

# New non-volatile and odorless organosulfur compounds anchored on ionic liquids. Recyclable reagents for Swern oxidation

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**Abstract**—A new class of odorless and non-volatile organosulfur compounds grafted to imidazolium ionic liquid scaffold has been synthesized. The sulfoxides can be used effectively for the oxidation of primary allylic and benzylic alcohols into aldehydes and secondary alcohols to ketones under Swern oxidation conditions and the corresponding sulfides can be recovered and recycled.

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## 1. Introduction

Organosulfur compounds have played an important role in organic chemistry.<sup>1</sup> An array of organosulfur compounds have been introduced for use in pesticides, medicines,<sup>2</sup> and more recently material sciences.<sup>3</sup> Many organosulfur reagents have important use in synthetic organic chemistry.<sup>4</sup> Volatile organosulfur compounds, especially thiols, often have very unpleasant smells and some are toxic.<sup>2</sup> These properties have reduced their attractiveness for applications. We report here the synthesis of a new class of organosulfur compounds anchored on the imidazolium scaffold commonly used for ionic liquids. Ionic liquids have received much attention in recent years as environmentally benign reaction media for organic reactions.<sup>5</sup> This is due to some intriguing properties of ionic liquids: high thermal and chemical stability, non-flammability, lack of measurable vapor pressure and high loading capacity. By modifying the structure of the cation or the anion, the solubilities of the ionic liquids can be tuned readily so that they can phase separate from organic as well as aqueous media. By anchoring the sulfur function to the ionic liquid moiety, we expect to render the organosulfur compounds non-volatile, and easily recoverable and recyclable. We then demonstrate the application of these new organosulfur compounds as reagents for the Swern oxidation.

## 2. Results and discussion

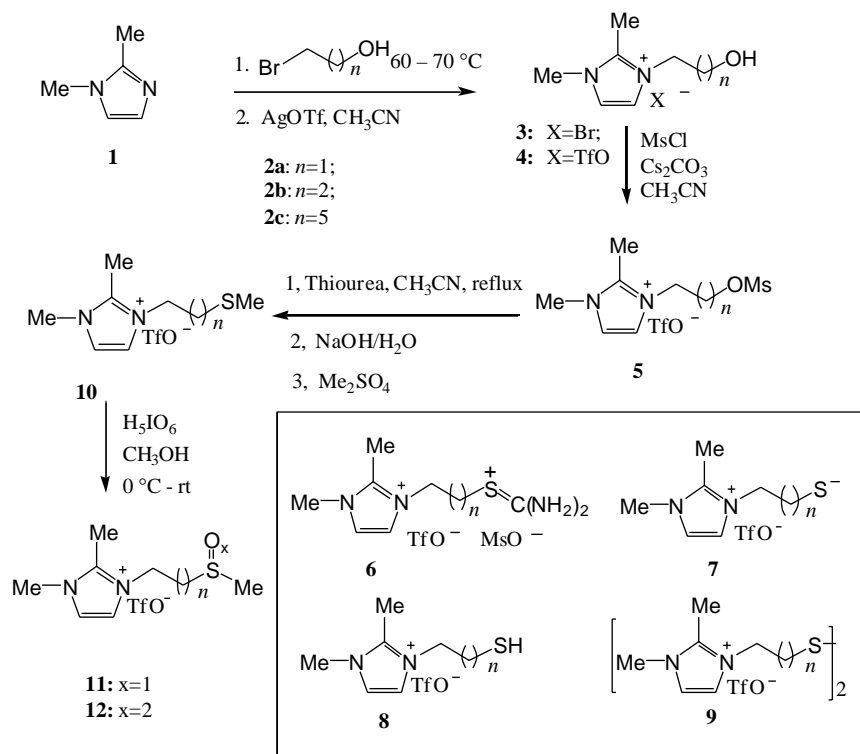
The preparation of the ionic liquid-supported sulfur compounds started from 1,2-dimethylimidazole **1** and

