Supplementary Information

for

Organocatalytic Synthesis of Perfluorophenylsulfides via Thiolation of Trimethyl(perfluorophenyl)silanes and Thiosulfonates

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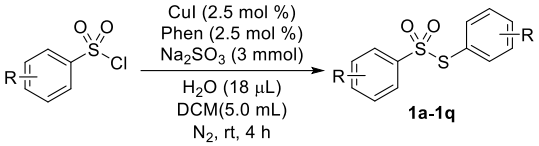
1. General Information

Unless otherwise indicated, all reactions were conducted under N_2 atmosphere in oven-dried glassware with magnetic stirring bar. All other chemicals were obtained from commercial supplies and used as received without any further purification. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F_{254}. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz, 100 MHz and 376 MHz, respectively), Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ^1H NMR and ^{13}C NMR. High-resolution mass spectra (HRMS) were obtained on a Q Exactive mass spectrometry equipped with an APCI source from Thermo Scientific.

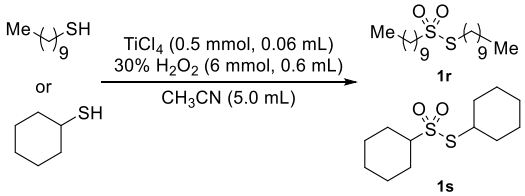
2. Experimental Section

2.1 General procedure for synthesis of substrates 1a-1q:



Substrates **1a-1q** were prepared according to the known literature.[1] CuI (2.5 mol%) and 1, 10-Phen·H_2O (2.5 mol%) were added to a mixture of arenesulfonyl chloride (1 mmol), sodium sulfite (3 mmol) and H_2O (18 μL) in DCM (5 mL), then the mixture was stirred at room temperature for 4 h under a nitrogen atmosphere (monitored by TLC). After completion of the reaction, the mixture was diluted with CH_2Cl_2 and washed with water, the organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (200−300 mesh) using petroleum ether and CH_2Cl_2 (v/v = 1:1) as the eluent to give thiosulfonate.

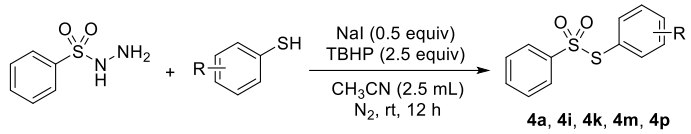
2.2 General procedure for synthesis of substrates 1r-1s:



Substrates **1r** and **1s** were prepared according to the known literature.[2] To a mixture of thiol (2 mmol) and 30% H_2O_2 (6 mmol, 0.6 mL) in CH_3CN (5 mL), $TiCl_4$ (0.5 mmol, 0.06 mL) was added. The mixture was then reacted at room temperature. After consumption of the starting material detected by TLC, the mixture was poured into H_2O (15 mL). The aqueous phase was extracted with EtOAc (2×5 mL), the combination of organic phase was subsequently dried over anhydrous Na_2SO_4. The solvent was removed under vacuum affording crude product which was purified by

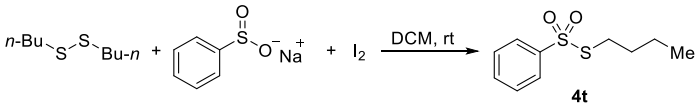
flash column chromatography on silica gel (200−300 mesh) using a mixture of petroleum ether and EtOAc (v/v = 10:1) as eluent to obtain clean thiosulfonate.

2.3 General procedure for synthesis of substrates 4a, 4i, 4k, 4m, 4p:



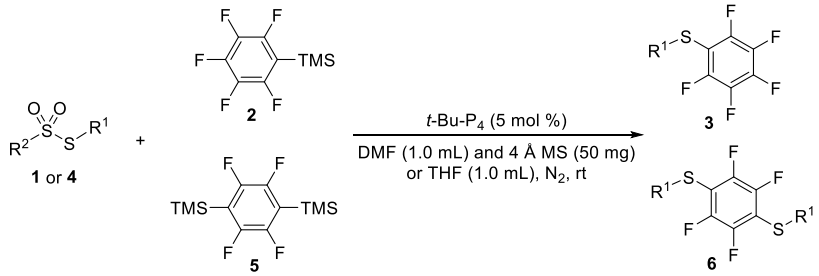
Substrates **4a, 4i, 4k, 4m, 4p** were prepared according to the known literature.[3] To a mixture of sulfonyl hydrazide (0.6 mmol), thiol (0.4 mmol), sodium iodide (0.2 mmol) in CH_3CN (2.5 mL) was added TBHP (1.0 mmol). The reaction mixture was then stirred at room temperature for 12 h. After removal of the solvent, the residue was subsequently purified by flash column chromatography on silica gel (200−300 mesh) using ethyl acetate in petroleum ether (v/v = 1:1) as the eluent to afford pure thiosulfonate.

2.4 Procedure for synthesis of substrates 4t:



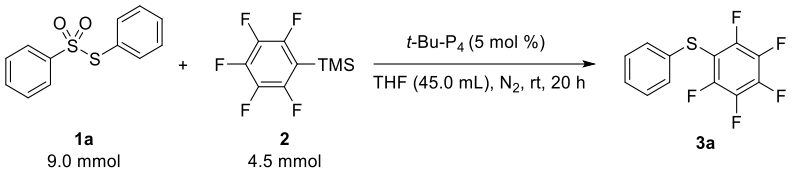
To a dried 50 mL bottom flask equipped with a magnetic stirring bar, was charged with dibutyl disulfide (0.5 mmol), sodium benzenesulfinate (1.6 mmol), iodine (1.0 mmol) and DCM (10 mL). The mixture was stirred for 22 h at room temperature. Then, $Na_2S_2O_3$ solution (0.10 M) was added to quench the excess of iodine. After separation of reaction mixtrure, the organic phase was washed with brine and dried. The organic solvent was removed under vacuum to give *S*-butyl benzenesulfonothioate **4t** as a yellow oil.[4]

2.5 General procedure for synthesis of products:



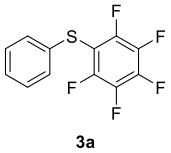
To an oven-dried 10 mL Schlenk tube was added thiosulfonate **1** or **4** (0.2 mmol), then the tube was evacuated under vacuum and charged with N_2. Under N_2 atmosphere, the anhydrous THF or DMF (1.0 mL) in combination with 4 Å MS (50 mg), trimethyl(perfluorophenyl)silane **2** or **5** (0.1 mmol) and *t*-Bu-P_4 (5 mol %) was added successively with stirring. After completion of the reaction, the solvent was removed under vacuum and the crude product was purified by flash column chromatography on silica gel (200−300 mesh, petroleum ether as the eluent) to afford clean product **3** and **6**.

2.6 Gram-scale preparation of 3a:

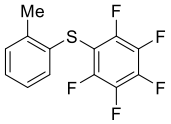


To an oven-dried 100 mL three-necked flask was added thiosulfonate **1a** (9.0 mmol, 2.253 g), then the reaction flask was evacuated under vacuum and charged with N_2. Under N_2 atmosphere, the anhydrous THF (45.0 mL), trimethyl(pentafluorophenyl)silane **2** (4.5 mmol, 1.085 g), *t*-Bu-P_4 (5 mol%, 0.143 g) was added successively with stirring. After completion of the reaction, the mixture was diluted with EtOAc and washed with water. The organic layer was separated, dried and filtered which was then removed under vacuum. The residue was purified by flash column chromatography on silica gel (200−300 mesh, petroleum ether as the eluent) to afford clean product **3a** (1.156 g, 93% yield).

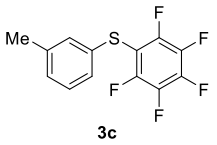
2.7 Characterization of products:


3a

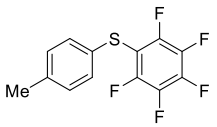
(perfluorophenyl)(phenyl)sulfane (3a) (known compound)[5]**:** white solid (26.8 mg, 97% yield); mp: 48–49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 7.32–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1–148.8 (m), 146.6–146.5 (m), 143.6–143.3 (m), 141.1–140.7 (m), 139.5–139.0 (m), 136.9–136.5 (m), 133.1, 130.7, 129.6, 128.1, 109.5–108.8 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.61– -131.74 (m, 2F), -151.25– -151.40 (m, 1F), -160.33– -160.51 (m, 2F); IR (KBr, thin film): 3062, 2927, 1638, 1513, 1488, 1265, 1095, 981, 862, 741 cm^{-1}.


3b

(perfluorophenyl)(o-tolyl)sulfane (3b) (known compound)[5]**:** colorless liquid (18.9 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.14 (m, 3H), 7.13–7.07 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.6 (m), 146.4–146.1 (m), 143.3–142.8 (m), 140.9–140.3 (m), 139.3–138.9 (m), 136.8–136.3 (m), 131.1, 130.8, 128.2, 126.9, 109.3–108.6 (m), 20.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.79– -131.91 (m, 2F), -151.75– -151.89 (m, 1F), -160.44– -160.62 (m, 2F); IR (KBr, thin film): 3064, 2921, 1637, 1513, 1490, 1144, 1094, 981, 859, 748 cm^{-1}.

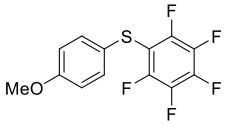

3c

(perfluorophenyl)(m-tolyl)sulfane (3c) (known compound)[5]**:** colorless liquid (21.5 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.11 (m, 3H), 7.08 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.6 (m), 146.5–146.2 (m), 143.5–143.0 (m), 140.9–140.5 (m), 139.4, 139.3–138.8 (m), 136.8–136.3 (m), 132.6, 131.2, 129.2, 128.9, 127.7, 109.4–108.8 (m), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.63– -131.76 (m, 2F), -151.44– -151.57 (m, 1F), -160.42– -160.59 (m, 2F); IR (KBr, thin film): 3065, 2925, 1637, 1513, 1488, 1379, 1092, 981, 862, 775 cm^{-1}.



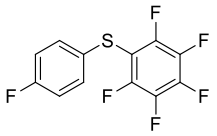
3d

(perfluorophenyl)(p-tolyl)sulfane (3d) (known compound)[5]**:** white solid (23.8 mg, 82% yield); mp: 39–40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8–148.7 (m), 146.4–146.0 (m), 143.3–142.9 (m), 140.8–140.3 (m), 139.3–138.8 (m), 138.5, 136.7–136.3 (m), 131.5, 130.2, 129.2, 110.1–109.5 (m), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.01– -132.14 (m, 2F), -151.86– -152.00 (m, 1F), -160.58– -160.75 (m, 2F); IR (KBr, thin film): 3052, 2926, 1637, 1512, 1488, 1290, 1095, 981, 860, 750 cm^{-1}.



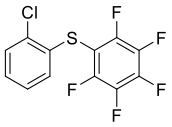
3e

(4-methoxyphenyl)(perfluorophenyl)sulfane (3e) (known compound)[5]: colorless liquid (26.6 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 6.90–6.74 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 148.6–148.3, 146.2–145.9 (m), 143.2–142.8 (m), 140.6–140.2 (m), 139.2–138.8 (m), 136.7–136.2 (m), 134.7, 122.8, 115.0, 111.1–110.5 (m), 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.66– -132.77 (m, 2F), -152.38– -152.52 (m, 1F), -160.75– -160.92 (m, 2F); IR (KBr, thin film): 3109, 2926, 1629, 1515, 1491, 1211, 1089, 991, 854, 709 cm^{-1}.



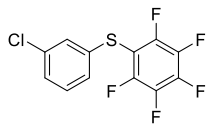
3f

(4-fluorophenyl)(perfluorophenyl)sulfane (3f): colorless liquid (21.8 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.40 (m, 2H), 7.06–6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 161.6, 148.8–148.4 (m), 146.3–145.9 (m), 143.6–142.9 (m), 141.0–140.5 (m), 139.3–138.9 (m), 136.8–136.3 (m), 134.1, 134.0, 131.4, 131.3, 127.8, 116.8, 116.5, 116.4, 116.2, 109.9–109.3 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.11– -132.23 (m, 2F), -151.21– -151.35 (m, 1F), -160.23– -160.40 (m, 2F); IR (KBr, thin film): IR (KBr, thin film): 3184, 2922, 1887, 1513, 1488, 1233, 1095, 980, 860, 742 cm^{-1}; HRMS (APCI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_5F_6S$, 295.0016, Found, 295.0013.



3g

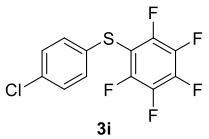
(2-chlorophenyl)(perfluorophenyl)sulfane (3g): white solid (24.8 mg, 80% yield); mp: 54–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24–7.14 (m, 2H), 7.08–7.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2–148.8 (m), 146.7–146.4 (m), 144.0–143.6 (m), 139.6–139.1 (m), 137.0–136.6 (m), 134.1, 132.2, 130.4, 130.2, 128.8, 127.7, 107.6–106.9 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.03– -136.17 (m, 2F), -155.40– -155.54 (m, 1F), -165.0 – -165.25 (m, 2F); IR (KBr, thin film): 3071, 2919, 1636, 1515, 1491, 1286, 1097, 983, 861, 748 cm^{-1}; HRMS (APCI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_5ClF_5S$, 310.9721, Found, 310.9716.



3h

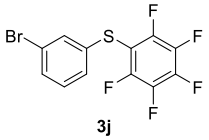
(3-chlorophenyl)(perfluorophenyl)sulfane (3h)： colorless liquid (24.5 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.6 Hz, 1H), 7.25–7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0–148.7 (m), 146.5–146.2 (m), 144.0–143.5 (m), 141.4–140.9 (m), 139.4–139.0 (m), 136.9–136.4 (m), 135.2, 134.9, 130.4, 129.9, 128.3, 128.2, 108.2–107.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.22– -131.34 (m, 2F), -150.10– -150.24 (m, 1F), -159.75– -159.92 (m, 2F); IR (KBr, thin film): 3064, 2926,

1636, 1515, 1491, 1286, 1089, 983, 869, 778 cm^{-1}; HRMS (APCI) *m/z*: $[M-H]^-$ Calcd. for $C_{12}H_3ClF_5S$, 308.9569, Found, 308.9569.



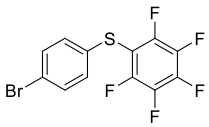
3i

(4-chlorophenyl)(perfluorophenyl)sulfane (3i) (known compound)[6]**:** white solid (26.0 mg, 84% yield); mp: 45–46 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.5 (m), 146.4–146.1 (m), 143.7–143.2 (m), 141.1–140.7 (m), 139.4–138.9 (m), 136.8–136.4 (m), 134.4, 132.2, 131.3, 129.6, 109.0–108.4 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.63– -131.76 (m, 2F), -150.65– -150.79 (m, 1F), -159.98– -160.16 (m, 2F); IR (KBr, thin film): 3042, 2924, 1638, 1512, 1488, 1292, 1095, 981, 861, 745 cm^{-1}.



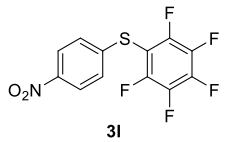
3j

(3-bromophenyl)(perfluorophenyl)sulfane (3j): colorless liquid (31.2 mg, 88% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 1.6 Hz, 2H), 7.43–7.36 (m, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.20–7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0–148.7 (m), 146.5–146.2 (m), 143.9–143.5 (m), 141.4–140.9 (m), 139.4–139.0 (m), 136.9 – 136.4 (m), 135.1, 132.7, 131.1, 130.7, 128.8, 123.2, 108.3–107.7 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.22– -131.34 (m, 2F), -151.11– -151.25 (m, 1F), -159.76– -159.92 (m, 2F); IR (KBr, thin film): 3126, 2924, 1638, 1513, 1492, 1291, 1093, 981, 863, 750 cm^{-1}; HRMS (APCI) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_5BrF_5S$, 354.9215, Found, 354.9211.



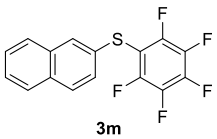
3k

(4-bromophenyl)(perfluorophenyl)sulfane (3k) (known compound)[7]**:** white solid (30.8 mg, 87% yield); mp: 64–65 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.39 (m, 2H), 7.25–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.6 (m), 146.4–146.1 (m), 143.8–143.3 (m), 141.2–140.7 (m), 139.4–138.9 (m), 136.9–136.4 (m), 132.6, 132.2, 132.0, 122.4, 108.8–108.2 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.54– -131.66 (m, 2F), -150.53– -150.67 (m, 1F), -159.93– -160.10 (m, 2F); IR (KBr, thin film): 3075, 2925, 1637, 1513, 1489, 1292, 1094, 981, 862, 729 cm^{-1}.



3l

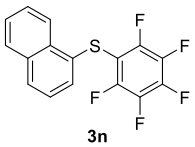
(4-nitrophenyl)(perfluorophenyl)sulfane (3l) (known compound)[8]**:** white solid (28.9 mg, 90% yield); mp: 89–90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20–8.11 (m, 2H), 7.35–7.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2–148.8 (m), 146.7, 146.6–146.3 (m), 144.6–144.1 (m), 142.5, 142.0–141.5 (m), 139.6–139.1 (m), 137.1–136.6 (m), 127.9, 124.5, 105.9–105.3 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.27– -130.39 (m, 2F), -148.02– -148.16 (m, 1F), -158.71– -158.87 (m, 2F); IR (KBr, thin film): 3101, 2919, 1636, 1515, 1484, 1340, 1089, 975, 854, 740 cm^{-1}.



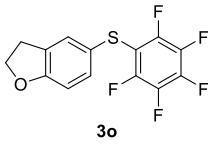
3m

naphthalen-2-yl(perfluorophenyl)sulfane (3m) (known compound)[9]**:** white solid (25.4 mg, 78% yield); mp: 66–67 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.2 Hz, 1H), 7.82–7.72 (m, 3H), 7.53–7.45 (m, 2H), 7.41–7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0–148.7 (m), 146.5–146.2 (m), 143.6–143.1 (m), 141.1–140.6 (m), 139.4–138.9 (m), 136.8–136.4 (m), 133.6, 132.6, 130.0, 129.9, 129.3, 127.8, 127.7, 127.5, 127.0, 126.8, 109.3–108.8 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.58–

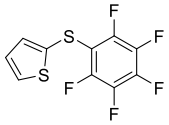
-131.71 (m, 2F), -151.12– -151.27 (m, 1F), -160.21– -160.38 (m, 2F); IR (KBr, thin film): 3064, 2912, 1629, 1515, 1484, 1256, 1097, 975, 816, 748 cm^{-1}.



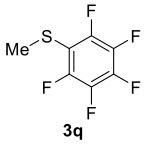
naphthalen-1-yl(perfluorophenyl)sulfane (3n): white solid (22.2 mg, 68% yield); mp: 81–82 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.8 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 7.2, 0.4 Hz, 1H), 7.64–7.58 (m, 1H), 7.57–7.50 (m, 1H), 7.39 (dd, *J* = 8.0, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.6 (m), 146.5–146.1 (m), 143.2–142.8 (m), 140.7–140.2 (m), 139.3–138.8 (m), 136.8–136.3 (m), 134.2, 133.2, 132.0, 129.7, 129.3, 128.7, 127.3, 126.6, 125.6, 124.8, 109.8–109.2 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.77– -132.90 (m, 2F), -151.83– -151.98 (m, 1F), -160.42– -160.59 (m, 2F); IR (KBr, thin film): 3059, 2927, 1637, 1518, 1492, 1256, 1087, 981, 802, 748 cm^{-1}; HRMS (APCI) *m/z*: $[M-H]^-$ Calcd. for $C_{16}H_6F_5S$, 325.0115, Found, 325.0110.



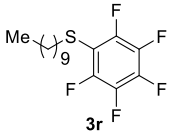
5-((perfluorophenyl)thio)-2,3-dihydrobenzofuran (3o): colorless liquid (15.9 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.58 (t, *J* = 8.8 Hz, 2H), 3.18 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 148.6–148.3 (m), 146.2–145.8 (m), 143.1–142.7 (m) , 140.5–140.2 (m), 139.2–138.7 (m), 136.7–136.2 (m), 134.0, 130.3, 128.7, 122.2, 111.4–110.10 (m), 110.2, 71.7, 29.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.72– -132.84 (m, 2F), -152.52– -152.66 (m, 1F), -160.79– -160.96 (m, 2F); IR (KBr, thin film): 2963, 2902, 1601, 1510, 1483, 1234, 1090, 979, 857, 816 cm^{-1}; HRMS (APCI) *m/z*: $[M]^+$ Calcd. for $C_{14}H_7F_5OS$, 318.0137, Found, 318.0140.



2-((perfluorophenyl)thio)thiophene (3p) (known compound)[10]**:** colorless liquid (21.4 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.38–7.33 (m, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6–148.3 (m), 146.1–145.8 (m), 143.7–143.2 (m), 141.2–140.7 (m), 139.2–138.7 (m), 136.7–136.2 (m), 131.5, 129.3, 127.7, 110.8–110.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.62– -132.75 (m, 2F), -151.21– -151.35 (m, 1F), -160.29– -160.45 (m, 2F); IR (KBr, thin film): 3109, 2926, 1636, 1515, 1491, 1218, 1089, 983, 854, 709 cm^{-1}.

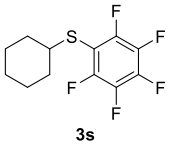


methyl(perfluorophenyl)sulfane (3q) (known compound)[11]**:** colorless liquid (18.8 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5–148.2 (m), 146.1–145.7 (m), 142.5–142.1 (m), 140.0–139.5 (m), 139.2–138.7 (m), 136.7–136.2 (m), 111.3–110.7 (m), 18.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.57– -133.69 (m, 2F), -153.79– -153.93 (m, 1F), -161.26– -161.43 (m, 2F); IR (KBr, thin film): 3360, 3185, 2919, 2851, 1659, 1636, 1469, 1416, 1271, 740 cm^{-1}.



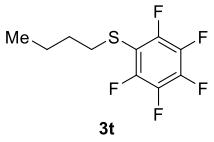
decyl(perfluorophenyl)sulfane (3r) (known compound)[12]**:** colorless liquid (25.8 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (t, *J* = 7.2 Hz, 2H), 1.59–1.50 (m, 2H), 1.45–1.21 (m, 16H), 0.91–0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9–148.6 (m), 146.5–146.2 (m), 142.6–142.2 (m), 140.1–139.6 (m), 139.2–138.7 (m), 136.6–136.2

(m), 109.8–109.2 (m), 35.0, 31.9, 29.8, 29.5, 29.4, 29.3, 29.1, 28.3, 22.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.64– -132.76 (m, 2F), -153.30– -153.44 (m, 1F), -161.21– -161.38 (m, 2F); IR (KBr, thin film): 2926, 2859, 1636, 1515, 1484, 1294, 1089, 983, 861, 725 cm^{-1}.



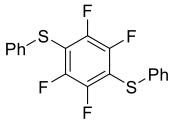
3s

cyclohexyl(perfluorophenyl)sulfane (3s) (known compound)[13]**:** white solid (20.9 mg, 74% yield); mp: 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23–3.04 (m, 1H), 1.94–1.83 (m, 2H), 1.83–1.74 (m, 2H), 1.66–1.56 (m, 1H), 1.41–1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2–148.9 (m), 146.8–146.5 (m), 142.8–142.4 (m), 140.1–139.8 (m), 139.1–138.5 (m), 136.6–136.1 (m), 108.5–107.8 (m), 47.5, 33.3, 25.8, 25.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.40– -131.51 (m, 2F), -152.59– -152.72 (m, 1F), -161.20– -161.36 (m, 2F); IR (KBr, thin film): 3092, 2919, 1636, 1515, 1484, 1271, 1089, 975, 861, 717 cm^{-1}.



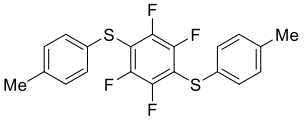
3t

butyl(perfluorophenyl)sulfane (3t) (known compound)[14]**:** colorless liquid (22.2 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (t, *J* = 7.6 Hz, 2H), 1.58–1.49 (m, 2H), 1.48–1.37 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0–148.6 (m), 146.5–146.2 (m), 142.6–142.2 (m), 140.2–139.7 (m), 139.2–138.7 (m), 136.7–136.2 (m), 109.8–109.1 (m), 34.7, 31.8, 21.5, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.66– -132.77 (m, 2F), -153.23– -153.37 (m, 1F), -161.18– -161.33 (m, 2F); IR (KBr, thin film): 3657, 2924, 2855, 2363, 2043, 1715, 1652, 1558, 1498, 1458 cm^{-1}.



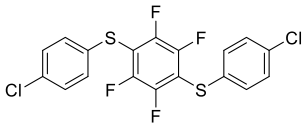
6a

(perfluoro-1,4-phenylene)bis(phenylsulfane) (6a) (known compound)[15]: white solid (14.6 mg, 40% yield); mp: 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 4H), 7.33–7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4–148.0 (m), 145.9–145.5 (m), 132.6, 131.0, 129.4, 128.1, 115.5–115.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.03.



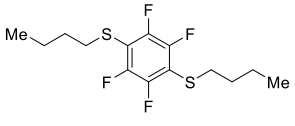
6b

(perfluoro-1,4-phenylene)bis(p-tolylsulfane) (6b) (known compound)[15]: white solid (21.3 mg, 54% yield); mp: 104–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3–147.8 (m), 145.8–145.3 (m), 138.5, 131.8, 130.1, 128.9, 115.8–115.4 (m), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.63.



6c

(perfluoro-1,4-phenylene)bis((4-chlorophenyl)sulfane) (6c) (known compound)[5]: white solid (16.1 mg, 37% yield); mp: 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.30–7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3–147.9 (m), 145.7–145.4 (m), 134.6, 132.7, 130.8, 129.6, 115.5–114.8 (m); ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -131.82.



6d

(perfluoro-1,4-phenylene)bis(butylsulfane) (6d) (known compound)[15]: colorless liquid (7.5 mg, 23% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (t, *J* = 7.2 Hz, 2H), 1.60–1.54 (m,

2H), 1.49–1.38 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4–148.0 (m), 145.8–145.5 (m), 114.6–114.2 (m), 34.4, 31.8, 21.5, 13.5, 0.1 (t, *J* =3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.06.

