The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b02811 • Publication Date (Web): 21 Dec 2016

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Synthesis of Aryl(2,4,6-trimethoxyphenyl)iodonium Trifluoroacetate Salts

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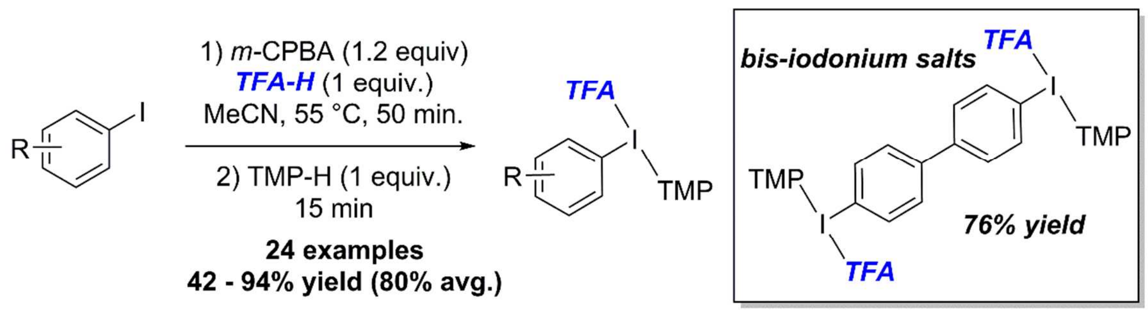
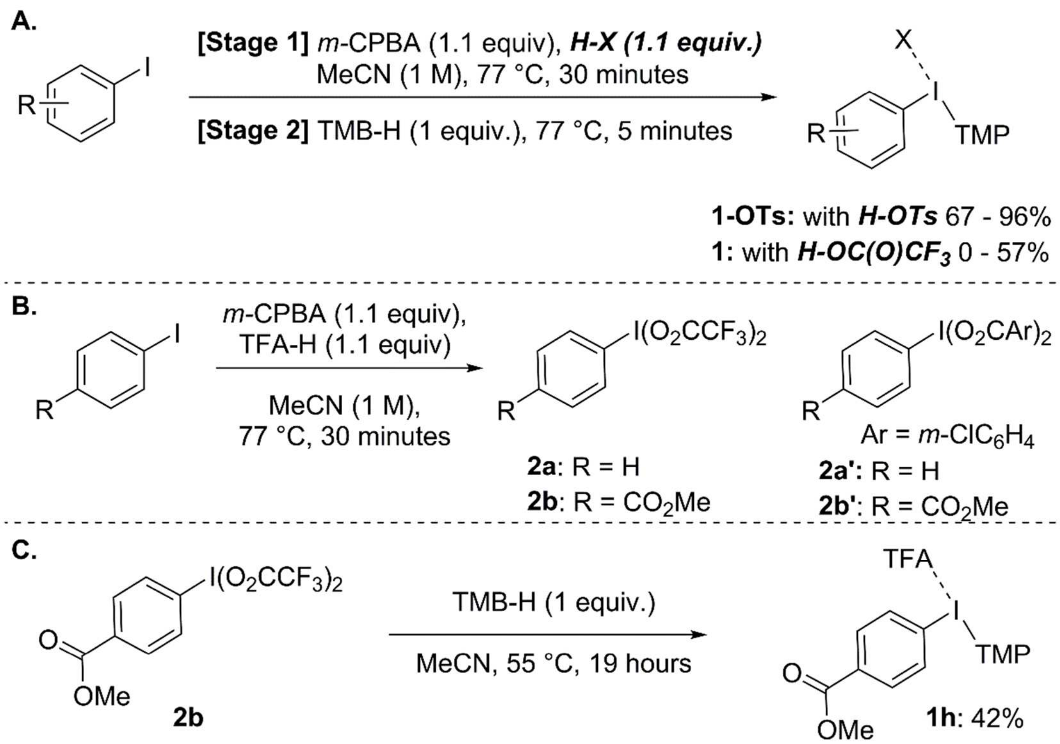


Abstract: The direct synthesis of aryl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate salts from aryl iodides is described. Stoichiometric quantities of trifluoroacetic acid and trimethoxybenzene are used as the counter anion and auxiliary precursors, respectively, under oxidizing conditions. The reaction occurs at mild temperature, is broad in scope, and does not require a separate anion exchange step to install the trifluoroacetate group. The intermediacy of two distinct dicarboxy aryl-λ^3-iodanes is hypothesized in the mechanism.

One-pot reactions are an efficient and attractive means to prepare diaryliodonium salts from commercial arene building blocks and direct access to triflate,[1] tosylate,[2] and tetrafluoroborate[3] salts have been well described, particularly in the past decade. While these methods have been a primary driving force for the utilization of diaryliodonium salts in novel arylation reactions,[4] direct access to diaryliodonium salts incorporating other counter anions are relatively limited. Specifically, although diaryliodonium trifluoroacetates are useful salts in their own right,[5] we were surprised to find that a well-established synthesis from aryl iodides has not been reported;[6,7] although they are suggested as intermediates in the synthesis of diaryliodonium triflates with trifluoroacetic acid as solvent.[1b,c] Given empirical evidence for the importance of counter anion identity on reactivity,[4] the development of methods that deliver diaryliodonium trifluoroacetates directly, without recourse to anion exchange, would enable reaction development with these reagents.

