Organocatalysis

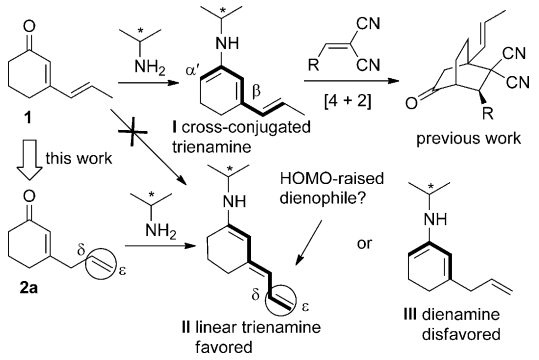
DOI: 10.1002/ange.201307460

Trienamines Derived from Interrupted Cyclic 2,5-Dienones: Remote δ,ε-C=C Bond Activation for Asymmetric Inverse-Electron-Demand Aza-Diels–Alder Reaction**

Xin Feng, Zhi Zhou, Chao Ma, Xiang Yin, Rui Li, Lin Dong, and Ying-Chun Chen**

A special challenge in the field of asymmetric catalysis is the realization of remote stereocontrol.[1] The problem can be extended to remote sites which must be activated to ensure better reactivity. While most early examples of remote asymmetric inductions rely on enzyme catalysis or intramolecular relay of chiral information through the substrate,[2] current studies have demonstrated that chiral catalysts can facilitate enantioselectivity in variety of reactions.[3] In particular, our group and the group of Jørgensen found that the well-established enamine chemistry of saturated carbonyl compounds could be expanded to polyconjugated 2,4-dienals based on the principle of vinylogy,[4] thus leading to the remote ε-site activation and still allowing highly stereoselective cycloadditions at β,ε-sites of in situ formed linear trienamine intermediates.[5] Moreover, such an activation mode was successfully applied to 2,4-dienone analogues. Unfortunately, it was not possible to utilize 2,4-dienones with an enolizable α′-alkyl substitution because the cross-conjugated trienamine species were preferably generated.[6]

In fact, we also found that the cyclic 2,4-dienone **1** would predominantly generate the cross-conjugated trienamine **I**, catalyzed by a primary amine, and then react with a dienophile by a α′,β-regioselective [4+2] annulation pathway (Scheme 1).[7] To overcome the inherent preference for the formation of cross-conjugated trienamines from 2,4-dienones bearing an enolizable α′-alkyl group, we envisaged that an appropriately positioned δ,ε-C=C bond, as shown for the interrupted 3-allyl cyclohexen-2-one **2a** (Scheme 1), would induce the generation of the desired polyconjugated linear trienamine **II**, rather than the dienamine[8] **III** which has a higher energy.[9] Thus, the electron-donating effects of the amine could be transmitted through the conjugated π system,



Scheme 1. Strategy for the formation of linear trienamine intermediate.

and raise the HOMO energy of the remote δ,ε-C=C group to participate in asymmetric reactions.

Based on the above considerations, we initially investigated the reaction of the 2,5-dienone **2a** and the 1-azadiene **3a**, containing a 1,2-benzoisothiazole-1,1-dioxide moiety,[10] in the presence of 9-amino-9-deoxyepiquinidine (**C1**) and benzoic acid (**A1**).[11] To our gratification, the reaction proceeded smoothly in toluene at 35 °C, and the inverse-electron-demand aza-Diels–Alder cycloaddition product **4a** was isolated in 63 % yield with exclusive δ,ε-regioselectivity.[12–14] More pleasingly, both diastereo- (*endo*, > 19:1) and enantioselectivity (98 % *ee*) are remarkable, even though the δ,ε-C=C bond is quite remote from chiral amine catalyst (Table 1, entry 1).[15] It should be addressed that almost no reaction occurred for the reaction of the conjugated 2,4-dienone **1** and **3a** under the same catalytic conditions, thus further verifying that the appropriately positioned δ,ε-C=C bond is crucial for inducing the formation of the required linear trienamine intermediate. 9-Amino-9-deoxyepiquinine (**C2**) afforded the product with the opposite configuration in excellent stereoselectivity (Table 1, entry 2), but **C3**, having with a free OH group, failed to catalyze the reaction (Table 1, entry 3). The acid additives had significant effects on the reaction. Salicylic acid (**A2**) produced better reactivity (Table 1, entry 4), and a slower reaction and even poor conversion was observed by using either **A3** or **A4** (Table 1, entries 5 and 6). Other solvents were tolerated though lower yields were obtained (Table 1, entries 7–10). Notably, the reaction still proceeded smoothly with a decreased amount (10 mol % or 5 mol %) of **C1** in combination with **A2**, and better results were obtained after a longer reaction time (Table 1, entries 11 and 12).

