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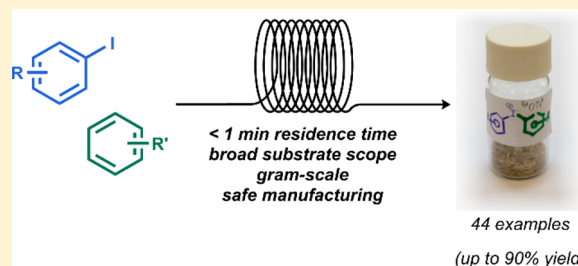
Flow Synthesis of Diaryliodonium Triflates

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S 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.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 compounds⁸ 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 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.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 that 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 the Supporting Information). Assuming full conversion, we calculated the reaction enthalpy using the following equation, $\Delta H_R = m \times C_p \times \Delta T$, where m and C_p are the mass and the heat capacity of the solvent, respectively (C_p 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.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 three times each). With the C_p value of DCE known ($C_p = 129.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$),¹⁴ we were able to directly calculate the respective enthalpy values. Interestingly, very high ΔH_R 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).¹⁵ Such exothermic transformations can be carried out safely in continuous-flow microreactors as the micro-environment results in an excellent heat dissipation rate.¹⁶

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, $750 \mu\text{m}$ i.d., $0.1\text{--}3.0 \text{ mL}$). To avoid microreactor clogging, the mixer and reactor

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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

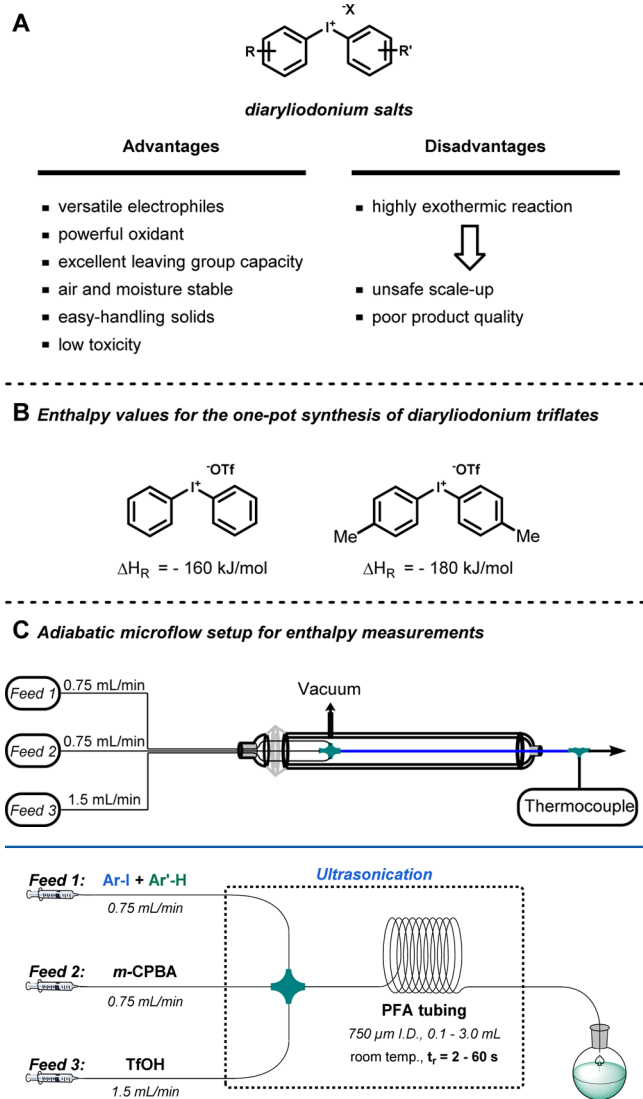


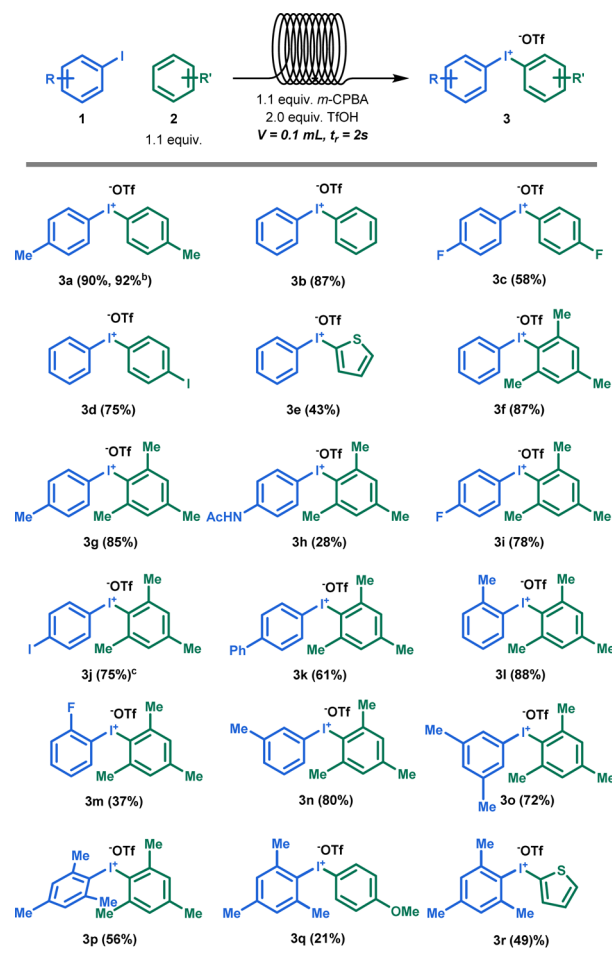
Figure 1. Schematic representation of the microflow setup.

79 were submerged in an ultrasonic bath.¹⁷ The reaction between
80 4-iodotoluene (**1a**) and toluene (**2a**) in the presence of *m*-
81 CPBA and TfOH was selected as the benchmark for our
82 reaction optimization studies (see the [Supporting Information](#)).
83 Optimal reaction conditions were obtained with 1.1 equiv of **2a**
84 and *m*-CPBA, and 2 equiv of TfOH and dichloroethane (DCE)
85 as the solvent in a 100 μL microreactor. The reaction was
86 remarkably fast and was completed within 2 s residence time.
87 Notably, the desired di-*p*-tolyliodonium triflate **3a** could be
88 obtained on a gram scale (2.04 g, 89%) in excellent yield as
89 pure and simple to handle crystals ([Figure 2](#)). Analogous batch
90 experiments resulted in a lower yield (69% yield) of **3a** as an
91 inferior-quality powder precipitate.
92 With the optimized conditions in hand, we sought to
93 demonstrate the generality of our flow protocol ([Table 1](#)).
94 Within a 2 s residence time, a diverse set of both symmetrical
95 and unsymmetrical diaryliodonium triflates was synthesized in
96 fair to excellent yield on a gram scale (5–10 mmol scale).



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

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



^aReaction 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. ^b10 mmol scale reaction.

