General Information:

Reactions were set-up in the open air (not in a glove box) and were stirred with Teflon-coated magnetic stir bars. All reactions were performed in oven-dried, screw-cap test-tubes with Teflon seals under an atmosphere of argon. Toluene was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvent was further purified by passing it under argon pressure through two packed columns of neutral alumina and copper (II) oxide. Flash chromatography was performed on a Biotage Isolera 4 using SNAP 25g prepacked silica cartriges and a solvent gradient of dichloromethane:hexane (0 → 80%) unless otherwise noted. The preparation of (COD)Pd($CH_2TMS)_2$ has been previously described and it is commercially available from Aldrich[1]. The preparation of BrettPhos has also been previously described and it is available from Strem and Aldrich[2]. All quaternary ammonium salts were purchased from either Alfa or Aldrich and the bulk stored in a glovebox. Small quantities (~2 g) were periodically removed in glass vials and used immediately (within 3 h). AgF was purchased from Aldrich and stored as is in the glovebox. Anhydrous MeCN and anhydrous CS_2 were purchased from Aldrich in Sure-Seal® bottles and used as received. All aryl bromides were purchased from Matrix Scientific, Aldrich or Alfa unless otherwise noted and used as received. Yields refer to isolated yields of compounds greater than 95% purity as determined by gas chromatography and ^{1}H NMR. Quoted yields are representative and so may differ slightly from the average values given in Tables 2 and 3, as well Scheme 3.

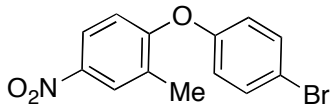
^{1}H NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 500 MHz. ^{13}C NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 126 MHz. ^{19}F NMR spectra were recorded on a Varian Inova-500 NMR spectrometer in deuterochloroform operating at 471 MHz. Chemical shifts are quoted relative to residual solvent in the case of ^{1}H and ^{13}C NMR spectra and relative to $CFCl_3$ as zero in the case of ^{19}F NMR spectra. The following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet. NMR spectra were acquired at 298 K. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer as thin films on KBr plates. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). GC analyses were performed on an Agilent 6970 equipped with an FID detector and a Hewlett Packard 10 m × 0.2 mm HP-1 capillary column using dodecane as an internal standard. Melting points were determined on a

Mel-Temp II capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Nocross, GA.

Procedure for the Synthesis of $AgSCF_3$:[3]

To an oven dried 200 mL Schlenk flask equipped with a stir bar was added 15 g of dry AgF. The flask was fitted with a glass stopper and evacuated and refilled with Ar (this procedure was repeated a total of three times). Under Ar pressure, the stopper was removed and replaced with a reflux condenser. The system was once again evacuated and refilled with Ar (this procedure was also repeated a total of three times). Dry MeCN was injected into the flask in two 50 mL portions via the side arm followed by 15 mL of CS_2. The flask was then placed into a preheated 80˚C oil bath with efficient stirring. After several minutes the reaction mixture became brown in color. After 14 h the reaction mixture was black, at which time the flask was removed from the oil bath and the contents were allowed to cool to room temperature. The reflux condenser was replaced with a distillation head and excess CS_2 was removed by distillation. The remaining solvent was removed under reduced pressure with the aid of a rotary evaporator to produce a black residue, which was then redissolved in EtOAc and filtered through a pad of celite. The flask was then wrapped in aluminum foil and the solvent was once again removed under reduced pressure with the aid of a rotary evaporator. The resulting yellow solid was dissolved in a minimum amount of MeCN to produce a clear yellow solution, which was transferred to a 500 mL round bottom flask wrapped in aluminum foil. Approximately 300 mL of Et_2O was carefully layered on top of the yellow solution. The flask was stoppered and left at room temperature overnight after which it was placed in a freezer set to -20˚C for 24 h to produce an off-white solid. The flask was removed from the freezer and the solution was filtered while cold to collect the white material, 7.5g (90%). The white solid was kept in a refrigerator (5 °C) with the exclusion of light.

Procedure for the Synthesis of 1-(4-Bromophenoxy)-2-methyl-4-nitrobenzene:



4-bromophenol (858 mg, 5 mmol, 1 equiv) and K_2CO_3 (1.8 g, 12.5 mmol, 2.5 equiv) were added to a 100 mL round bottom flask equipped with a stir bar. The flask was stoppered with a rubber septum and evacuated and refilled three times with Ar. Subsequently, 10 mL of DMSO were added to the mixture and the flask was placed

into a preheated 70 °C oil bath for 30 min. The solution was then removed form the oil bath and allowed to cool to room temperature. 2-chloro-4-nitrotoluene was added as a solid to the reaction mixture. The flask was then placed into an oil bath and heated to 110 °C for 12 hours. The flask was removed from the oil bath and allowed to cool to room temperature. The solution was diluted with Et_2O and poured into a separatory funnel. The organic layer was washed three times with water followed by brine, dried over Mg_2SO_4 and filtered. The filtrate was then concentrated under reduced pressure with the aid of a rotary evaporator and the residue was purified via silica gel column chromatography (1% EtOAc in hexanes) to afford the pure compound as a pale yellow solid (1.44g, 93% yield), m.p. 57.2-58.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.3 Hz, 1H), 7.99 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.29 (s), 155.27 (s), 143.66 (s), 133.92 (s), 130.48 (s), 127.58 (s), 123.89 (s), 122.09 (s), 118.17 (s), 116.97 (s), 17.07 (s). IR (film) ν_{max} 3091.03, 295.21, 2851.65, 2019.97, 1892.11, 1616.37, 1594.71, 1578.89, 1518.20, 1480.85, 1343.51, 1245.75, 1209.41, 1092.78, 1068.76, 1010.62, 931.81, 898.87, 844.90, 824.27, 802.71, 746.29, 650.07 cm^{-1}. Anal. Calcd. For $C_{14}H_{10}BrNO_3$: C, 50.67; H, 3.27. Found: C, 50.77; H, 3.31

Procedure for the Examination of Various Trifluoromethylthiolate Salts:

(COD)Pd(CH_2TMS)$_2$ (1.9 mg, 0.005 mmol, 2.5 mol%), BrettPhos (3.0 mg, 0.0055 mmol, 2.75 mol%) and 4-(4-bromophenyl)morpholino (48.4 mg, 0.2 mmol) were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (3x). After which 2 mL of dry toluene was added to the tube. The solution was placed into a preheated 80˚C oil bath with stirring for 60 s. The tube was removed from the oil bath generating solution **A**.

In an N_2 glovebox the SCF_3 salt (0.26 mmol, 1.3 equiv) was added to a flame dried 16 mL re-sealable screw cap tube equipped with a magnetic stir bar. The tube was evacuated and refilled with Ar (3x). Solution **A** was added via cannula. The tube containing solution **A** was then washed with 2 mL of dry toluene, which was then cannulated over once more. The tube was placed into a preheated 80˚C oil bath with stirring for 14 h at which point the tube was removed and allowed to cool. Dodecane (45 μL, 0.20 mmol) was added to the cooled reaction tube. The reaction tube was then opened and the reaction mixture diluted with EtOAc. The resulting solution was analyzed using GC and GC/MS methods.

Procedure for the Examination of Various Quaternary Ammonium Salt Additives:

(COD)Pd($CH_2TMS)_2$ (1.9 mg, 0.005 mmol, 2.5 mol%), BrettPhos (3.0 mg, 0.0055 mmol, 2.75 mol%) and 4-(4-bromophenyl)morpholino (48.4 mg, 0.2 mmol) were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (3x). After which 2 mL of dry toluene was added to the tube. The solution was placed into a preheated 50˚C oil bath with stirring for 60 s. The tube was removed from the oil bath generating solution **A**.

$AgSCF_3$ (54.0 mg, 0.26 mmol, 1.3 equiv) and a quaternary ammonium salt additive (0.26 mmol, 1.3 equiv) were added to a flame dried 16 mL re-sealable screw cap tube equipped with two magnetic stir bars. The tube was evacuated and refilled with Ar (3x). Solution **A** was added via cannula. The tube containing solution **A** was then washed with 2 mL of dry toluene, which was then cannulated over once more. The tube was placed into a preheated 80˚C oil bath with stirring for 14 h after which point the tube was removed and allowed to cool. Dodecane (45 μL, 0.20 mmol) was added to the cooled reaction tube. The reaction tube was opened and the reaction mixture diluted with EtOAc. The resulting solution was analyzed using GC and GC/MS methods.

Procedure for the Examination of Various Ligands:

(COD)Pd($CH_2TMS)_2$, Ligand and 4-(4-bromophenyl)morpholino (48.4 mg, 0.2 mmol) were added to a flame dried 8 mL test tube with Teflon screw cap equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (3x). After which 2 mL of dry toluene was added to the tube. The solution was placed into a preheated 80˚C oil bath with stirring for 60 s. The tube was removed from the oil bath generating solution **A**.

$AgSCF_3$ (54 mg, 0.26 mmol, 1.3 equiv) and $Ph(Et)_3NI$ (80 mg, 0.26 mmol, 1.3 equiv) were added to a flame dried 16 mL re-sealable screw cap tube equipped with a magnetic stir bar. The tube was evacuated and refilled with Ar (3x). Solution **A** was added via cannula. The tube containing solution **A** was then washed with 2 mL of toluene, which was then cannulated over once more. The tube was placed into a preheated 80 °C oil bath with stirring for 1-2 h at which point the tube was removed and allowed to cool. Dodecane (45 μL, 0.20 mmol) was added to the cooled reaction tube. The reaction tube was then opened and the reaction mixture diluted with EtOAc. The resulting solution was analyzed using GC and GC/MS methods.

General Procedure A:

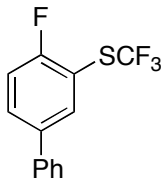
(COD)Pd($CH_2TMS)_2$ (5.8 mg, 0.015 mmol, 1.5 mol%), BrettPhos (8.9 mg, 0.0165 mmol, 1.65 mol%) and 1 mmol of starting aryl bromide, if solid, were added to a flame dried 8 mL test tube with Teflon screw cap

equipped with magnetic stir bar. The tube was sealed and evacuated and refilled with Ar (3x). After which 2 mL of dry toluene was added to the tube as well as aryl bromide if liquid. The solution was placed into a preheated 80˚C oil bath for 60 s. The tube was removed from the oil bath generating solution **A**.

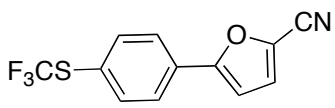
$AgSCF_3$ (280 mg, 1.3 mmol, 1.3 equiv) and $(Ph)(Et)_3NI$ (400 mg, 1.3 mmol, 1.3 equiv) were added to a flame dried 16 mL re-sealable screw cap tube equipped with two magnetic stir bars. The tube was evacuated and refilled with Ar (3x). Solution **A** was added via cannula. The tube containing solution **A** was then washed with 3 mL of toluene which was then cannulated over once more. The tube was placed into a preheated 80 °C oil bath with stirring for 2 h at which point the tube was removed and allowed to cool. The reaction mixture was then filtered through Si_2O eluting with EtOAc. The solvent was removed under reduced pressure and the residue was purified via silica gel column chromotagraphy.

General Procedure B:

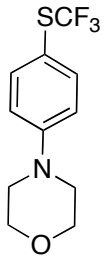
As General Procedure A but with XPhos as ligand.



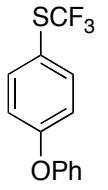
4-Fluoro-3-((trifluoromethyl)thio)-1,1'-biphenyl. Following general procedure A, 4-fluoro-3-bromo-1,1'-biphenyl (251 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a clear colorless oil (259.8 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.67 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.60 δ 7.53 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.58 (s), 162.61 (s), 142.47 (s), 136.41 (d, *J* = 3.2 Hz), 135.53 (d, *J* = 18.1 Hz), 130.60 (s), 130.41 (q, *J* = 308.1 Hz), 130.12 (s), 129.52 (d, *J* = 8.2 Hz), 125.78 (s), 116.63 (d, *J* = 21.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.71 (s), -114.47 δ -114.59 (m). IR (film) ν_{max}1609.44, 1514.40, 1471.51, 1237.92, 1160.72, 1117.48, 1098.31, 1082.37, 837.39, 791.78, 694.48 cm $^{-1}$. Anal. Calcd. For $C_{13}H_8F_4S$: C, 57.35; H, 2.96. Found: C, 57.24; H, 2.95.



5-(4-((Trifluoromethyl)thio)phenyl)furan-2-carbonitrile. Following general procedure A, 5-(4-bromophenyl)furan-2-carbonitrile (248 mg, 1 mmol) was used. Purification via column chromatography provided the compound as an orange solid (258.5 mg, 96%), m.p. 77.3-81.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 δ 7.65 (m, 4H), 7.17 (d, *J* = 3.7 Hz, 1H), 6.81 (d, *J* = 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.59 (s), 137.37 (d, *J* = 0.8 Hz), 131.44 (s), 128.56 (q, *J* = 308.5 Hz), 126.60 (s), 126.24 (s), 126.14 (dd, *J* = 4.3, 2.2 Hz), 124.70 (s), 112.22 (s), 108.50 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.48 (s). IR (film) ν_{max} 2231.21, 1478.49, 1123.61, 1087.13, 1024.82, 838.42, 796.26 cm^{-1}. Anal. Calcd. For $C_{12}H_6F_3NOS$: C, 53.53; H, 2.25. Found: C, 53.43; H, 2.12.

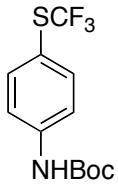


4-(4-((Trifluoromethyl)thio)phenyl)morpholine. Following general procedure A, 4-(4-bromophenyl)morpholine (242 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a pale yellow oil (262 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 3.88 δ 3.82 (m, 2H), 3.25 δ 3.19 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.59 (s), 138.61 (d, *J* = 0.5 Hz), 130.45 (q, *J* = 308.3 Hz), 115.92 (s), 113.03 (q, *J* = 2.0 Hz), 67.31 (s), 48.60 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.17 (s). IR (film) ν_{max} 2966.02, 2857.40, 1594.34, 1502.18, 1451.02, 1381.75, 1352.25, 1305.79, 1263.12, 1240.05, 1122.89, 1051.78, 928.78, 819.87, 754.13, 670.94, 579.60, 557.18, 528.69, 472.80 cm^{-1} Anal. Calcd. For $C_{11}H_{12}F_3NOS$: C, 50.18; H, 4.59. Found: C, 50.47; H, 4.68.

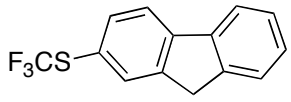


4-Phenoxy-((trifluoromethyl)thio)benzene. Following general procedure A, 4-Phenoxy-bromobenzene (249 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a colorless oil (263 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 δ 7.61 (m, 2H), 7.47 δ 7.40 (m, 2H), 7.28 δ 7.21 (m, 1H), 7.16 δ 7.09 (m, 2H), 7.07 δ 7.03 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.18 (s), 156.34 (s), 139.10 (d, *J* = 0.7 Hz), 130.81 (s), 130.36 (q, *J* = 308.1 Hz), 125.32 (s), 120.84 (s), 119.34 (s), 117.96 (q, *J* = 2.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.66 (s). IR (film) ν_{max} 1582.89, 1488.04, 1280.75, 1246.21,

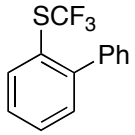
1118.86, 1084.24, 869.61, 835.22, 755.96, 692.86 cm^{-1}. Anal. Calcd. For $C_{13}H_9F_3OS$: C, 57.77; H, 3.36. Found: C, 58.01; H, 3.46.



