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N-Heterocyclic Carbene/Lewis Acid Strategy for the Stereoselective Synthesis of Spirocyclic Oxindole−Dihydropyranones

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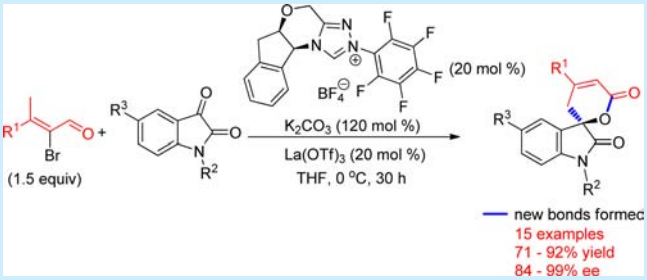
Supporting Information

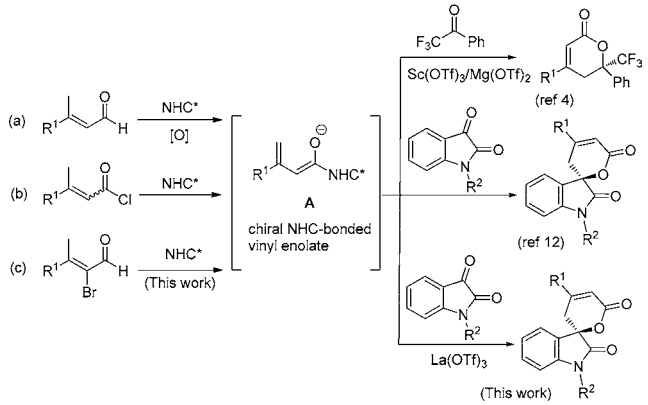
ABSTRACT: Under the cooperative catalysis of NHC/Lewis acid, the mild, straightforward [4 + 2] annulation of α-bromo-α,β-unsaturated aldehydes bearing γ-H with isatin derivatives gave spirocyclic oxindole−dihydropyranones stereoselectively. This approach is particularly attractive due to the concise construction, avoidance of external oxidants, and the potential utilization value of final products in molecular biology and pharmacy.



In recent decades, *N*-heterocyclic carbenes (NHCs) have been proven to be excellent organocatalysts for various organic reactions. In addition to the widely known benzoin condensation and Stetter reaction, the utility of the NHCs as organocatalysts has recently been extended to a host of other reactions such as ring-opening polymerization, homoenolate formations, and transesterification reactions.[1] Asymmetric reactions catalyzed by chiral NHCs have also achieved noticeable progress in the past years.[2,3] Furthermore, cooperative catalysis, which was pioneered by Scheidt, by combining Lewis acids with NHCs to provide new modes of activating molecules, is emerging as a powerful strategy in asymmetric synthesis.[1g,3] Recently, Chi et al. demonstrated that enantioselective control involving the relatively remote enal γ-carbon could be nicely accomplished through the introduction of $Sc(OTf)_3$ or $Sc(OTf)_3/Mg(OTf)_2$ as a relatively strong Lewis acid cocatalyst (Scheme 1, eq a).[4] A literature survey revealed that the use of a Lewis acid in conjunction with an NHC could also enhance yield and enantioselectivity and reverse diastereoselectivity.[3,5,6]

Indole and dihydropyranone are important structural motifs prevalent in many biologically active natural products; thus, they are important not only to synthetic but also to medicinal chemists.[7] So far, several strategies including oxidative spirocyclization,[8] metal-mediated multistep transformations,[9] Prins-type cyclization[10] and amino enyne catalysis[11] have been developed for the efficient assembly of a spirocyclic oxindole-pyranone architecture, an attractive combination of pharmacologically interesting pyran and oxindole units. Besides, Ye et al. reported an enantioselective NHC-catalyzed annulation of unsaturated acyl chlorides with isatin derivatives to prepare spirocyclic oxindole−dihydropyranones via NHC-bonded vinyl enolate **A** in 2011 (Scheme 1, eq b).[12] Our previous work showed that achiral NHCs are capable of activating 2-bromo-2-enal bearing γ-H to react with isatin derivatives to give racemic

