Supporting Information

Radical Fluoroalkylthiolation of Aldehydes with $PhSO_2SR_f$ ($R_f = CF_3$, C_2F_5, CF_2H or CH_2F): A General Protocol for the Preparation of Fluoroalkylthioesters

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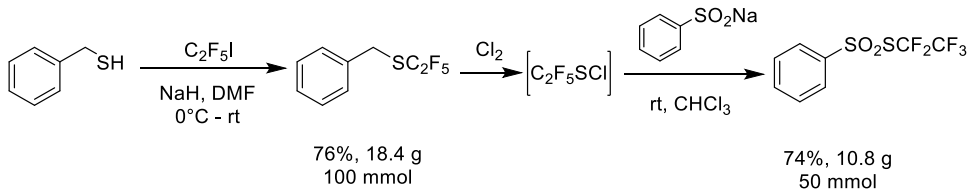
General information. All reactions were maintained under an argon atmosphere unless otherwise stated. All solvents were purified by standard method. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz, 125 MHz, 100 MHz, 375 MHz spectrometer (400 MHz for ^{1}H ; 100 MHz or 125 MHz for ^{13}C; 375 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz); The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

Materials. Aldehydes were received from commercial sources. $PhSO_2SCF_3$,[1] $PhSO_2SCF_2H$[2] and $PhSO_2SCH_2F$[3] were prepared according to the procedures reported in the literature. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

General procedure for the synthesis of S-(pentafluoroethyl) benzenesulfonothioate

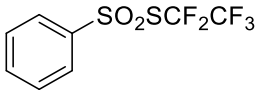


Benzyl(pentafluoroethyl)thioether

To a suspension of NaH (120 mmol) in anhydrous DMF (100 mL) was added mercaptan (11.5 mL, 100 mmol) at room temperature with stirring. The mixture was stirred for 1 h and was cooled to 0 °C. 2-Iodo pentafluoroethane (23.6 mL, 200 mmol) was added dropwise. The mixture was stirred and allowed to warm to room temperature. An aqueous solution of NH_4Cl (50 mL) was added and the mixture was extracted with diethyl ether (350 mL × 3). The organic layer was combined and washed with water and brine, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash chromatograph on silica gel (eluent: petroleum ether) to give benzyl(pentafluoroethyl)thioether as a colorless oil (18.4 g, 76%).

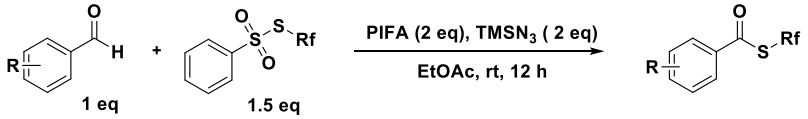
S-(Pentafluoroethyl)benzenesulfonothioate

A solution of Cl_2 in $CHCl_3$ (71 mL, 0.840 mol/L, 60 mmol) was placed into three-neck round bottom flask equipped with a stirring bar. (12.3 g, 50.0 mmol) benzyl(pentafluoroethyl)thioether was added at 0 °C and the reaction was stirred for 1 h. Sodium benzenesulfinate (12.3 g, 75.0 mmol) was added quickly at 0 °C and the mixture was stirred for another 2 h at room temperature. The mixture was filtered. The solvent of the filtrate was evaporated in *vacuo*. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to give S-(pentafluoroethyl)benzenesulfonothioate as a colorless oil (10.8 g, 74%).



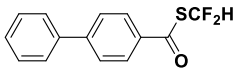
S-(Pentafluoroethyl)benzenesulfonothioate. Yield 74%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.00 (d, *J* = 8.0 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 7.60 (t, *J* = 7.9 Hz, 2 H) ; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K, TMS) δ -83.32 (t, *J* = 3.5 Hz, 3 F), -91.17(q, *J* = 4.0 Hz, 2 F), -121.25 (m, 2 F) ; ^{13}C NMR (126 MHz, $CDCl_3$, 293 K, TMS) δ 125.16, 135.27, 129.66, 127.65, 122.07, 119.73 (tq, *J* = 295.6 Hz, *J* = 42.4 Hz), 117.66 (qt, *J* = 285.4, 34.6 Hz) ppm. IR (KBr): ν_{max} = 3071, 1582, 1477, 1450, 1325, 1220, 1107, 1077, 999, 954, 753, 716, 682, 645, 538 cm^{-1}. MS (EI): 292.77 (100). HRMS (EI) for $C_8H_5F_5O_2S_2$: Calcd: 291.9651; Found: 291.9657.

General procedure for the fluoroalkylthiolation of aldehydes



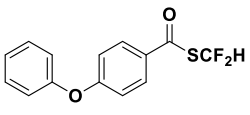
Aldehyde (0.300 mmol), PIFA (258 mg, 0.600 mmol), S-(fluoromethyl)benzenesulfonothionate (0.450 mmol), EtOAc (1.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under an atmosphere of argon. $TMSN_3$ (69 mg, 0.600 mmol) was added. The tube was quickly sealed with a rubber stopper. The reaction was stirred at room temperature for 12 h. The mixture was concentrated under vacuum. The residue was purified by flash column chromatography (eluent: petroleum ether: ethyl acetate = 100:1). The yields of the products were calculated based on aldehyde.

S-(Difluoromethyl)(1,1'-biphenyl)-4-carbothioate 2a



The general procedure conducted with (1,1'-biphenyl)-4-carbaldehyde (54.7 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258.0 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.60 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)(1,1'-biphenyl)-4-carbothioate **2a** (71 mg, 90%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 2 H), 7.70 (d, J = 8.3 Hz, 2 H), 7.61 (d, J = 7.9 Hz, 2 H), 7.52 (t, J = 56.0 Hz, 1 H), 7.51 – 7.40 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.33 (d, J = 55.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7, 147.6, 139.2, 134.2, 129.1, 128.7, 128.2, 127.6, 127.3, 120.6 (t, J = 270.2 Hz) ppm. MS (EI): m/z (%) 152 (100). HRMS (EI) for $C_{14}H_{10}F_2OS$ Calcd: 264.0420; Found: 264.0432. IR (KBr): ν_{max} = 1674, 1601, 1219, 1040, 913, 765,646 cm^{-1}. M.P.: 82-83 °C.

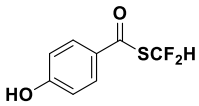
S-(Difluoromethyl)-4-phenoxybenzothioate 2b



The general procedure conducted with 4-phenoxybenzaldehyde (59.5 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.600 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.60 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)

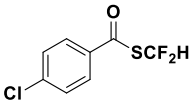
4-phenoxybenzothioate **2b** (76 mg, 90%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2 H), 7.47 (t, *J* = 56.0 Hz, 1 H), 7.41 (t, *J* = 7.9 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 7.07 (d, *J* = 7.7 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.28 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6, 163.6, 154.9, 130.2, 130.0, 129.8, 125.2, 120.7 (t, *J* = 271.7 Hz), 120.5, 117.4 ppm. MS (EI): m/z (%) 197 (M^+-SCF_2H, 100). HRMS (EI) for $C_{14}H_{10}F_2O_2S$ Calcd: 280.0370; Found: 280.0363. IR (KBr): ν_{max} = 1681, 1585, 1502, 1489, 1251, 1079, 901, 753 cm^{-1}.

S-(Difluoromethyl) 4-hydroxybenzothioate 2c



The general procedure conducted with 4-hydroxybenzaldehyde (36.6 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl) 4-hydroxybenzothioate **2c** (40 mg, 66%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 2 H), 7.43 (t, *J* = 55.3 Hz, 1 H), 6.87 (d, *J* = 7.5 Hz, 2 H), 5.62 (s, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.31 (d, *J* = 55.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.7, 161.3, 130.4, 128.7, 120.7 (t, *J* = 269.8 Hz), 115.9 ppm. MS (EI): m/z (%) 121 (M^+-SCF_2H, 100). HRMS (EI) for $C_8H_6F_2O_2S$ Calcd: 204.0057; Found: 204.0063. IR (KBr): ν_{max} = 1652, 1578, 1214, 1070, 899, 658 cm^{-1}.

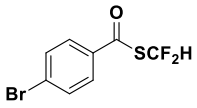
S-(Difluoromethyl)-4-chlorobenzothioate 2d[4]



The general procedure conducted with 4-chlorobenzaldehyde (42.2 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-4-chlorobenzothioate **2d** (45 mg, 67%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 2.9 Hz, 2 H), 7.46 (t, *J* = 55.2 Hz, 1 H); ^{19}F NMR (376 MHz,

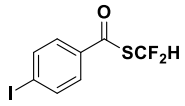
$CDCl_3$) δ -99.30 (d, J = 55.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 141.4, 133.8, 129.4, 128.9, 120.3 (t, J = 271.7 Hz) ppm.

S-(Difluoromethyl)-4-bromobenzothioate 2e[4]



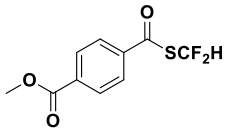
The general procedure conducted with 4-bromobenzaldehyde (55.5 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-4-bromobenzothioate **2e** (58 mg, 72%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.46 (t, J = 55.1 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.30 (d, J = 55.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4, 134.3, 132.4, 130.1, 128.9, 120.3 (t, J = 271.0 Hz) ppm.

S-(Difluoromethyl) 4-iodobenzothioate 2f[4]



The general procedure conducted with 4-iodobenzaldehyde (69.6 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl) 4-iodobenzothioate **2f** (47 mg, 50%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2 H), 7.59 – 7.55 (m, 2 H), 7.46 (t, J = 56.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.29 (d, J = 55.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7, 138.4, 134.8, 128.7, 120.2 (t, J = 271.8 Hz), 103.0 ppm.

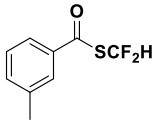
Methyl 4-(((difluoromethyl)thio)carbonyl)benzoate 2g[4]



The general procedure conducted with methyl 4-formylbenzoate (49.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258

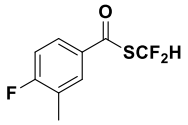
mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave methyl 4-(((difluoromethyl)thio)carbonyl)benzoate **2g** (45 mg, 61%) as a white solid (eluent: petroleum ether: ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2 H), 7.92 (d, *J* = 8.3 Hz, 2 H), 7.46 (t, *J* = 55.1 Hz, 1 H), 3.93 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.39 (d, *J* = 55.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0, 165.7, 138.7, 135.5, 130.2, 127.5, 120.3 (t, *J* = 271.3 Hz), 52.7 ppm.

S-(Difluoromethyl)-3-methylbenzothioate 2h[4]



The general procedure conducted with 3-methylbenzaldehyde (36.1 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-3-methylbenzothioate **2 H** (31 mg, 51%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.68 (m, 2 H), 7.47 (t, *J* = 56.0 Hz, 1 H), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.40 – 7.34 (m, 1 H), 2.41 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.53 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 139.1, 136.7, 135.6, 128.9, 128.0, 124.8, 120.6 (t, *J* = 270.1 Hz), 21.2 ppm.

