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Asymmetric Mannich Reaction and Construction of Axially Chiral Sulfone-Containing Styrenes in One Pot from α-Amido Sulfones Based on the Waste−Reuse Strategy

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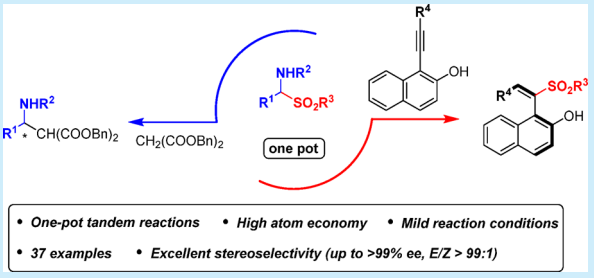
Supporting Information

ABSTRACT: A simultaneous asymmetric Mannich reaction and the construction of axially chiral sulfone-containing styrenes in one pot from α-amido sulfones based on the waste−reuse strategy was demonstrated. A series of chiral β-amino diesters and axially chiral sulfone-containing styrenes with various functional groups were synthesized in good to excellent yields and enantioselectivities under mild conditions. In addition, this protocol has been successfully applied to synthesize the anti-HIV drug Maraviroc and chiral trichloro derivatives.



The development of efficient synthetic methods is one of the central themes in chemistry. With the development of synthetic chemistry, especially the demand for green chemistry,[1] the atom economy[2] of a reaction becomes an extremely important subject. Therefore, the design and application of atom-economical and selective organic transformations are important and challenging.

α-Amido sulfones[3] as stable precursors of reactive N-protected imine derivatives are widely used in Mannich reactions[4] for the synthesis of chiral nitrogen derivatives, which can be readily transformed into valuable optically active compounds, such as β-amino acids and β-lactams. In particular, the instability of some primary aliphatic imines owing to rapid imine−enamine tautomerization requires the in situ generation of carbamate-protected alkyl imines from α-amido sulfones. Undoubtedly, a number of useful catalytic asymmetric variants with α-amido sulfones as substrates are available.[5] However, the limited application of existing catalytic methods is mainly caused by the low atomic utilization of α-amido sulfones since the sulfone groups are discarded in the form of metal sulfone salts after the reaction. Generally, the atom efficiency of α-amido sulfones in Mannich reaction is 50−60%. The sulfone functionality itself is gaining increasing concern in synthetic chemistry, especially in the synthesis of peptide-based inhibitors.[6] Therefore, it is necessary to develop a practical method for the full utilization of α-amido sulfones. To our knowledge, catalytic enantioselective reactions for the full utilization of α-amido sulfones have not been reported to date (Scheme 1).

During the last decades, the waste−reuse strategy[7] has emerged as a promising method for improving the synthesis efficiency. Inspired by the works from O'Brien,[7a] Zhou,[7b] Mandal,[7c] et al., we presumed that the use of a "waste−reuse strategy" would address the above-mentioned problems of α-amido sulfones. Before this conceptually simple idea is addressed, the following three problems should be solved: improving the reactivity of sulfinate salts in organic solvent, the discovery of an asymmetric catalytic reaction involving sulfinate salts, and a suitable catalytic system for both the above reaction and Mannich reaction. Based on the accomplishments of enantioselective Mannich reaction and our recent achievements on vinylidene *ortho*-quinone methide (VQM),[8] we envisioned that if we could develop a catalytic system for both enantioselective Mannich reaction and nucleophilic addition of sulfinate salts to vinylidene *ortho*-quinone methide then we would achieve the full utilization of

Scheme 1. Asymmetric One-Pot Tandem Reactions of Vinylidene *ortho*-Quinone Methide (VQM) and α-Amido Sulfones