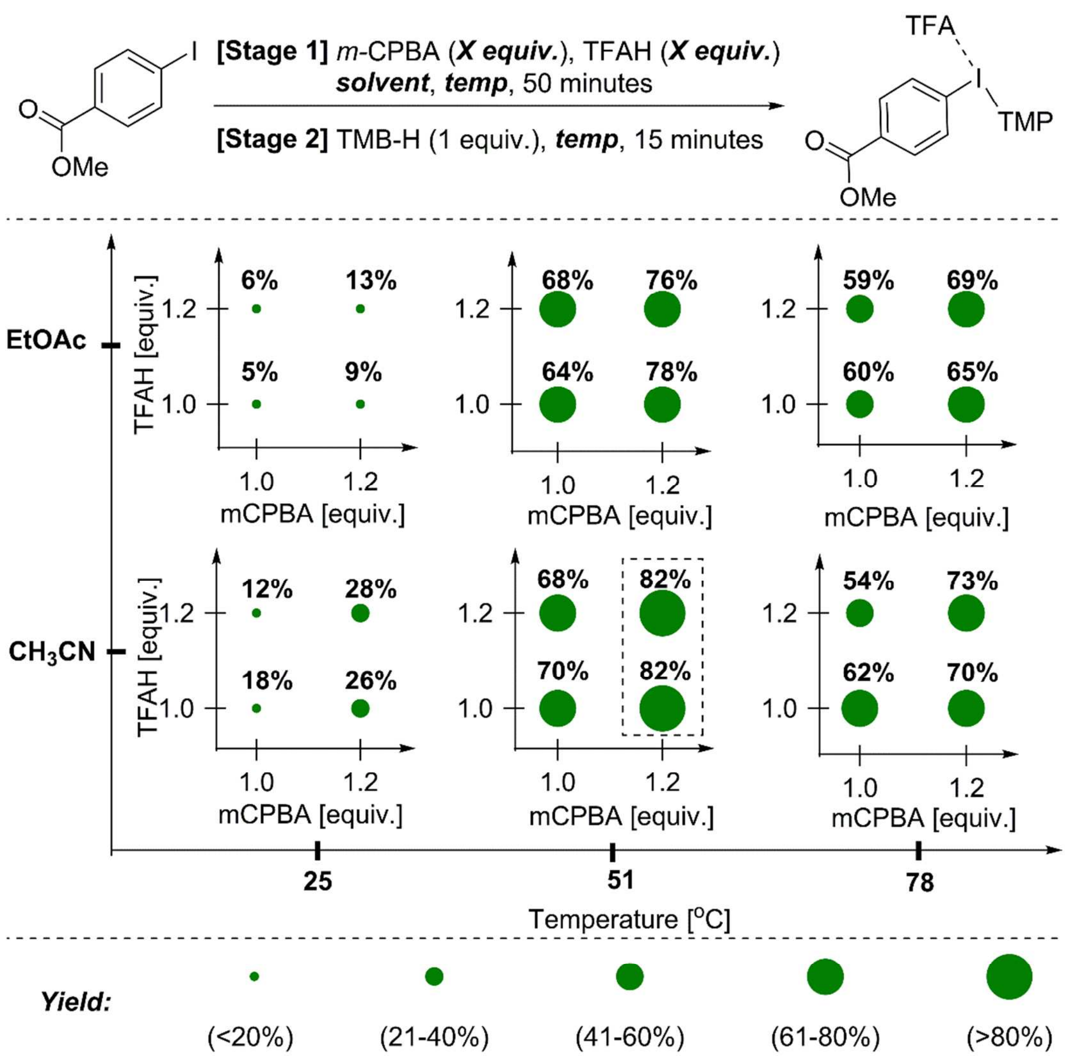
We have recently described the *N*-arylation of alicyclic amines with aryl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate salts[8] wherein the TFA-salts were prepared by first synthesizing the OTs-salts and then performing a counter anion exchange with NaTFA.[2e] While accessible, the yields for the TFA-salts over this two-step procedure varied widely (15 – 85%; average 51%)[8] and we viewed this as an impractical procedure[9] for future reaction development with aryl(TMP)iodonium trifluoroacetate salts. We initially explored the possibility of replacing toluenesulfonic acid with trifluoroacetic acid in a direct synthesis from aryl iodides with *m*-CPBA as oxidant,[2e] but this resulted in low and variable yields (Scheme 1A).[10] The combination of toluenesulfonic acid and *m*-CPBA is known to produce heteroleptic aryl-λ^3-iodanes, such as [hydroxyl(tosyloxy)iodo]arenes, from aryl iodides.[2e,11] In this vein, we investigated the oxidation of an aryl iodide with *m*-CPBA in the presence of stoichiometric trifluoroacetic acid. However, we did not observe clean formation of a single aryl-λ^3-iodane, although we did observe [bis(trifluoroacetoxy)iodo]arenes **2a** and **2b** (Scheme 1B) and other unidentifiable signals in the crude ^{19}F-NMR spectra.[12] Additionally, peaks consistent with the structures **2a'** and **2b'** were observed in the crude ^{1}H NMR spectra.[12,13] Reaction of **2b** with trimethoxybenzene in acetonitrile at 55 °C produced **1h** in 42% yield (Scheme 1C). Given the observation of several aryl-λ^3-iodane intermediates under these conditions, we were intrigued by the possibility that a dynamic equilibrium between these intermediates may be amenable to optimization and lead to a practical direct synthesis of aryl(TMP)iodonium trifluoroacetate salts from aryl iodides.

Scheme 1. Identification and reactivity of potential reaction intermediates.



