Organic LETTERS

Letter

pubs.acs.org/OrgLett

Palladium-Catalyzed Asymmetric Cycloadditions of Vinylcyclopropanes and in Situ Formed Unsaturated Imines: Construction of Structurally and Optically Enriched Spiroindolenines

Ze-Shui Liu, Wen-Ke Li, Tai-Ran Kang, Long He,* and Quan-Zhong Liu*

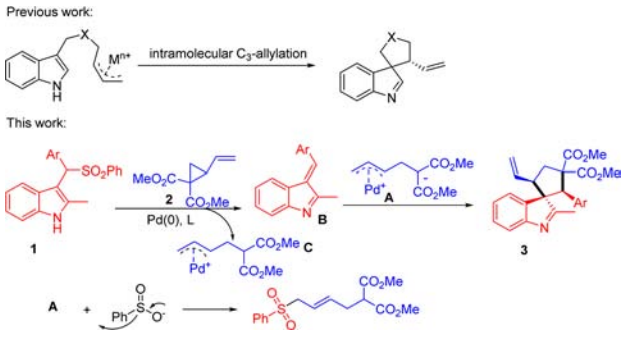
Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, College of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637002, P. R. China

Supporting Information

ABSTRACT: A palladium-catalyzed (3 + 2) cycloaddition of vinyl cyclopropane and α,β-unsaturated imines generated in situ from aryl sulfonyl indoles is reported. The reaction proceeds with high diastereoselectivity to provide the optically enriched spirocyclopentane-1,3′-indolenines in up to 74% yield and with up to 97% ee, which contains an all-carbon quaternary center and two tertiary stereocenters. The reaction involves a first conjugate addition of the carbon anion of zwitterionic π-allylpalladium complex from vinyl cyclopropane to the in situ formed unsaturated imine followed by a palladium-catalyzed intramolecular C_3-allylation of indole.

The spiroindolenine and spiroindoline units are ubiquitous and constitute the structural core in numerous natural products and biologically active molecules, including commercial drugs.[1] Numerous efforts have been devoted to the efficient synthesis of spiroindolenine nucleus structure;[2] however, efficient and rapid approaches for spiroindolenines are still very limited. Most methods for spiroindolenines employed function-alized indole compounds such as oxindoles and methyleneindo-linones.[2] Quite recently, the intramolecular allylic alkylations of indole and analogies have been developed for spiroindolenines using palladium,[3] iridium,[4] gold[5] and ruthenium[6] as the catalysts (Scheme 1). The protocol was successfully employed in the intermolecular allylations of indole anologies. To streamline substantial advances in this area, new catalytic asymmetric methodologies for the construction of structurally diverse spiroindolenines using simple substances are more appealing.

Scheme 1. Dearomatization of Indole



Vinyl cyclopropane derivatives with electron-withdrawing groups are known to act as 1,3-dipoles in the presence of a palladium catalyst. The in situ generated dipoles are reactive in the cycloaddition reaction with dipolarophiles such as olefins,[7] isocyanates,[8] imines,[9] and aldehydes[10] forming the functionally enriched cyclic products.

The easily available sulfonyl indoles are known to be a precursor of α,β-unsaturated imines in the presence of a base. The in situ formed α,β-unsaturated imines are reactive toward varieties of nucleophiles such as malononitrile, aldehydes, naphthols, and nitroalkenes using metal or organic catalysts.[11] Organic or inorganic bases are required during the reaction. Vinyl cyclopropanes bearing electron-withdrawing groups are readily transformed to the amphiphilic ion in the presence of a palladium catalyst. We reasoned that the carbon anion of the amphiphilic species could act as a transient base and deprive a proton from aryl sulfonyl indole, allowing the formations of the transient α,β-unsaturated imines and benzenesulfinic anion. The α,β-unsaturated imines would act as a dipolarophile and a [3 + 2] cycloaddition of zwitterionic π-allylpalladium complex from vinyl cyclopropane would proceed to yield a five-membered spiroindolenines (Scheme 1). Although spiroindolenine have been previously accessed by enantioselective intramolecular allylic dearomatization reactions,[3−6] the known procedure requires an indole molecule with an allylic alcohol or ester preinstalled at the right position on the indole ring. Our procedure allows sulfonyl indoles and vinyl cyclopropane

