Supporting Information

Silver-Mediated Trifluoromethylthiolation–Iodination of Arynes

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General Information

NMR spectra were obtained on a Varian MR400 (400 MHz for ^{1}H; 377 MHz for ^{19}F; 100 MHz for ^{13}C), or a Varian MR500 (500 MHz for ^{1}H; 125MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as internal reference. $CDCl_3$ was referenced to -77.00 ppm in ^{13}C and 7.26 ppm in ^{1}H NMR spectra. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of quartets (tq), multiplet (m), and broad resonance (br).

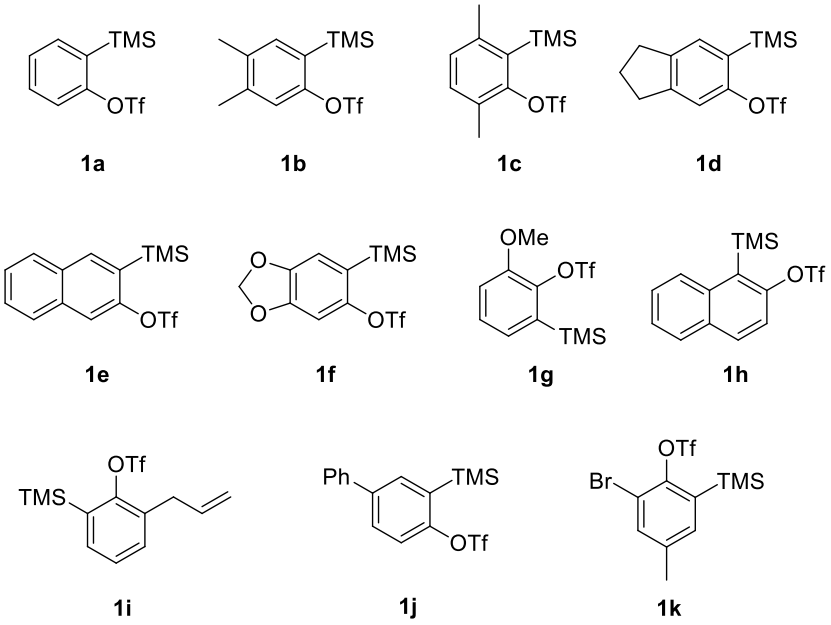
Materials and Methods

Cesium fluoride (>99%) was obtained from Acros. Unless otherwise noted, all other reagents were purchased from commercial suppliers (Aldrich, Alfa, Acros, TCI) and used as received. MeCN was distilled from CaH_2. 1-iodophenylacetylene[1] and $AgSCF_3$[2] were prepared according to literature procedures. All syntheses were conducted using standard Schlenk techniques or in an inert atmosphere glovebox unless otherwise stated.

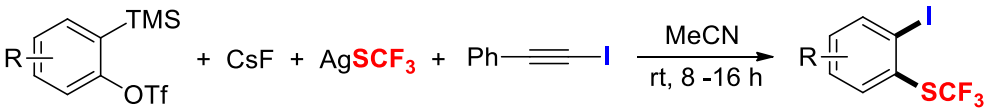
Experimental Details

Preparation of Aryne precursors

Aryne precursors **1a-j** were synthesized according to the literature procedures.[3]



General Procedure for Silver Mediated Trifluoromethylthiolation-Iodination of Arynes

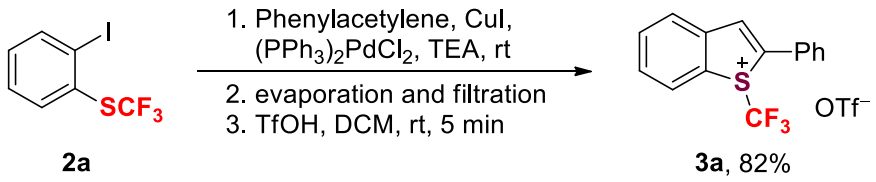


A solution of Aryne precursor (0.5 mmol, 1 equiv) and 1-iodophenylacetylene (228 mg, 1.0 mmol, 2 equiv) in 10 mL of MeCN was added to a mixture of $AgSCF_3$ (314 mg, 1.5 mmol, 3 equiv) and CsF (304mg, 2 mmol, 4 equiv) in 10 mL of MeCN. The reaction mixture was vigorously stirred at room temperature for 8-16 h. After evaporation the reaction solvent, the residue was diluted with hexane and filtered through a short pad of silica gel. The residue was further washed with hexane for three times. The filtrate was then evaporated and the residue was purified by silica gel flash

column chromatograph using hexane as an eluent (Rf from 0.4 to 0.9).

Note: For aryne precursors **1b-1d**, 6 equiv of CsF is needed in order to achieve a full conversion.

Synthesize of Yagupolskii-Umemoto Type Reagent



To a mixture of $(Ph_3P)_2PdCl_2$ (26 mg, 0.02 equiv) and CuI (3.2 mg, 0.01 equiv) the substrate **2a** (497 mg, 1.63 mmol, 1 equiv) and phenylacetylene (230 mg, 2.25 mmol, 1.4 equiv) was added in 4 mL of anhydrous TEA. The reaction mixture was stirred overnight at room temperature. After evaporation the reaction solvent, the residue was diluted with hexane and filtered through a short pad of silica gel. The residue was further washed with hexane for three times. The filtrate was then evaporated and a colorless oil was obtained.

The crude Sonogashira coupling product was dissolved in 4 mL of anhydrous DCM and vigorously stirred at room temperature. Then TfOH (0.36 mL, 2 equiv) was added dropwise. After the reaction was stirred for 5 min at room temperature, 35 mL of Et_2O was added and a large quantity of powder was precipitated. This powder was filtered and washed with Et_2O several times. The product **3a** (596 mg, 82%) was obtained as a yellow powder, generally, further purification is not needed.

(For further purification of this product, the precipitate can be re-dissolved in DCM and precipitated with Et_2O.)

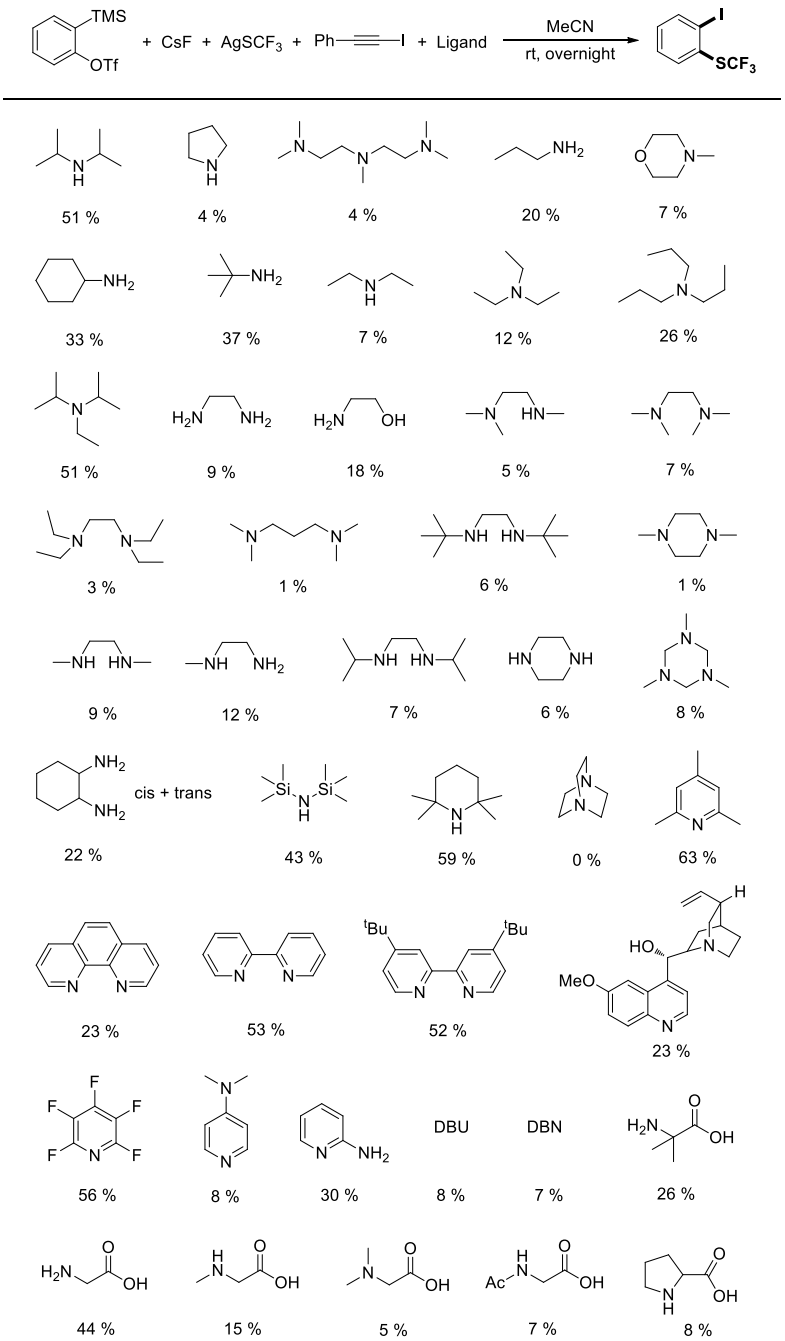
Note: This reagent is unstable in solution (e.g. MeCN). Thus after 24 h an obvious decomposition of a CD_3CN solution can be observed in both ^1H and ^{19}F NMR spectra.

Identification of regioselective isomers

The regioselectivity of this reaction was assigned on the basis of well-known selectivities in nucleophilic additions to unsymmetrical arynes[4] and our previously work.[5]

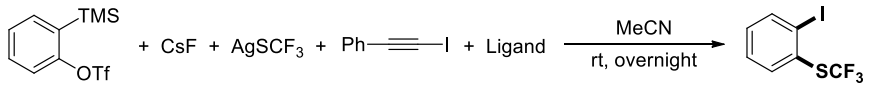
Optimiziation of Trifluoromethylthiolation-Iodination of Aryne

To improve the reaction efficiency, a number of ligands were tested as additives. The screening experiments are reported in Table S1 (N ligands) and Table S2 (P, S ligands).

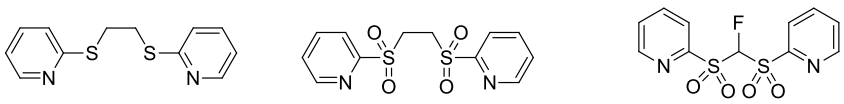


Reaction conditions: benzyne precursor (0.1 mmol, 1 equiv), CsF (4 equiv), $AgSCF_3$ (1.5 equiv), 1-iodophenyl acetylene (2 equiv), MeCN (4 mL). Yields were determined by ^{19}F NMR.

Table S1



Ph_2P–(CH$_2$)$_n$–PPh_2	n = 1, 6 % n = 2, 2 % n = 3, 7 % n = 4, 15 % n = 5, 8 % n = 6, 15 %	DPE Phos	PPh_3	PCy_3
		34 %	9 %	3 %

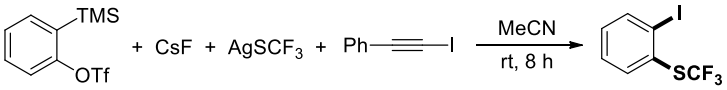


53 %	60 %	28 %

Reaction conditions: benzyne precursor (0.1 mmol, 1 equiv), CsF (4 equiv), $AgSCF_3$ (1.5 equiv), 1-iodophenyl acetylene (2 equiv), MeCN (4 mL). Yields were determined by ^{19}F NMR.

Table S2

The screening experiments (variation of reactant ratio) are reported in Table S3.

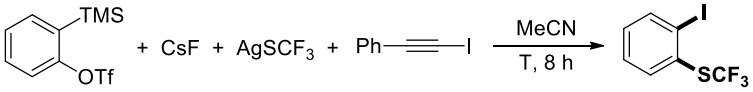


Entry[a]	$AgSCF_3$	Ph—≡—I	Yields (%)
1	1.5	1.5	63
2	1.5	2	64
3	1.5	3	59
4	2	1.5	62
5	2	2	65
6	2	3	67
7	3	1.5	68
8	3	2	69
9	3	3	70

[a]Reaction conditions: benzyne precursor (0.1 mmol, 1 equiv), CsF (4 equiv), MeCN (4 mL). Yields were determined by ^{19}F NMR.

Table S3

Reaction temperature was also screened, see Table S4.



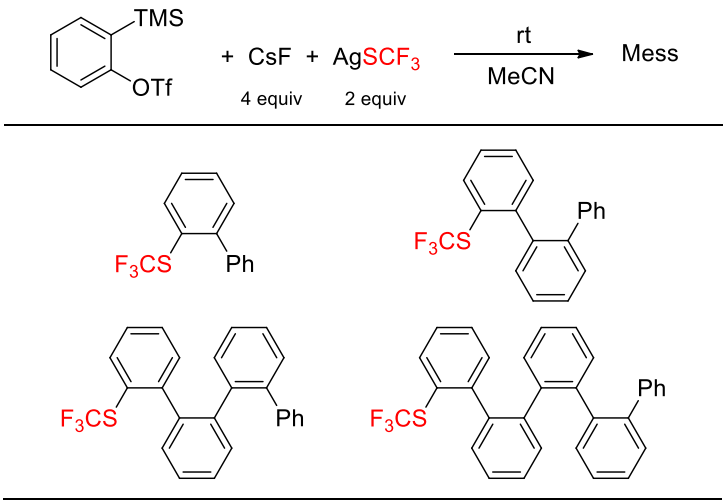
Entry[a]	T (°C)	Yields
1	0	63%
2	20	67%
3	30	61%
4	40	53%
5	50	43%

[a]Reaction conditions: benzyne precursor (0.1 mmol, 1 equiv), CsF (4 equiv), $AgSCF_3$ (3 equiv), 1-iodophenylacetylene (2 equiv), MeCN (4 mL). Yields were determined by ^{19}F NMR.

Table S4

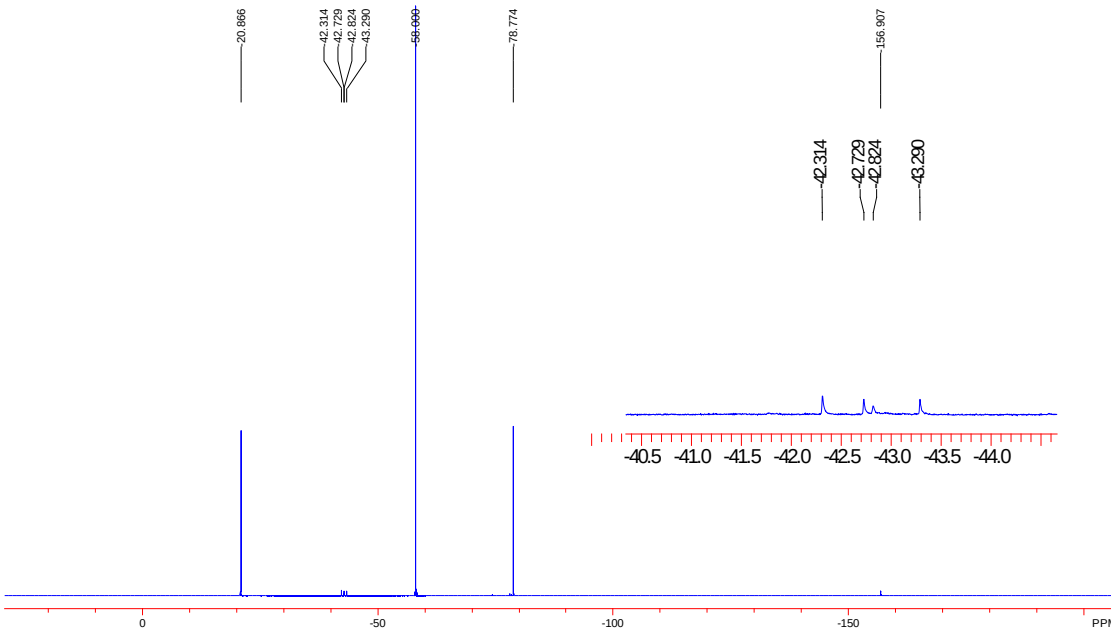
Experiments for Mechanistic Investigations

Direct trifluoromethylthiolation of benzyne (in the absence of trapping agents)

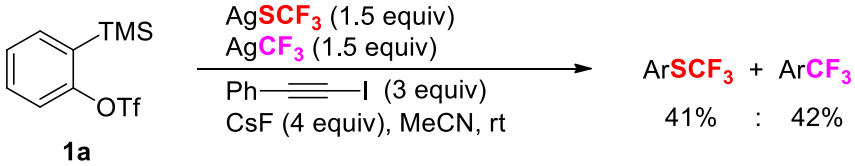


observed by ^{19}F NMR and GC-MS

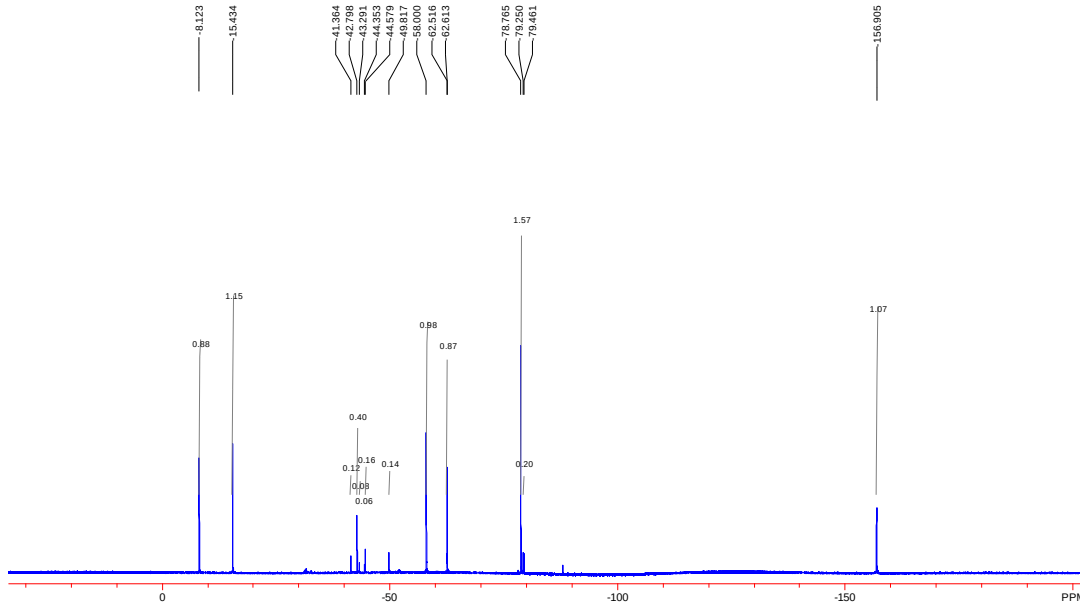
^{19}F NMR spectrum:

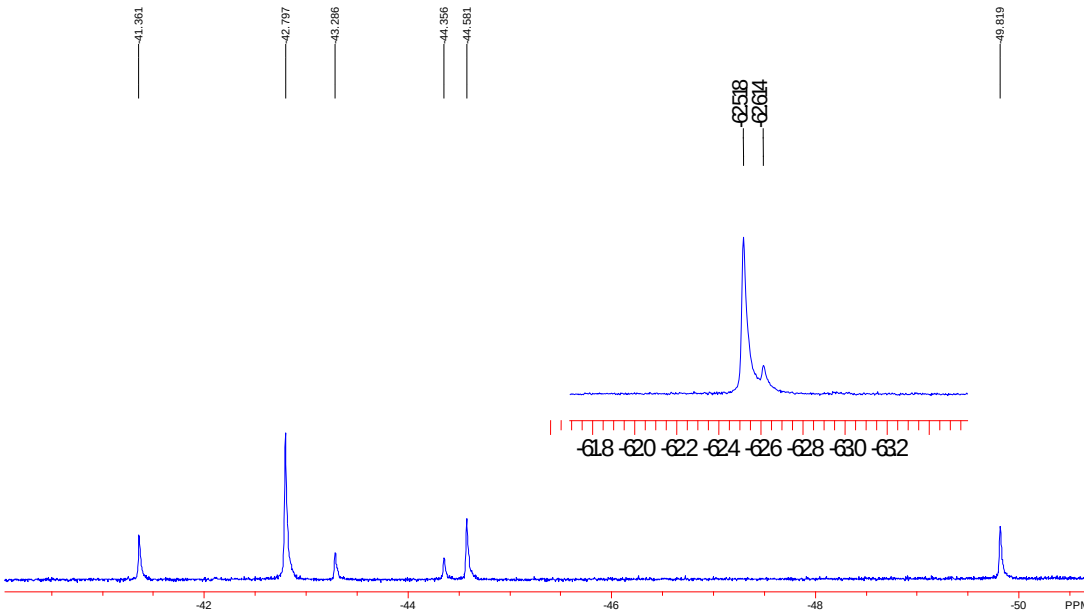


An investigation into the reactivity of $AgCF_3$ and $AgSCF_3$ with benzyne



^{19}F NMR spectrum:





Note: **CF_3I** (-8.12 (s)); **$AgSCF_3$** (-15.43 (s)); **$ArSCF_3$** (mixture: -41.36 (s), -42.80 (s), -43.28 (s), -44.35 (s), -44.58 (s), -49.82 (s)); **$PhOCF_3$** (internal standard: -58.00 (s)); **$ArCF_3$** (including *ortho*-CF_3-iodobenzene: -62.52 (s) and $PhCF_3$: -62.61 (s)); **OTf^-** in MeCN (-78.77 (s)); **CF_3H** (-79.36 (d, J = 79.5 Hz)); **TMSF** (-156.91 (m))

The ratio of $ArSCF_3$/$ArCF_3$ is 0.98/1.00, indicating a similar insertion reactivity of $AgSCF_3$ compared with $AgCF_3$.

