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Asymmetric organocatalysis

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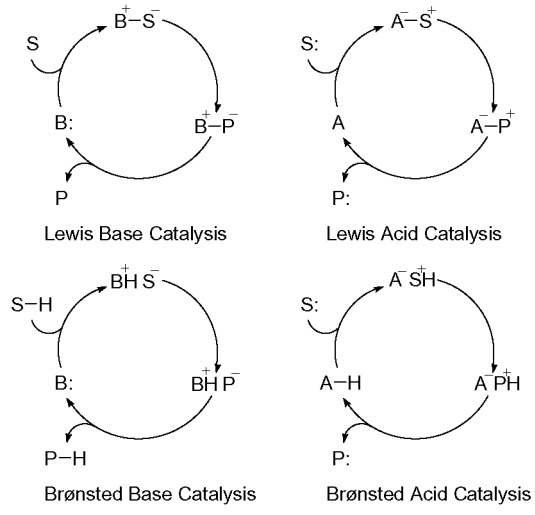
The field of asymmetric organocatalysis is rapidly developing and attracts an increasing number of research groups around the world. Here we present a brief overview of this area, guided by a mechanistic classification. Accordingly, organocatalysts are categorized as either Lewis base, Lewis acid, Brønsted base, or Brønsted acid catalysts.

Introduction

Enzymes are enormously efficient and enantioselective. While chemists use mostly metal-based catalysts, about half of known enzymes do not contain metals in their active sites. In recent years it has been established that small organic molecules, in addition to metal complexes and biocatalysts, can be highly selective and efficient catalysts. As a consequence, organocatalysis is gaining importance in asymmetric synthesis, complementing bio- and metal-catalysis. Although the first examples were reported several decades ago,[1] the area of enantioselective organocatalysis became a main focus of research only recently.[2] This article provides an overview of this exciting and rapidly growing field.

Most but not all organocatalysts can be broadly classified as Lewis bases, Lewis acids, Brønsted bases, and Brønsted acids. The corresponding (simplified) catalytic cycles are shown in Scheme 1. Accordingly, Lewis base catalysts (B:) initiate the catalytic cycle *via* nucleophilic addition to the substrate (S). The resulting complex undergoes a reaction and then releases the product (P) and the catalyst for further turnover. Lewis acid catalysts (A) activate nucleophilic substrates (S:) in a similar manner. Brønsted base and acid catalytic cycles are initiated *via* a (partial) deprotonation or protonation, respectively. We have structured the text by describing recent examples of the different catalysis types illustrated in the context of asymmetric catalysis. A major limitation of our mechanistic classification approach is the typical lack of information on the mechanisms of most organocatalytic reactions, in particular kinetic data.[3] However, we feel this drawback to be more than counterbalanced with the obvious benefit of giving the field a somewhat logical structure.



Scheme 1 Organocatalytic cycles.

Lewis base catalysis

The majority of organocatalysts are N-, C-, O-, P-, and S-based Lewis bases that operate through diverse mechanisms

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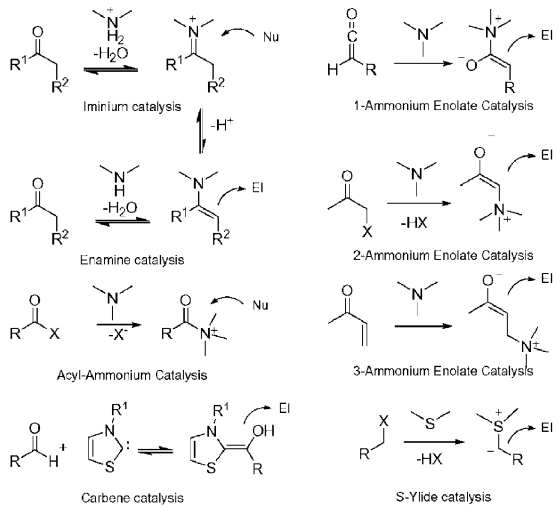
and convert the substrates either into activated nucleophiles or electrophiles. Typical reactive intermediates are iminium ions, enamines, acyl ammonium ions, 1-, 2-, or 3-ammonium enolates, *etc.* (Scheme 2).

