

Supporting Information

Scalable electrochemical synthesis of diaryliodonium salts

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General Methods

Chemicals were purchased from Sigma Aldrich, Alfa Aesar, and FluoroChem and were used as received without purification or drying. Solvents were used as received without drying. Thin layer chromatography (TLC) was performed on precoated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualized by UV radiation (254 nm). Automated column chromatography was performed on a Biotage® Isolera Four using Biotage® cartridges SNAP Ultra. ^1H NMR and ^{13}C NMR spectra were measured on Bruker Ascend 400 or 600 apparatus and were referenced to the solvent peak. Chemical shifts δ were given in ppm and the multiplicity of the signals was reported as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplet, m = multiplet, b = broad. The coupling constants (J) in Hertz. Mass spectrometric measurements were performed at Innovative Physical Organic Solutions (IPOS), University of Huddersfield on Agilent 1290 HPLC + 6530 QTOF instrument. Ions were generated by Electrospray ionisation (ESI).

Electrolysis cells

Electrasyn 2.0: Screening of reaction conditions and synthesis of diaryliodonium salts (scope of substrates) were performed using ElectraSyn 2.0 machine, using 5 mL glass vial equipped with glassy carbon (GC) anode and Pt cathode.

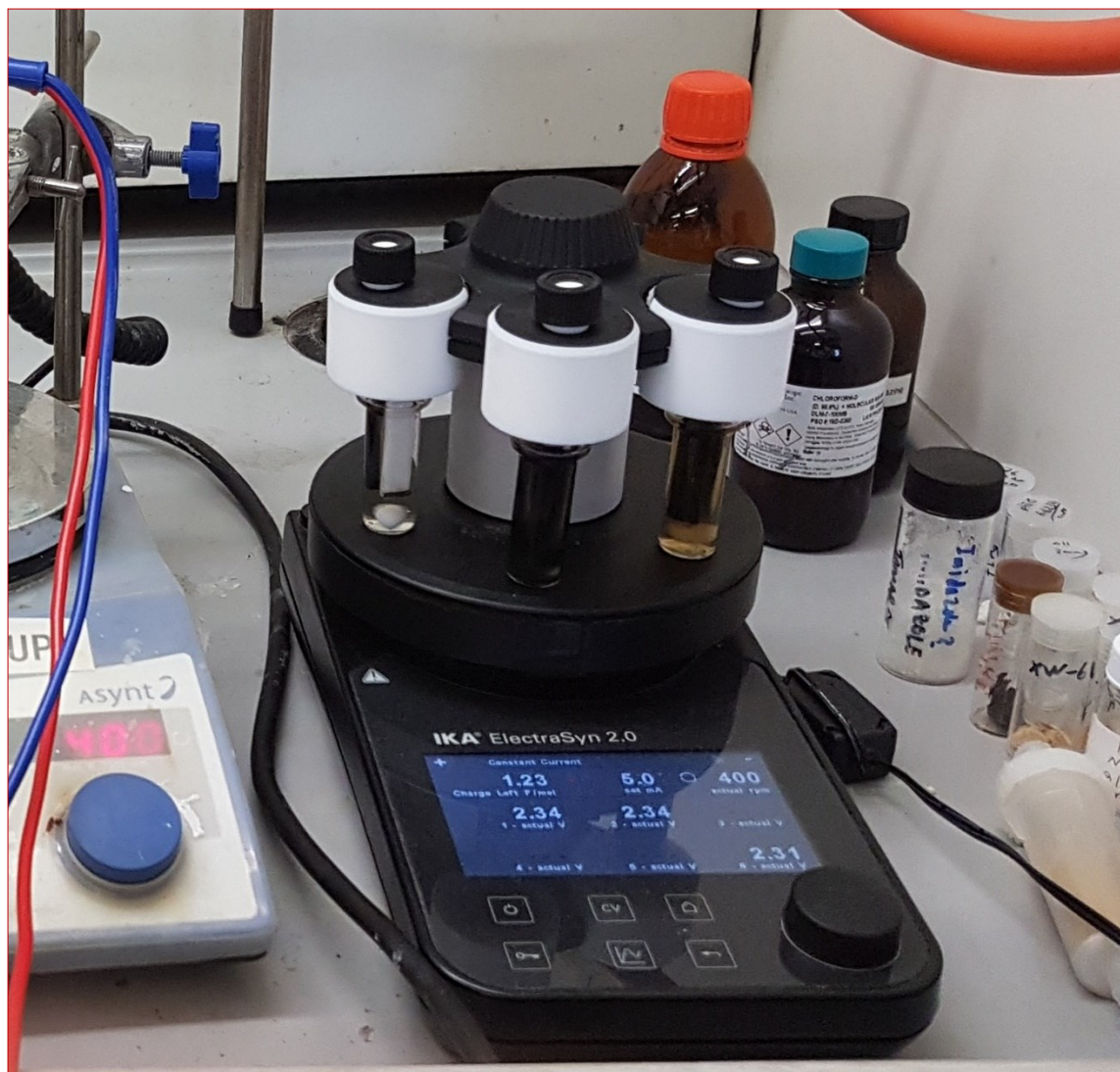


Figure S1. ElectraSyn in action.

Beaker-type cell: Scale-up / solvent recycling experiments were done using a homemade beaker-type cell. The cell is made using a 250 mL beaker and equipped with three parallel square (5 x 5 cm) electrodes, with 0.7 cm interelectrode gap between each pair. The three parallel electrodes are in order: glassy carbon (anode), platinum (cathode), and glassy carbon (anode). Each GC anode was connected to one positive (+) output of the power supply (TTi Ex354RT triple, 300W), two negative outputs (-) of the power supply were connected to the common Pt cathode.

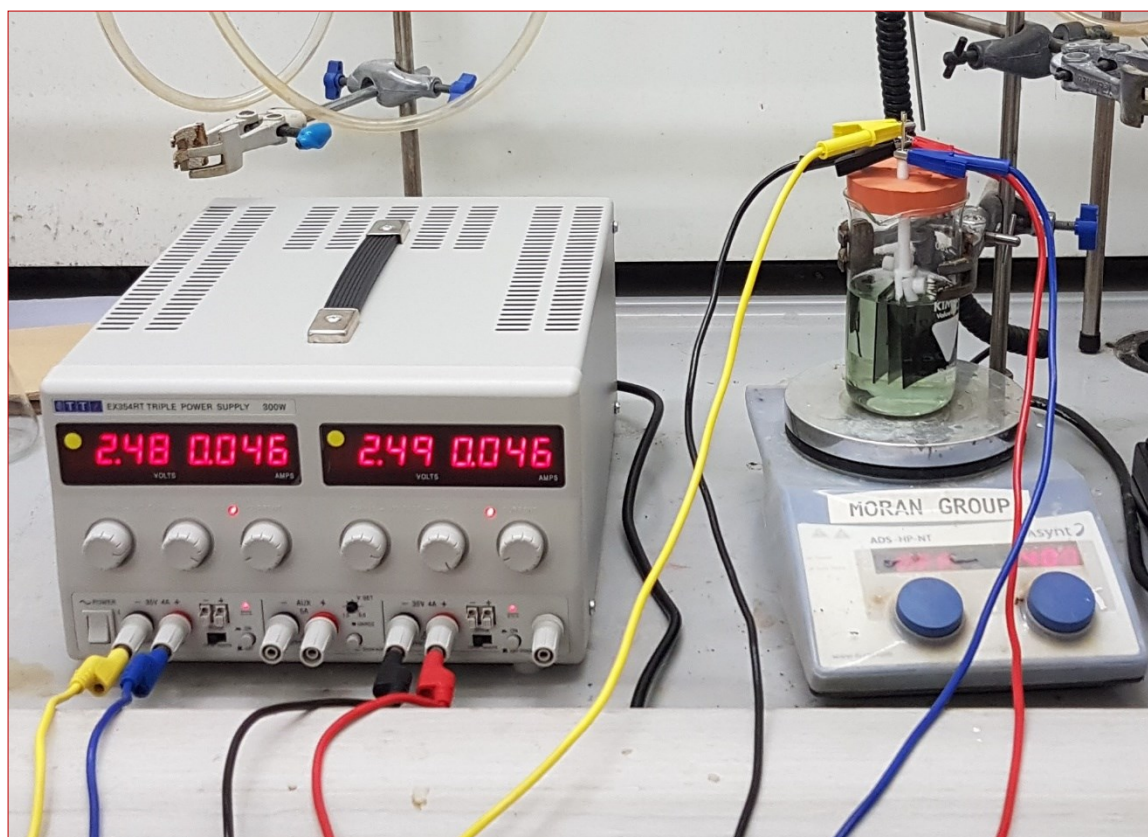
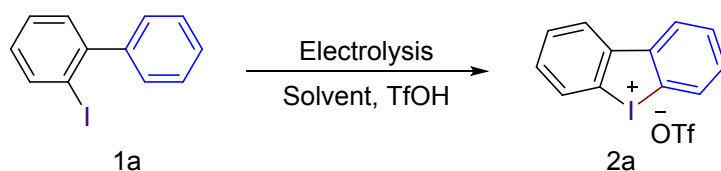


Figure S2. Actual setup of the scale-up experiments using a homemade beaker-type electrolysis cell.

Table S1. Solvent screening^[a]

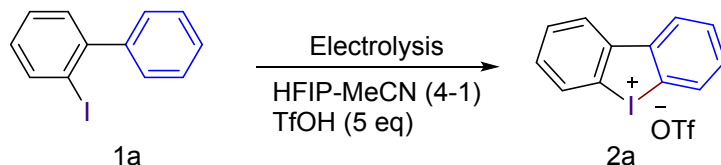


No	Solvent	2a [Yield%]
1 ^b	TFE	---
2 ^c	HFIP	70
3	MeCN	80
4 ^d	DCM	33
5 ^d	EtOAc	30
7	TFE-MeCN (4:1)	83
8	HFIP-MeCN (4:1)	95
9	HFIP-MeCN (3:2)	87
10	HFIP-MeCN (1:1)	83

^[a]Electrolyses were carried out with ElectroSyn 2.0 machine, using 5 mL glass vial equipped with glassy carbon (GC) anode and Pt cathode; electrode immersed area: 2.8 cm². Reaction conditions: 2-iodobiphenyl (**1a**, 42 mg, 26 μ L, 0.15 mmol) dissolved in 5 mL solvent, TfOH (113 mg, 67 μ L, 0.75 mmol, 5 equiv.), **constant current: 5 mA; time 120.6 min (2.5 F)**. ^bThe electrolysis could not be completed

due to very high cell voltage. ^cThe cell voltage started high (12 V) and dropped gradually till it reached 5 V prior the end of the electrolysis. ^dThe voltage was high, MeCN (0.4 mL) was added to enable completion of the electrolysis. TFE = 2,2,2-Trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Table S2. Concentration and current screening^[a]

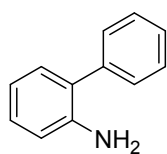
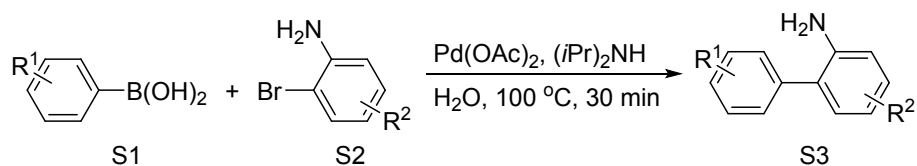


No	Current[mA]	Charge [F]	1a [mol/L]	2a [Yield%]
1	5	2.5	0.03	95
2	7.5	2.5	0.03	88
3	10	2.5	0.03	89
4	5	2.0	0.03	78
5	5	2.25	0.03	86
6	5	2.5	0.04	93
7	5	2.5	0.05	95
7	5	2.5	0.06	96
8 ^b	5	2.5	0.1	85

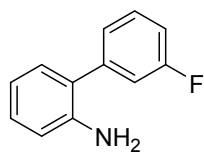
^[a]Electrolyses were carried out with ElectraSyn 2.0 machine, using 5 mL glass vial equipped with glassy carbon (GC) anode and Pt cathode; electrode immersed area: 2.8 cm². Reaction conditions: 2-iodobiphenyl (**1a**) dissolved in 5 mL solvent, TfOH (5 equiv.), constant current electrolysis. ^bProduct **2a** started to precipitate during the electrolysis and was accompanied by gradual increase of the cell voltage. TFE = 2,2,2-Trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Synthesis of aminobiaryl precursors (GP 1)

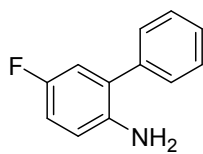
Aminobiaryl precursors **S3a-x** were prepared by Suzuki-Miyaura coupling between *o*-bromoaniline derivatives **S2** and the corresponding arylboronic acids **S1** according to a literature procedure.^[1] A mixture of *o*-bromoanilines (5.0 mmol, 1 equiv.), arylboronic acids (7.5 mmol, 1.5 equiv.), diisopropylamine (10.0 mmol, 2 equiv.), Pd(OAc)₂ (0.25 mol%, 2.8 mg), H₂O (10.0 mL) was stirred at 100 °C for 30 min. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (Pet. ether/EtOAc). Products **S3a-S3n**, **S3p-S3r** and **S3v** are known compounds, their spectral data are in good agreement with literature.^[2–10]



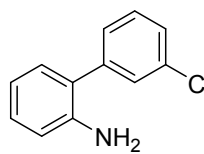
S3a^[2]



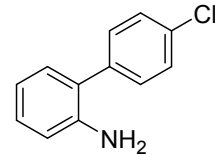
S3b^[3]



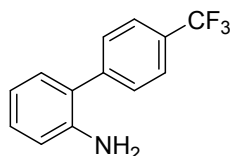
S3b'^[3]



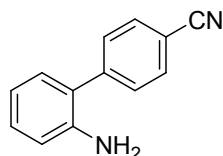
S3c^[3]



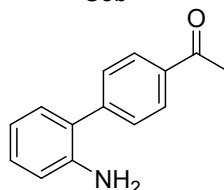
S3d^[3]



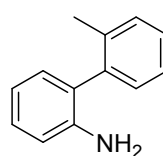
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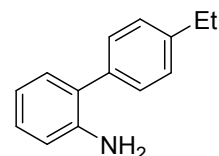
S3f^[4]



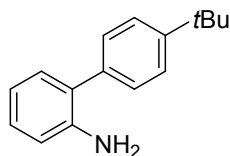
S3g^[5]



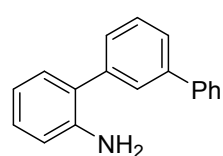
S3h^[3]



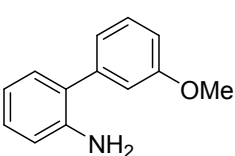
S3i^[4]



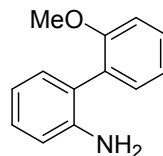
S3j^[4]



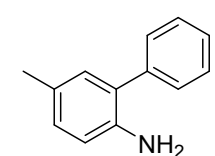
S3k^[5]



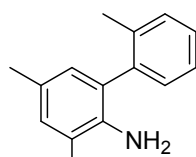
S3l^[3]



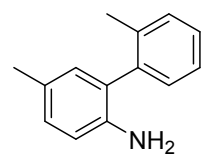
S3m^[6]



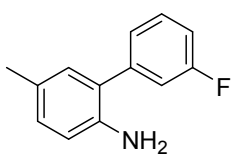
S3n^[3]



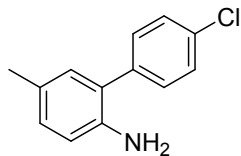
S3o



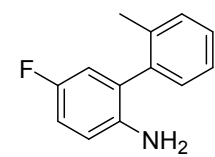
S3p^[8]



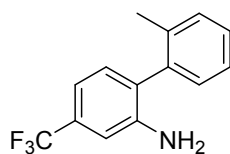
S3q^[9]



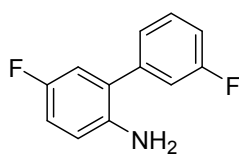
S3r^[9]



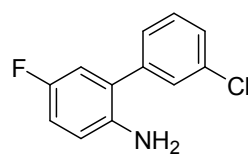
S3s



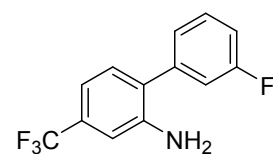
S3t



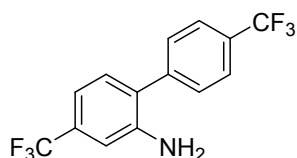
S3u



S3v^[10]



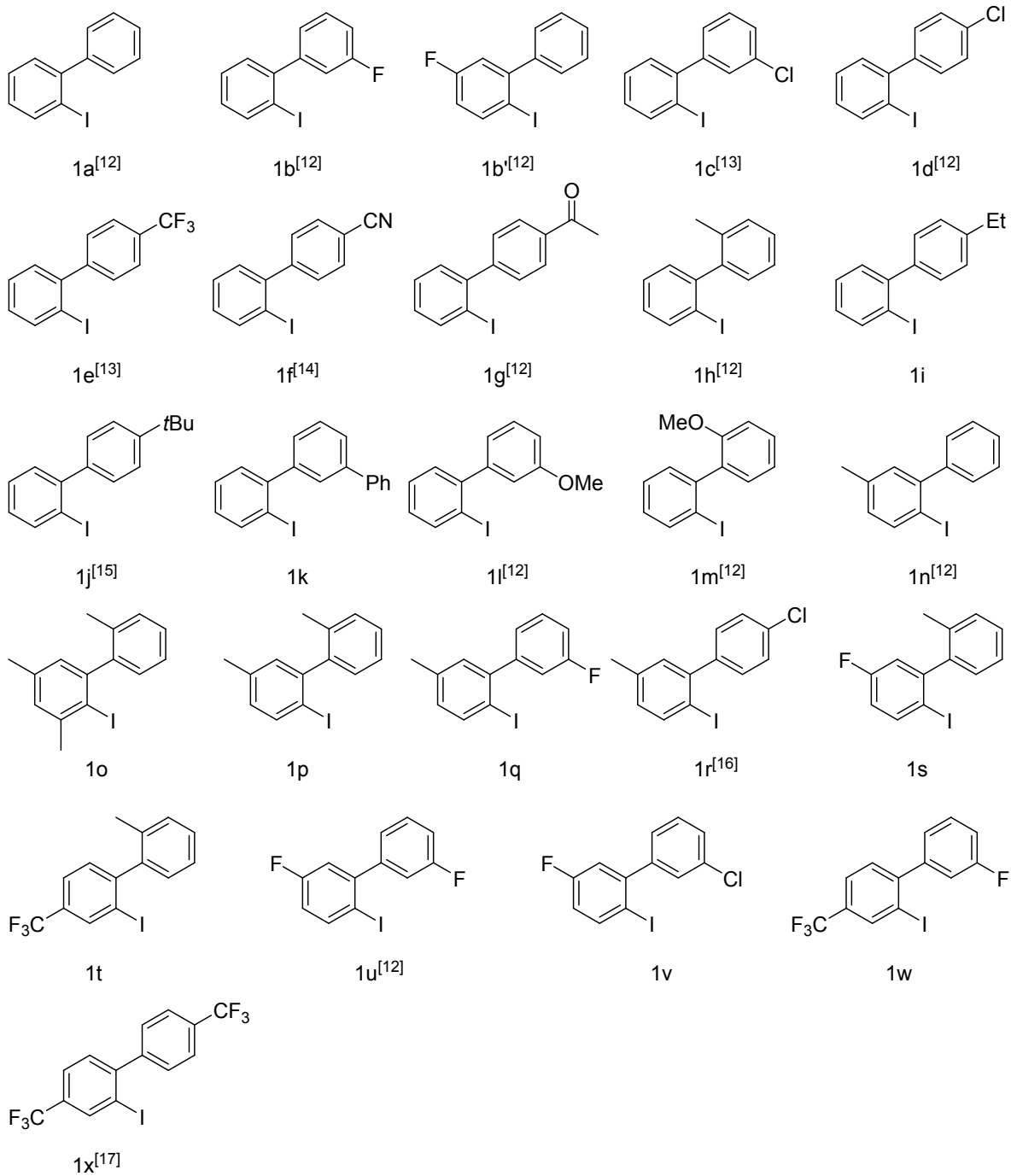
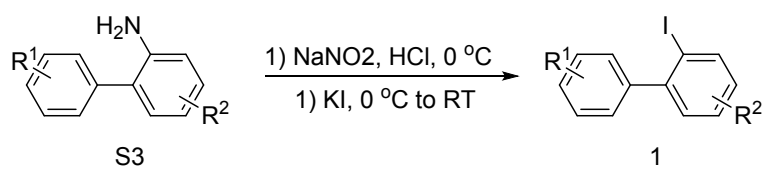
S3w



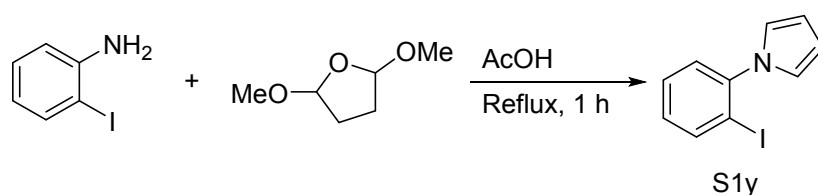
S3x

Synthesis of iodobiaryl substrates (GP 2)

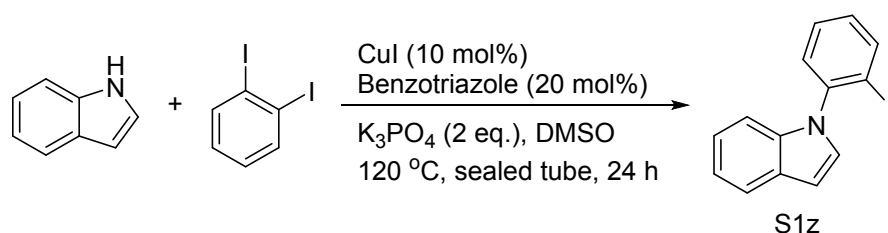
Iodobiphenyl precursors **1a-x** were prepared by Sandmeyer reaction of the prepared aminobiphenyls **S3** according to a literature procedure.^[11] A solution of conc. HCl (36-38%; 0.75 mL, 2.03 mmol, 1.35 equiv.) in water (3 mL) was added slowly to the prepared 2-aminobiphenyls **S3** (1.5 mmol, 1.0 equiv.) at 0 °C in portions. After stirring for 1 h at 0 °C, the aqueous solution of NaNO₂ (2.25 mmol, 1.5 equiv.) in water (2.0 mL) was added dropwise to the reaction mixture below 5 °C and stirred for 1 h in ice-bath. Then an aqueous solution of KI (3.0 mmol, 2.0 equiv.) in water (3.0 mL) was added dropwise and the reaction mixture was stirred at room temperature overnight. Saturated aqueous NaHCO₃ was added to neutralize the acid and adjust the solution to pH > 7, then extracted with ethyl acetate (3x5 mL). The combined organic phases were dried over anhydrous MgSO₄ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether unless otherwise noted) to give the desired 2-iodobiphenyls **1**. Products **1a-1h**, **1j**, **1l-1n**, **1r**, **1u**, and **1x** are known compounds, their spectral data are in good agreement with literature.^[12-17]



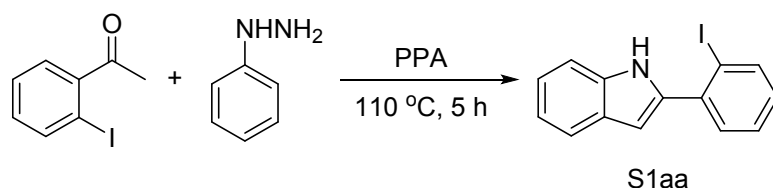
Synthesis of heterocyclic substrates **1y**, **1z**, and **1aa**



1-(2-iodophenyl)pyrrole (S1y) was prepared according to literature procedure.^[18,19] Spectral data are in good agreement with literature.^[18,19]

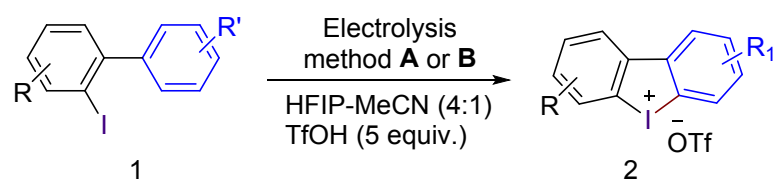


1-(2-iodophenyl)-1H-indole (S1z) was prepared according to literature procedure.^[18] Spectral data are in good agreement with literature.^[18]



1-(2-iodophenyl)-1H-indole (S1aa) was prepared according to literature procedure.^[11,20] Spectral data are in good agreement with literature.^[20]

Electrochemical synthesis of diaryliodonium salts **2**



Method A: A solution of 2-iodobiaryls **1** (0.3 mmol) in a mixture of HFIP (4 mL) and acetonitrile (1 mL) containing TfOH (225 mg, 133 μ L, 1.5 mmol, 5 equiv.) was electrolysed using an ElectraSyn undivided cell equipped with glassy carbon anode and platinum cathode under constant current of 5 mA with stirring (400 rpm) for 4.02 h (2.5 F). After electrolysis, the electrodes were rinsed with acetonitrile and combined with the reaction mixture. The mixture was concentrated under reduced pressure and

the residue was treated with cooled diethyl ether and left in the fridge overnight. The formed solid was collected by filtration and washed with cooled diethyl ether and air dried.

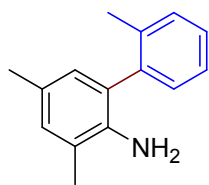
Method B: A solution of 2-iodobiphenyl **1** (0.3 mmol) in a mixture of HFIP (4 mL) and acetonitrile (1 mL) containing TfOH (225 mg, 133 μ L, 1.5 mmol, 5 equiv.) was electrolysed using an ElectraSyn undivided cell equipped with platinum anode and platinum cathode under constant current of 5 mA alternating polarity each 20 s, with stirring (400 rpm) for 4.02 h (2.5 F). After electrolysis, the electrodes were rinsed with acetonitrile and combined with the reaction mixture. The mixture was concentrated under reduced pressure and the residue was treated with cooled diethyl ether and left in the fridge overnight. The formed solid was collected by filtration and washed with cooled diethyl ether and air dried.

Gram-scale electrochemical synthesis of diaryliodonium salt **2a and solvent recovery / recycling**

Method C: Using a beaker-type homemade electrolysis cell (Figure S2), a solution of 2-iodobiphenyl **1a** (2.80 g, 1.76 mL, 10 mmol) in a mixture of HFIP (130 mL) and acetonitrile (32 mL) containing TfOH (7.5 g, 4.42 mL, 50 mmol, 5 equiv.) was electrolysed with stirring (400 rpm) under constant current of 92 mA (46 mA on each of the two anodes, $j = 1.84 \text{ mA/cm}^2$) for 5.83 h (2.5 F). After electrolysis, the mixture was concentrated under reduced pressure[†] and the residue was stirred with cooled diethyl ether for 20 min, the formed precipitate (**2a**) was filtered off and washed with cooled diethyl ether then oven dried (80 °C). The combined ether filtrate and wash was kept in the fridge overnight to give an additional small crop of product **2a** (total yield 4.17 g, 97%).

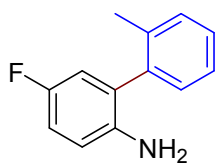
[†]Using rotary evaporator, the recovered solvent mixture (>97%) was completed to 162 mL with HFIP-MeCN (4:1) and reused.

2',3,5-Trimethyl-[1,1'-biphenyl]-2-amine (S3o)



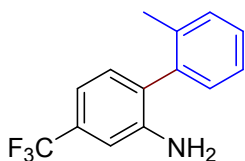
Pale yellow solid (0.624 g, 59%). ^1H NMR (400 MHz, CDCl_3) δ = 7.33 – 7.28 (m, 2H), 7.26 (ddd, J =6.4, 4.5, 2.6 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.93 (dd, J =1.3, 0.6 Hz, 1H), 6.75 (dd, J =1.4, 0.5 Hz, 1H), 3.34 (s, 2H), 2.28 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 139.32, 139.20, 137.10, 130.33, 130.28, 130.23, 128.36, 127.67, 127.52, 127.02, 126.23, 122.41, 20.56, 19.91, 17.93 ppm. HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{18}\text{N}^+$ $[\text{M}+\text{H}]^+$ 212.1434, found 212.1434.

5-Fluoro-2'-methyl-[1,1'-biphenyl]-2-amine (S3s)



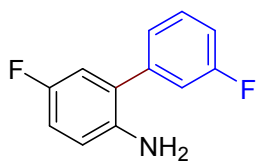
Reddish oil (0.916 g, 91%). ^1H NMR (400 MHz, CDCl_3) δ = 7.31 (dd, J =5.4, 1.4 Hz, 2H), 7.27 (ddd, J =8.9, 4.9, 2.7 Hz, 1H), 7.19 (dd, J =6.7, 1.3 Hz, 1H), 6.89 (td, J =8.5, 3.0 Hz, 1H), 6.77 (dd, J =9.1, 3.0 Hz, 1H), 6.70 (dd, J =8.7, 4.8 Hz, 1H), 3.41 (s, 2H), 2.19 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 156.12 (d, $^1J_{\text{C-F}}$ =236.3 Hz), 139.82 (d, $^4J_{\text{C-F}}$ =2.0 Hz), 137.72 (d, $^5J_{\text{C-F}}$ =1.3 Hz), 136.92, 130.53, 129.92, 128.72 (d, $^3J_{\text{C-F}}$ =7.2 Hz), 128.20, 126.38, 116.54 (d, $^2J_{\text{C-F}}$ =22.0 Hz), 116.06 (d, $^3J_{\text{C-F}}$ =7.8 Hz), 114.88 (d, $^2J_{\text{C-F}}$ =22.2 Hz), 19.71 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ = -127.16 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{13}\text{FN}^+$ $[\text{M}+\text{H}]^+$ 202.1027, found 202.1028.

2'-Methyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (S3t)



Yellow oil (0.980 g, 78%). ^1H NMR (400 MHz, CDCl_3) δ = 7.32 (dd, J =5.0, 1.3 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.18 (d, J =6.8 Hz, 1H), 7.11 (d, J =7.8 Hz, 1H), 7.05 (dd, J =7.8, 1.0 Hz, 1H), 7.00 – 6.98 (m, 1H), 3.68 (s, 2H), 2.17 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 144.21, 137.39, 136.88, 133.22, 130.71 (q, $^2J_{\text{C-F}}$ =32.0 Hz), 130.63, 130.60, 129.83, 128.40, 126.50, 124.42 (q, $^1J_{\text{C-F}}$ =272.1 Hz), 114.73 (q, $^4J_{\text{C-F}}$ =3.9 Hz), 111.45 (q, $^4J_{\text{C-F}}$ =3.8 Hz), 19.71 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ = -62.65 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{13}\text{F}_3\text{N}^+$ $[\text{M}+\text{H}]^+$ 252.0995, found 252.0993.

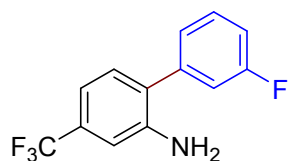
3',5-Difluoro-[1,1'-biphenyl]-2-amine (S3u)



Yellow oil (1.02 g, quant.). ^1H NMR (400 MHz, CDCl_3) δ = 7.42 (td, J =8.0, 6.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.17 (ddd, J =9.8, 2.5, 1.6 Hz, 1H), 7.07 (tdd, J =8.5, 2.6, 0.9 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.70 (dd, J =8.7, 4.8 Hz, 1H), 3.63 (s, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ =

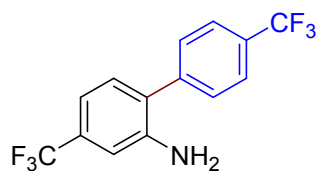
163.14 (d, $^1J_{C-F}$ = 247.0 Hz), 156.43 (d, $^1J_{C-F}$ = 236.7 Hz), 140.82 (dd, $^{3,4}J_{C-F}$ = 7.7, 1.6 Hz), 139.49 (d, $^4J_{C-F}$ = 2.1 Hz), 130.64 (d, $^3J_{C-F}$ = 8.5 Hz), 127.39 (dd, $^{3,4}J_{C-F}$ = 7.2, 1.9 Hz), 124.76 (d, $^4J_{C-F}$ = 3.0 Hz), 116.90 (d, $^3J_{C-F}$ = 7.7 Hz), 116.65 (d, $^2J_{C-F}$ = 22.7 Hz), 116.08 (d, $^2J_{C-F}$ = 21.5 Hz), 115.53 (d, $^2J_{C-F}$ = 22.3 Hz), 114.68 (d, $^2J_{C-F}$ = 21.0 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -112.24 -126.82 ppm. HRMS (ESI) Calcd for $C_{12}H_{10}F_2N^+$ $[M+H]^+$ 206.0776, found 206.0775.

3'-Fluoro-4-(trifluoromethyl)-[1,1'-biphenyl]-2-amine (S3w)



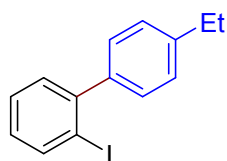
Yellow oil (1.12 g, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44 (td, J = 8.0, 6.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.16 (ddd, J = 9.7, 2.4, 1.7 Hz, 1H), 7.10 (tdd, J = 8.4, 2.6, 0.9 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.99 (d, J = 0.7 Hz, 1H), 3.94 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.21 (d, $^1J_{C-F}$ = 247.3 Hz), 143.94, 140.49 (d, $^3J_{C-F}$ = 7.7 Hz), 131.20 (q, $^2J_{C-F}$ = 32.2 Hz), 130.85, 130.76, 129.22, 124.69 (d, $^4J_{C-F}$ = 2.9 Hz), 124.23 (q, $^1J_{C-F}$ = 272.3 Hz), 116.05 (d, $^2J_{C-F}$ = 21.6 Hz), 115.12 (q, $^4J_{C-F}$ = 3.9 Hz), 114.97 (d, $^2J_{C-F}$ = 21.0 Hz), 112.19 (q, $^4J_{C-F}$ = 3.9 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.85, -111.96 ppm. HRMS (ESI) Calcd for $C_{13}H_{10}F_4N^+$ $[M+H]^+$ 256.0744, found 256.0745.

4,4'-Bis(trifluoromethyl)-[1,1'-biphenyl]-2-amine (S3x)



Yellowish solid (1.42 g, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.9 Hz, 1H), 7.08 (dd, J = 7.9, 0.9 Hz, 1H), 7.01 (s, 1H), 3.91 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.94, 142.09, 133.23, 131.52 (q, $^2J_{C-F}$ = 32.2 Hz), 130.89, 130.20 (q, $^2J_{C-F}$ = 32.6 Hz), 129.45, 129.01, 126.17 (q, $^4J_{C-F}$ = 3.7 Hz, 2C), 124.17 (q, $^1J_{C-F}$ = 272.2 Hz, 2CF₃), 115.27 (q, $^4J_{C-F}$ = 3.8 Hz), 112.33 (q, $^4J_{C-F}$ = 3.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.63, -62.93 ppm. HRMS (ESI) Calcd for $C_{14}H_{10}F_6N^+$ $[M+H]^+$ 306.0712, found 306.0709.

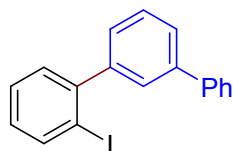
4'-Ethyl-2-iodo-1,1'-biphenyl (1i)



Colourless oil (361 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.94 (dd, J = 7.9, 1.1 Hz, 1H), 7.37 (td, J = 7.4, 1.2 Hz, 1H), 7.32-7.23 (m, 5H), 7.01 (ddd, J = 7.9, 7.4, 1.8 Hz, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.72,

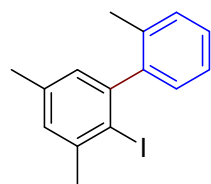
143.74, 141.63, 139.60, 130.31, 129.30, 128.72, 128.22, 127.53, 98.95, 28.73, 15.52 ppm. HRMS (ESI) Calcd for $C_{14}H_{13}I^+$ $[M]^+$ 308.0056, found 308.0057.

2-Iodo-1,1':3',1''-terphenyl (1k)



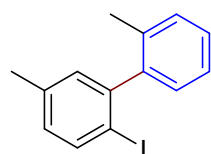
Colourless oil (486 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.99 (dd, J =8.0, 1.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.66 (d, J =1.0 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.62-7.59 (m, 1H), 7.54 – 7.49 (m, 1H), 7.49 – 7.43 (m, 2H), 7.41 (dd, J =7.1, 1.2 Hz, 1H), 7.40 – 7.38 (m, 1H), 7.38 – 7.31 (m, 2H), 7.06 (ddd, J =7.9, 7.1, 2.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.59, 144.67, 141.00, 140.89, 139.71, 130.26, 129.02, 128.93, 128.58, 128.41, 128.32, 128.22, 127.54, 127.34, 126.48, 98.78 ppm. HRMS (ESI) Calcd for $C_{18}H_{13}I^+$ $[M]^+$ 356.0056, found 356.0056.

2-Iodo-2',3,5-trimethyl-1,1'-biphenyl (1p)



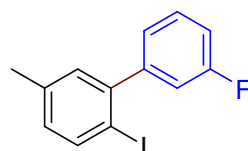
Colourless oil (295 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.21 (m, 3H), 7.09 – 7.03 (m, 2H), 6.84 (d, J =1.6 Hz, 1H), 2.51 (s, 3H), 2.30 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.55, 145.68, 141.96, 137.58, 135.72, 129.89, 129.37, 129.27, 127.80, 127.15, 125.61, 103.04, 29.64, 20.87, 20.13 ppm. HRMS (ESI) Calcd for $C_{15}H_{15}I^+$ $[M]^+$ 322.0213, found 322.0213.

2-Iodo-2',5-dimethyl-1,1'-biphenyl (1q)



Colourless oil (273 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, J =8.1 Hz, 1H), 7.34 – 7.21 (m, 3H), 7.09 – 7.03 (m, 2H), 6.87 (d, J =7.9 Hz, 1H), 2.33 (s, 3H), 2.09 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.67, 144.52, 138.70, 138.14, 135.76, 130.70, 129.97, 129.83, 129.29, 127.99, 125.63, 96.00, 21.08, 20.14 ppm. HRMS (ESI) Calcd for $C_{14}H_{13}I^+$ $[M]^+$ 308.0056, found 308.0058.

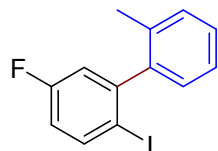
3'-Fluoro-2-iodo-5-methyl-1,1'-biphenyl (1r)



Yellow oil (298 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, J =8.1 Hz, 1H), 7.38 (dd, J =7.8, 1.9 Hz, 1H), 7.14 – 7.02 (m, 4H), 6.89 (ddd, J =8.1, 2.2, 0.6 Hz, 1H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.35 (d, $^1J_{C-F}$ = 246.1 Hz), 146.30 (d, $^3J_{C-F}$ = 7.9 Hz), 145.22 (d, $^4J_{C-F}$ = 2.0 Hz), 139.47, 138.37, 131.05, 130.31, 129.59 (d, $^3J_{C-F}$ = 8.4 Hz), 125.25 (d, $^4J_{C-F}$ = 3.0 Hz), 116.56 (d, $^2J_{C-F}$ = 21.9 Hz), 114.57 (d, $^2J_{C-F}$ = 20.9 Hz), 94.06, 21.02 ppm. ^{19}F

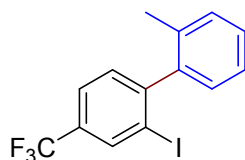
NMR (376 MHz, DMSO) δ = -113.33 ppm. HRMS (ESI) Calcd for $C_{13}H_{10}FI^+$ $[M]^+$ 311.9806, found 311.9805.

5-Fluoro-2-iodo-5'-methyl-1,1'-biphenyl (1t)



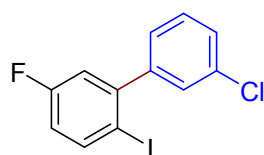
Yellow oil (275 mg, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.87 (dd, J =8.7, 5.6 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.30 – 7.25 (m, 2H), 7.06 (d, J =7.7 Hz, 1H), 6.98 (dd, J =9.1, 3.0 Hz, 1H), 6.83 (td, J =8.5, 3.0 Hz, 1H), 2.09 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.91 (d, $^1J_{C-F}$ =248.5 Hz), 148.78 (d, $^3J_{C-F}$ =7.7 Hz), 143.47 (d, $^4J_{C-F}$ =1.5 Hz), 140.16 (d, $^3J_{C-F}$ =7.9 Hz), 135.52, 130.16, 129.01, 128.46, 125.81, 117.15 (d, $^2J_{C-F}$ =21.8 Hz), 116.34 (d, $^2J_{C-F}$ =21.7 Hz), 93.17 (d, $^4J_{C-F}$ =3.2 Hz), 20.03 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -114.47 ppm. HRMS (ESI) Calcd for $C_{13}H_{10}FI^+$ $[M]^+$ 311.9806, found 311.9806.

2-Iodo-2'-methyl-4-(trifluoromethyl)-1,1'-biphenyl (1u)



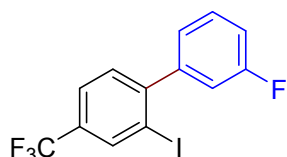
Yellow oil (337 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, J =0.8 Hz, 1H), 7.67 (ddd, J =7.9, 1.7, 0.6 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.05 (d, J =7.6 Hz, 1H), 2.08 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.72, 143.31, 135.85 (q, $^4J_{C-F}$ =3.8 Hz), 135.39, 133.13, 130.93 (q, $^2J_{C-F}$ =32.9 Hz), 130.25, 129.94, 128.87, 128.64, 125.12 (q, $^4J_{C-F}$ =3.6 Hz), 123.08 (q, $^1J_{C-F}$ =272.8 Hz), 99.94, 20.07 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -62.52 ppm. HRMS (ESI) Calcd for $C_{14}H_{10}F_3I^+$ $[M]^+$ 361.9774, found 361.9772.

3'-Chloro-5-fluoro-2-iodo-1,1'-biphenyl (1w)



Pale yellow oil (382 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.89 (dd, J =8.7, 5.6 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.21 (dt, J =6.6, 1.8 Hz, 1H), 7.04 (dd, J =9.1, 3.0 Hz, 1H), 6.83 (ddd, J =8.6, 8.1, 3.0 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.94 (d, $^1J_{C-F}$ =248.9 Hz), 147.09 (d, $^3J_{C-F}$ =7.6 Hz), 144.84 (d, $^4J_{C-F}$ =1.6 Hz), 140.94 (d, $^3J_{C-F}$ =7.8 Hz), 134.09, 129.57, 129.36, 128.37, 127.51, 117.45 (d, $^2J_{C-F}$ =22.5 Hz), 116.83 (d, $^2J_{C-F}$ =21.6 Hz), 91.23 (d, $^4J_{C-F}$ =3.4 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.07 ppm. HRMS (ESI) Calcd for $C_{12}H_7ClFI^+$ $[M]^+$ 331.9260 found 331.9261.

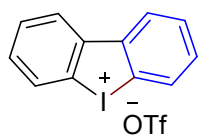
3'-Fluoro-2-iodo-4-(trifluoromethyl)-1,1'-biphenyl (1x)



Yellow oil (390 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, J =0.8 Hz, 1H), 7.66 (dd, J =8.0, 1.1 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.17 – 7.09 (m, 2H), 7.05 (ddd, J =9.4, 2.4, 1.7 Hz, 1H) ppm.

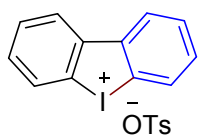
^{13}C NMR (101 MHz, CDCl_3) δ = 162.44 (d, $^1J_{\text{C-F}}$ = 247.1 Hz), 149.06, 145.01 (d, $^3J_{\text{C-F}}$ = 7.9 Hz), 136.55 (q, $^4J_{\text{C-F}}$ = 3.9 Hz), 131.37 (q, $^2J_{\text{C-F}}$ = 33.0 Hz), 130.15, 130.04 (d, $^3J_{\text{C-F}}$ = 8.4) Hz, 125.24 (q, $^4J_{\text{C-F}}$ = 3.6 Hz), 124.95 (d, $^4J_{\text{C-F}}$ = 3.0 Hz), 122.95 (q, $^1J_{\text{C-F}}$ = 272.8 Hz), 116.34 (d, $^2J_{\text{C-F}}$ = 22.3 Hz), 115.41 (d, $^2J_{\text{C-F}}$ = 21.0 Hz), 98.02 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -62.63, -112.56 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_7\text{F}_4\text{I}^+ [\text{M}]^+$ 365.9523, found 365.9525.

Dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2a)



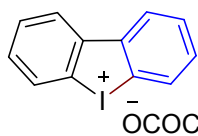
Pale yellow solid (124 mg, 96%). ^1H NMR (400 MHz, DMSO) δ = 8.49 (dd, J =7.9, 1.3, 2H), 8.22 (dd, J =8.2, 0.9, 2H), 7.90 – 7.81 (m, 2H), 7.72 (ddd, J =8.5, 7.4, 1.4, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 141.76, 131.14, 130.75, 130.62, 127.05, 121.65 120.70 (q, $^1J_{\text{C-F}}$ = 322.4 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_8\text{I}^+ [\text{M-OTf}]^+$ 278.9665, found 278.9662. Spectral data are in good agreement with literature.^[21,22]

Dibenzo[b,d]iodol-5-ium 4-methylbenzenesulfonate (2a1)



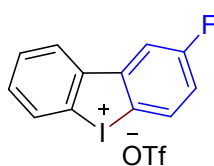
Pale yellow solid (126 mg, 93%). ^1H NMR (400 MHz, DMSO) δ = 8.47 (dd, J =7.9, 1.3 Hz, 2H), 8.26 (dd, J =8.3, 0.9 Hz, 2H), 7.89 – 7.80 (m, 2H), 7.70 (ddd, J =8.5, 7.4, 1.4 HZ, 2H), 7.53 (d, J =8.1 Hz, 2H), 7.13 (d, J =7.8 Hz, 2H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 145.31, 141.75, 137.89, 131.01, 130.67 (2C), 128.16, 126.95, 125.50, 121.65, 20.78 ppm. Spectral data are in good agreement with literature.^[23]

Dibenzo[b,d]iodol-5-ium 2,2,2-trifluoroacetate (2a2)



Pale yellow solid (82 mg, 70%). ^1H NMR (400 MHz, DMSO) δ = 8.45 (dd, J =7.8, 0.9 Hz, 2H), 8.27 (d, J =7.9 Hz, 2H), 7.83 (t, J =7.2 Hz, 2H), 7.73 – 7.65 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 141.75, 130.90, 130.72, 130.58, 126.82, 121.89 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -73.49 ppm. Spectral data are in good agreement with literature.^[23]

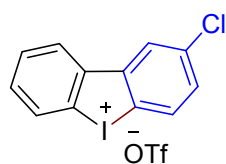
2-Fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2b)



Pale yellow solid (118 mg, 88%). ^1H NMR (400 MHz, DMSO) δ = 8.52 (dd, J =8.3, 1.1 Hz, 1H), 8.30 (dd, J =8.2, 1.2 Hz, 1H), 8.16 (dd, J =8.1, 0.7 Hz, 1H), 7.88 (ddd, J =8.3, 1.3, 1H), 7.75– 7.68 (m, 2H), 7.57 (t, J =7.9 Hz, 1H), 2.89 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO)

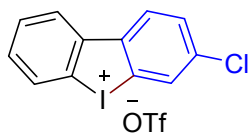
δ = 164.07 (d, $^1J_{\text{C-F}}$ = 247.0 Hz), 144.41 (d, $^3J_{\text{C-F}}$ = 9.5 Hz), 140.84 (d, $^4J_{\text{C-F}}$ = 3.0 Hz), 132.56 (d, $^3J_{\text{C-F}}$ = 9.2 Hz), 131.72, 130.84, 130.66, 127.55, 122.27, 120.71 (q, $^1J_{\text{C-F}}$ = 322.2 Hz), 118.56 (d, $^2J_{\text{C-F}}$ = 24.0 Hz), 115.62 (d, $^4J_{\text{C-F}}$ = 2.1 Hz), 114.03 (d, $^2J_{\text{C-F}}$ = 25.2 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.77, -110.61 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_7\text{FI}^+ [\text{M-OTf}]^+$ 296.9571, found 296.9568. Spectral data are in good agreement with literature.^[24]

2-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2c)



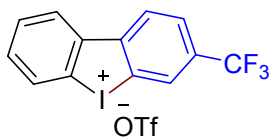
Pale yellow solid (135 mg, 97%). ^1H NMR (400 MHz, DMSO) δ = 8.66 (d, J = 2.3, 1H), 8.58 (dd, J = 7.9, 1.1, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 1H), 7.86 (t, J = 7.2 Hz, 1H), 7.79-7.70 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 143.84, 140.54, 136.40, 132.06, 131.70, 130.78, 130.65, 130.56, 127.54, 126.68, 122.22, 120.68 (q, $^1J_{\text{C-F}}$ = 322.5 Hz), 119.50 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.74 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_7\text{ClI}^+ [\text{M-OTf}]^+$ 312.9275, found 312.9273. Spectral data are in good agreement with literature.^[24]

3-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2d)



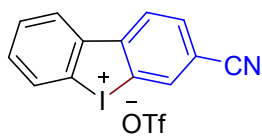
Pale yellow solid (132 mg, 95%). ^1H NMR (400 MHz, DMSO) δ = 8.52 – 8.43 (m, 2H), 8.23 – 8.18 (m, 2H), 7.94 (dd, J = 8.5 Hz, 2.0, 1H), 7.90 – 7.83 (m, 1H), 7.78 – 7.71 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 140.80, 140.62, 134.52, 131.38, 131.09, 130.83, 130.52, 129.87, 127.98, 127.31, 122.31, 122.08, 120.69 (q, $^1J_{\text{C-F}}$ = 322.3 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_7\text{ClI}^+ [\text{M-OTf}]^+$ 312.9275, found 312.9275. Spectral data are in good agreement with literature.^[14]

3-(Trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2e)



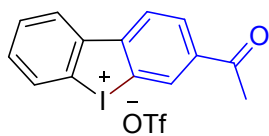
White solid (115 mg, 77%). ^1H NMR (400 MHz, DMSO) δ = 8.71 (d, J = 8.3 Hz, 1H), 8.62 (dd, J = 7.9, 1.3 Hz, 1H), 8.54 (d, J = 0.8 Hz, 1H), 8.31 – 8.20 (m, 2H), 7.96 – 7.88 (m, 1H), 7.86 – 7.75 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 145.69, 140.31, 132.32, 130.96, 130.68, 130.20, 129.87, 128.07, 127.66, 127.50, 123.35 (q, $^1J_{\text{C-F}}$ = 272.8 Hz), 122.99, 122.13, 120.69 (q, $^1J_{\text{C-F}}$ = 322.3 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -60.99, -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_7\text{F}_3\text{I}^+ [\text{M-OTf}]^+$ 346.9539, found 346.9540. Spectral data are in good agreement with literature.^[21]

3-Cyanodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2f)



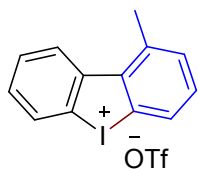
White solid (118 mg, 87%). ^1H NMR (400 MHz, DMSO) δ = 8.67 (d, J =8.3 Hz, 1H), 8.61 (dd, J =7.9, 1.3 Hz, 1H), 8.53 (d, J =1.4 Hz, 1H), 8.33 (dd, J =8.2, 1.5 Hz, 1H), 8.25 (dd, J =8.2, 0.9 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.85 – 7.78 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 145.97, 140.25, 134.28, 134.21, 132.53, 130.94, 130.63, 128.22, 127.33, 123.28, 121.74, 120.67 (q, $^1J_{\text{C-F}}$ =322.5 Hz), 117.50, 112.40 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_7\text{IN}^+$ [M-OTf] $^+$ 303.9618, found 303.9619. Spectral data are in good agreement with literature.^[21]

3-Acetyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2g)



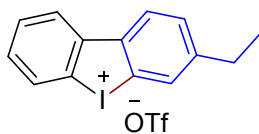
Yellow solid (111 mg, 79%). ^1H NMR (400 MHz, DMSO) δ = 8.73 (d, J =1.5 Hz, 1H), 8.66 – 8.56 (m, 2H), 8.39 (dd, J =8.2, 1.5 Hz, 1H), 8.25 (d, J =8.2 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.82 – 7.75 (m, 1H), 2.70 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 196.27, 145.50, 140.64, 137.98, 132.10, 130.92, 130.77, 130.65, 130.20, 128.00, 127.02, 122.85, 122.29, 26.99 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{10}\text{IO}^+$ [M-OTf] $^+$ 320.9771, found 320.9769. Spectral data are in good agreement with literature.^[14]

1-Methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2h)



White solid (125 mg, 94%). ^1H NMR (400 MHz, DMSO) δ = 8.52 (dd, J =8.3, 1.1 Hz, 1H), 8.30 (dd, J =8.2, 1.2 Hz, 1H), 8.16 (dd, J =8.1, 0.7 Hz, 1H), 7.88 (ddd, J =8.3, 7.4, 1.3 Hz, 1H), 7.76–7.68 (m, 2H), 7.57 (t, J =7.8 Hz, 1H), 2.89 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.76, 139.96, 139.47, 134.53, 130.87, 130.77, 130.62, 130.27, 129.89, 128.61, 122.05, 120.61, 23.31 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.77 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{I}^+$ [M-OTf] $^+$ 292.9822, found 292.9822. Spectral data are in good agreement with literature.^[21]

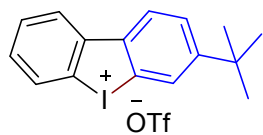
3-Ethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2i)



White solid (116 mg, 85%). ^1H NMR (400 MHz, DMSO) δ = 8.42 (dd, J =7.9, 1.3 Hz, 1H), 8.37 (d, J =8.1 Hz, 1H), 8.19 (dd, J =8.2, 0.9 Hz, 1H), 8.02 (d, J =1.3 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.73 – 7.65 (m, 2H), 2.80 (q, J =7.6 Hz, 2H), 1.27 (t, J =7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz,

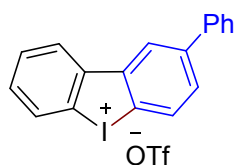
DMSO) δ = 147.57, 141.72, 139.40, 130.68, 130.56, 129.09, 126.78, 126.73, 121.86, 121.34, 120.68 (q, $^1J_{C-F}$ = 322.4 Hz), 28.18, 15.15 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.74 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}\text{I}^+$ [M-OTf] $^+$ 306.9978, found 306.9977.