References

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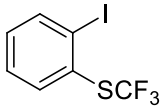
Analytical Data

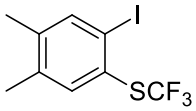
(2-Iodophenyl)(trifluoromethyl)sulfane (2a):[6]



2a

Colorless oil (102 mg, 65%); Rf 0.9 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.13 (td, *J* = 7.9 Hz, 1.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.17 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.7, 137.1, 131.9, 130.49 (q, *J* = 2.1 Hz), 129.44 (q, *J* = 309.6 Hz), 129.2, 108.0; **GC-MS**: 303.9 (M^+).

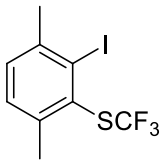
(2-Iodo-4,5-dimethylphenyl)(trifluoromethyl)sulfane (2b):



2b

Colorless oil (96 mg, 58%); Rf 0.85 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.55 (s, 1H), 2.24 (s, 3H), 2.23 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.61 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0, 141.3, 138.34, 138.29, 129.5 (q, *J* = 309.6 Hz), 126.8, 104.8, 19.3, 19.1; **GC-MS**: 331.9 (M^+); **HRMS (EI)**: Calcd for $C_9H_8F_3IS$, 331.9343; Found 331.9338.

(2-Iodo-3,6-dimethylphenyl)(trifluoromethyl)sulfane (2c):

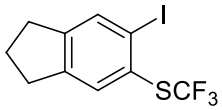


2c

Colorless oil (107 mg, 64%); Rf 0.95 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8

Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 2.65 (s, 3H), 2.52 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.28 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 142.6, 132.5, 130.4, 129.73 (q, *J* = 310.8 Hz), 129.69 (q, *J* = 1.8 Hz), 119.5, 31.2, 24.1; **GC-MS**: 331.9 (M^+); **HRMS (EI)**: Calcd for $C_9H_8F_3IS$, 331.9343; Found 331.9337.

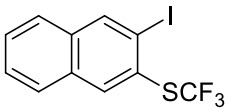
(6-Iodo-2,3-dihydro-1H-inden-5-yl)(trifluoromethyl)sulfane (2d):



2d

White solid (79 mg, 46%); Rf 0.85 (PE); **Mp** 32-37 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.65 (s, 1H), 2.90 (m, 4H), 2.11 (p, *J* = 7.5 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.67 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 146.4, 136.4, 133.2, 129.6 (q, *J* = 309.6 Hz), 127.0, 105.3, 32.4, 32.3, 25.5; **GC-MS**: 344.0 (M^+); **HRMS (EI)**: Calcd for $C_{10}H_8F_3IS$, 343.9343; Found 343.9339.

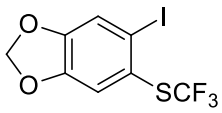
(3-Iodonaphthalen-2-yl)(trifluoromethyl)sulfane (2e):



2e

White solid (85 mg, 48%); Rf 0.8 (PE); **Mp** 69-70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.35 (s, 1H), 7.83 (d, *J* = 7.1 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.64 – 7.50 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.53 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.9, 138.0, 135.2, 132.9, 129.5 (q, *J* = 311.1 Hz), 128.8, 128.2, 127.5, 126.5, 126.4, 102.8; **GC-MS**: 353.9 (M^+); **HRMS (EI)**: Calcd for $C_{11}H_6F_3IS$, 353.9187; Found 353.9190.

5-Iodo-6-(trifluoromethylthio)benzo[d][1,3]dioxole (2f):

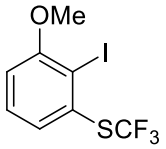


2f

White solid (115 mg, 61%); Rf 0.5 (PE); **Mp** 49-50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.40 (s, 1H), 7.27 (s, 1H), 6.06 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -43.05 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 149.0, 129.4 (q, *J* = 310.2 Hz), 121.7, 119.7, 116.5, 102.6, 99.1; **GC-MS**: 347.9 (M^+); **HRMS (EI)**: Calcd for $C_8H_4F_3IO_2S$, 347.8929; Found 347.8930.

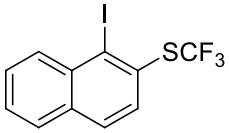
(2-Iodo-3-methoxyphenyl)(trifluoromethyl)sulfane (2g):



2g

Colorless oil (117 mg, 70%); Rf 0.4 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 3.91 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.93 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 132.3 (d, *J* = 2.1 Hz), 129.8, 129.6 (q, *J* = 309.6 Hz), 128.4 (d, *J* = 1.0 Hz), 112.2, 99.8, 56.8; **GC-MS**: 333.9 (M^+); **HRMS (EI)**: Calcd for $C_8H_6F_3IOS$, 333.9136; Found 333.9130.

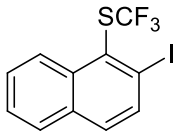
(1-Iodonaphthalen-2-yl)(trifluoromethyl)sulfane (2ha):



2ha

White solid (82 mg, 46%); Rf 0.85 (PE); **Mp** 57-58 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 7.89 – 7.73 (m, 3H), 7.68 – 7.53 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.53 (m, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ135.99, 134.64, 133.71, 131.08 (d, *J* = 0.8 Hz), 130.18 (d, *J* = 2.0 Hz), 129.68 (q, J = 310.0 Hz), 129.59, 128.76, 128.33, 128.21, 115.31; **GC-MS**: 354.0 (M^+); **HRMS (EI)**: Calcd for $C_{11}H_6F_3IS$, 353.9187; Found 353.9185.

(2-Iodonaphthalen-1-yl)(trifluoromethyl)sulfane (2hb):

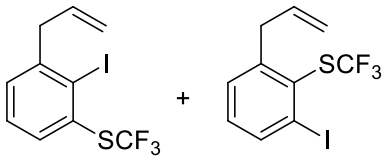


2hb

Colorless oil (49 mg, 28%); Rf 0.85 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.61 – 7.55 (m, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -40.87 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.76, 136.73, 133.57, 133.18, 129.44 (q, *J* = 311.9 Hz), 128.64, 128.46, 127.86, 127.27 (d, *J* = 1.7 Hz), 127.06; **GC-MS**: 354.0 (M^+); **HRMS (EI)**: Calcd for $C_{11}H_6F_3IS$, 353.9187; Found 353.9181.

(2-Allyl-6-iodophenyl)(trifluoromethyl)sulfane &

(3-allyl-2-iodophenyl)(trifluoromethyl)sulfane (2i):

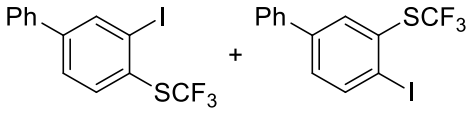


2i (3.2:1)

Colorless oil (108 mg, 63%); Rf 0.8 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, **1H**), 7.33 (t, *J* = 7.6 Hz, **1H**), 7.27 (d, *J* = 9.9 Hz, 1H & **1H**), 7.10 (t, *J* = 7.8 Hz, 1H), 6.03 – 5.85 (m, 1H & **1H**), 5.18 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.13 – 5.00 (m, 1H & **2H**), 3.83 (d, *J* = 6.6 Hz, 2H), 3.62 (d, *J* = 6.4 Hz, **2H**); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -41.38 (s, 3F), -42.31 (s, **3F**); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6, 146.2, 139.2, 136.0, 135.2, 134.5, 132.9, 131.9, 131.3, 130.5, 129.6 (q, *J* = 309.6 Hz), 129.4 (q, *J* = 310.8 Hz), 128.8, 117.3, 117.1, 114.4, 112.7, 47.1, 41.0; **GC-MS**: 343.9 (M^+); **HRMS (EI)**: Calcd for $C_{10}H_8F_3IS$, 343.9343; Found 343.9340.

(3-Iodo-[1,1'-biphenyl]-4-yl)(trifluoromethyl)sulfane compound with

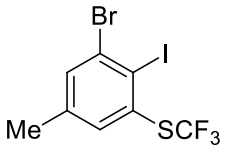
(4-iodo-[1,1'-biphenyl]-3-yl)(trifluoromethyl)sulfane (2j):



2j (1.3:1)

Colorless oil (142 mg, 74%); Rf 0.8 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.51 – 7.40 (m, 6H), 7.33 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.00 (s, 3F), -42.19 (s, 3F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.17, 142.72, 140.95, 139.14, 138.60, 138.06, 137.15, 135.60, 132.32, 130.63, 129.52 (q, *J* = 309.7 Hz), 129.48 (q, *J* = 309.9 Hz), 129.12, 129.06, 128.63, 128.34, 128.22, 127.88, 127.19, 126.92, 108.54, 106.23; **GC-MS**: 380.0 (M^+); **HRMS (EI)**: Calcd for $C_{13}H_8F_3IS$, 379.9343; Found 379.9341.

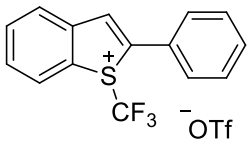
(3-Bromo-2-iodo-5-methylphenyl)(trifluoromethyl)sulfane (2k):



2k

Colorless oil (63 mg, 32%); Rf 0.85 (PE); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H & 1H), 2.31 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -42.09 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.58, 135.45 (d, *J* = 1.2 Hz), 135.27, 132.95, 131.79, 129.56 (q, *J* = 310.0 Hz), 110.68, 20.54; **GC-MS**: 395.9 (M^+); **HRMS (EI)**: Calcd for $C_8H_5BrF_3IS$, 395.8292; Found 395.8297.

2-Phenyl-1-(trifluoromethyl)-1H-benzo[b]thiophen-1-ium trifluoromethanesulfonate (3a):[7]

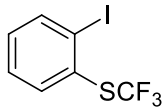


3a

Yellow powder (596 mg, 82%); **^{1}H NMR** (400 MHz, CD_3CN) δ 8.41 (d, *J* = 8.2 Hz, 1H), 8.33 (s, 1H), 8.10 – 8.02 (m, 2H), 7.92 – 7.80 (m, 3H), 7.69 – 7.61 (m, 3H); **^{19}F NMR**

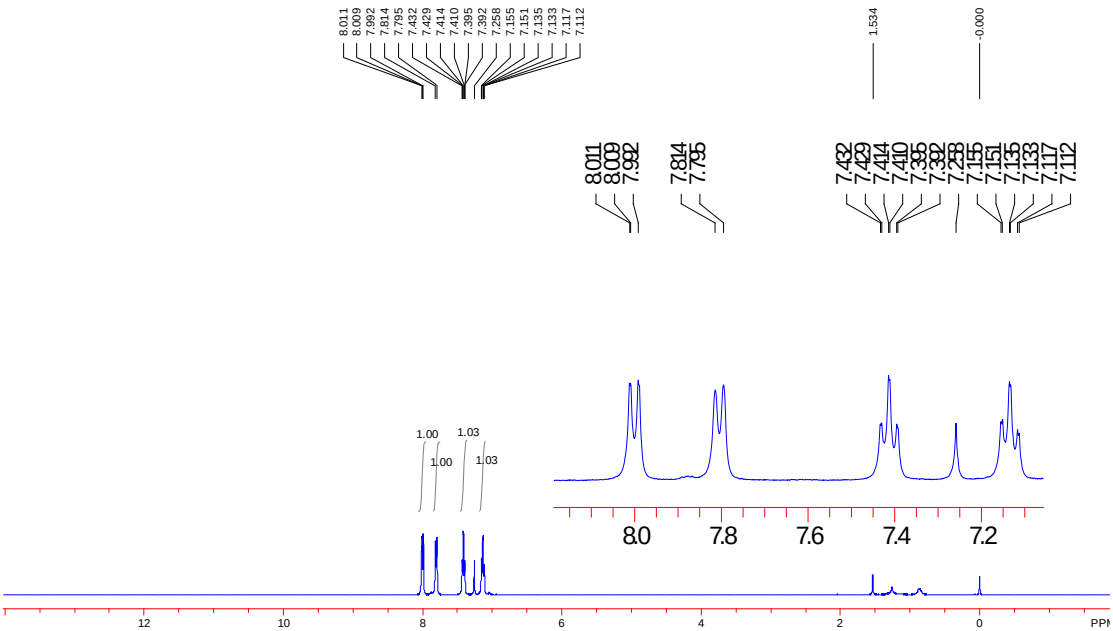
(376 MHz, CD_3CN) δ -50.82 (s, 3F), -79.37 (s, 3F); **^{13}C NMR** (100 MHz, CD_3CN) δ 146.19, 140.67, 137.76 (d, *J* = 3.0 Hz), 135.47 (d, *J* = 5.1 Hz), 133.13, 133.08, 131.07, 130.72, 129.60, 128.83, 127.87 (d, *J* = 3.8 Hz), 124.14 (q, *J* = 330.3 Hz), 123.69, 122.16 (q, *J* = 324.1 Hz).

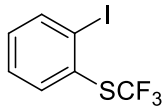
NMR Spectra of Product



2a

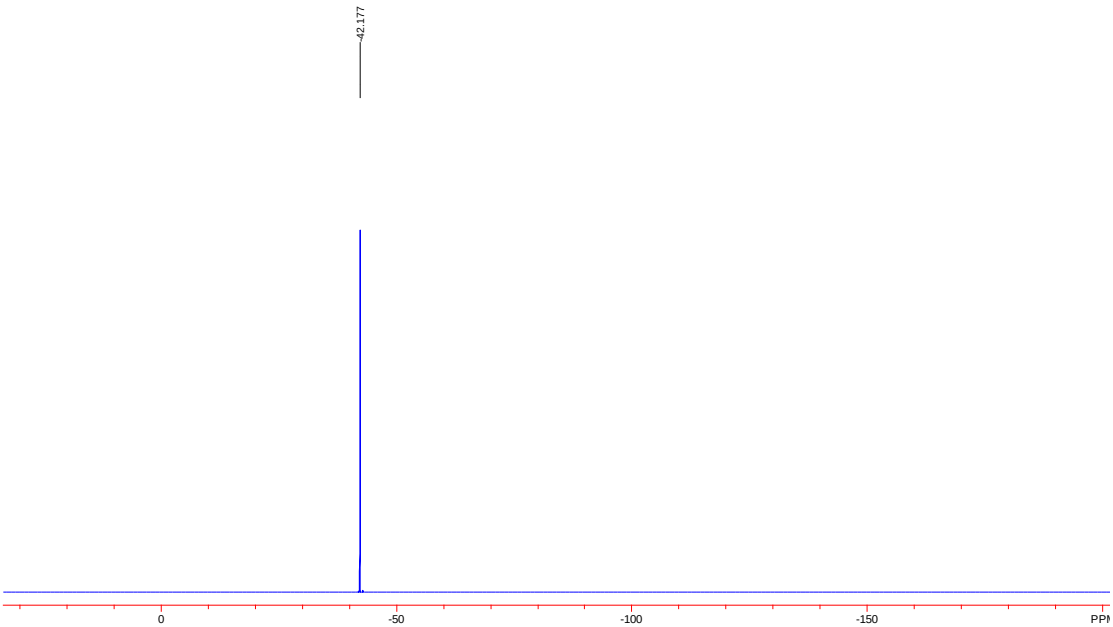
^{1}H NMR (400 MHz, $CDCl_3$)

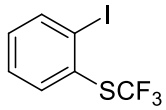




2a

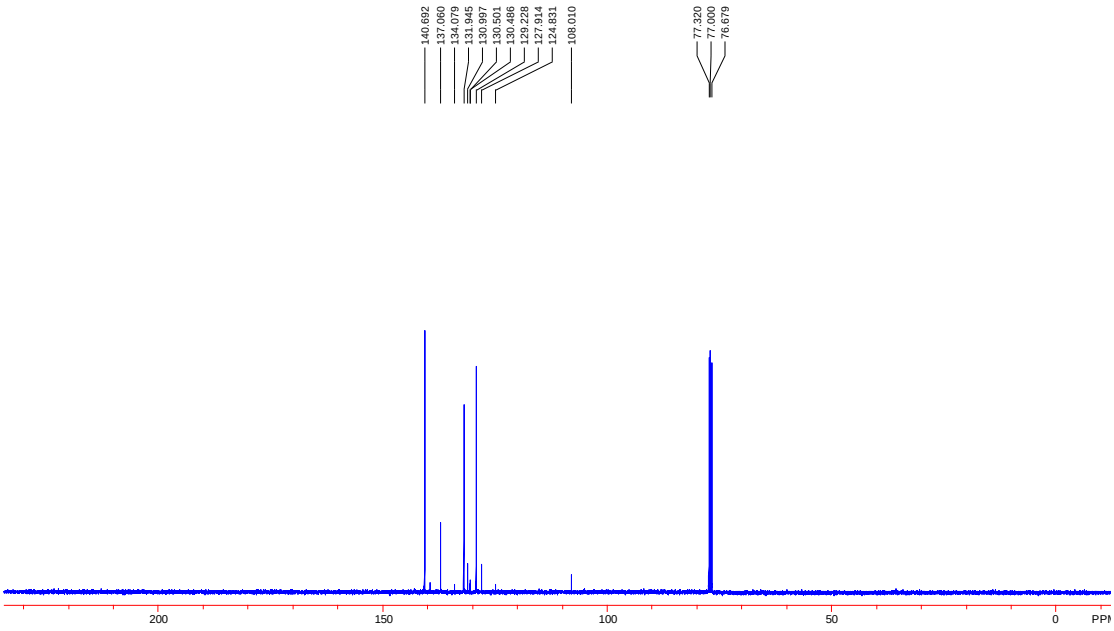
^{19}F NMR (376 MHz, $CDCl_3$)

