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Asymmetric Catalytic [4+3] Cycloaddition Reactions

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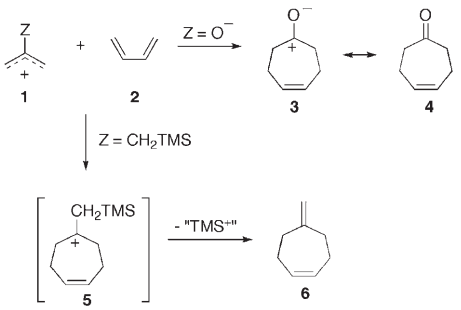
Abstract: Although the [4+3] cycloaddition reaction has seen considerable attention over the past 10–15 years, only a few investigations have been dedicated to the development of a catalytic, asymmetric process. This short review covers some of the advances made in the area of absolute stereocontrol in this higher order cycloaddition and will hopefully serve as an inspiration towards the development of asymmetric, catalytic versions of the reaction.

Keywords: carbocations; chiral auxiliaries; cycloaddition; diastereoselectivity; enantioselectivity; oxyallyl

1 Introduction

The [4+3] cycloaddition reaction involves the cycloaddition of an allylic cation or its equivalent with a diene to produce a seven-membered ring.[1] The generic reaction is shown in Scheme 1. A product may



Scheme 1. A general scheme for the [4+3] cycloaddition reaction showing two different terminating groups.

be produced directly, or an intermediate may form that evolves in accord with the nature of the "terminating" group Z. For example, when Z is an oxyanion (O^-), a cycloheptenone (**3**/**4**) is formed directly. In other cases, such as when Z is a trimethylsilylmethylene group, an intermediate cation (**5**) might be formed, which rapidly loses the silyl group to form a product (**6**) with an exocyclic methylene group.

The [4+3] cycloaddition can proceed by either a concerted or a stepwise mechanism.[2] In the latter case, it is formally not a cycloaddition at all. The occurrence of either mechanism is dependent on the structure of both reactants and the reaction conditions. Generally, one can expect more reactive cations and electron-rich dienes to react in a stepwise fashion, while less reactive cations and less reactive dienes will tend to combine *via* a concerted process. However, these are only guidelines and are certainly not rigid. It is likely that some of the mechanistic ambiguities associated with this process have delayed the development of catalytic, asymmetric versions of the reaction.

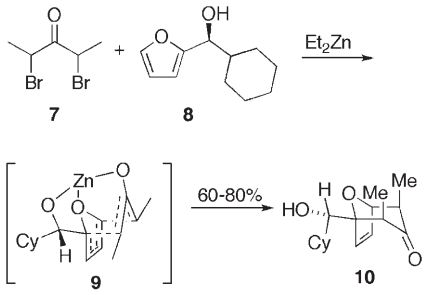
2 Stoichiometric Asymmetric [4+3] Cycloaddition Reactions

The vast majority of approaches to asymmetric [4+3] cycloaddition reactions have involved stoichiometric approaches, i.e., the use of chiral auxiliaries. Highly diastereoselective processes often result from such approaches. As this area has been reviewed recently,[3] only a few highlights will be discussed. Reactions that involve high diastereoselectivity, but from whose cycloadducts the original source of stereogenicity has not been removed, will not be covered, with a few exceptions.

Michael Harmata was born in Chicago, Illinois in 1959. He received his AB with honors and highest distinction in chemistry from the University of Illinois-Chicago in 1980. He studied carbanion-accelerated Claisen rearrangements with Scott Denmark, obtaining his Ph.D. from the University of Illinois-Champaign/Urbana in 1985. As an NIH postdoctoral fellow, he conducted research on the synthesis of the neocarzinostatin chromophore at Stanford University under the guidance of Paul Wender. He began his independent career at the University of Missouri-Columbia in 1986 and is now the Norman Rabjohn Distinguished Professor of Chemistry at that institution. When not doing chemistry, he enjoys being with his family, roller skating, stamp collecting and reading.

2.1 Chiral Dienes

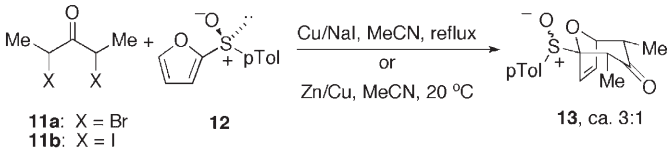
The Lautens group showed that certain chiral dienes could exhibit very high diastereofacial selectivity in the [4+3]cycloaddition reaction.[4] For example, the reaction of **7** with furan **8** in the presence of diethylzinc afforded the cycloadduct **10** with very high stereoselectivity (Scheme 2). The basis for this selectivity



Scheme 2. Diastereoselective [4+3]cycloaddition reaction using a chiral furan.

was explained as a result of chelate formation and coordination of the oxyallyl oxygen to the zinc as shown in **9**. This resulted in not only high diastereofacial selectivity, but an *exo* (extended) approach of the oxyallyl to the diene, a rather unusual result. To the best of our knowledge, one application,[5] but no further exploration or extension of this reaction has appeared in print.

