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A Flow Synthesis of Diaryliodonium Triflates

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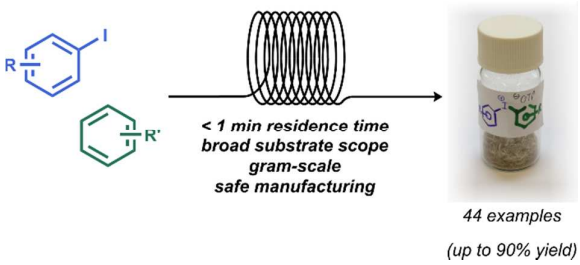
Abstract: A safe and scalable synthesis of diaryliodonium triflates was achieved using a practical continuous-flow design. A wide array of electron-rich to electron-deficient arenes could readily be transformed to their respective diaryliodonium salts on gram-scale, with residence times varying from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



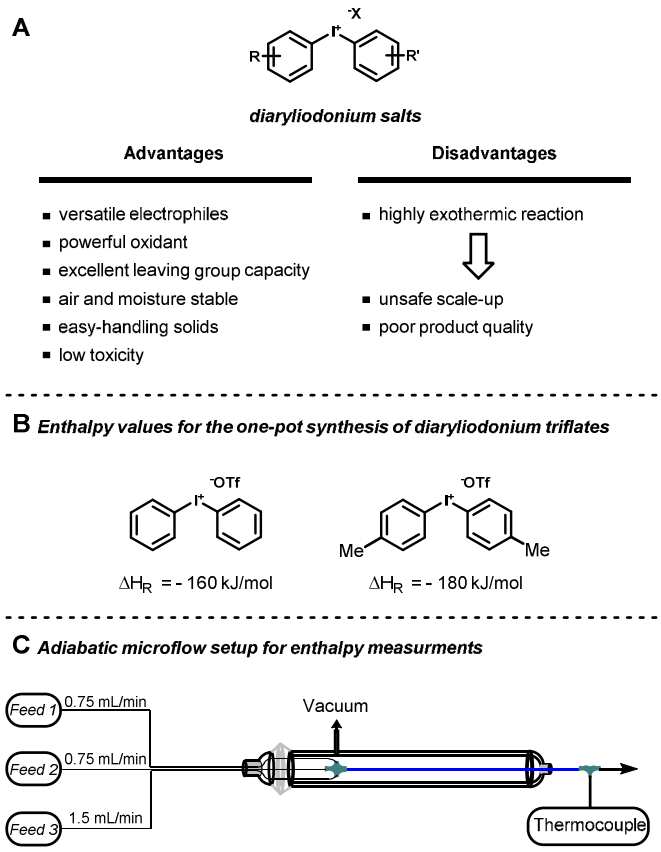
Introduction

In recent years, the applications of aryl electrophile sources, such as hypervalent iodinated compounds, have become increasingly important in synthetic organic chemistry.[1] In particular, diaryl-λ^3-iodanes, also known as diaryliodonium salts, have been extensively used in numerous arylation procedures.[2] 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.[3] Furthermore, diaryliodonium salts can be used as an electrophilic aryl source to couple with a wide variety of nucleophiles allowing the preparation of sulfides,[4] ethers,[5] amines,[6] esters[7] and nitro compounds,[8] as well as the α-arylation on enolates.[9]

Given the apparent importance of diaryliodonium salts, many syntheses have been developed to prepare these compounds.[10] 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.[11] 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, scalable and provides a broad substrate scope.

Results and Discussion

To quantify the thermodynamic data of highly exothermic reactions, reaction calorimetry is typically used.[12] In order to rapidly determine the unknown reaction enthalpy (ΔH_R) of the diaryliodonium salt synthesis, we developed an operationally simple adiabatic continuous-flow device which allowed us to calculate ΔH_R values via in-line ΔT measurements (See Scheme 1c). Hereto, 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 Supporting Information). Assuming full conversion, we calculated the reaction enthalpy using the following equation $\Delta H_R = m*Cp*\Delta T$, where m and Cp are the mass and the heat capacity of the solvent respectively (Cp 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.[13] Next, we carried out the synthesis of diphenyliodonium triflate and di-*p*-tolyliodonium triflate in the adiabatic microfluidic device and ΔT values were measured (reactions were performed 3 times each). With the Cp value of DCE known (Cp = 129.4 $J.mol^{-1}.K^{-1}$)[14], we were able to directly calculate the respective enthalpy values. Interestingly, very high ΔH_R values between -160 kJ/mol for to -180 kJ/mol were observed highlighting the need for a safe and reliable method to scale the reaction conditions (Scheme 1).[15] Such exothermic transformations can be carried out safely in continuous-flow microreactors, since the micro environment results in an excellent heat dissipation rate.[16]



Scheme 1: (A) Advantages and disadvantages of diaryliodonium salts. (B) Enthalpy measurement of the diaryliodonium salt synthesis in an adiabatic microreactor. (C) Flow setup used for the enthalpy measurements.

