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CHAPTER 1

DIOXIRANE OXIDATIONS OF COMPOUNDS OTHER THAN ALKENES

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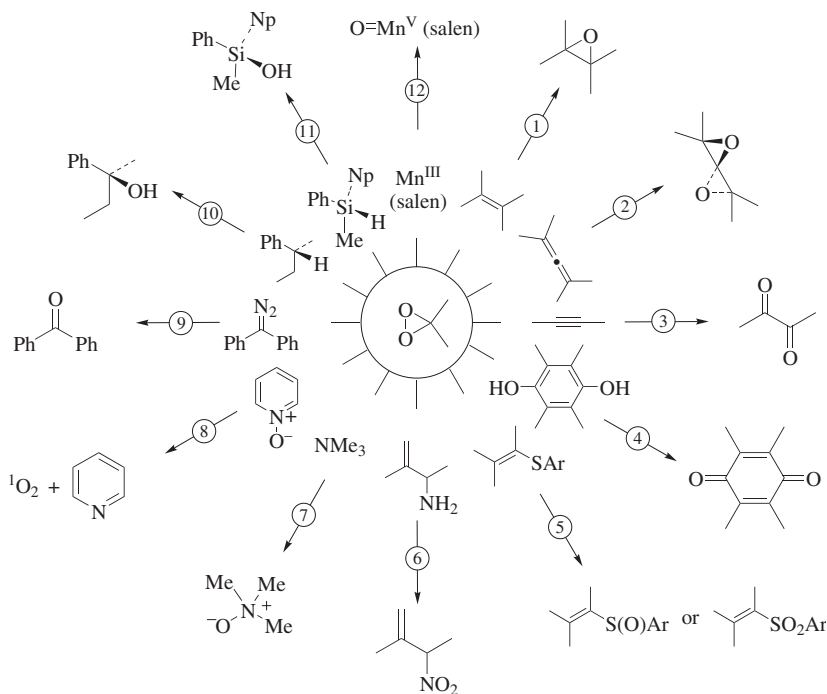
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INTRODUCTION

Epoxidations, heteroatom oxidations, and Y–H insertions constitute the best investigated oxidations by dioxiranes. An overview of these transformations is displayed in the rosette of Scheme 1. These preparatively useful oxidations have been extensively reviewed during the last decade.^{1–14} In a previous chapter,¹⁵ we presented the epoxidation of double bonds [π bonds in simple alkenes and those functionalized with electron donors (ED), electron acceptors (EA), and with both ED and EA substituents; case 1 in the rosette] with either isolated or in situ generated dioxiranes. The recent developments in the dioxirane-mediated asymmetric epoxidation have also been extensively covered there.¹⁵ The present chapter concerns the remaining oxidations in the rosette of Scheme 1, that is, epoxidation of the double bonds in the cumulenes, such as allenes (transformation 2), acetylenes (transformation 3), and arenes (transformation 4); the oxidation of heteroatom functionalities, mainly lone pairs on sulfur (transformation 5), on nitrogen (transformations 6 and 7), and on oxygen as the deoxygenation of *N*-oxides (transformation 8); the oxidation of C=Y functionalities (e.g., transformation 9), Y–H insertions (σ bonds) such as C–H in alkanes (transformation 10) and Si–H in silanes (transformation 11); and the oxidation of organometallic substrates including metal (transformation 12) and ligand-sphere oxidation.

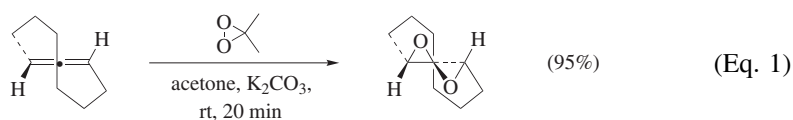


Scheme 1. An overview of dioxirane oxidations (Np = 1-naphthyl).

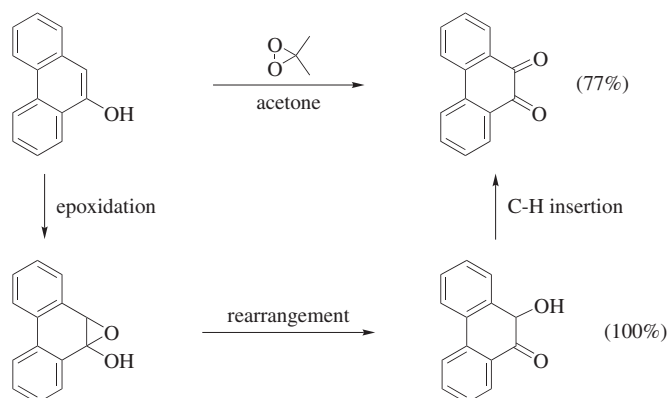
MECHANISM

Allenes, Alkynes, and Arenes

Although the products of the dioxirane oxidation of allenes, alkynes, and arenes are usually more complex than those of the epoxidation of simple C=C double bonds, the initial step of the oxidation is usually epoxidation. Therefore, the same mechanism that has been extensively discussed in the previous chapter¹⁵ also applies in these reactions. The oxygen transfer proceeds with complete retention of the initial olefin configuration through the concerted spiro transition state.¹⁵ An example is shown in Eq. 1, in which the oxidation of the chiral allene proceeds in nearly quantitative yield (95%) with preservation of the starting allene configuration in the spiro-bisepoxide.¹⁶



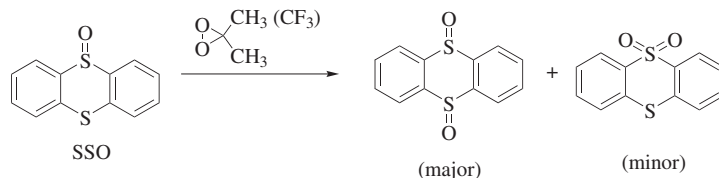
Since the initial epoxidation products of the allenes, alkynes, and arenes are usually labile substances, they may undergo subsequent reactions, which include further oxidation by dioxirane other than epoxidation. For example, in the dimethyldioxirane (DMD) oxidation of the phenanthrene derivative in Scheme 2,¹⁷ the second oxidation by DMD involves C-H insertion instead of epoxidation.



Scheme 2. DMD oxidation of 9-hydroxyphenanthrene.

Heteroatom Substrates

Through a detailed study of the competitive oxidation of the sulfide versus sulfide functionalities in thianthrene 5-oxide (SSO),¹⁸ a pronounced electrophilic character has been demonstrated for DMD and methyl(trifluoromethyl)dioxirane (TFD).^{19,20} Thus, dioxiranes prefer to oxidize the sulfide over the sulfoxide functionality, a typical behavior of an electrophilic oxidant (Scheme 3). Also, the

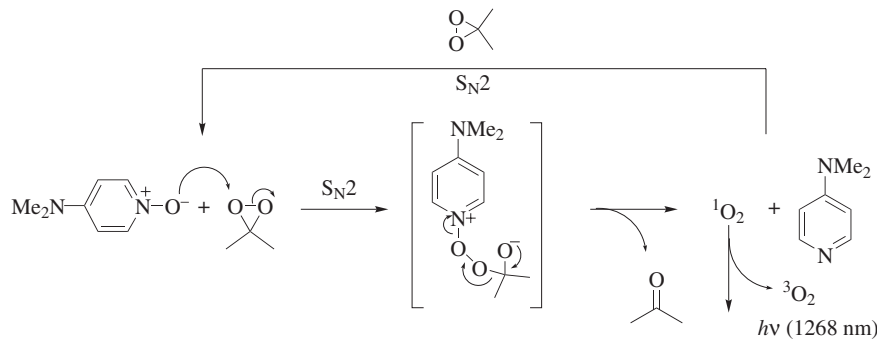


Scheme 3. Competitive oxidation of the sulfide vs. sulfoxide functionalities in thianthrene-5-oxide (SSO) by the dioxiranes DMD and TFD.

kinetic data⁶ for the oxidation of sulfides and sulfoxides have revealed the electrophilic character of dioxiranes. Thus, the heteroatom oxidations by dioxirane are generally explained in terms of a S_N2-type attack of the heteroatom lone pair on the dioxirane peroxide σ*-orbital.^{21,22}

A possible single-electron-transfer (SET) mechanism in N-oxidations^{23,24} has been discounted²¹ on the basis of kinetic experiments by comparing the relative rates of oxygen transfer by DMD with those of alkylation by methyl iodide. For the latter, an S_N2 mechanism unequivocally applies. Similar reactivities (linear correlation of rates) for N-oxidation also establish the S_N2 pathway for dioxirane oxidations. This conclusion is supported by a kinetic study of the DMD oxidation of substituted *N,N*-dimethylanilines.²⁵

The heterolytic mechanism is presumably also valid for a variety of oxygen-type nucleophiles, e.g., amine *N*-oxides, ClO⁻, HO⁻, HOO⁻, RO⁻, ROO⁻, RC(O)OO⁻, and ⁻OS(O)₂OO⁻, which all catalyze the decomposition of dioxiranes with the evolution of molecular oxygen.^{26,27} A typical case is illustrated with 4-dimethylaminopyridine *N*-oxide in Scheme 4.²⁶ The chemiluminescence emitted by the generated singlet oxygen confirms the heterolytic nature of the dioxirane decomposition.²⁶ Further support for this mechanism has been provided by theoretical work, from which it was concluded that the oxidation of primary amines by DMD does not proceed by a radical process.²⁸



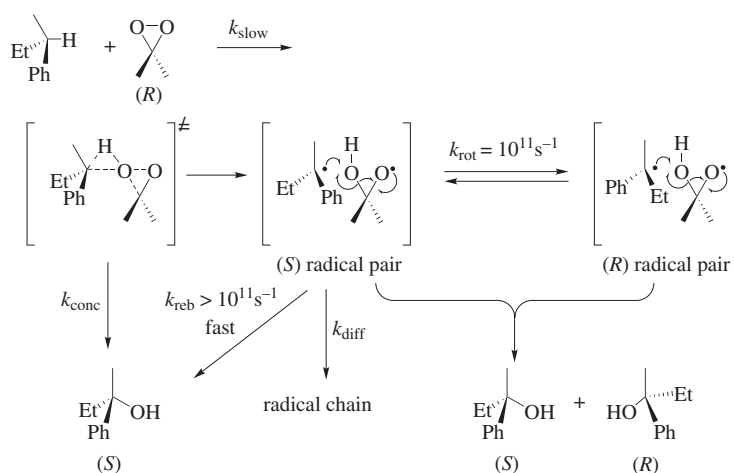
Scheme 4. S_N2 Mechanism for the *N*-oxide-induced decomposition of DMD.

Alkanes and Silanes

Two mechanisms have been suggested for the insertion of an oxygen atom into the Y–H bond of alkanes and silanes. Abundant evidence, which includes kinetics,²⁹ kinetic isotope effects,³⁰ and stereoselectivity,³¹ all unequivocally support a concerted oxenoid-type mechanism (Figure 1).

Nonetheless, radical reactivity has been observed recently and interpreted in terms of the dioxirane diradical as the active oxidant, in particular, the so-called “molecule-induced homolysis.”^{32–35} It has also been proposed³⁶ that alkane hydroxylation may proceed by a rate-determining oxygen insertion into the alkane C–H bond to generate a caged radical pair, followed by very fast collapse (oxygen rebound) to hydroxylated products (Scheme 5).

That hydroxylation of (*R*)-2-phenylbutane proceeds with 100% retention to furnish (*S*)-2-phenylbutan-2-ol for both DMD³⁷ and TFD³¹ sheds serious doubt on the involvement of out-of-cage radical intermediates in such C–H oxidations (Eq. 2).



Scheme 5. Concerted oxenoid-type (k_{conc}) vs. oxygen-rebound (k_{reb}) mechanisms for C–H insertion by DMD.

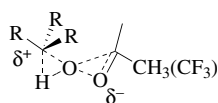
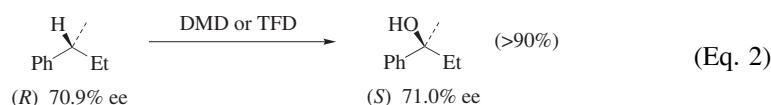
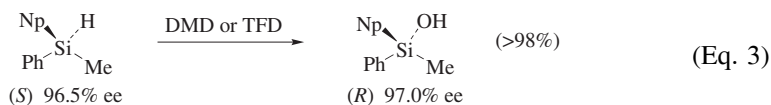


Figure 1. Concerted oxenoid-type transition state for C–H insertion.

The tertiary benzyl radical derived from this optically active substrate is one of the fastest radical clocks (the configurational persistence of this radical is estimated to be about 10^{-11} seconds)³⁸ and serves as a definitive probe for the intervention of radical intermediates. Thus, as shown in Scheme 5,³⁷ if a caged radical pair is formed, collapse with configurational conservation by oxygen rebound (k_{reb}) must be faster than diffusion out of the cage (k_{diff}), as well as in-cage isomerization (k_{rot}), since such competitive processes would lead to racemization.

As in the C–H oxidation of (*R*)-2-phenylbutane (Eq. 2), the hydroxylation of the (+)-(*S*)-(α -Np)PhMeSiH silane enantiomer by both dioxiranes DMD and TFD proceeds with complete retention of configuration to afford (+)-(*R*)-(α -Np)PhMeSiOH (Eq. 3).^{39,40} Therefore, a similar mechanism would appear to apply for the oxidation of C–H and Si–H bonds.



Most recent theoretical work on oxygen transfer for C–H insertion supports the concerted spiro oxenoid-type mechanism, in which the transition structure has considerable dipolar and also some diradical character.^{41–43} Under typical preparative conditions, for example, in the presence of molecular oxygen, it was concluded that a concerted mechanism applies for the C–H insertion.

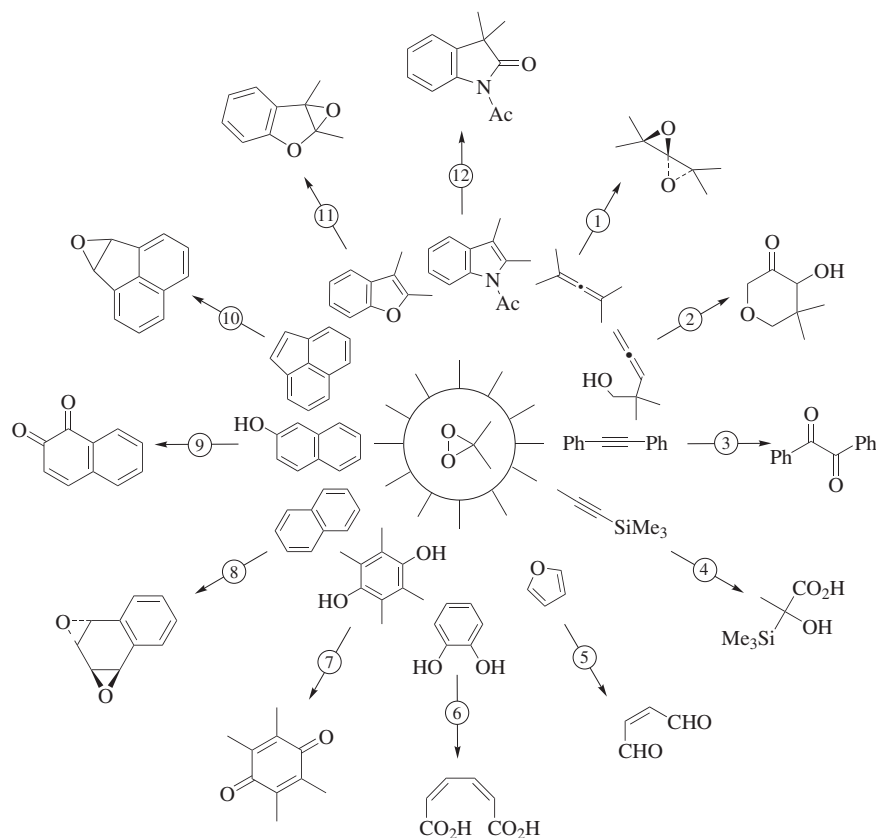
SCOPE AND LIMITATIONS

The oxidation of double bonds (π bonds) in cumulenes (allenes, acetylenes) and arenes, of heteroatom functionalities (lone-pair electrons), of transition-metal complexes, and Y–H insertions (σ bonds) has been successfully performed, either with isolated or with in situ generated dioxiranes. Thus, a broad spectrum of substrates has been oxidized by dioxiranes. The pertinent examples are listed in Tables 1–7 (see Tabular Survey). An isolated (distilled) acetone solution [DMD (isol.)] is the most often used dioxirane owing to its convenient preparation and relatively low cost. Although methyl(trifluoromethyl)dioxirane (TFD) is considerably more reactive than DMD, its application is limited because of its high cost and the high volatility of trifluoroacetone. With DMD (isol.), the scale of the reaction is usually limited to 100 mmol because DMD (isol.) is quite dilute (ca. 0.08 M). In the case of TFD (ca. 0.6 M), the prohibitive cost of trifluoroacetone obliges small-scale (ca. 10 mmol) applications. When a large-scale preparation is desired, the in situ mode [DMD (in situ)] is recommended, for which both biphasic^{44–47} and homogeneous^{48,49} media are available. It should be kept in mind that when one operates in aqueous solution, both the substrate and the oxidized products should resist hydrolysis and persist at temperatures above 0°. An advantage of the in situ mode is that it may be carried out with less than stoichiometric amounts (<0.5 equiv.) of ketone, which is important for enantioselective oxidations.^{50–54}

Allenes, Alkynes, and Arenes

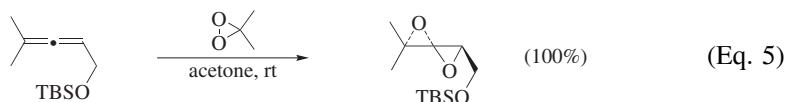
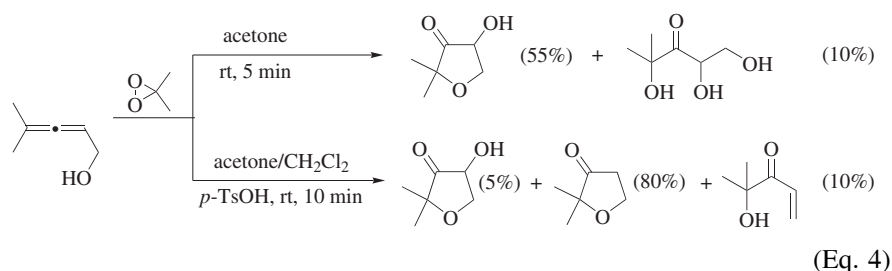
Representative examples of oxidations of allenes, alkynes, and arenes are collected in the rosette of Scheme 6.

The products of dioxirane oxidation of allenes depend on the reaction conditions and the substrate structure. Unfunctionalized allenes give the corresponding spiro-bisepoxides usually in good yields^{16,54} at subambient temperatures when dry dioxirane solution is employed (Eq. 1).¹⁶ If the allene is unsymmetrically substituted, a mixture of regioisomers is obtained, and the selectivity is highly dependent on the allene structure.^{16,55} Since these spiro-bisepoxides are labile toward hydrolysis, the in situ oxidation mode is not recommended. If the allene substrate contains a hydroxy functionality, the latter will react with the spiro-bisepoxide intermediate to form ring-opened and/or rearranged products.^{56–58} The final products may be cyclic or acyclic, depending on the reaction conditions, the chain-length of the substituent that contains the hydroxy functionality, and the other substituents on the allene. For example, when the hydroxyallene



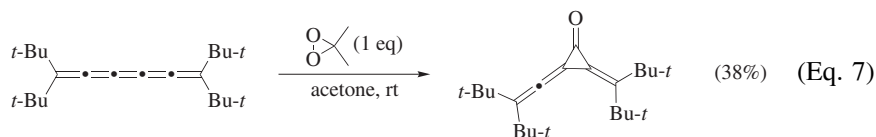
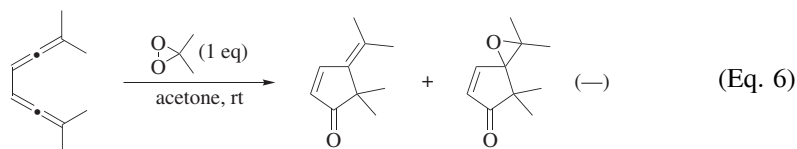
Scheme 6. An overview of dioxirane oxidations of allenes, alkynes, and arenes.

in Eq. 4 is oxidized with an acetone solution of DMD,⁵⁷ the hydroxyfuranone is obtained as the major product (upper route), together with minor amounts of open-chain material. In the presence of catalytic amounts of *p*-TsOH (lower route), however, the above hydroxy-substituted heterocycle is a minor product. On protection of the hydroxy functionality as a silyl ether, these complications are avoided, and the spiro-bisepoxide is obtained (Eq. 5).⁵⁷



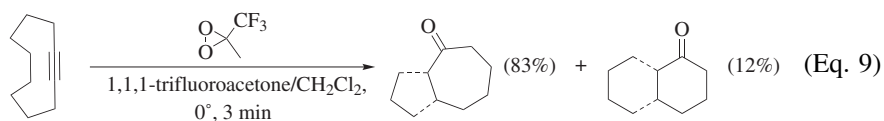
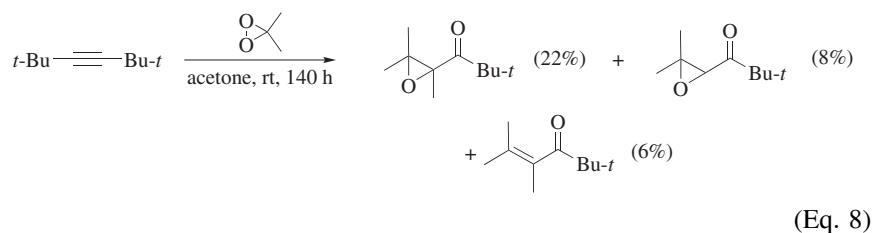
Other reactive functionalities in the allene, such as amine,⁵⁸ amide,⁵⁸ aldehyde,⁵⁹ carboxylic acid,⁶⁰ oxime,⁵⁸ and even ketone⁵⁹ groups, will open the spiro-bisepoxide intermediate and lead to substrate-specific products. These multifunctionalized heterocyclic and acyclic products should be of potential use in organic synthesis.

The oxidation of (bis)allenes and higher cumulenes has been much less studied. Nevertheless, one example of the DMD oxidation of a bisallene yields a cyclopentenone and an exocyclic epoxide (Eq. 6).⁶¹ The epoxide presumably arises from further oxidation of the exomethylenic double bond. A higher-order cumulene has also been oxidized with DMD to give an unusual cyclopropanone in 38% yield (Eq. 7).⁶²

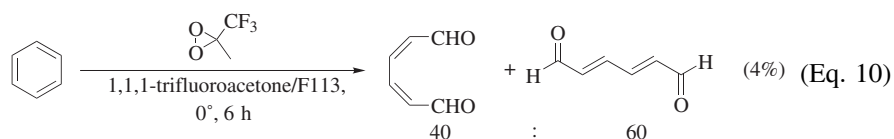


The oxidation of alkynes appears to be little studied, most likely because of the complexity of the product composition obtained in this oxidation. The oxyfunctionalized intermediates, presumably oxirenes, are much more labile than allene oxides and have so far not been detected. This oxidation is usually not

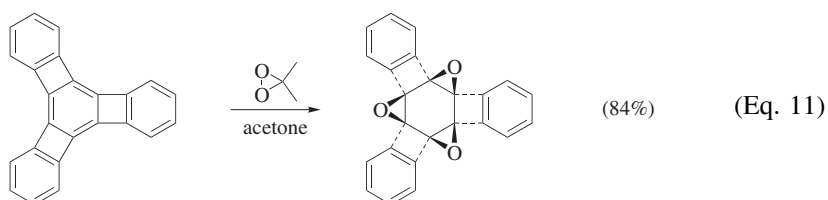
useful for synthetic purposes since extensively rearranged products are obtained in poor yields, especially with open-chain alkynes (Eq. 8).⁶³ The cyclic alkyne in Eq. 9, however, gives well-defined bicyclic rearrangement products in good yields when oxidized with TFD at 0° (Eq. 9).⁶⁴



In contrast, dioxirane oxidation of arenes is a useful reaction and has been thoroughly studied. Among the arenes and heteroarenes, benzene is the most difficult to oxidize. It is inert toward DMD oxidation and, thus, it has been employed as solvent in the biphasic oxidation mode with in situ generated DMD.⁴⁷ Nonetheless, benzene has been oxidized with the more reactive TFD in a fluorinated solvent, affording two isomeric dialdehydes in low yield (Eq. 10).⁶⁵

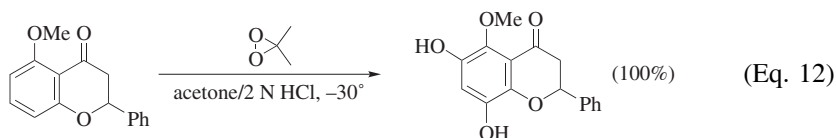


Electron-rich substituted benzenes are more reactive. For example, phenols and naphthols have been oxidized by DMD to the corresponding quinones.^{17,66} Oxidation of the arene substrate in Eq. 11 leads to the tris(epoxide) in high yield.⁶⁷ This transformation demonstrates the usefulness of dioxiranes in the oxidation of arenes, since such a tris(epoxide) would be difficult to make by any other route.

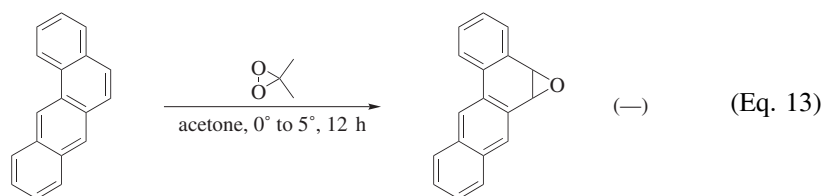


Recently, methoxy-substituted benzenes have been hydroxylated to phenols with isolated DMD under acidic conditions at subambient temperatures (Eq. 12).⁶⁸

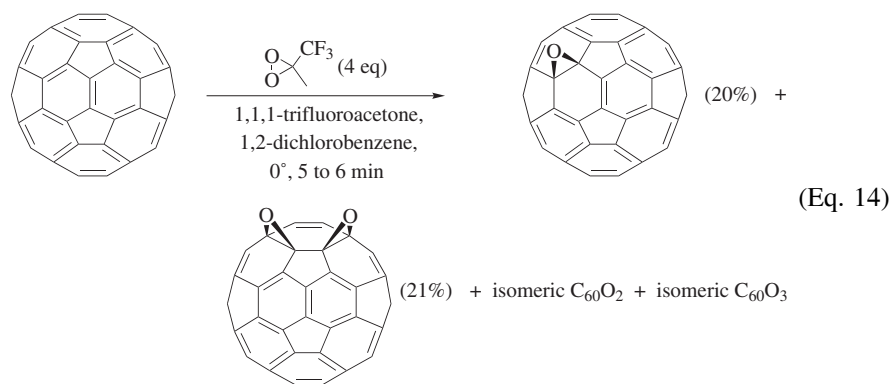
The overall reaction at first appears to be a direct CH insertion, but actually epoxidation takes place followed by an acid-catalyzed rearrangement of the intermediary epoxide.



Indene, naphthalene, and polycyclic arenes are more reactive and thus susceptible to both DMD and TFD oxidation. For example, the tetracyclic arene in Eq. 13 is oxidized by DMD to furnish the corresponding epoxide.⁶⁹ Such arene epoxides are of special interest since they are biologically active metabolites of carcinogenic polycyclic aromatic hydrocarbons.^{69,70}

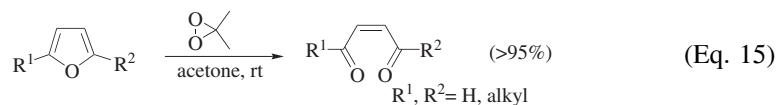


A highlight of arene oxidation by dioxirane reagents is that of the fullerene C₆₀. DMD leads mainly to the monoxide,⁷¹ but the more reactive TFD yields dioxides and even some trioxides of C₆₀ (Eq. 14).⁷²

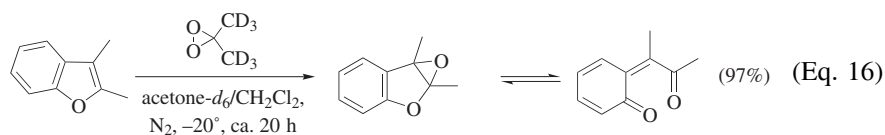


Furan-type heteroarenes are usually more reactive towards dioxirane oxidation than arenes. When subjected to oxidation by DMD (isol.), furan and its 2,5-disubstituted derivatives^{73,74} lead to the ring-opened enediones shown in Eq. 15,⁷³ which are useful building blocks in synthesis.^{73,75} The intermediary mono-epoxide of 2,3-dimethylfuran is presumably involved in the epoxidation with *d*₆-DMD (prepared in *d*₆-acetone), but could not be detected by NMR

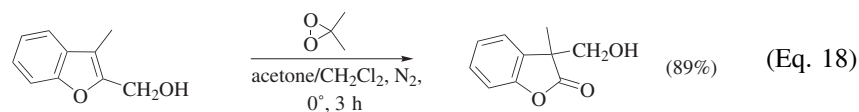
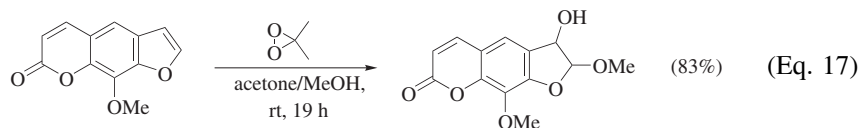
spectroscopy even at -100° ; only the rearrangement product hex-3-ene-2,5-dione was observed.⁷⁶



Related benzofurans also form labile epoxides when epoxidized by dry dioxirane solutions at low temperature under an inert atmosphere; they are sufficiently persistent to be detected at low temperatures.⁷⁷⁻⁸⁶ Depending on the substituents of the heterocycle, the epoxide may undergo opening to dicarbonyl products. Thus, the labile epoxide derived from 2,3-dimethylbenzofuran (Eq. 16) rearranges at -20° to the *o*-quinomethide.^{79,87,88} To characterize this epoxide by NMR spectroscopy, fully deuterated DMD was employed for the oxidation; the epoxide was directly detected in situ at -78° without work-up.⁷⁹ This example further emphasizes the importance and convenience of isolated dioxiranes for the synthesis of exceedingly labile oxy-functionalized substances.

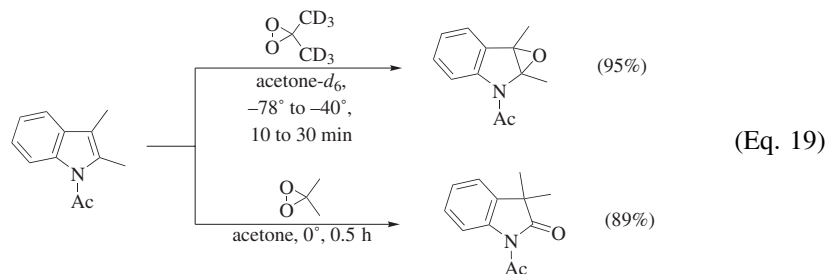


In view of the high reactivity of the benzofuran oxides, ring-opened products are formed in the presence of nucleophiles. For example, when the epoxidation of the structurally related 8-methoxypsoralen was carried out in the presence of MeOH, the hydroxy ether was obtained in good yield as ring-opened product (Eq. 17).⁸⁵ Elevated temperatures lead to rearrangement products as in the oxidation of benzofuran. Thus, when the reaction is carried out at 0° , the rearranged product in Eq. 18 is obtained from the intermediary epoxide by migration of the hydroxymethyl group.⁸⁹

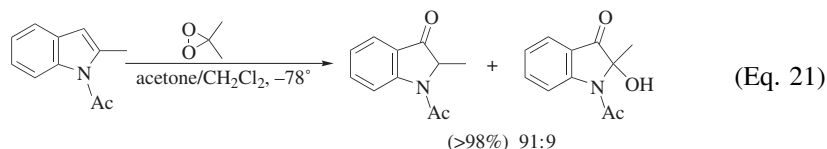
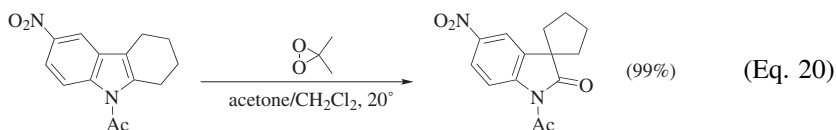


Dioxirane oxidation of the aromatic ring in nitrogen-containing heteroarenes may be even more complex. Since amine nitrogen atoms are more nucleophilic than an arene C=C double bond, N-oxidation usually precedes epoxidation. For example, the oxidation of pyridines takes place at the nitrogen atom to give the corresponding *N*-oxides as the sole products (see the section on Heteroatom

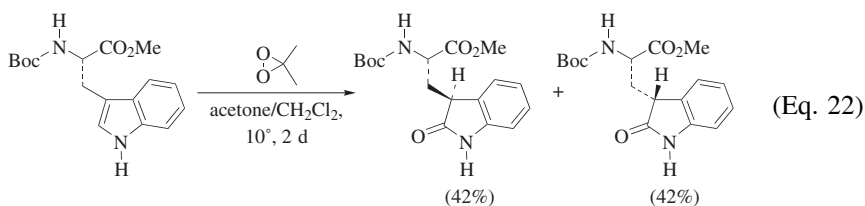
Substrates). Nonetheless, acetylation of the nitrogen functionality may sufficiently suppress N-oxidation, as illustrated for the *N*-acetylated indole in Eq. 19.^{90,91}

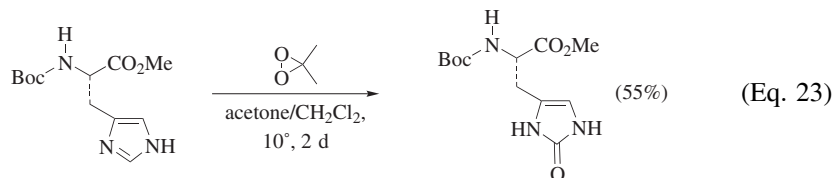


Analogous to the benzofuran example above, the corresponding labile epoxide is produced (upper pathway), when the indole is oxidized with DMD at low temperature (-78°).⁹⁰ In contrast, the rearranged product⁹¹ is obtained when the oxidation is run at subambient temperature (lower pathway). The latter rearrangement has been used for the synthesis of spiro lactams (Eq. 20).⁹² Variation of the substitution pattern of indoles may permit other rearrangements to take place. For example, the oxidation of the indole shown in Eq. 21 yields the respective benzopyrroldihydroindole instead of a lactam.⁹² The minor product presumably results from overoxidation of the pyrrolidone enol tautomer.



Currently little is known about dioxirane oxidations of unprotected indoles. One example is given in Eq. 22, for which the diastereomeric lactams are obtained.⁹³ Examples of dioxirane oxidations of heteroarenes with more than one nitrogen atom are also scarce. An example is the DMD oxidation of a substituted imidazole (Eq. 23), which furnishes an imidazolone in moderate yield.⁹³ In contrast, the DMD oxidation of 1,2,4-triazole results in a complex mixture of unidentified products.⁹⁴

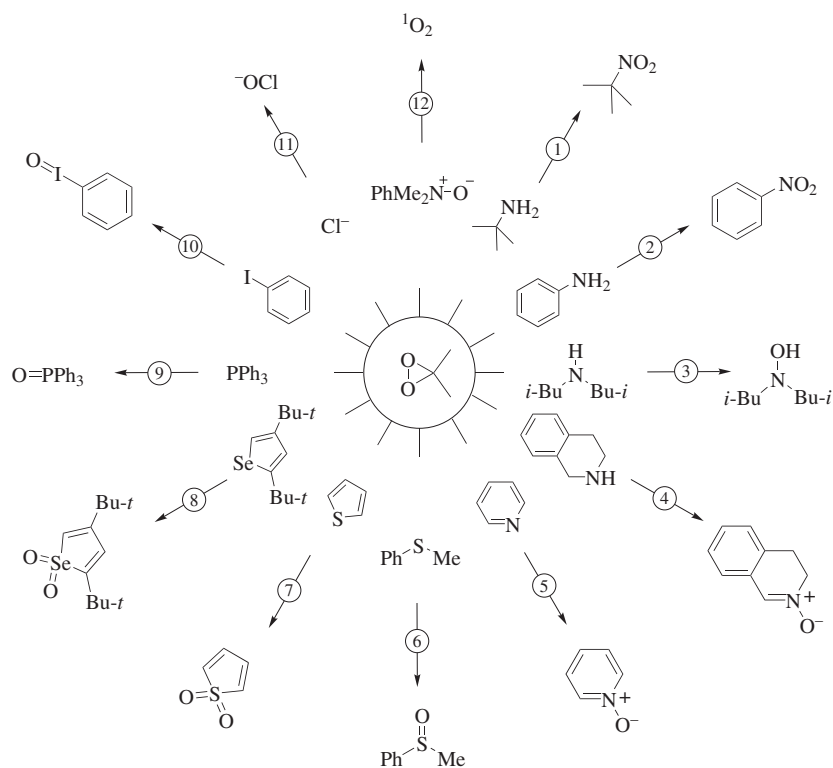




The oxidation of sulfur-containing heteroarenes such as thiophenes takes place only on sulfur, as will be discussed in the next section.

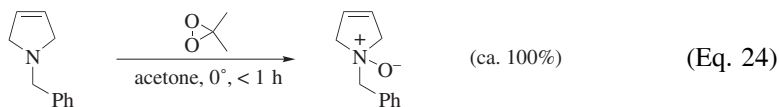
Heteroatom Substrates

Electrophilic dioxiranes are particularly reactive towards heteroatom substrates, for which the electron lone-pair serves as the nucleophile in the oxygen transfer. Because of the importance of their oxidation products, substrates that contain nitrogen, sulfur, and C=Y functionalities are among the best studied. Some typical examples are collected in the rosette of Scheme 7. These oxidations will be discussed separately according to the type of heteroatom that is oxidized, mainly nitrogen and sulfur.

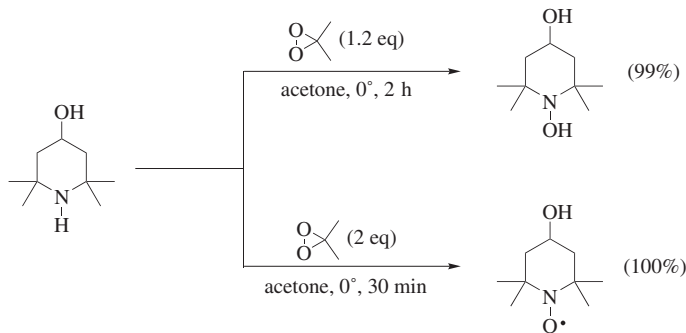


Scheme 7. An overview of dioxirane oxidations of heteroatom substrates.

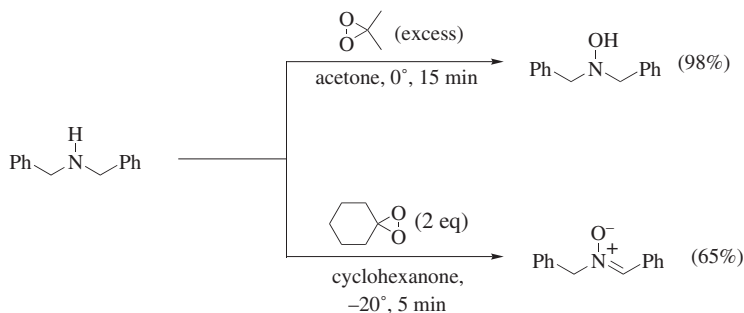
Nitrogen. Irrespective of whether the nitrogen atom in the substrate is sp^3 or sp^2 hybridized, it is readily oxidized by either isolated or in situ generated dioxiranes. The outcome of the dioxirane oxidation of an sp^3 -hybridized nitrogen depends on the structure of the amine. Tertiary amines give cleanly the *N*-oxides, as illustrated in Eq. 24. Particularly noteworthy is the selective oxidation of the nitrogen atom, without epoxidation of the double bond.⁹⁵ Oxidation of secondary amines is more complex. If the secondary amine does not bear α -hydrogen atoms, the product is usually the expected hydroxylamine; however, the latter may be further oxidized by excess DMD to the corresponding nitroxyl radical. An illustrative example is shown in Scheme 8;^{96,97} it should be noted that the alcohol functionality survives, which demonstrates the greater reactivity of the amino group towards DMD oxidation.



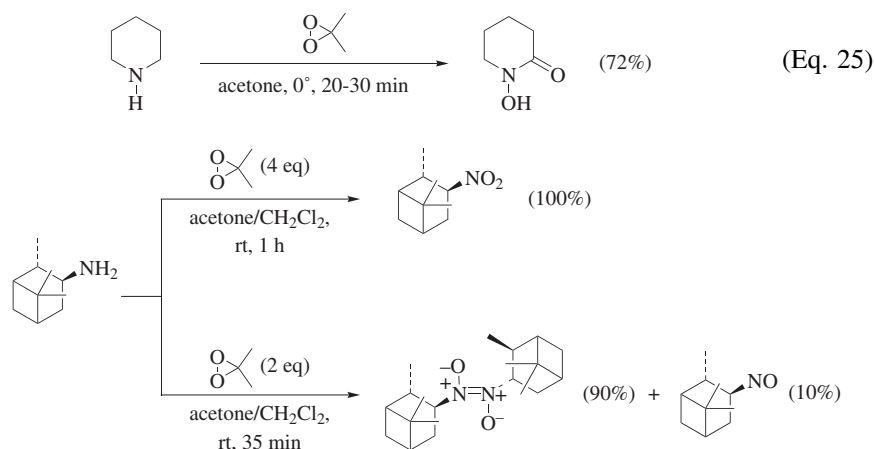
If the secondary amine bears α -hydrogen atoms, the product can be either a nitron or a hydroxylamine, depending on the reaction conditions. For example, *N,N*-dibenzylamine is oxidized to the hydroxylamine with DMD at 0° (upper pathway),⁹⁶ whereas the nitron is obtained upon treatment with two equivalents of cyclohexanone dioxirane at -20° (lower pathway) (Scheme 9).⁹⁸ Other products may also be obtained, as illustrated in the DMD oxidation of piperidine; here the hydroxamic acid is obtained in good yield (Eq. 25).⁹⁹ Primary amines usually give a complex mixture of products, which may contain hydroxylamine, oxime, nitroso, nitro, and sometimes even azoxy compounds. However, reaction conditions may be chosen to favor one of these products. Thus, a preparatively valuable method is the DMD oxidation of aliphatic and aromatic amines to the corresponding nitro compounds. For example, the optically active amine in Scheme 10 is oxidized with excess DMD to the respective nitroalkane in quantitative yield



Scheme 8. DMD oxidation of a secondary amine.



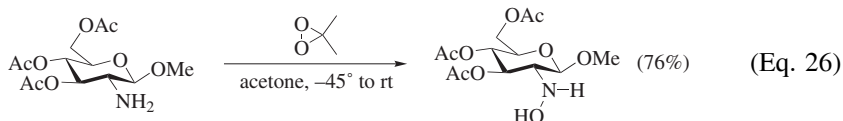
Scheme 9. DMD oxidation of *N,N*-dibenzylamine.

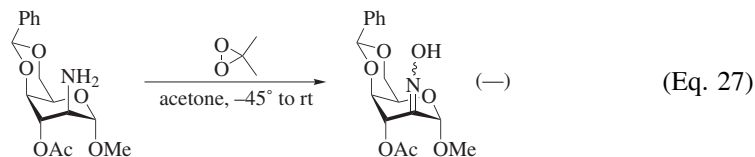


Scheme 10. DMD oxidation of a primary amine.

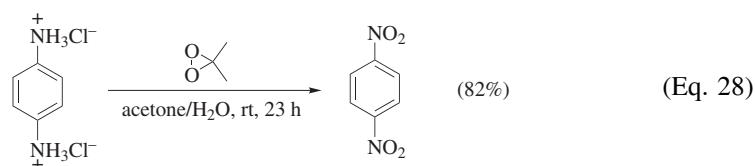
(upper pathway).²² If an insufficient amount (2 equiv.) of DMD is used, the nitroso and the azoxy products are obtained instead (lower pathway).²²

At subambient temperature, primary amines are converted either into hydroxylamines or into oximes by DMD. This transformation can be synthetically useful, as, for example, in the oxidation of the amino sugar derivative in Eq. 26 to the corresponding hydroxylamine in good yield. However, the related amino sugar in Eq. 27 is oxidized to the oxime under identical reaction conditions.¹⁰⁰ Clearly, structural features of the amino sugar strongly influence the course of the oxidation.

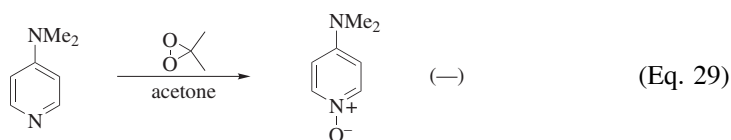




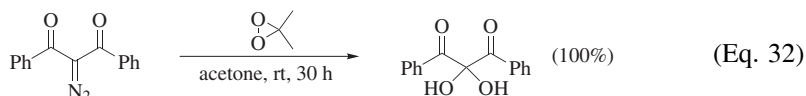
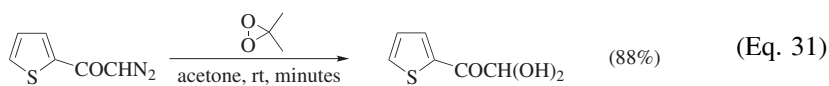
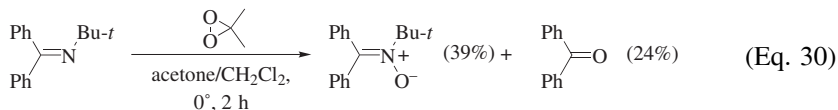
Although amines are readily oxidized by dioxiranes, the corresponding amides persist and are, therefore, often used to protect amines. Protection of the amine by protonation may also be employed, but since ammonium salts dissociate into the free amine, it is essential to conduct the oxidation under strongly acidic conditions; otherwise the oxidation will still take place slowly (Eq. 28).¹⁰¹



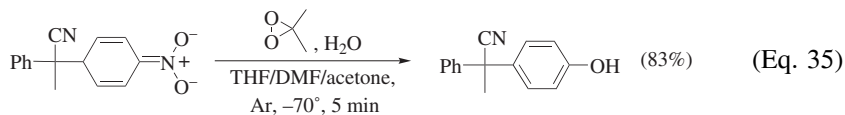
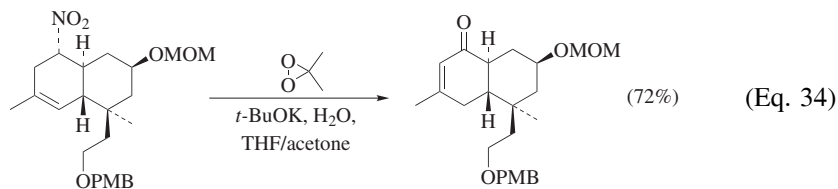
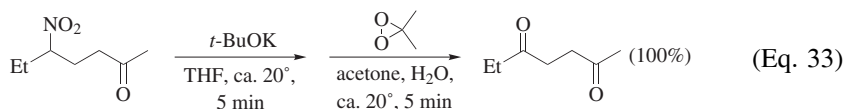
The oxidation of sp^2 -hybridized nitrogen generally falls into two categories: namely, heteroarenes and isolated C=N bonds. The nitrogen-containing arenes usually afford *N*-oxides. Thus, pyridines are generally oxidized to pyridine *N*-oxides. An interesting example is given in Eq. 29 in which the pyridine nitrogen atom is selectively oxidized rather than the dimethylamino group.²¹ Since the resulting *N*-oxide may further react with DMD to give *N,N*-dimethylaminopyridine and singlet oxygen, as illustrated in Scheme 4, it is not possible to achieve full conversion of the substrate in such situations.²¹



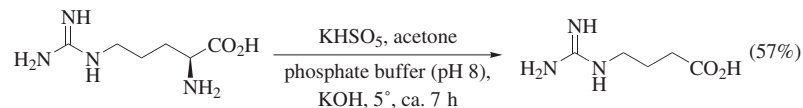
Oxidation of the nitrogen atom in isolated C=N bonds is complicated by the fact that the initial oxidation product may be further oxidized by dioxirane with cleavage of the C=N bond. For example, *N*-alkylated imines are oxidized by DMD to a mixture of nitrones and ketones (Eq. 30)¹⁰². When imines without substituents on the nitrogen atom are treated with DMD, the main products are oximes,¹⁰² which in turn may be further oxidized by excess dioxirane to the corresponding ketones or aldehydes. The method thus serves as a useful deprotection method for oximes. Similarly, diazoalkanes yield cleavage products (ketones, aldehydes, or their hydrates),^{103–106} when oxidized by DMD (Eq. 31).¹⁰³ This oxidation has been employed to prepare tricarbonyl compounds (Eq. 32),¹⁰⁵ and as such comprises a convenient method for the preparation of these reactive substances.



The DMD oxidation of nitronate anions, generated in situ from nitroalkanes, also affords carbonyl compounds through cleavage of the carbon-nitrogen bond (Eq. 33),¹⁰⁷ and in effect constitutes an oxidative Nef reaction.¹⁰⁸ This efficient new method has been successfully employed in the synthesis of the AB ring system of norzoanthamine (Eq. 34).¹⁰⁹ In a similar manner, the σ^{H} adducts generated in situ from nitroarenes by the addition of a carbanion are efficiently oxidized by DMD to the corresponding phenols (Eq. 35).^{110,111} This transformation comprises the first method for the direct oxidation of nitroarenes to phenols.



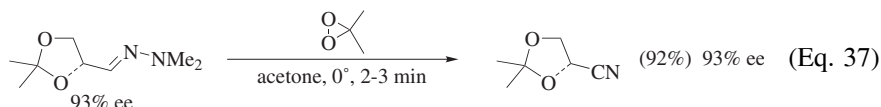
Similar oxidative cleavage reactions have been reported for several α -amino acids. Thus, when arginine is oxidized by DMD under in situ conditions, 4-guanidinobutanoic acid is obtained in moderate yield (Eq. 36).¹¹²



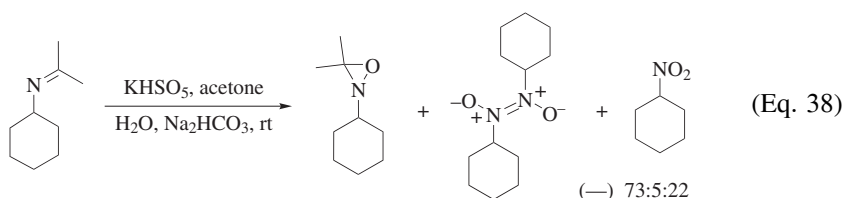
(Eq. 36)

The oxidation of *N,N*-dimethylhydrazone by DMD at 0° produces the corresponding nitriles (Eq. 37)¹¹³. What is remarkable about this useful oxidation is

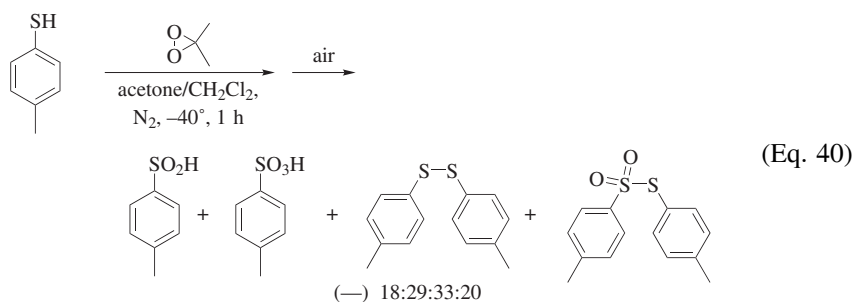
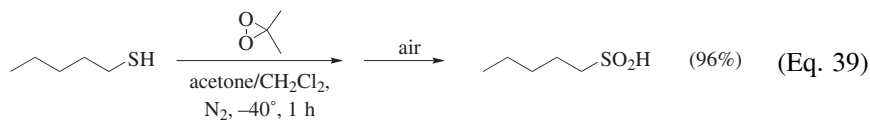
that no racemization takes place at the stereogenic center, which again emphasizes the mild reaction conditions.

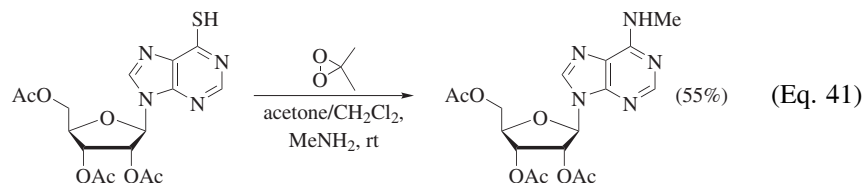


Dioxirane-mediated epoxidation of the C=N bond of imines to oxaziridines is rare, but examples are known for the in situ method (Eq. 38).¹¹⁴

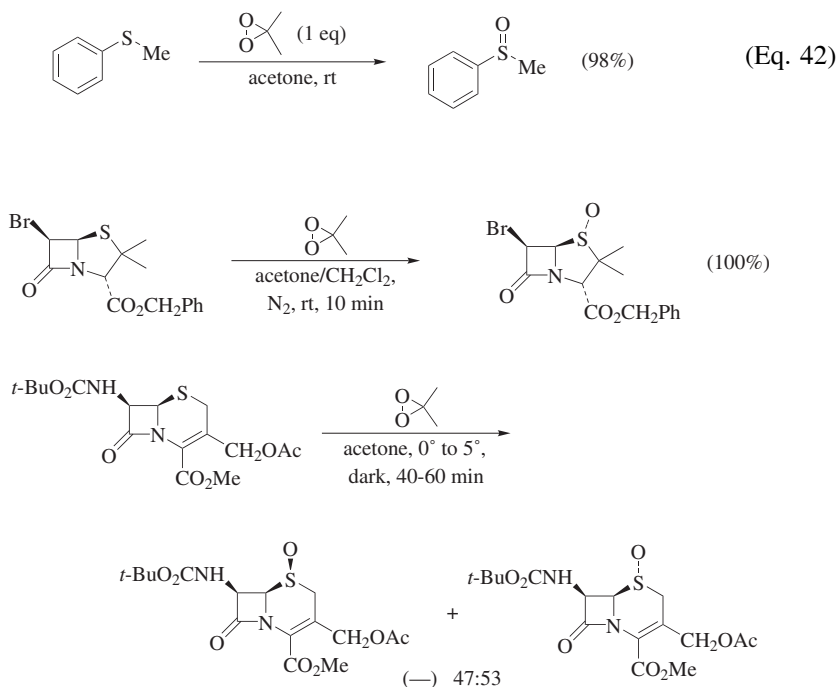


Sulfur and Selenium. In general, sulfur-containing substrates are more reactive toward dioxirane than nitrogen compounds. Thus, the oxidation of aliphatic thiols by DMD (isol.) at low temperature leads to sulfonic acids in good yield (Eq. 39).¹¹⁵ However, under the same reaction conditions, benzyl mercaptan affords a complex mixture of benzylsulfonic acid, benzylsulfonic acid, dibenzyl disulfide, dibenzyl thiosulfonate, and benzaldehyde.¹¹⁵ Similarly, DMD (isol.) oxidation of *p*-methylthiophenol displays this complexity (Eq. 40).¹¹⁵ The latter oxidations are, thus, not synthetically useful, given the multiple products formed; however, the oxidation of 9*H*-purine-6-thiols in the presence of an amine nucleophile produces ribonucleoside analogs in useful yields.^{116–120} An example of such a mercaptan oxidation with DMD (isol.) in the presence of methylamine is illustrated in Eq. 41. This reaction confirms that thiols are more reactive toward DMD oxidation than primary amines, as would be expected from the nucleophilicity of mercaptans compared with amines.¹⁵

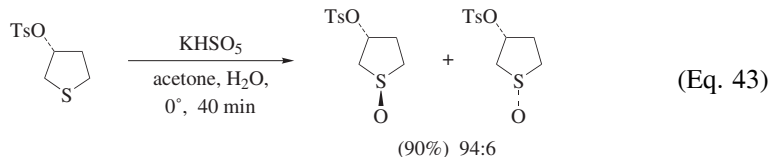




A sulfide may be oxidized by dioxirane to either the sulfoxide or sulfone, depending on the number of equivalents of the oxidant employed (Scheme 3). As pointed out already, sulfides are more readily oxidized than sulfoxides and, therefore, the sulfoxide product may be selectively obtained by employing only one equivalent of DMD (Eq. 42).¹²¹ Since methyl phenyl sulfide is prochiral, DMD oxidation affords the racemic sulfoxide. Similarly, if a chiral sulfide is employed, diastereomeric sulfoxides are expected. For example, DMD (in situ) oxidation of the tetrahydrothiophene derivative shown in Eq. 43 furnishes mainly one diastereomeric *S*-oxide with excellent stereocontrol (94:6).¹²² Such high diastereoselective oxidations are not general, as illustrated for the two similar substrates shown in Scheme 11.^{123,124} For the five-membered-ring sulfide (upper equation), the *cis* diastereomer is formed exclusively, whereas for the six-membered cyclic sulfide (lower equation) both diastereomeric sulfoxides are obtained in about equal amounts.

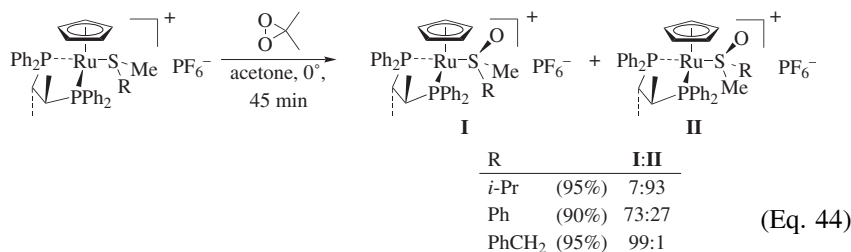


Scheme 11. Sulfoxidation of cyclic sulfides by DMD (isol.).

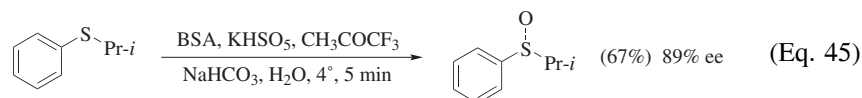


There is only one report on the diastereoselective oxidation of a chiral acyclic sulfide by DMD. In this case, the exocyclic sulfide is oxidized with low diastereoselectivity to the corresponding sulfoxide.¹²⁵

To achieve better diastereomeric control, prochiral sulfides have been coordinated to chiral organometallic complexes and then oxidized with DMD (isol.).^{126–129} As is evident from Eq. 44,¹²⁶ the diastereoselectivity depends highly on the structure of the sulfide, and as such, the outcome is difficult to predict. After decomplexation, enantiomerically enriched sulfoxides are obtained. The overall process qualifies, therefore, as an indirect enantioselective oxidation.



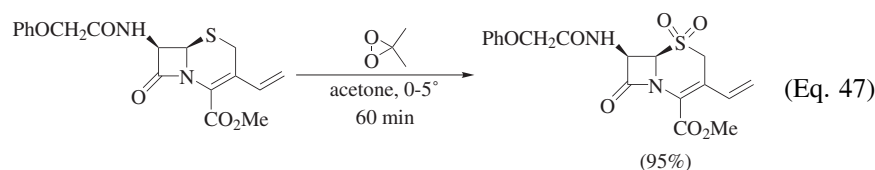
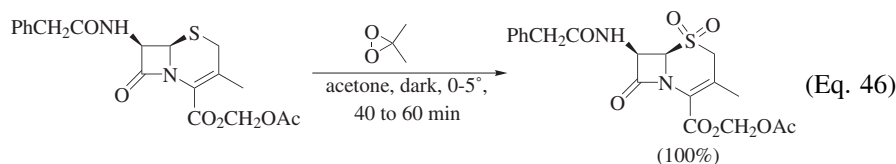
Enantioselective oxidation of sulfides by achiral dioxirane may be performed with bovine serum albumin (BSA). In the presence of this protein, prochiral sulfides have been oxidized by TFD (in situ) to enantioenriched sulfoxides in moderate to good enantioselectivities (up to 89% ee).^{130,131} A typical example is shown in Eq. 45.^{130,131}



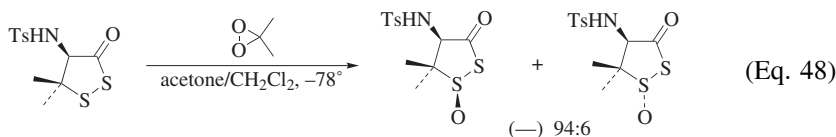
Enantioselective oxidation of a prochiral sulfide with an optically active dioxirane has not yet been accomplished. An attempt with methyl phenyl sulfide as substrate and in situ generated fructose-derived dioxirane, which has been successfully employed in asymmetric epoxidation,^{15,132} resulted in an enantiomeric excess of less than 5%.⁹⁴

If two or more equivalents of dioxirane are used, the sulfone is the main product. An illustrative example with DMD (isol.) is shown in Eq. 46.¹²⁴ It is noteworthy that both alkenyl¹²⁴ and alkynyl¹³³ sulfides are oxidized by dioxirane to the corresponding sulfones without epoxidation of the C–C multiple

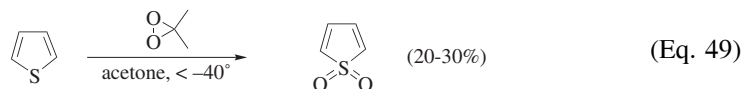
bonds (Eq. 47).¹²⁴ As expected, the dioxirane oxidation of a sulfoxide affords the corresponding sulfone.¹³⁴



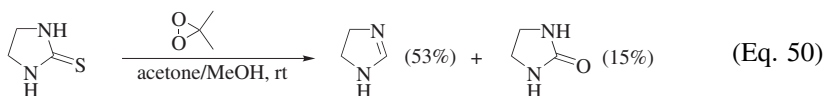
Oxidation of disulfides, trisulfides, and polysulfides by DMD usually leads to a mixture of multiple products,^{135,136} and is not of synthetic importance. Useful selectivities have been observed with DMD (isol.) only when one of the sulfur atoms in the disulfide is substituted by an electron-withdrawing group (Eq. 48).¹³⁷

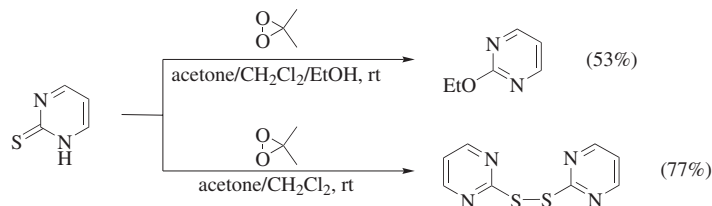


Dioxirane oxidation of sulfur-containing heteroarenes, such as substituted thiophenes, takes place exclusively on the sulfur atom.¹³⁸⁻¹⁴¹ At subambient temperature, the oxidation products are usually the corresponding thiophene 1,1-dioxides. Recently, the oxidation of thiophene with DMD (isol.) below -40° afforded the elusive parent thiophene 1,1-dioxide, which was isolated (Eq. 49).¹⁴⁰ When the oxidation was carried out at higher temperature, the thiophene 1,1-dioxide decomposed to other products.^{140,141}



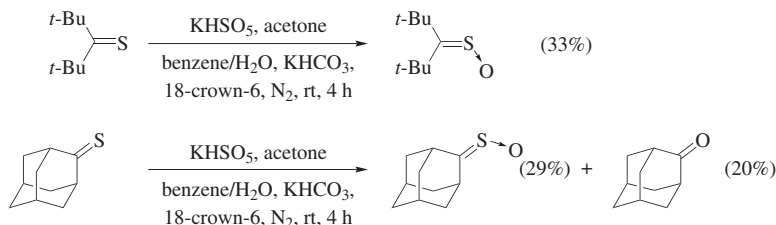
Dioxirane oxidation of the C=S bond in the thiourea functionality of some heterocycles leads to desulfurization products. A typical example is shown for a cyclic thiourea with DMD (isol.) in Eq. 50.¹⁴² This oxidation is, however, complex since disulfides and other products may be formed (Scheme 12).¹⁴²⁻¹⁴⁴



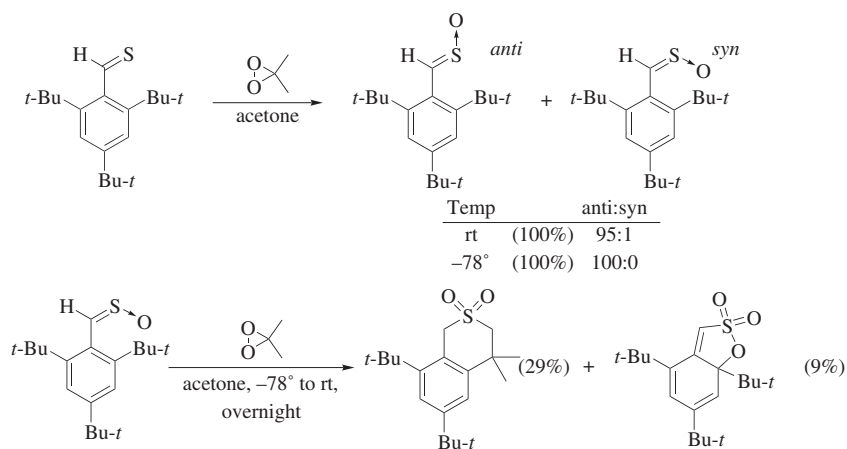


Scheme 12. Oxidation of 1H-pyrimidine-2-thione by DMD (isol.).

The dioxirane oxidation of the C=S functionality in thioketones to thioketone *S*-oxides is quite rare. Examples are collected in Scheme 13.^{145,146} The yields of the *S*-oxides from bis(*tert*-butyl)thione and adamantane-2-thione by DMD (in situ) are quite low because of further oxidation. Thiobenzaldehyde derivatives with bulky substituents, however, are oxidized by DMD (isol.) to the corresponding *S*-oxides both in good yield and with high diastereoselectivity;¹⁴⁷ further oxidation of the *syn* diastereomer by DMD (isol.) gives two unusual products in low yields (Scheme 14).¹⁴⁷

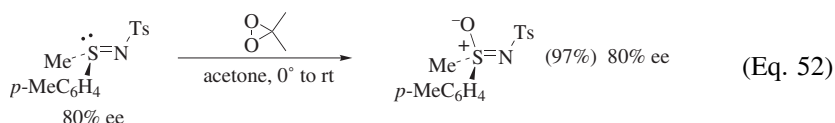
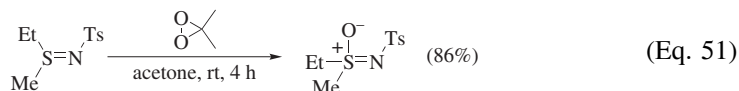


Scheme 13. Oxidation of thioketones by DMD (in situ).

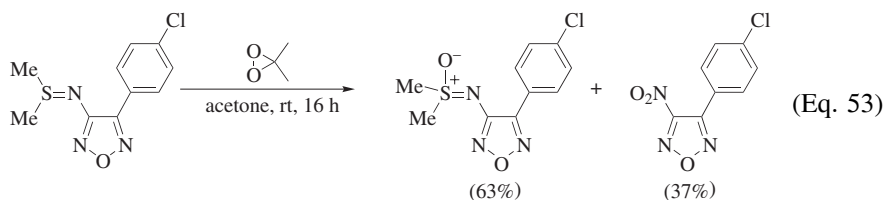


Scheme 14. DMD (isol.) oxidation of a thioaldehyde and its *syn*-*S*-oxide.

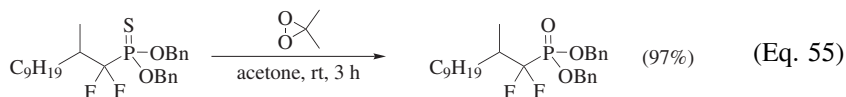
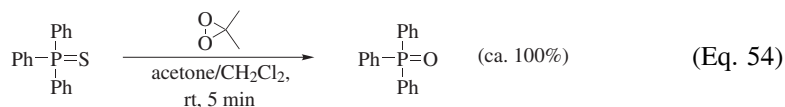
Oxidation of N-tosylated or N-acylated sulfilimines with DMD (isol.) takes place selectively on sulfur to give sulfoximines in good yields (Eq. 51).¹⁴⁸ The oxidation by DMD (isol.) is stereoselective so that a chiral sulfoximine may be obtained from an optically active sulfilimine with complete preservation of the initial enantiomeric purity (Eq. 52).¹⁴⁸



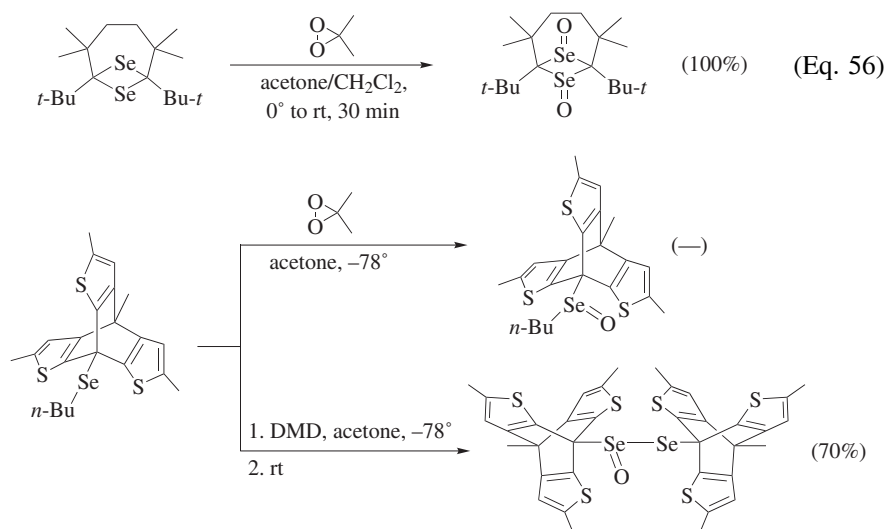
With the more reactive TFD (isol.), some sulfoxides and sulfones are also formed via cleavage of the S=N bond.¹⁴⁸ When the N atom of the sulfilimine bears a heterocyclic ring instead of an acyl or tosyl group, DMD (isol.) oxidation leads to a mixture of S- and N-oxidations, as evidenced by the presence of the nitro product (Eq. 53).¹⁴⁹ With wet DMD (isol.), N-oxidation represents the major process (63% vs. 37%).¹⁴⁹ These results suggest that the chemoselectivity of S versus N oxidation by DMD (isol.) of sulfilimine depends on the electron density of the heteroatoms.



In the oxidation of phosphine sulfides by DMD (isol.), desulfurization affords the corresponding phosphine oxides in nearly quantitative yields (Eq. 54).¹⁵⁰ Similarly, a thiophosphonate is converted into the phosphonate by oxidation with DMD (isol.), as shown in Eq. 55.¹⁵¹



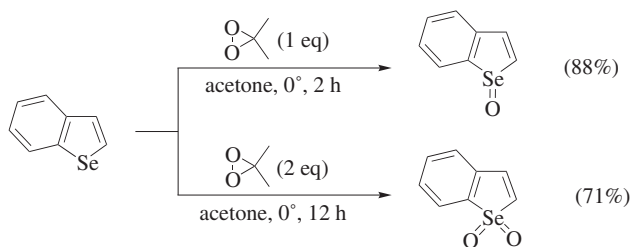
Selenides react with dioxirane like their sulfur analogs to give selenoxides, but the selenium atom is more reactive than the sulfur atom. Since selenoxides are much more labile than sulfoxides, good yields are usually only obtained



Scheme 15. Oxidation of a selenide by DMD (isol.).

for selenoxides with bulky substituents (Eq. 56).¹³⁴ In some cases more complex products may be obtained because of the labile nature of the selenoxides (Scheme 15).¹⁵²

Oxidation of selenophenes by DMD (isol.)^{153–155} at subambient temperatures gives selenophene 1-oxides or 1,1-dioxides in good yields. The amount of DMD used determines which product predominates (Scheme 16).¹⁵³ These results are comparable to those obtained with their sulfur counterparts.^{138–141}



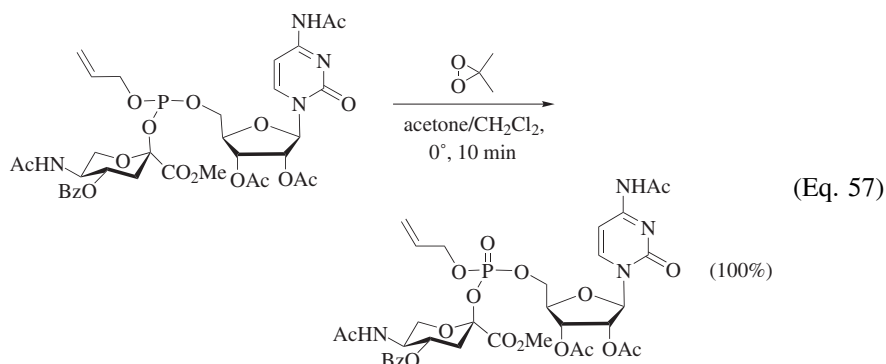
Scheme 16. Oxidation of benzoselenophene by DMD (isol.).

Phosphorus. Trivalent phosphorus compounds are readily oxidized by various oxidants; however, the oxidation of such substrates by dioxiranes has been sparsely studied. Since only a handful of examples are available in the literature, little may be said about general trends in reactivity and/or selectivity. Clearly, more detailed studies are needed to define the scope and limitations

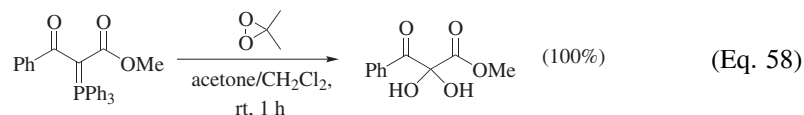
of this oxidation. Nonetheless, the phosphorus atom is readily oxidized by other reagents, such that it is questionable whether dioxiranes need to be used.

Triphenylphosphine is a favorite substrate for testing the oxidation of trivalent phosphorus. DMD (isol.) leads to triphosphine oxide quantitatively under a variety of conditions.^{121,156} DMD (in situ) has also been used, although the product yield was not specified.^{121,157}

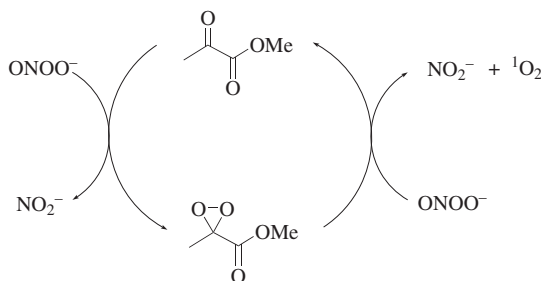
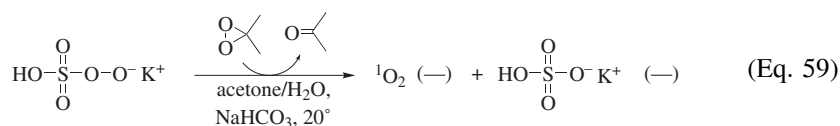
The selective oxidation of the phosphite functionality in nucleoside derivatives bearing a modified sugar on the trivalent phosphorus atom produces the corresponding nucleotides in nearly quantitative yields (Eq. 57).¹⁵⁸ In this reaction, the phosphorus atom is, as expected, selectively oxidized by the dioxirane, without epoxidation of the allylic double bond. Furthermore, this phosphorus oxidation may offer an expedient way of synthesizing unusual nucleotides.



A case of pentavalent phosphorus atom oxidation is documented for α,α -dicarbonylphosphoranes. When oxidized by DMD (isol.), the corresponding tricarbonyl compounds (as their hydrates) are obtained in excellent yields (Eq. 58).¹⁵⁹ These results are comparable with the DMD oxidation of similar diazo compounds¹⁰⁴ discussed above (cf. Eq. 32).



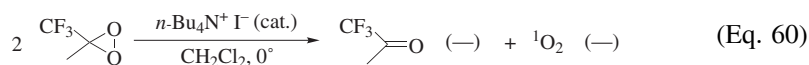
Oxygen. Dioxiranes also oxidize several types of oxygen functionalities, which include peroxides, N-oxides, and N-oxyl radicals. In most of these oxidations, molecular oxygen is produced. Thus, KHSO_5 , which is used as reagent for the generation of dioxiranes, reacts with DMD (isol.) to generate oxygen gas, KHSO_4 , and acetone as products (Eq. 59).¹⁶⁰ This reaction also takes place under in situ conditions and is responsible for the acetone-catalyzed decomposition of KHSO_5 , the process that actually led to the discovery of dimethyldioxirane.¹⁶¹ The molecular oxygen that is released in this oxidation is the electronically excited singlet oxygen, as confirmed by the characteristic chemiluminescence emission.¹⁶² Similarly, the catalytic decomposition of peroxyxynitrite by ketones,



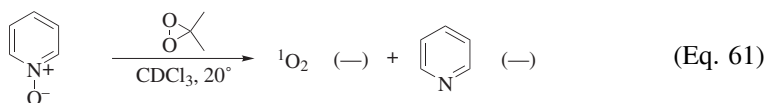
Scheme 17. Catalytic decomposition of peroxyxynitrite by methyl pyruvate.

such as methyl pyruvate, is rationalized in terms of peroxyxynitrite oxidation by the in situ generated dioxirane (Scheme 17).¹⁶³

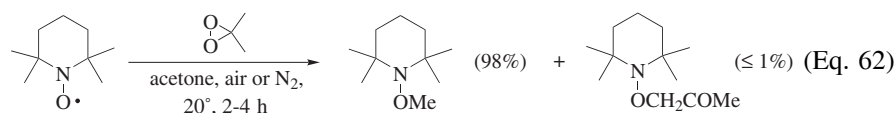
Potassium superoxide (KO_2) decomposes DMD in acetone solution, releasing singlet oxygen as detected by chemiluminescence.⁹⁴ Furthermore, a catalytic amount of $n\text{-Bu}_4\text{NI}$ efficiently converts two molecules of TFD into singlet oxygen and trifluoroacetone (Eq. 60).¹⁶⁴



Aliphatic and aromatic tertiary amine oxides also react with dioxiranes to generate free amines and singlet oxygen (Eq. 61).^{26,165} Since the N -oxide is prepared by DMD oxidation of the tertiary amine, treatment of the latter with excess DMD causes decomposition of the DMD by the in situ formed N -oxide, with concomitant release of O_2 .²⁶ The mechanism of this oxidation is presented in Scheme 4.

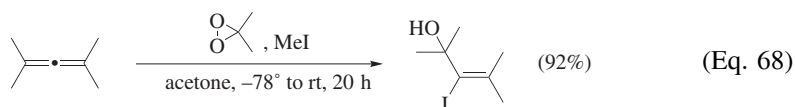
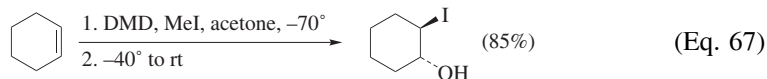
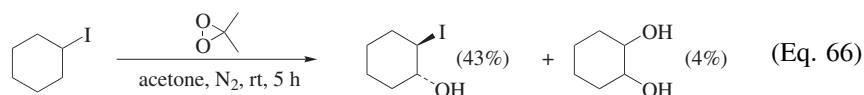
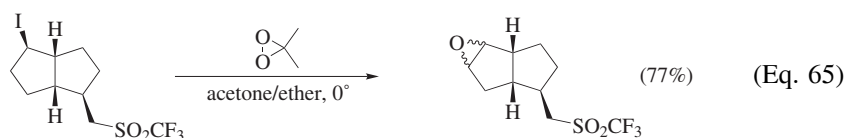
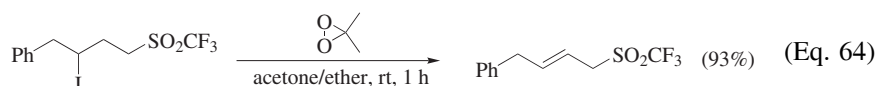
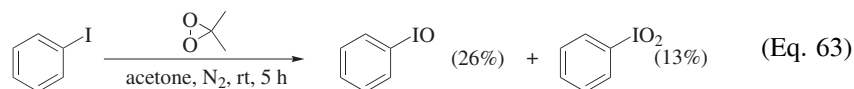


The dioxirane oxidation of an N -oxyl radical is illustrated in Eq. 62.^{23,166} The reaction follows a complex radical mechanism to give two O -alkylated products.



Halogens. There are only a few reports on the dioxirane oxidation of halogen-containing compounds. The oxidation of the chloride ion to the hypochlorite ion by DMD (in situ) has been known since the very beginning of dioxirane chemistry. In fact, this reaction constitutes the first example of a dioxirane oxidation.¹⁶¹ Iodometry,^{121,167} which utilizes the oxidation of iodide anion under acidic conditions, serves as the method for quantitative determination of dioxirane concentration.

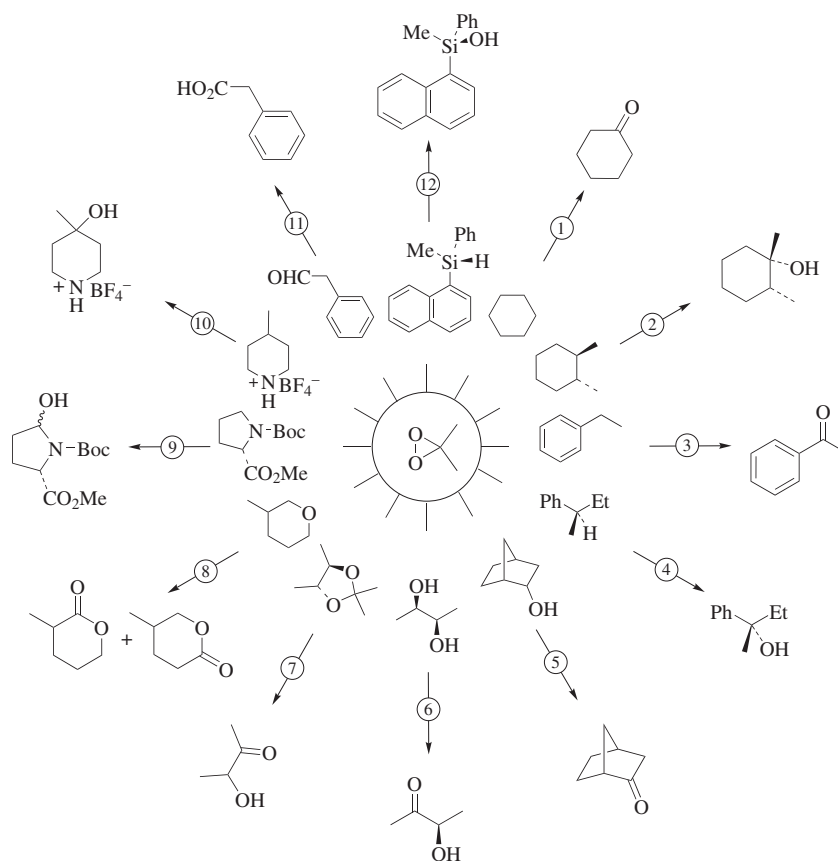
Organoiodides are also prone to dioxirane oxidation, as illustrated by the DMD oxidation of iodobenzene to a mixture of iodobenzene and iodylbenzene (Eq. 63).¹⁶⁸ In contrast, alkyl iodides afford labile primary oxidation products, which eliminate the oxidized iodine functionality resulting in alkenes (Eq. 64).¹⁶⁹ In such oxidations, the alkene product may be converted to an epoxide, as illustrated when the cyclic iodide in Eq. 65 is oxidized by DMD (isol.).¹⁶⁹ The oxidation of iodocyclohexane by DMD (isol.) under nitrogen leads to the iodohydrin and diol as unexpected products (Eq. 66).¹⁶⁸ The formation of iodohydrin, the major product, clearly reveals that hypoiodous acid (HOI) is generated in situ, which in turn adds to the liberated cyclohexene. Indeed, when methyl iodide is oxidized by moist DMD (isol.) at subambient temperature in the presence of cyclohexene, the corresponding iodohydrin is obtained (Eq. 67).¹⁷⁰ When an allene is used as substrate for this reaction, an allylic alcohol with a vinyl iodo functional group is obtained in high yield (Eq. 68).¹⁷¹



Alkanes and Silanes

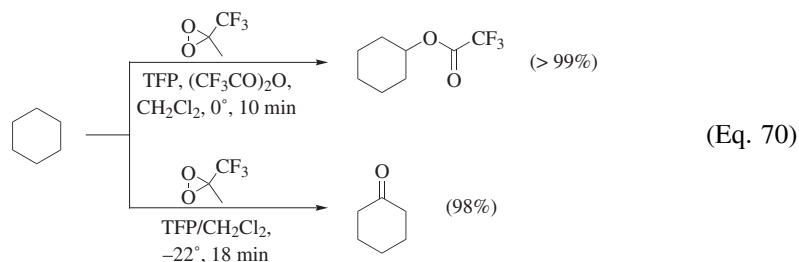
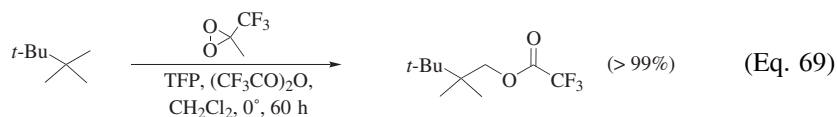
One of the highlights of dioxirane chemistry is the facile oxidation of C–H and Si–H σ bonds. Some typical examples of these oxidations are collected in the rosette of Scheme 18. Both DMD (isol.) and TFD (isol.) are employed for the oxidation of alkanes; TFD is more effective than DMD. In a few cases in situ generated dioxiranes have also been employed for this purpose.

Alkanes. Usually, alkanes are difficult to functionalize, but dioxiranes, especially TFD (isol.), effect hydroxylation under mild conditions. Their reactivity order follows the sequence primary < secondary < tertiary < benzylic < allylic C–H bonds. Only one example of hydroxylation by TFD (isol.) at a primary position of an unfunctionalized alkane (without secondary and tertiary C–H bonds) appears to have been reported (Eq. 69);¹⁷² in contrast, papers on hydroxylation at a secondary position are relatively abundant. For example, cyclohexane gives cyclohexanone as the only product in high yield (98%) under exceedingly

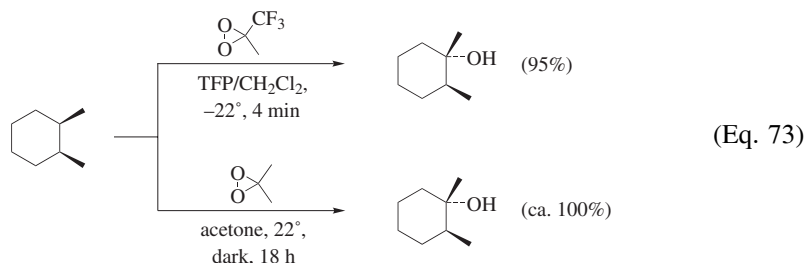
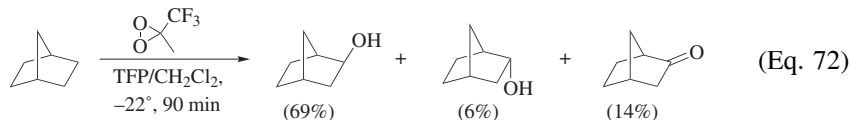
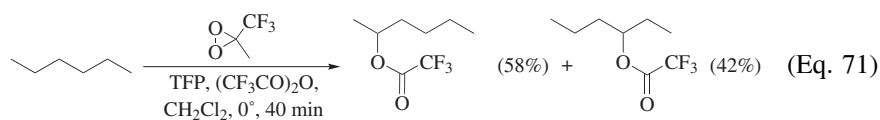


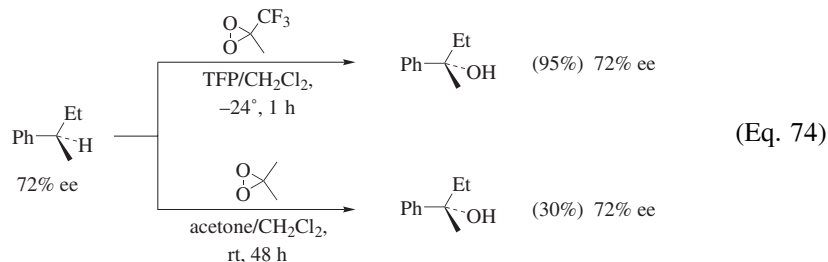
Scheme 18. An overview of dioxirane oxidations of alkanes and silanes.

mild conditions (Eq. 70). The primary oxidation product, namely cyclohexanol, is more reactive toward dioxirane oxidation than cyclohexane. Oxidation of the secondary alcohol may be circumvented by in situ acylation with trifluoroacetic anhydride (Eq. 70). Related cycloalkanes follow this reactivity pattern.^{30,172,173}

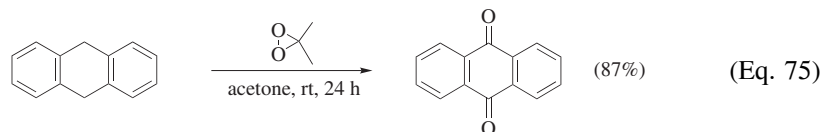


When *n*-alkanes are used, a mixture of regioisomeric ketones is usually obtained,¹⁷² unless the intermediary secondary alcohols are again protected in situ through acylation (Eq. 71).¹⁷³ Oxidation of bicyclic substrates usually affords a mixture of diastereomers (Eq. 72).³⁰ That the hydroxylation of a tertiary C–H bond is preferred over primary and secondary C–H bonds is exemplified in the oxidation of *cis*-1,2-dimethylcyclohexane by either DMD (isol.)¹⁷⁴ or TFD (isol.) (Eq. 73).³⁰ The resulting tertiary alcohol of this C–H insertion also demonstrates that oxygen transfer takes place stereoselectively, i.e., with complete retention at the stereogenic center. Absolute stereoretention has been rigorously confirmed by employing optically active 2-phenylbutane as substrate (Eq. 74).³¹

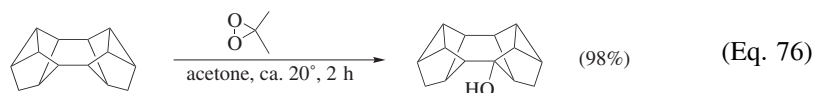




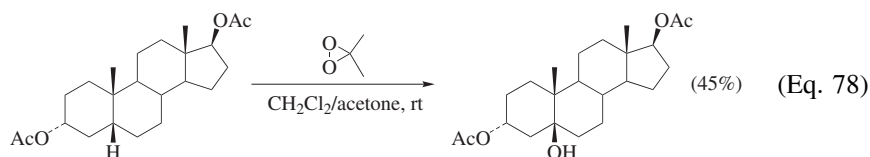
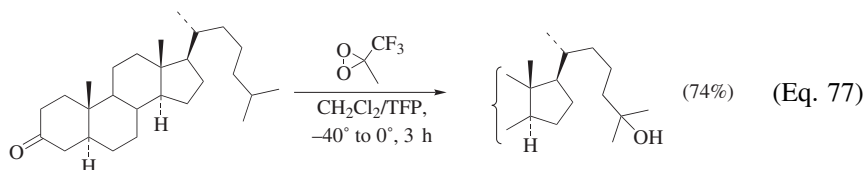
Benzylic C–H bonds are particularly reactive toward dioxirane oxidation, with numerous examples documented in the literature.¹⁷⁵ A preparatively useful approach is shown in Eq. 75, in which a benzhydryl C–H bond is oxyfunctionalized.¹⁷⁶



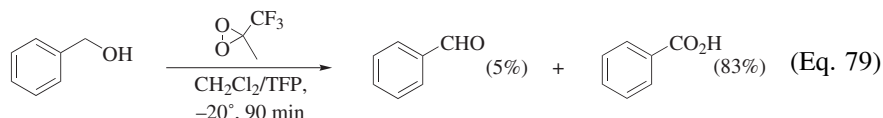
The oxidation of alkanes by dioxiranes is a convenient and useful method in organic synthesis. For example, the polycyclic substrate in Eq. 76¹⁷⁷ is hydroxylated in near quantitative yield by DMD (isol.). Such a transformation would be difficult to realize with conventional oxidants. Similarly, all four bridgehead positions in adamantane may be hydroxylated by TFD (isol.) on repetitive oxidation, affording the tetrahydroxy derivative.¹⁷⁸



Tertiary C–H bonds in the side chains of several steroids have also been selectively hydroxylated (Eq. 77).¹⁷⁹ In the absence of such C–H bonds, the tertiary C–H bond at the junction of the A and B rings is hydroxylated (Eq. 78).¹⁸⁰ This chemoselectivity derives presumably from steric factors, since the tertiary C–H bond in the side chain is sterically more exposed.

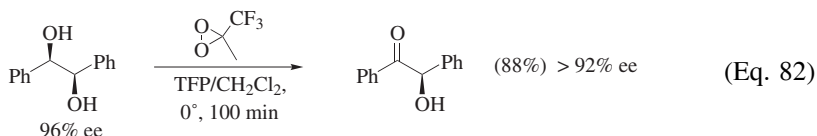
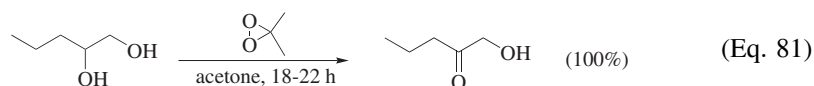
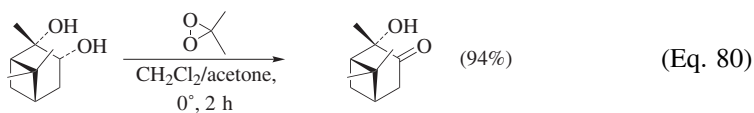


Carbon-hydrogen bonds adjacent to functional groups on the carbon atom are usually more reactive toward dioxirane oxidation, as has already been illustrated for alcohols. Primary alcohols, although much less reactive compared to secondary alcohols, are oxidized to aldehydes and/or carboxylic acids (Eq. 79).²⁹

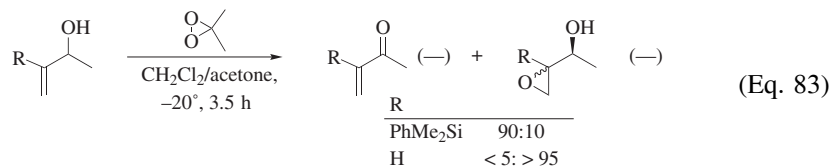


The same reaction may be responsible for the slow decomposition of DMD (isol.) in methanol.¹⁸¹ Consequently, primary and secondary alcohols are not recommended as solvents for conducting oxidations with DMD (isol.) and especially TFD (isol.).

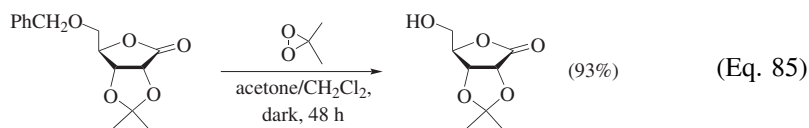
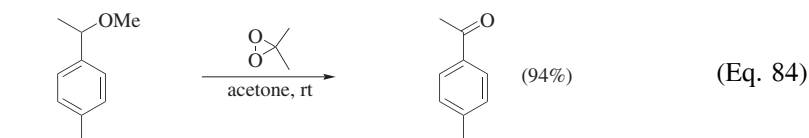
The oxidation of secondary alcohols, which is actually a very facile reaction, leads to the corresponding ketone as the product; expectedly, the tertiary hydroxy functionality is not oxidized (Eq. 80).¹⁸² The reactivity difference between primary and secondary alcohols may be exploited for chemoselective oxidation, as shown in Eq. 81.¹⁸³ Such oxidative transformations of vicinal diols to the corresponding α -hydroxy carbonyl products are particularly useful in organic synthesis, since the latter comprise valuable building blocks. In view of the mild oxidation conditions, this transformation has been employed for the preparation of optically active α -hydroxy ketones from the corresponding diols, as exemplified in Eq. 82.¹⁸⁴ Since the requisite enantioenriched diols may be readily obtained by a Sharpless dihydroxylation, this oxidation constitutes a convenient and effective entry into non-racemic α -hydroxy ketones.



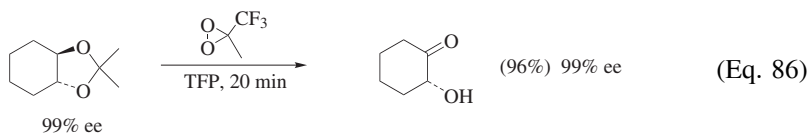
Oxidation of C–H bonds is usually more difficult than epoxidation; however, steric effects can cause allylic C–H oxidation to compete efficiently with epoxidation.¹⁸⁵ In the reaction shown in Eq. 83 the large silyl group directs the DMD oxidation preferably toward C–H insertion (for a detailed discussion see ref. 15).



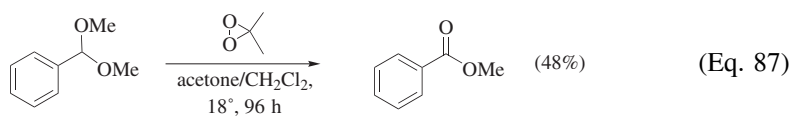
Conversion of the alcohol into the corresponding ether derivative reduces reactivity; however, DMD (isol.), and even more so TFD (isol.), oxidize such substrates to their respective carbonyl products (Eq. 84).¹⁸⁶ Since even ethers, such as diethyl ether and tetrahydrofuran, may be cleaved by dioxiranes, they are not recommended as solvents for dioxirane oxidations. Indeed, for the successful preparation of TFD (isol.), use of ether-free 1,1,1-trifluoropropan-2-one (TFP) is essential.¹⁸⁷ Nevertheless, when properly controlled, oxidation of ethers provides a useful method for the deprotection of the benzyl group in carbohydrates (Eq. 85).^{188,189}

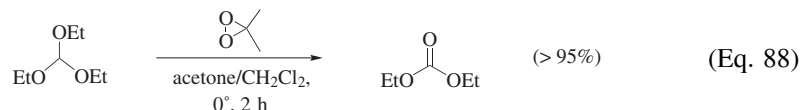


Acetals of vicinal diols are also subject to α -oxidation by dioxirane, especially with the more reactive TFD (isol.). For example, oxidative cleavage of an acetal functionality to the corresponding α -hydroxy ketone (Eq. 86)¹⁹⁰ constitutes a convenient deprotection protocol, coupled with an alcohol oxidation. Like the oxidation of vicinal diols, the second stereogenic center is preserved. Although further oxidation of α -hydroxy ketones to 1,2-diketones is possible, such reactions are sluggish because of electronic reasons, in that the α -carbonyl group deactivates the C-H bond. Thus, 1,2-diketones are not usually formed in appreciable amounts in the dioxirane oxidation of vicinal diols or their acetals.^{184,190}

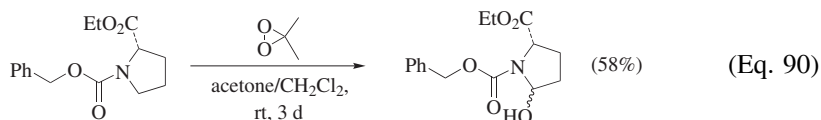
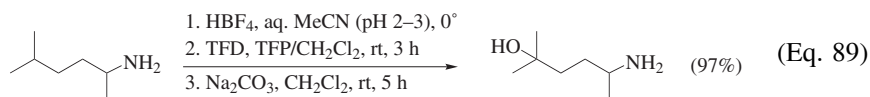


Dioxirane oxidation of the acetals of aldehydes leads to esters (Eq. 87),^{189,191} similarly, oxidation of orthoformates furnishes carbonates (Eq. 88).¹⁹¹

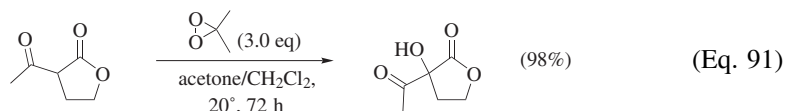




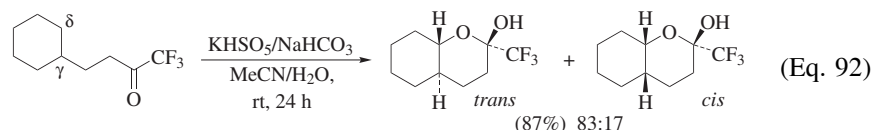
Direct oxidation of the C–H bond in an amine is not feasible given the much higher reactivity of the nitrogen atom; however, protection of the amino group as the ammonium salt (strongly acidic conditions must be used to tie up all of the amine) or as an amide will suppress the nitrogen oxidation effectively (for a detailed discussion of chemoselective dioxirane oxidation see ref. 15). A typical example is shown in Eq. 89.¹⁹² Unlike for alcohols, the α -hydroxylation of an amine is rare. One such example is shown in Eq. 90,⁹³ for which the hydroxylation is made possible by protection of the amine as a carbamate.



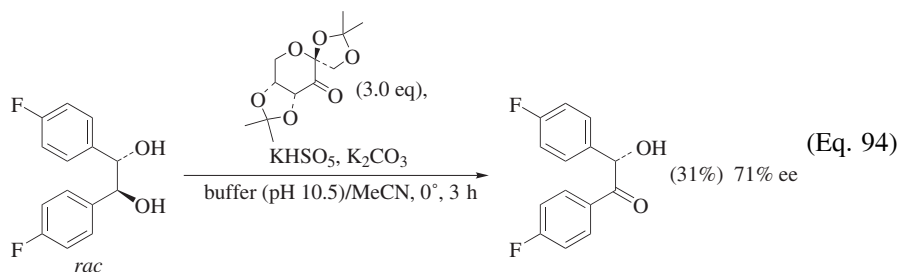
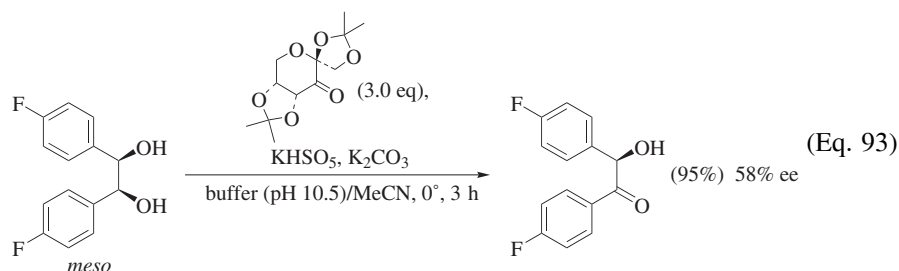
The acidic C–H bond of 1,3-dicarbonyl compounds is also reactive toward dioxirane (both isolated and in situ generated) oxidation (Eq. 91).¹⁹³ Although the oxidation appears like a C–H insertion, the possibility that epoxidation of the enolate is involved cannot be ruled out. The fact that this oxidation may be catalyzed by either Ni(OAc)₂ or Ni(acac)₂ implies involvement of enolate intermediates.¹⁹⁴



As is evident from the above discussion, C–H oxidation is a highly chemoselective reaction. The chemoselectivity is mainly governed by the reactivity of the chemically different C–H bonds, and sometimes by steric factors when the reactivities are similar. In the special situation illustrated in Eq. 92,¹⁹⁵ an in situ generated intramolecular dioxirane chemoselectively oxidizes the C–H bond at the δ site rather than the usually more reactive tertiary hydrogen (γ site) because of a more favorable concerted six-membered cyclic transition state.¹⁹⁵ Moreover, the equatorial C–H bond is preferentially oxidized such that the *trans* product dominates.

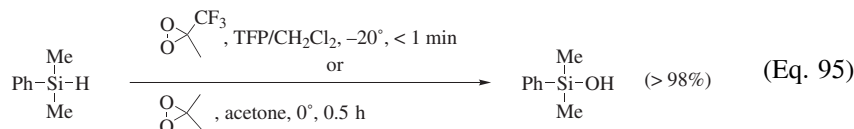


As C–H oxidation by dioxiranes is a stereoselective reaction, an attractive opportunity arises to carry out enantioselective C–H oxidations by employing optically active dioxiranes; however, such asymmetric C–H oxidations by dioxiranes are still largely unexplored. The only known example of enantioselective C–H oxidation appears to be the oxidation of vicinal diols by an in situ generated fructose-derived dioxirane.^{196,197} Through either the desymmetrization of meso-diols (Eq. 93) or the kinetic resolution of racemic diols (Eq. 94), enantioenriched α -hydroxy ketones may be obtained in up to 71% ee.¹⁹⁷ The desymmetrization of the acetals of meso-diols leads to higher enantioselectivities compared with that of meso-diols, but the conversion is lower because of their reduced reactivity.¹⁹⁷

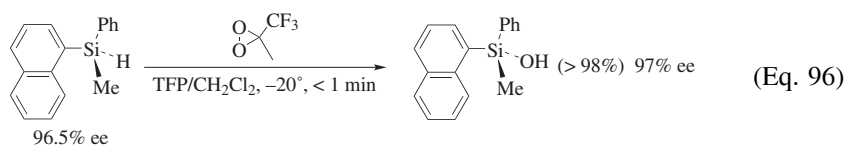


Since presently not much is known about enantioselective C–H oxidation with optically active dioxiranes, more research in this important area is needed. Analogous to the recent development of dioxirane-mediated asymmetric epoxidations, we expect progress in asymmetric C–H functionalization with chiral dioxiranes in the near future. The problem resides in designing more persistent and reactive optically active ketones as the dioxirane precursors.

Silanes. The Si–H bond in silanes is weaker than the C–H bond in alkanes; therefore, the oxidation of silanes is more facile. Nevertheless, only a few examples of silane oxidation by dioxiranes are known. Oxidation of dimethylphenylsilane by TFD (isol.)³⁹ or DMD (isol.)¹⁹⁸ affords the silanol in high yield, as shown in Eq. 95. As in the case of C–H oxidation, TFD is significantly more reactive than DMD toward the Si–H bond. The mild and neutral conditions lead exclusively to silanol product without any formation of disiloxane.



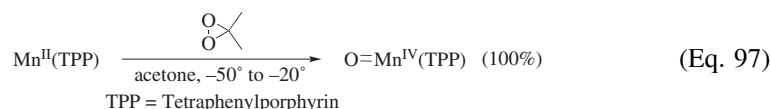
Like C–H oxidation, Si–H oxidation of silanes by dioxirane is also stereoselective. As displayed in Eq. 96, the original configuration of the silane is preserved during the oxidation.³⁹ The hydroxylation of silanes has also been applied to organometallic substrates (see the following section).



Organometallic Compounds

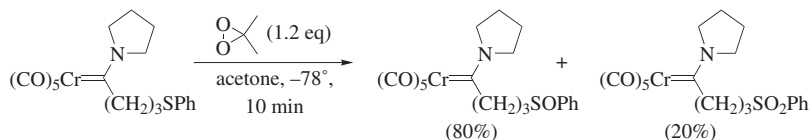
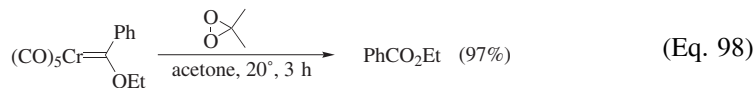
Oxidation of organometallic compounds by dioxiranes is usually more complex since both the metal center as well as the organic ligands may be oxidized. The examples presented in this section include both types of oxidations. Unless redox chemistry at the metal center complicates matters, the more electron-rich organic ligand in the organometallic complex usually undergoes direct oxidation (epoxidation, heteroatom oxidation, σ -bond insertion) by the dioxirane more readily than the metal center. In the case of highly reactive electron-rich alkenes, direct non-selective epoxidation prevails.

Dioxirane oxidation of the metal center leads to a higher oxidation state of the metal. For example, the DMD oxidation of a manganese(II) porphyrin complex at subambient temperature leads to the manganese(IV) derivative in quantitative yield (Eq. 97).¹⁹⁹ Analogously, manganese(III) and iron complexes are oxidized under similar conditions.¹⁹⁹ The use of DMD (isol.) as a stoichiometric oxygen donor in the Jacobsen–Katsuki epoxidation with the manganese-salen catalyst enables the enantioselective epoxidation of prochiral olefins under homogeneous conditions.^{200–203} Since the oxidation of the manganese is much faster than the epoxidation of the olefin, good to excellent enantiomeric excesses are obtained for the epoxides.^{200–203}



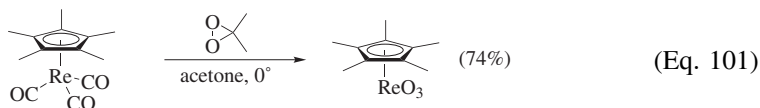
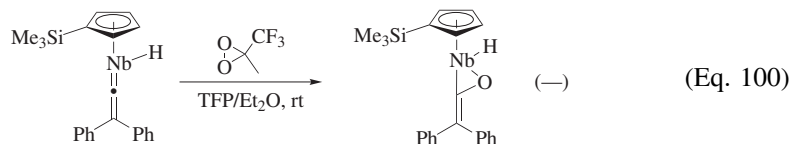
Dioxirane oxidation of metal-carbene complexes usually leads to demetalation.^{204–207} A specific example of such an oxidation by DMD (isol.) is shown in Eq. 98.²⁰⁴ When the ligands of the metal complex contain a functionality that is more prone to oxidation, demetallation may be suppressed (Eq. 99).²⁰⁸ With

even an excess of DMD (2.2 equiv.), a mixture of sulfoxide and the sulfone products is formed exclusively (93% yield) without demetallation.²⁰⁸



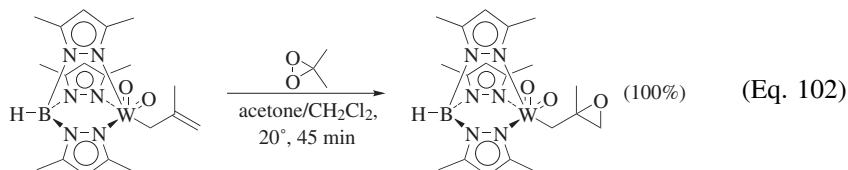
(Eq. 99)

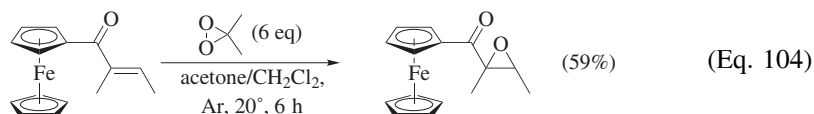
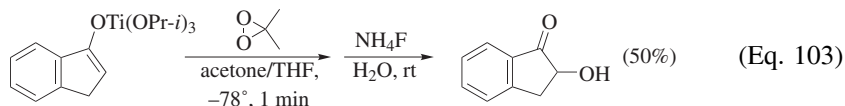
In an unusual example, the niobium complex shown in Eq. 100 is oxidized by TFD (isol.) to the metallaoxirane.²⁰⁹ Selective oxidative decarbonylation reactions of several rhenium and molybdenum carbonyl complexes by DMD (isol.) have also been observed; a particular case for rhenium is given in Eq. 101.²¹⁰



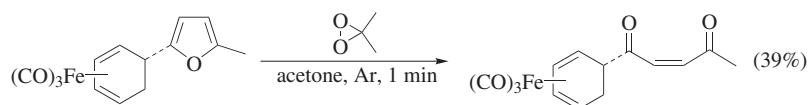
The dioxirane oxidation of ligands in organometallic complexes is more abundant. The chemical nature of the ligand determines whether the oxidation takes place at a π bond (epoxidation), at a lone pair (heteroatom oxidation), or at a σ bond (Si-H insertion).

Organometallic substrates with ligands that contain a reactive C=C double bond may undergo epoxidation. For example, the tungsten complex shown in Eq. 102 is epoxidized by DMD (isol.) in quantitative yield at ambient temperature.²¹¹ Similarly, titanium enolates are functionalized by DMD (isol.) to the corresponding α -hydroxy ketones after acidic workup (Eq. 103).²¹² When enantiomerically pure enolates bearing titanium TADDOLates as chiral ligands are subjected to this oxidation, enantiomerically enriched α -hydroxy ketones are obtained.²¹² If the metal complex is sufficiently robust, even electron-poor double bonds may be epoxidized under more strenuous conditions, as illustrated for the ferrocene derivative shown in Eq. 104.²¹³



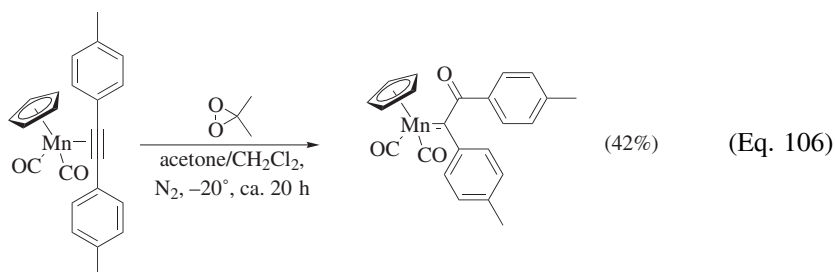


When the C=C double bond is, however, directly coordinated to the metal center, the reactivity drops. For example, oxidation of an iron complex by DMD (isol.) takes place only at the more electron-rich furan ring (Eq. 105).²¹⁴ Thus, the iron-tricarbonyl fragment may be utilized as an oxidatively resistant protecting group for the 1,3-diene functionality.

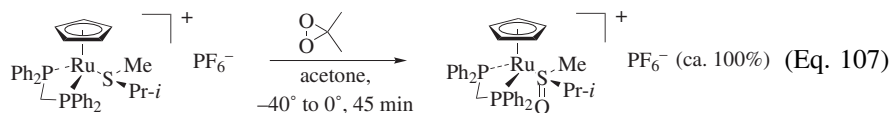


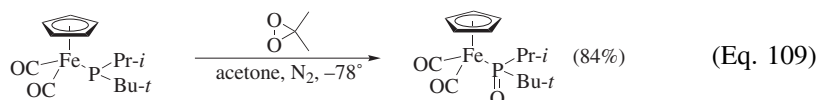
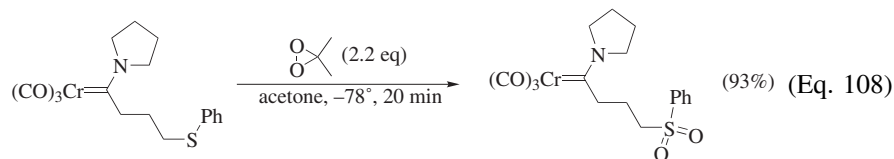
(Eq. 105)

Dioxirane oxidation of cyclopentadiene, ligands widely used in organometallic complexes, has not been reported. Apparently, the complexed cyclopentadiene ligand resists dioxirane oxidation. In contrast, the metal-coordinated triple bond in a manganese-acetylene complex is oxidized by DMD (isol.) to a manganese-carbene complex, as illustrated in Eq. 106.²¹⁵

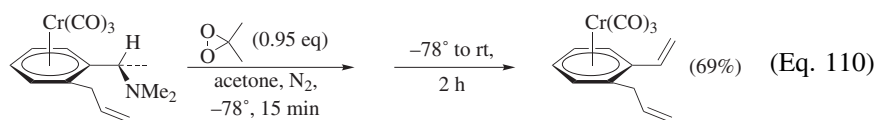


For ligands with a heteroatom functionality (sulfur, phosphorus, or nitrogen), the heteroatom is usually the preferred site of dioxirane oxidation. These oxidations usually follow the general trends presented in the section on Heteroatom Substrates (see above); sulfides are oxidized to sulfoxides (Eq. 107)¹²⁷ and/or sulfones (Eq. 108),²⁰⁸ and phosphines to phosphine oxides (Eq. 109).²¹⁶

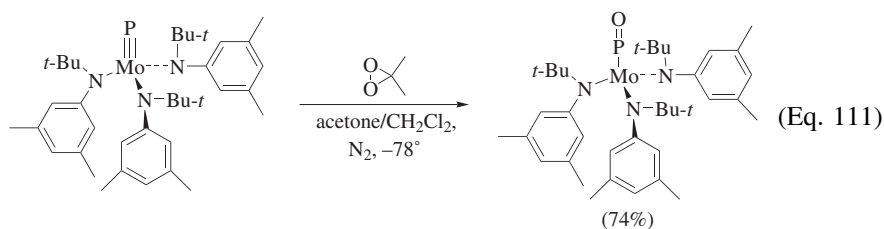




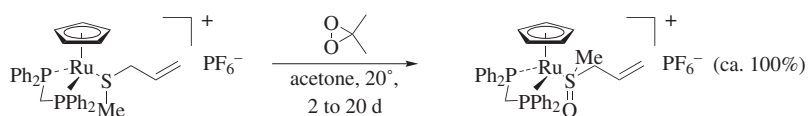
A tertiary amine ligand affords the *N*-oxide with DMD (isol.), which may eliminate hydroxylamine on warming to room temperature, thus generating the vinyl group in the final product (Eq. 110).²¹⁷ This result illustrates that the nitrogen functionality is more readily oxidized than an alkenyl double bond.



Notably, oxidation of a molybdenum complex having a molybdenum-phosphorus triple bond occurs at the trivalent phosphorus ligand, affording the corresponding complex with a P=O functionality (Eq. 111).²¹⁸



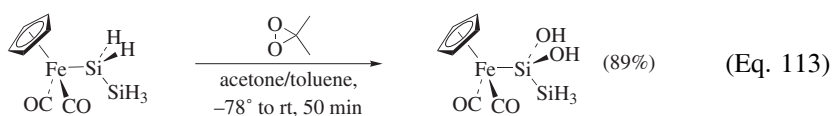
DMD (isol.) mediated oxidation of a ruthenium complex having both sulfide and double-bond functionalities reveals once again that the sulfur atom is more prone to oxidation than the C=C double bond, even though the sulfide functionality is coordinated to the metal center (Eq. 112).²¹⁹ The corresponding epoxide may only be obtained once the sulfur atom has been functionalized.²¹⁹



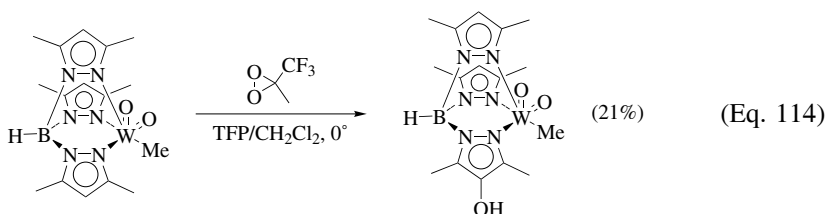
(Eq. 112)

Insertion of oxygen into Si-H with DMD or TFD when Si-H is a component of an organometallic substrate has also been documented. For example, organometallic complexes with silane ligands are successfully hydroxylated by

DMD (isol.).^{220–227} A preparatively valuable example of the regioselective double hydroxylation of a ferriodisilane is shown in Eq. 113.²²⁷



Insertion into a CH bond of a ligand belonging to an organometallic compound is much more difficult. The only case known to date is the TFD (isol.) oxidation of the tungsten-boron complex in Eq. 114,²¹¹ in which hydroxylation of the pyrazole ligand occurs.



COMPARISON WITH OTHER METHODS

The three reaction types of dioxiranes presented in this chapter, namely π -bond oxidation (epoxidation) of allenes, acetylenes, and arenes, lone-pair oxidation of heteroatom substrates (N, S, P heteroatoms), and σ -bond oxidation (CH/SiH insertions) of alkanes and silanes, are quite different in their nature. Consequently, in comparing the dioxirane performance with other oxidants, it is convenient and even essential, to deal with these three classes separately in this subsection. It should, however, be kept in mind that the general features are quite similar, such that considerable overlap in the oxidative behavior exists for these substrates.

Allenes, Acetylenes, and Arenes

The dioxirane oxidation of cumulenes, acetylenes, and aromatic compounds all entail initial formation of epoxides. Some of these epoxides are rather labile and the final oxidation product may be structurally altered. Such functionalizations are to be classified as epoxidation reactions, which have been thoroughly covered in a previous chapter on dioxirane chemistry.¹⁵ The interested reader should consult that coverage for details; herein we reiterate only the more specifically applicable features in regard to oxidants other than dioxiranes.

As cumulenes and arenes are more sluggishly epoxidized than alkenes, potent oxidizing agents must be employed. For example, perhydrates (hexafluoroacetone/ H_2O_2),^{228,229} oxaziridines,^{230–232} and the Payne oxidation reagents ($\text{MeCN}/\text{H}_2\text{O}_2/\text{HO}^-$)^{233–235} are hardly suitable. In addition, oxidations catalyzed by most transition metals (Co, Cr, Mn, Mo, Ti, V, W) are relatively ineffective for these substrates. An exception is rhenium, which in the form of methyltrioxorhenium

(MTO), efficiently oxidizes cumulenes and arenes, with the advantage that the MTO/H₂O₂ oxidant operates catalytically.⁴⁰

It is most unfortunate that the usually highly efficient enantioselective Jacobsen–Katsuki epoxidation with chiral manganese-salen complexes is not applicable to functionalize cumulenes and arenes to the corresponding optically active oxidation products. Similarly, the optically active ketones (such as Shi's fructose-derived ketone^{132,236}) employed in the catalytic, enantioselective, in situ mode of epoxidation are also ineffective for these substrates because of their low oxidative reactivity.

Peracids (most frequently *m*CPBA) are usually employed for the oxidation of cumulenes, acetylenes, and arenes, but as already pointed out,^{77–86} isolated dioxiranes are more advantageous for the preparation of labile epoxides. The disadvantage of peracids resides in the fact that acid-sensitive substrates and/or products must be avoided. When the acidity is buffered, the substrate and resulting epoxide must resist hydrolysis. Such limitations are not an issue when isolated dioxiranes are used, but the in situ mode of generating dioxiranes is subject to the same disadvantages as for peracids. The benefits of dioxirane chemistry should be conspicuous for the oxidation of allenes, acetylenes, and arenes.

Heteroatom Substrates

Of the substrates considered in this chapter, those with heteroatoms are the easiest to oxidize, such that many oxidizing agents are available. For some heteroatoms, particularly divalent sulfur/selenium and more so trivalent phosphorus compounds, even H₂O₂ without activation will do, although the rate of oxidation is relatively slow. In the context of reactivity, dioxiranes present no definite advantages as heteroatom oxidants over the traditional ones such as peracids²³⁷ and transition-metal catalysts.²³⁸ (For a detailed comparison of the reactivity and selectivity of the methyltrioxorhenium (MTO) catalyst with dioxiranes, see a recent review.⁴⁰)

On the contrary, overoxidation by the more reactive dioxiranes may be a more serious problem to control. Whereas sp³-type (amines, hydroxylamine, hydrazines) and sp²-type (imines, oximes, hydrazones, heteroarenes) nitrogen-containing substances are readily oxidized to a plethora of products, the direct oxidation of the sp-type nitrogen atom in nitriles to the corresponding nitrile oxides is still a difficult task even for the highly reactive TFD. Similarly, the oxidative functionalization of amides and imides lacks suitable oxidizing agents, since neither dioxiranes nor traditional oxidants serve this purpose.

A unique chemical property of dioxiranes is their propensity to oxidize oxygen-type nucleophiles (e.g., HO₂⁻, RO₂⁻, RC(O)O₂⁻, ClO⁻) to molecular oxygen; the latter is formed in the singlet-excited state, namely singlet oxygen.^{26,27} This unusual transformation appears not to have an equivalent among other oxidants. It is a consequence of the high electrophilic character of the dioxiranes, which makes them amenable for attack by the oxygen-centered nucleophile on the peroxide bond of the dioxirane. Some amine *N*-oxides¹⁶⁵ also engage in this type of reaction and are deoxygenated into singlet-excited molecular oxygen and the free amine, again a unique chemical behavior of dioxiranes.

As for enantioselective oxidations, specifically sulfoxidation, the chiral dioxiranes, such as Shi's fructose-based dioxirane,^{132,236} are inferior to the asymmetric oxygen transfer catalyzed by transition metals, namely the $\text{Ti}(\text{OR})_4/t\text{-BuO}_2\text{H}$ oxidant (Kagan sulfoxidation²³⁹). The ability, however, to achieve the asymmetric efficiency delivered by oxidative enzymes²⁴⁰ and microorganisms^{241,242} is still a formidable task in oxidation chemistry, particularly for chiral dioxiranes. Nevertheless, sulfoxides of high enantiomeric purity may be obtained through the sequence of desymmetrizing a prochiral sulfide by complexation with a transition metal based chiral auxiliary, followed by DMD oxidation, and final removal of the chiral auxiliary.¹²⁶ Such methodology should be able to compete in efficacy with the established protocols such as the Kagan enantioselective sulfoxidation.²³⁹

The dioxirane-related oxaziridines, which in optically active form deliver sulfoxides with enantioselectivities up to 98% ee, are effective for asymmetric sulfoxidation.^{243,244} Oxaziridinium salts also show promise and offer potential, but, as yet, enantioselectivity of only about 35% ee has been achieved.²⁴⁵

Alkanes and Silanes

Indisputably, the greatest challenge in oxidation chemistry is still the direct functionalization of unactivated C–H bonds. It is especially desirable to carry out such insertion reactions enantioselectively under catalytic conditions. Nature has perfected oxygen-atom insertions into C–H bonds by developing efficacious enzymes for this purpose, namely the oxidases and oxygenases.²⁴⁶ Along these lines, biomimetic oxidants based on chemical catalysts have been developed,²⁴⁷ most notably for the remote hydroxylation of steroids.^{248–250}

Although as yet the dioxiranes do not offer a general method for the enantioselective functionalization of hydrocarbons, it should be appreciated that these readily accessible oxidants, especially the simple structures DMD and TFD, work as impressively as they do. In this context, we reiterate that such non-metal-catalyzed C–H insertions by dioxiranes may take place highly stereoselectively as, for example, with complete retention of configuration in the hydroxylation of (*R*)-2-phenylbutane (see Scheme 5) by DMD.³⁷ Indeed, even a few asymmetric C–H oxidations with optically active dioxiranes, such as Shi's fructose-derived system,^{196,197} have been reported to occur in substantial enantiomeric excess, under quasi-catalytic conditions. These simple metal-free functionalizations of alkanes approach the efficiency of enzymatic C–H insertions. However, their catalytic efficiency still needs to be improved. The future challenges in dioxirane chemistry lie in enhancing the catalytic reactivity of these oxidants to achieve high enantioselectivity.

There are only a few alternative chemical methods that are competitive with dioxiranes; most comprise metal-catalyzed and radical-type C–H oxidations. One such method is the so-called "Gif oxidation,"²⁵¹ which is of limited synthetic utility because complex product mixtures are usually obtained.²⁵² A detailed comparison of metal-catalyzed C–H insertion with methyltrioxorhenium (MTO) and with dioxiranes has been made recently.⁴⁰ Generally, the performance (reactivity, selectivity) of the dioxiranes is better, but the MTO/H₂O₂ oxidant offers excellent catalytic efficiency. An effective nonmetal-type C–H oxidation of alcohols

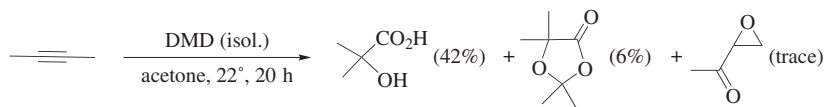
to ketones is catalyzed by the TEMPO nitroxyl radical, which has the advantage over dioxiranes that C=C double bonds may be present, since this reagent does not effect epoxidation.^{253–263} In fact, this method may be used for the kinetic resolution of secondary alcohols to afford ee values of up to 98% by engaging chiral binaphthyl-based nitroxyl radicals.²⁶⁴

Silanes are more readily oxidized than alkanes, since the Si–H bond (ca. 77 kcal/mol) is considerably weaker than the C–H bond (ca. 99 kcal/mol). The advantages of dioxiranes for oxygen insertion into Si–H bonds has been amply emphasized;^{39,198} a competitive alternative is the catalytic MTO/H₂O₂ oxidant.⁴⁰ For oxidation of optically active silanes, the urea/H₂O₂ adduct (UHP) should be employed instead of hydrogen peroxide to obtain enantioselectivities comparable to those of dioxiranes.¹⁹⁹

EXPERIMENTAL CONDITIONS

Caution! The dioxiranes DMD and TFD are volatile peroxides and must be handled with care. The oxidations should be carried out in a hood with good ventilation. Inhalation and direct exposure to skin must be avoided! Although no explosions have been reported for dioxiranes, all safety precautions should be employed!

EXPERIMENTAL PROCEDURES

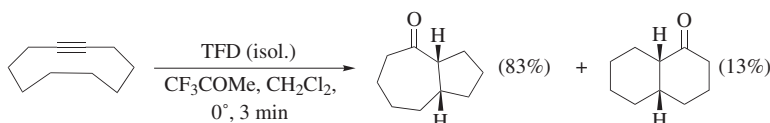


2-Hydroxy-2-methylpropanoic Acid [Oxidation of an Alkyne with DMD (isol.)].⁶³ To a magnetically stirred solution of 2-butyne (216 mg, 4.00 mmol) in acetone (5.0 mL) in a 250-mL flask, was added a solution of DMD in acetone (140 mL, 0.060 M, 8.40 mmol) at room temperature (ca. 22°). The progress of the reaction was followed by GLC analysis, which indicated the presence of three products in the ratio of 10 : 15 : 75. After 20 hours, the excess acetone was removed on a rotary evaporator (20°, 15 mmHg), the dark yellow residue (25 mL) was subjected to fractional distillation (80°, 5 mmHg) to afford a colorless material which solidified. The solid was recrystallized from CH₂Cl₂/hexane to give 174 mg (42%) of 2-hydroxy-2-methylpropanoic acid as colorless needles, mp 77–79°; ¹H NMR (CDCl₃) δ 1.50 (s, 6H), 6.30 (br s, 2H); ¹³C NMR (CDCl₃): δ 27.0, 72.2, 181.4; EIMS *m/z* (%): 89 (5), 59 (100), 45 (7), 44 (4), 43 (53).

The yellow distillate contained two other products, which were separated by preparative GLC. One of the products was obtained in trace amount and identified

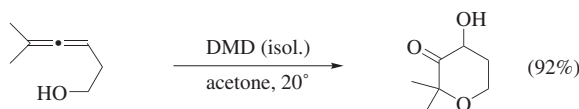
as 1-oxiranylethanone: ^1H NMR (CDCl_3) δ 2.06 (s, 3H), 2.90 (dd, $J = 5.7$, 2.5 Hz, 1H), 3.01 (dd, $J = 5.7$, 4.7 Hz, 1H), 3.40 (dd, $J = 4.6$, 2.5 Hz, 1H); ^{13}C NMR (CDCl_3) δ 23.7, 45.8, 53.7, 205.5. EIMS m/z (%): 87 (M + H, 1), 86 (M^+ , 17), 85 (13), 71 (18), 55 (7), 53 (1), 44 (3), 43 (100).

The other product, 2,2,5,5-tetramethyl-1,3-dioxolane-4-one, was isolated by distillation (80° , 5 mmHg) as a colorless liquid (18 mg, 6%); IR (KBr) 2990, 2936, 1797, 1466, 1380, 1301, 1192, 1076, 1015, 931, 868, 838 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.48 (s, 6H), 1.58 (s, 6H); ^{13}C NMR (CDCl_3) δ 26.5, 28.6, 77.2, 109.3, 175.7; EIMS m/z (%): 130 (1.3), 129 (M-CH₃, 22), 101 (20), 100 (8), 59 (81), 58 (39), 43 (100).



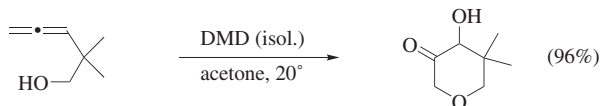
***cis*-Bicyclo[5.3.0]decan-2-one [Oxidation of an Alkyne with TFD (isol.)].⁶⁴**

A 25-mL flask was charged with cyclodecyne (136 mg, 1.00 mmol) and a trifluoroacetone solution of TFD (isol.) (20.0 mL, 0.010 M, 2.00 mmol) at 0° . After magnetic stirring for 3 minutes, the volatiles were removed on a rotary evaporator (10° , 15 mmHg), and the residue was purified by column chromatography on silica gel, to give the title compound (126 mg, 83%); ^{13}C NMR (50 MHz, CDCl_3) δ 21.0, 21.7, 22.1, 23.1, 28.0, 29.7, 43.4, 58.3, 59.2, 206.5. Further elution resulted in isolation of *cis*-bicyclo[4.4.0]decan-2-one (22 mg, 13%): ^{13}C NMR (50 MHz, CDCl_3) δ 24.5, 25.4, 26.2, 27.8, 32.5, 32.2, 40.4, 43.2, 54.6, 214.0.

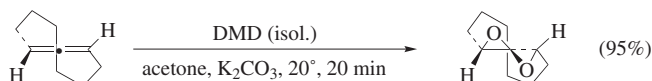


6-Hydroxy-2,2-dimethyl-3-oxacyclohexanone [Oxidation of an Allene with DMD (isol.)].⁵⁷

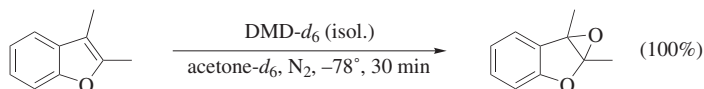
A 25-mL flask at 20° was charged with 5-methyl-3,4-hexadien-1-ol (22 mg, 0.20 mmol) and a solution of DMD (12.0 mL, 0.100 M, 1.20 mmol) under vigorous stirring. Removal of the solvent on a rotary evaporator (20° , 15 mmHg), followed by chromatographic purification on silica gel, afforded the title compound as a colorless liquid (26 mg, 92%); IR 3425, 1720, 1158, 1076 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.37 (s, 3H), 1.39 (s, 3H), 1.99 (m, 1H), 2.51 (m, 1H), 3.20–3.80 (br s, 1H), 3.87 (ddd, $J = 13.0$, 5.0, 2.0 Hz, 1H), 4.05 (ddd, $J = 13.0$, 12.0, 4.0 Hz, 1H), 4.55 (dd, $J = 12.0$, 7.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.6, 23.8, 36.3, 59.0, 70.1, 80.3, 212.0. EIMS m/z (%): 145 (14), 127 (9), 116 (10), 99 (2), 87 (11), 85 (5), 83 (100), 71 (3). HRMS calcd for $\text{C}_7\text{H}_{13}\text{O}_3$ (M + H), 145.0860, found 145.0865.



6-Hydroxy-5,5-dimethyl-3-oxacyclohexanone [Oxidation of an Allene with DMD (isol.)].⁵⁷ A 25-mL flask was charged at 20° with 2,2-dimethyl-3,4-pentadien-1-ol (20 mg, 0.180 mmol) and a solution of DMD (18.0 mL, 0.100 M, 1.80 mmol) under vigorous magnetic stirring. Removal of the excess solvent on a rotary evaporator (20°, 15 mmHg), followed by chromatographic purification on silica gel afforded 6-hydroxy-5,5-dimethyl-3-oxacyclohexanone as a colorless liquid (25 mg, 96%); IR 3460, 1727, 1248, 1106 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.94 (s, 3H), 1.08 (s, 3H), 3.40–3.50 (br s, 1H), 3.63 (dd, *J* = 15.0, 12.0 Hz, 2H), 4.00 (dd, *J* = 14.4, 1.2 Hz, 1H), 4.02 (br s, 1H), 4.13 (dd, *J* = 14.4, 0.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 17.7, 22.6, 42.8, 72.7, 76.4, 81.0, 206.9. EIMS *m/z* (%): 145 (23), 144 (16), 127 (4), 101 (5), 85 (37), 71 (100). HRMS calcd for C₇H₁₃O₃ (M + H), 145.0860, found 145.0865.

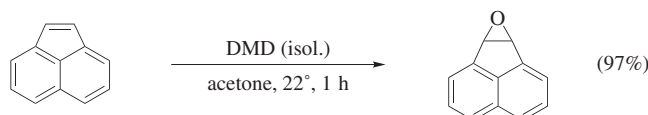


2,5-Hexamethylene-1,4-dioxaspiro[2.2]pentane [Diepoxidation of a Cyclic Allene with DMD (isol.)].¹⁶ To a stirred solution of DMD (0.100 M, 4.44 mmol) in acetone (40.0 mL) dried over K₂CO₃, was added the cyclic allene (112 mg, 0.900 mmol) at 20°. Stirring was continued for 20 minutes at the same temperature. The solvent was removed on a rotary evaporator (20°, 15 mmHg), and the product was separated from the K₂CO₃ by triturating with ether (3 × 10 mL). The combined ether triturates were filtered, dried (MgSO₄), and concentrated (20°, 15 mmHg) to give the title compound (135 mg, 95%) as a colorless oil; IR 1626, 1605 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35–1.42 (m, 6H), 1.49–1.54 (m, 2H), 1.69–1.74 (m, 2H), 2.12–2.18 (m, 2H), 3.75 (dd, *J* = 6.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 20.1, 24.7, 27.4, 60.1, 84.3; EIMS *m/z* (%): 154 (8), 130 (29), 98 (100), 82 (83), 69 (65). HRMS calcd for C₉H₁₄O₂, 154.0994, found 154.1000.



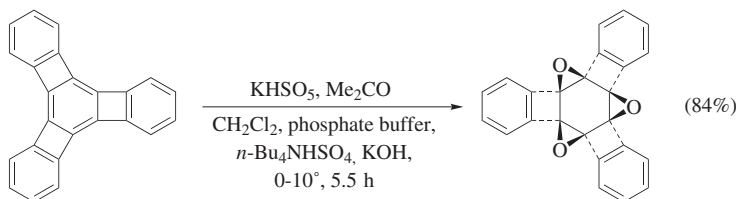
2,3-Epoxy-2,3-dihydro-2,3-dimethylbenzo[*b*]furan [Epoxidation of a Benzofuran with DMD-*d*₆ (isol.)].⁸⁷ A 5-mm NMR tube was charged with an acetone-*d*₆ solution of 2,3-dimethylbenzo[*b*]furan (113 μL, 0.220 M, 25 μmol) at –78° under a N₂ atmosphere. By means of a syringe, a well-dried (over 4 Å molecular sieves) DMD-*d*₆ (isol.) solution in acetone-*d*₆ (500 μL, 0.0500 M, 25 μmol) was added rapidly at –78°. After 30 minutes, the NMR tube was

submitted to low-temperature (-50°) ^{13}C -NMR spectroscopy, which revealed that the olefinic carbon resonances in 2,3-dimethylbenzo[*b*]furan were replaced by the characteristic epoxide resonances for the product. At temperatures higher than 0° , complete decomposition of the epoxide occurred within 30 minutes.



1,2-Epoxyacenaphthene [Epoxidation of an Arene with DMD (isol.)].²⁶⁵

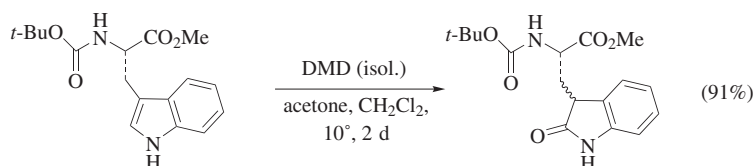
To a magnetically stirred solution of acenaphthylene (611 mg, 4.02 mmol) in acetone (5.0 mL) was added an acetone solution of DMD (66.0 mL, 0.0620 M, 4.09 mmol) at room temperature (ca. 20°). The progress of the reaction was monitored by GLC, which indicated that acenaphthylene was converted into its 1,2-epoxide within one hour. Removal of the solvent on a rotary evaporator (20° , 15 mmHg) afforded a white solid, which was taken up into CH_2Cl_2 (30 mL) and dried over Na_2SO_4 . After removal of the drying agent, the solvent was removed on a rotary evaporator first at 20° , 15 mmHg and subsequently at 20° , 5 mmHg, to give the analytically pure oxide (654 mg, 97%), mp $83\text{--}84^{\circ}$; ^1H NMR (CDCl_3) δ 4.81 (s, 2H), 7.39–7.77 (m, 6H).



Bisbenzo[3',4']cyclobuta[1',2':1,2:1'',2'':3,4]biphenyleno[1,8*b*-*b*:2,3-*b*':4,4-*a*-*b*'']trisoixirene [Epoxidation of an Arene with DMD (in situ)].⁶⁷

To a solution of tris(benzocyclobutadieno)cyclohexatriene (1.50 g, 5.06 mmol) in an acetone/ CH_2Cl_2 mixture (350 mL, 5 : 2 v/v) contained in a 1000-mL three-necked flask were added phosphate buffer (50 mL) and tetra-*n*-butylammonium hydrogen sulfate (200 mg, 0.590 mmol). A solution of potassium monoperoxysulfate (46.0 g, 30.2 mmol) in water (225 mL) was added dropwise under vigorous magnetic stirring at $0\text{--}10^{\circ}$ over 1.5 hours. The pH was maintained at 7.5–8.5 by the dropwise addition of an aqueous solution of KOH (2–3%). The reaction mixture was stirred for an additional 4 hours and then mixed with an equal volume of ice-cold water. The reaction mixture was extracted with CH_2Cl_2 (1×150 mL), the extract was washed with ice-cold water (3×100 mL), and the combined organic layers were dried (K_2CO_3). The solvent was removed on a rotary evaporator (20° , 15 mmHg) and the solid residue was purified by preparative TLC on silica gel with CH_2Cl_2 /hexane (1 : 1) as eluent. Recrystallization from the same solvent mixture gave the oxide as colorless plates (1.48 g, 84%), mp $180\text{--}182^{\circ}$;

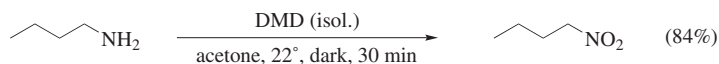
IR (KBr) 1613, 1512, 1495, 1463, 1430, 1339, 1261, 1154, 1094, 1003, 918, 861, 802, 751 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (m, 6H), 7.46 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 76.3, 122.6, 131.5, 143.71. EIMS m/z (%): 348 (M^+ , 11), 316 (8), 261 (10), 248 (9), 176 (21), 175 (100), 174 (11), 156 (61), 135 (22), 127 (20), 123 (30), 121 (22), 107 (18), 85 (11), 73 (38).



Methyl Boc- β -(2,3-dihydro-2-oxo-indol-3-yl)alaninate [Oxidation of an Indole with DMD (isol.)].⁹³

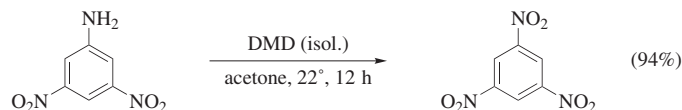
A 10-mL flask equipped with a magnetic stirring bar was charged with a solution of Boc-Trp-OMe (292 mg, 0.910 mmol) in CH_2Cl_2 (5.0 mL). After cooling to 10° by means of an ice bath, a freshly prepared acetone solution of DMD (23.0 mL, 0.100 M, 2.30 mmol) was added. Stirring was continued for 2 days at 10° . The solvent was removed (10° , 15 mmHg) and the residue was purified by flash column chromatography on silica gel, with a mixture of EtOAc and hexane as eluent, to afford two diastereoisomers (A : B = 1 : 1, 91% yield). Diastereomer A: $[\alpha]^{25}_{\text{D}} - 221.4^\circ$ (c 1.0, CHCl_3); ^1H NMR (200 MHz, CDCl_3) δ 1.38 (s, 9H), 2.39–2.57 (m, 2H), 3.76 (s, 3H), 4.19–4.32 (m, 1H), 5.44 (s, 1H), 6.59–6.62 (m, 1H), 6.63–6.84 (m, 1H), 7.09–7.20 (m, 1H), 7.21–7.31 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3): δ 28.2, 41.4, 52.3, 59.8, 81.2, 84.3, 110.5, 119.4, 123.2, 130.3, 148.3, 154.1, 173.9, 175.2; EIMS m/z (%): 334 (M^+ , 18). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5$: C, 61.06, H, 6.63, N, 8.38. Found: C, 61.0, H, 6.59, N, 8.15.

Diastereomer B: $[\alpha]^{25}_{\text{D}} + 83.6^\circ$ (c 1.0, CHCl_3); ^1H NMR (200 MHz, CDCl_3) δ 1.42 (s, 9H), 2.57–2.64 (m, 2H), 3.64 (s, 3H), 4.58–4.78 (m, 1H), 5.30–5.45 (m, 1H), 6.88–7.05 (m, 2H), 7.12–7.32 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 28.2, 42.1, 52.2, 61.8, 81.6, 98.6, 115.1, 121.9, 123.2, 130.2, 149.1, 154.5, 172.4, 173.9; EIMS m/z (%): 334 (M^+ , 16). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5$: C, 61.06, H, 6.63, N, 8.38. Found: C, 61.10, H, 6.63, N, 8.19.

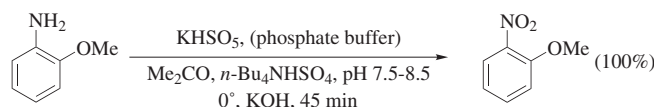


1-Nitrobutane [Oxidation of a Primary Aliphatic Amine with DMD (isol.)].²⁶⁶

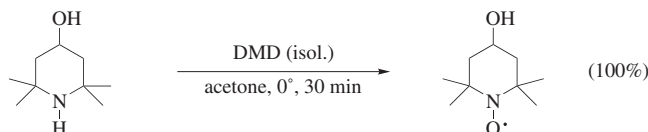
A 150-mL flask was charged with a solution of *n*-butylamine (52 mg, 0.700 mmol) in acetone (5.0 mL), and an acetone solution of DMD (95.0 mL, 0.050 M, 4.80 mmol). The mixture was stirred at room temperature (ca. 20°) for 30 minutes in the dark. The solvent was removed on a rotary evaporator (20° , 20 mmHg), to afford the title compound (62 mg, 84%).



1,3,5-Trinitrobenzene [Oxidation of a Primary Aromatic Amine with DMD (isol.)].¹⁰¹ To a stirred solution of 3,5-dinitroaniline (30 mg, 0.165 mmol) in acetone (5.0 mL) was added an acetone solution of DMD (30.0 mL, 0.0600 M, 1.80 mmol) at room temperature (ca. 20°). After the reaction mixture was stirred for 12 hours, excess solvent was removed on a rotary evaporator (20°, 15 mmHg), and the residue was purified by preparative TLC on silica gel with CH₂Cl₂/hexane (1 : 1) as eluent. The product streak was scraped from the plate and extracted from the silica gel with CH₂Cl₂ (15 mL) that contained 5% methanol. Evaporation of the volatiles under reduced pressure (20°, 15 mmHg) gave 1,3,5-trinitrobenzene (33 mg, 94%), mp 121–122°.

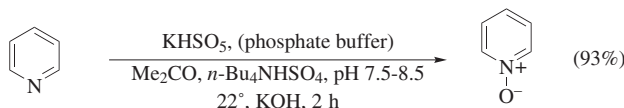


***o*-Nitroanisole [Oxidation of a Primary Aromatic Amine with DMD (in situ)].**²⁶⁷ A 500-mL, three-necked round-bottomed flask, fitted with two addition funnels and a pH electrode, was charged with *o*-anisidine (1.10 mL, 10.0 mmol), CH₂Cl₂ (100 mL), acetone (100 mL), an aqueous solution of sodium phosphate (50 mL, 0.080 M), and tetra-*n*-butylammonium hydrogen sulfate (170 mg, 0.500 mmol). In one of the addition funnels was placed an aqueous solution of KHSO₅ (150 mL, 20.0 g, 32.0 mmol), and in the other an aqueous solution of KOH (100 mL, 150 mL). After the mixture was cooled to 0°, the aqueous solution of KHSO₅ was added dropwise over 30 minutes, while maintaining the pH between 7.5–8.5 by dropwise addition of an aqueous solution of KOH (2.00 N). After addition, the mixture was stirred at the same temperature for 15 minutes and then treated with 1 mL of methyl sulfide to destroy residual peroxide. The suspended material was removed by filtration and the organic layer was washed with water (50 mL), dried (MgSO₄), and concentrated (20°, 15 mmHg). The residue was purified by column chromatography on silica gel (50 g) with CH₂Cl₂ as eluent to afford *o*-nitroanisole (1.50 g, 100%).



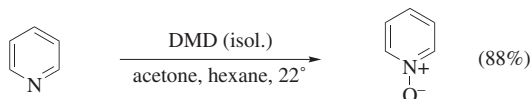
1-Oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine [Oxidation of a Hindered Secondary Amine with DMD (isol.)].⁹⁷ To a magnetically stirred solution of 2,2,6,6-tetramethylpiperidinol (312 mg, 2.00 mmol) in acetone (20 mL) in a

100-mL flask was slowly added a pale yellow stock solution of DMD (60.0 mL, 0.0670 M, 4.00 mmol) at 0° (ice bath). The reaction mixture turned to deep yellow within 10 minutes. After stirring was continued for another 30 minutes, the solvent was removed on a rotary evaporator (20°, 15 mmHg) to afford the nitroxide (354 mg, 100%) as a bright yellow powder, mp 71–72°.



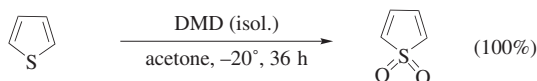
Pyridine *N*-Oxide, Method A [Oxidation of Pyridine with DMD (in situ)].¹²¹

To a 500-mL, three-necked flask, equipped with a mechanical stirrer, was added pyridine (1.00 g, 12.6 mmol), acetone (5 mL, 68.0 mmol), and phosphate buffer (50 mL). An aqueous solution of potassium monoperoxysulfate (100 mL, 18.3 g, 29.8 mmol) was added dropwise by means of an addition funnel. Simultaneously, an aqueous solution of KOH (1.00 N) was added in portions to maintain the pH at 7.5–8.0. After completion of the addition, the reaction mixture was stirred for 2 hours, then extracted with CH₂Cl₂ (4 × 30 mL). The combined extracts were dried (MgSO₄) and concentrated (20°, 15 mmHg). The residue was crystallized from a CH₂Cl₂/hexane mixture to afford the pyridine oxide (1.10 g, 93%) as a white crystalline solid, mp 64–65° (lit.²⁶⁸ mp 65–66°); ¹H NMR (60 MHz, CDCl₃) δ 7.30–7.50 (m), 8.3–8.5 (m).



Pyridine *N*-Oxide, Method B [Oxidation of Pyridine with DMD (isol.)].¹²¹

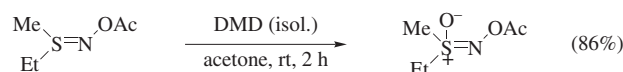
To a stirred mixture of an acetone solution of pyridine (0.50 mL, 0.200 M, 7.90 mg, 0.10 mmol) and a hexane solution of decane (0.50 mL, 0.100 M) was added an acetone solution of DMD (1.00 mL, 0.116 M, 0.116 mmol) at room temperature (ca. 20°). The solvent was removed (20°, 15 mmHg) leaving pyridine *N*-oxide (8.4 mg, 88%).



Thiophene 1,1-Dioxide [Oxidation of Thiophene with DMD (isol.)].¹⁴¹

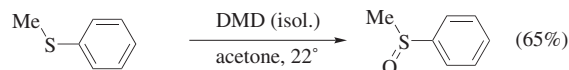
A 50-mL flask was charged with an acetone solution of thiophene (10.0 mL, 84 mg, 1.00 mmol) at –20° and an acetone solution of DMD (isol.) (30 mL, 0.100 M, 3.00 mmol) was added rapidly under magnetic stirring at –20°. Stirring was continued at the same temperature for 36 hours. The solvent and unreacted DMD were removed (below –40°, 5 mmHg) to afford pure thiophene 1,1-dioxide as

colorless plates (116 mg, ca. 100%); UV (CHCl_3) 245 (870) and 288 (1070) nm; IR (neat) 1152, 1306, 1327, 1530, 3100, 3175 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , -40°) δ 6.53–6.61 (m, 2H), 6.75–6.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , -40°) δ 129.3, 113.1; HRMS calcd for $\text{C}_4\text{H}_4\text{O}_2\text{S}$, 115.9932, found 115.9931.



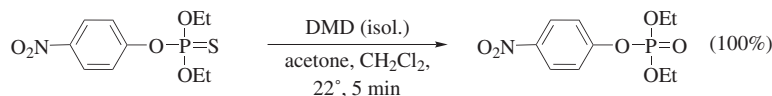
S-Ethyl-S-methyl-N-(acetyl)sulfoximine [Oxidation of a Sulfilimine with DMD (isol.)].¹⁴⁸

A 25-ml flask, supplied with a magnetic stirrer, was charged with a solution of the substituted sulfilimine (20 mg, 0.150 mmol) in acetone (5 mL). An acetone solution of DMD (4.0 mL, 0.080 M, 0.32 mmol) was added dropwise at 0° . The reaction mixture was stirred for 2 hours at room temperature; the reaction progress was monitored by TLC (silica gel). After complete consumption of the sulfilimine, the solvent was removed (20° , 15 mmHg) and the residue was purified by column chromatography on silica gel with a mixture of $\text{Et}_2\text{O}/\text{MeOH}$ (95 : 5) as eluent, affording the sulfoximine (20 mg, 86%) as an oil; ^1H NMR (300 MHz, CDCl_3) δ 1.40 (t, $J = 7.0$ Hz, 3H), 2.40 (s, 3H), 3.30 (s, 3H), 3.50 (q, $J = 7.0$ Hz, 2H), 7.20–7.80 (m, 4H). Anal. Calcd for $\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$: C, 40.25, H, 7.43, N, 9.39. Found: C, 40.01, H, 7.33, N, 9.46.



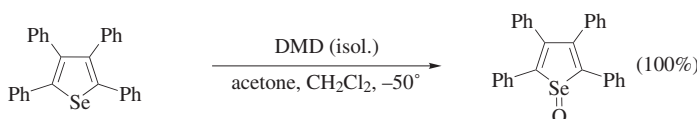
Methyl Phenyl Sulfoxide [Oxidation of a Thioether with DMD (isol.)].¹²¹

A 10-mL flask was charged with a solution of phenyl methyl sulfide (13.6 mg, 0.11 mmol) in acetone (0.50 mL) and an acetone solution of DMD (0.58 mL, 0.189 M, 0.110 mmol) at ca. 20° . The reaction mixture was stirred at room temperature (ca. 22°) until consumption of the sulfide was complete as determined by GC analysis. The solvent was removed under reduced pressure (20° , 15 mmHg) and the crude product was purified by preparative TLC on silica gel by elution with a mixture of hexane and EtOAc to afford the solid phenyl methyl sulfoxide (11 mg, 65%).

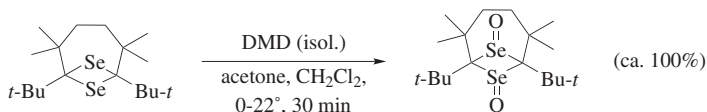


Diethyl 4-Nitrophenylphosphate [Oxidation of a Thiophosphate with DMD (isol.)].¹⁵⁰ An acetone solution of DMD (200 mL, 0.100 M, 20.0 mmol), dried over 4 Å molecular sieves, was added rapidly to a magnetically stirred dry CH_2Cl_2 solution of *O,O*-diethyl *O*-(4-nitrophenyl)thiophosphate (10.0 mL, 29 mg, 0.100 mmol) at room temperature (ca. 20°). After standing for 5 minutes, the crude

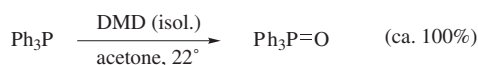
reaction mixture was diluted with pentane (10 mL) and dried (MgSO_4). The drying agent was removed by filtration and washed with pentane (5 mL), and the filtrate was concentrated on a rotary evaporator (20° , 15 mmHg), affording the title compound (27 mg) in quantitative yield; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.38 (t, $J = 7.0$ Hz, 3H), 1.39 (t, $J = 7.0$ Hz, 3H), 4.25 (q, $J = 7.0$ Hz, 2H), 4.32 (q, $J = 7.0$ Hz, 2H), 7.38 (dd, $J = 9.0$ Hz, 1.0 Hz, 2H), 8.24 (dd, $J = 9.0$, 1.0 Hz, 2H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3) δ 15.9, 16.1, 65.2, 65.3, 120.4, 125.0, 148.2, 155.7; $^{31}\text{P NMR}$ δ -6.6.



Tetraphenylselenophene 1-Oxide [Oxidation of a Selenophene with DMD (isol.)].¹⁵⁵ A cold (-50°) acetone solution of DMD (11.50 mL, 0.086 M, 1.00 mmol) was added to a cold (-50°), vigorously stirred dry CH_2Cl_2 solution of tetraphenylselenophene (2.0 mL, 435 mg, 1.00 mmol). After complete addition, the solvent was removed (-40° , 0.001 mmHg), to afford the title compound (451 mg) in quantitative yield; IR (KBr) 3056, 1596, 1573, 1487, 1444, 817, 788, 761, 743, 710, 693 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.91 (d, $J = 7.2$ Hz, 4H), 7.10 (t, $J = 7.2$ Hz, 4H), 7.16 (t, $J = 7.2$ Hz, 2H), 7.19–7.27 (m, 6H), 7.29–7.36 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 128.0, 128.1, 128.6, 128.8, 129.4, 129.5, 131.9, 134.7, 147.2, 150.0; $^{77}\text{Se NMR}$ (76 MHz, CDCl_3) δ 1014. Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{OSe}$: C, 74.50, H, 4.47. Found: C, 73.98, H, 4.44.

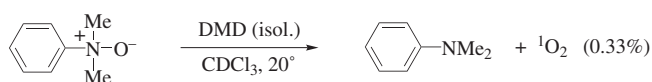


1,6-Di-tert-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo[4.1.1]octane 7-endo, 8-endo-Dioxide [Oxidation of a Selenoether with DMD (isol.)].¹³⁴ To a stirred solution of the starting diselenetane (65 mg, 0.160 mmol) in CH_2Cl_2 (10 mL) was added an acetone solution of DMD (5.0 mL, 0.082 M, 0.410 mmol) in three portions at 0° . The mixture was warmed to room temperature (ca. 20°) and magnetically stirred for 30 minutes. The solvent was removed (20° , 20 mmHg) to give spectroscopically pure title compound (70 mg, ca. 100%) as a colorless powder, which decomposed above 80° ; IR (KBr) 824 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.23–1.30 (m, 2H), 1.47 (s, 6H), 1.51 (s, 18H), 1.73 (s, 6H), 4.30–4.37 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 28.4, 31.6, 35.4, 38.8, 43.9, 49.0, 97.3. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{Se}_2\text{O}_2$: C, 49.09, H, 7.78. Found: C, 48.63, H, 7.74.

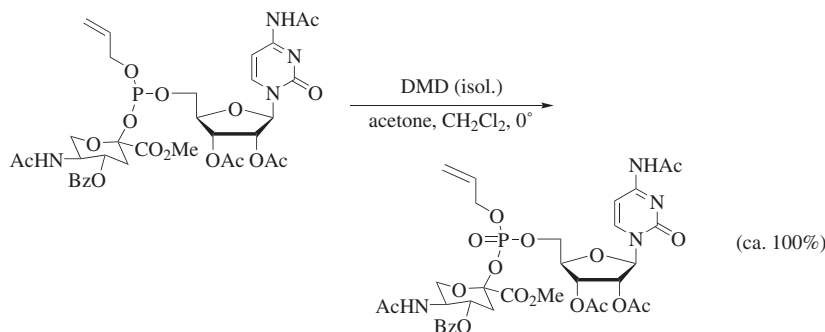


Triphenylphosphine Oxide [Oxidation of a Phosphine with DMD (isol.)].¹²¹

To a stirred solution of triphenylphosphine (26 mg, 0.100 mmol) in acetone (0.50 mL) was added a freshly prepared acetone solution of DMD (0.50 mL, 0.185 M, 6.9 mg, 0.0900 mmol) at room temperature (ca. 20°). Capillary GC was used to monitor the reaction progress by injecting 1.0- μ L aliquots of the reaction mixture at intervals of 15–30 minutes (the peak areas of the triphenylphosphine and its oxide product were compared). Removal of the solvent (20°, 15 mmHg) afforded triphenylphosphine oxide (27.8 mg, ca. 100%).

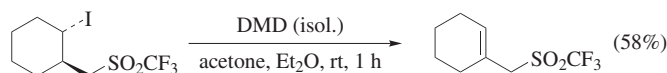
**Singlet-Oxygen Generation by Oxidation of *N,N*-Dimethylaniline *N*-Oxide with DMD (isol.).¹⁶⁵**

To a stirred solution of *N,N*-dimethylaniline *N*-oxide in CDCl_3 (1.0 mL, 0.50 mM) was added a CDCl_3 solution of DMD (0.080 M, 3 equiv.) at 20°. The reaction mixture was magnetically stirred at this temperature for 10 minutes. The consumption of the dioxirane was monitored by means of the peroxide test (KI/HOAc), while the amount of singlet oxygen (0.33%) was determined by its characteristic IR chemiluminescence at 1268 nm using a photodiode detector.

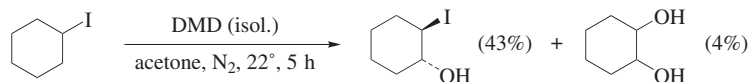
**[(2*S*,4*S*,5*S*)-5-Acetylamino-4-benzoyloxy-2-methoxycarbonyltetrahydropyran-2-yl] Propen-2-yl *N*-Acetyl-2',3'-di-*O*-acetyl-5'-cytidylate [Oxidation of a Phosphite to a Phosphate with DMD (isol.)].¹⁵⁸**

To a cold (0°) stirred solution of the starting phosphite (9.7 mg, 0.0120 mmol) in CH_2Cl_2 (1 mL) was added an acetone solution of DMD (162 μ L, 0.083 M, 0.0310 mmol) at 0°. After 10 minutes, the reaction mixture was concentrated on a rotary evaporator (0°, 15 mmHg) to give the title compound (9.9 mg, 100%) as a colorless foam (the product was contaminated with the α -linked diastereomer); ^1H NMR (500 MHz, CDCl_3) δ 1.89 (s, 4.3H), 1.91 (s, 3.2H), 2.02 (s, 6.6H), 2.08 (s, 12.0H), 2.15 (s, 15.2H), 2.22 (s, 4.4H), 2.25 (s, 3.7H), 2.74 (dd, $J = 13.5, 4.8$ Hz, 1H), 2.92 (dd, $J = 13.7, 4.5$ Hz, 1.4H), 3.32 (dd, $J = 14.9, 4.4$ Hz, 0.2H), 3.76–3.80

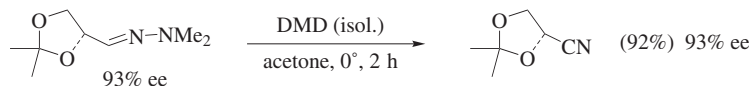
(m, 1.8H), 3.80 (m, 1.8H), 3.82 (s, 3.4H), 3.85–3.90 (m, 1.8H), 4.18–4.22 (m, 2.6H), 4.29–4.49 (m, 10.2H), 4.54–4.63 (m, 4.0H), 4.69 (t, $J = 7.4$ Hz, 2.0H), 5.26–5.40 (m, 6.6H), 5.44 (d, $J = 3.6$ Hz, 2.5H), 5.47–5.54 (m, 1.5H), 5.64 (dd, $J = 4.8, 4.0$ Hz, 1.0H), 5.89–6.02 (m, 2.6H), 6.24 (d, $J = 2.8$ Hz, 1.0H), 6.37 (d, $J = 6.2$ Hz, 0.9H), 6.67 (d, $J = 7.7$ Hz, 0.8H), 6.95 (d, $J = 8.7$ Hz, 0.8H), 7.36–7.48 (m, 7.9H), 7.53–7.58 (m, 2.5H), 7.83 (d, $J = 7.3$ Hz, 0.5H), 7.92–8.02 (m, 5.4H), 8.56 (d, $J = 7.7$ Hz, 1.1H), 8.90 (s, 1.2H), 9.12 (s, 0.9H); ^{31}P NMR (203 Hz, CDCl_3) δ -4.54, -4.60.



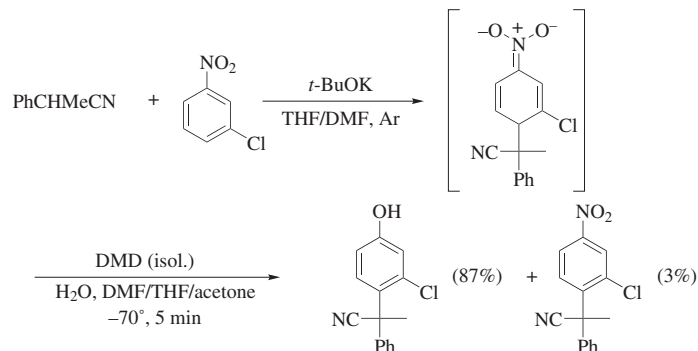
1-[(Trifluoromethyl)sulfonyl]methylcyclohexene [Oxidation of an Idoalkane with DMD (isol.).]¹⁶⁹ A 10-mL flask, equipped with a magnetic stirring bar, was charged at 25° with 356 mg (1.00 mmol) of *trans*-1-iodo-2-[(trifluoromethyl)sulfonyl]methylcyclohexane in ether (5 mL) and an acetone solution of DMD (20.0 mL, 0.100 M, 2.00 mmol). After the mixture was stirred at 25° for 1 hour, the solvent was removed (10°, 15 mmHg) and the product was dried to give the title alkene (132 mg, 58%) as a colorless oil.



***trans*-2-Iodocyclohexanol [Oxidation of Iodocyclohexane with DMD (isol.).]**¹⁶⁸ A 25-mL, round-bottomed flask was charged with an acetone solution of DMD (11.0 mL, 0.090 M, 1.0 mmol) at ca. 20° under a N_2 atmosphere. While stirring magnetically, the cyclohexyl iodide (210 mg, 1.00 mmol) was added. After five hours, GLC analysis indicated formation of *trans*-2-iodocyclohexanol (102 mg, 43%) and 1,2-cyclohexanediol (5 mg, 4%).

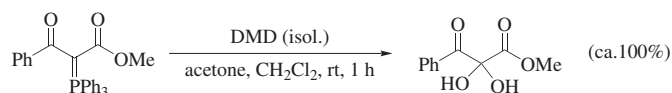


(*S*)-4-Cyano-2,2-dimethyl-1,3-dioxalane [Conversion of a Hydrazone into a Nitrile with DMD (isol.).]¹¹³ A cold (0°) solution of DMD (0.100 M, 1.00 mmol) in acetone (10.0 mL) was added to a cold (0°) acetone solution of (+)-2,3-*O*-isopropylidene-D-glyceraldehyde *N,N*-dimethylhydrazone (5 mL, 86 mg, 0.50 mmol, enantiomeric purity 93%) with vigorous magnetic stirring. The reaction progress was monitored by GLC analysis, which indicated that the starting material was converted into the nitrile product within 2 hours. Removal of the acetone on a rotary evaporator (20°, 15 mmHg) afforded the title compound (58 mg, 92%); $[\alpha]_{\text{D}} + 1.36$ (c 1.33, CHCl_3), 93% optically pure.



2-(2-Chloro-4-hydroxyphenyl)-2-phenylpropionitrile [Tandem Nucleophilic Addition/Conversion of a Nitrobenzene into a Phenol with DMD (isol.)].¹¹⁰

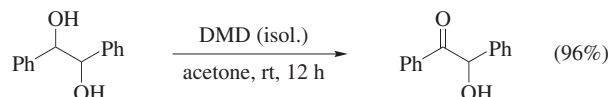
An oven dried, 100-mL, three-necked, round-bottom flask, equipped with a magnetic stirring bar, was charged with t -BuOK (123 mg, 1.10 mmol) and THF (20 mL) at -70° under an argon gas atmosphere. A solution of 2-phenylpropionitrile (131 mg, 1.00 mmol) and 1-chloro-3-nitrobenzene (157 mg, 1.00 mmol) in DMF (1.0 mL) was added at -70° within 2 minutes via syringe. The resulting mixture was magnetically stirred for 5 minutes, and a precooled (-70°) acetone solution of DMD (14.5 mL, 1.20 mmol, 0.0830 M) was added in one portion. After 5 minutes, H_2O (18.0 μL , 1.00 mmol) was added. The mixture was stirred for an additional 5 minutes, hydrolyzed with saturated aqueous NH_4Cl (1.0 mL), raised to 20° , and dried over MgSO_4 . The drying agent was removed by filtration, washed with THF (3×20 mL), and the solvent was evaporated (30° , 12 mmHg). The residue was purified by chromatography on silica gel (4 : 1 hexane/EtOAc, followed by 2 : 1 hexane/EtOAc as eluents) to give the nitro compound (8.6 mg, 3%) as a minor product, and the title phenol (223 mg, 87%) as colorless flakes, mp 180 – 182° ; IR (KBr) 3375, 2236, 1607, 1575, 1495, 1430, 1312, 1291, 1215 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.09 (s, 3H), 5.69 (br s, 1H), 6.81–6.89 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.91–6.94 (d, $J = 2.6$ Hz, 1H), 7.20–7.39 (m, 5H), 7.42–7.50 (d, $J = 8.6$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 29.6, 44.8, 113.9, 118.9, 122.0, 125.8, 127.5, 128.6, 128.8, 129.0, 135.3, 141.3, 156.5; EIMS m/z (%): 257 (M^+), 242 (100), 222, 215, 207, 206, 195, 177, 165, 152, 89, 77. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{ClNO}$: C, 69.91, H, 4.69, N, 5.43, Cl, 13.76. Found: C, 69.74, H, 4.43, N, 5.29, Cl, 13.83.



