ROYAL SOCIETY OF CHEMISTRY

Check for updates

Asymmetric synthesis of polysubstituted methylenecyclobutanes *via* catalytic [2+2] cycloaddition reactions of *N*-allenamides†

Xia Zhong, Qiong Tang, Pengfei Zhou, Ziwei Zhong, Shunxi Dong, * Xiaohua Liu and Xiaoming Feng *
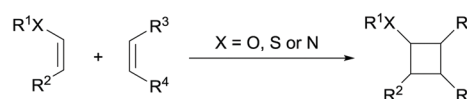
A highly enantioselective [2+2] cycloaddition reaction of alkylidene malonates with the internal C=C bond of *N*-allenamides was developed with a Mg^{II}/*N*,*N*′-dioxide complex as a catalyst. Various polysubstituted methylenecyclobutanes were afforded in good yields (up to 99%) and excellent enantioselectivities (up to 96% ee) under mild conditions. The utility of the donor–acceptor cyclobutane product was demonstrated as a masked 1,4-dipole in the formal [4+2] annulation reaction with a silyl enol ether.

Cyclobutanes are not only important structural motifs in numerous biologically significant molecules, but also used as key intermediates for the synthesis of many bioactive compounds and drugs.[1] Among them, heteroatom-substituted cyclobutanes, and in particular the *N*-substituted ones, have received much attention. The introduction of aminocyclobutanes into peptides resulted in foldamers with interesting properties ranging from cell-penetrating agents to low-molecular-weight gelators.[2] On the other hand, heteroatom-substituted cyclobutanes bearing electron-donating and withdrawing groups could serve as masked 1,4-dipoles in cycloaddition reactions.[3] Regarding the methods for the construction of heteroatom-substituted cyclobutanes, the most efficient one is the [2+2] cycloaddition reaction (Scheme 1a). In the past several decades, the synthesis of heteroatom-substituted cyclobutanes *via* [2+2] cycloaddition were achieved successfully using photocatalysts, Lewis acids, amine-catalysts or transition metal catalysts.[4] However, compared with the well-established chiral alkoxy[5] and alkyl sulphanyl[6] substituted cyclobutanes, the synthetic strategies of enantioenriched amino-cyclobutanes were mainly focused on photocatalysis,[7] and other routes are rare.[8]
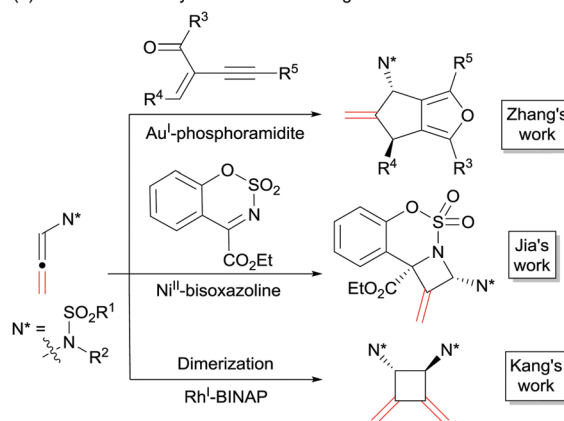
Due to the presence of the electron-withdrawing group on nitrogen, *N*-allenamides show higher stability than the

corresponding allenamines. In the past two decades, *N*-allenamides have been employed as versatile reagents in organic synthesis.[9] In *N*-allenamides, the delocalization of the nitrogen lone pair toward the allenic moiety creates an electronic bias, leading to consecutive addition of electrophiles and nucleophiles in a highly regioselective manner. The impressive examples of such elegant transformations are cycloaddition reactions, in which either the terminal C=C or internal C=C bond could participate, leading to a diverse array of carbo- and heterocyclic structures. Highly enantioselective cycloaddition
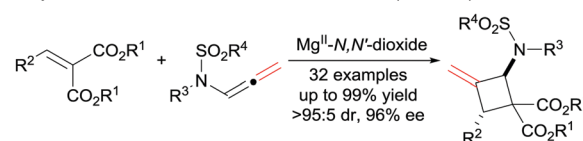

Scheme 1 The synthesis of heteroatom-substituted cyclobutanes and cycloaddition reactions of internal C=C of *N*-allenamides.