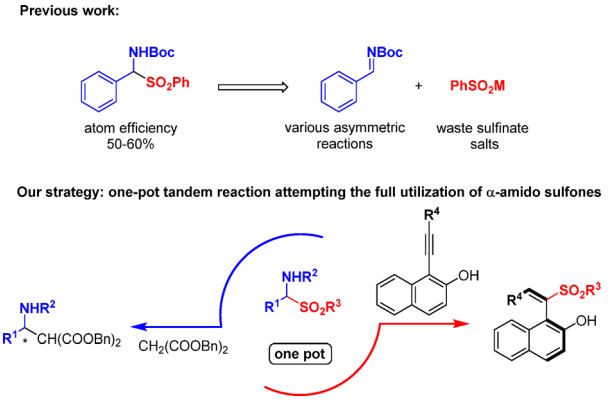


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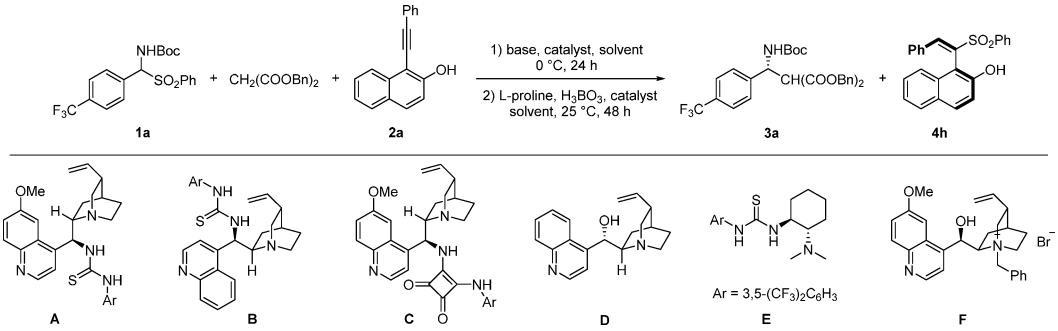
Table 1. Optimization of Reaction Conditions[a]



		solvent			3a		4h	
entry	catalyst	step 1	step 2	base	yield (%)[b]	ee (%)[c]	yield (%)[b]	ee (%)[c]
1	**A**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	95	95	75	99
2	**A**	CH_2Cl_2	CH_2Cl_2	K_2CO_3 (0.1 M)	85	42	65	85
3	**A**	CH_2Cl_2	CH_2Cl_2	Cs_2CO_3 (0.1 M)	90	76	90	45
4	**A**	CH_2Cl_2	CH_2Cl_2	KF (0.1 M)	60	49	85	99
5	**B**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	90	−95	70	−99
6	**C**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	60	85	75	74
7	**D**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	90	80	65	70
8	**E**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	90	93	70	98
9	**F**	CH_2Cl_2	CH_2Cl_2	Na_2CO_3 (0.1 M)	85	−17	<5	-
10	**A**	**CH_2Cl_2**	**$CHCl_3$**	**Na_2CO_3 (0.1 M)**	**95**	**95**	**90**	**99**
11	**A**	CH_2Cl_2	acetone	Na_2CO_3 (0.1 M)	95	93	50	92
12	**A**	CH_2Cl_2	THF	Na_2CO_3 (0.1 M)	90	90	55	98
13	**A**	CH_2Cl_2	EtOAc	Na_2CO_3 (0.1 M)	90	92	65	98
14	**A**	CH_2Cl_2	1,4-dioxane	Na_2CO_3 (0.1 M)	90	93	60	95

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), dibenzylmalonate (0.2 mmol, 1.0 equiv), and catalyst (10 mol %) in CH_2Cl_2 (0.4 mL) at 0 °C were added into chilled base solution (0.1 M, 2.0 mL, 1.0 equiv) in one portion. The resulting biphasic reaction mixture was stirred at 0 °C for 24 h. Then the reaction mixture was concentrated under the reduced pressure. Compound **2a** (0.2 mmol, 1.0 equiv), catalyst (10 mol %), L-proline (10 mol %), and H_3BO_3 (1.5 equiv) were dissolved in solvent (2.0 mL) and stirred at 25 °C for 48 h. [b]Isolated yield. [c]The ee value was determined by HPLC analysis.

α-amido sulfones in one-pot tandem reactions.[9] Herein, we reported our preliminary results on the strategy, which provided facile access to axially chiral styrenes[10] and valuable chiral β-amino acid derivatives with excellent enantioselectivities and yields.