bromoalkyl alcohols **2** (Scheme 1). The reaction was conducted without solvent at 60–70 °C and the product **3** was obtained in nearly quantitative yield simply by washing the reaction mixture with diethyl ether to remove the trace amount of unreacted starting materials. This was followed by anion exchange to give the triflate salt **4** quantitatively. Mass spectroscopic analysis showed that the anion exchange was complete based on the spectra on anions, which showed the absence of bromide anion. Sodium triflate also worked for the anion exchange reaction, but the reaction went faster with silver triflate. The methanesulfonylation of alcohols **4** was conducted at room temperature under the basic condition provided by Cs<sub>2</sub>CO<sub>3</sub> in acetonitrile. This gave excellent yields of product mesylates **5**. The inorganic salt was simply removed by filtration and the organic impurity was easily washed away with diethyl ether. The mesylates **5** were then transformed to the ionic liquid-supported sulfides **10** in one pot with a sequence of reactions but without need of purification of the intermediate products. First, treatment of **5** with thiourea in acetonitrile gave the thiuronium salt **6**.<sup>6</sup> Base hydrolysis of **6** gave the odorless ionic liquid-supported thiol **8** together with the disulfide **9** as a mixture. The sole formation of pure thiol **8** was difficult even though a number of reaction conditions were tested including using different bases such as LiOH, NaOH, KOH and CsOH, or solvents such as THF and acetonitrile, and temperature from room temperature to 60 °C. This is due to ease of thiol oxidative dimerization in air under basic conditions. However, we were able to trap the thiolate intermediate **7** readily as the methyl sulfide **10** by quenching the base hydrolytic reaction mixture with dimethyl sulfate.<sup>7</sup> The conversion of the ionic liquid **4** to the sulfur compound **10** could be achieved in >92% overall yield with no need of chromatographic

**Keywords:** Odorless organosulfur compounds; Ionic liquids; Swern oxidation; Supported reagents.

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Scheme 1. Preparation of ionic liquid-grafted sulfides and sulfoxides.

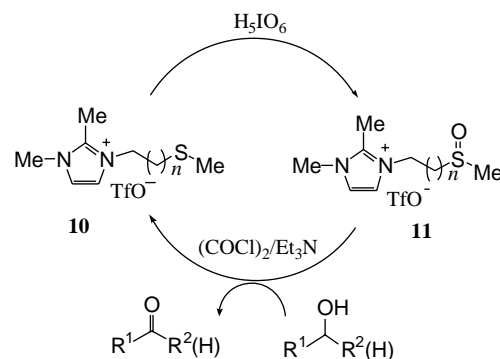
purification of intermediates and there was no foul smell released in any of the operations. This is because in all the reaction steps, the products were separated from the excess organic or inorganic reagents by simply washing with organic or aqueous solvents, an advantage, which we have demonstrated previously in ionic liquid-supported synthesis of small molecules,<sup>8</sup> oligopeptides<sup>9</sup> and oligosaccharides.<sup>10</sup> The whole synthetic sequence was odor-free as no volatile organosulfur compounds were used or generated. Previously, sulfur containing imidazolium ionic liquid had been synthesized from *N*-methylimidazole and 2-(chloroethyl)ethyl sulfide.<sup>11</sup> However, this involved the use of odorous volatile sulfur compound for the synthesis, and ethyl sulfoxides in general are not used for Swern oxidation.

The oxidation of the sulfides **10** with periodic acid generated very cleanly the sulfoxides **11** without over-oxidation to the sulfone **12** under the experimental condition.<sup>12</sup> Potassium periodate did not oxidize **10** under neutral conditions, but under acidic conditions converted **10** to a mixture of sulfoxide **11** as well as sulfone **12** in a ratio of 3 to 1 according to  $^1\text{H}$  NMR spectra. *m*-Chloroperoxybenzoic acid (*m*CPBA) also oxidized the sulfide **10** to give similar results as acidified potassium periodate. The oxidation of the sulfides with peracetic acid, on the other hand, proceeded slowly at room temperature. It only generated a very small amount of sulfoxide **11** after stirring for 24 h at room temperature.

