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C_2 Symmetry and Asymmetric Induction

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Contents

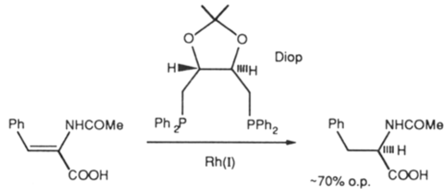
James K. Whitesell received his B.S. degree from The Pennsylvania State University in 1966 and the Ph.D. degree from Harvard University in 1971 under the direction of R. B. Woodward. After a 2-year postdoctoral stay at the Woodward Research Institute in Basel, Switzerland, he began his independent research at the University of Texas at Austin, where he currently holds the position of Professor of Chemistry. He conducts research on methods for the analysis and control of stereochemistry within complex molecular arrays and has made major contributions in the area of absolute stereochemical control through asymmetric induction. Recently, he has turned his attention to extending methods for the control of arrangements within molecules to fixing the relative orientations between molecules. Results in this latter area will have wide-ranging applications in material science.

I. Introduction

Upon first inspection, it might appear that the introduction of a symmetry element within a chiral auxiliary would be antithetical to the stated objective of achieving asymmetric induction in a chemical transformation. In fact, the enantioface differentiation almost universally relied upon to provide asymmetric induction requires only that the auxiliary lack mirror or inversion symmetry and, therefore, need not be asymmetric, only dissymmetric.[1] In the majority of scenarios for absolute stereochemical control, the presence of a C_2 symmetry axis within the chiral auxiliary can serve the very important function of dramatically reducing the number of possible competing, diastereomeric transition states. While a number of researchers in this area have noted parenthetically the importance of this symmetry element in their rational design of chiral auxiliaries, there has been to this point no comprehensive review predicated on this fundamental concept.[2]

It is my purpose in collecting this body of chemistry in one place to provide an avenue whereby researchers interested in asymmetric induction can continue this fascinating yet subtle area of stereochemical control with full knowledge of auxiliaries that have been designed and used in the past. A "sales pitch" for this symmetry element will not be made beyond the tabulation of the obviously successful results to appear below. It would be inappropriate in many cases to make a cross comparison between reactions using auxiliaries both with and without this symmetry because almost universally that is not the only feature of the stereochemical directors that is different. In addition, it is common for results for different auxiliaries to be reported from different laboratories where conditions and methods are likely different. Finally, caution is always advised when dealing with complex yet subtle issues of reaction mechanisms as there are many transformations in organic synthesis that are not yet well understood. Care is especially warranted in the area of absolute stereochemical control where there are generally only two possible outcomes (either *R* or *S*), and any transition-state model has, a priori, a 50% probability of being consistent with the observed outcome. Nonetheless, it is almost universally observed that auxiliaries with C_2 symmetry elements perform in their capacity as stereochemical directors to provide higher levels of absolute stereochemical control as compared to those totally lacking in symmetry.

There are three seminal contributions in the area of C_2-symmetry chiral auxiliaries to which research in this area can be traced. Kagan's[4,5] introduction of Diop is especially significant not only because this is historically the first C_2 chiral auxiliary but as well represents the first general, high-level (95:5), catalytic asymmetric induction process (eq 1). Johnson's[6] mediation of the cation-induced cyclization to a decalin with high levels



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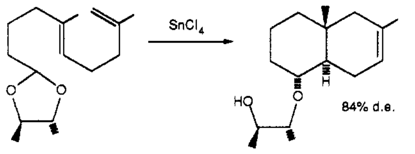
of stereochemical control based on a ketal derived from a C_2-symmetric glycol (eq 2) stimulated a large array of studies on similar ketal/acetal systems, many of which provide synthetically useful levels of absolute stereochemical control. Finally, our own introduction of 2,5-dimethylpyrrolidine[7,8] as the amine component in enamine alkylation stands as the first example of a monodentate C_2 auxiliary (eq 3).



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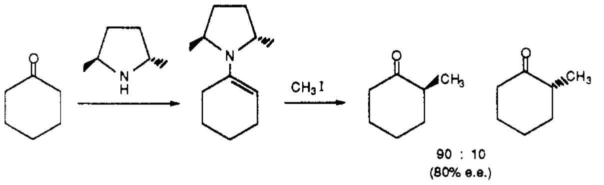

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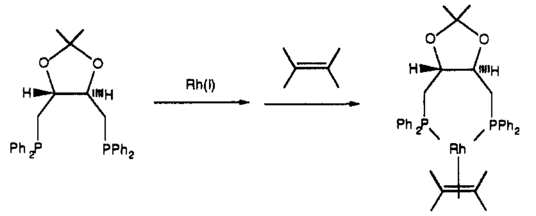
It is important to note here parenthetically that the strictest interpretation of the C_2 symmetry element would not apply to many of the auxiliaries so far introduced *in their ground-state arrangements.* For example, dimethylpyrrolidine, in which the nitrogen is sp^3 hybridized, lacks this symmetry element and, under most circumstances, 2,3-butanediol would as well have this possible symmetry element broken, for example, by internal hydrogen bonding that would differentiate the two oxygens. Nonetheless, both of these materials function as if the symmetry element was present since the impact of this symmetry upon the efficacy of the auxiliary explicitly depends on the lack of stereochemistry for atoms lying on the pseudo-C_2 axis rather than on the identity of the two sides of the auxiliary molecule. For example, in Johnson's ketal cyclization the use of a C_2-symmetric glycol avoids the generation of a chiral center at the ketal carbon as would have been the case if an unsymmetric glycol had been employed. Likewise, the incorporation of a "C_2-symmetric" amine into an enamine avoids the rotational isomerism that is present with unsymmetric amines. Even greater subtleties are possible, as it has been shown, at least in the solid state, that not all enamines have a planar arrangement about nitrogen.[9]

As might be appreciated, there is no simple way to search the literature for the particular topic chosen for this review. Citations included come from the author's personal knowledge (obviously stimulated by a keen interest in this area) as well as by citation searching of seminal papers in this area. Many additional citations were found by visually scanning annual reports (Royal Society of Chemistry) for molecules with high symmetry. My apologies are extended to those who have contributed to this area but were missed by these search routines.