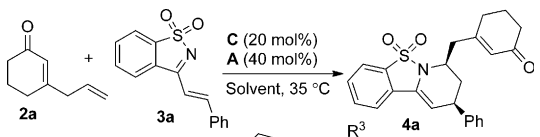
Consequently, a number of cyclic 2,5-dienones and electron-deficient 1-azadienes were investigated (Table 2). For the reactions of **2a**, a variety of 3-vinyl-1,2-benzoisothia-

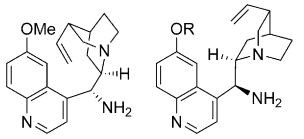
[*] X. Feng,[+] Z. Zhou,[+] C. Ma, X. Yin, Prof. Dr. R. Li, Dr. L. Dong, Prof. Dr. Y.-C. Chen
Key Laboratory of Drug-Targeting and Drug Delivery System of the Ministry of Education, West China School of Pharmacy, and State Key Laboratory of Biotherapy, West China Hospital, Sichuan University, Chengdu, 610041 (China)
E-mail: ycchen@scu.edu.cn
Prof. Dr. Y.-C. Chen
College of Pharmacy, Third Military Medical University
Chongqing, 400038 (China)
[+] These authors contributed equally to this work.

[**] We are grateful for financial support from the NSFC (21125206, 21021001 and 21372160) and the National Basic Research Program of China (973 Program, 2010CB833300).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307460.

Table 1: Screening of reaction conditions for the inverse-electron-demand aza-Diels–Alder reaction of **2a** and **3a**.[a]





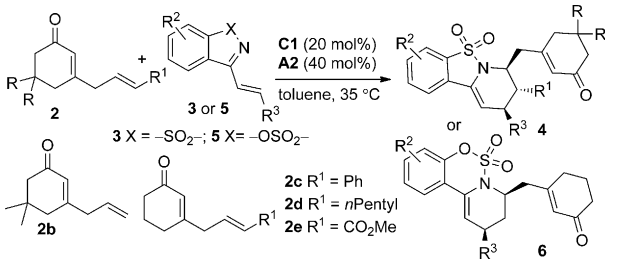
C1 | **C2** R = Me, **C3** R = H | **A1** $R^2 = R^3 = H$, **A2** R^2 = OH, R^3 = H, **A3** R^2 = OMe, R^3 = H, **A4** R^2 = H, R^3 = OH

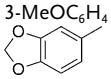
Entry	Cat	Acid	Solvent	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**C1**	**A1**	toluene	16	63	98
2	**C2**	**A1**	toluene	24	56	−95
3	**C3**	**A1**	toluene	24	–	–
4	**C1**	**A2**	toluene	13	92	>99.5
5	**C1**	**A3**	toluene	22	77	99
6	**C1**	**A4**	toluene	48	<20	–
7	**C1**	**A2**	CH_2Cl_2	19	84	99
8	**C1**	**A2**	THF	24	70	99
9	**C1**	**A2**	EtOAc	36	73	99
10	**C1**	**A2**	CH_3CN	17	77	99
11[d]	**C1**	**A2**	toluene	26	85	>99
12[e]	**C1**	**A2**	toluene	38	80	>99

