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Hydrogen-Bond-Directed Formal [5 + 1] Annulations of Oxindoles with Ester-Linked Bisenones: Facile Access to Chiral Spirooxindole δ-Lactones

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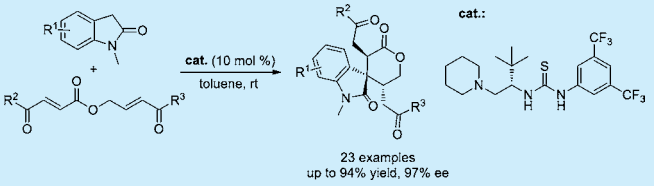
Supporting Information

ABSTRACT: A novel bifunctional thiourea catalyzed formal [5 + 1] cycloaddition of oxindoles and ester-linked bisenones was successfully developed. This strategy involves two sequential Michael additions, leading to spirooxindole δ-lactones with three contiguous stereocenters including an all-carbon quaternary center with high diastereo- and enantioselectivites. In addition, a remarkable N-substituent effect was observed on the reactivity and selectivity.



Lactones are unique structural units frequently found in a wide variety of naturally occurring molecules and pharmaceuticals. Multisubstituted lactones are of particular synthetic significance due to their capacity as synthetic intermediates toward complex molecules.[1] Consequently, great efforts have been directed recently toward the development of the catalytic asymmetric synthesis of lactones and their derivatives. As a result, a multitude of elegant methods for the construction of five-membered lactones have been reported,[2] such as well-documented NHC-catalyzed [3 + 2] cycloaddition[3] and carboxylic acid involved halocyclizations.[4] By contrast, reliable and flexible methods for the construction of six-membered lactones are very rare despite the prevalence of these unique architectures in various natural products and bioactive molecules (Figure 1).[5,6] Furthermore, it is still a great challenge to stereoselectively construct δ-lactones bearing all-carbon quaternary chiral centers. To our knowledge, there is no precedent for the enantioselective synthesis of spirocyclic δ-lactone with all-carbon quaternary centers so far.[7]

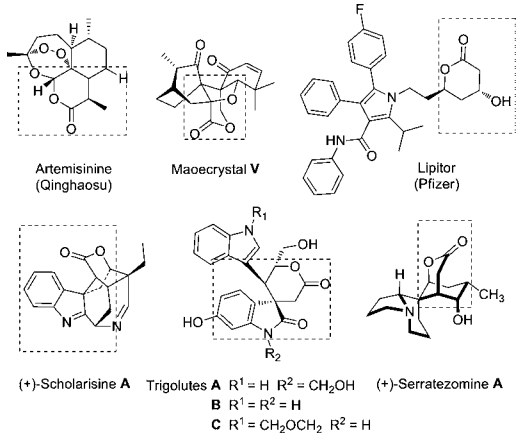


Figure 1. Represented δ-lactone-containing natural products and drugs.

Construction of complex chiral molecular architectures from simple achiral materials is a main focus of research in organic chemistry. Significant progress in this area has been made through organocatalytic asymmetric cascade/tandem reactions due to their ability toward facile assembly of complex and diverse molecules as well as their operational simplicity and environmental friendliness.[8] With our strong interest in developing novel and practical organocatalytic cascade reactions,[9] and also inspired by the previous achievements in the hydrogen-bonding activation of various Michael acceptors toward nucleophilic attack of oxindole,[10,11] we reasoned that ester-linked bisenones could serve as powerful reaction partners in a tandem Michael/Michael process promoted by a suitable bifunctional hydrogen-bonding donor catalyst. More importantly, this formal [5 + 1] cycloaddition process will lead to a spirooxindole δ-lactone with three continuous stereocenters,[12] which is an important structural motif in many natural products and biological active molecules (Scheme 1).