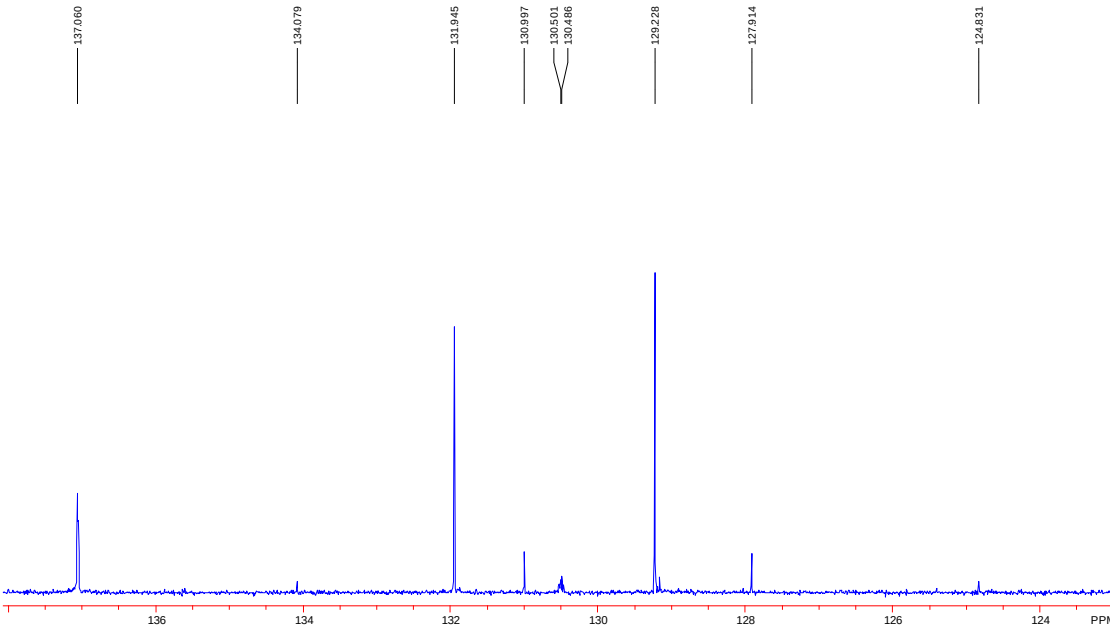


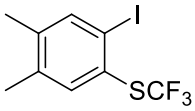


2a

^{13}C NMR (100 MHz, $CDCl_3$)

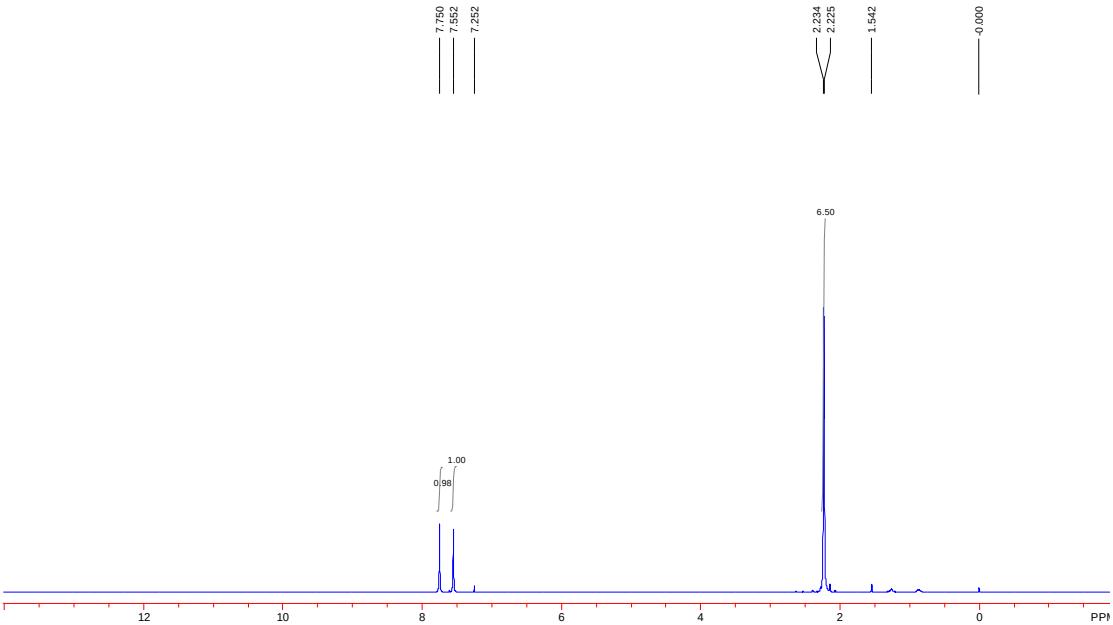


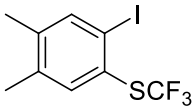




2b

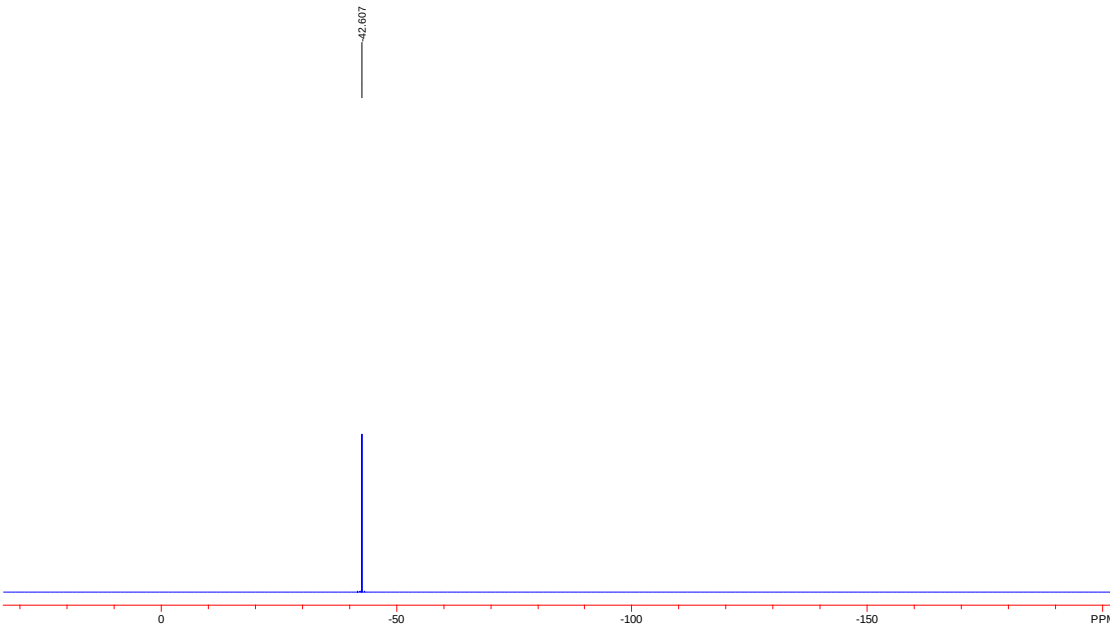
^{1}H NMR (400 MHz, $CDCl_3$)

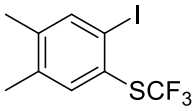




2b

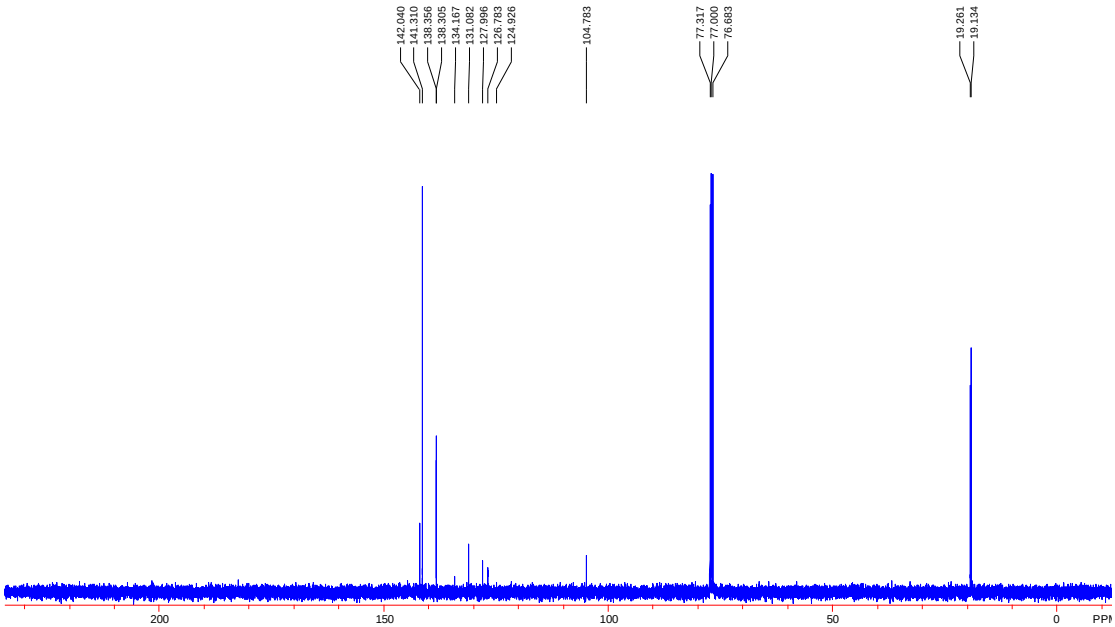
^{19}F NMR (376 MHz, $CDCl_3$)

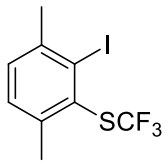




2b

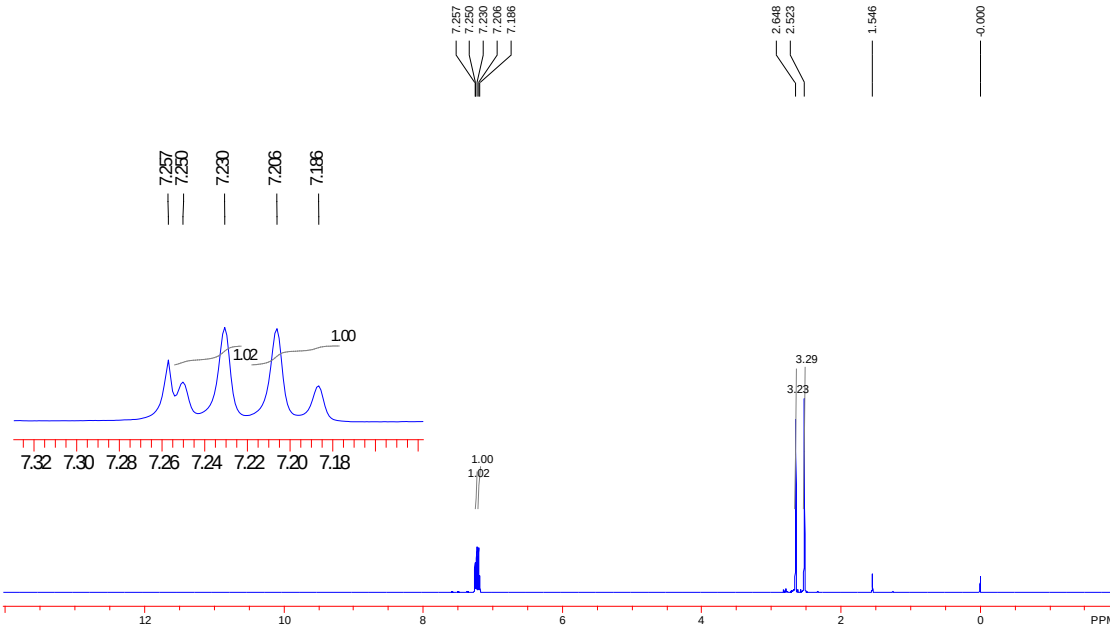
^{13}C NMR (100 MHz, $CDCl_3$)

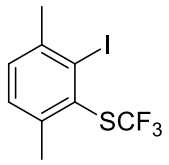




2c

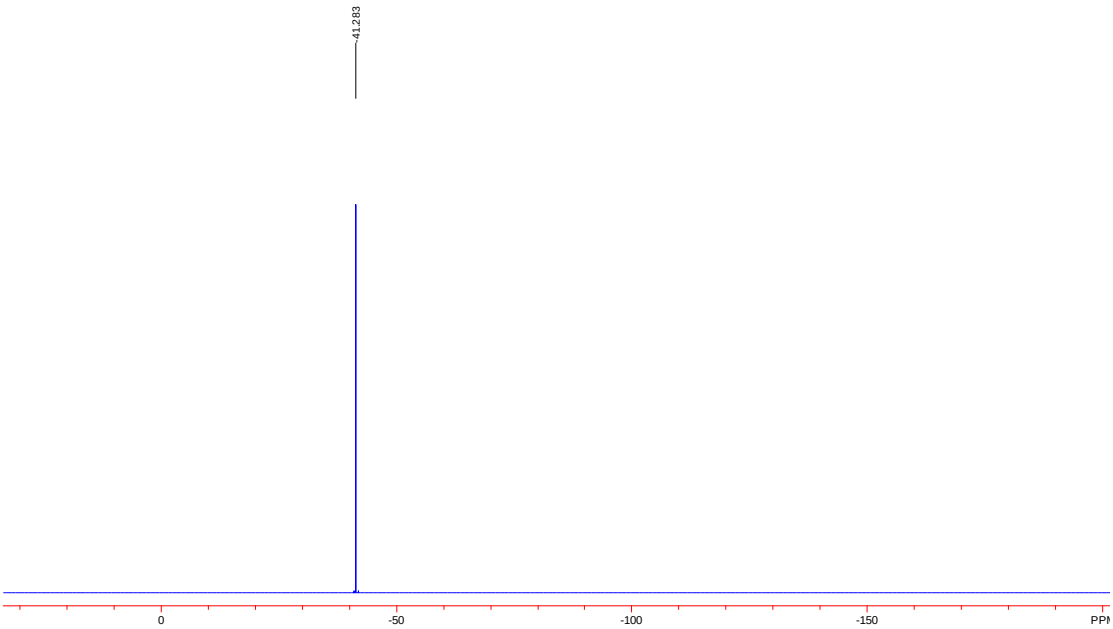
^{1}H NMR (400 MHz, $CDCl_3$)

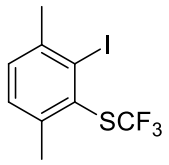




2c

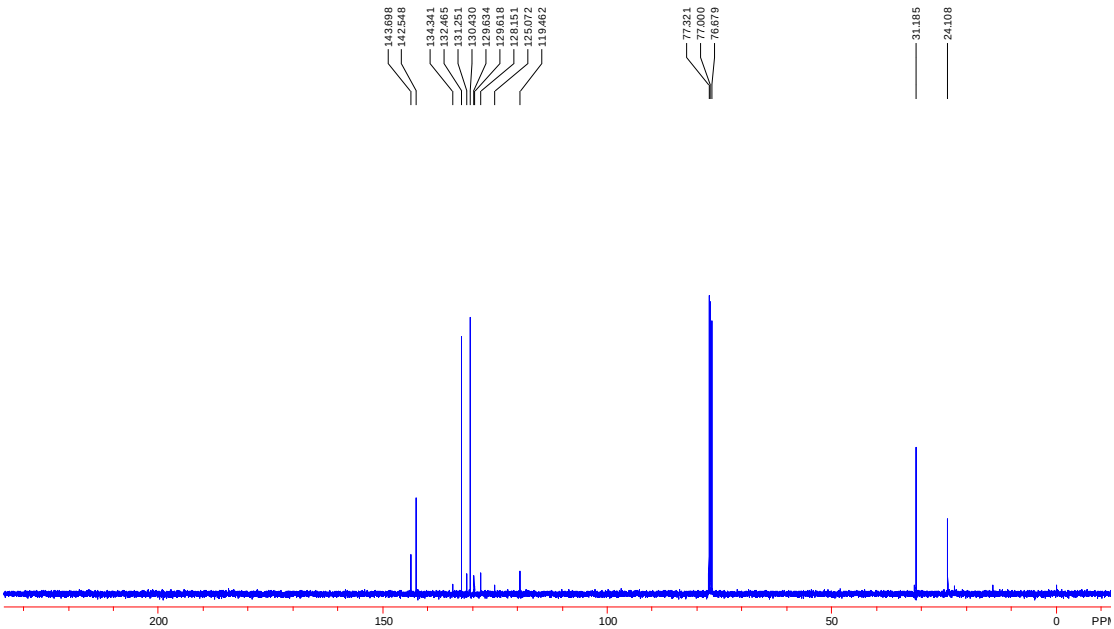
^{19}F NMR (376 MHz, $CDCl_3$)

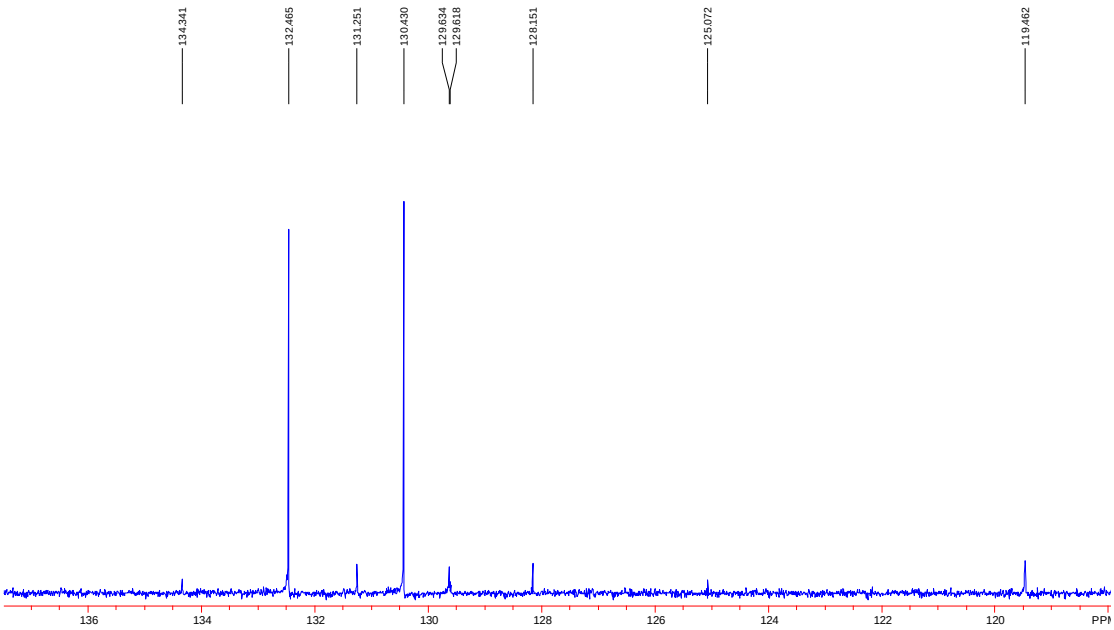


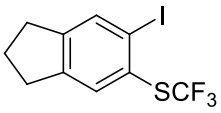


2c

^{13}C NMR (100 MHz, $CDCl_3$)

