

The Concise Synthesis of Spiro-Cyclopropane Compounds via the Dearomatization of Indole Derivatives

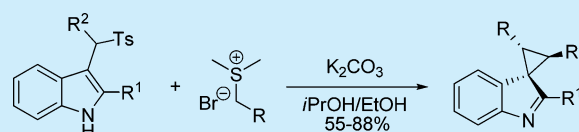
Jing Luo,[†] Bo Wu,[‡] Mu-Wang Chen,[‡] Guo-Fang Jiang,^{*,†} and Yong-Gui Zhou^{*,‡}

[†]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

[‡]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Supporting Information

ABSTRACT: A concise synthesis of spiro-cyclopropane compounds from indole derivatives and sulfur ylides has been developed via a dearomatization strategy. Moreover, the spiro-cyclopropane compounds could be conveniently transformed to rearomatized indole derivatives in the presence of acids.

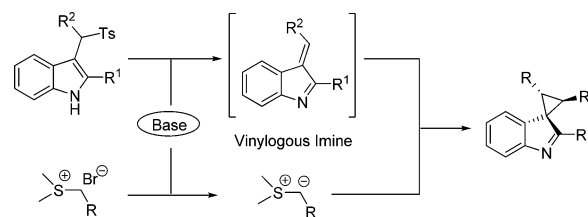


Dearomatization reactions are important transformations of aromatic compounds because they directly lead to a variety of ring systems.¹ Additionally, they are highly efficient for constructing quaternary carbon centers² and used as the key steps in the total synthesis of many natural products.³ In this regard, dearomatization reactions of indoles,⁴ pyridines,⁵ phenols,⁶ pyrroles,⁷ etc., have been developed. Among them, compounds with an indole skeleton have attracted enormous attention because of the important biological activities of their derivatives.⁸ Dearomatization reaction of indoles has been extensively studied over the past decades, with particular focuses on alkylative dearomatization⁹ and oxidative dearomatization.¹⁰ In addition, the Diels–Alder pathway with various dienophiles¹¹ and organocatalyzed Michael/Mannich cyclization cascade reactions were also demonstrated in dearomatization reactions of indoles.¹² Besides, several transition-metal-catalyzed dearomatization reactions of indoles were also documented.¹³ Although great progress has been made in the dearomatization reaction of indoles, most of the methods required harsh conditions and designed catalysts that are currently commercially unavailable. Thus, to develop a facile and efficient method for a dearomatization reaction of indole derivatives from readily available starting materials would be of considerable significance in organic chemistry.

Spiro-cyclopropane structure motifs are ubiquitous and prevalent in various anticancer agents and pharmaceuticals.¹⁴ In addition, they also serve as valuable synthetic intermediates for a wide range of organic compounds.¹⁵ Therefore, the construction of spiro-cyclopropane skeletons has achieved extensive attention, and a plethora of efficient methods have been developed for the synthesis of these important structures, including from alkenes by Simmons–Smith and related reactions or with ylides, transition-metal-catalyzed carbene transfer, Michael-initiated ring closure (MIRC), and organocatalytic cyclopropanation, which have been described in the literature.^{16,17}

The use of an arylsulfonyl group as an auxiliary group is still a prominent synthetic strategy in organic synthesis.¹⁸ Recently, the utilization of the arylsulfonyl group in connection with indole has attracted intriguing interests. The sulfonyl moiety at the benzylic position of 3-substituted indoles acts as a good leaving group, which enables the generation of vinylogous imines intermediates under basic conditions. The generating vinylogous imines intermediates are equal to α,β -unsaturated imines, which are able to react with numerous nucleophiles.¹⁹ Considering that sulfur ylides act as a nucleophile under the basic condition,²⁰ the vinylogous imine intermediates can be generated from arenesulfonylindole under the mild basic conditions. We envisioned that ylides could react with the vinylogous imine intermediates to furnish the spiro-cyclopropane compounds (Scheme 1). Herein, we report an efficient

Scheme 1. Synthesis of Spiro-Cyclopropane Compounds via the Dearomatization of Indoles



dearomatization reaction of indole derivatives in which arylsulfonyl group acts as a leaving group with sulfonium salts under mild conditions to synthesize spiro-cyclopropane compounds.