Scheme 1. Formation of NHC-Bounded Vinyl Enolate from Unsaturated Acyl Chlorides, Oxidation of Enal, or 2-Bromo-2-enal



spirocyclic oxindole−dihydropyranones via a similar intermediate.[13d] To continue our work on NHC-catalyzed cascade synthesis of heterocycles,[13] in this paper, we report an enantioselective assembly of a spirocyclic oxindole−pyranone scaffold by the reaction of 2-bromo-2-enal with isatin derivatives catalyzed by chiral *N*-heterocyclic carbene in combination with La-based Lewis acid (Scheme 1, eq c).

Considering that the catalyst plays a key role in the whole reaction process, we first explored the influence of catalysts by taking the reaction of 2-bromo-3-methylbut-2-enal (**1a**) with *N*-methylisatin (**2a**) as an initial platform. Catalyst **5** derived from aminoindanol displayed promising catalytic activity during the preliminary screening. However, in the absence of the Lewis acid as cocatalyst, only 19−41% ee was observed in all cases

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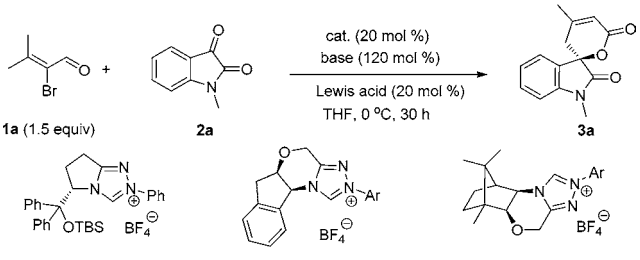
(Table 1, entries 2–4). When this reaction was performed under the relatively bulky triazolium compounds **4** and **6**, trace or no formation of **3a** was observed (Table 1, entries 1 and 5–6). Recent success employing Lewis acids with NHC catalysis prompted us to investigate this reaction using a NHC/Lewis acid approach instead of modifying the NHC catalysts to control the enantioselectivity outcome.[3,4] Thus, we investigated the precatalysts **5a–c** in the presence of $Yb(OTf)_3$ further, and triazolium salt **5b** was found to be the best (Table 1, entries 7–9). With the optimal catalyst in hand, several other Lewis acids were screened [$Y(OTf)_3$, $Sc(OTf)_3$, $La(OTf)_3$, $Ti(OiPr)_4$, $Al(OiPr)_3$] (Table 1, entries 10–14). Encouraging results emerged that the product ee jumped from 45 to 75% when $La(OTf)_3$ was used as a Lewis acid cocatalyst (Table 1, entry 8 vs 12). The reaction in the presence of $Y(OTf)_3$ or $Sc(OTf)_3$ showed a slightly lower ee than $La(OTf)_3$ (Table 1, entries 10 and 11). For $Ti(OiPr)_4$ and $Al(OiPr)_3$, product **3a** was not obtained (Table 1, entries 13 and 14). A catalyst loading test indicated that 20 mol % of **5b** would be better (Table 1, entries 15 and 16). Subsequently, the influences of different temperatures, solvents, bases, and the amount of base required on the reaction of **1a** and **2a** were examined to optimize the reaction conditions (Table 1, entries 17–30). Finally, we found that THF was the best solvent among THF, toluene, ether, and CH_2Cl_2, and K_2CO_3 was superior to Cs_2CO_3 in terms of both reaction yield and enantioselectivity at 0 °C, the optimal temperature, affording **3a** with 94% ee in 82% yield (Table 1, entry 24). The optimization studies revealed that decreasing or increasing the loading of base was not beneficial.