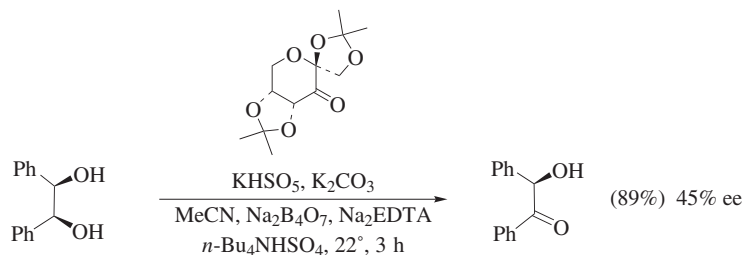
Methyl 3-Phenyl-2,2-dihydroxy-3-oxopropionate [Oxidation of a Phosphorane to a Ketone Hydrate with DMD (isol.)].¹⁵⁹

A 25-mL, round-bottomed flask was charged with a solution of methyl-3-oxo-3-phenyl-2-(triphenylphosphoranylidene)propionate (219 mg, 0.500 mmol) in CH_2Cl_2 (2.0 mL). Under

vigorous magnetic stirring, an acetone solution of DMD (15.0 mL, 1.5 mmol, 0.100 M) was added and the stirring continued at room temperature for one hour until all the starting material had been consumed as monitored by TLC. The reaction mixture was concentrated (20°, 15 mmHg) and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc, 1 : 1 as eluent) to give the product as a yellow oil (105 mg, ca. 100%); IR (neat) 3600–3300, 3060, 2940, 1760, 1750, 1690, 1600, 1450, 1440, 1230, 1130, 1100, 1010 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.66 (s, 3H), 5.81 (br s, 2H), 7.38–7.44 (m, 2H), 7.54–7.58 (m, 1H), 8.05–8.08 (m, 2H); ^{13}C NMR (CDCl_3) δ 53.4, 91.9, 128.6, 129.0, 129.8, 131.1, 170.1, 191.4; HRMS ($M + H$) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_5$, 211.0603, found 211.0606.

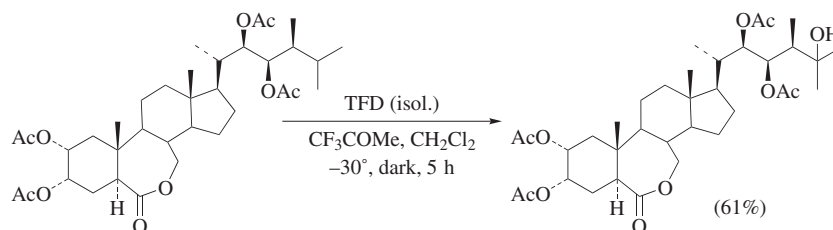


Benzoin. Method A [Oxidation of a Benzyl Alcohol to an Aryl Ketone with DMD (isol.)].²⁶⁹ A 25-mL flask was charged with hydrobenzoin (214 mg, 1.00 mmol) in acetone (1.0 mL) at room temperature, and then a solution (at ca. 20°) of DMD (1.50 mmol, 0.080 M) in acetone (19.0 mL) was added rapidly under vigorous magnetic stirring. The solvent was removed by distillation (20°, 15 mmHg) on a Vigreux column, and the residue was purified by flash column chromatography on silica gel with 1 : 1 hexane/EtOAc as eluent, to afford the benzoin (204 mg, 96%).



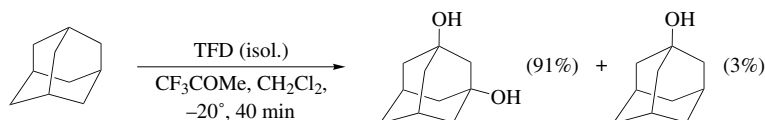
(R)-Benzoin. Method B [Catalytic Asymmetric Oxidation of Hydrobenzoin].¹⁹⁷ To a MeCN solution of *meso*-hydrobenzoin (1.5 mL, 21.4 mg, 0.100 mmol) was added the ketone catalyst 1,2:4,5-bis-*O*-(1-methylethylidene)- β -*D*-*erythro*-2,3-hexodiulo-2,6-pyranose (77.5 mg, 0.300 mmol), Bu_4NHSO_4 (1.5 mg, 4.0 μmol), and $\text{Na}_2\text{B}_4\text{O}_7$ (1.0 mL, 0.050 M) in aqueous Na_2EDTA (4×10^{-4} M) while stirring magnetically at 0°. Solutions of potassium monoperoxy sulfate (92.0 mg, 0.150 mmol) and K_2CO_3 (87.0 mg, 0.630 mmol), each in an aqueous solution (0.65 mL) of Na_2EDTA (4×10^{-4} M), were added simultaneously using syringes over a period of 2 hours. The mixture was stirred for another hour and then diluted with H_2O (20 mL), extracted with ether (3×20 mL), washed with H_2O (2×10 mL), and dried over MgSO_4 . After removal of the solvent on a rotary evaporator (20°, 20 mmHg), the residue was purified by

column chromatography (silica gel) to give the recovered ketone (40–60%) and benzoin (18.9 mg, 89%), with an ee value of 45% for the R enantiomer.



2,3,22,23-Tetra-*O*-acetyl-25-hydroxybrassinolide [Hydroxylation of a Tertiary Carbon Center with TFD (isol.)].²⁷⁰

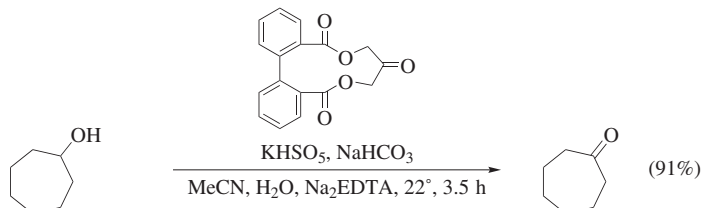
To a stirred solution of 2,3,22,23-tetra-*O*-acetylbrassinolide (20 mg, 0.0300 mmol) in dry CH_2Cl_2 (0.40 mL) was added dropwise a trifluoroacetone solution of TFD (0.20 mL, 0.50 M, 0.10 mmol) at -30° . The reaction mixture was stirred magnetically in the dark for 5 hours at -30° . The solvent was removed on a rotary evaporator (20° , 15 mmHg), and the residue was purified by flash chromatography on silica gel (2:1 hexane/EtOAc as eluent) to give the title compound (12.5 mg, 61%) as colorless needles, mp $226\text{--}229^\circ$; ^1H NMR (600 MHz, CDCl_3) δ 0.73 (s, 3H), 0.98 (s, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 1.04 (d, $J = 7.3$ Hz, 3H), 1.15 (s, 3H), 1.16 (m, 1H), 1.18 (m, 2H), 1.22 (s, 3H), 1.25 (m, 1H), 1.27 (m, 1H), 1.28 (m, 1H), 1.41 (m, 1H), 1.62 (m, 2H), 1.66 (dq, $J = 7.3, 1.0$ Hz, 1H), 1.68 (m, 1H), 1.73 (m, 1H), 1.75 (s, 1H), 1.76 (m, 1H), 1.92 (m, 1H), 1.93 (m, 1H), 1.98 (m, 1H), 2.00 (s, 6H), 2.02 (s, 3H), 2.09 (m, 1H), 2.11 (s, 3H), 2.29 (ddd, $J = 15.1, 12.2, 2.4$ Hz, 1H), 2.99 (dd, $J = 12.2, 4.4$ Hz, 1H), 4.04 (dd, $J = 12.2, 9.3$ Hz, 1H), 4.12 (dd, $J = 12.2, 1.0$ Hz, 1H), 4.87 (ddd, $J = 12.2, 4.4, 2.4$ Hz, 1H), 5.12 (dd, $J = 9.3, 1.0$ Hz, 1H), 5.37 (m, 1H), 5.49 (dd, $J = 9.3, 1.0$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 9.1, 11.7, 12.7, 15.5, 20.8, 21.1, 21.2, 22.2, 24.7, 26.6, 28.1, 28.6, 29.3, 37.1, 38.4, 38.9, 39.2, 39.4, 42.1, 42.5, 43.4, 51.3, 52.4, 58.4, 68.0, 68.9, 70.4, 72.3, 72.4, 75.5, 170.0, 170.2, 170.5, 171.0, 175.0; HRMS (FAB) ($M + H$) calcd for $\text{C}_{36}\text{H}_{57}\text{O}_{11}$, 665.3901, found, 665.3900.



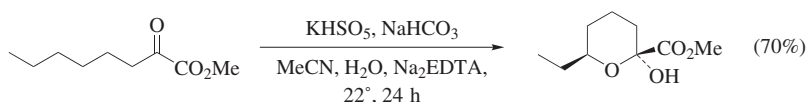
1,3-Dihydroxyadamantane [Dihydroxylation of Adamantane with TFD (isol.)].¹⁷⁸

A solution of TFD (4.60 mL, 0.50 M, 2.30 mmol) in trifluoroacetone/ CH_2Cl_2 (2:1 v/v) at -20° was added to a solution of adamantane (136 mg, 0.100 mmol) in CH_2Cl_2 (5 mL) also at -20° , while stirring vigorously magnetically. The progress of the reaction was followed by GLC analysis, which indicated that 97% of the adamantane was converted to its hydroxylated products in 40 minutes. Removal of the solvent on a rotary evaporator (-20° , 15 mmHg)

afforded a mixture of the 1,3-dihydroxyadamantane (156 mg, 91%) and the monohydroxy adamantane (4.6 mg, 3%).

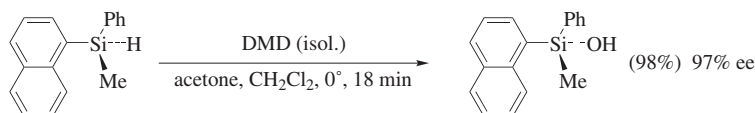


Cycloheptanone [Oxidation of a Secondary Alcohol to a Ketone under In Situ Catalytic Conditions].⁵² To a vigorously stirred solution of cycloheptanol (38.4 mg, 0.300 mmol) in MeCN (1.5 mL), was added an aqueous Na₂EDTA solution (4×10^{-4} M) of 7*H*-dibenzo[*g,i*]-1,5-dioxacycloundecin-5,8,11(9*H*)-trione (catalyst, 1.0 mL, 17.6 mg, 0.0600 mmol) at room temperature (ca. 20°). A mixture of KHSO₅ (282 mg, 0.600 mmol) and NaHCO₃ (156 mg) was added in portions, and consumption of the alcohol was complete after 4 hours as confirmed by GLC analysis. The reaction mixture was poured into water (20 mL), extracted with CH₂Cl₂ (3 × 30 mL), and dried (Na₂SO₄). After removal of the solvent on a rotary evaporator (20°, 15 mmHg), the residue was purified by flash column chromatography (Et₃N-buffered silica gel) to give cycloheptanone (34.4 mg, 91%).

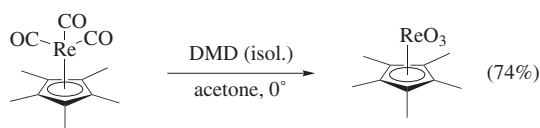


Methyl (*S,*S**)-6-Ethyl-2-hydroxytetrahydropyran-2-carboxylate [Hydroxylation of a Secondary Carbon Center under In Situ Catalytic Conditions].**¹⁹⁵

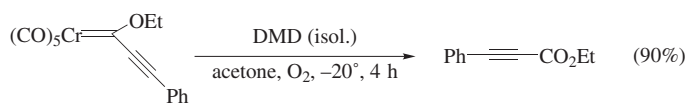
To a magnetically stirred MeCN solution (30 mL) of methyl-2-oxo-octanoate (86 mg, 0.50 mmol) was added an aqueous Na₂EDTA solution (20 mL, 4×10^{-4} M), followed by a mixture of KHSO₅ (1.54 g, 2.5 mmol) and NaHCO₃ (0.65 g) at ca. 20° over a period of 1 hour. After stirring for 24 hours, the reaction mixture was poured into brine (10 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried (MgSO₄), and the solvent was removed on a rotary evaporator (20°, 15 mmHg). The residue was purified by flash column chromatography on silica gel (1 : 4 EtOAc/hexane as eluent) to give the title compound (66 mg, 70%) as a colorless syrup; ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, *J* = 7.5 Hz, 3H), 1.20–1.74 (m, 6H), 1.79–1.97 (m, 2H), 3.60 (s, 1H), 3.82 (s, 3H), 3.85 (m, 1H); ¹³C NMR (68 MHz, CDCl₃) δ 9.8, 18.4, 28.8, 30.0, 30.4, 53.1, 72.5, 94.8, 171.7; EIMS *m/z* (%): 171 (M⁺ – OH, 14), 130 (12), 129 (100), 111 (41).



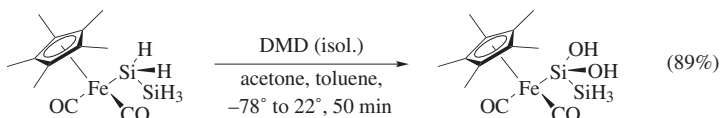
(*R*)-Methylphenyl(1-naphthyl)silanol [Hydroxylation of a Silane with TFD (isol.)].³⁹ A cold (-20°) 1,1,1-trifluoropropanone solution of TFD (80.0 mL, 0.500 M, 4.00 mmol) was rapidly added to a cold (-20°) solution of 96.5% optically pure (*R*)-methylphenyl(1-naphthyl)silane (0.992 g, 4.00 mmol) in dry CH_2Cl_2 (30 mL). Capillary GC analysis indicated complete consumption of the silane immediately on addition of the oxidant. Removal of the solvent on a rotary evaporator ($10-20^{\circ}$, 80–100 mmHg) afforded very pure (97% ee) silanol (1.03 g, 98%).



(η^5 -Pentamethylcyclopentadienyl)trioxorhenium [Oxidation of a Rhenium Complex with DMD (isol.)].²¹⁰ A 100-ml flask, equipped with a magnetic stirring bar, was charged with a chilled (0°) anhydrous acetone solution of $\text{Cp}^*\text{Re}(\text{CO})_3$ (20 mL, 80 mg, 0.20 mmol) and an acetone solution of DMD (25.0 mL, 0.05 M, 1.25 mmol) was added dropwise at 0° . The reaction terminated within a few minutes under immediate gas evolution, accompanied by a slight darkening of the pale yellow solution. The solvent was removed on a rotary evaporator (20° , 15 mmHg) until a volume of ca. 3 mL remained. Hexane (15 mL) was added to the residue, and the resulting solution cooled to 0° for 3 hours to afford the title compound (54 mg, 74%) as yellow needles; IR (KBr) 913 and 878 cm^{-1} .



Ethyl Phenylpropiolate [Oxidation of a Fischer Carbene Complex with DMD (isol.)].²⁰⁵ To a vigorously stirred acetone solution of the Fischer carbene complex (10 mL, 99 mg, 0.28 mmol), previously filtered over Celite and protected from light at -20° , was added an acetone solution of DMD (13.6 mL, 0.041 M, 0.56 mmol) dropwise over 4 hours. The reaction progress was monitored by TLC (silica gel), which indicated complete consumption of the complex within minutes. The solvent was evaporated (room temperature, 20 mmHg), the residue taken up in CH_2Cl_2 (10 mL), and the chromium oxides were removed by filtration through Celite. The solvent was removed on a rotary evaporator (room temperature, 20 mmHg) to afford pure ethyl phenylpropiolate (44 mg, 90%).



[Dicarbonyl(η^5 -pentamethylcyclopentadienyl)ferrio]-1,1-dihydroxydisilane [Hydroxylation of an Iron-Complexed Silane with DMD (isol)].²²⁷ A cold (-78°) acetone solution of DMD (11.0 mL, 1.3 M, 0.84 mmol) was added to a solution of $\text{Me}_5\text{Cp}(\text{CO})_2\text{FeSi}_2\text{H}_5$ (130 mg, 0.420 mmol) in toluene (5 mL) at -78° while stirring magnetically. After complete addition (ca. 10 minutes), the color of the reaction mixture changed from yellow to orange. Subsequently, the temperature of the reaction mixture was raised to ca. 20° and after 80 minutes a material precipitated. The solvent was removed (20° , 15 mmHg), the residue was washed with pentane (10 mL) and dried over MgSO_4 to give the title compound (98 mg, 89%) as a yellow powder, mp $65-66^\circ$; IR (toluene) 1931, 1986, 2107, 3479 cm^{-1} ; ^1H NMR (400 MHz, benzene- d_6) δ 3.57 (s, 1J (SiH) = 182 Hz, 3H), 2.28 (br s, 2H), 1.58 (s, 15H); ^{13}C NMR (100 MHz, benzene- d_6) δ 9.7, 95.7, 215.9; ^{29}Si NMR (benzene- d_6) δ -95.26 (s), 96.70 (s). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{FeO}_4\text{Si}_2$: C, 42.35, H, 5.92. Found C, 42.26, H, 6.01.

TABULAR SURVEY

The oxidation of allenes, alkynes, arenes, heteroatom substrates, alkanes and silanes, and organometallic compounds is presented in the appended tables. The tabular survey covers the literature reported through March, 2005.

The tables are arranged in the order of the discussion in the section on Scope and Limitations. Thus, the data on the oxidation of allenes and alkynes, arenes, heteroatom substrates, alkanes and silanes, and organometallic compounds by isolated dioxiranes (DMD and TFD) are presented in Tables 1A, 2A, 3A–3E, 4A, 5A, 5E, and 6. Oxidations with in situ generated dioxiranes of allenes, alkynes, arenes, heteroatom substrates, and alkanes are shown in Tables 1B, 2B, 3F–H, 4B, and 5C. Regioselective oxidations of alkanes by isolated dioxiranes are compiled in Table 5B. Asymmetric oxidations of alkanes by in situ generated dioxiranes are shown in Table 5D. Miscellaneous oxidations are presented in Table 7.

The entries within each table are arranged in order of increasing carbon number of the substrates. The carbon count is based on the total number of carbon atoms. Yields of products are given in parentheses, and an em-dash (—) indicates that no yield was reported in the original reference. Data on conversion (% conv.) are included in the product column, preferentially in subtables, and labeled as such. Ratios of different products or diastereomers are given without parentheses. For those reactions that were carried out both with and without a co-solvent, the cosolvent is enclosed in parentheses to indicate that its use is optional.

The following abbreviations are used in the tables:

Ac	acetyl
Ad	adamantyl
Bn	benzyl
Bz	benzoyl
Boc	<i>tert</i> -butyloxycarbonyl

Cbz	benzyloxycarbonyl
Cp	cyclopentadienyl
Cy	cyclohexyl
de	diastereomeric excess
DEK	diethyl ketone
DMD	dimethyldioxirane
DMD (in situ)	in situ generated dioxirane
DMD (isol.)	isolated dimethyldioxirane in acetone
DMD- <i>d</i> ₆ (isol.)	isolated hexadeuterated dimethyldioxirane in acetone- <i>d</i> ₆
DMIPS	dimethylisopropylsilyl
DMM	dimethoxymethane
dr	diastereomeric ratio
EDTA	ethylenediaminetetraacetic acid
Na ₂ EDTA	disodium salt of ethylenediaminetetraacetic acid
F112	1,1,1,2-tetrachlorodifluoroethane
ee	enantiomeric excess
LDA	lithium diisopropylamide
Ms	methanesulfonyl
MOM	methoxymethyl
Naph	naphthyl
NPhth	<i>N</i> -phthalimido
Oxone [®]	potassium monoperoxysulfate (2KHSO ₅ •KHSO ₄ •K ₂ SO ₄)
PMB	<i>p</i> -methoxybenzyl
PMP	<i>p</i> -methoxyphenyl
PG	protecting group
PPTS	pyridinium <i>p</i> -toluenesulfonate
TAS	tris(dimethylamino)sulfonium difluorotrimethyl siliconate
TBDPS	<i>tert</i> -butyldiphenylsilyl
TBS	<i>tert</i> -butyldimethylsilyl
TES	triethylsilyl
Tf	trifluoromethanesulfonyl (trifyl)
TFD	methyl(trifluoromethyl)dioxirane
TFD (in situ)	in situ generated methyl(trifluoromethyl)dioxirane
TFD (isol.)	isolated methyl(trifluoromethyl)dioxirane
TFP	1,1,1-trifluoro-2-propanone
TIPS	triisopropylsilyl
TMP	tetramesitylporphyrin
TMS	trimethylsilyl
Tp	hydridotris(1-pyrazoylborate)
Tp*	3,5-dimethylhydridotris(1-pyrazoylborate)
TPP	tetraphenylporphyrin
TPS	triphenylsilyl
Ts	<i>p</i> -toluenesulfonyl

TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₄ 	DMD, acetone, rt, 20 h	+	63																
C ₅ 	DMD, acetone, rt, 10 min		56, 57, 60																
C ₅₋₇ 	DMD, acetone, rt, 10 min	 or 	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>n</th> <th>Product</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>1</td> <td>I (55)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1</td> <td>II (89)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>2</td> <td>I (92)</td> </tr> </tbody> </table>	R ¹	R ²	n	Product	Me	H	1	I (55)	H	Me	1	II (89)	Me	H	2	I (92)
R ¹	R ²	n	Product																
Me	H	1	I (55)																
H	Me	1	II (89)																
Me	H	2	I (92)																
C ₆ 	DMD, acetone, rt, 140 h		63																
	DMD, acetone, rt, 5 min		56, 57, 60																
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min		56, 57, 60																
	1. Lewis acid/ligand (pre-mixed, 9.0 eq), furan 2. DMD (3-5 eq), CH ₂ Cl ₂ , 8-10 h	 + 	271																

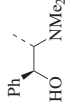
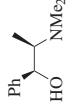
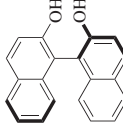
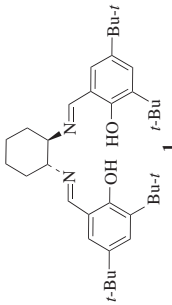
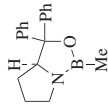
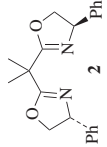
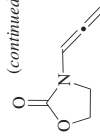
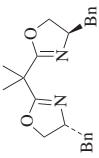
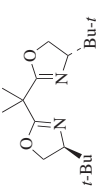
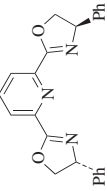
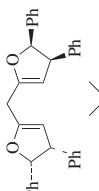
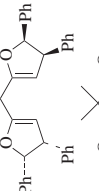
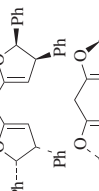
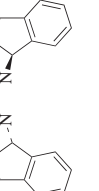
Ligand	eq	Lewis Acid (eq)	Temp	I % ee	II % ee	
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	(48)	8
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	(58)	2
	1.3	Zn(OTf) ₂ (1.1)	-55°	(0)	(70)	21
	1.0	Co(OAc) ₂ ·4H ₂ O (1.1)	-55°	(0)	(—)	(—)
1	1.0	Co(OAc) ₂ ·4H ₂ O (0.25)	-55°	(0)	(46)	1
	0.25	—	-78°	(0)	(40)	3
	1.3	Sn(OTf) ₂ (1.1)	-55°	(0)	(48)	5
2	0.32	MgI ₂ (0.25)	-78°	(0)	(46)	3
2	1.1	Cu(OTf) ₂ (0.85)	-55°	(62)	78	(0)
2	0.32	Cu(OTf) ₂ (0.25)	-78°	(46)	74	(0)

TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Ligand	Conditions		Product(s) and Yield(s) (%)			Refs.
		eq	Lewis Acid (eq)	Temp	I	II	
<p>C₆</p>  <p>(continued from previous page)</p>		1.2	Cu(OTf) ₂ (1.1)	-55°	(53)	(0)	—
		0.32	Cu(OTf) ₂ (0.25)	-78°	(0)	(46)	10
		0.32	Cu(OTf) ₂ (0.25)	-78°	(54)	(0)	—
		0.32	Cu(OTf) ₂ (0.25)	-78°	(46)	(82)	—
		0.32	Cu(OTf) ₂ (0.25)	-78°	(46)	(90)	—
		0.12	Cu(OTf) ₂ (0.10)	-78°	(76)	(59)	—
		0.32	Cu(OTf) ₂ (0.25)	-78°	(84)	(2)	—

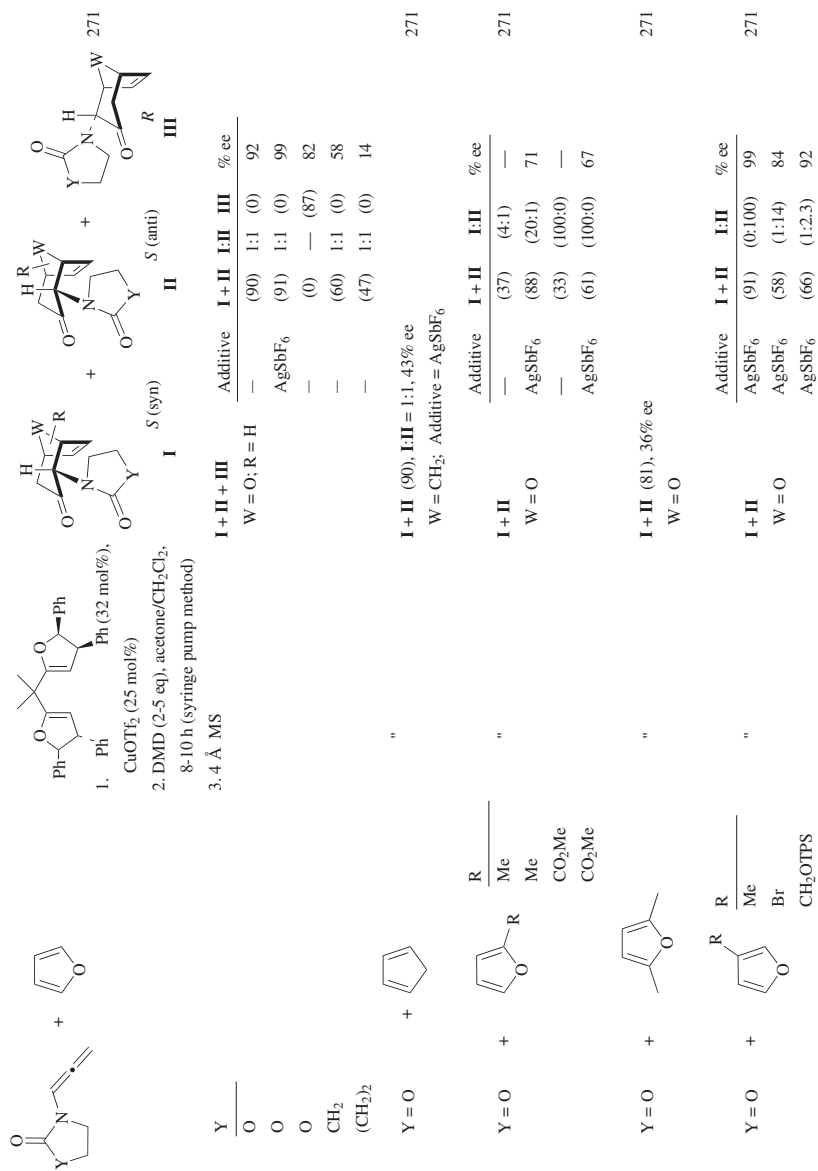

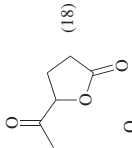
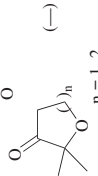
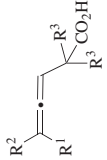
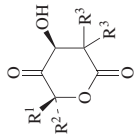
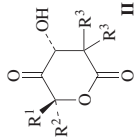
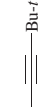
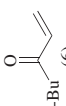

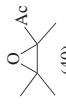
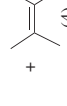



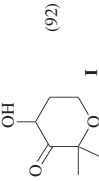



TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																			
	DMD (6-10 eq), acetone, rt, 0.5-2 h	 (18)	272																			
	DMD, TsOH, acetone	 (19)	56																			
	DMD, acetone	 I  II	60																			
		<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>(76)</td> <td>40:60</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>(96)</td> <td>50:50</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>H</td> <td>Me</td> <td>(84)</td> <td>40:60</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I + II	I:II	Me	H	H	(76)	40:60	Me	Me	Me	(96)	50:50	<i>n</i> -Pr	H	Me	(84)	40:60
R ¹	R ²	R ³	I + II	I:II																		
Me	H	H	(76)	40:60																		
Me	Me	Me	(96)	50:50																		
<i>n</i> -Pr	H	Me	(84)	40:60																		
	DMD, acetone, rt, 20 h	 (6) +  (18) +  (40)	63																			
		 (4) +  (3) +  (9)																				
	DMD, acetone, rt	 (92) I	57																			
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min	 (79) + I (10)	57																			

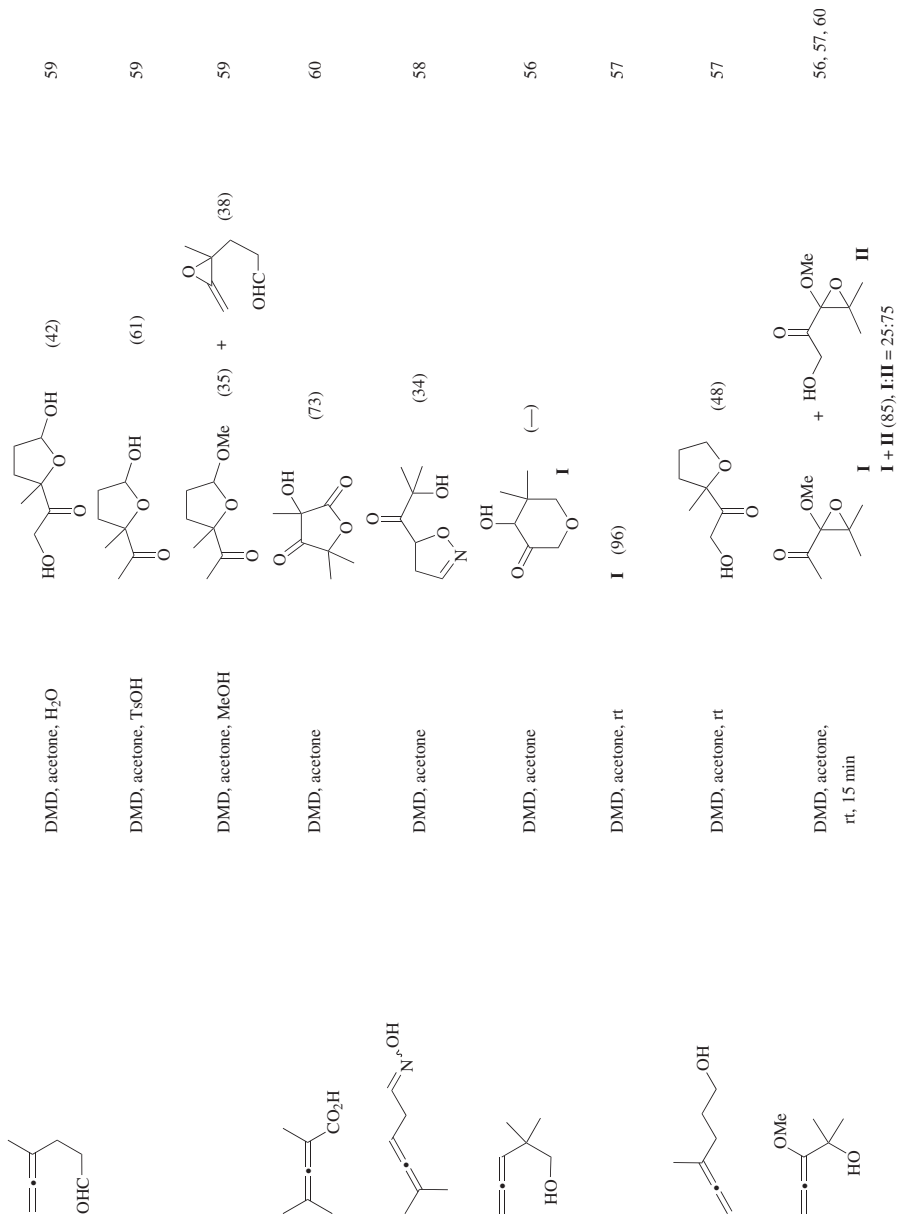

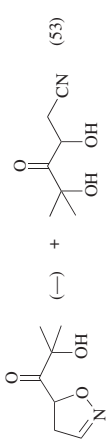

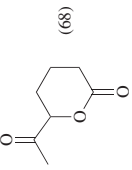
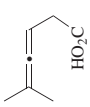
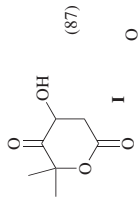
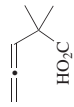
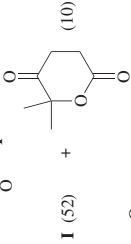
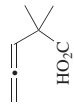
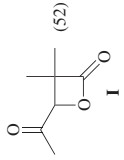
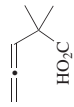

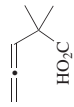
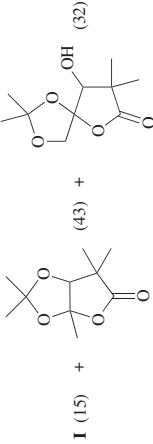
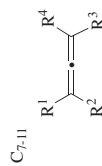
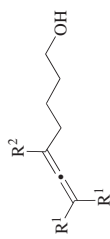
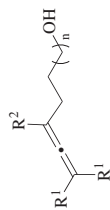
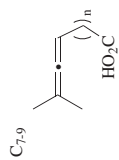
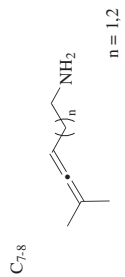
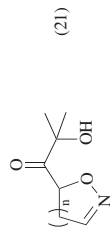


TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇	DMD, acetone, K ₂ CO ₃	 (-) + (53)	58
 C ₇	DMD (6-10 eq), K ₂ CO ₃ , acetone, rt, 0.5-2 h	 (68)	272
 C ₇	DMD (6-10 eq), acetone, rt, 0.5-2 h	 (87)	272
 C ₇	DMD (6-10 eq), NaHCO ₃ , acetone, rt, 0.5-2 h	 I (52) + (10)	272
 C ₇	DMD (6-10 eq), acetone, rt, 0.5-2 h	 I (52)	272
 C ₇	DMD (6-10 eq), acetone, NaHCO ₃ , rt, 0.5-2 h	 I (84)	272
 C ₇	DMD (6-10 eq), acetone, TsOH, rt, 0.5-2 h	 I (15) + (43) + (32)	272

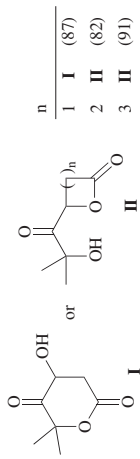


DMD, acetone



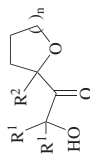
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DMD, acetone



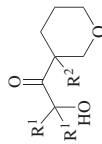
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DMD, acetone



56

DMD, acetone, rt



57

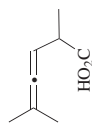
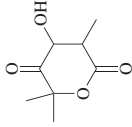
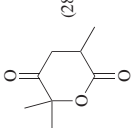
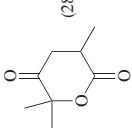

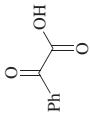
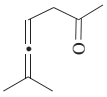
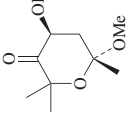
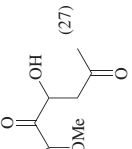
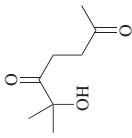
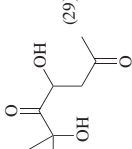

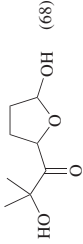
DMD, acetone



55

R^1	R^2	R^3	R^4	Temp	Time	I+II
Me	Me	Me	Me	-50°	30 min	(44) 50:50
Me	Me	<i>n</i> -Bu	H	rt	10 min	(95) 90:10
Me	Me	<i>t</i> -Bu	H	rt	10 min	(84) 100:0
<i>n</i> -Bu	<i>n</i> -Bu	H	H	-40°	1.5 h	(80) 50:50
<i>n</i> -Oct	H	H	H	-40°	2.5 h	(50) 83:17

TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (6-10 eq), acetone, rt, 0.5 to 2 h	 I (92)	272
	DMD (6-10 eq), NaHCO ₃ , acetone, rt, 0.5-2 h	 I (54) +  (28)	272
	DMD, acetone, CH ₂ Cl ₂ , 0°, 6 h	 (12) + PhCHO (38)	64
	TFD, TFP, CH ₂ Cl ₂ , 0°, 7 min	PhCHO (49)	64
	DMD, acetone, CH ₂ Cl ₂ , MeOH, 3 Å MS	 (47) +  (27)	59
	DMD, acetone, H ₂ O	 (58) +  (29)	59
	DMD, acetone, H ₂ O	 (68)	59

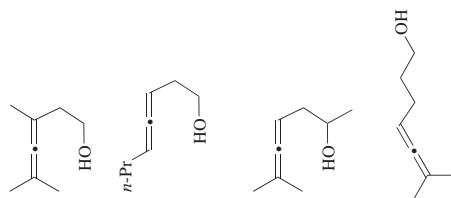
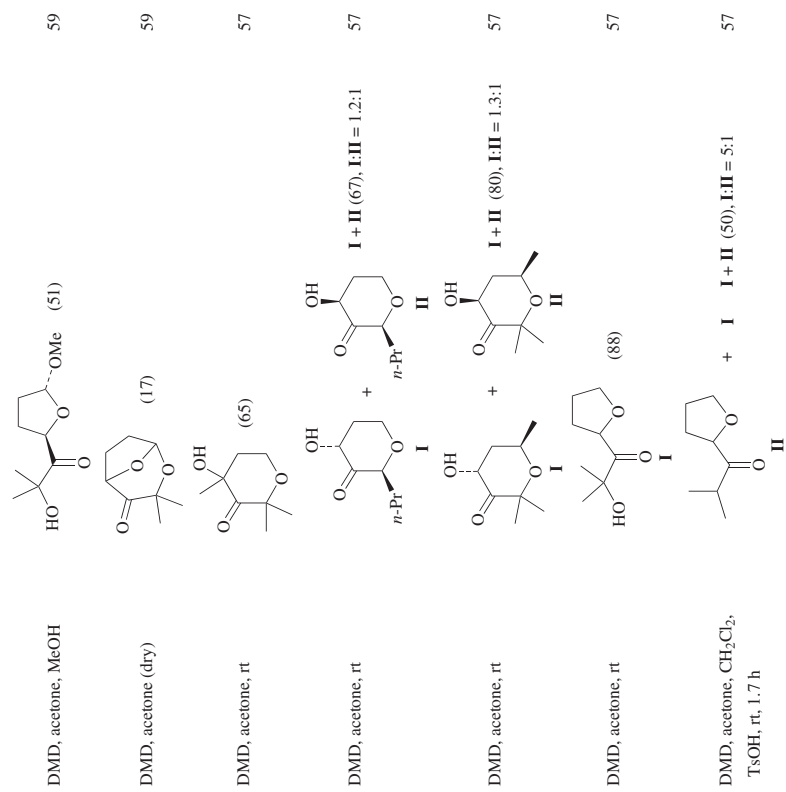


TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (6-10 eq), acetone, rt, 0.5-2 h	 I 1 (82) II 2 (71)	272
	DMD (6-10 eq), Cs ₂ CO ₃ , acetone, rt, 0.5-2 h	 I + II I 1 (100) II 2 (83)	272
	DMD, acetone, K ₂ CO ₃ , rt, 20 min		16
	DMD (6-10 eq), acetone, rt, 0.5-2 h	 I (96)	272
	DMD (6-10 eq), acetone NaHCO ₃ , rt, 0.5-2 h	 I (44) + II (11)	272
	DMD (6-10 eq), acetone, TsOH, rt, 0.5-2 h	 I + II (88), I:II = 1:4	272
	DMD, acetone, rt	 HO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH (66)	57
	DMD, acetone, KOAc, rt	 AcO-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH (63)	57

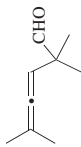
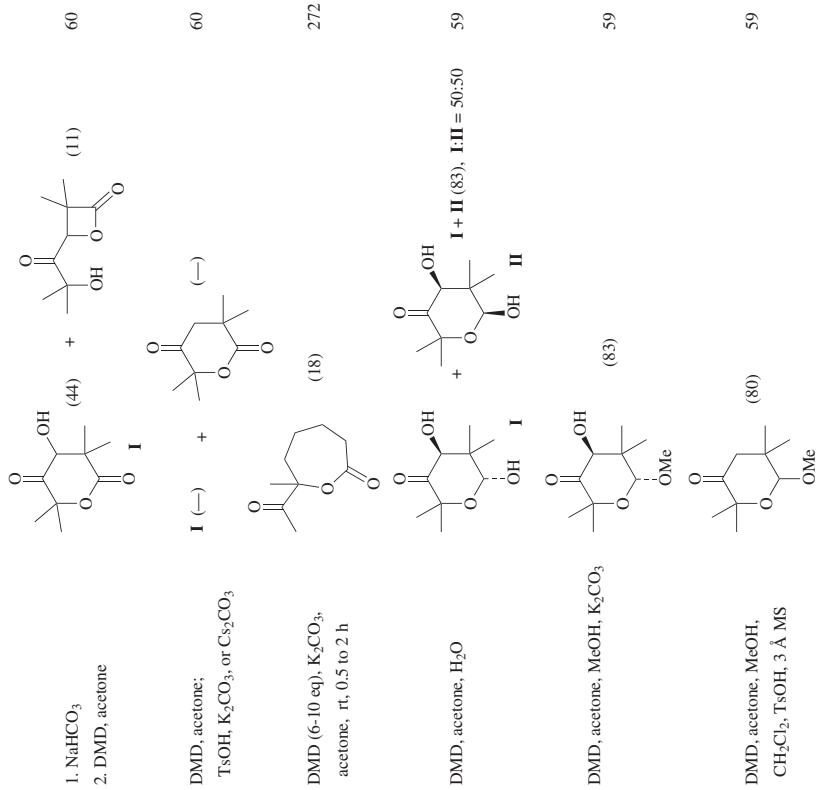
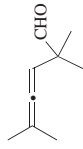
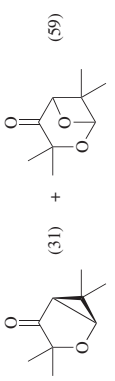
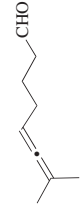
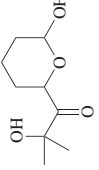
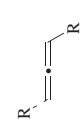
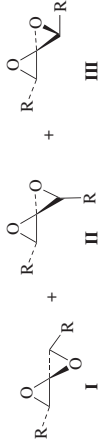
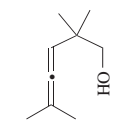
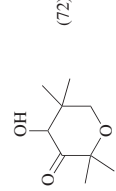
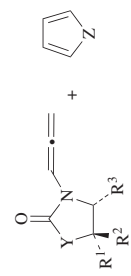
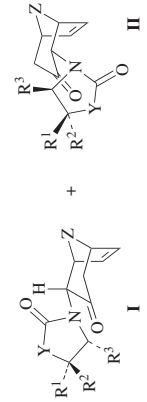


TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	DMD, acetone (dry), CH ₂ Cl ₂ , 3 Å MS		59												
	DMD, acetone, H ₂ O		59												
	DMD, acetone, K ₂ CO ₃ , rt		16												
		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Pr</td> <td>20 min</td> <td>1:1:0.15 (99)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>20 min</td> <td>2:1:0 (75)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>25 min</td> <td>1:0:0 (98)</td> </tr> </tbody> </table>	R	Time	I:II:III	<i>n</i> -Pr	20 min	1:1:0.15 (99)	<i>i</i> -Pr	20 min	2:1:0 (75)	<i>t</i> -Bu	25 min	1:0:0 (98)	
R	Time	I:II:III													
<i>n</i> -Pr	20 min	1:1:0.15 (99)													
<i>i</i> -Pr	20 min	2:1:0 (75)													
<i>t</i> -Bu	25 min	1:0:0 (98)													
	DMD, acetone, rt		57												
	DMD (2-3 eq), acetone, THF, -40 to 50°		273												

R ¹	R ²	R ³	Y	Z	I + II	I:II
H	H	<i>i</i> -Pr	O	O	(70)	55:45
H	H	Ph	O	CH ₂	(40)	> 95:5
H	H	PhCH ₂	O	O	(67)	77:23
Me	H	Ph	NMe	O	(60)	> 95:5
Me	H	Ph	NMe	CH ₂	(83)	> 96:4
H	H	Ph ₂ CH	O	O	(74)	> 95:5
H	H	Ph ₂ CH	O	CH ₂	(62)	93:7
Ph	Ph	<i>i</i> -Pr	O	O	(72)	94:6

C₁₀

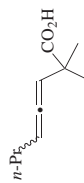
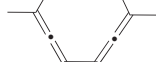
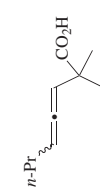
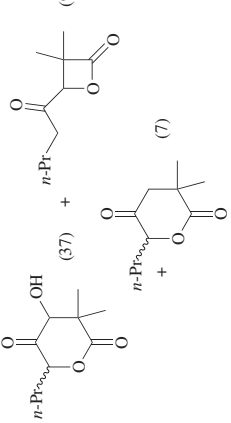
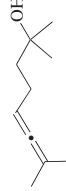
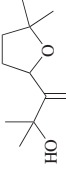
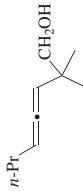
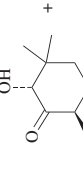
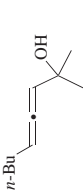
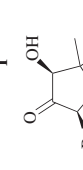

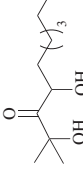



TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD (6-10 eq), Na ₂ CO ₃ , acetone, rt, 0.5-2 h		272
	DMD, acetone, rt		57
	DMD, acetone, rt		57
	DMD, acetone, rt		56, 57, 60
	DMD, acetone, rt		56, 57
	DMD (dry), acetone, rt		57

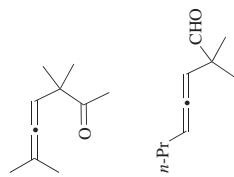
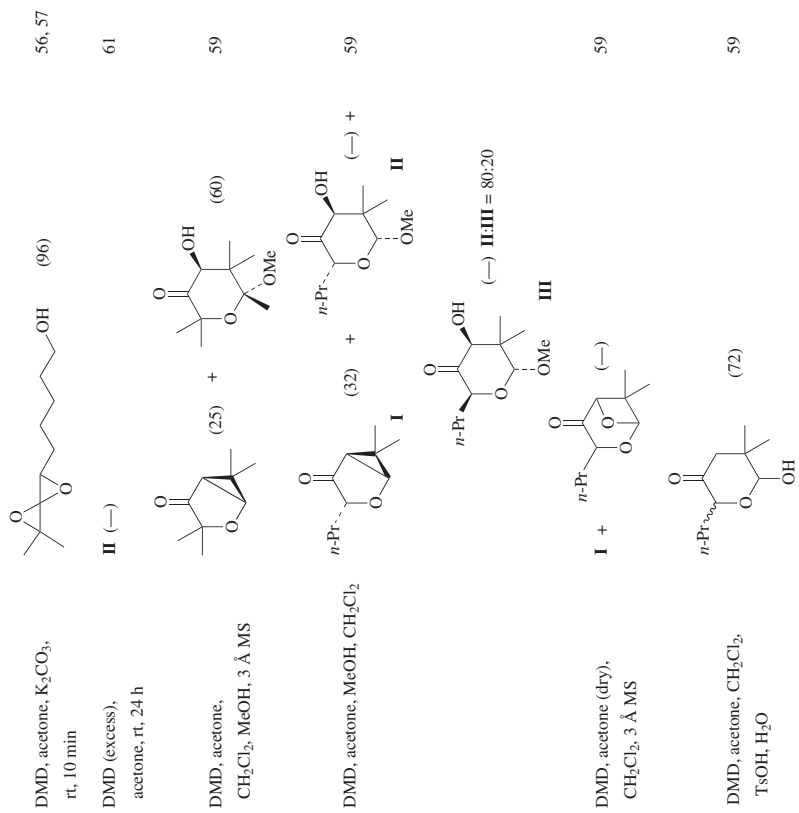


TABLE 1A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

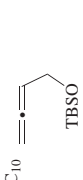
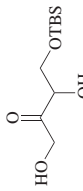
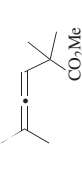
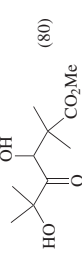
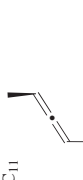
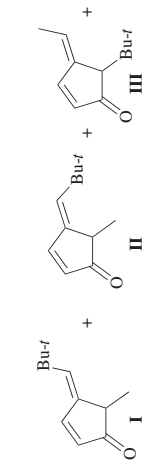
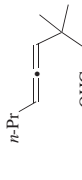
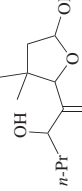
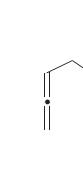
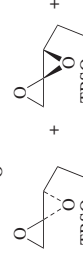
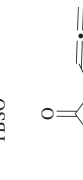
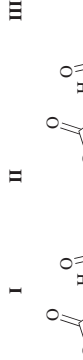
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀	DMD, acetone, rt	 (37)	57
 C ₁₁	DMD (6-10 eq), acetone, rt, 0.5-2 h	 (80)	272
 C ₁₁	DMD, acetone, rt, 24 h	 I + II + III + IV (-), III:II:IV = 26:30:28:16	61
 n-Pr	DMD, acetone, H ₂ O	 (90)	59
 TBSO	DMD, acetone, MgSO ₄ , rt	 I + II + III (100), III:II = 3.4:1.4	57
 TBSO	DMD (2-5 eq), acetone, CH ₂ Cl ₂	 I + II	274

TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

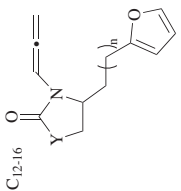
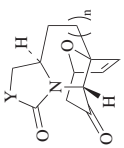
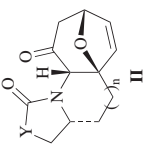
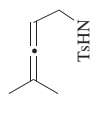

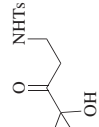
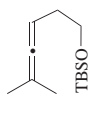
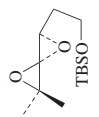

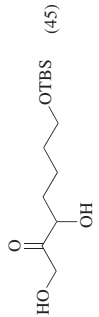
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
 C ₁₂₋₁₆	DMD (2-5 eq), acetone, CH ₂ Cl ₂	 I +  II	274				
	Addition Method	Additive	Y	n	Temp	I + II	E:II
	syringe-pumped	—	O	0	-45°	(82)	> 96:4
	syringe-pumped	—	O	0	rt	(77)	> 96:4
	cannulated	—	O	0	-45°	(75)	> 96:4
	cannulated	—	O	1	-45°	(75)	> 96:4
	cannulated	ZnCl ₂	O	1	-78°	(30)	95:5
	syringe-pumped	—	O	2	-45°	(30)	87:13
	syringe-pumped	—	O	2	rt	(70)	83:17
	syringe-pumped	—	O	3	rt	(57)	70:30
	syringe-pumped	—	CH ₂	1	rt	(90)	87:13
	cannulated	—	CH ₂	1	-45°	(85)	93:7
	syringe-pumped	—	CH ₂	3	rt	(40)	52:48
 C ₁₃	DMD, acetone, TsOH	 (42) +  NHTs	(-)	58			
 C ₁₃	DMD, acetone, NaHCO ₃ , rt	 (93)		57			
 C ₁₃	DMD, acetone, NaHCO ₃ , -78° to rt, 5 h	 (45)		57			

TABLE I.A. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)



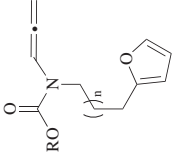
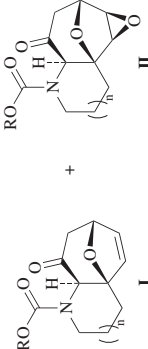
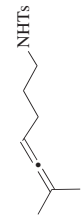
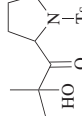
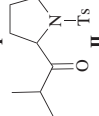
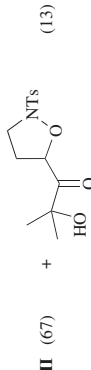
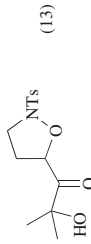
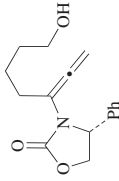
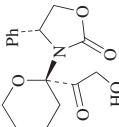
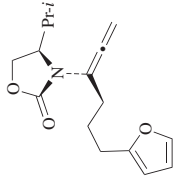
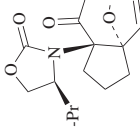
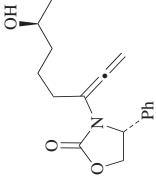
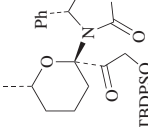
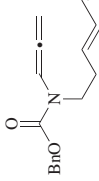
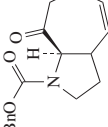
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	DMD, acetone, rt	 (—) dr 67:33	57																				
	DMD (2-3 eq), acetone, CH ₂ Cl ₂ , -45°		274																				
		<table border="1"> <thead> <tr> <th>R</th> <th>n</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td><i>t</i>-Bu</td> <td>0</td> <td>(80)</td> <td>(14)</td> </tr> <tr> <td>Bn</td> <td>0</td> <td>(75)</td> <td>(—)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>1</td> <td>(< 5)</td> <td>(—)</td> </tr> <tr> <td>Bn</td> <td>1</td> <td>(< 5)</td> <td>(—)</td> </tr> </tbody> </table>	R	n	I	II	<i>t</i> -Bu	0	(80)	(14)	Bn	0	(75)	(—)	<i>t</i> -Bu	1	(< 5)	(—)	Bn	1	(< 5)	(—)	
R	n	I	II																				
<i>t</i> -Bu	0	(80)	(14)																				
Bn	0	(75)	(—)																				
<i>t</i> -Bu	1	(< 5)	(—)																				
Bn	1	(< 5)	(—)																				
	DMD, acetone, NaHCO ₃	 (64)	58																				
	DMD, acetone, TsOH	 (81) + I (—)	58																				
	DMD, acetone, K ₂ CO ₃	 II (67) +  (13)	58																				

TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₆	DMD (2-5 eq), acetone, -40°, 2 h	 I (88)	275
 C ₁₇	DMD (2-5 eq) cumulated, acetone/CH ₂ Cl ₂ , -78°, 5-15 min	 (65) dr 95:5	276
 C ₁₇	1. DMD, acetone 2. TBDPSCl, imidazole, CH ₂ Cl ₂ , 2 h	 (46)	275
 C ₁₇	DMD (2-5 eq) syringe- pumped, acetone, CH ₂ Cl ₂ , -45°	 I + II (65), I:II = 53:47	274

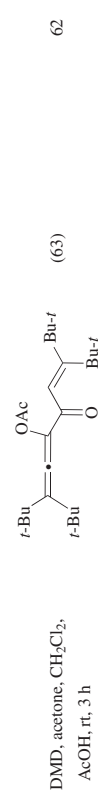
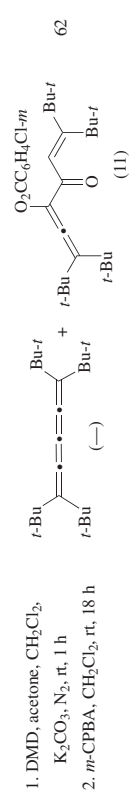
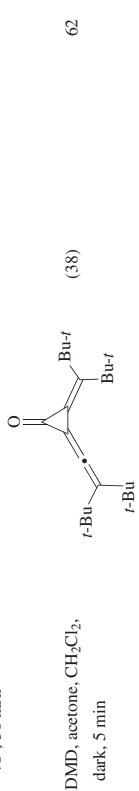
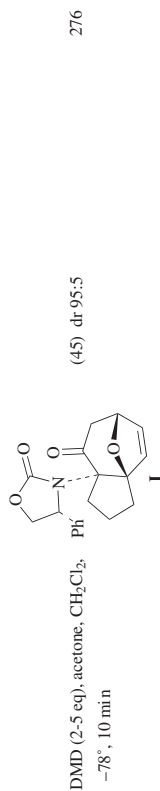
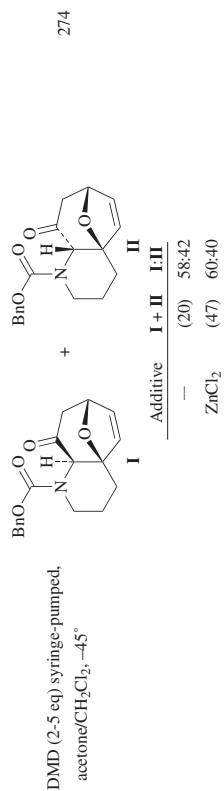
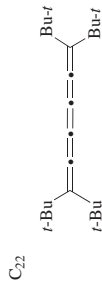
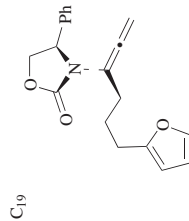
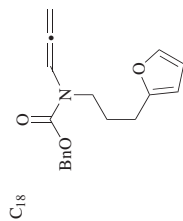
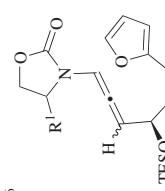
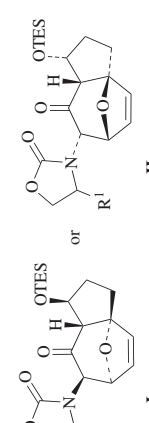
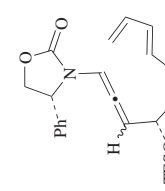
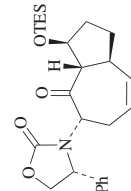
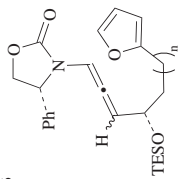


TABLE IA. OXIDATION OF ALLENES AND ALKYNES BY ISOLATED DIOXIRANES (Continued)

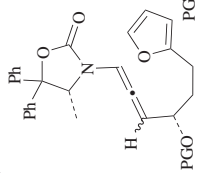
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C_{22-26}</p>	<p>DMD (2.5 eq), acetone, CH_2Cl_2, -78°, 5-15 min</p>	<p>  I II </p>	276
<p>C_{25}</p> 	<p>DMD (2.5 eq), acetone, CH_2Cl_2, -78°, 5-15 min</p>	<p>  I </p>	276
	<p>Allene isomer</p> <p>P/M 3:1 P/M 1:1 P M</p>	<p>I II dr</p> <p>(65) (—) 71:29 (—) (60) 90:10 (—) (60) 95:5 (—) (60) 95:5</p>	
	<p>Allene isomer</p> <p>M P</p>	<p>dr</p> <p>(30) < 5:95 (34) < 5:95</p>	

C₂₅₋₂₆



n	Allene isomer	
	I	P
1	1	M
2	P/M	1:1
3	P/M	1:1

C₂₈₋₃₂



PG	Allene isomer	
	TES	Ac
TES	P/M	2.5:1
Ac	P/M	2.5:1

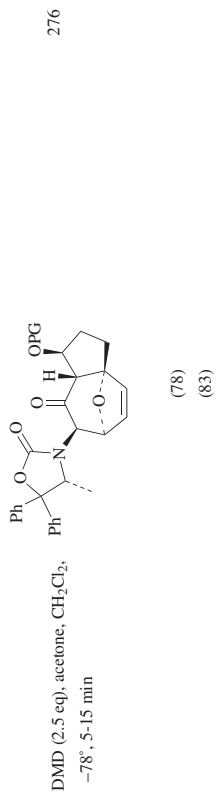
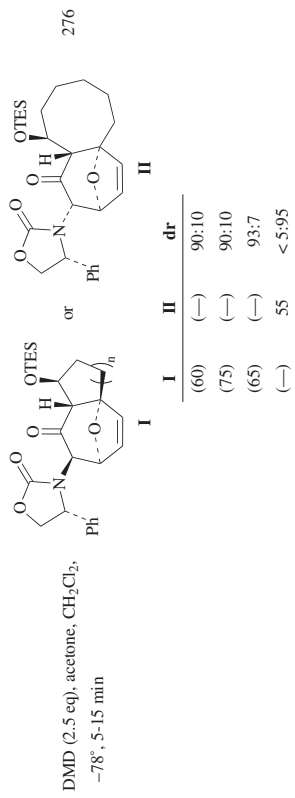


TABLE IB. OXIDATION OF ALLENES AND ALKYNES BY IN SITU GENERATED DIOXIRANES


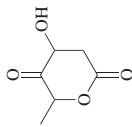

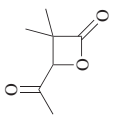

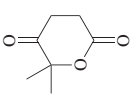
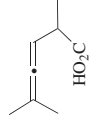
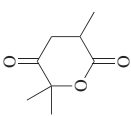
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₆	Oxone [®] , NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	 (42)	272
 C ₇	Oxone [®] , NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	 (72)	272
 C ₈	Oxone [®] , NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	 (67)	272
 C ₈	Oxone [®] , NaHCO ₃ , acetone, CH ₂ Cl ₂ , H ₂ O, rt, 2 h	 (74)	272
Ph—C≡C—C≡C—	Oxone [®] , acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 10 ⁵ , 40 h	PhCHO I (6) + PhCO ₂ H II (15) + PhCH ₂ CO ₂ H III (52)	64
	Oxone [®] , acetone, phosphate buffer (pH 7.5), CH ₂ Cl ₂ , Bu ₄ NHSO ₄ , 10 ⁵ , 8 h	I (25) + II (20) + III (19)	64

TABLE 1B. OXIDATION OF ALLENES AND ALKYNES BY IN SITU GENERATED DIOXIRANES (Continued)

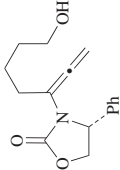
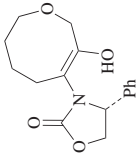
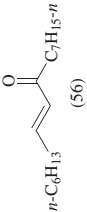
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₆</p> 	<p>Oxone[®], acetone, CH₂Cl₂, H₂O (1:1:2), rt, 2-3 h</p>	 <p>(40)</p>	275
<p><i>n</i>-C₇H₁₅-C≡C-C₇H₁₅-<i>n</i></p>	<p>Oxone[®], acetone, phosphate buffer (pH 7.5), CH₂Cl₂, Bu₄NHSO₄, 5°, 16 h</p>	 <p>(56)</p> <p>+ <i>n</i>-C₇H₁₅-<i>n</i> + C₇H₁₅-<i>n</i> (12)</p>	64

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES


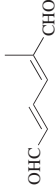
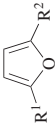
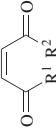

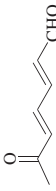
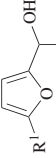
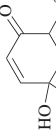


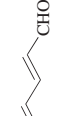
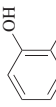
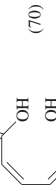
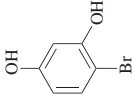
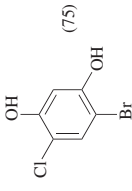
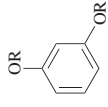
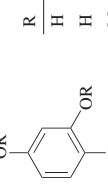
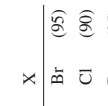
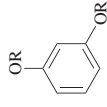
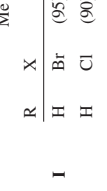
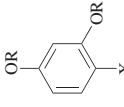
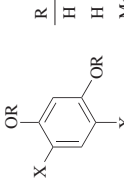
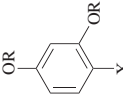
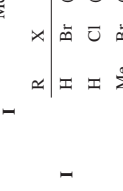
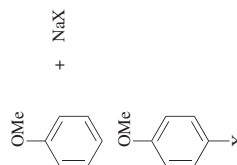
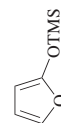
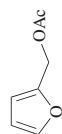
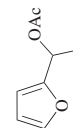
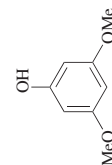
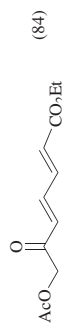
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄ 	1. DMD, acetone, 0°, 30 min 2. Ph ₃ PC(Me)CHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h	 (84)	75
C ₄₊₁₀ 	DMD, acetone, rt	 (> 95)	73
C ₅ 	1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h	 (73)	75
C ₅₋₆ 	DMD, acetone, rt	 (> 95)	73
C ₆ 	TFD, TFP, F113, 0°, 6 h	 +  I + II (4), I:II = 1:1.5	65
	TFD, acetone, TFP, -20°, 1 h	 (70)	277

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
 C_6	+ NaCl DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min	 (75)	278												
 C_{6-8}	+ HX DMD, acetone, rt, 1 min	 (75)  <table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>X</td></tr> <tr><td>H</td><td>Br</td></tr> <tr><td>H</td><td>Cl</td></tr> <tr><td>Me</td><td>Br</td></tr> <tr><td>Me</td><td>Cl</td></tr> </table>	R	X	H	Br	H	Cl	Me	Br	Me	Cl	278		
R	X														
H	Br														
H	Cl														
Me	Br														
Me	Cl														
	+ NaX DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min	 <table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>X</td></tr> <tr><td>H</td><td>Br</td></tr> <tr><td>H</td><td>Cl</td></tr> <tr><td>Me</td><td>Br</td></tr> <tr><td>Me</td><td>Cl</td></tr> <tr><td>Me</td><td>I</td></tr> </table>	R	X	H	Br	H	Cl	Me	Br	Me	Cl	Me	I	278
R	X														
H	Br														
H	Cl														
Me	Br														
Me	Cl														
Me	I														
	+ HX DMD, acetone, rt, 1 min	 <table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>X</td></tr> <tr><td>H</td><td>Br</td></tr> <tr><td>H</td><td>Cl</td></tr> <tr><td>Me</td><td>Br</td></tr> <tr><td>Me</td><td>Cl</td></tr> </table>	R	X	H	Br	H	Cl	Me	Br	Me	Cl	278		
R	X														
H	Br														
H	Cl														
Me	Br														
Me	Cl														
	+ NaX DMD, acetone, 10% H ₂ SO ₄ , rt, 1 min	 <table border="1" style="display: inline-table; vertical-align: middle;"> <tr><td>R</td><td>X</td></tr> <tr><td>H</td><td>Br</td></tr> <tr><td>H</td><td>Cl</td></tr> <tr><td>Me</td><td>Br</td></tr> <tr><td>Me</td><td>Cl</td></tr> <tr><td>Me</td><td>I</td></tr> </table>	R	X	H	Br	H	Cl	Me	Br	Me	Cl	Me	I	278
R	X														
H	Br														
H	Cl														
Me	Br														
Me	Cl														
Me	I														

C₇C₈

1. DMD, acetone, 0°, 30 min
2. Ph₃PCHCO₂Et,
CH₂Cl₂, acetone, 0° to rt, 3 h



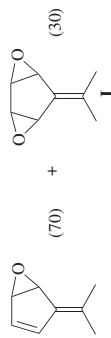
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1. DMD, acetone, 0°, 30 min
2. Ph₃PCHCO₂Et,
CH₂Cl₂, acetone, 0° to rt, 3 h



75

DMD (1.1 eq), acetone,
CH₂Cl₂, N₂, -10°, 3 h

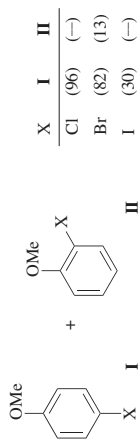


279

DMD (2.5 eq), acetone,
CH₂Cl₂, N₂, 0°, 3 h

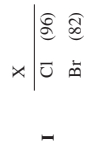
I (91)

279



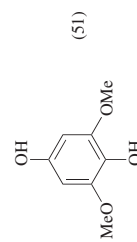
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DMD, acetone, 10% H₂SO₄,
rt, 1 min



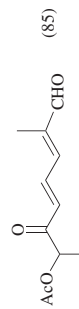
278

DMD, CH₂Cl₂, 0° to rt, 2 h



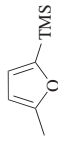
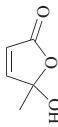
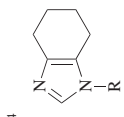
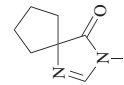


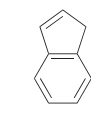
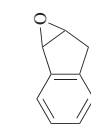
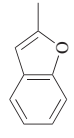
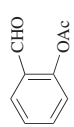
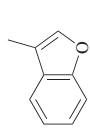
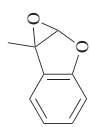
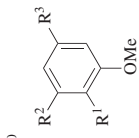
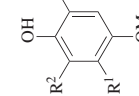
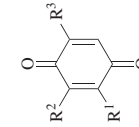
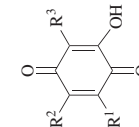
280

1. DMD, acetone, 0°, 30 min
2. Ph₃PC(Me)CHO,
CH₂Cl₂, acetone, 0° to rt, 3 h



75

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

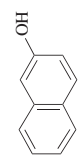
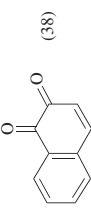
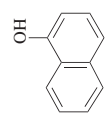
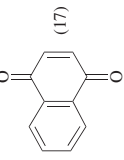
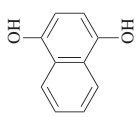
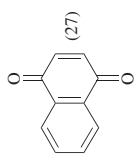
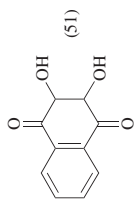
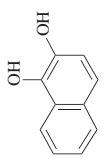
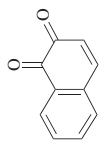
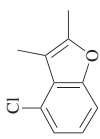
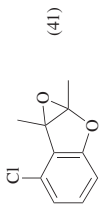
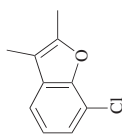
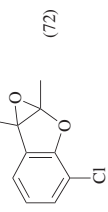
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt	 (>95)	73
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 1.5 h	 (73)  (70)  (60) SO ₂ NMe ₂ (—)	281
	DMD, acetone, 1 h	 (96)	265
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 20°, 19 h	 (35)	89
	DMD- <i>d</i> ₆ , acetone- <i>d</i> ₆ , N ₂ , -55°, 4 h	 (—)	89
	DMD, acid, acetone, 0°, N ₂	 I +  II +  III	282

R ¹	R ²	R ³	Acid	Time	I	II	III
MeO	H	Me	—	360 min	(—)	(3)	(11)
MeO	H	Me	H ₂ SO ₄	60 min	(—)	(8)	(2)
H	MeO	Me	—	300 min	(—)	(—)	(12)
H	MeO	Me	H ₂ SO ₄	45 min	(1)	(35)	(5)
H	MeO	Me	H ₃ PMo ₁₂ O ₄₀	300 min	(1)	(38)	(2)
Me	MeO	MeO	—	30 min	(26)	(—)	(—)
Me	MeO	MeO	H ₂ SO ₄	60 min	(—)	(50)	(—)
Me	MeO	MeO	H ₃ PMo ₁₂ O ₄₀	30 min	(—)	(23)	(—)
Me	MeO	MeO	H ₃ PO ₄	30 min	(—)	(51)	(—)
Me	MeO	MeO	CF ₃ CO ₂ H	30 min	(—)	(46)	(—)
Me	MeO	MeO	AcOH	30 min	(6)	(16)	(—)
MeO	MeO	Me	—	390 min	complex mixture		
MeO	MeO	Me	H ₂ SO ₄	240 min	(11)	(14)	(—)

R	Temp	Time
H	0°	3 h (98)
CH ₂ OH	0°	3 h (89)
CO ₂ Et	20°	48 h (72)
Ph(MeO)CH	0°	9 h (77)

Structure	Reaction Conditions	Product
	DMD, acetone, CH ₂ Cl ₂ , N ₂	
	TFD, CH ₂ Cl ₂ , TFP, -20°, 30 min	
	TFD, CH ₂ Cl ₂ , TFP, -22°, 40 min	
	DMD, CH ₂ Cl ₂ , 0° to rt, 10 min	

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone	 (38)	17
	DMD, acetone	 (17) + I (14)	17
	DMD, acetone, Ar, 20°, 24 h	 (27) +  (51)	66
	DMD, acetone	 (100)	17
	DMD, acetone, N ₂ , -40°, 11 h	 (41)	79
	DMD, acetone, N ₂ , -40°, 9 h	 (72)	79

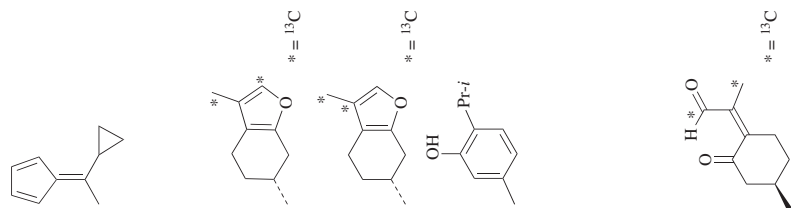
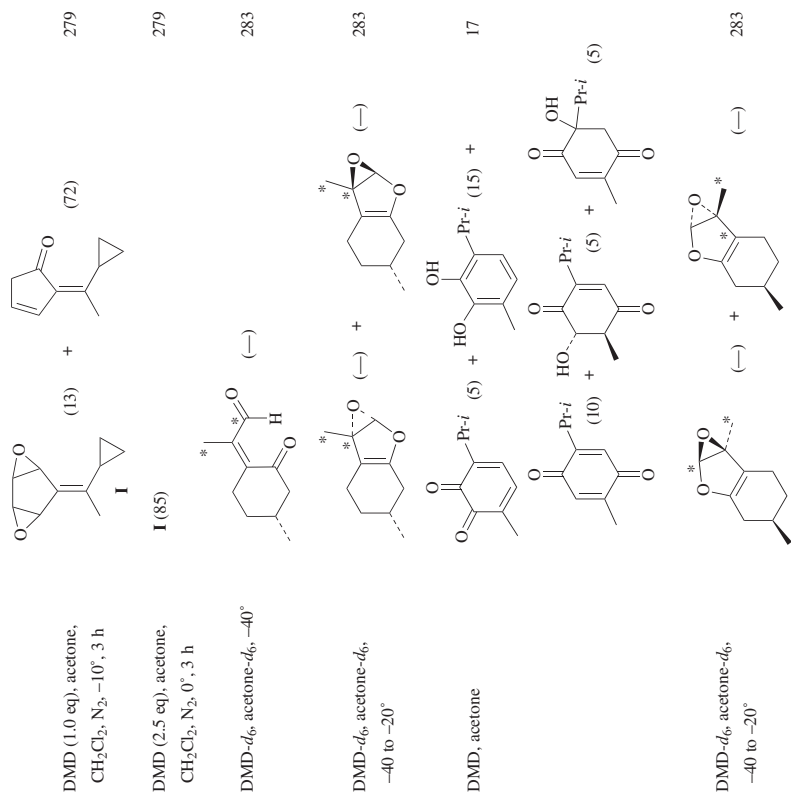
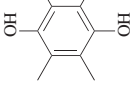
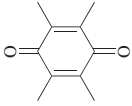
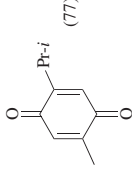
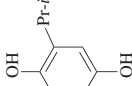
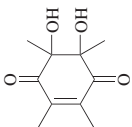
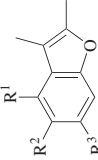
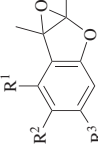
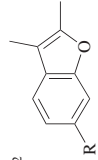
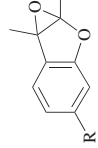
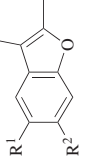
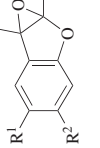
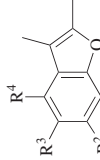
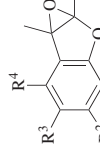
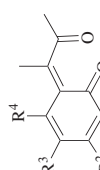


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{10}	DMD, acetone, Ar, 20°, 1.5 h	 (72) +  (77)	66
 C_{10-11}	DMD, acetone	 (11)	17
 C_{10-12}	DMD, acetone, CH_2Cl_2 , N_2 , -78 to -20°, 0.5 to 3 h	 (100)	77, 79
 C_{10-18}	DMD- d_6 , acetone- d_6 , N_2 , -78°, 0.5 h	 (100)	87
 C_{10-18}	DMD, acetone, N_2 , -40°, 11-12 h	 (100)	79
 C_{10-18}	DMD, acetone, CH_2Cl_2 , N_2	 I +  II	82

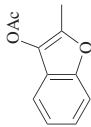
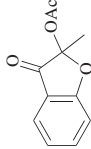
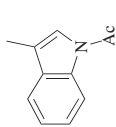
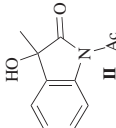
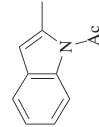
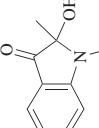
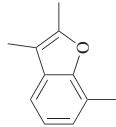
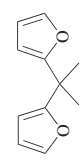
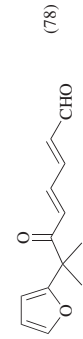
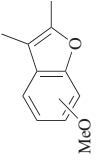
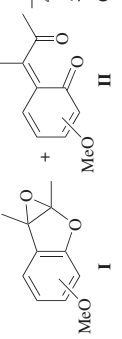
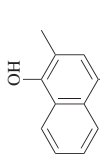
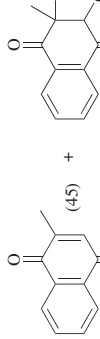
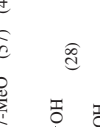
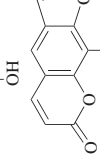
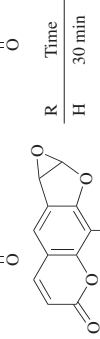
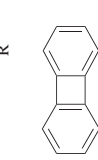

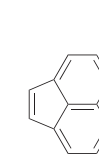

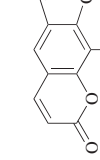
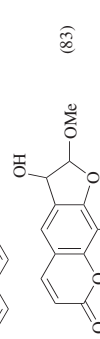
R ¹	R ²	R ³	R ⁴	Temp	Time	% Convn	Products
Cl	H	H	H	-20°	10 h	> 95	I
H	Cl	H	H	-35°	6 h	79	I
H	H	Cl	H	-20°	9 h	71	I
H	H	H	Cl	-20°	8 h	92	I
H	H	H	H	-40°	7 h	> 95	I
Me	H	H	H	-45°	3 h	95	I
H	Me	H	H	-50°	2 h	> 95	I+II (31:69)
H	H	Me	H	-40°	3 h	> 95	I
H	H	H	Me	-35°	4 h	> 95	I
H	MeO	H	H	-60°	0.5 h	> 95	II
H	H	<i>r</i> -Bu	H	-30°	2 h	> 95	I
H	<i>r</i> -Bu	H	<i>r</i> -Bu	-45°	3 h	> 95	I
							
					DMD, acetone, CH ₂ Cl ₂ , 0°, 9 h		I
							I
					DMD, acetone, CH ₂ Cl ₂ , -78°		I + II (>98), II = 11:1
							II
							I
					DMD, acetone, CH ₂ Cl ₂ , -78°		I + II (>98), II = 10:1
							II
					DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 3 h		I

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMD, acetone, 0°, 30 min 2. Ph ₃ PCHCHO, CH ₂ Cl ₂ , acetone, 0° to rt, 3 h	 (78)	75
	DMD, acetone, -70 to -20°, 3 to 5 h		I 81 II 81
	DMD, acetone, Ar, 20°, 24 h	 (45) +  (28)	66
	TFD, TFP, CH ₂ Cl ₂ , N ₂ , -78 to -40°	 (29)	84
	DMD, acetone, 20°, 24 h	 (97)	284
	DMD, acetone, rt, 1 h	 (83)	265
	DMD, acetone, MeOH, rt, 19 h	 (85)	85

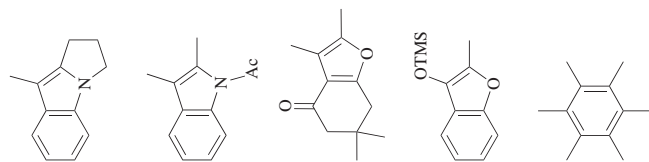
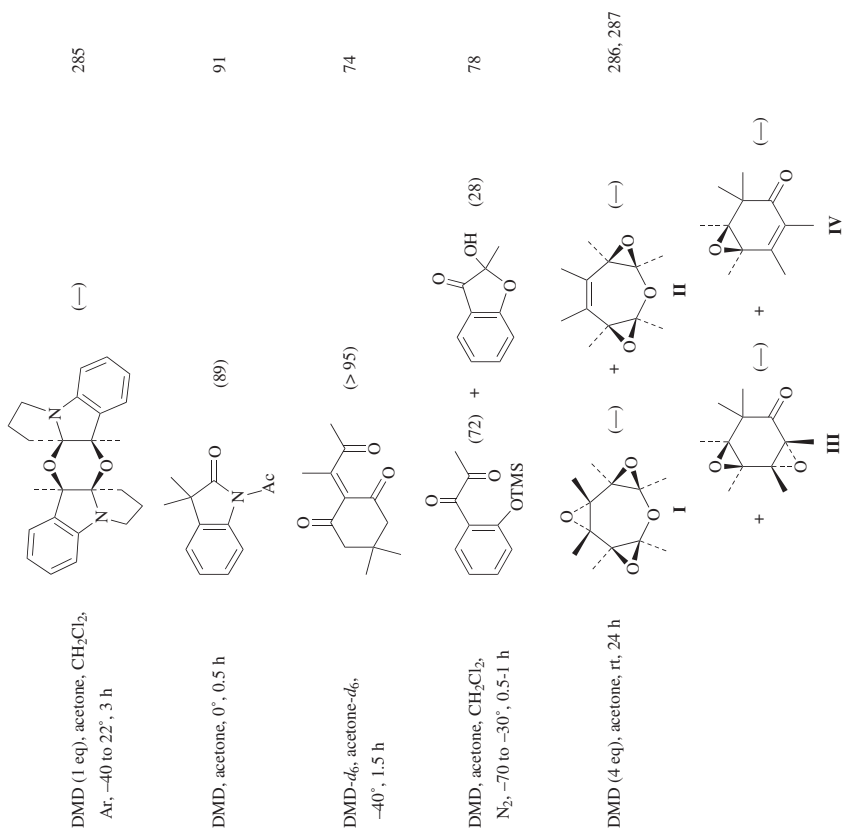
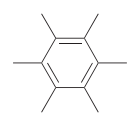
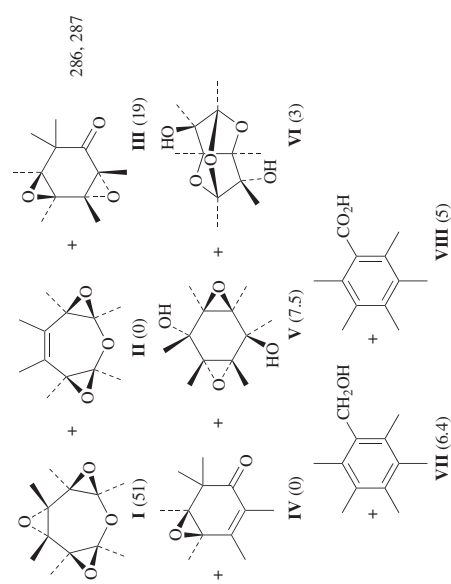


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₂	DMD (5 eq), acetone, rt, 48 h		286, 287
	DMD (2 eq), acetone, rt, 5 h	I (5) + II (29) + IV (5) + III (traces)	286, 287
	DMD (6 eq), acetone, -25°, 72 h	I (-) + II (-) + IV (-) + V (-) + III (traces) + VII (traces)	286, 287
	DMD (6 eq), acetone, NaHCO ₃ , rt, dark, 64 h	I (-) + II (-) + III (-), I:II:III = 58:27:15	286, 287
	DMD (> 6 eq), acetone, NaHCO ₃ , rt, dark, > 76 h	I (-) + III (-), I:III = 90:10	286, 287
	Dry DMD (6 eq), acetone, rt, 96 h	I (-) + II (-) + VII (-), I:II:VII = 58:15:27	286, 287
	DMD (6 eq), acetone, TsOH, rt, 96 h	I (-) + III (-) + V (traces) + VII (traces), I:III = 15:85	286, 287

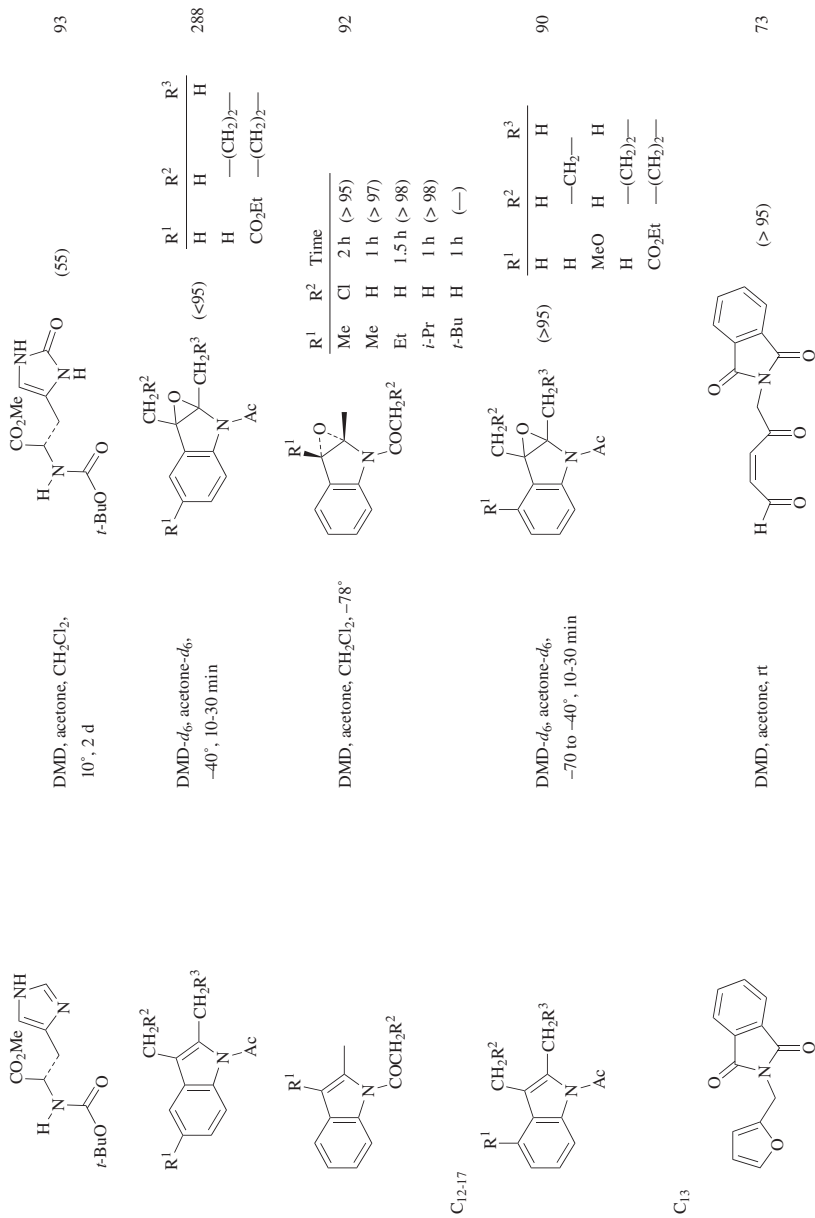




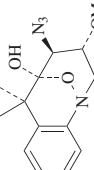
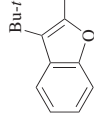
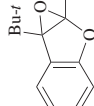
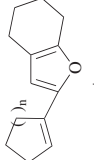
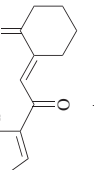
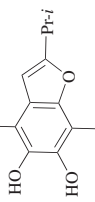
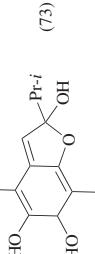
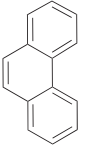
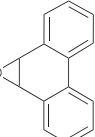
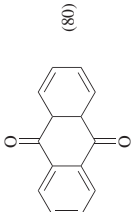
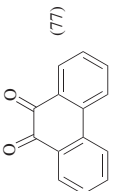
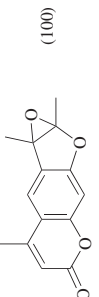
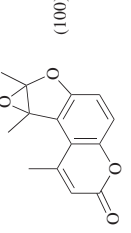
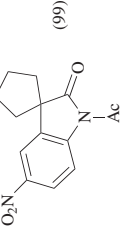


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₃	DMD (1.0 eq), acetone, CH ₂ Cl ₂ , N ₂ , -10°, 3 h	 (67) +  I (89)	279
 C ₁₃	DMD (3.1 eq), acetone, CH ₂ Cl ₂ , N ₂ , 0°, 4 h	 (59)	279
 C ₁₃	DMD, acetone, H ₂ O	 (> 95)	89
 C ₁₃	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 3 h	 (100)	290
 C ₁₃	DMD, acetone, CH ₂ Cl ₂ , -20°	 (73)	291
 C ₁₄	DMD, acetone, MeCN, 26°	 (83)	121

Ethylmethylidioxirane, 2-butanone, MeCN, rt	I (–)	121
TFD, TFP, –20°, 5 min	I (74)	173
DMD, acetone, 22°, 20 h	I (–)	173
TFD, CH ₂ Cl ₂ , TFP, –20°, 8 min	I (96)	65
TFD, CH ₂ Cl ₂ , TFP, 0°, 30 min	 (80)	65
DMD, acetone	 (77)	17
DMD, acetone, CH ₂ Cl ₂ , N ₂ , –78 to –20°, 16 h	 (100)	84
DMD, acetone, CH ₂ Cl ₂ , N ₂ , –78° to –20°, 22 h	 (100)	84
DMD, acetone, CH ₂ Cl ₂ , 20°	 (99)	91

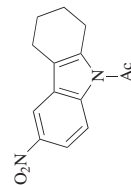
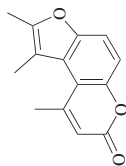
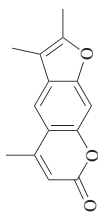
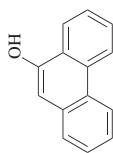
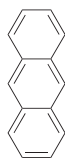
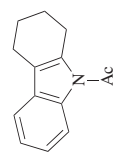
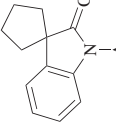
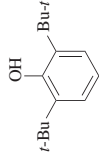
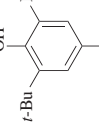
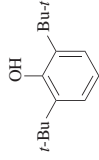
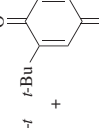
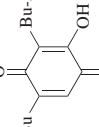
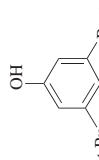
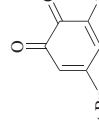
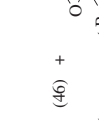

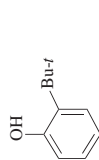
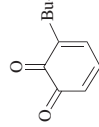

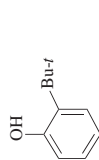
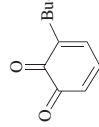


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, 0°, 0.5 h		91
	DMD, acetone, CH ₂ Cl ₂ , -78°		92
	TFD, TFP, CH ₂ Cl ₂ , N ₂ , 0°, 1 min	 + 	277
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 48 h	 +  + 	277
	DMD, acetone	 + 	17
	DMD, acetone		17

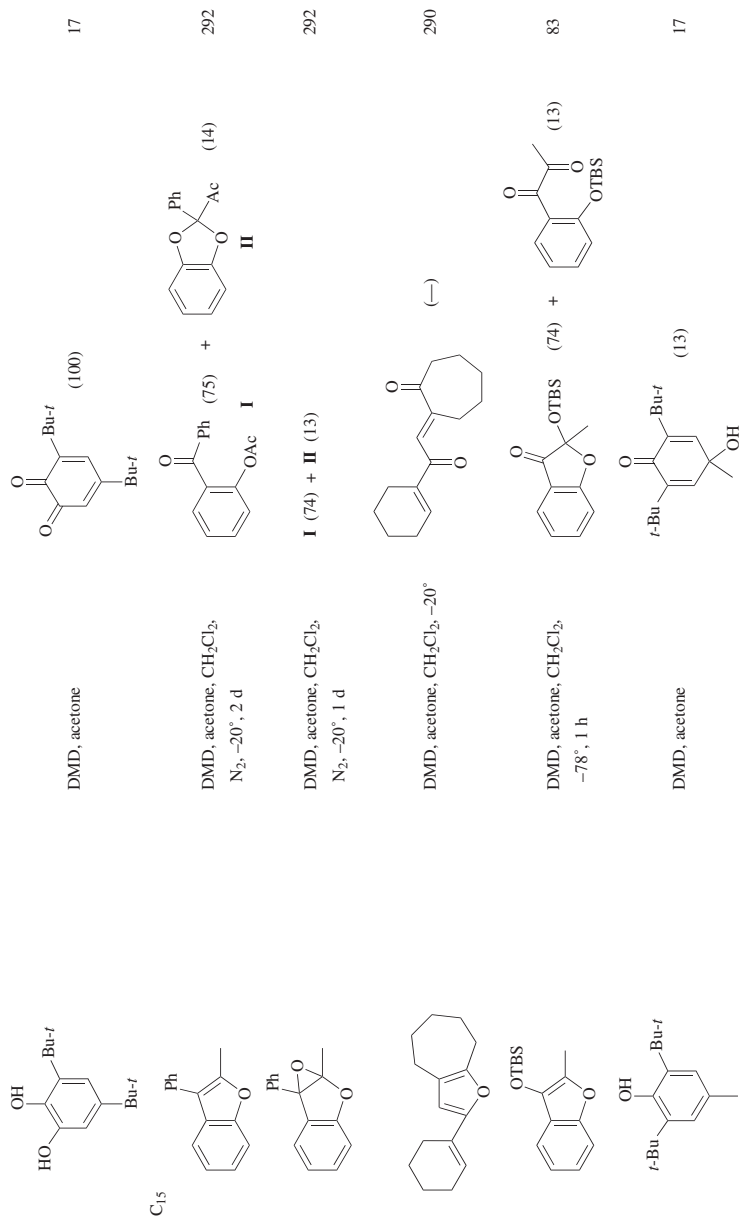
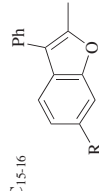
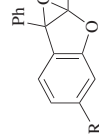
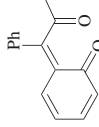
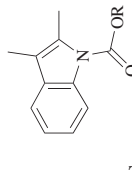
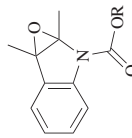
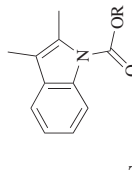
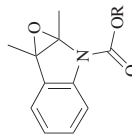
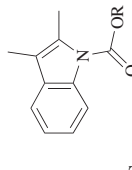
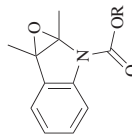
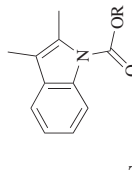
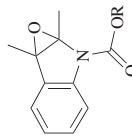
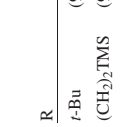
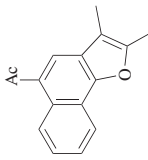
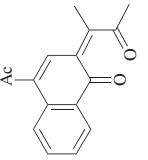
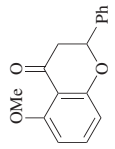
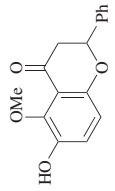
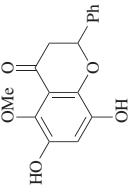
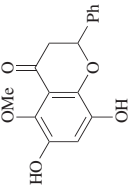
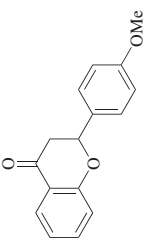
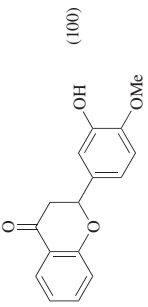
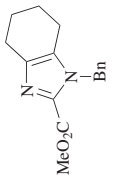
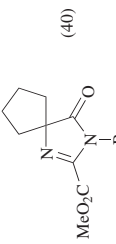


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
 C _{15.16}	DMD, acetone, -70 to -20°, 4 h	 I +  II <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>I</td> <td>II</td> </tr> <tr> <td>H</td> <td>(100)</td> <td>(—)</td> </tr> <tr> <td>MeO</td> <td>(—)</td> <td>(100)</td> </tr> </table>	R	I	II	H	(100)	(—)	MeO	(—)	(100)	80			
R	I	II													
H	(100)	(—)													
MeO	(—)	(100)													
 C _{15.17}	DMD, acetone, N ₂ , -78 to -10°	<table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>Time</td> </tr> <tr> <td>H</td> <td>7 h (100)</td> </tr> <tr> <td>MeO</td> <td>1 h (100)</td> </tr> </table>  I <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R</td> <td>(95)</td> </tr> <tr> <td>t-Bu</td> <td>(93)</td> </tr> <tr> <td>(CH₂)₂TMS</td> <td>(93)</td> </tr> </table>	R	Time	H	7 h (100)	MeO	1 h (100)	R	(95)	t-Bu	(93)	(CH ₂) ₂ TMS	(93)	293
R	Time														
H	7 h (100)														
MeO	1 h (100)														
R	(95)														
t-Bu	(93)														
(CH ₂) ₂ TMS	(93)														
 C _{15.17}	DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 3 h	 I <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> </tr> <tr> <td>H</td> <td>H (98)</td> </tr> <tr> <td>Me</td> <td>H (97)</td> </tr> <tr> <td>Me</td> <td>Me (98)</td> </tr> </table>	R ¹	R ²	H	H (98)	Me	H (97)	Me	Me (98)	294				
R ¹	R ²														
H	H (98)														
Me	H (97)														
Me	Me (98)														
 C _{15.17}	DMD, acetone, CH ₂ Cl ₂ , -78°, 10-20 min; 20°, 60-140 min	 I <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> </tr> <tr> <td>H</td> <td>H (98)</td> </tr> <tr> <td>Me</td> <td>H (97)</td> </tr> <tr> <td>Me</td> <td>Me (98)</td> </tr> </table>	R ¹	R ²	H	H (98)	Me	H (97)	Me	Me (98)	295				
R ¹	R ²														
H	H (98)														
Me	H (97)														
Me	Me (98)														
 C _{15.17}	DMD, acetone, N ₂	 I +  II <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> </tr> <tr> <td>H</td> <td>H (98)</td> </tr> <tr> <td>Me</td> <td>H (97)</td> </tr> <tr> <td>Me</td> <td>Me (98)</td> </tr> </table>	R ¹	R ²	H	H (98)	Me	H (97)	Me	Me (98)	86				
R ¹	R ²														
H	H (98)														
Me	H (97)														
Me	Me (98)														

R ¹	R ²	R ³	Temp	Time	I	II	
H	H	H	-78° to -10°	7 h		(-)	278
MeO	H	NO ₂	-78° to -20°	3 h		(-)	(>95)
MeO	H	H	-78° to -20°	1 h		(-)	(>95)
Ac	H	H	-78° to 0°	14 h		(-)	(-)
MeO	MeO	H	-78° to -20°	1 h		(-)	(>95)
 C ₁₆			DMD, acetone, rt		R		
			DMD, acetone, 0-5°, 12 h		H	(72)	69
			TFD (1.1 eq), CH ₂ Cl ₂ , TFP, -20°, 5 min		Me	(87)	65
			TFD (2.2 eq), CH ₂ Cl ₂ , TFP, -20°, 5 min				65
			DMD, acetone, 0-5°, 12 h				69
			DMD, acetone, CH ₂ Cl ₂ , N ₂ , -78 to -20°, 5 h				84

TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{16}	DMD, acetone, CH_2Cl_2 , N_2 , -78 to -20° , 7 h	 (100)	84
	DMD, acetone, rt	 (35-40)	68
	DMD, acetone, 2 N HCl, -30°	 (100)	68
	DMD, acetone, 2 N HCl, -30°	 (100)	68
	DMD (1.5 eq), acetone, CH_2Cl_2 , rt, 2 h	 (40)	281

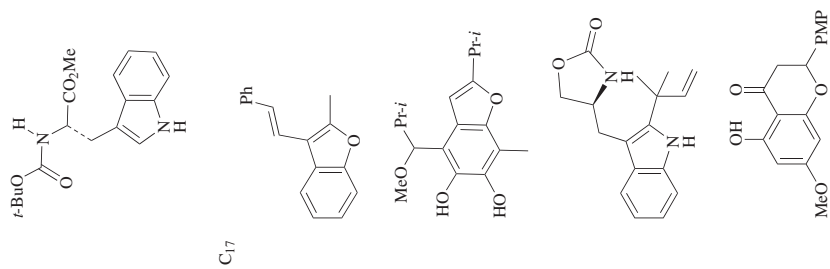
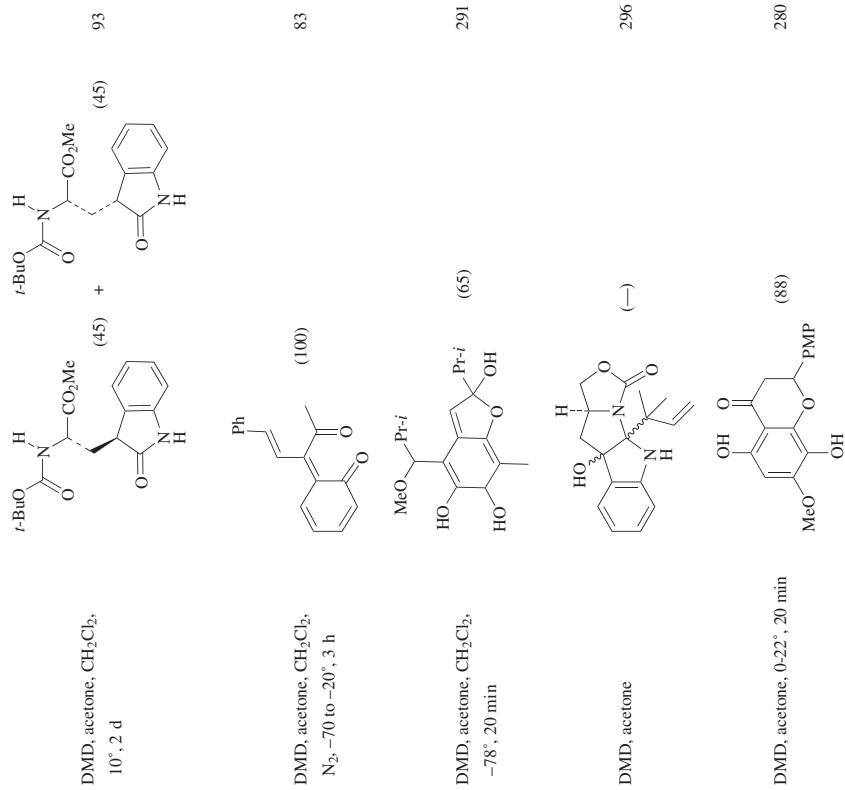
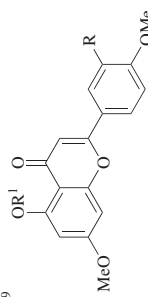

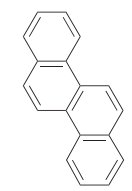
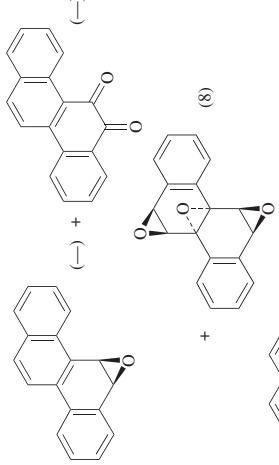
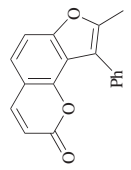
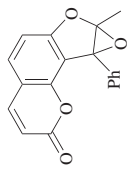
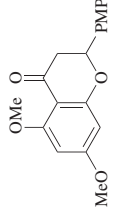
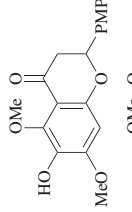

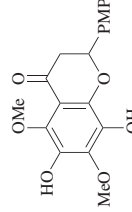


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{17-19}	1. DMD, CH_2Cl_2 , 2 h 2. Me_2SO_4 , acetone, K_2CO_3 , 60°, 1 h	 R R ¹ H H (85) Me H (55) Me Me (38)	280
 C_{18}	DMD, acetone, rt, dark, 72 h	 (–) + (–)	70
 (100)	DMD, acetone, CH_2Cl_2 , N_2 , –78 to –20°, 14 h	 (84)	84
 (35-40)	DMD, acetone, rt	 (68)	68
 (100)	DMD, acetone, 2 N HCl, –30°	 (68)	68

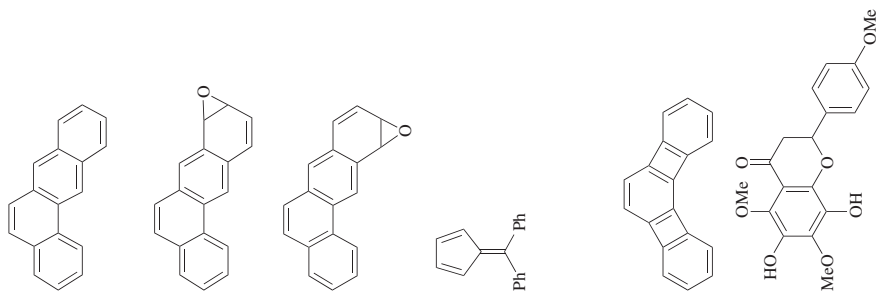
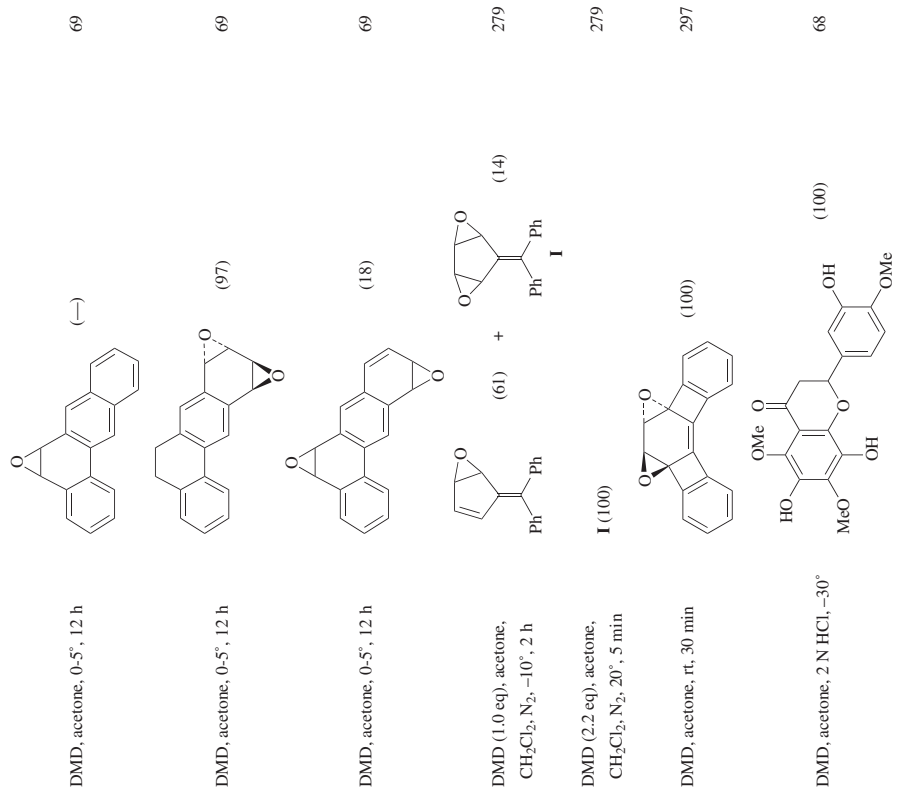
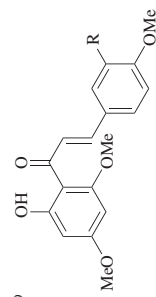
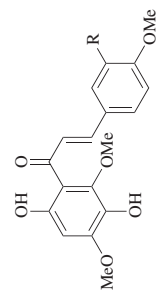
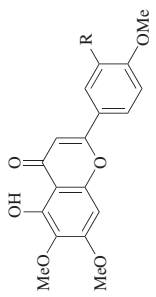
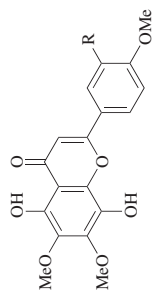
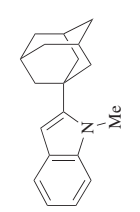
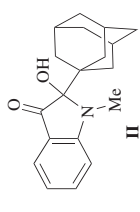
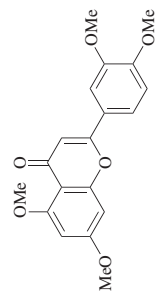
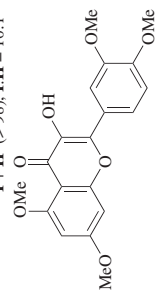
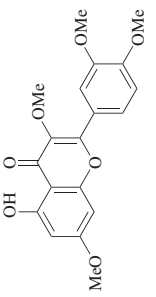
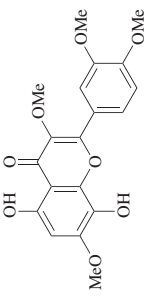


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{18-19}	DMD, CH_2Cl_2 , 0° to rt, 1 h	 R H (76) OMe (65)	280
 C_{19}	DMD, CH_2Cl_2 , 1 h	 R H (90) OMe (90)	280
 C_{19}	DMD, acetone, CH_2Cl_2 , -78°	 I + II (> 98), I:II = 10:1	92
	DMD, CH_2Cl_2 , N_2 , 30 min	 (86)	280
	DMD, CH_2Cl_2 , 50 min	 (89)	280

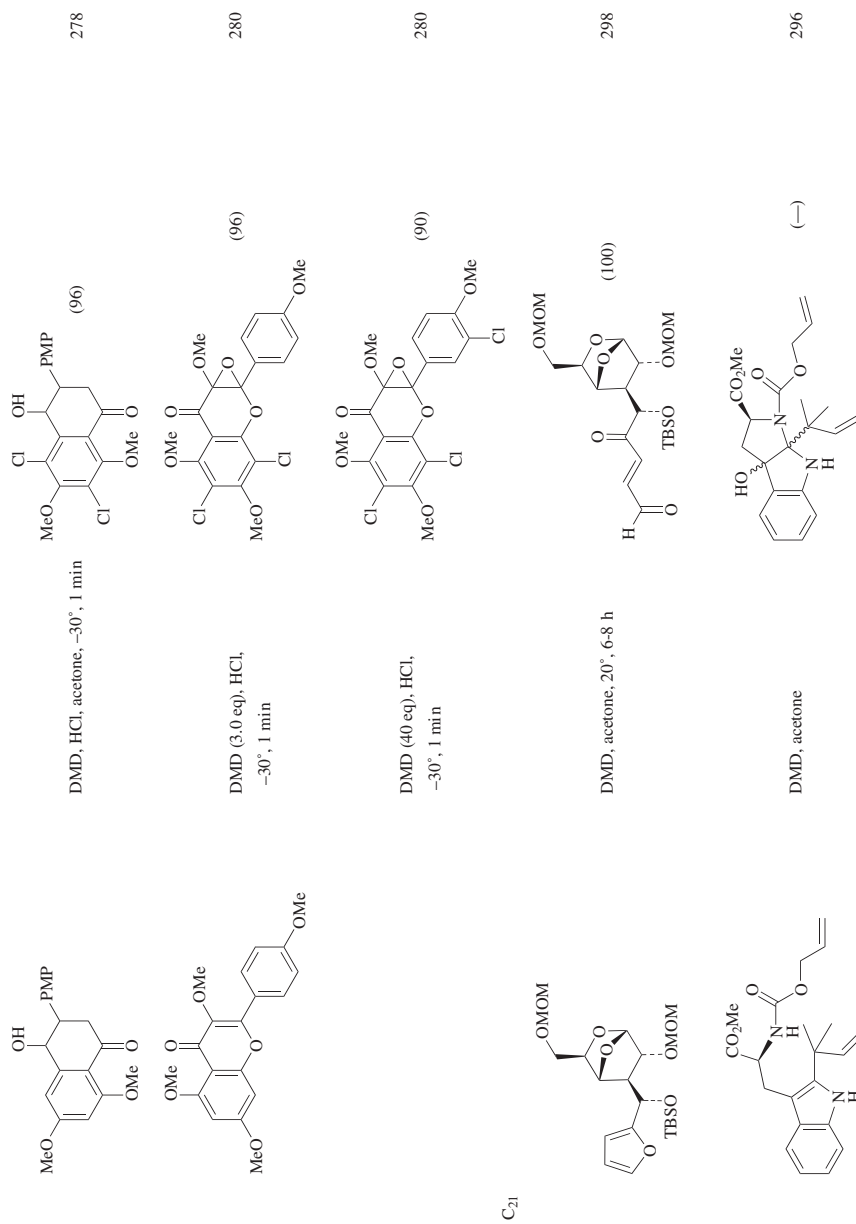
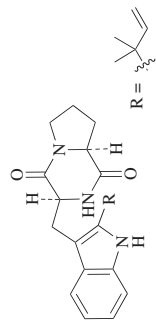

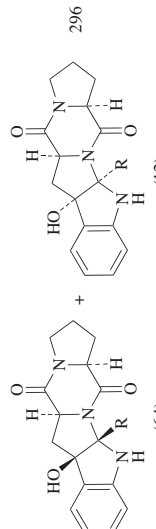
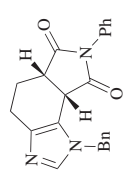
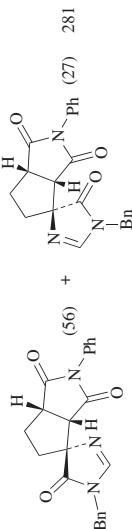
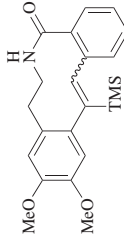
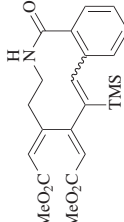
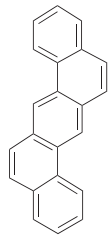
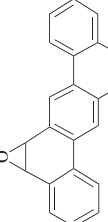
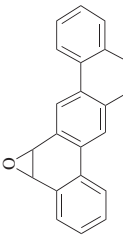
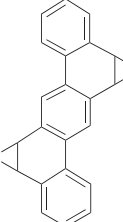


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₁</p>  <p>R = </p>	DMD (4 eq), acetone, CH ₂ Cl ₂ , -78 to 0°, 2.5 h	 <p>(64) + (12)</p>	296
<p>C₂₂</p> 	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 2 h	 <p>(56) + (27)</p>	281
	TFD, TFP, CH ₂ Cl ₂ , rt, 9 h	 <p>(90)</p>	299, 300
	DMD, acetone, 0-5°, 12 h	 <p>(-)</p>	69
	DMD, acetone, 0-5°, 12 h	 <p>(16)</p>	69

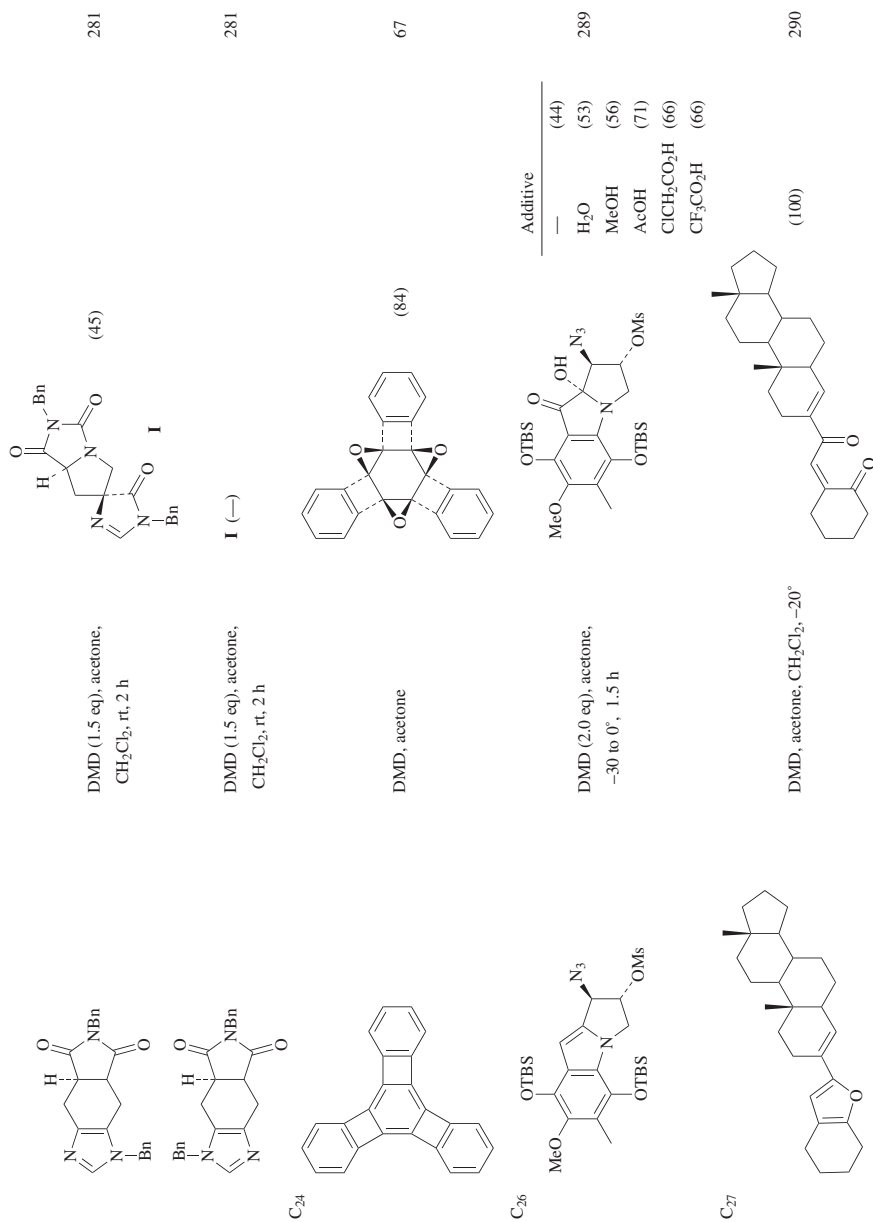
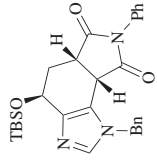
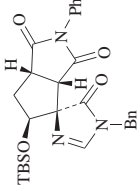
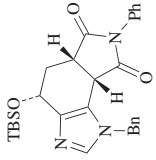
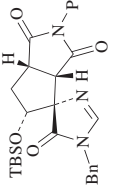
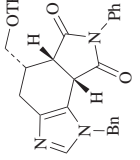
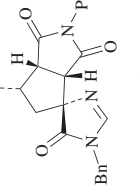
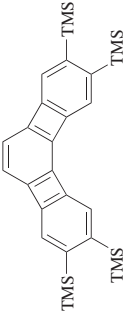
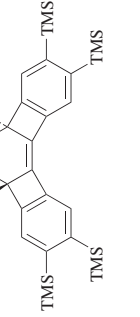

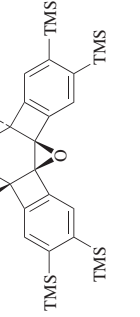
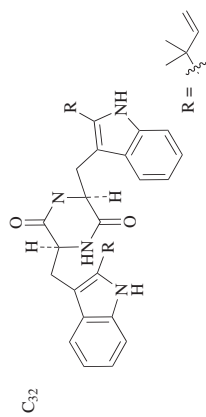
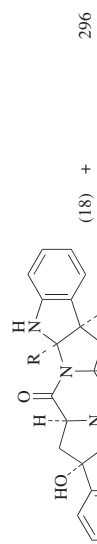


TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

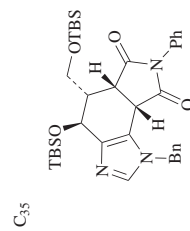
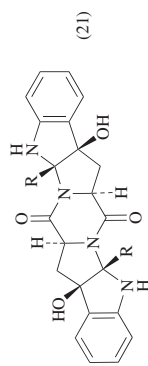
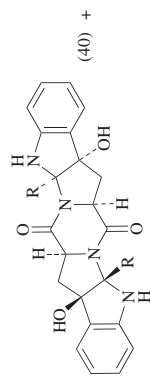
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₈</p>	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , -78°, 2 h	 <p>(82)</p>	281
 <p>C₂₉</p>	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , -78°, 2 h	 <p>(44)</p>	281
 <p>C₂₉</p>	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , rt, 1 h	 <p>(60)</p>	281
 <p>C₃₀</p>	DMD, acetone, rt, 1 h	 <p>(100)</p>	297
 <p>C₃₀</p>	DMD, acetone, rt, 6 h	 <p>(26)</p>	297



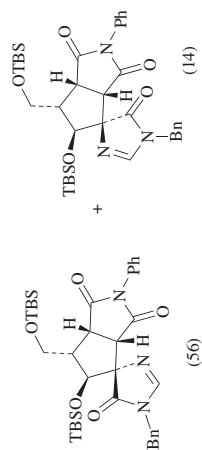
DMD (4 eq), acetone,
CH₂Cl₂, -78 to 0°, 25 h



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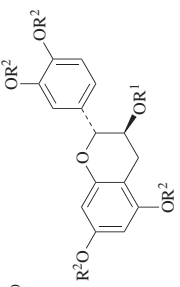
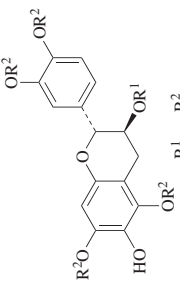
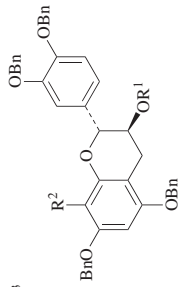
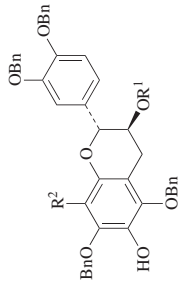


DMD (1.5 eq), acetone,
CH₂Cl₂, rt, 2 h

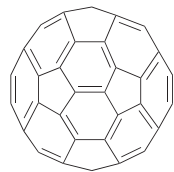


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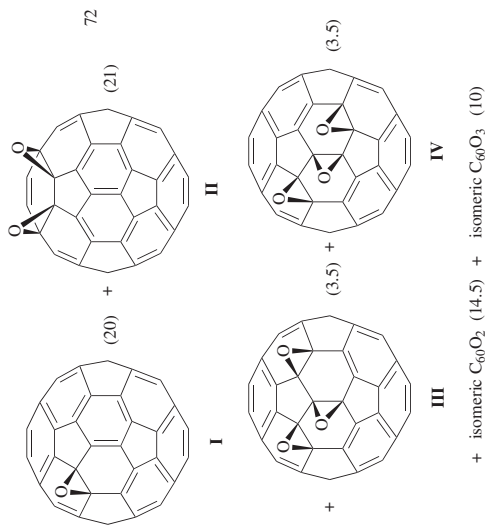
TABLE 2A. OXIDATION OF ARENES AND HETEROARENES BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																					
 <p>C₄₃₋₅₀</p>	DMD, acetone, -15°, 0.6 h	 <p>301</p>																						
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Bn</td> <td>(10-15)</td> </tr> <tr> <td>Bn</td> <td>Bn</td> <td>(13)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	Bn	(10-15)	Bn	Bn	(13)													
R ¹	R ²	Yield (%)																						
H	Bn	(10-15)																						
Bn	Bn	(13)																						
 <p>C₄₃₋₅₃</p>	DMD, acetone	 <p>301</p>																						
	<table border="1"> <thead> <tr> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>-40°</td> <td>7.5 h</td> <td>(33-36)</td> </tr> <tr> <td>-30°</td> <td>36 h</td> <td>(37)</td> </tr> <tr> <td>-40°</td> <td>7.5 h</td> <td>(38)</td> </tr> <tr> <td>-15°</td> <td>0.6 h</td> <td>(30-40)</td> </tr> <tr> <td>-40°</td> <td>7.5 h</td> <td>(34)</td> </tr> <tr> <td>-30°</td> <td>20 h</td> <td>(49)</td> </tr> </tbody> </table>	Temp	Time	Yield (%)	-40°	7.5 h	(33-36)	-30°	36 h	(37)	-40°	7.5 h	(38)	-15°	0.6 h	(30-40)	-40°	7.5 h	(34)	-30°	20 h	(49)		
Temp	Time	Yield (%)																						
-40°	7.5 h	(33-36)																						
-30°	36 h	(37)																						
-40°	7.5 h	(38)																						
-15°	0.6 h	(30-40)																						
-40°	7.5 h	(34)																						
-30°	20 h	(49)																						
	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Br</td> <td></td> </tr> <tr> <td>H</td> <td>CF₃CO</td> <td></td> </tr> <tr> <td>Bn</td> <td>CHO</td> <td></td> </tr> <tr> <td>Bn</td> <td>CO₂H</td> <td></td> </tr> <tr> <td>Bn</td> <td>CH₂OAc</td> <td></td> </tr> <tr> <td>Bn</td> <td>CF₃CO</td> <td></td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	Br		H	CF ₃ CO		Bn	CHO		Bn	CO ₂ H		Bn	CH ₂ OAc		Bn	CF ₃ CO			
R ¹	R ²	Yield (%)																						
H	Br																							
H	CF ₃ CO																							
Bn	CHO																							
Bn	CO ₂ H																							
Bn	CH ₂ OAc																							
Bn	CF ₃ CO																							

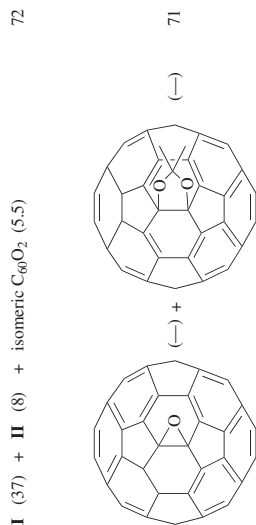
C_{60}



TFD (4 eq), TFP,
1,2-dichlorobenzene,
0°, 6 min



TFD (1.2 eq), TFP,
1,2-dichlorobenzene,
0°, 5 min



DMD, toluene, acetone,
rt, 12 h

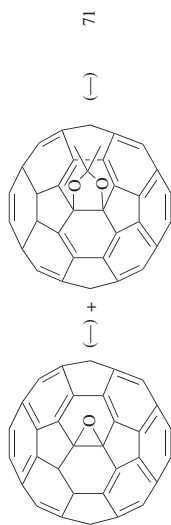
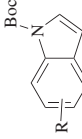
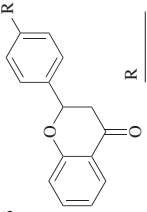
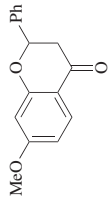
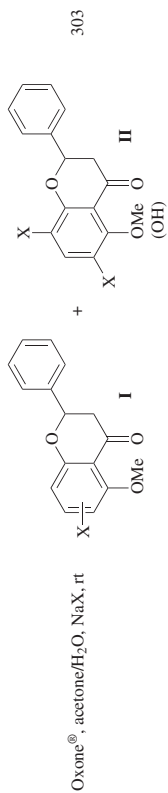


TABLE 2B. OXIDATION OF ARENES AND HETEROARENES BY IN SITU GENERATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₃₋₁₄</p> 	<p>1. (<i>i</i>-Pr)₃B, LDA, THF 2. Oxone®, NaOH, acetone, THF, H₂O, NaHSO₃</p>	<p>R</p> <p>5-Me (89) 4-Cl (70) 7-Me (63) 5-Br (62) H (78)</p>	302
<p>C₁₅₋₁₆</p> 	<p>Oxone®, acetone/H₂O (v/v 1:1), NaX, rt</p> <p>X (eq) Time</p> <p>Br (1) 3 h Br (1) 0.3 h Cl (1) 1 h Cl (4) 0.3 h</p>	<p>Product</p> <p>6-Br (97) 3,6-Br₂ (74) 6-Cl (85) 3,6-Cl₂ (55)</p>	303
<p>C₁₆</p> 	<p>Oxone®, acetone/H₂O (v/v 1:1), NaX, rt</p> <p>X (eq) Time</p> <p>Br (10) 0.3 h Br (5) 0.5 h Cl (4) 6 h Cl (5) 0.5 h</p>	<p>I</p> <p>MeO, Ph, X</p> <p>II</p> <p>MeO, Ph, X</p> <p>I (97) II (—) (—) (98) (38) (30) (—) (98)</p>	303

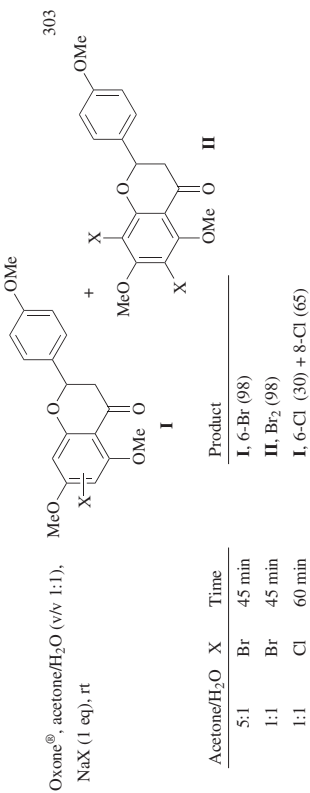


Oxone®, acetone/H₂O, NaX, rt

Acetone/H ₂ O	X (eq)	Time
5:1	Br (1)	0.5 h
1:1	Br (1)	0.25 h
5:1	Cl (1)	2 h
1:1	Cl (3)	0.25 h

Product

I, 6-Br (19) + 8-Br (79)
II, 5-OMe (58) + **II**, 5-OH, Br₂ (36)
I, 8-Cl (59) + **II**, Cl₂ (16)
II, Cl₂ (98)



Oxone®, acetone/H₂O (v/v 1:1),
NaX (1 eq), rt

Acetone/H ₂ O	X	Time
5:1	Br	45 min
1:1	Br	45 min
1:1	Cl	60 min

Product

I, 6-Br (98)
II, Br₂ (98)
I, 6-Cl (30) + 8-Cl (65)

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES


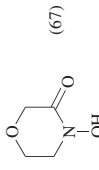

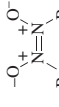








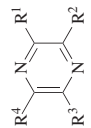
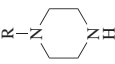
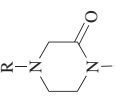
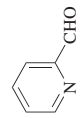

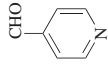
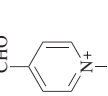
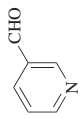

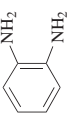

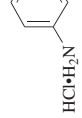

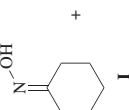
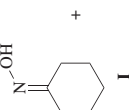
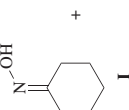
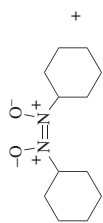
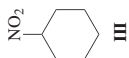
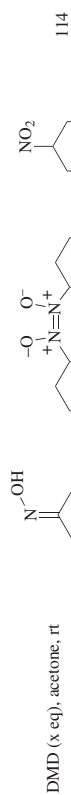
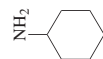
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₀ NO ₂ ⁻	DMD, acetone, rt, 0.5 h	NO ₃ ⁻ (—)	163																
C ₄ 	DMD, acetone, 0°, 20-30 min	 (67)	99																
<i>n</i> -BuNH ₂	DMD (x eq), acetone, rt	 I +  II +  III +  IV	114																
	x Additives	I II III IV																	
	5 —	(20) ^a (34) ^a < 5 ^b (25)																	
	6 NaHCO ₃	(24) (36) (trace) (15)																	
	6 K ₂ CO ₃	(16) (58) (trace) (—)																	
	DMD, acetone, dark, rt, 30 min	III (84)	266																
	DMD, acetone, dark, rt, 30 min	 (87)	266																
<i>t</i> -BuNH ₂	DMD, acetone, dark, rt, 30 min	<i>t</i> -BuNO ₂ (90)	266																
C ₄₋₅ 	DMD, acetone, 0°, 20 to 30 min	 1 (27)  2 (72)	99																
C ₄₋₆ 	DMD, acetone, rt, 18-48 h	<table border="1"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> <td>R⁴</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Cl</td> <td>Me</td> <td>H</td> </tr> <tr> <td>H</td> <td>Cl</td> <td>Cl</td> <td>H</td> </tr> </table>	R ¹	R ²	R ³	R ⁴	H	Cl	H	H	Me	Cl	Me	H	H	Cl	Cl	H	304
R ¹	R ²	R ³	R ⁴																
H	Cl	H	H																
Me	Cl	Me	H																
H	Cl	Cl	H																

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{5-12} 	DMD, acetone, 0°, 20-30 min	R  CHO (89) PhCH ₂ O ₂ C (67) 4-AcC ₆ H ₄ (85)	99
C_6 	DMD, acetone, 20°, 1 h	 (60)	307
	DMD, acetone, 20°, 2 h	 (98)	307
	DMD, acetone, 20°, 1 h	 (98)	307
	DMD, acetone, 20°, 1 h	 (100)	308
$HCl \cdot H_2N$ 	DMD, acetone, H ₂ O, rt, 23 h	 (82)	101



x	Time	I	II	III
3.5	—	(40)	(21)	(trace)
5	NaHCO ₃	(21)	(46)	(—)
5	K ₂ CO ₃	(25)	(33)	(—)
7	CH ₂ Cl ₂	(20)	(48)	(—)
10	—	(24)	(39)	(trace)
10	reverse addition	10 ^a	50 ^a	40 ^a
7	—	(—)	60 ^a	40 ^a
7	dark	(—)	70 ^a	30 ^a

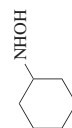
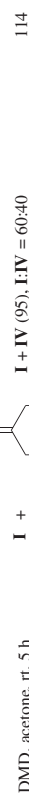
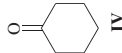
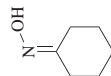
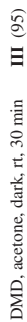
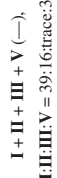
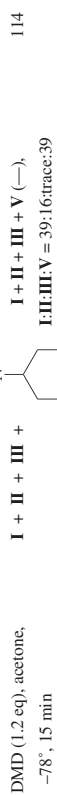
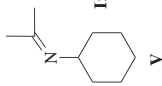
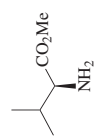
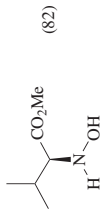

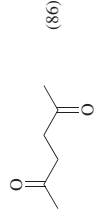
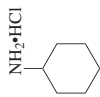
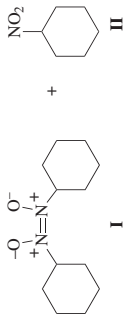



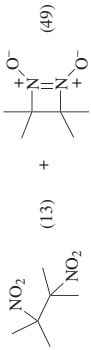


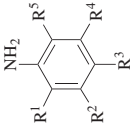
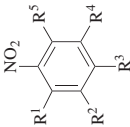


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_6	DMD, acetone, -45° to rt	 (82)	100
 C_6	DMD, acetone, 0° , 1 h	 (86)	308
 C_6	DMD, acetone, rt, 1 h	 I + II (—), I:II = 26:53 I + II (—), I:II = 90:10	114
 C_6	DMD, acetone, H_2O , rt, 30 min	 (20)	101
 C_6	DMD, acetone, 0° , 1 h	 (13) + (49)	308
 C_{6-7}	DMD, acetone, H_2O , rt, 23 h	 (60)	101
 C_{6-7}	DMD, acetone, dark, 22°	 (60)	101, 266


R ¹	R ²	R ³	R ⁴	R ⁵	Time	
H	H	Cl	H	H	30 min	(97)
Cl	H	Cl	H	Cl	10 h	(98)
F	H	H	H	F	10 h	(96)
H	H	H	H	H	30 min	(97)
NH ₂	H	H	H	H	6 h	(85)
NO ₂	H	H	H	H	6 h	(65)
H	NO ₂	H	H	H	30 min	(97)
H	H	NO ₂	H	H	30 min	(98)
H	NO ₂	H	NO ₂	H	overnight	(94)
H	H	Me	H	H	30 min	(98)
H	H	CF ₃	H	H	2 h	(93)
H	H	CN	H	H	30 min	(90)
H	H	CO ₂ H	H	H	30 min	(95)
H	H	MeO	H	H	30 min	(94)
H	H	Ac	H	H	30 min	(95)
						C ₇
						(91)
					Cyclohexanone dioxirane, acetone, cyclohexanone, CH ₂ Cl ₂ , -10°, 20 min	98
						(100)
					DMD, acetone, 0°, < 1 h	95
						(100)
					DMD, acetone, 0°, < 1 h	95

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

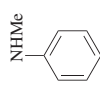
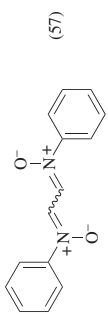
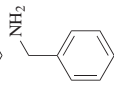
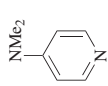
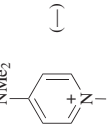
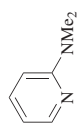
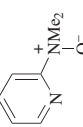
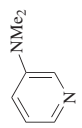
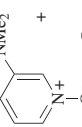
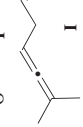
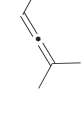
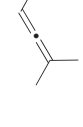





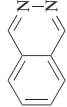
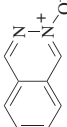
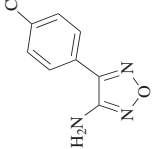
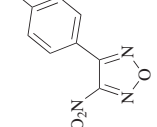
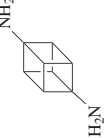
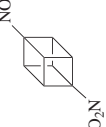
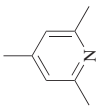

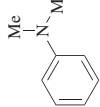
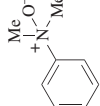
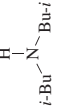

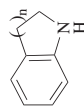
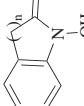
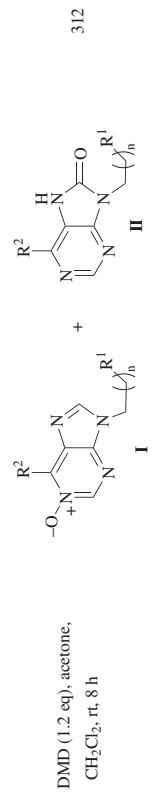
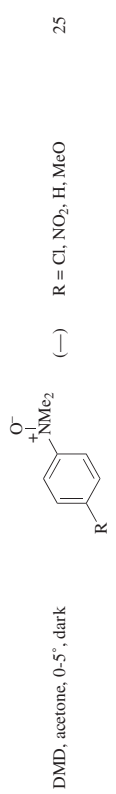
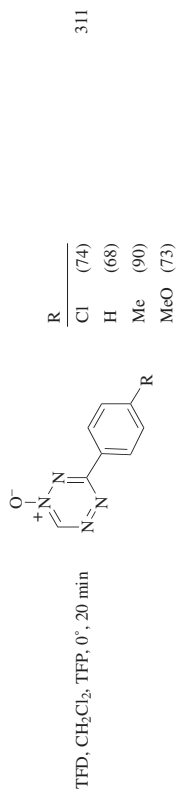
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	DMD, acetone, 0°, 5 min	 (57)	309												
	DMD (6 eq), acetone, rt	<table border="0"> <tr> <td>—</td> <td>—</td> <td>E:Z</td> </tr> <tr> <td>—</td> <td>(60)</td> <td>—</td> </tr> <tr> <td>NaHCO₃</td> <td>(69)</td> <td>9:1</td> </tr> <tr> <td>K₂CO₃</td> <td>(65)</td> <td>8:1</td> </tr> </table>	—	—	E:Z	—	(60)	—	NaHCO ₃	(69)	9:1	K ₂ CO ₃	(65)	8:1	114
—	—	E:Z													
—	(60)	—													
NaHCO ₃	(69)	9:1													
K ₂ CO ₃	(65)	8:1													
	DMD, acetone	 (—)	21												
	DMD, acetone	 (—)	21												
	DMD, acetone	 +  +  +  +  +  +  +  +  + +													

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

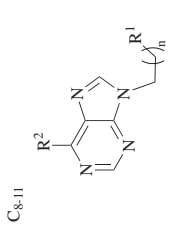
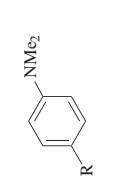
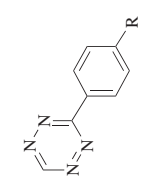
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone	 (—)	21
	DMD, acetone	 (—)	149
	DMD, acetone, CH ₂ Cl ₂ , rt, 48 h	 (80)	101
	DMD, acetone, 0°, < 1 h	 (100)	95
	DMD, acetone, 0°, < 1 h	 (100)	95
	DMD, acetone, 0°, 10 min	 (97)	96
	DMD, acetone, 0°, 20-30 min	 1 (54) 2 (83)	99



Ar =

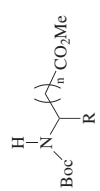
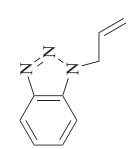
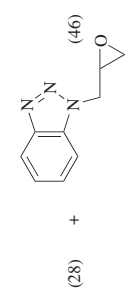
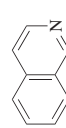
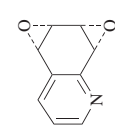
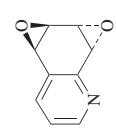
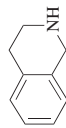
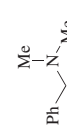
Catalyst A: R³ = OMe, R⁴ = Cl
 Catalyst B: R³ = Cl, R⁴ = H

Catalyst	I	II
A	(-)	(98)
B	(93)	(-)
A	(98)	(-)
A	(92)	(-)
B	(94)	(-)
B	(95)	(-)
A	(15)	(30)
A	(95)	(-)
B	(97)	(-)
A	(91)	(-)
B	(93)	(-)



R ¹	R ²	n
OH	NH ₂	3
OH	NH ₂	3
OH	H	3
OH	NH ₂	2
OH	NH ₂	2
OH	NH ₂	4
OH	NH ₂	4
Me	NH ₂	4
Me	NH ₂	4
OAc	NH ₂	3
OAc	NH ₂	3

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
		R	n	x	Time	
C_{8-12} 	TFD (x eq), TFP, CH ₂ Cl ₂ , -20 to 0°	H	0	2.0	5 h (82)	313
		<i>i</i> -Pr	0	3.1	6 h (75)	
C_9 	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 24 h; rt, 12 h	H	4	2.0	8 h (74)	
		(28) +			 (46)	310
	DMD, acetone, 0°, < 1 h	(100)				95
	DMD, acetone, 10°, 3 h	(99)				314
	DMD, acetone, 10°, 3 h	(93)				314
	DMD, acetone, 0°, 20-30 min	(48)				99
	DMD, acetone, 0°, < 1 h	(100)				95

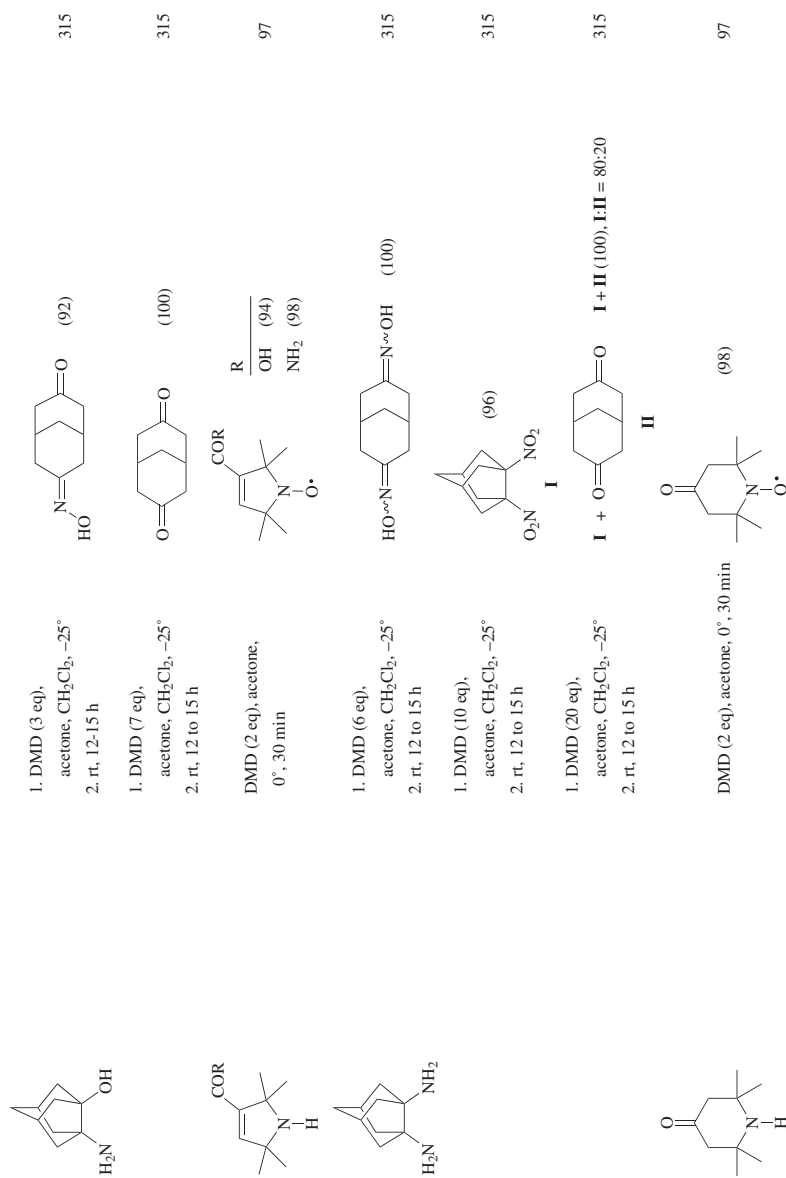
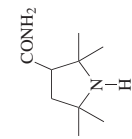
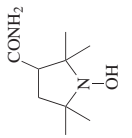
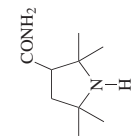
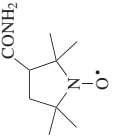
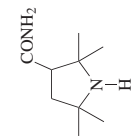
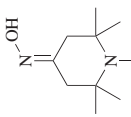
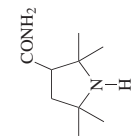
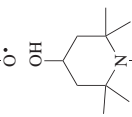
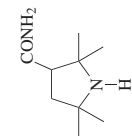
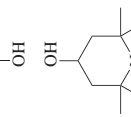
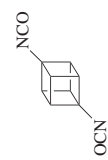
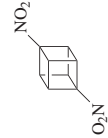


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₉	DMD, acetone, 0°, 2 h	 (96)	96
 C ₉	DMD (2 eq), acetone, 0°, 30 min	 (100)	97
 C ₉	DMD (2 eq), acetone, 0°, 30 min	 (99)	97
 C ₉	DMD, acetone, 0°, 2 h	 (99)	96
 C ₉	DMD (2 eq), acetone, 0°, 30 min	 (100)	97
 C ₁₀	DMD, acetone, H ₂ O, dark, N ₂ , rt, 1.5 h	 (85)	316

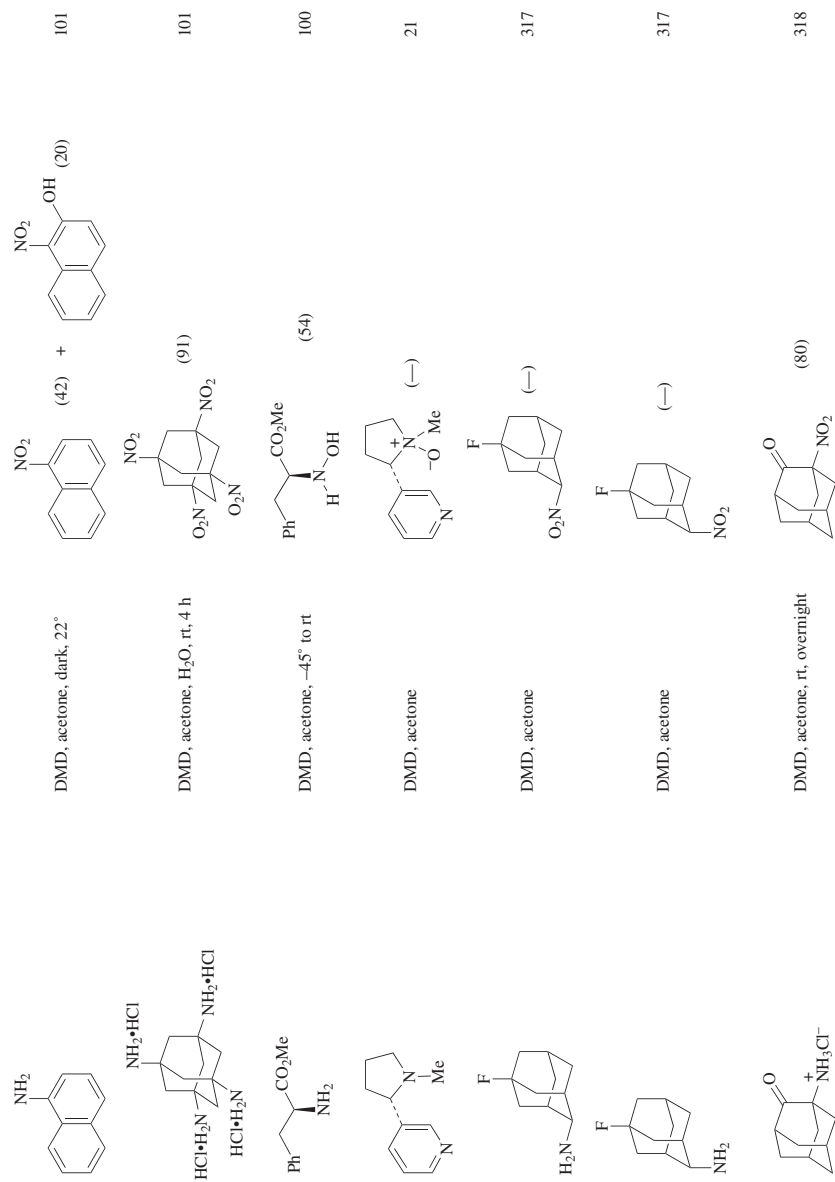


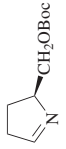

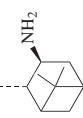
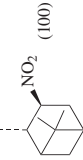


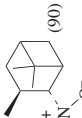
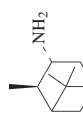
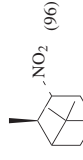


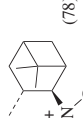
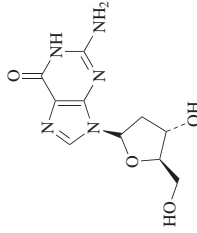
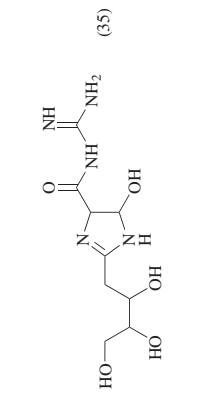
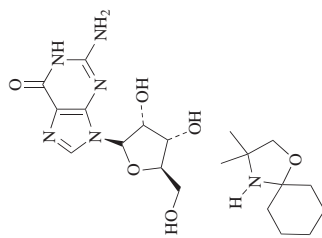
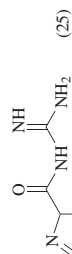


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, dark, rt, 30 min	 (95)	266
	TFD (1.2 eq), TFP, CH ₂ Cl ₂ , -78°, 1 h	 (100)	319
	DMD, acetone, CH ₂ Cl ₂ , rt, 1 h	 (100)	22
	DMD (insufficient amount), acetone, CH ₂ Cl ₂ , rt, 35 min	 (10) +  (90)	22
	DMD, acetone, CH ₂ Cl ₂ , rt, 1 h	 (96)	22
	DMD (insufficient amount), acetone, CH ₂ Cl ₂ , rt, 35 min	 (22) +  (78)	22
	DMD (2.5 eq), acetone, 90°, 5 h	 (35)	320

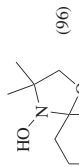


320



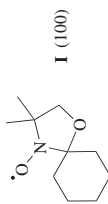
DMD (2.5 eq), acetone, 90°, 5 h

96



DMD, acetone, 0°, 2 h

97



DMD (2 eq), acetone, 0°, 30 min

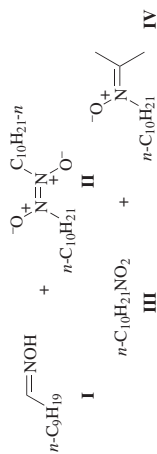
98

Cyclohexanone dioxirane,
acetone, cyclohexanone,
20°, 10 min

98

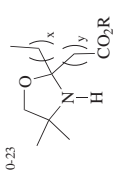
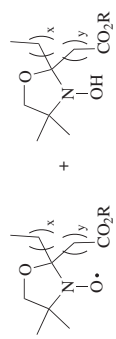
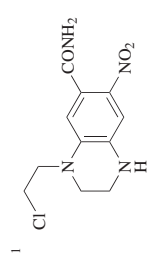
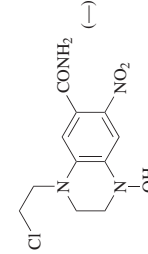
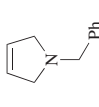
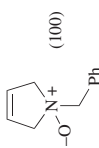
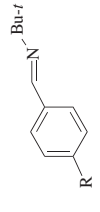
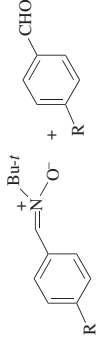
Acetone, cyclohexanone,
-20°, 10 min

114

 $n\text{-C}_{10}\text{H}_{21}\text{NH}_2$

Additives	I	II	III	IV
—	(51)	(18)	(8)	(3)
NaHCO ₃	(43)	(13)	(trace)	(17)
K ₂ CO ₃	(73)	(18)	(trace)	(—)

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C_{10-23}</p>  <p style="text-align: center;"> $\begin{matrix} x & y & R \\ 0 & 2 & Me \\ 1 & 3 & Me \\ 6 & 3 & Me \\ 6 & 3 & [(CH_2)_2O]_3Me \end{matrix}$ </p>	DMD, acetone, 0°, 30 min		321
<p>C_{11}</p> 	DMD, acetone, 0°, 10 min		322
	DMD, acetone, 0°, < 1 h		95
	DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h		102

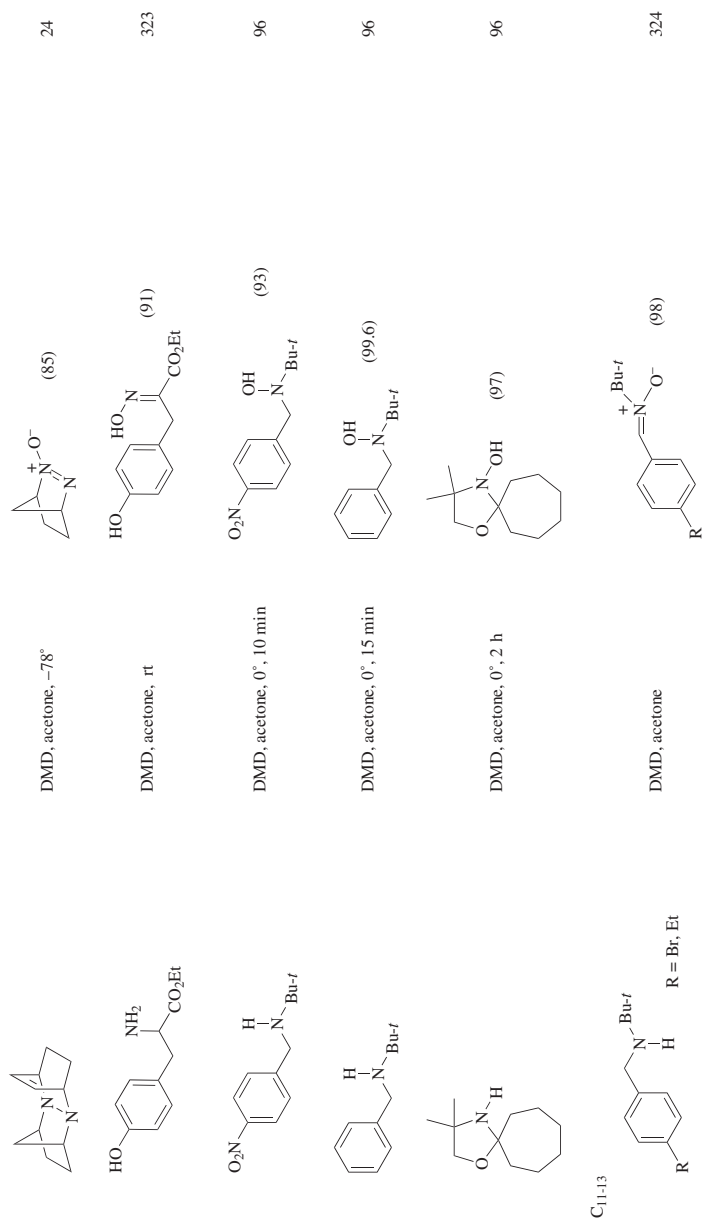
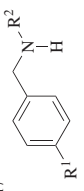
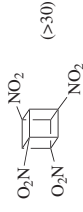
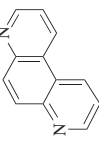
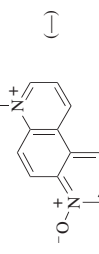
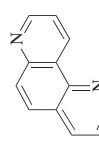
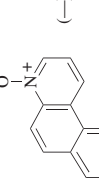
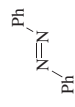
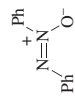


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₁₋₁₇	DMD, acetone, 0°, 10 min	 R ¹ R ² Cl <i>t</i> -Bu (99) F <i>t</i> -Bu (99) NO ₂ <i>t</i> -Bu (95) H <i>t</i> -Bu (96) CF ₃ <i>t</i> -Bu (98) Me <i>t</i> -Bu (99) MeO <i>t</i> -Bu (98) <i>t</i> -Bu <i>t</i> -Bu (99) Cl Ph (96) H Ph (98) H Bn (96) H 1-Ad (99)	309
 C ₁₂	DMD, acetone, H ₂ O, overnight	 (>30)	325
	DMD, acetone	 (—)	21
	DMD, acetone	 (—)	21
	DMD, acetone, dark, rt, 30 min	 (96)	266

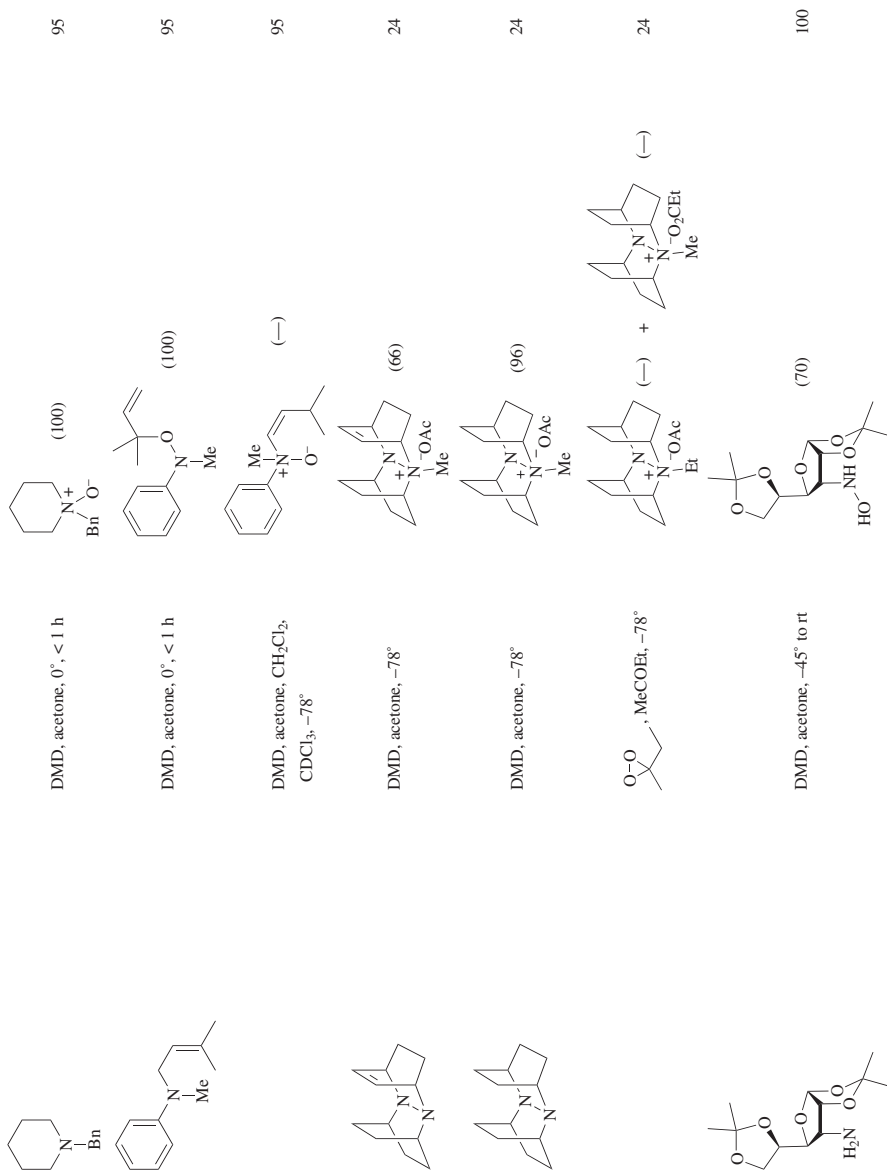
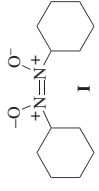

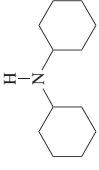
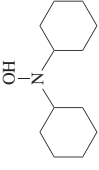
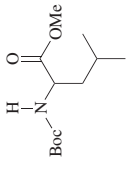
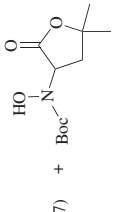

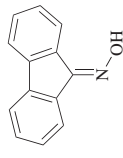
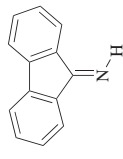
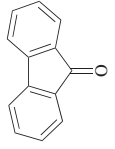
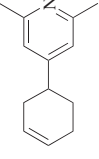
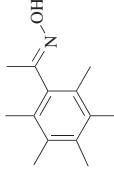
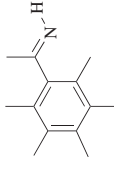
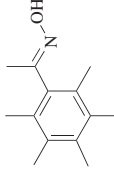
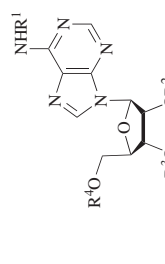
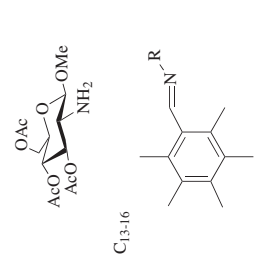
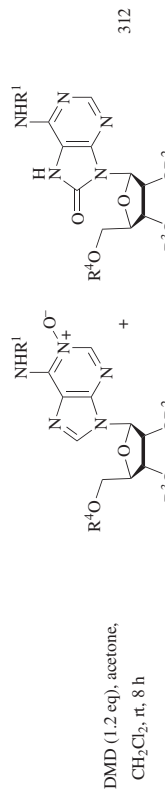
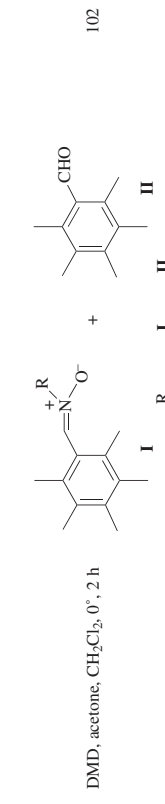
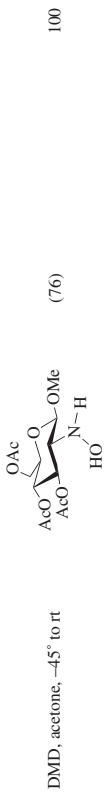
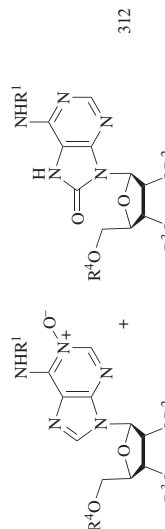
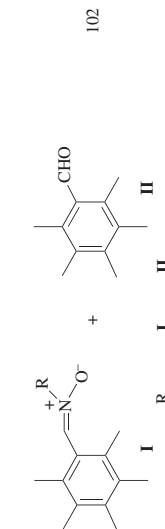


TABLE 3.A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

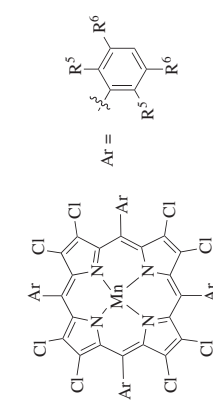
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 I	DMD, acetone, rt, 6 h	 II	114
 (82)	DMD, acetone, 0°, 10 min	 (82)	96
 (57)	TFD (5 eq), TFP, CH ₂ Cl ₂ , -20 to 0°, 6 h	 (21)	313
 (100)	DMD, acetone, 0°, < 1 h	 (90)	95
 (90)	DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	 (2)	102
 (100)	DMD, acetone, 0°, < 1 h	 (39)	95
 (39)	DMD, acetone, CH ₂ Cl ₂ , 0°, 2 h	 (39)	102



R ¹	R ²	R ³	R ³
Ac	Ac	Ac	Ac
Ac	Ac	Ac	Ac
H	-C(Me) ₂ -	H	H
H	-C(Me) ₂ -	H	H
H	-C(Me) ₂ -	H	H
H	-C(Me) ₂ -	H	H


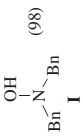
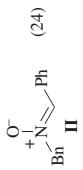

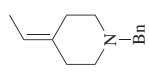
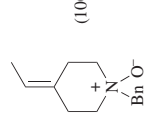
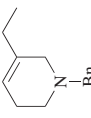
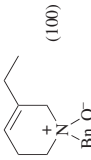
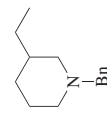
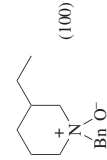
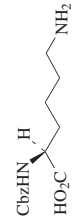
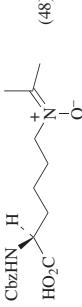



Catalyst	I	II
A	(93)	(-)
B	(93)	(-)
A	(25)	(70)
A	(-)	(76)
B	(88)	(-)
B	(81)	(-)



Catalyst A: R⁵ = OMe, R⁶ = Cl
 Catalyst B: R⁵ = Cl, R⁶ = H

TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{14}	DMD, acetone, 0°, 15 min	 I (98)	96
	Cyclohexanone dioxirane, cyclohexanone, 20°, 5 min	 I (68) + II (24)	98
	Cyclohexanone dioxirane (2 eq), cyclohexanone, 20°, 5 min	 II (65)	98
	DMD, acetone, 0°, < 1 h	 (100)	95
	DMD, acetone, 0°, < 1 h	 (100)	95
	DMD, acetone, 0°, < 1 h	 (100)	95
	1. SOCl ₂ , MeOH 2. DMD, acetone, -78°	 (48)	326
	1. SOCl ₂ , MeOH, -5° to rt, overnight 2. NaHCO ₃ , rt 3. DMD, acetone, -78°, 5-10 min	 (48)	327

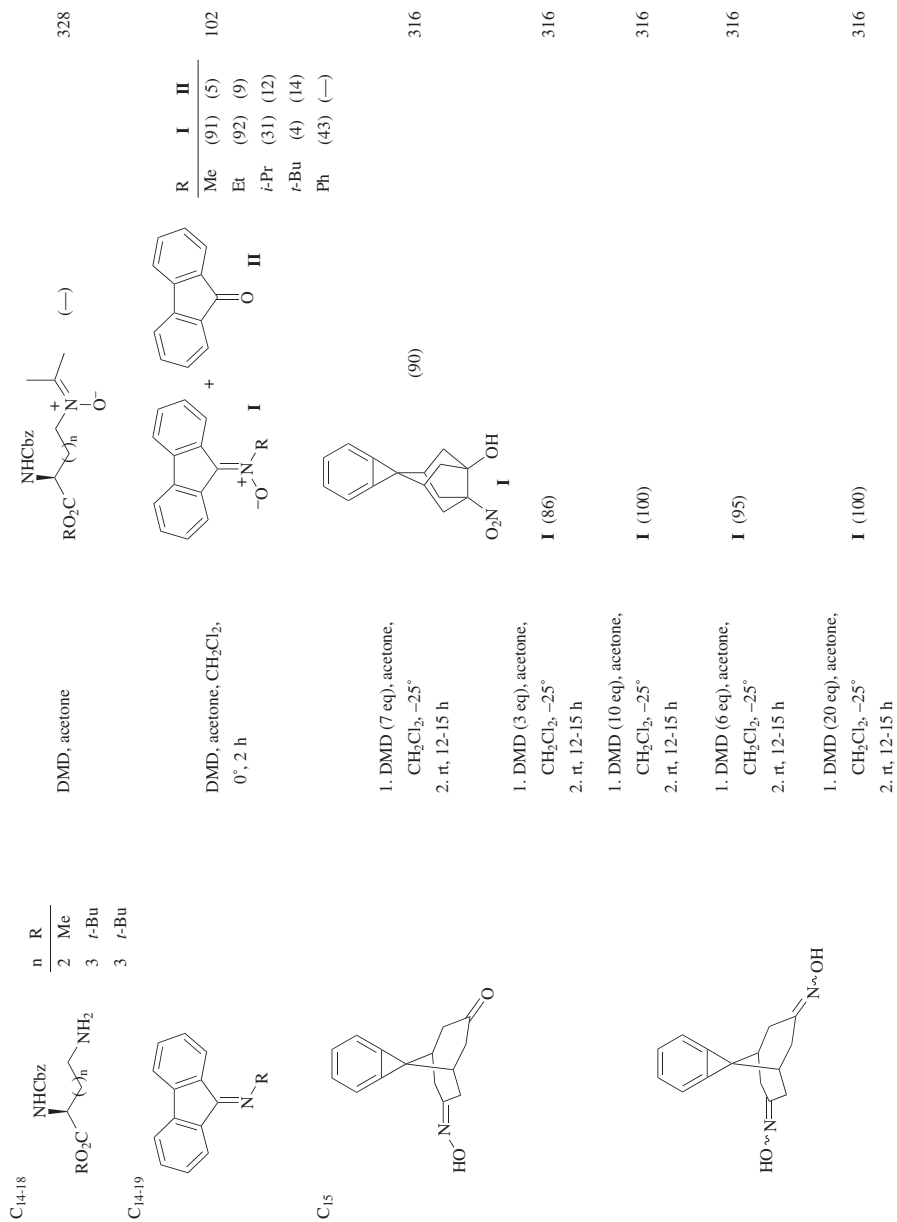


TABLE 3.A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₅</p>	<p>DMD, acetone, 0°, < 1 h</p>	<p>(—)</p>	95
	<p>1. DMD (3 eq), acetone, CH₂Cl₂, -25° 2. rt, 12-15 h</p>	<p>(100)</p>	316
	<p>1. DMD (6 eq), acetone, CH₂Cl₂, -25° 2. rt, 12-15 h</p>	<p>(100)</p>	316
	<p>1. DMD (12 eq), acetone, CH₂Cl₂, -25° 2. rt, 12-15 h</p>	<p>(96)</p> <p>I</p>	316
<p>C₁₆</p>	<p>DMD, acetone, -45° to rt</p>	<p>(—)</p>	100

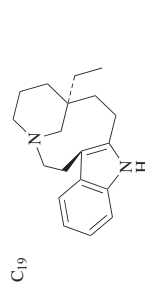
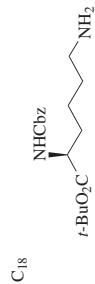
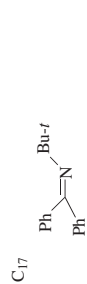
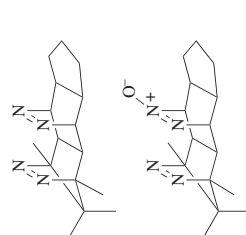
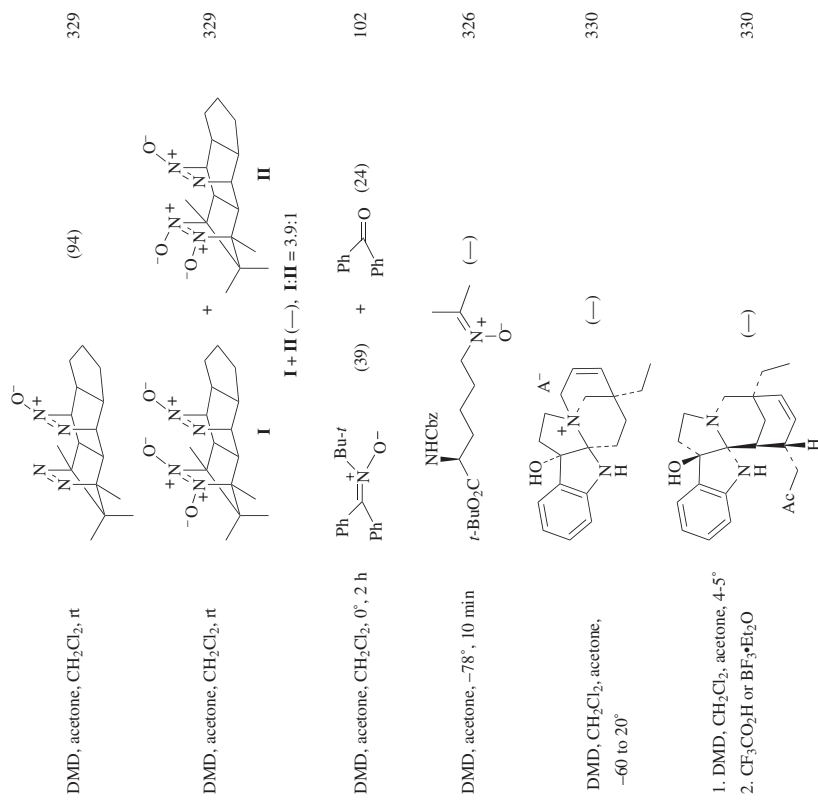
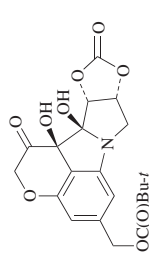
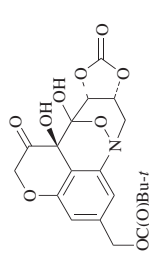
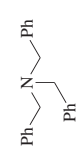
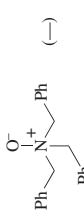
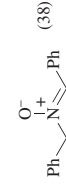


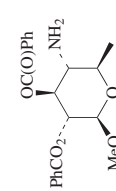
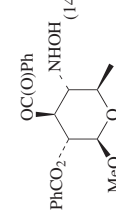
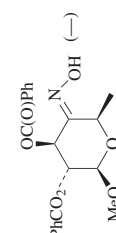


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₃₀	DMD, acetone	 (—) 331	
	DMD, acetone, -78°	 (—) 95	
	DMD, acetone, 0°, < 1 h	PhCHO (31) +  (38) 95	
	DMD, acetone, -45° to rt	 (75) 100	
	DMD, acetone, -45° to rt	 (14) +  (—) 332	

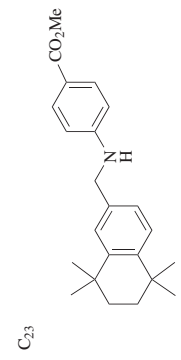
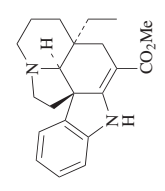
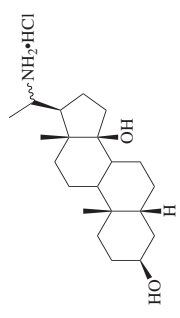
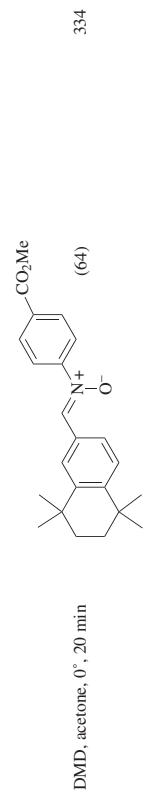
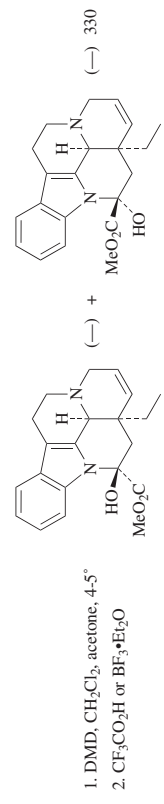
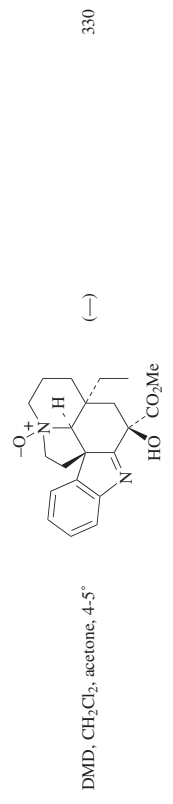
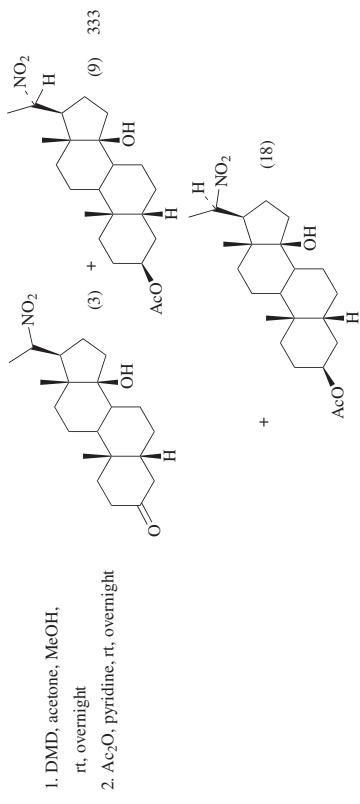
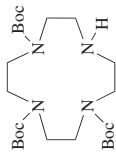
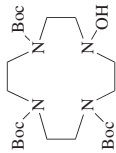
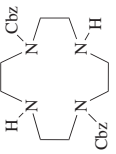
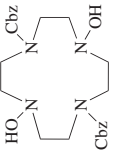
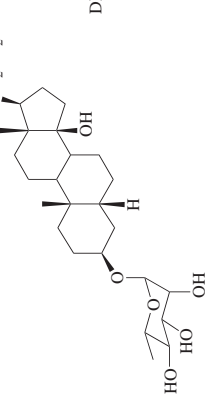
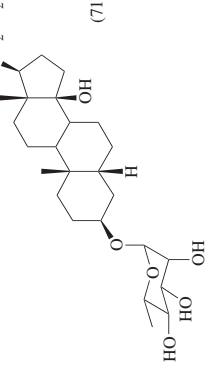
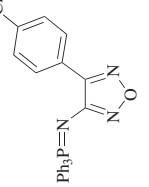
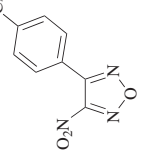
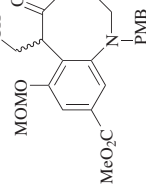
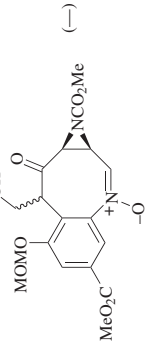


TABLE 3.A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₃	DMD, acetone, 0° to rt, 4 h	 (81)	335
 C ₂₄	DMD, acetone, 0° to rt, 70 min	 (46)	335
 C ₂₆	DMD, acetone, MeOH, 30 min	 (71)	336
	DMD, acetone	 (—) + Ph ₃ PO (—)	149
	TFD, CH ₂ Cl ₂ , -22°	 (—)	337

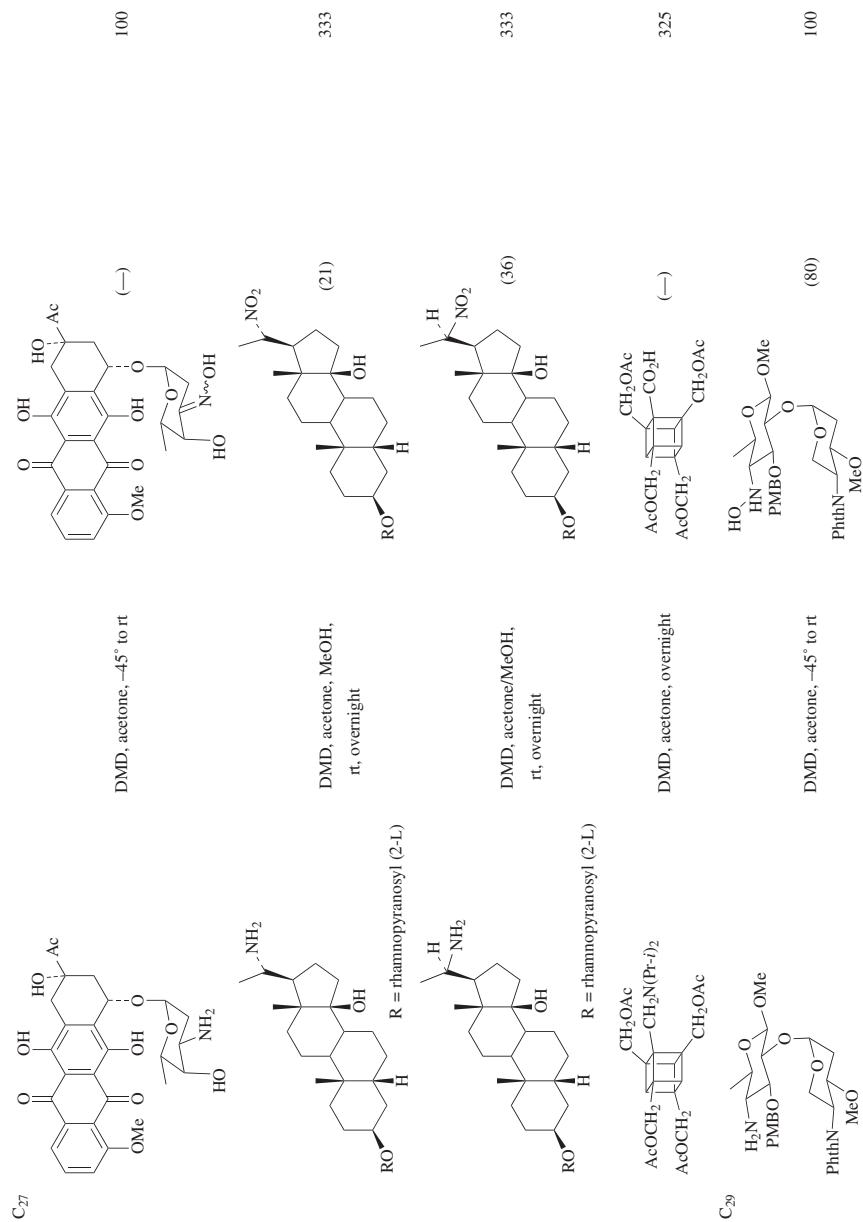
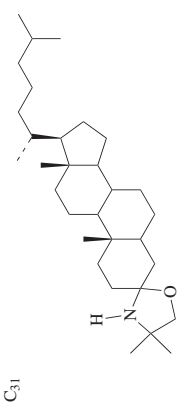
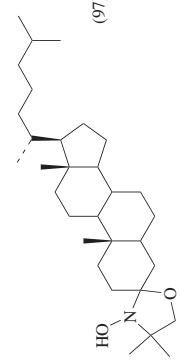
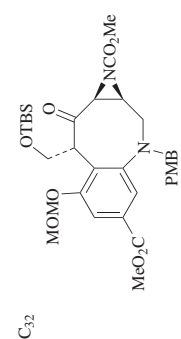
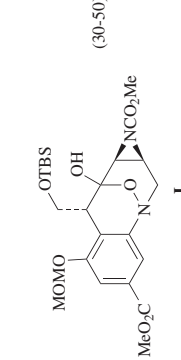
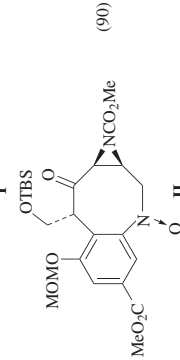
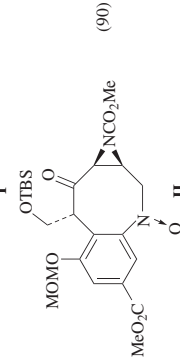
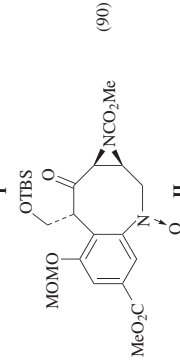
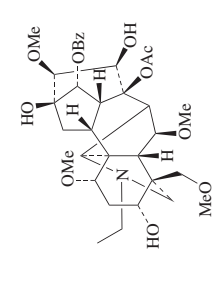
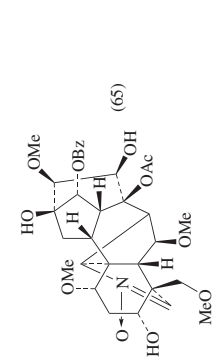
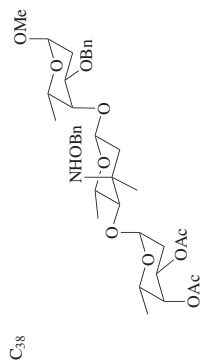


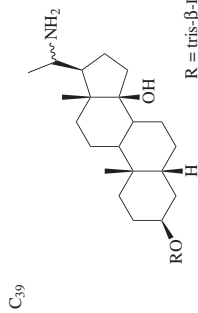
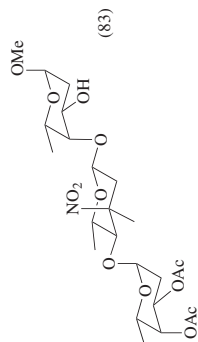
TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₃₁	DMD, acetone, 0°, 2 h	 (97)	96
 C ₃₂	DMD, CH ₂ Cl ₂ , sat K ₂ CO ₃ , 0° to rt, 7 h	 (30-50)	337
		 I	
		 II	
		I:II = 1:1	
	DMD, CH ₂ Cl ₂ , 0°-rt	 (90)	337
	DMD, CH ₂ Cl ₂ , sat NaHCO ₃ , 0° to rt		337
 C ₃₄	DMD, acetone, -20°	 (65)	338



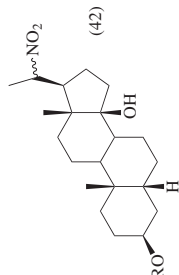
DMD, acetone, -78° to rt, 24 h

339



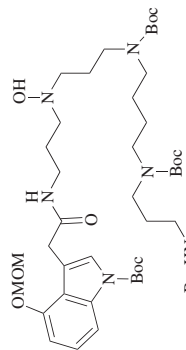
DMD, acetone, CH₂Cl₂, rt, 15 min

333



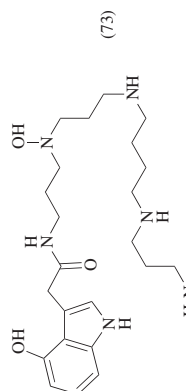
C₄₅

R = tris-β-D-digitoxosyl

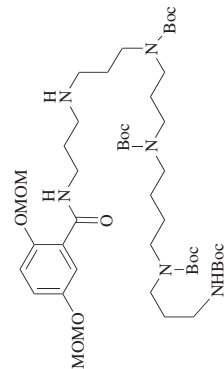


DMD, acetone, HCl, Ar, 1 h

340



C₄₇



1. DMD, acetone, N₂, 0°, 15 min
2. NaCNBH₃, AcOH, rt, 2 h

340

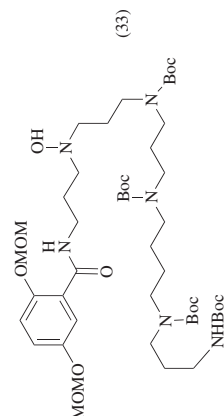
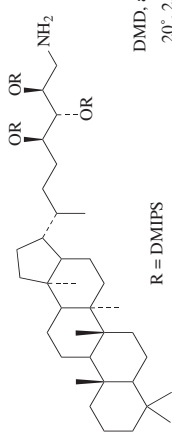
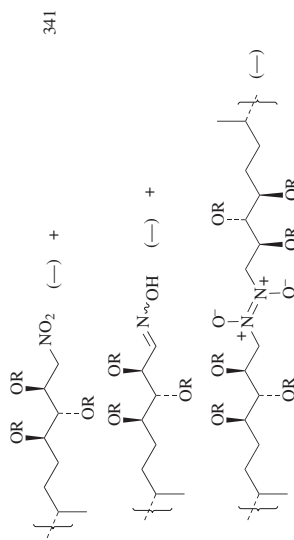
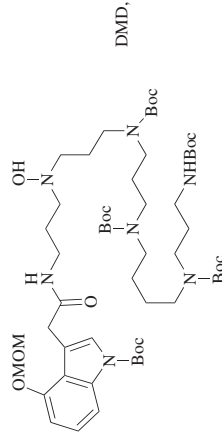
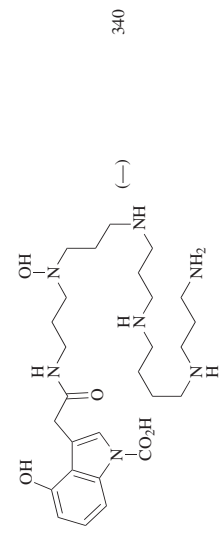


TABLE 3A. NITROGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₅₀</p>  <p>R = DMIPS</p>	DMD, acetone, CH ₂ Cl ₂ , 20°, 2.5 h	 <p>341</p>	
<p>C₅₃</p> 	DMD, acetone, HCl, Ar, 1 h	 <p>340</p>	

^a The two products were obtained as a mixture.