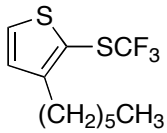
-Butyl (4-((trifluoromethyl)thio)phenyl)carbamate. Following general procedure A, tert-Butyl (4-bromophenyl)carbamate (272 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a white solid (263 mg, 91%), m.p. 93.4-94.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 6.98 (s, 1H), 1.51 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.23 (s), 141.95 (s), 138.20 (s), 130.30 (q, *J* = 308.1 Hz), 119.59 (s), 117.75 (q, *J* = 2.1 Hz), 81.95 (s), 28.89 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.65 (s). IR (film) ν_{max} 3329.19, 2988.12, 1699.19, 1587.43, 1525.85, 1402.61, 1371.69, 1312.17, 1127.98, 836.17, 773.97, 672.85, 522.71 cm^{-1}. Anal. Calcd. For $C_{12}H_{14}F_3NO_2S$: C, 49.14; H, 4.81. Found: C, 49.24; H, 4.75.



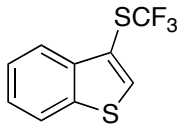
2-((Trifluoromethyl)thio)fluorine. Following general procedure A, 2-bromofluorene (245 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a pale yellow solid (259 mg, 97%), m.p. 44.5-47.8 °C. Note: the starting material was contaminated with 5% of 2,7-dibromofluorene, as a result the ^{19}F NMR spectrum exhibits a second, minor fluorine signal corresponding to 5% of 2,7-bis((trifluoromethyl)thio)fluorene. These two compounds are inseparable by column chromatography. The yield has been corrected for this impurity. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.79 δ 7.64 (m, 3H), 7.58 δ 7.52 (m, 1H), 7.47 δ 7.38 (m, 1H), 3.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.14 (s), 145.05 (s), 144.39 (s), 140.93 (s), 135.93 (d, *J* = 0.7 Hz), 133.73 (d, *J* = 0.7 Hz), 130.66 (q, *J* = 308.2 Hz), 128.63 (s), 127.75 (s), 125.86 (s), 122.37 (q, *J* = 2.1 Hz), 121.26 (s), 121.21 (s), 37.35 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.15 (s). IR (film) ν_{max} 3066.87, 2898.42, 1603.59, 1466.72, 1450.07, 1410.34, 1111.22, 1073.50, 829.35, 767.41, 732.25, 592.42, 461.39, 416.97 cm^{-1}. Anal. Calcd. For $C_{14}H_9F_3S$: C, 63.15; H, 3.41. Found: C, 62.89; H, 3.41.



4-((Trifluoromethyl)thio)-1,1'-biphenyl.[4] Following general procedure B, 4-bromo-1,1'-biphenyl (233 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% XPhos (15.7 mg). Purification via column chromatography provided the compound as a colorless oil (244 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.58 (td, *J* = 7.5, 1.3 Hz, 1H), 7.55 δ 7.46 (m, 5H), 7.45 δ 7.40 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.68 (s), 141.03 (s), 137.94 (d, *J* = 0.9 Hz), 132.07 (s), 131.46 (s), 130.47 (s), 130.38 (q, *J* = 308.5 Hz), 129.04 (s), 128.74 (s), 128.46 (s), 124.07 (dd, *J* = 3.7, 1.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.11 (s). IR (film) ν_{max} 3060.97, 3030.76, 2927.66, 1948.39, 1587.68, 1466.00, 1447.50, 1430.45, 1107.02, 1074.22, 1037.25, 1008.09, 758.02, 700.00, 614.29 cm^{-1}. Anal. Calcd. For $C_{13}H_9F_3S$: C, 61.41; H, 3.57. Found: C, 61.30; H, 3.64.

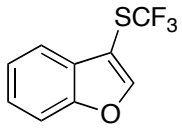


3-Hexyl-2-((trifluoromethyl)thio)thiophene. Following general procedure A, 3-hexyl-2-bromothiophene (247 mg, 1 mmol) was used along with 3.5 mol% (COD)Pd(CH_2TMS_2) (13.6 mg) and 3.85 mol% BrettPhos (20.7 mg). Purification via column chromatography provided the compound as a colorless oil (249 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 5.4 Hz, 1H), 7.07 (d, *J* = 5.5 Hz, 1H), 3.09 – 2.66 (m, 2H), 1.64 (dt, *J* = 15.5, 7.6 Hz, 2H), 1.37 (tdd, *J* = 10.5, 7.9, 5.1 Hz, 6H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.95 (d, *J* = 0.8 Hz), 132.91 (s), 129.79 (s), 129.29 (q, *J* = 311.0 Hz), 115.75 (dd, *J* = 4.7, 2.4 Hz), 32.35 (s), 31.13 (s), 29.78 (s), 29.65 (s), 23.31 (s), 14.73 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.95 (s). IR (film) ν_{max} 2929.43, 2859.56, 1523.88, 1466.92, 1395.96, 1117.80, 839.88, 754.91, 736.45, 659.91, 497.80 cm^{-1}. Anal. Calcd. For $C_{11}H_{15}F_3S_2$: C, 49.23; H, 5.63. Found: C, 49.49; H, 5.83.

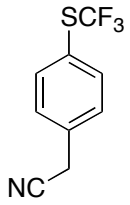


3-((Trifluoromethyl)thio)benzo[b]thiophene. Following general procedure A, 3-bromobenzothiophene (213 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (217.5 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.1, 0.4 Hz, 1H), 7.99 (s, 1H), 7.95 δ 7.89 (m, 1H), 7.56 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.52 δ 7.45 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.20 (s),

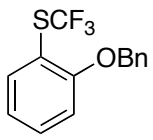
140.15 (s), 138.66 (d, J = 1.0 Hz), 130.04 (q, J = 309.9 Hz), 126.12 (d, J = 2.5 Hz), 126.09 (s), 123.62 (s), 123.58 (s), 115.97 (q, J = 2.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.75 (s). IR (film) ν_{max} 3102.09, 3059.97, 2927.53, 2274.12, 1913.00, 1792.20, 1651.05, 1584.28, 1480.22, 1454.92, 1421.76, 1317.46, 1255.44, 1107.70, 1063.23, 962.79, 838.40, 754.96, 730.99, 703.99, 606.21 cm^{-1} . Anal. Calcd. For $C_9H_5F_3S_2$: C, 46.14; H, 2.15. Found: C, 46.40; H, 2.26.



3-((Trifluoromethyl)thio)benzofuran. Following general procedure A, 3-bromobenzofuran (197 mg, 1 mmol) was used along with 3.5 mol% (COD)Pd(CH_2TMS_2) (13.6 mg) and 3.85 mol% BrettPhos (20.7 mg). Purification via column chromatography provided the compound as a colorless oil (218 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.79 (dd, J = 6.1, 2.8 Hz, 1H), 7.66 – 7.54 (m, 1H), 7.49 – 7.36 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.19 (s), 152.29 (d, J = 1.2 Hz), 129.67 (q, J = 309.8 Hz), 128.75 (s), 126.37 (s), 124.84 (s), 120.74 (d, J = 0.6 Hz), 112.70 (s), 103.95 (dd, J = 5.3, 2.6 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.40 (s). IR (film) ν_{max} 1531.97, 1449.90, 1253.30, 1112.40, 1014.83, 853.98, 745.36, 610.17 cm^{-1}.

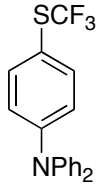


2-(4-((trifluoromethyl)thio)phenyl)acetonitrile.[5] Following general procedure A, 2-(4-bromophenyl)acetonitrile (196 mg, 1 mmol) was used along with 2 mol% (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol% BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a yellow oil (211.5 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 3.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.65 (d, J = 0.8 Hz), 133.89 (s), 130.15 (q, J = 308.1 Hz), 129.80 (s), 125.10 (q, J = 2.2 Hz), 117.86 (s), 24.08 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.85 (s). IR (film) ν_{max} 3066.62, 2926.19, 2253.47, 1923.91, 1599.82, 1495.68, 1412.15, 1115.88, 1086.84, 1018.86, 838.60, 799.92, 755.92, 570.38, 532.31, 501.04 cm^{-1}.

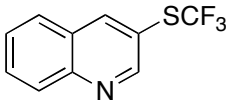


2-(Benzyloxy)-((trifluoromethyl)thio)benzene. Following general procedure A, 2-(benzyloxy)-bromobenzene (263 mg, 1 mmol) was used along with 2 mol% (COD)Pd(CH_2TMS_2) (7.78 mg)

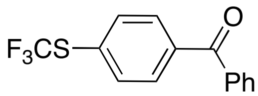
and 2.2 mol% BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (273 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.53 δ 7.46 (m, 3H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.07 (ddd, *J* = 6.7, 3.4, 2.4 Hz, 2H), 5.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.40 (s), 139.32 (s), 137.16 (s), 133.61 (s), 130.58 (q, *J* = 308.9 Hz), 129.42 (s), 128.77 (s), 127.72 (s), 122.25 (s), 114.02 (s), 113.78 (d, *J* = 1.2 Hz), 71.33 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.37 (s). IR (film) ν_{max} 3068.01, 2928.67, 1583.50, 1477.33, 1443.18, 1380.53, 1281.14, 1250.72, 1111.30, 1062.45, 755.77, 696.24 cm^{-1}. Anal. Calcd. For $C_{14}H_{11}F_3OS$: C, 59.15; H, 3.90. Found: C, 59.23; H, 3.98.



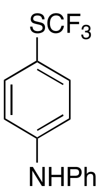
N,N-Diphenyl-4-((trifluoromethyl)thio)aniline. Following general procedure A, N,N-diphenyl-4-bromoaniline (324 mg, 1 mmol) was used along with 2 mol% (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol% BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (338 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.39 (dd, *J* = 8.3, 7.5 Hz, 4H), 7.29 δ 7.23 (m, 4H), 7.23 δ 7.18 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.25 (s), 147.54 (s), 138.39 (s), 130.52 (q, *J* = 308.5 Hz), 130.43 (s), 126.48 (s), 125.18 (s), 122.40 (s), 115.33 (d, *J* = 1.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.96 (s). IR (film) ν_{max} 3036.97, 1582.95, 1491.51, 1331.58, 1316.23, 1284.84, 1116.86, 1088.70, 826.15, 754.96, 696.26, 522.71 cm^{-1}. Anal. Calcd. For $C_{19}H_{14}F_3NS$: C, 66.07; H, 4.09. Found: C, 66.16; H, 4.14.



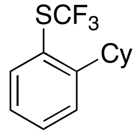
3-((Trifluoromethyl)thio)quinoline. Following general procedure A, 3-bromoquinoline (208 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless solid (220.5 mg, 96%), m.p. 42.8-44.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.1 Hz, 1H), 8.49 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.94 δ 7.68 (m, 2H), 7.68 δ 7.47 (m, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.1 Hz, 1H), 8.49 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.94 δ 7.68 (m, 2H), 7.68 δ 7.47 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.62 (s). IR (film) ν_{max} 3038.86, 1616.58, 1565.41, 1358.42, 1143.05, 1131.95, 1113.51, 1081.70, 956.02, 913.81, 785.79, 755.83, 648.17 cm^{-1}. Anal. Calcd. For $C_{10}H_6F_3NS$: C, 52.40; H, 2.64. Found: C, 52.21; H, 2.52



4-((Trifluoromethyl)thio)benzaphenone. Following general procedure A, 4-bromobenzophenone (261 mg, 1 mmol) was used along with 2 mol% (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol% BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a pale yellow solid (234 mg, 83%), m.p. 67.8-70.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 9.6, 7.5, 1.6 Hz, 4H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.64 δ 7.57 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.14 (s), 140.14 (s), 137.47 (s), 136.22 (d, *J* = 0.6 Hz), 133.68 (s), 131.38 (s), 130.74 (s), 130.07 (q, *J* = 308.4 Hz), 129.77 (dd, *J* = 4.2, 2.1 Hz), 129.19 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.06 (s). IR (film) ν_{max} 1654.00, 1578.58, 1396.12, 1285.17, 1114.11, 1081.89, 847.44, 731.07, 696.46, 665.30 cm^{-1}. Anal. Calcd. For $C_{14}H_9F_3OS$: C, 59.57; H, 3.21. Found: C, 59.85; H, 3.19

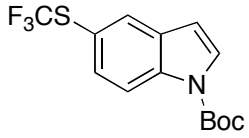


N-Phenyl-4-((trifluoromethyl)thio)aniline. Following general procedure A, N-phenyl-4-bromoaniline (248 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (264.5 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.29 (s). IR (film) ν_{max} 3401.73, 1587.40, 1507.52, 1319.13, 1116.19, 1088.41, 822.33, 752.58, 697.30 cm^{-1}. Anal. Calcd. For $C_{13}H_{10}F_3NS$: C, 57.98; H, 3.74. Found: C, 57.89; H, 3.65.

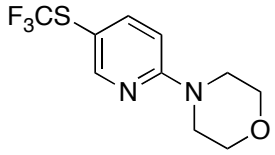


2-Cyclohexyl-((trifluoromethyl)thio)benzene. Following general procedure B, 2-cyclohexyl-bromobenzene (239 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol%

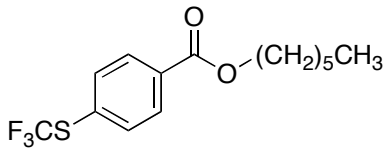
XPhos (15.7 mg). Purification via column chromatography provided the compound as a colorless oil (264.5 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.49 (td, *J* = 7.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.25 (td, *J* = 7.7, 1.6 Hz, 1H), 3.63 δ 3.27 (m, 1H), 2.07 δ 1.67 (m, 5H), 1.63 δ 1.40 (m, 4H), 1.37 δ 1.19 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.73 (s), 138.99 (d, *J* = 0.4 Hz), 132.20 (s), 130.40 (q, *J* = 308.3 Hz), 128.20 (s), 127.22 (s), 123.57 (dd, *J* = 3.6, 1.7 Hz), 42.07 (s), 34.86 (s), 27.50 (s), 26.86 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.95 (s). IR (film) ν_{max} 2929.78, 2854.56, 1471.68, 1449.71, 1119.09, 1101.59, 1036.40, 758.59, 497.98 cm^{-1} Anal. Calcd. For $C_{13}H_{15}F_3S$: C, 59.98; H, 5.81. Found: C, 59.96; H, 5.93



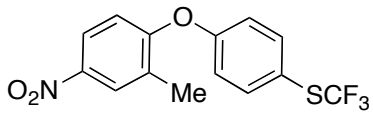
-Butyl 5-((trifluoromethyl)thio)-1H-indole-1-. Following general procedure A, *tert*-Butyl 5-bromo-1H-indole-1- (296 mg, 1 mmol) was used. Purification via column chromatography provided the compound as a colorless solid (311 mg, 98%), m.p. 43.7-44.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 1.5 Hz, 1H), 7.68 (d, *J* = 3.6 Hz, 1H), 7.60 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 1.71 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.98 (s), 137.14 (s), 132.67 (s), 132.16 (s), 130.59 (q, *J* = 307.9 Hz), 130.47 (s), 128.04 (s), 118.13 (dd, *J* = 4.0, 1.9 Hz), 116.74 (s), 107.60 (s), 85.11 (s), 28.74 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.73 (s). IR (film) ν_{max} 2982.41, 1741.32, 1453.10, 1371.67, 1342.33, 1156.49, 1135.85, 1115.89, 1084.84, 1023.84, 765.79, 726.28 cm^{-1}. Anal. Calcd. For $C_{14}H_{14}F_3NO_2S$: C, 52.99; H, 4.45. Found: C, 53.15; H, 4.49



4-(5-((Trifluoromethyl)thio)pyridin-2-yl)morpholine. Following general procedure A, 4-(5-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a pale yellow solid (258.5 mg, 98%), m.p. 79.2-82.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.2 Hz, 1H), 7.64 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.57 (d, *J* = 8.9 Hz, 1H), 3.79 δ 3.67 (m, 4H), 3.59 δ 3.45 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.51 (s), 156.21 (s), 145.68 (s), 130.01 (q, *J* = 308.8 Hz), 108.31 (dd, *J* = 3.9, 1.9 Hz), 107.32 (s), 67.19 (s), 45.56 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -44.70 (s). IR (film) ν_{max} 2972.62, 2906.71, 2854.08, 1587.30, 1494.11, 1251.56, 1145.38, 1108.98, 942.35, 805.01 cm^{-1}.



