Photochemical Synthesis of Highly Functionalized Cyclopropyl Ketones

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A series of di- and trisubstituted cyclopropyl ketones **11** were prepared by irradiation of ketones **3** and **5**, which bear a leaving group adjacent to the carbonyl C-atom. The required ketones **3** could be easily synthesized either by functionalization of ketones **1** with a hypervalent iodine reagent, **2**, or by *O*-sulfonylation of α-hydroxy ketones **7**. The nitrates **5** were obtained by treatment of the corresponding α-bromo ketones with $AgNO_3$. The irradiation of **3** and **5** must be performed in the presence of an acid scavenger (1-methyl-1*H*-imidazole) to obtain the cyclopropanes **11** in good yields. The synthetic efficiency of the method was, among other things, demonstrated by the preparation of a highly strained bicyclo[2.1.0]pentane **11i** in good yield. The mechanism of the photochemical cyclization was investigated by means of photokinetic measurements, as well as by quantum-chemical calculations. It was shown that the presence of the leaving group substantially influences all steps of the photochemical reaction cascade. The X-ray crystal structures of **11j** and *exo*-**11k** were also determined.

1. Introduction. – Cyclopropanes represent a unique class of cyclic compounds due to both the enormous synthetic potential and the broad occurrence as a structure element of natural products. Though cyclopropanes may be considered formally as the smallest cycloalkanes, the electronic properties of this small ring differ substantially from those of larger homologues. The high reactivity of cyclopropanes and the distinct tendency for ring opening can be explained by the considerable ring strain (27 kcal/mol).

Currently, organic chemists have a variety of methods for the preparation of cyclopropanes [1]. Most convenient methods are cycloaddition reactions of a carbene or a carbenoid with an alkene. This applies to such popular reactions as the *Simmons-Smith* reaction [2] and the reaction of diazoalkanes with alkenes in the presence of transition-metal catalysts[1]). On the other hand, only few efficient cyclization methods are known [4].

Photochemical methods, which often fit the latter concept, are attractive alternatives to the thermal reactions. From thermodynamic point of view, the ring closure is facilitated because the excitation energy of the photochemical process may compensate the energy needed for the construction of the ring strain. One photochemical reaction that has proven to be particularly useful for the synthesis of carbo- and heterocyclic compounds, is the *Norrish–Yang* reaction [5]. In the most popular type of this reaction, a photochemically excited C=O group abstracts a H-atom from the γ-position to give the 1,4-biradical, which can subsequently cyclize to the cyclobutane. This special type of the *Norrish–Yang* reaction is also called *Yang* cyclization (*cf. Scheme 1,a*).

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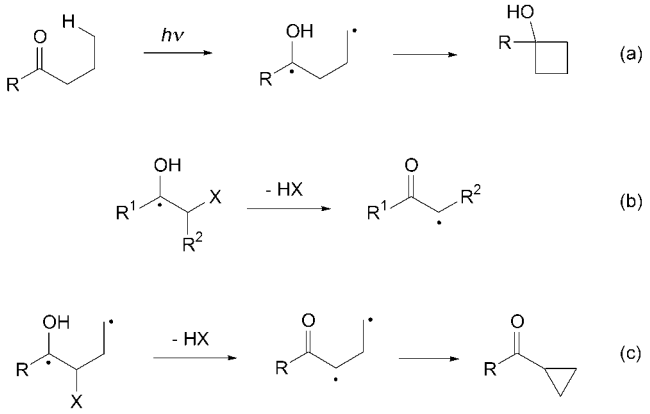
[1]) For Cu, see [3a]; for Rh, see [3b]; for Pd, see [3c]; for Mo, see [3d].

Scheme 1. Yang *Cyclization* (a), *Acid Elimination in OH-Substituted Radicals* (b), *and Spin-Center Shift in Biradicals* (c)



While many applications of the *Norrish – Yang* reaction on the synthesis of four-, five-, and six-membered rings are known, it was utilized for a very limited number of cyclopropane syntheses [6]. In most of these cases, it was either proven or it is very likely that the initial step is a photoelectron transfer (PET) and, consequently, the method is limited to reactants bearing functional groups with a low oxidation potential in a particular position. Unfortunately, the preparative value is restricted because electron-rich cyclopropanes undergo oxidative ring opening easily.

In this paper, we report a novel photochemical method for the preparation of benzoylcyclopropanes (for a preliminary communication, see [7]). The basic idea of our approach is to make use of a well-known behavior of radicals, namely the tendency of OH-substituted radicals bearing a leaving group at the adjacent atom, to undergo rapid elimination of an acid. During this process, the location of the highest spin density is shifted to the neighboring atom, as shown in *Scheme 1,b*.

If the concept of acid elimination in OH-substituted radicals is applied to biradicals formed in the *Norrish – Yang* reaction, the number of atoms between the radical centers could be altered, which consequently influences the size of ring formed in the reaction. Thus, if 1,4-biradicals formed by γ-H abstraction are subjected to acid elimination, 1,3-biradicals are produced, and, therefore, cyclopropanes could be prepared (*Scheme 1,c*). We propose to call this approach '*spin-center shift* in biradicals'.

Naturally, only few reactions of monoradicals can be applied to biradicals due to their very short lifetimes [8]. On the other hand, based on the well-known velocities of acid elimination in OH-substituted radicals, this process should be fast enough to proceed within the lifetime of a triplet biradical, whereas singlet biradicals will presumably be too short-lived. As discussed below in detail, we found that only biradicals derived from esters of very strong acids undergo the spin-center shift. Especially, sulfonates and nitrates have proved to be reliable.

In this work, the preparation of such sulfonates and nitrates as well as their photochemical transformation to cyclopropyl ketones will be discussed. Furthermore,

mechanistic details of the reaction will be clarified by means of density-functional theory calculations.

2. Results and Discussion. – 2.1. *Preparation of 2-Oxoalkyl Sulfonates and Nitrates.* To investigate the photochemical cyclization of reactants bearing a broad variety of different substituents, we needed some flexible methods for the introduction of the leaving group. In this work, we used three different synthetic routes.

The simplest and most-convenient method for preparation of 2-oxoalkyl sulfonates is the treatment of ketones with hypervalent iodine reagents (*Method A*, *Scheme 2*). Thus, ketones **1** react with 1-hydroxy-1-phenyl-λ^3-iodanyl methanesulfonate (**2**) to the corresponding 2-oxoalkyl methanesulfonates **3** [9]. Unfortunately, this method works well only when the side chain R is not branched. Ketones with branched residues R afforded the desired products at best in low yields. In these cases, we switched from sulfonate to nitrate as the leaving group. 2-Oxoalkyl nitrates **5** can be prepared easily by bromination of ketones to α-bromo ketones **4** and subsequent exchange of bromide for nitrate with $AgNO_3$ (*Method B*) [10]. It should be noted that 2-oxoalkyl nitrates are highly sensitive even against weak bases and easily undergo a disproportionation to 1,2-diketones [11].

The second way to 2-oxoalkyl sulfonates starts with primary alcohols **6**, which were first oxidized to the corresponding aldehydes by means of pyridinium chlorochromate (PCC). Afterwards, the aldehydes were treated with lithiated 2-phenyl-2-(trimethylsilyloxy)acetonitrile, which may be considered a benzoyl anion equivalent. This 'Umpolung' approach was originally developed by *Hünig* and *Marschner* [12][2]). The obtained α-silyloxy ketones were desilylated to give α-hydroxy ketones **7** in good yields (*Table 1*).

The next step, the sulfonylation of the OH group, turned out to be somewhat difficult. Treating of α-hydroxy ketones **7** with MsCl or TsCl led in some cases to products that were contaminated with the corresponding α-chloro ketones, probably formed by a S_N2 displacement of sulfonate by chloride. This drawback may be circumvented by utilization of sulfonyl anhydrides instead of chlorides. Nevertheless, another side reaction takes place when mesyl anhydride is used. Especially when the reactant is sterically hindered, and, therefore, an excess of the reagents is required, an intramolecular aldol reaction between the Me group of methanesulfonate and the C=O group is observed, as already described [14]. Therefore, tosyl anhydride is the reagent of choice (*Method C*). The three methods for the preparation of 2-oxoalkyl sulfonates and 2-oxoalkyl nitrates are summarized in *Scheme 2* (*cf. Tables 1* and *2*).

The required ketones **1** and alcohols **6** are either commercially available or were prepared according to literature procedures. In some cases, new syntheses were developed, which are summarized in *Scheme 3* and will be briefly outlined.

The *Michael* addition of ethyl cyanoacetate **9** to phenyl vinyl ketone **8** afforded the α-cyano δ-oxo ester **10**, which was converted to the δ-oxo nitrile **1e** according to the

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[2]) We also considered to prepare the ketones **8** by *Corey–Seebach* reaction [13], but orienting investigation revealed that the cleavage of 1,3-dithiane ring of the primary product from the reaction between the lithiated 2-phenyl-1,3-dithiane and an aldehyde is often accompanied by an oxidation of the OH group to give 1,2-diketones.

Scheme 2. *Preparation of 2-Oxoalkyl Sulfonates* **3** *and 2-Oxoalkyl Nitrates* **5**

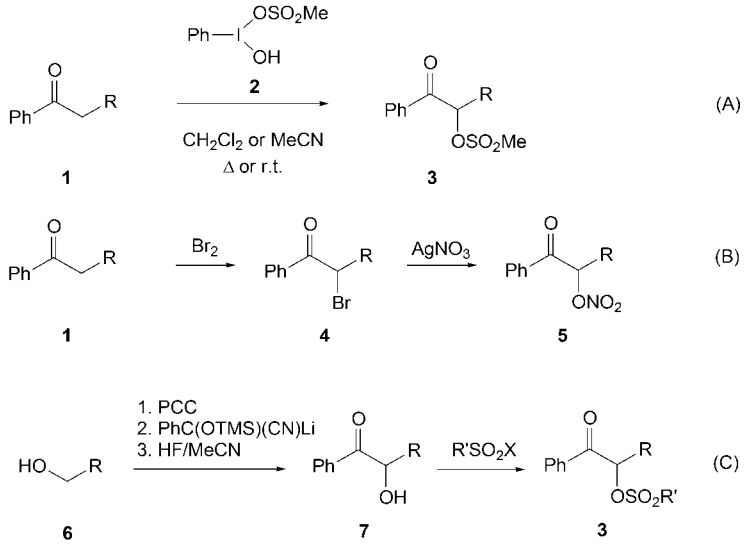


Table 1. *Synthesis of 2-Hydroxy Ketones* **7**[a])

Reactant	R	Product	Yield [%][b])
6a[c])	$BnO(CH_2)_2$	**7a**	63
6b[c])	PhCH(Me)	**7b**	73
6c[c]**)**	$CH_2{=}CH(CH_2)_2$	**7c**	43
6d	$PhC{\equiv}C(CH_2)_2$	**7d**	45
6e	Cyclopropyl-$(CH_2)_2$	**7e**	38
6f[c])	Cyclobutyl	**7f**	73
6g[c])	Cyclopentyl	**7g**	75
6h	Indan-2-yl	**7h**	68
6i[c])	Cyclohexyl	**7i**	71
6j	4-(*t*-Bu)-cyclohexyl	**7j**	57
6k	Tetrahydropyran-4-yl	**7k**	63
6l	*N*-Tosylpiperidin-4-yl	**7l**	56
6m[c])	*N*-Boc-piperidin-4-yl	**7m**	67

[a]) See *Scheme 3*. [b]) Three steps (1. PCC, 2. PhC(OTMS)(CN)Li, 3. HF/MeCN). [c]) Commercially available.

procedure described by *Krapcho* [15]. The commercially available pentenol **6c** was used as a reactant for the preparation of 3-cyclopropylpropan-1-ol (**6e**) by the *Simmons–Smith* cyclopropanation [2]. The straightforward ring opening of oxetane by lithium acetylides catalyzed by $BF_3 \cdot Et_2O$ [16] was utilized for the preparation of pentynol **6d**. The $HOCH_2$-substituted carbo- and heterocyclic compounds **6f**–**6m** are either commercially available (**6f**,**g**,**i**,**m**) or could be easily synthesized by $BH_3 \cdot Me_2S$ reduction of the corresponding carboxylic acids (for details, see *Exper. Part*).

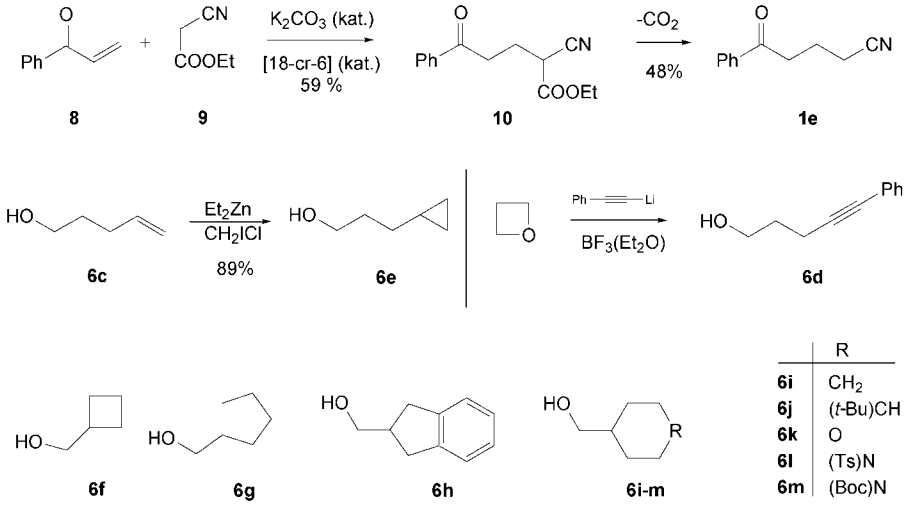
2.2. *Photochemical Cyclization to Cyclopropyl Ketones* **11.** – As mentioned above, in the course of the *Norrish–Yang* reaction, the O-atom of an excited C=O group

Table 2. *Syntheses of 2-Oxoalkyl Sulfonates* **3** *and 2-Oxoalkyl Nitrates* **5**.

Reactant	*Method*	Product	R	X	Yield [%]
1a[a])	*A*	**3a**	Et	MsO	85
1b[a])	*A*	**3b**	Pr	MsO	80
1c[a])	*A*	**3c**	i-Pr	MsO	33
1d[a])	*A*	**3d**	$Ph(CH_2)_2$	MsO	48
1e	*A*	**3e**	$NC(CH_2)_2$	MsO	70
7a	*C*	**3f**	$BnO(CH_2)_2$	MsO	75
7b	*C*	**3g**	PhCH(Me)	MsO	79
7c	*C*	**3h**	$CH_2{=}CH(CH_2)_2$	TsO	82
7d	*C*	**3i**	$PhC{\equiv}(CH_2)_2$	TsO	77
7e	*C*	**3j**	Cyclopropyl-$(CH_2)_2$	TsO	91
7f	*C*	**3k**	Cyclobutyl	TsO	74
7g	*C*	**3l**	Cyclopentyl	TsO	91
7h	*C*	**3m**	Indan-2-yl	TsO	82
7i	*C*	**3n**	Cyclohexyl	TsO	88
7j	*C*	**3o**	4-(*t*-Bu)-cyclohexyl	TsO	87
7k	*C*	**3p**	Tetrahydropyran-4-yl	TsO	84
7l	*C*	**3q**	*N*-Tosylpiperidin-4-yl	TsO	81
7m	*C*	**3r**	*N*-Boc-piperidin-4-yl	TsO	87
1f[b])	*B*	**5a**	MeOCOCH(Me)	NO_3	67[c])
1g[b])	*B*	**5b**	MeOCOCH(Bn)	NO_3	33[c])

[a]) Commercially available. [b]) See [17]. [c]) Two steps.

Scheme 3. *Synthesis of Some Ketones* **1** *and Alcohols* **6** *Used as Reactants*

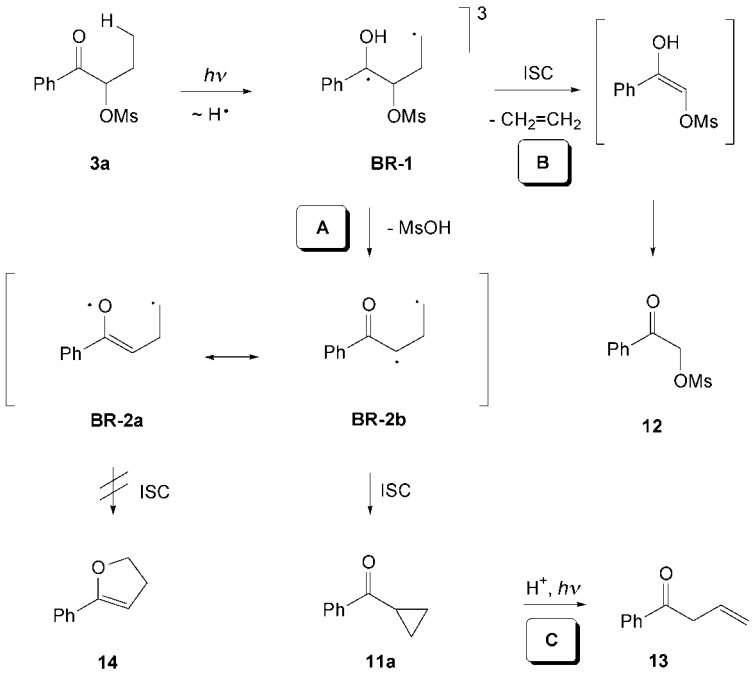


preferably attacks a C–H bond at the γ-position. Resulting from the H-migration, a 1,4-biradical is formed (*cf. Scheme 1*). Referring to the lifetimes of those biradicals, one must first distinguish between singlet and triplet biradicals. The former are very short-lived [18], and it is, therefore, unlikely that any chemical reaction could take place other than those affording closed-shell products (cleavage and cyclization). This

situation is completely different in the case of triplet biradicals. Their lifetimes range from 10 ns to 1 μs. Lifetimes of *ca.* 100 ns are most commonly observed [19]. Though these values do not seem to be large from the practical chemist's point of view, they are large enough for several chemical processes to occur while triplet biradicals persist. The elimination of an acid from an OH-substituted radical bearing a leaving group at the adjacent atom is one such fast reaction [20]. To ensure that only triplet biradicals are formed, we always used the benzoyl chromophore because it is well-known that, upon irradiation, benzoyl ketones are transferred solely to the n-π^*-excited triplet state [5].