We commenced our investigations by designing a suitable continuous-flow setup (Figure 1). Our design consists of three individual feeds that allows 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 submerged in an ultrasonic bath.[17] 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 Supporting Information). Optimal reaction conditions were obtained with 1.1 equivalents of **2a** and *m*-CPBA, 2 equivalents of TfOH and dichloroethane (DCE) as the solvent in a 100 µL microreactor. The reaction was remarkably fast and was completed within 2 seconds residence time. Notably, the desired di-*p*-tolyliodonium triflate **3a** could be obtained on 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.

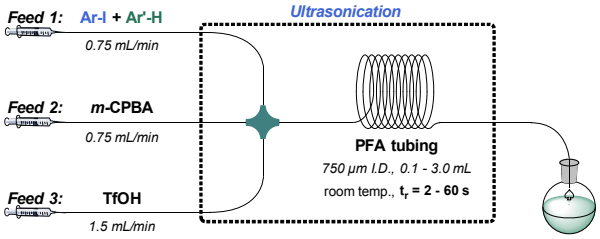


Figure 1. Schematic representation of micro flow setup.

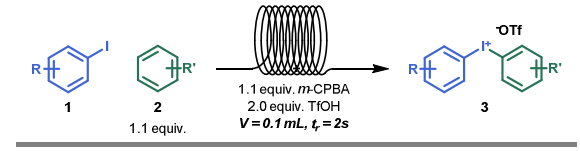
Figure 2. Comparison of the solids obtained after precipitation of di-*p*-tolyliodonium triflate (**3a**) produced either in batch (left) or flow (right).

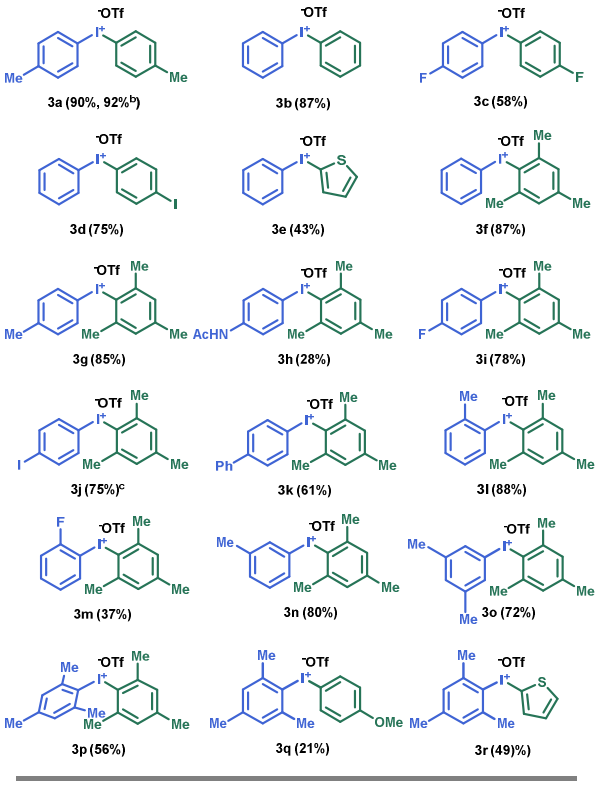
With the optimized conditions in hand, we sought to demonstrate the generality of our flow protocol (Table 1). Within 2 seconds residence time, a diverse set of both symmetrical and unsymmetrical diaryliodonium triflates were synthesized in fair to excellent yield on gram-scale (5-10 mmol scale). Symmetrical diaryliodonium triflates were readily produced in good to excellent yields (**3a**-**3c**). By using different (hetero)arenes, unsymmetrical diaryliodonium salts were synthesized (**3d**-**3e**). Furthermore, the use of sterically hindered mesitylene was well tolerated, providing access to a diverse set of aryl-mesityliodonium triflates (**3f**-**3p**). These compounds are of high interest in cross coupling and C–H arylation chemistry since they allow selective transfer of the functionalized aryl groups to the substrate. Aryl iodides bearing strong electron-donating substituents (*e.g.*, anisoles) or electron-rich heteroaromatic iodides (*e.g.*, thiophene) were

incompatible with the reaction conditions. However, these diaryliodonium triflates 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 re-optimization of the reaction conditions (See *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 equivalents) and TfOH (3.0 equivalents). 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).