We initiated the study by investigating the reaction of substrate **2** and **3** under the catalysis of **1a** in toluene at room temperature. The desired product was obtained in good yield and ee with only one diastereomer formed, although a prolonged reaction time was needed when the N-substituent was Bn group (Table 1, entry 1). It seemed that the steric hindrance of the Bn substituent remarkably reduced the reactivity of the substrate. When we changed the EWG group of **3** to an Ac or formyl group, the desired products were obtained with a very low yield (Table 1, entries 2 and 3). The Bz was observed to be a better EWG group of **3**. To enhance

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Scheme 1. Hydrogen-Bond-Directed Double Michael Reactions

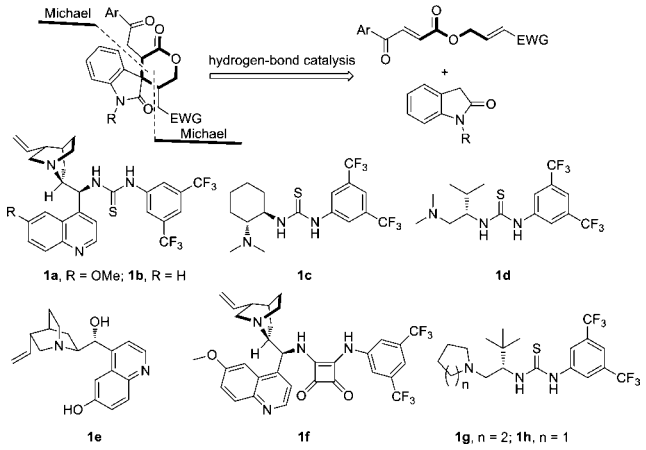
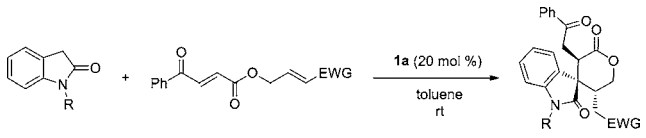


Table 1. Effects of the N-Substituent of Oxindole[a]



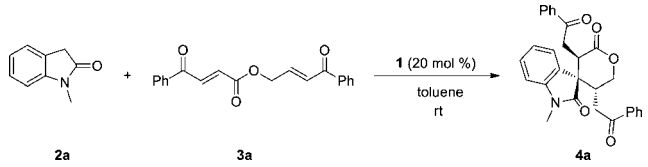
entry	R	EWG	t (h)	yield[b] (%)	ee[c] (%)
1	Bn	Bz	168	73	92
2	Bn	Ac	72	19	ND
3	Bn	formyl	72	19	ND
4[d]	Boc	Bz	12	90	73
5	CO_2Et	Bz	5	99	20
6	Ac	Bz	72	30	5
7	H	Bz	72	22	ND
8	Ph	Bz	72	56	20
9	Et	Bz	72	27	ND
10	Me	Bz	72	67	92

[a]Unless otherwise noted, the reaction was carried out with **2** (0.15 mmol), **3** (0.1 mmol), and **1a** (20 mol %) in 0.5 mL of toluene at room temperature. [b]The isolated yield. [c]Determined by HPLC. [d]The reaction was carried out at −78 °C.

the reactivity of the oxindoles, the N-substituent was replaced by the more electron-withdrawing Boc group. The reaction was accelerated a few times even at −78 °C albeit with a poor ee (Table 1, entry 2). It seemed that the N-substituent had a great influence on the reaction in terms of the yield and ee. Then we examined a series of N-substituents, both the electron-withdrawing and -donating ones. The results are outlined in Table 1. Considering the efficiency and selectivity, the reaction with the methyl substituted oxindole **2a** gave the best results (entry 8: yield 67%, ee 92%).

