Catalytic and non-catalytic selective aryl transfer from (mesityl)iodonium(III) salts to diarylsulfide compounds

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Received 01-28-2022  Accepted Manuscript 03-18-2022  Published on line 04-11-2022

Abstract

We report a facile synthesis of triarylsulfonium triflates by selective aryl transfer from readily available mesityl iodonium(III) salts to diarylsulfides in the presence of a copper catalyst. The advantage of our protocol is that the iodonium(III) salts bearing a mesitylene (Mes) auxiliary efficiently promote selective S-arylation of diarylsulfides to produce the desired triarylsulfonium triflates without the formation of Mes-derived byproduct salts.

Keywords: Hypervalent compounds, iodine, diaryliodonium(III) salts, ligand transfer selectivity, sulfonium salts
Introduction

Triarylsulfonium salts, one of the useful and important classes of sulfonium salts from an industrial point of view, have a wide range of applications, e.g., as acid generators in photolithography or as photoinitiators in cationic polymerization.\(^1\)\(^-\)\(^2\) Recently, triarylsulfonium salts have received considerable attention in organic synthesis as radical precursors and cross-coupling partners in metal-catalysis.\(^3\) Several synthetic routes for preparing triarylsulfonium salts have thus been reported so far.\(^4\) Among them, aryl transfer from diaryliodonium(III) salts to diarylsulfides under simple operation is one of the most reliable approaches.\(^5\)-\(^8\) In early studies, around 1960s, non-catalytic arylation of Ph\(_2\)S with Ph\(_2\)I\(^+\)BF\(_4\)^- under harsh conditions (180 °C, 35 h) was reported to afford Ph\(_3\)S\(^+\)BF\(_4\)^- in a moderate yield (ca. 65%).\(^5\) In 1978, Crivello et al. reported a faster and better-yield aryl transfer reaction in the presence of catalytic Cu(OBz).\(^2\) (Scheme 1A),\(^6\) but the reaction used a limited number of diaryliodonium(III) salts (Ar\(^1\)Ar\(^2\)I\(^+\)X\(^-\); Ar\(^1\) = Ar\(^2\)) possessing non-nucleophilic counter anions such as BF\(_4\)^-, AsF\(_6\)^-, and PF\(_6\). In 2014, Ciufolini et al. demonstrated that diaryliodonium(III) triflates effectively arylate diarylsulfide compounds under transition-metal-free conditions (Scheme 1B).\(^7\) The synthetic method is an attractive and economically advantageous approach, but mixtures of two types of aryl-transferred triarylsulfonium triflates were obtained in the case of diaryliodonium(III) triflates having Ar\(^1\) ≠ Ar\(^2\). Thus, developing a more practical method that enables the use of various diaryliodonium(III) salts is still required to expand the synthetic scope for triarylsulfonium salts with greater structural diversities.

A) Cu(II)-catalyzed S-arylation: J. V. Crivello et al. (1978)

\[
\text{Ph-S-Ph} + \text{Ar}\(_2\)I\(^+\)X^- \xrightarrow{\text{Cu(II) cat.}} \text{Ph}^+\text{S}^-\text{Ph} \quad X = \text{BF}_4^-, \text{AsF}_6^-, \text{PF}_6^-\text{etc.}
\]

B) Metal-free S-arylation: M. A. Ciufolini et al. (2014)

\[
\text{Ph-S-Ph} + \text{Ar}^1\text{OTf}^+ \quad \text{Ar}^2, \text{Ar}^1\text{OTf}^+ \quad \text{Ar}^1\text{OTf}^+ \quad \text{Ar}^2\text{OTf}^+
\]

Scheme 1. S-Arylation of diarylsulfides with diaryliodonium(III) salts.