Table 1. Scope of diaryliodonium triflates using electron-neutral and electron-rich aryl iodides.[a]

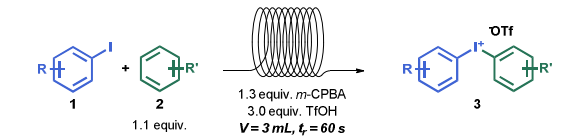


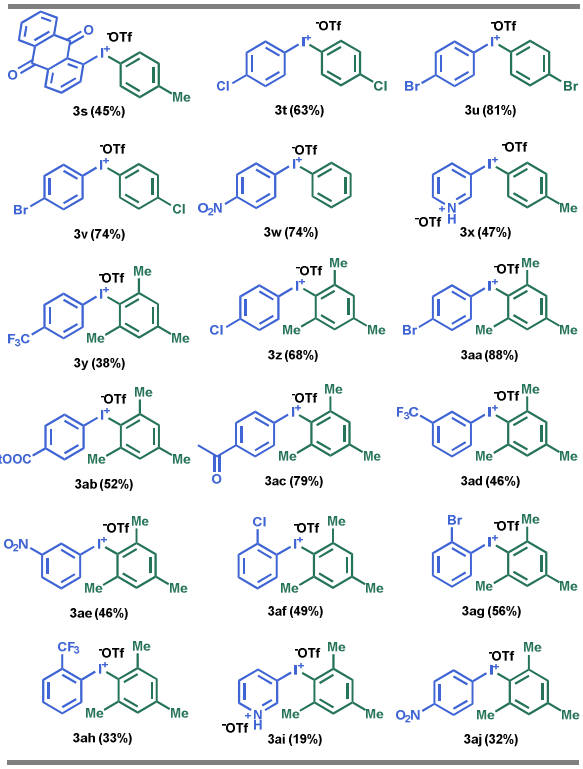


[a]Reaction conditions: feed 1: 5.0 mmol of aryl iodide (**1**), 5.5 mmol of arene (**2**) in 25 mL of DCE; feed 2: 5.5 mmol of *m*-CPBA in 25 mL of DCE; feed 3: 10 mmol of TfOH in 50 mL of DCE. Throughput distribution feed 1 / feed 2 / feed 3 was 1:1:2. [b]10 mmol scale reaction

Finally, with the aim of developing a flow 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 equivalents *m*-CPBA, 4.1-10 equivalents of arene and 5 equivalents TfOH (See 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* substituted diaryliodonium analogues were obtained as the only regioisomer. However, when using toluene as the substrate, several other regioisomers were obtained with the *ortho-para* isomer being the most abundant (**3ak**). However, the selectivity could be completely tuned towards the *ortho-para* isomer by decreasing the reaction temperature to 0 °C.

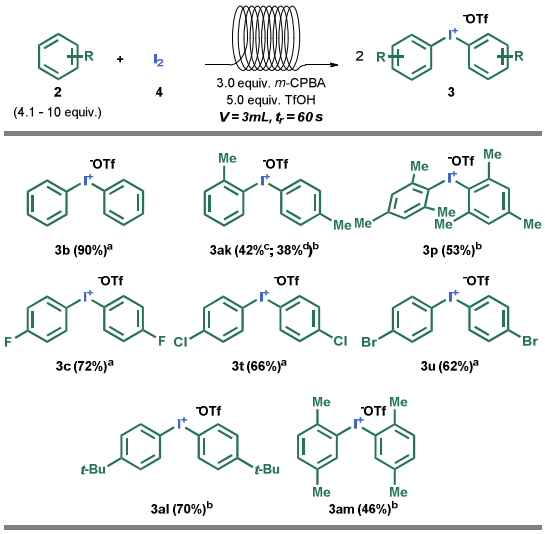
Table 2. Scope of diaryliodonium triflates with electron-deficient substrates.[a]





[a]Reaction conditions: feed 1: 5.0 mmol of 1, 5.5 mmol 2 in 25 mL of DCE; feed 2: 6.5 mmol of *m*-CPBA in 25 mL of DCE; feed 3: 15 mmol of TfOH in 50 mL of DCE. Throughput distribution feed 1 / feed 2 / feed 3 was 1:1:2.

Table 3. Scope of symmetric diaryliodonium triflates derived from arenes and molecular iodine .[a]



[a]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 TfOH 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. [b]4.1 equiv. of arene are used. [c]Selectivity at room temperature: ortho-para 90% para-para 5% and ortho-ortho 5%. [d]Selectivity at 0°C: ortho-para >96%.