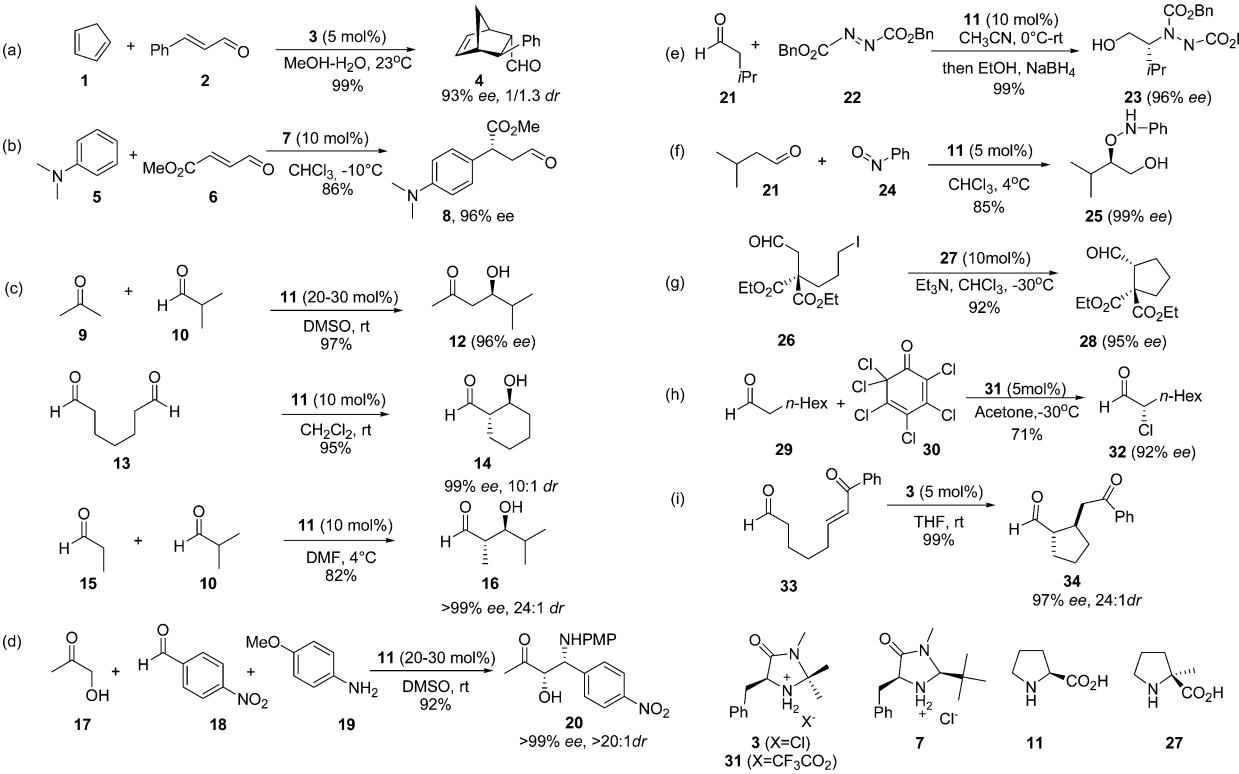


Scheme 2 Examples of Lewis base organocatalysis.

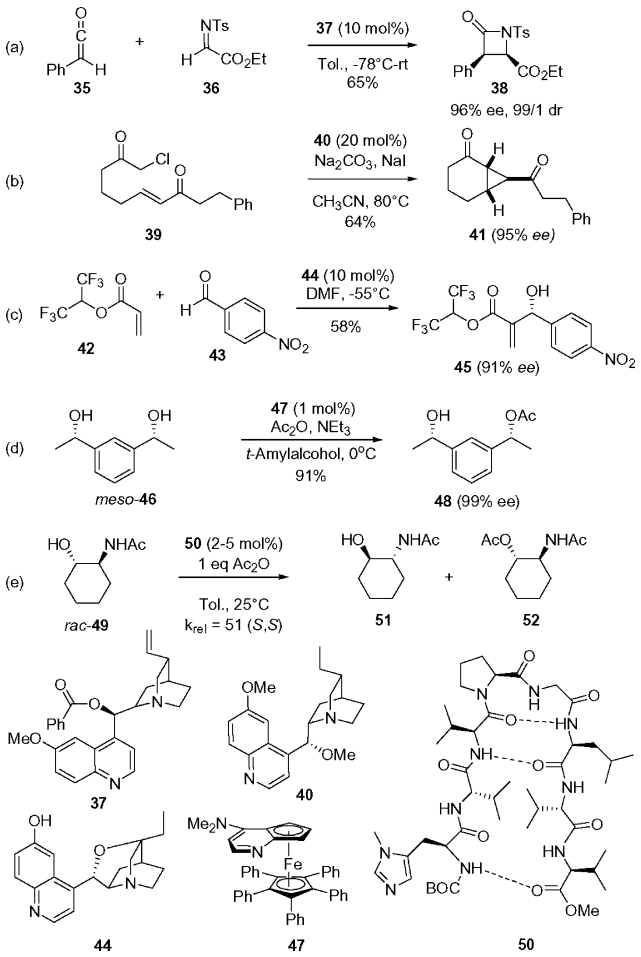
In *iminium catalysis*, the active species is an iminium ion formed by the reversible reaction of an amine catalyst with a carbonyl substrate. The higher reactivity of the iminium ion compared to the carbonyl species is utilized to facilitate reactions such as Knoevenagel condensations, cyclo- and nucleophilic additions, and cleavage of σ-bonds adjacent to the α-carbon.[4] The pioneering example of modern iminium catalysis is Macmillan's enantioselective Diels–Alder reaction of α,β-unsaturated aldehydes and ketones[5] with dienes using the chiral imidazolidinone catalyst **3** (Scheme 3a).[4b] The condensation of the α,β-unsaturated aldehyde with the enantiopure amine catalyst forms an activated iminium ion with lowered LUMO energy, which reacts with the diene leading to a Diels–Alder cycloaddition. This concept has been further extended to other reactions of α,β-unsaturated aldehydes, such as [3 + 2] cycloaddition with nitrones (up to 98% yields, *dr* = 98 : 2, and 99% *ee*),[4c,6] Friedel–Crafts alkylation with pyrroles,[7] indoles,[8] and benzenes (Scheme 3b)(up to 97% yield and 99% *ee*),[9] and Mukaiyama–Michael reactions (up to 93% yield and 98% *ee*),[10] achieving high yields and enantioselectivities. Other recent examples that may involve iminium catalysis are the Michael addition of malonates[11] and nitroalkanes[12] to enones using (*S*)-proline or a similar catalyst system that presumably activates the enone (Michael acceptor) by forming an iminium intermediate.

Enamine catalysis involves a catalytically generated enamine intermediate that is formed *via* deprotonation of an iminium ion and that reacts with various electrophiles or undergoes pericyclic reactions. The first example of asymmetric enamine catalysis was the Hajos–Parrish–Eder–Sauer–Wiechert reaction,[1b] an intramolecular aldol reaction catalyzed by proline. About 30 years later, List *et al.*, followed by other research groups, discovered proline-catalyzed enantioselective intermolecular aldol reactions (Scheme 3c),[13,14] Mannich reactions (Scheme 3d)[15] and Michael additions,[16] opening up new areas for enamine catalysis.[17] This concept has also been extended to highly enantioselective α-functionalizations of aldehydes and ketones such as aminations (Scheme 3e),[18–20] hydroxylations (Scheme 3f),[21,22] alkylations (Scheme 3g),[23] chlorinations (Scheme 3h)[24,25] and an intramolecular Michael reaction (Scheme 3i).[26]

In the case of *1-ammonium enolate catalysis*, a ketene interacts with a nucleophilic amine catalyst (typically a quinine or quinidine derivative) forming a 1-ammonium enolate intermediate which reacts with electrophiles *e.g.* ketenes (up to 88% yield and 97% *ee*),[27] aldehydes (up to 98% *ee*)[28] or imines (up to 65% yield and 99% *ee*) (Scheme 4a),[29] forming the corresponding lactones or lactams. Very recently, Gaunt *et al.*[30] reported the cinchona alkaloid catalyzed inter- and intramolecular cyclopropanation of α-halo ketones with electron withdrawing alkenes, which proceed through a catalytically generated ammonium ylide or 2-ammonium enolate species (Scheme 4b). Hatakeyama and co-workers[31] reported the enantioselective Baylis–Hillmann reaction of aldehydes with acrylates using quinidine catalysts



Scheme 3 Examples of enantioselective iminium and enamine catalysis.