The conversion of alcohols to aldehydes and ketones is one of the key functional transformations in organic chemistry. The Swern oxidation and its numerous variations<sup>13,14</sup> have

been used extensively for that purpose. A major drawback of the Swern oxidation is that dimethyl sulfide, generated in stoichiometric amount, is volatile, malodorous, toxic and difficult to be recovered. This mitigates against its use on a large scale. A number of research groups have attempted to overcome the problem by using polymer-supported sulfoxide reagents,<sup>15</sup> fluorosulfoxides<sup>16</sup> or dodecyl methyl sulfoxide.<sup>17</sup> Each of these has some inherent deficiencies. In the dodecyl methyl sulfoxide case, recovery of the product sulfide was difficult. The fluorosulfoxides and sulfides are likely to be expensive and relatively volatile. Polymer-supported sulfoxide reagents,<sup>15</sup> whether using insoluble or soluble polymer support, usually have a low loading level of the effective functional group.

We examined therefore the ionic liquid-supported sulfoxides **11** as recoverable and recyclable reagents for the Swern oxidation reaction (Scheme 2).



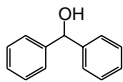
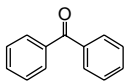
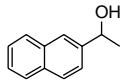
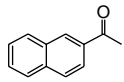
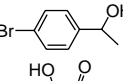
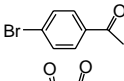
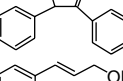
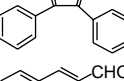
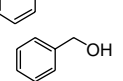
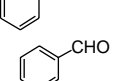
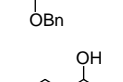
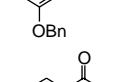
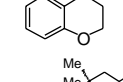
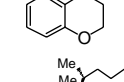
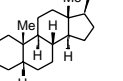
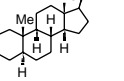
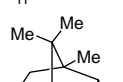
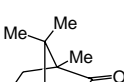
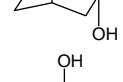
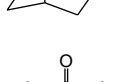
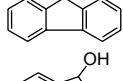
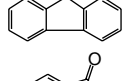
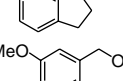
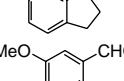
Scheme 2. Recycle of ionic liquid-supported sulfides and sulfoxides in Swern oxidation.

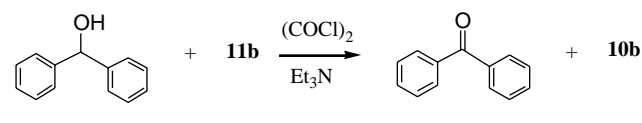
The Swern oxidations were conducted under standard conditions, using oxalyl chloride as activator and triethylamine as base in acetonitrile/dichloromethane at low temperature. The ionic liquid-attached sulfoxides **11b** or **11c** were quite reactive. A number of alcohols were converted to the corresponding aldehydes or ketones in high yields (Table 1). The carbonyl product was easily separated from the ionic liquid anchored sulfide **10** (**b** or **c**) by simple phase separations with diethyl ether after Swern oxidation. However, it should be pointed out that the sulfoxide **11a**, which has two methylene spacers between the ionic liquid moiety and the sulfoxide part, did not work well as Swern oxidation reagent. It is possible that facile  $\beta$  elimination may have occurred leading to the fragmentation of the imidazolium moiety from the sulfoxide. The oxidation of secondary alcohols to the corresponding ketones worked very efficiently under the reaction conditions (Table 1). On the other hand, oxidation of primary alcohols to aldehydes appears to have worked well only for benzylic or allylic alcohols.

Simple aliphatic primary alcohols tended to give low yield, possibly because the sulfoxide **11b** or **11c** reagent was not employed in large excess, in contrast to what was normally used for DMSO.<sup>14</sup> We have conducted one reaction on a larger (10–50 mmol) scale for the oxidation of benzhydrol to benzophenone. The isolated yield of the product was 91%.

The use of ionic liquid-supported reagents allows for the opportunity of recovery and recycle. The sulfide **10b** or **10c**, insoluble in ether, was recovered after aqueous treatment with  $K_2CO_3$  and extraction with acetonitrile/dichloromethane.<sup>18</sup> The recovered sulfide **10b** or **10c** can be re-oxidized with periodic acid and used for the Swern oxidation again. Oxidation of benzhydrol to benzophenone was chosen as an example to test the recovery and recycling efficiency of the **11b** ↔ **10b** system. The results are summarized in Table 2, which show that the product yields and recovered sulfide yields were still quite acceptable after four recycles (Table 2).<sup>18</sup>

