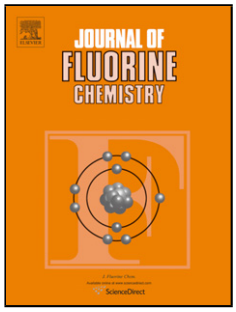

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Unsymmetrical Diaryliodonium Phenyltrifluoroborate Salts: Synthesis, Structure and Fluorination

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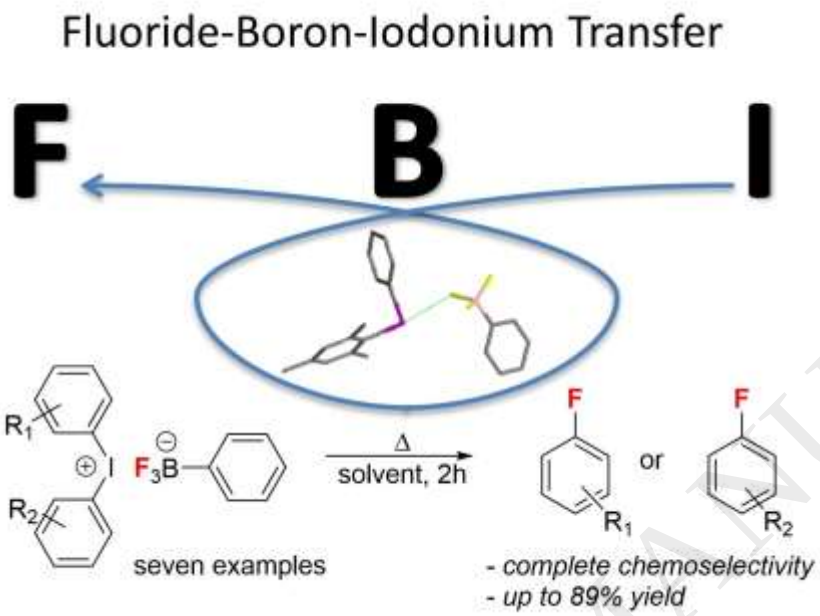
France

Graphical Abstract



Highlights:

- This is the first report of fluoride transfer from an aryltrifluoroborate to an aryl cation generated from an aryliodonium salt that favors the more electron-rich aryl cation.

Abstract

The unprecedented reaction of organotrifluoroborates salts of unsymmetrical diaryliodoniums to give aryl fluorides is presented. This preliminary report describes the first synthesis of unsymmetrical diaryliodonium phenyltrifluoroborates along with an exemplary x-ray crystal structure, and explores their reactivity regarding the fluorination of the diaryliodonium cation. Fluorination was found to be chemoselective, providing exclusively hindered aryl fluoride products in moderate to good yields (up to 89%).

1 Introduction

Hypervalent iodine compounds are immensely useful reagents; specifically, unsymmetrical diaryl-λ^3-iodanes (diaryliodonium salts) have received considerable attention owing to their efficient functionalization of aryl groups with a variety of nucleophiles under both metal-free and metal-mediated conditions.[1, 2] Of particular interest is the utility of these reagents as aryl fluoride precursors when reacted with a source of fluoride anion (F^-).[3, 4] This methodology has been extended to solid-supported systems[5] and metal catalysed processes.[6] Importantly, these reagents have been used to afford fluoroaromatic compounds and ^{18}F-labelled radiopharmaceuticals.[7-20]

Given the potential of this methodology, considerable attention has focused on the mechanism underlying these transformations along with an ensuing optimisation of reaction parameters including solvent selection to limit ligand exchange,[21, 22] the inhibition of radical decomposition pathways,[23] critical mechanistic insights that govern the selectivity of aryl ring fluorination,[24-28] and the design of auxiliary “dummy” ligands to enhance the regioselectivity of aryl fluorination.[10, 17, 25, 29] Despite the large number of publications on the direct fluorination of diaryliodonium salts, most reports have relied on alkali metal fluorides (KF and CsF). Less commonly, tetramethylammonium fluoride (TMAF) and potassium tetrafluoroborate (KBF_4) have found use as sources of anionic fluoride.

We have recently explored the potential of organotrifluoroborates as sources of anionic fluoride[30] in the fluoro-dediazoniation of *in-situ*-generated aryl diazonium salts in the

Balz-Schiemann reaction in which an arenium cation is implicated.[31] Although fragmentation to an arenium cation is also possible in the case of diaryliodonium cations, typically a concerted addition-elimination mechanism has prevailed. Hence, we wished to explore the potential for organotrifluoroborates to transfer fluoride from boron–to–carbon in the case of iodonium salts. Remarkably, such a transfer is unprecedented despite an extensive body of literature that has addressed the reaction of organotrifluoroborates and diaryliodonium salts in palladium-catalysed C-C bond formation,[32, 33] and more recently in terms of bifunctional reagents, comprising an iodonium and trifluoroborate on the same arene.[34]

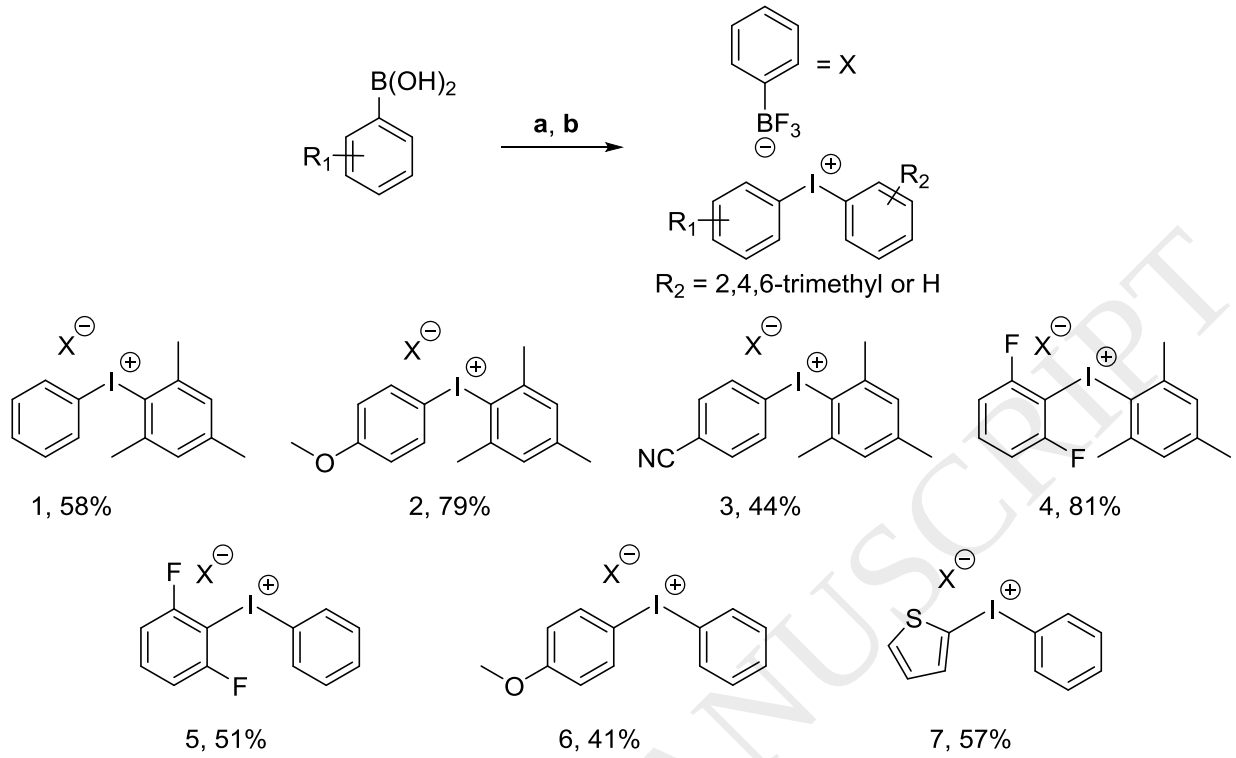
As no report has described the formation of aryl fluorides as products of reactions involving organotrifluoroborates and diaryliodonium salts, we decided to explore this reactivity by applying organotrifluoroborates towards the fluorination of these substrates, as this might appear as an unexpected reaction path in reaction featuring both reagents. Hence, we synthesised and characterised seven unsymmetrical diaryliodonium phenyltrifluoroborate salts in a preliminary exploration of their chemical reactivity to give aryl fluoride products.