We initially investigated the envisioned tandem reaction as follows (Table 1). The initial Mannich reaction of **1a** and $CH_2(COOBn)_2$ catalyzed by 10 mol % catalyst quinine-derived thiourea catalyst **A**[11] proceeded in CH_2Cl_2 at 0 °C. After the consumption of **1a**, as shown by TLC analysis, a combination of **2a**, H_3BO_3, and L-proline was added, and the reaction was stirred for 48 h at 25 °C. According to the above one-pot sequential protocol, various reaction conditions were screened. First, several inorganic bases were investigated. Among the tested inorganic bases, Na_2CO_3 gave the best result in terms of yields and enantioselectivities of both **3a** and **4h**. We then screened several bifunctional catalysts with different backbones. Compared with quinine-derived thiourea catalyst **A**, cinchonine-derived thiourea **B** afforded a comparable result in terms of yields and enantioselectivities and the opposite absolute configuration. In the presence of quinine-derived squareamide catalyst **C** and cinchonine **D**, the desired products were obtained in low yields and enantioselectivities. These results emphasize the importance of the functionality of thiourea catalysts. When the Takemoto catalyst **E** was employed, the desired products were generated smoothly with excellent enantioselectivities. However, phase transfer catalyst **F** was proven to be completely ineffective in this one-pot strategy. Finally, solvents were screened. The excellent yield and enantioselectivity were achieved when the solvent in the second step was changed to $CHCl_3$.

After establishing the methodology, the asymmetric Mannich reaction and the construction of axially chiral sulfone-containing styrenes in one pot from α-amido sulfones have been subsequently studied (Scheme 2). A variety of α-amido sulfones were applicable to this reaction based on 1-(phenylethynyl)naphthalen-2-ol **2a**. The aromatic, heteroaromatic, secondary alkyl, and primary alkyl α-amido sulfones were tested according to this protocol under the optimum reaction conditions in the presence of 10 mol % of the thiourea catalyst **A**. Excellent enantioselectivities (86−96% ee) and yields (31−98%) of desired β-amino diesters were obtained (Scheme 2). For the aromatic α-amido sulfones, the electronic properties of the substituents at the aromatic ring did not show the significant impact on the reactivity or selectivity (85−98% yields and 87−95% ee, Scheme 2, **3a**−**3k**). The opposite isomer of **3g** could be obtained with catalyst **B**. It is commonly difficult for the alkyl substrates to provide the high enantioselectivity in asymmetric catalysis. Gratifyingly, in our cases, all the alkyl α-amido sulfones including primary alkyl and secondary alkyl could successfully deliver the corresponding β-amino diesters with excellent enantioselectivies (86−96% ee) and good yields (Scheme 2, **3l**−**3t**). It is noteworthy that the corresponding **4h** has been furnished with moderate yields and enantioselectivities (87−99% ee) in all the above cases. Moreover, the scopes of the α-amido sulfones bearing various