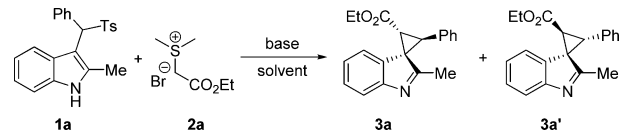
Initially, our investigation was launched with 2-methyl-substituted arenesulfonylindole **1a** (1.0 equiv), sulfonium salt **2a** (1.5 equiv), K_2CO_3 (3.0 equiv) as the base in CH_2Cl_2

Received: January 22, 2014

Published: May 6, 2014

(Table 1). Delightfully, the spiro-cyclopropane products **3a** and **3a'** were obtained with 71% yield and a ratio of 3:1. Next, a

Table 1. Optimization for the Reaction of 2-Methylarenesulfonylindole **1a with Sulfonium Salt **2a**^a**



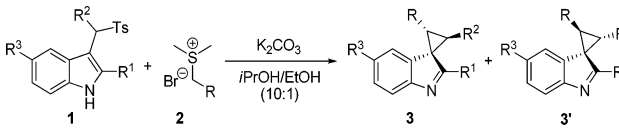
entry	solvent	base	yield (%) ^b	dr ^c
1	CH ₂ Cl ₂	K ₂ CO ₃	74	3:1
2	toluene	K ₂ CO ₃	<5	–
3	CH ₃ OH	K ₂ CO ₃	26	4:1
4	EtOH (E)	K ₂ CO ₃	87	6:1
5	<i>i</i> PrOH (P)	K ₂ CO ₃	55	19:1
6	E/P (1:1)	K ₂ CO ₃	83	7:1
7	E/P (1:5)	K ₂ CO ₃	84	8:1
8	E/P (1:10)	K ₂ CO ₃	83	13:1
9	E/P (1:10)	Cs ₂ CO ₃	66	6:1
10	E/P (1:10)	DIPEA	75	7:1
11	E/P (1:10)	Na ₂ CO ₃	61	15:1
12	E/P (1:10)	KO ^t Bu	<5	–

^aCondition: 0.25 mmol **1a**, 0.375 mmol **2a**, 0.75 mmol base, 3.3 mL of solvent, room temperature, 12 h. ^bIsolated yields of the mixture of **3a** and **3a'**. ^cAll of the dr (**3a/3a'**) were determined by ¹H NMR spectroscopy. E/P: EtOH/*i*PrOH.

series of solvents were examined, and to our delight, high yield was obtained from EtOH (87%, Table 1, entry 4), and *i*PrOH gave the excellent 19:1 of diastereoselectivity (Table 1, entry 5). Thus, the next screening was focused on the mixed solvents. When the ratio of *i*PrOH/EtOH was 10:1, the yield could be retained, and the diastereoselectivity could be raised up to 13:1 (Table 1, entry 8); several other bases were also examined, and moderate yields and diastereoselectivities were obtained (Table 1, entries 9–11). So, the optimal conditions were established, K₂CO₃ as the base and *i*PrOH/EtOH (10:1) as the solvent.

With the optimized conditions in hand, we explored the reaction scope using a variety of 2-substituted arenesulfonylindoles **1** and sulfonium salts **2** as listed in Table 2. A range of sulfonium salts were examined, and medium to good yields and excellent diastereoselectivities were achieved (55–78% yields, dr = 13:1 to >20:1, Table 2, entries 2–5). Especially, when R was aryl carbonyl, up to >20:1 diastereoselectivity were obtained. The steric and electronic property of the aryl substituents had little effect on the yield and diastereoselectivity for substituents R² (Table 2, entries 7–13); all of them could get satisfactory yields and diastereoselectivity. The electronic nature of the indole core had little influence on the outcome of the reactions; when the sulfonylindoles with fluorine or methyl as substituent at the 5-position of the indole ring, both gave excellent yields and satisfactory diastereoselectivities (Table 2, entries 14–15). It is worthy of note that when the 2-position of the indole ring was phenyl, the diastereoselectivity was reversed (Table 2, entry 16), which may ascribe to the change of geometry of C=C bond and relative stability of vinylogous imine intermediate due to steric hindrance of phenyl group. To our delight, the 2-position unsubstituted sulfonyl indoles were also suitable reaction partners using ethanol as solvent and provided the desired products in good yields and excellent diastereoselectivities (Table 2, entries 17–20).²¹