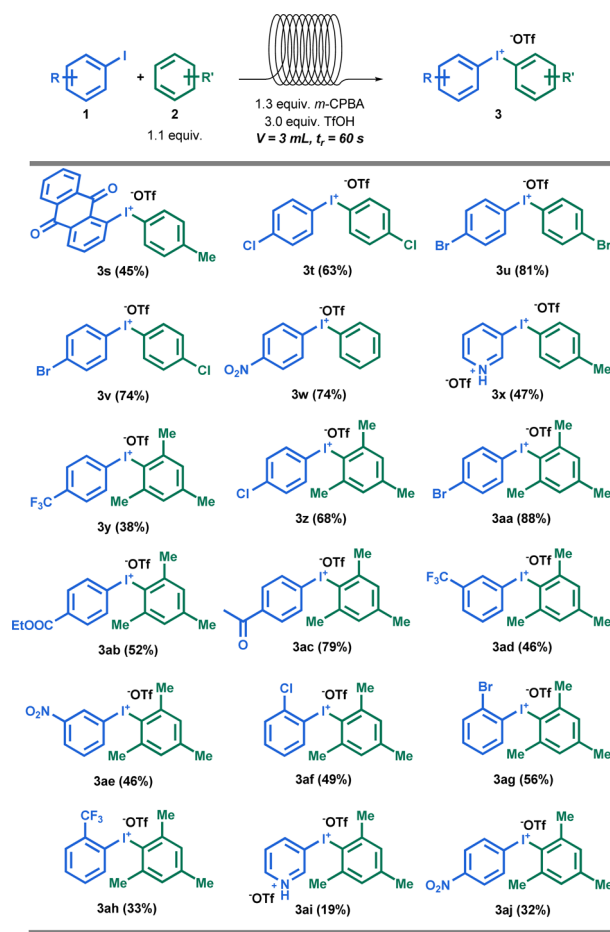
Symmetrical diaryliodonium triflates were readily produced in 97 good to excellent yields (**3a**–**3c**). Using different (hetero)- 98 arenes, unsymmetrical diaryliodonium salts were synthesized 99 (**3d**, **3e**). Furthermore, the use of sterically hindered mesitylene 100 was well-tolerated, providing access to a diverse set of aryl 101 mesityliodonium triflates (**3f**–**3p**). These compounds are of 102 high interest in cross-coupling and C–H arylation chemistry 103 because they allow selective transfer of the functionalized aryl 104 groups to the substrate. Aryl iodides bearing strong electron- 105

106 donating substituents (e.g., anisoles) or electron-rich hetero-
107 aromatic iodides (e.g., thiophene) were incompatible with the
108 reaction conditions. However, these diaryliodonium triflates
109 could be accessed when using the mesityl iodide with the
110 corresponding (hetero)arenes, albeit in a lower yield (**3q** and
111 **3r**).

112 Aryl iodides with electron-withdrawing functional groups
113 proved particularly challenging. However, after a minor
114 reoptimization of the reaction conditions (see the Supporting
115 Information), it was found that these compounds could be
116 obtained in good yields by increasing the reactor volume to 3
117 mL and using an excess of *m*-CPBA (1.3 equiv) and TfOH (3.0
118 equiv). Aryl iodides bearing *ortho*, *meta*, and *para* electron-
119 withdrawing substituents (e.g., halogens, nitro, esters, ketones)
120 were all well-tolerated, yielding the targeted diaryliodonium
121 triflates in synthetically useful yields (32–90% yield) (Table 2).
122 Also, 3-iodopyridine (**3x** and **3ai**) and 1-iodoanthraquinone
123 (**3s**) could be subjected to the flow conditions, resulting in the
124 desired compounds in fair yields (19–47% yield).

125 Finally, with the aim of developing a flow protocol utilizing
126 cheap and easily available starting materials, we chose to oxidize
127 simple arenes using molecular iodine to yield the corresponding
128 symmetrical diaryliodonium triflates. Optimal results were

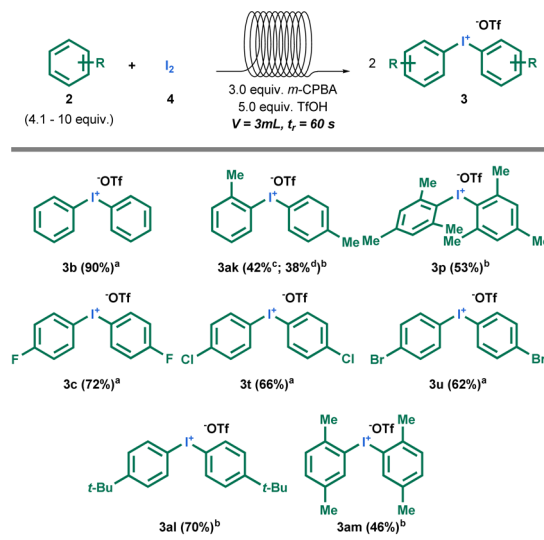
Table 2. Scope of Diaryliodonium Triflates with Electron-Deficient Substrates^a



^aReaction conditions. Feed 1: 5.0 mmol of **1**, 5.5 mmol of **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.

obtained using iodine as the limiting reagent along with 3
equiv of *m*-CPBA, 4.1–10 equiv of arene, and 5 equiv of TfOH
(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*

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



^aReaction 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. ^b4.1 equiv of arene was used. ^cSelectivity at room temperature: *ortho*–*para* 90%, *para*–*para* 5%, and *ortho*–*ortho* 5%. ^dSelectivity at 0 °C: *ortho*–*para* >96%.

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 toward the *ortho*–*para* isomer by
decreasing the reaction temperature to 0 °C.

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 a 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 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

161 reported in parts per million (ppm) downfield relative to CDCl_3 (7.26
162 ppm) and $\text{DMSO}-d_6$ (2.50 ppm); all $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are
163 reported in ppm relative to CDCl_3 (77.2 ppm) and $\text{DMSO}-d_6$ (39.52
164 ppm). HRMS (ESI/APCI multimode ionization source, TOF-MSD
165 analyzer) was measured with direct infusion in a 50:50 flow of 5 mM
166 NH_4OAc in water/MeOH. NMR data were processed using the
167 MestReNova 9.0.1 software package. Known products were
168 characterized by comparison to the corresponding ^1H NMR and ^{13}C
169 NMR from literature. Melting points were determined with a Buchi B-
170 540 capillary melting point apparatus in open capillaries and are
171 uncorrected. The names of all products were generated using the
172 PerkinElmer ChemBioDraw Ultra v.12.0.2 software package.

173 **General Procedure for the Diaryliodonium Salt Synthesis**
174 **with Electron-Neutral and Electron-Rich Substrates (GP1).** A 25
175 mL oven-dried volumetric flask was charged with 4-iodotoluene (**1a**,
176 1.09 g, 5.0 mmol) and toluene (**2a**, 506 mg, 5.5 mmol). Next, a second
177 25 mL oven-dried volumetric flask was charged with *meta*-
178 chloroperbenzoic acid ($\leq 77\%$) (1.24 g, 5.5 mmol). Both the flasks
179 were fitted with a septum and were degassed by alternating vacuum
180 and argon backfill. Dichloroethane was added via syringe to make a
181 25.0 mL solution in both flasks. Both the solutions were charged in 30
182 mL NORM-JECT syringes and were fitted to a single syringe pump.
183 Afterwards, a 50 mL oven-dried volumetric flask fitted with a septum
184 and was degassed by alternating vacuum and argon backfill and
185 charged with 20 mL of dichloroethane. Trifluoromethanesulfonic acid
186 (0.9 mL, 10.0 mmol) was added carefully with a syringe, and
187 dichloroethane was added via syringe to make a 50.0 mL solution. The
188 solution was charged in a 60 mL NORM-JECT syringe and fitted to a
189 second syringe pump. All syringes were connected to a PEEK cross-
190 mixer (500 μm i.d.) and subsequently connected to the inlet of the 0.1
191 mL PFA capillary tubing (750 μm i.d.). The cross-mixer and
192 microreactor were submerged in a sonication bath, and sonication
193 was applied during operation. The first syringe pump (containing two
194 syringes) was operated at 2×0.75 mL/min, and the second syringe
195 pump was operated at 1.5 mL/min (total 3 mL/min flow rate, 2 s
196 residence time). The outlet of the reactor was fitted to an argon-filled
197 round-bottom flask with septum via a needle connection. An argon-
198 filled balloon was attached in order to ensure a constant pressure. The
199 reaction mixture was evaporated under reduced pressure at the
200 rotavap. Residue was dissolved in diethyl ether and evaporated again at
201 the rotavap. This procedure was repeated three times, and then the
202 residue was dissolved in a minimum amount of acetone, followed by
203 addition of diethyl ether until a cloudy solution was obtained. Next,
204 the resulting mixture was kept in the freezer (-26 $^\circ\text{C}$) overnight.
205 Formed crystals were filtered off and washed with a minimum of
206 diethyl ether.