[a] Unless noted otherwise, reactions were performed with 2,5-dienone **2a** (0.15 mmol), 1-azadiene **3a** (0.1 mmol), amine **C** (20 mol%) and acid (40 mol%) in solvent (1.0 mL) at 35 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis on a chiral stationary phase; d.r. > 19:1 by ^{1}H NMR analysis. [d] With 10 mol% of **C1** and 20 mol% of **A2**. [e] With 5 mol% of **C1** and 10 mol% of **A2**. THF = tetrahydrofuran.

zole-1,1-dioxides (**3**) having a variety of aryl or heteroaryl groups were well tolerated, thus giving the corresponding tetrahydropyridines in excellent yields (Table 2, entries 1–13). 1-Azadienes (**3**) with branched alkyl groups exhibited a similar reactivity (Table 2, entries 14 and 15),[16] and those with either electron-withdrawing or electron-donating groups on the 1,2-benzoisothiazole-1,1-dioxide moiety also result in high yields and *ee* values (Table 2, entries 16 and 17). In contrast, a few substituted cyclic 2,5-dienones were tested in the reactions with **3a**. Excellent results were attained for the 2,5-dienone **2b** having 5′,5′-dimethyl groups (entry 18). The 2,5-dienones **2c** and **2d**, having an ε-aryl and alkyl group, respectively, delivered cycloadducts having three contiguous stereogenic centers (Table 2, entries 19 and 20). Even the 2,5-dienone **2e**, having an electron-withdrawing ethoxycarbonyl group at the ε-site, showed comparable reactivity (Table 2, entry 21). In addition, the analogous cyclic 1-azadienes **5** with a 1,2,3-benzoxathiazine-2,2-dioxide motif[17] reacted smoothly, thus delivering another type of heterocycles (**6**) in high yield and with excellent enantioselectivity (Table 2, entries 22–25). Furthermore, the reactions of some 1-azadienes with **2a** catalyzed by **C2** were explored. The cycloadducts having an opposite configuration to those obtained with **C1** were generally produced with excellent *ee* values and with moderate yields (Table 2, data within parentheses).[18]

Table 2: Substrate scope and limitations.[a]

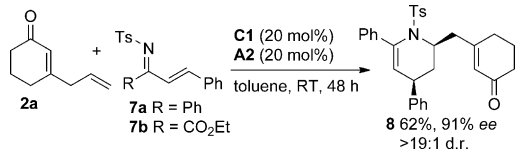


Entry	2	R^2	R^3	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**2a**	H	Ph	13 (39)	**4a**, 92 (69)	>99.5 (−95)
2	**2a**	H	3-MeC_6H_4	15	**4b**, 88	>99.5
3	**2a**	H	3-$MeOC_6H_4$	13 (48)	**4c**, 90 (73)	99 (−95)
4	**2a**	H		16	**4d**, 89	99
5	**2a**	H	3-FC_6H_4	16	**4e**, 93	>99
6	**2a**	H	2-ClC_6H_4	16 (37)	**4f**, 90 (71)	>99 (−96)
7	**2a**	H	4-BrC_6H_4	15	**4g**, 94	>99.5
8	**2a**	H	4-$CF_3C_6H_4$	17 (42)	**4h**, 89 (77)	>99.5 (−96)
9	**2a**	H	2-F-4-BrC_6H_3	14	**4i**, 92	>99.5
10	**2a**	H	1-naphthyl	14	**4j**, 90	>99.5
11	**2a**	H	2-naphthyl	13	**4k**, 93	>99.5
12	**2a**	H	2-furyl	14	**4l**, 93	>99
13	**2a**	H	2-thienyl	17	**4m**, 91	>99.5
14	**2a**	H	*i*Propyl	12	**4n**, 89	>99.5
15	**2a**	H	*c*Hexyl	12	**4o**, 85	>99.5
16	**2a**	6-Br	Ph	12	**4p**, 87	>99.5
17	**2a**	5,7-Me_2	Ph	17	**4q**, 91	>99[d]
18	**2b**	H	Ph	12	**4r**, 87	>99.5
19	**2c**	H	Ph	12	**4s**, 87	>99.5
20	**2d**	H	Ph	46	**4t**, 61	99
21	**2e**	H	Ph	44	**4u**, 73	96
22	**2a**	H	Ph	21 (17)	**6a**, 83 (72)	96 (−95)
23	**2a**	H	4-MeC_6H_4	23	**6b**, 85	97
24	**2a**	H	4-$CF_3C_6H_4$	21	**6c**, 80	94
25	**2a**	H	2-thienyl	22	**6d**, 89	96