2 Results and Discussion

2.1 Synthesis of Unsymmetrical Diaryliodonium Phenyltrifluoroborate Salts

A series of unsymmetrical diaryliodonium tetrafluoroborates (BF_4^-) was first synthesised using $BF_3{\cdot}OEt_2$ as a Lewis acid in CH_2Cl_2 (Scheme 1). Variations of steric demand were achieved by reacting iodomesitylene diacetate ($MesI(OAc)_2$) and phenyliodine(III) diacetate (PIDA), while aryl boronic acids were used to introduce electronic and steric

variations on the second aryl fragment. In addition, a diaryliodonium salt with either a methoxy or a nitrile at the para-positions was synthesized to address the respective effects of electron-releasing and electron-withdrawing substituents. Synthesis of the unsymmetrical diaryliodonium phenyltrifluoroborate salts was achieved via facile anion exchange. Indeed, following overnight stirring in MeCN, precipitated KBF_4 was filtered from the reaction mixture. The salts were purified by Et_2O-induced precipitation from concentrated CH_2Cl_2 solutions to furnish the desired salts in moderate to excellent yields over two steps (Scheme 1). Anion exchange gave nearly quantitative conversion while the purity of all diaryliodonium phenyltrifluoroborate salts was confirmed by ^{1}H-, ^{19}F-, and ^{11}B-NMR spectroscopy along with elemental analysis and high-resolution mass spectrometry.



Scheme 1 Scope of unsymmetrical diaryliodonium salts synthesised (isolated yields). **a**, (i) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 10 minutes, (ii) $MesI(OAc)_2$ or PIDA, 0 °C then room temperature, 18 hours. **b**, potassium phenyltrifluoroborate, MeCN, room temperature, 18 hours. Reported yields are over two synthetic steps.

2.2 Structure of Diaryliodonium Phenyltrifluoroborate Salts

Single crystals, suitable for X-ray analysis, of **1** were obtained by slow solvent evaporation; the salt crystallised in the orthorhombic P_{bca} space group (Figure 1). Carbon-Iodine bond lengths, for both mesityl and phenyl rings are essentially identical at 2.114(2) and 2.115(2) Å, respectively. The iodonium cation adopts T-shaped geometry, as expected for a λ^3-iodane,[2] evidenced by a C-I-C angle of 95.46(8)°. Additionally, the aryl fragments are almost perpendicular with an angle of 87.7° between the planes of both rings. An interaction between the phenyltrifluoroborate anion and diaryliodonium cation is evidenced by a short contact interaction (2.856(2) Å) between one F-atom on the trifluoroborate and the electrophilic I(III) centre. Notably, such a short distance, in the

solid state, between the F-atom on the phenyltrifluoroborate and the I(III) centre of the diaryliodonium appears highly favourable for the desired fluoride transfer.

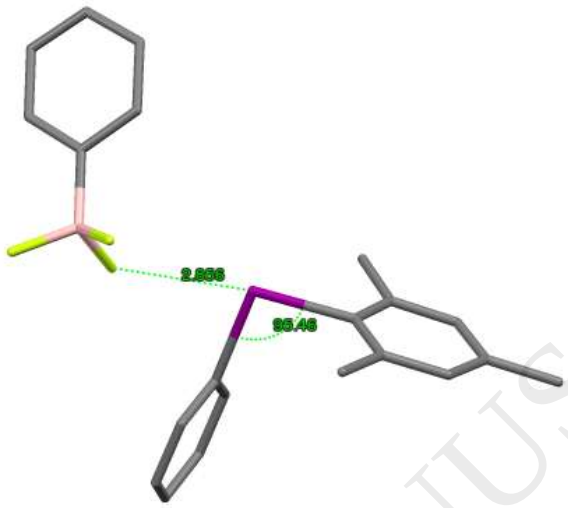


Figure 1 X-ray crystal structure of 1 with selected angles (°) and short contact interaction (Å). Carbon in grey, iodine in purple, boron in pink, fluorine in green/yellow. Hydrogen atoms are omitted for clarity.

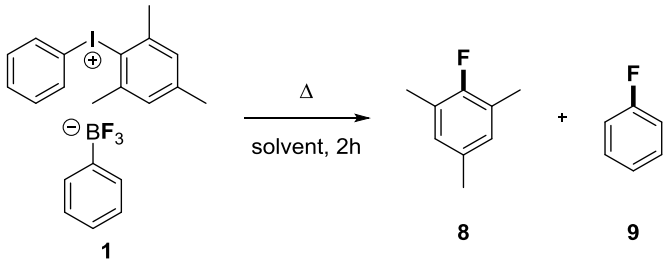
2.3 Fluorination Studies

We began by studying the decomposition of **1** in various solvents at different temperatures to determine if any fluorinated products could be detected (Table **1**, for full solvent screen please refer to ESI). Based on the above observation in the solid state, we focused on poorly dissociating solvents. Generally, low boiling solvents resulted in no conversion of **1** (Table 1, entries 1 and 2) however, trace yields of 2-fluoro-1,3,5-trimethylbenzene (**8**) were observed in $CHCl_3$ and THF (Table 1, entries 3 and 4); otherwise, unreacted and/or deborylated **1** were observed by ^{19}F-NMR spectroscopy (signals observed corresponding to phenyltrifluoroborate and/or tetrafluoroborate, respectively). Higher boiling solvents such as benzene, MeCN and DMF, which have been extensively used in the decomposition of diaryliodonium fluorides and

tetrafluoroborates,[3, 35] did not result in any fluorinated products (Table 1, entries 5, 6 and 7, respectively). However, yields could be increased by employing high-boiling, non-polar solvents such as toluene, xylenes and in particular 1,2-dichlorobenzene, which provided **8** in 22% yield (Table 1, entries 8-10). The use of non-polar, high-boiling, solvents is consistent with previous reports of improved yields.[3, 22]