207 **General Procedure for the Diaryliodonium Salt Synthesis**
208 **with Electron-Deficient Substrates (GP2).** A 25 mL oven-dried
209 volumetric flask was charged with 4-iodonitrobenzene (**1b**, 1.25 g, 5.0
210 mmol) and mesitylene (**2b**, 0.76 mL, 5.5 mmol). Next, a second 25
211 mL oven-dried volumetric flask was charged with *meta*-chloroperben-
212 zoic acid ($\leq 77\%$) (1.5 g, 6.5 mmol). Both the flasks were fitted with a
213 septum and were degassed by alternating vacuum and argon backfill.
214 Dichloroethane was added via syringe to make a 25.0 mL solution in
215 both flasks. Both the solutions were charged in 30 mL NORM-JECT
216 syringes and were fitted to a single syringe pump. Afterwards, a 50 mL
217 oven-dried volumetric flask was fitted with a septum and was degassed
218 by alternating vacuum and argon backfill and charged with 40 mL of
219 dichloroethane. Trifluoromethanesulfonic acid (1.3 mL, 15 mmol) was
220 added carefully with a syringe, and dichloroethane was added via
221 syringe to make a 50.0 mL solution. The solution was charged in a 60
222 mL NORM-JECT syringe and fitted to a second syringe pump. All
223 syringes were connected to a PEEK cross-mixer (500 μm i.d.) and
224 subsequently connected to the inlet of the 3.0 mL PFA capillary tubing
225 (750 μm i.d.). The cross-mixer and microreactor were submerged in a
226 sonication bath, and sonication was applied during operation. The first
227 syringe pump (containing two syringes) was operated at 2×0.75 mL/
228 min, and the second syringe pump was operated at 1.5 mL/min (total
229 3 mL/min flow rate, 60 s residence time). The outlet of the reactor
230 was fitted to an argon-filled round-bottom flask with septum via a

needle connection. An argon-filled balloon was attached in order to 231
ensure a constant pressure. The reaction mixture was evaporated 232
under reduced pressure at the rotavap. Residue was dissolved in 233
diethyl ether and evaporated again at the rotavap. This procedure was 234
repeated three times, and then the residue was dissolved in a minimum 235
amount of acetone, followed by addition of diethyl ether until a cloudy 236
solution was obtained. Next, the resulting mixture was kept in the 237
freezer (-26 $^\circ\text{C}$) overnight. Formed crystals were filtered off and 238
washed with a minimum of diethyl ether. 239

240 **General Procedure for the Diaryliodonium Salt Synthesis**
241 **with Iodine (GP3).** A 10 mL oven-dried volumetric flask was charged
242 with iodine (**4**, 507 mg, 2 mmol) and the arene (**2**, 8.2–20 mmol).
243 Next, a second 10 mL oven-dried volumetric flask was charged with
244 *meta*-chloroperbenzoic acid ($\leq 77\%$) (1.5 g, 6 mmol). Both the flasks
245 were fitted with a septum and were degassed by alternating vacuum
246 and argon backfill. Dichloroethane was added via syringe to make a 10
247 mL solution in both flasks. Both the solutions were charged in 10 mL
248 NORM-JECT syringes and were fitted to a single syringe pump.
249 Afterwards, a 25 mL oven-dried volumetric flask was fitted with a
250 septum and was degassed by alternating vacuum and argon backfill and
251 charged with around 15 mL of dichloroethane. Trifluoromethane-
252 sulfonic acid (0.9 mL, 10.0 mmol) was added carefully with a syringe,
253 and dichloroethane was added via syringe to make a 20.0 mL solution.
254 The solution was charged in a 20 mL NORM-JECT syringe and fitted
255 to a second syringe pump. All syringes were connected to a PEEK
256 cross-mixer (500 μm i.d.) and subsequently connected to the inlet of
257 the 3 mL PFA capillary tubing (750 μm i.d.). The cross-mixer and
258 microreactor were submerged in a sonication bath, and sonication was
259 applied during operation. The first syringe pump (containing two
260 syringes) was operated at 2×0.75 mL/min, and the second syringe
261 pump was operated at 1.5 mL/min (total 3 mL/min flow rate, 60 s
262 residence time). The outlet of the reactor was fitted to an argon-filled
263 round-bottom flask with septum via a needle connection. An argon-
264 filled balloon was attached in order to ensure a constant pressure. The
265 reaction mixture was evaporated under reduced pressure at the
266 rotavap. Residue was dissolved in diethyl ether and evaporated again at
267 the rotavap. This procedure was repeated five times, and then the
268 residue was dissolved in a minimum amount of acetone, followed by
269 addition of diethyl ether until a cloudy solution was obtained. Next,
270 the resulting mixture was kept in the freezer (-26 $^\circ\text{C}$) overnight.
271 Formed crystals were filtered off and washed with a minimum of
272 diethyl ether.

273 *Di-*p*-tolyliodonium Trifluoromethanesulfonate (3a).*¹⁸ GP1 was
274 used on a 5 mmol scale. Purification by recrystallization in diethyl
275 ether afforded the product as gray solids (2.04g, 89%): mp 131–133
276 $^\circ\text{C}$ (lit.¹⁸ 121–123 $^\circ\text{C}$); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.15–8.05
(m, 4H), 7.31 (d, $J = 8.1$ Hz, 4H), 2.32 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101
277 MHz, $\text{DMSO}-d_6$) δ 142.5, 135.0, 132.3, 120.8 (q, $J = 322.3$ Hz), 113.1,
278 20.8. 279

280 *Diphenyliodonium Trifluoromethanesulfonate (3b).*¹⁹ GP1 was
281 used on a 5 mmol scale. Purification by recrystallization in diethyl
282 ether afforded the product as off-white solids (1.89 g, 88%). GP3 was
283 used on a 4 mmol scale. Purification by recrystallization in diethyl
284 ether afforded the product as off-white solids (1.55 g, 90%): mp 169–
285 173 $^\circ\text{C}$ (lit.¹⁹ 172–174 $^\circ\text{C}$); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.27
286 (d, $J = 8.0$ Hz, 4H), 7.64 (t, $J = 7.4$ Hz, 2H), 7.52 (t, $J = 7.7$ Hz, 4H);
287 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO}-d_6$) δ 135.2, 132.1, 131.8, 120.8 (q,
288 $J = 322.3$ Hz), 116.5.

289 *Bis(4-fluorophenyl)iodonium Trifluoromethanesulfonate (3c).*^{2c}
290 GP1 was used on a 5 mmol scale. Purification by recrystallization in
291 diethyl ether afforded the product as gray solids (1.35 g, 58%). GP3
292 was used on a 4 mmol scale. Purification by recrystallization in diethyl
293 ether afforded the product as gray solids (1.34 g, 72%): mp 168–170
294 $^\circ\text{C}$ (lit.^{2c} 168–170 $^\circ\text{C}$); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.39–8.22
295 (m, 4H), 7.42 (t, $J = 8.9$ Hz, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO}-$
296 d_6) δ 164.4 (d, $J = 251.5$ Hz), 138.4 (d, $J = 9.1$ Hz), 122.7 (q, $J = 322.6$
297 Hz), 119.8, 119.6, 111.6 (d, $J = 3.0$ Hz); ^{19}F NMR (376 MHz, $\text{DMSO}-$
298 d_6) δ -77.75, -106.60 (tt, $J = 9.0, 5.0$ Hz).