2.8 References

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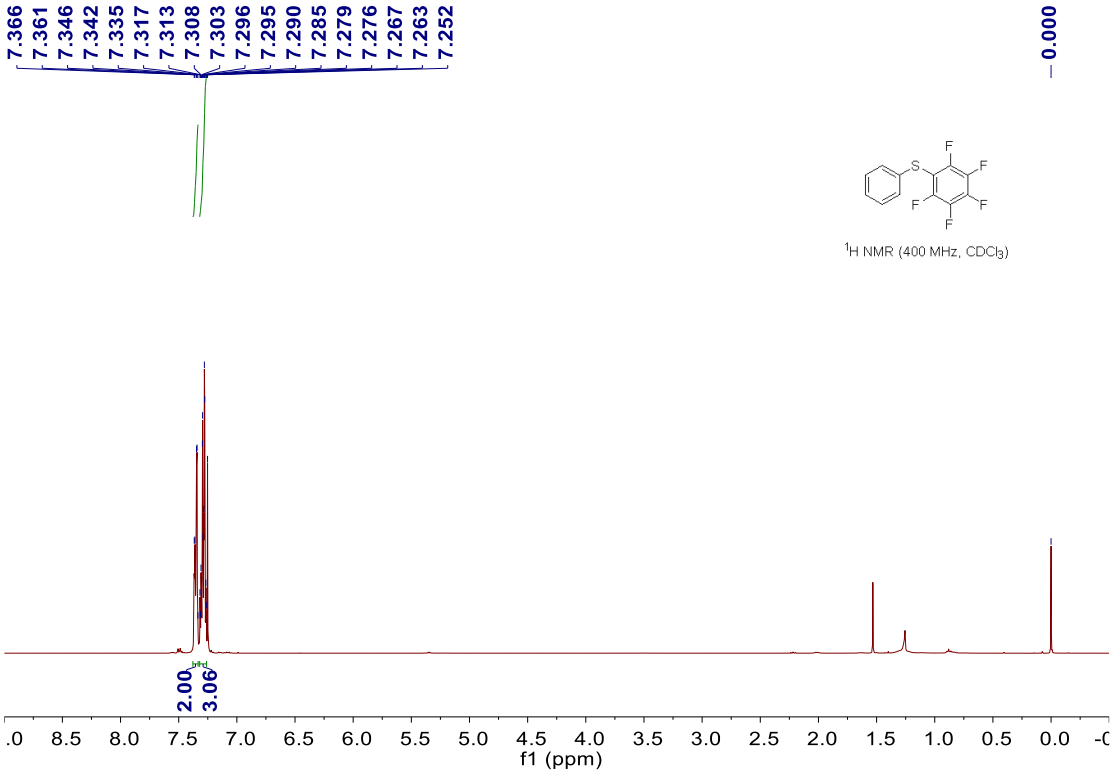
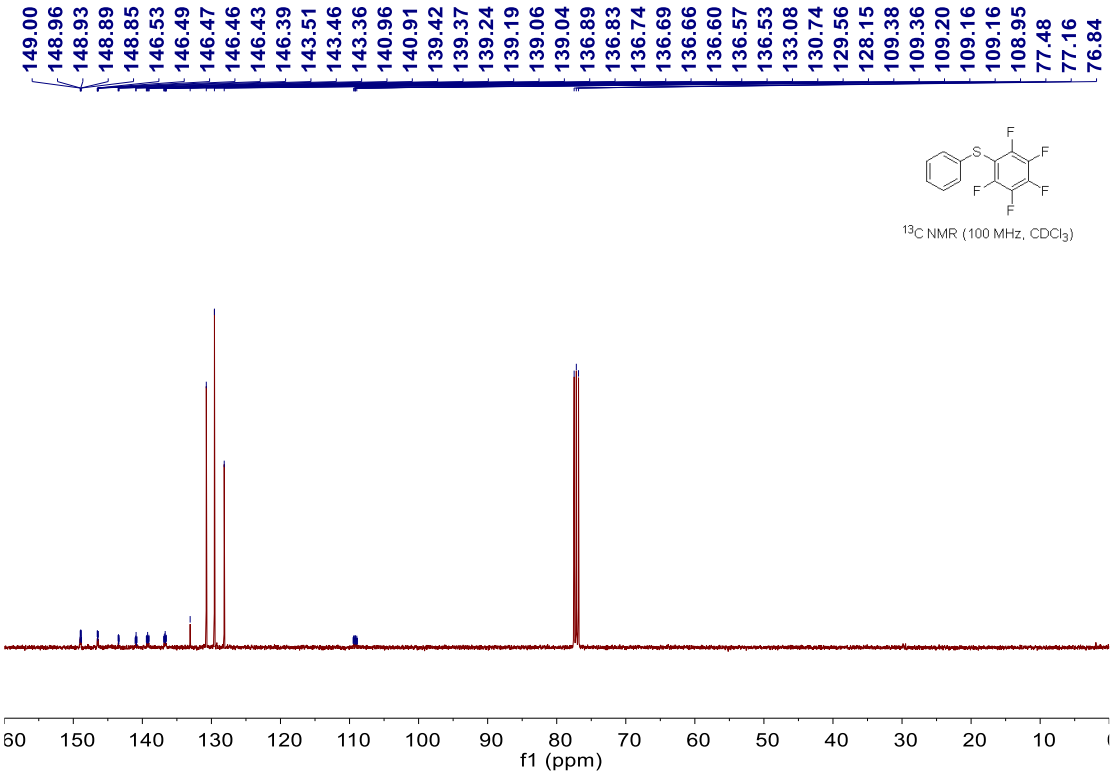
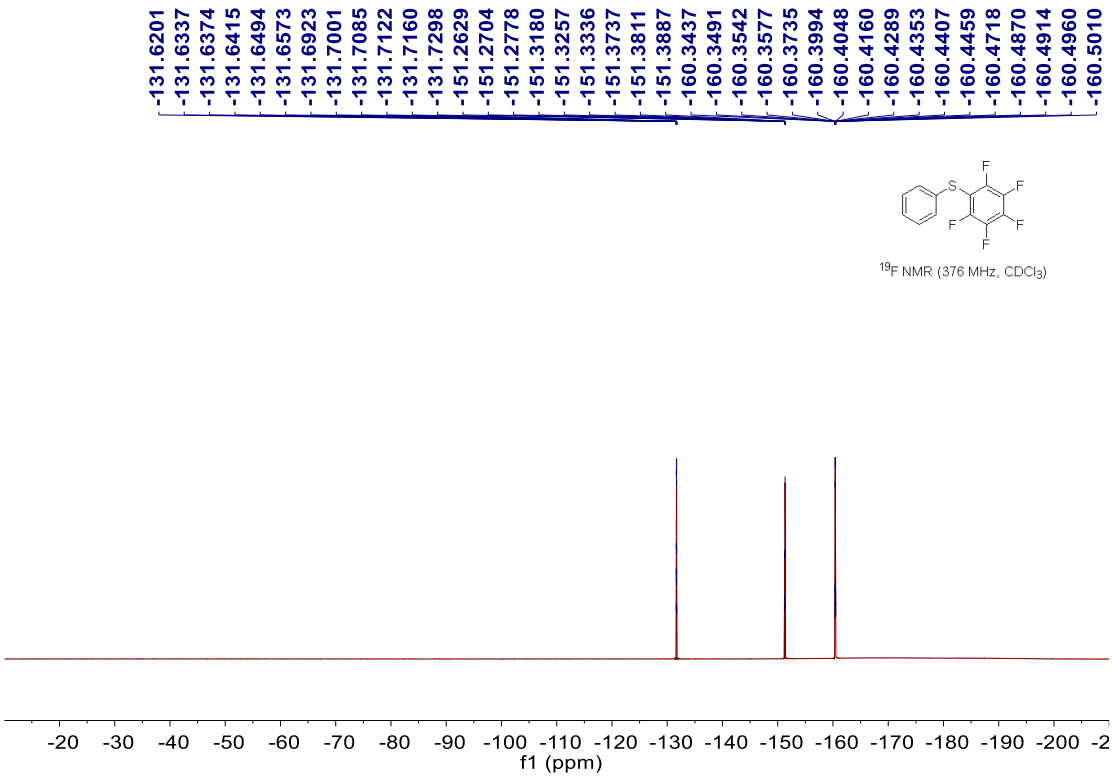
3. Copies of NMR spectra of products

3a



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-131.6573
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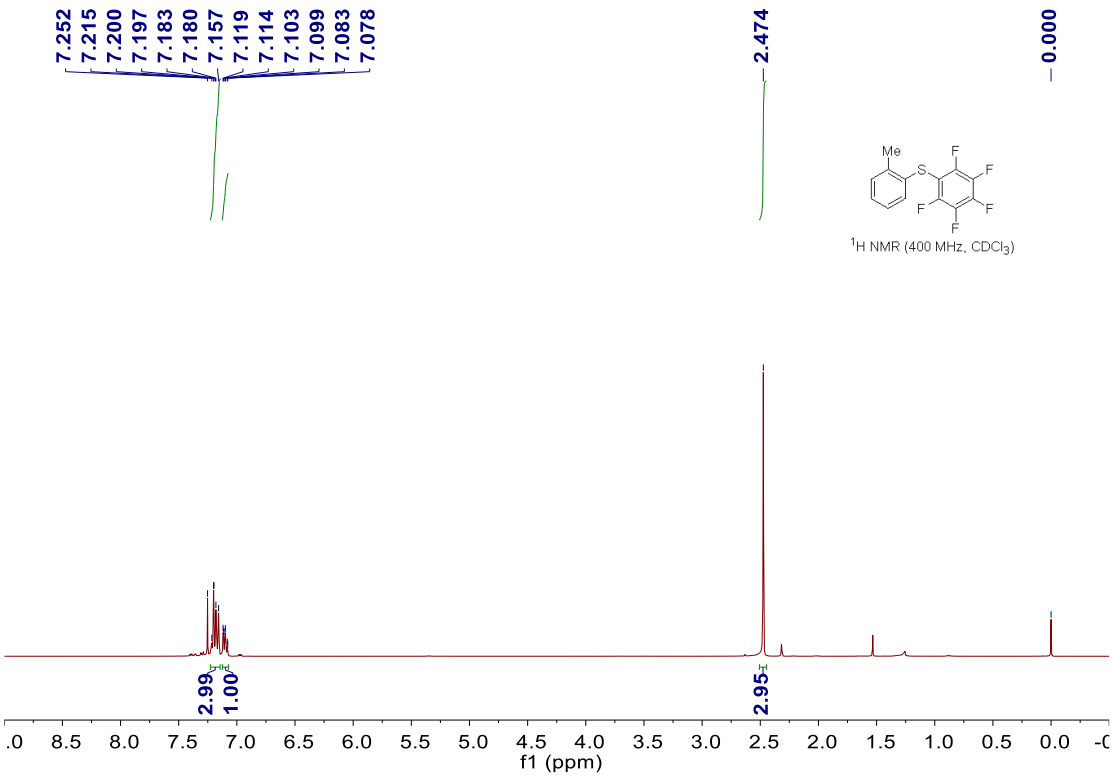
-131.7160
-131.7298
-151.2629
-151.2704
-151.2778
-151.3180
-151.3257
-151.3336
-151.3737
-151.3811
-151.3887
-160.3437
-160.3491
-160.3542
-160.3577
-160.3735
-160.3994
-160.4048
-160.4160
-160.4289
-160.4353
-160.4407
-160.4459
-160.4718
-160.4870
-160.4914
-160.4960
-160.5010
F
S
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

3b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7.215
7.200
7.197
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7.180
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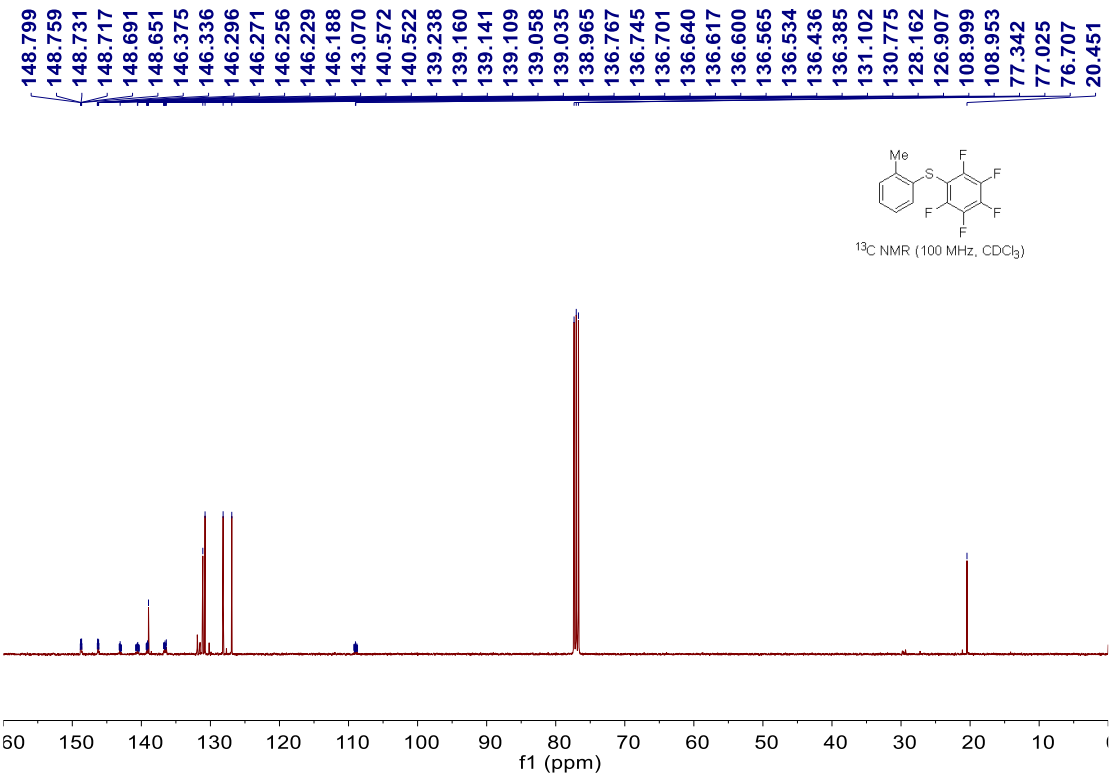
7.119
7.114
7.103
7.099
7.083
7.078
2.474
0.000
Me
F
S
F
F
F
F
1H NMR (400 MHz, CDCl3)
2.99
1.00
2.95
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)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140.522
139.238
139.160
139.141
139.109
139.058
139.035
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136.767
136.745
136.701
136.640
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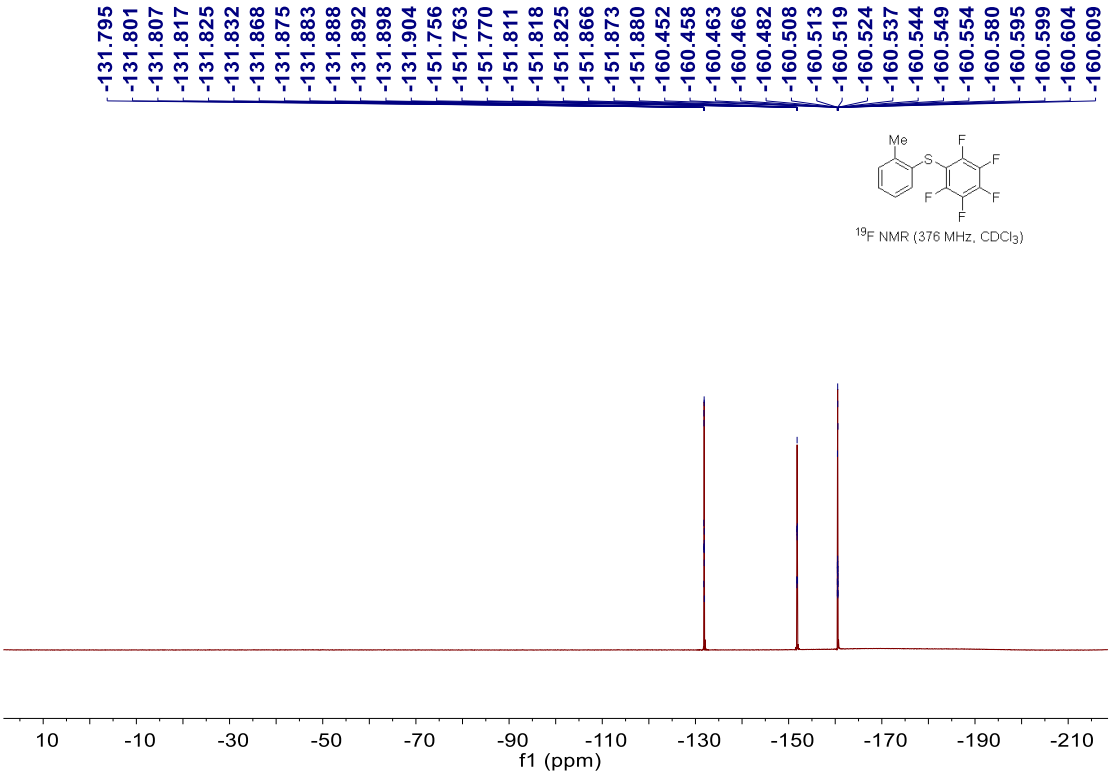
136.600
136.565
136.534
136.436
136.385
131.102
130.775
128.162
126.907
108.999
108.953
77.342
77.025
76.707
20.451
Me
S
F
F
F
F
F
13C NMR (100 MHz, CDCl3)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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-131.898
-131.904
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-151.763
-151.770
-151.811
-151.818
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-151.866
-151.873
-151.880
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-160.458
-160.463
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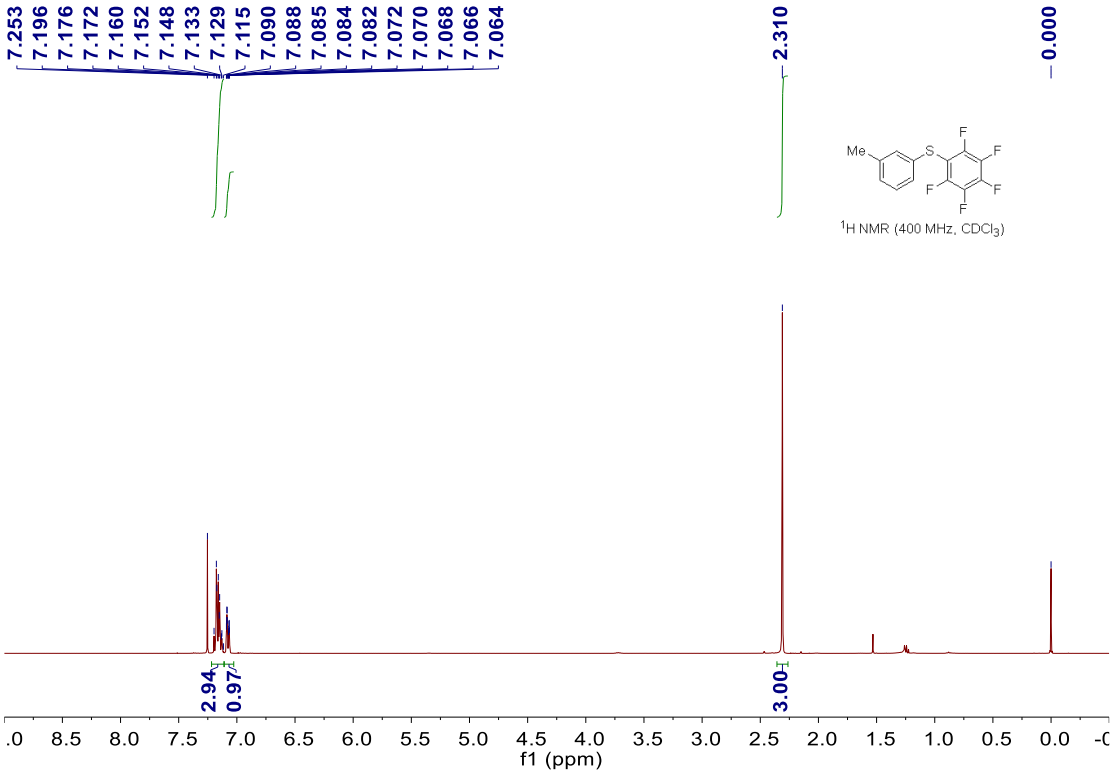
-160.482
-160.508
-160.513
-160.519
-160.524
-160.537
-160.544
-160.549
-160.554
-160.580
-160.595
-160.599
-160.604
-160.609
Me
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

3c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7.084
7.082
7.072
7.070
7.068
7.066
7.064
2.310
0.000
Me
S
F
F
F
F
F
1H NMR (400 MHz, CDCl3)
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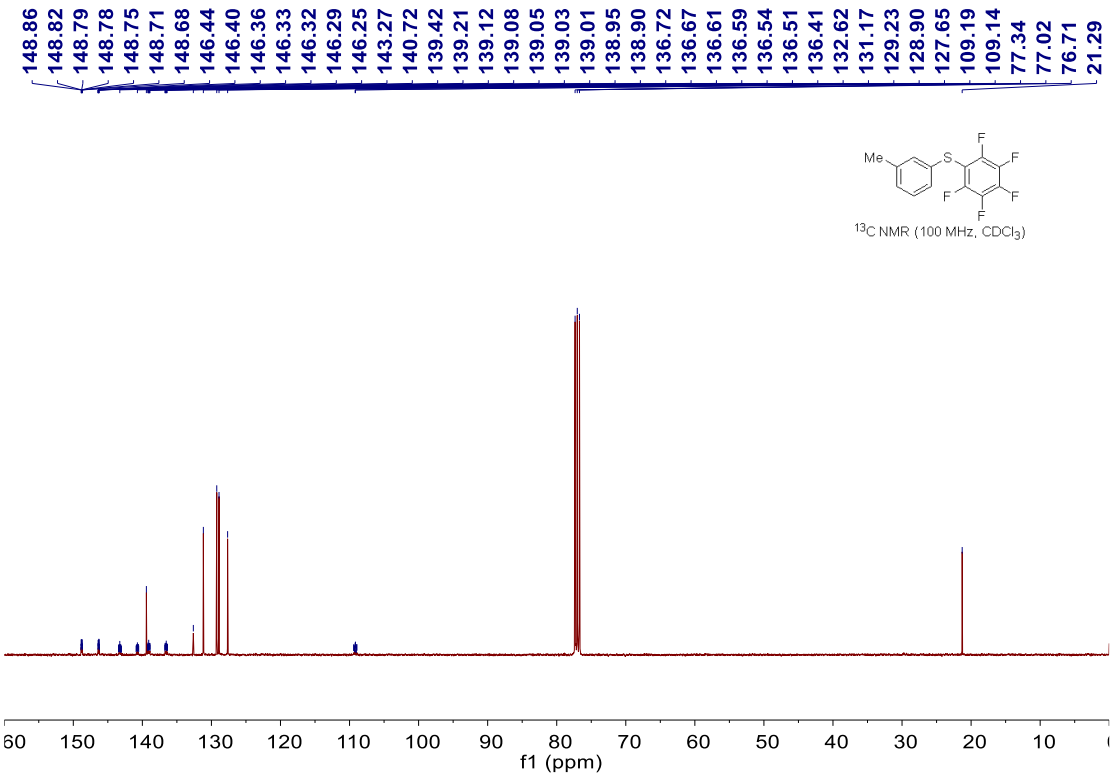
0.97
3.00
f1 (ppm)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146.25
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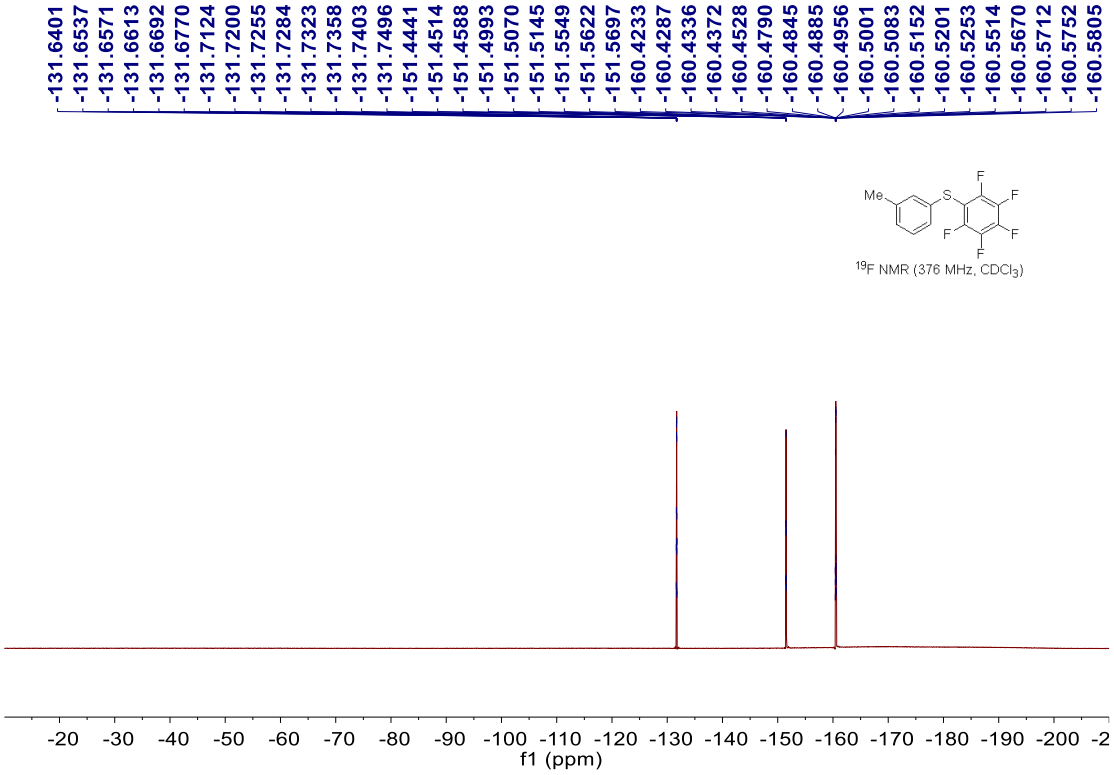
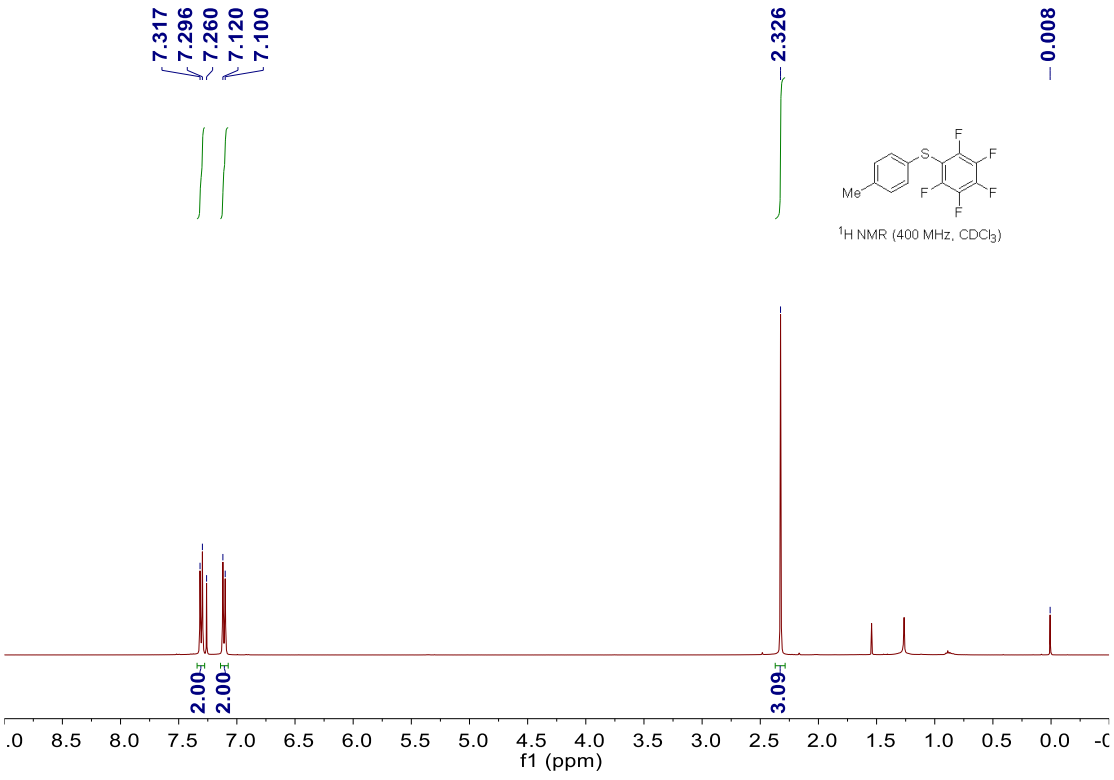
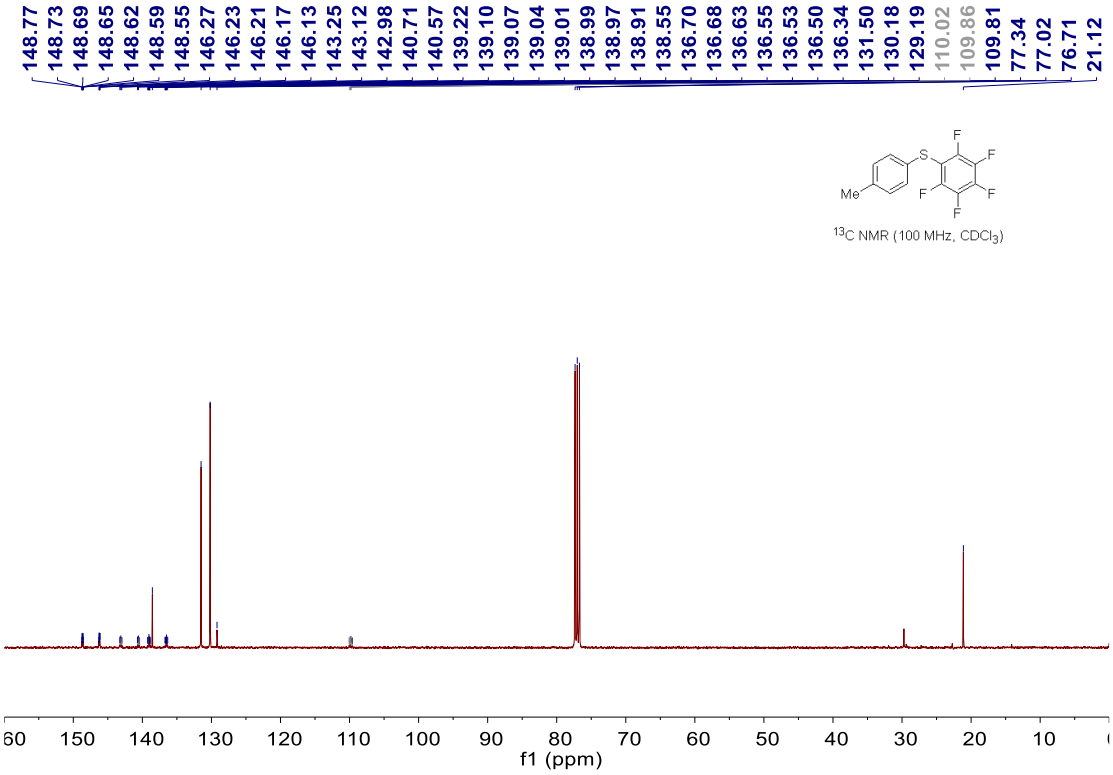
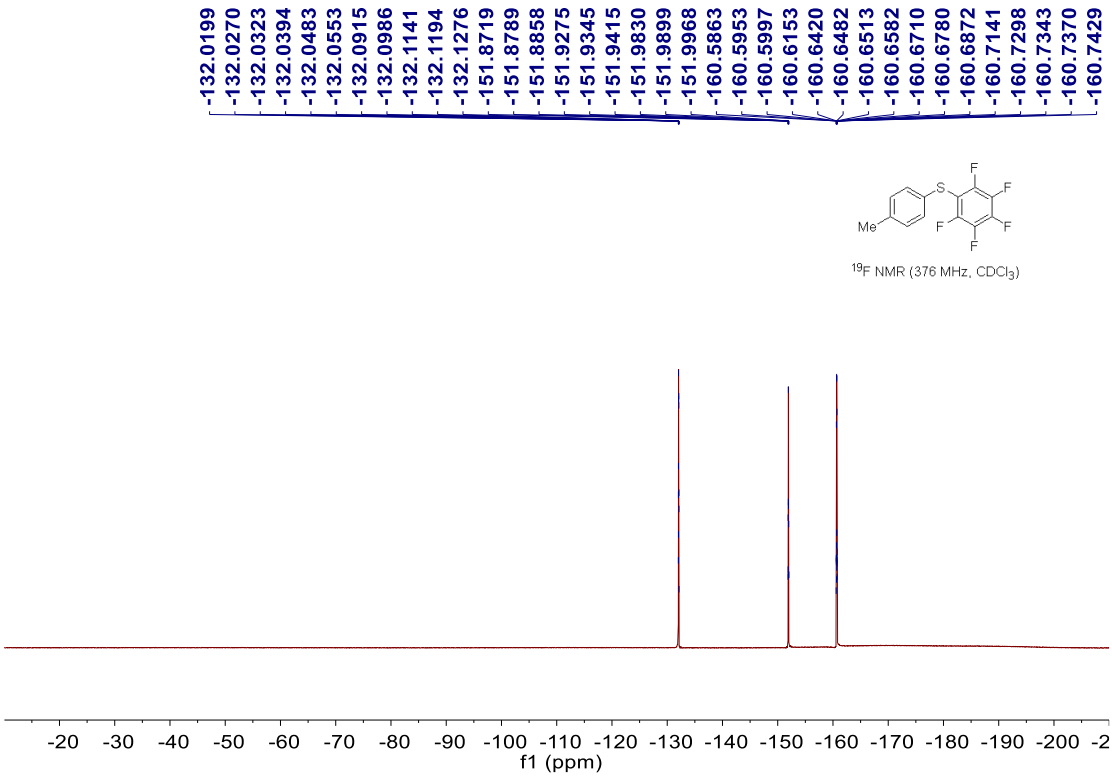
139.42
139.21
139.12
139.08
139.05
139.03
139.01
138.95
138.90
136.72
136.67
136.61
136.59
136.54
136.51
136.41
132.62
131.17
129.23
128.90
127.65
109.19
109.14
77.34
77.02
76.71
21.29
Me
S
F
F
F
F
F
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-131.6401
-131.6537
-131.6571
-131.6613
-131.6692
-131.6770
-131.7124
-131.7200
-131.7255
-131.7284
-131.7323
-131.7358
-131.7403
-131.7496
-151.4441
-151.4514
-151.4588
-151.4993
-151.5070
-151.5145
-151.5549
-151.5622
-151.5697
-160.4233
-160.4287
-160.4336
-160.4372
-160.4528
-160.4790
-160.4845
-160.4885
-160.4956
-160.5001
-160.5083
-160.5152
-160.5201
-160.5253
-160.5514
-160.5670
-160.5712
-160.5752
-160.5805
Me
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