^b This value is the ratio of this compound in the crude products.

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES

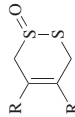
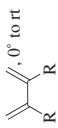
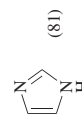
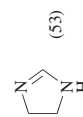
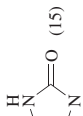
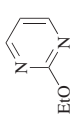
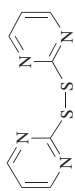
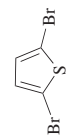
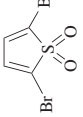
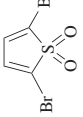


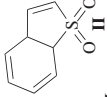
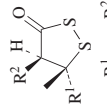
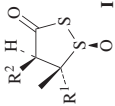
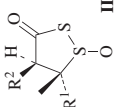
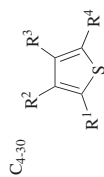
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₀ ³⁴ S ₈	DMD, acetone, CH ₂ Cl ₂ , 0°, 1 h	³⁴ S ₂ O (—)	342
S ₈	1. DMD, CH ₂ Cl ₂ , benzene, acetone, 0°, 1 h	 R	R (33)
	2.  , 0° to rt	R	Ph (27)
C ₂₋₅	DMD, CH ₂ Cl ₂ , benzene, acetone, 0°, 1 h	S ₂ O (—)	343
	1. DMD, acetone, CH ₂ Cl ₂ , N ₂ , -40°, 1 h 2. Air	RSO ₂ H	R Et (73) <i>n</i> -Pr (74) <i>i</i> -Pr (90) <i>n</i> -Bu (84) <i>i</i> -Bu (95) <i>n</i> -C ₃ H ₁₁ (96)
C ₃	DMD, acetone, MeOH, rt	 (81)	142
	DMD, acetone, MeOH, rt	 (53) +  (15)	142
C ₄	DMD, acetone, CH ₂ Cl ₂ , EtOH, rt	 (53)	143
	DMD, acetone, CH ₂ Cl ₂ , rt	 (77)	143

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

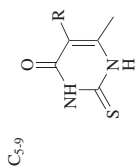
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_4	DMD, acetone, several days	 (27) 	344
	DMD, acetone, temp 1; solvent removal, temp 2 Temp 1 Time Temp 2	 (I) +  (II) 88:12 91:9 100:0	141, 345, 346,
 C_{4+13}	DMD, acetone, CH_2Cl_2 , -78°	 (I) +  (II) I:II 2:1 8:1 18:1 5:1 2:1 15:1 8:1	137



DMD, acetone, CH₂Cl₂, rt

R ¹	R ²	R ³	R ⁴
Br	H	H	Br
Et	H	H	H
Me	H	H	Me
Et	H	H	Ac
Bn	H	H	Bn
Ph	Ph	Ph	Ph
PhCO	Ph	Ph	Bz

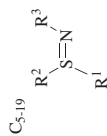
138



DMD, acetone, CH₂Cl₂, rt

R	I	II
H	(55)	(32)
<i>t</i> -Bu	(40)	(37)

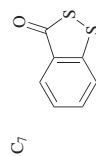
143



DMD, acetone, rt

R ¹	R ²	R ³	Time
Me	Et	Ac	2 h (86)
Me	Et	Ts	4 h (86)
Me	4-ClC ₆ H ₄	Ts	6 h (49)
Me	Ph	Ts	6 h (72)
Me	4-MeC ₆ H ₄	Ts	6 h (77)
Me	4-MeOC ₆ H ₄	Ts	6 h (86)
Ph	Ph	Ts	6 h (64)

148



DMD (1-2 eq), acetone, rt

R ¹	R ²	R ³
(-)	(-)	(-)

347

DMD (4 eq), acetone, rt, 2-4 h

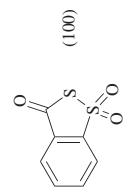


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)




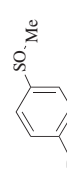
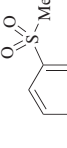
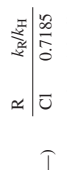
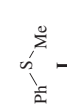




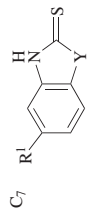
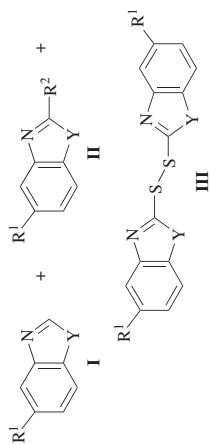
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
C_7 	TFD, vigorous conditions	 (—) +  (—) (—)	348																												
	DMD, acetone	 (—)  (—) R $\frac{kg/k_H}{Cl}$ NO ₂ 0.2762 H 1.0000 Me 1.337 MeO 1.857	349																												
 I	DMD, acetone, rt	 (65)	121																												
	DMD, CCl ₄ , minutes	 (—)	156, 157																												
	TFD, solvent, 0°	 II +  III (—)	348																												
	I:TFD Solvent	<table border="1"> <thead> <tr> <th>I:TFD</th> <th>Solvent</th> <th>I:II:III</th> <th>III:II</th> </tr> </thead> <tbody> <tr> <td>1:1</td> <td>CH₂Cl₂</td> <td>42:12:46</td> <td>3.8</td> </tr> <tr> <td>10:1</td> <td>CH₂Cl₂</td> <td>93:3:4</td> <td>1.3</td> </tr> <tr> <td>2:1</td> <td>CH₂Cl₂</td> <td>68:9:23</td> <td>2.6</td> </tr> <tr> <td>2:1</td> <td>CH₂Cl₂/acetone (1:19)</td> <td>71:8:21</td> <td>2.6</td> </tr> <tr> <td>2:1</td> <td>CH₂Cl₂/CH₃CN (1:19)</td> <td>68:9:23</td> <td>2.6</td> </tr> <tr> <td>2:1</td> <td>CH₂Cl₂/CF₃CH₂OH (1:7)</td> <td>66:18:16</td> <td>0.9</td> </tr> </tbody> </table>	I:TFD	Solvent	I:II:III	III:II	1:1	CH ₂ Cl ₂	42:12:46	3.8	10:1	CH ₂ Cl ₂	93:3:4	1.3	2:1	CH ₂ Cl ₂	68:9:23	2.6	2:1	CH ₂ Cl ₂ /acetone (1:19)	71:8:21	2.6	2:1	CH ₂ Cl ₂ /CH ₃ CN (1:19)	68:9:23	2.6	2:1	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:7)	66:18:16	0.9	
I:TFD	Solvent	I:II:III	III:II																												
1:1	CH ₂ Cl ₂	42:12:46	3.8																												
10:1	CH ₂ Cl ₂	93:3:4	1.3																												
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2:1	CH ₂ Cl ₂ /CH ₃ CN (1:19)	68:9:23	2.6																												
2:1	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:7)	66:18:16	0.9																												

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.														
 C ₇	DMD (1.5 eq), CH ₂ Cl ₂ , -50 to 30°, 5 h	(48) + (trace) + (trace) + (trace)	351														
 C ₇	DMD (2.2 eq), CH ₂ Cl ₂ , 0°, 3 h	I (88)	351														
 C ₇	DMD, CH ₂ Cl ₂ , 0°	(98)	351														
 C ₇₋₈	DMD, acetone	(—)	349														
		<table border="1"> <thead> <tr> <th>R</th> <th>k_p/k_H</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>0.6356</td> </tr> <tr> <td>Cl</td> <td>0.6598</td> </tr> <tr> <td>NO₂</td> <td>0.2093</td> </tr> <tr> <td>H</td> <td>1.0000</td> </tr> <tr> <td>Me</td> <td>1.237</td> </tr> <tr> <td>MeO</td> <td>1.548</td> </tr> </tbody> </table>	R	k _p /k _H	Br	0.6356	Cl	0.6598	NO ₂	0.2093	H	1.0000	Me	1.237	MeO	1.548	
R	k _p /k _H																
Br	0.6356																
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NO ₂	0.2093																
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MeO	1.548																



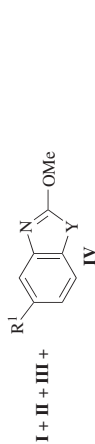
DMD, CH₂Cl₂, acetone, rt



142

R ¹	R ²	Y	I	II	III
H	AcCH ₂	O	(18)	(37)	(42)
H	—	S	(—)	(—)	(95)
Me	OH	NH	(55)	(18)	(—)

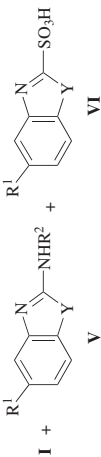
DMD, acetone, CH₂Cl₂,
MeOH, rt



142

R ¹	Y	I	II	III	IV
H	O	(11)	(13)	(0)	(72)
H	S	(—)	(—)	(88)	(—)
Me	NH	(20)	(—)	(—)	(74)

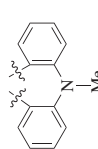
DMD, acetone,
R²NH₂, CH₂Cl₂, rt



142

R ¹	R ²	Y	I	V	VI
H	H	O	(20)	(68)	(—)
H	H	S	(—)	(—)	(9)
Me	H	NH	(—)	(75)	(—)
Me	Et	NH	(21)	(62)	(—)
Me	<i>n</i> -Pr	NH	(29)	(54)	(—)
Me	<i>n</i> -Bu	NH	(35)	(57)	(—)

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions		Product(s) and Yield(s) (%)				Refs.
	Solvent	TFD (x eq), TFP, 0°	R ¹	R ²	x	% Conv.	
$C_{7,13}$ R^1-S-R^2			$R^1-S(=O)-R^2$	$R^1-S(=O)-R^2$	$R^1-S(=O)-R^2$		352
$-ArN(Me)Ar-$							
							
	Solvent	TFD (x eq), TFP, 0°	R ¹	R ²	x	% Conv.	I II III
	CH ₂ Cl ₂		Ph	Me	0.5	31	(27) (73) 2.7
	CCl ₄		Ph	Me	0.5	25	(20) (80) 4.0
	CH ₂ Cl ₂ /acetone (1:19)		Ph	Me	0.5	29	(28) (72) 2.6
	CH ₂ Cl ₂ /MeCN (1:19)		Ph	Me	0.5	32	(28) (72) 2.6
	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)		Ph	Me	0.5	34	(53) (47) 0.9
	CH ₂ Cl ₂ /CF ₃ CO ₂ H (2 eq)		Ph	Me	0.5	40	(50) (50) 1.0
	CH ₂ Cl ₂ /CF ₃ CO ₂ H (10 eq)		Ph	Me	0.5	41	(66) (34) 0.53
	CH ₂ Cl ₂ /CF ₃ CO ₂ H (20 eq)		Ph	Me	0.5	53	(73) (27) 0.36
	CH ₂ Cl ₂ /CF ₃ CO ₂ H (1:19)		Ph	Me	0.5	46	(100) (—) 0.0
	CH ₂ Cl ₂		Ph	Me	1.0	58	(21) (79) 3.8
	CH ₂ Cl ₂ /DMSO (1 eq)		Ph	Me	1.0	42	(28) (72) 2.6
	CH ₂ Cl ₂ /DMSO (3 eq)		Ph	Me	1.0	27	(32) (68) 2.1
	CH ₂ Cl ₂ /DMSO (5 eq)		Ph	Me	1.0	23	(40) (60) 1.5
	CH ₂ Cl ₂		4-NCC ₆ H ₄	Me	0.5	31	(45) (54) 1.2
	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)		4-NCC ₆ H ₄	Me	0.5	44	(77) (23) 0.3
	CH ₂ Cl ₂		Ph	Ph	0.5	45	(36) (64) 1.8
	CCl ₄		Ph	Ph	0.5	22	(28) (72) 2.6
	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)		Ph	Ph	0.5	30	(61) (39) 0.6
	CH ₂ Cl ₂		-ArN(Me)Ar-	-ArN(Me)Ar-	0.5	21	(31) (69) 2.2
	CCl ₄		-ArN(Me)Ar-	-ArN(Me)Ar-	0.5	18	(13) (87) 6.7
	CH ₂ Cl ₂ /CF ₃ CH ₂ OH (1:19)		-ArN(Me)Ar-	-ArN(Me)Ar-	0.5	25	(87) (13) 0.15
	CH ₂ Cl ₂		-ArN(Me)Ar-	-ArN(Me)Ar-	1.0	41	(27) (73) 2.7
	CH ₂ Cl ₂ /CH ₃ CO ₂ H (15:1)		-ArN(Me)Ar-	-ArN(Me)Ar-	1.0	52	(42) (58) 1.4
	CH ₂ Cl ₂ /CH ₃ CO ₂ H (1.7:1)		-ArN(Me)Ar-	-ArN(Me)Ar-	1.0	75	(69) (31) 0.45
	CH ₂ Cl ₂ /t-BuOH (1.7:1)		-ArN(Me)Ar-	-ArN(Me)Ar-	1.0	64	(35) (65) 1.9

Dioxirane (x eq), CH₂Cl₂,
TFP, acetone, 0°

Dioxirane	R ¹	R ²	x	% Conv.	I	II	III
TFD	Ph	CF ₃	0.5	48	(>99)	(—)	(—)
TFD	4-ClC ₆ H ₄	Me	0.5	30	(38)	(62)	1.6
TFD	4-O ₂ NC ₆ H ₄	Me	0.5	35	(47)	(51)	1.1
DMD	Ph	Me	1.0	95	(95)	(5)	<0.1
DMD	Ph	Me	0.5	55	(100)	(—)	0.0
TFD	Ph	Me	1.0	58	(21)	(79)	3.8
TFD	Ph	Me	0.5	31	(27)	(73)	2.7
TFD	Ph	Me	0.33	20	(35)	(65)	1.9
TFD	Ph	Me	0.33 ^a	20	(40)	(60)	1.5
TFD	Ph	Me	0.2	13	(38)	(61)	1.6
TFD	Ph	Me	0.1	7	(43)	(57)	1.3
TFD	4-NCC ₆ H ₄	Me	0.5	34	(46)	(55)	1.2
TFD	4-MeC ₆ H ₄	Me	0.5	27	(24)	(76)	3.2
TFD	4-MeOC ₆ H ₄	Me	0.5	30	(29)	(71)	2.4
DMD	<i>n</i> -Bu	<i>n</i> -Bu	1.0	90	(94)	(6)	<0.1
TFD	<i>n</i> -Bu	<i>n</i> -Bu	1.0	63	(29)	(71)	2.5
TFD	<i>n</i> -Bu	<i>n</i> -Bu	0.33	22	(41)	(59)	1.4
TFD	<i>n</i> -Bu	<i>n</i> -Bu	0.1	7	(43)	(57)	1.3
TFD	Ph	Ph	0.5	45	(36)	(64)	1.8
DMD	—ArN(Me)Ar—	—	0.5	49	(100)	(—)	0.0
TFD	—ArN(Me)Ar—	—	1.0	41	(27)	(73)	2.7
TFD	—ArN(Me)Ar—	—	0.5	21	(31)	(69)	2.2
TFD	—ArN(Me)Ar—	—	0.33	19	(34)	(66)	1.9
DMD	Bn	Bn	1.0	93	(96)	(4)	<0.1
TFD	Bn	Bn	1.0	63	(27)	(73)	2.7
TFD	Bn	Bn	0.5	30	(36)	(64)	1.8
TFD	Bn	Bn	0.33	22	(41)	(59)	1.4
TFD	Bn	Bn	0.1	7	(43)	(57)	1.3

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																
C_{7-14} R^1-S-R^2	TFD (x eq), TFP, CH_2Cl_2	R^1-S-R^2 + $R^1-S(=O)-R^2$ I II	352																																																																																
		<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>x</th> <th>Temp</th> <th>% Conv.</th> <th>I</th> <th>II</th> <th>II:I</th> </tr> </thead> <tbody> <tr><td>Ph</td><td>Me</td><td>0.5</td><td>0°</td><td>31</td><td>(27)</td><td>(73)</td><td>2.7</td></tr> <tr><td>Ph</td><td>Me</td><td>0.5</td><td>-40°</td><td>31</td><td>(32)</td><td>(68)</td><td>2.1</td></tr> <tr><td>Ph</td><td>Me</td><td>0.5</td><td>-80°</td><td>35</td><td>(49)</td><td>(51)</td><td>1.1</td></tr> <tr><td>Ph</td><td>Me</td><td>0.33</td><td>0°</td><td>20</td><td>(35)</td><td>(65)</td><td>1.9</td></tr> <tr><td>Ph</td><td>Me</td><td>0.33</td><td>-40°</td><td>22</td><td>(41)</td><td>(59)</td><td>1.4</td></tr> <tr><td>Ph</td><td>Me</td><td>0.33</td><td>-80°</td><td>24</td><td>(54)</td><td>(46)</td><td>0.8</td></tr> <tr><td>Bn</td><td>Bn</td><td>0.5</td><td>0°</td><td>30</td><td>(36)</td><td>(64)</td><td>1.8</td></tr> <tr><td>Bn</td><td>Bn</td><td>0.5</td><td>-40°</td><td>34</td><td>(41)</td><td>(59)</td><td>1.4</td></tr> <tr><td>Bn</td><td>Bn</td><td>0.5</td><td>-80°</td><td>38</td><td>(58)</td><td>(42)</td><td>0.7</td></tr> </tbody> </table>	R^1	R^2	x	Temp	% Conv.	I	II	II:I	Ph	Me	0.5	0°	31	(27)	(73)	2.7	Ph	Me	0.5	-40°	31	(32)	(68)	2.1	Ph	Me	0.5	-80°	35	(49)	(51)	1.1	Ph	Me	0.33	0°	20	(35)	(65)	1.9	Ph	Me	0.33	-40°	22	(41)	(59)	1.4	Ph	Me	0.33	-80°	24	(54)	(46)	0.8	Bn	Bn	0.5	0°	30	(36)	(64)	1.8	Bn	Bn	0.5	-40°	34	(41)	(59)	1.4	Bn	Bn	0.5	-80°	38	(58)	(42)	0.7	
R^1	R^2	x	Temp	% Conv.	I	II	II:I																																																																												
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C_7 $Ph-S-Me$	TFD (1.0 eq), TFP, solvent, additive, 0°		352																																																																																
		<table border="1"> <thead> <tr> <th>Additive^b</th> <th>Eq</th> <th>Solvent</th> <th>% Convn</th> <th>I</th> <th>II</th> <th>^{18}O</th> <th>II:I</th> </tr> </thead> <tbody> <tr><td>$CF_3C(^{18}OH)_2CH_3$</td><td>100</td><td>$CH_2Cl_2/MeCN$ (1:4)</td><td>56</td><td>(34)</td><td>(23)</td><td>(66)</td><td>1.7</td></tr> <tr><td>$H_2^{18}O$</td><td>100</td><td>CH_2Cl_2/CF_3CH_2OH (1:4)</td><td>41</td><td>(33)</td><td>(11)</td><td>(67)</td><td>6</td></tr> <tr><td>$H_2^{18}O, CF_3CO_2H$</td><td>100, 2.5</td><td>CH_2Cl_2/CF_3CH_2OH (1:4)</td><td>67</td><td>(47)</td><td>(21)</td><td>(53)</td><td>5</td></tr> <tr><td>$CF_3C^{18}O_2H$</td><td>200</td><td>CH_2Cl_2</td><td>54</td><td>(94)</td><td>(1.1)</td><td>(6)</td><td>0.5</td></tr> </tbody> </table>	Additive ^b	Eq	Solvent	% Convn	I	II	^{18}O	II:I	$CF_3C(^{18}OH)_2CH_3$	100	$CH_2Cl_2/MeCN$ (1:4)	56	(34)	(23)	(66)	1.7	$H_2^{18}O$	100	CH_2Cl_2/CF_3CH_2OH (1:4)	41	(33)	(11)	(67)	6	$H_2^{18}O, CF_3CO_2H$	100, 2.5	CH_2Cl_2/CF_3CH_2OH (1:4)	67	(47)	(21)	(53)	5	$CF_3C^{18}O_2H$	200	CH_2Cl_2	54	(94)	(1.1)	(6)	0.5																																									
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$H_2^{18}O, CF_3CO_2H$	100, 2.5	CH_2Cl_2/CF_3CH_2OH (1:4)	67	(47)	(21)	(53)	5																																																																												
$CF_3C^{18}O_2H$	200	CH_2Cl_2	54	(94)	(1.1)	(6)	0.5																																																																												
	Dioxirane (III), solvent, 0°	$Ph-S-CD_3$ I + $Ph-S(=O)-CD_3$ V + $Ph-S(=O)-Me$ VI	352																																																																																
	Dioxirane	<table border="1"> <thead> <tr> <th>Solvent</th> <th>I:II:III (molar)</th> <th>II:VI</th> <th>I:II</th> <th>VI:IV</th> </tr> </thead> <tbody> <tr><td>DMD</td><td>$CH_2Cl_2/acetone$ (1:1)</td><td>1:1:1</td><td>13:80:7</td><td>93:7</td><td>13.4</td><td>0.1</td></tr> <tr><td>TFD</td><td>CH_2Cl_2</td><td>1:1:1</td><td>58:11:31</td><td>66:34</td><td>2.1</td><td>2.8</td></tr> <tr><td>TFD</td><td>CH_2Cl_2</td><td>1:3:1</td><td>73:9:18</td><td>80:20</td><td>2.3</td><td>2.0</td></tr> <tr><td>TFD</td><td>CH_2Cl_2/CF_3CH_2OH (1:9)</td><td>1:1:1</td><td>53:21:26</td><td>70:30</td><td>2.4</td><td>1.2</td></tr> </tbody> </table>	Solvent	I:II:III (molar)	II:VI	I:II	VI:IV	DMD	$CH_2Cl_2/acetone$ (1:1)	1:1:1	13:80:7	93:7	13.4	0.1	TFD	CH_2Cl_2	1:1:1	58:11:31	66:34	2.1	2.8	TFD	CH_2Cl_2	1:3:1	73:9:18	80:20	2.3	2.0	TFD	CH_2Cl_2/CF_3CH_2OH (1:9)	1:1:1	53:21:26	70:30	2.4	1.2																																																
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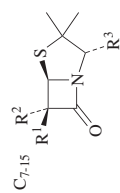
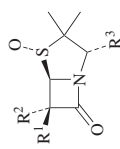
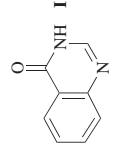
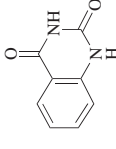
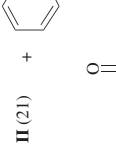

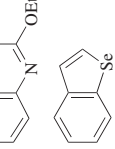

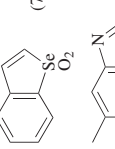

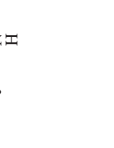



C_{7-15}			(100)	R ¹	R ²	R ³	
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , rt, 10 min			Br	Br	CO ₂ H	123
				Br	Br	CH ₂ OH	
				Br	Br	CO ₂ CH ₂ OC(O)Bu- <i>t</i>	
				Br	Br	CO ₂ Bn	
				Br	F	CO ₂ Bn	
				Br	H	CO ₂ Bn	
				F	H	CO ₂ Bn	
				Br	Br	CO ₂ Bn	
	DMD, CH ₂ Cl ₂ , acetone, rt		I (45) +				143
	DMD, acetone, H ₂ O, rt		II (21) +				143
	DMD, acetone, CH ₂ Cl ₂ , EtOH, rt		(45)				143
	DMD (1 eq), acetone, 0°, 2 h		(88)				153
	DMD (2 eq), acetone, 0°, 12 h		(71)				153
	DMD, acetone, CH ₂ Cl ₂ , MgSO ₄ , rt		(75)				142

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

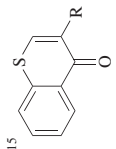
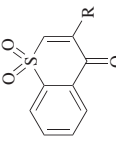
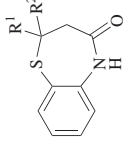
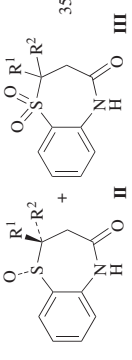
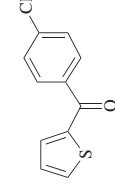
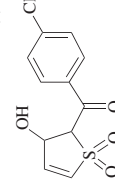
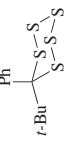
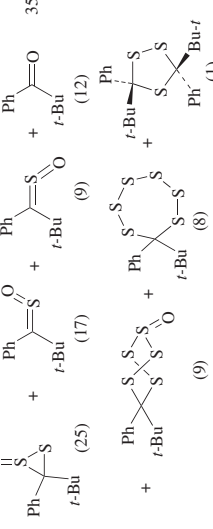
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} \text{O} \\ \parallel \\ t\text{-Bu}-\text{S}-\text{S}-\text{Bu}-t \\ \text{O} \end{array} $	DMD, acetone, N ₂ , -78°, 1 h	(83) + $t\text{-BuS}_x\text{O}_y$ (—)	350
$ \begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ t\text{-Bu}-\text{S}-\text{S}-\text{S}-\text{Bu}-t \\ \text{O} \quad \text{O} \end{array} $	DMD, acetone, N ₂ , -78°	(63)	350
$ \begin{array}{c} \text{S}-\text{R} \\ \\ \text{C}_6\text{H}_3(\text{OH})_2 \\ \text{R} = \text{Me, Et, } n\text{-Pr} \end{array} $	DMD, acetone, 0°	(45) + (45)	353
$ \begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{P}=\text{O} \\ \\ \text{R}^3 \end{array} $	DMD, acetone, CH ₂ Cl ₂ , rt, 5 min	(100)	150
$ \begin{array}{c} \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \\ \quad \quad \\ \text{MeO} \quad \text{MeO} \quad 1,3,4\text{-Cl}_3\text{C}_6\text{H}_2\text{O} \\ \text{MeO} \quad \text{MeO} \quad 3\text{-Me-4-O}_2\text{NC}_6\text{H}_3\text{O} \\ \text{EtO} \quad \text{EtO} \quad 1,4\text{-Cl}_7\text{-4-BrC}_6\text{H}_5\text{O} \\ \text{EtO} \quad \text{EtO} \quad 4\text{-O}_2\text{NC}_6\text{H}_4\text{O} \\ n\text{-Bu} \quad n\text{-Bu} \\ \text{Ph} \quad \text{Ph} \end{array} $	DMD (2 eq), acetone, 1-38 h	(—)	154
$ \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_3(\text{OH})_2 \\ \text{R} \end{array} $	DMD, acetone, 0°	(45) + (45)	353

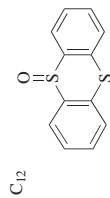
C ₉₋₁₅	R ¹	R ²	DMD (x eq), acetone, CH ₂ Cl ₂ , 0-5°	I		cis:trans I II	354
				% Conv.	II		
	H	H	1.42	86	(93)	— (4.8)	
	H	H	3.25	100	(—)	— (96)	
	Cl	Me	2.25	98	(86)	— (1.3)	
	Cl	Me	3.17	100	(0)	60:40 (86)	
	H	Me	2.01	91	(81)	— (14)	
	H	Me	3.00	100	(—)	59:41 (85)	
	Me	Me	1.80	100	(88)	— (8.9)	
	Me	Me	3.50	100	(—)	61:39 (84)	
	H	Ph	2.12	100	(77)	— (16)	
	H	Ph	4.10	100	(—)	70:30 (92)	

C ₁₀	R	DMD, acetone, CH ₂ Cl ₂ , 5°, 3 h	I		139
			OSi(<i>i</i> -Pr) ₃ (25)	SnMe ₃ (65)	
	Cl	DMD, acetone, rt, 16 h	(63)	(37)	149
		Wet DMD, acetone, rt	I (36) + II (64)		149

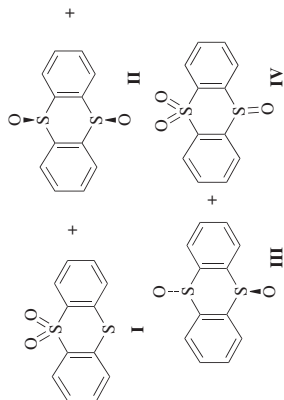
C ₁₀	R	DMD, acetone, CH ₂ Cl ₂	I		355
			OSi(<i>i</i> -Pr) ₃ (25)	SnMe ₃ (65)	
	Cl	DMD, acetone, CH ₂ Cl ₂	(100)		355

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																			
<p>C₁₀₋₁₅</p> 	DMD, acetone, cyclohexanone, -20°, 10 min		356																																			
	DMD (x eq.), acetone, CH ₂ Cl ₂ , 0 to 5°		357																																			
<p>R¹ R²</p> <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>Me</td> <td>Me</td> </tr> <tr> <td>2-furyl</td> <td>H</td> </tr> <tr> <td>2-furyl</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	Me	H	Me	Me	2-furyl	H	2-furyl	H	Ph	H	Ph	H	x	<table border="1"> <thead> <tr> <th>I+II</th> <th>III</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>(71)</td> <td>(3)</td> <td>23:77</td> </tr> <tr> <td>(66)</td> <td>(11)</td> <td>50:50</td> </tr> <tr> <td>(88)</td> <td>(6)</td> <td>0:100</td> </tr> <tr> <td>(58)</td> <td>(35)</td> <td>0:100</td> </tr> <tr> <td>(63)</td> <td>(8)</td> <td>0:100</td> </tr> <tr> <td>(0)</td> <td>(98)</td> <td>—</td> </tr> </tbody> </table>	I+II	III	I:II	(71)	(3)	23:77	(66)	(11)	50:50	(88)	(6)	0:100	(58)	(35)	0:100	(63)	(8)	0:100	(0)	(98)	—	
R ¹	R ²																																					
Me	H																																					
Me	Me																																					
2-furyl	H																																					
2-furyl	H																																					
Ph	H																																					
Ph	H																																					
I+II	III	I:II																																				
(71)	(3)	23:77																																				
(66)	(11)	50:50																																				
(88)	(6)	0:100																																				
(58)	(35)	0:100																																				
(63)	(8)	0:100																																				
(0)	(98)	—																																				
<p>C₁₁</p> 	DMD, acetone, H ₂ O, rt		358																																			
	DMD, CH ₂ Cl ₂ , acetone, -20° to rt		359																																			



Dioxirane, acetone, CH₂Cl₂,
additive, 1 h



360, 361

Dioxirane	Additive	Temp	% Conv.	I	II	III	IV
TFD	—	-78°	21	(0.8)	(3.1)	(96)	(0.2)
TFD	—	0°	20	(2.8)	(3.9)	(85)	(8.1)
DMD	—	-50°	52	(6.8)	(3.1)	(90)	(0.1)
DMD	—	0°	56	(12)	(3.9)	(84)	(0.3)
DMD	MeOH	0°	35	(8.8)	(160)	(75)	(—)
DMD	AcOH	0°	35	(6.5)	(130)	(80)	(—)
DMD	CF ₃ CO ₂ H	0°	53	(1.6)	(5.7)	(93)	(—)
Methyl(isopropyl)dioxirane	—	-40°	44	(4.3)	(1.2)	(94)	(—)
Methyl(isopropyl)dioxirane	—	0°	44	(13)	(2.50)	(84)	(—)
Methyl(isopropyl)dioxirane	CF ₃ CO ₂ H	0°	42	(—)	(2.5)	(98)	(—)
Cyclohexanone dioxirane	—	-70°	46	(5.8)	(11)	(82)	(1.9)
Cyclohexanone dioxirane	—	0°	46	(12)	(12)	(76)	(0.9)
Cyclohexanone dioxirane	CF ₃ CO ₂ H	0°	45	(1.0)	(13)	(86)	(—)



Phenyl(trifluoromethyl)-
dioxirane, MeCN, 20°, 30 min
Ph-S(=O)-Ph
I (—)

362

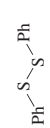
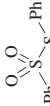
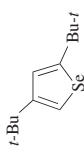

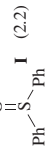
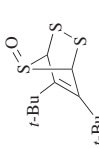
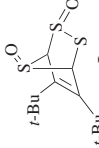
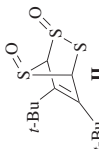
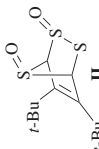
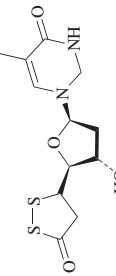
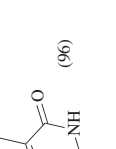
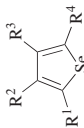
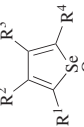
Diphenyldioxirane, 20°, 1.5 h
I (19)

363

Bis(4-methoxy)phenyldioxirane,
20°, 1.5 h
I (42)

363

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 30°		5
	DMD, CH ₂ Cl ₂ , acetone, -50°	(100)	155
	Diphenyldioxirane, 20°, 1.5 h		363
	Bis(4-methoxyphenyl)dioxirane, 20°, 1.5 h		363
	DMD, acetone, -18°		364
	DMD, acetone, rt, 2h		365
	DMD (2 eq), acetone, 0° to rt, 1-38 h		153

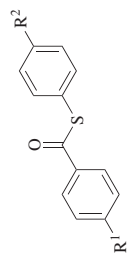
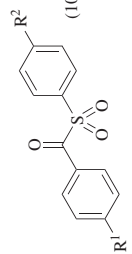
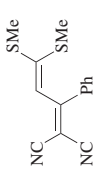
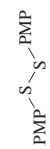
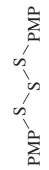




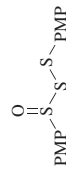
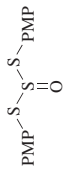


R ¹	R ²	R ³	R ⁴		
<i>t</i> -Bu	H	<i>t</i> -Bu	H		
Me	Ph	Ph	Me	(97)	
4-ClC ₆ H ₄	4-ClC ₆ H ₄	4-ClC ₆ H ₄	4-ClC ₆ H ₄	(97)	
Ph	Ph	Ph	Ph	(69)	
4-MeC ₆ H ₄	4-MeC ₆ H ₄	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(97)	
4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	(89)	
				(99)	
					DMD, acetone, cyclohexanone, -20°, 10 min
					(-)
					DMD, acetone, CH ₂ Cl ₂ , EtOH, rt
					(91)
					DMD (2 eq), acetone, 20°, 30 min
					(95)
					DMD, acetone, CH ₂ Cl ₂ , N ₂ , rt, 10 min
					(100)
					DMD, acetone, CH ₂ Cl ₂ , N ₂ , -30°, 2-4 h
					(-)

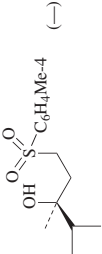
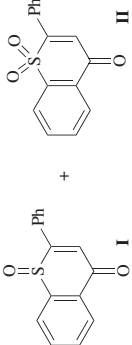
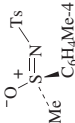
C₁₃

C₁₃₋₁₄

C₁₃₋₁₅

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																			
C_{13-15} 	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 30°	 (100)	<table border="0"> <tr> <td></td> <td>R¹</td> <td>R²</td> </tr> <tr> <td></td> <td>H</td> <td>H</td> </tr> <tr> <td></td> <td>H</td> <td>Me</td> </tr> <tr> <td></td> <td>H</td> <td>MeO</td> </tr> <tr> <td></td> <td>Me</td> <td>Me</td> </tr> <tr> <td></td> <td>Me</td> <td>MeO</td> </tr> </table>		R ¹	R ²		H	H		H	Me		H	MeO		Me	Me		Me	MeO	367
	R ¹	R ²																				
	H	H																				
	H	Me																				
	H	MeO																				
	Me	Me																				
	Me	MeO																				
C_{14} PhS—C≡C—SPh	DMD, acetone, 20°, 1 h	(—)	133																			
	DMD, acetone, cyclohexanone, -20°, 10 min	(—)	368																			
	DMD, acetone	(—)	135																			
	DMD, acetone-d ₆ , -20°	 I  II +  III +  IV	(—)	135																		
	DMD, acetone-d ₆ , -20°	I (—) + II (—) + III (—) + IV (—) + other products (—)	135																			
	DMD, acetone, CH ₂ Cl ₂ , rt	 I +  II	135																			

		I (←) + II (←)	135
TFD, acetone, TFP or CH ₂ Cl ₂ , TFP, rt		I (←)	135
TFD, acetone, TFP, -80°		III (←) + other products	135
DMD, acetone-d ₆ , -20°			369
DMD, acetone, rt, 5 h			354
DMD (1.2 eq), solvent, 0°, 24 h			
	Solvent	% Conv.	I:II
	CCl ₄	29	7:93
	CCl ₄ /acetone (9:1)	25	12:88
	acetone	15	35:65
	CCl ₄ /MeOH (1:1)	29	48:52
	CHCl ₃	21	60:40
	CCl ₄ /AcOH (1:1)	25	66:34
DMD, acetone, 0° to rt			

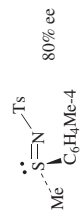
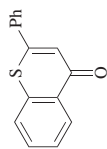
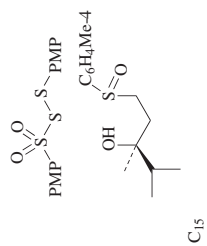
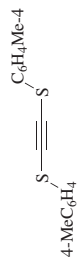


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

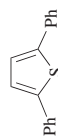
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
<p>C₁₅</p>	DMD, acetone, CH ₂ Cl ₂ , ROH, rt		117															
		<table border="1"> <thead> <tr> <th>ROH</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>(95)</td> <td>(—)</td> </tr> <tr> <td>MeOH</td> <td>(22)</td> <td>(70)</td> </tr> <tr> <td>EtOH</td> <td>(18)</td> <td>(65)</td> </tr> <tr> <td><i>n</i>-BuOH</td> <td>(20)</td> <td>(75)</td> </tr> </tbody> </table>	ROH	I	II	—	(95)	(—)	MeOH	(22)	(70)	EtOH	(18)	(65)	<i>n</i> -BuOH	(20)	(75)	
ROH	I	II																
—	(95)	(—)																
MeOH	(22)	(70)																
EtOH	(18)	(65)																
<i>n</i> -BuOH	(20)	(75)																
	DMD (4 eq), CH ₂ Cl ₂ , acetone, -78°, 1 h; rt, 4 h		370															
	DMD, CH ₂ Cl ₂ , acetone, -20°		370															
	DMD (4 eq), CH ₂ Cl ₂ , acetone, -20°		370															
<p>C_{15,21}</p>	DMD, acetone, rt, 3 h		136															
		<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>III</th> <th>IV</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Bu</td> <td>(31)</td> <td>50:50</td> <td>(4)</td> </tr> <tr> <td>1-Ad</td> <td>(38)</td> <td>50:50</td> <td>(12)</td> </tr> </tbody> </table>	R	I + II	III	IV	<i>n</i> -Bu	(31)	50:50	(4)	1-Ad	(38)	50:50	(12)	(25)			
R	I + II	III	IV															
<i>n</i> -Bu	(31)	50:50	(4)															
1-Ad	(38)	50:50	(12)															

C₁₆



DMD, acetone, 20°, 3 h

133



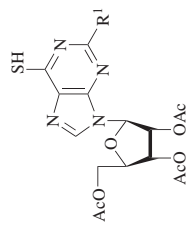
DMD (1 eq), acetone,
CH₂Cl₂, 20°

140

I + II (40), EII = 75:25

DMD (2 eq), acetone,
CH₂Cl₂, 0°, 4 h

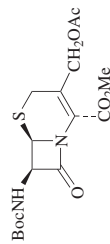
140



DMD, acetone, CH₂Cl₂,
R¹NH₂, rt

116, 117,
118, 119,
120, 144

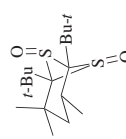
R ¹	R ²
H	H (75)
H	Me (55)
NHAc	H (65)
NHAc	Me (63)
NHAc	Et (67)
NHAc	4-MeC ₆ H ₄ (69)
SH	H (53)
SH	Me (46)



DMD, acetone, dark, 0-5°,
40-60 min

124

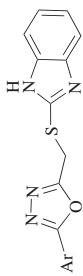
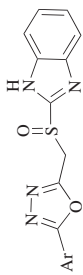
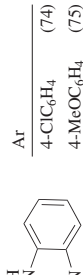
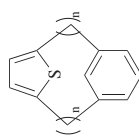
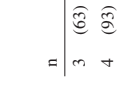

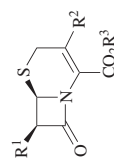


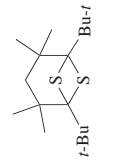

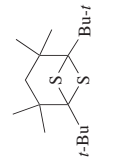

I + II (-), EII = 47:53



DMD, acetone, CH₂Cl₂,
0° to rt, 1 h

134

TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₆₋₁₇	DMD (2-4 eq), acetone, rt, 30 min	 (74)  (75)	372
 C ₁₆₋₁₈	DMD (5-8 eq), acetone, rt, 30 min	 (90)  (91)	372
 C ₁₆₋₁₂	DMD, acetone, CH ₂ Cl ₂ , rt	 (63)  (93)	138
 C ₁₇	DMD, acetone, 0-5°; dark, 40-60 min	 (100)	124
 C ₁₇	1. DMD, acetone, CH ₂ Cl ₂ , 0° 2. rt, 1 h	 (98)	134

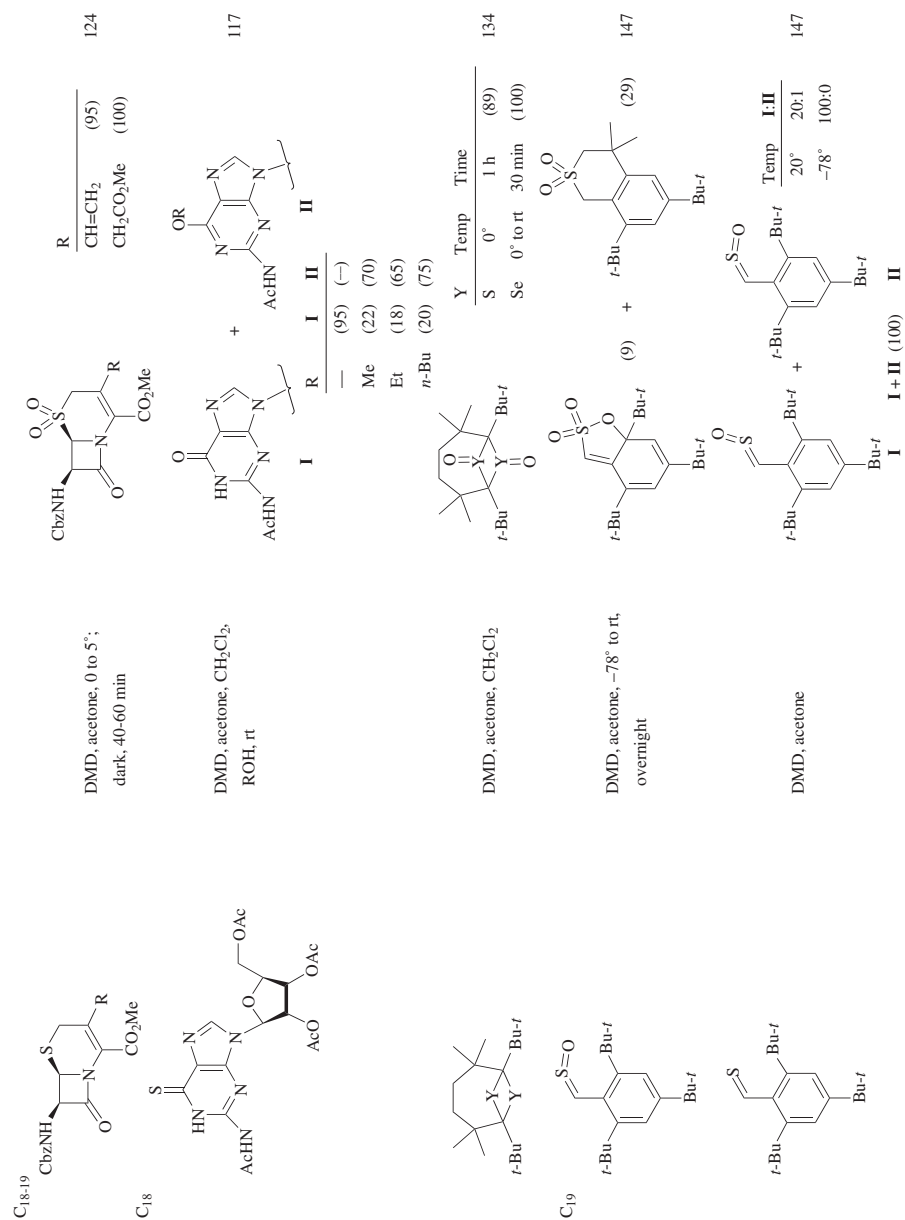


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₀</p>	<p>1. DMD (1 eq), CH₂Cl₂, -78° to rt, 6 h 2. KOAc, AcOH, -78° to rt 3. KOH, EtOH, H₂O, rt</p>	<p>(52) + (40)</p>	373
<p>C₂₀₋₂₉</p>	<p>DMD, acetone, 0 to 5°; dark, 4 days</p>	<p>dr</p> <p>(85) 83:17 (95) — (85) 83:17 (95) —</p>	124
<p>C₂₁₋₃₁</p>	<p>1. DMD, acetone, rt 2. Toluene, heating</p>	<p>(38) (35)</p> <p>(65) (—) (52) (—) (85) (—) (67) (15) (82) (—) (61) (—)</p>	374
		<p>I</p> <p>+</p> <p>II</p>	
		<p>R¹ R² R³ Ar</p> <p>H H Ph H H 4-MeOC₆H₄ MeO H Ph H H 2,4-(MeO)₂C₆H₃ MeO H 4-MeOC₆H₄ H H 2,4,6-(MeO)₃C₆H₂ H 4-MeOC₆H₄ 2,4,6-(MeO)₃C₆H₂</p>	

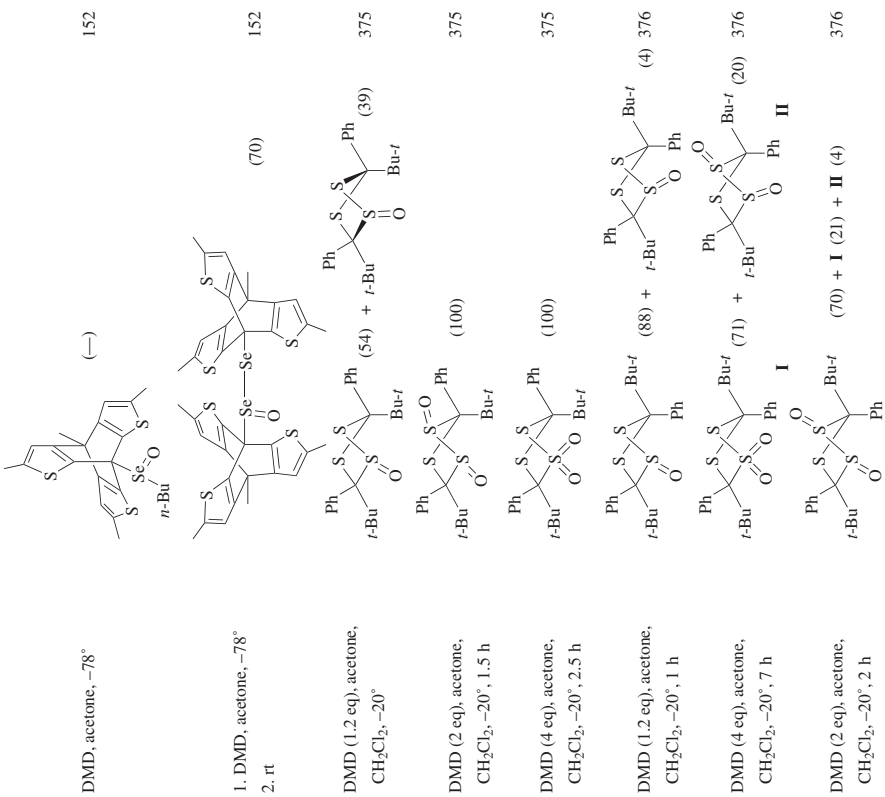
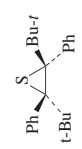
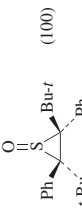
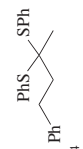

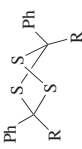
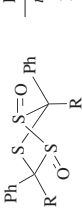
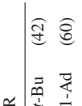

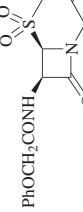
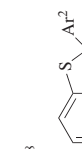
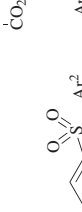


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₂</p> 	DMD (1 eq), acetone, CH ₂ Cl ₂ , 0°, 10 min	 (100)	376
<p>C₂₂₋₃₄</p> 	DMD, acetone, -78° to rt	 (87)	377
<p>C₂₃</p> 	DMD (4 eq), acetone, CH ₂ Cl ₂ , -20°, 1 h	 R  R -t-Bu (42) 1-Ad (60)	267
<p>C₂₃</p> 	DMD, acetone, 0-5°, dark, 40-60 min	 (95) CO ₂ CH ₂ C ₆ H ₄ NO ₂ -4	124
<p>C₂₃₋₂₈</p> 	DMD, acetone, CH ₂ Cl ₂ , rt, 16 h	 Ar ¹ Ar ² Ph (84) Ph 2-AcOC ₆ H ₄ (81) Ph 4-AcOC ₆ H ₄ (88) Ph 4-AcOC ₆ H ₄ (83) 4-(<i>i</i> -Pr)C ₆ H ₄ 2-AcOC ₆ H ₄ (94) 3-ClC ₆ H ₄ 2-AcOC ₆ H ₄ (91) 4-ClC ₆ H ₄ 2-AcOC ₆ H ₄ (94) 2,4-Cl ₂ C ₆ H ₃ 2-AcOC ₆ H ₄ (78) 3,4-Cl ₂ C ₆ H ₃ 2-AcOC ₆ H ₄ (81) 4-ClC ₆ H ₄ 4-AcOC ₆ H ₄ (84) 2,4-Cl ₂ C ₆ H ₃ 4-MeC ₆ H ₄ (78)	378

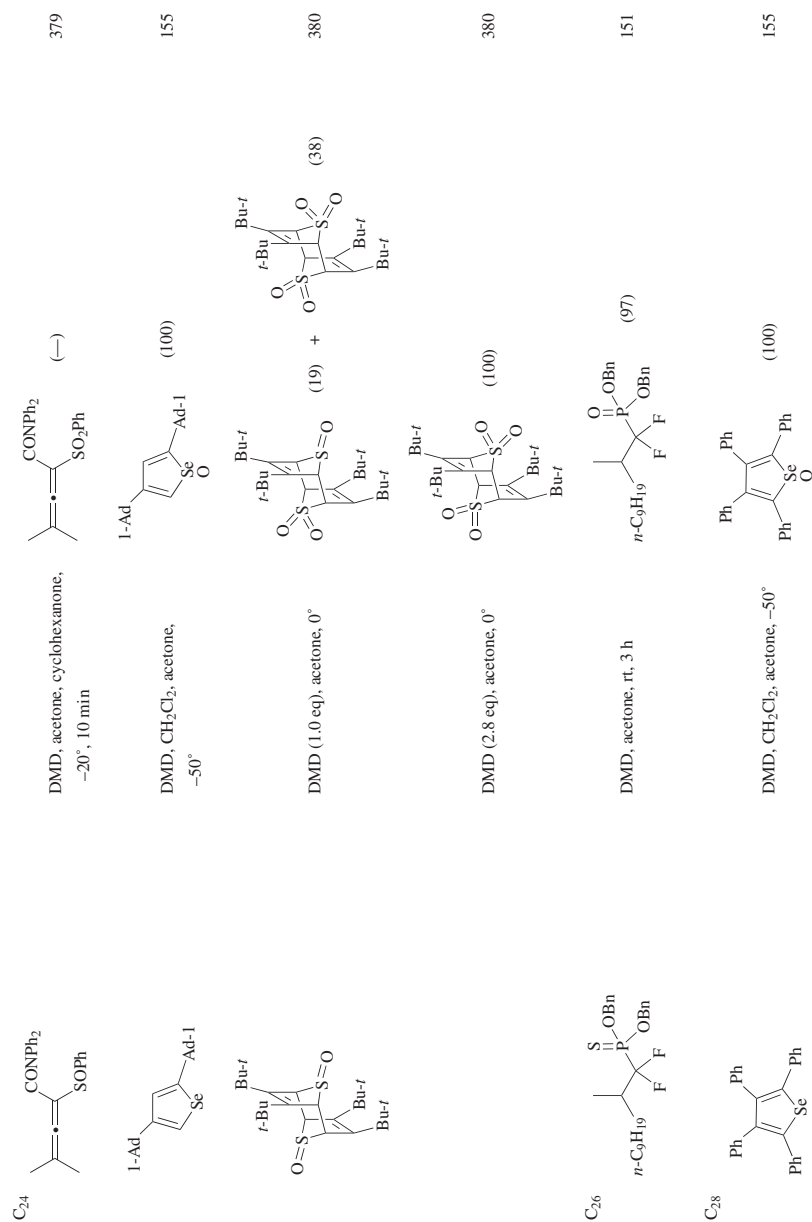
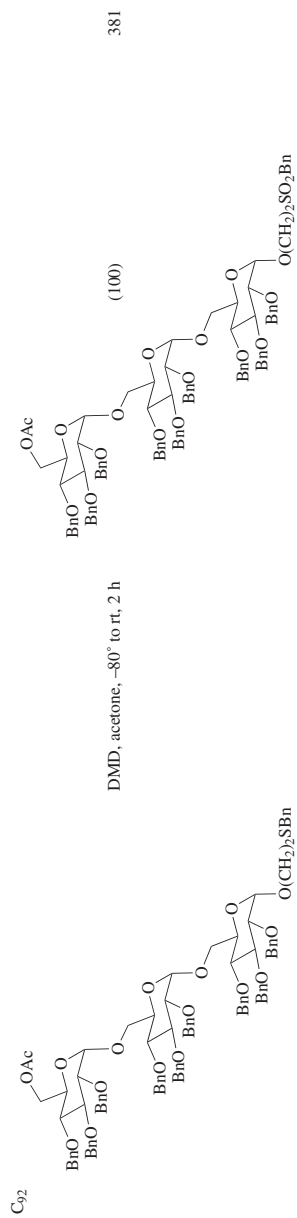


TABLE 3B. SULFUR AND SELENIUM OXIDATION BY ISOLATED DIOXIRANES (Continued)

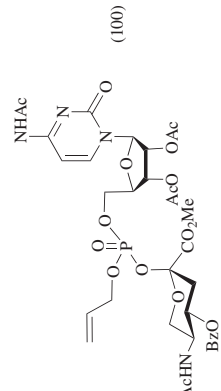
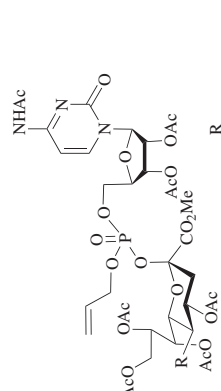


Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₉</p> <p>Ar = Ph, 4-FC₆H₄, 4-ClC₆H₄</p>	DMD, acetone, 0° to rt	<p>(−)</p>	371
<p>C₃₆</p>	1. DMD, acetone, rt 2. Toluene, heating	<p>(41)</p>	374
<p>C₃₈</p>	DMD, acetone, CH ₂ Cl ₂ , 0°, 30 min	<p>(77) dr 2.5:1</p>	125
<p>C₆₅</p>	DMD, acetone, −80° to rt, 2 h	<p>(100)</p>	381
<p>C₆₅</p>	DMD, acetone, −80° to rt, 2 h	<p>(100)</p>	381



^a Methyl(trifluoromethyl)dioxirane (TFD) was added dropwise.

^b The percent isotopic oxygen labeling for these compounds was as follows : CF₃C(¹⁸O)H₂CH₃: 49%; H₂¹⁸O: 98%; CF₃C(¹⁸O)₂H: 49%.

TABLE 3C. PHOSPHORUS OXIDATION BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₈ Ph ₃ P	DMD, acetone	Ph ₃ P=O I (100)	121
	DMD, acetone, -70 to -50°	I (-)	156
	DMD, CDCl ₃	I (-)	157
C ₃₄	DMD, acetone, CH ₂ Cl ₂ , 0°, 10 min	 (100)	158
C ₃₈₋₄₄	DMD, acetone, CH ₂ Cl ₂ , rt, 10 min	 (98)	158
		 (100)	
		 (99)	

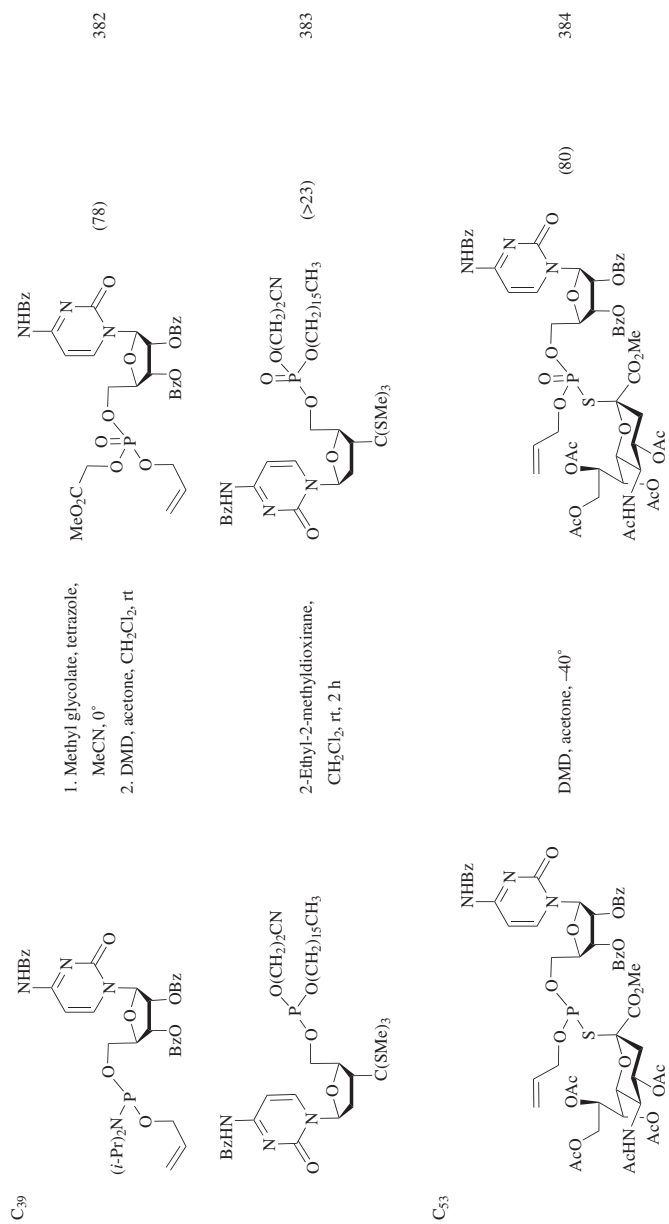



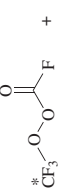



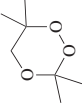
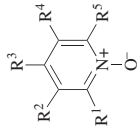
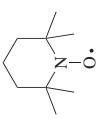
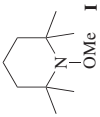
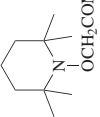
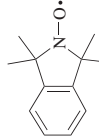
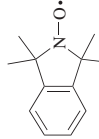
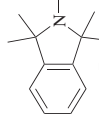
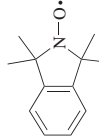


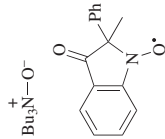
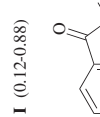
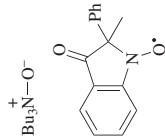
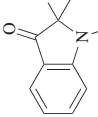
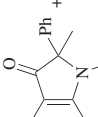
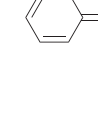
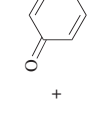


TABLE 3D. OXYGEN OXIDATION BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
C ₀ HSO ₅ ⁻	DMD, acetone/H ₂ O, NaHCO ₃ , 20°	O ₂ (—) + HSO ₄ ⁻ (—)	160																														
C ₁ 	F ₂ C=O, C ₈ F ₄ , -50°, 20 h	 n = 1, 2, 3	385																														
 * = ¹³ C	F ₂ C=O, C ₈ F ₄ , -50°, 16 h	*  + (—)  (—) n = 1, 2, 3	385																														
C ₃ 	TFD, CH ₂ Cl ₂ , <i>n</i> -Bu ₄ Ni, 0°, 5 min	O ₂ (96)	164																														
	DMD, acetone, dark, rt, 5-10 d	 (—)	121																														
C ₅₋₈ 	BF ₃ , acetone, ether, 0°	MeCO ₂ Me (—)	121																														
	DMD, CDCl ₃ , 20°	¹ O ₂ I <table border="1" data-bbox="1071 651 1234 924"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>R⁵</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>H</td> <td>H</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>H</td> <td>Me</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me₂N</td> <td>H</td> <td>H</td> </tr> </tbody> </table> (30)	R ¹	R ²	R ³	R ⁴	R ⁵	H	H	H	H	H	Me	H	H	H	Me	H	Me	Me	H	H	Me	H	Me	H	Me	H	H	Me ₂ N	H	H	165
R ¹	R ²	R ³	R ⁴	R ⁵																													
H	H	H	H	H																													
Me	H	H	H	Me																													
H	Me	Me	H	H																													
Me	H	Me	H	Me																													
H	H	Me ₂ N	H	H																													

				R ¹	R ²	R ³	R ⁴	R ⁵		
C ₅₋₁₂		TFD, TFA, 20°	I	H	H	H	H	H	165	
				Me	H	H	H	Me	(4.8)	
				H	Me	Me	H	H	(1.3)	
				Me	H	Me	H	Me	(0.2)	
				H	H	Me ₂ N	H	H	(0.6)	
				H	H	Me ₂ N	H	H	(5)	
				R	Y					
		DMD, CDCl ₃ , 20°	I	Me	O				165	
				PhCH ₂	CH ₂				(0.08-0.60)	
									(0.04-0.09)	
C ₆	TMS ¹⁸ O ¹⁸ OSO ₃ TMS	Cyclohexanone, CH ₂ Cl ₂ , He, -80 to -10°, 10 h	I + II + III	³² O ₂ (−) + ³⁴ O ₂ (−) + ³⁶ O ₂ (−) I:II:III = 92.7:6.4:0.9						386
C ₇		DMD, acetone, 0°	¹ O ₂ (−) + ¹ O ₂ (−)							26
		DMD, acetone	¹ O ₂ (−) + ¹ O ₂ (−)							26
		DMD, CDCl ₃ , 20°	¹ O ₂ (0.33)							165
C ₈	PhMe ₂ N ⁺ O ⁻	TFD, TFA, 20°	¹ O ₂ (0.02)							165
C ₉										

TABLE 3D. OXYGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_9	DMD, acetone, air or N_2 , 20°, 2-4 h	 OMe I (>98) +  OCH ₃ COMe (<1)	166
 C_{12}	TFD, TFA, 0°, 2-4 h	1O_2 (>96)	166
 C_{12}	TFD, CH_2Cl_2 , 0°, 2 h	 OMe I (8)	23
 C_{12}	TFD, hv, CH_2Cl_2 , -10°	 OCF ₃ I (39) +  OCF ₃ I (20)	23
 C_{15}	TFD, TFA, 20°	 OMe I (0.12-0.88)	165
 C_{15}	Dioxirane, acetone, 0°	 OMe I +  Ph II +  Ph III +  Ph IV	166
Dioxirane	Time	I II III IV	
DMD	3 h	(16) (8.5) (18) (12)	
TFD	30 min	(12) (14) (19) (21)	

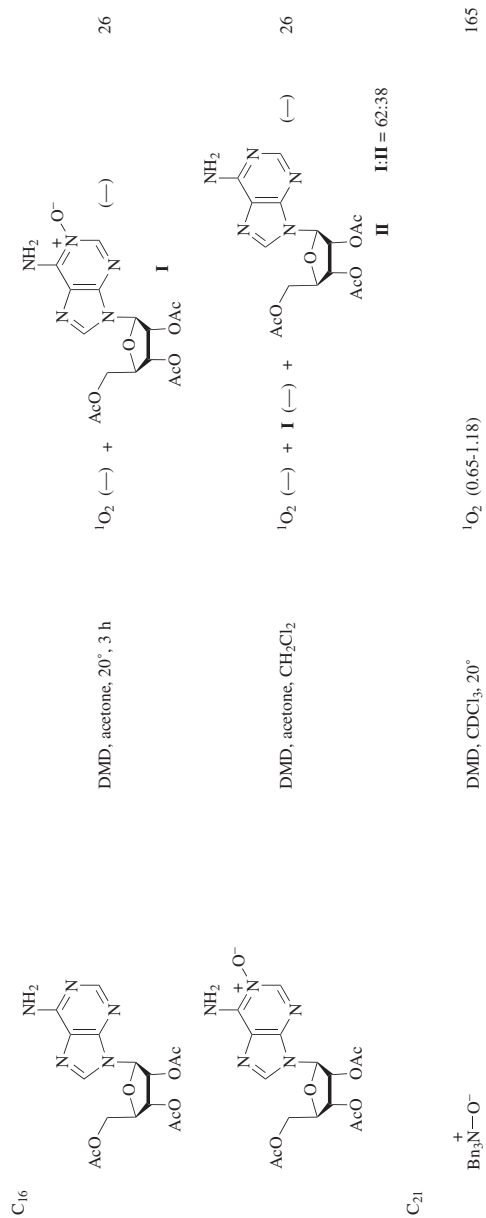

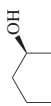

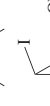



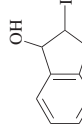

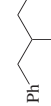

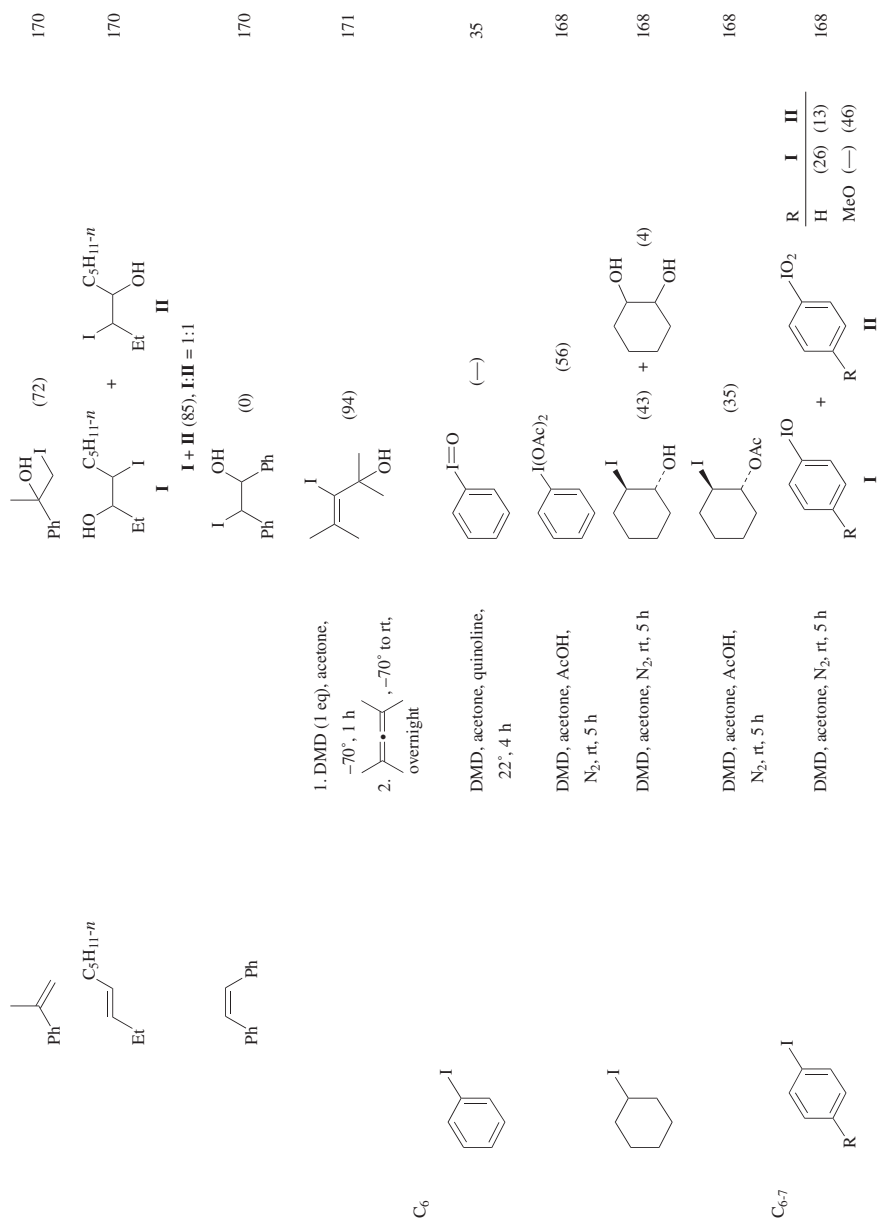


TABLE 3E. HALOGEN OXIDATION BY ISOLATED DIOXIRANES

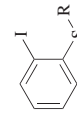
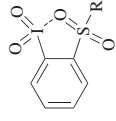
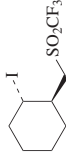
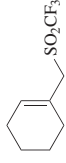
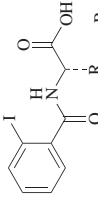
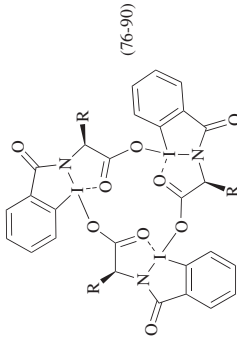
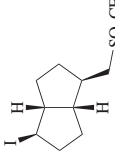
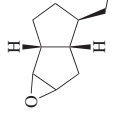
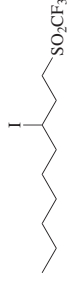

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₀	LiI	TFD, TMSCl, CH ₂ Cl ₂ , 0°, 20 min	(—)	164												
C ₁	CH ₃ I	1. DMD (1 eq), acetone, -70°, 1 h 2. Alkene, -70° to rt, 20 h	 (78)  (85)  (9)  (72)	170 170 170 170												
	 		<table border="1"> <tr> <td>Ar</td> <td></td> </tr> <tr> <td>4-ClC₆H₄</td> <td>(82)</td> </tr> <tr> <td>Ph</td> <td>(85)</td> </tr> <tr> <td>4-CF₃C₆H₄</td> <td>(44)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>(75)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>(60)</td> </tr> </table>	Ar		4-ClC ₆ H ₄	(82)	Ph	(85)	4-CF ₃ C ₆ H ₄	(44)	4-MeC ₆ H ₄	(75)	4-MeOC ₆ H ₄	(60)	170
Ar																
4-ClC ₆ H ₄	(82)															
Ph	(85)															
4-CF ₃ C ₆ H ₄	(44)															
4-MeC ₆ H ₄	(75)															
4-MeOC ₆ H ₄	(60)															
			 (82)	170												
			 I +  II	I + II (85), I:II = 65:35 170												



C₆


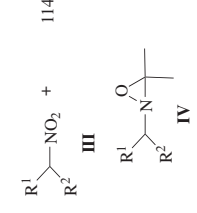

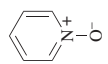

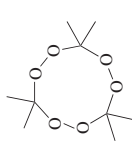


C₆₋₇

TABLE 3E. HALOGEN OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{7-8}	DMD, acetone, CH_2Cl_2 , 0° , 8 h	 R OMe (89) OEt (84)	387
 C_8	DMD, acetone, ether, rt, 1 h	 (58)	169
 C_{9-13}	DMD, acetone, rt, 8 h	 (76-90)	388
 C_{10}	DMD, acetone, ether, 0°	 (77)	169
	DMD, acetone, ether, rt, 1 h	 (80)	169

C ₁₀₋₁₆		DMD, acetone, rt, 8 h		R (S)-NHCH(Me)CO ₂ Me (96) (S)-NHCH(Bn)CO ₂ Me (68) (S)-NHCH(<i>i</i> -Pr)CO ₂ Me (84) (S)-NHCH(<i>i</i> -Bu)CO ₂ Me (63) (R)-NHCH(Ph)Me (67)	387, 389
C ₁₀₋₁₇		DMD, acetone, rt		R (S)-CH(Me)CO ₂ Me (R)-CH(Me)CO ₂ Me (S)-CH(Bn)CO ₂ Me (S)-CH(<i>i</i> -Bu)CO ₂ Me CH ₂ CH ₂ CO ₂ H CH(Me)CH ₂ CO ₂ H (R)-CH(Ph)CH ₃ (45-73)	390
C ₁₁		DMD, acetone, ether, rt, 1 h		(93)	169
C ₁₆	(<i>n</i> -Bu) ₄ NI	TFD, CH ₂ Cl ₂ , 0°	I ₂ (—)	(—)	164
		TFD, PhCOCl, CH ₂ Cl ₂ , 0°, 10 min		(—)	164

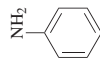
TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4+11} 	Oxone® (x eq), acetone, H ₂ O, NaHCO ₃ , rt		114
C_5 	Oxone®, acetone, H ₂ O (pH 7.5-8.0), 2 h		121
C_5 	Oxone®, acetone, 50°, 16 h		121
C_5 	Oxone®, acetone		121
	x	Solvent	
	R ¹	R ²	
	<i>n</i> -Pr	H	I (24) (30) 6 ^a 27 ^a
	<i>n</i> -Pr	H	(40) (40) 12 ^a (—)
	—(CH ₂) ₅ —	—	(10) (43) 18 ^a 14 ^a
	—(CH ₂) ₅ —	—	12 ^a 60 ^a 14 ^a 14 ^a
	—(CH ₂) ₅ —	—	12 ^a 50 ^a 18 ^a 20 ^a
	—(CH ₂) ₅ —	—	2 ^a 26 ^a 72 ^a (—)
	—(CH ₂) ₅ —	—	(—) 14 ^a 86 ^a (—)
	—(CH ₂) ₅ —	—	(—) (11) (65) (—)
	Ph	H	(55) (—) (—) 38 ^a
	Ph	H	(52) (—) (—) (trace)
	<i>n</i> -C ₉ H ₁₉	H	(15) (35) 5 ^a (37)
	<i>n</i> -C ₉ H ₁₉	H	(—) (64) (9) 13 ^a
			I II III IV

			pH	
			7.0	(72)
			7.5	(85)
			8.0	(94)
			8.5	(96)
			9.0	(95)
			9.5	(86)
				(17.5)
				(78)
				(98)
				(34)
				(57)

Oxone[®], cyclohexanone,
buffer (pH)

C₆

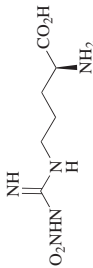


Oxone[®], acetone, CH₂Cl₂,
phosphate buffer (pH 7.5-8.5),
aq. KOH, (*n*-Bu)₄NHSO₄,
0°, 45 min

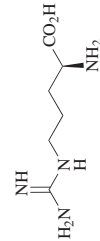
Oxone[®], THF, acetone, CH₂Cl₂,
phosphate buffer (pH 7.5-8.5),
aq. KOH, (*n*-Bu)₄NHSO₄,
0°, 15 min

Oxone[®],

acetone, CH₂Cl₂,
phosphate buffer (pH 7.5-8.5),
aq. KOH, (*n*-Bu)₄NHSO₄,
0°, 45 min

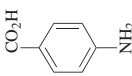

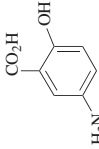
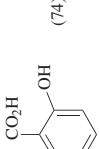


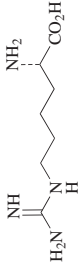

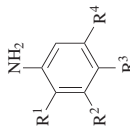
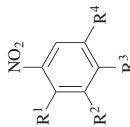


Oxone[®], acetone, phosphate
buffer (pH 8.0), KOH,
5°, 7 h



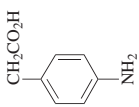
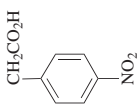
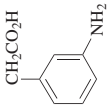
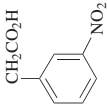
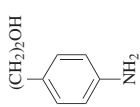
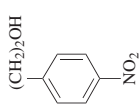
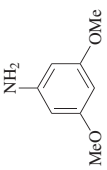
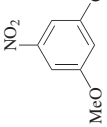
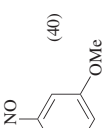
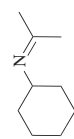
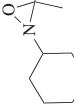
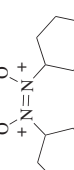
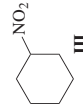
Oxone[®], acetone, phosphate
buffer (pH 8.0), KOH, 5°, 7 h

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_7	Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	 (73)	392
	Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	 (74)	392
	Oxone [®] , acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h	 I + II (88), II = 3:1	112
	Oxone [®] , acetone, phosphate buffer (pH 8.0), KOH, 5°, 7 h	 (56)	112
 C_{7-9}	Oxone [®] , acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5-8.5), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°, 45 min	 R ¹ R ² R ³ R ⁴	267

R ¹	R ²	R ³	Time	Yield (%)	Structure	Reference
H	CO ₂ Me	H	0.5 h	(100)		267
H	CO ₂ Me	H	1 h	(100)		267
CO ₂ Me	H	H	3 h	(100)		267
CO ₂ H	H	H	3.5 h	(96)		267
CN	H	H	3 h	(96)		267
H	Br	H	3.5 h	(70)		267
H	Et	H	12 h	(65)		267
H	SO ₃ H	H	4 h	(—)		267
H	SO ₃ NBu ₄	H	0.5 h	(97)		267
H	CH ₂ OH	H	1 h	(—)		267
H	CH ₂ CO ₂ H	H	4 h	(—)		267
H	CH ₂ NHBoc	H	9.5 h	(60)		267
CO ₂ Me	H	Me	3.5 h	(96)		267
H	CO ₂ Me	H	0.5 h	(100)		267
H	CO ₂ Me	H	1 h	(100)		267
CO ₂ Me	H	H	3 h	(100)		267
CO ₂ H	H	H	3.5 h	(96)		267
CN	H	H	3 h	(96)		267
H	Br	H	3.5 h	(70)		267
H	Et	H	12 h	(65)		267
H	SO ₃ H	H	4 h	(—)		267
H	SO ₃ NBu ₄	H	0.5 h	(97)		267
H	CH ₂ OH	H	1 h	(—)		267
H	CH ₂ CO ₂ H	H	4 h	(—)		267
H	CH ₂ NHBoc	H	9.5 h	(60)		267
CO ₂ Me	H	Me	3.5 h	(96)		267
H	CO ₂ Me	H	0.5 h	(100)		267
H	CO ₂ Me	H	1 h	(100)		267
CO ₂ Me	H	H	3 h	(100)		267
CO ₂ H	H	H	3.5 h	(96)		267
CN	H	H	3 h	(96)		267
H	Br	H	3.5 h	(70)		267
H	Et	H	12 h	(65)		267
H	SO ₃ H	H	4 h	(—)		267
H	SO ₃ NBu ₄	H	0.5 h	(97)		267
H	CH ₂ OH	H	1 h	(—)		267
H	CH ₂ CO ₂ H	H	4 h	(—)		267
H	CH ₂ NHBoc	H	9.5 h	(60)		267
CO ₂ Me	H	Me	3.5 h	(96)		267
H	CO ₂ Me	H	0.5 h	(100)		267
H	CO ₂ Me	H	1 h	(100)		267
CO ₂ Me	H	H	3 h	(100)		267
CO ₂ H	H	H	3.5 h	(96)		267
CN	H	H	3 h	(96)		267
H	Br	H	3.5 h	(70)		267
H	Et	H	12 h	(65)		267
H	SO ₃ H	H	4 h	(—)		267
H	SO ₃ NBu ₄	H	0.5 h	(97)		267
H	CH ₂ OH	H	1 h	(—)		267
H	CH ₂ CO ₂ H	H	4 h	(—)		267
H	CH ₂ NHBoc	H	9.5 h	(60)		267
CO ₂ Me	H	Me	3.5 h	(96)		267

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	 (81)	392
	Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	 (81)	392
	Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	 (73)	392
	Oxone [®] , acetone, CH ₂ Cl ₂ , phosphate buffer (pH 7.5-8.5), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°, 45 min	 (20) +  (40)	267
	Oxone [®] , acetone, H ₂ O, NaHCO ₃ , rt	 I +  II +  III I + II + III (→), I:II:III = 73:5:22	114

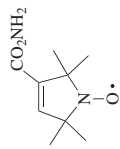
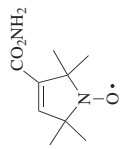
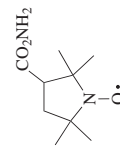
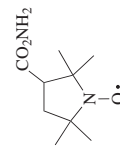
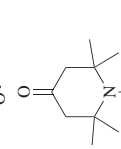
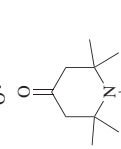
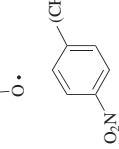
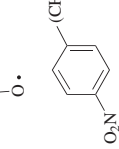
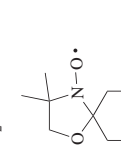
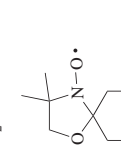
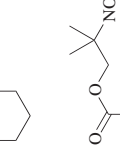
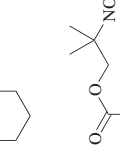
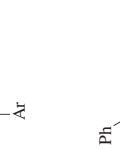
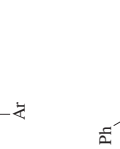
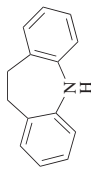
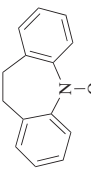
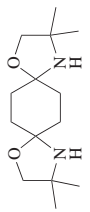
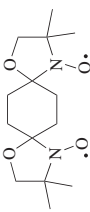
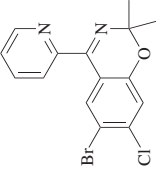
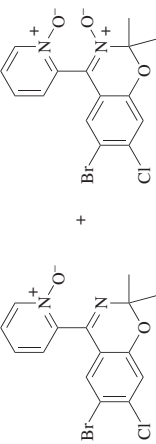

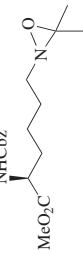
		Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	(85)	394
		Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	(82)	394
		Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	(75)	394
		Oxone [®] , acetone, H ₂ O, NaOH, NaHCO ₃ , EDTA, 2-18°, 4 h	(84)	392
		Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	(93)	394
		Oxone [®] , TFA, NaHCO ₃ , MeCN, H ₂ O, Na ₂ EDTA, rt, 1 h	Ar Ph 3-O ₂ NC ₆ H ₄ 2,6-Cl ₂ C ₆ H ₃	(99) (—) (—)
		Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	(83)	394

TABLE 3F. NITROGEN OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C14	Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	 (89)	394
 C15	Oxone [®] , acetone, CH ₂ Cl ₂ , Na ₂ HPO ₄ buffer (pH 7.5-8.0), aq. KOH, (<i>n</i> -Bu) ₄ NHSO ₄ , 0°	 (90)	394
 C15	Oxone [®] (2.3 eq), acetone, H ₂ O, CH ₂ Cl ₂ , buffer salt (x eq)	 I II (76) (4) (79) (2) (86) (3) (84) (3) (79) (2)	396
 C15	Oxone [®] , acetone, H ₂ O, NaHCO ₃ , Ar, rt, 30 min	 (67)	327

^a This value is the ratio of the products in the crude mixture.

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES

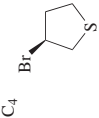
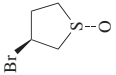
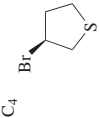
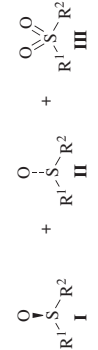
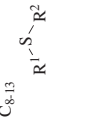

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
C ₄ 	Oxone [®] , acetone, H ₂ O, 0-5°, 75 min	 (67)	397				
C ₇₋₁₃ 	Oxone [®] , acetone, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		130, 131				
				Time	I + II	III	I:II
				180 min	(98)	(-)	53.5:46.5
				180 min	(85)	(-)	62:38
				60 min	(51)	(-)	49.5:50.5
				60 min	(77)	(-)	66:34
				105 min	(68)	(-)	82:18
				120 min	(56)	(5)	10.5:89.5
				120 min	(70)	(-)	13.5:86.5
				120 min	(50)	(11)	64.5:35.5
				85 min	(40)	(14)	45.5:54.5
				25 min	(45)	(5)	24:76
				180 min	(30)	(14)	84:16
				C ₈₋₁₃ 	Oxone [®] , PhCOCF ₃ , bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		130, 131
135 min	(80)	(-)	45.5:54.5				
180 min	(78)	(5)	52:48				
120 min	(96)	(-)	18:82				
90 min	(37)	(10)	14.5:85.5				
150 min	(22)	(3)	86.5:13.5				

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions			Product(s) and Yield(s) (%)		Refs.		
	x	Time	Temp	I	II			
$\begin{array}{c} \text{R}^1-\text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \end{array}$	Oxone® (x eq.), acetone, buffer (pH 7.5-8.0), NaHCO ₃ , EDTA			$\begin{array}{c} \text{O} \\ \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{I} \end{array} + \begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{II} \end{array}$		398		
	H	0.65	5 min	0-2°	(98.6)		(-)	
	H	1.35	1-2 h	rt	(-)		(96.7)	
	CO ₂ H	0.65	5 min	0-2°	(76.8)		(-)	
	CO ₂ H	1.35	1-2 h	rt	(-)		(92.6)	
	H	0.65	5 min	0-2°	(81.5)		(-)	
	H	1.35	1-2 h	rt	(-)		(92.8)	
	CH ₂ OH	0.65	5 min	0-2°	(46.6)		(-)	
	CH ₂ OH	1.35	1-2 h	rt	(-)		(83.4)	
	H	0.65	5 min	0-2°	(95.0)		(-)	
	H	1.35	1-2 h	rt	(-)		(35)	
	$\begin{array}{c} \text{R}^1-\text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \end{array}$	Oxone®, cyclohexanone, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°			$\begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{I} \end{array} + \begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{II} \end{array}$		130, 131	
		Time			I + II			I:II
240 min			(60)	53:47				
120 min			(46)	42:58				
$\begin{array}{c} \text{R}^1-\text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \end{array}$		Oxone®, TFP, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°			$\begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{I} \end{array} + \begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{II} \end{array} + \begin{array}{c} \text{O} \\ // \\ \text{S}-\text{R}^2 \\ \\ \text{C}_6\text{H}_4 \\ \text{III} \end{array}$			130, 131
		Time			I + II	I:II		
4-MeC ₆ H ₄			(60)	53:47				
Ph			(46)	42:58				

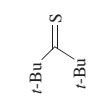
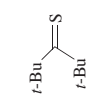
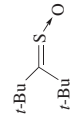
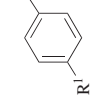
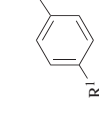
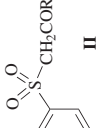
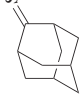
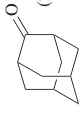
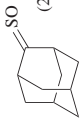
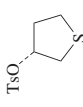
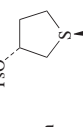
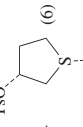
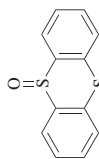
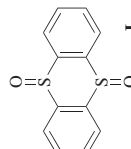
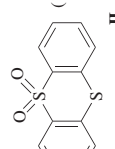
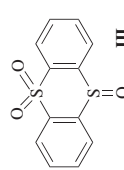
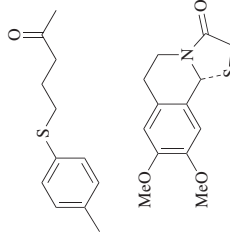
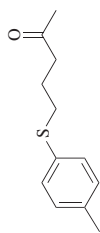
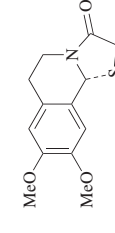
C ₉	R ¹	R ²	Time	I + II	III	I:II	146
							
	4-MeC ₆ H ₄	Me	10 min	(78)	(5)	52:48	
	4-MeC ₆ H ₄	Et	60 min	(66)	(12)	80.5:19.5	
	Ph	<i>i</i> -Pr	5 min	(67)	(—)	5.5:94.5	
	Ph	<i>t</i> -Bu	5 min	(55)	(—)	16.5:83.5	
	Ph	Bz	5 min	(20)	(21)	86:14	
	4-MeC ₆ H ₄	Bz	5 min	(95)	(—)	69:31	
C _{9,15}			Oxone®, acetone, benzene, H ₂ O, 18-crown-6, KHCO ₃ , N ₂ , rt, 4 h		(33)		146
		SCH ₂ COR ²	Oxone®, bovine serum albumin, NaHCO ₃ , Na ₂ EDTA, buffer (pH 7.2-7.8), 4°		I		130, 131
	R ¹	R ²	Time	I % ee		II	
	H	Me	40 min	(100)	6	(—)	
	Me	Me	30 min	(100)	72	(—)	
	H	<i>i</i> -Pr	10 min	(84)	35	(—)	
	Me	<i>i</i> -Pr	10 min	(94)	82	(—)	
	Me	<i>t</i> -Bu	30 min	(83)	79	(—)	
	Me	Ph	20 min	(59)	9	(10)	
C ₁₀			Oxone®, acetone, benzene, H ₂ O, 18-crown-6, KHCO ₃ , N ₂ , rt, 4 h		(20)		146
C ₁₁			Oxone®, acetone, H ₂ O, 0°, 40 min		(94)		122

TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₂</p> 	<p>Oxone®, acetone, phosphate buffer (pH 7.5), 18-crown-6, EDTA, 0° to rt, 24 h</p>	<p>(4) +  I +  II +  III (6)</p> <p>(16) + 399</p>	400
<p>C₁₃</p> 	<p>Oxone®, carbonyl compound, 18-crown-6, CH₂Cl₂, H₂O, 0°</p>	<p>I + II + III</p>	400
	<p>Ketone or aldehyde</p>	<p>I + II + III</p>	
	<p>acetone</p>	<p>(10.1)</p>	
	<p><i>t</i>-BuCOMe</p>	<p>59:15:26</p>	
	<p>cyclohexanone</p>	<p>(5.33)</p>	
	<p><i>t</i>-BuCHO</p>	<p>61:31:8</p>	
		<p>(1.88)</p>	
		<p>58:30:12</p>	
		<p>(5.04)</p>	
	<p>Oxone®, bovine serum albumin, NaHCO₃, Na₂EDTA, buffer (pH 7.2-7.8), 4°, 140 min</p>	<p> (63) 84% ee</p>	130, 131
	<p>Oxone®, CHCl₃, MeOH H₂O, 0°, 30 min</p>	<p> (68)</p>	401

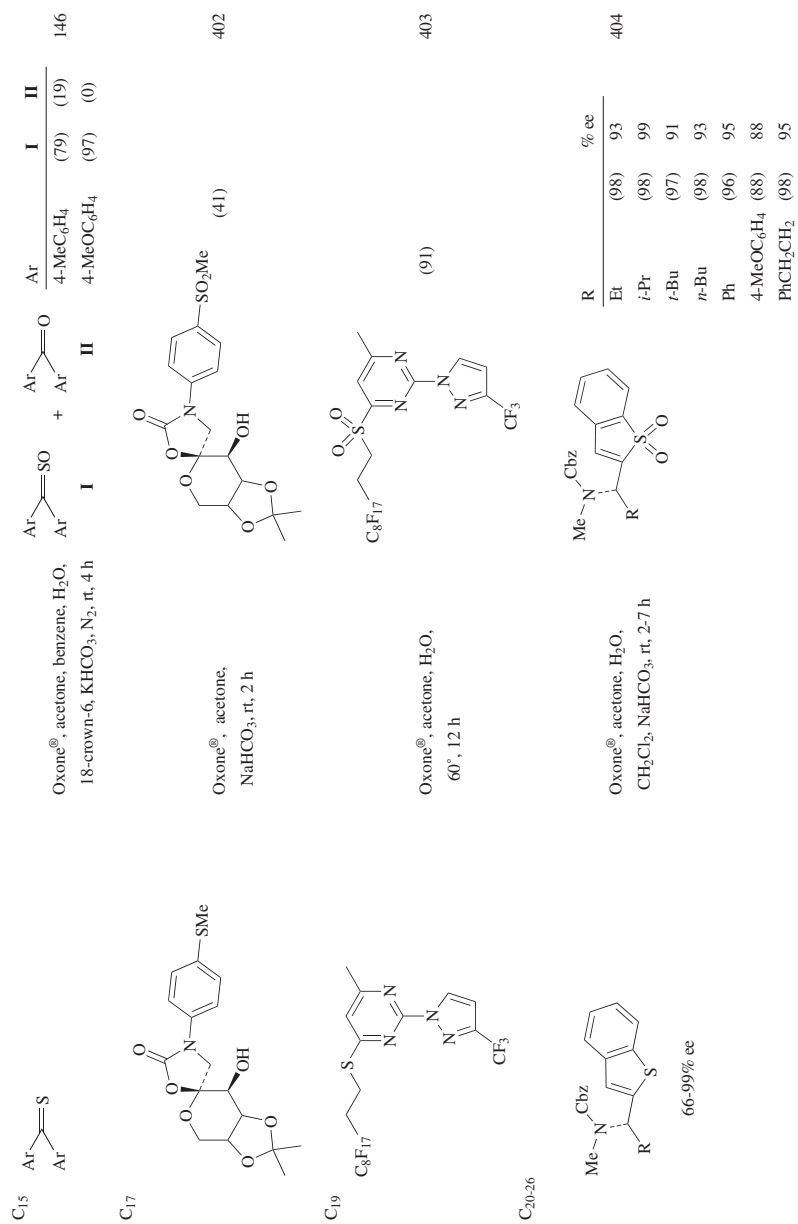


TABLE 3G. SULFUR OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

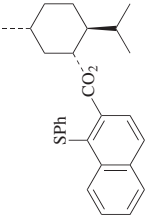
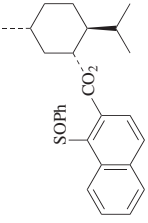
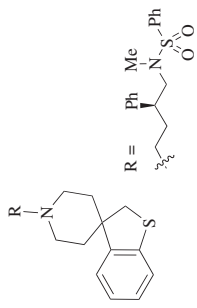
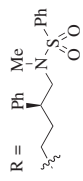
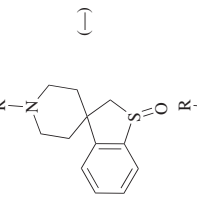
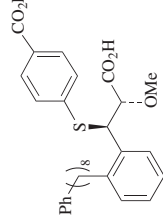
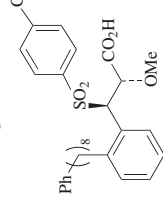
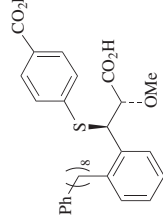
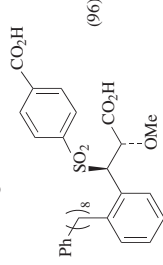
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>Oxone[®], acetone, MeCN, H₂O, NaHCO₃, 5°, 20 h</p>	 <p>(51) dr 58:42</p>	405
 <p>R = </p>	<p>Oxone[®] (1.2 eq), MeOH, -20°, 2-5 min</p>	 <p>(−)</p>	406
	<p>Oxone[®] (3 eq), MeOH, rt</p>	 <p>(−)</p>	406
	<p>Oxone[®], acetone, buffer (pH 7.5-8.0), NaHCO₃, EDTA, rt</p>	 <p>(96)</p>	398

TABLE 3H. OXIDATION OF OTHER HETEROATOMS BY IN SITU GENERATED DIOXIRANES

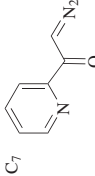
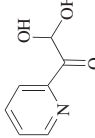
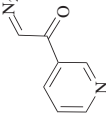
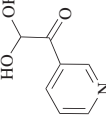
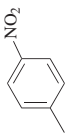
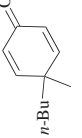
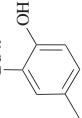

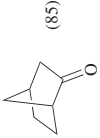
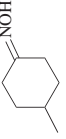
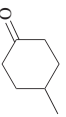
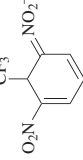
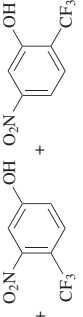
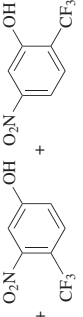
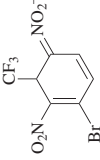
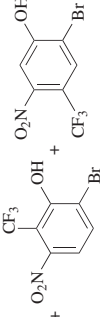
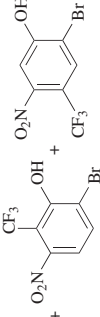
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₀	Oxone [®] , ketone, buffer (pH 9.0)	Cl ⁻	161										
		<table border="1"> <thead> <tr> <th>Ketone</th> <th><i>k_{rel}</i></th> </tr> </thead> <tbody> <tr> <td>—</td> <td>< 0.1</td> </tr> <tr> <td>acetone</td> <td>1.0</td> </tr> <tr> <td>cyclohexanone</td> <td>6.1</td> </tr> <tr> <td><i>N,N</i>-dimethyl-4-oxopiperidinium nitrate</td> <td>1300</td> </tr> </tbody> </table>	Ketone	<i>k_{rel}</i>	—	< 0.1	acetone	1.0	cyclohexanone	6.1	<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	1300	
		Ketone	<i>k_{rel}</i>										
—	< 0.1												
acetone	1.0												
cyclohexanone	6.1												
<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	1300												
ONO ₂ ⁻	163												
C ₁₈	Oxone [®] , acetone, phosphate buffer, KOH, < 0°, 10 min	<table border="1"> <thead> <tr> <th>Ketone</th> <th><i>k_{rel}</i></th> </tr> </thead> <tbody> <tr> <td>—</td> <td>< 0.1</td> </tr> <tr> <td>acetone</td> <td>1.0</td> </tr> <tr> <td>cyclohexanone</td> <td>9.4</td> </tr> <tr> <td><i>N,N</i>-dimethyl-4-oxopiperidinium nitrate</td> <td>1400</td> </tr> </tbody> </table>	Ketone	<i>k_{rel}</i>	—	< 0.1	acetone	1.0	cyclohexanone	9.4	<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	1400	
		Ketone	<i>k_{rel}</i>										
		—	< 0.1										
acetone	1.0												
cyclohexanone	9.4												
<i>N,N</i> -dimethyl-4-oxopiperidinium nitrate	1400												
Ph ₃ P	121												

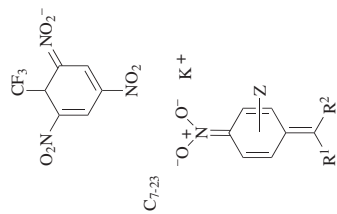
TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₋₉ 	1. <i>t</i> -BuOK, THF, 20°, 5 min 2. DMD, H ₂ O, acetone, 20°, 5 min	 R OH (-) SPh (25) SO ₂ Ph (-)	407
C ₅ 	DMD, acetone, rt, min	 EtO ₂ C OH OH (100)	103
C ₅₋₉ 	DMD, acetone, rt	 (EtO) ₂ P OH OH (100)	408
R-N=C=S	1. DMD, acetone, N ₂ , rt, 15 min 2. Isopropylamine, 0°, 1.5 h	 R <i>n</i> -Bu (71) Ph (89) Bn (84) BnCH ₂ (67)	409
	1. <i>t</i> -BuOK, THF, 20°, 5 min 2. DMD, H ₂ O, acetone, 20°, 5 min	 R ¹ R ² R ¹ R ² (CH ₂) ₂ CO ₂ Me (73) (CH ₂) ₂ CN (86) (CH ₂) ₂ COMe (99) (CH ₂) ₂ CO ₂ Me (90) (CH ₂) ₂ CO ₂ Me (83)	107
C ₅₋₂₃ 	DMD, acetone, rt	 R ¹ R ² R ¹ R ² I or II 	105

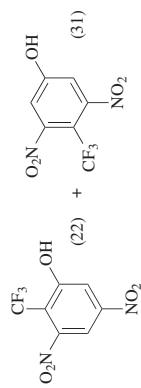
R ₁	R ²	Time	Product
Me	Me	16 h	II (95)
Me	EtO	10 h	I (100)
-(CH ₂) ₃ -		26 h	I (93)
EtO	EtO	29 h	II (100)
-CH ₂ C(Me) ₂ CH ₂ -		20 h	II (89)
-(1,2-C ₆ H ₄)-		20 h	II (100)
Me	Ph	24 h	II (98)
OEt	Ph	35 h	I (94)
Ph	Ph	30 h	II (100)
(-)-menthO	(-)-menthO	10 h	II (100)
C ₆		DMD, acetone, rt, 2 h	
		DMD, acetone, rt, min	
		1. BuLi, THF, Ar, -70°, 5 min 2. DMD, acetone, H ₂ O, THF, Ar, -70°, 6 min	
		DMD, H ₂ O, -70°, 15 min	

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

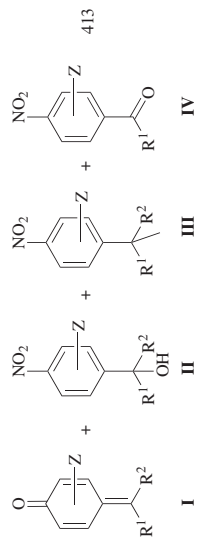
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₇	DMD, acetone, rt, min	 (100)	103
	DMD, acetone, rt, min	 (100)	103
	1. <i>n</i> -BuLi, THF, Ar, -70°, 5 min 2. DMD, acetone, H ₂ O, -70°, 5 min	 (16) +  (7)	111
	DMD, acetone, rt, 1 h	 (85)	411
	DMD, acetone, 0°, 30 min	 (80)	411
	DMD, H ₂ O, -70°, 15 min	 (47) +  (18)	410
	DMD, H ₂ O, -70°, 15 min	 (29) +  (6)	410



DMD, H₂O, -70°, 15 min



410

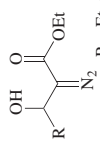
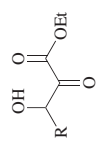
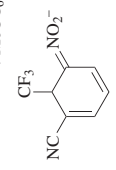
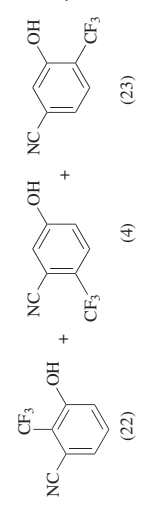
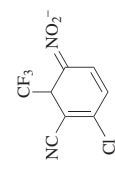
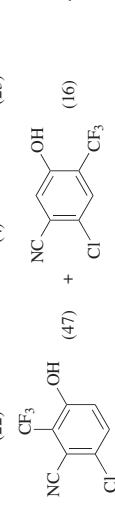
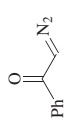
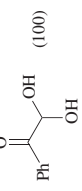
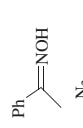
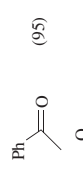
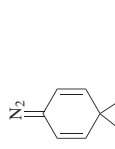
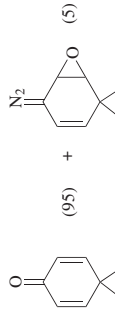
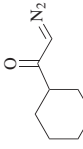
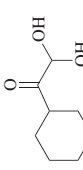


DMD, acetone, THF, Ar,
20°, 5 min

R ¹	R ²	Z
Me	Me	H
H	SO ₂ Ph	H
Me	SO ₂ Ph	H
Ph	CO ₂ Me	H
Ph	Ph	2-Cl
Ph	Ph	3-Cl
Ph	Ph	2-I
Ph	Ph	H
-(9-fluorenyl)-	H	H
Ph	Ph	3-CN
Ph	Ph	2-MeO
Ph	Ph	3-MeO
Ph	4-ClC ₆ H ₄	3-MeO
Ph	1-Naph	H
Ph	Ph	(CH) ₄

I	II	III	IV
(-)	(85)	(-)	(-)
(-)	(-)	(-)	(60)
(-)	(-)	(-)	(33)
(-)	(63)	(-)	(-)
(58)	(30)	(-)	(-)
(61)	(10)	(-)	(-)
(33)	(38)	(-)	(-)
(51)	(28)	(18)	(-)
(-)	(99)	(-)	(-)
(64)	(-)	(-)	(-)
(58)	(36)	(-)	(-)
(44)	(13)	(30)	(-)
(40)	(26)	(33)	(-)
(75)	(20)	(-)	(-)
(91)	(-)	(-)	(-)

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-17}  R = Et, <i>i</i> -Bu, <i>c</i> -C ₃ H ₉ , <i>n</i> -C ₆ H ₁₃ , Ph, 3-BrC ₆ H ₄ , 4-FC ₆ H ₄ , 2-MeOC ₆ H ₄ , 4-MeOC ₆ H ₄ , 3-CF ₃ C ₆ H ₄ , 4-PhC ₆ H ₄	DMD, acetone, -35°, 15-30 min	 (—)	412
C_8 	DMD, H ₂ O, -70°, 15 min	 (22) + (23)	410
	DMD, H ₂ O, -70°, 15 min	 (47) + (16)	410
	DMD, acetone, rt, min	 (100)	103
	DMD, acetone, rt, 24 h	 (95)	411
	DMD, acetone, CH ₂ Cl ₂ , 0°, 1 min	 (95) + (5)	106
	DMD, acetone, rt, min	 (96)	103

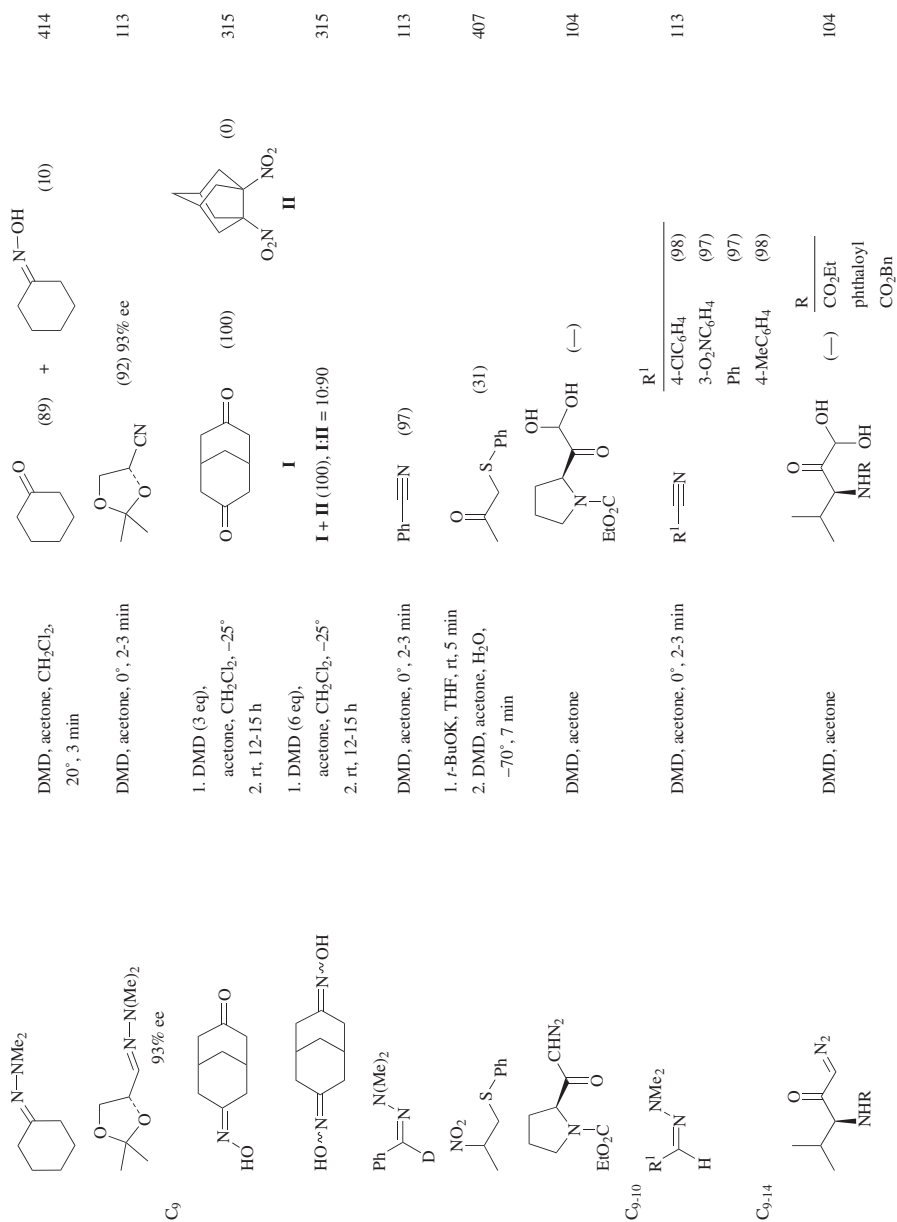
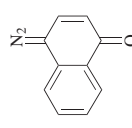
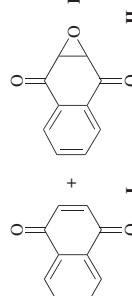
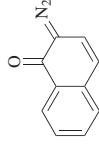
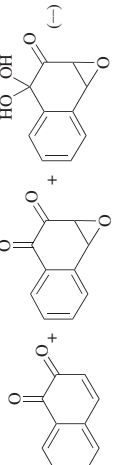
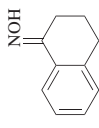
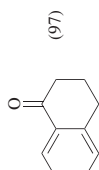
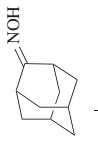
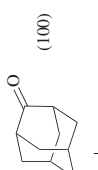
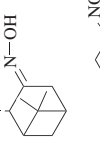
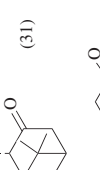
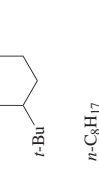
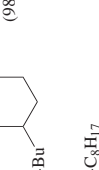




TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{10}	DMD, acetone, rt, 2 h	 I + II (—), II = 70:30	106
	DMD, acetone, rt, 2 h	 I + II + III (—), I : (II+III) = 30:70	106
	DMD, acetone, rt, 24 h	 (97)	411
	DMD, acetone, 0°, 5 min	 (100)	411
	DMD, acetone, rt, 0.5 h	 (31)	22
	DMD, acetone, 0°, 30 min	 (98)	411
	DMD, acetone, 0°, 10 min	 (94)	411

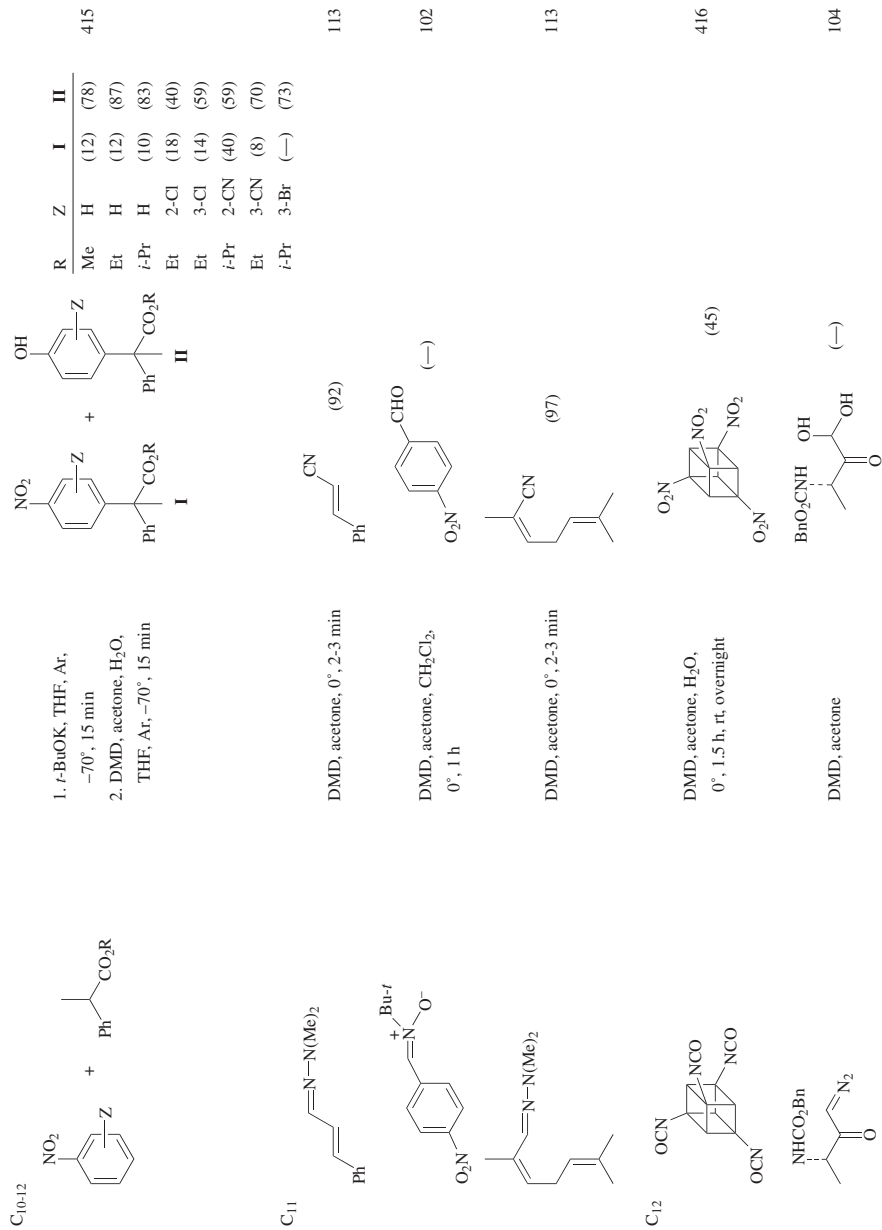


TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

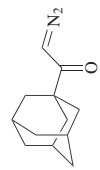
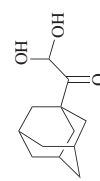
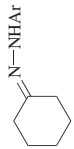
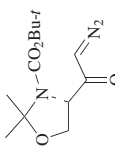
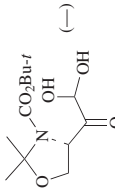
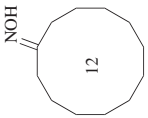
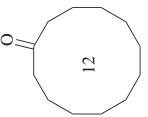
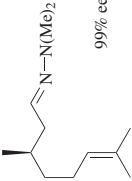
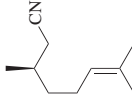
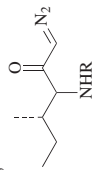
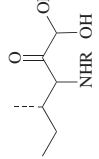
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt	 (100)	103
	DMD, acetone (or TFD, TFP), CH ₂ Cl ₂	Ar 2,4-(O ₂ N) ₂ C ₆ H ₃ DMD 2° 6 h (92) 2,4-(O ₂ N) ₂ C ₆ H ₃ TFD 0° 90 min (95) 4-O ₂ NC ₆ H ₄ DMD 20° 3 h (91) 4-O ₂ NC ₆ H ₄ TFD 0° 30 min (92) Ph DMD 20° 30 min (94)	414
	DMD, acetone	 (—)	104
	DMD, acetone, rt, 1 h	 (100)	411
	DMD, acetone, 0°, 2-3 min	 (92) 98% ee	113
	DMD, acetone	 R CO ₂ Bu-t CO ₂ Bn	104

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
<p>C₁₄</p>	DMD, acetone, rt	(100)	106						
	DMD, acetone, rt	(100)	106						
<p>C₁₅</p>	DMD, acetone, CH ₂ Cl ₂ , 20°	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>NO₂</td> <td>2 h (82)</td> </tr> <tr> <td>H</td> <td>30 min (92)</td> </tr> </tbody> </table>	R	Time	NO ₂	2 h (82)	H	30 min (92)	414
R	Time								
NO ₂	2 h (82)								
H	30 min (92)								
	DMD, H ₂ O	(81)	417						
	DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min	(72)	110						
	DMD, H ₂ O, DMF, THF, acetone, Ar, -70°, 5 min	(69-77)	110						

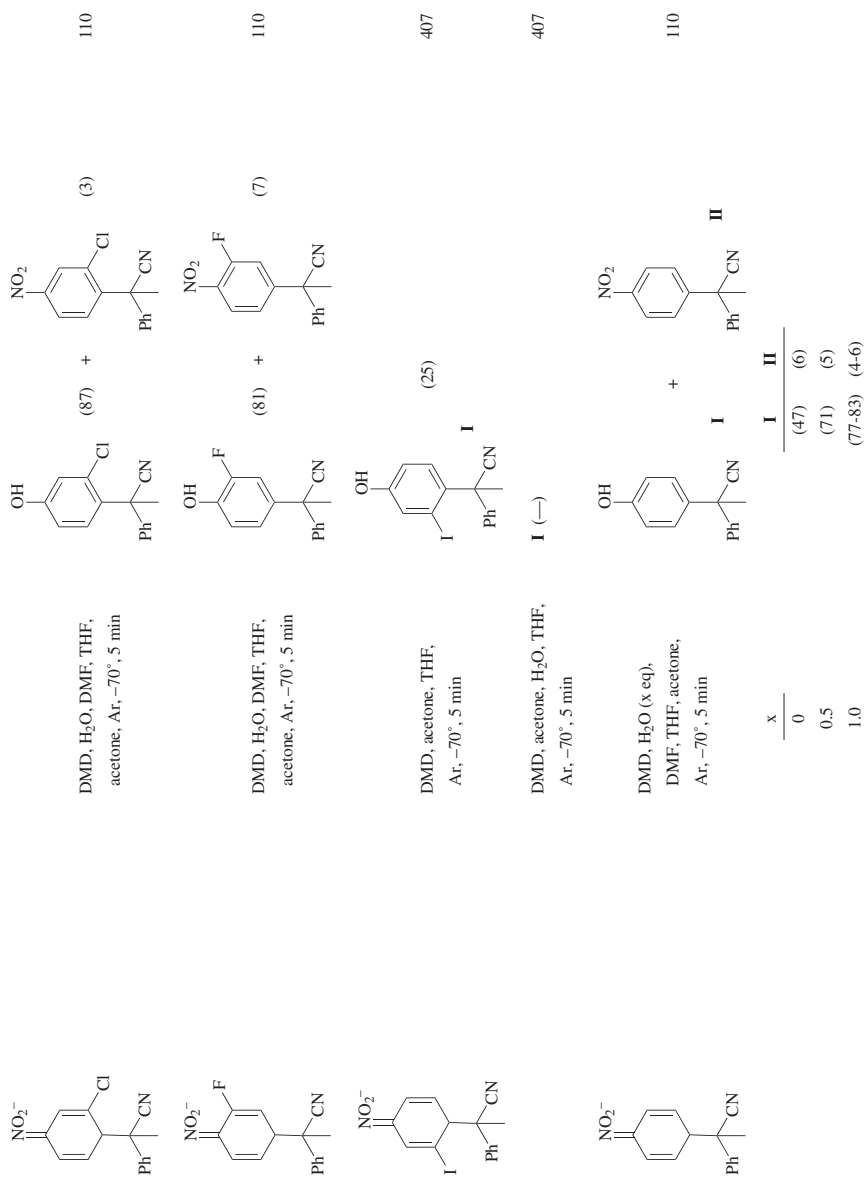
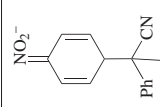
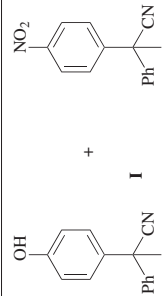
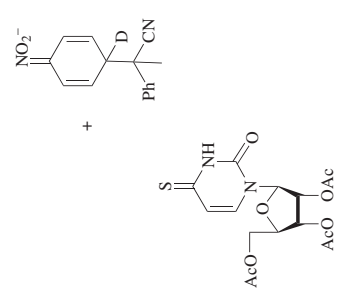
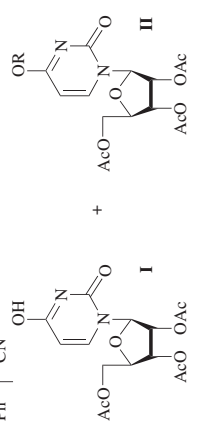


TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C15	Dioxirane, THF, Ar, -70°, 5 min	 I + II	111
	Dioxirane Solvent	I (trace) (trace) II (77-83) (4-6) (33-63) (4-5) (38) (10) (32) (9)	
	DMD	acetone	—
	DMD	acetone	H ₂ O
	DMD	acetone	MeOH
	TFD	TFP	—
	TFD	TFP	H ₂ O
 	DMD, acetone, THF, Ar, -70°, 5 min	 I + II	111
		(-) $K_{Hf}/K_{D} = 1.01 \pm 0.01$	
	DMD, acetone, CH ₂ Cl ₂ , additive, rt	I + II R H I + II (95) II = 1:1 Me (22) (70) Et (18) (65) <i>n</i> -Pr (15) (70) <i>n</i> -Bu (20) (75)	144
	Additive		

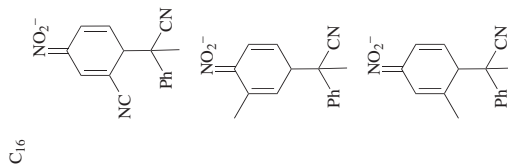
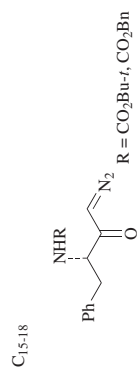
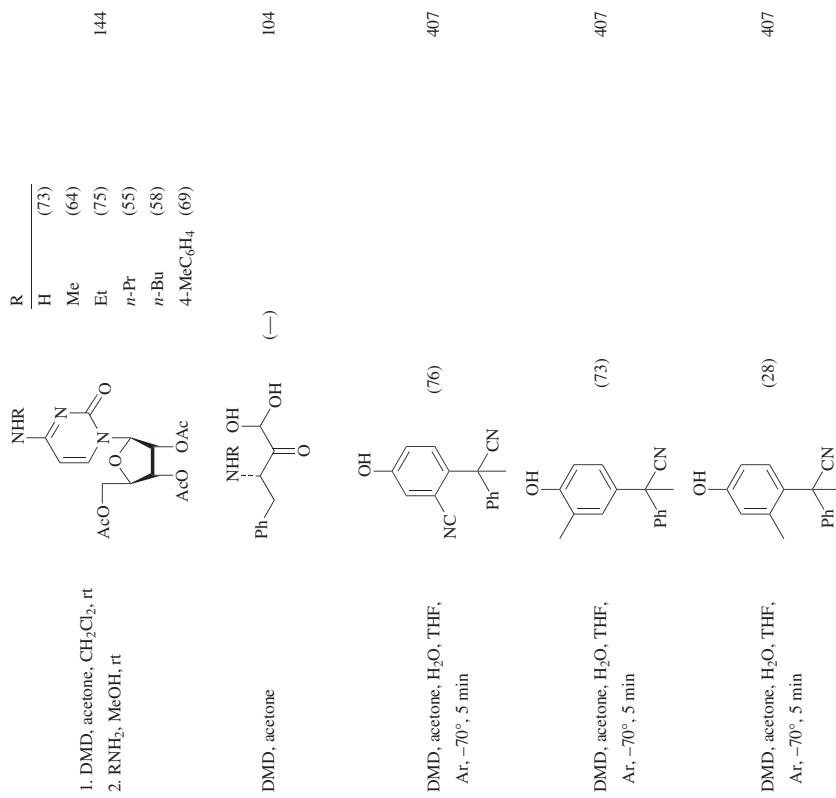


TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₇</p>	DMD, acetone	 (-)	104
<p>C₁₈</p>	DMD, acetone, rt, 2 h	 (97)	418
<p>C₁₈</p>	DMD, acetone, CH ₂ Cl ₂ , MeNH ₂ , rt	 (83)	116, 117, 118, 119, 120, 144
<p>C₁₉</p>	DMD, acetone, H ₂ O, THF, Ar, -70°, 5 min	 (65)	407
<p>C₁₉</p>	DMD, acetone, solvent, Ar, 20°, 5 min	 I	27
		 II	
		 III	

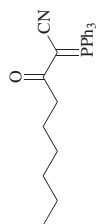
M ⁺	Solvent	% Conv.	I:III
Li ⁺	THF	83	17:63:16
Na ⁺	THF	88	33:47:16
K ⁺	THF	95	48:26:17
CaMg ⁺	THF	96	0:80:3
<i>t</i> -Bu ₄ N ⁺	THF	97	0:95:0
K ⁺	DMF	93	29:60:8
K ⁺	THF/DMF (3:1)	91	37:45:14
K ⁺	toluene	90	51:33:15

C ₂₁₋₂₂	Reaction Conditions	Yields (%)
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min	Z: 82 (12) H: 74 (8) 2-Cl: 64 (15) 3-Cl: 69 (—) 3-CN: 417 (—)
	1. <i>N,N,N',N'</i> -Tetramethylguanidine, CH ₂ Cl ₂ , 0°	419
	2. DMD, acetone	104
	DMD, acetone	104
	DMD, acetone	104

C ₂₂	Reaction Conditions	Yields (%)
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min	78
	1. <i>N,N,N',N'</i> -Tetramethylguanidine, CH ₂ Cl ₂ , 0°	419
	DMD, acetone, CH ₂ Cl ₂ , TsOH, rt, 10 min	104
	1. <i>N,N,N',N'</i> -Tetramethylguanidine, CH ₂ Cl ₂ , 0°	104
	2. DMD, acetone	104
	DMD, acetone	104

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

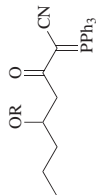
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₄	1. <i>t</i> -BuOK, THF, H ₂ O 2. DMD, acetone	 (72)	109
 C ₂₆	DMD, MeOH, acetone, rt	 (32) +	420
 C _{26,28}	DMD, MeOH, acetone, rt	 (85)	420
 C _{26,28}	DMD, MeOH, acetone, rt	 (56)	420
 C ₂₇	DMD, acetone, CH ₂ Cl ₂ , rt, 1 h	 R ¹ Me (100) R ² <i>t</i> -Bu (> 82) Cl(CH ₂) ₂ <i>t</i> -Bu (100) Ph Me (100)	159
 C ₂₇	DMD, acetone, CH ₂ Cl ₂ , 20°, 15 min	 (96)	414



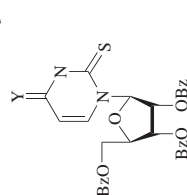
C₂₈



C₂₈₋₃₂

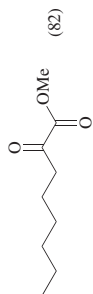


C₃₀



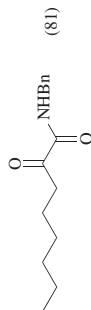
Y
O
O
O
S

DMD, MeOH, acetone, rt



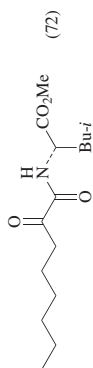
420

DMD, BnNH₂, CH₂Cl₂, acetone, -78°



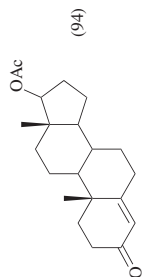
420

DMD, H₂N, CO₂Me, Bu-*i*, CH₂Cl₂, acetone, -78°



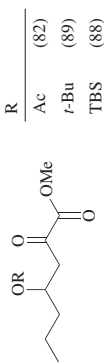
420

DMD, acetone, CH₂Cl₂, 20°, 1 h



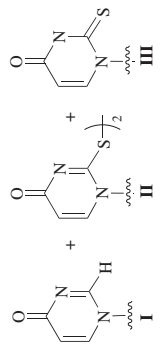
414

DMD, MeOH, acetone, rt



420

DMD, acetone, CH₂Cl₂, additive, rt



144

Additive	I	II	III
—	(43)	(20)	(—)
ROH	(37)	(26)	(—)
RNH ₂	(24)	(15)	(—)
—	(38)	(22)	(8)

TABLE 4A. C=Y OXIDATION BY ISOLATED DIOXIRANES (Continued)

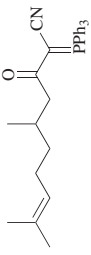
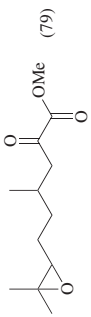
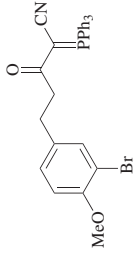
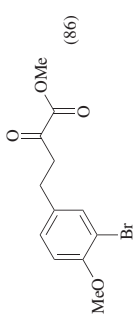
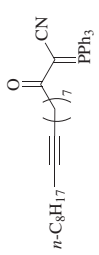
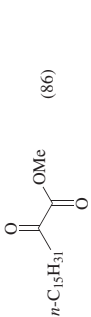
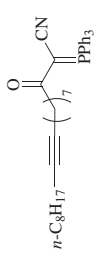
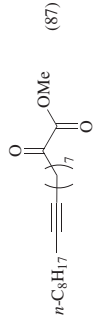
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₀		DMD (2.4 eq), MeOH, acetone, 0°	 (79)	420
C ₃₆		DMD, MeOH, acetone, rt	 (86)	420
C ₃₈		DMD, acetone, MeOH	 (86)	159
C ₃₈		DMD, MeOH, acetone, 0°	 (87)	420

TABLE 4B. C=Y OXIDATION BY IN SITU GENERATED DIOXIRANES


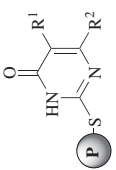
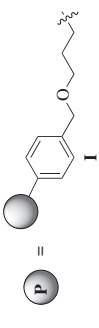
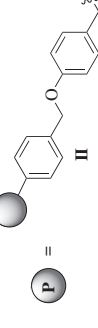

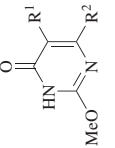
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C_{4-13} 	Oxone [®] , wet alumina, microwave	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td><i>n</i>-Pr</td> <td>(84)</td> <td>(87)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(95)</td> <td>(99)</td> </tr> <tr> <td>2-O₂NC₆H₄</td> <td>H</td> <td>(98)</td> <td>(99)</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>H</td> <td>(98)</td> <td>(98)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(89)</td> <td>(94)</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>H</td> <td>(94)</td> <td>(90)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>H</td> <td>(90)</td> <td>(82)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>Me</td> <td>(82)</td> <td>(86)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(86)</td> <td></td> </tr> </tbody> </table>	R ¹	R ²	I	II	Me	<i>n</i> -Pr	(84)	(87)	Ph	H	(95)	(99)	2-O ₂ NC ₆ H ₄	H	(98)	(99)	4-O ₂ NC ₆ H ₄	H	(98)	(98)	Ph	Me	(89)	(94)	4-MeC ₆ H ₄	H	(94)	(90)	4-MeOC ₆ H ₄	H	(90)	(82)	4-MeOC ₆ H ₄	Me	(82)	(86)	Ph	Ph	(86)		421
R ¹	R ²	I	II																																								
Me	<i>n</i> -Pr	(84)	(87)																																								
Ph	H	(95)	(99)																																								
2-O ₂ NC ₆ H ₄	H	(98)	(99)																																								
4-O ₂ NC ₆ H ₄	H	(98)	(98)																																								
Ph	Me	(89)	(94)																																								
4-MeC ₆ H ₄	H	(94)	(90)																																								
4-MeOC ₆ H ₄	H	(90)	(82)																																								
4-MeOC ₆ H ₄	Me	(82)	(86)																																								
Ph	Ph	(86)																																									
C_{5-11}    	Oxone [®] (3 eq), dioxane, H ₂ O, 12 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(98)</td> <td>(95)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(83)</td> <td>(78)</td> </tr> <tr> <td>H</td> <td>CH₂CO₂Et</td> <td>(78)</td> <td>(65)</td> </tr> <tr> <td>H</td> <td>Bn</td> <td>(85)</td> <td>(70)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	Me	(98)	(95)	Me	Me	(83)	(78)	H	CH ₂ CO ₂ Et	(78)	(65)	H	Bn	(85)	(70)	422																				
R ¹	R ²	I	II																																								
H	Me	(98)	(95)																																								
Me	Me	(83)	(78)																																								
H	CH ₂ CO ₂ Et	(78)	(65)																																								
H	Bn	(85)	(70)																																								
	Oxone [®] (3 eq), MeOH, 12 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(95)</td> <td>(96)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>(72)</td> <td>(70)</td> </tr> <tr> <td>H</td> <td>CH₂CO₂Et</td> <td>(67)</td> <td>(56)</td> </tr> <tr> <td>H</td> <td>Bn</td> <td>(77)</td> <td>(73)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	H	Me	(95)	(96)	Me	Me	(72)	(70)	H	CH ₂ CO ₂ Et	(67)	(56)	H	Bn	(77)	(73)	422																				
R ¹	R ²	I	II																																								
H	Me	(95)	(96)																																								
Me	Me	(72)	(70)																																								
H	CH ₂ CO ₂ Et	(67)	(56)																																								
H	Bn	(77)	(73)																																								

TABLE 4B. C=Y OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₁₄</p>	<p>Oxone[®], acetone, NaHCO₃ H₂O, 0°, 1 h</p>	<p>(83)</p>	423
<p>C₃₀</p>	<p>Oxone[®], dioxane, H₂O, 12 h</p>	<p>(40)</p>	422

= Merrifield resin

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES




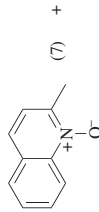
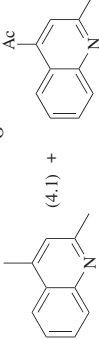
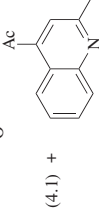




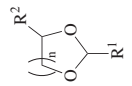
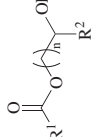
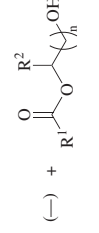

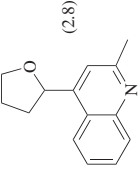
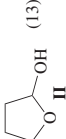

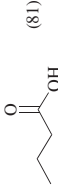

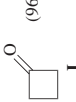




Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt, 2 h	 (—)	121
	DMD, 2-Me-quinoline, CF ₃ CO ₂ H, 0°, 8 h	 (77) +  (4.1) +  (4.2)	35
	DMD, acetone, rt, 2 h	 Et (—)	121
	TFD, TFP, CH ₂ Cl ₂ , -20°, 8 min	 (>88)	29
	DMD, acetone, 20°	 (—) +  (—)	424
		k (x 10 ³ l mol ⁻¹ s ⁻¹)	
		4.83 ± 0.35	
		33.0	
		24.8 ± 1.2	
		0.61 ± 0.06	
		0.74 ± 0.01	
		1.36 ± 0.09	
		45.0 ± 2.2	
		3.2 ± 0.05	
		9.25 ± 0.42	

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, 2-Me-quinoline, CF ₃ CO ₂ H, acetone, 0°, 8 h	I (23) + II (3.2) +  (2.8)	35
	DMD, acetone, CH ₂ Cl ₂ , 0°, 70 h	 (13) + II	191
	TFD, TFP, CH ₂ Cl ₂ , 0°, 10 min	I (65) + II (30)	191
	TFD, TFP, CH ₂ Cl ₂ , -20°, 10 min	 (81)	29
	TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	 (96)	29
	TFD, TFP, CH ₂ Cl ₂ , -20°, 4 min	I (59)	29
	TFD, TFP, CH ₂ Cl ₂ , -20°, 12 min	 (92)	29
	TFD, TFP, CH ₂ Cl ₂ , -20°, 12 min	 (86)	29

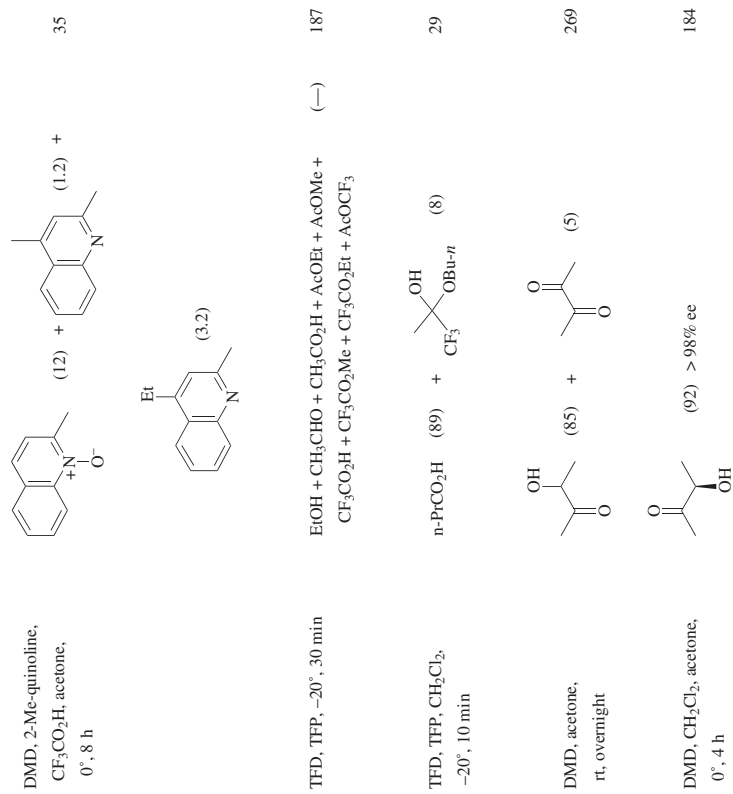




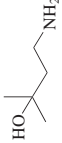
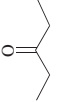

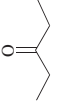


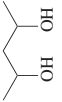
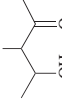
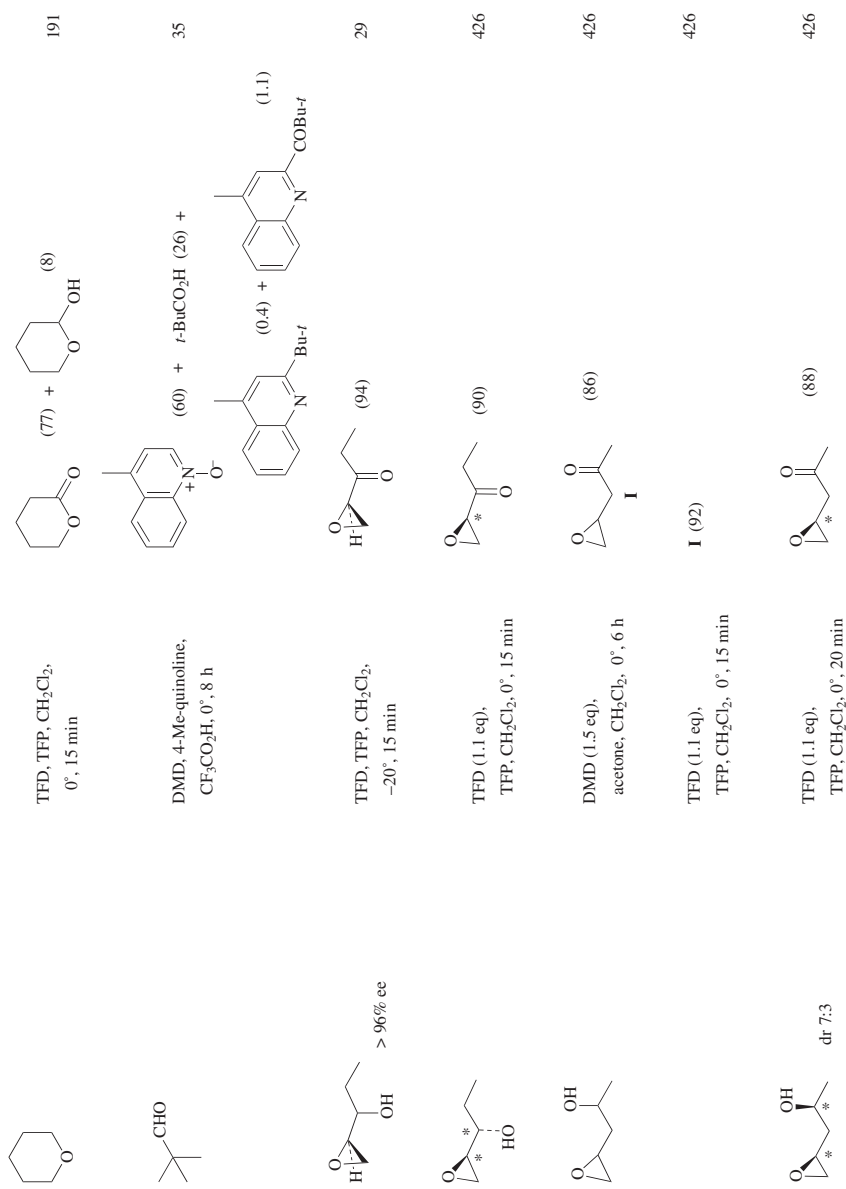


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

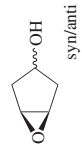
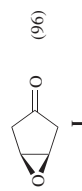
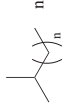
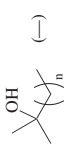
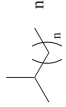
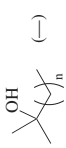
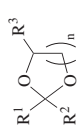
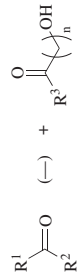
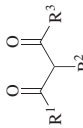
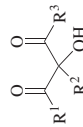
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
 x M	DMD, acetone, or TFD, TFP	 + 	425				
	Dioxirane (M)	Temp	Time	% Conv.	I	II	
	DMD (0.018)	20°	60 min	40	(89)	(11)	
	DMD (0.018)	20°	150 min	75	(70)	(30)	
	DMD (0.002)	20°	15 min	60	(>99)	(—)	
	DMD (0.002)	20°	27 min	82	(>99)	(—)	
	DMD (0.024)	20°	150 min	70	(>99)	(—)	
	DMD (0.002)	20°	120 min	25	(>99)	(—)	
	DMD (0.002)	20°	90 min ^d	35	(>99)	(—)	
	TFD (0.002)	0°	5 min	95	(79)	(21)	
	TFD (0.001)	0°	30 min	35	(92)	(8)	
	1. aq. HBF ₄ , MeCN, (pH 2-3), 0°						
	2. TFD, CH ₂ Cl ₂ , rt, 3 h						
	3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h						
						 (90)	192
	1. aq. HBF ₄ , MeCN, (pH 2-3), 0°						
	2. TFD, CH ₂ Cl ₂ , rt, 10 h						
	3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h						
						 (93)	192
	TFD, TFP, Et ₂ O, -20°					 + other products	187
	TFD, CCl ₄ , 0°, 10 min					 (90)	191
	DMD, acetone, rt, overnight					 (95)	269



> 96% ee

dr 7:3

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₅</p>  <p>syn/anti 6:4</p>	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 3 h	 <p>I (96)</p>	426
<p>C₅₋₈</p>  <p>n = 1, 2, 3, 4</p>	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min	<p>I (96)</p>  <p>(-)</p>	426
<p>C₅₋₈</p>  <p>n = 1, 2, 3, 4</p>	DMD, acetone, rt, 1-2 d	 <p>(-)</p>	427
	DMD, acetone, 20°	 <p>(-) + (-)</p>	424
		k (x 10 ³ l mol ⁻¹ s ⁻¹)	
		0.38 ± 0.05	
		0.54 ± 0.04	
		0.42 ± 0.01	
		9.25 ± 0.42	
<p>C₅₋₁₃</p> 	DMD, catalyst, acetone, H ₂ O, 20°		194

R ₁	R ²	R ³	Catalyst	Time	% Conv.
OMe	H	OMe	—	24 h	15
OMe	H	OMe	Ni(OAc) ₂	16 h	>95
—O(CH ₂) ₂ —	Me	Me	—	3.5 h	90
—O(CH ₂) ₂ —	Me	Me	Ni(acac) ₂	3.5 h	>95
Me	H	OEt	—	24 h	35
Me	H	OEt	Ni(OAc) ₂	24 h	>95
—O(CH ₂) ₂ —	OEt	OEt	—	5 h	46
—O(CH ₂) ₂ —	OEt	OEt	Ni(OAc) ₂	5 h	84
—(CH ₂) ₃ —	OEt	OEt	—	3.5 h	75
—(CH ₂) ₃ —	OEt	OEt	Ni(acac) ₂	3.5 h	>95
OEt	Me	OEt	—	120 h	—
OEt	Me	OEt	Ni(OAc) ₂	12 h	47
—(CH ₂) ₄ —	Et	Et	—	3 h	88
—(CH ₂) ₄ —	Et	Et	Ni(OAc) ₂	3 h	90
Me	Bn	OEt	—	4.25 h	11
Me	Bn	OEt	Ni(acac) ₂	4.25 h	78

R ¹	R ²	R ³	Reaction Conditions	Yield
			TFD, TFP, CH ₂ Cl ₂ , -12.5°	29
			DMD (3.0 eq), acetone, 20°, 72 h	193
			DMD, acetone, rt, 24 h	428

C₆

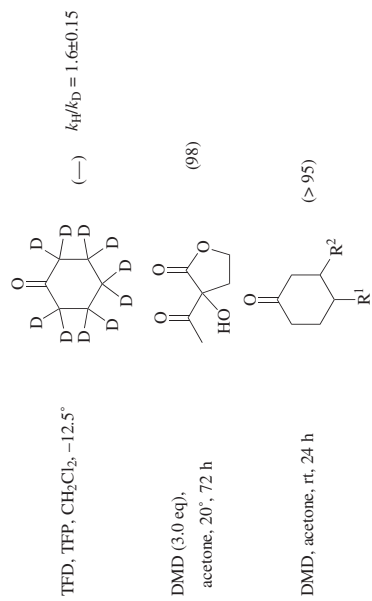

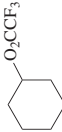

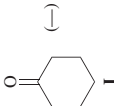





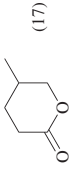


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 10 min	 (> 99)	172
	DMD, CCl ₃ Br, acetone, (O ₂)	 +  (—)	429
	TFD, TFP, CH ₂ Cl ₂ , -22°, 18 min	I (98)	30, 173
	TFD, TFP, -20°, 30 min	I (95)	173
	DMD, acetone, rt	 (30+50)	429
	TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	I (97)	29
	DMD, acetone, O ₂ , 22°, 6 h	I (—)	35
	DMD, acetone, Ar, 22°, 6 h	I (45) + AcOMe (27.2) + MeOH (13.5) + AcOCH ₂ Ac (12.1) + CH ₄ (—)	34, 35
	DMD, acetone, CH ₂ Cl ₂ , 18°, 96 h	 (9) +  (17)	191
	TFD, TFP, CH ₂ Cl ₂ , -10°, 15 min	I (32) + II (49)	191

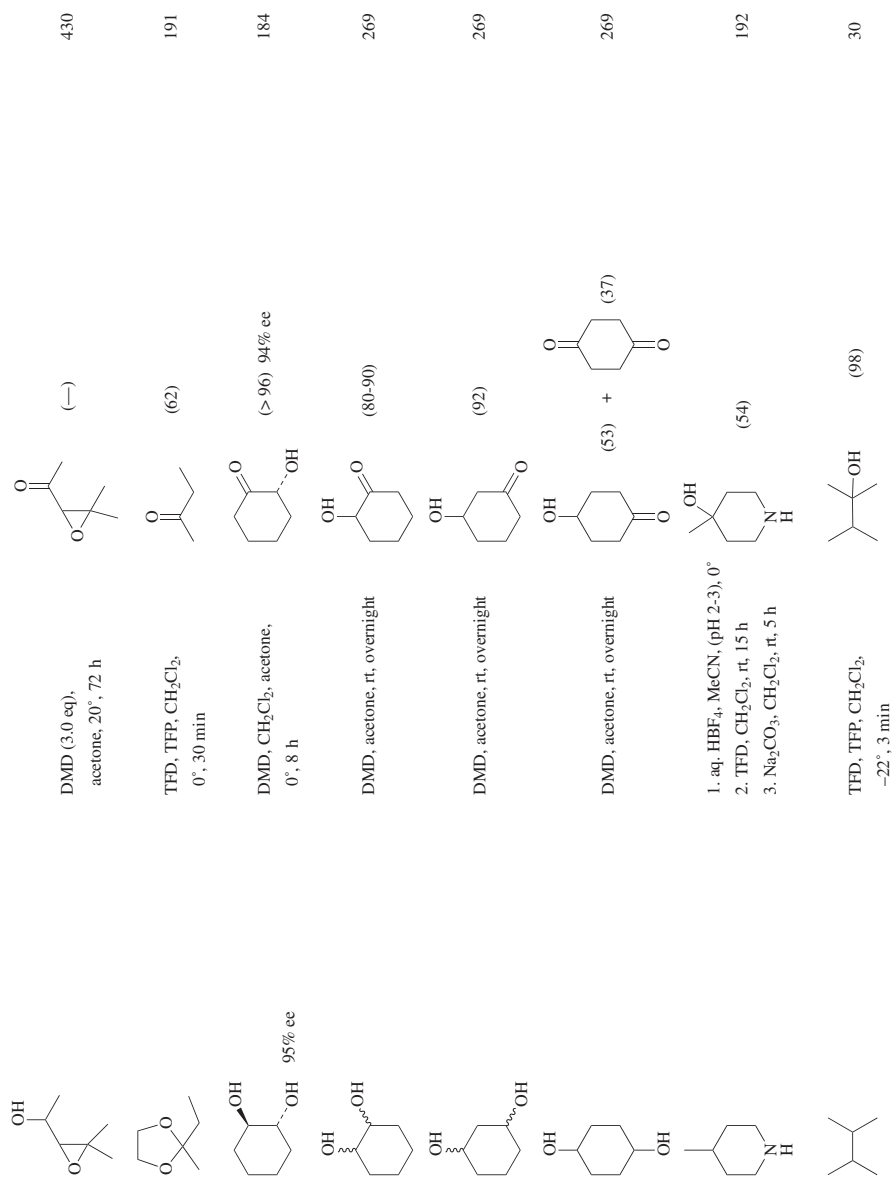


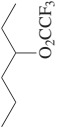

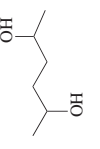
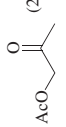
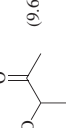
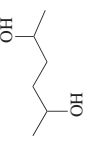
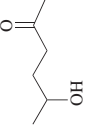
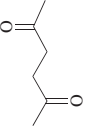

