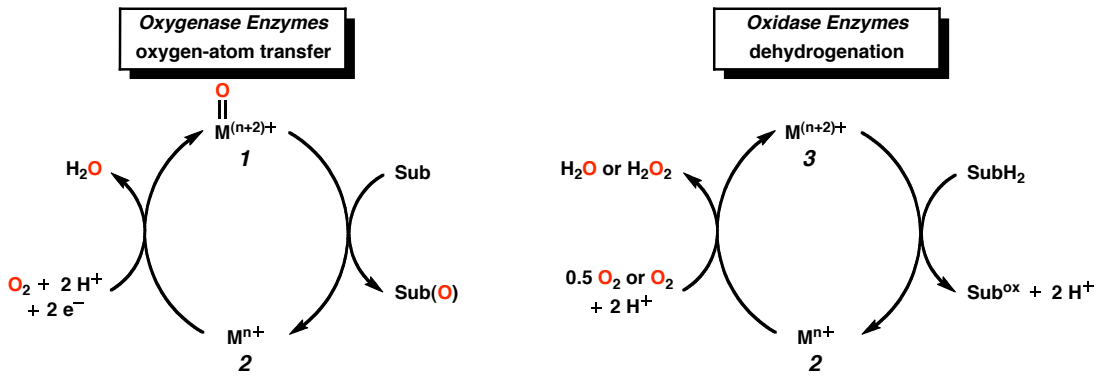
CHAPTER 1

Introduction to Enantioselective Oxidation Chemistry

1.1 Oxidation in Biological Systems

The selective oxidation of organic molecules is vital to biological systems. All aerobic organisms utilize molecular oxygen to perform cellular respiration. These redox processes with oxygen are mediated by metalloenzymes and can be divided into two classes (Figure 1.1.1). Oxygenases catalyze the transfer of oxygen atoms to the organic substrate via an intermediate metal-oxo species (**1**). Oxygenation of the substrate results in a reduced metal species (**2**). Reoxidation by molecular oxygen, two protons, and two electrons reforms the metal-oxo and generates water as a byproduct. Oxidases, on the other hand, do not involve oxygen-atom transfer to the substrate. Instead, the metal oxidant (**3**) catalyzes a formal dehydrogenation, resulting in the loss of two electrons and two protons from the substrate and the formation of a reduced metal species (**2**). Molecular oxygen then acts as an electron acceptor, regenerating the oxidized metal species (**3**). Water or hydrogen peroxide is the byproduct of these oxidations.

Figure 1.1.1 Oxygenase and oxidase enzymes.



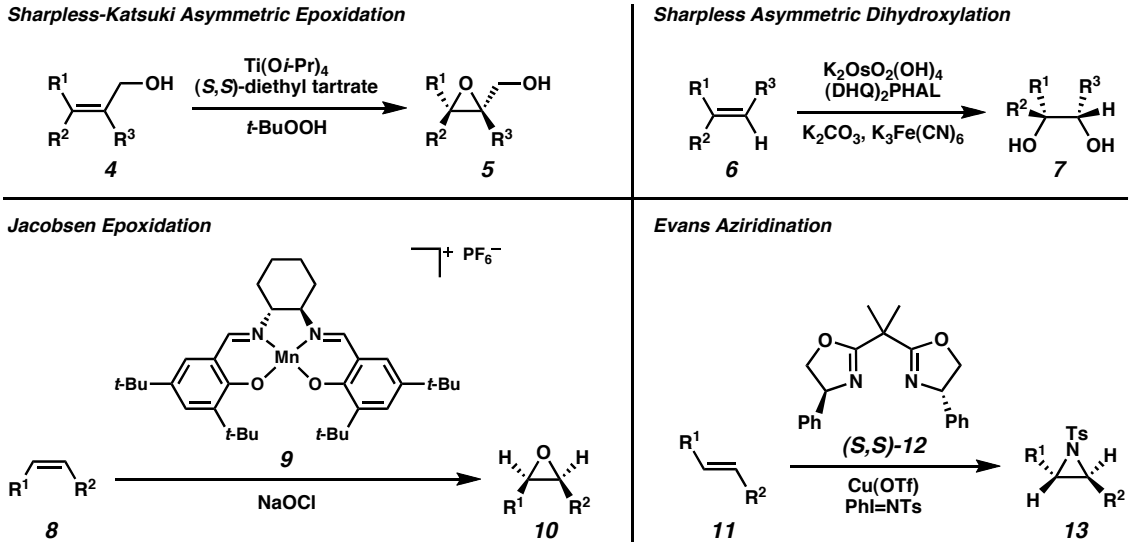
1.2 Enantioselective Oxidations in Synthetic Chemistry

1.2.1 Oxygenase-Type Reactions

Oxidation is also an essential process in synthetic chemistry. The exquisite substrate specificity and selectivity demonstrated with metalloenzymes has inspired many chemists to design synthetic catalysts to replicate nature. Recently, asymmetric oxidative processes have emerged as an important area for the construction of complex molecules.