3-(*tert*-Butyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2j)



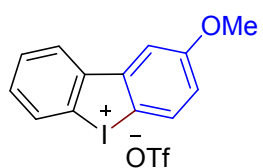
White solid (109 mg, 75%). ^1H NMR (400 MHz, DMSO) δ = 8.44 (dd, J = 8.0, 1.2 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 1.8 Hz, 1H), 8.20 (dd, J = 8.2, 0.7 Hz, 1H), 7.91 (dd, J = 8.3, 1.8 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.71 – 7.65 (m, 1H), 1.38 (s, 9H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 154.46, 141.61, 139.20, 130.72, 130.69, 130.59, 128.37, 126.83, 126.69, 126.64, 122.13, 121.43, 120.68 (q, $^1J_{C-F}$ = 322.5 Hz), 35.49, 30.86 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{16}\text{I}^+$ [M-OTf] $^+$ 335.0291, found 335.0292. Spectral data are in good agreement with literature.^[25,26]

2-Phenyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2k)



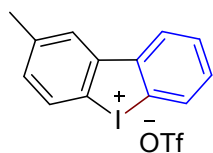
Grey solid (90 mg, 59%). ^1H NMR (400 MHz, DMSO) δ = 8.73 (d, J = 1.9 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.99 (dd, J = 8.6, 2.0 Hz, 1H), 7.90 – 7.85 (m, 3H), 7.75 – 7.68 (m, 1H), 7.55 (t, J = 7.4 Hz, 2H), 7.51 – 7.45 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.80, 142.49, 141.62, 138.17, 131.23, 130.92, 130.66, 130.53, 129.38, 129.15, 128.62, 127.53, 127.31, 124.87, 121.86, 120.71 (q, $^1J_{C-F}$ = 322.2 Hz), 120.13 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.73 ppm. HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{12}\text{I}^+$ [M-OTf] $^+$ 354.9978, found 354.9977.

2-Methoxydibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2l)



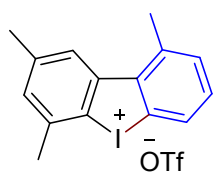
Grey solid (Method A: 31 mg, 44%, based on 0.15 mmol; Method B: 119 mg, 87%, based on 0.3 mmol). ^1H NMR (400 MHz, DMSO) δ = 8.54 (dd, J = 8.0, 1.3 Hz, 1H), 8.19 (dd, J = 8.3, 0.9 Hz, 1H), 8.04 (d, J = 6.2 Hz, 1H), 8.02 (s, 1H), 7.87 – 7.81 (m, 1H), 7.70 (ddd, J = 8.5, 7.3, 1.4 Hz, 1H), 7.31 (dd, J = 9.1, 2.8 Hz, 1H), 3.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 161.64, 143.30, 141.52, 131.26, 131.18, 130.64, 130.61, 127.37, 121.79, 120.70 (q, $^1J_{C-F}$ = 322.4 Hz), 118.41, 111.62, 110.52, 56.16 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{IO}^+$ [M-OTf] $^+$ 308.9771, found 308.9770. Spectral data are in good agreement with literature.^[22]

2-Methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2n)



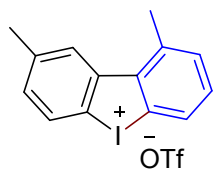
White solid (130 mg, 98%). ^1H NMR (400 MHz, DMSO) δ = 8.43 (dd, J =8.0, 1.2 Hz, 1H), 8.32 (d, J =1.0 Hz, 1H), 8.19 (dd, J =8.2, 0.8 Hz, 1H), 8.05 (d, J =8.4 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.73 – 7.66 (m, 1H), 7.53 (dd, J =8.4, 1.3 Hz, 1H), 2.51 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 141.70, 141.65, 140.94, 132.03, 130.98, 130.67, 130.59, 130.12, 127.32, 126.87, 121.67, 120.68 (q, $^1J_{\text{C-F}}$ =322.4 Hz), 117.93, 20.75 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.74 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{10}\text{I}^+ [\text{M-OTf}]^+$ 292.9822, found 292.9820. Spectral data are in good agreement with literature.^[24]

1,6,8-Trimethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2o)



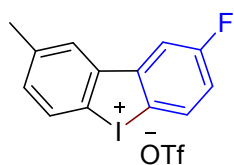
Light brown solid (114 mg, 81%). ^1H NMR (400 MHz, DMSO) δ = 8.29 (d, J =8.1 Hz, 1H), 8.10 (s, 1H), 7.72 (d, J =7.0 Hz, 1H), 7.56 (t, J =7.5 Hz, 1H), 7.42 (s, 1H), 2.88 (s, 3H), 2.66 (s, 3H), 2.51 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.97, 141.04, 140.35, 140.12, 138.76, 134.68, 131.31, 129.54, 129.14, 128.50, 122.04, 121.45, 120.69 (q, $^1J_{\text{C-F}}$ =322.3 Hz), 25.54, 23.19, 21.03 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.77 ppm. HRMS (ESI) Calcd for $\text{C}_{135}\text{H}_{14}\text{I}^+ [\text{M-OTf}]^+$ 321.0135, found 321.0137.

1,8-Dimethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2p)



Brown solid (129 mg, 94%). ^1H NMR (400 MHz, DMSO) δ = 8.28 (s, 1H), 8.14 (d, J =8.3 Hz, 2H), 7.69 (d, J =7.4 Hz, 1H), 7.58 – 7.50 (m, 2H), 2.89 (s, 3H), 2.54 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.74, 140.68, 139.83, 139.25, 134.39, 131.03, 130.85, 130.32, 129.66, 128.52, 122.00, 120.68 (q, $^1J_{\text{C-F}}$ =322.5 Hz), 116.79, 23.27, 21.17 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.74 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{12}\text{I}^+ [\text{M-OTf}]^+$ 306.9978, found 306.9977.

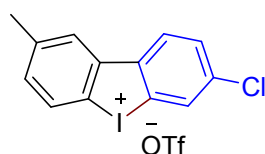
2-Fluoro-8-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2q)



White solid (125 mg, 91%). ^1H NMR (400 MHz, DMSO) δ = 8.39 (dd, J =10.0, 2.9 Hz, 1H), 8.19 (dd, J =9.0, 5.2 Hz, 1H), 8.05 (d, J =8.4 Hz, 1H), 7.64 – 7.52 (m, 3H), 2.88 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 164.06 (d, $^1J_{\text{C-F}}$ =246.9 Hz), 144.36 (d, $^3J_{\text{C-F}}$ =9.4 Hz), 141.12, 140.80 (d, $^4J_{\text{C-F}}$ =3.1 Hz), 132.64, 132.58 (d, $^3J_{\text{C-F}}$ =9.6 Hz), 130.22, 127.90, 120.73 (q, $^1J_{\text{C-F}}$ =322.3 Hz), 118.61, 118.44 (d, $^2J_{\text{C-F}}$ =24.2 Hz), 115.67 (d, $^4J_{\text{C-F}}$ =2.2

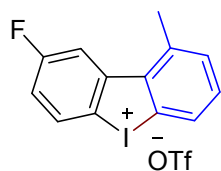
Hz), 113.88 (d, $^2J_{\text{C-F}}=25.3$ Hz), 20.78 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.78, -110.69 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_9\text{FI}^+ [\text{M-OTf}]^+$ 310.9727, found 310.9725.

7-Chloro-2-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2r)



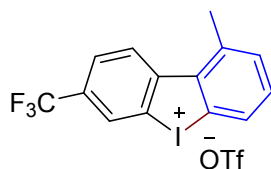
White solid (134 mg, 94%). ^1H NMR (400 MHz, DMSO) δ = 8.45 (dd, $J=8.6, 1.2$ Hz, 1H), 8.35 (s, 1H), 8.20 (d, $J=1.4$ Hz, 1H), 8.05 (d, $J=8.4$ Hz, 1H), 7.95 (dd, $J=8.5, 2.0$ Hz, 1H), 7.56 (d, $J=8.5$ Hz, 1H), 2.51 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 141.14, 140.77, 140.63, 134.42, 132.34, 131.11, 130.11, 129.91, 127.89, 127.69, 122.42, 120.70 (q, $^1J_{\text{C-F}}=322.4$ Hz), 118.46, 20.76 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.78 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_9\text{ClI}^+ [\text{M-OTf}]^+$ 326.9432, found 326.9431.

8-Fluoro-1-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2s)



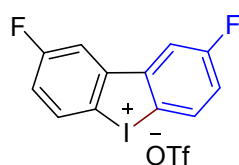
White solid (123 mg, 89%). ^1H NMR (400 MHz, DMSO) δ = 8.30 (dd, $J=9.0, 5.6$, 1H), 8.25 (dd, $J=11.2, 2.7$, 1H), 8.16 (d, $J=8.1$, 1H), 7.72 (d, $J=7.4$, 1H), 7.67 – 7.57 (m, 2H), 2.90 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.82 (d, $J_{\text{C-F}}=246.1$ Hz), 145.31 (d, $J_{\text{C-F}}=9.3$ Hz), 140.83, 138.75 (d, $J_{\text{C-F}}=2.9$ Hz), 134.90, 132.86 (d, $J_{\text{C-F}}=9.4$ Hz), 130.86, 129.04, 123.12, 121.70 (q, $J_{\text{C-F}}=322.3$ Hz), 118.03 (d, $J_{\text{C-F}}=7.6$ Hz), 117.78 (d, $J_{\text{C-F}}=10.2$ Hz), 115.07 (d, $J_{\text{C-F}}=2.4$ Hz), 23.41 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75, -109.62 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_9\text{FI}^+ [\text{M-OTf}]^+$ 310.9727, found 310.9724.

1-Methyl-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2t)



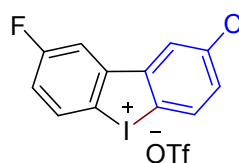
White solid (103 mg, 67%). ^1H NMR (400 MHz, DMSO) δ = 8.71 (d, $J=8.6$ Hz, 1H), 8.64 (d, $J=1.0$ Hz, 1H), 8.22 (t, $J=7.9$ Hz, 2H), 7.78 (d, $J=7.4$ Hz, 1H), 7.67 (t, $J=7.8$ Hz, 1H), 2.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = ^{13}C NMR (101 MHz, DMSO) δ = 146.47, 140.91, 138.05, 134.63, 130.96, 130.94, 128.61, 127.48, 127.44, 127.40, 123.37, 123.27 (q, $^1J_{\text{C-F}}=272.6$ Hz), 121.25, 120.68 (q, $^1J_{\text{C-F}}=322.3$ Hz), 23.17 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -61.16, -77.76 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{I}^+ [\text{M-OTf}]^+$ 360.9696, found 360.9694.

2,8-Difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2u)



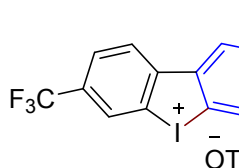
White solid (120 mg, 86%). ^1H NMR (400 MHz, DMSO) δ = 8.49 (dd, J =9.8, 2.8 Hz, 2H), 8.21 (dd, J =9.1, 5.1 Hz, 2H), 7.62 (td, J =8.8, 2.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.96 (d, $^1J_{\text{C-F}}$ =247.3 Hz), 143.28 (dd, $^{3,4}J_{\text{C-F}}$ =9.5, 3.0 Hz), 132.56 (d, $^3J_{\text{C-F}}$ =9.2 Hz), 120.69 (q, $^1J_{\text{C-F}}$ =322.3), 119.06 (d, $^2J_{\text{C-F}}$ =24.1 Hz), 116.21 (d, $^4J_{\text{C-F}}$ =2.1 Hz), 114.41 (d, $^2J_{\text{C-F}}$ =25.3 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76, -110.41 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_6\text{F}_2\text{I}^+$ [M-OTf] $^+$ 314.9477, found 314.9477. Spectral data are in good agreement with literature.^[27]

2-Chloro-8-fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2v)



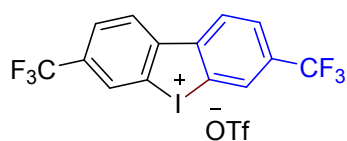
White solid (131 mg, 91%). ^1H NMR (400 MHz, DMSO) δ = 8.70 (d, J =2.2 Hz, 1H), 8.56 (dd, J =9.9, 2.7 Hz, 1H), 8.21 (dd, J =9.0, 5.1 Hz, 1H), 8.19 (d, J =8.8 Hz, 1H), 7.78 (dd, J =8.8, 2.2 Hz, 1H), 7.63 (td, J =8.8, 2.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.97 (d, $^1J_{\text{C-F}}$ =247.3 Hz), 143.07 (d, $^3J_{\text{C-F}}$ =9.6 Hz), 142.80 (d, $^4J_{\text{C-F}}$ =3.0 Hz), 136.45, 132.49 (d, $^3J_{\text{C-F}}$ =9.3 Hz), 132.07, 131.17, 127.13, 120.68 (q, $^1J_{\text{C-F}}$ =322.3 Hz), 120.15, 119.09 (d, $^2J_{\text{C-F}}$ =24.1 Hz), 116.23 (d, $^4J_{\text{C-F}}$ =2.2 Hz), 114.48 (d, $^2J_{\text{C-F}}$ =25.4 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76, -110.41 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_6\text{ClFI}^+$ [M-OTf] $^+$ 330.9181, found 330.9181.

2-Fluoro-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2w)



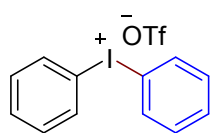
White solid (122 mg, 79%). ^1H NMR (400 MHz, DMSO) δ = 8.74 (d, J =8.3 Hz, 1H), 8.61 (dd, J =9.7, 2.8 Hz, 1H), 8.53 (d, J =0.8 Hz, 1H), 8.30 – 8.21 (m, 2H), 7.69 (td, J =8.8, 2.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 164.00 (d, $^1J_{\text{C-F}}$ =247.7 Hz), 144.65, 142.85 (d, J =9.5 Hz), 132.60 (d, J =9.3 Hz), 130.50 (q, J =32.7 Hz), 128.12, 127.76 (q, J =3.3 Hz), 127.48 (q, J =4.3 Hz), 123.23 (q, $^1J_{\text{C-F}}$ =273.0 Hz), 122.72, 120.68 (q, $^1J_{\text{C-F}}$ =322.2 Hz), 119.68 (d, J =24.2 Hz), 116.94 (d, J =2.1 Hz), 115.01 (d, J =25.4 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -61.10, -77.78, -110.21 ppm. HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_6\text{F}_4\text{I}^+$ [M-OTf] $^+$ 364.9445, found 364.9447.

3,7-Bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2x)



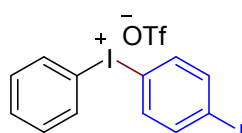
White solid (136 mg, 80%). ^1H NMR (400 MHz, DMSO) δ = 8.84 (d, J =8.3 Hz, 2H), 8.56 (d, J =0.8 Hz, 2H), 8.30 (dd, J =8.3, 1.1 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 144.20, 131.04 (q, $^2J_{\text{C-F}}$ = 32.9 Hz), 128.72, 127.90 (q, $^4J_{\text{C-F}}$ = 3.3 Hz), 127.51 (q, $^4J_{\text{C-F}}$ = 4.0 Hz), 123.50, 123.21 (q, $^1J_{\text{C-F}}$ = 273.1 Hz), 120.68 (q, $^1J_{\text{C-F}}$ = 322.3) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -61.17, -77.80 ppm. HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_6\text{F}_6\text{I}^+$ $[\text{M-OTf}]^+$ 414.9413, found 414.9413. Spectral data are in good agreement with literature.^[28]

Diphenyliodonium trifluoromethanesulfonate (5a)



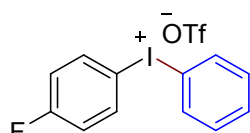
White solid (103 mg, 80%). ^1H NMR (400 MHz, DMSO) δ = 8.25 (d, J =7.5 Hz, 4H), 7.67 (d, J =7.4 Hz, 2H), 7.53 (d, J =7.6 Hz, 4H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 135.17, 132.06, 131.76, 120.70 (q, $^1J_{\text{C-F}}$ = 322.3 Hz), 116.49 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.72 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{10}\text{I}^+$ $[\text{M-OTf}]^+$ 280.9822, found 280.9821. Spectral data are in good agreement with literature.^[29]

(4-Iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (5b)



White solid (152 mg, 91%). ^1H NMR (400 MHz, DMSO) δ = 8.24 (d, J =7.4 Hz, 2H), 8.00 (d, J =8.5 Hz, 2H), 7.90 (d, J =8.5 Hz, 2H), 7.67 (t, J =7.4 Hz, 1H), 7.53 (t, J =7.8 Hz, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 140.34, 136.72, 135.13, 132.10, 131.76, 120.62 (q, $^1J_{\text{C-F}}$ = 322.3 Hz), 116.65, 115.82, 100.27 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_9\text{I}_2^+$ $[\text{M-OTf}]^+$ 406.8788, found 406.8786. Spectral data are in good agreement with literature.^[29]

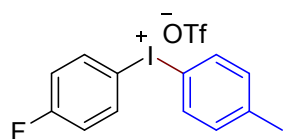
(4-Fluorophenyl)(phenyl)iodonium trifluoromethanesulfonate (5c)



White solid (114 mg, 85%). ^1H NMR (400 MHz, DMSO) δ = 8.36 – 8.29 (m, 2H), 8.25 (dd, J =8.3, 1.0 Hz, 2H), 7.67 (t, J =7.4 Hz, 1H), 7.54 (t, J =7.7 Hz, 2H), 7.46 – 7.37 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.99 (d, $^1J_{\text{C-F}}$ = 251.4 Hz), 138.09 (d, $^3J_{\text{C-F}}$ = 9.1 Hz), 135.10, 132.14, 131.81, 120.71 (q, $^1J_{\text{C-F}}$ = 322.2 Hz), 119.25 (d, $^2J_{\text{C-F}}$ = 22.8 Hz), 116.96, 110.79 (d, $^4J_{\text{C-F}}$ = 3.1 Hz) ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75, -106.69 ppm. HRMS (ESI)

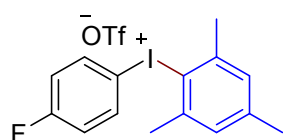
Calcd for $C_{12}H_9FI^+ [M-OTf]^+$ 298.9727, found 298.9724. Spectral data are in good agreement with literature.^[30,31]

(4-Fluorophenyl)(p-tolyl)iodonium trifluoromethanesulfonate (5d)



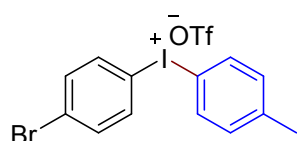
White solid (111 mg, 80%). ^1H NMR (400 MHz, DMSO) δ = 8.31 – 8.26 (m, 2H), 8.13 (d, J =8.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.34 (d, J =8.0 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.93 (d, $^1J_{C-F}$ = 251.3 Hz), 142.66, 137.92 (d, $^3J_{C-F}$ = 9.0 Hz), 135.09, 132.4, 120.71 (q, $^1J_{C-F}$ = 322.3 Hz), 119.17 (d, $^2J_{C-F}$ = 22.8 Hz), 113.34, 110.94 (d, $^4J_{C-F}$ = 3.0 Hz), 20.88 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76, -106.89 ppm. HRMS (ESI) Calcd for $C_{13}H_{11}FI^+ [M-OTf]^+$ 312.9884, found 312.9882. Spectral data are in good agreement with literature.^[30]

(4-Fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (5f)



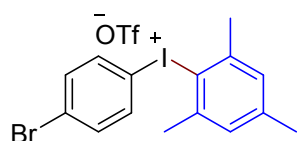
White solid (122 mg, 83%). ^1H NMR (400 MHz, DMSO) δ = 8.07 – 8.03 (m, 2H), 7.39 – 7.35 (m, 2H), 7.22 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 163.77 (d, $^1J_{C-F}$ = 251.1 Hz), 143.19, 141.53, 137.33 (d, $^3J_{C-F}$ = 8.9 Hz), 129.81, 122.92, 120.69 (q, $^1J_{C-F}$ = 322.3 Hz), 119.26 (d, $^2J_{C-F}$ = 22.8 Hz), 108.63 (d, $^4J_{C-F}$ = 3.0 Hz), 26.27, 20.53 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76, -107.25 ppm. HRMS (ESI) Calcd for $C_{15}H_{15}FI^+ [M-OTf]^+$ 341.0197, found 341.0197. Spectral data are in good agreement with literature.^[29]

(4-Bromophenyl)(p-tolyl)iodonium trifluoromethanesulfonate (5g)



White solid (110 mg, 70%). ^1H NMR (400 MHz, DMSO) δ = 8.16 – 8.10 (m, 4H), 7.76 – 7.72 (m, 2H), 7.34 (d, J =8.0 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.70, 136.88, 135.16, 134.57, 132.41, 126.09, 120.68 (q, $^1J_{C-F}$ = 322.4 Hz), 115.19, 113.13, 20.86 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.73 ppm. HRMS (ESI) Calcd for $C_{13}H_{11}BrI^+ [M-OTf]^+$ 372.9083, found 372.9085.

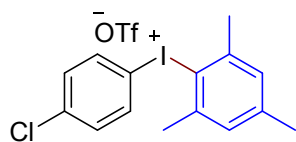
(4-Bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (5h)



White solid (134 mg, 81%). ^1H NMR (400 MHz, DMSO) δ = 7.91 – 7.86 (m, 1H), 7.74 – 7.67 (m, 1H), 7.23 (s, 1H), 2.59 (s, 3H), 2.30 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 143.28, 141.61, 136.31, 134.69, 129.86, 125.81, 122.71, 120.69 (q, $^1J_{C-F}$ = 322.3 Hz), 113.02,

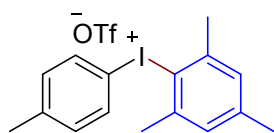
26.30, 20.54 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.76 ppm. HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{BrI}^+ [\text{M-OTf}]^+$ 400.9396, found 400.9391. Spectral data are in good agreement with literature.^[29,32]

(4-Chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (5i)



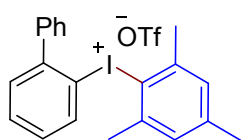
White solid (117 mg, 77%). ^1H NMR (400 MHz, DMSO) δ = 7.97 (d, J =8.8 Hz, 2H), 7.58 (d, J =8.8 Hz, 2H), 7.23 (s, 2H), 2.59 (s, 6H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 143.28, 141.61, 137.02, 136.25, 131.81, 129.86, 122.79, 120.70 (q, $^1J_{\text{C-F}}$ =322.4 Hz), 112.33, 26.30, 20.55 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{15}\text{ClI}^+ [\text{M-OTf}]^+$ 356.9901, found 356.9897. Spectral data are in good agreement with literature.^[29,33]

Mesityl(*p*-tolyl)iodonium trifluoromethanesulfonate (5j)



White solid (142 mg, 97%). ^1H NMR (400 MHz, DMSO) δ = 7.89 – 7.85 (m, 2H), 7.30 (d, J =8.1, 2H), 7.20 (s, 2H), 2.59 (s, 6H), 2.33 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 142.99, 142.26, 141.46, 134.56, 132.47, 129.74, 122.71, 120.70 (q, $^1J_{\text{C-F}}$ =322.3 Hz), 110.90, 26.29, 20.79, 20.52 ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.75 ppm. HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{18}\text{I}^+ [\text{M-OTf}]^+$ 337.0448, found 337.0447. Spectral data are in good agreement with literature.^[29,32]

[1,1'-Biphenyl]-2-yl(mesityl)iodonium trifluoromethanesulfonate (5m)



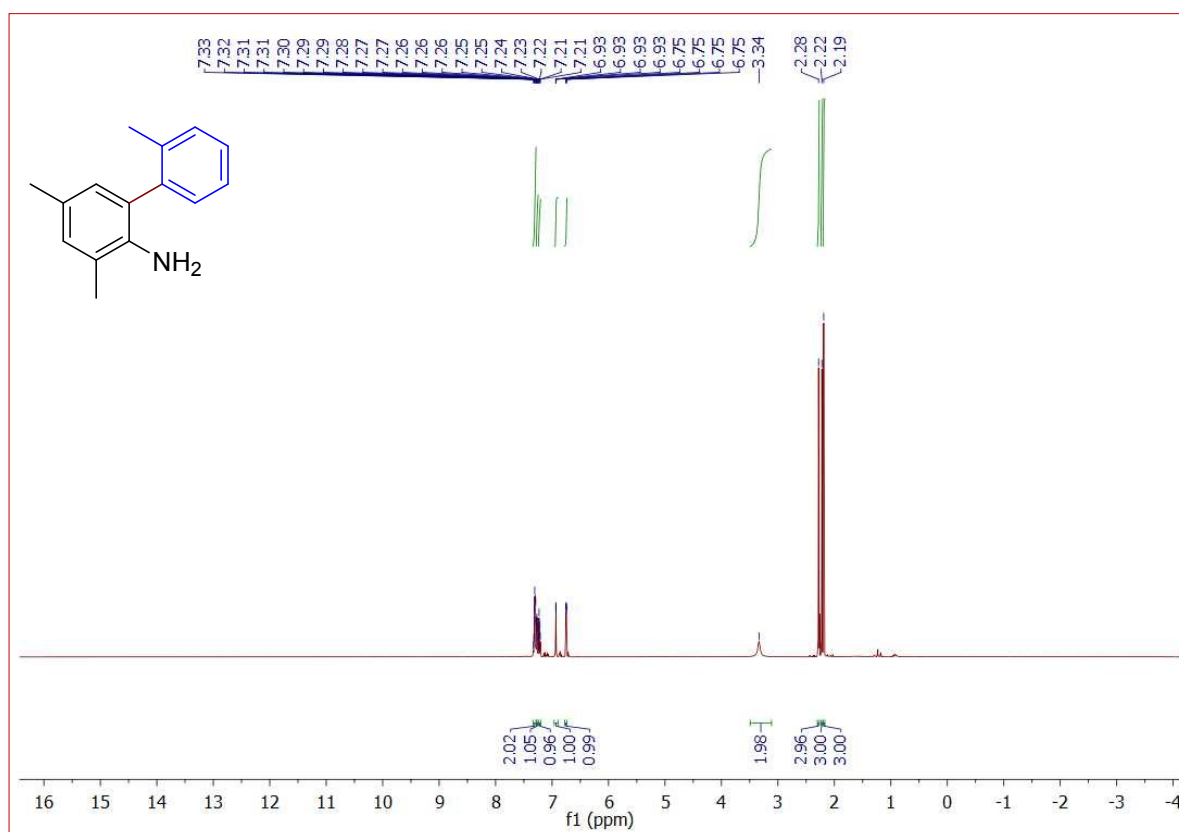
White solid (94 mg, 57%). ^1H NMR (400 MHz, DMSO) δ = 8.45 (dd, J =8.0, 0.8 Hz, 1H), 7.75 (td, J =7.5, 1.1 Hz, 1H), 7.59 – 7.49 (m, 5H), 7.45 – 7.39 (m, 2H), 7.04 (s, 2H), 2.23 (s, 3H), 2.06 (s, 6H). ppm. ^{13}C NMR (101 MHz, DMSO) δ = 144.90, 142.86, 141.80, 140.73, 138.31, 132.75, 132.08, 130.36, 129.58, 129.31, 129.02, 128.96, 122.05, 120.68 (q, $^1J_{\text{C-F}}$ =322.4 Hz), 117.05, 25.49, 20.36. ppm. ^{19}F NMR (376 MHz, DMSO) δ = -77.73 ppm. HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{I}^+ [\text{M-OTf}]^+$ 399.0604, found 399.0603.

References

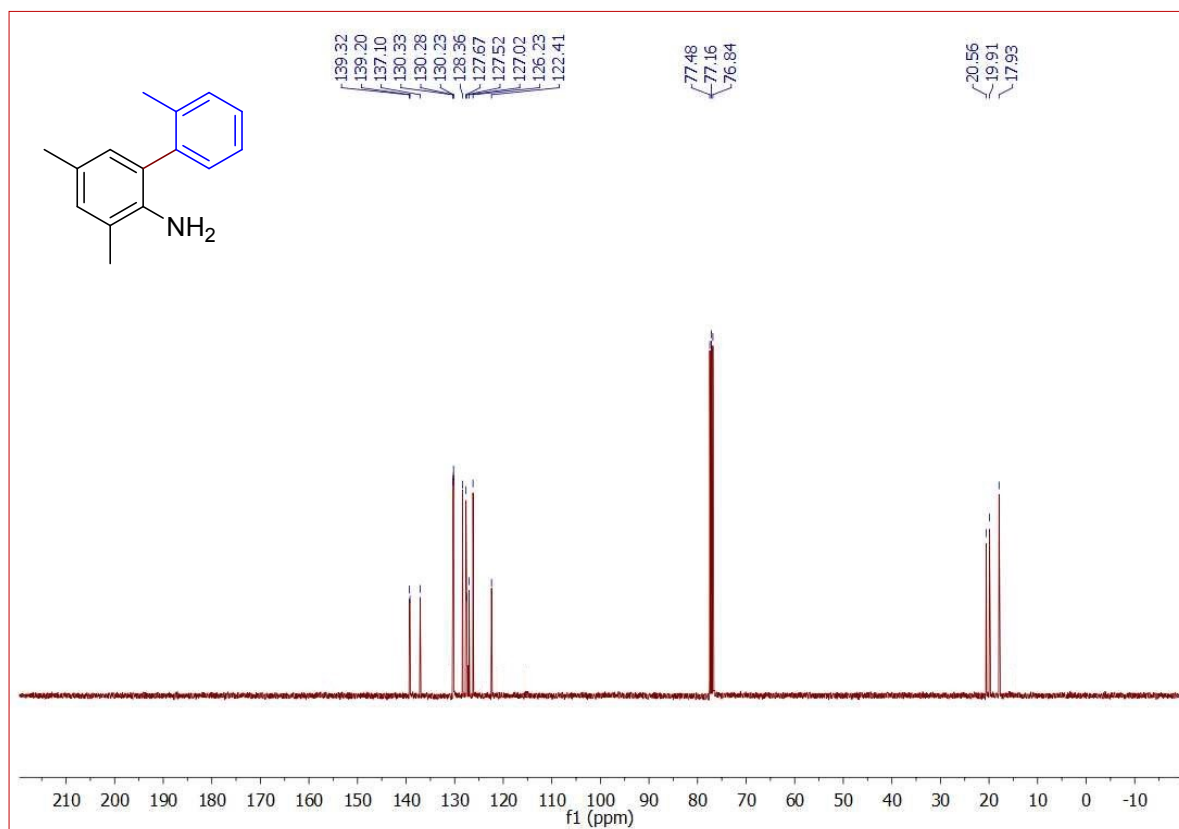
- [1] Y. Gao, Z. Cai, S. Li, G. Li, *Org. Lett.* **2019**, *21*, 3663–3669.
- [2] L. Zhao, C. Hu, X. Cong, G. Deng, L. L. Liu, M. Luo, X. Zeng, *J. Am. Chem. Soc.* **2021**, jacs.0c12318.
- [3] Z. Liang, R. Feng, H. Yin, Y. Zhang, *Org. Lett.* **2013**, *15*, 4544–4547.
- [4] B. J. Stokes, B. Jovanović, H. Dong, K. J. Richert, R. D. Riell, T. G. Driver, *J. Org. Chem.* **2009**, *74*, 3225–3228.
- [5] Q. Jiang, D. Duan-Mu, W. Zhong, H. Chen, H. Yan, *Chem. - A Eur. J.* **2013**, *19*, 1903–1907.
- [6] F. Willig, J. Lang, A. C. Hans, M. R. Ringenberg, D. Pfeffer, W. Frey, R. Peters, *J. Am. Chem. Soc.* **2019**, *141*, 12029–12043.
- [7] J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu, J. Hu, *Angew. Chemie Int. Ed.* **2016**, *55*, 2743–2747.
- [8] B. Fang, J. Hou, J. Tian, W. Yu, J. Chang, *Org. Biomol. Chem.* **2020**, *18*, 3312–3323.
- [9] M. Hartmann, C. G. Daniliuc, A. Studer, *Chem. Commun.* **2015**, *51*, 3121–3123.
- [10] O. Fischer, J. Hofmann, H. Rampp, J. Kaindl, G. Pratsch, A. Bartuschat, R. V. Taudte, M. F. Fromm, H. Hübner, P. Gmeiner, et al., *J. Med. Chem.* **2020**, *63*, 4349–4369.
- [11] W. Li, G. Xiao, G. Deng, Y. Liang, *Org. Chem. Front.* **2018**, *5*, 1488–1492.
- [12] G. Shi, D. Chen, H. Jiang, Y. Zhang, Y. Zhang, *Org. Lett.* **2016**, *18*, 2958–2961.
- [13] S. Pan, H. Jiang, Y. Zhang, D. Chen, Y. Zhang, *Org. Lett.* **2016**, *18*, 5192–5195.
- [14] B. Wu, N. Yoshikai, *Angew. Chemie Int. Ed.* **2015**, *54*, 8736–8739.
- [15] T. Furusawa, T. Morimoto, Y. Nishiyama, H. Tanimoto, K. Kakiuchi, *Chem. - An Asian J.* **2016**, *11*, 2312–2315.
- [16] R. Möckel, J. Hille, E. Winterling, S. Weidemüller, T. M. Faber, G. Hilt, *Angew. Chemie Int. Ed.* **2018**, *57*, 442–445.
- [17] C. Zhu, D. Wang, D. Wang, Y. Zhao, W.-Y. Sun, Z. Shi, *Angew. Chemie Int. Ed.* **2018**, *57*, 8848–8853.
- [18] H. Liu, T. Duan, Z. Zhang, C. Xie, C. Ma, *Org. Lett.* **2015**, *17*, 2932–2935.
- [19] V. Mamane, P. Hannen, A. Fürstner, *Chem. - A Eur. J.* **2004**, *10*, 4556–4575.
- [20] I. Bennacef, C. N. Haile, A. Schmidt, A. O. Koren, J. P. Seibyl, J. K. Staley, F. Bois, R. M. Baldwin, G. Tamagnan, *Bioorg. Med. Chem.* **2006**, *14*, 7582–7591.
- [21] M. Jiang, J. Guo, B. Liu, Q. Tan, B. Xu, *Org. Lett.* **2019**, *21*, 8328–8333.

- [22] D. Zhu, Q. Liu, B. Luo, M. Chen, R. Pi, P. Huang, S. Wen, *Adv. Synth. Catal.* **2013**, 355, 2172–2178.
- [23] Y. Wu, X. Peng, B. Luo, F. Wu, B. Liu, F. Song, P. Huang, S. Wen, *Org. Biomol. Chem.* **2014**, 12, 9777–9780.
- [24] N. Nguyen, D. W. Wilson, G. Nagalingam, J. A. Triccas, E. K. Schneider, J. Li, T. Velkov, J. Baell, *Eur. J. Med. Chem.* **2018**, 148, 507–518.
- [25] Z. Liu, D. Zhu, B. Luo, N. Zhang, Q. Liu, Y. Hu, R. Pi, P. Huang, S. Wen, *Org. Lett.* **2014**, 16, 5600–5603.
- [26] J. Bin Lee, M. H. Jeon, J. K. Seo, G. von Helden, J.-U. Rohde, B. S. Zhao, J. Seo, S. Y. Hong, *Org. Lett.* **2019**, 21, 7004–7008.
- [27] G. Akimoto, M. Otsuka, K. Miyamoto, A. Muranaka, D. Hashizume, R. Takita, M. Uchiyama, *Chem. - An Asian J.* **2018**, 13, 913–917.
- [28] M. Ding, W. Hua, M. Liu, F. Zhang, *Org. Lett.* **2020**, 22, 7419–7423.
- [29] G. Laudadio, H. P. L. Gemoets, V. Hessel, T. Noël, *J. Org. Chem.* **2017**, 82, 11735–11741.
- [30] Z. Gonda, Z. Novák, *Chem. - A Eur. J.* **2015**, 21, 16801–16806.
- [31] M. D. Hossain, T. Kitamura, *Tetrahedron* **2006**, 62, 6955–6960.
- [32] K. Aradi, Á. Mészáros, B. L. Tóth, Z. Vincze, Z. Novák, *J. Org. Chem.* **2017**, 82, 11752–11764.
- [33] A. E. Allen, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2011**, 133, 4260–4263.

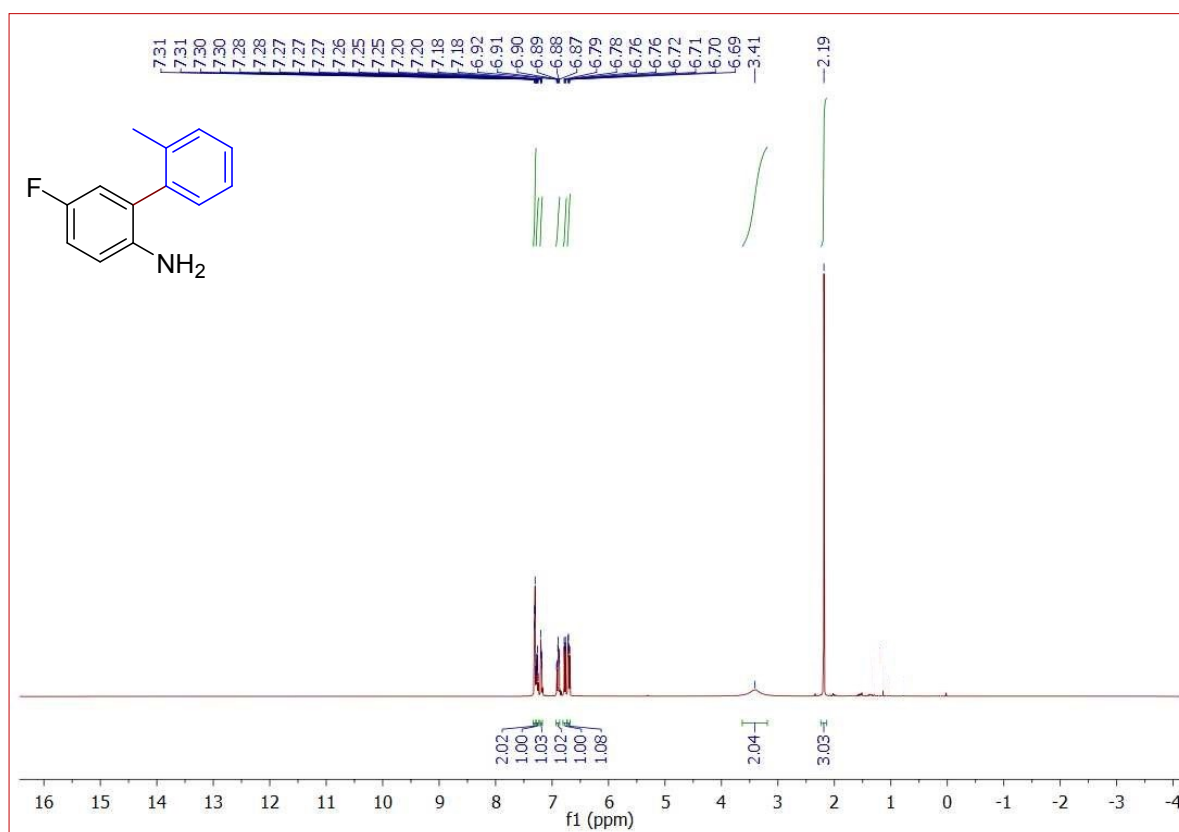
2',3,5-Trimethyl-[1,1'-biphenyl]-2-amine (**S3o**), ^1H NMR



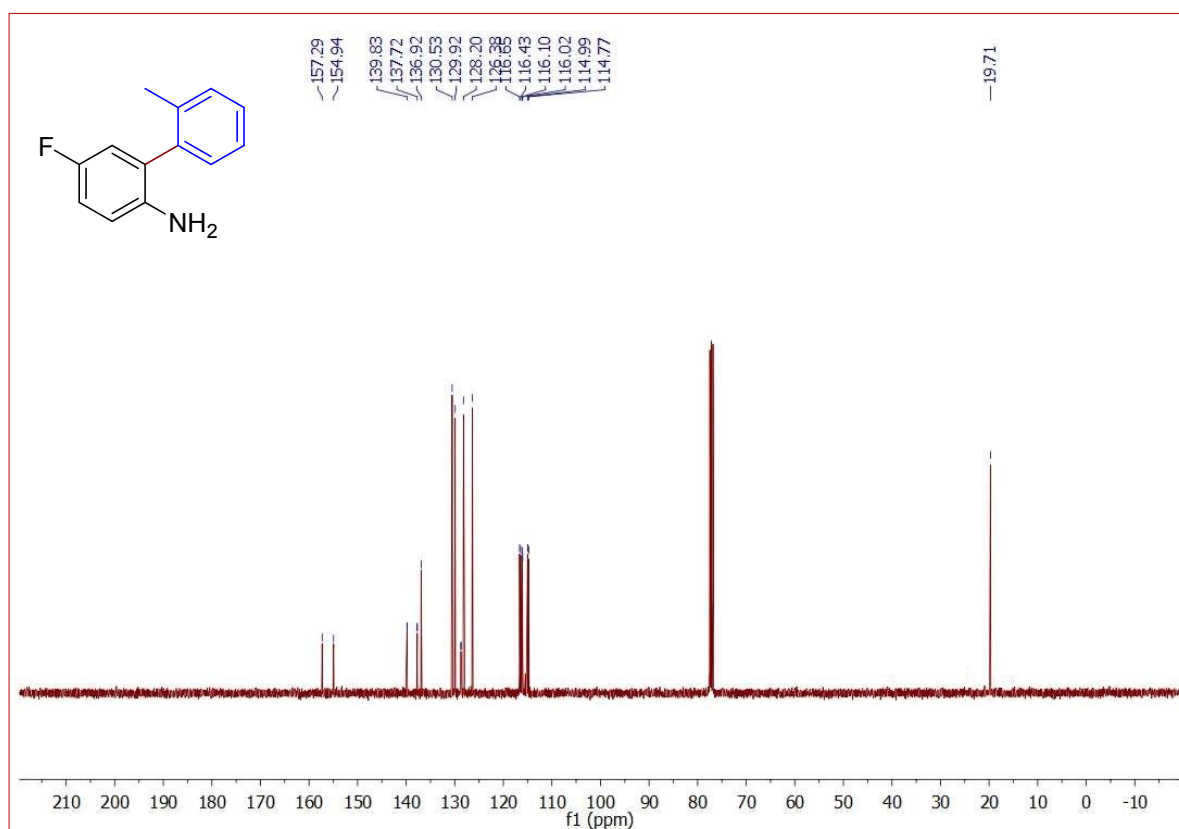
2',3,5-Trimethyl-[1,1'-biphenyl]-2-amine (**S3o**), ^{13}C NMR



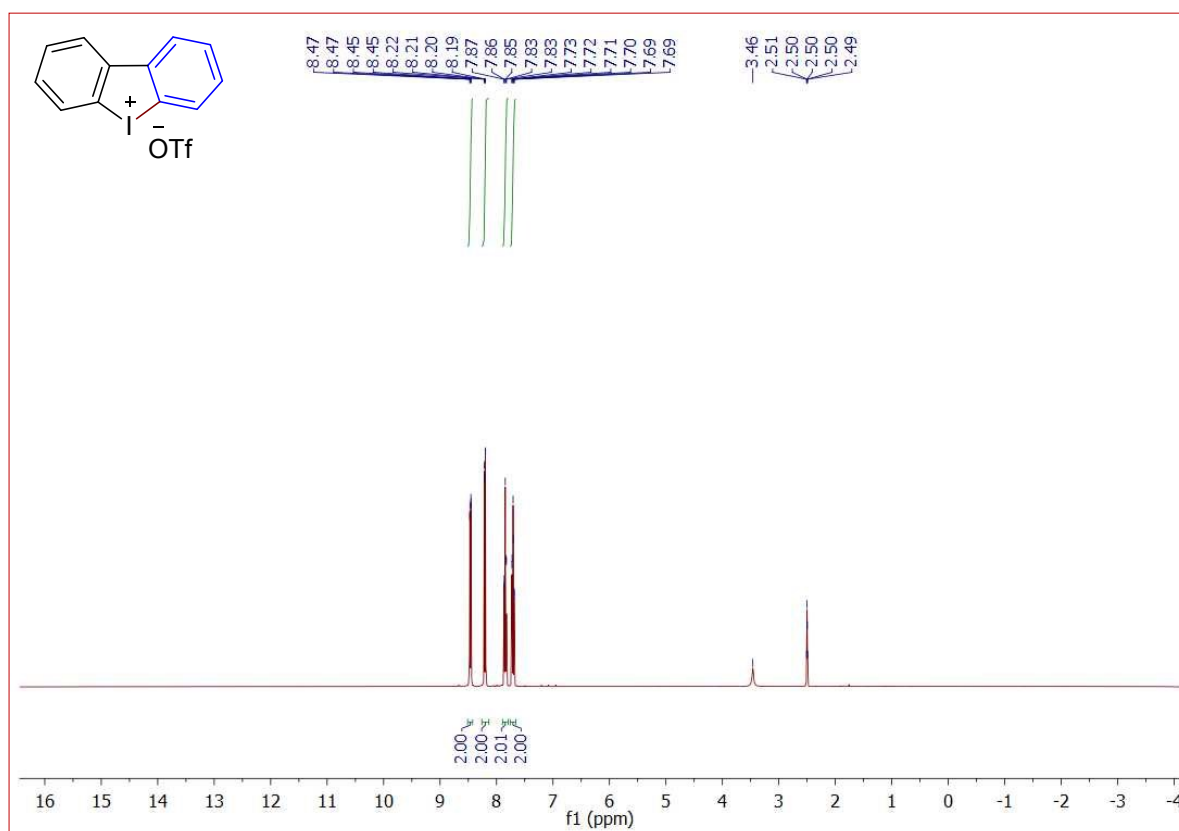
5-Fluoro-2'-methyl-[1,1'-biphenyl]-2-amine (**S3s**), ^1H NMR



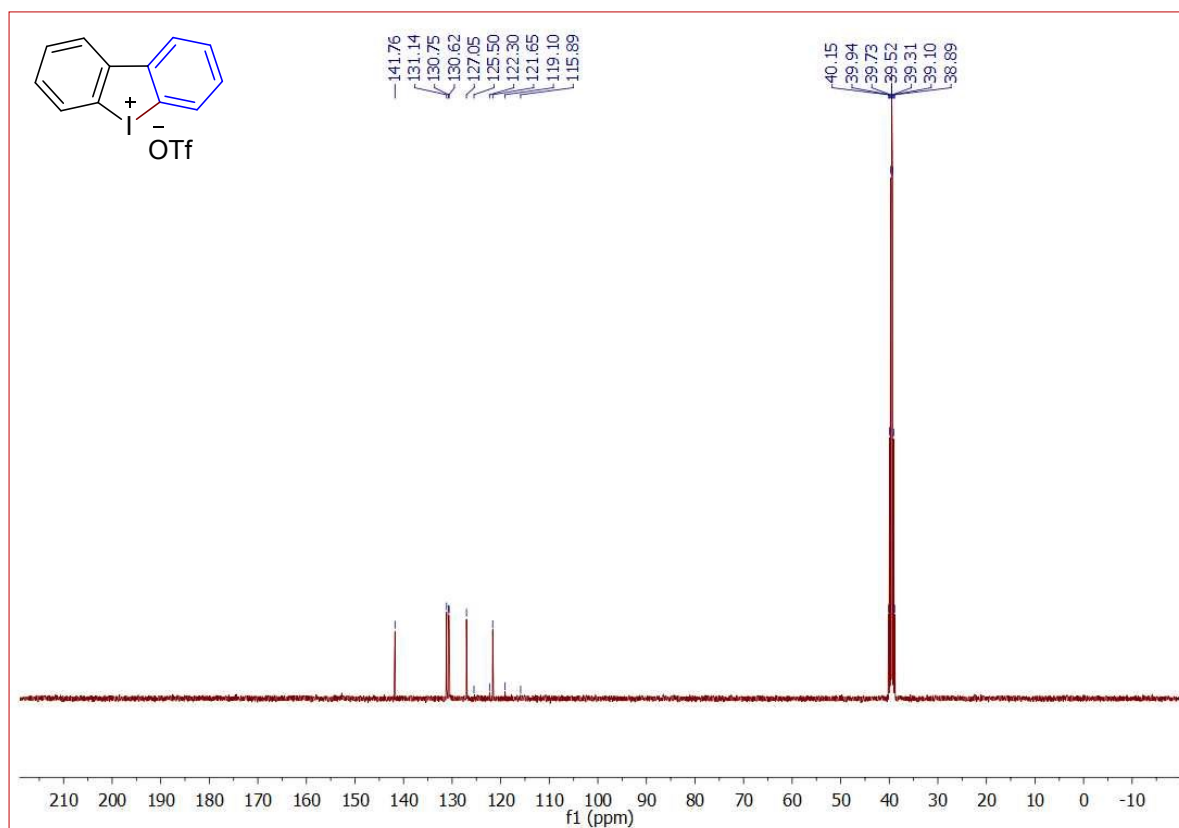
5-Fluoro-2'-methyl-[1,1'-biphenyl]-2-amine (**S3s**), ^{13}C NMR