Montaña and co-workers examined the [4+3]cycloaddition of a variety of chiral furans with a zinc or copper oxyallyl.[6] The reduction of 2,4-diiodo-3-pentanone in the presence of furan **12** afforded a diastereomeric mixture of cycloadducts, generally in a ratio of about 3:1 (Scheme 3). This ratio was essentially in-



Scheme 3. Diastereoselective [4+3]cycloaddition using a chiral arylsulfinyl furan.

dependent of the reaction conditions, including the metal reductant, the solvent and the reaction temperature (20 or 60 °C). The diastereoselectivity of such processes using other chiral furans was very low. However, given that only a single dienophile was used and that the scope of functionalization possible to make a diene chiral is quite broad, this strategy bears continued examination.

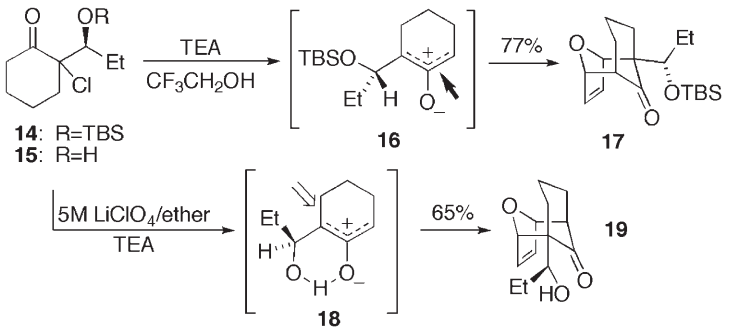
2.2 Chiral Cations

The development of chiral allylic cations has had a greater impact on asymmetric [4+3]cycloadditions than the development of chiral dienes. This parallels similar trends in the Diels–Alder reaction. Most of the chiral cation development has focused on heteroatom-stabilized species.[7] However, there is one interesting example in which this was not the case.

2.2.1 "Unstabilized" Oxyallylic Species

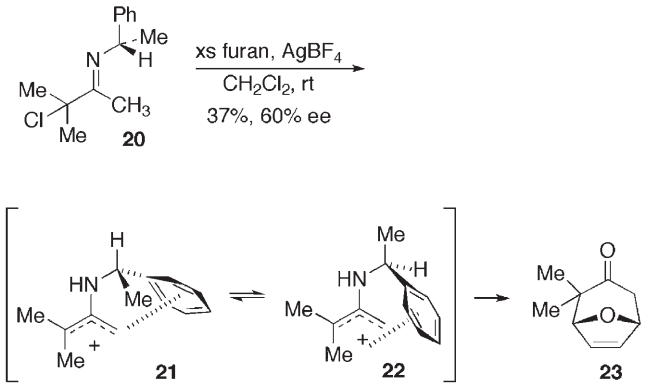
Cha and co-workers reported an elegant approach to asymmetric [4+3]cycloaddition reactions.[8] Treatment of **14** with triethylamine in trifluoroethanol in the presence of furan afforded the cycloadduct **17** as a single stereoisomer (Scheme 4). The rationale for this stereochemical result is based on the formation of an oxyallylic cation whose conformation is that shown in **16**. Attack of the diene on the least hindered face of this intermediate *via* an *endo* (compact) transition state affords the product. Interestingly, with a precursor having no protecting group on the hydroxy moiety, the cycloadduct **19** could be produced with very high selectivity, presumably *via* **18**.

Kende and Huang reported that the reaction of chiral imines of certain chloroketones could give [4+3] cycloadducts in moderate yields and with fair enantioselectivities.[9] In their best case, treatment of the imine **20** with silver tetrafluoroborate in the presence



Scheme 4. [4+3] cycloaddition of a cyclic, chiral cation.

of furan gave the cycloadduct **23** in 37% yield with an enantiomer excess of 60% (Scheme 5). A model for the stereocontrol that incorporated some data on



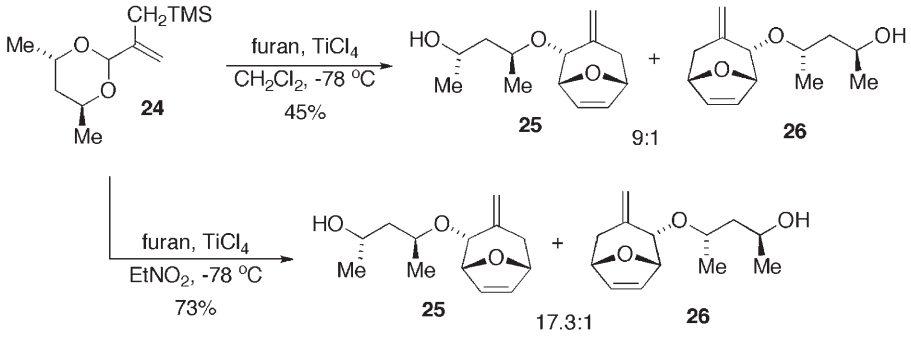
Scheme 5. [4+3] cycloaddition of α-chloroimines.

reactivity differences suggested that an equilibrium existed between **21** and **22**. In **21**, both faces of the allylic cation are sterically encumbered, while in **22** only the *si* face of the cation is blocked, affording access to the *re* face to the incoming diene.