Oxygenase-type reactions have been explored extensively, and numerous examples of catalytic asymmetric oxidations involving heteroatom transfer to the substrate have been demonstrated (Figure 1.2.1).[1] Sharpless and Katsuki developed one of the first widely applicable processes, utilizing readily available reagents to selectively epoxidize allylic alcohols with *tert*-butyl hydroperoxide as the stoichiometric oxygen atom donor (**4**→**5**).[2] Later, Sharpless was able to achieve the asymmetric dihydroxylation of olefins with an osmium catalyst and potassium ferricyanide as the terminal oxidant (**6**→**7**).[3] Jacobsen also reported an enantioselective epoxidation of olefins with manganese catalyst **9** and bleach as the oxidant (**8**→**10**).[4] Evans has shown that a copper(I) complex with bisoxazoline (*S*,*S*)-**12** catalyzes the aziridination of olefins with *N*-tosyliminobenzyliodinane (**11**→**13**).[5] Each of these oxidative systems involves heteroatom transfer to the organic substrate, though none utilize molecular oxygen as the terminal oxidant as in oxygenase enzymes.

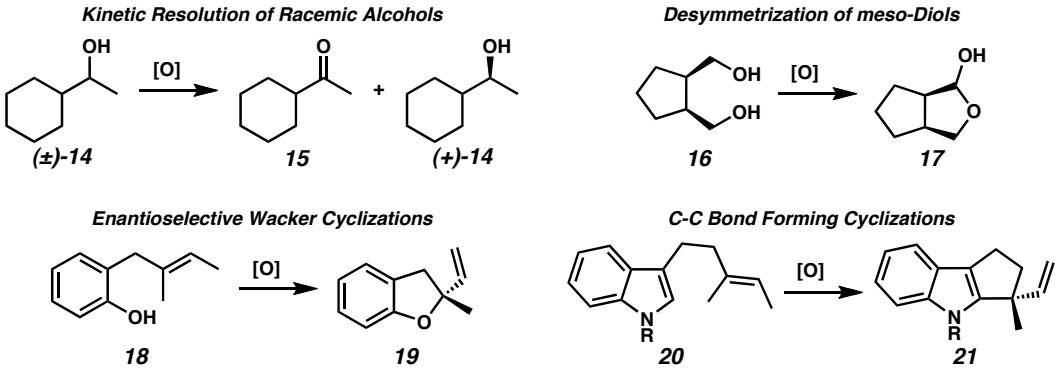
Figure 1.2.1 Synthetic asymmetric oxygenase-type chemistry.



1.2.2 Oxidase-Type Reactions

Synthetic variants of oxidase-type reactions, which involve a formal dehydrogenation rather than heteroatom transfer, have also been demonstrated. Asymmetric versions, however, have been much less explored. The scarcity of these methods is somewhat understandable, as dehydrogenation is a complexity-minimizing process.[6] While enantioselective oxygenase-type transformations involve asymmetric induction in the *construction* of substrate-heteroatom bonds, oxidase-type reactions often result in the formation of unsaturated bonds through the *destruction* of stereogenic centers. Nevertheless, the Stoltz laboratory at the California Institute of Technology envisioned a number of dehydrogenative processes that could be amenable to asymmetric catalysis (Figure 1.2.2). While long-term goals included asymmetric Wacker-type cyclizations (**18**→**19**)[7] and C–C bond forming cyclizations (**20**→**21**),[8] the initial focus of the project has been the kinetic resolution of secondary alcohols (e.g., (±)-**14**→**15** + (+)-**14**) and the related desymmetrization of *meso*-diols (**16**→**17**).

Figure 1.2.2 Proposed synthetic asymmetric oxidase-type chemistry.



