Flow synthesis of diaryliodonium triflates

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Flow Synthesis of Diaryliodonium Triflates

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Supporting Information

ABSTRACT: A safe and scalable synthesis of diaryliodonium triflates was achieved using a practical continuous-flow design. A wide array of electron-rich to electron-deficient arenes could readily be transformed to their respective diaryliodonium salts on a gram scale, with residence times varying from 2 to 60 s (44 examples).

INTRODUCTION

In recent years, the applications of aryl electrophile sources, such as hypervalent iodinated compounds, have become increasingly important in synthetic organic chemistry. In particular, diaryl-I-iodanes, also known as diaryliodonium salts, have been extensively used in numerous arylation procedures. Such diaryliodonium salts can be considered as both strong electrophiles and powerful oxidants, which allows chemists to reach higher oxidation states with Pd or Cu complexes and to carry out the targeted transformations at milder reaction conditions. Furthermore, diaryliodonium salts can be used as an electrophilic aryl source to couple with a wide variety of nucleophiles, allowing the preparation of sulfides, ethers, amines, esters, and nitro compounds as well as the α-arylation on enolates.

Given the apparent importance of diaryliodonium salts, many syntheses have been developed to prepare these compounds. The most practical reaction conditions involve the reaction of iodoarenes with a suitable oxidant to give I+III followed by a ligand exchange with an arene. An improved one-pot version was developed by Olofsson et al. using meta-chloroperbenzoic acid (m-CPBA) as the oxidant and trifluoromethanesulfonic acid (TfOH) to yield diaryliodonium triflates directly. However, such oxidative reaction conditions are typically very exothermic and thus represent a substantial safety risk when carried out on a large scale. Herein, we present a flow synthesis of diaryliodonium triflates which is fast and scalable and provides a broad substrate scope.

RESULTS AND DISCUSSION

To quantify the thermodynamic data of highly exothermic reactions, reaction calorimetry is typically used. In order to rapidly determine the unknown reaction enthalpy (ΔHₚ) of the diaryliodonium salt synthesis, we developed an operationally simple adiabatic continuous-flow device that allowed us to calculate ΔHₚ values via in-line ΔT measurements (see Scheme 1c). Here, a custom-made glass tube was designed, and the cross-micromixer and microreactor were placed inside. High vacuum was applied to the system in order to create adiabatic conditions (for more details about the setup, see the Supporting Information). Assuming full conversion, we calculated the reaction enthalpy using the following equation,

ΔHₚ = m × Cp × ΔT, where m and Cp are the mass and the heat capacity of the solvent, respectively (Cp values of substrates were neglected, which is fair given the dilution). A thermocouple was connected to the T-mixer at the end of the microreactor, which allowed us to have in-line temperature measurements. The calibration of the adiabatic system was performed using the well-known neutralization reaction of sodium hydroxide with hydrochloric acid. Next, we carried out the synthesis of diphenyliodonium triflate and diphenyliodonium triflate in the adiabatic microfluidic device, and ΔT values were measured (reactions were performed three times each). With the Cp value of DCE known (Cp = 129.4 J mol⁻¹K⁻¹), we were able to directly calculate the respective enthalpy values. Interestingly, very high ΔHₚ values between −160 and −180 kJ/mol were observed, highlighting the need for a safe and reliable method to scale the reaction conditions (Scheme 1).

Such exothermic transformations can be carried out safely in continuous-flow microreactors as the micro-environment results in an excellent heat dissipation rate.

We commenced our investigations by designing a suitable continuous-flow setup (Figure 1). Our design consists of three individual feeds that allow separation of the hazardous reagents and control of the reaction stoichiometry by adjusting the individual flow rates. The different reagent streams were merged in a cross-micromixer and subsequently introduced in a perfluoroalkoxy capillary reactor (PFA, 750 μm i.d., 0.1−3.0 mL). To avoid microreactor clogging, the mixer and reactor were placed inside. High vacuum was applied to the system in order to create adiabatic conditions (for more details about the setup, see the Supporting Information). Assuming full conversion, we calculated the reaction enthalpy using the following equation,
were submerged in an ultrasonic bath. The reaction between 4-iodotoluene (1a) and toluene (2a) in the presence of m-CPBA and TfOH was selected as the benchmark for our reaction optimization studies (see the Supporting Information). Optimal reaction conditions were obtained with 1.1 equiv of 2a and m-CPBA, and 2 equiv of TfOH and dichloroethane (DCE) as the solvent in a 100 μL microreactor. The reaction was remarkably fast and was completed within 2 s residence time. Notably, the desired di-p-tolyliodonium triflate (3a) could be obtained on a gram scale (2.04 g, 89%) in excellent yield as pure and simple to handle crystals (Figure 2). Analogous batch experiments resulted in a lower yield (69% yield) of 3a as an inferior-quality powder precipitate.