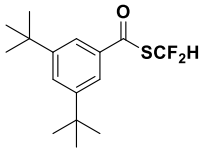
S-(Difluoromethyl)-4-fluoro-3-methylbenzothioate 2i



The general procedure conducted with 4-fluoro-3-methylbenzaldehyde (41.4 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-4-fluoro-3-methylbenzothioate **2i** (58 mg, 88%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 2 H), 7.46 (t, *J* = 55.2 Hz, 1 H), 7.10 (t, *J* = 8.7 Hz, 1 H), 2.32 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.37 (d, *J* = 55.2 Hz), -105.76 (ddd, *J* = 9.1, 6.8, 3.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.9, 166.6, 164.1, 129.5 (dd, *J* = 371.4, 8.3 Hz), 129.1 (dd, *J* = 526.2, 18.2 Hz), 120.5 (t, *J* = 270.4 Hz), 116.0, 115.78 (s), 14.5 (d, *J* = 3.3 Hz)

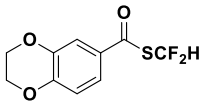
ppm. MS (EI): m/z (%) 137 (M^+-SCF_2H, 100). HRMS (EI) for $C_9H_7F_3OS$ Calcd: 220.0170; Found: 220.0168. IR (KBr): ν_{max} = 1688, 1500, 1252, 1080, 952, 669 cm^{-1}.

S-(Difluoromethyl)-3,5-di-*tert*-butylbenzothioate 2j



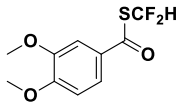
The general procedure conducted with 3,5-di-tert-butylbenzaldehyde (65.5 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-3,5-di-*tert*-butylbenzothioate **2j** (82 mg, 91%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 200:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 3 H), 7.49 (t, *J* = 55.3 Hz, 1 H), 1.35 (s, 18 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.53 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 152.1, 135.4, 129.2, 121.9, 120.8 (t, *J* = 270.7 Hz), 35.1, 31.3 ppm. MS (EI): m/z (%) 152 (100). HRMS (EI) for $C_{16}H_{22}F_2OS$ Calcd: 300.1359; Found: 300.1362. IR (KBr): ν_{max} = 2965, 1686, 1599, 1365, 1192, 1081, 978, 827, 742, 699 cm^{-1}.

S-(Difluoromethyl)-2,3-dihydrobenzo[b](1,4]dioxine-6-carbothioate 2k



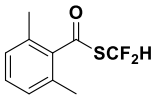
The general procedure conducted with 2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbaldehyde (49.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbothioate **2k** (62 mg, 84%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 56.0 Hz, 1 H), 7.43 – 7.37 (m, 2 H), 7.01 – 6.75 (m, 1 H), 4.26-4.33 (m, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.37 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4, 149.4, 143.6, 129.0 (t, *J* = 2.5 Hz), 121.8, 120.7 (t, *J* = 269.7 Hz), 117.7, 117.0, 64.7, 64.0 ppm. MS (EI): m/z (%) 163 (M^+-SCF_2H, 100). HRMS (EI) for $C_{10}H_8F_2O_3S$ Calcd: 246.0162; Found: 246.0163. IR (KBr): ν_{max} = 1693, 1306, 1047, 824, 799, 672 cm^{-1}. M.P.: 80-81 °C.

S-(Difluoromethyl)-3,4-dimethoxybenzothioate 2l



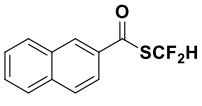
The general procedure conducted with 3,4-dimethoxybenzaldehyde (49.9 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-3,4-dimethoxybenzothioate **2l** (51 mg, 69%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.5, 2.1 Hz, 1 H), 7.46 (t, *J* = 56.0 Hz, 1 H), 7.35 (d, *J* = 2.0 Hz, 1 H), 6.89 (d, *J* = 8.5 Hz, 1 H), 3.94 (s, 3 H), 3.91 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.29 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6, 154.6, 149.2, 128.4, 122.6, 120.7 (t, *J* = 269.7 Hz), 110.4, 109.4, 56.2, 56.1 ppm. MS (EI): m/z (%) 165 (M^+-SCF_2H, 100). HRMS (EI) for $C_{10}H_{10}F_2O_3S$ Calcd: 248.0319; Found: 248.0318. IR (KBr): ν_{max} = 1514, 1270, 1077, 763, 669 cm^{-1}. M.P.: 60-61 °C

S-(Difluoromethyl)-2,6-dimethylbenzothioate 2m



The general procedure conducted with 2,6-dimethylbenzaldehyde (40.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-2,6-dimethylbenzothioate **2m** (58 mg, 90%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 55.1 Hz, 1 H), 7.21-7.25 (m, 1 H), 7.04 (d, *J* = 7.7 Hz, 2 H), 2.34 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.42 (d, *J* = 55.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 138.7, 133.7, 130.5, 128.0, 120.0 (t, *J* = 271.7 Hz), 19.0 ppm. MS (EI): m/z (%) 152 (100). HRMS (EI) for $C_{10}H_{10}F_2OS$ Calcd: 216.0420; Found: 216.0426. IR (KBr): ν_{max} = 1701, 1193, 1080, 883, 789, 757, 669 cm^{-1}.

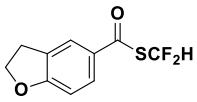
S-(Difluoromethyl)-naphthalene-2-carbothioate 2n[4]



The general procedure conducted with 2-naphthaldehyde (46.9 mg, 0.300 mmol), S-

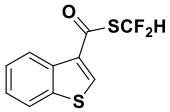
(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-naphthalene-2-carbothioate **2n** (60 mg, 84%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 7.95 (d, *J* = 8.1 Hz, 1 H), 7.92 – 7.83 (m, 3 H), 7.67 – 7.56 (m, 2 H), 7.55 (t, *J* = 56.0 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.29 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 136.3, 132.8 (t, *J* = 2.5 Hz), 132.2, 129.7, 129.4, 129.0, 127.9, 127.4, 122.6, 120.6 (t, *J* = 270.2 Hz) ppm.

S-(Difluoromethyl)-2,3-dihydrobenzofuran-5-carbothioate 2o



The general procedure conducted with 2,3-dihydrobenzofuran-5-carbaldehyde (44.5 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-2,3-dihydrobenzofuran-5-carbothioate **2o** (52 mg, 75%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 2 H), 7.46 (t, *J* = 55.4 Hz, 1 H), 6.82 (d, *J* = 8.2 Hz, 1 H), 4.69 (t, *J* = 8.8 Hz, 2 H), 3.26 (t, *J* = 8.8 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.30 (d, *J* = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.3, 165.9, 130.0, 128.6, 128.4, 125.0, 120.9 (t, *J* = 269.4 Hz), 109.7, 72.6, 28.8 ppm. MS (EI): m/z (%) 147 (M^+-SCF_2H, 100). HRMS (EI) for $C_{10}H_8F_2O_2S$ Calcd: 230.0213; Found: 230.0218. IR (KBr): ν_{max} = 2129, 1675, 1606, 1248, 1073, 936, 602 cm^{-1}.

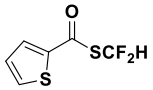
S-(Difluoromethyl)-benzo[b]thiophene-3-carbothioate 2p



The general procedure conducted with benzo[b]thiophene-3-carbaldehyde (48.7 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-benzo[b]thiophene-3-carbothioate **2p** (50 mg, 68%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d,

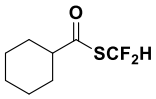
J = 7.9 Hz, 1 H), 8.36 (s, 1 H), 7.94 – 7.79 (m, 1 H), 7.53 (t, J = 55.3 Hz, 1 H), 7.52 – 7.41 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.22 (d, J = 55.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 139.8, 137.9, 135.2, 133.3, 126.4, 126.1, 124.6, 122.5, 120.4 (t, J = 271.7 Hz) ppm. MS (EI): m/z (%) 161 (M^+-SCF_2H, 100). HRMS (EI) for $C_{10}H_6F_2OS_2$ Calcd: 243.9828; Found: 243.9836. IR (KBr): ν_{max} = 1673, 1491, 1459, 1049, 814, 736 cm^{-1}. M.P.: 30-31^{o}C.

S-(Difluoromethyl)-thiophene-2-carbothioate 2q[4]



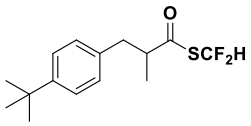
The general procedure conducted with thiophene-2-carbaldehyde (33.6 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-thiophene-2-carbothioate **2q** (23 mg, 40%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 2 H), 7.48 (t, J = 56.0 Hz, 1 H), 7.20 – 7.12 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.80 (d, J = 55.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 140.3, 135.1, 132.9, 128.4, 120.3 (t, J = 271.0 Hz) ppm.

S-(Difluoromethyl)-cyclohexanecarbothioate 2r[4]



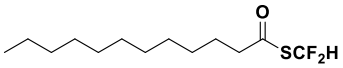
The general procedure conducted with cyclohexanecarbaldehyde (33.6 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl)-cyclohexanecarbothioate **2r** (31 mg, 53%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 200:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 56.0 Hz, 1 H), 2.48 (tt, J = 11.2, 3.5 Hz, 1 H), 2.04 – 1.88 (m, 2 H), 1.87 – 1.72 (m, 2 H), 1.72 – 1.59 (m, 1 H), 1.52 – 1.36 (m, 2 H), 1.34 – 1.12 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.12 (d, J = 55.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 120.3 (t, J = 269.5 Hz), 53.4, 28.9, 25.4, 25.2 ppm.

S-(Difluoromethyl) 3-(4-(*tert*-butyl)phenyl)-2-methylpropanethioate 2s



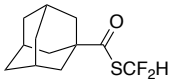
The general procedure conducted with 3-(4-(*tert*-butyl)phenyl)-2-methylpropanal (61.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl) 3-(4-(*tert*-butyl)phenyl)-2-methylpropanethioate **2s** (73 mg, 85%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 200:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 56.0 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 3.09 - 3.04 (m, 1 H), 2.92 - 2.86 (m, 1 H), 2.67 - 2.62 (m, 1 H), 1.30 (s, 9 H), 1.20 (d, *J* = 6.9 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.59 – -110.53 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 149.9, 135.0, 128.9, 125.7, 120.4 (t, *J* = 270.1 Hz), 51.6, 38.9, 34.7, 31.6, 16.8 ppm. MS (EI): m/z (%) 147 (100). HRMS (EI) for $C_{15}H_{20}F_2OS$ Calcd: 286.1203; Found: 286.1197. IR (KBr): ν_{max}= 2965, 1716, 1457, 1294, 1083, 954, 787, 567 cm^{-1}.