1.3 Oxidative Kinetic Resolution of Alcohols

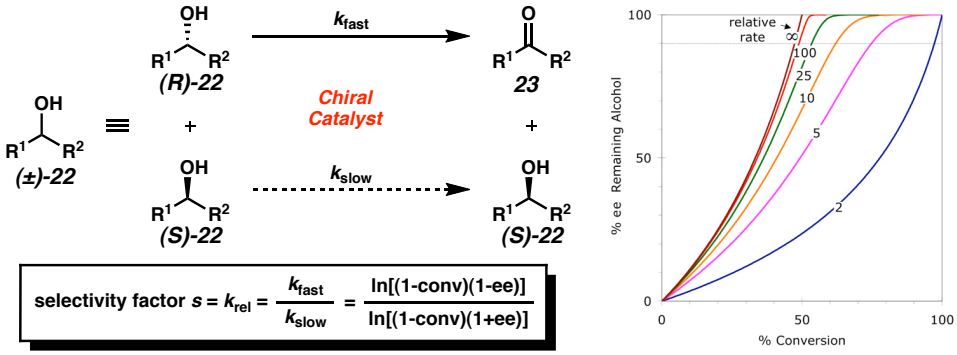
1.3.1 Kinetic Resolutions

Of all oxidase-type dehydrogenative processes, the oxidation of alcohols to carbonyl compounds is one of the most fundamental in organic chemistry.[9] Though a wide variety of oxidants have been used for these transformations,[10] comparatively few catalytic enantioselective variants are known. These enantioselective alcohol oxidations require the selective destruction of a stereocenter in a stereoablative kinetic resolution process.[11,12]

A kinetic resolution separates the two enantiomers of a racemic mixture by exploiting their unequal rates of reaction with an enantioenriched reagent or catalyst (Figure 1.3.1).[12c] One enantiomer (e.g., (*R*)-**22**) reacts faster with the enantioenriched catalyst, with rate k_{fast}, to provide product **23**. The other enantiomer ((*S*)-**22**) reacts much more slowly (k_{slow}). Ideally, the reaction is terminated when all or most of the faster-reacting enantiomer has been converted to product **23**. The remaining enantioenriched starting material ((*S*)-**22**) and product **23** can be separated by standard techniques. The selectivity factor (*s*) of a resolution is determined by measuring the relative rates of

reaction of the two enantiomers ($k_{rel} = k_{fast} / k_{slow}$). In practice, the selectivity factor is usually determined by measuring the total conversion of starting material to product and the enantiomeric excess of the recovered starting material.[12a] For an ideal system, the chiral reagent or catalyst maintains the same relative enantiomeric preference throughout the reaction, so the selectivity factor remains constant. As shown in the graph in Figure 1.3.1, the enantiomeric excess of the starting material always increases with increasing conversion for any kinetic resolution with a selectivity factor greater than 1. Thus, kinetic resolutions have the ability to provide compounds of high enantiomeric excess for even modestly selective processes at higher levels of conversion.

Figure 1.3.1 Kinetic resolution overview.

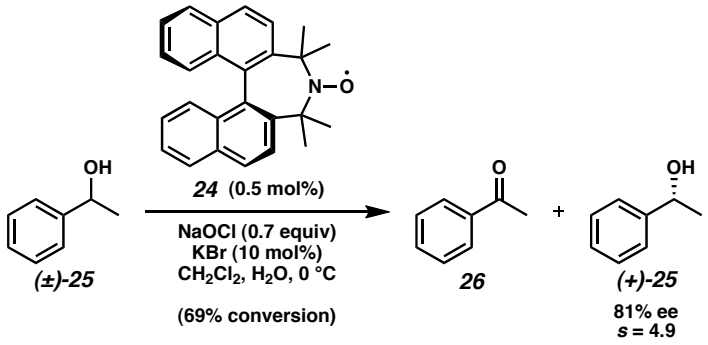


1.3.2 Previous Catalytic Enantioselective Alcohol Oxidations

At the beginning of our efforts in this area, only a few approaches to the nonenzymatic catalytic asymmetric oxidation of alcohols had been reported.[13] Several groups have utilized nitroxyl radicals for this process. Rychnovsky found that binaphthyl radical **24** catalyzes the oxidation of (±)-1-phenylethanol ((±)-**25**) to acetophenone (**26**) with bleach as the terminal oxidant, leaving enantioenriched alcohol (+)-**25** (Scheme 1.3.1).[14] Low catalyst loadings could be used, though only modest selectivity was