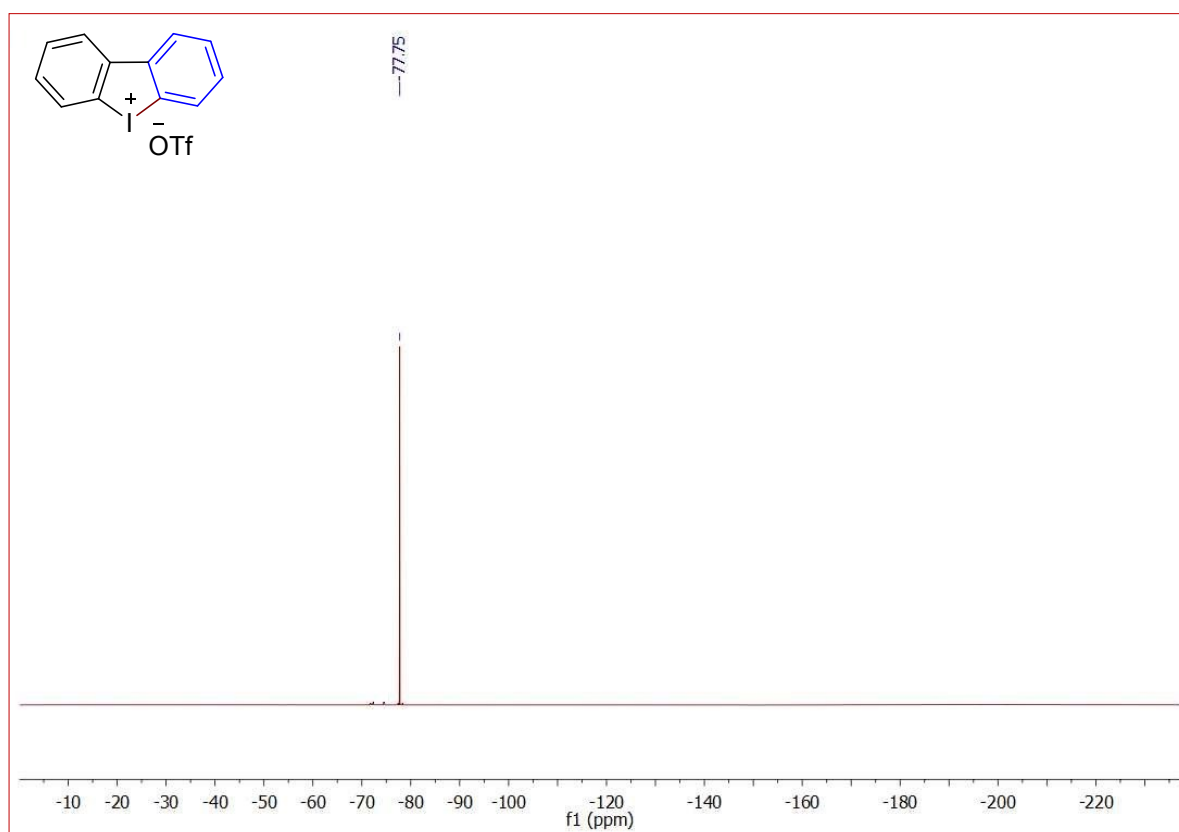
Dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2a**), ^1H NMR



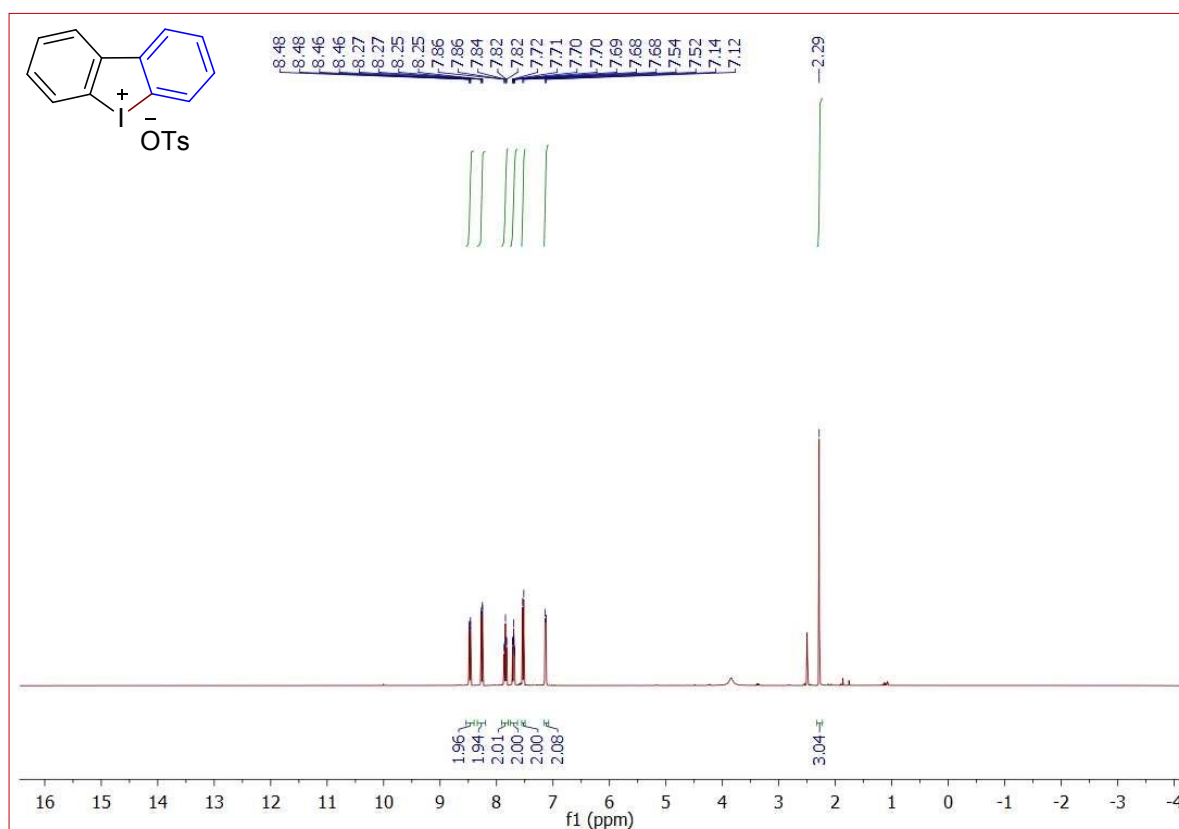
Dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2a**), ^{13}C NMR



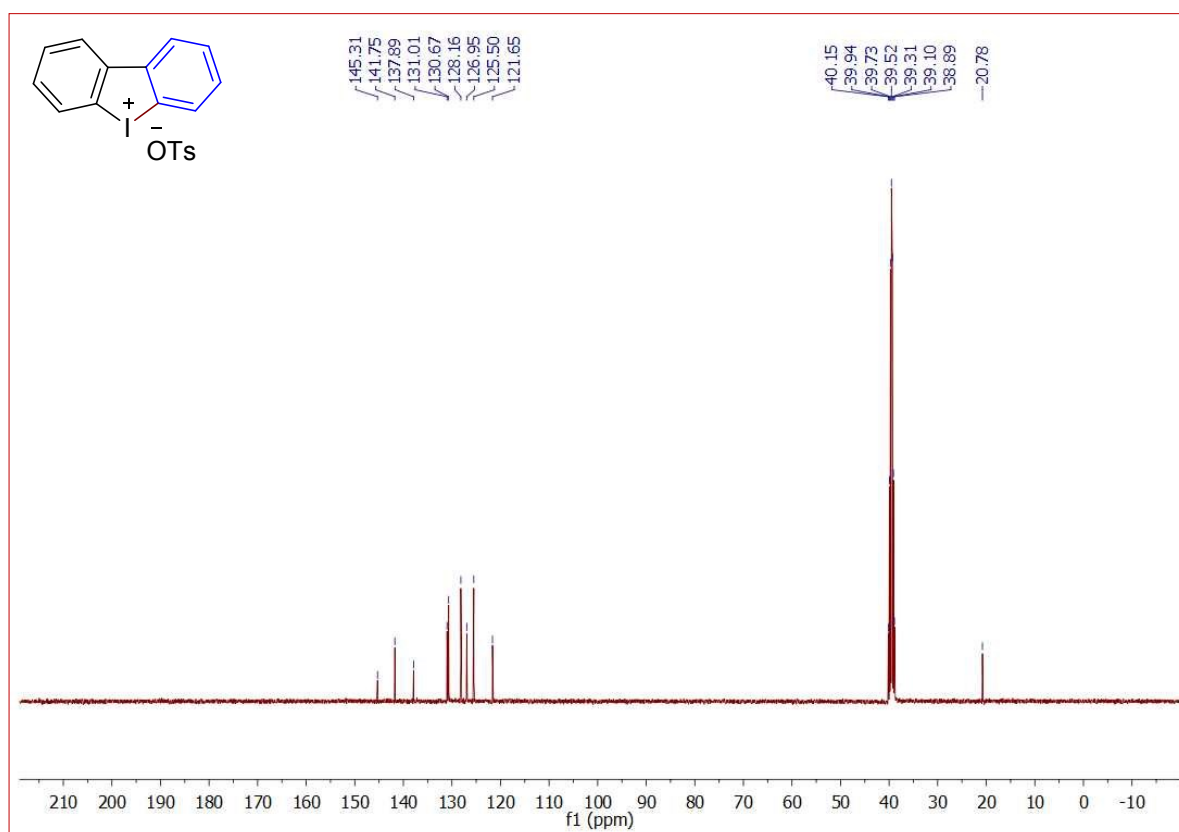
Dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2a**), ^{19}F NMR



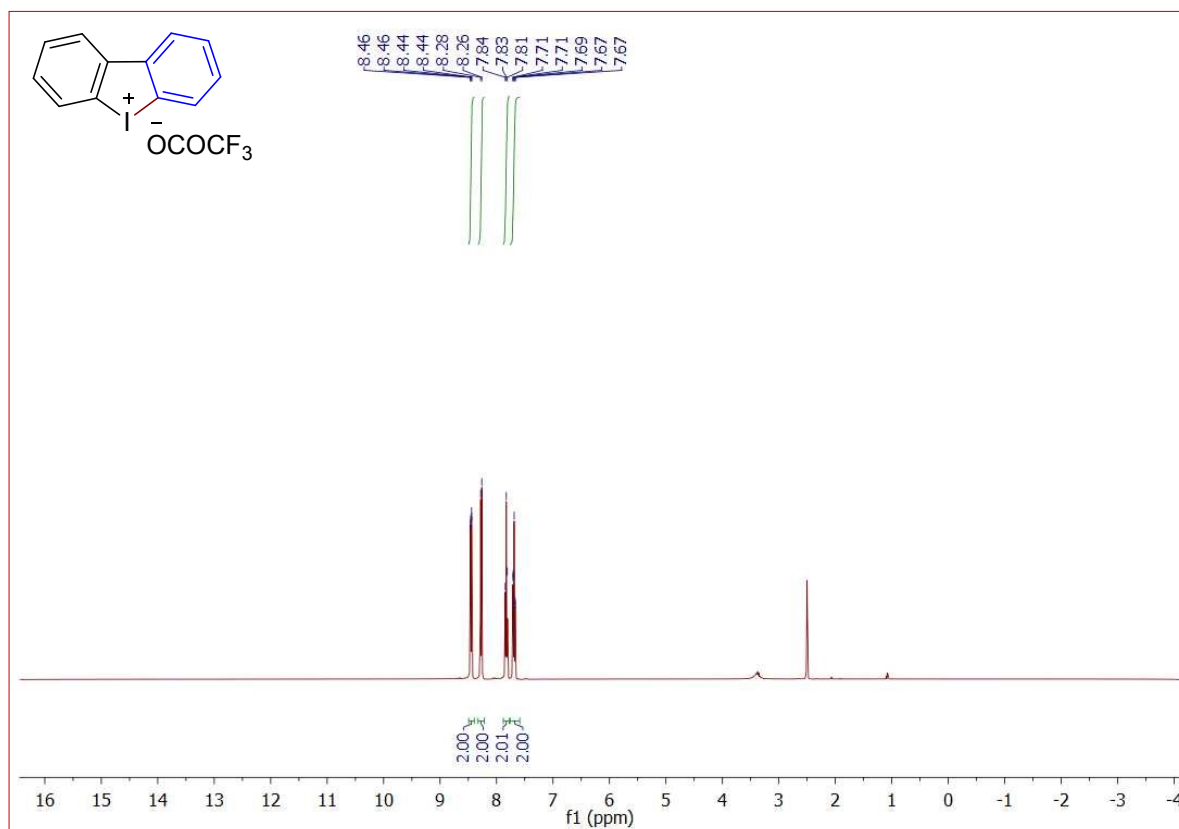
Dibenzo[b,d]iodol-5-ium 4-methylbenzenesulfonate (**2a1**), ^1H NMR



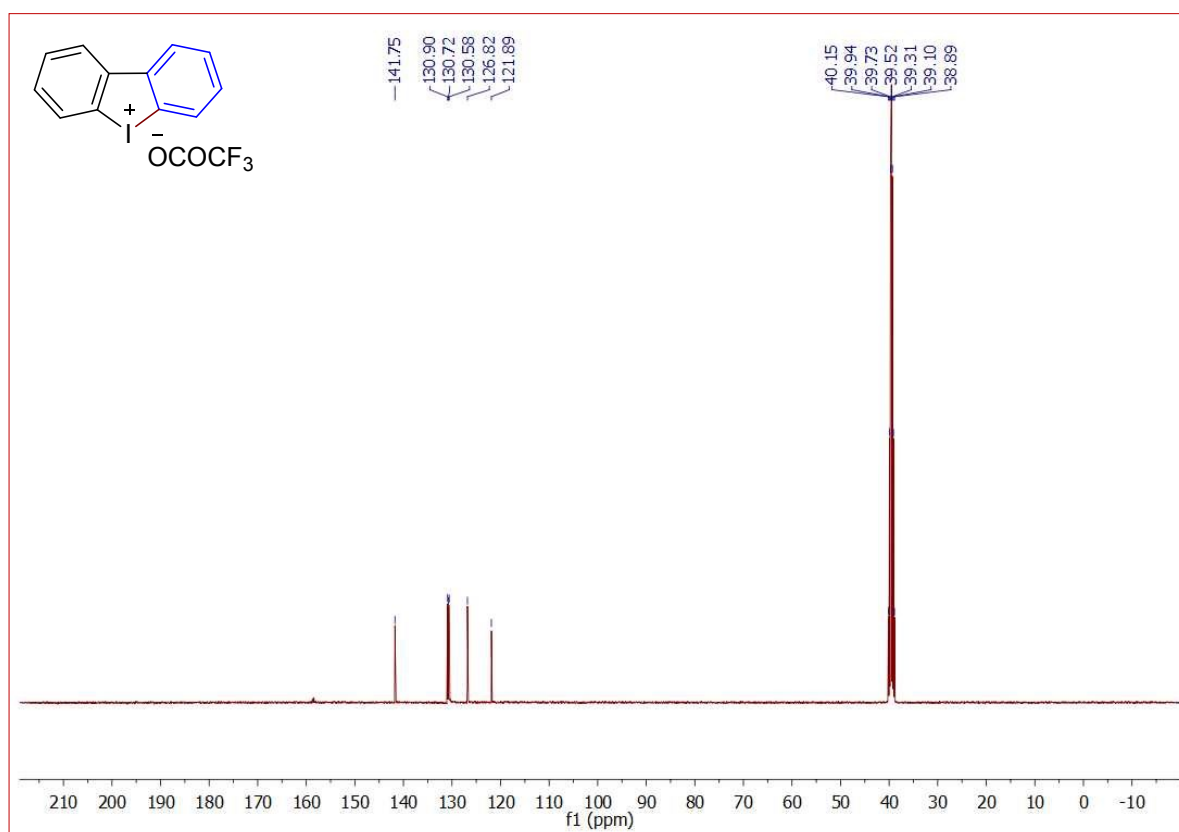
Dibenzo[b,d]iodol-5-ium 4-methylbenzenesulfonate (**2a1**), ^{13}C NMR



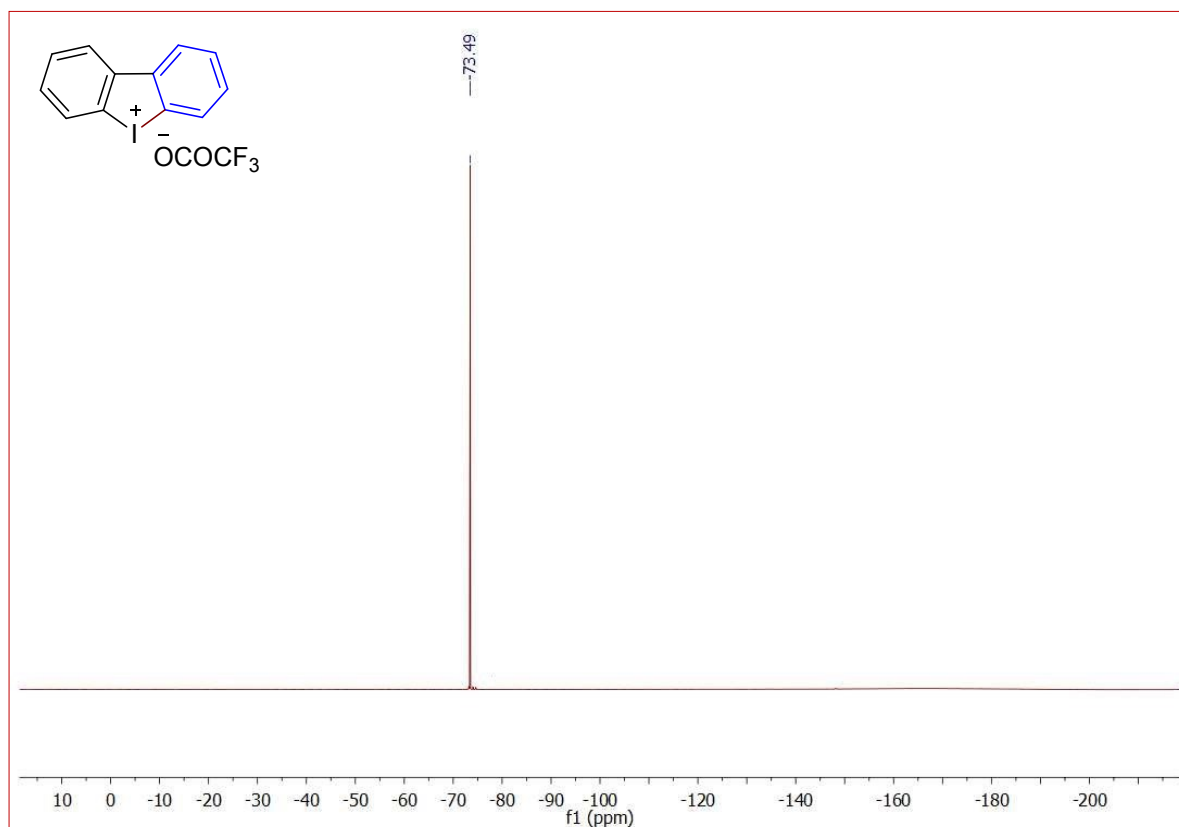
Dibenzo[b,d]iodol-5-ium 2,2,2-trifluoroacetate (**2a2**), ^1H NMR



Dibenzo[b,d]iodol-5-ium 2,2,2-trifluoroacetate (**2a2**), ^{13}C NMR



Dibenzo[b,d]iodol-5-ium 2,2,2-trifluoroacetate (**2a2**), ^{19}F NMR



Fc1ccc(cc1)[C+]([O-])S(=O)(=O)c2ccccc2

Chemical structure: 2-(4-fluorophenyl)-1-phenylethan-1-yl trifluoromethanesulfonate (OTf).

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.5-8.6 ppm), a triflate singlet (3.40 ppm), and a fluorine quartet (2.50 ppm). Integration values are provided for each signal group.

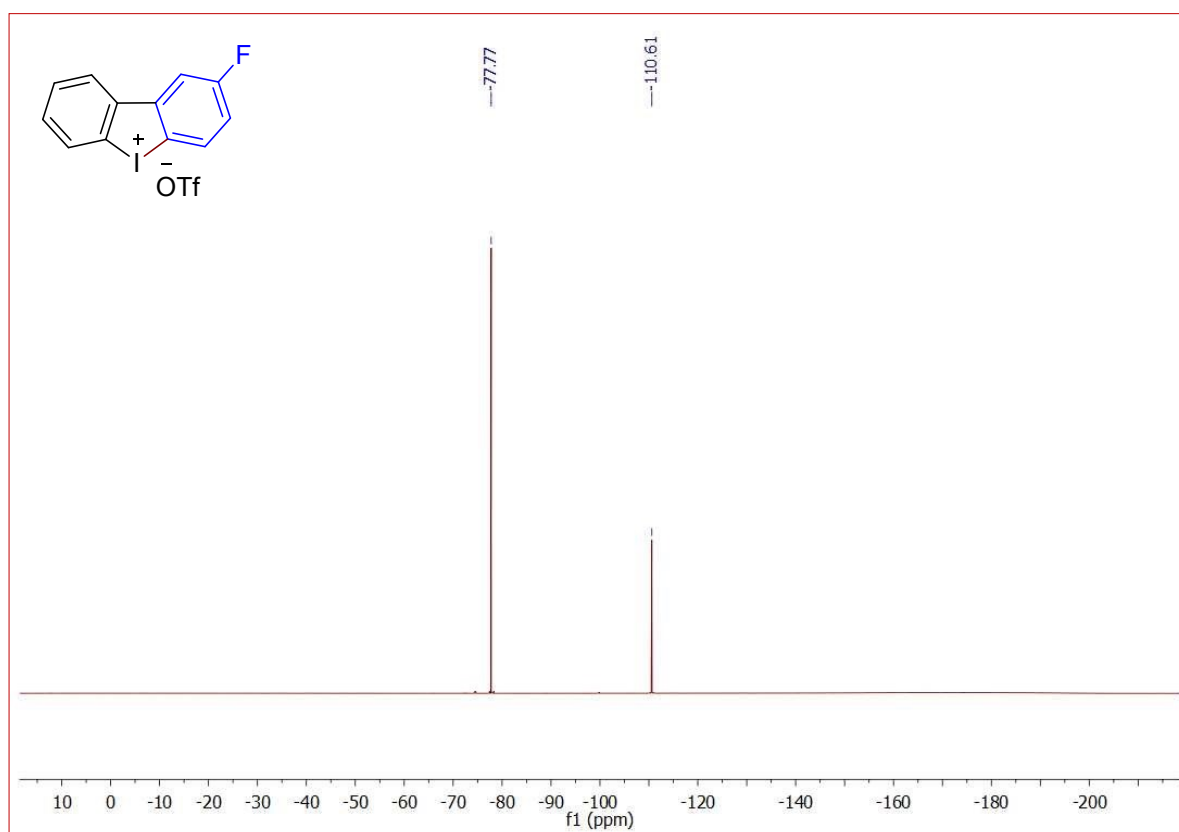
Chemical Shift (ppm)	Integration
8.55	1.00
8.54	1.00
8.53	1.98
8.52	1.02
8.50	1.00
8.49	1.00
8.47	1.00
8.47	1.00
8.24	1.00
8.23	1.00
8.22	1.00
8.22	1.00
8.21	1.00
8.21	1.00
8.21	1.00
8.20	1.00
7.89	1.00
7.89	1.00
7.87	1.00
7.86	1.00
7.85	1.00
7.76	1.00
7.76	1.00
7.74	1.00
7.74	1.00
7.72	1.00
7.72	1.00
7.64	1.00
7.63	1.00
7.61	1.00
7.61	1.00
7.59	1.00
7.58	1.00
3.40	2.51
2.51	2.50
2.50	2.50
2.50	2.50
2.49	2.49

Chemical structure: Fc1ccc(cc1)[C+]([I-])c2ccccc2

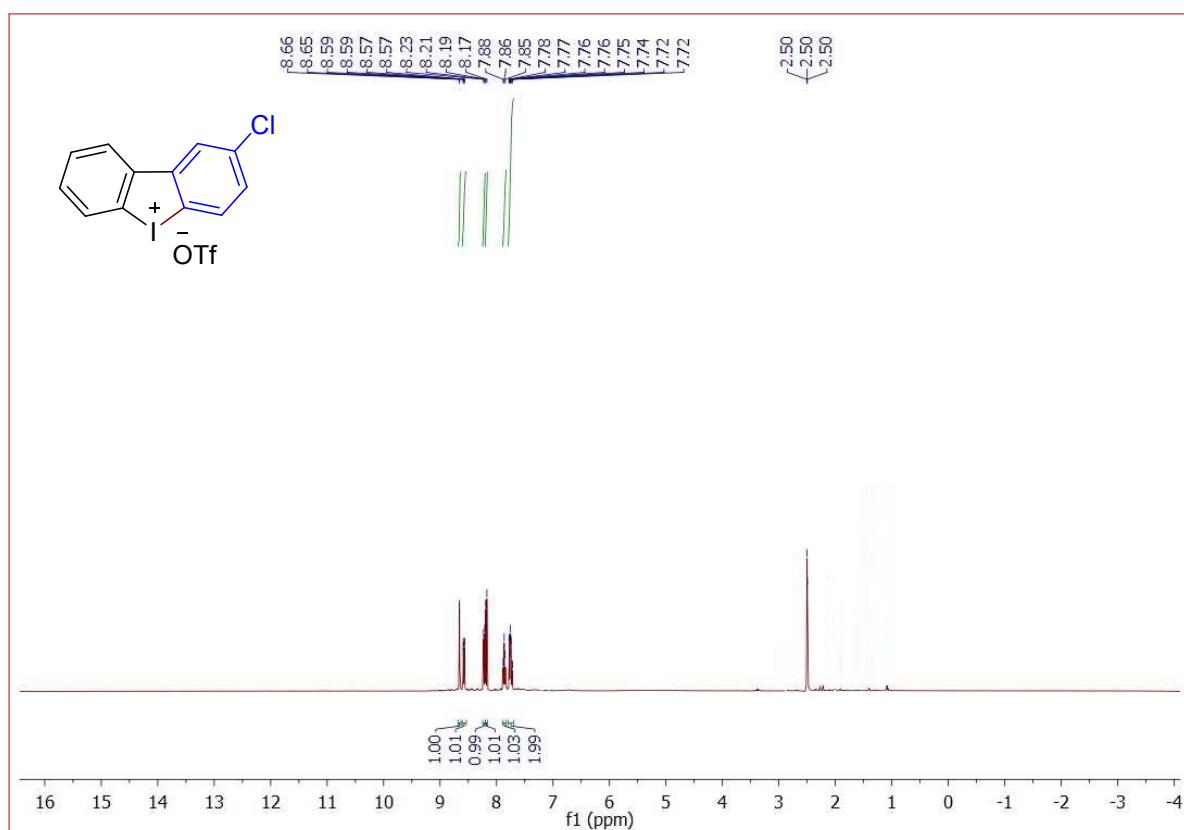
¹³C NMR peaks (ppm):

Peak (ppm)
165.30
162.84
144.46
144.36
140.85
140.82
132.61
132.51
131.72
130.84
130.66
127.55
125.51
122.31
122.27
119.11
118.68
118.44
115.90
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115.61
114.16
113.91
40.15
39.94
39.73
39.53
39.31
39.10
38.89

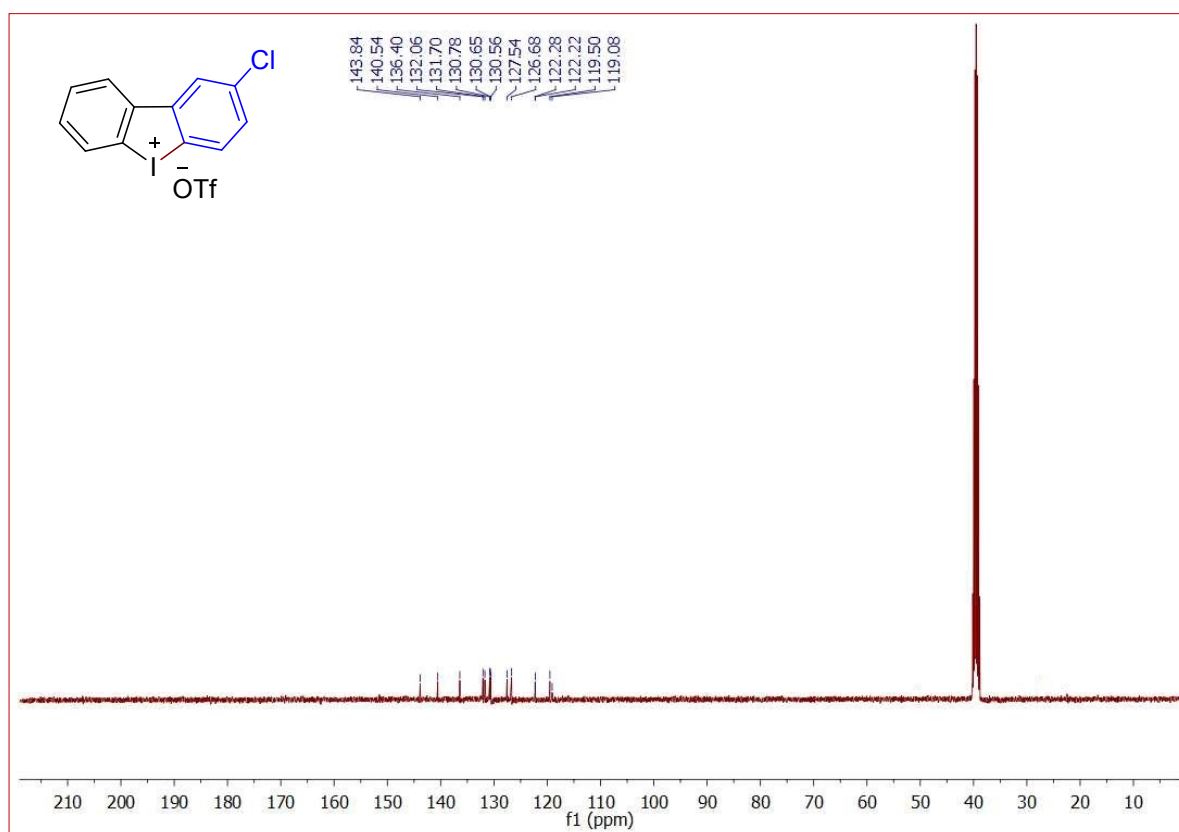
2-Fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2b**), ^{19}F NMR



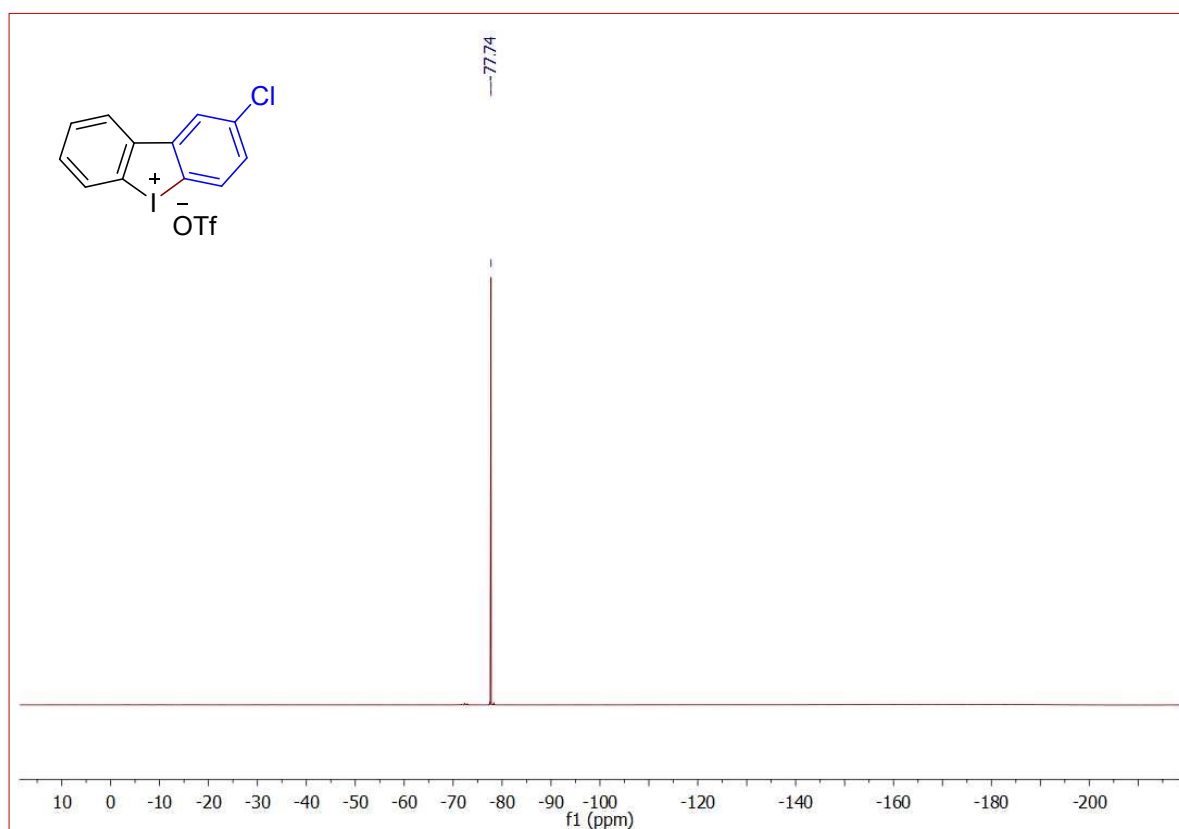
2-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2c**), ^1H NMR



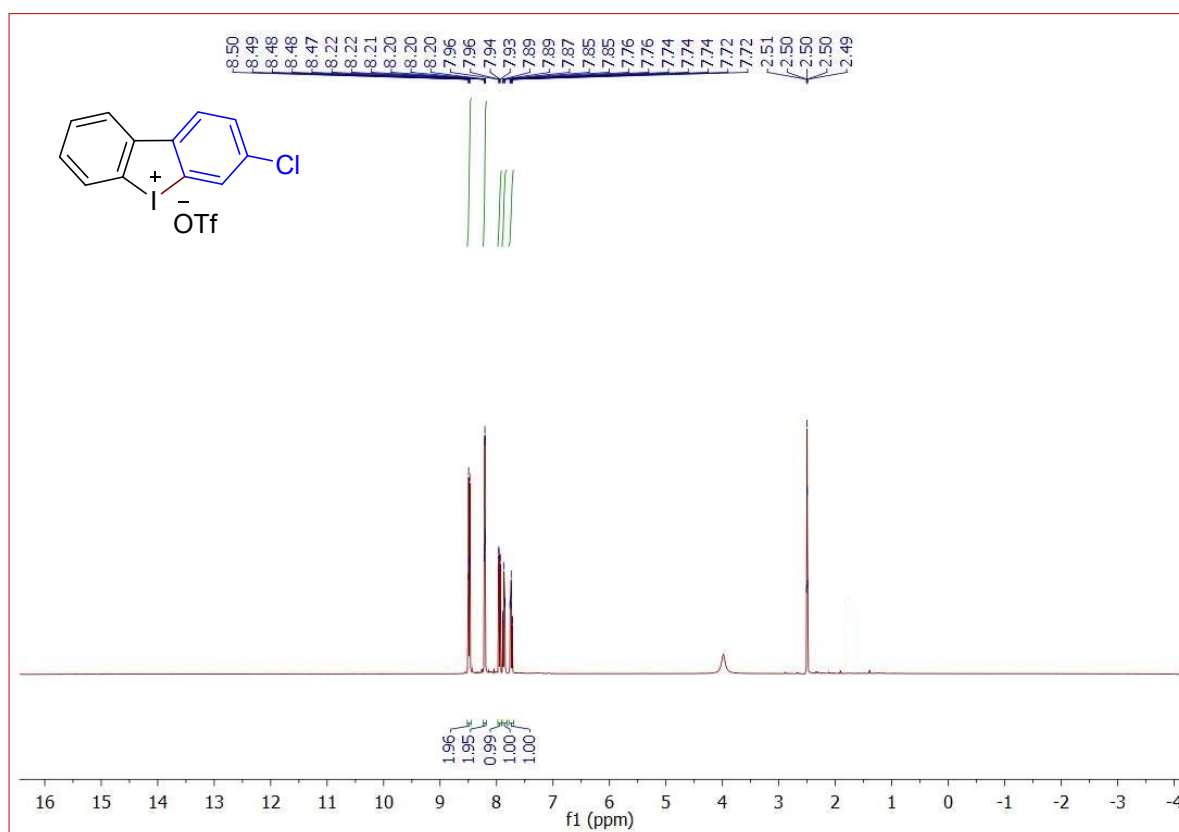
2-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2c**), ^{13}C NMR



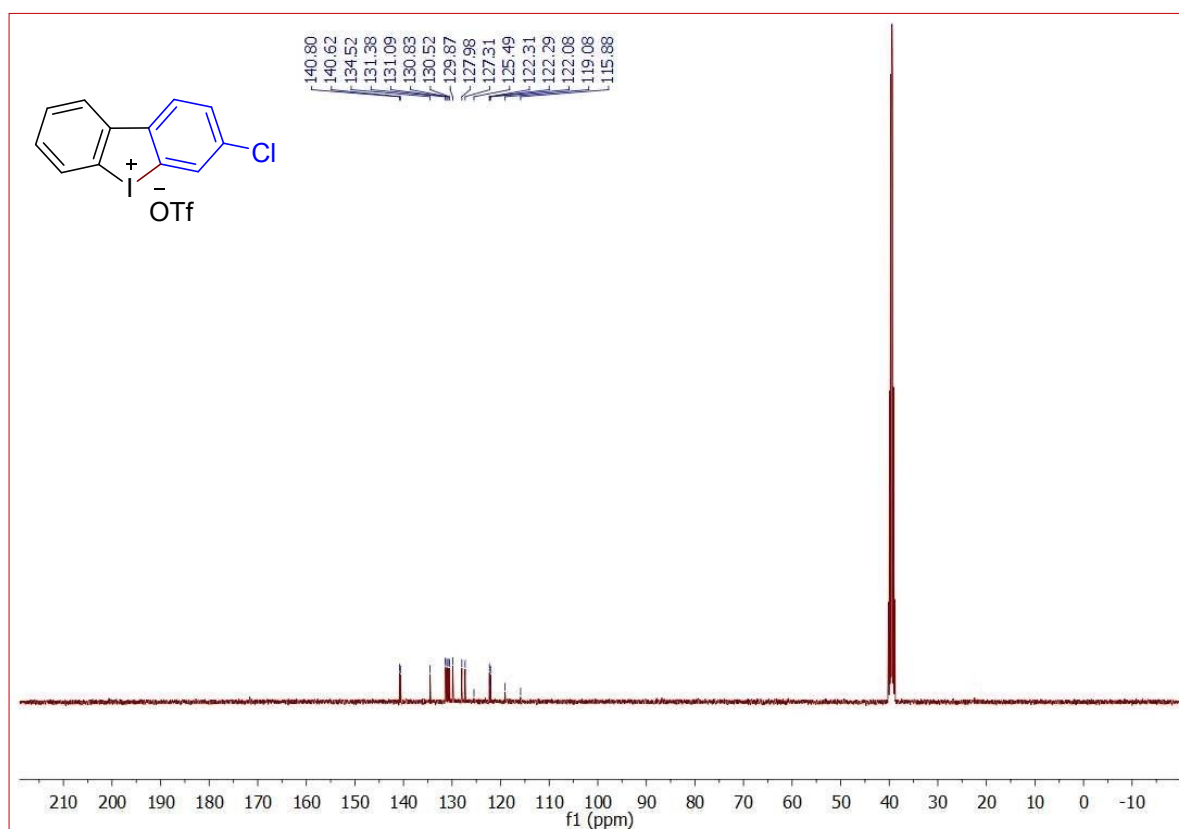
2-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2c**), ^{19}F NMR



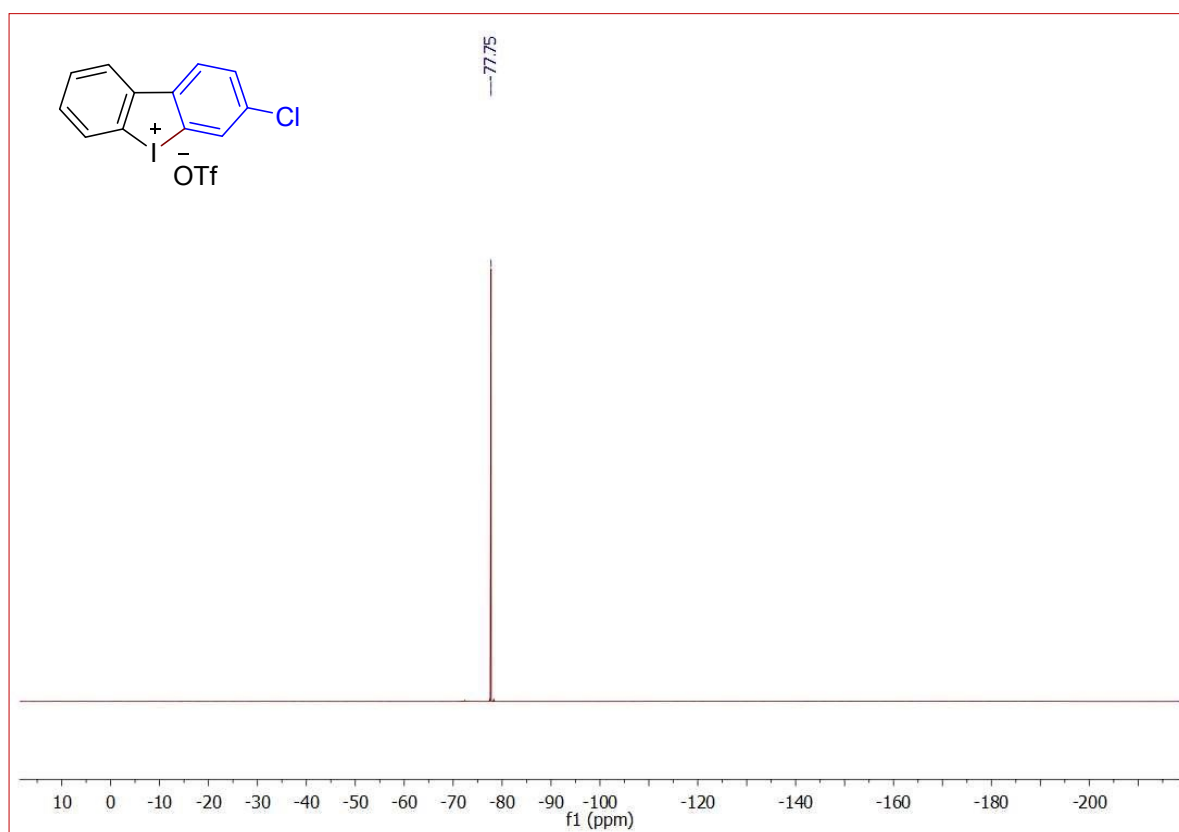
3-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2d**), ^1H NMR



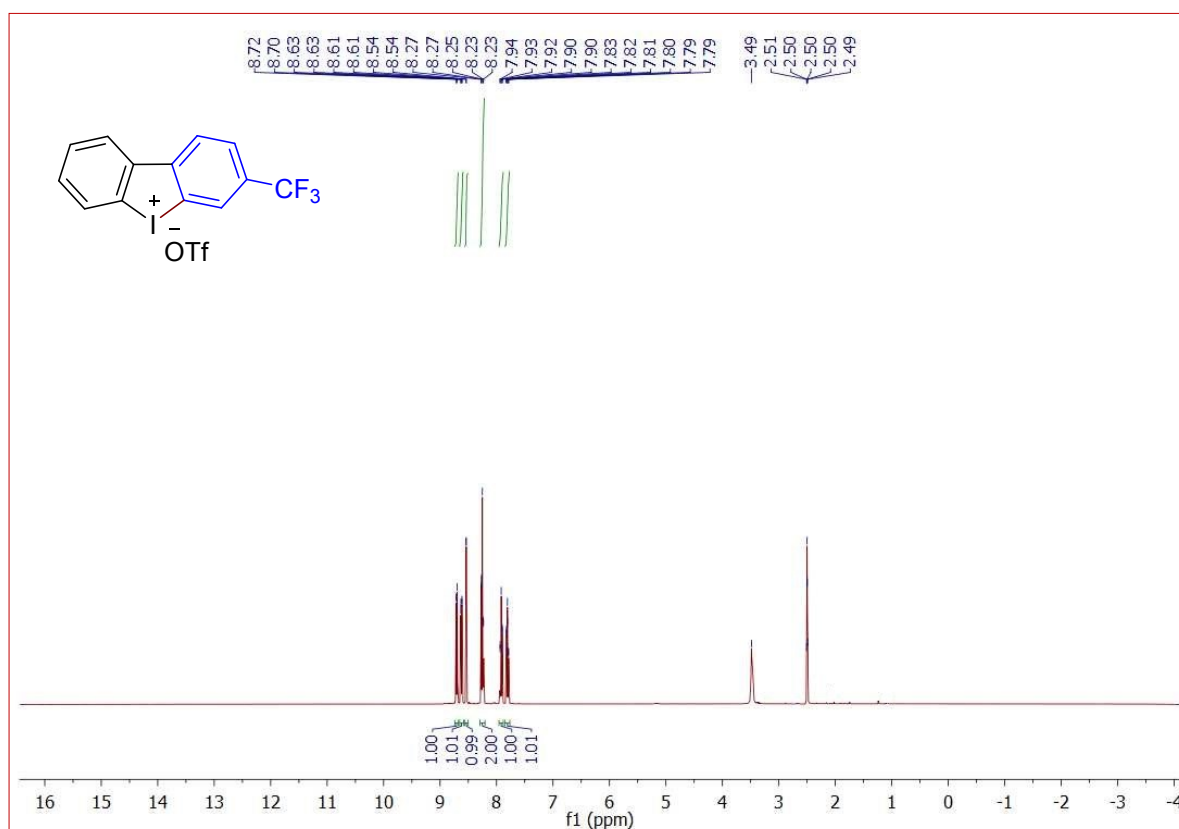
3-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2d**), ^{13}C NMR



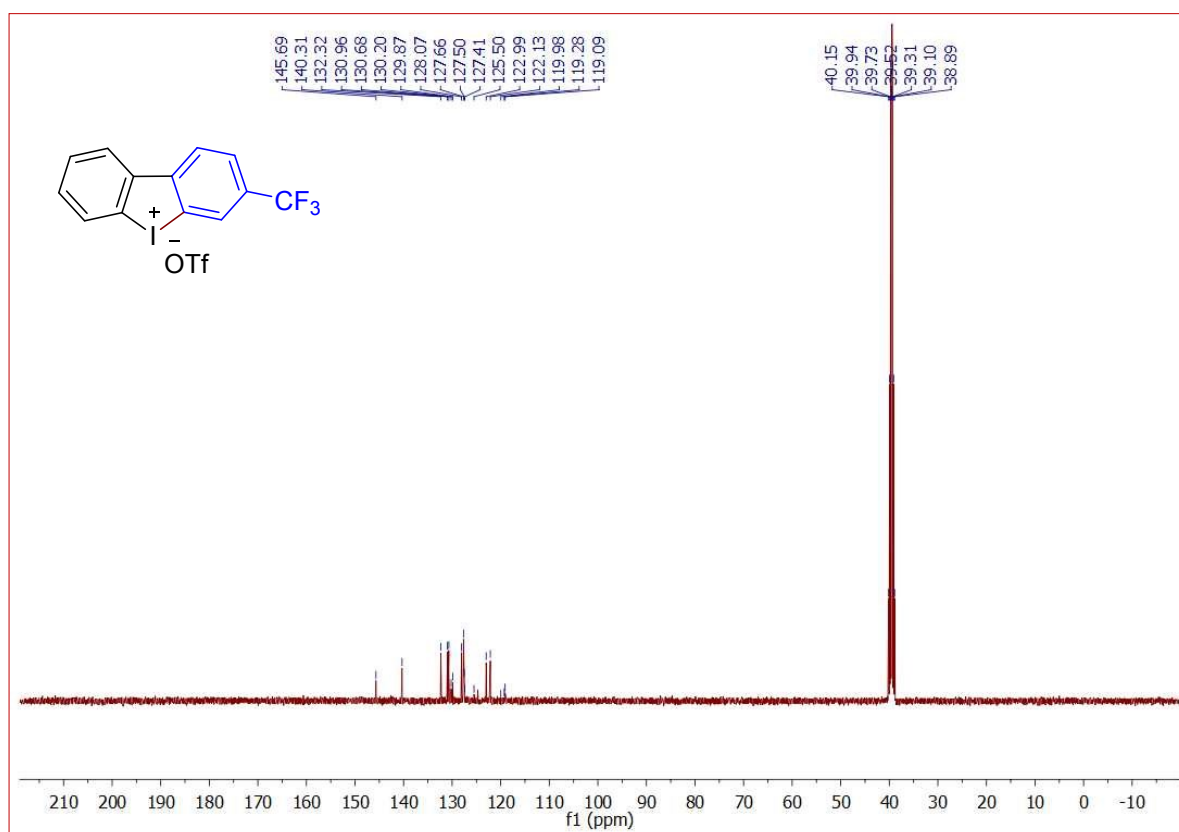
3-Chlorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2d**), ^{19}F NMR