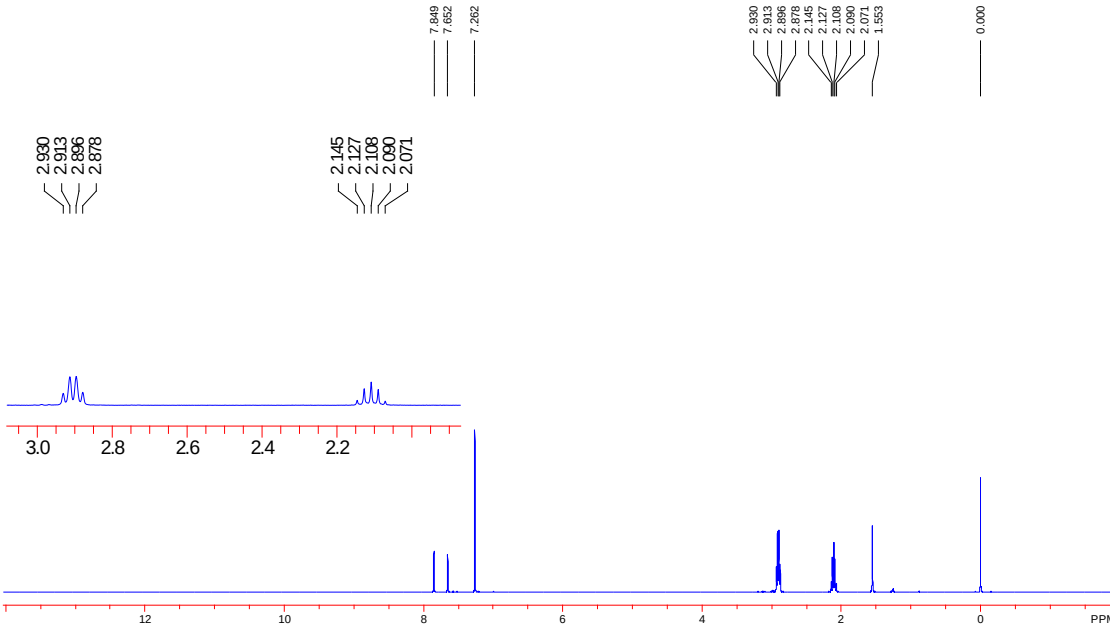


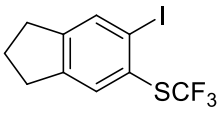




2d

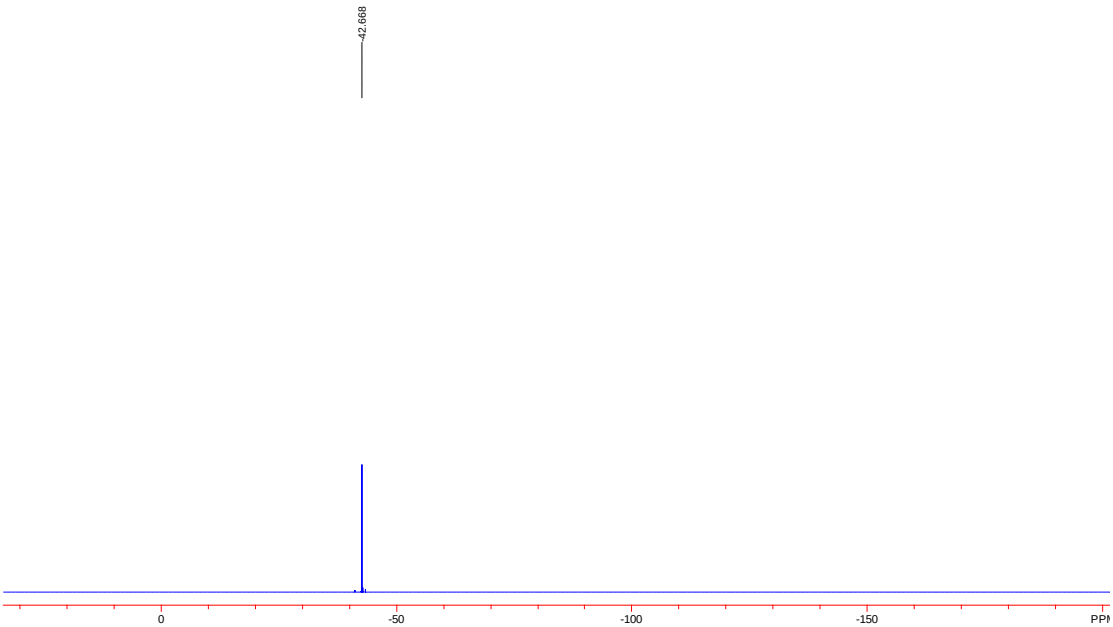
^{1}H NMR (400 MHz, $CDCl_3$)

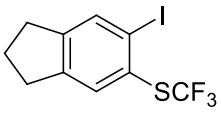




2d

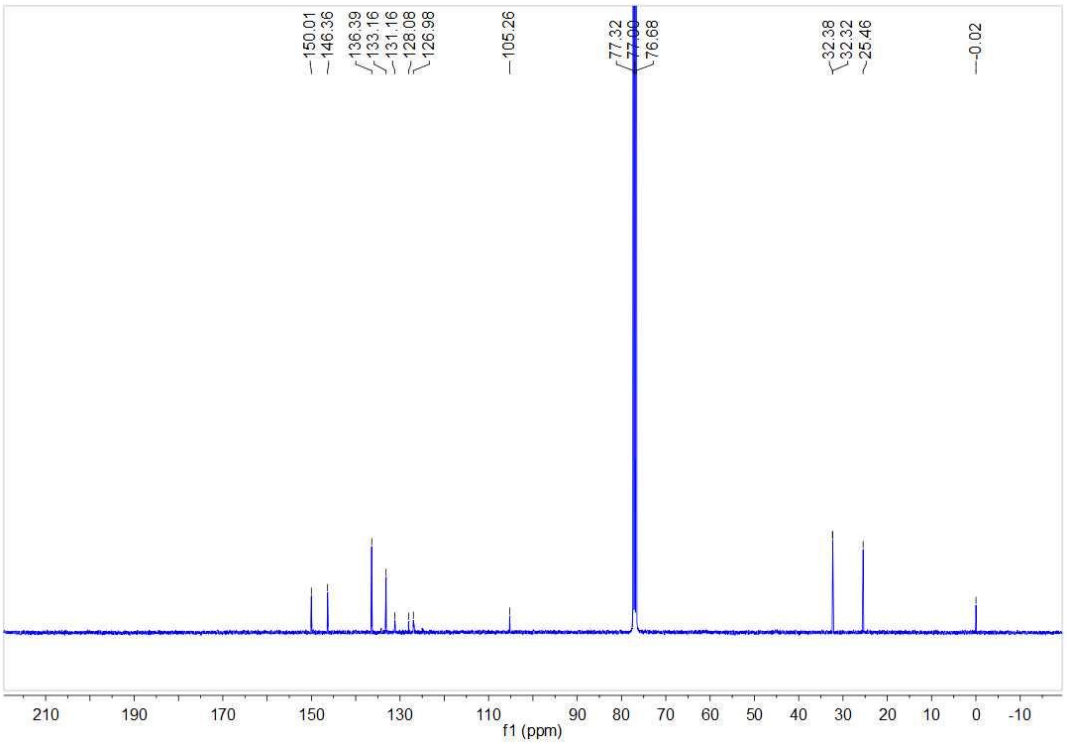
^{19}F NMR (376 MHz, $CDCl_3$)

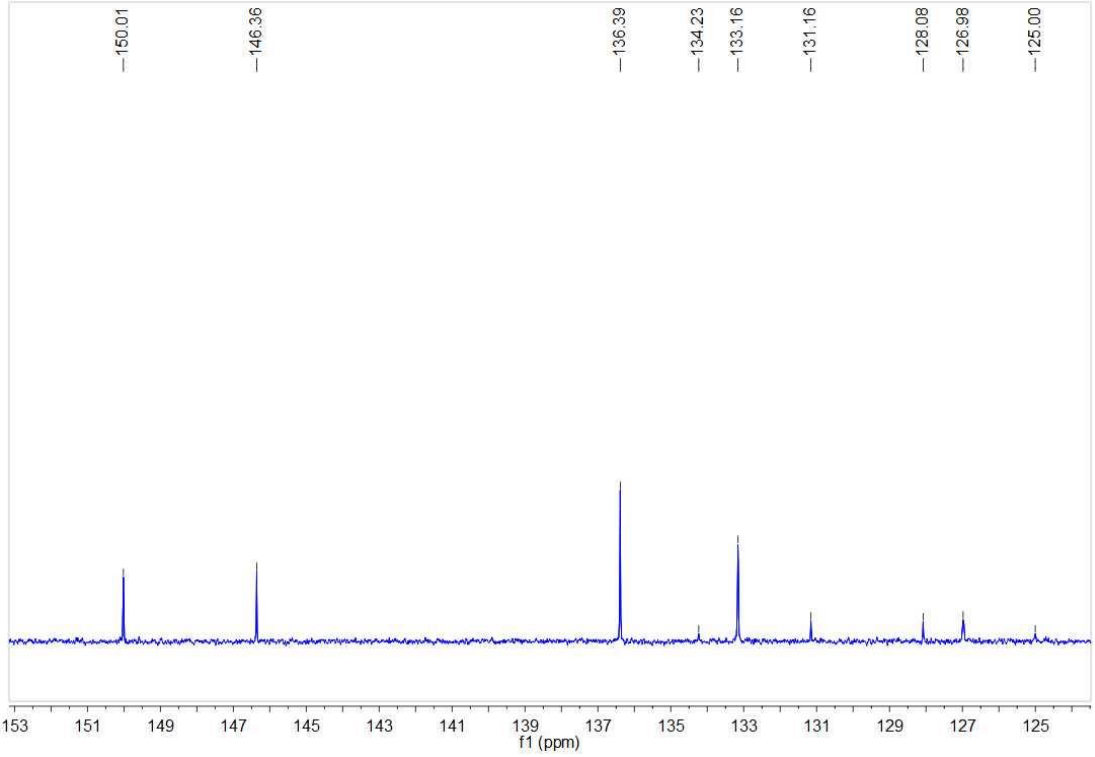


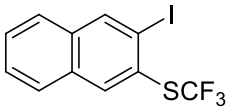


2d

^{13}C NMR (100 MHz, $CDCl_3$)

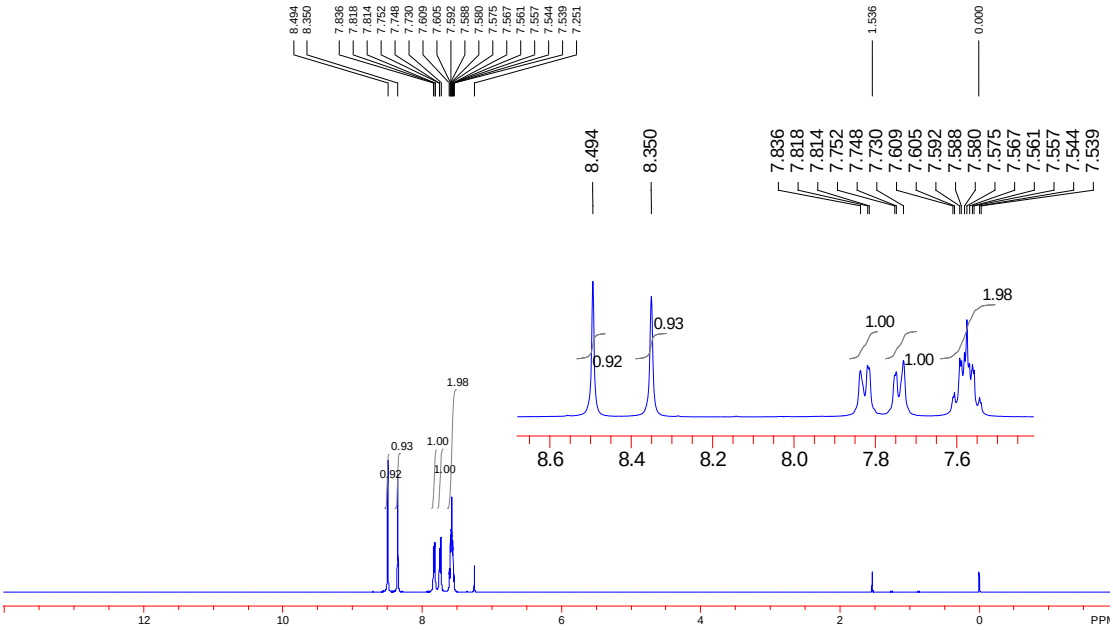


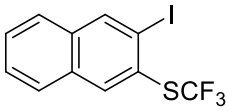




2e

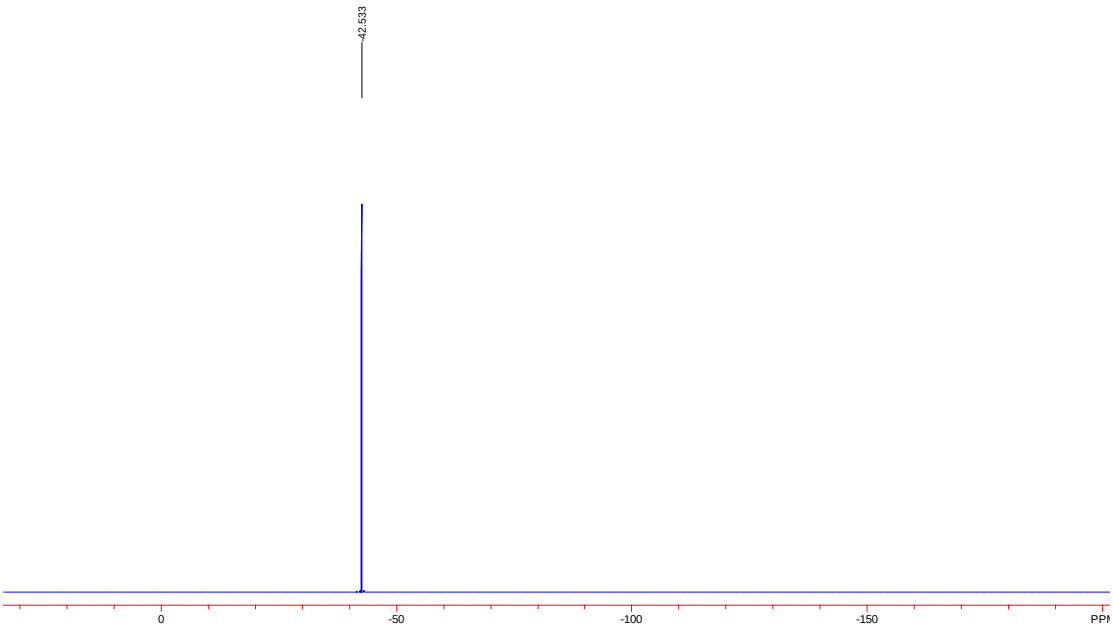
^{1}H NMR (400 MHz, $CDCl_3$)

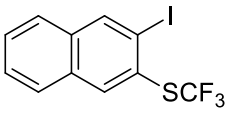




2e

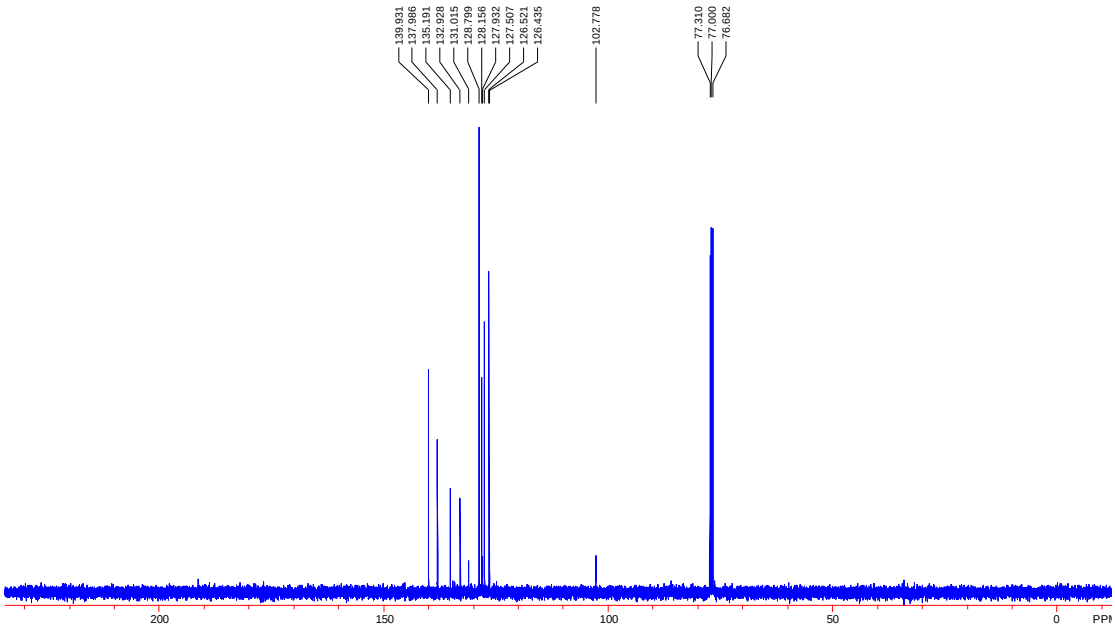
^{19}F NMR (376 MHz, $CDCl_3$)

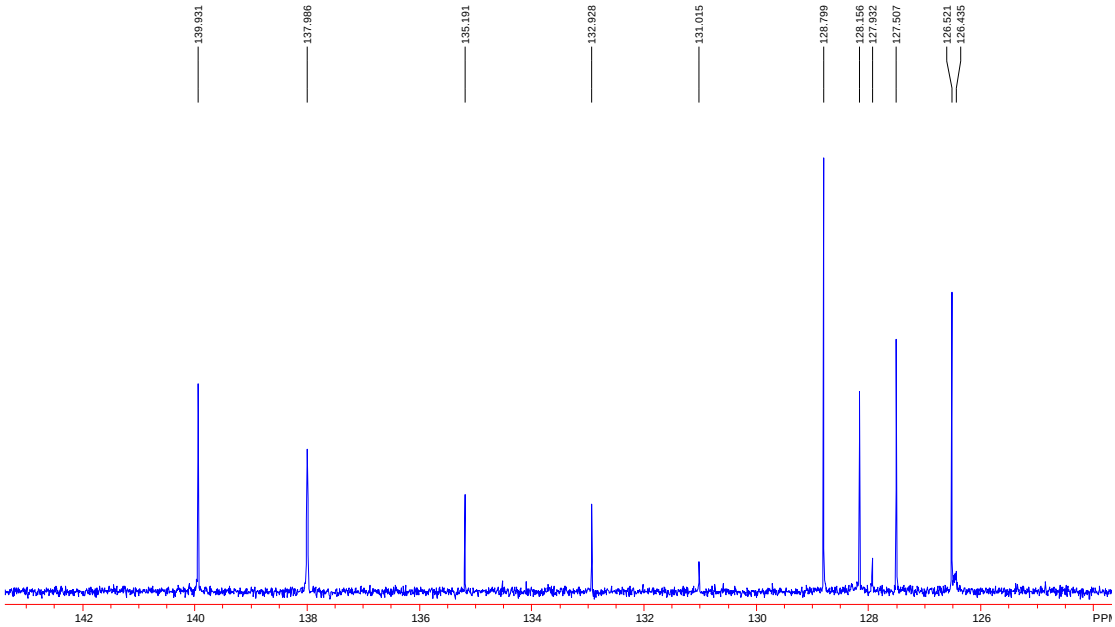


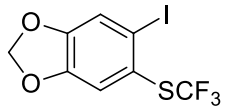


2e

^{13}C NMR (100 MHz, $CDCl_3$)