Table 2. Scope for the Reaction of Arenesulfonylindoles **1 with Sulfonium Salts **2**^a**



entry	R ¹ /R ² /R ³	2	3 , yield ^b (%)	dr ^c
1	Me/Ph/H	2a	3a , 83	13:1
2	Me/Ph/H	2b	3b , 78	13:1
3	Me/Ph/H	2c	3c , 60	>20:1
4	Me/Ph/H	2d	3d , 55	>20:1
5	Me/Ph/H	2e	3e , 71	>20:1
6	Me/ <i>n</i> -Pentyl/H	2a	3f , 56	>20:1
7	Me/4-MeC ₆ H ₄ /H	2a	3g , 88	14:1
8	Me/3-MeC ₆ H ₄ /H	2a	3h , 86	13:1
9	Me/2-MeC ₆ H ₄ /H	2a	3i , 84	13:1
10	Me/4-ClC ₆ H ₄ /H	2a	3j , 82	14:1
11	Me/3-ClC ₆ H ₄ /H	2a	3k , 75	12:1
12	Me/4-BrC ₆ H ₄ /H	2a	3l , 81	15:1
13	Me/3-MeOC ₆ H ₄ /H	2a	3m , 69	11:1
14	Me/Ph/5-Me	2a	3n , 88	12:1
15	Me/Ph/5-F	2a	3o , 83	10:1
16	Ph/4-BrC ₆ H ₄ /H	2a	3p , 70	1:5
17 ^d	H/Ph/H	2a	3q , 82	>20:1
18 ^d	H/4-ClC ₆ H ₄ /H	2a	3r , 81	>20:1
19 ^d	H/4-BrC ₆ H ₄ /H	2a	3s , 83	>20:1
20 ^d	H/ <i>n</i> -Pentyl/H	2a	3t , 85	>20:1

^aCondition: 0.25 mmol **1**, 0.375 mmol **2**, 0.75 mmol K₂CO₃, 3.0 mL of *i*PrOH, 0.3 mL of EtOH, room temperature, 12 h. ^bIsolated yields of the mixture of **3** and **3'**. ^cAll of the dr (**3/3'**) were determined by ¹H NMR spectroscopy. ^d3.3 mL of EtOH was used.

The structure and stereochemistry of spiro-cyclopropanes **3a** (Figure 1), **3p**, and **3p'** were verified by the combination of

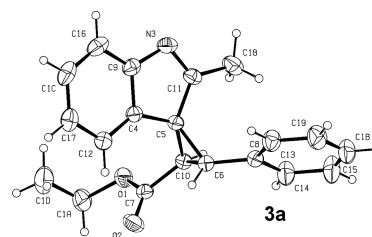


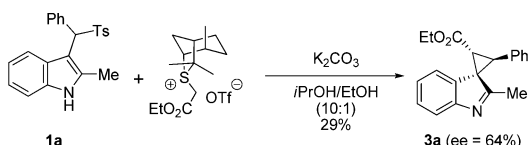
Figure 1. X-ray crystal structure of compound **3a**.

NMR, HRMS spectroscopy, and single-crystal X-ray diffraction analysis (for X-ray crystal structure of **3p** and **3p'**, see the Supporting Information).²²

Furthermore, a preliminary study on the enantioselective version of this dearomatization reaction was also tried. Using the known chiral sulfonium salts²³ originally developed by Aggarwal, only moderate enantioselectivity 64% ee and low yield (29%) were obtained (Scheme 2). These promising results demonstrated the potential for synthesis of the chiral spiro-cyclopropane derivatives, although more efficient catalytic systems need to be developed.