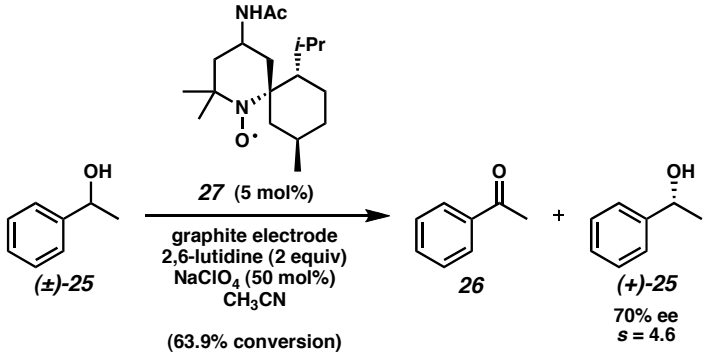
observed across a range of secondary alcohols ($s \leq 7.1$). Further studies with other chiral nitroxyl radicals led to even lower selectivity.[15]

Scheme 1.3.1 Rychnovsky's chiral TEMPO-based oxidation.



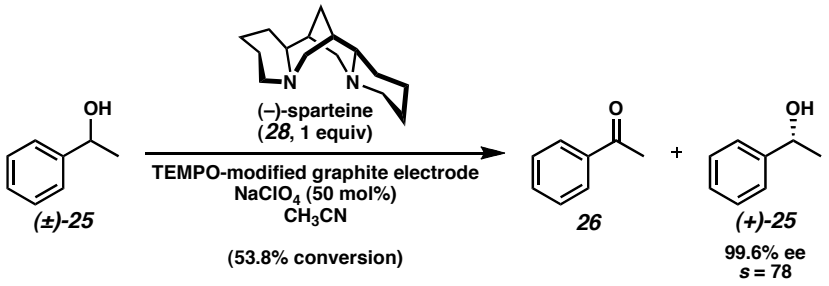
Catalytic nitroxyl radicals have also been used in electrolytic oxidation of alcohols. Kashiwagi and Bobbitt performed the enantioselective oxidation of alcohol (±)-**25** using a graphite electrode and chiral *N*-oxyl **27** (Scheme 1.3.2).[16] Again, the observed selectivity was modest for several substrates (s = 4.1–4.6). Tanaka reported a similar system utilizing Rychnovsky's *N*-oxyl **24** under electrolytic conditions that displayed improved selectivity ($s \leq 16$) at temperatures below 23 °C.[17]

Scheme 1.3.2 Chiral nitroxyl oxidation under electrolysis.



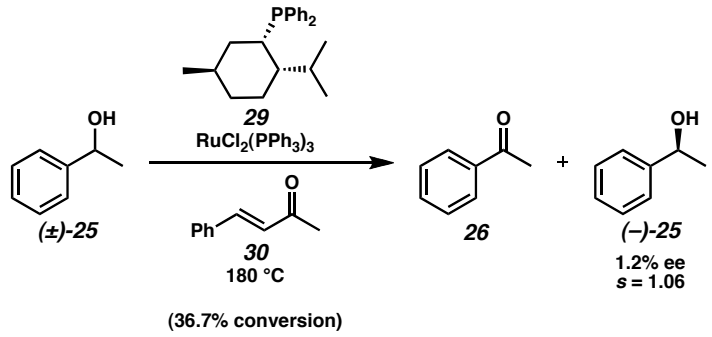
Osa and Bobbitt also demonstrated an oxidative kinetic resolution using an achiral nitroxyl radical. Utilizing a TEMPO-modified graphite electrode and the chiral diamine (–)-sparteine (**28**), highly enantioenriched alcohol (+)-**25** was recovered (Scheme 1.3.3).[18] Several other secondary alcohols also exhibited impressive selectivity factors (s = 56-184). The researchers postulated that (–)-sparteine (**28**) acts as a chiral base in the resolution. Oxidations conducted with (–)-strychnine as the chiral base were less selective.

Scheme 1.3.3 Nitroxyl oxidation with a chiral base.