Notably, the desired di-p-tolyliodonium triflate 3a could be obtained on a gram scale (2.04 g, 89%) in excellent yield as pure and simple to handle crystals (Figure 2). Analogous batch experiments resulted in a lower yield (69% yield) of 3a as an inferior-quality powder precipitate.

With the optimized conditions in hand, we sought to demonstrate the generality of our flow protocol (Table 1). Within a 2 s residence time, a diverse set of both symmetrical and unsymmetrical diaryliodonium triflates was synthesized in fair to excellent yield on a gram scale (5–10 mmol scale).

**Table 1. Scope of Diaryliodonium Triflates Using Electron-Neutral and Electron-Rich Aryl Iodides**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl Iodide</th>
<th>Ararene</th>
<th>Feed 1</th>
<th>Feed 2</th>
<th>Feed 3</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-iodotoluene (1a)</td>
<td>Toluene (2a)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3a</td>
<td>90%</td>
</tr>
<tr>
<td>2</td>
<td>3,4-dimethoxytoluene (1b)</td>
<td>Toluene (2a)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3b</td>
<td>87%</td>
</tr>
<tr>
<td>3</td>
<td>3-methyl-4-iodotoluene (1c)</td>
<td>Toluene (2a)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3c</td>
<td>59%</td>
</tr>
<tr>
<td>4</td>
<td>2-iodoanisole (1d)</td>
<td>Toluene (2a)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3d</td>
<td>79%</td>
</tr>
<tr>
<td>5</td>
<td>2-iodoanisole (1d)</td>
<td>Naphthalene (2b)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3e</td>
<td>43%</td>
</tr>
<tr>
<td>6</td>
<td>2-iodoanisole (1d)</td>
<td>Mesitylene (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3f</td>
<td>79%</td>
</tr>
<tr>
<td>7</td>
<td>2-iodoanisole (1d)</td>
<td>4-methoxybiphenyl (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3g</td>
<td>89%</td>
</tr>
<tr>
<td>8</td>
<td>2-iodoanisole (1d)</td>
<td>3,5-dimethoxybiphenyl (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3h</td>
<td>28%</td>
</tr>
<tr>
<td>9</td>
<td>2-iodoanisole (1d)</td>
<td>4-nitroacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3i</td>
<td>79%</td>
</tr>
<tr>
<td>10</td>
<td>2-iodoanisole (1d)</td>
<td>4-iodoacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3j</td>
<td>79%</td>
</tr>
<tr>
<td>11</td>
<td>2-iodoanisole (1d)</td>
<td>2-iodoacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3k</td>
<td>61%</td>
</tr>
<tr>
<td>12</td>
<td>2-iodoanisole (1d)</td>
<td>2,4-dimethoxyacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3l</td>
<td>89%</td>
</tr>
<tr>
<td>13</td>
<td>2-iodoanisole (1d)</td>
<td>2,4-dichloroacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3m</td>
<td>37%</td>
</tr>
<tr>
<td>14</td>
<td>2-iodoanisole (1d)</td>
<td>2,4-dinitroacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3n</td>
<td>89%</td>
</tr>
<tr>
<td>15</td>
<td>2-iodoanisole (1d)</td>
<td>2,4-dimethoxyacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3o</td>
<td>72%</td>
</tr>
<tr>
<td>16</td>
<td>2-iodoanisole (1d)</td>
<td>2,4-dichloroacetophenone (2c)</td>
<td>5.0 mmol</td>
<td>5.5 mmol</td>
<td>10 mmol</td>
<td>3p</td>
<td>49%</td>
</tr>
</tbody>
</table>

**Scheme 1. (A) Advantages and Disadvantages of Diaryliodonium Salts, (B) Enthalpy Measurement of the Diaryliodonium Salt Synthesis in an Adiabatic Microreactor, and (C) Flow Setup Used for the Enthalpy Measurements**
donating substituents (e.g., anisoles) or electron-rich hetero-
aromatic iodides (e.g., thiophene) were incompatible with the
reaction conditions. However, these diaryliodonium tri
flates could be accessed when using the mesityl iodide with the
corresponding (hetero)arenes, albeit in a lower yield (3q and
3r).