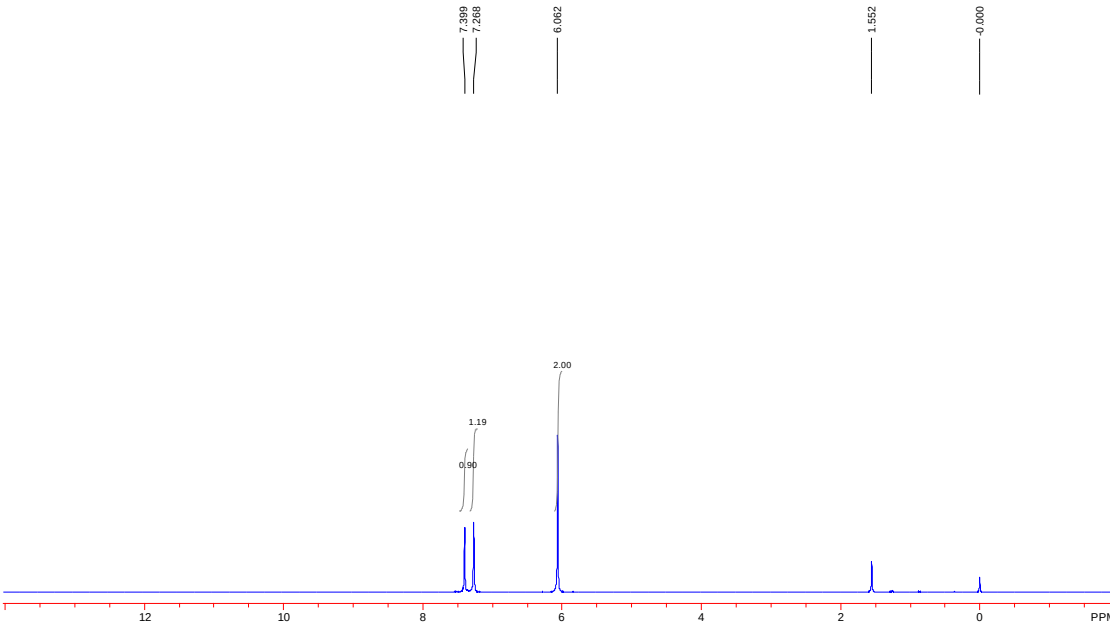


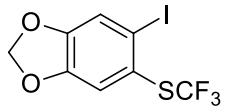




2f

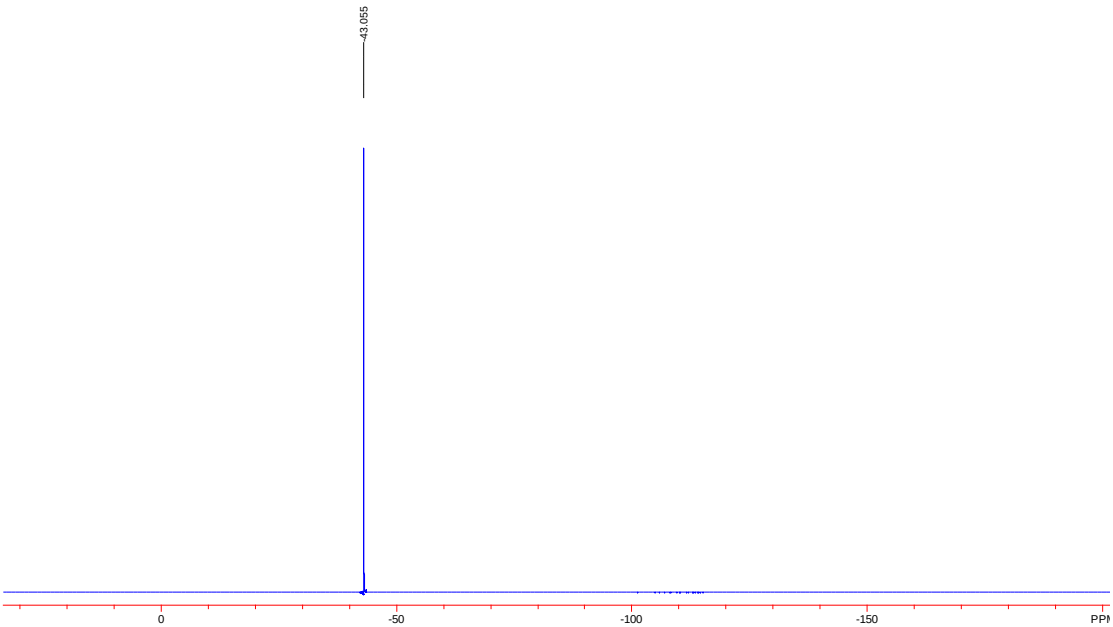
^{1}H NMR (400 MHz, $CDCl_3$)

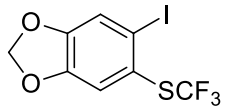




2f

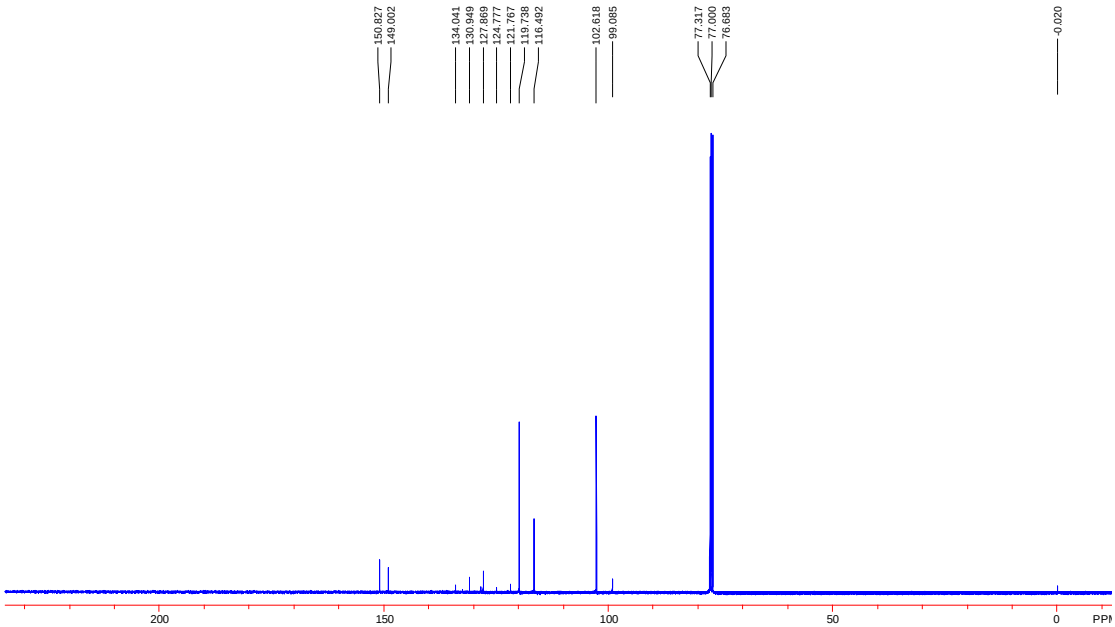
^{19}F NMR (376 MHz, $CDCl_3$)

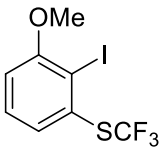




2f

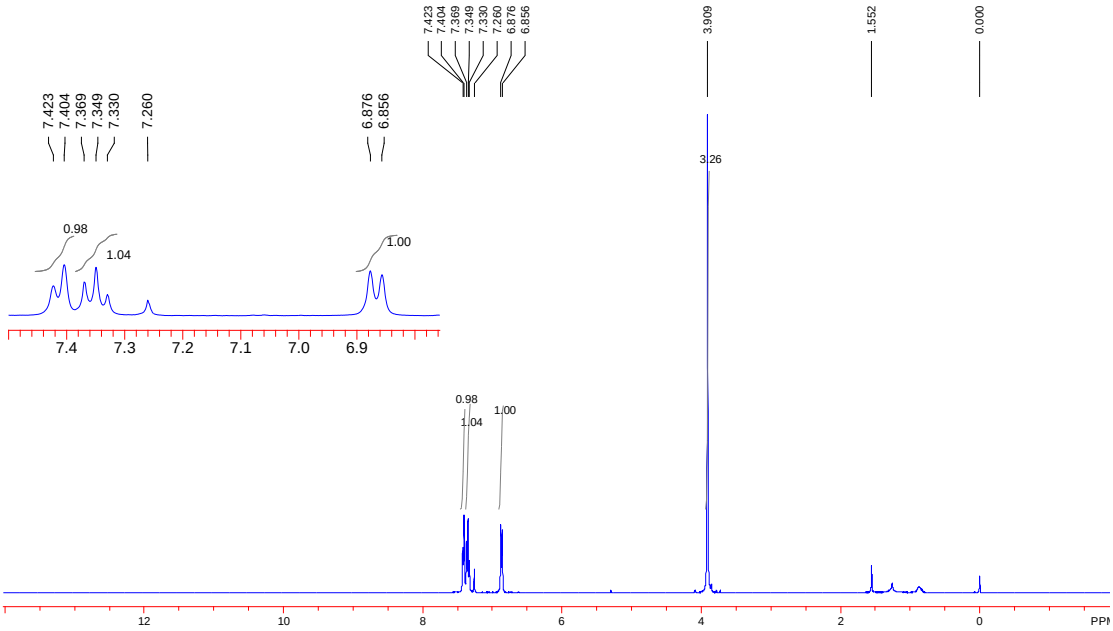
^{13}C NMR (100 MHz, $CDCl_3$)

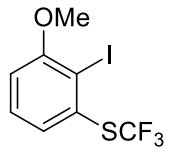




2g

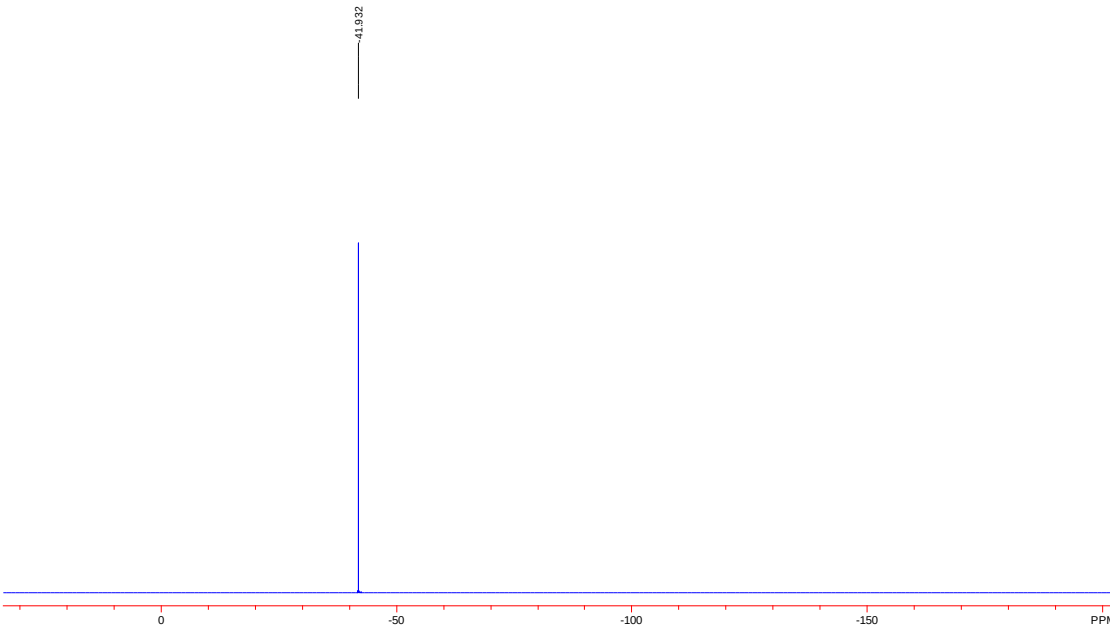
^{1}H NMR (400 MHz, $CDCl_3$)

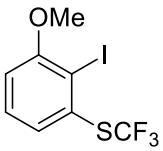




2g

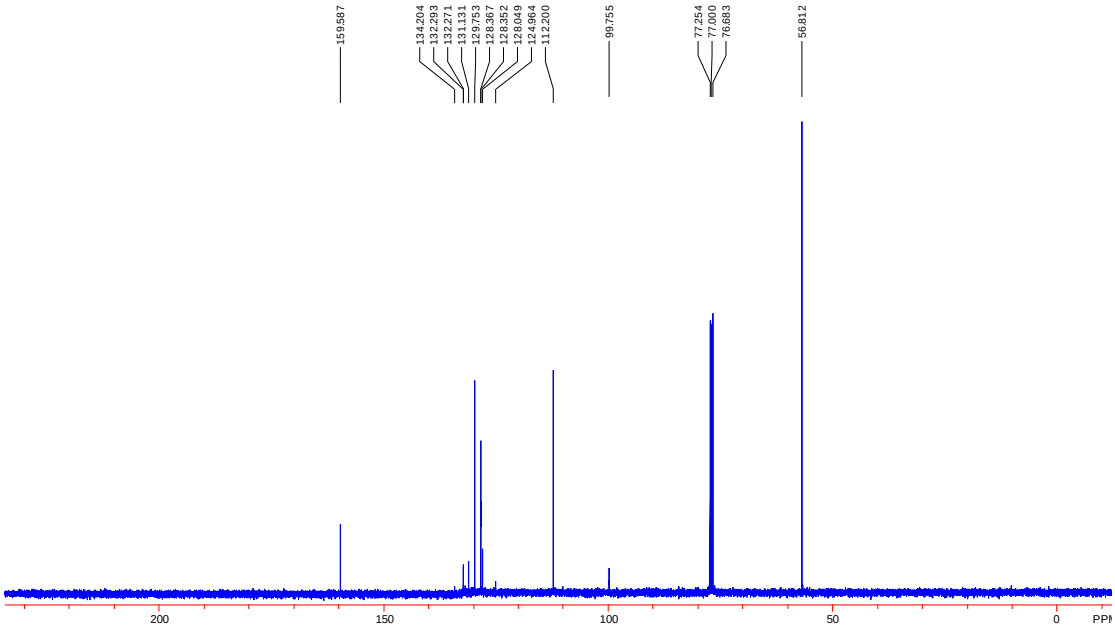
^{19}F NMR (376 MHz, $CDCl_3$)

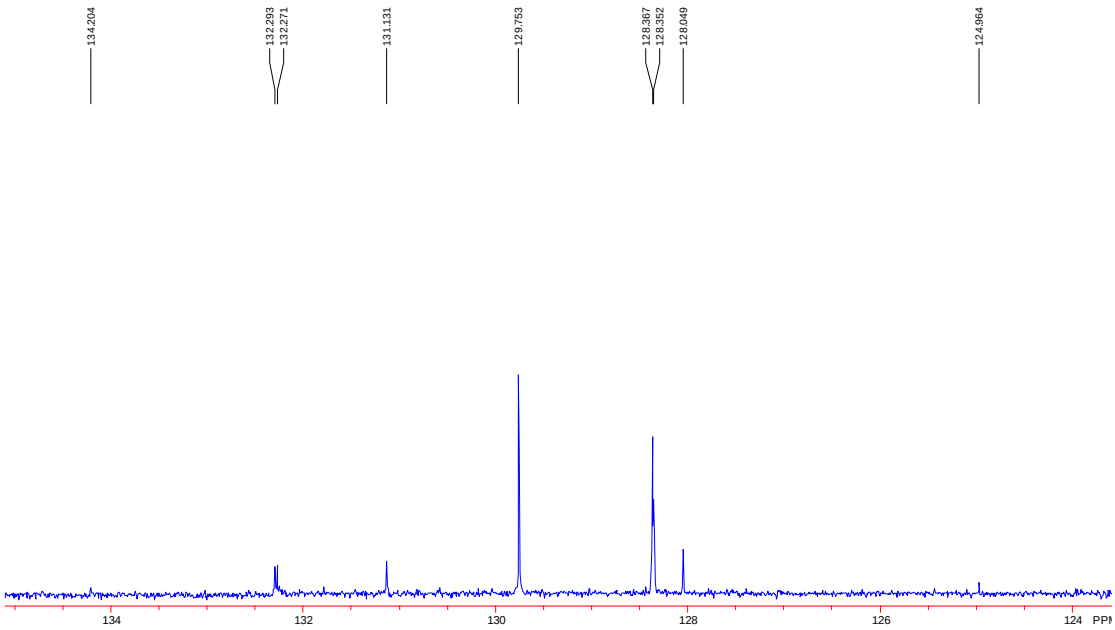


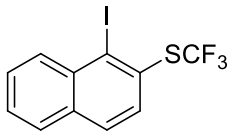


2g

^{13}C NMR (100 MHz, $CDCl_3$)

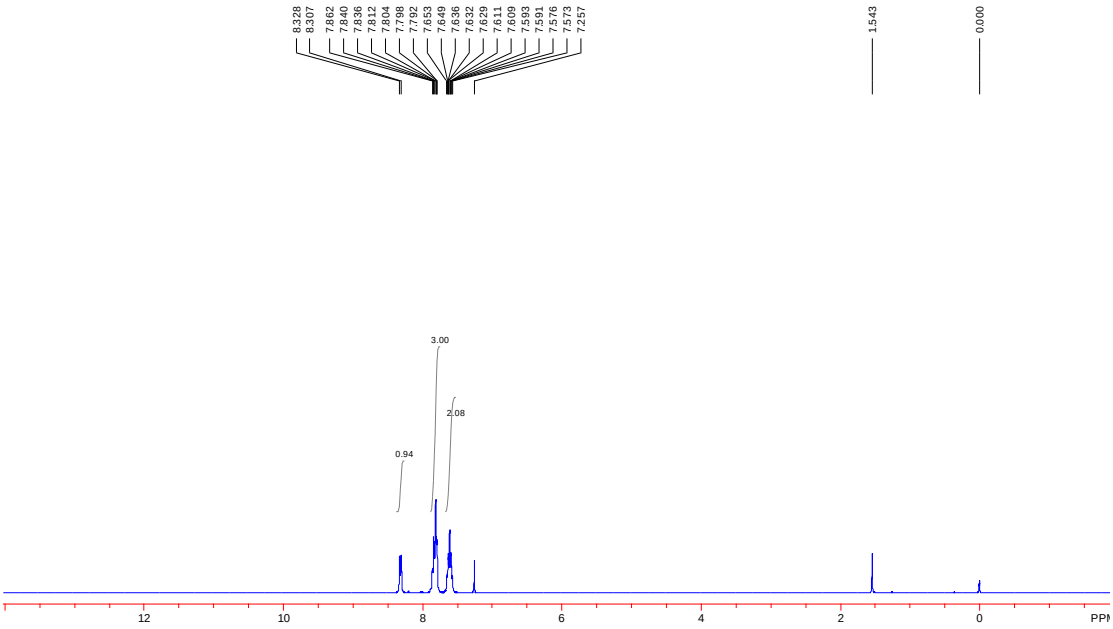


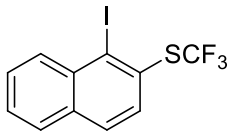




2ha

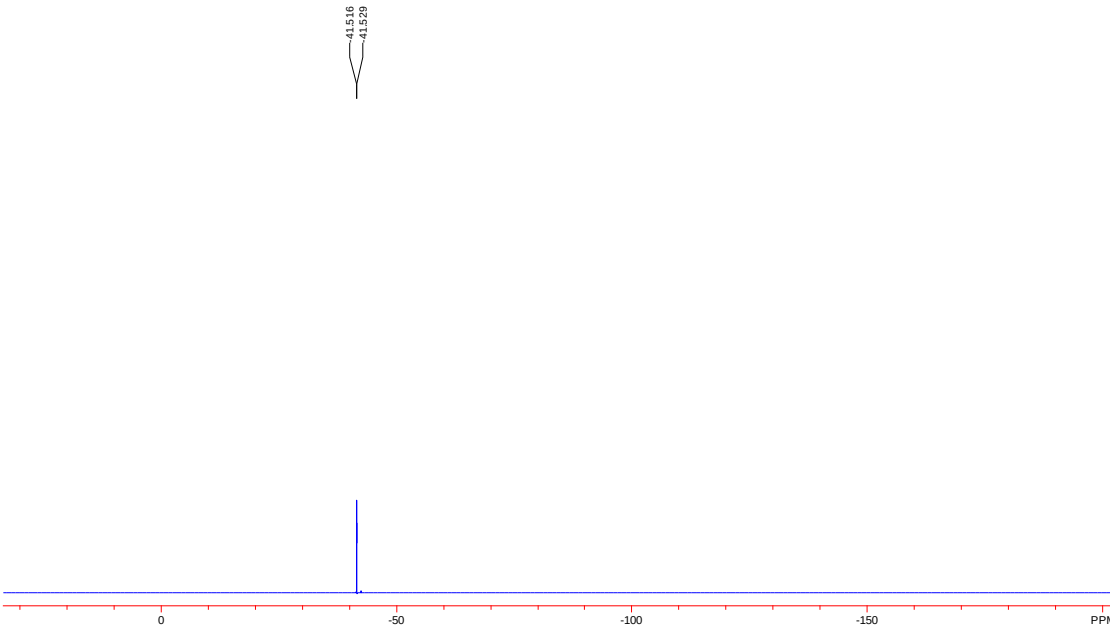
^{1}H NMR (400 MHz, $CDCl_3$)