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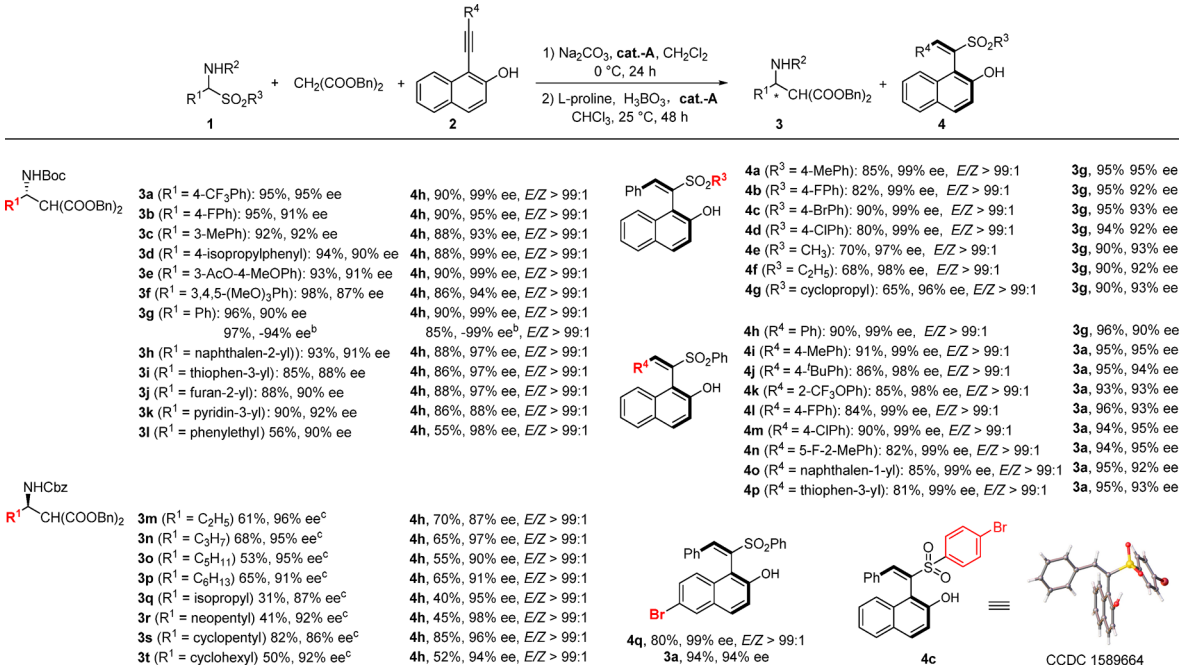
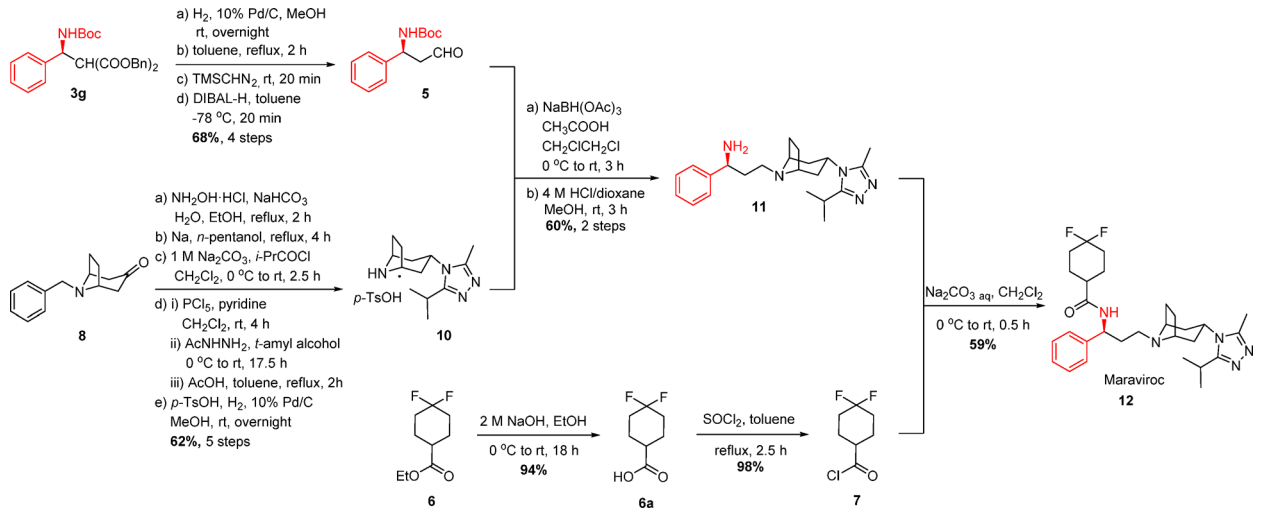
Scheme 2. Substrate Scope[a]



[a]Reaction conditions: **1** (0.2 mmol, 1.0 equiv), dibenzylmalonate (0.2 mmol, 1.0 equiv), and **cat.-A** (10 mol %) in CH_2Cl_2 (0.4 mL) at 0 °C were added into chilled Na_2CO_3 solution (0.1 M, 2.0 mL, 1.0 equiv) in one portion. The resulting biphasic reaction mixture was stirred at 0 °C for 24 h. Then the reaction mixture was concentrated under the reduced pressure. The compound **2** (0.2 mmol, 1.0 equiv), **cat.-A** (10 mol %), L-proline (10 mol %), and H_3BO_3 (1.5 equiv) were dissolved in $CHCl_3$ (2.0 mL) and stirred at 25 °C for 48 h. [b]The reaction was carried out with **cat.-B**. [c]The reaction was carried out in Cs_2CO_3 solution (0.1 M, 2.0 mL, 1.0 equiv) at 0 °C for 24 h.