S-(Difluoromethyl) dodecanethioate 2t[4]



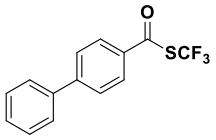
The general procedure conducted with dodecanal (55.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl) dodecanethioate **2t** (55 mg, 69%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 200:1). ^{1}H NMR (400 MHz, CDCl3) δ 7.28 (t, *J* = 55.1 Hz, 1 H), 2.60 (t, *J* = 7.4 Hz, 2 H), 1.97 – 1.59 (m, 2 H), 1.28 - 1.24 (m, 16 H), 0.86 (t, J = 6.7 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.05 (d, *J* = 55.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 120.4 (t, *J* = 269.8 Hz), 45.2 (t, *J* = 2.2 Hz), 32.1, 29.8, 29.8, 29.6, 29.5, 29.4, 29.0, 25.1, 23.0, 14.3 ppm.

S-(Difluoromethyl) (3r,5r,7r)-adamantane-1-carbothioate 2u[4]



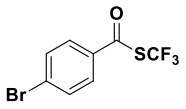
The general procedure conducted with (3r,5r,7r)-adamantane-1-carbaldehyde (49.3 mg, 0.300 mmol), S-(difluoromethyl)benzenesulfonothionate (101 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(difluoromethyl) (3r,5r,7r)-adamantane-1-carbothioate **2u** (52 mg, 71%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 200:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 55.5 Hz, 1 H), 2.07 (s, 3 H), 1.90 - 1.85 (m, 6 H), 1.76 - 1.67 (m, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.01 (d, *J* = 55.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 120.6 (t, *J* = 269.1 Hz), 49.6, 38.7, 36.2, 27.9 ppm.

S-(Trifluoromethyl)(1,1'-biphenyl)-4-carbothioate 3a



The general procedure conducted with (1,1'-biphenyl)-4-carbaldehyde (54.7 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)(1,1'-biphenyl)-4-carbothioate **3a** (75 mg, 89%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2 H), 7.77 – 7.67 (m, 2 H), 7.65 – 7.57 (m, 2 H), 7.54 – 7.38 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.52 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 147.9, 139.2, 133.8, 129.1, 128.8, 128.3,128.1 (q, *J* = 311.1 Hz), 127.8, 127.3 ppm. MS (EI): m/z (%) 181 (M^+-SCF_3, 100). HRMS (EI) for $C_{14}H_9F_3OS$ Calcd: 282.0326; Found: 282.0331. IR (KBr): ν_{max} = 1704, 1600, 1404, 1223, 1152, 891, 647 cm^{-1}. M.P.: 68-70 ^{o}C.

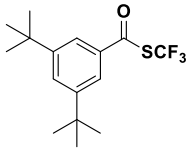
S-(Trifluoromethyl)-4-bromobenzothioate 3b



The general procedure conducted with 4-bromobenzaldehyde (55.5 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)-4-bromobenzothioate **3b** (60 mg, 70%) as a white solid (eluent: petroleum ether: ethyl

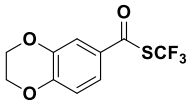
acetate = 100:1), M.P.: 55-56°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2 H), 7.64 (d, *J* = 8.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.58 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.5, 133.8, 132.6, 130.5, 129.0, 127.8 (q, *J* = 311.1 Hz) ppm. MS (EI): m/z (%) 183 (M^+-SCF_3, 100). HRMS (EI) for $C_8H_4BrF_3OS$ Calcd: 283.9118; Found: 283.9124. IR (KBr): ν_{max} = 1701, 1582, 1152, 1103, 905, 636 cm^{-1}.

S-(Trifluoromethyl)-3,5-di-*tert*-butylbenzothioate 3c



The general procedure conducted with 3,5-di-*tert*-butylbenzaldehyde (65.5 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)-3,5-di-*tert*-butylbenzothioate **3c** (91 mg, 95%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1 H), 7.69-7.67 (m, 2 H), 1.34 (s, 18 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.78 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 152.3, 134.9, 129.5, 128.2 (q, *J* = 310.1 Hz), 121.9, 35.1, 31.2 ppm. MS (EI): m/z (%) 217 (M^+-SCF_3, 100). HRMS (EI) for $C_{16}H_{21}F_3OS$ Calcd: 318.1265; Found: 318.1252. IR (KBr): ν_{max} = 2966, 1722, 1365, 1108, 972 736 cm^{-1}.

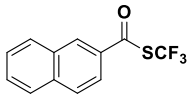
S-(Trifluoromethyl)-2,3-dihydrobenzo[*b*](1,4]dioxine-6-carbothioate 3d



The general procedure conducted with ,3-dihydrobenzo[*b*](1,4)dioxine-6-carbaldehyde (49.3 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)-2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbothioate **3d** (76 mg, 96%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2 H), 7.00 – 6.84 (m, 1 H), 4.40 – 4.18 (m, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.61 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.4, 149.8, 143.8, 128.5, 128.2 (q, *J* = 310.1 Hz), 121.9, 117.9, 117.1, 64.8, 64.1 ppm. MS (EI):

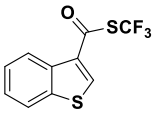
m/z (%) 163 (M^+-SCF_3, 100). HRMS (EI) for $C_{10}H_7F_3O_3S$ Calcd: 264.0068; Found: 264.0061. IR (KBr): ν_{max} = 1705, 1508, 1299, 1144, 804 cm^{-1}. M.P.: 51-53°C.

S-(Trifluoromethyl)-naphthalene-2-carbothioate 3e



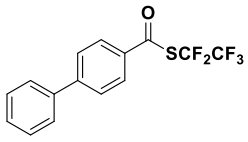
The general procedure conducted with 2-naphthaldehyde (46.9 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)-naphthalene-2-carbothioate **3e** (67 mg, 87%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1 H), 7.94 (d, *J* = 7.9 Hz, 1 H), 7.88 (t, *J* = 8.5 Hz, 2 H), 7.84-7.81 (m, 1 H), 7.69 – 7.62 (m, 1 H), 7.62 – 7.55 (m, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.54 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.2, 136.4, 132.4, 132.3, 129.9, 129.8, 129.6, 129.3, 128.2 (q, *J* = 315.1 Hz), 128.0, 127.6, 122.6 ppm. MS (EI): m/z (%) 155 (M^+-SCF_3, 100). HRMS (EI) for $C_{12\ H7}F_3OS$ Calcd: 256.0170; Found: 256.0177. IR (KBr): ν_{max} = 1696, 1140, 822, 751 cm^{-1}. M.P.: 47-49 °C.

S-(Trifluoromethyl)-benzo[*b*]thiophene-3-carbothioate 3f



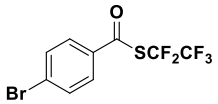
The general procedure conducted with benzo[b]thiophene-3-carbaldehyde (48.7 mg, 0.300 mmol), S-(trifluoromethyl)benzenesulfonothioate (109 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(trifluoromethyl)-benzo[*b*]thiophene-3-carbothioate **3f** (71 mg, 90%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (t, *J* = 9.3 Hz, 1 H), 8.31 (s, 1 H), 7.84 (t, *J* = 9.2 Hz, 1 H), 7.60 – 7.38 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.14 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 139.8, 138.2, 135.1, 132.8, 128.0 (q, *J* = 311.1 Hz), 126.6, 126.4, 124.7, 122.5 ppm. MS (EI): m/z (%) 161 (M^+-SCF_3, 100). HRMS (EI) for $C_{10}H_5F_3OS_2$ Calcd: 261.9734; Found: 261.9732. IR (KBr): ν_{max} = 1704, 1459, 1155, 1089, 1049, 804, 735 cm^{-1}. M.P.: 42-43 °C.

S-(Pentafluoroethyl)(1,1'-biphenyl)-4-carbothioate 4a



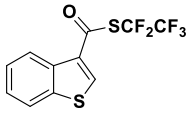
The general procedure conducted with (1,1'-biphenyl)-4-carbaldehyde (54.7 mg, 0.300 mmol), S-(pentafluoroethyl)benzenesulfonothioate (132 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(pentafluoroethyl)(1,1'-biphenyl)-4-carbothioate **4a** (83 mg, 83%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2 H), 7.71 (d, J = 8.3 Hz, 2 H), 7.62 (d, J = 7.2 Hz, 2 H), 7.54 – 7.34 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.47 (t, J = 2.9 Hz), -93.81 (q, J = 3.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.3, 148.0, 139.1, 134.0, 129.1, 128.9, 128.5, 127.8, 127.3, 120.3 (m), 118.2 (m) ppm. MS (EI): m/z (%) 161 (M^+-SC_2F_5, 100). HRMS (EI) for $C_{15}H_9F_5OS$ Calcd: 332.0294; Found: 332.0290. IR (KBr): ν_{max} = 1710, 1601, 1319, 1215, 1104, 966, 883, 767, 645 cm^{-1}. M.P.: 36-38 °C

S-(Pentafluoroethyl)-4-bromobenzothioate 4b



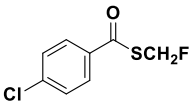
The general procedure conducted with 4-bromobenzaldehyde (55.5 mg, 0.300 mmol), S-(pentafluoroethyl)benzenesulfonothioate (132 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(pentafluoroethyl)-4-bromobenzothioate **4b** (63 mg, 63%) as a white solid (eluent: petroleum ether: ethyl acetate = 200:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2 H), 7.71 – 7.60 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.50 (t, J = 2.9 Hz), -93.85 (q, J = 3.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 129.3, 127.8, 125.8, 124.3, 115.2 (m), 113.3 (m) ppm. MS (EI): m/z (%) 183 (M^+-SC_2F_5, 100). HRMS (EI) for $C_9H_4BrF_5OS$ Calcd: 333.9086; Found: 333.9081. IR (KBr): ν_{max} = 1698, 1582, 1213, 1129, 970, 895, 752, 635 cm^{-1}. M.P.: 47-48 °C.

S-(Pentafluoroethyl)-benzo[*b*]thiophene-3-carbothioate 4c



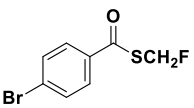
The general procedure conducted with benzo[*b*]thiophene-3-carbaldehyde (48.7 mg, 0.300 mmol), S-(pentafluoroethyl)benzenesulfonothioate (132 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(pentafluoroethyl)-benzo[*b*]thiophene-3-carbothioate **4c** (70 mg, 75%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.9 Hz, 1 H), 8.40 (s, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.64 – 7.41 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.44 (t, *J* = 3.0 Hz), -92.94 (q, *J* = 3.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 139.7, 138.7, 135.1, 132.9, 126.6, 126.4, 124.6, 122.5, 120.1 (m), 118.1 (m) ppm. MS (EI): m/z (%) 161 (M^+-SC_2F_5, 100). HRMS (EI) for $C_{11}H_5F_5OS_2$ Calcd: 311.9702; Found: 311.9704. IR (KBr): ν_{max} = 1708, 1490, 1215, 1096, 960, 799, 732 cm^{-1}.