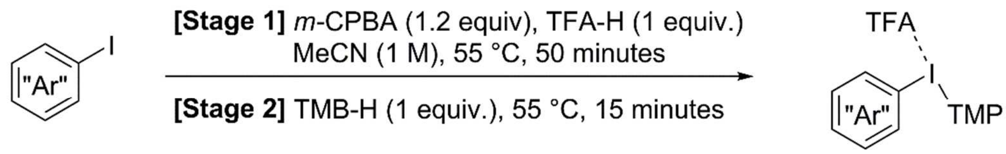
We previously used design of experiment to optimize the reaction conditions for the synthesis of aryl(TMP)iodonium tosylates which provided insight into the contribution of each variable;[2e] temperature had the largest contribution on yield. We noted during our initial screening experiments that each stage required longer reaction time with trifluoroacetic acid relative to toluene sulfonic acid. Therefore, stage 1 was held for 50 minutes and stage 2 was held for 15 minutes in our current optimization studies. We focused on temperature, stoichiometry of *m*-CPBA and trifluoroacetic acid (TFAH), and solvent in the optimization of reaction conditions with trifluoroacetic acid as the acid source (Scheme 2). Higher yields are consistently observed in acetonitrile over ethyl acetate as solvent (Scheme 2). Moreover, in acetonitrile consistently higher yields were observed with a slight excess of *m*-CPBA (1.2 equiv.), whereas the stoichiometry of trifluoroacetic acid appeared to have little influence on yield (Scheme 2). The temperature had a dramatic influence on yield and a maximum yield was obtained at 51 °C as compared to 25 and 78 °C (Scheme 2). Based on these experiments the optimal conditions selected to evaluate the scope of the reaction were *m*-CPBA 1.2 equiv., TFAH 1 equiv., at 50 °C in acetonitrile.

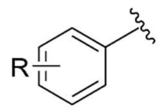
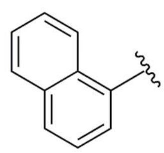
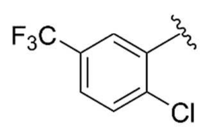
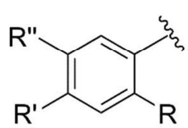
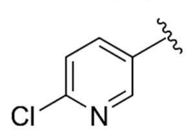
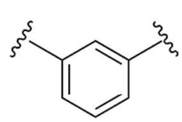
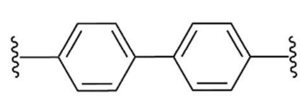
Scheme 2. Effect of variables on reaction yield.



The reaction scope is presented in Table 1. The scope aryl iodide substrates that participate in this reaction is broad (> 20 examples) and the reactions proceed with high yield (77% average yield). Electron-rich and electron-deficient aryl iodides are compatible in this reaction as evidenced by the 14 examples that bear mono-functionalized aryl moieties (Table 1, entries 1 – 14, **1a-n**, 70-94%). Polyfunctional aryl moieties are also compatible and this point reinforces the importance of using unsymmetrical iodonium salts for nucleophile arylation reactions (Table 1, entries 15 – 21, **1o-u**, 68 – 88%). Moreover, the synthesis of (1-naphthyl)(TMP)iodonium trifluoroacetate was possible under these conditions which we were unable to isolate in our previous work.[2e] The synthesis of pyridine-containing **1v** is also possible, albeit in moderate yield of 42% and may allow *C*-3 functionalization of the pyridyl moiety (Table 1, entry 22).[14] The oxidation of two iodide groups on a substrate to yield bis(iodonium) compounds was also possible here and **1w** and **1x** were obtained in 90 and 76% yield, respectively (Table 1, entry 23 and 24). The Mes group, which is useful in both metal-catalyzed[4,15] and metal-free[16] reactions, may also be introduced by this method, albeit in moderate yield (Table 1, **1b** and **1f**, 51 and 49%, respectively).

Table 1. Reaction scope.



Entry	"Ar" moiety		Yield (%)
1 (**1a**)		R = H	94[b]
2 (**1b**)		R = 4-Me	93 (51)[c]
3 (**1c**)		R = 4-*i*-Pr	82
4 (**1d**)		R = 4-*t*-Bu	89
5 (**1e**)		R = 4-F	93[b]
6 (**1f**)		R = 4-Cl	81 (49)[c]
7 (**1g**)		R = 4-Br	86[b]
8 (**1h**)		R = 4-CO_2Me	84
9 (**1i**)		R = 4-CN	80
10 (**1j**)		R = 4-NO_2	70
11 (**1k**)		R = 4-Ph	75
12 (**1l**)		R = 3-CN	84
13 (**1m**)		R = 3-NO_2	76
14 (**1n**)		R = 3-CF_3	83
15 (**1o**)			68[d]
16 (**1p**)			69
17 (**1q**)		R = H, R' = F, R" = Cl	80
18 (**1r**)		R = H, R' = Me, R" = Cl	88
19 (**1s**)		R = H, R' = Me, R" = Br	81
20 (**1t**)		R = H, R' = Me, R" = NO_2	82
21 (**1u**)		R = Me, R' = F, R" = Br	80
22 (**1v**)			42
23 (**1w**)[c]			90
24 (**1x**)[c]			76

[a]Conditions: aryl iodide (1 mmol, 1 equiv.), *m*-CPBA (1.2 mmol, 1.2 equiv.), TFAH (1 mmol, 1 equiv.), MeCN (1 mL), 55 °C, 50 min, 1,3,5-trimethoxybenzene (1 mmol, 1 equiv.), 55 °C, 15 min. [b]Reaction conducted on 2 mmol-scale of aryl iodide. [c]Mesitylene (1.5 mmol, 1 equiv.) instead of 1,3,5-trimethoxybenzene, 77°C for 22h. [d]EtOAc (1 mL) used as solvent.