Conclusions

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 the diaryliodonium triflates on gram-scale with excellent purity in a time-efficient fashion. We believe that the developed flow protocol will find widespread use in both 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 of BD Discardit II® or NORM-JECT®. Syringe pumps were purchased from Chemix Inc. model Fusion 200 Touch. Used ultrasonicator was VWR USC300T. ^{1}H (400MHz), ^{13}C (100MHz) and ^{19}F (376 MHz) NMR spectra were recorded on ambient temperature using a Bruker-Avance 400 or Mercury 400. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to $CDCl_3$ (7.26 ppm) and DMSO-d_6 (2.50 ppm), all $^{13}C\{^{1}H\}$NMR spectra are reported in ppm relative to $CDCl_3$ (77.2 ppm) and DMSO-d_6 (39.52 ppm). HRMS (ESI/APCI multimode ionization source, TOF-MSD analyzer), were measured with direct infusion in a 50:50 flow of 5mM NH_4OAc in water / MeOH. NMR data was processed using the MestReNova 9.0.1 software package. Known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C 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 salts synthesis with electron-neutral and electron-rich substrates (GP1): A 25 mL oven-dried volumetric flask was charged with 4-iodotoluene (**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*-chloroperbenzoic acid (≤ 77%) (1.24 g, 5.5 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 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. After, a 50 mL oven-dried volumetric flask fitted with a septum and was degassed by alternating vacuum and argon backfill and charged with around 20 mL dichloroethane. Trifluoromethanesulfonic acid (0.9 mL, 10.0 mmol) was added carefully with a syringe and dichloroethane was added via syringe to make a 50.0 mL solution. The solution was charged in a 60 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 0.1 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. First syringe pump (containing 2 syringes) was operated at 2x 0.75 mL/min and the second syringe pump was operated at 1.5 mL/min (total 3 mL/min flow rate, 2 seconds 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, then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until cloudy solution is obtained. Next, the resulted 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 salts 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*-chloroperbenzoic acid (≤ 77%) (1.5 g, 6.5 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 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. After, a 50 mL oven-dried volumetric flask fitted with a septum and was degassed by alternating vacuum and argon backfill and charged with around 40 mL dichloroethane. Trifluoromethanesulfonic acid (1.3 mL, 15 mmol) was added carefully with a syringe and dichloroethane was added via syringe to make a 50.0 mL solution. The solution was charged in a 60 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 3.0 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. First syringe pump (containing 2 syringes) was operated at 2x 0.75 mL/min and the second syringe pump was

operated at 1.5 mL/min (total 3 mL/min flow rate, 60 seconds 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, then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until cloudy solution is obtained. Next, the resulted 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 salts 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*-chloroperbenzoic 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. After, a 25 mL oven-dried volumetric flask was fitted with a septum and was degassed by alternating vacuum and argon backfill and charged with around 15 mL dichloroethane. Trifluoromethanesulfonic acid (0.9 mL, 10.0 mmol) was added carefully with a syringe and 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. First syringe pump (containing 2 syringes) was operated at 2x 0.75 mL/min and the second syringe pump was operated at 1.5 mL/min (total 3 mL/min flow rate, 60 seconds 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, then the residue was dissolved in a minimum amount of acetone, followed by addition of diethyl ether until cloudy solution is obtained. Next, the resulted mixture was kept in the freezer (-26 °C) overnight. Formed crystals were filtered off and washed with a minimum of diethyl ether.

*di-p-tolyliodonium trifluoromethanesulfonate (**3a**)*.[18] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (2.04g, 89%). Mp. 131-133 °C (Lit. 121-123 °C)[18]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 – 8.05 (m, 4H), 7.31 (d, J = 8.1 Hz, 4H), 2.32 (s, 6H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 142.5, 135.0, 132.3, 120.8 (q, J = 322.3 Hz), 113.1, 20.8.

*diphenyliodonium trifluoromethanesulfonate (**3b**)*.[19] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (1.89 g, 88%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (1.55 g, 90%). Mp. 169-173 °C (Lit. 172-174 °C)[19]. ^{1}H NMR (400 MHz, DMSO-d_6) 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). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 135.2, 132.1, 131.8, 120.8 (q, J = 322.3 Hz), 116.5.

*bis(4-fluorophenyl)iodonium trifluoromethanesulfonate (**3c**)*.[2c] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (1.35 g, 58%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (1.34 g, 72%). Mp. 168-170 °C (Lit. 168-170 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 – 8.22 (m, 4H), 7.42 (t, J = 8.9 Hz, 4H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) 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).^{19}F NMR (376 MHz, DMSO-d_6) δ -77.75, -106.60 (tt, J = 9.0, 5.0 Hz).

*(4-iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (**3d**)*.[19] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (2.09 g, 75%). Mp. 144-148 °C (Lit. 146-148 °C)[19]. ^{1}H NMR (400 MHz, DMSO-d_6) δ

8.24 (d, *J* = 7.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H). $^{13}C\{^{1}H\}$NMR (101 MHz, DMSO-d_6) δ 140.39, 136.75, 135.16, 132.14, 131.80, 120.67 (q, *J* = 322.4 Hz), 116.67, 115.83, 100.28.

*phenyl(thiophen-2-yl)iodonium trifluoromethanesulfonate (**3e**)*.[2c] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light brown solids (937 mg, 43%). Mp. 143-146 °C (Lit. 144-146 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 – 8.21 (m, 2H), 8.07 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.97 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.58 – 7.47 (m, 2H), 7.18 (dd, *J* = 5.3, 3.8 Hz, 1H). $^{13}C\{^{1}H\}$NMR (101 MHz, DMSO-d_6) δ 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 (**3f**)*.[20] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (2.05g, 87%). Mp. 148-150 °C (Lit. 137-138 °C)[20]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 – 7.94 (m, 2H), 7.69 – 7.60 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.22 (s, 2H), 2.62 (s, 6H), 2.29 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, DMSO-d_6) δ 143.1, 141.6, 134.5, 131.9, 129.8, 122.6, 120.7 (q, *J* = 322.3 Hz), 114.5, 26.3, 20.5.