S-(Monofluoromethyl)-4-chlorobenzothioate 5a



The general procedure conducted with 4-chlorobenzaldehyde (42.2 mg, 0.300 mmol), S-(monofluoromethyl)benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(monofluoromethyl) 4-chlorobenzothioate **5a** (27 mg, 44%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 5.97 (d, *J* = 50.1 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.23 (t, *J* = 50.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 140.8, 134.2, 129.2, 129.0, 80.6 (d, *J* = 216.1 Hz) ppm. MS (EI): m/z (%) 139 (M^+-SCH_2F, 100). HRMS (EI) for C_8H_6ClFOS Calcd: 203.9812; Found: 203.9817. IR (KBr): ν_{max} = 1683, 1587, 1401, 1208, 1091, 907, 844, 639 cm^{-1}.

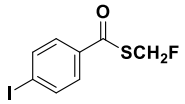
S-(Monofluoromethyl)-4-bromobenzothioate 5b



The general procedure conducted with 4-bromobenzaldehyde (55.5 mg, 0.300 mmol), S-(monofluoromethyl)benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-

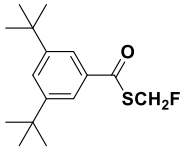
(monofluoromethyl)-4-bromobenzothioate **5b** (46 mg, 61%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 5.98 (d, *J* = 50.1 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.27 (t, *J* = 50.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 134.7, 132.3, 129.6, 129.2, 80.6 (d, *J* = 216.3 Hz) ppm. MS (EI): m/z (%) 183 (M^+-SCH_2F, 100). HRMS (EI) for C_8H_6BrFOS Calcd: 247.9307; Found: 247.9313. IR (KBr): ν_{max} = 1680, 1583, 958, 831, 639 cm^{-1}. M.P.: 69-70 °C.

S-(Monofluoromethyl)-4-iodobenzothioate 5c



The general procedure conducted with 4-iodobenzaldehyde (69.6 mg, 0.300 mmol), S-(monofluoromethyl) benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(monofluoromethyl)-4-iodobenzothioate **5c** (60 mg, 67%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, CDC_3) δ 7.84 (d, *J* = 8.3 Hz, 2 H), 7.66 (d, *J* = 8.3 Hz, 2 H), 5.97 (d, *J* = 50.1 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.29 (t, *J* = 50.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 138.2, 135.2, 128.9, 102.4, 80.5 (d, *J* = 216.2 Hz) ppm. MS (EI): m/z (%) 152 (100). HRMS (EI) for C_8H_6FIOS Calcd: 295.9168; Found: 295.9175. IR (KBr): ν_{max} = 1679, 1577, 959, 828,639 cm^{-1}.

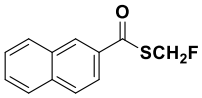
S-(Monofluoromethyl) 3,5-di-*tert*-butylbenzothioate 5d



The general procedure conducted with 3,5-di-tert-butylbenzaldehyde (65.5 mg, 0.300 mmol), S-(monofluoromethyl)benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(monofluoromethyl)-3,5-di-*tert*-butylbenzothioate **5d** (74 mg, 87%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2 H), 7.69 (s, 1 H), 6.00 (d, *J* = 50.3 Hz, 2 H), 1.35 (s, 18 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.23 (t, *J* = 50.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 151.7, 135.6,

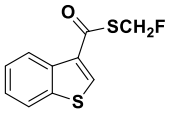
128.6, 122.0, 80.8 (d, J = 214.6 Hz), 35.0, 31.3 ppm. MS (EI): m/z (%) 217 (M^+-SCH_2F, 100). HRMS (EI) for $C_{16}H_{23}FOS$ Calcd: 282.1454; Found: 282.1461. IR (KBr): ν_{max} = 2964, 1686, 1191, 981, 828, 745, 701 cm^{-1}.

S-(Monofluoromethyl)-naphthalene-2-carbothioate 5e



The general procedure conducted with 2-naphthaldehyde (46.9 mg, 0.300 mmol), S-(monofluoromethyl)benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(monofluoromethyl)-naphthalene-2-carbothioate **5e** (50 mg, 75%) as a colorless oil (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1 H), 8.06 – 7.93 (m, 2 H), 7.93 – 7.83 (m, 2 H), 7.59 (m, 2 H), 6.05 (d, J = 50.3 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -196.47 (t, J = 50.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 136.1, 133.2, 132.3, 129.7, 129.0, 128.8, 127.9, 127.2, 123.1, 80.8 (d, J = 215.3 Hz) ppm. MS (EI): m/z (%) 155 (M^+-SCH_2F, 100). HRMS (EI) for $C_{12\ H9}FOS$ Calcd: 220.0358; Found: 220.0359. IR (KBr): ν_{max} = 1680, 1163, 1122, 982, 831, 750 cm^{-1}.

S-(Monofluoromethyl)-benzo[*b*]thiophene-3-carbothioate 5f



The general procedure conducted with benzo[b]thiophene-3-carbaldehyde (48.7 mg, 0.300 mmol), S-(monofluoromethyl)benzenesulfonothioate (93 mg, 0.450 mmol), PIFA (258 mg, 0.600 mmol), $TMSN_3$ (69 mg, 0.600 mmol) in EtOAc (1.0 mL) gave S-(monofluoromethyl)-benzo[*b*]thiophene-3-carbothioate **5f** (52 mg, 76%) as a white solid (eluent: petroleum ether: ethyl acetate = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.2 Hz, 1 H), 8.45 (s, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.52-7.42 (m, 2 H), 6.02 (d, J = 50.4 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.56 (t, J = 50.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 139.8, 137.5, 135.5, 133.7, 126.2, 125.9, 124.8, 122.4, 80.8 (d, J = 215.7 Hz) ppm. MS (EI): m/z (%) 161 (M^+-SCH_2F, 100). HRMS (EI) for $C_{10}H_7FOS_2$ Calcd: 225.9922; Found: 225.9925. IR (KBr): ν_{max} = 3093, 1665, 1492, 1459, 1109, 969, 757 cm^{-1}. M.P.: 59-61 °C.

Reference

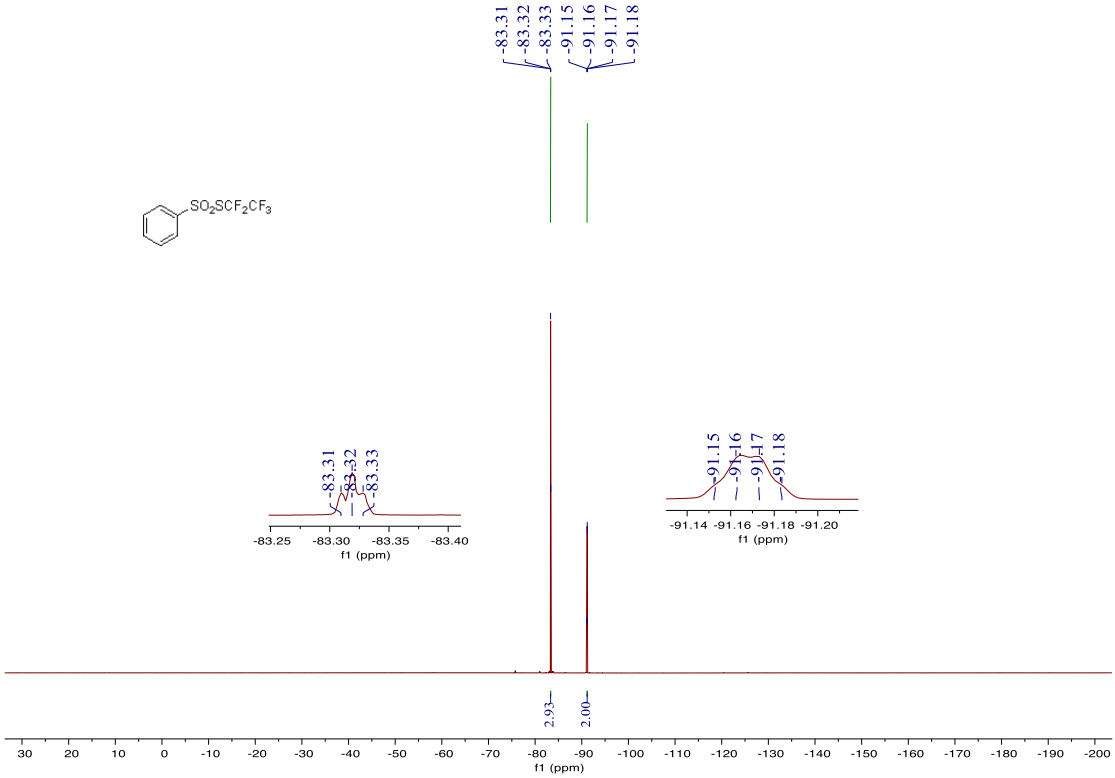
1. Shao, X.-X.; Xu, C.-F.; Lu, L.; Shen, Q. *J. Org. Chem.* **2015**, *80*, 3012

2. Zhu, D.-H.; Shao, X.-X.; Hong, X.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2016**, *55*, 15807.

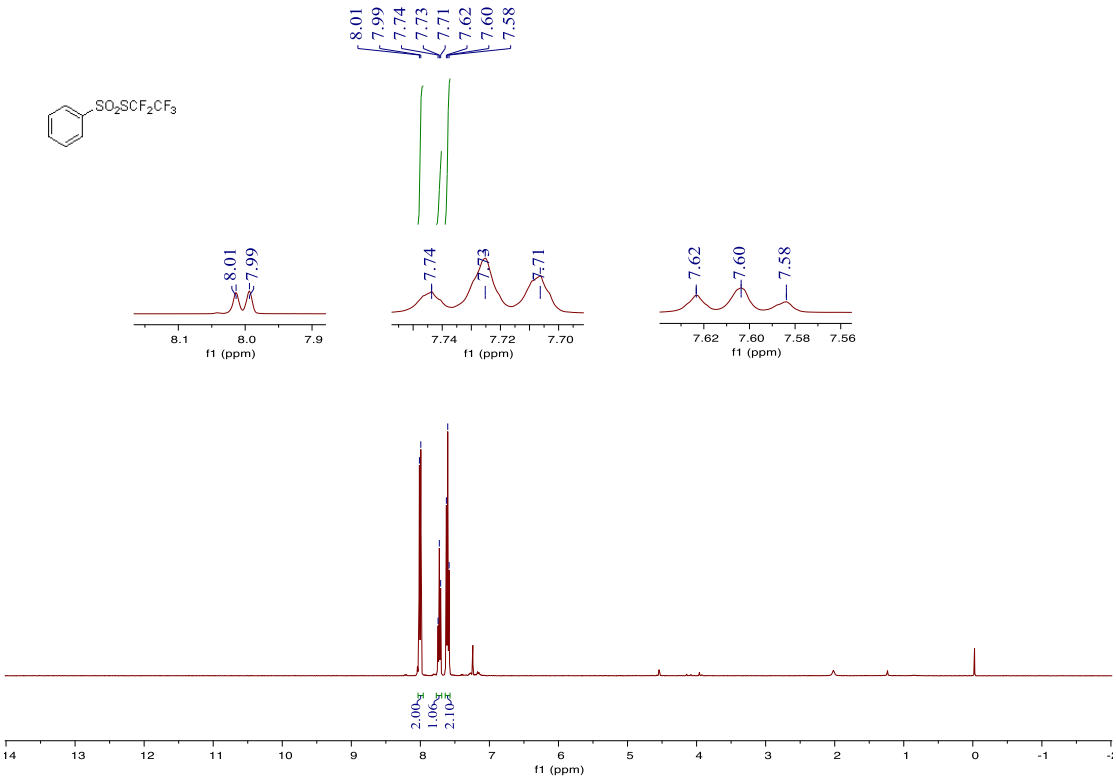
3. Zhao, Q.-C.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2017**, *56*, 11575

4. Guo, S.-H.; Zhang, X.-L.; Pan, G.-F.; Zhu, X.-Q.; Gao, Y.-R.; Wang, Y.-Q. *Angew. Chem. Int. Ed*. **2018**, *57*, 1663 –1667.