Table 1. Swern oxidation using ionic liquid-supported sulfoxides

Entry	Sulfoxide	Substrate	Product	Yield (%)
1	<b>11b</b>			90
2	<b>11b</b>			95
3	<b>11b</b>			86
4	<b>11b</b>			85
5	<b>11b</b>			88
6	<b>11b</b>			95
7	<b>11b</b>			82
8	<b>11b</b>			85
9	<b>11b</b>			90
10	<b>11c</b>			95
11	<b>11c</b>			82
12	<b>11c</b>			97

**Table 2.** Recycle of ionic liquid-supported sulfide **10b** in Swern oxidation of benzhydrol to benzophenone


Recycle times	1	2	3	4
Product yield (%)	90	87	86	81
Recovered sulfide (%)	88	82	82	80

### 3. Conclusions

We have prepared a class of novel sulfur containing compounds anchored onto an imidazolium ionic liquid scaffold. Because of the lack of vapour pressure of these ionic liquids, the sulfur compounds do not possess odor. The sulfoxide compounds **11b** and **11c** can be used effectively for the oxidation of alcohols to carbonyl compounds under the Swern oxidation conditions. The product sulfide **10b** can be recovered easily from the reaction mixture and regenerated to **11b** and thus reused for at least 4 cycles.

### 4. Experimental

#### 4.1. General

The procedures to make ionic liquid-attached compounds with two, three, six methylene spacers in the Scheme 1 were the same.

**4.1.1. 1-(3'-Hydroxypropyl)-2,3-dimethylimidazolium triflate (4b).** To a flask containing 1,2-dimethylimidazole (10.0 mL, 113 mmol) was added 3-bromopropanol (10.0 mL, 114 mmol). The mixture was heated to 70 °C and stirred for 2 h under nitrogen and then cooled to room temperature. The crude product solidified during the cooling process. The solid was washed with diethyl ether for four times and dried in vacuo for 3 h to afford

**4.1.2. 1-(3'-Hydroxypropyl)-2,3-dimethylimidazolium bromide (3b).** As white solid (26.2 g, 98% yield). Mp 58–60 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.24 (d, 1H, *J* = 2 Hz), 7.20 (d, 1H, *J* = 2 Hz), 4.10 (t, 2H, *J* = 7.2 Hz), 3.65 (s, 3H), 3.50 (t, 2H, *J* = 6.4 Hz), 2.48 (s, 3H), 1.93 (m, 2H); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 144.5, 122.4, 120.9, 58.2, 45.3, 35.0, 31.6, 9.4; HRMS (ESI): calcd for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>O (M<sup>+</sup>) 155.1179, found: 155.1178.

To a solution of 1-(3'-hydroxypropyl)-2,3-dimethylimidazolium bromide (**3b**) (4.97 g, 21.1 mmol) in dry acetonitrile (20 mL) was added silver triflate (5.43 g, 21.1 mmol). The mixture was stirred for 2 h in the dark under nitrogen. The mixture was filtered to remove the yellow salt and the filtrate was evaporated by rotary evaporation under vacuum and dried in vacuo to generate the product **4b** as a clear liquid with a very light brown color (6.42 g, 100% yield). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.27 (d, 1H, *J* = 1.8 Hz), 7.23 (d, 1H, *J* = 1.8 Hz), 4.12 (t, 2H, *J* = 7.2 Hz), 3.68 (s, 3H), 3.53 (t, 2H, *J* = 6.3 Hz), 2.51 (s, 3H), 1.96 (m, 2H); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 144.5, 122.4, 120.9,

58.1, 45.2, 34.9, 31.6, 9.1; HRMS (ESI): calcd for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>O (M<sup>+</sup>) 155.1179, found: 155.1180.

**4.1.3. 1-(2'-Hydroxyethyl)-2,3-dimethylimidazolium triflate (4a).** Yield: 100% as clear liquid; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.28 (d, 1H, *J* = 2.0 Hz), 7.24 (d, 1H, *J* = 2.0 Hz), 4.15 (t, 2H, *J* = 5.6 Hz), 3.82 (t, 2H, *J* = 6 Hz), 3.69 (s, 3H), 2.51 (s, 3H); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 144.5, 122.5, 121.2, 60.2, 50.4, 35.0, 9.4; HRMS (ESI): calcd for C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O (M<sup>+</sup>) 141.1018, found: 141.1022.