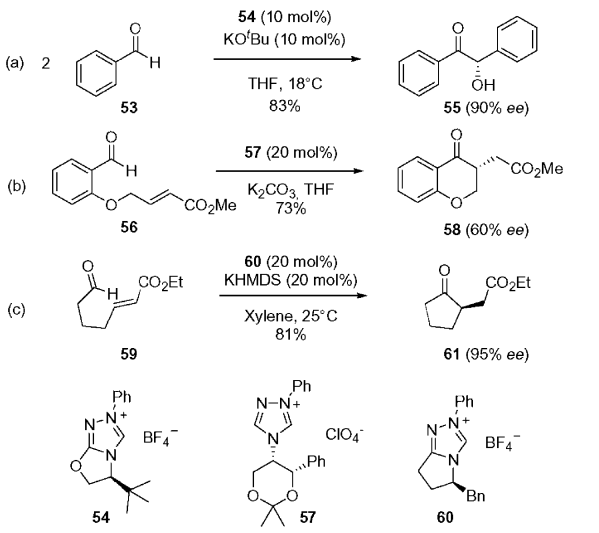


Scheme 4 Other examples of enantioselective *N*-based Lewis base catalysis.

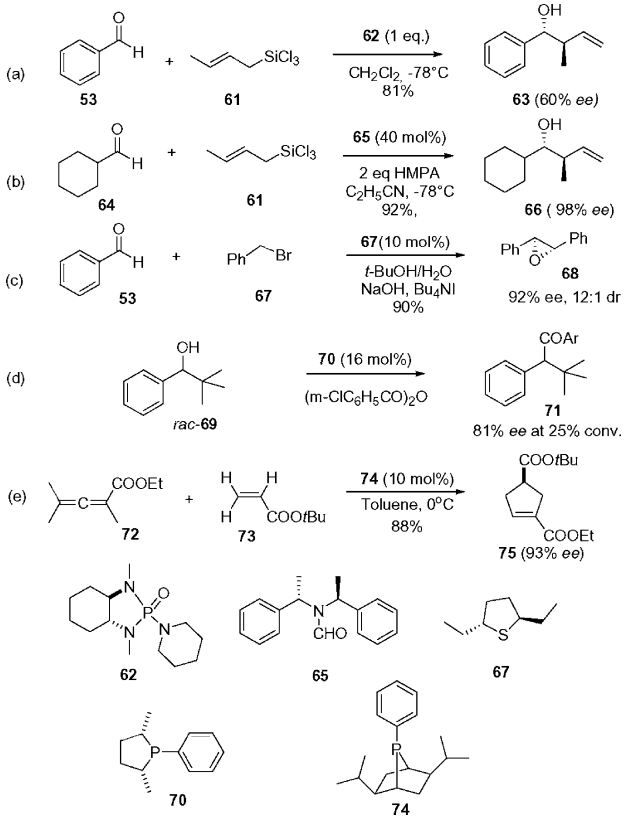
(up to 58% yield and 99% *ee*) proceeding through the formation of a 3-ammonium enolate species (Scheme 4c). Important examples of *acyl-ammonium catalysis* are acyl-transfer reactions. Fu *et al.*[32] developed planar chiral DMAP analogues such as **47** for kinetic resolutions and desymmetrizations (Scheme 4d). Miller *et al.*[33] developed peptide catalysts containing an *N*-alkylimidazole substructure that presumably form acyl imidazolium intermdediates on reaction with acetic anydride and catalyze the kinetic resolution of alcohols (Scheme 4e). Here enhanced rigidity and increased structural complexity lead to highly enantioselective catalysts.

In carbene catalysis the carbene catalyst reacts with the aldehyde forming the nucleophilic Breslow intermediate, facilitating addition to an electrophile (Scheme 2). Typical examples of carbene catalysis[34] include reactions that take advantage of umpolung aldehyde reactivity, wherein an acyl anion equivalent reacts with an electrophile *e.g.* aldehyde (benzoin condensation),[35] or an electron-deficient olefin (Stetter reaction). Enders *et al.* achieved the enantioselective benzoin condensation of aromatic aldehydes (up to 100% yield and 95% *ee*) using a *tert*-leucine-derived nucleophilic carbene catalyst **54** (Scheme 5a). Rovis and co-workers[36] reported examples of the enantioselective intramolecular Stetter reaction (Scheme 5b,c) using triazolium catalysts **57** and **60**.

Denmark *et al.*[37] and Iseki *et al.*[38] reported chiral phosphoramides (**62**) and formamides (**65**) as Lewis base catalysts for the enantioselective allylation and crotylation of aromatic and aliphatic aldehydes (Scheme 6a,b). Metzner and co-workers developed an asymmetric conversion of aldehydes to oxiranes using sulfonium ylides (Scheme 6c).[39] Vedejs *et al.*[40] reported enantioselective acylations using chiral phosphine catalysts (Scheme 6d). In another example of Lewis base catalysis, Zhang



Scheme 5 Carbenes as asymmetric organic catalysts.

