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New reaction and new catalyst—a personal perspective

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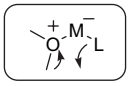
Abstract—A number of new synthetic methods are reviewed. Most of the methods are based on aluminum, boron, tin, silver Lewis acids and/or Brønsted acid catalysts. Concepts of combined acid catalysis and super Brønsted acid catalysis are also summarized. These methods are useful for selective organic transformations including simple natural product synthesis.

1. Introduction

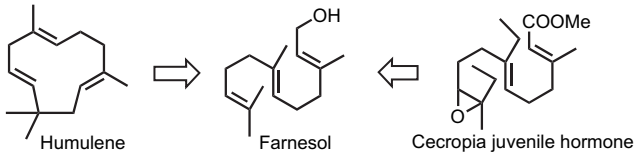
Although I am not a good Japanese chess (Shogi) player, I admire one famous professional player, the late Kozo Masuda (1918–1991), the most gifted Shogi player of his era. He became a professional Shogi player while in his youth. After years of practice and dedication, he quickly climbed the ranks of the best and became the champion in 1957. His popularity did not derive from being an undefeatable champion; rather what was so special about his game was that he invented completely novel strategies and tactics in his matches. I was amazed by this and indeed I am sure it was not a simple task. Famous professional Shogi players today make use of the same conservative strategies in their games. When people asked Mr. Masuda why he insisted on inventing new strategies, his answer was simple: "I would like to devote my life solely to creating unbeaten path" (shinn te isshou).

I respect his philosophy greatly and feel that his attitude to Shogi exemplifies the ideal of a synthetic chemist. This way of thinking is essential to preserving and making certain this lovely science is immortalized. Described herein is a small contribution from our laboratories on organic synthesis, particularly regarding the molecular design and engineering of reagents and catalysts.

2. Aluminum amide: Lewis acid–Lewis base cooperative system



In my early days, I was interested in synthesizing several sesquiterpenes from simple and readily available farnesol. Although this is not actually a biomimetic route, the invention of possible synthetic routes is still quite challenging (Scheme 1). For example, how can we prepare juvenile hormone and humulene from farnesol?



Scheme 1.

Scheme 2 is one of our answers to this question. A key step of synthesis is a vanadium-catalyzed epoxidation, which resulted from fruitful collaboration with Professor Barry Sharpless.[1] The reaction proceeds with exceedingly high *erythro* selectivities. The following steps proceed stereoselectively: copper alkylation and dehydration to generate the key framework. Although the reaction of epoxides with a strong base constitutes a well-known synthetic method for preparation of the starting allylic alcohols, the inefficiency of this process led us to develop a new method: the aluminum amides for this rearrangement.[2]

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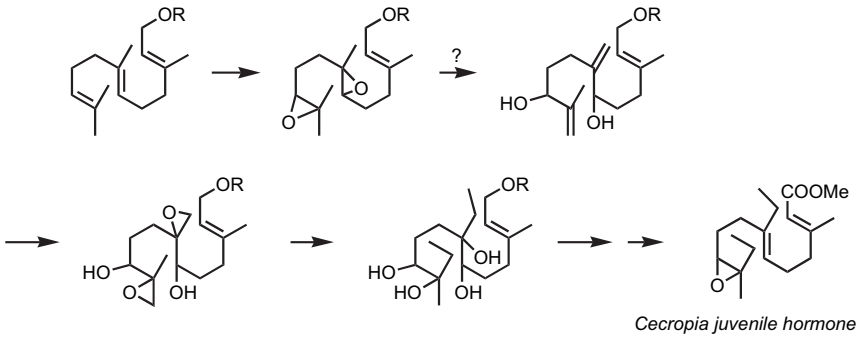
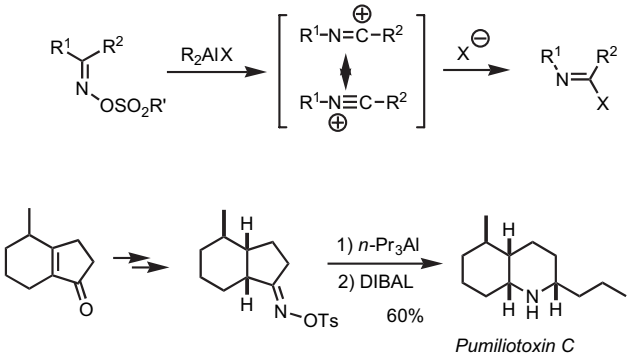


Scheme 2.

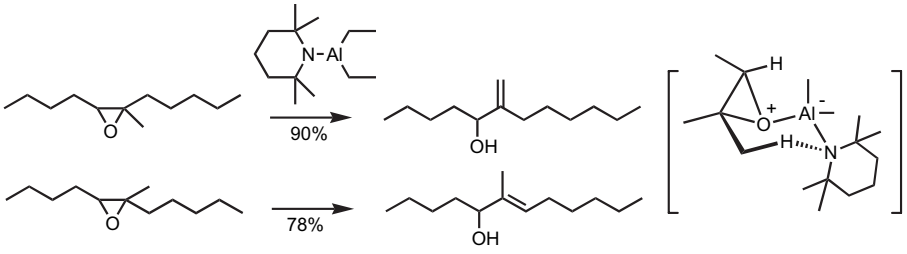
The rearrangement proceeded smoothly using bulky aluminum amides. Thus, diethylaluminum 2,2,6,6-tetramethylpiperide reacted with the epoxide smoothly and gave the allylic alcohols highly efficiently. The observed strict regioselectivity originated from the stereoselective coordination of a sterically less hindered epoxide lone pair with the nitrogen of aluminum amide. Thus, the Lewis basicity of nitrogen was increased significantly by coordination of epoxide to aluminum. This was a new Lewis acid–Lewis base cooperative reaction system (Scheme 3).

The stereoselective synthesis of humulene is shown in Scheme 4. The key step of the synthesis is the palladium-catalyzed medium ring cyclization, the first transition metal catalyzed cyclization of a medium and a large ring. The base-catalyzed elimination of oxetane to generate homoallylic alcohol proceeds smoothly using aluminum amide, a transformation similar to that described above.[3]

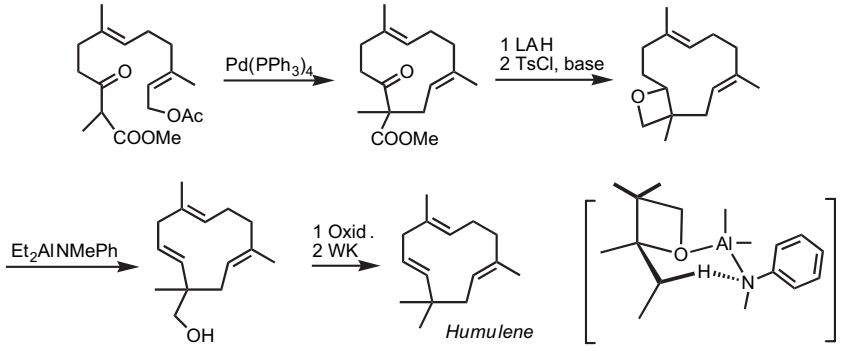
These Lewis acid–Lewis base cooperating systems are not only effective as an intramolecular system. The intermolecular version of the process was developed as follows. Reexamination of Beckmann rearrangement using organoaluminum reagents under aprotic conditions led to the abstraction of the sulfonyl group, followed by capture of the intermediary iminocarbocation or alkylidyneammonium ion with the nucleophilic group (X; R_2AlX (X=H, R, SR′, SeR′)) on the aluminum. Thus, aluminum reagents act not only as a Lewis acid but also as a base.[4] This method opens a new synthetic entry to a variety of alkaloids such as pumiliotoxin C (Scheme 5).[5]



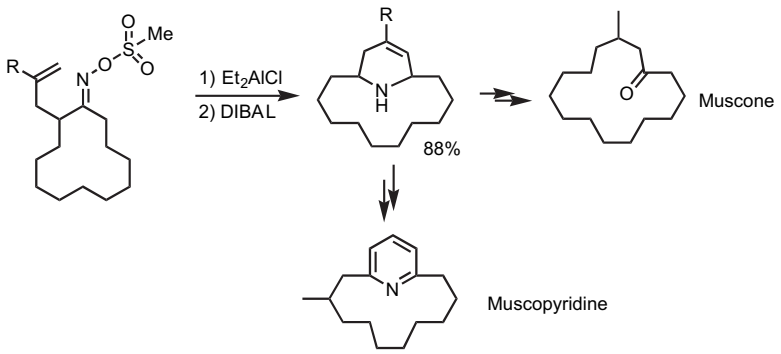
Scheme 5.



Scheme 3.



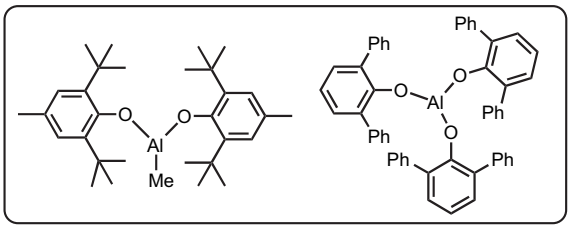
Scheme 4.



Scheme 6.

The intermediary iminocarbocation or alkylidyneammonium ion generated by an organoaluminum can also be trapped intramolecularly with olefinic groups.[6] This interesting rearrangement–cyclization sequence can be extended to an efficient synthesis of muscopyridine (Scheme 6).[7]

3. Bulky aluminum reagents

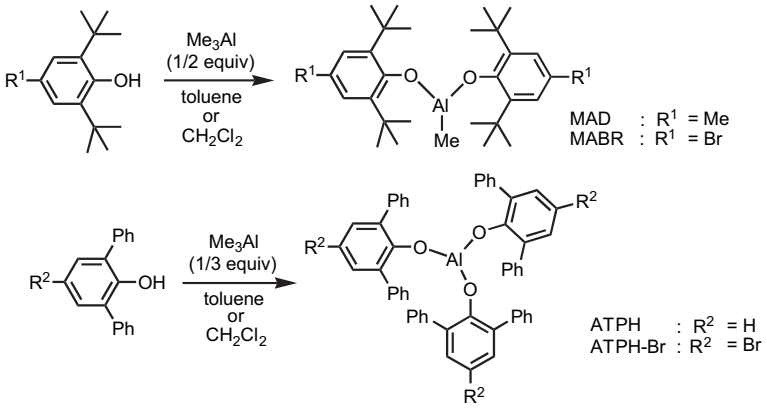


Most aluminum compounds in solution exist as dimeric, trimeric, or higher oligomeric structures. In contrast, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) and aluminum tris(2,6-diphenylphenoxide) (ATPH) are monomeric in organic solvent. Lewis acidity of these reagents decreases with the coordination of more electron-donating aryloxides, but this can be compensated for by loosening of the aggregation. Compared with classical Lewis acids, the significant steric effect of our aluminum reagents plays an important role in selective organic synthesis.[8–10]

These bulky aluminum reagents can be prepared from sterically hindered phenols. Thus, MAD and ATPH are readily prepared by treatment of Me_3Al with a corresponding amount of the phenol in toluene (or in CH_2Cl_2) at room temperature for 0.5–1 h with exclusion of air and moisture. The reactivity of a phenol toward Me_3Al largely depends on the stereochemistry of the phenol (Scheme 7).

The X-ray crystal structure of the *N*,*N*-dimethylformamide–ATPH complex[11] disclosed that three arene rings of ATPH form a propeller-like arrangement around the aluminum center, and hence ATPH has a cavity with C_3 symmetry. In contrast, the X-ray crystal structure of the benzaldehyde–ATPH complex shows that the cavity surrounds the carbonyl substrate upon complexation with slight distortion from C_3 symmetry. A particularly notable structural feature of these aluminum–carbonyl complexes is the Al–O–C angles and Al–O distances, which clarify that the size and shape of the cavity are flexible and change depending on the substrates. According to these models, the cavity should be able to differentiate carbonyl substrates, which when accepted into the cavity should exhibit unprecedented reactivity under the steric and electronic environments of the arene rings (Fig. 1).

Selective 1,6-addition of alkyllithiums to aromatic carbonyl substrates such as benzaldehyde or acetophenone was achieved with ATPH to give functionalized cyclohexadienyl compounds (Scheme 8).[12] According to the molecular structure of the benzaldehyde–ATPH complex, it is obvious that the *para*-position of benzaldehyde is deshielded by the three



Scheme 7.