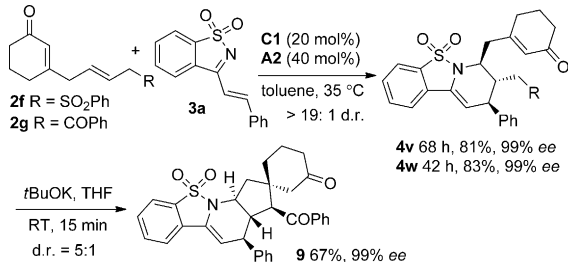
[a] Unless noted otherwise, reactions were performed with 2,5-dienone **2** (0.15 mmol), 1-azadiene **3** or **5** (0.1 mmol), amine **C1** (20 mol%) and acid **A2** (40 mol%) in toluene (1.0 mL) at 35 °C. Data in paralethes obtained with amine **C2**. [b] Yield of isolated product. [c] Determined by HPLC analysis using a chiral stationary phase; d.r. > 19:1 by ^{1}H NMR analysis. [d] The absolute configuration of **4q** was determined by X-ray analysis. See the Supporting Information.[19] The other products were assigned by analogy.

Apart from the cyclic 1-azadienes **3** and **5**, we also investigated the asymmetric cycloadditions of acyclic *N*-tosyl-1-azadienes which have been widely used for aza-Diels–Alder reactions.[13] The substrate **7a**, derived from chalcone, exhibited acceptable reactivity in the presence of **C1** and **A2**. The cycloadduct **8** was obtained with high diastereo- and enantioselectivity, albeit in moderate yield. A reduced amount of the acid additive slowed the hydrolysis of the imine group of **7a**, but the more labile 1-azadiene **7b**, having an α-ethoxycarbonyl group, failed to deliver the aza-cycloadduct because of rapid decomposition of the ketimine group under the catalytic conditions (Scheme 2).

The remaining cyclic enone motif of the cycloadducts encouraged us to design appropriately functionalized sub-



Scheme 2. Asymmetric aza-Diels–Alder reaction with acyclic *N*-tosyl-1-azadienes.

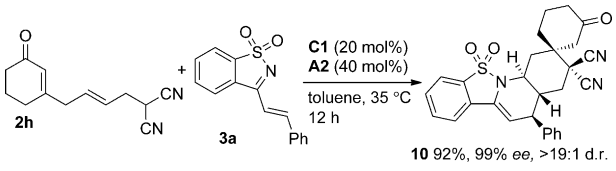


Scheme 3. Sequential reactions with multifunctional 2,5-dienones.

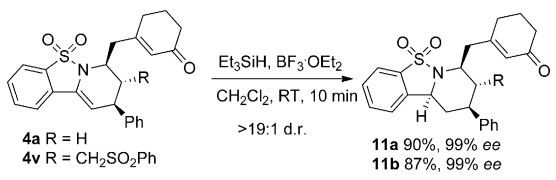
strates to access more complex frameworks. As outlined in Scheme 3, both **2f** and **2g**, bearing an activated methylene group at the ω-site, enabled a highly δ,ε-regioselective inverse-electron-demand aza-Diels–Alder reaction with **3a** to give the cycloadducts **4v** and **4w**, respectively. A diastereoselective cyclization with **4w** was efficiently promoted by adding *t*BuOK,[20] thus producing **9** as a separable single enantiomer, which possesses five fused and spirocyclic rings and five stereogenic centers.