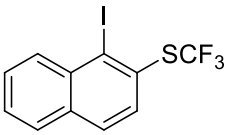




2ha

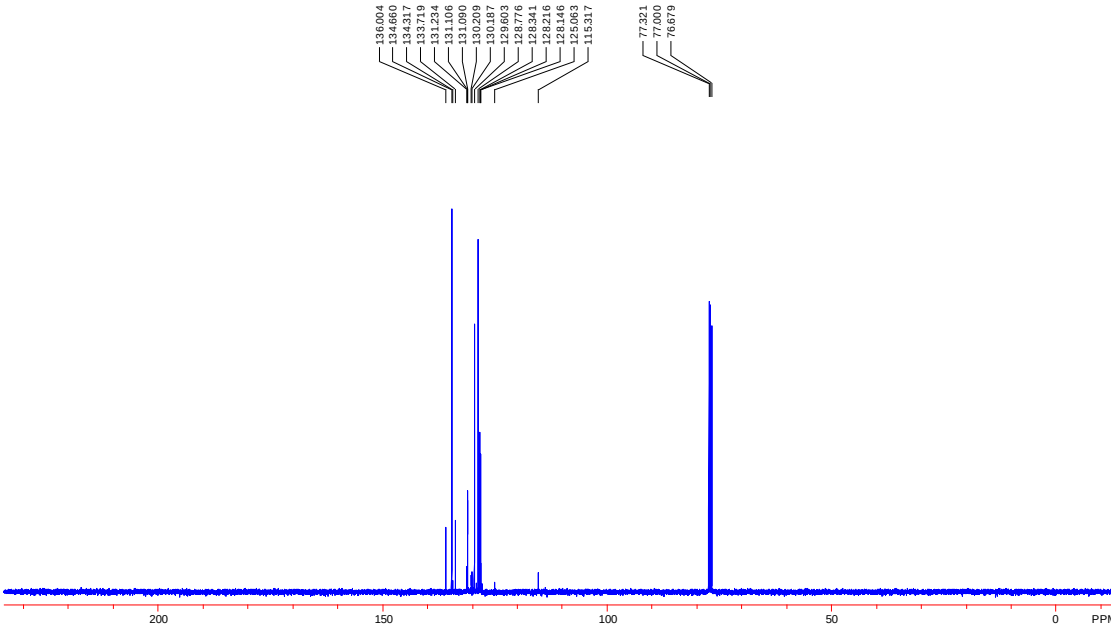
^{19}F NMR (376 MHz, $CDCl_3$)

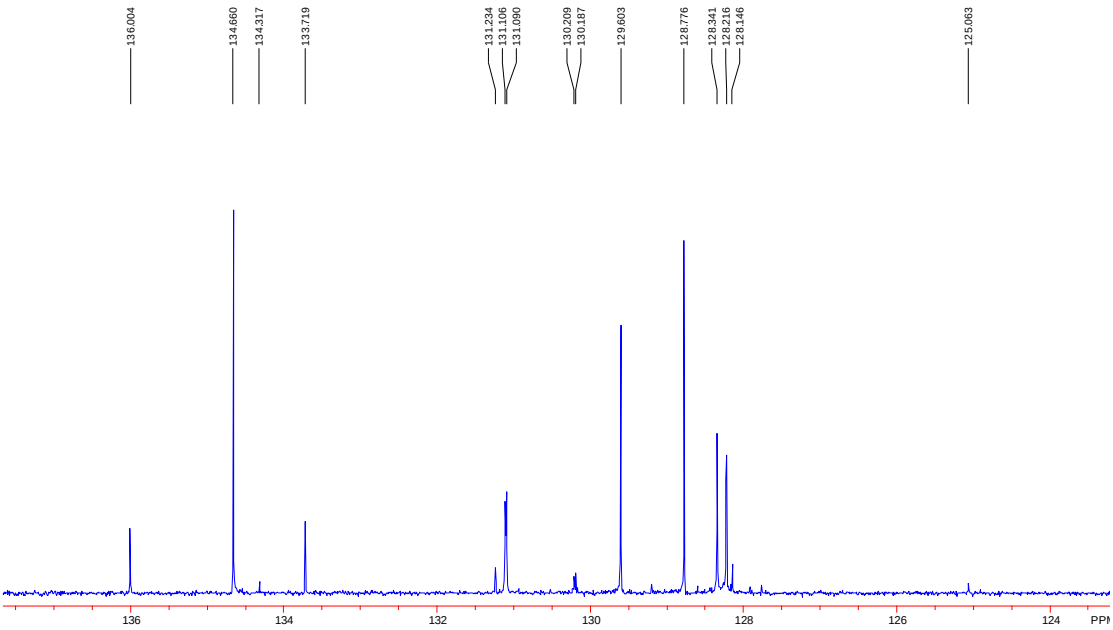


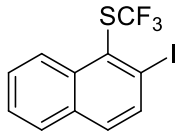


2ha

^{13}C NMR (100 MHz, $CDCl_3$)

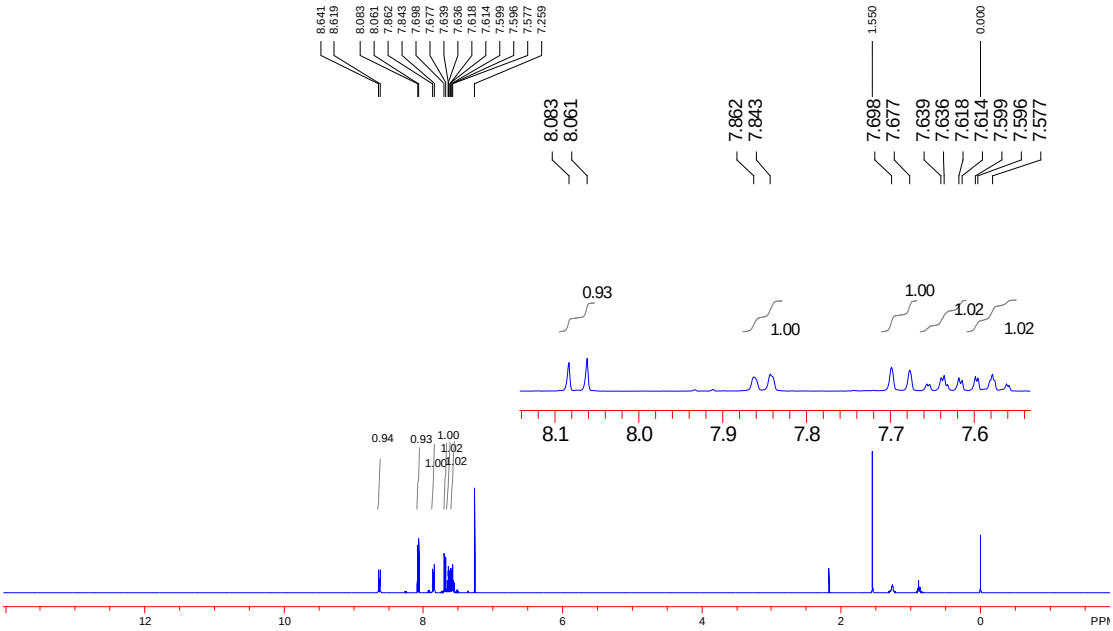


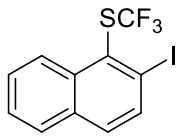




2hb

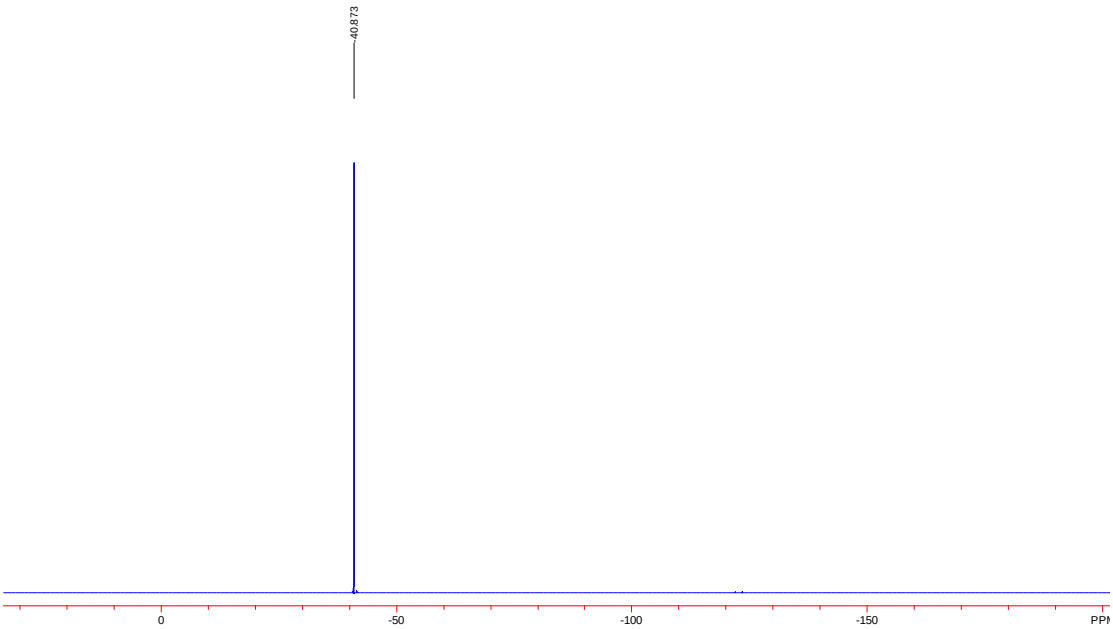
^{1}H NMR (400 MHz, $CDCl_3$)

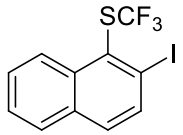




2hb

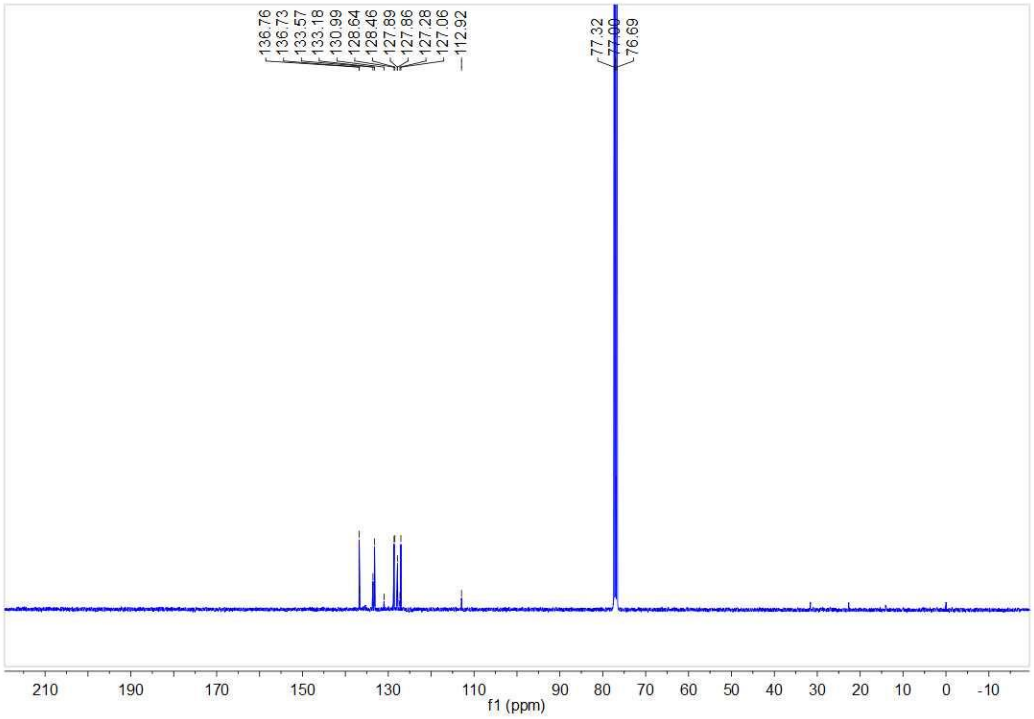
^{19}F NMR (376 MHz, $CDCl_3$)

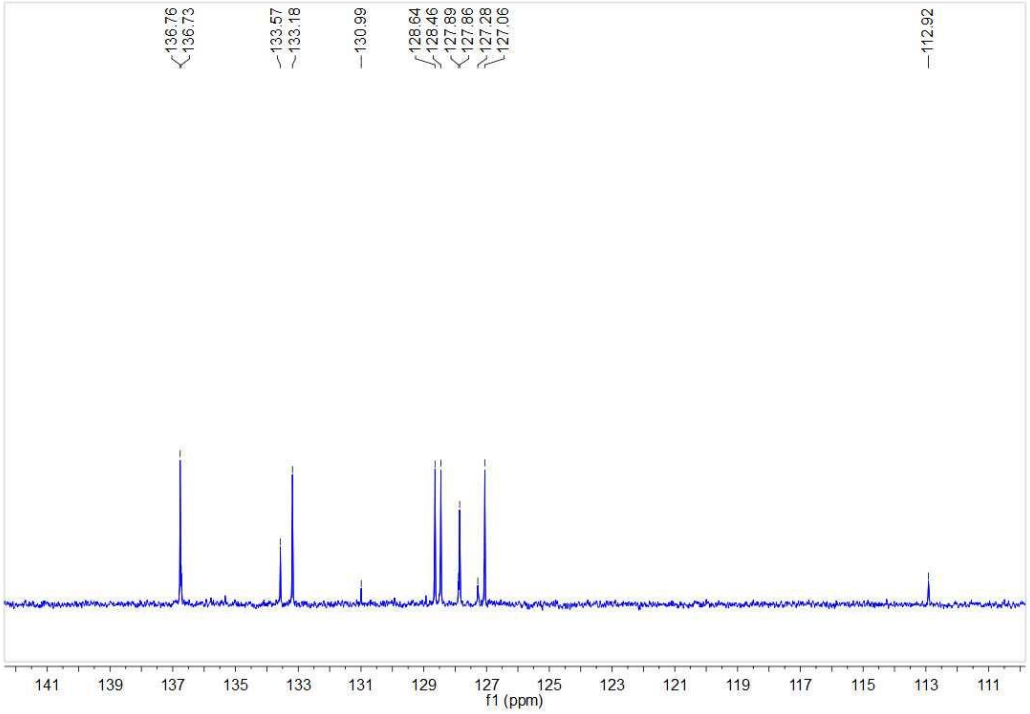


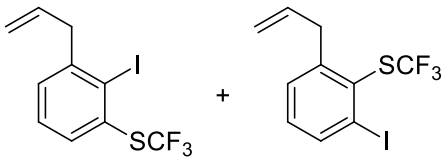


2hb

^{13}C NMR (100 MHz, $CDCl_3$)

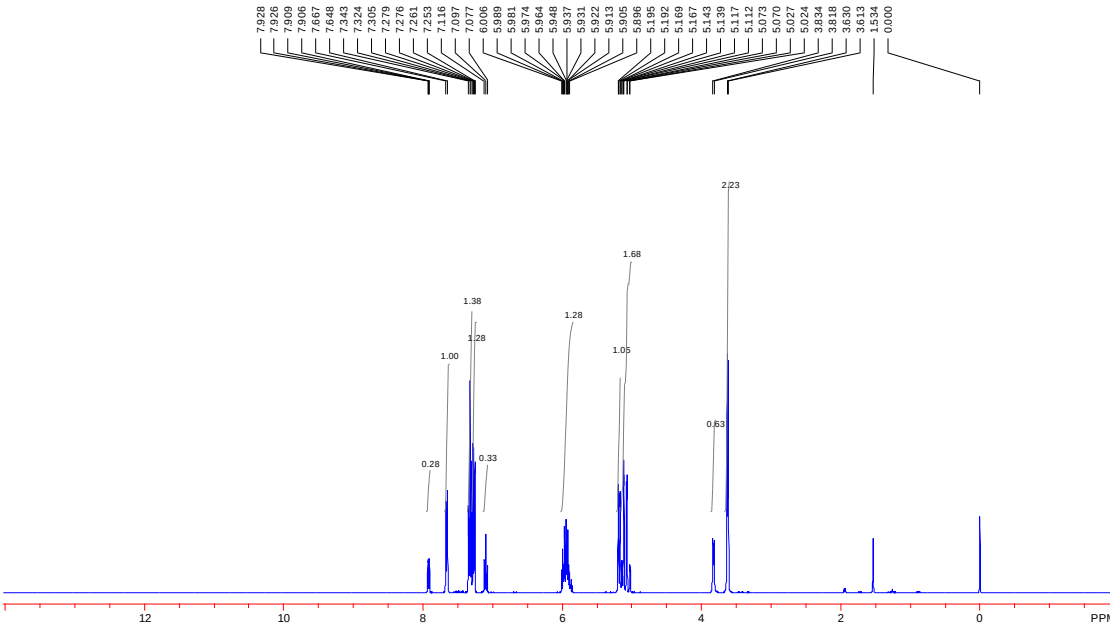


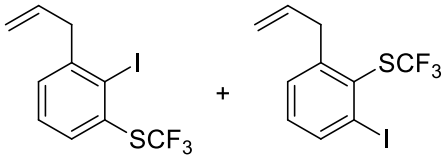




2i

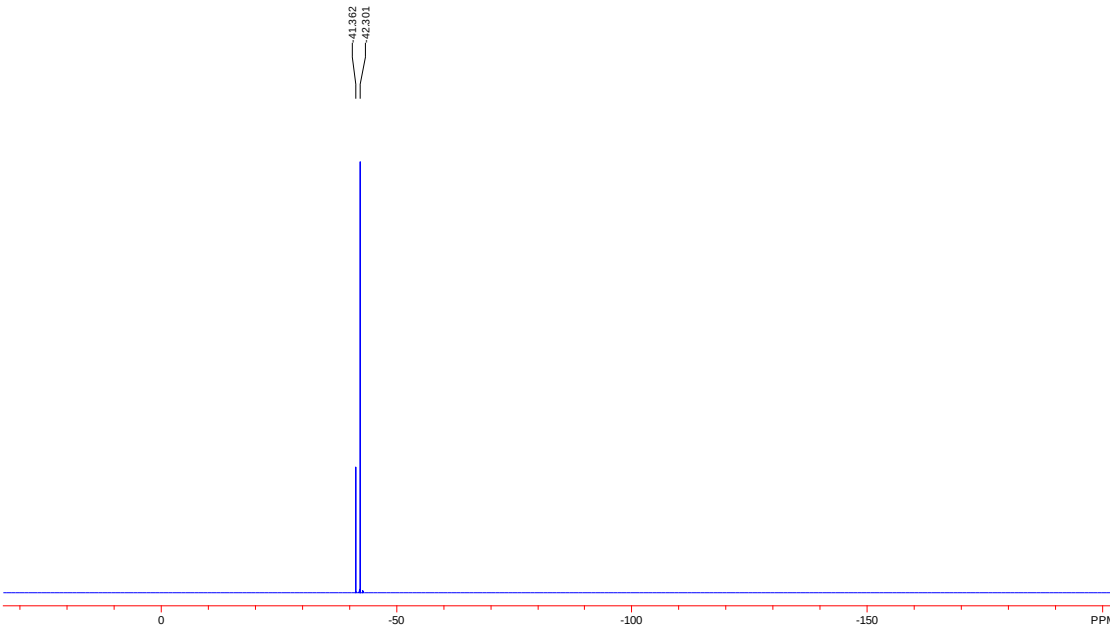
^{1}H NMR (400 MHz, $CDCl_3$)