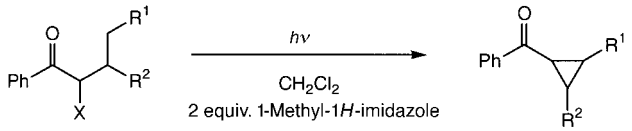
Reaction conditions for the cyclopropane synthesis were optimized by chosing the simplest reactant, 1-benzoylpropyl methanesulfonate (**3a**), for systematic photochemical investigations. The results are depicted in *Scheme 4*. Upon irradiation ($\lambda_{irr.} \geq$ 300 nm), **3a** readily provides the desired cyclopropyl phenyl ketone (**11a**; *Path A*), but the yields depend considerably on the solvent used. Whereas CH_2Cl_2 furnished satisfactory results, in Et_2O we observed the products of a *Norrish*-Type-II cleavage from the primarily formed biradical **BR-1** (*Path B*). Obviously, the acid elimination step is not much faster than the conventional deactivation processes of 1,4-biradicals. On the other hand, the irradiation in CH_2Cl_2 revealed another serious problem. In the course of the photolysis, a very strong acid is formed (MsOH), and, whereas cyclopropyl phenyl ketone **11a** itself is stable under the irradiation conditions, it readily undergoes ring opening to the unsaturated ketone **13** when acid is present (*Path C*). Therefore, the addition of an acid scavenger is necessary. The scavenger must fulfill two

Scheme 4. *Photochemical Behavior of 1-Benzoylpropyl Methanesulfonate* (**3a**)



preconditions, namely, its basicity and nucleophilicity must not be sufficient to attack the sensitive sulfonate moiety, and its oxidation potential must be high enough to avoid quenching of the excited C=O group by charge transfer [21]. After testing various compounds, we found that 1-methyl-1*H*-imidazole is most suitable. Applying the optimized conditions (CH_2Cl_2, 2 equiv. 1-methyl-1*H*-imidazole, irradiation wavelength > 300 nm), we obtained the cyclopropyl ketone **11a** in 87% yield (*Table 3*).

Table 3. *Synthesis of Cyclopropyl Phenyl Ketones* **11**.



3/5 **11**

Reactant	R^1	R^2	X	Product	Yield [%]	Remarks[a])
3a	H	H	MsO	**11a**	87	
3b	Me	H	MsO	**11b**	63	*trans* + 16% **15**
3c	H	Me	MsO	**11b**	90	*trans*
3d	Ph	H	MsO	**11c**	78	*cis*/*trans* 63 : 37
3e	CN	H	MsO	**11d**	65	*trans*
3f	BnO	H	MsO	**11e**	46	*trans*
3g	H	Ph	MsO	**11c**	44	*cis*/*trans* 63 : 37
3h	CH_2=CH	H	TsO	**11f**	80	*cis*/*trans* 50 : 50
3i	PhC≡C	H	TsO	**11g**	34	*cis*/*trans* 60 : 40 + 42% **3i**
3j	Cyclopropyl	H	TsO	**11h**	68	*cis*/*trans* 30 : 70
3k	$-(CH_2)_2-$		TsO	**11i**	61	*exo* + 7% **16**
3l	$-(CH_2)_3-$		TsO	**11j**	80	*exo*
3m	$-C_6H_4(CH_2)-$[b])		TsO	**11k**	78	*exo/endo* 80 : 20
3n	$-(CH_2)_4-$		TsO	**11l**	86	*exo*
3o	$-(CH)_2CH(t\text{-Bu})CH_2-$		TsO	**11m**	79	*exo*
3p	$-(CH)_2OCH_2-$		TsO	**11n**	74	*exo*
3q	$-(CH)_2N(Ts)CH_2-$		TsO	**11o**	78	*exo*
3r	$-(CH)_2N(BOC)CH_2-$		TsO	**11p**	69	*exo*
5a	H	MeOCO	NO_3	**11q**	59	*trans*
5b	Ph	MeOCO	NO_3	**11r**	37	1,2-*trans*-2,3-*cis*

[a]) The indicated ratios represent the photostationary equilibrium. [b]) **3m** = 2-[α-(Tosyloxy)phenacyl]indan.

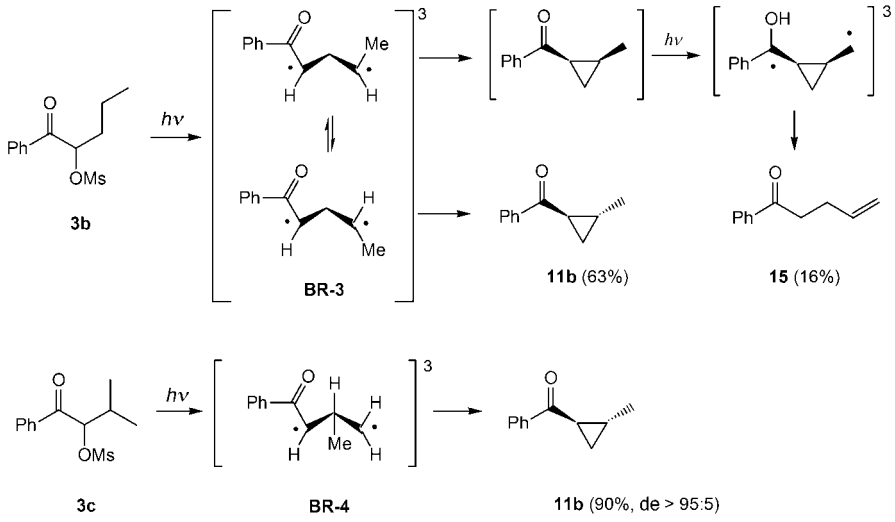
Another interesting phenomenon must be mentioned here. The biradicals **BR-2** may be considered to exist as two mesomeric species **BR-2a** and **BR-2b** that differ in the position of the spin center in the enolate radical moiety. Whereas **BR-2b** gives the desired cyclopropane **11a**, the products of **BR-2a** would be the dihydrofuran **14**. We recently reported the photochemical synthesis of 1,3-oxazin-4-ones; in this case, the enolate radical moiety reacted solely as an O-centered radical [22]. In the case of biradicals **BR-2**, we isolated exclusively the cyclopropyl ketone **11a**, and no indication for the formation of **14** was found. Obviously, the regioselectivity of the ring closure of biradicals formed in the course of a *spin-center shift* sensitively depends on the functional groups present between the two radical centers (*Scheme 4*).

To verify that the new method represents a general route to highly functionalized cyclopropyl ketones, we investigated the photochemical behavior of differently substituted ketones **3** and **5**. It must be noted that products **11** of the photochemical ring closure still contain the same chromophore as the reactants **3** and **5**, and, therefore, one must take into account both internal light filtering and photochemical reactions of the products. Whereas the former is obviously not a problem, as shown by the high product yield of **11a**, the photochemical reactivity of cyclopropanes **11** deserves special attention.

The introduction of alkyl groups into the resulting cyclopropanes raises an interesting question. It is well-known that cyclopropyl phenyl ketones bearing a *cis*-oriented alkyl group at the cyclopropane ring undergo efficient ring opening by intramolecular H-transfer, followed by a *Norrish*-Type-II cleavage of the biradical [23]. Therefore, when ring closure of Me-substituted ketones **3b** and **3c** does not proceed stereoselectively, a mixture of the *trans*-substituted cyclopropane **11b** and the unsaturated ketone **15** is expected. We found that the stereoselectivity of the ring closure and, consequently, the extent to which **15** is formed, remarkably depends on the position of the Me group. 1-Benzoylbutyl methanesulfonate (**3b**) furnishes 63% of *trans*-2-methylcyclopropyl phenyl ketone (**11b**) together with 16% of the unsaturated ketone **15**, whereas **11b** is the only product of the irradiation of 1-benzoyl-2-methylpropyl methanesulfonate (**3c**). This result can be explained easily by consideration of the appropriate 1,3-biradicals. In **BR-3**, a 1,3-interaction between benzoyl (Bz) and Me group causes an only moderate diastereoselectivity, while, in **BR-4**, a much stronger 1,2-interaction is responsible for the high selectivity (*Scheme 5*).

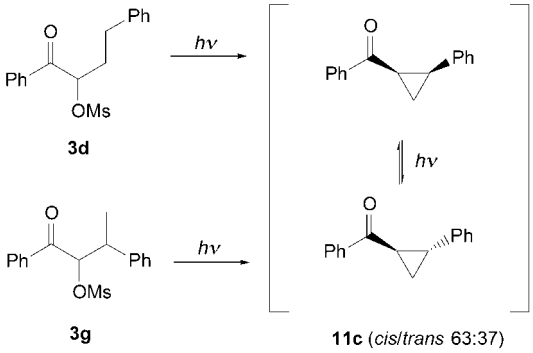
The stereochemical course of the cyclization of γ- and β-Ph substituted phenyl propyl ketones **3d** and **3g** was surprising at first. No matter at which position the Ph

Scheme 5. *Photochemical Behavior of Ketones* **3b** *and* **3c**



group was placed, we always obtained a 63 : 37 mixture of diastereoisomers of phenyl 2-phenylcyclopropyl ketone (**11c**), although the yields differed significantly. The same ratio of diastereoisomers was obtained by irradiation of each of the pure isomers *cis*-**11c** and *trans*-**11c**. Obviously, aryl-substituted cyclopropyl phenyl ketones undergo photochemical *cis*/*trans* isomerization (*Scheme 6*) [24]. The slightly preferred formation of the *cis*-isomer may be explained by a weak π-π interaction between the Bz group and the Ph group.

Scheme 6. *Photochemical Behavior of Ketones* **3d** *and* **3g**

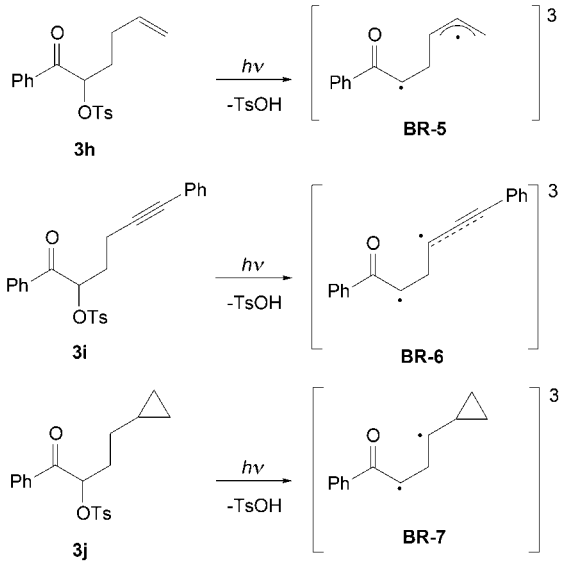


The particular importance of dipole–dipole interactions with respect to the diastereoselectivity of the ring closure is revealed by the photochemical behavior of esters **5a** and **5b**, the nitrile **3e**, and the ether **3f**. In all of these cases, only the *trans*-configured products were obtained. The only moderate yields upon irradiation of nitrates **5a** and **5b** arise not so much from photochemical but from purely thermal side reactions. They are highly sensitive to the presence of base, even the very weak base 1-methyl-1*H*-imidazole. The photochemical behavior of **5b** is remarkable, because the product **11r** also contains a Ph group, and one would expect, referring to the isomerization of **11c**, that a mixture of diastereoisomers would be formed. But, in spite of low yields due to thermal decomposition, we isolated only the product with 1,2-*trans*-2,3-*cis*-configuration. Obviously, the ring closure is dominated by dipole–dipole interactions between the two C=O-bearing residues.

Compounds **3h** and **3i**, bearing vinyl and phenylethynyl groups at the terminal C-atom, respectively, generate triplet biradicals **BR-5** and **BR-6**. In **BR-5**, the remote radical center is part of an allyl moiety, whereas **BR-6** contains a propargyl moiety at the same position (*Scheme 7*). From thermodynamic point of view, one would expect that the cyclization of **BR-5** occurs in a 1,5-fashion to give a cyclopentene as product. On the other hand, **BR-6** could undergo ring closure to a cyclobutenylcarbene without a change in spin state[3]). An analogous cyclization of 1-alkynyl-1,5-biradicals was described recently [25]. However, in both cases the cyclopropyl ketones **11f** and **11g**

[3]) DFT Calculations (B3PW91/6-31G*) revealed that the cyclization of the triplet pent-1-yne-3,5-diyl biradical to triplet (cyclobut-1-enyl)carbene is exothermic (*ca.* 8 kcal/mol).

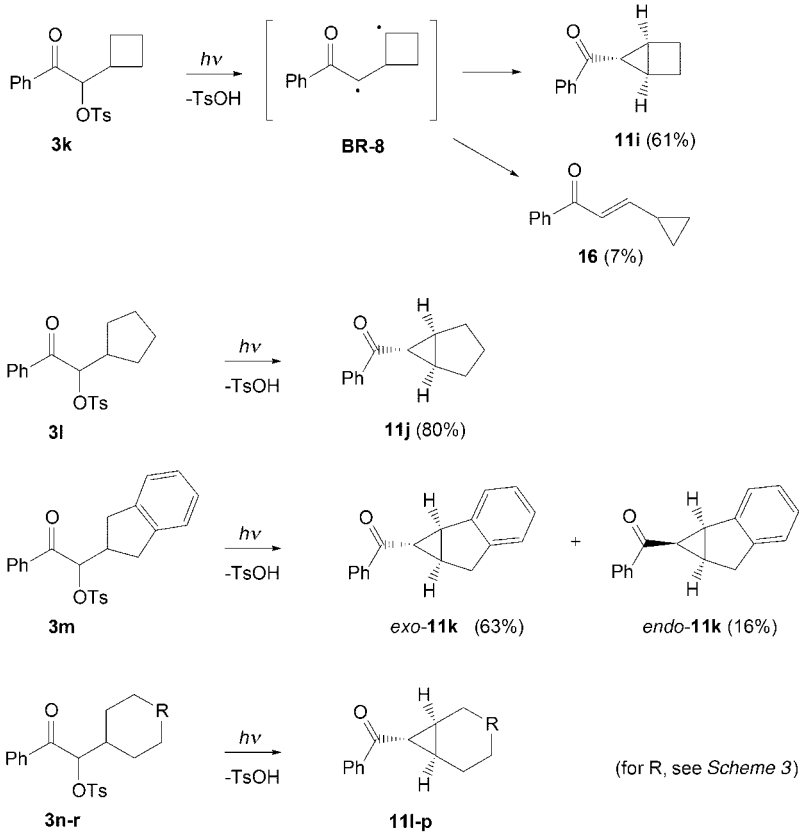
Scheme 7. *Formation of Biradicals* **BR-5**–**BR-7** *from 4-Vinyl-* (**3h**)*, 4-(Phenylethinyl)-* (**3i**)*, and 4-(Cyclopropyl)-* (**3j**) *2-(tosyloxy)butyrophenones*



were obtained as diastereoisomeric mixture. Apparently, the ring closure proceeds very fast, and, therefore, there is no time for the conformational changes necessary for the alternative 1,5- and 1,4-cyclization. To substantiate this hypothesis, we prepared the 4-cyclopropyl-2-(tosyloxy)-1-phenylbutan-1-one (**3j**). It is well-known that cyclopropylcarbinyl radicals undergo a very fast ring opening ($k = 4.0 \cdot 10^7\ s^{-1}$), and this reaction was often utilized for the determination of radical lifetimes [26]. Consequently, the formation of dicyclopropyl ketone **11h** in 68% yield and without any indication of an opening of the terminal cyclopropyl ring proves that the sum of the lifetimes of the primarily formed 1,4-biradical and biradical **BR-7** is considerably smaller than 25 ns. This value is in good agreement with the data previously described by *Caldwell et al.* for diarylcyclopropanes [27] (*Scheme 7*).

Bicyclic compounds bearing a cyclopropane moiety are wide-spread in natural products, and, therefore, we decided to apply our method to the synthesis of these interesting molecules. Irradiation of readily accessible ketones **3k**–**3r** furnished the desired bicyclic ketones **11i**–**11p** in good-to-excellent yields. It is noteworthy that, in all cases with exception of **3m**, only the *exo*-diastereoisomer could be isolated. The synthesis of bicyclo[2.1.0]pent-5-yl phenyl ketone ('benzoyl housane') **11i** is particularly interesting by virtue of the considerable ring strain of this compound. In addition to **11i**, we isolated the unsaturated ketone **16** in 7% yield. To clarify whether **16** is an alternative product of biradical **BR-8** or is formed by a subsequent photochemical reaction of housane **11i**, we irradiated **11i** separately and found that no formation of **16** occurs (*Scheme 8*).

Scheme 8. *Preparation of Bicyclic Ketones* **11i** *and* **11p**.



The configuration of the bicyclic compounds **11i**–**11p** was unambiguously established by X-ray analyses of **11j** and *exo*-**11k** (*Fig. 1* and *Table 4*)[4]).