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, P. R. China. E-mail: xmfeng@scu.edu.cn, dongs@scu.edu.cn; Fax: +86 28 85418249; Tel: +86 28 85418249

reactions involving the terminal C≡C bond were well studied.[10] In contrast, only a few of the reactions occurring at the internal C≡C bond have been established in the asymmetric version to date. In 2015, Zhang and co-workers described the asymmetric formal [3+2] cycloaddition reaction of 2-(1-alkynyl)-2-alken-1-ones with the internal C≡C bond of N-allenamides using Au[I]-chiral phosphoramidite as the catalyst.[11a] Last year, an asymmetric [2+2] reaction of ketimines with the internal C≡C bond of N-allenamides was realized by Jia et al. in the presence of Ni[II]-chiral bisoxazoline (Scheme 1b).[11b] Recently, the group of Kang developed the internal C≡C bond involved asymmetric dimerization of N-allenamides in the presence of Rh[I]-BINAP.[11c] In addition, an elegant intramolecular [2+2] cycloaddition reaction of alkenes with the internal C≡C bond of N-allenamide was disclosed by Arisawa in 2016.[12] Herein, we disclose a highly enantioselective intermolecular [2+2] cyclo-addition reaction, providing a direct access to amino-substituted methylenecyclobutanes[13] with a Mg(OTf)$_2$/N,N'-dioxide complex as the catalyst.[14] Diverse ranges of functionalized aminocyclo-butanes were obtained in moderate to good yields with excellent diastereo- and enantioselectivities (Scheme 1c).

The optimization of the reaction conditions was carried out by taking the reaction of alkylidene malonate (**1a**) and N-allenamide (**2a**) as the model reaction. Initially, identification of the metal salts indicated that Mg(OTf)$_2$ exhibited higher activity than other metal salts in the presence of chiral N,N'-dioxide **L-PrPr$_2$** (for details, see the ESI†). The desired product **3a** was obtained in 18% yield with a moderate ee value (46% ee). Subsequently, various chiral N,N'-dioxide ligands complexing with Mg(OTf)$_2$ were evaluated, suggesting that **L-PiPr$_2$** was superior to **L-PrPr$_2$** and **L-RaPr$_2$** in terms of enantioselectivities (Table 1, entries 1–3). Changing the 2,6-diisopropylaniline moiety to 2,4,6-trimethylaniline provided better results (65% yield, 75% ee; Table 1, entry 4). After careful screening of the solvents, CH$_2$ClCH$_2$Cl was proved to be the best choice, and the cyclo-addition product can be obtained 63% yield with 77% ee (Table 1, entry 5). To our delight, the reactivity and enantio-selectivity of the reaction increased with the addition of NaBAr$^F_4$ as an additive, which was proposed to be used for exchanging the counterion (80% yield and 79% ee; Table 1, entry 6).[15] Lowering the temperature to 20 °C and switching the alkylidene malonate **1a** to **1d** gained further improvement (86% yield and 90% ee; Table 1, entries 7 and 8). Finally, 99% yield was afforded when 2.0 equivalents of **2a** were used (Table 1, entry 9).

With the optimized reaction conditions in hand (Table 1, entry 9), the scope of alkylidene malonates **1** was investigated by reacting with N-allenamide **2a** (Table 2). Both reactivities and enantioselectivities gradually reduced with the increase of steric hindrance of the ester group (Table 2, entries 1–3). The positions of substituents on the phenyl ring in alkylidene malonates **1** showed a significant influence on the results (Table 2, entries 4–15). Generally, alkylidene malonates **1e**−**j** bearing para-substituents regardless of electron-donating and electron-withdrawing groups are all tolerated well, providing the desired products in high yields and ee values (92–99% yield, 92–95% ee; Table 2, entries 4–9). The reaction with **1g** was performed on a

Table 1 Optimization of the reaction conditions[a]

Entry	Ligand	Solvent	Yield[b] (%)	ee[c] (%)
1	**L-PrPr$_2$**	CH$_2$Cl$_2$	18	46
2	**L-RaPr$_2$**	CH$_2$Cl$_2$	53	23
3	**L-PiPr$_2$**	CH$_2$Cl$_2$	29	47
4	**L-PiMe$_3$**	CH$_2$Cl$_2$	65	75
5	**L-PiMe$_3$**	CH$_2$ClCH$_2$Cl	63	77
6[d]	**L-PiMe$_3$**	CH$_2$ClCH$_2$Cl	80	79
7[de]	**L-PiMe$_3$**	CH$_2$ClCH$_2$Cl	80	85
8[def]	**L-PiMe$_3$**	CH$_2$ClCH$_2$Cl	86	90
9[defg]	**L-PiMe$_3$**	CH$_2$ClCH$_2$Cl	99	90