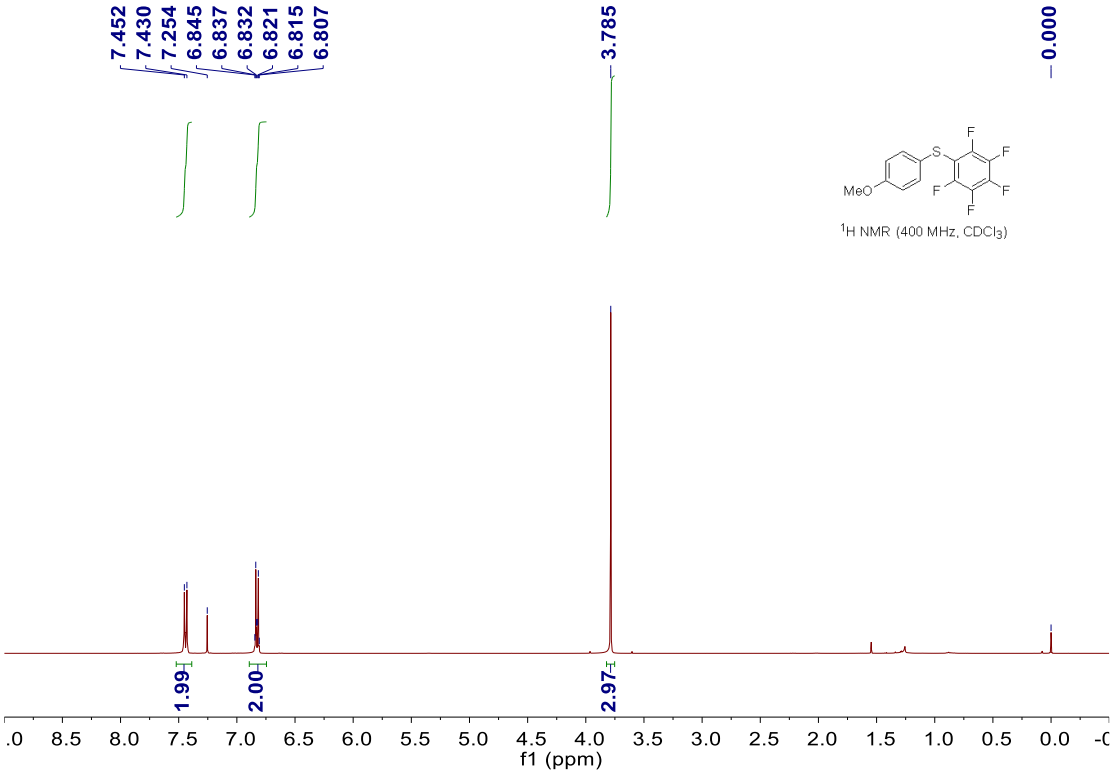
3d

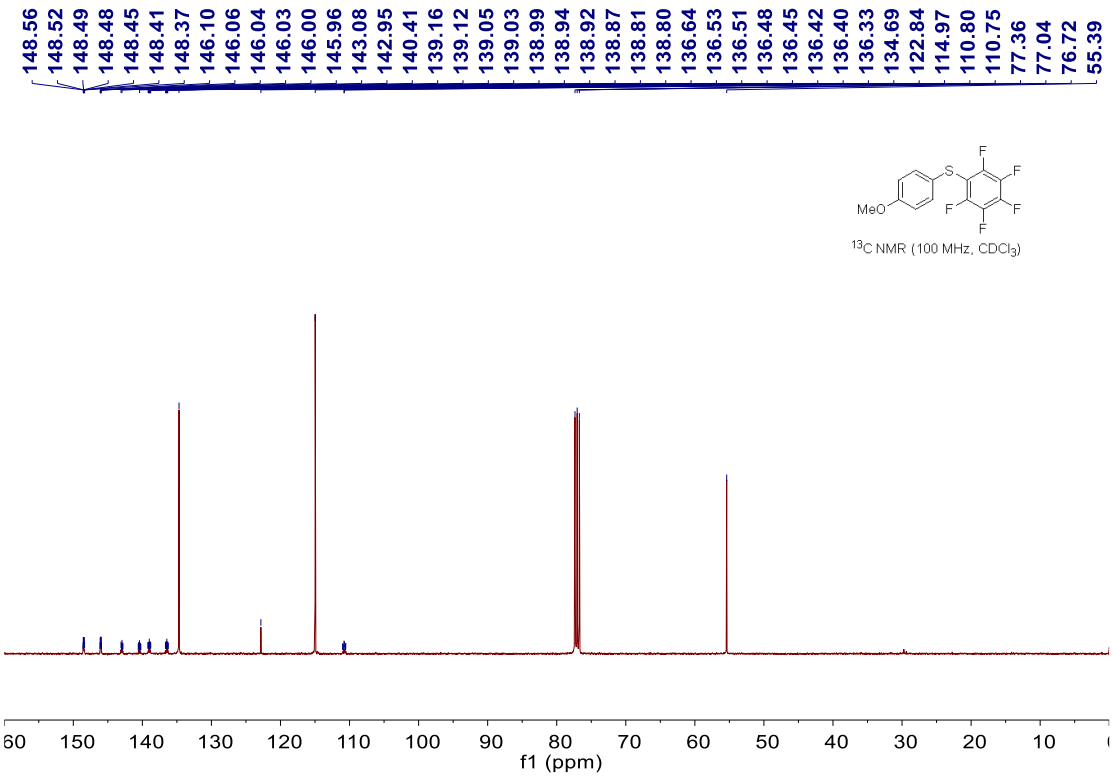

7.317
7.296
7.260
7.120
7.100
2.326
0.008
Me
S
F
F
F
F
F
1H NMR (400 MHz, CDCl3)
2.00
2.00
3.09
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

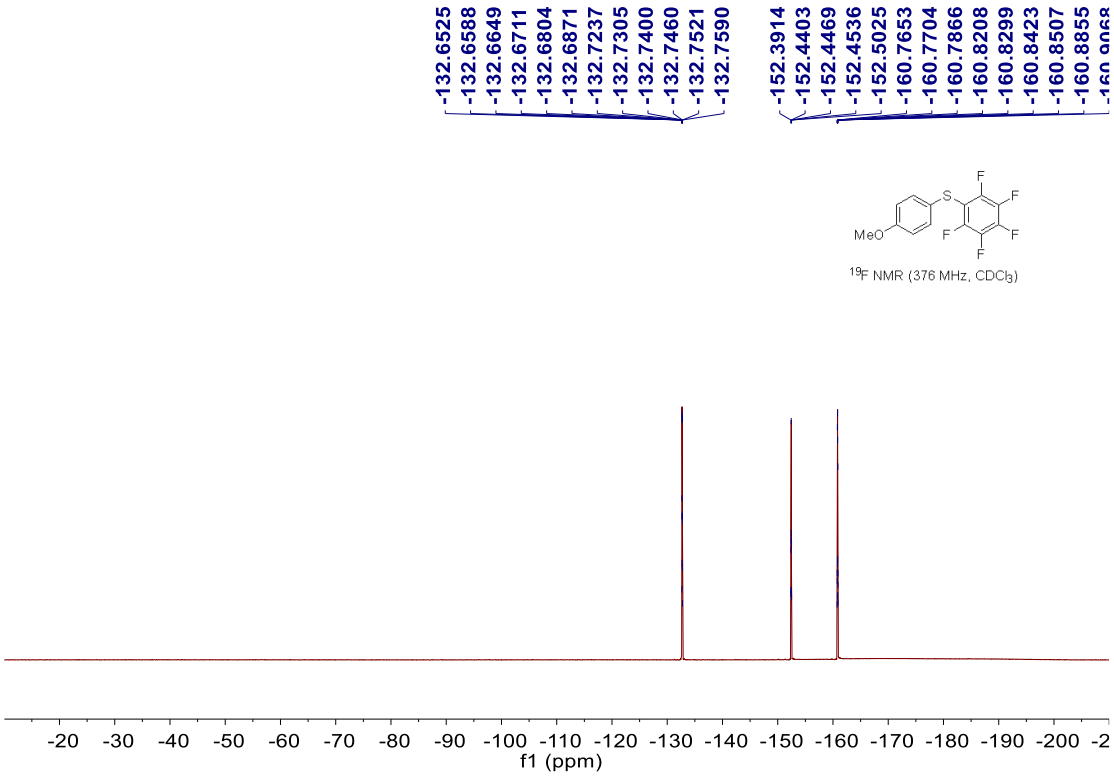

148.77
148.73
148.69
148.65
148.62
148.59
148.55
146.27
146.23
146.21
146.17
146.13
143.25
143.12
142.98
140.71
140.57
139.22
139.10
139.07
139.04
139.01
138.99
138.97
138.91
138.55
136.70
136.68
136.63
136.55
136.53
136.50
136.34
131.50
130.18
129.19
110.02
109.86
109.81
77.34
77.02
76.71
21.12
F
S
F
Me
F
F
F
13C NMR (100 MHz, CDCl3)
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-132.0199
-132.0270
-132.0323
-132.0394
-132.0483
-132.0553
-132.0915
-132.0986
-132.1141
-132.1194
-132.1276
-151.8719
-151.8789
-151.8858
-151.9275
-151.9345
-151.9415
-151.9830
-151.9899
-151.9968
-160.5863
-160.5953
-160.5997
-160.6153
-160.6420
-160.6482
-160.6513
-160.6582
-160.6710
-160.6780
-160.6872
-160.7141
-160.7298
-160.7343
-160.7370
-160.7429
F
S
F
Me
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

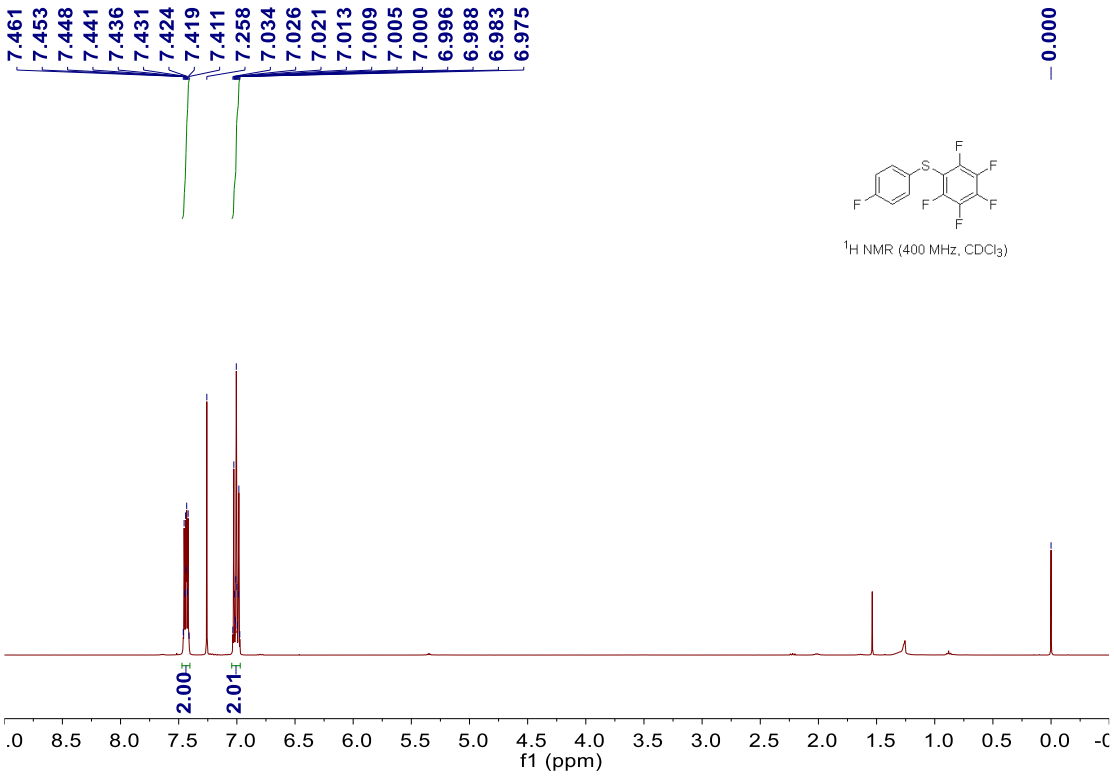
3e

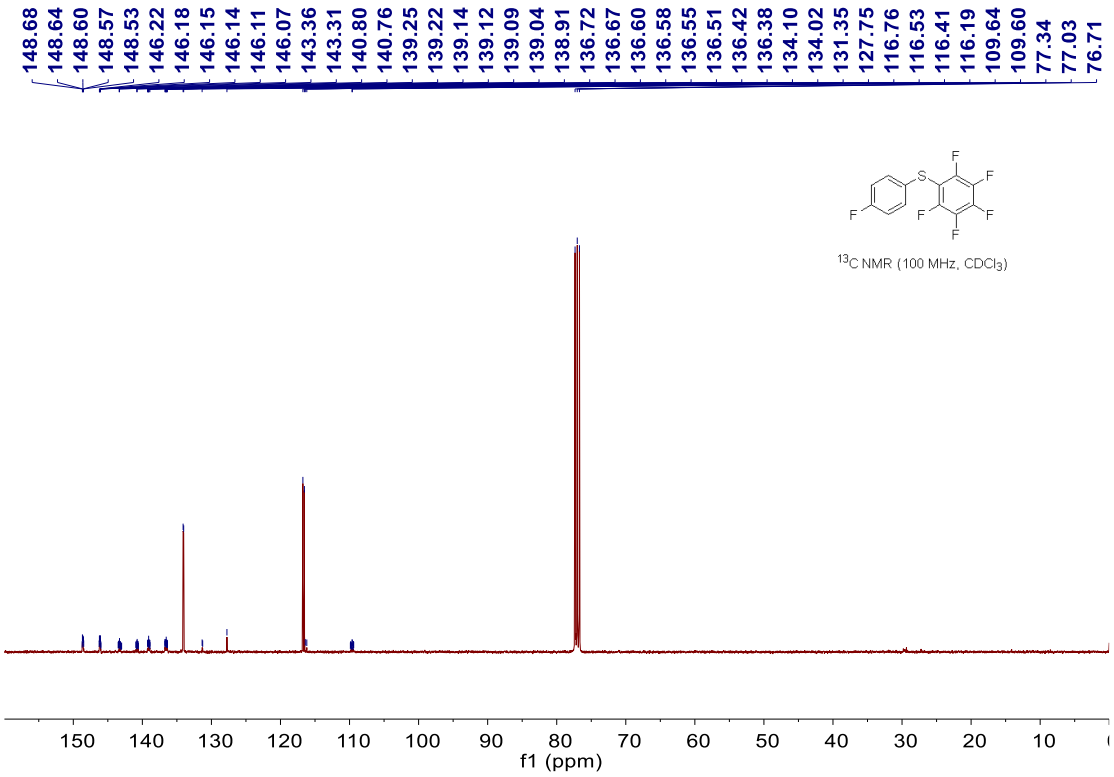

7.452
7.430
7.254
6.845
6.837
6.832
6.821
6.815
6.807
3.785
0.000
MeO
F
S
F
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
1.99
2.00
2.97
f1 (ppm)

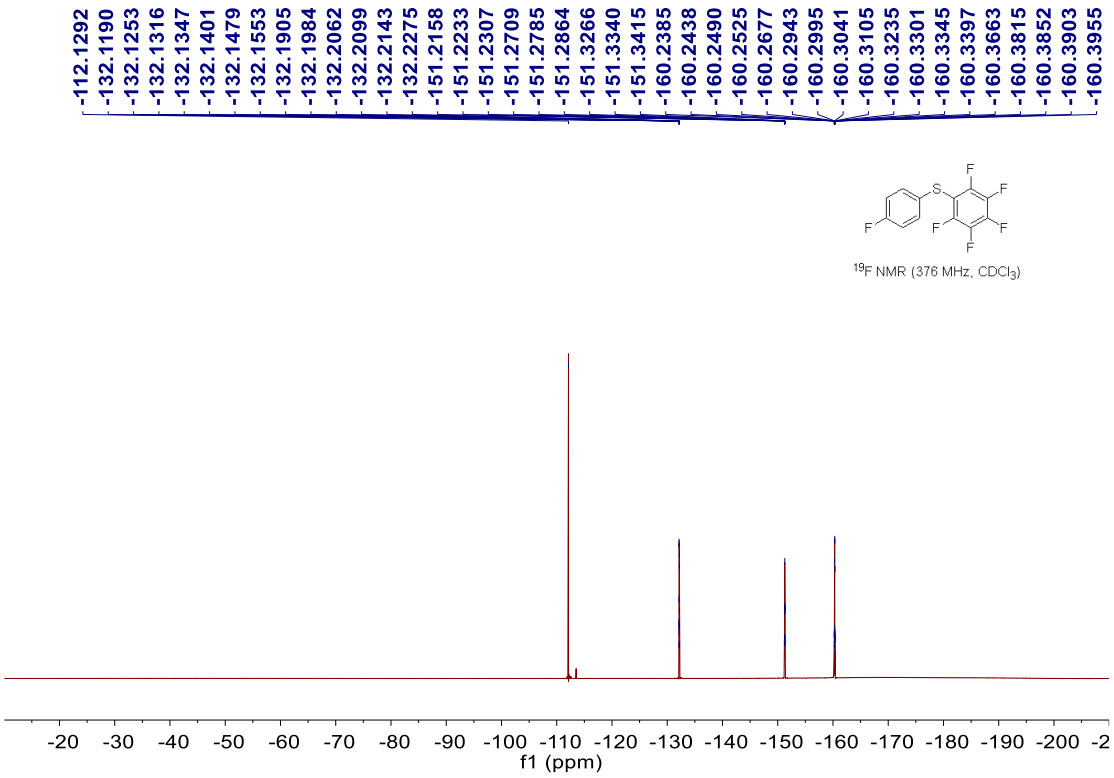

148.56
148.52
148.49
148.48
148.45
148.41
148.37
146.10
146.06
146.04
146.03
146.00
145.96
143.08
142.95
140.41
139.16
139.12
139.05
139.03
138.99
138.94
138.92
138.87
138.81
138.80
136.64
136.53
136.51
136.48
136.45
136.42
136.40
136.33
134.69
122.84
114.97
110.80
110.75
77.36
77.04
76.72
55.39
MeO
F
S
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-132.6525
-132.6588
-132.6649
-132.6711
-132.6804
-132.6871
-132.7237
-132.7305
-132.7400
-132.7460
-132.7521
-132.7590
-152.3914
-152.4403
-152.4469
-152.4536
-152.5025
-160.7653
-160.7704
-160.7866
-160.8208
-160.8299
-160.8423
-160.8507
-160.8855
MeO
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

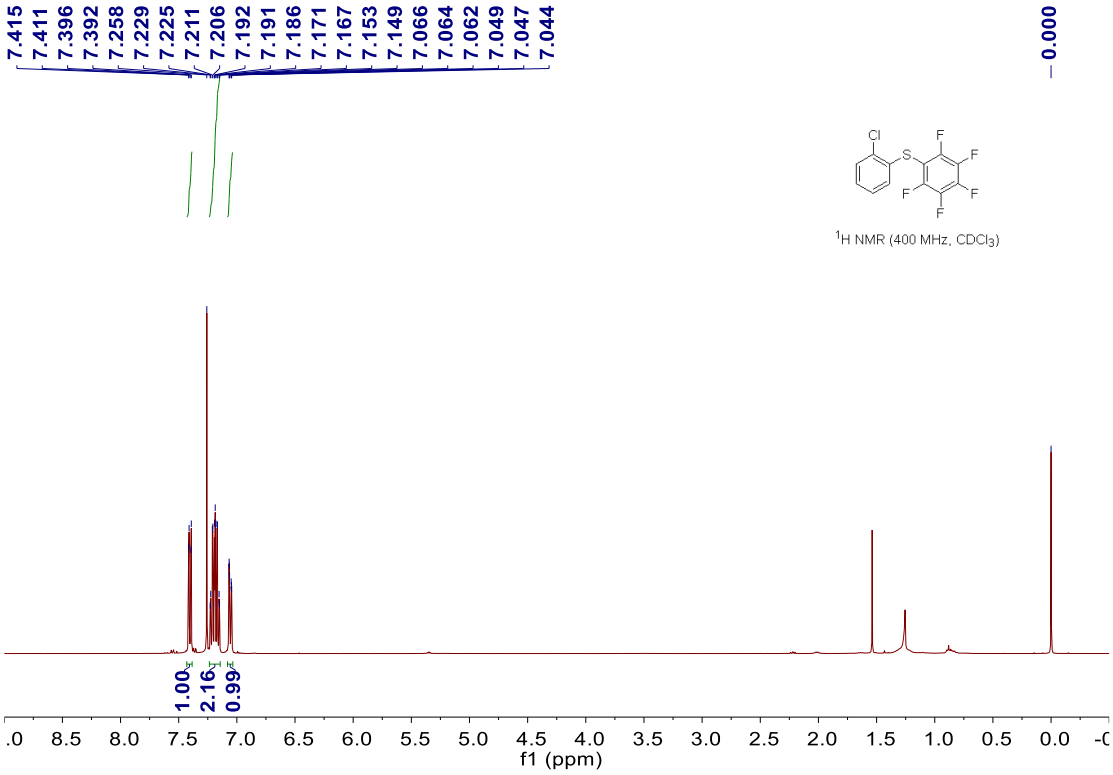
3f

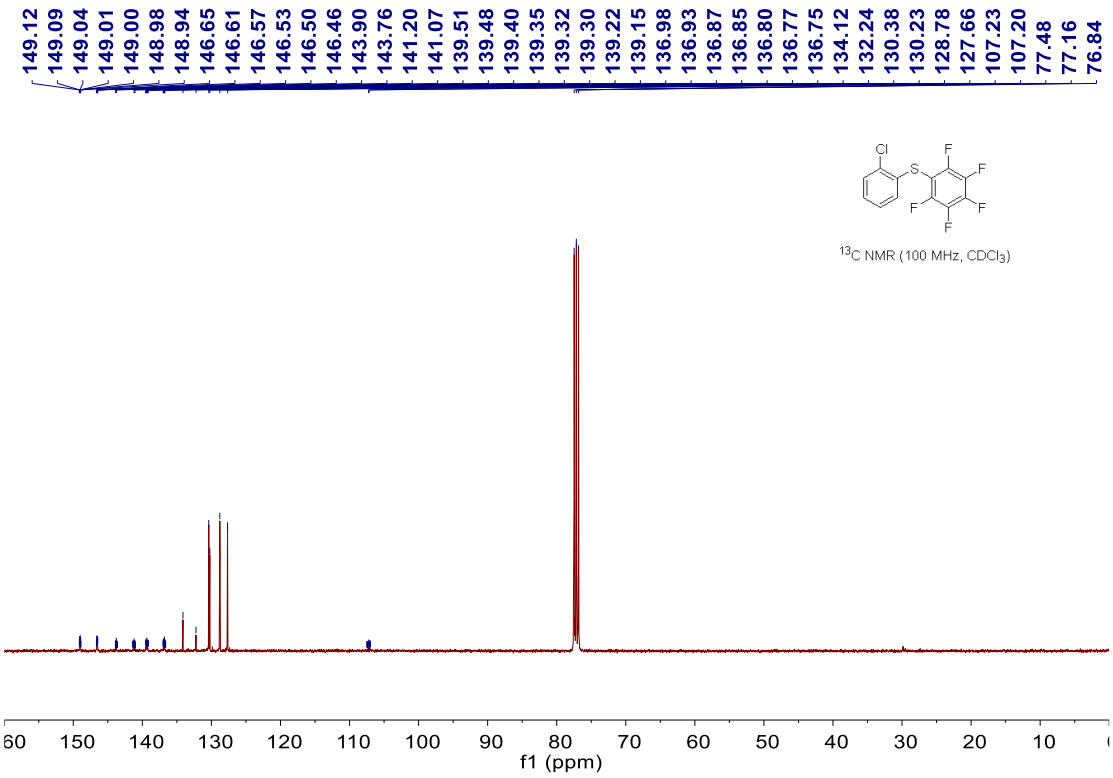

7.461
7.453
7.448
7.441
7.436
7.431
7.424
7.419
7.411
7.258
7.034
7.026
7.021
7.013
7.009
7.005
7.000
6.996
6.988
6.983
6.975
0.000
1H NMR (400 MHz, CDCl3)
2.00
2.01
f1 (ppm)

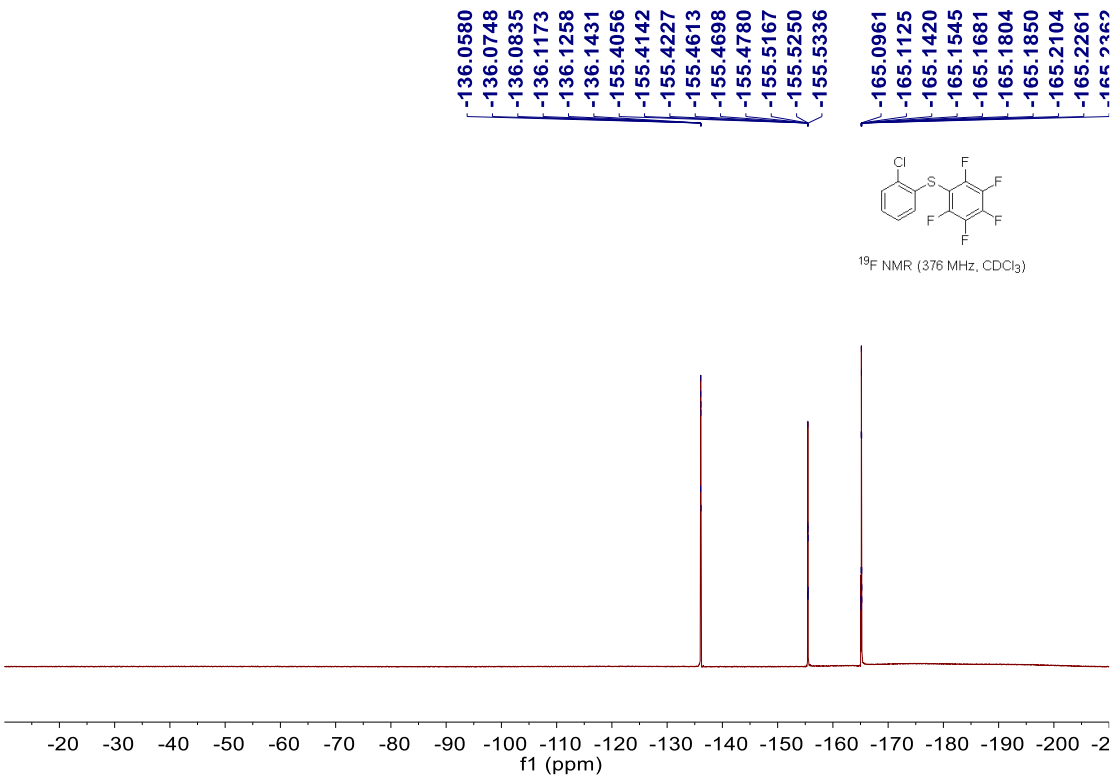

148.68
148.64
148.60
148.57
148.53
146.22
146.18
146.15
146.14
146.11
146.07
143.36
143.31
140.80
140.76
139.25
139.22
139.14
139.12
139.09
139.04
138.91
136.72
136.67
136.60
136.58
136.55
136.51
136.42
136.38
134.10
134.02
131.35
127.75
116.76
116.53
116.41
116.19
109.64
109.60
77.34
77.03
76.71
13C NMR (100 MHz, CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-112.1292
-132.1190
-132.1253
-132.1316
-132.1347
-132.1401
-132.1479
-132.1553
-132.1905
-132.1984
-132.2062
-132.2099
-132.2143
-132.2275
-151.2158
-151.2233
-151.2307
-151.2709
-151.2785
-151.2864
-151.3266
-151.3340
-151.3415
-160.2385
-160.2438
-160.2490
-160.2525
-160.2677
-160.2943
-160.2995
-160.3041
-160.3105
-160.3235
-160.3301
-160.3345
-160.3397
-160.3663
-160.3815
-160.3852
-160.3903
-160.3955
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