2.3. *Photokinetic Investigations and Quantum-Chemical Calculations.* The efficient cyclization of ketones **3** and **5** to cyclopropyl ketones **11** brings up some questions. Though we did not determine the exact quantum yields of this reaction, the very rapid decomposition of the reactants upon irradiation clearly indicates that this process must be considerably more efficient than the 'classical' *Norrish–Yang* reaction. To investigate the reasons for this efficiency, we determined the rate constant of the initial intramolecular H-transfer for both 2-[(methylsulfonyl)oxy]-1-phenylbutan-1-one (**3a**) and 1-phenylbutan-1-one (**1a**). Thus, the rates of photochemical decomposition of **1a** and **3a** in the presence of different amounts of the triplet quencher 2,5-

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[4]) Crystallographic data (excluding structure factors) for **11j** and *exo*-**11k** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication No. CCDC-192089 (**11j**) and CCDC-193677 (*exo*-**11k**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 4. *Crystallographic Data of* **11j** *and* exo-**11k**

	11j	*exo*-**11k**
Empirical formula	$C_{13}H_{14}O$	$C_{17}H_{14}O$
Formula weight	186.24	234.28
Temp.	180(2) K	180(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	*P* 21/*n*	*P* 21 21 21
Unit-cell dimensions	$a = 6.290(3)$ Å, $\alpha = 90°$	$a = 5.6170(6)$ Å, $\alpha = 90°$
	$b = 8.815(5)$ Å, $\beta = 99.98(5)°$	$b = 7.9674(9)$ Å, $\beta = 90°$
	$c = 18.103(8)$ Å, $\gamma = 90°$	$c = 26.487(4)$ Å, $\gamma = 90°$
V	988.5(9) Å^3	1185.4(3) Å^3
Z, $D_{calc.}$	4, 1.251 Mg/m^3	4, 1.313 Mg/m^3
Absorption coefficient	0.077 mm^{-1}	0.080 mm^{-1}
F(000)	400	496
Crystal size	$0.88 \times 0.80 \times 0.56$ mm	$0.60 \times 0.40 \times 0.12$ mm
θ Range	2.28 – 27.48°	2.98 – 25.23°
Limiting indices	$-8 \le h \le 8$, $-11 \le k \le 11$, $-23 \le l \le 4$	$-6 \le h \le 6$, $-9 \le k \le 9$, $-31 \le l \le 31$
Reflections collected / unique	4499 / 2217 (R(int) = 0.0233)	6933/1292 (R(int) = 0.0466)
Completeness to $\theta = 27.48$	97.8%	99.8%
Max./min. transmission	0.9581 and 0.9352	0.9905 and 0.9536
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2217 / 0 / 184	1292 / 0 / 220
Goodness-of-fit on F^2	1.066	0.881
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0398$, $wR2 = 0.1081$	$R1 = 0.0264$, $wR2 = 0.0488$
R Indices (all data)	$R1 = 0.0421$, $wR2 = 0.1108$	$R1 = 0.0424$, $wR2 = 0.0510$
Extinction coefficient	0.068(7)	0.0103(15)
$\Delta\rho$ (max; min)	0.332 and −0.164 e.A^{-3}	0.119 and −0.131 e.A^{-3}

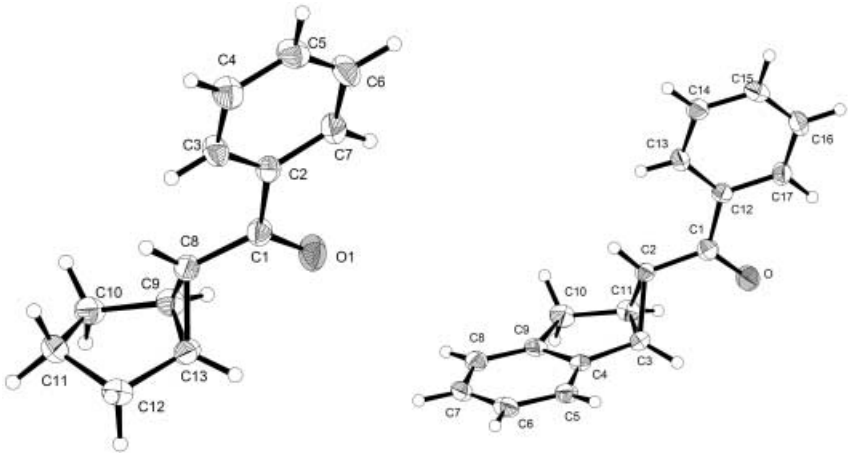


Fig. 1. *X-Ray structure of* **11j** *and* exo-**11k**

dimethylhexadiene were measured, and the lifetimes of triplet excited ketones were determined by *Stern – Volmer* plots. We found lifetimes of 115 ns for **1a** (which is in good agreement with the values published in [28]), and, surprisingly, only 3.4 ns for **3a**. Obviously, the leaving groups influence the reaction course not even at the stage of the

first biradical (**BR-1**; *Scheme 4*), but already in the initial stage of intramolecular H-transfer.

To discover an explanation for these findings, we performed DFT calculations on two simple model systems, 2-(mesyloxy)butanal (**I**) and butanal (**VI**) (B3PW91/6-311++G**//B3PW91/6-31G*; for details, see *Exper. Part*; the structures are collected in *Fig. 2*, the energies are summarized in *Table 5*). The first remarkable

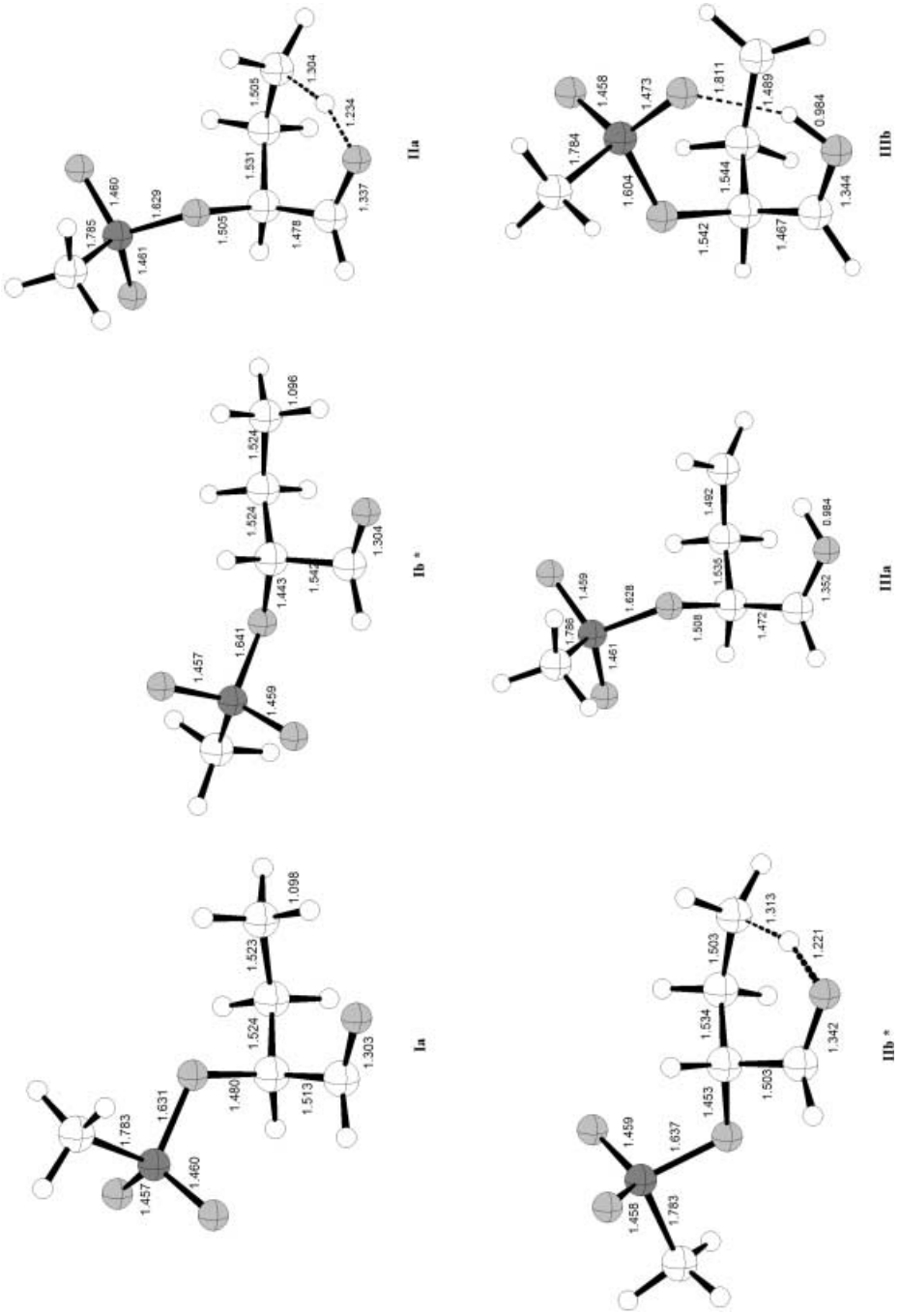
Table 5. *Calculated Energies of Species* **I**–**VIII**

Entry	E[a]) [a.u.]	ZPE[b]) [kcal/mol]	E + ZPE [kcal/mol]	E_{REL}[c]) [kcal/mol]
Ia	– 895.3836451	96.81	– 561765.38	± 0.0
Ib	– 895.3802291	96.69	– 561763.35	+ 2.0
IIa	– 895.3715884	93.71	– 561760.91	+ 4.5
IIb	– 895.3664576	93.72	– 561757.69	+ 7.7
IIIa	– 895.3857923	96.15	– 561767.39	– 2.0
IIIb	– 895.3827549	95.98	– 561765.66	– 0.3
IV	– 895.3798296	95.35	– 561764.44	+ 0.9
V	– 895.4018012	93.94	– 561779.64	– 14.3
VI	– 232.3230499	69.63	– 145715.40	± 0.0
VII	– 232.3081846	66.70	– 145709.01	+ 6.4
VIII	– 232.3234866	69.02	– 145716.29	– 0.9

[a]) Electronic energy (B3PW91/6-311++G**). [b]) Zero-point vibrational energy (B3PW91/6-31G*). [c]) Energy differences referring to **Ia** and **VI**, respectively.

result concerns the preferred conformation of the triplet state of **I**. In the *gauche* conformer with the lowest energy **Ia**, the C–O(Ms) bond is nearly eclipsed to the p_z orbital of the C-atom of the C=O group (dihedral angle O–C–C–O = – 69.02°, the C=O C-atom is considerably pyramidalized). The other conformer **Ib**, the O–C–C–O dihedral angle of which amounts to – 178.42°, is by 2 kcal/mol less favorable. Furthermore, the C–O(Ms) bond of **Ia** is significantly stretched compared with **Ib**, whereas the (carbonyl)C–(α)C bond of **Ia** is remarkably shorter than the corresponding bond of **Ib**. This phenomenon becomes understandable with the qualitative MO scheme depicted in *Scheme 9*. By combination of three orbitals of the C=O group (π, n, π^*) and two orbitals of the C–O(Ms) bond (σ,σ^*) five localized MOs are obtained. In the ground state, the n orbital of the C=O group represents the HOMO and the combination ($\pi^* + \sigma^*$) the LUMO. The latter MO is characterized by a σ^* antibonding contribution of the C–O(Ms) bond and a π-bonding contribution of the (carbonyl)C–(α)C bond. Upon photochemical n-π^* excitation, this orbital is singly occupied, explaining the above-mentioned changes in bond length.

The structural and energetic differences between **Ia** and **Ib**, caused by the above discussed hyperconjugation between C–O(Ms) bond and the excited C=O group, increase by turning to the transition states **IIa** and **IIb** of the intramolecular H-transfer. The energy of **IIb**, which corresponds to **Ib**, is by 3.2 kcal/mol higher than the energy of **IIa**. Furthermore, the presence of the leaving group in **I** lowers the activation barrier of the H-transfer by *ca.* 2 kcal/mol, compared with the unsubstituted 1-phenylbutan-1-one (**VI**) and the corresponding transition state **VII**. The initially formed biradical


1.460
1.785
1.629
1.461
1.505
1.531
1.478
1.505
1.304
1.234
1.337
IIa
1.096
1.524
1.524
1.304
1.443
1.542
1.641
1.457
1.459
IIb *
1.098
1.523
1.524
1.303
1.631
1.480
1.513
1.783
1.460
1.457
Ia
1.458
1.473
1.811
1.489
0.984
1.784
1.604
1.544
1.344
1.542
1.467
IIIb
1.492
1.459
1.628
1.535
0.984
1.786
1.508
1.472
1.352
1.461
IIIa
1.313
1.503
1.221
1.534
1.342
1.453
1.503
1.459
1.637
1.458
1.783
IIb *

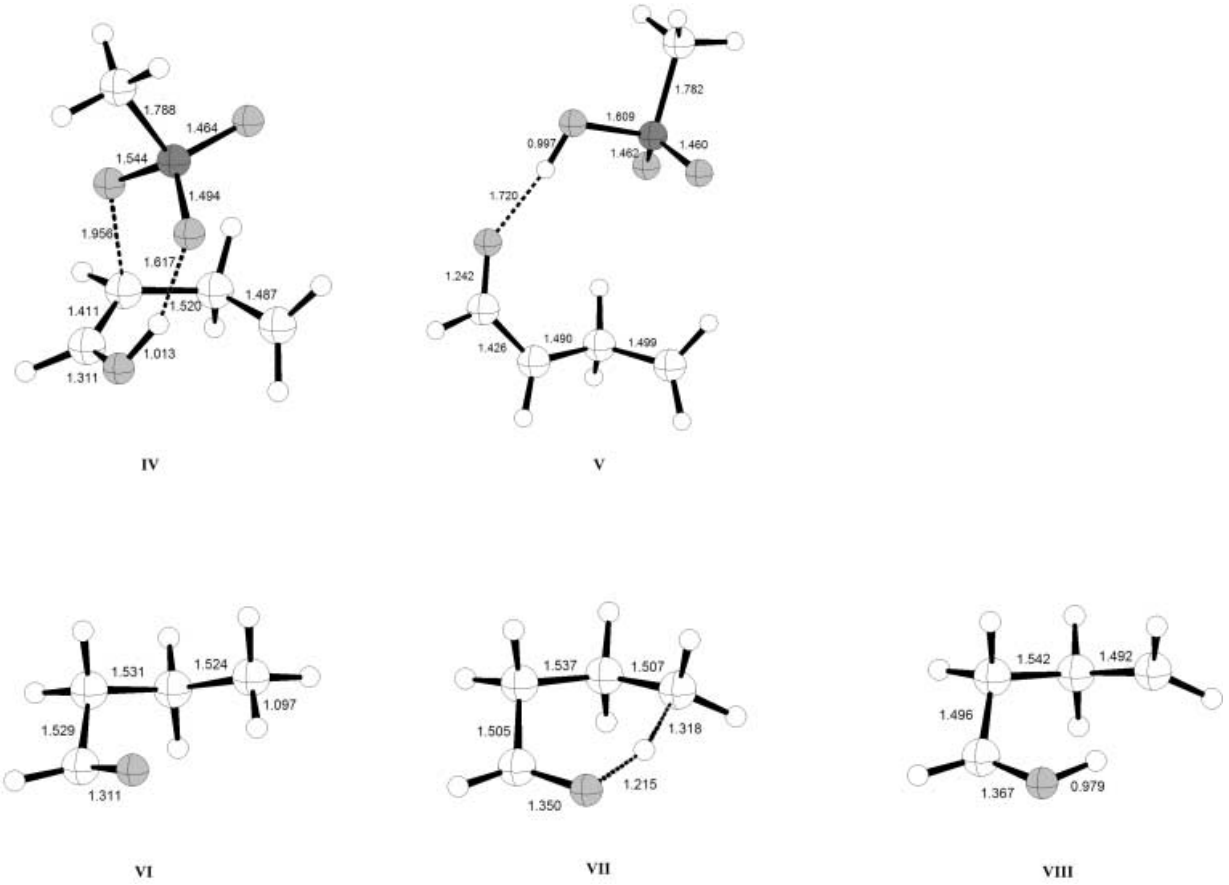
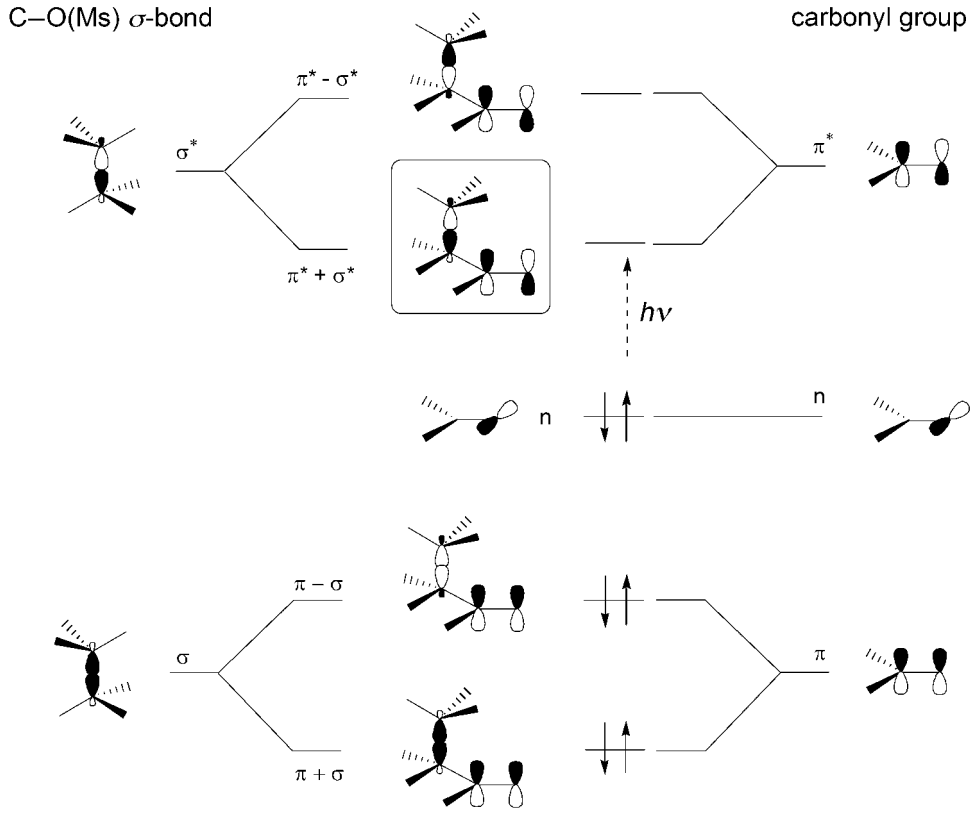


Fig. 2. *Calculated structures* **I**–**VIII**. *) The structures were mirrored for better clearness.

Scheme 9



conformer **IIIa** may be converted to another conformer **IIIb** by rotation around the C–O(Ms) bond. Conformer **IIIb**, which is slightly less favorable from an energetic point of view, is characterized by an intramolecular H-bond between the OH group and an O-atom of the Ms group. The structure of this conformer already indicates the subsequent elimination of MsOH *via* the transition state **IV**. Thus, the C–O(Ms) bond in **IIIb** is remarkably stretched, compared with **IIIa** (1.508 *vs.* 1.542 Å). The acid elimination giving the H-bonded complex **V** between the 1-oxobutane-2,4-diyl biradical and MsOH occurs *via* a very low activation barrier of 1.2 kcal/mol. Bearing in mind that this step is certainly irreversible, one now has found the key for understanding the high efficiency of the reaction. It is well-known that the main reason for the low quantum yields of the triplet *Norrish–Yang* reaction is the H back-transfer, which proceeds with a simultaneous intersystem crossing to the singlet state [5e]. When a leaving group is present, as in the model system **I** or in compounds **3** and **5**, the H back-transfer competes with the very fast and, above all, irreversible acid elimination. Consequently, the high efficiency of the cyclopropyl ketone formation is now clearly understandable.

3. Conclusions. – In the present study, we describe a novel and straightforward method for the preparation of highly functionalized cyclopropyl ketones **11**. The method is based on the *Norrish–Yang* reaction of ketones, which bear a leaving group adjacent to the C=O C-atom. In such cases, the primarily formed biradicals are subject to rapid and efficient acid elimination. The main feature of this process is the shift of spin density from the former C=O C-atom to the C-atom that bears the leaving group. Therefore, we call this overall process *spin-center shift*.

Our method is not only suitable for preparation of monocyclic cyclopropanes (*i.e.*, **11a–11h, 11q**, and **11r**) but also permits the synthesis of bicyclic compounds (*i.e.*, **11i–11p)**. The formation of highly strained 'housane' **11i** in good yield is particularly remarkable because it impressively demonstrates the preparative potential of the method.

Though the mechanism of our photochemical cyclopropane synthesis and the 'classical' *Norrish–Yang* reaction agree in some points, there are also appreciable differences. We found by triplet-quenching experiments that the rate of the initial H-abstraction by the excited C=O group becomes larger by approximately two orders of magnitude as a result of introduction of the leaving group. Furthermore, we observed a high efficiency of product formation, even though the formed cyclopropyl ketones **11** bear the same chromophoric group as the reactants **3** and **5**. These experimental findings could be easily explained by the results of density-functional calculations on model systems **I–VIII** bearing a CHO group instead of the Bz group in **3** and **5**. At present, further applications of the method to more-complicated molecules are under investigation.