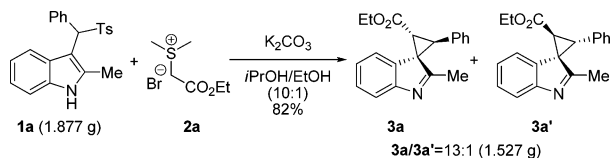
It is noted that the model substrates **1a** and **2a** could also be carried out at a gram scale. As illustrated in Scheme 3, the target

Scheme 2. Synthesis of Chiral Spiro-Cyclopropane with the Chiral Sulfonium Salt



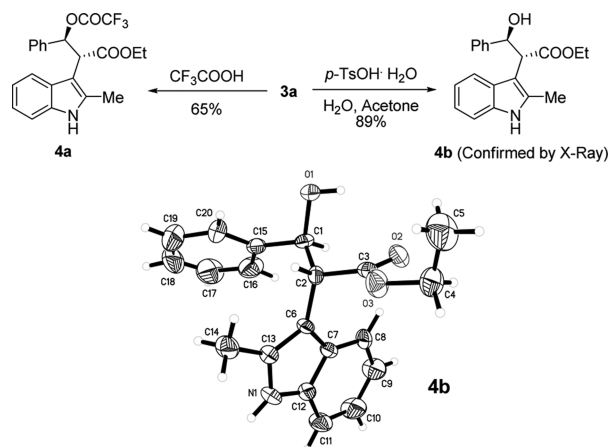
products **3a** and **3a'** could be obtained in 82% yield and the diastereoselectivity could be kept with 13:1.

Scheme 3. Scale-up of Model Substrates



In order to explore the application of our methodology, we tried to transform them to rearomatized 2,3-disubstituted indole derivatives (Scheme 4). Pleasingly, when trifluoroacetic

Scheme 4. Selective Transformations of **3a** to Rearomatized Indole Derivatives



acid was added, the expected rearomatized product **4a** was obtained in 65% yield with excellent diastereoselectivity; trifluoroacetic acid served as both acid and nucleophile in this reaction. When water was chosen as nucleophile, the product hydroxyl ester **4b** could also be obtained with 89% yield with excellent diastereoselectivity. The single-crystal of **4b**²⁴ was successfully obtained and confirmed the relative configuration (see the Supporting Information).

In conclusion, we have developed a concise and efficient dearomatization method for the rapid and facile synthesis of spiro-cyclopropane compounds via the vinylogous imine intermediates generated from readily available arenesulfonylindoles and sulfonium salts under mild basic conditions. This methodology provides a succinct access to substituted spiro-cyclopropane derivatives. Moreover, the spiro-cyclopropanes could be conveniently transformed to rearomatized indole derivatives with excellent yields in the presence of acids. Our ongoing studies are focused on an asymmetric version of this reaction.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, X-ray structures, data for the determination of enantiomeric excess, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: gfjiang@hnu.edu.cn.

*E-mail: ygzhou@dicp.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (J1210040) and the National Basic Research Program of China (2010CB833300).