Hexyl 4-((trifluoromethyl)thio)benzoate. Following general procedure A, Hexyl 4-bromobenzoate (285 mg, 1 mmol) was used along with 2 mol% (COD)Pd(CH_2TMS_2) (7.78 mg) and 2.2 mol% BrettPhos (11.8 mg). Purification via column chromatography provided the compound as a colorless oil (298.5 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.82 δ 1.63 (m, 2H), 1.52 δ 1.37 (m, 2H), 1.36 δ 1.24 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.15 (s), 136.20 (d, *J* = 0.8 Hz), 136.20 (d, *J* = 0.8 Hz), 131.03 (s), 130.32 (dd, *J* = 4.2, 2.1 Hz), 130.00 (q, *J* = 308.3 Hz), 66.25 (s), 32.12 (s), 29.30 (s), 26.35 (s), 23.21 (s), 14.59 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -42.20 (s). IR (film) ν_{max} 2959.03, 2933.12, 2860.72, 1726.32, 1597.35, 1468.47, 1399.69, 1305.74, 1273.46, 1017.39, 856.38, 764.98, 692.89, 502.89 cm^{-1}. Anal. Calcd. For $C_{13}H_{15}F_3O_2S$: C, 54.89; H, 5.59. Found: C, 55.09; H, 5.71



1-(4-((Trifluoromethyl)thio)phenoxy)-2-methyl-4-nitrobenzene.[6] Following general procedure A, 1-(4-bromophenoxy)-2-methyl-4-nitrobenzene (308 mg, 1 mmol) was used along with 3 mol% (COD)Pd(CH_2TMS_2) (11.7 mg) and 3.3 mol% BrettPhos (17.7 mg). Purification via column chromatography provided the compound as a colorless oil (314 mg, 95%), m.p. 62-63 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.7 Hz, 1H), 8.03 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.21 δ 7.00 (m, 2H), 6.93 (d, *J* = 8.9 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.19 (s), 159.02 (s), 144.34 (s), 139.34 (s), 131.42 (s), 130.16 (q, *J* = 308.2 Hz), 127.68 (s), 123.89 (s), 120.33 (s), 119.99 (dd, *J* = 4.4, 2.2 Hz), 118.73 (s), 16.97 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -43.48 (s). IR (film) ν_{max} 3092.96, 2928.72, 2856.16, 2270.72, 2023.09, 1903.95, 1617.82, 1581.03, 1522.70, 1485.23, 1345.34, 1247.74, 1213.91, 1117.85, 1087.46, 1013.59, 931.93, 900.25, 856.71, 830.53, 803.93, 747.36, 519.60 cm^{-1}. Anal. Calcd. For $C_{14}H_{10}F_3NO_3S$: C, 51.06; H, 3.06. Found: C, 51.30; H, 3.06

References:

[1] D. A. Watson, M. J. Su, G. Teverovskiy, Y. Zhang, J. Garcia-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661.
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[4] T. Umemoto, S. Ishihara, *J. Am. Chem. Soc.* **1993**, *115*, 2156.
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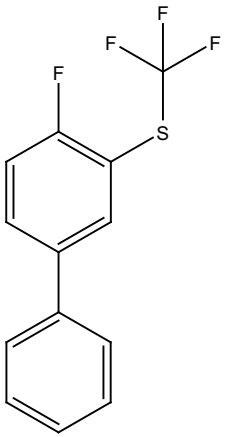
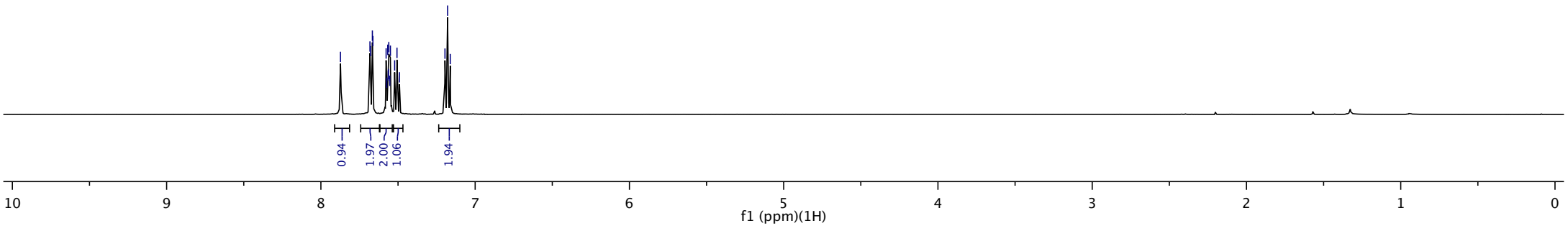
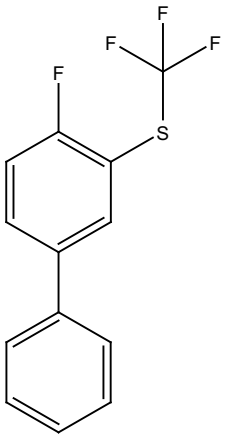

F
F
F
F
S

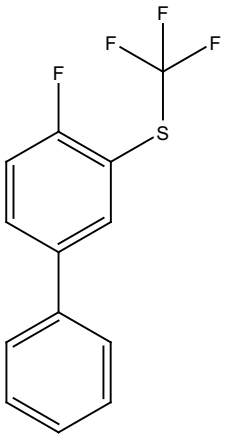

7.87
7.68
7.67
7.66
7.57
7.56
7.55
7.20
7.18
7.16


0.94
1.97
2.00
1.06
1.94
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)



164.58
162.61
142.47
136.43
136.40
135.60
135.46
134.08
131.63
130.60
130.12
129.55
129.49
129.18
116.55

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)



-42.71

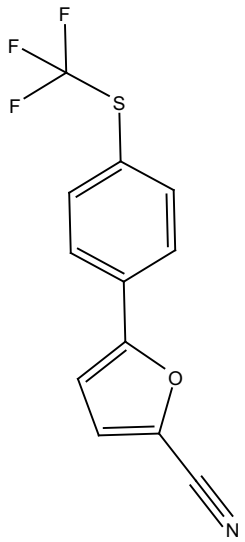
-114.50
-114.52
-114.53
-114.54
-114.56

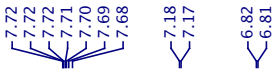
3.05

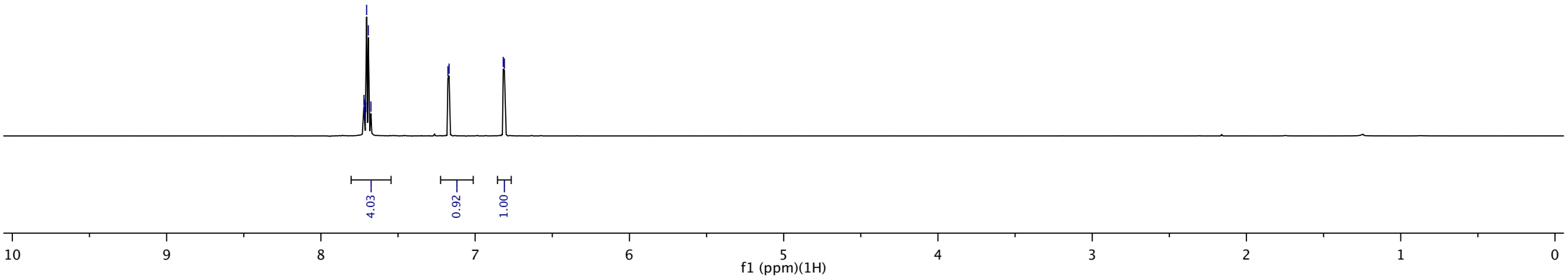
0.95

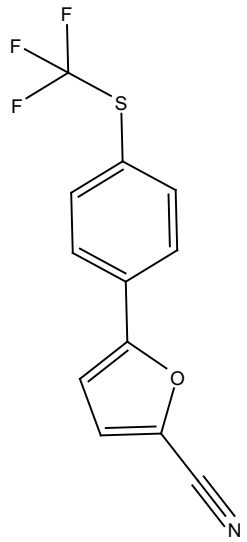
−20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140

f1 (ppm)(19F)

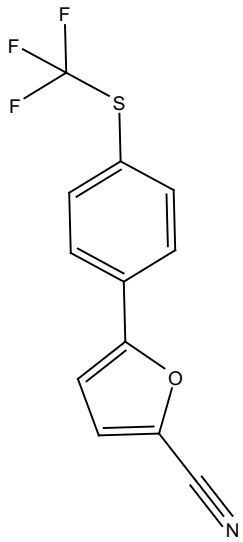

F
F
F
S
O
N


7.72
7.72
7.72
7.71
7.70
7.69
7.68
7.18
7.17
6.82
6.81

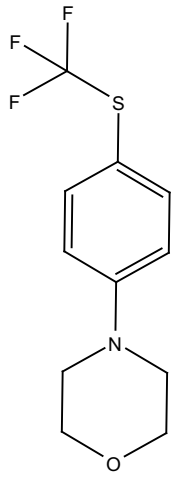

4.03
0.92
1.00
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)


F
F
F
S
O
N

157.59
137.37
137.37
133.81
131.44
131.35
128.90
126.60
126.45
126.24
126.16
126.14
126.13
126.11
124.70
112.22
108.50
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S
O
N

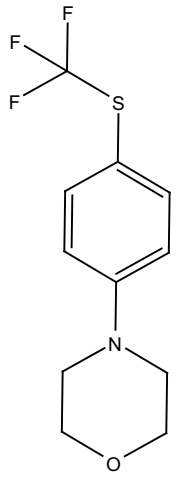
-42.48
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)



7.54
7.52
6.89
6.87
3.86
3.85
3.84
3.23
3.22
3.21

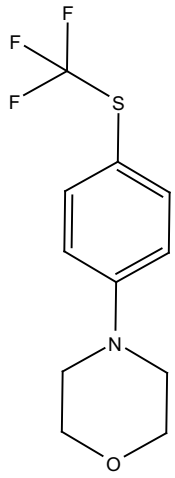
1.03
1.02
2.03
2.10

10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

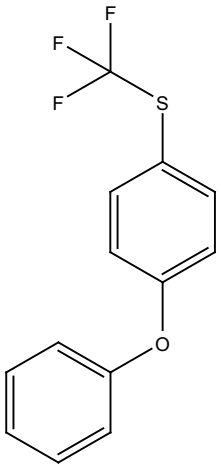


153.59
138.61
138.61
134.13
131.68
129.23
126.78
115.92
113.06
113.04
113.03
113.01
67.31
48.60

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S
N
O

-44.17
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

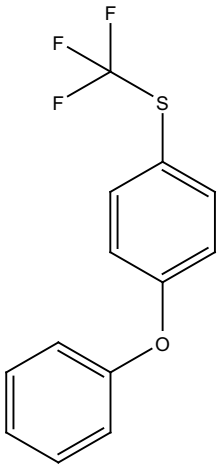


7.66 7.65 7.64 7.64 7.63 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.23 7.23 7.23 7.14 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.12 7.12 7.11 7.07 7.06 7.05 7.05 7.04 7.04

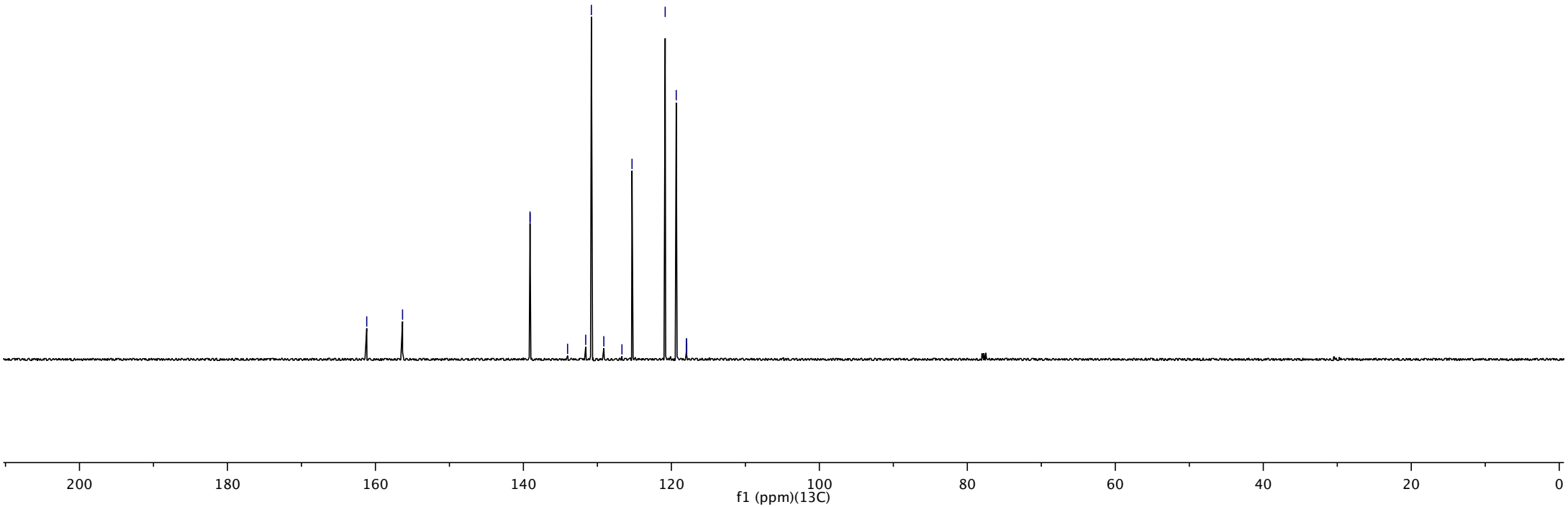
2.03 2.00 1.00 1.91 2.03

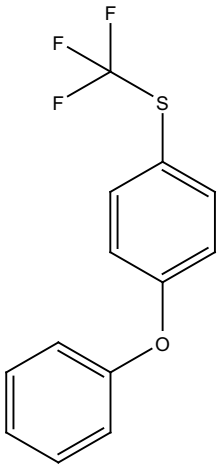
10 9 8 7 6 5 4 3 2 1 0

f1 (ppm)(1H)