Under the optimized reaction conditions, the generality of the reaction was briefly explored (Table 2). It was found that isatins with both electron-withdrawing groups (4-F, 4-Br) and electron-donating groups (4-Me) were compatible with the reaction conditions. Small substituents such as methyl on the N atom or with electron-donating substituents on the aromatic ring of isatins reacted well with **1a** to give the products with relatively high enantioselectivities (Table 2, entries 1, 5, 6, 11, and 12). Others such as ethyl, allyl, or benzyl in place of methyl on the *N*-atom were also tolerated. Gratifyingly, when the *β*-methyl group of the enal was changed to a phenyl group or a

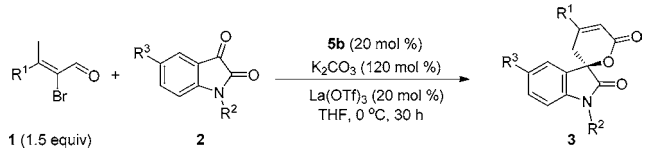
Table 1. Optimization of the Reaction Conditions



entry	precat. (mol %)	Lewis acid	base (mol %)	solvent	*t* (°C)	yield (%)[a]	ee (%)[b]
1	**4**(15)	-	Cs_2CO_3(115)	THF	0	-	-
2	**5a**(15)	-	Cs_2CO_3(115)	THF	0	83	-41[c]
3	**5b**(15)	-	Cs_2CO_3(115)	THF	0	39	-35[c]
4	**5c**(15)	-	Cs_2CO_3(115)	THF	0	64	-19[c]
5	**6a**(15)	-	Cs_2CO_3(115)	THF	0	-	-
6	**6b**(15)	-	Cs_2CO_3(115)	THF	0	trace	-
7	**5a**(15)	$Yb(OTf)_3$	Cs_2CO_3(115)	THF	0	62	3
8	**5b**(15)	$Yb(OTf)_3$	Cs_2CO_3(115)	THF	0	70	45
9	**5c**(15)	$Yb(OTf)_3$	Cs_2CO_3(115)	THF	0	46	13
10	**5b**(15)	$Y(OTf)_3$	Cs_2CO_3(115)	THF	0	68	72
11	**5b**(15)	$Sc(OTf)_3$	Cs_2CO_3(115)	THF	0	72	70
12	**5b**(15)	$La(OTf)_3$	Cs_2CO_3(115)	THF	0	79	75
13	**5b**(15)	$Ti(OiPr)_4$	Cs_2CO_3(115)	THF	0	-	-
14	**5b**(15)	$Al(OiPr)_3$	Cs_2CO_3(115)	THF	0	-	-
15	**5b**(10)	$La(OTf)_3$	Cs_2CO_3(110)	THF	0	trace	-
16	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	THF	0	80	78
17	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	THF	10	91	69
18	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	THF	5	85	72
19	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	THF	-5	78	72
20	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	THF	-10	77	64
21	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	CH_2Cl_2	0	29	54
22	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	toluene	0	23	14
23	**5b**(20)	$La(OTf)_3$	Cs_2CO_3(120)	ether	0	56	41
24	**5b(20)**	**$La(OTf)_3$**	**K_2CO_3(120)**	**THF**	**0**	**82**	**94**
25	**5b**(20)	$La(OTf)_3$	Na_2CO_3(120)	THF	0	56	81
26	**5b**(20)	$La(OTf)_3$	DBU(120)	THF	0	13	16
27	**5b**(20)	$La(OTf)_3$	DIPEA(120)	THF	0	39	25
28	**5b**(20)	$La(OTf)_3$	KOtBu(120)	THF	0	45	87
29	**5b**(20)	$La(OTf)_3$	K_2CO_3(110)	THF	0	66	93
30	**5b**(20)	$La(OTf)_3$	K_2CO_3(130)	THF	0	71	91

[a]Yield of the isolated product. [b]Determined by HPLC. [c]The minus ee value indicate that (−)-**3a** was isolated as the major isomer.