Given well-established reactivity and selectivity rules for λ^3-iodane intermediates with nucleophiles, we expected the major product to be **8** due to electronic and the so-called "*ortho*" effects.[1, 26, 27, 36] Radical scavengers, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), have successfully increased fluorination yields by suppressing the propagation of *in situ* generated aryl radicals that arise through homolytic cleavage of the aryl-I bond.[23] However, under our reaction conditions, the addition of TEMPO did not improve reaction efficiencies (Table 1, entries 11 and 12), corroborating heterolysis.

Table 1 Solvent optimisation for the decomposition of **1**



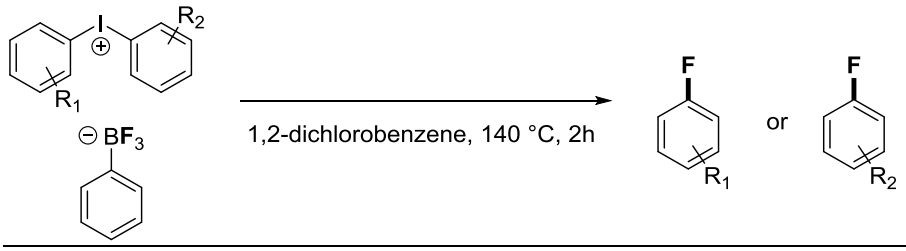
1 8 9

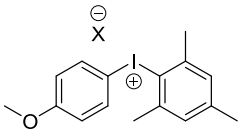
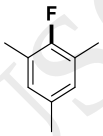
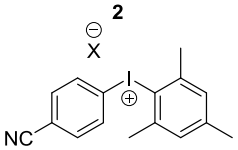
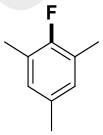
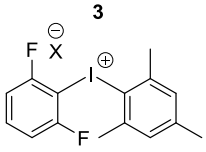
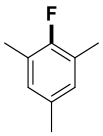
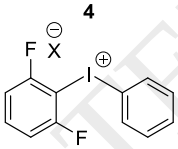
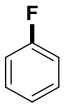
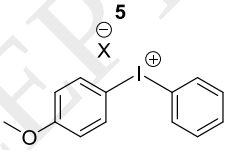
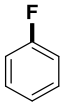
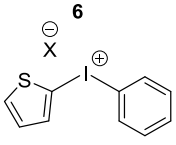
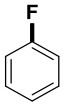
			Product distribution (%)[a]	
Entry	Solvent	Temperature (°C)	8	9
1[b]	Et_2O	80	-	-
2[b]	CH_2Cl_2	80	-	-
3[b]	$CHCl_3$	80	trace	-
4[b,c]	THF	80	trace	-
5[b]	Benzene	100	-	-
6[b]	MeCN	100	-	-
7[b,c]	DMF	140	-	-
8[b]	Toluene	140	8	-
9[b,c]	Xylenes	140	8	trace
10[b,c]	1,2-dichlorobenzene	140	22	trace
11[c,d]	1,2-dichlorobenzene	140	15	-
12[c,e]	1,2-dichlorobenzene	140	21	-

Reaction conditions: 1 (0.05 mmol), solvent (1.0 mL) in pressure vial with Teflon lined cap, heated at indicated temperature for 2 hours. [a] Yields determined by ^{19}F-NMR using 2,2,2-trifluoroethanol as an internal standard. [b] unreacted 1 observed by ^{19}F-NMR. [c] deborylation observed by ^{19}F-NMR. [d] 0.2 eq. TEMPO added to reaction mixture. [e] 1.0 eq. TEMPO added to reaction mixture.

Having determined 1,2-dichlorobenzene as the optimal solvent we investigated the decomposition of salts **2**-**7** (Table 2). Salt **2** decomposed selectively provided **8** in 16% yield (Table 2, entry 1), while 4-fluoroanisole went undetected despite predictions to the contrary as both aryl rings are electron-rich. Salt **3** decomposed selectively to furnish **8** as the sole product in good yield (62%) (Table 2, entry 2); this is surprising as the expected product should be 4-fluorobenzonitrile since this would arise from the most electron-deficient arene and should therefore be preferentially fluorinated according to the well-accepted mechanism. Similarly, **4** provided **8** as the only product in excellent yields (89%) contrary to the prediction that 1,2,3-trifluorobenzene would have resulted based on both electronic and "*ortho*" effects (Table 2, entry 3). More surprisingly, **5**, which was expected to selectively decompose to 1,2,3-trifluorobenzene, provided fluorobenzene (**9**) as the sole product, albeit in only 13% yield (Table 2, entry 4). The decomposition of **6** and **7** delivered only trace amounts (<2%) of the expected product **9**; no traces 4-fluoroanisole or 2-fluorothiophene were detected (Table 2, entries 5 and 6, respectively), perhaps due to the energetic availability of lower lying radical decomposition pathways. Considering the decomposition of salts **1**-**4**, one appreciates an emergent trend of increasing yields of 2-fluoro-1,3,5-trimethylbenzene. The increase in yields correlates with increasing electron-deficiency of the second aryl fragment in the order 4-OMe < H < 4-CN < 2,6-di-F.

Table 2 Product distribution from the decomposition of salts **2-7**

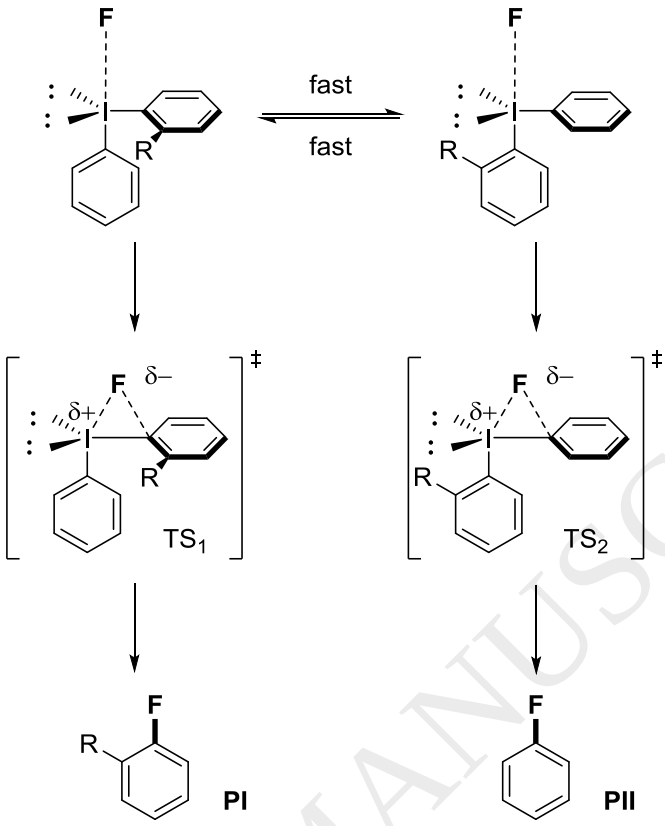


Entry	Compound	Product distribution (%)[a]
1	 **2**	 16
2	 **3**	 62
3	 **4**	 89
4	 **5**	 13
5[b]	 **6**	 trace
6[b]	 **7**	 trace