Diaryliodonium(III) salts have found numerous applications as electrophilic arylating agents toward nucleophiles, and the nature of the aryl moiety and anionic counterpart alter their chemical and physical properties.\(^9\)-\(^11\) Over the past few decades, diaryliodonium(III) salts (Ar\(^1\)Ar\(^2\)I\(^+\)X\(^-\)) with Ar\(^1\) = Ar\(^2\) were preferred over those with Ar\(^1\) ≠ Ar\(^2\) in order to avoid selectivity issues of aryl transfer processes. Recently, aiming at selective aryl transfer reactions, specific diaryliodonium(III) salts incorporating a non-transferable dummy group such as mesityl (Mes)\(^12\)-\(^14\) and an auxiliary 2,4,6-trimethoxyphenyl (TMP)\(^15\)-\(^19\) have been studied by scientists including our research group. In our continuous study of diaryliodonium(III) salts-mediated reactions,\(^20\),\(^21\) we report herein diaryliodonium(III) triflates bearing a mesitylene (Mes) auxiliary to facilitate selective S-arylation of diarylsulfides to form triarylsulfonium triflates without the formation of Mes-derived byproduct salts (Scheme 2).
Scheme 2. This work: selective S-arylation of diarylsulfides with (mesityl)iodonium(III) triflates.

Results and Discussion

In a pilot experiment, we first examined the S-arylation of diphenylsulfide 1a in the presence of copper(II) acetate monohydrate using mesityl(p-tolyl)iodonium(III) triflate 2a (Table 1). When sulfide 1a was reacted with 1.2 equivalent of iodonium(III) triflate 2a with 10 mol % of copper(II) acetate monohydrate at 130 °C under solvent-free conditions, the reaction proceeded smoothly and yielded the arylation product 3aa with an 80% and 91% yields (Entries 1 and 2, respectively). It is notable that the sulfonium salt 3aa was solely obtained by selective p-tolyl transfer in high yields without the formation of a potential byproduct, diphenyl(mesityl)sulfonium salt. The copper(II)-catalyzed aryl transfer of (mesityl)iodonium(III) salts was reported in other arylation reactions, in which the oxidative addition of copper(II) to the mesityl group did not occur due to its high steric bulkiness. The use of 1,2-dichloroethane (DCE) as solvent also resulted in a good yield with selective formation of 3aa, though the reaction time in this case was prolonged (Entries 3 and 4). Lowering the reaction temperature to 100 °C increased the yield to 96% (Entries 5 and 6). The usage of anhydrous copper(II) acetate was not effective, and provided an inferior result in comparison with the use of copper(II) acetate monohydrate (Entry 7). Moreover, when the reaction was performed with equimolar amounts of diphenylsulfide 1a and iodonium(III) triflate 2a, the yield was slightly decreased (Entry 8). It should be noted that the copper(II) catalyst plays an important role in accelerating the reaction rate; the use of 5 mol % of copper(II) gave p-tolyl transfer product 3aa with an 88% yield at 100 °C (Entry 9), while the same product was not obtained at all in the absence of the copper(II) catalyst (Entry 10).
Table 1. Optimization of the reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Temp</th>
<th>Solvent</th>
<th>Time</th>
<th>Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>130 °C</td>
<td>none</td>
<td>30 min</td>
<td>80%</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>130 °C</td>
<td>none</td>
<td>2 h</td>
<td>91%</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>130 °C</td>
<td>DCE</td>
<td>2 h</td>
<td>79%</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>130 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>77%</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>100 °C</td>
<td>DCE</td>
<td>2 h</td>
<td>89%</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>100 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>96%</td>
</tr>
<tr>
<td>7$^c$</td>
<td>10</td>
<td>100 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>89%</td>
</tr>
<tr>
<td>8$^d$</td>
<td>10</td>
<td>100 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>80%</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>100 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>88%</td>
</tr>
<tr>
<td>10</td>
<td>none</td>
<td>100 °C</td>
<td>DCE</td>
<td>15 h</td>
<td>nd</td>
</tr>
</tbody>
</table>

$^a$1a (0.1 M); $^b$isolated yield of sulfonium salt 3aa; $^c$Cu(OAc)$_2$ was used; $^d$equimolar amounts of 1a and 2a were used.