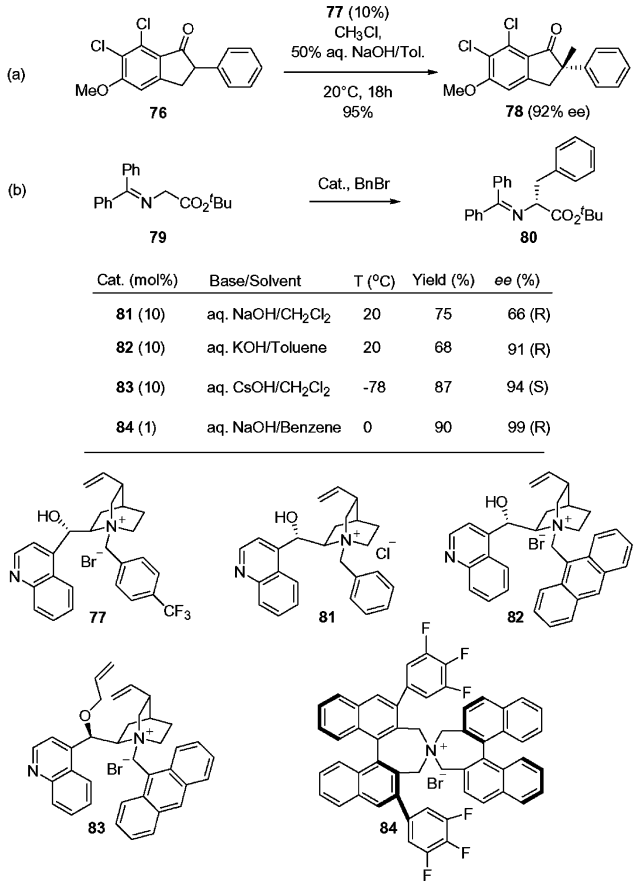


Scheme 6 Examples for O- S- and P-based chiral Lewis base catalysts.

and co-workers developed chiral phosphine catalyzed [3 + 2] cycloadditions of 2,3-butadienoates and electron-deficient olefins (up to 92% yield and 93% *ee*) (Scheme 6e).[41]

Lewis acid catalysis

An important class of organic catalysts that can be considered as Lewis acids are phase transfer catalysts. A group at Merck developed the first efficient chiral phase-transfer catalyst, *N*-benzyl cinchoninium salt **77** for the asymmetric α-methylation of indanone **76** in 95% yield and 92% *ee* (Scheme 7a).[42] Using similar cinchonine and cinchonidine catalysts, O'Donnel *et al.*[43] achieved the α-alkylation of protected glycine derivative **79** to furnish α-amino acids enantioselectively. Later on, the research groups of Lygo and Corey independently developed *N*-anthracenyl cinchonidium salts **82** and **83** as second-generation

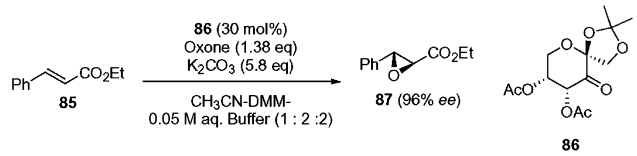


Cat. (mol%)	Base/Solvent	T (°C)	Yield (%)	*ee* (%)
81 (10)	aq. $NaOH/CH_2Cl_2$	20	75	66 (R)
82 (10)	aq. KOH/Toluene	20	68	91 (R)
83 (10)	aq. $CsOH/CH_2Cl_2$	-78	87	94 (S)
84 (1)	aq. NaOH/Benzene	0	90	99 (R)

Scheme 7 Enantioselective phase transfer catalysis.

chiral phase transfer catalysts, achieving remarkably high asymmetric inductions (up to 99.5%) in the α-alkylation of glycine derivatives.[44,45] Recently, Maruoka and co-workers developed highly efficient and enantioselective C_2-symmetric chiral spiro ammonium salt catalysts such as **84**, derived from commercially available (*S*)- or (*R*)-1,1′-bi-2-naphthol, and successfully applied them to enantioselective α-alkylations as well as aldol and Michael reactions.[46–49]

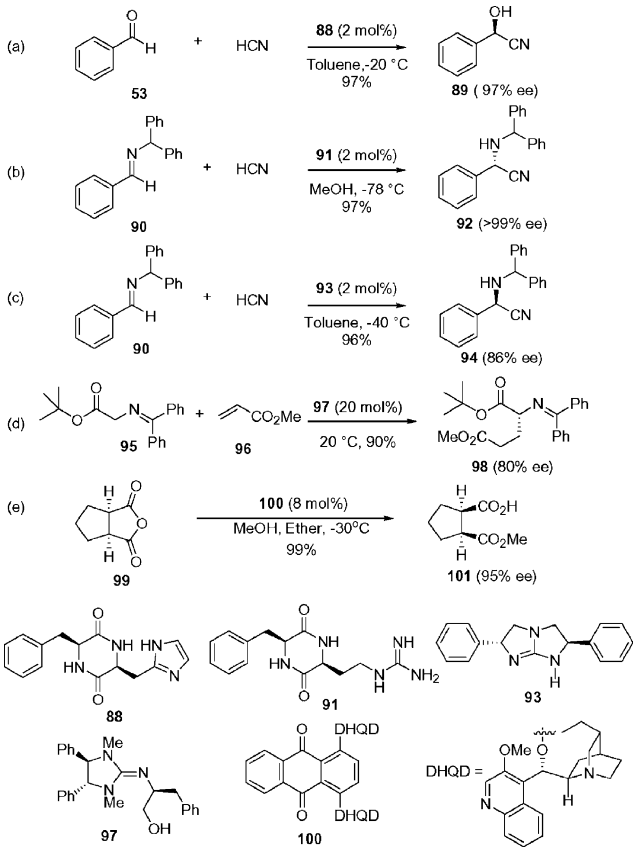
Another important example of Lewis acid catalysis is the epoxidation of olefins using chiral dioxiranes generated *in situ* from chiral ketone catalysts and Oxone (potassium peroxomonosulfate) as oxidant.[50] Shi *et al.* developed elegant D-fructose derived ketone catalysts for the enantioselective epoxidation of stilbenes,[51] α,β-unsaturated esters[52] and terminal olefins (Scheme 8).[53]



Scheme 8 A ketone-catalyzed enantioselective epoxidation of an olefin.