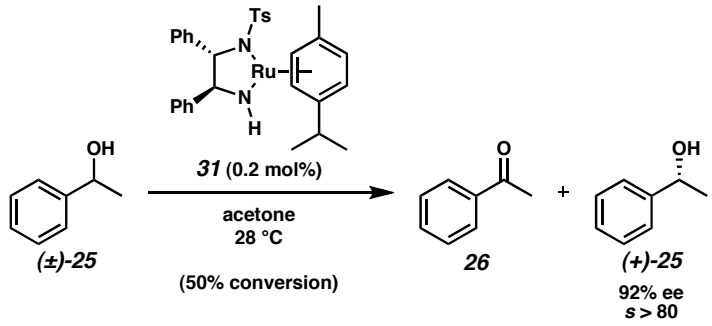
Transition metal catalysts have also been used to effect enantioselective alcohol oxidation. Ohkubo disclosed the earliest example of a nonenzymatic oxidative kinetic resolution of a secondary alcohol in 1976 (Scheme 1.3.4).[19] Extremely low levels of enantioselectivity were observed in the oxidation of (±)-1-phenylethanol ((±)-**25**) with a ruthenium catalyst and menthol-derived phosphine **29**. While not a synthetically useful transformation, this process served as an important conceptual proof for later oxidative kinetic resolutions by transfer hydrogenation. Saburi and Yoshikawa subsequently found that a rhodium hydride species with bisphosphine (–)-DIOP as a chiral ligand could catalyze the oxidative desymmetrization of a *meso*-diol by transfer hydrogenation with modest selectivity.[20]

Scheme 1.3.4 Ohkuba ruthenium-catalyzed transfer hydrogenation.



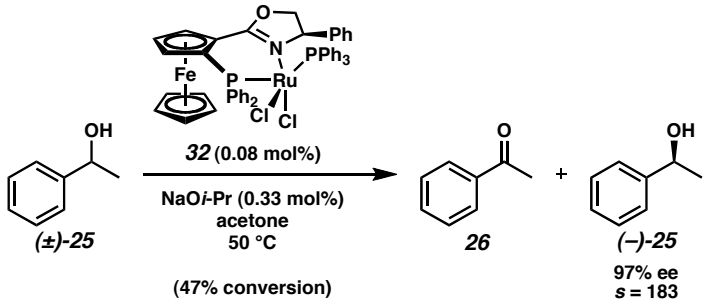
More recently, Noyori demonstrated the asymmetric oxidation of alcohol (±)-**25** with ruthenium arene complex **31** under transfer hydrogenation conditions with acetone as the terminal oxidant (Scheme 1.3.5).[21] Highly selective oxidations were observed with this system, with *s* factors for some alcohols above 100.

Scheme 1.3.5 Noyori ruthenium-catalyzed transfer hydrogenation.



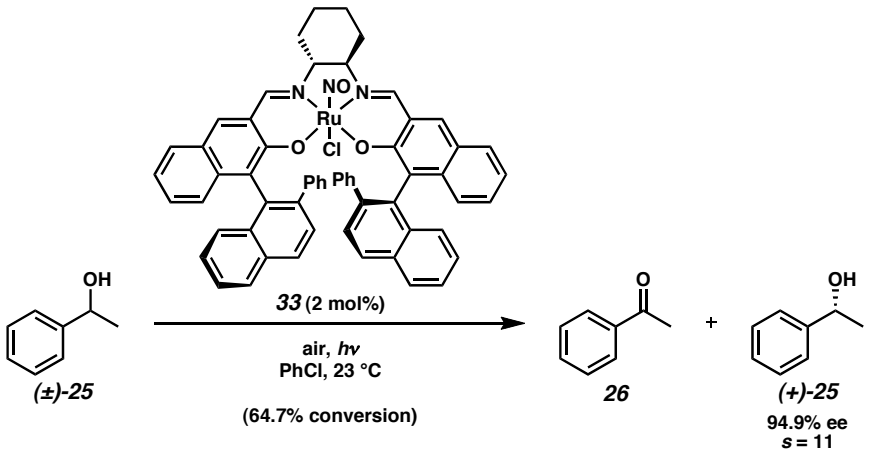
Uemura has demonstrated a similar system with a different chiral ligand (Scheme 1.3.6).[22] Ferrocenylphosphine catalyst **32** promoted transfer hydrogenation with acetone to afford alcohol (–)-**25** with outstanding selectivity. This system was active even at extremely low catalyst loadings, and a range of substrates could be resolved to high enantiomeric excesses.

Scheme 1.3.6 Uemura ruthenium-catalyzed transfer hydrogenation.