**4.1.4. 1-(6'-Hydroxyhexyl)-2,3-dimethylimidazolium triflate (4c).** Yield: 100% as clear liquid; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 7.21 (d, 1H, *J* = 2.4 Hz), 7.17 (d, 1H, *J* = 2.4 Hz), 3.98 (t, 2H, *J* = 6.9 Hz), 3.64 (s, 3H), 3.46 (t, 2H, *J* = 6.6 Hz), 2.46 (s, 3H), 1.70 (m, 2H), 1.42 (m, 2H), 1.23 (m, 4H); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 144.2, 122.2, 120.8, 61.9, 48.3, 34.8, 31.4, 29.2, 25.5, 24.9, 9.1; HRMS (ESI): calcd for C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>O (M<sup>+</sup>) 197.1648, found: 197.1646.

**4.1.5. Compound 5b.** To a flask containing **4b** (6.00 g, 19.7 mmol) and cesium carbonate (8.05 g, 24.7 mmol) was added acetonitrile (30 mL). The mixture was cooled to 0 °C and methanesulfonyl chloride (2.30 mL, 29.6 mmol) was added dropwise. After 2 h of stirring at 0 °C, the mixture was warmed to room temperature and stirring continued for 20 h. The insoluble inorganic salt was filtered off and the filtrate was evaporated by rotary evaporation and dried in vacuo overnight. The crude product was washed with diethyl ether for four times to afford white solid product **5b** (7.31 g, 97% yield). Mp 47–49 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.25 (d, 1H, *J* = 2.0 Hz), 7.21 (d, 1H, *J* = 2.0 Hz), 4.23 (t, 2H, *J* = 5.6 Hz), 4.16 (t, 2H, *J* = 7.2 Hz), 3.64 (s, 3H), 3.06 (s, 3H), 2.46 (s, 3H), 2.19 (m, 2H); <sup>13</sup>C NMR (400 MHz, D<sub>2</sub>O): δ 144.7, 122.6, 120.9, 68.2, 44.8, 36.6, 34.9, 28.8, 9.2; HRMS (ESI): calcd for C<sub>9</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>S (M<sup>+</sup>) 233.0954, found: 233.0953.

**4.1.6. Compound 5a.** Yield: 94% as clear liquid; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.30 (d, 1H, *J* = 1.6 Hz), 7.23 (d, 1H, *J* = 1.6 Hz), 4.51 (t, 2H, *J* = 4.8 Hz), 4.42 (t, 2H, *J* = 5.6 Hz), 3.65 (s, 3H), 3.05 (s, 3H), 2.49 (s, 3H); <sup>13</sup>C NMR (400 MHz, D<sub>2</sub>O): δ 145.4, 122.8, 121.3, 68.6, 47.3, 36.9, 35.1, 9.5; HRMS (ESI): calcd for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S (M<sup>+</sup>) 219.0795, found: 219.0798.

**4.1.7. Compound 5c.** Yield: 95% as clear liquid; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 7.16 (d, 1H, *J* = 2.4 Hz), 7.12 (d, 1H, *J* = 2.4 Hz), 4.15 (t, 2H, *J* = 6.0 Hz), 3.94 (t, 2H, *J* = 7.2 Hz), 3.58 (s, 3H), 3.00 (s, 3H), 2.41 (s, 3H), 1.68 (m, 2H), 1.59 (m, 2H), 1.28 (m, 2H), 1.17 (m, 2H); <sup>13</sup>C NMR (400 MHz, CD<sub>3</sub>CN): δ 144.6, 122.5, 121.0, 71.1, 48.4, 36.8, 35.1, 29.5, 28.9, 25.6, 25.0, 9.6; HRMS (ESI): calcd for C<sub>12</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S (M<sup>+</sup>) 275.1424, found: 275.1420.

**4.1.8. Compound 10b.** To a flask containing **5b** (1.00 g, 2.61 mmol) and thiourea (0.32 g, 4.20 mmol) was added dry acetonitrile (20 mL). The mixture was refluxed for 10 h under nitrogen. After removing the solvent, NaOH (0.42 g, 10.5 mmol) and degassed water (20 mL) were added and the mixture was stirred at 45 °C overnight under nitrogen. Dimethyl sulfate (0.30 mL, 3.15 mmol) was added and the mixture was stirred at room temperature for 20 h.