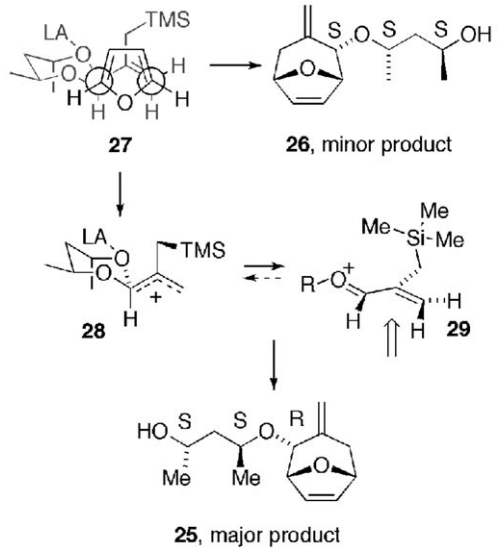
2.2.2 Chiral Vinyl Oxocarbenium Ions

In 1997, we reported the first example of a Lewis acid-mediated diastereoselective reaction between a chiral allylic acetal and furan. The reaction of **24** and furan in the presence of $TiCl_4$ in CH_2Cl_2 afforded the [4+3] cycloaddition products **25** and **26** in 45% yield as a 9:1 ratio of diastereomers (Scheme 6).[10] Further improvements, including a change in solvent to nitroethane, led to a process in which the yield had improved to 73% and the ratio of **25**:**26** increased to 17.3:1.[11] Other Lewis acids generally gave the same direction of stereoselection, though not necessarily to the same extent. Attempts to perform the reaction catalytically with $TiCl_4$ gave low yields, but high diastereoselection (*ca.* 26:1). The basis for this selectivity change has not been determined, though it may lie in the exact nature of the species that undergoes the cycloaddition process.[12]

It is interesting to note that the major diastereomer in these reactions is not that which is predicted by the standard models associated with nucleophilic ring opening of 2,4-pentanediol acetals, as illustrated in Scheme 7.[12,13] Coordination of the Lewis acid to the oxygen on the carbon bearing the axial methyl group polarizes the carbon-oxygen acetal bond and results in bond formation *via* what often appears to be an S_N2 cleavage of the acetal. Mechanistic issues in acetal ring openings are complex and still not com-



Scheme 6. [4+3] cycloaddition of a chiral, allylic acetal.

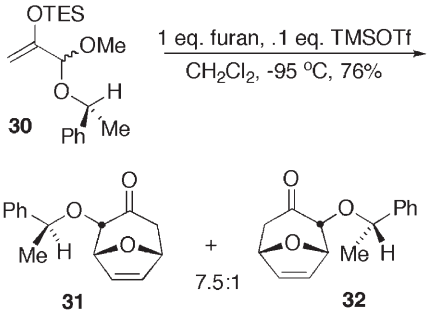


Scheme 7. Mechanistic rationale for the stereochemical outcome of the [4+3]cycloaddition of **24** with furan.

pletely resolved, but the observation of high selectivity that does not correlate with this standard model is relatively unusual. Conformational effects that are not readily apparent may play a role. One possibility is that the orientation of the TMS group affects the facial selectivity, since a TMS group perpendicular to the pi system of any carbocationic intermediate adds another degree of chirality to the system. So standard opening of the acetal shown in **27** might produce an intermediate like the intimate ion pair **28** or the free oxocarbenium ion **29** whose TMS group is oriented in a way that minimizes its interaction with the Lewis acid in the Lewis acid-acetal complex. While this intermediate exists in this conformation, attack by nucleophilic dienes should occur on the face opposite the TMS group. This is precisely what we observed. On the other hand, cyclopentadiene reacted with **24** to afford a 1.7:1 mixture of diastereomers and it is expected to be a better nucleophile than furan. This might imply a more rapid reaction on intermediates, each of which reacts selectively, but gives opposite stereochemical outcomes, or a single species that reacts without selectivity.