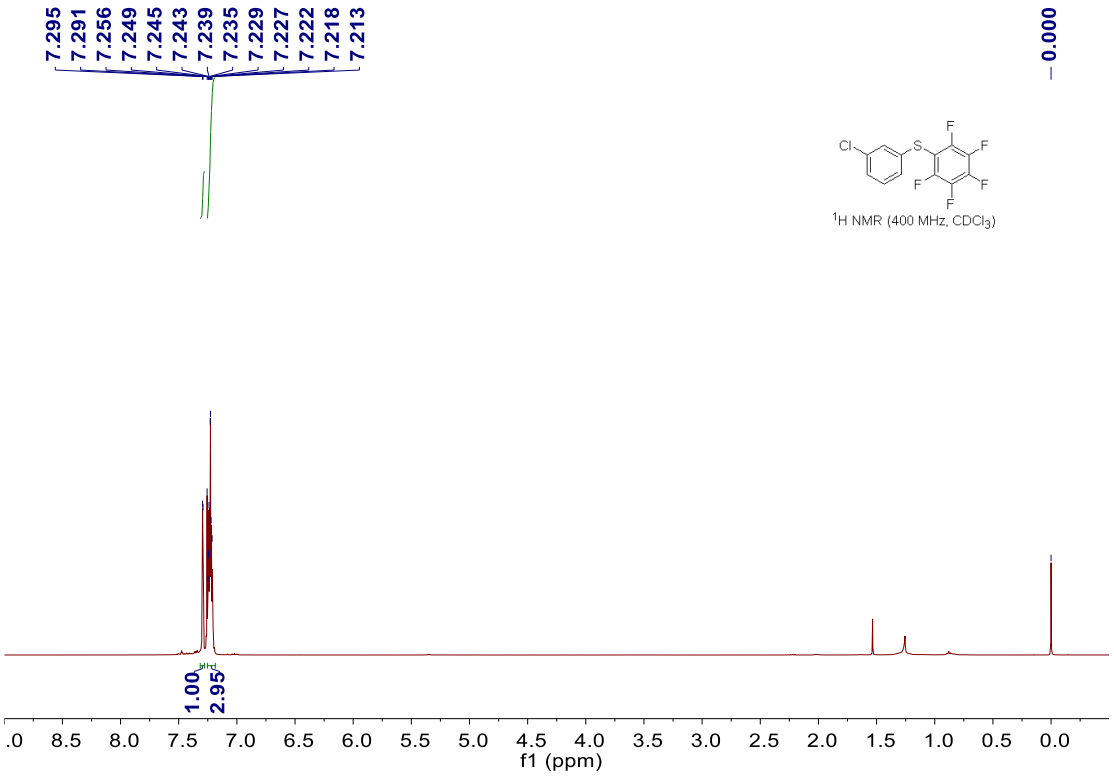
3g

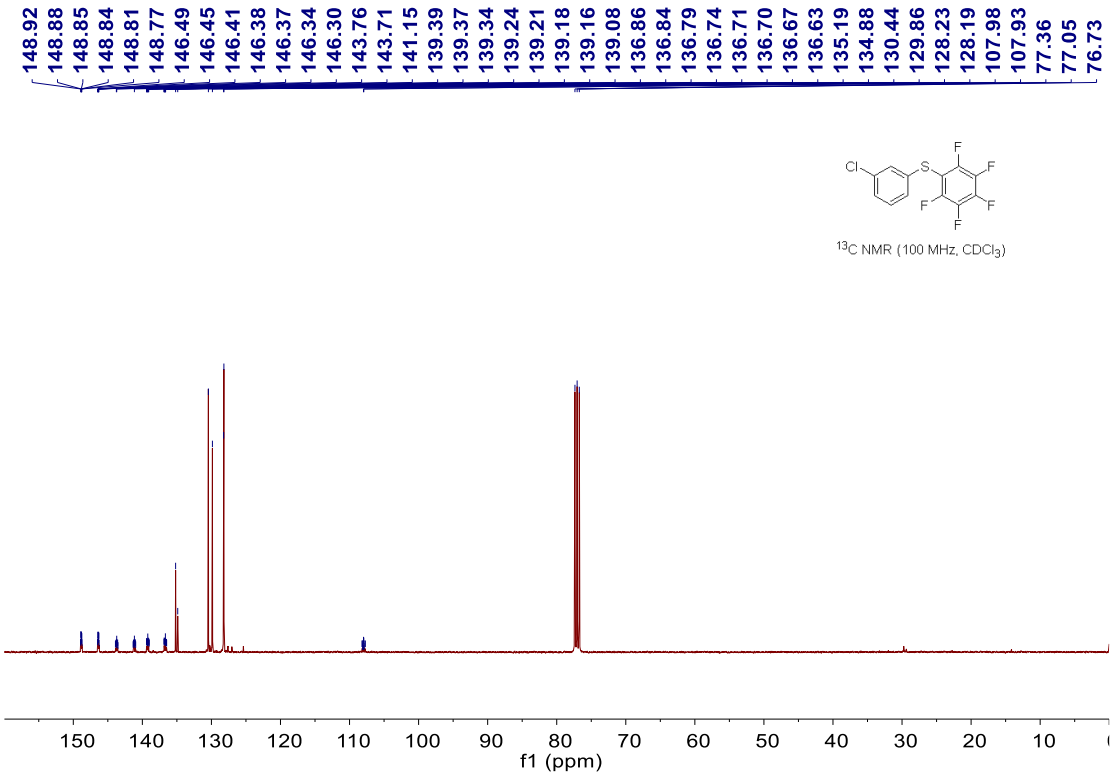

7.415
7.411
7.396
7.392
7.258
7.229
7.225
7.211
7.206
7.192
7.191
7.186
7.171
7.167
7.153
7.149
7.066
7.064
7.062
7.049
7.047
7.044
0.000
Cl
S
F
F
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
2.16
0.99
f1 (ppm)

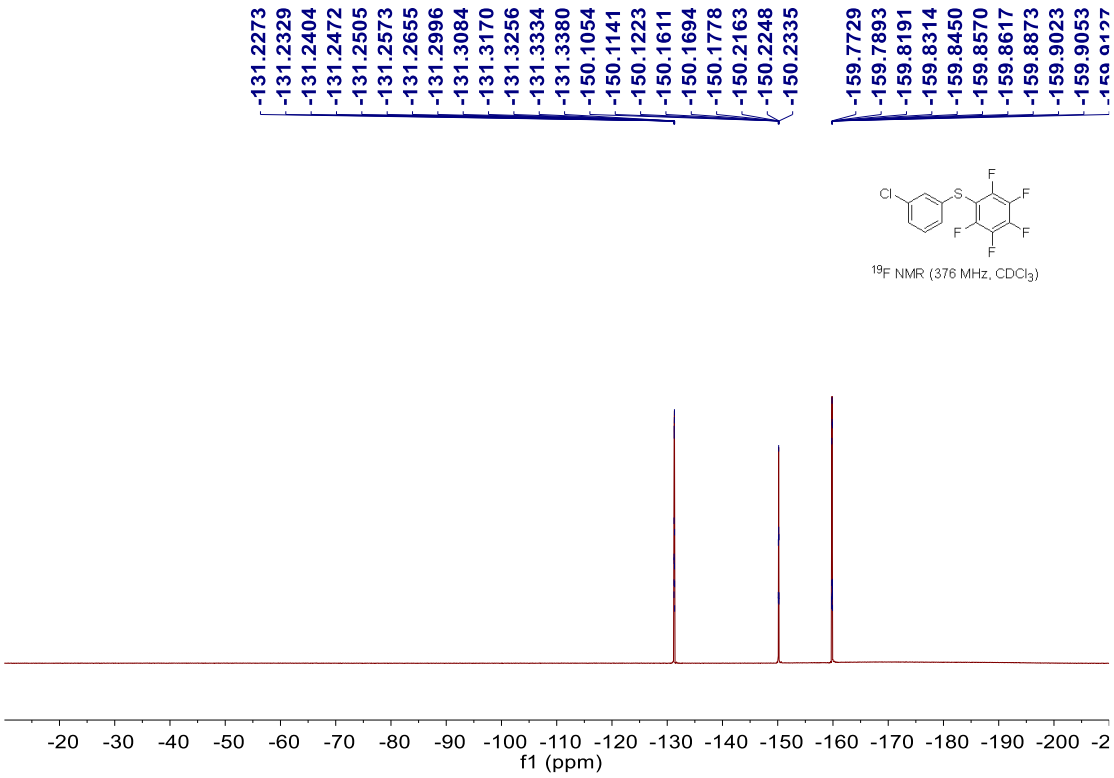

149.12
149.09
149.04
149.01
149.00
148.98
148.94
146.65
146.61
146.57
146.53
146.50
146.46
143.90
143.76
141.20
141.07
139.51
139.48
139.40
139.35
139.32
139.30
139.22
139.15
136.98
136.93
136.87
136.85
136.80
136.77
136.75
134.12
132.24
130.38
130.23
128.78
127.66
107.23
107.20
77.48
77.16
76.84
Cl
S
F
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-136.0580
-136.0748
-136.0835
-136.1173
-136.1258
-136.1431
-155.4056
-155.4142
-155.4227
-155.4613
-155.4698
-155.4780
-155.5167
-155.5250
-155.5336
-165.0961
-165.1125
-165.1420
-165.1545
-165.1681
-165.1804
-165.1850
-165.2104
-165.2261
Cl
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

3h


7.295
7.291
7.256
7.249
7.245
7.243
7.239
7.235
7.229
7.227
7.222
7.218
7.213
0.000
Cl
S
F
F
F
F
F
1H NMR (400 MHz, CDCl3)
1.00
2.95
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.92
148.88
148.85
148.84
148.81
148.77
146.49
146.45
146.41
146.38
146.37
146.34
146.30
143.76
143.71
141.15
139.39
139.37
139.34
139.24
139.21
139.18
139.16
139.08
136.86
136.84
136.79
136.74
136.71
136.70
136.67
136.63
135.19
134.88
130.44
129.86
128.23
128.19
107.98
107.93
77.36
77.05
76.73
Cl
S
F
F
F
F
F
13C NMR (100 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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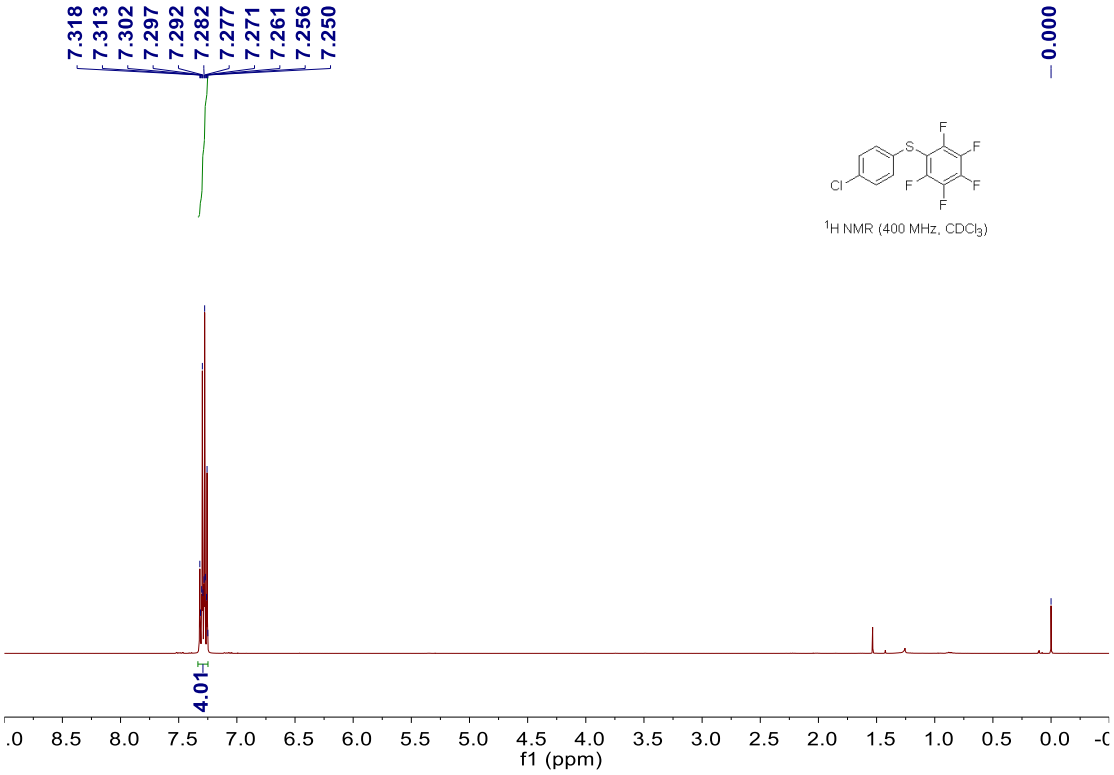
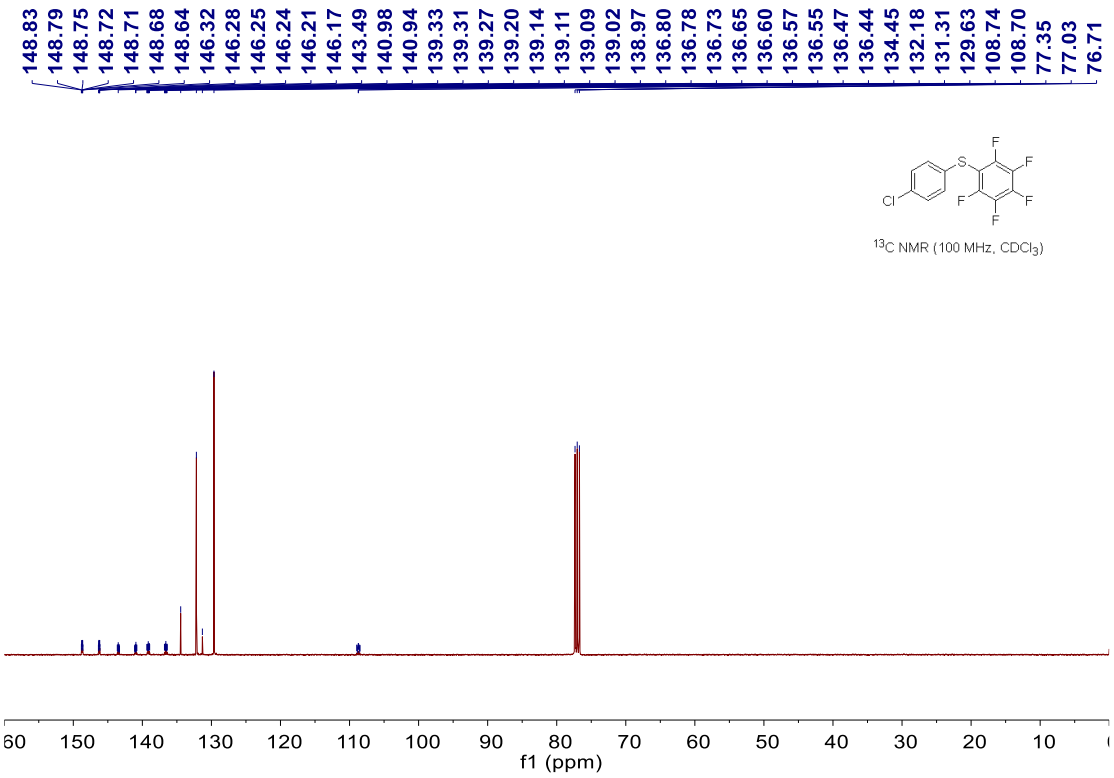
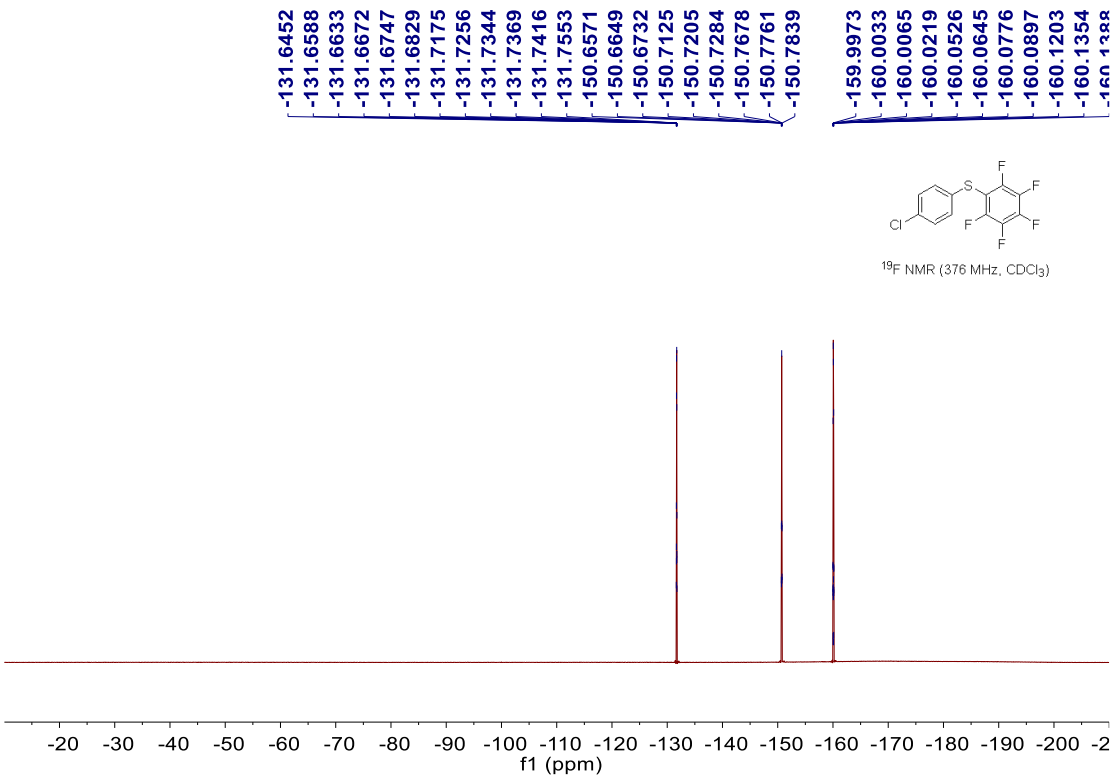
-131.2329
-131.2404
-131.2472
-131.2505
-131.2573
-131.2655
-131.2996
-131.3084
-131.3170
-131.3256
-131.3334
-131.3380
-150.1054
-150.1141
-150.1223
-150.1611
-150.1694
-150.1778
-150.2163
-150.2248
-150.2335
-159.7729
-159.7893
-159.8191
-159.8314
-159.8450
-159.8570
-159.8617
-159.8873
-159.9023
-159.9053
Cl
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

3i


7.318
7.313
7.302
7.297
7.292
7.282
7.277
7.271
7.261
7.256
7.250
0.000
F
S
F
Cl
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
4.01
f1 (ppm)


148.83
148.79
148.75
148.72
148.71
148.68
148.64
146.32
146.28
146.25
146.24
146.21
146.17
143.49
140.98
140.94
139.33
139.31
139.27
139.20
139.14
139.11
139.09
139.02
138.97
136.80
136.78
136.73
136.65
136.60
136.57
136.55
136.47
136.44
134.45
132.18
131.31
129.63
108.74
108.70
77.35
77.03
76.71
F
S
F
Cl
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)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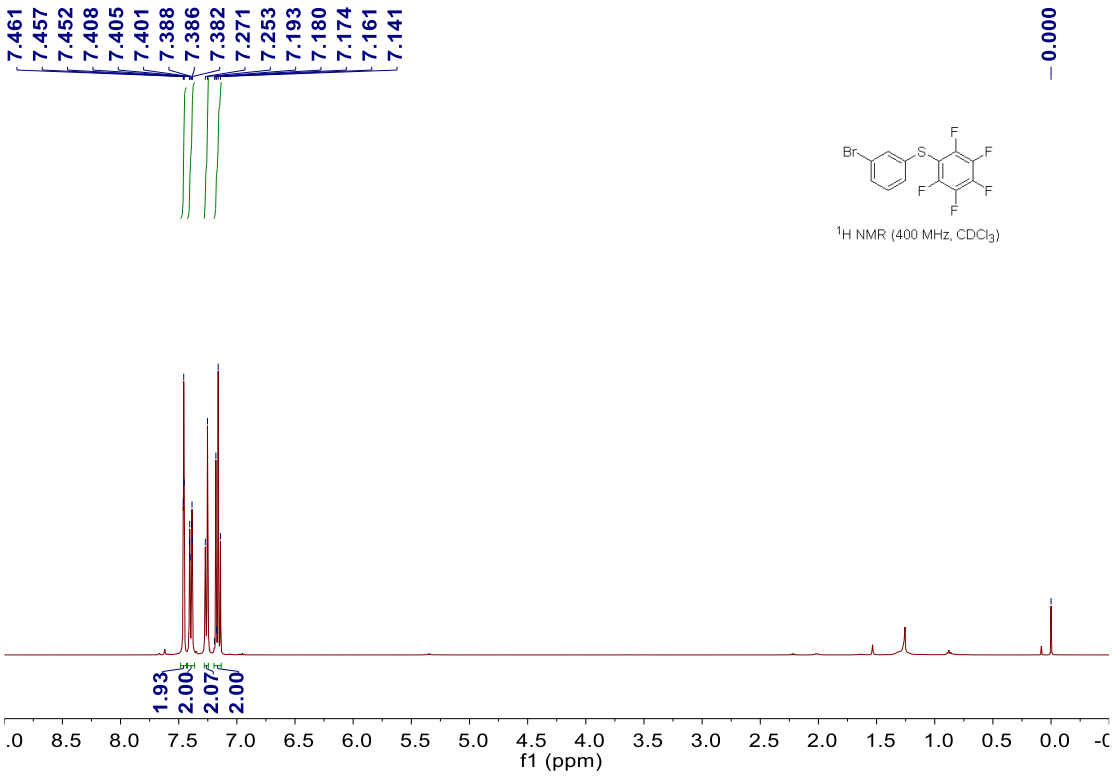
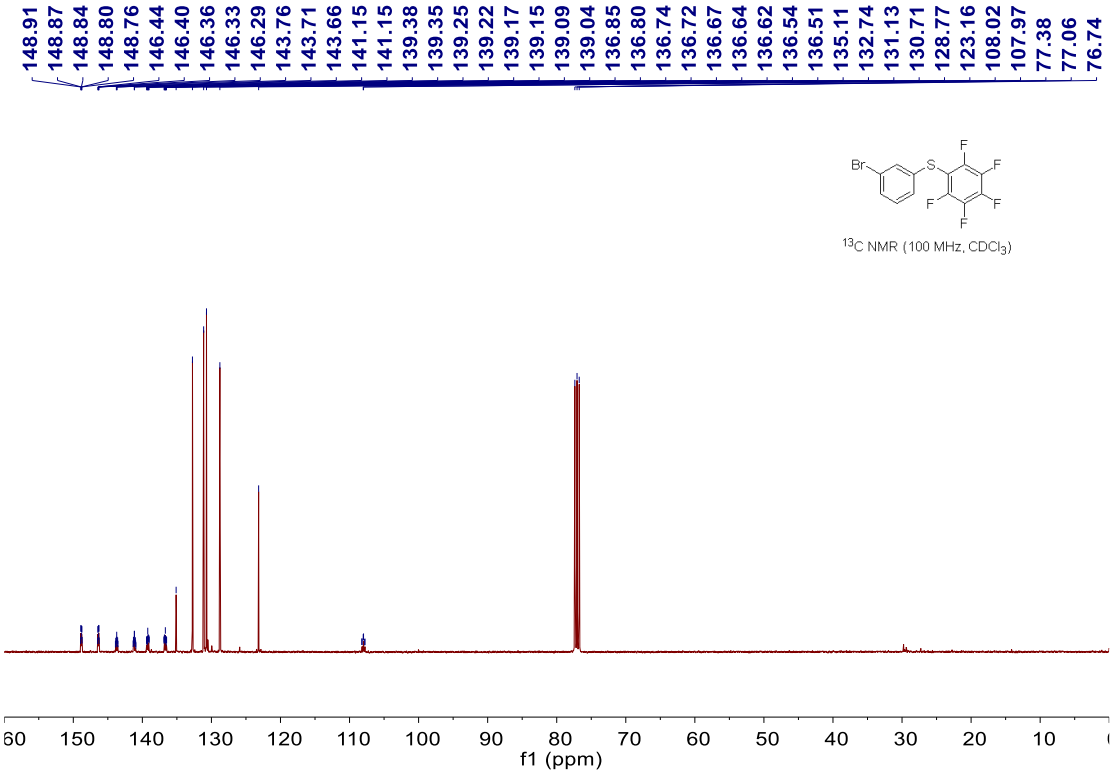
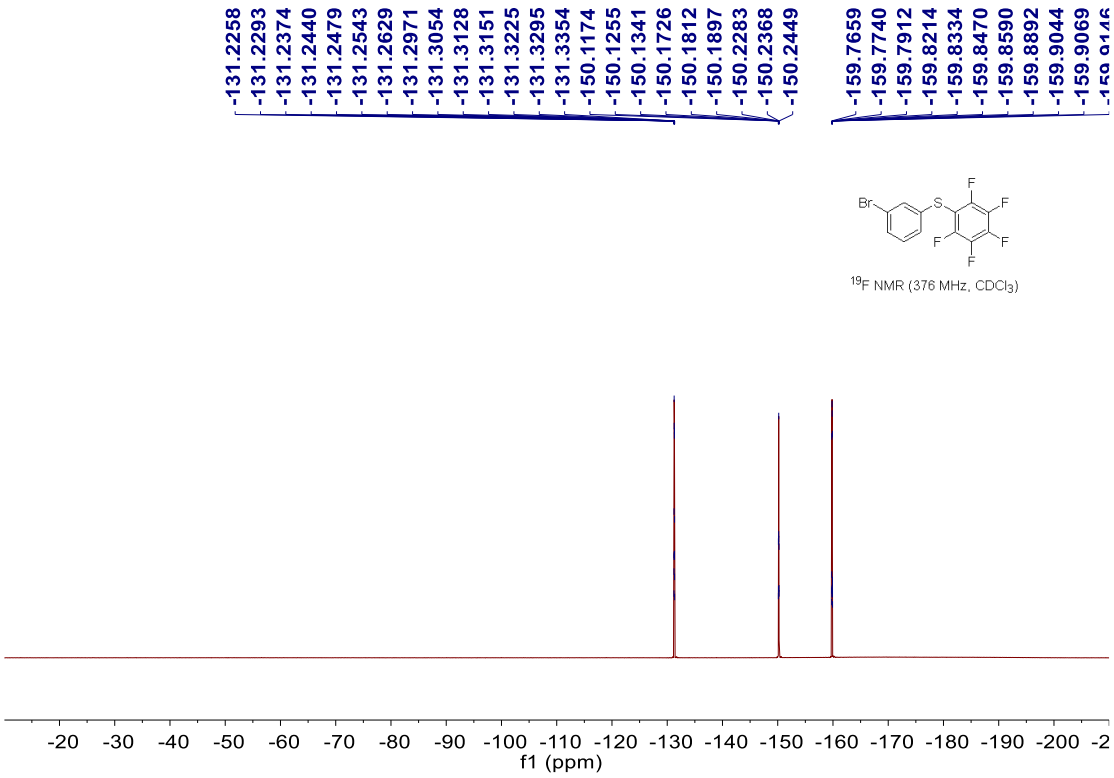
-131.6633
-131.6672
-131.6747
-131.6829
-131.7175
-131.7256
-131.7344
-131.7369
-131.7416
-131.7553
-150.6571
-150.6649
-150.6732
-150.7125
-150.7205
-150.7284
-150.7678
-150.7761
-150.7839
-159.9973
-160.0033
-160.0065
-160.0219
-160.0526
-160.0645
-160.0776
-160.0897
-160.1203
-160.1354
Cl
S
F
^{19}F NMR (376 MHz, CDCl$_3$)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

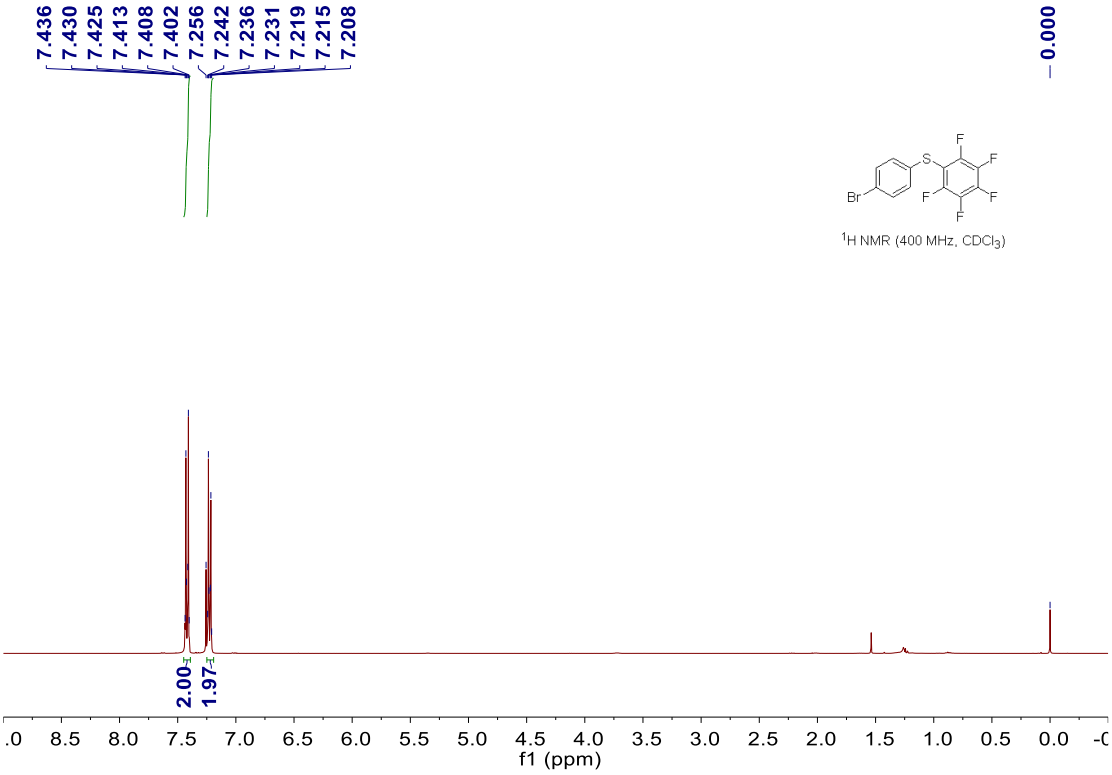
3j

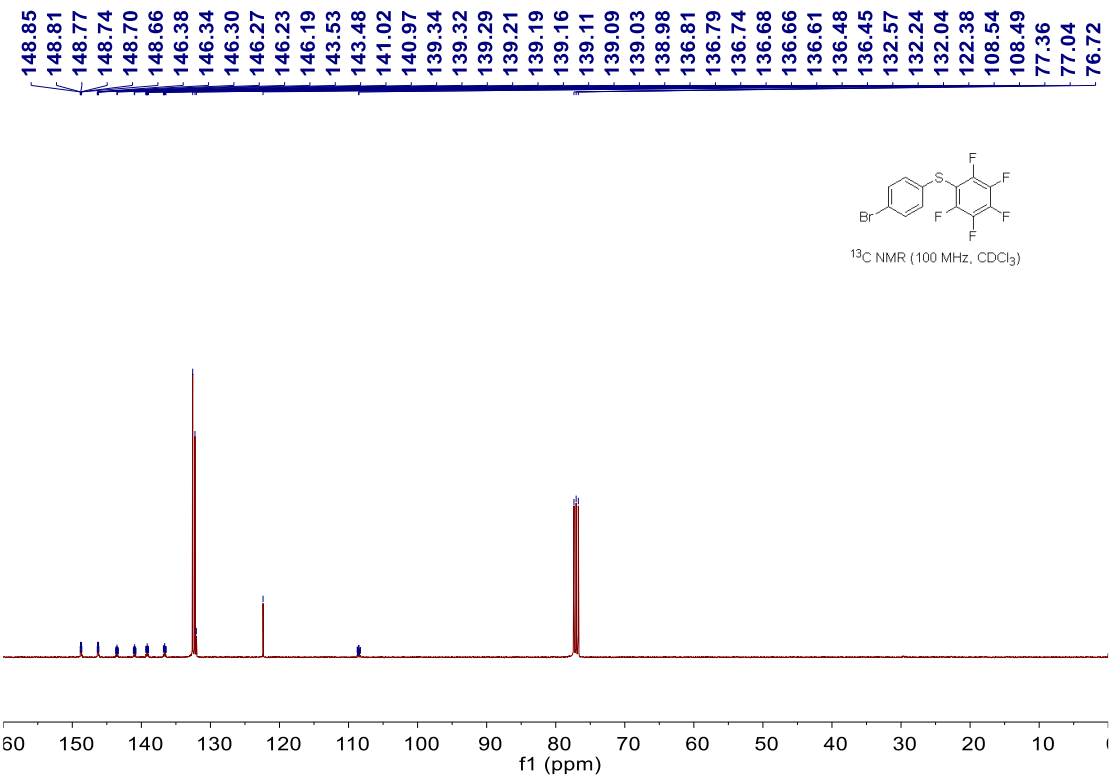

7.461
7.457
7.452
7.408
7.405
7.401
7.388
7.386
7.382
7.271
7.253
7.193
7.180
7.174
7.161
7.141
0.000
Br
S
F
^{1}H NMR (400 MHz, CDCl$_3$)
1.93
2.00
2.07
2.00
f1 (ppm)