[a] Unless otherwise noted, all reactions were performed with ligand (10 mol%), Mg(OTf)$_2$ (10 mol%), **1a** (0.10 mmol) and **2a** (0.10 mmol) in solvent (1.0 mL) at 35 °C under N$_2$ for 48 h. The dr values (>95:5) were determined via ^{1}H NMR of the crude mixture. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] NaBAr$^F_4$ {NaB[3,5-(F$_3$C)$_2$C$_6$H$_3$]$_4$} (20 mol%) was added as an additive. [e] At 20 °C for 48 h. [f] **1d** (0.10 mmol) was used instead of **1a**. [g] 0.20 mmol of **2a** was used.

gram scale and obtained comparable results (1.02 g, 92% yield and 95% ee, Table 2, entry 6). The meta-substituted ones displayed similar reactivities but the ee values of the products **3k–3m** decreased slightly (70–99% yield, 85–89% ee; Table 2, entries 10–12), and the 3,4-disubstituted alkylidene malonate afforded comparable results (Table 2, entry 13). In contrast, a sharp decrease in both reactivities and enantioselectivities was observed for ortho-substituted substrates (Table 2, entries 14 and 15). Pleasingly, the reaction of fused-ring-substituted alkylidene malonate proceeded well, and the adduct **3q** was isolated in 99% yield with 88% ee (Table 2, entry 16). Moreover, the heteroaromatic cycle derived ones also performed the reaction with moderate ee values (58–98% yield, 51–84% ee, Table 2, entries 17–20). It should be noted that only one of the diastereomers was detected in all of these cases. To our delight, the catalyst system was also effective for aliphatic substrates, affording excellent enantioselectivities (93–96% ee) and high diastereoselectivities (85:15–92:8 dr; Table 2, entries 21–24). Interestingly, cinnamyl-substituted alkylidene malonate was also suitable with high regioselectivity (Table 2, entry 25).

Then, various substituted N-allenamides were examined. As shown in Table 3, N-allenamides with different substituents were applicable, giving the corresponding products in 85–99% yield and 88–91% ee (Table 3, entries 1–6). The absolute con-figuration of compound **4d** was determined to be (2R, 4R) by X-ray single crystallographic analysis.[16]

Table 2 Substrate scope of the alkylidene malonates 1^a

| Entry	R^1/R^2	Yield (%)	dr	ee (%)
1	Me/Ph (**3a**)	99	>95:5	87
2	Et/Ph (**3b**)	95	>95:5	87
3	^{i}Pr/Ph (**3c**)	31	>95:5	67
4	Bn/4-FC$_6$H$_4$ (**3e**)	94	>95:5	93
5	Bn/4-ClC$_6$H$_4$ (**3f**)	99	>95:5	95
6^b	Bn/4-BrC$_6$H$_4$ (**3g**)	99 (92)	>95:5	95 (95)
7	Bn/4-MeC$_6$H$_4$ (**3h**)	93	>95:5	93
8	Bn/4-^{i}PrC$_6$H$_4$ (**3i**)	92	>95:5	92
9	Bn/4-PhC$_6$H$_4$ (**3j**)	98	>95:5	92
10	Bn/3-ClC$_6$H$_4$ (**3k**)	99	>95:5	87
11	Bn/3-BrC$_6$H$_4$ (**3l**)	99	>95:5	89
12	Bn/3-MeC$_6$H$_4$ (**3m**)	70	>95:5	85
13	Bn/3,4-Me$_2$C$_6$H$_3$ (**3n**)	91	>95:5	84
14	Bn/2-ClC$_6$H$_4$ (**3o**)	52	>95:5	39
15	Bn/2-MeC$_6$H$_4$ (**3p**)	32	>95:5	48
16	Bn/2-naphthyl (**3q**)	99	>95:5	88
17	Bn/2-thienyl (**3r**)	86	>95:5	74
18	Bn/2-benzothienyl (**3s**)	98	>95:5	84
19	Bn/2-furanyl (**3t**)	58	>95:5	51
20	Bn/2-benzofuranyl (**3u**)	92	>95:5	67
21^c	Bn/^{i}Pr (**3v**)	95	89:11	96
22^c	Bn/cyclohexyl (**3w**)	83	85:15	96
23^c	Bn/^{i}Bu (**3x**)	86	92:8	92
24^c	Bn/^{n}Bu (**3y**)	57	92:8	93
25^c	Bn/Ph⌒ (**3z**)	49	91:9	88