299 *(4-Iodophenyl)(phenyl)iodonium Trifluoromethanesulfonate*
300 *(3d).*¹⁹ GP1 was used on a 5 mmol scale. Purification by 300

301 recrystallization in diethyl ether afforded the product as off-white
302 solids (2.09 g, 75%): mp 144–148 °C (lit.¹⁹ 146–148 °C); ¹H NMR
303 (400 MHz, DMSO-*d*₆) δ 8.24 (d, *J* = 7.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz,
304 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8
305 Hz, 2H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 140.39, 136.75,
306 135.16, 132.14, 131.80, 120.67 (*q*, *J* = 322.4 Hz), 116.67, 115.83,
307 100.28.

308 **Phenyl(thiophen-2-yl)iodonium Trifluoromethanesulfonate**
309 **(3e)**.^{2c} GP1 was used on a 5 mmol scale. Purification by
310 recrystallization in diethyl ether afforded the product as light brown
311 solids (937 mg, 43%): mp 143–146 °C (lit.^{2c} 144–146 °C); ¹H NMR
312 (400 MHz, DMSO-*d*₆) δ 8.29–8.21 (m, 2H), 8.07 (dd, *J* = 3.8, 1.3 Hz,
313 1H), 7.97 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.71–7.63 (m, 1H), 7.58–7.47
314 (m, 2H), 7.18 (dd, *J* = 5.3, 3.8 Hz, 1H); ¹³C{¹H} NMR (101 MHz,
315 DMSO-*d*₆) δ 140.9, 137.8, 135.1, 132.6, 132.2, 130.1, 121.2 (*q*, *J* =
316 322.2 Hz), 119.8, 101.2.

317 **Mesityl(phenyl)iodonium Trifluoromethanesulfonate (3f)**.²⁰ GP1
318 was used on a 5 mmol scale. Purification by recrystallization in diethyl
319 ether afforded the product as off-white solids (2.05g, 87%): mp 148–
320 150 °C (lit.²⁰ 137–138 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.06–
321 7.94 (m, 2H), 7.69–7.60 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.22 (s,
322 2H), 2.62 (s, 6H), 2.29 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-
323 *d*₆) δ 143.1, 141.6, 134.5, 131.9, 129.8, 122.6, 120.7 (*q*, *J* = 322.3 Hz),
324 114.5, 26.3, 20.5.

325 **Mesityl(*p*-tolyl)iodonium Trifluoromethanesulfonate (3g)**.²⁰ GP1
326 was used on a 5 mmol scale. Purification by recrystallization in diethyl
327 ether afforded the product as white solids (2.07g, 85%): mp 181–183
328 °C (lit.²⁰ 183–184 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.87 (d, *J*
329 = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (s, 2H), 2.60 (s, 6H),
330 2.33 (s, 3H), 2.29 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO) δ
331 143.0, 142.2, 141.4, 134.5, 132.5, 129.7, 122.7, 110.9, 26.3, 20.8, 20.5.

332 **(4-Acetamidophenyl)(mesityl)iodonium Trifluoromethanesulfonate**
333 **(3h)**. GP1 was used on a 5 mmol scale. Purification by
334 recrystallization in diethyl ether afforded the product as off-white
335 solids (741 mg, 28%): mp 136–138 °C; ¹H NMR (399 MHz, DMSO-
336 *d*₆) δ 10.28 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H),
337 7.20 (s, 2H), 2.60 (s, 6H), 2.28 (s, 3H), 2.05 (s, 3H); ¹³C{¹H} NMR
338 (100 MHz, DMSO) δ 169.5, 143.4, 142.8, 141.8, 136.3, 130.2, 123.4,
339 122.7, 122.0, 106.3, 26.7, 24.6, 21.0; HRMS (ESI) calcd for
340 C₁₇H₁₉F₃INO [M – OTf]⁺ 380.0506, found 380.0514.

341 **(4-Fluorophenyl)(mesityl)iodonium Trifluoromethanesulfonate**
342 **(3i)**.²⁰ GP1 was used on a 5 mmol scale. Purification by
343 recrystallization in diethyl ether afforded the product as gray solids
344 (1.96 g, 80%): mp 173–176 °C (lit.²⁰ 177–178 °C); ¹H NMR (400
345 MHz, CDCl₃) δ 7.73 (dd, *J* = 8.5, 4.7 Hz, 2H), 7.10 (d, *J* = 4.9 Hz,
346 4H), 2.63 (s, 6H), 2.35 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ
347 164.7 (d, *J* = 255.0 Hz), 144.6, 142.5, 135.7 (d, *J* = 8.7 Hz), 130.5,
348 121.2, 120.3 (*q*, *J* = 319.8 Hz), 119.8 (d, *J* = 22.9 Hz), 105.3 (d, *J* = 3.4
349 Hz), 27.2, 21.3; ¹⁹F NMR (376 MHz, CDCl₃) δ –78.40, –106.01
350 (ddd, *J* = 12.8, 8.2, 4.7 Hz).

351 **(4-Iodophenyl)(mesityl)iodonium Trifluoromethanesulfonate**
352 **(3j)**. GP1 was used on a 5 mmol scale. Purification by recrystallization
353 in diethyl ether afforded the product as dark white solids (2.24 g,
354 75%): mp 193–195 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.86 (d, *J*
355 = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.23 (s, 2H), 2.58 (s, 6H),
356 2.30 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 143.5, 141.7,
357 141.6, 140.4, 136.8, 136.0, 129.9, 129.82, 122.7, 122.6, 116.3 (*q*, *J* =
358 397.4 Hz), 99.7, 26.3, 20.5.

359 **[1,1'-Biphenyl]-4-yl(mesityl)iodonium Trifluoromethanesulfonate**
360 **(3k)**. GP1 was used on a 5 mmol scale. Purification by recrystallization
361 in diethyl ether afforded the product as pale green solids (1.67 g,
362 61%): mp 185–187 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* =
363 8.6 Hz, 2H), 7.63–7.58 (m, 2H), 7.54–7.39 (m, 5H), 7.14 (s, 2H),
364 2.67 (s, 6H), 2.38 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.4,
365 144.9, 142.7, 138.5, 133.5, 131.1, 130.7, 129.3, 129.0, 127.3, 120.5,
366 109.9, 27.4, 21.3; HRMS (ESI) calcd for C₂₁H₂₀I [M – OTf]⁺
367 399.0604, found 399.0585.

368 **Mesityl(*o*-tolyl)iodonium Trifluoromethanesulfonate (3l)**.²⁰ GP1
369 was used on a 5 mmol scale. Purification by recrystallization in diethyl
370 ether afforded the product as white solids (2.09g, 86%): mp 170–172

°C (lit.²⁰ 167–168 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.38
371 (m, 3H), 7.17 (td, *J* = 7.7, 7.1, 2.0 Hz, 1H), 7.11 (s, 2H), 2.60 (s, 9H),
372 2.36 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.8, 142.7, 140.4,
373 133.7, 132.7, 132.6, 130.9, 130.0, 120.5 (*q*, *J* = 321.8 Hz), 119.7, 115.8,
374 27.1, 25.05, 21.2.