Scheme 3. Synthesis of Maraviroc



substituted groups on sulfone were also investigated. Both the *para*-substituted groups on the aromatic ring and alkyl-substituted groups of the sulfone group were perfectly compatible with the reaction conditions, and the corresponding products with 65−90% yields and 96−99% ee (Scheme 2, **4a**−**4g**) were obtained. Next, **1a** was selected as the precursor of sodium sulfinate and *N*-carbamoyl imine. A series of substrates with different substituents could be converted enantioselectively into the desired axially chiral styrenes. First, the substrates with substituents on the 2-aryl moiety were examined. The electron-donating groups including methyl, *tert*-butyl, and trifluoromethoxyl were perfectly compatible with the reaction conditions, and the corresponding products were obtained with 85−91% yields and 98−99% ee (Scheme 2, **4i**−**4k**). The electron-withdrawing groups such as fluoro and chloro could successfully deliver the desired products with excellent enantioselectivies and *E*/*Z* selectivities (99% ee, *E*/*Z* > 99:1) (Scheme 2, **4l**−**4n**). In addition, the naphthyl was also tolerated in this protocol, and the product **4o** was obtained in 85% yield and 99% ee. Furthermore, the substrate with the electron-rich heterocyclic ring, such as thienyl, smoothly gave the axially chiral sulfone-containing styrene with excellent to near-perfect enantioselectivity (Scheme 2, **4p**). Subsequently, the substituent at the naphthol

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moiety of 1-(phenylethynyl)naphthalen-2-ol was further evaluated. For example, the bromo group on the ring of the naphthol successfully afforded the corresponding product **4q** in 80% yield and 99% ee. It is noteworthy that the corresponding β-amino diesters **3a**/**3g** have been furnished with excellent yields and enantioselectivities (90−96% yields, 90−95% ee) in all the above cases.

The synthetic applicability of chiral Mannich adducts obtained by this one-pot reaction from α-amido sulfones through the waste−reuse strategy was highlighted by the asymmetric synthesis of the anti-HIV drug Maraviroc[12] (Scheme 3). Maraviroc (UK-427,857) is a CCR-5 receptor antagonist developed and discovered by Pfizer and was approved by the FDA in 2007 for the treatment of HIV. Maraviroc is the first small-molecule CCR5 antagonist, and now it is commercially available as Selzentry.

Since the introduction of Maraviroc as a potent anti-HIV agent, diverse synthetic routes have been developed in recent years. Our approach toward the synthesis of Maraviroc started from the chiral β-amino diester **3g**, followed by a series of reactions including debenzylation, decarboxylation, methylation, and reduction to give the corresponding amino aldehyde **5**. After reductive amination between the amino aldehyde **5** and amine **10** and subsequent deprotection of the Boc group, the key intermediate amine **11** was obtained in 60% yield. The acylation reaction of **11** with a toluene solution of the acid chloride **7**, which was converted from commercially available ethyl 4,4-difluorocyclohexanecarboxylate **6** through simple chemical transformations, afforded Maraviroc under modified Schotten−Baumann conditions.

To show the synthetic utility of this newly developed protocol, the transformation of axially chiral styrenes was carried out. The trichloro derivatives could be obtained with moderate yields and enantioselectivities. Moreover, the structure and absolute configuration of the product were further confirmed by X-ray crystallography (please see Supporting Information for details).

In summary, we demonstrated a simultaneous asymmetric Mannich reaction and the construction of axially chiral sulfone-containing styrenes in one pot from α-amido sulfones based on the waste−reuse strategy and synthesized a series of chiral β-amino diesters and axially chiral sulfone-containing styrenes with various functional groups in good to excellent yields and enantioselectivies under mild conditions. In addition, the chiral β-amino diester was successfully applied to synthesize the anti-HIV drug Maraviroc, verifying the synthetic applicability of this protocol. Furthermore, the axially chiral sulfone-containing styrenes could be easily converted into chiral trichloro derivatives through asymmetric chlorinative dearomatization. Further applications of this reaction are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02087.