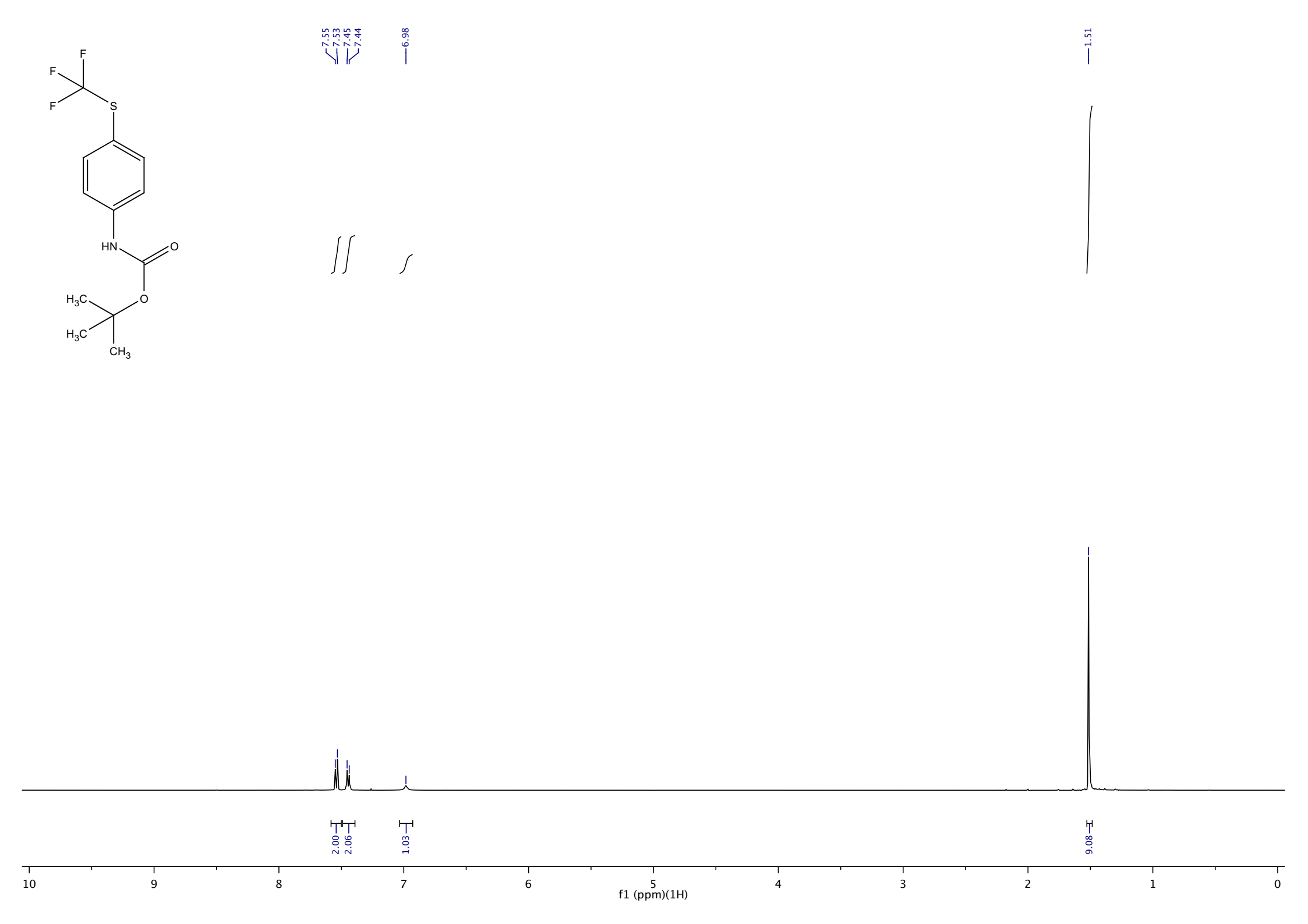


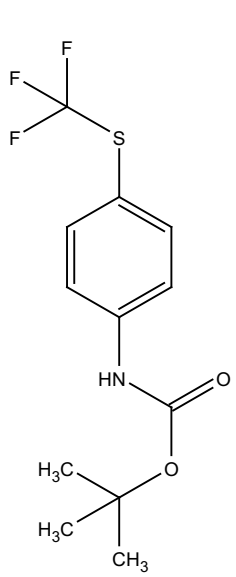
161.18
156.34
139.10
139.10
134.03
131.58
130.81
129.13
126.68
125.32
120.84
119.34
117.98
117.97
117.95
117.93




F
F
F
S
O

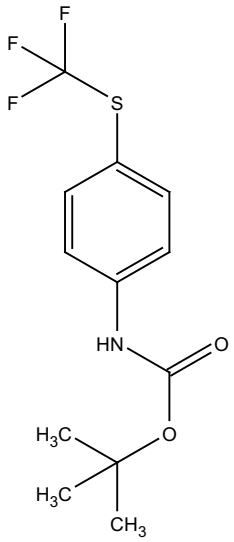
-43.66
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


F
F
F
S
HN
O
O
H3C
H3C
CH3
7.55
7.53
7.45
7.44
6.98
1.51
2.00
2.06
1.03
9.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

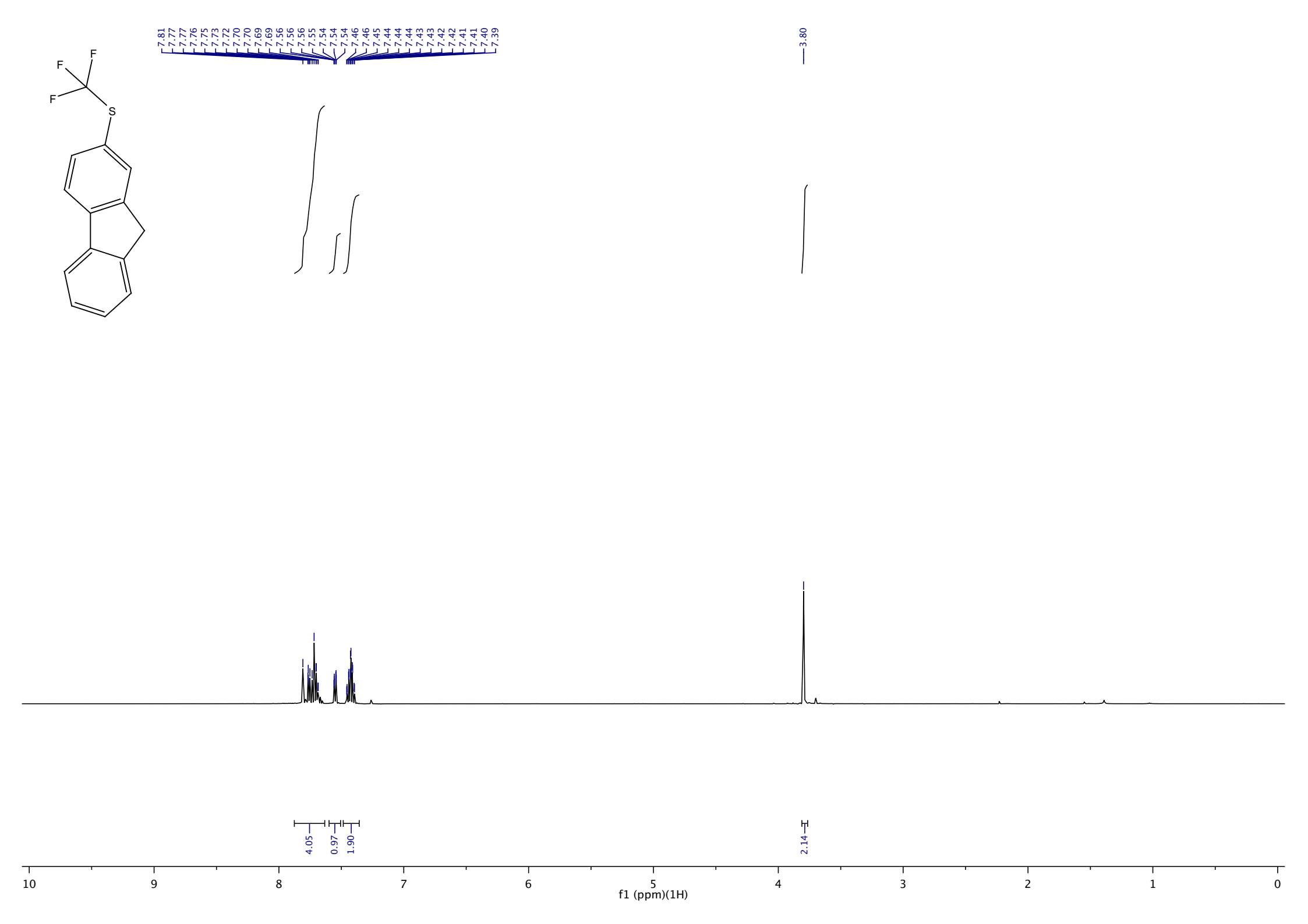


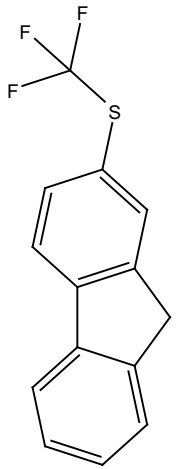
153.23
141.95
138.20
133.97
131.52
129.07
126.62
119.59
117.77
117.76
117.74
117.72
81.95
28.89

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S
HN
O
O
H3C
H3C
CH3

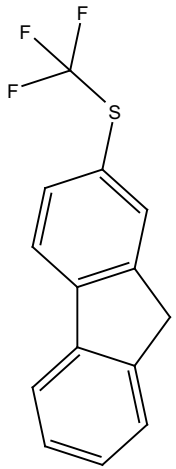
-43.65
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


7.81
7.77
7.77
7.76
7.75
7.73
7.72
7.70
7.70
7.69
7.69
7.56
7.56
7.55
7.54
7.54
7.54
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
3.80
F
F
F
S
4.05
0.97
1.90
2.14
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

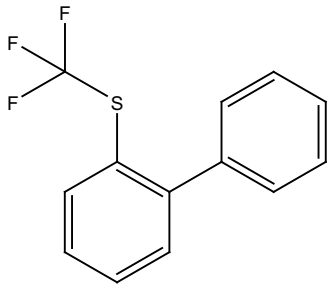


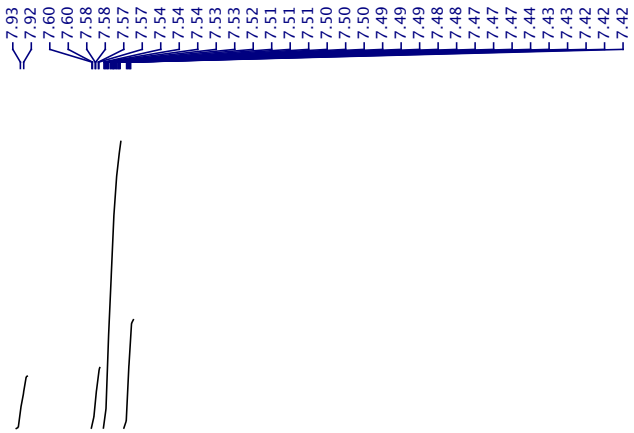
145.14
145.05
144.39
140.93
135.93
135.93
133.73
133.73
131.89
129.44
128.63
127.75
125.86
121.26
121.21
37.35

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S

-43.15
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


F
F
F
S


7.93
7.92
7.60
7.60
7.58
7.58
7.58
7.57
7.57
7.54
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.49
7.49
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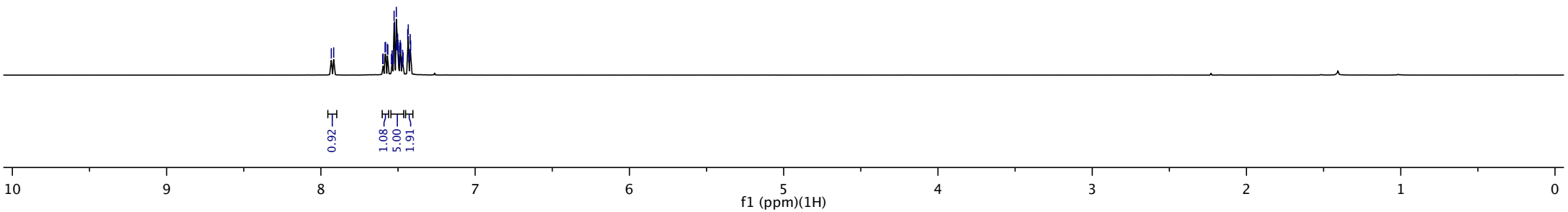
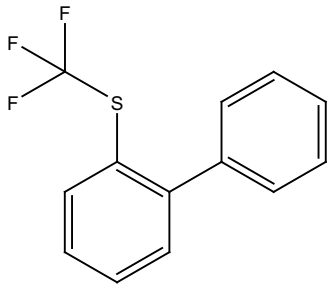
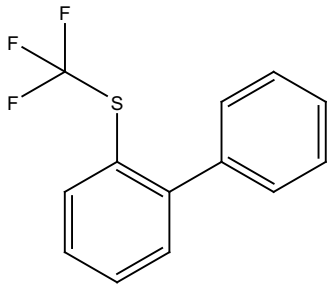
7.44
7.43
7.43
7.42
7.42
7.42


0.92
1.08
5.00
1.91
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

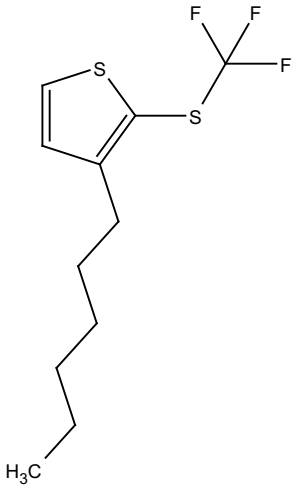


148.68
141.03
137.95
137.94
131.46
130.47
129.04
128.74
124.08
124.06
124.05

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S

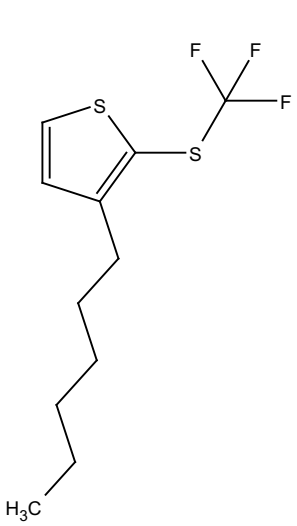
-42.11
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)



7.54
7.53
7.07
7.06
2.83
2.81
2.80
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.38
1.37
1.36
1.36
0.96
0.94
0.93

