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Regiospecific One-Pot Synthesis of Diaryliodonium Tetrafluoroborates from Arylboronic Acids and Aryl Iodides

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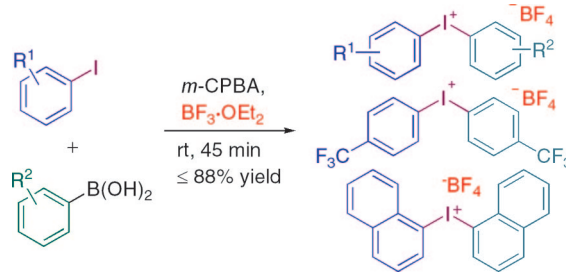

Diaryliodonium salts have recently received considerable attention as mild arylation reagents in organic synthesis. This paper describes a regiospecific, sequential one-pot synthesis of symmetrical and unsymmetrical diaryliodonium tetrafluoroborates, which are the most popular salts in metal-catalyzed arylations. The protocol is fast and high-yielding and has a large substrate scope. Furthermore, the corresponding diaryliodonium triflates can conveniently be obtained via an in situ anion exchange.

Introduction

Hypervalent iodine reagents are efficient alternatives to toxic heavy metal-based oxidants and expensive organometallic catalysts in many organic transformations. Compounds such as iodosylbenzene, (diacetoxyiodo)benzene, Dess−Martin periodinane and *o*-iodoxybenzoic acid (IBX) are frequently employed in natural product synthesis as mild, selective, and efficient oxidation reagents.[1–4]

Diaryliodonium salts constitute another class of iodine(III) reagents, having two carbon ligands bound to iodine. Their use in organic transformations has recently gained considerable attention, as their properties resemble those of organometallic complexes with Hg, Pb, and Pd.[5] Diaryliodonium salts are often applied in metal-catalyzed coupling reactions,[5,6] in α-arylations of carbonyl compounds,[7–10] as photoinitiators in polymerizations,[11,12] as benzyne generators,[13] and also as precursors to ^{18}F-labeled radioligands.[14]

Symmetric diaryliodonium salts are usually preferred in arylation reactions. However, the aryl moieties in unsymmetrical salts can often be differentiated electronically or sterically, thus enabling selective reactions with iodobenzene as the only side product.[6,15] Diaryliodonium salts with halide anions are generally sparingly soluble in many organic solvents, whereas triflate and tetrafluoroborate salts have good solubility. Another attractive property with the latter anions is their weak or nonexistent nucleophilicity, which makes them easily applicable in synthesis.[6,16]

Synthetic routes to diaryliodonium salts usually consist of two to three reaction steps, commonly followed by an anion exchange.[17–19] Although shorter routes have been reported, they

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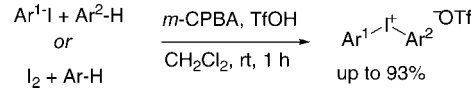
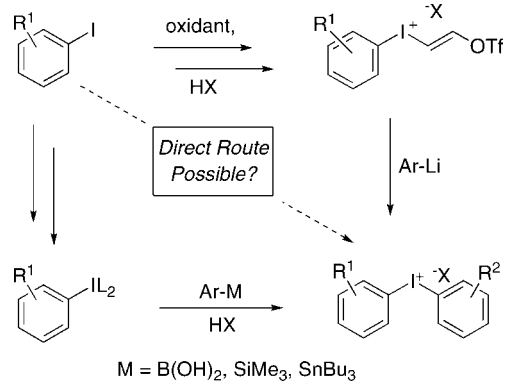
SCHEME 1. One-Pot Synthesis of Diaryliodonium Triflates



SCHEME 2. Regiospecific Routes to Diaryliodonium Salts



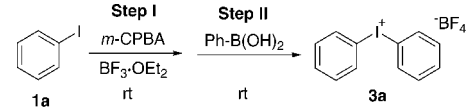
require the use of toxic chromium reagents[20] or inorganic iodine(III) reagents that need to be prepared in advance.[21–23] During the past few years, some one-pot procedures starting from arenes and iodoarenes or iodine have been developed, yielding both unsymmetrical and symmetrical salts.[24–28] The one-pot reaction developed in our laboratory employs *m*-CPBA and triflic acid, delivering diaryliodonium triflates in high yields and short reaction times (Scheme 1).[24,25]

A common feature of almost all synthetic routes is the electrophilic aromatic substitution of an arene onto an iodine(III) intermediate. High para selectivity is usually obtained, which limits the number of salts that can be obtained by these methods. Symmetric salts with ortho and meta substitutents are only accessible by a limited number of routes. These employ preformed iodine(III) reagents and lithiated arenes,[29,30] arylboronic acids,[31,32] stannanes,[19,33] or silanes[34] (Scheme 2).

