# High-Yielding One-Pot Synthesis of Diaryliodonium Triflates from Arenes and Iodine or Aryl Iodides

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# SUPPORTING INFORMATION

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# 1. General experimental conditions:

NMR spectra were recorded using DMSO- $d_6$ , CDCl<sub>3</sub> or MeOD- $d_4$  as solvent. DMSO- $d_6$  was the solvent of choice in most cases, as all salts were soluble. Chemical shifts are given in ppm relative to TMS for CDCl<sub>3</sub>, the residual peak of DMSO (<sup>1</sup>H NMR  $\delta$  2.50, <sup>13</sup>C NMR 39.52) or MeOD (<sup>1</sup>H NMR  $\delta$  3.31, <sup>13</sup>C NMR 49.00) as internal standard, with multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), integration and coupling constants (Hz). In the IR spectra, only the strongest/structurally most important peaks (n, cm<sup>-1</sup>) are listed. The reactions were carried out in sealed tubes to allow for reaction temperatures above the boiling point of CH<sub>2</sub>Cl<sub>2</sub>. Reactions with long reaction times (> 1 h) were protected from light using alumina foil. Dichloromethane was freshly distilled from CaH<sub>2</sub> and TfOH (≥99%) was stored under Ar atmosphere. The percentage of active oxidizing agent in *m*CPBA was determined by iodometric titration.<sup>1</sup> All other chemicals were used as received without further purification.

# 2. Synthesis of Diaryliodonium Salts 3:

#### 2.1 General Procedure for the Synthesis of Electron-Rich Salts:

$$\begin{array}{cccc} Ar^{1}-I &+ & Ar^{2}-H & \xrightarrow{\text{mCPBA},} & & & & \\ \textbf{1} & \textbf{2} & & & & \\ \end{array} \xrightarrow{} & Ar^{1} \xrightarrow{I^{+}} Ar^{2} & & \\ \textbf{3} & & & \\ \end{array}$$

*m*-Chloroperbenzoic acid (65% active oxidant, 66 mg, 0.25 mmol) and aryl iodide **1** (0.23 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in a sealed tube. The arene **2** (0.25 mmol) was added and the solution was cooled to the tabulated temperature followed by dropwise addition of TfOH (40  $\mu$ L, 0.45 mmol), resulting in a slight heat increase and change of color from a clear to a yellow transparent solution. The solution was stirred at the indicated temperature and time and concentrated *in vacuo* while still cold. Et<sub>2</sub>O (1-2 mL) was added and the mixture was stirred at rt for 10 min to precipitate out an off-white solid. The flask was stored in the freezer for 30 min, then the solid was filtered off, washed with cold Et<sub>2</sub>O and dried under vacuum to give diaryliodonium salt **3**.

Entry	Aryl Iodide	Arene	<b>T</b> (°C)	Time (min)	Product	Yield (%)
1	1a	2c	0	10	3c	85
2	1a	2d	-78	10 + 10	3d	87
3	1a	2e	-78	10 + 10	3e	82
4 <sup><i>a</i></sup>	1b	2a	0	45	3c	71
5	1b	2c	rt	10	3f	52
6	1c	2a	rt	10	3g	85
7	1c	2c	rt	10	3h	87
$8^a$	<b>1</b> e	2 <b>d</b>	0	15	3k	53

 Table S1: Reaction conditions for electron rich arenes.

<sup>*a*</sup> 3.0 equiv. of TfOH was used.

#### **2.2 General Procedure for Less Reactive Substrates:**

Ar<sup>1</sup>-I + Ar<sup>2</sup>-H 
$$\xrightarrow{\text{mCPBA},}$$
 Ar<sup>1</sup>-I<sup>+</sup>  $\xrightarrow{\text{OTf}}$   
1 2 Ar<sup>2</sup>

Performed as described in section 2.1 apart from that *m*CPBA, **1** and **2** were dissolved in  $CH_2Cl_2$  (1 mL), TfOH was added dropwise at rt and the mixture was heated to 80 °C for the time given in Table S2.

Entry	Aryl Iodide	Arene	Time	Product	Yield (%)	
$1^a$	1a	2a	10 min	<b>3</b> a	85	
2	1a	2b	2 h	<b>3</b> b	85	
3	1d	2a	14.5 h	<b>3i</b>	85	
4 <sup><i>a</i></sup>	1e	2a	2 h	3ј	60	

Table S2: Reaction conditions for less reactive aryl iodides/ arenes.

<sup>*a*</sup> 3.0 equiv. of TfOH was used.