Reaction conditions: precursor (0.05 mmol), 1,2-dichlorobenzene (1.0 mL) in pressure vial with Teflon lined cap, heated at 140 °C for 2 hours, X = phenyltrifluoroborate.[a] Yields determined by ^{19}F-NMR using 2,4-dinitrofluorobenzene as an internal standard.[b] Deborylation observed by ^{11}B and ^{19}F-NMR (BF_4^- peak detected).

The reactivity and selectivity observed in the decomposition of diaryliodonium salts **1**-**7** seem to implicate a mechanism that differs from the accepted one for the fluorination of diaryliodonium fluorides.[24, 27] Generally, fluorination of diaryliodonium salts with F^- is thought to proceed under Curtin-Hammett control whereby the ratio of fluorinated products is dependent on the difference in the free energies of transition states derived from the two conformers of the λ^3-iodane intermediate (Scheme 2).

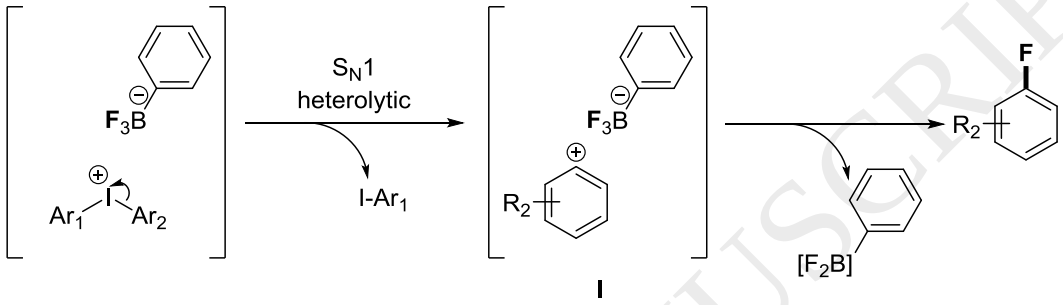
Given that such selectivity is not observed for the decomposition of **3**, **4** and **5**, our findings suggest that the product distribution is determined by irreversible fragmentation of the iodonium cation to give the more stable aryl cation, by analogy to fluorodediazoniation. Indeed if unsymmetrical diaryliodonium phenyltrifluoroborate salts were undergoing fluorination following the accepted mechanism for fluorination of iodonium salts depicted in Scheme 2, we would expect to detect the formation of both aryl fluoride products (Scheme 2, PI and PII) and those distributions should be comparable to previously reported examples, [6] as the transition states would be identical irrespective of the source of F^-. As the observed distributions are not consistent with past reports, the phenyltrifluoroborate cannot be transferring F^- to one of two rapidly exchanging conformers.



Scheme 2 Accepted mechanism for the fluorination of diaryliodonium salts with F^-

Instead, based on our recent report on the reaction of a range of diazonium salts, we propose a mechanism whereby thermolysis of the diaryliodonium salt results in the heterolytic cleavage of the I-Ar_1 bond, forming an aryl iodide and the aryl cation. This is directly analogous to dediazoniation that occurs upon aryl diazonium salt decomposition in the Balz-Schiemann reaction wherein the mesityldiazonium gave the highest yields. Hence, fluorination of the aryl cation likely occurs within the tight ion pair **I** such that fluoride transfer proceeds directly from phenyltrifluoroborate (Scheme 3). This may account for the trend of increasing yields with more electron-deficient aryl ligands; Indeed within the diaryliodonium, Ar_2–I^+–Ar_1, I-Ar_1 becomes an increasingly activated leaving group leading to more efficient fluorination. This mechanism may explain the considerably

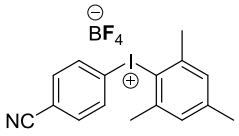
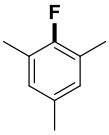
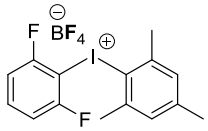
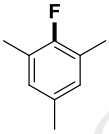
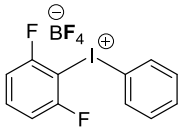
higher yields of fluoromesitylene that arise from fluorination of the sterically hindered and kinetically more stable aryl cation; such reactivity parallels our findings in the fluorination of sterically hindered anilines using organotrifluoroborates in a Balz-Schiemann type transformation.[31]



Scheme 3 Proposed mechanism for the fluorination of diaryliodonium salts with phenyltrifluoroborate

This mechanism would also be consistent with the results observed for the decomposition of unsymmetrical diaryliodonium tetrafluoroborates **3a** and **4a** which displayed identical selectivity and yields as their corresponding phenyltrifluoroborate salts (Table 3, entries 1 and 2). Surprisingly, we did not observe any conversion to aryl fluorides when using tetrafluoroborate salt **5a** (Table 3, entry 3) in contrast to its corresponding phenyltrifluoroborate salt **5** (Table 2, entry 4). This result suggests that phenyltrifluoroborate may serve a unique role as a fluorinating agent compared to BF_4^-.

Table 3 Product distribution for the decomposition of salts **3a** – **5a**

Entry	Compound	Product distribution (%)[a]
1	 **3a**	 62
2	 **4a**	 89
3	 **5a**	no conversion

Reaction conditions: precursor (0.05 mmol), 1,2-dichlorobenzene (1.0 mL) in pressure vial with Teflon lined cap, heated at 140 °C for 2 hours. [a] Yields determined by ^{19}F-NMR using 2,4-dinitrofluorobenzene as an internal standard.