375
376 **(2-Fluorophenyl)(mesityl)iodonium Trifluoromethanesulfonate**
377 **(3m)**.²¹ GP1 was used on a 5 mmol scale. Purification by
378 recrystallization in diethyl ether afforded the product as white solids
379 (907 mg, 37%): mp 157–159 °C (lit.²¹ 161–162 °C); ¹H NMR (399
380 MHz, CDCl₃) δ 7.81 (ddd, *J* = 7.8, 5.8, 1.6 Hz, 1H), 7.59 (dddd, *J* =
381 8.6, 7.2, 5.4, 1.6 Hz, 1H), 7.35–7.19 (m, 2H), 7.08 (s, 2H), 2.68 (s,
382 6H), 2.34 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.5 (d, *J* =
383 252.1 Hz), 144.6, 142.7, 136.1, 135.2 (d, *J* = 8.0 Hz), 130.6, 127.6 (d, *J* =
384 3.3 Hz), 121.5, 117.6 (d, *J* = 21.8 Hz), 98.0 (d, *J* = 23.9 Hz), 27.1,
385 21.2; ¹⁹F NMR (376 MHz, CDCl₃) δ –78.35, –95.37 to –96.24 (m).

386 **Mesityl(*m*-tolyl)iodonium Trifluoromethanesulfonate (3n)**.²¹ GP1
387 was used on a 5 mmol scale. Purification by recrystallization in diethyl
388 ether afforded the product as off-white solids (1.94 g, 80%): mp 169–
389 171 °C (lit.²¹ 171–172 °C); ¹H NMR (399 MHz, CDCl₃) δ 7.58 (s,
390 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.8
391 Hz, 1H), 7.10 (s, 2H), 2.62 (s, 6H), 2.35 (s, 6H); ¹³C{¹H} NMR (100
392 MHz, CDCl₃) δ 144.6, 143.3, 142.7, 133.6, 132.9, 132.1, 130.5, 129.9,
393 120.5 (*q*, *J* = 320.5 Hz), 120.2, 111.6, 27.3, 21.5, 21.3.

394 **(3,5-Dimethylphenyl)(mesityl)iodonium Trifluoromethanesulfonate**
395 **(3o)**. GP1 was used on a 5 mmol scale. Purification by
396 recrystallization in diethyl ether afforded the product as off-white
397 solids (1.80 g, 72%): mp 200–203 °C; ¹H NMR (399 MHz, CDCl₃) δ
398 7.28 (s, 2H), 7.14 (s, 1H), 7.11 (s, 2H), 2.63 (s, 6H), 2.36 (s, 3H),
399 2.30 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.6, 142.9, 142.7,
400 134.0, 130.6, 130.5, 120.7 (*q*, *J* = 321.3 Hz), 120.0, 111.4, 27.3, 21.5,
401 21.3; HRMS (ESI) calcd for C₁₇H₂₀I [M – OTf]⁺ 351.0604, found
402 351.0616.

403 **Dimesityliodonium Trifluoromethanesulfonate (3p)**.¹⁹ GP1 was
404 used on a 5 mmol scale. Purification by recrystallization in diethyl
405 ether afforded the product as brown solids (1.44 g, 56%). GP3 was
406 used on a 4 mmol scale. Purification by recrystallization in diethyl
407 ether afforded the product as brown solids (1.08 g, 53%): mp 183–
408 186 °C (lit.¹⁹ 187–188 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s,
409 4H), 2.51 (s, 12H), 2.33 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ
410 144.0, 142.4, 131.1, 117.4, 26.3, 21.1.

411 **Mesityl(4-methoxyphenyl)iodonium Trifluoromethanesulfonate**
412 **(3q)**.^{2c} GP1 was used on a 5 mmol scale. Purification by
413 recrystallization in diethyl ether afforded the product as dark gray
414 solids (502 mg, 20%): mp 148–150 °C (lit.^{2c} 148–151 °C); ¹H NMR
415 (400 MHz, CDCl₃) δ 7.69–7.57 (m, 2H), 7.10 (s, 2H), 6.98–6.85 (m,
416 2H), 3.82 (s, 3H), 2.64 (s, 6H), 2.35 (s, 3H); ¹³C{¹H} NMR (101
417 MHz, CDCl₃) δ 162.8, 144.7, 142.4, 135.5, 130.6, 121.0, 118.3, 99.9,
418 55.9, 27.2, 21.3.

419 **Mesityl(thiophen-2-yl)iodonium Trifluoromethanesulfonate (3r)**.
420 GP1 was used on a 5 mmol scale. Purification by recrystallization in
421 diethyl ether afforded the product as light brown solids (1.20 g, 50%):
422 mp 160–162 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 3.8, 1.2
423 Hz, 1H), 7.61 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.11–7.04 (m, 3H), 2.73 (s,
424 6H), 2.33 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.5, 141.7,
425 139.7, 135.8, 130.6, 129.8, 125.7, 120.3 (*q*, *J* = 319.6 Hz), 94.5, 27.2,
426 21.2; HRMS (ESI) calcd for C₁₃H₁₄IS [M – OTf]⁺ 328.9855, found
427 328.9857.

428 **(9,10-Dioxo-9,10-dihydroanthracen-1-yl)(*p*-tolyl)iodonium Tri-**
429 **fluoromethanesulfonate (3s)**. GP2 was used on a 5 mmol scale.
430 Purification by recrystallization in diethyl ether afforded the product as
431 light gray solids (1.29 g, 45%): mp 225–230 °C; ¹H NMR (400 MHz,
432 DMSO-*d*₆) δ 8.47–8.41 (m, 1H), 8.39 (dd, *J* = 7.0, 2.0 Hz, 1H), 8.30
433 (dd, *J* = 7.2, 1.9 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 2H), 8.09 (qd, *J* = 7.3,
434 1.7 Hz, 2H), 8.02 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.36
435 (dd, *J* = 8.2, 1.0 Hz, 1H), 2.52 (s, 3H); ¹³C{¹H} NMR (101 MHz,
436 DMSO) δ 185.3, 181.2, 144.9, 138.1, 137.3, 136.9, 136.3, 135.7, 133.7,
437 133.3, 132.2, 131.9, 130.4, 129.9, 128.2, 127.8, 114.7, 108.4, 21.7;
438 HRMS (ESI) calcd for C₂₁H₁₄IO₂ [M – OTf]⁺ 425.0033, found
439 425.0030.