With the selection of the appropriate N-substituent, we started to optimize the reaction conditions with **2a** and **3a** as the model substrates. First, a series of bifunctional thiourea catalysts were examined with other conditions unchanged (Table 2).[13] As better results were produced by the quinine thiourea **1a**, other bifunctional hydrogen-bond catalysts derived from the cinchona alkaloid were tested. Unfortunately, they all failed to give a satisfactory result (Table 2, entries 2, 5, and 6). The catalysts **1c** and **1d** derived from diaminocyclohexane and L-valine resulted in a slight decrease in the selectivity or yield (Table 2, entries 3 and 4). And catalysts **1e** and **1f**, with a

Table 2. Optimization of the Reaction Parameters[a]



entry[b]	1	catalyst loading (mol %)	t (h)	yield[c] (%)	ee[d] (%)
1	**1a**	20	72	67	92
2	**1b**	20	72	60	91
3	**1c**	20	72	67	−84
4	**1d**	20	96	61	91
5	**1e**	20	96	NR	ND
6	**1f**	20	96	44	88
7	**1g**	20	72	94	93
8	**1h**	20	72	69	82
9	**1g**	15	72	91	94
10	**1g**	10	72	82	96
11	**1g**	5	72	40	97
12[e]	**1g**	10	72	87	92
13[e]	**1g**	5	72	50	96

[a]Unless otherwise noted, the reaction was carried out with **2a** (0.15 mmol), **3a** (0.1 mmol), and **1** in 0.5 mL of toluene at room temperature. [b]For all entries, the dr > 25:1. [c]The isolated yield. [d]Determined by HPLC. [e]The reactions were carried out with **2a** (0.3 mmol), **3a** (0.2 mmol), and **1** in 0.5 mL of toluene.

hydrogen-bond donor other than thiourea, gave disappointing results (Table 2, entries 5 and 6). Then we changed **1d** to its analogs **1g** and **1h** bearing bulky substituents. The results demonstrated that **1g** was the best catalyst for this lactone-forming reaction, which might be due to the dihedral and relative crowding of the two groups of the catalyst. Now with the best catalyst found, the solvent of the reaction was further optimized. Toluene was determined to be the best solvent for this reaction (see Supporting Information). Considering that the loading of catalyst (20 mol %) was a little too high, we tried to investigate the influence of the catalyst loading on the reaction. Despite a positive correlation between catalyst loading and reactivity, we found that reducing the catalyst loading slightly enhanced the enantioinduction (Table 2, entries 9−11). To increase the reaction yield, a higher concentration (0.4 M) of the catalyst was tested. The yield increased as expected but the ee decreased (Table 2, entries 12 and 13). Considering the yield and ee, 10 mol % catalyst in 0.5 mL of toluene was found to meet the requirement (Table 2, entry 10). Given the above results, the optimal conditions included using catalyst **1g** (10 mol %) in toluene (0.5 mL) at room temperature for 72 h.

Under the optimal conditions, the substrate scope of the lactone-forming reaction was investigated and the results are outlined in Table 3. A variety of substituents on oxindoles and dienones were well tolerated in this catalytic system, providing the desired products in moderate to high yields (up to 94%) with excellent enantioselectivities (up to 97% ee) and diastereoselectivities (>25:1). The position of the substituents on the phenyl ring of oxindole has no significant impact on the yield and enantioselectivity (Table 3, entry 2 vs 3 and 4 vs 5). In contrast, the substituents with different electronic features gave quite different results. Those substrates with electron-withdrawing substituents gave higher yields but a lower ee (Table 3, entries 2−5), while the yield was very low but the ee was higher when the substrates with electron-donating

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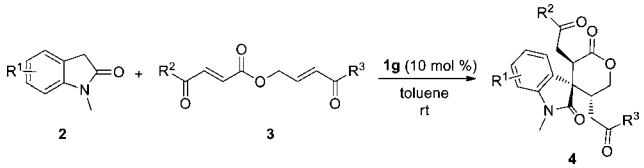
Table 3. Substrate Scope of the Organocatalytic Tandem Reaction[a]