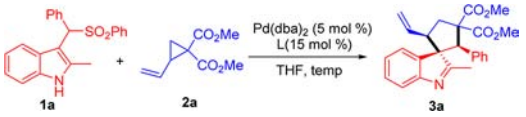
Received: November 21, 2014
Published: December 19, 2014

dx.doi.org/10.1021/ol503383x | *Org. Lett.* 2015, 17, 150−153

derivatives as the starting material and assembles the five-membered spiroindolenines with three contiguous stereocenters in one step. The chemistry includes the first formation of the transient α,β-unsaturated imine, conjugate addition of carbon anion of zwitterionic allylpalladium complex, and palladium-catalyzed intramolecular allylation of indole in one pot reaction.

Initially, sulfonyl indole **1a** and vinyl cyclopropane derivative **2a** (2 equiv) were stirred in THF at room temperature in the presence of $Pd(dba)_2$ and dppb. We were pleased that the desired product **3a** was observed as a sole isomer in 25% yield (entry 1, Table 1). Other phosphine ligands were investigated, and the

Table 1. Optimization of the Reaction of Sulfonyl indole 1a and Vcp 2a[a]



entry	ligand	yield[b] (%)	ee[c] (%)	dr[d]
1[e]	Dppb	25		>20:1
2[e]	PMe_3	77		>20:1
3	PMe_3	84		>20:1
4	L_1	89	47	>20:1
5	L_2	57	53	>20:1
6	L_3	35	11	>20:1
7	L_4	25	25	>20:1
8	L_5	57	39	>20:1
9	L_6	70	81	>20:1
10	L_7	70	89	>20:1
11[f]	L_7	69	90	>20:1
12[g]	L_7	73	87	>20:1
13[h]	L_7	74	61	>20:1
14[i]	L_7	73	96	>20:1
15[j]	L_7	69	89	>20:1
16[k]	L_7	67	87	>20:1
17[l]	L_7	53	67	>20:1
18[m]	L_7	29	64	>20:1

[a]Reaction conditions: 0.1 mmol of **1a**, 0.3 mmol of **2a**, 5 mol % of $Pd(dba)_2$, 15 mol % of ligand at 10 °C using THF as the solvent. [b]Isolated yield. [c]Determined by HPLC. [d]Determined by ^{1}HNMR of crude product. [e]0.2 mmol of **2a** was employed. [f]Carried out at 0 °C. [g]Carried out at 25 °C. [h]Carried out at 40 °C. [i]50 mg of 4 Å MS was added, and the reaction was carried out at 0 °C. [j]0.1 equiv of ethanol was added. [k]0.1 equiv of water was added. [l]0.1 equiv of sodium acetate was added. [m]Carried out under oxygen atmosphere.

results showed that PMe_3 was the best choice and afforded the highest yield (entry 2, Table 1; for other achiral ligands, see the Supporting Information). Increasing the amount of Vcp to 3 equiv resulted in a significant increase in the yield. Solvent screening found that THF was the best among the solvents examined (results not shown in Table 1; see the Supporting Information). In all cases, the reaction demonstrated excellent diastereoselectivity and only a single stereoisomer was isolated in all cases.