This work was supported by the *Deutsche Forschungsgemeinschaft* (DFG, We 1830-3/1-2). We also thank *B. Ziemer* for the X-ray-analysis of **11j** and *exo*-**11k**

Experimental Part

General. The following reagents were commercially available: *1-phenylbutan-1-one* (**1a**), *1-phenylpentan-1-one* (**1b**), *3-methyl-1-phenylbutan-1-one* (**1c**), *1,4-diphenylbutan-1-one* **1d**, *3-benzyloxypropan-1-ol* (**6a**), *2-phenylpropan-1-ol* (**6b**), *pent-4-en-1-ol* (**6c**), *cyclobutylmethanol* (**6f**), *cyclopentylmethanol* (**6g**), *cyclohexylmethanol* (**6i**), *1-[(*tert-*butoxy)carbonyl]piperidine-4-methanol* (**6m**), *ethyl 2-cyanoacetate* (**9**), trans-4-(tert-*butyl*)-*cyclohexanecarboxylic acid* (**17**), *piperidine-4-carboxylic acid* (**18**). The following reagents were prepared according to literature procedures: *methyl 2-methyl-4-oxo-4-phenylbutanoate* (**1f**) [17], *methyl 2-benzyl-4-oxo-4-phenylbutanoate* (**1g**) [17], *1-hydroxy-1-phenyl-*λ^3*-iodanyl methanesulfonate* (HMIB; **2**) [28], *2-phenyl-2-(trimethylsilyloxy)acetonitrile* [29], p-*toluenesulfonic anhydride* [30], *5-Phenylpent-4-yn-1ol* (**6d**) [16], *phenyl vinyl ketone* **8** [31], *indan-2-carboxylic acid* (**19**) [32], *3,4,5,6-tetrahydro-2*H-*pyran-4-carboxylic acid* (**20**) [33]. THF and Et_2O were dried over Na metal in the presence of benzophenone as an indicator of dryness and distilled at atmospheric pressure. CH_2Cl_2 and 1,2-dichloroethane were dried by heating under reflux over P_2O_5 and distilled at atmospheric pressure. All moisture-sensitive reagents were transferred *via* syringe under N_2 or Ar; moisture-sensitive reactions were carried out under N_2 or Ar. Flash column chromatography (FCC): silica gel, 230–400 mesh (*Fluka*). Anal. TLC: precoated *Merck* silica gel *60* F_{254} plates; detection by UV light. M.p.: *Büchi 530*, uncorrected. IR: *Perkin-Elmer-881*, solids as KBr pastes, liquids and oils on NaCl crystals as film, in cm^{-1}. NMR: $CDCl_3$, CD_2Cl_2, and (D_6)DMSO solns.; *Bruker DPX-300* equipment; chemical shifts δ in ppm; calibration: $CDCl_3$ (^{1}H: 0.00 ppm = Me_4Si; ^{13}C: 77.0 ppm), (D_6)DMSO (^{1}H: 2.49 ppm; ^{13}C: 39.5 ppm), CD_2Cl_2 (^{1}H: 5.32 ppm; ^{13}C: 53.8 ppm); Some compounds were obtained as mixture of two diastereoisomers. In these cases, the data of the minor product are given in square brackets; the relative configuration of the products were determined by NOE, NOESY, ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-COSY experiments. EI-MS: *Hewlett-Packard 5995 A*, 70 eV at 293–593 K, *m*/*z* (%). HR-EI-MS: *MSI Concept 1 H*. Elemental Analysis were carried out by the analytical laboratory of the Institute of Chemistry of the Humboldt-University Berlin. Photochemistry: prep.

irradiations with a 150-W high pressure Hg-arc lamp (*Hanau*); anal. irradiations with a 500-W high pressure Hg-arc lamp (*OSRAM HBO-500*), UV cuvette 1 × 1 cm, filter *WG 295* (*Schott*).

Quantum-Chemical Calculations. The geometry optimization of molecules **I** – **VIII** were performed with the program package Gaussian 98 [34], the B3PW91 hybrid functional[5]), and the 6-31G* basis set. At the same level of theory, frequency calculations were carried out to characterize each structure as minimum (**Ia**,**b**, **IIIa**,**b**, **V**, **VI**, and **VIII)** or transition state (**IIa**,**b**, **IV**, and **VII**) and to obtain the zero-point vibrational energies. Afterwards, single-point calculations were performed with the same DFT functional and the extended basis set 6-311 ++ G** basis set in order to obtain improved energies.

General Procedure A (*GP A*) *for the 2-Mesyloxylation of Ketones* **1a** – **1e**. To a stirred mixture of the appropriate ketone **1a** – **1e** (10.0 mmol) in MeCN or CH_2Cl_2 (25 ml) was added HMIB (**2**; 3.16 g, 10.0 mmol). The mixture was stirred at r.t. or heated under reflux until TLC indicated disappearance of the ketone **1**. The mixture was concentrated to an oil (when MeCN was used as solvent), diluted with CH_2Cl_2 (25 ml), washed with brine (25 ml) and H_2O (25 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Purification of the residue by FCC (petroleum ether/AcOEt 10 : 1 – 10 : 3) gave the 2-mesyloxy ketones **3a** – **3e**.

General Procedure B (*GP B*) *for the Synthesis of 2-Hydroxy Ketones* **7a** – **7m**. The appropriate alcohol **6a** – **6m** (20.0 mmol) in CH_2Cl_2 (10 ml) was added in one portion to a magnetically stirred suspension of PCC (6.47 g, 30.0 mmol) in anh. CH_2Cl_2 (50 ml). After TLC indicated disappearance of the alcohol (1.5 – 4 h), the supernatant liquid was decanted from the black gum and filtered through a short column of *Florisil*, *Celite*, and silica gel. The insoluble residue was washed five times with 25-ml portions of Et_2O. The combined org. layers were passed through the same short column, and the solvent was removed under reduced pressure. The aldehyde was used immediately for the next reaction without further purification. In a dry 250-ml two-necked round-bottomed flask fitted with a N_2 bubbler, a rubber septum, and a magnetic stir bar was placed dry Et_2O (50 ml) and $(i\text{-}Pr)_2NH$ (2.23 g, 22.0 mmol). The soln. was cooled to – 78° (dry ice/acetone), and 22.0 mmol of a 1.6M solution of BuLi in hexane was added dropwise. After 0.5 h, a soln. of 20.0 mmol of freshly distilled 2-phenyl-2-(trimethylsilyloxy)acetonitrile and dry Et_2O (5 ml) was added dropwise, and the resultant mixture was stirred for 0.75 h, followed by a dropwise addition of the aldehyde in 5 ml dry Et_2O. The mixture was kept at – 70° for an additional 2 – 3 h and quenched by addition of sat. aq. NH_4Cl soln. (30 ml). After warming to r.t., the aq. layer was extracted with Et_2O (2 × 20 ml), and the combined org. extracts were washed with sat. aq. NH_4Cl soln. (2 × 30 ml) and dried ($MgSO_4$). Concentration *in vacuo* gave a yellow-brown oil that was dissolved in 30 ml of MeCN. The magnetically stirred soln. was cooled to 0°, and HF (40%, aq.) was added dropwise until TLC indicated completion of the desilylation. After addition of solid $NaHCO_3$, the mixture was stirred for an additional 0.5 h, diluted with Et_2O (30 ml), filtered, dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by FCC (petroleum ether/AcOEt 100 : 5 – 10 : 3) gave the 2-hydroxy ketones **7a** – **7m**.

General Procedure C (*GP C*) *for the Mesylation of 2-Hydroxy Ketones* **7a** and **7b**. To a magnetically stirred soln. of the appropriate 2-hydroxy ketone **7a** or **7b** (15.0 mmol) and dry CH_2Cl_2 (30 ml) were added at 0° Et_3N (1.52 g, 15.0 mmol) and MsCl (1.72 g, 15.0 mmol). After TLC indicated completion of the reaction (0.5 – 3 h), the mixture was diluted with CH_2Cl_2 (20 ml), washed with 2M HCl (20 ml), and sat. aq. $NaHCO_3$ soln. (3 × 20 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by FCC (petroleum ether/AcOEt 10 : 1 – 10 : 3) gave the 2-mesyloxy ketones **3f** and **3g**.

General Procedure D (*GP D*) *for the Tosylation of 2-Hydroxy Ketones* **7c** – **7m**. To a magnetically stirred soln. of the appropriate 2-hydroxy ketone **7c** – **7m** (15.0 mmol) and dry CH_2Cl_2 (30 ml) were added at 0° pyridine (1.19 g, 15.0 mmol) and Ts_2O (4.90 g, 15.0 mmol). After TLC indicated completion of the reaction (0.5 – 6 h), the mixture was diluted with CH_2Cl_2 (20 ml), washed with 2M HCl (20 ml) and sat. aq. $NaHCO_3$ soln. (3 × 20 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by FCC (petroleum ether/AcEtO 10 : 1 – 10 : 3) gave the 2-tosyloxy ketones **3h** – **3r**.

General Procedure E (*GP E*) *for the 2-Bromination of Ketones* **1f** and **1g**. To a magnetically stirred soln. of the appropriate ketone **1f** or **1g** (30.0 mmol) and CH_2Cl_2 (50 ml) was added dropwise Br_2 (4.79 g, 30.0 mmol) in 30 ml of CH_2Cl_2 until no discoloration of the mixture was observed. Complete conversion was detected by TLC. Evaporation *in vacuo* gave the 2-bromo ketones **4a** and **4b**.

General Procedure F (*GP F*) *for the 2-Nitrooxylation of 2-Bromo Ketones* **4a** and **4b**. To a soln. of the appropriate 2-bromo ketone **4a** or **4b** (10.0 mmol) and dry MeCN (100 ml) was added $AgNO_3$ (80.0 mmol), and

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[5]) B3PW91 is *Becke*'s 3-parameter functional [35a] with the nonlocal correlation provided by the *Perdew 91* expression [35b].

the mixture was stirred at r.t. until TLC indicated complete conversion (2–10 d). The mixture was filtered to remove AgBr partially. Remaining AgBr could be removed after concentration *in vacuo*, addition of Et_2O (20 ml), and filtration. Evaporation under reduced pressure and purification of the residue by FCC (petroleum ether/AcOEt 10:1–10:3) gave the 2-nitrooxy ketones **5a** and **5b**.

General Procedure G (*GP G*) *for the Synthesis of Alcohols* **6h**, **6j**, **6k**, and **6l**. To a magnetically stirred soln. of $BH_3 \cdot Me_2S$ (3.65 g, 48.0 mmol) and dry THF (100 ml) was added the appropriate carboxylic acid **17**, **19**, **20**, and **21** (40.0 mmol) in dry THF (20 ml). The mixture was refluxed until TLC indicated complete conversion of the carboxylic acid (1–3 h). After removing the solvent under reduced pressure, the residue was hydrolyzed by addition of H_2O at 0°. The aq. layer was extracted with CH_2Cl_2 (3 × 50 ml), and the combined org. extracts were washed with sat. aq. $NaHCO_3$ soln. (2 × 50 ml) and dried ($MgSO_4$). Concentration *in vacuo* gave the alcohols **6h**, **6j**, **6k**, and **6l**.

General Procedure H (*GP H*) *for the Photochemical Synthesis of Cyclopropyl Phenyl Ketones* **11a**–**11d** and **11f**–**11r**. Irradiations of ketones **3a**–**3e**, **3g**–**3r**, **5a**, and **5b** were performed in CH_2Cl_2 (200 or 400 ml) at concentrations of 0.01 mmol/ml in the presence of 1-methyl-1*H*-imidazole (2 equiv.), with a high-pressure Hg-arc lamp (150 W). Light of wavelength below 300 nm was absorbed with a *Pyrex*™ glass jacket between the lamp and the reaction vessel. The reaction was monitored by TLC and aborted when the reactant had completely disappeared (30–60 min). The soln. was washed with H_2O (2 × 100 ml), dried ($MgSO_4$), and concentrated *in vacuo* to 10% of the original volume. To the soln. was added silica gel (5 g), and the remaining solvent was removed under reduced pressure. The residue was purified immediately by FCC (petroleum ether/AcOEt 100:3–100:15) to give the **11a**–**11d** and **11f**–**11r**.

Ethyl 2-Cyano-5-oxo-5-phenylpentanoate (**10**). To a magnetically stirred soln. of **8** (1.32 g, 10.0 mmol), **9** (1.13 g, 10.0 mmol) in dry THF (40 ml) were added K_2CO_3 (0.14 g, 1.01 mmol) and 18-crown-6 (0.27 g, 1.02 mmol). After 45 min, TLC indicated complete conversion of the reactants. The mixture was hydrolyzed with H_2O (10 ml), diluted with Et_2O (100 ml), washed with H_2O (2 × 100 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by FCC (petroleum ether/AcOEt 100:15) gave **10** (1.45 g, 59%). Colorless solid. M.p. 89–91°. IR (KBr): 1744, 1731, 1686, 1597, 1580, 1449, 1365, 1208. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00–7.92 (*m*, 2 H); 7.62–7.55 (*m*, 1 H); 7.52–7.42 (*m*, 2 H); 4.28 (*q*, *J* = 7.2, 2 H); 3.82 (*dd*, *J* = 6.0, 8.3, 1 H); 3.25 (*t*, *J* = 7.2, 2 H); 2.55–2.25 (*m*, 2 H); 1.32 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.6, 165.7 (C=O); 136.1 (arom. C_q); 133.5, 128.6, 127.8 (arom. CH); 116.3 (C_q); 62.9 (CH_2); 36.4 (CH); 34.6 (CH_2); 23.9 (CH_2); 13.9 (Me). EI-MS: 245 (16, M^+), 133 (16), 105 (100, $PhCO^+$), 77 (48, Ph^+), 51 (8). Anal. calc. for $C_{14}H_{15}NO_3$ (245.27): C 68.56, H 6.16, N 5.71; found: C 68.67, H 6.36, N 5.33.

5-Oxo-5-phenylpentanenitrile (**1e**). The ester **10** (1.23 g, 5.01 mmol), NaCl (0.30 g, 5.13 mmol) and H_2O (2 ml) in DMSO (18 ml) were refluxed until TLC indicated complete conversion of **10** (20 h). The mixture was diluted with H_2O (60 ml) and extracted with Et_2O (6 × 50 ml). The combined org. extracts were washed with H_2O (2 × 100 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by FCC (petroleum ether/AcOEt 10:2) gave **1e** (0.41 g, 48%). Colorless oil. IR (film): 1684, 1597, 1448, 1234, 691. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00–7.92 (*m*, 2 H); 7.62-7.53 (*m*, 1 H); 7.52–7.42 (*m*, 2 H); 3.17 (*t*, *J* = 7.2, 2 H); 2.52 (*t*, *J* = 7.2, 2 H); 2.11 (*quint.*, *J* = 7.2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.0 (C=O); 136.3 (arom. C_q); 133.3, 128.6, 127.8 (arom. CH); 119.3 (C_q); 36.2 (CH_2); 19.6 (CH_2); 16.5 (CH_2). EI-MS: 173 (8, M^+), 105 (100, $PhCO^+$), 77 (41, Ph^+), 51 (15). Anal. calc. for $C_{11}H_{11}NO$ (173.21): C 76.28, H 6.40, N 8.09; found: C 75.92, H 6.28, N 8.17.

1-Benzoylpropyl Methanesulfonate (**3a**). *GP A* (CH_2Cl_2, 24 h reflux) starting from **1a** afforded **3a** in 85% yield. Colorless solid. M.p. 59–60°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.96–7.92 (*m*, 2 H); 7.67–7.62 (*m*, 1 H); 7.55–7.50 (*m*, 2 H); 5.92–5.87 (*m*, 1 H); 3.15 (*s*, 3 H); 2.19–1.90 (*m*, 2 H); 1.08 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 195.2 (C=O); 134.1 (arom. C_q); 134.1, 129.0, 128.5 (arom. CH); 82.2 (CH); 39.3 (Me); 26.0 (CH_2); 9.5 (Me). IR (KBr): 1689, 1356, 1175, 959, 910, 864, 698. EI-MS: 146 (5, $[M - MsOH]^+$), 105 (100, $PhCO^+$), 77 (35, Ph^+), 51 (13). Anal. calc. for $C_{11}H_{14}O_4S$ (242.29): C 54.53, H 5.82, S 13.23; found: C 54.53, H 5.92, S 13.43.

1-Benzoylbutyl Methanesulfonate (**3b**). *GP A* (CH_2Cl_2, 24 h reflux) starting from **1b** afforded **3b** in 80% yield. Colorless solid. M.p. 59–61°. IR (KBr): 1690, 1354, 1210, 1171, 977, 933, 701. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.96–7.92 (*m*, 2 H); 7.68–7.61 (*m*, 1 H); 7.54–7.48 (*m*, 2 H); 5.96–5.91 (*m*, 1 H); 3.13 (*s*, 3 H); 1.97–1.84 (*m*, 2 H); 1.62–1.50 (*m*, 2 H); 0.94 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.3 (C=O); 134.1 (arom. C_q); 134.1, 129.0, 128.5 (arom. CH); 80.1 (CH); 39.3 (Me); 34.4 (CH_2); 18.4 (CH_2); 13.4 (CH_3). EI-MS: 160 (5, $[M - MsOH]^+$), 105 (100, $PhCO^+$), 77 (28, Ph^+), 55 (7), 51 (8). Anal. calc. for $C_{12}H_{16}O_4S$ (256.32): C 56.23, H 6.29, S 12.51; found: C 55.63, H 6.21, S 12.66.

1-Benzoyl-2-methylpropyl Methanesulfonate (**3c**). *GP A* (CH_2Cl_2, 24 h r.t.) starting from **1c** afforded **3c** in 33% yield. Colorless solid. M.p. 69–71°. IR (KBr): 1696, 1363, 1178, 974, 941, 874, 694. ^{1}H-NMR (300 MHz,

$CDCl_3$): 7.93–7.89 (*m*, 2 H); 7.66–7.59 (*m*, 1 H); 7.54–7.48 (*m*, 2 H); 5.78–5.76 (*d*, *J* = 4.2, 1 H); 3.12 (*s*, 3 H); 2.41–2.30 (*m*, 1 H); 1.12 (*t*, *J* = 6.8, 3 H); 0.92 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.3 (C=O); 134.7 (arom. C_q), 134.0, 128.9, 128.4 (arom. CH); 85.4 (CH); 39.1 (Me); 31.1 (CH); 19.2 (Me); 16.2 (Me). EI-MS: 160 (4, $[M - MsOH]^+$), 105 (100, $PhCO^+$), 77 (28, Ph^+), 55 (10), 51 (9). Anal. calc. for $C_{12}H_{16}O_4S$ (256.32): C 56.23, H 6.29, S 12.51; found: C 55.82, H 6.15, S 12.73.