Aryl iodides with electron-withdrawing functional groups
proved particularly challenging. However, after a minor
reoptimization of the reaction conditions (see the Supporting
Information), it was found that these compounds could be
obtained in good yields by increasing the reactor volume to 3
mL and using an excess of m-CPBA (1.3 equiv) and TIOH (3.0
equiv). Aryl iodides bearing ortho, meta, and para electron-
withdrawing substituents (e.g., halogens, nitro, esters, ketones)
were all well-tolerated, yielding the targeted diaryliodonium
triﬂates in synthetically useful yields (32–90% yield) (Table 2).

Also, 3-iodopyridine (3x and 3ai) and 1-iodoanthraquinone
(3s) could be subjected to the ﬂow conditions, resulting in the
desired compounds in fair yields (19–47% yield).

Finally, with the aim of developing a fl ow protocol utilizing
cheap and easily available starting materials, we chose to oxidize
simple arenes using molecular iodine to yield the corresponding
symmetrical diaryliodonium triﬂates. Optimal results were
obtained using iodine as the limiting reagent along with 3
equiv of m-CPBA, 4.1–10 equiv of arene, and 5 equiv of TIOH
(see the Supporting Information). Moderate to excellent yields
were obtained for the synthesis of symmetrical diaryliodonium
salts (38–90%) (Table 3). In most cases, the para–para–
para isomer was isolated. Notably, the selectivity at 0 °C: ortho–para >96%.

In summary, we have developed a fast, scalable, and safe
continuous-ﬂow protocol to prepare various symmetrical and
unsymmetrical diaryliodonium triﬂates. Our protocol displayed
a broad substrate scope of electron-rich to electron-deﬁcient
substrates (44 examples, yields up to 90%). Notably, the
reaction could be completed in a matter of seconds, allowing
the preparation of diaryliodonium triﬂates on a gram scale
with excellent purity in a time-eﬃcient process. We believe that
the developed ﬂow protocol will ﬁnd widespread use in both
academia and industry given the synthetic relevance of
diaryliodonium salts.

Table 2. Scope of Diaryliodonium Triﬂates with Electron-
Deﬁcient Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a(45%)</td>
<td></td>
</tr>
<tr>
<td>3b(62%)</td>
<td></td>
</tr>
<tr>
<td>3c(81%)</td>
<td></td>
</tr>
<tr>
<td>3d(54%)</td>
<td></td>
</tr>
<tr>
<td>3e(74%)</td>
<td></td>
</tr>
<tr>
<td>3f(85%)</td>
<td></td>
</tr>
<tr>
<td>3g(28%)</td>
<td></td>
</tr>
<tr>
<td>3h(38%)</td>
<td></td>
</tr>
<tr>
<td>3i(79%)</td>
<td></td>
</tr>
<tr>
<td>3j(91%)</td>
<td></td>
</tr>
<tr>
<td>3k(30%)</td>
<td></td>
</tr>
<tr>
<td>3l(68%)</td>
<td></td>
</tr>
<tr>
<td>3m(69%)</td>
<td></td>
</tr>
<tr>
<td>3n(88%)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Scope of Symmetric Diaryliodonium Triﬂates
Derived from Arenes and Molecular Iodine

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a(70%)</td>
<td></td>
</tr>
<tr>
<td>3b(76%)</td>
<td></td>
</tr>
<tr>
<td>3c(68%)</td>
<td></td>
</tr>
<tr>
<td>3d(40%)</td>
<td></td>
</tr>
<tr>
<td>3e(49%)</td>
<td></td>
</tr>
<tr>
<td>3f(37%)</td>
<td></td>
</tr>
<tr>
<td>3g(45%)</td>
<td></td>
</tr>
<tr>
<td>3h(20%)</td>
<td></td>
</tr>
<tr>
<td>3i(22%)</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions. Feed 1: 2.0 mmol of 4, 10 equiv of 2 in 10 mL
of DCE. Feed 2: 6.0 mmol of m-CPBA in 10 mL of DCE. Feed 3: 10
mmol of TIOH in 10 mL of DCE. Syringe pumps were used to add
reagents to the reactor. Throughput distribution, feed 1/ feed 2/ feed 3
was 1:1:2. All reactions were performed at room temperature.