To realize the asymmetric version of the reaction, various commercially available ligands (Figure 1) were screened, and the results are summarized in Table 1. To our delight, Me-Duphos (L_1) did generate the desired product albeit with only 47% ee (entry 4, Table 1). Other ligands such as L_2, L_3, and L_4 all provided less desired results (entries 5−7). Inspired by the successful application of chiral phosphoramidites in dearomatization,[4] we investigated the effects of chiral phosphoramidites on the reaction. Although the L_5 yielded only 39% ee, the bulky ligand L_6 with S_a,R,R configuration delivered good enantioselectivities (entry 9). The R_a,R,R configuration for L_7 matched in the reaction provided the best results in terms of enantioselectivities and yield (entry 10). The temperature had a slight effect on the reaction (entries 11−13), low temperature led to better selectivity but the reaction proceeded much more slowly. Increasing the temperature resulted in the decreased enantioselectivity. Finally, addition of molecular sieves (4 Å) gave the best yield and ee value (entry 14). It should be mentioned that protonic solvent such as ethanol and water had almost no influence on the reaction. Addition of 10 mol % of ethanol with respect to **1a** resulted in almost no alteration in yield and enantioselectivity (entry 15 vs 10, Table 1). In presence of 10 mol % of water, the reaction proceeded smoothly although the results were less desired (87% ee, entry 16). On the basis of this observation, we surmised that the microenvironment from molecular sieves is responsible for achieving good enantioselectivity. Alkaline conditions were necessary for the desulfonylation of sulfonyl indole to generate the intermediate imine. With this regard, 10 mol % anhydrous sodium acetate was added, both yield and enantioselectivity were significantly decreased (53% yield, 67% ee, entry 17). Oxygen was deleterious for the reaction; exposure of the reaction to air resulted in 29% yield and 64% ee (entry 18).

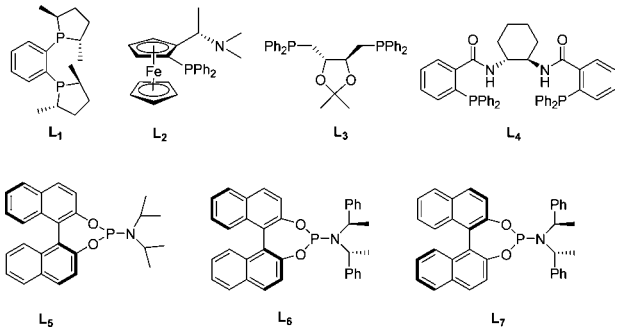
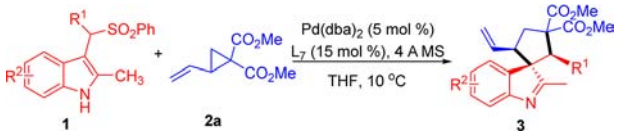


Figure 1. Representative ligands surveyed in this work.

With the optimal conditions for the reaction established, the reaction scope was investigated. As summarized in Table 2, various sulfonyl indoles were compatible affording the corresponding spiroindolenine in good yields and excellent enantioselectivities. Generally speaking, the steric hindrance of sulfonyl indoles had a significant impact on both the yield and enantioselectivities. The substrates with substitutents on the *para*- or *meta*-position on the phenyl ring on the carbon attached directly to sulfonyl group were tolerable, affording the desired products in good yields and with excellent ee values regardless of the electronic nature of substitutents. However, *ortho*-substituted substrates provided low yields or enantioselectivities. For examples, 3- and 4-chlorophenyl-substituted sulfonyl indoles afforded better yields and enantioselectivitities compared to 2-chloro substituted one (entires 3−4 vs entry 2). 2-Bromophenyl-substituted sulfonyl indoles delivered only 45% yield and 64% ee (entry 5). Methyl-substituted substrates also showed the same trend (entries 8−10). The electronic nature of substituents had no dramastic effects on the reaction. For example, both electron-withdrawing groups such as chloro, bromo, methoxy, nitro, or nitrile and electron-donating groups such as methyl provided good yields and excellent enantioselectivities (entries 3, 4, 6, 7, and 9−14). 1-Naphthyl- or furanyl-derived substrate gave less

dx.doi.org/10.1021/ol503383x | *Org. Lett.* 2015, 17, 150−153

Table 2. Enantioselective Cycloaddition of Sulfonyl indoles 1 and Vcp 2a[a]