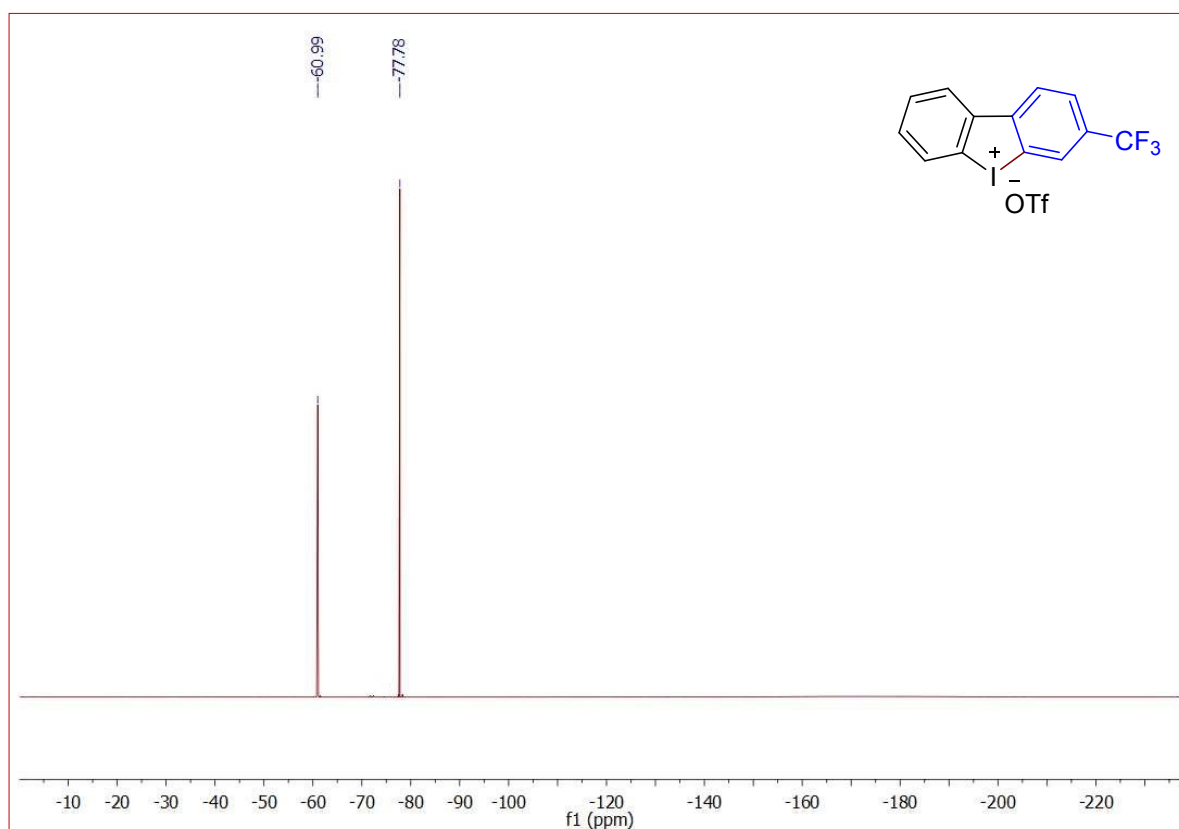
3-(Trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2e**), ^1H NMR



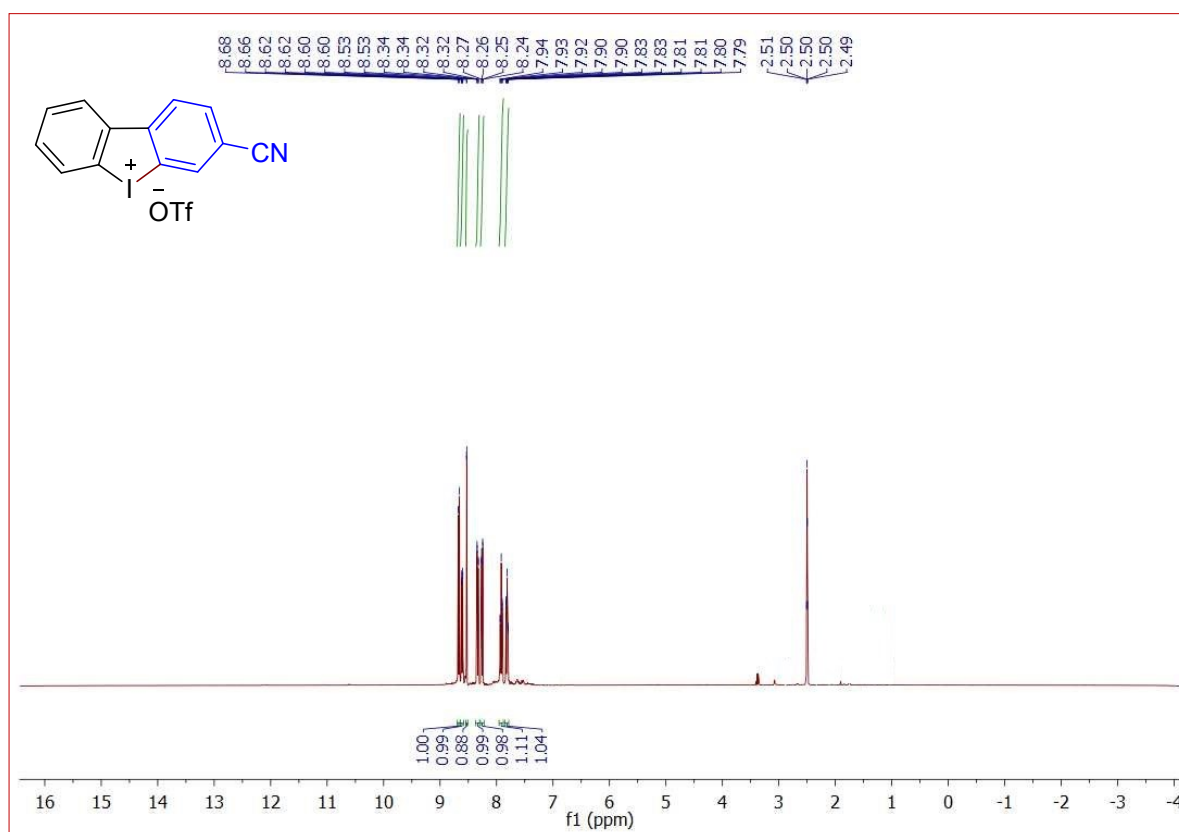
3-(Trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2e**), ^{13}C NMR



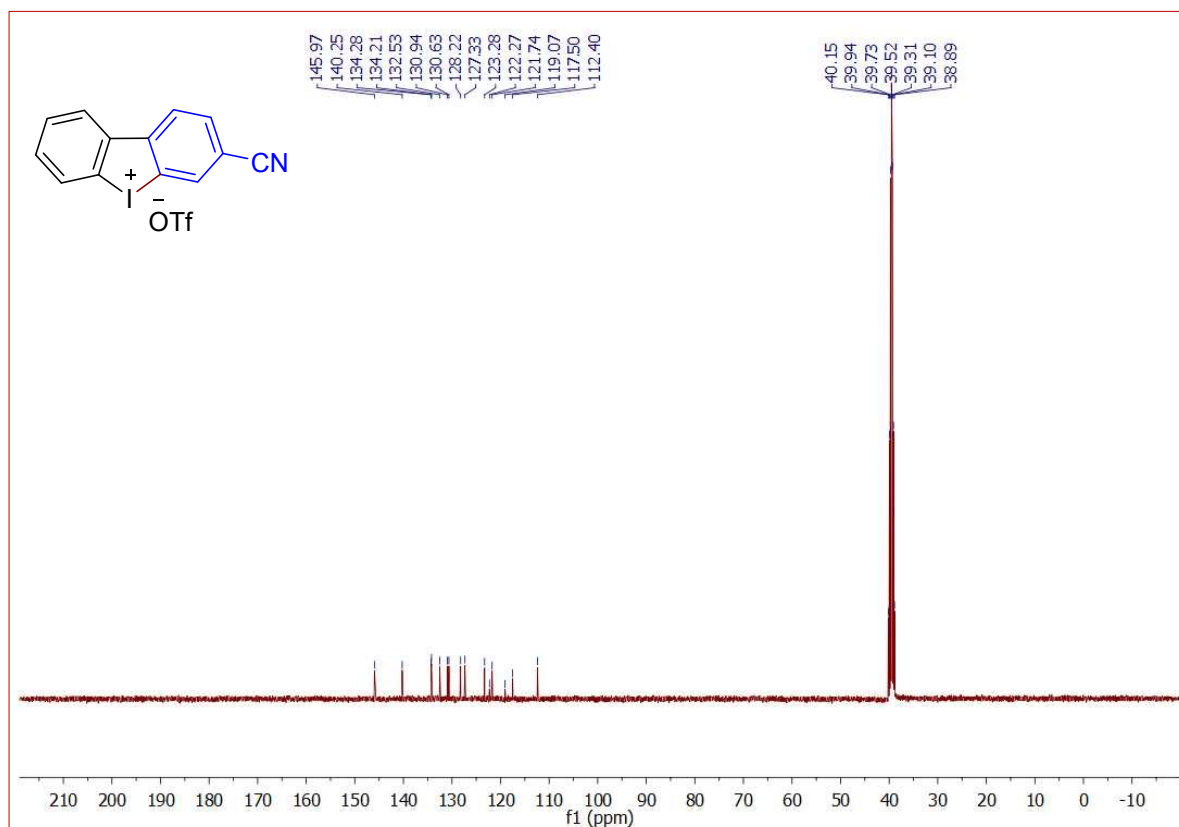
3-(Trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2e**), ^{19}F NMR



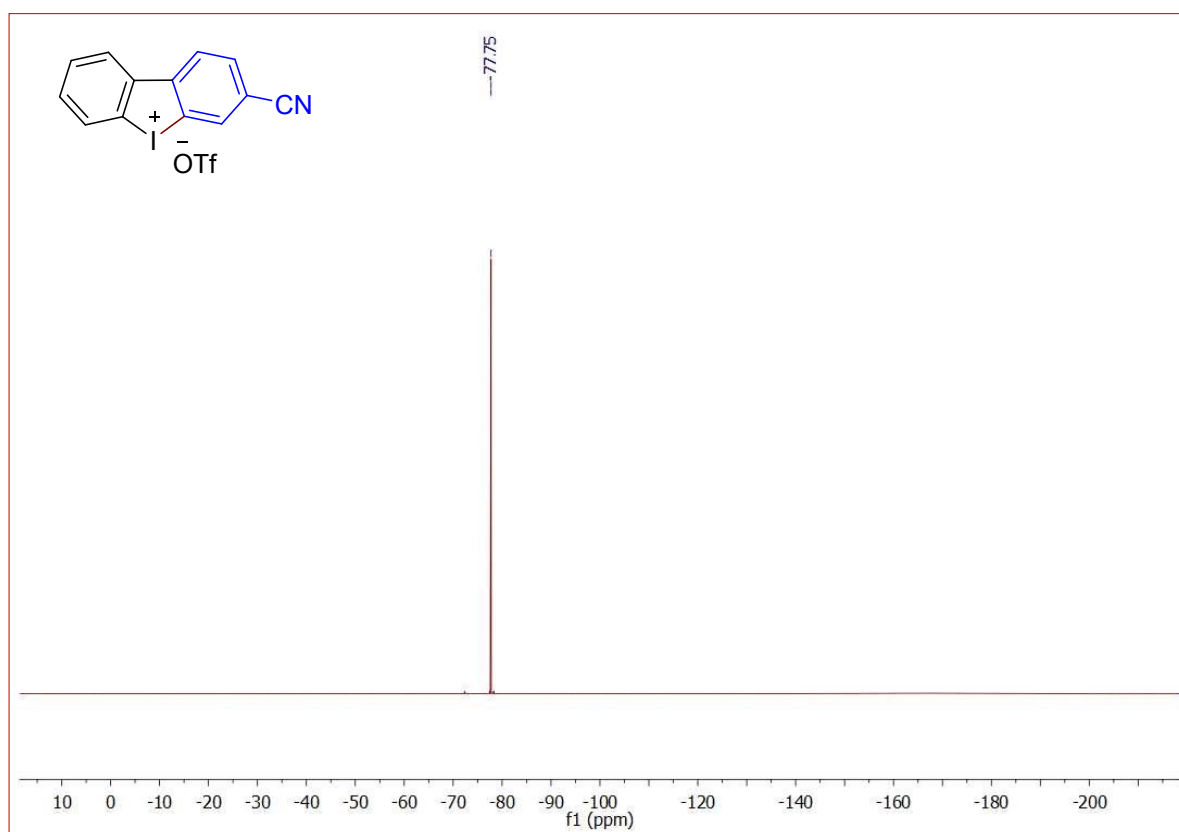
3-Cyanodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2f), ^1H NMR



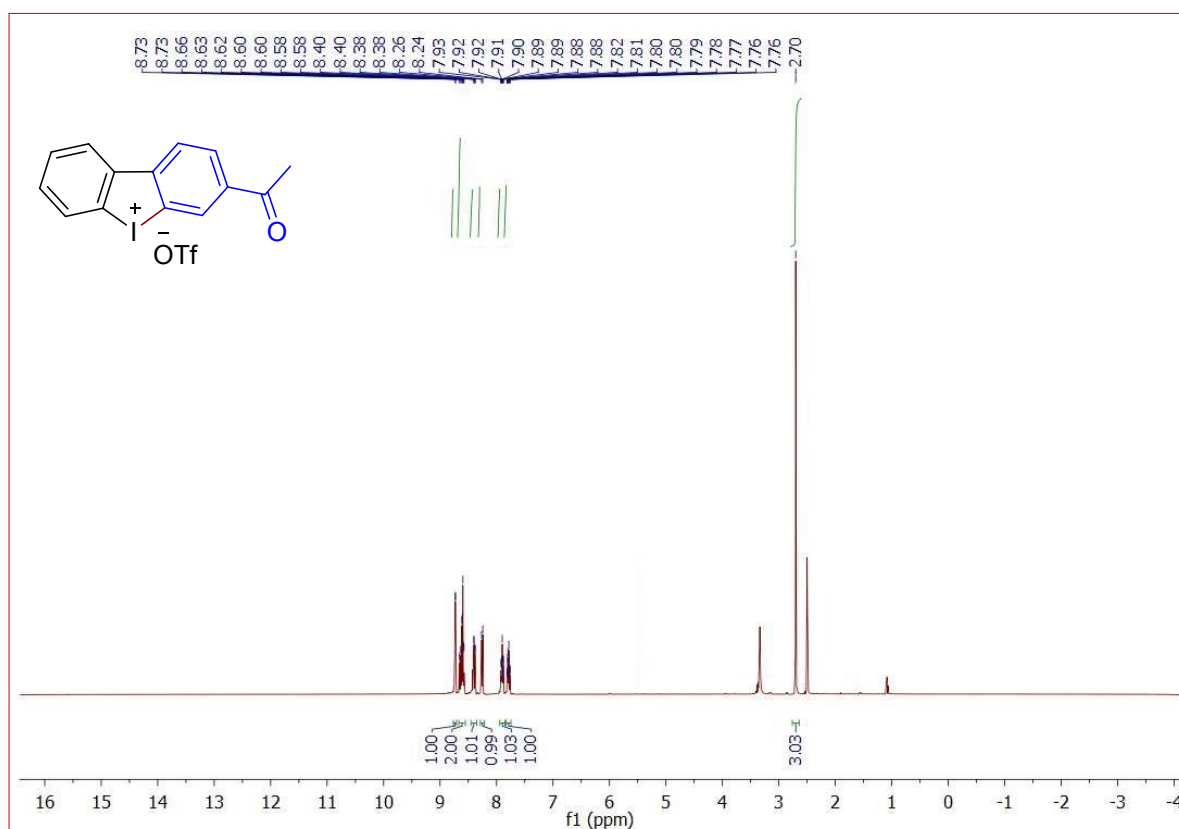
3-Cyanodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (2f), ^{13}C NMR



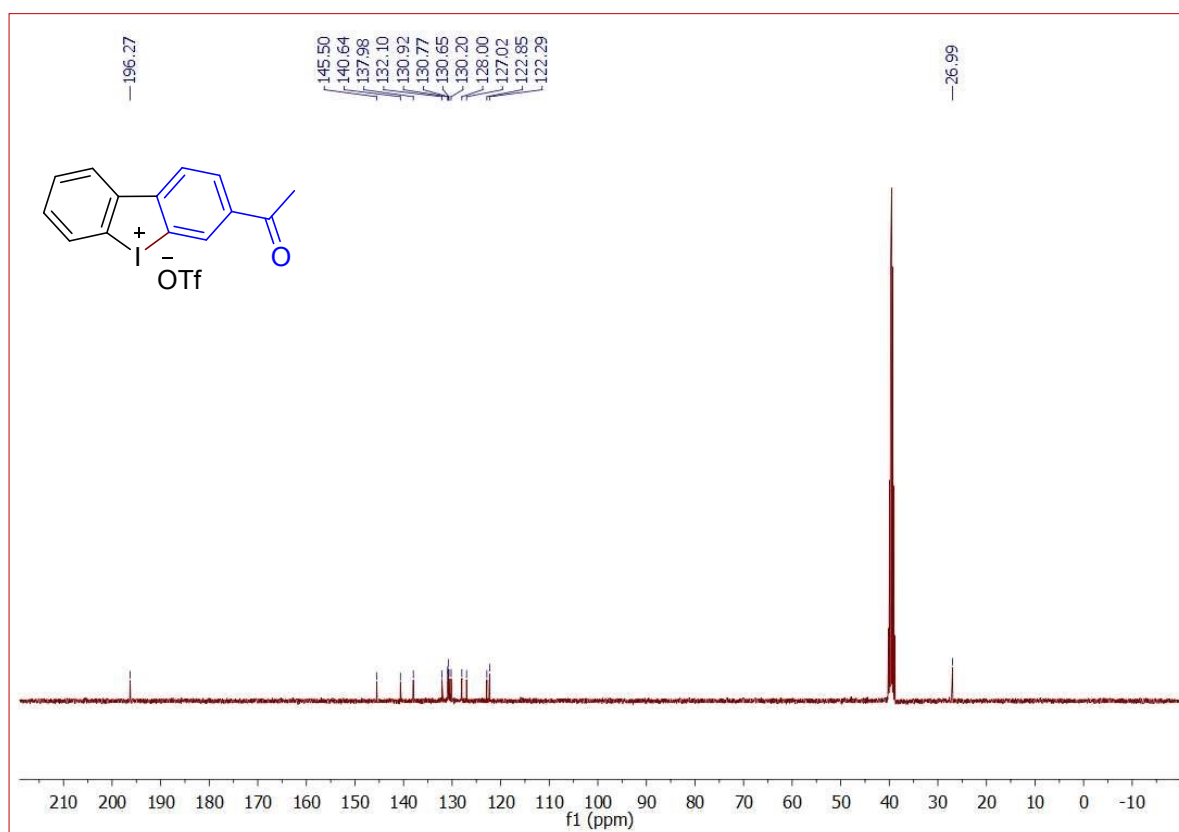
3-Cyanodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2f**), ^{19}F NMR



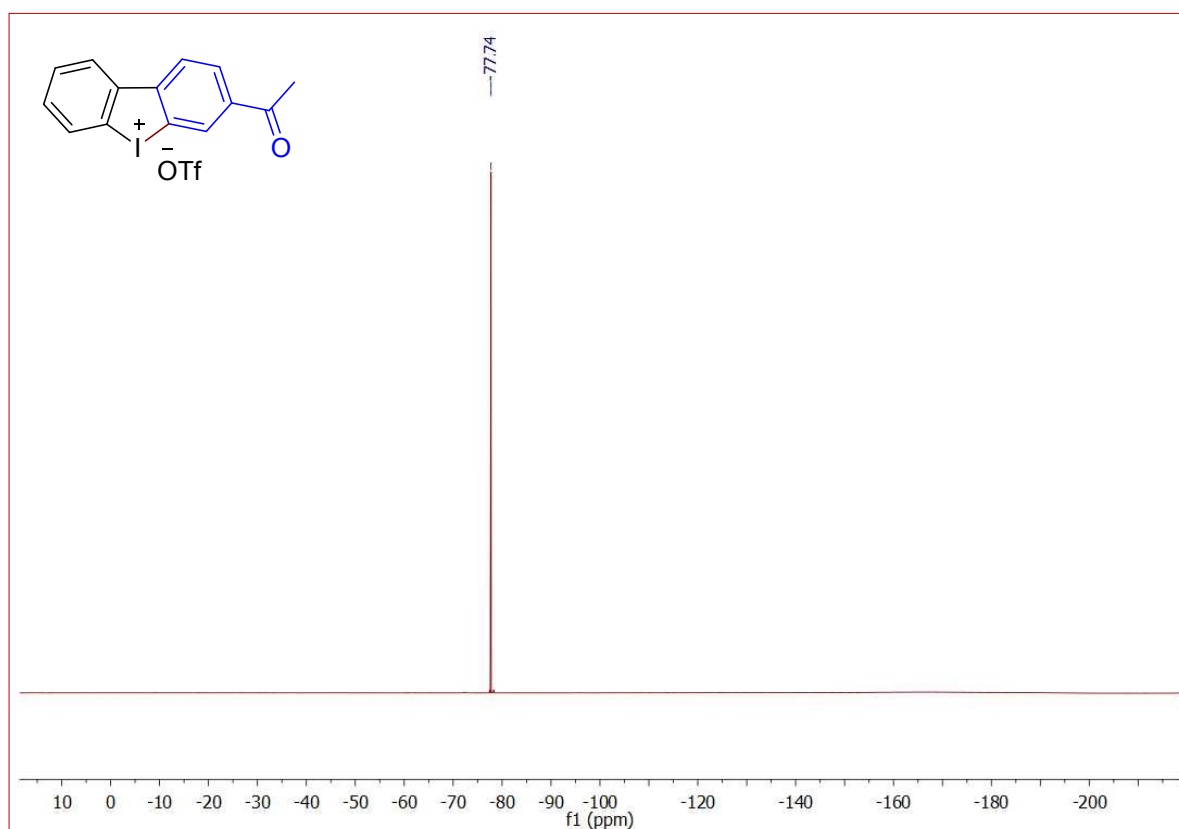
3-Acetyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**), ^1H NMR



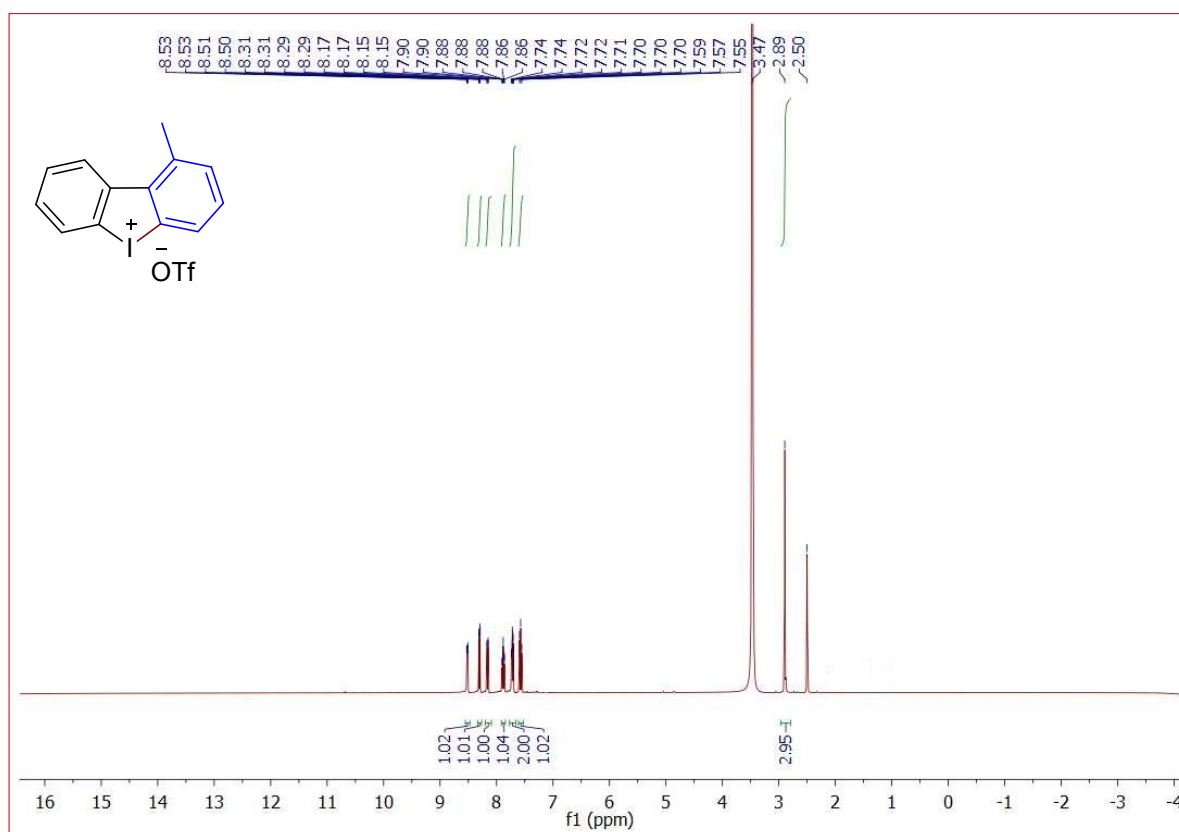
3-Acetyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**), ^{13}C NMR



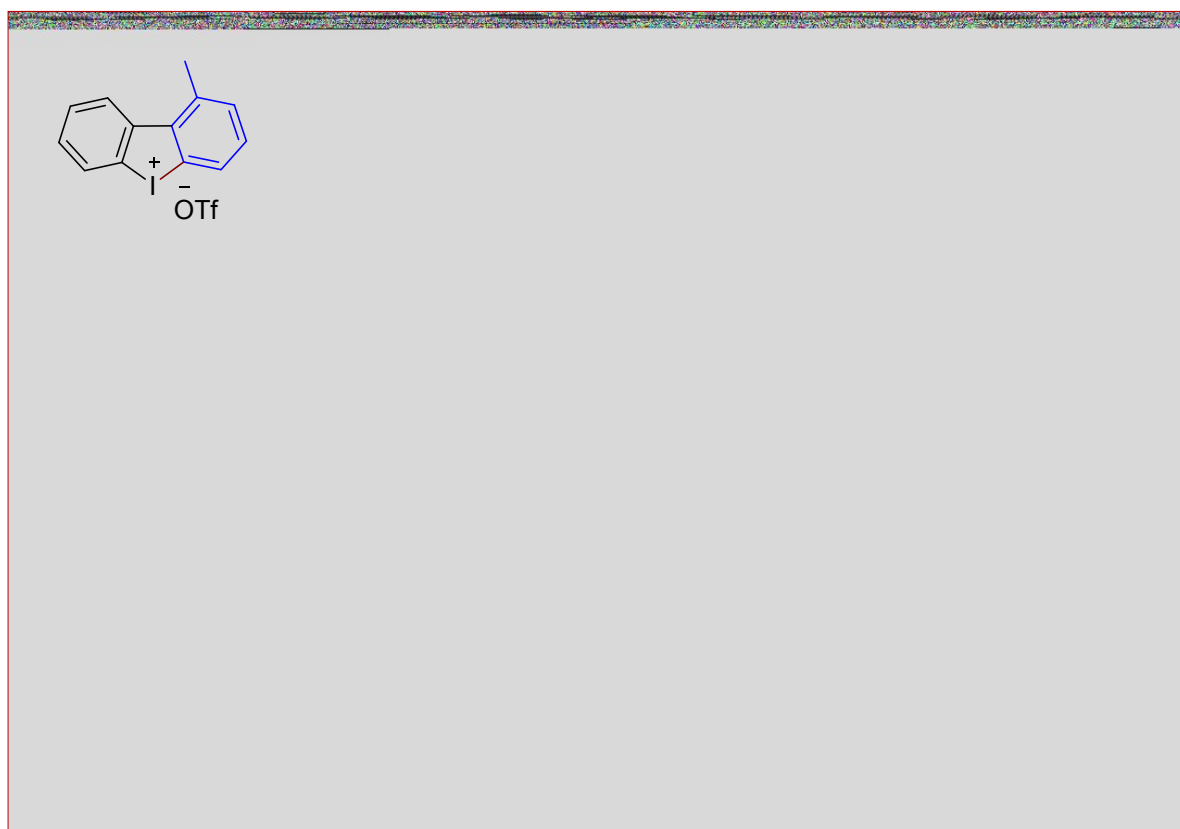
3-Acetyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2g**), ^{19}F NMR



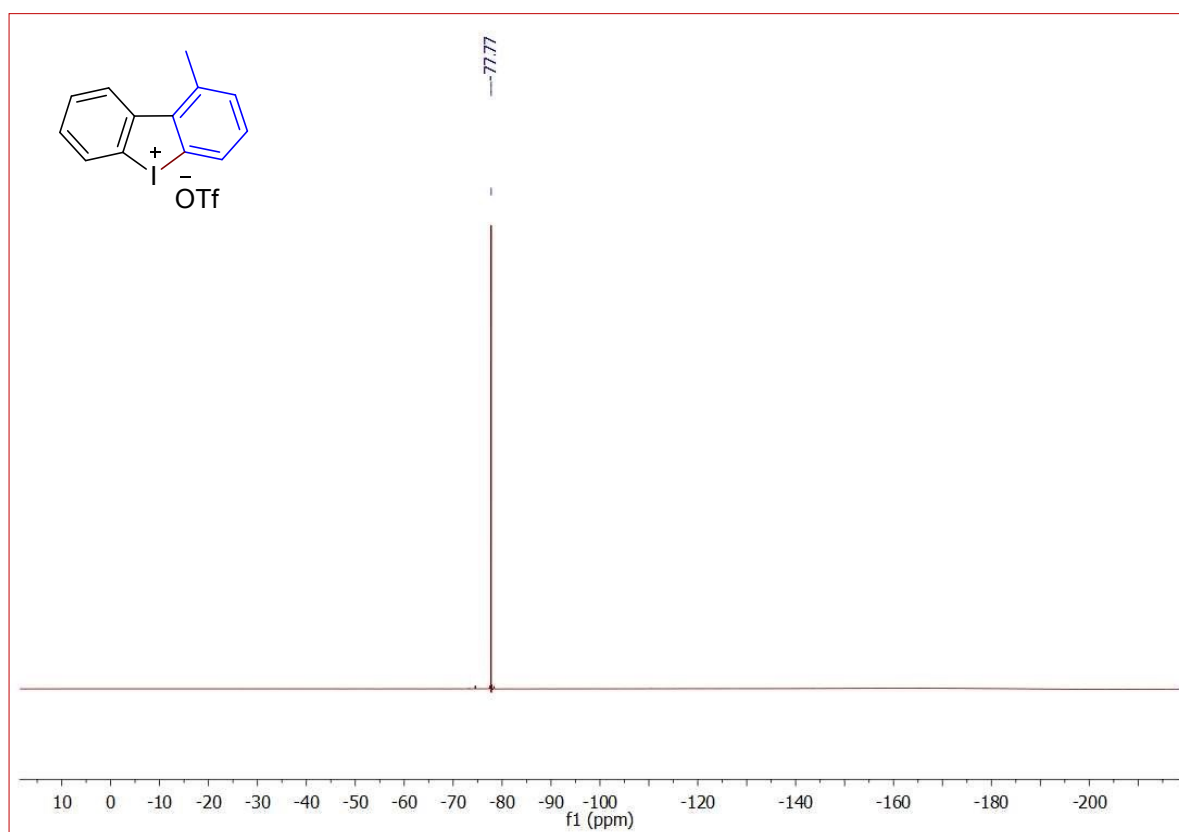
1-Methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2h**), ^1H NMR



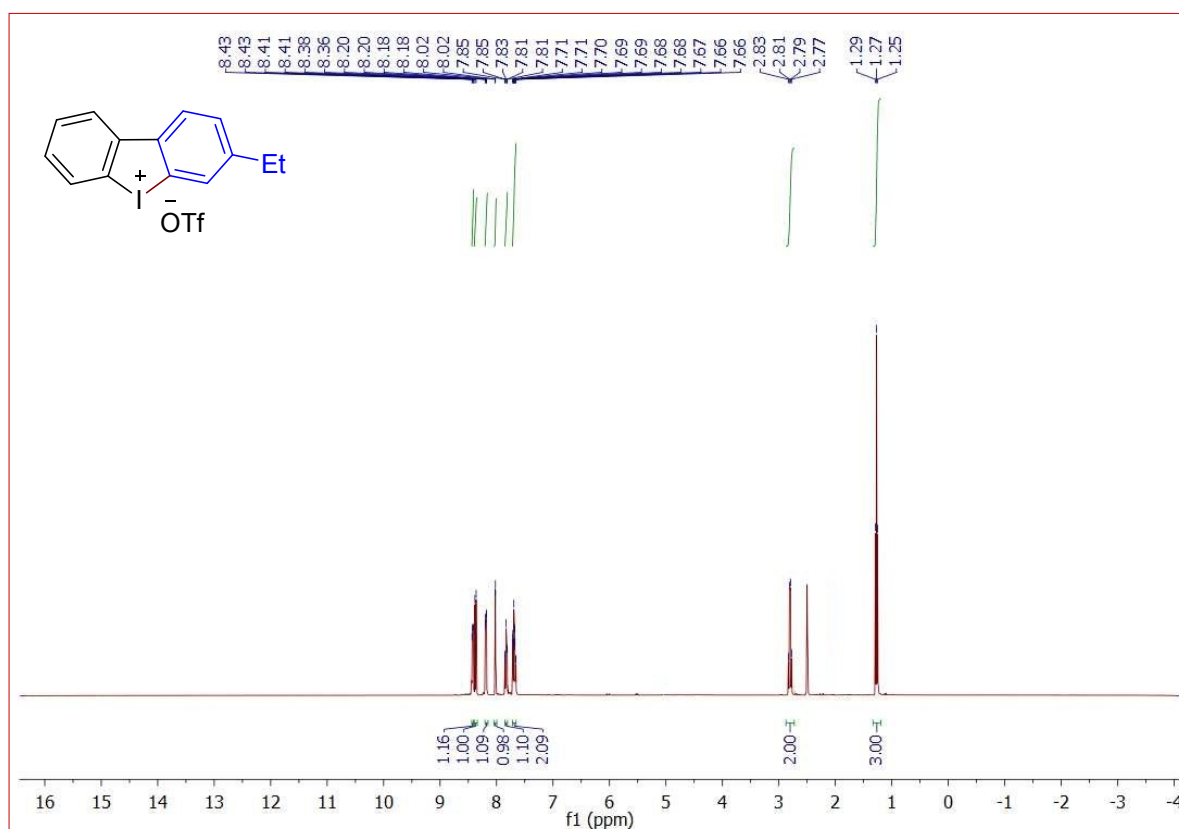
1-Methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2h**), ^{13}C NMR



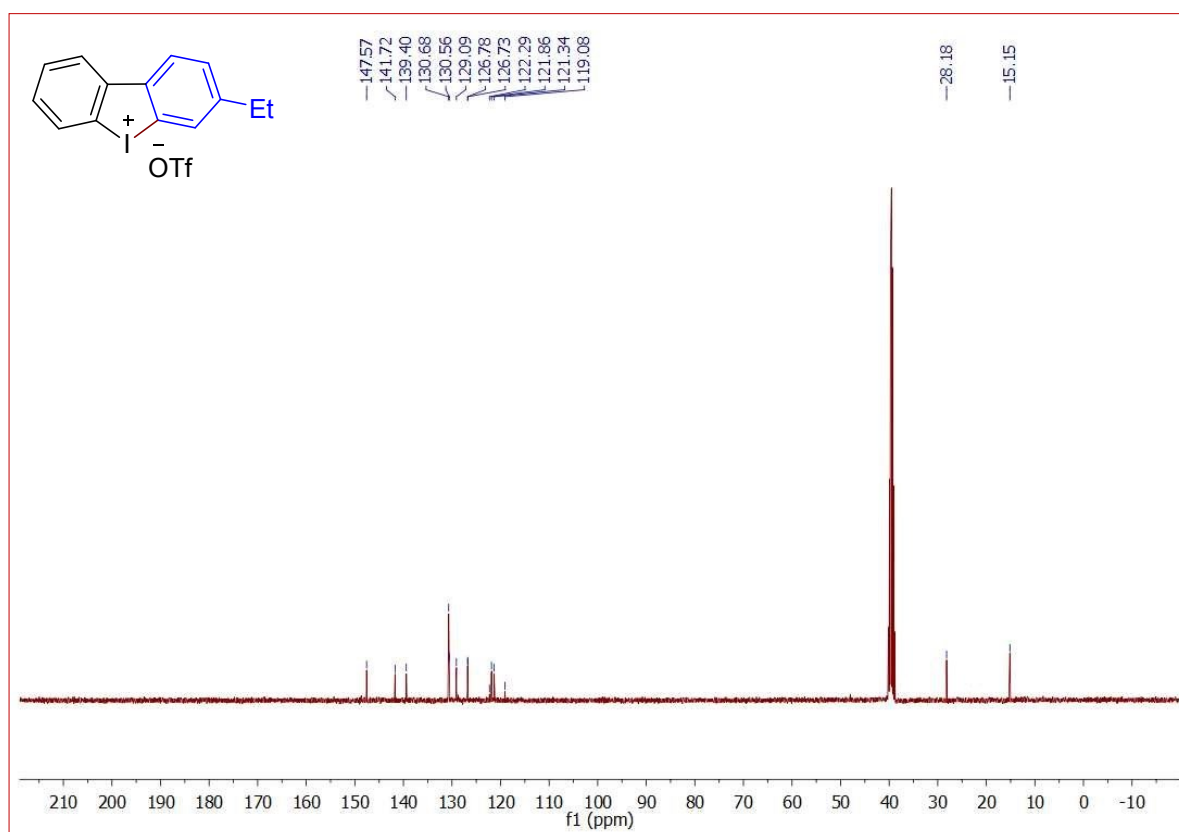
1-Methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2h**), ^{19}F NMR



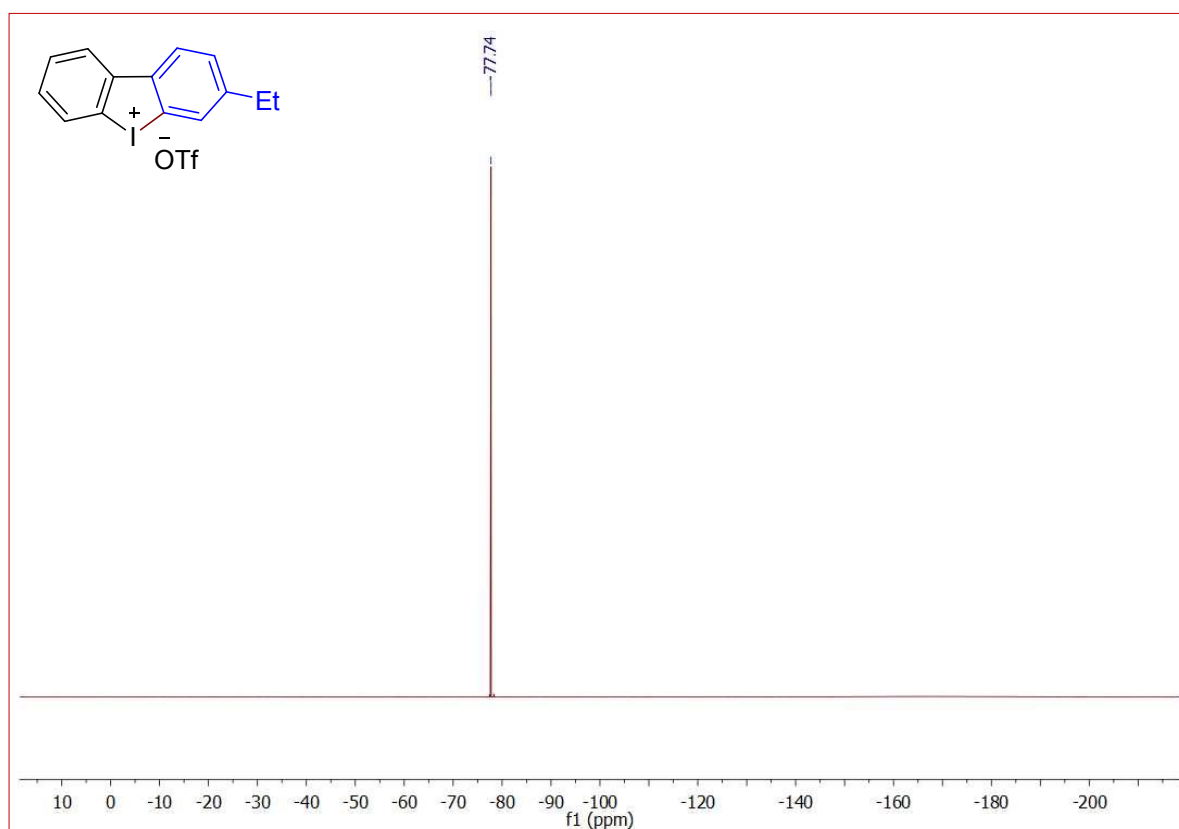
3-Ethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2i**), ^1H NMR



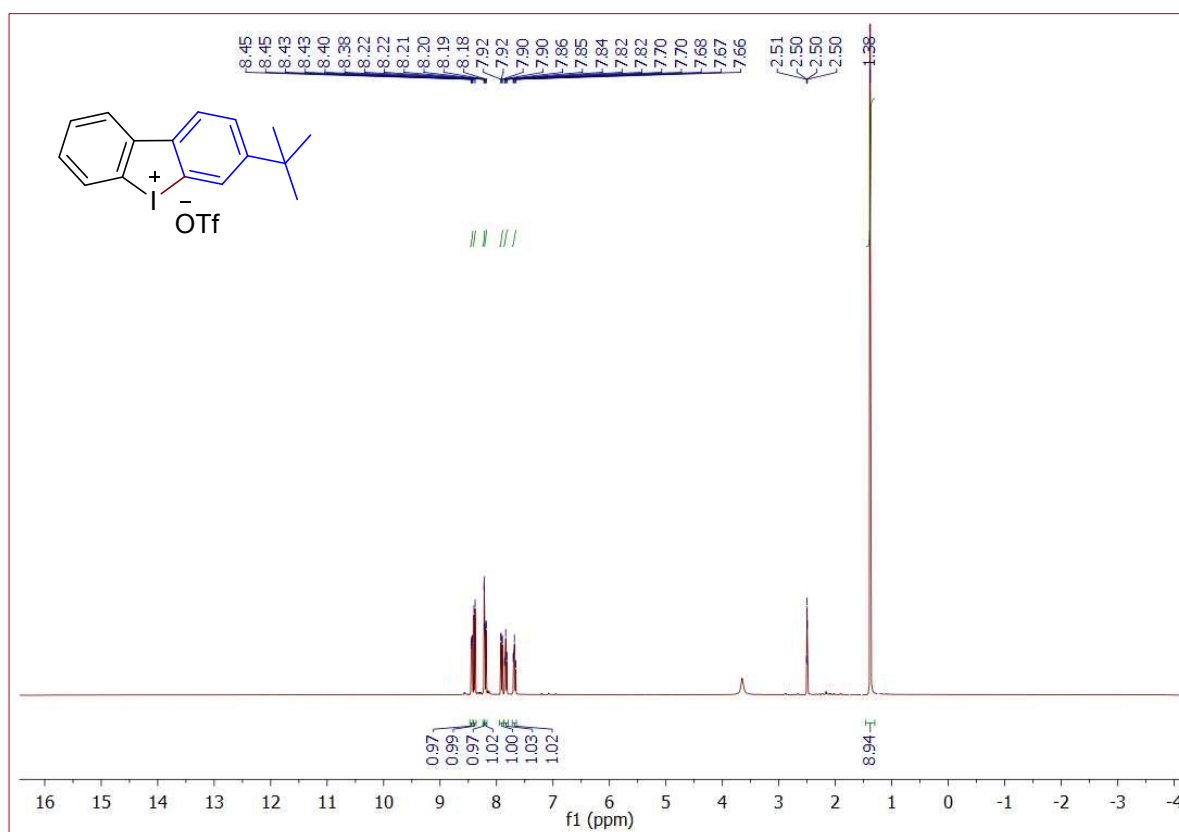
3-Ethyl-dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2i**), ^{13}C NMR



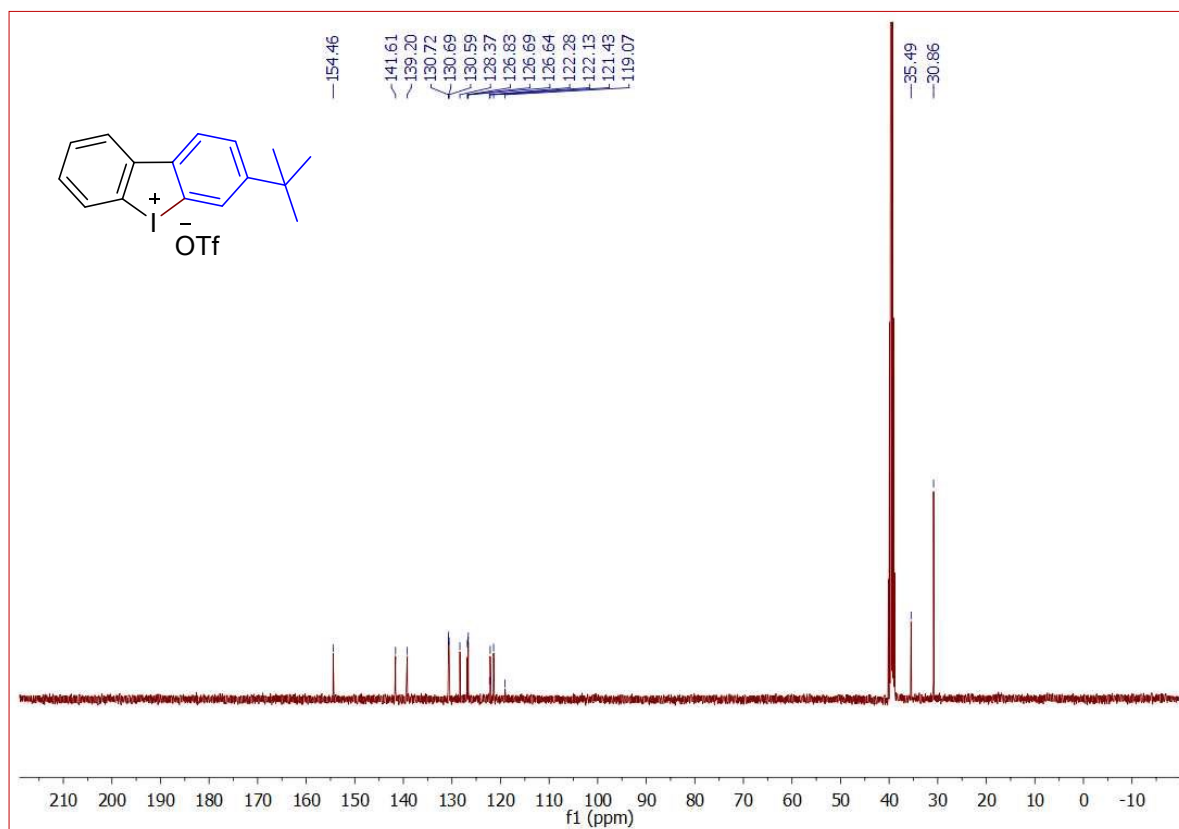
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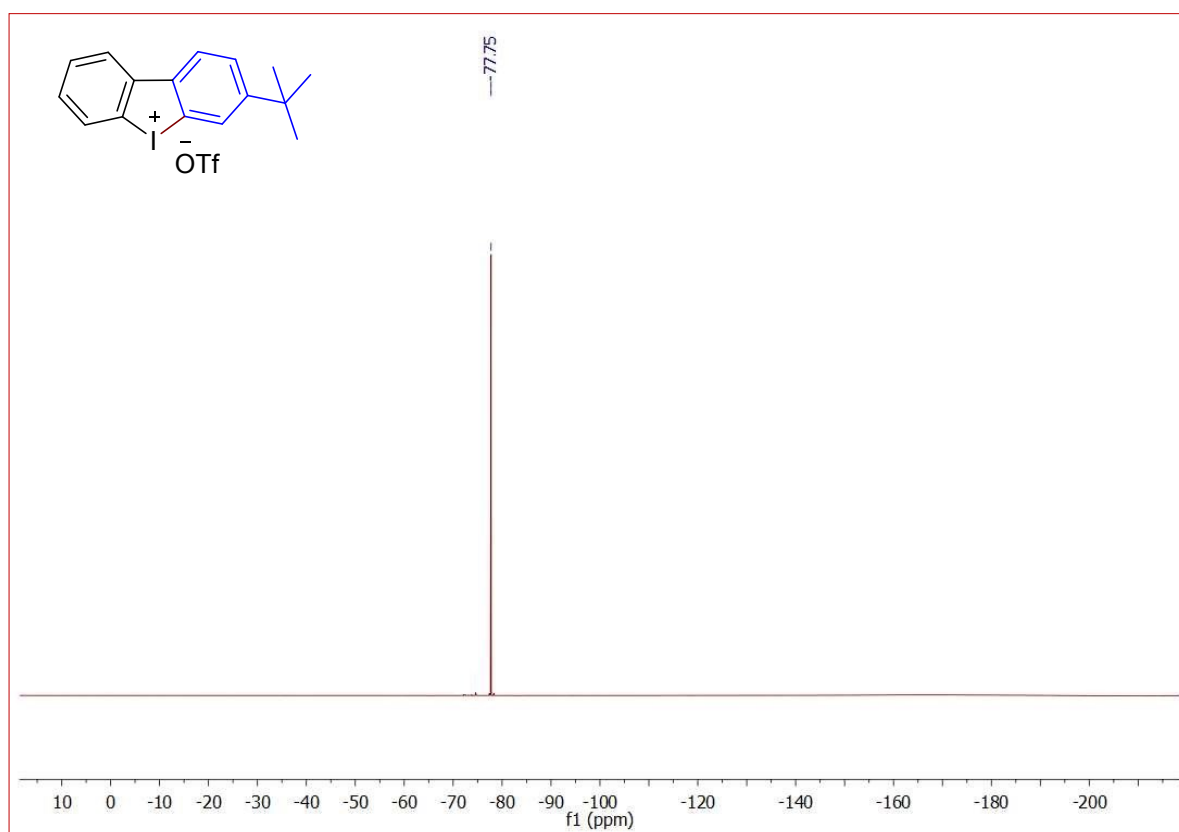
3-(*tert*-Butyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2j**), ¹H NMR



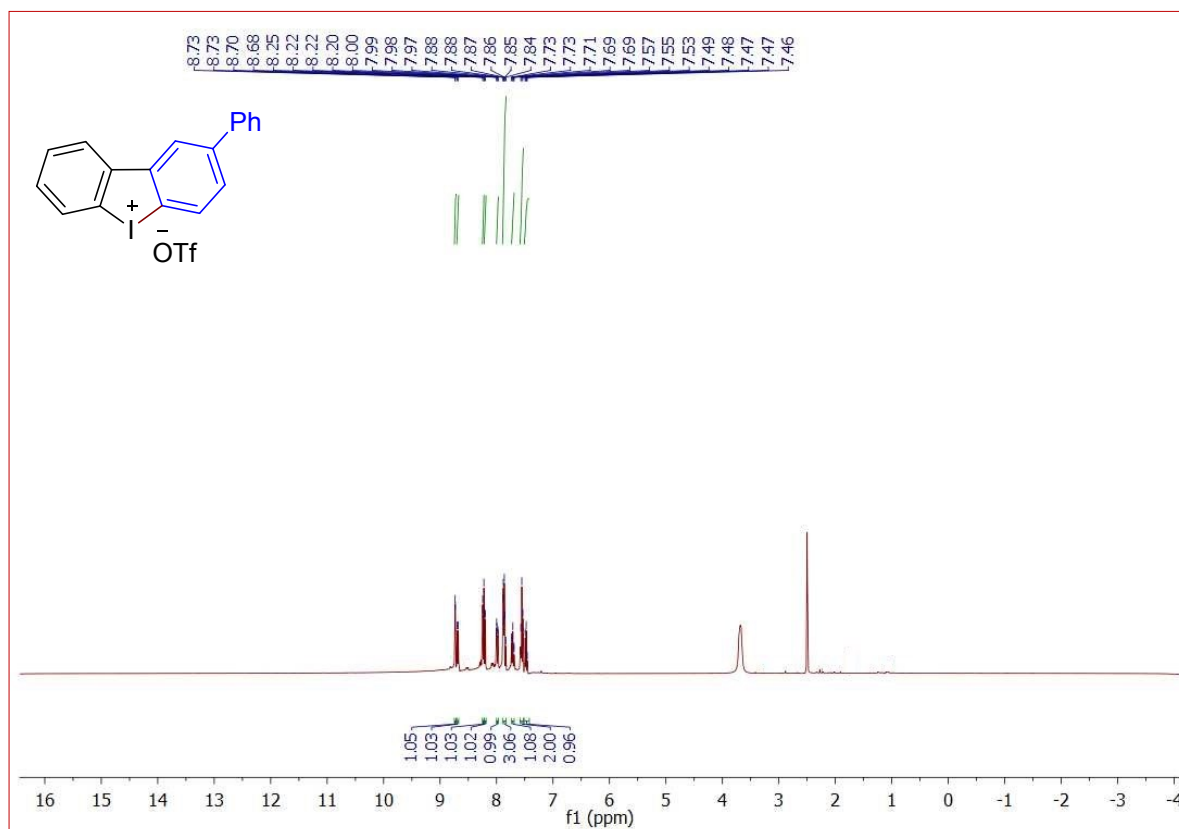
3-(*tert*-Butyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2j**), ¹³C NMR