Results and Discussion

To widen the scope of easily accessible diaryliodonium salts and circumvent the need for preformed iodine(III) reagents, we envisioned a *regiospecific* one-pot reaction starting from iodoarenes and a suitably activated arene source. Arylboronic acids were selected due to their high reactivity and low toxicity compared to silanes and stannanes, respectively. The protocol would employ *m*-CPBA, which has recently been used in several iodine oxidations,[35–39] and a suitable acid, the anion of which would end up in the salt. The use of boron trifluoride etherate was deemed interesting, as it could give rise to diaryliodonium *tetrafluoroborates* without an extra anion-exchange step.[40–42] Tetrafluoroborate salts have been employed in several recent papers on Pd-catalyzed arylation reactions,[6,43,44] but there is no general way to synthesize them.[31,45–48]

TABLE 1. Optimization of the Synthesis of 3a[a]



entry	$BF_3 \cdot OEt_2$ (equiv)	step I (min)	*T* (°C)	step II (min)	yield (%)[b]
1	2.0	<1	rt	60	29
2	2.0	15	rt	60	59
3	2.0	30	rt	60	75
4	2.0	60	rt	60	78
5	2.0	30	0	60	47
6	2.0	30	40	60	61
7	2.0	30	rt	30	74
8	2.5	30	rt	30	80
9	2.5	30	rt	15	82
10	3.0	30	rt	15	78
11[c]	2.5	30	rt	15	83

[a] Reaction conditions: **1a** (0.27 mmol) and *m*-CPBA (0.30 mmol) were dissolved in CH_2Cl_2 (1 mL), $BF_3 \cdot OEt_2$ was added, and the reaction was stirred at the indicated temperature for the time given in step I. **2a** (0.30 mmol) was subsequently added at 0 °C, and the mixture was then stirred at rt for the time given in step II. [b] Isolated yield. [c] 1 g scale, see the Experimental Section for details.

When the model substrates iodobenzene (**1a**) and phenylboronic acid (**2a**) were reacted in the presence of *m*-CPBA[49] and boron trifluoride at room temperature, diphenyl salt **3a** was indeed formed, albeit in low yield (Table 1, entry 1). An unwanted reaction between *m*-CPBA and **2a** was observed,

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(49) In our first report on *m*-CPBA oxidation of aryl iodides, the *m*-CPBA was used without drying (ref 24). However, new, commercially available cans of *m*-CPBA were found to contain large and variable amounts of H_2O, and drying under vacuum at room temperature for 1 h was necessary to obtain reproducible results. The percentage of active oxidizing agent was determined by iodometric titration; see the Supporting Information for further details.

which could explain the low yield. Fortunately, a short preoxidation time before addition of **2a** was sufficient to dramatically increase the yield of **3a** (entries 2−4). Temperature variation did not improve the results, either during the preoxidation (entries 5 and 6) or in the second step. The use of 2.5 equiv of $BF_3 \cdot OEt_2$ resulted in a faster reaction, and **3a** was isolated in high yield after only 45 min reaction time (entries 8 and 9). Salt **3a** was easily isolated by fast elution of the crude reaction mixture through a silica plug followed by precipitation from diethyl ether.[50] Furthermore, the protocol was easily scaled up to 1 g without loss in yield or purification efficiency (entry 11).

To investigate the scope of this reaction, the optimized conditions were subsequently applied to other substrates. Iodobenzene was reacted with electron-deficient and electron-rich arylboronic acids **2** to give unsymmetrical salts **3b**−**p** in high yields (Table 2). The halide-substituted arylboronic acids **2b**−**f** participated excellently in the reaction, yielding ortho-, meta- and para-substituted salts **3b-3f** (entries 2−6). Likewise, *o*- and *m*-methyl-substituted boronic acids **2g**,**h** delivered salts **3g**,**h** (entries 7 and 8). Sterically hindered substrates like 2,6-dimethylboronic acid **2i** could also be employed (entry 9).