entry	R^1	R^2	3	yield[b] (%)	ee[c] (%)
1	Ph	H	**3a**	71	96
2	2-ClPh	H	**3b**	39	91
3	3-ClPh	H	**3c**	73	96
4	4-ClPh	H	**3d**	69	97
5	2-BrPh	H	**3e**	45	64
6	3-MeOPh	H	**3f**	69	95
7	4-MeOPh	H	**3g**	73	95
8	2-MePh	H	**3h**	<5	
9	3-MePh	H	**3i**	66	95
10	4-MePh	H	**3j**	73	96
11	4-FPh	H	**3k**	71	97
12	4-BrPh	H	**3l**	69	93
13	4-CNPh	H	**3m**	74	96
14	4-NO_2Ph	H	**3n**	72	92
15	1-naphthyl	H	**3o**	73	78
16	2-furanyl	H	**3p**	76	85
17	Ph	5-OMe	**3q**	70	91
18	Ph	5-Cl	**3r**	73	80
19	Ph	5-Me	**3s**	67	92
20	4-BrPh	5-Me	**3t**	69	93
21	4-ClPh	5-Cl	**3u**	67	96

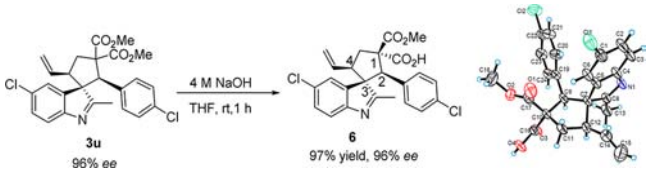
[a]Reaction conditions: 0.1 mmol of **1**, 0.3 mmol of **2a**, 5 mol % of $Pd(dba)_2$, 15 mol % of $\mathbf{L_7}$, 50 mg of 4 Å MS, 1 mL of THF, 10 °C; in all cases, only one diastereoisomer was observed. [b]Isolated yield. [c]Determined by chiral HPLC.

desired enantioselectivities, and this perhaps resulted from the steric hindrance (entries 15 and 16).

On the other hand, substitution on indole ring resulted in less desired enantioselectivities. For example, substitution with 5-chloro, 5-methyl, and 5-methoxy at the indole ring resulted in good to excellent selectivities. Electron-donating groups acheived better enantioselectivities than electron-withdrawing groups (entries 17−19). From the experiment, substitution on phenyl ring on the carbon attached directly to sulfonyl group had a significant effect on the outcome of the reaction (entries 20 and 21). Although substitution with chlorine atom at the 5-position of indole resulted in only 80% ee, introduction of another chlorine atom at 4-position of phenyl on the carbon attached directly to sulfonyl group afforded excellent enantioselectivities (entry 21). It should be noted that only one isomer was obtained in all cases by ^{1}HNMR analysis of the crude product. The other esters of vinyl cyclopropane dicarboxylate were also examined, but both the yields and selectivities were less satisfactory (see the Supporting Information).

All of the cycloaddition products are oil. To determine the absolute configuration of product **3**, **3u** underwent diastereoselective hydrolysis in 4 M aqueous NaOH solution at room temperature to afford the diastereomerically pure monoester **6** in 97% yield with no erosion in enantioselectivity (Scheme 2). After recrystallization from a mixed solvent of hexane and ethyl acetate, a crystal suitable for X-ray diffraction was obtained and the absolute configuration of **6** was thus assigned to be (1*R*,2*S*,3*R*,4*R*) (see the Supporting Information). The absolute

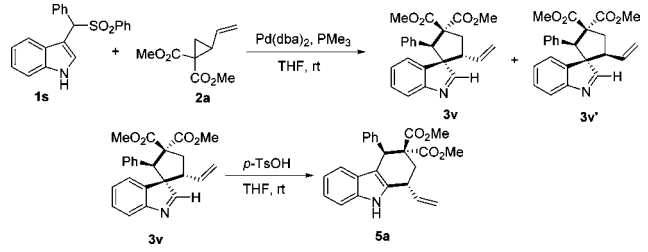
Scheme 2. Determination of Absolute Configuration of Cycloadducts



configuration of other cycloadducts was tentatively assigned by analogy.