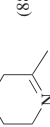
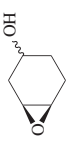
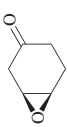


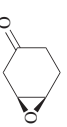


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 40 min	 (58) +  (42)	172
<i>i</i> -Pr-O-Pr- <i>i</i>	DMD, acetone, Ar, 22°, 6 h	CH ₄ (-) +  (38.4) + MeOH (12.1)	34, 35
	DMD, acetone, DEK, Ar, 22°, 6 h	AcO  (2.1) + AcO  (9.6)	35
	DMD, acetone, rt, overnight	 (50) +  (25)	269
	1. aq. HBF ₄ , MeCN (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (88)	192
	DMD (1.6 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h	 (83)	426
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min	II (88)	426
	TFD (3.0 eq), acetone, 0°, 3 h	 (67)	426

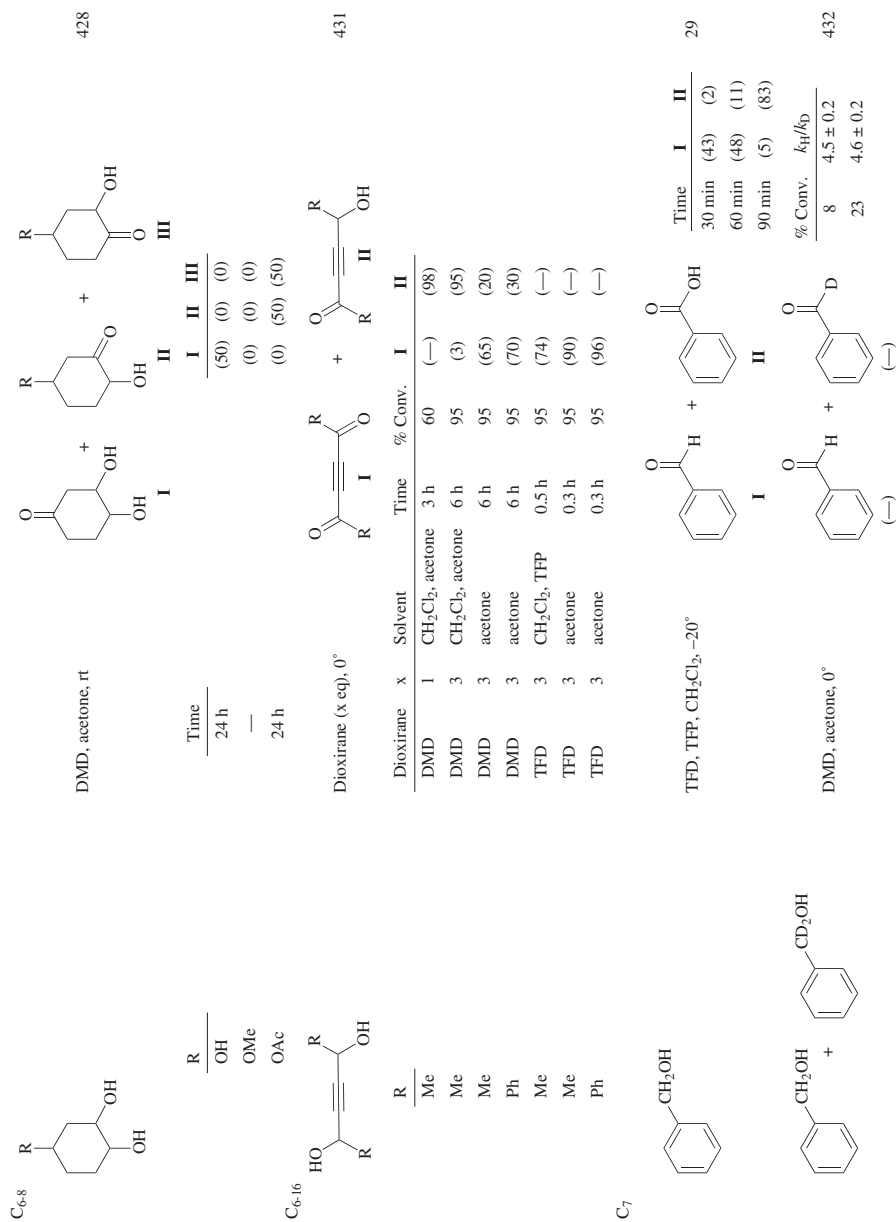
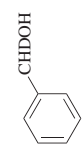
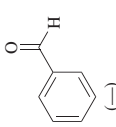
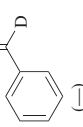

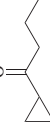

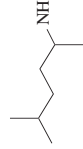
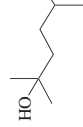


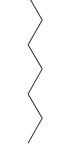
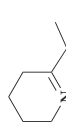
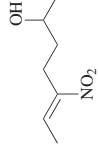
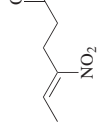





TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, 0°	 +  (—)	432
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min	 (40) +  (4)	433
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 3 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (97)	192
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 10 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (96)	192
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (94)	192
	DMD, acetone, rt, overnight	 (75)	434
	TFD, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 40 min	 (5) +  (95)	172

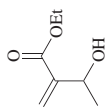
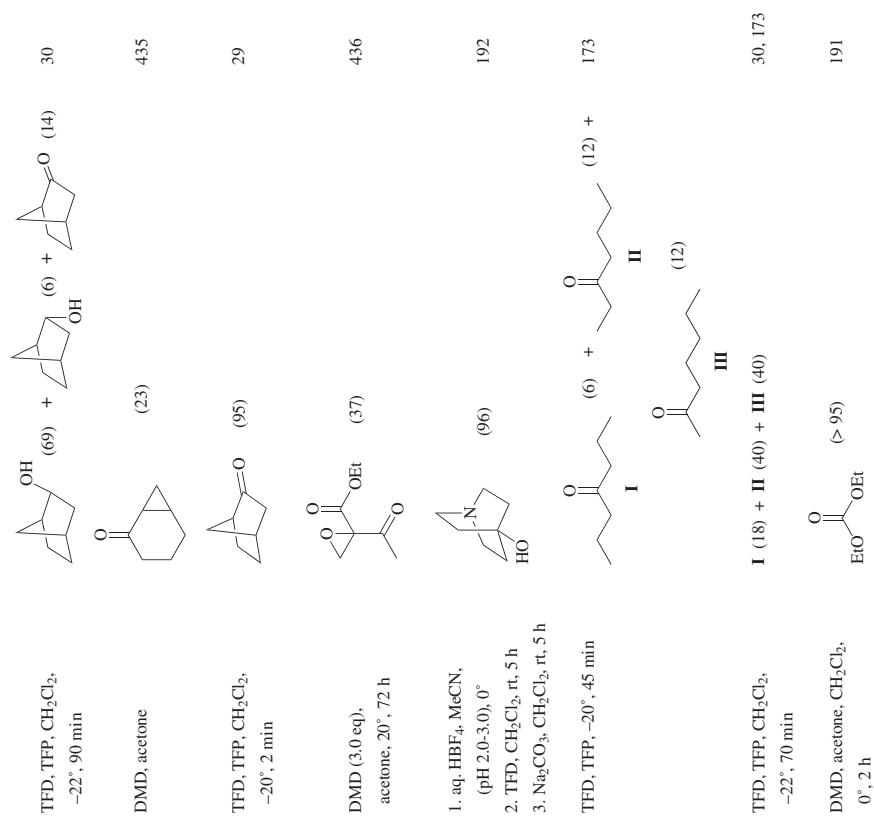
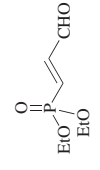
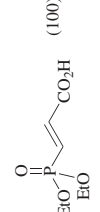

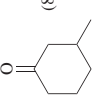


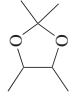

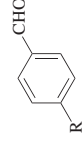
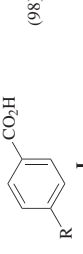





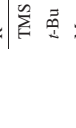


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
 C_7	DMD, acetone, rt, 4 d	 (100)	437										
	TFD, TFP, CH_2Cl_2 , -22° , 8 min	 (8)	30										
 98% ee	TFD, TFP, CH_2Cl_2 , 0° , 40 min	 (> 96) 98% ee	190										
	TFD, TFP, CH_2Cl_2 , 0° , 20 min	 (> 94)	190										
 C_{7-8}	DMD, acetone, rt, dark, 18 h	 (98)	438										
 C_{7-10}	DMD, acetone, rt, dark, N_2 or Ar	 I (52 ± 8)	438										
	1. TFD, CH_2Cl_2 , -40° 2. $(CF_3CO)_2O$	 + 	439										
		k_{eq}/k_{ax} <table border="1"> <thead> <tr> <th>C-3</th> <th>C-4</th> </tr> </thead> <tbody> <tr> <td>2.92</td> <td>2.61</td> </tr> <tr> <td>1.35</td> <td>1.10</td> </tr> <tr> <td>1.34</td> <td>0.90</td> </tr> <tr> <td>0.44</td> <td>0.52</td> </tr> </tbody> </table>	C-3	C-4	2.92	2.61	1.35	1.10	1.34	0.90	0.44	0.52	
C-3	C-4												
2.92	2.61												
1.35	1.10												
1.34	0.90												
0.44	0.52												

R = Br, NO_2 , H, CN, Me, MeO

R = Br, NO_2 , H, MeO

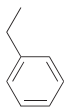
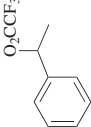
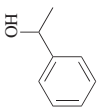
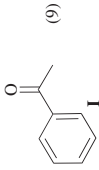
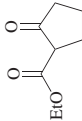
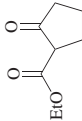
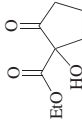


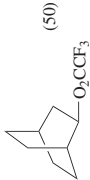


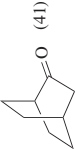
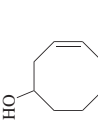

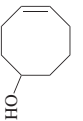
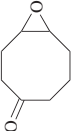
R = TMS, *t*-Bu, Me, CF_3

R ¹	R ²	n	Structure	Reaction Conditions	Yield (%)	k _H /k _D
Me	OH	1		DMD, acetone, rt, 15 min to 2 d	427	—
Et	OH	0				
Me	OH	2				
Me	Me	2				
Et	OH	3				
C ₈						
				DMD, acetone, O ₂ , 20°, 6 h	35	(0.75)
			I (1.98) + BnOAc II (4.02) + AcOMe (2.52) + MeOH (0.546) + AcOCH ₂ Ac (0.504) + CH ₄ (—)	DMD, acetone, Ar, 20°, 6 h	35	—
			I + II (—), I : II = 13:87	DMD, acetone, Ar, 60°, 6 h	35	—
			I (—)	DMD, acetone, 20°	168	—
			I (2) + II (4)	DMD, acetone, N ₂ (Ar), 20°	168	—
			I (2) + II (14)	DMD, acetone, N ₂ , 60°	168	—
				DMD, acetone, rt, 30 min	176	(80)
			I + II	DMD, acetone, rt	175	—

I	II	k ₂ (x 10 ⁻² Mol ⁻¹ s ⁻¹)
(73)	(2)	2.24±0.06
(70)	(3,5)	0.63±0.02
(70)	(2)	2.05±0.06

R ¹	R ²	k _H /k _D
H	H	—
D	H	3.55
H	D	1.09

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFD, TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 20 min	 (9)	172
	TFD, TFP, CH ₂ Cl ₂ , 0°, 80 min	 (9)	30
	TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	I (97)	29
	DMD (3.0 eq), acetone, 20°, 72 h	 (100)	193
	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 2 min	 (50) +  (50)	172
	TFD, TFP, CH ₂ Cl ₂ , -22°, 2 min	 (56) +  (41)	30
	DMD (2.1 eq), acetone, CH ₂ Cl ₂ , 20°, 24 h	 (>95)	440
	DMD (2.2 eq), acetone, CH ₂ Cl ₂ , 20°, 24 h	 (85)	440

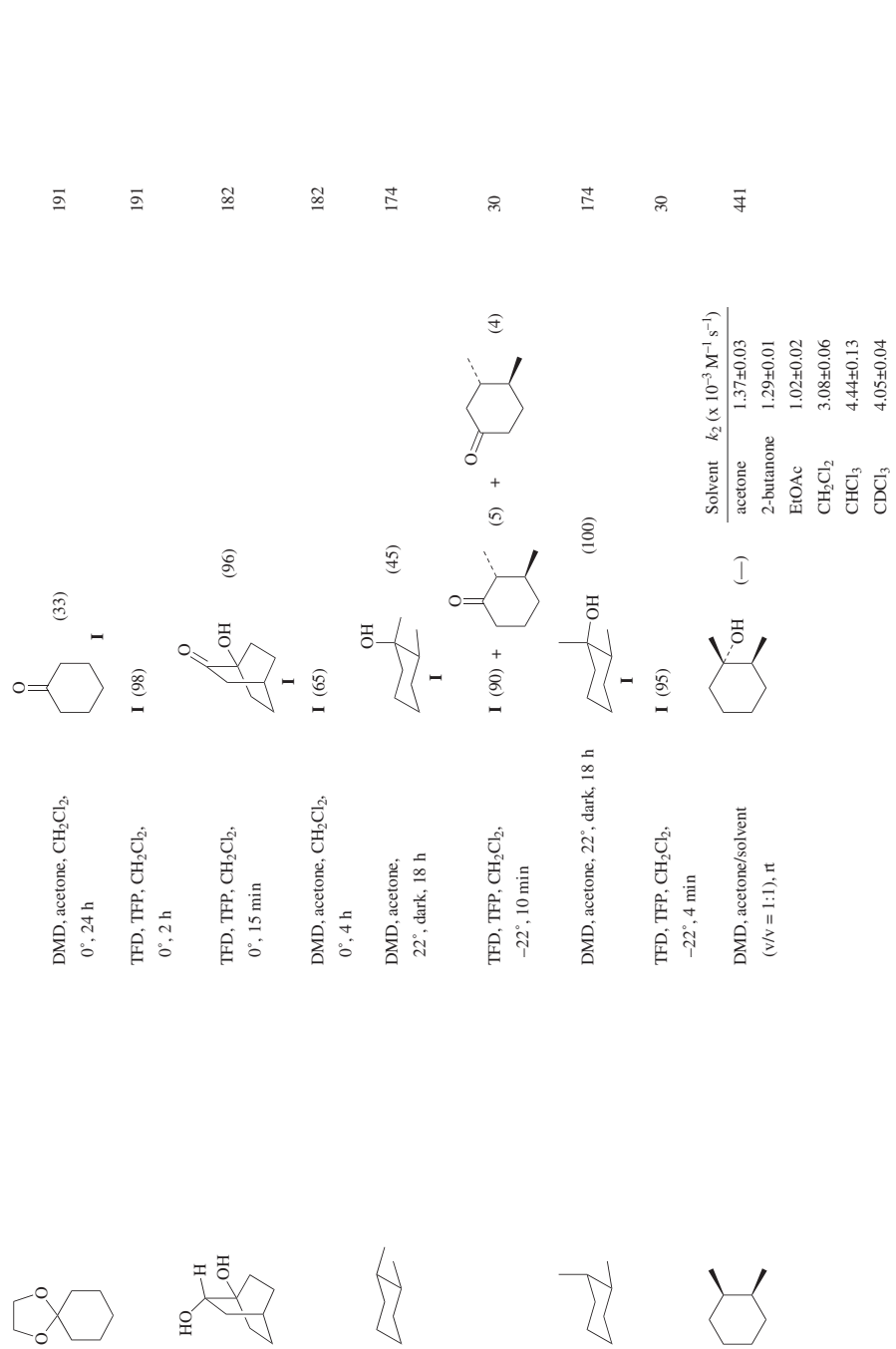
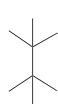
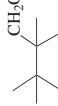
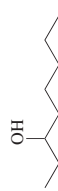


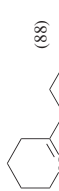
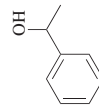
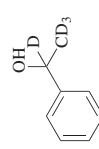
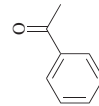


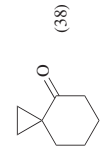
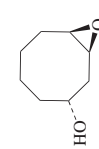
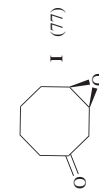



TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	TFP, (CF ₃ CO) ₂ O, CH ₂ Cl ₂ , 0°, 60 h	 (99)	172										
	TFD, TFP, CH ₂ Cl ₂ , -20°, 20 min	 (99)	29										
	1. aq. HBF ₄ , MeCN, (pH 2.0-3.0), 0° 2. TFD, CH ₂ Cl ₂ , rt, 8 h 3. Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 5 h	 (88)	192										
 + 	DMD, acetone, 0°	 +  (—)	<table border="1" data-bbox="795 567 925 735"> <tr> <td>% Conv.</td> <td>k_{H1} / k_D</td> </tr> <tr> <td>6</td> <td>1.00 ± 0.02</td> </tr> <tr> <td>11</td> <td>0.99 ± 0.02</td> </tr> <tr> <td>18</td> <td>1.01 ± 0.02</td> </tr> <tr> <td>32</td> <td>0.98 ± 0.02</td> </tr> </table>	% Conv.	k_{H1} / k_D	6	1.00 ± 0.02	11	0.99 ± 0.02	18	1.01 ± 0.02	32	0.98 ± 0.02
% Conv.	k_{H1} / k_D												
6	1.00 ± 0.02												
11	0.99 ± 0.02												
18	1.01 ± 0.02												
32	0.98 ± 0.02												
	TFD (1.2 eq), TFP, CH ₂ Cl ₂ , 0°, 35 min	 (38)	433										
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 6 h	 (77)	427										
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 10 min	 (86)	427										

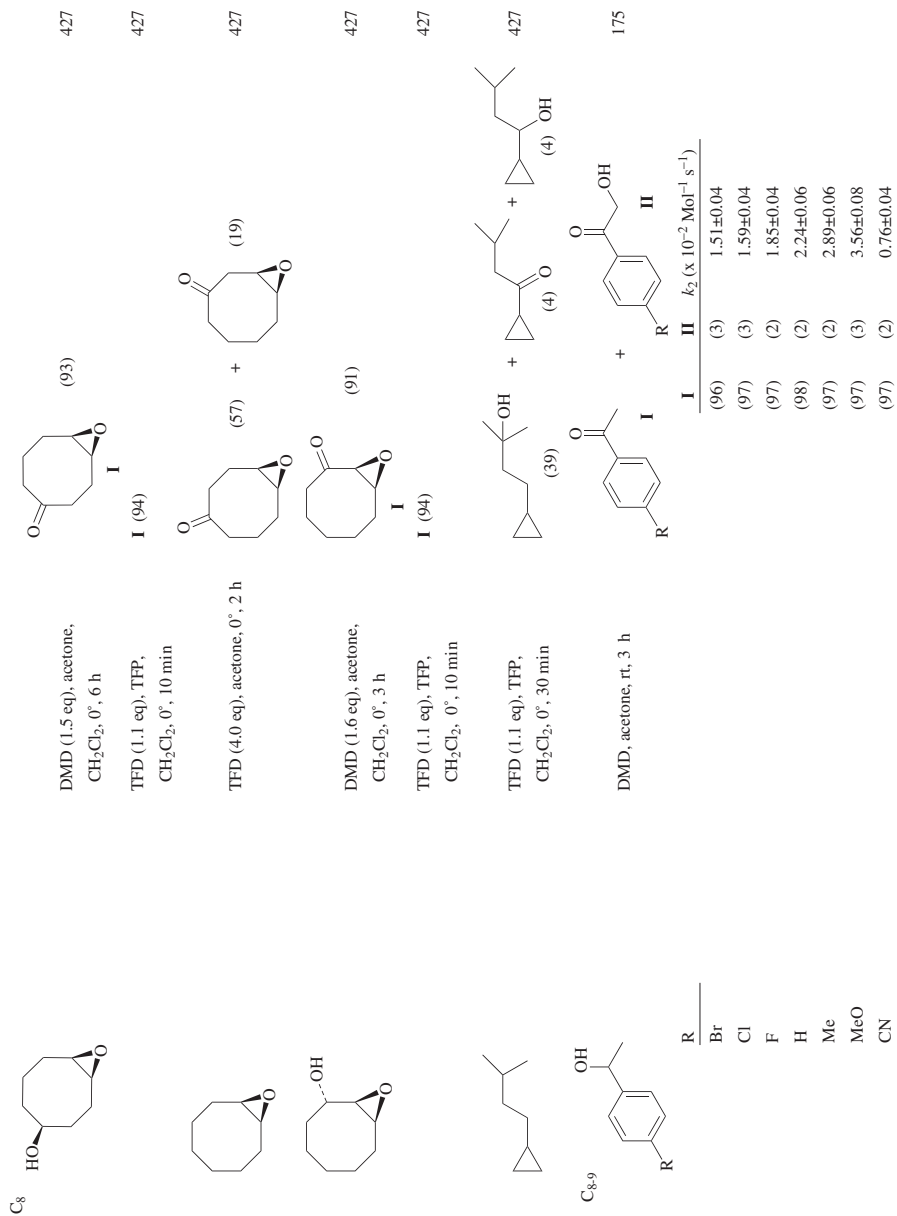

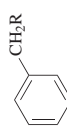
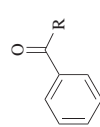


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.		
		R ¹	R ²	R ³			
<p>C₈₋₁₃</p> 	DMD, acetone, rt	Ph	Me	H	(98)	175	
		Ph	Et	H	(92)		
		Ph	<i>n</i> -Pr	H	(92)		
		Ph	<i>i</i> -Pr	H	(90)		
		Ph	<i>t</i> -Bu	H	(90)		
		Ph	Ph	H	(96)		
		Ph	<i>c</i> -C ₃ H ₅	H	(92)		
		Bn	Me	H	(85)		
		Ph	Me	Me	(90)		
		Ph	Et	Me	(81)		
		Ph	<i>n</i> -Pr	Me	(86)		
		Ph	<i>i</i> -Pr	Me	(48)		
		Ph	<i>t</i> -Bu	Me	(24)		
		Ph	Ph	Me	(84)		
		Ph	<i>c</i> -C ₃ H ₅	Me	(88)		
		Bn	Me	Me	(80)		
		Ph	Me	TMS	(95)		
Ph	Me	Ac	(96)				
<p>C₈₋₁₆</p> 	DMD, acetone, dark, rt, 3 d		R				
			Me	(6.9)			
			Et	(22)			
			<i>t</i> -Bu	(2.7)			
			Ph	(3.2)			
			PhCH ₂	(22)			
			Ph(CH ₂) ₂	(28)			
			Ph(CH ₂) ₃	(99)			
			Ph(CH ₂) ₄	(16)			

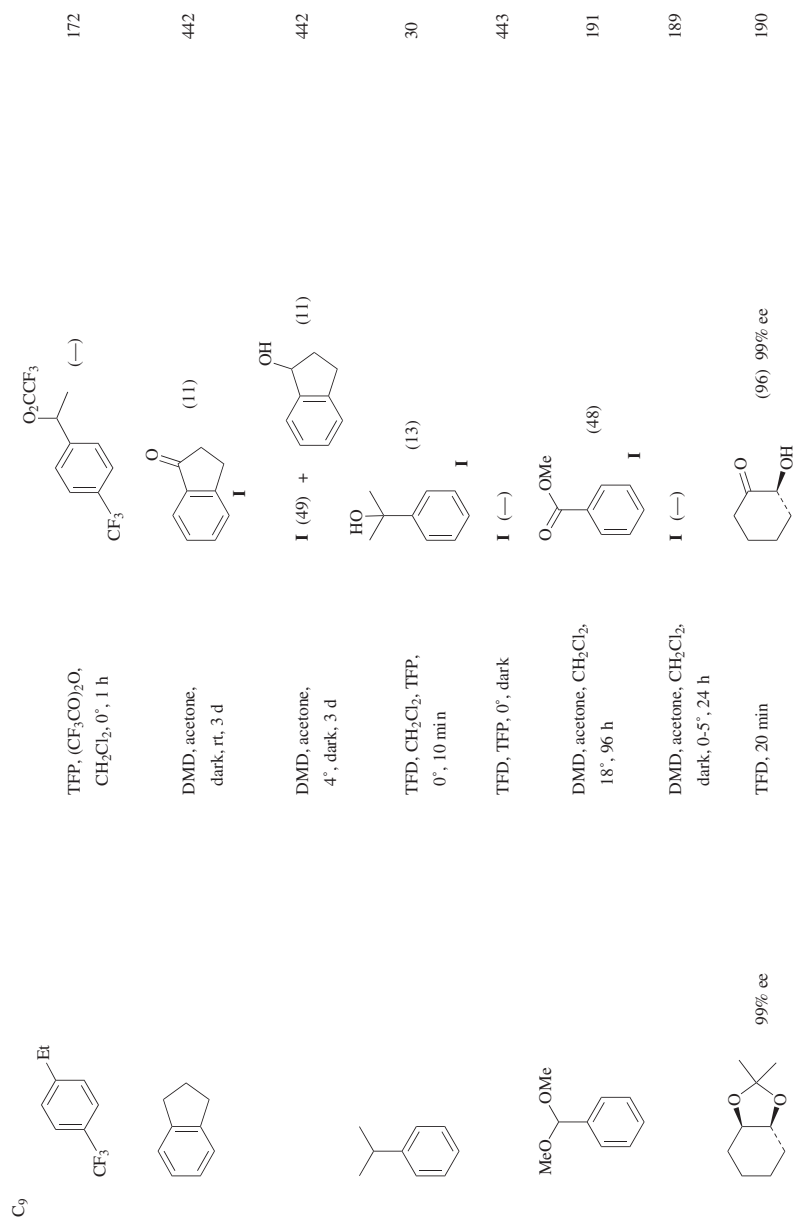
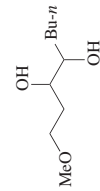
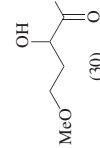
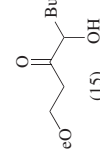
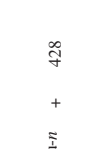
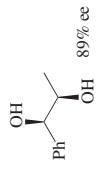
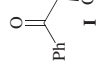
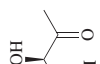
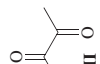

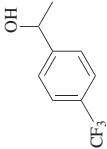
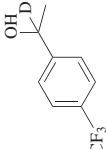
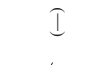
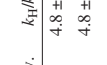
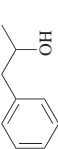
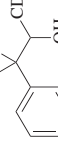


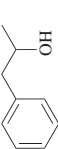
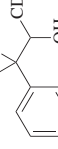




TABLE 5A. C–H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
 <chem>COc1ccc(cc1)C(O)CC</chem>	DMD (6 eq), acetone, rt, 72 h	 <chem>COc1ccc(cc1)C(=O)CC</chem> +  <chem>COc1ccc(cc1)C(O)CC</chem> +  <chem>COc1ccc(cc1)C(=O)CC</chem>	428										
 <chem>CC(O)c1ccccc1</chem> 89% ee	DMD, CH ₂ Cl ₂ , acetone, 0°, 22 h	 <chem>CC(O)c1ccccc1</chem> +  <chem>CC(O)c1ccccc1</chem> +  <chem>CC(O)c1ccccc1</chem> +  <chem>CC(O)c1ccccc1</chem>	184										
 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	TFD, CH ₂ Cl ₂ , TFP, 0°, 40 min	 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	184										
 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	DMD, acetone, 0°	 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	432										
 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	DMD, acetone, 0°	 <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem> +  <chem>CC(O)c1ccc(cc1)C(F)(F)F</chem>	432										
		<table border="1"> <thead> <tr> <th>% Conv.</th> <th><i>k_H</i>/<i>k_D</i></th> </tr> </thead> <tbody> <tr> <td>4</td> <td>0.98 ± 0.2</td> </tr> <tr> <td>8</td> <td>0.98 ± 0.2</td> </tr> <tr> <td>17</td> <td>1.01 ± 0.2</td> </tr> <tr> <td>35</td> <td>0.98 ± 0.2</td> </tr> </tbody> </table>	% Conv.	<i>k_H</i> / <i>k_D</i>	4	0.98 ± 0.2	8	0.98 ± 0.2	17	1.01 ± 0.2	35	0.98 ± 0.2	
% Conv.	<i>k_H</i> / <i>k_D</i>												
4	0.98 ± 0.2												
8	0.98 ± 0.2												
17	1.01 ± 0.2												
35	0.98 ± 0.2												

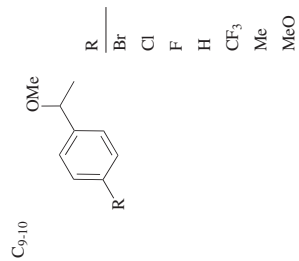
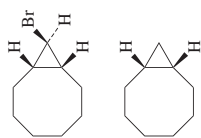
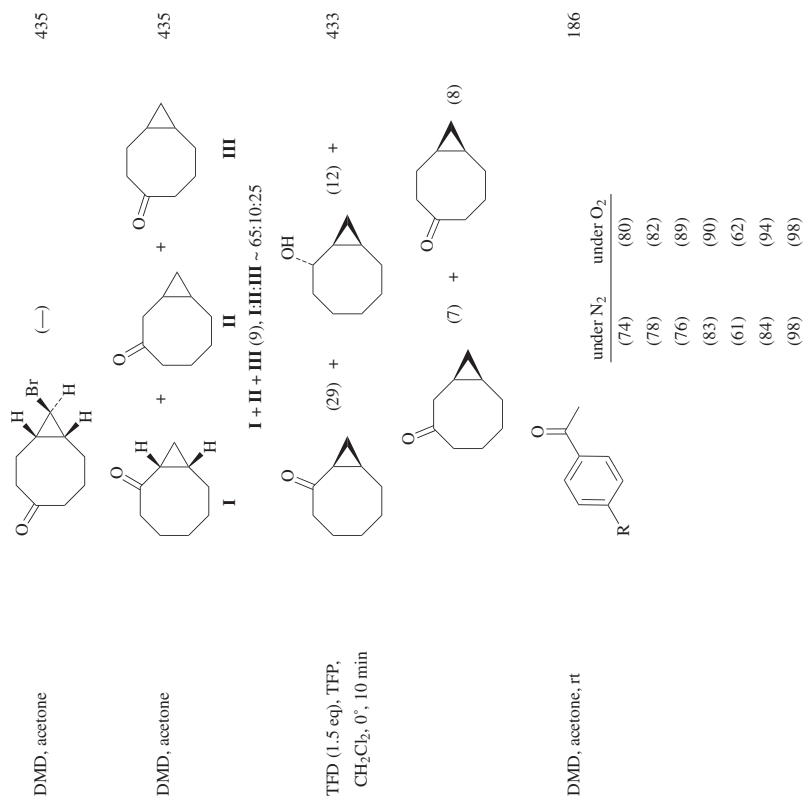
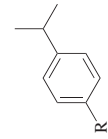
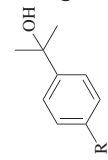
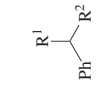
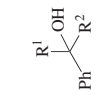
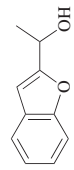
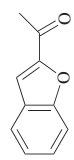
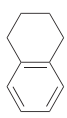
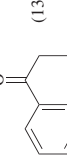
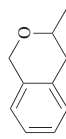
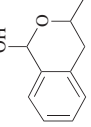



TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, rt	 R k_{rel} I 0.14±0.01 H 1.00±0.00 OH 10.17±0.50 Me 1.91±0.01 MeO 3.58±0.10 Ac 0.047±0.0002 PhO 7.05±0.40	444
	DMD, acetone, dark, rt, 3 d	 R ¹ R ² Me (13.4) Ph (1.0) Ph <i>t</i> -Bu (0.5) Ph Ph (17.5)	442
	DMD, acetone, CH ₂ Cl ₂ , N ₂ , 0°, 12 h	 (38)	89
	DMD, acetone, dark, rt, 3 d	 (13)	442
	DMD (2 eq), acetone, rt, 30 min	 I + II (100), I:II = 70:30	176
	DMD (3 eq), acetone, rt, 60 min	 II (100)	176

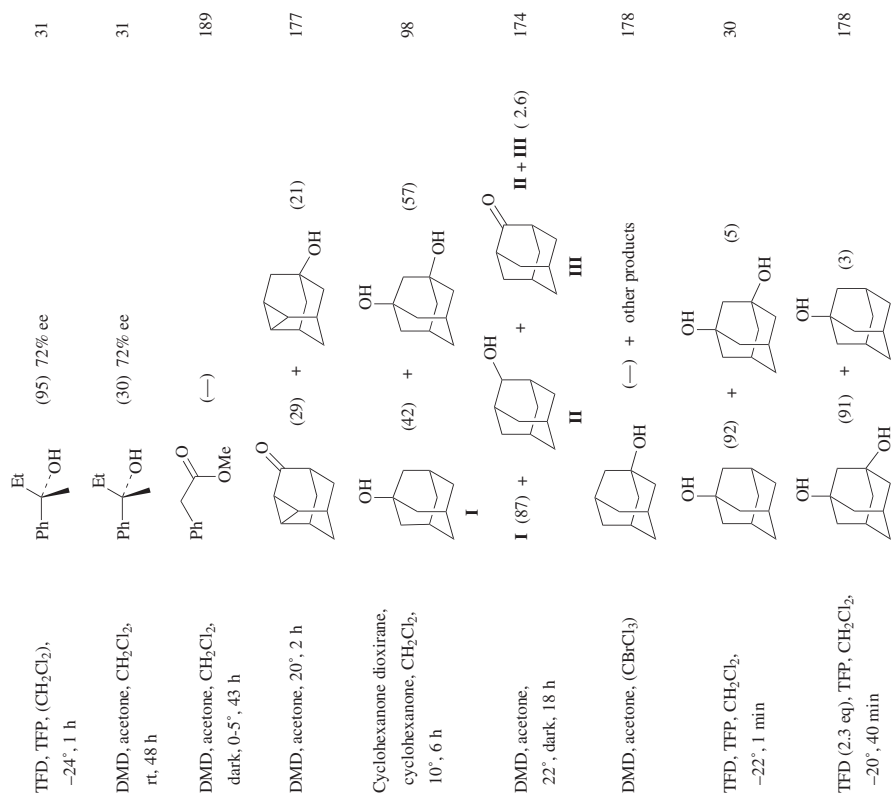

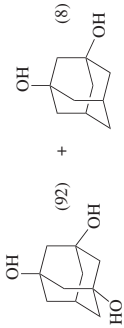

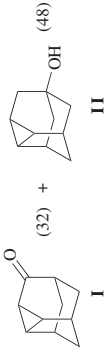

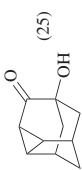
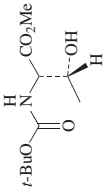
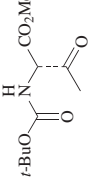

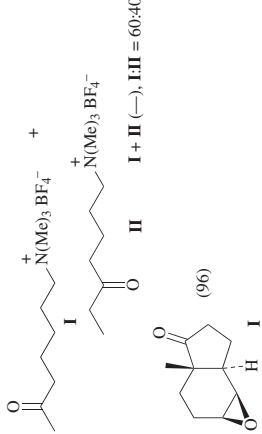
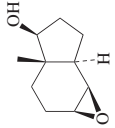
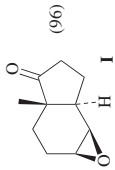
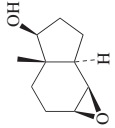



TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀			
	TFD (6 eq), TFP, CH ₂ Cl ₂ , -20°, 2 h		178
	TFD (2 eq), TFP, CH ₂ Cl ₂ , 0°, 1.5 h		433
	TFD (4 eq), TFP, CH ₂ Cl ₂ , 0°, 1.5 h		433
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d		93
	TFD, CH ₂ Cl ₂ , MeCN (pH 2.0-3.0), 0°, 15 h		192
	DMD (1.5 eq), acetone, CH ₂ Cl ₂ , 0°, 2.5 h		427
	TFD (1.1 eq), TFP, CH ₂ Cl ₂ , 0°, 15 min		427

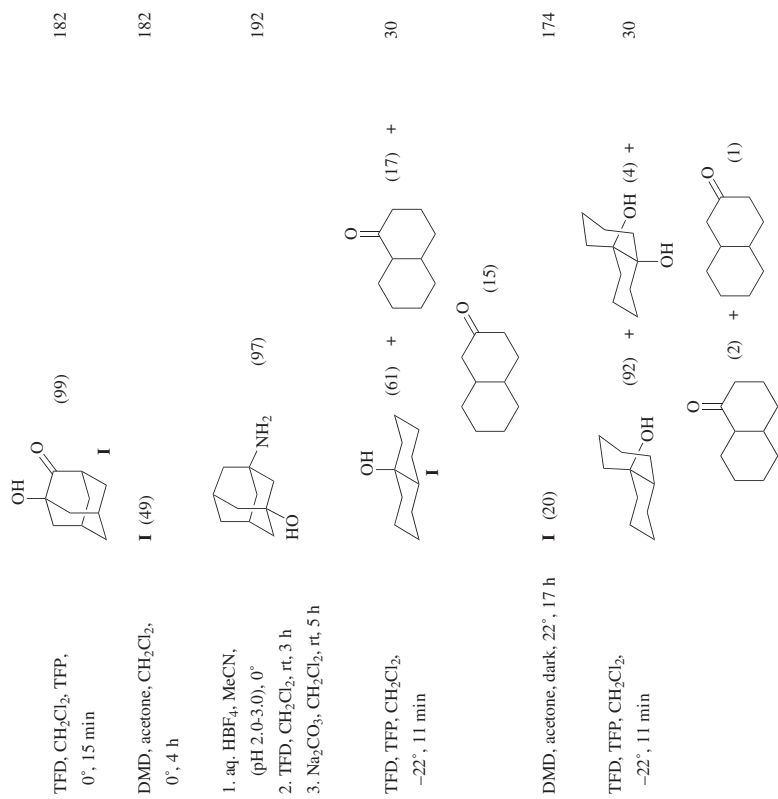

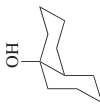
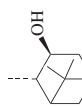
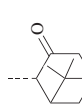
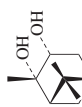
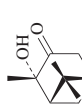
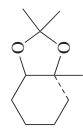
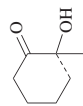

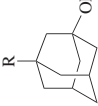


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMD, acetone, 22°, dark, 17 h	 (84)	174
	DMD, acetone, rt, 8 h	 (99)	22
	DMD, acetone/CH ₂ Cl ₂ , 0°, 2 h	 (94)	182
	TFD, 15 min	 (98)	190
	DMD, acetone, rt	 (—)	444
		k_2 (10 ⁻³ M ⁻¹ s ⁻¹)	
R		0.290±0.011	
Br		0.213±0.007	
Cl		2.978±0.099	
H		1.430±0.063	
OH		0.957±0.049	
CO ₂ H		0.406±0.006	
Ac		0.557±0.04	
CO ₂ Et			

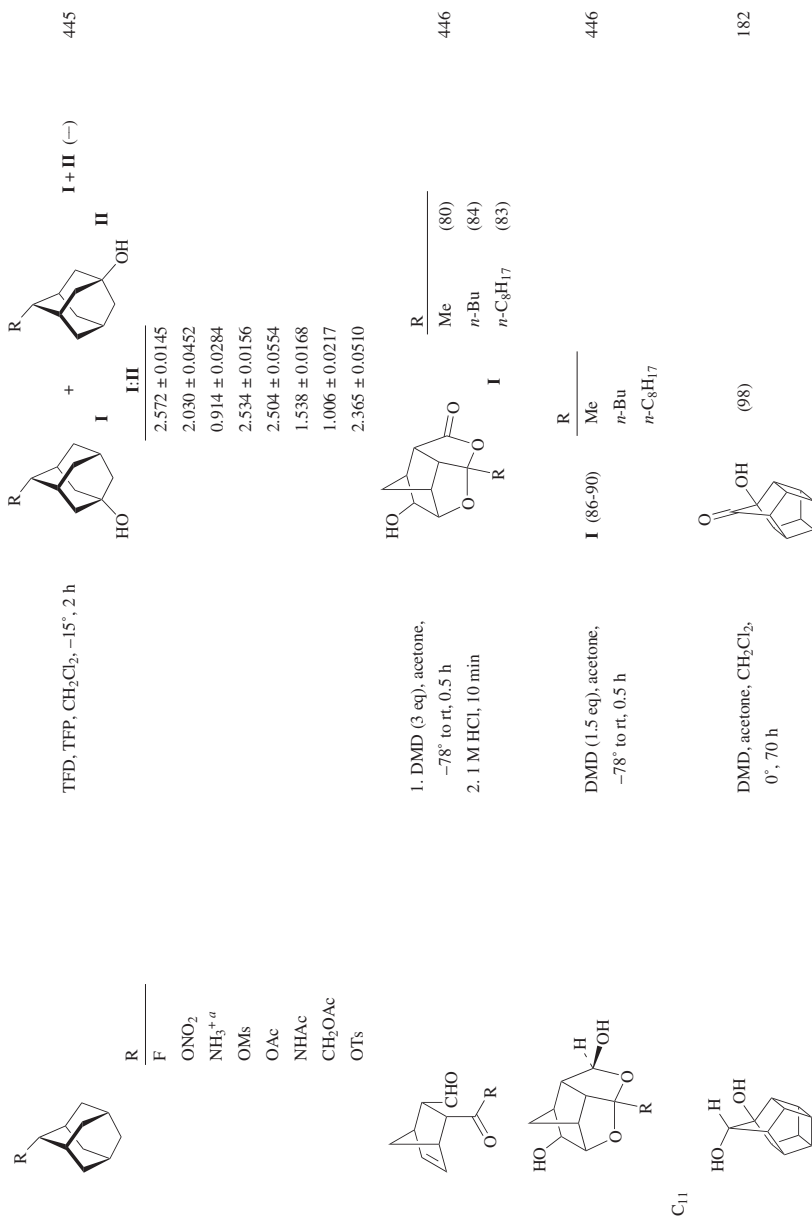
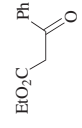
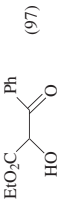

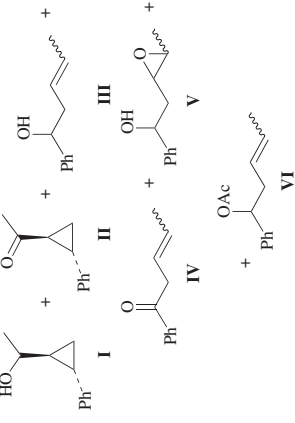
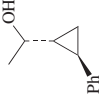
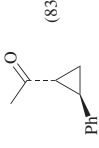
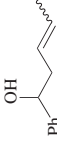



TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
 C_{11}	DMD, acetone, CH_2Cl_2 , MgSO_4	 (97)	206																				
	DMD, acetone, atmos., rt, 2 h	 I + II + III + IV + V + VI	38																				
	DMD	 (83)	38																				
	DMD	 (5) + (25)	38																				
	Atmos.	<table border="1"> <thead> <tr> <th>I</th> <th>II</th> <th>III + IV + V</th> <th>VI</th> </tr> </thead> <tbody> <tr> <td>(0.3)</td> <td>(2.1)</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>(0.3)</td> <td>(1.7)</td> <td>(0.05)</td> <td>(0.14)</td> </tr> <tr> <td>(0.3)</td> <td>(2.2)</td> <td>(0.08)</td> <td>(0.01)</td> </tr> <tr> <td>(0.3)</td> <td>(1.7)</td> <td>(0.05)</td> <td>(0.09)</td> </tr> </tbody> </table>	I	II	III + IV + V	VI	(0.3)	(2.1)	(—)	(—)	(0.3)	(1.7)	(0.05)	(0.14)	(0.3)	(2.2)	(0.08)	(0.01)	(0.3)	(1.7)	(0.05)	(0.09)	
I	II	III + IV + V	VI																				
(0.3)	(2.1)	(—)	(—)																				
(0.3)	(1.7)	(0.05)	(0.14)																				
(0.3)	(2.2)	(0.08)	(0.01)																				
(0.3)	(1.7)	(0.05)	(0.09)																				

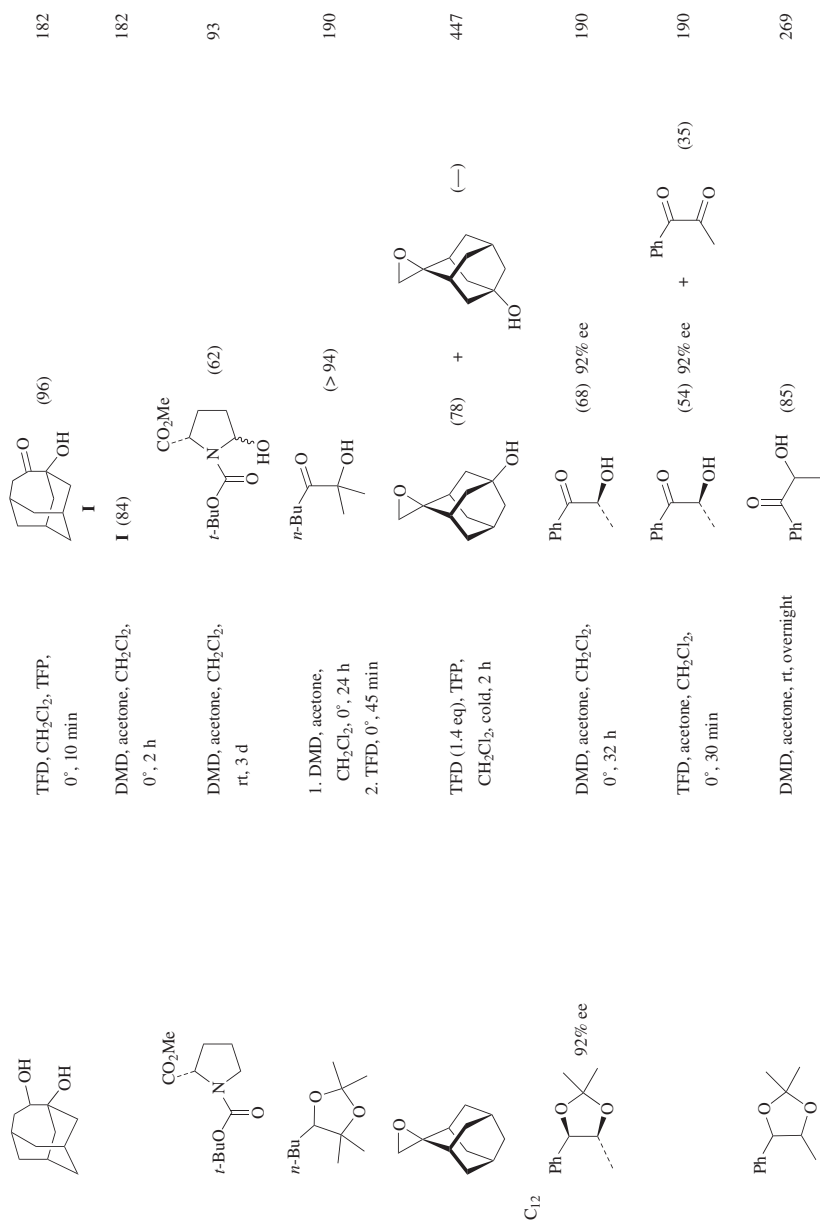
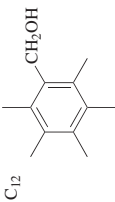
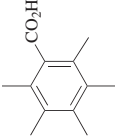
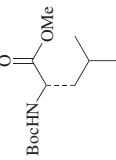
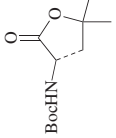
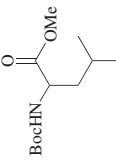
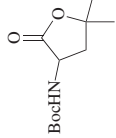
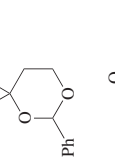
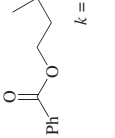
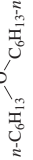





TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₂	DMD, acetone, rt, 3 d	 (-)	287
	DMD, CH ₂ Cl ₂ , acetone, rt, 3 d	 (42)	93, 448
	DMD (6 eq), acetone, CH ₂ Cl ₂ , 20°, 120 h	 (15)	310
	DMD, acetone, 20°	 (-) + $k = 4.52 \pm 0.27 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$	424
 <i>n</i> -C ₆ H ₁₃ -O-C ₆ H ₁₃ - <i>n</i>	TFD, TFP, -20°, 30 min	 <i>n</i> -C ₆ H ₁₃ OH (-) + <i>n</i> -C ₃ H ₁₁ CHO (-) + <i>n</i> -C ₃ H ₁₁ CO ₂ H (-) + <i>n</i> -C ₆ H ₁₃ CO ₂ C ₆ H ₁₃ - <i>n</i> (-) + <i>n</i> -C ₆ H ₁₃ OCF ₃ (-) + <i>n</i> -C ₃ H ₁₁ CO ₂ C ₆ H ₁₃ - <i>n</i> (-) + <i>n</i> -C ₃ H ₁₁ CO ₂ C ₆ H ₁₃ - <i>n</i> (-)	187
	TFD (1.2 eq), TFP, CH ₂ Cl ₂ , 0°, 20 min	 (>90)	433

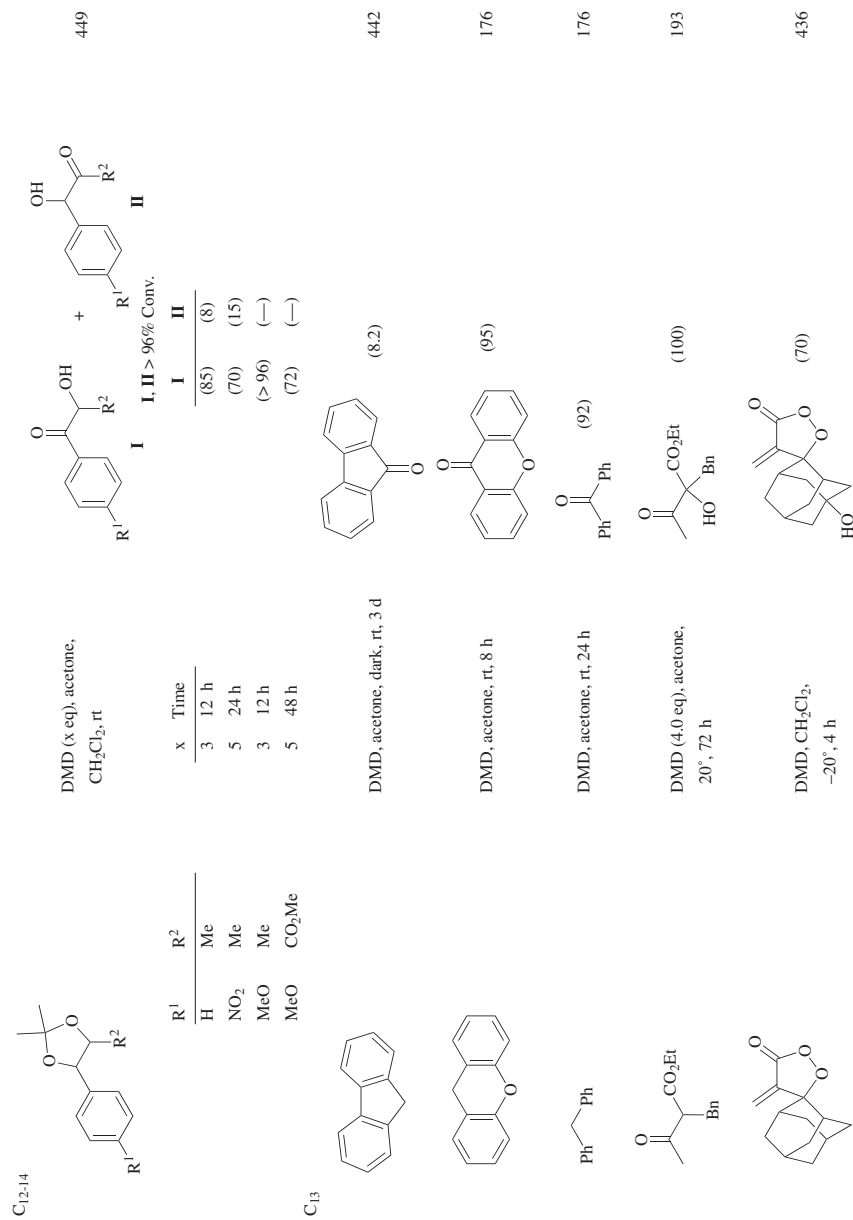

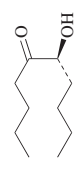
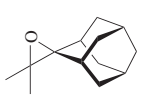
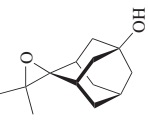
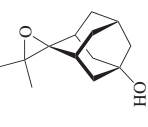
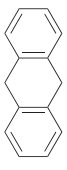
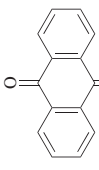
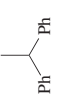
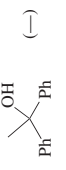
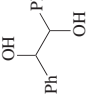
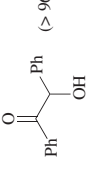
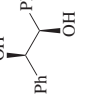
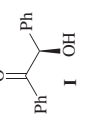
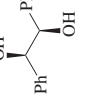
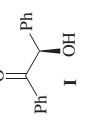


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₃	TFD, 0°, 35 min	 (> 70) 96% ee	190
 C ₁₄	TFD (1.4 eq), TFP, CH ₂ Cl ₂ , cold, 2 h	 (42) +  (28)	447
 C ₁₄	DMD, acetone, rt, 24 h	 (87)	176
	TFD, TFP, dark, 0°	 (—)	443
	DMD, acetone, rt, overnight	 (> 96)	269
	DMD, CH ₂ Cl ₂ , acetone, 0°, 48 h	 (46) > 92% ee I	184
	TFD, CH ₂ Cl ₂ , TFP, 0°, 100 min	 (88) > 92% ee I	184

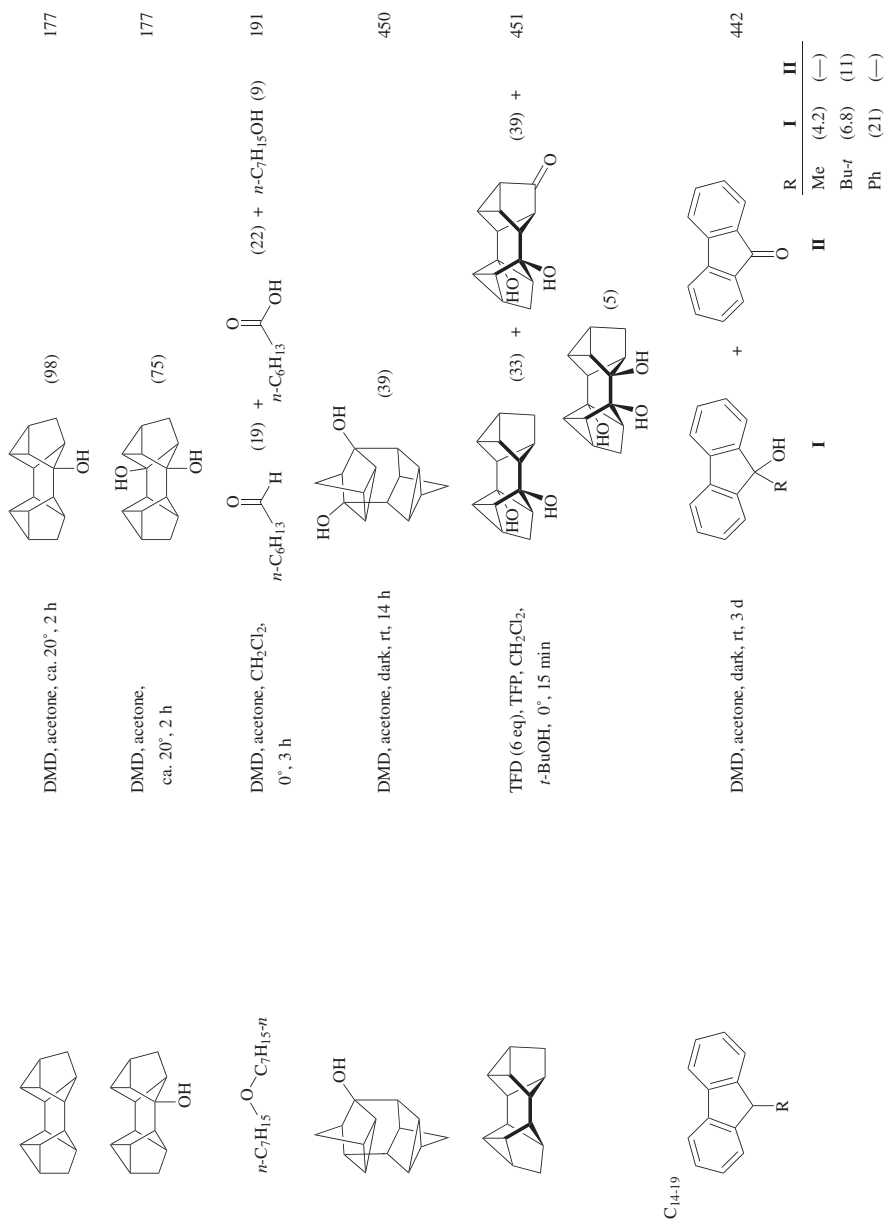
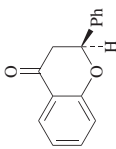
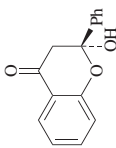
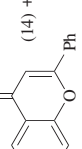
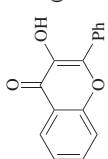
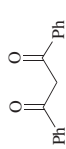
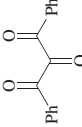
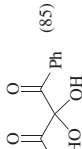
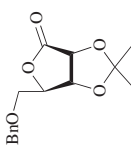
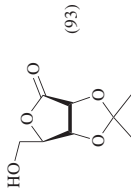
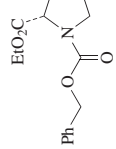
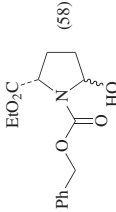
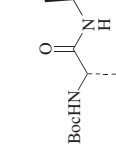
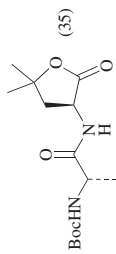


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₅	DMD, acetone, CH ₂ Cl ₂ , rt	 (27) +  (14) +  (10)	452
	DMD (4.0 eq), acetone, N ₂ , 20°, 96 h	 (15) + Ph  (85)	193
	DMD, acetone, CH ₂ Cl ₂ , dark, 48 h	 (93)	188
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d	 (58)	93
	DMD, acetone, CH ₂ Cl ₂ , rt, 3 d	 (35)	93, 448

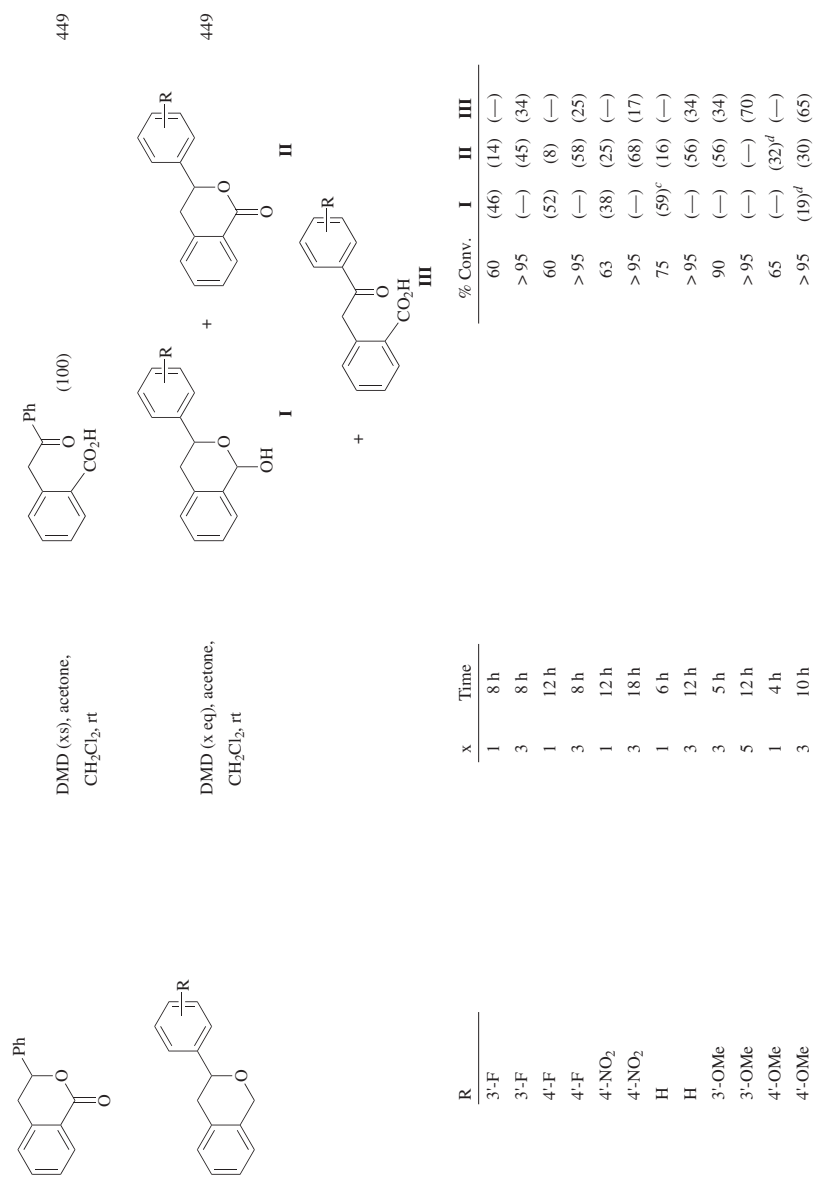
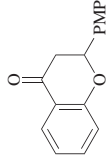
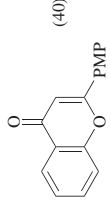

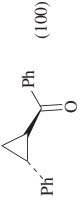
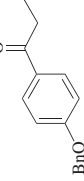
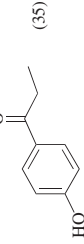
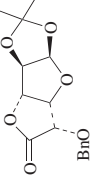
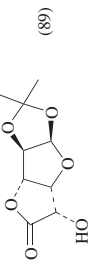
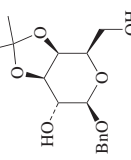
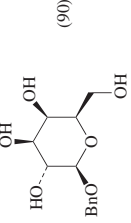
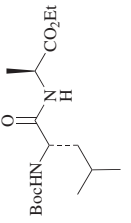
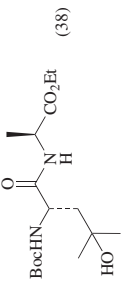
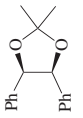



TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{16}	DMD, acetone, rt	 (40)	68
	DMD, acetone, rt, 11 h	 (100)	453
	DMD, CH_2Cl_2 , acetone, dark, 20°, 45 h	 (35)	189
	DMD, acetone, CH_2Cl_2 , dark, rt, 48 h	 (89)	188
	DMD, acetone, CH_2Cl_2 , dark, rt, 48 h	 (90)	188
	DMD, acetone, CH_2Cl_2 , rt, 3 d	 (38)	93, 448
 97% ee	TFD, 50 min	 (92) 97% ee	190

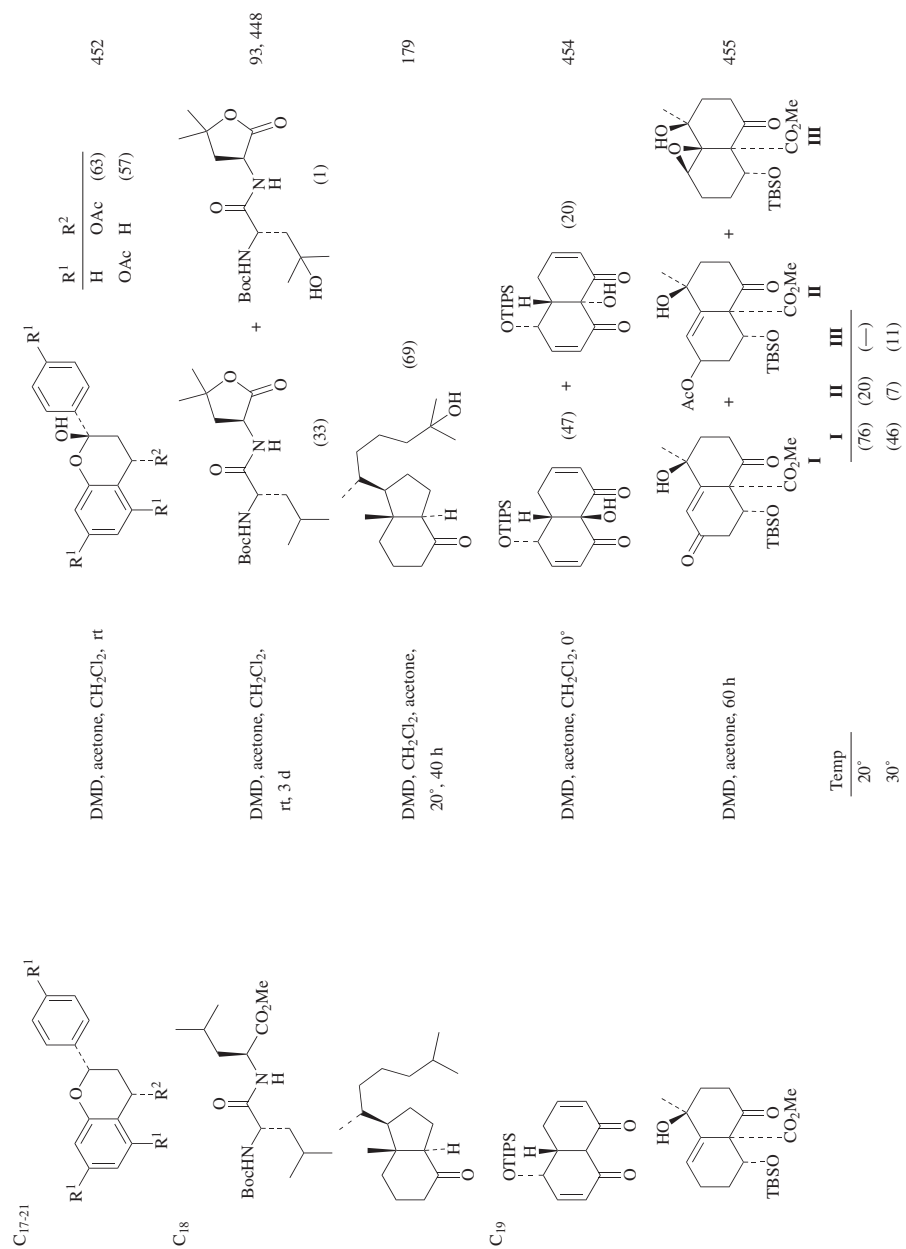
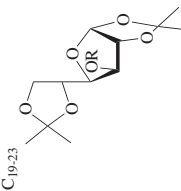
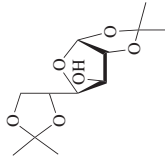
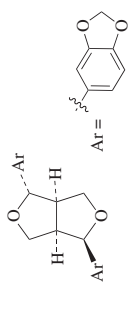
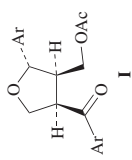
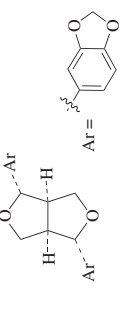
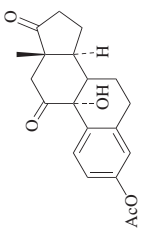
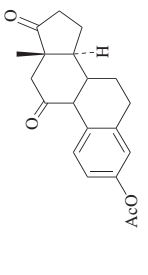
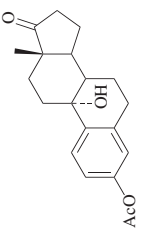
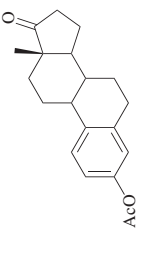
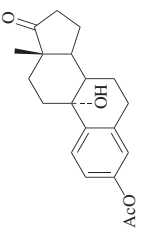


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C _{19,23}	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	 R 4-BrC ₆ H ₄ CH ₂ (85) Bn (87) 4-CNC ₆ H ₄ CH ₂ (87) 2-naphthyl-CH ₂ (90)	188
 C ₂₀	1. DMD, acetone, -20°, 2 d 2. Ac ₂ O, pyridine	 I (80)	456
 I (75)	1. DMD, acetone, -20°, 2 d 2. Ac ₂ O, pyridine	 I (74)	456
 (74)	DMD, acetone, 20°, 22 h	 I (80)	457
 (80)	DMD, acetone, 20°, 22 h	 I (80)	457

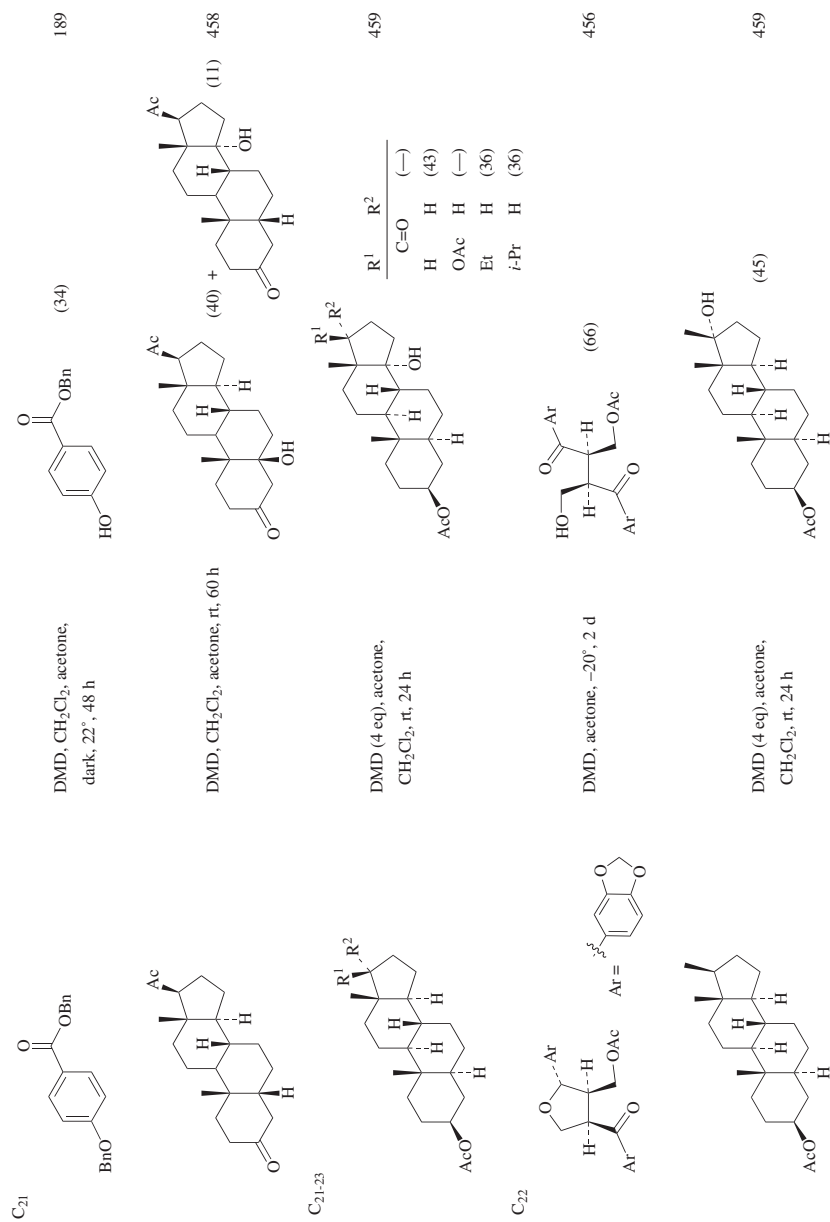
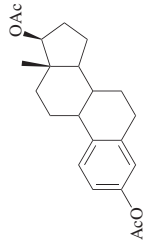
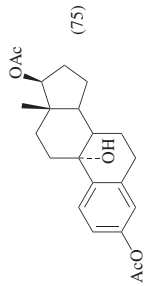
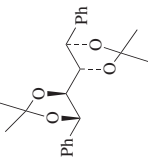
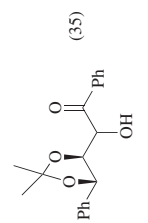
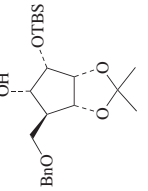
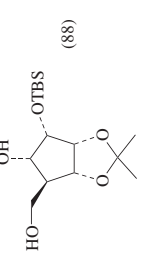
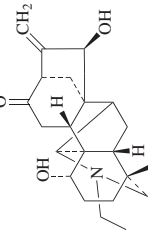
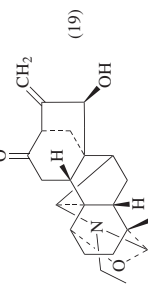


TABLE 5.A. C–H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₂	DMD, acetone	 (75)	460
 (35)	TFD, TFP, CH ₂ Cl ₂ , 0°, 2.5 h	 (88)	190
 (85)	DMD, acetone, CH ₂ Cl ₂ , dark, rt, 48 h	 (85)	188
 (19)	DMD, acetone, <i>t</i> -BuOH, –20°	 (19)	338

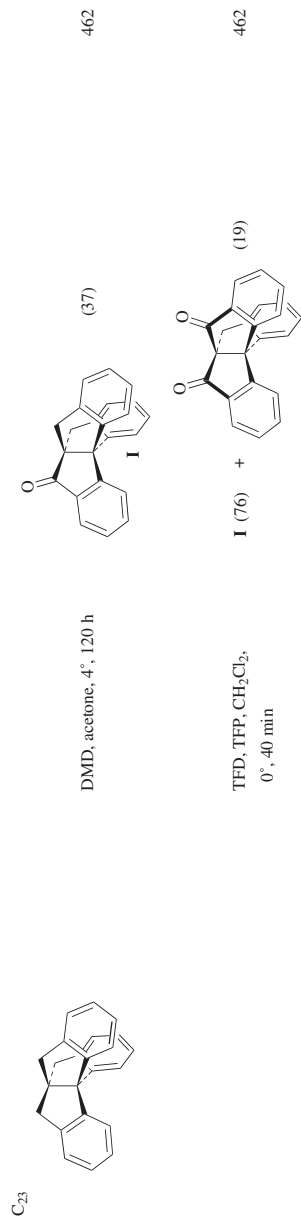
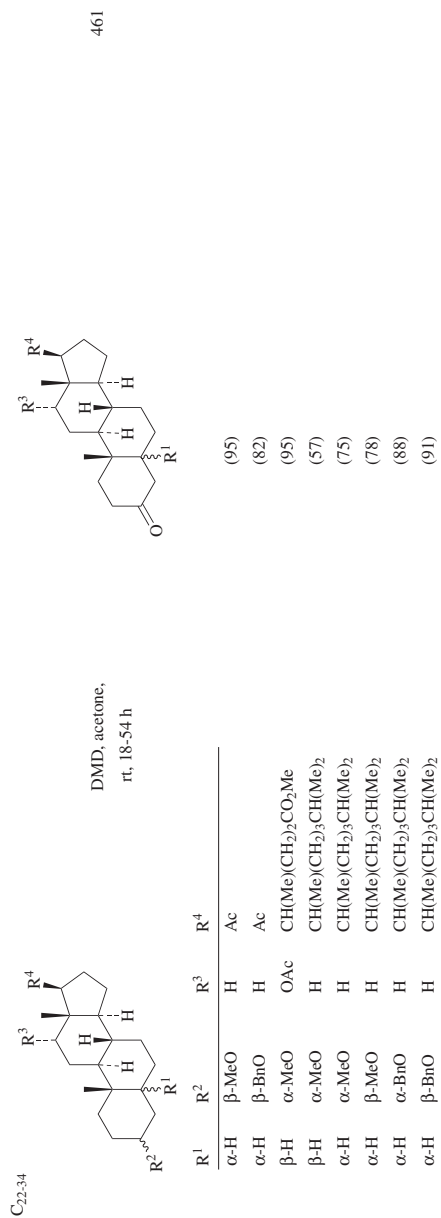
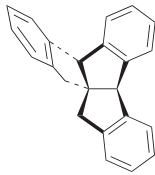
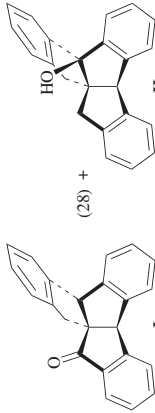
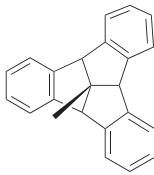
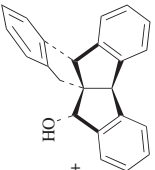
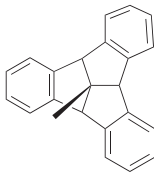
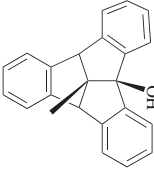
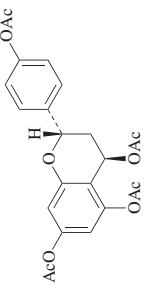
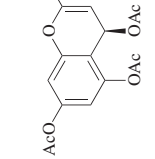
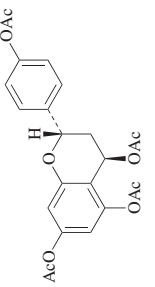
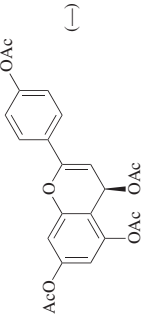
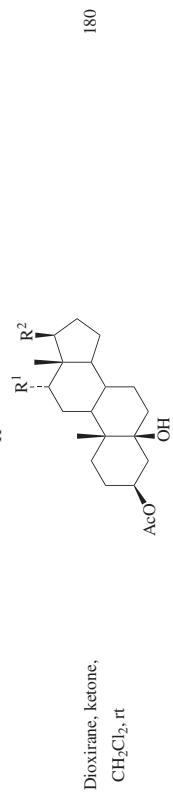
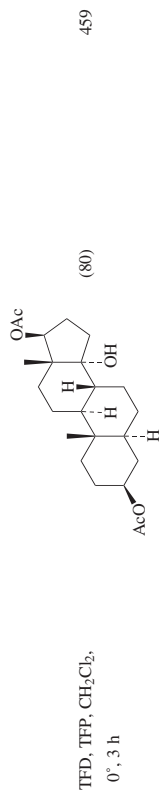
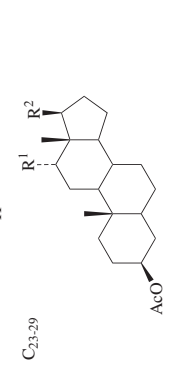
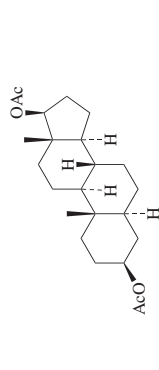
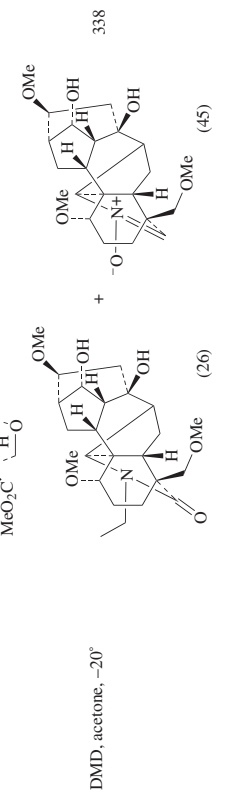
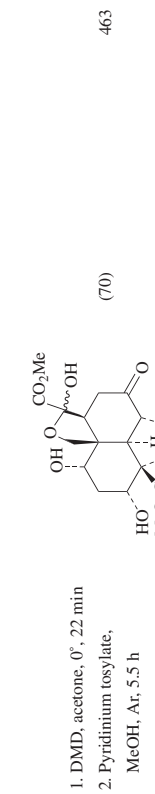


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₂₃	DMD, acetone, 4°, 96 h	 (28) + (16)	462
	TFD, TFP, CH ₂ Cl ₂ , -20°, 2.5 h	 I (16) + II (15) + (8)	462
	DMD, acetone, 20°, 120 h	 I (10)	462
	TFD, TFP, CH ₂ Cl ₂ , -20°, 40 min	 I (35)	462
	DMD, acetone, CH ₂ Cl ₂ , rt	 (11)	452



Dioxirane	Ketone
DMD	(45)
DMD	acetone (26)
TFD	acetone (60)
DMD/TFD	acetone, TFP (—)
DMD	acetone (—)



R ¹	R ²
H	OAc
H	CH(Me)(CH ₂) ₂ CO ₂ Me
H	CH(Me)(CH ₂) ₂ CO ₂ Me
OAc	CH(Me)(CH ₂) ₂ CO ₂ Me
H	CH(Me)(CH ₂) ₃ CH(Me) ₂

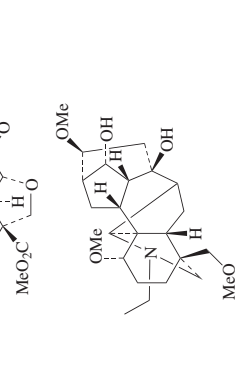
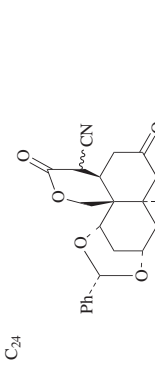
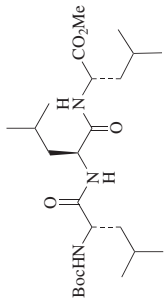
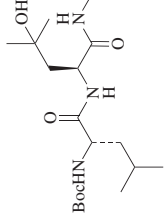
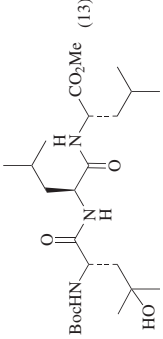
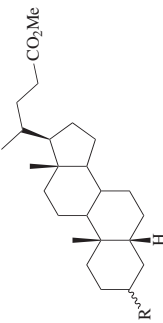
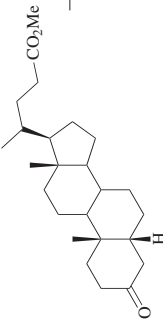
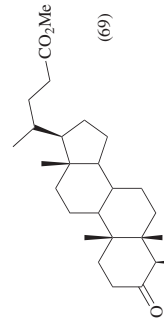
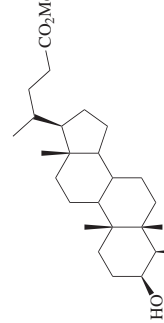
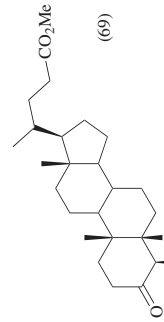


TABLE 5.A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₄</p>	DMD, acetone, rt, 3 d	 (40) +  (13)	93
 <p>C₂₅</p>	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 0.5 h	 (90)  (83)	464
	DMD (2 eq), CHCl ₃ , CH ₂ Cl ₂ , acetone, rt, 1.5 h	 (69)	464

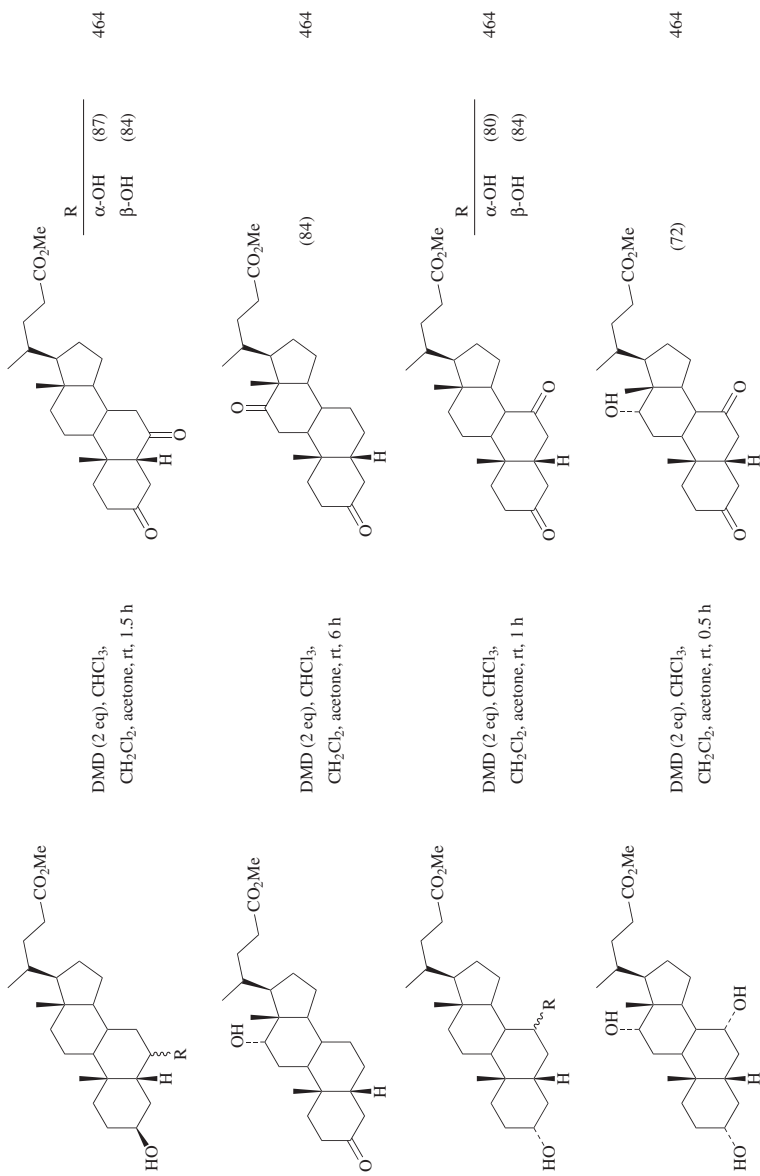


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <chem>CC12CCC3C(C1)C(O)C(O)C3C2CC(=O)OC</chem> (83)	DMD (2 eq), CHCl_3 , CH_2Cl_2 , acetone, rt, 1.5 h	 (83)	464
 <chem>CC12CCC3C(C1)C(O)C(O)C3C2CC(=O)OC</chem> (87)	DMD (2 eq), CHCl_3 , CH_2Cl_2 , acetone, rt, 0.5 h	 (87)	464
 <chem>CC12CCC3C(C1)C(O)C=C3C2CC(=O)OC</chem> (55)	DMD (2 eq), CHCl_3 , CH_2Cl_2 , acetone, rt, 1 h	 (55)	464
 <chem>CC12CCC3C(C1)C(O)C=C3C2CC(=O)OC</chem> I + II (83), III = 3:1	DMD (2 eq), CHCl_3 , CH_2Cl_2 , acetone, rt, 1 h	 I + II (83), III = 3:1	464

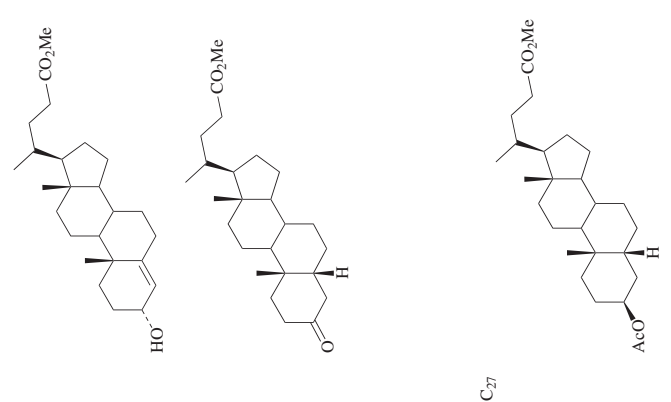
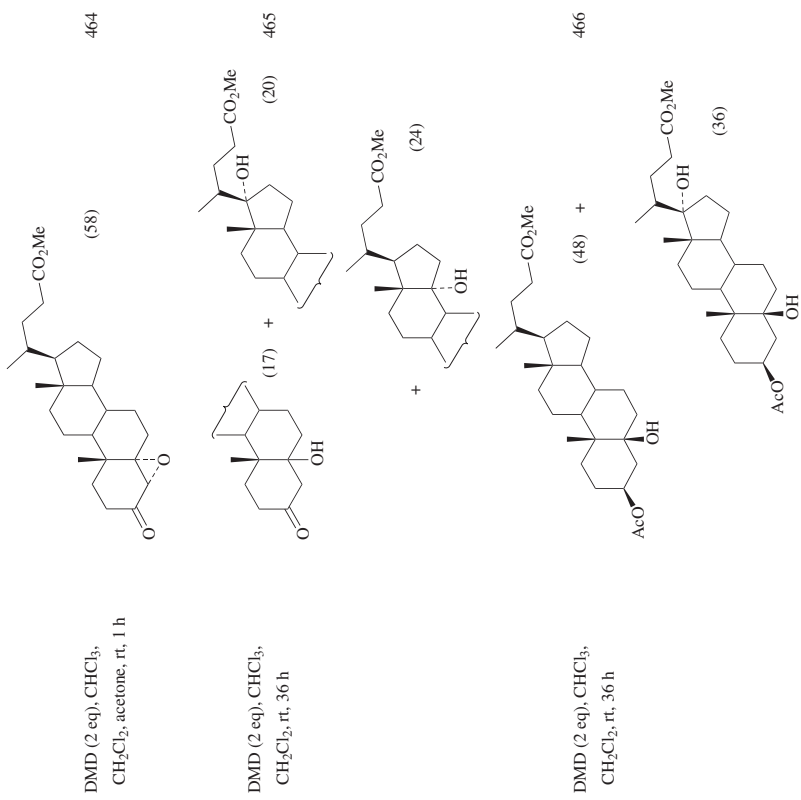
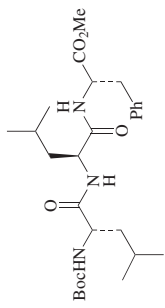
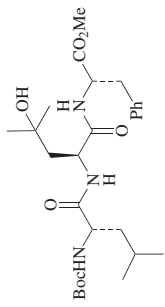
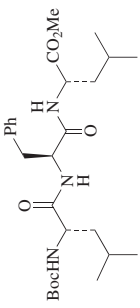
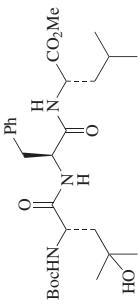
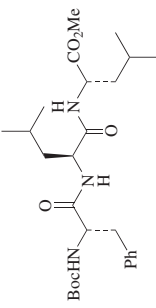
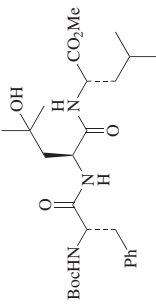
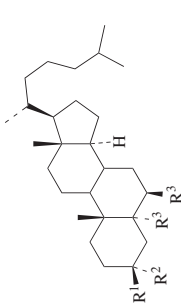
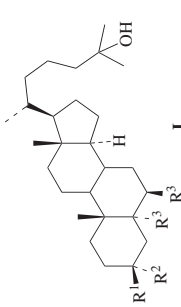

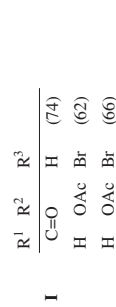


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
 <p>C₂₇</p>	DMD, acetone, rt, 3 d	 <p>(43)</p>	93												
	DMD, acetone, rt, 3 d	 <p>(41)</p>	93												
	DMD, acetone, rt, 3 d	 <p>(38)</p>	93												
 <p>C₂₇₋₂₉</p>	DMD, CH ₂ Cl ₂ , acetone, 20°, 24 h	 <p>I</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> </tr> <tr> <td>C=O</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>Br</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>H</td> </tr> </table>	R ¹	R ²	R ³	C=O	H	H	H	OAc	Br	H	OAc	H	179 (29) (44) (24)
R ¹	R ²	R ³													
C=O	H	H													
H	OAc	Br													
H	OAc	H													
 <p>I</p>	TFD, CH ₂ Cl ₂ , TFP, -40 to 0°, 3 h	 <p>I</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> </tr> <tr> <td>C=O</td> <td>H</td> <td>H</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>Br</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>Br</td> </tr> </table>	R ¹	R ²	R ³	C=O	H	H	H	OAc	Br	H	OAc	Br	179 (74) (62) (66)
R ¹	R ²	R ³													
C=O	H	H													
H	OAc	Br													
H	OAc	Br													

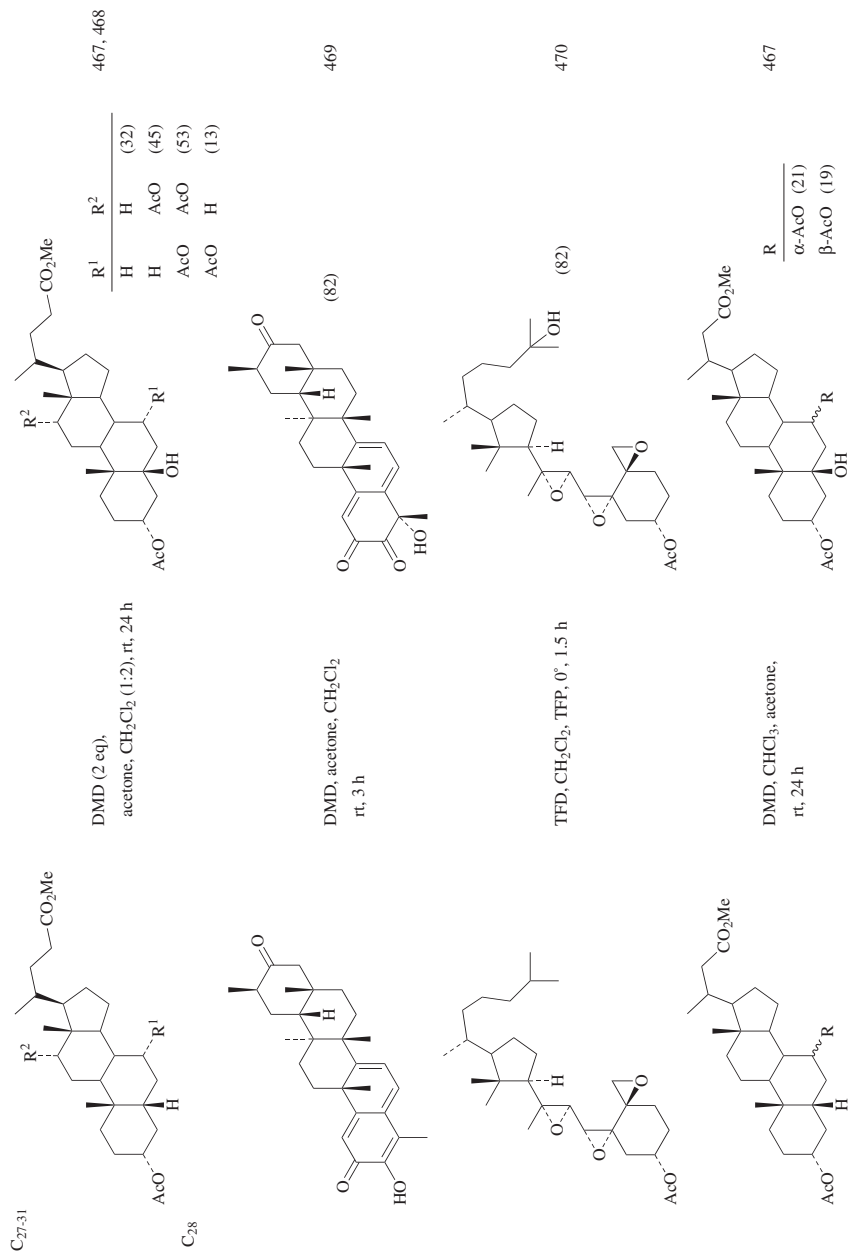


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>(35)</p>	DMD, CH ₂ Cl ₂ , acetone, rt, 48 h	<p>(56)</p>	458
<p>I (44)</p>	TFD, CH ₂ Cl ₂ , TFP, <i>t</i> -BuOH, -10°, 25 min	<p>(54)</p>	462
<p>I (44)</p>	TFD, CH ₂ Cl ₂ , TFP, 0°, 20 min	<p>(53)</p>	443
<p>I (44)</p>	TFD, CH ₂ Cl ₂ , TFP, <i>t</i> -BuOH, -10°, 25 min	<p>(54)</p>	462
<p>I (44)</p>	TFD, CH ₂ Cl ₂ , TFP, 0°, 15 min	<p>(53)</p>	443

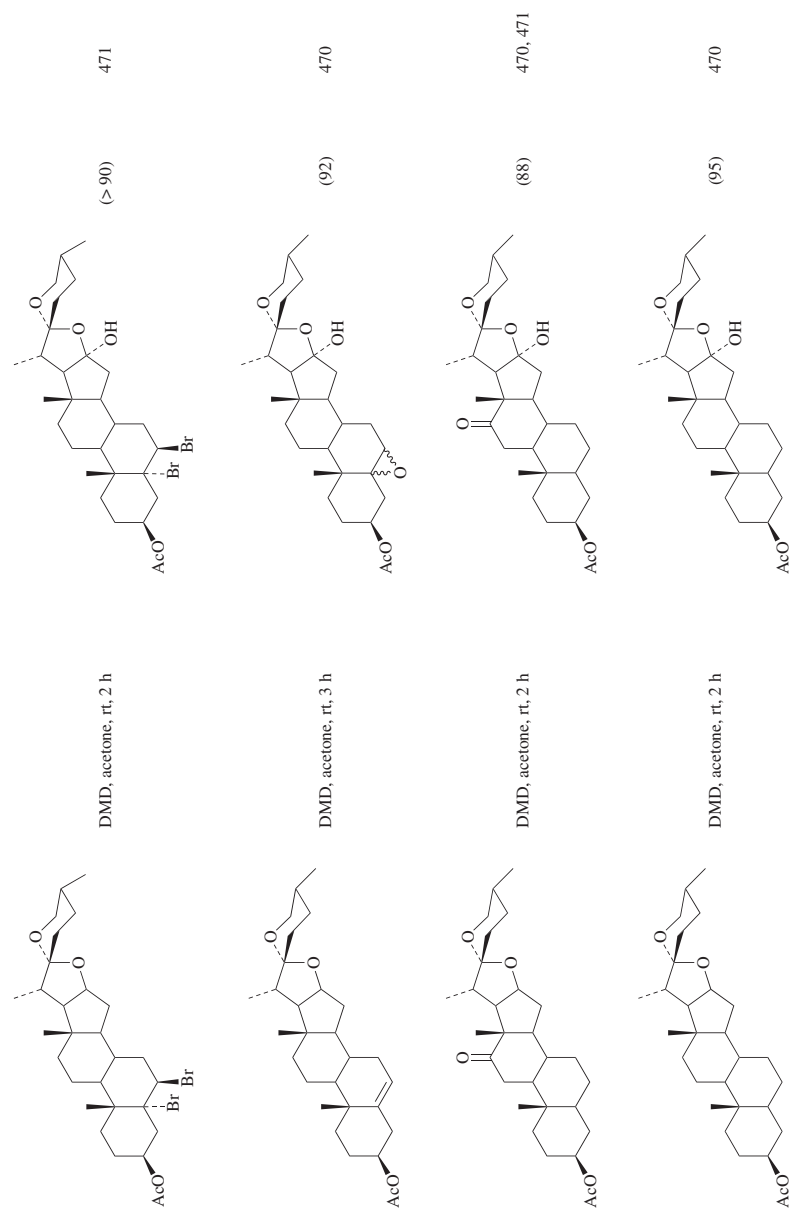
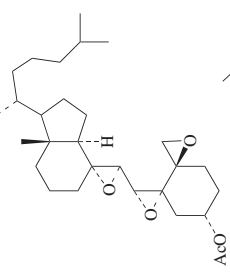
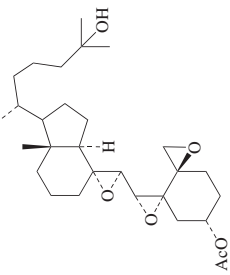
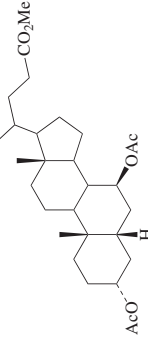
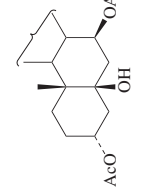
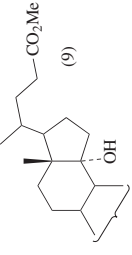
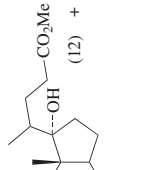
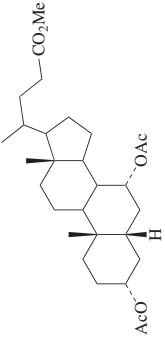
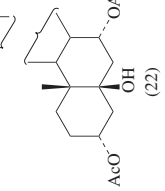
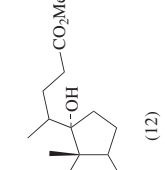
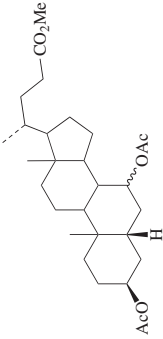
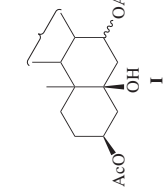
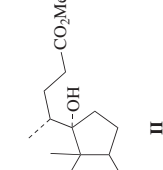
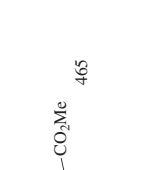
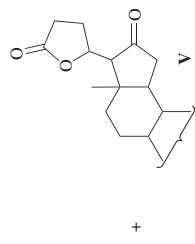
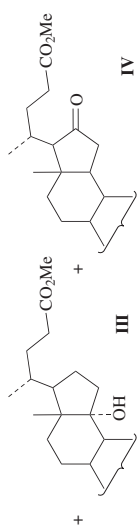
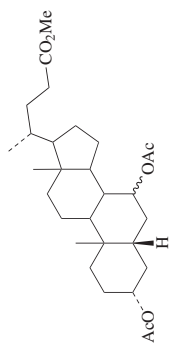


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

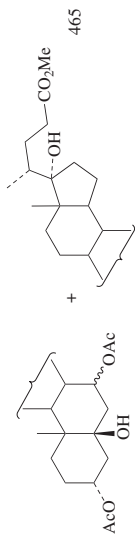
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₉</p>	TFD (3 eq), CH ₂ Cl ₂ , TFP (9:1), 0°, 1.5 h	 <p>(82)</p>	469
	DMD, CHCl ₃ , acetone, rt, 24 h	 <p>(12)</p> <p>+  <p>(9)</p> <p>+  <p>(12)</p> <p>+ 467</p> </p></p>	467
	DMD, CHCl ₃ , acetone, rt, 24 h	 <p>(22)</p> <p>+  <p>(12)</p> <p>+ 467</p> </p>	467
 <p>I</p>	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt	 <p>I</p> <p>+  <p>(12)</p> <p>+  <p>II</p> <p>+ 465</p> </p></p>	465



Time	I + II	III	IV	V
12 h	(trace)	(6)	(6)	(4)
24 h	(4)	(10)	(11)	(6)
36 h	(7)	(15)	(16)	(11)
48 h	(14)	(20)	(22)	(15)

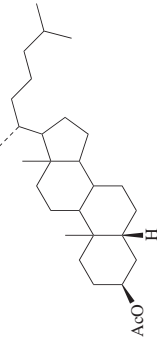
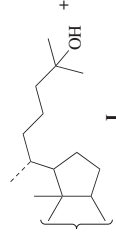
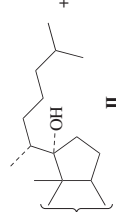
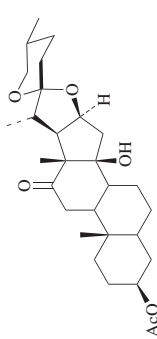
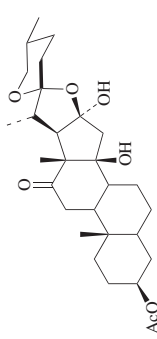
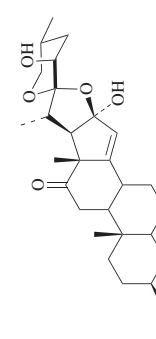


DMD, CH₂Cl₂, CHCl₃, rt

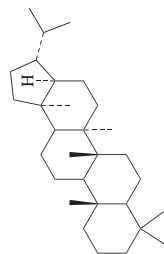


Time	I	II	III
12 h	(21)	(10)	(2)
24 h	(35)	(14)	(7)
36 h	(39)	(18)	(14)
48 h	(45)	(16)	(18)

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

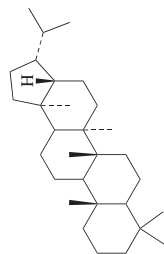
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
 C ₂₉	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt	 I	465																
		 II																	
	DMD (2.2 eq), CH ₂ Cl ₂ , rt, 7 d	 (82)	471																
		 (99)	471																
		<table border="1"> <thead> <tr> <th>Time</th> <th>I</th> <th>II</th> <th>III + IV</th> </tr> </thead> <tbody> <tr> <td>12 h</td> <td>(37)</td> <td>(3)</td> <td>(5)</td> </tr> <tr> <td>24 h</td> <td>(45)</td> <td>(8)</td> <td>(12)</td> </tr> <tr> <td>36 h</td> <td>(39)</td> <td>(19)</td> <td>(29)</td> </tr> </tbody> </table>	Time	I	II	III + IV	12 h	(37)	(3)	(5)	24 h	(45)	(8)	(12)	36 h	(39)	(19)	(29)	
Time	I	II	III + IV																
12 h	(37)	(3)	(5)																
24 h	(45)	(8)	(12)																
36 h	(39)	(19)	(29)																

C₃₀



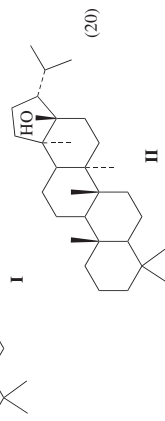
DMD, acetone, CH₂Cl₂,
rt, 21 h

472



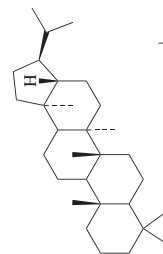
DMD, acetone, CH₂Cl₂,
rt, 12 h

472



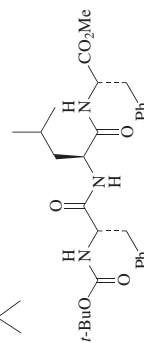
I (50) + **II** (30)

472



DMD, acetone, CH₂Cl₂,
rt, 21 h

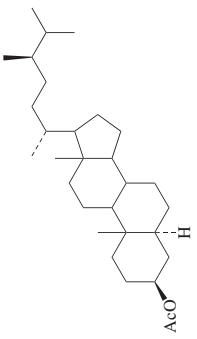
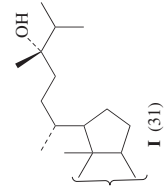
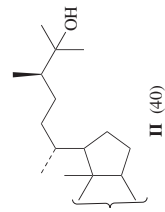
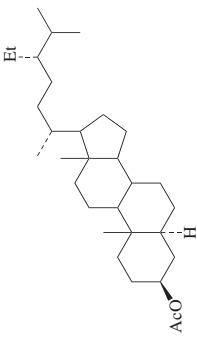
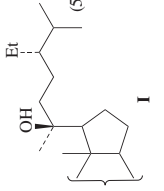
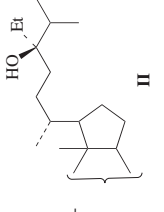
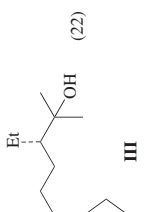
472



DMD, acetone, rt, 3 d

93

TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₃₀</p>	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 24 h	 <p>I (31)</p> <p>+</p>  <p>II (40)</p>	465
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 36 h	I (33) + II (30)	465
 <p>C₃₁</p>	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 12 h	 <p>I</p> <p>(5) +</p>  <p>II (10)</p> <p>+</p>  <p>III (22)</p>	465
	DMD, CH ₂ Cl ₂ , CHCl ₃ , rt, 24 h	(5) + I (8) + II (18) + III (22)	465

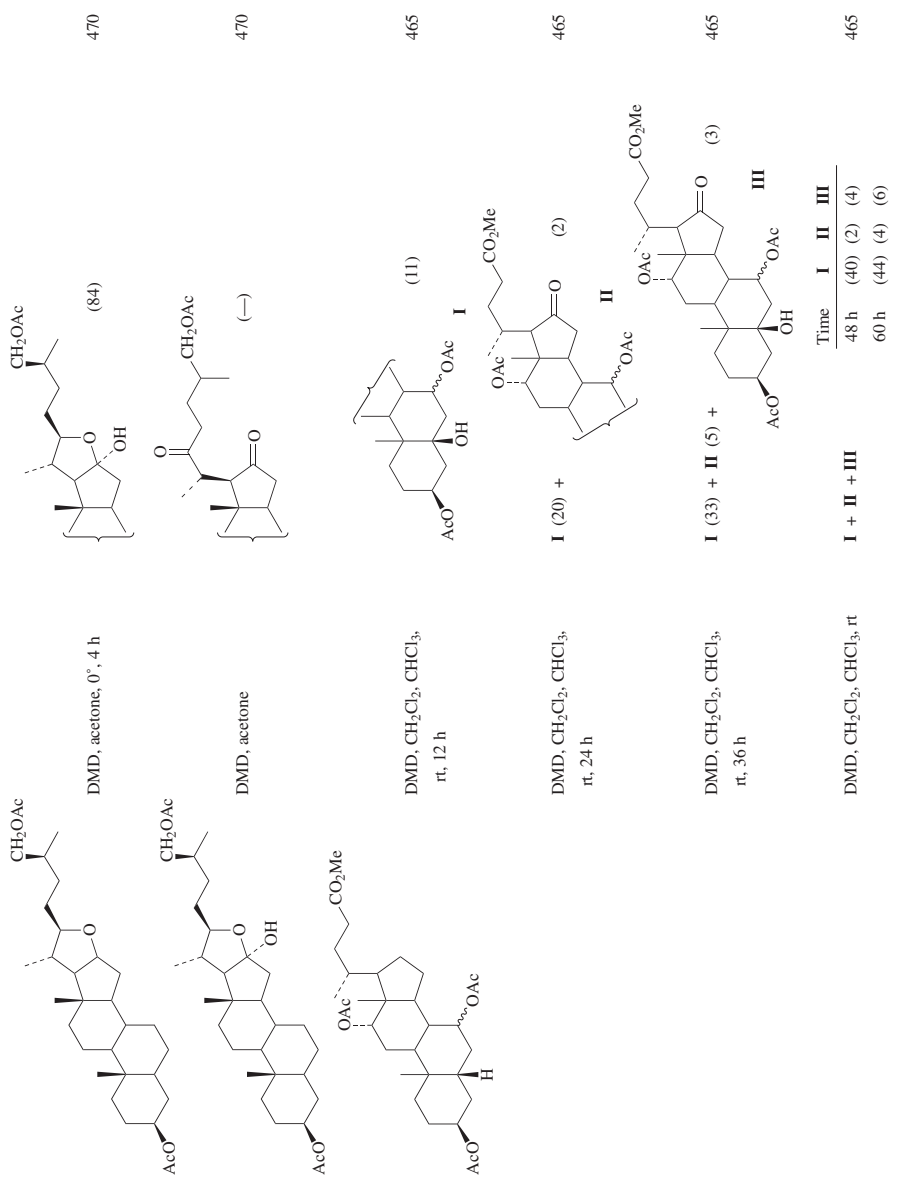
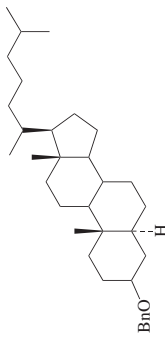
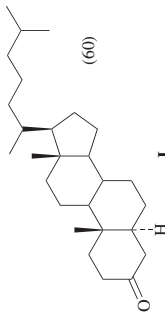
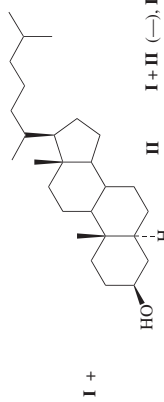
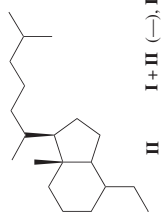
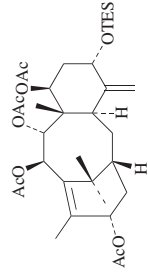
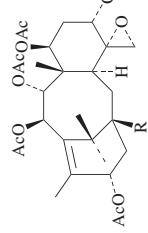
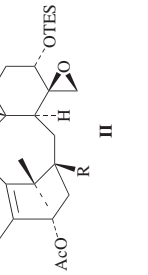


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₃₄	DMD (2 eq), CH ₂ Cl ₂ , acetone, dark, 22°, 15 h	 I (60)	189
	DMD (1 eq), CH ₂ Cl ₂ , acetone, dark, 22°, 14 h	 I +  II I + II (—), I:II = 3:1	189
	DMD (15 eq), acetone, rt, 48 h	 I +  II	473
	DMD (30 eq), acetone, rt, 48 h	I + II R = OH (90)	473
	DMD (25-30 eq), acetone, rt, 48 h	I R = OH (—)	473
	DMD (25-30 eq), acetone, rt, 48 h	II R = OH (—)	473

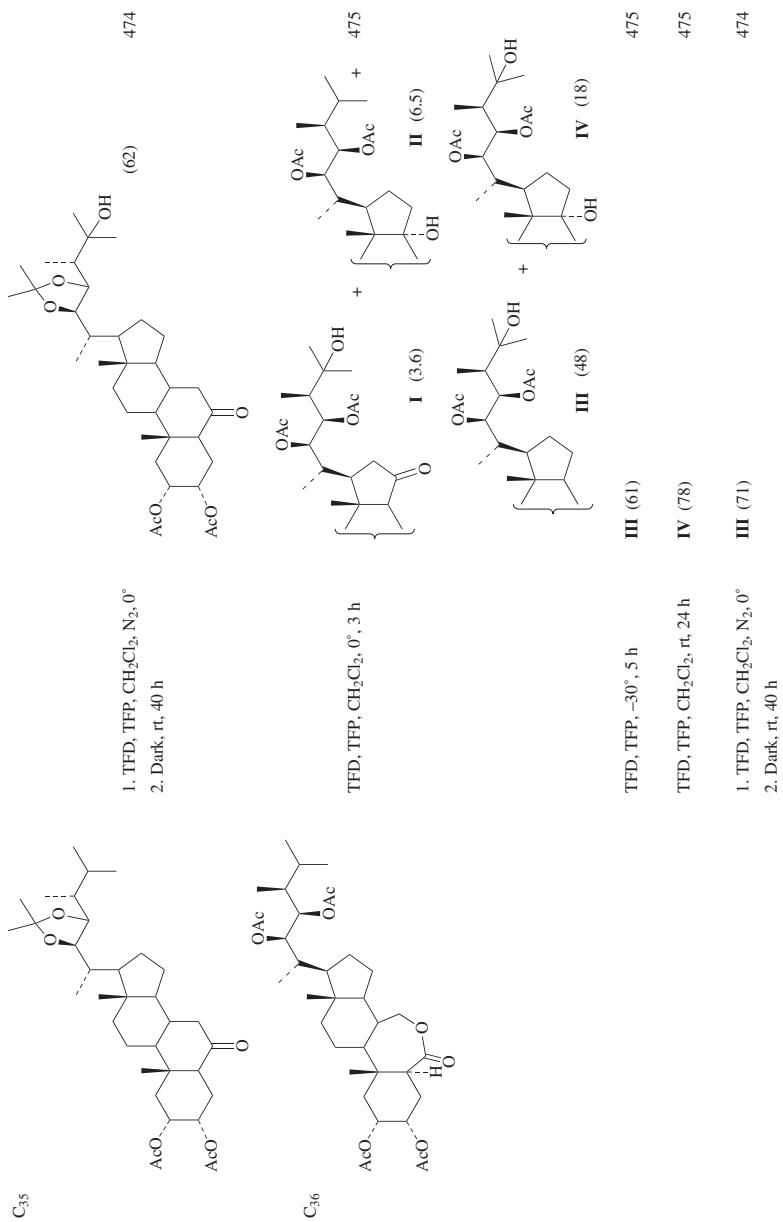
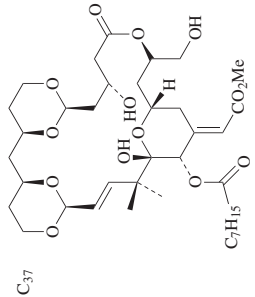
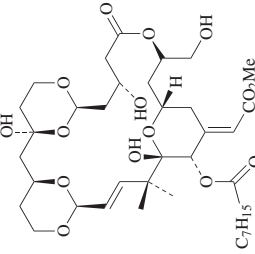
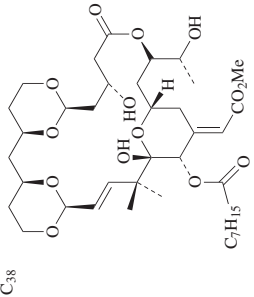
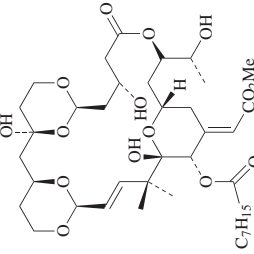
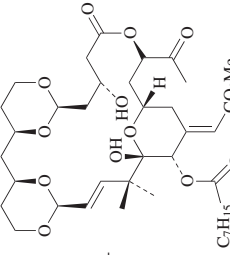
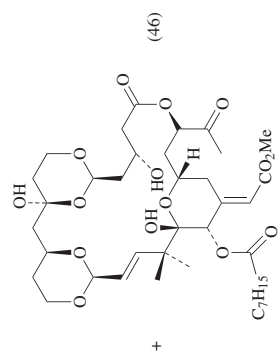


TABLE 5A. C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₃₇</p> 	DMD, acetone, rt, 48 h	<p>(70)</p> 	476
<p>C₃₈</p> 	DMD, acetone, rt, 48 h	<p>(9)</p> 	476
		<p>(26)</p> 	



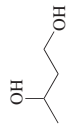
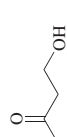
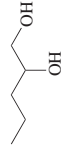
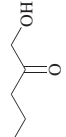
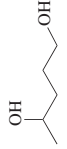

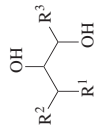
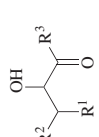
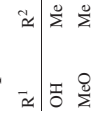
^a Reaction was run using solutions purged with pure, oxygen-free nitrogen gas.

^b The reaction was carried out under N₂.

^c The diastereomer ratio was 10:1.

^d The value includes 14% of an oxo aldehyde byproduct.

TABLE 5B. REGIOSELECTIVE C–H OXIDATION BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																										
C ₄ 	DMD, acetone, rt, 18–22 h	 (90)	183																																																																																										
C ₅ 	DMD, acetone, rt, 18–22 h	 (100)	183																																																																																										
	DMD, acetone, rt, 18–22 h	 (60)	183																																																																																										
C ₅₋₁₁ 	DMD, acetone, CH ₂ Cl ₂ , rt	 +  I II	428																																																																																										
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>OH</td> <td>Me</td> <td>Me</td> <td>—</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>MeO</td> <td>Me</td> <td>Me</td> <td>—</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>AcO</td> <td>Me</td> <td>Me</td> <td>24 h</td> <td>(90)</td> <td>(—)</td> </tr> <tr> <td>Br</td> <td><i>n</i>-Pr</td> <td>Me</td> <td>48 h</td> <td>(95)</td> <td>(—)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td><i>n</i>-Pr</td> <td>48 h</td> <td>(76)</td> <td>(14)</td> </tr> <tr> <td>AcO</td> <td>H</td> <td><i>n</i>-Pr</td> <td>36 h</td> <td>(83)</td> <td>(—)</td> </tr> <tr> <td>N₃</td> <td>H</td> <td><i>n</i>-C₅H₁₁</td> <td>48 h</td> <td>(95)</td> <td>(—)</td> </tr> <tr> <td>OH</td> <td>H</td> <td><i>n</i>-C₅H₁₁</td> <td>24 h</td> <td>(59)</td> <td>(—)</td> </tr> <tr> <td>CH₂OH</td> <td>H</td> <td><i>n</i>-Bu</td> <td>48 h</td> <td>(38)</td> <td>(38)</td> </tr> <tr> <td>OH</td> <td>Me</td> <td><i>n</i>-C₅H₁₁</td> <td>—</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>CH₂OMe</td> <td>H</td> <td><i>n</i>-Bu</td> <td>24 h</td> <td>(30)</td> <td>(15)</td> </tr> <tr> <td>CH₂OAc</td> <td>H</td> <td><i>n</i>-Bu</td> <td>24 h</td> <td>(60)</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>Me</td> <td><i>n</i>-C₅H₁₁</td> <td>36 h</td> <td>(60)</td> <td>(—)</td> </tr> <tr> <td>OAc</td> <td>Me</td> <td><i>n</i>-C₅H₁₁</td> <td>48 h</td> <td>(70)</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	I	II	OH	Me	Me	—	(—)	(—)	MeO	Me	Me	—	(—)	(—)	AcO	Me	Me	24 h	(90)	(—)	Br	<i>n</i> -Pr	Me	48 h	(95)	(—)	MeO	H	<i>n</i> -Pr	48 h	(76)	(14)	AcO	H	<i>n</i> -Pr	36 h	(83)	(—)	N ₃	H	<i>n</i> -C ₅ H ₁₁	48 h	(95)	(—)	OH	H	<i>n</i> -C ₅ H ₁₁	24 h	(59)	(—)	CH ₂ OH	H	<i>n</i> -Bu	48 h	(38)	(38)	OH	Me	<i>n</i> -C ₅ H ₁₁	—	(—)	(—)	CH ₂ OMe	H	<i>n</i> -Bu	24 h	(30)	(15)	CH ₂ OAc	H	<i>n</i> -Bu	24 h	(60)	(—)	OMe	Me	<i>n</i> -C ₅ H ₁₁	36 h	(60)	(—)	OAc	Me	<i>n</i> -C ₅ H ₁₁	48 h	(70)	(—)	
R ¹	R ²	R ³	Time	I	II																																																																																								
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AcO	Me	Me	24 h	(90)	(—)																																																																																								
Br	<i>n</i> -Pr	Me	48 h	(95)	(—)																																																																																								
MeO	H	<i>n</i> -Pr	48 h	(76)	(14)																																																																																								
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CH ₂ OH	H	<i>n</i> -Bu	48 h	(38)	(38)																																																																																								
OH	Me	<i>n</i> -C ₅ H ₁₁	—	(—)	(—)																																																																																								
CH ₂ OMe	H	<i>n</i> -Bu	24 h	(30)	(15)																																																																																								
CH ₂ OAc	H	<i>n</i> -Bu	24 h	(60)	(—)																																																																																								
OMe	Me	<i>n</i> -C ₅ H ₁₁	36 h	(60)	(—)																																																																																								
OAc	Me	<i>n</i> -C ₅ H ₁₁	48 h	(70)	(—)																																																																																								

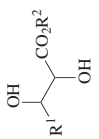
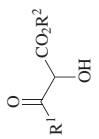
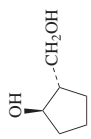
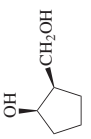
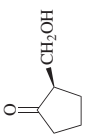
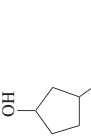
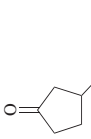
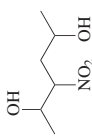
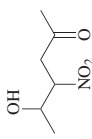
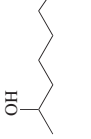
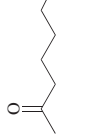
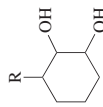
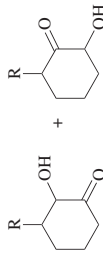
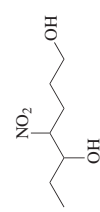
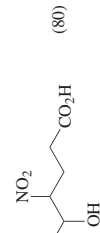
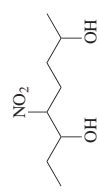
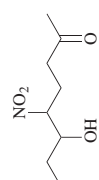
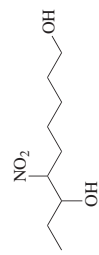
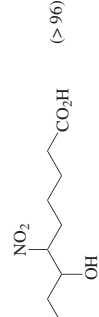
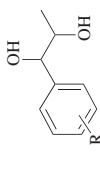
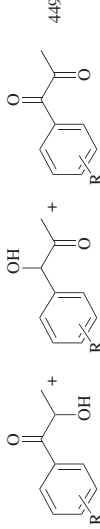
C ₅₋₁₃		DMD, acetone, CH ₂ Cl ₂ , rt, 72 h		R ¹ R ² Me Me (80) <i>c</i> -C ₆ H ₁₁ Et (57) <i>n</i> -C ₉ H ₁₉ Me (< 10)	449
C ₆		DMD, acetone, rt, 18-22 h	mixture		183
		DMD, acetone, rt, 18-22 h		(85)	183
		DMD, acetone, rt, 18-22 h		(82)	434
		DMD, acetone, rt, overnight		(-)	434
		DMD, acetone, rt, 18-22 h		(60)	183

TABLE 5B. REGIOSELECTIVE C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																												
 C ₆₋₈	DMD, acetone, rt	 <table border="1" data-bbox="560 724 787 1018"> <thead> <tr> <th>R</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>24 h</td> <td>(> 95)</td> <td>(—)</td> </tr> <tr> <td>N₃</td> <td>48 h</td> <td>(> 95)</td> <td>(—)</td> </tr> <tr> <td>OH</td> <td>48 h</td> <td>(> 95)</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>48 h</td> <td>(74)</td> <td>(16)</td> </tr> <tr> <td>AcO (syn, syn)</td> <td>24 h</td> <td>(> 95)</td> <td>(—)</td> </tr> <tr> <td>AcO (anti, syn)</td> <td>24 h</td> <td>(> 95)</td> <td>(—)</td> </tr> </tbody> </table>	R	Time	I	II	Br	24 h	(> 95)	(—)	N ₃	48 h	(> 95)	(—)	OH	48 h	(> 95)	(—)	OMe	48 h	(74)	(16)	AcO (syn, syn)	24 h	(> 95)	(—)	AcO (anti, syn)	24 h	(> 95)	(—)	428
R	Time	I	II																												
Br	24 h	(> 95)	(—)																												
N ₃	48 h	(> 95)	(—)																												
OH	48 h	(> 95)	(—)																												
OMe	48 h	(74)	(16)																												
AcO (syn, syn)	24 h	(> 95)	(—)																												
AcO (anti, syn)	24 h	(> 95)	(—)																												
 C ₇	DMD, acetone, rt, overnight	 (80)	434																												
 C ₈	DMD, acetone, rt, overnight	 (55)	434																												
 C ₉	DMD, acetone, rt, overnight	 (> 96)	434																												
 C ₉₋₁₀	DMD, CH ₂ Cl ₂ , acetone, rt		449																												

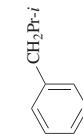
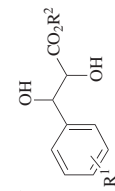
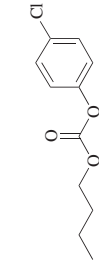
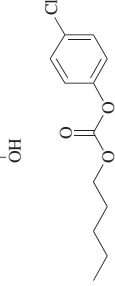
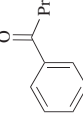
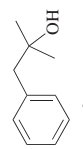
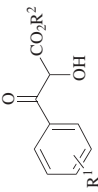
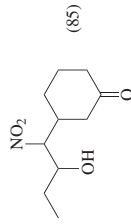
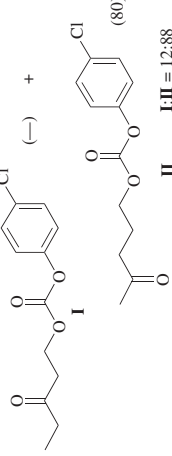

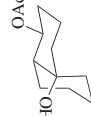
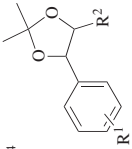
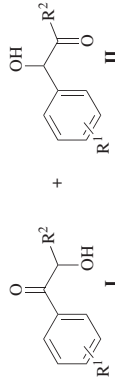
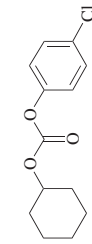
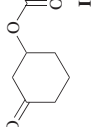
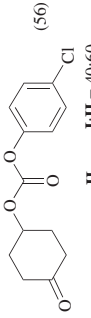
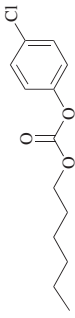
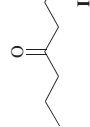
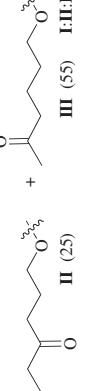

R	Time	% Conv.	I:II
4-NO ₂	12 h	>96	52:32:16
2-NO ₂	24 h	>96	15:44:41
H	24 h	>96	0:82:18
4-MeO	12 h	>96	66:14:20
			
			
			
			
			
			
			
			
			
			I:II = 12:88
DMD, acetone, dark, rt, 3 d			
DMD, CH ₂ Cl ₂ , acetone, rt			
TFD, CH ₂ Cl ₂ , -20°, 48 h			
DMD, acetone, rt, overnight			
TFD, CH ₂ Cl ₂ , -20°, 48 h			

TABLE 5B. REGIOSELECTIVE C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
	TFD, CH ₂ Cl ₂ , -20°, 48 h	 (97)	477																														
	DMD, acetone, rt		449																														
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>4-NO₂</td> <td>Me</td> <td>24 h</td> <td>(70)</td> <td>(15)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>12 h</td> <td>(85)</td> <td>(8)</td> </tr> <tr> <td>H</td> <td>CO₂Me</td> <td>—</td> <td>(—)</td> <td>(—)</td> </tr> <tr> <td>4-MeO</td> <td>Me</td> <td>12 h</td> <td>(>96)</td> <td>(—)</td> </tr> <tr> <td>4-MeO</td> <td>CO₂Me</td> <td>48 h</td> <td>(72)</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	Time	I	II	4-NO ₂	Me	24 h	(70)	(15)	H	Me	12 h	(85)	(8)	H	CO ₂ Me	—	(—)	(—)	4-MeO	Me	12 h	(>96)	(—)	4-MeO	CO ₂ Me	48 h	(72)	(—)	
R ¹	R ²	Time	I	II																													
4-NO ₂	Me	24 h	(70)	(15)																													
H	Me	12 h	(85)	(8)																													
H	CO ₂ Me	—	(—)	(—)																													
4-MeO	Me	12 h	(>96)	(—)																													
4-MeO	CO ₂ Me	48 h	(72)	(—)																													
	TFD, CH ₂ Cl ₂ , -20°, 48 h	 I +  II (56) I:II = 40:60	477																														
	TFD, CH ₂ Cl ₂ , -20°, 48 h	 I (—) +  II (25) +  III (55) I:II:III = 14:29:57	477																														

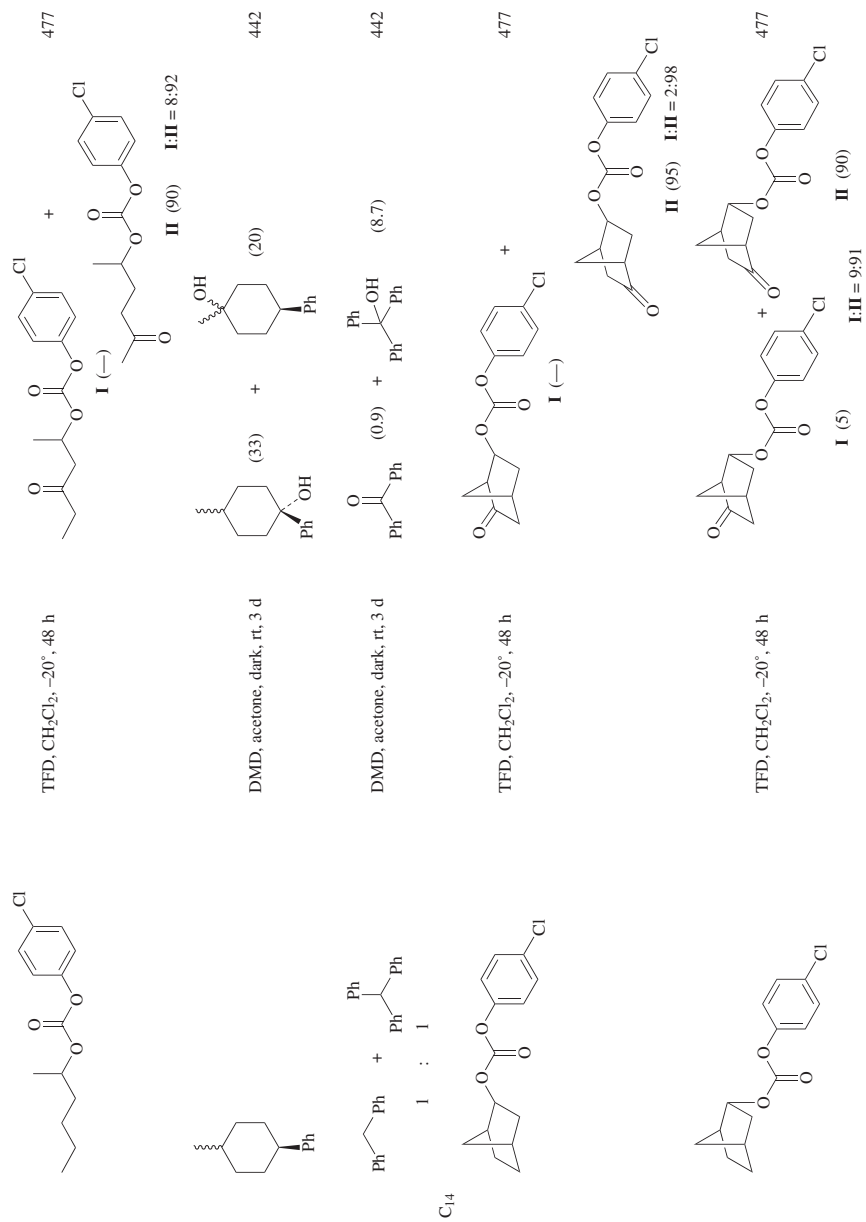


TABLE 5B. REGIOSELECTIVE C-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

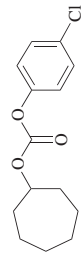
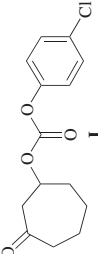
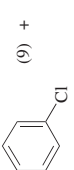
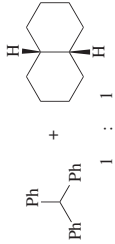
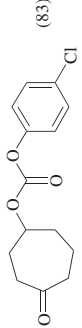
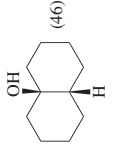

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <chem>Clc1ccc(cc1)OC(=O)C2CCCCC2</chem>	TFD, CH ₂ Cl ₂ , -20°, 48 h	 I  (9) +	477
 <chem>CC1(C2CCCCC2)OCC1C3(C4CCCCC4)C(C5=CC=CC=C5)(C6=CC=CC=C6)O</chem>	DMD, acetone, dark, rt, 3 d	 (83) II I:II = 15:85  (46)  (0.6) +	442

TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES


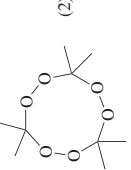
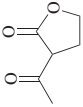
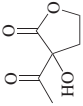
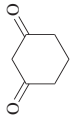

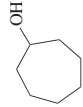
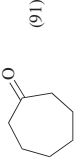


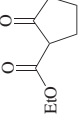
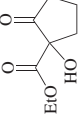
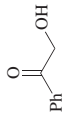
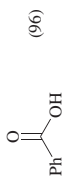
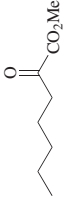
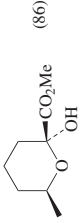
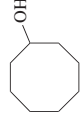
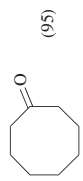
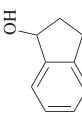
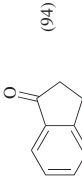
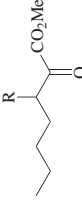
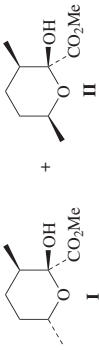

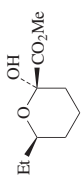
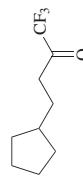
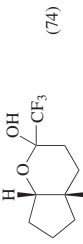
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂ 	Oxone [®] , acetone, rt, 5 h	CH ₃ CO ₂ H (–) +  (2)	121
C ₆ 	Oxone [®] , acetone, phosphate buffer (pH 7.3-7.5), CH ₂ Cl ₂ , KF, 20°, 1 h	 (85)	193
	Oxone [®] , acetone, H ₂ O, NaHCO ₃	 (14)	478
C ₇ 	Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 3.5 h	 (91)	52
C ₈ 	Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 3.5 h	 (80)	52
	Oxone [®] , acetone, phosphate buffer (pH 7.3-7.5), CH ₂ Cl ₂ , KF, 20°, 1 h	 (85)	193

TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
	Oxone [®] , acetone, H ₂ O, NaHCO ₃	 (96)	478												
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , rt, 24 h	 (86)	195												
	Oxone [®] , ketone 1, NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 4 h	 (95)	52												
	Oxone [®] , ketone 1, NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 5 h	 (94)	52												
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt	 I + II	479												
		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>7 h</td> <td>(80)</td> <td>3.4:1</td> </tr> <tr> <td>OMe</td> <td>24 h</td> <td>(9)</td> <td>1:1</td> </tr> </tbody> </table>	R	Time	I + II	I:II	Me	7 h	(80)	3.4:1	OMe	24 h	(9)	1:1	
R	Time	I + II	I:II												
Me	7 h	(80)	3.4:1												
OMe	24 h	(9)	1:1												
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 (70)	195												
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 (74)	480												

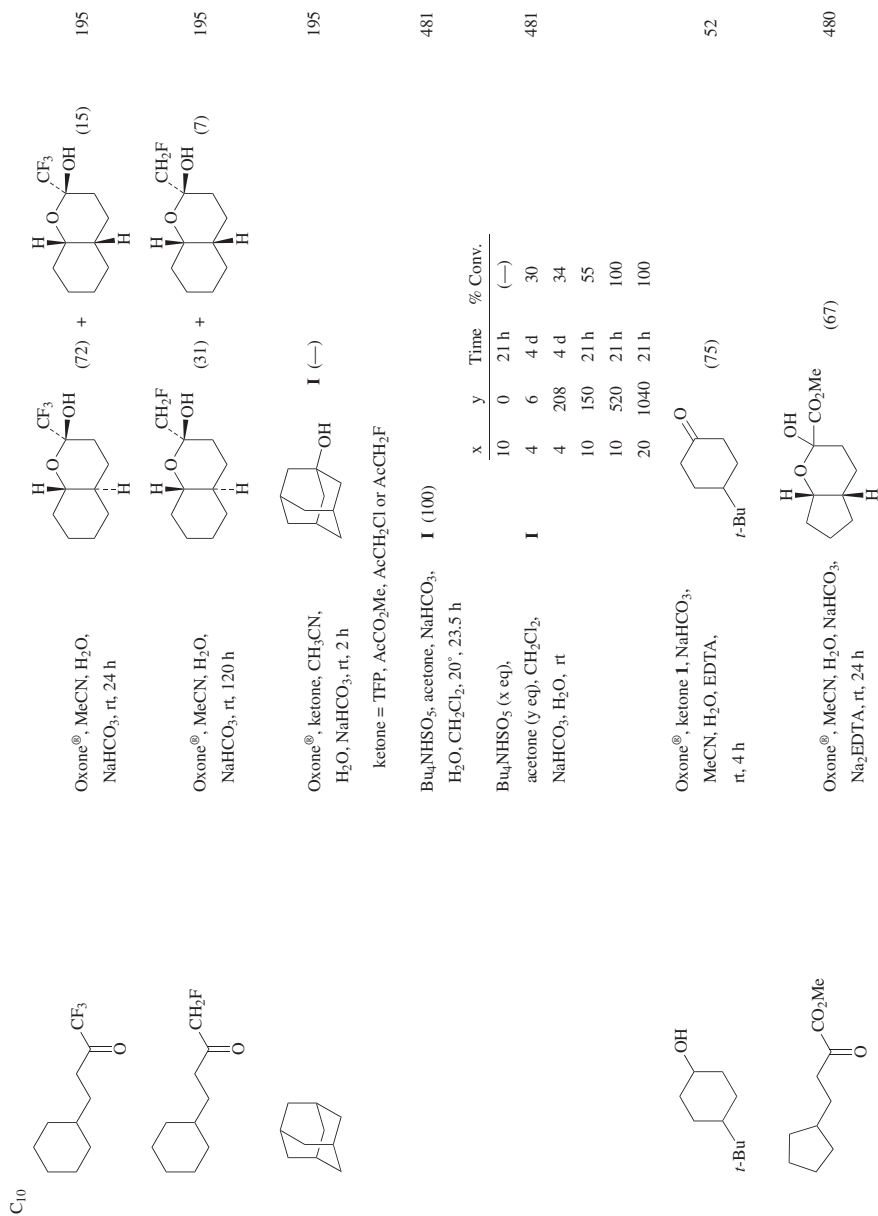
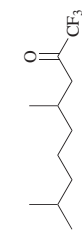
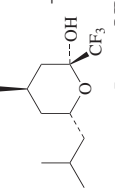
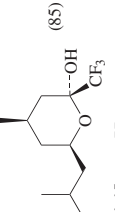
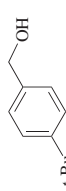
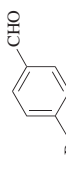








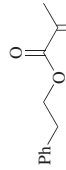



TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	 I +  II I:II = 1:15	479
	Oxone [®] , ketone 1 , NaHCO ₃ , MeCN, H ₂ O, EDTA, rt, 12 h	 (77)	52
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , rt, 24 h	 (78)	195
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , rt, 24 h	 (66) +  (17)	195
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , rt, 72 h	 I +  II X I II Cl (56) (21) F (41) (14)	195
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 120 h	 (93)	480

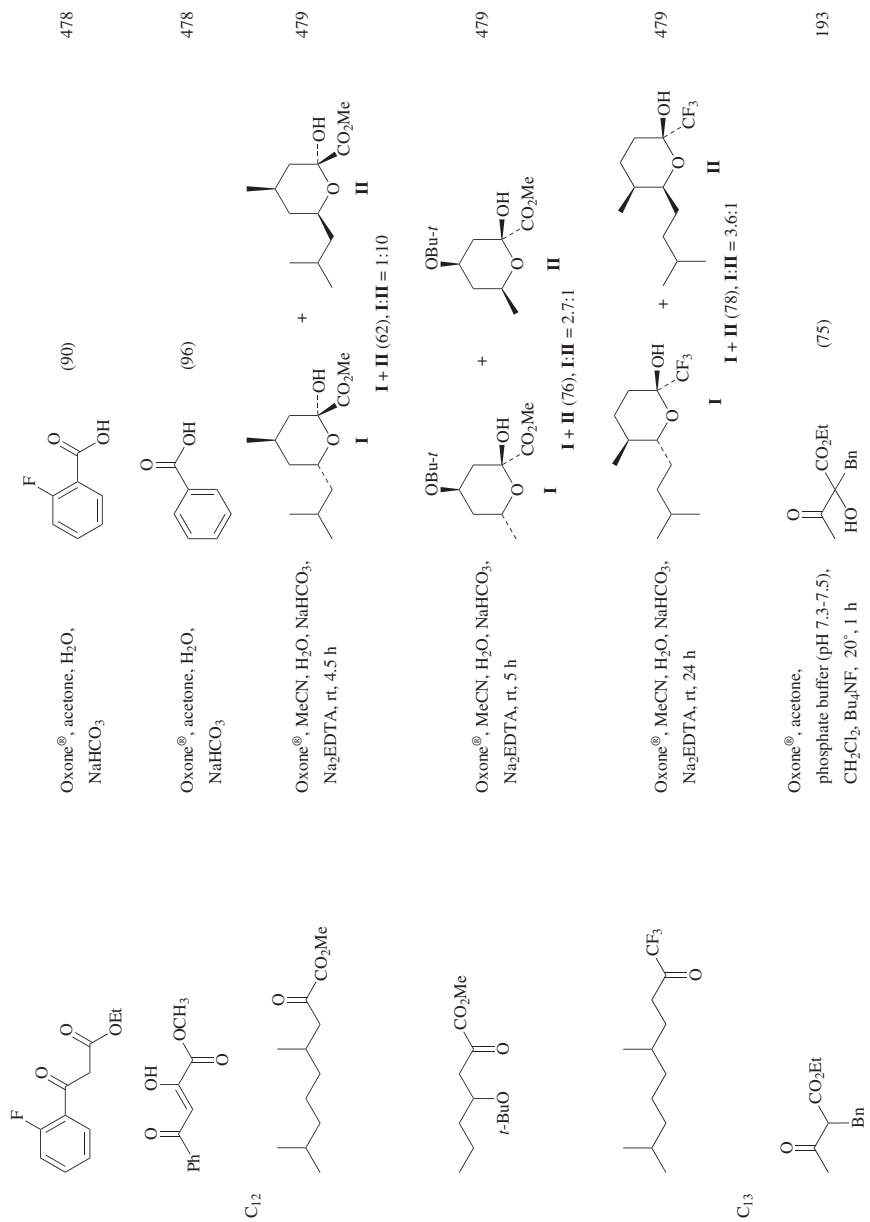


TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Oxone [®] , acetone, CH ₂ Cl ₂ , H ₂ O, NaHCO ₃ , 0°, 2 h 2. rt, 12 h	(38) + (1)	450
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 27 h	I + II I + II (58), I:II = 2.7:1	479
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 6 h	(78) 73% ee + (8)	480
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 24 h	(73)	480
	Oxone [®] , MeCN, H ₂ O, NaHCO ₃ , Na ₂ EDTA, rt, 20 h	I + II I + II (43), I:II = 2.3:1	479

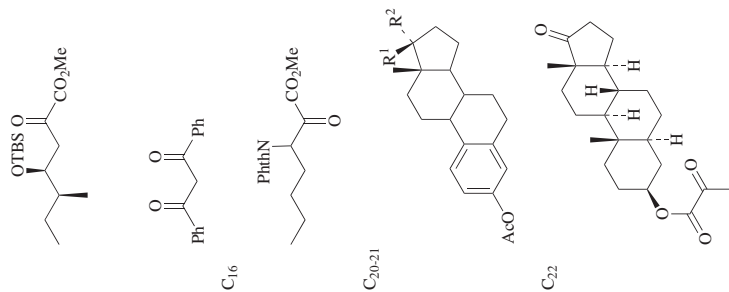
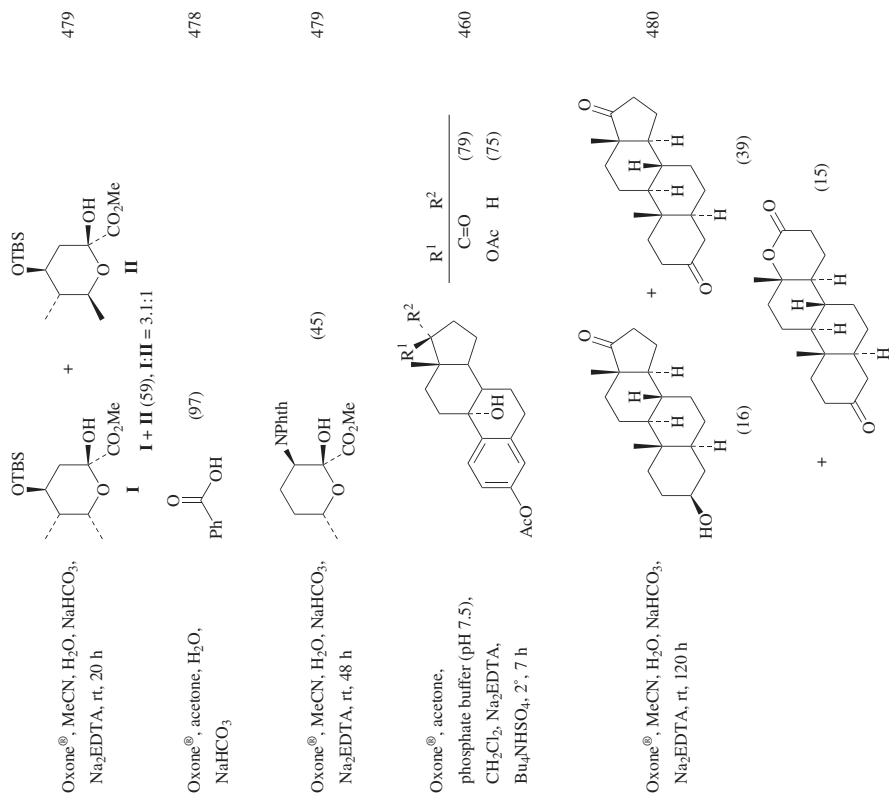
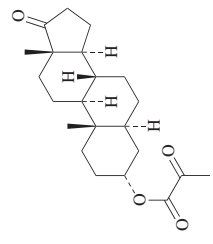
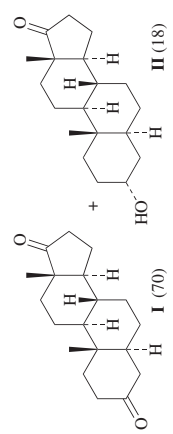
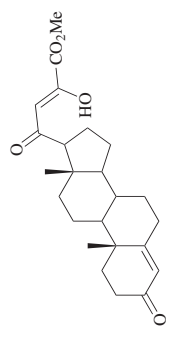
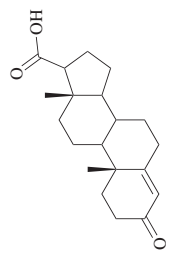
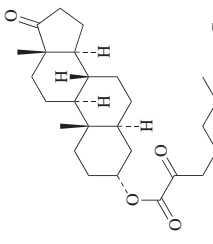
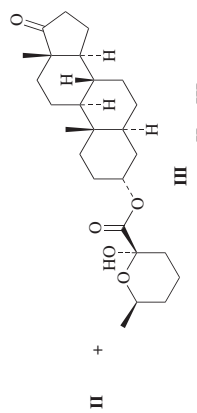
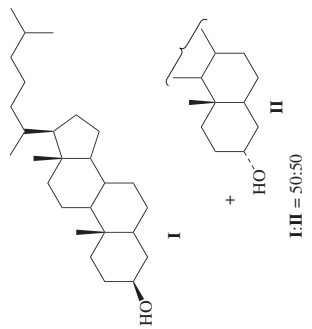


TABLE 5C. C-H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₂</p>	<p>Oxone[®], MeCN, H₂O, NaHCO₃, Na₂EDTA, rt, 120 h</p>	 <p>I (70) + II (18)</p>	480
 <p>C₂₄</p>	<p>Oxone[®], acetone, H₂O, NaHCO₃, 0° to rt, 15 min</p>	 <p>(87)</p>	478
 <p>Conc. 1.5 mM 10 mM</p>	<p>Oxone[®], MeCN, H₂O, NaHCO₃, Na₂EDTA, rt, 120 h</p>	 <p>II + III</p> <p>(69) (34) (15) (42)</p>	480

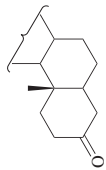
C₂₇



Oxone[®], acetone, CH₂Cl₂,
phosphate buffer (pH 7.5),
Bu₄NHSO₄, 0-5°

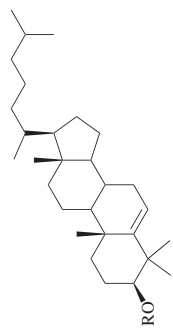
I + II +
I + II (-), I:II
= 35:65

(-)



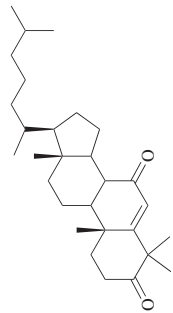
482

C₂₉₋₃₁



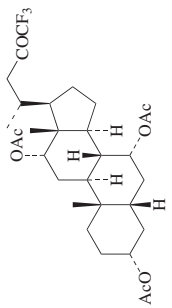
Oxone[®], acetone, CH₂Cl₂,
phosphate buffer (pH 7.5),
Bu₄NHSO₄, 0-5°

R
H (36)
Ac (44)



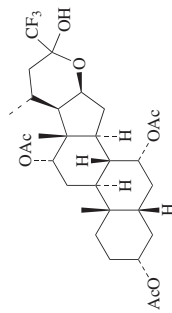
482

C₃₀



Oxone[®], MeCN, H₂O, NaHCO₃,
Na₂EDTA, rt, 24 h

(77)



480

TABLE 5C. C–H OXIDATION BY IN SITU GENERATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₃₁</p>	<p>Oxone®, MeCN, H₂O, NaHCO₃, Na₂EDTA, rt, 24 h</p>	<p>(58)</p>	195, 480
<p>C₃₅</p>	<p>Oxone®, MeCN, H₂O, NaHCO₃, Na₂EDTA, rt, 41 d</p>	<p>(3) + (4) + (10) + (17) + (6)</p>	480

TABLE 5D. ASYMMETRIC C-H OXIDATION BY IN SITU GENERATED OPTICALLY ACTIVE DIOXIRANES

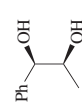
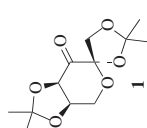
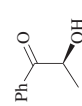
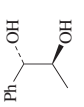
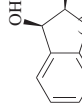
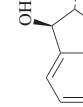
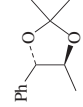
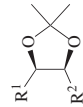
Substrate	Conditions	Product(s) and Conversions(s) (%)	Refs.												
<p>C₉</p>  <p>racemic</p>	<p>Oxone[®], K₂CO₃, ketone, buffer (pH 10.5), MeCN, 0°, 2 h</p> <p>Ketone = </p>	<p> I + II (34), I:II = 89:11</p> <p>23% ee + 8% ee</p>	197												
<p>C₉₋₁₀</p>  <p>racemic</p>	<p>Oxone[®], K₂CO₃, ketone I, buffer (pH 10.5), MeCN, 0°, 2 h</p>	<p>I + II (20), I:II 11% ee, II:I = 84:16</p>	197												
<p>C₉₋₁₀</p>  <p>racemic</p>	<p>Oxone[®], K₂CO₃, ketone I, buffer (pH 10.5), MeCN, 0°, 2 h</p>	<table border="1"> <thead> <tr> <th>n</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>1 (30)</td> <td>9</td> </tr> <tr> <td>2 (18)</td> <td>14</td> </tr> </tbody> </table>	n	% ee	1 (30)	9	2 (18)	14	197						
n	% ee														
1 (30)	9														
2 (18)	14														
<p>C₁₂</p>  <p>racemic</p>	<p>Oxone[®], K₂CO₃, ketone I, buffer (pH 10.5), MeCN, 0°, 2 h</p>	<table border="1"> <thead> <tr> <th>n</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>1 (26)</td> <td>20</td> </tr> <tr> <td>2 (8)</td> <td>5</td> </tr> </tbody> </table>	n	% ee	1 (26)	20	2 (8)	5	197						
n	% ee														
1 (26)	20														
2 (8)	5														
<p>C₁₂₋₁₉</p> 	<p>Oxone[®], K₂CO₃, ketone I, buffer (pH 10.5), MeCN, DMMF, 0°, 5 h</p>	<p>(<5), 11% ee</p>	196, 197												
<p>meso or rac</p> 	<p>Oxone[®], K₂CO₃, ketone I, buffer (pH 10.5), MeCN, DMMF, 0°, 5 h</p>	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>Me</td> <td>(6) 44</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(10) 63</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>4-MeC₆H₄</td> <td>(10) 65</td> </tr> </tbody> </table>	R ¹	R ²	% ee	Ph	Me	(6) 44	Ph	Ph	(10) 63	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(10) 65	197
R ¹	R ²	% ee													
Ph	Me	(6) 44													
Ph	Ph	(10) 63													
4-MeC ₆ H ₄	4-MeC ₆ H ₄	(10) 65													

TABLE 5D. ASYMMETRIC C–H OXIDATION BY IN SITU GENERATED OPTICALLY ACTIVE DIOXIRANES (Continued)

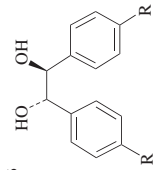
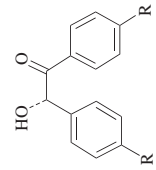
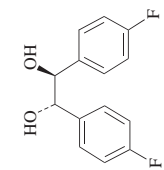
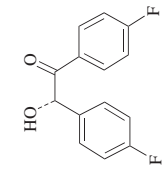
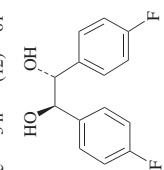
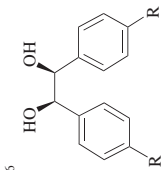
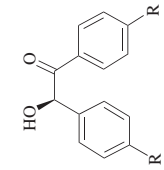
Substrate	Conditions	Product(s) and Conversions(s) (%)	Refs.																									
<p>C₁₄₋₁₆</p> 	Oxone [®] , ketone 1 , K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>2 h (10)</td> <td>74</td> </tr> <tr> <td>Cl</td> <td>2 h (11)</td> <td>70</td> </tr> <tr> <td>H</td> <td>3 h (51)</td> <td>65</td> </tr> <tr> <td>CN</td> <td>2.5 h (6)</td> <td>75</td> </tr> <tr> <td>Me</td> <td>3 h (12)</td> <td>61</td> </tr> </tbody> </table>	R	Time	% ee	Br	2 h (10)	74	Cl	2 h (11)	70	H	3 h (51)	65	CN	2.5 h (6)	75	Me	3 h (12)	61	197						
R	Time	% ee																										
Br	2 h (10)	74																										
Cl	2 h (11)	70																										
H	3 h (51)	65																										
CN	2.5 h (6)	75																										
Me	3 h (12)	61																										
<p>C₁₄</p> 	Oxone [®] (0.75 eq), ketone 1 , K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°, 1.5 h	  I + II (10), I 71% ee, II 11% ee	197																									
	Oxone [®] (1.5 eq), ketone 1 , K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°, 3 h	I + II (31), I 69% ee, II 28% ee	197																									
<p>C₁₄₋₁₆</p> 	Oxone [®] , ketone 1 , K ₂ CO ₃ , buffer (pH 10.5), MeCN, 0°		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>2 h (61)</td> <td>58</td> </tr> <tr> <td>Cl</td> <td>3 h (56)</td> <td>54</td> </tr> <tr> <td>F</td> <td>3 h (89)</td> <td>58</td> </tr> <tr> <td>H</td> <td>3 h (95)</td> <td>45</td> </tr> <tr> <td>CN</td> <td>3 h (< 5)</td> <td>60</td> </tr> <tr> <td>Me</td> <td>3 h (92)</td> <td>30</td> </tr> <tr> <td>MeO</td> <td>3 h (95)</td> <td>24</td> </tr> </tbody> </table>	R	Time	% ee	Br	2 h (61)	58	Cl	3 h (56)	54	F	3 h (89)	58	H	3 h (95)	45	CN	3 h (< 5)	60	Me	3 h (92)	30	MeO	3 h (95)	24	197
R	Time	% ee																										
Br	2 h (61)	58																										
Cl	3 h (56)	54																										
F	3 h (89)	58																										
H	3 h (95)	45																										
CN	3 h (< 5)	60																										
Me	3 h (92)	30																										
MeO	3 h (95)	24																										

TABLE 5E. Si-H OXIDATION BY ISOLATED DIOXIRANES

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.	
		R ¹	R ²	R ³	Time		
C _{5,18} $\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{Si}-\text{H} \\ \\ \text{R}^3 \end{array}$	DMD, acetone, (CCl ₄), rt	$\begin{array}{c} \text{R}^1 \\ \\ \text{R}^2-\text{Si}-\text{OH} \\ \\ \text{R}^3 \end{array}$	Me	Me	15 min	483	
			Et	Et	< 5 min		
C ₆ $\begin{array}{c} \text{Et} \\ \\ \text{Et}-\text{Si}-\text{H} \\ \\ \text{Et} \end{array}$	TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min	$\begin{array}{c} \text{Et} \\ \\ \text{Et}-\text{Si}-\text{OH} \\ \\ \text{Et} \end{array}$	Me	Me	< 5 min	39	
			Ph	H	30min		
			TMSO	Me	30 min		
			Ph	Me	< 5 min		
C ₈ $\begin{array}{c} \text{Me} \\ \\ \text{Ph}-\text{Si}-\text{H} \\ \\ \text{Me} \end{array}$	TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min	$\begin{array}{c} \text{Me} \\ \\ \text{Ph}-\text{Si}-\text{OH} \\ \\ \text{Me} \end{array}$	Me	Me	3 h	39	
			Ph	TMS	< 1 min		
C ₉ $\begin{array}{c} \text{TMS} \\ \\ \text{TMS}-\text{Si}-\text{H} \\ \\ \text{TMS} \end{array}$	DMD, acetone, Ar	$\begin{array}{c} \text{TMS} \\ \\ \text{TMS}-\text{Si}-\text{OH} \\ \\ \text{TMS} \end{array}$	TMS	TMS		483	
	Additive	I	I	II			
	Temp	20°	20°	20°	(79)		(16)
	Time	< 1 min	< 1 min	< 1 min	(> 99)		(—)
		—	-70°	10 min	(> 99)		(—)
	hν	-70°	10 min	(88)	(5)		
	DMD, (CF ₃ CO) ₂ O, acetone, CCl ₄ , Ar, 20°, < 1 min	$\begin{array}{c} \text{TMS} \\ \\ \text{TMS}-\text{Si}-\text{O}-\text{C}(=\text{O})-\text{CF}_3 \\ \\ \text{TMS} \end{array}$	(90)	TMS	TMS	483	
			(10)	TMS	TMS		

TABLE 5E. Si-H OXIDATION BY ISOLATED DIOXIRANES (Continued)

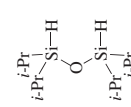
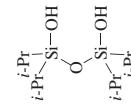
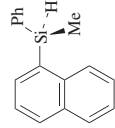
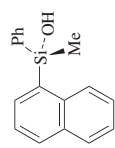
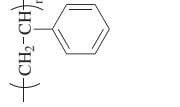
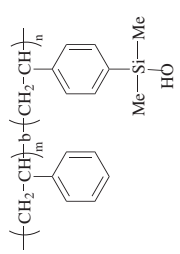
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C12	DMD, acetone, CCl ₄ , rt	 (> 99)	483
 C17	TFD, TFP, CH ₂ Cl ₂ , -20°, < 1 min; or, DMD, acetone, CH ₂ Cl ₂ , 0°, 18 min	 (> 98), 97% ee	39
 Cx	DMD, acetone, 0°	 (-)	484

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES

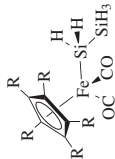
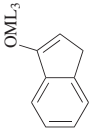
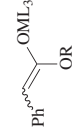
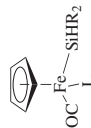
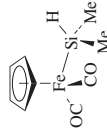
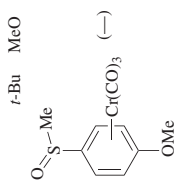
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₇₋₁₂</p> 	DMD, acetone, toluene, -78° to rt, 50 min	<p>R</p> <p>H (89)</p> <p>Me (89)</p>	227
<p>C₉₋₁₉</p> 	1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h	<p>M L₃</p> <p>Na — (32)</p> <p>Ti (<i>i</i>-PrO)₃ (50)</p> <p>Ti Cp₂Cl (70)</p>	212
<p>C₉₋₂₂</p> 	1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h	<p>R M L₃</p> <p>Me Na — (60)</p> <p><i>t</i>-Bu Ti (<i>i</i>-PrO)₃ (12)</p> <p><i>t</i>-Bu Ti Cp₂Cl (67)</p>	212
<p>C₉₋₃₈</p> 	DMD, acetone; or acetone, CH ₂ Cl ₂	<p>L R</p> <p>Temp Time</p> <p>CO Me 0° 6 h (46)</p> <p>CO <i>t</i>-Bu -78° 0.3 h (98)</p> <p>CO Ph 0° 2.5 h (86)</p> <p>CO 2-MeC₆H₄ 0° 0.5 h (85)</p> <p>PPh₃ 2-MeC₆H₄ -78° 0.5 h (43)</p>	220
<p>C₁₀</p> 	DMD, acetone, -78°, 1 h; rt, 1 h	(67)	485

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

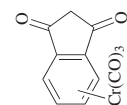
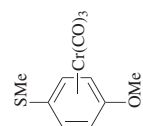
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
 C_{10}	DMD (1.0 eq), acetone, CH_2Cl_2 , -65° , 10 min	 (88)	486								
 C_{10-11}	DMD (2.0 eq), acetone, CH_2Cl_2 , -65° , 10 min	 (70)	486								
 C_{10-11}	DMD (1.0 eq), acetone, CH_2Cl_2 , -65° , 10 min	<table border="1"> <thead> <tr> <th>n</th> <th>R</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Me (88)</td> </tr> <tr> <td>2</td> <td>Me (-)</td> </tr> <tr> <td>1</td> <td>Et (89)</td> </tr> </tbody> </table>	n	R	1	Me (88)	2	Me (-)	1	Et (89)	486
n	R										
1	Me (88)										
2	Me (-)										
1	Et (89)										
 C_{10-13}	DMD, acetone, toluene, -78° , 2 h	 (34-71)	221								
 C_{10-13}	DMD, acetone, 20°	 (100) + Cr_2O_3 (-)	487								
 C_{10-14}	1. DMD, acetone, N_2 , -78° , 15 min 2. rt, 1 h	 I	128, 129								
 C_{10-14}		 II	128, 129								

R ¹	R ²	R ³	I	II	I:II
Me	H	H	I + II (93)	(78)	1:1
Me	Me	H	(—)	(78)	10:90
Me	H	MeO	(33)	(33)	50:50
Me	MeO	H	(—)	(80)	7:93
Et	MeO	H	(—)	(39)	15:85
<i>i</i> -Pr	MeO	H	(56)	(—)	70:30
<i>t</i> -Bu	Me	H	(92)	(—)	98:2
Me	<i>t</i> -Bu	H	(—)	(45)	6:94
<i>t</i> -Bu	MeO	H	(77)	(—)	98:2

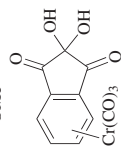


DMD, acetone, 20°

487



317



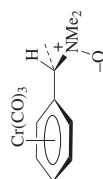
DMD, acetone, -28°, 1 min

488

1. DMD (0.95 eq), acetone, N₂,
-78°, 15 min
2. -78° to rt, 2 h

217

R
I (48)
Ac (69)
CH₂=CHCH₂ (69)
Bu₃Sn (20)

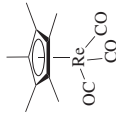
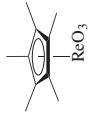
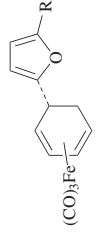
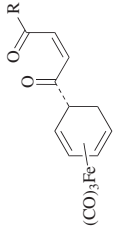
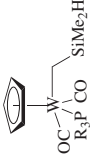
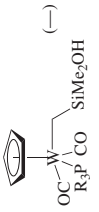
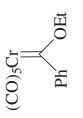
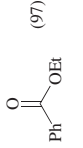
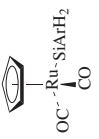

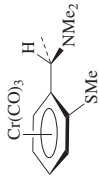
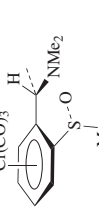

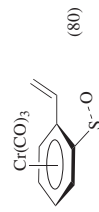


1. DMD, acetone, N₂,
-78°, 15 min
2. -78° to rt, 2 h

217



TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{13}	DMD, acetone, 0°	 (74)	210
 C_{13-14}	DMD, acetone, Ar, 1 min	 (39)	214
 C_{13-28}	DMD, acetone	 (97)	489
 C_{14}	DMD, acetone, 20°, 3 h	 (68)	204
 C_{14}	DMD, acetone, toluene, -78° to rt, 60 min	 (63)	226
 C_{14}	1. DMD (1,2 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h	 (80)	217
 C_{14}	1. DMD (2,4 eq), acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h	 (80)	217