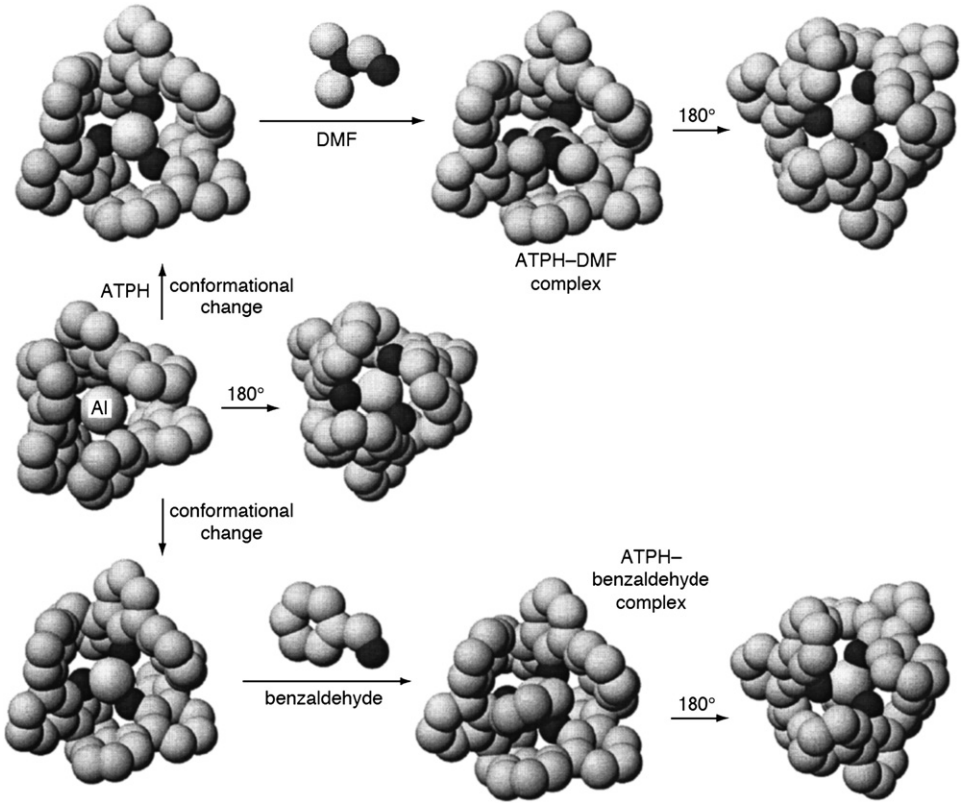
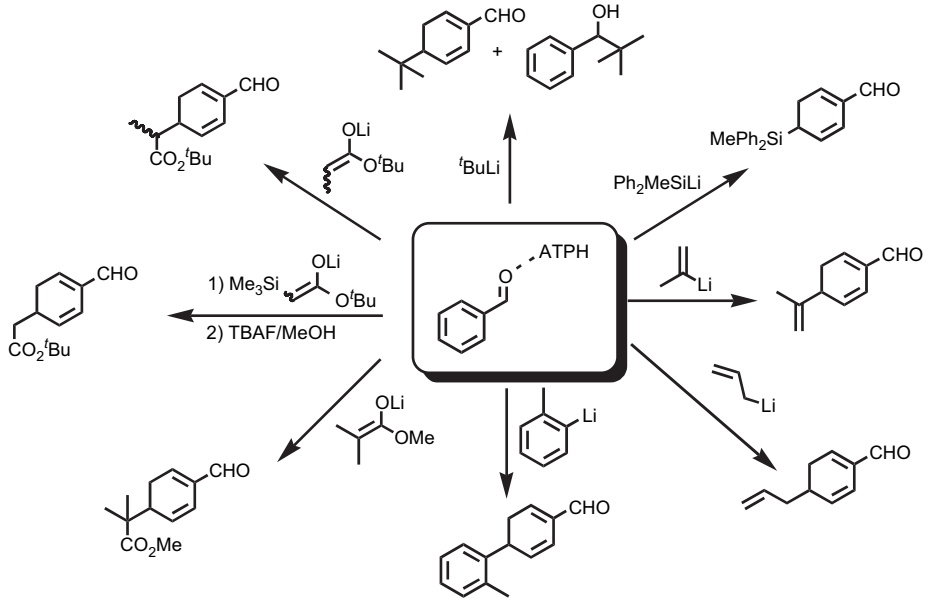


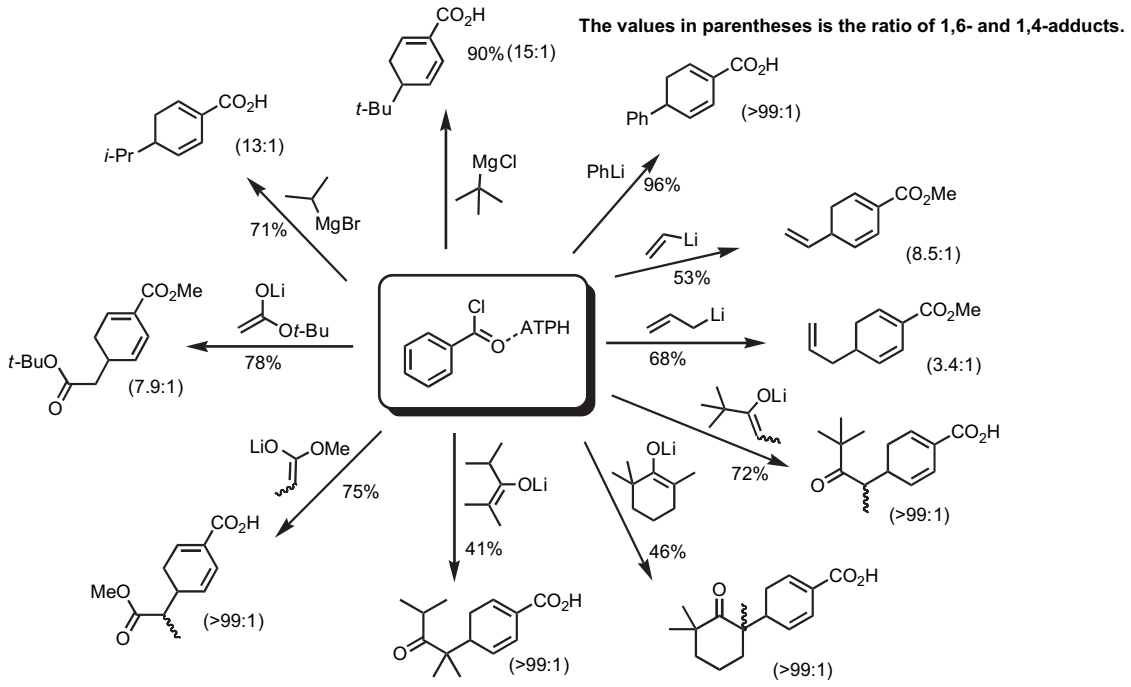
Figure 1.

arene rings, which effectively block the *ortho*-position as well as the carbonyl carbon from nucleophilic attack. Although conjugate addition to the ATPH–PhCHO complex did not proceed effectively with smaller nucleophiles, we were able to illustrate that ATPH–ArCOCl is superior to ATPH–PhCHO for the nucleophilic dearomatic functionalization. Several analytical and spectral data showed that the ATPH–PhCOCl complex was more reactive than ATPH–PhCHO (Scheme 9).[13]

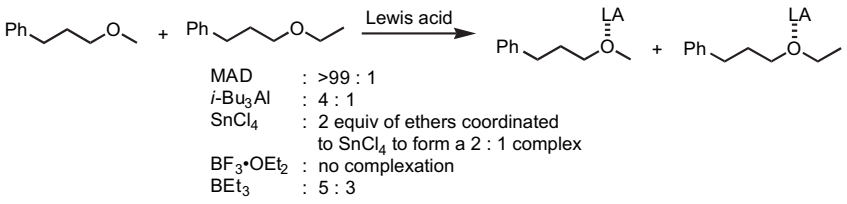
A similar concept was used in a number of different organic transformations, all of which used the selective coordination of Lewis base including carbonyl compounds to ATPH or MAD. Several examples are shown in Schemes 10–19.



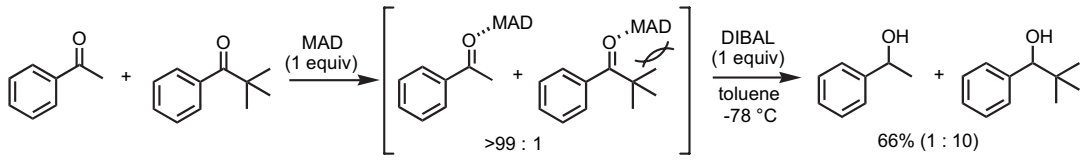
Scheme 8.



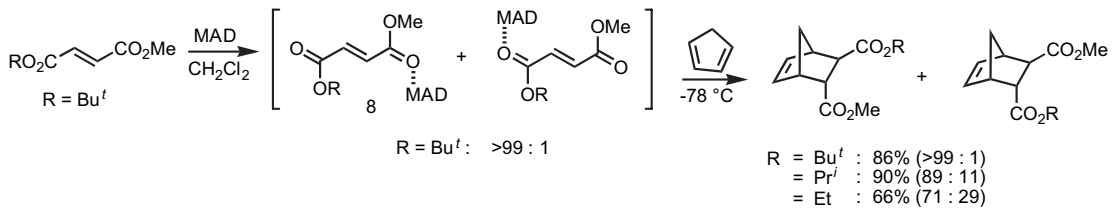
Scheme 9.



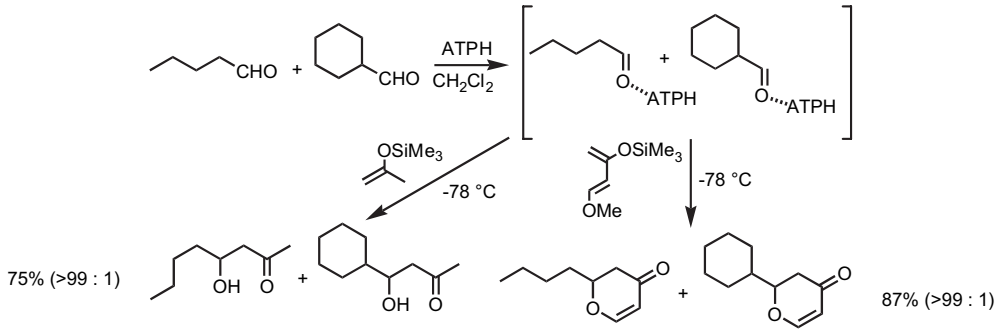
Scheme 10. Discrimination of two different ethers with MAD.[14]



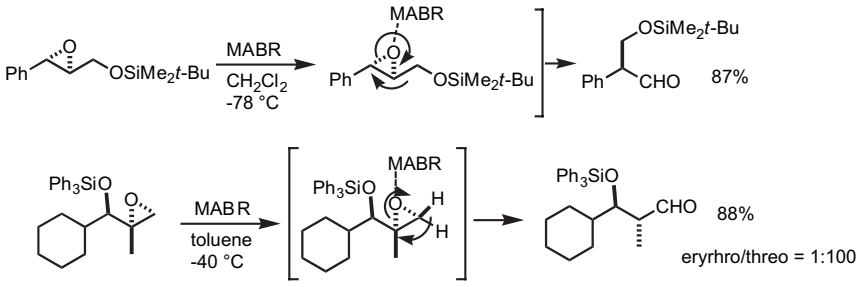
Scheme 11. Discrimination of two different ketones with MAD.[15,16]



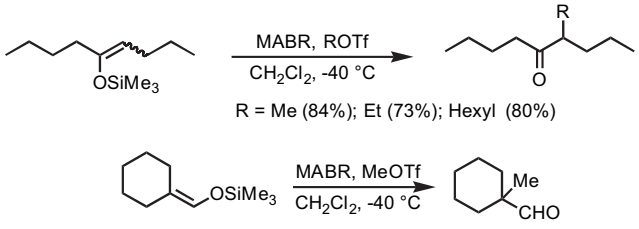
Scheme 12. Discrimination of two different esters with MAD.[17,18]