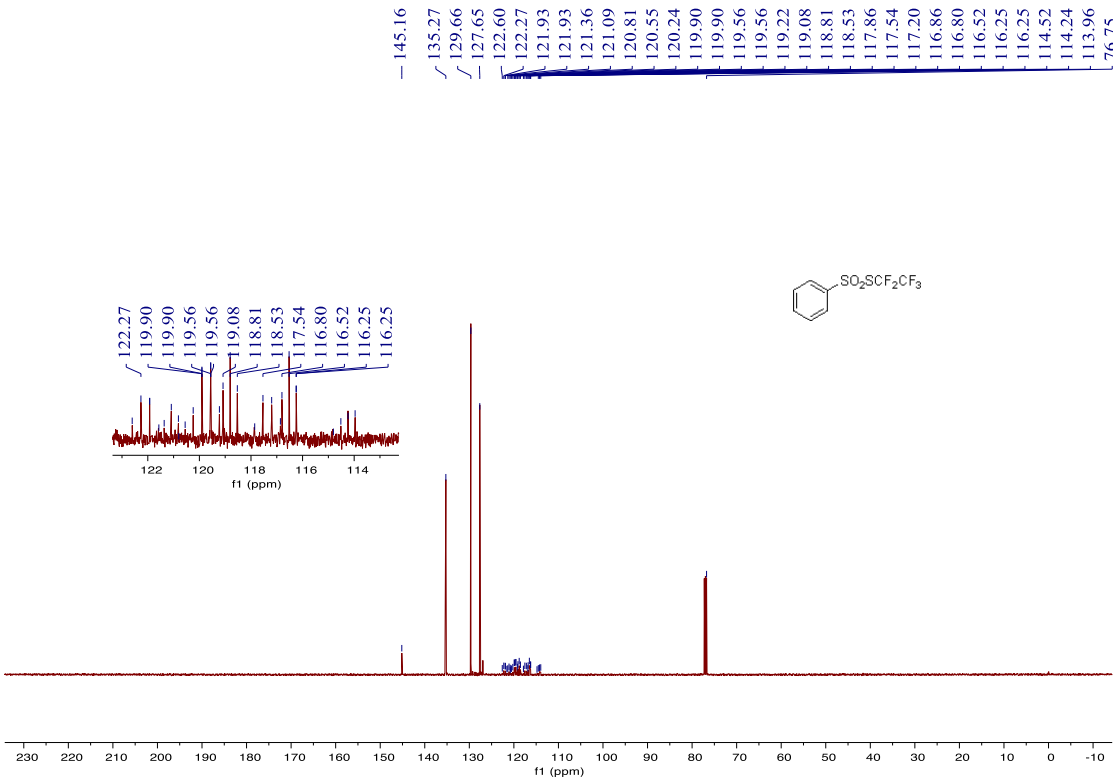
^{19}F NMR spectrum of S-(pentafluoroethyl) benzenesulfonothioate



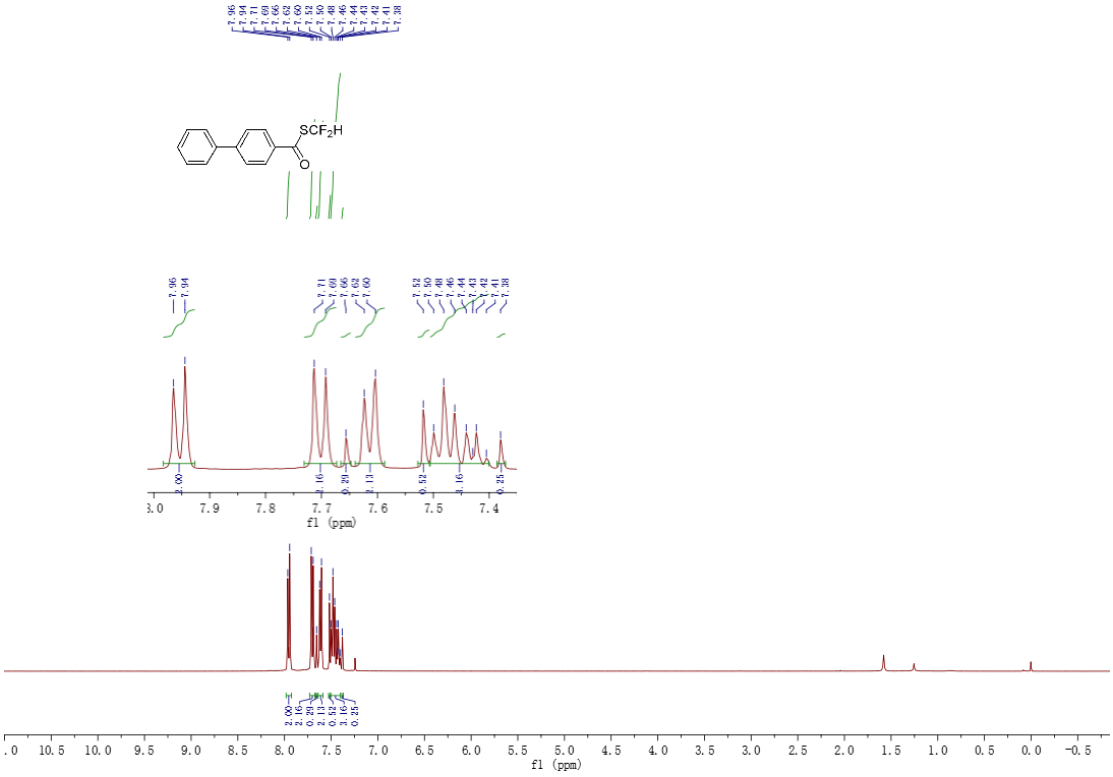
^{1}H NMR spectrum of S-(pentafluoroethyl) benzenesulfonothioate



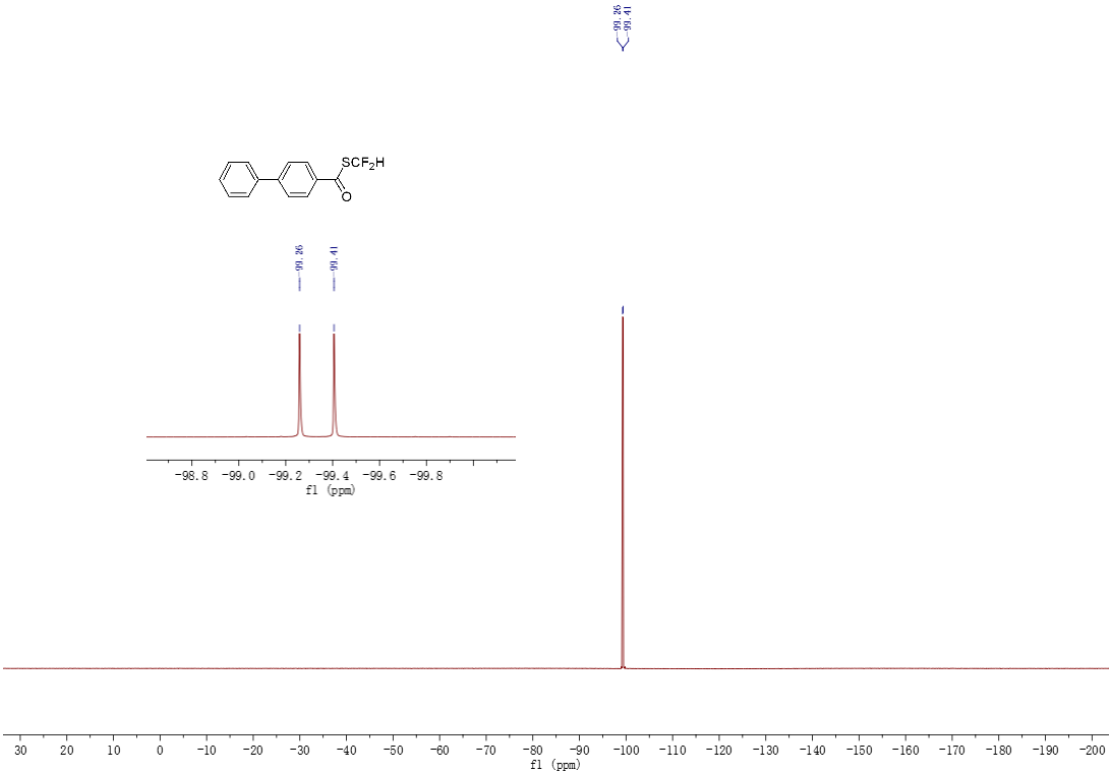
^{13}C NMR spectrum of S-(pentafluoroethyl) benzenesulfonothioate