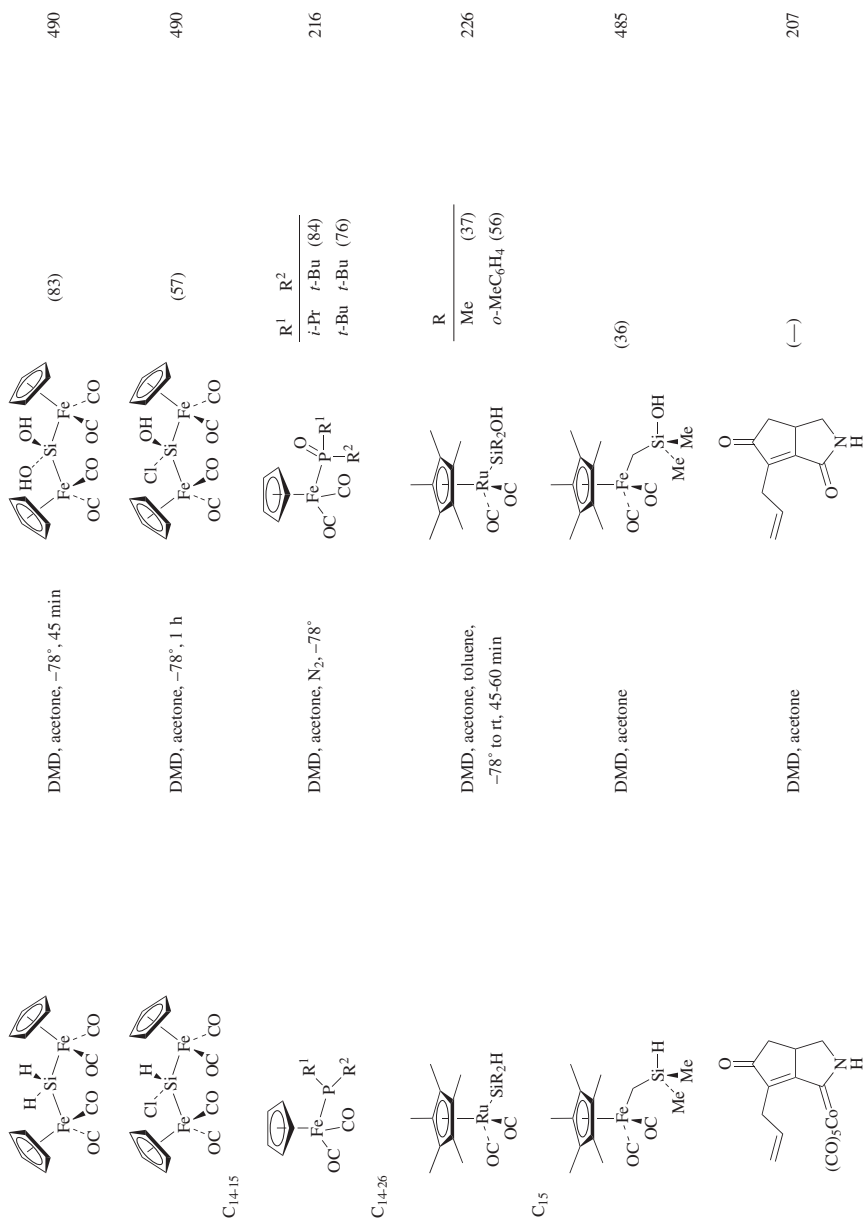
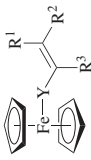
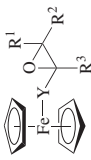




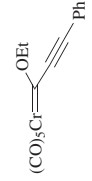



TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions			Product(s) and Yield(s) (%)	Refs.		
	Y	R ¹	R ²				
C ₁₅₋₁₉				DMD (x eq), acetone, CH ₂ Cl ₂ , gas		213	
	CO	Me	H	x Time Temp Gas			
	CO	Me	H	6.0 5 h 20° Ar (24)			
	CO	Me	H	9.0 9 h 20° Ar (44)			
	CO	Me	H	12.0 14 h 20° Ar (58)			
	CO	H	Me	6.0 6 h 20° Ar (59)			
	CO	H	Me	6.0 24 h 20° O ₂ (38)			
	CH ₂	Me	H	3.0 40 min 0° Ar (66)			
	CH ₂	Me	H	3.0 10 min 20° Ar (75)			
	CH ₂	Me	H	3.0 1 min 56° Ar (63)			
	CH ₂	Me	H	4.0 1 min 56° Ar (76)			
	CH ₂	Me	H	3.0 25 min 20° O ₂ (28)			
	CH ₂	H	Me	3.0 15 min 20° Ar (67)			
	CH ₂	H	Me	3.0 30 min 20° O ₂ (53)			
	CO	H	H	6.0 8 h 20° Ar (30)			
	CH ₂	H	H	6.0 45 min 20° Ar (38)			
C ₁₅₋₂₁				DMD, acetone, -78° to rt, 25 min		 (89)  (95)	223
C ₁₆				DMD, O ₂ , acetone, -20°, 4 h TFD, O ₂ , TFP, -20°, 4 h	 (90) I (91)	204, 205 205	

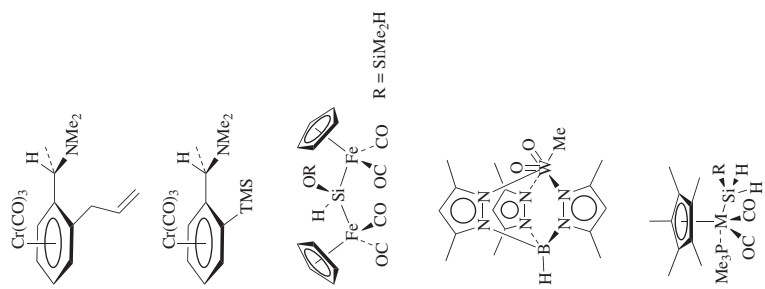
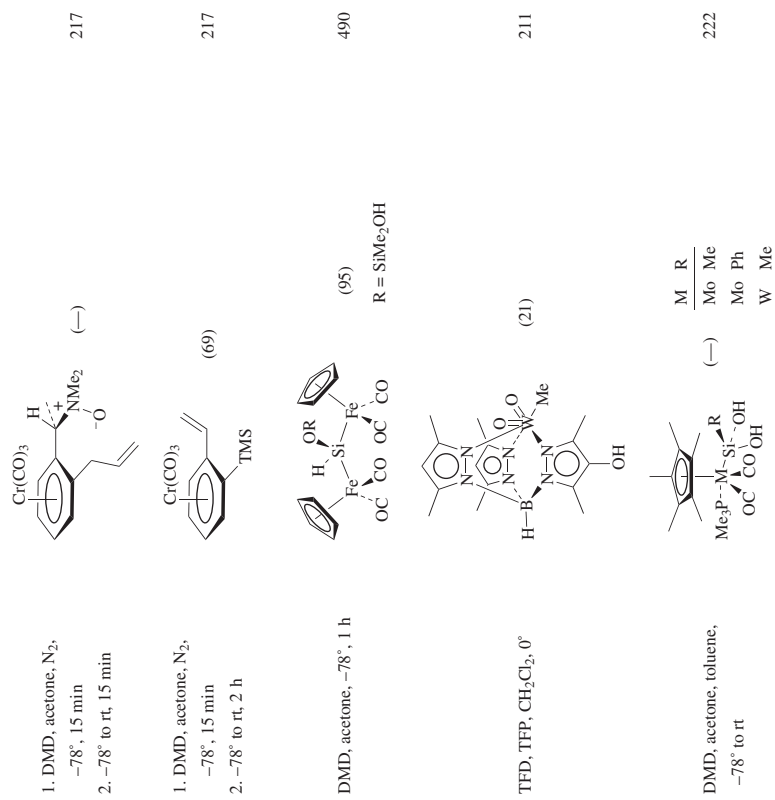
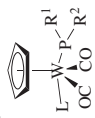
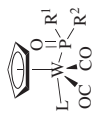
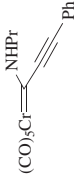
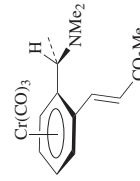
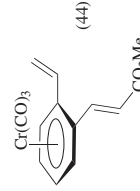


TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{16,22}$ 	DMD, acetone, solvent, N_2 , -78°		216
	Solvent	(—)	
	<i>t</i> -Bu	(88)	
	H	(80)	
	Me	(69)	
	2-MeC ₆ H ₄	(67)	
	PMe ₃	Ph	
C_{17} 	DMD, O ₂ , acetone, -20° , 4 h	Ph—C≡C—CONHPt (94)	204
$Et_4N^+ TpMo(CO)_3^-$	DMD, acetone, Ar, rt, 15 min	$Et_4N^+ TpMoO_3^-$ (59)	210
$Et_4N^+ Tp^*Mo(CO)_3^-$	DMD, acetone, Ar, rt, 15 min	$Et_4N^+ Tp^*MoO_3^-$ (—)	210
	1. DMD, acetone, N ₂ , -78° , 15 min 2. -78° to rt, 2 h	 (44)	217

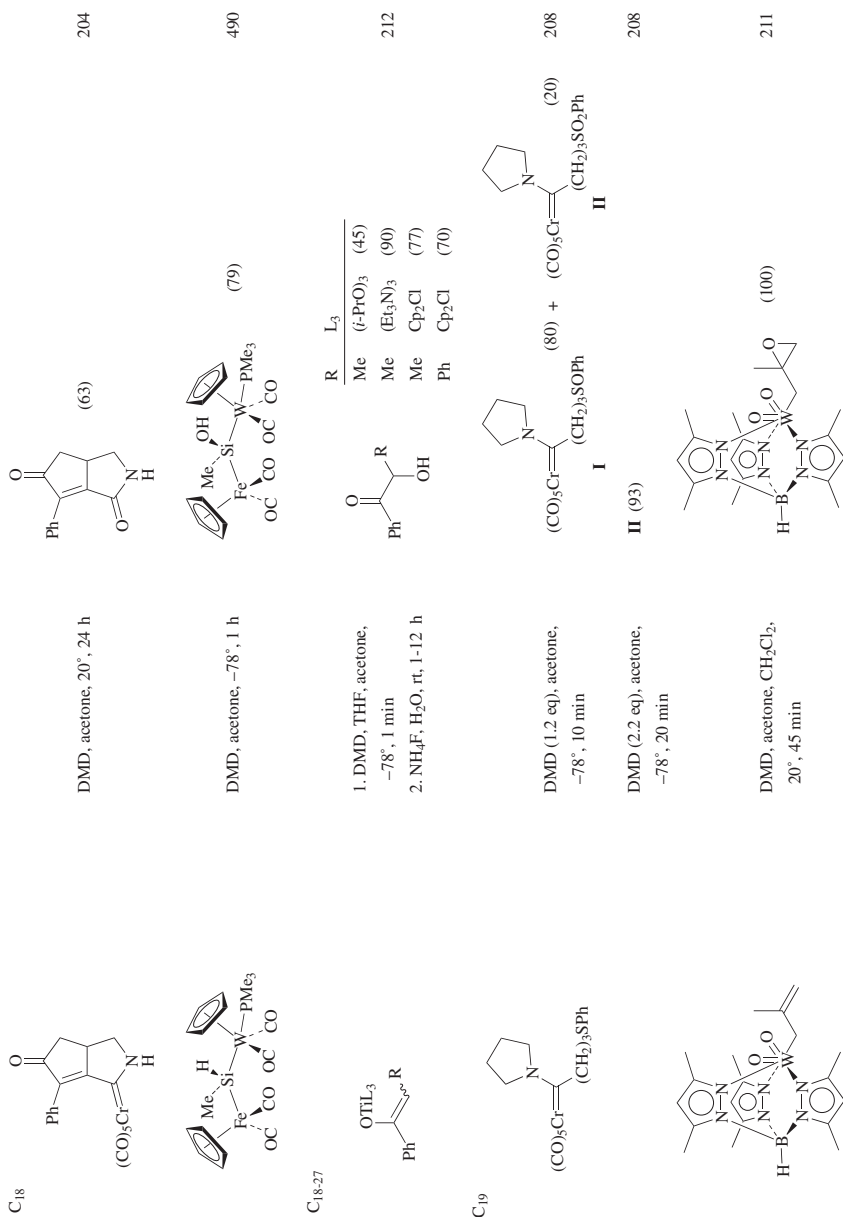
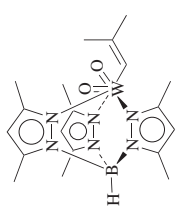
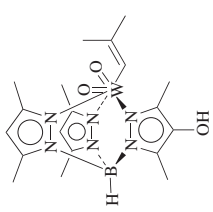
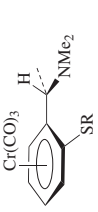
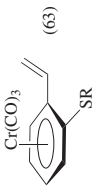
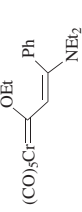
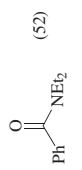
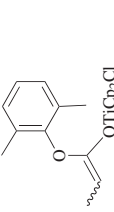
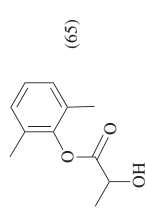
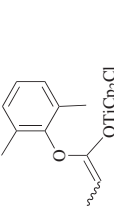
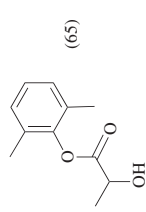
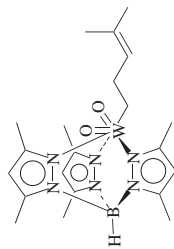


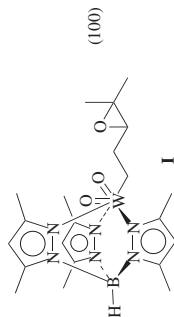
TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
 C ₁₉	DMD, acetone, CH ₂ Cl ₂ , 20°, 45 min	 (39)	211						
 C ₁₉₋₂₀	1. DMD, acetone, N ₂ , -78°, 15 min 2. -78° to rt, 2 h	 (63)	<table border="1"> <tr> <td>R</td> <td></td> </tr> <tr> <td>Ph</td> <td>(84-85)</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>(81-95)</td> </tr> </table>	R		Ph	(84-85)	4-MeOC ₆ H ₄	(81-95)
R									
Ph	(84-85)								
4-MeOC ₆ H ₄	(81-95)								
 C ₂₀	DMD, acetone, 20°	 (52)	206						
 C ₂₁	1. DMD, CH ₂ Cl ₂ , acetone, -30° 2. Et ₃ OBF ₄ , CH ₂ Cl ₂ , acetone, -70°	 (65)	206						
 C ₂₁	1. DMD, THF, acetone, -78°, 1 min 2. NH ₄ F, H ₂ O, rt, 1-12 h	 (65)	212						

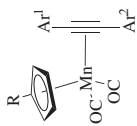


DMD, acetone, CH_2Cl_2 ,
20°, 0.5 h

211



C_{21-24}



TFD, TFP, CH_2Cl_2 , 0°

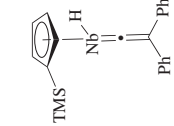
211

I (83)

R	Ar^1	Ar^2	
H	Ph	Ph	(30)
Me	Ph	Ph	(25)
H	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(42)
Me	Ph	4-MeOC ₆ H ₄	(27)
Me	4-MeOC ₆ H ₄	Ph	(-)
Me	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(41)
Me	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	(-)
Me	4-MeC ₆ H ₄	4-MeOC ₆ H ₄	(29)

DMD, acetone, CH_2Cl_2 ,
 N_2 , -20°, 20 h

215

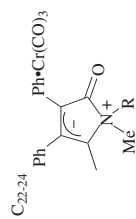


C_{22}

TFD, TFP, Et₂O, rt

209

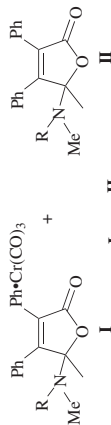
(-)



C_{22-24}

DMD, acetone, rt

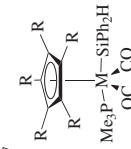
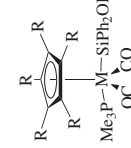
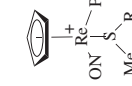
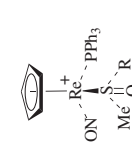

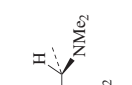

491

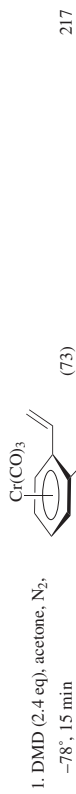


I **II**
(20) (75)
(47) (-)

R
Me
c-C₃H₅

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{22-27}	1. DMD, acetone, toluene, -78° , 30 min 2. rt, 1 h	 M R Cr H (79) Mo Me (64) W Me (89)	224
 C_{24}	DMD, acetone, 0° , 45 min	 I II ON ⁻ PPh ₃ + ON ⁻ PPh ₃ Me ⁺ O R Me ⁺ O Me	492
 R BF ₄ ⁻ BF ₄ ⁻ BF ₄ ⁻ BF ₄ ⁻ TfO ⁻ TfO ⁻ TfO ⁻ TfO ⁻ TfO ⁻	Time 2.3 h 2.0 h 3.0 h 5.6 h 2.6 h 3.0 h 2 d 4 d —	I II % ee (67) (—) 96 (49) (24) 100 (84) (10) 91 (100) (—) 85 (53) (21) 39 (84) (11) 38 (77) (—) 79 (58) (—) 100 (32) (—) —	
 C_{25}	1. DMD (0.95 eq), acetone, N ₂ , -78° , 15 min 2. -78° to rt, 2 h	 (85)	217



L ¹	L ²	R ¹	R ²	Time	dr
Ph ₃ P	Me ₂ P(CH ₂) ₂ PPh ₂	Me	<i>i</i> -Pr	45 min	(100) 80:20
	CO	Me	<i>i</i> -Pr	2 h	(45) 64:36
	Me ₂ P(CH ₂) ₂ PPh ₂	Me	Ph	45 min	(100) 80:20
	Me ₂ P(CH ₂) ₂ PPh ₂	Me	Bz	45 min	(100) 75:25
Ph ₃ P	CO	Me	Ph	2 h	(100) 54:46
	Me ₂ P(CH ₂) ₂ PPh ₂	<i>i</i> -Pr	Bz	45 min	(10) 67:33
Ph ₃ P	CO	Me	Bz	2 h	(30) 62:38
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	<i>i</i> -Pr	45 min	(100) 93:7
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	Ph	45 min	(100) 73:27
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	<i>c</i> -C ₆ H ₁₁	45 min	(70) 92:8
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Me	Bz	45 min	(100) > 99:1
(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	(<i>S,S</i>)-Ph ₂ PCH(Me)CH(Me)PPh ₂	Et	Bz	45 min	(5) 95:5

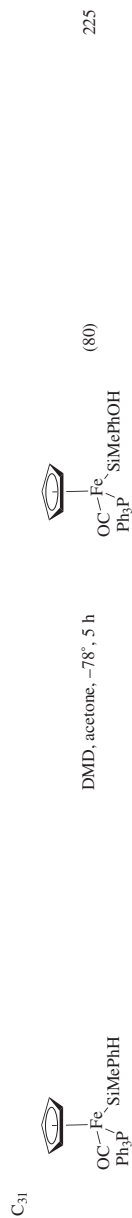
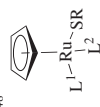
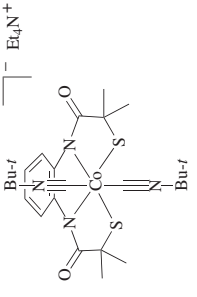
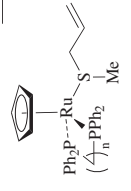
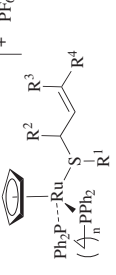
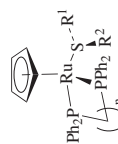


TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₃₁₋₄₈</p>  <p>$L^1-Ru-SR$ L^2</p>	DMD, acetone, CH ₂ Cl ₂ , -40°, 10 min	<p>L^1 CO</p> <p>L^2 PPh₃</p> <p>R Bn</p> <p>(ca. 90)</p> <p>Ph₂P(CH₂)₂PPh₂ Me</p> <p>Ph₂P(CH₂)₂PPh₂ Ph</p> <p>PPh₃ Bn</p> <p>PPh₃ Me</p> <p>PPh₃ Ph</p> <p>PPh₃ Bn</p>	486
<p>C₃₂</p>  <p>$Bu-t$ Et_4N^+</p>	DMD (4,4 eq), acetone, -30°, 1 h	(-)	493
<p>C₃₄₋₃₅</p>  <p>Ph_2P PF_6^-</p> <p>$(C_n)PPh_2$ Me</p>	DMD, acetone, 20°, 2-20 d	<p>n</p> <p>1 (69)</p> <p>2 (73)</p>	219
<p>C₃₄₋₄₂</p>  <p>Ph_2P PF_6^-</p> <p>$(C_n)PPh_2$ Me</p>	DMD, acetone, 20°, 2-20 d	<p>R¹</p> <p>R²</p> <p>R³</p> <p>R⁴</p>	219

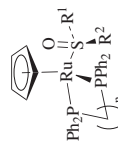
	n	R ¹	R ²	R ³	R ⁴	dr
(35)	1	Me	H	H	H	61:39
(24)	1	Et	H	H	H	55:45
(33)	2	Me	H	H	H	70:30
(50)	1	Me	H	Me	Me	72:28
(27)	2	Et	H	H	H	55:45
(37)	1	Me	—(CH ₂) ₃ —	H	H	48:38:9:5
(51)	1	Et	H	Me	Me	74:26
(46)	2	Me	H	Me	Me	79:21
(36)	1	Et	—(CH ₂) ₃ —	H	H	47:43:6:4
(41)	2	Me	—(CH ₂) ₃ —	H	H	30:30:23:17
(48)	2	Et	H	Me	Me	71:29
(29)	1	Ph	H	H	H	72:28
(32)	2	Et	—(CH ₂) ₃ —	H	H	84:6:6:4
(32)	2	Ph	H	H	H	78:22
(35)	1	Ph	H	Me	Me	71:29
(32)	1	Ph	—(CH ₂) ₃ —	H	H	58:25:17
(43)	2	Ph	H	Me	Me	59:41

C₄₄51



n	R ¹	R ²
1	Me	<i>i</i> -Pr
2	Me	<i>i</i> -Pr
1	Me	Ph
2	Me	Ph
1	Me	Bz
2	Me	Bz
1	<i>i</i> -Pr	Bz
2	<i>i</i> -Pr	Bz

DMD, acetone,
-40° to 0°, 45 min



(100)
(100)
(100)
(100)
(100)
(100)
(20)
(—)

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $	DMD, acetone, CH_2Cl_2 , N_2 , -78°	 (74)	218										
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$		 + PF_6^-											
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$	DMD, acetone, 0° , 45 min	 + PF_6^-	(> 90)										
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$	DMD, acetone, 0° , 45 min	 + PF_6^-	126										
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$	DMD, acetone, 0° , 45 min	 + PF_6^-	<table border="0"> <tr> <td>R</td> <td>de</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>86</td> </tr> <tr> <td>Cy</td> <td>84</td> </tr> <tr> <td>Ph</td> <td>46</td> </tr> <tr> <td>Bz</td> <td>98</td> </tr> </table>	R	de	<i>i</i> -Pr	86	Cy	84	Ph	46	Bz	98
R	de												
<i>i</i> -Pr	86												
Cy	84												
Ph	46												
Bz	98												
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$	DMD, acetone, 0° , 45 min	 + PF_6^-	126										
$ \begin{array}{c} \text{Ar} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{P} \\ \\ \text{M} \\ \\ \text{N}-\text{Bu}-t \\ \\ \text{Ar} \end{array} $ $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$	DMD, acetone, 0° , 45 min	 + PF_6^-	<table border="0"> <tr> <td>R</td> <td>I; II</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(95) 7:93</td> </tr> <tr> <td>Ph</td> <td>(90) 73:27</td> </tr> <tr> <td>Bn</td> <td>(95) 99:1</td> </tr> </table>	R	I; II	<i>i</i> -Pr	(95) 7:93	Ph	(90) 73:27	Bn	(95) 99:1		
R	I; II												
<i>i</i> -Pr	(95) 7:93												
Ph	(90) 73:27												
Bn	(95) 99:1												



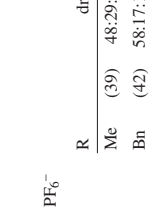
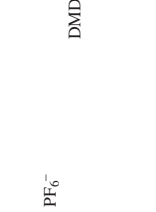
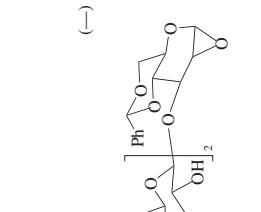
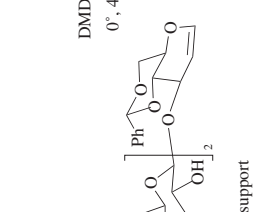
C ₃₈₋₃₉	 <p>R = Ph, Bn</p>	DMD, acetone, 0°, 45 min	 <p>(> 90)</p>	126
C ₃₈₋₄₄		DMD, acetone, 20°, 2-4 d		219
C ₄₀		DMD, acetone, CH ₂ Cl ₂ , 0°, 40 min		494
C ₄₄	<p>Fe^{II}(TPP)</p> <p>Mn^{II}(TPP)</p> <p>CiMn^{III}(TPP)</p> <p>HO-Mn^{III}(TPP)</p> <p>Mn^{III}(TPP)</p>	<p>DMD, acetone, -10°</p> <p>DMD, acetone, -50 to -20°</p> <p>DMD, acetone, -10°</p> <p>DMD, acetone, -10°</p> <p>DMD, acetone, -10°</p>	<p>[Fe^{III}(TPP)]₂O (→)</p> <p>O=Mn^{IV}(TPP) I (100)</p> <p>I (100)</p> <p>I (100)</p> <p>I (100)</p>	<p>198</p> <p>198</p> <p>198</p> <p>198</p> <p>198</p>

TABLE 6. OXIDATION OF ORGANOMETALLICS BY ISOLATED DIOXIRANES (Continued)

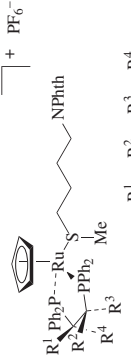
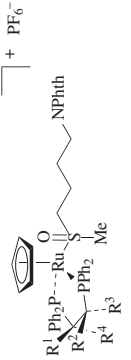
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{44-46} 	DMD, acetone, 0°, 2 h	 + PF ₆ ⁻	495
C_{56} Fe ^{II} (TMP)	DMD, acetone, -10°	O=Fe ^{IV} (TMP) (100)	198
C_{88} [Fe ^{III} (TPP)] ₂ O	DMD, acetone, -10°	O=Fe ^{IV} (TTP) (—)	198
[Mn ^{III} (TPP)] ₂ O	DMD, acetone, -10°	O=Mn ^{IV} (TTP) (100)	198

TABLE 7. MISCELLANEOUS OXIDATIONS BY ISOLATED DIOXIRANES


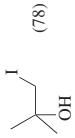

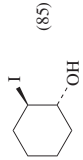

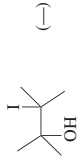



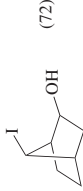
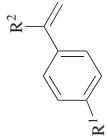
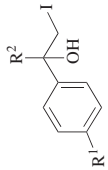

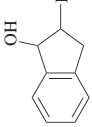
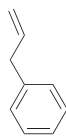
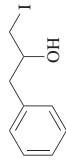
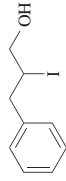

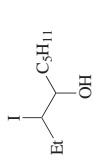
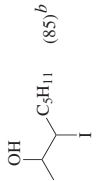
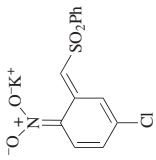
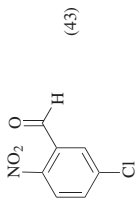

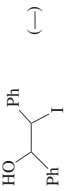
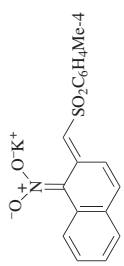
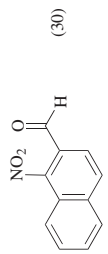
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (78)	170
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (85)	170
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (—)	170
	DMD, acetone, CH_2Cl_2 , 0° or 15°	 (—)	496
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (72)	170
	1. DMD, MeI, acetone, -70° 2. -40° to rt		170
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (82)	170

TABLE 7. MISCELLANEOUS OXIDATIONS BY ISOLATED DIOXIRANES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 +  (84) ^a	170
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 +  (85) ^b	170
	DMD, acetone, THF, Ar, 20°, 5 min	 (43)	413
	1. DMD, MeI, acetone, -70° 2. -40° to rt	 (43)	170
	DMD, acetone, THF, Ar, 20°, 5 min	 (30)	413

^a These two products were obtained as a mixture in a ratio of 65:35.

^b These two products were obtained as a mixture in a ratio of 50:50.

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CHAPTER 2

ELECTROPHILIC FLUORINATION WITH N-F REAGENTS

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INTRODUCTION

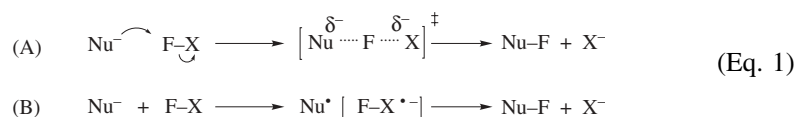
The synthesis of selectively fluorinated molecules is an important challenge in organic chemistry. This topic has received considerable attention because of the utility of fluorinated compounds in a wide variety of disciplines. There are three types of fluorinations depending on whether the fluorine atom is radical, anionic, or cationic. Fluorine radicals are of little synthetic use because of the difficulties in controlling their reactivity. Fluorine, which is the most electronegative of all elements, is utilized in nucleophilic as well as electrophilic fluorinations. Fluorine acts as an electrophile when it is polarized in a positive sense by combination with a group containing electronegative elements. Molecular fluorine is the simplest reagent of this type; however, its safe handling is difficult because of its high toxicity, and its selectivity is poor because it leads to nonselective radical processes.¹ Therefore, stable, selective, and safe reagents are crucial to the development of electrophilic fluorination.

A considerable number of electrophilic fluorinating agents have been reported. Importantly, they are all made using molecular fluorine, which poses major hazards for the nonspecialist. Initially, alternative sources of positive fluorine were designed around reagents possessing the O-F moiety (i.e., fluoroxy perfluoroalkanes, acyl hypofluorites, and sulfonyl hypofluorites); however, several limitations have precluded their widespread use and commercial production has been discontinued.² Subsequently, N-F reagents emerged as generally safer and easier to handle selective sources of electrophilic fluorine. N-F reagents offer a range of fluorinating powers, and some of them are available commercially. Two classes of N-F reagents are known: neutral N-F reagents (R_2N-F) and quaternary ammonium N-F reagents ($R_3NF^+A^-$). The electron density on the nitrogen can be tuned by varying the adjacent groups. The fluorinating power of neutral N-F reagents is increased by adjacent carbonyl or sulfonyl groups, with sulfonimides providing the most electrophilic F^+ donors. *N*-Fluoro quaternary ammonium salts are usually more powerful electrophilic fluorinating reagents than those of the neutral N-F class, with the exception of *N*-fluorobis(trifluoromethanesulfonyl) imide [$(CF_3SO_2)_2NF$], which is no longer commercially available. The popularity of N-F reagents comes from the fact that they possess a long shelf life; several are commercially available, and they can be handled safely in glassware. The main drawback with N-F reagents is the preferential use of molecular fluorine for their preparation, thus limiting their synthesis to specialized laboratories.

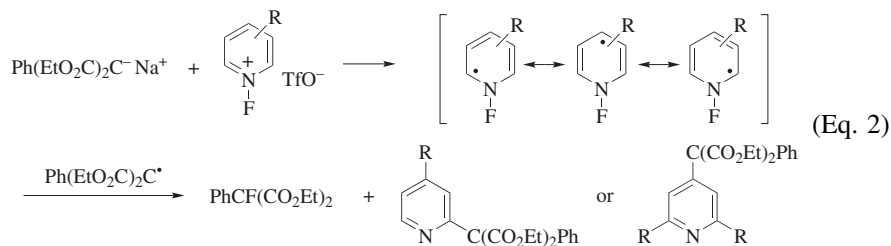
This review deals with the preparation and the use of all types of electrophilic fluorinating reagents possessing the N-F moiety. The synthesis of fluorinated compounds by formation of a C-F bond by electrophilic fluorination is covered, but the formation of heteroatom-F bonds (for example B-F, P-F, and S-F bonds) is not. The chemistry of fluorine-18 organic compounds is not covered.³⁻⁵ Inorganic N-F compounds such as trifluoroamine *N*-oxide,^{6,7} dinitrogen difluoride,⁸ fluorine nitrate,⁹ and tetrafluoroammonium or fluorodiazonium salts¹⁰⁻¹² are not considered in this chapter nor is the use of xenon difluoride and its homologs.¹³ Several reviews of electrophilic fluorination have been published.^{1,14-30}

MECHANISM

In electrophilic fluorination the symbol "F⁺" is often used to denote transfer of fluorine, although neither free nor solvated fluoronium ion is believed to be involved because of the very high molar enthalpy of formation of gaseous fluoronium ion (1760 kJ mol⁻¹). Since the introduction of the N-F reagents, the mechanism of electrophilic fluorination has been the subject of controversy. There are two possible mechanistic pathways (Eq. 1). Mechanism A involves the classical S_N2 pathway and is invoked for the fluorination of nucleophilic substrates. The displacement of X⁻ in a direct attack by the nucleophile on the fluorine atom is interpreted as a simple nucleophilic substitution reaction. Mechanism B involves a single-electron transfer (SET) followed by a very fast recombination of the radical derived from the nucleophile and the radical anion derived from the F-X reagent in a tight pair within a solvent cage. The fluorine atom is transferred to the nucleophilic moiety and the X residue leaves as an anion.

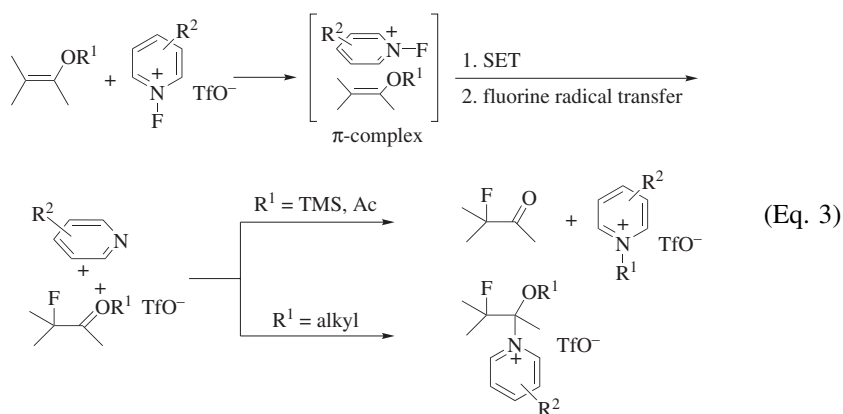


Alkyl and aryl Grignard reagents, which are prone to undergo SET, react with *N*-fluoropyridinium salts (FP) to give the fluorinated products, whereas organolithiums do not.³¹ The greater reactivity of FP toward Grignard reagents supports the SET mechanism. However, organolithium reagents are also reported to react by SET.³² Thus, caution should be taken when invoking the SET mechanism with FP reagents. On the other hand, syntheses of fluorobenzene from phenyllithium or phenylmagnesium bromide with *N*-fluoro-*o*-benzenedisulfonimide (NFOBS), which give similar yields and small amounts of biphenyl, provide support for the S_N2 mechanism.³³ Reactions of sodium diethyl phenylmalonate with various *N*-fluoropyridinium triflates (FP-OTf) give the expected fluorinated products along with diethyl phenyl(2-pyridyl)malonate or diethyl phenyl(4-pyridyl)malonate byproducts that can be explained by the SET mechanism, as shown in Eq. 2.³¹

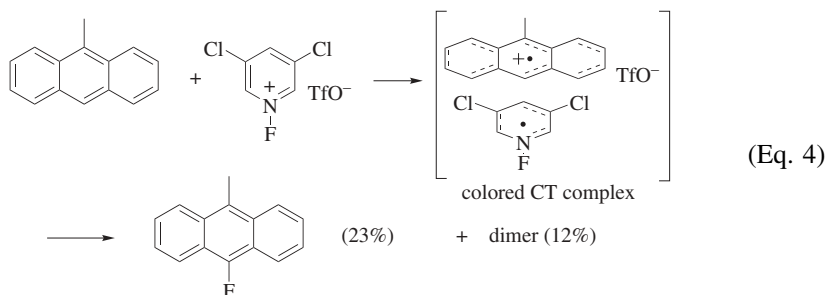


The fluorination of enol derivatives with FP reagents proceeds through the formation of a π-complex, followed successively by electron and fluorine radical transfers (Eq. 3).³¹ The oxocarbenium salt undergoes subsequent conversion to α-fluoro ketones (R¹ = SiMe₃, Ac) or to β-F alkylpyridinium salts (R¹ = alkyl).

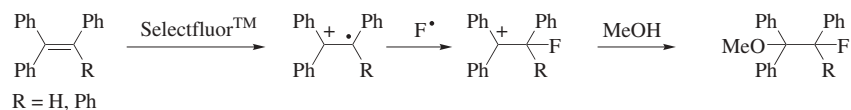
An oxocarbenium salt that further rearranges has also been suggested in the reaction of norbornene with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (SelectfluorTM).³⁴



Initial formation of a colored charge-transfer (CT) complex followed by an SET mechanism was invoked in the reaction of alkenes and aromatics with *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides.³⁵ Support for this hypothesis includes the fact that 1,4-dinitrobenzene, an efficient electron-transfer quencher, inhibits the fluorination of *trans*- β -methylstyrene.³⁵ The ortho-directed fluorination of *N,N*-dimethylaniline by perfluoropiperidine was also explained in terms of a localized single-electron transfer process within a CT complex.³⁶ Further evidence for the SET mechanism was found in the reaction of 2-naphthol with *N*-fluoro-3,5-dichloropyridinium triflate (3,5-Cl₂FP-OTf) in which the initial orange color of the π -complex formed between the reagent and the substrate disappears as fluorination proceeds.³¹ Similar conclusions have been drawn from experiments with 2,6-dimethoxynaphthalene or 9-methylantracene (Eq. 4).^{37,38} In these reactions, the fluorinating agent 3,5-Cl₂FP-OTf interacts with electron-rich aromatics to form electron-donor-acceptor complexes with characteristic CT absorption bands. Photo-excitation at the CT band dramatically increases the rate and yield of the fluorination.³⁷

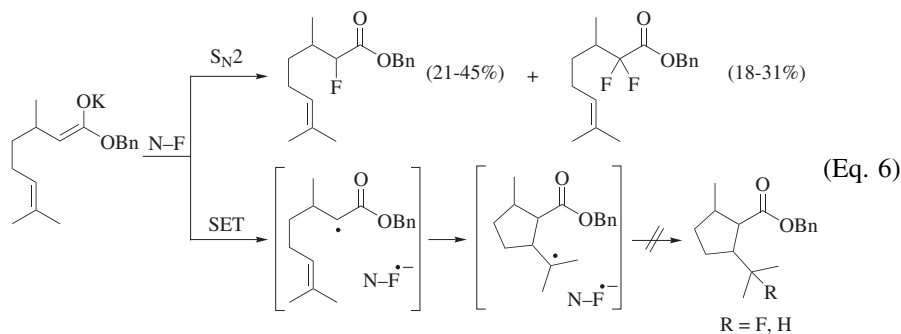


Electrospray ionization ESI-MS and ESI-MS/MS experiments were conducted to monitor the reactions of triphenylethylene and tetraphenylethylene with SelectfluorTM in which detection and characterization of radical cationic intermediates support an SET mechanism for electrophilic fluorination as depicted in Eq. 5.^{39,40}



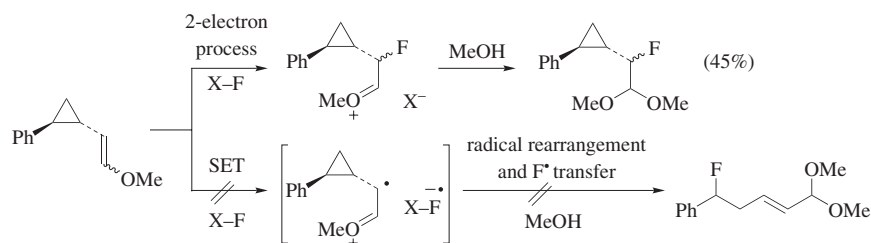
(Eq. 5)

Judicious experiments were carried out to analyze the question of SET vs. nucleophilic substitution in electrophilic fluorination. A potassium ester enolate containing a 5-hexenyl carbon chain was designed as a radical clock, which should cyclize to a cyclopentylmethyl radical intermediate if electron transfer occurs. The complete absence of the cyclic fluorinated product was considered as proof that the fluorination does not occur via free-radical intermediates (Eq. 6).^{41,42}



(Eq. 6)

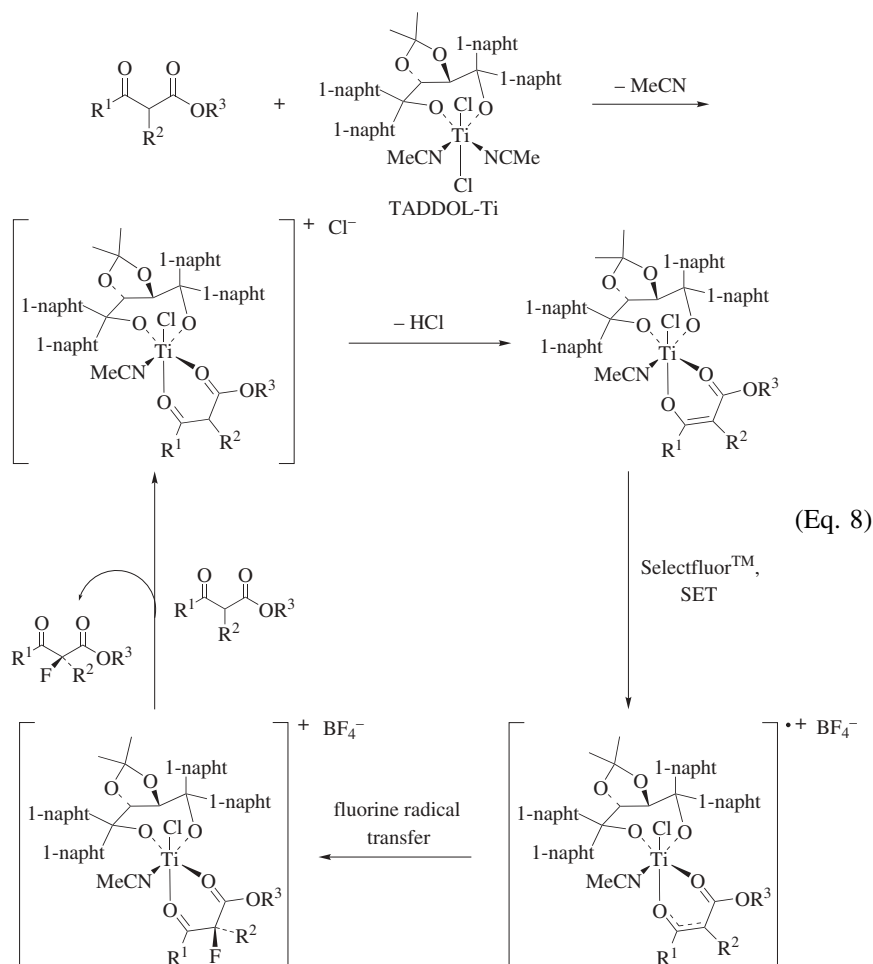
Radicals formed on hypersensitive radical probes containing a phenylcyclopropyl moiety are expected to trigger the opening of the cyclopropyl ring at a rate of 10^{11} sec^{-1} .⁴³ However, no product characteristic of a radical process is found in reactions of the cyclopropyl compound shown in Eq. 7 with SelectfluorTM or with *N*-fluorobenzenesulfonimide (NFSI); formation of the fluorinated product was ascribed to a two-electron process.



(Eq. 7)

The mechanism of fluorine transfer between SelectfluorTM and dimethylcyclo[3.3.1]nonane has been investigated by a semiempirical PM3 method.⁴⁴ It

was demonstrated that the mechanism corresponds to an S_N2 substitution involving single-electron transfer synchronous with the cleavage of the N-F bond and formation of the C-F bond. The arguments for an S_N2 pathway are quite convincing; however, the possibility of electron transfer followed by a very fast recombination within a solvent cage to fluorinated products cannot be ruled out. Computational QM/MM first-principle molecular dynamics and experimental investigations in the TADDOL-Ti catalyzed fluorination of β -keto esters with SelectfluorTM strongly support an SET mechanism as a pathway for fluorine transfer.⁴⁵ One electron is removed from the neutral titanium-enolato complex which acts as a reducing agent, whereas SelectfluorTM is the electron acceptor. The resulting intermediate consists of a singlet diradical which recombines to create the new carbon-fluorine bond (Eq. 8).



The lifetime of the intermediate radicals is estimated at a few femtoseconds, 10^4 times shorter than the time required for ring opening of the phenylcyclopropyl

radical.⁴⁵ It was concluded from these studies and from the fact that Selectfluor™ lacks a polarizable π -electron donor center to stabilize the fluorine radical that the unstabilized fluorine radical would combine immediately with the radical cation resulting from an SET on the substrate.

The reaction of various types of substrates with different fluorinating agents has been investigated; however, the question of mechanism is as yet unresolved and it is possible that different substrates are fluorinated by different mechanisms. The difference between mechanisms A and B (Eq. 1) can be very difficult to establish, and even methods to study extremely fast reactions may not allow a definitive elucidation of the mechanism of electrophilic fluorination.⁴⁶

SCOPE AND LIMITATIONS

Electrophilic Fluorinating Agents

A wide range of substrates have been successfully fluorinated with electrophilic fluorinating agents. The choice of a fluorinating agent is mainly determined by its fluorinating power and its availability. Whereas a reagent such as *N*-fluorobis(trifluoromethanesulfonyl)imide, $(\text{CF}_3\text{SO}_2)_2\text{NF}$, is much more reactive than others, applications are limited because of its commercial unavailability. Concerning the fluorinating power of N–F reagents, extensive qualitative information has been obtained through their chemical and electrochemical reactivities, and computational studies.^{20,47–55} The reaction of N–F class fluorinating reagents with solvents has also been studied in detail.⁵⁶

Chiral, enantiopure fluorinating agents are not discussed here, but will be described in the enantioselectivity section (see later in the text).

***N*-Fluorosulfonamides and *N*-Fluorosulfonimides.** The development of these two classes of neutral *N*-fluoro compounds has been based on two principles: the enhancement of fluorinating power by decreasing the electron density at the nitrogen atom, and the use of electron-withdrawing groups to stabilize the resulting anion after the loss of fluorine from nitrogen. *N*-Fluorosulfonamides (Fig. 1) are prepared by treatment of *N*-alkyl- or *N*-arylsulfonamides with molecular fluorine^{57–59} or perchloryl fluoride, FClO_3 ,⁶⁰ under a variety of conditions. The alkali metal salts of the parent sulfonamides can also be fluorinated with molecular fluorine.⁶¹ Alternatively, a transfer fluorination of the potassium salts of the sulfonamides with *N*-fluorobenzenesulfonimide gives the corresponding *N*-fluorosulfonamides.⁶²

N-Fluorosulfonamides are among the weakest fluorinating agents. This type of N–F compound, which possesses only a single sulfonyl group and an *N*-alkyl or *N*-aryl substituent, is not reactive enough to fluorinate less reactive substrates such as enol ethers or arenes. In addition, since α -hydrogen atoms are present in the *N*-alkyl residue, *N*-fluoro-*N*-alkylsulfonamide reagents readily undergo hydrogen fluoride elimination by base. Use of a nonpolar solvent or solvent mixture suppresses elimination.⁶⁹ *N*-Fluorosulfonamides possessing an *N*-*tert*-butyl group as the *N*-alkyl residue were designed to circumvent the

			$\begin{array}{c} \text{O}_2 \\ \\ \text{R}^1\text{-S}-\text{N}-\text{F} \\ \\ \text{R}^2 \end{array}$		
R ¹	R ²	Ref	R ¹	R ²	Ref
CF ₃	4-(2,3,5,6-F ₄ -pyridinyl)	57, 61	4-MeC ₆ H ₄	Me	69
CF ₃	4-(2,5,6-F ₃ -pyrimidyl)	57	4-MeC ₆ H ₄	<i>t</i> -Bu	69
CF ₃	Me	59, 63	4-MeC ₆ H ₄	<i>c</i> -C ₆ H ₁₁	69
CF ₃	<i>n</i> -Bu	59	4-MeC ₆ H ₄	exo-2-norbornyl	69
CF ₃	<i>t</i> -Bu	64	4-MeC ₆ H ₄	endo-2-norbornyl	69
C ₂ F ₅	alkyl	59	4-MeC ₆ H ₄	CH ₂ Bu- <i>t</i>	69
C ₈ F ₁₇	alkyl	59	4-MeC ₆ H ₄	<i>n</i> -Bu	59, 65
C ₆ F ₅	<i>n</i> -Pr	59, 65	4-MeC ₆ H ₄	<i>n</i> -Pr	59, 65
C ₆ F ₅	CH ₂ Bu- <i>t</i>	59, 65	<i>n</i> -Bu	CH ₂ Bu- <i>t</i>	69
4-FC ₆ H ₄	alkyl	59, 66	<i>t</i> -Bu	Me	59, 65
4-CF ₃ C ₆ H ₄	alkyl	59	<i>t</i> -Bu	<i>n</i> -Bu	59, 65
Ph	<i>t</i> -Bu	67, 68	<i>t</i> -Bu	CH ₂ Bu- <i>t</i>	59, 65

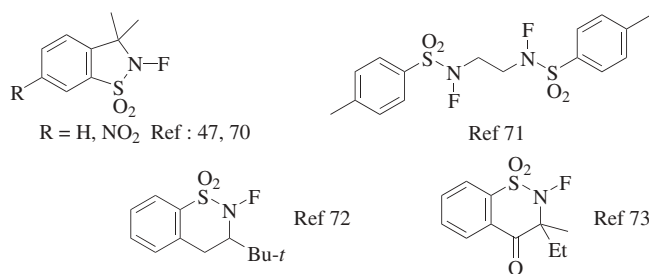
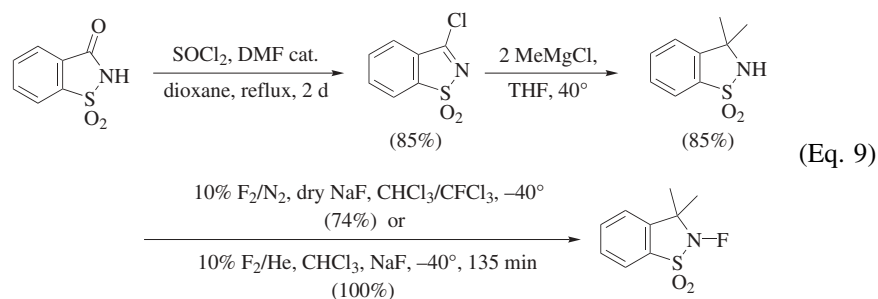


Figure 1. *N*-Fluorosulfonamides.

elimination reaction, but the reagents were obtained in low yields. The three-step preparation of the saccharin-derived *N*-fluorosultam shown in Eq. 9 furnishes a versatile fluorinating agent; it shows increased stability since it lacks an α -hydrogen atom.^{70,74–77} The fluorination step for its preparation is performed with molecular fluorine diluted in nitrogen.⁷⁴ The reaction can also be carried out with perchloryl fluoride, FClO₃, which presents drawbacks such as unwanted chlorination side-reactions, potential explosions, unavailability, and difficult handling.⁷³ The saccharin-derived *N*-fluorosultam is a white crystalline solid melting at 114–116°; the ¹⁹F NMR signal is at δ 9.8 ppm in CDCl₃.⁷⁰



N-Fluorosulfonylimides constitute a superior class of electrophilic fluorinating agents that are effective in the fluorination of aromatics, alkenes, carbanions, and ketone enolates. The reactivity is enhanced by decreasing the electron density on nitrogen by the two sulfonyl groups that also stabilize the resulting anion formed by the loss of fluorine from nitrogen. In particular, *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides, $(R_fSO_2)_2NF$, are some of the most powerful electrophilic fluorinating agents. Symmetric, dissymmetric, cyclic, and difunctional *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides are known (Fig. 2).^{63,78,79} They are all stable for prolonged periods at room temperature and are preferably stored in fluoropolymer plastic containers. Storage in Pyrex results in a slow etching of the glass.⁶³

The preparation and characterization of *N*-fluoroimidodisulfonyl fluoride, $(FSO_2)_2NF$, is described but its application in electrophilic fluorination is not reported.⁸⁰ *N*-Fluorobis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2NF$, is especially attractive because of its favorable physical properties and high reactivity, but is no longer commercially available.^{63,78,81,82} A five-step synthesis produces $(CF_3SO_2)_2NF$ in 76% yield based on the starting trifluoromethanesulfonyl fluoride. Formation of the N–F bond is accomplished by treating neat bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2NH$, with undiluted molecular fluorine in a sealed metal bomb.^{81,83} Alternatively, fluorination of $(CF_3SO_2)_2NH$ or its lithium salt with diluted molecular fluorine provides milder fluorination conditions.⁸⁴ The ¹⁹F NMR spectrum shows a signal at $\delta -33.7$ ppm in $CDCl_3$, which is upfield from $CFCl_3$ (internal standard).⁶³

N-Fluorobis[(alkyl)sulfonyl]imides and *N*-fluorobis[(aryl)sulfonyl]imides are hydrocarbon analogs of the above-mentioned class of reagents. The two most extensively studied reagents of this class are *N*-fluorobenzenesulfonylimide (NFSI) and *N*-fluoro-*o*-benzenedisulfonylimide (NFOBS) (Fig. 3). These reagents display high reactivity, stability, and ease of preparation, and are the ones of choice for the selective electrophilic monofluorination of enolates and carbanions.

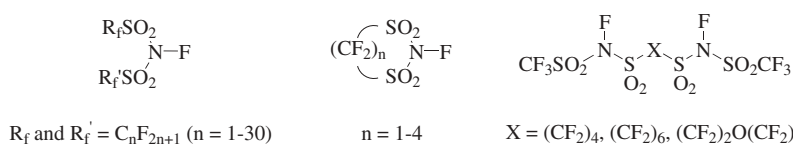


Figure 2. *N*-Fluorobis[(perfluoroalkyl)sulfonyl]imides.

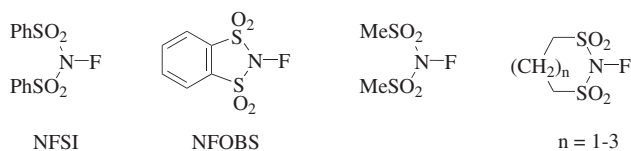
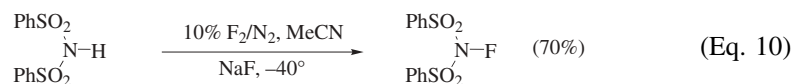
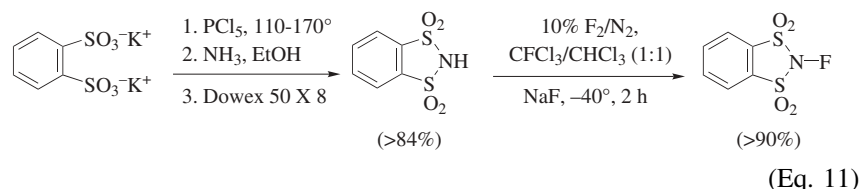


Figure 3. *N*-Fluorobis[(aryl)sulfonyl]imides and *N*-Fluorobis[(alkyl)sulfonyl]imides.

NFSI is one of the most popular fluorinating agents and is commercially available. It can be readily prepared in 70% yield by treatment of (bis)benzenesulfonimide in acetonitrile solution with 10% molecular fluorine in nitrogen at -40° (Eq. 10).^{85,86} *N*-Fluorosulfonimides can also be prepared from an alkali metal salt of a sulfonimide.⁸⁷ NFSI is a stable, easy-to-handle, crystalline solid that is soluble in many common solvents. Its reactivity is situated between the *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides and the *N*-fluoroalkylsulfonamides.



NFOBS is a stable, easily prepared, and commercially available fluorinating agent.^{33,88} *o*-Benzenedisulfonimide, the precursor of NFOBS, is prepared in two steps from the dipotassium salt of *o*-benzenedisulfonic acid by conversion to the disulfonyl chloride with phosphorus pentachloride followed by treatment with an ethanolic ammonia solution. NFOBS is obtained by passing molecular fluorine in nitrogen through a solution of *o*-benzenedisulfonimide in trichlorofluoromethane/chloroform (1 : 1). Optimized conditions of concentration, temperature, and time give NFOBS in better than 90% yield as a white crystalline solid melting at $139-141^\circ$ with decomposition (Eq. 11). The ^{19}F NMR spectrum shows a signal at $\delta -12$ ppm in C_6D_6 , which is upfield from CFCl_3 (internal standard).^{33,88}



Other *N*-fluorobis[(alkyl)sulfonyl]imides include *N*-fluorobis(methanesulfonyl)imide⁸⁹ and *N*-fluoro[1,3,2]dithiazinane-1,1,3,3-tetraoxide^{89,90} (Fig. 3).

***N*-Fluorocarboxamides.** *N*-Fluorocarboxamides have received little attention and have not gained much popularity except for ^{18}F -*N*-fluorolactams, which have found utility in the field of radiofluorination reactions.⁹¹ A number of *N*-fluoroamides,^{66,92} *N*-fluorolactams,⁹² *N*-fluorocarbamates,⁹³ and *N*-fluoroureas⁹⁴ have been synthesized but have not been exploited as electrophilic fluorinating agents. Similarly, the potential of *N*-fluoroperfluorosuccinimide and *N*-fluoroperfluoroglutarimide has not been studied (Fig. 4).⁹⁵

For example, perfluoro-*N*-fluoro-*N*-(4-pyridyl)acetamide] is prepared by direct fluorination of the corresponding sodium salt with molecular fluorine. Applications are limited to those reported by the group that synthesized this reagent.⁹⁶ On the other hand, *N*-fluoro-2-pyridone is obtained by reaction of 5% fluorine in nitrogen and 2-(trimethylsiloxy)pyridine in trichlorofluoromethane at -78° (Eq. 12).⁹⁷ It is a white solid melting at $50-53^\circ$, and is used in the

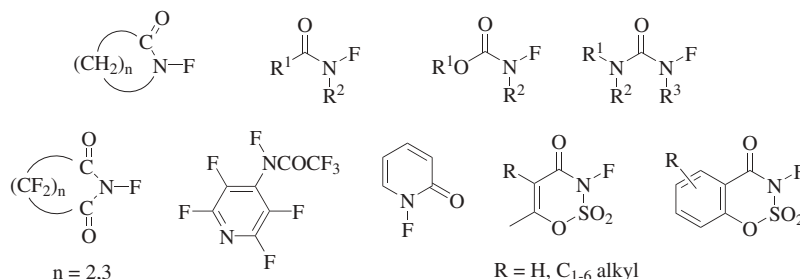
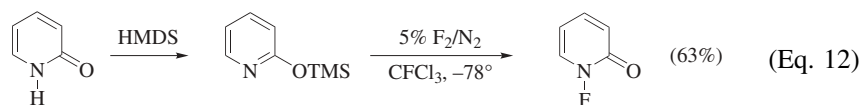


Figure 4. *N*-Fluorocarboxamides.

preparation of some fluoromalonates⁹⁷ as well as in the fluorination of enamines and Grignard reagents.⁹⁸ The driving force for this fluorinating agent is the rearomatization of the pyridine nucleus after fluorination. The 6-chloro and 3,4,5,6-tetrachloro derivatives are known but have not been used as fluorinating agents.⁹⁹



N-Fluorooxathiazinone dioxides (Fig. 4) are prepared by the fluorine or alkali metal fluoride fluorination.^{100–102} They possess both a carbonyl and a sulfonyl group that decreases the electron density on the nitrogen. Purification of these reagents is rather difficult since they are not stable in air at room temperature, with the exception of the fused-ring derivative that is a stable, effective fluorinating agent obtained in 83% yield as a solid melting at 61°. ¹⁰⁰ Various derivatives with different substitution patterns on the aromatic ring have been synthesized.¹⁰¹ Fluorination of a variety of substrates can be carried out in a wide range of solvents including apolar solvents such as hexane.

Neutral *N*-Fluoro Heterocycles. *N*-Fluoroperfluoropiperidine (Fig. 5) is the first N–F compound reported to act as a fluorinating agent, but it has received little attention because its preparation yield by Simons electrochemical fluorination in anhydrous hydrogen fluoride is only 13% from 2-fluoropyridine,^{103–105} and it is a volatile liquid boiling at 49.5°. The morpholino analog of the piperidine is also prepared by Simons electrochemical fluorination,¹⁰⁶ as well as the *N*-fluoroperfluoro-2,2,6,6-tetramethylpiperidine (Fig. 5, R = CF₃).¹⁰⁷ The latter compound was devised to maximize the electrophilic character of the fluorine atom of the NF group and to eliminate problems caused by the release of fluoride or by dehydrofluorination. Polymeric analogs have been described, but are difficult to prepare by a LaMar direct fluorination procedure (Fig. 5).^{108,109}

The synthetic utility of *N*-fluoro-2,4-dinitroimidazole (NF-2,4-DNI) (Fig. 6) has been tested in the fluorination of polycyclic aromatic hydrocarbons.¹¹⁰ This

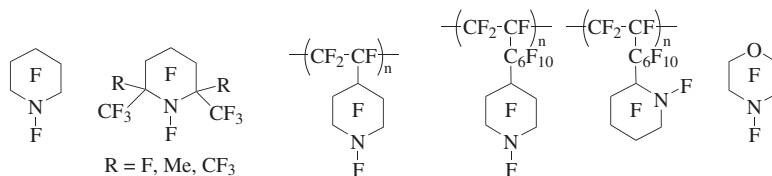


Figure 5. *N*-Fluoroperfluoropiperidines and *N*-Fluoroperfluoromorpholine.

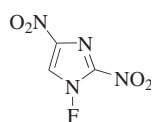


Figure 6. *N*-Fluoro-2,4-dinitroimidazole.

reagent is obtained as a white solid by fluorination of 2,4-dinitroimidazole with 5% molecular fluoride in nitrogen. The electron-withdrawing effect of the nitro groups was expected to weaken the N-F bond, allowing transfer fluorination under mild conditions.

***N*-Fluoroammonium Compounds.** Because *N*-fluoroperfluoropiperidine liberates the imidoyl fluoride perfluoro-1-azacyclohex-1-ene, which competes with its progenitor for the substrate, *N*-fluoroammonium compounds capable of effecting site-selective fluorination were sought. *N*-Fluoroammonium salts have the advantage of releasing fairly innocuous tertiary amines. *N*-Fluoropiperidinium chlorates (Fig. 7) are obtained by reaction of the piperidines with perchloryl fluoride, but have not been exploited in electrophilic fluorination.^{111,112}

N-Fluoroquinuclidinium fluoride (NFQN-F), which is obtained by direct fluorination of quinuclidine in trichlorofluoromethane at low temperature (Scheme 1), is an extremely hygroscopic, white solid melting at 126–128°. It is also not perceptibly soluble in a wide range of solvents.^{114,115} *N*-Fluoroammonium trifluoroacetates and heptafluoropropionates are also hygroscopic and, like the fluorides, are best manipulated by using dry-box techniques.¹¹⁴ Analogs obtained by exchanging the fluoride counterion for another anionic species, including BF₄⁻, Ph₄B⁻, TfO⁻, PF₆⁻, FSO₃⁻, and CF₃SO₃⁻, solve the hygroscopicity and insolubility problems.¹¹⁴ On the other hand, *N*-fluoroquinuclidinium triflate

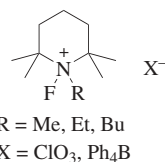
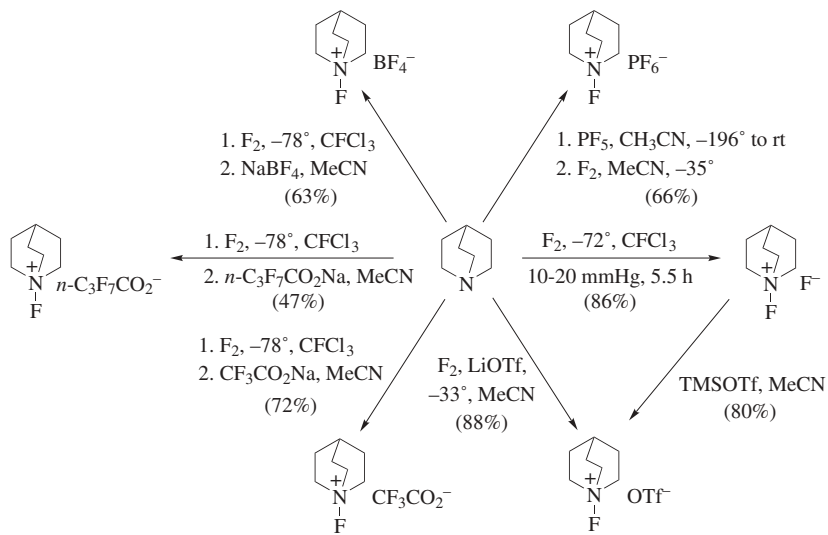


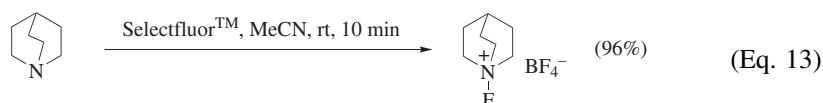
Figure 7. *N*-Fluoropiperidinium salts.



Scheme 1. Preparation of *N*-fluoroquinuclidinium salts.

(NFQN-OTf) is a non-hygroscopic, white solid stable in air below 180° that is easier to use than the corresponding fluoride.^{116,117} It is prepared in high yield in a one-pot procedure (Scheme 1).¹¹⁷ Alternatively, fluorine smoothly attacks quinuclidine pentafluorophosphorane in acetonitrile to give the corresponding *N*-fluoroquinuclidinium hexafluorophosphate (NFQN- PF_6) (Scheme 1); quinuclidine trifluoroborane and quinuclidine sulfur trioxide give the corresponding *N*-fluoroquinuclidinium salts (NFQN-X, X = BF_4 , FSO_3) (Scheme 1).¹¹⁸

N-Fluoroquinuclidinium tetrafluoroborate can also be prepared by transfer fluorination of quinuclidine with SelectfluorTM in excellent yield (Eq. 13).¹¹⁹



Among diamine analogs of *N*-fluoroquinuclidine, the 1,4-difluoro-1,4-diazo-niabicyclo[2.2.2]octane (or triethylenediamine, TEDA) salts (Fig. 8, R = F) possess a higher fluorine content and are more powerful by virtue of the strong electron-withdrawing effect of the second FN^+ group. However, the synthesis is difficult and only one electrophilic fluorine is transferred per molecule because of self-defluorination of the mono *N*-fluoro salt.¹²⁰⁻¹²³ Quaternization of one of the two bridgehead nitrogens prior to fluorination provides a range of F-TEDA salts having reactivity tuned through variation in the electronegativity of the quaternizing group; however, no persuasive evidence for a counter-anion effect was noted (Fig. 8).^{124,125}

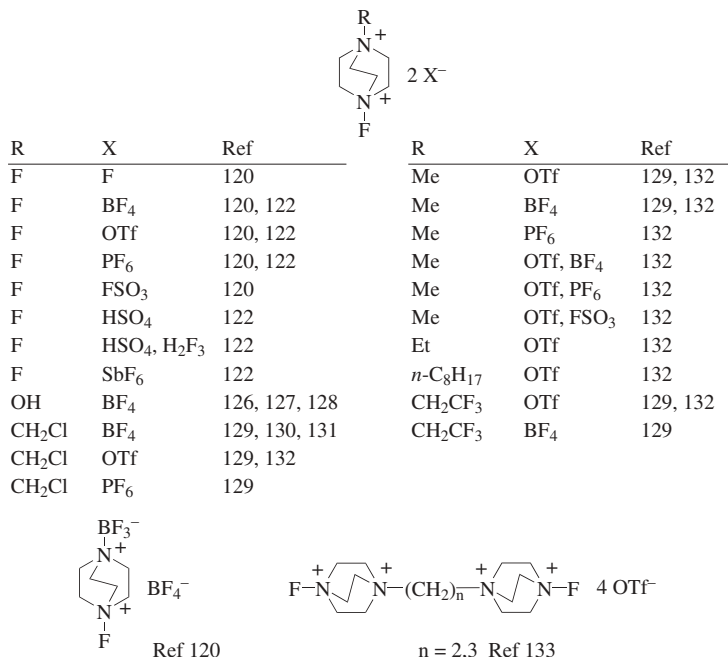


Figure 8. F-TEDA salts.

These reagents belong to the SelectfluorTM family, the best known of which is 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate), which is simply called SelectfluorTM (Fig. 9). The second most popular fluorinating agent of this family is 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate), which is called AccufluorTM or NFTh (Fig. 9).¹²⁶

Electrochemical studies⁵¹ and chemical behavior in fluorination of a wide range of organic substrates indicate that the fluorinating power of SelectfluorTM is superior to most of the N-F reagents and approaches closely that of *N*-fluorobis[(trifluoromethyl)sulfonyl]imide. The fluorinating power within the SelectfluorTM family increases with increasing electron-withdrawing power of the R group (Me \approx Et \approx *n*-octyl < CH₂Cl < CH₂CF₃). SelectfluorTM is a white solid. It is a user-friendly, air- and moisture-stable, non-volatile, high-melting

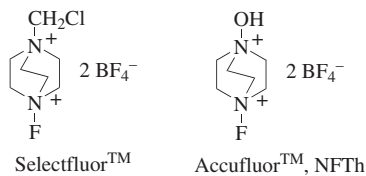
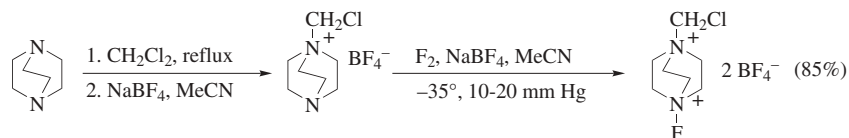


Figure 9. The two most popular F-TEDA salts.

reagent (apparent mp 190°) capable of introducing fluorine into organic molecules with a remarkably broad scope of reactivity.^{46,129,134,135} SelectfluorTM is very soluble in cold water (176 g/L at 20°) and in dilute hydrochloric acid, moderately soluble in acetonitrile (50 g/L at 20°), dimethylformamide, and slightly soluble in acetone. It decomposes in dilute aqueous sodium hydroxide and reacts rapidly with cold dimethyl sulfoxide and slowly with dimethylformamide on heating.¹³⁴ In addition, it does not require special equipment or handling techniques. The most convenient process for preparing SelectfluorTM is depicted in Eq. 14. Chloromethylation of TEDA in refluxing dichloromethane is followed by anion metathesis to incorporate the tetrafluoroborate anion. Then, fluorination is carried out in acetonitrile at -35° in the presence of sodium tetrafluoroborate either in a closed system with neat fluorine or using a flow method by passing a fluorine-nitrogen blend through the solution (Eq. 14).¹³⁰⁻¹³²

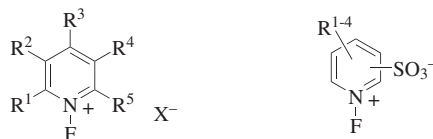


(Eq. 14)

Another fluorination process involves Lewis acid adducts obtained by treatment of the TEDA monoquaternary salts with, for example, boron trifluoride-diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$). The 1 : 1 TEDA monoquat- BF_3 adduct salts are then treated with molecular fluorine to give the SelectfluorTM reagents.¹³⁶ To complete the SelectfluorTM family, the 1,2- or 1,3-bis(4-fluoro-1,4-diazoniabicyclo[2.2.2]oct-1-yl)ethane and -propane tetratrilates (Fig. 8) have been prepared by the closed-system fluorination technique.¹³³

***N*-Fluoroiminium Compounds.** *N*-Fluoropyridinium salts are relatively easy to make. They are stable and nonhygroscopic, with the exception of the fluoride salts that decompose to 2-fluoropyridine and hydrogen fluoride explosively at temperatures above -2° .¹³⁷⁻¹³⁹ In practice, fluorinations with *N*-fluoropyridinium fluorides can be carried out only at temperatures below -20° . Replacement of the fluoride by other, less nucleophilic counter-anions or internal salts greatly improves the stability of the reagents.¹⁴⁰⁻¹⁵⁰ Optimal media for *N*-fluoropyridiniums are dichloromethane, tetrahydrofuran, and acetonitrile, whereas dimethyl sulfoxide, dimethylformamide, and 1-methyl-2-pyrrolidone cause decomposition to yield 2-pyridone as a major product. A very large number of reagents of this type have been synthesized, each with a different pyridine derivative (Fig. 10).^{21,151,152}

Counteranion-bound *N*-fluoropyridinium salts, such as *N*-fluoropyridinium-2-, -3-, and -4-sulfonates are poorly soluble in organic solvents and thus exhibit low reactivity. Addition of a strong acid converts the reagents into the more reactive *N*-fluorosulfopyridinium salts that accelerate fluorinations.¹⁴⁰ Most conveniently,



R¹-R⁵ = H, halogen, alkyl, aryl, acyl, acyloxy, alkoxy, alkoxy, alkoxy, aryloxy, aryloxy, OH, acylthio, amido, carbamoyl, nitro, cyano, alkanesulfonyl, alkanesulfonyloxy, arenesulfonyl, arenesulfonyloxy, sulfonate

R¹, R², R³, R⁴, R⁵ = combinations to make cyclic structures

X = conjugate base of Brønsted acids excluding Cl, Br, I; X may be bonded to R¹-R⁵

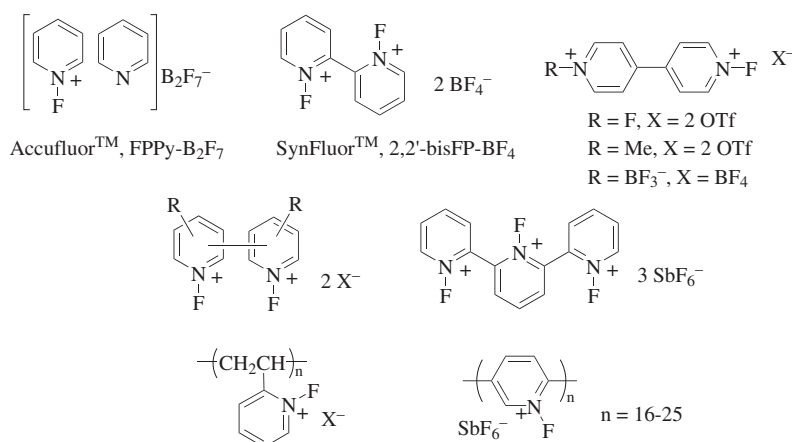
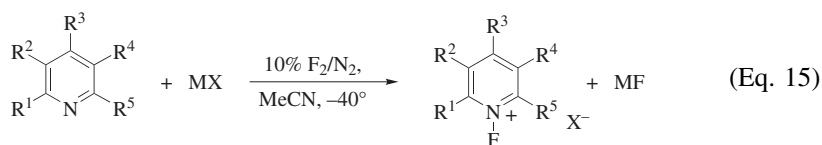
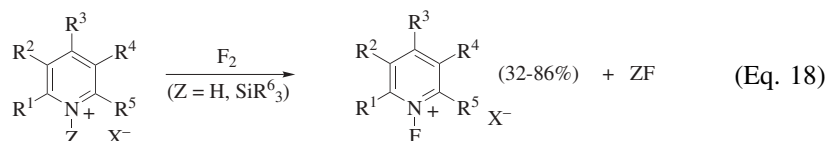
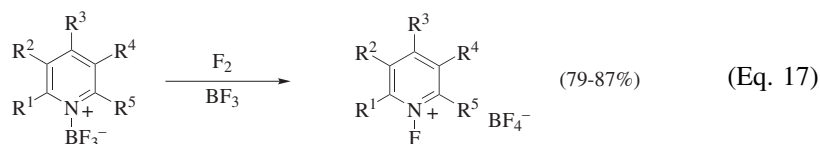
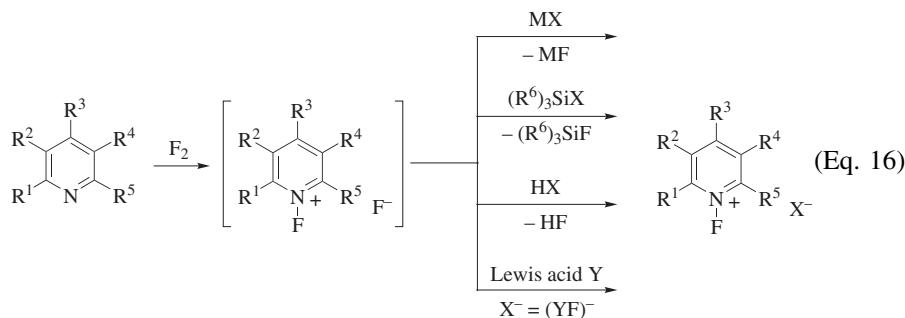


Figure 10. *N*-Fluoropyridinium fluorinating agents.

pyridinium salts are prepared by bubbling molecular fluorine through a solution of the pyridine and an inorganic salt in acetonitrile at low temperature (Eq. 15). Alternatively, in situ generated pyridinium fluorides are treated with inorganic salts, silyl esters, Brønsted acids, or Lewis acids (Eq. 16).^{99,153} Pyridinium salts can also be prepared by reaction of an adduct of the parent pyridine with a Lewis acid such as boron trifluoride with molecular fluorine (Eq. 17), by reaction of a preformed Brønsted acid salt of the parent pyridine with molecular fluorine, or by reaction of an *N*-trimethylsilylpyridinium triflate with molecular fluorine in acetonitrile at -40° (Eq. 18).^{99,141,153}





The fluorinating ability of *N*-fluoropyridinium salts is tuned by introduction of electron-withdrawing or -donating substituents on the pyridine ring.^{31,154} Electron-withdrawing groups enhance the fluorinating power, thus making the agents suitable for reactions with aromatics, whereas electron-donating groups decrease the fluorinating power, thus making the agents ideal for reactions with carbanions. Size-controlled particles of *N*-fluoropyridinium agents, produced by pulverization in a spray dryer, have improved reactivity.¹⁵⁵ *N*-Fluoropyridinium salts are stable, crystalline solids with melting points ranging from 90° to above 300°, which usually do not require special handling, with the exception of perchlorates that can undergo violent explosions. These reagents are more reactive than *N*-fluoroammonium salts with the exception of the Selectfluor™ family. This class comprises several commercially available representatives. Among them is the *N*-fluoropyridinium pyridine heptafluorodiborate, Accufluor™, FPPy-B₂F₇ (Fig. 10), which is conveniently prepared by the reaction of fluorine with the pyridine-boron trifluoride complex.^{156,157} *N*-*N'*-Difluoro-2,2'-bipyridinium bis(tetrafluoroborate), Synfluor™ (Fig. 10), and related salts are highly reactive electrophilic fluorinating agents with the highest effective fluorine content of their class since both of the fluorine atoms are effective for fluorination.^{158–161} Synfluor™ can be synthesized in 89% yield in one pot by introducing boron trifluoride into 2,2'-bipyridine at 0°, followed by molecular fluorine diluted with nitrogen. Other -2,4'-, -3,3'-, -4,4'- bipyridinium salts, as well as higher homologs (trimers and polymers) with high effective fluorine content, have been synthesized (Fig. 10).^{133,161–163}

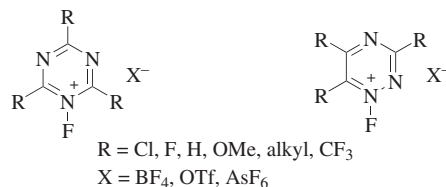
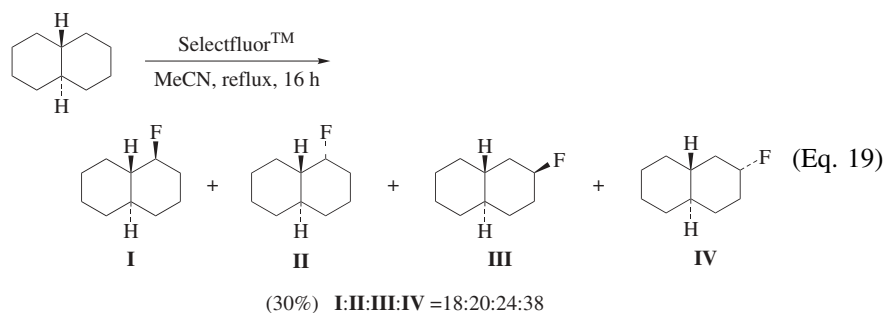


Figure 11. *N*-Fluorotriazinium fluorinating agents.

Other examples that may be included in this group of *N*-fluoroiminium compounds are the *N*-fluorotriazinium fluorinating agents (Fig. 11). *N*-Fluoro-1,3,5- and *N*-fluoro-1,2,4-triazin-ium compounds have been prepared from the corresponding triazines in acetonitrile at -35° in the presence of triflic acid in a flow fluorination reactor with a blend of fluorine and nitrogen (1 : 9, v/v).^{164–168} These reagents are moisture-sensitive solids that are best manipulated in a drybox under argon. *N*-Fluoro-1,3,5-triazin-ium compounds are used for the fluorination of aromatic substrates.¹⁶⁵

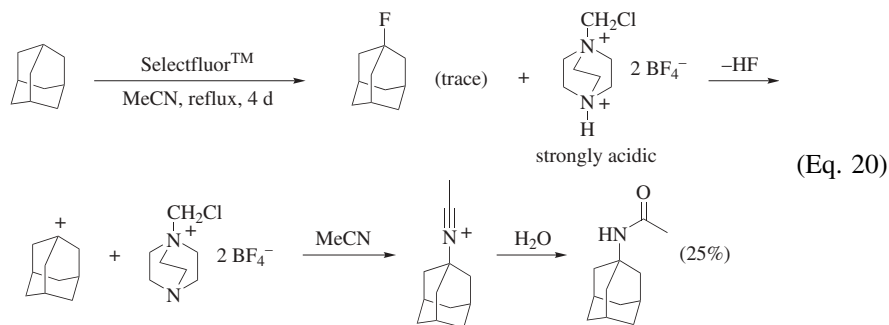
Electrophilic Fluorinations

Fluorination of Alkanes. Most reactions with electrophilic fluorinating agents involve transformation of a carbon-hydrogen bond to a carbon-fluorine bond at a carbon atom that is either sp^2 hybridized or that bears a negative charge. Selective electrophilic fluorination at a tertiary sp^3 carbon atom in a one-step process can be achieved with molecular fluorine¹⁶⁹ but is very difficult with N-F reagents. However, selective fluorination of a range of hydrocarbons (e.g., cyclohexane, decane, adamantane, norbornane, and decalins) at tertiary or secondary carbon atoms can be achieved with SelectfluorTM.^{170–172} An example of direct electrophilic fluorination of *trans*-decalin is shown in Eq. 19. The preferential fluorination of the secondary centers of *trans*- (or *cis*-) decalin by SelectfluorTM is attributed to the sterically hindered fluorinating agent which, unlike molecular fluorine, does not access the electronically preferred tertiary sites.¹⁷² An electrophilic mechanism is envisaged.



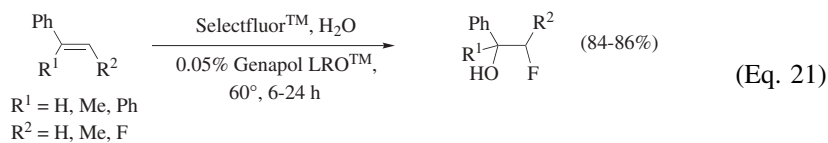
Preferably, the fluorination is conducted with alkyl nitriles as the reaction media. However, fluorination of alkanes in acetonitrile suffers from the formation

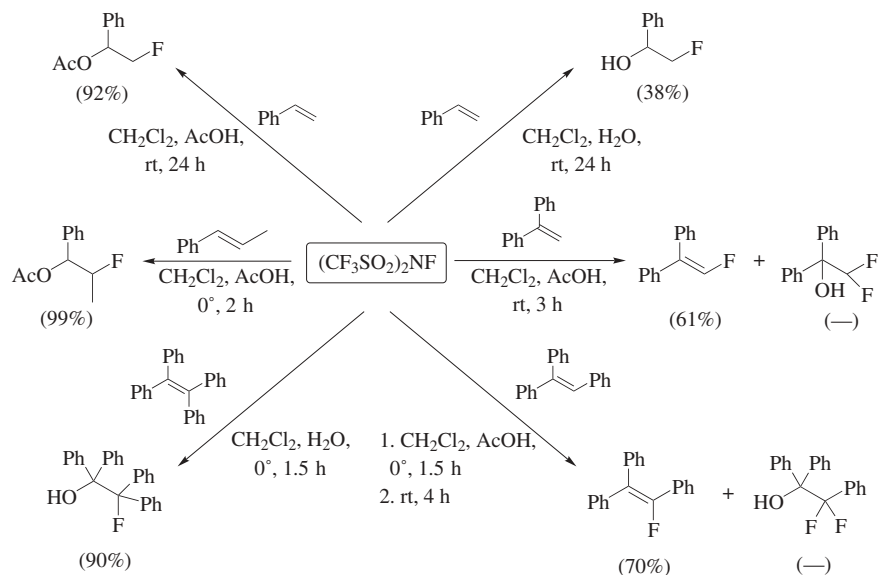
of amide derivatives after prolonged reaction as a result of the highly acidic reaction medium (Eq. 20).¹⁷²



Addition to π Bonds (Alkenes and Alkynes). The electrophilic fluorination of alkenes is performed with the most reactive N–F reagents such as $(\text{CF}_3\text{SO}_2)_2\text{NF}$, 2,3,4,5,6- $\text{Cl}_5\text{FP-OTf}$, and Selectfluor™. These reactions are addition or addition-elimination processes in which the intermediacy of a β -fluoro carbocation is postulated. As a consequence, groups that stabilize the carbocation significantly enhance the reactivity of the alkene. Reactions conducted with $(\text{CF}_3\text{SO}_2)_2\text{NF}$ in solvents of low nucleophilicity such as chloroform, dichloromethane, tetrahydrofuran, diethyl ether, and Freon™-113 give complex product mixtures. However, with excess electron-rich alkenes, some fluorinated products can be isolated. The carbocation intermediate eliminates a proton to form the fluorinated alkene or attacks the starting alkene to give a dimer. The monofluorinated alkene reacts further with the N–F reagent to give additional fluorinated products.³⁵ In solvents of higher polarity such as water, alcohols, acetic acid, hydrochloric acid, or hydrogen fluoride/pyridine, reaction of $(\text{CF}_3\text{SO}_2)_2\text{NF}$ with alkenes gives fluoro carbocation intermediates that are captured by the nucleophilic solvent; therefore, the expected Markovnikov addition products are obtained. Depending on the reaction conditions and the structure of the substrate, the fluorination of styrene and its derivatives gives various products (Scheme 2).³⁵

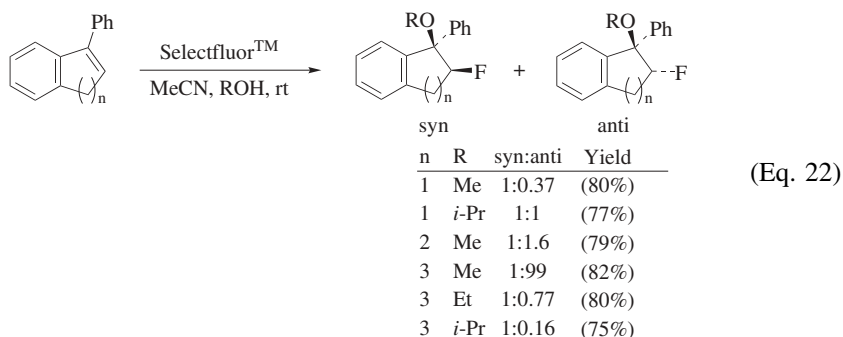
Selectfluor™ and NFlth can also be used for the synthesis of vicinal fluorohydroxy, fluoromethoxy, fluoroacetoxy, and difluoro compounds from phenyl-substituted alkenes. Both the nature of the substituents and the configuration of the alkene moderately affect the syn:anti ratio.^{126,173–176} For example, selective and effective fluorination of styrene derivatives occurs in water with Selectfluor™ in the presence of the surfactant sodium lauryl ether sulfate (Genapol LRO™) (Eq. 21).¹⁷⁷



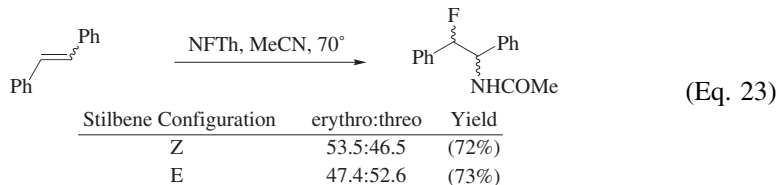


Scheme 2. Reactions of $(\text{CF}_3\text{SO}_2)_2\text{NF}$ with alkenes.

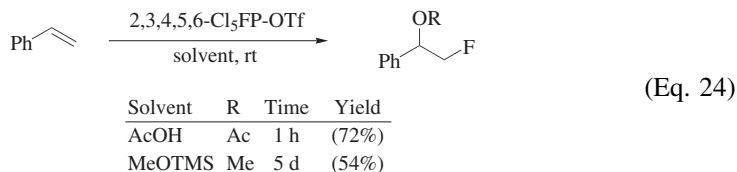
With phenyl-substituted benzocycloenes, the stereochemical outcome is strongly dependent on the ring size and structure of the alcohol. In the five-membered ring system, the syn diastereomer is favored with methanol, whereas the anti isomer is the major product in the six-membered ring system. The alcohol also has a strong impact on the syn:anti ratio observed in seven-membered ring systems (Eq. 22).^{174,178}



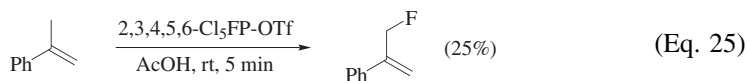
Selective fluorination of alkenes can also be achieved with the solvent acetonitrile as the nucleophile. Alkenes are converted into vicinal fluoro acetamides in good yields and poor diastereoselectivity with the aid of NFlth or SelectfluorTM in a Ritter-type reaction (Eq. 23).^{179,180}



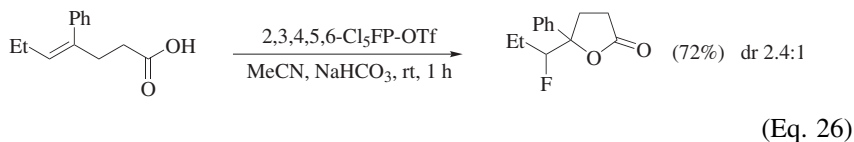
Of the *N*-fluoropyridinium salts, the most powerful ones including 2,3,4,5,6-Cl₅FP-OTf, *N*-fluoropyridinium-2-sulfonate, and 2,2'-bisFP-BF₄ have sufficient reactivity to fluorinate alkenes, whereas milder *N*-fluoropyridinium salts do not.^{31,161} Styrene and derivatives are easily fluorinated in the presence of acetic acid at room temperature to give the fluoroacetoxy addition products with Markovnikov regioselectivity (Eq. 24). Because methanol and ethanol decompose the fluorinating agent, their trimethylsilyl ethers can be used to provide the corresponding addition products in moderate yields (Eq. 24).³¹



The same treatment of α -methylstyrene gives α -fluoromethylstyrene by elimination of a proton (Eq. 25).³¹ Alternatively, α -fluoromethylstyrene is obtained by reaction with 2,3,4,5,6-Cl₅FP-OTf in dichloromethane in the presence of 2-fluoropyridine as an acid trap.³¹

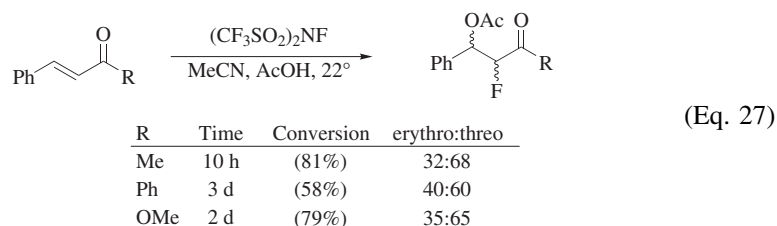


When the nucleophile is a functional group of the substrate, an intramolecular cyclization takes place.^{181,182} Fluorolactonization of 4-alkenoic acid derivatives with *N*-fluoropentachloropyridinium triflate proceeds regioselectively through a 5-exo ring closure with poor diastereoselectivity (Eq. 26).¹⁸²

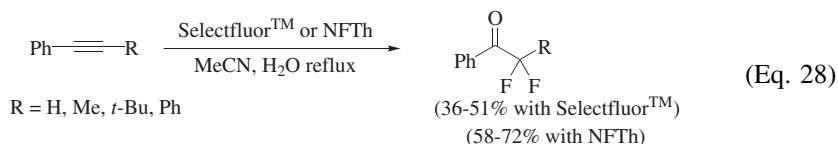


Alkenes contained within α,β -unsaturated carbonyl compounds are also susceptible to fluorination with (CF₃SO₂)₂NF in acetic acid (Eq. 27).^{35,83} Similarly,

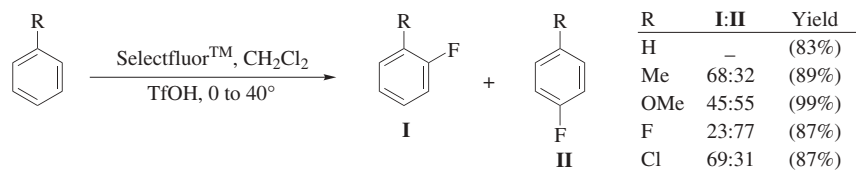
pyrimidine bases react with SelectfluorTM in water to generate the corresponding fluorohydrins with the fluorine atom at C-5.¹⁸³



In contrast, fluorinations of alkynes, which are less reactive towards electrophilic reagents than alkenes, are rare.^{184,185} Substituted phenylacetylenes react with SelectfluorTM or NFTh in refluxing acetonitrile/water following Markovnikov regioselectivity to give α,α -difluoroketones as sole products in moderate yields (Eq. 28). Under similar conditions, 1-decyne is not fluorinated.¹⁸⁴



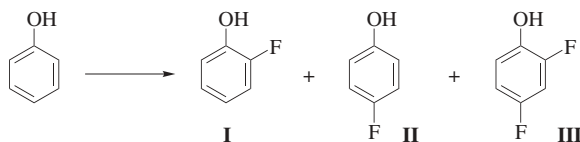
Electrophilic Aromatic Substitution. The direct electrophilic fluorination of aromatics complements other available methods for the synthesis of fluoroaromatics such as the Balz-Schiemann reaction and the Halex process. Whereas the use of molecular fluorine usually results in low selectivity because of the radical nature of the fluorination,¹⁸⁶ N-F fluorinating agents have emerged as selective sources of electrophilic fluorine for the fluorination of aromatics. Electron-donor substituents are often necessary to promote the reaction, although benzene and polycyclic aromatic hydrocarbons can also be efficiently fluorinated. The yield varies with the fluorinating power of the reagent and reaction conditions. A wide range of fluorinating agents have been evaluated; some are not reactive enough to fluorinate aromatics. Fluorination of benzene is realized with *N*-fluorobis(trifluoromethanesulfonyl)imide,⁶³ 2,6-(CO₂Me)₂FP-OTf,¹⁵⁰ and perfluoro *N*-(4-pyridyl) *N*-fluoromethanesulfonamide⁶¹ in modest yields. Fluorination of benzene with SelectfluorTM in dichloromethane in the presence of trifluoromethanesulfonic acid proceeds in 83% yield (Eq. 29).¹⁸⁷ Excellent yields are also obtained with other aromatics such as halobenzenes, toluene, anisole, naphthalene, and mesitylene. The mechanism of these fluorinations may involve in situ formation of protonated trifluoromethanesulfonyl hypofluoride as the de facto electrophilic fluorinating agent. A noteworthy fact is that fluorobenzene is mainly fluorinated at the para position, indicating the π -donor ability of the fluorine atom.¹⁸⁸



(Eq. 29)

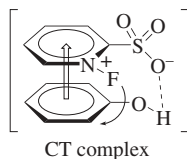
Fluorination of naphthalene usually results in mixtures of up to five mono- and difluoro derivatives.^{189–191} However, the conditions described in Eq. 29 afford 1-fluoronaphthalene and 3-fluoronaphthalene quantitatively in a ratio of 3:2.¹⁸⁷ Several polycyclic aromatic hydrocarbons such as pyrene, phenanthrene, and anthracene derivatives, are fluorinated with the aid of *N*-fluoro-2,4-dinitroimidazole, giving mixtures of regioisomers in modest yields (3–27%).¹¹⁰

Monosubstituted aromatics often give mixtures of ortho and para isomers. However, a good choice of fluorinating agent and reaction conditions allows highly selective ortho-fluorination to be achieved. Products of monofluorination are obtained in most reactions, although multiple fluorinations occur with the most reactive fluorinating agents. For example, reaction of *N*-fluoropyridinium-2-sulfonates with phenol yields ortho isomers exclusively (Eq. 30).¹⁴⁰ The substitution ortho to the hydroxy group is in accordance with an electrophilic fluorination mechanism.



Fluorinating agent	Solvent	Temp	Time	Conversion	I:II:III
FP-OTf	TCE	100°	24 h	(75%)	51:18:6
2,4-Cl ₂ FP-OTf	CH ₂ Cl ₂	reflux	5 h	(73%)	60:18:7
2,2'-bisFP-BF ₄	MeCN	reflux	8 h	(77%)	39:33:5
2-SO ₃ -4,6-(CF ₃) ₂ FP	CH ₂ Cl ₂	rt	13 h	(87%)	84:1:0
2-SO ₃ FP	TCE	reflux	1.5 h	(81%)	100:0:0
2-SO ₃ -6-ClFP	TCE	100°	49 h	(95%)	100:0:0

(Eq. 30)

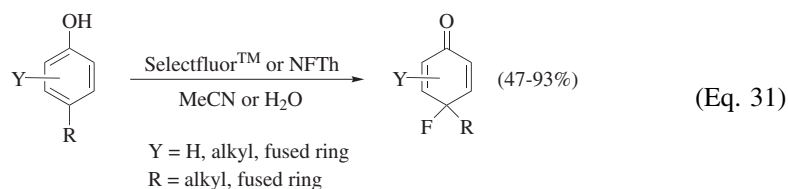


The formation of a charge-transfer complex between the aromatic ring of the phenol and the pyridinium ring of the reagent, additionally stabilized by hydrogen bonding between the sulfonate and the hydroxy group, has been proposed to rationalize the high regioselectivity (Eq. 30). The exclusive ortho-fluorination erodes with the use of polar solvents or acids that destroy the hydrogen bonding. The highly regioselective ortho-fluorination of aniline derivatives and phenol

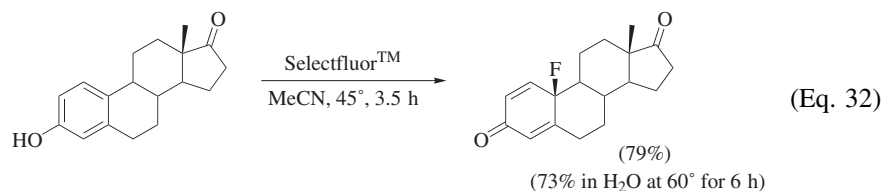
trimethylsilyl ether by *N*-fluoropyridinium-2-sulfonate was explained in a similar fashion.^{31,140} The ortho regioselectivity is lost in the fluorination of anisole and 4-fluoroanisole is the predominant product.¹⁴⁰

A huge number of disubstituted aromatics as well as tri- and tetrasubstituted aromatics have been fluorinated (see Table 4 of the Tabular Survey). Among the media utilized for electrophilic fluorination, imidazolium-based ionic liquids dissolve SelectfluorTM for reaction with reactive aromatics in moderate yields.¹⁸⁹ Microwave-promoted fluorination of electron-rich aromatics with SelectfluorTM or NFTh proceeds in acetonitrile at 150° for 10 minutes to afford products in comparable yields to those obtained by prolonged heating in refluxing acetonitrile.¹⁹²

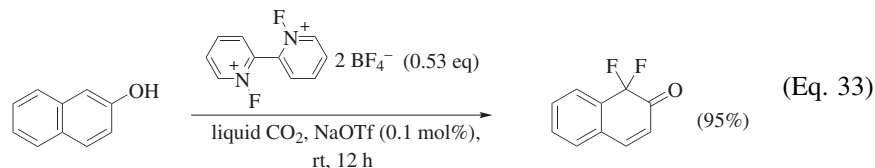
The N-F fluorinating agents are also strong oxidants, a fact that is responsible for the competition between fluorofunctionalization and oxidation. As a consequence, the selectivity of fluorination reactions can decrease when oxidizable functional groups or heteroatoms are present in the substrates. The hydroxy group in phenols and naphthols, for instance, is prone to both competitive oxidation and fluorofunctionalization reactions. Thus, 4-substituted phenols react with SelectfluorTM or NFTh in acetonitrile to give 4-fluorocyclohexa-2,5-dienone derivatives as shown in Eq. 31; only trace amounts of fluoro aromatic compounds are detected.¹⁹³ A water solution of SelectfluorTM can be used for this reaction.¹⁷⁷



To illustrate this method, estrogen steroids are readily converted into 10 β -fluoro-1,4-estradiene-3-one derivatives in high yields (Eq. 32).¹⁹⁴ In contrast, the use of *N*-fluoropyridinium salts on A-ring aromatic steroids gives fluorination of the aromatic ring with high regioselectivity in some reactions.^{31,195-197}



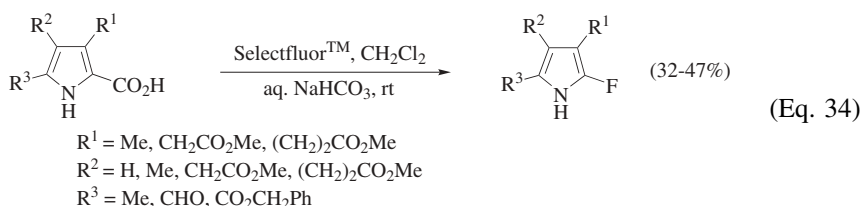
The electrophilic fluorination of 2-naphthol with *N,N'*-difluoro-2,2'-bipyridinium bis(tetrafluoroborate) can be conducted in liquid carbon dioxide in the presence of a catalytic amount of sodium triflate. The reaction proceeds in high yield without byproduct formation (Eq. 33).¹⁵⁸



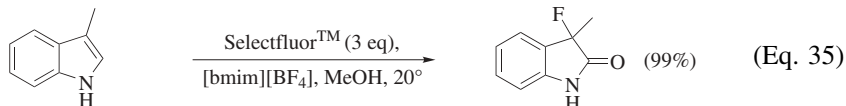
Fluorination of aromatics has also been achieved via electrophilic fluorination of metalated intermediates. In particular, directed ortho-lithiation of substituted aromatics followed by fluorination provides regioisomerically pure fluoroaromatic compounds (see the fluorodemetalation section).

Fluorination of Heterocycles. Examples of fluorination of both aromatic and non-aromatic heterocycles are considered here. The electrophilic fluorination of aromatic heterocycles has been less studied than the fluorination of arenes. Nevertheless, a number of fluoropyrroles,¹⁹⁸ -furans,¹⁹⁹ -thiophenes,²⁰⁰ -pyrrolo[2,3-*d*]pyrimidines,²⁰¹ -quinolines,²⁰² and -indoles^{203–206} have been prepared either by direct fluorination or by fluorodecarboxylation using SelectfluorTM or, for some indoles, 2,4,6-Me₃FP-OTf.

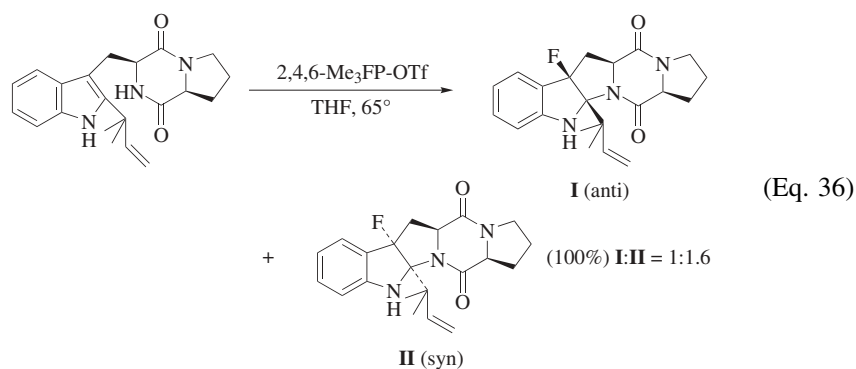
Highly substituted pyrrolecarboxylic acids react with SelectfluorTM in dichloromethane and aqueous sodium bicarbonate at room temperature to give the corresponding α -fluoropyrroles by fluorodecarboxylation in 32–47% yields (Eq. 34).¹⁹⁸ The fluorodecarboxylation of bromofuroic acids using SelectfluorTM proceeds in lower yields (<27%).¹⁹⁹



Direct fluorination has been studied on indole derivatives. The fluorination of *N*-tosylindole with SelectfluorTM in acetonitrile and methanol gives 3-fluoro-2-methoxy-1-(4-toluenesulfonyl)indoline in 38% yield.²⁰⁵ This result is in agreement with the observed reactivity between alkenes and SelectfluorTM in the presence of methanol. The reaction of 3-substituted indoles, including derivatives of tryptophan and serotonin, with SelectfluorTM in acetonitrile/water allows an efficient synthesis of 3-fluorooxindoles together with small amounts of non-fluorinated oxindoles.²⁰³ The choice of solvent can suppress the formation of side products. Use of solvent mixtures such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄])/methanol or 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆])/methanol results in high chemoselectivity and yields (Eq. 35).²⁰⁶

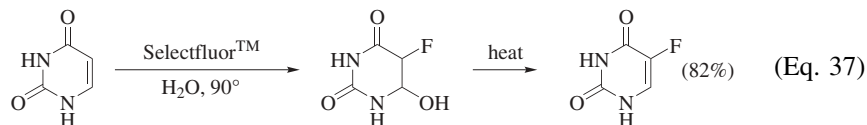


With a suitably positioned internal nucleophile tethered to the 3-position, a fluorination-cyclization reaction provides an elegant method for the synthesis of fluorobrevianamide **E** as shown in Eq. 36.²⁰⁴ In this example, 2,4,6-Me₃FP-OTf is preferred to SelectfluorTM, producing higher yields.

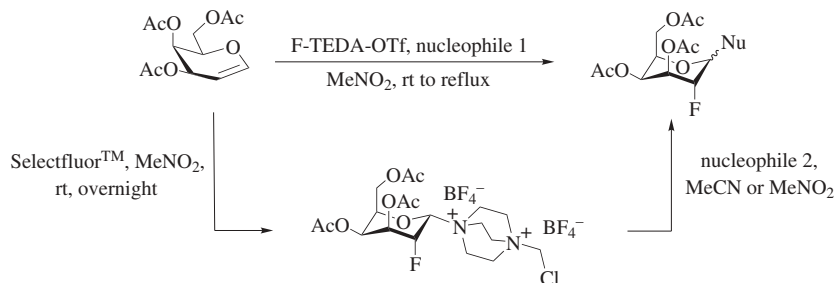


A number of aromatic heterocycles have been fluorinated via electrophilic fluorination of metalated intermediates (see the fluorodemetalation section).

Among the non-aromatic heterocycles, the fluorination of pyrimidine nucleoside bases with SelectfluorTM represents a practical and direct route to 5-fluoropyrimidine bases. For example, when uracil is heated at 90° in water with SelectfluorTM, the fluorohydrin is obtained as an 8:1 diastereomeric mixture, which is dehydrated on sublimation to give the anti-cancer agent 5-fluorouracil (Eq. 37).¹⁸³ This methodology can also be applied to nucleosides in acetonitrile in the presence of water, methanol, or acetic acid.¹⁸³



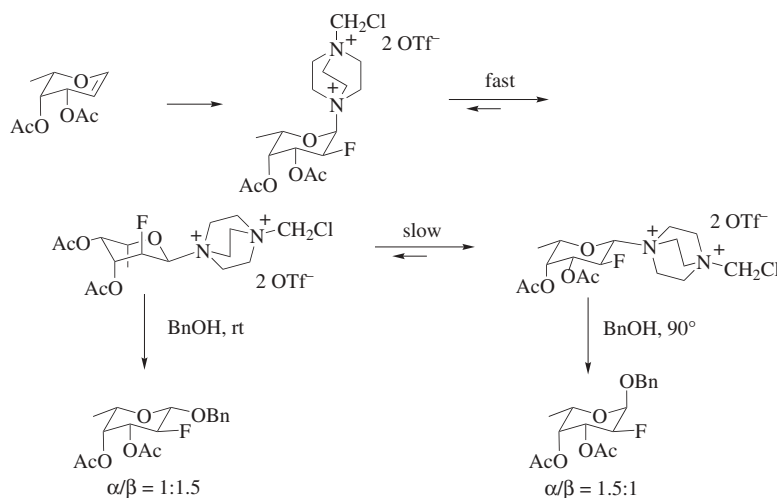
Fluorination of Glycols. The electrophilic fluorination-nucleophilic addition reaction across the double bond of glycols constitutes an attractive approach to the synthesis of 2-deoxy-2-fluoro carbohydrates.²⁰⁷ Introduction of fluorine with F-TEDA salts occurs regioselectively at C-2 and the [TEDA-CH₂Cl] moiety adds at the anomeric position, yielding a 1-[TEDA-CH₂Cl]-2-fluoro saccharide, which reacts further at room temperature or at higher temperature with various nucleophiles. The reaction may be carried out in one pot⁴³ or the intermediate may be isolated and reacted with a nucleophile (Eq. 38).²⁰⁸



Nucleophile 1 = H₂O, alcohols, phenols, protected sugars, amines, diphenyl phosphoric acid
 Nucleophile 2 = sodium azide, magnesium bromide, potassium 4-nitrophenolate,
 potassium 2,4-dinitrophenolate, 2,4-bis(trimethylsilyl)thymine

(Eq. 38)

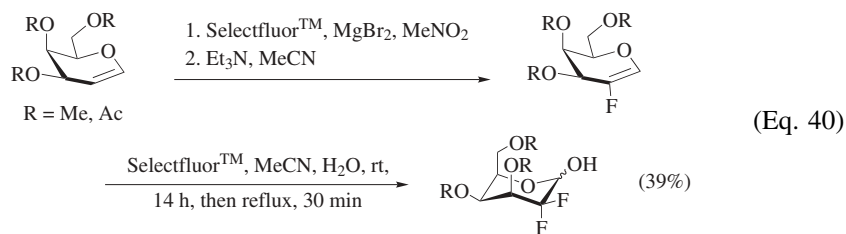
The stereochemical outcome of the fluorination-glycosylation sequence consists of a concerted syn addition of the F-TEDA salt to the alkene functionality of the glycal leading to an *N*-glycosyl ammonium compound, which slowly anomerizes to the more thermodynamically stable trans isomer (Eq. 39). The configuration and the protecting group at the 4-position of glycals direct fluorination stereoselectivity. In the galactose and fucose series, the addition of F-TEDA-OTf gives exclusively equatorially fluorinated products even with acetate-protected hydroxy groups. Glucals having hydroxy groups protected with various esters give fluorinated products with fluorine equatorial/axial ratios depending on the steric size of the protected group (Ac: F-eq/ax = 45 : 55, Bz: F-eq/ax = 75 : 25, Piv: F-eq/ax = 90 : 10). The anomeric α/β distribution depends on the nucleophile, the reaction temperature, and solvent effects (Eq. 39).



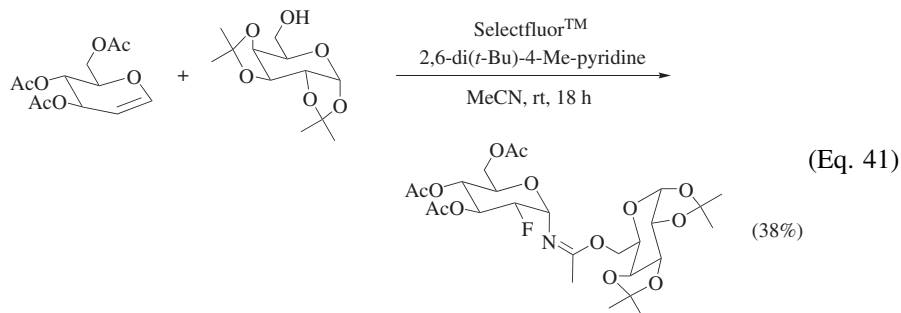
(Eq. 39)

A double fluorination-glycosylation sequence on 2-deoxyhex-1-enitol allows the synthesis of 2,2-difluorosaccharides (Eq. 40). In the first sequence, magnesium

bromide is used as nucleophile and a subsequent elimination of the resulting anomeric bromide with triethylamine affords the vinylic fluoride, which is then subjected to the second sequence with SelectfluorTM in the presence of water.²⁰⁹



SelectfluorTM or F-TEDA-OTf is used in the fluorination-glycosylation sequence; however, the former sometimes results in the formation of 1,2-difluoro derivatives as major side products, presumably resulting from the attack of fluoride liberated from the tetrafluoroborate anion.⁴³ Reactions with F-TEDA-OTf are optimal in nitromethane. Dimethylformamide may be used when water is the nucleophile. Acetonitrile participates in the reaction with attack at the anomeric position and subsequent addition of the nucleophile at the nitrile carbon (Eq. 41), but acetonitrile may be used when the desired nucleophile is present in excess.⁴³

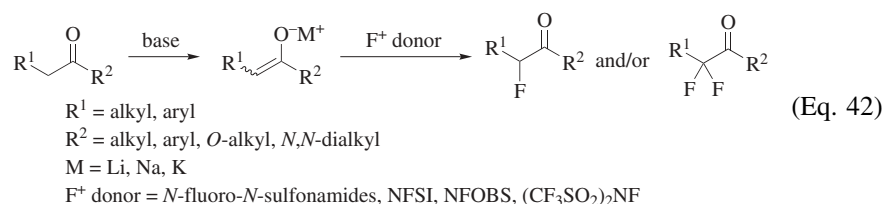


Although pyranosyl glycols are generally employed, furanosyl glycols can also be used successfully²¹⁰ as well as exo furanosyl glycols²¹¹ in the synthesis of nucleoside analogs.

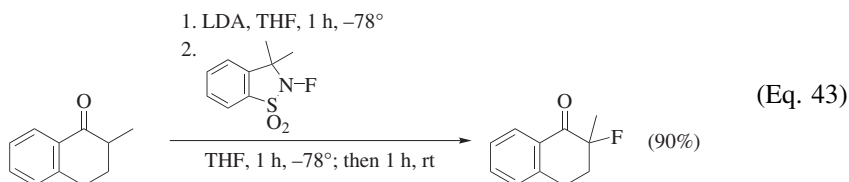
Fluorination of Metal Enolates. Enolates are central intermediates in the fluorination of a large number of substrates. Processes for their generation are well documented and are not detailed in this section. The fluorination of a carbonyl compound via its enolate is generally more facile than the direct fluorination of the carbonyl compound (see next section). Indeed, some neutral nucleophilic substrates are inert toward fluorination whereas their enolates are easily fluorinated in high yields.

Metal Enolates of Monocarbonyl Compounds. In the monocarbonyl compound series, the selective fluorination of enolates into mono- and difluorinated

carbonyl compounds has been studied in detail using various fluorinating agents (Eq. 42).⁷⁶



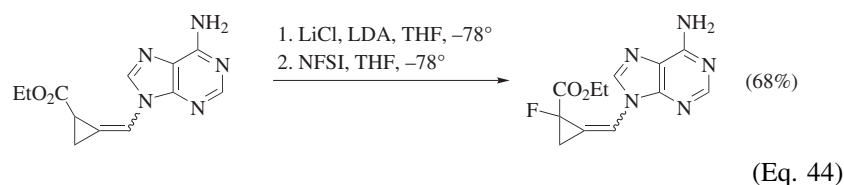
Of the fluorinating agents, 2-fluoro-3,3-dimethyl-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide consistently provides better yields of fluorinated products than do acyclic *N*-fluoro-*N*-alkylsulfonamides.^{69,70,76} However, selectivity and yields are strongly dependent on the enolate counterion and the acidity of the protons α to the carbonyl group. The selectivity for mono- versus difluorinated products decreases in the order $\text{Li} > \text{Na} > \text{K}$. Less acidic substrates can be monofluorinated selectively with the selectivity decreasing in the order amide > ester > ketone. The ratio of mono- to difluorinated products reflects the competition between the reaction of the starting enolate with the fluorinating agent and the deprotonation of the initially formed monofluorinated product by the starting enolate. The selectivity is generally improved at low reaction temperature. Use of slightly more than two equivalents of both the base and the fluorinating agent mainly affords difluorinated products. It should be noted that competitive reaction of the fluorinating agent with the base leads to side reactions and moderate yields of the desired fluorinated products. With tetrasubstituted enolates derived from a variety of 2-substituted indanone and tetralone derivatives, fluorination with cyclic *N*-fluorobenzenesulfonamides provides the desired fluorinated products in good to excellent yields (Eq. 43).^{70,72,73}



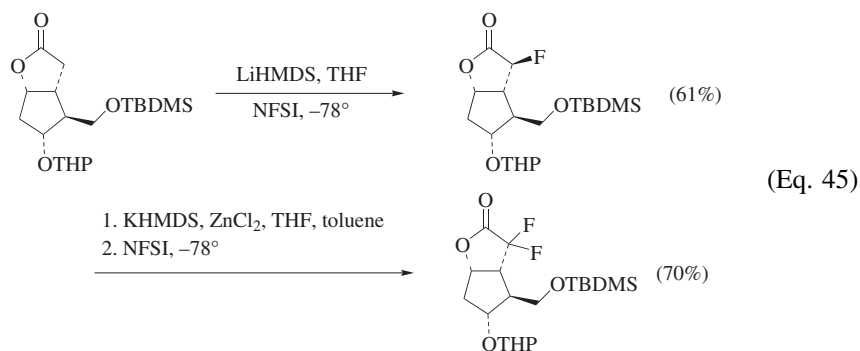
The trends defined in the study with 2-fluoro-3,3-dimethyl-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide are also valid for the use of other fluorinating agents. However, when NFSI or NFOBS are used, the monofluorinated products are obtained in significantly better yields: 80–95% for ketone enolates and 53–70% for ester enolates.^{33,85,212} Alternatively, the lithium enolates of esters, amides, and ketones react with *N*-fluorobis[(trifluoromethyl)sulfonyl]imide in tetrahydrofuran at -80° to afford the α -fluorination products in good yields (63–87%). Under such conditions, it is claimed that the formation of α,α -difluoro carbonyl compounds never occurs.²¹³ The F-TEDA type reagents are not very effective for the

fluorination of metal enolates because of a competing Hofmann-type elimination in the strongly basic medium.

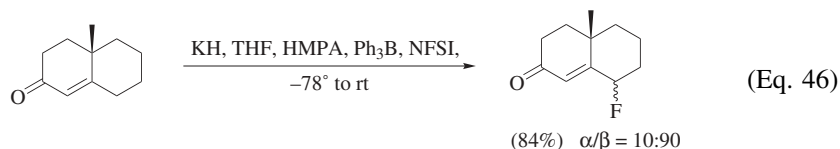
The synthesis of fluoromethylenecyclopropane analogs of nucleosides as anti-viral agents illustrates the fluorination reaction of ester enolates. In the reaction shown in Eq. 44, it is necessary to include lithium chloride in the protocol to achieve high yields.^{214,215}



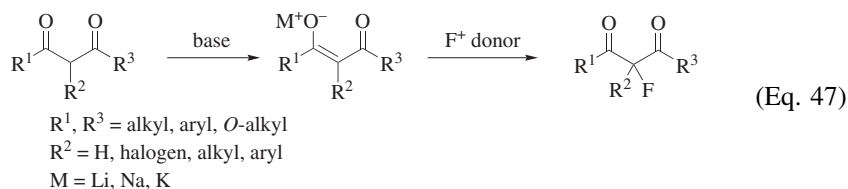
An example of the importance of the reaction conditions on difluorination is given for the synthesis of difluorinated Corey lactone in Eq. 45. The starting lactone is treated with lithium hexamethyldisilazide, LiHMDS, in tetrahydrofuran and monofluorinated with NFSI at -78° in 61% yield. With excess base and NFSI, the difluorolactone could not be obtained. On the other hand, the difluorolactone is obtained in 70% yield after metal exchange with zinc chloride and fluorination with NFSI.²¹⁶



α,β -Unsaturated carbonyl substrates undergo γ -fluorination via the reaction of the corresponding potassium dienoxo borates with NFSI to afford γ -fluoro enones in good yields (Eq. 46).²¹⁷ This methodology has been extended to the more structurally complex steroids. The replacement of triphenylborane with 2-phenylbenzo[1,3,2]dioxaborole affords γ -fluorosteroidal enones in 58–82% yield as a mixture of α/β isomers.²¹⁷

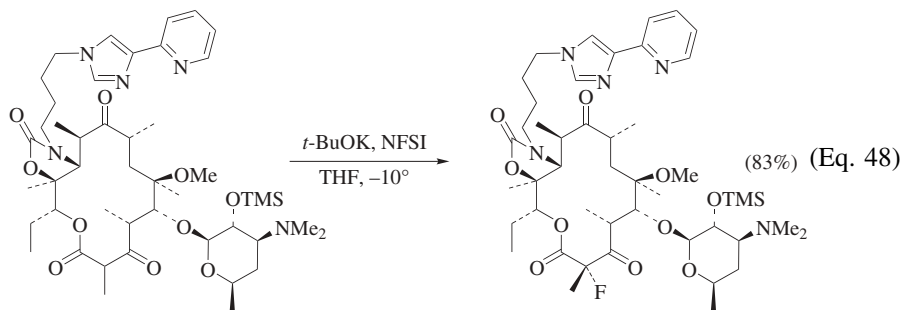


Metal Enolates of β -Dicarbonyl Compounds. The metal enolates of not only β -dicarbonyl compounds (β -diketones, β -keto esters, β -diesters) but also α -cyano esters²¹⁸ react with *N*-fluorobis(trifluoromethanesulfonyl)imide,^{219,220} *N*-fluoro-2-pyridone,⁹⁷ *N*-fluoroperfluoropiperidine,^{106,107} *N*-fluorosulfonamides,^{42,69,70} *N*-fluorosulfonimides,^{83,85,221} *N*-fluoroquinuclidinium salts,^{113,115} F-TEDA salts,^{122,173,218,221–224} and *N*-fluoropyridinium salts^{31,150,225} to give mono- or difluoro β -dicarbonyl compounds (Eq. 47).



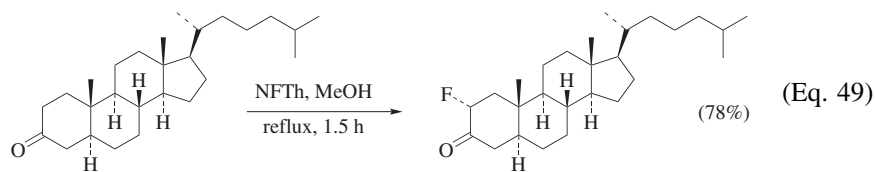
Reaction of α -monosubstituted dicarbonyl compounds gives α -monofluoro compounds whereas α,α -difluoro compounds are formed when unsubstituted dicarbonyl compounds react with two equivalents of fluorinating agent.²²⁶ Control of monofluorination for unsubstituted dicarbonyl compounds is difficult since the starting enolate is a strong base that can generate the enolate of the monofluoro compound. To suppress the undesired difluorination, the enolate can be added slowly to the fluorinating agent at low temperature. The direct fluorination of β -dicarbonyl compounds without preformation of their alkali enolates is discussed in the next section. It is generally an efficient method. However, in the case of β -dicarbonyl compounds with low enol content such as β -diesters, only the enolates are reactive.²²³

The yields depend on a variety of factors such as the substrate, base, fluorinating agent, order of addition, and reaction temperature. Sodium hydride is an appropriate base to generate the enolate, and tetrahydrofuran is the most utilized solvent. Acetonitrile or dimethylformamide is used as the cosolvent when SelectfluorTM is the fluorinating agent. The reaction temperature for fluorination of enolates varies from -78° to room temperature. For example, 2-fluoroketolide antibiotics are synthesized by electrophilic fluorination at the β -keto ester moiety as shown in Eq. 48. Here, the introduction of a fluorine atom at C-2 is beneficial to the overall antibacterial spectrum.²²⁷

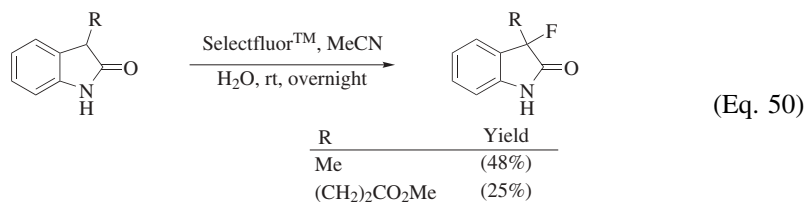


Direct Fluorination of Carbonyl Compounds. Monocarbonyl Compounds.

Activation of carbonyl compounds through enolate anions, enol ethers, enol esters, or enamines is usually necessary for effective α -fluorination, especially for fluorination of ketones. On the other hand, direct α -fluorination of ketones is possible. The reaction is best performed in refluxing methanol with NFTh, although SelectfluorTM, NFSI, and 2,6-Cl₂FP-BF₄ can also be utilized. Acetonitrile can be used as the solvent,²²⁸ but the keto-enol equilibrium is less favorable and ketones possessing an activated aromatic ring give aromatic fluorination products regioselectively.²²⁹ This method has been applied to a comprehensive range of substrates and produces α -fluoro ketones regioselectively without prior activation. The reaction tolerates the presence of functional groups such as an activated aromatic or an oxidizable heteroatom. Interestingly, 5 α -cholestan-3-one is readily transformed into 2 α -fluoro-5 α -cholestan-3-one in 78% yield (Eq. 49).²³⁰ This direct synthesis compares favorably with the method consisting of the fluorination of the corresponding silyl enol ether with *N*-fluoropyridinium triflate.²³¹

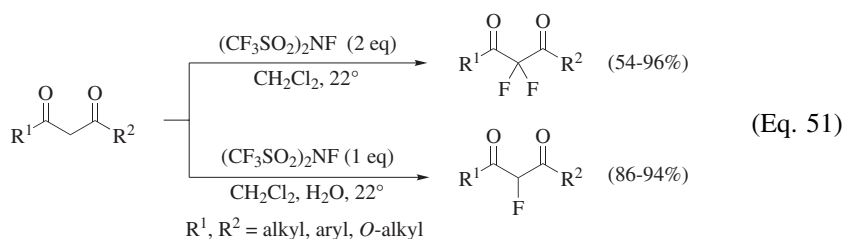


The direct fluorination of oxindoles at C-3 has been carried out with SelectfluorTM in an acetonitrile/water system (Eq. 50).²⁰³ However, the yields are much lower than those obtained in the fluorination of indoles (see section on fluorination of heterocycles).

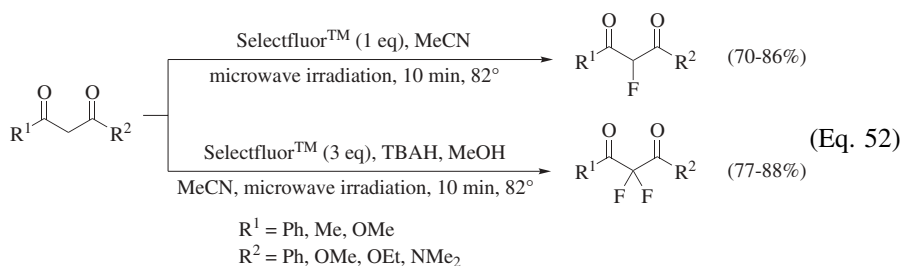


β -Dicarbonyl Compounds. The ease of fluorination of β -dicarbonyl compounds increases with their enol content in the order β -diketones > β -keto esters \gg β -diesters. Direct fluorination can be readily performed using (CF₃SO₂)₂NF in acetic acid or chloroform at room temperature.²¹³ Hydrocarbons, other halogenated solvents, ethers, acetonitrile, and benzonitrile are equally effective solvents in the fluorination of 2-chloro-3-oxobutyric acid ethyl ester.²¹³ Because some products are sensitive to the acidity of the formed bis(trifluoromethanesulfonyl)imide, the fluorination can be performed in the presence of sodium bicarbonate to neutralize the imide through its sodium salt. The fluorination of unsubstituted β -dicarbonyl compounds can be controlled to give either monofluorination or difluorination by choosing the reaction conditions. Indeed, the monofluorination products can be obtained exclusively if the strongly

acidic bis(trifluoromethylsulfonyl)imide, which causes the enolization of the monofluorinated product, is removed by conducting the reaction in a biphasic water/dichloromethane solvent system (Eq. 51).²²⁰

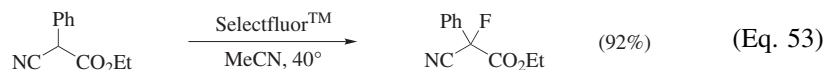


β -Dicarbonyl compounds are also fluorinated directly with NFOBS and NFSI in good to high yields. When water is added as a cosolvent, monofluorination increases at the expense of difluorination only in the case of NFOBS; difluorination prevails in the case of NFSI because its sulfonimide byproduct has limited solubility in water.³³ SelectfluorTM reacts with cyclic β -keto esters,²³² acyclic β -keto esters,^{223,224,233} β -diketones,^{134,223} and β -keto amides²²³ at room temperature in solvents such as ethanol, tetrahydrofuran, or acetonitrile. Under these neutral conditions, difluorination proceeds very slowly. However, the sodium enolate of the monofluoro intermediate reacts rapidly to give the difluoro derivative in excellent yield.²²³ The rate of the fluorination is dramatically accelerated under microwave irradiation; in particular, difluorination of β -diesters can be realized within 10 minutes with SelectfluorTM in the presence of tetrabutylammonium hydroxide (TBAH) (Eq. 52).²³⁴



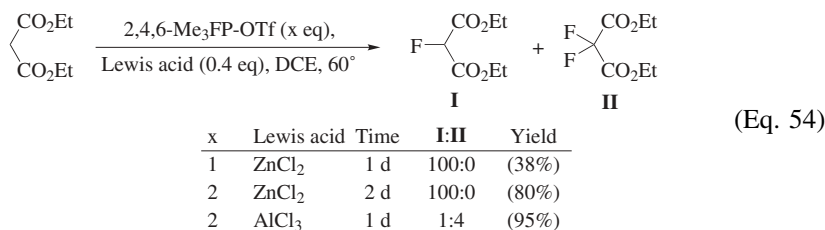
When water is used as the solvent, addition of an anionic surfactant compound (sodium lauryl ether sulfate, Genapol LROTM), which acts as an emulsifier of the substrate, promotes the fluorination with water-soluble SelectfluorTM within a reasonable reaction time (3 hours at 60°). Unfortunately, monofluorinated products could not be selectively obtained under these conditions.¹⁷⁷

The nitrile group is compatible with SelectfluorTM as demonstrated in the fluorination of cyano esters, a substrate type equivalent to β -dicarbonyl compounds (Eq. 53).²²³

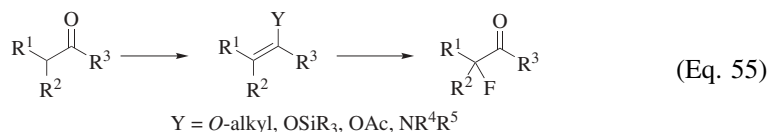


Several *N*-fluoropyridinium and bis(*N*-fluoropyridinium) salts serve in the fluorination of β -dicarbonyl compounds.^{140,150,158,161} The fluorinations are commonly run in acetonitrile or in dichloromethane at reflux with the most powerful reagents of the family in yields ranging from 46 to 98%. Fluorination of unsubstituted β -dicarbonyl compounds gives the monofluorination products almost exclusively.¹⁴⁰

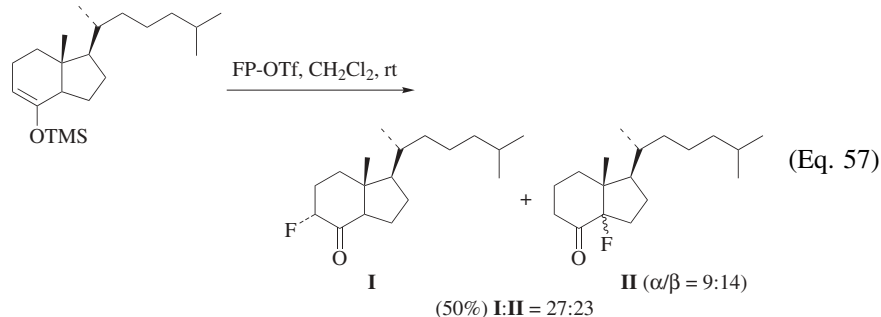
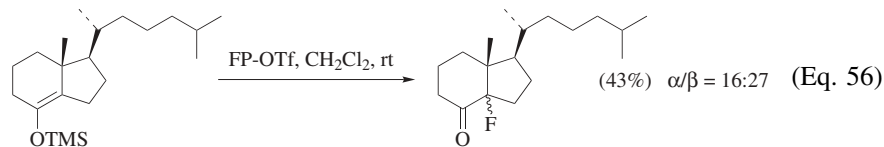
As these reactions proceed via the enol form of the substrate, a substoichiometric quantity of a Lewis acid can accelerate the fluorination by promoting the enolization process. Zinc chloride catalyzes fluorination of active methylene compounds with *N*-fluoro-2,4,6-trimethylpyridinium triflate³¹ or with NFTh in the presence of either imidazole or collidine as an added base.²³⁵ The strong Lewis acid aluminum chloride is capable of promoting the difluorination of diethyl malonate in 76% yield whereas this product is difficult to obtain via an alkali enolate (Eq. 54).³¹



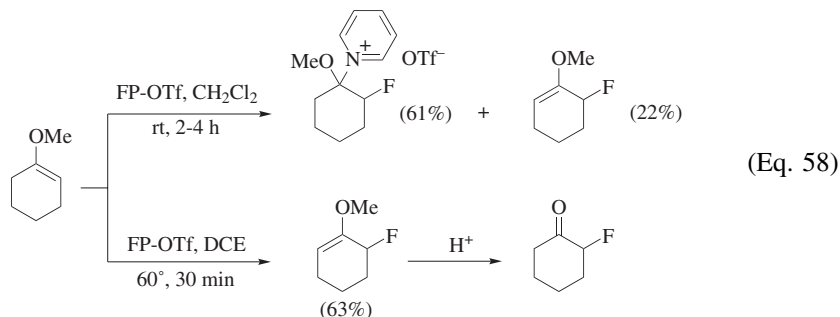
Fluorination of Enol Derivatives, Enamines, and Imines. The introduction of a fluorine atom adjacent to a carbonyl group can also be achieved by reaction of an electrophilic fluorinating agent with masked carbonyl compounds such as alkyl enol ethers, silyl enol ethers, enol esters, and enamines (Eq. 55).



This method allows the monofluorination of ketones and esters. Enol derivatives of aldehydes have been used rarely in electrophilic fluorination.²³⁶ Recent work in this area has focused on the enantioselective introduction of a fluorine atom onto prochiral silyl enol ethers (see enantioselectivity section). Regioselectivity in the fluorination of unsymmetrical ketones can be attained by the regiocontrolled formation of the enol derivatives. Nevertheless, examples are reported in which the regiochemical integrity of the silyl enol ether is not preserved. Fluorinated synthons suitable for the synthesis of 9- and 14-fluorovitamins D₃ are prepared either from the thermodynamic silyl enol ether (Eq. 56) or from the kinetic silyl enol ether (Eq. 57). Fluorination of the thermodynamic silyl enol ether with *N*-fluoropyridinium triflate gives the expected 14-fluoro C/D ring ketone whereas a mixture of regioisomeric 9- and 14-fluoro C/D ring ketones is obtained starting from the kinetic silyl enol ether.²³⁷

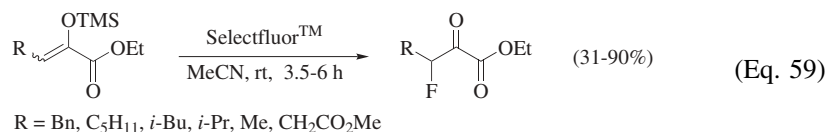


Alkyl enol ethers are generally poor substrates for electrophilic fluorination.^{150,235} 1-Methoxy-1-cyclohexene reacts smoothly with FP-OTf at room temperature to give a mixture of addition product and allyl fluoride derivative. At higher temperature, the allyl fluoride is obtained exclusively, which is then subjected to acid hydrolysis to give the 2-fluorocyclohexanone (Eq. 58).³¹

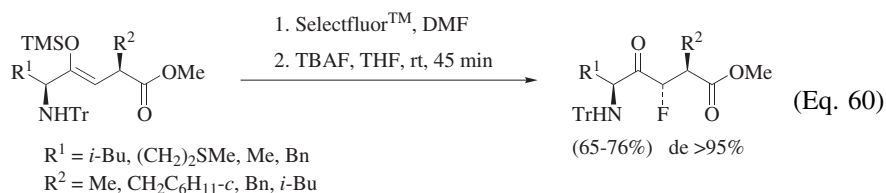


Reactions with other enol derivatives proceed generally in good to excellent yields with the most powerful fluorinating agents, such as F-TEDA salts, *N*-fluoropyridinium salts, NFSI, and NFOBS. Some common solvents are acetonitrile, dimethylformamide, and dichloromethane.

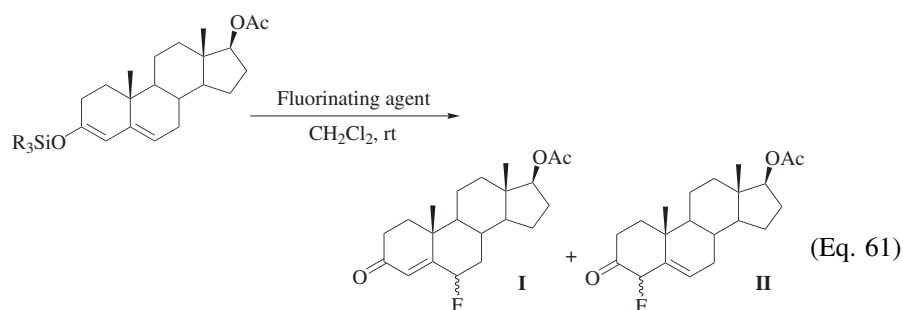
Silyl enol ethers can be used when the carbonyl substrates have insufficient enol content for direct fluorination or when SelectfluorTM is ineffective at fluorinating highly reactive metal enolates.²³⁸⁻²⁴⁴ This method is illustrated in the preparation of β -fluoro- α -keto esters as shown in Eq. 59.²⁴⁵



A stereocontrolled synthesis of dipeptides possessing an α -fluoro keto peptide bond mimic has been developed that involves the fluorination of a silyl enol ether as the key step (Eq. 60). The use of SelectfluorTM in dimethylformamide or acetonitrile is rather sluggish. In contrast, the fluorination conducted in the presence of tetrabutylammonium fluoride (TBAF) leads to smooth fluorination in good yields (65–76%).²³⁹



Among the substrates that have been extensively studied in electrophilic fluorination are silyl enol ether and enol acetate derivatives of steroids. Positions 6 and 16 of 3-keto steroids are mainly targeted in fluorination with SelectfluorTM and *N*-fluoropyridinium salts. With α,β -unsaturated silyl enol ether derivatives of steroids, fluorination occurs regioselectively at the 6-position with moderately powerful *N*-fluoropyridinium salts (Eq. 61). *N*-Fluoropyridinium triflate gives lower regioselectivity and yield than the counteranion-bound salt, 2-SO₃-4-MeFP. Polar solvents such as acetonitrile or dimethylformamide decrease the selectivity. The regioselectivity increases with the bulk of the silyl moiety, and exclusive 6-fluorination is achieved with the triisopropylsilyl group. In addition, preferential β -stereoselective fluorination at the 6-position is observed.¹⁴⁰

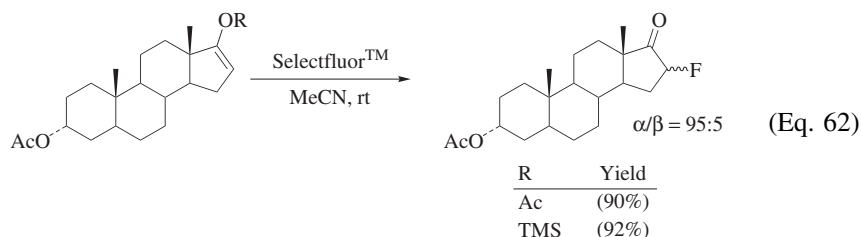


R	Fluorinating agent	Conversion	I (α : β):II
Me	FP-OTf	(51%)	2.4 (1:1.8):1
Me	2-SO ₃ -4-MeFP	(77%)	14 (1:3.5):1
Et	2-SO ₃ -4-MeFP	(90%)	>92 (1:3.5):1
<i>i</i> -Pr	FP-OTf	(41%)	4.1 (1:1.5):1
<i>i</i> -Pr	2-SO ₃ -4-MeFP	(93%)	100 (1:3.8):1

When the fluorination is conducted with 2,2'-bisFP-OTf in the presence of sodium bicarbonate as an acid trap, a 2.4 : 1 mixture of 6- and 4-fluoro isomers is obtained. On the other hand, fluorination of the corresponding enol acetate derivative gives the 6-fluoro compound exclusively in 82% yield ($\alpha/\beta = 1 : 1.7$).¹⁶¹

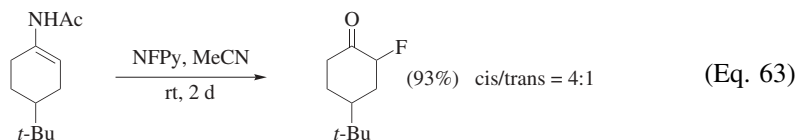
Similarly, NFluor selectively fluorinates a dienol acetate and a methyl dienol ether at the 6-position in acetonitrile in 89 and 72% yields, respectively.²³⁵

The C-16 fluorination of steroids is also very efficiently carried out. 16-Fluoro steroids are obtained in high yields with excellent α/β stereoselectivity on fluorination of either an enol acetate or a silyl enol ether (Eq. 62).¹⁷³

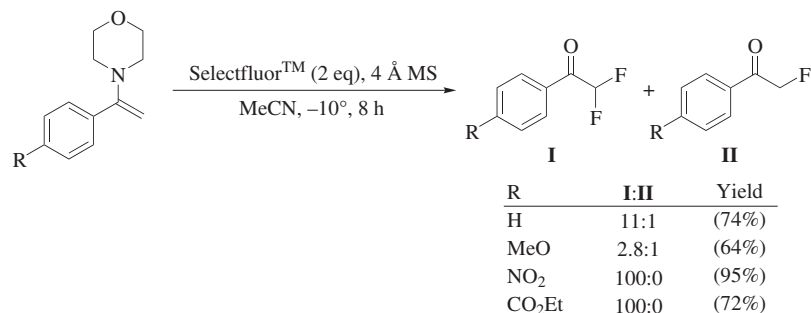


In steroids possessing two reaction sites of conjugated and non-conjugated enol acetates, *N*-fluoropyridinium triflate reacts at the conjugated site only. On the other hand, a steroid having both a conjugated enol acetate and a silyl enol ether moiety is selectively fluorinated at the silyl enol ether.¹⁵⁰

As nitrogen analogs of enols, enamines are easily available substrates for the introduction of a fluorine atom at the α -position of carbonyl compounds. Moreover, the reactivity of enamines toward electrophilic fluorination is improved relative to enol esters because the nitrogen atom donates electrons to the double bond. A variety of enamines possessing an acetylamino group (Eq. 63)¹⁵⁷ and the more reactive dialkylamino and morpholino enamines react with electrophilic fluorinating agents to produce monofluorinated carbonyl compounds.^{31,98,113,129}

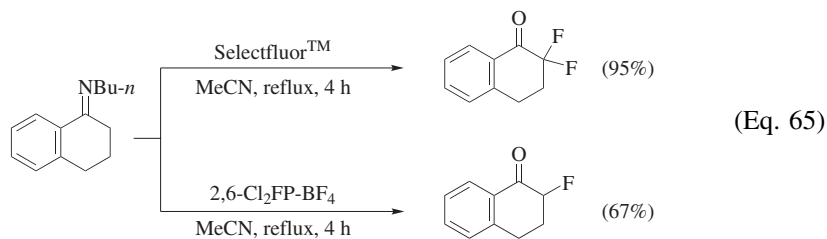


Difluorination of monocarbonyl compounds is not easy. However, the difluorination of their enamine derivatives proceeds with 2.4 equivalents of *N*-fluoro-bis(trifluoromethanesulfonyl)imide in dichloromethane in the presence of sodium carbonate, which is added to neutralize the bis(trifluoromethanesulfonyl)imide formed during the reaction. Reducing the quantity of fluorinating agent produces mixtures of mono- and difluorinated products.²⁴⁶ With the more widely used SelectfluorTM, difluorinated products predominate in the fluorination of the morpholino enamine of acetophenone derivatives (Eq. 64).²⁴⁷ In this reaction, it is crucial to regenerate the monofluorinated enamine in order to obtain a second fluorination. The addition of molecular sieves to the reaction mixture increases the yield and the ratio of di- to monofluorination, whereas the presence of electron-withdrawing groups on the aromatic ring results in exclusive formation of difluorinated products.



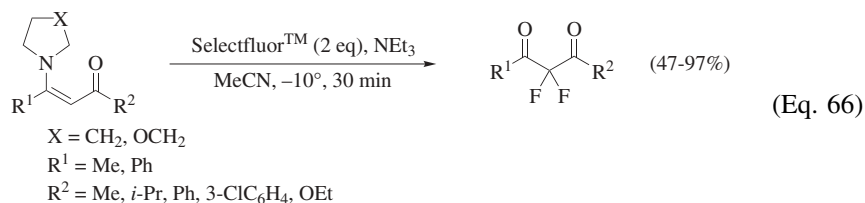
(Eq. 64)

When the method is applied to propiophenone instead of acetophenone, the monofluorinated product is obtained as the major product in high yield, even when two equivalents of SelectfluorTM are used. It has been proposed that the methyl group attached to the position at which the fluorination occurs has a significant effect on the reaction by reducing the acidity of the proton, precluding enolization and further fluorination.²⁴⁷ However, *N*-butylimines of a variety of substrates, some including the propiophenone motif, have been successfully difluorinated with SelectfluorTM in refluxing dry acetonitrile in good yields (73–89%).²⁴⁸ Screening of various fluorinating agents has shown that *N*-fluoro-2,6-dichloropyridinium tetrafluoroborate is inefficient for difluorination because the fluorination stops at the stage of the α -fluoro ketone (Eq. 65).²⁴⁸



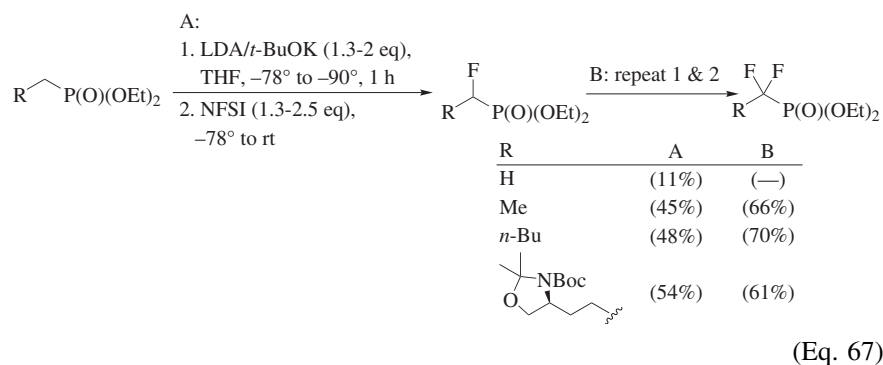
(Eq. 65)

Pyrrolidino- and morpholino enamine derivatives of β -diketones and β -keto esters are transformed into difluorinated carbonyl compounds with two equivalents of SelectfluorTM in the presence of one equivalent of triethylamine, which helps to regenerate the monofluorinated enamine (Eq. 66).²⁴⁷

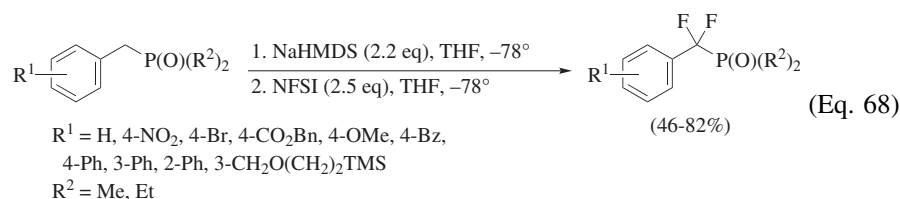


(Eq. 66)

Fluorination of Organophosphorus Compounds. A number of α,α -difluorophosphonates have been synthesized as analogs of biological phosphates, but experimental and theoretical reports indicate that α -monofluorophosphonates would be better mimics.^{249,250} α -Monofluorophosphonates are isoacidic mimics of phosphates, they are metabolically stabilized, and they possess excellent features for receptor binding. In addition, the CHF stereochemistry does affect enzyme-binding.²⁵¹ NFSI is the most frequently used fluorinating agent for the fluorination of organophosphorus compounds; SelectfluorTM, $(CF_3SO_2)_2NF$, and NFOBS are less utilized. Alkyl phosphonates react with a strong base (e.g., lithium diisopropylamide or *n*-butyllithium) to generate an unstabilized carbanion α to the phosphorus atom, and reaction with NFSI gives a mixture of α -mono- and α -difluorophosphonates in modest to good yields.^{252,253} Monofluorination can be achieved by reaction of a mixture of LDA and *t*-BuOK with the alkylphosphonate at -90° to -78° followed by the addition of NFSI (Eq. 67).²⁵⁴ Difluorinated phosphonates can be obtained by repetition of this procedure.



Stabilization of an α -phosphoryl anion by aryl, arenesulfonyl, or trialkylsilyl groups allows the fluorination to proceed more efficiently. SelectfluorTM has been successfully employed when arenesulfonyl groups are used to stabilize the anion.^{173,255,256} Several benzylic phosphonates possessing various functional groups on the phenyl ring can be difluorinated in good yields using sodium hexamethyldisilazide (NaHMDS, 2.2 equivalents) and NFSI (2.5 equivalents) (Eq. 68). The procedure is compatible with methyl or ethyl phosphonate esters but not with *tert*-butyl esters.²⁵⁷



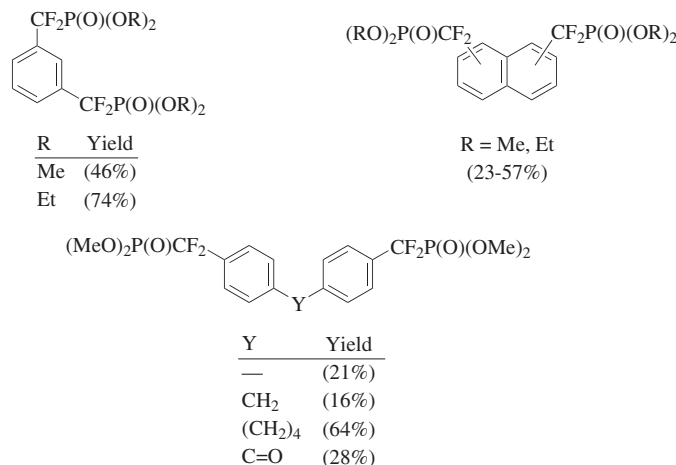
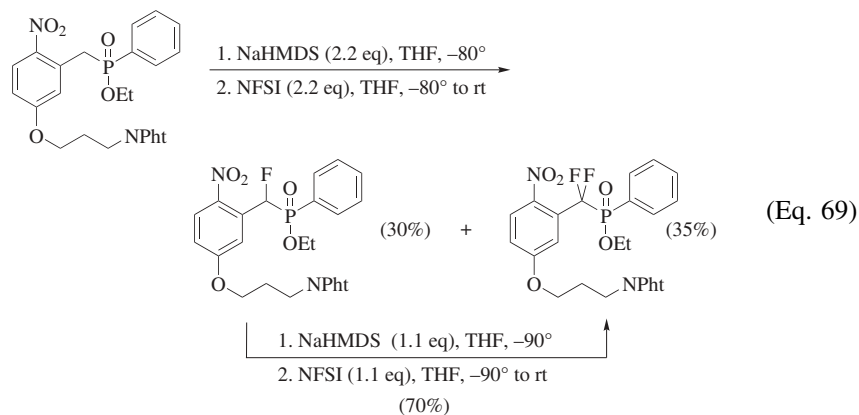


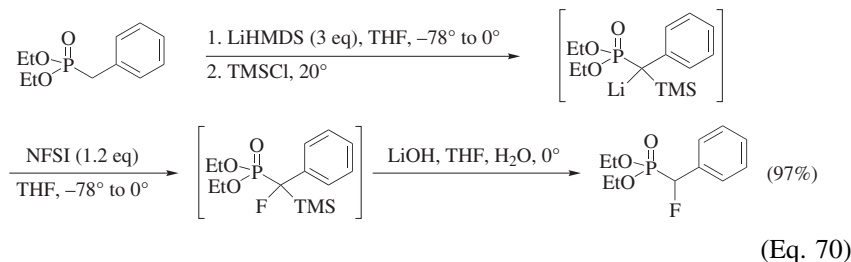
Figure 12. Fluorinated benzylic phosphonates.

Benzene, naphthalene, and diphenyl systems bearing two benzyl phosphonate moieties can also be fluorinated using adequate amounts of base and NFSI (Fig. 12).^{257,258}

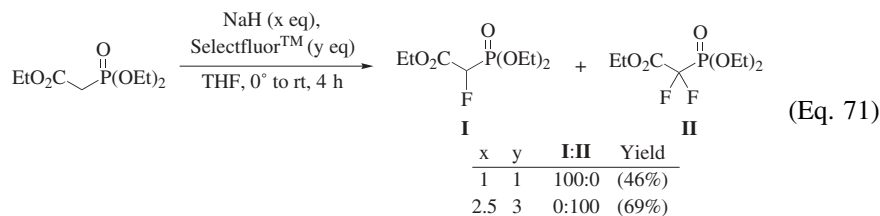
The arylphosphinate shown in Eq. 69 reacts with NFSI with sequential replacement of both hydrogen atoms of the methylene group to give an overall 56% yield of α,α -difluorophosphinate. In this example, NaHMDS is used as the base whereas the difluorination procedure on nonactivated alkylphosphinate requires the use of *t*-BuLi and gives a modest 14% overall yield.²⁵⁹



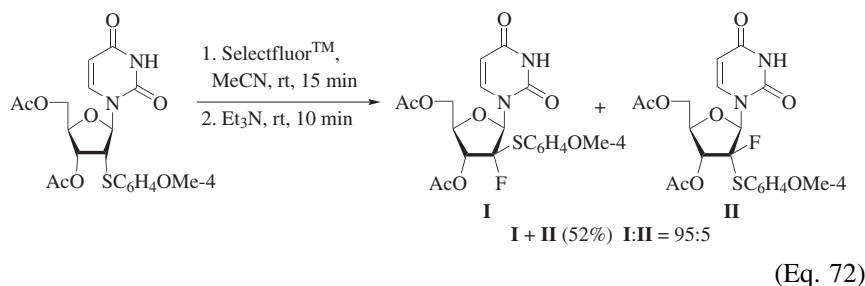
Controlled monofluorination of benzylic phosphonates can be achieved with the aid of a trimethylsilyl group, formed in situ, which acts as a temporary anion-stabilizing group and that is cleaved afterwards with an oxygen nucleophile (Eq. 70).^{260,261} This sequence has also been carried out in 74–89% overall yields with LDA as the base.²⁶²



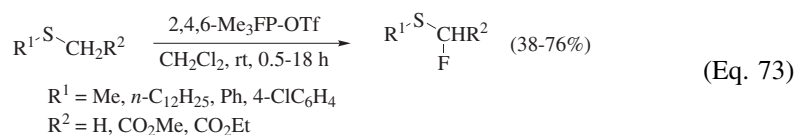
α -Fluorinated β -alkoxycarbonyl phosphonates are prepared from the corresponding β -alkoxycarbonyl phosphonates by fluorination with NFOBS or SelectfluorTM.^{33,263} By adjusting the molar ratio of base and SelectfluorTM, the monofluoro or the difluoro compound can be obtained selectively (Eq. 71).²⁶³ Enantioselective fluorinations of β -alkoxycarbonyl phosphonates are discussed in the enantioselectivity section.



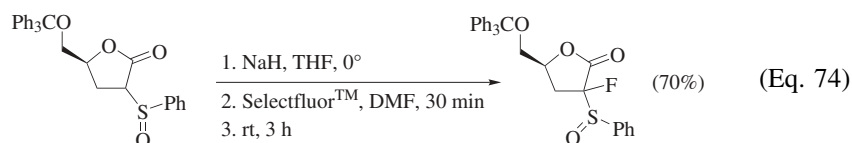
Fluorination of Organosulfur Compounds. Syntheses of α -fluoro-substituted sulfides, sulfoxides, sulfones, and sulfonates have been described. α -Fluoro-sulfides are particularly interesting since they have found applications as enzyme inhibitors, as ¹⁹F NMR probes in proteins, and as synthons for vinylic fluorides. The fluorination of sulfides is considered in this section even though the first step involves attack by sulfur. Sulfides bearing α -hydrogen atoms react rapidly with SelectfluorTM in acetonitrile at room temperature, forming fluorosulfonium salts which undergo a Pummerer-like rearrangement on treatment with base (triethylamine or DBU) to produce α -fluorosulfides.^{173,264} This method may be used to introduce a fluorine atom at C_{2'}, C_{3'}, and C_{5'} of a variety of nucleosides. The fluorination is carried out at room temperature by reaction with SelectfluorTM in acetonitrile followed by addition of triethylamine; a mixture of diastereomers is obtained (Eq. 72).²⁶⁵



The reaction of sulfides with various *N*-fluoropyridinium salts has been also examined under very mild conditions in dichloromethane at room temperature (Eq. 73).²⁶⁶ Triflates are more reactive than the corresponding tetrafluoroborates, and *N*-fluoro-2,4,6-trimethylpyridinium triflate gives the best yields. The pyridine derivative liberated in the reaction acts as a base in the Pummerer-like rearrangement.

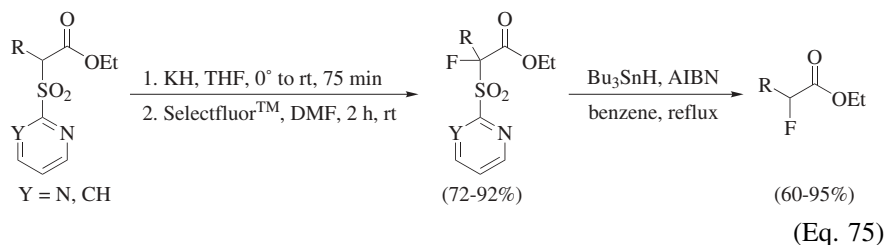


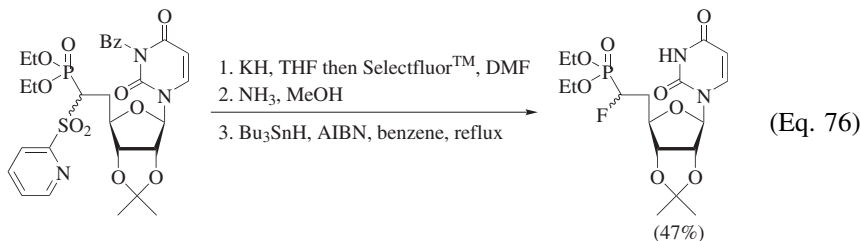
There are a few reports that describe the electrophilic fluorination of sulfoxides. Preformed α -sodium- β -keto sulfoxides are fluorinated with SelectfluorTM to form the α -fluorosulfoxides as a mixture of diastereoisomers as demonstrated in the synthesis of the fluoro furanose unit of the anti-HIV-active nucleoside, β -FddA (Eq. 74).²⁶⁷ The fluorination does not take place without preliminary deprotonation with sodium hydride; without deprotonation, oxidation to the corresponding sulfone occurs.



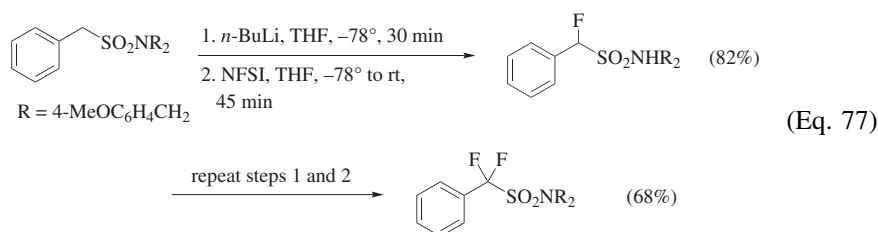
α -Fluorination of enantiomerically pure β -keto sulfoxides by SelectfluorTM does not alter the sulfinyl stereocenter and affords thermodynamic mixtures of diastereoisomeric α -monofluorinated β -keto sulfoxides in reasonable yields.²⁶⁸

There are numerous reports of α -fluorination of sulfones. For example, the α -fluorination of carbethoxyalkyl α -pyrimidin-2-yl sulfones with SelectfluorTM followed by desulfonylation provides a route for the preparation of α -fluoro carbonyl compounds (Eq. 75).²⁶⁹ This methodology has been successfully extended to the preparation of α -fluorophosphonates²⁵⁶ and applied to the synthesis of a homonucleoside α -fluoromethylene phosphonate (Eq. 76).²⁵⁵ In both studies, the sulfone group is utilized as an activating moiety for α -fluorination and is then removed from the carboxylate or the phosphonate esters.



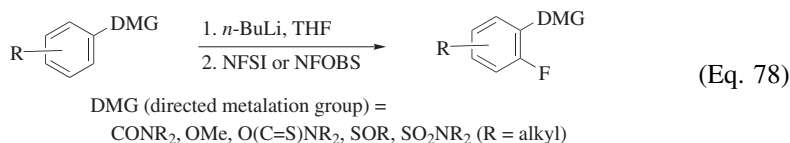


Fluorination of benzylic sulfonic compounds is well documented. α -Carbanions of sulfones, sulfonate esters, or sulfonamides are generated with strong bases such as NaHMDS or *n*-BuLi in tetrahydrofuran at low temperature and react with NFSI to give α -fluoro or α -difluorosulfonyl compounds in good yields.^{270,271} Rather higher yields of difluorinated products are obtained by sequential fluorination as illustrated in the synthesis of an inhibitor of carbonic anhydrase (Eq. 77).²⁷¹



Difluoromethyl benzyldisulfonates having a neopentyl or a trichloroethyl ester group are prepared in moderate to good yields whereas other ester groups (methyl, ethyl, *iso*-propyl) yield only decomposition products.^{272–275}

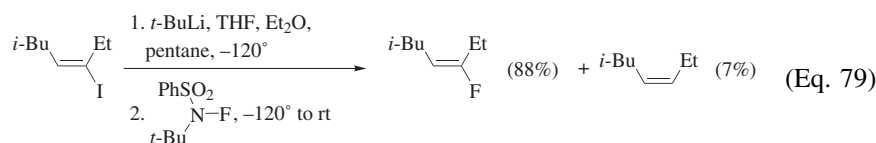
Fluorodemetalation. This method, which utilizes a metalation intermediate prior to effecting the electrophilic fluorination step, overcomes problems associated with direct electrophilic fluorinations that do not proceed regioselectively. Electrophilic fluorination of organometallic species is of broad interest and has been developed since selective metalations can be achieved. Thus, regioselective fluorination of aromatics can be accomplished in a two-step sequence: metalation followed by electrophilic fluorination. A range of ortho-lithiated carbon-, oxygen-, and sulfur-based directed metalation group systems undergo reaction with NFSI or NFOBS (Eq. 78).^{33,276–282} In some examples, NFSI leads to phenylsulfonyl transfer rather than electrophilic fluorination.



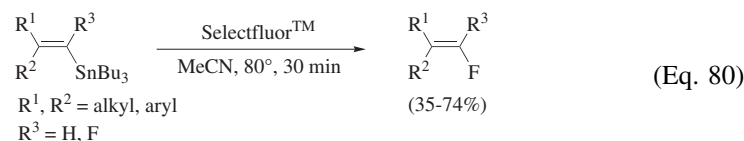
N-Alkyl *N*-fluorobenzenesulfonamides,⁶¹ *N*-fluoroquinuclidinium triflate,⁶⁹ and perfluoro-*N*-fluoro-*N*-(4-pyridyl)methanesulfonamide⁶¹ also fluorinate ortho-metalated substituted aromatic compounds. Aryl and alkyl organometallics

(lithium and Grignard reagents), which are strongly basic carbanions, are preferably fluorinated with reagents for which β -elimination of hydrogen fluoride is precluded. Grignard reagents generally react at 0° whereas organolithium compounds are preferably fluorinated in good yields at -78° . Several examples are given in the literature.^{31,42,61,68,69,85,98,100,150}

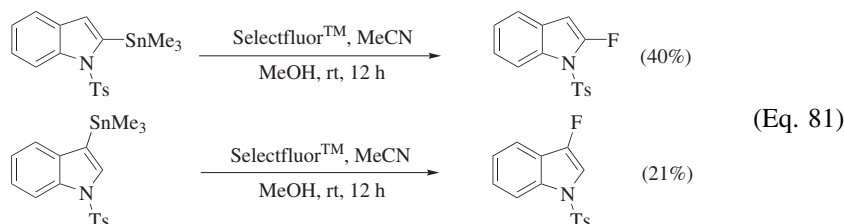
The reaction of *N*-(*tert*-butyl) *N*-fluorobenzenesulfonamide with alkenyl-lithium reagents, which are obtained from the corresponding iodoalkenes, affords the fluoroalkenes in high yields with retention of configuration. Small amounts of non-fluorinated alkenes are present with the fluoroalkenes as shown in Eq. 79.^{67,283,284} Alkenyl iodides serve as starting materials while alkenyl mercurials give fluoroalkenes in very poor yields.



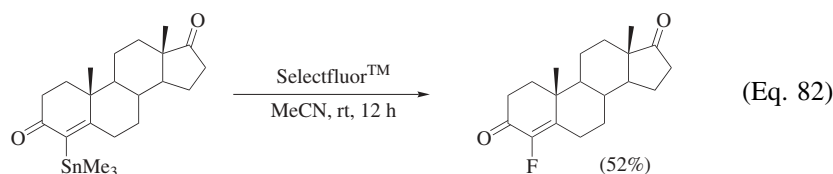
The reaction of terminal vinyl stannanes and fluorovinyl stannanes with SelectfluorTM in refluxing acetonitrile is a facile method for the synthesis of mono- and difluoroalkenes, respectively (Eq. 80).²⁸⁵



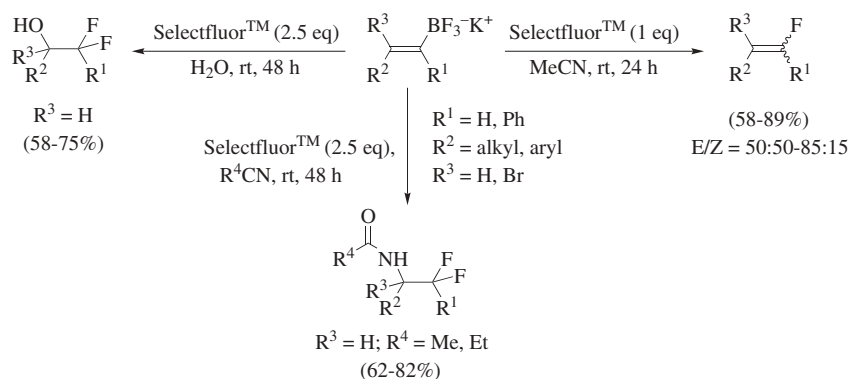
Fluorination of 2- and 3-trimethylstannylindoles with SelectfluorTM gives 2- and 3-fluoroindoles, respectively (Eq. 81), demonstrating the ability of organometallic species to direct the electrophilic fluorination and to overcome the usual preference for indoles to react with electrophiles in the 3-position.²⁰⁵



Another example of the regioselective fluorination of a trimethylstannyl derivative is given for the fluoro steroid in Eq. 82.²⁵³

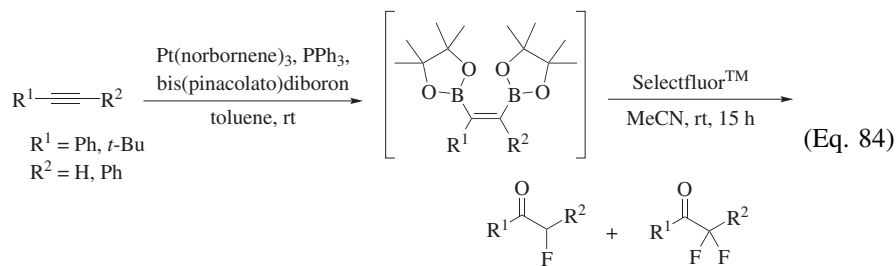


Likewise, alkenyl trifluoroborates react with SelectfluorTM to give fluoroalkenes in 58–89% yield, although with complete loss of stereochemistry. Difluoromethyl-substituted alcohols and amides are obtained with two equivalents of SelectfluorTM in water or a nitrile solvent, respectively (Eq. 83).²⁸⁶ The same reaction products can be obtained from reaction of alkenyltrimethylsilanes with SelectfluorTM (see later in the text).²⁸⁷



(Eq. 83)

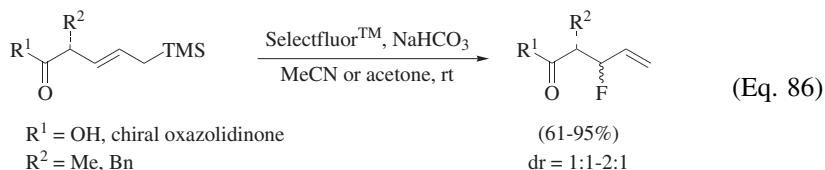
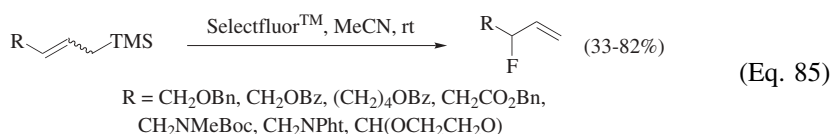
The catalytic diboration of alkynes to give intermediate alkenyl diboronates, followed by electrophilic fluorination with SelectfluorTM, produces α -fluorinated and α,α -difluorinated carbonyl compounds depending on the amount of fluorinating agent. This approach complements other methods for the synthesis of such compounds. With one equivalent of SelectfluorTM, mixtures of mono- and difluorinated carbonyl compounds are obtained, whereas the addition of more than two equivalents of SelectfluorTM favors the formation of α,α -difluorinated carbonyl compounds with up to 95% yield (Eq. 84).²⁸⁸



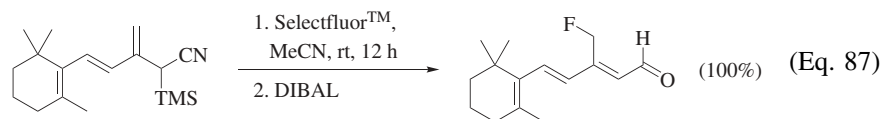
(Eq. 84)

The fluorodesilylation of aryl-, vinyl-, allyl-, and propargyltrialkylsilanes can be achieved with electrophilic sources of cationic fluorine to prepare a variety of fluorine-containing compounds.²⁸⁹ These reactions are run most efficiently with SelectfluorTM. Fluorodesilylation of phenyltrimethylsilane occurs in low yield (19%).²⁸⁹ The reaction with alkenyltrimethylsilanes affords fluoroalkenes with loss of stereochemistry, and difluoromethyl-substituted amides, alcohols, or ethers

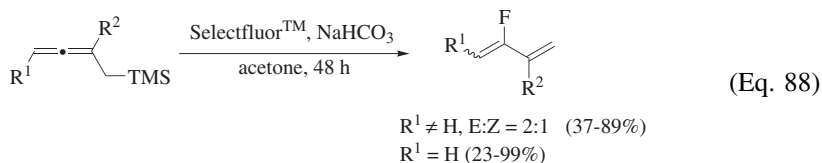
when an excess of SelectfluorTM is used in the presence of various nucleophiles (see Eq. 83 for similar products obtained from alkenyl trifluoroborates).²⁸⁷ Allylsilanes are also good substrates for fluorodesilylation conducted in acetonitrile at room temperature with one equivalent of SelectfluorTM to afford various functionalized allylic fluorides (Eq. 85).²⁹⁰ Importantly, when R is a carbonyl group, the reaction fails. Starting from the enantiopure allylsilanes shown in Eq. 86, mixtures of diastereomeric allylic fluorides are obtained with a poor level of diastereocontrol.²⁹¹



The synthesis of 19-fluoro- β -(ionylidene)acetaldehyde is a nice example of the application of the fluorodesilylation of allylsilanes (Eq. 87).²⁹²



Electrophilic fluorodesilylation can also be applied to allenyltrimethylsilanes as an entry into 2-fluorodienes with various substitution patterns (Eq. 88).²⁹³

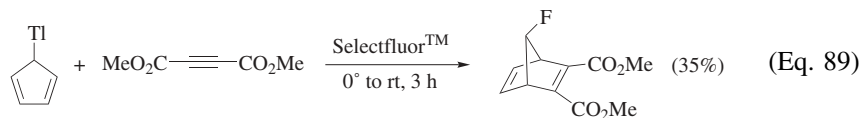


In terms of mechanism, fluorodesilylation involves an addition-elimination pathway via a carbocationic intermediate. The trimethylsilyl group controls the regioselectivity of the addition by virtue of the stabilization of the cation β to the silicon.