Table 2. Enantioselective Synthesis of Spirocyclic Oxindole–Dihydropyranones



entry	R^1	R^2	R^3	product	yield (%)[a]	ee(%)[b]
1	Me	Me	H	**3a**	82	94
2	Me	Et	H	**3b**	80	88
3	Me	allyl	H	**3c**	85	88
4	Me	Bn	H	**3d**	76	84
5	Me	Me	Me	**3e**	74	91
6	Me	Et	Me	**3f**	87	89
7	Me	Bn	Me	**3g**	90	87
8	Me	allyl	Me	**3h**	92	88
9	Me	Me	F	**3i**	77	85
10	Me	Me	Br	**3j**	84	85
11[c]	Ph	Me	H	**3k**	76	90
12[c]	Ph	Me	Me	**3l**	71	95
13[c]	4-MeC_6H_4	Me	Me	**3m**	77	96
14[c]	4-BrC_6H_4	Me	Me	**3n**	87	99
15[c]	4-$MeOC_6H_4$	Me	Me	**3o**	72	98

[a]Yield of the isolated product. [b]Determined by HPLC. [c]Reaction time: 45 h.

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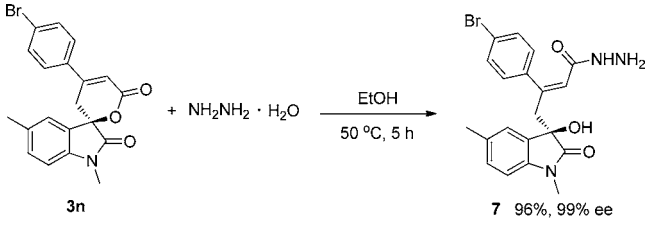
para-substituted phenyl group, such as 4-MeC_6H_4, 4-BrC_6H_4, or 4-$MeOC_6H_4$, the reaction went smoothly as well to give the desired product in good yield and excellent enantioselectivity exhibiting an outstanding adaptability (Table 2, entries 11−15). These results highlighted the wide application scope of the cooperative catalysis of NHC/Lewis acid.

The optical rotation data and HPLC analysis data of spirocyclic oxindole−dihydropyranone **3k** were found to be in good agreement with those reported in the literature; thus, the absolute configuration could be determined by comparison.[12] In addition, the configuration of compound **3a** was further confirmed by single-crystal X-ray analysis. Other product configurations were deduced based on analogy (see the Supporting Information for further details.)

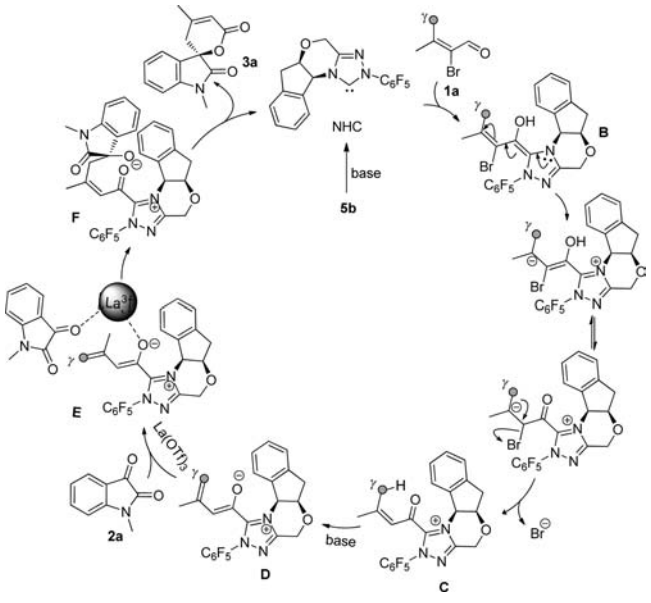
A further transformation exemplified the synthetic utility of the products of this NHC-catalyzed cascade reaction successfully. Hydrazinolysis of spirocyclic oxindole **3n** with hydrazine hydrate afforded the ring-opened product **7**, an integration of 3-hydroxyoxindole, and cinnamohydrazide with biological and synthetic potential, in excellent yield with high enantiopurity (Scheme 2).[14]