After the pH of the mixture was adjusted to 7 with the addition of aqueous HCl, the mixture was freeze dried to remove water. Acetonitrile was added to the residue to extract the product. The acetonitrile solution was filtered to remove the insoluble inorganic salt, and the filtrate was rotary evaporated under vacuum and then dried in vacuo to give product **10b** as clear oil (0.87 g, 99% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.22 (d, 1H,  $J=2.4$  Hz), 7.17 (d, 1H,  $J=2.4$  Hz), 4.08 (t, 2H,  $J=6.8$  Hz), 3.62 (s, 3H), 2.47 (s, 3H), 2.41 (t, 2H,  $J=6.8$  Hz), 1.97 (m, 5H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.5, 122.5, 120.8, 46.9, 34.9, 29.9, 28.3, 14.4, 9.2; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{17}\text{N}_2\text{S}$  ( $\text{M}^+$ ) 185.1107, found: 185.1103.

**4.1.9. Compound 10a.** Yield: 99% as clear oily liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.28 (d, 1H,  $J=2.0$  Hz), 7.21 (d, 1H,  $J=2.0$  Hz), 4.22 (t, 2H,  $J=6.4$  Hz), 3.66 (s, 3H), 2.83 (t, 2H,  $J=6.4$  Hz), 2.51 (s, 3H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.7, 122.4, 121.1, 47.2, 35.0, 33.4, 14.7, 9.4; HRMS (ESI): calcd for  $\text{C}_8\text{H}_{15}\text{N}_2\text{S}$  ( $\text{M}^+$ ) 171.0950, found: 171.0949.

**4.1.10. Compound 10c.** Yield: 98% as clear oily liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.16 (d, 1H,  $J=1.8$  Hz), 7.13 (d, 1H,  $J=1.8$  Hz), 3.94 (t, 2H,  $J=7.2$  Hz), 3.60 (s, 3H), 2.42 (s, 3H), 2.36 (t, 2H,  $J=7.2$  Hz), 1.92 (s, 3H), 1.65 (m, 2H), 1.43 (m, 2H), 1.52 (m, 4H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.2, 122.2, 120.8, 48.3, 34.7, 33.4, 29.1, 28.3, 27.6, 25.3, 14.4, 9.1; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{23}\text{N}_2\text{S}$  ( $\text{M}^+$ ) 227.1576, found: 227.1575.

**4.1.11. Compound 11b.** To a solution of **10b** (5.05 g, 15.1 mmol) in methanol (50 mL), which was cooled with ice bath, was added dropwise a solution of periodic acid (3.45 g, 15.1 mmol) in methanol (15 mL). The mixture was stirred at 0 °C for 2 h. The ice bath was removed and stirring was continued for 20 h. To the orange mixture was added aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the orange color disappeared. The solvent methanol was removed by rotary evaporation in vacuo and water was removed by freeze drying. To the residue was then added the mixed solvent (100 mL) of acetonitrile and dichloromethane (v/v = 1:1). After filtering off the inorganic salt, the filtrate was rotary evaporated under vacuum and dried in vacuo to afford the product as white sticky foam (5.18 g, 98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.24 (d, 1H,  $J=2$  Hz), 7.17 (d, 1H,  $J=2$  Hz), 4.14 (t, 2H,  $J=7.2$  Hz), 3.61 (s, 3H), 2.84–2.72 (m, 2H), 2.56 (s, 3H), 2.45 (s, 3H), 2.15 (m, 2H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.6, 122.7, 120.8, 49.1, 46.9, 37.1, 35.1, 23.0, 9.4; HRMS (ESI): calcd for  $\text{C}_9\text{H}_{17}\text{N}_2\text{SO}$  ( $\text{M}^+$ ) 201.1056, found: 201.1056.