■ REFERENCES

- (1) (a) Newhouse, T.; Baran, P. S.; Hoffmann, R. W. *Chem. Soc. Rev.* **2009**, *38*, 3010. (b) Ortiz, F. L.; Iglesias, M. J.; Fernández, I.; Sánchez, C. M. A.; Gómez, G. R. *Chem. Rev.* **2007**, *107*, 1580.
- (2) (a) Liu, Q.; Rovis, T. *J. Am. Chem. Soc.* **2006**, *128*, 2552. (b) Gong, J.; Lin, G.; Li, C.-C.; Yang, Z. *Org. Lett.* **2009**, *11*, 4770. (c) Jia, M.-Q.; You, S.-L. *Synlett* **2013**, 1201.
- (3) For reviews, see: (a) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993. (b) Rasso, G.; Zanardi, F.; Battistini, L.; Casiraghi, G. *Chem. Soc. Rev.* **2000**, *29*, 109. For selected examples: (a) Cha, J. Y.; Huang, Y.; Pettus, T. R. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9519. (b) Zuo, Z.; Xie, W.; Ma, D. *J. Am. Chem. Soc.* **2010**, *132*, 13226. (c) Zuo, Z.; Ma, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 12008. (d) Horning, B. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, *135*, 6442.
- (4) For recent reviews on dearomatization of indoles, see: (a) Zhuo, C.-X.; Zhang, W.; You, S.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 12662. (b) Roche, S. P.; Porco, J. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 4068. (c) Chen, Q.-A.; Ye, Z.-S.; Duan, Y.; Zhou, Y.-G. *Chem. Soc. Rev.* **2013**, *42*, 497.
- (5) For dearomatization of pyridines reviews, see: (a) Lavilla, R. J. *Chem. Soc., Perkin Trans. 1* **2002**, 1141. (b) Comin, D. L. *J. Heterocycl. Chem.* **1999**, *36*, 1491. For selected examples see: (a) Wang, S.-G.; Zhang, W.; You, S.-L. *Org. Lett.* **2013**, *15*, 1488. (b) Dai, C.; Liang, B.; Stephenson, C. R. J. *Beilstein. J. Org. Chem.* **2012**, *8*, 986. (c) Mousseau, J. J.; Fortier, A.; Charette, A. B. *Org. Lett.* **2010**, *12*, 516. (d) Sun, Z.; Yu, S.; Ding, Z.; Ma, D. *J. Am. Chem. Soc.* **2007**, *129*, 9300. (e) Wang, S.-G.; You, S.-L. *Angew. Chem., Int. Ed.* **2014**, *53*, 2194.
- (6) For dearomatization of phenols reviews, see: (a) Ding, Q.; Ye, Y.; Fan, R. *Synthesis* **2013**, 1. (b) Pouységu, L.; Deffieux, D.; Quideau, S. *Tetrahedron* **2010**, *66*, 2235. (c) Quideau, S.; Pouységu, L.; Deffieux, D. *Synlett* **2008**, 467. For selected examples, see: (a) Li, Y.; Zhang, L.; Zhang, L.; Wu, Y.; Gong, Y. *Eur. J. Org. Chem.* **2013**, *2013*, 8039. (b) Xu, Q.-L.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 2579. (c) Yin, Q.; You, S.-L. *Org. Lett.* **2012**, *14*, 3526. (d) 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. (e) Vo, N. T.; Pace, R. D. M.; O'Hara, F.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 404. (f) Zhuo, C.-X.; You, S.-L. *Angew. Chem., Int. Ed.* **2013**, *52*, 10056.
- (7) For selected examples of dearomatization of pyrroles, see: (a) Mulcahy, J. V.; Bois, J. D. *J. Am. Chem. Soc.* **2008**, *130*, 12630. (b) Wang, D.-S.; Ye, Z.-S.; Chen, Q.-A.; Zhou, Y.-G.; Yu, C.-B.; Fan, H.-J.; Duan, Y. *J. Am. Chem. Soc.* **2011**, *133*, 8866. (c) Zhuo, C.-X.; Liu, W.-B.; Wu, Q.-F.; You, S.-L. *Chem. Sci.* **2012**, *3*, 205. (d) Wu, K.-J.; Dai, L.-X.; You, S.-L. *Chem. Commun.* **2013**, *49*, 8620.