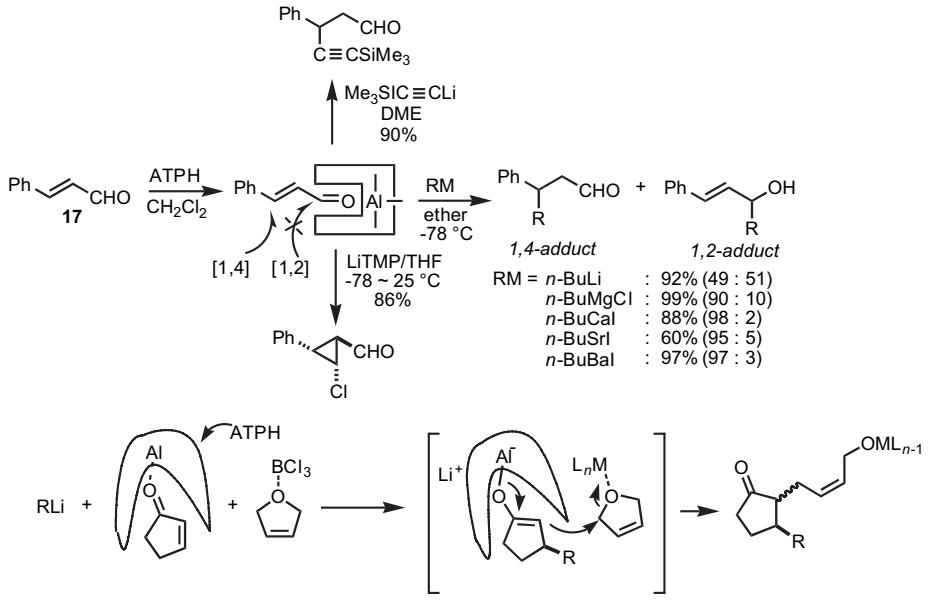
Scheme 13. Discrimination of two different aldehydes with MAPH and ATPH.[19]



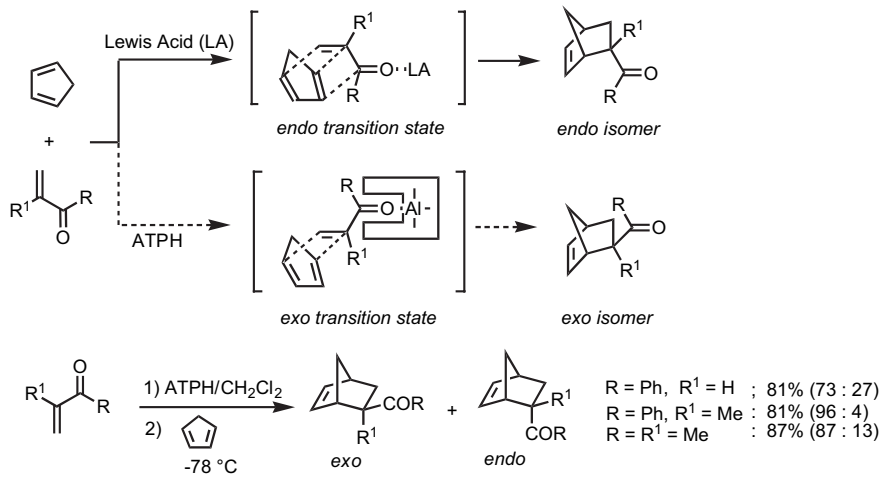
Scheme 14. Stereoselective epoxide rearrangement.[20,21]



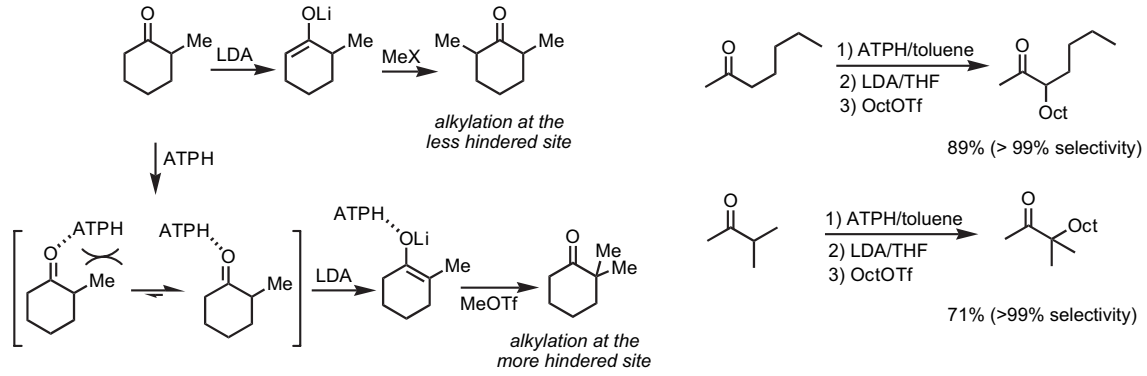
Scheme 15. Primary alkylation of carbonyl compounds.[22]



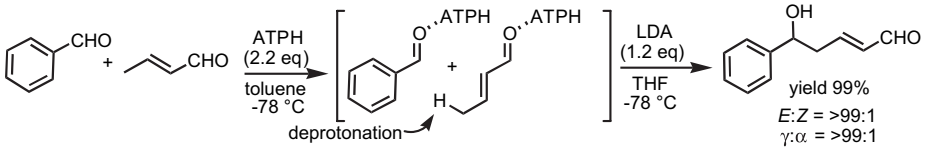
Scheme 16. Conjugate addition to unsaturated carbonyl compounds.[11,23,24]



Scheme 17. *exo*-Selective Diels–Alder reaction.[25]

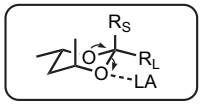


Scheme 18. Selective alkylation at the α-carbon of unsymmetrical ketones.[26]



Scheme 19. New directed aldol condensation between two different carbonyl compounds.[27,28]

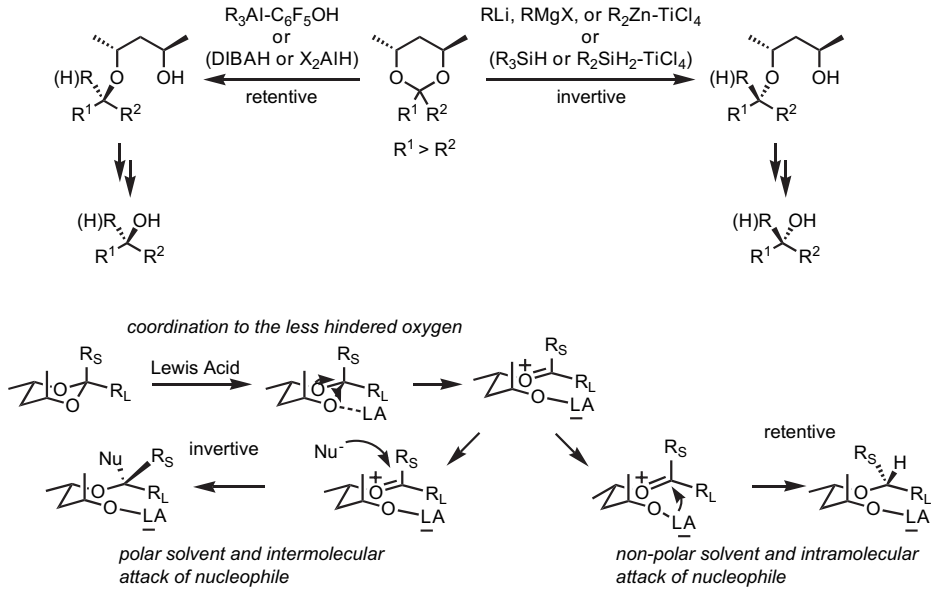
4. Chiral acetal and its application in organic synthesis



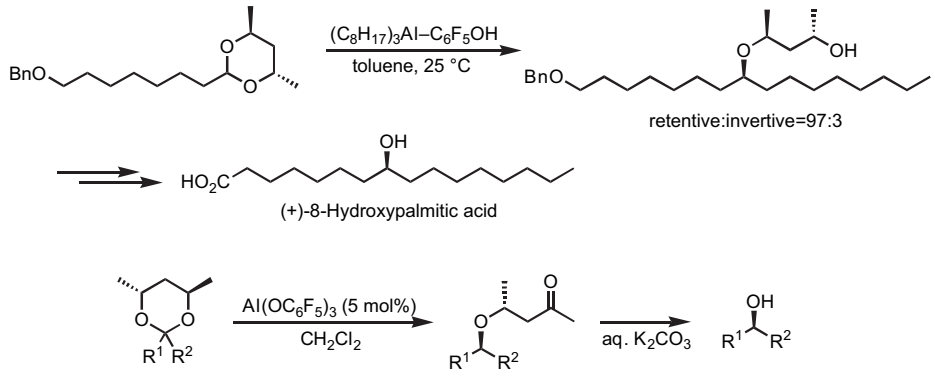
Chiral acetals derived from aldehydes and (2*R*,4*R*)-2,4-pentanediol are cleaved selectively by organoaluminum reagents.[29–33] The reaction proceeds via the retentive-alkylation process with >95% selectivity in most cases. The reaction of acetals derived from (2*R*,4*R*)-2,4-pentanediol and ketones in the presence of a catalytic amount of aluminum pentafluorophenoxide produces reductively cleaved products with high diastereoselectivity. The reaction is a useful means of diastereoselective cleavage of acetals: an intramolecular Meerwein–Ponndorf–Verley reductive and Oppenauer oxidative reaction on an acetal template (Scheme 20).[34]

In sharp contrast, alkylative cleavage of the same chiral acetals using Lewis acid–alkylmetal systems and reductive cleavage of the same acetals using Lewis acid–trialkylsilane or dialkylsilane systems occur inversely.[32,35–38] Examples of this concept in synthesis are shown in Scheme 21.

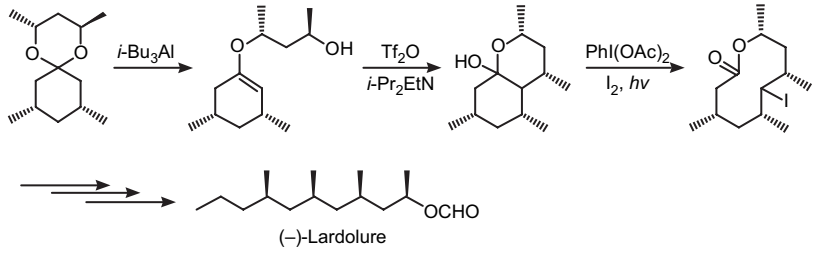
(−)-Lardolure has been synthesized based on this discovery.[39] Thus, the compound was prepared elegantly by intramolecular cyclization of vinyl ether alcohol derived from spiroacetal via triisobutylaluminum and further ring enlargement of the afforded bicyclic hemiacetals. In this simple total synthesis, the entire chirality of the product was transferred from optically active 2,4-pentanediol (Scheme 22).



Scheme 20.

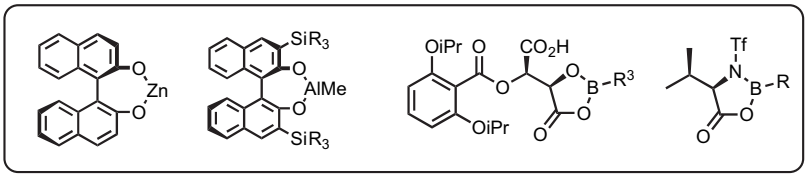


Scheme 21.



Scheme 22.

5. Chiral Lewis acid catalysis



In 1988 an ASI workshop on 'Selectivities in Lewis acid-promoted reactions' was held in Greece, during which I proposed the mechanism of our asymmetric propargylation reaction using chiral allenyl boronic ester.[40] In an enantioface differentiating process, the chiral nucleophile was added to the carbonyl group of aldehydes, thus allowing the preparation of the chiral propargylic alcohols.[41] Based on the *anti*-coplanar complex structure of carbonyl–boron–allene

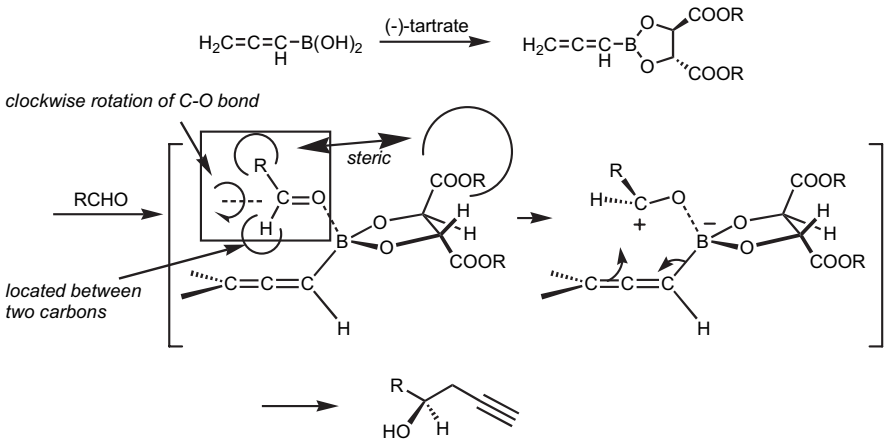
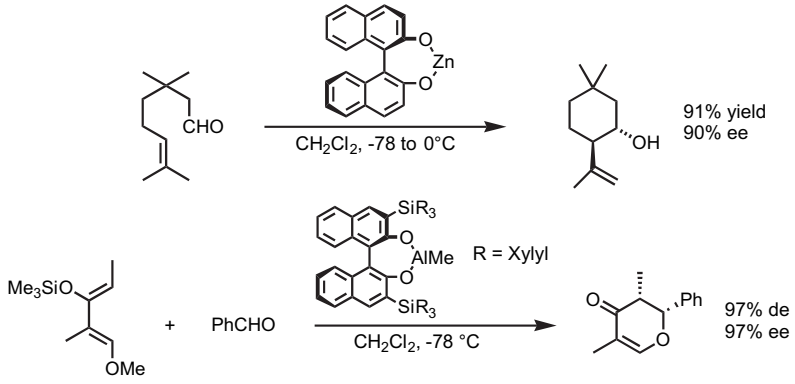


Figure 2. Rotation of C–O bond after coordination of Lewis acid reagent.