Related studies of vinyl oxocarbenium ions have been carried out by Hoffman and co-workers. They reported that the chiral acetal **30** afforded good levels of diastereoselectivity upon reaction with furan dienes in the presence of a Lewis acid (Scheme 8).[14] The process required temperatures below −95 °C for reasonable diastereoselection. Changing the phenyl group in **30** to a 2-naphthyl group improved the stereoselection.[15]

The basis for the stereocontrol is proposed to be π-stacking, as exemplified by the transition state models



Scheme 8. [4+3]cycloaddition of chiral acetal **30**.

33 and **34** (Figure 1). This requires considerable distortion from the expected geometry of the oxygen atom in the cationic intermediate. Nevertheless, the

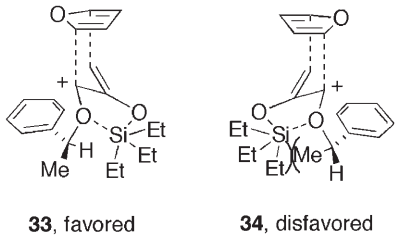


Figure 1. Mechanistic rationale for the selectivity in [4+3]cycloadditions of **30**.

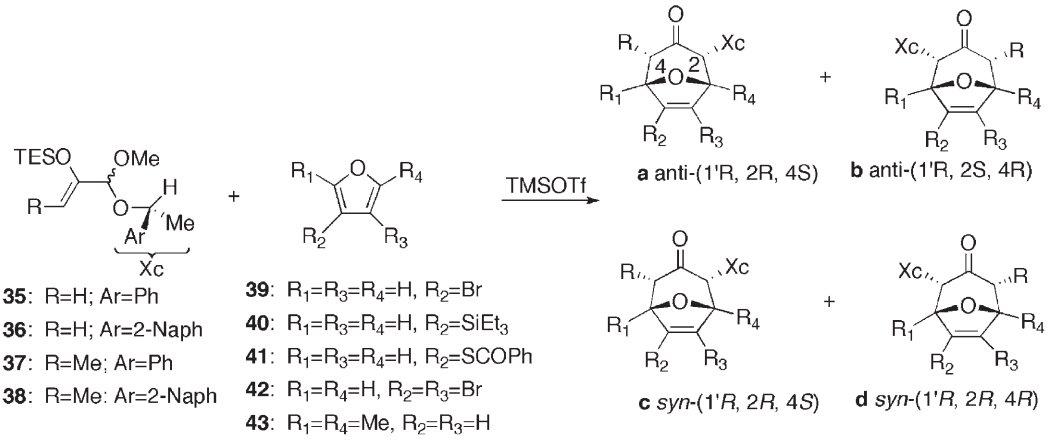
process works. When various substituted furans were used as dienes in studies with these chiral cations, stereoselectivity and regioselectivity were often high.[16] Some of the results are summarized in Table 1. The high regioselectivity and diastereoselectivity that can be observed in many cases is impressive. As interesting is the loss of facial selectivity when 2,5-dimethylfuran (**43**) is used as a diene. This has been explained by invoking a steric interaction between the methyl groups and the dienophiles that disrupts the π-stacking thought to be responsible for high facial selectivity in other examples.

2.2.3 Chiral Vinyl Iminium Ions

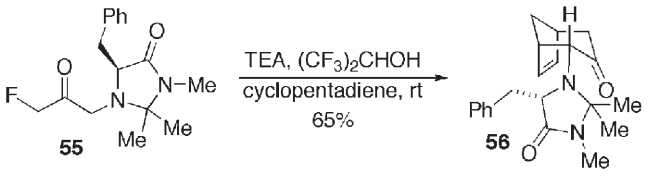
Myers and Barbay published an interesting 4+3 cycloaddition reaction as part of their work on α-amino-α′-fluoro ketones.[17] In a single example, these workers showed that ketone **55** reacted with cyclopentadiene to afford a 65% yield of **56**, along with other diastereomers (Scheme 9). This was the first example of the use of a vinyl iminium ion in an asymmetric [4+3]cycloaddition reaction.

More recently, the Hsung group has developed a unique approach to vinyl iminium ions in the context of their work on allenamide chemistry.[18] For example, oxidation of **57** with dimethyldioxirane (DMDO) in the presence of 10 equivalents of furan (CH_2Cl_2,

Table 1. [4+3] cycloaddition of chiral acetals **35–38** with substituted furans.