A large collection of molecules with C_2 symmetry were uncovered during the compilation of this review material that have not yet been (and perhaps never will be) used as chiral auxiliaries. Nonetheless, we would assume that most readers of this review find symmetry an aesthetically pleasing topic and we have therefore included these molecules in section IV.

II. C_2 Chiral Auxiliaries for Asymmetric Induction

We have chosen to divide the discussions of chiral auxiliaries into two major classes based upon the crude differentiation as monodentate versus bidentate ligands. This distinction is rather artificial as it depends in many cases upon the species on which attention is focused. For example, Kagan's Diop ligand is clearly bidentate, yet the complex of the ligand with a metal interacts with the alkene substrate in a monodentate fashion (eq 4), while, of course, all molecules with this symmetry require the presence of two identical portions of the molecule. Our choice of class in many cases was made based upon the features of the auxiliaries as they might be stored. Further subdivision is made based upon the heteroatom involved and again, this distinction is somewhat arbitrary (phosphorus or rhodium in the example above). In any event the subclassifications are consistent.



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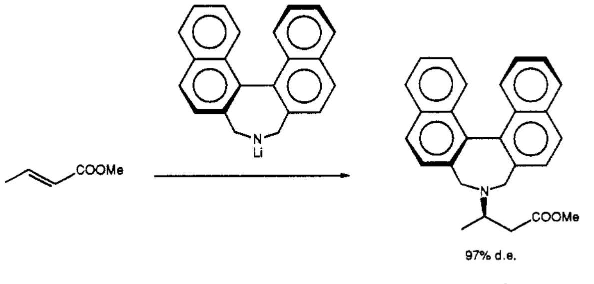
A. Monodentate Auxiliaries

i. Amines

Reports in this area have been very sparse, certainly in part because of the relative difficulty of preparing auxiliaries of this type. Indeed, our examinations of possible applications of 2,5-dimethylpyrrolidine to asymmetric induction[10] have been seriously hampered by the difficulty with which this amine can be prepared, notwithstanding alternate routes contributed by Harding[11] and Schlessinger.[12] Part of the difficulty associated with the synthesis of this simple amine is the result of a preference for many reactions to form the cis (or meso, and thus achiral) diastereomer. This difficulty is obviated in the binaphthyl amine used by Hawkins[13,14] as its lithium amide anion in a conjugate addition reaction (eq 5).



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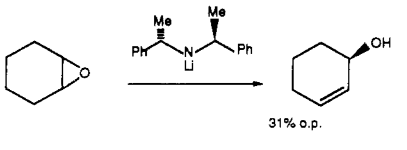
Alternatively, the C_2 amine used by us[10] for enantioselective deprotonation in the rearrangement of a meso epoxide to a chiral allylic alcohol (eq 6) can be formed in preference to the meso isomer (~80:20) by



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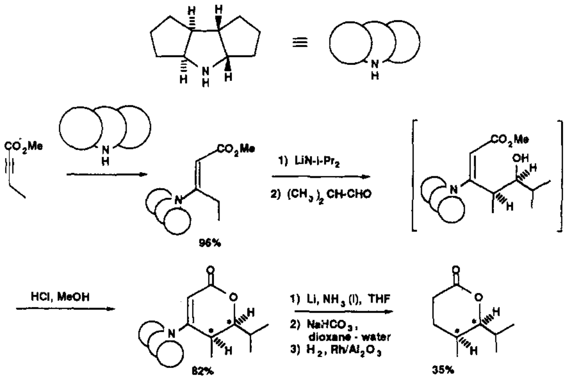
reductive amination of α-phenethylamine.[15] In addition, we[16] have recently introduced a new tricyclic amine and demonstrated (eq 7) its use in the alkylation of a vinylogous urethane.[17]



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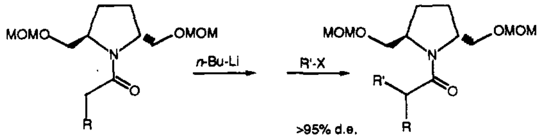
A number of applications have been found for *trans*-2,5-bis(methoxymethylene)pyrrolidine (eq 8,[18] 9,[19,20] 10,[21] and 11[22,23]), all of which proceed with surprisingly high levels of asymmetric induction. It is possible that one of the oxygens of the auxiliary is effective as a ligand for the metal ions involved in these reactions.



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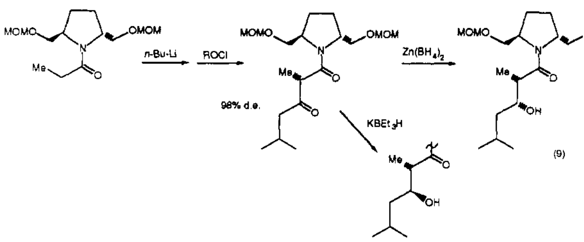

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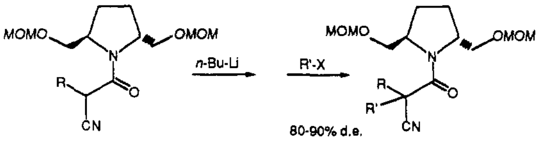

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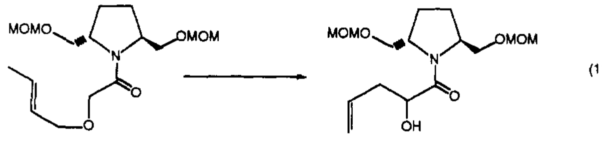

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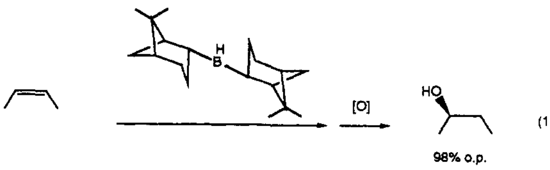
ii. Boranes

The early, seminal contributions of Brown[24-26] in the construction and application of chiral boranes set the stage for recent and highly successful contributions from others. Initial difficulties associated with obtaining the reagent diisopinocampheylborane in a state of high enantiomeric excess have been mainly overcome, and high levels of optical purities of alcohols can be obtained by hydroboration of alkenes in certain cases, as for example, with *cis*-2-butene (eq 12).[27] Conversely, application of either diisopinocampheylborane or a derived lithium borohydride reagent for the reduction of aliphatic, acyclic ketones was less successful (eq 13).