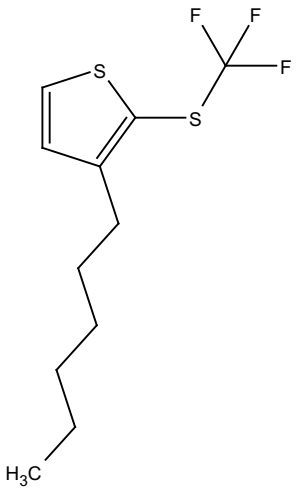
0.94
1.02
2.10
2.16
6.17
3.00

10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

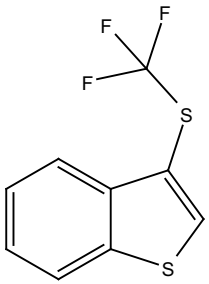


153.95
153.94
133.00
132.91
130.52
129.79
128.05
125.58
115.78
115.76
115.74
115.72
32.35
31.13
29.78
29.65
23.31
14.73

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)


F
F
F
S
S
H3C

-44.95
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

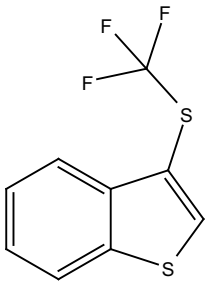


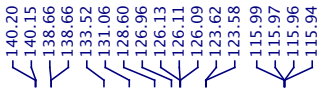
8.12 8.12 8.10 8.10 7.99 7.93 7.93 7.92 7.91 7.91 7.91 7.57 7.57 7.56 7.56 7.54 7.54 7.50 7.50 7.50 7.50 7.48 7.48 7.48 7.47 7.47 7.47 7.47

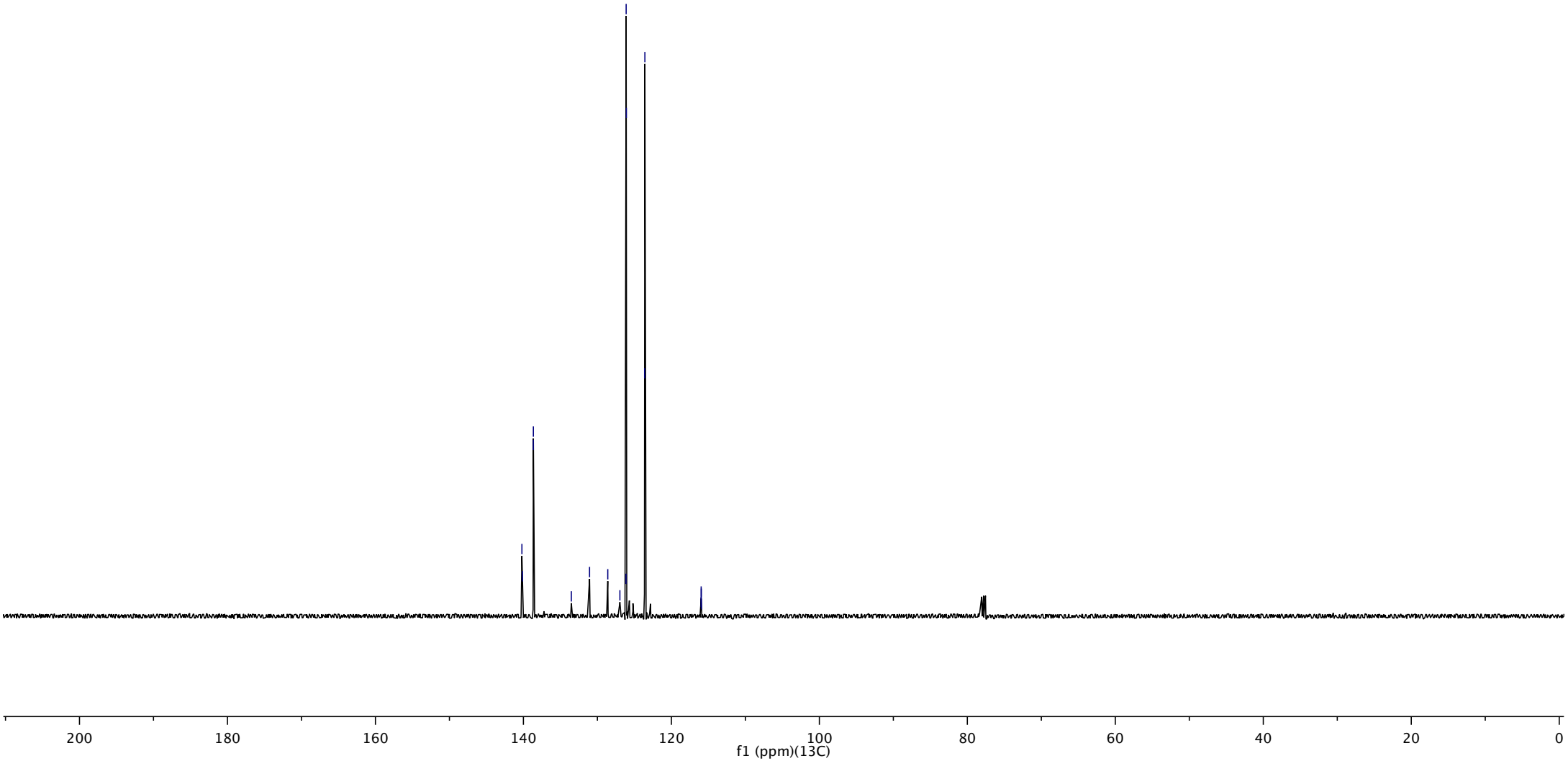
1.00 0.91 0.95 1.10 1.11

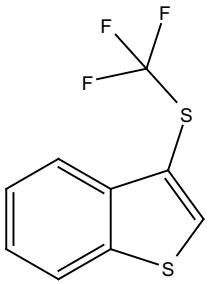
10 9 8 7 6 5 4 3 2 1 0

f1 (ppm)(1H)

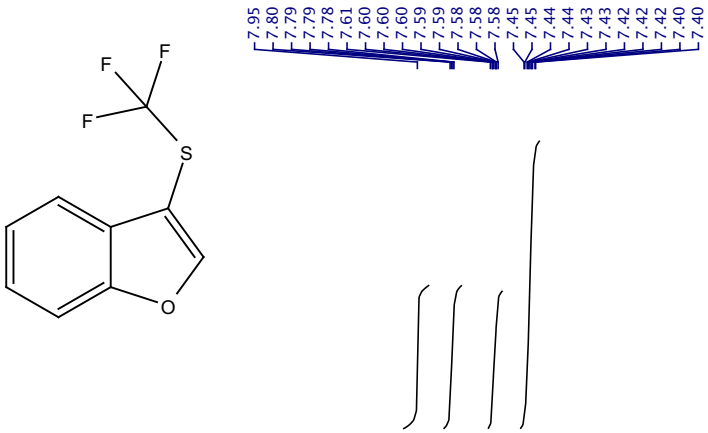

F
F
F
S
S


140.20
140.15
138.66
138.66
133.52
131.06
128.60
126.96
126.13
126.11
126.09
123.62
123.58
115.99
115.97
115.96
115.94


200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)



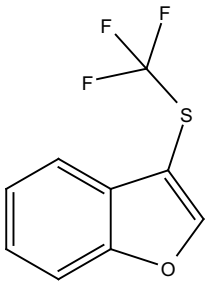
^{19}F NMR (471 MHz, $CDCl_3$) δ -42.75 (s).



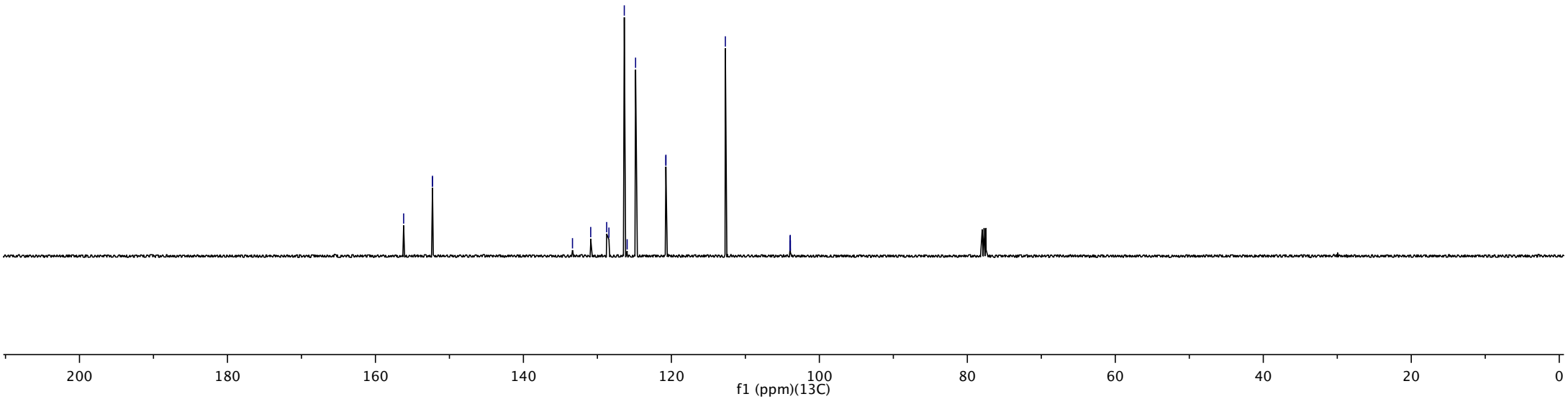
7.95
7.80
7.79
7.79
7.78
7.61
7.60
7.60
7.60
7.59
7.59
7.58
7.58
7.58
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.40
7.40

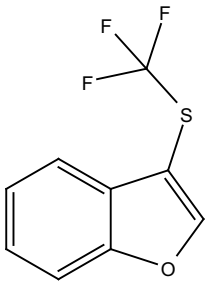
1.00
1.00
0.96
2.00

10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)(1H)

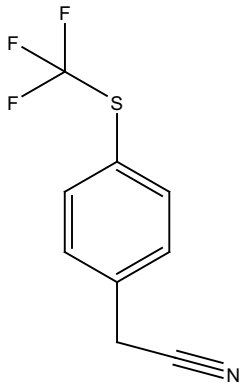


156.19
152.30
152.29
133.37
130.90
128.75
128.44
126.37
125.98
124.84
120.75
120.74
112.70
103.98
103.96
103.94
103.91

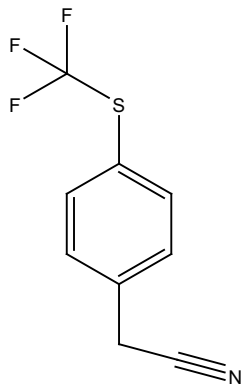



F
F
F
S
O

-43.40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

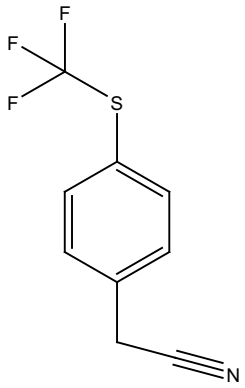

F
F
F
S
N

7.69
7.67
7.42
7.40
3.79
1.95
1.97
2.08
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

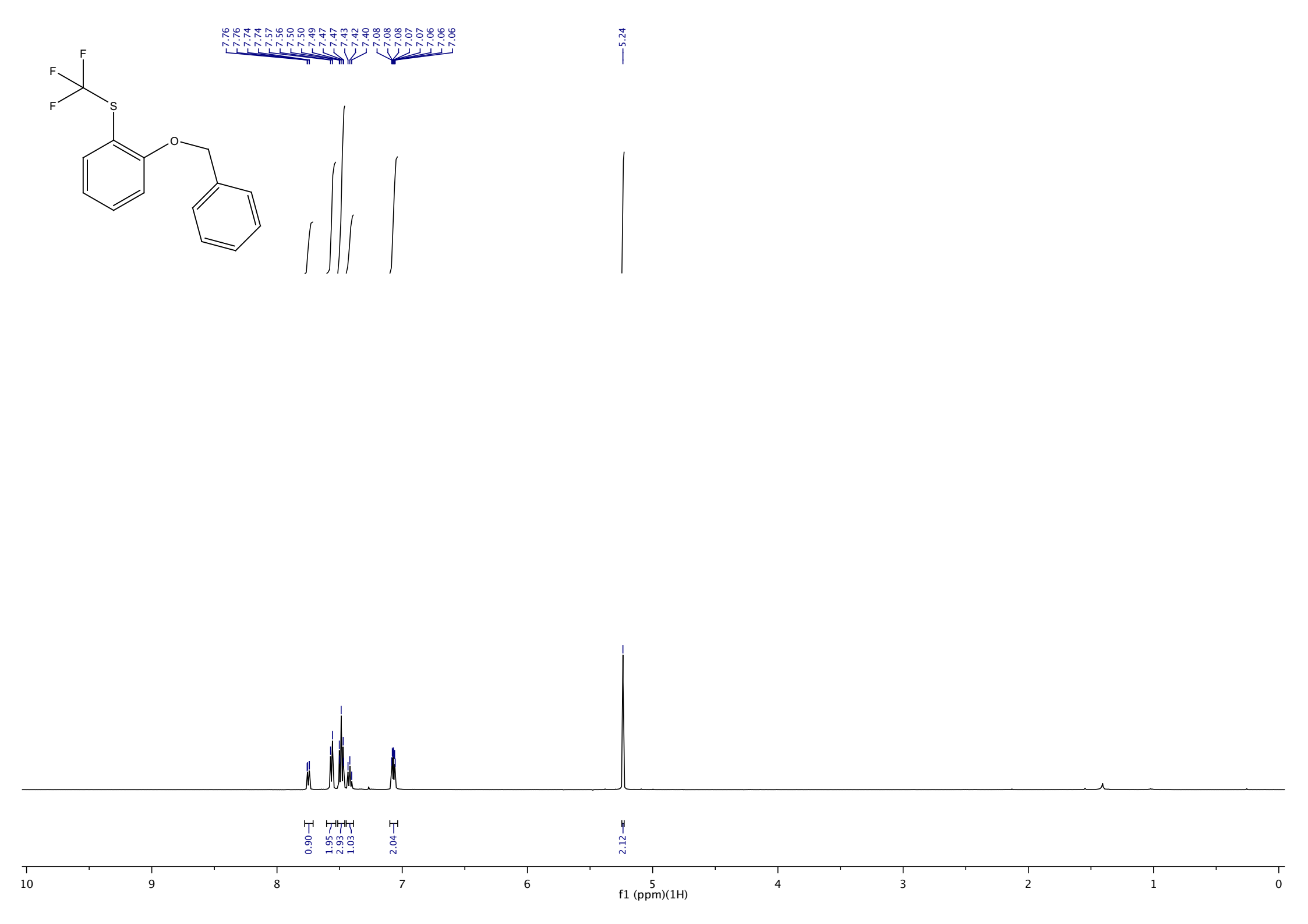


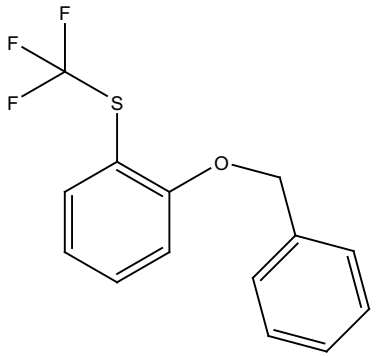
137.65
137.64
133.89
133.82
131.37
129.80
128.92
126.47
125.11
125.09
125.07
117.86
24.08