3 Conclusions

In summary, we have described the synthesis and full characterisation of an abbreviated series of unsymmetrical diaryliodonium phenyltrifluoroborate salts. The fluorination of these salts was investigated by thermal decomposition in various solvents and was found to be most efficient at high temperatures in non-polar solvents. Fluorination of all salts was observed to be completely chemoselective, providing a single aryl fluoride in low to excellent yields. The observed selectivity contrasts with that observed in the decomposition of diaryliodonium fluorides; these differences suggest that fluorination occurs via fluoride transfer to an aryl cation that forms *in situ*, as seen similarly in the fluorination of aryl diazonium salts. These preliminary results expand the repertoire of

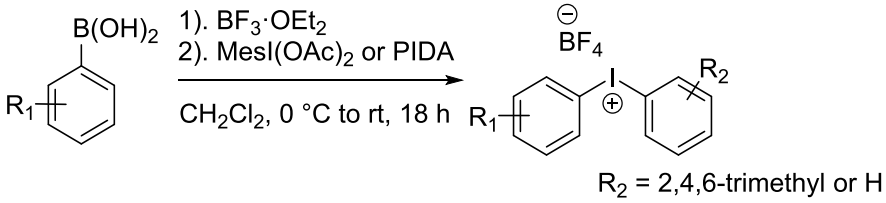
organotrifluoroborates as new, versatile, and intriguing sources of nucleophilic fluorine with potential for use in the context of ^{18}F-labeled organotrifluoroborates.[37]

We believe that this work uncovers an unexpected reactivity of organotrifluoroborates with diaryliodonium salts thus highlighting potential reactivity when both reagents are mixed. Although yields are low, we expect that these preliminary findings may prompt further investigations of this reaction. Moreover, we suggest that these results paves the way for future developments as demonstrated by recent work of Hu and coworkers;[38] hence it is expected that suitable additives including oxidants or catalytic metals may enhance yields substantially.

4 Experimental

All chemicals were purchased from commercial sources and used as received unless otherwise noted. Solvents, MeCN and CH_2Cl_2, were dried and distilled using standard methods (MeCN dried over activated 3A molecular sieves, CH_2Cl_2 obtained from a PureSolv solvent purification system). All reactions were performed in oven-dried glassware under argon atmosphere unless otherwise stated. Deuterated solvents for NMR spectroscopic analysis were purchased from Euriso-top. NMR spectroscopy experiments were performed in deuterated solvents. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F spectra were recorded on 300 Avance (300 MHz), 400 Avance (400 MHz) and 400 AvanceIII (400 MHz) Bruker spectrometers. All spectra were recorded at ambient temperature (298 K). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual protium in the solvents (^{1}H) or the solvent carbon (^{13}C) as internal standards. ^{19}F spectra of aryl fluorides were referenced to 2,4-dinitrofluorobenzene or 2,2,2-trifluoroethanol as internal standards (1 equivalent). Multiplicity of signals is indicated using the following abbreviations: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), q_B (1:1:1:1 of peaks arising from coupling to ^{11}B with S=3/2, midpoint of signal reported), dd (doublet of doublets), dt (doublet of triplet), ddt (doublet of doublet of triplet), dddt (doublet of doublet of doublet of triplet), tt (triplet of triplet) and m (multiplet). ^{13}C signals arising from the quaternary carbon bearing the trifluoroborate group were not always observed and therefore were not always listed. Reactions were monitored using Merck Silica gel 60 F_{254} glass backed plates. TLC plates were visualized by UV fluorescence (λ= 254 nm) and one of the following stains: $KMNO_4$ or HBQ. Flash column chromatography was performed using VWR Chemicals Silica gel 60 – 200 µm. IR spectra were recorded on a PerkinElmer Frontier FT-IR spectrometer with frequencies expressed in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using either electrospray ionization (ESI) or desorption chemical ionization (DCI) using a Waters GCT Premier or Sciex QTRAP 4500 AB or Thermo Fisher Scientific DSQ II spectrometers. X-ray crystallography was performed on single crystal diffractometers: Agilent Gemini, Bruker Nonius and Bruker Kappa Apex II. Crystal and refinement data are collected in the ESI. Crystallographic data has been deposited to the Cambridge Crystallographic Data Centre as CCDC 1879815.

General procedure for the synthesis of unsymmetrical diaryliodonium tetrafluoroborates:



A round-bottom flask was charged with a stir bar, arylboronic acid (1 eq.) and CH_2Cl_2 (0.1 M), the reaction mixture was stirred and cooled to 0 °C in an ice-water bath and then $BF_3{\cdot}OEt_2$ (3 eq.) was added, this solution was stirred at 0 °C for 10 minutes. In a separate flask $MesI(OAc)_2$ or PIDA (1.1 eq) was dissolved in CH_2Cl_2 (0.37 M) and added dropwise to the reaction mixture at 0 °C. The resulting solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was then transferred directly onto a plug of Silica gel and washed with CH_2Cl_2, the product was then eluted with CH_2Cl_2/MeOH (9.5:0.5). Collected fractions were concentrated under reduced pressure then dropped on Et_2O to precipitate the product which was collected by filtration and further washed with Et_2O.

(2,4,6-trimethylphenyl)(phenyl)iodonium tetrafluoroborate (**1a**)

Isolated as a white fluffy powder (408.6 mg, 99%). IR ν_{max}/cm^{-1} (neat film): 2989, 2970, 2901, 1473, 1445, 1057, 736. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 – 7.94 (m, 2H), 7.67 – 7.60 (m, 1H), 7.54 – 7.47 (m, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.1 (C_q), 141.6 (C_q), 134.5 (CH), 131.9 (CH), 131.8 (CH), 129.8 (CH), 122.5 (C_q), 115.0 (C_q), 26.2 (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -145.58 – -150.82 (m). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.29 (s). HRMS-ESI (*m/z*): found $[M]^+$ 323.0295, calc'd $C_{15}H_{16}I^+$ requires 323.0297.

(4-methoxyphenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (**2a**)

Isolated as a grey powder (262.8 mg, 59%). IR ν_{max}/cm^{-1} (neat film): 2989, 2973, 2901, 1582, 1569, 1486, 1302, 1259, 1051, 1027, 827. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 – 7.89 (m, 2H), 7.19 (s, 2H), 7.06 – 7.01 (m, 2H), 3.78 (s, 3H), 2.60 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7 (C_q), 142.9 (C_q), 141.3 (C_q), 136.6 (CH), 129.7 (CH), 123.0 (C_q), 117.50 (CH), 103.3 (C_q), 55.7 (CH_3), 26.2 (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -146.91 – -149.49 (m). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.30 (s). HRMS-ESI (*m/z*): found $[M]^+$ 353.0402, calc'd $C_{16}H_{18}IO^+$ requires 353.0402.

(4-cyanophenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (**3a**)

Isolated as a beige powder (208.9 mg, 48%). IR ν_{max}/cm^{-1} (neat film): 2989, 2970, 2901, 2237, 1482, 1066, 832. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H), 7.25 (s, 2H), 2.58 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.5 (C_q), 141.8 (C_q), 135.1 (CH), 134.9 (CH), 130.0 (CH), 122.6 (C_q), 119.4 (C_q), 117.4 (C_q), 114.4 (C_q), 26.3 (CH_3), 20.6 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -146.91 – -149.84 (m). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.30 (s). HRMS-ESI (*m/z*): found $[M]^+$ 348.0254, calc'd $C_{16}H_{15}IN^+$ requires 348.0249.