*mesityl(p-tolyl)iodonium trifluoromethanesulfonate (**3g**)*.[20] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (2.07g, 85%). Mp. 181-183 °C (Lit. 183-184 °C)[20]. ^{1}H NMR (400 MHz, DMSO- d_6) δ 7.87 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.21 (s, 2H), 2.60 (s, 6H), 2.33 (s, 3H), 2.29 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, DMSO) δ 143.0, 142.2, 141.4, 134.5, 132.5, 129.7, 122.7, 110.9, 26.3, 20.8, 20.5.

*(4-acetamidophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3h**)*. GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white off solids (741 mg, 28%). Mp. 136-138 °C. ^{1}H NMR (399 MHz, DMSO-d_6) δ 10.28 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.20 (s, 2H), 2.60 (s, 6H), 2.28 (s, 3H), 2.05 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, DMSO) δ 169.5, 143.4, 142.8, 141.8, 136.3, 130.2, 123.4, 122.7, 122.0, 106.3, 26.7, 24.6, 21.0. HRMS (ESI) calculated for $C_{17}H_{19}F_3INO$ $[M\text{-}OTf]^+$: 380.0506, found: 380.0514.

*(4-fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3i**)*.[20] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (1.96 g, 80%). Mp. 173-176 °C (Lit. 177-178 °C)[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.5, 4.7 Hz, 2H), 7.10 (d, J = 4.9 Hz, 4H), 2.63 (s, 6H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$ δ 164.7 (d, *J* = 255.0 Hz), 144.6, 142.5, 135.7 (d, *J* = 8.7 Hz), 130.5, 121.2, 120.3 (q, *J* = 319.8 Hz), 119.8 (d, *J* = 22.9 Hz), 105.3 (d, *J* = 3.4 Hz), 27.2, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.40, -106.01 (ddd, J = 12.8, 8.2, 4.7 Hz).

*(4-iodophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3j**)*. GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as dark white solids (2.24 g, 75%). Mp. 193-195 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.23 (s, 2H), 2.58 (s, 6H), 2.30 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, DMSO-d_6) δ 143.5, 141.7, 141.6, 140.4, 136.8, 136.0, 129.9, 129.82, 122.7, 122.6, 116.3 (q, *J* = 397.4 Hz), 99.7, 26.3, 20.5.

*[1,1'-biphenyl]-4-yl(mesityl)iodonium trifluoromethanesulfonate (**3k**)*. GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as pale green solids (1.67 g, 61%). Mp. 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.54 – 7.39 (m, 5H), 7.14 (s, 2H), 2.67 (s, 6H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 145.4, 144.9, 142.7, 138.5, 133.5, 131.1, 130.7, 129.3, 129.0, 127.3, 120.5, 109.9, 27.4, 21.3. HRMS (ESI) calculated for $C_{21}H_{20}I$ $[M\text{-}OTf]^+$: 399.0604, found: 399.0585.

*mesityl(o-tolyl)iodonium trifluoromethanesulfonate (**3l**)*.[20] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (2.09g, 86%). Mp. 170-172 °C (Lit. 167-168 °C)[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 3H), 7.17 (td, J = 7.7, 7.1, 2.0 Hz, 1H), 7.11 (s, 2H), 2.60 (s, 9H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ 144.8, 142.7, 140.4, 133.7, 132.7, 132.6, 130.9, 130.0, 120.5 (q, *J* = 321.8 Hz), 119.7, 115.8, 27.1, 25.05, 21.2.

*(2-fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3m**)*.[21] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (907 mg, 37%). Mp. 157-159 °C (Lit. 161-162 °C)[21]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.81 (ddd, *J* = 7.8, 5.8, 1.6 Hz, 1H), 7.59 (dddd, *J* = 8.6, 7.2, 5.4, 1.6 Hz, 1H), 7.35 – 7.19 (m, 2H), 7.08 (s, 2H), 2.68 (s, 6H), 2.34 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 160.5 (d, *J* = 252.1 Hz), 144.6, 142.7, 136.1, 135.2 (d, *J* = 8.0 Hz), 130.6, 127.6 (d, *J* = 3.3 Hz), 121.5, 117.6 (d, *J* = 21.8 Hz), 98.0 (d, *J* = 23.9 Hz), 27.1, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.35, -95.37 – -96.24 (m).