Scheme 2. Hydrazinolysis of Spirocyclic Oxindole 3n



The catalytic cycle of this NHC-catalyzed reaction is possibly initiated by the addition of the NHC to the 2-bromo-2-enal **1a** to give the Breslow intermediate **B**, which is then transformed into **C** through $a^3 \rightarrow d^3$ umpolung and debromination (Scheme 3).[13b,15] With the aid of base, the acylazoliumion **C** is deprotonated at the γ-position to give the vinyl enolate **D**. It then undergoes nucleophilic addition to isatin **2a** via intermediate **F**, eventually affording product **3a**. Similar to Chi's report,[4] the La(III) Lewis acid may, like the Sc(III) Lewis acid, have good affinities for carbonyl oxygens and carboxylates in multisite coordination to bring the ketone electrophile into close proximity with intermediate **D**, as illustrated by **E**. To some extent, this coordination enhances the chiral induction exerted by the chiral NHC catalyst.

Scheme 3. Possible Catalytic Cycle



In conclusion, we have developed a chiral NHC/Lewis acid catalyzed [4 + 2] annulation of α-bromo-α,β-unsaturated aldehydes bearing γ-H with isatin derivatives to prepare spirocyclic oxindole−dihydropyranones in good yield and with high enantioselectivity. This approach is particularly attractive due to the avoidance of external oxidants and the potential utilization value of final products in molecular biology and pharmaceuticals. This paper promotes the development of the powerful strategy of combining umpolung catalysis of NHC with Lewis acid activation. New applications related to this strategy are underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization of the products. 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) For reviews, see: (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (b) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691. (c) Moore, J. L.; Rovis, T. *Top. Curr. Chem.* **2010**, *291*, 77. (d) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Jose, A.; Sreekumar, V. *Chem. Soc. Rev.* **2011**, *40*, 5336. (e) Rong, Z.-Q.; Zhang, W.; Yang, G.-Q.; You, S.-L. *Curr. Org. Chem.* **2011**, *15*, 3077. (f) Grossmann, A.; Enders, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 314. (g) Cohen, D. T.; Scheidt, K. A. *Chem. Sci.* **2012**, *3*, 53. (h) Vora, H. U.; Wheeler, P.; Rovis, T. *Adv. Synth. Catal.* **2012**, *354*, 1617. (i) Knappke, C. E. I.; Imami, A.; Jacobi von Wangelin, A. *ChemCatChem.* **2012**, *4*, 937. (j) Studer, A.; De Sarkar, S.; Biswas, A.; Samanta, R. C. *Chem.—Eur. J.* **2013**, *19*, 4664. For recent advances, see: (k) Jia, M.-Q.; Liu, C.; You, S.-L. *J. Org. Chem.* **2012**, *77*, 10996. (l) DiRocco, D. A.; Rovis, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 5904. (m) Jia, M.-Q.; You, S.-L. *Chem. Commun.* **2012**, *48*, 6363. (n) Bhunia, A.; Yetra, S. R.; Bhojgude, S. S.; Biju, A. T. *Org. Lett.* **2012**, *14*, 2830. (o) Sun, L.-H.; Liang, Z.-Q.; Jia, W.-Q.; Ye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 5803. (p) Mo, J.; Shen, L.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 8588. (q) Fu, Z.; Xu, J.; Zhu, T.; Leong, W. W. Y.; Chi, Y. R. *Nat. Chem.* **2013**, *5*, 835. (r) Chen, X.-Y.; Xia, F.; Cheng, J.-T.; Ye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 10644. (s) Jia, M.-Q.; Liu, C.; You, S.-L. *ACS Catal.* **2013**, *3*, 622. (t) Cheng, J.; Huang, Z.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 8592.