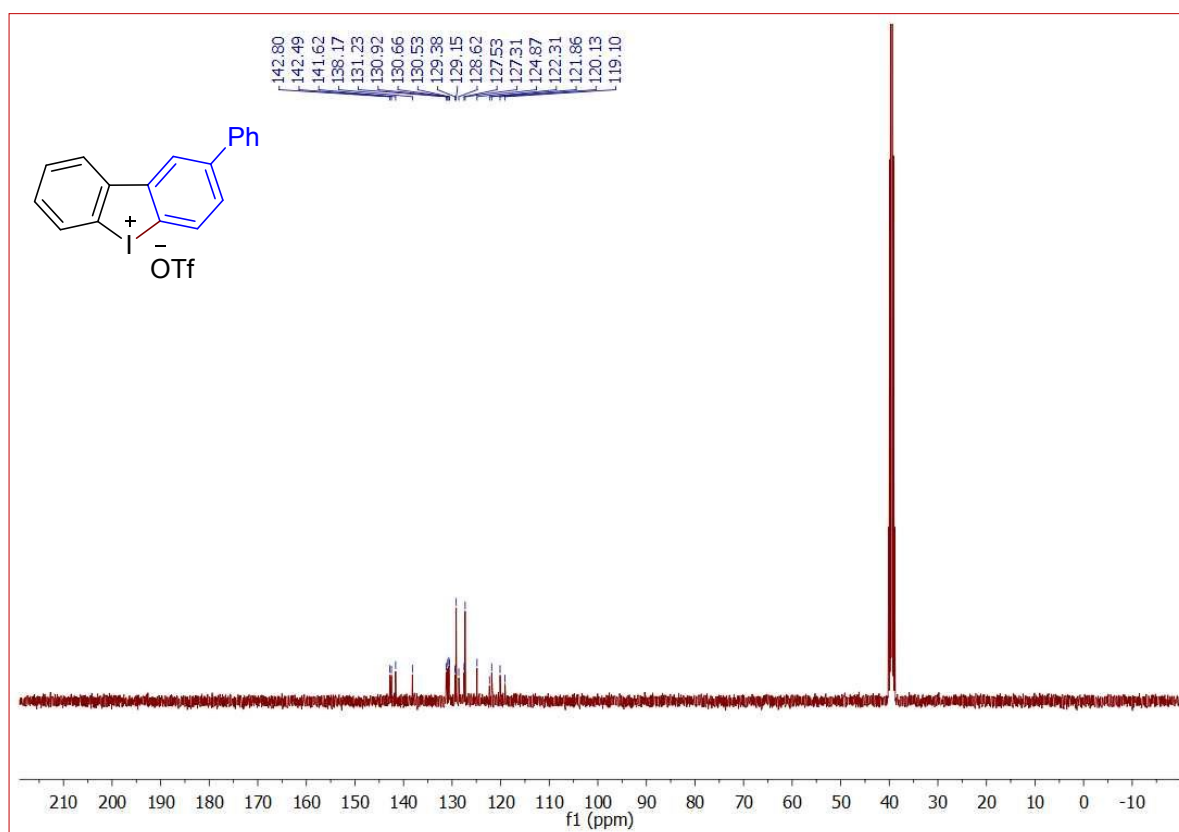
3-(*tert*-Butyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2j**), ^{19}F NMR



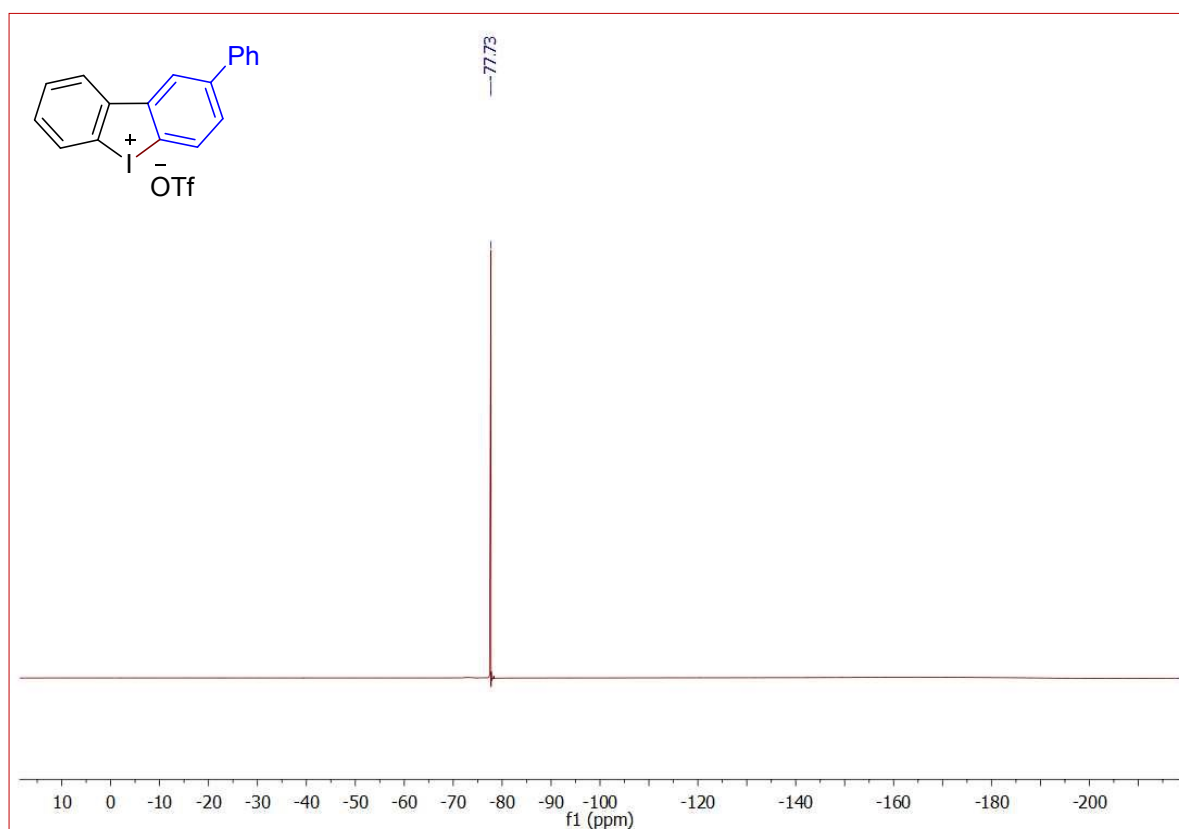
2-Phenyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2k**), ^1H NMR



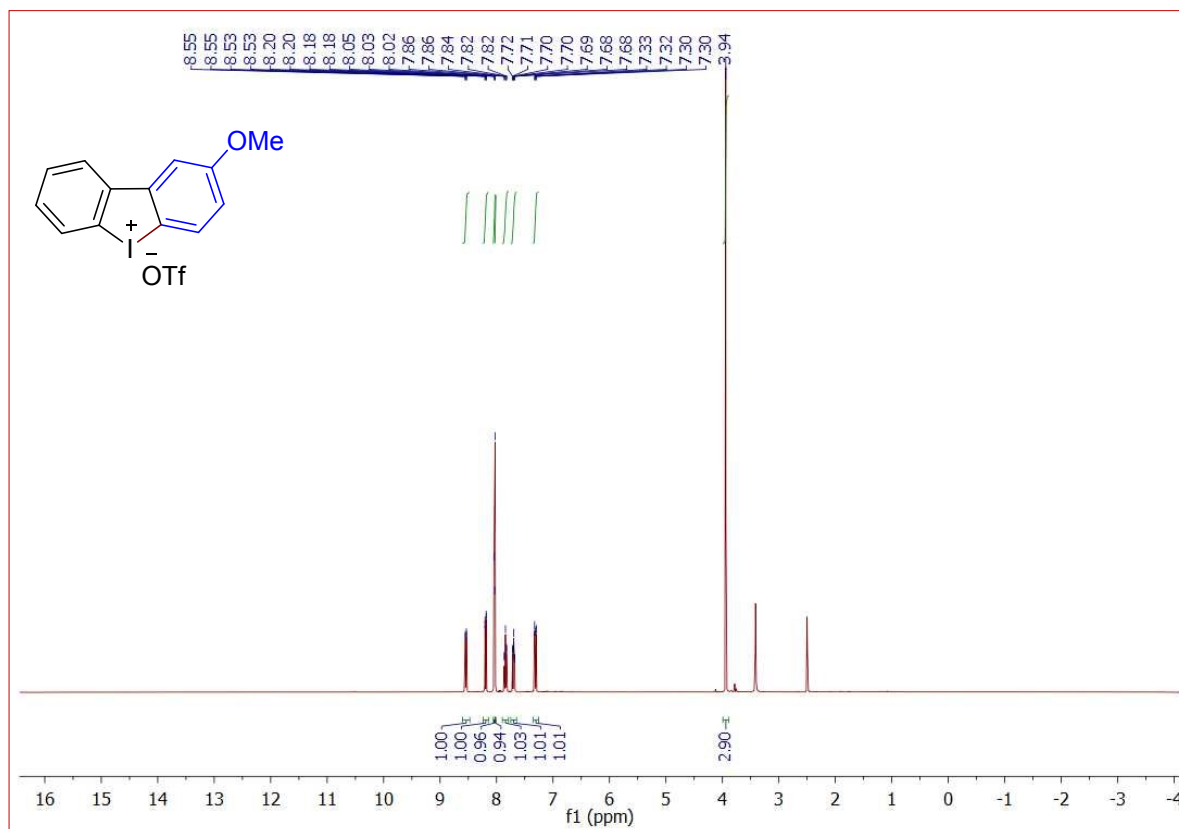
2-Phenyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2k**), ^{13}C NMR



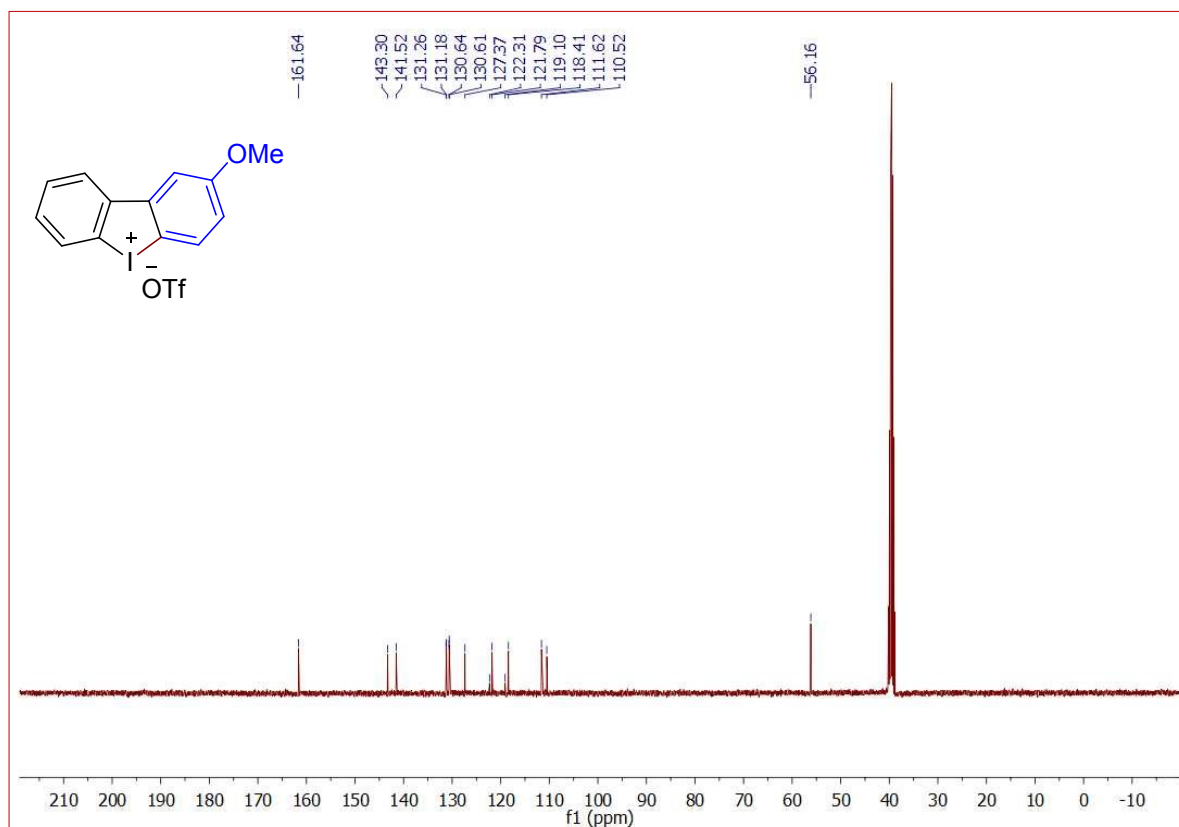
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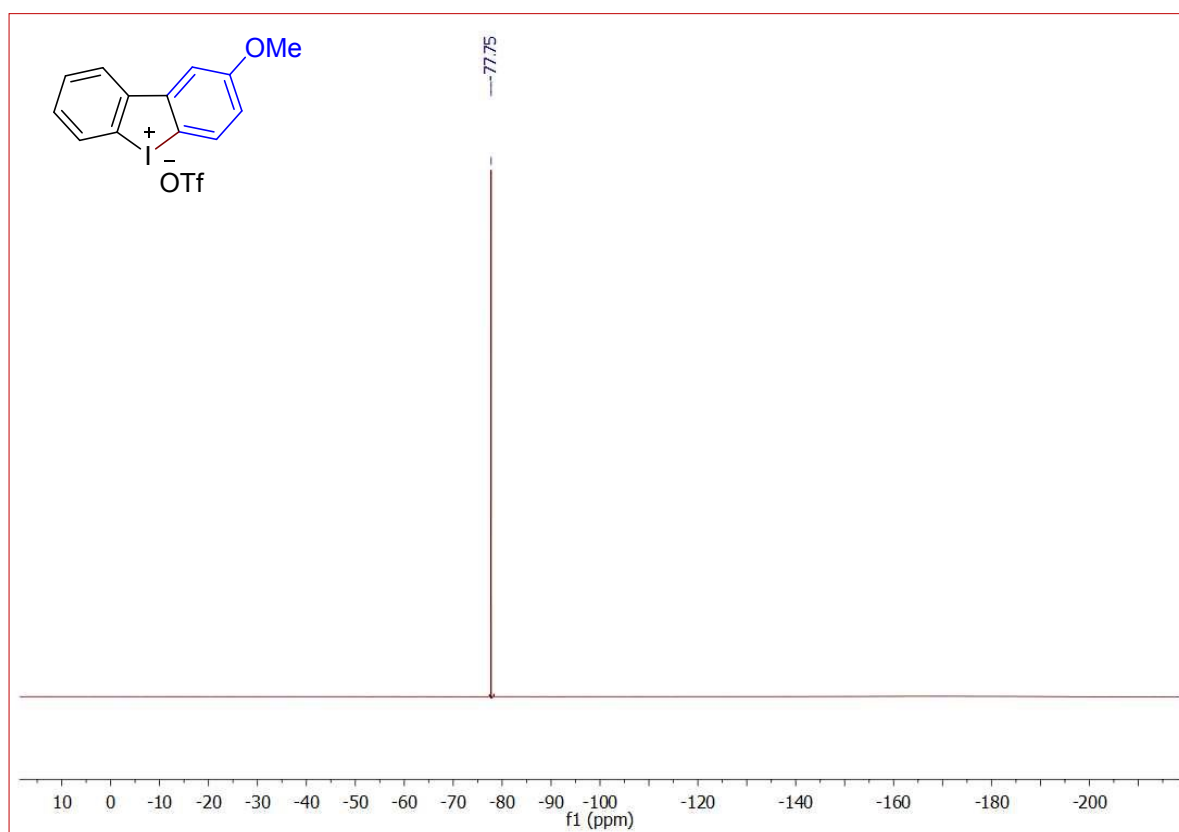
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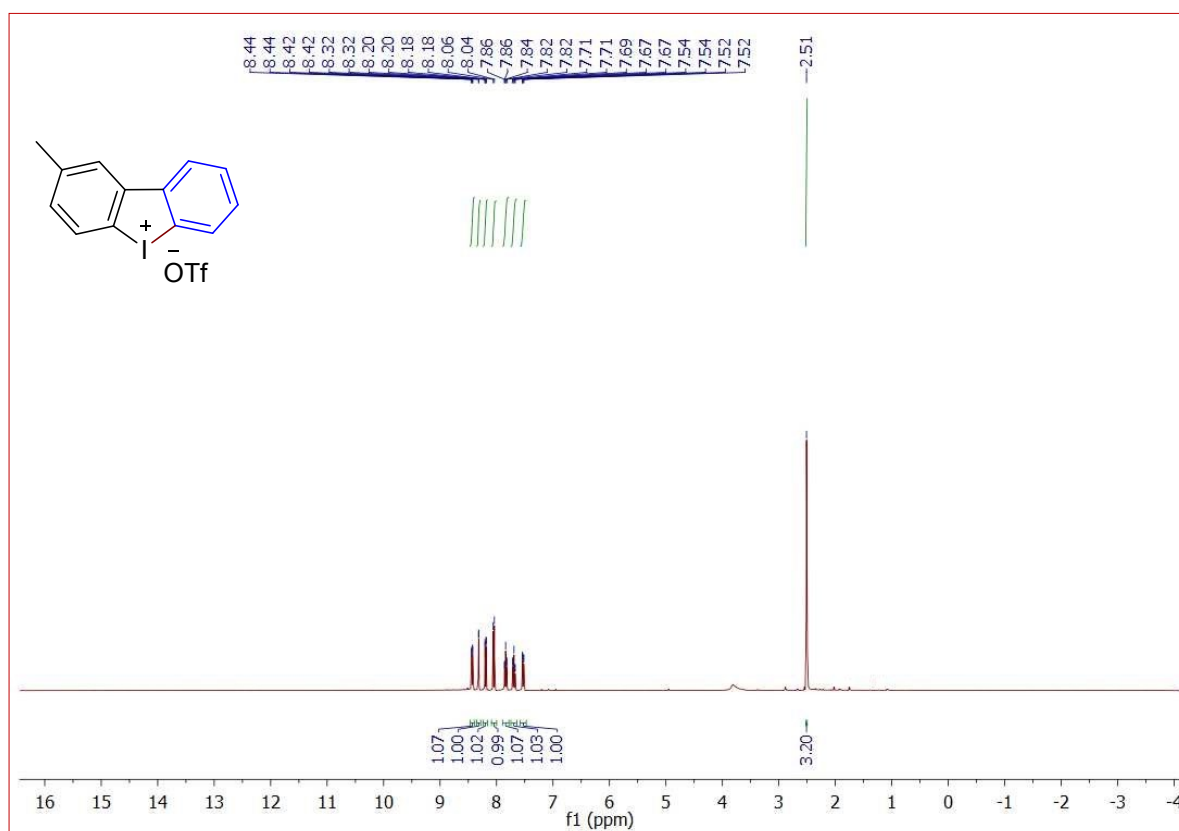
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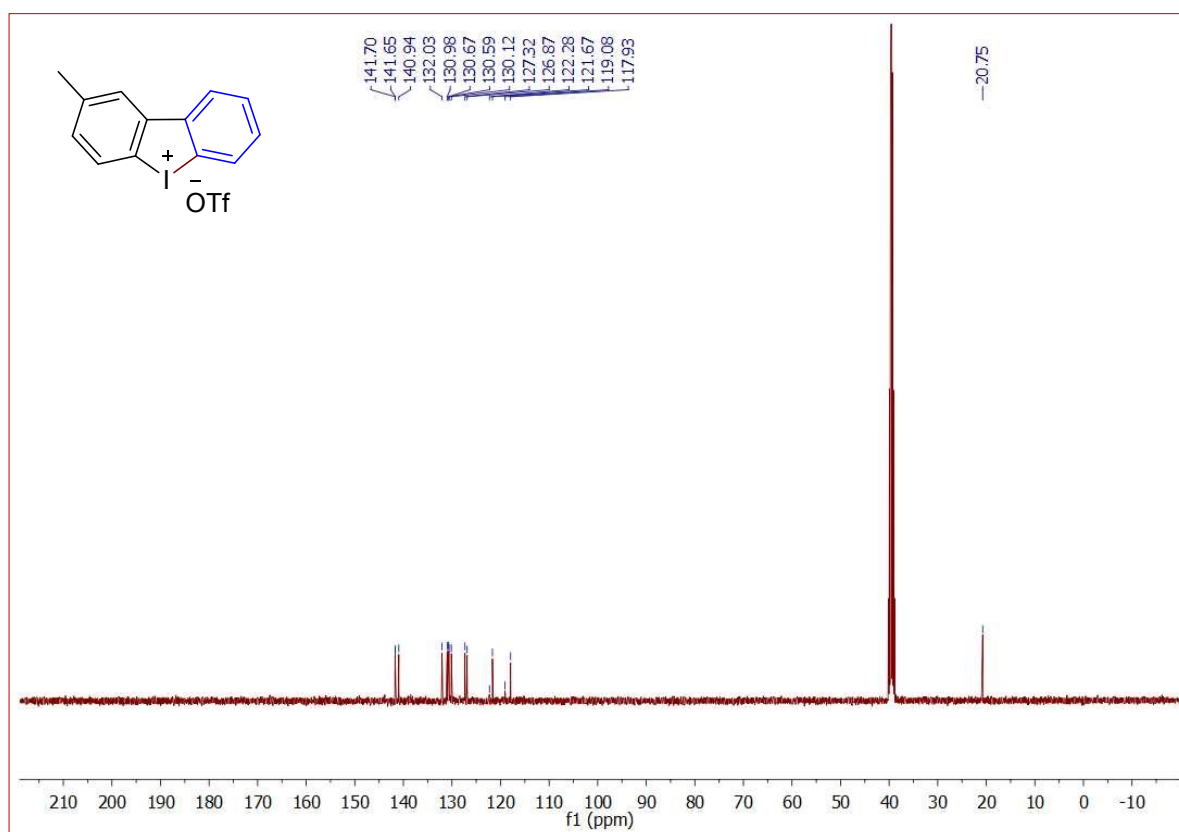
2-Methoxydibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2l**), ^{19}F NMR



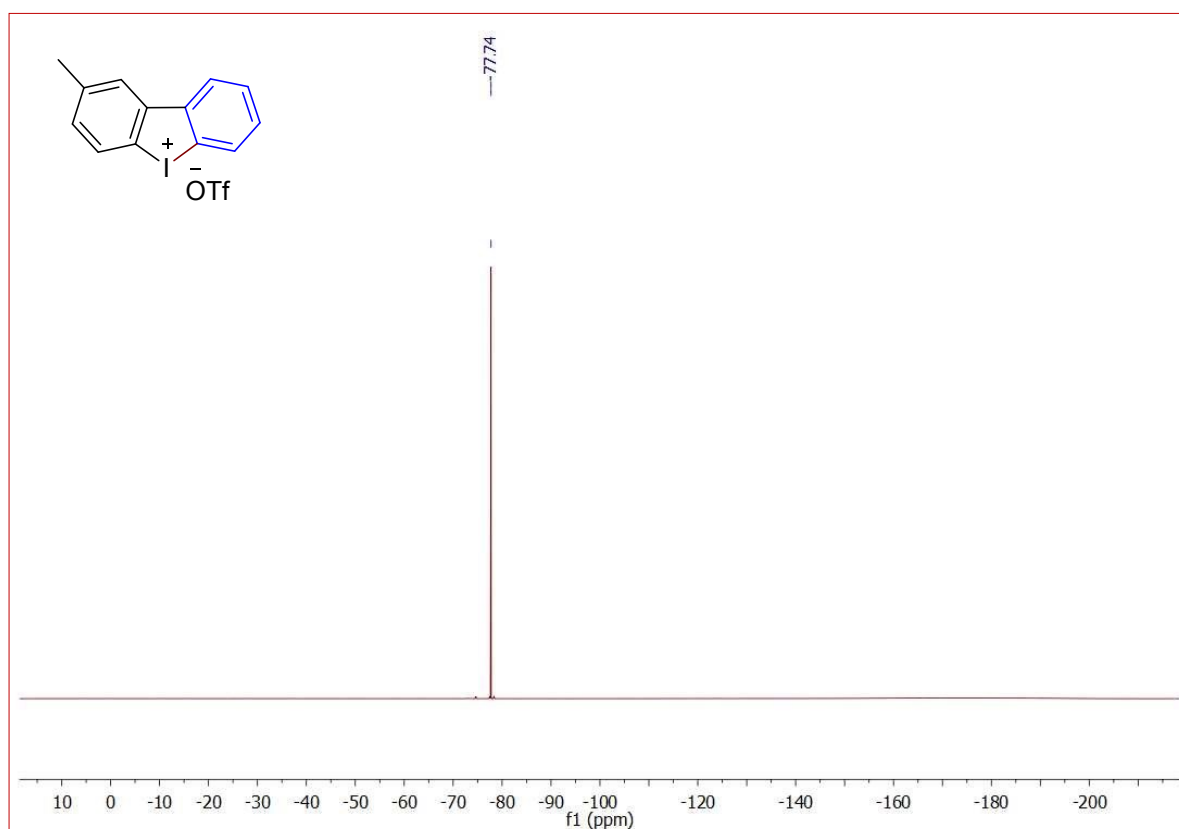
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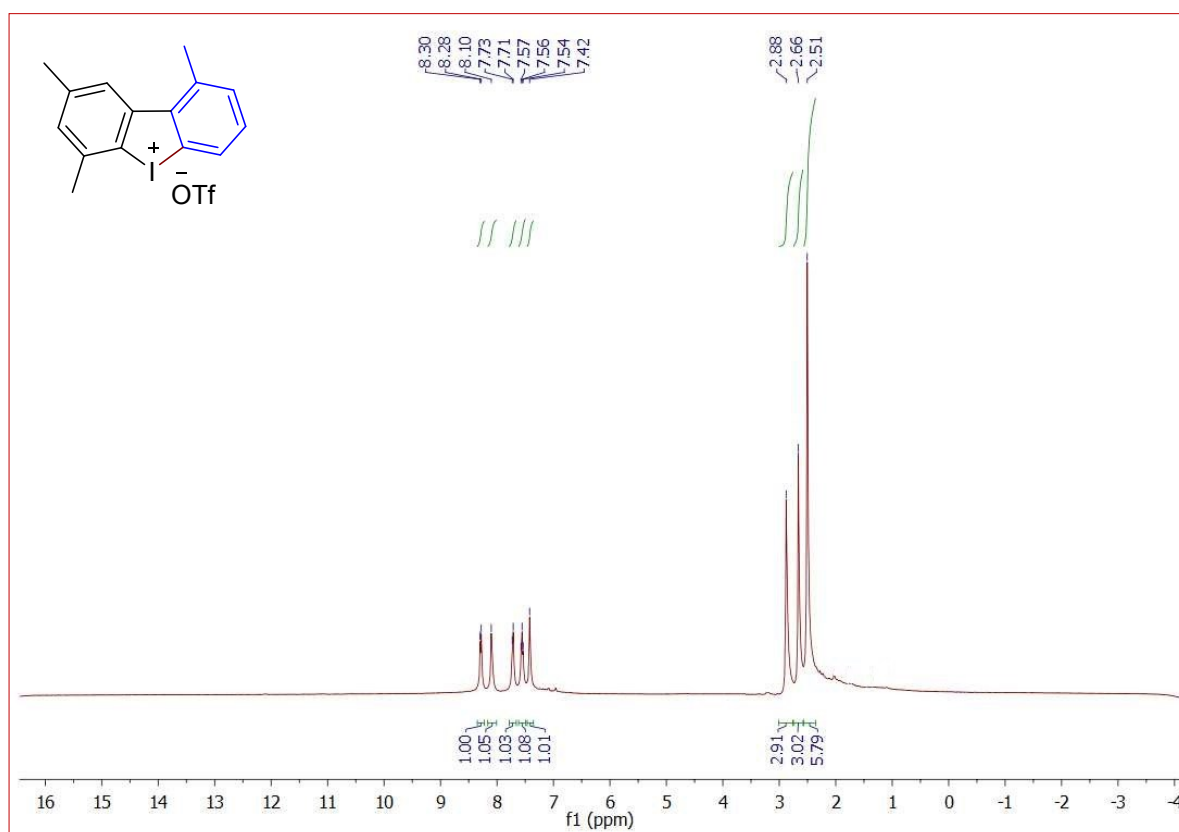
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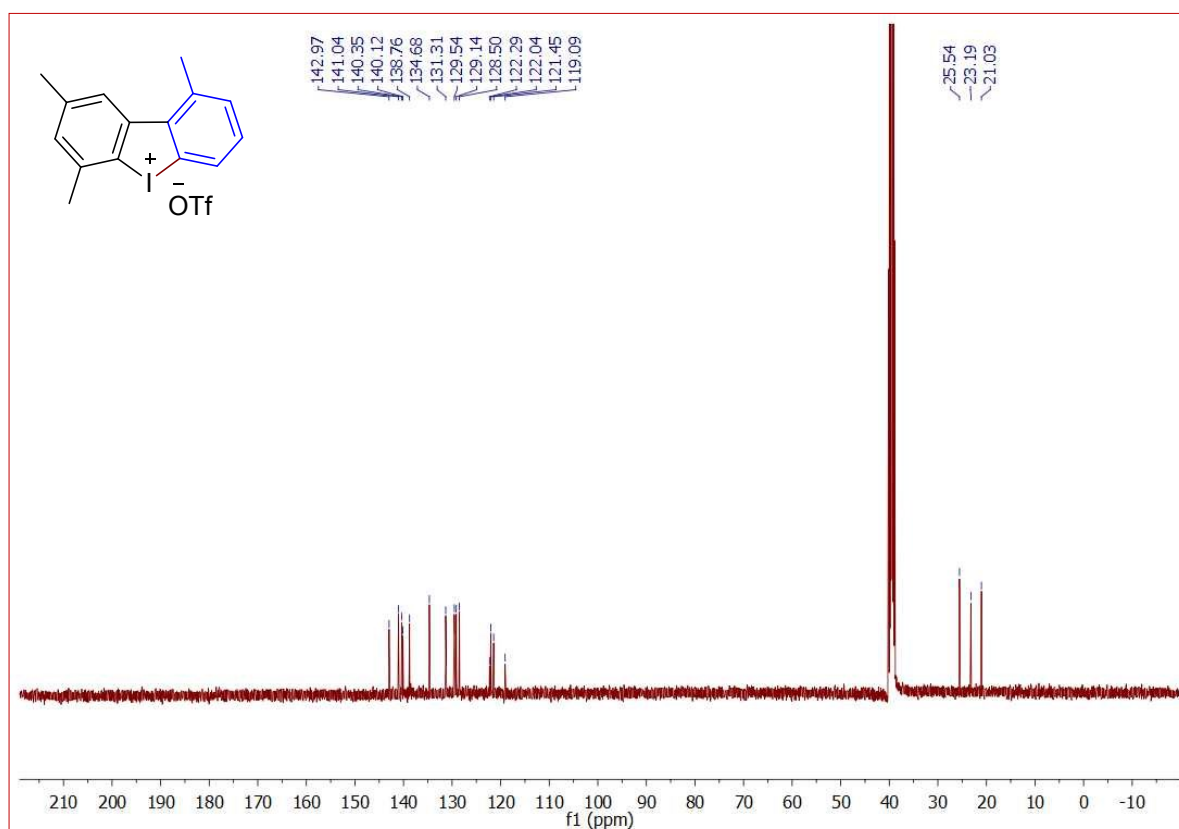
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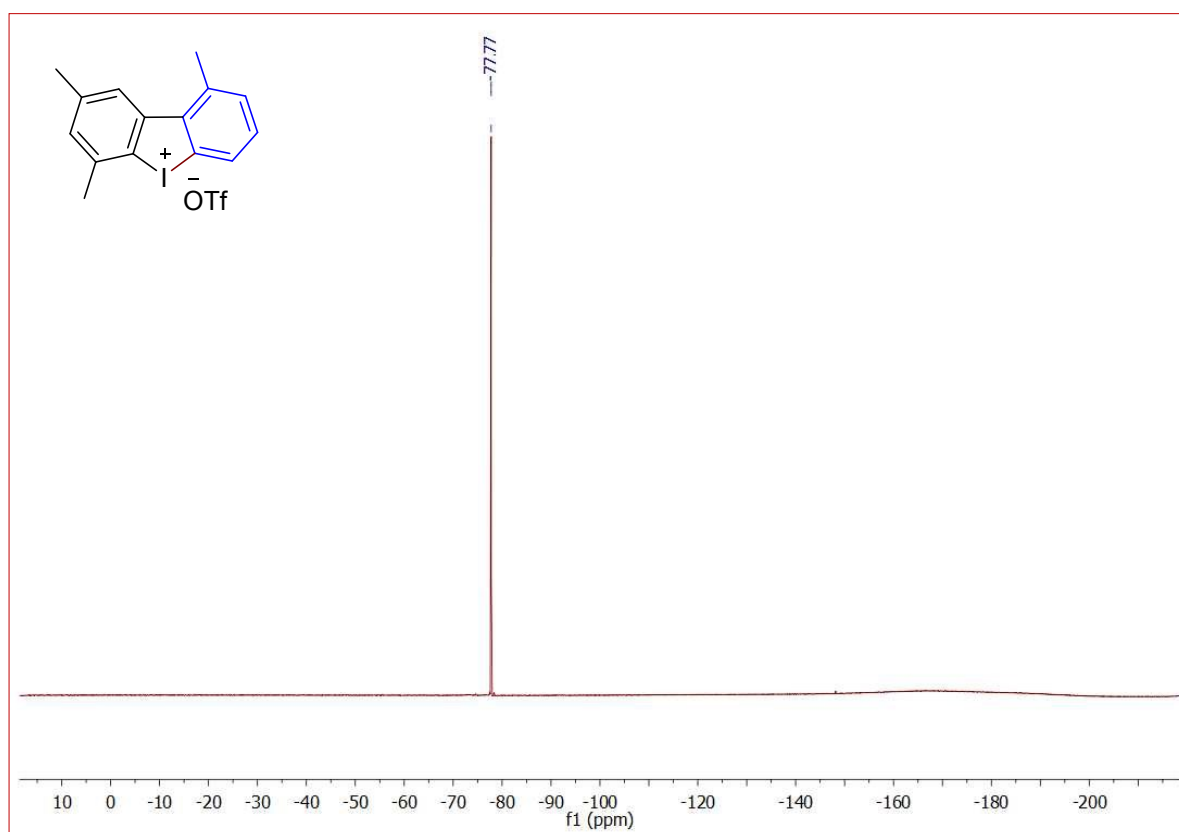
1,6,8-Trimethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2o**), ^1H NMR



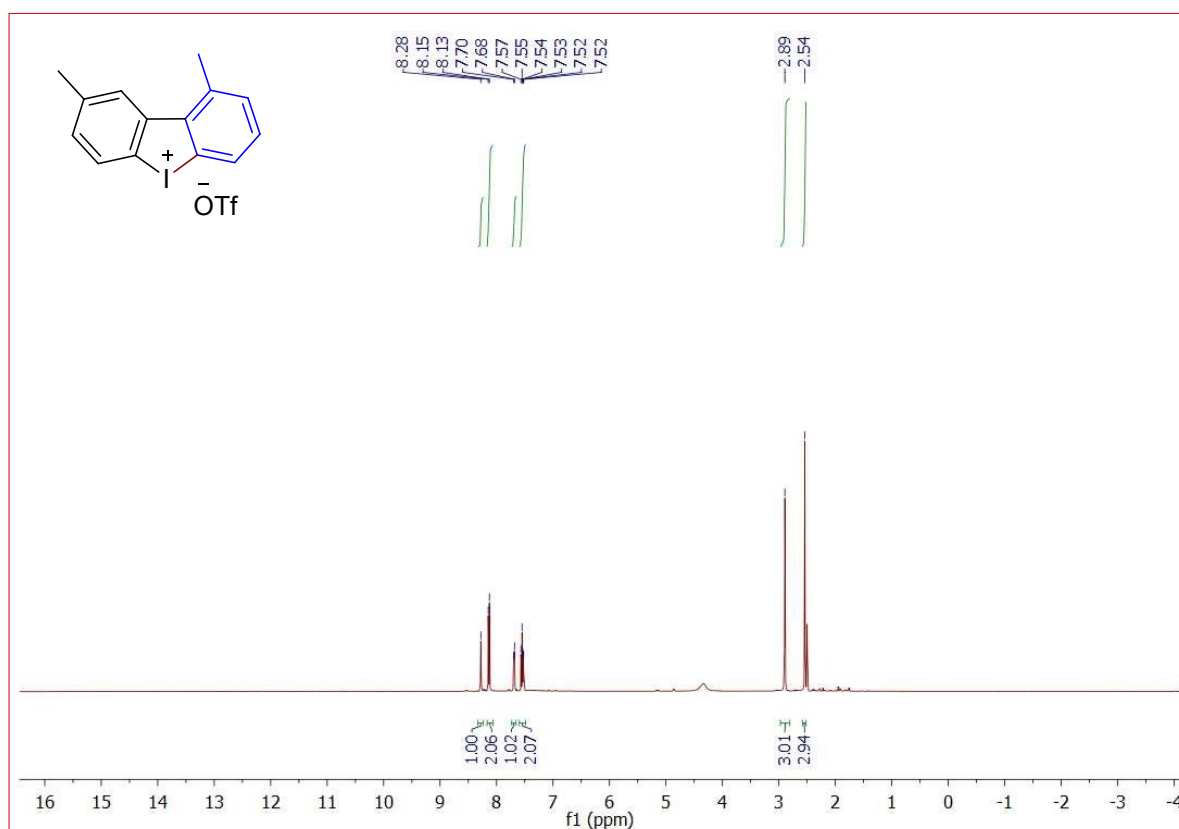
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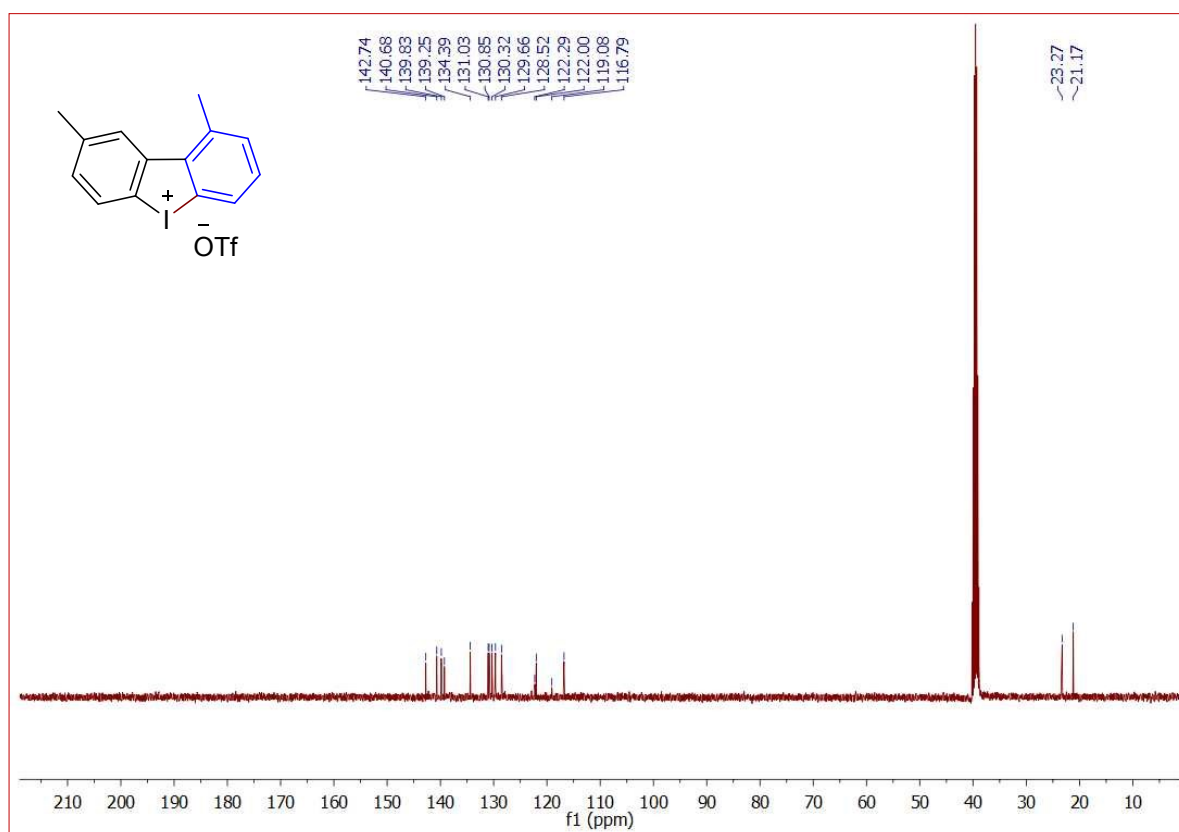
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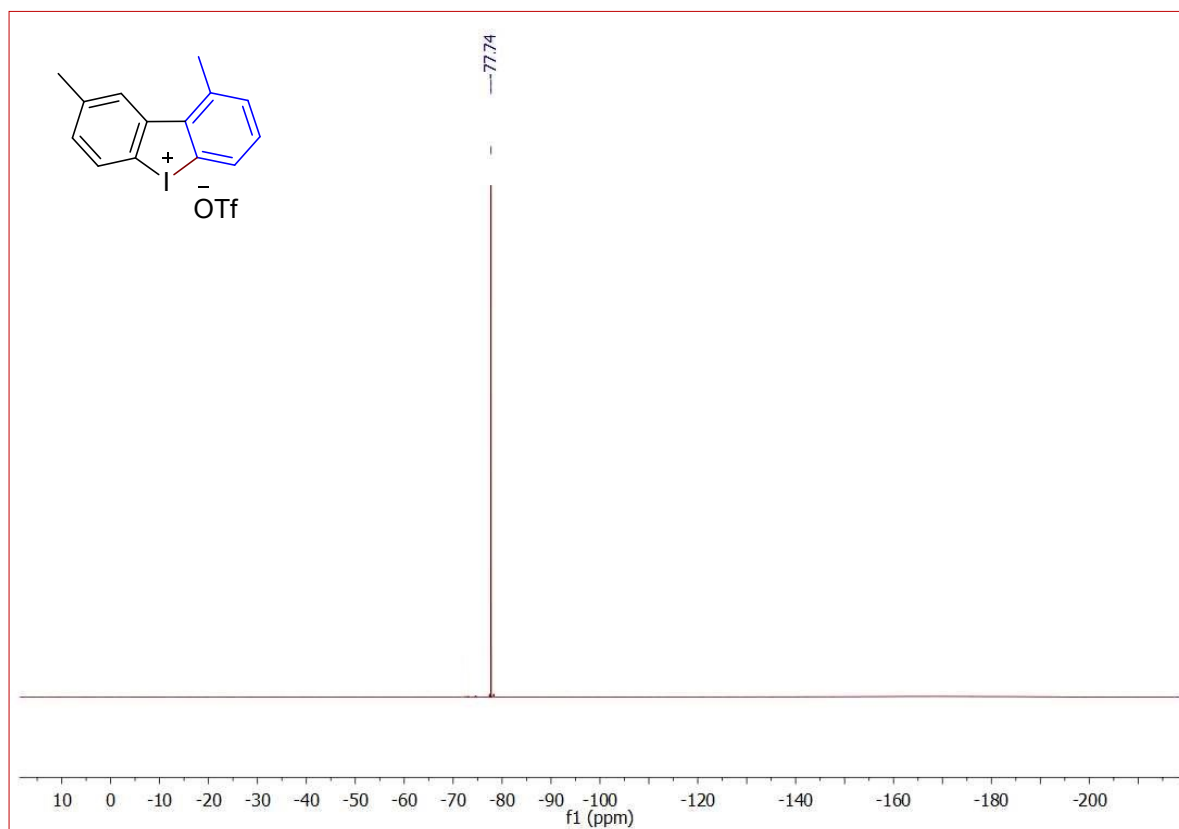
1,8-dimethyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2p**), ^1H NMR



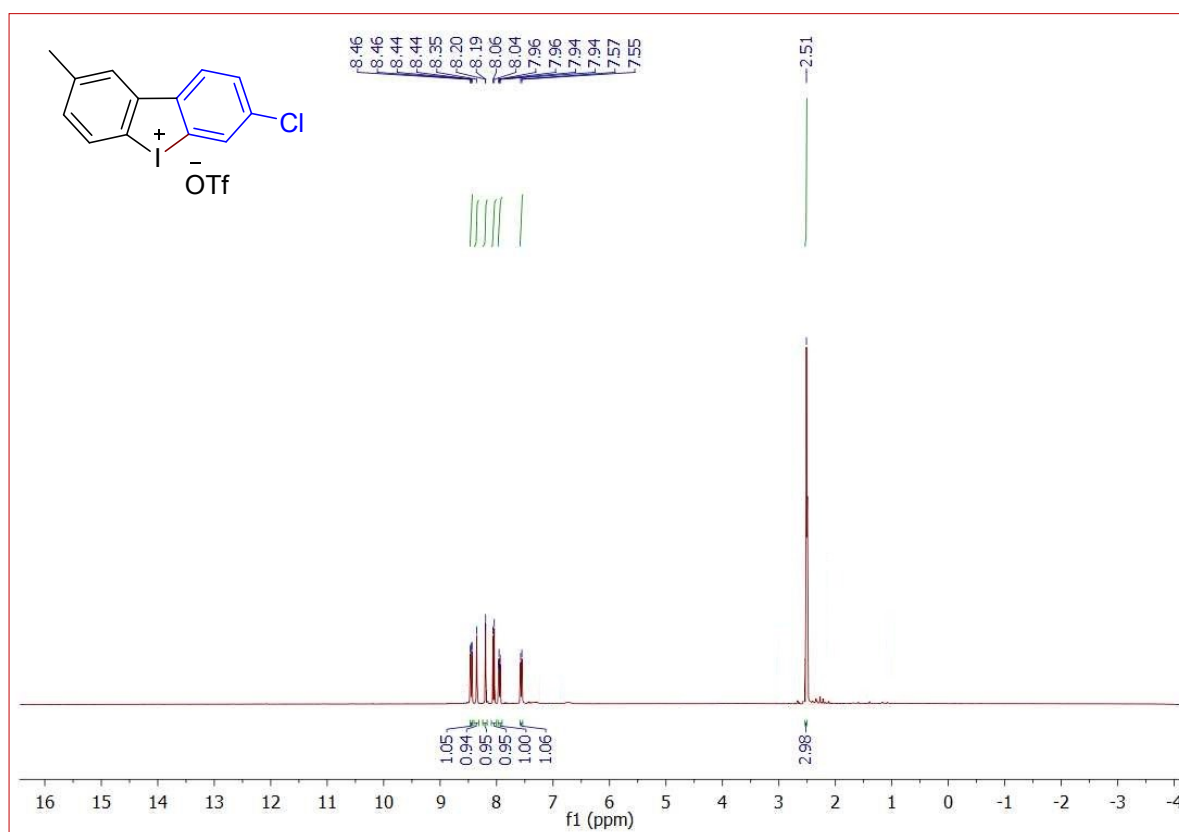
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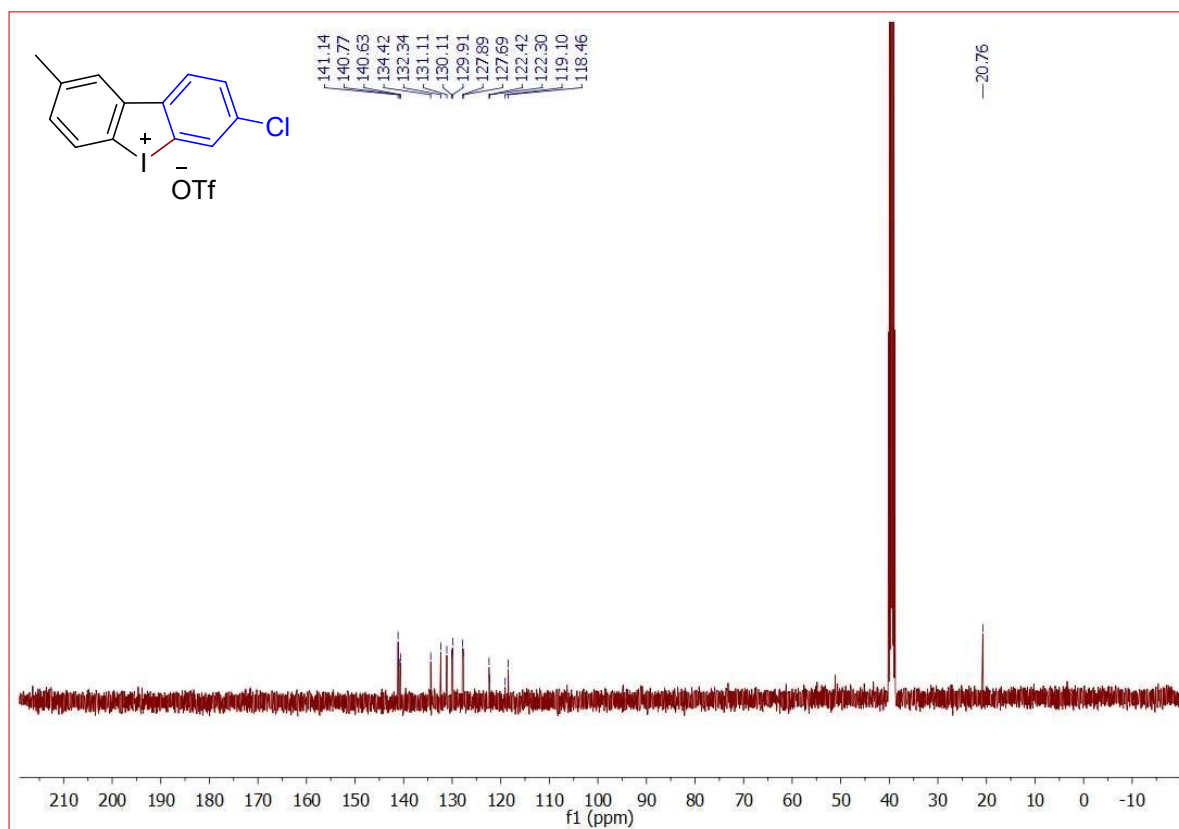
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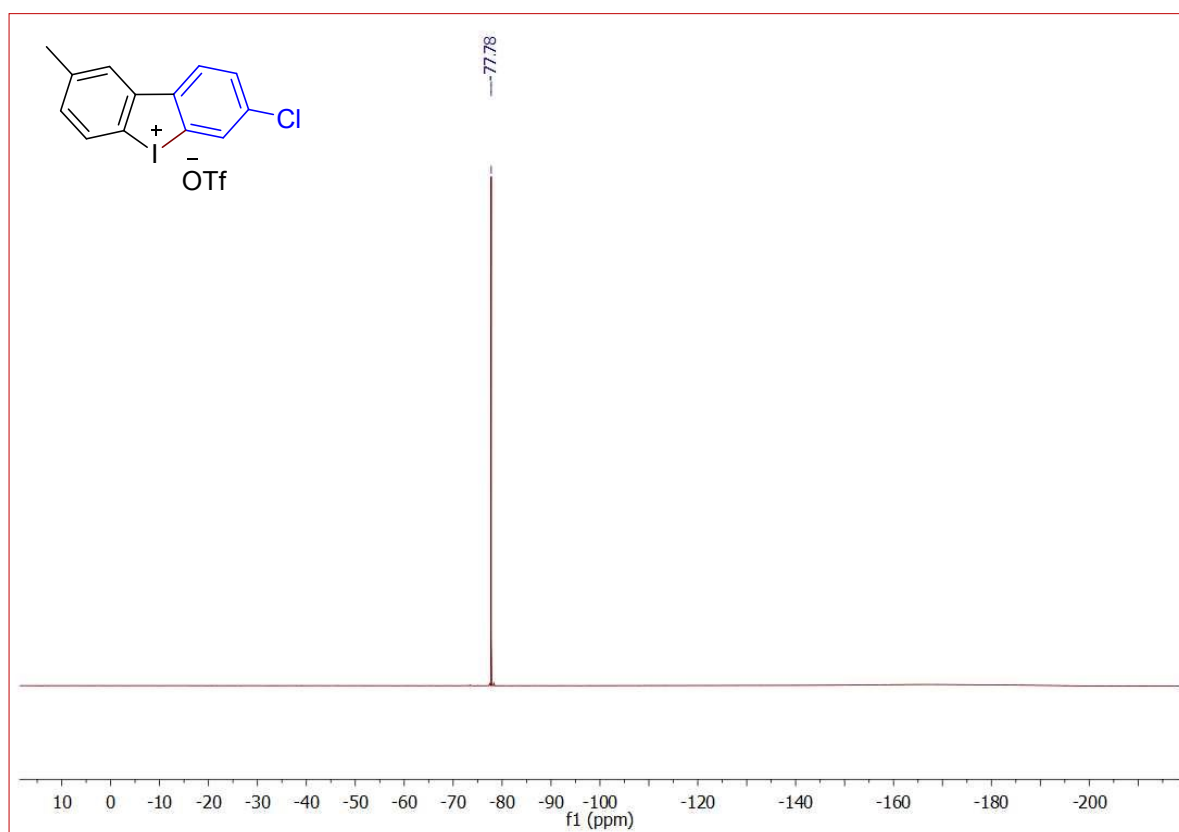
7-Chloro-2-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2r**), ^1H NMR