entry[b]	R^1	R^2	R^3	yield[c] (%)	ee[d] (%)
1	H	Ph	Ph	82 (**4a**)	96
2	4-Cl	Ph	Ph	94 (**4b**)	88
3	6-Cl	Ph	Ph	90 (**4c**)	90
4	5-Br	Ph	Ph	86 (**4d**)	88
5	6-Br	Ph	Ph	92 (**4e**)	90
6	5-Me	Ph	Ph	55 (**4f**)	97
7	H	2-F-Ph	Ph	81 (**4g**)	88
8	H	4-F-Ph	Ph	90 (**4h**)	93
9	H	4-Br-Ph	Ph	82 (**4i**)	93
10	H	2-Cl-Ph	Ph	88 (**4j**)	95
11	H	3-Cl-Ph	Ph	87 (**4k**)	90
12	H	4-Cl-Ph	Ph	84 (**4l**)	92
13	H	2-Me-Ph	Ph	80 (**4m**)	95
14	H	3-Me-Ph	Ph	84 (**4n**)	94
15	H	4-Me-Ph	Ph	88 (**4o**)	93
16	H	2-naphthyl	Ph	87 (**4p**)	93
17	H	2-thienyl	Ph	80 (**4q**)	90
18	H	4-NO_2-Ph	Ph	71 (**4r**)	88
19	H	4-CF_3-Ph	Ph	78 (**4s**)	90
20	H	Ph	4-Me-Ph	93 (**4t**)	94
21	H	Ph	2-Cl-Ph	58 (**4u**)	97
22	H	Ph	4-Cl-Ph	86 (**4v**)	93
23	H	Ph	2-furyl	82 (**4w**)	96

[a]Unless otherwise noted, the reaction was carried out with **2** (0.15 mmol), **3** (0.1 mmol), and **1g** (10 mol %) in 0.5 mL of toluene at room temperature for 72 h. [b]For all entries, the dr > 25:1. [c]The isolated yield. [d]Determined by HPLC.

substituents were used due to the lower reactivity at the C3 position (Table 3, entry 6). Subsequently, an array of dienones **3** were examined using the double Michael reaction. We were happy to find that substrates with various substituents on both of the phenyl rings or with other aromatic systems were well tolerated in our reaction. The position and electronic nature of the substituents on aromatic rings had a slight influence on the results probably because of the long distance between the aromatic rings and the reaction sites. The stereochemistry of **4i** was determined based on the X-ray crystallography (Figure 2).[14]

With regard to the reaction mechanism, a catalyst-controlled pathway of this lactone-forming reaction was proposed based on our experimental results, although at this stage a substrate-controlled pathway could not be ruled out. As shown in Scheme 2, initially, the oxindole and enone are synergistically

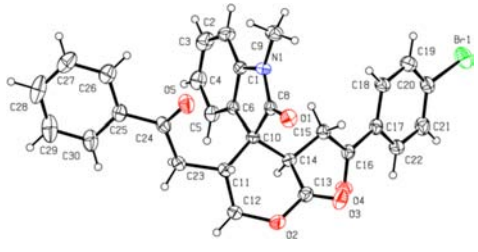
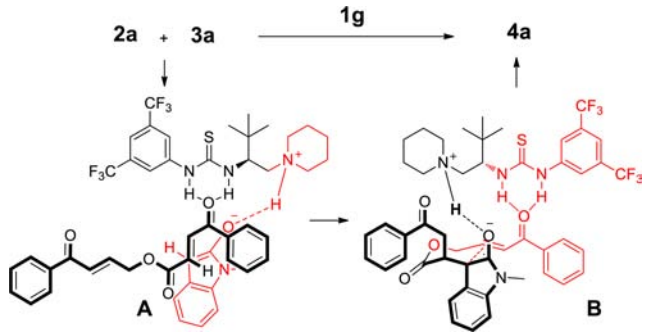


Figure 2. X-ray crystal structure of compound **4i**.