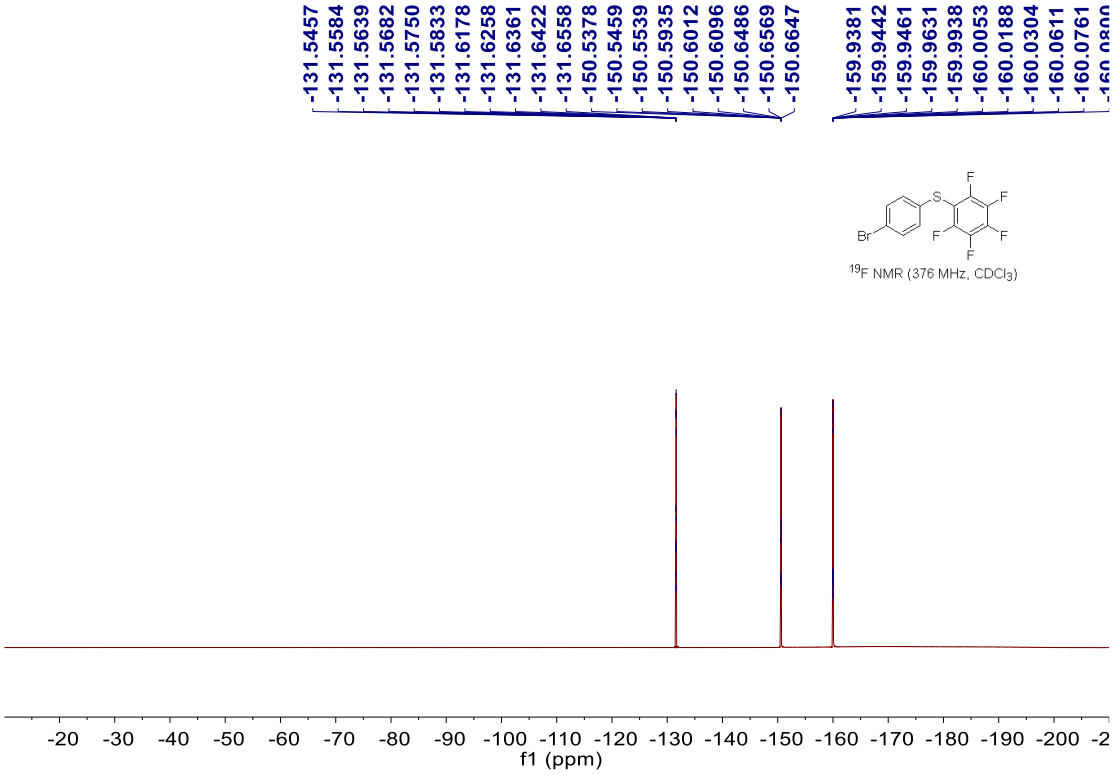

148.91
148.87
148.84
148.80
148.76
146.44
146.40
146.36
146.33
146.29
143.76
143.71
143.66
141.15
141.15
139.38
139.35
139.25
139.22
139.17
139.15
139.09
139.04
136.85
136.80
136.74
136.72
136.67
136.64
136.62
136.54
136.51
135.11
132.74
131.13
130.71
128.77
123.16
108.02
107.97
77.38
77.06
76.74
Br
S
F
F
F
F
F
13C NMR (100 MHz, CDCl3)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-131.2258
-131.2293
-131.2374
-131.2440
-131.2479
-131.2543
-131.2629
-131.2971
-131.3054
-131.3128
-131.3151
-131.3225
-131.3295
-131.3354
-150.1174
-150.1255
-150.1341
-150.1726
-150.1812
-150.1897
-150.2283
-150.2368
-150.2449
-159.7659
-159.7740
-159.7912
-159.8214
-159.8334
-159.8470
-159.8590
-159.8892
-159.9044
-159.9069
Br
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

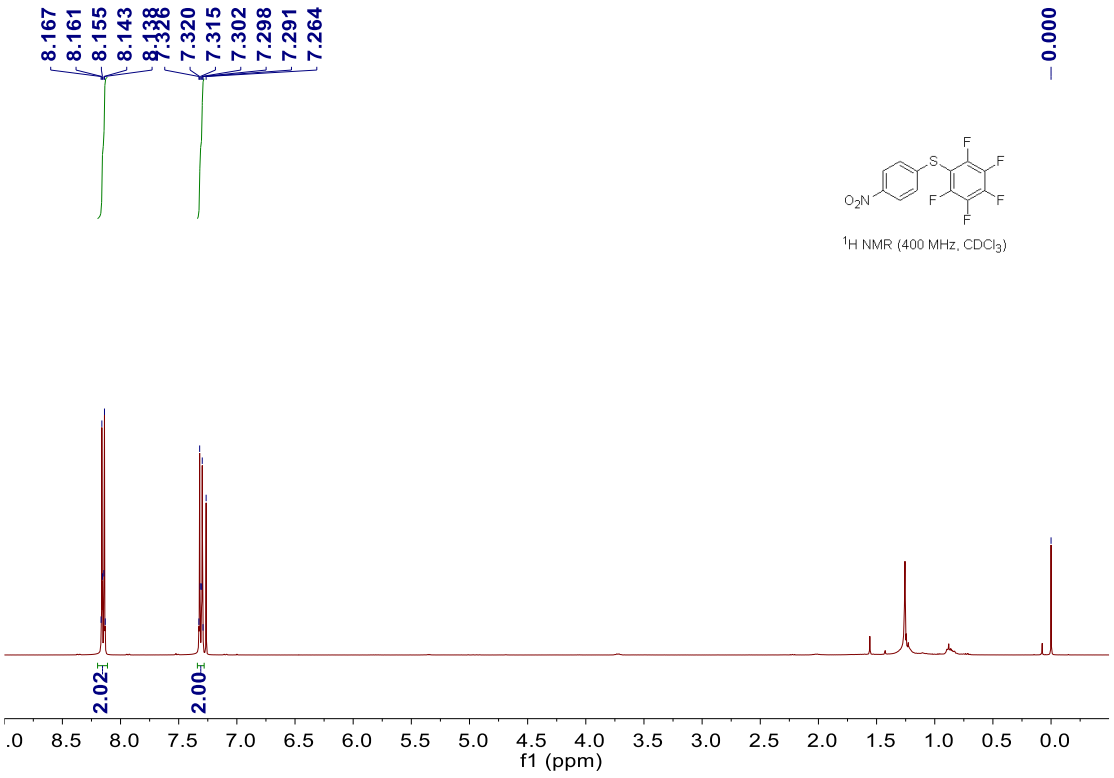
3k

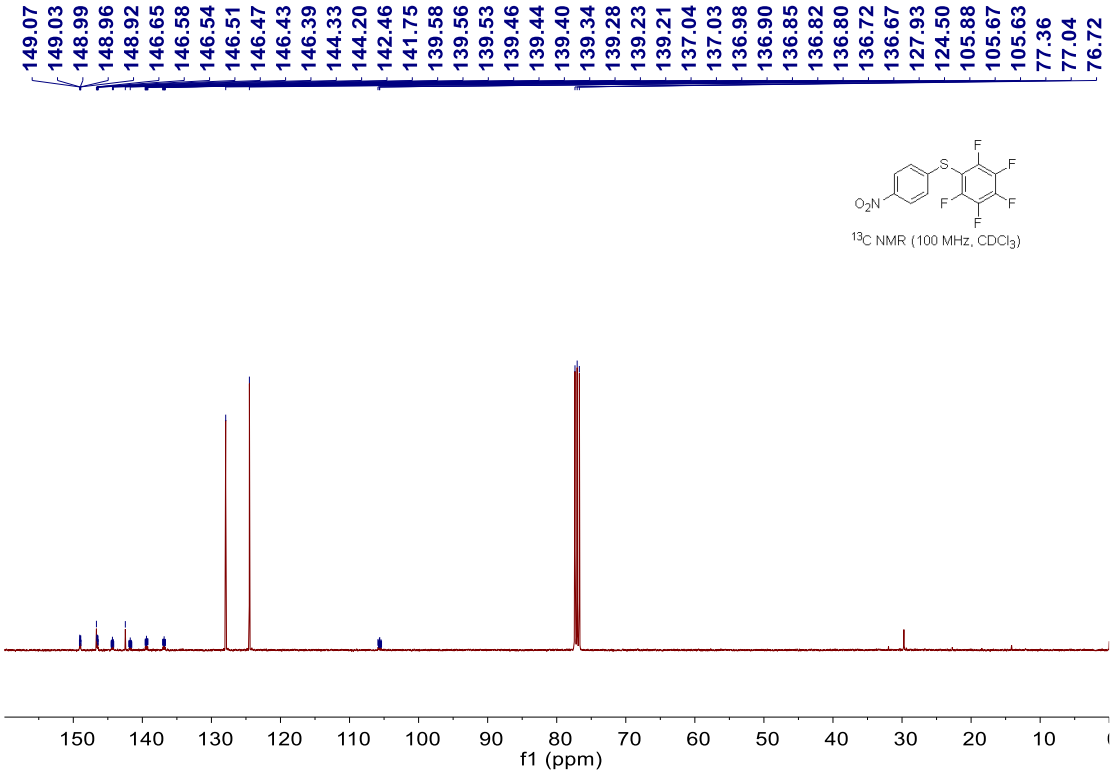

7.436
7.430
7.425
7.413
7.408
7.402
7.256
7.242
7.236
7.231
7.219
7.215
7.208
0.000
Br
S
F
F
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
1.97
f1 (ppm)

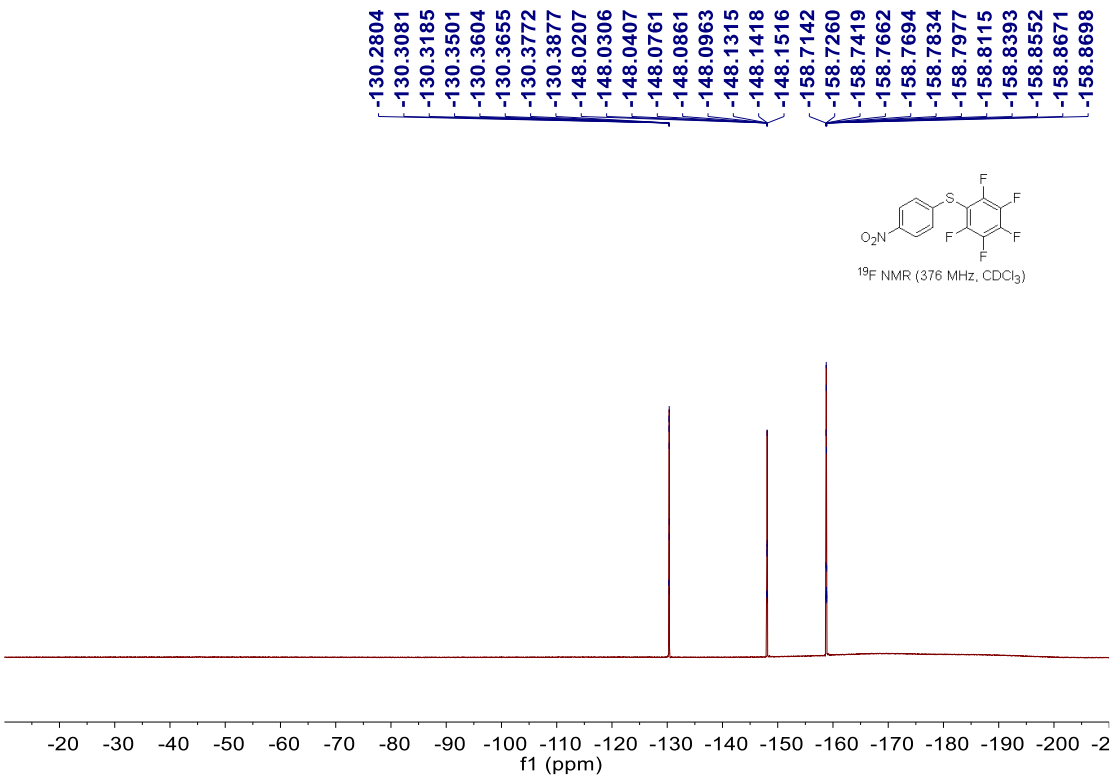

148.85
148.81
148.77
148.74
148.70
148.66
146.38
146.34
146.30
146.27
146.23
146.19
143.53
143.48
141.02
140.97
139.34
139.32
139.29
139.21
139.19
139.16
139.11
139.09
139.03
138.98
136.81
136.79
136.74
136.68
136.66
136.61
136.48
136.45
132.57
132.24
132.04
122.38
108.54
108.49
77.36
77.04
76.72
Br
S
F
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-131.5457
-131.5584
-131.5639
-131.5682
-131.5750
-131.5833
-131.6178
-131.6258
-131.6361
-131.6422
-131.6558
-150.5378
-150.5459
-150.5539
-150.5935
-150.6012
-150.6096
-150.6486
-150.6569
-150.6647
-159.9381
-159.9442
-159.9461
-159.9631
-159.9938
-160.0053
-160.0188
-160.0304
-160.0611
-160.0761
Br
S
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

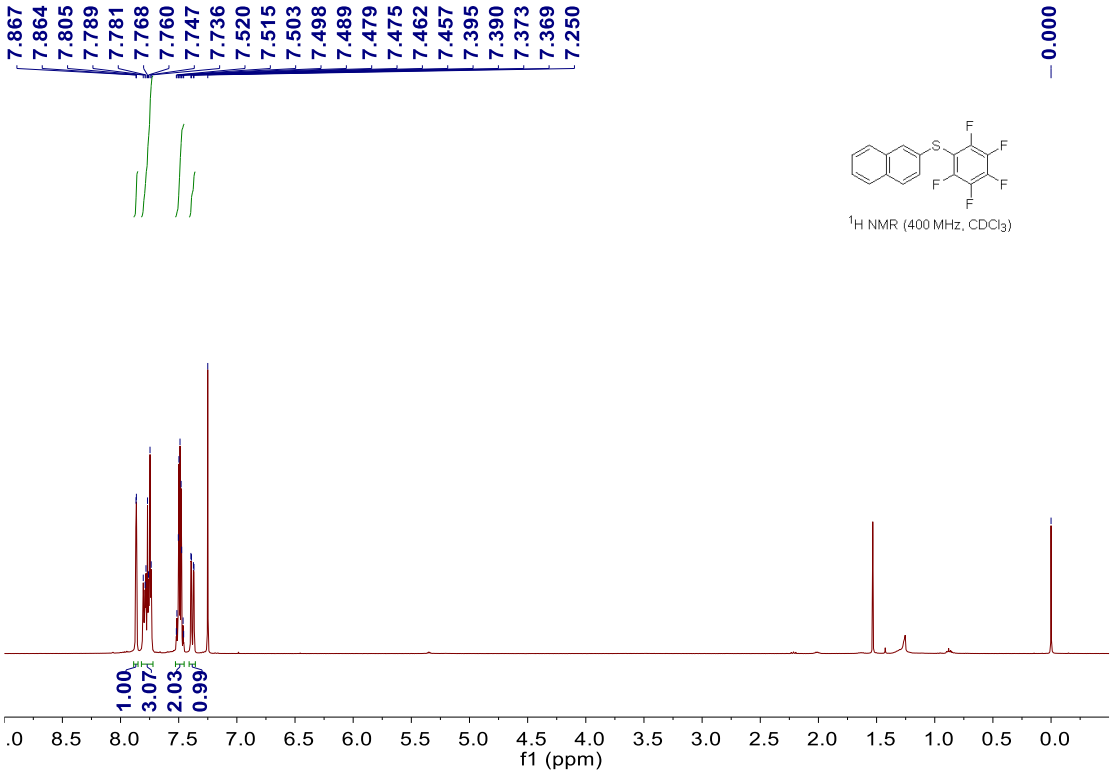
3l

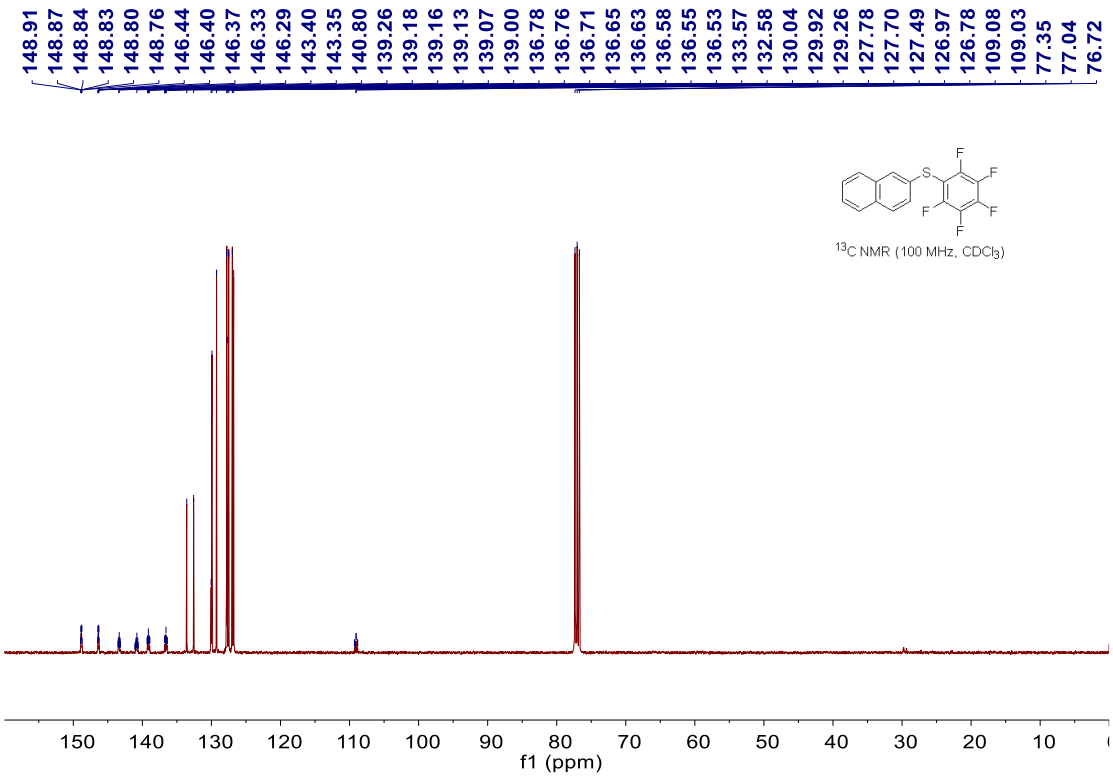

8.167
8.161
8.155
8.143
7.320
7.315
7.302
7.298
7.291
7.264
0.000
O2N
S
F
1H NMR (400 MHz, CDCl3)
2.02
2.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

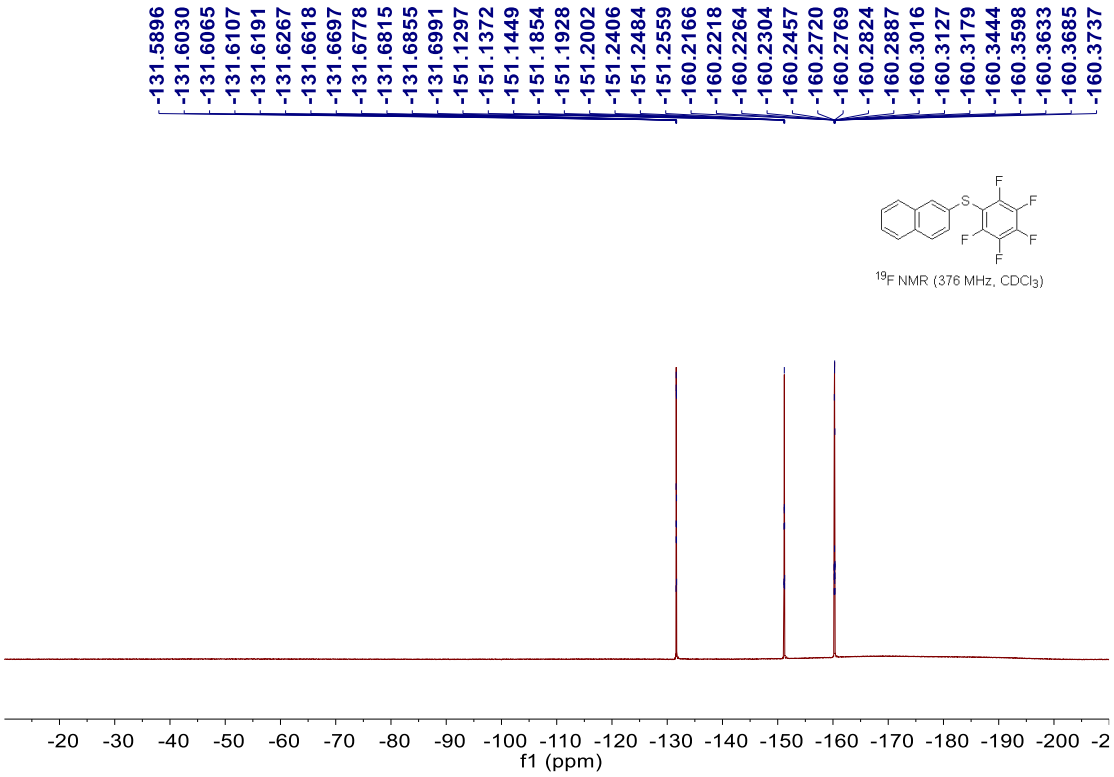

149.07
149.03
148.99
148.96
148.92
146.65
146.58
146.54
146.51
146.47
146.43
146.39
144.33
144.20
142.46
141.75
139.58
139.56
139.53
139.46
139.44
139.40
139.34
139.28
139.23
139.21
137.04
137.03
136.98
136.90
136.85
136.82
136.80
136.72
136.67
127.93
124.50
105.88
105.67
105.63
77.36
77.04
76.72
^{13}C NMR (100 MHz, CDCl$_3$)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-130.2804
-130.3081
-130.3185
-130.3501
-130.3604
-130.3655
-130.3772
-130.3877
-148.0207
-148.0306
-148.0407
-148.0761
-148.0861
-148.0963
-148.1315
-148.1418
-148.1516
-158.7142
-158.7260
-158.7419
-158.7662
-158.7694
-158.7834
-158.7977
-158.8115
-158.8393
-158.8552
-158.8671
-158.8698
^{19}F NMR (376 MHz, CDCl$_3$)
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

3m


7.867
7.864
7.805
7.789
7.781
7.768
7.760
7.747
7.736
7.520
7.515
7.503
7.498
7.489
7.479
7.475
7.462
7.457
7.395
7.390
7.373
7.369
7.250
0.000
F
S
F
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
3.07
2.03
0.99
f1 (ppm)


148.91
148.87
148.84
148.83
148.80
148.76
146.44
146.40
146.37
146.33
146.29
143.40
143.35
140.80
139.26
139.18
139.16
139.13
139.07
139.00
136.78
136.76
136.71
136.65
136.63
136.58
136.55
136.53
133.57
132.58
130.04
129.92
129.26
127.78
127.70
127.49
126.97
126.78
109.08
109.03
77.35
77.04
76.72
F
S
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)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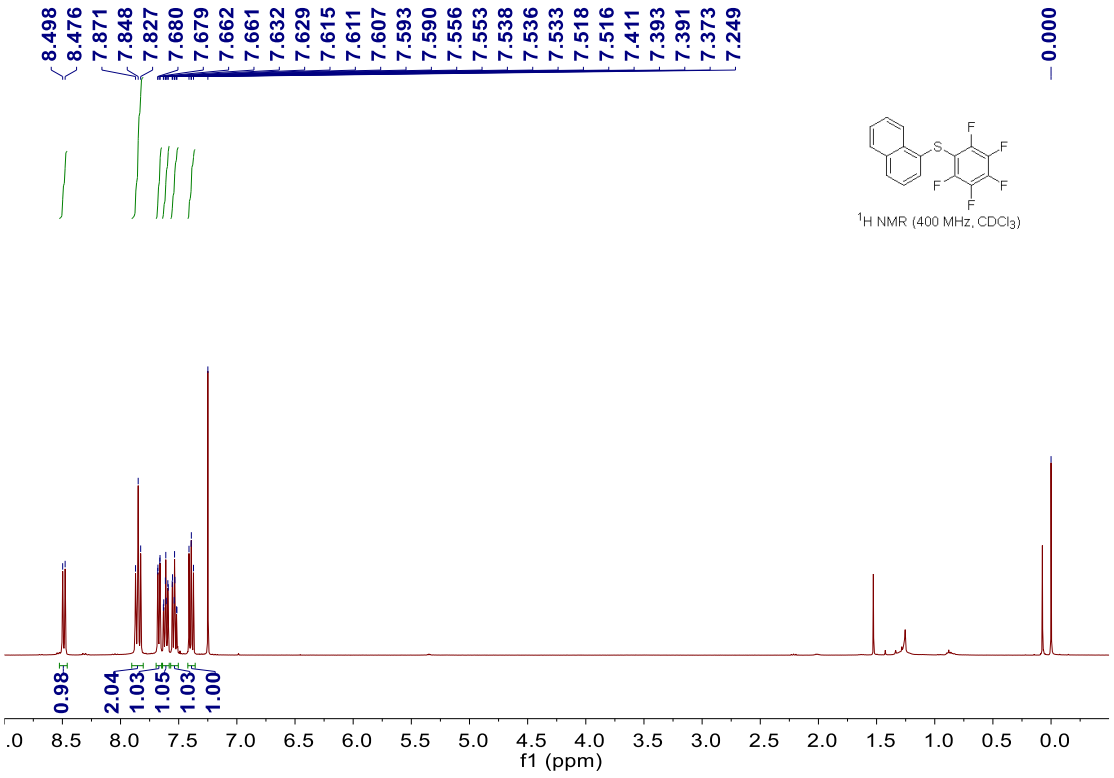
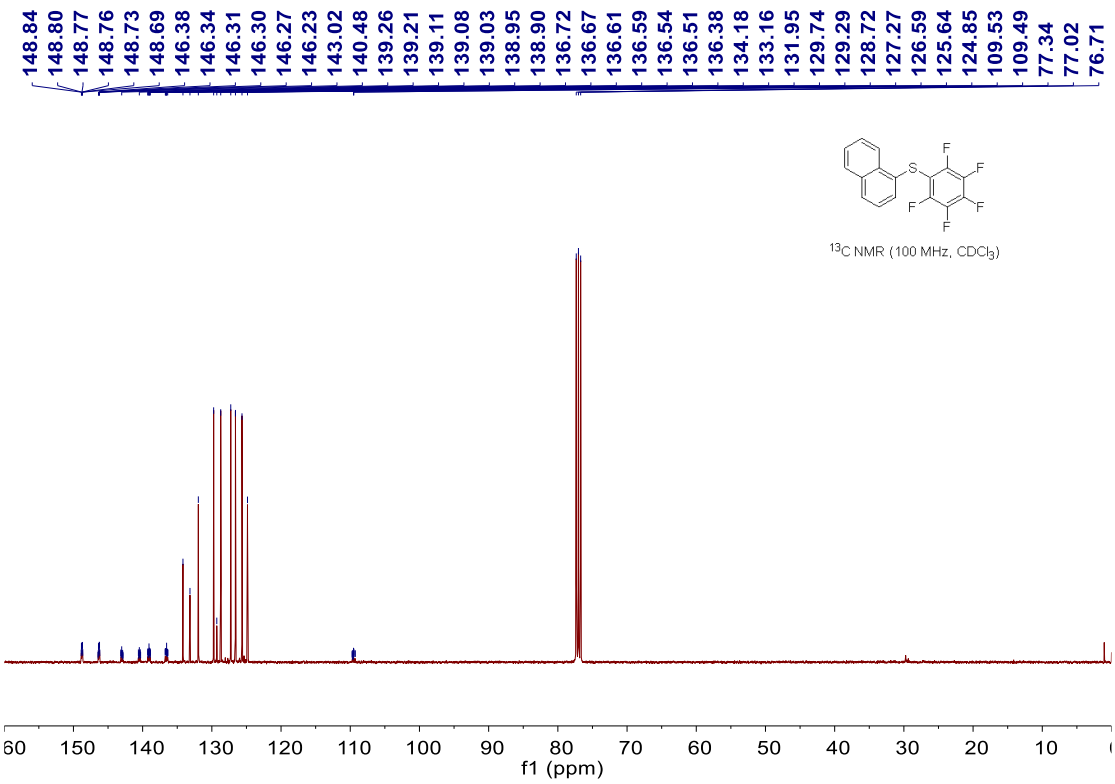
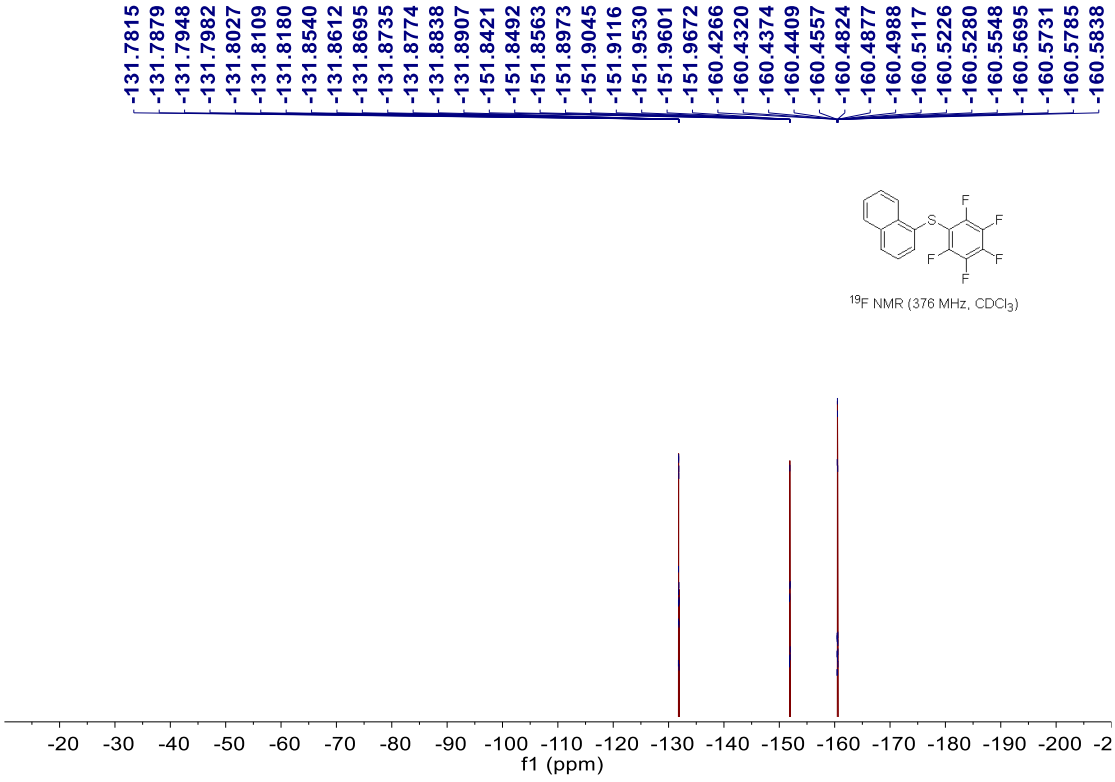
-131.6030
-131.6065
-131.6107
-131.6191
-131.6267
-131.6618
-131.6697
-131.6778
-131.6815
-131.6855
-131.6991
-151.1297
-151.1372
-151.1449
-151.1854
-151.1928
-151.2002
-151.2406
-151.2484
-151.2559
-160.2166
-160.2218
-160.2264
-160.2304
-160.2457
-160.2720
-160.2769
-160.2824
-160.2887
-160.3016
-160.3127
-160.3179
-160.3444
-160.3598
-160.3633
-160.3685
-160.3737
F
S
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

