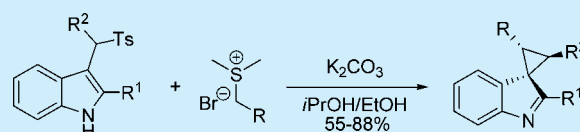


## The Concise Synthesis of Spiro-Cyclopropane Compounds via the Dearomatization of Indole Derivatives

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## 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.

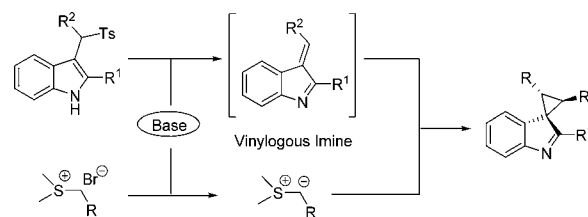


Dearomatization reactions are important transformations of aromatic compounds because they directly lead to a variety of ring systems.<sup>1</sup> Additionally, they are highly efficient for constructing quaternary carbon centers<sup>2</sup> and used as the key steps in the total synthesis of many natural products.<sup>3</sup> In this regard, dearomatization reactions of indoles,<sup>4</sup> pyridines,<sup>5</sup> phenols,<sup>6</sup> pyrroles,<sup>7</sup> etc., have been developed. Among them, compounds with an indole skeleton have attracted enormous attention because of the important biological activities of their derivatives.<sup>8</sup> Dearomatization reaction of indoles has been extensively studied over the past decades, with particular focuses on alkylative dearomatization<sup>9</sup> and oxidative dearomatization.<sup>10</sup> In addition, the Diels–Alder pathway with various dienophiles<sup>11</sup> and organocatalyzed Michael/Mannich cyclization cascade reactions were also demonstrated in dearomatization reactions of indoles.<sup>12</sup> Besides, several transition-metal-catalyzed dearomatization reactions of indoles were also documented.<sup>13</sup> 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.<sup>14</sup> In addition, they also serve as valuable synthetic intermediates for a wide range of organic compounds.<sup>15</sup> 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.<sup>16,17</sup>

The use of an arylsulfonyl group as an auxiliary group is still a prominent synthetic strategy in organic synthesis.<sup>18</sup> 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  $\alpha,\beta$ -unsaturated imines, which are able to react with numerous nucleophiles.<sup>19</sup> Considering that sulfur ylides act as a nucleophile under the basic condition,<sup>20</sup> 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.

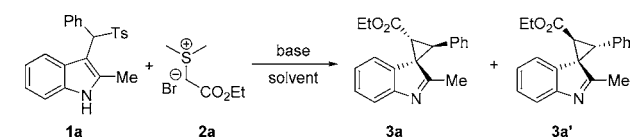
Initially, our investigation was launched with 2-methyl-substituted arenesulfonylindole **1a** (1.0 equiv), sulfonium salt **2a** (1.5 equiv),  $K_2CO_3$  (3.0 equiv) as the base in  $CH_2Cl_2$

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(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**<sup>a</sup>**



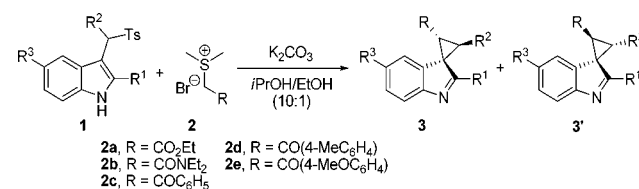
entry	solvent	base	yield (%) <sup>b</sup>	dr <sup>c</sup>
1	CH <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	74	3:1
2	toluene	K <sub>2</sub> CO <sub>3</sub>	<5	—
3	CH <sub>3</sub> OH	K <sub>2</sub> CO <sub>3</sub>	26	4:1
4	EtOH (E)	K <sub>2</sub> CO <sub>3</sub>	87	6:1
5	<i>i</i> PrOH (P)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

<sup>a</sup>Condition: 0.25 mmol **1a**, 0.375 mmol **2a**, 0.75 mmol base, 3.3 mL of solvent, room temperature, 12 h. <sup>b</sup>Isolated yields of the mixture of **3a** and **3a'**. <sup>c</sup>All of the dr (**3a**/**3a'**) were determined by <sup>1</sup>H 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, K<sub>2</sub>CO<sub>3</sub> 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 R<sup>2</sup> (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).<sup>21</sup>

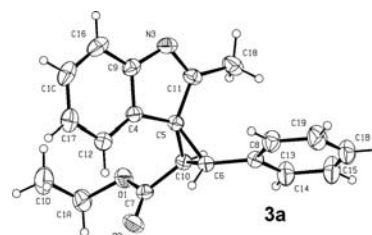
**Table 2. Scope for the Reaction of Arenesulfonylindoles **1** with Sulfonium Salts **2**<sup>a</sup>**



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

<sup>a</sup>Condition: 0.25 mmol **1**, 0.375 mmol **2**, 0.75 mmol K<sub>2</sub>CO<sub>3</sub>, 3.0 mL of *i*PrOH, 0.3 mL of EtOH, room temperature, 12 h. <sup>b</sup>Isolated yields of the mixture of **3** and **3'**. <sup>c</sup>All of the dr (**3**/**3'**) were determined by <sup>1</sup>H NMR spectroscopy. <sup>d</sup>3.3 mL of EtOH was used.

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



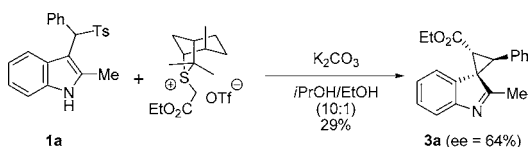
**Figure 1.** X-ray crystal structure of compound **3a**.

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

Furthermore, a preliminary study on the enantioselective version of this dearomatization reaction was also tried. Using the known chiral sulfonium salts<sup>23</sup> 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.

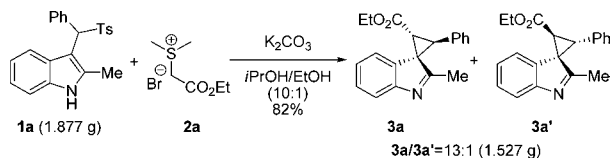
It is noted that the model substrates **1a** and **2a** could also be carried out at a gram scale. As illustrated in Scheme 3, the target

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



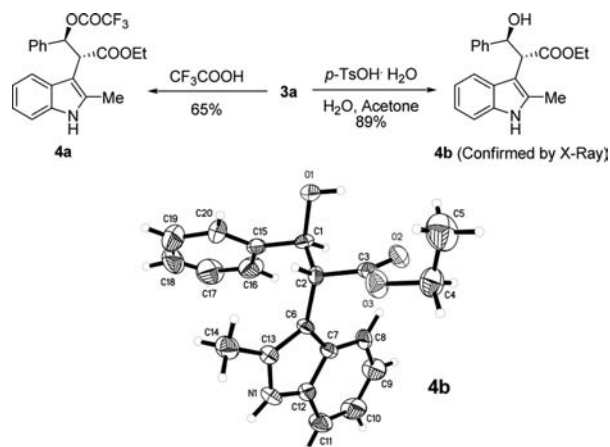
products 3a and 3a' could be obtained in 82% yield and the diastereoselectivity could be kept with 13:1.

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 acid

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<sup>24</sup> 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>.

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### Notes

The authors declare no competing financial interest.

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