^{a} Reaction conditions are identical to those in entry 9 of Table 1. ^{b} The value in parentheses was obtained when conducted on a gram scale (1.5 mmol of **1g**). ^{c} Carried out with **L-PiEt$_2$Me** (10 mol%) in CHCl$_2$CHCl$_2$ (1.0 mL) for 48 h.

Table 3 Substrate scope of the N-allenamides 2^a

Entry	R^3/R^4	Yield (%)	ee (%)
1	Ph/Ph (**4a**)	95	90
2	Ph/4-MeOC$_6$H$_4$ (**4b**)	99	90
3	Ph/4-^{t}BuC$_6$H$_4$ (**4c**)	99	90
4	Ph/Me (**4d**)	85	91 (2R, 4R)
5	Ph/1-naphthyl (**4e**)	98	88
6	4-MeC$_6$H$_4$/4-MeC$_6$H$_4$ (**4f**)	99	91

^{a} Reaction conditions are identical to those in entry 9 of Table 1.

To evaluate the practicality of this catalytic system, the reduction of **3a** with LiAlH$_4$ generated the 1,3-diol derivative **5**, which can be reduced continuously to the compound **6** in excellent yield with high diastereoselectivity (Scheme 2a). In addition, the product **3a** was successfully used as a masked 1,4-dipole in the [4+2] annulation reaction with silyl enol ether **7** in the presence of SnCl$_4$ (Scheme 2b), and the products **8a** and
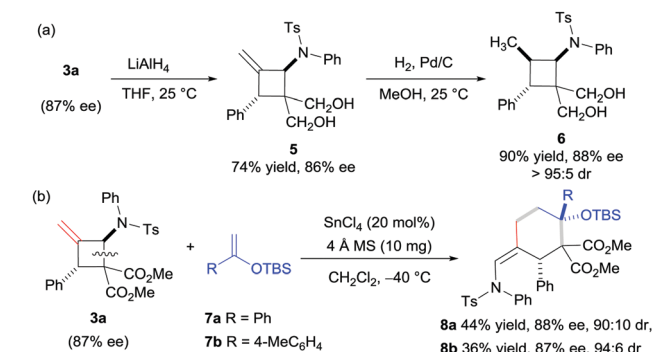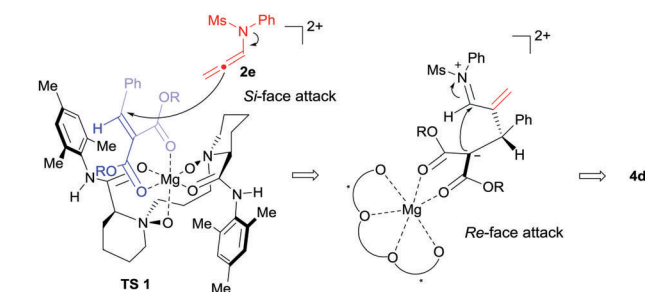
Scheme 2 Transformation of the products.

Fig. 1 Proposed transition state model.

8b were obtained in moderate yields and high diastereoselectivities along with a maintained ee value (for the proposed mechanism, see the ESI†). The relative configuration of compound **8a** was assigned via X-ray single crystallographic analysis.[16]

Based on the previous work[14] and the absolute configuration of the product **4d**, a possible transition state model was proposed to elucidate the origin of chiral induction in the [2+2] cycloaddition reaction. As shown in Fig. 1, chiral N,N'-dioxide and alkylidene malonate **1d** coordinated to Mg^{II} in tetradentate and bidentate fashions respectively to form a slightly distorted hexahedral complex. The Re-face of the substrate **1d** was shielded by the substituted aniline group on the ligand. Consequently, N-allenamide **2e** approached from the Si-face of the substrate to form the zwitterionic intermediate, which subsequently underwent cyclization from the Re-face of the imine moiety to afford **4d**.