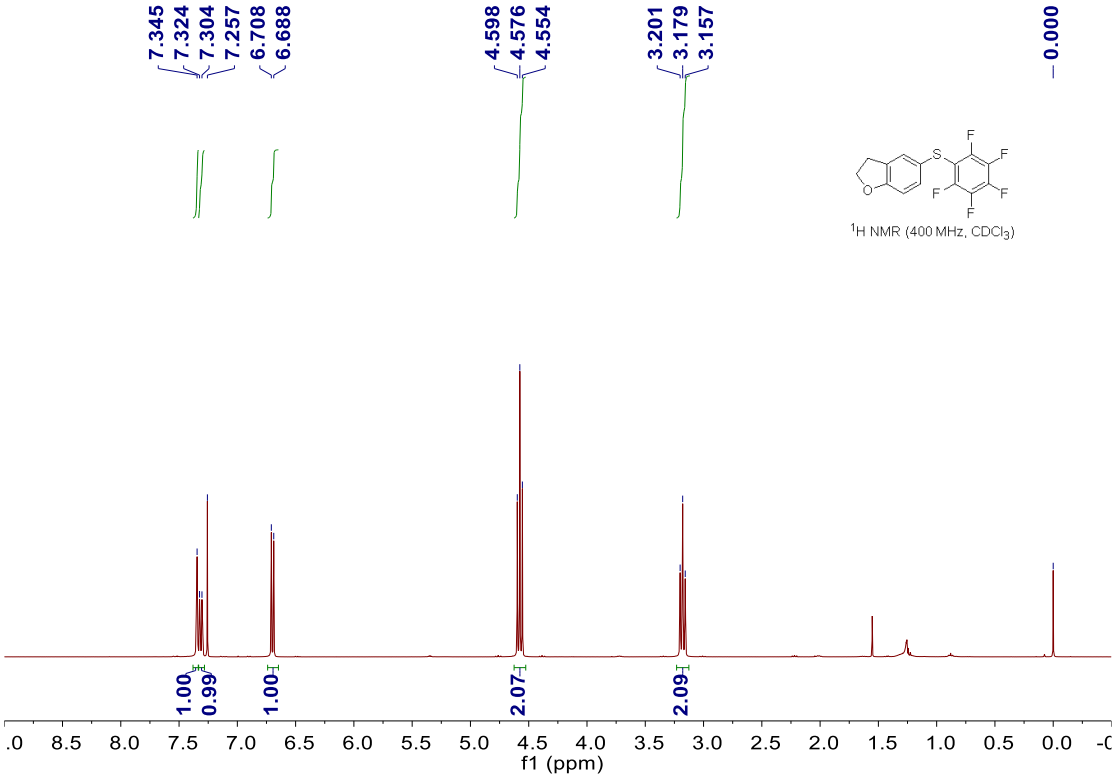
3n

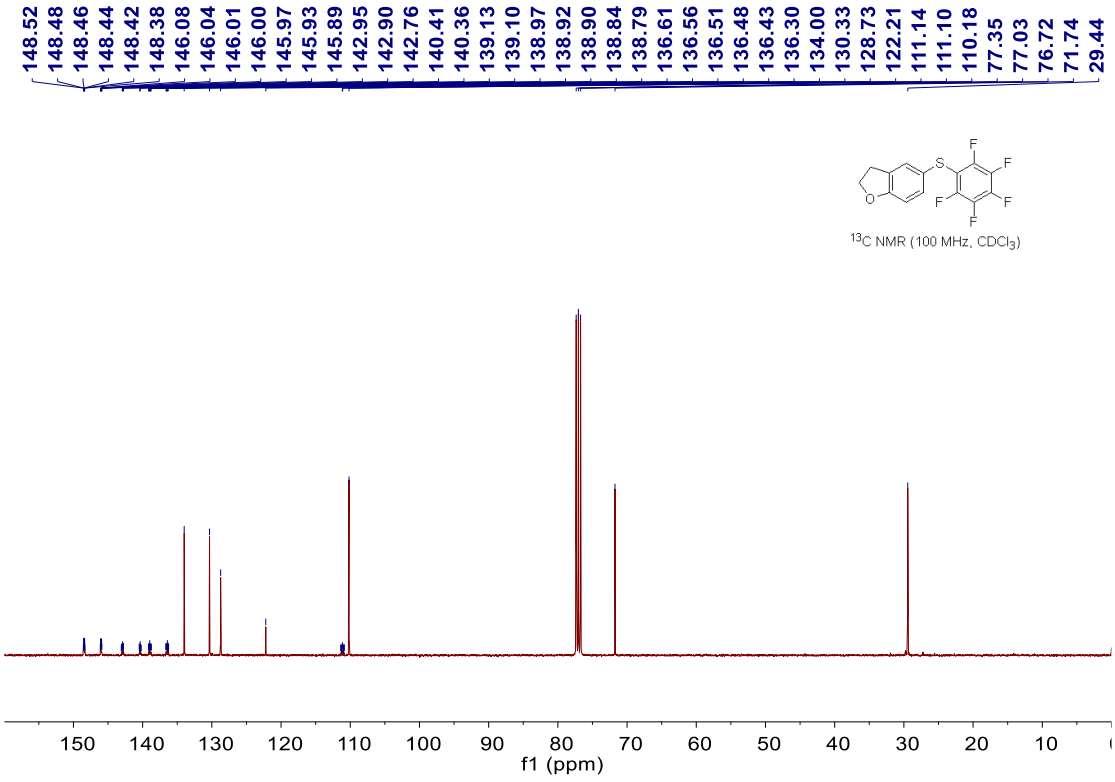

8.498
8.476
7.871
7.848
7.827
7.680
7.679
7.662
7.661
7.632
7.629
7.615
7.611
7.607
7.593
7.590
7.556
7.553
7.538
7.536
7.533
7.518
7.516
7.411
7.393
7.391
7.373
7.249
0.000
F
S
F
F
F
F
1H NMR (400 MHz, CDCl3)
0.98
2.04
1.03
1.05
1.03
1.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

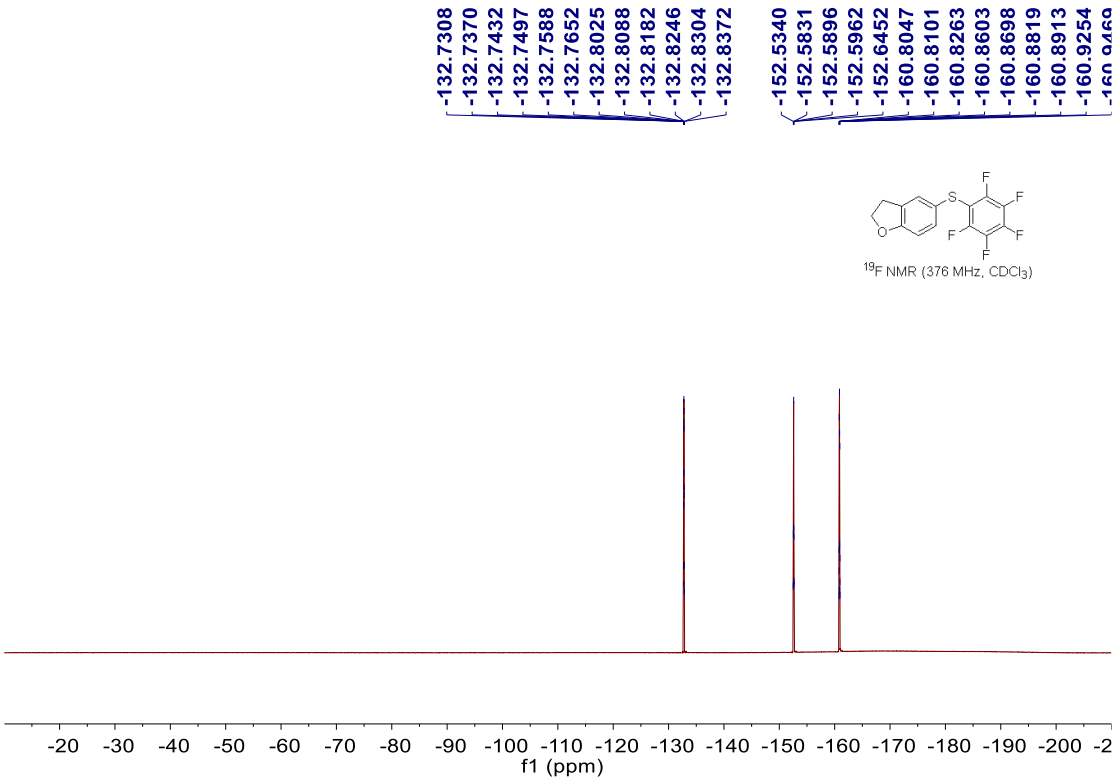

148.84
148.80
148.77
148.76
148.73
148.69
146.38
146.34
146.31
146.30
146.27
146.23
143.02
140.48
139.26
139.21
139.11
139.08
139.03
138.95
138.90
136.72
136.67
136.61
136.59
136.54
136.51
136.38
134.18
133.16
131.95
129.74
129.29
128.72
127.27
126.59
125.64
124.85
109.53
109.49
77.34
77.02
76.71
F
S
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-131.7815
-131.7879
-131.7948
-131.7982
-131.8027
-131.8109
-131.8180
-131.8540
-131.8612
-131.8695
-131.8735
-131.8774
-131.8838
-131.8907
-151.8421
-151.8492
-151.8563
-151.8973
-151.9045
-151.9116
-151.9530
-151.9601
-151.9672
-160.4266
-160.4320
-160.4374
-160.4409
-160.4557
-160.4824
-160.4877
-160.4988
-160.5117
-160.5226
-160.5280
-160.5548
-160.5695
-160.5731
-160.5785
-160.5838
F
S
F
F
F
F
^{19}F NMR (376 MHz, CDCl$_3$)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

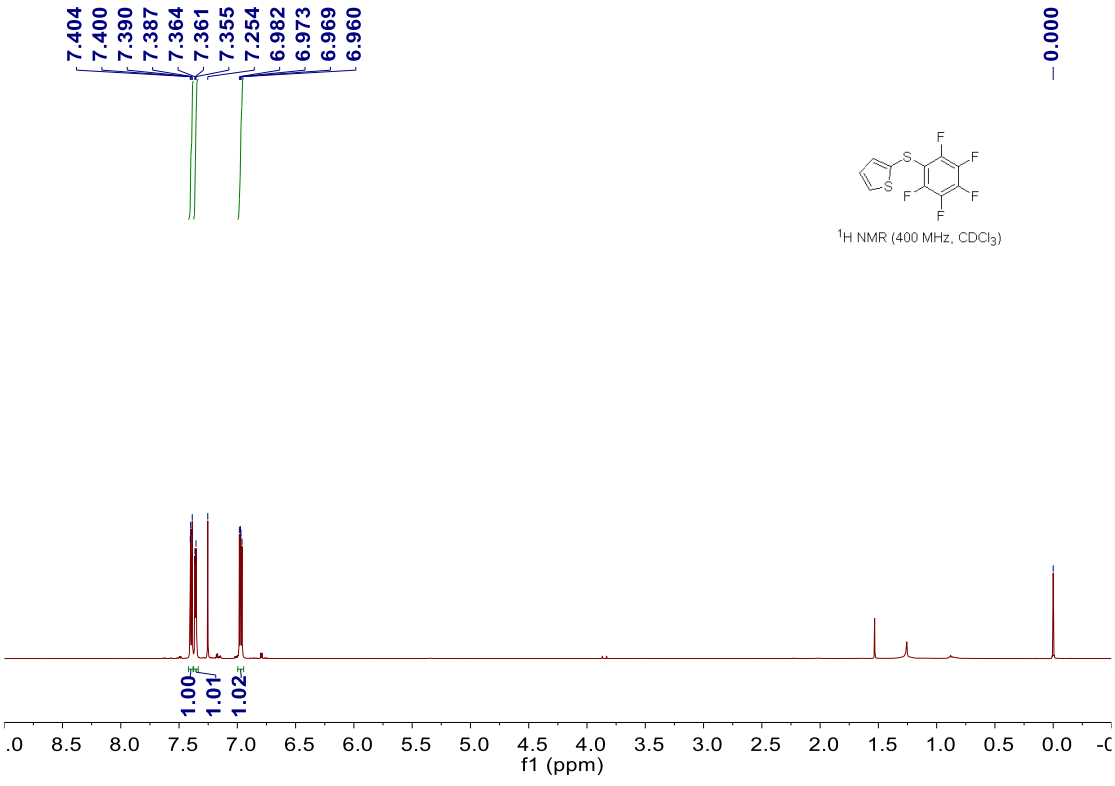
3o

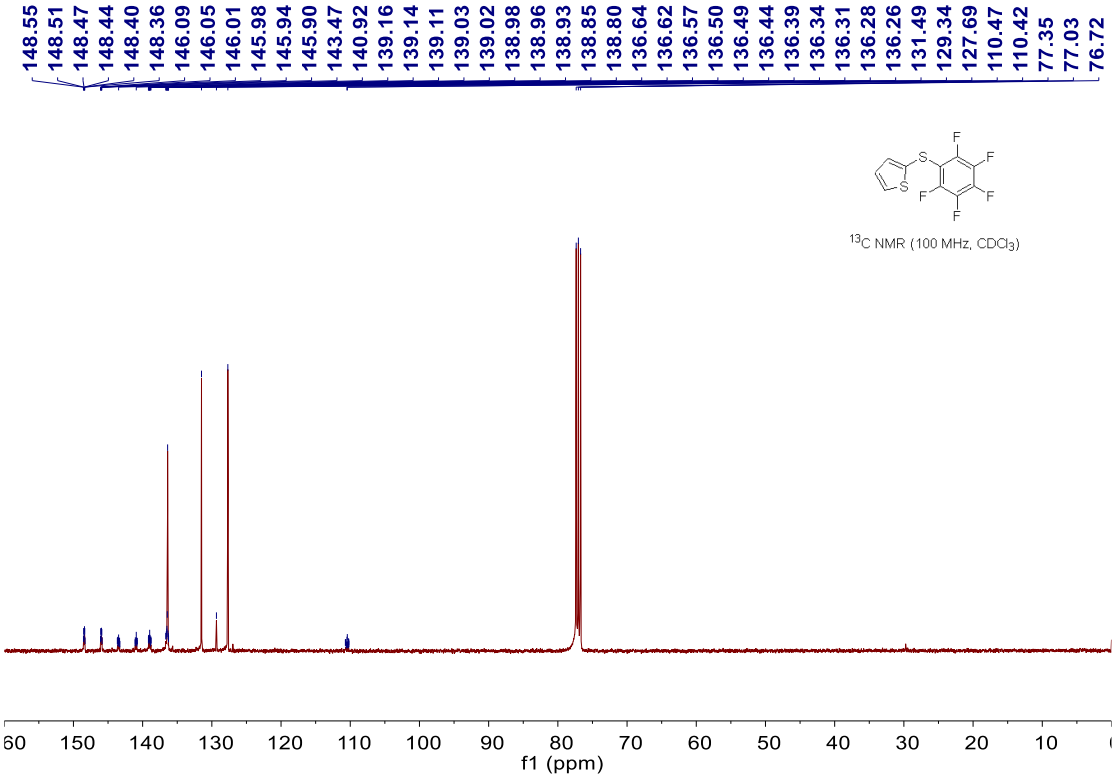

7.345
7.324
7.304
7.257
6.708
6.688
4.598
4.576
4.554
3.201
3.179
3.157
0.000
1H NMR (400 MHz, CDCl3)
1.00
0.99
1.00
2.07
2.09
f1 (ppm)

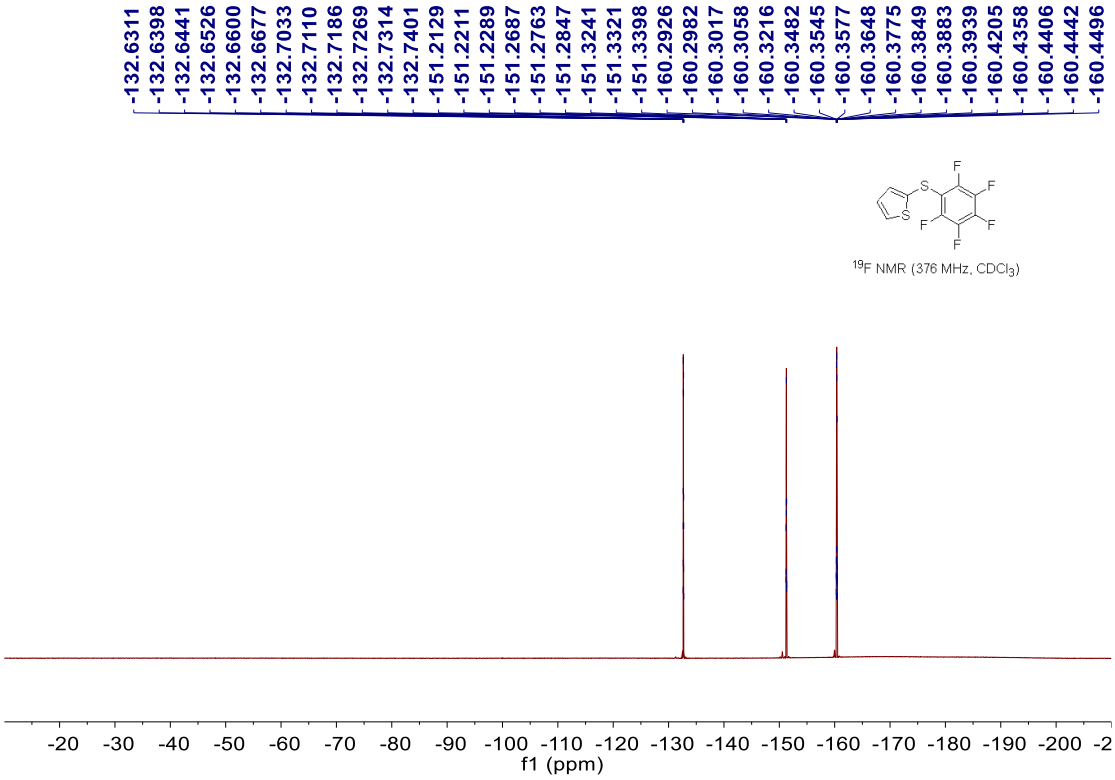

148.52
148.48
148.46
148.44
148.42
148.38
146.08
146.04
146.01
146.00
145.97
145.93
145.89
142.95
142.90
142.76
140.41
140.36
139.13
139.10
138.97
138.92
138.90
138.84
138.79
136.61
136.56
136.51
136.48
136.43
136.30
134.00
130.33
128.73
122.21
111.14
111.10
110.18
77.35
77.03
76.72
71.74
29.44
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-132.7308
-132.7370
-132.7432
-132.7497
-132.7588
-132.7652
-132.8025
-132.8088
-132.8182
-132.8246
-132.8304
-132.8372
-152.5340
-152.5831
-152.5896
-152.5962
-152.6452
-160.8047
-160.8101
-160.8263
-160.8603
-160.8698
-160.8819
-160.8913
-160.9254
F
S
O
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

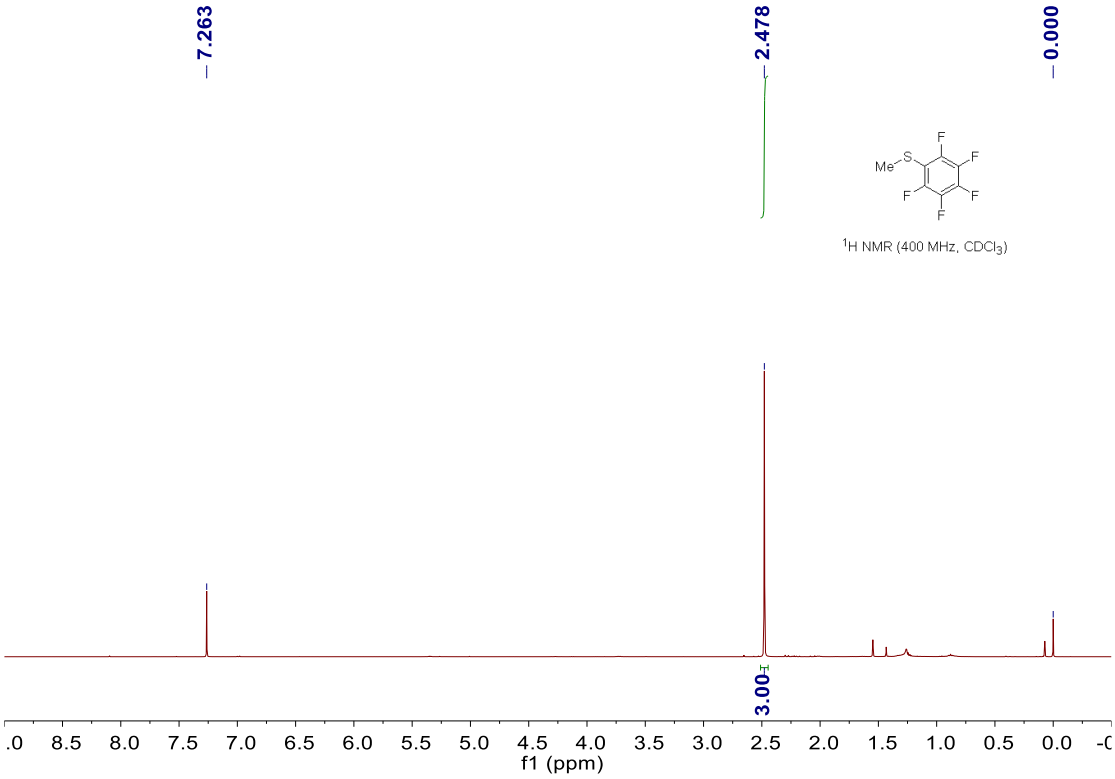
3p

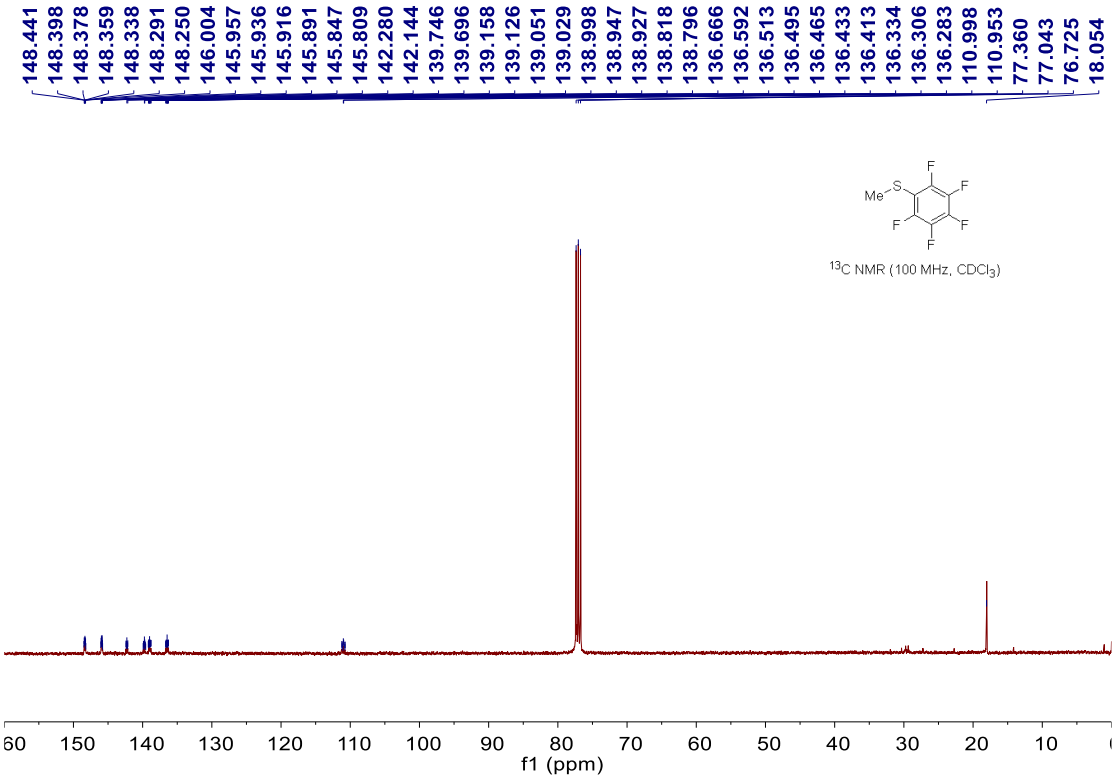

7.404
7.400
7.390
7.387
7.364
7.361
7.355
7.254
6.982
6.973
6.969
6.960
0.000
F
S
S
F
F
F
F
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.02
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

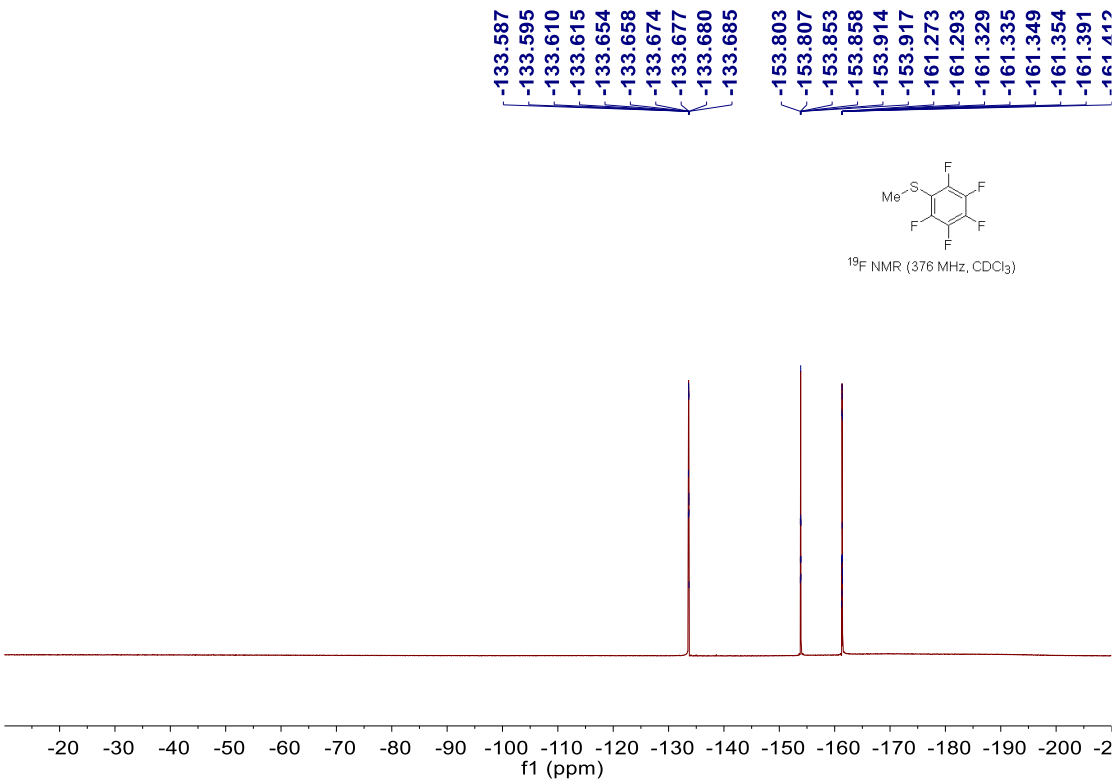

148.55
148.51
148.47
148.44
148.40
148.36
146.09
146.05
146.01
145.98
145.94
145.90
143.47
140.92
139.16
139.14
139.11
139.03
139.02
138.98
138.96
138.93
138.85
138.80
136.64
136.62
136.57
136.50
136.49
136.44
136.39
136.34
136.31
136.28
136.26
131.49
129.34
127.69
110.47
110.42
77.35
77.03
76.72
F
S
S
F
F
F
F
13C NMR (100 MHz, CDCl3)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-132.6311
-132.6398
-132.6441
-132.6526
-132.6600
-132.6677
-132.7033
-132.7110
-132.7186
-132.7269
-132.7314
-132.7401
-151.2129
-151.2211
-151.2289
-151.2687
-151.2763
-151.2847
-151.3241
-151.3321
-151.3398
-160.2926
-160.2982
-160.3017
-160.3058
-160.3216
-160.3482
-160.3545
-160.3577
-160.3648
-160.3775
-160.3849
-160.3883
-160.3939
-160.4205
-160.4358
-160.4406
-160.4442
-160.4496
F
S
S
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