1-Benzoyl-3-phenylpropyl Methanesulfonate (**3d**). *GP A* (MeCN, 24 h reflux) starting from **1d** afforded **3d** in 48% yield. Colorless solid. M.p. 52–57°. IR (KBr): 1692, 1361, 1354, 1174, 934, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73–7.69 (*m*, 2 H); 7.62–7.55 (*m*, 1 H); 7.45–7.39 (*m*, 2 H); 7.37–7.19 (*m*, 5 H); 5.91–5.86 (*m*, 1 H); 3.15 (*s*, 3 H); 2.98–2.77 (*m*, 2 H); 2.28–2.16 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 195.0 (C=O); 139.5, 133.7 (arom. C_q); 134.1, 128.9, 128.7, 128.4, 126.5 (arom. CH); 80.0 (CH); 39.4 (Me); 34.0 (CH_2); 31.1 (CH_2). EI-MS: 222 (3, $[M - MsOH]^+$), 214 (17, $PhCOCH_2OMs^+$), 135 (40), 105 (100, $PhCO^+$), 91 (26, $PhCH_2^+$), 77 (39, Ph^+), 51 (11). Anal. calc. for $C_{17}H_{18}O_4S$ (318.39): C 64.13, H 5.70, S 10.07; found: C 63.83, H 5.83, S 9.89.

1-Benzoyl-3-cyanopropyl Methanesulfonate (**3e**). *GP A* (MeCN, 24 h reflux) starting from **1e** afforded **3e** in 70% yield. Colorless solid. M.p. 60–62°. IR (KBr): 1727, 1698, 1364, 1289, 1278, 1173, 943. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.97–7.93 (*m*, 2 H); 7.71–7.65 (*m*, 1 H); 7.58–7.52 (*m*, 2 H); 6.05 (*dd*, *J* = 3.8, 8.7, 1 H); 3.18 (*s*, 3 H); 2.73–2.51 (*m*, 2 H); 2.45–2.33 (*m*, 1 H); 2.29–2.16 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 193.5 (C=O); 133.3 (arom. C_q); 134.8, 129.3, 128.5 (arom. CH); 125.9 (C_q); 77.9 (CH); 39.4 (Me); 28.2 (CH_2); 13.4 (CH_2). EI-MS: 105 (100, $PhCO^+$), 77 (33, Ph^+), 51 (10). Anal. calc. for $C_{12}H_{13}NO_4S$ (267.30): C 53.92, H 4.90, N 5.24, S 12.00; found: C 53.68, H 4.78, N 5.41, S 12.32.

4-Benzyloxy-2-hydroxy-1-phenylbutan-1-one (**7a**). *GP B* starting from **6a** afforded **7a** in 63% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.95–7.89 (*m*, 2 H); 7.63–7.25 (*m*, 8 H); 5.32–5.28 (*m*, 1 H); 4.48 (*s*, 2 H); 3.70–3.60 (*m*, 2 H); 2.27–2.16 (*m*, 1 H); 1.86–1.75 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.8 (C=O); 138.2, 129.6 (arom. C_q); 133.7, 128.9, 128.5, 128.0, 127.9, 127.6 (arom. CH); 73.1 (CH_2); 70.6 (CH); 66.1 (CH_2); 36.1 (CH_2).

*(2*SR*,3*RS*)-2-Hydroxy-1,3-diphenylbutan-1-one* (**7b**). *GP B* starting from **6b** afforded **7b** in 63% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.96–7.89 (*m*, 2 H); 7.60–7.10 (*m*, 8 H); 5.27–5.23 (*m*, 1 H); 3.23 (*dq*, *J* = 7.2, 1 H); 1.08 (*d*, *J* = 7.2, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.4 (C=O), 143.8, 133.9 (arom. C_q); 134.0, 128.9, 128.6, 128.5, 127.7, 126.8 (arom. CH); 77.0 (CH); 43.3 (CH); 13.3 (Me). NMR Data: identical to those reported in [12].

2-Hydroxy-1-phenyl-hex-5-en-1-one (**7c**). *GP B* starting from **6c** afforded **7c** in 43% yield. Colorless oil. IR (film): 3472, 2926, 1681, 1597, 1449, 1271, 1076, 980, 915, 699. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.95–7.86 (*m*, 2 H); 7.67–7.58 (*m*, 1 H); 7.57–7.47 (*m*, 2 H); 5.87–5.73 (*m*, 1 H); 5.13–5.97 (*m*, 3 H); 3.75 (*d*, *J* = 6.4, OH); 2.39–2.16 (*m*, 2 H); 2.01–1.89 (*m*, 1 H); 1.68–1.57 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.9 (C=O); 137.3 (olef. CH); 133.5 (arom. C_q); 133.9, 128.9, 128.5 (arom. CH); 115.7 (olef. CH_2); 72.3 (CH); 35.0 (CH_2); 29.1 (CH_2). EI-MS: 190 (4, M^+), 136 (20), 105 (100, $PhCO^+$), 77 (42, Ph^+), 51 (17). Anal. calc. for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.63, H 7.27.

1,6-Diphenyl-2-hydroxy-hex-5-yn-1-one (**7d**). *GP B* starting from **6d** afforded **7d** in 45% yield. Colorless oil. IR (film): 1688, 1598, 1490, 1450, 1272, 757, 693. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.84–7.78 (*m*, 2 H); 7.46–7.39 (*m*, 1 H); 7.33–7.19 (*m*, 4 H); 7.14–7.08 (*m*, 3 H); 5.18–5.09 (*m*, 1 H); 3.62 (*d*, *J* = 6.0, OH); 2.65–2.51 (*m*, 1 H); 2.49–2.35 (*m*, 1 H); 2.09–1.95 (*m*, 1 H); 1.66–1.52 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.4 (C=O); 133.2, 123.5 (arom. C_q); 134.0, 131.5, 128.8, 128.6, 128.2, 127.7 (arom. CH); 88.8, 81.7 (C_q); 71.8 (CH); 35.1 (CH_2); 15.8 (CH_2). EI-MS: 264 (14, M^+), 158 (18), 136 (100), 105 (80, $PhCO^+$), 91 (15, $PhCH_2^+$), 77 (84, Ph^+), 51 (16). Anal. calc. for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found: C 81.53, H 5.97.

4-Cyclopropyl-2-hydroxy-1-phenylbutan-1-one (**7e**). *GP B* starting from **6e** afforded **7e** in 38% yield. Colorless oil. IR (film): 3474, 3076, 3000, 2930, 2855, 1682, 1597, 1449, 1273, 1085, 1016, 984, 698. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.81 (*m*, 2 H); 7.59–7.51 (*m*, 1 H); 7.49–7.38 (*m*, 2 H); 5.05 (*dd*, *J* = 3.4, 8.3, 1 H); 1.99–1.85 (*m*, 1 H); 1.64–1.48 (*m*, 1 H); 1.45–1.33 (*m*, 1 H); 1.29–1.13 (*m*, 1 H); 0.67–0.51 (*m*, 1 H); 0.44–0.25 (*m*, 2 H); 0.04–(−0.08) (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 192.4 (C=O); 134.4 (arom. C_q); 133.9, 128.8, 128.5 (arom. CH); 72.8 (CH); 35.9 (CH_2); 29.9 (CH_2); 10.4 (CH); 4.7 (CH_2); 4.1 (CH_2). EI-MS: 204 (3, M^+), 136 (17), 120 (18), 105 (100, $PhCO^+$), 77 (49, Ph^+), 51 (13). Anal. calc. for $C_{13}H_{16}O_2$ (204.26): C 76.44, H 7.90; found: C 76.12, H 7.72.

2-Cyclobutyl-2-hydroxy-1-phenylethan-1-one (**7f**). *GP B* starting from **6f** afforded **7f** in 73% yield. Colorless solid. M.p. 38–40°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.93–7.85 (*m*, 2 H); 7.60–7.51 (*m*, 1 H); 7.50–7.40 (*m*, 2 H); 5.02 (*d*, *J* = 3.8, 1 H); 3.97 (*s*, OH), 2.81–2.67 (*m*, 1 H); 2.36–2.20 (*m*, 1 H); 2.02–1.68 (*m*, 4 H); 1.60–1.45 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 200.7 (C=O); 133.8 (arom. C_q); 133.3, 128.3, 128.0 (arom. CH); 73.9 (CH); 39.1 (CH); 23.7 (CH_2); 20.4 (CH_2); 17.6 (CH_2). IR (KBr): 3440, 2936, 2853, 1676, 1597, 1579,

1407, 1277, 1216, 1144. EI-MS: 190 (11, M^+), 105 (100), 85 (65), 77 (94, Ph^+), 67 (82), 51 (79), 41 (65), 39 (46). Anal. calc. for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.83, H 7.84.

2-Cyclopentyl-2-hydroxy-1-phenylethan-1-one (**7g**). *GP B* starting from **6g** afforded **7g** in 75% yield. Colorless solid. M.p. 52–54°. IR (KBr): 3444, 2960, 2868, 1676, 1597, 1579, 1448, 1278, 1104. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.82 (*m*, 2 H); 7.59–7.50 (*m*, 1 H); 7.48–7.39 (*m*, 2 H); 5.08 (*dd*, *J* = 5.7, 3.0, 1 H); 3.59 (*d*, *J* = 6.4, OH); 2.27–2.11 (*m*, 1 H); 1.79–1.05 (*m*, 8 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 202.1 (C=O); 134.2 (arom. C_q); 133.8, 128.8, 128.4 (arom. CH); 74.4 (CH); 43.8 (CH); 29.5 (CH_2); 25.8 (CH_2); 25.7 (CH_2); 24.3 (CH_2). EI-MS: 204 (3, M^+), 136 (66), 105 (81), 81 (100), 77 (93, Ph^+), 51 (77), 41 (82), 39 (61). Anal. calc. for $C_{13}H_{16}O_2$ (204.26): C 76.44, H 7.90; found: C 76.18, H 7.67.

2-Hydroxy-2-(indan-2-yl)-1-phenylethan-1-one (**7h**). *GP B* starting from **6h** afforded **7h** in 68% yield. Colorless crystals. M.p. 124–125°. IR (KBr): 3438, 2942, 2922, 1677, 1599, 1580, 1449, 1272, 1230, 1114. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.90–7.85 (*m*, 2 H); 7.59–7.52 (*m*, 1 H); 7.48–7.40 (*m*, 2 H); 7.12–6.97 (*m*, 4 H); 5.22 (*d*, *J* = 2.6, 1 H); 3.70 (br., *s*, OH); 3.24–3.13 (*m*, 1 H); 3.03–2.67 (*m*, 3 H); 2.42–2.32 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 201.8 (C=O); 142.5, 142.2, 134.0 (arom. C_q); 134.1, 128.9, 128.5, 126.3, 124.3, 124.2 (arom. CH); 73.8 (CH); 44.3 (CH); 35.7 (CH_2); 31.4 (CH_2). EI-MS: 252 (2, M^+), 224 (5), 146 (33), 105 (100, $PhCO^+$), 91 (44, $PhCH_2^+$), 77 (28, Ph^+), 51 (6). HR-EI-MS: 252.11497 ($C_{17}H_{16}O_2$; calc. 252.11503). Anal. calc. for $C_{17}H_{16}O_2$ (252.31): C 80.93, H 6.93; found: C 80.57, H 6.53.

2-Cyclohexyl-2-hydroxy-1-phenylethan-1-one (**7i**). *GP B* starting from **6i** afforded **7i** in 71% yield. Colorless solid. M.p. 83–85°. IR (KBr): 3440, 2933, 2853, 1679, 1597, 1578, 1448, 1275, 1216, 1108. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.94–7.88 (*m*, 2 H); 7.66–7.59 (*m*, 1 H); 7.55–7.47 (*m*, 2 H); 4.94 (*dd*, *J* = 6.4, 2.3, 1 H); 3.60 (*d*, *J* = 6.8, OH); 1.85–1.48 (*m*, 6 H); 1.31–0.93 (*m*, 5 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 202.2 (C=O); 134.2 (arom. C_q); 133.8, 128.8, 128.5 (arom. CH); 77.3 (CH); 42.6 (CH); 30.2 (CH_2); 26.5 (CH_2); 25.8 (2 CH_2); 24.8 (CH_2). EI-MS: 218 (7, M^+), 136 (67), 107 (53), 95 (100), 77 (91, Ph^+), 67 (33), 55 (58), 51 (47), 41 (65), 39 (28). Anal. calc. for $C_{14}H_{18}O_2$ (218.29): C 77.03, H 8.31; found: C 76.55, H 8.23.

trans-*2-[4-(*tert-*Butyl)cyclohexyl]-2-hydroxy-1-phenylethan-1-one* (**7j**). *GP B* starting from **6j** afforded **7j** in 57% yield. Colorless solid. M.p. 81–82°. IR (KBr): 3504, 2937, 2862, 1672, 1598, 1579, 1449, 1263, 1216, 1127, 984. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86–7.81 (*m*, 2 H); 7.59–7.52 (*m*, 1 H); 7.47–7.40 (*m*, 2 H); 4.89 (*d*, *J* = 2.6, 1 H); 3.27 (br., *s*, OH); 1.85–1.72 (*m*, 2 H); 1.68–1.57 (*m*, 2 H); 1.56–1.44 (*m*, 1 H); 1.16–1.09 (*m*, 2 H); 0.95–0.63 (*m*, 3 H); 0.71 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 202.2 (C=O); 134.2 (arom. C_q); 133.8, 128.8, 128.4 (arom. CH); 76.8 (CH); 47.3 (CH); 42.5 (CH); 32.3 (C_q); 30.4 (CH_2); 27.4 (3 Me); 27.2 (CH_2); 26.5 (CH_2); 24.9 (CH_2). EI-MS: 274 (3, M^+), 151 (33), 136 (58), 105 (63, $PhCO^+$), 95 (60), 81 (41), 77 (33, Ph^+), 57 (100), 41 (28). Anal. calc. for $C_{18}H_{26}O_2$ (274.40): C 78.79, H 9.55; found: C 78.28, H 9.64.

*2-Hydroxy-1-phenyl-2-(3,4,5,6-tetrahydro-2*H*-pyran-3-yl)ethan-1-one* (**7k**). *GP B* starting from **6k** afforded **7k** in 63% yield. Colorless solid. M.p. 113–115°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87–7.81 (*m*, 2 H); 7.62–7.54 (*m*, 1 H); 7.50–7.42 (*m*, 2 H); 4.92 (*d*, *J* = 2.3, 1 H); 3.97–3.88 (*m*, 1 H); 3.86–3.77 (*m*, 1 H); 3.34–3.21 (*m*, 1 H); 3.17–3.04 (*m*, 1 H); 2.15–1.75 (*m*, 3 H); 1.60–1.51 (*m*, 1 H); 0.99–0.89 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 201.5 (C=O); 133.9 (arom. C_q); 134.1, 128.9, 128.4 (arom. CH); 76.0 (CH); 67.7 (CH_2); 67.3 (CH_2); 39.8 (CH); 25.2 (CH_2); 25.0 (CH_2). EI-MS: 220 (1, M^+), 105 (100, $PhCO^+$), 77 (53, Ph^+), 51 (18). Anal. calc. for $C_{18}H_{16}O_3$ (220.26): C 70.89, H 7.32; found: C 70.48, H 7.19.

2-Hydroxy-2-{1-[(4-methylphenyl)sulfonyl]piperidin-4-yl}-1-phenylethan-1-one (**7l**). *GP B* starting from **6l** afforded **7l** in 56% yield. Colorless solid. M.p. 102–105°. IR (KBr): 3481, 2924, 2849, 1677, 1596, 1448, 1366, 1268, 1161, 1093, 934. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79–7.73 (*m*, 2 H); 7.58–7.47 (*m*, 3 H); 7.44–7.36 (*m*, 2 H); 7.23–7.17 (*m*, 2 H); 4.92–4.86 (*m*, 1 H); 3.83–3.73 (*m*, 1 H); 3.70–3.60 (*m*, 1 H); 2.32 (*s*, 3 H); 2.15–2.05 (*m*, 1 H); 1.97–1.38 (*m*, 5 H); 1.13–1.03 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 201.2 (C=O); 143.4, 133.7, 132.9 (arom. C_q); 134.2, 129.5, 129.0, 128.3, 127.6 (arom. CH); 75.4 (CH); 46.2 (CH_2); 45.7 (CH_2); 39.9 (CH); 28.3 (CH_2); 23.7 (CH_2); 21.4 (Me). EI-MS: 373 (1, M^+), 355 (4), 268 (14), 238 (14), 200 (44), 155 (48, Ts^+), 112 (24), 105 (76, $PhCO^+$), 91 (100, $PhCH_2^+$), 82 (58), 77 (42, Ph^+), 42 (30). Anal. calc. for $C_{20}H_{23}NO_4S$ (373.47): C 64.32, H 6.21, N 3.75, S 8.59; found: C 63.93, H 6.11, N 3.99, S 8.46.

*2-{1-[(*tert-*Butoxy)carbonyl]piperidin-4-yl}-2-hydroxy-1-phenylethan-1-one* (**7m**). *GP B* starting from **6m** afforded **7m** in 67% yield. Colorless solid. M.p. 99–101°. IR (KBr): 3407, 2939, 2852, 1676, 1429, 1366, 1234, 1169, 1137. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87–7.81 (*m*, 2 H); 7.62–7.54 (*m*, 1 H); 7.50–7.41 (*m*, 2 H); 4.93 (*d*, *J* = 3.0, 2 H); 4.15–4.06 (*m*, 1 H); 4.04–3.93 (*m*, 1 H); 2.62–2.50 (*m*, 1 H); 2.44–2.31 (*m*, 1 H); 1.90–1.71 (*m*, 1 H); 1.71–1.59 (*m*, 2 H); 1.36 (*s*, 9 H); 1.33–1.23 (*m*, 1 H); 1.06–0.97 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 201.5, 154.6 (C=O); 133.9 (arom. C_q); 134.2, 129.0, 128.5 (arom. CH); 79.5 (C_q), 76.0 (CH); 43.8 (br., CH_2); 43.2 (br., CH_2); 40.9 (CH); 29.0 (CH_2); 28.4 (3 Me); 24.2 (CH_2). EI-MS: 245 (5), 202 (4), 140 (9), 105 (34, $PhCO^+$),

82 (43), 77 (29, Ph^+), 57 (100), 41 (37). Anal. calc. for $C_{18}H_{25}NO_4$ (319.40): C 67.69, H 7.89, N 4.39; found: C 67.35, H 7.57, N 4.60.