*mesityl(m-tolyl)iodonium trifluoromethanesulfonate (**3n**)*.[21] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (1.94 g, 80%). Mp. 169-171 °C (Lit. 171-172 °C)[21]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.10 (s, 2H), 2.62 (s, 6H), 2.35 (s, 6H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 144.6, 143.3, 142.7, 133.6, 132.9, 132.1, 130.5, 129.9, 120.5 (q, *J* = 320.5 Hz), 120.2, 111.6, 27.3, 21.5, 21.3.

*(3,5-dimethylphenyl)(mesityl)iodonium trifluoromethanesulfonate (**3o**)*. GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as off white solids (1.80 g, 72%). Mp. 200-203 °C. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.14 (s, 1H), 7.11 (s, 2H), 2.63 (s, 6H), 2.36 (s, 3H), 2.30 (s, 6H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 144.6, 142.9, 142.7, 134.0, 130.6, 130.5, 120.7 (q, *J* = 321.3 Hz), 120.0, 111.4, 27.3, 21.5, 21.3. HRMS (ESI) calculated for $C_{17}H_{20}I$ [M-OTf]$^{+}$: 351.0604, found: 351.0616.

*dimesityliodonium trifluoromethanesulfonate (**3p**)*.[19] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.44 g, 56%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.08 g, 53%).Mp. 183-186 °C (Lit. 187-188 °C)[19]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 4H), 2.51 (s, 12H), 2.33 (s, 6H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 144.0, 142.4, 131.1, 117.4, 26.3, 21.1.

*mesityl(4-methoxyphenyl)iodonium trifluoromethanesulfonate (**3q**)*.[2c] GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as dark grey solids (502 mg, 20%). Mp. 148-150 °C (Lit. 148-151 °C).[2c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 2H), 7.10 (s, 2H), 6.98 – 6.85 (m, 2H), 3.82 (s, 3H), 2.64 (s, 6H), 2.35 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 162.8, 144.7, 142.4, 135.5, 130.6, 121.0, 118.3, 99.9, 55.9, 27.2, 21.3.

*mesityl(thiophen-2-yl)iodonium trifluoromethanesulfonate (**3r**)*. GP1 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light brown solids (1.20 g, 50%). Mp. 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.2 Hz, 1H), 7.61 (dd, J = 5.4, 1.2 Hz, 1H), 7.11 – 7.04 (m, 3H), 2.73 (s, 6H), 2.33 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 144.5, 141.7, 139.7, 135.8, 130.6, 129.8, 125.7, 120.3 (q, *J* = 319.6 Hz), 94.5, 27.2, 21.2. HRMS (ESI) calculated for $C_{13}H_{14}IS$ [M-OTf]$^{+}$: 328.9855, found: 328.9857.

*(9,10-dioxo-9,10-dihydroanthracen-1-yl)(p-tolyl)iodonium trifluoromethanesulfonate (**3s**)*. GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light grey solids (1.29 g, 45%). Mp. 225-230 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 – 8.41 (m, 1H), 8.39 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.30 (dd, *J* = 7.2, 1.9 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 2H), 8.09 (qd, *J* = 7.3, 1.7 Hz, 2H), 8.02 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 8.2, 1.0 Hz, 1H), 2.52 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO) δ 185.3, 181.2, 144.9, 138.1, 137.3, 136.9, 136.3, 135.7, 133.7, 133.3, 132.2, 131.9, 130.4, 129.9, 128.2, 127.8, 114.7, 108.4, 21.7. HRMS (ESI) calculated for $C_{21}H_{14}IO_2$ [M-OTf]$^{+}$: 425.0033, found: 425.0030.

*bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (**3t**)*.[2c] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (1.57 g, 63%). GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (1.32 g, 66%). Mp. 183-187 °C (Lit. 185-186 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 – 8.08 (m, 4H), 7.75 – 7.47 (m, 4H). ^{13}C{^{1}H}NMR (101 MHz, DMSO) δ 137.9, 137.4, 132.3, 115.2.

*bis(4-bromophenyl)iodonium trifluoromethanesulfonate (**3u**)*.[2c] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white solids (2.37 g, 81%). GP3 was used on a 4 mmol scale. Purification by recrystallization in

diethyl ether to afford the product as white solids (1.46 g, 62%). Mp. 183-188 °C (Lit. 185-190 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 8.6 Hz, 4H), 7.77 (d, J = 8.6 Hz, 4H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 137.0, 134.7, 126.3, 115.4.

*(4-bromophenyl)(4-chlorophenyl)iodonium trifluoromethanesulfonate (**3v**)*. GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white needles (2.01g, 74%). Mp. 201-204 °C. ^{1}H NMR (399 MHz, DMSO-d_6) δ 8.31 – 8.23 (m, 2H), 8.26 – 8.13 (m, 2H), 7.86 – 7.71 (m, 2H), 7.70 – 7.58 (m, 2H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 138.0, 137.5, 137.5, 135.2, 132.3, 126.8, 121.2 (q, *J* = 322.5 Hz), 115.9, 115.1. HRMS (ESI) calculated for $C_{12}H_8BrClI$ [M-OTf]$^+$: 392.8537, found: 392.8553.