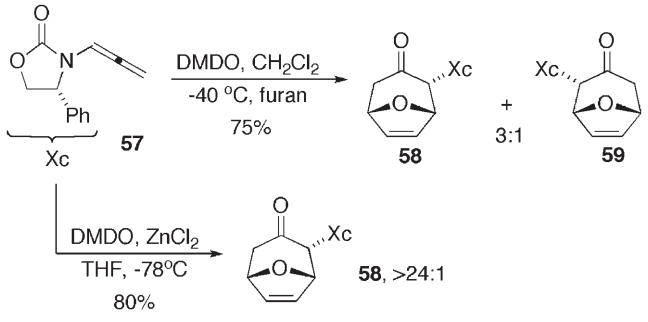


Entry	Acetal	Furan	Product	Diastereoselectivity (a+c):(b+d)	Regioselectivity (a+b):(c+d)	Yield [%]
1	**35**	**39**	**44**	7:1	10:1	50
3	**35**	**40**	**45**	7:1	1.3:1	74
4	**36**	**40**	**46**	6:1	1.3:1	73
5	**35**	**41**	**47**	1.2:1	6:1	79
6	**36**	**41**	**48**	1.5:1	6:1	74
7	**37**	**41**	**49**	17:1	17:1	75
8	**38**	**41**	**50**	13.1	14:1	75
	35	**42**	**51**	17:1	-	50
	36	**42**	**52**	16:1	-	49
	35	**43**	**53**	1.2:1	-	49
	36	**43**	**54**	1.5:1	-	47



Scheme 9. The first example of a [4+3] cycloaddition of a chiral vinyl iminium ion.

−40 °C) afforded a 75% yield of **58** and **59** in a ratio of 3:1 (Scheme 10).



Scheme 10. Oxidation and subsequent [4+3] cycloaddition of a chiral allenamide.

While solvent changes had no effect on diastereoselectivity, it was found that the use of zinc chloride as an additive resulted in an increased yield and very high diastereoselection. The rationale for this outcome combines the inherent preference for an *endo* (compact) approach of the dienophile to the diene in 4+3 cycloadditions with facial selectivity being based on minimization of steric interactions, such that approach occurs from the least hindered face of the chelated vinyl iminium ion (**60**, Figure 2).

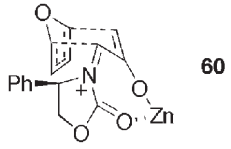
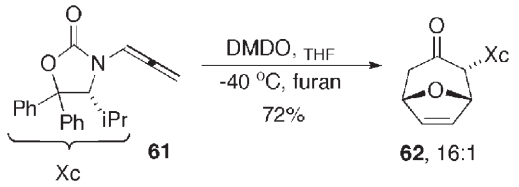


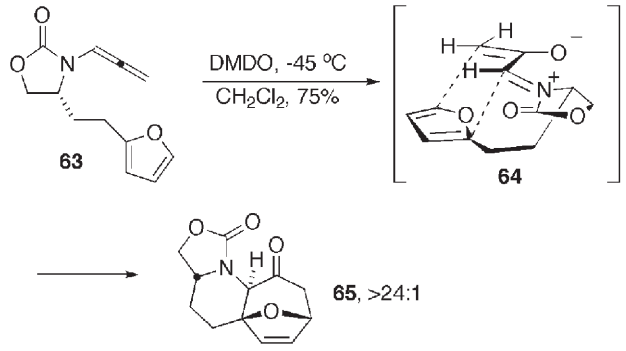
Figure 2. Model for the stereoselection observed in the [4+3] cycloaddition of **57** in the presence of $ZnCl_2$.

However, some allenamides with different chiral auxiliaries studied did not benefit from the addition of zinc chloride. Further, **61** reacted with furan upon oxidation in the absence of zinc chloride to afford **62** with very high diastereoselectivity (Scheme 11).



Scheme 11. High diastereoselectivity in the oxidation/[4+3] cycloaddition of a chiral allenamide in the absence of $ZnCl_2$.

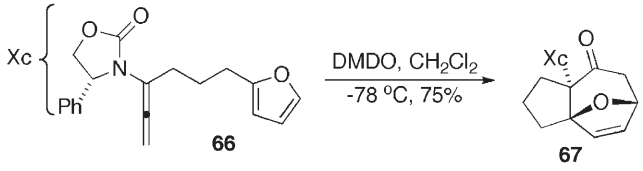
This chemistry has also been used in intramolecular [4+3]cycloaddition reactions to good effect.[19] The reaction of **63** with excess DMDO in acetone/CH_2Cl_2 at −45 °C afforded **65** in 75% yield with a diastereoselectivity of greater than 24:1 (Scheme 12). This and



Scheme 12. Diastereoselective intramolecular [4+3]cycloaddition of a chiral allenamide.

other examples of the reaction fit the mechanistic model shown in **64** in which the vinyl iminium ion adopts a W configuration and the reaction proceeds by *exo* (extended) approach of the dienophile to the diene. The tether thus introduces some constraints on how the reactants may approach each other. Zinc chloride had no effect on the stereochemical outcome of the intramolecular processes.

When intramolecular reactions were conducted with allenamides bearing a chiral auxiliary not incorporated into the tether, the stereochemical outcomes of the reactions remained impressive. Oxidation of **66** in CH_2Cl_2 at −78 °C afforded **67** as a nearly pure diastereomer in 75% yield (Scheme 13).



Scheme 13. Intramolecular [4+3]cycloaddition of an "α-tethered" chiral allenamide.