In conclusion, we have demonstrated a practical and high-yielding method to access diverse and highly-functionalized aryl(TMP)iodonium trifluoroacetate salts directly from aryl iodides. This method utilizes commercially available reagents, is straight forward to conduct, is functional group tolerant, and provides a mild approach to trifluoroacetate salts that does not require a subsequent anion exchange step. We anticipate that this method will engender the use of iodonium trifluoroacetate salts in organic synthesis.

Experimental Section

General considerations. Commercially available reagents and solvents were used without further purification unless stated otherwise. *m*-CPBA was dried over-night under vacuum. **2b** was prepared by literature procedure.[17] ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer at 298 K, unless stated otherwise. The following abbreviations are used to indicate the multiplicity of the signals: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets. IR data were obtained as thin films. High-resolution mass spectrometry (HRMS) data were obtained by electrospray ionization (ESI) with an ion trap mass analyzer. Melting points (m.p.) are reported uncorrected.

General procedure for unsymmetrical aryl(TMP)iodonium trifluoroacetate synthesis (1a – 1x). Aryl iodide (1 mmol, 1 equiv) and acetonitrile (1 mL) were added to a 5 mL vial, equipped with a magnetic stir bar. *m*-CPBA (1.2 mmol, 0.208 g, 1.2 equiv) was added in one portion, followed by the drop-wise addition of TFA (1 mmol, 76 μL, 1 equiv). After sealing the tube with a screw-cap, the reaction was placed in an oil bath set to 55°C and stirred. After 50 min, 1,3,5-

trimethoxybenzene (1 mmol, 0.168 g, 1 equiv) was added in one portion and the mixture was stirred at 55°C for 15 min. The post-reaction mixture was removed from heat and concentrated under reduced pressure and the crude residue was triturated with diethyl ether (10 mL). The solid was collected by vacuum filtration and washed by slurry filtration with diethyl ether (3 × 10 mL). After drying under reduced pressure, the diaryliodonium salt was obtained in analytically pure form.

Phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1a. Isolated as a white solid (0.907 g, 94%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (dd, J_1 = 8.4 Hz, J_2 = 1.0 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 8.1 Hz, 2H), 6.16 (s, 2H), 3.87 (s, 6H), 3.86 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ (ppm): 166.8, 161.9 (q, J_{C-F} = 34.0 Hz), 160.7, 133.9, 131.4, 131.2, 117.2, 116.7 (q, J_{C-F} = 295.1 Hz), 91.5, 86.0, 56.9, 56.0. ^{19}F{^{1}H}-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.3. FT-IR: 3071 (br), 2986 (br), 2954 (br), 2850 (br), 1676 (s), 1580 (s), 1460 (m), 1161 (m), 1112 (s), 795(m), 716 (m) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^{+}$ calcd. for $C_{15}H_{16}IO_3^{+}$: 371.0139, found: 371.0133. M.p. (Et_2O): 160-165 °C.

4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1b. Isolated as a white solid (0.462 g, 93%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 6.15 (s, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 2.33 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ (ppm): 166.70, 161.71 (q, J_{C-F} = 34.0 Hz), 160.56, 141.98, 133.96, 132.15, 116.68 (q, J_{C-F} = 295.1 Hz), 113.41, 91.47, 85.93, 56.84, 55.96, 21.33. ^{19}F{^{1}H}-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.2. FT-IR: 2990 (br), 2949 (br), 2885 (br), 2852 (br), 1655 (m), 1581 (s), 1458 (m), 1162 (s), 1117 (s), 795 (s), 716 (s) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^{+}$ calcd. for $C_{16}H_{18}IO_3^{+}$: 385.0295, found: 385.0289. M.p. (Et_2O): 163-165 °C.

4-*iso*propylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1c. Isolated as a white solid (0.432 g, 82%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.16 (s, 2H), 3.88 (s, 6H), 3.86 (s, 3H), 2.88 (m, 1H), 1.20 (d, J = 6.9 Hz, 6H).

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ (ppm): 166.7, 161.8 (q, J_{C-F} = 33.9 Hz), 160.6, 152.6, 134.0, 129.7, 116.7 (q, J_{C-F} = 295.1 Hz), 113.4, 91.5, 85.9, 56.8, 56.0, 34.0, 23.7. $^{19}F\{^1H\}$-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.3. FT-IR: 3054 (br), 3014 (br), 2969 (br), 2947 (br), 1659 (s), 1580 (s), 1463 (m), 1410 (m), 1160 (s), 1121 (s), 795 (m), 719 (m) cm^{-1}. HR-MS (EI) *m/z* $[M\text{-}TFA]^+$ calcd. for $C_{18}H_{22}IO_3^+$: 413.0608, found: 413.0600. M.p. (Et_2O): 168-171 °C.

4-*tert*-butylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1d. Isolated as a white solid (0.480 g, 89%) ^1H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.83 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 6.46 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H), 1.24 (s, 9H). $^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$) δ (ppm): 166.7, 161.9 (q, J_{C-F} = 34.0 Hz), 160.7, 154.9, 133.7, 128.7, 116.7 (q, J_{C-F} = 294.9 Hz), 113.3, 91.5, 85.9, 56.9, 56.0, 35.1, 31.1. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4. FT-IR: 2970 (br), 2951 (br), 2904 (br), 2867 (br), 1670 (s), 1657 (s), 1585 (s), 1409 (m), 1159 (s), 1121 (s), 794 (m), 718 (m) cm^{-1}. HR-MS (EI) *m/z* $[M\text{-}TFA]^+$ calcd. for $C_{19}H_{24}IO_3^+$: 427.0765, found: 427.0755. M.p. (Et_2O): 180-185 °C.