- (8) (a) Sundberg, R. J. *Indoles*; Academic Press: San Diego, 1996. (b) d'Ischia, M.; Napolitano, A.; Pezzella, A. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A. R., Ramsden, C. A., Scriven, E. F. V., Taylor, R. J. K., Eds.; Elsevier: Oxford, 2008; Vol. 3, p 353. (c) Wang, D.-S.; Tang, J.; Zhou, Y.-G.; Chen, M.-W.; Yu, C.-B.; Duan, Y.; Jiang, G.-F. *Chem. Sci.* **2011**, *2*, 803. (d) Wang, D.-S.; Chen, Q.-A.; Li, W.; Yu, C.-B.; Zhou, Y.-G.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 8909.
- (9) For selected examples on alkylative dearomatization, see: (a) Chen, J.; Cook, M. J. *Org. Lett.* **2013**, *15*, 1088. (b) Zhang, X.; Liu, W.-B.; Wu, Q.-F.; You, S.-L. *Org. Lett.* **2013**, *15*, 3746. (c) Zhang, X.; Yang, Z.-P.; Liu, C.; You, S.-L. *Chem. Sci.* **2013**, *4*, 3239. (d) Zhu, S.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2012**, *134*, 10815. (e) Wu, Q.-F.; Zheng, C.; You, S.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 1680. (f) Wu, Q.-F.; He, H.; Liu, W.-B.; You, S.-L. *J. Am. Chem. Soc.* **2010**, *132*, 11418.
- (10) For selected examples, see: (a) Sunazuka, T.; Hirose, T.; Shirahata, T.; Harigaya, Y.; Hayashi, M.; Komiyama, K.; Omura, S.; Smith, A. B. *J. Am. Chem. Soc.* **2000**, *122*, 2122. (b) Liang, J.-L.; Yuan, S.-X.; Chan, P. W. H.; Che, C.-M. *Tetrahedron Lett.* **2003**, *44*, 5917.
- (11) Gioia, C.; Hauville, A.; Bernardi, L.; Fini, F.; Ricci, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9236.
- (12) For selected examples, see: (a) Cai, Q.; Zheng, C.; Zhang, J.-W.; You, S.-L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8665. (b) Heurreux, N.; Wouters, J.; Markó, L. E. *Org. Lett.* **2005**, *7*, 5245. (c) Zhang, Z.; Antilla, J. C. *Angew. Chem., Int. Ed.* **2012**, *51*, 11778. (d) Cai, Q.; Liu, C.; Liang, X.-W.; You, S.-L. *Org. Lett.* **2012**, *14*, 4588. (e) Cai, Q.; You, S.-L. *Org. Lett.* **2012**, *14*, 3040. (f) Liu, C.; Zhang, W.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 4525.
- (13) For selected examples, see: (a) Austin, J. F.; Kim, S.-G.; Sinz, C. J.; Xiao, W.-J.; MacMillan, D. W. C. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5482. (b) Kimura, M.; Futamata, M.; Mukai, R.; Tamaru, Y. *J. Am. Chem. Soc.* **2005**, *127*, 4592. (c) Kagawa, N.; Malerich, J. P.; Rawal, V. H. *Org. Lett.* **2008**, *10*, 2381. (d) Wu, K.-J.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2012**, *14*, 3772. (e) Xiong, H.; Xu, H.; Liao, S.; Xie, Z.; Tang, Y. *J. Am. Chem. Soc.* **2013**, *135*, 7851. (f) Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6802. (g) Zhang, H.; Hong, L.; Kang, H.; Wang, R. *J. Am. Chem. Soc.* **2013**, *135*, 14098.
- (14) (a) Wessjohann, L. A.; Brandt, W.; Thiemann, T. *Chem. Rev.* **2003**, *103*, 1625. (b) Charette, A. B.; Lebel, H. *J. Am. Chem. Soc.* **1996**, *118*, 10327. (c) Barrett, A. G. M.; Kasdorf, K. *J. Am. Chem. Soc.* **1996**, *118*, 11030.
- (15) For some reviews, see: (a) Wong, H. N. C.; Hon, M. Y.; Tse, C. W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) Kulinkovich, O. G. *Chem. Rev.* **2003**, *103*, 2597. (c) Brackmann, F.; de Meijere, A. *Chem. Rev.* **2007**, *107*, 4493.
- (16) For some reviews, see: (a) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183. (b) Lebel, H.; Marcoux, J. F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977. (c) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (d) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307.