**4.1.12. Compound 11a.** Yield: 99% as thick oil;  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.33 (d, 1H,  $J=2.4$  Hz), 7.26 (d, 1H,  $J=2.4$  Hz), 4.53 (t, 2H,  $J=6.0$  Hz), 3.68 (s, 3H), 3.33 (m, 1H), 3.24 (m, 1H), 2.68 (s, 3H), 2.55 (s, 3H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.9, 123.0, 121.0, 52.1, 42.3, 37.5, 35.2, 9.5; HRMS (ESI): calcd for  $\text{C}_8\text{H}_{15}\text{N}_2\text{SO}$  ( $\text{M}^+$ ) 187.0900, found: 187.0898.

**4.1.13. Compound 11c.** Yield: 96% as thick oil;  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.16 (d, 1H,  $J=2.1$  Hz), 7.13 (d, 1H,  $J=2.1$  Hz), 3.95 (t, 2H,  $J=6.9$  Hz), 3.59 (s, 3H), 2.71

(m, 2H), 2.52 (s, 3H), 2.42 (s, 3H), 1.67 (m, 2H), 1.58 (m, 2H), 1.35 (m, 2H), 1.19 (m, 2H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  144.2, 122.2, 120.8, 52.8, 48.3, 36.7, 34.9, 29.0, 27.5, 25.4, 22.0, 9.2; HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{23}\text{N}_2\text{SO}$  ( $\text{M}^+$ ) 243.1526, found: 243.1525.

## 4.2. General procedure for the Swern oxidation

A solution of ionic liquid-attached sulfoxide **11** (0.9 mmol, 3 equiv) in dichloromethane (2.5 mL) and acetonitrile (2.5 mL) was cooled to  $-78$  °C and oxalyl chloride (0.9 mmol, 3 equiv) was added dropwise. The mixture was stirred at  $-78$  °C for 40 min and then the alcohol (0.3 mmol, 1 equiv) solution in dichloromethane (2.5 mL) was added dropwise in 10 min. After stirring at low temperature for 1.5 h, triethylamine (0.25 mL, 6 equiv) was added and the mixture was slowly warmed to room temperature. The solvent was removed by rotary evaporation and the product in the residue was extracted with diethyl ether (6 mL) for five times. The ether extract was evaporated by rotary evaporation in vacuo. The product residue was subject to flash column chromatography (silica gel 60A, 230–400 mesh) using hexane and ethyl acetate as eluant to afford the pure product.

## 4.3. Swern oxidation in larger scale

A solution of ionic liquid-attached sulfoxide **11b** (16.73 g, 48 mmol) in dichloromethane (50 mL) and acetonitrile (75 mL) was cooled to  $-78$  °C and oxalyl chloride (4.8 mL, 55 mmol) was added dropwise. The mixture was stirred at  $-78$  °C for 40 min and then the alcohol benzhydrol (2.92 g, 16 mmol) solution in dichloromethane (25 mL) was added dropwise in 10 min. After stirring at low temperature for 1.5 h, triethylamine (14 mL, 100 mmol) was added and the mixture was slowly warmed to room temperature in 2 h. The solvent was removed by rotary evaporation and the product in the residue was extracted with diethyl ether (60 mL) for 10 times. The ether extract was evaporated by rotary evaporation in vacuo. The product residue was subject to flash column chromatography (silica gel 60A, 230–400 mesh) using hexane and ethyl acetate as eluant to afford the product benzophenone (2.62 g, 91% yield).

## 4.4. General procedure to recover ionic liquid-attached sulfide after Swern oxidation

After the extraction of the product with diethyl ether described above, water (10 mL) was added to the residue. The aqueous phase was collected and to which  $\text{K}_2\text{CO}_3$  (0.16 g, 1.1 mmol) was added. The aqueous phase was stirred for 3 h at room temperature and water was removed by freeze-dry by lypholyser. To the solid residue was then added acetonitrile (10 mL), dichloromethane (5 mL) and anhydrous  $\text{Na}_2\text{SO}_4$ . The mixture was stirred for 20 min to extract the expected sulfide into the organic phase. After filtering off the insoluble inorganic salts, the organic filtrate was evaporated by rotary evaporation under vacuum and dried in vacuo to generate the recovered ionic liquid-attached sulfide **10** (Table 2). The NMR spectra of the recovered sulfide showed the same NMR as that of **10** before reaction. The recovered sulfide was used as is for the next cycle. The recovery yield was about 80%, due to



mechanical loss associated with the small scale experimental conditions.

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