In summary, we have developed a chiral Mg^{II}/N,N'-dioxide catalyst system to realize the asymmetric [2+2] cycloaddition of alkylidene malonates with the proximal C=C bond of N-allenamides. A wide range of aminocyclobutanes was obtained in moderate to excellent yields (up to 99%) with excellent ee values (up to 96% ee). The utility of the product was demonstrated as a masked 1,4-dipole in highly diastereoselective cycloaddition with silyl enol ether **7**. Furthermore, a possible transition state mode was proposed to explain the origin of the chiral induction.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews, see: (*a*) E. Lee-Ruff and G. Mladenova, *Chem. Rev.*, 2003, **103**, 1449; (*b*) V. M. Dembitsky, *Phytomedicine*, 2014, **21**, 1559; (*c*) J.-P. Deprés, P. Delair, J.-F. Poisson, A. Kanazawa and A. E. Greene, *Acc. Chem. Res.*, 2016, **49**, 252. For select examples, see: (*d*) K. Tanino, M. Takahashi, Y. Tomata, H. Tokura, T. Uehara, T. Narabu and M. Miyashita, *Nat. Chem.*, 2011, **3**, 484; (*e*) X.-K. Kuang, J. Zhu, L. Zhou, L. Wang, S. R. Wang and Y. Tang, *ACS Catal.*, 2018, **8**, 4991.

2 For select examples on aminocyclobutanes as amino acids, see: (*a*) G. Jiménez-Osés, F. Corzana, J. H. Busto, M. Pérez-Fernández, J. M. Peregrina and A. Avenoza, *J. Org. Chem.*, 2006, **71**, 1869; (*b*) A. Fetnández-Tejada, F. Corzana, J. H. Busto, G. Jiménez-Osés, J. M. Peregrina and A. Avenoza, *Chem. – Eur. J.*, 2008, **14**, 7042; (*c*) E. Gorrea, P. Nolis, E. Torres, E. D. Silva, D. B. Amabilino, V. Branchadell and R. M. Ortuño, *Chem. – Eur. J.*, 2011, **17**, 4588; (*d*) A. Sorrenti, O. Illa, R. Pons and R. M. Ortuño, *Langmuir*, 2015, **31**, 9608; (*e*) M. Alauddin, E. Gloaguen, V. Brenner, B. Tardivel, M. Mons, A. Zehnacker-Rentien, V. Declerck and D. J. Aitken, *Chem. – Eur. J.*, 2015, **21**, 16479; (*f*) A. Sorrenti, O. Illa, R. M. Ortuño and R. Pons, *Langmuir*, 2016, **32**, 6977.

3 For selected reviews on cyclobutanes as 1,4-dipoles, see: (*a*) F. de Nanteuil, F. De Simone, R. Frei, F. Benfatti, E. Serrano and J. Waser, *Chem. Commun.*, 2014, **50**, 10912; (*b*) H.-U. Ressig and R. Zimmer, *Angew. Chem., Int. Ed.*, 2015, **54**, 5009; (*c*) N. Vemula and B. L. Pagenkopf, *Org. Chem. Front.*, 2016, **3**, 1205. For select examples, see: (*d*) A. Levens, A. Ametovski and D. W. Lupton, *Angew. Chem., Int. Ed.*, 2016, **55**, 16136; (*e*) L. K. B. Garve, A. Kreft, P. G. Jones and D. B. Werz, *J. Org. Chem.*, 2017, **82**, 9235; (*f*) L.-W. Feng, H. Ren, H. Xiong, P. Wang, L. Wang and Y. Tang, *Angew. Chem., Int. Ed.*, 2017, **56**, 3055; (*g*) J.-L. Hu, L. Zhou, L. Wang, Z. Xie and Y. Tang, *Chin. J. Chem.*, 2018, **36**, 47.