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with excellent purity in a time-eﬃcient manner. We believe that
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academia and industry given the synthetic relevance of
diaryliodonium salts.

■ EXPERIMENTAL SECTION

All reagents and solvents were used as received without further
purification. All capillary tubing and microﬂuidic ﬁttings were
purchased from IDEX Health & Science. Used syringes were from
BD Discardit II or NORM-JECT. Syringe pumps were purchased from
Chemix Inc. model Fusion 200 Touch. Used ultrasonicator was VWR
USC300T. 1H (400 MHz), 13C (100 MHz), and 19F (376 MHz)
nMR spectra were recorded at ambient temperature using a Bruker
Avance 400 or Mercury 400 spectrometer. 1H NMR spectra are
obtained using iodine as the limiting reagent along with 3
equiv of m-CPBA, 4.1–10 equiv of arene, and 5 equiv of TIOH
(see the Supporting Information). Moderate to excellent yields
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salts (38–90%) (Table 3). In most cases, the para–para–
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academia and industry given the synthetic relevance of
diaryliodonium salts.
reported in parts per million (ppm) downfield relative to CDCl₃ (7.26 ppm) and DMSO-d₆ (2.50 ppm); all ¹³C NMR spectra are reported in ppm relative to CDCl₃ (77.2 ppm) and DMSO-d₆ (39.52 ppm). HRMS (ESI/APCI multimode ionization source, TOF-MSD analyzer) was measured with direct infusion in a 50:50 flow of 5 mM NH₄OAc in water/MEOH. NMR data were processed using the MestReNova 9.0.1 software package. Known products were characterized by comparison to the corresponding H NMR and ¹³C NMR from literature. Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and are uncorrected. The names of all products were generated using the PerkinElmer ChemBioDraw Ultra v.12.0.2 software package.

### General Procedure for the Diaryliodonium Salt Synthesis with Electron-Neutral and Electron-Rich Substrates (GP1)

A 25 mL oven-dried volumetric flask was charged with 4-iodonitrobenzene (1a, 1.09 g, 5.0 mmol) and toluene (2a, 506 mg, 5.5 mmol). Next, a second 25 mL oven-dried volumetric flask was charged with meta-chloroperoxybenzoic acid (≤77%) (1.5 g, 6 mmol). Both the flasks were filled carefully with a septum and were degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 50.0 mL solution. The solution was charged in a 60 mL NORM-JECT syringe and was charged with dichloroethane was added via syringe to make a 10 mL solution in both flasks. Both the solutions were charged in 10 mL NORM-JECT syringes and were charged to a single syringe pump. Afterwards, a 25 mL oven-dried volumetric flask was filled with a septum and was degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 50.0 mL solution. Both the syringes were fitted with a septum and were degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 25.0 mL solution in both flasks. Both the solutions were charged in 30 mL NORM-JECT syringes and were fitted to a single syringe pump. Afterwards, a 50 mL oven-dried volumetric flask fitted with a septum was fitted with a septum and was degassed by alternating vacuum and argon backfill and charged with 20 mL of dichloroethane. Trifuoromethanesulfonic acid (0.9 mL, 10.0 mmol) was added carefully with a syringe, and the residue was dissolved in diethyl ether and evaporated again at an argon-protected residence time. The outlet of the reactor was fitted to an argon-filled round-bottom flask with septum via a needle connection. An argon-filled balloon was attached in order to ensure a constant pressure. The reaction mixture was evaporated under reduced pressure at the rotavap. Residue was dissolved in diethyl ether and evaporated again at the rotavap. This procedure was repeated three times, and then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until a cloudy solution was obtained. Next, the reacting mixture was kept in the freezer (−26 °C) overnight. Formed crystals were filtered off and washed with a minimum of diethyl ether.