Brønsted base catalysis

Typical examples of organic Brønsted base catalysis in asymmetric synthesis are hydrocyanation reactions *e.g.* cyanohydrin synthesis and the Strecker reaction. Inoue and co-workers studied the addition of HCN to various aldehydes using cyclopeptide **88** as a catalyst, achieving high asymmetric inductions (Scheme 9a).[54] Lipton and co-workers used a similar cyclopeptide **91** for the Strecker reaction of various *N*-benzhydryl imines to α-aminonitriles (Scheme 9b).[55] Corey and Grogan reported the Strecker reaction using a synthetic chiral C_2-symmetric



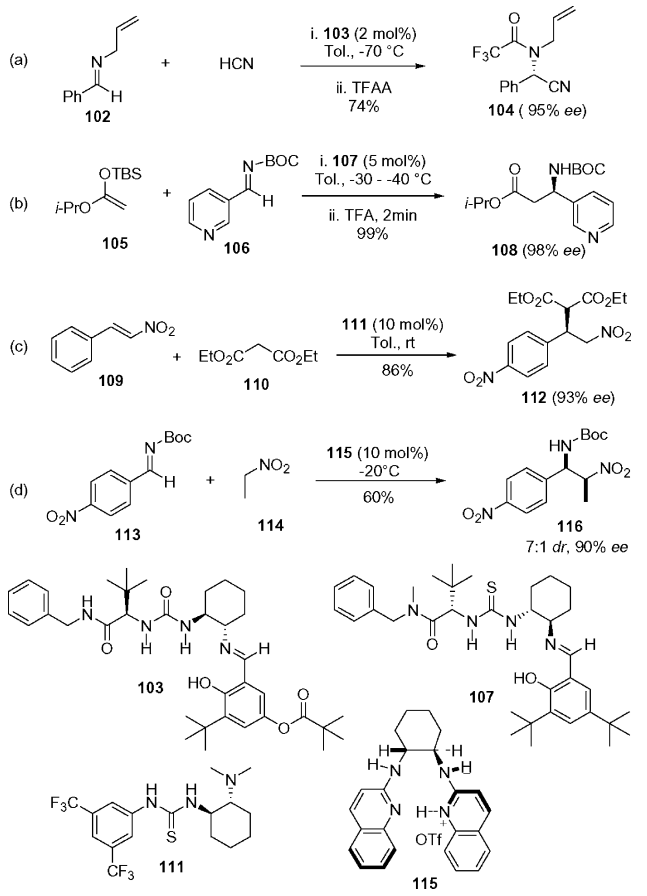
Scheme 9 Organic Brønsted base catalysis.

guanidine **93** (Scheme 9c).[56] In these cases, hydrogen cyanide interacts with the nitrogen base by hydrogen bonding to form a cyanide ion, which can then add to the carbonyl compound or the imine coordinated with the peptide/guanidine hydrogen through hydrogen bonding. Another example of Brønsted base catalysis is the Michael reaction of a prochiral glycine derivative *tert*-butyl diphenyliminoacetate in the presence of a modified guanidine **97** under solvent free conditions (Scheme 9d).[57] Deng and co-workers[58] reported the desymmetrization of cyclic *meso*-anhydrides such as **99** by alcoholysis using commercially available modified cinchona alkaloids (*e.g.* **100** (Scheme 9e). Mechanistic studies suggest that the amine catalyst operates by general base catalysis, activating the alcohol *via* hydrogen bonding for nucleophilic attack on the anhydride.

Brønsted acid catalysis

Recently, catalysis through hydrogen bonding[59] has been introduced as a powerful methodology for asymmetric catalysis. Similarly to enzymatic catalysis where H-bonding to a transition state occurs, this type of catalysis may be described as general acid catalysis.

For example, Jacobsen and co-workers developed enantioselective Strecker (Scheme 10a),[60] Mannich (Scheme 10b),[61] hydrophosphonylation,[62] and Pictet–Spengler[63] reactions of imines, using urea and thiourea catalyst-motifs. These catalysts seem to activate the imine substrate by forming hydrogen bonds from the urea hydrogens to the imine nitrogen in a bridging mode. Takemoto and co-workers demonstrated that chiral thiourea derivatives with neighboring tertiary amino groups function as bifunctional organic catalysts, activating nitro compounds for enantioselective aza-Henry[64] and Michael[65] reactions. The thiourea moiety interacts with the nitro group *via* hydrogen-bonding activation and the neighboring tertiary amino group activates the nucleophile. For example, nitroolefins react with malonates in the presence of **111**, forming the corresponding Michael adducts in up to 93% *ee* (Scheme 10c).



Scheme 10 Examples for N–H-based enantioselective Brønsted acid catalysts.

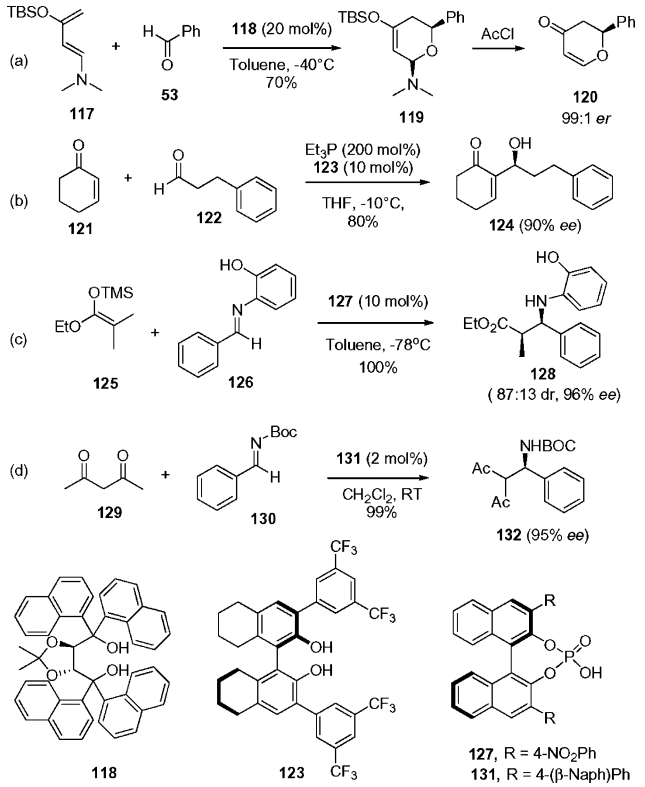
Johnston *et al.*[66] reported an enantioselective chiral proton source (containing a polar ionic hydrogen bond) as a catalyst for the aza-Henry reaction. For example, the reaction of nitroethane and the *p*-nitrobenzylimine **113** in the presence of **115** yielded the corresponding aza-Henry adduct in 90% *ee* (Scheme 10c).