#### 2.3 General procedure for direct synthesis of salts 3 from arenes and iodine:

4.4.11		mCPBA,	,ı <sup>+</sup> <sup>−</sup> OTf		
4 Ar-H	+ I <sub>2</sub>	TfOH CH <sub>2</sub> Cl <sub>2</sub>	Ar Ar		
2			3		

*m*-Chloroperbenzoic acid (65% active oxidant, 123 mg, 0.47 mmol) and iodine (30.0 mg, 0.12 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) in a sealed tube, which resulted in a dark purple solution that was cooled to 0 °C. Arene **2** (4.1-10 equiv, see Table S3) was added followed by dropwise addition of TfOH (41  $\mu$ L, 0.47 mmol), resulting in a slight heat increase and change of color to a yellow transparent solution. The solution was stirred at the indicated temperature and time (Table S3). Workup and purification was performed as described in section 2.1.

Entry	Arene	<b>T</b> (°C)	Time	Product	Yield (%)
	(equiv.)				
1	<b>2a</b> (4.1)	80	10 min	3a	78
2	<b>2a</b> (10)	rt	22 h	<b>3</b> a	81
3	<b>2c</b> (10)	rt	2 h	<b>3h</b> + <b>3f</b> (3:1)	52
4	<b>2c</b> (4.1)	0	1 h	3h	31
5	<b>2f</b> (10)	rt	21 h	31	57
6	<b>2g</b> (10)	rt	19 h	3m	24

**Table S3:** Reaction conditions for the reaction of arenes with iodine.

# 3. Analytical data of diaryliodonium salts 3:

# **Diphenyliodonium triflate (3a):**<sup>2 3</sup>



Synthesized according to section 2.2, but in 2 ml  $CH_2Cl_2$ , in 85% yield or according to section 2.3 in 81% yield. **3a** can also be synthesized according to Table 1; either at rt or at 40 °C in 89% yield. Analytical data were in agreement with previous reports.

# (4-Iodophenyl)(phenyl)iodonium triflate (3b):<sup>3</sup>



Synthesized according to section 2.2 in 85% yield as a white solid. Analytical data were in agreement with previous reports.

### (4-Methylphenyl)(phenyl)iodonium triflate (3c):<sup>4</sup>



Synthesized according to section 2.1 (Table 1, entry 1) in 85% yield and as an offwhite solid. Can also be obtained as described in Table 1, entry 4, using 3 equiv TfOH, in 71% yield. The <sup>13</sup>C NMR given in reference 4 is in accordance with our data, whereas the <sup>1</sup>H NMR differs. mp: 120-121 °C (lit<sup>4</sup>: 122-125 °C); IR (film): 3082, 3060, 2922, 1258, 1170, 1026 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.21 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 8.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H).

# (4-Methoxyphenyl)(phenyl)iodonium triflate (3d):<sup>4</sup>



Synthesized according to section 2.1, apart from that TfOH was added at rt and the reaction was stirred for 10 min at rt before cooling to -78 °C and slow addition of arene **2d** (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The reaction was then stirred at -78 °C for 10 min, delivering **3d** in 87% yield as an off-white solid. Analytical data were in agreement with previous reports.

### (2-Thienyl)(phenyl)iodonium triflate (3e):<sup>5</sup>



Synthesized according to section 2.1 apart from that TfOH was added at rt and the reaction was stirred for 10 min at rt before cooling to -78 °C and slow addition of arene **2e** (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The reaction was then stirred at -78 °C for 10 min, giving **3e** in 82% yield as a grey solid. Analytical data were in agreement with previous reports.

Bis(4-methylphenyl)iodonium triflate (3f):<sup>6</sup>



Synthesized according to section 2.1 in 52% yield as an off-white solid. The <sup>13</sup>C NMR given in reference 6 is in accordance with our data, whereas the <sup>1</sup>H NMR differs. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.08 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  142.5, 135.0, 132.3, 120.7 (q, *J* = 320 Hz, *C*F<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 113.0, 20.8; HRMS (ESI): calcd for C<sub>14</sub>H<sub>14</sub>I ([M – TfO<sup>-</sup>]<sup>+</sup>): 309.0135; found 309.0131.

#### (2-Methylphenyl)(phenyl)iodonium triflate (3g):<sup>7</sup>



Synthesized according to section 2.1 to give **3g** in 85% yield as an off-white solid. Analytical data have not been given in previous reports. <sup>1</sup>H NMR (400 MHz, DMSO $d_6$ ):  $\delta$  8.39 (d, J = 7.8 Hz, 1H), 8.20 (d, J = 7.7 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.57 (m, 2H),7.51 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 6.2 Hz, 1H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ): 140.6, 137.1, 135.0, 132.9, 132.0, 131.8, 131.4, 129.3, 121.4, 120.7 (q, J = 320 Hz,  $CF_3SO_3^-$ ), 115.9, 25.0; HRMS (ESI): calcd for  $C_{13}H_{12}I$  ([M – TfO<sup>-</sup>]<sup>+</sup>): 294.9978; found 294.9985.

