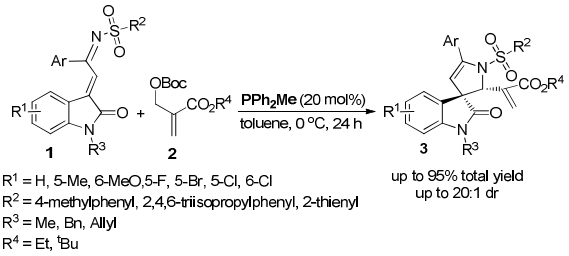
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Regio- and Diastereoselective Construction of 1',2'-Dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates through Phosphine-catalyzed [4+1] Annulation of Morita-Baylis-Hillman Carbonates with Oxindole-Derived α,β-Unsaturated Imines

Yu Lei,[a] Xiao-Nan Zhang,[a] Xue-Yan Yang,[a] Qin Xu[a] and Min Shi*[a,b]*



Phosphine-catalyzed [4+1] annulation of Morita-Baylis-Hillman (MBH) carbonates with oxindole-derived α,β-unsaturated imines has been developed, giving the corresponding 1',2'-dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates in moderate to good yields and diastereoselectivities under mild conditions.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Regio- and Diastereoselective Construction of 1',2'-Dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates through Phosphine-catalyzed [4+1] Annulation of Morita-Baylis-Hillman Carbonates with Oxindole-Derived α,β-Unsaturated Imines

Yu Lei,[a] Xiao-Nan Zhang,[a] Xue-Yan Yang,[a] Qin Xu*[a] and Min Shi*[a,b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Phosphine-catalyzed [4+1] annulation of Morita-Baylis-Hillman (MBH) carbonates with oxindole-derived α,β-unsaturated imines has been developed, giving the corresponding 1',2'-dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates in moderate to good yields with moderate to good diastereoselectivities under mild conditions.

The spirooxindole backbones have drawn tremendous interest in the area of synthetic organic chemistry and medicinal chemistry since they are the core structures in a variety of pharmacological agents and natural alkaloids[1] and have various types of biological activities.[2] For example, the 1',2'-dihydrospiro[indoline-3,3'-pyrrol]-2-one featuring the molecular structures of spirotryprostatin B is one of the mammalian cell cycle inhibitors.[1d] Moreover, the spiro[indoline-3,3'-pyrrolidin]-2-one skeleton as a structural characteristic has been found in alkaloid rhynchophylline (Figure 1).[1b] Therefore, they have recently become one of the most attractive synthetic targets for organic chemists. Subsequently, many kinds of elegant synthetic approaches have been thus far developed for their syntheses.[3]

Over the past decade, nucleophilic phosphine catalysis has made significant progress[4] and phosphine-mediated/catalyzed annulations have emerged as a powerful tool for the synthesis of a variety of unique carbo- and heterocyclic frameworks.[5] In this arena, Lu and coworkers first reported a series of intra- and intermolecular [3+n] annulations (n = 2, 4, 6) using Morita-Baylis-Hillman (MBH) carbonates as 1,3-dipoles with various electron-deficient olefins catalyzed by tertiary phosphine, affording the corresponding cycloadducts in good yield and high regioselectivities under mild conditions.[6] Furthermore, [3+2] annulations of allenoates/alkynes or MBH acetate/carbonates with electron-deficient alkenes or imines have been widely explored and established as an effective method for constructing a wide range of highly functionalized five-membered ring systems.[7] Apart from phosphine-catalyzed [3+2] annulations, phosphine-catalyzed [4+1] annulations are also efficient methodologies to construct functionalized five-membered carbo- and heterocycles. Recently, Zhang,[8] Huang,[9] He,[10] Shi,[11] Lu[12] and Fu[13] as well as their co-workers have developed many [4+1] annulations utilizing MBH carbonates, maleimides[14] or others as 1,1-dipoles with various electron-deficient alkenes to obtain the desired heterocyclic products in high yields under mild conditions, respectively also along with their asymmetric versions. Another type of [4+1] annulation was disclosed by Tong[15] in 2010, using 2,3-butadienoate as a C_4 synthon under phosphine catalysis to construct cyclopentene containing products.