This implies an *endo* (compact) approach of the sickle-configured oxyallylic cation to the diene as shown in **68** (Figure 3).

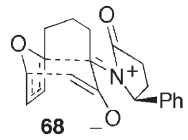
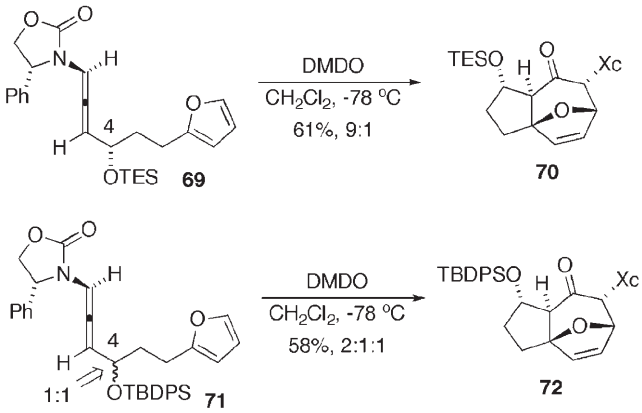


Figure 3. Model for the stereoselectivity observed in the oxidation/[4+3]cycloaddition of **66**.

Substrates in which the chiral auxiliary had been transposed to the terminal end of the allene also generally underwent selective [4+3]cycloadditions. For example, oxidation of **69** afforded **70** as a 9:1 mixture of diastereomers (Scheme 14), the major isomer resulting from a transition structure represented by **73**



Scheme 14. A study of double diastereoselection in the [4+3]cycloaddition of chiral allenamides.

and/or **74** (Figure 4). On the other hand, the process conducted with **71** (Scheme 14), which was an 1:1 epimeric mixture at carbon 4, afforded three cycload-

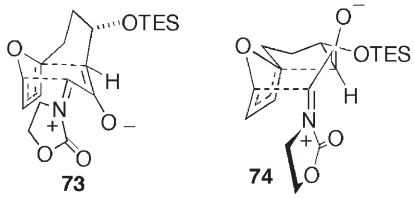


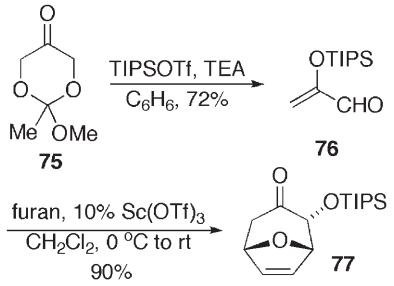
Figure 4. Two possible transition structures that account for the formation of **70** (Ph groups omitted for clarity).

ducts in a ratio of 2:1:1 (58%). Although not directly comparable because of the protecting group difference, the implication is that the stereochemical rela-

tionships in **69** represent the "matched" case. Whether lower diastereoselectivity in the "mismatched" case is due to loss of *endo* selectivity or another factor is not clear. Finally, it should be noted that the stereogenic axis associated with the allene had no effect on the stereochemical outcome of these reactions.

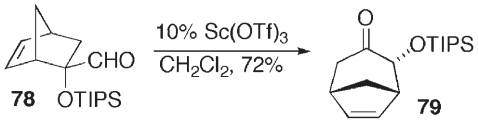
3 Catalytic [4+3] Cycloadditions Reactions

Examples of catalytic [4+3] cycloadditions are relatively rare. We showed that treatment of **76** with 10 mol % of scandium(III) triflate resulted in the formation of the 4+3 cycloadduct **77** in high yield with complete diastereoselectivity (Scheme 15).[20]



Scheme 15. Catalytic [4+3] cycloaddition reaction of acrolein **76**.

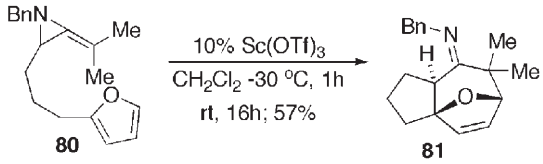
How this reaction occurs has been the subject of some speculation. Davies and Dai suggested that the reaction proceeded by a [4+2] cycloaddition followed by a ring expansion, by showing that the adduct **78** gave **79** on treatment with scandium triflate (Scheme 16).[21]



Scheme 16. Catalytic conversion of a [4+2] cycloadduct into a [4+3] cycloadduct.

However, based on high level computations, Domingo and co-workers suggested that the process does not involve any real cycloaddition component but rather proceeds *via* Michael addition of furan to **76** followed by ring closure.[22]

In an elegant demonstration of the synthetic utility of alkylidene aziridines, Shipman and co-workers demonstrated that treatment of **80** with 10 mol % of the same Lewis acid affords the adduct **81** in 57 % yield as a single diastereomer (Scheme 17).[23]



Scheme 17. Catalytic [4+3] cycloaddition of an alkylideneaziridine.