Scheme 23.

moieties, we postulated the clockwise rotation of the O–C bond prior to C–C bond formation (Fig. 2).

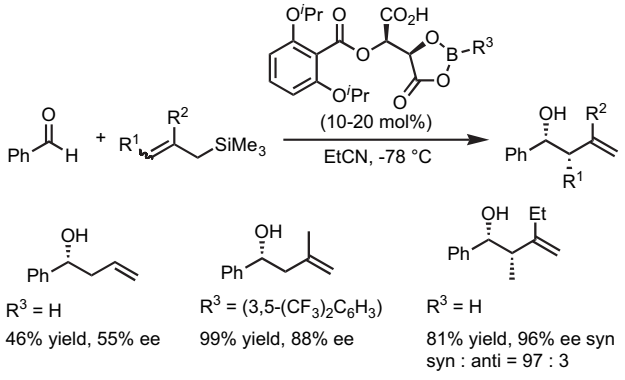
The reaction scheme shown in Figure 2 demonstrates that the symmetry element coordinated on the metal center does have a significant effect on the direction of the C–O rotation and thus on the asymmetric induction of the reaction. Thus, we initiated our projects for development of the chiral Lewis acid catalyst, which has C_n symmetry elements.

On this basis, chiral Lewis acid catalyst, which has the C_2 symmetry element was designed and tested for various asymmetric syntheses. Thus, in 1985 we reported a zinc reagent and in 1988 a bulky aluminum reagent.[42,43] The zinc reagent was used for asymmetric cyclization of unsaturated aldehyde and the aluminum reagent was used for asymmetric hetero-Diels–Alder reaction with Danishefsky diene. Both reagents effectively discriminate the enantioface of aldehydes (Scheme 23).

This work was the forerunner of a vast amount of present-day research on the binaphthol based chiral Lewis acid catalyst. Furthermore, we and other groups have reported various kinds of chiral Lewis acid catalysts, which have C_2 symmetry elements and all of them have proven quite effective for asymmetric carbon–carbon bond forming processes.[27,44] Not only main group metal catalysts but also transition metal catalysts having the C_2 symmetric structure can be used for asymmetric synthesis via selective activation of carbonyls.[45]

The first catalytic enantioselective Sakurai–Hosomi allylation was reported in 1991 by our laboratory (Scheme 24).[46] Allylation of both aromatic and aliphatic aldehydes proceeded smoothly in the presence of 10–20 mol % of chiral (acyloxy)borane (CAB) complex. Unfortunately, simple allyltrimethylsilane was not sufficiently reactive under the conditions used.

In 1996 we reported the second generation of the catalyst, the BINAP–silver catalyst, and the reaction turned out to be highly selective and reliable under mild reaction conditions using allyltributyltin as an allylating reagent. BINAP–AgOTf is an excellent catalyst for the catalytic enantioselective allylation, methallylation, *anti*-selective



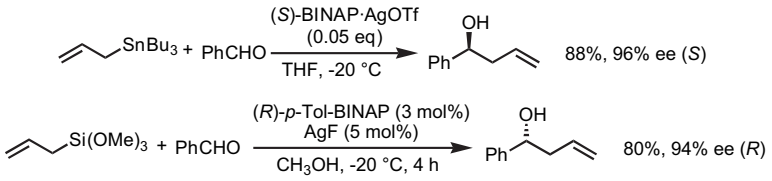
Scheme 24.

crotylation, pentadienylation, and aldol reaction using corresponding allyltributyltin reagents (Scheme 25).[47] Subsequently, we have reported enantioselective addition of allylic trimethoxysilanes to aldehydes catalyzed by BINAP–AgF system (Scheme 25).[45] It should be noted that, when BINAP–AgOTf complex was used as a catalyst, a racemic homoallylic alcohol was obtained in only 5% yield. Both systems gave higher reactivity and enantioselectivity compared with the other previously reported Lewis acid-catalyzed methods using allyltributyltin.

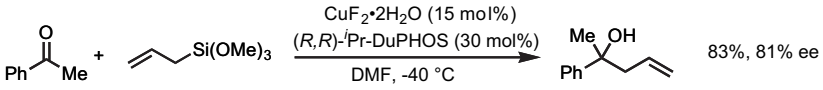
In 2002 Shibasaki developed the general catalytic allylation of ketones using allyltrimethoxysilane catalyzed by CuCl–TBAT (Scheme 26).[48,49] This is the first catalytic enantioselective Sakurai–Hosomi allylation of acetophenone. Although the observed enantioselectivity was relatively low, it was improved to 81% ee by choosing the ligand of DuPHOS under the proper reaction conditions.

Our AgF system also gave us good selectivity after careful examination of reaction conditions, especially catalyst study. We earlier stated that more than three complexes exist between silver and diphosphine (Fig. 3). According to these studies, different reactivities and selectivities were given by different complexes and it is important to generate *a single silver complex* to achieve a high stereoselective reaction; the ^{31}P NMR of (a 1:1 mixtures of AgF and ligand) revealed that (*R*)-DIFLUORPHOS gave predominantly 1:1 complex **A**, presumably due to the poor electron-donating ability of the phosphorus atoms. With this catalyst in hand, we observed 86% ee with acetophonone using 2 mol % of catalyst.[50]

This catalyst system can be applied to various simple ketones and corresponding tertiary homoallylic alcohols were obtained with excellent enantioselectivities (up to 96% ee) (Scheme 27).



Scheme 25.



Scheme 26.

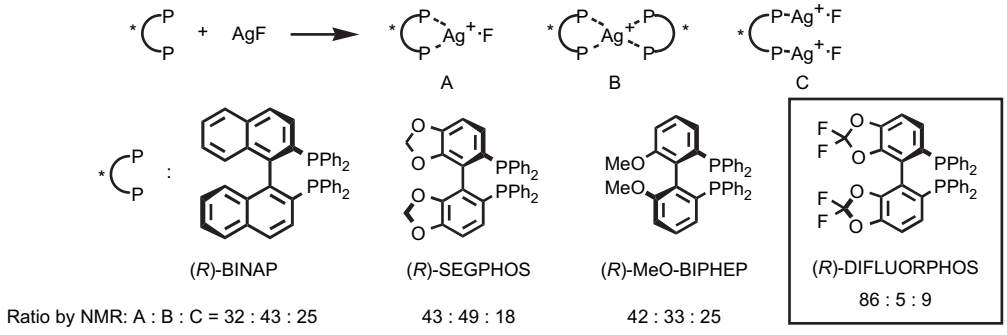
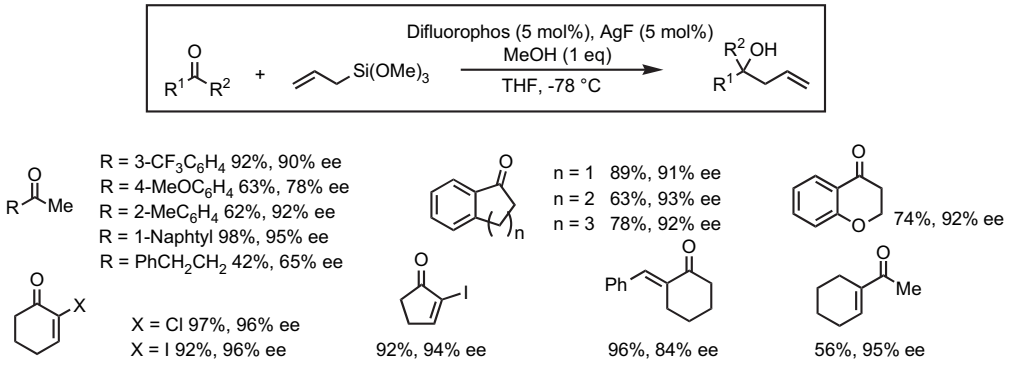
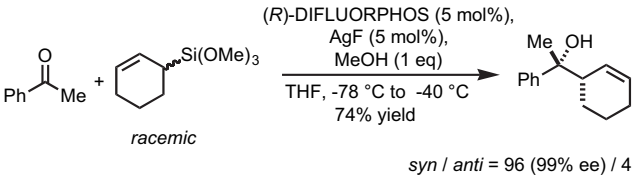


Figure 3. BINAP–Ag complex.



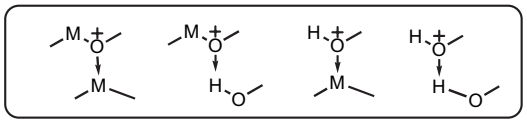
Scheme 27.

Even more interestingly, the regio-, diastereo- and enantioselective crotylation has been achieved. *E*- or *Z*-crotyltrimethoxysilane gave a similar diastereomer ratio with high enantioselectivities. This finding introduces the utility of racemic allylsilanes for the enantioselective Sakurai–Hosomi allylation reaction,[50] which is an additional example of dynamic kinetic asymmetric transformation (DYKAT) of palladium proposed by Trost but a version with a different nucleophilic addition (Scheme 28).[51]



Scheme 28.

6. Combined acid catalysis



In 1988 we reported a chiral Lewis acid catalyst of an acyloxyboron with a tartaric acid ligand.[52] This was the first chiral Lewis acid catalyst for aldol, ene, and Diels–Alder reactions. The high reactivity of the tartaric acid derived catalyst may originate from intramolecular hydrogen bonding of the terminal carboxylic acid to the alkoxy oxygen (Fig. 4).

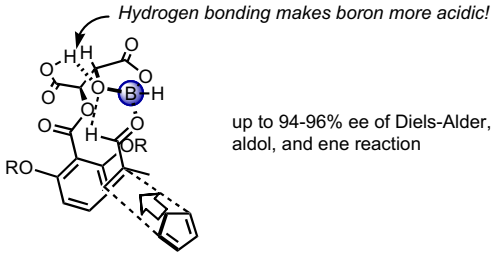
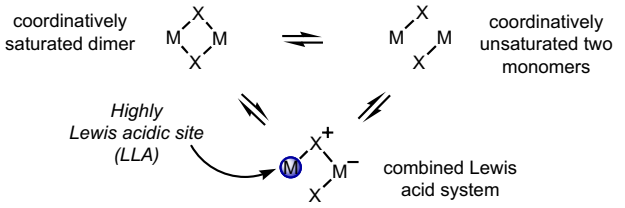


Figure 4.

This was our first example of the 'combined acids system'.[53] It is known that coordinatively unsaturated monomers are far more Lewis acidic than doubly bridged coordinatively saturated dimers.[54] A mono-coordinated complex, however, can generate and is even more Lewis acidic than the monomer through the formation of a singly bridged dimer. This species is the combined acid catalyst (Scheme 29).



Scheme 29. Association of Lewis acid (LM).

It should be emphasized that we anticipated a more or less intramolecular assembly of such combined systems rather than intermolecular arrangements. Thus, proper design of the catalyst structure is essential for success. The concept of combined acids, which can be classified into Brønsted acid-assisted Lewis acid (BLA), Lewis acid-assisted Lewis acid (LLA), Lewis acid-assisted Brønsted acid (LBA), and Brønsted acid-assisted Brønsted acid (BBA), can be a useful tool for designing asymmetric catalysis, because combining such acids will bring out their inherent reactivity by associative interaction and also provide a more organized structure, both of which allow the securing of an effective asymmetric environment (Fig. 5).