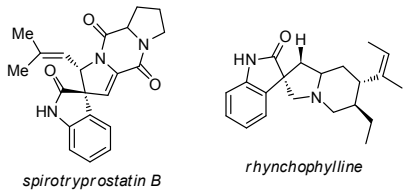


Figure 1. Selected examples of natural products with spirooxindole motifs

α,β-unsaturated imines as synthetically useful C_2 or C_4 synthons have been widely utilized to construct multifunctional five- and six-membered heterocycles.[10a, 16, 17] Our group has reported an efficient method to construct spiro-fused six-membered heterocycles through [4+2] annulations of vinyl ketones with oxindole-derived α,β-unsaturated imines in the presence of phosphine.[17c] However, to the best of our knowledge, there has been no report on phosphine-catalyzed synthesis of isatin-based spiro-fused five-membered heterocycles through [4+1] annulation by oxindole-derived α,β-unsaturated imines.[17] Herein, we wish to disclose a phosphine-catalyzed regio- and diastereoselective [4+1] annulation of MBH carbonates with oxindole-derived α,β-unsaturated imines to produce 1',2'-dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates in moderate to good yields and

[a] *Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China.*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China. E-mail: mshi@mail.sioc.ac.cn.*

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of new compounds, and CCDC 1024783 and 1019412. See DOI: 10.1039/b000000x/

moderate to good diastereoselectivities under mild conditions (Scheme 1).

Scheme 1. Phosphine-catalyzed annulations of oxindole-derived α,β-unsaturated imines to construct six- or five-membered spiro heterocyclic compounds

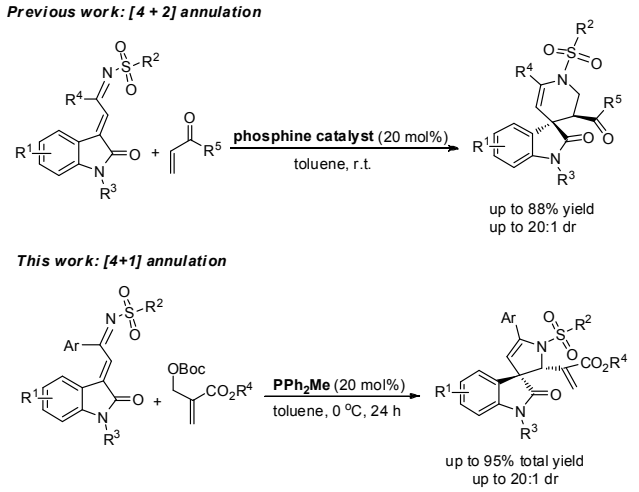
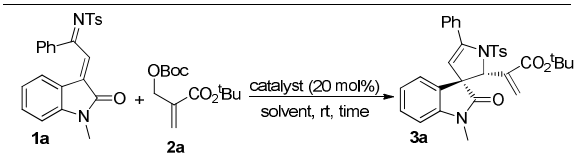


Table 1. Optimization of reaction conditions for the [4+1] annulation

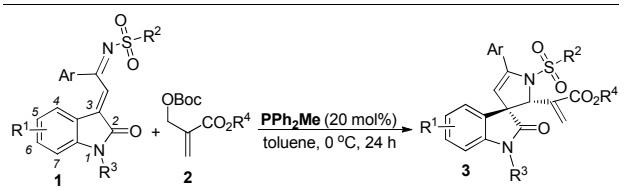


entry	catalyst	solvent	time (h)	yield (%)[a]	dr (%)[b]
1	PPh_3	toluene	24	90	1.2:1
2	P(*p*-$MeOC_6H_4$)$_3$	toluene	24	78	4:1
3	P(*p*-FC_6H_4)$_3$	toluene	48	82	1.6:1
4	PPh_2Me	toluene	24	90	5.5:1
5	$PPhMe_2$	toluene	12	89	1.2:1
6	PBu_3	toluene	12	55	1.1:1
7	dppb	toluene	24	60	4:1
8	PPh_2Me	CH_2Cl_2	24	69	2:1
9	PPh_2Me	THF	24	66	3:1
10	PPh_2Me	MeCN	24	65	3:1
11	PPh_2Me	Et_2O	24	81	3:1
12[c]	PPh_2Me	toluene	24	88	8:1

[a] Yield was determined by ^{1}H NMR spectroscopic data of crude products using 1,3,5-trimethoxybenzene as a calibrated internal standard. [b] Determined by ^{1}H NMR spectroscopic data of crude products. [c] The reaction mixtures were stirred at 0 °C.