200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)(13C)

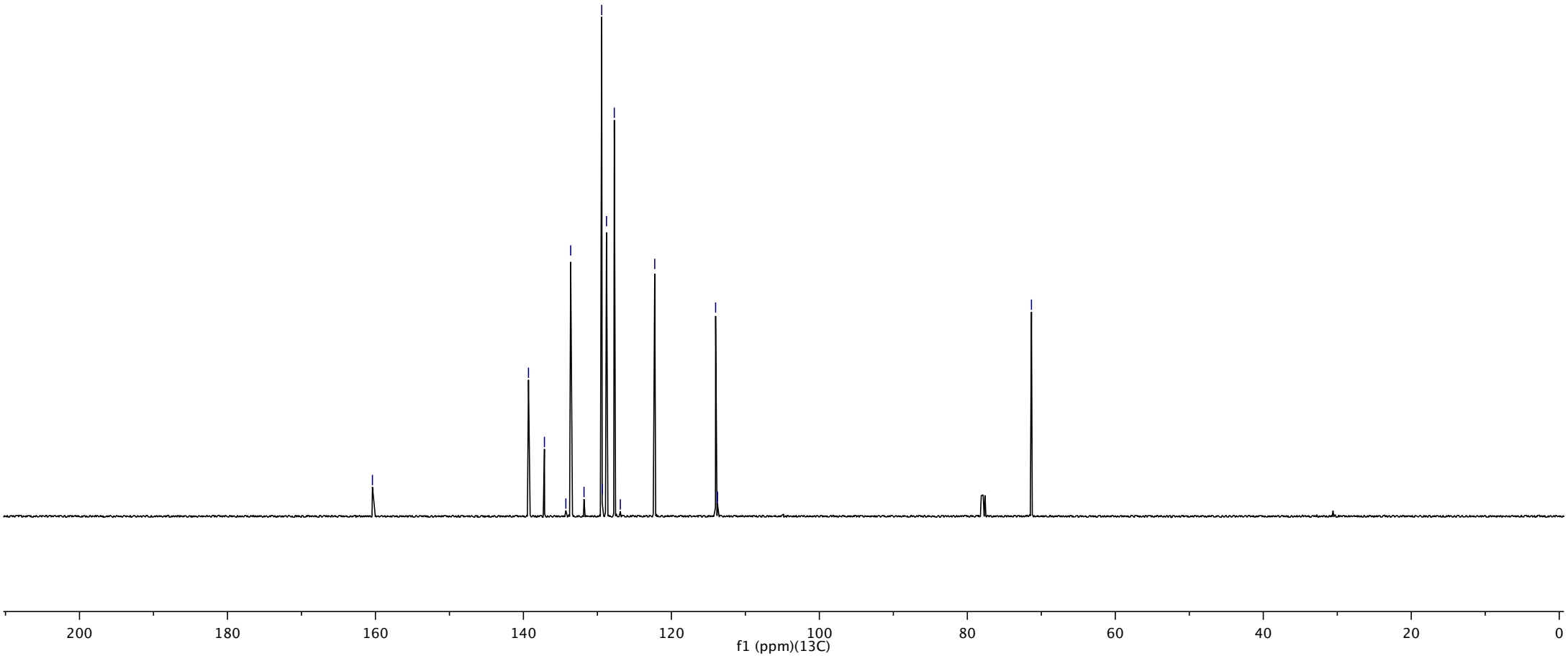

F
F
F
S
N

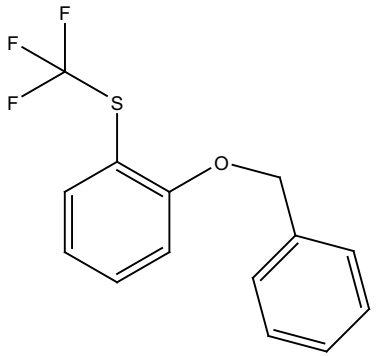
-42.85
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


F
F
F
S
O
7.76
7.76
7.74
7.74
7.57
7.56
7.50
7.50
7.49
7.47
7.47
7.43
7.42
7.40
7.08
7.08
7.08
7.07
7.07
7.06
7.06
7.06
5.24
0.90
1.95
2.93
1.03
2.04
2.12
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

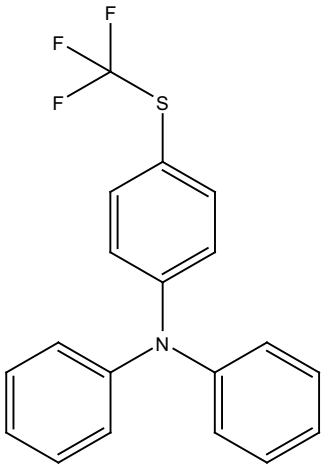


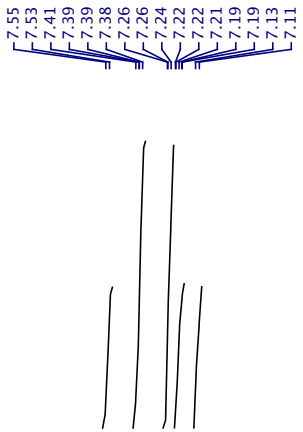
160.40
139.32
137.16
134.26
133.61
131.81
129.42
129.35
128.77
127.72
126.90
122.25
114.02
113.78
113.77
71.33

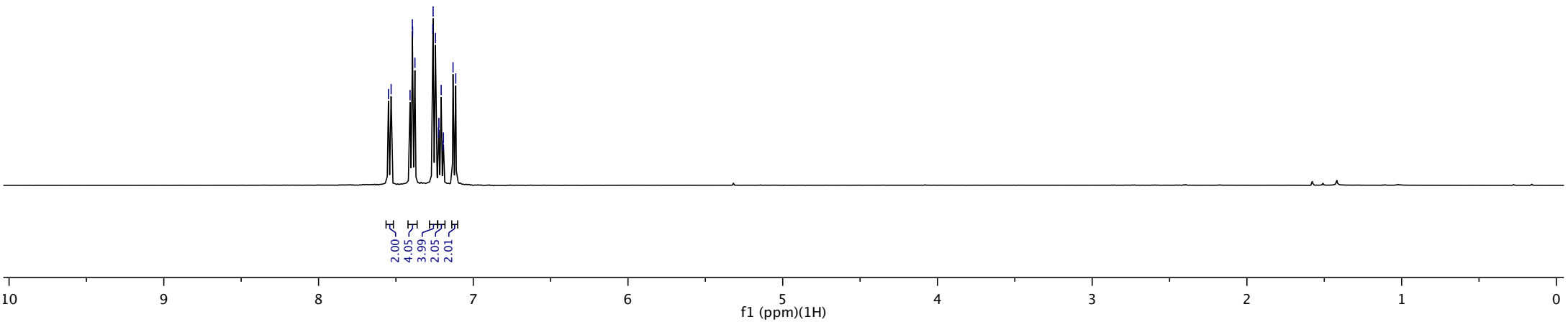


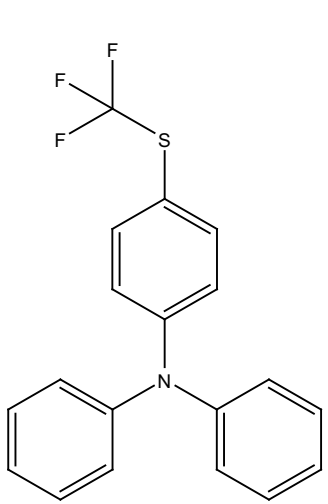

F
F
F
S
O

-42.37
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

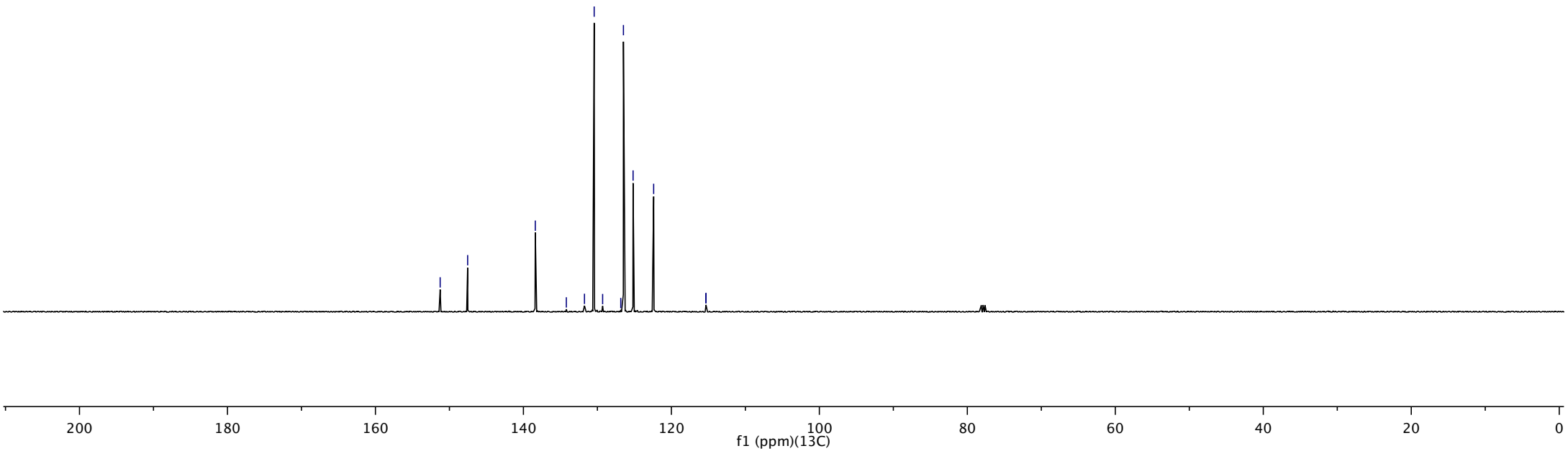

F
F
F
S
N

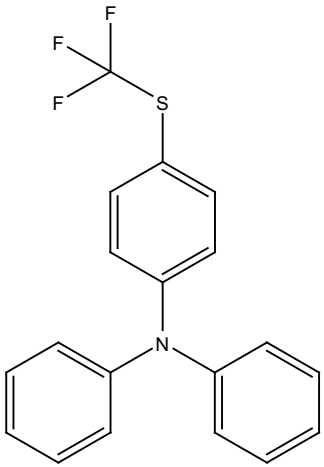

7.55
7.53
7.41
7.39
7.39
7.38
7.26
7.26
7.24
7.22
7.22
7.21
7.19
7.19
7.13
7.11


2.00
4.05
3.99
2.05
2.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

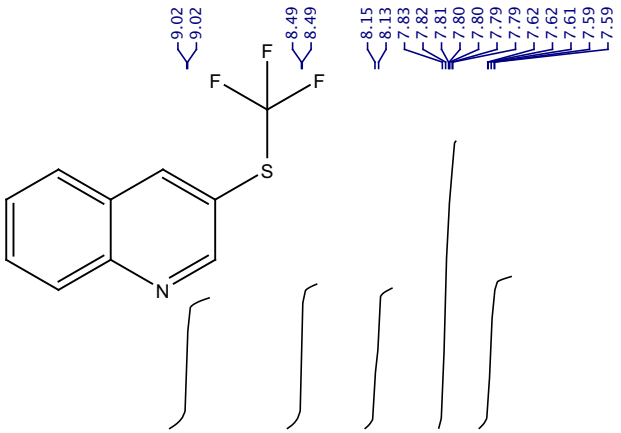


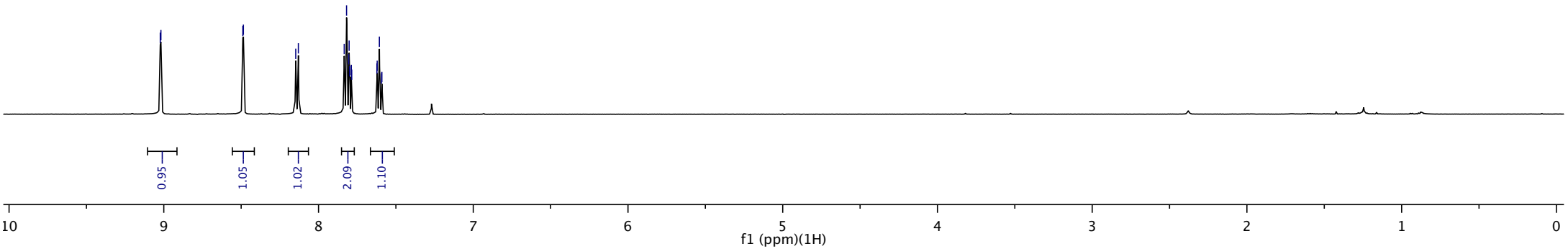
151.25
147.54
138.39
134.20
131.75
130.43
129.29
126.84
126.48
125.18
122.40
115.34
115.32