Scheme 2. Proposed Mechanism of the Spirooxindole δ-Lactone-Forming Tandem Reaction



activated by the bifunctional thiourea via the formation of intermediate **A**, which immediately undergoes the intramolecular Michael addition to generate the enone-tethered intermediate **B**. Subsequently an intermolecular Michael reaction of the oxindole with the *Si*-face of the tethered enone delivers the final product and regenerates the catalyst. The excellent enantio- and diastereoselectivities of the product may be ascribed to the stable six-membered transition state of intermediate **B**. The catalyst **1g** gave better results than other bifunctional thiourea catalysts probably because its dihedral and the relative crowding of the two groups generated a more stable six-membered transition state.[13c] Furthermore, the remarkable N-substituted effect was observed, probably because of not only the different C3 reactivity with a different substituent but also the nonbonding interaction between the substituent and the phenyl ring of the enone. This may explain why the methyl substituted oxindole has a faster reaction rate than the benzyl substituted one, which has more steric hindrance and may have a $\pi-\pi$ interaction with the phenyl ring of enone.

In conclusion, we have developed a novel formal [5 + 1] cyclization of oxindoles and ester-linked bisenones catalyzed by a simple bifunctional thiourea. The trisubstituted spirooxindole δ-lactones with three contiguous stereocenters including an all-carbon quaternary center were obtained with high diastereoselectivities (>25:1) and enantioselectivities (up to 97%). In addition, dramatic effects of N-substituents of the oxindole on this reaction with respect to reactivity and selectivity were observed. Further investigation of this chemistry toward mechanism rationale and synthetic applications is underway.

■ ASSOCIATED CONTENT

Supporting Information

Additional optimization of reaction parameters, experimental procedure and characterization data for all new compounds, X-ray crystal structure data (CIF) for compound **4i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Janecki, T. *Natural lactones and lactams, synthesis, occurrence, and biological activity*; Wiley-VCH: Weinheim, 2013. (b) Ley, S. V.; Cox, L. R.; Meek, G. *Chem. Rev.* **1996**, *96*, 423. (c) Mulzer, J.; Öhler, E. *Chem. Rev.* **2003**, *103*, 3753.

(2) For selected examples, see: (a) Kreimerman, S.; Ryu, L.; Minakata, S.; Komatsu, M. *Org. Lett.* **2000**, *2*, 389. (b) Babu, S. A.; Yasuda, M.; Okabe, Y.; Shibata, L.; Baba, A. *Org. Lett.* **2006**, *8*, 3029. (c) Qabaja, G.; Wilent, J. E.; Benavides, A. R.; Bullard, G. E.; Petersen, K. S. *Org. Lett.* **2013**, *15*, 1266. (d) Steward, K. M.; Gentry, E. C.; Johnson, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 7329.

(3) (a) Burstein, C.; Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 6205. (b) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370. (c) Li, Y.; Zhao, Z.-A.; He, H.; You, S.-L. *Adv. Synth. Catal.* **2008**, *350*, 1885. (d) Hirano, K.; Piel, I.; Glorius, F. *Adv. Synth. Catal.* **2008**, *350*, 984.

(4) (a) Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B. *J. Am. Chem. Soc.* **2010**, *132*, 3298. (b) Murai, K.; Matsushita, T.; Nakamura, A.; Fukushima, S.; Shimura, M.; Fujioka, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9174. (c) Jiang, X. J.; Tan, C. K.; Zhou, L.; Yeung, Y. Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 7771. (d) Yousefi, R.; Ashtekar, K. D.; Whitehead, D. C.; Jackson, J. E.; Borhan, B. *J. Am. Chem. Soc.* **2013**, *135*, 14524.