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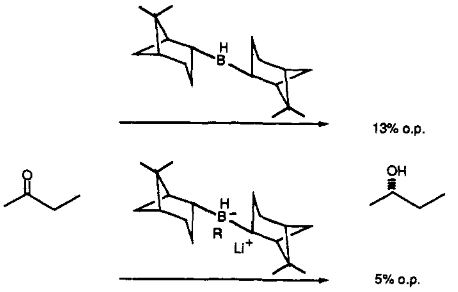

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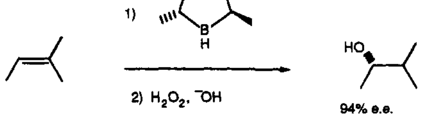
More recently, Masamune has prepared *trans*-2,5-dimethylborolane and demonstrated high levels of asymmetric induction in hydroboration of alkenes[28] (eq 14) as well as in reduction of simple ketones with a derived lithium borohydride reagent[29,30] (eq 15).



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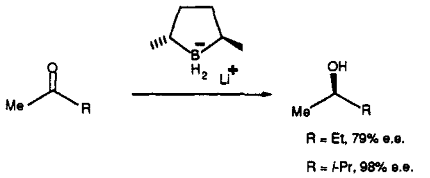

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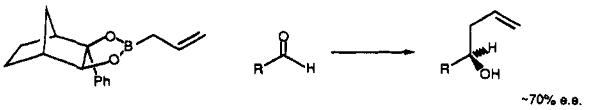
Additional and significant applications of C_2-symmetric borane reagents are found in the area of carbon–carbon bond formation. Hoffmann was the first to report asymmetric induction in the reaction of an allylborane reagent derived from a chiral borane with an aldehyde[31-33] (eq 16) and was first to report double stereodifferentiation in the reaction of these chiral reagents with chiral aldehydes.[34]



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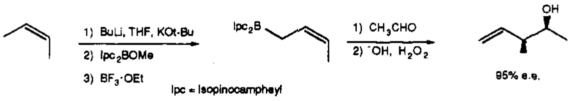
Further contributions in the area of chiral allylborane reagents have been made by Yamamoto,[35] Midland,[36] Roush,[37,38] and Brown,[29] with the results reported by Roush and Brown representing the highest levels of stereochemical control (eq 17 and 18).



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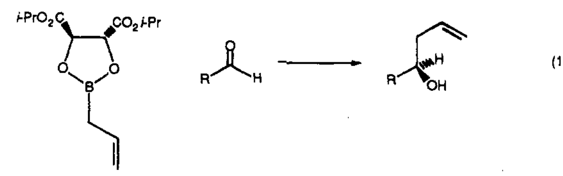

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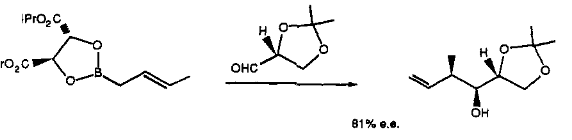

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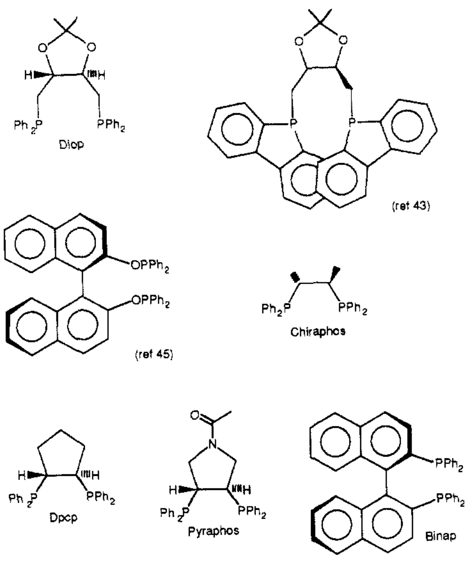
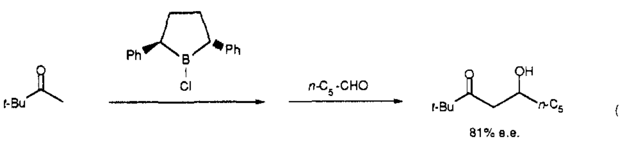


Figure 1.

Reetz[40] has demonstrated good control in the aldol reaction of the boron enolate of acyclic ketones derived from *trans*-2,5-diphenylborolane with aldehydes (eq 20), while an alkylative rearrangement with exceptional asymmetric induction has been reported (eq 21).[41]



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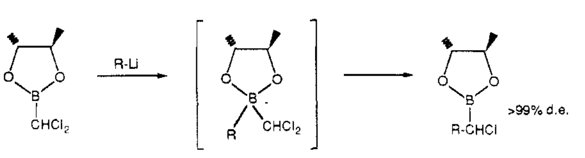

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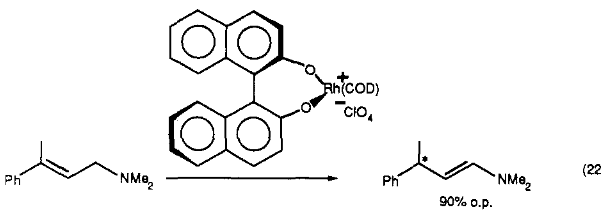
B. Bidentate Auxiliaries