Based on the above results, the 2,5-dienone **2h**, having a more reactive malononitrile moiety, was designed. Thus, the first cascade-induced trienamine-iminium catalysis with **2h** and **3a** could be realized,[21] directly producing the polycyclic compound **10** in excellent yield and with almost enantiomerical purity (Scheme 4).

As illustrated in Scheme 5, the enamide functionality of the aza-cycloadducts **4** could be chemoselectively reduced with Et_3SiH and $BF_3{\cdot}OEt_2$ without affecting the enone or other groups.[11] The piperidine derivatives **11a** and **11b** were efficiently obtained in high yield and with exclusive diastereoselectivity from **4a** and **4v**, respectively. More structural diversity and complexity might be introduced from the cyclic enone moiety based on previously established methodologies.[22]



Scheme 4. Cascade induced trienamine-iminium catalysis.



Scheme 5. Chemoselective reduction of enamide group.

In conclusion, we have developed an unprecedented asymmetric inverse-electron-demand aza-Diels–Alder reaction with interrupted cyclic 2,5-dienones and electron-deficient 1-azadienes under the catalysis of chiral amines derived from quinidine or quinine. The success of this novel catalytic mode relies on the rational design of the polyunsaturated ketone substrates, which contain an appropriately positioned δ,ε-C=C bond to induce the in situ generation of HOMO-raised linear trienamine species. In contrast to early examples of trienamine catalysis,[5,6] the current cycloaddition exhibits exclusive remote δ,ε-regioselectivity, and excellent catalytic efficacy and stereocontrol were observed for the reactions of a variety of substrates with substantial scope. Moreover, an aza-Diels–Alder reaction/Michael addition process was developed by introducing a functional group to the 2,5-dienone substrates. The cascade reaction efficiently constructed frameworks having high structural and stereogenic complexity. We believe that this strategy would help overcome the limitations of more types of unsaturated ketone substrates bearing α′-enolizable alkyl groups in other aminocatalytic asymmetric reactions. More results will be reported in due course.

Received: August 24, 2013
Revised: September 24, 2013
Published online: November 8, 2013

Keywords: cycloadditions · heterocycles · organocatalysis · stereoselectivity · synthetic methods

[1] For reviews, see: a) H. Sailes, A. Whiting, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1785; b) K. Mikami, M. Shimizu, H.-C. Zhang, B. E. Maryanoff, *Tetrahedron* **2001**, *57*, 2917; c) J. Clayden, *Chem. Soc. Rev.* **2009**, *38*, 817.

[2] For selected examples, see: a) P. Linnane, N. Magnus, P. Magnus, *Nature* **1997**, *385*, 799; b) J. Clayden, A. Lund, L. Vallverdu, M. Helliwell, *Nature* **2004**, *431*, 966; c) S.-i. Shirokawa, M. Kamiyama, T. Nakamura, M. Okada, A. Nakazaki, S. Hosokawa, S. Kobayashi, *J. Am. Chem. Soc.* **2004**, *126*, 13604; d) T. Sammakia, D. M. Johns, G. Kim, M. A. Berliner, *J. Am. Chem. Soc.* **2005**, *127*, 6504; e) Y. Nishioka, T. Yamaguchi, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 8160; f) E. García-Urdiales, I. Alfonso, V. Gotor, *Chem. Rev.* **2005**, *105*, 313; g) D. L. Hughes, J. J. Bergan, J. S. Amato, M. Bhupathy, J. L. Leazer, J. M. McNamara, D. R. Sidler, P. J. Reider, E. J. J. Grabowski, *J. Org. Chem.* **1990**, *55*, 6252.