The synthesis of electron-deficient iodonium salts generally requires heating and prolonged reaction times. It was therefore surprising that salts **3j**−**m**, obtained from electron-deficient boronic acids with varying substitution patterns, could be isolated in good yields in only 45 min (entries 10−13). Electron-rich substrates, such as *p*-methoxy- and 1-naphthylboronic acids **2o**,**p**, delivered salts **3o**,**p** in high yields when the reactions were performed at low temperature (entries 15 and 16). Unfortunately, *m*-methoxyphenylboronic acid did not give the expected meta-substituted iodonium salt. A para-substituted salt was obtained instead, presumably via the electrophilic aromatic substitution pathway, which reflects a limitation to the protocol.

The synthesis of symmetric diaryliodonium tetrafluoroborates was subsequently investigated. Substituted symmetric salts are generally difficult to obtain, as the system either becomes too unreactive (electron-poor substrates) or too reactive (electron-rich substrates). Reported procedures are generally limited in scope and give moderate yields.[14−16] Gratefully, our protocol delivered both electron-poor and electron-rich salts, as depicted in Table 3.

The halogenated iodoarenes **1b** and **1c** were smoothly oxidized and coupled with **2b** and **2e**, respectively, yielding symmetric salts **3q**,**r** (entries 2 and 3). Likewise, 2-iodotoluene (**1d**) and *o*-methyl-substituted boronic acid **2g** gave salt **3s** (entry 4). Again, the deactivated substrates showed high reactivity, giving salts **3t**−**v** within 1.5 h at rt (entries 5−7). The highly activated iodoarenes **1h** and **1i** also participated in the reactions with the corresponding arylboronic acids (**2o**,**p**), but even at −78 °C side reactions took place and moderate yields were obtained (entries 8 and 9). An alternative route to highly activated symmetrical diaryliodonium tetrafluoroborates is the conversion from the corresponding tosylates with an in situ anion exchange.[26]

Although the yields in entries 5−9 are moderate, the synthesis should be appealing due to its simplicity, short reaction time, easy purification, and large substrate scope.

Diaryliodonium triflates are frequently applied in synthesis. As shown in Scheme 1, we have previously developed an efficient one-pot synthesis of triflate salts. That methodology is for mechanistical reasons limited to certain substitution patterns, and it was therefore of interest to investigate whether the boronic acid route could be used also to obtain diaryliodonium triflates with previously unobtainable substituents. Although the reaction indeed worked with triflic acid, higher yields were obtained when boron trifluoride was used followed by an in situ anion exchange with triflic acid. This is exemplified by the synthesis of bis(2-fluorophenyl)iodonium triflate (**4**), which was isolated in 75% yield by addition of triflic acid to the crude mixture after complete conversion to diaryliodonium salt **3q** (Scheme 3).

Conclusions

To summarize, we have demonstrated an efficient and fast one-pot synthesis of symmetric and unsymmetric diaryliodonium tetrafluoroborates from iodoarenes and arylboronic acids. Both electron-deficient and electron-rich salts can be synthesized in a regiospecific manner, and the substitution pattern can easily be varied. An in situ anion exchange with triflic acid gives access also to the corresponding diaryliodonium triflates.