#### 2-Methylphenyl(4-methylphenyl)iodonium triflate (3h):<sup>8</sup>



Synthesized according to section 2.1 in 87% yield as an off-white solid. Also synthesized as described in section 2.3 as a regioisomeric mixture with **3f** (ratio **3h**:**3f** 3:1) in 52% combined yield or as the single regioisomer in 31% yield. Analytical data were in agreement with previous reports. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.36 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.57 (m, 2H), 7.32 (m, 3H) 2.60 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  142.5, 140.5, 137.0, 135.0, 132.8, 132.4, 131.4, 129.3, 121.5, 120.7 (q, *J* = 321 Hz, *C*F<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 112.2, 25.0, 20.8; HRMS (ESI): calcd for C<sub>14</sub>H<sub>14</sub>I ([M – TfO<sup>-</sup>]<sup>+</sup>): 309.0135; found 309.0140.

#### (4-Nitrophenyl)(phenyl)iodonium triflate (3i):<sup>3</sup>



Synthesized according to section 2.2 in 85% yield as a white solid. Analytical data were in agreement with previous reports.

(6-Chloro-pyridin-3-yl)(phenyl)iodonium triflate (3j):<sup>9</sup>



Synthesized according to section 2.2, apart from that 3 equiv TfOH was used, delivering **3j** in 60% yield as a white solid. Analytical data have not been given in previous reports. m.p.: 153-155 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.17 (d, *J* = 2.3 Hz, 1H), 8.70 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.28 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  154.3, 153.4, 145.5, 135.2, 132.4, 132.0, 127.6, 120.7 (q, *J* = 322 Hz, *C*F<sub>3</sub>SO<sub>3</sub><sup>¬</sup>), 116.9, 114.2; IR (film): 3084, 3055, 1554, 1445, 1260, 1172, 1027 cm<sup>-1</sup>; HRMS (ESI): calcd for C<sub>11</sub>H<sub>8</sub>CIIN ([M – TfO<sup>-</sup>]<sup>+</sup>): 315.9384; found 315.9393.

#### (6-chloro-pyridin-3-yl)(4-methoxyphenyl)iodonium triflate (3k):



Synthesized according to section 2.1, apart from that TfOH (3 equiv) was added at rt and the reaction was stirred for 10 min at rt before cooling to -78 °C and slow addition of arene **2d** (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The reaction was then stirred at -78 °C for 10 min, delivering **3k** in 53% yield as a slightly grey solid. m.p.: 101-103 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.12 (d, *J* = 2.1 Hz, 1H), 8.64 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.20 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 2H) 3.80 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  162.2, 154.0, 153.2, 145.3, 137.3, 127.5, 120.7 (q, *J* = 321 Hz, *C*F<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 117.7, 114.6, 105.7, 55.8; IR (film): 3090, 3047, 1572, 1443, 1258, 1172, 1026 cm<sup>-1</sup>; HRMS (ESI): calcd for C<sub>12</sub>H<sub>10</sub>ClINO ([M – TfO<sup>-</sup>]<sup>+</sup>): 345.9490; found 345.9501.

#### **Bis(4-chlorophenyl)iodonium triflate (3l):**



Synthesized according to section 2.3 in 57% yield as a single regioisomer. m.p.: 181-183 °C; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.26 (d, J = 8.6 Hz, 4H), 7.63 (d, J = 8.6 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  139.8, 136.8, 132.5, 120.0 (q, J = 318 Hz,  $CF_3SO_3^-$ ), 111.2; IR (film): 3086, 1260, 1172, 1026 cm<sup>-1</sup>; HRMS (ESI): calcd for C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>I ([M – TfO<sup>-</sup>]<sup>+</sup>): 348.9042; found 348.9041.

#### **Bis**(2,4-dimethyl-5-nitrophenyl)iodonium triflate (3m):



Synthesized according to section 2.3 in 24% yield as a single regioisomer. m.p.: 200-202 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.10 (s, 2H), 7.70 (s, 2H), 2.65 (s, 6H), 2.53 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  147.5, 146.4, 137.9, 135.1, 132.9, 120.7 (q, *J* = 320 Hz, *C*F<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 117.4, 24.7, 19.6; IR (film): 3095, 1523, 1342, 1261, 1173, 1024 cm<sup>-1</sup>; HRMS (ESI): calcd for C<sub>16</sub>H<sub>16</sub>IN<sub>2</sub>O<sub>4</sub> ([M – TfO<sup>-</sup>]<sup>+</sup>): 427.0149; found 427.0145.

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# 4. NMR spectra of diaryliodonium salts 3:

<sup>1</sup>H NMR-spectra for compounds **3a-m** and <sup>13</sup>C NMR-spectra for compounds **3g,h,j-m** follow on the coming pages.







































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