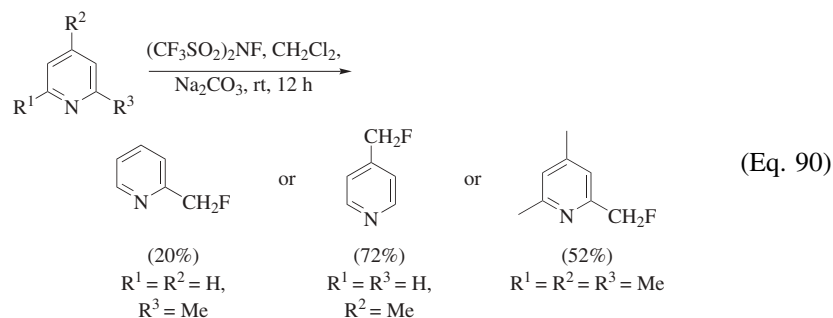
A single example of fluorination of trichlorophenylsilane with *N*-fluoroquinclidinium fluoride has been reported to give fluorobenzene in a low 22% yield; the reaction is presumably triggered by fluoride attack on silicon.^{113,115}

Fluorination of cyclopentadienylthallium with SelectfluorTM generates 5-fluorocyclopentadiene in situ, which can be trapped by suitable dienophiles to form

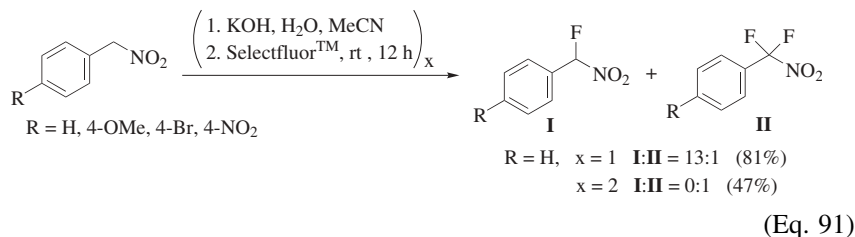
7-fluorobicyclo[2.2.1]heptenes having exclusively the syn orientation as exemplified in Eq. 89.²⁹⁴



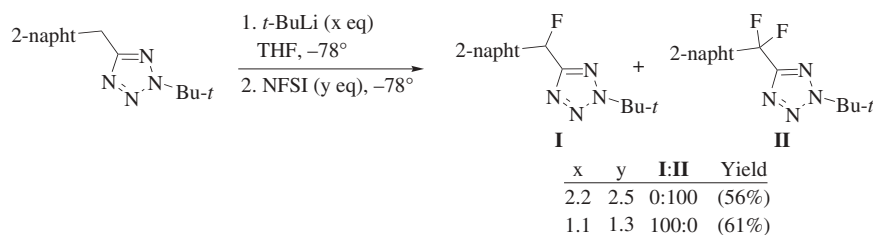
Miscellaneous Substrates. The selective fluorination of diverse organic compounds is the subject of this section. For instance, the preparation of 2- or 4-fluoromethylpyridines is realized with *N*-fluorobis(trifluoromethanesulfonyl)imide in dichloromethane at room temperature. In these reactions, the presence of sodium carbonate is necessary to suppress the formation of unreactive pyridinium salts which are generated by the strongly acidic bis(trifluoromethanesulfonyl)imide co-product (Eq. 90).²⁴⁶ It has been proposed that tautomers of methylpyridines having an enamine-like structure are fluorinated on the methylene site of the enamine. However, in some instances, small quantities of fluoropyridines are formed.



Fluorination at a benzylic position bearing an electron-withdrawing group (nitro, cyano, tetrazolyl, or sulfonate) has been studied in detail with various fluorinating agents. In a first step, deprotonation with a base is required at the benzylic position. By choosing an appropriate base and using proper amounts of the base and fluorinating agent, the substrates can be mono- or difluorinated in moderate to high yields. As shown in Eq. 91, phenylnitromethane and derivatives react in aqueous potassium hydroxide with Selectfluor™ under stoichiometric conditions to yield monofluorinated products selectively. Repeating the deprotonation-fluorination sequence in one pot gives exclusive access to the difluorinated product, albeit in a moderate yield.²¹⁸

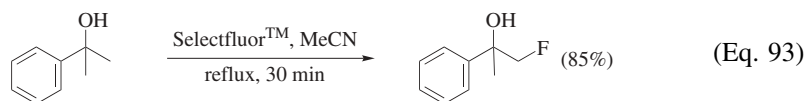


Similarly, benzylic α,α -difluoro-substituted nitriles, tetrazoles, and sulfonates can be prepared by electrophilic fluorination of benzylic carbanions generated by means of strong bases (*t*-BuLi, LDA, NaHMDS). The fluorination can be performed either with NFSI^{272,275} or NFOBS.³³ Furthermore, the use of slightly more than one equivalent of base and fluorinating agent allows good control of the monofluorination reaction (Eq. 92).^{33,272}

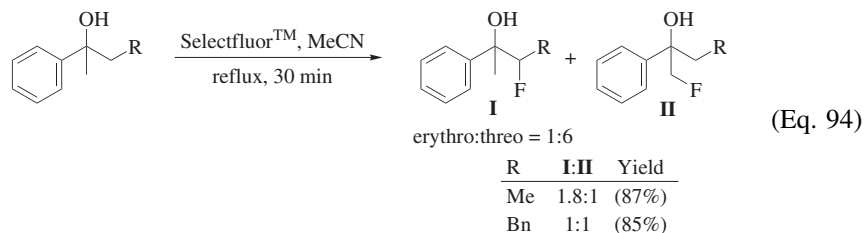


(Eq. 92)

The synthesis of vicinal fluorohydrins from aryl- and alkyl-substituted tertiary alcohols can be achieved with SelectfluorTM in acetonitrile in high yields (Eq. 93).²⁹⁵ An additional phenyl group geminal to the OH group improves the yield of vicinal fluorohydrin formation. By choosing such substrates, the competitive oxidation of the hydroxy functional group by the fluorinating agent is obviously suppressed. With dialkyl(phenyl)-substituted alcohols having two different alkyl groups, a pair of regioisomers is formed with diastereomeric mixtures for one (Eq. 94) or both of the regioisomers.²⁹⁵ The reaction presumably proceeds through the styrene intermediate.



(Eq. 93)

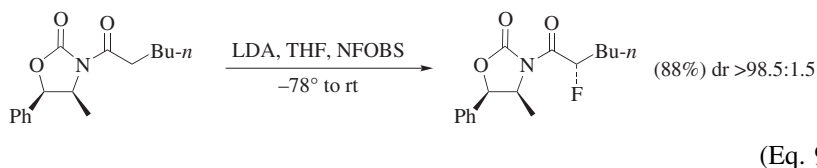


(Eq. 94)

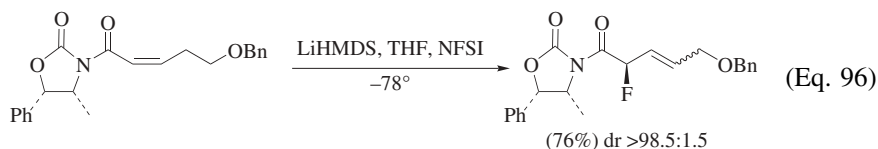
Diastereoselectivity

Intramolecular stereocontrol by an enantiomerically pure substrate is the origin of a diastereoselective reaction. The existing stereogenic center remains incorporated in the product or can be removed after formation of the new fluorinated stereogenic center. In this section, only the synthetic routes that require the temporary attachment of a chiral auxiliary (i.e., chiral auxiliary approach) are covered. Other examples were discussed previously in context with particular substrates.

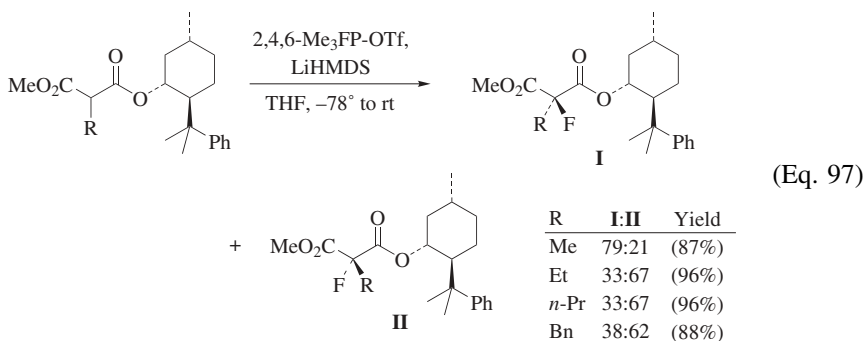
Highly diastereoselective electrophilic fluorinations have been developed using chiral oxazolidinones as auxiliaries and NFSI or NFOBS as the fluorinating agent. Good to excellent diastereoselectivities are obtained by selective approach of the fluorinating agent from the less hindered *si* face of the chiral imide enolate (Eq. 95).^{296–301} The fluorination is suggested to occur by an S_N2-type mechanism for transfer of fluorine to the enolate species.³³



Deconjugative electrophilic fluorination of lithium dienolates of α,β -unsaturated chiral oxazolidinones with NFSI proceeds with complete diastereoselectivity whereas NFOBS is less selective. This difference is attributed to the greater steric bulk of NFSI (Eq. 96).^{297,302,303} This strategy has been successfully applied to the synthesis of biologically important fluoro nucleosides,²⁹⁹ fluoro carbohydrates,³⁰² and to the synthesis of a phosphotyrosyl mimetic.³⁰⁴

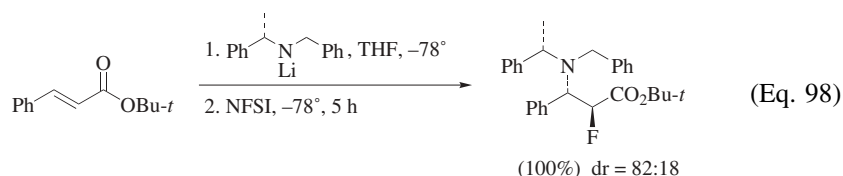


Diastereoselective fluorination of the lithium enolates of (1*R*,3*R*,4*S*)-8-phenylmenthyl β -keto esters with *N*-fluoro-2,4,6-trimethylpyridinium triflate allows the construction of quaternary fluorinated stereogenic centers with moderate diastereoselectivity (Eq. 97).^{305–307} Of the substrates evaluated, the one where R is methyl displays diastereoselectivity in electrophilic fluorination opposite to that involving other R groups; in these reactions the R group, which is responsible for enolate conformation, causes preferred access to one of the enolate faces.

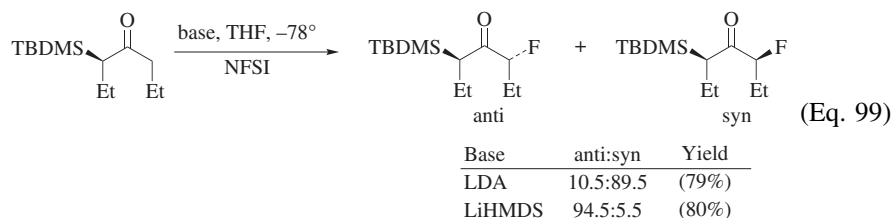


Some diastereoselective fluorinations of β -keto esters bearing a chiral auxiliary (e.g. cholesteryl ester³⁰⁸ and L-menthyl esters^{309–311}) have been conducted in the presence of a chiral transition-metal catalyst (see next section). In these reactions, a double stereodifferentiation was expected; however, the stereoselectivity was lower or equal to that observed with achiral ester derivatives.

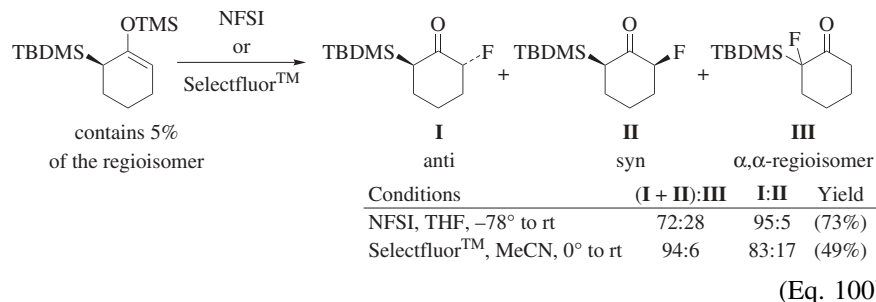
A tandem conjugate addition of a chiral lithium amide to *tert*-butyl cinnamate followed by a diastereoselective electrophilic fluorination of the intermediate enolate by NFSI provides β -amino α -fluoro esters (Eq. 98).³¹²



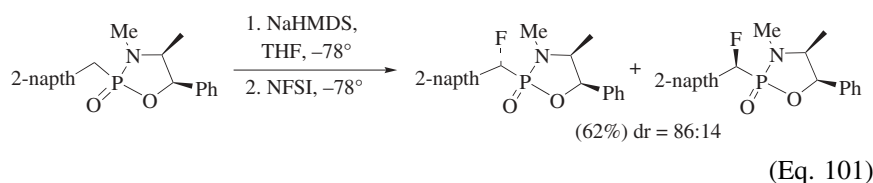
Diastereoselective electrophilic fluorination of enantiopure α -silyl ketones places the fluorine atom at the α' position. The α -silyl group provides stereocontrol for fluorination and is subsequently removed. High diastereomeric ratios are obtained for cyclic ketones, whereas lower dr values are measured for acyclic ketones. In most cases, replacement of LDA by LiHMDS, which causes different enolate geometries, allows reverse diastereoselectivity to be obtained (Eq. 99). Either enantiomer (after removal of the chiral auxiliary) can be produced by choosing the *Z*- or *E*-enolate geometry: LDA provides *E*-enolates which give *syn* isomers, whereas LiHMDS provides *Z*-enolates which give *anti* isomers. This method is restricted to the synthesis of α -fluoro ketones that lack unsaturation because ozone is necessary to remove the chiral auxiliary.^{313,314}



This concept can be applied to silyl enol ethers; however, the fluorination gives rise to a significant amount of regioisomers (Eq. 100). The unpredictable formation in various amounts (up to 100%) of the regioisomer bearing the fluorine atom on the carbon bearing the silyl group is obviously a disadvantage of the method.³¹⁴



A variety of phosphoramidates bearing *trans*-(*R,R*)-1,2-bis(*N*-methylamino) cyclohexane or (–)-ephedrine as a chiral auxiliary react with NFSI to give α -monofluoroalkylphosphonates.³¹⁵ The diastereoselectivity is strongly dependent on the nature of the base and counterion with dr values ranging from 51:49 to 86:14. LiHMDS gives good results with chiral diaminophosphoramidates, whereas NaHMDS is preferred when ephedrine is the auxiliary (Eq. 101).



Enantioselectivity

There are several methods for conducting enantioselective electrophilic fluorination.^{316–320} The use of chiral, nonracemic N–F or [N–F]⁺ reagents is the most general approach. With the aid of a stoichiometric, chiral fluorinating agent, a prochiral substrate is transformed into a chiral product with concomitant creation of a fluorine-bearing stereogenic center. Another approach involves transition-metal catalysis of the fluorination of 1,3-dicarbonyl compounds and β -keto phosphonates. Since enolization of 1,3-dicarbonyl compounds is promoted by Lewis acids, chiral transition-metal catalysts have been investigated, and are found to produce enantioenriched α -fluorinated 1,3-dicarbonyl compounds. The substrates are usually β -keto esters. Enantioselective organocatalytic α -fluorination of aldehydes and ketones has also been accomplished. β -Keto esters and β -keto phosphonates have been produced with moderate enantioselectivities using phase transfer catalyzed fluorination. On the other hand, organocatalytic fluorination of aldehydes and ketones with chiral pyrrolidine or imidazolidinone derivatives gives very high enantioselectivities.

The first enantioselective fluorinating agents were the camphor-derived *N*-fluorosultams **1a–d** (Fig. 13). They are prepared by passing a mixture of 10% (v/v) molecular fluorine in nitrogen through a solution of the corresponding camphorsultam in CHCl₃/CFCl₃ at –40° in the presence of powdered NaF as the HF-scavenger.

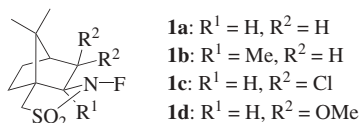
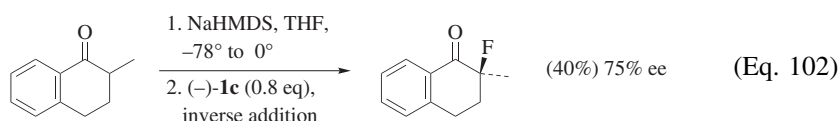
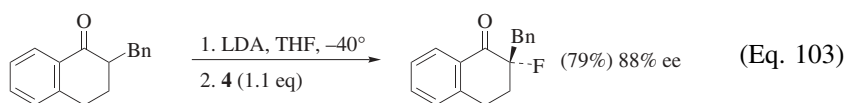


Figure 13. Camphor-derived *N*-fluorosultams.

The fluorination of various prochiral metal enolates of ketones, esters, and β -keto esters affords α -fluoro carbonyl compounds in modest yields and with up to 75% ee (Eq. 102).^{321–324} However, most of the ee values are in the range 10% to 40%.



Other examples of chiral fluorinating agents include the nonracemic, acyclic *N*-fluorosulfonamides **2** and **3a,b** (Fig. 14).³²⁵ Their preparations utilize either diluted molecular fluorine or perchloryl fluoride. However, they display poor reactivity toward metalated enolates and are not very stable under the reaction conditions. Poor yields ($\leq 53\%$) and only moderate ee values of up to 54% are obtained.³²⁵ Several enantiopure, cyclic *N*-fluorosulfonamides **4–6** (Fig. 14) have been designed and tested for electrophilic fluorination of aryl ketone enolates.^{326–330} *N*-Fluorosulfonamide **4** exhibits excellent enantioselectivity, producing ee values as high as 88%, and affords good chemical yields (Eq. 103).³²⁶



Although satisfactory enantiomeric excesses of up to 88% are attained in the fluorination of metal enolates, the *N*-F reagents present two sizeable drawbacks: their arduous multi-step syntheses, and the necessity of handling molecular

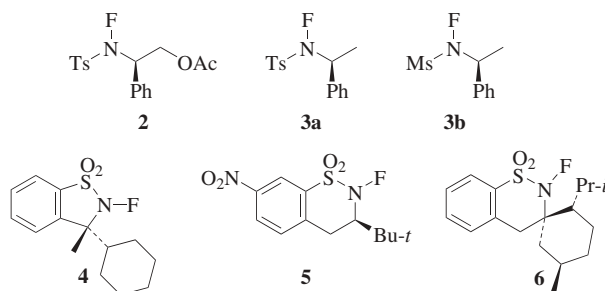


Figure 14. Chiral *N*-F fluorinating agents.

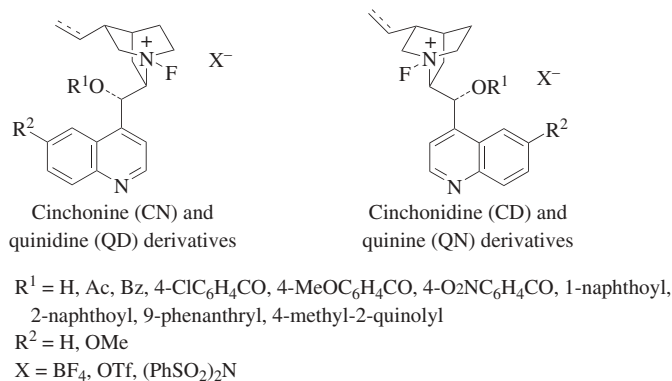
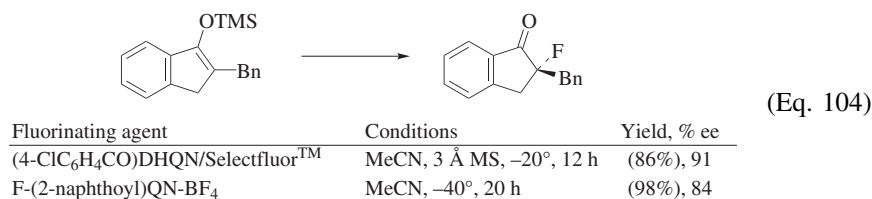


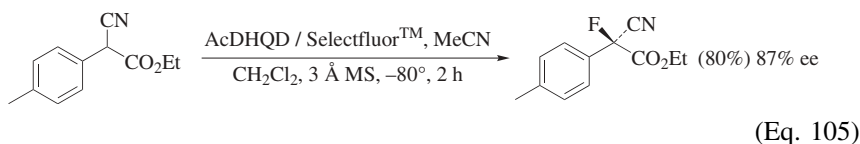
Figure 15. $[\text{N-F}]^+$ Reagents from cinchona alkaloids.

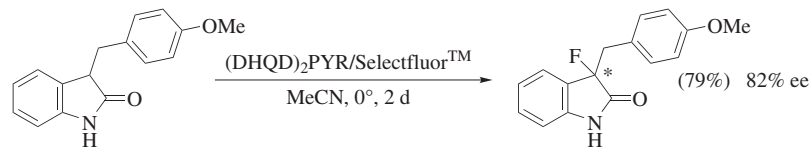
fluorine or perchloryl fluoride. A major breakthrough in the field of enantioselective electrophilic fluorination came from the development of a different class of reagents: the $[\text{N-F}]^+$ ammonium salts of cinchona alkaloids (Fig. 15). These fluorinating agents are easily obtained in a one-step transfer-fluorination of cinchona alkaloids with the aid of SelectfluorTM, or can be generated in situ from the same reagents.^{331–335} In addition, such reagents benefit from the commercial availability of both SelectfluorTM and the cinchona alkaloids. Several achiral fluorinating agents (SelectfluorTM, NFlth, NFSI, and 2,6-Cl₂FP-BF₄) are efficient fluorine-transfer reagents.³³⁶

Unlike the chiral, neutral N–F reagents, the $[\text{N-F}]^+$ ammonium salts of cinchona alkaloids are employed for the fluorination of a number of substrates: ketone and ester enolates, β -keto esters, α -cyano esters, silyl enol ethers, nitrile anions, and oxindoles. These reagents possess a stronger fluorinating power than the neutral N–F reagents, allowing the fluorination of enol derivatives such as silyl enol ethers (Eq. 104).^{334,337}



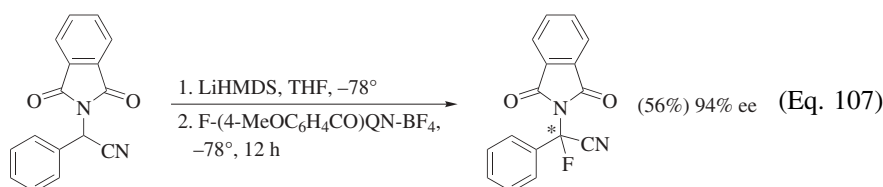
Among the most interesting substrates used in the enantioselective electrophilic fluorination are α -cyano arylacetates (Eq. 105)³³⁴ and oxindoles (Eq. 106).³³⁴



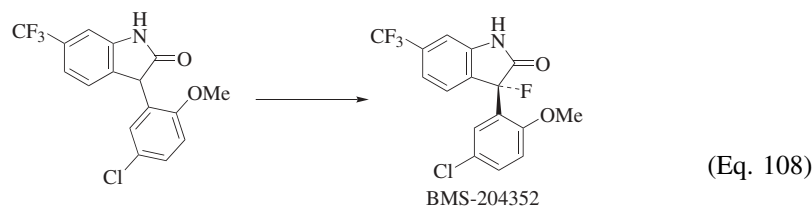


(Eq. 106)

Applications of these $[N-F]^+$ reagents include the enantioselective syntheses of α -fluoro- α -amino acid derivatives (Eq. 107),³³⁸ fluoropeptides,³³⁹ BMS-204352, a potent opener of maxi-K channels (Eq. 108),^{340–342} and 20-deoxy-20-fluorocamptothecin (Eq. 109).³⁴³

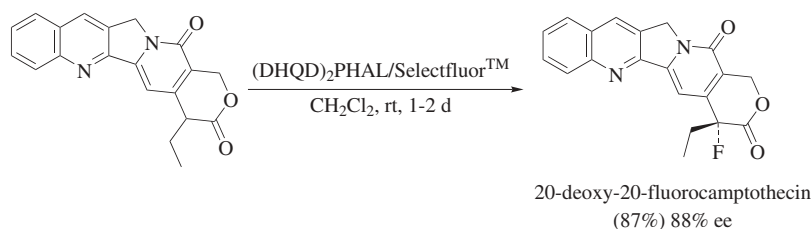


(Eq. 107)



(Eq. 108)

Fluorinating agent	Conditions	Yield, % ee
(DHQN) ₂ AQN/Selectfluor [™]	MeCN, CH ₂ Cl ₂ , -80°, 12 h	(94%), 84
F-(2-naphthoyl)QN-BF ₄	DABCO, THF, MeCN, CH ₂ Cl ₂ , -78°, 12 h	(96%), 88

20-deoxy-20-fluorocamptothecin
(87%) 88% ee

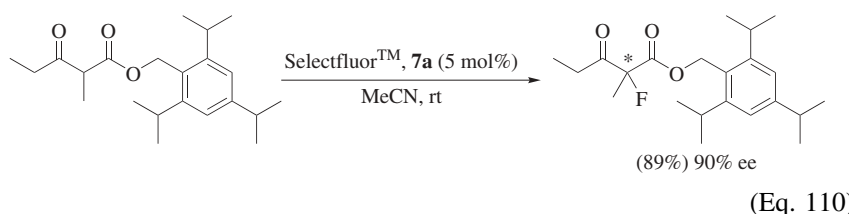
(Eq. 109)

These charged $[N-F]^+$ reagents are soluble in acetonitrile and also in a wide variety of ionic liquids. In the latter, electrophilic fluorinations of silyl enol ethers performed at room temperature produce the target α -fluoro carbonyl compounds in both yields and ee values similar to those obtained in acetonitrile at -40° . In addition, the cinchona alkaloids can be immobilized in the ionic liquid, allowing recovery and reuse.³⁴⁴ Grafting cinchona alkaloids onto a polystyrene support constitutes another approach to recycling the source of chirality in the enantioselective electrophilic fluorination.³⁴⁵ Here again, the enantiodiscriminating

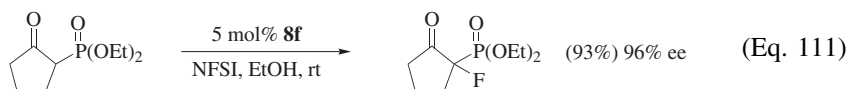
properties of the polymer-bound reagents are similar in all respects to those of non-supported analogs.

The ease of preparation and generality of fluorination make the $[N-F]^+$ class of reagents the best choice for enantioselective electrophilic fluorination. Attempts to perform a catalytic electrophilic fluorination of silyl enol ethers with the aid of cinchona alkaloids failed because the fluorination by the stoichiometric reagent is faster than the fluorine transfer, leading to racemic fluorinated products. A partial solution of this drawback was found by conducting the fluorination on acyl enol ethers, which are less reactive than the silyl enol ethers, in the presence of sodium acetate.³⁴⁶

Catalytic enantioselective electrophilic fluorination under transition-metal catalysis succeeds with α -monosubstituted β -keto esters and β -keto phosphonates that have the requisite ease of enol (or enolate) formation. Chiral transition-metal catalysts **7a** and **b**,^{45,308,309,347–350} **8a–g**,^{351–356} **9a** and **9b**,^{310,311,357,358} and **10**³⁵⁹ (Fig. 16) have been utilized, and their efficiency is clearly demonstrated by the high ee values of the fluorinated products. For example, α -fluoro β -keto esters are obtained using $TiCl_2[(R,R)\text{-TADDOLato}]$ complex **7a** with enantiomeric excesses up to 90% (Eq. 110).³⁰⁸ The more sterically hindered complex **7a** gives rise to higher enantioselectivities than **7b**; **7a** is also the more effective catalyst.



Interestingly, palladium complexes **8a–d** can be immobilized and reused in ionic liquids with excellent reproducibility even after ten consecutive cycles. For example, the enantioselective electrophilic fluorination of 2-methyl-3-oxo-3-phenylpropionic acid *tert*-butyl ester with **8b** in [hmim][BF₄] gives the corresponding fluorinated product in 93% yield with 92% ee, and still in 67% yield with 91% ee after ten cycles.³⁵² The synthesis of α -fluoro- β -keto phosphonates can be realized in high enantiomeric excesses (94–98% ee) using chiral palladium complexes **8e** or **8f** and NFSI (Eq. 111),^{360,361} or **8g** and NFSI (87–97% ee).³⁶²



Bisoxazoline-copper (II) complexes are also efficient for the catalytic fluorination of both acyclic and cyclic β -keto esters using NFSI as the achiral fluorinating agent. Catalysts **9a** (Fig. 16) do not lead to enantioselectivities as high as those observed with catalysts **7** or **8** whereas catalyst **9b** [Fig. 16,

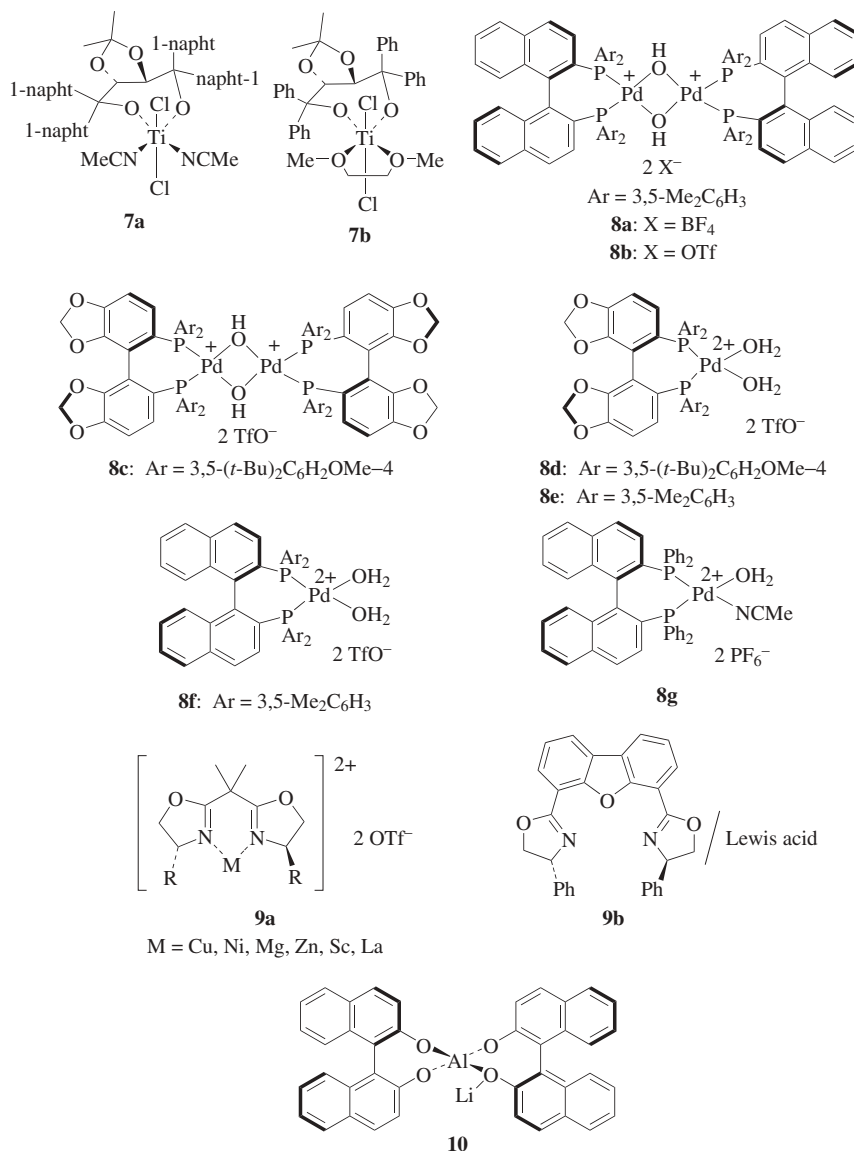
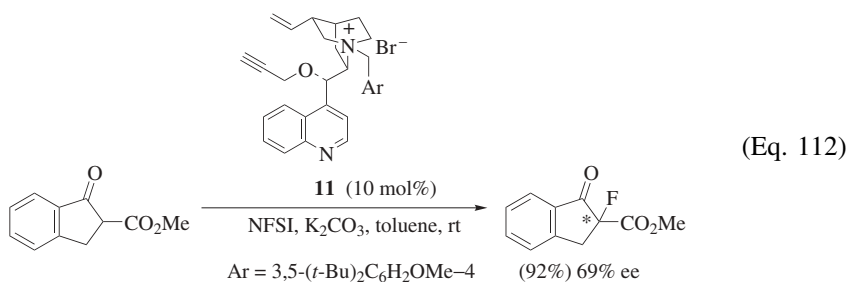


Figure 16. Chiral transition-metal catalysts.

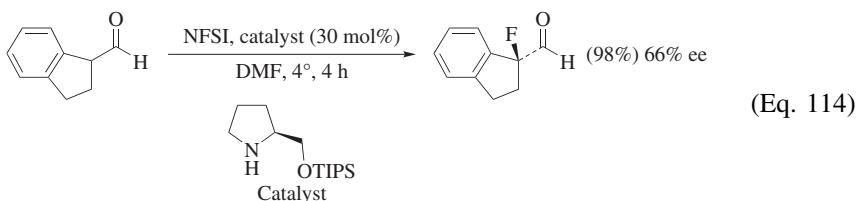
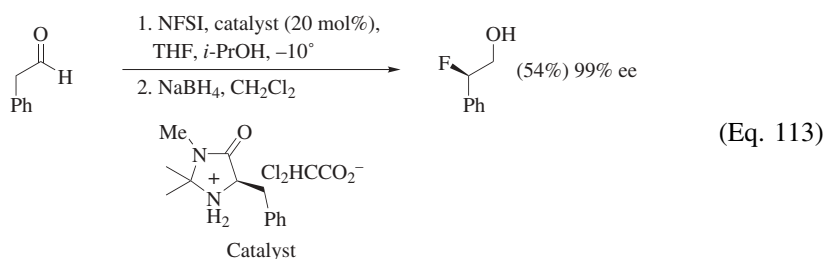
Lewis acid = Ni(ClO₄)·6H₂O] generates enantioselectivities up to 99%.³¹¹ As little as 0.1 mol% of catalyst **9a** (M = Cu, R = Ph) can be used; the addition of 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) is crucial for achieving high enantioselectivity.³⁵⁷ Importantly, a simple change of the metal salt allows the preparation of either of the two enantiomers.³¹⁰ Other combinations of chiral

ligands with various metals and fluorinating agents have been evaluated. In particular, the Al-Li-BINOL complex **10** allows the preparation of α -fluoro β -keto esters in high yields with moderate ee values; up to 67%.³⁵⁹ The combination of chiral bisoxazoline **9b** and $\text{Zn}(\text{ClO}_4)_2$ also catalyzes the fluorination of β -keto phosphonates in up to 91% ee³⁵⁸ and β -keto esters in up to 99% ee.³¹¹

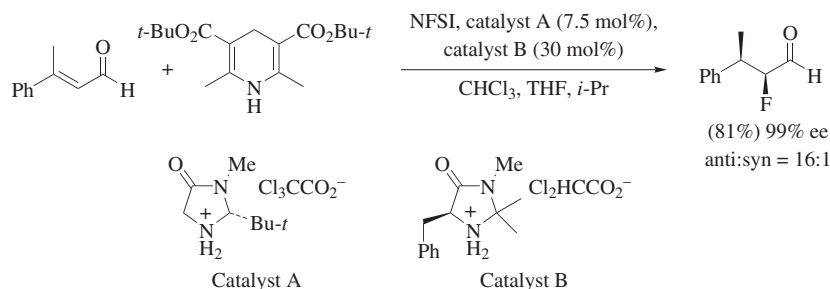
Organocatalysis is an alternative approach that induces high to very high enantioselectivities. The use of the cinchonine-derived quaternary ammonium salt **11** as a chiral phase-transfer catalyst with an achiral fluorinating agent allows the enantioselective fluorination of β -keto esters (Eq. 112)³⁶³ and α -cyano esters.³⁶⁴



Direct organocatalytic enantioselective fluorination of aldehydes and ketones employs proline derivatives or imidazolidinones. α -Fluorocyclohexanone is obtained at a modest 36% ee with SelectfluorTM in the presence of 23 mol% of *trans*-4-hydroxy-*L*-proline.³⁶⁵ Higher enantioselectivities are attained in the organocatalyzed fluorination of aldehydes.^{366–368} A screening of electrophilic fluorinating agents shows a preference for NFSI rather than SelectfluorTM or pyridinium salts. Linear aldehydes allow high enantioselectivities of up to 99% (Eq. 113),^{366–368} whereas α -branched aldehydes that generate quaternary chiral centers give moderate ee values of up to 66% (Eq. 114).³⁶⁸

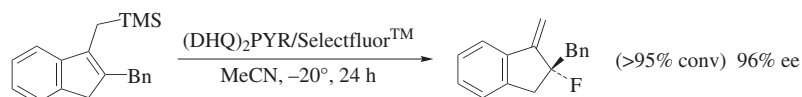


Exposure of α,β -unsaturated aldehydes to a tandem reaction that combines transfer hydrogenation conditions using Hantzsch esters and NFSI in the presence of one or a combination of two organocatalysts allows the formal addition of hydrogen fluoride with very high levels of enantio- and diastereoselection (Eq. 115).³⁶⁹



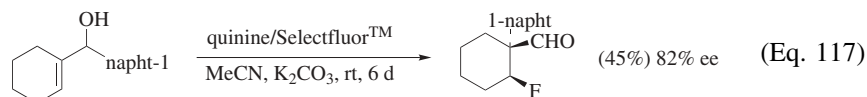
(Eq. 115)

α -Fluoro carbonyl compounds are not the sole targets of the enantioselective electrophilic fluorination; allylic fluorides can be obtained by the electrophilic fluorodesilylation of allyl silanes. With *N*-fluoroammonium salts of cinchona alkaloid derivatives generated in situ, some fluoro allylic compounds are obtained in high conversions with excellent enantioselectivities (Eq. 116).^{370–372}



(Eq. 116)

A quinine/Selectfluor™ combination allows the fluorination of allylic alcohols with subsequent rearrangement to give diastereomerically pure α -quaternary- β -fluoro aldehydes in moderate yields and good enantioselectivities (Eq. 117).³⁷³



COMPARISON WITH OTHER METHODS

Single-step transformation of C–H to C–F linkages requires sources of electrophilic fluorine (F^+) or radical fluorine (F^\bullet). The very reactive, molecular fluorine, when used under highly controlled conditions, can be a source of these fluorinating species. Such reactions are highly substrate dependent, but often in a predictable manner. When direct fluorination is possible, this route can potentially have the lowest cost for introducing electrophilic fluorine.^{17,374–378} Reactions of fluorine at ambient temperatures tend to be homolytic in nature because of the

weak F–F bond (37.7 kcal/mol), thus leading frequently to extensive decomposition. However, ionic addition of fluorine occurs when the reaction is carried out at low temperature with diluted fluorine in helium or nitrogen, and in a high dielectric constant solvent with a proton source to suppress radical processes. Sulfuric acid or formic acid are excellent solvents to promote electrophilic (rather than radical) fluorination. These can be used with or without other polar high dielectric solvents such as acetonitrile. Formic acid gives fewer problems with some aromatic substrates (such as competing sulfonation, hydrolysis of nitriles, etc.). Substrates such as β -dicarbonyl compounds^{379,380} and substituted benzenes^{381,382} give high yields of fluorinated products. The former react mainly at the central carbon atom whereas the latter react at the expected site of electrophilic attack.

Reagents containing the O–F group contributed to the rapid development of organofluorine chemistry. This class of reagents includes fluoroxytrifluoromethane (CF₃OF), fluoroxyperfluoroalkanes (R_fOF), bis(fluoroxy)difluoromethane [CF₂(OF)₂], perfluoroacyl hypofluorites (R_fCO₂F), acetyl hypofluorite (MeCO₂F) and higher homologs (RCO₂F), trifluoromethanesulfonyl hypofluorite (CF₃SO₂OF), pentafluorosulfur hypofluorite (SF₅OF), and cesium fluorooxysulfate (CsSO₄F).^{2,383–385} These compounds are electrophilic sources of fluorine and are generally more selective than molecular fluorine. Hypofluorites, however, have not received wide acceptance, and their use has declined dramatically in recent years because of difficulties in handling and danger associated with their very strong oxidizing power. Consequently, N–F reagents have surpassed O–F reagents in stability, safety, and handling convenience.

Perchloryl fluoride (FCIO₃), in which the fluorine atom is bound to the chlorine atom of the perchloryl function, ably fluorinates organic substrates such as aromatics and stabilized carbanions. However, the manipulation of perchloryl fluoride is too problematic for general use: it can decompose explosively, and it leads to unwanted chlorinated by-products.^{386,387}

Xenon difluoride (XeF₂) and higher fluorides (XeF₄, XeF₆) are also very effective for the fluorination of nucleophilic substrates, but the commercial use of XeF₂ is limited owing to its high cost.^{13,388–390}

Hypervalent difluoroiodoarenes are used as fluorinating agents. Fluorination of β -dicarbonyl compounds, silyl enol ethers, α -phenylsulfanyl esters, α -seleno carboxylic acid, and acetamides using iodotoluene difluoride is an apparent electrophilic fluorination. From a mechanistic standpoint, the carbon-fluorine bond formation occurs through a nucleophilic fluorination; for this reason, hypervalent difluoroiodoarenes are not considered further in this chapter.^{391–398}

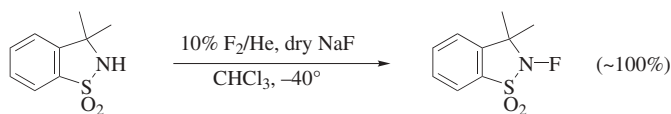
EXPERIMENTAL CONDITIONS

Caution. Fluorine is a poisonous, corrosive, flammable, pale yellow to greenish gas, with an irritating pungent odor. It is extremely reactive, and is a powerful oxidant that reacts violently with many materials. It is toxic by inhalation or ingestion.

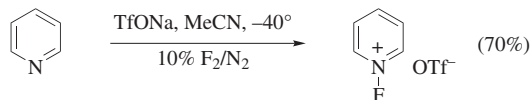
Molecular fluorine is not directly used in electrophilic fluorination with N-F reagents; however, the syntheses of all the N-F reagents require molecular fluorine or a reagent made from it. The safe handling of molecular fluorine requires a high level of expertise and special apparatus. Molecular fluorine is prepared by the electrolysis of a solution of anhydrous hydrogen fluoride that contains potassium fluoride (KF/2HF is an ionic liquid at about 100°).³⁹⁹ Chemical methods for the generation of molecular fluorine have also been reported.^{400–403} Cylinders of F₂/N₂ or F₂/He blends and the particularly hazardous neat F₂ are commercially available. The rate of uptake of fluorine and the reaction temperature must be carefully controlled to prevent free-radical side reactions. Low reaction temperatures in the range –80° to –30° are adequate. The fluorination reactions with molecular fluorine are carried out in Pyrex[®] glass reaction vessels^{22,113} or in a polytetrafluoroethylene flask for experiments in which aqueous HPF₆ or HSbF₆·6H₂O are used.¹²² Fluorination reactions with N-F reagents are conducted in glass vessels.

EXPERIMENTAL PROCEDURES

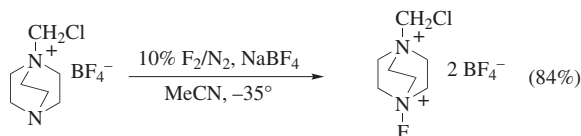
Preparation of Fluorinating Agents



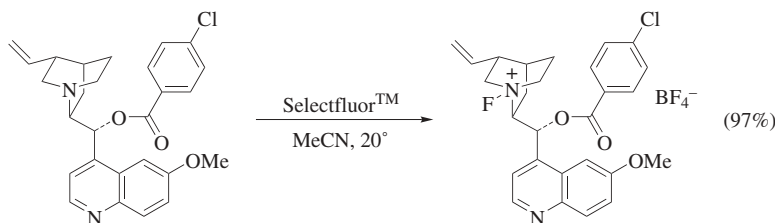
2-Fluoro-3,3-dimethyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide [with F₂].⁴⁰⁴ A conical glass flask (1000 mL) was charged with anhydrous powdered sodium fluoride (60 g oven dried at 200° for 24 hours), anhydrous CHCl₃ (600 mL), and 3,3-dimethyl-2,3-dihydro-1,2-benzo[d]isothiazole-1,1-dioxide (20 g, 101 mmol), and the resulting mixture was magnetically stirred at room temperature under nitrogen until the latter compound had completely dissolved. The reaction vessel was immersed in a cryo-cooled, thermostatically controlled (–40°) ethanol bath. A mixture of 10% (v/v) fluorine in helium (spectral purity) (slightly more than one equivalent) was added by means of a fritted glass tube to the vigorously stirred reaction mixture at a flow rate of 210 mL/minute for 135 minutes, while the external bath temperature was maintained at –35 to –40°. The cold bath was removed and the reaction mixture was purged of fluorine gas with bubbling nitrogen at a flow rate of 525 mL/minute for 45 minutes. The sodium fluoride–hydrogen fluoride complex was removed from the reaction mixture by frit filtration and rinsed copiously with chloroform. The combined chloroform solution was evaporated to dryness in vacuo and the residue was sublimed (55°/0.01 mm Hg) to afford the title product (21.5 g) almost quantitatively as a white solid, mp 111–112°; ¹H NMR (300 MHz, CDCl₃) δ 1.78 (d, *J* = 3.54 Hz, 6H), 7.34–7.93 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 26.2 (d, *J* = 9.1 Hz), 69.8 (d, *J* = 11.6 Hz), 123.0, 123.9, 129.8, 131.4, 135.1, 144.2; ¹⁹F NMR (282 MHz, CDCl₃): δ –47.3.



***N*-Fluoropyridinium Triflate, FP-OTf [with F₂].²²** This procedure is described in *Organic Syntheses*.



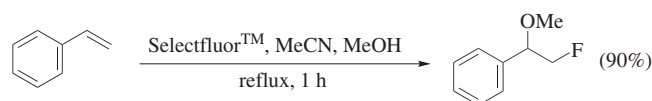
1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(Tetrafluoroborate), SelectfluorTM [Flow Method with F₂].¹³² A homogeneous 1 : 9 (v/v) mixture of F₂ (6.2 g, 16.3 mmol) and N₂ was passed at a rate of 130 mL/minute through a cold (−35°) vigorously stirred solution of 1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrafluoroborate (2.0 g, 8.0 mmol) and sodium tetrafluoroborate (0.88 g, 8.0 mmol) in dry MeCN (100 mL). The mixture was filtered to remove sodium tetrafluoroborate, the filtrate was evaporated, and the white residue was washed with acetone and dried in vacuo to provide SelectfluorTM (2.4 g, 6.8 mmol, 84%), mp 225° (decomp.); ¹H NMR (300 MHz, D₂O) δ 4.47 (t, *J* = 7.5 Hz, 6H), 4.90 (q, *J* = 7.6 Hz, 6H), 5.52 (s, 2H); ¹³C NMR (75 MHz, D₂O) δ 54.8 (m), 58.4 (d, *J* = 15.2 Hz), 70.0 (m); ¹⁹F NMR (188.8 MHz, D₂O) δ 125.6 (br s, NF⁺), −72.3 (BF₄⁻).



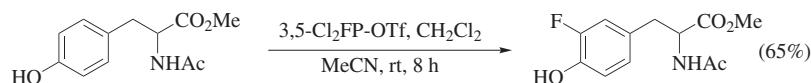
9-*O*-(4-Chlorobenzoyl)-*N*-fluoroquininium Tetrafluoroborate [F-(4-ClC₆H₄CO)QN-BF₄] [by Transfer Fluorination with SelectfluorTM].³³⁸ SelectfluorTM (4.82 g, 13.6 mmol) in MeCN (30 mL) was added slowly to an equimolar amount of 9-*O*-4-chlorobenzoylquinine (6.50 g, 13.6 mmol) in MeCN (20 mL). The reaction was complete within 20 minutes. Acetonitrile was removed under reduced pressure and the resulting white solid was dissolved in a small amount of acetone. Then a solution of H₂SO₄ (96%, 1.13 g, 10.9 mmol) in acetone (100 mL) was added dropwise to precipitate 1-chloromethyl-4-hydro-1,4-diazoniabicyclo[2.2.2]octane hydrogen sulfate tetrafluoroborate, which was removed by filtration. Addition of Et₂O to the filtrate gave a precipitate, which was washed

with a 1 : 1 v/v mixture of Et₂O and acetone, and dried in vacuo. The product crystallized from acetone on cooling to afford colorless crystals of the title compound (97% yield), mp 156°; ¹H NMR (300 MHz, acetone-*d*₆) δ 2.44 (m, 1H), 2.67 (m, 2H), 2.87 (m, 1H), 3.31 (m, 1H), 3.58 (m, 1H), 4.10 (s, 3H), 4.49 (m, 1H), 4.62 (m, 1H), 4.87 (m, 2H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.22 (d, *J* = 16.9 Hz, 1H), 5.25 (m, 1H), 5.90 (m, 1H), 7.61–7.72 (m, 4H), 7.84 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.29–8.37 (m, 4H), 9.09 (d, *J* = 5.6 Hz, 1H); ¹³C NMR (75 MHz, acetone-*d*₆) δ 26.0, 28.3, 28.4, 44.2, 57.2, 59.7 (d, *J* = 8.7 Hz), 68.1 (d, *J* = 5.1 Hz), 69.4 (d, *J* = 8.7 Hz), 73.5 (d, *J* = 8.7 Hz), 102.8, 119.3, 121.1, 126.4, 128.3, 128.4, 128.7, 130.6, 133.2, 136.9, 137.2, 141.6, 144.1, 149.6, 162.1, 164.9; ¹⁹F NMR (282 MHz, acetone-*d*₆/CFCl₃) δ 44.6 (1F), –149.7 (4F); HRMS (FAB) calcd for C₂₇H₂₇ClF₂N₂O₃ (M + H), 481.1694, found, 481.1697.

Electrophilic Fluorinations

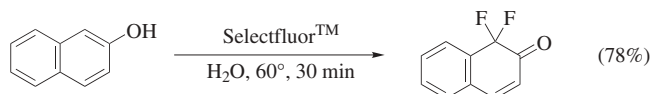


2-Fluoro-1-methoxy-1-phenylethane [Fluorination of an Alkene with Selectfluor™].¹⁷⁴ To a solution of styrene (208 mg, 2.0 mmol) in MeCN (20 mL) and methanol (2 mL) was added Selectfluor™ (709 mg, 2.0 mmol). The reaction mixture was stirred for 1 hour at reflux, then diluted with CH₂Cl₂ (40 mL), washed with 10% aqueous sodium bicarbonate solution and H₂O, and dried (Na₂SO₄). The pure product was obtained in 90% yield after column chromatography on silica gel, bp 110°/25 mm Hg; ¹H NMR (100 MHz, CDCl₃) δ 3.30 (s, 3H), 4.0–4.9 (m, 3H), 7.0–7.6 (m, 5H); ¹⁹F NMR (376 MHz, CDCl₃) δ 220.5 (td, *J* = 49.4, 4.0 Hz); MS *m/z*: M⁺ 154. Anal. Calcd for C₉H₁₁FO: C, 70.11; H, 7.19. Found: C, 70.13; H, 7.26.

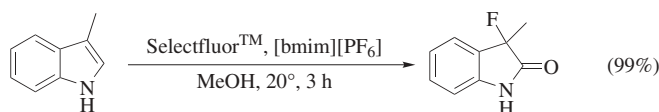


2-Acetylamino-3-(3-fluoro-4-hydroxyphenyl)propionic Acid Methyl Ester [Fluorination of an Arene with 3,5-Cl₂FP-OTf].⁴⁰⁵ 2-Acetylamino-3-(4-hydroxyphenyl)propionic acid methyl ester (400 mg, 1.68 mmol) and 3,5-Cl₂FP-OTf (632 mg, 2 mmol) were stirred under nitrogen in 10 mL of dry CH₂Cl₂/MeCN (9 : 1). After 8 hours, the starting material and reagent were consumed as verified by a KI paper test and TLC. The reaction mixture was poured into 10 mL of water, neutralized with sodium bicarbonate, and the layers were separated. The organic layer was washed with 10 mL of H₂O, dried (Na₂SO₄), and concentrated under reduced pressure. The crude product was purified by silica gel chromatography with 60% EtOAc in petroleum ether as eluent. The title product was obtained in 65% yield (280 mg); ¹H NMR (CD₃OD) δ 1.91 (s, 3H), 2.8–3.0

(m, 2H), 3.67 (s, 3H), 4.59 (dd, $J = 8.8, 5.7$ Hz, 1H), 6.77–6.84 (m, 2H), 6.89 (dd, $J = 12.9, 1.7$ Hz, 1H); ^{19}F NMR (CD_3OD) $\delta -140.3$ (t, $J = 12$ Hz).

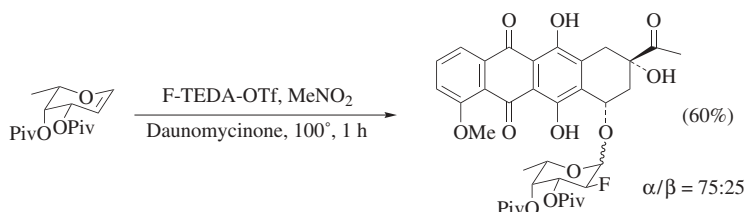


1,1-Difluoro-2(1H)-naphthalenone [Difluorination of a Phenol with SelectfluorTM].¹⁷⁷ A demineralized water solution of the surfactant Genapol LROTM (5 mL, 0.05%) was poured over naphthalen-2-ol (144 mg, 1.0 mmol) and the suspension was magnetically stirred in a glass vessel for 10 minutes at 60°. SelectfluorTM (745 mg, 2.1 mmol) was added, and the reaction mixture was stirred at 60° until the consumption of the reagent was established by a KI starch paper test (30 minutes). Water (10 mL) was added to the mixture, which, after cooling to room temperature, was extracted with *tert*-butyl methyl ether (20 mL). The organic layer was washed with H₂O (20 mL) and dried (Na_2SO_4), and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2) to give the title product (78%) as yellow crystals: mp 48–50°; IR (KBr) 1694, 1252, 1042, 835, 770 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.23 (dt, 1H, $J_{\text{HH}} = 10$ Hz, $J_{\text{HF}} = 2$ Hz, H3), 7.20–8.06 (m, 5H, ArH and H4); ^{13}C NMR (75 MHz, CDCl_3) δ 107.3 (d, $J_{\text{CF}} = 244.7$ Hz, C1), 123.2 (C4), 127.6 (t, $J_{\text{CF}} = 8.5$ Hz, C3), 130.0, 131.0, 132.0, 145.8 (CArH), 130.2 (t, $J_{\text{CF}} = 8.1$ Hz, C4a), 133.2 (t, $J_{\text{CF}} = 23.6$ Hz, C4b), 187.4 (t, $J_{\text{CF}} = 24.4$ Hz, CO); ^{19}F NMR (56.4 MHz, CDCl_3) $\delta -101.5$ (d, $J = 2$ Hz); EIMS (70 eV) m/z : M^+ 180 (60), 152 (75), 151 (100), 133 (52), 114 (60).



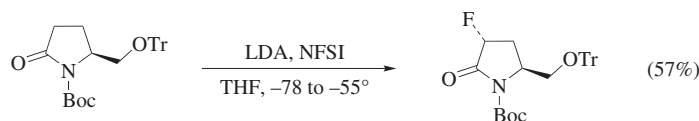
3-Fluoro-3-methyl-1,3-dihydroindol-2-one [Fluorination of a Heterocycle with SelectfluorTM].²⁰⁶ 3-Methyl-1H-indole (13.3 mg, 0.1 mmol) in [bmim][PF₆] (0.3 mL) and MeOH (0.1 mL) was stirred at room temperature under argon for 10 minutes. SelectfluorTM (107 mg, 0.3 mmol) was added and the resulting solution was stirred at 20°. After 3 hours the reaction mixture was completely extracted with Et₂O (as checked by TLC). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was purified by silica gel chromatography (pentane/EtOAc, 1:1) to afford the pure title product in 99% yield; IR 3065, 2991, 1752, 1488, 1272 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.76 (d, $J = 22.2$ Hz, 3H), 6.93 (d, $J = 7.7$ Hz, 1H), 7.09 (t, $J = 7.3$ Hz, 1H), 7.30 (m, 2H), 9.18 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 19.5 (d, $J = 29.3$ Hz), 89.6 (d, $J = 183.7$ Hz), 109.1, 121.6, 122.7, 125.9 (d, $J = 18.5$ Hz), 129.4, 138.5, 174.0

(d, $J = 21.2$ Hz); ^{19}F NMR (282 MHz, CDCl_3) $\delta -153.7$ (q, $J = 21.5$ Hz); MS m/z : M^+ 165 (93), 137 (81), 117 (96).



7-*O*-(2-Deoxy-2-fluoro-3,4-*O*-dipivaloyl- α -L-fucopyranosyl)daunomycinone [Tandem Fluorination–Glycosylation of a Glycal with SelectfluorTM].⁴³

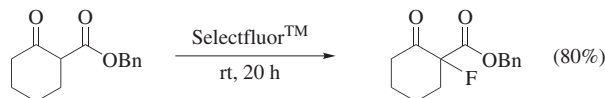
To a mixture of dipivaloyl-L-fucal (149.2 mg, 0.5 mmol) and 4 Å dry molecular sieves (200 mg) in dry MeNO_2 (4 mL) was added F-TEDA-OTf (263.3 mg, 0.55 mmol). After 6 hours of stirring at room temperature under argon, a solution of daunomycinone (219.1 mg, 0.55 mmol) in MeNO_2 (1 mL) was added quickly, and the solution was stirred at 100° for 1 hour. The mixture was poured into 100 mL of CH_2Cl_2 , filtered through Celite, and concentrated. The resulting mixture was chromatographed to give the title product in 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 1.12 (s, 9H), 1.18 (d, $J_{5'-6'} = 6.6$ Hz, 3H), 1.28 (s, 9H), 2.21 (d, $J_{\text{ax-eq}} = 15.0$ Hz, 1H), 2.33 (dd, $J = 3.7$ Hz, $J_{\text{ax-eq}} = 15.0$ Hz, 1H), 2.42 (s, 3H), 3.01 (d, $J_{\text{ax-eq}} = 19.1$ Hz, 1H), 3.27 (dd, $J = 1.5$ Hz, $J_{\text{ax-eq}} = 19.1$ Hz, 1H), 4.08 (s, 3H), 4.20 (s, 1H), 4.41 (m, 1H), 4.74 (ddd, $J_{2'-1'} = 4.1$ Hz, $J_{2'-3'} = 10.3$ Hz, $J_{2'-\text{F}} = 49.9$ Hz, 1H), 5.23 (dt, $J_{3'-4'} = 2.9$ Hz, $J_{3'-2'} = 10.3$ Hz, 1H), 5.38 (t, $J_{4'-3'} = 2.9$ Hz, 1H), 5.44 (dd, $J_{7-8\text{ax}} = 3.7$ Hz, $J_{7-8\text{eq}} = 5.9$ Hz, 1H), 5.74 (d, 1H), 7.78 (d, $J_{3-2} = 8.1$ Hz, 1H), 7.78 (t, $J_{1-2} = 8.1$ Hz, 1H), 8.04 (d, $J_{1-2} = 8.1$ Hz, 1H), 13.27 (s, 1H), 14.01 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 15.8, 24.9, 26.9, 27.3, 29.7, 33.8, 35.5, 56.7, 66.0, 68.4 (d, $J_{4'-\text{F}} = 18.1$ Hz), 69.3, 71.2 (d, $J_{3'-\text{F}} = 7.6$ Hz), 76.5, 85.1 (d, $J_{2'-\text{F}} = 192.6$ Hz), 98.4 (d, $J_{1'-\text{F}} = 9.5$ Hz), 111.5, 111.6, 118.4, 119.8, 121.0, 133.1, 134.7, 135.6, 135.7, 155.7, 156.3, 161.0, 177.2, 177.3, 186.8, 187.1, 211.2; ^{19}F NMR (376 MHz, CDCl_3) $\delta -205.7$ (dd, $J = 9.9, 49.7$ Hz).



(3*R*,5*S*)-1-(*tert*-Butyloxycarbonyl)-3-fluoro-5-(trityloxymethyl)-2-pyrrolidinone [Fluorination of a Lactam Lithium Enolate with NFSI].⁴⁰⁶

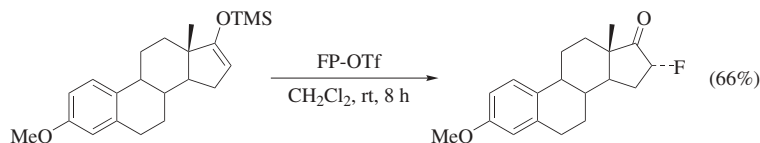
Diisopropylamine (1.59 g, 15.73 mmol) was added to THF (100 mL), and the solution was cooled to -78° in a dry ice/2-PrOH bath. A 1.6 M solution of *n*-BuLi (8.73 mL, 13.98 mmol) was added slowly and the resulting solution was stirred for 1 hour. A solution of (*S*)-1-(*tert*-butoxycarbonyl)-5-(trityloxymethyl)-2-pyrrolidinone (4.0 g, 8.74 mmol) in THF (7 mL) was added slowly. The resulting

light yellow solution was stirred at -78° for 45 minutes and then at -55° for 5 min. A solution of NFSI (4.13 g, 13.11 mmol) in THF (15 mL) was added and the reaction mixture was stirred at -55° for 35 minutes. The reaction was quenched with saturated aqueous NH_4Cl solution, and the flask was warmed to room temperature. The THF was removed in vacuo and the resulting residue was partitioned between EtOAc and H_2O . After the layers were separated, the aqueous layer was extracted with EtOAc. The combined organic layers were dried (Na_2SO_4), filtered, and evaporated to leave an orange residue that was purified by two sequential silica gel column chromatographies: (1) hexanes/EtOAc, 4:1; (2) CHCl_3 /EtOAc, 19:1, to give the desired product as a white solid (2.4 g, 5.0 mmol, 57%). The samples for elemental analysis and X-ray crystal structure determination were obtained by crystallization from EtOH; R_f 0.40 (hexanes/EtOAc, 4:1); mp 130 – 134° ; $[\alpha]_D^{23} -1.63^{\circ}$ (c 0.61, MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 1.50 (s, 9H), 2.32 (m, 2H), 2.97 (dd, $J = 9.9, 2.1$ Hz, 1H), 3.66 (dt, $J = 9.9, 2.6, 2.2$ Hz, 1H), 4.27 (d, $J = 9.1$ Hz, 1H), 5.56 (dt, $J = 53.1, 8.9$ Hz, 1H), 7.29 (m, 15H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 28.2, 30.7 (d, $^2J_{\text{C-F}} = 18.9$ Hz), 54.5, 63.6, 84.1, 86.9, 88.2 (d, $^1J_{\text{C-F}} = 187$ Hz), 127.6, 128.3, 128.6, 143.4, 149.5, 169.7 (d, $^2J_{\text{C-F}} = 20.8$ Hz); ^{19}F NMR (CDCl_3 , 282.38 MHz) δ -110.6 (dd, $J = 53.6, 25.4$ Hz); MS (FAB), (3-NBA with Na^+) m/z : (M + Na) 498 (61.6), 398 (69.5), 243 (100.0), 136 (25.6); HRMS (FAB) (3-NBA with Na^+) calcd for $\text{C}_{29}\text{H}_{30}\text{FNO}_4\text{Na}$ (M + Na), 498.2056, found, 498.2054. Anal. Calcd for $\text{C}_{29}\text{H}_{30}\text{FNO}_4$: C, 73.24; H, 6.36; N, 2.95. Found: C, 72.84; H, 6.27; N, 2.84.

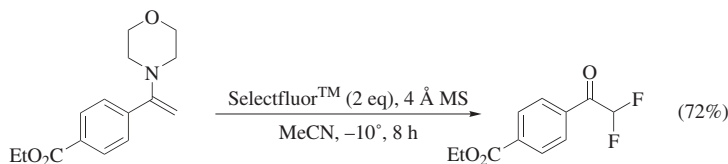


Benzyl 2-Fluorocyclohexanone-2-carboxylate [Direct Fluorination of a Keto Ester with Selectfluor™].²²⁴

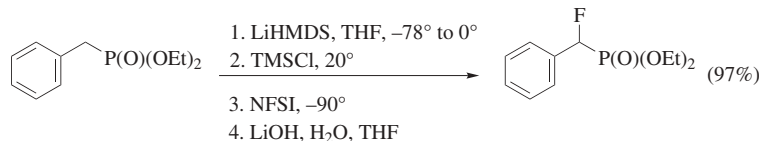
To benzyl cyclohexanone-2-carboxylate (1.50 g, 6.46 mmol) in MeCN (65 mL) was added Selectfluor™ (2.29 g, 6.46 mmol) in one portion. The reaction mixture was stirred for 20 hours at room temperature. After removal of the solvent, the residue was taken up in CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The organic layer was washed with water and dried over MgSO_4 , filtered, and evaporated. The crude product was purified by flash chromatography (petroleum ether/EtOAc, 90:10) to afford the title product as a colorless liquid (1.30 g, 80% yield); IR (neat) 2980, 2890, 1760, 1730 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.74–1.98 (m, 4H), 2.08–2.24 (m, 1H), 2.36–2.63 (m, 2H), 2.65–2.79 (m, 1H), 5.24 (d, $J = 12.1$ Hz, 1H), 5.29 (d, $J = 12.1$ Hz, 1H), 7.30–7.42 (m, 5H); ^{13}C NMR (CDCl_3 , 75.5 MHz) δ 20.8 (d, $J = 5.2$ Hz), 26.6, 36.0 (d, $J = 21.4$ Hz), 39.6, 67.8, 96.4 (d, $J = 196.8$ Hz), 128.3, 128.6, 128.7, 134.8, 166.8 (d, $J = 25.1$ Hz), 201.8 (d, $J = 19.9$ Hz); ^{19}F NMR (CDCl_3 , 235 MHz) δ 160.97 (ddd, $J = 21.9, 13.7, 5.1$ Hz); GC-MS (CI) m/z 91 (10), 108 (29), 134 (5), 250 (4), 268 (100).



16 α -Fluoro-3-methoxy-1,3,5(10)-estratrien-17-one [Fluorination of a Ketone Silyl Enol Ether with FP-OTf].²² A 125-mL, round-bottomed flask containing 3-methoxy-17-trimethylsilyloxy-1,3,5(10),16-estratetraene (8.6 g, 24 mmol) was purged with argon, and dry CH₂Cl₂ (50 mL) was added. *N*-Fluoropyridinium triflate (6.5 g, 26 mmol) was added in one portion, and the mixture was stirred at 20–25° for 8 hours. The reaction mixture was poured into water and extracted with CH₂Cl₂ (3 × 60 mL). The combined organic extracts were washed with saturated sodium bicarbonate solution and then with water, and dried over MgSO₄. The drying agent was removed by filtration and the solution was evaporated to dryness with a rotary evaporator. The resulting pale yellow solid was purified by column chromatography on silica gel with CH₂Cl₂ as eluent to give the title compound in 66% yield (4.8 g) as a colorless solid; IR (KBr) 2900, 2850, 1750, 1600, 1500, 1460, 1440, 1310, 1240, 1030, 1000 cm⁻¹; ¹H NMR (360 MHz, CDCl₃/CFCl₃) δ 0.95 (s, 3H), 3.77 (s, 3H), 5.13 (dd, *J* = 50.6, 7.3 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 1H); ¹⁹F NMR (338 MHz, CDCl₃) δ -192.7 (m); MS *m/z* 304 (2.7), 303 (21.5), 302 (M⁺, 100), 301 (3.7).

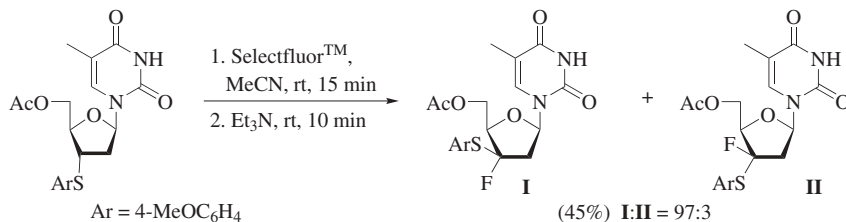


4-Difluoroacetylbenzoic Acid Ethyl Ester [Difluorination of an Enamine with Selectfluor™].²⁴⁷ To a mixture of Selectfluor™ (746 mg, 2 mmol) and 4 Å molecular sieves (2 g) in 20 mL of anhydrous MeCN cooled to -10° under nitrogen was added a single portion of 4-(1-morpholin-4-yl-vinyl)benzoic acid ethyl ester (261 mg, 1 mmol) in anhydrous MeCN (5 mL). After the reaction mixture was stirred for 7–8 hours at -10°, it was filtered, and 2.5 g of silica gel was added to the filtrate. The solvent was removed under vacuum and the remaining solid was purified by chromatography using hexanes/EtOAc as eluent to give the difluorinated product in 72% yield as a white solid, mp 57–58°; IR (KBr) 2989, 1711, 1610, 1471, 1398, 1371, 1291, 1239, 1181, 1137, 1112, 1059, 1021, 971, 883, 843, 769, 726, 694, 661 cm⁻¹; ¹H NMR (CDCl₃) δ 1.44 (t, *J* = 7.1 Hz, 3H), 4.44 (q, *J* = 7.1 Hz, 2H), 6.30 (t, *J* = 53.4 Hz, 1H), 8.12–8.22 (AB system, *J* = 8.7 Hz, 4H); ¹³C NMR (CDCl₃) δ 15.1, 62.5, 112.0 (t, *J* = 254.0 Hz), 130.4 (t, *J* = 2.4 Hz), 130.8, 135.3 (t, *J* = 2.0 Hz), 136.6, 166.2, 188.1 (t, *J* = 25.9 Hz); ¹⁹F NMR (CDCl₃) δ -122.0 (d, *J* = 53.7 Hz); GC-MS (EI) *m/z* M⁺ 228, 213, 207, 183, 177, 155, 149, 127, 121, 104, 93. Anal. Calcd for C₁₁H₁₀F₂O₃: C, 57.90; H, 4.42. Found: C, 57.66; H, 4.43.



Diethyl α -Fluorobenzylphosphonate [Fluorodesilylation of an α -Silylphosphonate with NFSI].²⁶¹

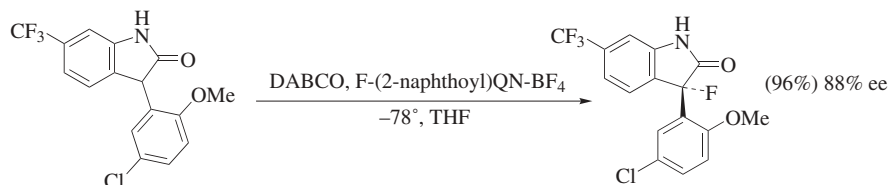
A freshly titrated solution of *n*-BuLi (4.69 ml of a 1.6 M solution in hexane, 7.5 mmol) was added to THF (20 mL) cooled to -78° . A mixture of hexamethyldisilazane (1.33 g, 8.25 mmol) and diethyl benzylphosphonate (2.5 mmol, 570 mg) in THF (20 mL) was slowly added at this temperature via a dropping funnel. The reaction mixture was warmed slowly to 20° and TMSCl (0.3 g, 2.75 mmol) in THF (10 mL) was added rapidly. After 15 minutes, the reaction mixture was cooled to -90° , and NFSI (1.02 g, 3.25 mmol) in THF (20 mL) was added slowly. After 15 minutes at this temperature, the reaction mixture was warmed gradually to 0° and treated at this temperature with an excess of LiOH in H_2O (15 mL) for 15 minutes. The organic layer was washed with a 1 M LiOH solution (2×15 mL), and then poured with stirring into a mixture of 3 M HCl (20 mL), CH_2Cl_2 or Et_2O (20 mL), and ice (10 g). After two extractions with CH_2Cl_2 (2×20 mL) of the aqueous layer, the combined organic layers were dried (MgSO_4), and the solvents evaporated under reduced pressure to afford the title product as a pale-yellow oil. Further purification by column chromatography on silica gel (hexane/EtOAc, 70:30) afforded the pure fluorinated product in 97% yield; ^1H NMR δ 1.30 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H), 1.32 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H), 4.01–4.24 (m, 4H), 5.75 (dd, $^2J_{\text{PH}} = 7.9$ Hz, $^2J_{\text{FH}} = 44.6$ Hz, 1H), 7.41–7.54 (m, 5H); ^{13}C NMR (CDCl_3) δ 16.8 (d, $^3J_{\text{PC}} = 5.2$ Hz), 64.1 (dd, $^2J_{\text{PC}} = 7.0$ Hz, $^4J_{\text{FC}} = 18.2$ Hz), 89.9 (dd, $^1J_{\text{PC}} = 170.5$ Hz, $^1J_{\text{FC}} = 184.2$ Hz), 127.3 (t, $^3J_{\text{PC}} = ^3J_{\text{FC}} = 6.0$ Hz), 129.0 (d, $^4J_{\text{FC}} = 2.4$ Hz), 129.7, 133.4 (d, $^2J_{\text{FC}} = 18.4$ Hz); ^{31}P NMR (CDCl_3) δ 13.0 (d, $^2J_{\text{PF}} = 85.6$ Hz); ^{19}F NMR (CDCl_3) δ -200.6 (d, $^2J_{\text{PF}} = 85.6$ Hz); MS (CI) m/z : 247 (100, $M + 1$), 264 (44, $M + 18$).



5'-O-Acetyl-3'-fluoro-3'-(*R*)-(4-methoxyphenyl)-3'-thiothymidine [Fluorination of a Thioether with SelectfluorTM].²⁶⁵

A solution of the thioaryl-substituted nucleoside (203.2 mg, 0.5 mmol) in MeCN (5 mL) under N_2 was

treated with SelectfluorTM (177 mg, 0.5 mmol) and stirred at room temperature for 15 minutes. Triethylamine (68 μ L, 0.5 mmol) was added and stirring was continued for an additional 10 minutes. The solution was poured into EtOAc (50 mL), washed with H₂O (2 \times 25 mL) and then with saturated NaHCO₃ solution (25 mL), dried (Na₂CO₃), filtered, and concentrated in vacuo. Flash chromatography on silica gel (EtOAc/hexane, 70 : 30) afforded the pure title product (95 mg, 45%); ¹H NMR (300 MHz, DMSO-*d*₆) δ 1.80 (s, 3H), 2.10 (s, 3H), 2.25–2.40 (m, 1H), 2.55–2.75 (m, 1H), 3.80 (s, 3H), 4.25–4.60 (m, 3H), 6.10 (dd, 1H), 7.05 (d, 2H), 7.55 (d, 2H), 7.60 (s, 1H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 13.2, 20.5, 51.5, 55.7, 63.0, 82.5, 83.7, 84.0, 110.2, 115.7, 118.5, 136.0, 137.7, 150.5, 161.7, 164.2, 170.2; ¹⁹F NMR (282 MHz, DMSO-*d*₆) δ –110.0; HRMS (M + H) calcd for C₁₉H₂₁FN₂O₆S, 425.1183, found, 425.1150.



(S)-3-(5-Chloro-2-methoxyphenyl)-3-fluoro-6-trifluoromethyl-1,3-dihydroindol-2-one [Enantioselective Fluorination of an Oxindole with F-(2-Naphthoyl)QN-BF₄].³⁴⁰ To a solution of 1,4-diazabicyclo[2.2.2]octane (35 mg, 0.31 mmol) in THF (1 mL) was added 3-(5-chloro-2-methoxyphenyl)-6-trifluoromethyl-1,3-dihydroindol-2-one (48 mg, 0.14 mmol) at 20°. The mixture was stirred for 30 minutes and the temperature was lowered to –78°. A solution of *N*-fluoro-2-naphthoylquininium tetrafluoroborate (99 mg, 0.17 mmol) in a mixture of MeCN (3 mL) and CH₂Cl₂ (4 mL) was added over a period of 1 hour. The mixture was stirred overnight, during which time the temperature rose from –78° to 0°. The reaction was then quenched with H₂O (8 mL). The aqueous phase was extracted with CH₂Cl₂ and the organic phase was washed with brine, dried (MgSO₄), and concentrated. Purification by silica gel chromatography (CH₂Cl₂/MeOH, 96 : 4) afforded the title compound in 96% yield with 88% ee. The ee value was determined by chiral HPLC (Chiracel OD-H column, 10% 2-PrOH/hexane, 1 mL/minute, 254 nm; retention times: S isomer, 6.0 minutes; R isomer, 7.8 minutes); ¹H NMR (300 MHz, CDCl₃) δ 3.58 (d, *J* = 7.2 Hz, 3H), 6.83 (d, *J* = 8.7 Hz), 7.21 (m, 2H), 7.37 (d, *J* = 2.7 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 9.46 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 56.4, 91.0 (d, *J* = 190.0 Hz), 107.8, 113.1, 120.7, 122.3, 125.8, 126.4 (d, *J* = 26.8 Hz), 126.7, 126.9, 126.9, 130.7, 134.5, 143.2 (d, *J* = 0.1 Hz), 154.1 (d, *J* = 0.1 Hz), 174.5 (d, *J* = 20.0 Hz); ¹⁹F NMR (282 MHz, CDCl₃/CFCl₃) δ –63.4 (d, *J* = 3.0 Hz, 3F), –160.5 (s, 1F).

TABULAR SURVEY

The tabular survey includes all examples found in the literature through December, 2005. The literature survey was conducted by computer search of *Chemical Abstracts* and by direct inspection of the literature.

The tables are arranged in the order of the discussion in the Scope and Limitations. Tables 1–12 compile the electrophilic fluorination of alkanes, alkenes, alkynes, arenes, heterocycles, glycols, carbonyl compounds, enol derivatives, enamines, imines, organophosphorus compounds, organosulfur compounds, and others. Substrates containing both phosphorus and sulfur atoms are only listed in Table 10 (Organosulfur Compounds). Diastereoselective electrophilic fluorinations, for which a chiral auxiliary is used exclusively, are given in Table 13, while the enantioselective electrophilic fluorinations are collected in Table 14.

The entries within each table are arranged in order of increasing total number of carbon atoms of the substrate. Unreported yields are indicated using “(—)”.

The following abbreviations are used in the tables:

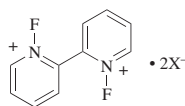
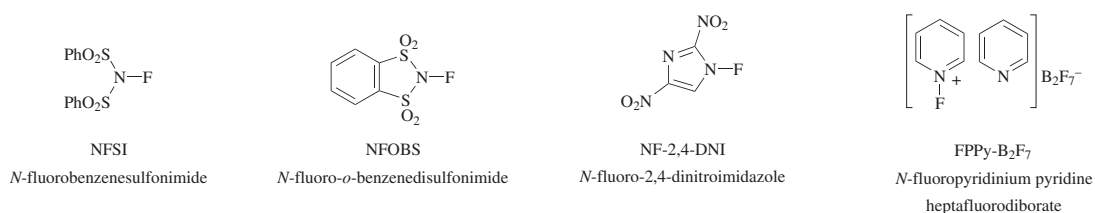
Ac	acetyl
AcDHCD	dihydrocinchonidine acetate
AcDHCN	dihydrocinchonine acetate
AcDHQD	dihydroquinidine acetate
AcDHQN	dihydroquinine acetate
Ad	adamantyl
AIBN	2,2'-azobis(isobutyronitrile)
(2-anthraquinoyl)DHQD	9- <i>O</i> -(2-anthraquinoyl)dihydroquinidine
(2-anthraquinoyl)DHQN	9- <i>O</i> -(2-anthraquinoyl)dihydroquinine
ATP	adenosine-5'-triphosphate
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][OTf]	1-butyl-3-methylimidazolium triflate
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluoro-phosphate
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
Bz	benzoyl
BzDHCD	dihydrocinchonidine benzoate
BzDHCN	dihydrocinchonine benzoate
BzDHQD	dihydroquinidine benzoate
BzDHQN	dihydroquinine benzoate
Cbz	benzyloxycarbonyl
CD	cinchonidine
(C ₆ F ₅ CO)DHQD	9- <i>O</i> -(2,3,4,5,6-pentafluorobenzoyl)dihydroquinidine
(C ₆ F ₅ CO)DHQN	9- <i>O</i> -(2,3,4,5,6-pentafluorobenzoyl)dihydroquinine

(C ₂ H ₅ CO)DHQD	9- <i>O</i> -propanoyldihydroquinidine
(4-ClC ₆ H ₄ CO)CN	9- <i>O</i> -(4-chlorobenzoyl)cinchonine
(4-ClC ₆ H ₄ CO)DHCD	9- <i>O</i> -(4-chlorobenzoyl)dihydrocinchonidine
(4-ClC ₆ H ₄ CO)DHQD	9- <i>O</i> -(4-chlorobenzoyl)dihydroquinidine
(4-ClC ₆ H ₄ CO)DHQN	9- <i>O</i> -(4-chlorobenzoyl)dihydroquinine
(4-ClC ₆ H ₄ CO)QN	9- <i>O</i> -(4-chlorobenzoyl)quinine
CN	cinchonine
Cyt	cytosine
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCA	dichloroacetic acid
DCE	1,2-dichloroethane
DHCD	dihydrocinchonidine
DHCN	dihydrocinchonine
DHQD	dihydroquinidine
(DHQD) ₂ AQN	dihydroquinidine anthraquinone-1,4-diyl diether
(DHQD) ₂ PHAL	dihydroquinidine 1,4-phthalazinediyl diether
(DHQD) ₂ PYR	dihydroquinidine 2,5-diphenyl-4,6-pyrimidinediyl diether
DHQN	dihydroquinine
(DHQN) ₂ AQN	dihydroquinine anthraquinone-1,4-diyl diether
(DHQN) ₂ PHAL	dihydroquinine 1,4-phthalazinediyl diether
(DHQN) ₂ PYR	dihydroquinine 2,5-diphenyl-4,6-pyrimidinediyl diether
DIBAL	diisobutylaluminum hydride
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DMTr	dimethoxytrityl
dr	diastereomeric ratio
ee	enantiomeric excess
[emim][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[emim][OTf]	1-ethyl-3-methylimidazolium triflate
FddA	9-(2',3'-dideoxy-2'-fluoro-D-threo-pentofuranosyl)adenine
Fmoc	9-fluorenylmethoxycarbonyl
Gal	galactose
Glc	glucose
HFIP	1,1,1,3,3,3-hexafluoroisopropyl alcohol
[hmim][BF ₄]	1-hexyl-3-methylimidazolium tetrafluoroborate
[hmim][PF ₆]	1-hexyl-3-methylimidazolium hexafluorophosphate
HMPA	hexamethylphosphoramide
KDA	potassium diisopropylamide

KHMDS	potassium hexamethyldisilazide
LDA	lithium diisopropylamide
LiHMDS	lithium hexamethyldisilazide
MCPBA	<i>meta</i> -chloroperoxybenzoic acid
(4-MeOC ₆ H ₄ CO)DHQD	9- <i>O</i> -(4-methoxybenzoyl)dihydroquinidine
(4-MeOC ₆ H ₄ CO)DHQN	9- <i>O</i> -(4-methoxybenzoyl)dihydroquinine
MOM	methoxymethyl
monoglyme	1,2-dimethoxyethane
MQE-DHQN	dihydroquinine 4-methyl-2-quinolyl ether
Ms	methanesulfonyl (mesyl)
MS	molecular sieves
MTBE	<i>tert</i> -butyl methyl ether
N ⁴ -Ac-Cyt(SiMe ₃) ₂	<i>N</i> -acetyl-bis(trimethylsilyl)cytosine
NaHMDS	sodium hexamethyldisilazide
napht	naphthyl
(1-naphthoyl)DHQD	9- <i>O</i> -(1-naphthoyl)dihydroquinidine
(1-naphthoyl)DHQN	9- <i>O</i> -(1-naphthoyl)dihydroquinine
3-nba	3-nitrobenzyl alcohol
NBS	<i>N</i> -bromosuccinimide
(4-O ₂ NC ₆ H ₄ CO)DHQD	9- <i>O</i> -(4-nitrobenzoyl)dihydroquinidine
(4-O ₂ NC ₆ H ₄ CO)DHQN	9- <i>O</i> -(4-nitrobenzoyl)dihydroquinine
P	pyridinium
PE-DHQN	dihydroquinine 9-phenanthryl ether
Pht	phthaloyl
Piv	pivaloyl
PMP	4-methoxyphenyl
Py	pyridine, pyridinyl
QD	quinidine
QN	quinine
R _f	fluorinated substituent
TADDOL	tetraaryl-1,3-dioxolan-4,5-dimethanol
TBAF	tetra- <i>n</i> -butylammonium fluoride
TBAH	tetra- <i>n</i> -butylammonium hydroxide
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
TCA	trichloroacetic acid
TCE	1,1,2-trichloroethane
TEDA	triethylenediamine
TES	triethylsilyl
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
<i>p</i> -Tol	<i>p</i> -tolyl

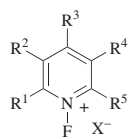
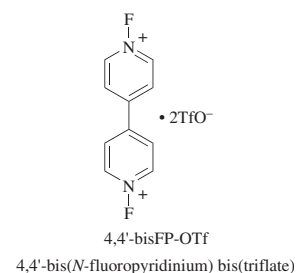
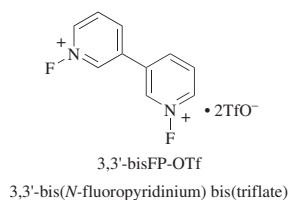
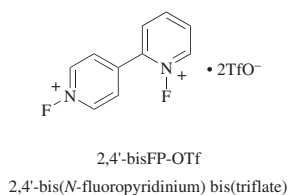
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
Tr	triphenylmethyl
trifluoroacetyl	9- <i>O</i> -trifluoroacetyldihydroquinine
DHQN	
Ts	<i>p</i> -toluenesulfonyl

CHART 1. ACRONYMS FOR FLUORINATION AGENTS USED IN TABLES



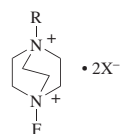
X

BF ₄	2,2'-bisFP-BF ₄ (SynFluor™)	2,2'-bis(<i>N</i> -fluoropyridinium) bis(tetrafluoroborate)
OTf	2,2'-bisFP-OTf	2,2'-bis(<i>N</i> -fluoropyridinium) bis(triflate)



R ¹	R ²	R ³	R ⁴	R ⁵	X		
H	H	H	H	H	OTf	FP-OTf	<i>N</i> -fluoropyridinium triflate
H	H	H	H	H	BF ₄	FP-BF ₄	<i>N</i> -fluoropyridinium tetrafluoroborate
H	H	H	H	H	SbF ₆	FP-SbF ₆	<i>N</i> -fluoropyridinium hexafluoroantimonate
H	H	H	H	H	ClO ₄	FP-ClO ₄	<i>N</i> -fluoropyridinium perchlorate
H	H	H	H	H	OSO ₂ C ₄ F _{9-n}	FP-OSO ₂ C ₄ F _{9-n}	<i>N</i> -fluoropyridinium perfluorobutyl sulfonate
Cl	H	H	H	CCl ₃	BF ₄	2-Cl-6-CCl ₃ FP-BF ₄	<i>N</i> -fluoro-2-chloro-6-trichloromethylpyridinium tetrafluoroborate
Cl	H	Cl	H	H	OTf	2,4-Cl ₂ FP-OTf	<i>N</i> -fluoro-2,4-dichloropyridinium triflate
H	Cl	H	Cl	H	OTf	3,5-Cl ₂ FP-OTf	<i>N</i> -fluoro-3,5-dichloropyridinium triflate
Cl	H	H	H	Cl	OTf	2,6-Cl ₂ FP-OTf	<i>N</i> -fluoro-2,6-dichloropyridinium triflate
Cl	H	H	H	Cl	BF ₄	2,6-Cl ₂ FP-BF ₄	<i>N</i> -fluoro-2,6-dichloropyridinium tetrafluoroborate
Cl	Cl	H	Cl	Cl	BF ₄	2,3,5,6-Cl ₅ FP-BF ₄	<i>N</i> -fluoro-2,3,5,6-tetrachloropyridinium tetrafluoroborate
Cl	Cl	Cl	Cl	Cl	OTf	2,3,4,5,6-Cl ₅ FP-OTf	<i>N</i> -fluoro-2,3,4,5,6-pentachloropyridinium triflate
SO ₃	H	H	H	H	—	2-SO ₃ FP	<i>N</i> -fluoropyridinium-2-sulfonate
SO ₃	H	H	H	Cl	—	2-SO ₃ -6-ClFP	<i>N</i> -fluoropyridinium-6-chloro-2-sulfonate
SO ₃	H	Et	H	H	—	2-SO ₃ -4-EtFP	<i>N</i> -fluoropyridinium-4-ethyl-2-sulfonate
SO ₃	H	Me	H	H	—	2-SO ₃ -4-MeFP	<i>N</i> -fluoropyridinium-4-methyl-2-sulfonate
SO ₃	H	H	H	Me	—	2-SO ₃ -6-MeFP	<i>N</i> -fluoropyridinium-6-methyl-2-sulfonate
SO ₃	H	H	CF ₃	H	—	2-SO ₃ -5-CF ₃ FP	<i>N</i> -fluoropyridinium-5-trifluoromethylpyridinium-2-sulfonate
SO ₃	H	CF ₃	H	CF ₃	—	2-SO ₃ -4,6-(CF ₃) ₂ FP	<i>N</i> -fluoro-4,6-di(trifluoromethyl)pyridinium-2-sulfonate
SO ₃	Cl	H	CF ₃	H	—	2-SO ₃ -3-Cl-5-CF ₃ FP	<i>N</i> -fluoro-3-chloro-5-trifluoromethylpyridinium-2-sulfonate
Me	H	H	H	Me	OTf	2,6-Me ₂ FP-OTf	<i>N</i> -fluoro-2,6-dimethylpyridinium triflate
Me	H	Me	H	Me	OTf	2,4,6-Me ₃ FP-OTf	<i>N</i> -fluoro-2,4,6-trimethylpyridinium triflate
H	H	<i>t</i> -Bu	H	H	OTf	4- <i>t</i> -BuFP-OTf	<i>N</i> -fluoro-4- <i>tert</i> -butylpyridinium triflate
CO ₂ Me	H	H	H	CO ₂ Me	OTf	2,6-(MeO ₂ C) ₂ FP-OTf	<i>N</i> -fluoro-2,6-di(carbomethoxy)pyridinium triflate
CH ₂ OMe	H	H	H	CH ₂ OMe	OTf	2,6-(MeOCH ₂) ₂ FP-OTf	<i>N</i> -fluoro-2,6-di(methoxymethyl)pyridinium triflate
CH ₂ OMe	H	CH ₂ OMe	H	CH ₂ OMe	OTf	2,4,6-(MeOCH ₂) ₃ FP-OTf	<i>N</i> -fluoro-2,4,6-tri(methoxymethyl)pyridinium triflate

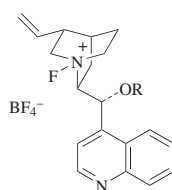
CHART 1. ACRONYMS FOR FLUORINATION AGENTS USED IN TABLES (Continued)



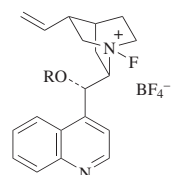
R	X		
CH ₂ Cl	BF ₄ ⁻	F-TEDA-BF ₄ (Selectfluor™)	1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate)
CH ₂ Cl	OTf	F-TEDA-OTf	1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(triflate)
OH	BF ₄ ⁻	NFth (Accufluor™)	1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate)



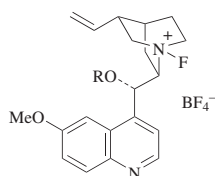
X			
BF ₄ ⁻	NFQN-BF ₄	<i>N</i> -fluoroquinuclidinium tetrafluoroborate	
OTf	NFQN-OTf	<i>N</i> -fluoroquinuclidinium triflate	
F	NFQN-F	<i>N</i> -fluoroquinuclidinium fluoride	
CF ₃ CO ₂ ⁻	NFQN-CF ₃ CO ₂ ⁻	<i>N</i> -fluoroquinuclidinium trifluoroacetate	
C ₃ F ₇ CO ₂ ⁻	NFQN-C ₃ F ₇ CO ₂ ⁻	<i>N</i> -fluoroquinuclidinium heptafluoropropionate	



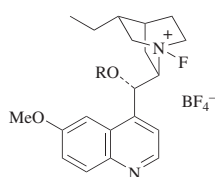
R			
H	F-CD-BF ₄	<i>N</i> -fluorocinchonidinium tetrafluoroborate	
4-ClC ₆ H ₄ CO	F-(4-ClC ₆ H ₄ CO)CD-BF ₄	<i>N</i> -fluorocinchonidinium 4-chlorobenzoyl ester tetrafluoroborate	
Ac	F-AcCD-BF ₄	<i>N</i> -fluoro- <i>O</i> -acetylcinchonidinium tetrafluoroborate	



R			
H	F-CN-BF ₄	<i>N</i> -fluorocinchoninium tetrafluoroborate	
4-ClC ₆ H ₄ CO	F-(4-ClC ₆ H ₄ CO)CN-BF ₄	<i>N</i> -fluorocinchoninium 4-chlorobenzoyl ester tetrafluoroborate	

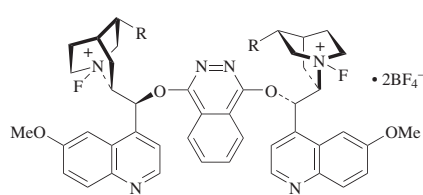


R			
H	F-QD-BF ₄	<i>N</i> -fluoroquinidinium tetrafluoroborate	
4-ClC ₆ H ₄ CO	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	<i>N</i> -fluoroquinidinium 4-chlorobenzoyl ester tetrafluoroborate	

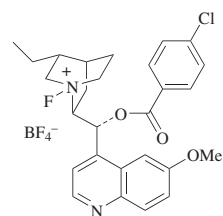


R			
Ac	F-AcDHQD-BF ₄	<i>N</i> -fluoro- <i>O</i> -acetyldihydroquinidinium tetrafluoroborate	
4-ClC ₆ H ₄ CO	F-(4-ClC ₆ H ₄ CO)DHQD-BF ₄	<i>N</i> -fluorodihydroquinidinium 4-chlorobenzoyl ester tetrafluoroborate	

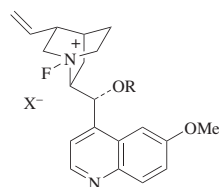
CHART 1. ACRONYMS FOR FLUORINATION AGENTS USED IN TABLES (Continued)

F-(DHQD)₂PHAL-BF₄

N-fluorodihydroquininium 1,4-phthalazinediyl diether
bis(tetrafluoroborate)

F-(4-ClC₆H₄CO)DHQN-BF₄

N-fluorodihydroquininium 4-chlorobenzoyl ester
tetrafluoroborate



R	X		
H	BF ₄	F-QN-BF ₄	<i>N</i> -fluoroquininium tetrafluoroborate
4-MeOC ₆ H ₄ CO	BF ₄	F-(4-MeOC ₆ H ₄ CO)QN-BF ₄	<i>N</i> -fluoroquininium 4-methoxybenzoyl ester tetrafluoroborate
4-ClC ₆ H ₄ CO	BF ₄	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	<i>N</i> -fluoroquininium 4-chlorobenzoyl ester tetrafluoroborate
4-ClC ₆ H ₄ CO	OTf	F-(4-ClC ₆ H ₄ CO)QN-OTf	<i>N</i> -fluoroquininium 4-chlorobenzoyl ester triflate
4-ClC ₆ H ₄ CO	N(SO ₂ Ph) ₂	F-(4-ClC ₆ H ₄ CO)QN-N(SO ₂ Ph) ₂	<i>N</i> -fluoroquininium 4-chlorobenzoyl ester benzenesulfonimide
4-O ₂ NC ₆ H ₄ CO	BF ₄	F-(4-O ₂ NC ₆ H ₄ CO)QN-BF ₄	<i>N</i> -fluoroquininium 4-nitrobenzoyl ester tetrafluoroborate
Ac	BF ₄	F-AcQN-BF ₄	<i>N</i> -fluoro- <i>O</i> -acetylquininium tetrafluoroborate
4-Me-2-quinolyl	BF ₄	F-MEQN-BF ₄	<i>N</i> -fluoroquininium 4-methyl-2-quinolyl ether tetrafluoroborate
9-phenanthryl	BF ₄	F-PEQN-BF ₄	<i>N</i> -fluoroquininium 9-phenanthryl ether tetrafluoroborate
1-naphthoyl	BF ₄	F-(1-naphthoyl)QN-BF ₄	<i>N</i> -fluoroquininium 1-naphthoyl ester tetrafluoroborate
2-naphthoyl	BF ₄	F-(2-naphthoyl)QN-BF ₄	<i>N</i> -fluoroquininium 2-naphthoyl ester tetrafluoroborate

CHART 2. CATALYSTS USED IN TABLE 14

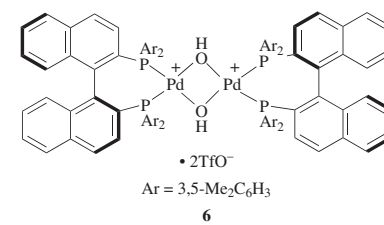
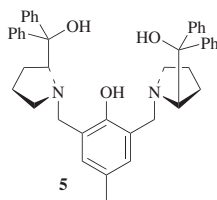
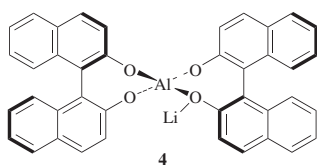
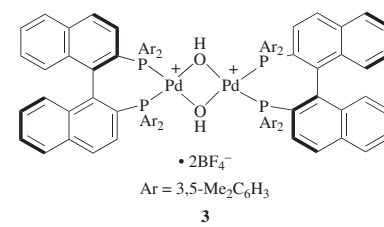
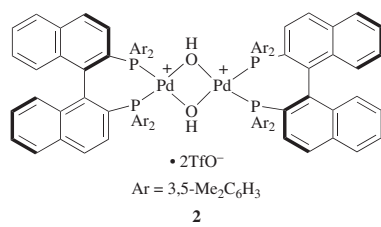
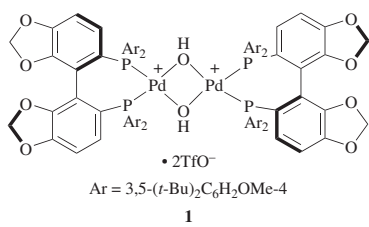


TABLE 1. FLUORINATION OF ALKANES










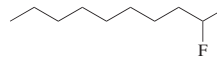
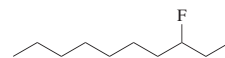
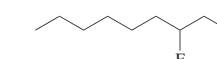
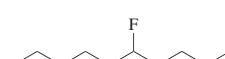
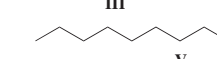
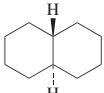
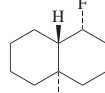
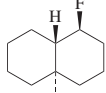
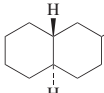
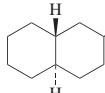
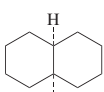
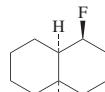
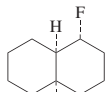
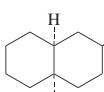
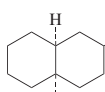



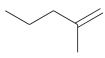















Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	Selectfluor™, MeCN, 65°, 26 h	 (21)	170, 171, 172
C ₇ 	Selectfluor™, MeCN, reflux, 16 h	 (34) +  (7)	172
C ₁₀ 	Selectfluor™, MeCN, reflux, 16 h	 (43) +  (8)	171, 172
	Selectfluor™, MeCN, 65°, 18 h	 I +  II +  III +  IV +  V I + II + III + IV + V (84), I:II:III:IV:V = 2.4:1.3:1:1:1	172
	Selectfluor™, MeCN, reflux, 4.5 h	 I +  II +  III +  IV I + II + III + IV (30), I:II:III:IV = 1:1.14:1.36:2.24	172
	Selectfluor™, MeCN, reflux, 1.5 h	 I +  II +  III +  IV I + II + III + IV (25), I:II:III:IV = 1.6:1.3:1:1.4	172

TABLE 2. FLUORINATION OF ALKENES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₆ 	(CF ₃ SO ₂) ₂ NF, CDCl ₃ , 0°	 (—)	35												
	NFTh, MeCN, 70°, 30 min	 (82)	179												
C ₇  	2,3,4,5,6-Cl ₃ FP-OTf, 2-FPy, AcOH, rt, 30 min	 (28)	31												
	Selectfluor TM , MeCN, MeOH, rt	 I (—) +  II (—) +  III (—) +  IV (—)	407												
		<table border="1"> <thead> <tr> <th>MeCN:MeOH (w/w)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>95:5</td> <td>31:30:20:19</td> </tr> <tr> <td>90:10</td> <td>15:25:26:34</td> </tr> <tr> <td>80:20</td> <td>7:13:33:45</td> </tr> <tr> <td>60:40</td> <td>11:7:33:49</td> </tr> </tbody> </table>	MeCN:MeOH (w/w)	I:II:III:IV	95:5	31:30:20:19	90:10	15:25:26:34	80:20	7:13:33:45	60:40	11:7:33:49			
MeCN:MeOH (w/w)	I:II:III:IV														
95:5	31:30:20:19														
90:10	15:25:26:34														
80:20	7:13:33:45														
60:40	11:7:33:49														
	Selectfluor TM , MeCN, H ₂ O, rt	I (—) + II (—) +  III (—) +  IV (—)	407												
		<table border="1"> <thead> <tr> <th>MeCN:H₂O (w/w)</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>95:5</td> <td>32:25:18:25</td> </tr> <tr> <td>90:10</td> <td>25:20:21:34</td> </tr> <tr> <td>80:20</td> <td>22:17:25:36</td> </tr> <tr> <td>60:40</td> <td>16:12:31:42</td> </tr> <tr> <td>40:60</td> <td>12:9:38:41</td> </tr> </tbody> </table>	MeCN:H ₂ O (w/w)	I:II:III:IV	95:5	32:25:18:25	90:10	25:20:21:34	80:20	22:17:25:36	60:40	16:12:31:42	40:60	12:9:38:41	
MeCN:H ₂ O (w/w)	I:II:III:IV														
95:5	32:25:18:25														
90:10	25:20:21:34														
80:20	22:17:25:36														
60:40	16:12:31:42														
40:60	12:9:38:41														

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TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C ₇ 	Selectfluor TM , MeCN, rt, 4 h	 I +  II	407																				
		I + II (—), I:II = 1:1																					
C ₈ 	NFTh, MeCN, H ₂ O, 80°, 1 h	 (90)	126																				
	Selectfluor TM , MeCN, MeOH, reflux, 1 h	 I (90)	174																				
	Selectfluor TM , MeCN, MeOH, 80°, 1 h	I (92)	126																				
	F ⁺ -N ⁺ (C ₆ H ₁₁) ₂ -F • 2BF ₄ ⁻ , MeCN/MeOH (1:1), 3 h, rt	I (25)	122																				
	2-SO ₃ -4,6-(CF ₃) ₂ FP, AcOH, rt	 I (24)	161																				
	F ⁺ -N ⁺ (C ₆ H ₁₁) ₂ -F • 2TfO ⁻ , AcOH, 5 h, rt	I (30)	122																				
	2,3,4,5,6-Cl ₃ FP-OTf, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>AcOH</td> <td>1 h</td> <td>(72)</td> </tr> <tr> <td>Ac</td> <td>AcOTMS</td> <td>3 d</td> <td>(56)</td> </tr> <tr> <td>Me</td> <td>MeOTMS</td> <td>5 d</td> <td>(54)</td> </tr> <tr> <td>Et</td> <td>EtOTMS</td> <td>18 d</td> <td>(29)</td> </tr> </tbody> </table>	R	Solvent	Time	Yield (%)	Ac	AcOH	1 h	(72)	Ac	AcOTMS	3 d	(56)	Me	MeOTMS	5 d	(54)	Et	EtOTMS	18 d	(29)	31
R	Solvent	Time	Yield (%)																				
Ac	AcOH	1 h	(72)																				
Ac	AcOTMS	3 d	(56)																				
Me	MeOTMS	5 d	(54)																				
Et	EtOTMS	18 d	(29)																				

428

	NFTh, MeCN, 70°, 1-24 h		<table border="1"> <thead> <tr> <th colspan="2">Y</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(79)</td> <td>179</td> </tr> <tr> <td>4-Cl</td> <td>(81)</td> <td></td> </tr> <tr> <td>3-NO₂</td> <td>(70)</td> <td></td> </tr> </tbody> </table>	Y			H	(79)	179	4-Cl	(81)		3-NO ₂	(70)	
Y															
H	(79)	179													
4-Cl	(81)														
3-NO ₂	(70)														
	NFTh, MeCN, 70°, 1-24 h	 	179 I + II (74)^a, I:II = 1:3												
	Selectfluor™, MeCN, reflux		408												
	Selectfluor™, HR ³ , MeCN, rt		173												
	(CF ₃ SO ₂) ₂ NF, AcOH, CH ₂ Cl ₂ , rt		35												

TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																																											
	Selectfluor™, sodium lauryl ether sulfate (0.05% aq), 60°, 6-24 h	(84-86)	177																																																																																											
	(CF ₃ SO ₂) ₂ NF, CH ₂ Cl ₂ , H ₂ O, 0°, 1.5 h	I + II	35																																																																																											
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(38)</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>(57)</td> <td>(28)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>H</td> <td>(98)</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>(90)</td> <td>(0)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I	II	H	H	H	(38)	(0)	Ph	H	H	(57)	(28)	Ph	Ph	H	(98)	(0)	Ph	Ph	Ph	(90)	(0)																																																																			
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	NFTh, R ⁴ H, MeCN	I	126, 235																																																																																											
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R ¹	R ²	R ³	R ⁴	Temp	Time	I																																																																																								
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
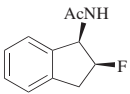
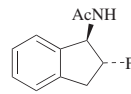
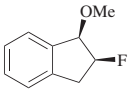
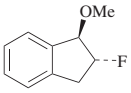

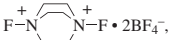
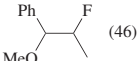
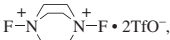
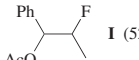



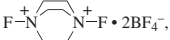
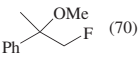
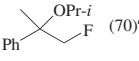
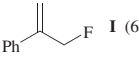
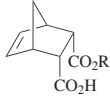
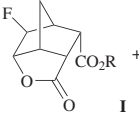
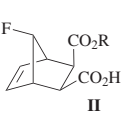
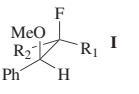
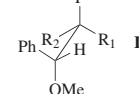
C ₉ 	Selectfluor TM , MeCN, MeOH, rt, 1 h	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>Ph</td> <td>OMe</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>OMe</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>OMe</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>H</td> <td>OMe</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	H	H	Ph	OMe	Ph	H	H	OMe	Ph	Me	H	OMe	Ph	Ph	H	OMe	174
	R ¹	R ²	R ³	R ⁴																			
	H	H	Ph	OMe																			
	Ph	H	H	OMe																			
Ph	Me	H	OMe																				
Ph	Ph	H	OMe																				
NFTh, MeCN, 70°, 1-24 h	 I +  II I + II (—), I:II = 1:1	179																					
NFTh, MeCN, MeOH, 35°, 60 min	 I +  II I + II (92), I:II = 60:40	126																					
Selectfluor TM , MeCN, MeOH, rt, 1 h	I + II (85), I:II = 58:42	178																					
	 MeCN/MeOH (1:1), rt, 10 min	 (46)	122																				
	 AcOH, rt, 15 min	 I (52)	122																				
 E:Z = 1:1	2,3,4,5,6-Cl ₃ FP-OTf, AcOH, rt, 20 min	I (80), threo:erythro = 1:1	31																				
	2,3,4,5,6-Cl ₃ FP-OTf, AcOH, rt, 20 min	I (80), threo:erythro = 1:1	31																				
	2,2'-bisFP-BF ₄ , AcOH, reflux, 15 min	I (51), dr = 1:1	161																				
	2-SO ₃ -4,6-(CF ₃) ₂ FP, AcOH, rt	I (51), dr = 1:1	161																				

TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₉ 	 MeCN/MeOH (1:1), rt, 15 min	 (70)	122															
	2,3,4,5,6-Cl ₃ FP-OTf, <i>i</i> -PrOH, rt, 10 min	 (70) ^d	31															
	2-SO ₃ -5-CF ₃ FP, Yb(OTf) ₃ , CH ₂ Cl ₂ , THF, rt, 9 h	 I (63)	409															
	2,3,4,5,6-Cl ₃ FP-OTf, AcOH, rt, 5 min	I (25)	31															
	2,3,4,5,6-Cl ₃ FP-OTf, 2-FPy, CH ₂ Cl ₂ , rt, 5 min	I (73) ^d	31															
C ₉₋₁₀ 	Selectfluor TM , MeCN, reflux	 I +  II <table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(53)</td> <td>traces</td> </tr> <tr> <td>Me</td> <td>(58)</td> <td>(8)</td> </tr> </tbody> </table>	R	I	II	H	(53)	traces	Me	(58)	(8)	408						
	R	I	II															
H	(53)	traces																
Me	(58)	(8)																
Selectfluor TM , MeCN, MeOH	 I +  II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>(75)</td> <td>50:50</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(75)</td> <td>28:72</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(78)</td> <td>55:45</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	Me	H	(75)	50:50	Ph	H	(75)	28:72	H	Ph	(78)	55:45	178
R ¹	R ²	I + II	I:II															
Me	H	(75)	50:50															
Ph	H	(75)	28:72															
H	Ph	(78)	55:45															

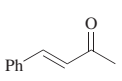
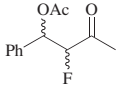
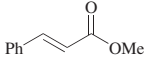
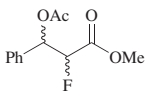
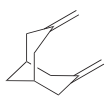
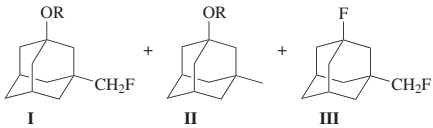
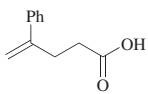
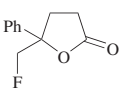
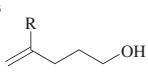

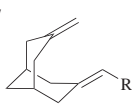
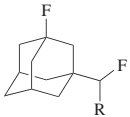
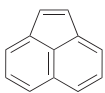
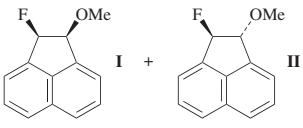
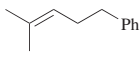
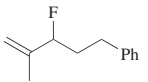
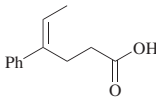
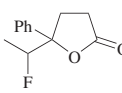
C ₁₀		R _f ¹ O ₂ S ₂ N-F, AcOH, 22° R _f ² O ₂ S ₂		83																																								
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TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																
C ₁₁ 	Fluorinating agent, MeCN, NaHCO ₃	 <table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>Temp</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>2,3,4,5,6-Cl₅FP-OTf</td> <td>rt</td> <td>1 h</td> <td>(69)</td> </tr> <tr> <td>2,6-Cl₂FP-OTf</td> <td>80°</td> <td>2 h</td> <td>(74)</td> </tr> <tr> <td>FP-OTf</td> <td>80°</td> <td>30 min</td> <td>(0)</td> </tr> </tbody> </table>	Fluorinating agent	Temp	Time	Yield (%)	2,3,4,5,6-Cl ₅ FP-OTf	rt	1 h	(69)	2,6-Cl ₂ FP-OTf	80°	2 h	(74)	FP-OTf	80°	30 min	(0)	182
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C ₁₁₋₁₃ 	2,3,4,5,6-Cl ₅ FP-OTf, NaHCO ₃ , MeCN	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>(49)</td> </tr> <tr> <td>PhCH₂CH₂</td> <td>(12)</td> </tr> </tbody> </table>	R	Yield (%)	Ph	(49)	PhCH ₂ CH ₂	(12)	182										
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C ₁₁₋₁₇ 	Selectfluor TM , monoglyme, reflux	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(93)</td> </tr> <tr> <td>Me</td> <td>(81)</td> </tr> <tr> <td>Ph</td> <td>(95)</td> </tr> </tbody> </table>	R	Yield (%)	H	(93)	Me	(81)	Ph	(95)	411								
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Ph	(95)																		
C ₁₂ 	Selectfluor TM , MeCN, MeOH, rt, 1 h	 <p>I + II (75), I:II = 50:50</p>	178																
	NFth, MeCN, MeOH, 35°, 10 min	I + II (89), I:II = 53:47	126																
	2,3,4,5,6-Cl ₅ FP-OTf, 2,6-(<i>t</i> -Bu) ₂ Py, THF, rt, 10 min	 (57)	31																
	2,3,4,5,6-Cl ₅ FP-OTf	 (85)	412																

		2,3,4,5,6-Cl ₅ FP-OTf, NaHCO ₃ , MeCN	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>cis:trans</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Ph</td> <td>(59) 1:2.5</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(20) 1:2.2</td> </tr> </tbody> </table>	R ¹	R ²	cis:trans	Me	Ph	(59) 1:2.5	Ph	Me	(20) 1:2.2	182																
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Solvent	Temp	I	II	III																									
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		Selectfluor TM , MeCN	(75)	178																									

TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
C ₁₄ 	Selectfluor TM , sodium lauryl ether sulfate (0.05% aq), 60°, 24 h	 I + II (—), I:II = 20:80	177						
	Selectfluor TM , MeCN, rt, 72 h; then H ₂ O	(85)	413						
	Selectfluor TM , sodium lauryl ether sulfate (0.05% aq), 60°, 24 h	I + II (—), I:II = 47:53	177						
	NFTh, MeCN, 70°, 1-24 h	<table border="1"> <thead> <tr> <th>Alkene</th> <th>erythro:threo</th> </tr> </thead> <tbody> <tr> <td>Z</td> <td>53:47 (72)</td> </tr> <tr> <td>E</td> <td>47:53 (73)</td> </tr> </tbody> </table>	Alkene	erythro:threo	Z	53:47 (72)	E	47:53 (73)	179
Alkene	erythro:threo								
Z	53:47 (72)								
E	47:53 (73)								
	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , MeCN, reflux, 1 h	(66)	181						
C ₁₄₋₂₀ 	(CF ₃ SO ₂) ₂ NF, AcOH, CH ₂ Cl ₂ , 0°, 1.5 h	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(61)</td> </tr> <tr> <td>Ph</td> <td>(70)</td> </tr> </tbody> </table>	R	I	H	(61)	Ph	(70)	35
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Ph	(55)								


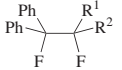
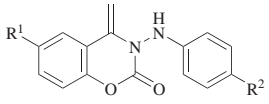
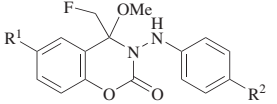
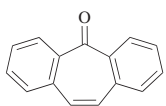
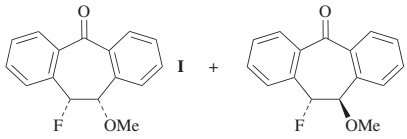
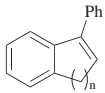
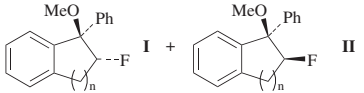
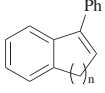
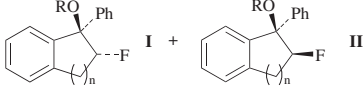
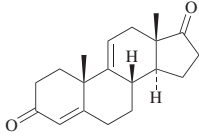
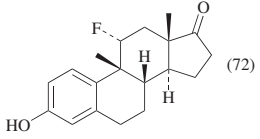

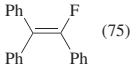
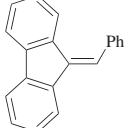
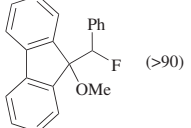
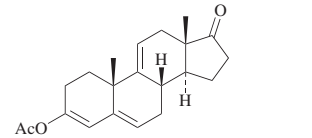
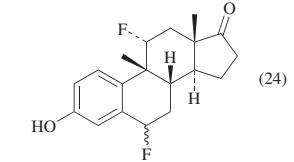
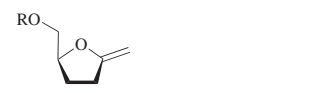
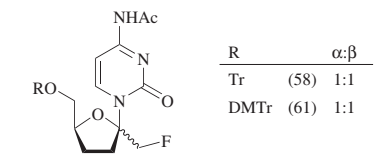
C ₁₄₋₂₆		(CF ₃ SO ₂) ₂ NF, (HF) _n Py, CH ₂ Cl ₂		<table border="1" data-bbox="1119 160 1241 264"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(0)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(96)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(100)</td> </tr> </tbody> </table>	R ¹	R ²		H	H	(0)	H	Ph	(96)	Ph	Ph	(100)	35																						
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C ₁₅		Selectfluor TM , MeCN, MeOH		<table border="1" data-bbox="1258 332 1380 413"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>Br</td> <td>(49)</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>(42)</td> </tr> </tbody> </table>	R ¹	R ²		Br	Br	(49)	Cl	H	(42)	414																									
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			<table border="1" data-bbox="1032 792 1319 975"> <thead> <tr> <th>n</th> <th>Temp</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>22°</td> <td>5 min</td> <td>(96)</td> <td>27:73</td> </tr> <tr> <td>1</td> <td>35°</td> <td>5 min</td> <td>(96)</td> <td>41:59</td> </tr> <tr> <td>1</td> <td>35°</td> <td>30 min</td> <td>(95)</td> <td>75:25</td> </tr> <tr> <td>1</td> <td>80°</td> <td>45 min</td> <td>(95)</td> <td>75:25</td> </tr> <tr> <td>2</td> <td>22°</td> <td>5 min</td> <td>(97)</td> <td>60:40</td> </tr> <tr> <td>3</td> <td>35°</td> <td>10 min</td> <td>(96)</td> <td>99:1</td> </tr> </tbody> </table>	n	Temp	Time	I + II	I:II	1	22°	5 min	(96)	27:73	1	35°	5 min	(96)	41:59	1	35°	30 min	(95)	75:25	1	80°	45 min	(95)	75:25	2	22°	5 min	(97)	60:40	3	35°	10 min	(96)	99:1	
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1	35°	30 min	(95)	75:25																																			
1	80°	45 min	(95)	75:25																																			
2	22°	5 min	(97)	60:40																																			
3	35°	10 min	(96)	99:1																																			

TABLE 2. FLUORINATION OF ALKENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C ₁₅₋₁₇ 	Selectfluor TM , ROH, MeCN, rt, 1 h	 <table border="1" data-bbox="1015 1480 1241 1756"> <thead> <tr> <th>n</th> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Me</td> <td>(80)</td> <td>27:73</td> </tr> <tr> <td>1</td> <td>Et</td> <td>(80)</td> <td>25:75</td> </tr> <tr> <td>1</td> <td><i>i</i>-Pr</td> <td>(77)</td> <td>50:50</td> </tr> <tr> <td>2</td> <td>Me</td> <td>(79)</td> <td>63:37</td> </tr> <tr> <td>2</td> <td>Et</td> <td>(74)</td> <td>60:40</td> </tr> <tr> <td>2</td> <td><i>i</i>-Pr</td> <td>(75)</td> <td>69:31</td> </tr> <tr> <td>3</td> <td>Me</td> <td>(82)</td> <td>99:1</td> </tr> <tr> <td>3</td> <td>Et</td> <td>(80)</td> <td>43:57</td> </tr> <tr> <td>3</td> <td><i>i</i>-Pr</td> <td>(75)</td> <td>14:86</td> </tr> </tbody> </table>	n	R	I + II	I:II	1	Me	(80)	27:73	1	Et	(80)	25:75	1	<i>i</i> -Pr	(77)	50:50	2	Me	(79)	63:37	2	Et	(74)	60:40	2	<i>i</i> -Pr	(75)	69:31	3	Me	(82)	99:1	3	Et	(80)	43:57	3	<i>i</i> -Pr	(75)	14:86	178
n	R	I + II	I:II																																								
1	Me	(80)	27:73																																								
1	Et	(80)	25:75																																								
1	<i>i</i> -Pr	(77)	50:50																																								
2	Me	(79)	63:37																																								
2	Et	(74)	60:40																																								
2	<i>i</i> -Pr	(75)	69:31																																								
3	Me	(82)	99:1																																								
3	Et	(80)	43:57																																								
3	<i>i</i> -Pr	(75)	14:86																																								
C ₁₉ 	Selectfluor TM , MeCN, 80°, 3 h	 (72)	415																																								
C ₂₀ 	Selectfluor TM , MeCN	 (75)	178																																								
	Selectfluor TM , MeOH, MeCN, rt, 1 h	 (>90)	174																																								

C ₂₁		Selectfluor TM , MeCN, 80°, 6 h	 (24)	415						
C ₂₅₋₂₇		N ⁴ -Ac-Cyt(SiMe ₃) ₂ , Selectfluor TM , MeNO ₂ , rt, 3 h	 <table border="1" data-bbox="1145 447 1319 539"> <thead> <tr> <th>R</th> <th>α:β</th> </tr> </thead> <tbody> <tr> <td>Tr (58)</td> <td>1:1</td> </tr> <tr> <td>DMTr (61)</td> <td>1:1</td> </tr> </tbody> </table>	R	α:β	Tr (58)	1:1	DMTr (61)	1:1	211
R	α:β									
Tr (58)	1:1									
DMTr (61)	1:1									

^a The reported value is the percent conversion based on starting material.

TABLE 3. FLUORINATION OF ALKYNES

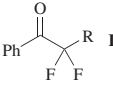
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
C ₈₋₁₄ Ph—C≡C—R	Selectfluor TM , MeCN, H ₂ O, reflux, 10-20 h	 <table border="1" data-bbox="1154 1028 1258 1159"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(36)</td> </tr> <tr> <td>Me</td> <td>(51)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>(48)</td> </tr> <tr> <td>Ph</td> <td>(51)</td> </tr> </tbody> </table>	R	I	H	(36)	Me	(51)	<i>t</i> -Bu	(48)	Ph	(51)	184
	R	I											
H	(36)												
Me	(51)												
<i>t</i> -Bu	(48)												
Ph	(51)												
	NFTh, MeCN, H ₂ O, 80°, 6-24 h	<table border="1" data-bbox="980 1205 1119 1343"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(58)</td> </tr> <tr> <td>Me</td> <td>(78)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>(72)</td> </tr> <tr> <td>Ph</td> <td>(72)</td> </tr> </tbody> </table>	R	I	H	(58)	Me	(78)	<i>t</i> -Bu	(72)	Ph	(72)	185
R	I												
H	(58)												
Me	(78)												
<i>t</i> -Bu	(72)												
Ph	(72)												

TABLE 4. FLUORINATION OF ARENES




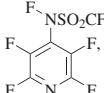
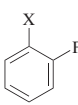
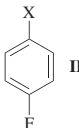

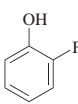
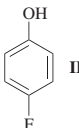
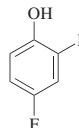

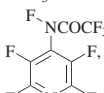
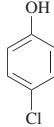
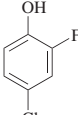
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
C ₆ 	(CF ₃ SO ₂) ₂ NF, neat, 22°, 18 h	 I (25)	63								
	2,6-(MeO ₂ C) ₂ FP-OTf, C ₆ H ₆ , reflux, 24 h	I (56) ^d	150								
	Selectfluor TM , TfOH, CH ₂ Cl ₂ , 0° to reflux, 20 h	I (83)	187								
	 F, C ₆ H ₆ , 60°	I (88) ^d	61								
	Selectfluor TM , TfOH, CH ₂ Cl ₂ , 0-40°, 36 h	 I +  II <table border="1" style="display: inline-table; vertical-align: middle;"> <tr> <td>X</td> <td>I + II</td> <td>I:II</td> </tr> <tr> <td>F</td> <td>(87)</td> <td>23:77</td> </tr> <tr> <td>Cl</td> <td>(87)</td> <td>69:31</td> </tr> </table>	X	I + II	I:II	F	(87)	23:77	Cl	(87)	69:31
X	I + II	I:II									
F	(87)	23:77									
Cl	(87)	69:31									
	F ⁺ -N ⁺ (CH ₂) ₃ -N ⁺ -F • 4TfO ⁻ , MeOH, 20°, 15 h	 I +  II +  III I + II (52), I:II = 60:40, III (0)	133								
	F ⁺ -N ⁺ (CH ₂) ₃ -N ⁺ -F • 2BF ₄ ⁻ , HCO ₂ H, rt, 15 min	I + II + III (48), I:II:III = 60:25:15	122								
	NFQN-OTf, NaOH (20%), rt	I + II + III (100) ^d , I:II:III = 1:1:1	114								
	1. NaH, THF, 20° 2. NFQN-OTf, THF, -10°	I + II (17), I:II = 1:2	114								

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	Fluorinating agent	I + II + III	31, 150
	Fluorinating agent	Solvent Temp Time I + II + III ^d I:II:III	
	2,4,6-Me ₃ FP-OTf	TCE 100° 24 h (75) 47:31:3	
	FP-OTf	TCE 100° 24 h (75) 51:18:6	
	2,4-Cl ₂ FP-OTf	CH ₂ Cl ₂ reflux 5 h (73) 60:18:7	
	2,6-(MeO ₂ C) ₂ FP-OTf	CH ₂ Cl ₂ rt 18 h (78) 10:8:1	
	2,2'-bisFP-BF ₄ , MeCN, reflux, 8 h	I + II + III (77), I:II:III = 39:33:5	161
	2,2'-bisFP-BF ₄ , NaOTf, MeCN, reflux, 5 h	I + II + III (80), I:II:III = 43:31:6	161
	2-SO ₃ -3-Cl-5-CF ₃ FP, TCE, 100°, 1.5 h	I + II (85) ^b , I:II = 88 ^c :<1:0	140
	2-SO ₃ -4,6-(CF ₃) ₂ FP, CH ₂ Cl ₂ , rt, 13 h	I + II (87) ^b , I:II = 84 ^c :1:0	140
	2-SO ₃ FP, TCE, reflux, 1.5 h	I (81) ^b , I = 55 ^c :0:0	31
	2-SO ₃ -6-ClFP, TCE, 100°, 49 h	I + II + III (95) ^b , I:II:III = 58 ^c :0:0	31
	 F, MeOH, 20°	I + II (91) ^d , I:II = 1:1	96
1. Formation of sodium phenolate 2. Perfluoropiperidine, pentane, 16 h	I + II (31), I:II = 3.5:1	36	
Selectfluor TM , MeOH, 20°	I + II (—), I:II = 3:2	134, 416	
Selectfluor TM , MeCN, microwaves, 150°, 1 h	I + II (24), I:II = 2:1	192	
	2,3,5,6-Cl ₄ FP-BF ₄ , TCE, 45°, 3 h	 I (81) ^d	417
	2,2'-bisFP-BF ₄ , DCE, 82°, 20 h	I (40)	158
	3,5-Cl ₂ FP-OTf, DCE, reflux, 23 h	I (54) ^d	31

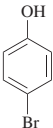
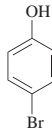
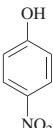
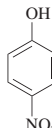
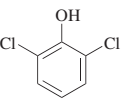
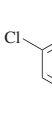
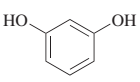
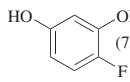
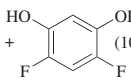
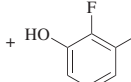
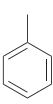
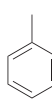
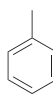
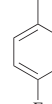
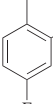
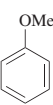
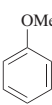
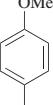
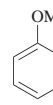
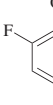


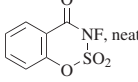
	2,3,5,6-Cl ₄ FP-BF ₄ , TCE, 45°, 6 h	 (87) ^a	417
	2,3,4,5,6-Cl ₅ FP-OTf, CH ₂ Cl ₂ , reflux, 17 h	 (89) ^a	31
	2-Cl-6-CCl ₃ FP-BF ₄ , TCE, 55°, 8 h	 (24) ^a	417
	2,2'-bisFP-BF ₄ , MeCN, reflux, 5 min	 (72) +  (10) +  (3)	161
	(CF ₃ SO ₂) ₂ NF, neat, 22°, 10 h	 I +  II +  III +  IV	418
		I + II + III (80)^a, I:II:III = 74:4:22, IV (0)	
	NFSI, toluene, reflux, 9 d	I + II + III (19)^a, I:II:III = 65:7:28	85
	Selectfluor TM , MeCN, reflux, 16 h	I + III (80), I:III = 75:25	173
	Selectfluor TM , TfOH, CH ₂ Cl ₂ , 0-40°, 24 h	I + III (89), I:III = 68:32	187
	Selectfluor TM , MeCN, microwaves, 150°, 30 min	I + III + IV (53), I:III:IV = 37:15:1	192

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	(CF ₃ SO ₂) ₂ NF, neat, 22°, 2 h	 I +  II +  III +  IV	63
		I + II (93), I:II = 74:26, III (0), IV (0)	
	NFOBS, 60°, 10 h	I + II (42), I:II = 60:40	33
	 F, C ₆ H ₆	I + II (98)^a, I:II = 75:25	61
	NFSI, 150°, 5 h	I + II + III (100)^a, I:II:III = 58:37:5	85
	NFth, MeCN, rt, 5 h	I + II (83), I:II = 29:71	235
	 F, MeCN, 60°	I + II (81)^a, I:II = 70:30	96
	 NF, neat, 150°, 5 h	I + II (77), I:II = 56:44	100
	Me ⁺ -N ⁻ Me ⁺ + 2TfO ⁻ , MeCN, 80°, 15 h	I + II (55), I:II = 50:50	133
	Fluorinating agent, reflux	I + II	140
	Fluorinating agent	Solvent Time I + II I:II	
	2-SO ₃ -4,6-(CF ₃) ₂ FP	TfOH, CH ₂ Cl ₂ 20 min (85) ^a 26:54	
	2-SO ₃ -4,6-(CF ₃) ₂ FP	CH ₂ Cl ₂ 29.5 h (80) ^a 30:46	
	2-SO ₃ -3-Cl-5-CF ₃ FP	TfOH, CH ₂ Cl ₂ 3 h (79) ^a 35:44	

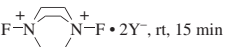
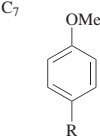
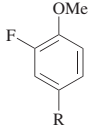
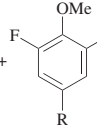
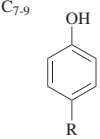
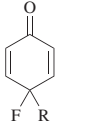
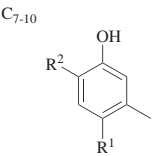
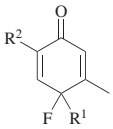
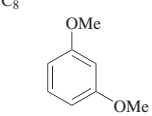
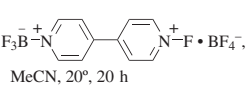
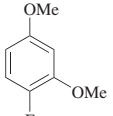
		Y	Solvent	I + II + IV	I:II:IV	
	I + II + IV	OTf	HCO ₂ H	(49)	43:49:8	122
		HSO ₄	HCO ₂ H	(61)	50:44:6	
		BF ₄	HCO ₂ H	(64)	47:45:8	
		SbF ₆	HCO ₂ H	(50)	44:46:10	
		SbF ₆	MeCN	(57)	54:37:9	
Selectfluor™, MeCN, H ₂ O, 40°	I + II (—), I:II = 50:50					134, 416
Selectfluor™, HCO ₂ H, rt, 15 min	I + II (5), I:II = 60:40					122
Fluorinating agent, 80°, 15 h	I + II					189
Fluorinating agent	Solvent	I + II	I:II			
Selectfluor™	[emim][OTf]	(56)	47:53			
Selectfluor™	[emim][BF ₄]	(42)	43:57			
Selectfluor™	[bmim][PF ₆]	(43)	48:52			
NFTh	[emim][OTf]	(30)	56:44			
FPPy-B ₂ F ₇	[emim][OTf]	(11)	54:46			
Fluorinating agent	I + II					419
Fluorinating agent	Solvent	Temp	Time	I + II	I:II	
Selectfluor™	MeCN	70°	3 h	(47)	60:40	
Selectfluor™	MeCN, PhNO ₂	70°	3 h	(55)	58:42	
Selectfluor™	CF ₃ CO ₂ H	50°	2.5 h	(42)	58:42	
NFTh	MeCN	70°	3 h	(58)	60:40	
2,6-Cl ₂ FP-BF ₄	MeCN	70°	3 h	(56)	64:36	
Selectfluor™, TfOH, CH ₂ Cl ₂ , 0–40°, 12 h	I + II (99), I:II = 9:11					187
Selectfluor™, MeCN, microwaves, 150°, 10 min	I + II + IV (32), I:II:IV = 9:6:1					192
NFTh, MeCN, microwaves, 150°, 10 min	I + II + III (42), I:II:III = 8:5:1					192
2,2'-bisFP-BF ₄ , MeCN, reflux, 9 h	I + II + IV (—), I:II:IV = 10:7:2					161
2,6-(MeO ₂ C) ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 24 h	I + II (—), I:II = 11:12					150
[(ClCN) ₃ F] ⁺ [BF ₄] ⁻ , MeCN, 0° to rt	I + II (—), I:II = 1:2					165, 167

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																						
	Selectfluor™, [emim][OTf], 80°, 15 h	 I +  II <table border="1" style="margin-left: 20px;"> <thead> <tr> <th></th> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>(50)</td> <td>95:5</td> <td></td> </tr> <tr> <td>F</td> <td>(24)</td> <td>100:0</td> <td></td> </tr> </tbody> </table>		R	I + II	I:II	Cl	(50)	95:5		F	(24)	100:0		189																																										
	R	I + II	I:II																																																						
Cl	(50)	95:5																																																							
F	(24)	100:0																																																							
	Fluorinating agent, MeCN, 22°	 <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Fluorinating agent</th> <th>R</th> <th>Time</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Selectfluor™</td> <td>Me</td> <td>20 h</td> <td>(52)</td> </tr> <tr> <td>NFTh</td> <td>Me</td> <td>20 h</td> <td>(45)</td> </tr> <tr> <td>Selectfluor™</td> <td><i>i</i>-Pr</td> <td>24 h</td> <td>(44)</td> </tr> <tr> <td>NFTh</td> <td><i>i</i>-Pr</td> <td>24 h</td> <td>(44)</td> </tr> </tbody> </table>	Fluorinating agent	R	Time	I:II	Selectfluor™	Me	20 h	(52)	NFTh	Me	20 h	(45)	Selectfluor™	<i>i</i> -Pr	24 h	(44)	NFTh	<i>i</i> -Pr	24 h	(44)	194																																		
Fluorinating agent	R	Time	I:II																																																						
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	Fluorinating agent, MeCN	 <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Fluorinating agent</th> <th>R¹</th> <th>R²</th> <th>Temp</th> <th>Time</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Selectfluor™</td> <td>Me</td> <td>H</td> <td>22°</td> <td>4.5 h</td> <td>(76)</td> </tr> <tr> <td>NFTh</td> <td>Me</td> <td>H</td> <td>22°</td> <td>4.5 h</td> <td>(74)</td> </tr> <tr> <td>Selectfluor™</td> <td><i>i</i>-Pr</td> <td>H</td> <td>22°</td> <td>7 h</td> <td>(71)</td> </tr> <tr> <td>NFTh</td> <td><i>i</i>-Pr</td> <td>H</td> <td>22°</td> <td>7 h</td> <td>(69)</td> </tr> <tr> <td>Selectfluor™</td> <td>Me</td> <td>Cl</td> <td>70°</td> <td>5 h</td> <td>(68)</td> </tr> <tr> <td>NFTh</td> <td>Me</td> <td>Cl</td> <td>70°</td> <td>5 h</td> <td>(66)</td> </tr> <tr> <td>Selectfluor™</td> <td>F</td> <td>H</td> <td>70°</td> <td>18 h</td> <td>(38)</td> </tr> <tr> <td>NFTh</td> <td>F</td> <td>H</td> <td>70°</td> <td>18 h</td> <td>(35)</td> </tr> </tbody> </table>	Fluorinating agent	R ¹	R ²	Temp	Time	I:II	Selectfluor™	Me	H	22°	4.5 h	(76)	NFTh	Me	H	22°	4.5 h	(74)	Selectfluor™	<i>i</i> -Pr	H	22°	7 h	(71)	NFTh	<i>i</i> -Pr	H	22°	7 h	(69)	Selectfluor™	Me	Cl	70°	5 h	(68)	NFTh	Me	Cl	70°	5 h	(66)	Selectfluor™	F	H	70°	18 h	(38)	NFTh	F	H	70°	18 h	(35)	194
Fluorinating agent	R ¹	R ²	Temp	Time	I:II																																																				
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		 I (52)	133																																																						

		I (40) MeCN, 20°, 15 h; then 60°, 20 h		133
		NFOBS, 0° to rt, 6 h		(48) 33
		Selectfluor™, MeCN, 22°, 4.5 h		I + II + III I (—), II + III (11), I:II:III = 85:5:10 420
		NFTh, MeCN, 22°, 4.5 h	I + II + III (—), I:II:III = 84:5:11	420
		Selectfluor™, H ₂ O, MeOH, rt, 18 h		(—) 421
		2,2'-bisFP-OTf, DCE, 82°, 20 h		I (50) 158
		3,5-Cl ₂ FP-OTf, DCE, reflux, 40 h		I (51) ^a 31
		Selectfluor™, [emim][OTf], 80°, 15 h		I + II + III (56), I:II:III = 93:6:1 189

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.						
	Selectfluor™, MeCN, reflux, 16 h		173						
	Selectfluor™, MeCN, reflux, 16 h		173						
	Selectfluor™, 80°, 15 h		<table border="1"> <thead> <tr> <th>Solvent</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>[emim][OTf]</td> <td>(51)</td> </tr> <tr> <td>[emim][BF₄]</td> <td>(24)</td> </tr> </tbody> </table> 189	Solvent	I	[emim][OTf]	(51)	[emim][BF ₄]	(24)
Solvent	I								
[emim][OTf]	(51)								
[emim][BF ₄]	(24)								
	Selectfluor™, MeCN, reflux, 16 h	I + II (97), I:II = 2:1	173						
	FP-OTf, TCE, 100°, 20 h		417						
	NFSI, neat, 100°, 18 h		I + II (40) ^a , I:II = 62:38 85						
	2,6-(MeO ₂ C) ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 48 h	I + II (53) ^a , I:II = 55:45	31						
	2,6-Cl ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 43 h	I + II (56) ^a , I:II = 70:30	31						
	2,3,4,5,6-Cl ₅ FP-OTf, CH ₂ Cl ₂ , 0° to rt, 23 h	I + II (60) ^a , I:II = 78:22	31						
	Selectfluor™, MeCN, reflux, 15 min	I + II (80), I:II = 62:38	129						
	Selectfluor™, MeCN, reflux	I + II (—), I:II = 62:38	134, 416						

C ₈₋₉		NFTh, MeCN, reflux, 0.5-4 h		$\frac{R}{OH}$ (55-65) $\frac{R}{OMe}$ (55-65)	229
		NFTh, MeCN, 6 h		$\frac{R}{Ac}$ Temp 40° I + II (84) 2:1 $\frac{R}{CO_2Et}$ 80° (88) 1:2.3	235
C ₈₋₁₀		perfluoropiperidine, pentane, 16 h		$\frac{R}{Me}$ Et	36, 422
C ₉		Selectfluor™, MeCN, 22°, 4.5 h			194
		NFTh, MeCN, 22°, 4.5 h			194
		Selectfluor™, MeCN, 22°, 4.5 h		I (-), II + III (13), I:II:III = 85:2.1:12.9	420
		NFTh, MeCN, 22°, 4.5 h		I + II + III (-), I:II:III = 84:4:12	420
		2,3,4,5,6-Cl ₅ FP-OTf, CH ₂ Cl ₂ , rt, 12 h		I + II (100) ^b , I:II = 42:0	31
		2,6-(MeO ₂ C) ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 3 h		I + II (79) ^a , I:II = 46:23	31

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
C ₉																																	
	Selectfluor™ (x eq), 2 h		423																														
		<table border="1"> <thead> <tr> <th>x</th> <th>Solvent</th> <th>Temp</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>MeCN</td> <td>-40° to 20°</td> <td>(62)</td> <td>(26)</td> </tr> <tr> <td>2</td> <td>MeCN</td> <td>-40° to 20°</td> <td>(0)</td> <td>(51)</td> </tr> <tr> <td>2</td> <td>MeCN (2 vol% H₂O)</td> <td>-21° to 20°</td> <td>(0)</td> <td>(56)</td> </tr> <tr> <td>2</td> <td>MeCN (20 vol% H₂O)</td> <td>20°</td> <td>(0)</td> <td>(58)</td> </tr> <tr> <td>2</td> <td>H₂O</td> <td>20°</td> <td>(0)</td> <td>(63)</td> </tr> </tbody> </table>	x	Solvent	Temp	I	II	1	MeCN	-40° to 20°	(62)	(26)	2	MeCN	-40° to 20°	(0)	(51)	2	MeCN (2 vol% H ₂ O)	-21° to 20°	(0)	(56)	2	MeCN (20 vol% H ₂ O)	20°	(0)	(58)	2	H ₂ O	20°	(0)	(63)	
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2	H ₂ O	20°	(0)	(63)																													
	$F_3B^+N^+ \text{ (pyridine)} \cdot BF_4^-$, MeCN, 20°, 18 h		133																														
	$Me^+N^+ \text{ (pyridine)} \cdot 2TfO^-$, MeCN, 20°, 18 h		133																														
	Selectfluor™ (1 eq), MeCN (2 vol% H ₂ O), 0-20°, 2 h		423																														
	2-SO ₃ -4,6-(CF ₃) ₂ FP, CH ₂ Cl ₂ , rt, 17 h		I + II (89) ^a , I:II = 34:1	140																													










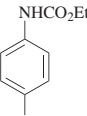
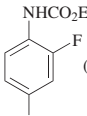
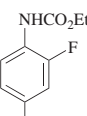
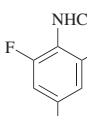
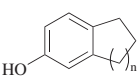
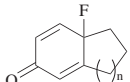
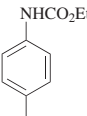
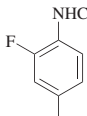
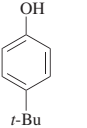
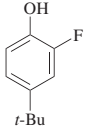
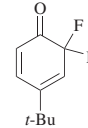
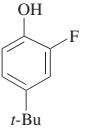
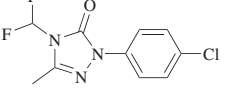
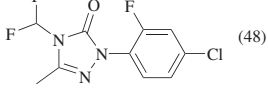
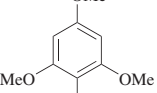
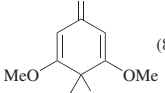
	2,2'-bisFP-BF ₄ , MeCN, reflux, 48 h	 I +  II +  III	161
		I + II + III (85), I:II:III = 56:38:6	
	2,6-(MeO ₂ C) ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 32 h	I + II + III (84), I:II:III = 56:38:6	150
	3,5-Cl ₂ FP-OTf, DCE, reflux, 5.5 h	I + II + III (89), I:II:III = 67:26:7	31
	2-SO ₃ -4,6-(CF ₃) ₂ FP, DCE, reflux, 2 h	I + II + III (87) ^a , I:II:III = 58:9:7	140
	NFTh, MeCN, reflux, 0.5-4 h	 I +  II	229
		I + II (55-65), I:II = 1:1	
	Selectfluor TM , [bmim][PF ₆], 80°, 15 h	 I (52)	189
	Selectfluor TM , TfOH, CH ₂ Cl ₂ , 0° to rt, 12 h	I (90)	187
	2,3,4,5,6-Cl ₅ FP-OTf, CH ₂ Cl ₂ , 0° to rt, 22 h	 (79) ^a	31
	2,3,4,5,6-Cl ₅ FP-OTf, CH ₂ Cl ₂ , 0° to rt, 22 h	 (74) ^a	31

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.										
	Fluorinating agent, MeCN, 22°, 4.5 h		194										
		<table border="1"> <thead> <tr> <th>n</th> <th>Fluorinating agent</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>SelectfluorTM (77)</td> </tr> <tr> <td>1</td> <td>NFTh (74)</td> </tr> <tr> <td>2</td> <td>SelectfluorTM (77)</td> </tr> <tr> <td>2</td> <td>NFTh (75)</td> </tr> </tbody> </table>	n	Fluorinating agent	1	Selectfluor TM (77)	1	NFTh (74)	2	Selectfluor TM (77)	2	NFTh (75)	
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1	Selectfluor TM (77)												
1	NFTh (74)												
2	Selectfluor TM (77)												
2	NFTh (75)												
	3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 38 h	 (56) ^a	31										
	Selectfluor TM , MeOH, reflux, 5 h	 I (49) +  II (12)	193										
	NFTh, MeOH, 60°, 2 h	II (72)	185										
	Selectfluor TM , MeOH, reflux, 5 h	II (80)	193										
	(Selectfluor TM , MeCN, 82°, 24 h) x 2	 (48)	424										
	Selectfluor TM (2 eq), MeCN, -40° to 20°, 2 h	 (81)	423										

	2,6-(MeO ₂ C) ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 25 h		31																		
	Selectfluor™		191																		
		<table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>I + II + III + IV</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>Selectfluor™</td> <td>MeCN</td> <td>reflux</td> <td>24 h</td> <td>(30)</td> <td>(—)</td> </tr> <tr> <td>Selectfluor™</td> <td>CF₃CO₂H</td> <td>70°</td> <td>4 h</td> <td>(75)</td> <td>3:1:0:0</td> </tr> </tbody> </table>	Fluorinating agent	Solvent	Temp	Time	I + II + III + IV	I:II:III:IV	Selectfluor™	MeCN	reflux	24 h	(30)	(—)	Selectfluor™	CF ₃ CO ₂ H	70°	4 h	(75)	3:1:0:0	
Fluorinating agent	Solvent	Temp	Time	I + II + III + IV	I:II:III:IV																
Selectfluor™	MeCN	reflux	24 h	(30)	(—)																
Selectfluor™	CF ₃ CO ₂ H	70°	4 h	(75)	3:1:0:0																
	Selectfluor™, [emim][OTf], 80°, 15 h	I + II + III (80), I:II:III = 91:7:2	189																		
	NFTh, MeCN, 80°, 30 min	I + II (82), I:II = 90:2	190																		
	Selectfluor™, TfOH, CH ₂ Cl ₂ , 0-40°, 12 h	I + II (100), I:II = 60:40	187																		
	NFTh, MeCN, 80°, 3 h		190																		
	Selectfluor™, MeCN, MeOH, rt, 5 min		425																		

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
	NFQN-X, MeCN, rt, 16 h		118																				
	3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , rt, 26 h	I + II (80) ^d , I:II = 84:11	31																				
	Fluorinating agent (0.53 eq), rt, 12 h	<table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>Solvent</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>2,2'-bisFP-OTf</td> <td>CO₂</td> <td>(99)</td> <td>1:8.9</td> </tr> <tr> <td>2,2'-bisFP-OTf</td> <td>MeCN</td> <td>(86)</td> <td>1:18.7</td> </tr> <tr> <td>2,2'-bisFP-BF₄</td> <td>CO₂</td> <td>(0)</td> <td>—</td> </tr> <tr> <td>2,2'-bisFP-BF₄, NaOTf</td> <td>CO₂</td> <td>(95)</td> <td>0:100</td> </tr> </tbody> </table>	Fluorinating agent	Solvent	I + II	I:II	2,2'-bisFP-OTf	CO ₂	(99)	1:8.9	2,2'-bisFP-OTf	MeCN	(86)	1:18.7	2,2'-bisFP-BF ₄	CO ₂	(0)	—	2,2'-bisFP-BF ₄ , NaOTf	CO ₂	(95)	0:100	158
	Fluorinating agent	Solvent	I + II	I:II																			
	2,2'-bisFP-OTf	CO ₂	(99)	1:8.9																			
	2,2'-bisFP-OTf	MeCN	(86)	1:18.7																			
	2,2'-bisFP-BF ₄	CO ₂	(0)	—																			
	2,2'-bisFP-BF ₄ , NaOTf	CO ₂	(95)	0:100																			
	2,2'-bisFP-BF ₄ , HCO ₂ H, rt, 10 min	I + II (79), I:II = 3.4:1	161																				
	NFTh, MeCN, rt, 30 min	II (92)	185																				
Selectfluor™, DMF, rt, 3 h	II (98)	426																					
Selectfluor™, MeOH, -196° to 20°	I + II (—), I:II = 2:1	134, 416																					
Fluorinating agent, MeCN, rt, 3 h	<table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Selectfluor™</td> <td>(100)^d</td> <td>73:27</td> </tr> <tr> <td>NFSI</td> <td>(30)^d</td> <td>100:0</td> </tr> <tr> <td>FPPy-B₂F₇</td> <td>(0)^d</td> <td>—</td> </tr> </tbody> </table>	Fluorinating agent	I + II	I:II	Selectfluor™	(100) ^d	73:27	NFSI	(30) ^d	100:0	FPPy-B ₂ F ₇	(0) ^d	—	193									
Fluorinating agent	I + II	I:II																					
Selectfluor™	(100) ^d	73:27																					
NFSI	(30) ^d	100:0																					
FPPy-B ₂ F ₇	(0) ^d	—																					
	MeCN, 80°, 15 h	I (60)	133																				
	MeCN, 20°, 1 h	I (71)	133																				

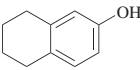
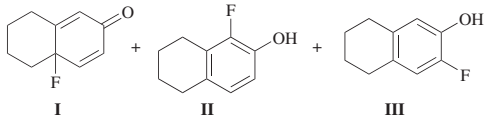
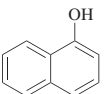
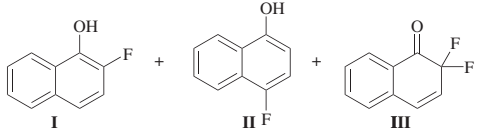
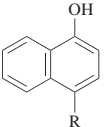
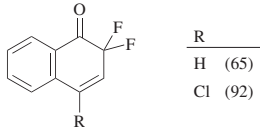
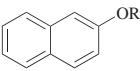
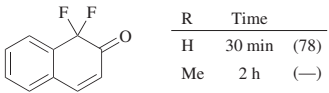
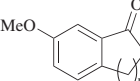
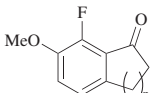
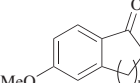
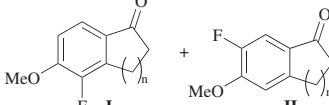
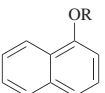
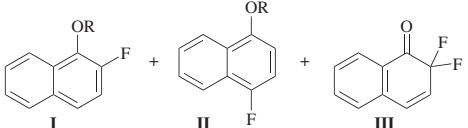
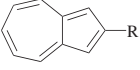
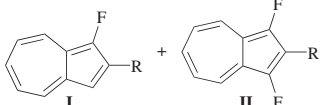
	$F^+N^+ \cdot F \cdot 2BF_4^-$ HCO ₂ H, MeOH, rt, 15 min	I + II (67), I:II = 57:43	122
	Selectfluor TM , MeCN, 22°, 4.5 h	 I (—), II + III (12), I:II:III = 85:10:5	420
	NFTh, MeCN, 22°, 4.5 h Selectfluor TM , H ₂ O, 60°, 2-6 h	I + II + III (—), I:II:III = 88:9:3 I (73.5)	420 177
	Fluorinating agent, MeCN, rt, 3 h	 I + II + III I:II:III Selectfluor TM (100) ^a 49:41:10 NFSI (70) ^a 88:0:12 FPPy-B ₂ F ₇ (0) ^a —	193
	2-SO ₃ -4,6-(CF ₃) ₂ FP, CH ₂ Cl ₂ , rt, 5 min	I + III (100) ^a , I:III = 63:3	140
	Selectfluor TM , MeOH, -196° to 20°	I + II (—), I:II = 2:1	134, 416
	FP-OTf, CH ₂ Cl ₂ , reflux, 22 h	I + II + III (85) ^a , I:II:III = 42:9:5	31
	NFTh, MeOH, 60°, 1 h	 R — H (65) Cl (92)	185

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Selectfluor TM , H ₂ O, 60°	 R — H 30 min (78) Me 2 h (—)	177
	NFTh, MeCN, reflux, 0.5-4 h	 n — 1 (68) 2 (55-65)	229
	NFTh, MeCN, reflux, 0.5-4 h	 I + II I:II n (55-65) 3:1 1 (55-65) 3:1 2 (55-65) 3:1	229
	NFTh, MeCN, 80°	 I + II + III I:II:III R — H 10 min (80) 45:42:13 Me 15 min (85) 48:48:4 <i>i</i> -Pr 10 min (85) 68:30:2	190
	2,4,6-Me ₃ FP-BF ₄ , MeCN, reflux, 30 min	 R I + II I:II H (24) 2:1 Me (55) 3.6:1 Ph (50) 1.9:1	427, 428

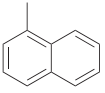
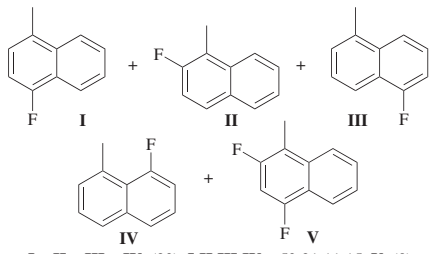
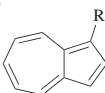
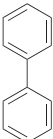
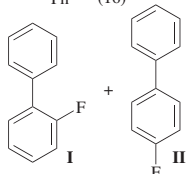
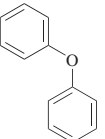
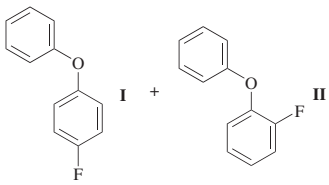
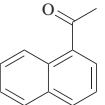
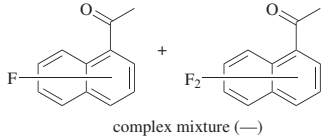
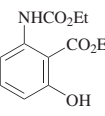
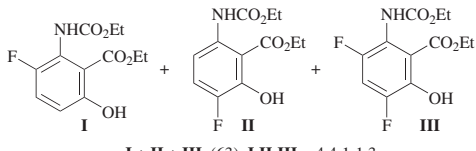
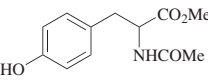
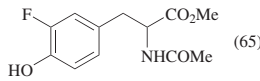
C ₁₁		Selectfluor TM , [bmim][PF ₆], 80°, 15 h		189				
		NFTh, MeCN, 80°, 3 h	I + II + V (65), I:II:V = 68:22:10	190				
C ₁₁₋₁₆		2,4,6-Me ₃ FP-OTf, MeCN, reflux, 3-8 h	I $\xrightarrow{\text{R}}$ (21) CHO	427				
		2,4,6-Me ₃ FP-OTf, MeCN, 60°, 1 h	I $\xrightarrow{\text{R}}$ (5) Me	427				
			I $\xrightarrow{\text{R}}$ (16) Ph	427				
C ₁₂		(R _f SO ₂) ₂ NF, 22°, 40 h		83				
		Fluorinating agent	I + II	419				
		Fluorinating agent	Solvent	Temp	Time	I + II	I:II	
		Selectfluor TM	MeCN	70°	97 h	(77)	78:22	
		Selectfluor TM	MeCN, PhNO ₂	70°	97 h	(73)	78:22	
		Selectfluor TM	CF ₃ CO ₂ H	60°	4 h	(69)	83:17	
		NFTh	MeCN	70°	96 h	(50)	77:23	
		2,6-Cl ₂ FP-BF ₄	MeCN	70°	24 h	(53)	60:40	

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
C ₁₂ 	Fluorinating agent		419				
	Fluorinating agent	Solvent	Temp	Time	I + II	I:II	
	Selectfluor TM	MeCN	70°	24 h	(65)	56:44	
	Selectfluor TM	MeCN, PhNO ₂	70°	24 h	(73)	56:44	
	Selectfluor TM	CF ₃ CO ₂ H	50°	4 h	(68)	59:41	
	NFTh	MeCN	70°	24 h	(62)	53:47	
	2,6-Cl ₂ FP-BF ₄	MeCN	70°	24 h	(72)	59:41	
	NFTh, MeCN, reflux, 0.5-4 h		229				
	3,5-Cl ₂ FP-OTf, DCE, reflux, 22 h		429				
		I + II + III (63), I:II:III = 4.4:1:1.3					
	3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , MeCN, rt, 8 h		405				

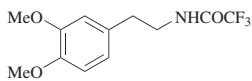
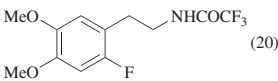
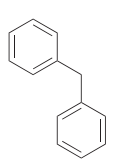
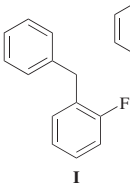
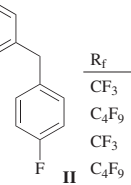
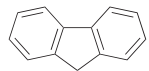
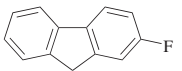
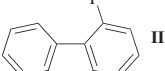
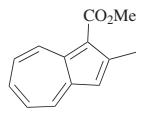
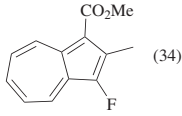
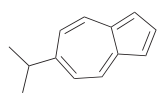
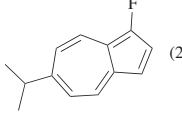
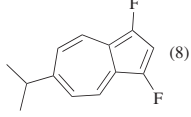
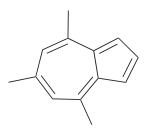
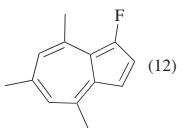
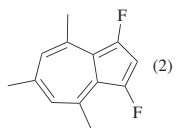
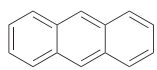
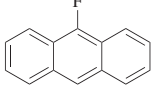
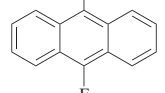
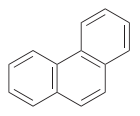
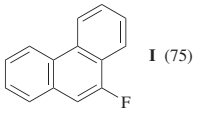
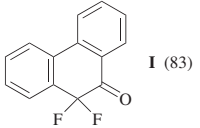
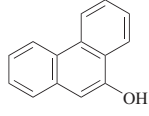
C ₁₃		3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , 35°, 10 h		405																								
		(R _f SO ₂) ₂ NF, 22°, 36 h	  <table border="1" data-bbox="1163 287 1414 424"> <thead> <tr> <th>R_f</th> <th>Solvent</th> <th>I + II</th> <th>I:II</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>CF₃</td> <td>CH₂Cl₂</td> <td>(63)^a</td> <td>71:29</td> <td>83</td> </tr> <tr> <td>C₄F₉</td> <td>CH₂Cl₂</td> <td>(34)^a</td> <td>72:28</td> <td></td> </tr> <tr> <td>CF₃</td> <td>MeCN</td> <td>(95)^a</td> <td>70:30</td> <td></td> </tr> <tr> <td>C₄F₉</td> <td>MeCN</td> <td>(94)^a</td> <td>76:24</td> <td></td> </tr> </tbody> </table>	R _f	Solvent	I + II	I:II	Yield (%)	CF ₃	CH ₂ Cl ₂	(63) ^a	71:29	83	C ₄ F ₉	CH ₂ Cl ₂	(34) ^a	72:28		CF ₃	MeCN	(95) ^a	70:30		C ₄ F ₉	MeCN	(94) ^a	76:24	
R _f	Solvent	I + II	I:II	Yield (%)																								
CF ₃	CH ₂ Cl ₂	(63) ^a	71:29	83																								
C ₄ F ₉	CH ₂ Cl ₂	(34) ^a	72:28																									
CF ₃	MeCN	(95) ^a	70:30																									
C ₄ F ₉	MeCN	(94) ^a	76:24																									
		Selectfluor TM , MeCN, 80°, 48 h	I + II (13), I:II = 76:24	430																								
		Selectfluor TM , CF ₃ CO ₂ H, 60°, 4 h	I + II (66), I:II = 64:36	430																								
		Selectfluor TM , MeCN, 80°, 4.5 h	 	430																								
			I + II (27), I:II = 67:33																									
		Selectfluor TM , CF ₃ CO ₂ H, 50°, 2 h	I + II (24), I:II = 55:45	430																								
		FP-BF ₄ , MeCN, reflux, 2 h		428																								
		Selectfluor TM , MeCN, MeOH, rt, 5 min	 	425																								

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	Selectfluor TM , MeCN, MeOH, rt, 5 min	 	425
C ₁₄ 	NF-2,4-DNI, DCE, reflux, 3 d	 	110
	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , reflux	I + II (55) ^a , I:II = 1.2:1	431
	Selectfluor TM , CF ₃ CO ₂ H, 70°, 4 h		191
	NFth, MeCN, reflux, 5 min	I (85)	190
	NFth, MeCN, H ₂ O, 80°, 1 h		185
	NFth, MeCN, rt, 2 h	I (79)	185
	Selectfluor TM , MeCN, rt, 2 h	I (49)	191, 193, 432

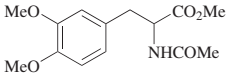
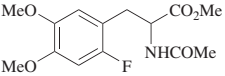
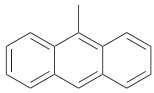
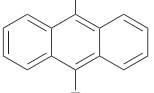
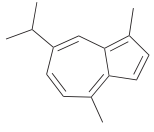
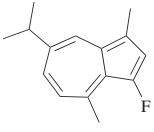
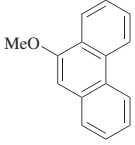
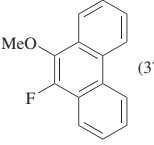
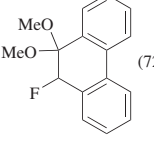
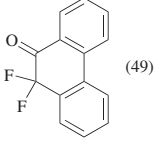
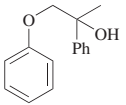
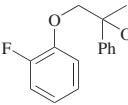
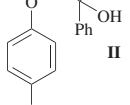
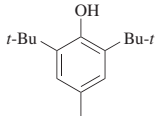
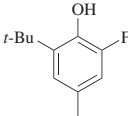
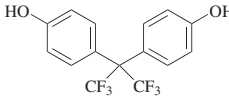
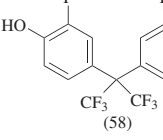
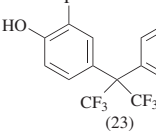
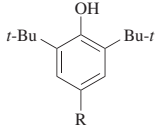
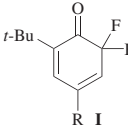
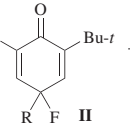
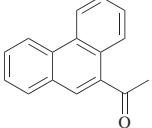
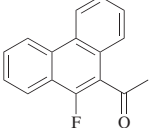
C ₁₅		3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , 35°, 8 h	 (30)	405
		NF-2,4-DNI, DCE, reflux, 3 d	 (7)	110
		Selectfluor TM , MeCN, MeOH, rt, 5 min	 (31)	425
		Selectfluor TM , CF ₃ CO ₂ H, rt, 4 h	 (37)	191, 432
		Selectfluor TM , MeOH, rt, 21 h	 (72)	191, 432
		Selectfluor TM , MeCN, rt, 4 h	 (49)	191, 432

TABLE 4. FLUORINATION OF ARENES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅		Selectfluor TM , MeCN, reflux	 I +  II I + II (—), I:II = 1.8:1	295
		Selectfluor TM , MeCN, 80°	 (100) ^a	433
		2,2'-bisFP-OTf, DCE, 82°, 20 h	 (58) +  (23)	158
C ₁₅₋₁₈		Selectfluor TM , MeCN, 10°	 I +  II R I + II I:II Me (80) 56:44 t-Bu (—) 80:20	433
C ₁₆		NFth, MeCN, reflux, 0.5-4 h	 (55-65)	229

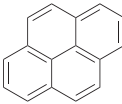
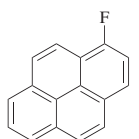
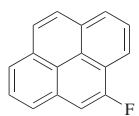
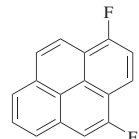
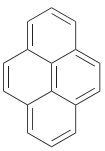
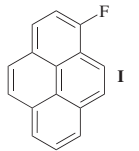
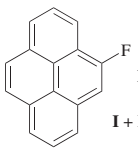
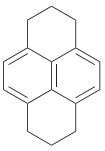
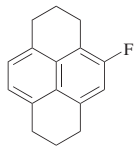
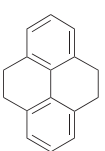
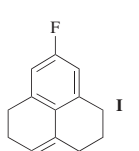
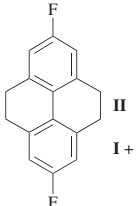
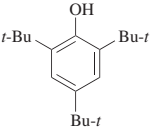
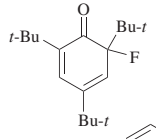
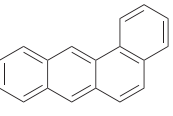
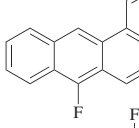
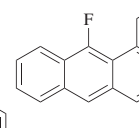
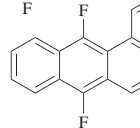
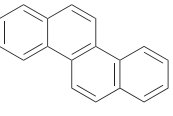
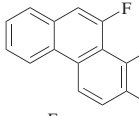
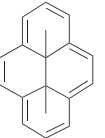
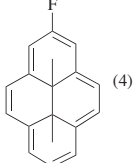
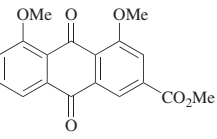
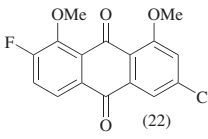
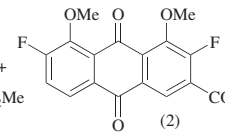
	NFTh, MeCN	 I +  II +  III	190																								
		<table border="1"> <thead> <tr> <th>Temp</th> <th>Time</th> <th>I + II + III</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>80°</td> <td>5 min</td> <td>(80)</td> <td>63:22:15</td> </tr> <tr> <td>60°</td> <td>30 min</td> <td>(75)</td> <td>64:16:20</td> </tr> <tr> <td>22°</td> <td>1 h</td> <td>(75)</td> <td>85:11:4</td> </tr> <tr> <td>10°</td> <td>2.5 h</td> <td>(75)</td> <td>90:10:<1</td> </tr> <tr> <td>5°</td> <td>5 h</td> <td>(75)</td> <td>93:7:<1</td> </tr> </tbody> </table>	Temp	Time	I + II + III	I:II:III	80°	5 min	(80)	63:22:15	60°	30 min	(75)	64:16:20	22°	1 h	(75)	85:11:4	10°	2.5 h	(75)	90:10:<1	5°	5 h	(75)	93:7:<1	
Temp	Time	I + II + III	I:II:III																								
80°	5 min	(80)	63:22:15																								
60°	30 min	(75)	64:16:20																								
22°	1 h	(75)	85:11:4																								
10°	2.5 h	(75)	90:10:<1																								
5°	5 h	(75)	93:7:<1																								
	NF-2,4-DNI, DCE, reflux, 3 d	 I +  II I + II (23), I:II = 9:1	110																								
	NF-2,4-DNI, DCE, reflux, 3 d	 (16)	110																								
	NF-2,4-DNI, DCE, reflux, 3 d	 I +  II I + II (12), I:II = 3:1	110																								

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	1. Formation of lithium phenolate 2. Perfluoropiperidine, pentane, C_6H_6 , 10 min	 (31)	36
	NF-2,4-DNI, DCE, reflux, 3 d	 I +  II +  III I + II + III (24), I:II:III = 4:1:2	110
	NF-2,4-DNI, DCE, reflux, 3 d	 (8)	110
	NF-2,4-DNI, DCE, reflux, 3 d	 (4)	110
	Selectfluor™, MeCN, reflux, 10 d	 (22) +  (2)	134

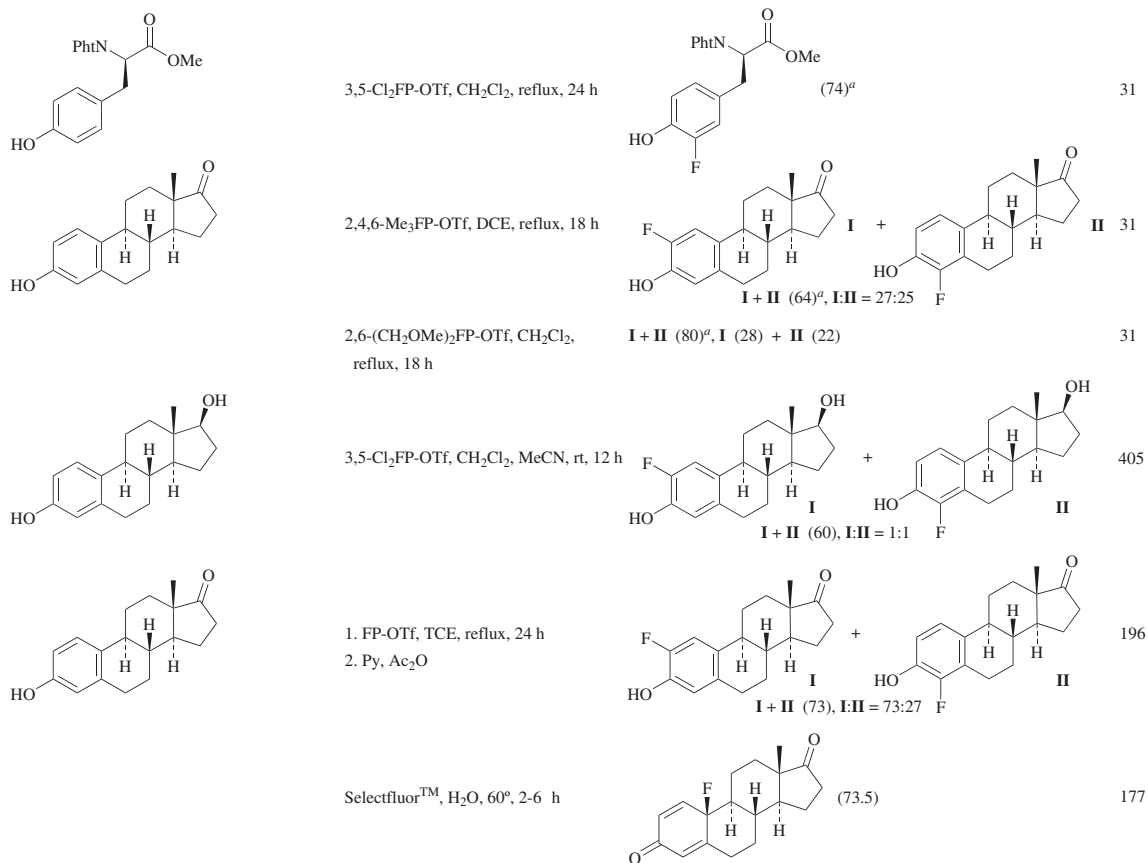


TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
 C ₁₈	FP-OTf, DCE, reflux, 18 h	 (28)	197																																				
 C ₁₈₋₁₉	Fluorinating agent, MeCN, 45°	<table border="1"> <thead> <tr> <th>R</th> <th>Fluorinating agent</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>SelectfluorTM</td> <td>3.5 h (79)</td> </tr> <tr> <td>H</td> <td>NFTh</td> <td>3.5 h (73)</td> </tr> <tr> <td>Me</td> <td>SelectfluorTM</td> <td>4 h (84)</td> </tr> <tr> <td>Me</td> <td>NFTh</td> <td>4 h (81)</td> </tr> </tbody> </table>	R	Fluorinating agent	Time	H	Selectfluor TM	3.5 h (79)	H	NFTh	3.5 h (73)	Me	Selectfluor TM	4 h (84)	Me	NFTh	4 h (81)	194																					
R	Fluorinating agent	Time																																					
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 C ₁₈₋₂₁	Fluorinating agent, MeCN, 45°	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>4 h (81)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>4 h (76)</td> </tr> <tr> <td>H</td> <td>H</td> <td>OH</td> <td>5 h (73)</td> </tr> <tr> <td>H</td> <td>H</td> <td>OH</td> <td>5 h (70)</td> </tr> <tr> <td>H</td> <td>C≡CH</td> <td>H</td> <td>4 h (78)</td> </tr> <tr> <td>H</td> <td>C≡CH</td> <td>H</td> <td>4 h (75)</td> </tr> <tr> <td>Me</td> <td>C≡CH</td> <td>H</td> <td>4.5 h (75)</td> </tr> <tr> <td>Me</td> <td>C≡CH</td> <td>H</td> <td>4.5 h (72)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time	H	H	H	4 h (81)	H	H	H	4 h (76)	H	H	OH	5 h (73)	H	H	OH	5 h (70)	H	C≡CH	H	4 h (78)	H	C≡CH	H	4 h (75)	Me	C≡CH	H	4.5 h (75)	Me	C≡CH	H	4.5 h (72)	194
R ¹	R ²	R ³	Time																																				
H	H	H	4 h (81)																																				
H	H	H	4 h (76)																																				
H	H	OH	5 h (73)																																				
H	H	OH	5 h (70)																																				
H	C≡CH	H	4 h (78)																																				
H	C≡CH	H	4 h (75)																																				
Me	C≡CH	H	4.5 h (75)																																				
Me	C≡CH	H	4.5 h (72)																																				

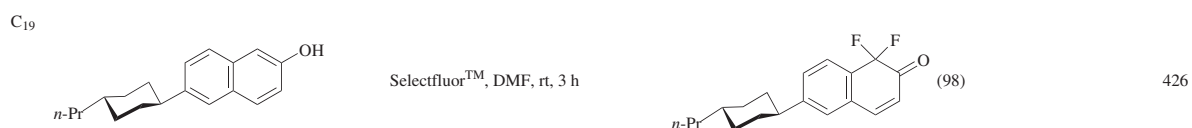
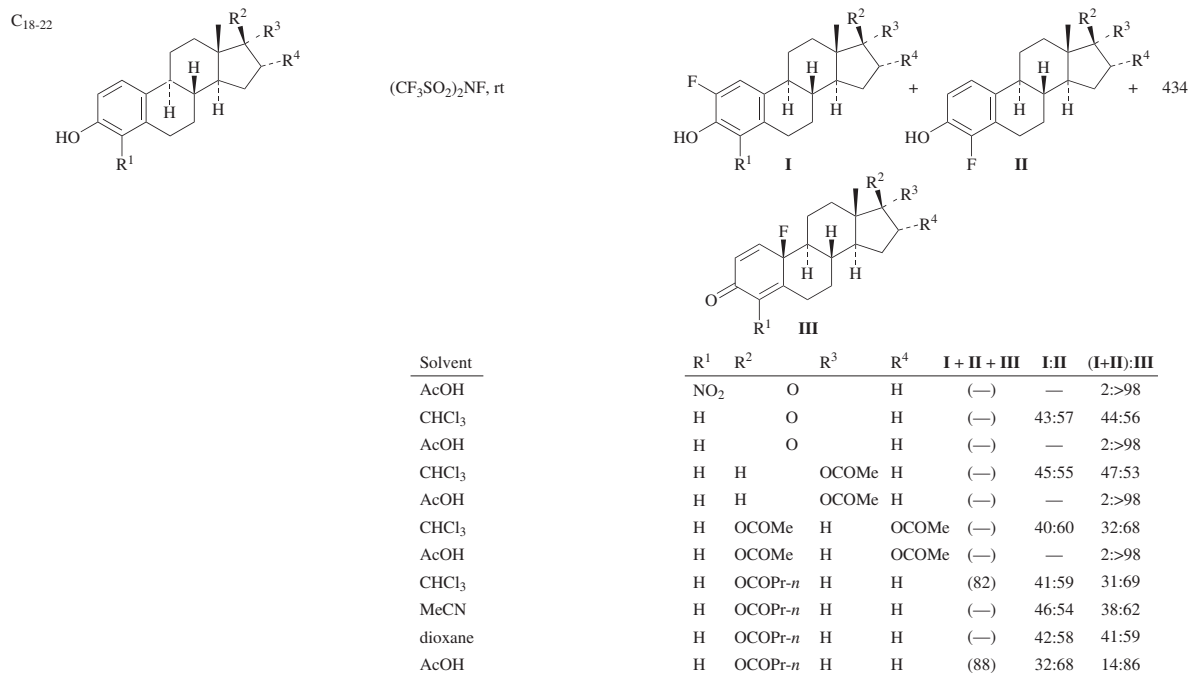


TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₉ 	FP-OTf, TCE, reflux, 4-6 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>(—)</td> <td>—</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>(—)</td> <td>—</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	H	Me	(—)	—	OMe	H	(—)	—	195
R ¹	R ²	I + II	I:II												
H	Me	(—)	—												
OMe	H	(—)	—												
C ₂₀ 	NF-2,4-DNI, DCE, reflux, 3 d	 (6)	110												
	NF-2,4-DNI, DCE, reflux, 3 d	 I + II + III (19), I:II:III = 3:3:1	110												

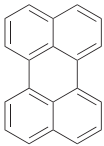
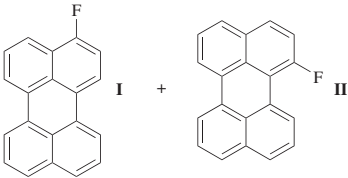
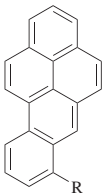
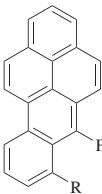
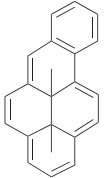
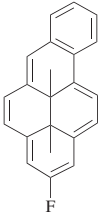
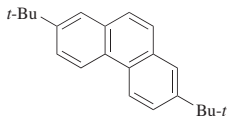
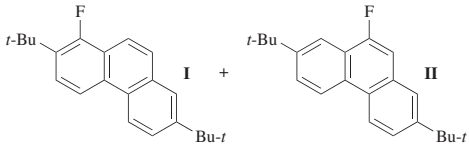
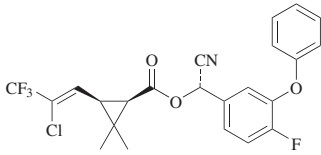
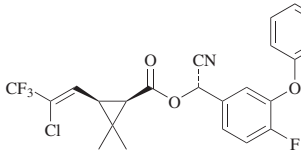
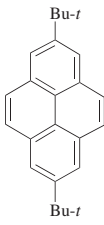
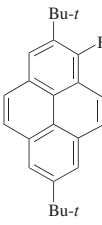
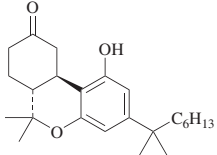
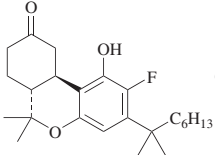
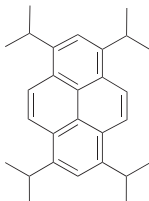
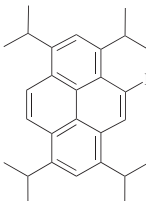
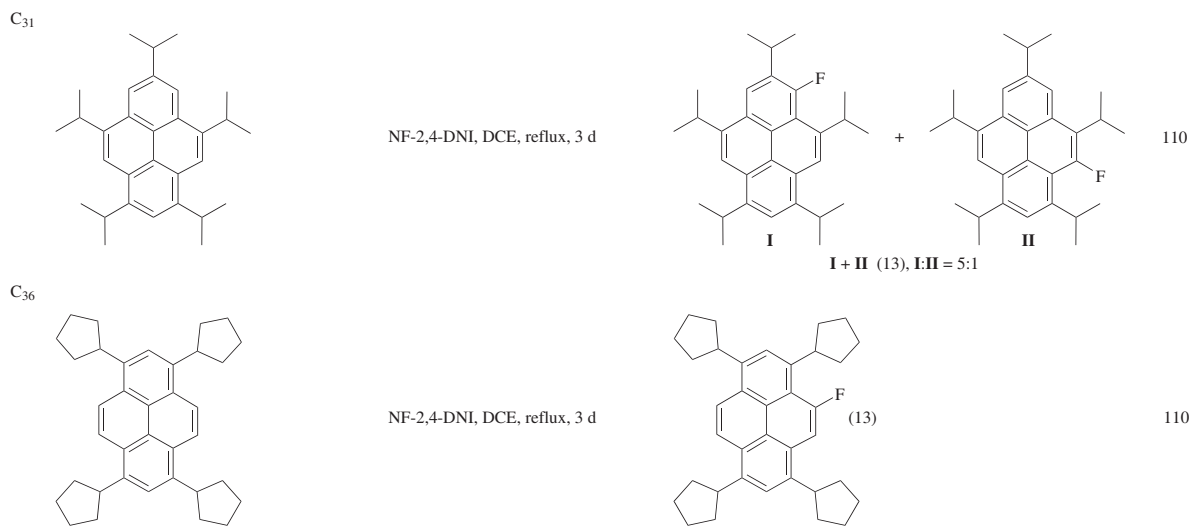
	NF-2,4-DNI, DCE, reflux, 3 d		110
		I + II (27), I:II = 2:1	
C ₂₀₋₂₁ 	NF-2,4-DNI, DCE, reflux, 3 d		110
		$\frac{R}{H} \quad (22)$ $\frac{R}{Me} \quad (18)$	
C ₂₂ 	NF-2,4-DNI, DCE, reflux, 3 d		110
		(4)	
	NF-2,4-DNI, DCE, reflux, 3 d		110
		I + II (3), I:II = 3:2	

TABLE 4. FLUORINATION OF ARENES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₃ 	Selectfluor™, MeCN, microwaves, 150°, 20 min	 (14)	192
C ₂₄ 	NF-2,4-DNI, DCE, reflux, 3 d	 (21)	110
	FP-OTf, CH ₂ Cl ₂ , rt, 1 d	 (88)	435
C ₂₈ 	NF-2,4-DNI, DCE, reflux, 3 d	 (18)	110



^a The reported value is the percent conversion based on starting material.