With the optimal reaction conditions identified (Table 1, entry 6), we explored the reaction scope of iodonium(III) triflates 2 for diphenylsulfide 1a. As shown in Table 2, diverse aryl(mesityl)iodonium(III) triflates 2 were found to undergo the desired sulfonium salt formation. Mesityl(phenyl)iodonium(III) triflate 2b and triflate 2c bearing an electron-donating methoxy group, as well as triflates 2d-f bearing electron-withdrawing groups, all produced the expected sulfonium salts 3ab-3af with yields of 75-97%, though a higher reaction temperature (130 °C) was necessary for improving the yields in some cases. The reaction of sulfide 1a and mesityl(naphthyl)iodonium(III) triflates 2g also proceeded to afford the corresponding product 3ag with a yield of 89%. When triflates 2h and 2i containing heteroaromatics, such as furan and thiophene, were subjected to the reaction conditions, the desired heteroaryl sulfonium salts 3ah and 3ai were also obtained with a 92% and 65% yield, respectively. The aryl transfer reaction of triflate 2j bearing a sterically bulky 2,4,6-trimethoxyphenyl (TMP) group did not smoothly proceed at 100 °C, while the corresponding product 3aj was obtained with a moderate yield (40%) when the temperature was increased to 130 °C. Note that all the sulfonium products 3aa-
3aj were selectively obtained in good yields without the formation of potential byproducts, Mes-derived sulfonium salts.

**Table 2. Scope of aryl(mesityl)iodonium(III) salts 2**

<table>
<thead>
<tr>
<th>Ar</th>
<th>S+Ph</th>
<th>R¹</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= Me</td>
<td>3aa: 96%</td>
</tr>
<tr>
<td>Mes</td>
<td>Ph</td>
<td>R¹= H</td>
<td>3ab: 95%</td>
</tr>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= OMe</td>
<td>3ac: 75%</td>
</tr>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= F</td>
<td>3ad: 95%</td>
</tr>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= CO₂Me</td>
<td>3ae: 97%</td>
</tr>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= CN</td>
<td>3af: 80%</td>
</tr>
<tr>
<td>Ph</td>
<td>S=Ph</td>
<td>R¹= CN</td>
<td>3ag: 89%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3ah: 92%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3ai: 65%</td>
</tr>
<tr>
<td>3aj: 40%</td>
</tr>
</tbody>
</table>

*Reactions were performed at 130 °C*

As summarized in Table 3, the generality of the aryl-transfer protocol using mesityl(phenyl)iodonium(III) triflate 2b for various diarylsulfides 1b-1i was also investigated under the optimized reaction conditions. Irrespective of the presence of the electron-donating or electron-withdrawing groups on the aromatic rings, diarylsulfides 1b-1e were capable of forming sulfonium salts 3bb-3eb in good to excellent yields. However, it was necessary to increase the temperature for accelerating the reaction of electron-rich diarylsulfide 1c. Arylation of p-nitrophenyl(phenyl)sulfide 1f also proceeded to afford the resulting product 3fb with a 68% yield. As for sterically hindered and electron-rich diarylsulfides 1g-1i, the reactions did not proceed smoothly at 100 °C. The corresponding sulfonium salts 3hb and 3ib could be obtained at 130 °C with yields of 66% and 95%, respectively, but the reaction of diarylsulfide 2g, bearing a sterically bulky and electron-rich mesityl group did not proceed even at an elevated temperature. Compared to the iodonium(III) salt scope, the ortho-aromatic substituents in diarylsulfides had little influence on the reaction progress (see the formations of diphenyl(2,4,6-trimethoxyphenyl)sulfoxonium triflate 3aj in Table 2 and 3ib in Table 3).
Table 3. Scope of diarylsulfides 1 coupled with mesityl(phenyl)iodonium(III) triflate 2b

<table>
<thead>
<tr>
<th>Ar1SAr2</th>
<th>R1= R2= Br (3bb): 95%</th>
<th>R1= R2= OMe (3cb): quant.a</th>
<th>R1= R2= CF3 (3db): 76%</th>
<th>R1= R2= NO2 (3eb): 56%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b-i</td>
<td>3gb: tracea</td>
<td>3hb: 66%a</td>
<td>3ib: 95%a (3aj)</td>
<td></td>
</tr>
</tbody>
</table>

a Reactions were performed at 130 °C.

It seems that the steric effect of the iodonium(III) mesityl group is the origin of the selective aryl transfer in this sulfonium salt formation. This is evident from the slow transfer of o-tolyl group from (mesityl)iodonium(III) triflate 2k to diphenylsulfide 1a with only a 37% formation of the corresponding sulfonium salt 3ak, while mesityl group was not transferred under the reaction conditions (Scheme 3). Furthermore, the reaction of iodonium(III) triflate 2l bearing a sterically bulky o-isopropylphenyl group did not proceed, and the sulfonium salt 3al was not obtained at all. This is the limitation of scope of the developed protocol, where the iodonium(III) salts 2 bearing ortho-substituents prevent the aryl transfer reaction. On the other hand, reaction of (o-isopropylphenyl)(p-tolyl)iodonium(III) triflate with diphenylsulfide 1a by the same copper catalysis selectively afforded p-tolyl transfer product, diphenyl(p-tolyl)sulfonium triflate, in a nearly quantitative yield. Therefore, such sterically hindered ortho-substituted aryl group would serve as a dummy ligand in diaryliodoninium(III) salts during the present aryl transfer process to diarylsulfide compounds.
Scheme 3. ortho-Group steric effect.