1-Benzoyl-3-(benzyloxy)propyl Methanesulfonate (**3f**). *GP C* starting from **7a** afforded **3f** in 75% yield. Colorless solid. M.p. 62–64°. IR (KBr): 1695, 1366, 1169, 1068, 971, 936, 737, 696. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.95–7.92 (*m*, 2 H); 7.61–7.55 (*m*, 1 H); 7.49–7.41 (*m*, 2 H); 7.39–7.26 (*m*, 5 H); 6.23–6.18 (*m*, 1 H); 4.50 (*s*, 2 H); 3.67–3.58 (*m*, 2 H); 3.07 (*s*, 3 H); 2.35–2.23 (*m*, 1 H); 2.12–2.00 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C=O); 137.8, 133.7 (arom. C_q); 133.9, 128.8, 128.5, 128.3, 127.6 (arom. CH); 78.2 (CH); 73.1 (CH_2); 64.8 (CH_2); 38.9 (Me); 32.9 (CH_2). EI-MS: 146 (19), 105 (100, $PhCO^+$), 91 (57, $PhCH_2^+$), 77 (51, Ph^+), 65 (12), 51 (17). Anal. calc. for $C_{18}H_{20}O_5S$ (348.41): C 62.05, H 5.79, S 9.20; found: C 61.77, H 5.70, S 9.28.

*(1*SR,*2*RS*)-1-Benzoyl-2-phenylpropyl Methanesulfonate* (**3g**). *GP C* starting from **7b** afforded **3g** in 79% yield. Colorless solid. M.p. 95–101°. IR (KBr): 1683, 1354, 1175, 1006, 957, 914, 866, 761, 697. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86–7.82 (*m*, 2 H); 7.59–7.52 (*m*, 1 H); 7.47–7.40 (*m*, 2 H); 7.29–7.13 (*m*, 5 H); 5.93 (*d*, J = 4.9, 1 H); 3.51–3.35 (*m*, 1 H); 2.88 (*s*, 3 H); 1.37 (*d*, J = 7.2, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 195.0 (C=O); 140.3, 134.7 (arom. C_q); 133.8, 128.8, 128.6, 128.3, 127.8, 127.5 (arom. CH); 84.5 (CH); 41.9 (CH); 38.7 (Me); 14.8 (Me). EI-MS: 222 (11, $[M - MsOH]^+$), 105 (100, $PhCO^+$), 77 (28, Ph^+), 51 (8). Anal. calc. for $C_{17}H_{18}O_4S$ (318.39): C 64.13, H 5.70, S 10.07; found: C 63.84, H 5.78, S 10.16.

1-Benzoylpent-4-enyl 4-Methylbenzene-1-sulfonate (**3h**). *GP D* starting from **7c** afforded **3h** in 82% yield. Yellowish oil. IR (film): 3068, 2925, 1704, 1597, 1448, 1364, 1190, 1175, 1096. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.80–7.74 (*m*, 2 H); 7.70–7.64 (*m*, 2 H); 7.54–7.47 (*m*, 1 H); 7.41–7.33 (*m*, 2 H); 7.20–7.14 (*m*, 2 H); 5.73–5.55 (*m*, 2 H); 4.97–4.86 (*m*, 2 H); 2.32 (*s*, 3 H); 2.21–1.79 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.8 (C=O); 145.0, 133.9, 133.1 (arom. C_q); 135.9 (olef. CH); 133.8, 129.7, 128.7, 128.6, 128.0 (arom. CH); 116.7 (olef. CH_2); 80.2 (CH); 31.8 (CH_2); 28.9 (CH_2); 21.6 (Me). EI-MS: 155 (15, Ts^+), 105 (100, $PhCO^+$), 91 (30, $PhCH_2^+$), 77 (39, Ph^+), 65 (14), 51 (12), 39 (11). Anal. calc. for $C_{19}H_{20}O_4S$ (344.43): C 66.26, H 5.85, S 9.31; found: C 65.94, H 5.48, S 9.69.

1-Benzoyl-5-phenylpent-4-ynyl 4-Methylbenzene-1-sulfonate (**3i**). *GP D* starting from **7d** afforded **3i** in 77% yield. Colorless solid. M.p. 99–101°. IR (KBr): 1702, 1596, 1363, 1189, 1176, 969, 886, 782. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87–7.78 (*m*, 2 H); 7.70–7.63 (*m*, 2 H); 7.48–7.40 (*m*, 1 H); 7.30 (*d*, J = 7.9, 2 H); 7.28–7.13 (*m*, 5 H); 7.07 (*d*, J = 7.9, 2 H); 5.84 (*dd*, J = 4.5, 7.9, 1 H); 2.39 (*t*, J = 7.2, 2 H); 2.17 (*s*, 3 H); 2.08–1.94 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 193.9 (C=O); 144.9, 133.6, 132.7, 123.0 (arom. C_q); 133.8, 131.3, 129.6, 128.6, 128.4, 128.1, 127.8, 127.7 (arom. CH); 87.0, 82.3 (C_q); 79.1 (CH); 31.4 (CH_2); 21.3 (Me); 15.5 (CH_2). EI-MS: 290 (15), 246 (10, $[M - TsOH]^+$), 155 (9, Ts^+), 135 (75), 115 (20), 105 (100, $PhCO^+$), 91 (35, $PhCH_2^+$), 77 (48, Ph^+), 65 (14), 51 (10). Anal. calc. for $C_{25}H_{21}O_4S$ (418.51): C 71.75, H 5.30, S 7.66; found: C 71.24, H 5.19, S 7.82.

1-Benzoyl-3-cyclopropylpropyl 4-Methylbenzene-1-sulfonate (**3j**). *GP D* starting from **7e** afforded **3j** in 91% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83–7.75 (*m*, 2 H); 7.69–7.63 (*m*, 2 H); 7.55–7.48 (*m*, 1 H); 7.42–7.34 (*m*, 2 H); 7.20–7.13 (*m*, 2 H); 5.62 (*t*, J = 6.8, 1 H); 2.32 (*s*, 3 H); 1.98–1.87 (*m*, 2 H); 1.32–1.17 (*m*, 2 H); 0.62–0.48 (*m*, 1 H); 0.42–0.28 (*m*, 2 H); 0.04–(–0.17) (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C=O); 144.9, 134.0, 133.2 (arom. C_q); 133.7, 129.6, 128.7, 128.6, 128.0 (arom. CH); 81.0 (CH); 32.8 (CH_2); 29.9 (CH_2); 21.6 (Me); 10.0 (CH); 4.7 (CH_2); 4.1 (CH_2). Anal. calc. for $C_{20}H_{22}O_4S$ (358.45): C 67.01, H 6.19, S 8.95; found: C 66.85, H 6.29, S 9.09.

1-Cyclobutyl-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate (**3k**). *GP D* starting from **7f** afforded **3k** in 74% yield. Colorless oil. IR (KBr): 1687, 1595, 1448, 1359, 1172, 969, 947. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.93–7.88 (*m*, 2 H); 7.68–7.60 (*m*, 3 H); 7.55–7.50 (*m*, 2 H); 7.18–7.12 (*m*, 2 H); 5.85 (*d*, J = 7.2, 1 H); 2.96–2.79 (*m*, 1 H); 2.32 (*s*, 3 H); 2.18–1.78 (*m*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C=O); 144.8, 134.7, 133.1 (arom. C_q); 134.0, 129.6, 128.9, 128.5, 128.0 (arom. CH); 83.0 (CH); 36.8 (CH); 23.3 (2 CH_2); 21.6 (Me); 17.9 (CH_2). EI-MS: 172 (3, $[M - TsOH]^+$), 155 (16, Ts^+), 105 (100, $PhCO^+$), 91 (38, $PhCH_2^+$), 77 (34, Ph^+), 65 (23), 51 (7). Anal. calc. for $C_{19}H_{20}O_4S$ (344.43): C 66.26, H 5.85, S 9.31; found: C 66.15, H 5.69, S 9.48.

1-Cyclopentyl-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate (**3l**). *GP D* starting from **7g** afforded **3l** in 91% yield. Colorless solid. M.p. 68–70°. IR (KBr): 2952, 2870, 1699, 1596, 1448, 1370, 1176, 941. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.82–7.75 (*m*, 2 H); 7.67–7.60 (*m*, 2 H); 7.53–7.45 (*m*, 1 H); 7.40–7.31 (*m*, 2 H); 7.16–7.10 (*m*, 2 H); 5.35 (*d*, J = 7.2, 1 H); 2.42–2.27 (*m*, 1 H); 2.30 (*s*, 3 H); 1.73–1.16 (*m*, 8 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.0 (C=O); 144.9, 134.5, 133.0 (arom. C_q); 133.6, 129.6, 128.7, 128.6, 128.0 (arom. CH); 84.2 (CH); 42.1 (CH); 28.4 (CH_2); 28.3 (CH_2); 25.2 (CH_2); 24.8 (CH_2); 21.5 (Me). EI-MS: 186 (5, $[M - TsOH]^+$), 155 (25, Ts^+), 105 (100, $PhCO^+$), 91 (44, $PhCH_2^+$), 81 (39), 77 (39, Ph^+), 65 (14), 51 (8). Anal. calc. for $C_{20}H_{22}O_4S$ (358.45): C 67.01, H 6.19, S 8.95; found: C 67.22, H 6.18, S 8.58.

*1-(2,3-Dihydro-1*H*-inden-2-yl)-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate* (**3m**). *GP D* starting from **7h** afforded **3m** in 82% yield. Colorless solid. M.p. 120–122°. IR (KBr): 1694, 1595, 1449, 1370, 1189,

1171, 933. ^{1}H-NMR (300 Hz, $CDCl_3$): 7.84–7.76 (*m*, 2 H); 7.65–7.60 (*m*, 2 H); 7.54–7.47 (*m*, 1 H); 7.40–7.32 (*m*, 2 H); 7.17–7.10 (*m*, 2 H); 7.04–6.97 (*m*, 4 H); 5.55 (*d*, *J* = 7.2, 1 H); 3.05–2.91 (*m*, 1 H); 2.90–2.80 (*m*, 2 H); 2.79–2.71 (*m*, 2 H); 2.35 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C=O); 145.0, 141.3, 141.2, 134.5, 132.8 (arom. C_q); 133.8, 129.6, 128.7, 128.6, 128.0, 126.6, 126.5, 124.4, 124.3 (arom. CH); 82.8 (CH); 42.0 (CH); 34.9 (CH_2); 34.7 (CH_2); 21.6 (Me). EI-MS: 290 (19), 234 (3, [*M* – TsOH]$^+$), 155 (17, Ts^+), 135 (100), 115 (14), 105 (62, $PhCO^+$), 91 (37, $PhCH_2^+$), 77 (42, Ph^+), 65 (12), 51 (9). Anal. calc. for $C_{24}H_{22}O_4S$ (406.50): C 70.91, H 5.46, S 7.89; found: C 70.49, H 5.65, S 7.74.

1-Cyclohexyl-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate (**3n**). *GP D* starting from **7i** afforded **3n** in 88% yield. Colorless solid. M.p. 64–67°. IR (KBr): 2932, 2853, 1689, 1597, 1449, 1366, 1172, 939. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.81–7.73 (*m*, 2 H); 7.66–7.59 (*m*, 2 H); 7.54–7.46 (*m*, 1 H); 7.41–7.32 (*m*, 2 H); 7.17–7.10 (*m*, 2 H); 5.28 (*d*, *J* = 5.9, 1 H); 2.30 (*s*, 3 H); 1.96–1.80 (*m*, 1 H); 1.78–1.35 (*m*, 5 H); 1.20–0.93 (*m*, 5 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.1 (C=O); 144.8, 134.8, 133.0 (arom. C_q); 133.6, 129.6, 128.6, 128.0 (arom. CH); 85.1 (CH); 40.5 (CH); 28.9 (CH_2); 27.8 (CH_2); 25.7 (2 CH_2); 25.5 (CH_2); 21.6 (Me). EI-MS: 200 (5, [*M* – TsOH]$^+$), 155 (22, Ts^+), 105 (100, $PhCO^+$), 95 (53), 91 (41, $PhCH_2^+$), 77 (38, Ph^+), 65 (12), 51 (7). Anal. calc. for $C_{21}H_{24}O_4S$ (372.48): C 67.72, H 6.49, S 8.61; found: C 67.40, H 6.22, S 8.43.

trans-*1-[4-(*tert-*Butyl)cyclohexyl]-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate* (**3o**). *GP D* starting from **7j** afforded **3o** in 87% yield. Colorless solid. M.p. 97–99°. IR (KBr): 2935, 2857, 1678, 1597, 1449, 1367, 1172, 941. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83–7.75 (*m*, 2 H); 7.67–7.60 (*m*, 2 H); 7.56–7.47 (*m*, 1 H); 7.40–7.31 (*m*, 2 H); 7.18–7.10 (*m*, 2 H); 5.68 (*d*, *J* = 6.2, 1 H); 2.31 (*s*, 3 H); 2.00–1.86 (*m*, 1 H); 1.82–1.66 (*m*, 3 H); 1.63–1.52 (*m*, 1 H); 1.35–1.08 (*m*, 2 H); 1.02–0.80 (*m*, 3 H); 0.70 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 196.2 (C=O); 144.8, 134.5, 132.4 (arom. C_q); 133.6, 129.6, 128.5, 128.3, 128.0 (arom. CH); 85.1 (CH); 47.4 (CH); 40.6 (CH); 32.4 (C_q); 29.3 (CH_2); 27.4 (3 Me); 26.6 (CH_2); 26.5 (CH_2); 21.6 (CH_2); 21.6 (Me). Anal. calc. for $C_{25}H_{32}O_4S$ (428.59): C 70.06, H 7.53, S 7.48; found: C 69.91, H 7.49, S 7.58.

*2-Oxo-2-phenyl-1-(3,4,5,6-tetrahydro-2*H*-pyran-4-yl)ethyl 4-Methylbenzene-1-sulfonate* (**3p**). *GP D* starting from **7k** afforded **3p** in 84% yield. Colorless solid. M.p. 139–141°. IR (KBr): 2954, 2857, 1697, 1596, 1449, 1369, 1237, 1210, 1181, 1090, 1071, 1009, 949, 934, 918, 876, 851, 718. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.82–7.77 (*m*, 2 H); 7.66–7.60 (*m*, 2 H); 7.57–7.49 (*m*, 1 H); 7.44–7.35 (*m*, 2 H); 7.18–7.12 (*m*, 2 H); 5.29 (*d*, *J* = 6.8, 2 H); 3.92–3.79 (*m*, 2 H); 3.26–3.15 (*m*, 2 H); 2.32 (*s*, 3 H); 2.20–2.08 (*m*, 1 H); 1.63–1.21 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6 (C=O); 145.1, 134.7, 132.8 (arom. C_q); 133.9, 129.7, 128.7, 128.5, 128.1 (arom. CH); 83.8 (CH); 67.3 (CH_2); 67.0 (CH_2); 38.0 (CH); 28.6 (CH_2); 28.0 (CH_2); 21.6 (Me). EI-MS: 374 (1, M^+), 269 (18), 202 (10, [M – TsOH]$^+$), 155 (60, Ts^+), 105 (100, $PhCO^+$), 91 (44, $PhCH_2^+$), 77 (34, Ph^+). Anal. calc. for $C_{20}H_{22}O_5S$ (374.45): C 64.15, H 5.92, S 8.56; found: C 63.94, H 5.98, S 8.72.

1-{1-[(4-Methylphenyl)sulfonyl]piperidin-4-yl}-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate (**3q**). *GP D* starting from **7l** afforded **3q** in 81% yield. Colorless solid. M.p. 97–99°. IR (KBr): 1691, 1597, 1448, 1357, 1338, 1163, 933. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.76–7.69 (*m*, 2 H); 7.65–7.58 (*m*, 2 H); 7.54–7.45 (*m*, 2 H); 7.40–7.31 (*m*, 1 H); 7.24–7.12 (*m*, 2 H); 5.25 (*d*, *J* = 6.4, 1 H); 3.75–3.60 (*m*, 2 H); 2.33 (*s*, 3 H); 2.32 (*s*, 3 H); 2.11–1.96 (*m*, 2 H); 1.85–1.62 (*m*, 2 H); 1.53–1.28 (*m*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.3 (C=O); 145.3, 143.6, 134.5, 132.8, 132.6 (arom. C_q); 134.0, 129.8, 129.6, 128.8, 128.6, 128.0, 127.6 (arom. CH); 83.0 (CH); 45.7 (CH_2); 45.6 (CH_2); 38.1 (CH); 27.4 (CH_2); 26.6 (CH_2); 21.6 (CH_3); 21.5 (Me). EI-MS: 355 (7, [*M* – TsOH]$^+$), 200 (60), 155 (26, Ts^+), 105 (100, $PhCO^+$), 91 (81, $PhCH_2^+$), 82 (37), 77 (30, Ph^+), 65 (19), 42 (10). Anal. calc. for $C_{27}H_{29}NO_6S_2$ (527.65): C 61.46, H 5.54, N 2.65, S 12.15; found: C 61.34, H 5.55, N 2.87, S 12.25.

*1-{1-[(*tert-*Butoxy)carbonyl]piperidin-4-yl}-2-oxo-2-phenylethyl 4-Methylbenzene-1-sulfonate* (**3r**). *GP D* starting from **7m** afforded **3r** in 87% yield. Colorless solid. M.p. 123–124°. IR (KBr): 1688, 1594, 1401, 1362, 1171, 925. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.81–7.75 (*m*, 2 H); 7.65–7.59 (*m*, 2 H); 7.56–7.49 (*m*, 1 H); 7.43–7.34 (*m*, 2 H); 7.18–7.11 (*m*, 2 H); 5.30 (*d*, *J* = 6.4, 1 H); 4.11–3.90 (*m*, 2 H); 2.59–2.43 (*m*, 2 H); 2.31 (*s*, 3 H); 2.10–1.96 (*m*, 1 H); 1.72–1.61 (*m*, 1 H); 1.35 (*s*, 9 H); 1.40–1.14 (*m*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6, 154.4 (C=O); 145.1, 134.6, 132.7 (arom. C_q); 133.9, 129.7, 128.7, 128.6, 128.0 (arom. CH); 83.6 (C_q); 43.6 (br., CH_2); 43.1(br., CH_2); 39.0 (CH); 28.3 (3 Me); 27.9 (CH_2); 27.1 (CH_2); 21.6 (Me). EI-MS: 301 (2, [*M* – TsOH]$^+$), 245 (16), 201 (15), 160 (16), 140 (13), 105 (100, $PhCO^+$), 96 (25), 91 (36, $PhCH_2^+$), 82 (76), 77 (49, Ph^+), 57 (93), 41 (65). Anal. calc. for $C_{25}H_{31}NO_6S$ (473.58): C 63.40, H 6.60, N 2.96, S 6.77; found: C 63.64, H 6.62, N 3.17, S 6.37.