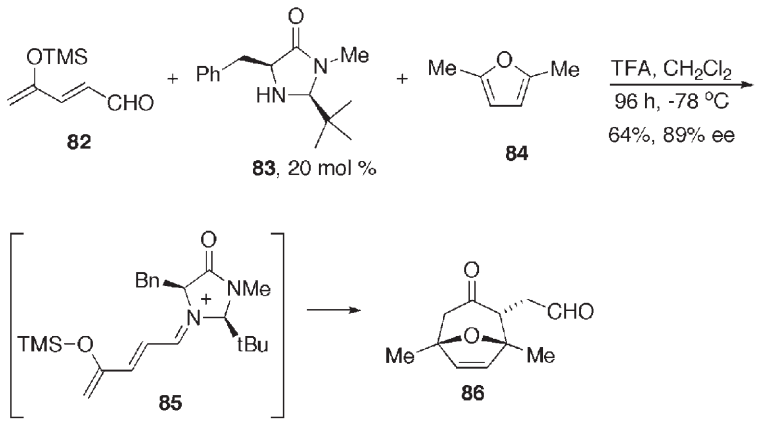
While neither of these observations has yet been converted to asymmetric, catalytic processes, they clearly demonstrated feasibility and lay the foundation for future studies.

4 Asymmetric Catalytic [4+3] Cycloaddition Reactions

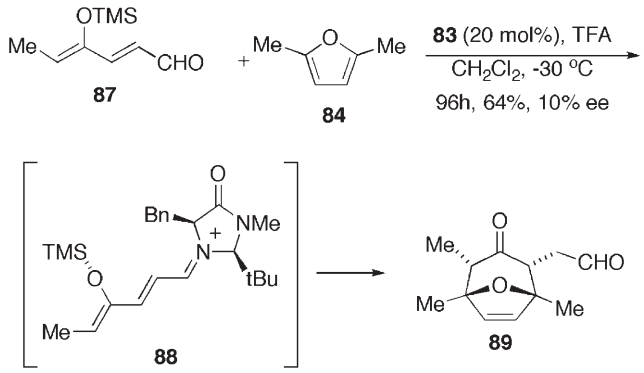
We reported the first example of an asymmetric, catalytic [4+3] cycloaddition reaction.[24] The reaction of dienal **82** with 2,5-dimethylfuran **84** in the presence of chiral amine **83** gave **86** in 64 % yield as a single diastereomer with an enantiomeric excess of 89 %, though the absolute stereochemistry of the product was not determined (Scheme 18). The organocatalytic reaction presumably proceeded through iminium ion **85**. Two other 2,5-disubstituted furans also gave good enantioselectivities under these conditions, while the reaction with furan itself gave low yields and moderate enantioselectivity.

Interestingly, the reaction between **87** and **84**, while completely diastereoselective, was only slightly enantioselective (Scheme 19). We rationalized this outcome on the basis of the structure of the presumed vinyl iminium ion intermediate **88**. For **85**, one can imagine a structure in which one face of the dienophile is blocked by the benzyl group of **83** and the OTMS group lies approximately in the plane of the iminium ion. With **88**, on the other hand, the OTMS group may be blocked from lying in the plane by the methyl group on the iminium ion (Figure 5). It would then point to the face opposite that blocked by the benzyl group. With both faces blocked, facial selective virtually vanishes and little net enantioselectivity is observed. This is a type of chiral relay that is not productive, however, the compounds we have designed to avoid the problem have yet to be tested.

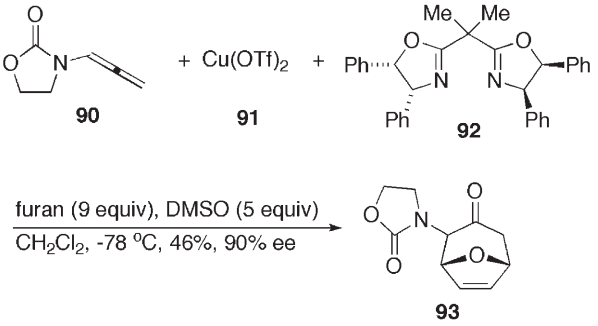
Hsung and Huang and made use of chiral Lewis acids in developing a different asymmetric, catalytic [4+3] cycloaddition reaction.[25] After exploration of a



Scheme 18. An asymmetric, organocatalytic [4+3]cycloaddition reaction.



Scheme 19. A failed asymmetric, organocatalytic [4+3]cycloaddition reaction.