*(4-nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate (**3w**)*.[2c] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as yellow solids (1.76 g, 74%). Mp. 178-183 °C (Lit. 180-185 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 – 8.45 (m, 2H), 8.35 – 8.27 (m, 4H), 7.74 – 7.65 (m, 1H), 7.61 – 7.50 (m, 2H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 149.4, 136.4, 135.5, 132.4, 131.96, 126.3, 122.6, 120.7 (q, *J* = 322.4 Hz), 116.9.

*mono(3-(p-tolyliodonio)pyridin-1-ium) bis(trifluoromethanesulfonate) (**3x**)*.[2c] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light yellow solids (1.40 g, 47%). Mp. 163-167 °C (Lit. 170-172 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.27 (d, *J* = 2.2 Hz, 1H), 8.82 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.64 (dt, *J* = 8.2, 1.8 Hz, 1H), 8.26 – 8.07 (m, 2H), 7.58 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 153.4, 152.1, 142.9, 142.3, 135.3, 132.5, 126.9, 120.7 (q, *J* = 323.3 Hz), 116.2, 113.0, 20.9.

*mesityl(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**3y**)*. GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.03 g, 38%). Mp. 202-205 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 2H), 2.59 (s, 6H), 2.31 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 143.5, 141.74, 135.0, 131.8, 129.9, 128.4 (d, *J* = 3.7 Hz), 124.7, 122.6, 120.5 (q, *J* = 295.3 Hz), 118.7, 26.3, 20.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.68, -77.75. HRMS (ESI) calculated for $C_{16}H_{15}F_3I$ [M-OTf]$^+$: 391.0165, found: 391.0183.

*(4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3z**)*.[20] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light grey solids (2.21 g, 87%). Mp. 161-163 °C (Lit. 132-133 °C)[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.40 – 7.34 (m, 2H), 7.11 (s, 2H), 2.62 (s, 6H), 2.36 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 144.8, 142.6, 138.9, 134.4, 132.5, 130.6, 120.9, 120.8 (q, *J* = 237.7 Hz), 108.9, 27.2, 21.3.

*(4-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3aa**)*.[20] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light grey solids (2.48 g, 90%). Mp. 187-190 °C (Lit. 179-180 °C)[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.09 (s, 2H), 2.61 (s, 6H), 2.34 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 144.6, 142. 6, 135.3, 134.7, 130.5, 126.9, 120.9, 120.3 (q, *J* = 319.9 Hz), 109.9, 27.2, 21.3.

*(4-(ethoxycarbonyl)phenyl)(mesityl)iodonium triflate (**3ab**)*.[20] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (1.39 g, 51%). Mp. 173-175 °C (Lit. 178-179 °C)[20]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 1.0 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.61 (s, 6H), 2.36 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.9, 144.8, 142.7, 133.7, 132.9, 132.8, 130.5, 120.7, 120.3 (q, *J* = 319.9 Hz), 116.5, 62.0, 27.2, 21.3, 14.3.

*(4-acetylphenyl)(mesityl)iodonium trifluoromethanesulfonate (**3ac**)*.[21] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as grey solids (2.03 g. 79%). Mp. 183-184 °C (Lit. 183-185 °C)[21]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.14 (s, 2H), 2.62 (s, 6H), 2.59 (s, 3H), 2.38 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 196.3, 145.1, 142.8, 139.6, 133.0, 131.6, 130.7, 120.4, 116.6, 27.3, 26.8, 21.3.

*mesityl(3-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**3ad**)*.[20] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.24 g, 46%). Mp. 180-182 °C (Lit. 181-183 °C)[20]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.12 (s, 2H), 2.63 (s, 6H), 2.36 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 144.9, 142.7, 134.2 (d, *J* = 33.8 Hz), 132.5, 130.6, 129.8 (d, *J* = 4.0 Hz), 128.6 (d, *J* = 3.7 Hz), 123.9, 121.2, 121.0, 120.2 (q, *J* = 319.2 Hz), 112.1, 27.2 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.05, -78.53.

*mesityl(3-nitrophenyl)iodonium trifluoromethanesulfonate (**3ae**)*. GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.19 g, 46%). Mp. 162-164 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (t, *J* = 2.0 Hz, 1H), 8.42 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 8.18 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 7.26 (s, 2H), 2.61 (s, 6H), 2.32 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 148.6, 143.6, 141.9, 139.7, 132.9, 130.0, 128.9, 126.4, 122.7, 120.7 (q, *J* = 322.1 Hz), 114.1, 26.4, 20.6. HRMS (ESI) calculated for $C_{15}H_{15}INO_2$ $[M\text{-}OTf]^+$: 368.0142, found: 368.0154.