4-fluorophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1e. Isolated as a white solid (0.935 g, 93%). ^1H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.97 (q, *J* = 4.0 Hz, 2H), 7.33 (t, *J* = 8.9 Hz, 2H), 6.46 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). $^{13}C\{^1H\}$-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.2, 163.6 (d, J_{C-F} = 250.2 Hz), 159.5, 158.2 (q, J_{C-F} = 30.9 Hz), 137.1 (d, J_{C-F} = 8.9 Hz), 118.8 (d, J_{C-F} = 22.7 Hz), 117.3 (q, J_{C-F} = 300.0 Hz), 110.9 (d, J_{C-F} = 3.1 Hz), 92.1, 88.1, 57.3, 56.1. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4, -107.5. FT-IR: 3074 (br), 3022 (br), 2988 (br), 2956 (br), 1683 (s), 1575 (s), 1157 (s), 1117 (s), 799 (s), 716 (s) cm^{-1}. HR-MS (EI) *m/z* $[M\text{-}TFA]^+$ calcd. for $C_{15}H_{15}FIO_3^+$: 389.0044, found: 389.0039. M.p. (Et_2O): 165-169 °C.

4-chlorophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1f. Isolated as a white solid (0.477 g, 81%). ^1H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.91 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). $^{13}C\{^1H\}$-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.2, 159.4, 157.9 (q, J_{C-F} = 30.6 Hz), 136.6, 136.1, 131.4, 117.3 (q, J_{C-F} = 300.9 Hz), 114.2, 92.1, 87.6, 57.3, 56.2. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4. FT-IR: 3081 (br), 3062 (br), 3000 (br), 2955 (br), 1682 (m), 1577 (s), 1345 (m), 1176 (s), 1116 (s), 794 (m), 715 (s) cm^{-1}. HR-MS (EI) *m/z* $[M-TFA]^+$ calcd. for $C_{15}H_{15}ClIO_3^+$: 404.9749, found: 404.9744. M.p. (Et_2O): 168-172 °C.

4-bromophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1g. Isolated as a white solid (0.969 g, 86%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 7.83 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 6.47 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.2, 159.4, 157.9 (q, J_{C-F} = 30.7 Hz), 136.2, 134.3, 125.3, 117.3 (q, J_{C-F} = 300.8 Hz), 114.9, 92.1, 87.5, 57.3, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4. FT-IR: 3085 (br), 3001 (br), 2948 (br), 2844 (br), 1656 (m), 1581 (s), 1352 (m), 1175 (s), 1118 (s), 799 (s), 716 (s) cm^{-1}. HR-MS (EI) *m/z* $[M-TFA]^+$ calcd. for $C_{15}H_{15}BrIO_3^+$: 448.9244, found: 448.9240. M.p. (Et_2O): 171-173 °C.

4-methylbenzoxycarbonyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1h. Isolated as a white solid (0.520 g, 84%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (br, 4H), 6.17 (s, 2H), 3.91 (s, 3H), 3.87 (s, 9H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ (ppm): 167.0, 165.7, 162.0 (q, J_{C-F} = 34.4 Hz), 160.7, 133.7, 132.7, 132.1, 121.9, 116.6 (q, J_{C-F} = 294.6 Hz), 91.6, 86.4, 56.9, 56.0, 52.7. ^{19}F{^{1}H}-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.3. Spectral data was in accordance with the literature.[8]

4-cyanophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1i. Isolated as a white solid (0.405 g, 80%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.06 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.6 Hz, 2H), 6.49 (s, 2H), 3.93 (s, 6H), 3.88 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.4, 159.5, 157.8 (q, J_{C-F} = 30.5 Hz), 134.8, 134.7, 121.2, 117.6, 117.3 (q, J_{C-F} = 301.0 Hz), 114.1, 92.2, 87.3, 57.4, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4. FT-IR: 3090 (br), 3022 (br), 2953 (br), 2845 (br), 2230 (m), 1713 (m), 1661 (s), 1578 (s), 1414 (m), 1162 (s), 1117 (s), 827 (s), 719 (s) cm^{-1}. HR-MS (EI) *m/z* $[M-TFA]^+$ calcd. for $C_{16}H_{15}INO_3^+$: 396.0091, found: 396.0086. M.p. (Et_2O): 166-167 °C.

4-nitrophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1j. Isolated as an off-white solid (0.273 g, 70%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.23 (d, J = 9.0 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H), 6.50 (s, 2H), 3.95 (s, 6H), 3.88 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.5, 159.5, 158.0 (q, $J_{C\text{-}F}$ = 30.8 Hz), 149.1, 135.4, 126.0, 122.8, 117.2 (q, $J_{C\text{-}F}$ = 300.7 Hz), 92.2, 87.6, 57.4, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.5. Spectral data was in accordance with the literature.[8]

4-biphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1k. Isolated as an off-white solid (0.362 g, 68%) using ethyl acetate as solvent. ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.48 (dd, J_1 = 7.4 Hz, J_2 = 0.8 Hz, 1H), 8.22 (dd, J_1 = 8.3 Hz, J_2 = 2.9 Hz, 2H), 8.03 (d, J = 8.1 Hz, 1H), 7.86-7.82 (m, 1H), 7.72-7.68 (m, 1H), 7.56 (t, J = 7.7 Hz, 1H), 6.39 (s, 2H), 3.95 (s, 6H), 3.80 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 165,9, 159.4, 157.8 (q, $J_{C\text{-}F}$ = 30.6 Hz), 137.4, 134.0, 132.9, 131.0, 129.3, 129.2, 127.7, 127.3, 119.5, 117.4 (q, $J_{C\text{-}F}$ = 301.1 Hz), 92.0, 87.3, 57.2, 56.1. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -75.4. Spectral data was in accordance with the literature.[2e]