We then examined the reaction of diphenylsulfide 1a using other specific iodonium(III) triflate 4 with a TMP group, which is used as a non-transferable dummy group in a range of metal-free and metal-catalyzed coupling reactions\textsuperscript{15-19} (Scheme 4). The reaction was completed within 30 min under the catalytic conditions. However, the TMP group did not work as a non-transferable aryl group and TMP-transferred sulfonium salt 3aj was obtained with a 95% yield. In the absence of the copper catalyst, TMP group was similarly transferred to afford the same sulfonium salt 3aj with a yield of 59%. Therefore, the TMP group is too electron-rich to be suitable for the present S-arylation of diarylsulfides 1, while the Mes group is a suitable auxiliary in iodonium(III) salts for the selective aryl transfer. As such, TMP-iodonium(III) salt 4 showed inherently different aryl transfer reactivity in the present case compared to other reported coupling reactions.\textsuperscript{19}

Scheme 4. TMP-group transfer from TMP-iodonium(III) salt 4.

Finally, a non-catalytic aryl transfer reactivity of mesityliodonium(III) salt was performed, as shown in Scheme 5. The reaction of diphenyl sulfide 1a and p-fluorophenyl(mesityl)iodonium(III) triflate 2d without the copper catalysis proceeded under the thermal conditions at 130 °C to form diphenyl(p-fluorophenyl)sulfonium triflate 3ad with a yield of 75%. Meanwhile, when the reaction was performed using 10 mol % of copper(II) acetate monohydrate at 130 °C, the same sulfonium salt 3ad was obtained with a yield of 87%. This result implied that the reaction would proceed faster and with a better yield in the presence of the copper catalyst. In contrast, selective aryl transfer occurred without the need of the copper catalyst, which was achieved by utilizing (mesityl)iodonium(III) triflate 2d. Accordingly, the Mes auxiliary of diaryliodonium(III) salts 2 is crucial...
for achieving the selective aryl transfer, and yielding single triarylsulfonium salts 3 in the present S-arylation of diarylsulfides 1.

\[ \text{Scheme 5. Non-catalytic selective aryl transfer from (mesityl)iodonium(III) salt 2d.} \]

**Conclusions**

We have developed a facile method for the preparation of a variety of triarylsulfonium triflates 3 by selective aryl-group transfer utilizing aryl(mesityl)iodonium(III) salts 2. It was revealed that the mesityl (Mes) group specifically contributes to the selective S-arylation of diarylsulfides 1 to form variety of the desired sulfonium triflates 3, and in which the ortho-steric effect of mesityliodonium(III) salts seems to prevent the formation of Mes-transferred byproducts.

**Experimental Section**

**General.** Diarylsulfides (1d, 1f, 1g, 1h, and 1i) \(^{23-26}\) and mesityliodonium(III) salts 2 \(^{14}\) were prepared according to the reported methods and our procedure. Other materials were used as received from commercial sources without further purification. Melting points (MPS) were measured using a Büchi B 545 apparatus and are uncorrected. Infrared (IR) spectra were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters (cm\(^{-1}\)) for strong and structurally important peaks. \(^1\)H and \(^{13}\)C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JMN-400 spectrometer operating at 400 MHz (\(^1\)H NMR) in CDCl\(_3\) and 100 MHz (\(^{13}\)C NMR) in DMSO-\(d_6\) at 25 °C. The chemical shifts in \(^1\)H and \(^{13}\)C NMR spectra were recorded relative to the residual solvent peaks (CDCl\(_3\): \(\delta\) 7.26, DMSO-\(d_6\): \(\delta\) 39.5). The date are reported as follows: chemical shift in ppm (\(\delta\)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were obtained using a Thermo Scientific Exactive Plus Orbitrap (Thermo Fisher Scientific, Inc., Waltham, MA, USA). Flash column chromatography and analytical thin layer chromatography (TLC) were carried out on Merck Silica gel 60 (230-400 mesh) and Merck Silica gel F\(_{254}\) plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254 nm).