Initially, we examined the reaction outcome of oxindole-derived α,β-unsaturated imine **1a** (0.1 mmol) with MBH carbonate **2a** (0.12 mmol, 1.2 equiv.) catalyzed by PPh_3 in toluene (1.0 mL) at room temperature. The desired [4+1] cycloadduct **3a** was obtained in 90% total yield along with 1.2:1 dr value within 24 h (Table 1, entry 1). To improve the dr value, other phosphines such as P(*p*-$MeOC_6H_4$)$_3$, P(*p*-FC_6H_4)$_3$, PPh_2Me, $PPhMe_2$, PBu_3, and dppb were further tested in this reaction and the results of these experiments are summarized in Table 1. It was found that PPh_2Me is the best catalyst, affording **3a** in 90% total yield along with 5.5:1 dr value (Table 1, entries 1-7). We next examined the solvent effects of this reaction in CH_2Cl_2, THF, MeCN or Et_2O. It was found that toluene is the best solvent in this reaction (Table 1, entries 8-11). Reducing the reaction temperature to 0 °C gave the corresponding annulation product **3a** in 88% total yield along with 8:1 dr (Table 1, entry 12). Therefore, the best reaction conditions have been determined as that using PPh_2Me (20 mol%) as the catalyst and carrying out the reaction in toluene at 0 °C within 24 hours.

Table 2. Substrate scope of the [4+1] annulation of **1** with **2**



entry[a]	Ar	R^1	R^2	R^3	R^4	yield[b] (%)	dr[c]
1	4-FC_6H_4	H	4-methylphenyl	Me	^{t}Bu	**3b**, 72	8:1
2	4-ClC_6H_4	H	4-methylphenyl	Me	^{t}Bu	**3c**, 84	8:1
3	4-BrC_6H_4	H	4-methylphenyl	Me	^{t}Bu	**3d**, 78	7:1
4	4-$MeOC_6H_4$	H	4-methylphenyl	Me	^{t}Bu	**3e**, 95	9:1
5	4-MeC_6H_4	H	4-methylphenyl	Me	^{t}Bu	**3f**, 86	7:1
6	4-$(CH_3)_3CC_6H_4$	H	4-methylphenyl	Me	^{t}Bu	**3g**, 88	7:1
7	4-$MeOC_6H_4$	5-Me	4-methylphenyl	Me	^{t}Bu	**3h**, 88	9:1
8	4-$MeOC_6H_4$	6-MeO	4-methylphenyl	Me	^{t}Bu	**3i**, 84	5:1
9	4-$MeOC_6H_4$	5-F	4-methylphenyl	Me	^{t}Bu	**3j**, 63	20:1
10	4-$MeOC_6H_4$	5-Cl	4-methylphenyl	Me	^{t}Bu	**3k**, 65	20:1
11	4-$MeOC_6H_4$	6-Cl	4-methylphenyl	Me	^{t}Bu	**3l**, 54	20:1
12	4-$MeOC_6H_4$	5-Br	4-methylphenyl	Me	^{t}Bu	**3m**, 68	20:1
13	C_6H_5	5-Cl	4-methylphenyl	Bn	^{t}Bu	**3n**, 62	12:1
14	C_6H_5	5-Cl	4-methylphenyl	Allyl	^{t}Bu	**3o**, 68	10:1
15	C_6H_5	H	2-thienyl	Me	^{t}Bu	**3p**, 84	9:1
16	4-$MeOC_6H_4$	H	2-thienyl	Me	^{t}Bu	**3q**, 80	8:1
17	4-MeC_6H_4	H	2-thienyl	Me	^{t}Bu	**3r**, 76	7:1
18	4-ClC_6H_4	H	2,4,6-triisopropylphenyl	Me	^{t}Bu	**3s**, 83	4:1
19	4-BrC_6H_4	H	2,4,6-triisopropylphenyl	Me	^{t}Bu	**3t**, 82	4:1
20	C_6H_5	H	4-methylphenyl	Me	Et	**3u**, 85	5:1

[a] **1** (0.2 mmol), **2** (0.3 mmol) and **PPh_2Me** (0.04 mmol) were stirred in 1.0 mL of toluene at 0 °C within 24h. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopic data of crude products.