Experimental procedure and characterization data for all the products (PDF)

Accession Codes

CCDC 1589664 and 1834661 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Constable, D. J. C.; Curzons, A. D.; Cunningham, V. L. *Green Chem.* **2002**, *4*, 521−527. (b) Anastas, P.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301−312.

(2) (a) Trost, B. M. *Science* **1991**, *254*, 1471−1477. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259−281. (c) Sheldon, R. A. *Pure Appl. Chem.* **2000**, *72*, 1233−1246. (d) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695−705. (e) Kang, B.; Fu, Z.; Hong, S. H. *J. Am. Chem. Soc.* **2013**, *135*, 11704−11707. (f) Yang, J.-M.; Li, Z.-Q.; Li, M.-L.; He, Q.; Zhu, S.-F.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2017**, *139*, 3784−3789. (g) Pitzer, L.; Sandfort, F.; Strieth-Kalthoff, F.; Glorius, F. *J. Am. Chem. Soc.* **2017**, *139*, 13652−13655.

(3) (a) Niess, B.; Jørgensen, K. A. *Chem. Commun.* **2007**, 1620−1622. (b) Marianacci, O.; Micheletti, G.; Bernardi, L.; Fini, F.; Fochi, M.; Pettersen, D.; Sgarzani, V.; Ricci, A. *Chem. - Eur. J.* **2007**, *13*, 8338−8351. (c) Lou, S.; Dai, P.; Schaus, S. E. *J. Org. Chem.* **2007**, *72*, 9998−10008. (d) Mazzotta, S.; Gramigna, L.; Bernardi, L.; Ricci, A. *Org. Process Res. Dev.* **2010**, *14*, 687−691. (e) Hernando, E.; Arrayás, R. G.; Carretero, J. C. *Chem. Commun.* **2012**, *48*, 9622−9624. (f) Wei, Y.; He, W.; Liu, Y.; Liu, P.; Zhang, S. *Org. Lett.* **2012**, *14*, 704−707. (g) Wang, H.-Y.; Zhang, J.-X.; Cao, D.-D.; Zhao, G. *ACS Catal.* **2013**, *3*, 2218−2221. (h) Wang, B.; Liu, Y.; Sun, C.; Wei, Z.; Cao, J.; Liang, D.; Lin, Y.; Duan, H. *Org. Lett.* **2014**, *16*, 6432−6435. (i) Shan, J.; Cui, B.; Wang, Y.; Yang, C.; Zhou, X.; Han, W.; Chen, Y. *J. Org. Chem.* **2016**, *81*, 5270−5277. (j) Yu, L.; Wu, X.; Kim, M. J.; Vaithiyanathan, V.; Liu, Y.; Tan, Y.; Qin, W.; Song, C. E.; Yan, H. *Adv. Synth. Catal.* **2017**, *359*, 1879−1891. (k) Lu, N.; Li, R.; Wei, Z.; Cao, J.; Liang, D.; Lin, Y.; Duan, H. *J. Org. Chem.* **2017**, *82*, 4668−4676.

(4) (a) List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 827−833. (b) Pojarliev, P.; Biller, W. T.; Martin, H. J.; List, B. *Synlett* **2003**, 1903−1905. (c) CÓRDOVA, A. *Acc. Chem. Res.* **2004**, *37*, 102−112. (d) Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048−6049. (e) Yang, J. W.; Stadler, M.; List, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 609−611. (f) Song, J.; Shih, H.-W.; Deng, L. *Org. Lett.* **2007**, *9*, 603−606. (g) Yang, J. W.; Chandler, C.; Stadler, M.; Kampen, D.; List, B. *Nature* **2008**, *452*, 453−455. (h) Verkade, J. M. M.; van Hemert, L. J. C.; Quaedflieg, P. J. L. M.; Rutjes, F. P. J. T. *Chem. Soc. Rev.* **2008**, *37*, 29−41. (i) Chandler, C.; Galzerano, P.; Michrowska, A.; List, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 1978−1980. (j) Probst, N.; Madarász, A.; Valkonen, A.; Pápai, I.; Rissanen, K.; Neuvonen, A.; Pihko, P. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 8495−8499. (k) Bae, H. Y.; Kim, M. J.; Sim, J. H.; Song, C. E. *Angew. Chem.,*