*(2-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3af**)*.[21] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.24 g, 49%). Mp. 171-172 °C (Lit. 167-168 °C)[21]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (td, *J* = 7.7, 1.4 Hz, 1H), 7.29 (td, *J* = 7.8, 7.4, 1.5 Hz, 1H), 7.17 (s, 2H), 7.09 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.62 (s, 6H), 2.40 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 145.4, 143.0, 135.5, 133.5, 132.5, 131.4, 131.0, 130.6, 120.8, 120.4 (q, *J* = 319.9 Hz), 112.5, 27.2, 21.3.

*(2-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (**3ag**)*.[21] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (1.54 g, 56%). Mp. 172-173 °C (Lit. 167-168 °C)[21]. ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 (td, *J* = 7.7, 1.5 Hz, 1H), 7.33 (ddd, *J* = 8.9, 7.5, 1.5 Hz, 1H), 7.20 (s, 2H), 6.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 2.61 (s, 6H), 2.41 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 145.6, 143.0, 134.6, 133.3, 131.5, 131.2, 131.0, 124.7, 121.6, 120.4 (q, *J* = 319.8 Hz), 115.4, 27.2, 21.4.

*mesityl(2-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (**3ah**)*.[21] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (891 mg, 33%). Mp. 176-178 °C (Lit. 180-181 °C)[21]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 7.8, 1.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 2H), 2.62 (s, 6H), 2.41 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 145.9, 143.1, 135.8, 133.1, 132.2, 131.4, 131.1, 129.6 (d, *J* = 4.8 Hz), 124.1, 121.9, 120.1 (q, *J* = 264.9 Hz), 107.5, 27.2, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.93, -78.44.

*3-(mesityliodonio)pyridin-1-ium bis(trifluoromethanesulfonate) (**3ai**)*.[2c] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as light yellow solids (592 mg, 19%). Mp. 155-158 °C (Lit. 138-141 °C)[2c]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (d, J = 2.3 Hz, 1H), 8.79 (dd, J = 4.8, 1.3 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 8.3, 4.7 Hz, 1H), 7.23 (s, 2H), 2.61 (s, 6H), 2.30 (s, 3H). ^{13}C{^{1}H}NMR (101 MHz, DMSO-d_6) δ 152.9, 151.9, 143.3, 142.1, 141.6, 129.9, 127.1, 122.6, 120.7 (q, *J* = 322.4 Hz), 114.2, 26.3, 20.5.

*mesityl(4-nitrophenyl)iodonium trifluoromethanesulfonate (**3aj**)*.[20] GP2 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (827 mg, 32%). Mp. 197-200 °C (Lit. 208 °C)[20]. ^{1}H NMR (399 MHz, DMSO-d_6) δ 8.26 (d, J = 8.4 Hz, 2H), 8.22 – 8.12 (m, 2H), 7.26 (s, 2H), 2.59 (s, 6H), 2.31 (s, 3H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6) δ 149.3, 143.6, 141.8, 135.5, 130.0, 126.2, 122.8 (q, *J* = 201.9 Hz), 26.3, 20.6.

*o-tolyl(p-tolyl)iodonium trifluoromethanesulfonate (**3ak**)*.[11b] GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (ortho-para 90%, para-para 5%, ortho-ortho 5%, 770 mg, 42%). Mp. 158-160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85 – 7.71 (m, 2H), 7.52 (td, *J* = 7.5, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22

(t, *J* = 5.4 Hz, 3H), 2.60 (s, 3H), 2.37 (s, 3H). $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ 143.4, 141.4, 137.6, 134.7, 133.5, 133.2, 132.1, 129.8, 120.4 (q, *J* = 320.0 Hz), 119.0, 109.0, 25.8, 21.5.

*bis(4-(tert-butyl)phenyl)iodonium trifluoromethanesulfonate (**3al**).*[22] GP3 was used on a 4 mmol scale. Purification by recrystallization in diethyl ether to afford the product as white needles (1.52 g, 70%). Mp. 163-165 °C (Lit. 164-165 °C)[22]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 4H), 7.43 – 7.36 (m, 4H), 1.23 (s, 18H). $^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ 156.7, 134.8, 129.7, 120.3 (d, *J* = 321.3 Hz), 109.4, 35.3, 31.0.

*bis(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (**3am**).*[11b] GP3 was used on a 5 mmol scale. Purification by recrystallization in diethyl ether to afford the product as brown solids (896 mg, 46%). Mp. 168-169 °C (Lit. 173-175 °C).[11b] ^{1}H NMR (399 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.33 (s, 4H), 2.56 (s, 6H), 2.34 (s, 6H). $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 140.6, 138.1, 136.9, 134.4, 132.0, 117.0, 25.1, 20.8.

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Supporting Information Available:

Description of reaction set-ups, optimization of reaction conditions and enthalpy measurements and spectral data of all products. This material is available free of charge via the Internet at http://pubs.acs.org

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