Rawal and co-workers[67] discovered that chiral alcohols catalyze the enantioselective hetero-Diels–Alder reaction of aldehydes with dienes. For instance, benzaldehyde and diene **117** in the presence of the chiral alcohol (*R*,*R*)-1-naphthyl TADDOL (**118**) formed the cycloadduct **119** as a single diastereomer, which was converted to dihydropyrone **120** (99 : 1 *er*) on treatment with acetyl chloride (Scheme 11a). It is proposed that the alcohol activates the carbonyl compound *via* hydrogen bonding. McDougal and Schaus[68] reported the enantioselective asymmetric Morita–Baylis–Hillman reaction catalyzed by a chiral BINOL-derived Brønsted acid **123** (Scheme 11b). Here the Brønsted acid promotes the conjugate addition step of the reaction, and then remains hydrogen-bonded to the resulting enolate in the enantioselectivity-determining aldehyde addition step.

Japanese groups have made the very exciting discovery that even relatively strong acids can be efficient asymmetric catalysts. Very recently, Akiyama *et al.*[69] and Terada *et al.*[70] reported Mannich reactions (Scheme 11c,d) and aza-Friedel–Crafts alkylations of aldimines using chiral Brønsted acid catalysts (**127**, **131**). To stay in enzyme-catalysis terminology, this catalysis may be classified as specific acid catalysis, as protonation of the substrate is likely to be occurring.

Conclusions

Selected recent developments in the area of asymmetric organocatalysis have been summarized in this review article. We have chosen a mechanistic classification, which in our opinion helps the organization of the field, although exact mechanisms



Scheme 11 Other examples of enantioselective Brønsted acid catalysis.

are not often available. Despite its deep roots, asymmetric organocatalysis is a relatively new and explosively growing field that, without doubt, will continue to yield impressive results for some time to come.

References

1 (*a*) H. Pracejus, *Justus Liebigs Ann. Chem.*, 1960, **634**, 9–22; (*b*) H. Pracejus, *Justus Liebigs Ann. Chem.*, 1960, **634**, 23–29; (*c*) Z. G. Hajos and D. R. J. Parrish, *J. Org. Chem.*, 1974, **39**, 1615–1621; (*d*) U. Eder, G. Sauer and R. Wiechert, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 496–497.

2 (*a*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2001, **40**, 3726–3748; (*b*) A. Berkessel and H. Gröger, *Asymmetric Organocatalysis*, VCH, Weinheim, 2004.

3 (*a*) C. Allemann, R. Gordillo, F. R. Clemente, P. H.-Y. Cheong and K. N. Houk, *Acc. Chem. Res.*, 2004, **37**, 558–569; (*b*) F. R. Clemente and K. N. Houk, *Angew. Chem., Int. Ed.*, 2004, **43**, 5766–5768; (*c*) P. H.-Y. Cheong and K. N. Houk, *J. Am. Chem. Soc.*, 2004, **126**, 13912–13913; (*d*) H. Iwamura, S. P. Mathew and D. G. Blackmond, *J. Am. Chem. Soc.*, 2004, **126**, 11770–11771; (*e*) S. P. Mathew, H. Iwamura and D. G. Blackmond, *Angew Chem., Int. Ed.*, 2004, **43**, 3317–3321; (*f*) H. Iwamura, D. H. Wells, S. P. Mathew, Jr., M. Klussmann, A. Armstrong and D. G. Blackmond, *J. Am. Chem. Soc.*, 2004, **126**, 16312–16313.

4 For examples, see: (*a*) Knoevenagel reaction, review: L. F. Tietze, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon Press, New York, 1991, vol. 2, pp. 341–394.; (*b*) Diels–Alder reaction:K. A. Ahrendt, C. J. Borths and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2000, **122**, 4243–4244; (*c*) 1,3-Dipolar cycloaddition: W. S. Jen, J. J. M. Wiener and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2000, **122**, 9874–9875; (*d*) Decarboxylation:J. P. Guthrie and F. Jordan, *J. Am. Chem. Soc.*, 1972, **94**, 9136.