With the optimized reaction conditions in hand, we next turned our attention to the scope and limitations of this reaction using a variety of oxindole-derived α,β-unsaturated imines **1** with MBH carbonates **2** and the results are summarized in Table 2. Using MBH carbonate **2a** as substrate, we examined its reaction with various substituted oxindole-derived α,β-unsaturated imines **1b-1t** and found that these [4+1] annulation proceeded smoothly to give the desired products in moderate to good yields. Substrates with electron-rich or electron-withdrawing substituents on the Ar group gave the corresponding products **3b-3g** in good yields (up to 95% yield) and good dr values (up to 9:1 dr), respectively (Table 2, entries 1-6). We next examined oxindole-derived α,β-unsaturated imines **1h-1o** bearing different substituents on their benzene rings of oxindole or having different N-protecting groups, and it was found that all of the reactions proceeded very well to produce the corresponding products **3h-3o** in moderate to good yields along with good dr values (Table 2, entries 7-14). It should be pointed out that when electron-withdrawing substituents were introduced on their benzene rings, the reactions afforded the desired products in slightly lower yields, but with better diastereoselectivities perhaps due to the electronic effect (Table 2, entries 9-14). When R^2 was a heteroaromatic group (R^2 = 2-thienyl), the

reactions also proceeded efficiently to produce the corresponding products **3p-3r** in good yields and good dr values, respectively (Table 2, entries 15-17). When R^2 was a sterically more bulky 2,4,6-triisopropylphenyl moiety, the desired spirooxindole products **3s** and **3t** could also be obtained in good yields, but in lower diastereoselectivities (Table 2, entries 18 and 19). The relative configuration of the major diastereoisomer of **3t** was assigned by X-ray diffraction (see the Supporting Information).[18] Ethyl 2-(((tert-butoxycarbonyl)oxy)methyl)acrylate **2b** was also used to react with **1a**, affording the corresponding product **3u** in 85% yield and moderate dr value (dr = 5:1) (Table 2, entry 20) and the configuration of the major diastereoisomer of **3u** was also assigned by X-ray diffraction. Its ORTEP drawing is shown in Figure 2 and the corresponding CIF data are presented in the Supporting Information.[18]

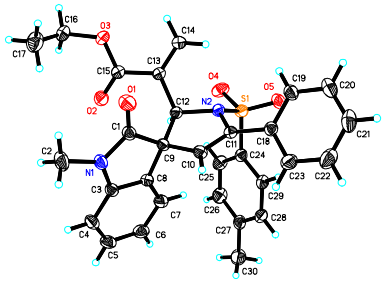
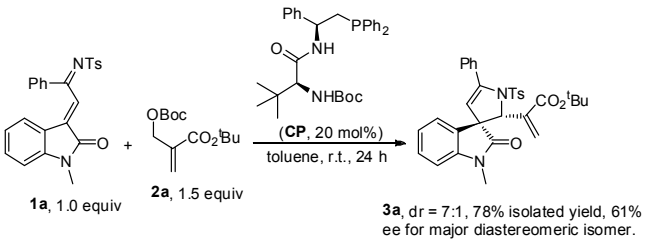


Figure 2. X-ray crystal structure of the major diastereomeric product **3u**

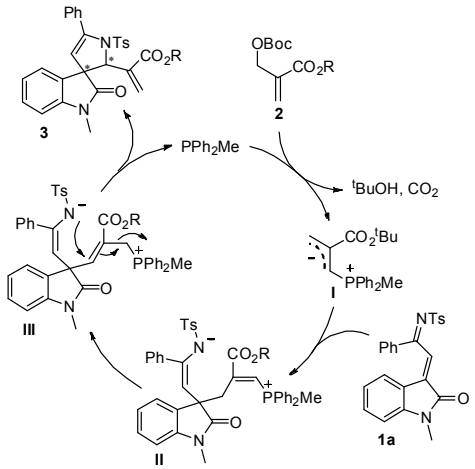
Next, we examined the asymmetric [4+1] annulation of **1a** with MBH carbonate **2a** using natural amino acid derived chiral phosphine catalyst **CP**,[18] giving the corresponding cycloadduct **3a** in 78% isolated yield along with 7:1 dr and 61% ee value for the major diastereomeric isomer in toluene at room temperature (Scheme 2).