Katsuki showed that ruthenium complex **33** was a catalyst for the oxidative kinetic resolution of several alcohols (Scheme 1.3.7).[23] Under photolysis conditions, (±)-1-phenylethanol ((±)-**25**) could be resolved to high ee. This system was the first to use molecular oxygen from dry air as the terminal oxidant, representing a major advance toward catalytic systems that truly mimic aerobic oxidase enzymes. This complex was also able to perform oxidative desymmetrizations of several *meso*-diols, albeit in a modest 59-67% ee.[24] More recently, improvements in selectivity were observed with 1,3-diketone additives.[25] Finally, Gross reported a ruthenium-porphyrin-catalyzed oxidative kinetic resolution with 2,6-dichloropyridine-*N*-oxide as the terminal oxidant, though the observed enantiomeric excesses were moderate (2-28% ee).[26]

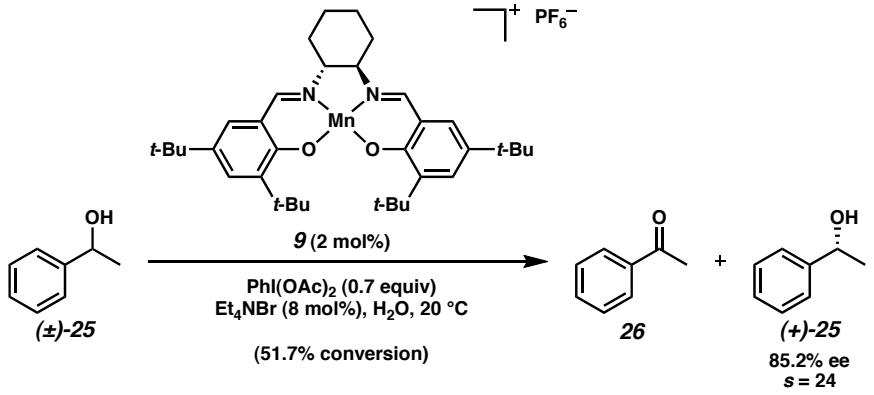
Scheme 1.3.7 Katsuki aerobic enantioselective alcohol oxidation.



1.3.3 Subsequent Enantioselective Alcohol Oxidations

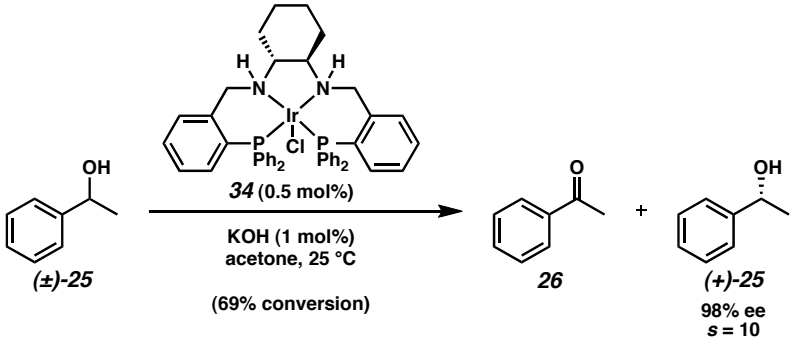
Subsequent to our initial publication on the palladium-catalyzed aerobic oxidative kinetic resolution of secondary alcohols, several other systems have been disclosed. Xia performed the enantioselective oxidation of alcohol (±)-**25** with cationic manganese(III) complex **9** and $PhI(OAc)_2$ as terminal oxidant (Scheme 1.3.8).[27] Based on an oxidation system previously reported by Katsuki,[28] water was found to be an excellent solvent for the resolutions with tetraethylammonium bromide as a phase transfer catalyst. Low to good selectivity (s = 1.1-24) was observed in the resolution of a variety of secondary alcohols. Some selectivity improvements were found with water/organic solvent mixtures.[29] A number of studies on the use of polymeric[30] and solid supported[31] catalysts for easier purification and catalyst recycling have also been reported.

Scheme 1.3.8 Manganese-catalyzed oxidation with $PhI(OAc)_2$.



Gao has found that iridium complex **34** catalyzes the oxidative kinetic resolution of benzylic alcohols (Scheme 1.3.9).[32] (±)-1-Phenylethanol ((±)-**25**) could be resolved to high enantiomeric excess under transfer hydrogenation conditions with acetone as stoichiometric oxidant, similar to previous ruthenium-based systems (Scheme 1.3.5 and Scheme 1.3.6).