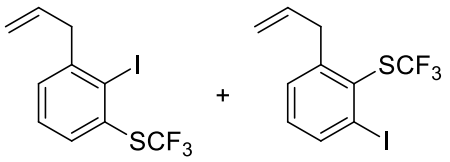




2i

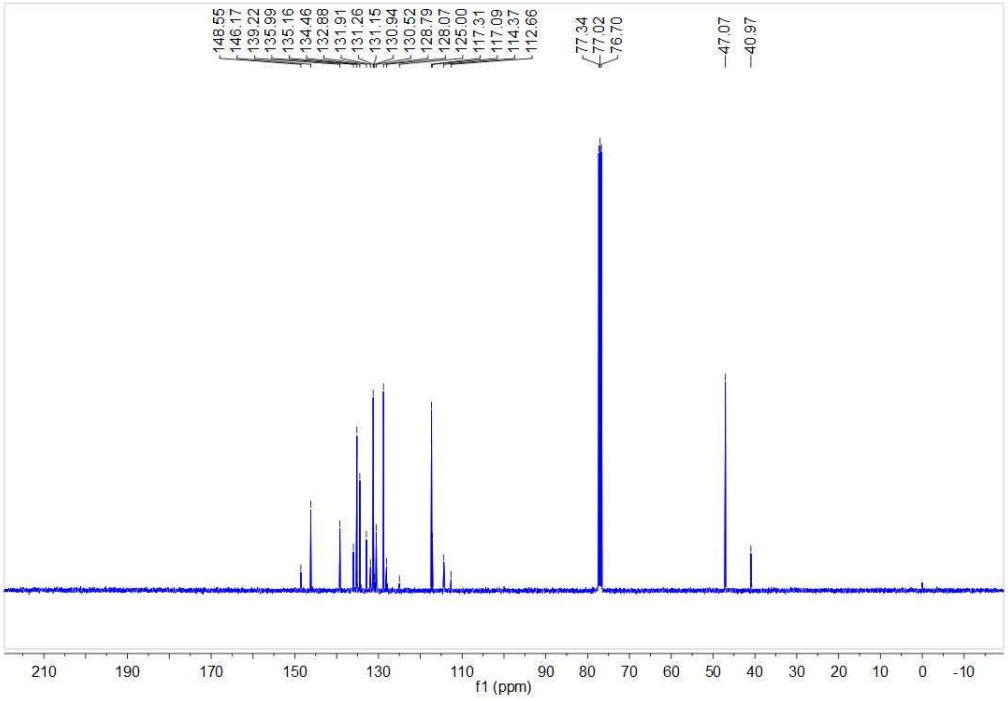
^{19}F NMR (376 MHz, $CDCl_3$)

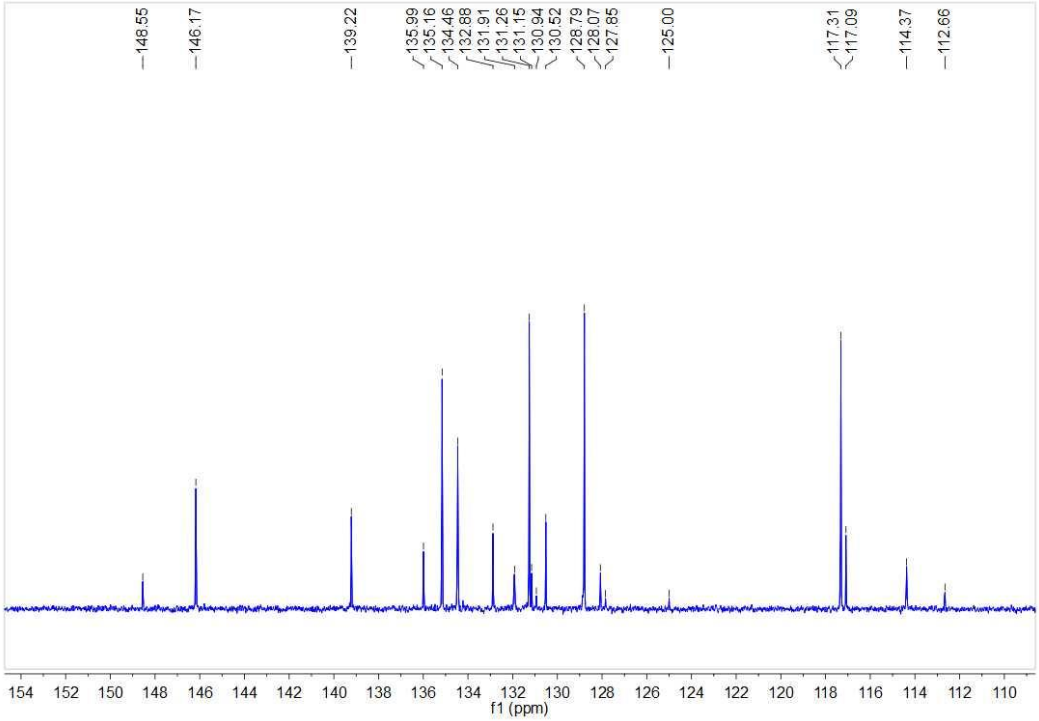


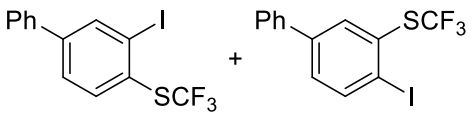


2i

^{13}C NMR (100 MHz, $CDCl_3$)

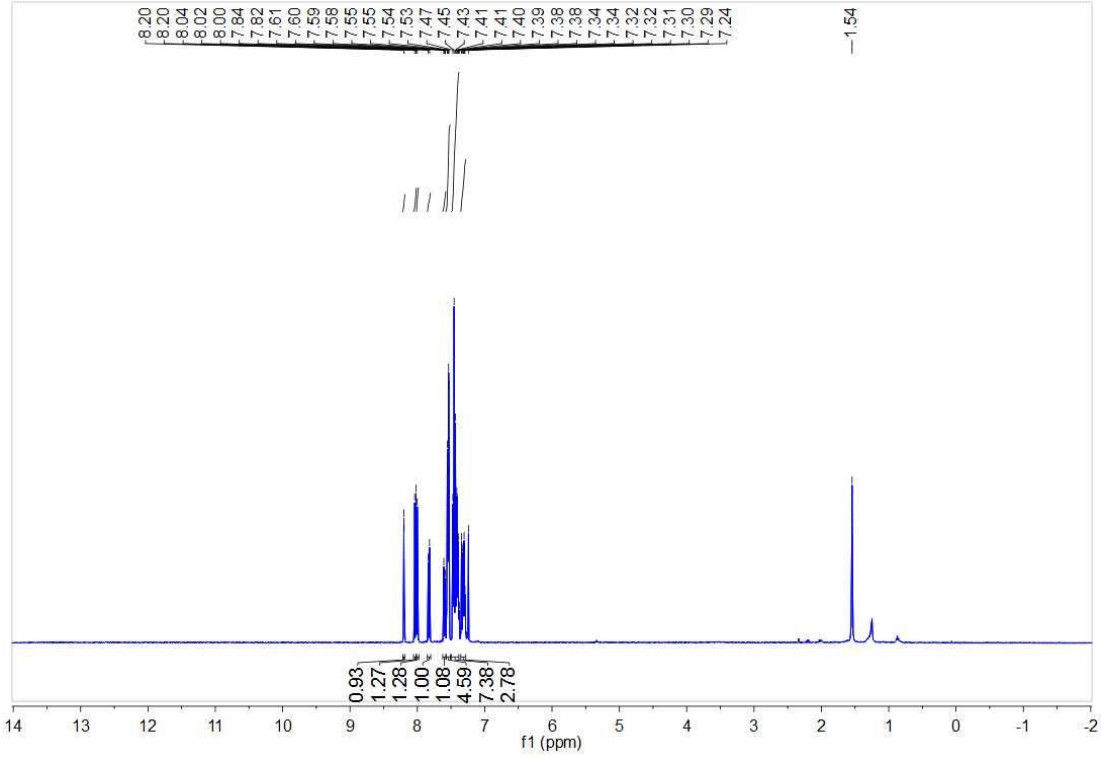


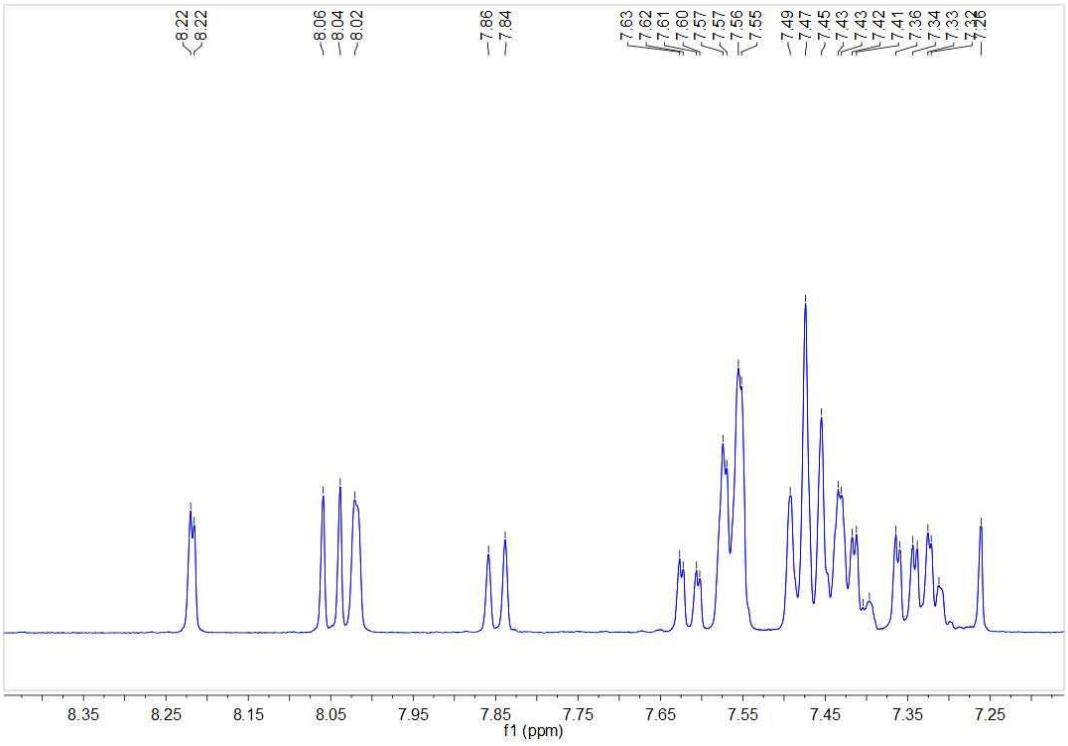


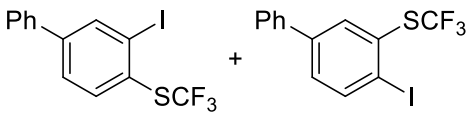


2j

^{1}H NMR (400 MHz, $CDCl_3$)

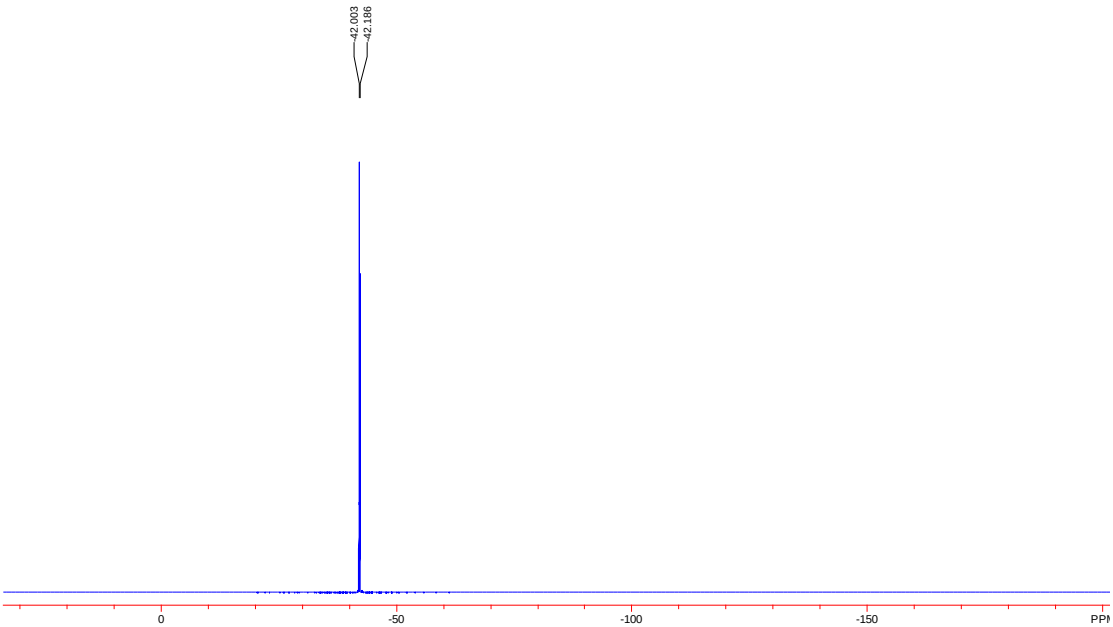


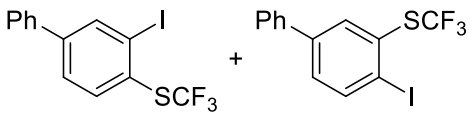




2j

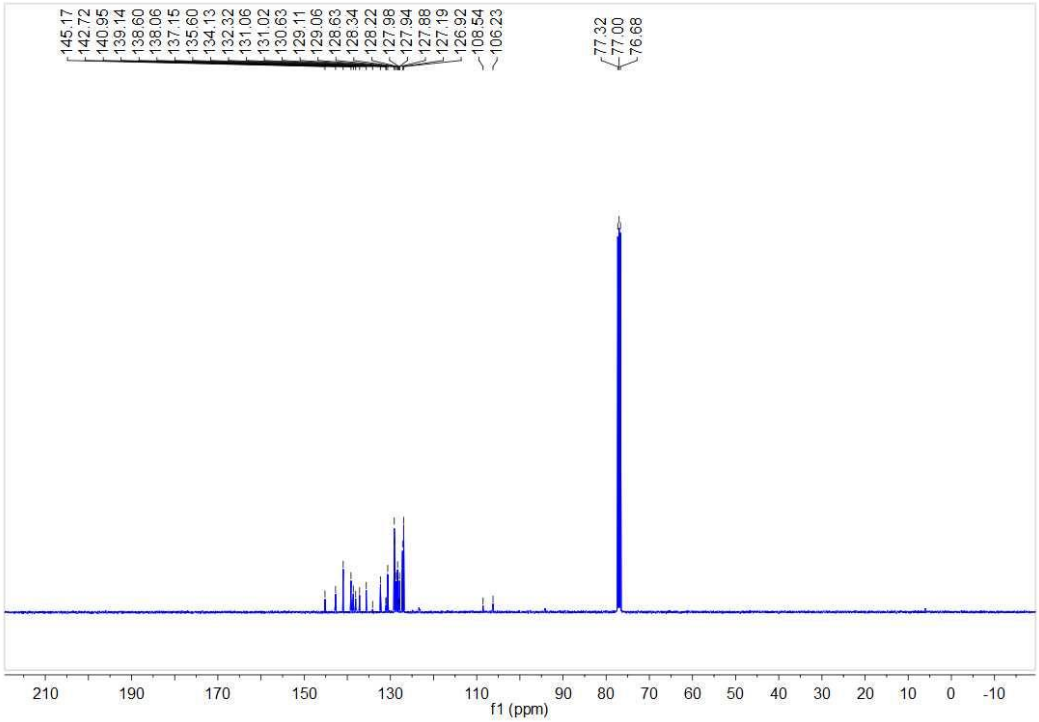
^{19}F NMR (376 MHz, $CDCl_3$)

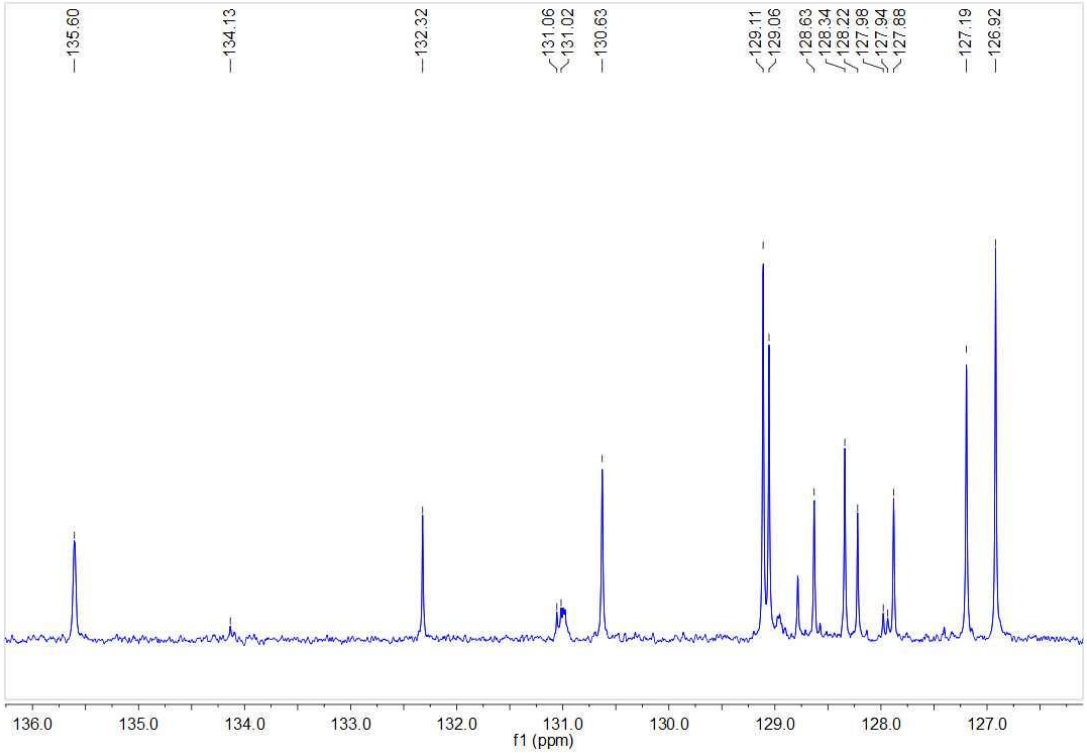


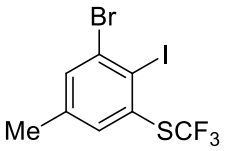


2j

^{13}C NMR (100 MHz, $CDCl_3$)