(5) (a) Cai, X.-H.; Tan, Q.-G.; Liu, Y.-P.; Feng, T.; Du, Z.-Z.; Li, W.-Q.; Luo, X.-D. *Org. Lett.* **2008**, *10*, 577. (b) Adams, G. L.; Carroll, P. J.; Smith, A. B., III. *J. Am. Chem. Soc.* **2013**, *135*, 519. (c) Smith, M. W.; Synder, S. A. *J. Am. Chem. Soc.* **2013**, *135*, 12964. (d) Lu, P.; Gu, Z.; Zakarian, A. *J. Am. Chem. Soc.* **2013**, *135*, 14552. (e) Bautista, E.; Toscano, A.; Calzada, F.; Díaz, E.; Yépez-Mulia, L.; Ortega, A. *J. Nat. Prod.* **2013**, *76*, 1970. (f) Igarashi, Y.; Zhou, T.; Sata, S.; Matsumoto, T.; Yu, L.; Oku, N. *Org. Lett.* **2013**, *15*, 5678. (g) Endo, A. *J. Med. Chem.* **1985**, *28*, 401. (h) Istvan, E. S.; Deisenhofer, J. *Science* **2001**, *292*, 1160. (i) Morita, H.; Arisaka, M.; Yoshida, N.; Kobayashi, J. *J. Org. Chem.* **2000**, *65*, 6241. (j) Ma, S.-S.; Mei, W.-L.; Guo, Z.-K.; Liu, S.-B.; Zhao, Y.-X.; Yang, D.-L.; Zeng, Y.-B.; Jiang, B.; Dai, H.-F. *Org. Lett.* **2013**, *15*, 1492. (k) Miller, L. H.; Su, X.-Z. *Cell* **2011**, *146*, 855.

(6) For selected examples, see: (a) Wang, L.; Thai, K.; Gravel, M. *Org. Lett.* **2009**, *11*, 891. (b) Liu, J.; Li, Z. *ACS Catal.* **2013**, *3*, 908. (c) Murai, K.; Matsushita, T.; Nakamura, A.; Hyogo, N.; Nakajima, J.; Fujioka, H. *Org. Lett.* **2013**, *15*, 2526.

(7) (a) Sun, L.-H.; Shen, L.-T.; Ye, S. *Chem. Commun.* **2011**, *47*, 10136. (b) Du, D.; Hu, Z.-Y.; Jin, J.-L.; Lu, Y.-Y.; Tang, W.-F.; Wang, B.; Lu, T. *Org. Lett.* **2012**, *14*, 1274.

(8) (a) Moyano, A.; Rios, R. *Chem. Rev.* **2011**, *111*, 4703. (b) Enders, D.; Grondal, C.; Hüttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570. (c) Grondal, C.; Jeanty, M.; Enders, D. *Nat. Chem.* **2010**, *2*, 167.

(9) (a) Duan, G.-J.; Ling, J.-B.; Wang, W.-P.; Luo, Y.-C.; Xu, P.-F. *Chem. Commun.* **2013**, *49*, 4625. (b) Tian, L.; Hu, X.-Q.; Li, Y.-H.; Xu, P.-F. *Chem. Commun.* **2013**, *49*, 7213. (c) Jia, Z.-X; Luo, Y.-C; Cheng, X.-N.; Xu, P.-F.; Gu, Y.-C. *J. Org. Chem.* **2013**, *78*, 6488. (d) Su, Y.; Ling, J.-B.; Zhang, S.; Xu, P.-F. *J. Org. Chem.* **2013**, *78*, 11053. (e) Jia, Z.-X.; Luo, Y.-C.; Wang, Y.; Chen, L.; Xu, P.-F.; Wang, B.-H. *Chem.—Eur. J.* **2012**, *18*, 12958. (f) Zhu, H.-L.; Ling, J.-B.; Xu, P.-F. *J. Org. Chem.* **2012**, *77*, 7737. (g) Ling, J.-B.; Su, Y.; Zhu, H.-L.; Wang, G.-Y.; Xu, P.-F. *Org. Lett.* **2012**, *14*, 1090. (h) Wang, Y.; Han, R.-G.; Zhao, Y.-L.; Yang, S.; Xu, P.-F.; Dixon, D. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9834.