Methyl 3-Bromo-2-methyl-4-oxo-4-phenylbutanoate (**4a**). *GP E* starting from **1f** afforded **4a** in 100% yield (mixture of diastereoisomers, ds 55:45; the data of the minor product are given in square brackets). Yellow-brown oil. IR (film): 1742, 1699, 1646, 1285, 1261, 858. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.06–8.00 (*m*, 2 H); 7.65–7.56 (*m*, 1 H); 7.54–7.45 (*m*, 2 H); 5.32 [5.34] (*d*, *J* = 9.8 [10.2], 1 H); 3.65 [3.78] (*s*, 3 H); 3.43–3.32 [3.54–3.45] (*m*, 1 H); 1.53 [1.26] (*d*, *J* = 7.2 [6.8], 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 193.1 [191.6], 174.1 [173.9] (C=O);

134.1 [134.3] (arom. C_q); 133.7 [134.0], 128.8 [128.7] (arom. CH); 52.2 (Me); 48.3 [45.8] (CH); 42.4 [43.7] (CH); 16.2 (Me). EI-MS: 105 (100, $PhCO^+$), 77 (35, Ph^+), 51 (13). Anal. calc. for $C_{12}H_{13}BrO_3$ (285.13): C 50.55, H 4.60, Br 28.02; found: C 50.68, H 4.61, Br 27.89.

Methyl 2-Benzyl-3-bromo-4-oxo-4-phenylbutanoate (**4b**). *GP E* starting from **1g** afforded **4b** in 100% yield (mixture of diastereoisomers, ds 60:40; the data of the minor product are given in square brackets). Yellow-brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.83 [7.94–7.90] (*m*, 2 H); 7.58–7.34 (*m*, 3 H); 7.28–7.03 (*m*, 5 H); 5.15 [5.28] (*d*, *J* = 10.6 [10.2], 1 H); 3.69–3.10 (*m*, 2 H); 3.45 [3.53] (*s*, 3 H); 2.89–2.70 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 192.9 [191.5], 172.5 [172.7] (C=O); 136.8 [137.1], 134.2 (arom. C_q); 133.7 [134.1], 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 127.1 [127.0] (arom. CH); 51.9 [51.3] (Me); 49.2 (CH); 45.9 [45.3] (CH); 35.8 [37.1] (CH_2).

Methyl 2-Methyl-3-(nitrooxy)-4-oxo-4-phenylbutanoate (**5a**). *GP F* starting from **4a** afforded **5a** in 67% yield (mixture of diastereoisomers, ds 75:25; the data of the minor product are given in square brackets). Colorless oil. IR (film): 1742, 1699, 1646, 1285, 1261, 1226, 858, 695. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.02–7.96 (*m*, 2 H); 7.69–7.63 (*m*, 1 H); 7.57–7.49 (*m*, 2 H); 6.60 [6.29] (*d*, *J* = 4.2 [7.5], 1 H); 3.74 [3.64] (*s*, 3 H); 3.26–3.10 (*m*, 1 H); 1.20 [1.48] (*d*, *J* = 7.2 [7.5], 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 192.4 [193.5], 171.4 [171.7] (C=O); 133.5 [131.9] (arom. C_q); 134.4 [134.5], 129.1 [130.3], 128.3 [128.7] (arom. CH); 81.5 [82.1] (CH); 52.7 [52.4] (Me); 39.7 [40.2] (CH); 10.2 [11.3] (CH). EI-MS: 105 (100, $PhCO^+$), 77 (53, Ph^+), 51 (14), 15 (10). Anal. calc. for $C_{12}H_{13}NO_6$ (267.23): C 53.93, H 4.90, N 5.24; found: C 54.43, H 4.89, N 5.66

Methyl 2-Benzyl-3-(nitrooxy)-4-oxo-4-phenylbutanoate (**5b**). *GP F* starting from **4b** afforded **5b** in 33% yield (mixture of diastereoisomers, ds 60:40; the data of the minor product are given in square brackets). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.94–7.00 (*m*, 10 H); 6.05 [6.43] (*d*, *J* = 5.3, 1 H); 3.59 [3.56] (*s*, 3 H); 3.46–3.38 (*m*, 1 H); 3.19–3.09 (*m*, 1 H); 2.98–2.86 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 193.0 [192.6], 170.0 [170.7] (C=O); 134.6 [134.0] (arom. C_q); 134.3, 134.1, 130.4, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 127.3, 126.8 (arom. CH); 80.6 [81.3] (CH); 52.3 [52.5] (Me); 48.0 [47.7] (CH); 34.0 [32.3] (CH_2).

3-(Cyclopropyl)propan-1-ol (**6e**). In a dry 250-ml two-necked round-bottomed flask fitted with a N_2 bubbler, a rubber septum and a magnetic stirrer bar were placed at 0° dry 1,2-dichloroethane (50 ml), Et_2Zn (44.4 ml, 0.9M in hexane, 40.0 mmol), and chloroiodomethane (14.2 g, 80.5 mmol). After stirring at r.t. for 45 min, **6c** (1.73 g, 20.1 mmol) in 5 ml of dry 1,2-dichloroethane was added dropwise to the mixture. After 16 h, the mixture was quenched with sat. aq. NH_4Cl soln. (50 ml), and, after phase separation, the aq. layer was extracted with CH_2Cl_2 (3 × 30 ml). The combined org. extracts were washed with brine (30 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Colorless liquid (1.79 g, 89%). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.61 (*t*, *J* = 6.8, 2 H); 1.65–1.50 (*m*, 2 H); 1.25–1.16 (*m*, 2 H); 0.66–0.53 (*m*, 1 H); 0.37–0.31 (*m*, 2 H); −0.02–(−0.09) (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 62.8 (CH_2); 32.7 (CH_2); 30.9 (CH_2); 10.6 (CH); 4.4 (CH_2).

*(2,3-Dihydro-1*H*-inden-2-yl)methanol* (**6h**). *GP G* starting from **19** afforded **6h** in 89% yield. Colorless oil. IR (film): 3600–3100, 2933, 2846, 1482, 1034, 741. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.20–7.05 (*m*, 4 H); 3.61 (*d*, *J* = 6.4, 2 H); 3.10–2.91 (*m*, 2 H); 2.76–2.60 (*m*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 142.6 (arom. C_q); 126.2, 124.6 (arom. CH); 66.5 (CH_2); 41.4 (CH); 35.7 (2 CH_2). EI-MS: 148 (52, M^+), 131 (95), 115 (100), 91 (21, $PhCH_2^+$). Anal. calc. for $C_{10}H_{12}O$ (148.20): C 81.04, H 8.16; found: C 81.03, H 7.91.

trans-*[4-(*tert*-Butyl)cyclohexyl]methanol* (**6j**). *GP G* starting from **17** afforded **6j** in 91% yield. Colorless oil. IR (film): 3600–3100, 2941, 2865, 1596, 1364, 1034. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.42 (*d*, *J* = 6.0, 2 H); 1.83–1.77 (*m*, 4 H, OH); 1.47–1.31 (*m*, 2 H); 0.82 (*s*, *t*-Bu); 1.04–0.80 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 68.8 (CH_2); 48.2 (CH); 40.6 (CH); 29.9 (2 CH_2); 27.6 (Me_3C); 26.7 (2 CH_2). EI-MS: 170 (1, M^+), 137 (7), 113 (52), 95 (88), 81 (36), 67 (11), 57 (100), 41 (46). Anal. calc. for $C_{11}H_{22}O$ (170.29): C 77.58, H 13.02; found: C 77.59, H 13.10.

*3,4,5,6-Tetrahydro-4(hydroxymethyl)-2*H*-pyran* (**6k**). *GP G* starting from **20** afforded **6k** in 99% yield. Colorless oil. ^{1}H-NMR (300 MHz, DMSO): 4.49 (*t*, *J* = 5.3, OH); 3.81 (*dd*, *J* = 10.9, 3.8, 2 H); 3.30–3.18 (*m*, 4 H); 1.59–1.50 (*m*, 3 H); 1.20–1.08 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, DMSO): 66.9 (2 CH_2); 66.2 (CH_2); 37.6 (CH); 29.6 (2 CH_2). Anal. calc. for $C_6H_{12}O_2$ (116.16): C 62.04, H 10.41; found: C 61.87, H 10.52.

{1-[(4-Methylphenyl)sulfonyl]piperidin-4-yl}methanol (**6l**). *GP G* starting from **21** afforded **6l** in 93% yield. Colorless solid. M.p. 110–112°. IR (KBr): 3556, 2943, 2917, 2858, 1596, 1331, 1158, 1094, 1028, 929, 908, 819, 728. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55 (*d*, *J* = 8.3, 2 H); 7.24 (*d*, *J* = 8.3, 2 H); 3.71 (*d*, *J* = 11.7, 2 H); 3.37 (*d*, *J* = 6.0, 2 H); 2.35 (*s*, 3 H); 2.22–2.10 (*m*, 2 H); 1.70 (*d*, *J* = 11.7, 2 H); 1.42–1.16 (*m*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 143.4, 133.1 (arom. C_q); 129.6, 127.6 (arom. CH); 67.0 (CH_2); 46.0 (2 CH_2); 37.8 (CH); 28.0 (2 CH_2); 21.5 (Me). EI-MS: 155 (11, Ts^+), 114 (100), 96 (22), 91 (53, $PhCH_2^+$), 65 (27), 55 (20), 42 (40), 31 (44). Anal. calc. for $C_{13}H_{19}NO_3S$ (269.36): C 57.97, H 7.11, N 5.20, S 11.90; found: C 58.04, H 7.06, N 5.09, S 11.91.

(Cyclopropyl)(phenyl)methanone (**11a**). *GP H* starting from **3a** afforded **11a** in 87% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.04–8.00 (*m*, 2 H); 7.56–7.44 (*m*, 3 H); 2.67 (*m*, 1 H); 1.28–1.20 (*m*, 2 H); 1.10–1.00 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 200.6 (C=O); 137.9 (arom. C_q); 132.6, 128.4, 127.9 (arom. CH); 17.1 (CH); 11.6 (2 CH_2). IR (film): 1667, 1148, 1385, 1225, 992, 706. EI-MS: 146 (17, M^+), 105 (100, $PhCO^+$), 77 (67, Ph^+), 51 (37), 41 (16), 39 (25). Anal. calc. for $C_{10}H_{10}O$ (164.19): C 82.16, H 6.89; found: C 81.96, H 6.93.

trans-*(2-Methylcyclopropyl)(phenyl)methanone* (**11b**). *GP H* starting from **3b** afforded **11b** in 63% yield and **15** in 16% yield (separated by FCC); starting from **3c** afforded **11b** in 90% yield.

Data of **11b**: Colorless oil. IR (film): 1665, 1448, 1402, 1222, 699. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.03–7.99 (*m*, 2 H); 7.57–7.45 (*m*, 3 H); 2.45–2.38 (*m*, 1 H); 1.67–1.56 (*m*, 1 H); 1.54–1.47 (*m*, 1 H); 1.23 (*d*, $J = 5.9$, 3 H); 0.94–0.87 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 200.0 (C=O); 138.0 (arom. C_q); 132.5, 128.4, 127.9 (arom. CH); 26.3 (CH); 21.2 (CH); 20.0 (CH_2); 18.2 (Me). EI-MS: 160 (15, M^+), 105 (100, $PhCO^+$), 77 (49, Ph^+), 57 (19), 55 (19), 51 (19), 43 (21). Anal. calc. for $C_{11}H_{12}O$ (160.21): C 82.46, H 7.55; found: C 81.78, H 7.54.

1-Phenylpent-4-en-1-one (**15**). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.00–7.96 (*m*, 2 H); 7.57–7.42 (*m*, 3 H); 5.98–5.83 (*m*, 1 H); 5.13–4.98 (*m*, 2 H); 3.10–3.04 (*m*, 2 H); 2.54–2.45 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.4 (C=O), 137.2 (CH), 136.9 (arom. C_q), 132.9, 128.5, 128.0 (arom. CH); 115.2 (CH_2); 37.7 (CH_2); 28.1 (CH_2).

(2-Methylcylopropyl)(phenyl)methanone (**11c**). *GP H* starting from **3d** afforded *cis*-**11c** in 49% yield and *trans*-**11c** in 29% yield; starting from **3g**, *cis*-**11c** in 28% yield and *trans*-**11c** in 16 % yield were obtained. Separation by FCC.

Data of cis-**11c**: Colorless solid. M.p. 67–69°. IR (KBr): 1661, 1448, 1390, 1217, 1004, 710. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.93–7.88 (*m*, 2 H); 7.54–7.47 (*m*, 1 H); 7.44–7.37 (*m*, 2 H); 7.22–7.08 (*m*, 5 H); 3.14–3.06 (*m*, 1 H); 2.94–2.84 (*m*, 1 H); 2.17–2.08 (*m*, 1 H); 1.50–1.42 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 196.1 (C=O); 138.6, 135.9 (arom. C_q); 132.5, 129.0, 128.4, 128.0, 127.9, 126.6 (arom. CH); 29.5 (CH); 27.0 (CH); 11.6 (CH_2). EI-MS: 222 (7, M^+), 115 (34), 105 (100, $PhCO^+$), 77 (86, Ph^+), 51 (38). Anal. calc. for $C_{16}H_{14}O$ (222.28): C 86.45, H 6.35; found: C 85.97, H 6.52.

Data of trans-**11c**: Colorless solid. M.p. 45–47°. IR (film): 1666, 1448, 1397, 1223, 1024, 697. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01–7.97 (*m*, 2 H); 7.59–7.52 (*m*, 1 H); 7.49–7.41 (*m*, 2 H); 7.35–7.16 (*m*, 5 H); 2.94–2.87 (*m*, 1 H); 2.74–2.67 (*m*, 1 H); 1.96–1.89 (*m*, 1 H); 1.59–1.52 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 198.5 (C=O); 140.5, 137.7 (arom. C_q); 132.9, 128.6, 128.1, 126.6, 126.2 (arom. CH); 30.0 (CH); 29.3 (CH); 19.2 (CH_2). EI-MS: 222 (6, M^+), 115 (31), 105 (100, $PhCO^+$), 77 (94, Ph^+), 51 (45). Anal. calc. for $C_{16}H_{14}O$ (222.28): C 86.45, H 6.35; found: C 85.72, H 6.36.

trans-*2-Benzoylcyclopropanecarbonitrile* (**11d**). *GP H* starting from **3e** afforded **11d** in 65% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.05–8.00 (*m*, 2 H); 7.69–7.62 (*m*, 1 H); 7.57–7.50 (*m*, 2 H); 3.31–3.24 (*m*, 1 H); 2.20–2.13 (*m*, 1 H); 1.72–1.60 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.0 (C=O); 136.2 (arom. C_q); 134.0, 128.9, 128.3 (arom. CH); 119.8 (C_q); 24.0 (CH); 16.8 (CH_2); 7.3 (CH). EI-MS: 171 (16, M^+), 105 (100, $PhCO^+$), 77 (46, Ph^+), 51 (20). HR-EI-MS: 171.19528 ($C_{11}H_9NO$; calc. 171.19530).

(2-Benzyloxycylopropyl)(phenyl)methanone (**11e**). *GP H* starting from **3f** failed, because FCC (silica gel) caused decomposition of the product. Therefore, **3f** (13.9 mg, 0.04 mmol) and 1-methyl-1*H*-imidazole (9.85 mg, 0.12 mmol) were irradiated in CD_2Cl_2 (0.7 ml) in a NMR tube (conditions: 500-W high-pressure Hg-arc lamp (*OSRAM HBO-500*), filter *WG 295* (*Schott*)). The yield was determined *via* ^{1}H-NMR by adding benzoine (0.04 mmol) after irradiation. Yield: 46%. ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.99–7.15 (*m*, 10 H), 4.61 (*d*, $J = 7.2$, 2 H); 3.77–3.71 (*m*, 1 H); 2.89–2.83 (*m*, 1 H); 1.63–1.57 (*m*, 1 H); 1.52–1.45 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, CD_2Cl_2): 195.2 (C=O); 137.5, 133.2 (arom. C_q); 134.0, 128.7, 128.5, 128.2, 127.7 (arom. CH); 73.2 (CH_2); 64.5 (CH); 26.3 (CH); 18.1 (CH_2).

(2-Ethenylcyclopropyl)(phenyl)methanone (**11f**). *GP H* starting from **3h** afforded **11f** as an inseparable *cis*/*trans* mixture (50:50) in 80% yield. Colorless oil. IR (film): 1665, 1448, 1383, 1223, 1018, 701. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.02–7.95 (*m*, 4 H); 7.60–7.42 (*m*, 6 H); 5.73–5.47 (*m*, 2 H); 5.26–5.23 (*m*, 1 H); 5.20–5.17 (*m*, 1 H); 5.05 (*dd*, $J = 10.2$, 1.5, 1 H (*trans*)); 4.98 (*dd*, $J = 10.0$, 1.9, 1 H (*cis*)); 3.00–2.91 (*m*, 1 H (*cis*)); 2.73-2.66 (*m*, 1 H (*trans*)); 2.31–2.14 (*m*, 2 H); 1.74–1.65 (*m*, 2 H); 1.36–1.28 (*m*, 1 H (*cis*)); 1.24–1.15 (*m*, 1 H (*trans*)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 198.6, 197.5 (C=O); 138.4 (olef. CH (*cis*)); 137.8 (arom. C_q); 134.9 (olef. CH (*trans*)); 132.8, 132.6, 128.5, 128.4, 128.0 (arom. CH); 116.1 (olef. CH_2 (*cis*)); 115.0 (olef. CH_2 (*trans*)); 29.4 (CH (*trans*)); 28.5 (CH (*cis*)); 26.6 (CH (*trans*)); 25.8 (CH (*cis*)); 18.1 (CH_2 (*trans*)); 14.2 (CH_2 (*cis*)). EI-MS: 171 (2, $[M-1]^+$); 105 (100, $PhCO^+$), 77 (43, Ph^+), 51 (17). Anal. calc. for $C_{12}H_{12}O$ (172.22): C 83.69, H 7.02; found: C 83.32, H 6.96.

(Phenyl)[2-(phenylethenyl)cyclopropyl]methanone (**11g**). *GP H* starting from **3i** afforded *cis*-**11g** in 20% yield, *trans*-**11g** in 14% yield and **3i** in 42% yield (separated by FCC).