- 440 *Bis(4-chlorophenyl)iodonium Trifluoromethanesulfonate (3t)*.^{2c}
 441 GP2 was used on a 5 mmol scale. Purification by recrystallization in
 442 diethyl ether afforded the product as white solids (1.57 g, 63%). GP3
 443 was used on a 4 mmol scale. Purification by recrystallization in diethyl
 444 ether afforded the product as white solids (1.32 g, 66%): mp 183–187
 445 °C (lit.^{2c} 185–186 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.42–8.08
 446 (m, 4H), 7.75–7.47 (m, 4H); ¹³C{¹H} NMR (101 MHz, DMSO) δ
 447 137.9, 137.4, 132.3, 115.2.
- 448 *Bis(4-bromophenyl)iodonium Trifluoromethanesulfonate (3u)*.^{2c}
 449 GP2 was used on a 5 mmol scale. Purification by recrystallization in
 450 diethyl ether afforded the product as white solids (2.37 g, 81%). GP3
 451 was used on a 4 mmol scale. Purification by recrystallization in diethyl
 452 ether afforded the product as white solids (1.46 g, 62%): mp 183–188
 453 °C (lit.^{2c} 185–190 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.17 (d, *J*
 454 = 8.6 Hz, 4H), 7.77 (d, *J* = 8.6 Hz, 4H); ¹³C{¹H} NMR (101 MHz,
 455 DMSO-*d*₆) δ 137.0, 134.7, 126.3, 115.4.
- 456 *(4-Bromophenyl)(4-chlorophenyl)iodonium Trifluoromethane-*
 457 *sulfonate (3v)*. GP2 was used on a 5 mmol scale. Purification by
 458 recrystallization in diethyl ether afforded the product as white needles
 459 (2.01 g, 74%): mp 201–204 °C; ¹H NMR (399 MHz, DMSO-*d*₆) δ
 460 8.31–8.23 (m, 2H), 8.26–8.13 (m, 2H), 7.86–7.71 (m, 2H), 7.70–
 461 7.58 (m, 2H); ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 138.0, 137.5,
 462 137.5, 135.2, 132.3, 126.8, 121.2 (q, *J* = 322.5 Hz), 115.9, 115.1;
 463 HRMS (ESI) calcd for C₁₂H₈BrClI [M – OTf]⁺ 392.8537, found
 464 392.8553.
- 465 *(4-Nitrophenyl)(phenyl)iodonium Trifluoromethanesulfonate*
 466 *(3w)*.^{2c} GP2 was used on a 5 mmol scale. Purification by
 467 recrystallization in diethyl ether afforded the product as yellow solids
 468 (1.76 g, 74%): mp 178–183 °C (lit.^{2c} 180–185 °C); ¹H NMR (400
 469 MHz, DMSO-*d*₆) δ 8.51–8.45 (m, 2H), 8.35–8.27 (m, 4H), 7.74–
 470 7.65 (m, 1H), 7.61–7.50 (m, 2H); ¹³C{¹H} NMR (101 MHz, DMSO-
 471 *d*₆) δ 149.4, 136.4, 135.5, 132.4, 131.96, 126.3, 122.6, 120.7 (q, *J* =
 472 322.4 Hz), 116.9.
- 473 *Mono(3-(p-tolyl)iodonio)pyridin-1-ium Bis-*
 474 *(trifluoromethanesulfonate) (3x)*.^{2c} GP2 was used on a 5 mmol
 475 scale. Purification by recrystallization in diethyl ether afforded the
 476 product as light yellow solids (1.40 g, 47%): mp 163–167 °C (lit.^{2c}
 477 170–172 °C); ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.27 (d, *J* = 2.2 Hz,
 478 1H), 8.82 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.64 (dt, *J* = 8.2, 1.8 Hz, 1H),
 479 8.26–8.07 (m, 2H), 7.58 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz,
 480 2H), 2.35 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 153.4,
 481 152.1, 142.9, 142.3, 135.3, 132.5, 126.9, 120.7 (q, *J* = 323.3 Hz), 116.2,
 482 113.0, 20.9.
- 483 *Mesityl(4-(trifluoromethyl)phenyl)iodonium Trifluoromethane-*
 484 *sulfonate (3y)*. GP2 was used on a 5 mmol scale. Purification by
 485 recrystallization in diethyl ether afforded the product as brown solids
 486 (1.03 g, 38%): mp 202–205 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ
 487 8.14 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 2H), 2.59
 488 (s, 6H), 2.31 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 143.5,
 489 141.74, 135.0, 131.8, 129.9, 128.4 (d, *J* = 3.7 Hz), 124.7, 122.6, 120.5
 490 (q, *J* = 295.3 Hz), 118.7, 26.0; ¹⁹F NMR (376 MHz, DMSO-*d*₆)
 491 δ –61.68, –77.75; HRMS (ESI) calcd for C₁₆H₁₅F₃I [M – OTf]⁺
 492 391.0165, found 391.0183.
- 493 *(4-Chlorophenyl)(mesityl)iodonium Trifluoromethanesulfonate*
 494 *(3z)*.²⁰ GP2 was used on a 5 mmol scale. Purification by
 495 recrystallization in diethyl ether afforded the product as light gray
 496 solids (2.21 g, 87%): mp 161–163 °C (lit.²⁰ 132–133 °C); ¹H NMR
 497 (400 MHz, CDCl₃) δ 7.67–7.60 (m, 2H), 7.40–7.34 (m, 2H), 7.11 (s,
 498 2H), 2.62 (s, 6H), 2.36 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ
 499 144.8, 142.6, 138.9, 134.4, 132.5, 130.6, 120.9, 120.8 (q, *J* = 237.7 Hz),
 500 108.9, 27.2, 21.3.
- 501 *(4-Bromophenyl)(mesityl)iodonium Trifluoromethanesulfonate*
 502 *(3aa)*.²⁰ GP2 was used on a 5 mmol scale. Purification by
 503 recrystallization in diethyl ether afforded the product as light gray
 504 solids (2.48 g, 90%): mp 187–190 °C (lit.²⁰ 179–180 °C); ¹H NMR
 505 (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz,
 506 2H), 7.09 (s, 2H), 2.61 (s, 6H), 2.34 (s, 3H); ¹³C{¹H} NMR (101
 507 MHz, CDCl₃) δ 144.6, 142.6, 135.3, 134.7, 130.5, 126.9, 120.9, 120.3
 508 (q, *J* = 319.9 Hz), 109.9, 27.2, 21.3.
- 509 *(4-(Ethoxycarbonyl)phenyl)(mesityl)iodonium Triflate (3ab)*.²⁰
 510 GP2 was used on a 5 mmol scale. Purification by recrystallization in
 511 diethyl ether afforded the product as gray solids (1.39 g, 51%): mp
 512 173–175 °C (lit.²⁰ 178–179 °C); ¹H NMR (399 MHz, CDCl₃) δ 8.01
 513 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 1.0 Hz, 2H),
 514 4.36 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 6H), 2.36 (s, 3H), 1.36 (t, *J* = 7.1 Hz,
 515 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 164.9, 144.8, 142.7, 133.7,
 516 132.9, 132.8, 130.5, 120.7, 120.3 (q, *J* = 319.9 Hz), 116.5, 62.0, 27.2,
 517 21.3, 14.3.
- 518 *(4-Acetylphenyl)(mesityl)iodonium Trifluoromethanesulfonate*
 519 *(3ac)*.²⁷ GP2 was used on a 5 mmol scale. Purification by
 520 recrystallization in diethyl ether afforded the product as gray solids
 521 (2.03 g, 79%): mp 183–184 °C (lit.²¹ 183–185 °C); ¹H NMR (399
 522 MHz, CDCl₃) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H),
 523 7.14 (s, 2H), 2.62 (s, 6H), 2.59 (s, 3H), 2.38 (s, 3H); ¹³C{¹H} NMR
 524 (100 MHz, CDCl₃) δ 196.3, 145.1, 142.8, 139.6, 133.0, 131.6, 130.7,
 525 120.4, 116.6, 27.3, 26.8, 21.3.
- 526 *Mesityl(3-(trifluoromethyl)phenyl)iodonium Trifluoromethane-*
 527 *sulfonate (3ad)*.²⁰ GP2 was used on a 5 mmol scale. Purification by
 528 recrystallization in diethyl ether to afford the product as brown solids
 529 (1.24 g, 46%): mp 180–182 °C (lit.²⁰ 181–183 °C); ¹H NMR (400
 530 MHz, CDCl₃) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.77 (d, *J* = 7.8
 531 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.12 (s, 2H), 2.63 (s, 6H), 2.36 (s,
 532 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 144.9, 142.7, 134.2 (d, *J* =
 533 33.8 Hz), 132.5, 130.6, 129.8 (d, *J* = 4.0 Hz), 128.6 (d, *J* = 3.7 Hz),
 534 123.9, 121.2, 121.0, 120.2 (q, *J* = 319.2 Hz), 112.1, 27.2 21.3; ¹⁹F
 535 NMR (376 MHz, CDCl₃) δ –63.05, –78.53.
- 536 *Mesityl(3-nitrophenyl)iodonium Trifluoromethanesulfonate*
 537 *(3ae)*. GP2 was used on a 5 mmol scale. Purification by
 538 recrystallization in diethyl ether afforded the product as brown solids
 539 (1.19 g, 46%): mp 162–164 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ
 540 8.82 (t, *J* = 2.0 Hz, 1H), 8.42 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 8.18 (ddd,
 541 *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 7.26 (s, 2H), 2.61 (s,
 542 6H), 2.32 (s, 3H); ¹³C{¹H} NMR (101 MHz, DMSO-*d*₆) δ 148.6,
 543 143.6, 141.9, 139.7, 132.9, 130.0, 128.9, 126.4, 122.7, 120.7 (q, *J* =
 544 322.1 Hz), 114.1, 26.4, 20.6; HRMS (ESI) calcd for C₁₅H₁₅INO₂ [M
 545 – OTf]⁺ 368.0142, found 368.0154.
- 546 *(2-Chlorophenyl)(mesityl)iodonium Trifluoromethanesulfonate*
 547 *(3af)*.²¹ GP2 was used on a 5 mmol scale. Purification by
 548 recrystallization in diethyl ether afforded the product as brown solids
 549 (1.24 g, 49%): mp 171–172 °C (lit.²¹ 167–168 °C); ¹H NMR (399
 550 MHz, CDCl₃) δ 7.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (td, *J* = 7.7, 1.4
 551 Hz, 1H), 7.29 (td, *J* = 7.8, 7.4, 1.5 Hz, 1H), 7.17 (s, 2H), 7.09 (dd, *J* =
 552 8.2, 1.4 Hz, 1H), 2.62 (s, 6H), 2.40 (s, 3H); ¹³C{¹H} NMR (100
 553 MHz, CDCl₃) δ 145.4, 143.0, 135.5, 133.5, 132.5, 131.4, 131.0, 130.6,
 554 120.8, 120.4 (q, *J* = 319.9 Hz), 112.5, 27.2, 21.3.
- 555 *(2-Bromophenyl)(mesityl)iodonium Trifluoromethanesulfonate*
 556 *(3ag)*.²¹ GP2 was used on a 5 mmol scale. Purification by
 557 recrystallization in diethyl ether afforded the product as brown solids
 558 (1.54 g, 56%): mp 172–173 °C (lit.²¹ 167–168 °C); ¹H NMR (399
 559 MHz, CDCl₃) δ 7.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 (td, *J* = 7.7, 1.5
 560 Hz, 1H), 7.33 (ddd, *J* = 8.9, 7.5, 1.5 Hz, 1H), 7.20 (s, 2H), 6.86 (dd, *J* =
 561 8.2, 1.4 Hz, 1H), 2.61 (s, 6H), 2.41 (s, 3H); ¹³C{¹H} NMR (100
 562 MHz, CDCl₃) δ 145.6, 143.0, 134.6, 133.3, 131.5, 131.2, 131.0, 124.7,
 563 121.6, 120.4 (q, *J* = 319.8 Hz), 115.4, 27.2, 21.4.
- 564 *Mesityl(2-(trifluoromethyl)phenyl)iodonium Trifluoromethane-*
 565 *sulfonate (3ah)*.²¹ GP2 was used on a 5 mmol scale. Purification by
 566 recrystallization in diethyl ether afforded the product as brown solids
 567 (891 mg, 33%): mp 176–178 °C (lit.²¹ 180–181 °C); ¹H NMR (400
 568 MHz, CDCl₃) δ 7.96–7.89 (m, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.54 (td,
 569 *J* = 7.8, 1.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.19 (s, 2H), 2.62 (s,
 570 6H), 2.41 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 145.9, 143.1,
 571 135.8, 133.1, 132.2, 131.4, 131.1, 129.6 (d, *J* = 4.8 Hz), 124.1, 121.9,
 572 120.1 (q, *J* = 264.9 Hz), 107.5, 27.2, 21.4; ¹⁹F NMR (376 MHz,
 573 CDCl₃) δ –59.93, –78.44.
- 574 *3-(Mesityliodonio)pyridin-1-ium Bis(trifluoromethanesulfonate)*
 575 *(3ai)*.^{2c} GP2 was used on a 5 mmol scale. Purification by
 576 recrystallization in diethyl ether afforded the product as light yellow
 577 solids (592 mg, 19%): mp 155–158 °C (lit.^{2c} 138–141 °C); ¹H NMR
 578 (400 MHz, DMSO-*d*₆) δ 9.06 (d, *J* = 2.3 Hz, 1H), 8.79 (dd, *J* = 4.8, 1.3