Scheme 2. Asymmetric [4+1] annulation catalyzed by chiral phosphine catalyst **CP**



On the basis of above experimental results and closely related reports,[6d, 8, 9, 10, 11] a plausible reaction mechanism has been outlined in Scheme 3. PPh_2Me attacks from the β-position of MBH carbonate **2** to take off carbon dioxide and t-BuOH, affording phosphorus ylide **I**, which undergoes the nucleophilic attack with α,β-unsaturated imine **1a** to give the corresponding intermediate **II**. Subsequent hydrogen transfer produces intermediate **III**, which is followed by a Michael addition and elimination of PPh_2Me to produce **3**.

Scheme 3. A plausible reaction mechanism.



In summary, we have developed an interesting phosphine-catalyzed regio- and diastereoselective [4+1] annulation of MBH carbonates with oxindole-derived α,β-unsaturated imines, affording the corresponding functionalized 1',2'-dihydrospiro[indoline-3,3'-pyrrol]-2'-yl)acrylates in moderate to good yields and dr values under mild conditions. A plausible reaction mechanism has also been proposed on the basis of previous literature. Further efforts in our laboratory will focus on exploring the more effective asymmetric version and possible application of this annulation in organic synthesis.

Acknowledgement: We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, and the National Natural Science Foundation of China (20472096, 21372241, 21361140350, 20672127, 21421091, 21372250, 21121062, 21302203 and 20732008).

Notes and references

1 For selected reviews, see: (a) C. Marti and E. M. Carreia, *Eur. J. Org. Chem*., 2003, 2209; (b) C. V. Galliford and K. A. Scheidt, *Angew. Chem., Int. Ed.,* 2007, **46**, 8748; (c) G. S. Singh and Z. Y. Desta, *Chem. Rev.,* 2012, **112**, 6104. For selected papers, see: (d) P. R. Sebahar and R. M. Williams, *J. Am. Chem. Soc.,* 2000, **122**, 5666; (e) A. H. Abdel-Rahman, E. M. Keshk, M. A. Hanna and Sh. M. EI-Bady, *Bioorg. Med. Chem*., 2004, **12**, 2483; (f) T.-L. Liu, Z.-Y. Xue, H.-Y. Tao and C.-J. Wang, *Org. Biomol. Chem.*, 2011, **9**, 1980; (g) T.-L. Liu, Z.-L. He, Q.-H. Li, H.-Y. Tao and C.-J. Wang, *Adv. Synth. Catal.* 2011, **353**, 1713; (h) Yiming Cao, X. Jiang, L. Liu, F. Shen, F. Zhang and R. Wang, *Angew. Chem. Int. Ed.* **2011**, **50**, 9124; (i) A. Awata and T. Arai, *Chem. Eur. J.* 2012, **18**, 8278.

2 (a) M. M.-C. Lo, C. S. Newmann, S. Nagayams, E. O. Perlstein and S. L. Schreiber, *J. Am. Chem. Soc*., 2005, **127**, 10130; (b) V. V. Vintonyak, K. Warburg, H. Kruse, S. Grimme, K. Hubel, D. Rauth and H. Waldmann, *Angew. Chem. Int. Ed.,* 2010, **49**, 5902; (c) G. K. Nutan, M. Modi, S. K. Gupta and R. K. Singh, *Eur. J. Med. Chem*., 2011, **46**, 1181.

3 For selected reviews, see: (a) A. B. Dounay and L. E. Overman, *Chem. Rev.*, 2003, **103**, 2945; (b) B. M. Trost and M. K. Brennan, *Synthesis.,* 2009, 3003; (c) F. Zhou, Y. Liu and J. Zhou, *Adv. Synth. Catal,*. 2010, **352**, 1381. For selected papers, see: (d) B. M. Trost, N. Cramer and S. M. Silverman, *J. Am. Chem. Soc.,* 2007, **129**, 12396; (e) X. Chen, Q. Wei, S. Luo, H. Xiao and L.-Z. Gong, *J. Am. Chem. Soc.,* 2009, **131**, 13819; (f) Q. Wei, and L.-Z. Gong, *Org. Lett.,* 2010, **12**, 1008.