There has been far more concentration of effort in the area of bidentate auxiliaries than there has been with those monofunctional species described in the previous section. These may in part be ascribed to the facility with which materials can be derived from tartaric acid and the fact that this material is readily available in both enantiomeric forms.

i. Phosphorus-Based Auxiliaries

This area has been recently and quite thoroughly reviewed[42] and will not be surveyed again here. Included in Figure 1 are the more prominent members of this group of ligands (Diop,[2] Chiraphos,[46] Dipamp,[47] Dpcp,[48] Pyraphos,[49] Binap,[50] Bdpp,[51] and the ligands without "handles" identified by their respective literature reference numbers). All have been used as auxiliary ligands for transition metals in a variety of reactions. While catalytic, homogeneous reduction of alkenes has received the greatest attention, other reactions catalyzed by transition metals have been examined, for example, the use of Binap for the isomerization of an allyl amine to the more stable enamine with concomitant formation of a chiral center (eq 22).[52]



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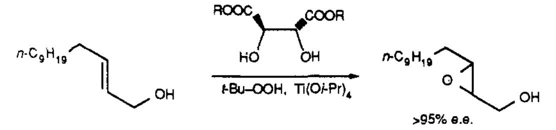
ii. Oxygen-Based Auxiliaries

This area appears to have received far more attention than any other save for the phosphine ligands (above), possibly in part because of the availability of C_2 species that can be derived from tartaric acid. One of the earliest uses of C_2-symmetric glycols was for the analysis of enantiomeric excesses in ketones through the formation of diastereomeric ketals.[53] By far the most significant result is the Sharpless epoxidation, a process that not only can provide high levels of asymmetric induction but uses in a catalytic fashion an auxiliary that can be readily obtained in both enantiomeric forms. There is a recent, comprehensive review of this area.[54]



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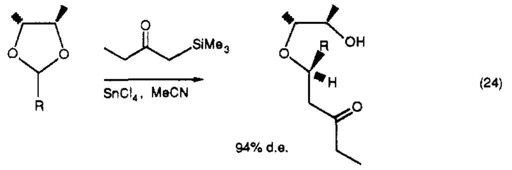
Other uses of bidentate oxygen species have focused on ketals and acetals, where induction has been observed at the acetal as well as the α and β carbons. Equations 24–31 demonstrate a range of transforma-



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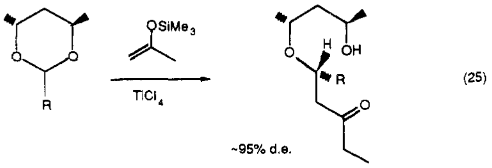

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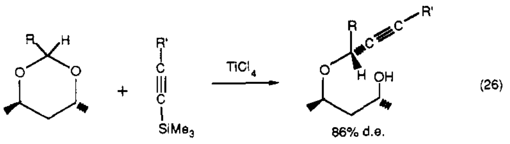

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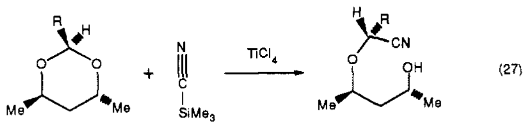

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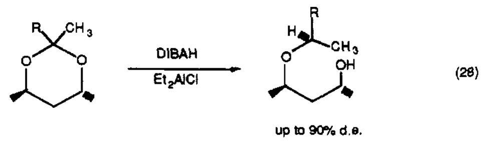

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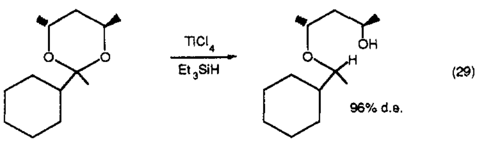

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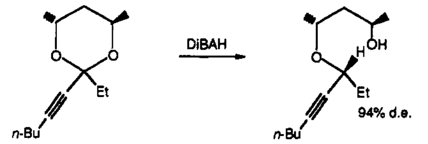

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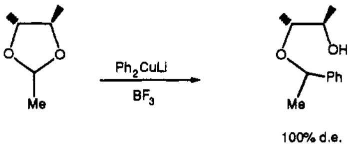
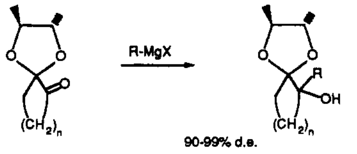


(31)

tions at the acetal carbon (eq 24,[55,56] 25,[57] 26,[58–60] 27,[61] 28,[62] 29,[63] 30,[64] and 31[65]). Alternatively, reaction at the carbon α to the acetal (eq 32,[66] 33,[67] and 34[68]) as well as at both the α and β carbons to form a three-membered ring (eq 35[69,70] and 36[71,72]) has been achieved with moderate to good levels of asymmetric induction. Addition to the β carbon has been achieved with surprisingly uniform results (except for the first example, eq 37[73,74]) across a range of systems with a variety of auxiliaries (eq 38,[75] 39,[76] 40,[77] and 41[78]).