(2) (a) Lv, H.; Jia, W.-Q.; Sun, L.-H.; Ye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8607. (b) Candish, L.; Forsyth, C. M.; Lupton, D. W. *Angew. Chem., Int. Ed.* **2013**, *52*, 9149. (c) Ma, C.; Jia, Z.-J.; Liu, J.-X.; Zhou, Q.-Q.; Dong, L.; Chen, Y.-C. *Angew. Chem., Int. Ed.* **2013**, *52*, 948. (d) Candish, L.; Lupton, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 58. (e) White, N. A.; DiRocco, D. A.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 8504. (f) Zhang, B.; Feng, P.; Sun, L.-H.; Cui, Y.; Ye, S.; Jiao, N. *Chem.—Eur. J.* **2012**, *18*, 9198. (g) Zhao, Y.-M.; Cheung, M. S.; Lin, Z.; Sun, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10359. (h) Kravina, A. G.; Mahatthananchai, J.; Bode, J. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 9433. (i) Wurz, N. E.; Daniliuc, C. G.; Glorius, F. *Chem.—Eur. J.* **2012**, *18*, 16297. (j) Iwahana, S.; Iida, H.; Yashima, E. *Chem.—Eur. J.* **2011**, *17*, 8009.

(3) (a) Raup, D. E. A.; Cardinal-David, B.; Holte, D.; Scheidt, K. A. *Nat. Chem.* **2010**, *2*, 766. (b) Cardinal-David, B.; Raup, D. E. A.; Scheidt, K. A. *J. Am. Chem. Soc.* **2010**, *132*, 5345. (c) Cohen, D. T.; Cardinal-David, B.; Roberts, J. M.; Sarjeant, A. A.; Scheidt, K. A. *Org. Lett.* **2011**, *13*, 1068. (d) Cohen, D. T.; Cardinal-David, B.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1678. (e) Dugal-Tessier, J.; O'Bryan, E. A.; Schroeder, T. B. H.; Cohen, D. T.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4963.

(4) Mo, J.; Chen, X.; Chi, Y. R. *J. Am. Chem. Soc.* **2012**, *134*, 8810.

(5) For a recent report combining NHC−homoenolates with Brønsted acid activation, see: Zhao, X.; DiRocco, D. A.; Rovis, T. *J. Am. Chem. Soc.* **2011**, *133*, 12466. For the impact of alkali metal salt effects on carbene-catalyzed reactions, see: (a) Phillips, E. M.; Riedrich, M.; Scheidt, K. A. *J. Am. Chem. Soc.* **2010**, *132*, 13179. (b) Ryan, S. J.; Candish, L.; Lupton, D. W. *J. Am. Chem. Soc.* **2011**, *133*, 4694. (c) Rong, Z.-Q.; Jia, M.-Q.; You, S.-L. *Org. Lett.* **2011**, *13*, 4080.

(6) For a computational study on NHC−Lewis acid processes, see: Domingo, L. R.; Zaragozá, R. J.; Arnó, M. *Org. Biomol. Chem.* **2011**, *9*, 6616. For a comparative study of Lewis acid strength, see: Kobayashi, S.; Busujima, T.; Nagayama, S. *Chem.—Eur. J.* **2000**, *6*, 3491.