4 For reviews, see: (*a*) F. Secci, A. Frongia and P. P. Piras, *Molecules*, 2013, **18**, 15541; (*b*) Y. Xu, M. L. Conner and M. K. Brown, *Angew. Chem., Int. Ed.*, 2015, **54**, 11918; (*c*) S. Poplata, A. Tröster, Y.-Q. Zou and T. Bach, *Chem. Rev.*, 2016, **116**, 9748. For examples, see: (*d*) B. Brown and L. S. Hegedus, *J. Org. Chem.*, 1998, **63**, 8012; (*e*) A. Avenoza, J. H. Busto, N. Canal, J. M. Peregrina and M. Pérez-Fernández, *Org. Lett.*, 2005, **7**, 3597; (*f*) A. Avenoza, J. H. Busto, L. Mata, J. M. Peregrina and M. Pérez-Fernández, *Synthesis*, 2008, 743; (*g*) A. Avenoza, J. H. Busto, N. Canal, F. Corzana, J. M. Peregrina, M. Pérez-Fernández and F. Rodríguez, *J. Org. Chem.*, 2010, **75**, 545; (*h*) F. de Nanteuil and J. Waser, *Angew. Chem., Int. Ed.*, 2013, **52**, 9009; (*i*) Z. Dobi, T. Holczbauer and T. Soós, *Eur. J. Org. Chem.*, 2017, 1391.

5 (*a*) E. Canales and E. J. Corey, *J. Am. Chem. Soc.*, 2007, **129**, 12686; (*b*) R. Brimioulle and T. Bach, *Angew. Chem., Int. Ed.*, 2014, **53**, 12921; (*c*) F. Yagishita, N. Takagishi, H. Ishikawa, Y. Kasashima, T. Mino and M. Sakamoto, *Eur. J. Org. Chem.*, 2014, 6366; (*d*) S. C. Coote, A. Pöthig and T. Bach, *Chem. – Eur. J.*, 2015, **21**, 6906; (*e*) K. L. Skubi, J. B. Kidd, H. Jung, I. A. Guzei, M.-H. Baik and T. P. Yoon, *J. Am. Chem. Soc.*, 2017, **139**, 17186.

6 (*a*) Y. Hayashi and K. Narasaka, *Chem. Lett.*, 1989, 793; (*b*) K. Narasaka, Y. Hayashi, H. Shimadzu and S. Niihata, *J. Am. Chem. Soc.*, 1992, **114**, 8869; (*c*) K. Narasaka, K. Hayashi and Y. Hayashi, *Tetrahedron*, 1994, **50**, 4529.

7 (*a*) S. C. Coote and T. Bach, *J. Am. Chem. Soc.*, 2013, **135**, 14948; (*b*) R. Brimioulle and T. Bach, *Science*, 2013, **342**, 840; (*c*) R. Brimioulle, A. Bauer and T. Bach, *J. Am. Chem. Soc.*, 2015, **137**, 5170; (*d*) H. Wang, X. Cao, X. Chen, W. Fang and M. Dolg, *Angew. Chem., Int. Ed.*, 2015, **54**, 14295; (*e*) A. Tröster, R. Alonso,

A. Bauer and T. Bach, *J. Am. Chem. Soc.*, 2016, **138**, 7808; (*f*) C. Wang and Z. Lu, *Org. Lett.*, 2017, **19**, 5888.

8 For selected examples on the asymmetric synthesis by other methods, see: (*a*) L. Ghosez, F. Mahuteau-Betzer, C. Genicot, A. Vallribera and J.-F. Cordier, *Chem. – Eur. J.*, 2002, **8**, 3411; (*b*) F. Mahuteau-Betzer and L. Ghosez, *Tetrahedron*, 2002, **58**, 6991; (*c*) D. J. Aitken, P. Caboni, H. Eijsberg, A. Frogia, R. Guillot, J. Ollivier, P. P. Piras and F. Secci, *Adv. Synth. Catal.*, 2014, **356**, 941; (*d*) N. Melis, L. Ghisu, R. Guillot, P. Caboni, F. Secci, D. J. Aitken and A. Frongia, *Eur. J. Org. Chem.*, 2015, 4358.

9 (*a*) L.-L. Wei, H. Xiong and R. P. Hsung, *Acc. Chem. Res.*, 2003, **36**, 773; (*b*) T. Lu, Z. Lu, Z.-X. Ma, Y. Zhang and R. P. Hsung, *Chem. Rev.*, 2013, **113**, 4862; (*c*) M. R. Fructos and A. Prieto, *Tetrahedron*, 2016, **72**, 355; (*d*) E. Manoni and M. Bandini, *Eur. J. Org. Chem.*, 2016, 3135.