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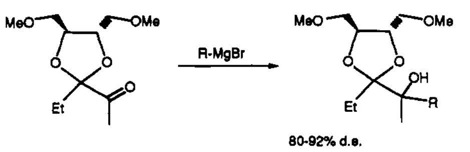

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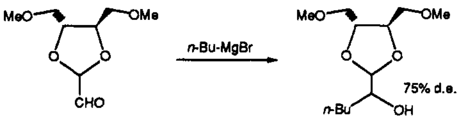

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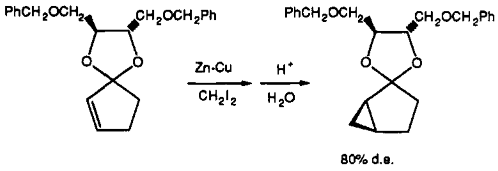

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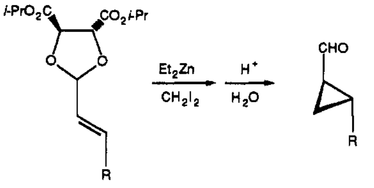

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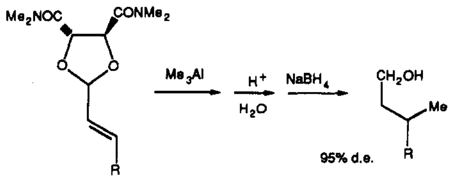

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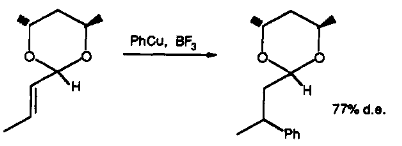

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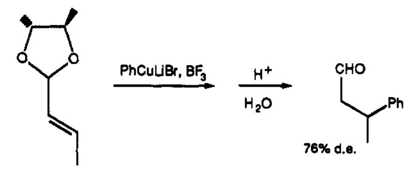

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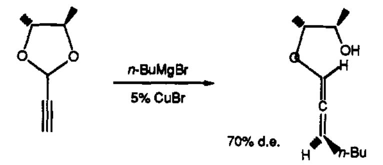

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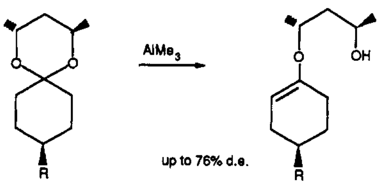

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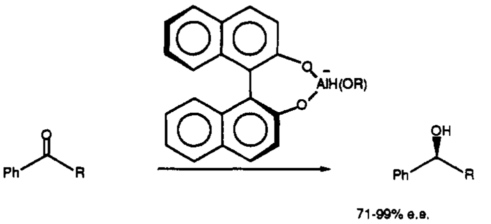
Over the years there have been many attempts to effect asymmetric induction with alkoxy-modified aluminum and boron hydride reagents derived from C_2-symmetric glycols. Early contributions came from Noyori[79–81] and represent potentially practical methods for stereochemical control both in the normal sense of asymmetric induction and for diastereomeric control (eq 42 and 43). While the highest levels of control have been achieved with the binaphthyl-derived aluminum reagents, those derived from other glycols as well as from glycols with boron (eq 44,[82] 45,[83] and 46[84]) have also been used successfully.



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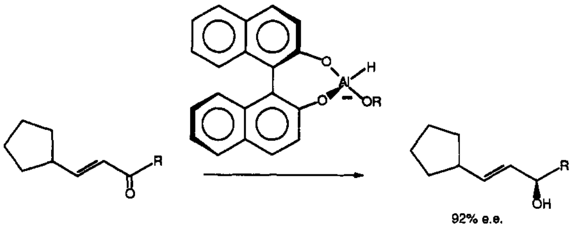

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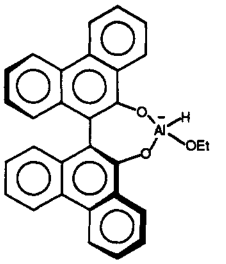

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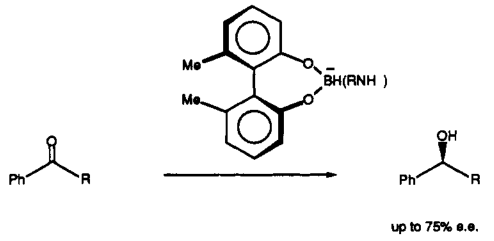
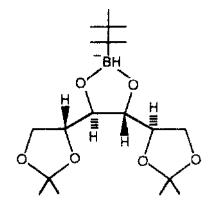
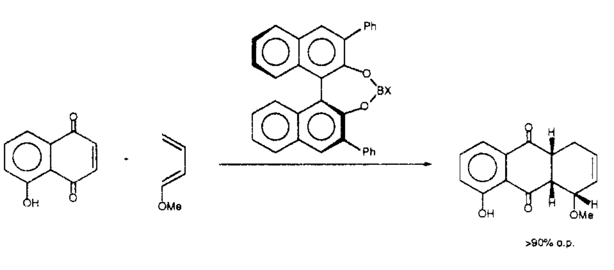


(45)

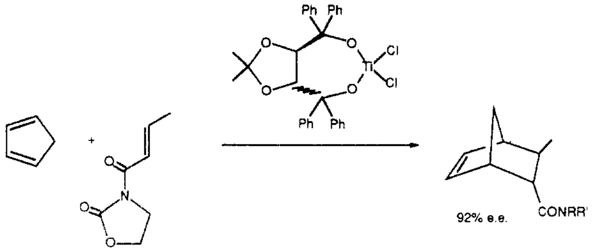


(46)

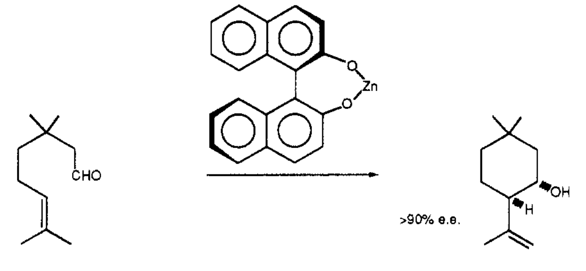
An unusually and possibly quite valuable observation of regio- and stereochemical control in Diels–Alder reactions has been made recently by Kelly (eq 47)[85] using a binaphthyl-derived boron reagent as a Lewis acid. Similar results have been observed with a titanium-based Lewis acid[86] (eq 48). Alternatively, a chiral zinc-based Lewis acid has been used by Yamamoto for an ene reaction equivalent[87] (eq 49).