Although excellent diastereoselectivties were observed in most cases, C_2-unsubstituted sulfonyl indole **1s** produced a diastereoisomeric mixture (**3v** + **3v′**) in 81% total yield, which could not be purified by simple choromatography (dr. 1.2:1). Fortunately, **3v** transformed to tetrahydrocarbazole **5a** while the **3v′** in which phenyl and vinyl groups are in a *cis*-relationship with each other (Scheme 3) is not reactive upon treatment of the mixture with catalytic amount of *p*-TsOH at room temperature.[12]

Scheme 3. Diastereoselective Cycloaddition of Vcp 2a and Sulfonyl indole 1s



A plausible mechanism for the reaction was proposed (Figure 2). In the presence of a palladium complex, dimethyl vinyl

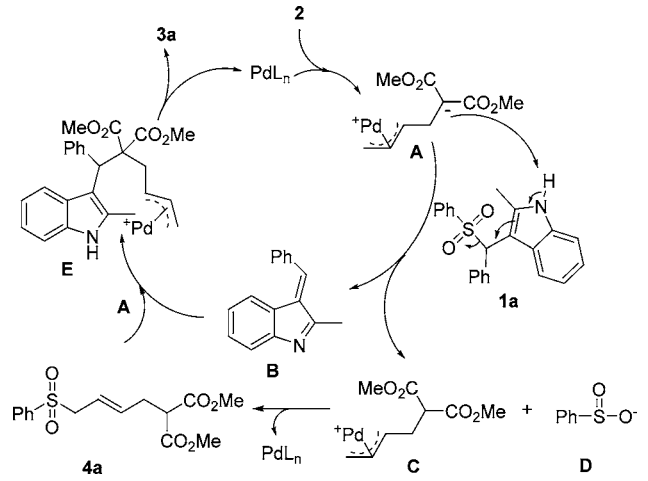


Figure 2. Plausible mechanism for the reaction.

cyclopropane ester **2** is cleaved and the corresponding 1,3-dipole species **A** is generated. The carbon anion of the dipole acts as a base to deprotonate **1a** and the expected α,β-unsaturated imine **B** and benzenesulfinate **D** are formed, respectively. Nucleophilic conjugate attack of 1,3-dipole to α,β-unsaturated imine **B** yields an indole-tethered allylic palladium **E**, and subsequent intramolecular dearomatization generates the spiroindolenine **3a**; reaction of benzenesulfinate **D** and allylic palladium **C** gives the

dx.doi.org/10.1021/ol503383x | *Org. Lett.* 2015, 17, 150−153

olefin **4a** observed in most cases.[13] Because 1 equiv of vinyl cyclopropane dicarboxylate **2a** was consumed, excessive amount of **2a** was required.

In summary, we have developed a highly diastereoselective and enantioselective synthetic approach for structurally and optically enriched spiroindolenines. The zwitterionic π-allylpalladium complex from vinyl cyclopropane derivatives acted as a base to deprotonate arenesulfonyl indoles forming the conjugate imines. First conjugate addition of amphiphilic ions and subsequent palladium-catalyzed intramolecular allylation afforded the spiroindolenines in good yields and diastereoselectivities and with up to excellent enantioselectivities. The application of other type of precursors of α,β-unsaturated imine are ongoing, and the results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectral data for all new compounds, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: longhe@cwnu.edu.cn.
*E-mail: quanzhongliu@cwnu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the NSFC (21102116) and the Innovative Research Team in College of Sichuan Province (14TD0016).

■ REFERENCES

(1) For selected examples of natural products containing spiroindolenine and spiroindoline, see: (a) Jadulco, R.; Edrada, R. A.; Ebel, R.; Berg, A.; Schau-mann, K.; Wray, V.; Steube, K.; Proksch, P. *J. Nat. Prod.* **2004**, *67*, 78. (b) Kawasaki, T.; Higuchi, K. *Nat. Prod. Rep.* **2005**, *22*, 761. (c) O'Connor, S. E.; Maresh, J. *J. Nat. Prod. Rep.* **2006**, *23*, 532. (d) Feng, T.; Li, Y.; Cai, X.-H.; Gong, X.; Liu, Y.-P.; Zhang, R.-T.; Zhang, X.-Y.; Tan, Q.-G.; Luo, X.-D. *J. Nat. Prod.* **2009**, *72*, 1836. (e) Liu, Y.-P.; Zhao, Y.-L.; Feng, T.; Cheng, G.-G.; Zhang, B.-H.; Li, Y.; Cai, X.-H.; Luo, X.-D. *J. Nat. Prod.* **2013**, *76*, 2322. (f) Zlotos, D. P.; Tränkle, C.; Holzgrabe, U.; Gűndisch, D.; Jensen, A. A. *J. Nat. Prod.* **2014**, *77*, 2006.