3-cyanophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1l. Isolated as a white solid (0.430 g, 84%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.47 (br, 1H), 8.19 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.3, 159.5, 158.1 (q, $J_{C\text{-}F}$ = 30.9 Hz), 138.8, 137.4, 135.1, 132.2, 117.2 (q, $J_{C\text{-}F}$ = 300.3 Hz), 117.1, 116.6, 113.6, 92.1, 87.7, 57.3, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4. Spectral data was in accordance with the literature.[8]

3-nitrophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1m. Isolated as a white solid (0.401 g, 76%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.70 (br, 1H), 8.39 (dd, J_1 = 8.2 Hz, J_2 = 1.9 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 8.1 Hz, 1H), 6.50 (s, 2H), 3.96 (s, 6H), 3.88 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.5, 159.5, 158.0 (q, $J_{C\text{-}F}$ = 30.8 Hz), 148.3, 139.8, 132.6, 128.5, 126.1, 117.2 (q, $J_{C\text{-}F}$ = 300.5 Hz), 116.2, 92.2, 87.7, 57.4, 56.2.

$^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.5. Spectral data was in accordance with the literature.[8]

3-trifluoromethylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1n. Isolated as a white solid (0.456 g, 83%). ^1H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.33 (s, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 6.48 (s, 2H), 3.94 (s, 6H), 3.87 (s, 3H). $^{13}C\{^1H\}$-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.4, 159.5, 158.1 (q, $J_{C\text{-}F}$ = 30.9 Hz), 138.0, 132.5, 131.1 (q, $J_{C\text{-}F}$ = 32.7 Hz), 130.7 (d, $J_{C\text{-}F}$ = 3.9 Hz), 128.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 123.0 (q, $J_{C\text{-}F}$ = 273.1 Hz), 117.2 (q, $J_{C\text{-}F}$ = 300.3 Hz), 116.8, 92.1, 87.7, 57.3, 56.2. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -61.4, -73.5. Spectral data was in accordance with the literature.[8]

1-naphtyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1o. Isolated as an off-white solid (0.362 g, 68%) using ethyl acetate as solvent. ^1H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.48 (dd, J_1 = 7.4 Hz, J_2 = 0.8 Hz, 1H), 8.22 (dd, J_1 = 8.3 Hz, J_2 = 2.9 Hz, 2H), 8.03 (d, J = 8.1 Hz, 1H), 7.86-7.82 (m, 1H), 7.72-7.68 (m, 1H), 7.56 (t, J = 7.7 Hz, 1H), 6.39 (s, 2H), 3.95 (s, 6H), 3.80 (s, 3H). $^{13}C\{^1H\}$-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 165,9, 159.4, 157.8 (q, $J_{C\text{-}F}$ = 30.6 Hz), 137.4, 134.0, 132.9, 131.0, 129.3, 129.2, 127.7, 127.3, 119.5, 117.4 (q, $J_{C\text{-}F}$ = 301.1 Hz), 92.0, 87.3, 57.2, 56.1. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -75.4. FT-IR: 3047 (br), 3013 (br), 2951 (br), 2839 (br), 1678 (m), 1656 (s), 1584 (s), 1341 (s), 1160 (s), 1123 (s), 802 (s), 717 (m) cm^{-1}. HR-MS (EI) m/z [M-TFA]$^+$ calcd. for $C_{19}H_{18}IO_3^+$: 421.0295, found: 421.0286. M.p. (Et_2O): 164-166 °C.

3-trifluoromethyl-6-chlorophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1p. Isolated as a white solid (0.407 g, 69%). ^1H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.63 (br, 1H), 8.04-7.97 (m, 2H), 6.44 (s, 2H), 3.92 (s, 6H), 3.85 (s, 3H). $^{13}C\{^1H\}$-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.2, 159.4, 157.8 (q, $J_{C\text{-}F}$ = 30.6 Hz), 140.2, 135.6 (d, $J_{C\text{-}F}$ = 3.9 Hz), 131.0, 130.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.1 (q, $J_{C\text{-}F}$ = 33.3 Hz), 122.6 (q, $J_{C\text{-}F}$ = 273.0 Hz), 120.1, 117.3 (q, $J_{C\text{-}F}$ = 300.8 Hz), 92.1, 87.6, 57.0, 56.1. $^{19}F\{^1H\}$-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -61.1, -73.4. Spectral data was in accordance with the literature.[8]

3-chloro-4-fluorophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1q. Isolated as a white solid (0.427 g, 80%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.23 (dd, J_1 = 6.8 Hz, J_2 = 2.2 Hz, 1H), 7.91-7.88 (m, 1H), 7.53 (t, J = 9.1 Hz, 1H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.3, 159.0 (d, J_{C-F} = 252.6 Hz), 159.4, 158.1 (q, J_{C-F} = 31.0 Hz), 136.1, 135.4 (d, J_{C-F} = 8.2 Hz), 121.8 (d, J_{C-F} = 18.6 Hz), 119.9 (d, J_{C-F} = 22.3 Hz), 117.2 (q, J_{C-F} = 300.2 Hz), 110.9 (d, J_{C-F} = 4.0 Hz), 92.1, 88.1, 57.3, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4, -110.4. FT-IR: 3082 (br), 3016 (br), 1686 (s), 1576 (s), 1466 (s), 1349 (s), 1120 (s), 825 (m), 715 (m), 697 (s) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^+$ calcd. for $C_{15}H_{14}ClFIO_3^+$: 422.9655, found: 422.9648. M.p. (Et_2O): 168 °C.