### General Procedure for the Diaryliodonium Salt Synthesis with Electron-Deficient Substrates (GP2)

A 25 mL oven-dried volumetric flask was charged with 4-iodonitrobenzene (1b, 1.25 g, 5.0 mmol) and mesitylene (2b, 0.76 mL, 5.5 mmol). Next, a second 25 mL oven-dried volumetric flask was charged with meta-chloroperoxybenzoic acid (≤77%) (1.5 g, 6.5 mmol). Both the flasks were filled with a septum and were degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 25.0 mL solution in both flasks. Both the solutions were charged in 30 mL NORM-JECT syringes and were fitted to a single syringe pump. Afterwards, a 50 mL oven-dried volumetric flask fitted with a septum was fitted with a septum and was degassed by alternating vacuum and argon backfill and charged with 40 mL of dichloroethane. Trifuoromethanesulfonic acid (1.3 mL, 15 mmol) was added carefully with a syringe, and the residue was dissolved in diethyl ether and evaporated again at an argon-protected residence time. The outlet of the reactor was fitted to an argon-filled round-bottom flask with septum via a needle connection. An argon-filled balloon was attached in order to ensure a constant pressure. The reaction mixture was evaporated under reduced pressure at the rotavap. Residue was dissolved in diethyl ether and evaporated again at the rotavap. This procedure was repeated three times, and then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until a cloudy solution was obtained. Next, the resulting mixture was kept in the freezer (−26 °C) overnight. Formed crystals were filtered off and washed with a minimum of diethyl ether.

### General Procedure for the Diaryliodonium Salt Synthesis with Iodine (GP3)

A 10 mL oven-dried volumetric flask was charged with iodine (4, 507 mg, 2 mmol) and the arene (2, 8.2–20 mmol). Next, a second 10 mL oven-dried volumetric flask was charged with meta-chloroperoxybenzoic acid (≤77%) (1.5 g, 6 mmol). Both the flasks were fitted with a septum and were degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 10 mL solution in both flasks. Both the solutions were charged in 10 mL NORM-JECT syringes and were fitted to a single syringe pump. Afterwards, a 25 mL oven-dried volumetric flask was filled with a septum and was degassed by alternating vacuum and argon backfill. Dichloroethane was added via syringe to make a 20.0 mL solution. The solution was charged in a 20 mL NORM-JECT syringe and fitted to a second syringe pump. All syringes were connected to a PEEK cross-mixer (500 μm i.d.) and subsequently connected to the inlet of the 3 mL PFA capillary tubing (750 μm i.d.). The cross-mixer and microreactor were submerged in a sonication bath, and sonication was applied during operation. The first syringe pump (containing two syringes) was operated at 2 × 0.75 mL/min, and the second syringe pump was operated at 1.5 mL/min (total 3 mL/min flow rate, 60 s residence time). The outlet of the reactor was fitted to an argon-filled round-bottom flask with septum via a needle connection. An argon-filled balloon was attached in order to ensure a constant pressure. The reaction mixture was evaporated under reduced pressure at the rotavap. Residue was dissolved in diethyl ether and evaporated again at the rotavap. This procedure was repeated five times, and then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until a cloudy solution was obtained. Next, the resulting mixture was kept in the freezer (−26 °C) overnight. Formed crystals were filtered off and washed with a minimum of diethyl ether.

### Di-p-tolyldiiodonium Trifuoromethanesulfonate (3a)

GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as gray solids (2.04 g, 89%): mp 131–133 °C (lit. 121–123 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 8.15–8.05 (m, 4H), 7.31 (d, J = 8.1 Hz, 4H), 2.32 (s, 6H); ¹³C{¹H} NMR (101 MHz, DMSO-d₆) δ 142.5, 135.8, 132.3, 120.8 (q, J = 322.3 Hz), 113.1, 27.8, 20.8.

### Diphenyldiiodonium Trifuoromethanesulfonate (3b)

GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as off-white solids (1.89 g, 88%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether afforded the product as off-white solids (1.55 g, 90%): mp 169–173 °C (lit. 172–174 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 8.27 (d, J = 8.0 Hz, 4H), 7.64 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.7 Hz, 4H); ¹³C{¹H} NMR (101 MHz, DMSO-d₆) δ 135.2, 132.1, 131.8, 120.8 (q, J = 322.3 Hz), 116.5.