(2) For selected reviews on spirooxindole synthesis, see: (a) Cheng, D.; Ishihara, Y.; Tan, B.; Barbas, C. F., III. *ACS Catal.* **2014**, *4*, 743. (b) Hong, L.; Wang, R. *Adv. Synth. Catal.* **2013**, *355*, 1023. (c) Dalpozzo, R.; Bartoli, G.; Bencivenni, G. *Chem. Soc. Rev.* **2012**, *41*, 7247. (d) Singh, G. S.; Desta, Z. Y. *Chem. Rev.* **2012**, *112*, 6104. For the original papers, see: (e) Ramachary, D. B.; Venkaiah, C.; Madhavachary, R. *Org. Lett.* **2013**, *15*, 3042. (f) Mao, H.; Lin, A.; Tang, Y.; Shi, Y.; Hu, H.; Cheng, Y.; Zhu, C. *Org. Lett.* **2013**, *15*, 4062. (g) Albertshofer, K.; Tan, B.; Barbas, C. F., III. *Org. Lett.* **2012**, *14*, 1834. (h) Tessier, J. D.; O'Bryan, E. A.; Schroeder, T. B. H.; Cohen, D. T.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4963. (i) Bergonzini, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 971. (j) Tan, B.; Zeng, X.; Leong, W. W. Y.; Shi, Z.; Barbas, C. F., III.; Zhong, G. *Chem.—Eur. J.* **2012**, *18*, 63. (k) Cao, Y.; Jiang, X.; Liu, L.; Shen, F.; Wang, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 9124. (l) Tan, B.; Candeias, N. R.; Barbas, C. F., III. *Nat. Chem.* **2011**, *3*, 473. (m) Tan, B.; Candeias, N. R.; Barbas, C. F., III *J. Am. Chem. Soc.* **2011**, *133*, 4672. (n) Jiang, X.; Cao, Y.; Wang, Y.; Liu, L.; Shen, F.; Wang, R. *J. Am. Chem. Soc.* **2010**, *132*, 15328. (o) Tian, X.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2013**, *52*, 5360. (p) Chen, X. H.; Wei, Q.; Luo, S. W.; Xiao, H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2009**, *131*, 13819.

(3) For selected reviews, see: (a) Zhuo, C.-X.; Zhang, W.; You, S.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 12662. (b) Zhuo, C.-X.; Zheng, C.; You, S.-L. *Acc. Chem. Rev.* **2014**, *47*, 2558. For palladium catalysis, see: (c) Bandini, M.; Melloni, A.; Piccinelli, F.; Sinisi, R.; Tommasi, S.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **2006**, *128*, 1424. (d) Kagawa, N.; Malerich, J. P.; Rawal, V. H. *Org. Lett.* **2008**, *10*, 2381. (e) Montgomery, T. D.; Nibbs, A. E.; Zhu, Y.; Rawal, V. H. *Org. Lett.* **2014**, *16*, 3480. (f) Montgomery, T. D.; Zhu, Y.; Kagawa, N.; Rawal, V. H. *Org. Lett.* **2013**, *15*, 1140.