BLA: in addition to Figure 4, Figure 6 exemplifies another boron based BLAs, which achieve high selectivity through the double effect of intramolecular hydrogen bonding interaction and attractive π–π donor–acceptor interaction in the transition state.[55]

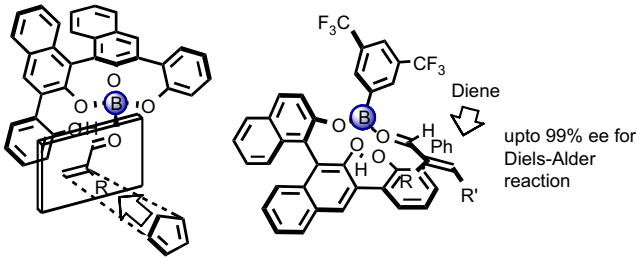


Figure 6. BLA for Diels–Alder reaction.

LLA: reactive Lewis acid-assisted Lewis acid (LLA) catalysts are relatively well known. Electron-deficient metal compounds can be further activated as electrophiles through hetero- and homodimeric associative interactions. However, full recognition of this synthetically powerful tool does not yet

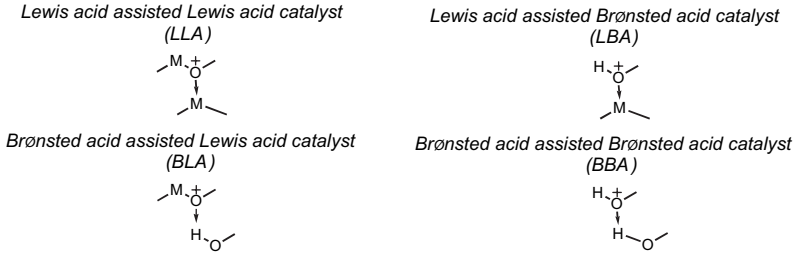
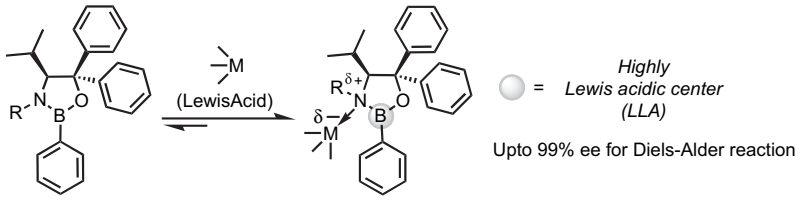
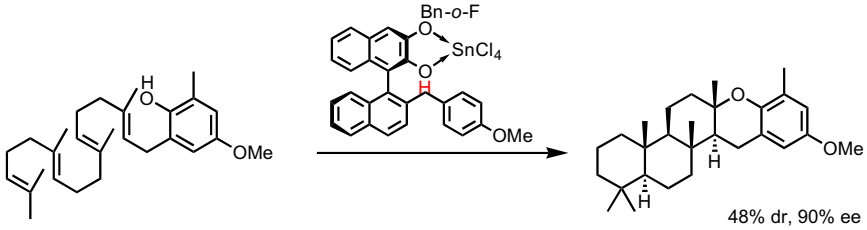


Figure 5. Combined acid catalyst.



Scheme 30.



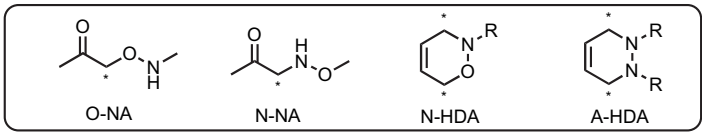
Scheme 31.

appear to be widespread. It may be further extended to include asymmetric catalysis design. Shown in Scheme 30 is an example of LLA of chiral boron reagent activated by various achiral Lewis acids including $SnCl_4$, $AlCl_3$, $FeCl_3$, and others.[56]

LBA: combining Lewis acids and Brønsted acids to give Lewis acid-assisted Brønsted acid (LBA) catalysts can provide an opportunity to design a unique chiral proton.[56] Namely, the coordination of a Lewis acid to the hetero atom of the Brønsted acid could significantly increase its original acidity (Scheme 31).[57]

BBA: hydrogen bonding can frequently be observed inside enzymes, and such a weak interaction has a crucial role in organizing their three dimensional structure. Additionally, the hydrogen bonding is often involved in the reaction inside the active site of an enzyme. Such an elegant device could be applicable to asymmetric catalysis. Especially for Brønsted acid catalysis, the design of these catalysts would result not only in formation of a highly organized chiral cavity but also in an increase in the Brønsted acidity of the terminal proton in a much milder way than that of the LBA system. We will discuss more details in the next section.[58]

7. Nitroso chemistry

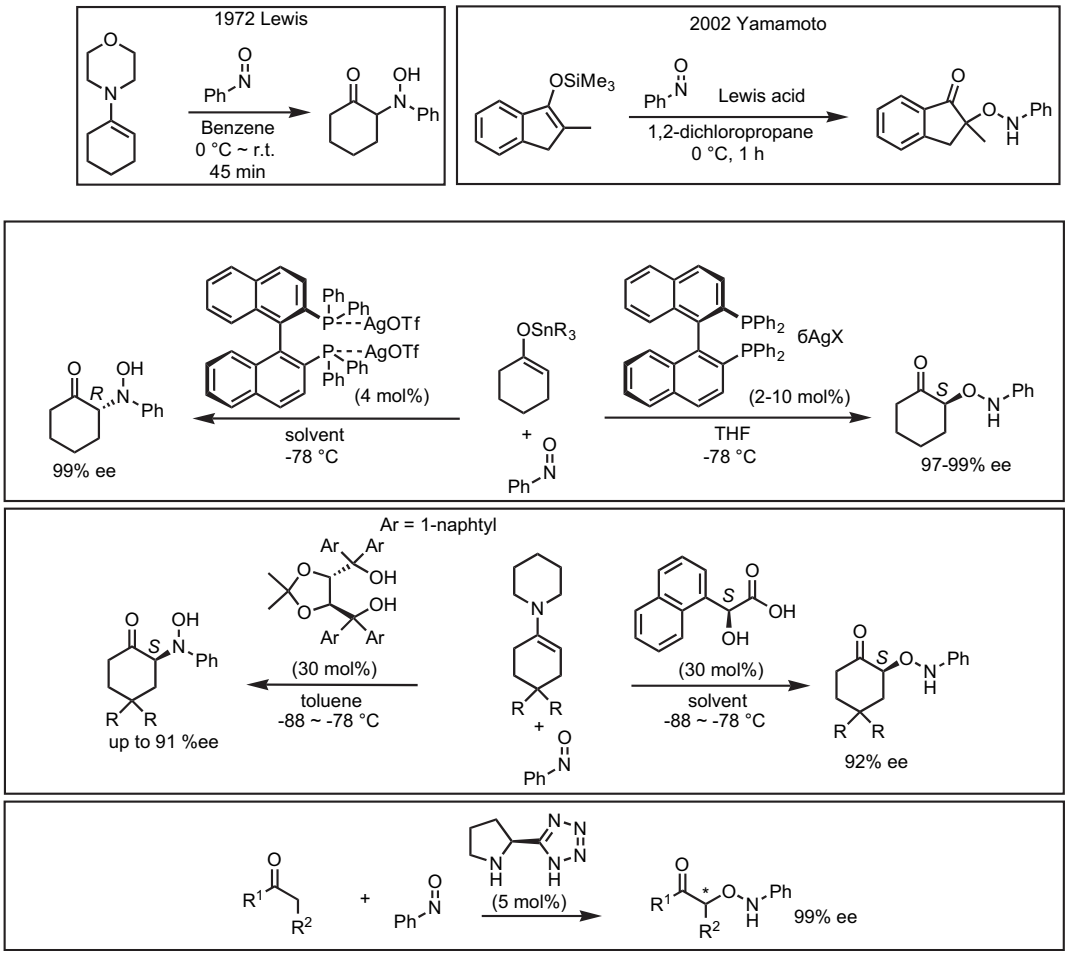


Recently, we discovered nitroso aldol (NA) reaction.[59] NA reaction is the reaction between carbonyl compound and nitroso derivative to generate either α-hydroxyamino ketone [*N*-NA)[60] or α-aminoxy ketone (*O*-NA), depending on the proper catalyst and reaction conditions. *N*-NA reaction has a lengthy history having been discovered by Lewis in 1972 using an enamine with nitrosobenzene.[61] Since hydroxyamino ketones can be dehydrated under acidic or basic conditions to generate imines or ketones, this addition–elimination process was reported even earlier.[62] The *O*-NA reaction, in contrast, has been discovered by us quite recently.[59] An asymmetric version of both *N*- and *O*-NA reactions has been accomplished either by metal or Brønsted acid (Scheme 32).[58,63–65]

Immediately after our reports, a succession of publications appeared on this very unique and important reaction. We recently published a review on this[66] and highlights have appeared by others.[67] Our review has been one of the most cited papers in Chemical Communications over the last year.

Almost simultaneously, catalytic asymmetric nitroso hetero-Diels–Alder (HDA) reaction was developed.[68,69] Nitroso HDA is a powerful process in organic synthesis because of the concurrent introduction of nitrogen, oxygen, and olefinic functional groups into an organic molecule in a single step. Asymmetric catalytic nitroso HDA has long been a dream of organic chemists because of the efficient creation of these chiral centers in a molecule. Our basic concept was based on the use of a pyridine moiety to aid in the coordination of the metal catalyst. This simple idea worked beautifully and we achieved the first true catalytic and asymmetric version of this useful transformation (Scheme 33). Recently we published a review article of these new HDA reactions, which has been recognized as one of the most frequently cited reviews of the journal in which it appeared.[70]

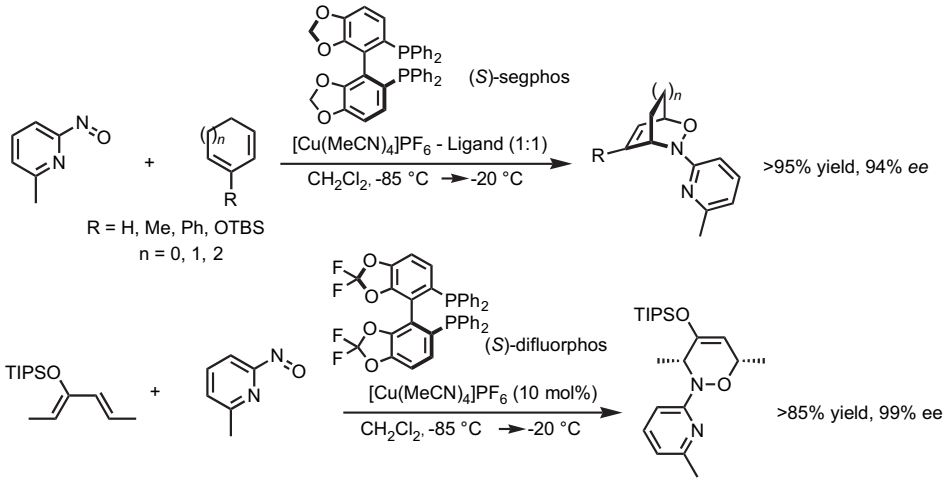
Immediately after these findings, we found that the organic catalyst system was also applicable to this HDA transformation.[71] Thus, starting from α,β-unsaturated carbonyl compound, either *O*- or *N*-NA reaction followed by the Michael addition sequence gave us a new heterocyclic product with virtually complete enantioselectivities. Although there are



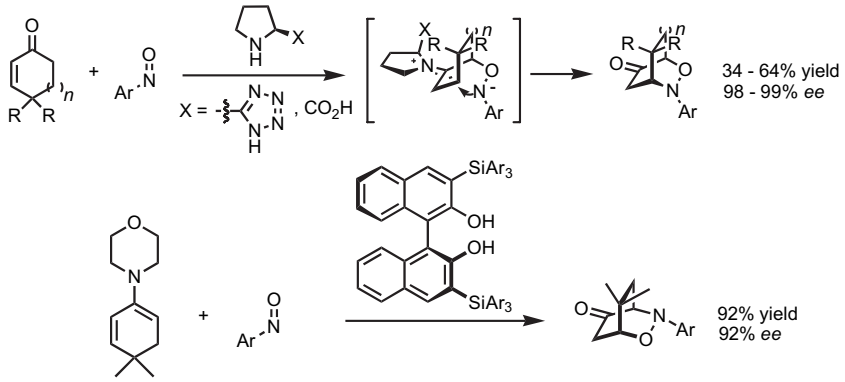
Scheme 32.

two possibilities for this transformation, *N*-NA and Michael or *O*-NA and Michael, we were able to establish the proper choice of catalyst to accomplish these two reactions selectively (Scheme 34).[72] While this transformation can be applied not only to unsaturated carbonyl compounds but not to simple 1,3-dienes, the utility of the method is quite broad.