Scheme 20. Asymmetric catalysis of an allenamide [4+3]cycloaddition reaction.

number of reaction conditions and ligands, they found that the oxidation of **90** in the presence of excess furan and 25 mol% of **92** and copper(II) triflate afforded cycloadduct **93** in 46% yield in 90% *ee* (Scheme 20). A change in counterion to SbF_6^- and the addition of molecular sieves improved the reaction dramatically in terms of yield, affording **93** in 99% *ee* in 91% yield. A summary of some other results is shown in Table 2. It is interesting that 2-substituted furans reacted with very high regioselectivity, but only modest enantioselectivity (Table 2, entries 2 and 3). Furthermore, 3-substituted furans gave good to excellent yields and excellent enantioselectivities and regioselectivities, save for the last entry. Steric effects presumably play a role in this reaction, making some substrates unsuitable partners, at least with respect to enantioselectivity. The rationale for the stereochemical outcomes of these reactions is shown in Figure 6. The chiral ligand/Lewis acid complex opens the allene oxide formed by oxidation of the allenamide to produce **103**, in which the copper ion is square planar. The faces of the intermediate are sterically different. An *endo* approach by the diene is preferred from the sterically less hindered top face. Steric interactions with 2- or 2,5-disubstituted dienes slide the dienes away from the chiral ligand, lowering

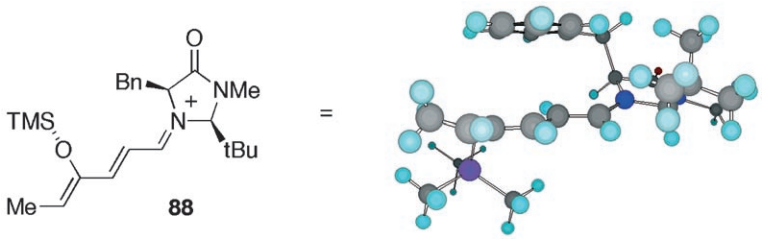
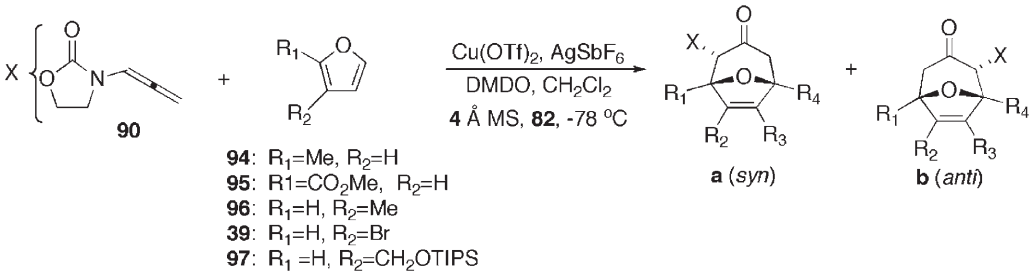


Figure 5. Putative structure of iminium ion **88**.

Table 2. Asymmetric catalysis of allenamide [4+3] cycloaddition reactions.



Entry	Furan	Product	*syn*:*anti*	ee [%]	Yield [%]
1	**94**	**98**	20:1	71	88
2	**95**	**99**	*syn* only	67	61
3	**96**	**100**	*anti* only	99	91
4	**39**	**101**	1:14	84	58
5	**97**	**102**	1:2.3	66	66

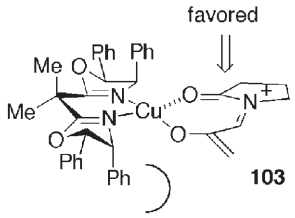


Figure 6. Rationale for the facial selectivity for the copper-catalyzed [4+3] cycloadditions in the presence of chiral ligand **92**.

enantioselectivity. Similar steric interactions with 3-substituted dienes result in a change in regioselectivity from *syn* to *anti*.

5 Summary and Future Prospects

Clearly, there is a great gaping hole in the development of catalytic, asymmetric [4+3] cycloadditions. We hope to contribute more to the development of this area, particularly in the context of organocatalysis. The reactions described herein lie more in the realm of what might be termed as classical organic chemistry (carbocations!). As such, they must compete with a growing variety of transition metal-catalyzed processes that can produce seven-membered and other medium-sized ring systems.[26] They in fact can compete, and as further advances are achieved, they will become even better. One part of synthetic organic chemistry is to take organic reactions and reinvent them as new methods and new concepts are introduced. We see this time and again with all sorts of reactions. This is happening and will occur further with [4+3] cycloadditions.

In a broader sense, this utilitarian aspect of synthesis is only one part of the discovery, invention, design and creation aspect of this art and science. First and foremost, synthetic organic chemistry is about learning how molecules interact and react with each other. This is as important and wondrous as learning about any other aspect of this universe, from theories of the subatomic world that challenge our ideas of existence, to the search for alien life and to studies of the vastness of the cosmos. Chemists see the universe in molecules, and create it as well. A broad view towards reactions, reactivity and interactivity will mean that synthetic organic chemistry is here to stay as an intellectual endeavor at the forefront of science. There are a myriad of opportunities waiting for us. Let us support each other as a community, and sculpt a future for our science that beckons the young and gratifies the old and, more often than not, provides benefits for all of humankind.

I hope some of us will do it studying [4+3] cycloadditions.

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