(4) For iridium catalysis, see: (a) Zhuo, C.-X.; Wu, Q.-F.; Zhao, Q.; Xu, Q.-L.; You, S.-L. *J. Am. Chem. Soc.* **2013**, *135*, 8169. (b) Zhang, X.; Han, L.; You, S.-L. *Chem. Sci.* **2014**, *5*, 1059. (c) Xu, Q.-L.; Dai, L.-X.; You, S.-L. *Chem. Sci.* **2013**, *4*, 97. (d) Wu, Q.-F.; Zheng, C.; You, S.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 1680. (e) Wu, Q.-F.; He, H.; Liu, W.-B.; You, S.-L. *J. Am. Chem. Soc.* **2010**, *132*, 11418. (f) Zhuo, C.-X.; Liu, W.-B.; Wu, Q.-F.; You, S.-L. *Chem. Sci.* **2012**, *3*, 205. (g) Wu, Q.-F.; Liu, W.-B.; Zhuo, C.-X.; Rong, Z.-Q.; Ye, K. Y.; You, S.-L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4455.

(5) For gold catalysis, see: (a) Jia, M.; Cera, G.; Perrotta, D.; Monari, M.; Bandini, M. *Chem.—Eur. J.* **2014**, *20*, 9875. (b) Bandini, M.; Bottoni, A.; Chiarucci, M.; Cera, G.; Miscione, G. P. *J. Am. Chem. Soc.* **2012**, *134*, 20690. (c) Cera, G.; Chiarucci, M.; Mazzanti, A.; Mancinelli, M.; Bandini, M. *Org. Lett.* **2012**, *14*, 1350. (d) Cera, G.; Crispino, P.; Monari, M.; Bandini, M. *Chem. Commun.* **2011**, *47*, 7803. (e) Bandini, M.; Eichholzer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9533.

(6) Zhang, X.; Yang, Z.-P.; Liu, C.; You, S.-L. *Chem. Sci.* **2013**, *4*, 3239.

(7) (a) Goldberg, A. F. G.; Stoltz, B. M. *Org. Lett.* **2011**, *13*, 4474. (b) Mei, L.; Wei, Y.; Xu, Q.; Shi, M. *Organometallics* **2012**, *31*, 7591. (c) Trost, B. M.; Morris, P. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 6167. (d) Li, W.-K.; Liu, Z.-S.; He, L.; Kang, T.-R.; Liu, Q.-Z. *Asian J. Org. Chem.* **2014**, DOI: 10.1002/ajoc.201402219.

(8) Trost, B. M.; Fandrick, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 11836.

(9) (a) Parsons, A. T.; Smith, A. G.; Neel, A. J.; Johnson, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 9688. (b) Larksarp, C.; Alper, H. *J. Org. Chem.* **1998**, *63*, 6229.

(10) (a) Parsons, A. T.; Johnson, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 3122. (b) Mei, L.; Wei, Y.; Xu, Q.; Shi, M. *Organometallics* **2013**, *32*, 3544. (c) Parsons, A. T.; Campbell, M. J.; Johnson, J. S. *Org. Lett.* **2008**, *10*, 2541.

(11) For the synthesis and applications of aryl sulfonyl indole, see: (a) Shaikh, R. R.; Mazzanti, A.; Petrini, M.; Bartoli, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8707. (b) Dobish, M. C.; Johnston, J. N. *Org. Lett.* **2010**, *12*, 5744. (c) Ballini, R.; Palmieri, A.; Petrini, M.; Shaikh, R. R. *Adv. Synth. Catal.* **2008**, *350*, 129. (d) Jing, L.; Wei, J.; Zhou, L.; Huang, Z.; Li, Z.; Wu, D.; Xiang, H.; Zhou, X. *Chem.—Eur. J.* **2010**, *16*, 10955. (e) Zhu, X.-L.; He, W.-J.; Yu, L.-L.; Cai, C.-W.; Zuo, Z.-L.; Qin, D.-B.; Liu, Q.-Z.; Jing, L.-H. *Adv. Synth. Catal.* **2012**, *354*, 2965.

(12) Zheng, C.; Wu, Q.-F.; You, S.-L. *J. Org. Chem.* **2013**, *78*, 4357.

(13) For sulfonyl anion surrogates, see: (a) Fernandez, M.; Uria, U.; Orbe, L.; Vicario, J. L.; Reyes, E.; Carrillo, L. *J. Org. Chem.* **2014**, *79*, 441. (b) Jin, Z.; Xu, J.; Yang, S.; Song, B.-A.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 12354.