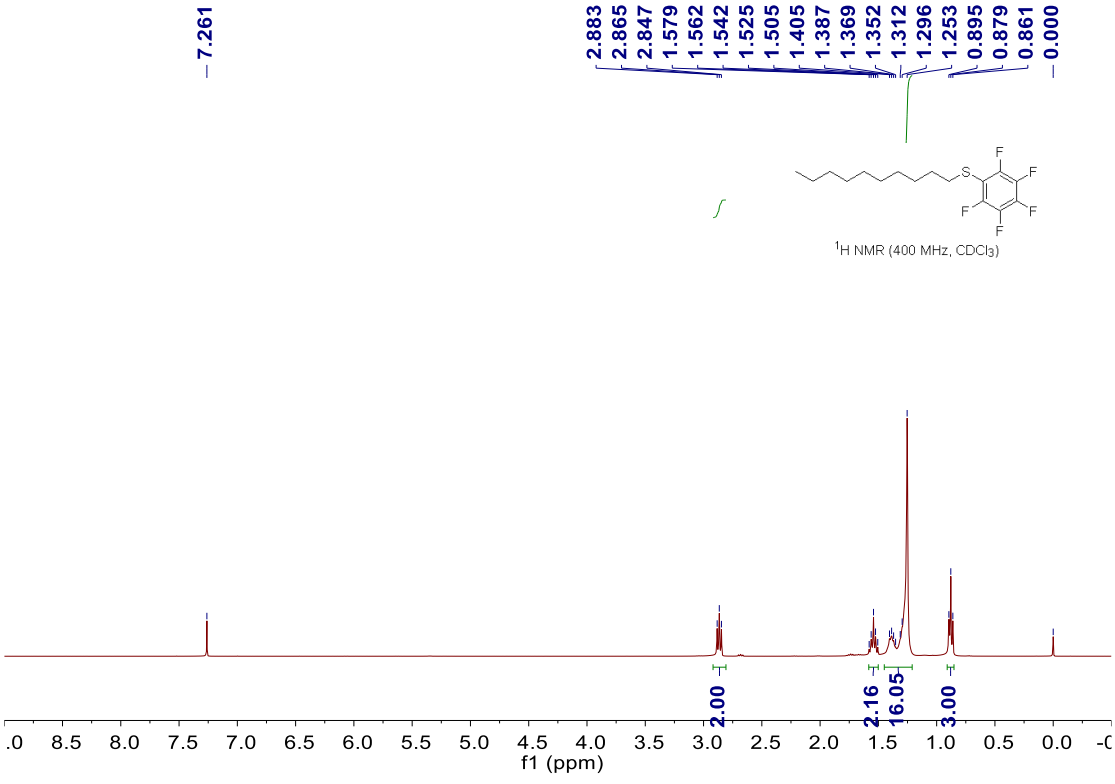
3q

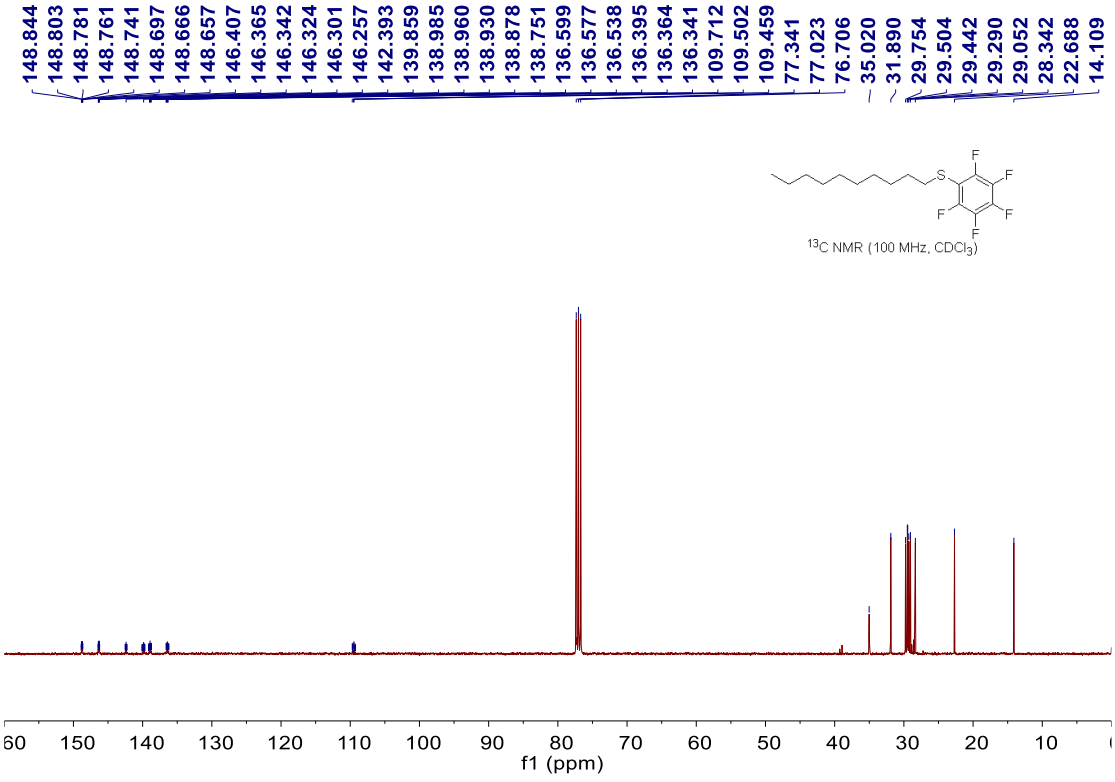

7.263
2.478
0.000
Me
S
F
F
F
F
F
^{1}H NMR (400 MHz, CDCl$_3$)
3.00
f1 (ppm)

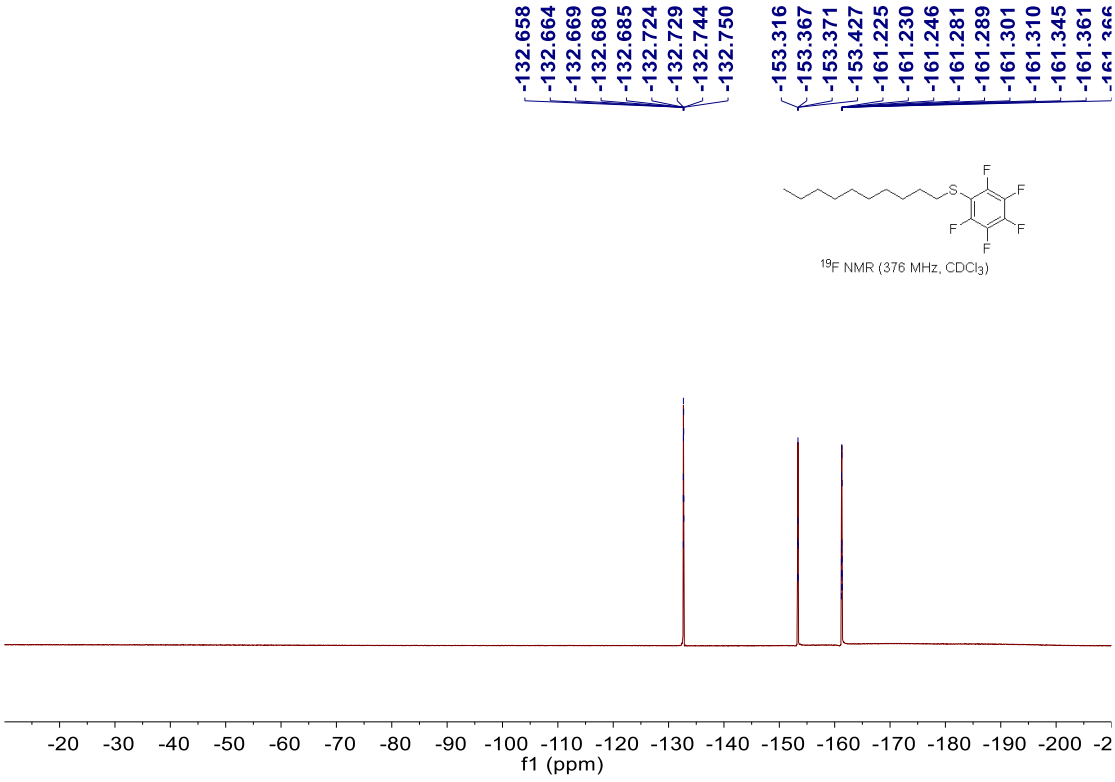

148.441
148.398
148.378
148.359
148.338
148.291
148.250
146.004
145.957
145.936
145.916
145.891
145.847
145.809
142.280
142.144
139.746
139.696
139.158
139.126
139.051
139.029
138.998
138.947
138.927
138.818
138.796
136.666
136.592
136.513
136.495
136.465
136.433
136.413
136.334
136.306
136.283
110.998
110.953
77.360
77.043
76.725
18.054
Me
S
F
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-133.587
-133.595
-133.610
-133.615
-133.654
-133.658
-133.674
-133.677
-133.680
-133.685
-153.803
-153.807
-153.853
-153.858
-153.914
-153.917
-161.273
-161.293
-161.329
-161.335
-161.349
-161.354
-161.391
Me
S
F
19F NMR (376 MHz, CDCl3)
f1 (ppm)

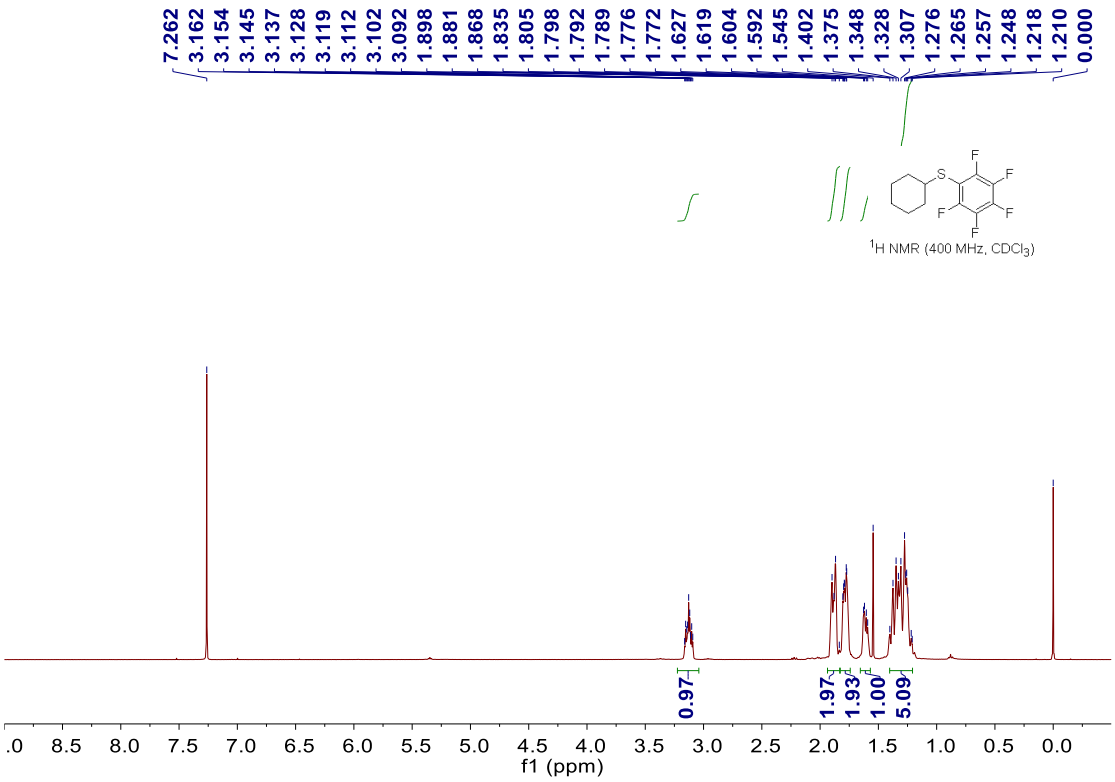
3r

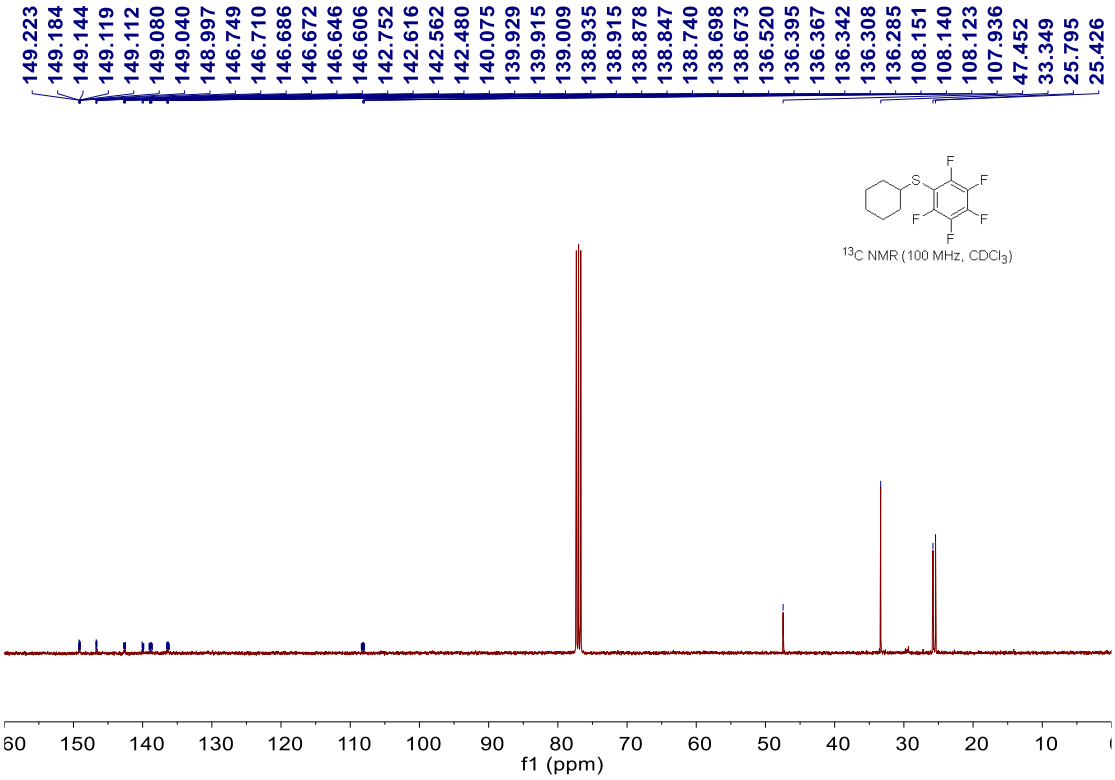

7.261
2.883
2.865
2.847
1.579
1.562
1.542
1.525
1.505
1.405
1.387
1.369
1.352
1.312
1.296
1.253
0.895
0.879
0.861
0.000
S
F
1H NMR (400 MHz, CDCl3)
2.00
2.16
16.05
3.00
f1 (ppm)

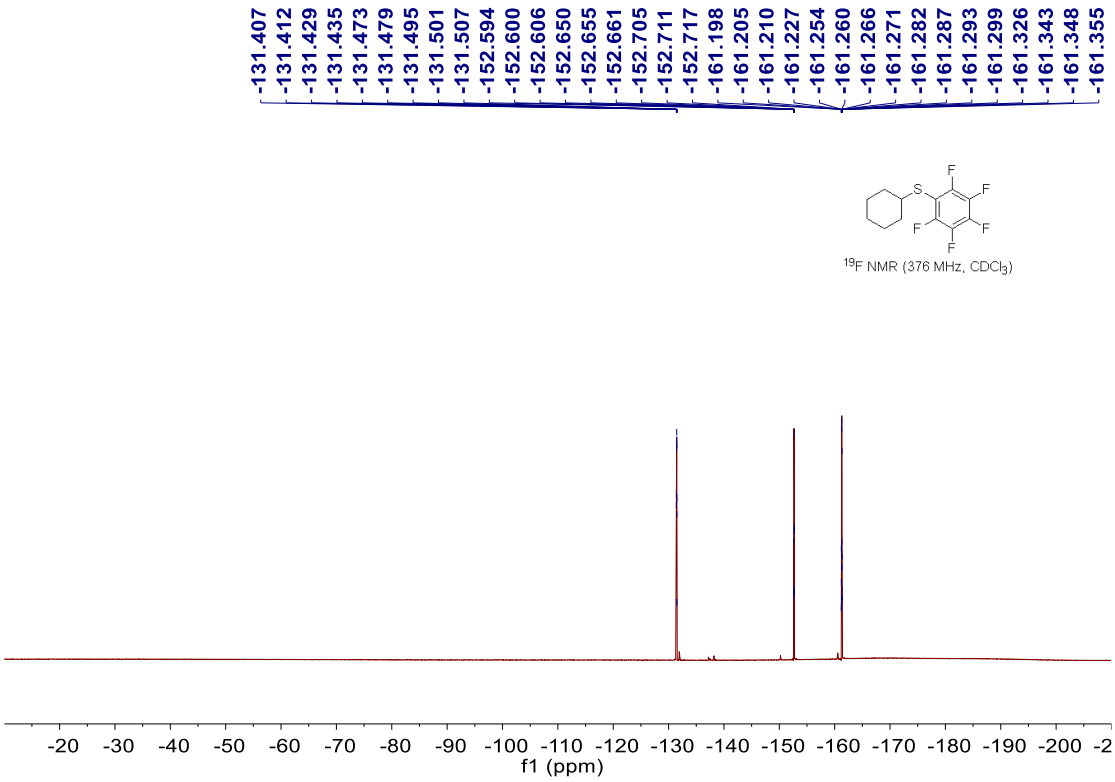

148.844
148.803
148.781
148.761
148.741
148.697
148.666
148.657
146.407
146.365
146.342
146.324
146.301
146.257
142.393
139.859
138.985
138.960
138.930
138.878
138.751
136.599
136.577
136.538
136.395
136.364
136.341
109.712
109.502
109.459
77.341
77.023
76.706
35.020
31.890
29.754
29.504
29.442
29.290
29.052
28.342
22.688
14.109
F
S
F
F
F
F
^{13}C NMR (100 MHz, CDCl$_3$)
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-132.658
-132.664
-132.669
-132.680
-132.685
-132.724
-132.729
-132.744
-132.750
-153.316
-153.367
-153.371
-153.427
-161.225
-161.230
-161.246
-161.281
-161.289
-161.301
-161.310
-161.345
-161.361
F
S
F
F
F
F
^{19}F NMR (376 MHz, CDCl$_3$)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

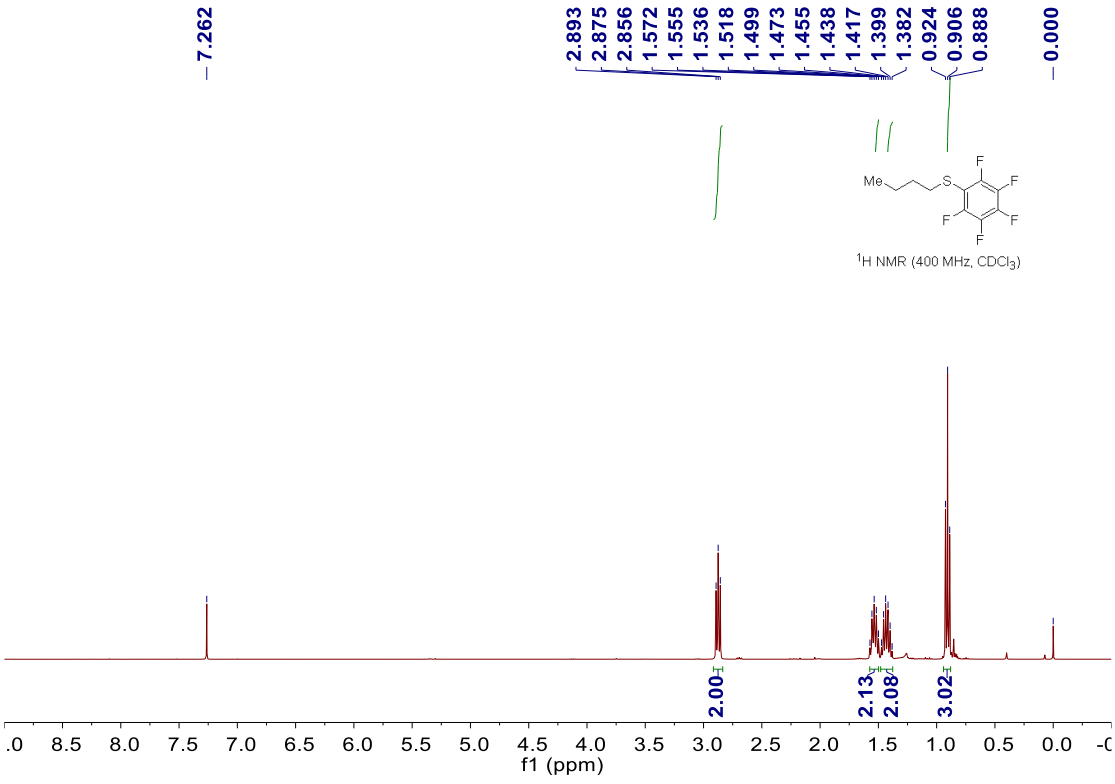
3s

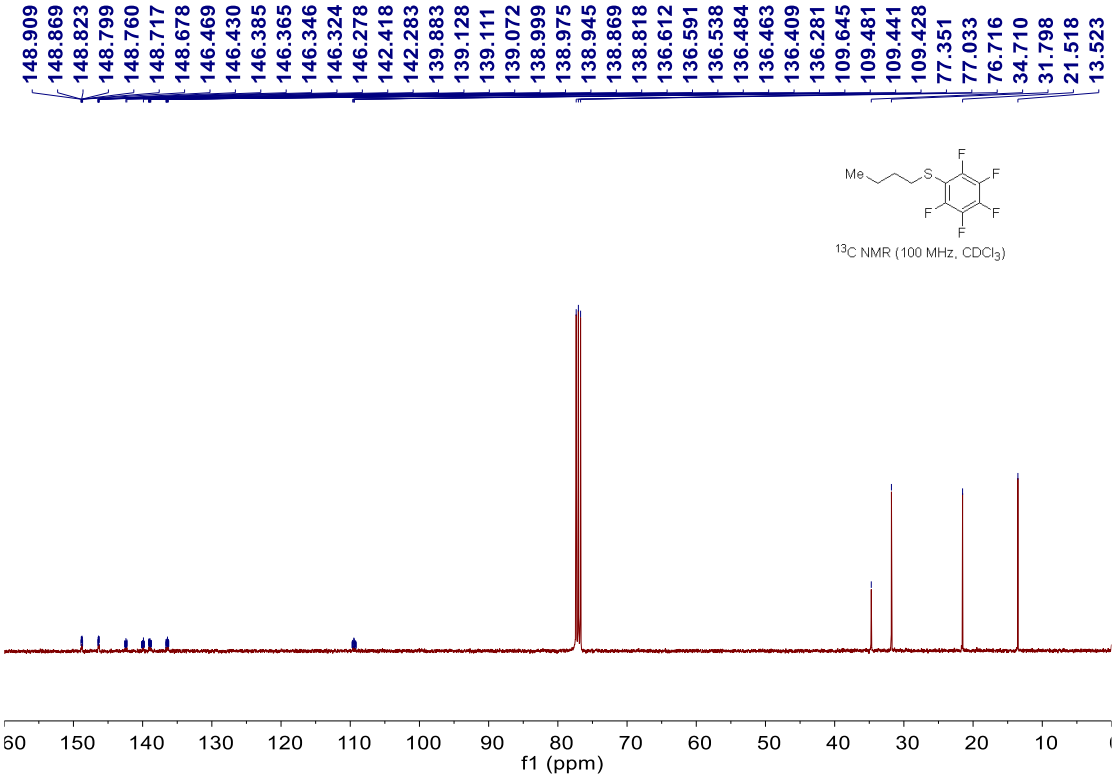

7.262
3.162
3.154
3.145
3.137
3.128
3.119
3.112
3.102
3.092
1.898
1.881
1.868
1.835
1.805
1.798
1.792
1.789
1.776
1.772
1.627
1.619
1.604
1.592
1.545
1.402
1.375
1.348
1.328
1.307
1.276
1.265
1.257
1.248
1.218
1.210
0.000
^{1}H NMR (400 MHz, CDCl$_3$)
0.97
1.97
1.93
1.00
5.09
f1 (ppm)

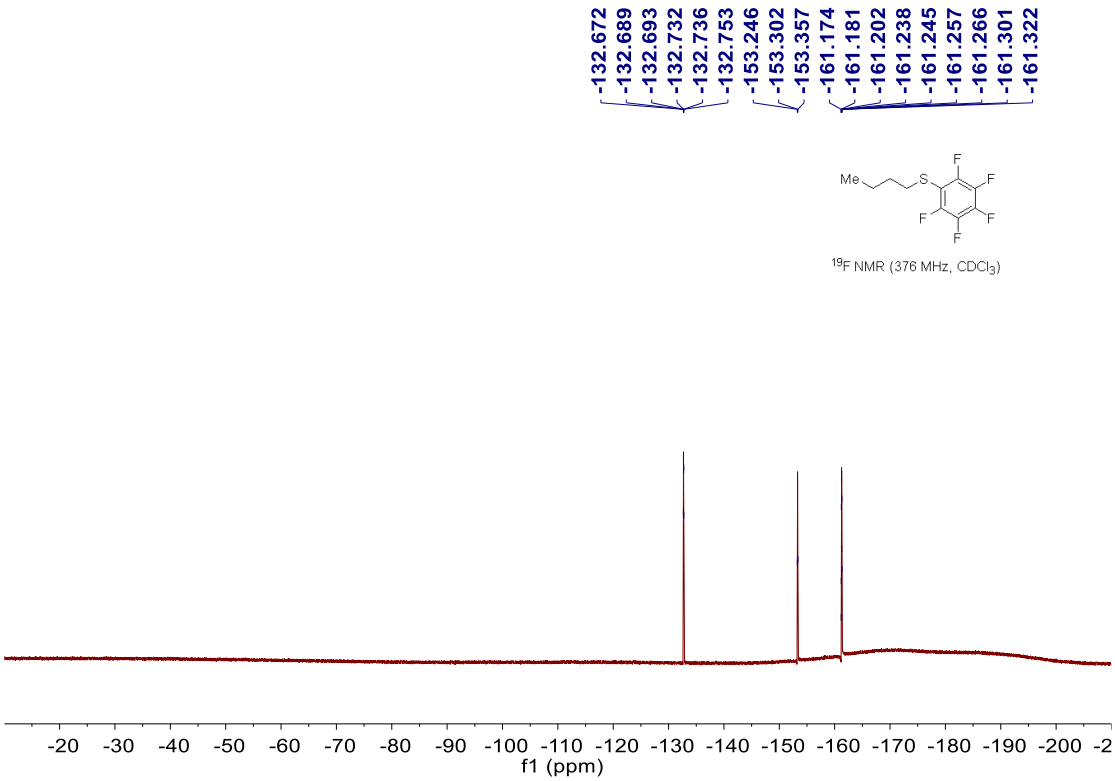

149.223
149.184
149.144
149.119
149.112
149.080
149.040
148.997
146.749
146.710
146.686
146.672
146.646
146.606
142.752
142.616
142.562
142.480
140.075
139.929
139.915
139.009
138.935
138.915
138.878
138.847
138.740
138.698
138.673
136.520
136.395
136.367
136.342
136.308
136.285
108.151
108.140
108.123
107.936
47.452
33.349
25.795
25.426
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-131.407
-131.412
-131.429
-131.435
-131.473
-131.479
-131.495
-131.501
-131.507
-152.594
-152.600
-152.606
-152.650
-152.655
-152.661
-152.705
-152.711
-152.717
-161.198
-161.205
-161.210
-161.227
-161.254
-161.260
-161.266
-161.271
-161.282
-161.287
-161.293
-161.299
-161.326
-161.343
-161.348
-161.355
F
S
F
F
F
F
19F NMR (376 MHz, CDCl3)
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

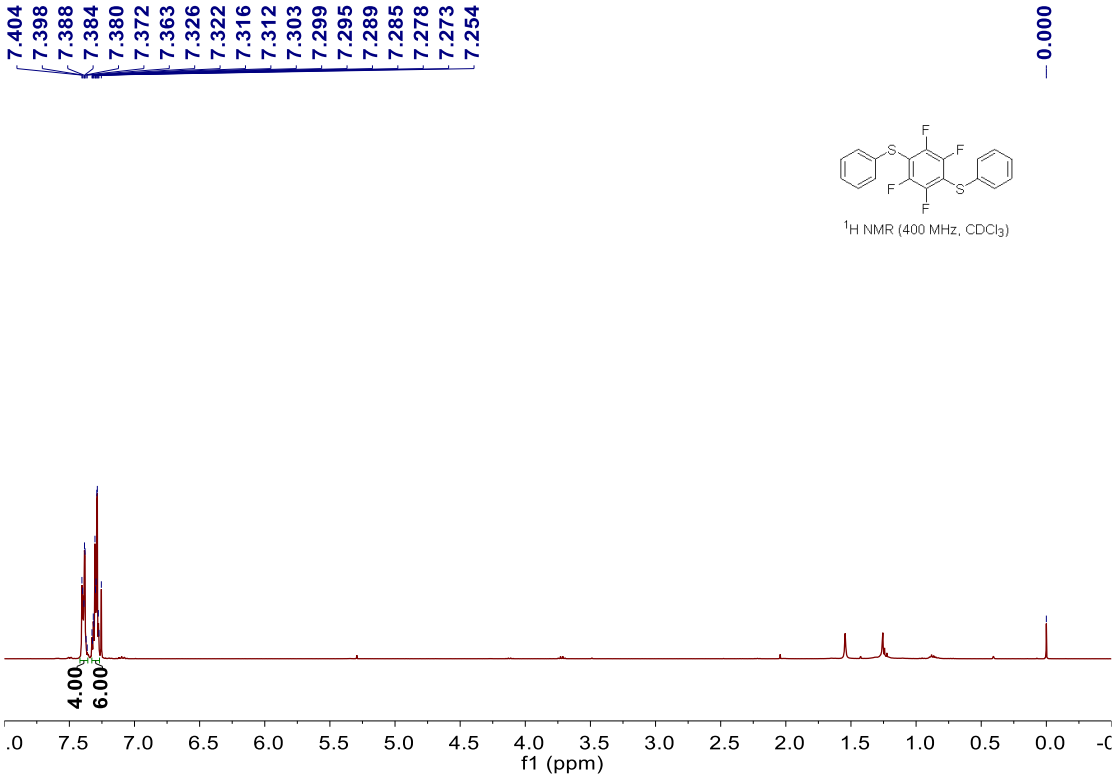
3t

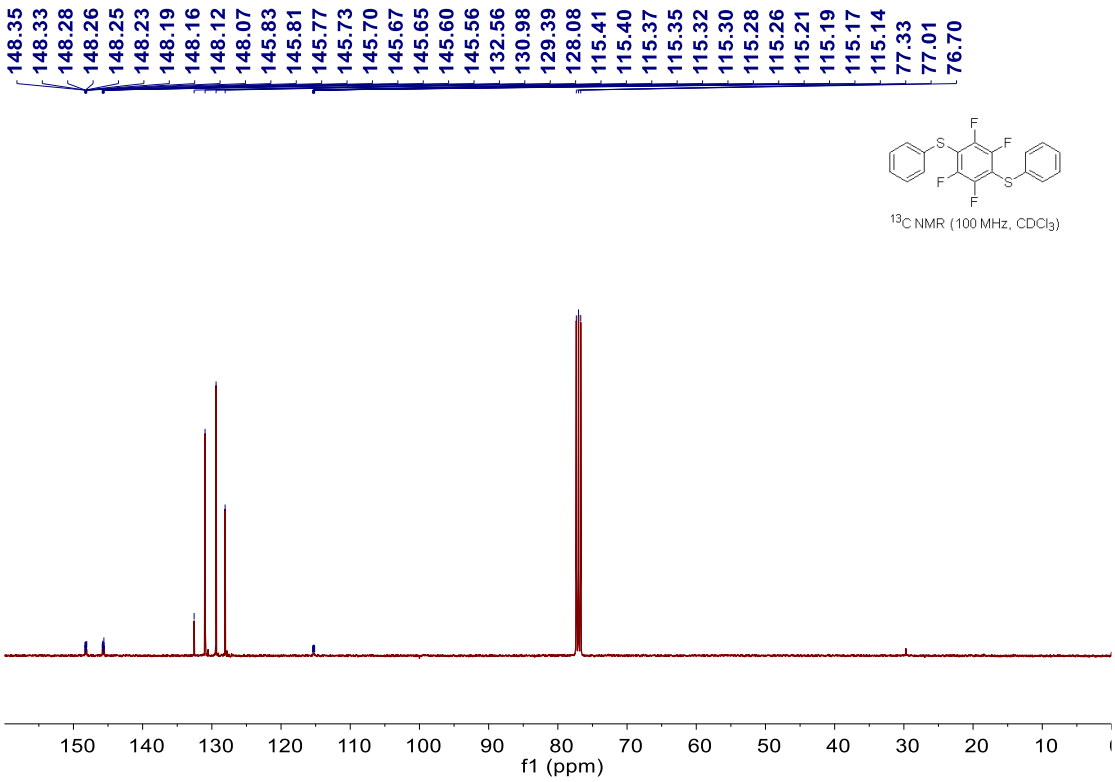

7.262
2.893
2.875
2.856
1.572
1.555
1.536
1.518
1.499
1.473
1.455
1.438
1.417
1.399
1.382
0.924
0.906
0.888
0.000
Me
S
F
F
F
F
F
1H NMR (400 MHz, CDCl3)
2.00
2.13
2.08
3.02
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