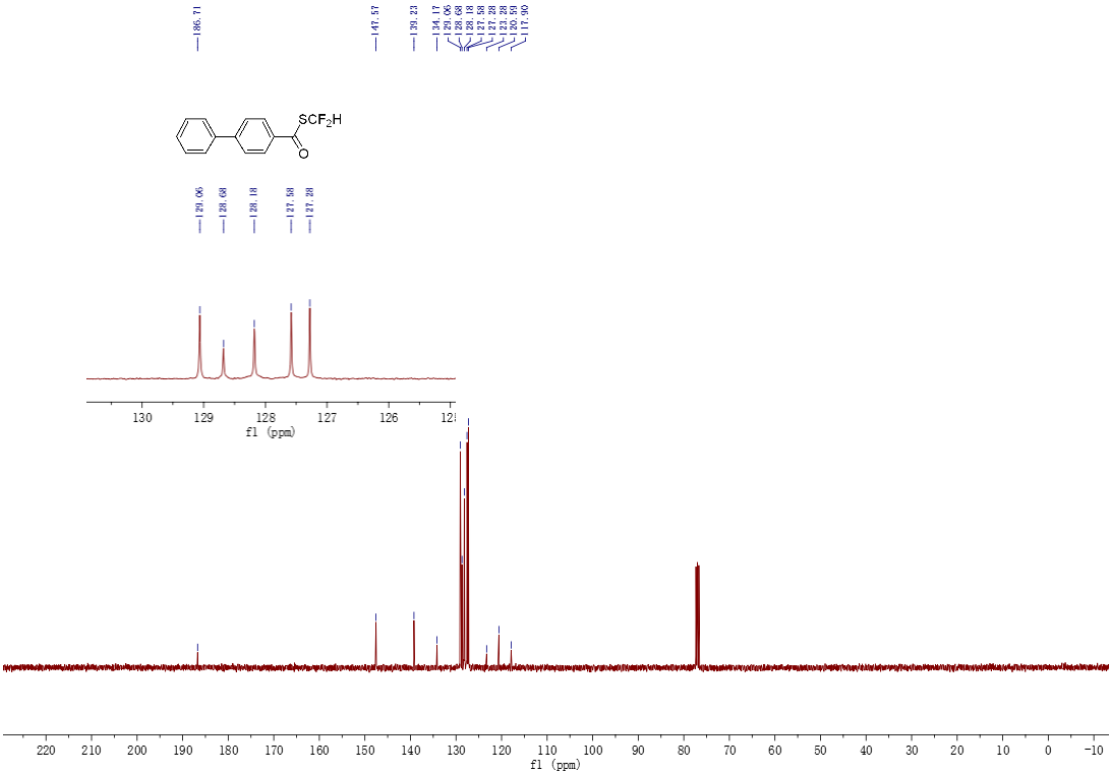
^{1}H NMR spectrum of S-(difluoromethyl)(1,1'-biphenyl)-4-carbothioate 2a



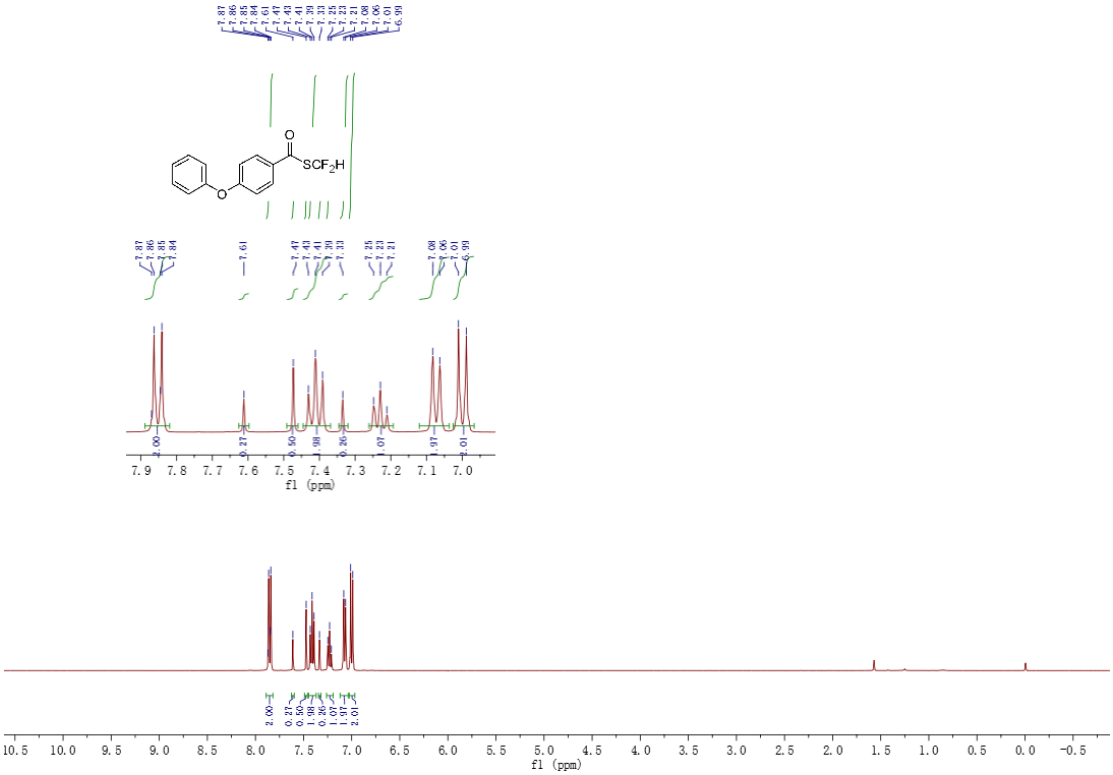
^{19}F NMR spectrum of S-(difluoromethyl)(1,1'-biphenyl)-4-carbothioate 2a



^{13}C NMR spectrum of S-(difluoromethyl)(1,1'-biphenyl)-4-carbothioate 2a



^{1}H NMR spectrum of S-(difluoromethyl)-4-phenoxybenzothioate 2b



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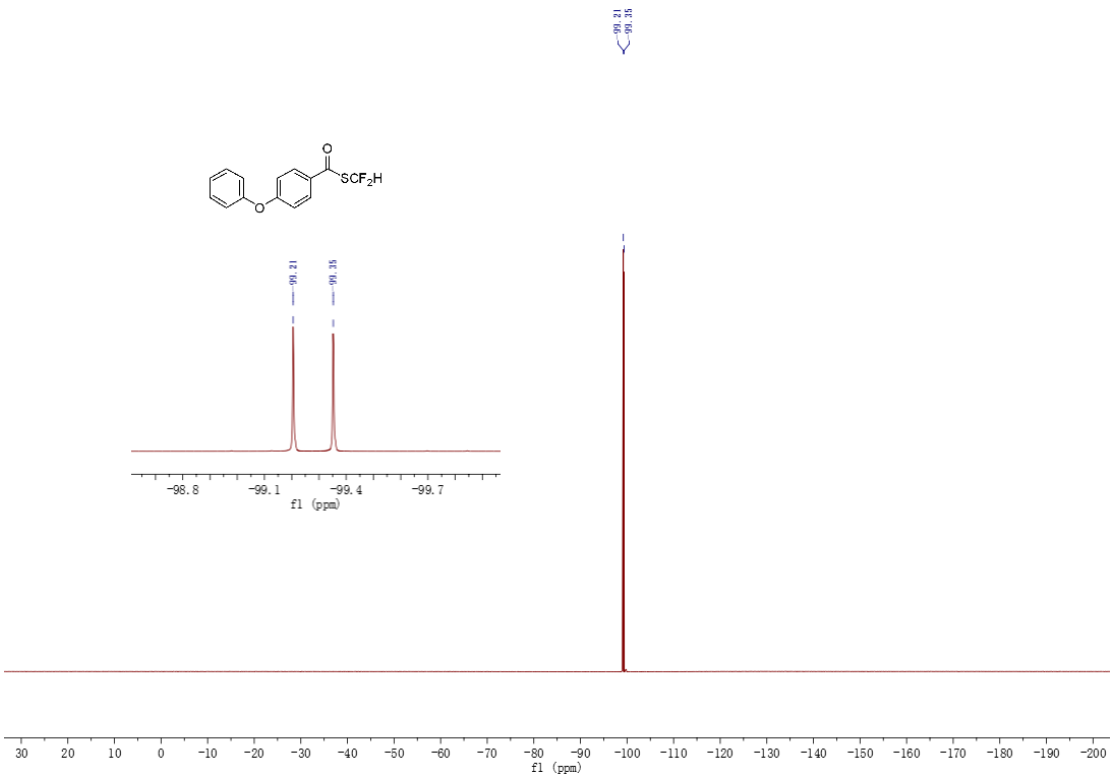