- (17) For recent examples, see: (a) Liao, W.-W.; Li, K.; Tang, Y. *J. Am. Chem. Soc.* **2003**, *125*, 13030. (b) Ma, S.; Jiao, N.; Yang, Q.; Zheng, Z. *J. Org. Chem.* **2004**, *69*, 6463. (c) Okamoto, N.; Sasaki, M.; Kawahata, M.; Yamaguchi, K.; Takeda, K. *Org. Lett.* **2006**, *8*, 1889. (d) Li, J.; Liao, S.-H.; Xiong, H.; Zhou, Y.-Y.; Sun, X.-L.; Zhang, Y.; Zhou, X.-G.; Tang, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 8838.
- (18) For reviews, see: (a) Palmieri, A.; Petrini, M.; Shaikh, R. R. *Org. Biomol. Chem.* **2010**, *8*, 1259. (b) Petrini, M. *Chem. Rev.* **2005**, *105*, 3949. (c) Nájera, C.; Yus, M. *Tetrahedron* **1999**, *55*, 10547.
- (19) For recent examples, see: (a) Johnson, J. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1326. (b) Li, Y.; Shi, F.-Q.; He, Q.-L.; You, S.-L. *Org. Lett.* **2009**, *11*, 3182. (c) Jing, L.; Wei, J.; Zhou, L.; Huang, Z.; Li, Z.; Wu, D.; Xiang, H.; Zhou, X. *Chem.—Eur. J.* **2010**, *16*, 10955. (d) Martinelli, F.; Palmieri, A.; Petrini, M. *Chem.—Eur. J.* **2011**, *17*, 7183. (e) Cao, L.-L.; Ye, Z.-S.; Jiang, G.-F.; Zhou, Y.-G. *Adv. Synth. Catal.* **2011**, *353*, 3352. (f) Chen, M.-W.; Cao, L.-L.; Ye, Z.-S.; Jiang, G.-F.; Zhou, Y.-G. *Chem. Commun.* **2013**, *49*, 1660. (g) Palmieri, A.; Petrini, M. *J. Org. Chem.* **2007**, *72*, 1863. (h) Ballini, R.; Palmieri, A.; Petrini, M.; Shaikh, R. R. *Adv. Synth. Catal.* **2008**, *350*, 129. (i) Shaikh, R. R.; Mazzanti, A.; Petrini, M.; Bartoli, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8707. (j) Dobish, M. C.; Johnston, J. N. *Org. Lett.* **2010**, *12*, 5744. (k) Ballini, R.; Gabrielli, S.; Palmieri, A.; Petrini, M. *Adv. Synth. Catal.* **2010**, *352*, 2459. (l) Zheng, B.-H.; Ding, C.-H.; Hou, X.-L.; Dai, L.-X. *Org. Lett.* **2010**, *12*, 1688. (m) Wang, J.; Zhou, S.; Lin, D.; Ding, X.; Jiang, H.; Liu, H. *Chem. Commun.* **2011**, *47*, 8355. (n) Huang, J.-Z.; Wu, X.; Gong, L.-Z. *Adv. Synth. Catal.* **2013**, *355*, 2531.
- (20) (a) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341. (b) McGarrigle, E. M.; Myers, E. L.; Illa, O.; Shaw, M. A.; Riches, S. L.; Aggarwal, V. K. *Chem. Rev.* **2007**, *107*, 5841. (c) Sun, X.-L.; Tang, Y. *Acc. Chem. Res.* **2008**, *41*, 937. (d) Aggarwal, V. K.; Hynd, G.; Picoul, W.; Vasse, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 9964.
- (21) For early examples on the synthesis of unsubstituted spirocyclopropane indolenine, see: (a) Arumugam, S.; Verkade, J. G. *J. Org. Chem.* **1997**, *62*, 4827. (b) Liu, X.; Verkade, J. G. *J. Org. Chem.* **1999**, *64*, 4840.
- (22) CCDC 970864, 970865 and 970863 separately contains the supplementary crystallographic data of **3a**, **3p**, and **3p'**. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- (23) For selected chiral sulfonium salts examples, see: (a) Illa, O.; Arshad, M.; Ros, A.; McGarrigle, E. M.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2010**, *132*, 1828. (b) Deng, X.-M.; Cai, P.; Ye, S.; Sun, X.-L.; Liao, W.-W.; Li, K.; Tang, Y.; Wu, Y.-D.; Dai, L.-X. *J. Am. Chem. Soc.* **2006**, *128*, 9730. (c) Zhou, Y.-G.; Hou, X.-L.; Dai, L.-X.; Xia, L.-J.; Tang, M.-H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 77.
- (24) CCDC 970862 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.