579 Hz, 1H), 8.42 (d, $J = 8.4$ Hz, 1H), 7.55 (dd, $J = 8.3, 4.7$ Hz, 1H), 7.23
 580 (s, 2H), 2.61 (s, 6H), 2.30 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz,
 581 DMSO- d_6) δ 152.9, 151.9, 143.3, 142.1, 141.6, 129.9, 127.1, 122.6,
 582 120.7 (q, $J = 322.4$ Hz), 114.2, 26.3, 20.5.
 583 **Mesityl(4-nitrophenyl)iodonium Trifluoromethanesulfonate**
 584 (**3aj**).²⁰ GP2 was used on a 5 mmol scale. Purification by
 585 recrystallization in diethyl ether afforded the product as brown solids
 586 (827 mg, 32%): mp 197–200 °C (lit.²⁰ 208 °C); ^1H NMR (399 MHz,
 587 DMSO- d_6) δ 8.26 (d, $J = 8.4$ Hz, 2H), 8.22–8.12 (m, 2H), 7.26 (s,
 588 2H), 2.59 (s, 6H), 2.31 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-
 589 d_6) δ 149.3, 143.6, 141.8, 135.5, 130.0, 126.2, 122.8 (q, $J = 201.9$ Hz),
 590 26.3, 20.6.
 591 ***o*-Tolyl(*p*-tolyl)iodonium Trifluoromethanesulfonate (**3ak**)**.^{11b}
 592 GP3 was used on a 4 mmol scale. Purification by recrystallization in
 593 diethyl ether afforded the product as brown solids (*ortho*–*para* 90%,
 594 *para*–*para* 5%, *ortho*–*ortho* 5%, 770 mg, 42%): mp 158–160 °C; ^1H
 595 NMR (400 MHz, CDCl_3) δ 8.09 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.85–7.71
 596 (m, 2H), 7.52 (td, $J = 7.5, 1.2$ Hz, 1H), 7.43 (dd, $J = 7.7, 1.7$ Hz, 1H),
 597 7.22 (t, $J = 5.4$ Hz, 3H), 2.60 (s, 3H), 2.37 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR
 598 (101 MHz, CDCl_3) δ 143.4, 141.4, 137.6, 134.7, 133.5, 133.2, 132.1,
 599 129.8, 120.4 (q, $J = 320.0$ Hz), 119.0, 109.0, 25.8, 21.5.
 600 ***Bis*(4-*tert*-butylphenyl)iodonium Trifluoromethanesulfonate**
 601 (**3al**).²² GP3 was used on a 4 mmol scale. Purification by
 602 recrystallization in diethyl ether afforded the product as white needles
 603 (1.52 g, 70%): mp 163–165 °C (lit.²² 164–165 °C); ^1H NMR (400
 604 MHz, CDCl_3) δ 7.87–7.76 (m, 4H), 7.43–7.36 (m, 4H), 1.23 (s,
 605 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 156.7, 134.8, 129.7, 120.3
 606 (d, $J = 321.3$ Hz), 109.4, 35.3, 31.0.
 607 ***Bis*(2,5-dimethylphenyl)iodonium Trifluoromethanesulfonate**
 608 (**3am**).^{11b} GP3 was used on a 5 mmol scale. Purification by
 609 recrystallization in diethyl ether afforded the product as brown solids
 610 (896 mg, 46%): mp 168–169 °C (lit.^{11b} 173–175 °C); ^1H NMR (399
 611 MHz, CDCl_3) δ 7.73 (s, 2H), 7.33 (s, 4H), 2.56 (s, 6H), 2.34 (s, 6H);
 612 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 140.6, 138.1, 136.9, 134.4, 132.0,
 613 117.0, 25.1, 20.8.