(10) (a) Singh, G. S.; Desta, Z. Y. *Chem. Rev.* **2012**, *112*, 6104. (b) Hong, L.; Wang, R. *Adv. Synth. Catal.* **2013**, *355*, 1023. (c) Liao, Y.-H.; Liu, X.-L.; Wu, Z.-J.; Du, X.-L.; Zhang, X.-M.; Yuan, W.-C. *Chem.—Eur. J.* **2012**, *18*, 6679.

(11) For selected reviews of chiral bifunctional thiourea catalysis, see: (a) Taylor, M. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1520. (b) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713. (c) Takemoto, Y. *Org. Biomol. Chem.* **2005**, *3*, 4299. (d) Schreiner, P. R. *Chem. Soc. Rev.* **2003**, *32*, 289. (e) Zhang, Z.; Schreiner, P. R. *Chem. Soc. Rev.* **2009**, *38*, 1187. (f) Yu, X.; Wang, W. *Chem.—Asian. J.* **2008**, *3*, 516. (g) Albrecht, Ł.; Jiang, H.; Jørgensen, K. A. *Chem.—Eur. J.* **2014**, *20*, 358. (h) Pihko, P. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2062. (i) Connon, S. J. *Chem.—Eur. J.* **2006**, *12*, 5418. For selected examples: (j) Andrés, J. M.; Manzano, R.; Pedrosa, R. *Chem.—Eur. J.* **2008**, *14*, 5116. (k) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X.; Takemoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 119. (l) Ramachary, D. B.; Sakthidevi, R.; Shruthi, K. S. *Chem.—Eur. J.* **2012**, *18*, 8008. (m) Ramachary, D. B.; Madhavachary, R.; Prasad, M. S. *Org. Biomol. Chem.* **2012**, *10*, 5825. (n) Ramachary, D. B.; Prasad, M. S.; Laxmi, S. V.; Madhavachary, R. *Org. Biomol. Chem.* **2014**, *12*, 574. (o) McCooey, S. H.; Connon, S. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6367. (p) Zhu, J.-L.; Zhang, Y.; Liu, C.; Zheng, A.-M.; Wang, W. *J. Org. Chem.* **2012**, *77*, 9813. (q) Tan, B.; Candeias, N. R.; Barbas, C. F., III. *Nat. Chem.* **2011**, *3*, 473. (r) Bui, T.; Syed, S.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2009**, *131*, 8758. (s) Tan, B.; Hernández-Torres, G.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2011**, *133*, 12354.

(12) (a) Wang, L.-L.; Peng, L.; Bai, J.-F.; Jia, L.-N.; Luo, X.-Y.; Huang, Q.-C.; Xu, X.-Y.; Wang, L.-X. *Chem. Commun.* **2011**, *47*, 5593. (b) Wu, B.; Liu, G.-G.; Li, M.-Q.; Zhang, Y.; Zhang, S.-Y.; Qiu, J.-R.; Xu, X.-P.; Ji, S.-J.; Wang, X.-W. *Chem. Commun.* **2011**, *47*, 3992. (c) Li, X.-M.; Wang, B.; Zhang, J.-M.; Yan, M. *Org. Lett.* **2011**, *13*, 374. (d) Wu, B.; Chen, J.; Li, M.-Q.; Zhang, J.-X.; Xu, X.-P.; Ji, S.-J.; Wang, X.-W. *Eur. J. Org. Chem.* **2012**, *12*, 1318. (e) Weber, M.; Frey, W.; Peters, R. *Chem.—Eur. J.* **2013**, *19*, 8342. (f) Li, X.; Yang, C.; Jin, J.-L.; Xue, X.-S.; Cheng, J.-P. *Chem.—Asian. J.* **2013**, *8*, 997.

(13) (a) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672. (b) Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org. Lett.* **2005**, *7*, 1967. (c) Gao, Y. J.; Ren, Q.; Wang, L.; Wang, J. *Chem.—Eur. J.* **2010**, *16*, 13068. (d) Storer, R. L.; Aciro, C.; Jones, L. H. *Chem. Soc. Rev.* **2011**, *40*, 2330. (e) Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906.

(14) CCDC 953783 contains 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.