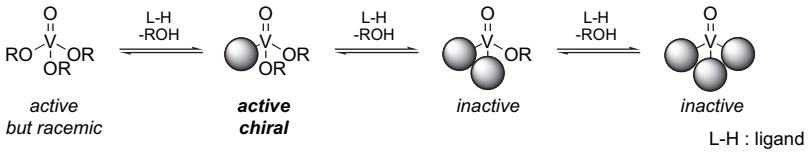
It should be noted that both of the above transformations (NA and HDA reactions) produced nitrogen–oxygen bond. This bond was cleaved efficiently and selectively after the reaction,[73] and nitrogen and oxygen were appropriately protected for the subsequent chemical transformations.



Scheme 33.

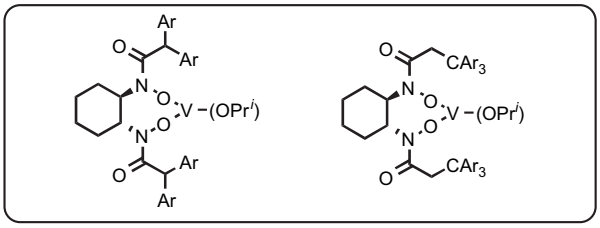


Scheme 34.



Scheme 35.

8. Asymmetric epoxidation of allylic and homoallylic alcohols



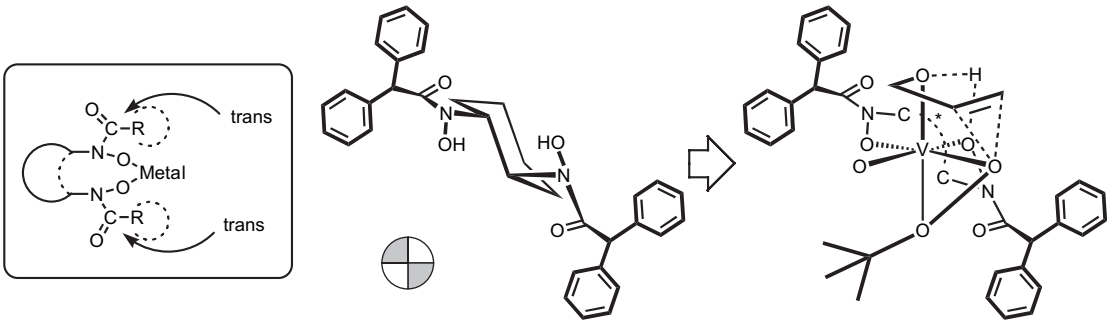
The asymmetric oxidation of olefins is a subject of intensive research in organic synthesis. The Sharpless asymmetric epoxidation protocol of allylic alcohol has proven to be an extremely useful means of synthesizing enantiomerically enriched epoxy alcohols. The huge contribution by Sharpless has long been justifiably recognized.[74] Thus, his titanium reagent was reported in 1980 and since then has had an enormous influence on modern organic synthesis. Although this is an excellent reaction, it should be renovated significantly in this century to fulfill the following conditions: (1) ligand design to achieve high enantioselectivity even for *Z*-olefins, (2) less than 1 mol % catalyst loading, (3) reaction conditions at 0 °C or room temperature for less time, (4) use of readily available and safe aqueous TBHP or CHP as an achiral oxidant instead of anhydrous TBHP, and (5) easy work-up procedure especially for small allylic alcohols.

In fact, because of these limitations Sharpless oxidation has not been applied on an industrial scale. In comparison with the well-known titanium catalysts, only a few examples of chiral vanadium catalysts for the epoxidation have been reported to date. As described earlier, we have applied vanadium-catalyzed epoxidation as the key step for selective synthesis of juvenile hormone, and we believe that vanadium is the catalyst of choice for stereoselective epoxidation of allylic alcohols. However, there is one important remaining issue to be solved before this excellent reagent will be a useful catalytic asymmetric tool. Since, during the course of oxidation, both vanadium(IV) and (V) are thought to exist as an oxovanadium(V) complex that has three alkoxy groups for substrate, hydroperoxides, and ligands, ligand design of chiral vanadium catalysts has never been successfully established to control such a complexation mode as proposed by Sharpless. In other words, if 1 equiv of ligand were added, the background epoxidation would be rather significant, and if a large excess ligand were used, the reaction would stop. This well-known 'ligand deceleration effect' should be resolved before this is made a true catalytic asymmetric process (Scheme 35).

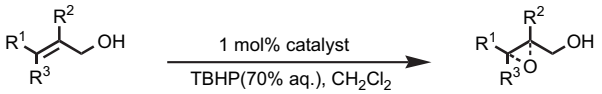
Our bishydroxamic acid catalyst system satisfies some of these conditions (Scheme 36).[75] This ligand is a bidentate ligand, which coordinates to vanadium rather strongly to prevent further coordination from the second hydroxamic acid ligand. In other words, the attachment of additional ligands to vanadium will be sterically restricted and doubly or triply coordinated species, which are believed to be inactive and to cause the ligand deceleration, should not be made problematic by this bishydroxamic acid ligand. Furthermore, the amide carbonyl oxygens are forced to direct toward the cyclohexane ring for steric reasons and the trans-geometry of hydroxamic acid, thus generated, will give us a more acidic metal center. In fact, careful molecular dynamic calculation shows that there is only a very little contribution of cis conformer of hydroxamic amides. Overall, the vanadium catalyst should create a pseudo C_2 symmetric structure as shown in Scheme 36.

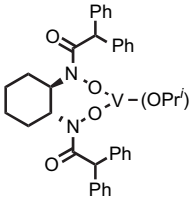
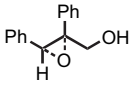
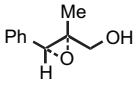
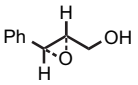
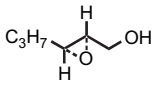
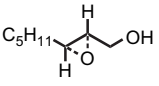
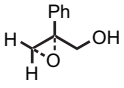
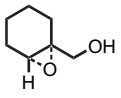
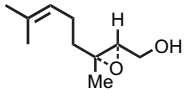
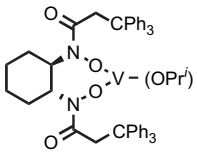
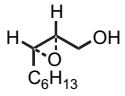
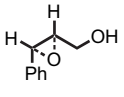
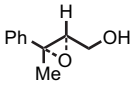
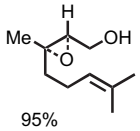
Using this system, we succeeded in asymmetric epoxidation of various allylic alcohols including cis and small allylic alcohols with high asymmetric inductions (Scheme 37). The reaction conditions are fairly robust and scalable.

Obviously, the success of the reaction comes from the design of a C_2-symmetric bishydroxamic acid ligand, which cleanly solves the ligand deceleration problems associated with previous vanadium-catalyzed systems. We recently accomplished the asymmetric epoxidation of homoallylic alcohols (Scheme 38), and these results can serve as a new and

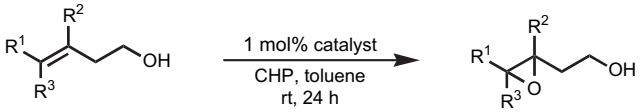


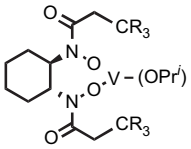
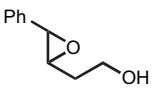
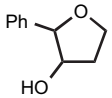
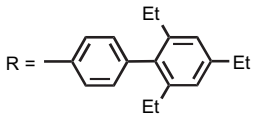
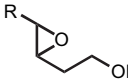
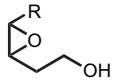
Scheme 36.



catalyst	ee (temp.(°C); t(h); yield(%))			
	 97% (-20; 48; 91)	 97% (-20; 48; 84)	 97% (-20; 60; 53)	 95% (-20; 72; 56)
	 95% (-20; 72; 51)	 95% (0; 48; 73)	 95% (-20; 48; 79)	 95% (-20; 48; 68)
	 95% (0; 72; 60)	 97% (-20; 120; 24)	 96% (-20; 48; 64)	 95% (-20; 48; 62)

Scheme 37.

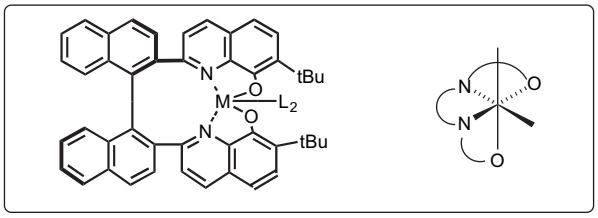


catalyst	% ee, Isolated % yield	
	 96% ee, 90%	 99% ee, 85%
	 $R=C_2H_5$ (93% ee, 85%) $R=C_5H_{11}$ (96% ee, 89%) $R=C_6H_{13}$ (98% ee, 92%)	 $R=C_2H_5$ (95% ee, 92%) $R=C_3H_7$ (97% ee, 90%) $R=C_4H_9$ (99% ee, 91%) $R=C_5H_{11}$ (99% ee, 90%)

Scheme 38.

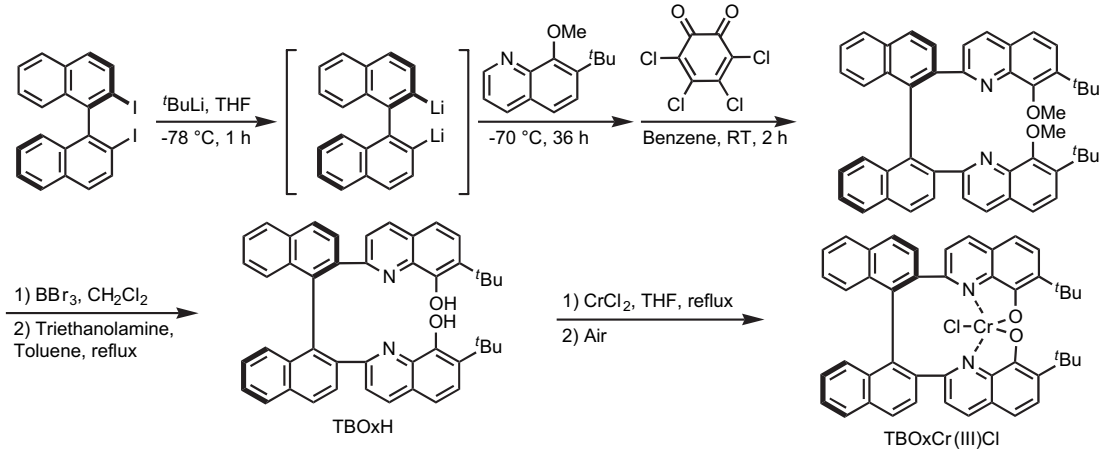
general tool for asymmetric oxidation in modern organic syntheses.[76]

9. 8-Hydroxyquinolino ligands as a cis-β configuration of metal catalyst

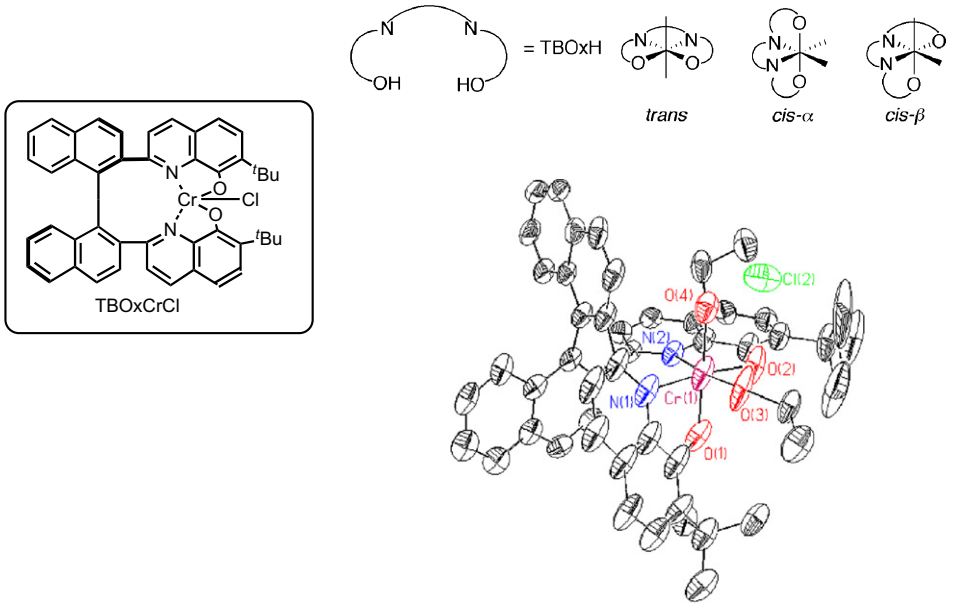


8-Hydroxyquinoline is a versatile ligand for metal ions. The derivatives of this heterocyclic system have been extensively studied from the viewpoint of analytical chemistry since 1926 and it is now widely used as one of the most reliable analytical tools of trace amount of metal ions by absorption spectrometric and fluorometric methods. In fact, 8-hydroxyquinoline (8-quinolinol) and its derivatives form stable metal complexes with almost all of the metal ions including Al, Be, Cu, Ce, Ca, Ga, In, Y, Fe, M, Mn, Mo, Sc, Sn, W, U, V, Nb, Ti, and Zr. We plan to make chiral ligand using this important heterocycles. The design of the ligand is quite simple: the two 8-hydroxyquinole is tethered with chiral binaphthyl moiety. Synthesis of a new chiral tethered bis(8-quinolinolato) (TBOxH) and its transformation to the chromium catalyst are shown in Scheme 39.[77]