### Bis(4-fluorophenyl)diiodonium Trifuoromethanesulfonate (3c)

GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as gray solids (1.35 g, 58%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether afforded the product as off-white solids (1.34 g, 72%): mp 168–170 °C (lit. 168–170 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 8.39–8.22 (m, 4H), 7.42 (t, J = 8.9 Hz, 4H); ¹³C{¹H} NMR (101 MHz, DMSO-d₆) δ 164.4 (d, J = 251.5 Hz), 138.4 (d, J = 9.1 Hz), 122.7 (q, J = 322.6 Hz), 119.8, 119.6, 111.6 (d, J = 3.0 Hz); ¹F NMR (376 MHz, DMSO-d₆) δ −77.75, −106.60 (t, J = 9.0, 5.0 Hz).

### (4-Iodophenyl)(phenyl)iodonium Trifuoromethanesulfonate (3d)

GP1 was used on a 5 mmol scale. Purification by 300
recrystallization in diethyl ether afforded the product as off-white solids (2.09 g, 75%): mp 144–148 °C (lit.19 146–148 °C); \( ^1\)H NMR (400 MHz, DMSO-\( d_6\)) \( \delta \) 8.24 (\( d, J = 6.0, 12.0 \) Hz), 9.00 (\( d, J = 8.5, 18.0 \) Hz), 7.90 (\( d, J = 8.5, 1.2 \) Hz), 7.68 (2H), 7.68 (4H, t, \( J = 7.4, 10.0 \) Hz), 7.54 (t, \( J = 7.8 \) Hz, 2H); \( ^1\)Cl(\( H \)) NMR (101 MHz, DMSO-\( d_6\)) \( \delta \) 139.0, 136.7, 135.16, 132.14, 131.80, 120.67 (\( q, J = 322.4 \) Hz), 116.67, 115.83, 100.28.

**Phenyl(2-fluorophenyl-2-yliodionium Trifluoromethanesulfonate (3f, 21)** GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as light brown solids (937 mg, 43%): mp 143–146 °C (lit.21 144–146 °C); \( ^1\)H NMR (400 MHz, DMSO-\( d_6\)) \( \delta \) 8.29–8.21 (\( d, J = 3.8, 13.8 \) Hz, 1H), 7.97 (\( d, J = 5.3, 1.3 \) Hz, 1H), 7.71–7.63 (2H), 7.58–7.47 (3m, 2H), 7.18 (2H, \( s, J = 7.8, 2.0 \) Hz, 1H), 7.14 (2H, \( s, J = 7.8, 1.7 \) Hz), 2.29 (2\( H, s \)); \( ^{13}\)C{\(^1\)H} NMR (100 MHz, DMSO-\( d_6\)) \( \delta \) 140.9, 137.8, 135.1, 132.6, 132.2, 130.1, 121.2 (\( q, J = 322.2 \) Hz), 119.8, 101.2.

**Mesityl(phenyl)iodonium Trifluoromethanesulfonate (3g, 21)** GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as light yellow solids (2.07 g, 85%): mp 181–183 °C (lit.21 137–138 °C); \( ^1\)H NMR (400 MHz, DMSO-\( d_6\)) \( \delta \) 8.06–8.08 (\( d, J = 3.9, 18.0 \) Hz, 2H), 7.69–7.60 (\( 2\ H, m \)), 7.51 (t, \( J = 7.8, 2.0 \) Hz, 2H), 7.22 (2H, \( s, J = 6.0 \) Hz, 2H); \( ^1\)F NMR (376 MHz, CDCl3) \( \delta \) 203.2; HRMS (ESI) calcd for C13H14I3S [M+OTf]^+ 380.0506, found 380.0514.