4 For selected reviews, see: (a) X. Lu, C. Zhang and Z. Xu, *Acc. Chem. Res.,* 2001, **34**, 535; (b) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.,* 2004, **346**, 1035; c) L.-W. Ye, J. Zhou and Y. Tang, *Chem. Soc. Rev.*, 2008, **37**, 1140; (d) B. J. Cowen and S. J. Miller, *Chem. Soc. Rev.*, 2009, **38**, 3102; (e) A. Marinetti and A. Voituriez, *Synlett.,* 2010, 174; (f) Z.-M. Wang, X.-Z. Xu and O. Kwon, *Chem. Soc. Rev.*, 2014, **43**, 2927.

5 For selected reviews, see: (a) S. E. Denmark and G. L. Beutner, *Angew. Chem., Int. Ed.*, 2008, **47**, 1560; (b) A. Marinetti and A. Voituriez, *Synlett*, 2010, 174; (c) S. Xu and Z. He, *Sci. Sin. Chim.*, 2010, **40**, 856.

6 (a) Y. Du, X. Lu and C. Zhang, *Angew. Chem., Int. Ed.*, 2003, **42**, 1035; (b) Y. Du, J. Feng and X. Lu, *Org. Lett.*, 2005, **7**, 1987; (c) J. Feng, X. Lu, A. Kong and X. Han, *Tetrahedron*, 2007, **63**, 6035; (d) S. Zheng and X. Lu, *Org. Lett.*, 2008, **10**, 4481; (e) S. Zheng and X. Lu, *Tetrahedron Lett.*, 2009, **50**, 4532; (f) S. Zheng and X. Lu, *Org. Lett.*, 2009, **11**, 3978; (g) .

7 (a) C.-W. Cho, J.-R. Kong and M. J. Krische, *Org. Lett*., 2004, **6**, 1337; (b) C.-W. Cho and M. J. Krische, *Angew. Chem. Int. Ed*., 2004, **43**, 6689; (c) B. M. Trost, R. M. Machacek and H. C. Tsui, *J. Am. Chem. Soc*., 2005, **127**, 7014; (d) Y.-S. Du, X.-L. Han and X.-Y. Lu, *Tetrahedron Lett*., 2004, **45**, 4967; (e) D. J. V. C. van Steenis, T. Marcelli, M. Lutz, A. L. Spek, J. H. van Maarseveen and H. Hiemstra, *Adv. Synth. Catal*., 2007, **349**, 281; (f) Y.-Q. Jiang, Y.-L. Shi and M. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 7202; (g) H.-L. Cui, X. Feng, J. Peng, J. Lei, K. Jiang and Y.-C. Chen, *Angew. Chem. Int. Ed*., 2009, **48**, 5737; (h) J. Peng, X. Huang, H.-L. Cui and Y.-C. Chen, *Org. Lett*., 2010, **12**, 4260; (i) T. Furukawa, T. Nishimine, E. Tokunaga, K. Hasegawa, M. Shiro and N. Shibata, *Org. Lett*., 2011, **13**, 3972; (j) T. Furukawa, J. Kawazoe, W. Zhang, T. Nishimine, E. Tokunaga, T. Matsumoto, M. Shiro and N. Shibata, *Angew. Chem. Int. Ed*., 2011, **50**, 9684; (k) F. Zhong, J. Luo, G. Y. Chen, X. Dou and Y. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 10222; (l) G.-Y. Chen, F. Zhong and Y. Lu, *Org. Lett.*, 2012, **14**, 3955; (m) B. Wang, X. Companyó, J. Li, A. Moyano and R. Rios, *Tetrahedron Lett.*, 2012, **53**, 4124; (n) R. Zhou, J.-F. Wang, H.-B. Song and Z.-J. He, *Org. Lett.*, 2011, **13**, 580; (o) M. Yang, T. Wang, S. Cao and Zhengjie He, *Chem. Commun.*, 2014, **50**, 13506.