**Procedure for sulfonium salt synthesis by aryl-group transfer using mesityliodonium(III) salt 2.** Diarylsulfide 1 (0.50 mmol), aryl(mesityl)iodonium(III) salt 2 (0.60 mmol, 1.2 equiv.) and Cu(OAc)\(_2\)-\(H_2O\) (9.9 mg, 0.05 mmol, 10 mol % relative to diarylsulfide 1) were dissolved in 1,2-dichloroethane (DCE, 5 mL) in a sealed tube. The reaction
mixture was stirred at the indicated temperature and time (see Table 1). It was then cooled to room temperature, and the resulting solution was purified by column chromatography on silica gel (dichloromethane/acetone) to give triarylsulfonium triflate 3. Sulfonium salts are generally light sensitive, and coloration of the compounds would occur during the column chromatography and evaporation.

**(4-Methylphenyl)diphenylsulfonium triflate (3aa).** Gray solid; mp 97-98 °C. IR: 3064, 2928, 1591, 1476 cm⁻¹. ¹H NMR: δ 2.46 (s, 3H, CH₃), 7.49 (d, J 8.3 Hz, 2H, ArH), 7.61 (d, J 8.8 Hz, 2H, ArH), 7.68-7.76 (m, 10H, ArH) ppm. ¹³C NMR: δ 21.0, 120.7 (q, J_CF 320.0 Hz, OTf), 121.4, 125.5, 131.1, 131.3, 131.4, 131.9, 134.2, 145.5 ppm.

**Triphenylsulfonium triflate (3ab).** Orange solid; mp 130-133°C. IR: 3064, 1582, 1476 cm⁻¹. ¹H NMR: δ 7.68-7.79 (m, 15H, ArH) ppm. ¹³C NMR: δ 120.7 (q, J_CF 320.0 Hz, OTf), 125.1, 131.2, 131.3, 134.3 ppm.

**(4-Methoxyphenyl)diphenylsulfonium triflate (3ac).** White solid; mp 84-85 °C. IR: 3095, 2845, 1588, 1496 cm⁻¹. ¹H NMR: δ 3.90 (s, 3H, CH₃), 7.20 (d, J 9.3 Hz, 2H, ArH), 7.68-7.76 (m, 12H, ArH) ppm. ¹³C NMR: δ 56.1, 114.0, 117.0, 120.7 (q, J_CF 321.0 Hz, OTf), 126.1, 130.7, 131.2, 133.9, 134.0, 163.9 ppm.

**(4-Fluorophenyl)diphenylsulfonium triflate (3ad).** Gray solid; mp 111-115 °C. IR: 3062, 1588, 1493 cm⁻¹. ¹H NMR: δ 7.37-7.41 (m, 2H, ArH), 7.67-7.78 (m, 10H, ArH), 7.84-7.87 (m, 2H, ArH) ppm. ¹³C NMR: δ 118.7 (d, J 23.1 Hz, Ar), 120.6 (d, J 3.3 Hz, Ar), 120.7 (q, J_CF 321.0 Hz, OTf), 125.3, 131.1, 131.3, 134.3, 134.6 (d, J 10.0 Hz, Ar), 165.3 (d, J 250.0 Hz, Ar) ppm. The same colored compound was obtained without the copper catalysis.

**(4-(Methoxycarbonyl)phenyl)diphenylsulfonium triflate (3ae).** White solid; mp 78 °C. IR: 3064, 2955, 1730, 1595, 1447 cm⁻¹. ¹H NMR: δ 3.97 (s, 3H, CH₃), 7.70-7.82 (m, 12H, ArH), 8.30 (d, J 8.8 Hz, 2H, ArH) ppm. ¹³C NMR: δ 52.9, 120.7 (q, J_CF 320.0 Hz, OTf), 124.8, 130.5, 131.4, 131.5, 131.7, 134.2, 164.9 ppm.