Experimental Section

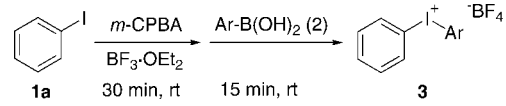
General Procedure for the Synthesis of Salts 3a−v. *m*-Chloroperbenzoic acid (81% active oxidant, 61 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (1 mL). To the solution was added aryl iodide **1a** (0.26 mmol) followed by $BF_3 \cdot OEt_2$ (81 μL, 0.65 mmol) at room temperature. The resulting yellow solution was stirred at rt for 30 min and then cooled to 0 °C, and arylboronic acid **2b** (40 mg, 0.29 mmol) was added. After 15 min of stirring at rt, the crude reaction mixture was applied on a silica plug (0.8 g) and eluted with CH_2Cl_2 (10 mL) to remove unreacted ArI and *m*-CBA, followed by CH_2Cl_2/MeOH (30 mL, 20:1), to elute the product, leaving any boric acid derivatives on the column. The latter solution was concentrated, and diethyl ether (1 mL) was added to the residue to induce a precipitation of salt **3b**, with any iodine(III) intermediates and BF_3 derivatives remaining in solution. (If precipitation is hard to obtain, a small amount of CH_2Cl_2 can be added.) The solution was allowed to stir for 15 min, and then the ether phase was decanted,[51] and the solid was washed twice more with diethyl ether (2 × 1 mL) and then dried in vacuo to give pure diaryliodonium tetrafluoroborate salt **3b** in 88% yield as a white solid: mp 141−143 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (1 H, ddd, J = 7.6, 6.0, 1.6 Hz), 8.23 (2 H, d, J = 7.2 Hz), 7.77−7.64 (2 H, m), 7.62−7.52 (3 H, m), 7.38 (1 H, td, J = 8.0, 1.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.2 (d, J = 248 Hz), 137.1, 135.6 (d, J = 8 Hz), 135.1, 132.3, 132.0, 127.7 (d, J = 3 Hz), 117.0, 116.8, 103.8 (d, J = 23.3 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ −97.45 (1 F), [−147.77, −147.82] (4 F); HRMS (ESI) calcd for $C_{12}H_9FI$ ([M − BF_4^-]$^+$) 298.9727, found 298.9718.

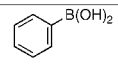
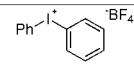
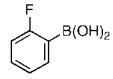
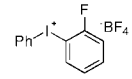
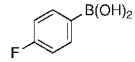
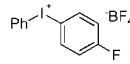
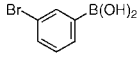
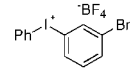
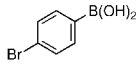
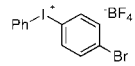
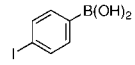
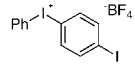
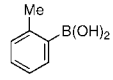
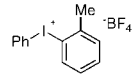
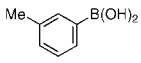
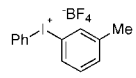
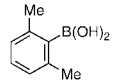
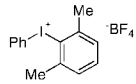
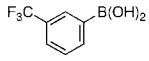
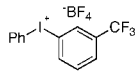
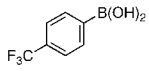
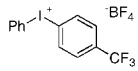
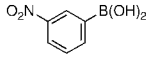
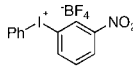
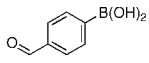
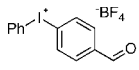
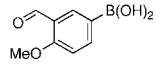
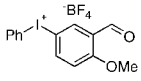
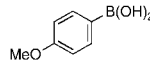
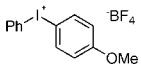
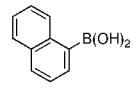
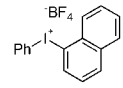
Large-Scale Synthesis of Diphenyliodonium Tetrafluoroborate (3a). *m*-Chloroperbenzoic acid (81% active oxidant, 640 mg, 3.0 mmol) was dissolved in CH_2Cl_2 (10 mL). To the solution was added iodobenzene (**1a**, 310 μL, 2.7 mmol) followed by slow addition of $BF_3 \cdot OEt_2$ (850 μL, 6.8 mmol) at room temperature. The resulting yellow solution was stirred at rt for 30 min and then cooled to 0 °C, and phenylboronic acid (**2a**, 370 mg, 3.0 mmol) was added. After 15 min of stirring at rt, the crude reaction mixture was applied on a silica plug (6.0 g) and eluted with CH_2Cl_2 (60 mL) followed by CH_2Cl_2/MeOH (120 mL, 20:1). The latter solution was concentrated, and diethyl ether (10 mL) was added to the residue to induce a precipitation. The solution was allowed to stir for 15 min, and then the ether phase was decanted. The solid was washed twice more with diethyl ether (2 × 10 mL) and then dried

(50) This purification was found both fast and highly efficient, and **3a** was obtained with high purity without need for recrystallization.

(51) Decantation of the filtrate proved to be better than filtration on a glass filter funnel, as the solid was initially rather sticky. After the washing procedure described above, it formed a solid that was easily collected.