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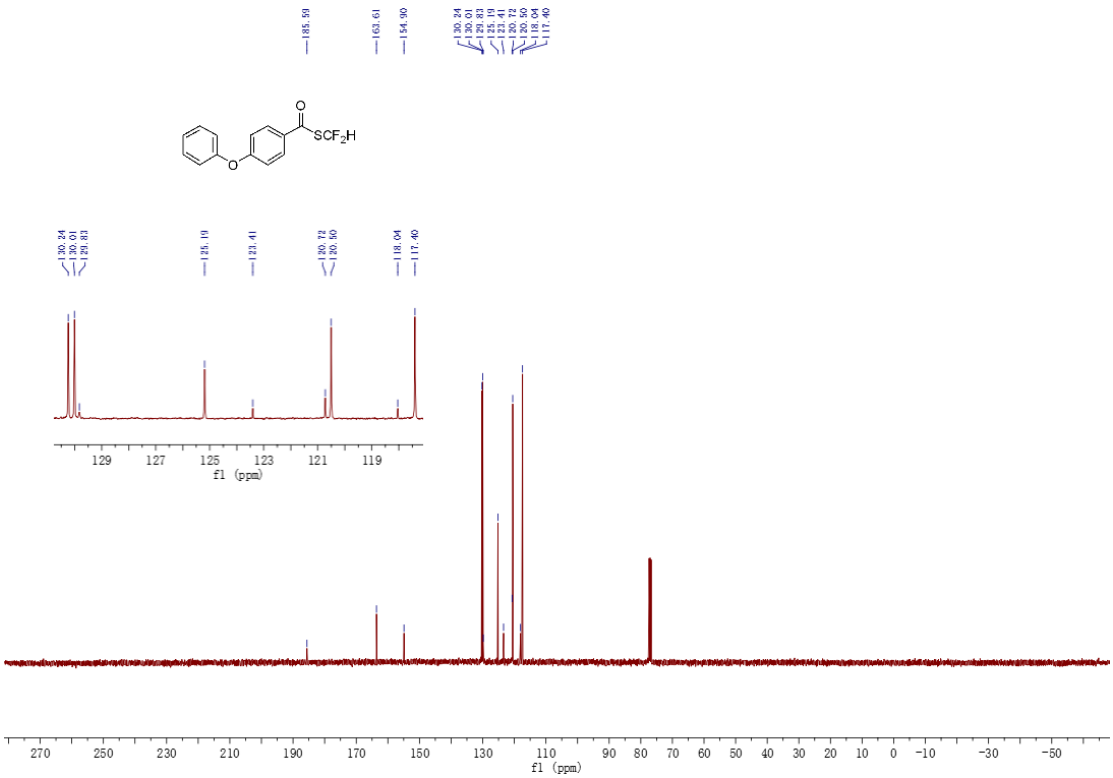
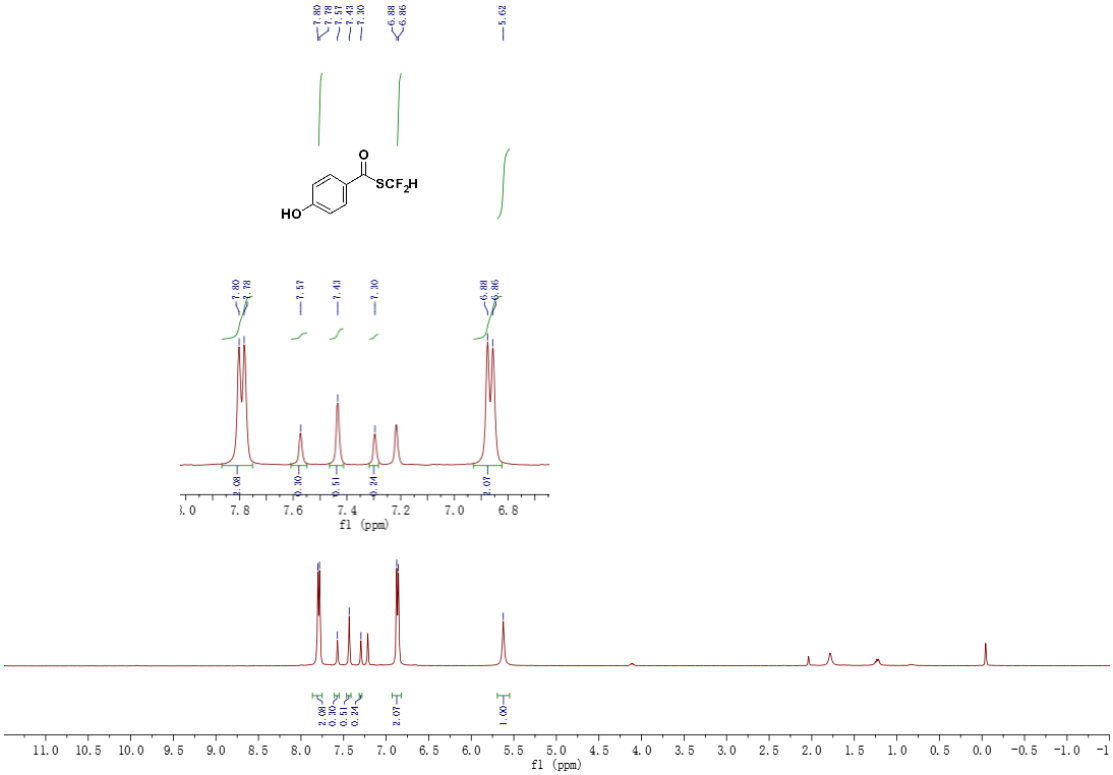
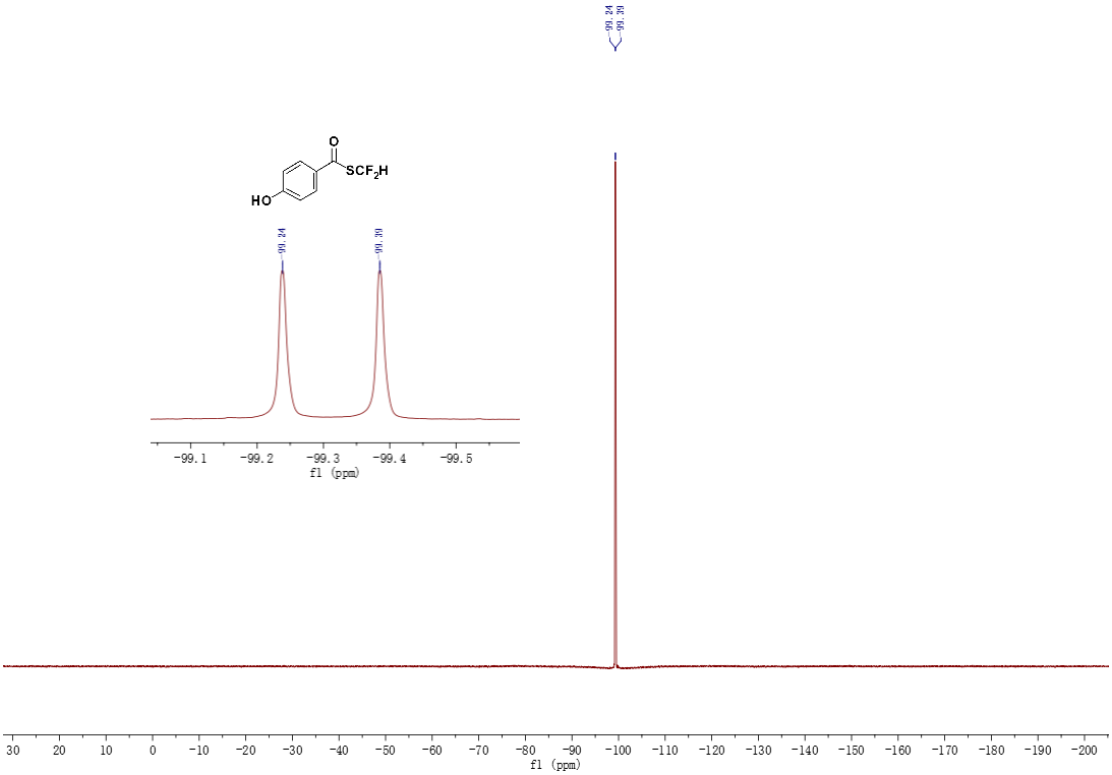


^{1}H NMR spectrum of S-(difluoromethyl)-4-hydroxybenzothioate 2c



^{19}F NMR spectrum of S-(difluoromethyl)-4-hydroxybenzothioate 2c



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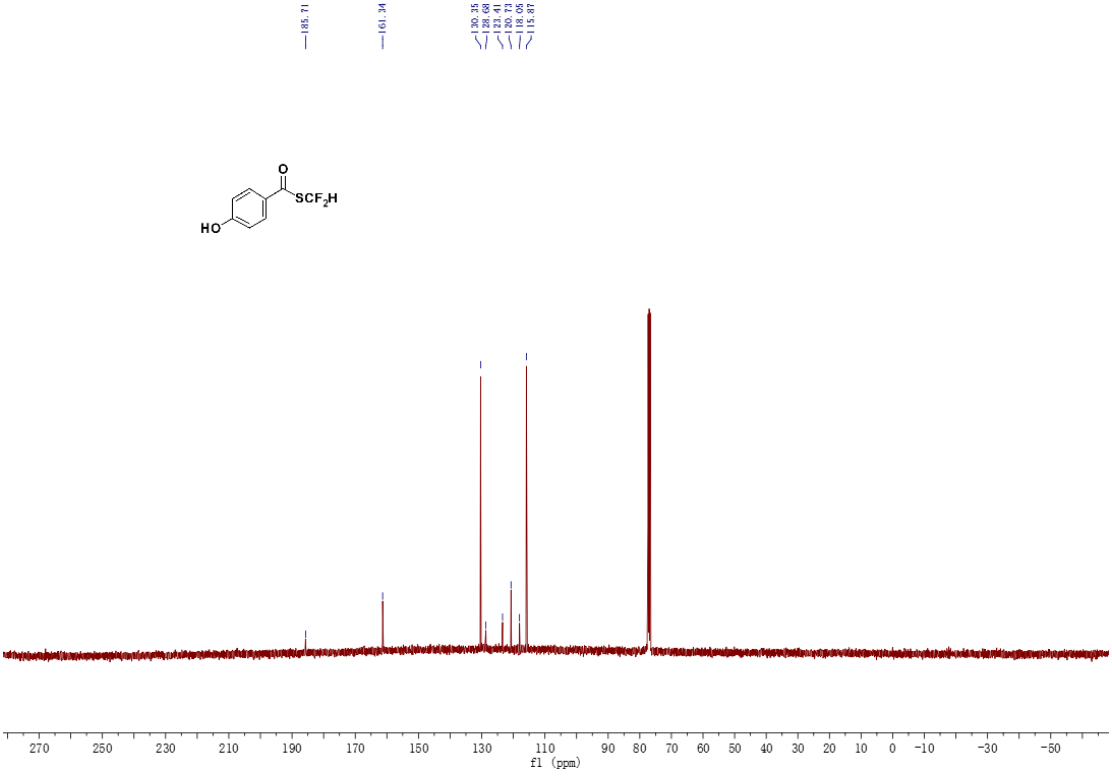
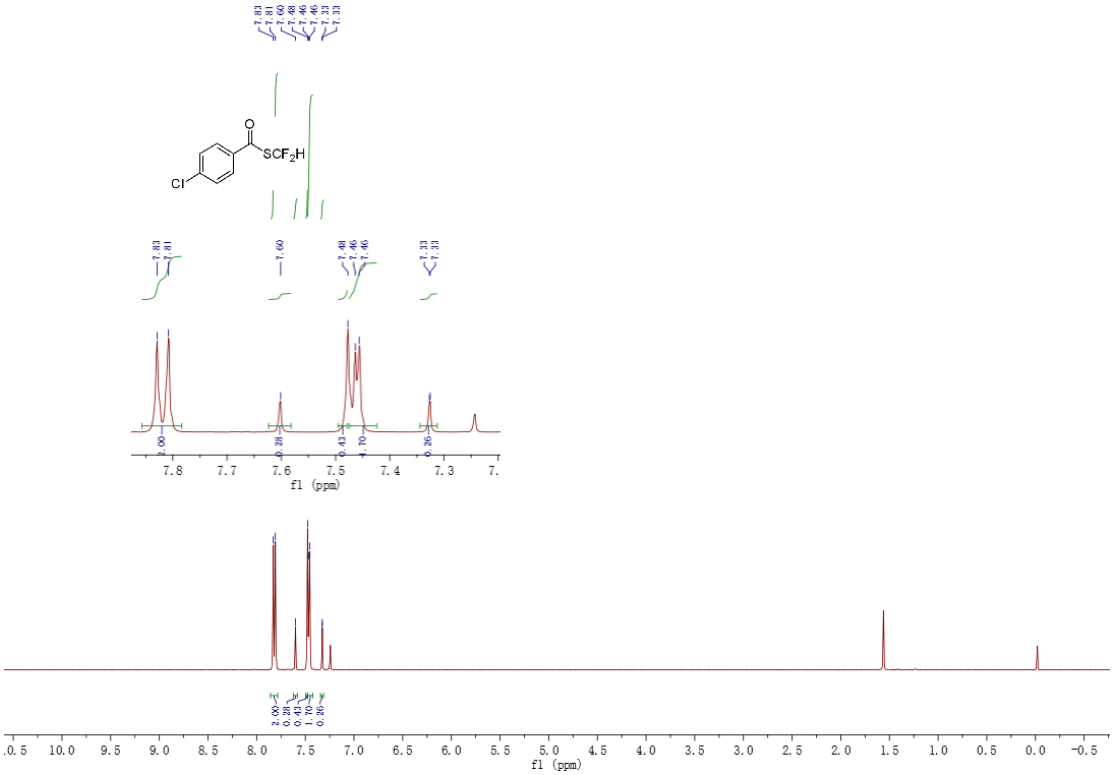
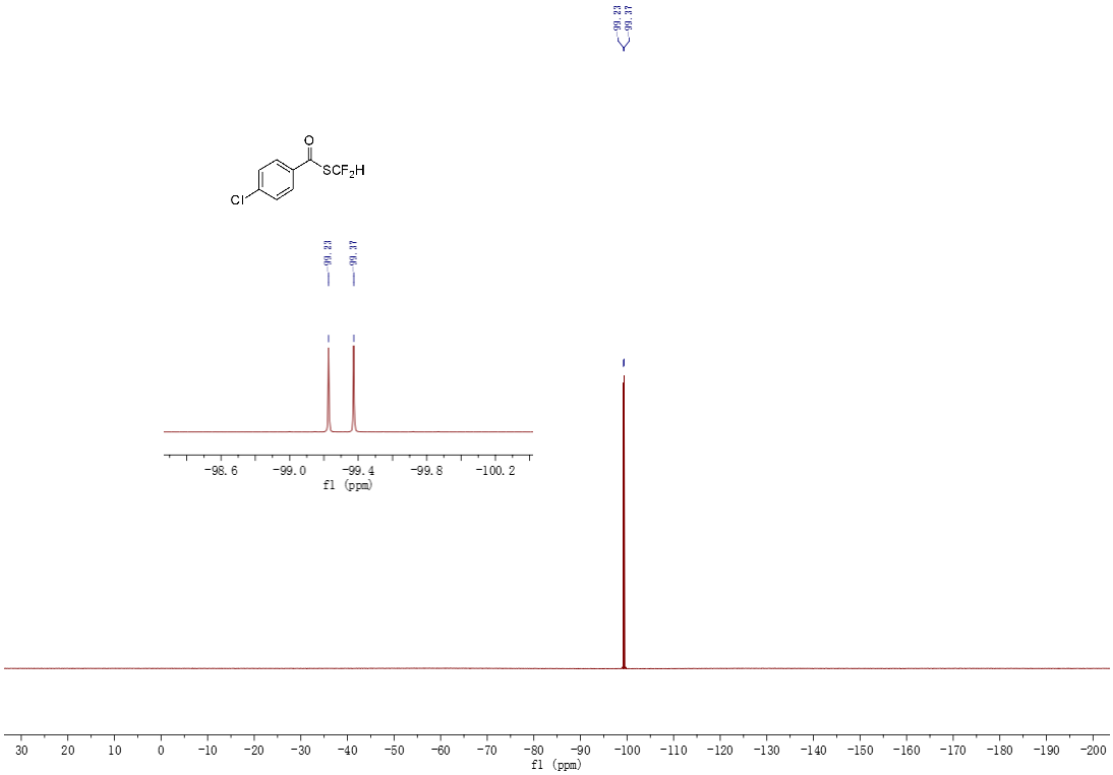