(7) (a) Edmondson, S.; Danishefsky, S. J.; Sepp-Lorenzino, L.; Rosen, N. *J. Am. Chem. Soc.* **1999**, *121*, 2147. (b) Sebahar, P. R.; Williams, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 5666. (c) Bagul, T. D.; Lakshmaiah, G.; Kawabata, T.; Fuji, K. *Org. Lett.* **2002**, *4*, 249. (d) Onishi, T.; Sebahar, P. R.; Williams, R. M. *Org. Lett.* **2003**, *5*, 3135. (e) Ding, K.; Lu, Y.; Nikolovska-Coleska, Z.; Wang, G.; Qiu, S.; Shangary, S.; Gao, W.; Qin, D.; Stuckey, J.; Krajewski, K.; Roller, P. P.; Wang, S. *J. Med. Chem.* **2006**, *49*, 3432. (f) Trost, B. M.; Cramer, N.; Bernsmann, H. *J. Am. Chem. Soc.* **2007**, *129*, 3086. (g) Galliford, C. V.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8748. (h) Yang, J.; Wearing, X. Z.; Le Quesne, P. W.; Deschamps, J. R.; Cook, J. M. *J. Nat. Prod.* **2008**, *71*, 1431. (i) Miller, K. A.; Tsukamoto, S.; Williams, R. M. *Nat. Chem.* **2009**, *1*, 63. (j) Trost, B. M.; Brennan, M. K. *Synthesis* **2009**, 3003. (k) Singh, G. S.; Desta, Z. Y. *Chem. Rev.* **2012**, *112*, 6104. (l) Dalpozzo, R.; Bartoli, G.; Bencivenni, G. *Chem. Soc. Rev.* **2012**, *41*, 7247. (m) Ramachary, D. B.; Venkaiah, C.; Madhavachary, R. *Org. Lett.* **2013**, *15*, 3042. (n) Cheng, D.; Ishihara, Y.; Tan, B.; Barbas, C. F. *ACS Catal.* **2014**, *4*, 743.

(8) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Lett.* **2013**, *15*, 5254.

(9) (a) Hojo, D.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem.,Int. Ed.* **2008**, *47*, 5820. (b) Shintani, R.; Hayashi, S.-y.; Murakami, M.; Takeda, M.; Hayashi, T. *Org. Lett.* **2009**, *11*, 3754.

(10) (a) Castaldi, M. P.; Troast, D. M.; Porco, J. A. *Org. Lett.* **2009**, *11*, 3362. (b) Wang, J.; Crane, E. A.; Scheidt, K. A. *Org. Lett.* **2011**, *13*, 3086.

(11) Ramachary, D. B.; Venkaiah, C.; Madhavachary, R. *Org. Lett.* **2013**, *15*, 3042.

(12) Shen, L.-T.; Shao, P.-L.; Ye, S. *Adv. Synth. Catal.* **2011**, *353*, 1943.

(13) (a) Yao, C.; Wang, D.; Lu, J.; Qin, B.; Zhang, H.; Li, T.; Yu, C. *Tetrahedron Lett.* **2011**, *52*, 6162. (b) Yao, C.; Wang, D.; Lu, J.; Li, T.; Jiao, W.; Yu, C. *Chem.—Eur. J.* **2012**, *18*, 1914. (c) Yao, C.; Jiao, W.; Xiao, Z.; Liu, R.; Li, T.; Yu, C. *Tetrahedron* **2013**, *69*, 1133. (d) Yao, C.; Xiao, Z.; Liu, R.; Li, T.; Jiao, W.; Yu, C. *Chem.—Eur. J.* **2013**, *19*, 456. (e) Yao, C.; Jiao, W.; Xiao, Z.; Xie, Y.; Li, T.; Wang, X.; Liu, R.; Yu, C. *RSC Adv.* **2013**, *3*, 10801.

(14) (a) Majumdar, P.; Pati, A.; Patra, M.; Behera, R. K.; Behera, A. K. *Chem. Rev.* **2014**, *114*, 2942. (b) Kumar, A.; Chimni, S. S. *RSC Adv.* **2012**, *2*, 9748. (c) De, P.; Bedos-Belval, F.; Vanucci-Bacque, C.; Baltas, M. *Curr. Org. Chem.* **2012**, *16*, 747. (d) Narang, R.; Narasimhan, B.; Sharma, S. *Curr. Med. Chem.* **2012**, *19*, 569.

(15) Sun, F.-G.; Sun, L. H.; Ye, S. *Adv. Synth. Catal.* **2011**, *353*, 3134.