5 A. B. Northrup and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 2458–2460.

6 S. Karlsson and H.-E. Högberg, Tetrahedron, *Asymmetry*, 2002, **13**, 923–926.

7 N. A. Paras and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2001, **123**, 4370–4371.

8 J. F. Austin and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 1172–1173.

9 N. A. Paras and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 7894–7895.

10 S. P. Brown, N. C. Goodwin and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2003, **125**, 1192–1194.

11 (*a*) M. Yamaguchi, T. Shiraishi and M. Hirama, *J. Org. Chem.*, 1996, **61**, 3520–3530; (*b*) N. Halland, P. S. Aburel and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2003, **42**, 661–664.
12 (*a*) S. Hanessian and V. Pham, *Org. Lett.*, 2000, **2**, 2975; (*b*) N. Halland, R. G. Hazell and K. A. Jørgensen, *J. Org. Chem.*, 2002, **67**, 8331–8338.
13 (*a*) B. List, R. A. Lerner and C. F. Barbas, *J. Am. Chem. Soc.*, 2000, **122**, 2395–2396; (*b*) W. Notz and B. List, *J. Am. Chem. Soc.*, 2000, **122**, 7386–7387; (*c*) B. List, P. Pojarliev and C. Castello, *Org. Lett.*, 2001, **3**, 573–575; (*d*) S. Bahmanyar, K. N. Houk, H. J. Martin and B. List, *J. Am. Chem. Soc.*, 2003, **122**, 2475–2479; (*e*) C. Pidathala, L. Hoang, N. Vignola and B. List, *Angew. Chem., Int. Ed.*, 2003, **42**, 2785–2788.
14 (*a*) A. B. Northrup and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 6798–6799; (*b*) A. Bøgevig, N. Kumaragurubaran and K. A. Jørgensen, *Chem. Commun.*, 2002, 620–621; (*c*) N. S. Chowdari, D. B. Ramachary, A. Córdova and C. F. Barbas III, *Tetrahedron Lett.*, 2002, **43**, 9591–9595; (*d*) A. Córdova, W. Notz and C. F. Barbas III, *J. Org. Chem.*, 2002, **67**, 301; (*e*) A. Córdova, W. Notz and C. F. Barbas III, *Chem. Commun.*, 2002, 3024–3025; (*f*) Y. Sekiguchi, A. Sasaoka, A. Shimomoto, S. Fujioka and H. Kotsuki, *Synlett*, 2003, 1655–1658; (*g*) A. Bøgevig, T. B. Poulsen, W. Zhuang and K. A. Jørgensen, *Synlett*, 2003, 1915–1918.
15 (*a*) B. List, *J. Am. Chem. Soc.*, 2000, **122**, 9336–9337; (*b*) B. List, P. Pojarliev, W. T. Biller and H. J. Martin, *J. Am. Chem. Soc.*, 2002, **124**, 827; (*c*) Y. Hayashi, W. Tsuboi, M. Shoji and N. Suzuki, *J. Am. Chem. Soc*, 2003, **125**, 11208; (*d*) Y. Hayashi, W. Tsuboi, I. Ashimine, T. Urushima, M. Shoji and K. Sakai, *Angew. Chem., Int. Ed.*, 2003, **42**, 3677; (*e*) A. Córdova, *Synlett*, 2003, 1651; (*f*) W. Notz, F. Tanaka, S. Watanabe, N. S. Chaudari, J. M. Turner, R. Thayumanavan and C. F. Barbas III, *J. Org. Chem.*, 2003, **68**, 9624.
16 (*a*) B. List, P. Pojarliev and H. J. Martin, *Org. Lett.*, 2001, **3**, 2423–2425; (*b*) D. Enders and A. Seki, *Synlett*, 2002, 26–28.
17 B. List, *Acc. Chem. Res.*, 2004, **37**, 548–557.
18 B. List, *J. Am. Chem. Soc*, 2002, **124**, 5656–5657.
19 N. Kumaragurubaran, K. Juhl, W. Zhuang, A. Bøgevig and K. A. Jørgensen, *J. Am. Chem. Soc*, 2002, **124**, 6254–6255.
20 A. Bøgevig, K. Juhl, N. Kumaragurubaran, W. Zhuang and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1790–1792.
21 (*a*) S. P. Brown, M. P. Brochu, C. J. Sinz and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2003, **125**, 10808–10809; (*b*) G. Zhong, *Angew. Chem., Int. Ed.*, 2003, **42**, 4247–4250; (*c*) Y. Hayashi, J. Yamaguchi, K. Hibino and M. Shoji, *Tetrahedron Lett.*, 2003, **44**, 8293–8296.
22 (*a*) Y. Hayashi, J. Yamaguchi, T. Sumiya and M. Shoji, *Angew. Chem., Int. Ed.*, 2004, **43**, 1112–1115; (*b*) A. Bøgevig, H. Sundéen and A. Córdova, *Angew Chem., Int. Ed.*, 2004, **43**, 1109–1112.
23 N. Vignola and B. List, *J. Am. Chem. Soc.*, 2004, **126**, 450–451.
24 M. P. Brochu, S. P. Brown and D. W. C. Macmillan, *J. Am. Chem. Soc.*, 2004, **126**, 4108–4109.
25 N. Halland, A. Braunton, S. Bachmann, M. Marigo and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2004, **126**, 4790–4791.
26 M. T. Hechavarria Fonseca and B. List, *Angew. Chem., Int. Ed.*, 2004, **43**, 3958–3960.
27 M. A. Calter, R. K. Orr and W. Song, *Org. Lett.*, 2003, **5**, 4745–4748.
28 (*a*) H. Wynberg and E. G. J. Staring, *J. Am. Chem. Soc.*, 1982, **104**, 166; (*b*) H. Wynberg and E. G. J. Staring, *J. Org. Chem.*, 1985, **50**, 1977–1979.
29 (*a*) A. E. Taggi, A. M. Hafez, H. Wack, B. Young, W. J. Drury III and T. Lectka, *J. Am. Chem. Soc.*, 2000, **124**, 7831–7832; (*b*) M. H. Shah, S. France and T. Lectka, *Synlett*, 2003, 1937–1939; (*c*) S. France, A. Weatherwax, A. E. Taggi and T. Lectka, *Acc. Chem. Res.*, 2004, **37**, 592–600.
30 (*a*) N. Bremeyer, S. C. Smith, S. V. Ley and M. J. Gaunt, *Angew. Chem., Int. Ed*, 2004, **43**, 2681–2684; (*b*) C. D. Papageorgiou, M. A. C. de Dios, S. V. Ley and M. J. Gaunt, *Angew. Chem., Int. Ed.*, 2004, **43**, 4641–4644.
31 Y. Iwabuchi, M. Nakatani, N. Yokoyama and S. Hatakeyama, *J. Am. Chem. Soc.*, 1999, **121**, 10219.
32 J. C. Ruble, J. Tweddell and G. C. Fu, *J. Org. Chem.*, 1998, **63**, 2794–2795.