Data of cis-**11g**: Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01–7.96 (*m*, 2 H); 7.54–7.47 (*m*, 1 H); 7.45–7.38 (*m*, 2 H); 7.23–7.17 (*m*, 2 H); 7.16–7.10 (*m*, 3 H); 3.00–2.91 (*m*, 1 H); 2.24–2.15 (*m*, 1 H); 1.85–1.78 (*m*, 1 H); 1.37–1.29 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.0 (C=O); 138.1, 123.2 (arom. C_q); 132.8, 131.8, 128.5, 128.2, 128.0, 127.7 (arom. CH); 87.0, 80.0 (C_q); 25.5 (CH); 14.7 (CH_2); 12.7 (CH). EI-MS: 246 (26, M^+), 230 (10), 165 (4), 128 (15), 105 (100, $PhCO^+$), 91 (20, $PhCH_2^+$), 77 (48, Ph^+), 51 (16). HR-EI-MS: 246.10446 ($C_{14}H_{18}O$; calc. 246.10447).

Data of trans-**11g**: Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.02–7.96 (*m*, 2 H); 7.57–7.50 (*m*, 1 H), 7.48–7.40 (*m*, 2 H); 7.37–7.31 (*m*, 2 H); 7.25–7.20 (*m*, 3 H); 3.04–2.96 (*m*, 1 H); 2.22–2.14 (*m*, 1 H); 1.73–1.65 (*m*, 1 H); 1.45–1.38 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 197.6 (C=O); 139.9, 123.1 (arom. C_q); 133.2, 131.7, 128.6, 128.3, 128.2, 128.0 (arom. CH); 90.1, 78.0 (C_q); 27.2 (CH); 19.8 (CH_2); 14.1 (CH). EI-MS: 246 (9, M^+), 230 (5), 165 (23), 147 (52), 128 (19), 105 (100, $PhCO^+$), 91 (34, $PhCH_2^+$), 77 (38, Ph^+), 51 (16). HR-EI-MS: 246.10442 ($C_{14}H_{18}O$; calc. 246.10447).

(2-Cyclopropylcyclopropyl)(phenyl)methanone (**11h**). *GP H* starting from **3j** afforded **11h** as an inseparable *cis*/*trans*-mixture (15:85) in 68% yield. Colorless oil.

Data of trans-**11h**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.97–7.91 (*m*, 2 H); 7.53–7.45 (*m*, 1 H); 7.44–7.36 (*m*, 2 H); 2.47–2.40 (*m*, 1 H); 1.60–1.50 (*m*, 1 H); 1.39–1.32 (*m*, 1 H); 0.90–0.79 (*m*, 2 H); 0.46–0.36 (*m*, 2 H); 0.17–0.11 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.8 (C=O); 139.0 (arom. C_q); 132.6, 128.5, 128.0 (arom. CH); 29.3 (CH); 24.5 (CH); 16.5 (CH_2); 12.2 (CH); 4.1 (CH_2); 2.8 (CH_2). EI-MS: 186 (9, M^+), 157 (13), 105 (100, $PhCO^+$), 77 (50, Ph^+), 51 (14). HR-EI-MS: 186.10443 ($C_{13}H_{14}O$; calc. 186.10447).

Data of cis-**11h**: ^{1}H-NMR (300 MHz, $CDCl_3$): 7.97–7.91 (*m*, 2 H); 7.53–7.45 (*m*, 1 H); 7.44–7.36 (*m*, 2 H); 2.69–2.60 (*m*, 1 H); 1.53–1.44 (*m*, 1 H); 1.10–1.00 (*m*, 2 H); 0.75–0.59 (*m*, 1 H); 0.49–0.39 (*m*, 2 H); 0.25–0.20 (*m*, 1 H); 0.06–(−0.02) (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 198.9 (C=O); 138.0 (arom. C_q); 132.4, 128.4, 128.0 (arom. CH); 29.8 (CH); 24.3 (CH); 13.3 (CH_2); 8.4 (CH); 4.9 (CH_2); 4.5 (CH_2). EI-MS: 186 (10, M^+), 157 (15), 105 (100, $PhCO^+$), 77 (50, Ph^+), 51 (14). HR-EI-MS: 186.10439 ($C_{13}H_{14}O$; calc. 186.10447).

exo-*(Bicyclo[2.1.0]pent-5-yl)(phenyl)methanone* (**11i**). *GP H* starting from **3k** afforded **11i** in 61% yield and **16** in 9% yield (separated by FCC).

Data of **11i**: Colorless oil. IR (film): 1664, 1448, 1399, 1372, 1224, 699. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.07–8.03 (*m*, 2 H); 7.63–7.50 (*m*, 3 H); 2.89 (*s*, 1 H); 2.40–2.34 (*m*, 2 H); 2.27 (*s*, 2 H); 1.72 (*d*, J = 7.9, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.2 (C=O); 138.1 (arom. C_q); 132.5, 128.3, 127.9 (arom. CH); 35.9 (CH); 30.2 (2 CH); 24.3 (2 CH_2). EI-MS: 172 (5, M^+), 144 (10), 105 (100, $PhCO^+$), 67 (13), 51 (18), 39 (14). HR-EI-MS: 172.08852 ($C_{12}H_{12}O$; calc. 172.08881). Anal. calc. for $C_{12}H_{12}O$ (172.22): C 83.69, H 7.02; found: C 83.10, H 7.20.

3-Cyclopropyl-1-phenylprop-2-enone (**16**). Colorless oil. IR (film): 1664, 1609, 1447, 1379, 1271, 938, 698. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.97–7.91 (*m*, 2 H); 7.57–7.42 (*m*, 3 H); 7.25 (*d*, J = 15.1, 1 H); 6.55 (*dd*, J = 10.2, 1 H); 1.79–1.64 (*m*, 1 H); 1.08–1.00 (*m*, 2 H); 0.78–0.70 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 189.9 (C=O); 155.3 (CH); 138.1 (arom. C_q); 132.4, 128.4, 128.3 (arom. CH); 122.8 (CH); 15.4 (CH); 9.2 (2 CH_2). EI-MS: 172 (23, M^+), 105 (100, $PhCO^+$), 77 (86, Ph^+), 51 (41), 39 (33). HR-EI-MS: 172.08849 ($C_{12}H_{12}O$; calc. 172.08881). Anal. calc. for $C_{12}H_{12}O$ (172.22): C 83.69, H 7.02; found: C 82.96, H 7.13.

exo-*(Bicyclo[3.1.0]hex-6-yl)(phenyl)methanone* (**11j**). *GP H* starting from **3l** afforded **11j** in 80% yield. Colorless crystals. M.p. 59–61°. IR (KBr): 1656, 1450, 1405, 1389, 1234, 687. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.99–7.91 (*m*, 2 H); 7.57–7.41 (*m*, 3 H); 2.47 (*t*, J = 3.0, 1 H); 2.17–2.10 (*m*, 2 H); 2.00–1.66 (*m*, 5 H); 1.36–1.19 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.8 (C=O); 138.2 (arom. C_q); 132.4, 128.3, 127.9 (arom. CH); 32.8 (2 CH); 27.5 (2 CH_2); 26.6 (CH); 20.6 (CH_2). EI-MS: 186 (100, M^+), 158 (72), 77 (79, Ph^+), 51 (89), 39 (75). HR-EI-MS: 186.10451 ($C_{13}H_{14}O$; calc. 186.10447). Anal. calc. for $C_{13}H_{14}O$ (186.25): C 83.83, H 7.58; found: C 83.45, H 7.34.

*(Phenyl)[(1*SR*,1a*RS*,6a*SR*)-1,1a,6,6a-Tetrahydrocyclopropa[a]indene-1-yl]methanone* (**11k**). *GP H* starting from **3m** afforded *exo*-**11k** in 62% yield and *endo*-**11k** in 16% yield (separated by FCC).

Data of exo-**11k**: Colorless crystals. M.p. 148–149°. IR (KBr): 1647, 1384, 1375, 1229, 1021, 757, 694. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.83 (*m*, 2 H); 7.49–7.42 (*m*, 1 H); 7.38–7.25 (*m*, 3 H); 7.18–7.06 (*m*, 3 H); 3.33–3.23 (*m*, 1 H); 3.13–3.02 (*m*, 2 H); 2.67–2.59 (*m*, 1 H); 2.19–2.16 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 198.2 (C=O); 144.2, 142.2, 137.6 (arom. C_q); 132.8, 128.5, 128.0, 126.4, 125.3, 123.9 (arom. CH); 38.3 (CH); 35.9 (CH); 35.8 (CH_2); 30.0 (CH). EI-MS: 234 (33, M^+), 129 (43), 105 (100, $PhCO^+$), 77 (41, Ph^+), 51 (10). Anal. calc. for $C_{17}H_{14}O$ (234.29): C 87.15, H 6.02; found: C 87.38, H 5.99.

Data of endo-**11k**: Colorless crystals. M.p. 70–72°. IR (KBr): 1666, 1448, 1399, 1231, 1220, 990, 760, 723, 712, 687. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83–7.78 (*m*, 2 H); 7.43–7.36 (*m*, 1 H); 7.33–7.25 (*m*, 2 H); 7.09–7.03 (*m*, 2 H); 7.01–6.94 (*m*, 1 H); 6.92–6.84 (*m*, 1 H); 3.55–3.46 (*m*, 1 H); 3.19–3.08 (*m*, 2 H); 2.61 (*t*, J = 8.3, 1 H); 2.42–2.34 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 196.7 (C=O); 144.0, 139.7, 138.1 (arom. C_q); 132.5,

128.2, 127.9, 126.4, 125.9, 124.6, 124.2 (arom. CH); 33.7 (CH); 32.4 (CH_2); 28.4 (CH); 24.4 (CH). EI-MS: 234 (30, M^+), 129 (51), 105 (100, $PhCO^+$), 77 (39, Ph^+), 51 (12). Anal. calc. for $C_{17}H_{14}O$ (234.29): C 87.15, H 6.02; found: C 87.26, H 6.17.

exo-*(Bicyclo[4.1.0]hept-7-yl)(phenyl)methanone* (**11l**). *GP H* starting from **3n** afforded **11l** in 86% yield. Colorless oil. IR (film): 1662, 1447, 1414, 1220, 693. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.99–7.91 (*m*, 2 H); 7.52–7.39 (*m*, 3 H); 2.45 (*t*, *J* = 4.0, 1 H); 2.05–1.86 (*m*, 4 H); 1.82–1.66 (*m*, 2 H); 1.42–1.21 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.7 (C=O); 138.0 (arom. C_q); 132.1, 128.1, 127.5 (arom. CH); 31.1 (CH); 26.3 (2 CH); 22.9 (2 CH_2); 20.8 (2 CH_2). EI-MS: 200 (78, M^+), 105 (100, $PhCO^+$), 77 (77, Ph^+), 51 (25). HR-EI-MS: 200.12008 ($C_{14}H_{16}O$; calc. 200.12012). Anal. calc. for $C_{14}H_{16}O$ (200.28): C 83.96, H 8.05; found: C 83.64, H 8.18.

*(1*SR*,3*SR*,6*RS*,7*RS*)-[3-(*tert*-Butyl)bicyclo[4.1.0.]hept-7-yl](phenyl)methanone* (**11m**). *GP H* starting from **3o** afforded **11m** in 79% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.93–7.87 (*m*, 2 H); 7.52–7.45 (*m*, 1 H); 7.44–7.37 (*m*, 2 H); 2.34 (*t*, *J* = 4.1, 1 H); 2.27–2.17 (*m*, 1 H); 2.04–1.90 (*m*, 2 H); 1.88–1.80 (*m*, 1 H); 1.55–1.42 (*m*, 3 H); 0.88–0.79 (*m*, 2 H); 0.78 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 196.0 (C=O); 138.2 (arom. C_q); 132.4, 128.4, 127.9 (arom. CH); 42.2 (CH); 32.3 (C_q); 32.1 (CH); 29.4 (CH); 27.3 (3 Me); 26.5 (CH); 25.2 (CH_2); 24.4 (CH_2); 24.3 (CH_2). EI-MS: 256 (23, M^+), 199 (23), 157 (33), 136 (38), 121 (34), 105 (100, $PhCO^+$), 77 (49, Ph^+), 57 (37). HR-EI-MS: 256.18267 ($C_{18}H_{24}O$; calc. 256.18272).

*(Phenyl)(*exo-*1a,2,4,5-tetrahydro-1*H,*5a*H-*cyclopropa[*c*]pyran-1-yl)methanone* (**11n**). *GP H* starting from **3p** afforded **11n** in 74% yield. Colorless needles. M.p. 31–33°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98–7.91 (*m*, 2 H); 7.53–7.46 (*m*, 1 H); 7.45–7.37 (*m*, 2 H); 3.98 (*d*, *J* = 11.7, 1 H); 3.81 (*dd*, *J* = 11.9, 3.2, 1 H); 3.73–3.61 (*m*, 1 H); 3.30–3.16 (*m*, 1 H); 2.70 (*t*, *J* = 4.1, 1 H); 2.05–1.86 (*m*, 3 H); 1.85–1.75 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.5 (C=O); 137.8 (arom. C_q); 132.7, 128.5, 128.0 (arom. CH); 65.0 (CH_2); 64.3 (CH_2); 30.4 (CH); 25.2 (CH); 22.9 (CH_2); 22.7 (CH). EI-MS: 202 (16, M^+), 157 (63), 144 (27), 105 (100, $PhCO^+$), 77 (64, Ph^+), 51 (22). HR-EI-MS: 202.09938 ($C_{13}H_{14}O_2$; calc. 202.09938).

*(Phenyl){*exo-*1a,2,4,5-tetrahydro-3-[(4-methylphenyl)sulfonyl]-1*H,*5*H-*cyclopropa[*c*]pyridin-1-yl}methane* (**11o**). *GP H* starting from **3q** afforded **11o** in 78% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.94–7.88 (*m*, 2 H); 7.61–7.48 (*m*, 3 H); 7.45–7.38 (*m*, 2 H); 7.30–7.24 (*m*, 2 H); 3.79 (*d*, *J* = 11.6, 1 H); 3.50–3.40 (*m*, 1 H); 2.82 (*dd*, *J* = 11.9, 3.6, 1 H); 2.71 (*t*, *J* = 4.3, 1 H); 2.37 (*s*, 3 H); 2.27 (*dt*, *J* = 11.5, 5.3, 1 H); 2.12–1.80 (*m*, 4 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 199.1 (C=O); 143.7, 137.4, 133.3 (arom. C_q); 133.0, 129.8, 128.6, 128.3, 127.6 (arom. CH); 44.2 (CH_2); 43.1 (CH_2); 29.5 (CH); 25.0 (CH); 23.2 (CH_2); 22.2 (CH); 21.5 (Me). EI-MS: 355 (1, M^+), 200 (100), 171 (14), 155 (18, Ts^+), 105 (94, $PhCO^+$), 91 (47, $PhCH_2^+$), 77 (33, Ph^+), 51 (7). HR-EI-MS: 355.12414 ($C_{20}H_{21}NO_3S$; calc. 355.12421).

*{*exo-*3-[(*tert*-Butoxy)carbonyl]-1a,2,4,5-tetrahydro-1*H,*5a*H-*cyclopropa[*c*]pyridin-1-yl}(phenyl)methanone* (**11p**). *GP H* starting from **3r** afforded **11p** in 69% yield. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.82 (*m*, 2 H); 7.64–7.55 (*m*, 1 H); 7.51–7.42 (*m*, 2 H); 3.83 (*d*, *J* = 11.2, 1 H); 3.50–3.40 (*m*, 1 H); 2.93–2.81 (*m*, 1 H); 2.67 (*t*, *J* = 4.8, 1 H); 2.32–2.23 (*m*, 1 H); 2.15–1.82 (*m*, 4 H); 1.35 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 201.5, 154.6 (C=O); 133.8 (arom. C_q); 134.2, 129.1, 128.7 (arom. CH); 80.1 (C_q); 42.8 (br., CH_2); 41.7 (br., CH_2); 32.5 (CH); 28.6 (CH_2); 28.4 (3 Me); 27.5 (CH); 23.2 (CH). EI-MS: 301 (1, M^+), 245 (16), 200 (15), 159 (16), 125 (20), 105 (57, $PhCO^+$), 77 (40, Ph^+), 57 (100), 51 (13). HR-EI-MS: 301.16783 ($C_{18}H_{23}NO_3$; calc. 301.16779).

trans-*Methyl 2-Benzoylcyclopropane-1-carboxylate* (**11q**). *GP H* starting from **5a** afforded **11q** in 59% yield. Colorless oil. IR (film): 1732, 1673, 1445, 1337, 1209, 1173, 711. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.04–8.00 (*m*, 2 H); 7.63–7.57 (*m*, 1 H); 7.52–7.46 (*m*, 2 H); 3.74 (*s*, 3 H); 3.24–3.17 (*m*, 1 H); 2.43–2.36 (*m*, 1 H); 1.68–1.57 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 197.0, 172.8 (C=O); 137.0 (arom. C_q); 133.4, 128.7, 128.3 (arom. CH); 52.2 (Me); 26.0 (CH); 24.4 (CH); 17.9 (CH_2). EI-MS: 204 (4, M^+), 149 (37), 105 (100, $PhCO^+$), 77 (59, Ph^+), 71 (24), 57 (32), 55 (23), 43 (28), 41 (26). Anal. calc. for $C_{12}H_{12}O_3$ (204.22): C 70.57, H 5.92; found: C 69.92, H 5.94.

*Methyl (1*SR*,2*SR*,3*RS*)-2-Benzoyl-3-phenylcyclopropane-1-carboxylate* (**11r**). *GP H* starting from **5b** afforded **11r** in 37% yield. Colorless solid. M.p. 64–66°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.96–7.92 (*m*, 2 H); 7.58–7.13 (*m*, 8 H); 3.79 (*s*, 3 H); 3.61–3.55 (*m*, 1 H); 3.39–3.32 (*m*, 1 H); 3.27–3.22 (*m*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 193.2, 172.7 (C=O); 137.5, 133.6 (arom. C_q); 133.2, 128.9, 128.8, 128.6, 128.2, 128.1, 127.3 (arom. CH); 52.4 (Me); 35.9 (CH); 35.0 (CH); 25.7 (CH). NMR Data: identical to those reported in [36].

1-[(4-Methylphenyl)sulfonyl]piperidine-4-carboxylic Acid (**21**). To a stirred soln. of **18** (10.0 g, 77.4 mmol) and 25 ml of 2N NaOH was added TsCl (16.2 g, 85.2 mmol). After 24 h, the mixture was washed with Et_2O (3 × 15 ml), acidified to pH 1, and extracted with CH_2Cl_2 (4 × 20 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Colorless solid (11.4 g, 52%). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.66–7.61 (*m*, 2 H); 7.35–7.30 (*m*, 2 H); 3.68–3.62 (*m*, 2 H); 2.44 (*s*, 3 H); 2.50–2.40 (*m*, 2 H); 2.33–2.24 (*m*,

1 H); 2.03–1.96 (*m*, 2 H); 1.89–1.79 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 179.6 (C=O); 143.7, 132.9 (arom. C_q); 129.7, 127.7 (arom. CH); 45.3 (2 CH_2); 39.7 (CH); 27.2 (2 CH_2); 21.5 (Me).

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Received October 31, 2002