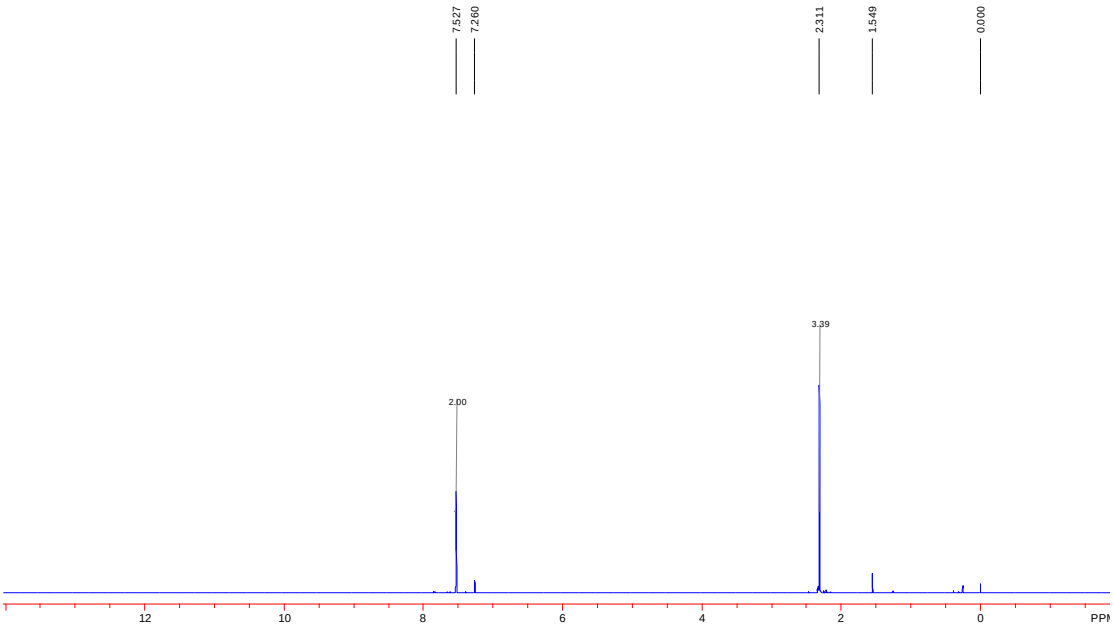


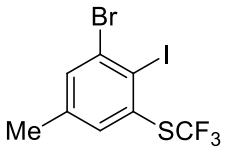




2k

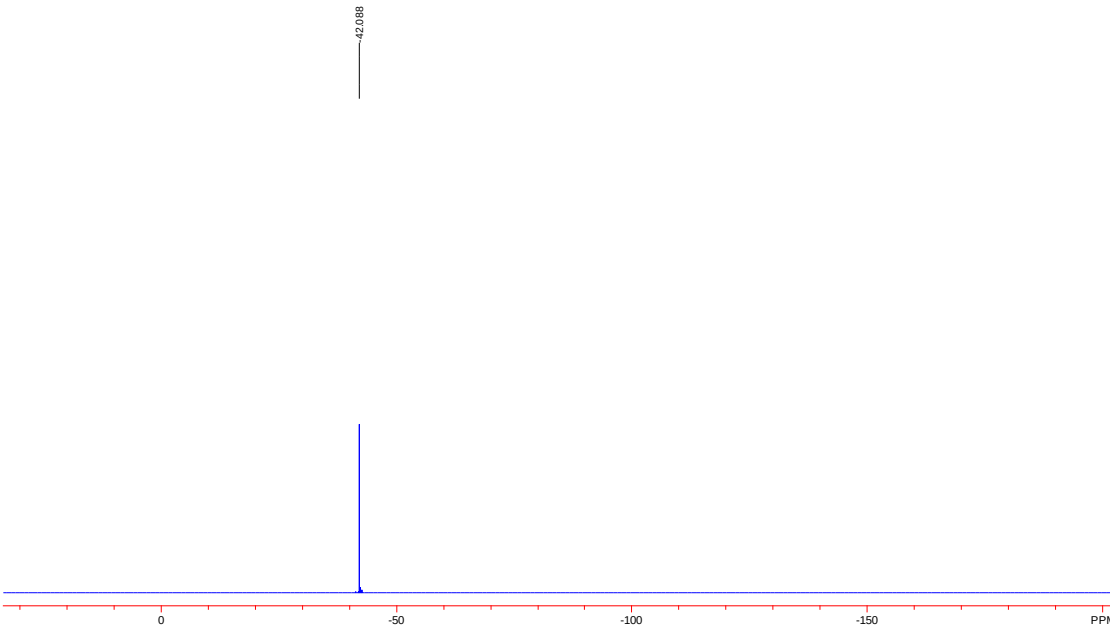
^{1}H NMR (400 MHz, $CDCl_3$)

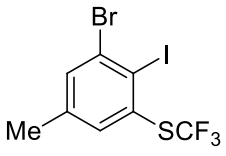




2k

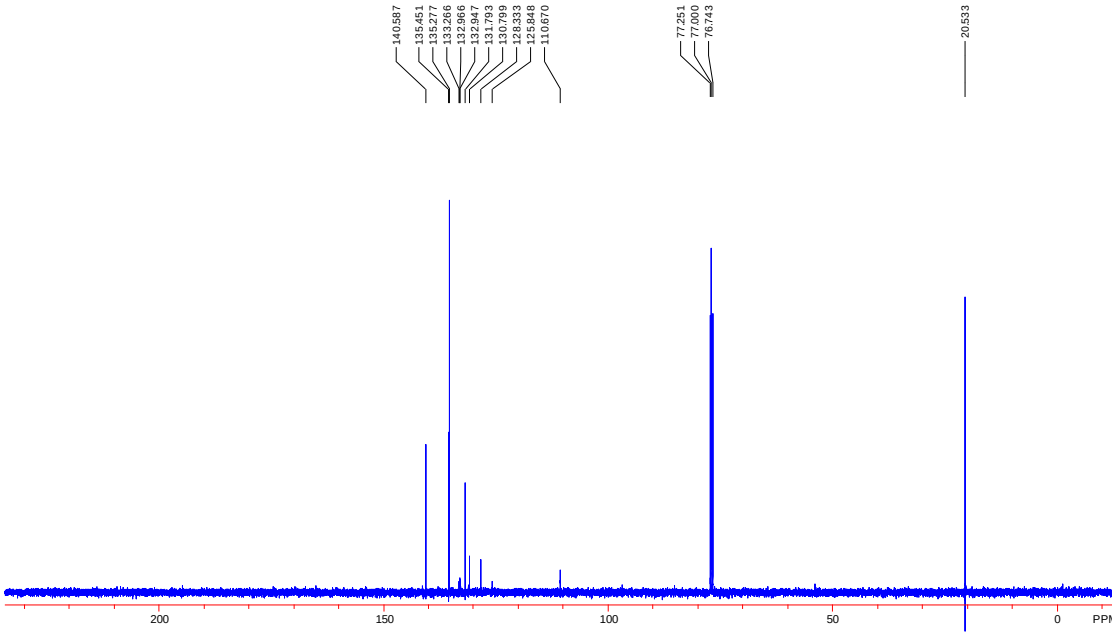
^{19}F NMR (376 MHz, $CDCl_3$)

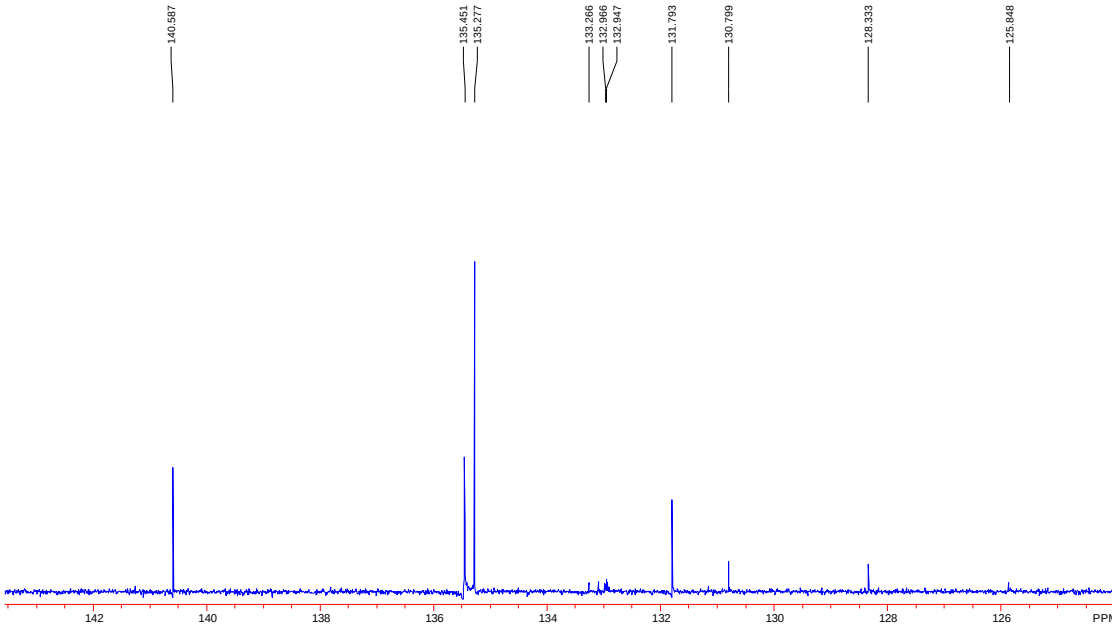


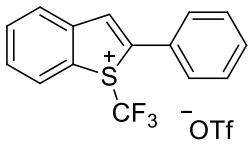


2k

^{13}C NMR (125 MHz, $CDCl_3$)

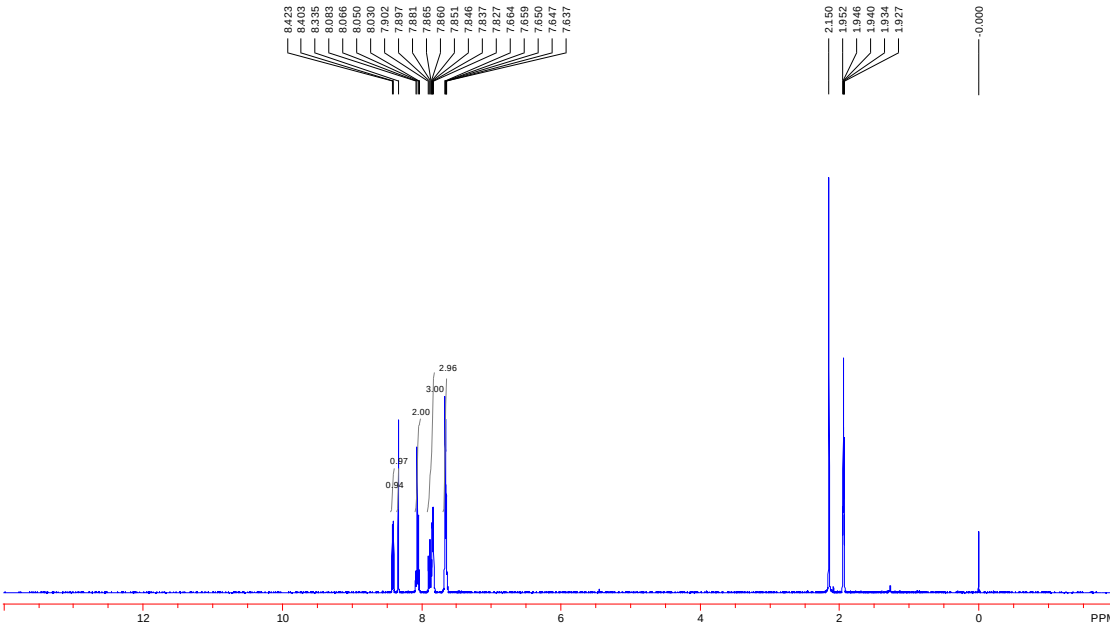


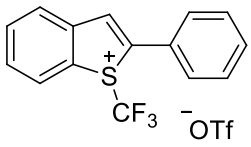




3a

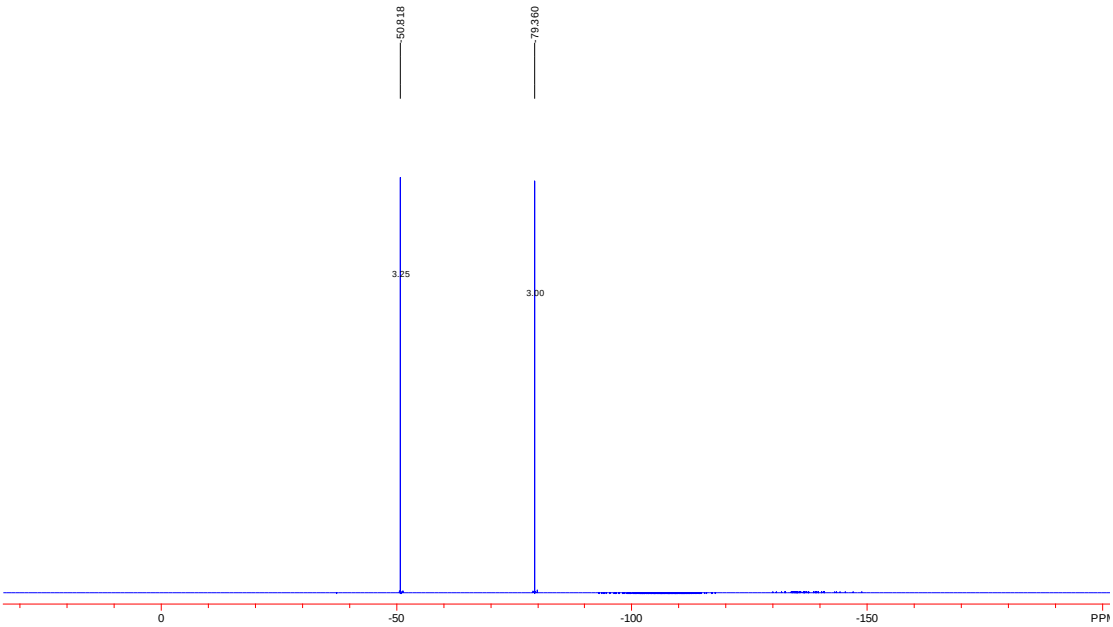
^{1}H NMR (400 MHz, CD_3CN)

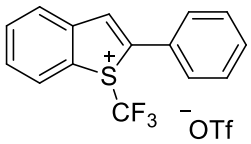


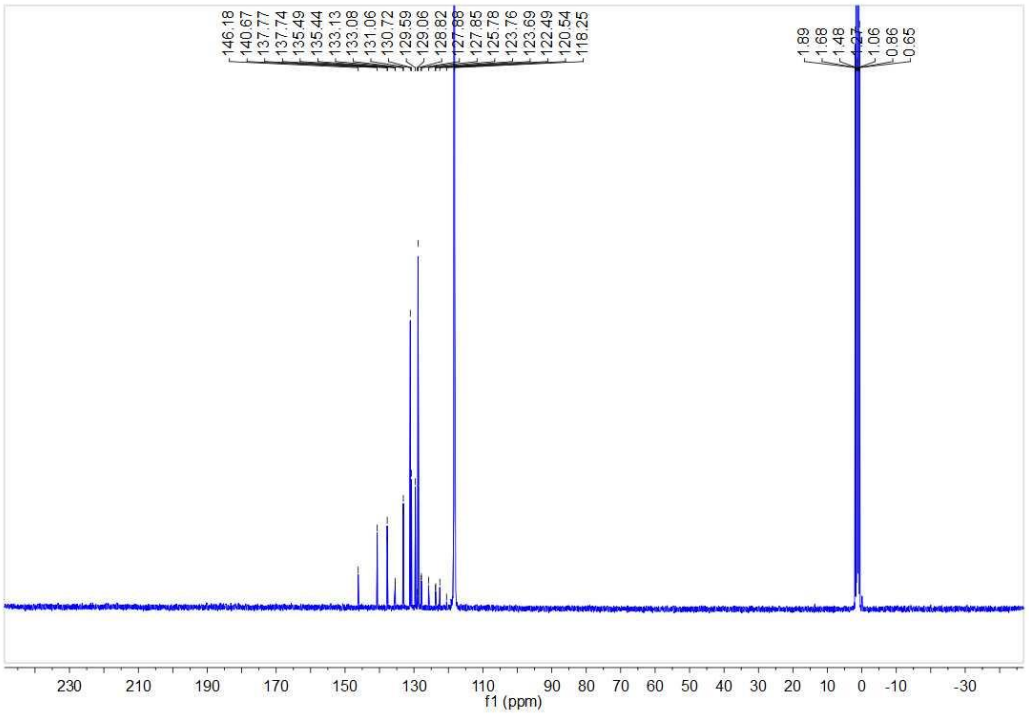
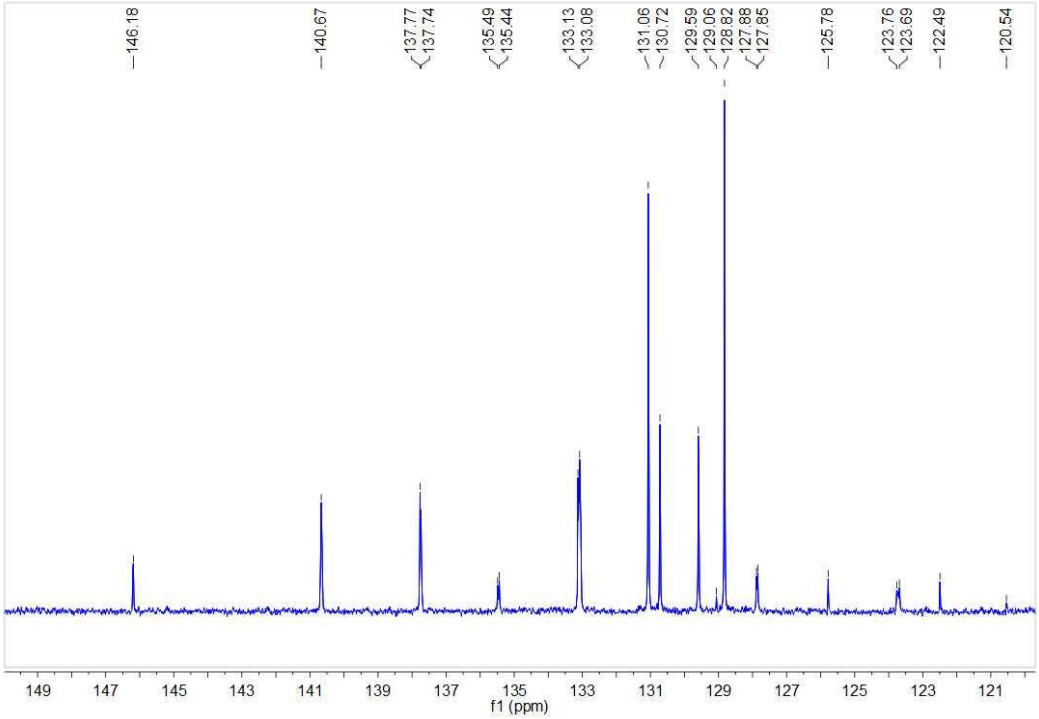


3a

^{19}F NMR (376 MHz, CD_3CN)





3a

^{13}C NMR (100 MHz, CD_3CN)