33 (*a*) S. J. Miller, G. T. Copeland, N. Papaioannou, T. E. Horstmann and E. M. Ruel, *J. Am. Chem. Soc.*, 1998, **120**, 1629–1630; (*b*) S. J. Miller, *Acc. Chem. Res.*, 2004, **37**, 601–610.
34 (*a*) J. S. Johnson, *Angew. Chem., Int. Ed*, 2004, **43**, 1326–1328; (*b*) D. Enders and T. Balensiefer, *Acc. Chem. Res.*, 2004, **37**, 534–541.
35 D. Enders and U. Kallfass, *Angew. Chem., Int. Ed.*, 2002, **41**, 1743–1744.
36 (*a*) M. S. Kerr, J. R. de Alaniz and T. Rovis, *J. Am. Chem. Soc.*, 2000, **124**, 10298–10299; (*b*) M. S. Kerr and T. Rovis, *Synlett*, 2003, 1934–1936.
37 S. E. Denmark, D. M. Coe, N. E. Pratt and B. D. Griedel, *J. Org. Chem.*, 1994, **59**, 6161–6163.
38 (*a*) K. Iseki, S. Mizuno, Y. Kuroki and Y. Kobayashi, *Tetrahedron Lett.*, 1998, **39**, 2767–2770; (*b*) K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto and Y. Kobayashi, *Tetrahedron*, 1997, **53**, 3513–3526; (*c*) K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto and Y. Kobayashi, *Tetrahedron Lett.*, 1996, **37**, 5149–5150.
39 (*a*) J. Zanardi, C. Leriverend, D. Aubert, K. Julienne and P. Metzner, *J. Org. Chem.*, 2001, **66**, 5620–5623; (*b*) V. K. Aggarwal and C. L. Winn, *Acc. Chem. Res*, 2004, **37**, 611–620.
40 E. Vedejs, O. Daugulis and S. T. Diver, *J. Org. Chem.*, 1996, **61**, 430–431.
41 G. Zhu, Z. Chen, Q. Jiang, D. Xiao, P. Cao and X. Zhang, *J. Am. Chem. Soc.*, 1997, **119**, 3836–3837.
42 U.-H. Dolling, P. Davis and E. J. J. Grabowski, *J. Am. Chem. Soc.*, 1984, **118**, 446–447.
43 (*a*) M. J. O'Donnell, W. D. Bennett and S. Wu, *J. Am. Chem. Soc.*, 1989, **111**, 2353–2355; (*b*) M. J. O'Donnell, *Acc. Chem. Res.*, 2004, **37**, 506–517.
44 B. Lygo and P. G. Wainwright, *Tetrahedron Lett.*, 1997, **38**, 8595–8598.
45 E. J. Corey, F. Xu and M. C. Noe, *J. Am. Chem. Soc.*, 1997, **119**, 12414–12415.
46 (*a*) K. Maruoka and T. Ooi, *Chem. Rev.*, 2003, **103**, 3013–3028; (*b*) T. Ooi and K. Maruoka, *Acc. Chem. Res.*, 2004, **37**, 526–533.
47 T. Ooi, M. Kameda and K. Maruoka, *J. Am. Chem. Soc.*, 1999, **121**, 6519.
48 (*a*) T. Ooi, M. Taniguchi, M. Kameda and K. Maruoka, *Angew. Chem., Int. Ed.*, 2002, **41**, 4542–4544; (*b*) T. Ooi, K. Doda and K. Maruoka, *J. Am. Chem. Soc.*, 2003, **125**, 2054.
49 T. Ooi, K. Doda and K. Maruoka, *J. Am. Chem. Soc.*, 2003, **125**, 9022–9023.
50 (*a*) R. Curci, M. Fiorentino and M. R. Serio, *J. Chem. Soc., Chem. Commun.*, 1984, 155–156; (*b*) R. Curci, L. D'Accolti, M. Fiorentino and A. Rosa, *Tetrahedron Lett.*, 1995, **36**, 5831–5834; (*c*) S. E. Denmark, D. C. Forbes, D. S. Hays, J. S. DePue and R. G. Wilde, *J. Org. Chem.*, 1995, **60**, 1391; (*d*) Y. Shi, *Acc. Chem. Res.*, 2004, **37**, 488–496; (*e*) D. Yang, *Acc. Chem. Res.*, 2004, **37**, 497–505.
51 (*a*) Y. Tu, Z.-X. Wang and Y. Shi, *J. Am. Chem. Soc.*, 1996, **118**, 9806–9807; (*b*) Z.-X. Wang, Y. Tu, M. Frohn and Y. Shi, *J. Org. Chem.*, 1997, **62**, 2328–2329.
52 X.-Y. Wu, X. She and Y. Shi, *J. Am. Chem. Soc.*, 2002, **124**, 8792–8793.
53 H. Tian, X. She, J. Xu and Y. Shi, *Org. Lett.*, 2001, **3**, 1929–1931.
54 K. Tanaka, A. Mori and S. Inoue, *J. Org. Chem.*, 1990, **55**, 181–185.
55 M. S. Iyer, K. M. Gigstad, N. D. Namdev and M. Lipton, *J. Am. Chem. Soc.*, 1996, **118**, 4910–4911.
56 E. J. Corey and M. J. Grogan, *Org. Lett.*, 1999, **1**, 157–160.
57 T. Ishikawa, Y. Araki, T. Kumamoto, H. Seki, K. Fukuda and T. Isobe, *Chem. Commun.*, 2002, 245–246.
58 (*a*) Y. Chen, S.-K. Tian and L Deng, *J. Am. Chem. Soc.*, 2000, **122**, 9542–9543; (*b*) S.-K. Tian, Y. Chen, J. Hang, L. Tang, P. Mcdaid and L. Deng, *Acc. Chem. Res*, 2004, **37**, 621–631.
59 (*a*) P. R. Schreiner, *Chem. Soc. Rev.*, 2003, **32**, 289–296; (*b*) P. M. Pihko, *Angew. Chem., Int. Ed.*, 2004, **43**, 2062–2064.
60 (*a*) M. S. Sigman and E. N. Jacobsen, *J. Am. Chem. Soc.*, 1998, **120**, 4901–4902; (*b*) M. S. Sigman, P. Vachal and E. N. Jacobsen, *Angew. Chem.*, 2000, **112**, 1336–1338.
61 A. G. Wenzel and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 12964–12965.
62 G. D. Joly and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 4102–4103.
63 M. S. Taylor and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 10558–10559.
64 T. Okino, S. Nakamura, T. Furukawa and Y. Takemoto, *Org. Lett.*, 2004, **6**, 625–627.
65 T. Okino, Y. Hoashi and Y. Takemoto, *J. Am. Chem. Soc.*, 2003, **125**, 12672–12673.
66 B. M. Nugent, R. A. Yoder and J. N. Johnston, *J. Am. Chem. Soc.*, 2004, **126**, 3418–3419.
67 Y. Huang, A. K. Unni, A. N. Thadani and V. H. Rawal, *Nature*, 2003, **424**, 146.
68 N. T. McDougal and S E. Schaus, *J. Am. Chem. Soc.*, 2003, **125**, 12094–12095.
69 T. Akiyama, J. Itoh, K. Yokota and K. Fuchibe, *Angew. Chem.*, 2004, **116**, 1592–1594.
70 (*a*) D. Uraguchi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356–5357; (*b*) D. Uraguchi, K. Sorimachi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356–5357.