[3] For selected examples, see: a) Y. Zhao, J. Rodrigo, A. H. Hoveyda, M. L. Snapper, *Nature* **2006**, *443*, 67; b) A. V. Malkov, A. J. P. S. Liddon, P. Ramírez-López, L. Bendová, D. Haigh, P. Kočovský, *Angew. Chem.* **2006**, *118*, 1460; *Angew. Chem. Int. Ed.* **2006**, *45*, 1432; c) C. A. Lewis, J. L. Gustafson, A. Chiu, J. Balsells, D. Pollard, J. Murry, R. A. Reamer, K. B. Hansen, S. J. Miller, *J. Am. Chem. Soc.* **2008**, *130*, 16358; d) P. W. N. M. van Leeuwen, D. Rivillo, M. Raynal, Z. Freixa, *J. Am. Chem. Soc.* **2011**, *133*, 18562; e) B. M. Trost, P. J. Morris, S. J. Sprague, *J. Am. Chem. Soc.* **2012**, *134*, 17823.

[4] a) R. C. Fuson, *Chem. Rev.* **1935**, *16*, 1; b) G. Casiraghi, L. Battistini, C. Curti, G. Rassu, F. Zanardi, *Chem. Rev.* **2011**, *111*, 3076.

[5] For an early example, see: a) Z.-J. Jia, H. Jiang, J.-L. Li, B. Gschwend, Q.-Z. Li, X. Yin, J. Grouleff, Y.-C. Chen, K. A. Jørgensen, *J. Am. Chem. Soc.* **2011**, *133*, 5053; for reviews, see: b) K. L. Jensen, G. Dickmeiss, H. Jiang, Ł. Albrecht, K. A. Jørgensen, *Acc. Chem. Res.* **2012**, *45*, 248; c) J.-L. Li, T.-Y. Liu, Y.-C. Chen, *Acc. Chem. Res.* **2012**, *45*, 1491; d) E. Arceo, P. Melchiorre, *Angew. Chem.* **2012**, *124*, 5384; *Angew. Chem. Int. Ed.* **2012**, *51*, 5290; e) I. Kumar, P. Ramaraju, N. A. Mir, *Org. Biomol. Chem.* **2013**, *11*, 709; f) H. Jiang, Ł. Albrecht, K. A. Jørgensen, *Chem. Sci.* **2013**, *4*, 2287.

[6] X.-F. Xiong, Q. Zhou, J. Gu, L. Dong, T.-Y. Liu, Y.-C. Chen, *Angew. Chem.* **2012**, *124*, 4477; *Angew. Chem. Int. Ed.* **2012**, *51*, 4401.

[7] X. Feng, Z. Zhou, R. Zhou, Q.-Q. Zhou, L. Dong, Y.-C. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 19942.

[8] D. B. Ramachary, Y. V. Reddy, *Eur. J. Org. Chem.* **2012**, 865.

[9] We have conducted preliminary DFT calculations at the B3LYP/6-31G(d) level of theory, the results of which indicate that the intermediate **III** has much higher energy than that of polyconjugated intermediate **II**. For more details, see the Supporting Information.

[10] R. A. Abramovitch, I. Shinkai, B. J. Mavunkel, K. M. More, S. O'Conner, G. H. Ooi, W. T. Pennington, P. C. Srinivasan, J. R. Stowers, *Tetrahedron* **1996**, *52*, 3339.

[11] For a comprehensive review of cinchona-based primary aminocatalysis, see: P. Melchiorre, *Angew. Chem.* **2012**, *124*, 9886; *Angew. Chem. Int. Ed.* **2012**, *51*, 9748.

[12] For inverse-electron-demand aza-Diels–Alder reactions by enamine or dienamine catalysis, see: a) B. Han, J.-L. Li, C. Ma, S.-J. Zhou, Y.-C. Chen, *Angew. Chem.* **2008**, *120*, 10119; *Angew. Chem. Int. Ed.* **2008**, *47*, 9971; b) B. Han, Z.-Q. He, J.-L. Li, R. Li, K. Jiang, T.-Y. Liu, Y.-C. Chen, *Angew. Chem.* **2009**, *121*, 5582; *Angew. Chem. Int. Ed.* **2009**, *48*, 5474.