TABLE 2. Synthesis of Salts 3 from PhI (1a) and Arylboronic Acids 2[a]



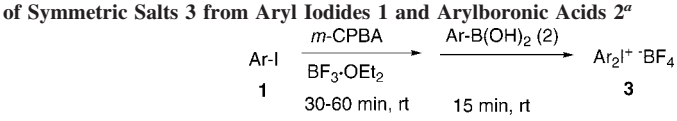
Entry	Ar-B(OH)$_2$	2	Product	3	Yield (%)[b]
1		**2a**		**3a**	82
2		**2b**		**3b**	88
3		**2c**		**3c**	58
4		**2d**		**3d**	75
5		**2e**		**3e**	78
6		**2f**		**3f**	73
7		**2g**		**3g**	80
8		**2h**		**3h**	84
9		**2i**		**3i**	81
10		**2j**		**3j**	73
11		**2k**		**3k**	69
12		**2l**		**3l**	56
13		**2m**		**3m**	65
14		**2n**		**3n**	85
15[c]		**2o**		**3o**	84
16[c]		**2p**		**3p**	81

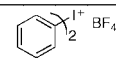
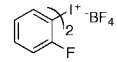
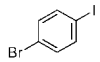
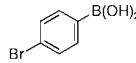
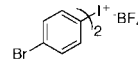
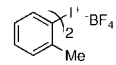
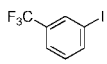
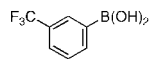
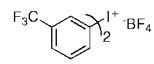
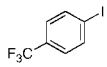
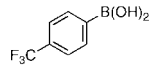
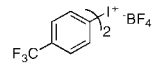
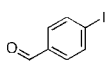
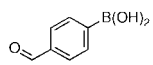
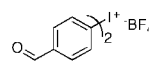
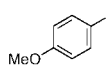
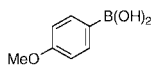
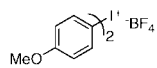
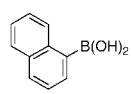
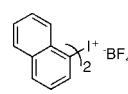
[a] Reaction conditions: **1a** (1.0 equiv) and *m*-CPBA (1.1 equiv) were dissolved in CH_2Cl_2 (1 mL), BF_3·OEt_2 (2.5 equiv) was added, and the reaction was stirred at rt for 30 min. **2** (1.1 equiv) was subsequently added at 0 °C, and the mixture was then stirred at rt for 15 min. [b] Isolated yield. [c] **2** was added at −78 °C.

in vacuo to give salt **3a** in 83% yield (825 mg). Analytical data were in agreement with previous reports; see the Supporting Information.

Modified Synthesis of Electron-Rich Salts 3w and 3x. *m*-Chloroperbenzoic acid (81% active oxidant, 68 mg, 0.30 mmol) was added to a sealed tube and dissolved in CH_2Cl_2 (1 mL). To

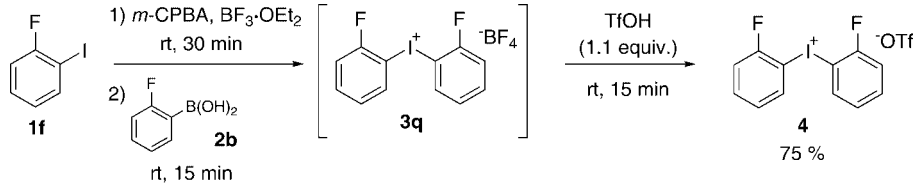
TABLE 3. Synthesis of Symmetric Salts 3 from Aryl Iodides 1 and Arylboronic Acids 2[a]



Entry	Ar-I	1	Ar-B(OH)$_2$	2	Product	3	Yield (%)[b]
1		**1a**		**2a**		**3a**	82
2		**1b**		**2b**		**3q**	85
3		**1c**		**2e**		**3r**	66
4		**1d**		**2g**		**3s**	74
5[c]		**1e**		**2j**		**3t**	51
6[c]		**1f**		**2k**		**3u**	56
7[d]		**1g**		**2m**		**3v**	31
8[e]		**1h**		**2o**		**3w**	46
9[e]		**1i**		**2p**		**3x**	37

[a] Reaction conditions: **1** (1.0 equiv.) and *m*CPBA (1.1 equiv.) were dissolved in CH_2Cl_2 (1 mL), $BF_3 \cdot OEt_2$ (2.5 equiv.) was added and the reaction was stirred at rt for 30 min. **2** (1.1 equiv.) was subsequently added at 0 °C, the mixture was then stirred at rt for 15 min. [b] Isolated yield. [c] 60 min preoxidation time. [d] In acetonitrile. [e] Special conditions were required, see the Experimental Section.