**Phenyl(4-methoxyphenyl)iodonium Trifluoromethanesulfonate (3h, 21)** GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as white solids (2.07 g, 88%): mp 183–184 °C; \( ^1\)H NMR (400 MHz, DMSO-\( d_6\)) \( \delta \) 8.78 (\( d, J = 8.0, 2.0 \) Hz, 2H), 7.31 (\( d, J = 8.1, 2.0 \)Hz, 2H), 7.21 (2H, \( s, J = 6.0 \) Hz, 2H), 2.33 (2\( H, s \)); \( ^1\)F NMR (376 MHz, CDCl3) \( \delta \) 203.2; 19F NMR (376 MHz, CDCl3) \( \delta \) –78.35, –95.37 to –96.24 (m, 8).
Bis(4-chlorophenyl)iodonium Trifluoromethanesulfonate (3t).\(^{2c}\)

GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as light yellow solids (1.57 g, 63%).

<table>
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<th>Compound</th>
<th>Formula</th>
<th>mp (°C)</th>
<th>IR (cm(^{-1}))</th>
<th>(^{1}H) NMR (400 MHz, CDCl(_3))</th>
<th>(^{19}F) NMR (376 MHz, CDCl(_3))</th>
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<td>(3t)</td>
<td>C(<em>{16})H(</em>{15})F(_3)I</td>
<td>123.4</td>
<td>133.1, 132.2, 131.4, 131.3, 131.2, 131.1, 129.6, 120.7 (q, (J = 322.4) Hz)</td>
<td>116.9, 115.9, 115.1, 115.4</td>
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Meso-3-(p-tolyliodonio)pyridin-1-ium Bis(trifluoromethanesulfonate) (3x).\(^{2c}\)

GP3 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as white solids (1.23 g, 81%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>mp (°C)</th>
<th>IR (cm(^{-1}))</th>
<th>(^{1}H) NMR (400 MHz, CDCl(_3))</th>
<th>(^{19}F) NMR (376 MHz, CDCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3x)</td>
<td>C(<em>{16})H(</em>{15})F(_3)I</td>
<td>123.4</td>
<td>133.1, 132.2, 131.4, 131.3, 131.2, 131.1, 129.6, 120.7 (q, (J = 322.4) Hz)</td>
<td>116.9, 115.9, 115.1, 115.4</td>
<td></td>
</tr>
</tbody>
</table>

(4-Nitrophenyl)(phenyl)iodonium Trifluoromethanesulfonate (3w).\(^{2c}\)

GP4 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as light yellow solids (1.76 g, 74%): mp 174–183 °C (lit.\(^{26}\) 178–185 °C); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (dd, \(J = 2.2, 1.1\) Hz), 7.27 (tt, \(J = 8.2, 1.1\) Hz), 7.16 (td, \(J = 8.2, 1.1\) Hz), 7.03 (t, \(J = 8.2, 1.1\) Hz), 6.89 (m, 4H), 3.93 (s, 3H), 13(C\(_{6}\)) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 134.3, 134.2, 133.5, 133.4, 133.2, 129.6, 120.7 (q, \(J = 322.4\) Hz), 116.2, 113.0, 20.9.

Mesityl(3-trifluoromethyl)methyl)iodonium Trifluoromethanesulfonate (3y).\(^{2c}\)

GP5 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as brown solids (1.9 g, 66%): mp 159–167 °C (lit.\(^{21}\) 165–167 °C); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (dd, \(J = 2.2, 1.1\) Hz), 7.17 (t, \(J = 7.8, 1.1\) Hz), 6.99 (m, 4H), 2.69 (s, 3H), 13(C\(_{6}\)) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.3, 143.2, 143.1, 133.5, 133.4, 133.2, 132.6, 129.6, 120.7 (q, \(J = 322.4\) Hz), 116.2, 113.0, 20.9.

(4-Chloro(phenyl)iodonium)iodonium Trifluoromethanesulfonate (3z).\(^{2c}\)

GP6 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether afforded the product as light yellow solids (2.48 g, 90%): mp 187–190 °C (lit.\(^{26}\) 179–180 °C); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 8.8, 2.2\) Hz), 7.50 (d, \(J = 8.8, 2.2\) Hz), 7.45 (s, 2H), 7.41 (s, 2H), 2.69 (s, 3H), 13(C\(_{6}\)) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.8, 144.6, 142.6, 135.3, 134.7, 133.0, 126.9, 120.9, 120.3 (q, \(J = 319.9\) Hz), 109.9, 27.2, 21.3.
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REFERENCES