(47)

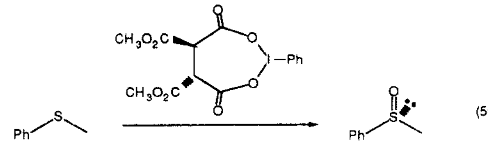


(48)



(49)

Finally, the novel, moderately selective oxidation of sulfides to sulfoxides has been reported by Imamoto[88] (eq 50).



(50)

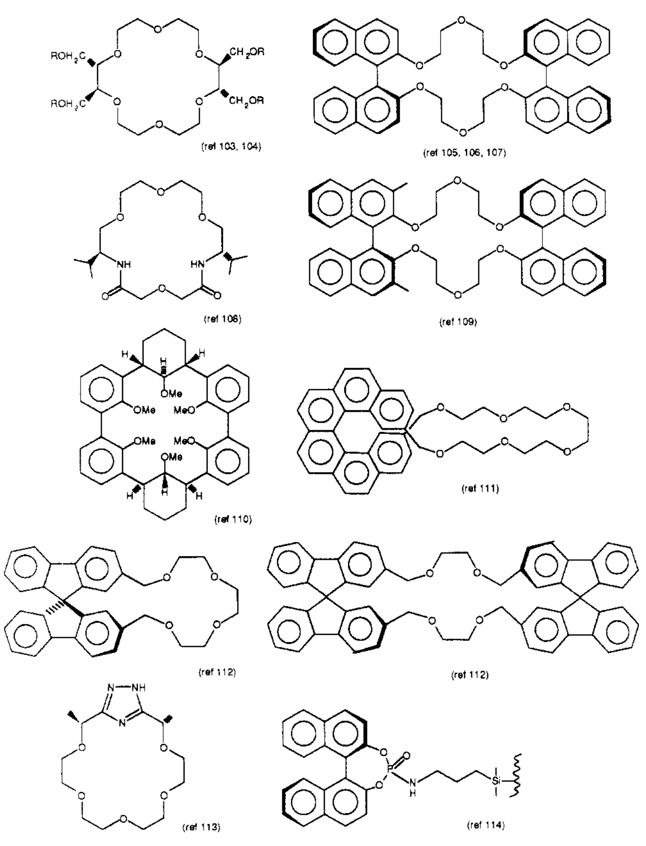
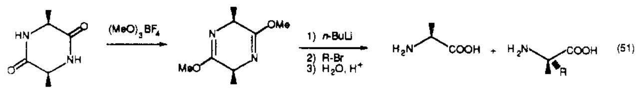


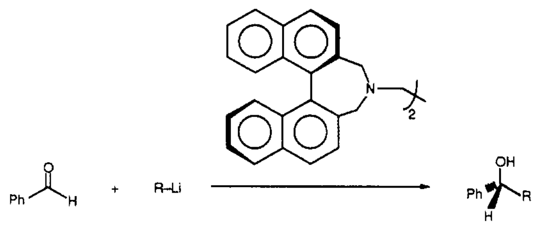
Figure 2.

iii. Nitrogen-Based Auxiliaries

There are significantly fewer examples of the application of bidentate nitrogen chiral auxiliaries than for the oxygen systems. In part this may be the result of the relatively greater difficulty with which nitrogen-based chiral centers can be incorporated in organic systems. Two of the earliest examples are the clever synthesis of amino acids by Schollkoph[89] (eq 51) and the control of face selectivity in additions of organolithium reagents to aldehydes by Cram[90] (eq 52).

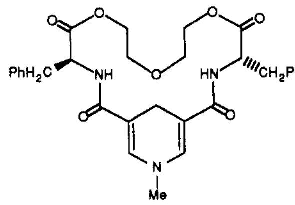


(51)

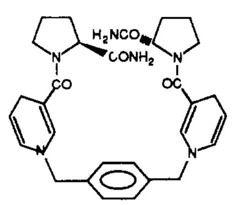


(52)

Other early contributions by Kellog[91-93] (eq 53) and Inouye[94] (eq 54) employed "mimics" of NADPH with dihydropyridines as hydride donors for reductions. This area



(53)



(54)