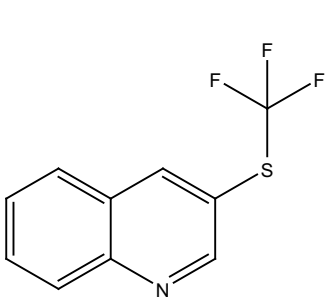



F
F
F
S
N

-43.96
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

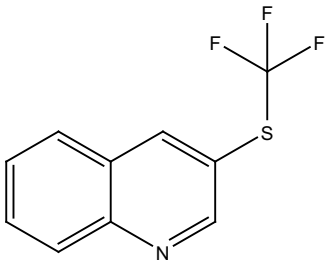

9.02
9.02
8.49
8.49
8.15
8.13
7.83
7.82
7.81
7.80
7.80
7.79
7.79
7.62
7.62
7.61
7.59
7.59
F
F
F
S
N


0.95
1.05
1.02
2.09
1.10
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

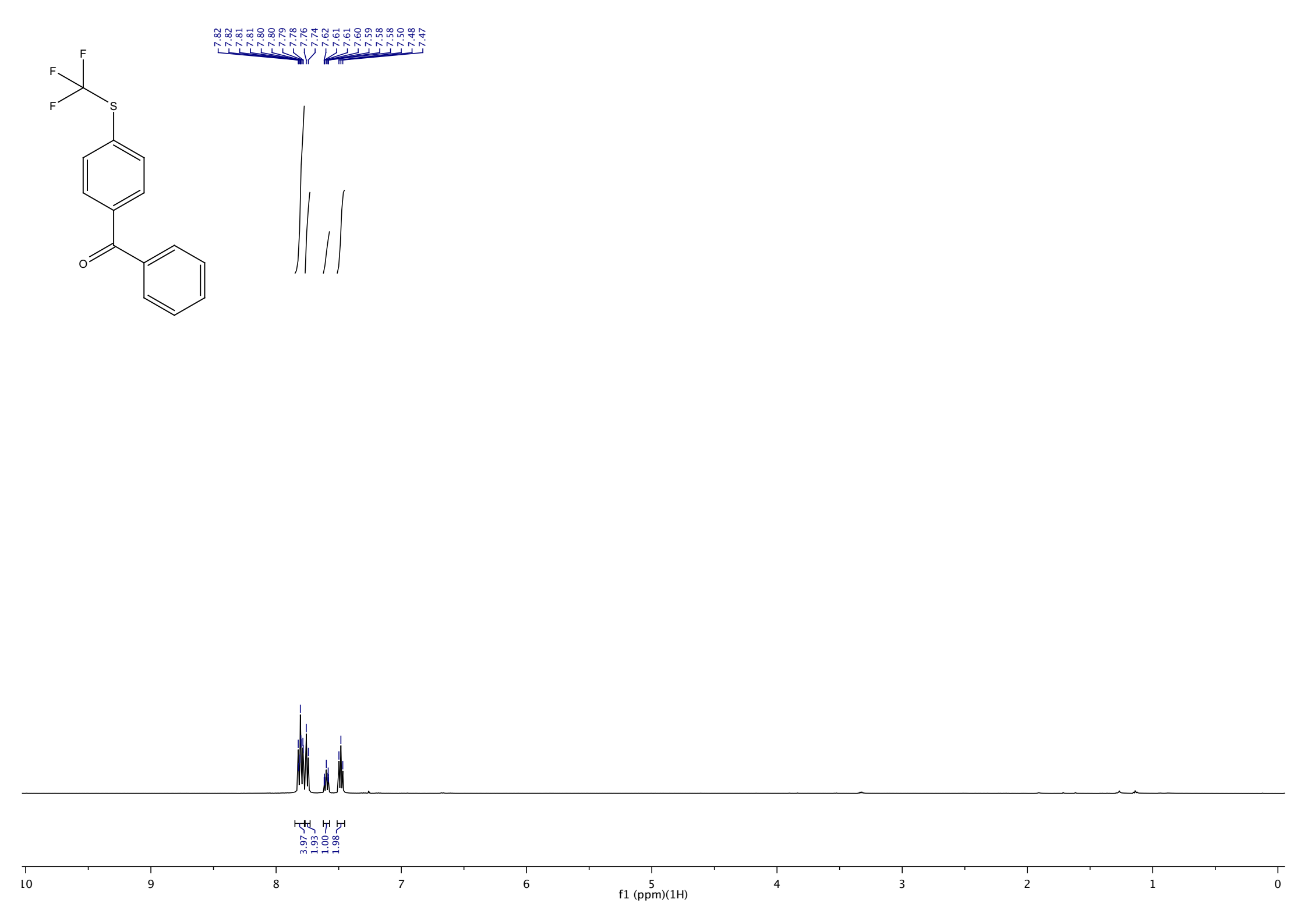


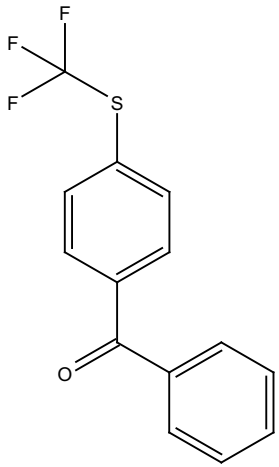
155.24
149.05
145.39
133.58
132.32
131.12
130.20
128.76
128.67
128.47
128.43
128.34
118.92
118.91
118.89

240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)(13C)


F
F
F
S
N

-42.62
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


7.82
7.82
7.81
7.81
7.80
7.80
7.79
7.78
7.76
7.74
7.62
7.61
7.61
7.60
7.59
7.58
7.58
7.50
7.48
7.47
F
F
F
S
O
3.97
1.93
1.00
1.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

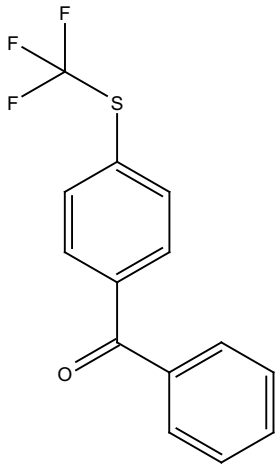


196.14

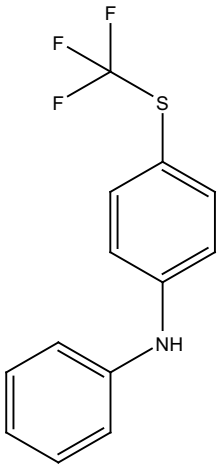
140.14
137.47
136.22
136.22
133.75
133.68
131.38
131.30
130.74
129.77
129.76
129.19
128.84
126.39

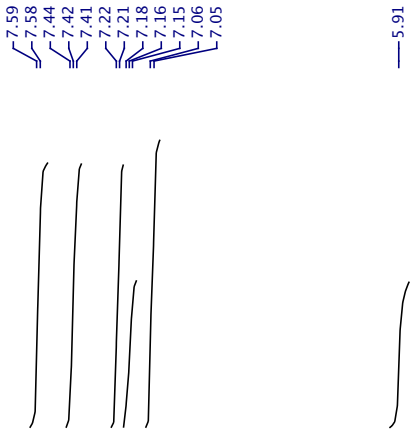
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40

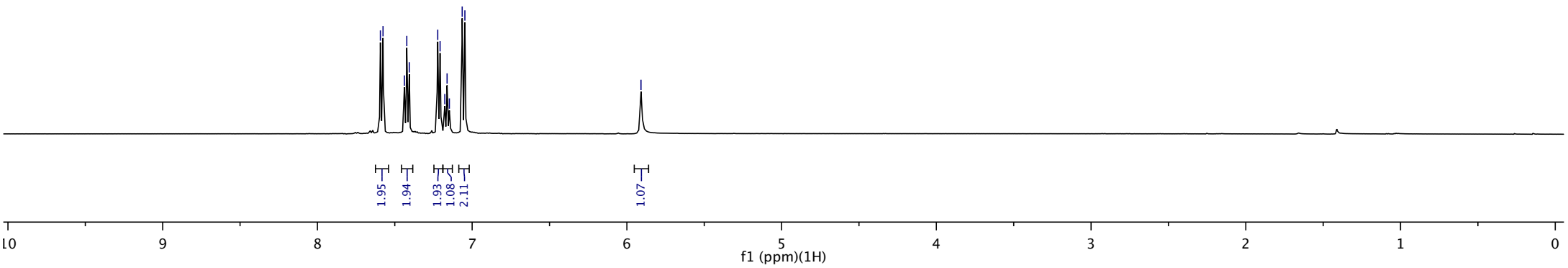
f1 (ppm)(13C)

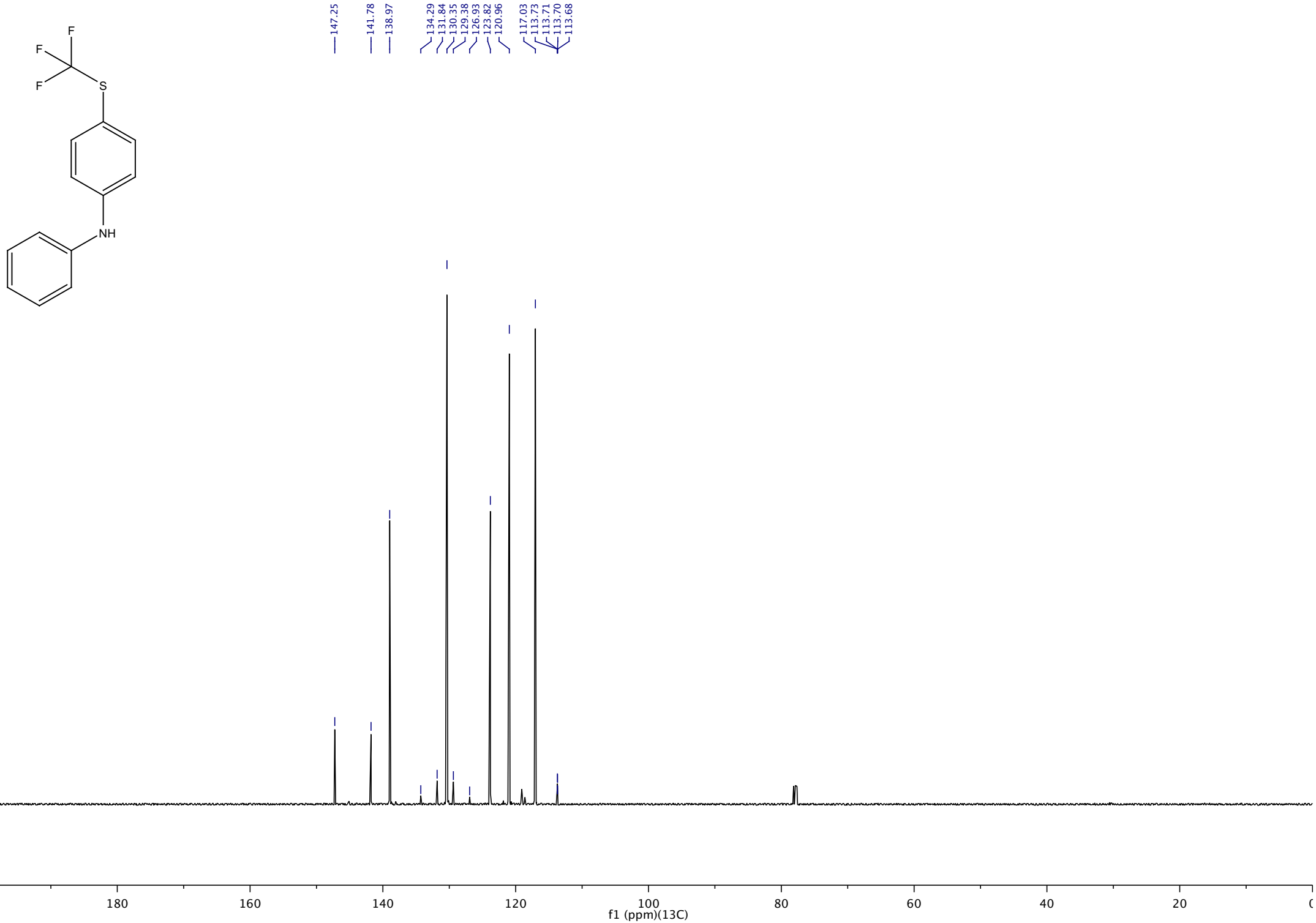

F
F
F
S
O

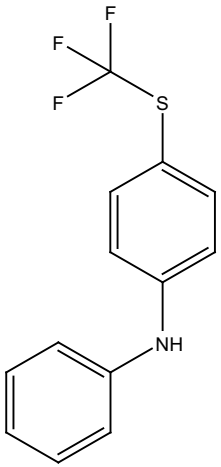
-42.06
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)


F
F
F
S
NH

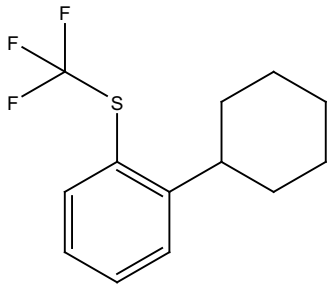

7.59
7.58
7.44
7.42
7.41
7.22
7.21
7.18
7.16
7.15
7.06
7.05
5.91


1.95
1.94
1.93
1.08
2.11
1.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

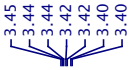

147.25
141.78
138.97
134.29
131.84
130.35
129.38
126.93
123.82
120.96
117.03
113.73
113.71
113.70
113.68
F
F
F
S
NH
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)


F
F
F
S
NH

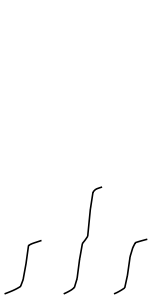
-44.29
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

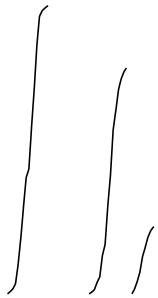

F
F
F
S

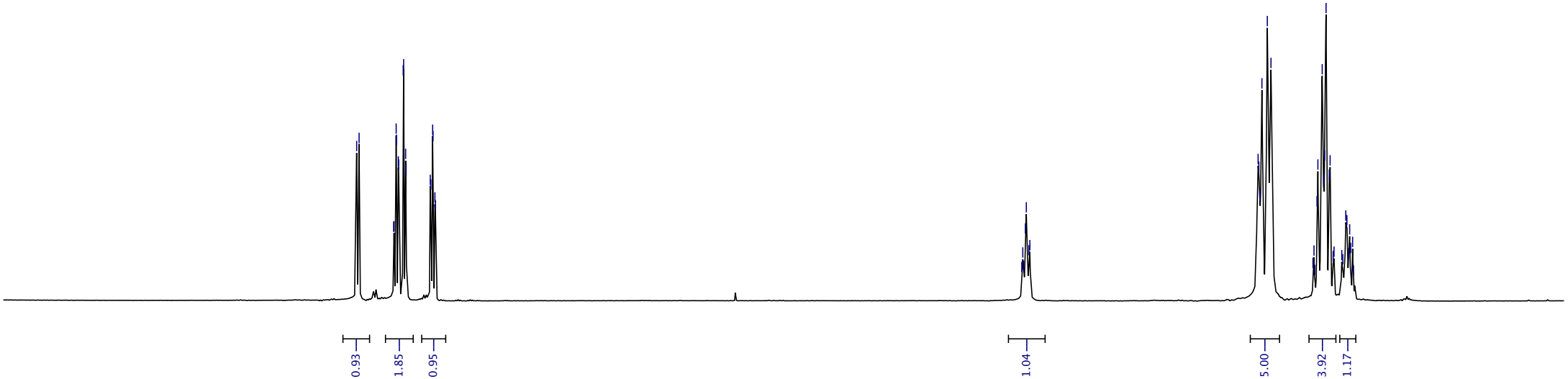

7.75
7.73
7.51
7.50
7.49
7.49
7.48
7.47
7.45
7.44
7.43
7.43
7.27
7.26
7.25
7.24
7.24


3.45
3.44
3.44
3.42
3.42
3.40
3.40


1.92
1.92
1.91
1.90
1.86
1.84
1.57
1.56
1.54
1.53
1.51
1.50
1.49
1.48
1.46
1.46
1.44
1.43
1.38
1.37
1.35
1.35
1.34
1.33
1.32



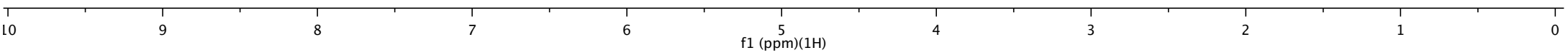


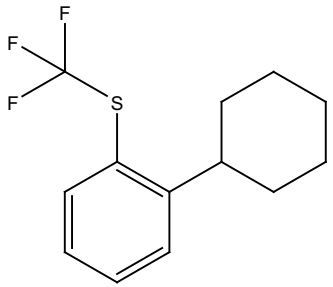


0.93
1.85
0.95

1.04

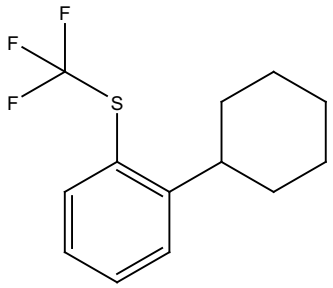
5.00
3.92
1.17


10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

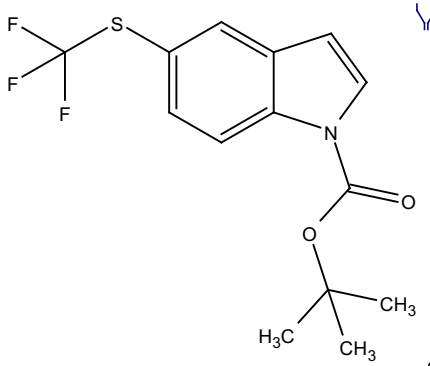


153.73
138.99
138.99
134.07
132.20
131.62
129.17
128.20
127.22
126.72
123.59
123.58
123.56
123.55
42.07
34.86
27.50
26.86