SCHEME 3. One-Pot Synthesis with in Situ Anion Exchange



the solution was added aryl iodide **1** (0.27 mmol), and the reaction mixture was placed in an 80 °C preheated oil bath. After 10 min, the vial was cooled to −78 °C, and a 0 °C mixture of $BF_3 \cdot OEt_2$ (85 μL, 0.68 mmol) and arylboronic acid **2** (37 mg, 0.30 mmol), dissolved in CH_2Cl_2 (1 mL), was transferred to the cooled reaction mixture through a cannula. The resulting dark solution was stirred for 30 min at −78 °C and brought up to room temperature, and the product was isolated as described in the general procedure. **Bis(4-methoxyphenyl)iodonium tetrafluoroborate (3w):** isolated in 46% yield as a gray solid; mp 170 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (4 H, d, J = 7.2 Hz), 7.06 (4 H, d, J = 7.2 Hz), 3.79 (6 H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 136.8, 117.3, 105.9, 55.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ [−147.78, −147.84] (4 F); HRMS (ESI) calcd for $C_{14}H_{14}IO_2$ ([M − BF_4^-]$^+$) 341.0033, found 341.0029. **Bis(1-naphthyl)iodonium tetrafluoroborate (3x):** isolated in 37% yield as a gray solid; mp 155 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (2 H, dd, J = 7.6, 0.8 Hz), 8.49 (2 H, d, J = 8.8 Hz), 8.21 (2 H, d, J = 8.0 Hz), 8.01 (2 H, d, J = 8.0 Hz), 7.81 (2 H, app td, J = 6.8, 1.2 Hz), 7.68 (2 H, app td, J = 8.0, 0.8 Hz), 7.57 (2 H, app td, J = 7.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.3, 134.2, 133.4, 130.9, 129.7, 129.4, 128.8, 128.0, 127.5, 119.2; ^{19}F NMR (376 MHz, DMSO-d_6) δ [−147.78, −147.84] (4 F); HRMS (ESI) calcd for $C_{20}H_{14}I$ ([M − BF_4^-]$^+$) 381.0135, found 381.0136.

Synthesis of Triflate Salt 4 via Tetrafluoroborate Salt 3q. *m*-Chloroperbenzoic acid (81% active oxidant, 58 mg, 0.27 mmol) was dissolved in CH_2Cl_2 (1 mL). To the solution was added 2-fluoroiodobenzene (**1b**, 0.25 mmol) followed by $BF_3 \cdot OEt_2$ (78 μL, 0.62 mmol) at room temperature. The resulting yellow solution was stirred for 30 min and cooled to 0 °C, followed by addition of 2-fluorophenylboronic acid (**2b**, 38 mg, 0.27 mmol). After 15 min of stirring at rt, triflic acid (24 μL, 0.27 mmol) was added at room temperature, and the mixture was stirred for an additional 15 min then isolated as described in the general procedure to give **4** in 75% yield as a white solid: mp 181−183 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.41 (2 H, ddd, J = 8.0, 6.4, 1.6 Hz), 7.74 (2 H, m), 7.59 (2 H, td, J = 8.4, 1.2 Hz), 7.38 (2 H, td, J = 8.0, 1.3 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.1 (d, J = 248.4 Hz), 137.1, 135.8 (d, J = 7.7 Hz), 127.8, 120.8 (q, 320.5 Hz, $F_3SO_3^-$), 116.8 (d, J = 22.1 Hz), 104.1 (d, J = 24.0 Hz); ^{19}F NMR (376 MHz,

DMSO-d_6) δ −77.3 (3 F, s, $CF_3SO_3^-$), −97.43 (2 F, m); HRMS (ESI) calcd for $C_{12}H_8F_2I$ ($[M - OTf^-]^+$) 316.9633, found 316.9624.

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Supporting Information Available: General experimental conditions, analytical data, and NMR spectra for salts **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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