**(4-Cyanophenyl)diphenylsulfonium triflate (3af).** Yellow viscous liquid. IR: 3092, 2235, 1595, 1476 cm⁻¹. ¹H NMR: δ 7.72-7.84 (m, 10H, ArH), 7.90 (d, J 9.3 Hz, 2H, ArH), 7.95 (d, J 8.8 Hz, 2H, ArH) ppm. ¹³C NMR: δ 116.4, 117.3, 120.7 (q, J_CF 321.0 Hz, OTf), 124.6, 130.6, 131.2, 131.5, 131.8, 131.8, 134.7 ppm. HRMS (DART) calcld for C₁₉H₁₄NS⁺ [M - OTf]⁺ 288.0841, found 288.0842.

**2-Naphthalenylidiphenylsulfonium triflate (3ag).** Brown viscous liquid. IR: 3061, 1581, 1502, 1476 cm⁻¹. ¹H NMR: δ 7.56 (dd, J 8.8 Hz, 2.0 Hz, 1H, ArH), 7.63-7.77 (m, 12H, ArH), 7.94 (d, J 8.3 Hz, 1H, ArH), 8.02 (d, J 8.8 Hz, 1H, ArH), 8.12 (d, J 9.3 Hz, 1H, ArH), 8.51 (d, J 2.0 Hz, 1H, ArH) ppm. ¹³C NMR: δ 120.7 (q, J_CF 321.0 Hz, OTf), 121.9, 124.7, 125.4, 128.2, 128.5, 129.1, 130.3, 131.3, 131.4, 131.6, 132.5, 134.1, 134.3, 134.6 ppm.

**(2-Furyl)diphenylsulfonium triflate (3ah).** Gray solid; mp 68-70 °C. IR: 3093, 1589, 1497 cm⁻¹. ¹H NMR: δ 6.78-6.80 (m, 1H, ArH), 7.64-7.69 (m, 4H, ArH), 7.71-7.76 (m, 2H, ArH), 7.82-7.84 (m, 4H, ArH), 7.99-8.00 (m, 1H, ArH), 8.03-8.04 (m, 1H, ArH) ppm. ¹³C NMR: δ 114.0, 120.7 (q, J_CF 320.0 Hz, OTf), 126.0, 128.1, 129.3, 130.6, 131.3, 134.2, 154.0 ppm. HRMS (DART) calcld for C₁₆H₁₃OS⁺ [M - OTf]⁺ 253.0682, found 253.0681.

**Diphenyl(2-thiénylsulfonium triflate (3ai).** Black solid; mp 94-96 °C. IR: 3090, 1580, 1476 cm⁻¹. ¹H NMR: δ 7.37-7.40 (m, 1H, ArH), 7.66-7.70 (m, 4H, ArH), 7.73-7.79 (m, 6H, ArH), 8.04 (dd, J 5.4, 1.5 Hz, 1H, ArH), 8.27 (dd, J 3.9, 1.5 Hz, 1H, ArH) ppm. ¹³C NMR: δ 120.1, 120.7 (q, J_CF 321.0 Hz, OTf), 127.8, 129.9, 130.3, 131.3, 134.3, 140.0, 141.0 ppm.

**Diphenyl(2,4,6-trimethoxyphenyl)sulfonium triflate (3aj).** Black viscous liquid. IR: 3094, 2951, 1596, 1475 cm⁻¹. ¹H NMR: δ 3.81 (s, 6H, CH₃), 3.98 (s, 3H, CH₃), 6.35 (s, 2H, ArH), 7.55 (d, J 7.8 Hz, 4H, ArH), 7.64 (t, J 7.6 Hz, 4H, ArH), 7.70 (t, J 7.1 Hz, 2H, ArH) ppm. ¹³C NMR: δ 56.6, 57.1, 87.0, 93.4, 120.8 (q, J_CF 320.0 Hz, OTf), 125.0, 129.9, 130.9, 133.4, 162.3, 166.8 ppm. The same colored compound was obtained without the copper catalysis.