3-chloro-4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1r. Isolated as a white solid (0.466 g, 88%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 7.98 (d, J = 1.8 Hz, 1H), 7.74 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H), 2.34 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.2, 159.4, 157.8 (q, J_{C-F} = 30.5 Hz), 139.8, 134.8, 133.7 (d, J_{C-F} = 8.1 Hz), 132.8, 117.3 (q, J_{C-F} = 301.2 Hz), 113.0, 92.1, 87.5, 57.3, 56.2, 30.7, 19.5. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4. FT-IR: 3100 (br), 3007 (br), 2949 (br), 2919 (br), 2843 (br), 1659 (s), 1585 (s), 1470 (m), 1347 (s), 1122 (s), 1055 (m), 809 (s), 718 (s) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^+$ calcd. for $C_{16}H_{17}ClIO_3^+$: 418.9905, found: 418.9900. M.p. (Et_2O): 168-173 °C.

3-bromo-4-methylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1s. Isolated as a white solid (0.467 g, 81%)- ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm):8.12 (d, J = 1.8 Hz, 1H), 7.77 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 6.47 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.2, 159.4, 157.8 (q, J_{C-F} = 30.5 Hz), 141.6, 136.6, 133.5 (q, J_{C-F} = 43.0 Hz), 125.5, 117.3 (q, J_{C-F} = 301.1 Hz), 113.2, 92.1, 87.5, 57.3, 56.2, 30.7, 22.3. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4. FT-IR: 3099 (br), 3008 (br), 2949 (br), 2843 (br), 1682 (m), 1660 (s), 1585 (s), 1466 (m), 1346 (s), 1121 (s), 1056 (m), 817 (s), 718 (s), 697 (m) cm^{-1}. HR-MS (EI) *m/z* $[M-TFA]^+$ calcd. for $C_{16}H_{17}BrIO_3$: 462.9400, found: 462.9398. M.p. (Et_2O): 180-181 °C.

4-methyl-3-nitrophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1t. Isolated as a yellow solid (0.444 g, 80%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.51 (d, J = 1.9 Hz, 1H), 8.06 (dd, J_1 = 8.2 Hz, J_2 = 1.9 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 6.48 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H), 2.52 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.4, 159.4, 157.9 (q, J_{C-F} = 30.7 Hz), 149.4, 138.1, 136.5, 135.4, 129.7, 117.3 (q, J_{C-F} = 300.7 Hz), 112.8, 92.1, 87.6, 57.4, 56.2, 19.4. ^{19}F-{^{1}H}NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4. Spectral data was in accordance with the literature.[8]

3-bromo-4-fluoro-6-methylphenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1u. Isolated as a yellow solid (0.494 g, 83%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.39 (d, J = 6.9 Hz, 1H), 7.60 (d, J = 9.9 Hz, 1H), 6.45 (s, 2H), 3.95 (s, 6H), 3.86 (s, 3H), 2.55 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.0, 160.1 (d, J_{C-F} = 250.7 Hz), 159.3, 158.1 (q, J_{C-F} = 30.9 Hz), 143.5 (d, J_{C-F} = 8.4 Hz), 140.9, 118.8 (d, J_{C-F} = 23.5 Hz), 117.2 (q, J_{C-F} = 300.4 Hz), 116.2 (d, J_{C-F} = 3.5 Hz), 106.7 (d, J_{C-F} = 22.1 Hz), 92.1, 87.8, 57.1, 56.1, 24.4. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.4, -102.9. FT-IR: 3096 (br), 3034 (br), 3000 (br), 2957 (br), 2852 (br), 1680 (m), 1594 (m), 1528 (m), 1345 (m), 1115 (s), 827 (s), 716 (m) cm^{-1}. HR-MS (EI) *m/z* $[M-TFA]^+$ calcd. for $C_{16}H_{16}BrFIO_3^+$: 480.9306, found: 480.9299. M.p. (Et_2O): 164-165 °C.

2-chloropyridine(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate 1v. Isolated as an off-white solid (0.220 g, 42%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm): 8.87 (d, J = 2.1 Hz, 1H), 8.36 (dd, J_1 = 8.5 Hz, J_2 = 2.4 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 6.46 (s, 2H), 3.95 (s, 6H), 3.87 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6) δ (ppm): 166.3, 159.3, 158.0 (q, J_{C-F} = 30.9 Hz), 153.5, 152.6, 145.0, 127.4, 117.2 (d, J_{C-F} = 300.4 Hz), 114.2, 92.1, 87.7, 57.3, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d_6) δ (ppm): -73.5. Spectral data was in accordance with the literature.[8]

1,3-phenyl(2,4,6-trimethoxyphenyl)diiodonium bis-trifluoroacetate 1w. Deviation from general procedure: *m*-CPBA (2.4 equiv.), TFA (2 equiv.), TMB (2 equiv.). Isolated as a white solid (0.800 g, 90%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 8.20 (t, J = 1.6 Hz, 1H), 8.08 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 6.48 (s, 4H), 3.90-3.88 (2s, 18H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.4, 159.4, 157.9 (q, J_{C-F} = 30.7 Hz), 137.7, 136.6, 134.2, 117.5, 117.3 (q, J_{C-F} = 300.8 Hz), 92.1, 87.5, 57.4, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4. FT-IR: 3079 (br), 2996 (br), 2956 (br), 2845 (br), 1663 (s), 1579 (s), 1348 (m), 1164 (s), 1118 (s), 797 (m), 716 (s) cm^{-1}. HR-MS (EI) *m/z* [M-2TFA]$^{2+}$ calcd. for $C_{12}H_{13}IO_3^{2+}$: 331.9904, found: 331.9904. M.p. (Et_2O): 189 °C.