(2,6-difluorophenyl)(2,4,6-trimethylphenyl)iodonium tetrafluoroborate (**4a**)

Isolated as a white powder (780.4 mg, 88%). IR ν_{max}/cm^{-1} (neat film): 3090, 3028, 2960, 2918, 1592, 1469, 1241, 1015, 994, 792. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (tt, $^{3}J_{HH}$ = 8.4, $^{4}J_{HF}$ = 6.7 Hz, 1H), 7.45 (dd, $^{3}J_{HH}$ = 8.4, $^{3}J_{HF}$ = 7.3 Hz, 2H), 7.23 (s, 2H), 2.61 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.6 (dd, $^{1}J_{CF}$ = 250.6, $^{3}J_{CF}$ = 5.9 Hz) (C_q), 143.5 (C_q), 141.6 (C_q), 137.0 (t, $^{3}J_{CF}$ = 10.1 Hz) (CH), 129.9 (CH), 122.8 (C_q), 113.48 – 113.1 (m) (CH), 91.7 (t, $^{2}J_{CF}$ = 28.1 Hz) (C_q), 25.9 (t, $^{6}J_{CF}$ = 1.8 Hz) (CH_3), 20.5 (CH_3). ^{19}F NMR (377 MHz, DMSO-d_6) δ -95.82 (t, J_{HF} = 7.0 Hz, 2F), -147.71 – -149.04 (m, 4F). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.29 (s). HRMS-ESI (*m/z*): found $[M]^+$ 359.0110, calc'd $C_{15}H_{14}F_2I^+$ requires 359.0108.

(2,6-difluorophenyl)(phenyl)iodonium tetrafluoroborate (**5a**)

Isolated as a white powder (267.4 mg, 66%). IR ν_{max}/cm^{-1} (neat film): 3096, 3058, 1591, 1467, 1447, 1241, 1054, 995, 987, 788, 744. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, J = 7.6 Hz, 2H), 7.80 (tt, $^{3}J_{HH}$ = 8.4, $^{4}J_{HF}$ = 6.7 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.55 (m, 2H), 7.46 (dd, $^{3}J_{HH}$ = 8.5, $^{3}J_{HF}$ = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.1 (dd, $^{1}J_{CF}$ = 251.0, $^{3}J_{CF}$ = 5.5 Hz) (C_q), 137.2 (t, $^{3}J_{CF}$ = 9.9 Hz) (CH), 135.2 (CH), 132.5 (CH), 132.2 (CH), 117.1 (C_q), 113.3 – 112.9 (m) (CH), 94.3 (t, $^{2}J_{CF}$ = 28.2 Hz) (C_q). ^{19}F NMR (377 MHz, DMSO-d_6) δ -96.40 (t, J_{HF} = 7.0 Hz, 2F), -147.60 – -149.53 (m, 4F). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.29 (s). HRMS-ESI (*m/z*): found $[M]^+$ 316.9647, calc'd $C_{12}H_8F_2I^+$ requires 316.9639.

(4-methoxyphenyl)(phenyl)iodonium tetrafluoroborate (**6a**)

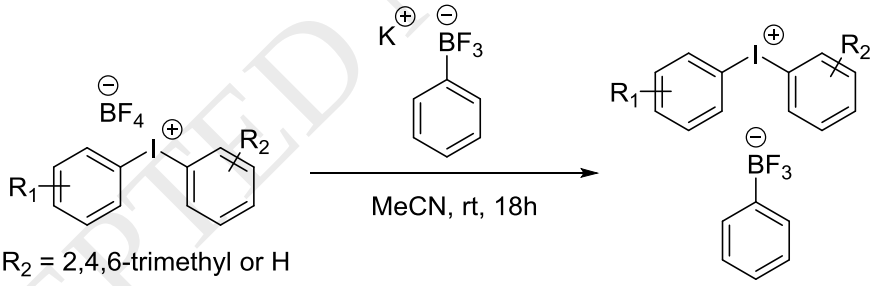
Isolated as a grey powder (199.3 mg, 51%). IR ν_{max}/cm^{-1} (neat film): 3196, 3097, 2951, 2846, 1573, 1489, 1302, 1260, 1181, 1047, 1013, 988, 830, 744. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (t, J = 9.3 Hz, 4H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0 (C_q), 137.3 (CH), 134.8 (CH), 131.9 (CH), 131.7 (CH), 117.5 (CH), 117.0 (C_q), 105.4 (C_q), 55.7 (CH_3). ^{19}F

NMR (376 MHz, DMSO-d_6) δ -148.05 – -148.35 (m). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.23 (s). HRMS-ESI (*m/z*): found $[M]^+$ 310.9935, calc'd $C_{13}H_{12}{}^{127}IO^+$ requires 310.9933.

(2-thienyl)(phenyl)iodonium tetrafluoroborate (**7a**)

Isolated as a burgundy powder (467.5 mg, 62%). IR ν_{max}/cm^{-1} (neat film): 3092, 1559, 1470, 1443, 1386, 1227, 1049, 1031, 1007, 988, 846, 739, 726. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (d, *J* = 7.5 Hz, 2H), 8.07 (s, 1H), 7.97 (d, *J* = 4.5 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.24 – 7.13 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.4 (CH), 137.4 (CH), 134.6 (CH), 132.1 (CH), 131.7 (CH), 129.7 (CH), 119.3 (C_q), 100.7 (C_q). ^{19}F NMR (376 MHz, DMSO-d_6) δ -147.95 – -148.54 (m). ^{11}B NMR (128 MHz, DMSO-d_6) δ -1.27 (s). HRMS-ESI (*m/z*): found $[M]^+$ 286.9393, calc'd $C_{10}H_8{}^{127}IS^+$ requires 286.9391.

General procedure for the synthesis of unsymmetrical diaryliodonium aryltrifluoroborates:



A round-bottom flask was charged with a stir bar, diaryliodonium tetrafluoroborate (1 eq.) and MeCN (0.1 M); to the stirring reaction mixture potassium phenyltrifluoroborate (1 eq.) was added in one portion and the mixture stirred at room temperature for 18 hours. The reaction mixture was passed through a 0.2 µm PTFE filter to remove insoluble impurities, and the filter washed with MeCN. The filtrate was then concentrated to dryness under reduced pressure, and then left under high vacuum for 6 hours. The remaining residue was triturated with CH_2Cl_2 and the solution passed through 0.2 µm PTFE filter to remove insoluble impurities. The filtrate was then concentrated to saturation and then dropped onto Et_2O to precipitate the product, which was collected by filtration and further washed with Et_2O.