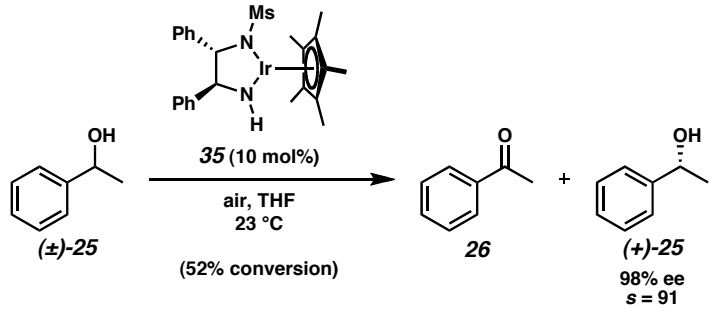
Scheme 1.3.9 Gao iridium-catalyzed transfer hydrogenation.



Another iridium catalyst (**35**) has demonstrated catalytic enantioselective oxidation with air as the terminal oxidant (Scheme 1.3.10).[33] Alcohol (±)-**25** was able to be resolved to high ee with excellent selectivity. Employing ligands related to the

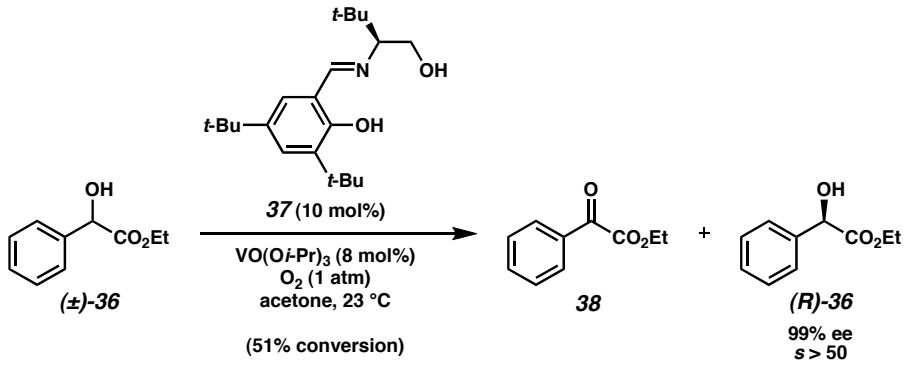
diimido ligand in Noyori's ruthenium catalyst (**31**), several other benzylic alcohols could be resolved under aerobic conditions as well.

Scheme 1.3.10 Ikariya iridium-catalyzed aerobic oxidation.



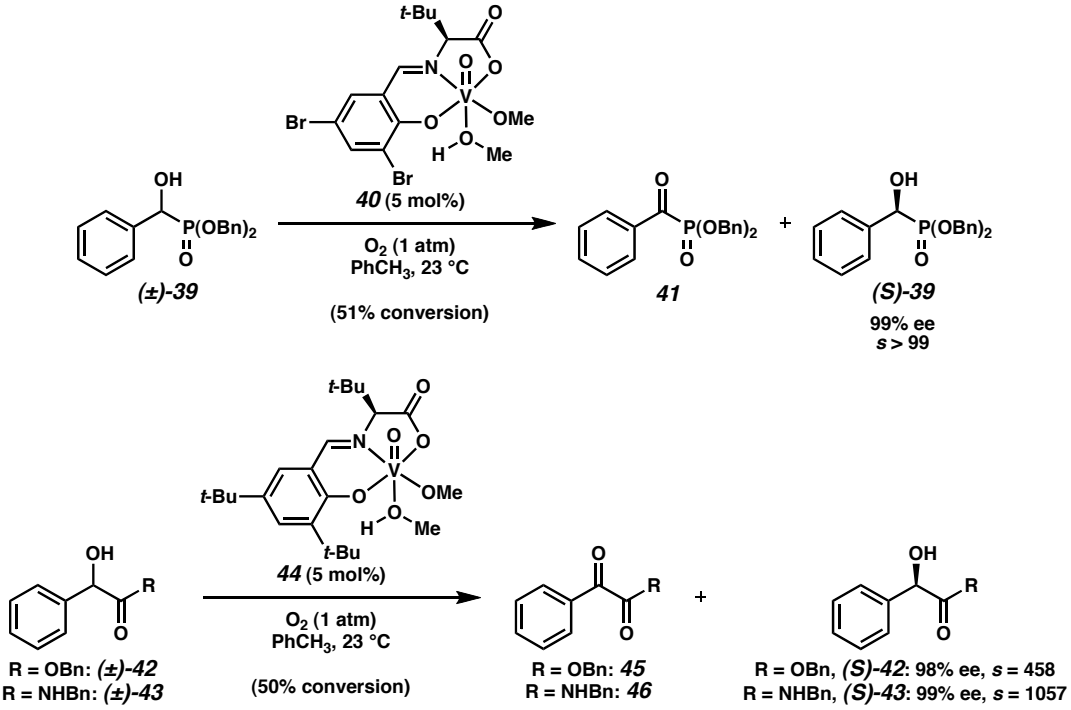
Toste has explored oxidative kinetic resolutions with vanadium catalysts.[34] salicylaldehyde-derived imine **37** proved to be an effective ligand for enantioselective oxidation of alcohols under an atmosphere of molecular oxygen as the terminal oxidant (Scheme 1.3.11). Indeed, (*R*)-ethyl mandelate ((*R*)-**36**) could be prepared with this highly selective oxidation. A number of α-hydroxyesters and also an α-hydroxyamide were resolved with good to excellent selectivity (*s* = 6-42). Interestingly, secondary alcohols without an adjacent ester or amide displayed poor reactivity with this system. Recently, Toste applied this methodology to the enantioselective total synthesis of (–)-octalactin A.[35]