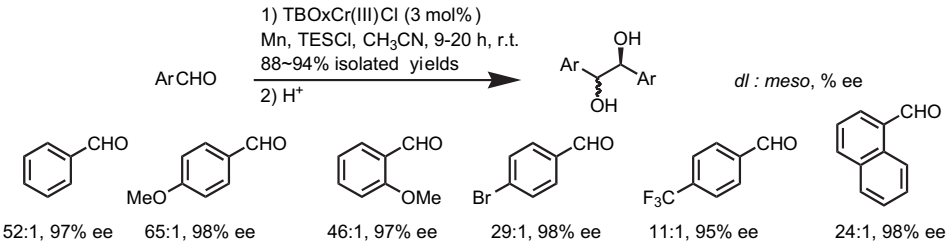
TBOxM may have a total of three geometric isomers, given that it adapts octahedral coordination. The X-ray structure of TBOxCrCl revealed that TBOxH ligand is bound to the metal center in a cis-β configuration (Scheme 40). A crystal structure of TBOxCrCl provided valuable information to begin our investigation based on this ligand system, since these metal complexes have all the necessary features of rigid cis-β-configuration to redeem the previously well-developed metal catalysts based on salen type ligands.



Scheme 39.



Scheme 40.



Scheme 41.

9.1. Catalytic asymmetric pinacol coupling reaction

Chiral 1,2-diols are structural motifs often found in various important natural products and have also proven valuable as chiral ligands and auxiliaries in stereoselective organic syntheses. Arguably, the most direct method to prepare 1,2-diols is a reductive coupling of simple aldehydes. However, the identification of a catalytic asymmetric pinacol coupling reaction has remained a challenge for organic chemistry since not only enantioselectivity but also diastereoselectivity (DL vs. *meso*) need to be controlled in a single bond-forming event. Thus, high stereoselectivity in pinacol coupling reaction has remained elusive even through stoichiometric protocols. Our new chiral tethered bis(8-quinolinolato) (TBOx) chromium catalyst offered an excellent solution to this challenging problem: the precatalyst (TBOx-Cr(III)Cl), co-reducing agent (Mn), the product scavenger (TESCl), and aldehyde were mixed in CH_3CN under an atmosphere of Ar at room temperature.[78] The isolated crude silyl ethers were treated with aqueous HCl in THF to afford diols in high yields and excellent enantio- and diastereoselectivities (Scheme 41).[77]

9.2. Catalytic asymmetric Nozaki–Hiyama allylation reaction

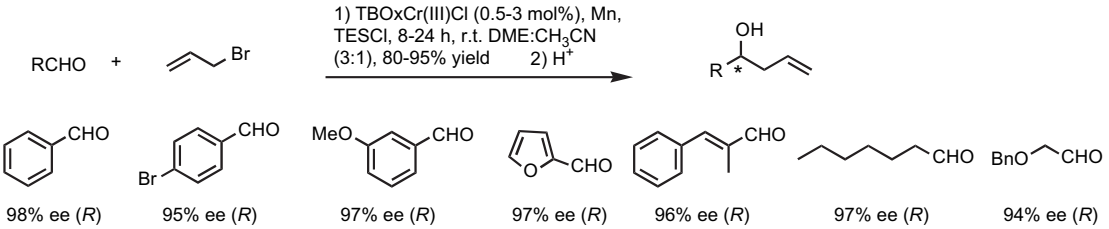
The addition of organochromium compounds to aldehydes, known as the Nozaki–Hiyama (NH) reaction,[79] has proven to be a powerful C–C bond formation method by virtue of its high chemo- and stereoselectivity and ease of the reaction under mild conditions. Catalytic asymmetric NH methodologies have been recognized as important and effective methods as environmentally friendly processes for the synthesis of chiral homoallylic alcohols.[80] Although there have been a limited number of reports on asymmetric catalysis of these reactions, the enantioselectivities, yields, and the scope of the substrates were not satisfactory. After carefully optimizing the experimental parameters, an easy reaction procedure was established for the NH allylation reaction of different aldehydes to afford homoallylic alcohols in good yields and good enantioselectivities (Scheme 42).[81] The catalyst loading could be decreased to 0.5 mol % while maintaining good yields and enantioselectivities.

9.3. Catalytic asymmetric allenylation reaction

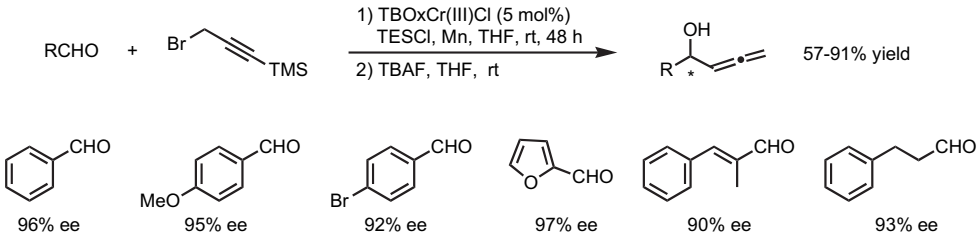
The allenylation reactions between aldehydes and propargylic halides catalyzed by chromium complexes are known to be very useful due to excellent chemoselectivity, broad compatibility with different functional groups, and an environmentally benign process. Only a very limited number of catalytic asymmetric allenylations have been reported. However, there are still some difficulties in terms of: (1) the enantioselectivities of α-allenic alcohols, (2) scope of substrates, and (3) the ease of operation with commercially available reagents. Our successful catalytic redox system was further applied to the asymmetric allenylation reaction between aldehydes and commercially available 1-trimethylsilyl-3-bromopropyne.[82] Under the optimized reaction conditions, a very wide scope of aldehydes were successfully allenylated in moderate to high yields with excellent enantioselectivities (Scheme 43). The aromatic aldehydes with either electron-donating or electron-withdrawing groups gave excellent enantioselectivities. Furthermore, bulky aryl aldehydes, heterocyclic aldehyde, α,β-unsaturated aldehyde, and aliphatic aldehydes proved to be good substrates for this method.

The allenylation reactions of aldehydes with terminally alkyl substituted propargylic bromide, which had never succeeded with high enantioselectivities by Cr-catalyzed asymmetric allenylation reactions, were also examined under the optimized reaction conditions and the results were excellent (Scheme 44).[82]

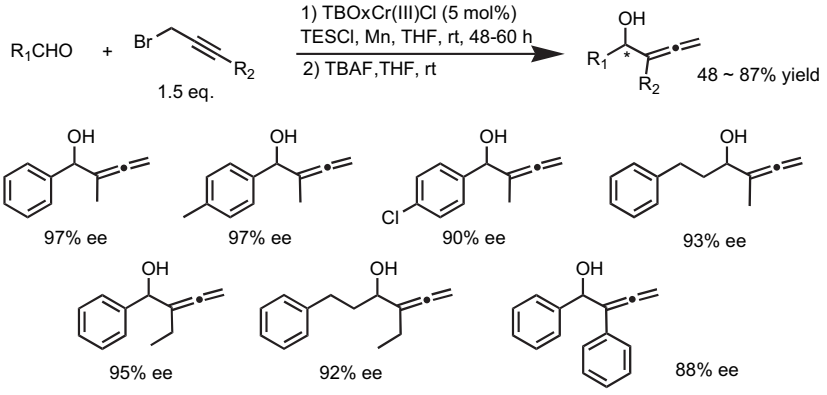
These three major contributions originated from our chiral ligand under redox conditions. However, we also found that the same chiral ligand is able to provide a unique and



Scheme 42.



Scheme 43.

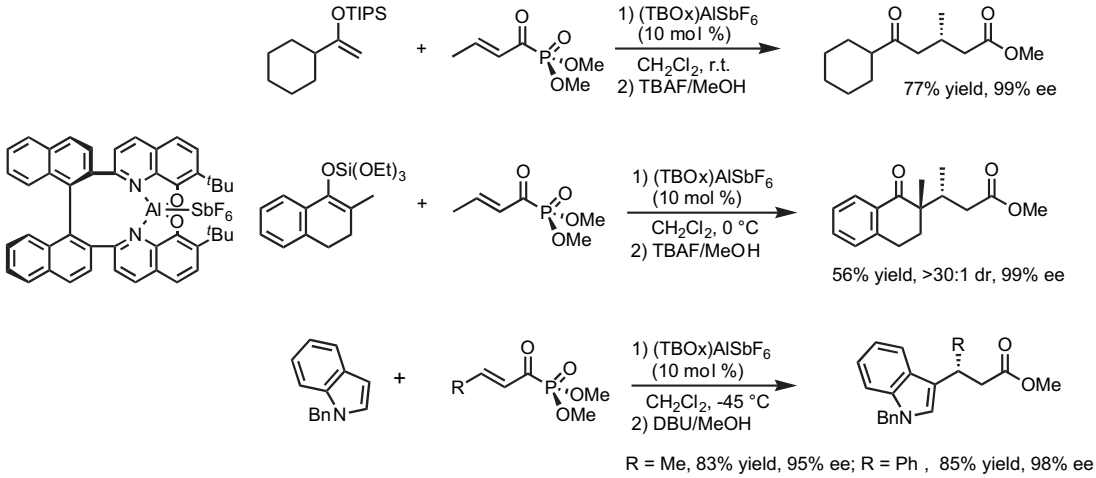


Scheme 44.

useful opportunity for generating new Lewis acid catalysts. Although we have authored a number of reports on various metal aryloxides including MAD and ATPH reagents, it was rather difficult to make them chiral. Our new chiral ligand gave us a simple solution to this long-standing issue. Thus, treatment of the ligand with alkylaluminum gave us quantitative conversion to the chiral aluminum aryloxides, which are excellent chiral Lewis acid catalysts and from which various asymmetric transformations are possible as shown in Scheme 45.