^b The reported value is the percent conversion determined by GLC.

^c The reported value is the percent product based on consumed phenol as determined by GLC.

TABLE 5. FLUORINATION OF HETEROCYCLES


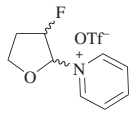
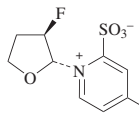
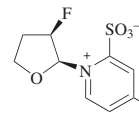
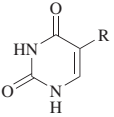
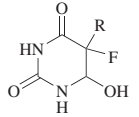

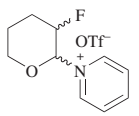
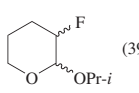
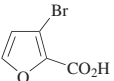
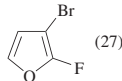
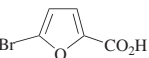
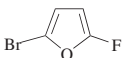
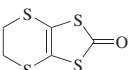
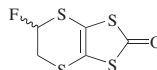
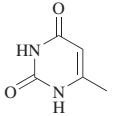
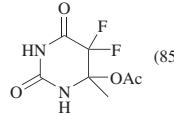

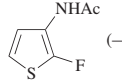
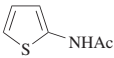
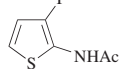
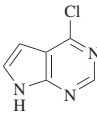
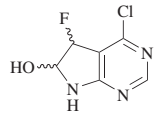
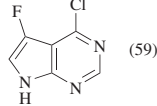
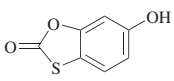
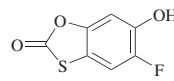
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
C ₄ 	FP-OTf, CH ₂ Cl ₂ , Py (2 mol%), reflux, 8 h	 (73), cis:trans = 1:1	31									
	2-SO ₃ -4-MeFP, CH ₂ Cl ₂ , reflux, 8 h	 (59) +  (16)	140									
C _{4,5} 	Selectfluor TM , H ₂ O, 90°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>4 h</td> <td>(82)</td> </tr> <tr> <td>Me</td> <td>3 h</td> <td>(95)</td> </tr> </tbody> </table>	R	Time	Yield (%)	H	4 h	(82)	Me	3 h	(95)	183
R	Time	Yield (%)										
H	4 h	(82)										
Me	3 h	(95)										
C ₅ 	FP-OTf, CH ₂ Cl ₂ , reflux, 7 h	 (86), cis:trans = 1:1	31									
	2,3,4,5,6-Cl ₅ FP-OTf, 2-FPy, <i>i</i> -PrOH, 5° to rt, 28 h	 (39), cis:trans = 1:1.5	31									
	Selectfluor TM , CCl ₄ , NaHCO ₃ (sat. aq), 20°, 1.5 h	 (27)	199									
	Selectfluor TM , CCl ₄ , NaHCO ₃ (sat. aq), 20°, 1.5 h	 (—)	199									
	Selectfluor TM , MeCN, 2 h	 (30)	436									
	(CF ₃ SO ₂) ₂ NF (2 eq), AcOH, rt, 2 d	 (85)	35									
C ₆ 	Selectfluor TM , MeCN, rt, 10 min	 (—)	200									
	Selectfluor TM , MeCN, rt, 10 min	 (—)	200									
	Selectfluor TM , MeCN, H ₂ O, rt, 4 h	 (41), trans:cis = 9:1	201									
	Selectfluor TM , MeCN, AcOH, 70°, 14 h	 (59)	201, 437									
C ₇ 	3,5-Cl ₂ FP-OTf, DCE, reflux	 (28)	438									

TABLE 5. FLUORINATION OF HETEROCYCLES (Continued)

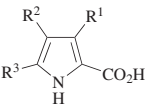
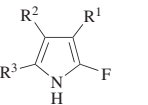
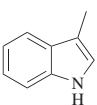
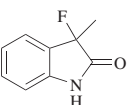
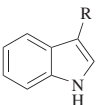
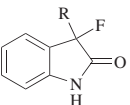
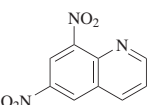
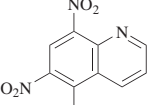
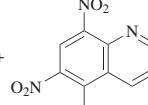
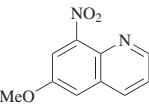
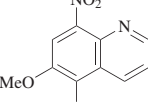
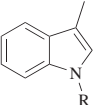
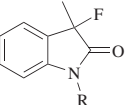
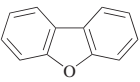
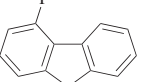
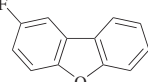
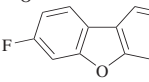
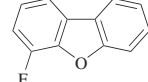
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																											
C ₇₋₂₀ 	Selectfluor TM , NaHCO ₃ (aq), CH ₂ Cl ₂ , rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>20 min</td> <td>(34)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>Me</td> <td>20 min</td> <td>(32)</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>CH₂CO₂Me</td> <td>CHO</td> <td>40 min</td> <td>(32)</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>CH₂CO₂Me</td> <td>Me</td> <td>20 min</td> <td>(37)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>CO₂Bn</td> <td>1 h</td> <td>(42)</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>CH₂CO₂Me</td> <td>CO₂Bn</td> <td>45 min</td> <td>(35)</td> </tr> <tr> <td>CH₂CO₂Me</td> <td>(CH₂)₂CO₂M</td> <td>CO₂Bn</td> <td>45 min</td> <td>(47)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Time		Me	H	Me	20 min	(34)	Me	Me	Me	20 min	(32)	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CHO	40 min	(32)	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	Me	20 min	(37)	Me	Me	CO ₂ Bn	1 h	(42)	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CO ₂ Bn	45 min	(35)	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ M	CO ₂ Bn	45 min	(47)	198			
R ¹	R ²	R ³	Time																																											
Me	H	Me	20 min	(34)																																										
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Me	Me	CO ₂ Bn	1 h	(42)																																										
(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CO ₂ Bn	45 min	(35)																																										
CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ M	CO ₂ Bn	45 min	(47)																																										
C ₉ 	Selectfluor TM , ROH, 20°	 <table border="1"> <thead> <tr> <th>Solvent</th> <th>ROH</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>[bmim][PF₆]</td> <td>MeOH</td> <td>3 h</td> <td>(99)</td> </tr> <tr> <td>[bmim][BF₄]</td> <td>MeOH</td> <td>3 h</td> <td>(99)</td> </tr> <tr> <td>[bmim][PF₆]</td> <td>EtOH</td> <td>12 h</td> <td>(88)</td> </tr> <tr> <td>[bmim][BF₄]</td> <td>EtOH</td> <td>12 h</td> <td>(92)</td> </tr> </tbody> </table>	Solvent	ROH	Time		[bmim][PF ₆]	MeOH	3 h	(99)	[bmim][BF ₄]	MeOH	3 h	(99)	[bmim][PF ₆]	EtOH	12 h	(88)	[bmim][BF ₄]	EtOH	12 h	(92)	206																							
Solvent	ROH	Time																																												
[bmim][PF ₆]	MeOH	3 h	(99)																																											
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C ₉₋₂₀ 	Selectfluor TM , MeCN, H ₂ O, rt, 16 h	 <table border="1"> <thead> <tr> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(71)</td> </tr> <tr> <td>CH₂CO₂Me</td> <td>(75)</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>(82)</td> </tr> <tr> <td>(CH₂)₂OAc</td> <td>(71)</td> </tr> <tr> <td>(CH₂)₃CO₂Me</td> <td>(77)</td> </tr> <tr> <td>(CH₂)₃OAc</td> <td>(69)</td> </tr> <tr> <td>(CH₂)₄OAc</td> <td>(64)</td> </tr> <tr> <td>(CH₂)₂CH(NHAc)CO₂Me</td> <td>(70)</td> </tr> <tr> <td>(CH₂)₂NPh</td> <td>(71)</td> </tr> <tr> <td>(CH₂)₂CH(NHCOC₆H₄NO₂-4)CO₂Me</td> <td>(92)</td> </tr> </tbody> </table>	R		Me	(71)	CH ₂ CO ₂ Me	(75)	(CH ₂) ₂ CO ₂ Me	(82)	(CH ₂) ₂ OAc	(71)	(CH ₂) ₃ CO ₂ Me	(77)	(CH ₂) ₃ OAc	(69)	(CH ₂) ₄ OAc	(64)	(CH ₂) ₂ CH(NHAc)CO ₂ Me	(70)	(CH ₂) ₂ NPh	(71)	(CH ₂) ₂ CH(NHCOC ₆ H ₄ NO ₂ -4)CO ₂ Me	(92)	203																					
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C ₁₀ 	NFSI, 130°, 3 h	 (38) +  (22)	202																																											
C ₁₀ 	NFSI, 130°, 3 h	 (38)	439																																											
C ₁₀₋₁₆ 	Selectfluor TM , MeCN, <i>i</i> -PrOH, rt, 16 h	 <table border="1"> <thead> <tr> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(96)</td> </tr> <tr> <td>Bn</td> <td>(66)</td> </tr> </tbody> </table>	R		Me	(96)	Bn	(66)	206																																					
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C ₁₂ 	Fluorinating agent	 I +  II +  III +  IV (0)	419																																											
	Fluorinating agent	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> <th>I + II + III</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>MeCN</td> <td>70°</td> <td>27 h</td> <td>(35)</td> <td>27:42:31</td> </tr> <tr> <td>MeCN/CH₂Cl₂ (9:1)</td> <td>70°</td> <td>27 h</td> <td>(30)</td> <td>26:42:32</td> </tr> <tr> <td>MeCN/MeOH (1:1)</td> <td>70°</td> <td>27 h</td> <td>(17)</td> <td>24:47:29</td> </tr> <tr> <td>MeCN/CF₃CO₂H (9:1)</td> <td>70°</td> <td>16 h</td> <td>(38)</td> <td>26:42:32</td> </tr> <tr> <td>SelectfluorTM</td> <td>CF₃CO₂H</td> <td>50°</td> <td>6 h</td> <td>(30)</td> <td>22:39:39</td> </tr> <tr> <td>NFTh</td> <td>MeCN</td> <td>70°</td> <td>24 h</td> <td>(35)</td> <td>26:42:32</td> </tr> <tr> <td>2,6-Cl₂FP-BF₄</td> <td>MeCN</td> <td>70°</td> <td>24 h</td> <td>(38)</td> <td>18:53:29</td> </tr> </tbody> </table>	Solvent	Temp	Time	I + II + III	I:II:III	MeCN	70°	27 h	(35)	27:42:31	MeCN/CH ₂ Cl ₂ (9:1)	70°	27 h	(30)	26:42:32	MeCN/MeOH (1:1)	70°	27 h	(17)	24:47:29	MeCN/CF ₃ CO ₂ H (9:1)	70°	16 h	(38)	26:42:32	Selectfluor TM	CF ₃ CO ₂ H	50°	6 h	(30)	22:39:39	NFTh	MeCN	70°	24 h	(35)	26:42:32	2,6-Cl ₂ FP-BF ₄	MeCN	70°	24 h	(38)	18:53:29	
Solvent	Temp	Time	I + II + III	I:II:III																																										
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	Selectfluor TM , [emim][OTf], 80°, 15 h	I + II + III (49), I:II:III = 20:41:39	189																																											
	Selectfluor TM , MeCN, microwaves, 150°, 10 min	II + III + IV (8), II:III:IV = 50:12:38	192																																											

TABLE 5. FLUORINATION OF HETEROCYCLES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Selectfluor™, CH ₂ Cl ₂ , NaHCO ₃ (aq), rt	 (37)	198
	FP-BF ₄ , MeCN, 80°, 180 h	 I + II	$\frac{R}{Ph} \quad \frac{I+II}{(12)} \quad \frac{I:II}{1.4:1}$ 4-ClC ₆ H ₄ (18) 2:1
	Selectfluor™, MeCN, R ³ OH, reflux, 3 h	 R ¹ R ² R ³ H Me H (96) OAc H H (80) OAc H Me (85) OAc H Ac (82)	183
	Selectfluor™, MeCN, THF, -40°	 R ¹ R ² H Me (48) H <i>i</i> -Pr (40) -(CH ₂) ₃ - (27) H Bn (42)	204
	Selectfluor™, sulfolane, 120°, 3 h	 (49)	441
	Selectfluor™, sulfolane, 130°	 (-) + (-)	441
	Selectfluor™, sulfolane, 120°, 3 h	 (39) + (10)	441
	Selectfluor™, MeCN, MeOH, reflux, 4 h	 (82)	183
	Selectfluor™, MeCN, MeOH	 (48)	205
	Selectfluor™, MeCN	 R Temp H reflux (32) Me reflux (34) OMe rt (28)	441

TABLE 5. FLUORINATION OF HETEROCYCLES (Continued)

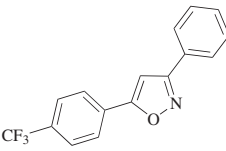
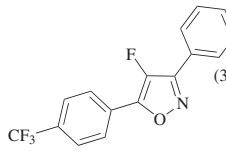
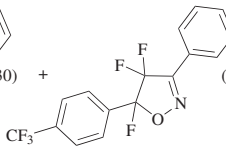
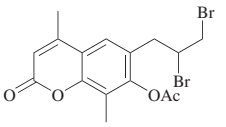
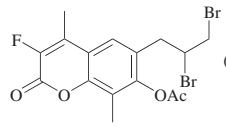
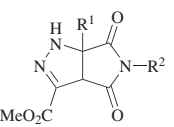
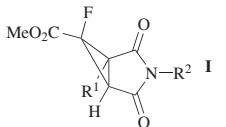
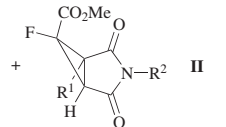
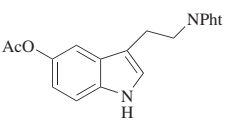
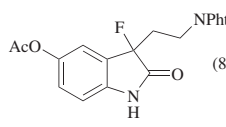
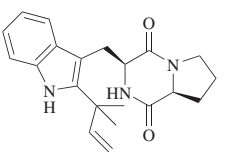
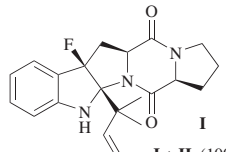
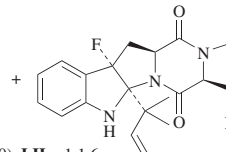
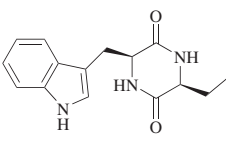
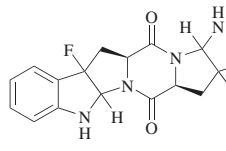
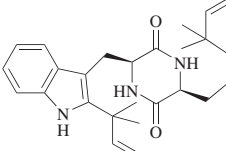
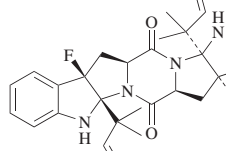
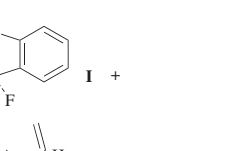
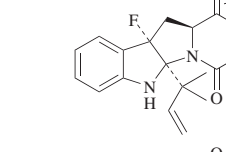
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C ₁₆ 	Selectfluor TM , sulfolane, 120°, 3 h	 (30) +  (10)	441																				
	Selectfluor TM , MeCN, reflux	 (14)	442																				
C ₁₉₋₂₁ 	FP-BF ₄ , MeCN, 80°, 150 h	 I +  II	440, 443																				
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>4-ClC₆H₄</td> <td>Ph</td> <td>(9)</td> <td>1.2:1</td> </tr> <tr> <td>4-ClC₆H₄</td> <td>4-MeC₆H₄</td> <td>(15)</td> <td>1.2:1</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>4-ClC₆H₄</td> <td>(11)</td> <td>1:1.5</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>4-MeC₆H₄</td> <td>(13)</td> <td>1.3:1</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	4-ClC ₆ H ₄	Ph	(9)	1.2:1	4-ClC ₆ H ₄	4-MeC ₆ H ₄	(15)	1.2:1	4-MeC ₆ H ₄	4-ClC ₆ H ₄	(11)	1:1.5	4-MeC ₆ H ₄	4-MeC ₆ H ₄	(13)	1.3:1	
R ¹	R ²	I + II	I:II																				
4-ClC ₆ H ₄	Ph	(9)	1.2:1																				
4-ClC ₆ H ₄	4-MeC ₆ H ₄	(15)	1.2:1																				
4-MeC ₆ H ₄	4-ClC ₆ H ₄	(11)	1:1.5																				
4-MeC ₆ H ₄	4-MeC ₆ H ₄	(13)	1.3:1																				
C ₂₀ 	Selectfluor TM , MeCN, H ₂ O, rt, overnight	 (82)	203																				
C ₂₁ 	2,4,6-Me ₃ FP-OTf, THF, 65°	 I +  II	204																				
		I + II (100), I:II = 1:1.6																					
C ₂₂ 	Selectfluor TM , MeCN, THF, -40°	 (44)	204																				
C ₃₂ 	2,4,6-Me ₃ FP-OTf, THF, 65°	 I +  II +  III	204																				
		I + II + III (77), I:II:III = 2:1:1																					

TABLE 5. FLUORINATION OF HETEROCYCLES (Continued)

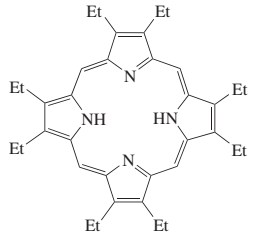
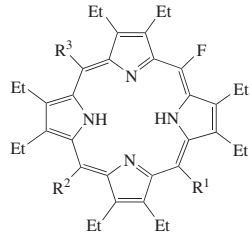
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
<p>C₃₆</p> 	2,3,4,5,6-Cl ₅ FP-OTf, C ₆ F ₆ , 50°, 12 h	 <table border="1" data-bbox="1241 1090 1388 1258"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(19)</td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>(6.5)</td> </tr> <tr> <td>H</td> <td>F</td> <td>H</td> <td>(6.5)</td> </tr> <tr> <td>F</td> <td>F</td> <td>H</td> <td>(15)</td> </tr> <tr> <td>F</td> <td>F</td> <td>F</td> <td>(20)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	H	H	H	(19)	F	H	H	(6.5)	H	F	H	(6.5)	F	F	H	(15)	F	F	F	(20)	444
R ¹	R ²	R ³	Yield (%)																								
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TABLE 6. FLUORINATION OF GLYICALS

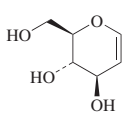
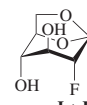
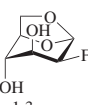
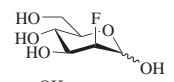
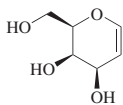
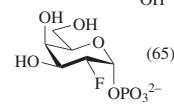
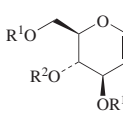
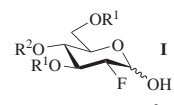
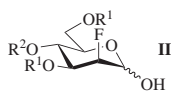
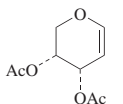
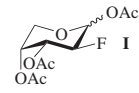
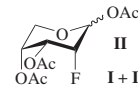
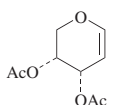
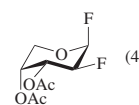
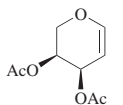
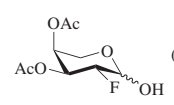
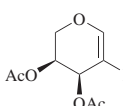
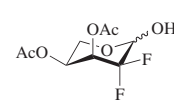
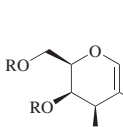
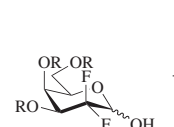
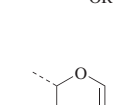
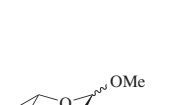
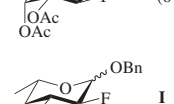
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																				
C ₆ 	Selectfluor™, MeNO ₂ , rt, overnight	 I +  II I + II (27), I:II = 1:3	445																																				
	Selectfluor™, H ₂ O, rt, 1 h	 (85), α:β = 1:1.5	210																																				
	F-TEDA-OTf, H ₂ O, 3 h; then kinase, ATP, 4 d	 (65)	446																																				
C ₆₋₂₇ 	Selectfluor™, MeNO ₂ , H ₂ O, rt, 16 h; then reflux, 1 h	 I +  II <table border="1" data-bbox="1006 631 1319 872"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(43)</td> <td>67:33</td> </tr> <tr> <td>Ac</td> <td>Ac</td> <td>(61)</td> <td>56:44</td> </tr> <tr> <td>Piv</td> <td>Piv</td> <td>(85)</td> <td>90:10</td> </tr> <tr> <td>Ac</td> <td>α-D-Glc(Ac)</td> <td>(66)</td> <td>62:38</td> </tr> <tr> <td>Ac</td> <td>β-D-Glc(Ac)</td> <td>(75)</td> <td>80:20</td> </tr> <tr> <td>Ac</td> <td>β-D-Gal(Ac)</td> <td>(65)</td> <td>78:22</td> </tr> <tr> <td>Bn</td> <td>Bn</td> <td>(93)</td> <td>51:49</td> </tr> <tr> <td>Bz</td> <td>Bz</td> <td>(74)</td> <td>80:20</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	H	H	(43)	67:33	Ac	Ac	(61)	56:44	Piv	Piv	(85)	90:10	Ac	α-D-Glc(Ac)	(66)	62:38	Ac	β-D-Glc(Ac)	(75)	80:20	Ac	β-D-Gal(Ac)	(65)	78:22	Bn	Bn	(93)	51:49	Bz	Bz	(74)	80:20	445
R ¹	R ²	I + II	I:II																																				
H	H	(43)	67:33																																				
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Bn	Bn	(93)	51:49																																				
Bz	Bz	(74)	80:20																																				
C ₉ 	1. Selectfluor™, MeNO ₂ , H ₂ O, rt; then reflux, 30 min 2. Acetylation	 I +  II I + II (68), I:II = 93:7	207, 208																																				

TABLE 6. FLUORINATION OF GLYICALS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	Selectfluor™, MeNO ₂ , rt; then reflux, 10-30 min	 (45)	208
	Selectfluor™, EtNO ₂ , H ₂ O, rt, 16 h; then reflux, 1 h	 (70)	447
	Selectfluor™, MeNO ₂ , H ₂ O, rt, 14 h; then reflux, 30 min	 (38)	209
C ₉₋₁₂ 	Selectfluor™, MeNO ₂ , H ₂ O, rt, 14 h; then reflux, 30 min	 (39) R Me (—) Ac	209
C ₁₀ 	F-TEDA-OTf, MeNO ₂ , rt, 6 h; then MeOH, 90°, 2 h	 (67), α:β = 4:6	43
	F-TEDA-OTf, MeNO ₂ , rt, 6 h; then BnOH, 90°, 2 h	 I (75), α:β = 1:1	43
	Selectfluor™, MeCN, BnOH, rt, 12 h	I (71), α:β = 0:1	210

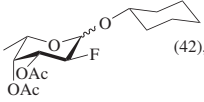
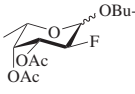
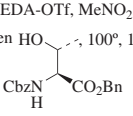
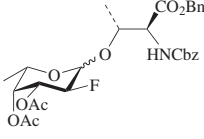
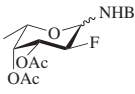
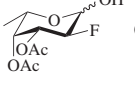
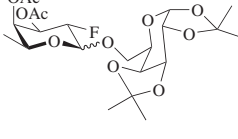
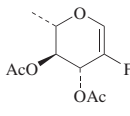
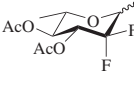
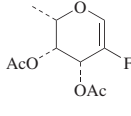
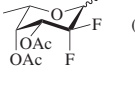
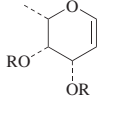
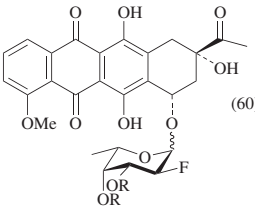
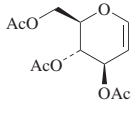
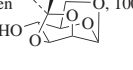
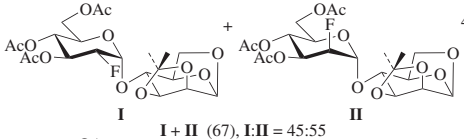

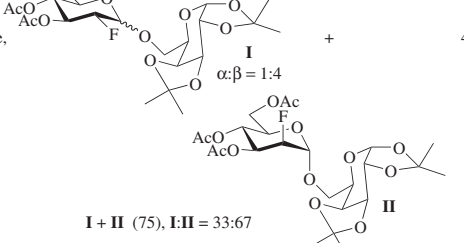
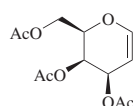
	F-TEDA-OTf, MeNO ₂ , rt, 6 h; then <i>c</i> -C ₆ H ₁₁ OH, 90°, 2 h	 (42), α:β = 55:45	43
	F-TEDA-OTf, MeNO ₂ , rt, 6 h; then <i>t</i> -BuOH, 90°, 2 h	 (48), α:β = 70:30	43
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then  , 100°, 1 h	 (55), α:β = 67:33	43
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then BnNH ₂ , 100°, 1 h	 (53), α:β = 80:20	43
	Selectfluor™, DMF, H ₂ O, rt, 12 h	 (97), α:β = 1:1	210
	1,2:3,4-di- <i>O</i> -isopropylidene- α -D-galactose, Selectfluor™, MeNO ₂ , rt, 2 h	 (40), α:β = 1:2	210
	Selectfluor™, MeNO ₂ , H ₂ O, rt, 14 h; then reflux, 30 min	 (65)	209

TABLE 6. FLUORINATION OF GLYCALs (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.								
	Selectfluor™, MeNO ₂ , H ₂ O, rt, 14 h; then reflux, 30 min	 (75)	209								
	F-TEDA-OTf, daunomycinone, 100°	 (60) <table border="1" data-bbox="1258 1572 1362 1687"> <thead> <tr> <th>R</th> <th>α:β</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>50:50</td> </tr> <tr> <td>Piv</td> <td>75:25</td> </tr> <tr> <td>Bz</td> <td>66:34</td> </tr> </tbody> </table>	R	α:β	Ac	50:50	Piv	75:25	Bz	66:34	43
R	α:β										
Ac	50:50										
Piv	75:25										
Bz	66:34										
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then  , 100°, 1 h	 I + II (67), I:II = 45:55	43								
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then 1,2:3,4-di- <i>O</i> -isopropylidene- α -D-galactose, 100°, 1 h	 I + II (75), I:II = 33:67	43								



Selectfluor™, potassium 2,4-dinitrophenolate, MeNO ₂ , reflux, 1 h		445
Selectfluor™, DMF, H ₂ O, rt, 12 h		210
Selectfluor™, 2,6-(<i>t</i> -Bu) ₂ -4-MePy, MeCN, BnOH, 4 Å MS, rt, 12 h		210
Selectfluor™, 1,2:3,4-di- <i>O</i> -isopropylidene- α - D-galactose, 2,6-(<i>t</i> -Bu) ₂ -4-MePy, MeCN		43
F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then 4-methoxyphenol, 100°, 1 h		43
Selectfluor™, MeNO ₂ , rt, overnight		207, 208
Selectfluor™, MeNO ₂ , H ₂ O, rt; then reflux		207, 208, 448
Selectfluor™, DMF, rt, 12 h		210

TABLE 6. FLUORINATION OF GLYICALS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																
	Selectfluor™, MeNO ₂ , MeOH, rt; then reflux		208																																
	Selectfluor™, MeNO ₂ , rt; then reflux		208																																
	NFSI, MeCN, 80°, 24 h		208																																
	Selectfluor™, MeNO ₂ , rt; then 50°, 1 h		445																																
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>Ac</td> <td>(25-45)</td> <td>1:1</td> </tr> <tr> <td>Piv</td> <td>Piv</td> <td>(25-45)</td> <td>10:1</td> </tr> <tr> <td>Ac</td> <td>α-D-Glc(Ac)</td> <td>(30)</td> <td>11:19</td> </tr> <tr> <td>Ac</td> <td>β-D-Glc(Ac)</td> <td>(26)</td> <td>5:8</td> </tr> <tr> <td>Ac</td> <td>β-D-Gal(Ac)</td> <td>(21)</td> <td>8:13</td> </tr> <tr> <td>Bn</td> <td>Bn</td> <td>(25-45)</td> <td>2:3</td> </tr> <tr> <td>Bz</td> <td>Bz</td> <td>(25-45)</td> <td>4:1</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	Ac	Ac	(25-45)	1:1	Piv	Piv	(25-45)	10:1	Ac	α -D-Glc(Ac)	(30)	11:19	Ac	β -D-Glc(Ac)	(26)	5:8	Ac	β -D-Gal(Ac)	(21)	8:13	Bn	Bn	(25-45)	2:3	Bz	Bz	(25-45)	4:1	
R ¹	R ²	I + II	I:II																																
Ac	Ac	(25-45)	1:1																																
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Ac	β -D-Gal(Ac)	(21)	8:13																																
Bn	Bn	(25-45)	2:3																																
Bz	Bz	(25-45)	4:1																																
	1. Selectfluor™, MeNO ₂ , rt, overnight; then H ₂ O, 75°, 75 min 2. Acetylation		445																																

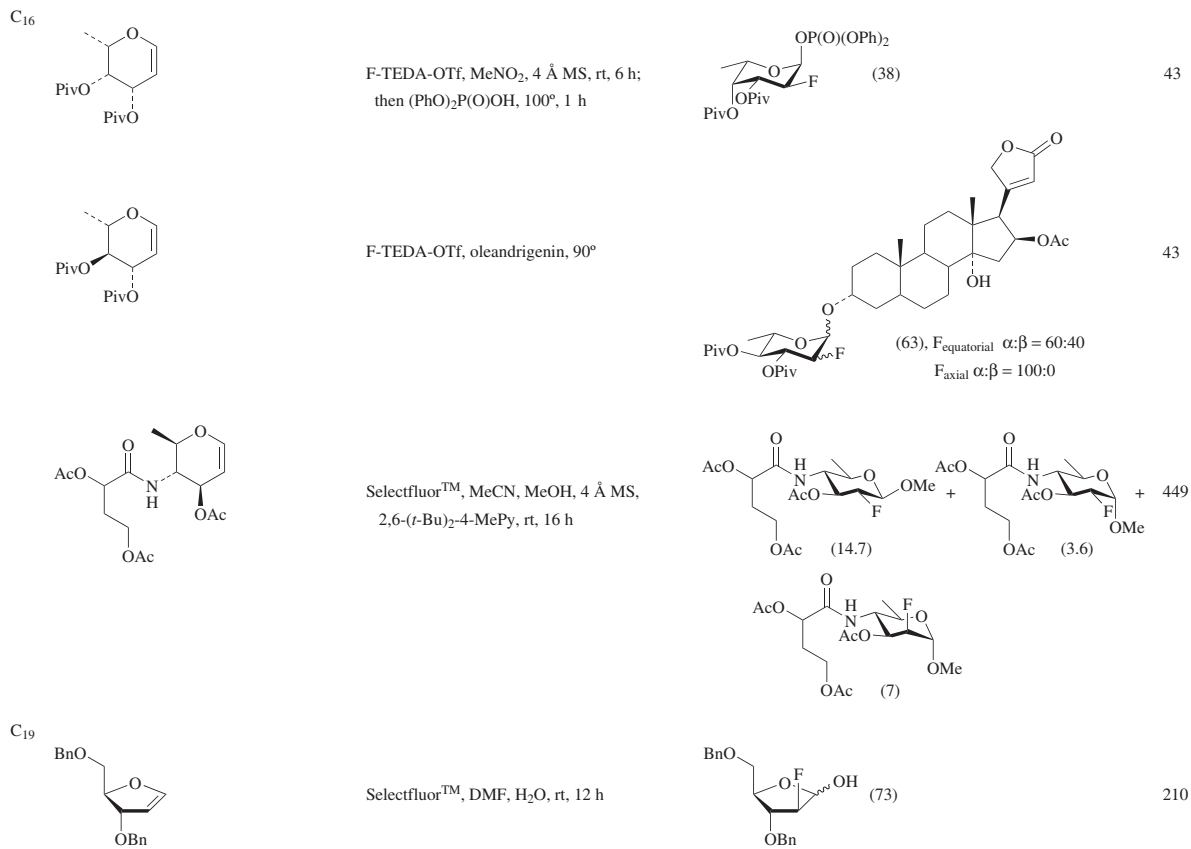
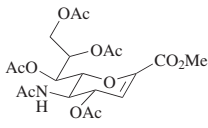
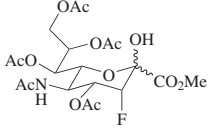
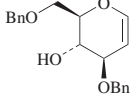
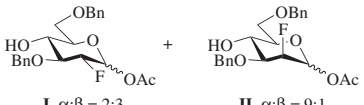
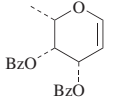
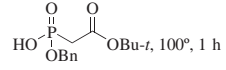
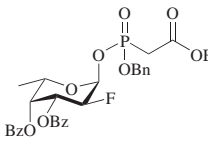
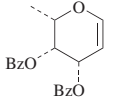
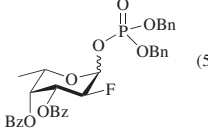
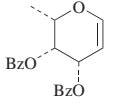
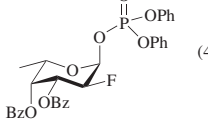


TABLE 6. FLUORINATION OF GLYCALs (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₀			
	Selectfluor™, DMF, H ₂ O, 60°, 12 h	 (80)	210, 450
	Selectfluor™, MeNO ₂ , AcOH, rt, 16 h; then reflux, 30 min	 I, α:β = 2:3 II, α:β = 9:1 I + II (25), I:II = 9:11	451
C ₂₀			
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then 	 (36)	43
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then (BnO) ₂ P(O)OH, 100°, 1 h	 (54), α:β = 40:60	43, 446
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then (PhO) ₂ P(O)OH, 100°, 1 h	 (44)	43

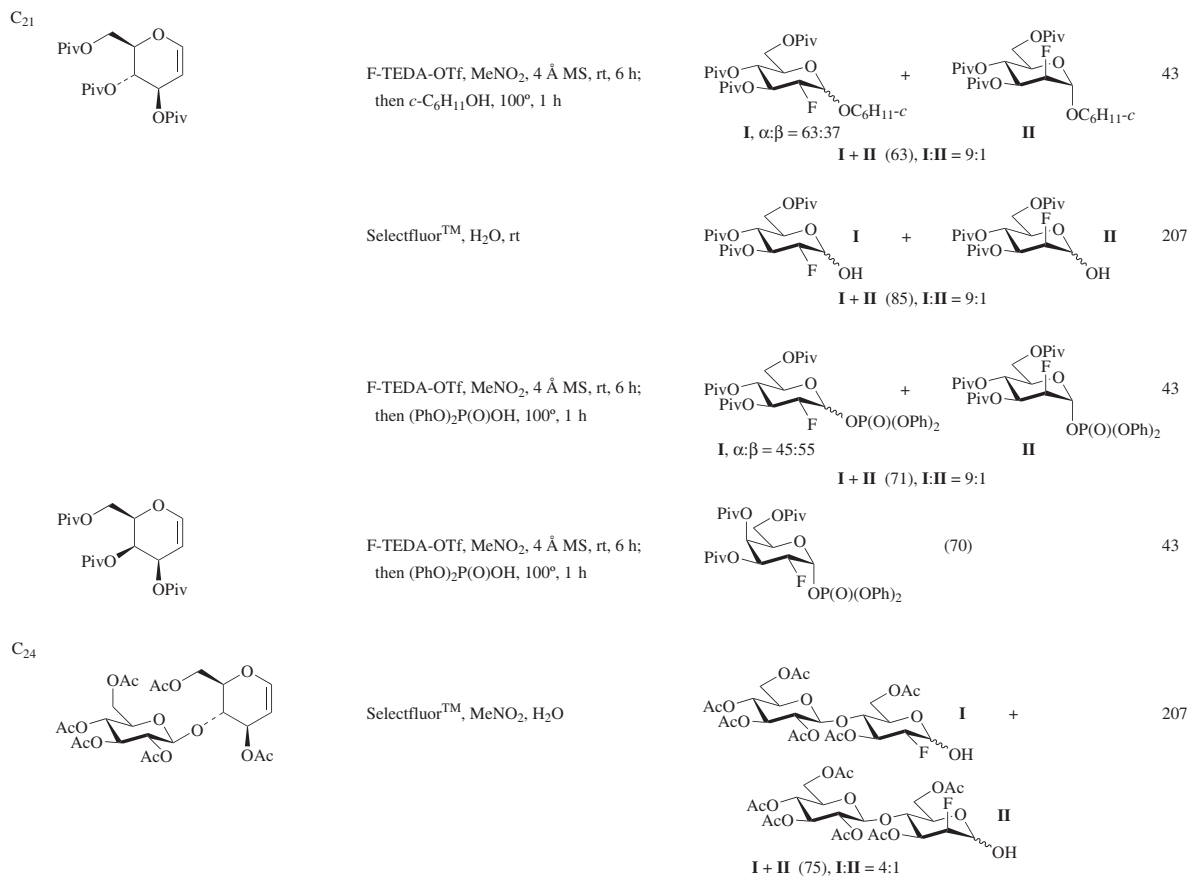


TABLE 6. FLUORINATION OF GLYCALs (Continued)

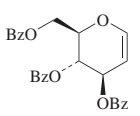
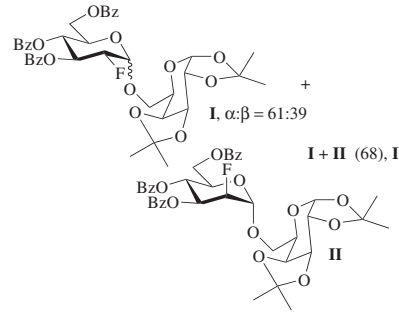
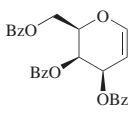
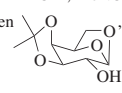
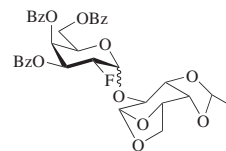
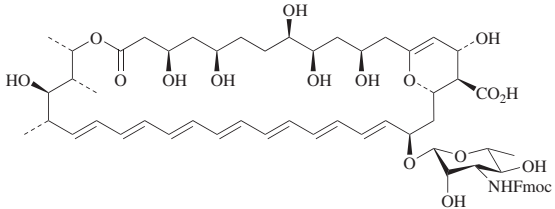
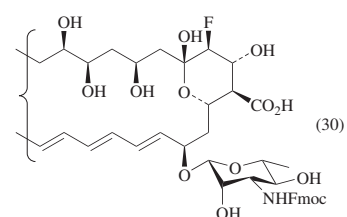
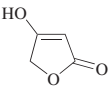
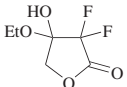
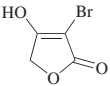
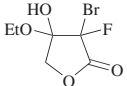
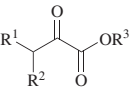
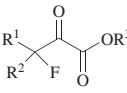
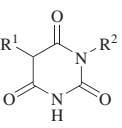
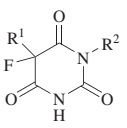


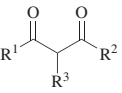
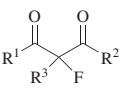
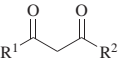
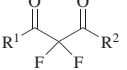
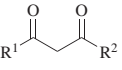
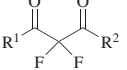
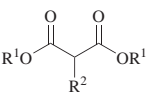
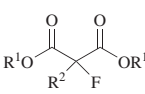
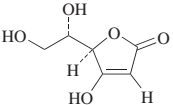
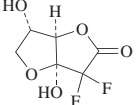
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C₂₇			
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then 1,2:3,4-di- <i>O</i> -isopropylidene- α -D-galactose, 100°, 1 h	 I , $\alpha:\beta = 61:39$ I + II (68), I:II = 3:1	43
	F-TEDA-OTf, MeNO ₂ , 4 Å MS, rt, 6 h; then  , 100°, 1 h	 (65), $\alpha:\beta = 79:21$	43
C₆₂			
	Selectfluor™, DMF/H ₂ O (3:1), rt, 1 h	 (30)	452

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C ₄ 	Selectfluor TM , EtOH, rt, 10 h	 (67)	232																																								
	Selectfluor TM , EtOH, rt, 10 h	 (87)	232																																								
C ₄₋₇ 	(CF ₃ SO ₂) ₂ NF, CHCl ₃ , 22°, 18-27 h	 (95)	213																																								
C ₄₋₁₁ 	(CF ₃ SO ₂) ₂ NF, AcOH, 20°, 10 min		453																																								
C ₅₋₈ 	NFth, MeCN, 80°, 8 h		228																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>(92)</td> </tr> <tr> <td>Me</td> <td>Et</td> <td>H</td> <td>(92)</td> </tr> <tr> <td>OMe</td> <td>Me</td> <td>H</td> <td>(90)</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>H</td> <td>(89)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(92)</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>H</td> <td>(83)</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>H</td> <td>H</td> <td>(90)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>(91)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>(91)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		H	Me	H	(92)	Me	Et	H	(92)	OMe	Me	H	(90)	Et	Me	H	(89)	Me	Me	H	(92)	Et	Me	H	(83)	<i>n</i> -Bu	H	H	(90)	Ph	H	H	(91)	Ph	Me	H	(91)	
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1	(70)																																										
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TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₋₈ 	(CF ₃ SO ₂) ₂ NF, CHCl ₃ , 22°, 1-6 h		213
C ₅₋₁₁ 	(CF ₃ SO ₂) ₂ NF (2 eq), CH ₂ Cl ₂ , 22°, 3-24 h		219, 220
C ₅₋₁₁ 	Selectfluor TM (3 eq), TBAH, MeOH, MeCN, microwaves, 82°, 10 min		234
C ₅₋₁₃ 	1. Formation of sodium enolate 2. (CF ₃ SO ₂) ₂ NF, THF, 22°		219, 220
C ₆ 	Selectfluor TM , THF, rt, 30 h	 (66)	233

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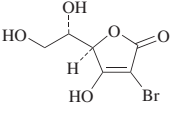
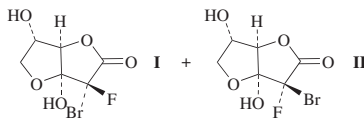

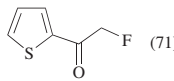
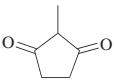
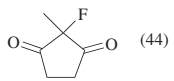
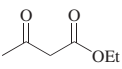
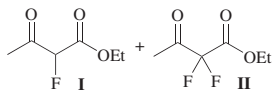
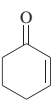
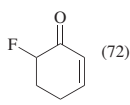
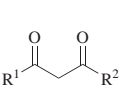
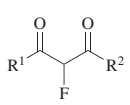
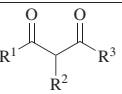
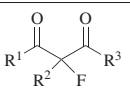
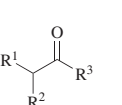
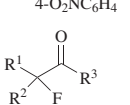
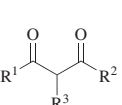
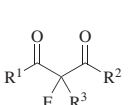
	Selectfluor TM , THF, rt, 23 h		233																
	NFTh, MeOH, reflux, 5 h	 (71)	230																
	1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, rt, 1 h	 (44)	31																
	2,4,6-Me ₃ FP-OTf (x eq), ZnCl ₂ (0.4 eq), DCE, 60°		<table border="1" data-bbox="1223 562 1414 654"> <thead> <tr> <th>x</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>1 d</td> <td>(81)</td> <td>5.75:1</td> </tr> <tr> <td>2</td> <td>12 h</td> <td>(96)</td> <td>1:2</td> </tr> </tbody> </table>	x	Time	I + II	I:II	1	1 d	(81)	5.75:1	2	12 h	(96)	1:2	31			
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2	12 h	(96)	1:2																
	NFTh, MeCN, 80°, 8 h	 (72)	228																
	Selectfluor TM (1 eq), MeCN, microwaves, 82°, 10 min		<table border="1" data-bbox="1085 826 1241 975"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>OEt</td> <td>(70)</td> </tr> <tr> <td>Ph</td> <td>OEt</td> <td>(81)</td> </tr> <tr> <td>Ph</td> <td>NMe₂</td> <td>(86)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(84)</td> </tr> </tbody> </table>	R ¹	R ²		Me	OEt	(70)	Ph	OEt	(81)	Ph	NMe ₂	(86)	Ph	Ph	(84)	234
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TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																						
	(CF ₃ SO ₂) ₂ NF, 22°, 4-14 h		219, 220																																																						
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	1. LDA, THF, -80° 2. (CF ₃ SO ₂) ₂ NF, THF, -80°, 10 min		213																																																						
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Ph	OEt	H	54 h	(22)																																																					
Ph	Ph	H	5 h	(84)																																																					
Ph	N(Me)CH(Ph)Me	H	67 h	(80)																																																					

C ₇		1. LDA, TMSCl, THF 2. FP-OTf, CH ₂ Cl ₂ , 13 h		454																								
		Selectfluor™, MeCN, rt, 19 h		134																								
		1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, 0°, 6 min		31																								
		2,4,6-Me ₃ FP-OTf (x eq), Lewis acid (0.4 eq), DCE	<table border="1"> <thead> <tr> <th>x</th> <th>Lewis acid</th> <th>Temp</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>ZnCl₂</td> <td>60°</td> <td>1 d</td> <td>(38)</td> <td>100:0</td> </tr> <tr> <td>2</td> <td>ZnCl₂</td> <td>60°</td> <td>2 d</td> <td>(80)</td> <td>100:0</td> </tr> <tr> <td>2</td> <td>AlCl₃</td> <td>80°</td> <td>1 d</td> <td>(95)</td> <td>20:80</td> </tr> </tbody> </table>	x	Lewis acid	Temp	Time	I + II	I:II	1	ZnCl ₂	60°	1 d	(38)	100:0	2	ZnCl ₂	60°	2 d	(80)	100:0	2	AlCl ₃	80°	1 d	(95)	20:80	31
x	Lewis acid	Temp	Time	I + II	I:II																							
1	ZnCl ₂	60°	1 d	(38)	100:0																							
2	ZnCl ₂	60°	2 d	(80)	100:0																							
2	AlCl ₃	80°	1 d	(95)	20:80																							
		1. NaH, toluene 2.	I + II (14), I:II = 64:36	97																								
		1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, 0°, 12 min		31																								
		2,2'-bisFP-BF ₄ , MeCN, reflux, 8 h		161																								

495

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₁₃ 	1. LDA, LiCl, THF, -78°, 45 min 2. NFSI, THF, -78°, 5 min	 R _____ H (62) 1-cytosine (49) 1-thymine (71) 9-adenine (68) 9-(2-amino-6-methoxy)purine (19)	214, 215
C ₈ 	1. LDA, NFSI, THF, -78° 2. Repeat step 1		455
	LDA, NFSI, THF	I (—)	406
	NFOBS, CH ₂ Cl ₂ , rt, 8 h		33
	NFSI, CH ₂ Cl ₂ , rt, 8 h	I (91)	33
	NFTh, MeCN, 80°, 10 h		228
	Selectfluor™, sodium lauryl ether sulfate (0.05% aq), 60°, 2-4 h		177

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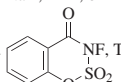
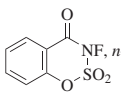
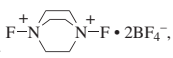
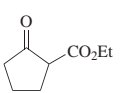
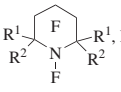
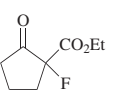
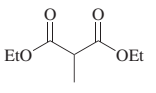
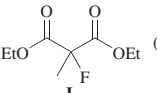
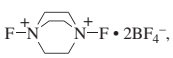
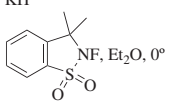
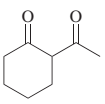
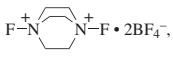
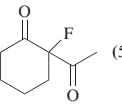
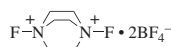
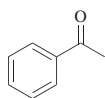
NFth, ZnCl ₂ (0.4 eq), imidazole (0.4 eq), MeCN, 50°, 24 h	I (70)	235
1. NaH, THF, 0°	I (77)	100
2.  , THF, rt, 30 min		
 <i>n</i> -hexane, 65°, 8 h	I (66)	100
1. Formation of sodium enolate	I (56)	106
2. Perfluoropiperidine, THF		
1. Formation of sodium enolate		
2.  , DMF/THF (1:1), -78° to rt, 1 h	I (75)	122
1. NaH, THF, 0° to rt, 90 min	I (95)	173
2. Selectfluor TM , THF, DMF, rt, 30 min		
3,5-Cl ₂ FP-OTf, CH ₂ Cl ₂ , reflux, 24 h	I (72)	150
2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , reflux, 48 h	I (83)	150
1. NaH, THF, 0°	I (78)	150
2. 2,4,6-Me ₃ FP-OTf, THF, 0°, 0.17 h		
2-SO ₃ -4,6-(CF ₃) ₂ FP, THF, rt, 46 h	I (84)	140
2,4,6-Me ₃ FP-OTf, ZnCl ₂ (0.4 eq), DCE, 60°, 18 h	I (67)	31

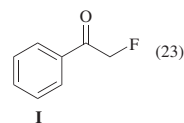
TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
C ₈ 	1. NaH, Et ₂ O, -50° 2.  , Et ₂ O, -50° to rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>F</td> <td>(56)</td> </tr> <tr> <td>F</td> <td>CF₃</td> <td>(47)</td> </tr> <tr> <td>Me</td> <td>CF₃</td> <td>(73)</td> </tr> <tr> <td>CF₃</td> <td>CF₃</td> <td>(78)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	F	F	(56)	F	CF ₃	(47)	Me	CF ₃	(73)	CF ₃	CF ₃	(78)	107
R ¹	R ²	Yield (%)																
F	F	(56)																
F	CF ₃	(47)																
Me	CF ₃	(73)																
CF ₃	CF ₃	(78)																
	1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, 0°, 10 min	 (78)	31, 150															
	1. NaH, THF, 0° to rt, 90 min 2. Selectfluor TM , THF, DMF, rt, 30 min	I (92)	173															
	1. Formation of sodium enolate 2.  , DMF, -60° to rt, 1 h	I (64)	122															
	1. KH 2.  , Et ₂ O, 0°	I (94)	42															
	1. Formation of sodium enolate 2. (CF ₃ SO ₂) ₂ NF, CCl ₄ , -10°, 2 h	I (96)	418															
	1. Formation of sodium enolate 2.  , DMF/THF (2:1), -60° to rt, 2.5 h	 (54)	122															

	I (80)	122
HCO ₂ H, 20°, 30 min		
2,2'-bisFP-OTf, MeCN, reflux, 5 min	I (85)	158
2,2'-bisFP-BF ₄ , MeCN, reflux, 3 h	I (71)	158
2,2'-bisFP-BF ₄ , NaOTf, MeCN, reflux, 10 min	I (82)	158
2,4'-bisFP-OTf, MeCN, reflux, 2 h	I (78)	161
3,3'-bisFP-OTf, MeCN, reflux, 5 h	I (70)	161
4,4'-bisFP-OTf, MeCN, reflux, 5 h	I (87)	161
FP-OTf, MeCN, reflux, 19 h	I (79)	161
2-SO ₃ -4,6-(CF ₃) ₂ FP, THF, rt, 1 h	I (83)	140



NFTh, MeCN, 80°, 48 h

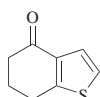


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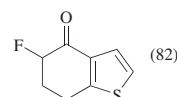
1. LDA, THF, -80°
2. (CF₃SO₂)₂NF, THF, -80°, 10 min

I (86)

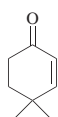
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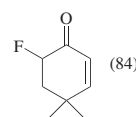
NFTh, MeOH, reflux, 1.2 h



230

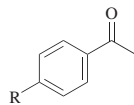
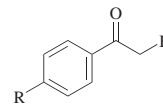
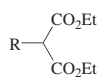
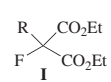
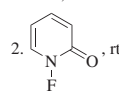

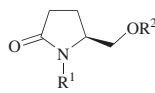
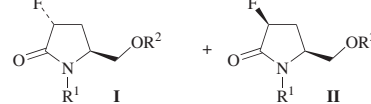
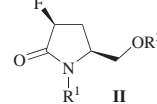


NFTh, MeOH, reflux, 0.5-3 h



230

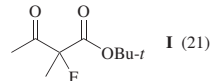
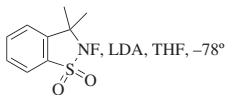
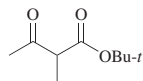
TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
C ₈₋₉ 	NFTh, MeOH, reflux, 0.5-4 h	 <table border="1" style="margin-left: 20px;"> <tr><td>R</td><td></td></tr> <tr><td>H</td><td>(80)</td></tr> <tr><td>OH</td><td>(75-85)</td></tr> <tr><td>OMe</td><td>(75-85)</td></tr> </table>	R		H	(80)	OH	(75-85)	OMe	(75-85)	229																																				
R																																															
H	(80)																																														
OH	(75-85)																																														
OMe	(75-85)																																														
C ₈₋₁₃ 	4-MeC ₆ H ₄ O ₂ S ₂ <i>t</i> -Bu-N-F, NaH, THF, rt	 <table border="1" style="margin-left: 20px;"> <tr><td>R</td><td>I</td></tr> <tr><td>Me</td><td>(53)</td></tr> <tr><td>Ph</td><td>(81)</td></tr> </table>	R	I	Me	(53)	Ph	(81)	69																																						
R	I																																														
Me	(53)																																														
Ph	(81)																																														
C ₈₋₁₄	1. NaH, toluene  rt	 <table border="1" style="margin-left: 20px;"> <tr><td>R</td><td>Time</td><td>I</td></tr> <tr><td>Me</td><td>1.7 h</td><td>(17)</td></tr> <tr><td>Ph</td><td>16 h</td><td>(39)</td></tr> <tr><td>Bn</td><td>16 h</td><td>(33)</td></tr> </table>	R	Time	I	Me	1.7 h	(17)	Ph	16 h	(39)	Bn	16 h	(33)	97																																
R	Time	I																																													
Me	1.7 h	(17)																																													
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Bn	16 h	(33)																																													
C ₈₋₃₁ 	LDA, NFSI, THF, -78°	 +  <table border="1" style="margin-left: 20px;"> <tr><td>R¹</td><td>R²</td><td>I + II</td><td>I:II</td></tr> <tr><td>-CMe₂-</td><td></td><td>(59)</td><td>55:45</td></tr> <tr><td>Boc</td><td>Me</td><td>(<38)</td><td>63:37</td></tr> <tr><td>Bn</td><td>Me</td><td>(70)</td><td>85:15</td></tr> <tr><td>Boc</td><td>TBDMS</td><td>(40)</td><td>62:38</td></tr> <tr><td>Bn</td><td>TBDMS</td><td>(68)</td><td>85:15</td></tr> <tr><td>4-MeOC₆H₄CH₂</td><td>TBDMS</td><td>(64)</td><td>83:17</td></tr> <tr><td>Bn</td><td>TIPS</td><td>(>50)</td><td>83:17</td></tr> <tr><td>Bn</td><td>TBDPS</td><td>(66)</td><td>77:23</td></tr> <tr><td>Boc</td><td>Tr</td><td>(20)</td><td>100:0</td></tr> <tr><td>Bn</td><td>Tr</td><td>(0)</td><td>—</td></tr> </table>	R ¹	R ²	I + II	I:II	-CMe ₂ -		(59)	55:45	Boc	Me	(<38)	63:37	Bn	Me	(70)	85:15	Boc	TBDMS	(40)	62:38	Bn	TBDMS	(68)	85:15	4-MeOC ₆ H ₄ CH ₂	TBDMS	(64)	83:17	Bn	TIPS	(>50)	83:17	Bn	TBDPS	(66)	77:23	Boc	Tr	(20)	100:0	Bn	Tr	(0)	—	406
R ¹	R ²	I + II	I:II																																												
-CMe ₂ -		(59)	55:45																																												
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4-MeOC ₆ H ₄ CH ₂	TBDMS	(64)	83:17																																												
Bn	TIPS	(>50)	83:17																																												
Bn	TBDPS	(66)	77:23																																												
Boc	Tr	(20)	100:0																																												
Bn	Tr	(0)	—																																												

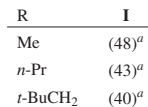
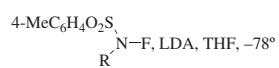
C ₉		1. Ph-CH ₂ -NH-Ph, <i>n</i> -BuLi, LiCl, -78° 2. NFSI, -78°, 30 min		(69), 70% ee	456												
		NFTh, MeCN, 80°, 12 h		(81)	228												
		NFOBS, CH ₂ Cl ₂ , rt, 8 h		(30)	33												
		Selectfluor TM , sodium lauryl ether sulfate (0.05% aq), 60°, 2-4 h		(74)	177												
	Ph-CH ₂ -CO ₂ Me	NFSI, KHMDS, MnBr ₂ , THF, -78° to 0°		(54)	457												
		1. Base, THF, -78° 2. NFOBS, -78° to rt, 2 h	<table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Base</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>NaHMDS</td> <td>(67)</td> <td>18:1</td> </tr> <tr> <td>LDA</td> <td>(64)</td> <td>18:1</td> </tr> <tr> <td>KHMDS</td> <td>(53)</td> <td>16:1</td> </tr> </tbody> </table>	Base	I + II	I:II	NaHMDS	(67)	18:1	LDA	(64)	18:1	KHMDS	(53)	16:1		33
Base	I + II	I:II															
NaHMDS	(67)	18:1															
LDA	(64)	18:1															
KHMDS	(53)	16:1															
		1. NaHMDS, THF, -78° to rt, 2 h 2. NFOBS, rt, 2 h		I (87)	33												

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

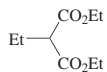
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉			
	1. NaHMDS, THF, -78° to rt, 2 h 2. NFSI, rt, 2 h		33
	LDA, NFSI, THF, -78° to rt NFTh, MeCN, 80°, 30 h	I (85) I (80)	85 228
	1. NaH (2 eq), THF, rt 2. Selectfluor TM (2 eq), rt		218
	2,2'-bisFP-BF ₄ , MeCN, reflux, 8 h		161
	2-SO ₃ -4,6-(CF ₃) ₂ FP, HFIP, rt, 30 min	I (98)	140
	NFTh, MeOH, reflux, 70 min		230
	NFTh, MeOH, reflux, 1.5 h		230
	NFTh, MeOH, reflux, 0.5-4 h		229



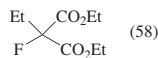
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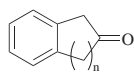
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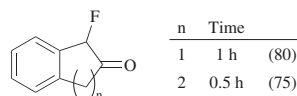
1. Formation of sodium enolate
2. Perfluoropiperidine, THF



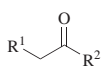
106

C₉₋₁₀

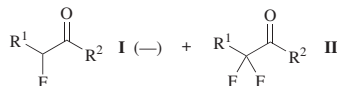
NFTh, MeCN, 80°



228



1. Base (2.4-3.6 eq), THF, -78°
2. (2.6-3.6 eq),
THF, -78° to rt



76

R ¹	R ²	Base	I:II
Ph	OMe	KHMDS	(53) 2:98
Me	Ph	KHMDS	(64) 5:95
Me	N(<i>Pr</i> - <i>i</i>) ₂	KDA	(42) 54:46
Me	Bn	KHMDS	(27) 33:67

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																											
C ₉₋₁₀ 	1. Base (1.2 eq), THF, -78° 2. (1.3-1.6 eq), THF, -78° to rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Base</th> <th>I</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>OMe</td> <td>LDA</td> <td>(40)</td> <td>95:5</td> </tr> <tr> <td>Ph</td> <td>OMe</td> <td>LiHMDS</td> <td>(33)</td> <td>>98:2</td> </tr> <tr> <td>Ph</td> <td>OMe</td> <td>NaHMDS</td> <td>(36)</td> <td>70:30</td> </tr> <tr> <td>Ph</td> <td>OMe</td> <td>KHMDS</td> <td>(27)</td> <td>53:47</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>LDA</td> <td>(53)</td> <td>97:3</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>LiHMDS</td> <td>(66)</td> <td>95:5</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>NaHMDS</td> <td>(56)</td> <td>78:22</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>KHMDS</td> <td>(40)</td> <td>50:50</td> </tr> <tr> <td>Me</td> <td>N(<i>Pr</i>-<i>i</i>)₂</td> <td>LDA</td> <td>(20)</td> <td>>98:2</td> </tr> <tr> <td>Me</td> <td>N(<i>Pr</i>-<i>i</i>)₂</td> <td>KDA</td> <td>(47)</td> <td>>98:2</td> </tr> <tr> <td>Me</td> <td>Bn</td> <td>LDA</td> <td>(<10)</td> <td>—</td> </tr> <tr> <td>Me</td> <td>Bn</td> <td>LiHMDS</td> <td>(<10)</td> <td>>98:2</td> </tr> <tr> <td>Me</td> <td>Bn</td> <td>NaHMDS</td> <td>(<10)</td> <td>—</td> </tr> <tr> <td>Me</td> <td>Bn</td> <td>KHMDS</td> <td>(58)</td> <td>90:10</td> </tr> </tbody> </table>	R ¹	R ²	Base	I	I:II	Ph	OMe	LDA	(40)	95:5	Ph	OMe	LiHMDS	(33)	>98:2	Ph	OMe	NaHMDS	(36)	70:30	Ph	OMe	KHMDS	(27)	53:47	Me	Ph	LDA	(53)	97:3	Me	Ph	LiHMDS	(66)	95:5	Me	Ph	NaHMDS	(56)	78:22	Me	Ph	KHMDS	(40)	50:50	Me	N(<i>Pr</i> - <i>i</i>) ₂	LDA	(20)	>98:2	Me	N(<i>Pr</i> - <i>i</i>) ₂	KDA	(47)	>98:2	Me	Bn	LDA	(<10)	—	Me	Bn	LiHMDS	(<10)	>98:2	Me	Bn	NaHMDS	(<10)	—	Me	Bn	KHMDS	(58)	90:10	76
R ¹	R ²	Base	I	I:II																																																																										
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C ₉₋₁₁ 	NFTh, MeCN, 80°, 8 h	 <table border="1"> <thead> <tr> <th>n</th> <th></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(88)</td> </tr> <tr> <td>2</td> <td>(88)</td> </tr> <tr> <td>3</td> <td>(82)</td> </tr> </tbody> </table>	n		1	(88)	2	(88)	3	(82)	228																																																																			
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1	(88)																																																																													
2	(88)																																																																													
3	(82)																																																																													
C ₉₋₁₂ 	Selectfluor™, MeCN, H ₂ O, rt, overnight	 <table border="1"> <thead> <tr> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(48)</td> </tr> <tr> <td>(CH₂)₂CO₂Me</td> <td>(25)</td> </tr> </tbody> </table>	R		Me	(48)	(CH ₂) ₂ CO ₂ Me	(25)	203																																																																					
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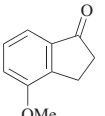
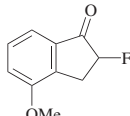
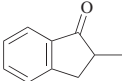
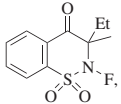
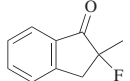

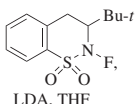
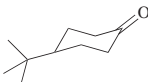

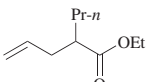
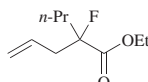
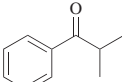
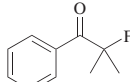
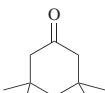
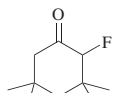
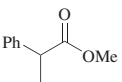
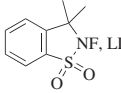
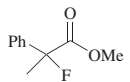
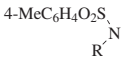
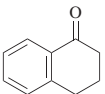
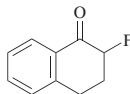
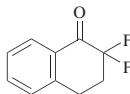
C ₁₀ 	NFTh, MeOH, reflux, 1 h	 (89)	230
	 LiHMDS, THF, -78° to -20°	 I (79)	73
	 LDA, THF	I (77)	72
	NFTh, MeCN, 80°, 2 h	 (85) ^d , cis:trans = 1:1.2	228
	1. LDA, HMPA, THF, -78° 2. NFSI, -78°, 2 h	 (86)	458
	NFTh, HF, MeCN, 80°, 12 h	 (74)	228
	NFTh, MeOH, reflux, 0.5-3 h	 (84)	230

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	 NF, LDA, THF, -78°	 I (55)	70
	 N-F, LDA, THF, -78°	I	70
	1. NaHMDS, THF, -78° to rt 2. NFOBS, rt	I (65)	33
	Fluorinating agent, reflux, 2 h	 I +  II (0)	230
	Fluorinating agent	Solvent I	
	2,6-Cl ₂ FP-BF ₄	MeCN (70)	
	2,6-Cl ₂ FP-BF ₄	MeOH (40)	
	NFSI	MeCN (0)	
	NFSI	MeOH (90)	
	Selectfluor TM	MeCN (18)	
	Selectfluor TM	MeOH (73)	
	NFTh	MeCN (54)	
	NFTh	MeOH (98)	
	1. Base (x eq), THF, -78° 2. NFOBS, 0° to rt	I + II	33
		Base x I + II I:II	
		NaHMDS 1.1 (80) 15:1	
		LDA 1.1 (77) 17:1	
		KHMDS 1.1 (51) 10:3	
		NaHMDS 2.1 (80) 2:3	
		LDA 2.1 (100) 9:11	

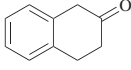
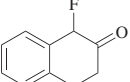
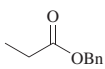
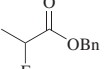

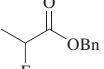

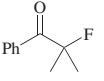
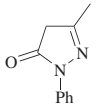
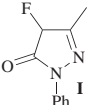
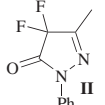
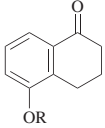
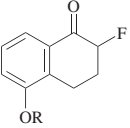
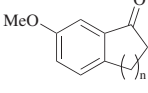
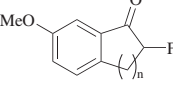
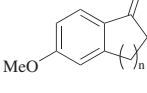
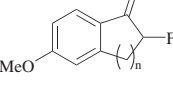
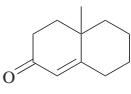
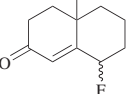
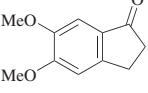
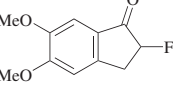
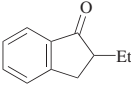
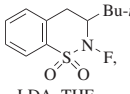
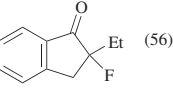
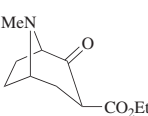
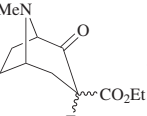
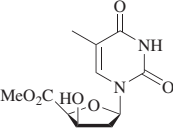
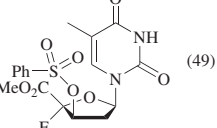
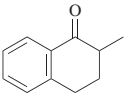
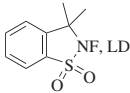
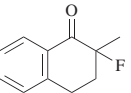
	NFTh, MeCN, PhNO ₂ , 80°, 0.5 h	 I (81)	228										
	2,2'-bisFP-BF ₄ , MeCN, reflux, 10 min	 I (38)	161										
	LDA, NFSI, THF, -78° to rt	 (47)	85										
	4-MeC ₆ H ₄ O ₂ S ₂ exo-2-norbornyl-N-F, KH, toluene, THF, -50°	 (81)	69										
	NFOBS, rt, 2 h	 I +  II	<table border="1"> <thead> <tr> <th>Solvent</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>CH₂Cl₂</td> <td>(42)</td> <td>0:1</td> </tr> <tr> <td>CH₂Cl₂, H₂O</td> <td>(30)</td> <td>1:3</td> </tr> </tbody> </table>	Solvent	I + II	I:II	CH ₂ Cl ₂	(42)	0:1	CH ₂ Cl ₂ , H ₂ O	(30)	1:3	33
Solvent	I + II	I:II											
CH ₂ Cl ₂	(42)	0:1											
CH ₂ Cl ₂ , H ₂ O	(30)	1:3											
C ₁₀₋₁₁ 	NFTh, MeOH, reflux		<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>30 min</td> <td>(77)</td> </tr> <tr> <td>Me</td> <td>15 min</td> <td>(84)</td> </tr> </tbody> </table>	R	Time		H	30 min	(77)	Me	15 min	(84)	230
R	Time												
H	30 min	(77)											
Me	15 min	(84)											
	NFTh, MeOH, reflux, 0.5-4 h		<table border="1"> <thead> <tr> <th>n</th> <th></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(75-85)</td> </tr> <tr> <td>2</td> <td>(90)</td> </tr> </tbody> </table>	n		1	(75-85)	2	(90)	229			
n													
1	(75-85)												
2	(90)												
	NFTh, MeOH, reflux, 0.5-4 h		<table border="1"> <thead> <tr> <th>n</th> <th></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(75-85)</td> </tr> <tr> <td>2</td> <td>(75-85)</td> </tr> </tbody> </table>	n		1	(75-85)	2	(75-85)	229			
n													
1	(75-85)												
2	(75-85)												

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	KH, HMPA, Ph ₃ B, NFSI	 (84), $\alpha:\beta = 10:90$	217
	NFTh, MeOH, reflux, 30 min	 (71)	230
	 LDA, THF	 (56)	72
	NaH; then Selectfluor TM , DMF	 (26-39)	222
	1. LDA, HMPA, THF, -78° to rt 2. <i>t</i> -BuLi, -78°, 1 h 3. NFSI, THF, -78° to 30°	 (49)	459
	 NF, LDA, THF, -78°	 I (90)	70

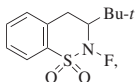
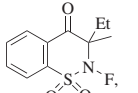
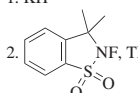
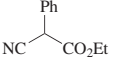
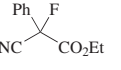
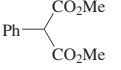
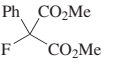
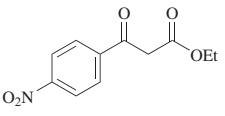
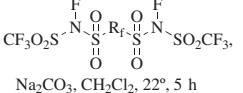
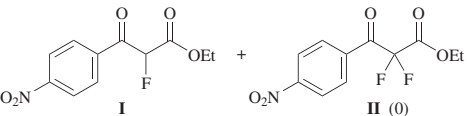
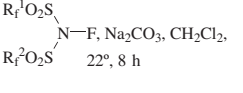
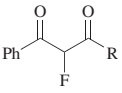
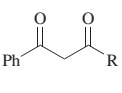


	$4\text{-MeC}_6\text{H}_4\text{O}_2\text{S}_2\text{N-F, LDA, THF, } -78^\circ$	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(13)^d</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>(20)^d</td> </tr> <tr> <td><i>t</i>-BuCH₂</td> <td>(57)^d</td> </tr> </tbody> </table>	R	I	Me	(13) ^d	<i>n</i> -Pr	(20) ^d	<i>t</i> -BuCH ₂	(57) ^d	70
R	I										
Me	(13) ^d										
<i>n</i> -Pr	(20) ^d										
<i>t</i> -BuCH ₂	(57) ^d										
	 LDA, THF	I (56)	72								
	 base, THF, -78° to -20°	<table border="1"> <thead> <tr> <th>Base</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>LiHMDS</td> <td>(72)</td> </tr> <tr> <td>NaHMDS</td> <td>(35)</td> </tr> </tbody> </table>	Base	I	LiHMDS	(72)	NaHMDS	(35)	73		
Base	I										
LiHMDS	(72)										
NaHMDS	(35)										
	1. NaHMDS, THF, -78° to rt 2. NFOBS, rt	I (95)	33								
	1. NaHMDS, THF, -78° to rt 2. NFSI, rt	I (50)	33								
	LDA, NFSI, THF, -95° to rt	I (50)	85								
	1. KH 2.  NF, THF, -78°	I (80)	42								
	Selectfluor TM , MeCN, 40°	 (92)	223								
	KH, NFSI, Et ₂ O, 0° to rt	 (47)	85								

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																								
C ₁₁ 	 Na ₂ CO ₃ , CH ₂ Cl ₂ , 22°, 5 h	 <table border="1"> <thead> <tr> <th>R_f</th> <th>I</th> <th>II (0)</th> </tr> </thead> <tbody> <tr> <td>(CF₂)₄</td> <td>(91)</td> <td></td> </tr> <tr> <td>(CF₂)₂O(CF₂)₂</td> <td>(90)</td> <td></td> </tr> </tbody> </table>	R _f	I	II (0)	(CF ₂) ₄	(91)		(CF ₂) ₂ O(CF ₂) ₂	(90)		79															
R _f	I	II (0)																									
(CF ₂) ₄	(91)																										
(CF ₂) ₂ O(CF ₂) ₂	(90)																										
	 R _f ¹ O ₂ S R _f ² O ₂ S N-F, Na ₂ CO ₃ , CH ₂ Cl ₂ , 22°, 8 h	<table border="1"> <thead> <tr> <th>R_f¹</th> <th>R_f²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>CF₃</td> <td>CF₃</td> <td>(80)</td> <td>93:7</td> </tr> <tr> <td>CF₃</td> <td>C₄F₉</td> <td>(83)</td> <td>89:11</td> </tr> <tr> <td>CF₃</td> <td>C₆F₁₃</td> <td>(77)</td> <td>93:7</td> </tr> <tr> <td>CF₃</td> <td>C₈F₁₇</td> <td>(80)</td> <td>93:7</td> </tr> <tr> <td>C₄F₉</td> <td>C₄F₉</td> <td>(80)</td> <td>91:9</td> </tr> </tbody> </table>	R _f ¹	R _f ²	I + II	I:II	CF ₃	CF ₃	(80)	93:7	CF ₃	C ₄ F ₉	(83)	89:11	CF ₃	C ₆ F ₁₃	(77)	93:7	CF ₃	C ₈ F ₁₇	(80)	93:7	C ₄ F ₉	C ₄ F ₉	(80)	91:9	83
R _f ¹	R _f ²	I + II	I:II																								
CF ₃	CF ₃	(80)	93:7																								
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C ₄ F ₉	C ₄ F ₉	(80)	91:9																								
	1. NaH, THF 2. Selectfluor TM , MeCN, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>OEt</td> <td>24 h (95)</td> </tr> <tr> <td>NMe₂</td> <td>27 h (73)</td> </tr> </tbody> </table>	R	Time	OEt	24 h (95)	NMe ₂	27 h (73)	223																		
R	Time																										
OEt	24 h (95)																										
NMe ₂	27 h (73)																										
C ₁₁₋₁₅ 	Selectfluor TM , sodium lauryl ether sulfate (0.05% aq), 60°, 3 h	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>OEt</td> <td>(67-85)</td> </tr> <tr> <td>Ph</td> <td>(67-85)</td> </tr> </tbody> </table>	R	I	OEt	(67-85)	Ph	(67-85)	177																		
R	I																										
OEt	(67-85)																										
Ph	(67-85)																										
	Selectfluor TM , MeCN	<table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>NMe₂</td> <td>40</td> <td>647 h (91)</td> </tr> <tr> <td>Ph</td> <td>rt</td> <td>192 h (78)</td> </tr> </tbody> </table>	R	Temp	Time	NMe ₂	40	647 h (91)	Ph	rt	192 h (78)	223															
R	Temp	Time																									
NMe ₂	40	647 h (91)																									
Ph	rt	192 h (78)																									
C ₁₂ 	NFth, MeOH, reflux, 0.5-3 h	 (83)	230																								

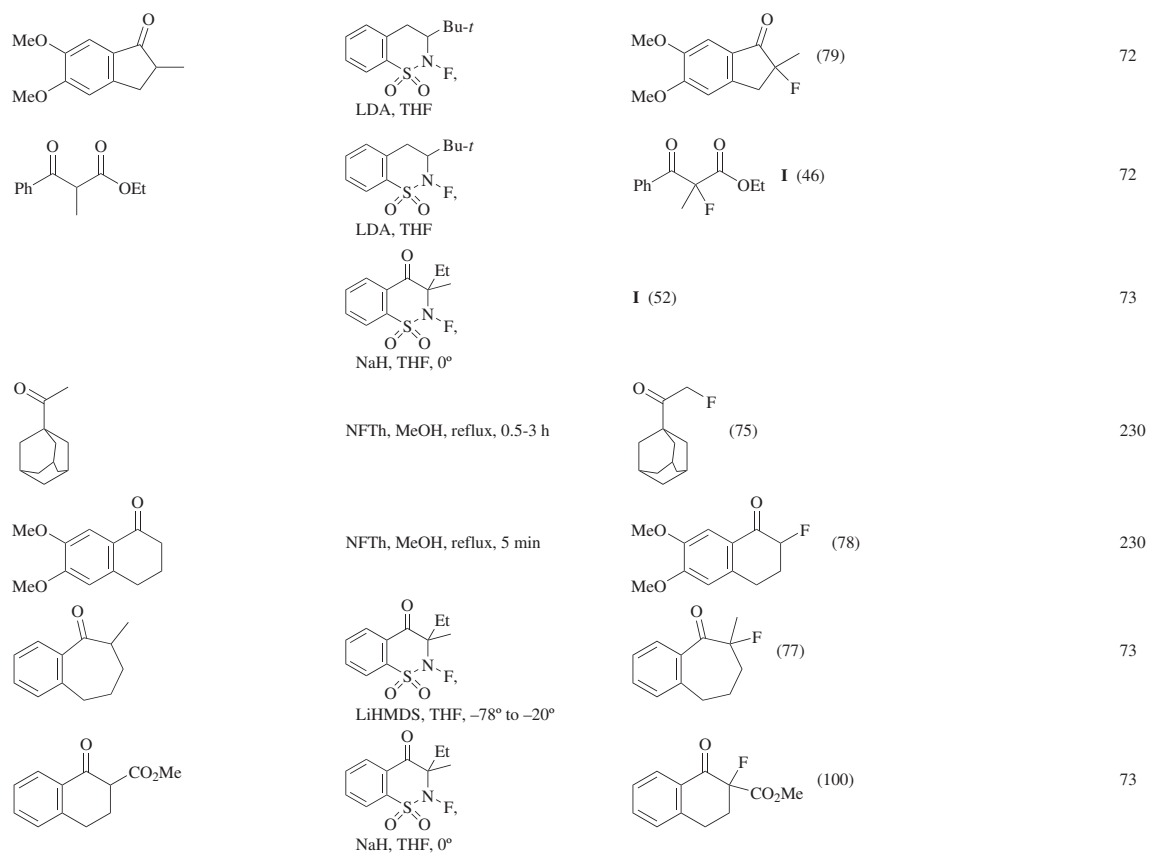
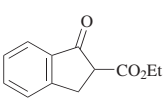
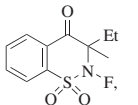
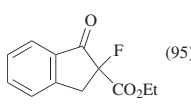
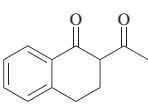
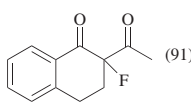
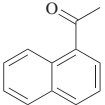
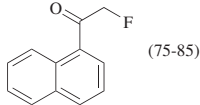
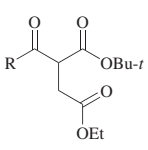
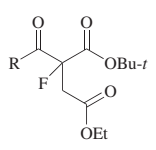
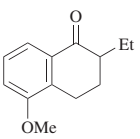
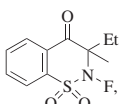
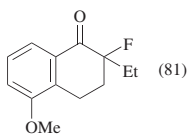


TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.														
C ₁₂ 	 NaH, THF, 0°	 (95)	73														
	Selectfluor™, sodium lauryl ether sulfate (0.05% aq), 60°, 2-4 h	 (91)	177														
	NFTh, MeOH, reflux, 0.5-4 h	 (75-85)	229														
C ₁₂₋₁₉ 	1. NaH, THF 2. Selectfluor™, DMF, rt, 3.5 h	 <table border="1" data-bbox="1111 1813 1232 2008"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(91)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>(97)</td> </tr> <tr> <td>C₆H₁₁</td> <td>(94)</td> </tr> <tr> <td>Ph</td> <td>(83)</td> </tr> <tr> <td>Bn</td> <td>(95)</td> </tr> <tr> <td>CH₂Bn</td> <td>(87)</td> </tr> </tbody> </table>	R	Yield (%)	Me	(91)	<i>i</i> -Bu	(97)	C ₆ H ₁₁	(94)	Ph	(83)	Bn	(95)	CH ₂ Bn	(87)	460
R	Yield (%)																
Me	(91)																
<i>i</i> -Bu	(97)																
C ₆ H ₁₁	(94)																
Ph	(83)																
Bn	(95)																
CH ₂ Bn	(87)																
C ₁₃ 	 LiHMDS, THF, -78° to -20°	 (81)	73														

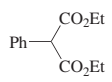
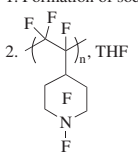
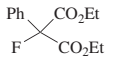
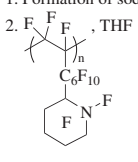
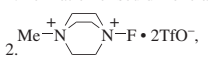
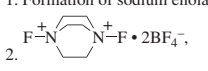
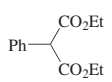
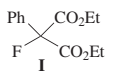
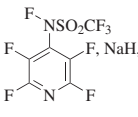
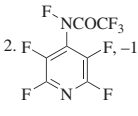
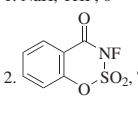
	1. Formation of sodium enolate 2.  , THF	 I (17)	108
	1. Formation of sodium enolate 2.  , THF	I (23)	108
	1. Formation of sodium enolate 2. Perfluoropiperidine, THF	I (68)	106, 108
	1. Formation of sodium enolate 2.  • 2TfO ⁻ , THF, DMF, rt, 30 min	I (93)	129
	1. Formation of sodium enolate 2.  • 2BF ₄ ⁻ , DMF/THF (1:1), -78° to rt, 2.5 h	I (74)	122
	1. Formation of sodium enolate 2. Selectfluor TM , THF, -10° to 20°	I (—)	134, 416

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
			Fluorinating agent	Solvent	
^{C13} 	1. NaH, THF, 0° 2. Fluorinating agent, rt	 I	FP-OTf (2) 4- <i>t</i> -BuFP-OTf (8) 2,6-Me ₂ FP-OTf (43) 2,4,6-Me ₃ FP-OTf (83) 2,4,6-Me ₃ FP-OTf (85) 2,4,6-Me ₃ FP-OTf (82) 2,4,6-(MeOCH ₂) ₃ FP-OTf (87)	THF (2) THF (8) THF (43) THF (83) DMF (85) DMSO (82) DMSO (87)	31
	1. NaH, THF 2.  , NaH, THF	I (93) ^d			57, 61
	1. NaH, THF 2.  , -10° to 20°	I (66) ^d			96
	1. NaH, THF, 0° 2.  , SO ₂ , THF, rt, 30 min	I (86)			100
	1. NaH, THF 2. NFQN-F, -10° to 20°	I (56)			113, 115
	1. NaH, THF 2. NFQN-OTf, -10° to 20°	I (52)			114

	1. NaH, THF 2. Selectfluor™, rt	Solvent MeCN THF, DMF	Time 20 h 30 min	I (93) (94)	173, 223
	NFOBS, rt, 4 h				33
		Solvent CH ₂ Cl ₂ CH ₂ Cl ₂ /H ₂ O		I + II (70) (79)	I:II 6.4:1 16:1
	NFTh, MeOH, reflux, 0.5-3 h				230
C ₁₃₋₁₉ 	(CF ₃ SO ₂) ₂ NF, CHCl ₃ , H ₂ O, 35°, 5 min				R H (91) Ph (92) 4-ClC ₆ H ₄ (90)
C ₁₄ 	1. 4-MeC ₆ H ₄ O ₂ S ₂ -N-F, exo-2-norbornyl <i>n</i> -BuLi, toluene, THF, -50° 2. CH ₂ N ₂				69
	1. LDA, HMPA, THF, -78° to rt 2. <i>t</i> -BuLi, -78°, 1 h 3. NFSI, THF, -78° to 0°				459

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.					
C ₁₄ 	Selectfluor™, MeCN, rt, 20 h		224					
C ₁₅ 	1. LDA, HMPA, THF, -78° 2. 4-MeC ₆ H ₄ O ₂ S ₂ -N-F, exo-2-norbornyl, -78° to rt		461					
	Fluorinating agent, rt, 2 h		33					
	Fluorinating agent	Solvent	I + II	I:II				
	NFOBS	CH ₂ Cl ₂	(52)	3.5:1				
	NFSI	CH ₂ Cl ₂	(92)	3.4:1				
	NFOBS	CH ₂ Cl ₂ /H ₂ O	(85)	17:1				
	NFSI	CH ₂ Cl ₂ /H ₂ O	(41)	7.2:1				
	2,2'-bisFP-BF ₄ , TfOH, MeCN, reflux, 2 d		I + II (86)	I:II = 5:38	161			
	2-SO ₃ -4,6-(CF ₃) ₂ FP, THF, rt, 16 h		I + II (71)	I:II = 66:<5	140			
	2-SO ₃ -4,6-(CF ₃) ₂ FP, HFIP, rt, 20 min		I + II (63)	I:II = 46:17	140			
	Selectfluor™ (3 eq), MeCN, microwaves, 82°, 10 min		I + II (83)	I:II = 1:40	234			
		x	Amine	Time	I + II	I:II		
	NFTh (x eq), ZnCl ₂ (0.4 eq), amine, MeCN, 50°	I + II	1	imidazole (0.4 eq)	24 h	(92)	6.2:1	235
			2	collidine (1 eq)	48 h	(68)	0:1	

	NFTh, MeOH, reflux, 0.5-3 h		230
	KHMDS, NFSI, THF, -78° to rt		85
	NaH, fluorinating agent, THF, rt		221
	<u>Fluorinating agent</u>	<u>I + II</u> <u>I:II</u>	
	NFSI	(85) 100:0	
	Selectfluor™	(65) 75:25	
	2,4,6-Me ₃ FP-OTf (2 eq), ZnCl ₂ (0.4 eq), DCE, 60°, 18 h		31
	(CF ₃ SO ₂) ₂ NF, CHCl ₃ , rt, 30 min		453
	2,4,6-Me ₃ FP-OTf, NaH, THF		225

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	4-MeC ₆ H ₄ O ₂ S-N-F, exo-2-norbornyl, KH, toluene, THF, -50°		69
	 LiHMDS, THF, -78° to -20°		73
	NFTh, MeOH, reflux, 0.5-4 h		229
	1. KHMDS, THF, -78° 2. Fluorinating agent, -78° to rt		41
	<u>Fluorinating agent</u>	<u>I + II</u> <u>I:II</u>	
	NFSI	(52) 40:60	
	NFQN-OTf	(63) 71:29	
		(61) 70:30	

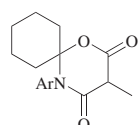
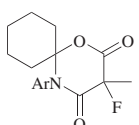
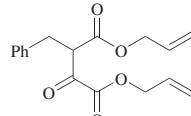
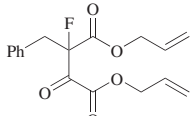
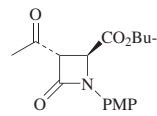
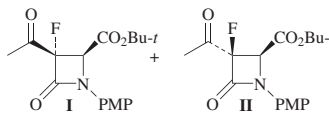
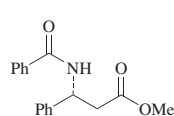
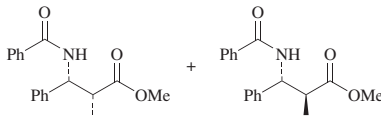
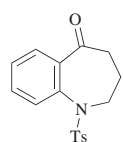
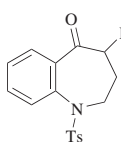
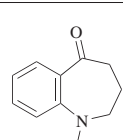
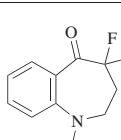
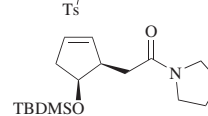
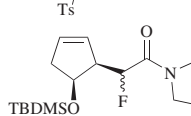
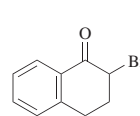
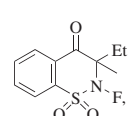
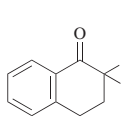
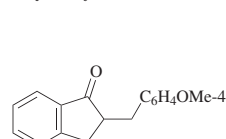
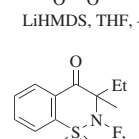
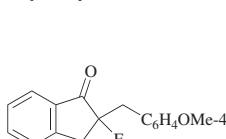
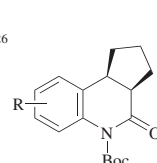
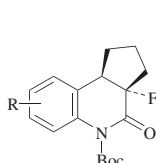
	1. NaH, DMF, 0° 2. 2,4,6-Me ₃ FP-OTf, -78°	 (100)	462																
	2,4,6-Me ₃ FP-OTf, NaH, THF	 (54)	225																
	NaH, NFSI, 1 h	 I + II (70)	<table border="1" data-bbox="1284 436 1406 551"> <thead> <tr> <th>Temp</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>20°</td> <td>85:15</td> </tr> <tr> <td>-15°</td> <td>95:5</td> </tr> </tbody> </table> 463	Temp	I:II	20°	85:15	-15°	95:5										
Temp	I:II																		
20°	85:15																		
-15°	95:5																		
	LDA, fluorinating agent, -78°, 6 h	 I + II	464																
	<table border="1" data-bbox="659 723 798 838"> <thead> <tr> <th>Fluorinating agent</th> </tr> </thead> <tbody> <tr> <td>NFOBS</td> </tr> <tr> <td>NFOBS</td> </tr> <tr> <td>NFSI</td> </tr> </tbody> </table>	Fluorinating agent	NFOBS	NFOBS	NFSI	<table border="1" data-bbox="1006 723 1215 838"> <thead> <tr> <th>Additive</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>—</td> <td>(82)</td> <td>35:65</td> </tr> <tr> <td>LiCl</td> <td>(94)</td> <td>44:56</td> </tr> <tr> <td>—</td> <td>(65)</td> <td>19:81</td> </tr> </tbody> </table>	Additive	I + II	I:II	—	(82)	35:65	LiCl	(94)	44:56	—	(65)	19:81	
Fluorinating agent																			
NFOBS																			
NFOBS																			
NFSI																			
Additive	I + II	I:II																	
—	(82)	35:65																	
LiCl	(94)	44:56																	
—	(65)	19:81																	
	1. LDA, THF, -78° 2. NFSI, -78°	 (78)	465																

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	2,2'-bisFP-BF ₄ , H ₂ SO ₄ , Me ₂ SO ₄ , MeCN, reflux, 72 h	 (77)	466
	NFSI, LDA, THF, -78°	 (95), dr = 8:1	467
	 LiHMDS, THF, -78° to -20°	 (96)	73
	 LiHMDS, THF, -78° to -20°	 (96)	73
	NFSI, KHMDs, THF, -78°	 (—) R H 8-Cl 6-F 7-CH ₂ OTBDMS 7-(CH ₂) ₂ OTBDMS 7-(CH ₂) ₃ OTBDMS	468

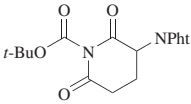
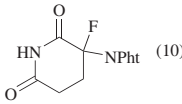
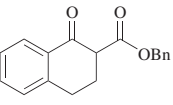
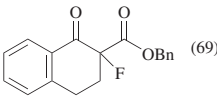
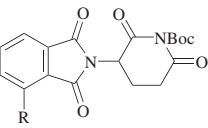
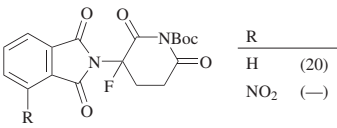
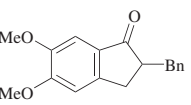
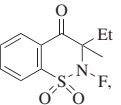
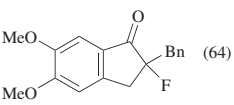
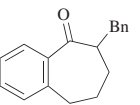
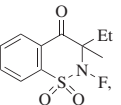
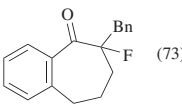
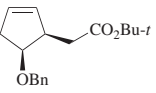
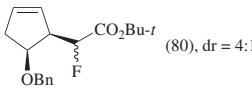
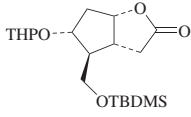
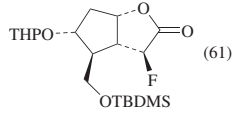
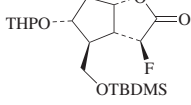
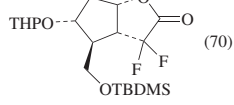
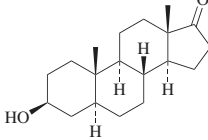
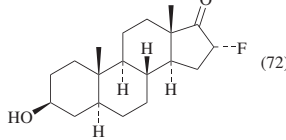
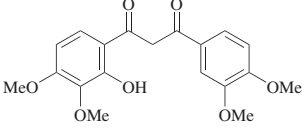
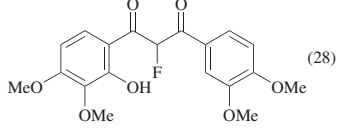
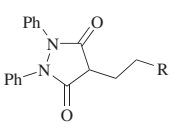
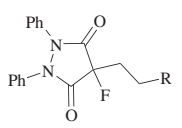
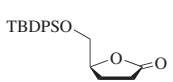
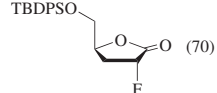
C ₁₈		1. <i>n</i> -BuLi, THF, -78°, 20 min 2. NFSI, -78° to rt 3. EtOAc, HCl, 1 h	 (10)	469
		Selectfluor TM , MeCN, rt, 19 h	 (69)	224
		NFSI, LiHMDS, THF	 $\begin{matrix} \text{R} \\ \text{H} \\ \text{NO}_2 \end{matrix}$ (20) (—)	469, 470
		 LiHMDS, THF, -78° to -20°	 (64)	73
		 LiHMDS, THF, -78° to -20°	 (73)	73
		NFSI, LDA, THF, -78°	 (80), dr = 4:1	467

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₉ 	LiHMDS, NFSI, THF, -78°	 (61)	216
	1. KHMDS, ZnCl ₂ , THF, toluene 2. NFSI, -78°	 (70)	216
	NFTh, MeOH, reflux, 1.5 h	 (72)	230
	NFSI, CH ₂ Cl ₂ , rt, 7 d	 (28)	471
C ₁₉₋₂₃ 	(CF ₃ SO ₂) ₂ NF, rt, 30 min	 $\begin{matrix} \text{R} & \text{Solvent} \\ \text{Et} & \text{AcOH} & (95) \\ \text{S(O)Ph} & \text{CHCl}_3 & (90) \end{matrix}$	453
C ₂₁ 	LiHMDS, NFSI, THF, -78°	 (70)	212

C ₂₂		NaH, THF, 0°; then Selectfluor™, DMF, rt, 20 h	(55)	224
		1. LiHMDS, THF, -78° 2. NFSI, -78°, 3 h	(>74)	472
C ₂₃		2,4,6-Me ₃ FP-OTf, NaH, THF	(78)	225
		LiHMDS, NFSI, THF, -78°	(95), dr = 70:30	473, 474
		1. KH, rt 2. NFSI, -78° to rt	(77)	475

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₄		1. LiHMDS, THF, -78° to -20° 2. NFSI, -78° to rt	(76)	476
C ₂₇		NFTh, MeOH, reflux, 1.5 h	(78)	230
		1. KH, HMPA 2. 2-Phenylbenzo[1,3,2]dioxaborole 3. NFSI	 I + II (62), I:II = 89:11	217
		1. KH, HMPA 2. 2-Phenylbenzo[1,3,2]dioxaborole 3. NFSI	 I + II (72), I:II = 81:19	217

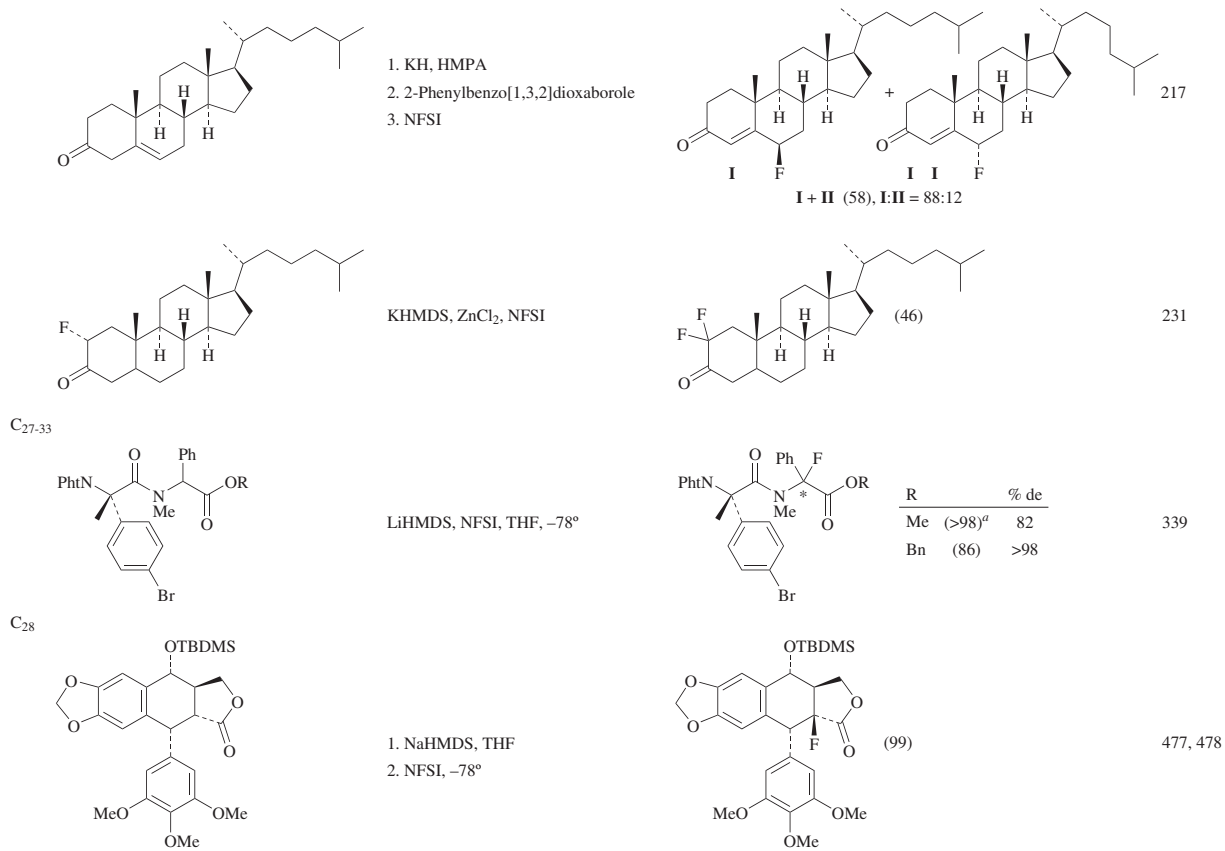


TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₈	1. KH, HMPA 2. 2-Phenylbenzo[1,3,2]dioxaborole 3. NFSI	I + II (69), I:II = 91:9	217
C ₂₉	LiHMDS, NFSI, THF, -78°, 5 h	(16)	479, 480
C ₂₈	1. KH, HMPA 2. 2-Phenylbenzo[1,3,2]dioxaborole 3. NFSI	I + II (82), I:II = 87:13	217

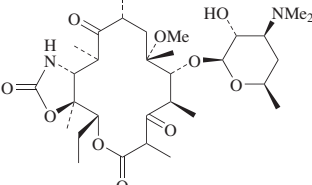
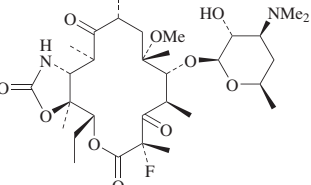
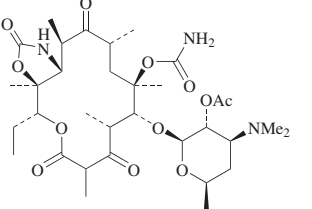
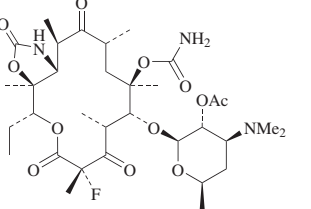
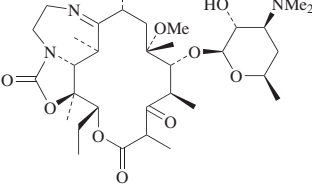
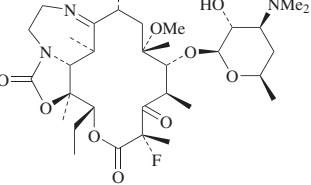
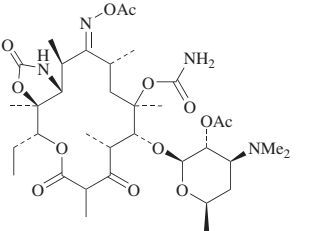
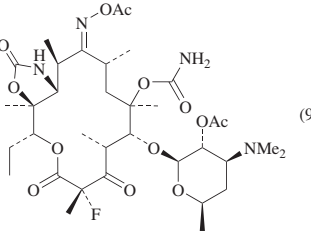
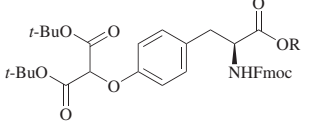
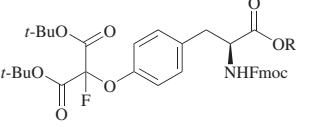
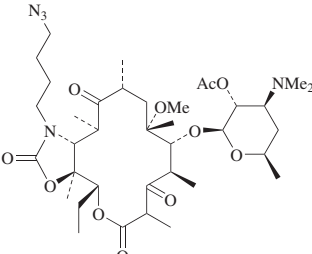
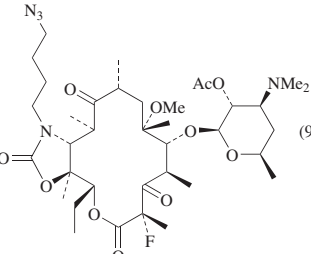
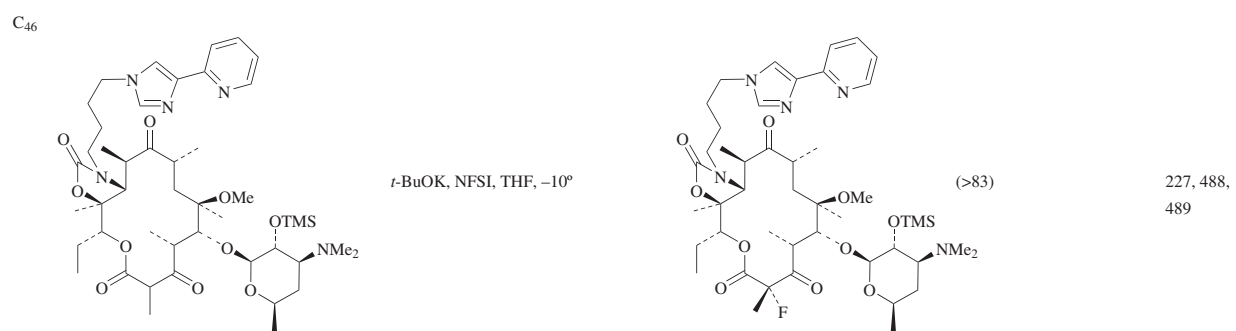
C ₃₁		Base, NFSI		(—)	481, 482
C ₃₃		NaHMDS; then Selectfluor TM , THF		(—)	483
		Base, NFSI		(—)	481, 482, 484

TABLE 7. FLUORINATION OF CARBONYL COMPOUNDS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃₅		NaHMDS, Selectfluor TM , THF	 (99)	483
C ₃₅₋₃₆		NFSI, NaHMDS, THF, -78°	 (89) R H Me	485
C ₃₇		NaH, NFSI, THF	 (90)	486, 487



^aThe reported value is the percent conversion based on starting material.

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES

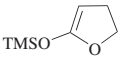

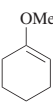
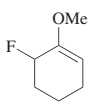
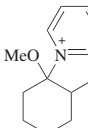
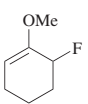
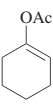
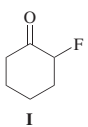
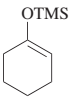
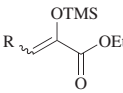
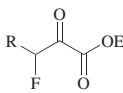
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
C ₇		NFOBS, CDCl ₃ , rt, 4 h	 I (31-40)	33																																												
		2,6-(MeOCH ₂) ₂ FP-OTf, CH ₂ Cl ₂ , rt, 3 h	I (50) ^a	31																																												
		2,6-(MeOCH ₂) ₂ FP-OTf, 2,6-(<i>t</i> -Bu) ₂ Py (2 eq), CH ₂ Cl ₂ , rt, 5 h	I (70-80) ^a	31																																												
		2,4,6-Me ₃ FP-OTf, 2,6-(<i>t</i> -Bu) ₂ Py (2 eq), CH ₂ Cl ₂ , rt, 12 h	I (30-40) ^a	31																																												
530		FP-OTf, CH ₂ Cl ₂ , reflux, 25 min	 I (59)	150																																												
		FP-OTf, DCE, 60°, 30 min	I (63)	31																																												
		FP-OTf, CH ₂ Cl ₂ , rt, 2-4 h	 (61) +  (22)	31																																												
C ₈		Fluorinating agent, reflux	 I	<table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>Solvent</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>FP-OTf</td> <td>MeCN</td> <td>14 h</td> <td>(30)</td> </tr> <tr> <td>2,4,6-Me₃FP-OTf</td> <td>MeCN</td> <td>1 d</td> <td>(<20)</td> </tr> <tr> <td>2,6-(MeOCH₂)₂FP-OTf</td> <td>DCE</td> <td>5 h</td> <td>(73)</td> </tr> </tbody> </table>	Fluorinating agent	Solvent	Time		FP-OTf	MeCN	14 h	(30)	2,4,6-Me ₃ FP-OTf	MeCN	1 d	(<20)	2,6-(MeOCH ₂) ₂ FP-OTf	DCE	5 h	(73)																												
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		FP-X, CH ₂ Cl ₂	I	150																																												
		FPPy-B ₂ F ₇ , MeCN, 0°, 1 h	I (37)	157																																												
		NFSI, CH ₂ Cl ₂ , rt, 24 h	I (46)	85																																												
		NFOBS, CH ₂ Cl ₂ , rt, 2.5 h	I (62-79)	33																																												
		NFSI, CH ₂ Cl ₂ , rt, 2.5 h	I (46)	33																																												
C ₉₋₁₅		Selectfluor™, MeCN, rt, 3.5-6 h		<table border="1"> <thead> <tr> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(31)</td> </tr> <tr> <td>CH₂CO₂Me</td> <td>(50)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(69)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>(89)</td> </tr> <tr> <td>C₅H₁₁</td> <td>(90)</td> </tr> <tr> <td>Bn</td> <td>(83)</td> </tr> </tbody> </table>	R		Me	(31)	CH ₂ CO ₂ Me	(50)	<i>i</i> -Pr	(69)	<i>i</i> -Bu	(89)	C ₅ H ₁₁	(90)	Bn	(83)	245																													
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TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

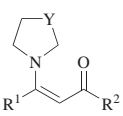
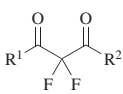
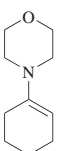

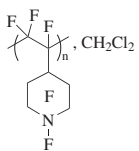
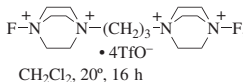
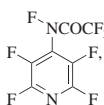
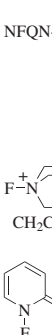
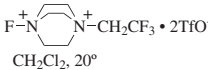

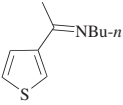
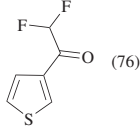
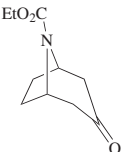
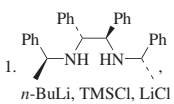
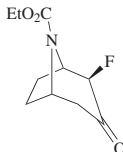
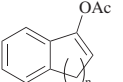
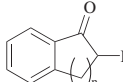
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																					
C ₉₋₁₉ 	Selectfluor TM (2 eq), Et ₃ N, MeCN, 10°, 30 min		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Y</th> <th></th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>CH₂</td> <td>(50)</td> </tr> <tr> <td>Me</td> <td>OEt</td> <td>CH₂</td> <td>(47)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>CH₂</td> <td>(71)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>OCH₂</td> <td>(89)</td> </tr> <tr> <td>Ph</td> <td>OEt</td> <td>CH₂</td> <td>(88)</td> </tr> <tr> <td>Ph</td> <td><i>i</i>-Pr</td> <td>CH₂</td> <td>(97)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>CH₂</td> <td>(81)</td> </tr> <tr> <td>Ph</td> <td>3-ClC₆H₄</td> <td>CH₂</td> <td>(95)</td> </tr> </tbody> </table>	R ¹	R ²	Y		Me	Me	CH ₂	(50)	Me	OEt	CH ₂	(47)	Me	Ph	CH ₂	(71)	Ph	Me	OCH ₂	(89)	Ph	OEt	CH ₂	(88)	Ph	<i>i</i> -Pr	CH ₂	(97)	Ph	Ph	CH ₂	(81)	Ph	3-ClC ₆ H ₄	CH ₂	(95)	247
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C ₁₀ 	Selectfluor TM , CH ₂ Cl ₂ , -196° to 20°	 I (—)	134, 416																																					
		 , CH ₂ Cl ₂	I (15)	108																																				
		 • 4TfO ⁻ CH ₂ Cl ₂ , 20°, 16 h	I (57)	133																																				
		 F, CH ₂ Cl ₂ , 20°	I (72) ^d	96																																				
	NFQN-X, CH ₂ Cl ₂ , -196° to 20°	<table border="1"> <thead> <tr> <th>X</th> <th></th> </tr> </thead> <tbody> <tr> <td>F</td> <td>(43)</td> </tr> <tr> <td>OTf</td> <td>(58)^a</td> </tr> <tr> <td>CF₃CO₂</td> <td>(67)^a</td> </tr> <tr> <td>C₃F₇CO₂</td> <td>(88)^a</td> </tr> <tr> <td>BF₄</td> <td>(62)^a</td> </tr> </tbody> </table>	X		F	(43)	OTf	(58) ^a	CF ₃ CO ₂	(67) ^a	C ₃ F ₇ CO ₂	(88) ^a	BF ₄	(62) ^a	113, 114, 115																									
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 • 2TfO ⁻ , CH ₂ Cl ₂ , 20°	I (81)	129																																						
 O, CH ₂ Cl ₂ , reflux, 24 h	I (44)	98																																						
	Selectfluor TM , MeCN, reflux, 8 h	 (76)	248																																					
	1.  <i>n</i> -BuLi, TMSCl, LiCl 2. Selectfluor TM	 (55), 60% ee	490																																					
C ₁₁₋₁₂ 	Selectfluor TM , sodium lauryl ether sulfate (0.05% aq), 60°, 1 h		<table border="1"> <thead> <tr> <th>n</th> <th></th> </tr> </thead> <tbody> <tr> <td>1</td> <td>(85-90)</td> </tr> <tr> <td>2</td> <td>(85-90)</td> </tr> </tbody> </table>	n		1	(85-90)	2	(85-90)	177																														
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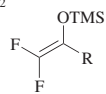

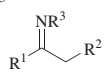


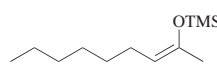
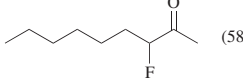
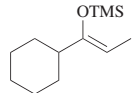
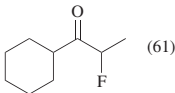
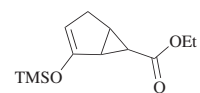
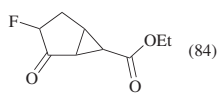
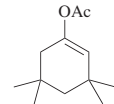
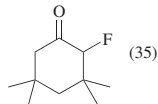
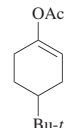
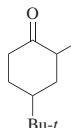
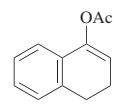
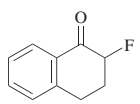
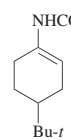
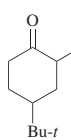
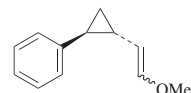
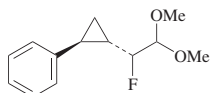
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																		
C ₁₁₋₁₂ 	Selectfluor TM , MeCN, CH ₂ Cl ₂ , -78° to 0°, 2 h	 R Ph (89) 4-ClC ₆ H ₄ (90) 4-CF ₃ C ₆ H ₄ (88) 4-MeC ₆ H ₄ (87)	491																																																																		
C ₁₁₋₁₃ 	(CF ₃ SO ₂) ₂ NF (x eq), CH ₂ Cl ₂ , Na ₂ CO ₃ , 22°, 5 h	 I +  II <table border="1" data-bbox="1006 493 1423 803"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>x</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr><td>Ph</td><td>H</td><td><i>n</i>-Pr</td><td>0.67</td><td>(33)</td><td>(15)</td></tr> <tr><td>Ph</td><td>H</td><td><i>n</i>-Pr</td><td>2.4</td><td>(0)</td><td>(82)</td></tr> <tr><td>4-MeC₆H₄</td><td>H</td><td><i>n</i>-Pr</td><td>0.67</td><td>(36)</td><td>(16)</td></tr> <tr><td>4-MeC₆H₄</td><td>H</td><td><i>n</i>-Pr</td><td>2.4</td><td>(0)</td><td>(83)</td></tr> <tr><td>Ph</td><td>Me</td><td><i>n</i>-Pr</td><td>0.67</td><td>(38)</td><td>(17)</td></tr> <tr><td>Ph</td><td>Me</td><td><i>n</i>-Pr</td><td>2.4</td><td>(0)</td><td>(58)</td></tr> <tr><td>4-BrC₆H₄</td><td>H</td><td><i>n</i>-Bu</td><td>0.67</td><td>(30)</td><td>(16)</td></tr> <tr><td>4-BrC₆H₄</td><td>H</td><td><i>n</i>-Bu</td><td>2.4</td><td>(0)</td><td>(78)</td></tr> <tr><td>4-MeOC₆H₄</td><td>H</td><td><i>n</i>-Bu</td><td>0.67</td><td>(26)</td><td>(17)</td></tr> <tr><td>4-MeOC₆H₄</td><td>H</td><td><i>n</i>-Bu</td><td>2.4</td><td>(0)</td><td>(70)</td></tr> </tbody> </table>	R ¹	R ²	R ³	x	I	II	Ph	H	<i>n</i> -Pr	0.67	(33)	(15)	Ph	H	<i>n</i> -Pr	2.4	(0)	(82)	4-MeC ₆ H ₄	H	<i>n</i> -Pr	0.67	(36)	(16)	4-MeC ₆ H ₄	H	<i>n</i> -Pr	2.4	(0)	(83)	Ph	Me	<i>n</i> -Pr	0.67	(38)	(17)	Ph	Me	<i>n</i> -Pr	2.4	(0)	(58)	4-BrC ₆ H ₄	H	<i>n</i> -Bu	0.67	(30)	(16)	4-BrC ₆ H ₄	H	<i>n</i> -Bu	2.4	(0)	(78)	4-MeOC ₆ H ₄	H	<i>n</i> -Bu	0.67	(26)	(17)	4-MeOC ₆ H ₄	H	<i>n</i> -Bu	2.4	(0)	(70)	246
R ¹	R ²	R ³	x	I	II																																																																
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C ₁₂ 	FP-OTf, CH ₂ Cl ₂ , reflux, 3 h	 (58)	31																																																																		
	FP-OTf, CH ₂ Cl ₂ , reflux, 10 h	 (61)	31																																																																		
	NFSI, CH ₂ Cl ₂ , rt, 16.5 h	 (84)	492																																																																		
	4-MeC ₆ H ₄ O ₂ S $\text{N}=\text{F}$, <i>exo</i> -2-norbornyl MeLi, toluene, THF, -20°	 (35)	69																																																																		
	FPPy-B ₂ F ₇ , MeCN, 80°, 18 h	 (62), <i>cis</i> : <i>trans</i> = 3:1	157																																																																		
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	FPPy-B ₂ F ₇ , MeCN, rt, 2 d	 (93), <i>cis</i> : <i>trans</i> = 4:1	157																																																																		
	Fluorinating agent, MeNO ₂ , MeOH, 4 Å MS	 Fluorinating agent F-TEDA-OTf (45) NFSI (40)	43																																																																		

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)


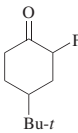
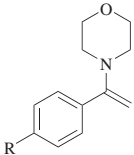
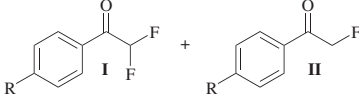
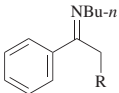
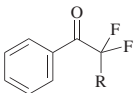
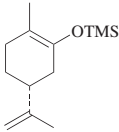
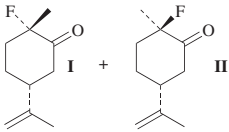
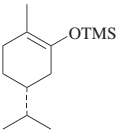
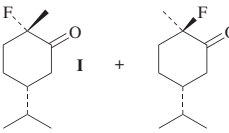
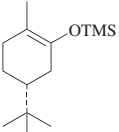
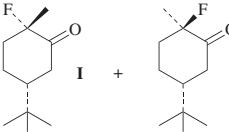
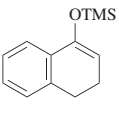
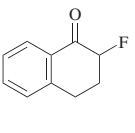
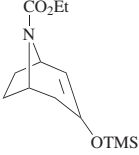
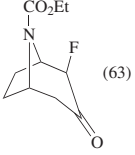
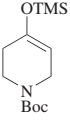
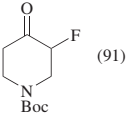
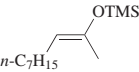
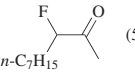
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.															
<p>C₁₂₋₁₃</p> 	NFTh, MeCN, rt, 5-6 h	 <table border="1"> <thead> <tr> <th>R</th> <th colspan="2">cis:trans</th> </tr> </thead> <tbody> <tr> <td>Ac</td> <td>(74)</td> <td>1:1.2</td> </tr> <tr> <td>Et</td> <td>(43)</td> <td>12.8:1</td> </tr> <tr> <td>TMS</td> <td>(44)</td> <td>9.8:1</td> </tr> </tbody> </table>	R	cis:trans		Ac	(74)	1:1.2	Et	(43)	12.8:1	TMS	(44)	9.8:1	235			
R	cis:trans																	
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Et	(43)	12.8:1																
TMS	(44)	9.8:1																
<p>C₁₂₋₁₅</p> 	Selectfluor TM (2 eq), MeCN, 4 Å MS, -10°, 8 h	 <table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>NO₂</td> <td>(95)</td> <td>1:0</td> </tr> <tr> <td>H</td> <td>(74)</td> <td>11:1</td> </tr> <tr> <td>MeO</td> <td>(64)</td> <td>2.8:1</td> </tr> <tr> <td>CO₂Et</td> <td>(72)</td> <td>1:0</td> </tr> </tbody> </table>	R	I + II	I:II	NO ₂	(95)	1:0	H	(74)	11:1	MeO	(64)	2.8:1	CO ₂ Et	(72)	1:0	247
R	I + II	I:II																
NO ₂	(95)	1:0																
H	(74)	11:1																
MeO	(64)	2.8:1																
CO ₂ Et	(72)	1:0																
<p>C₁₂₋₂₀</p> 	Selectfluor TM , MeCN, reflux, 4 h	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(77)</td> </tr> <tr> <td>Ph</td> <td>(73)</td> </tr> <tr> <td>Bn</td> <td>(85)</td> </tr> <tr> <td>C₈H₁₇</td> <td>(76)</td> </tr> </tbody> </table>	R	Yield (%)	H	(77)	Ph	(73)	Bn	(85)	C ₈ H ₁₇	(76)	248					
R	Yield (%)																	
H	(77)																	
Ph	(73)																	
Bn	(85)																	
C ₈ H ₁₇	(76)																	
<p>C₁₃</p> 	Selectfluor TM , DMF, 0°, 2 h	 <p>I + II (67), I:II = 51:49</p>	240, 493, 494															
	Selectfluor TM , DMF, 0°, 2 h	 <p>I + II (53), I:II = 54:46</p>	238															
	Selectfluor TM , DMF, 0°, 2 h	 <p>I + II (80), I:II = 43:57</p>	240, 493															
	NFOBS, CH ₂ Cl ₂ , rt, 4 h	 <p>(67)</p>	33															
	Selectfluor TM , MeCN, rt, 1 h	 <p>(63)</p>	490															
	Selectfluor TM , MeCN, rt	 <p>(91)</p>	241															
	FP-OTf, CH ₂ Cl ₂ , reflux, 3 h	 <p>(58)</p>	150															

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃		FP-OTf, CH ₂ Cl ₂ , rt, 2 h	I (65)	150
		NFOBS, CH ₂ Cl ₂ , rt, 3 h	I (71)	33
		FP-OTf, CH ₂ Cl ₂ , rt, 2 h	I (65)	31
		2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 2 h	I (71)	31
538		O, CH ₂ Cl ₂ , reflux, 61 h		98
		(CF ₃ SO ₂) ₂ NF, Na ₂ CO ₃ , CH ₂ Cl ₂ , 22°	I + II I + II (60), I:II = 90:10	246
		Selectfluor TM , MeCN, 4 Å MS, -10°, 8 h	I (89)	247
		Selectfluor TM , MeCN, reflux, 4 h	(70)	248
C ₁₃₋₁₅		Selectfluor TM , MeCN, reflux, 4 h	(89) (81)	248
C ₁₄		NFOBS, CH ₂ Cl ₂ , rt, 2.5 h	(86)	33
		Selectfluor TM , DMF, 0°	I + II I + II (80), I:II = 95:5	243
539		2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 2 h	(68)	31
		(CF ₃ SO ₂) ₂ NF (x eq), Na ₂ CO ₃ , CH ₂ Cl ₂ , 22°, 5 h	I + II x I + II I:II 0.67 (34) 65:35 2.4 (65) 0:100	246

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

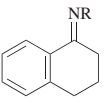
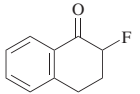
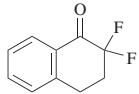
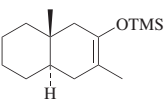
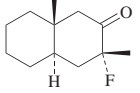
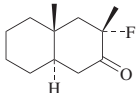
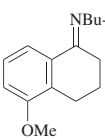
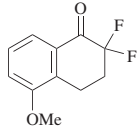
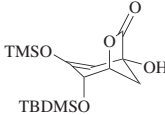
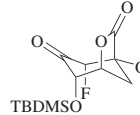
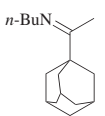
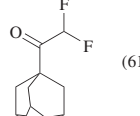
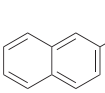
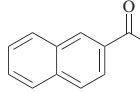
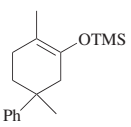
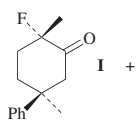
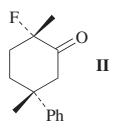
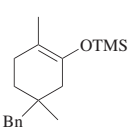
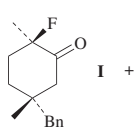
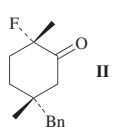
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.				
C ₁₄₋₁₈ 	Fluorinating agent (2 eq), reflux, 4 h	 I +  II	248				
				Fluorinating agent	R	Solvent	I + II
		Selectfluor TM		Bu- <i>n</i>	MeCN	(95)	0:100
		NFTh		Bu- <i>n</i>	MeCN	(91)	40:60
		NFSI		Bu- <i>n</i>	MeCN	(89)	12:88
		2,6-Cl ₂ FP-BF ₄		Bu- <i>n</i>	MeCN	(67)	100:0
		2,6-Cl ₂ FP-BF ₄		Bu- <i>n</i>	CH ₂ Cl ₂	(65)	100:0
		Selectfluor TM		CHMePh	MeOH	(88)	73:27
		Selectfluor TM		CHMePh	wet MeCN	(92)	25:75
		Selectfluor TM		CHMePh	MeCN	(93)	0:100
		NFTh		CHMePh	MeOH	(87)	56:44
		NFTh		CHMePh	wet MeCN	(92)	58:42
		NFTh		CHMePh	MeCN	(88)	40:60
		NFSI		CHMePh	MeOH	(84)	31:69
		NFSI		CHMePh	wet MeCN	(94)	21:79
NFSI	CHMePh	MeCN	(90)	13:87			
C ₁₅ 	Selectfluor TM , DMF, 0°	 (81)	243				
	Selectfluor TM , DMF, 0°	 (92)	243				
C ₁₆ 	Selectfluor TM , MeCN, reflux, 4 h	 (80)	248				
	Selectfluor TM , DMF, rt	 (89)	495				
	Selectfluor TM , MeCN, reflux, 12 h	 (61)	248				
	Selectfluor TM , MeCN, reflux, 4 h	 (82)	248				
C ₁₇ 	Selectfluor TM , DMF, 0°, 2 h	 I +  II I + II (92), I:II = 54:46	493				
C ₁₈ 	Selectfluor TM , DMF, 0°, 2 h	 I +  II I + II (83), I:II = 28:72	493				

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₈		 CH ₂ Cl ₂ , reflux, 49 h	 (33)	98
C ₁₉		1. LDA, TMSCl 2. 2,6-(MeOCH ₂) ₂ FP-OTf, K ₂ CO ₃ , CH ₂ Cl ₂ , rt	 (65)	31
		 C ₆ H ₆ , reflux, 9 h	 (66)	73
		Selectfluor™, MeCN, rt	 (—)	244
		Selectfluor™, MeCN, rt	 (85)	244
C ₂₀		Selectfluor™, DMF, rt; then Et ₃ N, CH ₂ Cl ₂ , rt	 (65)	222
		Selectfluor™, MeCN, rt	 (—)	244
		Selectfluor™, MeCN, rt	 I (91)	244
		FP-OTf, CH ₂ Cl ₂ , reflux	 I (94)	465
C ₂₁		FP-OTf, CH ₂ Cl ₂ , reflux	 I (27) + II (9)	237
		FP-OTf, CH ₂ Cl ₂ , rt	 III (14)	237
		FP-OTf, CH ₂ Cl ₂ , rt	 II (16) + III (27)	237

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

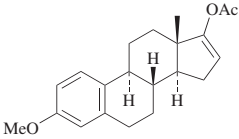
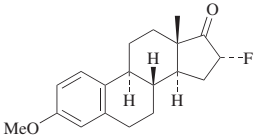
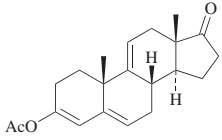
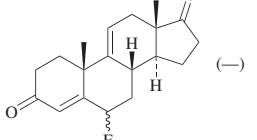
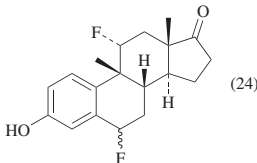
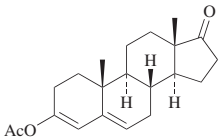
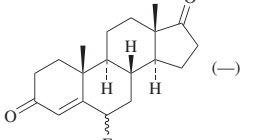
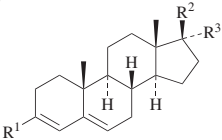
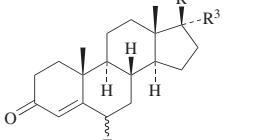
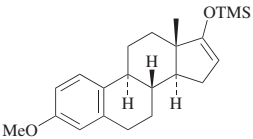
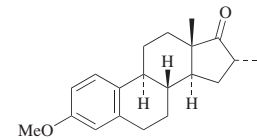
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₁ 	FPPy-B ₂ F ₇ , MeCN, 40°, 3 d	 (68), $\alpha:\beta = 81:1$	157
	Fluorinating agent, MeCN	 (—)	415
	Fluorinating agent	Temp Time $\alpha:\beta$	
	FPPy-B ₂ F ₇	40° 120 h 38:37	
	FPPy-B ₂ F ₇	80° 3 h 45:34	
	Selectfluor TM	0° 3 h 56:43	
	Selectfluor TM	80° 3 h 45:21	
	Selectfluor TM , MeCN, 6 h, 80°	 (24)	415
	Fluorinating agent, MeCN	 (—)	415
	Fluorinating agent	Temp Time $\alpha:\beta$	
	FPPy-B ₂ F ₇	40° 120 h 54:0	
	FPPy-B ₂ F ₇	80° 3 h 9:1	
	Selectfluor TM	0° 3 h 44:51	
	Selectfluor TM	80° 3 h 73:0	
C ₂₁₋₂₅ 	FPPy-B ₂ F ₇ , MeCN		157
		R ¹ R ² R ³ Temp Time $\alpha:\beta$	
		OAc O 80° 18 h (28) 6:1	
		OAc O 40° 4 d (60) 1:2	
		OAc OAc H 80° 5 d (57) 4:1	
		OAc OAc H 40° 2 d (96) 1:1	
		OAc Ac H 80° 6 h (36) 1:0	
		OAc Ac H 40° 3 d (46) 1:2	
		OTMS OTMS H rt 18 h (88) 1:3	
C ₂₂ 	FP-OTf, CH ₂ Cl ₂ , rt, 16 h	 (78)	22, 31

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

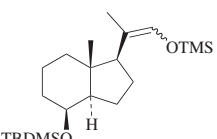
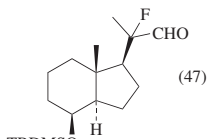
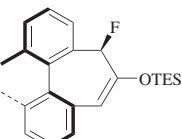
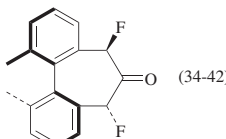
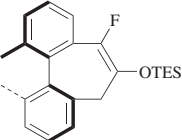
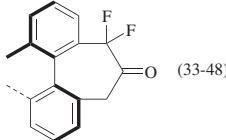
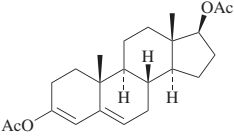
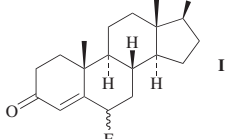
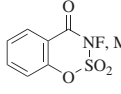
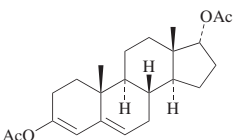
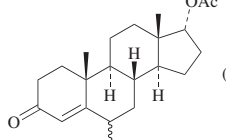
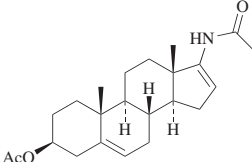
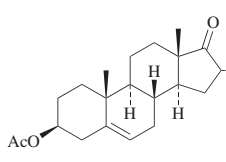
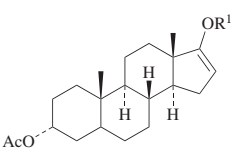
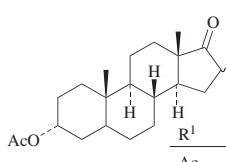
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
C ₂₂ 	NFSI, CH ₂ Cl ₂ , rt	 (47)	236		
C ₂₃ 	Selectfluor TM , DMF, rt	 (34-42)	222		
	Selectfluor TM , DMF, rt	 (33-48)	222		
	Fluorinating agent, MeCN	 I	415		
	Fluorinating agent	Temp	Time	I	α:β
	FPPy-B ₂ F ₇	40°	120 h	(<20) ^a	54:15
	FPPy-B ₂ F ₇	80°	3 h	(<20) ^a	39:46
	Selectfluor TM	0°	3 h	(>95) ^a	50:43
	Selectfluor TM	80°	3 h	(>95) ^a	50:32
	Selectfluor TM , MeCN, rt, 15 min	I	(95), α:β = 1:1.4	129	
	2,2'-bisFP-BF ₄ , NaHCO ₃ , MeCN, 70°, 1 h	I	(82), α:β = 1:1.7	161	
	NF, MeCN, rt, 24 h	I	(59), α:β = 1:2.5	100	
	FP-OTf, CH ₂ Cl ₂ , reflux, 10 h	I	(71), α:β = 1:2	150	
	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , reflux, 46 h	I	(55), α:β = 1:8.5	31	
	F ⁺ -N ⁺ Me ₂ -N ⁺ Me ₂ -F ⁻ • 2BF ₄ ⁻ , MeCN, -20°, 20 min	I	(81), α:β = 1:1.5	122	
	Selectfluor TM , MeCN, rt, 15 min	 (95), α:β = 42:58	173		
	FPPy-B ₂ F ₇ , MeCN, rt, 5 d	 (82), α:β = 15:1	157		
C ₂₃₋₂₄ 	Selectfluor TM , MeCN, rt	 α:β = 95:5	173		
		R ¹	Time		
		Ac	2 h	(90)	
		TMS	15 min	(92)	

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

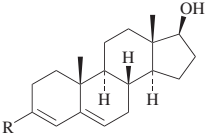
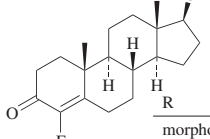
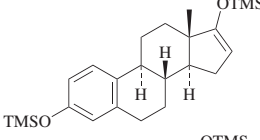
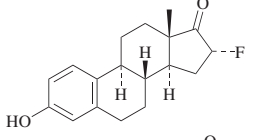
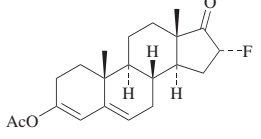
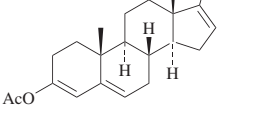
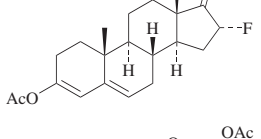
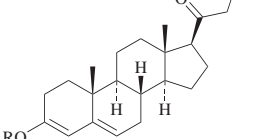
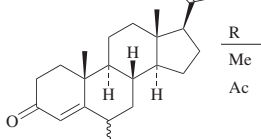
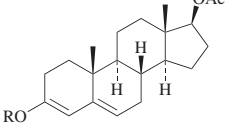
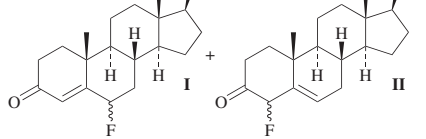
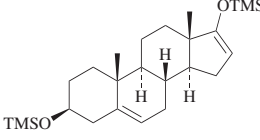
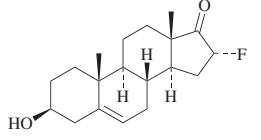
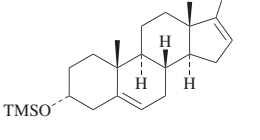
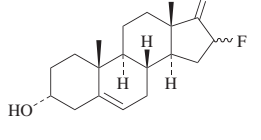
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																																	
	Fluorinating agent, CH ₂ Cl ₂ , MeCN, -15°		31																																																																	
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	2,4,6-Me ₃ FP-OTf			morpholinyl (54)																																																																
	FP-OTf			pyrrolidinyl (7)																																																																
	2,4,6-Me ₃ FP-OTf			pyrrolidinyl (13)																																																																
	FP-OTf, CH ₂ Cl ₂ , reflux, 1 h	 (50)	31																																																																	
	FP-OTf, CH ₂ Cl ₂ , reflux, 1 h			 (54)	150																																																															
	FP-OTf, CH ₂ Cl ₂ , reflux, 1 h	 (54)	150																																																																	
	FP-OTf, CH ₂ Cl ₂ , reflux, 1 h																																																																			
	NFTh, MeCN, rt		235																																																																	
				<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>$\alpha:\beta$</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>6 h (72)</td> <td>1:2.4</td> </tr> <tr> <td>Ac</td> <td>15 min (89)</td> <td>1:2.2</td> </tr> </tbody> </table>	R	Time	$\alpha:\beta$	Me	6 h (72)	1:2.4	Ac	15 min (89)	1:2.2																																																							
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	Fluorinating agent, rt	 <table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Time</th> <th>I + II</th> <th>I ($\alpha:\beta$):II</th> </tr> </thead> <tbody> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>24 h</td> <td>(72)^a</td> <td>13 (1:3.8):1</td> </tr> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>24 h</td> <td>(77)^a</td> <td>10 (1:4):1</td> </tr> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>30 h</td> <td>(35)^a</td> <td>6 (1:5):1</td> </tr> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>47 h</td> <td>(26)^a</td> <td>12 (1:3.8):1</td> </tr> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>4 h</td> <td>(51)^a</td> <td>2.4 (1:1.8):1</td> </tr> <tr> <td>TMS</td> <td>CH₂Cl₂</td> <td>20 h</td> <td>(77)^a</td> <td>14 (1:3.5):1</td> </tr> <tr> <td>TMS</td> <td>MeCN</td> <td>11 h</td> <td>(94)^a</td> <td>7.5 (1:3.4):1</td> </tr> <tr> <td>TMS</td> <td>DMF</td> <td>3.5 h</td> <td>(100)^a</td> <td>8 (1:3.9):1</td> </tr> <tr> <td>TBDMS</td> <td>CH₂Cl₂</td> <td>48 h</td> <td>(93)^a</td> <td>92 (1:3.8):1</td> </tr> <tr> <td>TES</td> <td>CH₂Cl₂</td> <td>66 h</td> <td>(90)^a</td> <td>>92 (1:3.5):1</td> </tr> <tr> <td>TIPS</td> <td>CH₂Cl₂</td> <td>90 h</td> <td>(93)^a</td> <td>100 (1:3.8):1</td> </tr> <tr> <td>TIPS</td> <td>CH₂Cl₂</td> <td>2.5 h</td> <td>(41)^a</td> <td>4.1 (1:1.5):1</td> </tr> </tbody> </table>	R	Solvent	Time	I + II	I ($\alpha:\beta$):II	TMS	CH ₂ Cl ₂	24 h	(72) ^a	13 (1:3.8):1	TMS	CH ₂ Cl ₂	24 h	(77) ^a	10 (1:4):1	TMS	CH ₂ Cl ₂	30 h	(35) ^a	6 (1:5):1	TMS	CH ₂ Cl ₂	47 h	(26) ^a	12 (1:3.8):1	TMS	CH ₂ Cl ₂	4 h	(51) ^a	2.4 (1:1.8):1	TMS	CH ₂ Cl ₂	20 h	(77) ^a	14 (1:3.5):1	TMS	MeCN	11 h	(94) ^a	7.5 (1:3.4):1	TMS	DMF	3.5 h	(100) ^a	8 (1:3.9):1	TBDMS	CH ₂ Cl ₂	48 h	(93) ^a	92 (1:3.8):1	TES	CH ₂ Cl ₂	66 h	(90) ^a	>92 (1:3.5):1	TIPS	CH ₂ Cl ₂	90 h	(93) ^a	100 (1:3.8):1	TIPS	CH ₂ Cl ₂	2.5 h	(41) ^a	4.1 (1:1.5):1	140
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TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

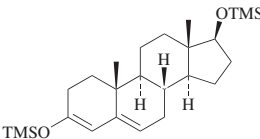
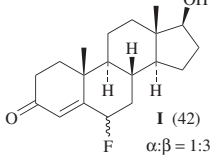
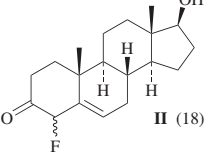
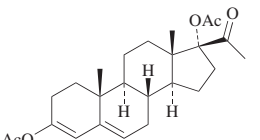
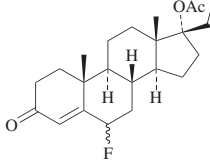
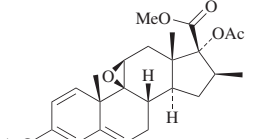
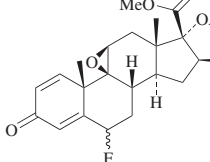
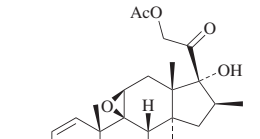
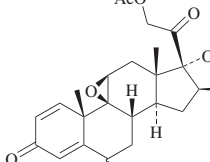

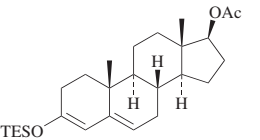
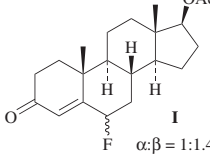
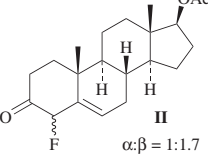
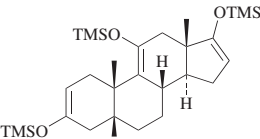
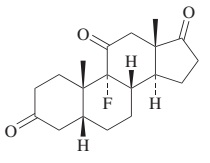
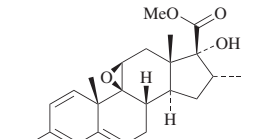
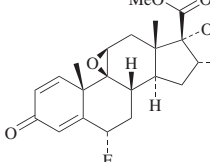
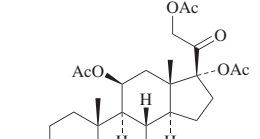
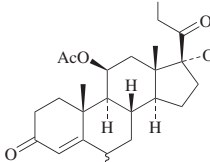
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₅</p> 	FP-OTf, CH ₂ Cl ₂ , rt, 1 h	 I (42)  II (18) α:β = 1:3	150
	Selectfluor TM , MeCN, rt, 15 min	 (90), α:β = 30:70	173
<p>C₂₆</p> 	Selectfluor TM , DMF, -5° to rt, 4 h	 (—), α:β = 70:30	496
	NFTh, MeCN, 0°, 12 h	 I (73), α:β = 93.5:6.5	497
	Selectfluor TM , MeCN, 1 h	I (—)	498
<p>C₂₇</p> 	2,2'-bisFP-BF ₄ , NaHCO ₃ , MeCN, rt, 30 min	 I  II α:β = 1:1.4 α:β = 1:1.7 I + II (65) ^a , I:II = 46:19	161
<p>C₂₈</p> 	FP-OTf, CH ₂ Cl ₂ , rt, 2 h	 (51)	31
<p>C₂₉</p> 	Selectfluor TM , MeCN, H ₂ O, 0°, 1 h	 (96)	499
	Selectfluor TM , MeCN, rt, 15 min	 (88), α:β = 47:53	173

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

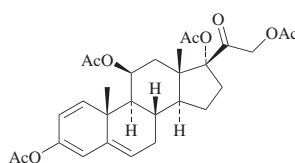
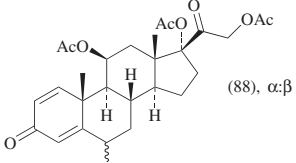
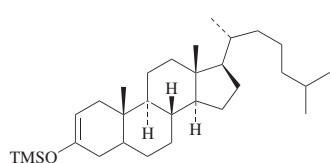
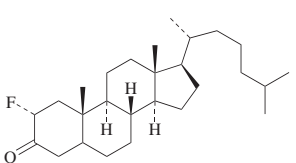
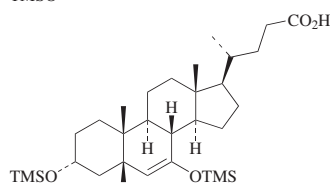
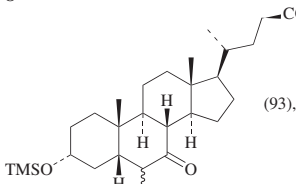
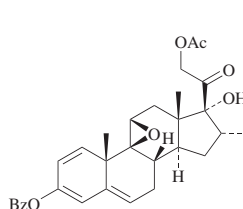
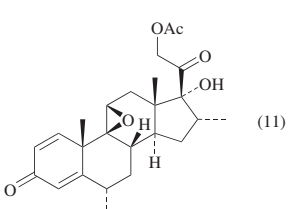
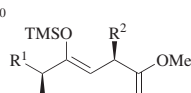
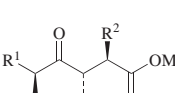
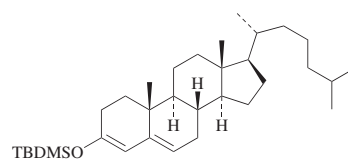
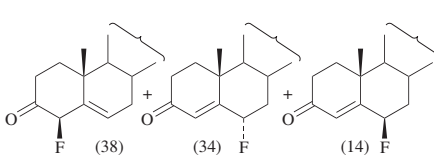
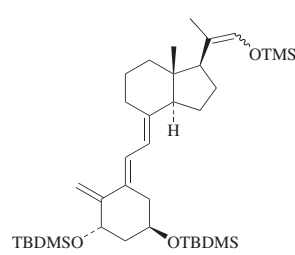
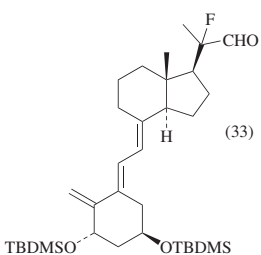
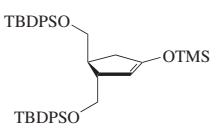
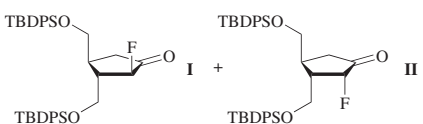
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																
	Selectfluor™, MeCN, rt, 15 min	 (88), $\alpha:\beta = 57:43$	173																																
	FP-OTf, CH ₂ Cl ₂ , reflux	 (79)	231																																
	Selectfluor™, MeCN, 20°, 6 h	 (93), $\alpha:\beta = 87:13$	500																																
	Selectfluor™, MeCN, Py, MeSO ₃ H, 0-5°	 (11)	501																																
	Selectfluor™, DMF; then TBAF, THF, rt, 45 min	 <table border="1" data-bbox="1058 1400 1406 1607"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> <th>% de</th> </tr> </thead> <tbody> <tr> <td>Bu-<i>i</i></td> <td>Me</td> <td>(76)</td> <td>>95</td> </tr> <tr> <td>Bu-<i>i</i></td> <td>CH₂C₆H₁₁-<i>c</i></td> <td>(73)</td> <td>>95</td> </tr> <tr> <td>(CH₂)₂SMe</td> <td>Bn</td> <td>(65)</td> <td>>95</td> </tr> <tr> <td>Me</td> <td>Bu-<i>i</i></td> <td>(75)</td> <td>>95</td> </tr> <tr> <td>Bn</td> <td>Pr-<i>n</i></td> <td>(68)</td> <td>>95</td> </tr> <tr> <td>Pr-<i>i</i></td> <td>Me</td> <td>(71)</td> <td>9</td> </tr> <tr> <td>CH₂OBn</td> <td>Bu-<i>i</i></td> <td>(74)</td> <td>28</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	% de	Bu- <i>i</i>	Me	(76)	>95	Bu- <i>i</i>	CH ₂ C ₆ H ₁₁ - <i>c</i>	(73)	>95	(CH ₂) ₂ SMe	Bn	(65)	>95	Me	Bu- <i>i</i>	(75)	>95	Bn	Pr- <i>n</i>	(68)	>95	Pr- <i>i</i>	Me	(71)	9	CH ₂ OBn	Bu- <i>i</i>	(74)	28	239, 502
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	FP-OTf, CH ₂ Cl ₂ , reflux, 5 h	 (38) (34) (14)	231																																
	NFSI, CH ₂ Cl ₂ , rt	 (33)	236																																

TABLE 8. FLUORINATION OF ENOL DERIVATIVES, ENAMINES, AND IMINES (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₄₂</p> 	Selectfluor TM , DMF, rt, 15 min	 <p>I + II (89), I:II = 1:1</p>	242

^aThe reported value is the percent conversion based on starting material.

TABLE 9. FLUORINATION OF ORGANOPHOSPHORUS COMPOUNDS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅₋₁₇ 	1. LDA, <i>t</i> -BuOK, THF, -78° to -90°, 1 h 2. NFSI, -78° to rt	 R H (11) Me (45) <i>n</i> -Bu (48) 	254
C ₆ 	1. BuLi, THF, -78° 2. (CF ₃ SO ₂) ₂ NF, THF, -78°	 I (51)	503
C ₆₋₁₀ 	1. LDA, THF, -78° 2. TMSCl, -78° to 0° to -78° 3. NFSI, -78° to 0°, 15 min 4. EtOLi, EtOH, THF, 0°	 R Me (89) <i>i</i> -Pr (74) <i>n</i> -Bu (85) <i>n</i> -C ₅ H ₁₁ (82)	262
C ₆₋₁₇ 	1. LDA, <i>t</i> -BuOK, THF, -78° to -90°, 1 h 2. NFSI, -78° to rt	 R Me (66) <i>n</i> -Bu (70) 	254
C ₈ 	NaH, Selectfluor TM , THF, rt	 (60)	505

555

TABLE 9. FLUORINATION OF ORGANOPHOSPHORUS COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 	NaH (<i>x</i> eq), Selectfluor TM (<i>y</i> eq), THF, 0° to rt, 4 h	 I + II x y I + II I:II 1 1 (46) ^a 100:0 2.5 3 (69) 0:100	263
	NFOBS, NaHMDS, -78° to 0°, 2 h	I (78)	33
	1. NaH, THF, 0° to rt 2. Selectfluor TM , DMF, rt, 140 min	I (17)	504
C ₉ 	NaH (1.3 eq), Selectfluor TM (1.5 eq), THF, 0° to rt, 4 h	 (85)	263
	NaH, Selectfluor TM , THF, 0°	 (52)	506
C ₉₋₁₈ 	1. NaHMDS (2.2 eq), THF, -78° 2. NFSI (2.5 eq), THF, -78°	 R ¹ R ² H Me (63) 4-NO ₂ Me (74) 4-NO ₂ Et (82) 4-Br Me (79) 4-Br Et (81) 4-OMe Me (80) 4-Ph Me (59) 3-Ph Me (60) 2-Ph Me (46) 3-CH ₂ O(CH ₂) ₂ TMS Me (79) 4-CO ₂ Bn Me (72) 4-COPh Et (70)	257

556

C ₁₁		1. Base (2.2 eq), THF, -78° 2. NFSI (2.5 eq), THF, -78°	<table border="1"> <thead> <tr> <th colspan="2">Base</th> </tr> </thead> <tbody> <tr> <td>KDA</td> <td>(39)</td> </tr> <tr> <td>LDA</td> <td>(33)</td> </tr> <tr> <td>NaHMDS</td> <td>(79)</td> </tr> <tr> <td>KHMDS</td> <td>(51)</td> </tr> <tr> <td>LiHMDS</td> <td>(29)</td> </tr> </tbody> </table>	Base		KDA	(39)	LDA	(33)	NaHMDS	(79)	KHMDS	(51)	LiHMDS	(29)	257						
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		1. <i>t</i> -BuLi (2.2 eq), THF, -90° 2. NFSI (2.2 eq), THF, -90° to rt		259																		
		1. <i>t</i> -BuLi (1.1 eq), THF, -90° 2. NFSI (1.1 eq), THF, -90° to rt		259																		
C ₁₁₋₁₂		1. LiHMDS, THF, -78° to 0° 2. TMSCl, 20° 3. NFSI, -90° 4. LiOH, H ₂ O, THF	<table border="1"> <thead> <tr> <th colspan="2">R</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(97)</td> </tr> <tr> <td>2-F</td> <td>(68)</td> </tr> <tr> <td>4-F</td> <td>(68)</td> </tr> <tr> <td>4-Cl</td> <td>(74)</td> </tr> <tr> <td>4-Br</td> <td>(76)</td> </tr> <tr> <td>4-OMe</td> <td>(79)</td> </tr> <tr> <td>3-Me</td> <td>(83)</td> </tr> <tr> <td>4-Me</td> <td>(90)</td> </tr> </tbody> </table>	R		H	(97)	2-F	(68)	4-F	(68)	4-Cl	(74)	4-Br	(76)	4-OMe	(79)	3-Me	(83)	4-Me	(90)	260, 261
R																						
H	(97)																					
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C ₁₂₋₁₆		1. NaHMDS, THF, -78° 2. NFSI, -78° to -20°	<table border="1"> <thead> <tr> <th colspan="2">R</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(46)</td> </tr> <tr> <td>Et</td> <td>(74)</td> </tr> </tbody> </table>	R		Me	(46)	Et	(74)	257, 258												
R																						
Me	(46)																					
Et	(74)																					
C ₁₃		NFSI, NaHMDS, THF		507																		

TABLE 9. FLUORINATION OF ORGANOPHOSPHORUS COMPOUNDS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
C ₁₃		<i>s</i> -BuLi, NFSI, -78°	 I + II (32), I:II = 84:16	508, 509																														
C ₁₆		1. NaHMDS (1.1 eq), THF, -80° 2. NFSI (1 eq), -80° to rt		510																														
		1. NaHMDS (2.2 eq), THF, -60° 2. NFSI (2.4 eq), -60° to rt		510																														
C ₁₆₋₂₀		1. NaHMDS, THF, -78° 2. NFSI, -78° to -20°	<table border="1"> <thead> <tr> <th>Substitution</th> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>2,7</td> <td>Me</td> <td>(57)</td> </tr> <tr> <td>2,6</td> <td>Me</td> <td>(23)</td> </tr> <tr> <td>1,5</td> <td>Me</td> <td>(46)</td> </tr> <tr> <td>1,3</td> <td>Me</td> <td>(55)</td> </tr> <tr> <td>1,6</td> <td>Me</td> <td>(51)</td> </tr> <tr> <td>2,7</td> <td>Et</td> <td>(49)</td> </tr> <tr> <td>2,6</td> <td>Et</td> <td>(23)</td> </tr> <tr> <td>1,5</td> <td>Et</td> <td>(48)</td> </tr> <tr> <td>1,7</td> <td>Et</td> <td>(46)</td> </tr> </tbody> </table>	Substitution	R		2,7	Me	(57)	2,6	Me	(23)	1,5	Me	(46)	1,3	Me	(55)	1,6	Me	(51)	2,7	Et	(49)	2,6	Et	(23)	1,5	Et	(48)	1,7	Et	(46)	258
Substitution	R																																	
2,7	Me	(57)																																
2,6	Me	(23)																																
1,5	Me	(46)																																
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1,5	Et	(48)																																
1,7	Et	(46)																																
C ₁₇		1. NaH, THF 2. Selectfluor™		292																														

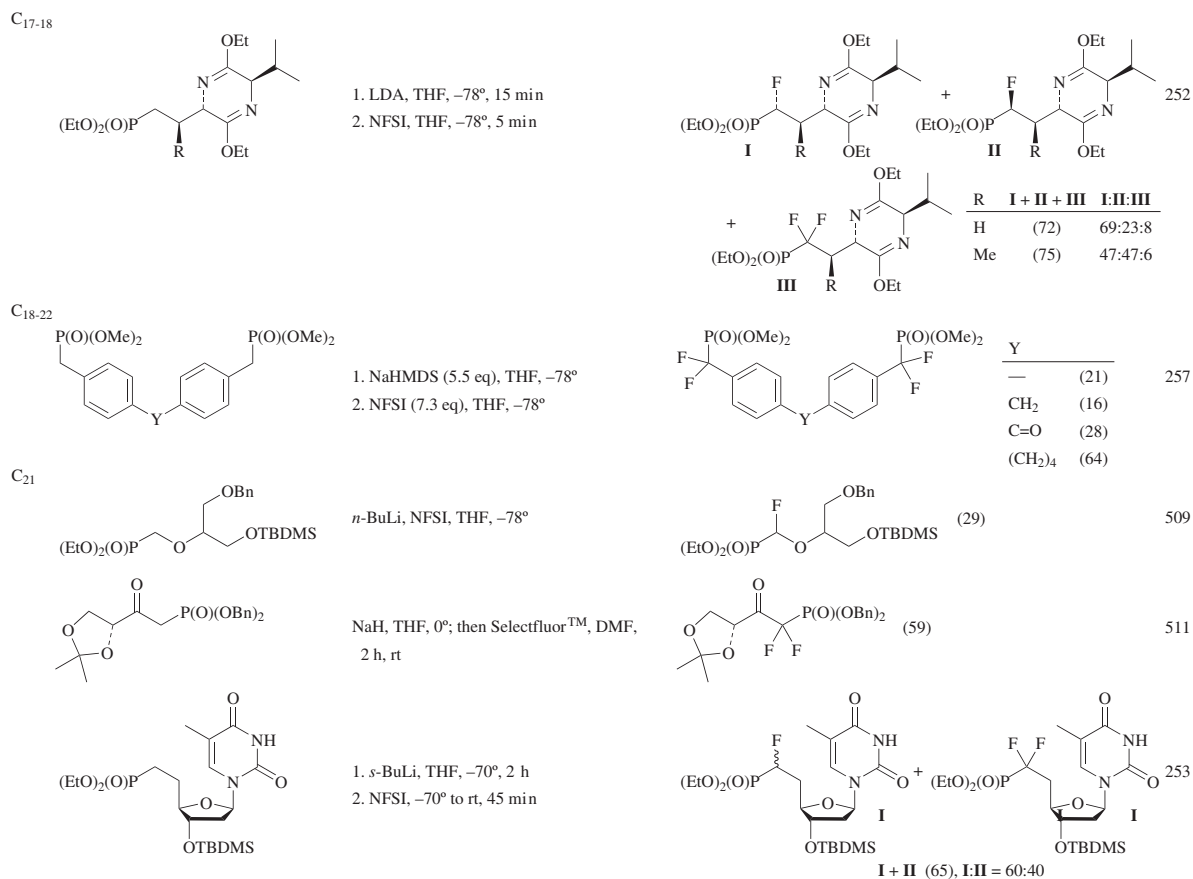
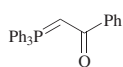


TABLE 9. FLUORINATION OF ORGANOPHOSPHORUS COMPOUNDS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
C₂₃₋₃₇												
	NaH, THF, 0° ; then Selectfluor™, DMF, 2 h, rt	 <table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>THP</td> <td>(55)</td> <td>(5)</td> </tr> <tr> <td>Tr</td> <td>(48)</td> <td>(5)</td> </tr> </tbody> </table>	R	I	II	THP	(55)	(5)	Tr	(48)	(5)	511
R	I	II										
THP	(55)	(5)										
Tr	(48)	(5)										
C₂₆												
	1. NaHMDS (2.2 eq), THF, -80° 2. NFSI (2.2 eq), THF, -80° to rt	 (30) + (35)	259									
	1. NaHMDS (1.1 eq), THF, -90° 2. NFSI (1.1 eq), THF, -90° to rt	(70)	259									

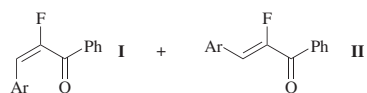


Method A:

1. NFSI, THF
2. ArCHO, 40-57 h

Method B:

1. NFSI, THF, -20° to rt, 3 h
2. LDA
3. ArCHO, 27-40 h

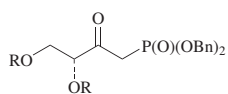


512

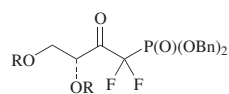
Method	Ar	I + II	I:II
A	4-O ₂ NC ₆ H ₄	(65)	95:5
B	4-O ₂ NC ₆ H ₄	(83)	90:10
A	4-ClC ₆ H ₄	(51)	100:0
B	4-ClC ₆ H ₄	(79)	100:0
A	Ph	(40)	98:2
B	Ph	(70)	95:5
B	4-FC ₆ H ₄	(72)	100:0
B	4-MeC ₆ H ₄	(81)	98:2

561

C₂₈



NaH, THF, 0°; then Selectfluor™, DMF,
2 h, rt



R	
EtO ₂ C(CH ₂) ₂	(90)
THP	(73)

511

^a The reported value is the percent conversion based on starting material.