1',1-biphenyl-bis-(2,4,6-trimethoxyphenyl)diiodonium bis-trifluoroacetate 1x. Deviation from general procedure: *m*-CPBA (2.4 equiv.), TFA (2 equiv.), TMB (2 equiv.). Isolated as an off-white solid (0.730 g, 76%). ^{1}H-NMR (400 MHz, DMSO-d$_6$) δ (ppm): 7.98 (d, J = 8.6 Hz, 4H), 7.73 (q, J = 8.7 Hz, 4H), 6.48 (s, 4H), 3.95 (s, 12H), 3.87 (s, 6H). ^{13}C{^{1}H}-NMR (101 MHz, DMSO-d$_6$) δ (ppm): 166.2, 159.4, 157.8 (q, J_{C-F} = 30.6 Hz), 141.2, 137.9, 134.8, 129.9, 129.3 (q, J_{C-F} = 35.1 Hz), 117.3 (q, J_{C-F} = 300.9 Hz), 116.0, 92.1, 87.3, 57.4, 56.2. ^{19}F{^{1}H}-NMR (376 MHz, DMSO-d$_6$) δ (ppm): -73.4. FT-IR: 3080 (br), 2988 (br), 2954 (br), 2852 (br), 1676 (m), 1660 (m), 1583 (s), 1342 (m), 1162 (s), 1118 (s), 990 (s), 796 (s), 718 (s) cm^{-1}. HR-MS (EI) *m/z* [M-2TFA]$^{2+}$ calcd. for $C_{15}H_{15}IO_3^{2+}$: 370.0060, found: 370.0060. M.p. (Et_2O): 215 °C.

General procedure for unsymmetrical aryl(mesityl)iodonium trifluoroacetate synthesis (1b-Mes and 1f-Mes). Aryl iodide (1 mmol, 1 equiv) and acetonitrile (1 mL) were added to a 5 mL vial, equipped with a magnetic stir bar. *m*-CPBA (1.2 mmol, 0.208 g, 1.2 equiv) was added in one portion, followed by the drop-wise addition of TFA (1 mmol, 76 µL, 1 equiv). After sealing the tube with a screw-cap, the reaction was placed in an oil bath set to 77°C and stirred. After 50 min, 1,3,5-trimethylbenzene (1.5 mmol, 413µL, 1.5 equiv) was added in one portion and the mixture was stirred at 77°C for 22h. The post-reaction mixture was removed from the heat, concentrated under reduced pressure and the crude residue was triturated with diethyl ether (10 mL). The solid was collected by vacuum filtration and washed by slurry filtration with diethyl ether (3 × 10 mL). After drying under reduced pressure the diaryliodonium salt was obtained in analytically pure form.

4-methylphenyl(2,4,6-trimethylphenyl)iodonium trifluoroacetate 1b-Mes. Isolated as a white solid (0.255 g, 51%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.05 (s, 2H), 2.63 (s, 6H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ (ppm): 161.7 (q, $J_{C\text{-}F}$ = 34.0 Hz), 143.4, 142.0, 141.9, 133.0, 133.5, 130.0, 122.8, 116.5 (q, $J_{C\text{-}F}$ = 295.1 Hz), 110.9, 27.0, 21.3, 21.1. ^{19}F{^{1}H}-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.3. FT-IR: 3058 (br), 3030 (br), 2990 (br), 2920 (br), 2864 (br), 1659 (s), 1453 (m), 1171 (s), 1124 (s), 824 (m), 797 (s), 715 (s) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^+$ calcd. for $C_{16}H_{18}I^+$: 337.0448, found: 337.0448. M.p. (Et_2O): 169-170 °C.

4-chlorophenyl(2,4,6-trimethylphenyl)iodonium trifluoroacetate 1f-Mes. Isolated as a white solid (0.231 g, 49%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 7.09 (s, 2H), 2.66 (s, 6H), 2.35 (s, 3H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$) δ (ppm): 161.6 (q, $J_{C\text{-}F}$ = 34.3 Hz), 143.6, 141.8, 137.8, 134.4, 131.7, 130.0, 123.2, 116.4 (q, $J_{C\text{-}F}$ = 294.9 Hz), 112.1 (d, $J_{C\text{-}F}$ = 10.1 Hz), 27.0, 21.1. ^{19}F{^{1}H}-NMR (376 MHz, $CDCl_3$) δ (ppm): -75.4. FT-IR: 3082 (br), 3063 (br), 2981 (br), 2924 (br), 2868 (br), 1656 (s), 1469 (m), 1384 (m), 1186 (s), 1172 (s), 1125 (s), 1085 (s), 999 (s), 825 (s), 812 (s), 796 (s), 717 (s) cm^{-1}. HR-MS (EI) *m/z* [M-TFA]$^+$ calcd. for $C_{15}H_{15}ClI^+$: 356.9902, found: 356.9904. M.p. (Et_2O): 162-163 °C.

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Notes

The authors declare no competing financial interest.

Acknowledgments

We acknowledge Portland State University and the donors of the American Chemical Society Petroleum Research Fund (PRF DNI1 #54405) for support of this research. V.C. is grateful to Université Paul Sabatier (Toulouse III) and Bourse à la mobilité de la Région Languedoc Roussillon Midi Pyrénées for financial support. A.H.S is grateful to Fulbright Norway for financial support. Thomas Seidl is thanked for helpful discussion during the preparation of this manuscript.

Supporting Information

Copies of ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H} NMR spectra of all new compounds is provided. This material is available free of charge via the Internet at http://pubs.acs.org

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