(2,4,6-trimethylphenyl)(phenyl)iodonium phenyltrifluoroborate (**1**)

Isolated as an off-white powder (54.7 mg, >99%). Colourless, single crystals suitable for X-ray analysis were grown by slow evaporation of a $CHCl_3$ solution. Mp: 114 – 127. IR ν_{max}/cm^{-1} (neat film): 3071, 3049, 3009, 2984, 1441, 1200, 1005, 986, 937, 906, 752, 743, 707. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 – 7.95 (m, 2H), 7.65 – 7.60 (m, 1H), 7.53 – 7.46 (m, 2H), 7.32 (d, J = 6.6 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.07 (dddt, J = 7.3, 5.9, 1.4, 0.7 Hz, 2H), 7.04 – 6.97 (m, 1H), 2.60 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.1 (C_q), 141.6 (C_q), 134.5 (CH), 131.9 (CH), 131.8 (CH), 131.3 (q, $^{3}J_{CF}$ = 1.7 Hz) (CH), 129.8 (CH), 126.2 (CH), 124.9 (CH), 122.6 (C_q), 114.5 (C_q), 26.3 (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.06 (q_B). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.15 (q, $^{1}J_{BF}$ = 52.0 Hz). HRMS-ESI (*m/z*): found $[M\text{-}C_6H_5BF_3]^+$ 323.0293, calc'd $C_{15}H_{16}I^+$ requires 322.0297, found $[M\text{-}C_{15}H_{16}I]^-$ 144.0474, calc'd $C_6H_5BF_3^-$ requires 144.0473. Anal. calc'd for $C_{21}H_{21}BF_3I$: C, 53.88; H, 4.52; N, 0.00. Found C, 52.85; H, 4.32; N, 0.02.

(4-methoxyphenyl)(2,4,6-trimethylphenyl)iodonium phenyltrifluoroborate (**2**)

Isolated as a grey powder (234.1 mg, 80%). Mp: 120-127. IR ν_{max}/cm^{-1} (neat film): 3085, 2970, 2845, 1571, 1486, 1253, 1195, 1020, 951, 941, 831, 754, 707. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 – 7.89 (m, 2H), 7.31 (d, J = 6.8 Hz, 2H), 7.19 (s, 2H), 7.10 – 6.97 (m, 5H), 3.78 (s, 3H), 2.60 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7 (C_q), 142.9 (C_q), 141.3 (C_q), 136.6 (CH), 131.3 (q, $^{3}J_{CF}$ = 1.9 Hz) (CH), 129.7 (CH), 126.2 (CH), 124.8 (CH), 123.0 (C_q), 117.5 (CH), 103.3 (C_q), 55.7 (CH_3), 26.2 (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.13 (q_B). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.11 (q, $^{1}J_{BF}$ = 53.1 Hz). HRMS-ESI (*m/z*): found $[M\text{-}C_6H_5BF_3]^+$ 353.0397, calc'd $C_{16}H_{18}IO^+$ requires 353.0402, found $[M\text{-}C_{16}H_{18}IO]^-$ 144.0477, calc'd $C_6H_5BF_3^-$ requires 144.0473. Anal. calc'd for $C_{22}H_{23}BF_3IO$: C, 53.05; H, 4.65; N, 0.00. Found C, 53.21; H, 4.60; N, 0.03.

(4-cyanophenyl)(2,4,6-trimethylphenyl)iodonium phenyltrifluoroborate (**3**)

Isolated as a white powder (206.2 mg, 91%). Mp: 135 – 143. IR ν_{max}/cm^{-1} (neat film): 3097, 3047, 3020, 3005, 2231, 1580, 1475, 1203, 948, 827, 751, 701. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 6.7 Hz, 2H), 7.25 (s, 2H), 7.07 (t, J = 7.1 Hz, 2H), 7.03 – 6.97 (m, 1H), 2.58 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.5 (C_q), 141.8 (C_q), 135.0 (CH), 134.9 (CH), 131.3 (q, $^{3}J_{CF}$ = 1.9 Hz) (CH), 130.0 (CH), 126.2 (CH), 124.8 (CH), 122.7 (C_q), 119.4 (C_q), 117.4 (C_q), 114.4 (C_q), 26.3 (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.12 (q_B). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.12 (q, $^{1}J_{BF}$ = 51.5 Hz). HRMS-ESI (*m/z*): found $[M\text{-}C_6H_5BF_3]^+$ 348.0250, calc'd $C_{16}H_{15}IN^+$ requires 348.0249, found $[M\text{-}C_{16}H_{15}IN]^-$ 144.0477,

calc'd $C_6H_5BF_3^-$ requires 144.0473. Anal. calc'd for $C_{22}H_{20}BF_3IN$: C, 53.59; H, 4.09; N, 2.84. Found C, 53.30; H, 3.84; N, 2.82.

(2,6-difluorophenyl)(2,4,6-trimethylphenyl)iodonium phenyltrifluoroborate (**4**)

Isolated as a white powder (520 mg, 92%). Mp: 158 – 167. IR ν_{max}/cm^{-1} (neat film): 3067, 3046, 3022, 3004, 2924, 1593, 1468, 1239, 1205, 1016, 995, 942, 925, 901, 892, 749. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (tt, $^3J_{HH}$ = 8.4, $^4J_{HF}$ = 6.7 Hz, 1H), 7.44 (dd, $^3J_{HH}$ = 8.4, $^3J_{HF}$ = 7.3 Hz, 2H), 7.31 (d, J = 6.7 Hz, 2H), 7.22 (s, 2H), 7.07 (t, J = 7.3 Hz, 2H), 7.03 – 6.97 (m, 1H), 2.61 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.6 (dd, $^1J_{CF}$ = 250.7, $^3J_{CF}$ = 6.0 Hz) (C_q), 143.5 (C_q), 141.6 (C_q), 137.0 (t, $^3J_{CF}$ = 10.1 Hz) (CH), 131.3 (q, $^3J_{CF}$ = 1.7 Hz) (CH), 129.9 (CH), 126.2 (CH), 124.9 (CH), 122.9 (C_q), 113.52 – 113.03 (m) (CH), 91.7 (t, $^2J_{CF}$ = 28.1 Hz) (C_q), 25.9 (t, $^6J_{CF}$ = 2.1 Hz) (CH_3), 20.5 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -95.84 (t, J_{HF} = 7.0 Hz, 2F), -139.10 (q_B, 3F). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.13 (q, $^1J_{BF}$ = 52.8 Hz). HRMS-ESI (*m/z*): found $[M\text{-}C_6H_5BF_3]^+$ 359.0112, calc'd $C_{15}H_{14}F_2I^+$ requires 359.0108, found $[M\text{-}C_{15}H_{14}F_2I]^-$ 144.0473, calc'd $C_6H_5BF_3^-$ requires 144.0473. Anal. calc'd for $C_{21}H_{19}BF_5I$: C, 50.04; H, 3.80; N, 0.00. Found C, 49.97; H, 3.43; N, 0.04.