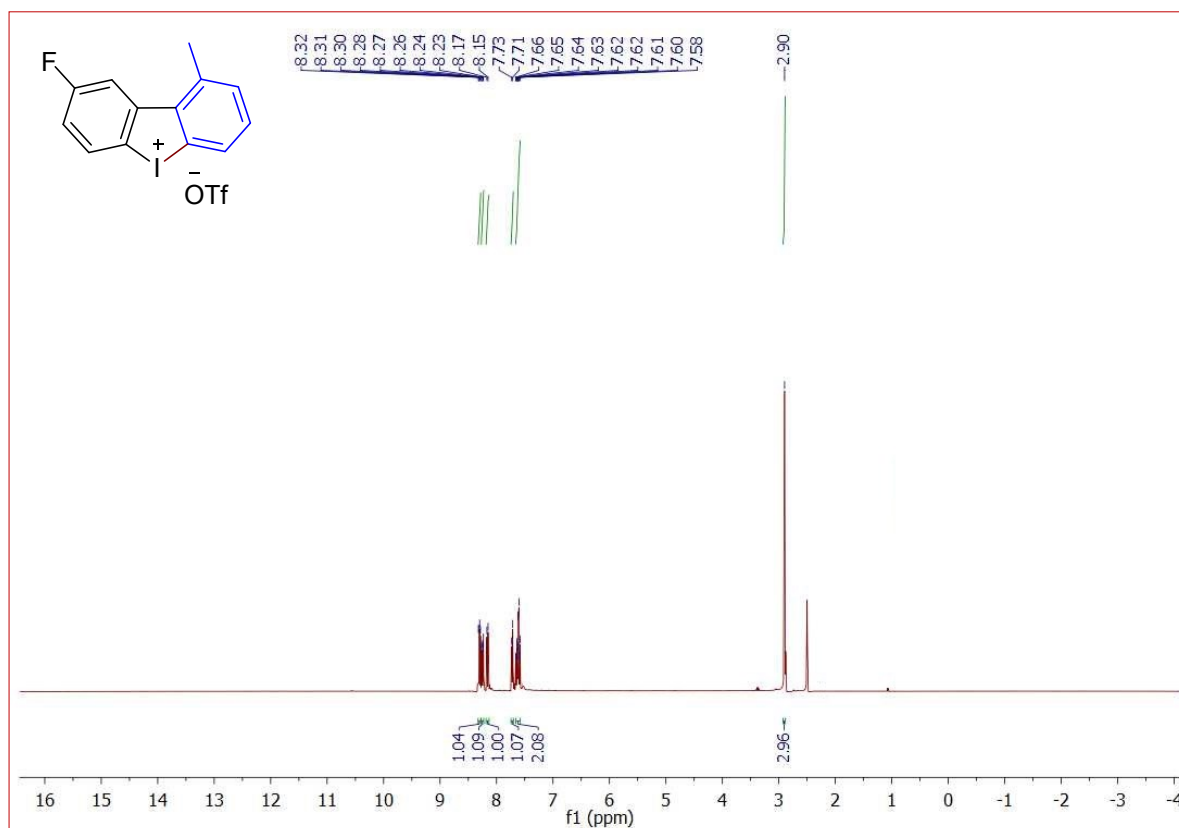
7-Chloro-2-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2r**), ^{13}C NMR



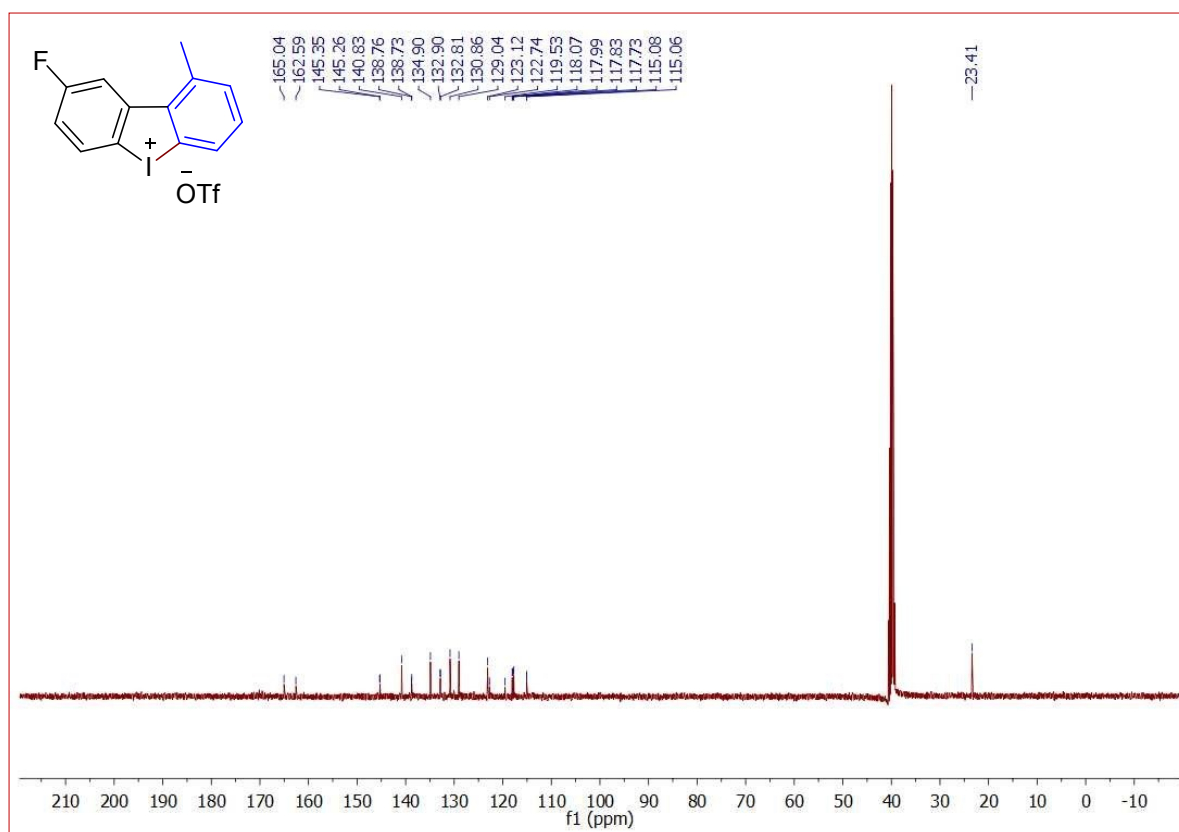
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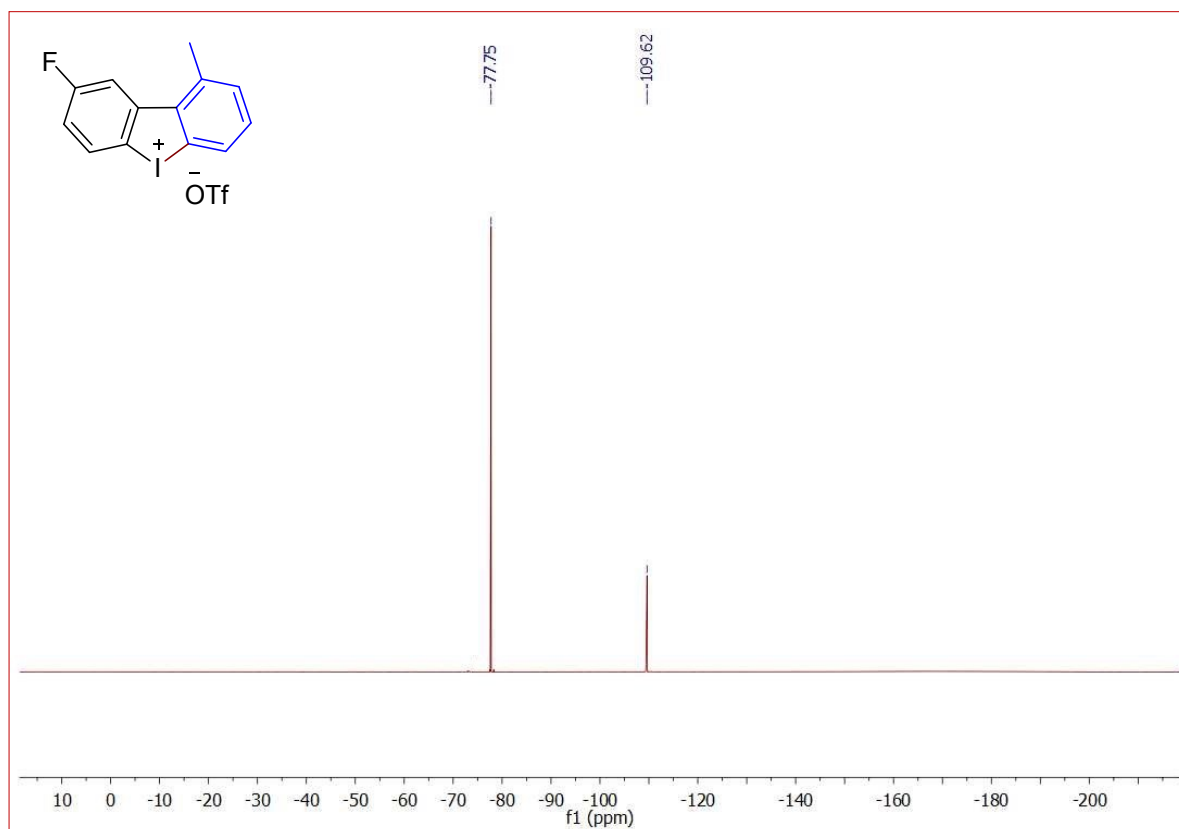
8-Fluoro-1-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2s**), ^1H NMR



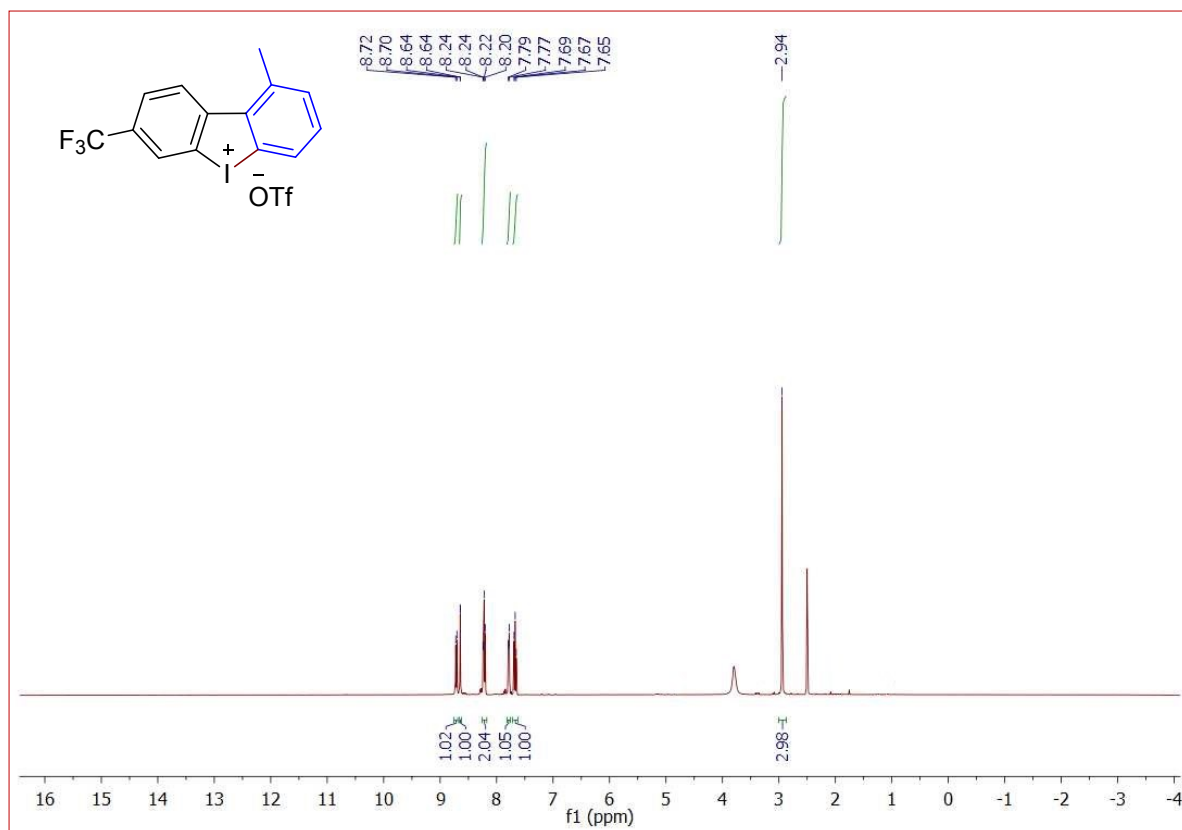
8-Fluoro-1-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2s**), ^{13}C NMR



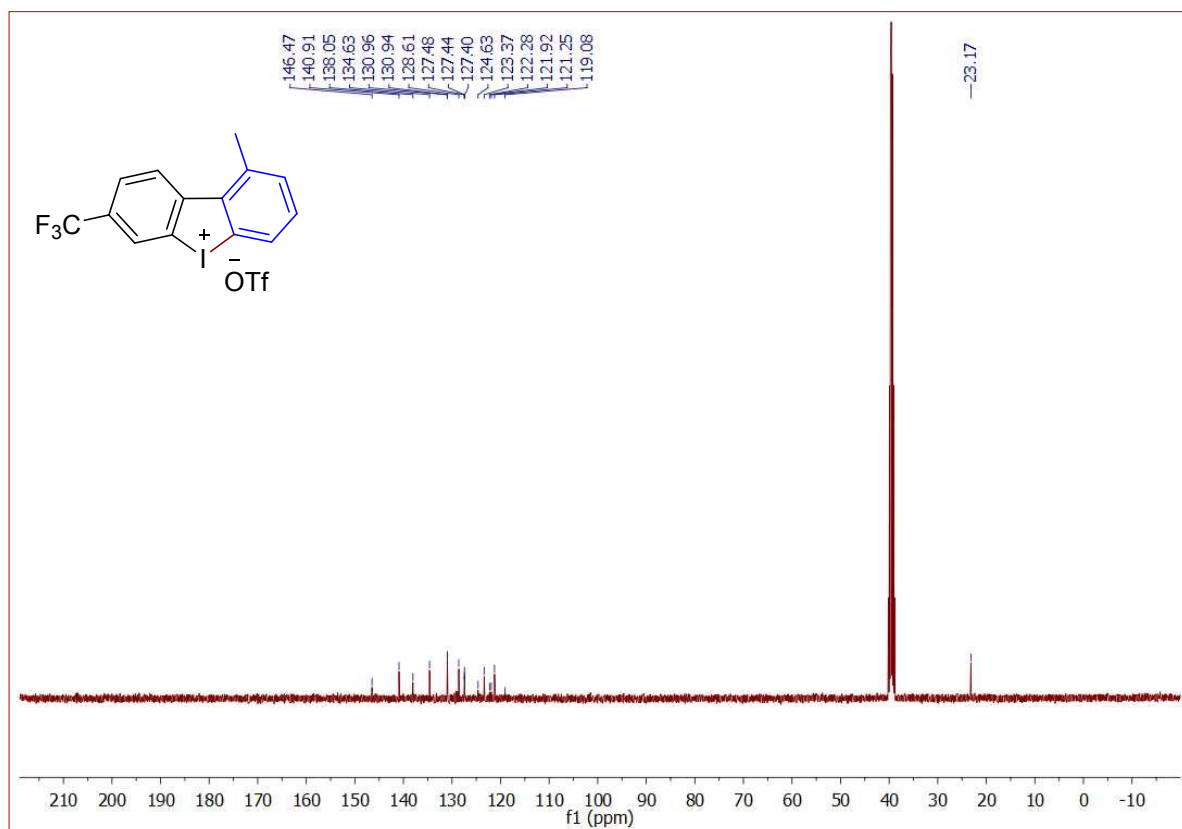
8-Fluoro-1-methyldibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2s**), ^{19}F NMR



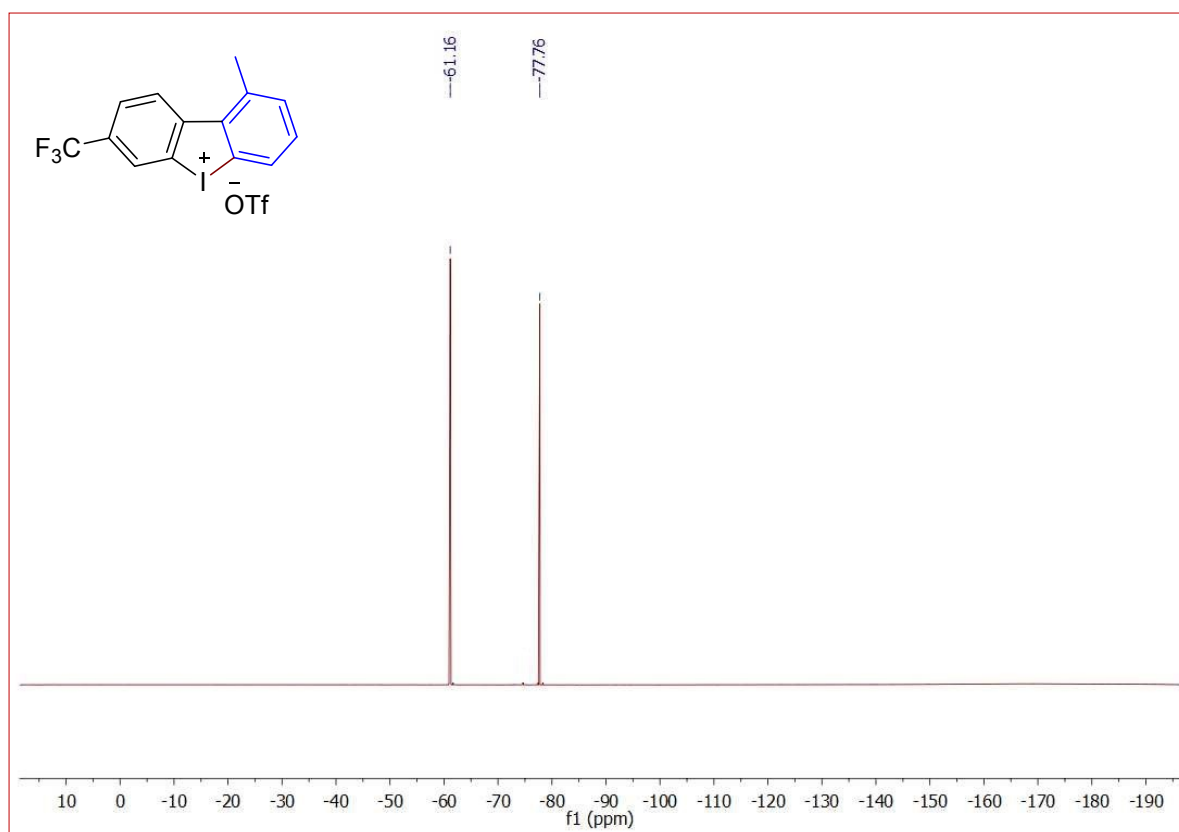
1-Methyl-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2t**), ^1H NMR



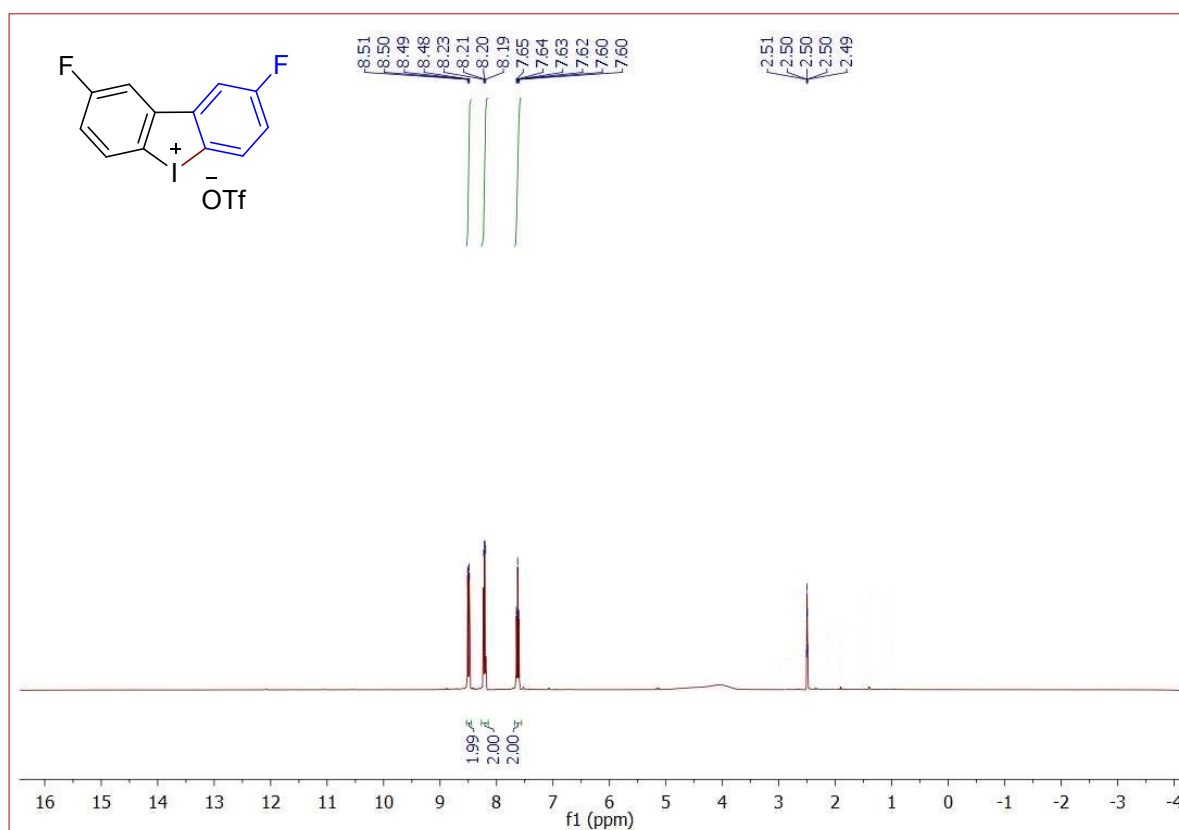
1-Methyl-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2t**), ^{13}C NMR



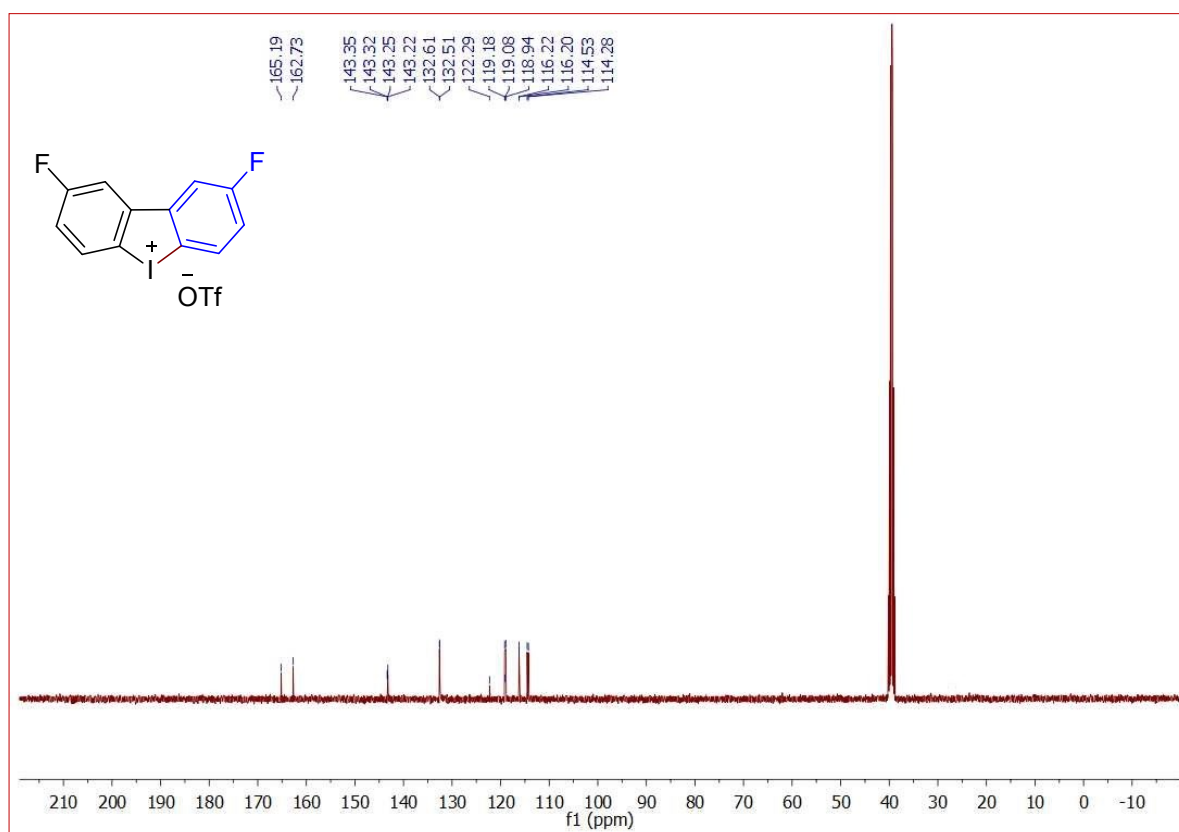
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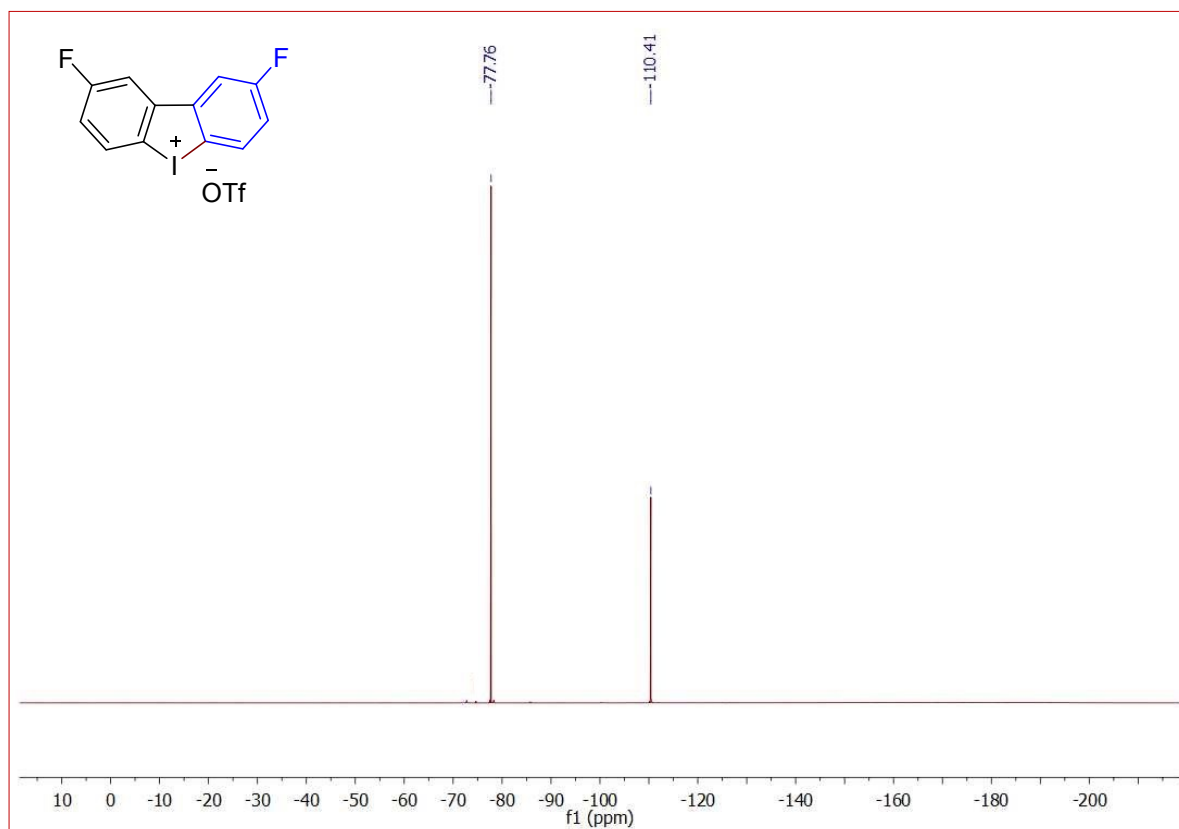
2,8-Difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2u**), ^1H NMR



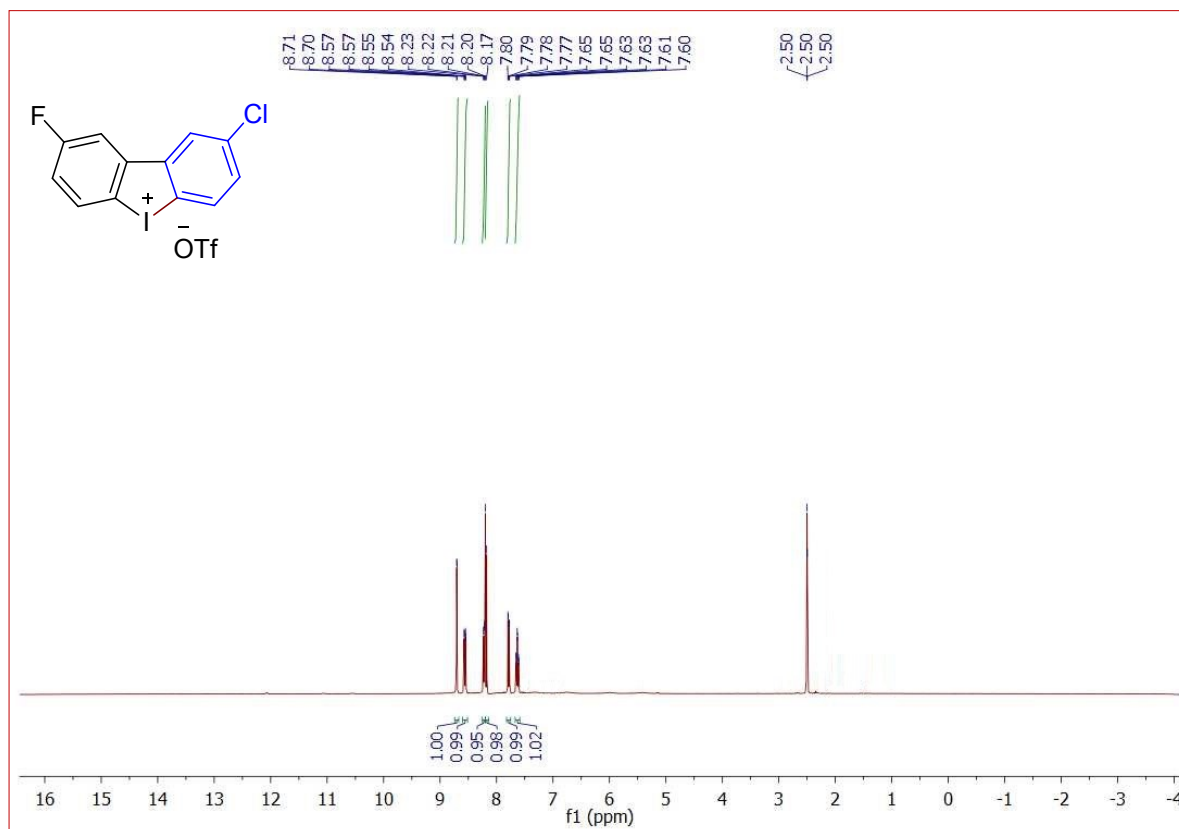
2,8-Difluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2u**), ^{13}C NMR



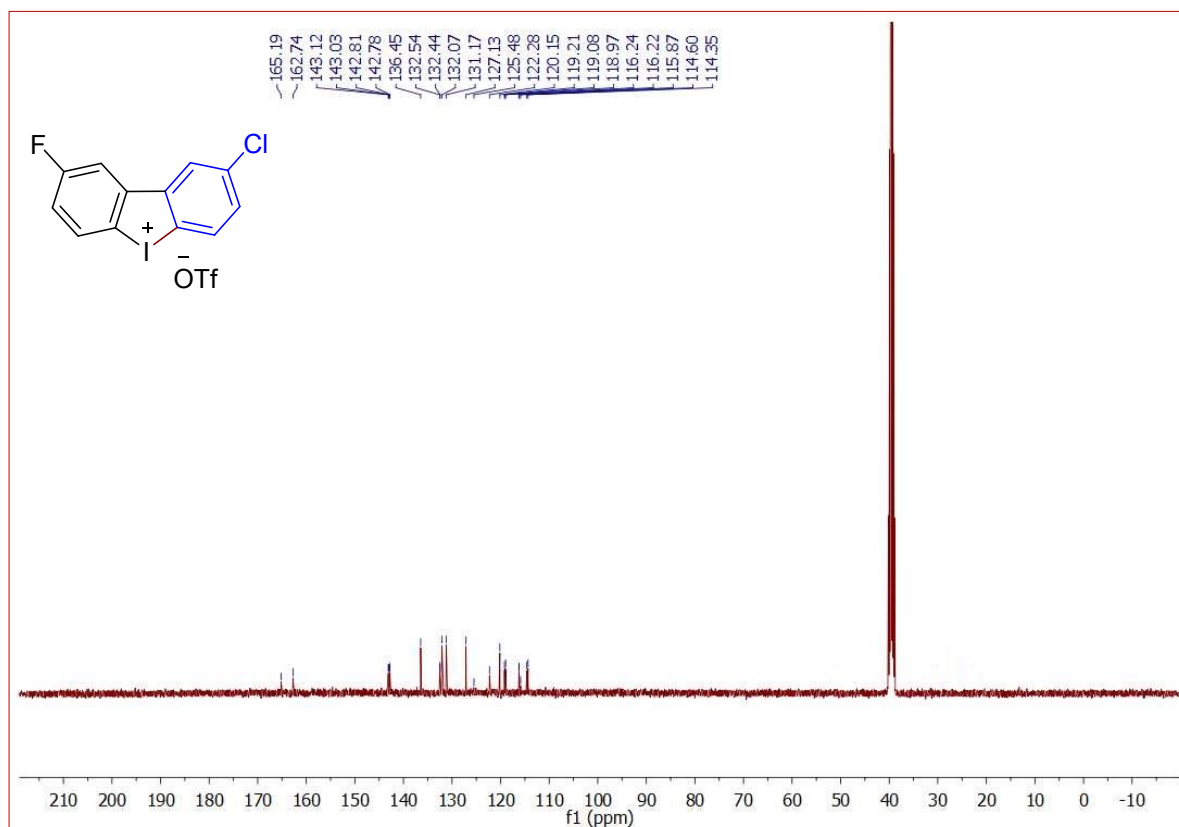
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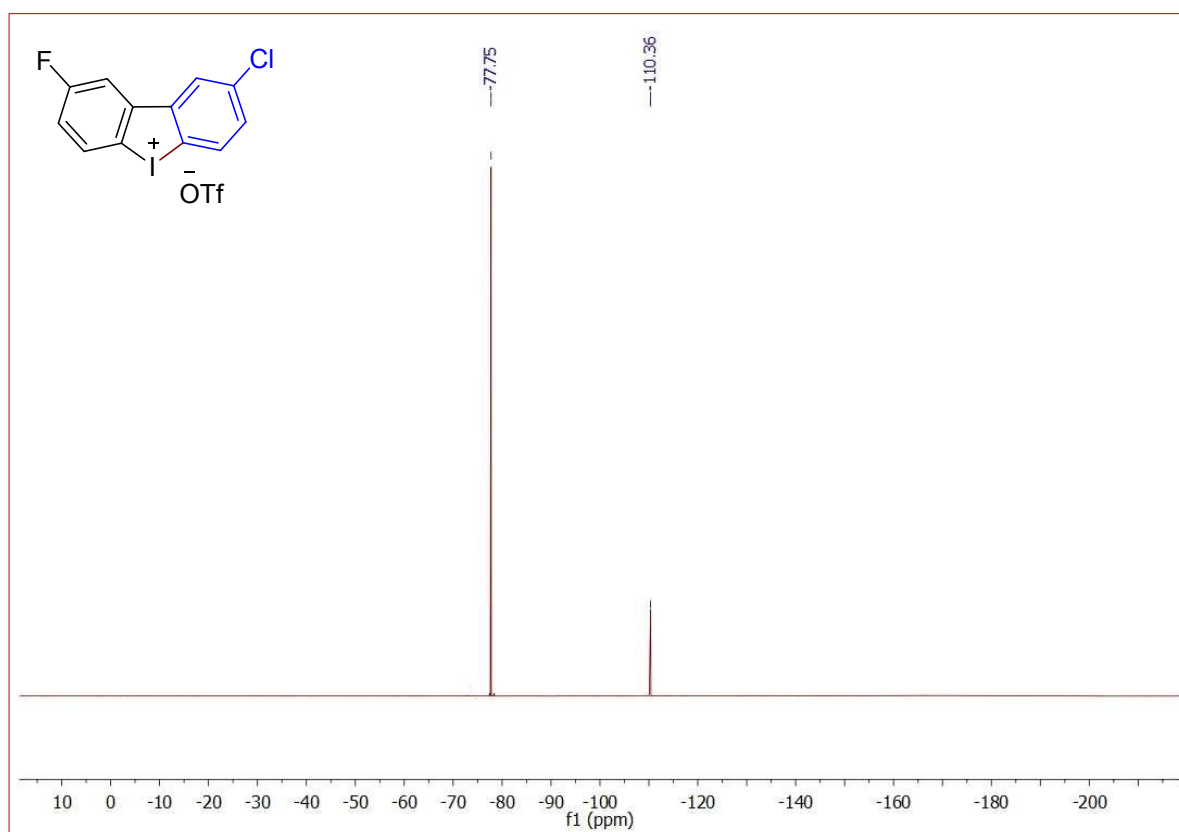
2-Chloro-8-fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2v**), ^1H NMR



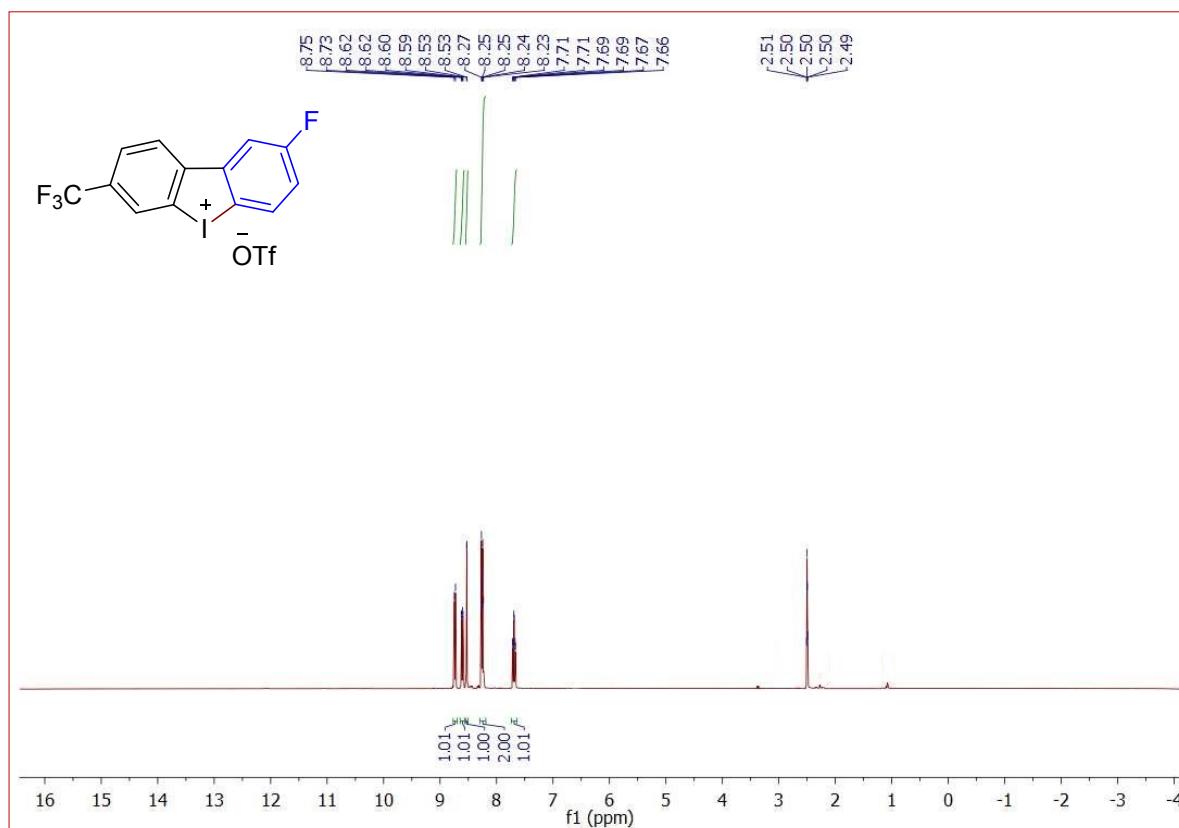
2-Chloro-8-fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2v**), ^{13}C NMR



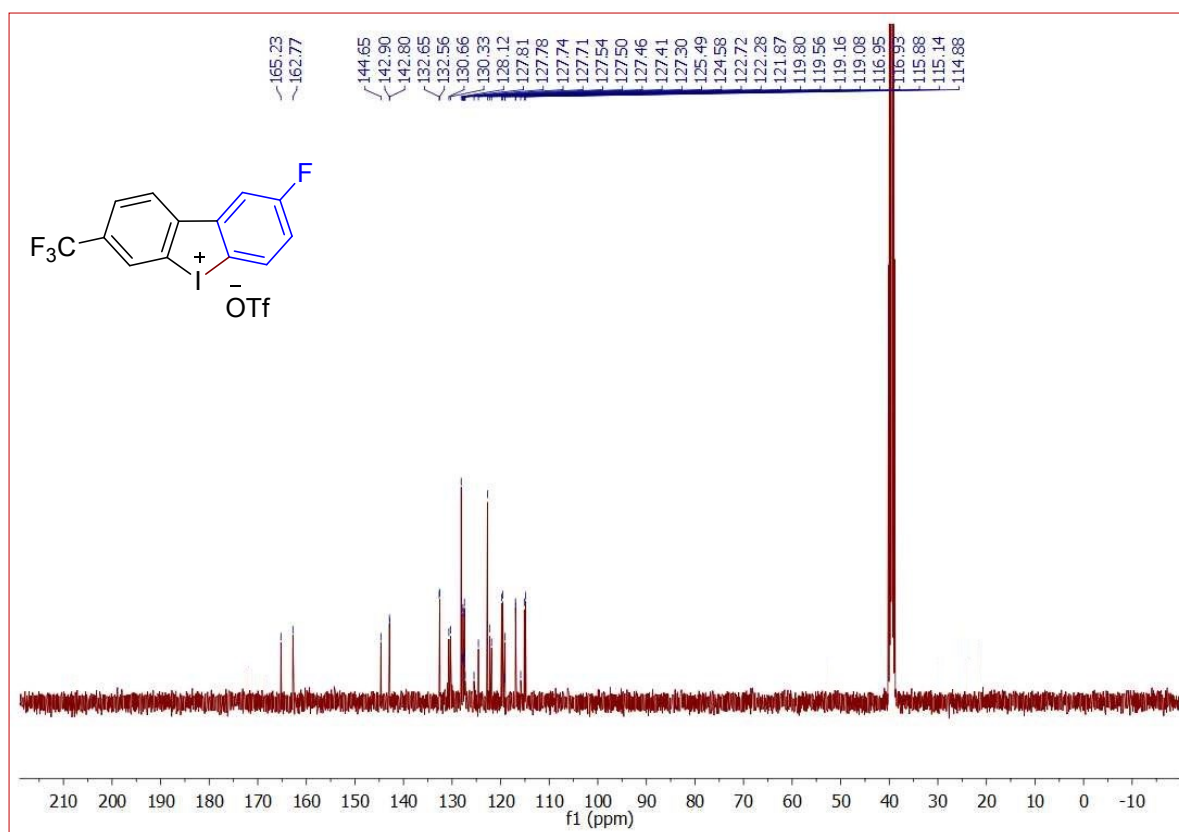
2-Chloro-8-fluorodibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2v**), ^{19}F NMR



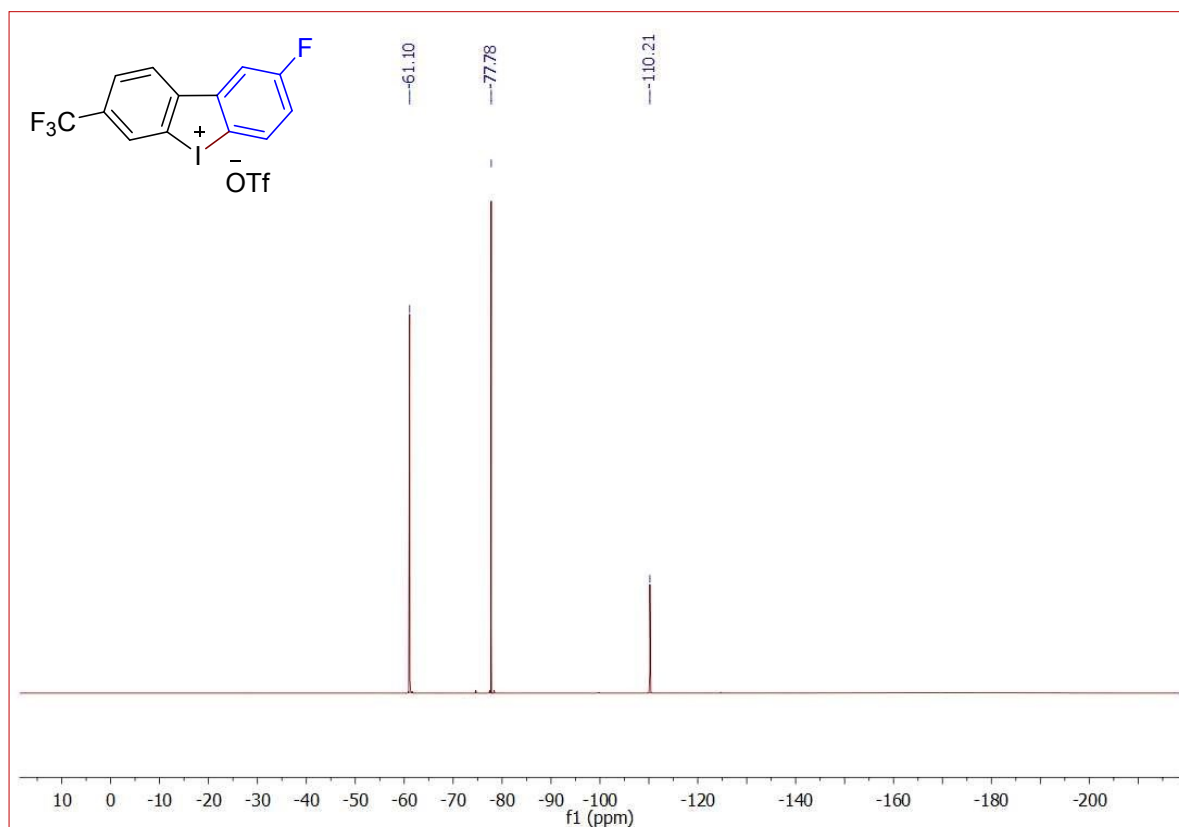
2-Fluoro-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2w**), ^1H NMR