614 ■ ASSOCIATED CONTENT

615 ● Supporting Information

616 The Supporting Information is available free of charge on the
 617 ACS Publications website at DOI: 10.1021/acs.joc.7b01346.

618 Description of reaction setups, optimization of reaction
 619 conditions and enthalpy measurements and spectral data
 620 of all products (PDF)

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629 Notes

630 The authors declare no competing financial interest.

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635 ■ REFERENCES

636 (1) (a) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*,
 637 9052–9070. (b) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656–
 638 3665. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523–
 639 2584.

(2) (a) Aradi, K.; Tóth, B.; Tolnai, G.; Novák, Z. *Synlett* **2016**, *27*, 640
 1456–1485. (b) Chan, L.; McNally, A.; Toh, Q. Y.; Mendoza, A.;
 641 Gaunt, M. J. *Chem. Sci.* **2015**, *6*, 1277–1281. (c) Gonda, Z.; Novák, Z.
 642 *Chem. - Eur. J.* **2015**, *21*, 16801–16806.
 (3) (a) Gemoets, H. P. L.; Laudadio, G.; Verstraete, K.; Hessel, V.;
 643 Noël, T. *Angew. Chem., Int. Ed.* **2017**, *56*, 7161–7165. (b) Sheng, J.;
 644 Su, X.; Cao, C.; Chen, C. *Org. Chem. Front.* **2016**, *3*, 501–504.
 645 (c) Duong, H. A.; Gilligan, R. E.; Cooke, M. L.; Phipps, R. J.; Gaunt,
 646 M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 463–466. (d) Phipps, R. J.;
 647 Gaunt, M. J. *Science* **2009**, *323*, 1593–1597. (e) Deprez, N. R.;
 648 Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924–1935. (f) Kalyani, D.;
 649 Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*,
 650 7330–7331.
 (4) (a) Wagner, A. M.; Sanford, M. S. *J. Org. Chem.* **2014**, *79*, 2263–
 651 2267. (b) Huang, X.; Zhu, Q.; Xu, Y. *Synth. Commun.* **2001**, *31*, 2823–
 652 2828.
 (5) Jalalian, N.; Ishikawa, E. E.; Silva, L. F.; Olofsson, B. *Org. Lett.* **2011**, *13*, 1552–1555.
 653 (6) Sandtorv, A. H.; Stuart, D. R. *Angew. Chem., Int. Ed.* **2016**, *55*,
 654 15812–15815.
 (7) Xu, X.; Wang, D.; Ge, C.; Yu, X.; Wan, H. *Synlett* **2016**, *27*,
 655 2616–2620.
 (8) Reitti, M.; Villo, P.; Olofsson, B. *Angew. Chem., Int. Ed.* **2016**, *55*,
 656 8928–8932.
 (9) (a) Aggarwal, V. K.; Olofsson, B. *Angew. Chem., Int. Ed.* **2005**, *44*,
 657 5516–5519. (b) Wang, D.; Ge, B.; Li, L.; Shan, J.; Ding, Y. *J. Org.*
 658 *Chem.* **2014**, *79*, 8607–8613. (c) Oh, C. H.; Kim, J. S.; Jung, H. H. *J.*
 659 *Org. Chem.* **1999**, *64*, 1338–1340. (d) Chen, K.; Koser, G. F. *J. Org.*
 660 *Chem.* **1991**, *56*, 5764–5767.
 (10) (a) Qin, L.; Hu, B.; Neumann, K. D.; Linstad, E. J.; McCauley,
 661 K.; Veness, J.; Kempinger, J. J.; DiMaggio, S. G. *Eur. J. Org. Chem.* **2015**,
 662 2015, 5919–5924. (b) Watts, K.; Gattrell, W.; Wirth, T. *Beilstein*
 663 *J. Org. Chem.* **2011**, *7*, 1108–1114. (c) Hossain, M. D.; Kitamura, T.
 664 *Tetrahedron* **2006**, *62*, 6955–6960. (d) Carroll, M. A.; Pike, V. W.;
 665 Widdowson, D. A. *Tetrahedron Lett.* **2000**, *41*, 5393–5396.
 666 (e) Kaźmierczak, P.; Skulski, L. *Synthesis* **1995**, *1995*, 1027–1032.
 (11) (a) Bielawski, M.; Olofsson, B. *Chem. Commun.* **2007**, 2521–
 667 2523. (b) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**,
 668 349, 2610–2618.
 (12) For a flow approach on reaction calorimetry, see: Glotz, G.;
 669 Knoechel, D. J.; Podmore, P.; Gruber-Woelfler, H.; Kappe, C. O. *Org.*
 670 *Process Res. Dev.* **2017**, *21*, 763–770.
 (13) Peper-Bienzeisler, R.; Fickenfrerichs, H.; Jansen, W. *CHEM-*
 671 *KON* **2012**, *19*, 21–28.
 (14) Hallén, D. *J. Chem. Thermodyn.* **1993**, *25*, 519–524.
 672 (15) Noël, T.; Su, Y.; Hessel, V. *Top. Organomet. Chem.* **2015**, *57*, 1–
 673 41.
 (16) (a) Kockmann, N.; Thenée, P.; Fleischer-Trebes, C.; Laudadio,
 674 G.; Noel, T. *React. Chem. Eng.* **2017**, *2*, 258–280. (b) Gemoets, H. P.
 675 L.; Su, Y.; Shang, M.; Hessel, V.; Luque, R.; Noel, T. *Chem. Soc. Rev.* **2016**,
 676 45, 83–117. (c) Movsisyan, M.; Delbeke, E. I. P.; Berton, J. K.
 677 E. T.; Battilocchio, C.; Ley, S. V.; Stevens, C. V. *Chem. Soc. Rev.* **2016**,
 678 45, 4892–4928. (d) Gutmann, B.; Cantillo, D.; Kappe, C. O. *Angew.*
 679 *Chem., Int. Ed.* **2015**, *54*, 6688–6728.
 (17) (a) Kuhn, S.; Noël, T.; Gu, L.; Heider, P. L.; Jensen, K. F. *Lab*
 680 *Chip* **2011**, *11*, 2488–2492. (b) Noël, T.; Naber, J. R.; Hartman, R. L.;
 681 McMullen, J. P.; Jensen, K. F.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*,
 682 287–290.
 (18) Pérez, J. M.; Cano, R.; McGlacken, G. P.; Ramón, D. J. *RSC Adv.* **2016**,
 683 6, 36932–36941.
 (19) Kitamura, T.; Matsuyuki, J.-i.; Nagata, K.; Furuki, R.; Taniguchi,
 684 H. *Synthesis* **1992**, *1992*, 945–946.
 (20) Bigot, A.; Williamson, A. E.; Gaunt, M. J. *J. Am. Chem. Soc.* **2011**,
 685 133, 13778–13781.
 (21) Sinai, Á.; Mészáros, Á.; Gáti, T.; Kudar, V.; Palló, A.; Novák, Z.
 686 *Org. Lett.* **2013**, *15*, 5654–5657.
 (22) Hossain, M. D.; Ikegami, Y.; Kitamura, T. *J. Org. Chem.* **2006**, *706*
 687 71, 9903–9905.