10 For selected examples of asymmetric cycloaddition of the terminal C=C bond of *N*-allenamides: (*a*) S. Suárez-Pantiga, C. Hernández-Díaz, E. Rubio and J. M. González, *Angew. Chem., Int. Ed.*, 2012, **51**, 11552; (*b*) J. Francos, F. Grande-Carmona, H. Faustino, J. Iglesias-Sigüenza, E. Díez, I. Alonso, R. Fernández, J. M. Lassaletta, F. López and J. L. Mascareñas, *J. Am. Chem. Soc.*, 2012, **134**, 14322; (*c*) G.-H. Li, W. Zhou, X.-X. Li, Q.-W. Bi, Z. Wang, Z.-G. Zhao, W.-X. Hu and Z. Chen, *Chem. Commun.*, 2013, **49**, 4770; (*d*) H. Faustino, I. Alonso, J. L. Mascareñas and F. López, *Angew. Chem., Int. Ed.*, 2013, **52**, 6526; (*e*) M. Jia, M. Monari, Q.-Q. Yang and M. Bandini, *Chem. Commun.*, 2015, **51**, 2320; (*f*) Y. Wang, P. Zhang, Y. Liu, F. Xia and J. Zhang, *Chem. Sci.*, 2015, **6**, 5564; (*g*) H. Hu, Y. Wang, D. Qian, Z.-M. Zhang, L. Liu and J. Zhang, *Org. Chem. Front.*, 2016, **3**, 759; (*h*) I. Varela, H. Faustino, E. Díez, J. Iglesias-Sigüenza, F. Grande-Carmona, R. Fernández, J. M. Lassaletta, J. L. Mascareñas and F. López, *ACS Catal.*, 2017, **7**, 2397; (*i*) V. Pirovano, M. Borri, G. Abbiat, S. Rizzato and E. Rossi, *Adv. Synth. Catal.*, 2017, **359**, 1912.

11 Enantioselective cycloaddition involving the internal C=C bond of *N*-allenamides: (*a*) Y. Wang, P. Zhang, D. Qian and J. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 14849; (*b*) R.-R. Liu, J.-P. Hu, J.-J. Hong, C.-J. Lu, J.-R. Gao and Y.-X. Jia, *Chem. Sci.*, 2017, **8**, 2811; (*c*) W.-F. Zheng, G.-J. Sun, L. Chen and Q. Kang, *Adv. Synth. Catal.*, 2018, **360**, 1790.

12 T. Nada, Y. Yoneshige, Y. Li, T. Matsumoto, H. Fujioka, S. Shuto and M. Arisawa, *ACS Catal.*, 2016, **6**, 3168.

13 For a review of methylenecyclobutane, see: A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2014, **114**, 7317.

14 For reviews on chiral *N*,*N*′-dioxides, see: (*a*) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574; (*b*) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.*, 2014, **1**, 298; (*c*) X. H. Liu, H. F. Zheng, Y. Xia, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2017, **50**, 2621; (*d*) X. H. Liu, S. X. Dong, L. L. Lin and X. M. Feng, *Chin. J. Chem.*, 2018, **36**, 791; (*e*) X. M. Feng, Z. Wang and X. H. Liu, Chiral Lewis Acid Rare-Earth Metal Complexes in Enantioselective Catalysis, in *Chiral Lewis Acids Top. Organomet. Chem.*, ed. K. Mikami, Springer, 2017, vol. 62, p. 147.

15 The BAr$^F_4$$^−$ ion might act as a large and noncoordinating counterion in the reaction. For a review, see: (*a*) I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066. For selected examples using BAr$^F_4$ as a counterion, see: (*b*) W.-J. Shi, Q. Zhang, J.-H. Xie, S.-F. Zhu, G.-H. Hou and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 2780; (*c*) B. Liu, S.-F. Zhu, W. Zhang, C. Chen and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 5834; (*d*) X. H. Zhao, X. H. Liu, H. J. Mei, J. Guo, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2015, **54**, 4032.

16 CCDC 1831461 (**4d**) and CCDC 1848226 (*rac*-**8a**), ESI†.