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₃ 	(CF ₃ SO ₂) ₂ NF, K ₂ CO ₃ , CH ₂ Cl ₂ , rt, 8 h	(45) + (31)	513
C ₄ 	(CF ₃ SO ₂) ₂ NF, K ₂ CO ₃ , CH ₂ Cl ₂ , rt, 12 h		513
C ₅ 	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 8 h	(46)	266
	1. Selectfluor TM , MeCN, rt; then Et ₃ N 2. <i>m</i> -CPBA, CH ₂ Cl ₂ , rt, 6 h	(58)	173
	Selectfluor TM , MeCN, rt, 2 h	(30)	436
C ₇ 	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 8 h	I (76)	266
	FP-OTf, CH ₂ Cl ₂ , rt, 7.5 h	I (48)	266
	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 4 h	I (49)	266
	FP-OTf, CH ₂ Cl ₂ , rt, 6 h	I (58)	266
C ₇₋₈ 	1. Selectfluor TM , MeCN, rt; then Et ₃ N 2. NBS, MeOH, H ₂ O, CH ₂ Cl ₂ , rt, 30 min	R Cl (51) H (48) Me (61)	173
C ₈ 	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 30 min	(44) + (33)	266
	Selectfluor TM , Et ₃ N, MeCN, rt, 40 min	(48)	264
	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 7.5 h	(39)	266
C ₈₋₁₃ 	1. <i>n</i> -BuLi (2.2 eq), THF, -78° to rt, 1 h 2. NFSI (2.5 eq), -78° to rt	R Me (11) Ph (32)	270
C ₉ 	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 23 h	(38)	266

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

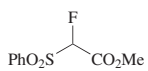
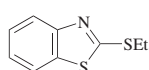
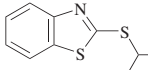
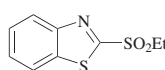
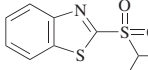
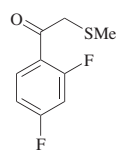
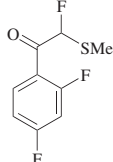
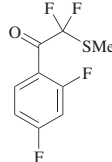
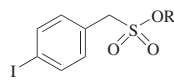
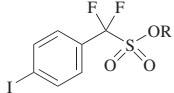
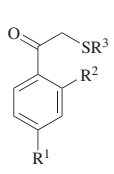
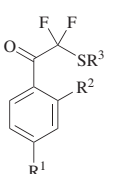
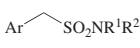
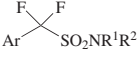
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																																								
$\text{PhO}_2\text{S}-\text{CH}_2-\text{CO}_2\text{Me}$	NaHMDS, NFOBS, -78° to 0° , 2 h	 I (86)	33																																																								
	NaHMDS, NFSI, -78° to 0° , 2 h	I (42)	33																																																								
	Selectfluor TM , Et ₃ N, rt, 16 h	 (35)	514																																																								
	Selectfluor TM , CH ₂ Cl ₂ , rt, 16 h	 (65)	515																																																								
	Fluorinating agent (3 eq)	 I +  II	515a																																																								
	<table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>Solvent</th> <th>Additive</th> <th>Temp</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>2,4,6-Me₃FP-OTf</td> <td>DCE</td> <td>—</td> <td>rt</td> <td>12 h</td> <td>(92)</td> <td>100:0</td> </tr> <tr> <td>2-SO₃-6-MeFP</td> <td>TCE</td> <td>—</td> <td>105°</td> <td>1.5 h</td> <td>(57)</td> <td>0:100</td> </tr> <tr> <td>2,4,6-Me₃FP-OTf</td> <td>TCE</td> <td>ZnBr₂</td> <td>105°</td> <td>2.5 h</td> <td>(82)</td> <td>0:100</td> </tr> </tbody> </table>	Fluorinating agent	Solvent	Additive	Temp	Time	I + II	I:II	2,4,6-Me ₃ FP-OTf	DCE	—	rt	12 h	(92)	100:0	2-SO ₃ -6-MeFP	TCE	—	105°	1.5 h	(57)	0:100	2,4,6-Me ₃ FP-OTf	TCE	ZnBr ₂	105°	2.5 h	(82)	0:100																														
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C_{9-12} 	NaHMDS, NFSI, THF, -78°	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>CH₂CCl₃</td> <td>(71)</td> </tr> <tr> <td>neopentyl</td> <td>(90)</td> </tr> </tbody> </table>	R	Yield (%)	CH ₂ CCl ₃	(71)	neopentyl	(90)	273																																																		
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C_{9-12} 	2,4,6-Me ₃ FP-OTf (3 eq), ZnBr ₂ , TCE, 105°, 0.5–3 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>(76)</td> </tr> <tr> <td>Cl</td> <td>Cl</td> <td>Me</td> <td>(72)</td> </tr> <tr> <td>F</td> <td>F</td> <td>Et</td> <td>(84)</td> </tr> <tr> <td>F</td> <td>F</td> <td><i>c</i>-C₃H₅</td> <td>(72)</td> </tr> <tr> <td>F</td> <td>F</td> <td>(CH₂)₂OAc</td> <td>(45)</td> </tr> <tr> <td>MeO</td> <td>H</td> <td>Me</td> <td>(64)</td> </tr> <tr> <td>CF₃</td> <td>H</td> <td>Me</td> <td>(60)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	H	H	Me	(76)	Cl	Cl	Me	(72)	F	F	Et	(84)	F	F	<i>c</i> -C ₃ H ₅	(72)	F	F	(CH ₂) ₂ OAc	(45)	MeO	H	Me	(64)	CF ₃	H	Me	(60)	515a																								
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Ar	R ¹	R ²	Yield (%)																																																								
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4-BrC ₆ H ₄	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	(84)																																																								
4-IC ₆ H ₄	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	(86)																																																								
4-O ₂ NC ₆ H ₄	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	(65)																																																								
3-BrC ₆ H ₄	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	(92)																																																								
4-MeC ₆ H ₄	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	2,4-(MeO) ₂ C ₆ H ₃ CH ₂	(76)																																																								

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

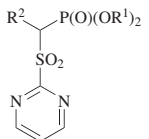
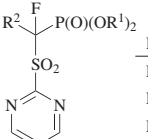

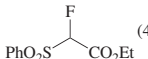
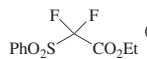
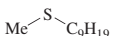
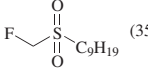
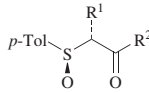
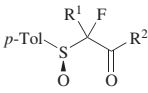
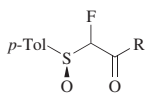
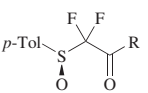
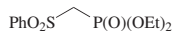
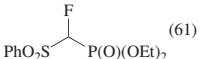
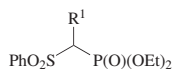
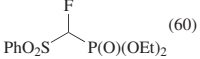
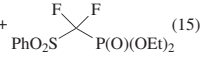
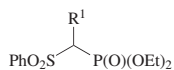
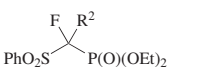
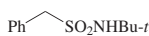

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																												
C ₉₋₂₁ 	KH, THF, 0°; then Selectfluor™, DMF, rt, 2 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>H</td> <td>(63)</td> </tr> <tr> <td>Et</td> <td>Me</td> <td>(80)</td> </tr> <tr> <td>Et</td> <td>(CH₂)₃CH=CH₂</td> <td>(55)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>Ph</td> <td>(61-80)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>2-BrC₆H₃OMe-5</td> <td>(50)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>2-naphthyl</td> <td>(61-80)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Et	H	(63)	Et	Me	(80)	Et	(CH ₂) ₃ CH=CH ₂	(55)	<i>i</i> -Pr	Ph	(61-80)	<i>i</i> -Pr	2-BrC ₆ H ₃ OMe-5	(50)	<i>i</i> -Pr	2-naphthyl	(61-80)	256																							
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<i>i</i> -Pr	2-naphthyl	(61-80)																																													
C ₁₀ 	1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, 0°, 12 min	 (49) +  (4)	31																																												
	1. Selectfluor™, MeCN, rt; then Et ₃ N 2. <i>m</i> -CPBA, CH ₂ Cl ₂ , rt, 6 h	 (35)	173																																												
C ₁₀₋₁₇ 	NaH, THF, 0°; then Selectfluor™, rt	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CH₂F</td> <td>5 h</td> <td>(23)</td> </tr> <tr> <td>H</td> <td>CHF₂</td> <td>12 h</td> <td>(19)</td> </tr> <tr> <td>H</td> <td>CF₃</td> <td>1.5 h</td> <td>(27)</td> </tr> <tr> <td>H</td> <td>CF₂Cl</td> <td>12 h</td> <td>(33)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>48 h</td> <td>(60)</td> </tr> <tr> <td>H</td> <td>2-pyridyl</td> <td>1 h</td> <td>(82)</td> </tr> <tr> <td>H</td> <td>4-pyridyl</td> <td>1 h</td> <td>(52)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>15 h</td> <td>(23)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>0.5 h</td> <td>(67)</td> </tr> <tr> <td>H</td> <td>CF=CHPh</td> <td>2 h</td> <td>(70)</td> </tr> </tbody> </table>	R ¹	R ²	Time	Yield (%)	H	CH ₂ F	5 h	(23)	H	CHF ₂	12 h	(19)	H	CF ₃	1.5 h	(27)	H	CF ₂ Cl	12 h	(33)	H	Me	48 h	(60)	H	2-pyridyl	1 h	(82)	H	4-pyridyl	1 h	(52)	H	Ph	15 h	(23)	Me	Ph	0.5 h	(67)	H	CF=CHPh	2 h	(70)	268
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	Selectfluor™, rt	 <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>CH₂F</td> <td>(27)</td> </tr> <tr> <td>CHF₂</td> <td>(41)</td> </tr> <tr> <td>CF₃</td> <td>(38)</td> </tr> <tr> <td>CF₂Cl</td> <td>(32)</td> </tr> <tr> <td>Me</td> <td>trace</td> </tr> <tr> <td>2-pyridyl</td> <td>trace</td> </tr> <tr> <td>4-pyridyl</td> <td>(17)</td> </tr> <tr> <td>Ph</td> <td>(20)</td> </tr> <tr> <td>CF=CHPh</td> <td>(15)</td> </tr> </tbody> </table>	R	Yield (%)	CH ₂ F	(27)	CHF ₂	(41)	CF ₃	(38)	CF ₂ Cl	(32)	Me	trace	2-pyridyl	trace	4-pyridyl	(17)	Ph	(20)	CF=CHPh	(15)	268																								
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C ₁₁ 	1. KH 2. Selectfluor™, <i>t</i> -BuOH, DMF, rt, 10 min	 (61)	173																																												
	1. NaH, THF 2. Selectfluor™, DMF	 (60) +  (15)	516																																												
	NaH, 0°; then fluorinating agent, rt	 <table border="1"> <thead> <tr> <th>Fluorinating agent</th> <th>R¹</th> <th>R²</th> <th>Solvent</th> <th>Time</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Selectfluor™</td> <td>H</td> <td>H</td> <td>THF/DMF</td> <td>30 min</td> <td>(60)</td> </tr> <tr> <td>2,4,6-Me₃FP-OTf</td> <td>I</td> <td>H</td> <td>THF</td> <td>60 min</td> <td>(55)</td> </tr> <tr> <td>NFSI</td> <td>I</td> <td>H</td> <td>THF</td> <td>60 min</td> <td>(53)</td> </tr> <tr> <td>Selectfluor™</td> <td>I</td> <td>H</td> <td>THF/DMF</td> <td>5 min</td> <td>(84)</td> </tr> <tr> <td>Selectfluor™</td> <td>Br</td> <td>Br</td> <td>THF/DMF</td> <td>5 min</td> <td>(85)</td> </tr> </tbody> </table>	Fluorinating agent	R ¹	R ²	Solvent	Time	Yield (%)	Selectfluor™	H	H	THF/DMF	30 min	(60)	2,4,6-Me ₃ FP-OTf	I	H	THF	60 min	(55)	NFSI	I	H	THF	60 min	(53)	Selectfluor™	I	H	THF/DMF	5 min	(84)	Selectfluor™	Br	Br	THF/DMF	5 min	(85)	516								
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	1. BuLi (2.2 eq), THF, -78° to 0° to -78° 2. NFSI (2.2 eq), THF, -78° to rt, 10 h	 (68)	271																																												

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

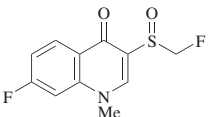
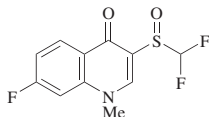
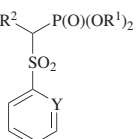
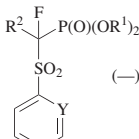
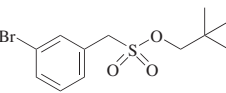
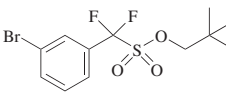
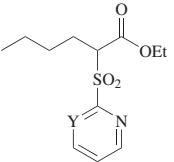
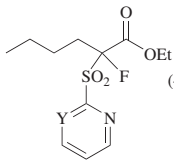
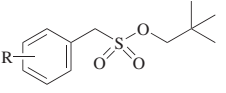
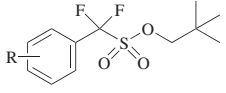
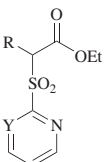
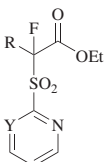
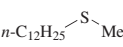
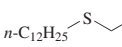
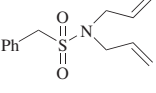
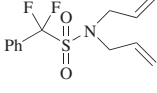
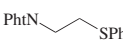
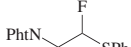
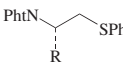
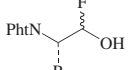
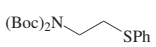
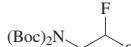
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																		
C11 	1. Selectfluor™, MeCN, rt 2. Et ₃ N	 (30)	517																		
C11-19 	KH, THF, 0°; then Selectfluor™, DMF, rt, 2 h	 (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Y</th> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>N</td> <td>Et</td> <td>Me</td> </tr> <tr> <td>N</td> <td><i>i</i>-Pr</td> <td>Ph</td> </tr> <tr> <td>CH</td> <td><i>i</i>-Pr</td> <td>Ph</td> </tr> </tbody> </table>	Y	R ¹	R ²	N	Et	Me	N	<i>i</i> -Pr	Ph	CH	<i>i</i> -Pr	Ph	256						
Y	R ¹	R ²																			
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N	<i>i</i> -Pr	Ph																			
CH	<i>i</i> -Pr	Ph																			
C12 	NFSI, NaHMDS, THF, -78° to rt	 (87)	274																		
C12-13 	KH, THF; then Selectfluor™, DMF	 (—) <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Y</th> </tr> </thead> <tbody> <tr> <td>N</td> </tr> <tr> <td>CH</td> </tr> </tbody> </table>	Y	N	CH	255															
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CH																					
C12-18 	1. Base, THF, -78° 2. NFSI, -78°	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> <th>Base</th> </tr> </thead> <tbody> <tr> <td>H</td> <td><i>t</i>-BuLi (81)</td> </tr> <tr> <td>4-NO₂</td> <td>NaHMDS (86)</td> </tr> <tr> <td>4-Br</td> <td>LDA (79)</td> </tr> <tr> <td>4-Me</td> <td>LDA (76)</td> </tr> <tr> <td>3-Ph</td> <td><i>t</i>-BuLi (59)</td> </tr> </tbody> </table>	R	Base	H	<i>t</i> -BuLi (81)	4-NO ₂	NaHMDS (86)	4-Br	LDA (79)	4-Me	LDA (76)	3-Ph	<i>t</i> -BuLi (59)	272						
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4-Me	LDA (76)																				
3-Ph	<i>t</i> -BuLi (59)																				
C12-22 	KH, THF, 0° to rt, 75 min; then Selectfluor™, DMF, 2 h, rt	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>Y</th> <th>R</th> </tr> </thead> <tbody> <tr> <td>N</td> <td><i>n</i>-Bu (92)</td> </tr> <tr> <td>N</td> <td>CH₂CH₂CH=CH₂ (86)</td> </tr> <tr> <td>N</td> <td>(CH₂)₃CH=CH₂ (88)</td> </tr> <tr> <td>CH</td> <td><i>n</i>-Bu (91)</td> </tr> <tr> <td>N</td> <td><i>n</i>-C₆H₁₃ (81)</td> </tr> <tr> <td>N</td> <td>(CH₂)₄CH=CH₂ (74)</td> </tr> <tr> <td>N</td> <td>(CH₂)₅CO₂Et (85)</td> </tr> <tr> <td>N</td> <td>(CH₂)₈OTBDMS (72)</td> </tr> </tbody> </table>	Y	R	N	<i>n</i> -Bu (92)	N	CH ₂ CH ₂ CH=CH ₂ (86)	N	(CH ₂) ₃ CH=CH ₂ (88)	CH	<i>n</i> -Bu (91)	N	<i>n</i> -C ₆ H ₁₃ (81)	N	(CH ₂) ₄ CH=CH ₂ (74)	N	(CH ₂) ₅ CO ₂ Et (85)	N	(CH ₂) ₈ OTBDMS (72)	269
Y	R																				
N	<i>n</i> -Bu (92)																				
N	CH ₂ CH ₂ CH=CH ₂ (86)																				
N	(CH ₂) ₃ CH=CH ₂ (88)																				
CH	<i>n</i> -Bu (91)																				
N	<i>n</i> -C ₆ H ₁₃ (81)																				
N	(CH ₂) ₄ CH=CH ₂ (74)																				
N	(CH ₂) ₅ CO ₂ Et (85)																				
N	(CH ₂) ₈ OTBDMS (72)																				
C13 	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 17.5 h	 (48)	266																		
	NaHMDS, NFSI, THF, -78°	 (86)	518																		
C16 	Selectfluor™, Et ₃ N, MeCN	 (32)	264																		
C17-23 	Selectfluor™, Et ₃ N, MeCN	 <table border="1" style="display: inline-table; vertical-align: middle;"> <thead> <tr> <th>R</th> </tr> </thead> <tbody> <tr> <td>Me (42)</td> </tr> <tr> <td><i>i</i>-Pr (30)</td> </tr> <tr> <td>Bn (65)</td> </tr> </tbody> </table>	R	Me (42)	<i>i</i> -Pr (30)	Bn (65)	264														
R																					
Me (42)																					
<i>i</i> -Pr (30)																					
Bn (65)																					
C18 	Selectfluor™, Et ₃ N, MeCN, rt, 25 min	 (20)	264																		

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

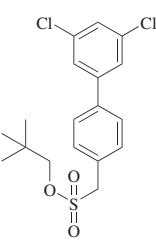
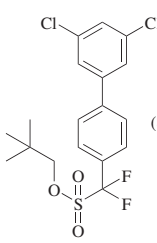
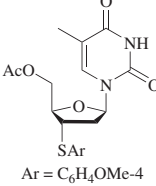
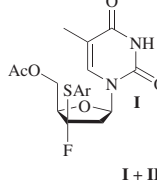
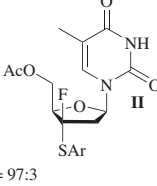
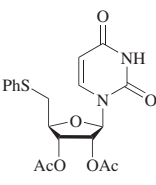
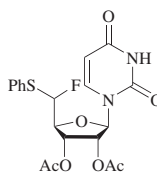
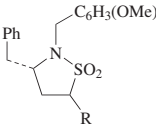
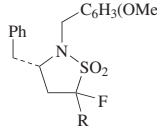
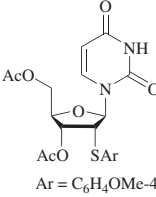
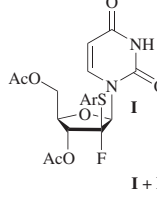
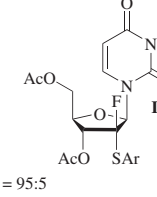
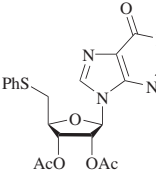
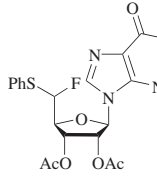
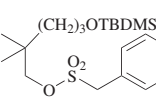
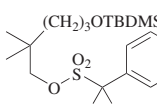
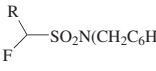

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₈		NFSI, NaHMDS, THF, -78° to rt	 (87)	274												
	 Ar = C ₆ H ₄ OMe-4	Selectfluor TM , MeCN; then Et ₃ N, rt, 25 min	 I +  II (45), I:II = 97:3	265												
C ₁₉		Selectfluor TM , MeCN; then Et ₃ N, rt, 25 min	 (42), dr = 60:40	265												
C ₁₉₋₂₅		NaHMDS, NFSI, THF, -78° to rt	 R	270												
			<table border="1"> <thead> <tr> <th>R</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>H (18)</td> <td>—</td> </tr> <tr> <td>Ph (90)</td> <td>1.7:1</td> </tr> </tbody> </table>	R	dr	H (18)	—	Ph (90)	1.7:1							
R	dr															
H (18)	—															
Ph (90)	1.7:1															
C ₂₀	 Ar = C ₆ H ₄ OMe-4	Selectfluor TM , MeCN; then Et ₃ N, rt, 25 min	 I +  II (52), I:II = 95:5	265												
		Selectfluor TM , MeCN; then Et ₃ N, rt, 25 min	 (46), dr = 66:34	265												
		NFSI, NaHMDS, THF, -78° to rt	 (88)	274												
C ₂₀₋₂₁		1. <i>n</i> -BuLi (1.3 eq), HMPA, THF, -78°, 1 h 2. NFSI (1.5 eq), -78° to rt	<table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me (33)</td> <td></td> </tr> <tr> <td>Et (50)</td> <td></td> </tr> </tbody> </table>	R	Yield (%)	Me (33)		Et (50)		270						
R	Yield (%)															
Me (33)																
Et (50)																
		1. <i>n</i> -BuLi (1.3 eq), HMPA, THF, -78°, 1 h 2. NFSI (1.5 eq), -78° to rt	<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H (60)</td> <td></td> </tr> <tr> <td>Et</td> <td>H (69)</td> <td></td> </tr> <tr> <td>Me</td> <td>Me (41)</td> <td></td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Me	H (60)		Et	H (69)		Me	Me (41)		270
R ¹	R ²	Yield (%)														
Me	H (60)															
Et	H (69)															
Me	Me (41)															

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

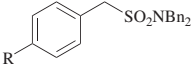
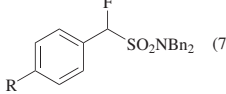
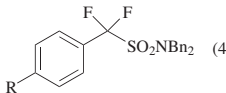
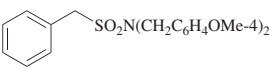
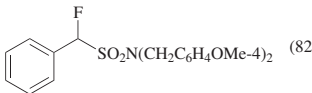
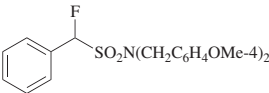
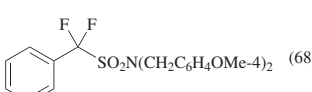
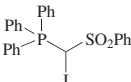
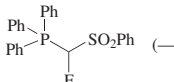
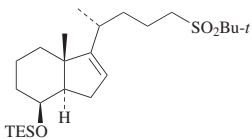
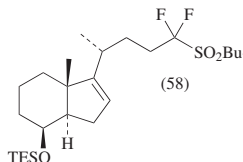
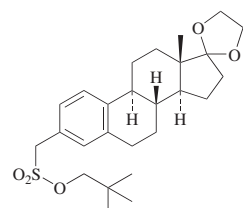
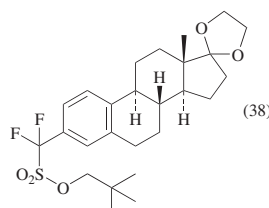
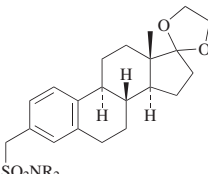
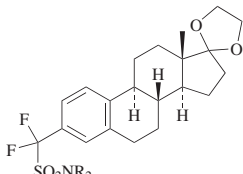
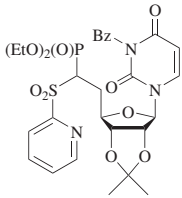
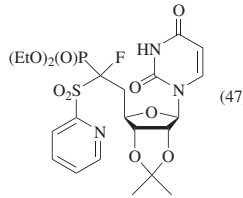
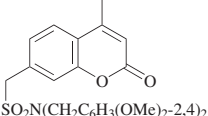
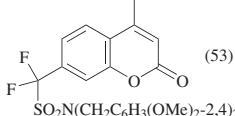
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₁ 	1. NaHMDS (1.1 eq), THF, -78° 2. NFSI (1.1 eq), THF, -78°	 (70)	$\frac{R}{H}$ NO ₂ 271
	1. NaHMDS (2.2 eq), THF, -78° 2. NFSI (2.2 eq), THF, -78°	 (40)	$\frac{R}{H}$ NO ₂ 271
C ₂₃ 	1. BuLi (1.1 eq), THF, -78° 2. NFSI (1.1 eq), THF, -78° to rt, 45 min	 (82)	271
	1. BuLi (1.1 eq), THF, -78° 2. NFSI (1.1 eq), THF, -78° to rt, 45 min	 (68)	271
C ₂₅ 	NaH, THF, 0°; then Selectfluor™, DMF, 0° to rt, 15 min	 (—)	516
	1. <i>n</i> -BuLi, -78° 2. NFSI, -78° to rt 3. Repeat steps 1 and 2	 (58)	519
C ₂₆ 	1. KHMDS, THF, -78°, 1 h 2. NFSI, -78°, 1 h 3. Repeat steps 1 and 2	 (38)	275
C ₂₇₋₃₀ 	NaHMDS, NFSI, THF, -78°		$\frac{R}{allyl}$ (83) CH ₂ C ₆ H ₃ (OMe) ₂ -2,4 (0) 518
C ₂₉ 	1. KH, THF; then Selectfluor™, DMF 2. NH ₃ , MeOH	 (47)	255
	NFSI, NaHMDS, THF, -78°	 (53)	270

TABLE 10. FLUORINATION OF ORGANOSULFUR COMPOUNDS (Continued)

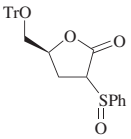
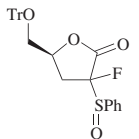
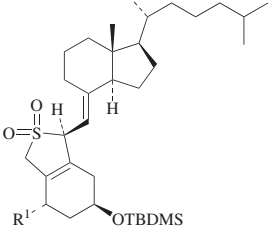
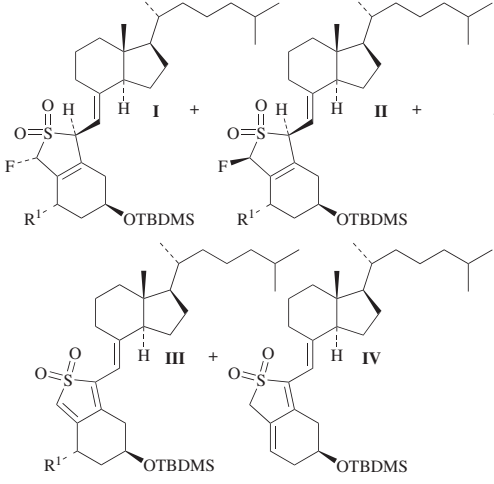
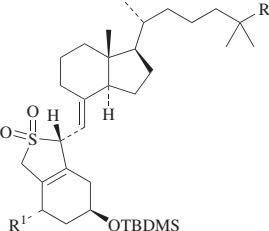
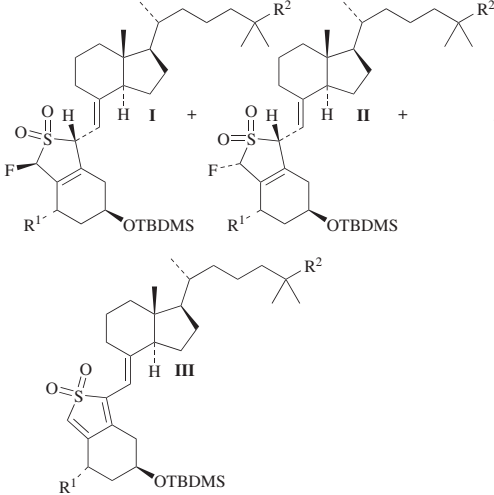
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																														
 C ₃₀	1. NaH, THF, 0° 2. Selectfluor™, DMF, 30 min; then rt, 3 h	 (70)	267																														
 C ₃₃₋₃₆	1. NFSI, HMPA, THF, -78° 2. Base, THF, 10 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>Base</th> <th>I + II + III + IV</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>OH</td> <td>LiHMDS</td> <td>(25)</td> <td>0:0:100</td> </tr> <tr> <td>H</td> <td>LiHMDS</td> <td>(55)</td> <td>55:19:26:0</td> </tr> <tr> <td>OMOM</td> <td>LDA</td> <td>(24)</td> <td>29:46:25:0</td> </tr> <tr> <td>OTMS</td> <td>LiHMDS</td> <td>(37)</td> <td>0:0:100</td> </tr> </tbody> </table>	R ¹	Base	I + II + III + IV	I:II:III:IV	OH	LiHMDS	(25)	0:0:100	H	LiHMDS	(55)	55:19:26:0	OMOM	LDA	(24)	29:46:25:0	OTMS	LiHMDS	(37)	0:0:100	520										
R ¹	Base	I + II + III + IV	I:II:III:IV																														
OH	LiHMDS	(25)	0:0:100																														
H	LiHMDS	(55)	55:19:26:0																														
OMOM	LDA	(24)	29:46:25:0																														
OTMS	LiHMDS	(37)	0:0:100																														
 C ₃₃₋₃₇	1. NFSI, HMPA, THF, -78° 2. Base, THF, 10 min	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Base</th> <th>I + II + III</th> <th>I:II:III</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>LiHMDS</td> <td>(52)</td> <td>52:16:32</td> </tr> <tr> <td>OMOM</td> <td>H</td> <td>LiHMDS</td> <td>(68)</td> <td>52:0:48</td> </tr> <tr> <td>OMOM</td> <td>H</td> <td>LDA</td> <td>(51)</td> <td>65:0:35</td> </tr> <tr> <td>OMOM</td> <td>H</td> <td><i>n</i>-BuLi</td> <td>(10)</td> <td>100:0:0</td> </tr> <tr> <td>OMOM</td> <td>OMOM</td> <td>LiHMDS</td> <td>(44)</td> <td>48:0:52</td> </tr> </tbody> </table>	R ¹	R ²	Base	I + II + III	I:II:III	H	H	LiHMDS	(52)	52:16:32	OMOM	H	LiHMDS	(68)	52:0:48	OMOM	H	LDA	(51)	65:0:35	OMOM	H	<i>n</i> -BuLi	(10)	100:0:0	OMOM	OMOM	LiHMDS	(44)	48:0:52	520, 521
R ¹	R ²	Base	I + II + III	I:II:III																													
H	H	LiHMDS	(52)	52:16:32																													
OMOM	H	LiHMDS	(68)	52:0:48																													
OMOM	H	LDA	(51)	65:0:35																													
OMOM	H	<i>n</i> -BuLi	(10)	100:0:0																													
OMOM	OMOM	LiHMDS	(44)	48:0:52																													

TABLE 11. FLUORODEMETALATIONS




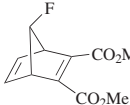
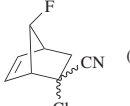
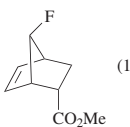
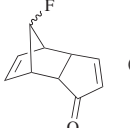


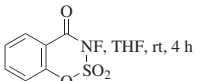
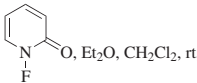


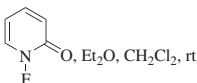


	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
C ₄		1. Formation of 2-thienyllithium 2. NFQN-BF ₄ , Et ₂ O, 0-20°	 (10) ^a	113	
C ₅		MeO ₂ C-C≡C-CO ₂ Me, Selectfluor TM , 0° to rt, 3 h	 (35)	294	
		H ₂ C=C(Cl)CN, Selectfluor TM , -41° to rt, 2.5 h	 (18)	294	
		H ₂ C=CHCO ₂ Me, Selectfluor TM , MeCN, 0° to rt, 3 h	 (17)	294	
		Selectfluor TM , 4-phenyl[1,2,4]triazole-3,5- dione, MeCN, rt, 4 h	 (39)	294	
C ₆		4-MeC ₆ H ₄ O ₂ S N-F, Et ₂ O, rt <i>t</i> -Bu	 I (50) ^a	69	
			THF, rt, 4 h	I (52)	100
			Et ₂ O, CH ₂ Cl ₂ , rt, 16 h	I (15)	98
		Selectfluor TM , Et ₂ O, rt, 16 h	I (61)	173	
		NFOBS, C ₆ D ₆ , 0° to rt, 2 h	I (74)	33	
		NFQN-F, Et ₂ O, 20°	I (26) ^a	113, 115	
		NFQN-OTf, Et ₂ O, 20°	I (26) ^a	114	
		Perfluoropiperidine, Et ₂ O	I (29)	106	
		F-TEDA-OTf, Et ₂ O, rt, 2 h	I (66)	129	
		C ₆		2,4,6-Me ₃ FP-OTf, THF, 0°, 0.17 h	I (58) ^a
NFOBS, C ₆ D ₆ , 0° to rt, 2 h	 (70)			33	
	Et ₂ O, CH ₂ Cl ₂ , rt, 16 h			 (11)	98
NFQN-F, Et ₂ O, 20°	 (20) ^a			113, 115	

TABLE 11. FLUORODEMETALATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																
C ₆ 	NFQN-F, THF, -50° to 20°	(22) ^a	113, 115																																
C ₆₋₁₄ 	Selectfluor TM , MeCN, rt, 24 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>E:Z</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Bu</td> <td>H</td> <td>(58) 50:50</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>H</td> <td>(89) 50:50</td> </tr> <tr> <td>H</td> <td>4-ClC₆H₄</td> <td>H</td> <td>(78) 50:50</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Br</td> <td>(65) 50:50</td> </tr> <tr> <td>H</td> <td>4-MeC₆H₄</td> <td>H</td> <td>(87) 50:50</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>H</td> <td>(71) 85:15</td> </tr> </tbody> </table>	R ¹	R ²	R ³	E:Z	H	Bu	H	(58) 50:50	H	Ph	H	(89) 50:50	H	4-ClC ₆ H ₄	H	(78) 50:50	H	Ph	Br	(65) 50:50	H	4-MeC ₆ H ₄	H	(87) 50:50	Ph	Ph	H	(71) 85:15	286				
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C ₇ 	4-MeC ₆ H ₄ O ₂ S N-F, exo-2-norbornyl <i>n</i> -BuLi, toluene, THF, rt 1. <i>n</i> -BuLi, Et ₂ O, reflux, 1 d 2. (CF ₃ SO ₂) ₂ NF, Et ₂ O, rt, 1 d 1. <i>n</i> -BuLi, Et ₂ O, reflux, 1 d 2. NFQN-OTf, TMEDA, 1 d	(24) I (60) I (60)	69 522 522																																
C ₈ 	 N-F, O, Et ₂ O, CH ₂ Cl ₂ , rt, 16 h 1. <i>n</i> -BuLi, TMEDA, Et ₂ O, reflux, 4 h 2. NFQN-OTf, rt	(5) (71)	98 522																																
	 NF, BuLi, THF, -78°	(—)	75																																
	1. <i>n</i> -BuLi, THF, -78°, 1 h 2. NFSI, THF, -78°, 15 min	(57)	278																																
	1. <i>i</i> -BuLi, THF, Et ₂ O, pentane, -120° 2. N-F, -120° to rt	I + II <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td>(71)</td> <td>(15)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(76)</td> <td>(10)</td> </tr> <tr> <td><i>n</i>-Pr</td> <td><i>n</i>-Pr</td> <td>(85)</td> <td>(3)</td> </tr> <tr> <td><i>i</i>-C₅H₁₁</td> <td>Me</td> <td>(75)</td> <td>(12)</td> </tr> <tr> <td>Me</td> <td><i>i</i>-C₅H₁₁</td> <td>(75)</td> <td>(12)</td> </tr> <tr> <td><i>i</i>-Bu</td> <td>Et</td> <td>(88)</td> <td>(7)</td> </tr> <tr> <td>Et</td> <td><i>i</i>-Bu</td> <td>(83)</td> <td>(7)</td> </tr> </tbody> </table>	R ¹	R ²	I	II	<i>n</i> -C ₆ H ₁₃	H	(71)	(15)	Ph	H	(76)	(10)	<i>n</i> -Pr	<i>n</i> -Pr	(85)	(3)	<i>i</i> -C ₅ H ₁₁	Me	(75)	(12)	Me	<i>i</i> -C ₅ H ₁₁	(75)	(12)	<i>i</i> -Bu	Et	(88)	(7)	Et	<i>i</i> -Bu	(83)	(7)	67, 283
R ¹	R ²	I	II																																
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C _{8-C10} 	1. <i>n</i> -BuLi, THF 2. Fluorinating agent Fluorinating agent	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Temp</th> </tr> </thead> <tbody> <tr> <td>NHMe</td> <td>Me</td> <td>-40° (71)</td> </tr> <tr> <td>NMe₂</td> <td>OMe</td> <td>-40° (55)</td> </tr> <tr> <td>NMe₂</td> <td>OMe</td> <td>-40° (47)</td> </tr> <tr> <td>NEt₂</td> <td>H</td> <td>0° (52)</td> </tr> </tbody> </table>	R ¹	R ²	Temp	NHMe	Me	-40° (71)	NMe ₂	OMe	-40° (55)	NMe ₂	OMe	-40° (47)	NEt ₂	H	0° (52)	276																	
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TABLE 11. FLUORODEMETALATIONS (Continued)

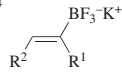
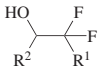
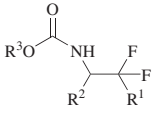

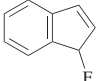
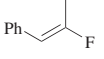
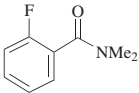
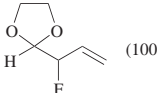
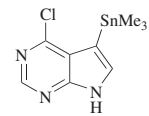
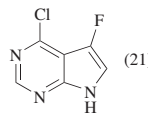
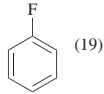
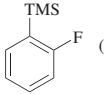
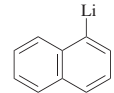
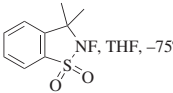
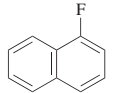
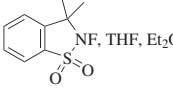
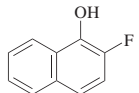
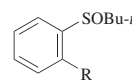
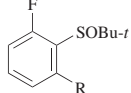
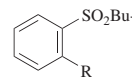
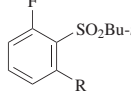
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C_9 	4-MeC ₆ H ₄ O ₂ S $N-F$, exo-2-norbornyl KH, toluene, THF, rt	 (31)	69																								
	NFSI, THF, Et ₂ O, pentane, -105° to rt	 (17)	85																								
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	Selectfluor TM , MeCN, rt, 48 h	 (100) ^a	290																								
	Selectfluor TM , MeCN, rt, 7 h	 (21)	523																								
	Selectfluor TM , MeCN, reflux, 64 h	 (19) +  (21)	289																								
	C_{10} 	 NF, THF, -75°	 I (72)	42																							
 NF, THF, Et ₂ O, 0°		I (17)	42																								
4-MeC ₆ H ₄ O ₂ S $N-F$, <i>t</i> -Bu, KH, THF, rt		 (60)	69																								
C_{10-15} 	1. <i>n</i> -BuLi, THF, -78° 2. Fluorinating agent		<table border="1"> <thead> <tr> <th>R</th> <th>Fluorinating agent</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>NFSI</td> <td>(74)</td> </tr> <tr> <td>H</td> <td>NFOBS</td> <td>(70)</td> </tr> <tr> <td>CONEt₂</td> <td>NFSI</td> <td>(26)</td> </tr> <tr> <td>CONEt₂</td> <td>NFOBS</td> <td>(31)</td> </tr> </tbody> </table>	R	Fluorinating agent	Yield (%)	H	NFSI	(74)	H	NFOBS	(70)	CONEt ₂	NFSI	(26)	CONEt ₂	NFOBS	(31)	276								
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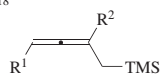
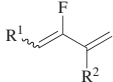
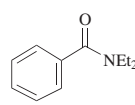
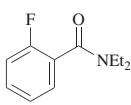
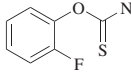
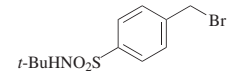
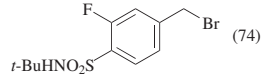
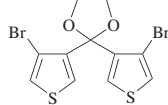
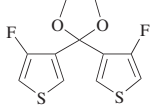
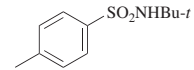
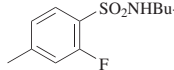
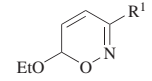
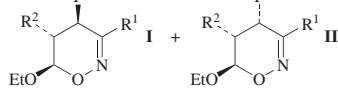
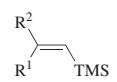


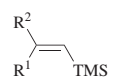

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
	Selectfluor TM , NaHCO ₃ , acetone, rt, 48 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> <th>E:Z</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CH₂OAc</td> <td>(23)</td> <td>—</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(99)</td> <td>—</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td>Me</td> <td>(37)</td> <td>2:1</td> </tr> <tr> <td>BnCH₂</td> <td>H</td> <td>(45)</td> <td>2:1</td> </tr> <tr> <td>H</td> <td>CH₂OBn</td> <td>(79)</td> <td>—</td> </tr> <tr> <td>BnCH₂</td> <td>Me</td> <td>(64)</td> <td>2:1</td> </tr> <tr> <td>BnOCH₂</td> <td>Me</td> <td>(89)</td> <td>2:1</td> </tr> <tr> <td><i>n</i>-C₅H₁₁</td> <td>Ph</td> <td>(66)</td> <td>2:1</td> </tr> <tr> <td>BnCH₂</td> <td>TMS</td> <td>(11)^a</td> <td>3:1</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	E:Z	H	CH ₂ OAc	(23)	—	H	Ph	(99)	—	<i>n</i> -C ₅ H ₁₁	Me	(37)	2:1	BnCH ₂	H	(45)	2:1	H	CH ₂ OBn	(79)	—	BnCH ₂	Me	(64)	2:1	BnOCH ₂	Me	(89)	2:1	<i>n</i> -C ₅ H ₁₁	Ph	(66)	2:1	BnCH ₂	TMS	(11) ^a	3:1	293
		R ¹	R ²	Yield (%)	E:Z																																						
		H	CH ₂ OAc	(23)	—																																						
		H	Ph	(99)	—																																						
		<i>n</i> -C ₅ H ₁₁	Me	(37)	2:1																																						
		BnCH ₂	H	(45)	2:1																																						
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<i>n</i> -C ₅ H ₁₁	Ph	(66)	2:1																																								
BnCH ₂	TMS	(11) ^a	3:1																																								
	1. <i>s</i> -BuLi, TMEDA, THF, -78°, 1 h 2. NFQN-OTf, rt, 16 h	 I (75)	522																																								
	<i>s</i> -BuLi, NFOBS, TMEDA, THF, -78°	I (10)	276																																								
	<i>s</i> -BuLi, NFSI, TMEDA, THF, -78°	 I (62)	276																																								
	<i>s</i> -BuLi, NFOBS, TMEDA, THF, -78°	I (0)	276																																								
	1. <i>n</i> -BuLi, THF, -40° to -30°, 2 h 2. NFSI, THF, 3 h	 (74)	279																																								
	BuLi, NFSI, THF, -78°	 (78)	524																																								
	4-MeC ₆ H ₄ O ₂ S ₂ N-F, exo-2-norbornyl <i>n</i> -BuLi, toluene, THF, rt	 (55)	69																																								
	1. R ² Li, THF, -78° 2. NFSI, -78° to rt	 I + II	525																																								
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>CH(OEt)₂</td> <td><i>n</i>-Bu</td> <td>(58)</td> <td>50:50</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(73)</td> <td>95:5</td> </tr> <tr> <td>Ph</td> <td><i>n</i>-Bu</td> <td>(44)</td> <td>95:5</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	CH(OEt) ₂	<i>n</i> -Bu	(58)	50:50	Ph	Ph	(73)	95:5	Ph	<i>n</i> -Bu	(44)	95:5																									
R ¹	R ²	I + II	I:II																																								
CH(OEt) ₂	<i>n</i> -Bu	(58)	50:50																																								
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Ph	<i>n</i> -Bu	(44)	95:5																																								
	Selectfluor TM , rt, 20 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> <th>Z:E</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>(32)</td> <td>65:35</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td>(45)^a</td> <td>80:20</td> </tr> <tr> <td>Et</td> <td>Ph</td> <td>(57)</td> <td>58:42</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Z:E	Ph	H	(32)	65:35	<i>n</i> -C ₆ H ₁₃	H	(45) ^a	80:20	Et	Ph	(57)	58:42	287																								
	R ¹	R ²	Yield (%)	Z:E																																							
	Ph	H	(32)	65:35																																							
<i>n</i> -C ₆ H ₁₃	H	(45) ^a	80:20																																								
Et	Ph	(57)	58:42																																								
Selectfluor TM , MeCN, rt, 80 h	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C₆H₁₃</td> <td>H</td> <td>(0)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(70)</td> </tr> <tr> <td>Et</td> <td>Ph</td> <td>(86)</td> </tr> <tr> <td><i>n</i>-C₆H₁₃</td> <td>Et</td> <td>(55)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	<i>n</i> -C ₆ H ₁₃	H	(0)	Ph	H	(70)	Et	Ph	(86)	<i>n</i> -C ₆ H ₁₃	Et	(55)	287																										
R ¹	R ²	Yield (%)																																									
<i>n</i> -C ₆ H ₁₃	H	(0)																																									
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<i>n</i> -C ₆ H ₁₃	Et	(55)																																									
	Selectfluor TM , R ³ OH, MeCN, rt, 5 d	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>H</td> <td>Me</td> <td>(75)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>H</td> <td>(45)</td> </tr> <tr> <td>Et</td> <td>Ph</td> <td>Me</td> <td>(79)</td> </tr> <tr> <td>Et</td> <td>Ph</td> <td>H</td> <td>(83)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	Ph	H	Me	(75)	Ph	H	H	(45)	Et	Ph	Me	(79)	Et	Ph	H	(83)	287																				
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TABLE 11. FLUORODEMETALATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																									
$n\text{-C}_{12}\text{H}_{25}\text{MgBr}$ $n\text{-C}_{12}\text{H}_{25}\text{MgCl}$	Selectfluor TM , Et ₂ O, rt, 16 h 2,4,6-Me ₃ FP-OTf, Et ₂ O, 0°, 0.5 h	$n\text{-C}_{12}\text{H}_{25}\text{F}$ (58) $n\text{-C}_{12}\text{H}_{25}\text{F}$ (75) ^a	173 31, 150																									
	$n\text{-BuLi}$, NFSI, THF, 0°		276																									
	$s\text{-BuLi}$, NFSI, THF, -78°		276																									
	$s\text{-BuLi}$, NFOBS, TMEDA, THF, -78°	I (48)	33																									
	1. $t\text{-BuLi}$, THF, Et ₂ O, pentane, -120° 2.	+	67, 283																									
C ₁₃ 	1. $n\text{-BuLi}$, THF, -78° 2. NFSI		526																									
	Selectfluor TM , MeCN, rt, 48 h		290																									
	1. $n\text{-BuLi}$, THF, -78°, 1 h 2. NFSI, THF, -78°, 15 min	 	278																									
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>I + II + III + IV</th> <th>I:II:III:IV</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>F</td> <td>(33)</td> <td>75:25:0:0</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(65)</td> <td>0:0:100:0</td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>(57)</td> <td>100:0:0:0</td> </tr> <tr> <td>F</td> <td>H</td> <td>F</td> <td>(57)</td> <td>0:0:0:100</td> </tr> </tbody> </table>	R ¹	R ²	R ³	I + II + III + IV	I:II:III:IV	H	H	F	(33)	75:25:0:0	H	H	H	(65)	0:0:100:0	F	H	H	(57)	100:0:0:0	F	H	F	(57)	0:0:0:100	
R ¹	R ²	R ³	I + II + III + IV	I:II:III:IV																								
H	H	F	(33)	75:25:0:0																								
H	H	H	(65)	0:0:100:0																								
F	H	H	(57)	100:0:0:0																								
F	H	F	(57)	0:0:0:100																								
C ₁₄ 	1. $n\text{-BuLi}$, Et ₂ O 2.		68																									
	NFSI, THF, Et ₂ O, -78° to rt		85																									
$n\text{-C}_{14}\text{H}_{29}\text{MgBr}$	4-MeC ₆ H ₄ O ₂ S N-F, exo-2-norbornyl toluene, Et ₂ O, -78°	$n\text{-C}_{14}\text{H}_{29}\text{F}$ (15)	69																									
	Selectfluor TM , MeCN, rt, 48 h		290																									

TABLE 11. FLUORODEMETALATIONS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		Selectfluor TM , MeCN, rt, 48 h	 (62)	287
C ₁₄₋₁₇		Selectfluor TM , MeCN, rt, 48 h	 n 1 (74) 4 (33)	290
C ₁₅		Selectfluor TM , MeCN, rt, 48 h	 (69)	290
		Selectfluor TM , MeCN, rt, 48 h	 (82)	290
		Selectfluor TM , MeCN, rt, 48 h	 (48)	287
		<i>n</i> -BuLi, NFSI, THF, -78°	 (59)	527
		Selectfluor TM , MeCN, rt	 I + II (61), I:II = 1:1	291
		1. <i>n</i> -BuLi, THF, -78° 2. NFSI	 (31)	526
C ₁₆		Selectfluor TM , MeCN, rt, 48 h	 (79)	290
		NFSI, NaHCO ₃ , acetone, 48 h	 (39)	293
		1. <i>n</i> -C ₆ H ₁₃ Li, Et ₂ O, -78° 2. NFSI, -78° to rt, 16 h	 (—)	528
C ₁₈		Selectfluor TM , MeCN, rt, 12 h	 (100)	292
		Selectfluor TM , MeCN, MeOH, rt, 12 h	 (40)	205
		Selectfluor TM , MeCN, MeOH, rt, 12 h	 (21)	205

TABLE 11. FLUORODEMETALATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.												
C ₁₉₋₂₅ 	Selectfluor TM , MeCN, rt	 <table border="1"> <tr> <td></td> <td>I + II</td> <td>I:II</td> </tr> <tr> <td>Me</td> <td>(82)</td> <td>1:1</td> </tr> <tr> <td>Bn</td> <td>(95)</td> <td>1.2:1</td> </tr> </table>		I + II	I:II	Me	(82)	1:1	Bn	(95)	1.2:1	291			
	I + II	I:II													
Me	(82)	1:1													
Bn	(95)	1.2:1													
C ₂₀ 	Selectfluor TM (x eq), MeCN, rt, 15 h	 <table border="1"> <tr> <td>x</td> <td>I</td> <td>II</td> </tr> <tr> <td>1</td> <td>(30-40)</td> <td>(50-60)</td> </tr> <tr> <td>2</td> <td>(0-10)</td> <td>(85-95)</td> </tr> <tr> <td>3</td> <td>(0-5)</td> <td>(95)</td> </tr> </table>	x	I	II	1	(30-40)	(50-60)	2	(0-10)	(85-95)	3	(0-5)	(95)	288
x	I	II													
1	(30-40)	(50-60)													
2	(0-10)	(85-95)													
3	(0-5)	(95)													
	1. <i>t</i> -BuLi, toluene, 0° 2. NFSI	(75)	529												
C ₂₀₋₂₁ 	1. <i>t</i> -BuLi, Et ₂ O, -78° 2. NFSI, THF, 0° to rt	 <table border="1"> <tr> <td>R</td> <td></td> </tr> <tr> <td>H</td> <td>(9)</td> </tr> <tr> <td>MeO</td> <td>(40)</td> </tr> </table>	R		H	(9)	MeO	(40)	281						
R															
H	(9)														
MeO	(40)														
C ₂₁ 	Selectfluor TM , MeCN, 80°, 30 min	(45)	285												
	1. <i>t</i> -BuLi, THF, Et ₂ O, pentane, -120° 2. -120° to rt	(80) + (13)	67, 283												
C ₂₂ 	<i>t</i> -BuLi, NFSI, THF, -78°	(42)	282												
	Selectfluor TM , MeCN, rt, 12 h	(52)	530												
	1. <i>t</i> -BuLi, THF, -78° 2. NFSI, 15 min	(24)	531												
C ₂₃ 	Selectfluor TM , MeCN, 80°, 30 min	(35)	285												

TABLE 11. FLUORODEMETALATIONS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.									
C ₂₄		NFSI, <i>n</i> -BuLi, THF, -78°, 1 h	(85)	532									
		Selectfluor TM , MeCN, 80°, 30 min	(42)	285									
C ₂₄₋₂₈		Selectfluor TM , MeCN, 80°, 30 min	<table border="1" style="margin-left: 20px;"> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> <tr> <td>Me</td> <td>EtO₂C</td> <td>(58)</td> </tr> <tr> <td>Me</td> <td>PhCO₂</td> <td>(74)</td> </tr> </table>	R ¹	R ²	Yield (%)	Me	EtO ₂ C	(58)	Me	PhCO ₂	(74)	285
R ¹	R ²	Yield (%)											
Me	EtO ₂ C	(58)											
Me	PhCO ₂	(74)											
C ₂₆		Selectfluor TM , MeCN, 80°, 30 min	(71)	285									
		Selectfluor TM , MeCN, N ₂ , rt, 15 h	(96)	288									
		Selectfluor TM , MeCN, air, rt, 15 h	(84)	288									
C ₂₉		Selectfluor TM , MeCN, rt, 12 h	(50)	530									
C ₃₂₋₄₄		1. NFSI, THF 2. <i>n</i> -BuLi, -78°	<table border="1" style="margin-left: 20px;"> <tr> <th>R</th> <th>Yield (%)</th> </tr> <tr> <td>Bn</td> <td>(—)</td> </tr> <tr> <td>Tr</td> <td>(51)</td> </tr> </table>	R	Yield (%)	Bn	(—)	Tr	(51)	533, 534			
R	Yield (%)												
Bn	(—)												
Tr	(51)												
C ₃₅		1. <i>s</i> -BuLi, THF, -70° to 0° 2. NFSI, -70° to 0°, 30 min	(18) + (3)	280									
C ₃₇		1. <i>n</i> -BuLi, THF, -70°, 10 min 2. NFSI, 20 min	(52)	535									

^a The reported value is the percent conversion based on starting material.

TABLE 12. MISCELLANEOUS FLUORINATIONS






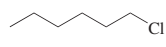
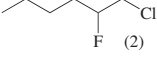
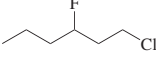
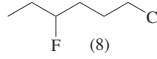
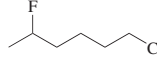
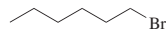
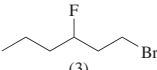
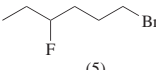
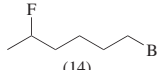
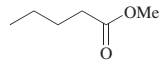
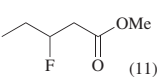
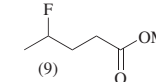




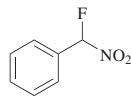
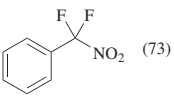
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																																								
C ₃ 	4-MeC ₆ H ₄ O ₂ S ₂ , <i>t</i> -Bu ⁺ N-F, TBAH, toluene, C ₆ H ₆ , -20°	 I (83) ^a	69																																								
	1. Formation of 2-lithio-2-nitropropane 2. NFQN-X, MeOH, 0°	I <table border="1" data-bbox="980 332 1171 493"> <thead> <tr> <th>X</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>(47)</td> </tr> <tr> <td>OTf</td> <td>(72)^a</td> </tr> <tr> <td>CF₃CO₂</td> <td>(56)^a</td> </tr> <tr> <td>C₃F₇CO₂</td> <td>(61)^a</td> </tr> <tr> <td>BF₄</td> <td>(50)^a</td> </tr> </tbody> </table>	X	I	F	(47)	OTf	(72) ^a	CF ₃ CO ₂	(56) ^a	C ₃ F ₇ CO ₂	(61) ^a	BF ₄	(50) ^a	113, 114, 115																												
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BF ₄	(50) ^a																																										
	Perfluoropiperidine, MeONa, MeOH, 0-20°	I (54)	103, 106																																								
C ₅₋₁₂ 	Selectfluor TM , base, MeCN, H ₂ O, 12 h	 I +  II (—)	218																																								
		<table border="1" data-bbox="1015 711 1362 987"> <thead> <tr> <th>R</th> <th>Base</th> <th>I</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>MeCO(CH₂)₂</td> <td>TBAH</td> <td>(88)</td> <td>37:1</td> </tr> <tr> <td>Ph</td> <td>KOH</td> <td>(81)</td> <td>13:1</td> </tr> <tr> <td>4-BrC₆H₄</td> <td>KOH</td> <td>(64)</td> <td>5.2:1</td> </tr> <tr> <td>4-O₂NC₆H₄</td> <td>KOH</td> <td>(83)</td> <td>7:1</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>KOH</td> <td>(79)</td> <td>12.4:1</td> </tr> <tr> <td>Bz</td> <td>KOH</td> <td>(40)</td> <td>1:0</td> </tr> <tr> <td>Bn</td> <td>TBAH</td> <td>(89)</td> <td>33:1</td> </tr> <tr> <td>PhCHOH</td> <td>KOH</td> <td>(30)</td> <td>1:0</td> </tr> <tr> <td>C₁₁H₂₃</td> <td>TBAH</td> <td>(98)</td> <td>1:0</td> </tr> </tbody> </table>	R	Base	I	I:II	MeCO(CH ₂) ₂	TBAH	(88)	37:1	Ph	KOH	(81)	13:1	4-BrC ₆ H ₄	KOH	(64)	5.2:1	4-O ₂ NC ₆ H ₄	KOH	(83)	7:1	4-MeOC ₆ H ₄	KOH	(79)	12.4:1	Bz	KOH	(40)	1:0	Bn	TBAH	(89)	33:1	PhCHOH	KOH	(30)	1:0	C ₁₁ H ₂₃	TBAH	(98)	1:0	
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C ₆ 	Selectfluor TM , MeCN, 82°, 16 h	 (2) +  (4) +  (8) +  (16)	171																																								
	Selectfluor TM , MeCN, 82°, 16 h	 (3) +  (5) +  (14)	171																																								
	Selectfluor TM , MeCN, 82°, 16 h	 (11) +  (9)	171																																								
	(CF ₃ SO ₂) ₂ NF, Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 12 h	 (20) ^a	246																																								
	(CF ₃ SO ₂) ₂ NF, Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 12 h	 (72)	246																																								
C ₇ 	Selectfluor TM , KOH, MeCN, H ₂ O	 (73)	218																																								

TABLE 12. MISCELLANEOUS FLUORINATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇₋₈ 	(Selectfluor TM , KOH, MeCN, H ₂ O, rt, 5-12 h) x 2	 R I I:II H (47) 1:0 218 Br (28) 1:0 O ₂ N (66) 10:1 MeO (41) 5:1	
C ₈ 	Selectfluor TM , NaH, DMF, 12 h		218
	Selectfluor TM , MeCN, 82°, 16 h		171
	(CF ₃ SO ₂) ₂ NF, Na ₂ CO ₃ , CH ₂ Cl ₂ , rt, 12 h		246
C ₈₋₁₄ 	1. Base, THF, -78° 2. NFSI, -78°	 R Base 4-O ₂ N NaHMDS (34) 272 4-Br LDA (19) 4-Me <i>t</i> -BuLi (44) 2-Me <i>t</i> -BuLi (37) 4-MeO <i>t</i> -BuLi (34) 3-MeO <i>t</i> -BuLi (56) 3-Ph <i>t</i> -BuLi (47)	
C ₉ 	1. BuLi, THF, -78° 2. Selectfluor TM , -78° to rt		218
	1. NaH, THF, 0° 2. 2,4,6-Me ₃ FP-OTf, THF, 0° to rt, 12 min		31
	1. NaHMDS, THF, -78° to 0° 2. NFOBS, 0°, 2 h		33
C ₉₋₁₇ 	Selectfluor TM , MeCN, reflux	 Ar R Ph Me (85) 295 Ph Ph (89) Ph 4-MeOC ₆ H ₄ (77) Ph 3-CF ₃ C ₆ H ₄ (90) 2-fluorenyl Me (68) 2-phenanthryl Me (55)	
C ₁₀ 	Selectfluor TM , MeCN, reflux	 I, erythro:threo = 1:6 II	I + II (87), I:II = 1.8:1 295
	NaHMDS, NFOBS, -78° to rt, 2 h		33

TABLE 12. MISCELLANEOUS FLUORINATIONS (Continued)

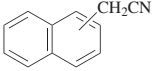
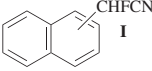
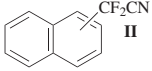
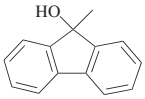
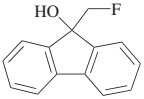
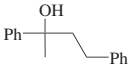
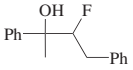
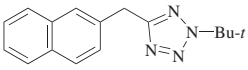
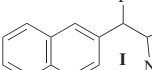
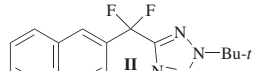
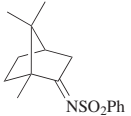
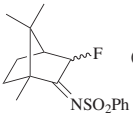
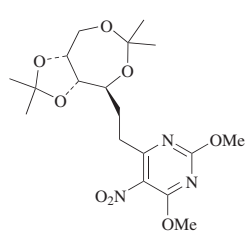
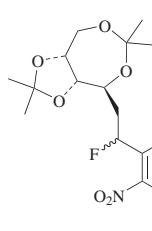
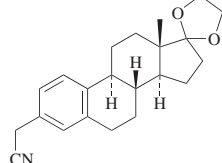
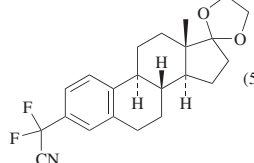
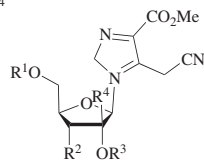
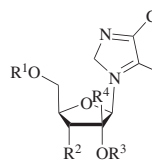
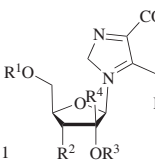
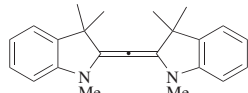
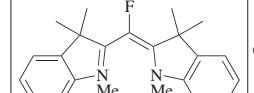
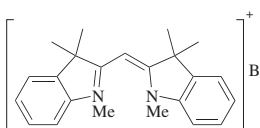
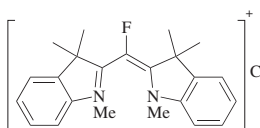
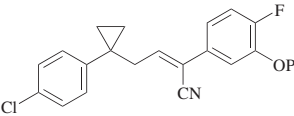
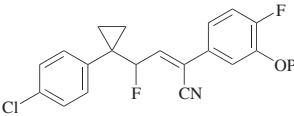
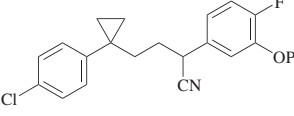
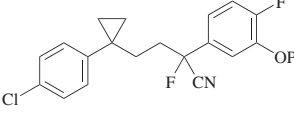
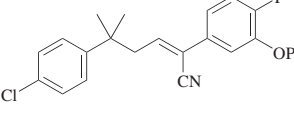
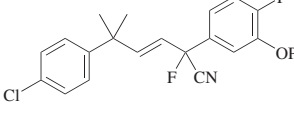
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.																				
C ₁₂ 	1. <i>t</i> -BuLi (x eq), THF, -78° 2. NFSI (y eq), -78°	 I +  II <table border="1" data-bbox="996 312 1277 422"> <thead> <tr> <th>Substrate</th> <th>x</th> <th>y</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>1-naphthyl</td> <td>2.2</td> <td>2.5</td> <td>(0)</td> <td>(46)</td> </tr> <tr> <td>2-naphthyl</td> <td>2.2</td> <td>2.5</td> <td>(0)</td> <td>(50)</td> </tr> <tr> <td>2-naphthyl</td> <td>1.1</td> <td>1.3</td> <td>(60)</td> <td>(0)</td> </tr> </tbody> </table>	Substrate	x	y	I	II	1-naphthyl	2.2	2.5	(0)	(46)	2-naphthyl	2.2	2.5	(0)	(50)	2-naphthyl	1.1	1.3	(60)	(0)	272
Substrate	x	y	I	II																			
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2-naphthyl	1.1	1.3	(60)	(0)																			
C ₁₄ 	Selectfluor™, MeCN, reflux	 (85)	295																				
C ₁₆ 	Selectfluor™, MeCN, reflux	 (85), erythro:threo = 1:6	295																				
	1. <i>t</i> -BuLi (x eq), THF, -78° 2. NFSI (y eq), -78°	 I +  II <table border="1" data-bbox="1260 789 1447 858"> <thead> <tr> <th>x</th> <th>y</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>2.2</td> <td>2.5</td> <td>(0)</td> <td>(56)</td> </tr> <tr> <td>1.1</td> <td>1.3</td> <td>(61)</td> <td>(0)</td> </tr> </tbody> </table>	x	y	I	II	2.2	2.5	(0)	(56)	1.1	1.3	(61)	(0)	272								
x	y	I	II																				
2.2	2.5	(0)	(56)																				
1.1	1.3	(61)	(0)																				
	NaHMDS, NFOBS, -78° to rt, 2 h	 (65), exo:endo = 10:90	33																				
C ₁₈ 	1. KDA, THF, -90° 2. NFSI, -78° to rt	 (20)	536																				
C ₂₂ 	<i>t</i> -BuLi, NFSI, THF, -78°	 (56)	275																				
C ₂₂₋₃₄ 	Selectfluor™, DMF, -45°	 I +  II (I:II = 1:1) <table border="1" data-bbox="1034 1896 1347 2006"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>I + II</th> </tr> </thead> <tbody> <tr> <td>4-MeC₆H₄CO</td> <td>H</td> <td>Ac</td> <td>H</td> <td>(65)</td> </tr> <tr> <td>Bz</td> <td>OBz</td> <td>Bz</td> <td>H</td> <td>(60)</td> </tr> <tr> <td>Bz</td> <td>OBz</td> <td>Bz</td> <td>Me</td> <td>(67)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	I + II	4-MeC ₆ H ₄ CO	H	Ac	H	(65)	Bz	OBz	Bz	H	(60)	Bz	OBz	Bz	Me	(67)	537
R ¹	R ²	R ³	R ⁴	I + II																			
4-MeC ₆ H ₄ CO	H	Ac	H	(65)																			
Bz	OBz	Bz	H	(60)																			
Bz	OBz	Bz	Me	(67)																			
C ₂₃ 	1. NFSI, THF, -5° to rt 2. NaClO ₄	 ⁺ ClO ₄ ⁻ (45)	538																				

TABLE 12. MISCELLANEOUS FLUORINATIONS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	NFSI, CH ₂ Cl ₂ , reflux, 3 d	 (41)	538
	1. LiHMDS, -78° to 0°, 1 h 2. NFSI, -78°	 (33)	539
	1. LiHMDS, -78° to 0°, 1 h 2. NFSI, -78°	 (—)	539
	1. LiHMDS, -78° to 0°, 1 h 2. NFSI, -78°	 (—)	539

^a The reported value is the percent conversion based on starting material.

TABLE 13. AUXILIARY-CONTROLLED DIASTERESELECTIVE ELECTROPHILIC FLUORINATIONS

Substrate	Conditions	Product(s), Yield(s) (%), and Diastereomeric Ratio (dr)	Refs.																																																																	
C ₆₋₁₃ 	1. Ph-CH ₂ -N(Ph)-Li, THF, -78° 2. NFSI, THF, -78°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Et</td> <td>(39)</td> <td>83:17</td> </tr> <tr> <td>Ph</td> <td><i>t</i>-Bu</td> <td>(100)</td> <td>82:18</td> </tr> </tbody> </table>	R ¹	R ²	I + II	I:II	Me	Et	(39)	83:17	Ph	<i>t</i> -Bu	(100)	82:18	312																																																					
R ¹	R ²	I + II	I:II																																																																	
Me	Et	(39)	83:17																																																																	
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C ₁₁₋₁₈ 	1. Base, THF, 0°, 4 h 2. NFSI, -78°	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Base</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>Me</td> <td>LDA</td> <td>(53)</td> <td>77.5:22.5</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>LiHMDS</td> <td>(65)</td> <td>12:88</td> </tr> <tr> <td>—(CH₂)₃—</td> <td></td> <td>LDA</td> <td>(81)</td> <td>1:>99</td> </tr> <tr> <td>—(CH₂)₃—</td> <td></td> <td>LiHMDS</td> <td>(70)</td> <td>12:88</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>LDA</td> <td>(79)</td> <td>89.5:10.5</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>LiHMDS</td> <td>(80)</td> <td>5.5:94.5</td> </tr> <tr> <td>—(CH₂)₄—</td> <td></td> <td>LDA</td> <td>(85)</td> <td>1:>99</td> </tr> <tr> <td>—(CH₂)₄—</td> <td></td> <td>LiHMDS</td> <td>(46)</td> <td>68.5:31.5</td> </tr> <tr> <td><i>n</i>-Pr</td> <td><i>n</i>-Pr</td> <td>LDA</td> <td>(81)</td> <td>82.5:17.5</td> </tr> <tr> <td><i>n</i>-Pr</td> <td><i>n</i>-Pr</td> <td>LiHMDS</td> <td>(75)</td> <td>9:91</td> </tr> <tr> <td>—CH₂N(Bn)CH₂—</td> <td></td> <td>LDA</td> <td>(69)</td> <td>1:>99</td> </tr> <tr> <td>—CH₂N(Bn)CH₂—</td> <td></td> <td>LiHMDS</td> <td>(84)</td> <td>6.5:93.5</td> </tr> </tbody> </table>	R ¹	R ²	Base	I + II	I:II	Me	Me	LDA	(53)	77.5:22.5	Me	Me	LiHMDS	(65)	12:88	—(CH ₂) ₃ —		LDA	(81)	1:>99	—(CH ₂) ₃ —		LiHMDS	(70)	12:88	Et	Et	LDA	(79)	89.5:10.5	Et	Et	LiHMDS	(80)	5.5:94.5	—(CH ₂) ₄ —		LDA	(85)	1:>99	—(CH ₂) ₄ —		LiHMDS	(46)	68.5:31.5	<i>n</i> -Pr	<i>n</i> -Pr	LDA	(81)	82.5:17.5	<i>n</i> -Pr	<i>n</i> -Pr	LiHMDS	(75)	9:91	—CH ₂ N(Bn)CH ₂ —		LDA	(69)	1:>99	—CH ₂ N(Bn)CH ₂ —		LiHMDS	(84)	6.5:93.5	314
R ¹	R ²	Base	I + II	I:II																																																																
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TABLE 13. AUXILIARY-CONTROLLED DIASTERESELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Conditions	Product(s), Yield(s) (%), and Diastereomeric Ratio (dr)	Refs.																																																																	
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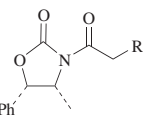
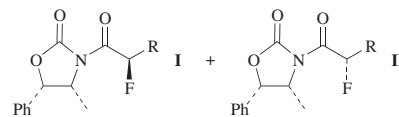
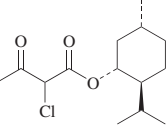
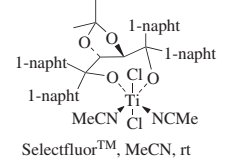
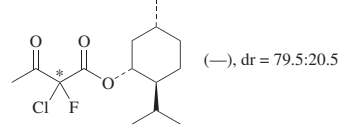
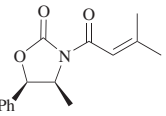
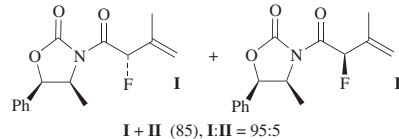
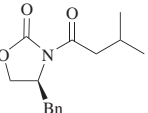
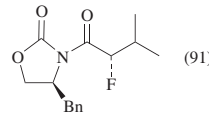
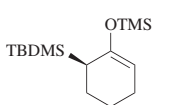
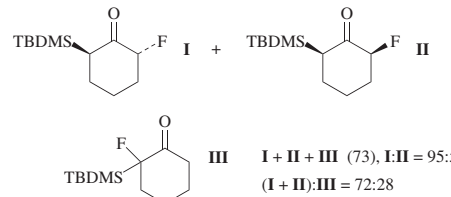
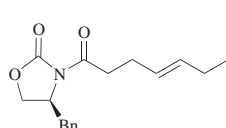
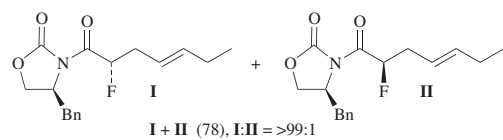
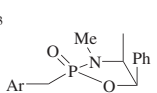
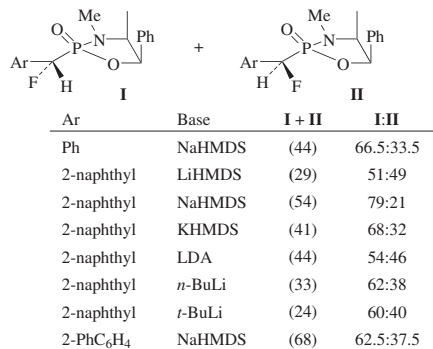
C ₁₃₋₁₈		NaHMDS, NFSI (inverse addition), THF, -78°		298												
			<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(77)</td> <td>93:7</td> </tr> <tr> <td>CH=CH₂</td> <td>(69)</td> <td>92:8</td> </tr> <tr> <td>Ph</td> <td>(85)</td> <td>>98.5:1.5</td> </tr> </tbody> </table>	R	I + II	I:II	Me	(77)	93:7	CH=CH ₂	(69)	92:8	Ph	(85)	>98.5:1.5	
R	I + II	I:II														
Me	(77)	93:7														
CH=CH ₂	(69)	92:8														
Ph	(85)	>98.5:1.5														
C ₁₄		 Selectfluor TM , MeCN, rt	 (-), dr = 79.5:20.5	309												
C ₁₅		NaHMDS, NFOBS, THF, -78° to rt	 I + II (85), I:II = 95:5	297												
		LiHMDS, NFSI, THF	 (91)	540												

TABLE 13. AUXILIARY-CONTROLLED DIASTERESELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Conditions	Product(s), Yield(s) (%), and Diastereomeric Ratio (dr)	Refs.																																				
C ₁₅ 	NFSI, THF, -78° to rt	 I + II + III (73), I:II = 95:5, (I + II):III = 72:28	314																																				
	Selectfluor TM , MeCN, 0° to rt	I + II + III (49), I:II = 83:17, (I + II):III = 94:6	314																																				
C ₁₇ 	LiHMDS, NFSI, THF, -78°	 I + II (78), I:II = >99:1	300																																				
C ₁₇₋₂₃ 	1. Base, THF, -78° 2. NFSI, -78°	 <table border="1"> <thead> <tr> <th>Ar</th> <th>Base</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>NaHMDS</td> <td>(44)</td> <td>66.5:33.5</td> </tr> <tr> <td>2-naphthyl</td> <td>LiHMDS</td> <td>(29)</td> <td>51:49</td> </tr> <tr> <td>2-naphthyl</td> <td>NaHMDS</td> <td>(54)</td> <td>79:21</td> </tr> <tr> <td>2-naphthyl</td> <td>KHMDS</td> <td>(41)</td> <td>68:32</td> </tr> <tr> <td>2-naphthyl</td> <td>LDA</td> <td>(44)</td> <td>54:46</td> </tr> <tr> <td>2-naphthyl</td> <td><i>n</i>-BuLi</td> <td>(33)</td> <td>62:38</td> </tr> <tr> <td>2-naphthyl</td> <td><i>t</i>-BuLi</td> <td>(24)</td> <td>60:40</td> </tr> <tr> <td>2-PhC₆H₄</td> <td>NaHMDS</td> <td>(68)</td> <td>62.5:37.5</td> </tr> </tbody> </table>	Ar	Base	I + II	I:II	Ph	NaHMDS	(44)	66.5:33.5	2-naphthyl	LiHMDS	(29)	51:49	2-naphthyl	NaHMDS	(54)	79:21	2-naphthyl	KHMDS	(41)	68:32	2-naphthyl	LDA	(44)	54:46	2-naphthyl	<i>n</i> -BuLi	(33)	62:38	2-naphthyl	<i>t</i> -BuLi	(24)	60:40	2-PhC ₆ H ₄	NaHMDS	(68)	62.5:37.5	315
Ar	Base	I + II	I:II																																				
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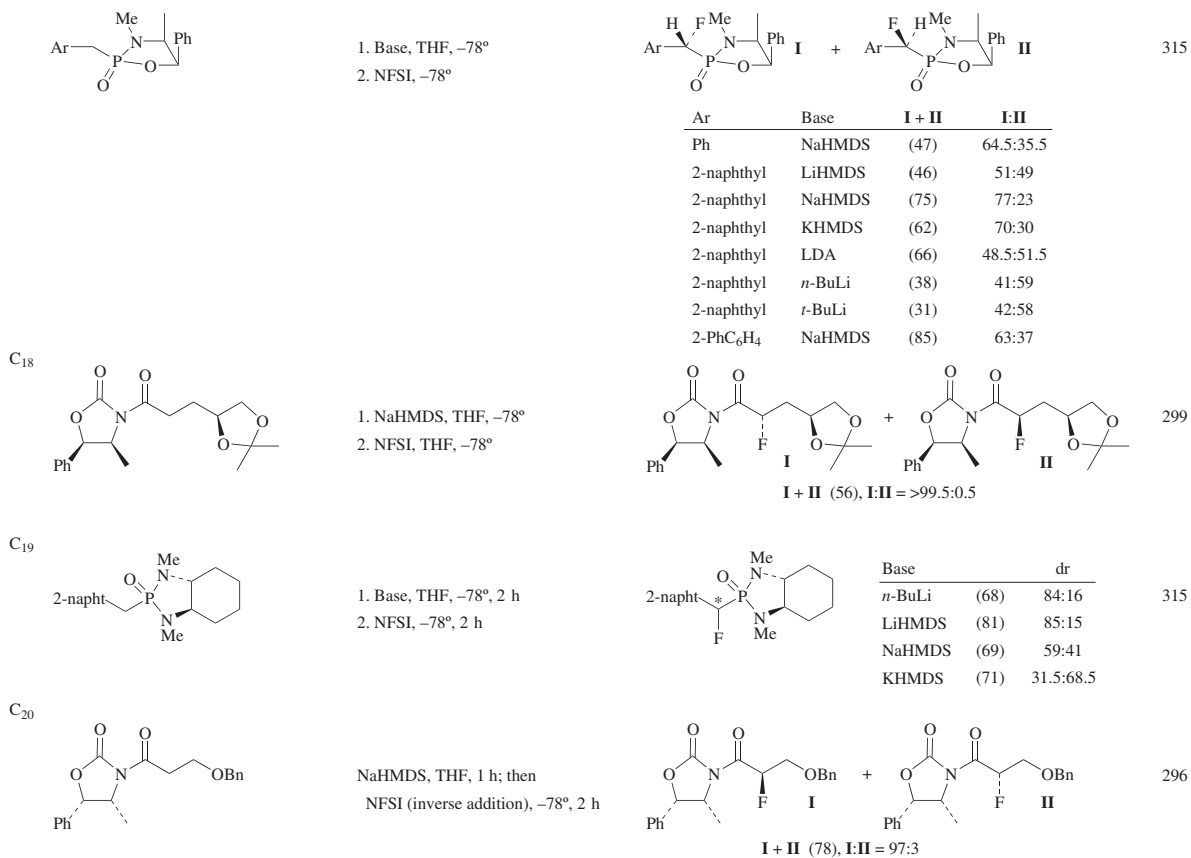


TABLE 13. AUXILIARY-CONTROLLED DIASTERESELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Conditions	Product(s), Yield(s) (%), and Diastereomeric Ratio (dr)	Refs.																															
	$[\text{Ph} \text{---} \text{N} \text{---} \text{M} \text{---} \text{N} \text{---} \text{Ph}]^{2+} \cdot 2\text{X}^-$, NFSI, THF		<table border="1"> <thead> <tr> <th>M</th> <th>X</th> <th>Temp</th> <th>Yield (%)</th> <th>dr</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>OTf</td> <td>-10°</td> <td>(99)</td> <td>77:23</td> </tr> <tr> <td>Ni</td> <td>ClO₄</td> <td>-10°</td> <td>(88)</td> <td>16.5:83.5</td> </tr> <tr> <td>Cu</td> <td>OTf</td> <td>-40°</td> <td>(94)</td> <td>58.5:41.5</td> </tr> <tr> <td>Ni</td> <td>ClO₄</td> <td>-40°</td> <td>(95)</td> <td>11.5:88.5</td> </tr> <tr> <td>Cu</td> <td>OTf</td> <td>20°</td> <td>(86)</td> <td>77.5:22.5</td> </tr> </tbody> </table>	M	X	Temp	Yield (%)	dr	Cu	OTf	-10°	(99)	77:23	Ni	ClO ₄	-10°	(88)	16.5:83.5	Cu	OTf	-40°	(94)	58.5:41.5	Ni	ClO ₄	-40°	(95)	11.5:88.5	Cu	OTf	20°	(86)	77.5:22.5	310
		M	X	Temp	Yield (%)	dr																												
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	Ni(ClO ₄) ₂ · 6H ₂ O, NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 2 h																																	
	NaH, Selectfluor TM , DMF, -50° to rt		(94), dr = (—)	541																														
			1. NaH, DMF, 0° 2. 2,4,6-Me ₃ FP-OTf, HMPA, THF, -78°		462																													
		<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(>91)</td> <td>94.5:5.5</td> </tr> <tr> <td>Et</td> <td>(>90)</td> <td>95:5</td> </tr> <tr> <td>Bn</td> <td>(>90)</td> <td>95:5</td> </tr> </tbody> </table>	R	I + II	I:II	Me	(>91)	94.5:5.5	Et	(>90)	95:5	Bn	(>90)	95:5																				
R	I + II	I:II																																
Me	(>91)	94.5:5.5																																
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Bn	(>90)	95:5																																

	LiHMDS, 2,4,6-Me ₃ FP-OTf, THF, -78° to rt		305, 306															
		<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(87)</td> <td>79:21</td> </tr> <tr> <td>Et</td> <td>(96)</td> <td>33:67</td> </tr> <tr> <td><i>n</i>-Pr</td> <td>(96)</td> <td>33:67</td> </tr> <tr> <td>Bn</td> <td>(88)</td> <td>38:62</td> </tr> </tbody> </table>	R	I + II	I:II	Me	(87)	79:21	Et	(96)	33:67	<i>n</i> -Pr	(96)	33:67	Bn	(88)	38:62	
R	I + II	I:II																
Me	(87)	79:21																
Et	(96)	33:67																
<i>n</i> -Pr	(96)	33:67																
Bn	(88)	38:62																
<p>C₂₂</p>	NaHMDS, THF, 1 h; then NFOBS, -78°, 2 h		302, 303															
	LiHMDS, THF, 1 h; then NFOBS, -78°, 2 h	I + II (80), I:II = 94:6	302, 303															
	LiHMDS, THF, -78°, 1 h; then NFSI, -78°, 2 h	I + II (76), I:II = >98.5:1.5	302, 303															
<p>C₂₄</p>	2,4,6-Me ₃ FP-OTf, CH ₂ Cl ₂ , rt, 30 h		542															
<p>C₂₇</p>	NaHMDS, NFSI, THF, -78°, 2 h		304															

TABLE 13. AUXILIARY-CONTROLLED DIASTERESELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Conditions	Product(s), Yield(s) (%), and Diastereomeric Ratio (dr)	Refs.						
<p>C₂₇</p> <p>Ar = 4-MeOC₆H₄</p>	1. NaH, DMF, 0° 2. 2,4,6-Me ₃ FP-OTf, HMPA, THF, -78°	<p>I + II (>90), I:II = 83.5:16.5</p>	462						
<p>C₂₇₋₃₃</p>	1. LiHMDS, THF, -78° 2. NFSI, -78°	<table border="1"> <thead> <tr> <th>R</th> <th>% dc</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>(>98)^a</td> </tr> <tr> <td>Bn</td> <td>(86)</td> </tr> </tbody> </table>	R	% dc	Me	(>98) ^a	Bn	(86)	339
R	% dc								
Me	(>98) ^a								
Bn	(86)								
<p>C₃₂</p> <p>R = </p>	Selectfluor TM , MeCN, rt	<p>I (≥80), dr = 60:40</p>	308						
	1-napht, 1-napht, 1-napht, MeCN, Cl, NCMe, Selectfluor TM , MeCN, rt	<p>I (≥80), dr = 80:20</p>	308						

^aThe reported value is the percent conversion based on starting material.

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS


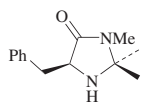
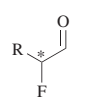

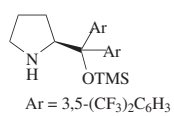


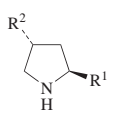


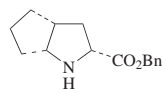

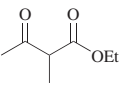
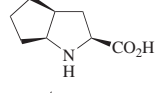
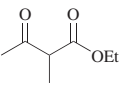
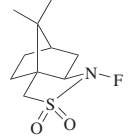
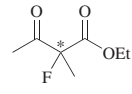
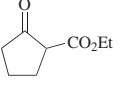
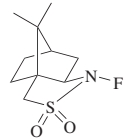
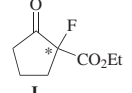
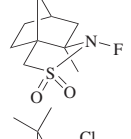
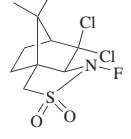
Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
See Chart 2 at the beginning of the Tabular Survey for catalyst structures that are indicated by bold numbers.				
C ₅₋₁₀ 	 (100 mol%)	NFSI, DMF, 4°	 R <i>i</i> -Pr (74), 96 <i>n</i> -Bu (40), 92 <i>n</i> -C ₆ H ₁₃ (94), 86 Bn (97), 88 <i>n</i> -C ₈ H ₁₇ (90), 88 oct-2-enyl (59), 93	368
C ₅₋₁₂ 	 Ar = 3,5-(CF ₃) ₂ C ₆ H ₃	1. NFSI, MTBE, rt 2. NaBH ₄ , MeOH, rt	 R Time <i>i</i> -Pr 6 h (>95) ^a , 96 <i>n</i> -Bu 28 h (>90) ^a , 91 <i>t</i> -Bu 2 h (>90) ^a , 97 <i>n</i> -C ₆ H ₁₃ 4 h (55), 96 <i>c</i> -C ₆ H ₁₁ 5 h (69), 96 Bn 2 h (74), 93 1-adamantyl 2 h (75), 96 BnO(CH ₂) ₃ 2 h (64), 91	366
C ₆ 		Selectfluor TM , MeCN, rt	 R ¹ R ² CO ₂ H H (43) ^b , 29 CONH ₂ H (42) ^b , 17 CH ₂ OMe H (56) ^b , 3 CO ₂ H OH (56) ^b , 34 CO ₂ H OTBDMS (60) ^b , 32 C(OH)Ph ₂ H (10) ^b , 2	365

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₆ 		Selectfluor TM , MeCN, rt	 (16) ^b , 7 I	365
C ₇ 		Selectfluor TM , MeCN, rt	I (35) ^b , 9	365
C ₇ 		LiH, Et ₂ O, rt	 (31), ≤10	321
C ₈ 		NaH, Et ₂ O, 0° to rt	 (63), 70 I	321
		KH, toluene, THF, 0° to rt	I (≤5), ≤10	321
		NaHMDS, THF, -78° to rt	I (41), 10	323
	"	NaH, Et ₂ O, -78° to rt	I (59), 34	323

	NaH, Et ₂ O, -78°	I (57), ≤5	323
	NaH, THF, 0°	I (23), 6	325
	NaH, THF, 0° to rt	I (20), 14	325
	NaH, THF, 0°	I (6), 30	325
F-CD-BF ₄	NaH, THF, MeCN, -40° to 20°	I (98), 40	332
	 NFSI, EtOH, 40°	 (57), 94	360
	 NFSI, THF, <i>i</i> -PrOH, -10°, 4 h	 I (79) ^b , 26	367
	 NFSI, THF, <i>i</i> -PrOH, -10°, 0.3 h	I (96) ^b , 63	367

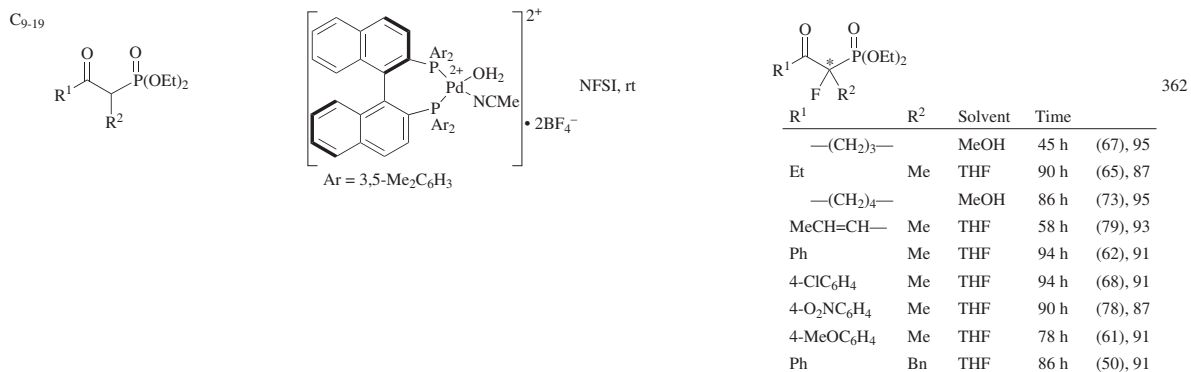
TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																															
	 CHCl ₂ CO ₂ ⁻	1. NFSI, THF, <i>i</i> -PrOH, -10° 2. NaBH ₄ , CH ₂ Cl ₂	 R F OH	<table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td><i>c</i>-C₆H₁₁</td> <td>(96)</td> <td>99</td> </tr> <tr> <td>Ph</td> <td>(54)</td> <td>99</td> </tr> <tr> <td>Bn</td> <td>(71)</td> <td>96</td> </tr> <tr> <td>EtO₂C(CH₂)₄</td> <td>(77)</td> <td>91</td> </tr> <tr> <td>Z-oct-5-enyl</td> <td>(81)</td> <td>94</td> </tr> <tr> <td><i>n</i>-C₉H₁₉</td> <td>(70)</td> <td>94</td> </tr> <tr> <td>non-8-enyl</td> <td>(79)</td> <td>94</td> </tr> <tr> <td><i>N</i>-Boc 4-piperidinyl</td> <td>(85)</td> <td>92</td> </tr> <tr> <td>1-adamantyl</td> <td>(82)</td> <td>98</td> </tr> </tbody> </table>	R	Yield (%)	% ee	<i>c</i> -C ₆ H ₁₁	(96)	99	Ph	(54)	99	Bn	(71)	96	EtO ₂ C(CH ₂) ₄	(77)	91	Z-oct-5-enyl	(81)	94	<i>n</i> -C ₉ H ₁₉	(70)	94	non-8-enyl	(79)	94	<i>N</i> -Boc 4-piperidinyl	(85)	92	1-adamantyl	(82)	98	367
R	Yield (%)	% ee																																	
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		NaHMDS, THF, -78° to rt	 Ph F OH (41), 0	323																															
	1	NFSI, EtOH, 20°	 OBu- <i>t</i> F (49), 91	351																															
	(DHQD) ₂ PYR, Selectfluor TM	MeCN, 0°, 2 d	 I (94), 67	334																															
	(DHQN) ₂ AQN, Selectfluor TM	MeCN, 0°, 2 d	I (56), 52	334																															
	 Ar = 3,5-(CF ₃) ₂ C ₆ H ₃	1. NFSI, toluene, 60° 2. NaBH ₄ , MeOH, rt	 Ph F OH (78), 48	366																															

	NFSI, THF, rt, 24 h		I (77), 16	368																																																																																
	NFSI, THF, rt, 24 h		I (75), 28	368																																																																																
	NFSI, THF, rt, 24 h		I	368																																																																																
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>CO₂H</td> <td>H</td> <td>H</td> <td>(94), 23</td> </tr> <tr> <td>CO₂Bu-<i>t</i></td> <td>H</td> <td>H</td> <td>(90), 13</td> </tr> <tr> <td>morpholinylcarbonyl</td> <td>H</td> <td>H</td> <td>(63), 8</td> </tr> <tr> <td>CO₂Bn</td> <td>H</td> <td>H</td> <td>(73), 28</td> </tr> <tr> <td>CH₂OH</td> <td>H</td> <td>H</td> <td>(70), 24</td> </tr> <tr> <td>CH₂OMe</td> <td>H</td> <td>H</td> <td>(83), 24</td> </tr> <tr> <td>CH₂OTIPS</td> <td>H</td> <td>H</td> <td>(90), 44</td> </tr> <tr> <td>CH₂NH₂</td> <td>H</td> <td>H</td> <td>(99), 12</td> </tr> <tr> <td>CH₂NHBu-<i>n</i></td> <td>H</td> <td>H</td> <td>(30), 12</td> </tr> <tr> <td>pyrrolidinylmethyl</td> <td>H</td> <td>H</td> <td>(84), 12</td> </tr> <tr> <td>pyrrolidinylmethyl, TFA</td> <td>H</td> <td>H</td> <td>(85), 16</td> </tr> <tr> <td>morpholinylmethyl</td> <td>H</td> <td>H</td> <td>(66), 16</td> </tr> <tr> <td>CH₂NHPh</td> <td>H</td> <td>H</td> <td>(88), 0</td> </tr> <tr> <td>5-1<i>H</i>-tetrazolyl</td> <td>H</td> <td>H</td> <td>(98), 38</td> </tr> <tr> <td>CO₂H</td> <td>OH</td> <td>H</td> <td>(93), 22</td> </tr> <tr> <td>CO₂H</td> <td>OBu-<i>t</i></td> <td>H</td> <td>(65), 27</td> </tr> <tr> <td>C(OH)Ph₂</td> <td>H</td> <td>H</td> <td>(34), 24</td> </tr> <tr> <td>Me</td> <td>H</td> <td>Me</td> <td>(19), 18</td> </tr> <tr> <td>CH₂OMe</td> <td>H</td> <td>CH₂OMe</td> <td>(42), 14</td> </tr> </tbody> </table>	R ¹	R ²	R ³		CO ₂ H	H	H	(94), 23	CO ₂ Bu- <i>t</i>	H	H	(90), 13	morpholinylcarbonyl	H	H	(63), 8	CO ₂ Bn	H	H	(73), 28	CH ₂ OH	H	H	(70), 24	CH ₂ OMe	H	H	(83), 24	CH ₂ OTIPS	H	H	(90), 44	CH ₂ NH ₂	H	H	(99), 12	CH ₂ NHBu- <i>n</i>	H	H	(30), 12	pyrrolidinylmethyl	H	H	(84), 12	pyrrolidinylmethyl, TFA	H	H	(85), 16	morpholinylmethyl	H	H	(66), 16	CH ₂ NHPh	H	H	(88), 0	5-1 <i>H</i> -tetrazolyl	H	H	(98), 38	CO ₂ H	OH	H	(93), 22	CO ₂ H	OBu- <i>t</i>	H	(65), 27	C(OH)Ph ₂	H	H	(34), 24	Me	H	Me	(19), 18	CH ₂ OMe	H	CH ₂ OMe	(42), 14	
R ¹	R ²	R ³																																																																																		
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TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.								
		NFSI, DMF, 4°	 <table border="1"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>CH₂OTIPS</td> <td>(92), 40</td> </tr> <tr> <td>5-1<i>H</i>-tetrazolyl</td> <td>(99), 45</td> </tr> <tr> <td>CO₂H</td> <td>(93), 28</td> </tr> </tbody> </table>	R	I	CH ₂ OTIPS	(92), 40	5-1 <i>H</i> -tetrazolyl	(99), 45	CO ₂ H	(93), 28	368
R	I											
CH ₂ OTIPS	(92), 40											
5-1 <i>H</i> -tetrazolyl	(99), 45											
CO ₂ H	(93), 28											
		NFSI, CH ₂ Cl ₂ , rt, 1 h	 (17) ^b , 48	366								
		NFSI, CH ₂ Cl ₂ , rt, 1 h	<table border="1"> <thead> <tr> <th>R</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>OH</td> <td>(<10)^b, 30</td> </tr> <tr> <td>NH₂</td> <td>(24)^b, 40</td> </tr> </tbody> </table>	R	I	OH	(<10) ^b , 30	NH ₂	(24) ^b , 40	366		
R	I											
OH	(<10) ^b , 30											
NH ₂	(24) ^b , 40											
	 Ar = 3,5-Me ₂ C ₆ H ₃	NFSI, EtOH, rt	 (82), 95	360								
	 Zn(ClO ₄) ₂	NFSI, CH ₂ Cl ₂ , rt	I (38), 91	358								



613

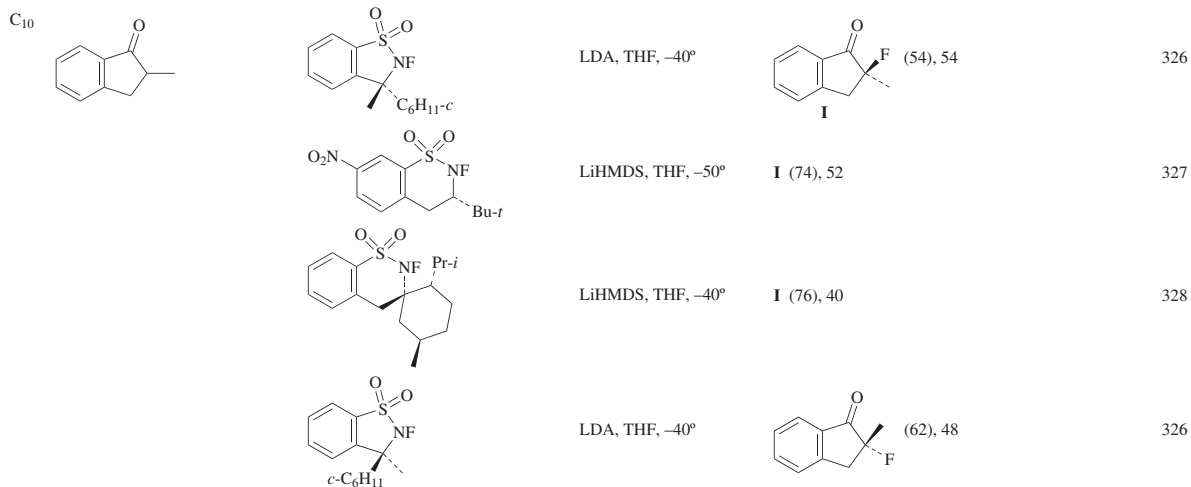
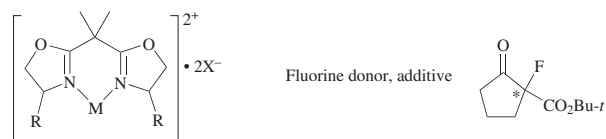


TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₀				
		LiHMDS, THF, -40°	I (69), 13	328
	1	NFSI, EtOH, 20°	I (90), 92	351
	2	NFSI, [bmim][BF ₄], rt	I (94), 91	352
	4	FP-BF ₄ , THF, HFIP, rt	I (58), 67	359
	4	FP-BF ₄ , THF, rt	I (65), 50	359
	5 • ZnEt₂	NFSI, Et ₂ O, rt	I (92), 36	359
		NFSI, CH ₂ Cl ₂ , rt	I (69), 92	347
		NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 2 h	I (84), 93	311

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R	M	X	Fluorine donor	Additive	Solvent	Temp	Time	
(<i>R</i>)-Ph	Cu	OTf	Selectfluor TM	none	CH ₂ Cl ₂	rt	16 h	(97), 36
(<i>R</i>)-Ph	Cu	OTf	FP-OTf	none	CH ₂ Cl ₂	rt	3 h	(98), 35
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	CH ₂ Cl ₂	rt	3 h	(84), 47
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	THF	rt	0.5 h	(96), 57
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	toluene	rt	2 h	(90), 73
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	Et ₂ O	rt	0.5 h	(95), 74
(<i>R</i>)-Ph	Mg	ClO ₄	NFSI	none	Et ₂ O	rt	48 h	(80), 7
(<i>R</i>)-Ph	Zn	OTf	NFSI	none	Et ₂ O	rt	12 h	(84), 74
(<i>R</i>)-Ph	Zn	OTf	NFSI	none	toluene	rt	48 h	(74), 47
(<i>R</i>)-Ph	Sc	OTf	NFSI	none	Et ₂ O	rt	2.5 h	(86), 17
(<i>R</i>)-Ph	La	OTf	NFSI	none	Et ₂ O	rt	48 h	(84), 14
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	Et ₂ O	rt	0.5 h	(96), 73
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	Et ₂ O	rt	0.5 h	(89), 72
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	Et ₂ O	0°	4 h	(86), 69
(<i>R</i>)-Ph	Cu	OTf	NFSI	none	Et ₂ O	-20°	48 h	(82), 72
(<i>R</i>)-Bn	Cu	OTf	NFSI	none	Et ₂ O	rt	2 h	(87), 5
(<i>S</i>)- <i>t</i> -Bu	Cu	OTf	NFSI	none	Et ₂ O	rt	2 h	(91), 20
(<i>R</i>)-Ph	Cu	OTf	NFSI	<i>i</i> -Pr ₂ NEt	Et ₂ O	rt	12 h	(90), 70
(<i>R</i>)-Ph	Cu	OTf	NFSI	2,6-lutidine	Et ₂ O	rt	12 h	(89), 70
(<i>R</i>)-Ph	Cu	OTf	NFSI	<i>t</i> -BuOK	Et ₂ O	rt	4 h	(94), 4
(<i>R</i>)-Ph	Cu	OTf	NFSI	3 Å MS	Et ₂ O	rt	36 h	(72), 70
(<i>R</i>)-Ph	Cu	OTf	NFSI	HFIP	Et ₂ O	rt	0.5 h	(96), 85
(<i>R</i>)-Ph	Cu	OTf	NFSI	HFIP	Et ₂ O	0°	0.5 h	(94), 82

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	2	NFSI, EtOH, 20°	(88), 87	351
		NFSI, [bmim][BF ₄], rt	I (80), 85	352
	(DHQD) ₂ PYR, Selectfluor TM	MeCN, 0°, 2 d	(79), 76	334
		(DHQN) ₂ AQN, Selectfluor TM	MeCN, 0°, 2 d	I (90), 58
	 	1. Catalyst (20 mol%), CHCl ₃ , -20° 2. E, 24 h E = CO ₂ Bu- <i>t</i> 3. NFSI, THF/ <i>i</i> -PrOH (9:1)	(60), 99, dr = 3:1	369
		1. E, 24 h E = CO ₂ Bu- <i>t</i> CHCl ₃ , -20°, 10 min 2. A (7.5 mol%), 30 h 3. NFSI, B (30 mol%), THF/ <i>i</i> -PrOH (9:1), -10°, 12 h	I (62), 99, dr = 9:1	369

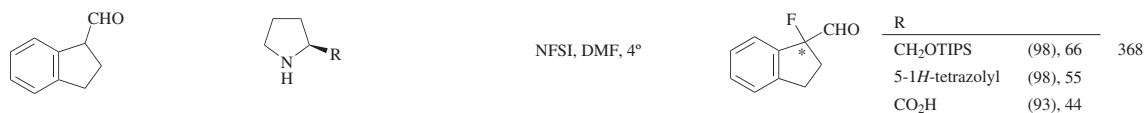
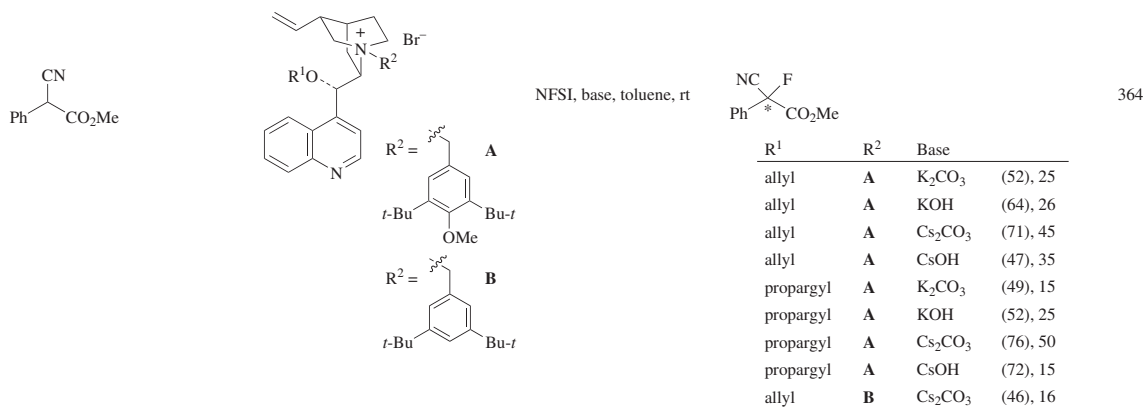
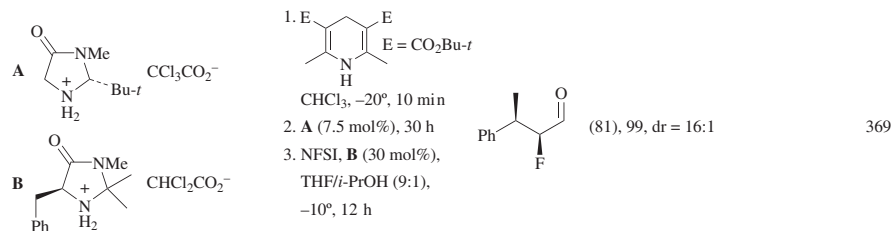


TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																																
	(30 mol%)	NFSI, DMF, 4°	<table border="1"> <thead> <tr> <th>R^1</th> <th>R^2</th> <th>Yield (%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CO_2H</td> <td>(29)^b</td> <td>29</td> </tr> <tr> <td>H</td> <td>CONH_2</td> <td>(50)^b</td> <td>22</td> </tr> <tr> <td>H</td> <td>CH_2OMe</td> <td>(30)^b</td> <td>32</td> </tr> <tr> <td>H</td> <td>CH_2OTIPS</td> <td>(30)^b</td> <td>37</td> </tr> <tr> <td>H</td> <td>5-1<i>H</i>-tetrazolyl</td> <td>(32)^b</td> <td>30</td> </tr> <tr> <td>H</td> <td>$\text{C}(\text{OH})\text{Ph}_2$</td> <td>(9)^b</td> <td>50</td> </tr> <tr> <td>CH_2OMe</td> <td>CH_2OMe</td> <td>(21)^b</td> <td>46</td> </tr> </tbody> </table>	R^1	R^2	Yield (%)	ee (%)	H	CO_2H	(29) ^b	29	H	CONH_2	(50) ^b	22	H	CH_2OMe	(30) ^b	32	H	CH_2OTIPS	(30) ^b	37	H	5-1 <i>H</i> -tetrazolyl	(32) ^b	30	H	$\text{C}(\text{OH})\text{Ph}_2$	(9) ^b	50	CH_2OMe	CH_2OMe	(21) ^b	46	368
R^1	R^2	Yield (%)	ee (%)																																	
H	CO_2H	(29) ^b	29																																	
H	CONH_2	(50) ^b	22																																	
H	CH_2OMe	(30) ^b	32																																	
H	CH_2OTIPS	(30) ^b	37																																	
H	5-1 <i>H</i> -tetrazolyl	(32) ^b	30																																	
H	$\text{C}(\text{OH})\text{Ph}_2$	(9) ^b	50																																	
CH_2OMe	CH_2OMe	(21) ^b	46																																	
	 Ar = 3,5-Me ₂ C ₆ H ₃	$\cdot 2\text{TfO}^-$ NFSI, EtOH, rt	 (93), 96	360																																
	 $\cdot 2\text{PF}_6^-$	NFSI, MeOH, rt	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>Yield (%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>12.5 h</td> <td>(56)</td> <td>67</td> </tr> <tr> <td>Et</td> <td>13.5 h</td> <td>(79)</td> <td>79</td> </tr> <tr> <td>Bn</td> <td>12.5 h</td> <td>(75)</td> <td>81</td> </tr> <tr> <td>$\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2-4$</td> <td>12 h</td> <td>(75)</td> <td>75</td> </tr> <tr> <td>CHPh₂</td> <td>10 h</td> <td>(62)</td> <td>83</td> </tr> </tbody> </table>	R	Time	Yield (%)	ee (%)	Me	12.5 h	(56)	67	Et	13.5 h	(79)	79	Bn	12.5 h	(75)	81	$\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2-4$	12 h	(75)	75	CHPh ₂	10 h	(62)	83	354								
R	Time	Yield (%)	ee (%)																																	
Me	12.5 h	(56)	67																																	
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$\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2-4$	12 h	(75)	75																																	
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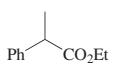
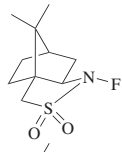
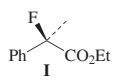
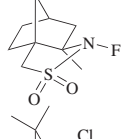
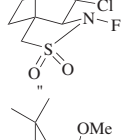
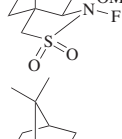
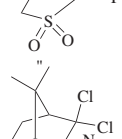
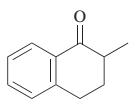
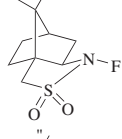
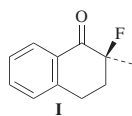
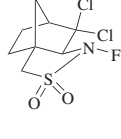

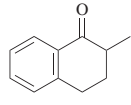
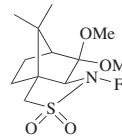
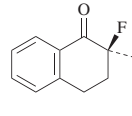
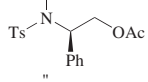
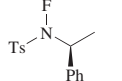

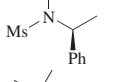
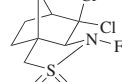



Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₁ 		LDA, THF, -78° to rt	 (27), 35	321
		LDA, THF, -78° to rt	I (34), ≤10	321
		LDA, THF, -78° to rt	I (62), 29	323
		NaHMDS, THF, -78°	I (54), 33	323
		NaHMDS, THF, -78°	I (55), <5	323
		LDA, THF, -78° to rt	 (<5), 35	321
		NaH, Et ₂ O, 0° to rt	I (28), 25	323
		LDA, THF, -78°	I (31), 10	323

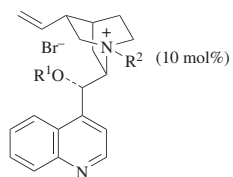
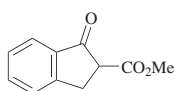
TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₁ 		NaHMDS, -78° to rt	 I (61), <5	323
		LDA, THF, -40° to 0°	I (12), 2	325
		KHMDS, THF, -40° to 0°	I (8), 8	325
		LDA, THF, -40° to 0°	I (16), 46	325
		KHMDS, THF, -40° to 0°	I (46), 46	325
		LiHMDS, THF, -40° to 0°	I (3), 46	325
		NaHMDS, THF, -40° to 0°	I (16), 32	325
		LDA, THF, -40° to 0°	I (11), 20	325
		NaHMDS, THF, -78° to 0°	I (41), 67	323
		NaHMDS, Et ₂ O, -78°	I (51), 6	323
		NaHMDS, -78°	I (53), 76	323
		NaHMDS, HMPA, -78°	I (24), 70	323
	LDA, ZnCl ₂ , THF, -78° to rt	I (33), 10	323	

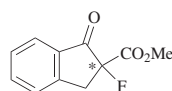
	LDA, THF, -40°	I (67), 74	326
"	LDA, HMPA, THF, -40°	I (65), 14	326
	LiHMDS, THF, -40°	I (65), 70	328
F-CN-BF ₄	NaH, THF, MeCN, -40° to 20°	I (70), 40	332
F-QD-BF ₄	NaH, THF, MeCN, -40° to 20°	I (87), 27	332
	LiHMDS, THF, -50°	 I (79), 62	327
F-CD-BF ₄	NaH, THF, MeCN, -40° to 20°	I (98), 50	332
F-CD-BF ₄	NaH, THF, MeCN, -60° to 20°	I (80), 56	332
F-QN-BF ₄	NaH, THF, MeCN, -40° to 20°	I (98), 20	332
	NaHMDS, THF, -78° (inverse addition)	I (40), 75	323
"	NaHMDS, THF, -78° to rt	I (50), 65	323

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

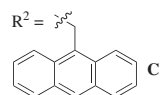
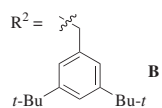
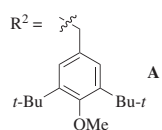
Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		LDA, THF, -40°	 I (73), 20	326
	3	NFSI, EtOH, -10°	 I (91), 94	351
		NFSI, Et ₂ O, HFIP, 20°	I (92), 63	357
	 Ni(ClO ₄) ₂ · 6H ₂ O	NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 2 h	I (86), 99	311
		Selectfluor™, MeCN, rt ^c	 I (53), 33	309



NFSI, base, toluene, rt



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R ¹	R ²	Base	
H	A	K ₂ CO ₃	(87), 20
allyl	A	K ₂ CO ₃	(91), 55
allyl	A	KOH	(84), 58
allyl	A	Cs ₂ CO ₃	(82), 21
allyl	A	RbOH	(80), 20
allyl	A	Rb ₂ CO ₃	(81), 41
benzyl	A	K ₂ CO ₃	(81), 28
propargyl	A	K ₂ CO ₃	(92), 69
propargyl	A	KOH	(89), 37
propargyl	A	KHCO ₃	(82), 15
propargyl	A	Cs ₂ CO ₃	(94), 60
propargyl	A	RbOH	(82), 27
propargyl	A	Rb ₂ CO ₃	(83), 36
propargyl	A	K ₂ CO ₃ ^d	(81), 36
propargyl	A	K ₂ CO ₃ ^e	(87), 68
propargyl	A	K ₂ CO ₃ ^f	(88), 6
propargyl	A	K ₂ CO ₃ ^g	(82), 13
allyl	B	K ₂ CO ₃	(84), 56
allyl	B	KOH	(83), 65
allyl	B	RbOH	(85), 60
benzyl	B	K ₂ CO ₃	(88), 20
H	C	K ₂ CO ₃	(82), 6
allyl	C	K ₂ CO ₃	(90), 66
allyl	C	KOH	(85), 60
allyl	C	Cs ₂ CO ₃	(87), 61
allyl	C	RbOH	(83), 38
allyl	C	Rb ₂ CO ₃	(86), 31
benzyl	C	K ₂ CO ₃	(83), 7

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TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	F-CD-BF ₄	NaH, THF, MeCN, -40° to 20°	 (95), 36	332
	AcDHQD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	 I (81), 83	334
	NFSI, Cs ₂ CO ₃ , toluene, rt		I (65), 42	364
	AcDHQD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	 (56), 68	334
	AcDHQD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	 (92), 80	334
	(DHQN) ₂ PHAL, Selectfluor TM	MeCN, 0°, 2 d	 (12), 40	334

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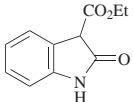
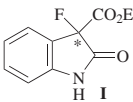
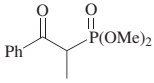
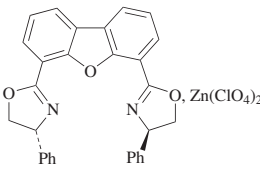
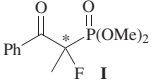
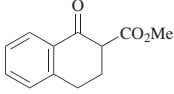
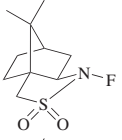
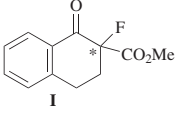
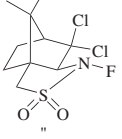
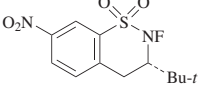
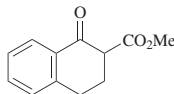
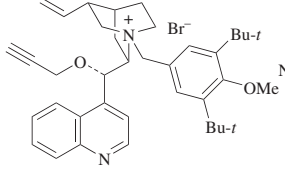
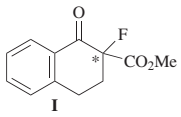
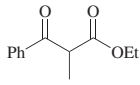
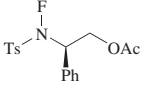
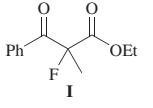
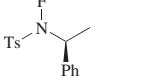
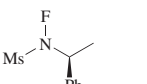
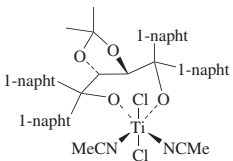
	(DHQD) ₂ PYR, Selectfluor TM	MeCN, 0°, 2 d	 (93), 37	334
	(DHQN) ₂ AQN, Selectfluor TM	MeCN, 0°, 2 d	I (91), 23	334
	 , Zn(ClO ₄) ₂	NFSI, CH ₂ Cl ₂ , rt	 (46), 70	358
	"	NFSI, CH ₂ Cl ₂ , reflux	I (77), 70	358
		NaHMDS, THF, -78° to rt	 (8), 14	323
		NaHMDS, THF, -78°	I (75), 25	323
	"	LDA, THF, -78°	I (25), 26	323
	"	KHMDS, THF, -78° (inverse addition)	I (90), 41	323
	"	LDA, THF, -78° (inverse addition)	I (87), 17	323
		LiHMDS, THF, -50°	I (73), 43	327

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		NFSI, RbOH, toluene, rt	 (87), 40	363
	"	NFSI, Cs ₂ CO ₃ , toluene, rt	I (88), 48	363
	AcDHQD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	I (26), 2	334
	DHQD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	I (79), 59	334
		NaH, THF, 0°	 (4), 8	325
		NaH, THF, 0°	I (21), 18	325
		NaH, THF, 0°	I (21), 6	325
		Selectfluor TM , MeCN, rt	I (71), 62	308

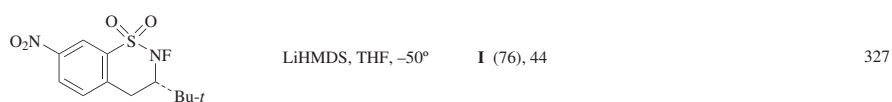
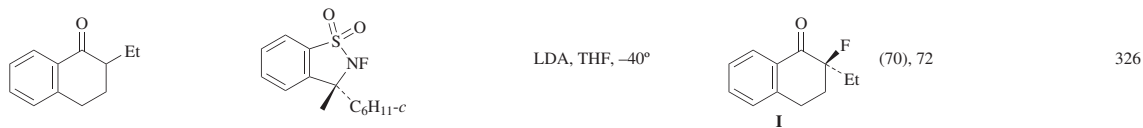
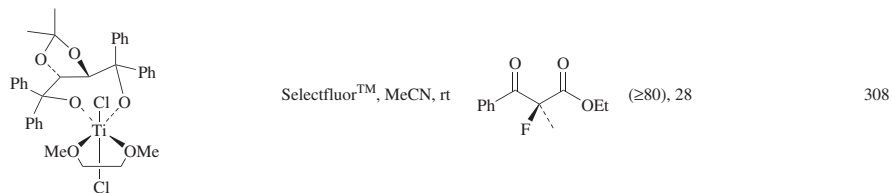
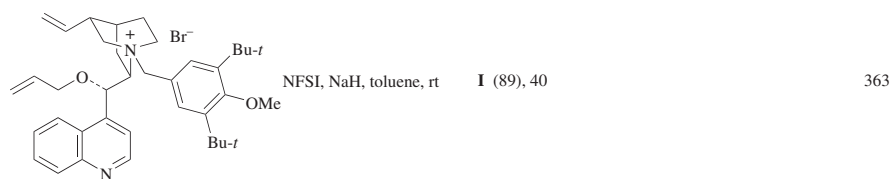
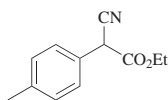


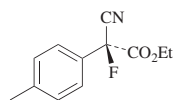
TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Selectfluor™, MeCN, rt	(78) , 91	347
		Selectfluor™, MeCN, rt	(50) , 88	347
		Selectfluor™, MeCN, rt	(63) , 51	347
		Selectfluor™, MeCN, rt	(85) , 62	347



Alkaloid, Selectfluor™

MeCN, CH₂Cl₂, -80°,
3-6 h



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Alkaloid

QN	(95), 20
BzDHQD	(83), 79
(4-O ₂ NC ₆ H ₄ CO)DHQD	(78), 67
(4-ClC ₆ H ₄ CO)DHQD	(97), 73
(2-anthraquinoyl)DHQD	(36), 78
(1-naphthoyl)DHQD	(88), 64
(4-MeOC ₆ H ₄ CO)DHQD	(27), 79
(C ₆ F ₅ CO)DHQD	(54), 47
AcDHQD	(80), 87
(C ₂ H ₅ CO)DHQD	(100), 72
(DHQD) ₂ PHAL	(76), 58
CN	(83), 4
DHCN	(93), 1
AcDHCN	(84), 7
BzDHCN	(86), 5
AcDHCD	(90), 12
BzDHCD	(82), 5

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TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₂ 	Alkaloid, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	 Alkaloid (4-ClC ₆ H ₄ CO)DHQN (100), 51 AcDHQN (89), 31 (C ₆ F ₅ CO)DHQN (91), 11 (C ₆ H ₅ CO)DHQN (82), 40 (2-anthraquinoyl)DHQN (34), 33 (DHQN) ₂ PHAL (93), 11 (DHQN) ₂ PYR (85), 48 QD (84), 23 DHQD (55), 29 CD (87), 9 DHCD (63), 3	334
		NFSI, K ₂ CO ₃ , toluene, rt	 I (92), 50	363
	"	NFSI, Cs ₂ CO ₃ , toluene, rt	I (91), 63	363
	AcDHQD, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	I (89), 78	334

630

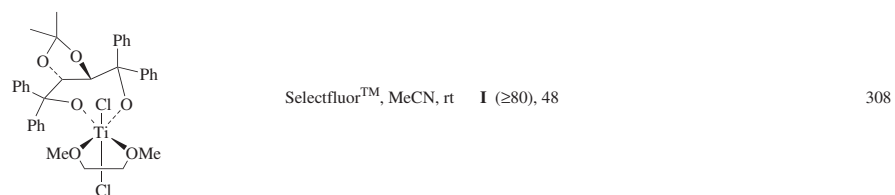
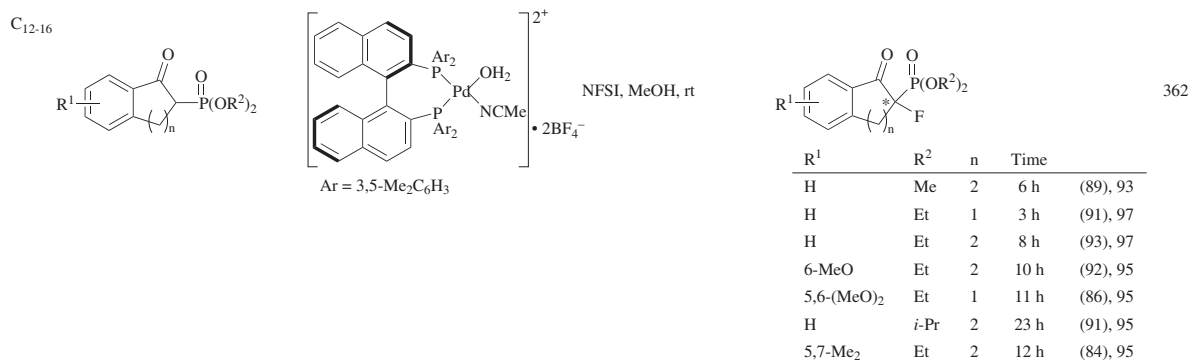


TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₃ 		NFSI, K ₂ CO ₃ , toluene, rt	 (74), 41	363
	"	NFSI, CsOH, toluene, rt	(78), 52	363
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 24 h	(>95) ^b , 28	370
	MQE-DHQN, Selectfluor TM	MeCN, -20°, 24 h	(>95) ^b , 32	
	PE-DHQN, Selectfluor TM	MeCN, -20°, 24 h	(>95) ^b , 48	
	(DHQN) ₂ PYR, Selectfluor TM	MeCN, -20°, 24 h	(>95) ^b , 60	
	(DHQN) ₂ PYR, Selectfluor TM	CH ₂ Cl ₂ , -20°, 24 h	(>95) ^b , 53	
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	MeCN, -40°	(97), 67	336
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	[bmim][PF ₆], rt	(89), 64	344
	F-(4-ClC ₆ H ₄ CO)QN-N(SO ₂ Ph) ₂	MeCN, -40°	(91), 62	336
	F-(4-O ₂ NC ₆ H ₄ CO)QN-BF ₄	[bmim][PF ₆], rt	(94), 65	344
	F-(4-MeOC ₆ H ₄ CO)QN-BF ₄	[bmim][PF ₆], rt	(82), 60	344
	F-(4-ClC ₆ H ₄ CO)CD-BF ₄	[bmim][PF ₆], rt	(99), 43	344
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(93), 54	335

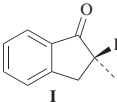
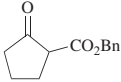
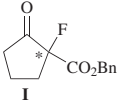
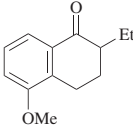
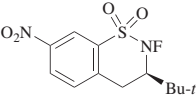
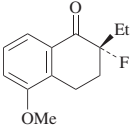
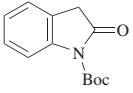
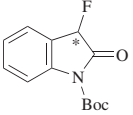
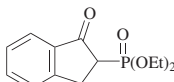
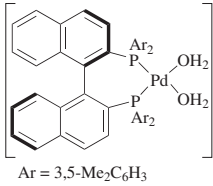
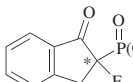
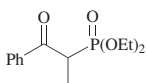
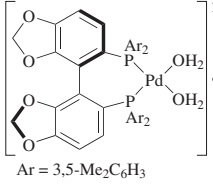
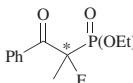
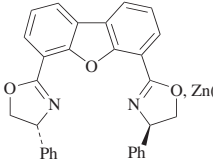
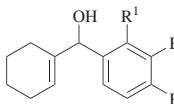
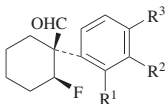
	F-(4-ClC ₆ H ₄ CO)CN-BF ₄	[bmim][PF ₆], rt		(91), 24	344
	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	[bmim][PF ₆], rt	I (96), 53		344
	AcDHQD, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h		(28), 25	334
	DHQN, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	I (55), 43		334
		LiHMDS, THF, -50°		(59), 60	327
	6 (2.5 mol%)	NFSI, rt			543
			Solvent	Time	
			THF	43 h (29), 21	
			THF/MeOH (5:1)	60 h (55), 60	
			THF/MeOH (1:1)	18 h (51), 84	
			DCE/MeOH (1:1)	18 h (53), 93	

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		• 2TfO ⁻ NFSI, EtOH, rt	 (84), 95	360
		• 2TfO ⁻ NFSI, EtOH, 40°	 I (38), 95	360
		NFSI, CH ₂ Cl ₂ , rt	I (59), 89	358
	"	NFSI, CH ₂ Cl ₂ , reflux	I (86), 88	358
	QN, Selectfluor™	MeCN, K ₂ CO ₃ , rt, 6 d		373

			R ¹	R ²	R ³	
			H	H	H	(33), 67
			H	—OCH ₂ O—	H	(39), 74
			OMe	H	H	(50), 71
			H	H	OMe	(41), 76
			H	OMe	H	(48), 54
			H	H	Me	(35), 70
			H	OMe	OMe	(42), 73
			—CH=CH—	—CH=CH—	H	(45), 82

C ₁₃₋₂₁			NFSI, MeOH, 0°		354																					
				<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th></th> </tr> </thead> <tbody> <tr> <td>Ph</td> <td>60 h</td> <td>(83), 99</td> </tr> <tr> <td>4-ClC₆H₄</td> <td>17 h</td> <td>(94), 85</td> </tr> <tr> <td>4-MeC₆H₄</td> <td>60 h</td> <td>(85), 93</td> </tr> <tr> <td>4-MeOC₆H₄</td> <td>72 h</td> <td>(85), 99</td> </tr> <tr> <td>2-naphthyl</td> <td>60 h</td> <td>(88), 93</td> </tr> <tr> <td>9-anthryl</td> <td>52 h</td> <td>(42), 91</td> </tr> </tbody> </table>	R	Time		Ph	60 h	(83), 99	4-ClC ₆ H ₄	17 h	(94), 85	4-MeC ₆ H ₄	60 h	(85), 93	4-MeOC ₆ H ₄	72 h	(85), 99	2-naphthyl	60 h	(88), 93	9-anthryl	52 h	(42), 91	
R	Time																									
Ph	60 h	(83), 99																								
4-ClC ₆ H ₄	17 h	(94), 85																								
4-MeC ₆ H ₄	60 h	(85), 93																								
4-MeOC ₆ H ₄	72 h	(85), 99																								
2-naphthyl	60 h	(88), 93																								
9-anthryl	52 h	(42), 91																								
C ₁₄			Selectfluor™, MeCN, rt		(40), 24																					
			NaH, Et ₂ O, 0° to rt		(28), 25																					

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																		
C ₁₄ 		NaHMDS, THF, -78° to rt	 I (22), 34	323																		
	"	NaHMDS, THF, 0° to rt	I (57), 26	323																		
	"	NaHMDS, Et ₂ O, -78° to rt	I (85), 37	323																		
	"	NaH, Et ₂ O, 0° to rt	I (95), 46	323																		
	"	NaH, Et ₂ O, 0° to rt (inverse addition)	I (95), 40	323																		
	"	KHMDS, THF, -78°	I (28), 20	323																		
		NaHMDS, -78°	I (83), 14	323																		
	"	LDA, THF, -78° to 0°	I (76), 14	323																		
	2	NFSI, EtOH, -20°	 I (85), 83	351																		
		NFSI	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th></th> </tr> </thead> <tbody> <tr> <td>THF</td> <td>-10°</td> <td>(65), 1</td> </tr> <tr> <td>CH₂Cl₂</td> <td>-10°</td> <td>(72), 71</td> </tr> <tr> <td>CH₂Cl₂</td> <td>-25°</td> <td>(83), 51</td> </tr> <tr> <td>CH₂Cl₂</td> <td>20°</td> <td>(92), 76</td> </tr> <tr> <td>CH₂Cl₂^h</td> <td>20°</td> <td>(87), 93</td> </tr> </tbody> </table>	Solvent	Temp		THF	-10°	(65), 1	CH ₂ Cl ₂	-10°	(72), 71	CH ₂ Cl ₂	-25°	(83), 51	CH ₂ Cl ₂	20°	(92), 76	CH ₂ Cl ₂ ^h	20°	(87), 93	310
Solvent	Temp																					
THF	-10°	(65), 1																				
CH ₂ Cl ₂	-10°	(72), 71																				
CH ₂ Cl ₂	-25°	(83), 51																				
CH ₂ Cl ₂	20°	(92), 76																				
CH ₂ Cl ₂ ^h	20°	(87), 93																				

		NFSI		I	310																					
			<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>THF</td> <td>-10°</td> <td>(89), 46</td> </tr> <tr> <td>CH₂Cl₂</td> <td>-10°</td> <td>(50), 39</td> </tr> <tr> <td>THF</td> <td>30°</td> <td>(77), 51</td> </tr> <tr> <td>Et₂O</td> <td>20°</td> <td>(72), 69</td> </tr> <tr> <td>MTBE</td> <td>20°</td> <td>(94), 60</td> </tr> <tr> <td>Et₂O^b</td> <td>20°</td> <td>(81), 70</td> </tr> </tbody> </table>	Solvent	Temp	I	THF	-10°	(89), 46	CH ₂ Cl ₂	-10°	(50), 39	THF	30°	(77), 51	Et ₂ O	20°	(72), 69	MTBE	20°	(94), 60	Et ₂ O ^b	20°	(81), 70		
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THF	-10°	(89), 46																								
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MTBE	20°	(94), 60																								
Et ₂ O ^b	20°	(81), 70																								
		NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 6 h		I (93), 99	311																					
	Ni(ClO ₄) ₂ • 6H ₂ O																									
		NFSI, Et ₂ O, HFIP, 20°		(56), 43	357																					
3		NFSI, EtOH, 20°		I (92), 91	351																					
2		NFSI, [bmim][BF ₄], rt		I (68), 91	352																					
2		NFSI, [bmim][OTf], rt		I (88), 92	352																					
2		NFSI, [hmim][BF ₄], rt		I (93), 92	352																					

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
		NFSI, EtOH, 20°		(96), 91	351
	Ar = 3,5-Me ₂ C ₆ H ₃				
		NFSI, EtOH, rt		(97), 94	360
	Ar = 3,5-Me ₂ C ₆ H ₃				
	(4-CIC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 24 h		(>95) ^b , 9	370
	(DHQN) ₂ PYR, Selectfluor TM	MeCN, -20°, 24 h	I	(>95) ^b , 22	370
	MQE-DHQN, Selectfluor TM	MeCN, -20°, 24 h	I	(>95) ^b , 30	370
	F-(4-CIC ₆ H ₄ CO)QN-BF ₄	[bmim][PF ₆], rt		(82), 82	344
	F-(2-naphthoyl)QN-BF ₄	[bmim][PF ₆], rt	I (98), 93		344
	(4-CIC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	I (99), 73		335

	F-CD-BF ₄	NaOH, THF, -40°		(93), 61	332
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor™	MeCN, -20°, 12 h		I (94), 42	335
	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	[emim][BF ₄], rt		(83), 22	344
	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	[bmim][PF ₆], rt		I (91), 34	344
	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	[hmim][PF ₆], rt		I (75), 34	344
	AcDHQD, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h		(82), 87	334
	 Ar = 3,5-Me ₂ C ₆ H ₃	• 2TfO ⁻ NFSI, THF, rt, 60 h		(20), 5	543
C ₁₄₋₁₉ 	 Ni(OAc) ₂ • 4H ₂ O	NFSI, CH ₂ Cl ₂ , 4 Å MS, rt	 R Time Me 35 h (73), 93 Ph 5 h (72), 96		311

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₄₋₂₁ 	6 (2.5 mol%)	NFSI, <i>i</i> -PrOH	 R ¹ R ² Temp Time Me H rt 5 h (86), 95 Me H 0° 18 h (85), 96 Et H rt 10 h (85), 92 MeC(O)CH ₂ H rt 2 h (85), 86 <i>i</i> -Bu H rt 2 h (85), 75 Ph H 0° 18 h (96), 90 4-FC ₆ H ₄ H rt 3 h (94), 84 4-MeC ₆ H ₄ H rt 3 h (97), 86 4-MeC ₆ H ₄ H 0° 18 h (92), 88 Bn H rt 4 h (72), 80 2-MeOC ₆ H ₄ CF ₃ rt 3 h (80), 75	543
C ₁₅ 	 Zn(ClO ₄) ₂	NFSI, CH ₂ Cl ₂ , rt	 I (41), 91	358
	"	NFSI, CH ₂ Cl ₂ , reflux	I (91), 90	358
	QN, Selectfluor™	K ₂ CO ₃ , MeCN, rt, 6 d	 (34), 65	373

	Alkaloid, Selectfluor™	MeCN, 0°, 2 d		Alkaloid		
				AcDHQD	(27), 37	334
				(4-ClC ₆ H ₄ CO)DHQN	(60), 7	
				DHQD	(17), 18	
				(4-ClC ₆ H ₄ CO)DHQD	(46), 38	
				DHCN	(19), 0	
				DHCD	(26), 7	
				AcDHCD	(32), 18	
				AcDHCN	(34), 9	
				(DHQN) ₂ AQN	(100), 78	
				(DHQD) ₂ PYR	(91), 72	
				(DHQD) ₂ AQN	(88), 10	
				(DHQN) ₂ PYR	(94), 42	
				(DHQN) ₂ PHAL	(74), 23	
				(DHQD) ₂ PHAL	(99), 62	
				AcDHQD ^f	(53), 44	
				(4-ClC ₆ H ₄ CO)DHQD	(77), 55	
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 8		370
	(DHQN) ₂ PYR, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 45		370
	PE-DHQN, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 21		370
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor™	MeCN, CH ₂ Cl ₂ , -50°, 12 h		(71), 67		335

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	AcDHQD, Selectfluor™	MeCN, CH ₂ Cl ₂ , -80°, 3-6 h	(87), 76	334
		NFSI, Cs ₂ CO ₃ , toluene, rt	 R ¹ R ²	364
			Ph CH ₂ C ₆ H ₅ (77), 61	
			Ph CH ₂ C ₆ H ₄ NO ₂ -4 (76), 73	
			4-FC ₆ H ₄ CH ₂ C ₆ H ₄ NO ₂ -4 (76), 73	
			4-ClC ₆ H ₄ CH ₂ C ₆ H ₄ NO ₂ -4 (72), 76	
		LDA, THF, -40°	(63), 54	326
		LiHMDS, THF, -40°	I (59), 54	328
		LiHMDS, THF, -50°	(40), 57	327

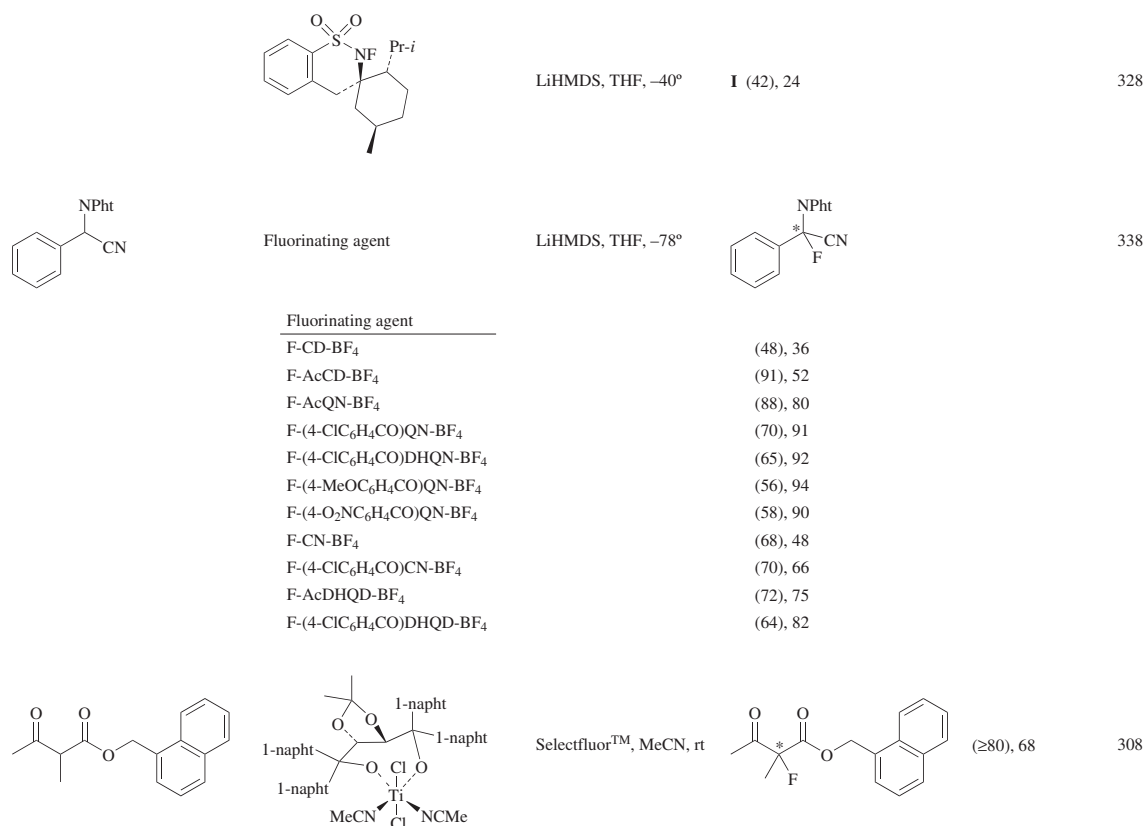
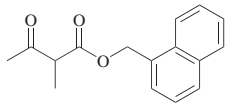
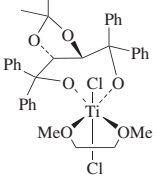
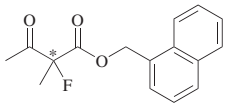
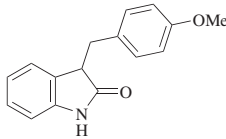
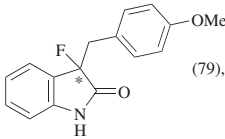
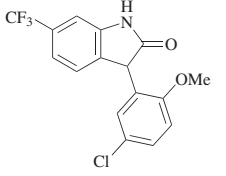
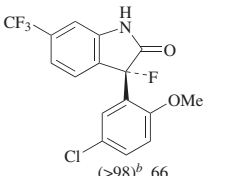
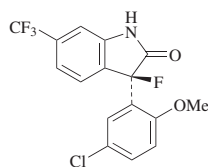


TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Selectfluor TM , MeCN, rt	 (≥ 80), 51	308
	(DHQD) ₂ PYR, Selectfluor TM	MeCN, 0 ^o , 2 d	 (79), 82	334
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	Quinuclidine, THF, MeCN, CH ₂ Cl ₂ , -78°	 (>98) ^b , 66	340
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	DABCO, THF, MeCN, CH ₂ Cl ₂ , -78°	(>98) ^b , 57	340
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	Cs ₂ CO ₃ , THF, MeCN, CH ₂ Cl ₂ , -78°	(>98) ^b , 84	340
	F-(2-naphthoyl)QN-BF ₄	Quinuclidine, THF, MeCN, CH ₂ Cl ₂ , -78°	(>98) ^b , 84	340
	F-(2-naphthoyl)QN-BF ₄	DABCO, THF, MeCN, CH ₂ Cl ₂ , -78°	(96), 88	340
	F-(2-naphthoyl)QN-BF ₄	Cs ₂ CO ₃ , THF, MeCN, CH ₂ Cl ₂ , -78°	(>98) ^b , 81	340

(DHQN) ₂ AQN, Selectfluor TM	EtOH, 0°, 1-2 h	(89), 8	341
(DHQN) ₂ AQN, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 12 h	(94), 84	341
(DHQN) ₂ PHAL, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 12 h	(75), 78	341
BzDHQN, Selectfluor TM	MeCN, 0°, 1-2 h	(94), 18	341
QN, Selectfluor TM	MeCN, 0°, 1-2 h	(91), 25	341
CD, Selectfluor TM	MeCN, 0°, 1-2 h	(90), 13	341
MQE-DHQN, Selectfluor TM	MeCN, 0°, 1-2 h	(93), 24	341
AcDHQN, Selectfluor TM	MeCN, 0°, 1-2 h	(93), 16	341
PE-DHQN, Selectfluor TM	MeCN, 0°, 1-2 h	(90), 2	341
BzDHCD, Selectfluor TM	MeCN, 0°, 1-2 h	(97), 11	341
(DHQN) ₂ PYR, Selectfluor TM	MeCN, 0°, 1-2 h	(90), 14	341
(DHQN) ₂ PHAL, Selectfluor TM	MeCN, 0°, 1-2 h	(89), 53	341
(DHQN) ₂ AQN, Selectfluor TM	MeCN, 0°, 1-2 h	(89), 74	341



F-(4-ClC ₆ H ₄ CO)QD-BF ₄	Quinuclidine, THF, MeCN, CH ₂ Cl ₂ , -78°	(>98) ^b , 66	340
F-(DHQD) ₂ PHAL-BF ₄	DABCO, THF, MeCN, CH ₂ Cl ₂ , -78°	(90), 88	340
QD, Selectfluor TM	EtOH, 0°, 1-2 h	(81), 18	341
(DHQD) ₂ PHAL, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 12 h	(93), 38	341
QD, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 12 h	(96), 68	341
(DHQD) ₂ PYR, Selectfluor TM	MeCN, 0°, 1-2 h	(93), 7	341

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₆ 	AcDHQD, Selectfluor TM	MeCN, 0°, 1-2 h	 I (82), 32	341
	QD, Selectfluor TM	MeCN, 0°, 1-2 h	I (98), 52	341
	CN, Selectfluor TM	MeCN, 0°, 1-2 h	I (94), 37	341
	BzDHQN, Selectfluor TM	MeCN, 0°, 1-2 h	I (88), 20	341
	BzDHQD, Selectfluor TM	MeCN, 0°, 1-2 h	I (97), 38	341
	(DHQD) ₂ AQN, Selectfluor TM	MeCN, 0°, 1-2 h	I (92), 3	341
	(DHQD) ₂ PHAL, Selectfluor TM	MeCN, 0°, 1-2 h	I (98), 54	341
C ₁₇ 	 Ts F OAc Ph	LDA, THF, -40° to -20°	 I (6), 9	325
	 Ts F Ph	LDA, THF, -40° to -20°	I (26), 54	325
	"	KHMDS, THF, -40° to -20°	I (53) 48	325
	 Ms F Ph	LDA, THF, -40° to -20°	I (8), 6	325
	 SO ₂ O NF Ph C ₆ H _{11-c}	LDA, THF, -40°	 I (79), 88	326

		LiHMDS, THF, -40°	I (61), 56	328
		LiHMDS, THF, -50°	 I (55), 49	327
	F-CD-BF ₄	NaH, THF, MeCN, -40° to 20°	I (96), 42	332
		LiHMDS, THF, -50°	 I (70), 69	327
		LiHMDS, THF, -40°	I (52), 51	328
		NFSI, Cs ₂ CO ₃ , toluene, rt	 I (64), 72	364

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

	Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₇			NFSI, Et ₂ O, HFIP, 20°	 (94), 35	357
		QN, Selectfluor TM	MeCN, K ₂ CO ₃ , rt, 6 d	 (37), 61	373
			NFSI, CH ₂ Cl ₂ , rt	 (71), 89	358
C ₁₈			LiHMDS, THF, -50°	 I (56), 60	327
			LiHMDS, THF, -40°	I (61), 33	328

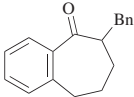
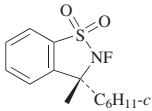
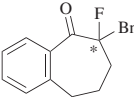
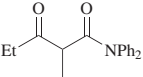
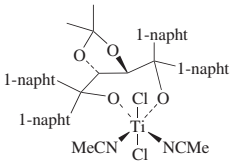
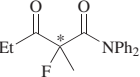
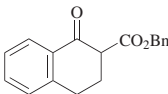
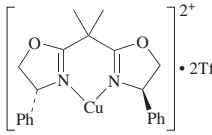
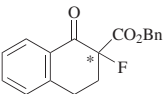
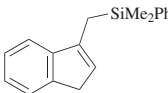
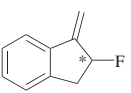
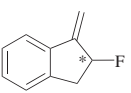
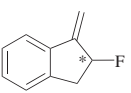
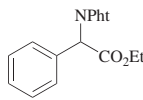
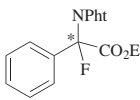
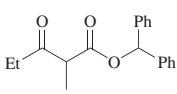
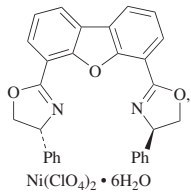
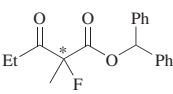
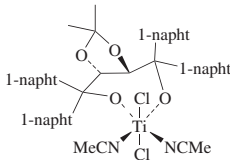
		LDA, THF, -40°		(39), 18	326
		Selectfluor™, MeCN, rt		(75), 55	347
		NFSI, Et ₂ O, HFIP, 20°		(92), 38	357
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 35	370
	MQE-DHQN, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 35	370
	(DHQN) ₂ PYR, Selectfluor™	MeCN, -20°, 24 h		I (>95) ^b , 73	370

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
	Fluorinating agent	LiHMDS, THF, -78°		338	
	Fluorinating agent				
	F-CD-BF ₄		(65), 8		
	F-AcCD-BF ₄		(87), 42		
	F-AcQN-BF ₄		(79), 76		
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄		(73), 68		
	F-(4-ClC ₆ H ₄ CO)DHQN-BF ₄		(86), 76		
	F-(4-MeOC ₆ H ₄ CO)QN-BF ₄		(64), 66		
	F-(4-O ₂ NC ₆ H ₄ CO)QN-BF ₄		(60), 60		
	F-CN-BF ₄		(62), 26		
	F-(4-ClC ₆ H ₄ CO)CN-BF ₄		(67), 28		
	F-AcDHQD-BF ₄		(60), 50		
	F-(4-ClC ₆ H ₄ CO)DHQD-BF ₄		(65), 38		
		NFSI, CH ₂ Cl ₂ , 4 Å MS, 0°, 18 h		I (75), 83	311
		Selectfluor™, MeCN, rt	I (≥80), 81	308	

		Selectfluor TM , MeCN, rt	I (≥80), 58	308
		QD, Selectfluor TM	MeCN, 0°, 3-6 h	(84), 35
		CN, Selectfluor TM	MeCN, 0°, 3-6 h	(94), 23
			THF, MeCN, -40°, 18 h	(98), 85
				334, 335
		(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(99), 89
		(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, CH ₂ Cl ₂ , -80°, 48 h	(86), 91
		QN, Selectfluor TM	MeCN, 0°, 3-6 h	(63), 44
		DHQN, Selectfluor TM	MeCN, 0°, 3-6 h	(67), 54
		(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, 0°, 3-6 h	(83), 81
		PE-DHQN, Selectfluor TM	MeCN, 0°, 3-6 h	(61), 72

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C ₁₉ 				
	MQE-DHQN, Selectfluor TM	MeCN, 0°, 3-6 h	(100), 70	334, 335
	CD, Selectfluor TM	MeCN, 0°, 3-6 h	(88), 42	334, 335
	(DHQN) ₂ PHAL, Selectfluor TM	MeCN, 0°, 3-6 h	(100), 82	334, 335
	(DHQN) ₂ PYR, Selectfluor TM	MeCN, 0°, 3-6 h	(100), 70	334, 335
	(DHQN) ₂ AQN, Selectfluor TM	MeCN, 0°, 3-6 h	(98), 70	334, 335
	BzDHQN, Selectfluor TM	MeCN, -20°, 12 h	(82), 90	334, 335
	(4-O ₂ NC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(61), 91	334, 335
	(4-MeOC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(80), 87	334, 335
	AcDHQN, Selectfluor TM	MeCN, -20°, 12 h	(67), 86	334, 335
	(1-naphthoyl)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(61), 87	334, 335
	(2-anthraquinoyl)DHQN, Selectfluor TM	MeCN, -20°, 12 h	(100), 86	334, 335
	TrifluoroacetylDHQN, Selectfluor TM	MeCN, -20°, 12 h	(43), 31	334, 335
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	MeCN, -40°	(98), 84	336
	F-(4-ClC ₆ H ₄ CO)QN-OTf	MeCN, -40°	(88), 81	336
	F-(4-ClC ₆ H ₄ CO)QN-N(SO ₂ Ph) ₂	MeCN, -40°	(94), 85	336
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	[hmim][PF ₆], rt	(89), 86	344
	F-(4-MeOC ₆ H ₄ CO)QN-BF ₄	[hmim][PF ₆], rt	(74), 84	344
	F-MEQN-BF ₄	[hmim][PF ₆], rt	(65), 66	344
	F-PEQN-BF ₄	[hmim][PF ₆], rt	(91), 74	344
	F-(1-naphthoyl)QN-BF ₄	[hmim][PF ₆], rt	(93), 86	344
	F-(2-naphthoyl)QN-BF ₄	[hmim][PF ₆], rt	(87), 84	344
	F-(4-ClC ₆ H ₄ CO)CD-BF ₄	[hmim][PF ₆], rt	(61), 73	344

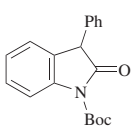
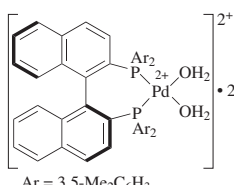
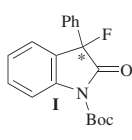
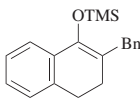
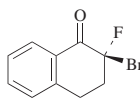
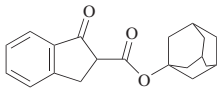
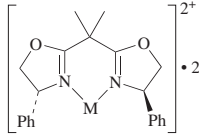
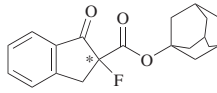

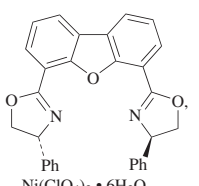
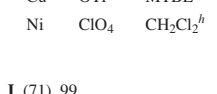
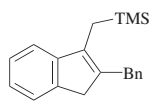
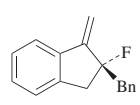
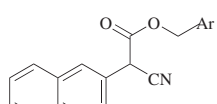
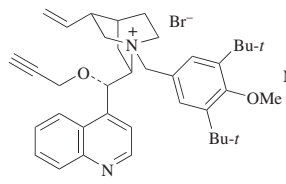
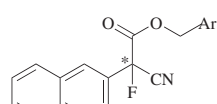
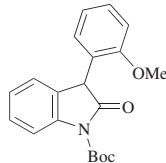
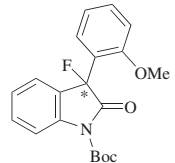
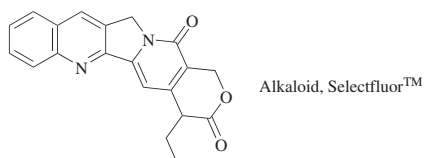
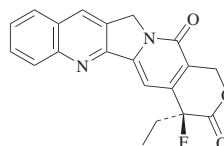
	 Ar = 3,5-Me ₂ C ₆ H ₃	• 2TfO ⁻ NFSI, rt		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>THF</td> <td>12 h</td> <td>(53), 81</td> </tr> <tr> <td><i>i</i>-PrOH</td> <td>3 h</td> <td>(66), 88</td> </tr> <tr> <td>acetone</td> <td>3 h</td> <td>(58), 89</td> </tr> </tbody> </table>	Solvent	Time	I	THF	12 h	(53), 81	<i>i</i> -PrOH	3 h	(66), 88	acetone	3 h	(58), 89	543																								
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acetone	3 h	(58), 89																																							
6 (5 mol%)	NFSI, <i>i</i> -PrOH, rt, 5 h	I (90), 88	543																																						
C ₂₀ 	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor TM	MeCN, -20°, 12 h	 (95), 71	335																																					
	 • 2X ⁻	NFSI		310																																					
				<table border="1"> <thead> <tr> <th>M</th> <th>X</th> <th>Solvent</th> <th>Temp</th> <th>I</th> </tr> </thead> <tbody> <tr> <td>Cu</td> <td>OTf</td> <td>THF</td> <td>-10°</td> <td>(81), 60 (-)</td> </tr> <tr> <td>Ni</td> <td>ClO₄</td> <td>CH₂Cl₂</td> <td>-10°</td> <td>(99), 68 (+)</td> </tr> <tr> <td>Cu</td> <td>OTf</td> <td>THF</td> <td>20°</td> <td>(86), 72 (-)</td> </tr> <tr> <td>Cu</td> <td>OTf</td> <td>Et₂O</td> <td>20°</td> <td>(85), 81 (-)</td> </tr> <tr> <td>Ni</td> <td>ClO₄</td> <td>CH₂Cl₂</td> <td>20°</td> <td>(88), 71 (+)</td> </tr> <tr> <td>Cu</td> <td>OTf</td> <td>MTBE</td> <td>20°</td> <td>(79), 84 (-)</td> </tr> <tr> <td>Ni</td> <td>ClO₄</td> <td>CH₂Cl₂^b</td> <td>20°</td> <td>(74), 79 (+)</td> </tr> </tbody> </table>	M	X	Solvent	Temp	I	Cu	OTf	THF	-10°	(81), 60 (-)	Ni	ClO ₄	CH ₂ Cl ₂	-10°	(99), 68 (+)	Cu	OTf	THF	20°	(86), 72 (-)	Cu	OTf	Et ₂ O	20°	(85), 81 (-)	Ni	ClO ₄	CH ₂ Cl ₂	20°	(88), 71 (+)	Cu	OTf	MTBE	20°	(79), 84 (-)	Ni	ClO ₄
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Cu	OTf	THF	-10°	(81), 60 (-)																																					
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Ni	ClO ₄	CH ₂ Cl ₂ ^b	20°	(74), 79 (+)																																					
	 Ni(ClO ₄) ₂ • 6H ₂ O	NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 2 h		311																																					
				I (71), 99	311																																				

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.															
C ₂₀ 	Alkaloid, Selectfluor TM	MeCN, -20°, 24 h	 <table border="1"> <thead> <tr> <th>Alkaloid</th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>(4-ClC₆H₄CO)DHQN</td> <td>(>95)^b</td> <td>85</td> </tr> <tr> <td>(DHQN)₂PYR</td> <td>(>95)^b</td> <td>96</td> </tr> <tr> <td>PE-DHQN</td> <td>(>95)^b</td> <td>84</td> </tr> <tr> <td>MQE-DHQN</td> <td>(>95)^b</td> <td>93</td> </tr> </tbody> </table>	Alkaloid	Yield (%)	% ee	(4-ClC ₆ H ₄ CO)DHQN	(>95) ^b	85	(DHQN) ₂ PYR	(>95) ^b	96	PE-DHQN	(>95) ^b	84	MQE-DHQN	(>95) ^b	93	370
Alkaloid	Yield (%)	% ee																	
(4-ClC ₆ H ₄ CO)DHQN	(>95) ^b	85																	
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PE-DHQN	(>95) ^b	84																	
MQE-DHQN	(>95) ^b	93																	
 Ar = C ₆ H ₄ NO ₂ -4		NFSI, Cs ₂ CO ₃ , toluene, rt	 (71), 76	364															
	6 (5 mol%)	NFSI, acetone, rt, 18 h	 (89), 76	543															



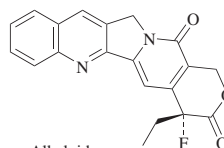
rt, 1-2 d



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Alkaloid	Solvent	
QD	MeCN	(49), 6
QD	MeCN/CHCl ₃	(70), 15
QD	CHCl ₃	(48), 21
QD	CH ₂ Cl ₂	(81), 32
CN	CH ₂ Cl ₂	(84), 27
DHQD	CH ₂ Cl ₂	(60), 19
AcDHQD	CH ₂ Cl ₂	(77), 34
(4-ClC ₆ H ₄ CO)DHQD	CH ₂ Cl ₂	(99), 7
(4-ClC ₆ H ₄ CO)DHQN	CH ₂ Cl ₂	(81), 6
(4-ClC ₆ H ₄ CO)DHCD	CH ₂ Cl ₂	(99), 9
(DHQD) ₂ AQN	CH ₂ Cl ₂	(87), 21
(DHQD) ₂ PHAL	CH ₂ Cl ₂	(87), 88
(DHQN) ₂ PYR	CH ₂ Cl ₂	(63), 22

Alkaloid, Selectfluor™

CH₂Cl₂, rt, 1-2 d

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Alkaloid	
QN	(64), 14
CD	(99), 32
AcDHQN	(70), 23
(4-ClC ₆ H ₄ CO)CN	(51), 25
(DHQN) ₂ AQN	(89), 8
(DHQN) ₂ PHAL	(98), 81
(DHQD) ₂ PYR	(63), 23

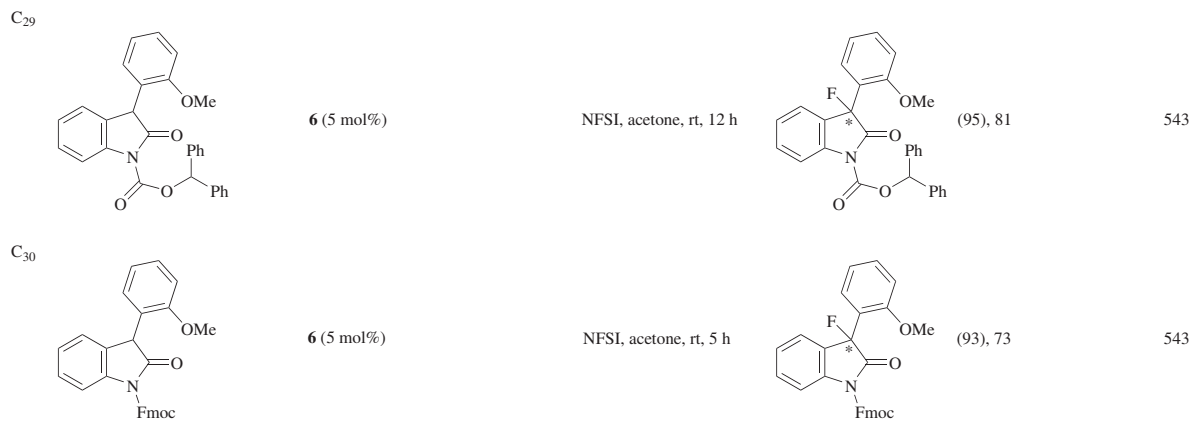
TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	(4-ClC ₆ H ₄ CO)DHQN, Selectfluor™	MeCN, -20°, 24 h	 I (>95) ^b , 53	370
	(DHQN) ₂ PYR, Selectfluor™	MeCN, -20°, 24 h	I (>95) ^b , 83	370
	PE-DHQN, Selectfluor™	MeCN, -20°, 24 h	I (>95) ^b , 64	370
	6 (2.5 mol%)	NFSI, acetone, 0°, 18 h	 I (90), 71	543
	Ni(OAc) ₂ · 4H ₂ O	NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 14 h	I (71), 93	311
	Ni(ClO ₄) ₂ · 6H ₂ O	NFSI, CH ₂ Cl ₂ , 4 Å MS, rt, 3 h	 (88), 95	311

		NFSI, Et ₂ O, HFIP, 20°		(88), 40	357
C ₂₂		Selectfluor TM , MeCN, rt		I (89), 90	308
		Selectfluor TM , MeCN, rt	I (≥80), 55		308
C ₂₂₋₃₀		Fluorinating agent	LiHMDS, THF, -78°		339
	Fluorinating agent				
	Fluorinating agent				
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	Me	Me	Me	(>98) ^b , 32
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	-(CH ₂) ₄ -	Me	Me	(>98) ^b , 34
	F-(4-ClC ₆ H ₄ CO)QD-BF ₄	-(CH ₂) ₄ -	Me	Me	(>98) ^b , 28
	F-(4-ClC ₆ H ₄ CO)CN-BF ₄	-(CH ₂) ₄ -	Me	Me	(95), 6
	F-(4-ClC ₆ H ₄ CO)CD-BF ₄	-(CH ₂) ₄ -	Me	Me	(95), 16
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	Me	Me	Bn	(88), 44
	F-(4-ClC ₆ H ₄ CO)QN-BF ₄	-(CH ₂) ₄ -	Bn	Bn	(92), 46

TABLE 14. ENANTIOSELECTIVE ELECTROPHILIC FLUORINATIONS (Continued)

Substrate	Fluorinating Agent or Catalyst	Conditions	Product(s) and Yield(s) (%), % ee	Refs.		
C ₂₃		Selectfluor TM , MeCN, rt		I (≥80), 82	308	
		Selectfluor TM , MeCN, rt	I (≥80), 59		308	
		NFSI, Et ₂ O, HFIP, 20°	I (72), 52		357	
C ₂₈		(DHQN) ₂ PYR, Selectfluor TM	MeCN, -20°, 24 h		(>95) ^b , 87	370



^a The yield reported is that of the aldehyde intermediate.

^b The reported value is the percent conversion based on starting material.

^c The substrate was generated in situ from the corresponding nonchlorinated molecule with the aid of *N*-chlorosuccinimide.

^d The reaction was carried out at -78° .

^e A 30 mol% concentration of catalyst was used.

^f The reaction was carried out in CH_2Cl_2 .

^g The reaction was carried out in THF.

^h The reaction was performed in the presence of 4 Å molecular sieves.

ⁱ The reaction was carried out with 3 equivalents of cinchona alkaloid and 1.5 equivalents of SelectfluorTM.

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