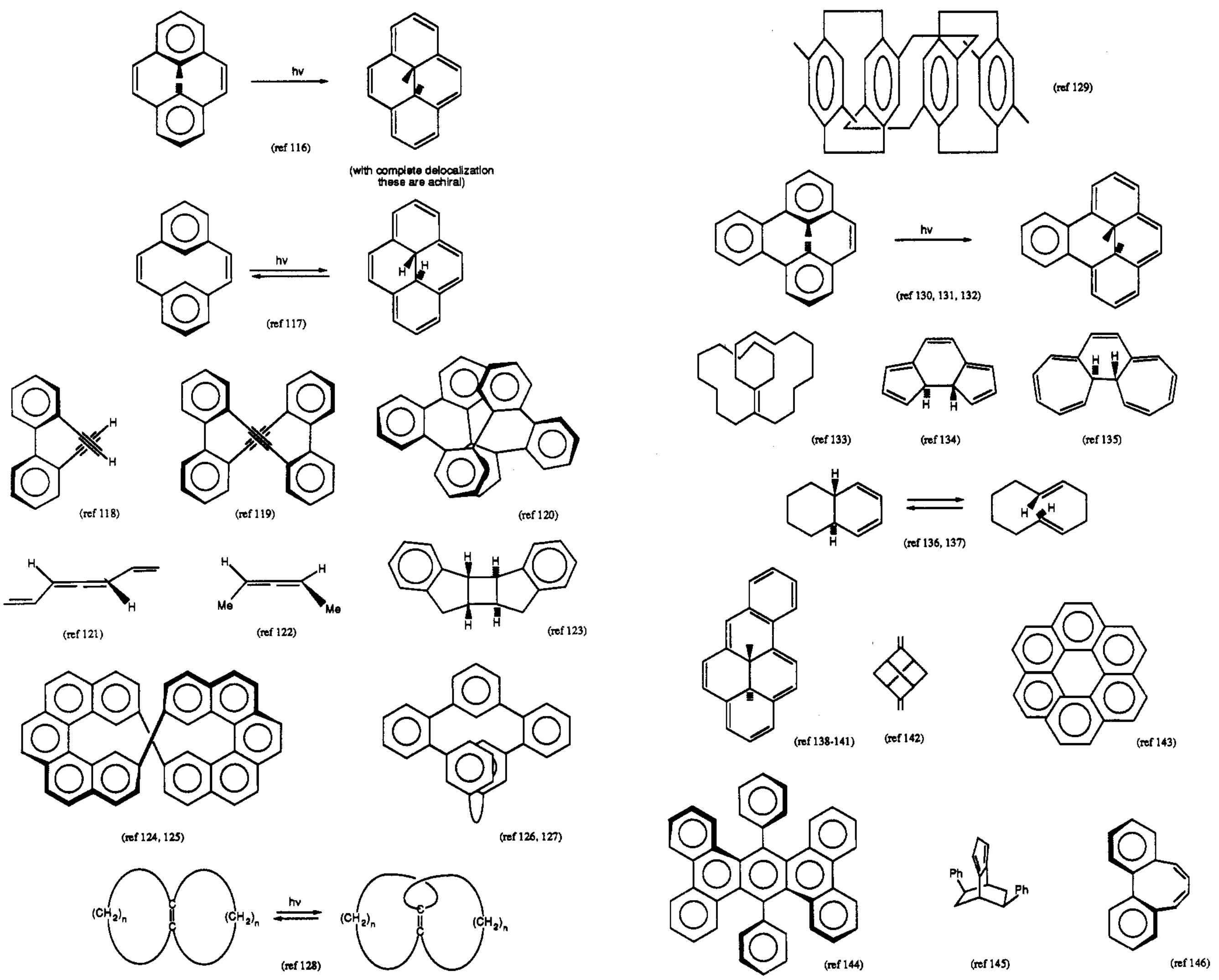


Figure 3.

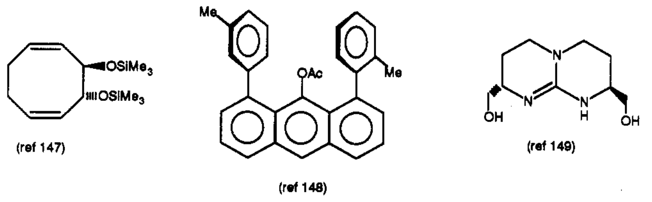
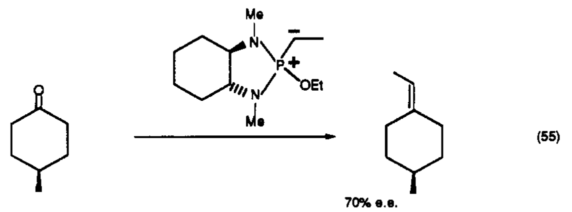


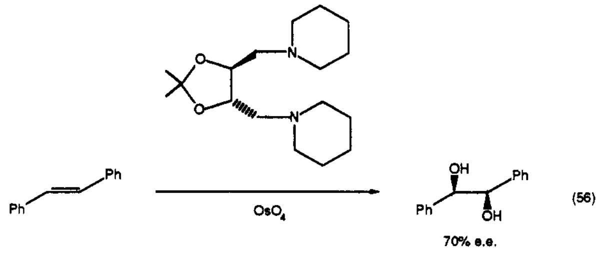
Figure 4.

has been recently reviewed.[95] Hanessian[96] has developed a chiral phosphonamide ylide based on a C_2 cyclohexyl diamine for olefination that provides good control of stereochemistry at "remote" centers (eq 55).

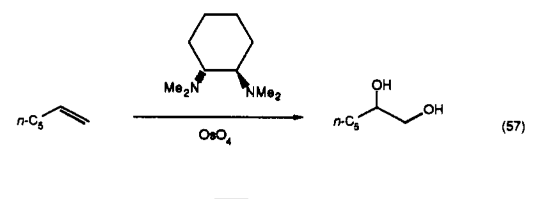


(55)

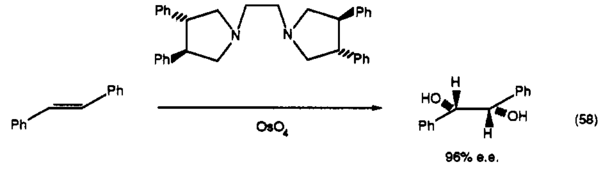
Possible applications of chiral 1,2-glycols are numerous, and thus addition of a chiral auxiliary to osmium tetraoxide reactions has been examined for some time[97,98] (eq 56 and 57; the amine in eq 57 has also been used as part of a chiral shift reagent system[99]), culminating recently in good levels of control with a variety of alkenes using a diamine with D_2 symmetry[100] (eq 58).



(56)



(57)



(58)

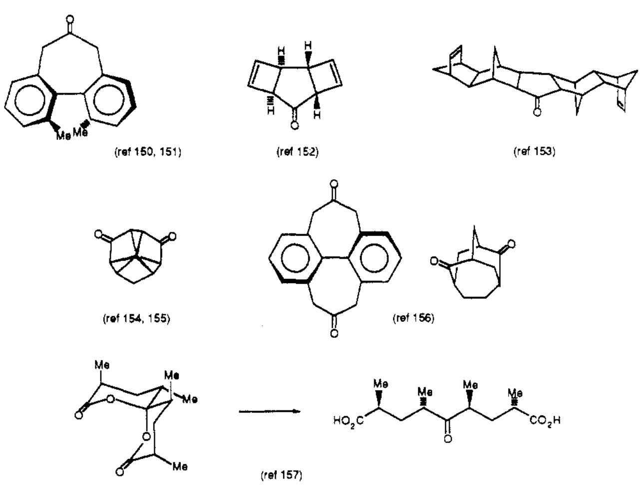


Figure 5.