240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)(13C)


F
F
F
S

-42.95
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)(19F)

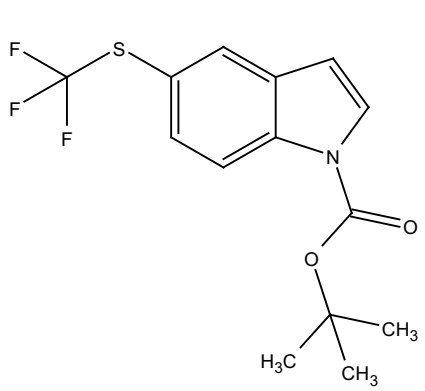


8.25
8.23
7.89
7.89
7.69
7.68
7.61
7.61
7.60
7.59
6.59
6.58
1.71

1.00
0.96
0.95
0.90
0.97
9.10

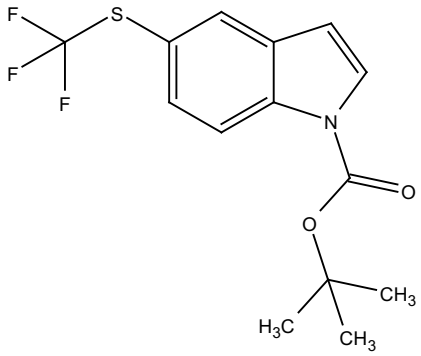
10
9
8
7
6
5
4
3
2
1
0

f1 (ppm)(1H)

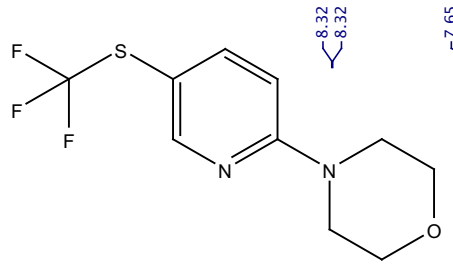


149.98
137.14
134.27
132.67
132.16
131.82
130.47
129.37
128.04
126.92
118.16
118.14
118.13
118.11
116.74
107.60
85.11
28.74

200
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)


F
F
F
S
N
O
O
CH3
H3C
CH3

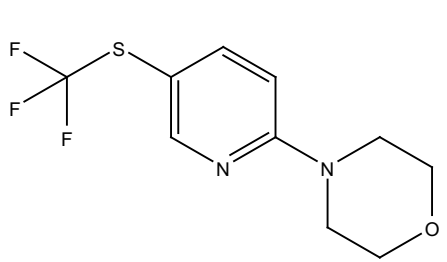
-43.73
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)(19F)



8.32
8.32
7.65
7.64
7.63
7.63
6.58
6.56
3.77
3.76
3.75
3.57
3.56
3.55

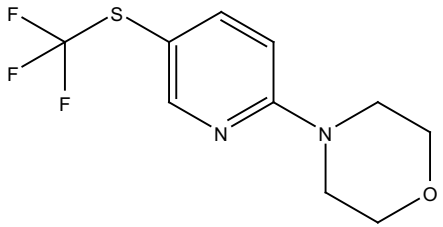
0.99
0.97
1.04
4.03
4.13

10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

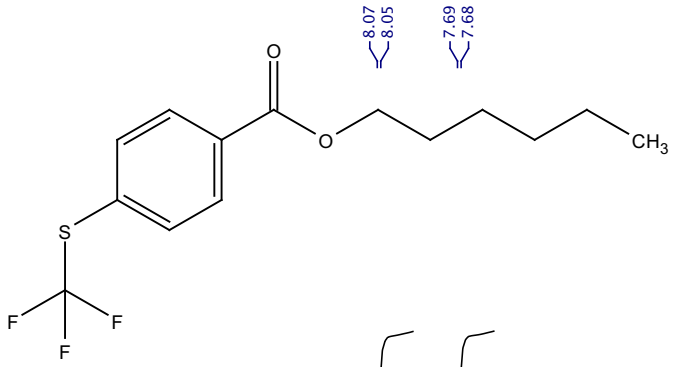


160.51
156.21
145.68
133.69
131.24
128.79
126.33
108.32
108.30
107.32
67.19
45.56

200
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)


F
F
F
S
N
N
O

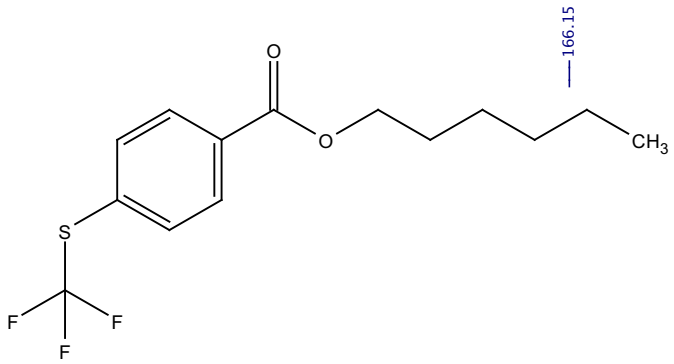
-44.70
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)(19F)



8.07
8.05
7.69
7.68
4.33
4.32
4.31
1.78
1.77
1.75
1.74
1.72
1.43
1.41
1.33
1.32
1.30
0.90
0.89
0.87

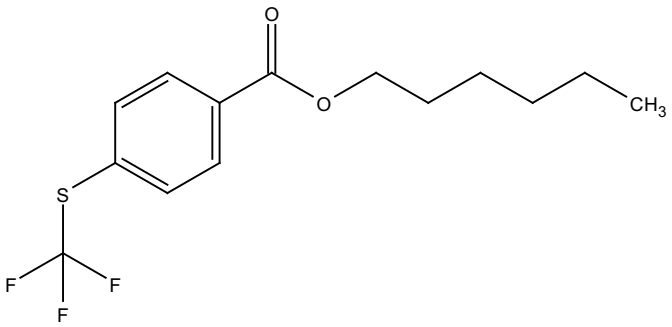
2.00
2.01
2.03
2.02
5.96
2.78

0 9 8 7 6 5 4 3 2 1 0
f1 (ppm)(1H)

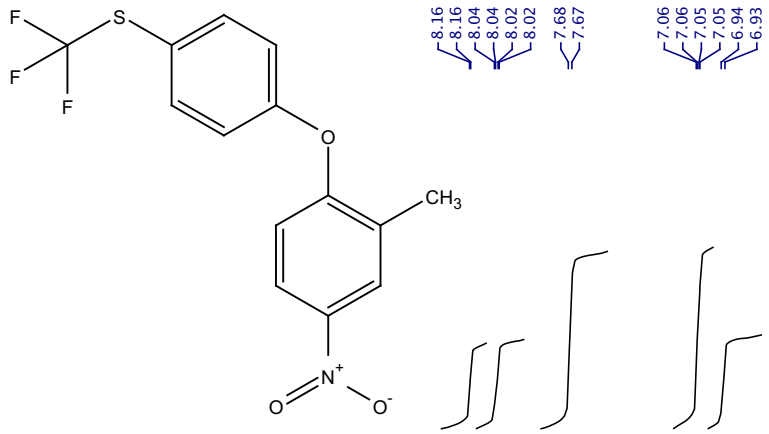


166.15
136.20
136.19
133.67
131.22
131.03
130.34
130.33
130.31
130.29
128.77
126.32
66.25
32.12
29.30
26.35
23.21
14.59

240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)(13C)


O
O
CH3
S
F
F
F

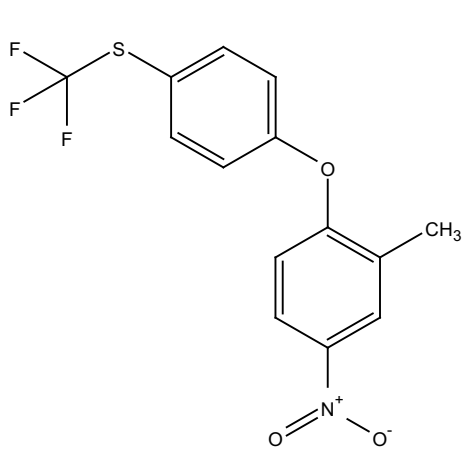
-42.20
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)(19F)



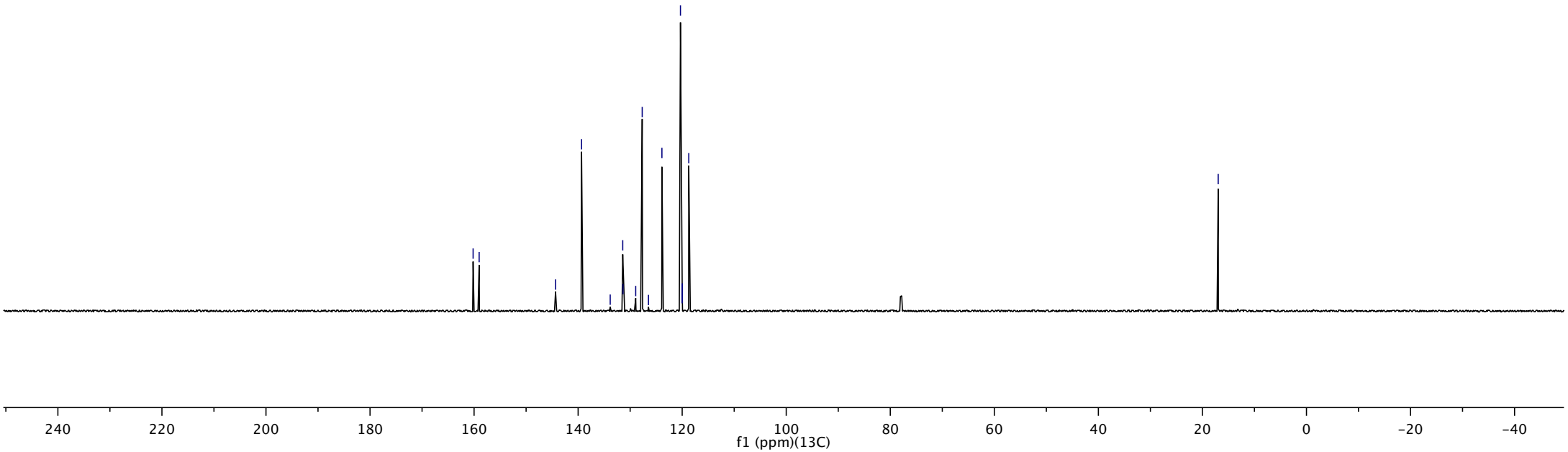
8.16
8.16
8.04
8.04
8.02
8.02
7.68
7.67
7.06
7.06
7.05
7.05
6.94
6.93
2.37

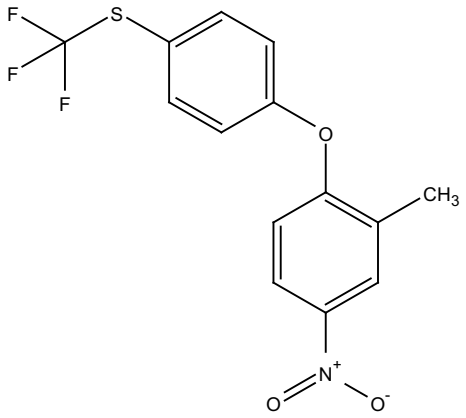
0.95
0.99
1.96
2.01
1.04
3.18

10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)(1H)

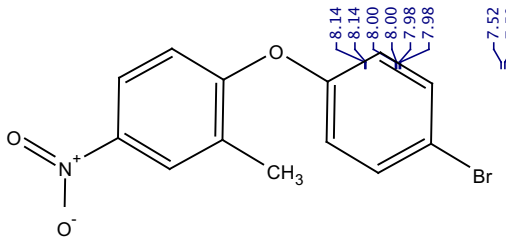


160.19
159.02
144.34
139.34
133.85
131.42
131.38
128.93
127.68
126.48
123.89
120.33
120.02
120.00
119.98
119.96
118.73
16.97




F
F
F
S
O
CH3
N+
O
O-

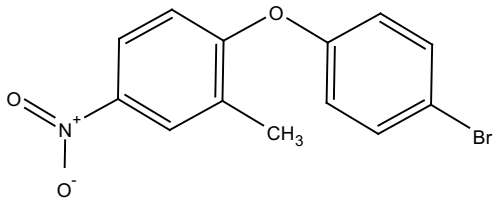
-43.48
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-8
f1 (ppm)(19F)



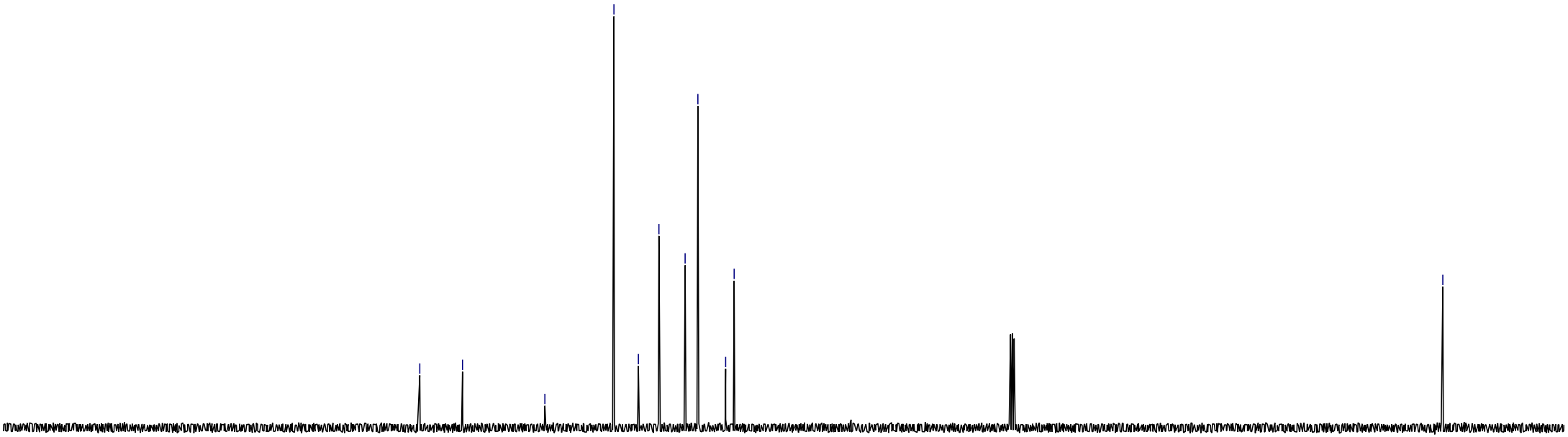
8.14
8.14
8.00
8.00
7.98
7.98
7.52
7.50
6.92
6.91
6.80
6.78
2.38

0.80
0.88
1.71
1.76
0.92
3.00

f1 (ppm)(1H)



161.29
155.27
143.66
133.92
130.48
127.58
123.89
122.09
118.17
116.97
17.07



200
180
160
140
120
100
80
60
40
20
f1 (ppm)(13C)