**Bis(4-bromophenyl)sulfonium triflate (3bb).** Orange solid; mp 108-110 °C. IR: 3087, 1566, 1473 cm⁻¹. ¹H NMR: δ 7.66 (d, J 8.8 Hz, 4H, ArH), 7.70-7.80 (m, 5H, ArH), 7.84 (d, J 8.8 Hz, 4H, ArH) ppm. ¹³C NMR: δ 120.7 (q, J_CF 321.0 Hz, OTf), 124.5, 124.8, 128.8, 131.4, 131.4, 133.2, 134.3, 134.5 ppm.
Bis(4-methoxyphenyl)phenylsulfonium triflate (3cb). Brown solid; mp 109-110 °C. IR: 3097, 2844, 1589, 1496 cm⁻¹. ¹H NMR: δ 3.90 (s, 6H, CH₃), 7.19 (d, J 9.3 Hz, 4H, ArH), 7.60-7.72 (m, 9H, ArH) ppm. ¹³C NMR: δ 56.1, 115.1, 116.9, 120.7 (q, J CF 321.0 Hz, OTf), 127.0, 130.2, 131.2, 133.4, 133.7, 163.8 ppm.

Bis(trifluoromethyl)phenylsulfonium triflate (3db). Red solid; mp 150-153 °C. IR: 3096, 1605, 1448 cm⁻¹. ¹H NMR: δ 7.76 (t, J 7.8 Hz, 2H, ArH), 7.82-7.85 (m, 3H, ArH), 7.96 (d, J 8.8 Hz, 4H, ArH), 7.99 (d, J 9.3 Hz, 4H, ArH) ppm. ¹³C NMR: δ 120.7 (q, J CF 321.0 Hz, OTf), 124.2, 128.1 (q, J 4.0 Hz, Ar), 130.3, 131.6, 132.2, 132.6, 133.9 (q, J 30.0 Hz, Ar), 134.9 ppm. HRMS (DART) calcd for C₂₁H₁₄F₉O₃S₂⁺ [M - OTf]⁺ 399.0637, found 399.0635.

Bis(nitrophenyl)phenylsulfonium triflate (3eb). Yellow solid; mp 110-114 °C. IR: 3108, 1606, 1531, 1476 cm⁻¹. ¹H NMR: δ 7.75-7.82 (m, 4H, ArH), 7.87 (t, J 7.1 Hz, 1H, ArH), 7.99 (d, J 9.3 Hz, 4H, ArH), 8.46 (d, J 9.3 Hz, 2H, ArH) ppm. ¹³C NMR: δ 120.7 (q, J CF 321.0 Hz, OTf), 124.2, 125.9, 131.6, 132.1, 132.3, 133.2, 135.1, 150.6 ppm. HRMS (DART) calcd for C₁₉H₁₄F₃N₂O₇S₂⁺ [M - OTf]⁺ 353.0591, found 353.0589.

Bis(2,4-dimethylphenyl)phenylsulfonium triflate (3hb). Red solid; mp 121-126 °C. IR: 3061, 2921, 1602, 1447 cm⁻¹. ¹H NMR: δ 2.42 (s, 6H, CH₃), 2.50 (s, 6H, CH₃), 6.89 (d, J 8.3 Hz, 2H, ArH), 7.27 (d, J 8.8 Hz, 2H, ArH), 7.33 (s, 2H, ArH), 7.64 (d, J 8.3 Hz, 2H, ArH), 7.73 (t, J 7.6 Hz, 2H, ArH), 7.79 (t, J 7.3 Hz, 1H, ArH) ppm. ¹³C NMR: δ 19.1, 21.0, 119.3, 120.8 (q, J CF 320.0 Hz, OTf), 122.4, 130.1, 130.3, 131.5, 131.9, 133.7, 134.8, 140.4, 145.6 ppm.

Diphenyl(o-tolyl)sulfonium triflate (3ak). Yellow solid; mp 95-96 °C. IR: 3064, 1606, 1534, 1476 cm⁻¹. ¹H NMR: δ 2.57 (s, 3H, CH₃), 7.07 (d, J 8.3, 1H, ArH), 7.46-7.52 (m, 2H, ArH), 7.63-7.81 (m, 11H, ArH) ppm. This compound was obtained as an inseparable mixture with mesityl(o-tolyl)iodonium(III) triflate 2k.

Acknowledgements

N.T. and T.D. acknowledge support from JSPS KAKENHI Grant Number 20K06980 (N.T.) and 19K05466 (T.D.), and the Ritsumeikan Global Innovation Research Organization (R-GIRO) project. R.K. is thankful to the J C Bose University of Science and Technology, YMCA, Faridabad (Seed Grant R&D/SG/2020-21/166) and HSCSIT, Science and Technology Department, Haryana (HSCSIT/R&D/2021/2935).

Supplementary Material

Supplementary data associated with this article is available in the Supplementary Material.

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