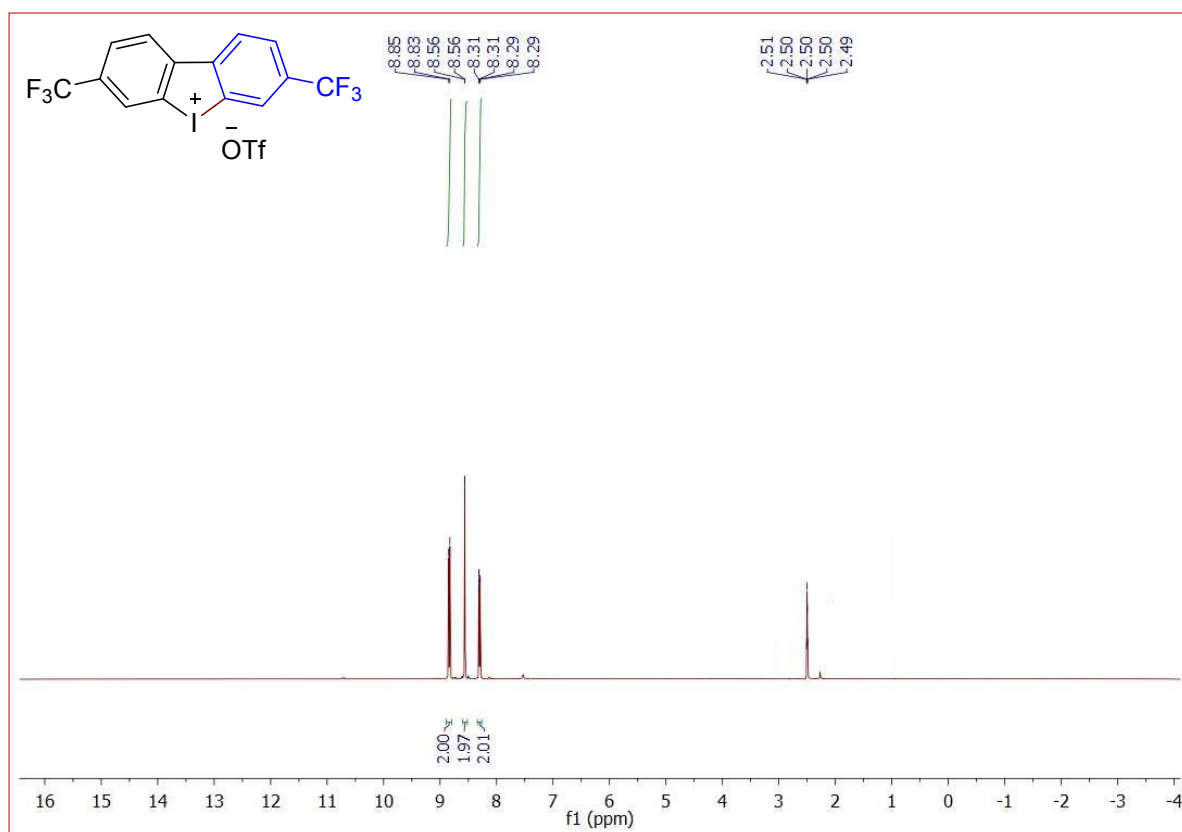
2-Fluoro-7-(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2w**), ^{13}C NMR



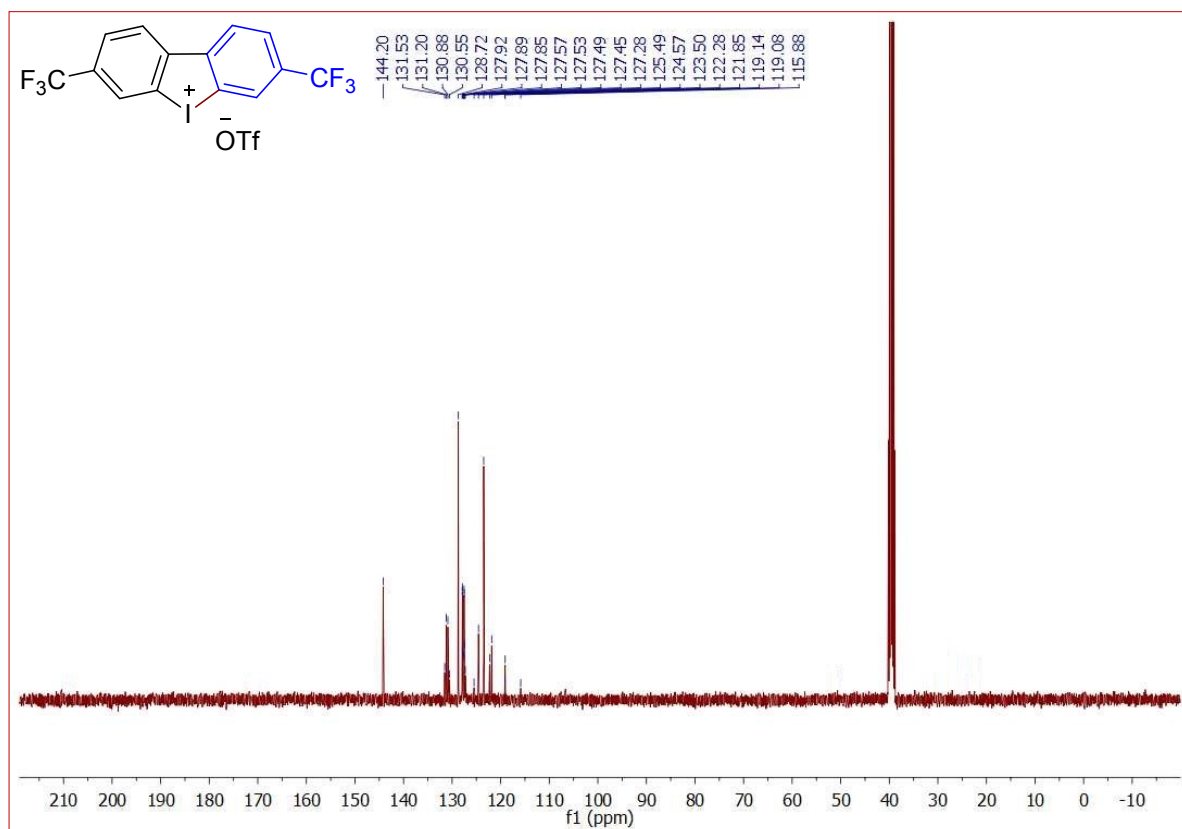
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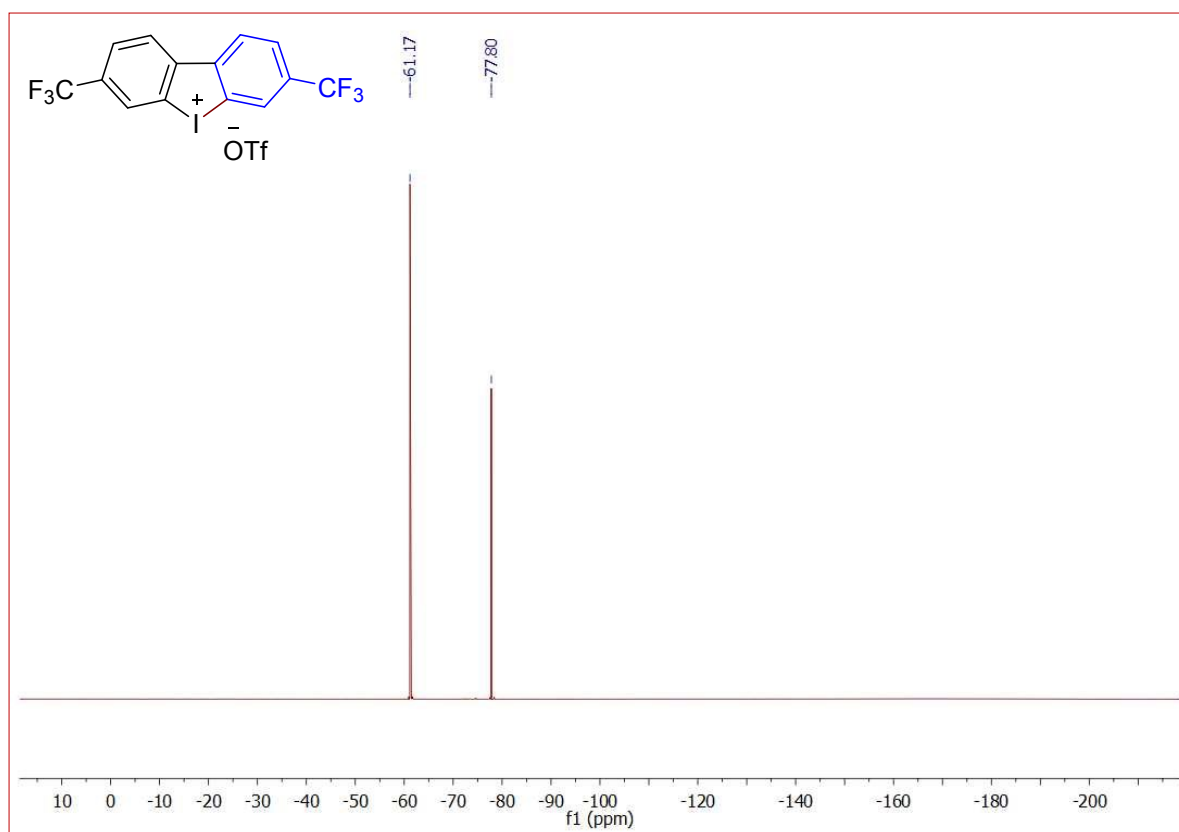
3,7-Bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2x**), ^1H NMR



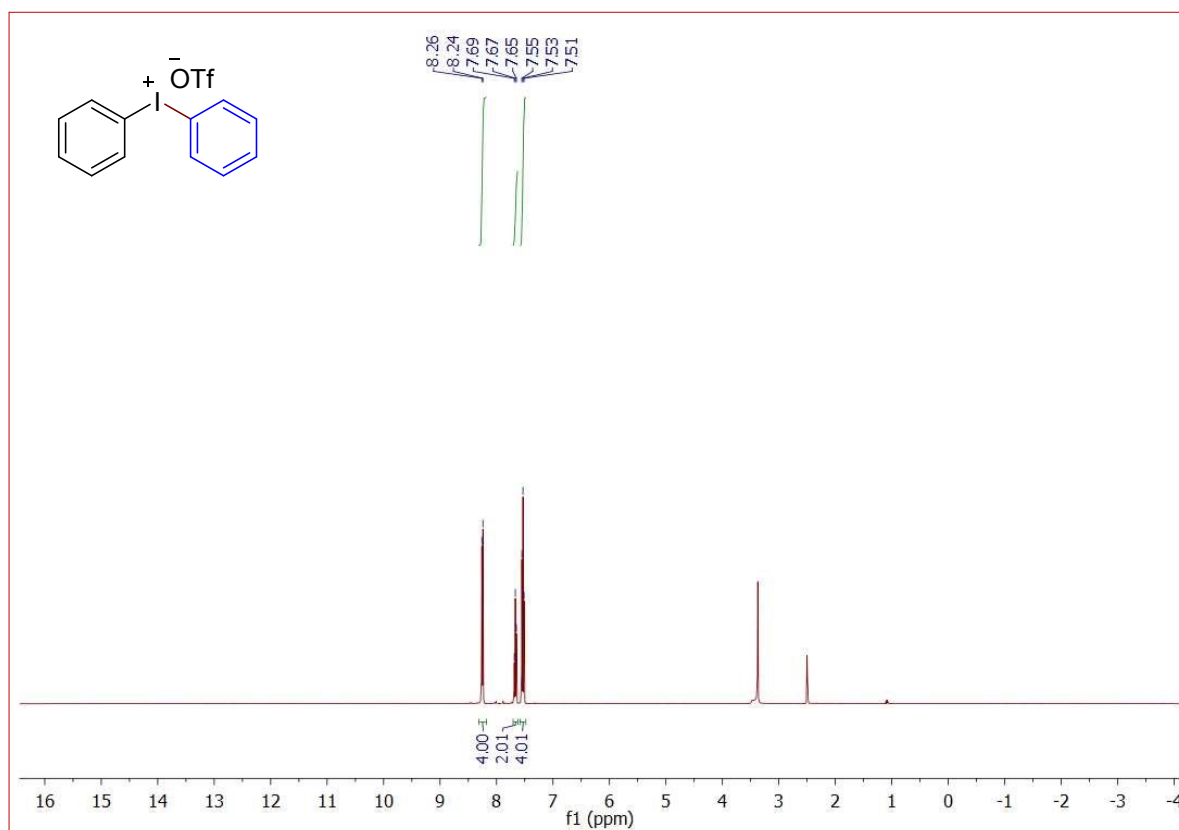
3,7-Bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2x**), ^{13}C NMR



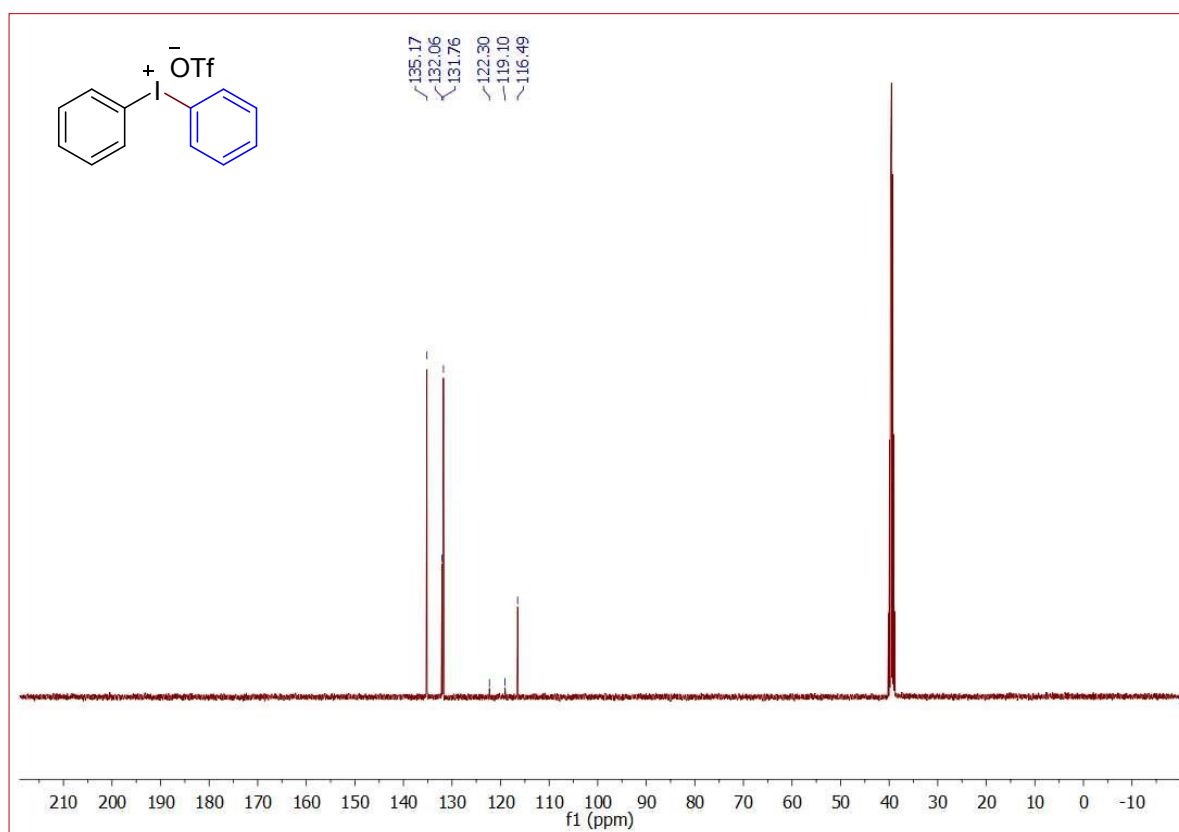
3,7-Bis(trifluoromethyl)dibenzo[b,d]iodol-5-ium trifluoromethanesulfonate (**2x**), ^{19}F NMR



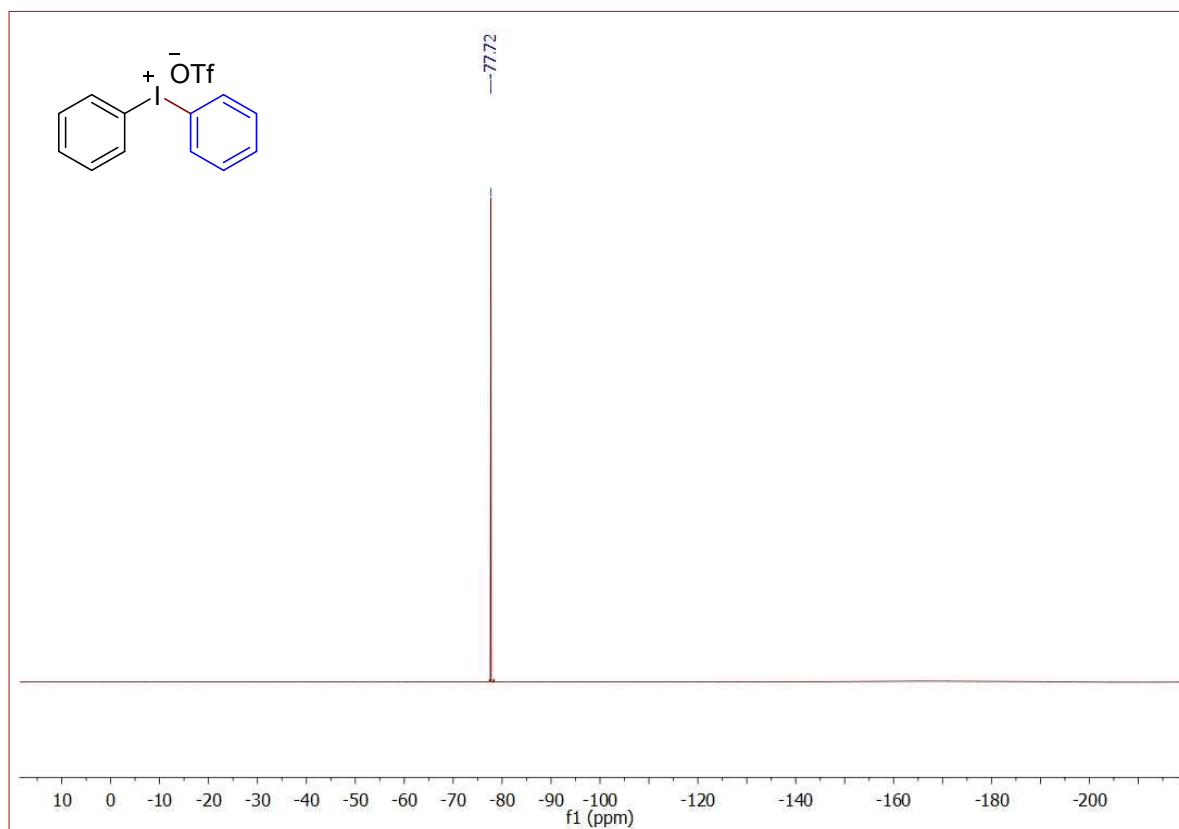
Diphenyliodonium trifluoromethanesulfonate (**5a**), ^1H NMR



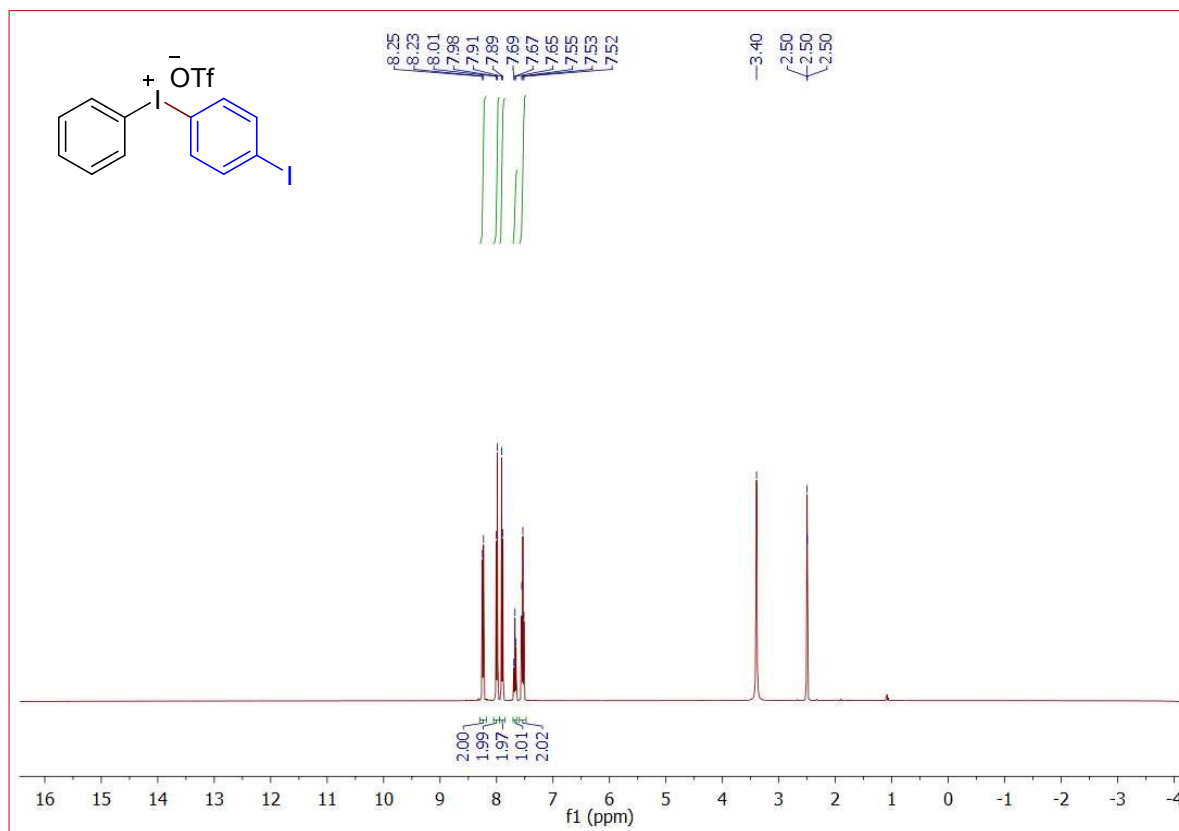
Diphenyliodonium trifluoromethanesulfonate (**5a**), ^{13}C NMR



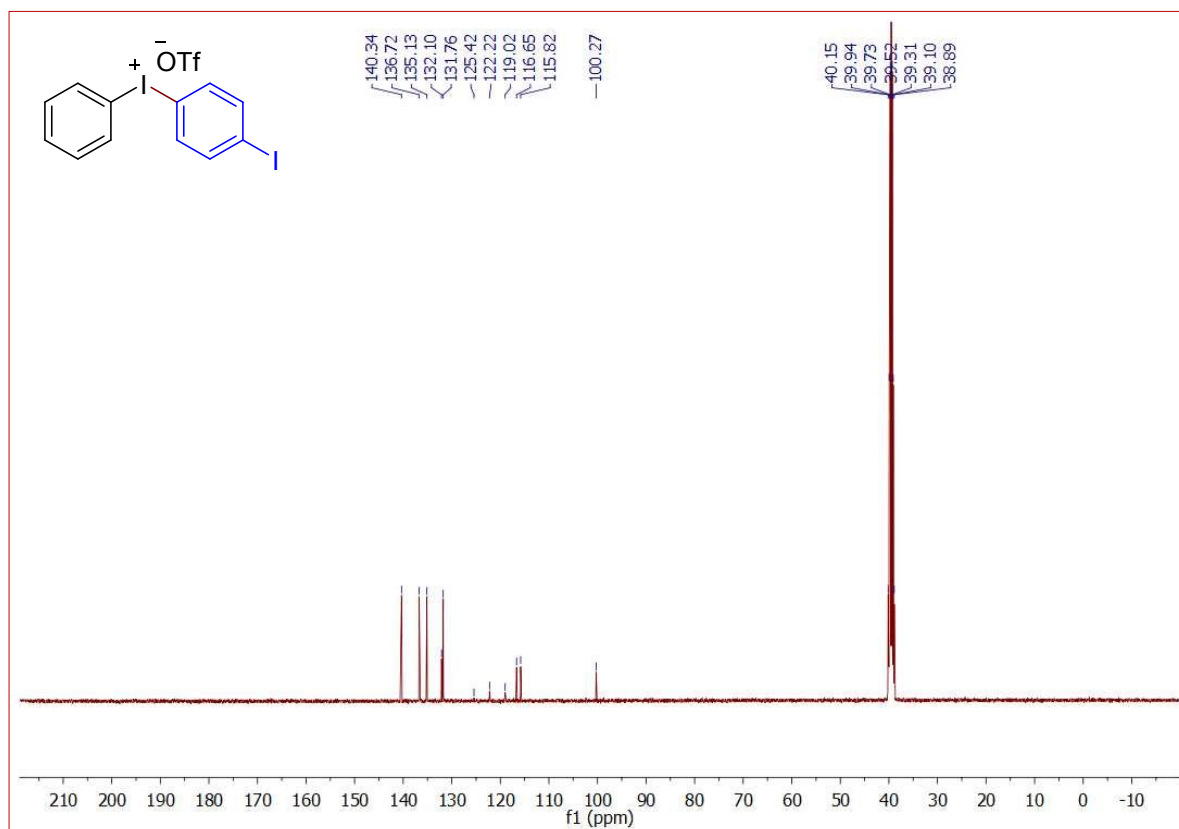
Diphenyliodonium trifluoromethanesulfonate (**5a**), ^{19}F NMR



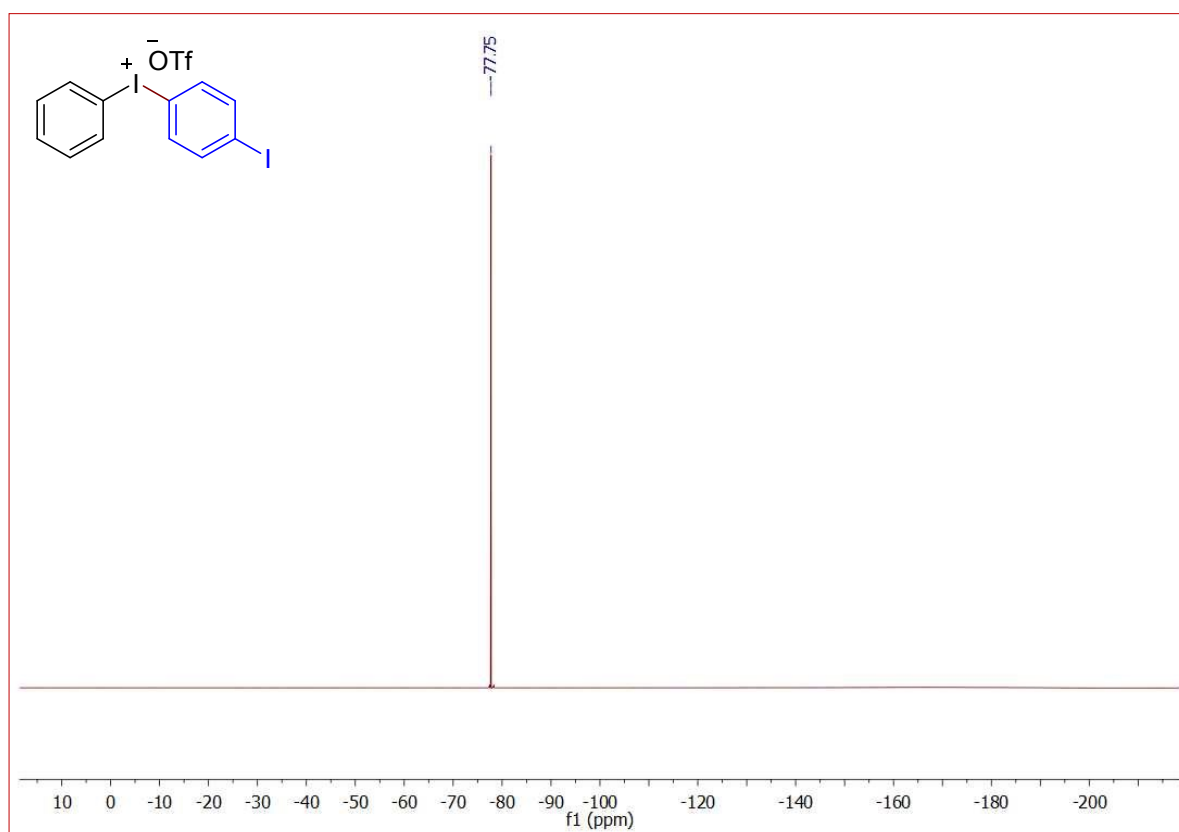
(4-Iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5b**), ^1H NMR



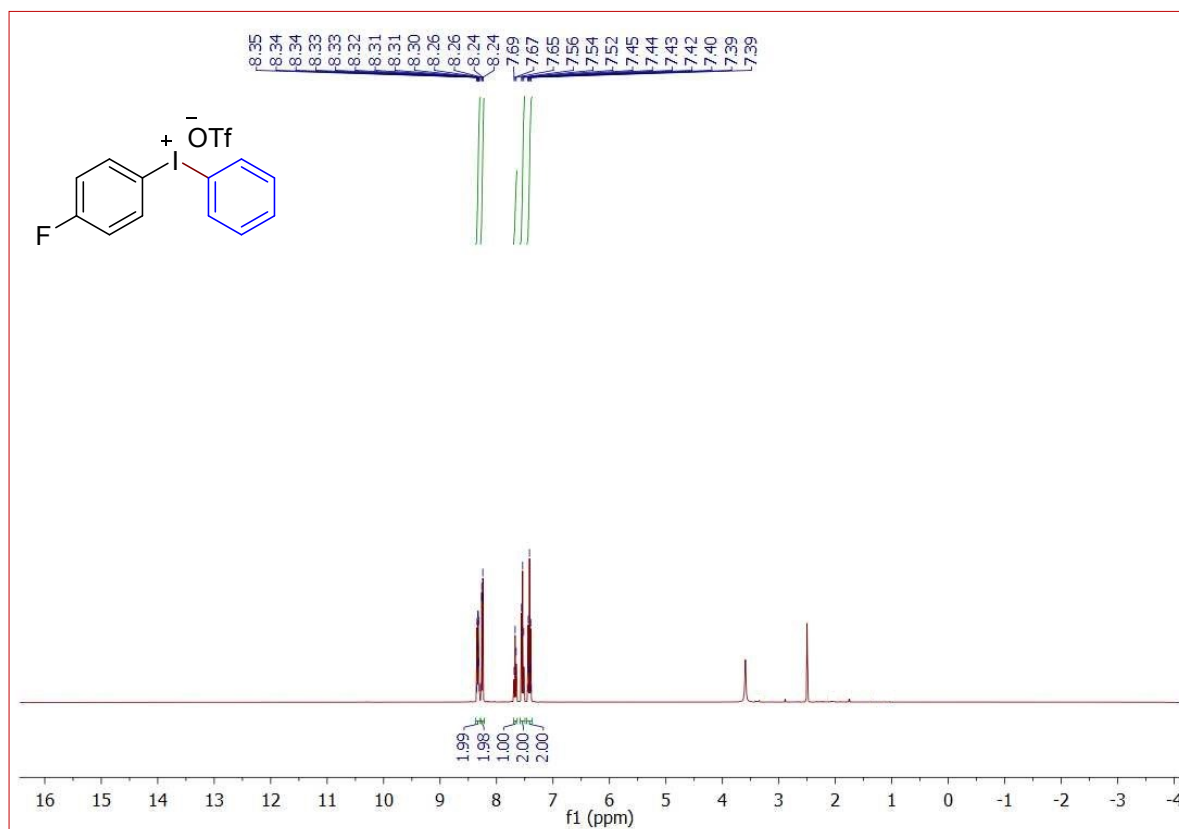
(4-Iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5b**), ^{13}C NMR



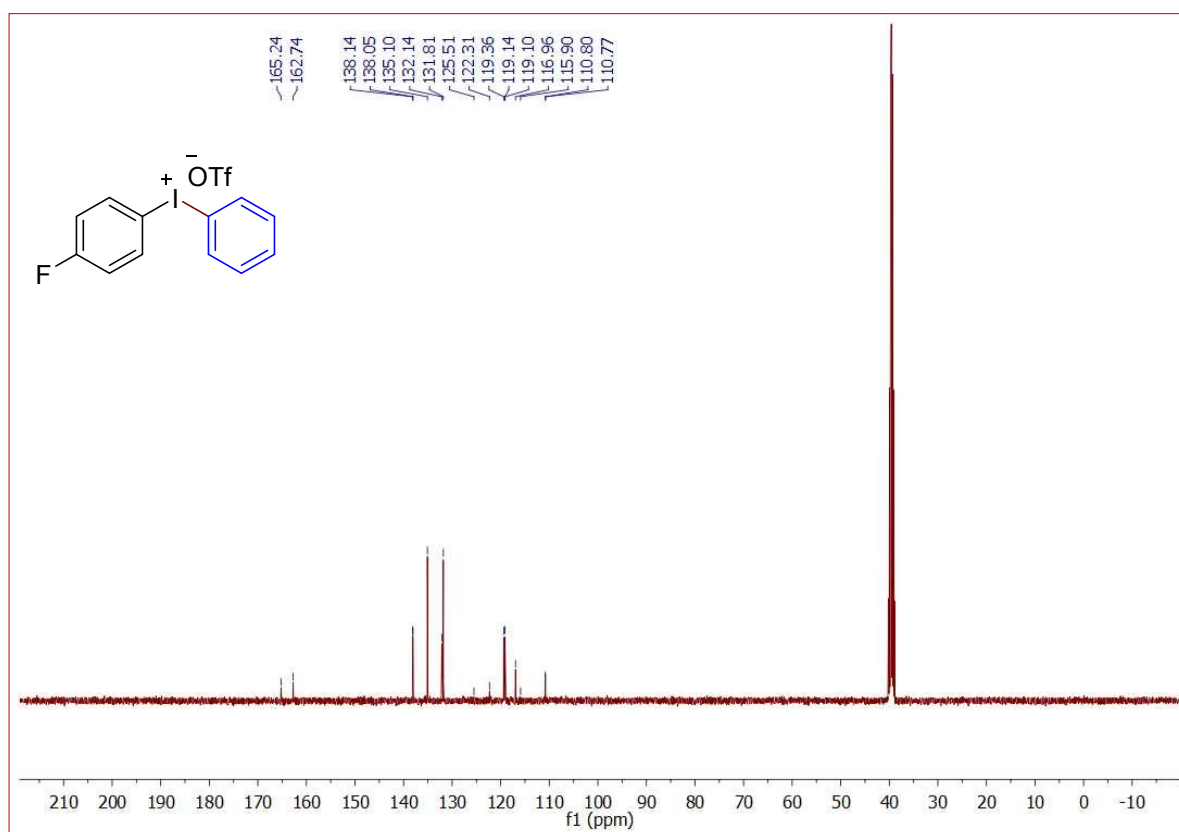
(4-Iodophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5b**), ^{19}F NMR



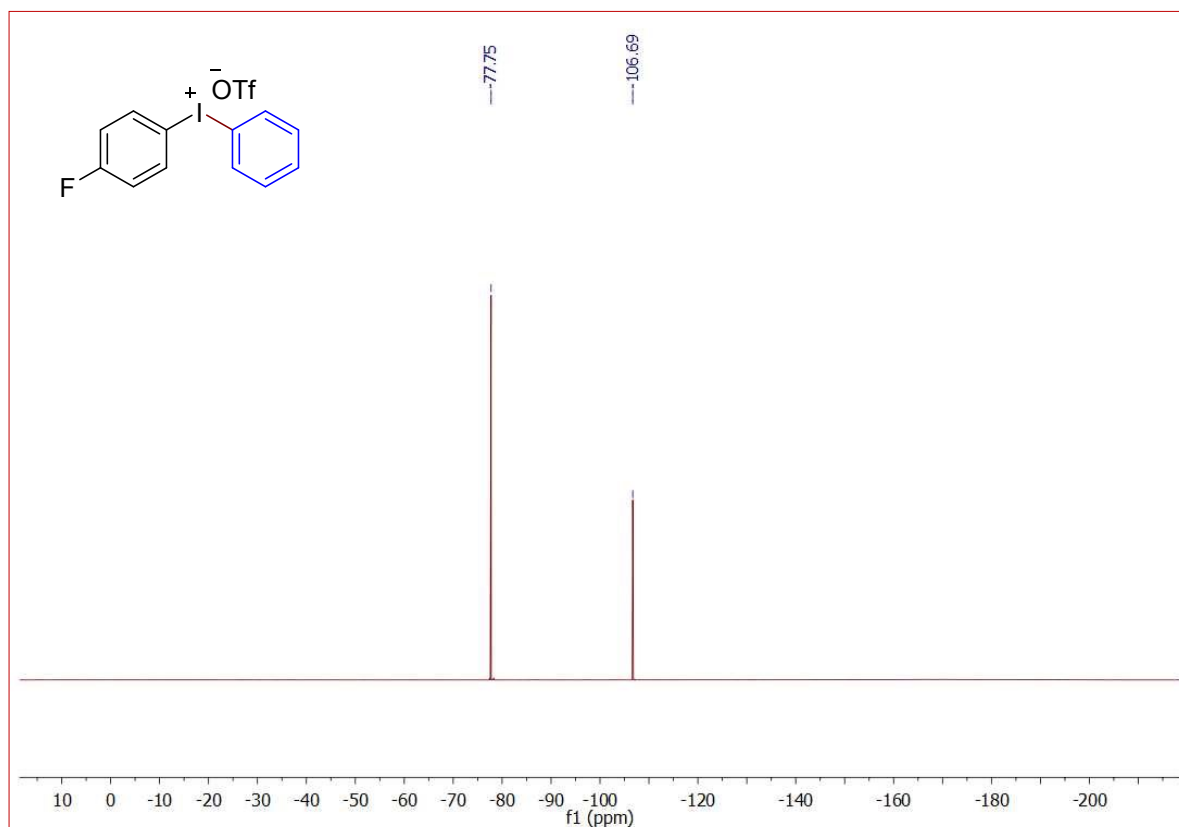
(4-Fluorophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5c**), ^1H NMR



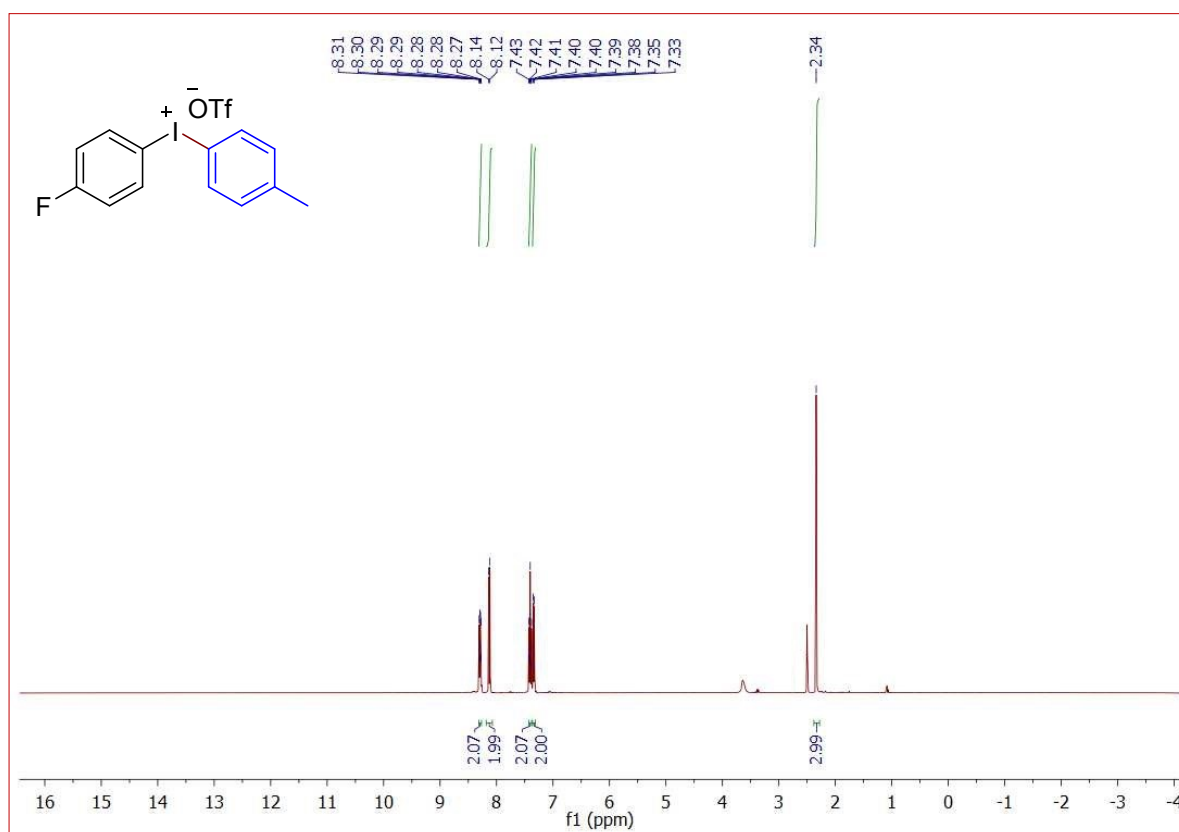
(4-Fluorophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5c**), ^{13}C NMR



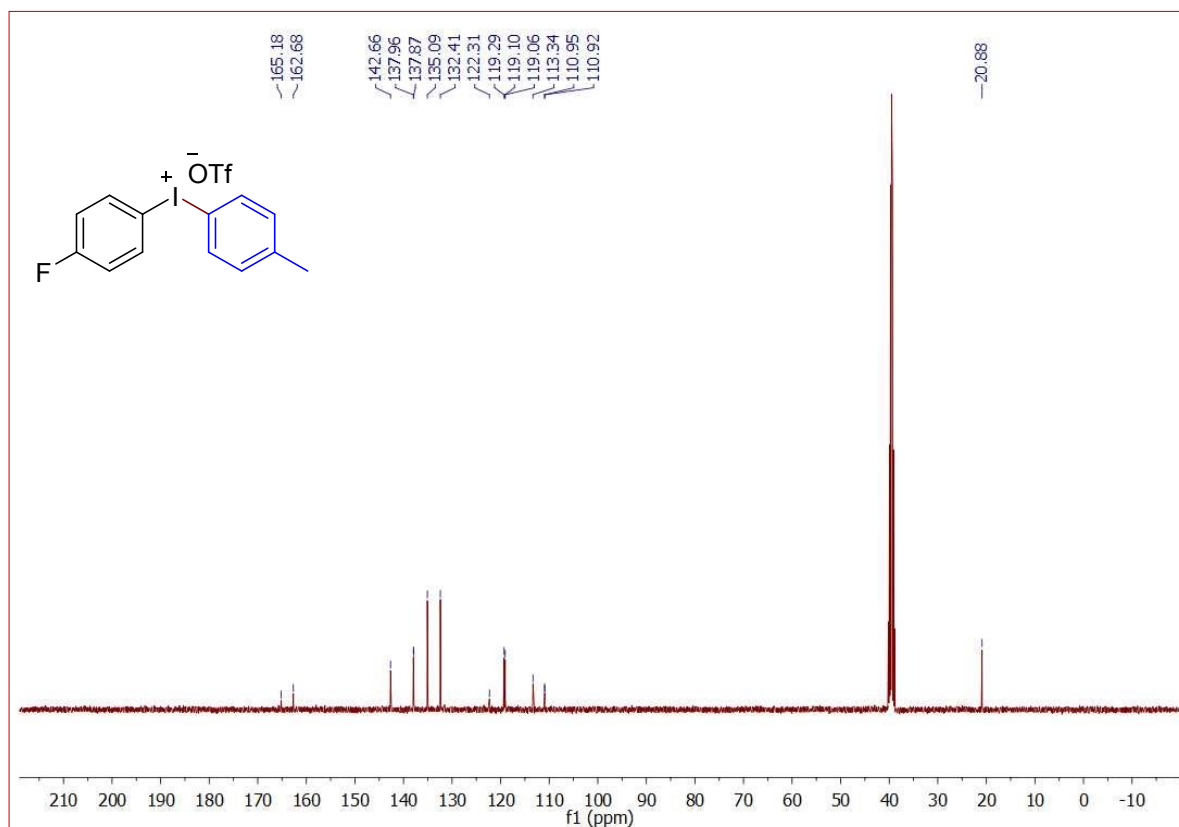
(4-Fluorophenyl)(phenyl)iodonium trifluoromethanesulfonate (**5c**), ^{19}F NMR



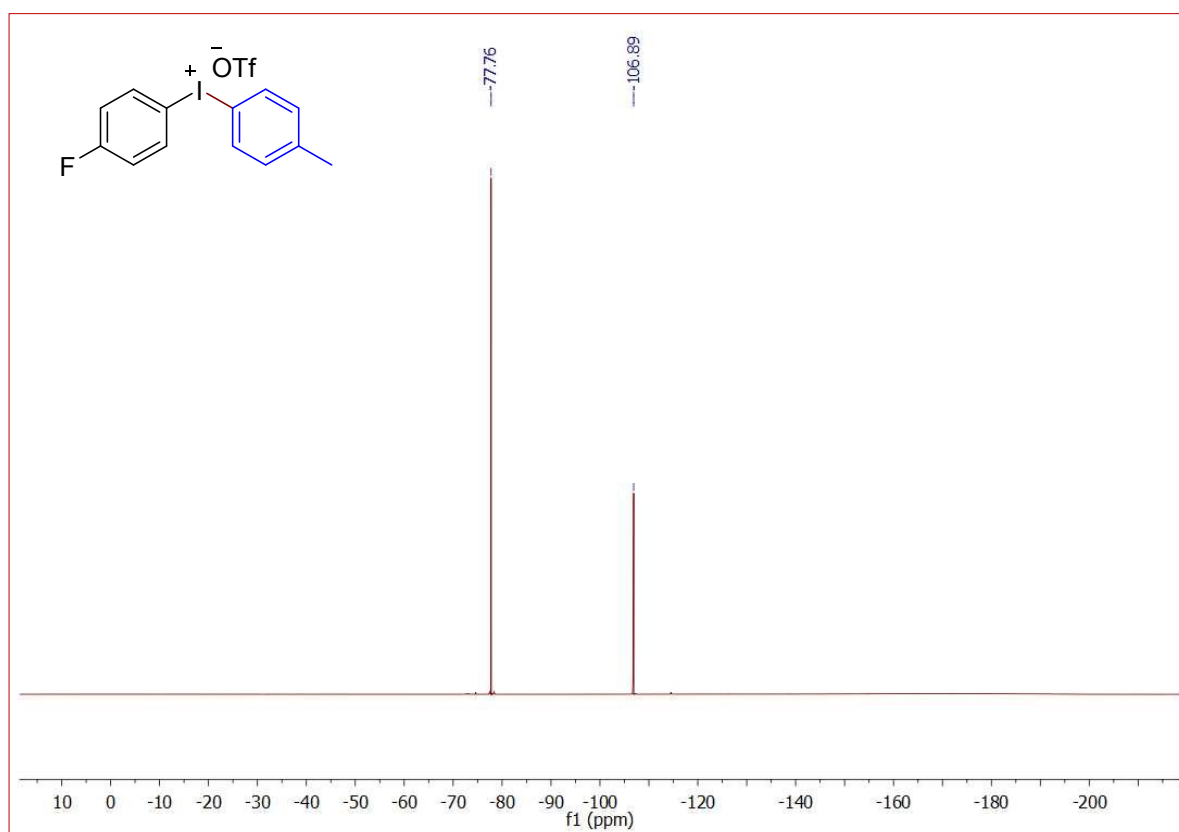
(4-Fluorophenyl)(p-tolyl)iodonium trifluoromethanesulfonate (**5d**), ^1H NMR



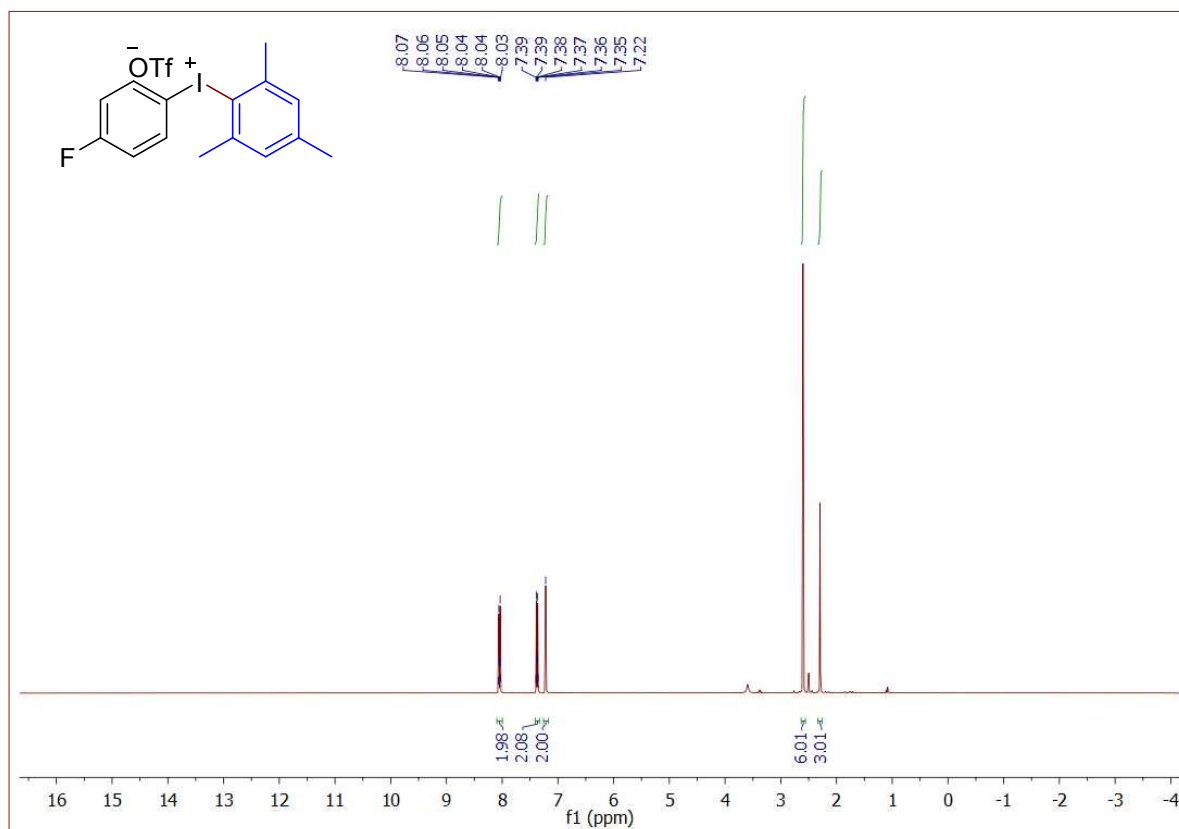
(4-Fluorophenyl)(p-tolyl)iodonium trifluoromethanesulfonate (**5d**), ^{13}C NMR