(2,6-difluorophenyl)(phenyl)iodonium phenyltrifluoroborate (**5**)

Isolated as a white powder (132.9 mg, 77%). Mp: 142 – 153. IR ν_{max}/cm^{-1} (neat film): 3080, 3066, 3049, 3007, 1593, 1467, 1242, 1206, 998, 946, 898, 788, 753, 706. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (d, J = 7.7 Hz, 2H), 7.80 (tt, $^4J_{HF}$ = 8.5, $^3J_{HH}$ = 6.7 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.31 (d, J = 6.9 Hz, 2H), 7.07 (t, J = 7.2 Hz, 2H), 7.00 (t, J = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.1 (dd, $^1J_{CF}$ = 251.0, $^3J_{CF}$ = 5.5 Hz) (C_q), 137.2 (t, $^3J_{CF}$ = 9.9 Hz) (CH), 135.2 (CH), 132.5 (CH), 132.2 (CH), 131.3 (q, $^3J_{CF}$ = 1.8 Hz) (CH), 126.2 (CH), 124.8 (CH), 117.1 (C_q), 113.1 (dd, $^2J_{CF}$ = 22.9, $^4J_{CF}$ = 2.8 Hz) (CH), 94.4 (t, $^2J_{CF}$ = 28.1 Hz) (C_q). ^{19}F NMR (377 MHz, DMSO-d_6) δ -96.41 (t, J_{HF} = 7.0 Hz, 2F), -139.12 (q_B, 3F). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.12 (q, $^1J_{BF}$ = 50.6 Hz). HRMS-ESI (*m/z*): found $[M\text{-}C_6H_5BF_3]^+$ 316.9644, calc'd $C_{12}H_8F_2I^+$ requires 316.9639, found $[M\text{-}C_{12}H_8F_2I]^-$ 144.0474, calc'd $C_6H_5BF_3^-$ requires 144.0473. Anal. calc'd for $C_{18}H_{13}BF_5I$: C, 46.80; H, 2.84; N, 0.00. Found C, 46.41; H, 2.25; N, 0.19.

(4-methoxyphenyl)(phenyl)iodonium phenyltrifluoroborate (**6**)

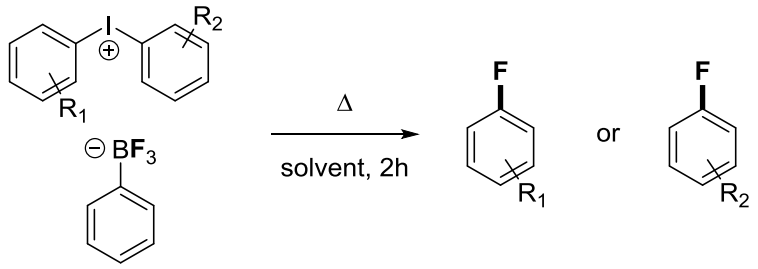
Isolated as a light grey powder (93.9 mg, 81%). IR ν_{max}/cm^{-1} (neat film): 3070, 3009, 2971, 2936, 2840, 1581, 1571, 1488, 1442, 1300, 1255, 1200, 1179, 1009, 990, 951, 904, 754.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 – 8.13 (m, 4H), 7.68 – 7.62 (m, 1H), 7.56 – 7.49 (m, 2H), 7.31 (d, J = 6.5 Hz, 2H), 7.11 – 7.04 (m, 4H), 7.03 – 6.97 (m, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.0 (C_q), 137.2 (CH), 134.8 (CH), 131.8 (CH), 131.6 (CH), 131.3 (q, $^{4}J_{C\text{-}F}$ = 1.7 Hz) (CH), 126.1 (CH), 124.8 (CH), 117.5 (CH), 117.0 (C_q), 105.3 (C_q), 55.7 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.14 (q_B). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.10 (q, $^{1}J_{BF}$ = 52.9 Hz). HRMS-ESI (*m/z*): found $[M]^+$ 310.9929, calc'd $C_{13}H_{12}{}^{127}IO^+$ requires 310.9933, found $[M]^-$ 144.0456, calc'd $C_6H_5{}^{10}BF_3^-$ requires 144.0473. Anal. calc'd for $C_{19}H_{17}BF_3IO$: C, 50.04; H, 3.76; N, 0.00. Found C, 49.91; H, 3.18; N, 0.06.

(2-thienyl)(phenyl)iodonium phenyltrifluoroborate (**7**)

Isolated as a light pink powder (318.7 mg, 92%). Mp: 110 – 115. IR ν_{max}/cm^{-1} (neat film): 3096, 3006, 1470, 1442, 1435, 1383, 1199, 1014, 1007, 988, 970, 890, 758, 736, 707. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 – 8.22 (m, 2H), 8.06 (dd, J = 3.8, 1.3 Hz, 1H), 7.97 (dd, J = 5.3, 1.3 Hz, 1H), 7.67 (ddt, J = 8.5, 7.0, 1.1 Hz, 1H), 7.54 (ddt, J = 8.2, 7.3, 1.3 Hz, 2H), 7.35 – 7.28 (m, 2H), 7.18 (dd, J = 5.3, 3.8 Hz, 1H), 7.07 (dddt, J = 7.4, 5.9, 1.4, 0.7 Hz, 2H), 7.04 – 6.98 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.4 (CH), 137.4 (CH), 134.6 (CH), 132.1 (CH), 131.7 (CH), 131.3 (q, $^{3}J_{CF}$ = 1.7 Hz) (CH), 129.7 (CH), 126.2 (CH), 124.8 (CH), 119.3 (C_q), 100.7 (C_q). ^{19}F NMR (376 MHz, DMSO-d_6) δ -139.11 (q_B). ^{11}B NMR (128 MHz, DMSO-d_6) δ 3.09 (q, $^{1}J_{BF}$ = 52.6 Hz). HRMS-ESI (*m/z*): found $[M]^+$ 286.9396, calc'd $C_{10}H_8{}^{127}IS^+$ requires 286.9391, found $[M]^-$ 144.0475, calc'd $C_6H_5{}^{10}BF_3^-$ requires 144.0473. Anal. calc'd for $C_{16}H_{13}BF_3IS$: C, 44.48; H, 3.03; N, 0.00. Found C, 44.16; H, 2.32; N, 0.00.

General procedure for the fluorination of unsymmetrical diaryliodonium phenyltrifluoroborates salts:



A 10 mL microwave vial was charged with the diaryliodonium phenyltrifluoroborate salt (0.05 mmol) and solvent (1 mL), the vial was capped and sealed with a crimper. The vial was placed in an oil bath at the specified temperature and stirred at the designated temperature for 2 hours. After cooling to room temperature, an internal standard was added to the crude reaction mixture followed by d^6-DMSO (0.5 mL) and the yield was determined by ^{19}F NMR spectroscopy.

Conflict of interest

There are no conflicts to declare.

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