[13] For selected stereoselective inverse-electron-demand aza-Diels–Alder reactions of 1-azadienes, see: a) R. C. Clark, S. S. Pfeiffer, D. L. Boger, *J. Am. Chem. Soc.* **2006**, *128*, 2587; b) M. He, J. R. Struble, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 8418; c) J. Esquivias, R. Gómez Arrayás, J. C. Carretero, *J. Am. Chem. Soc.* **2007**, *129*, 1480; d) X. Jiang, X. Shi, S. Wang, T. Sun, Y. Cao, R. Wang, *Angew. Chem.* **2012**, *124*, 2126; *Angew. Chem. Int. Ed.* **2012**, *51*, 2084; e) C. Simal, T. Lebl, A. M. Z. Slawin, A. D. Smith, *Angew. Chem.* **2012**, *124*, 3713; *Angew. Chem. Int. Ed.* **2012**, *51*, 3653; f) X. Zhao, K. E. Ruhl, T. Rovis, *Angew. Chem.* **2012**, *124*, 12496; *Angew. Chem. Int. Ed.* **2012**, *51*, 12330; g) X. Jiang, L. Liu, P. Zhang, Y. Zhong, R. Wang, *Angew. Chem.* **2013**, *125*, 11539; *Angew. Chem. Int. Ed.* **2013**, *52*, 11329.

[14] For selected reviews on Diels–Alder reactions, see: a) M. Behforouz, M. Ahmadian, *Tetrahedron* **2000**, *56*, 5259; b) D. H. Paull, J. Wolfer, J. W. Grebinski, A. Weatherwax, T. Lectka, *Chimia* **2007**, *61*, 240; c) X. Jiang, R. Wang, *Chem. Rev.* **2013**, *113*, 5515; d) H. B. Kagan, O. Riant, *Chem. Rev.* **1992**, *92*, 1007; e) E. J. Corey, *Angew. Chem.* **2002**, *114*, 1724; *Angew. Chem. Int. Ed.* **2002**, *41*, 1650; f) S. Reymond, J. Cossy, *Chem. Rev.* **2008**, *108*, 5359.

[15] For highly stereoselective remote δ-regioselective 1,6-addition with cyclic 2,4-dienones, see: a) X. Tian, Y. Liu, P. Melchiorre, *Angew. Chem.* **2012**, *124*, 6545; *Angew. Chem. Int. Ed.* **2012**, *51*, 6439; b) X. Tian, P. Melchiorre, *Angew. Chem.* **2013**, *125*, 5468; *Angew. Chem. Int. Ed.* **2013**, *52*, 5360; c) for a mechanistic study, see: A. Moran, A. Hamilton, C. Bo, P. Melchiorre, *J. Am. Chem. Soc.* **2013**, *135*, 9091.

[16] 1-Azadienes with a linear alkyl group have not been produced yet.

[17] M. Tripathi, D. N. Dhar, *J. Heterocycl. Chem.* **1988**, *25*, 1191.

[18] β-Allyl cyclopenten-2-one exhibited more complicated reactivity with **3a**; see the Supporting Information.

[19] CCDC 965414 (**4q**) and CCDC 965415 (**4v**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] Cycloadduct **4v** failed to undergo the intramolecular Michael addition.

[21] For reviews, see: a) X. Yu, W. Wang, *Org. Biomol. Chem.* **2008**, *6*, 2037; b) B. Westermann, M. Ayaz, S. S. van Berkel, *Angew. Chem.* **2010**, *122*, 858; *Angew. Chem. Int. Ed.* **2010**, *49*, 846; c) C. Grondal, M. Jeanty, D. Enders, *Nat. Chem.* **2010**, *2*, 167.

[22] a) J. B. Tuttle, S. G. Ouellet, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2006**, *128*, 12662; b) O. Lifchits, M. Mahlau, C. M. Reisinger, A. Lee, C. Farès, I. Polyak, G. Gopakumar, W. Thiel, B. List, *J. Am. Chem. Soc.* **2013**, *135*, 6677; c) I.-H. Chen, L. Yin, W. Itano, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 11664; d) T. L. May, J. A. Dabrowski, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 736.