DOI: 10.1021/acs.orglett.8b02087
Org. Lett. XXXX, XXX, XXX−XXX

Int. Ed. **2016**, *55*, 10825−10829. (l) Vaithiyanathan, V.; Kim, M. J.; Liu, Y.; Yan, H.; Song, C. E. *Chem. - Eur. J.* **2017**, *23*, 1268−1272.
(5) (a) Palomo, C.; Oiarbide, M.; Laso, A.; López, R. *J. Am. Chem. Soc.* **2005**, *127*, 17622−17623. (b) Fini, F.; Sgarzani, V.; Pettersen, D.; Herrera, R. P.; Bernardi, L.; Ricci, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7975−7978. (c) Yan, H.; Oh, J. S.; Lee, J.-W.; Song, C. E. *Nat. Commun.* **2012**, *3*, 1212. (d) Cao, D.; Chai, Z.; Zhang, J.; Ye, Z.; Xiao, H.; Wang, H.; Chen, J.; Wu, X.; Zhao, G. *Chem. Commun.* **2013**, *49*, 5972−5974. (e) Zheng, B.; Hou, W.; Peng, Y. *ChemCatChem* **2014**, *6*, 2527−2530. (f) Kim, M. J.; Xue, L.; Liu, Y.; Paladhi, S.; Park, S. J.; Yan, H.; Song, C. E. *Adv. Synth. Catal.* **2017**, *359*, 811−823. (g) Paladhi, S.; Park, S. Y.; Yang, J. W.; Song, C. E. *Org. Lett.* **2017**, *19*, 5336−5339.
(6) Lovejoy, B.; Welch, A. R.; Carr, S.; Luong, C.; Broka, C.; Hendricks, R. T.; Campbell, J. A.; Walker, K. A. M.; Martin, R.; Van Wart, H.; Browner, M. F. *Nat. Struct. Biol.* **1999**, *6*, 217−221.
(7) (a) O'Brien, C. J.; Tellez, J. L.; Nixon, Z. S.; Kang, L. J.; Carter, A. L.; Kunkel, S. R.; Przeworski, K. C.; Chass, G. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 6836−6839. (b) Cao, J.-J.; Zhou, F.; Zhou, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4976−4980. (c) Thalluri, K.; Nadimpally, K. C.; Paul, A.; Mandal, B. *RSC Adv.* **2012**, *2*, 6838−6845.
(8) (a) Wu, X.; Xue, L.; Li, D.; Jia, S.; Ao, J.; Deng, J.; Yan, H. *Angew. Chem., Int. Ed.* **2017**, *56*, 13722−13726. (b) Liu, Y.; Wu, X.; Li, S.; Xue, L.; Shan, C.; Zhao, Z.; Yan, H. *Angew. Chem., Int. Ed.* **2018**, *57*, 6491−6495. (c) Jia, S.; Chen, Z.; Zhang, N.; Tan, Y.; Liu, Y.; Deng, J.; Yan, H. *J. Am. Chem. Soc.* **2018**, *140*, 7056−7060.
(9) (a) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115−136. (b) Yuan, Y.; Li, X.; Ding, K. *Org. Lett.* **2002**, *4*, 3309−3311. (c) Nicolaou, K. C.; Montagnon, T.; Snyder, S. A. *Chem. Commun.* **2003**, 551−564. (d) Ramón, D. J.; Yus, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1602−1634. (e) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001−1020. (f) Seayad, J.; List, B. In *Multicomponent Reactions*; Zhu, J., Bienaymé, H., Eds.; Wiley-VCH: Weinheim, 2005; pp 277−299. (g) Broadwater, S. J.; Roth, S. L.; Price, K. E.; Kobašlija, M.; McQuade, D. T. *Org. Biomol. Chem.* **2005**, *3*, 2899−2906. (h) Chapman, C. J.; Frost, C. G. *Synthesis* **2007**, *2007*, 1−21. (i) Enders, D.; Grondal, C.; Hüttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570−1581. (j) Walji, A. M.; MacMillan, D. W. C. *Synlett* **2007**, *2007*, 1477−1489. (k) Dondoni, A.; Massi, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4638−4660. (l) Alaimo, P. J.; O'Brien, R., III; Johnson, A. W.; Slauson, S. R.; O'Brien, J. M.; Tyson, E. L.; Marshall, A.