9.4. Asymmetric Mukaiyama–Michael addition reaction

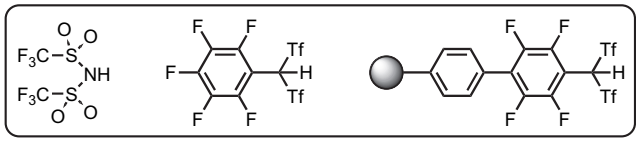
The Lewis acid-promoted conjugate addition of silylketene acetals and silyl enol ethers to α,β-unsaturated carbonyl derivatives, the Mukaiyama–Michael (MM) reaction, is an attractive alternative to the conventional metalloenolate process due to its mild reaction condition and frequently superior regioselection.[83] Catalytic asymmetric variants of this process have received extensive attention and continue to be powerful carbon–carbon bond forming reactions since these methods provide synthetically useful enantioenriched 1,5-dicarbonyl synthons. Whereas various catalysts developed for the MM reaction have centered on the use of silylketene acetals, silyl enol ethers have received relatively little attention in the context of asymmetric catalysis. This deficiency in the aforementioned reaction may arise, in part, from the decreased nucleophilicity of silyl enol ethers in comparison to that of silylketene acetals. It was found that a new chiral tethered bis(8-quinolinolato) (TBOx)



Scheme 45.

aluminum(III) complex effectively catalyzed the highly enantioselective MM reaction of silyl enol ethers, including tetrasubstituted enolates that provided access to enantiomerically enriched all-carbon quaternary centers, one of the most difficult problems for asymmetric synthesis (Scheme 45).[84]

10. Brønsted acid as a new tool for asymmetric synthesis



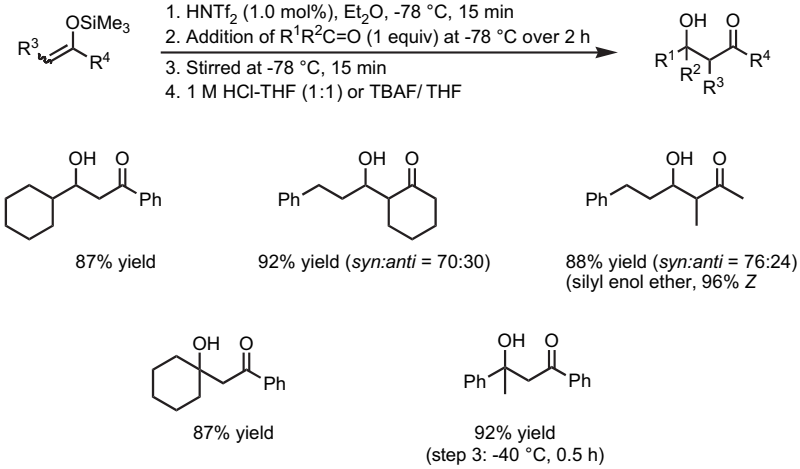
Brønsted acid stronger than 100% sulfuric acid is called super Brønsted acid by Gillespie.[85] High utility of these reagents has been demonstrated by simple Mukaiyama aldol reaction as shown in Scheme 46.[86]

Although the real catalyst in this scheme is not Brønsted acid but Me_3SiNTf_2, the high reactivity of this acid catalyst came from the high reactivity of Tf_2NH.[87] The trifluoromethanesulfonyl (triflyl, Tf) group is one of the strongest neutral electron-withdrawing groups. In particular, it greatly increases the acidity of hydrogen atoms at α-positions. The steric and electronic factors of the aromatic ring on arylbis(triflyl)methanes are expected to greatly influence their Brønsted acidity and their catalytic activity and selectivity for organic reactions. We have developed new strong carbon Brønsted acids, pentafluorophenylbis(triflyl)methane and polystyrene-bound tetrafluorophenylbis(triflyl)methane.[88] The synthesis of the resin-bound Brønsted acid has been accomplished by using the nucleophilic *para*-substitution reaction of lithium pentafluorophenylbis(triflyl)methide with lithiated polystyrenes as a key step. This is the first example of a highly acidic heterogeneous Brønsted acid catalyst that is effectively swollen by non-polar organic solvents, and its catalytic activities are superior to those of Nafion® SAC-13 (Scheme 47).[89]

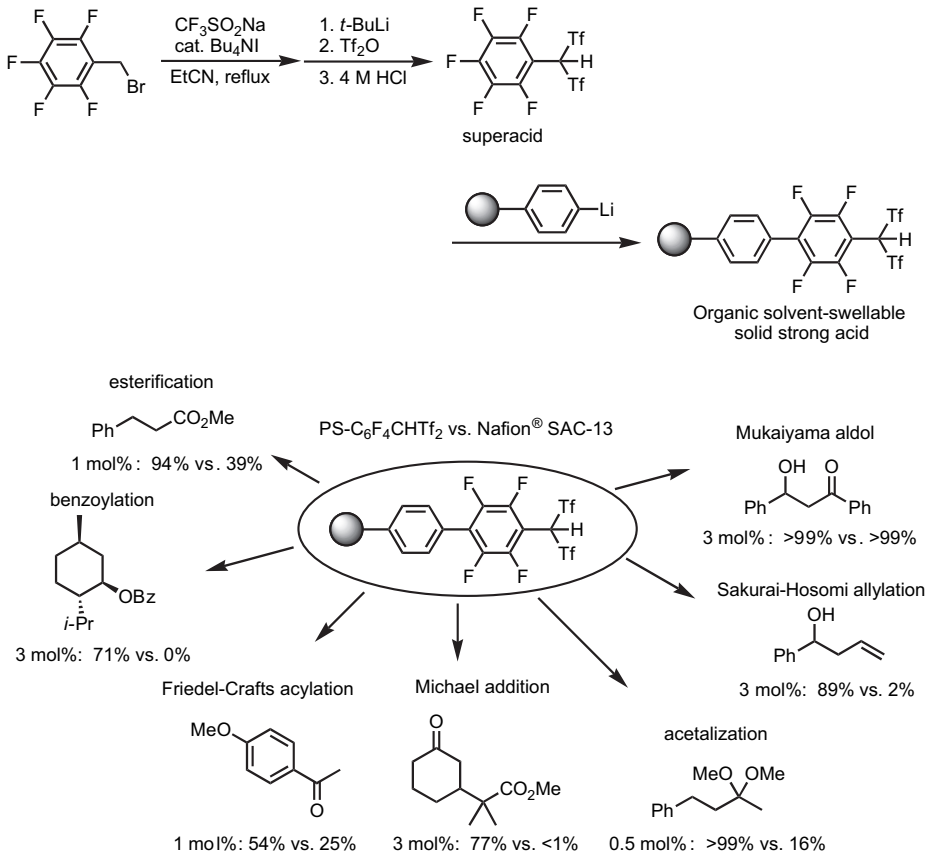
Metal free chiral Brønsted acid catalysis has recently emerged as a new class of chiral organic catalysis. Several quite nice chiral Brønsted acids such as urea/thiourea, alcohol, and phosphoric acid have already been reported as a chiral electron acceptor of carbonyl and imine compounds. However, compared with chiral metal Lewis acid catalysts, the utility of chiral Brønsted acid catalysts is still limited to the reactive substrates. This drawback can be overcome by designing the Brønsted acid catalyst with higher acidity, which, in turn, will be the most important challenge for Brønsted acid chemistry. In order to increase the acidity of Brønsted acids, it is necessary to increase the stability of the counter anion. We expected that strong chiral Brønsted acid would be achieved by introduction of =NTf group into the phosphoric acid. We have succeeded in preparing this super chiral Brønsted acid catalyst, which was able to move forward asymmetric Diels–Alder reaction of unsaturated ketones (Scheme 48).[90]

As described earlier, super Brønsted acid catalyst and super silyl catalyst are inextricably linked. This comes from the quick generation of silyl Lewis acid from super Brønsted acid and silyl enol ether (or allylsilane). Since Me_3SiNTf_2 is a moisture sensitive reagent, a small amount of water in the reaction mixture would cause its decomposition to give Me_3SiOH and $HNTf_2$. Me_3SiOH will react with Me_3SiNTf_2, and provide inert $Me_3SiOSiMe_3$ and $HNTf_2$. The regenerated $HNTf_2$ will readily react with allyltrimethylsilane and provide Me_3SiNTf_2 again.[87] The repetition of this cycle should produce strictly anhydrous conditions. Thus this catalytic cycle constitutes a self-repair system for Lewis acid catalysis. The same catalytic repair system will also be effective with silyl enol ether (Scheme 49).

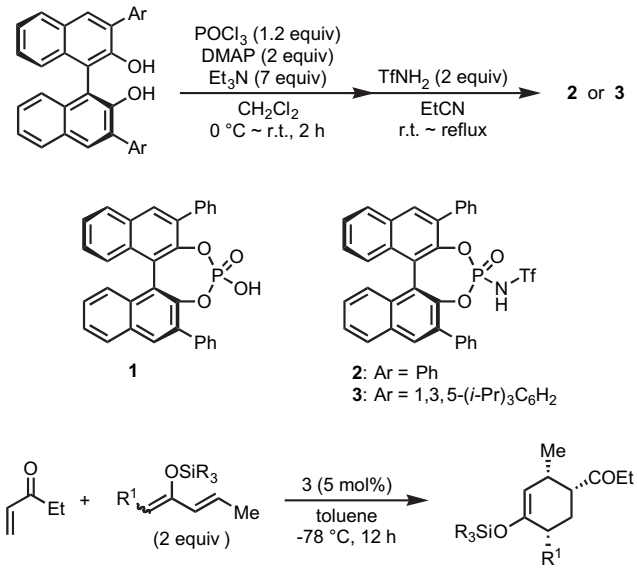
The trimethylsilyl (TMS) group is a widely used protecting group and Lewis acid, as well as an important functional group in certain substrates. For these reasons we deemed the TMS group to be 'generation one'. We have recently described that the use of triflimide as a catalyst initiator is very effective for the aldehyde cross-aldol reaction.[91] The success of this reaction proved to be the use of triflimide as the catalyst as well as the use of tris(trimethylsilyl)silyl (TTMSS)



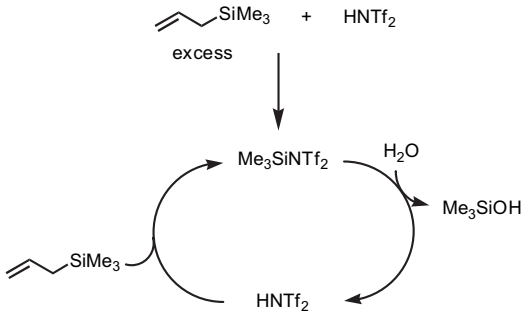
Scheme 46.



Scheme 47.



Scheme 48.

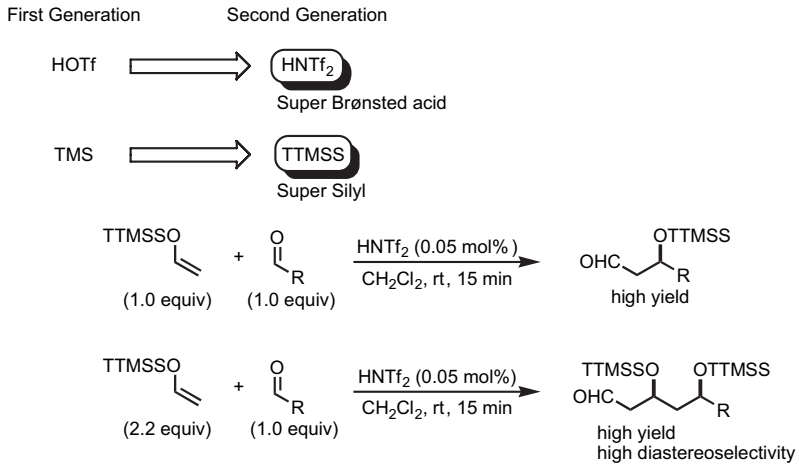


Scheme 49.

enol ethers.[92] The use of the TTMSS group, also referred to as the super silyl group, is one of the keys to this reaction and its unique reactivity caused us to consider it as a second-generation silyl group.

The exceptional diastereoselectivity 'control' and high reactivity of the TTMSS (super silyl) group can be attributed to the two classic arguments of sterics and electronics. The TTMSS group is extraordinarily bulky and has been reported to shield molecular skeletons effectively.[91] After the first addition and silyl transfer, the steric encumberment of this group is likely to kinetically slow down the addition of a second equivalent of nucleophile to a rate that does not compete with the rate of the first addition. When all of the aldehyde starting material have been consumed, a second addition occurs giving the products with high diastereoselectivity. After this second addition occurs, the aldehyde has β- and δ-TTMSSoxy groups and if catalyst coordination occurs, the complex is likely too bulky for further additions.

Intrigued by $TTMSSNTf_2$ catalysis, we used ^{29}Si NMR as an indicator of silicon Lewis acidity and found that the central



Scheme 50.

silicon of $TTMSSNTf_2$ was shifted significantly down-field (>6 ppm) compared to TMS and $TBSNTf_2$, and only slightly down-field from pentamethyldisilane–NTf_2 (62.2, 55.9, 55.5, and 60.8 ppm, respectively). This trend shows a considerable difference in the cationic nature of silyl groups with only silicon–carbon bonds versus those with silicon–silicon bonds. This high reactivity of silyl enol ether as well as super silyl cation is probably due to the high homo level of Si–Si and Si–C sigma bond (Scheme 50).

11. Conclusion

In the sunset of his life, Mr. Kozo Masuda chose to write, "Even after a long journey, the goal remains far away." (Tadorikite imada sanroku.) I believe the optimal designing in organic synthesis is still distant from the ultimate goal and I am sure that wonderful golden ages are yet to be experienced.

I would like to acknowledge many outstanding contributors in my research groups from Kyoto, Hawaii, Nagoya, and Chicago. If some of the chemistry mentioned in this review is significant, the honor should go to these individuals.

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