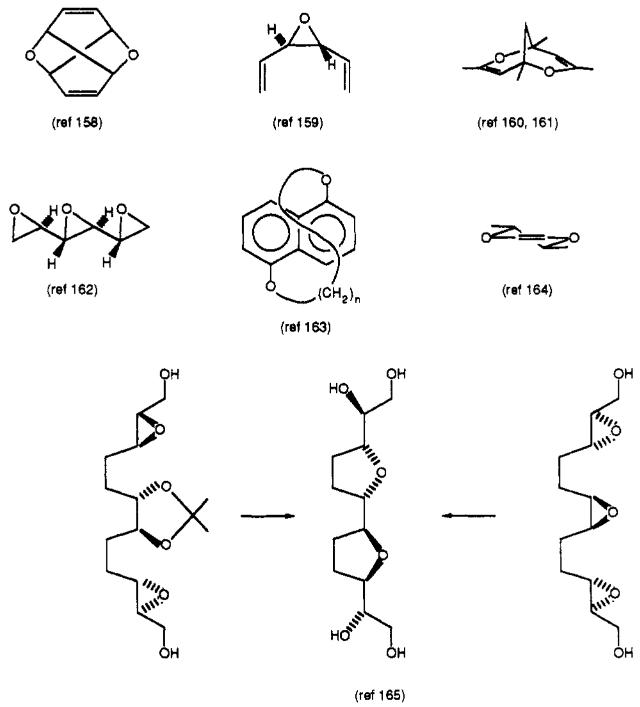
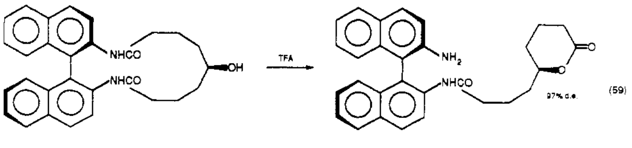


Figure 6.

Selectivity in the cleavage of a cyclic bislactam based on a binaphthyl diamine leads to the formation of a lactone with excellent asymmetric induction[101] (eq 59).



C. Polydentate Ligands

This group contains many fascinating members and represents an area of keen research interest among several active research groups. The area has been recently reviewed in depth[102] and thus, as with the phosphine ligands, we provide here (Figure 2) simply a representative collection of both historic and practical interest identified by their respective literature reference numbers. The last entry[114] is included here because it represents a species for chiral recognition as is typical with the crown ethers in Figure 2 and is polydentate in the sense of being polymer bound. The conjugate addition reaction illustrated in eq 60[115] typifies the contributions in the area of polydentate ligands that makes this avenue of research so fascinating.

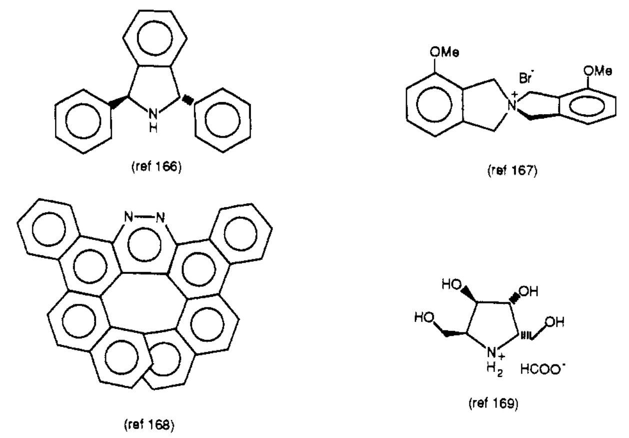


Figure 7.

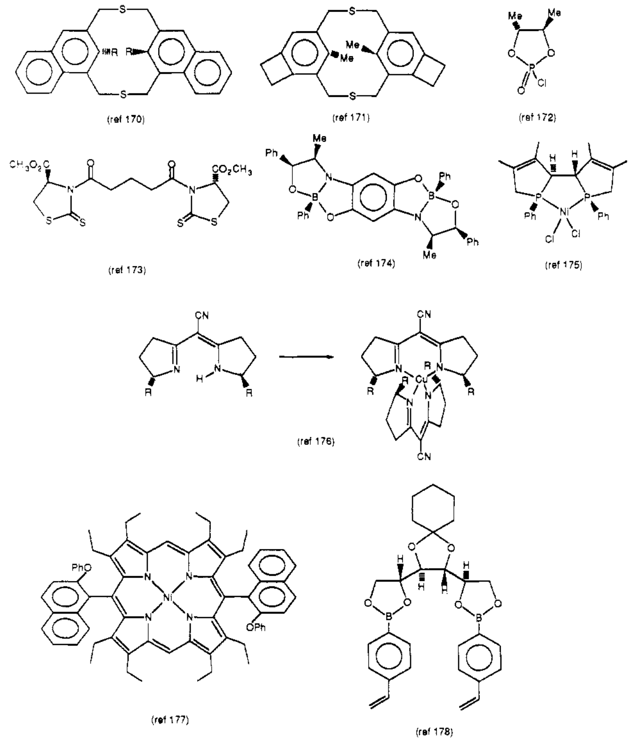
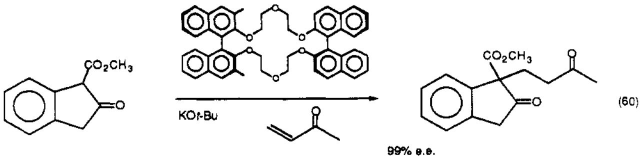


Figure 8.



III. Interesting C_2 Molecules

Figures 3–8 illustrate a range of molecules with diverse functionalities, all of which contain a C_2 axis of symmetry. They are collected without comment for the interest and fascination of the reader into groups based upon functionality present: hydrocarbons (Figure 3), alcohols (Figure 4), ketones (Figure 5), ethers (Figure

6), amines (Figure 7), and miscellaneous (Figure 8).

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