-L.; Ottinger, C. E.; Chacon, J. G.; Wallace, L.; Paulino, C. Y.; Connell, S. *Org. Lett.* **2008**, *10*, 5111−5114. (m) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993−3009. (n) Zhou, J. *Chem. - Asian J.* **2010**, *5*, 422−434. (o) Yang, B.-L.; Weng, Z.-T.; Yang, S.-J.; Tian, S.-K. *Chem. - Eur. J.* **2010**, *16*, 718−723.
(10) (a) Kawabata, T.; Yahiro, K.; Fuji, K. *J. Am. Chem. Soc.* **1991**, *113*, 9694−9696. (b) Baker, R. W.; Hambley, T. W.; Turner, P.; Wallace, B. J. *Chem. Commun.* **1996**, 2571−2572. (c) Hattori, T.; Date, M.; Sakurai, K.; Morohashi, N.; Kosugi, H.; Miyano, S. *Tetrahedron Lett.* **2001**, *42*, 8035−8038. (d) Zhao, H.; Hsu, D. C.; Carlier, P. R. *Synthesis* **2005**, *2005*, 1−16. (e) Mori, K.; Ohmori, K.; Suzuki, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5633−5637. (f) Mori, K.; Ohmori, K.; Suzuki, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5638−5641. (g) Kumarasamy, E.; Raghunathan, R.; Sibi, M. P.; Sivaguru, J. *Chem. Rev.* **2015**, *115*, 11239−11300. (h) Feng, J.; Li, B.; He, Y.; Gu, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 2186−2190. (i) Jolliffe, J. D.; Armstrong, R. J.; Smith, M. D. *Nat. Chem.* **2017**, *9*, 558−562. (j) Zheng, S.-C.; Wu, S.; Zhou, Q.; Chung, L. W.; Ye, L.; Tan, B. *Nat. Commun.* **2017**, *8*, 15238. (k) Feng, J.; Li, B.; Jiang, J.; Zhang, M.; Ouyang, W.; Li, C.; Fu, Y.; Gu, Z. *Chin. J. Chem.* **2018**, *36*, 11−14.
(11) (a) Tian, S.-K.; Chen, Y.; Hang, J.; Tang, L.; Mcdaid, P.; Deng, L. *Acc. Chem. Res.* **2004**, *37*, 621−631. (b) Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713−5743. (c) MacMillan, D. W. C. *Nature* **2008**, *455*, 304−308. (d) *Cinchona Alkaloids in Synthesis and Catalysis, Ligands, Immobilization and Organocatalysis*; Song, C. E., Ed.; Wiley-VCH: Weinheim, 2009. (e) Zhang, W.; Tan, D.; Lee, R.; Tong, G.; Chen, W.; Qi, B.; Huang, K.-W.; Tan, C.-H.; Jiang, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 10069−10073. (f) Zhu, B.; Zhang, W.; Lee, R.; Han, Z.; Yang, W.; Tan, D.; Huang, K.-W.; Jiang, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 6666−6670.
(12) (a) Haycock-Lewandowski, S. J.; Wilder, A.; Åhman, J. *Org. Process Res. Dev.* **2008**, *12*, 1094−1103. (b) Åhman, J.; Birch, M.; Haycock-Lewandowski, S. J.; Long, J.; Wilder, A. *Org. Process Res. Dev.* **2008**, *12*, 1104−1113. (c) Zhao, G.-L.; Lin, S.; Korotvička, A.; Deiana, L.; Kullberg, M.; Córdova, A. *Adv. Synth. Catal.* **2010**, *352*, 2291−2298.

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