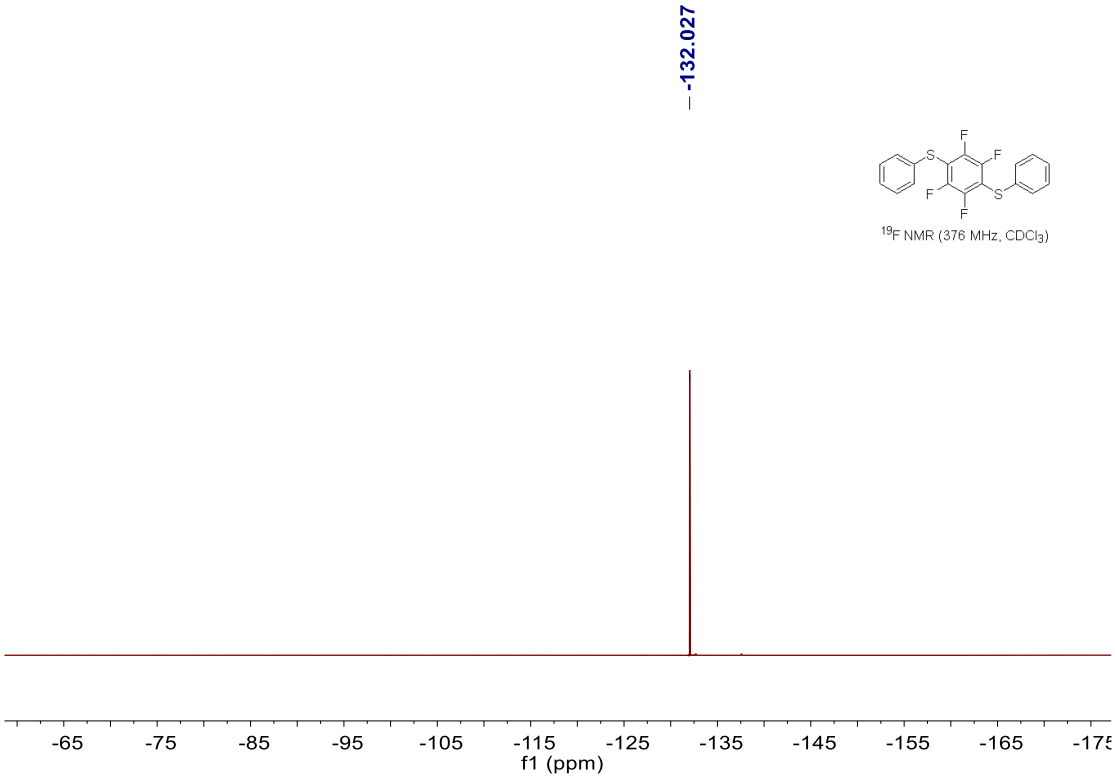

148.909
148.869
148.823
148.799
148.760
148.717
148.678
146.469
146.430
146.385
146.365
146.346
146.324
146.278
142.418
142.283
139.883
139.128
139.111
139.072
138.999
138.975
138.945
138.869
138.818
136.612
136.591
136.538
136.484
136.463
136.409
136.281
109.645
109.481
109.441
109.428
77.351
77.033
76.716
34.710
31.798
21.518
13.523
Me
S
F
F
F
F
F
13C NMR (100 MHz, CDCl3)
f1 (ppm)


-132.672
-132.689
-132.693
-132.732
-132.736
-132.753
-153.246
-153.302
-153.357
-161.174
-161.181
-161.202
-161.238
-161.245
-161.257
-161.266
-161.301
-161.322
Me
S
F
F
F
F
F
19F NMR (376 MHz, CDCl3)
f1 (ppm)

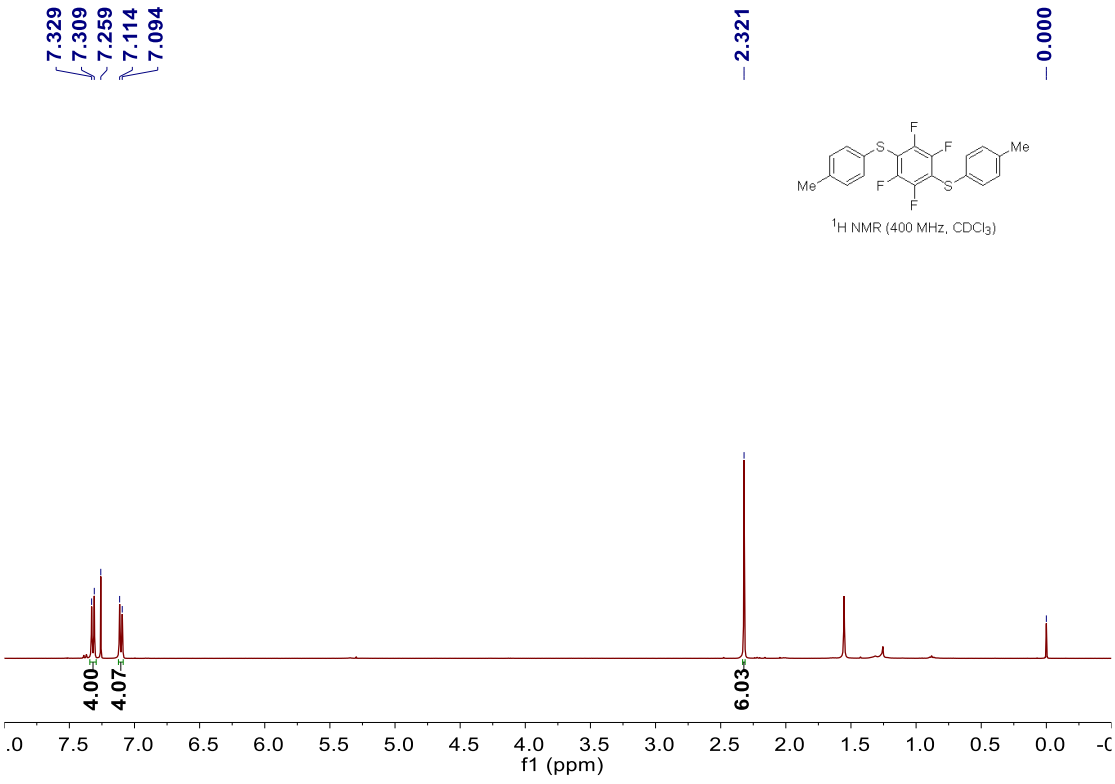
6a

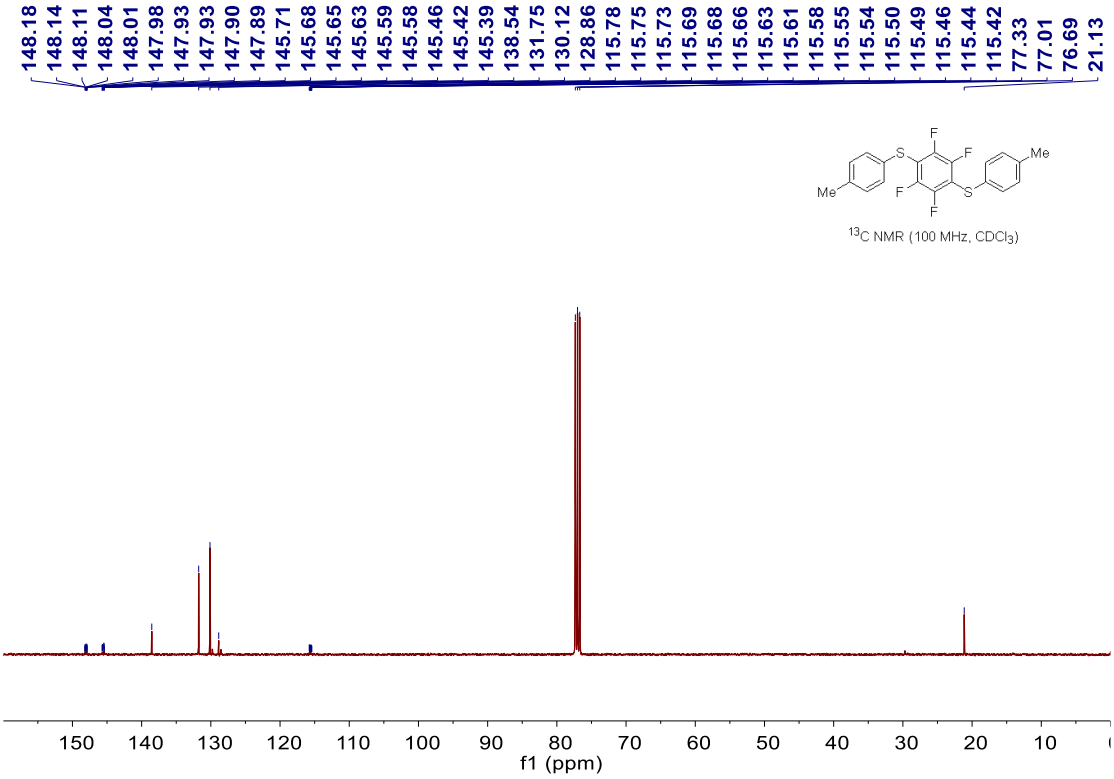

7.404
7.398
7.388
7.384
7.380
7.372
7.363
7.326
7.322
7.316
7.312
7.303
7.299
7.295
7.289
7.285
7.278
7.273
7.254
0.000
F
S
F
F
S
F
^{1}H NMR (400 MHz, CDCl$_3$)
4.00
6.00
f1 (ppm)

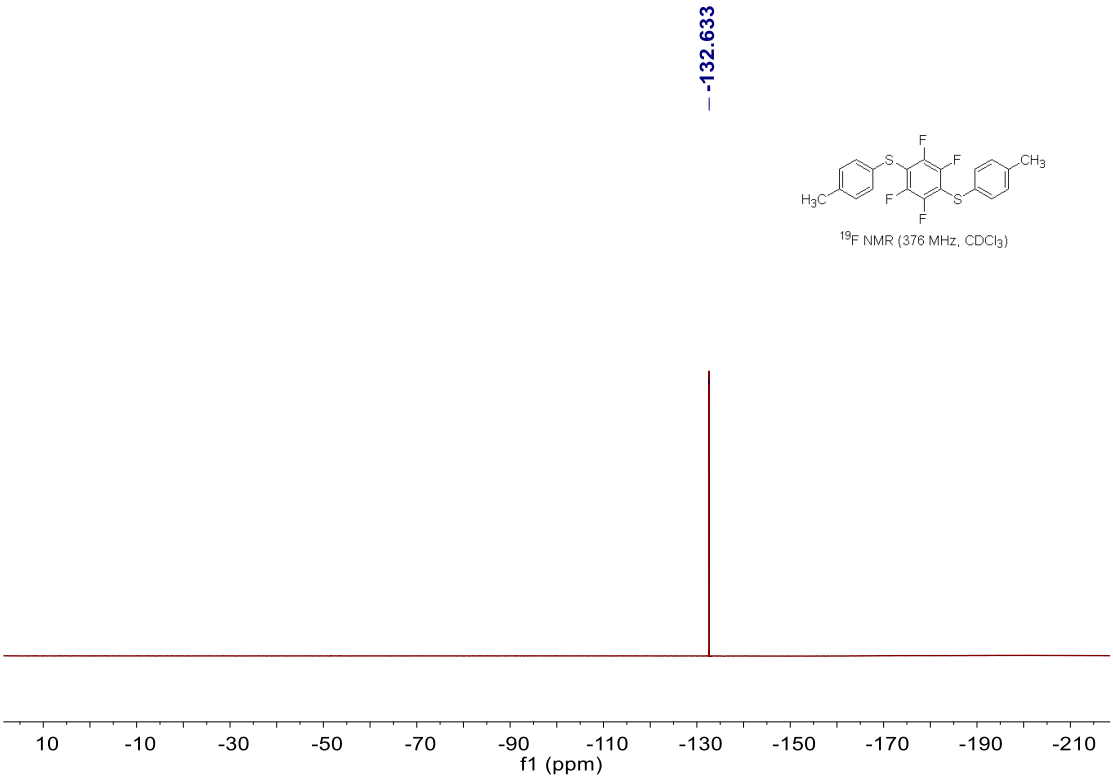

148.35
148.33
148.28
148.26
148.25
148.23
148.19
148.16
148.12
148.07
145.83
145.81
145.77
145.73
145.70
145.67
145.65
145.60
145.56
132.56
130.98
129.39
128.08
115.41
115.40
115.37
115.35
115.32
115.30
115.28
115.26
115.21
115.19
115.17
115.14
77.33
77.01
76.70
F
S
F
F
S
F
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


-132.027
F
S
F
F
S
F
19F NMR (376 MHz, CDCl3)
-65
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
f1 (ppm)

6b

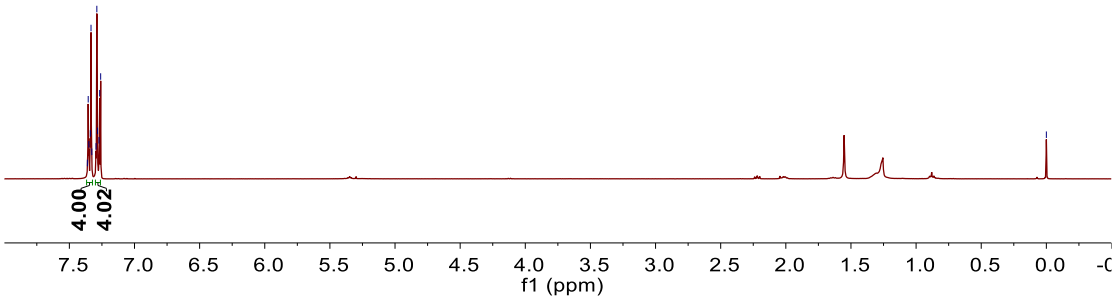

7.329
7.309
7.259
7.114
7.094
2.321
0.000
F
S
F
Me
Me
F
S
F
1H NMR (400 MHz, CDCl3)
4.00
4.07
6.03
f1 (ppm)

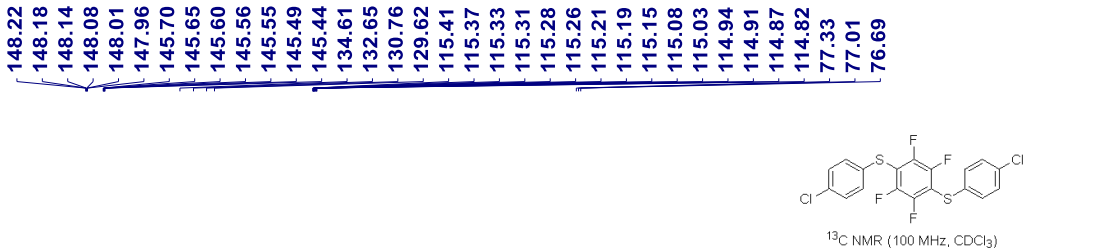

148.18
148.14
148.11
148.04
148.01
147.98
147.93
147.93
147.90
147.89
145.71
145.68
145.65
145.63
145.59
145.58
145.46
145.42
145.39
138.54
131.75
130.12
128.86
115.78
115.75
115.73
115.69
115.68
115.66
115.63
115.61
115.58
115.55
115.54
115.50
115.49
115.46
115.44
115.42
77.33
77.01
76.69
21.13
F
S
F
Me
Me
F
S
F
^{13}C NMR (100 MHz, CDCl$_3$)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-132.633
F
S
F
CH$_3$
H$_3$C
F
S
F
^{19}F NMR (376 MHz, CDCl$_3$)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

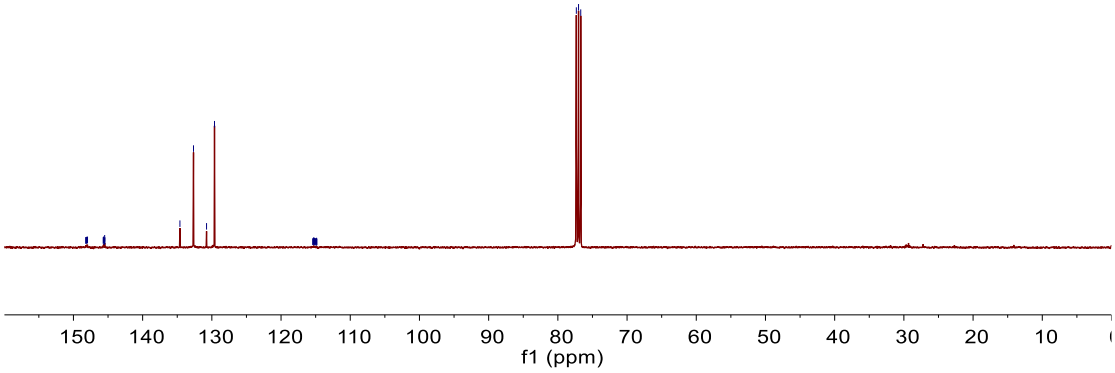
6c

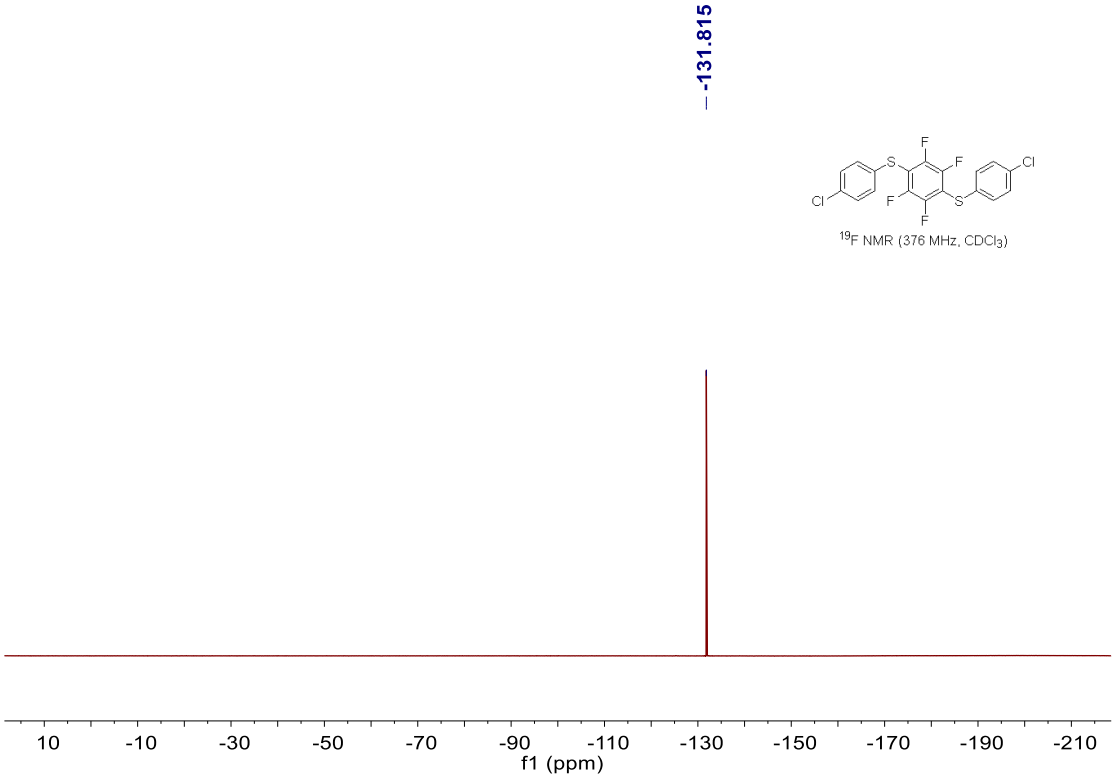
^{1}H NMR (400 MHz, $CDCl_3$)



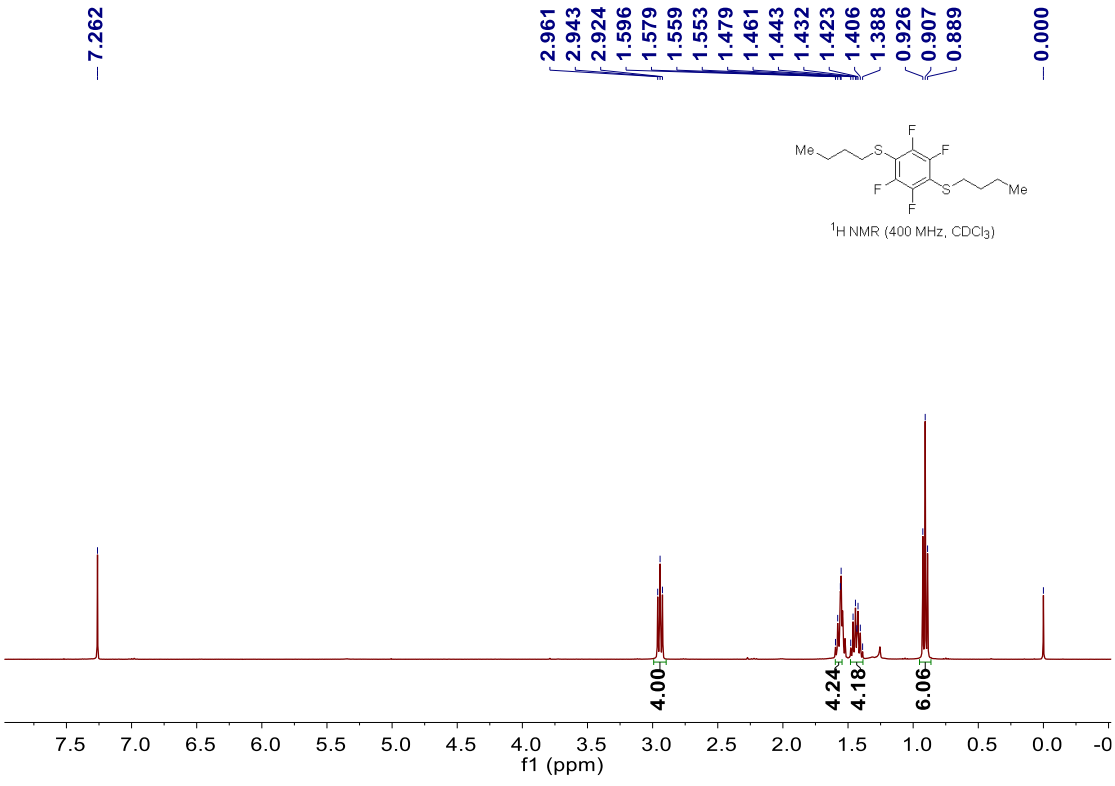


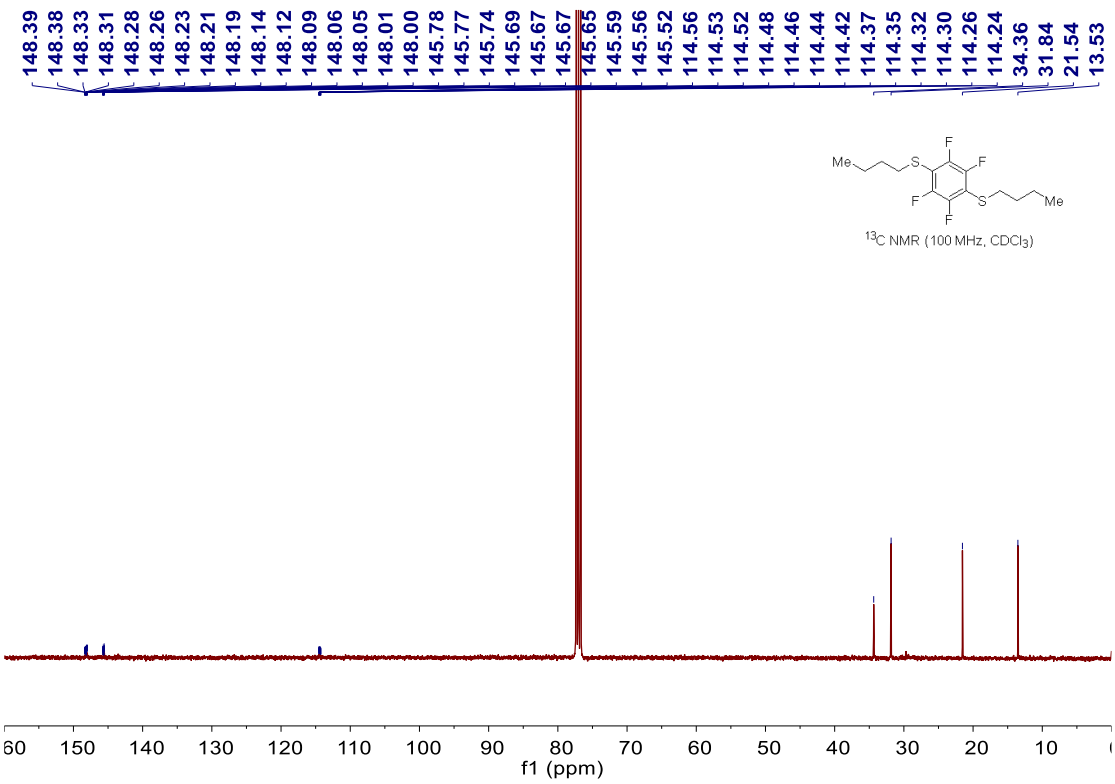
^{13}C NMR (100 MHz, $CDCl_3$)

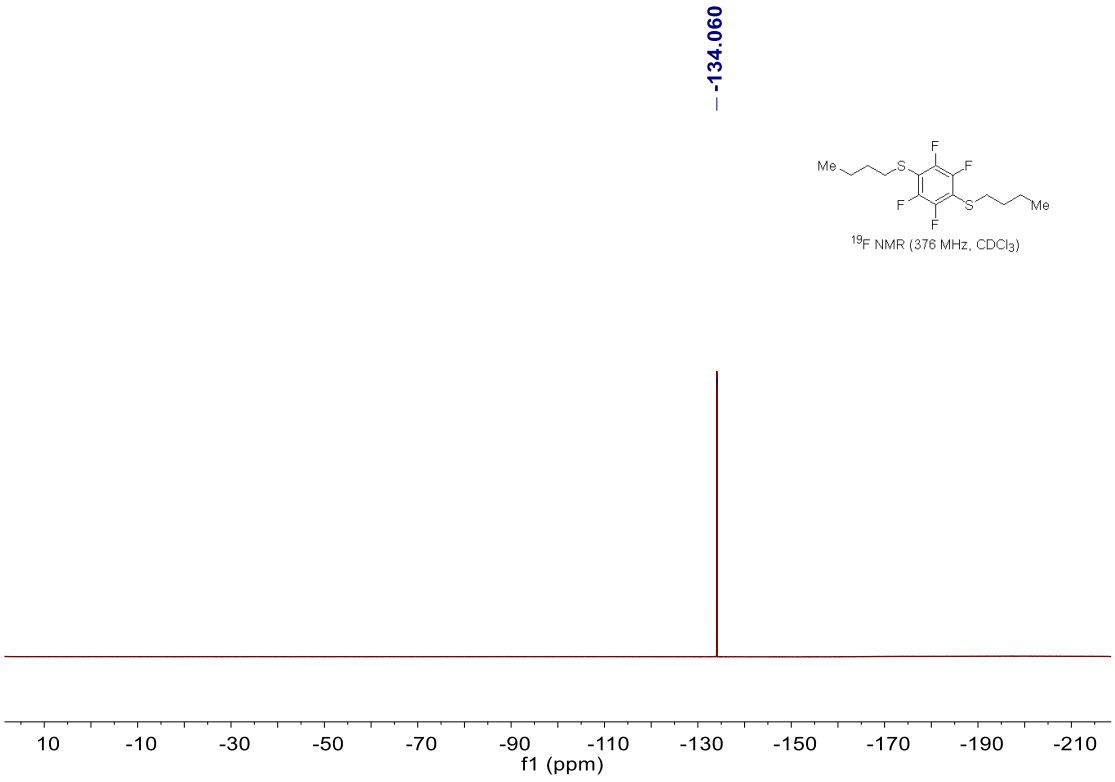



-131.815
F
S
F
Cl
F
S
Cl
F
19F NMR (376 MHz, CDCl3)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

6d


7.262
2.961
2.943
2.924
1.596
1.579
1.559
1.553
1.479
1.461
1.443
1.432
1.423
1.406
1.388
0.926
0.907
0.889
0.000
Me
S
F
F
F
S
Me
F
1H NMR (400 MHz, CDCl3)
4.00
4.24
4.18
6.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


148.39
148.38
148.33
148.31
148.28
148.26
148.23
148.21
148.19
148.14
148.12
148.09
148.06
148.05
148.01
148.00
145.78
145.77
145.74
145.69
145.67
145.67
145.65
145.59
145.56
145.52
114.56
114.53
114.52
114.48
114.46
114.44
114.42
114.37
114.35
114.32
114.30
114.26
114.24
34.36
31.84
21.54
13.53
Me
S
F
F
F
S
Me
F
13C NMR (100 MHz, CDCl3)
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-134.060
Me
S
F
F
F
S
Me
F
19F NMR (376 MHz, CDCl3)
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)