8 Z.-L. Chen and J.-L. Zhang, *Chem.-Asian J.*, 2010, **5**, 1542.

9 (a) P.-Z. Xie, Y. Huang and R.-Y. Chen, *Org. Lett.*, 2010, 12, 3768; (b) P.-Z. Xie, E.-Q Li, J. Zheng, X. Li, Y. Huang and R.-Y. Chen, *Adv. Synth. Catal.*, 2013, 355, 161.

10 (a) J.-J. Tian, R. Zhou, H.-B. Song and Z.-J. He, *J. Org. Chem.*, 2011, **76**, 2374; (b) R. Zhou, C. Duan, C.-J. Yang and Z.-J. He, Chem. *Asian J.*, 2014, **9**, 1183.

11 (a) X.-N. Zhang, H.-P. Deng, L. Huang, Y. Wei and M. Shi, *Chem. Commun.*, 2012, **48**, 8664; (b) F.-L. Hu, Y. Wei and M. Shi, *Chem. Commun.*, 2014, **50**, 8912; (c) Y. Wei and M. Shi, *Chem. Rev.* 2013, **113**, 6659; (d) Y. Wei and M. Shi, *Chem. Asian. J.* 2014, **9**, 2720.

12 X.-Y Han, W.-J. Yao, T.-L. Wang, Y.-R. Tan, Z.-Y. Yan, J. Kwiatkowski and Y.-X. Lu, *Angew. Chem. Int. Ed.*, 2014, **53**, 5643.

13 S. Kramer and G. C. Fu, *J. Am. Chem. Soc.,* 2015, **137**, 3803.

14 (a) X.-N. Zhang, G.-Q. Chen, X.-Y. Tang, Y. Wei and M. Shi, *Angew. Chem. Int. Ed.*, 2014, **53**, 10768; (b) M. Yang, T.-Y. Wang, S.-X. Cao and Z.-J. He, *Chem. Commun.*, 2014, **50**, 13506.

15 Q.-M. Zhang, L. Y and X.-F. Tong, *J. Am. Chem. Soc.,* 2010, **132**, 2551.

16 (a) B. Han, J.-L. Li, C. Ma, S.-J. Zhang and Y.-C. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 9971; (b) B. Han, Z.-Q. He, J.-L. Li, R. Li, K. Jiang, T.-Y. Liu and Y.-C. Chen, *Angew. Chem. Int. Ed.,* 2009, **48**, 5474; (c) Z.-G. Shi, Q.-J. Tong, W. W. Y. Leong and G.-F. Zhong, *Chem. Eur. J.,* 2012, **18**, 9802; (d) Z. Shi, P. Yu, T.-P. Loh and G. Zhong, *Angew. Chem. Int. Ed.*, 2012, **51**, 7825. (e) L. Hao, S.-J. Chen, J.-F. Xu, B. Tiwari, Z.-Q. Fu, T. Li, J.-Y, Lim and Y. R. Chi, *Org. Lett.,* 2013, **15**, 4956; (f) D.-D. Tang, Y. Wang, J.-R. Wang and P.-F. Xu, *Tetrahedron Lett.*, 2014, **55**, 4133; (g) E.-Q. Li, P.-H. Jia, L. Liang and Y. Huang, *ACS Catal.*, 2014, **4**, 600; (h) D. G. Stark, T. J. C. O'Riordan and A. D. Smith, *Org. Lett.,* 2014, **16**, 6496.

17 For N-heterocyclic carbene-catalyzed reactions of oxindole-derived α,β-unsaturated imines to construct spirocyclic oxindoles, see: (a) K. J. B. Tiwari and Y. R. Chi, *Org. Lett*., 2012, **14**, 2382; (b) L. Hao, C.-W. Chuen, R. Ganguly and Y. R. Chi, *Synlett.,* 2013, **24**, 1197; For phosphine-catalyzed asymmetric [4+2] annulation with oxindole-derived α,β-unsaturated imines, see: (c) X. N. Zhang, G.-Q. Chen, X. Dong, Y. Wei and M. Shi, *Adv. Synth. Catal.*, 2013, **355**, 3351.

18 The CIF data of major diastereoisomers of **3t** and **3u** have been deposited in CCDC with numbers 1024783 and 1019412.

19 S.-X. Wang, X.-Y. Han, F.-G. Zhong, Y.-Q. Wang and Y.-X. Lu, *Synlett.*, 2011, **19**, 2766.