Scheme 1.3.11 Toste vanadium-catalyzed aerobic oxidation.



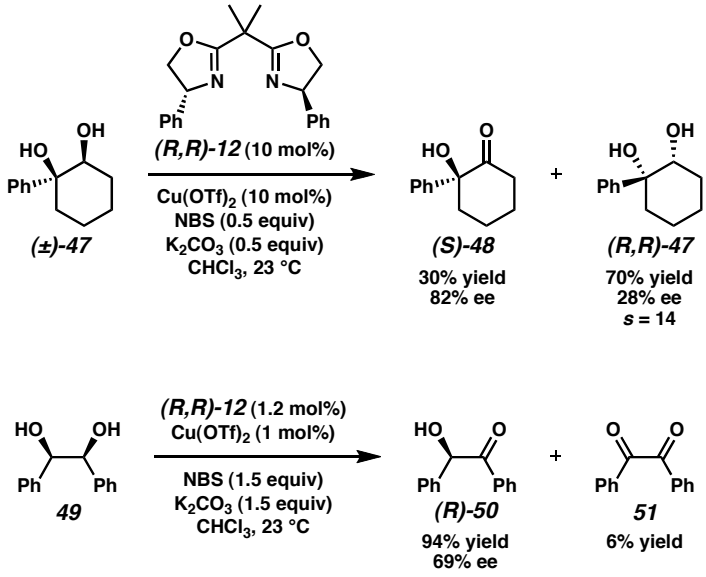
Chen subsequently reported a related system exploiting vanadium catalyst **40** with molecular oxygen as the stoichiometric oxidant to resolve phosphonate (±)-**39** with outstanding selectivity (Scheme 1.3.12).[36] Enantioselective oxidation of a range of other α-hydroxyphosphonate esters, frequently with selectivity factors over 100, was also accomplished with this aerobic system. Further developments by Chen led to a catalyst (**44**) that could resolve α-hydroxyesters and α-hydroxyamides with extremely high selectivity in some cases.[37] Vanadium clusters were found to be active catalysts for the aerobic oxidative kinetic resolution of α-hydroxythioesters.[38]

Scheme 1.3.12 Chen vanadium-catalyzed aerobic oxidations.



Onomura described an enantioselective oxidation with a copper catalyst and bisoxazoline (*R*,*R*)-**12** (Scheme 1.3.13).[39] This system successfully resolved a number of racemic 1,2-diols with *N*-bromosuccinimide as the terminal oxidant. Oxidation of cyclohexanediol (±)-**47** provided hydroxyketone (*S*)-**48** in 30% yield and 82% ee. Diol (*R*,*R*)-**47** was recovered in 70% yield and 28% ee, corresponding to a selectivity factor of 14. Desymmetrization of *meso*-hydrobenzoin (**49**) with low catalyst loading afforded (*R*)-benzoin ((*R*)-**50**) in 94% yield and 69% ee.

Scheme 1.3.13 Onomura copper-catalyzed enantioselective oxidations.



1.4 Conclusion

Inspired by biological systems, chemists have developed a number of asymmetric oxidations based on small molecule catalysis. While numerous transformations involving oxygenase-type reactivity have been reported, catalytic enantioselective oxidase-type reactivity has been relatively less explored. Even asymmetric variants of the ubiquitous alcohol oxidation have been limited. Despite efforts by a number of researchers, a mild, general, and selective method for the oxidative kinetic resolution of secondary alcohols has remained elusive. The discovery and development of a palladium-catalyzed aerobic system to achieve this goal is the subject of this thesis.

1.5 Notes and References

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