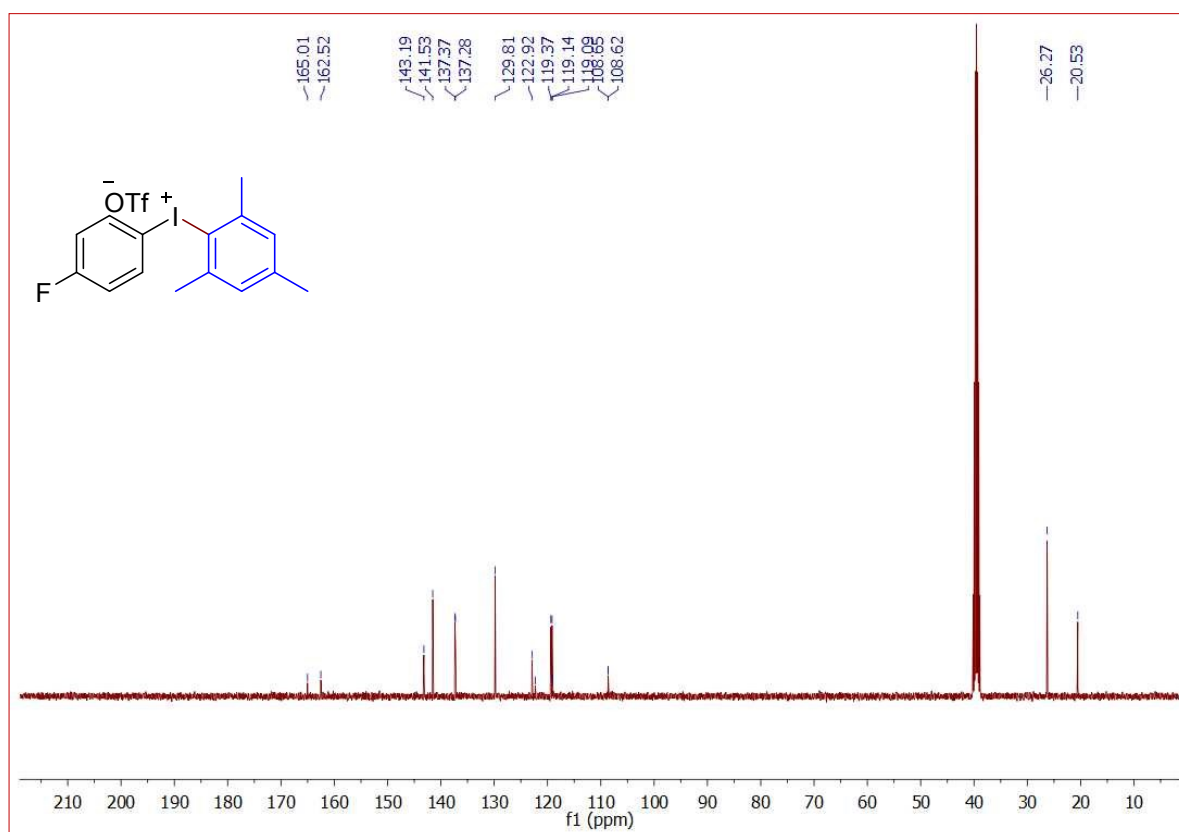
(4-Fluorophenyl)(p-tolyl)iodonium trifluoromethanesulfonate (**5d**), ^{19}F NMR



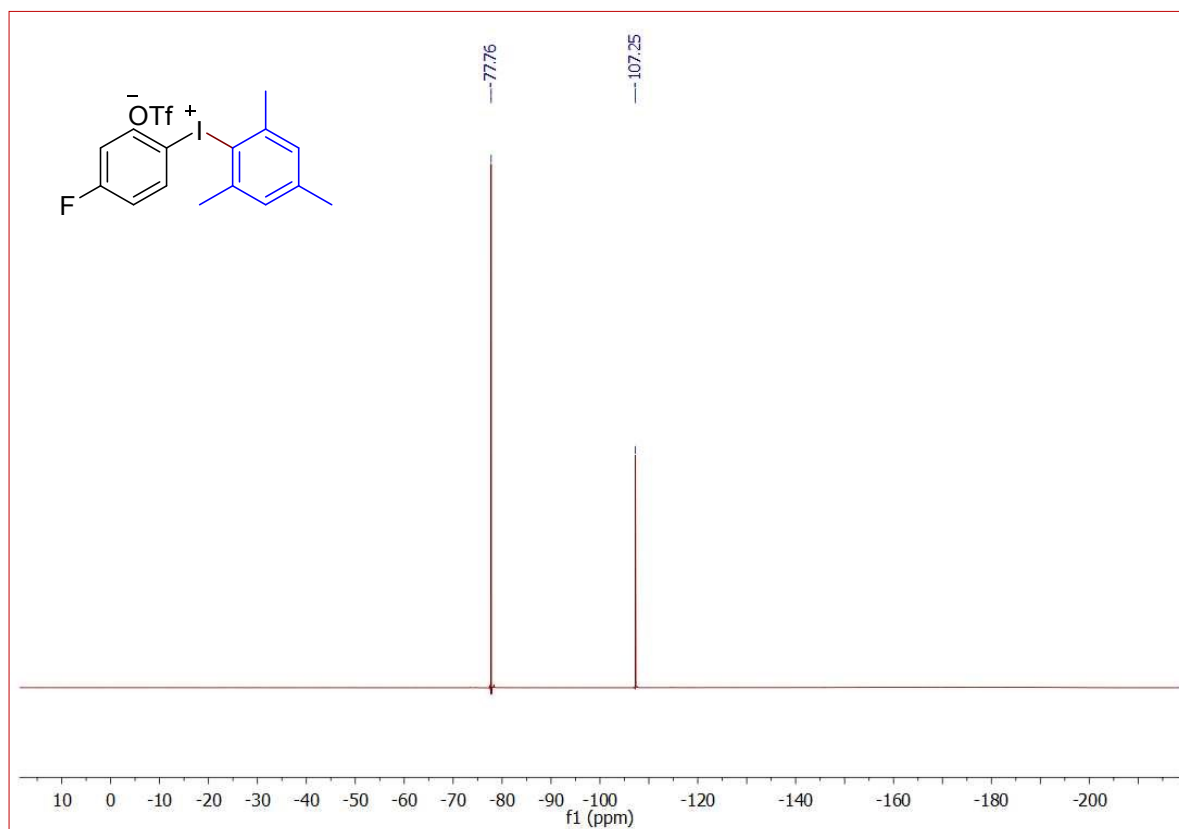
(4-Fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5f**), ^1H NMR



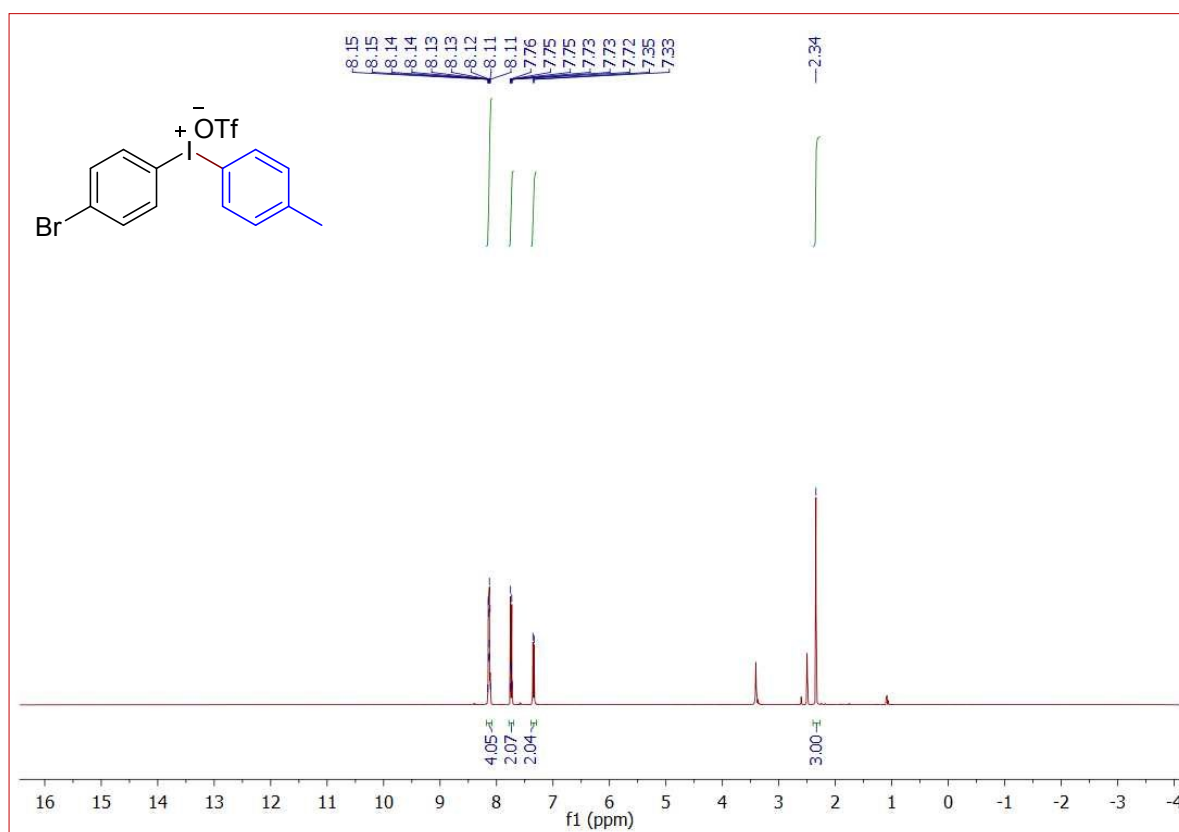
(4-Fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5f**), ^{13}C NMR



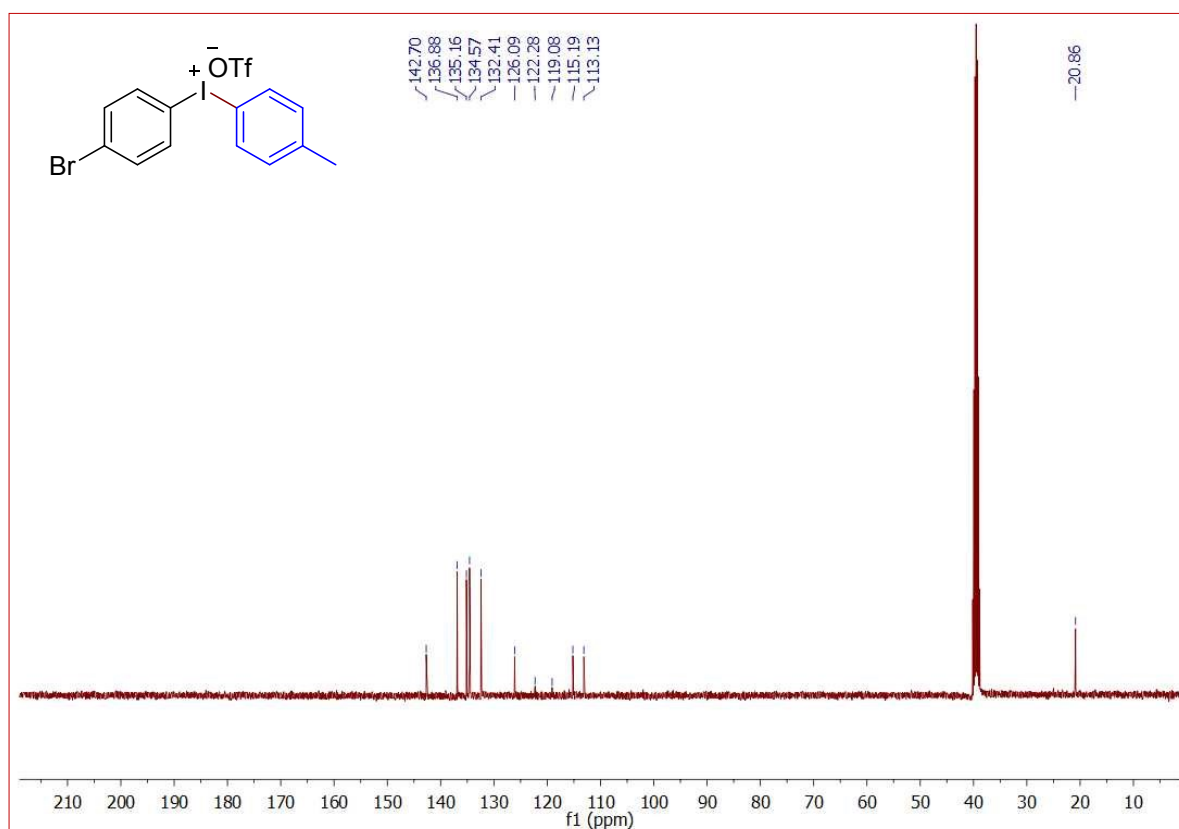
(4-Fluorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5f**), ^{19}F NMR



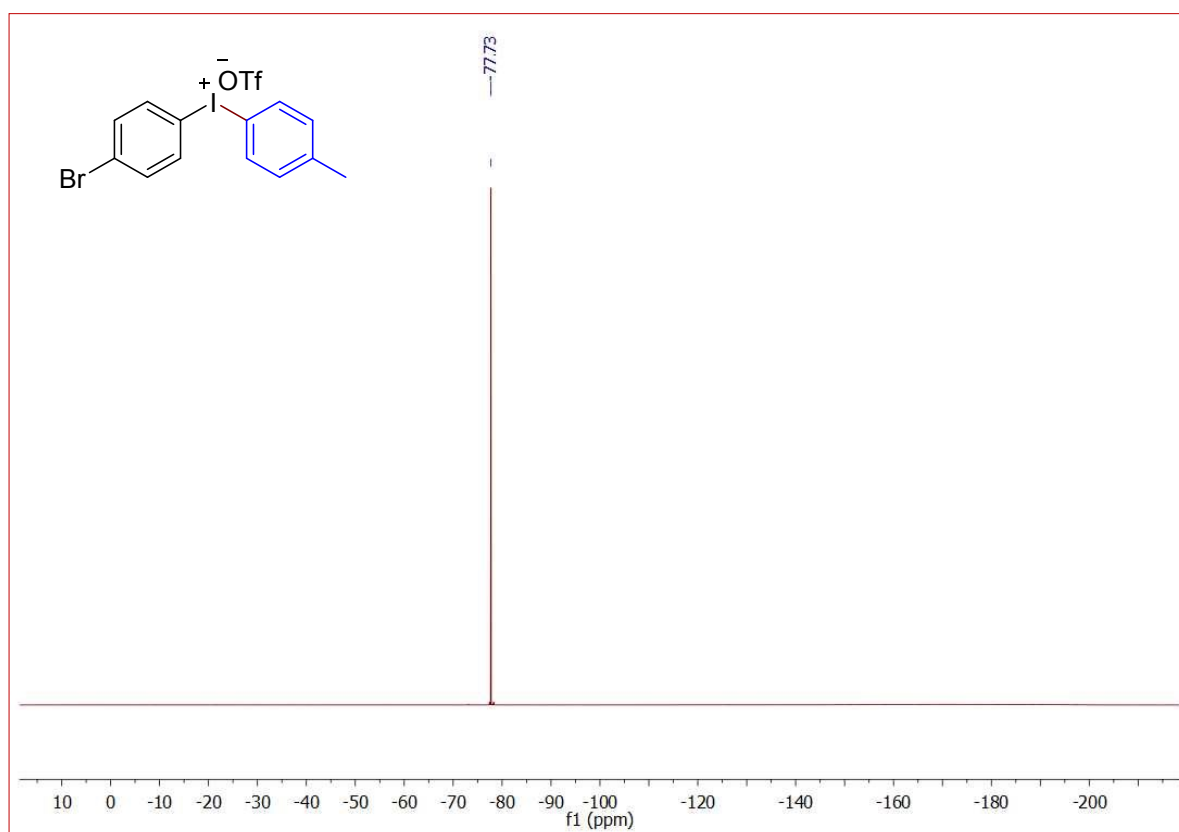
(4-Bromophenyl)(*p*-tolyl)iodonium trifluoromethanesulfonate (**5g**), ^1H NMR



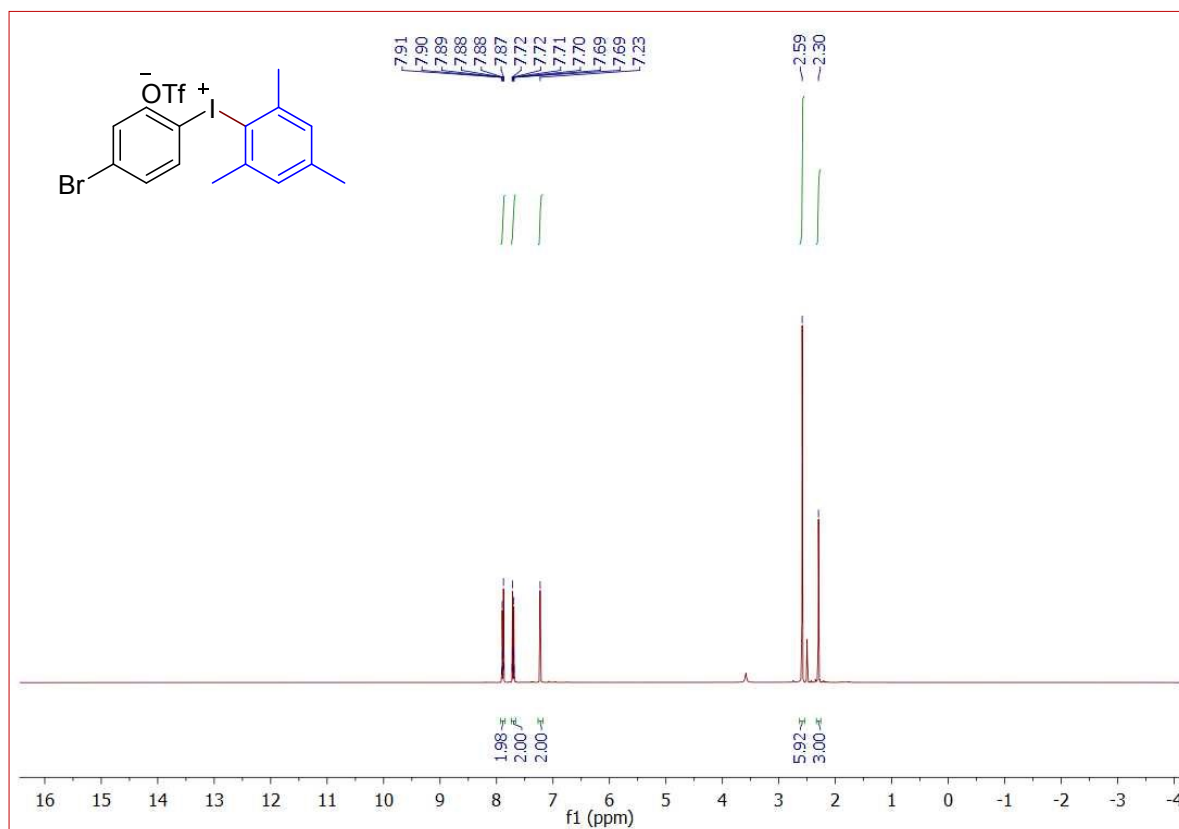
(4-Bromophenyl)(*p*-tolyl)iodonium trifluoromethanesulfonate (**5g**), ^{13}C NMR



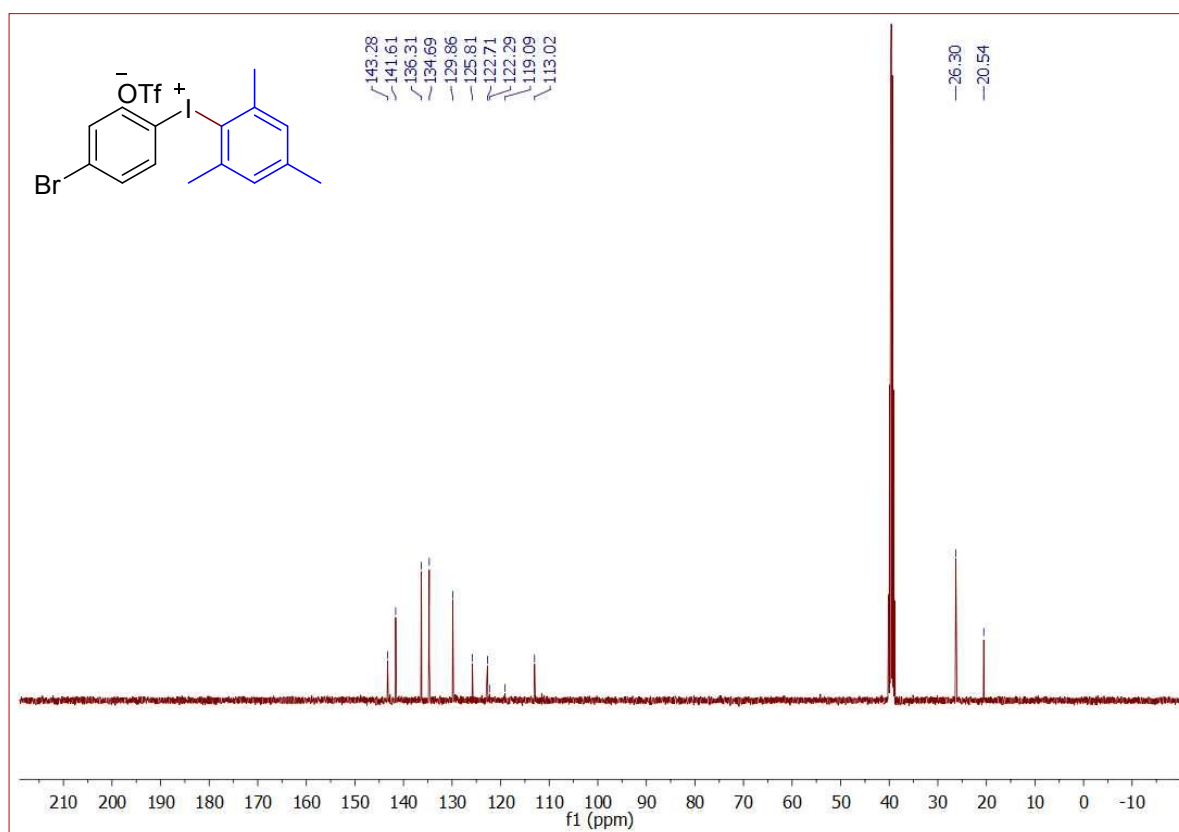
(4-Bromophenyl)(*p*-tolyl)iodonium trifluoromethanesulfonate (**5g**), ^{19}F NMR



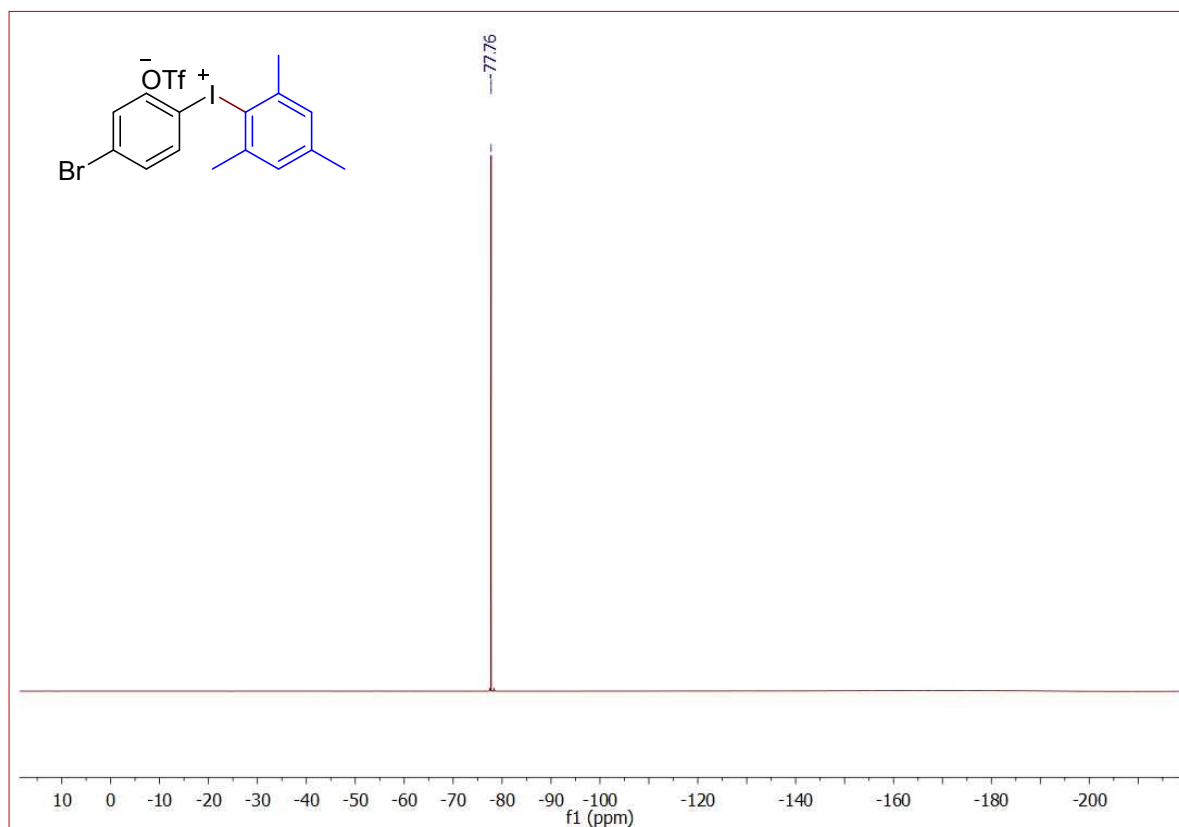
(4-Bromophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5h**), ^1H NMR



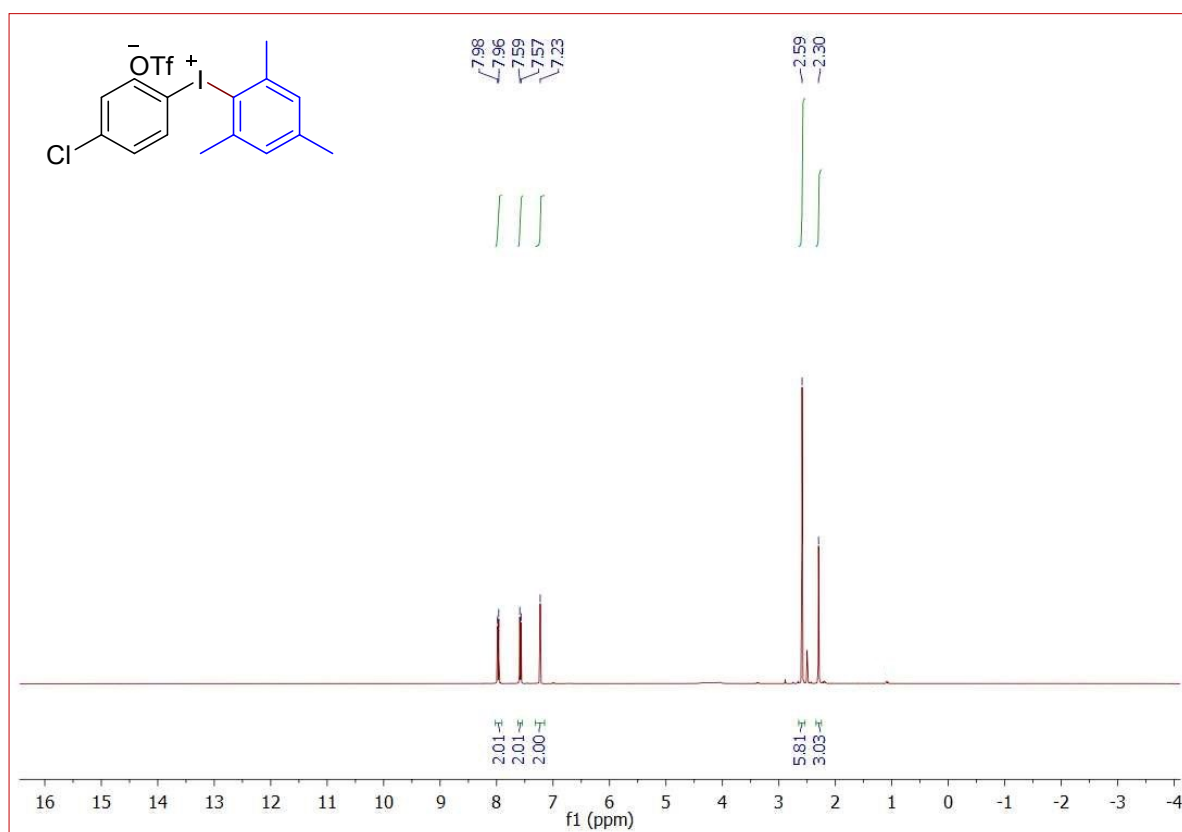
(4-Bromophenyl)(mesityl)iodonium trifluoromethanesulfonate **(5h)**, ^{13}C NMR



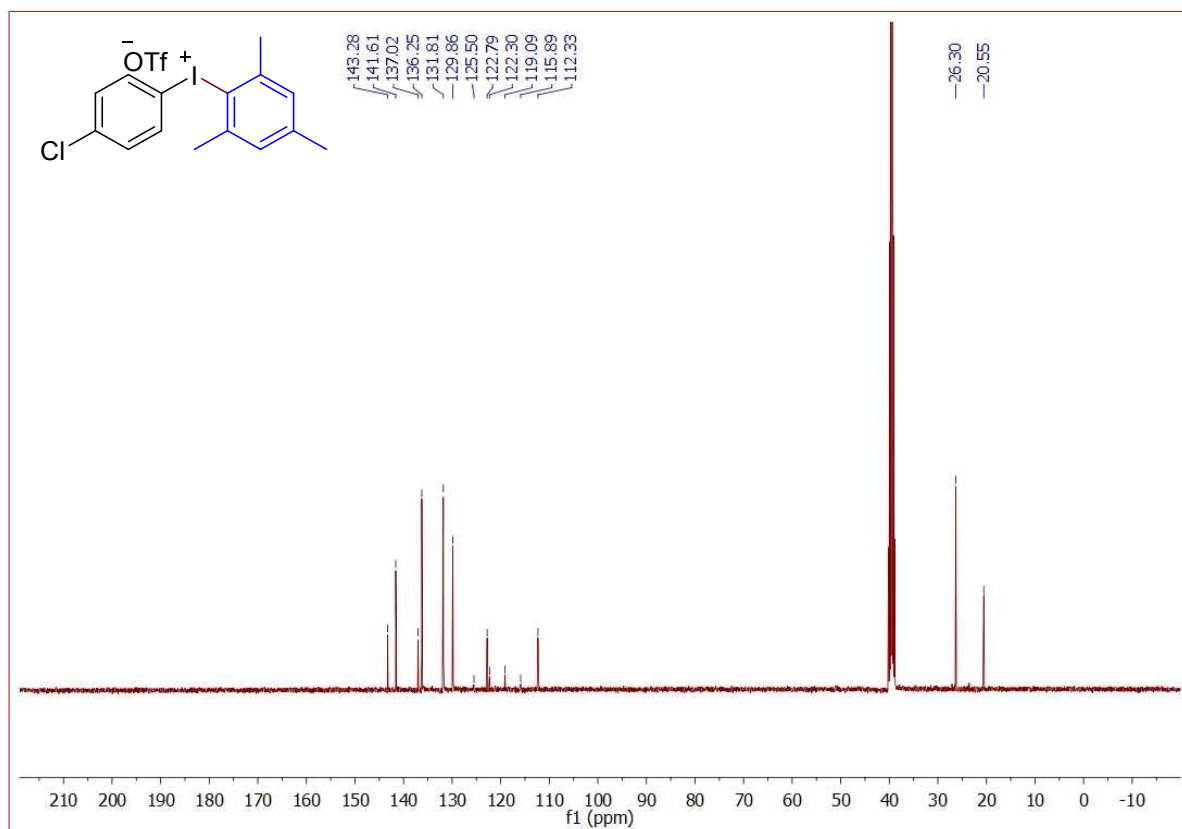
(4-Bromophenyl)(mesityl)iodonium trifluoromethanesulfonate **(5h)**, ^{19}F NMR



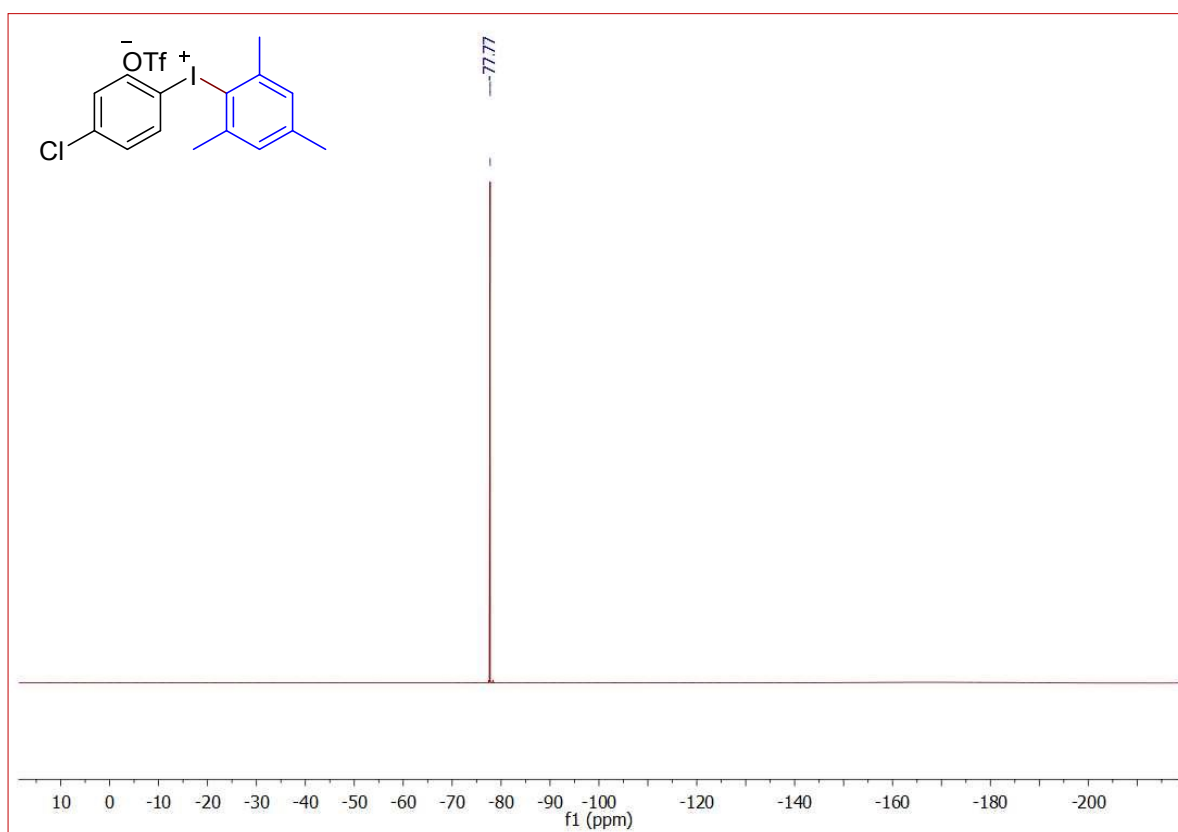
(4-Chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5i**), ^1H NMR



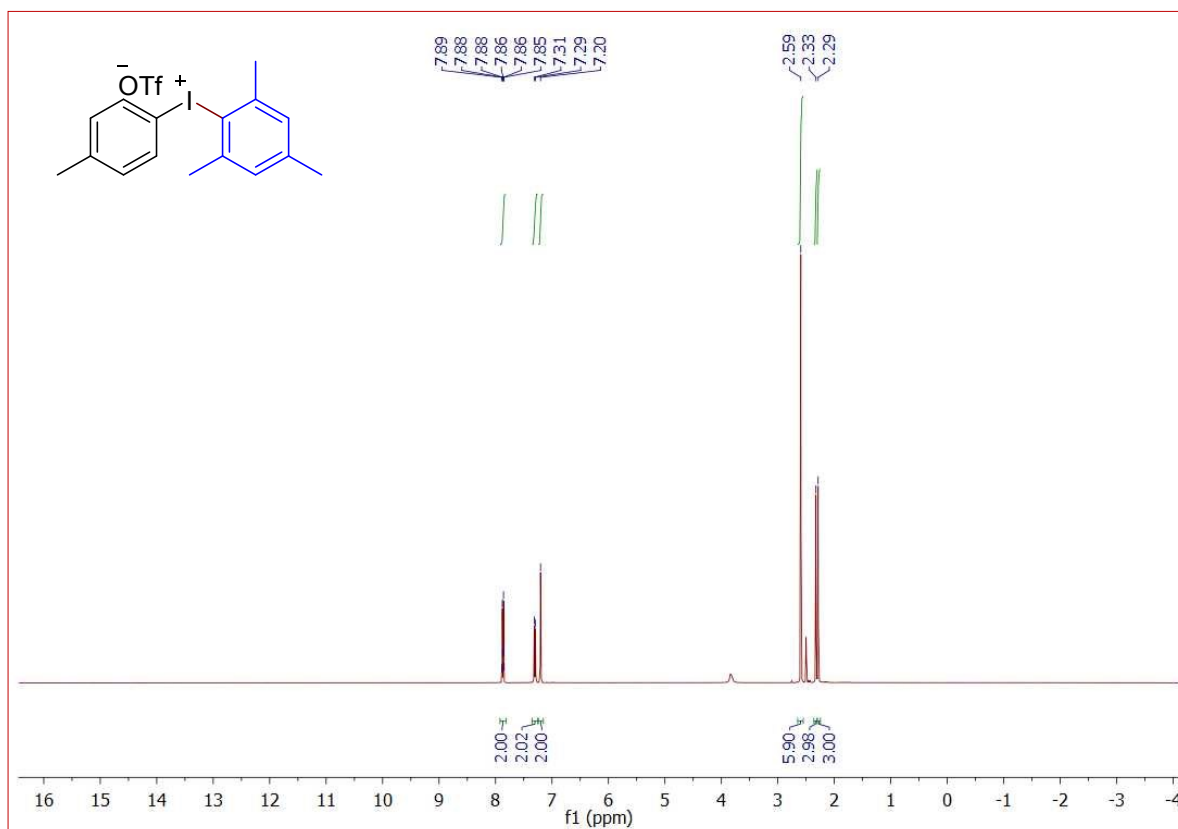
(4-Chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (**5i**), ^{13}C NMR



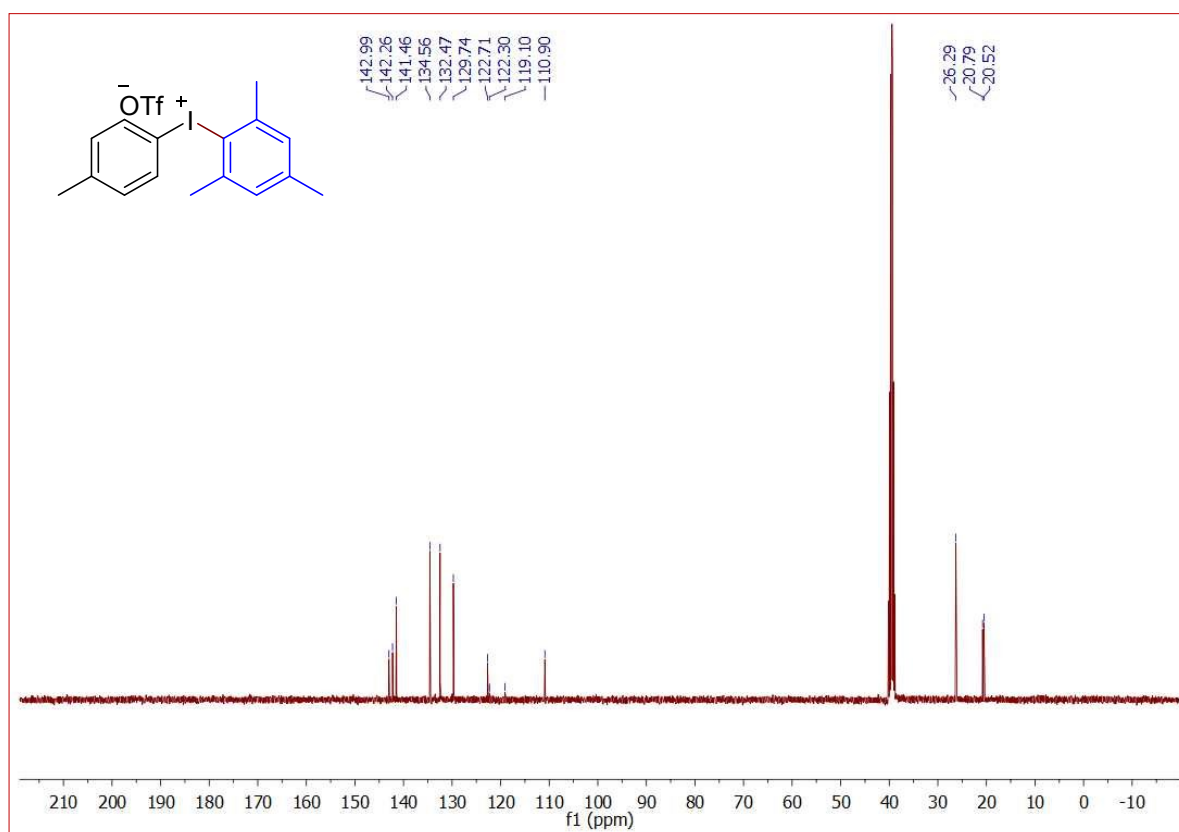
(4-Chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate **(5i)**, ^{19}F NMR



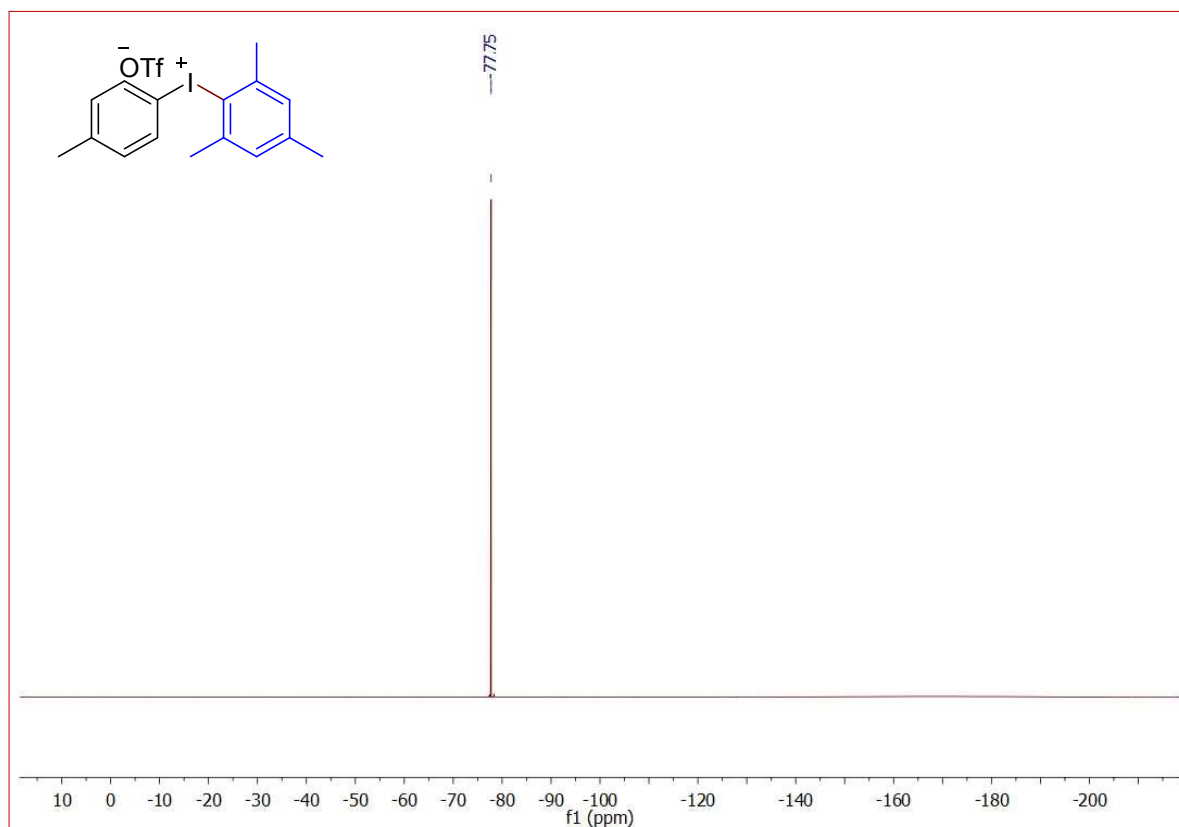
Mesityl(*p*-tolyl)iodonium trifluoromethanesulfonate **(5j)**, ^1H NMR



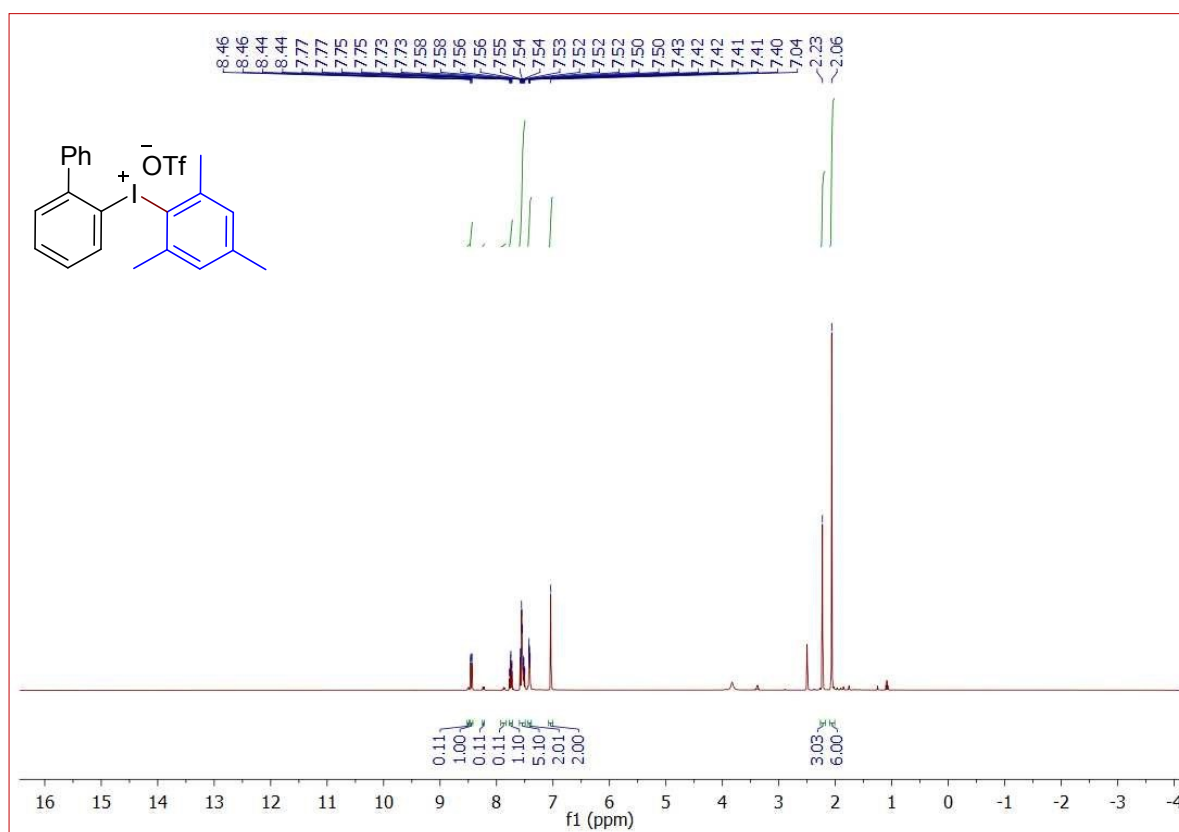
Mesityl(*p*-tolyl)iodonium trifluoromethanesulfonate (**5j**), ^{13}C NMR



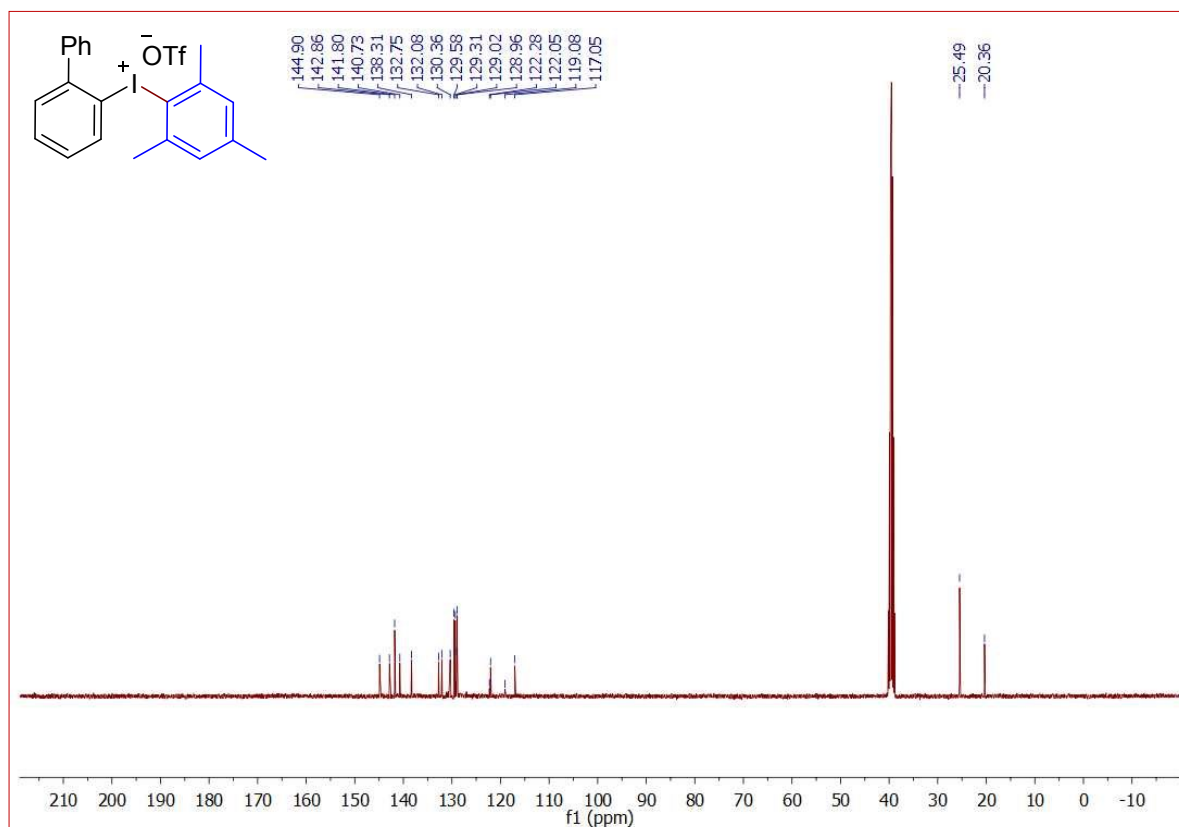
Mesityl(*p*-tolyl)iodonium trifluoromethanesulfonate (**5j**), ^{19}F NMR



[1,1'-Biphenyl]-2-yl(mesityl)iodonium trifluoromethanesulfonate (**5m**), ^1H NMR



[1,1'-Biphenyl]-2-yl(mesityl)iodonium trifluoromethanesulfonate (**5m**), ^{13}C NMR



[1,1'-Biphenyl]-2-yl(mesityl)iodonium trifluoromethanesulfonate (**5m**), ^{19}F NMR