^{1}H NMR spectrum of S-(difluoromethyl)-4-chlorobenzothioate 2d



^{19}F NMR spectrum of S-(difluoromethyl)-4-chlorobenzothioate 2d



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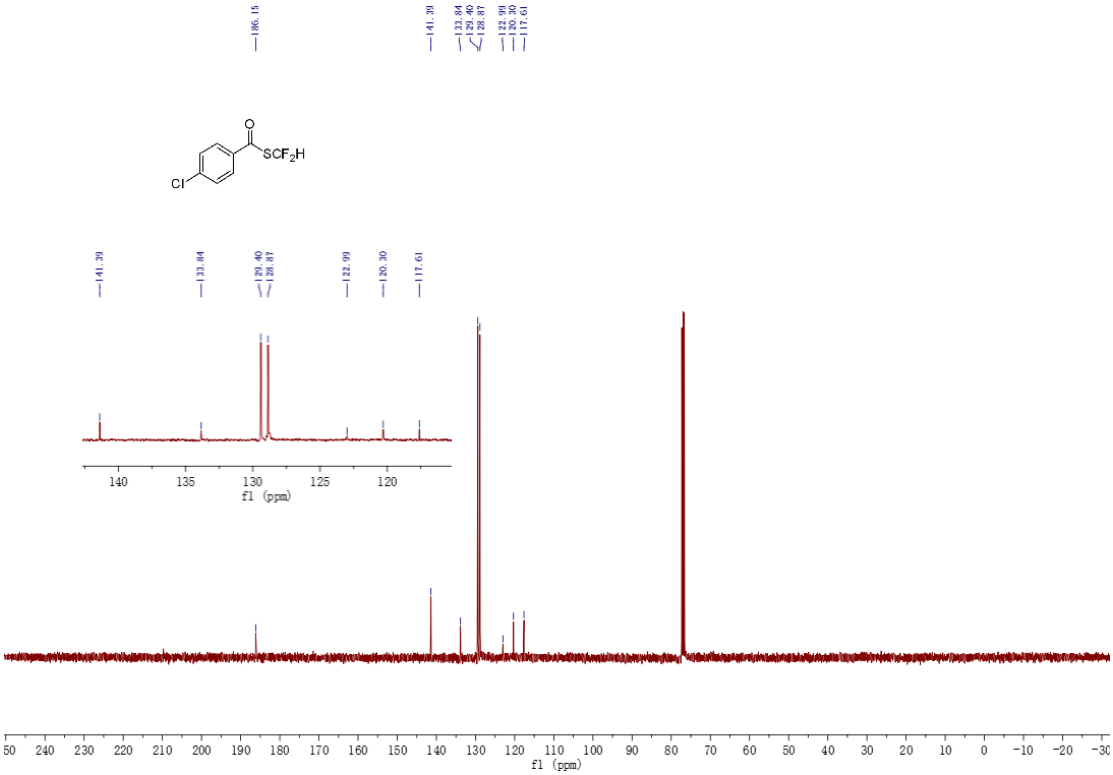
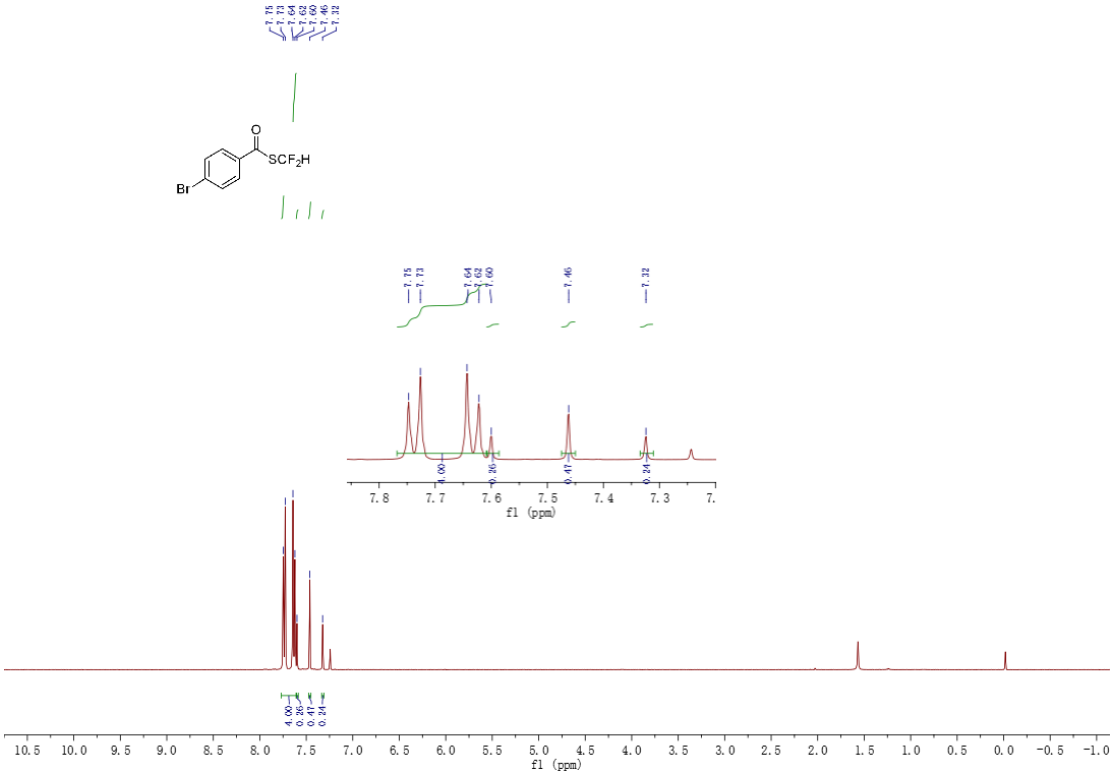
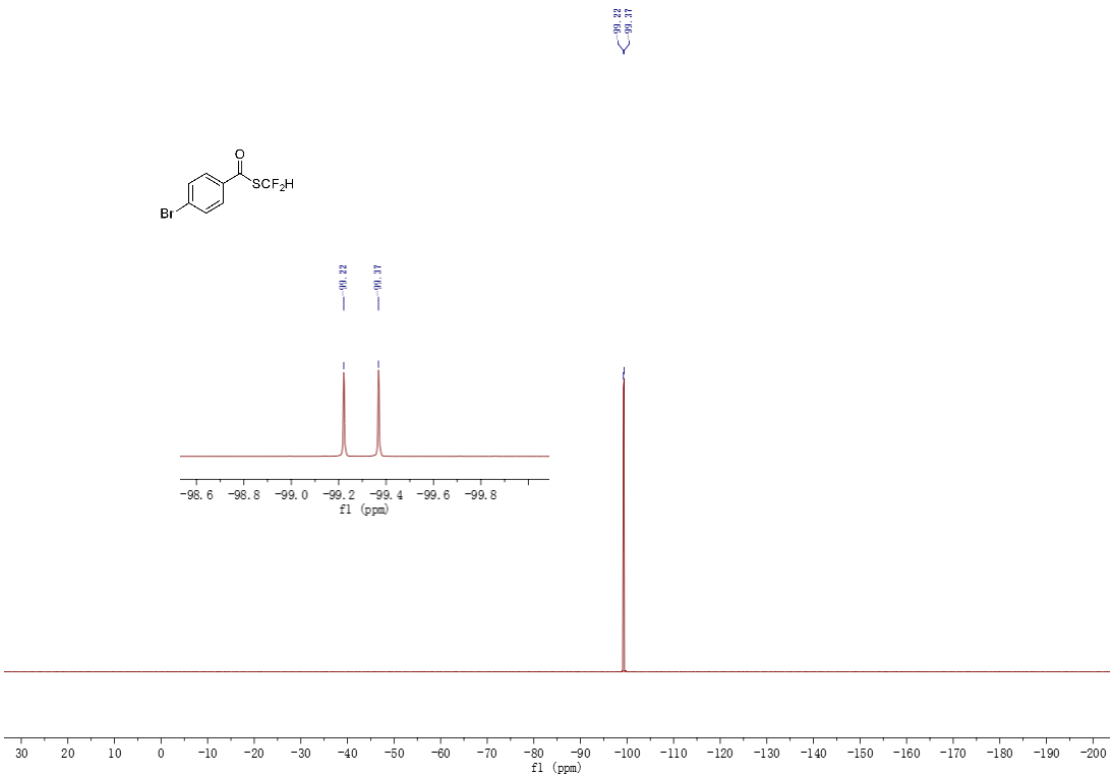


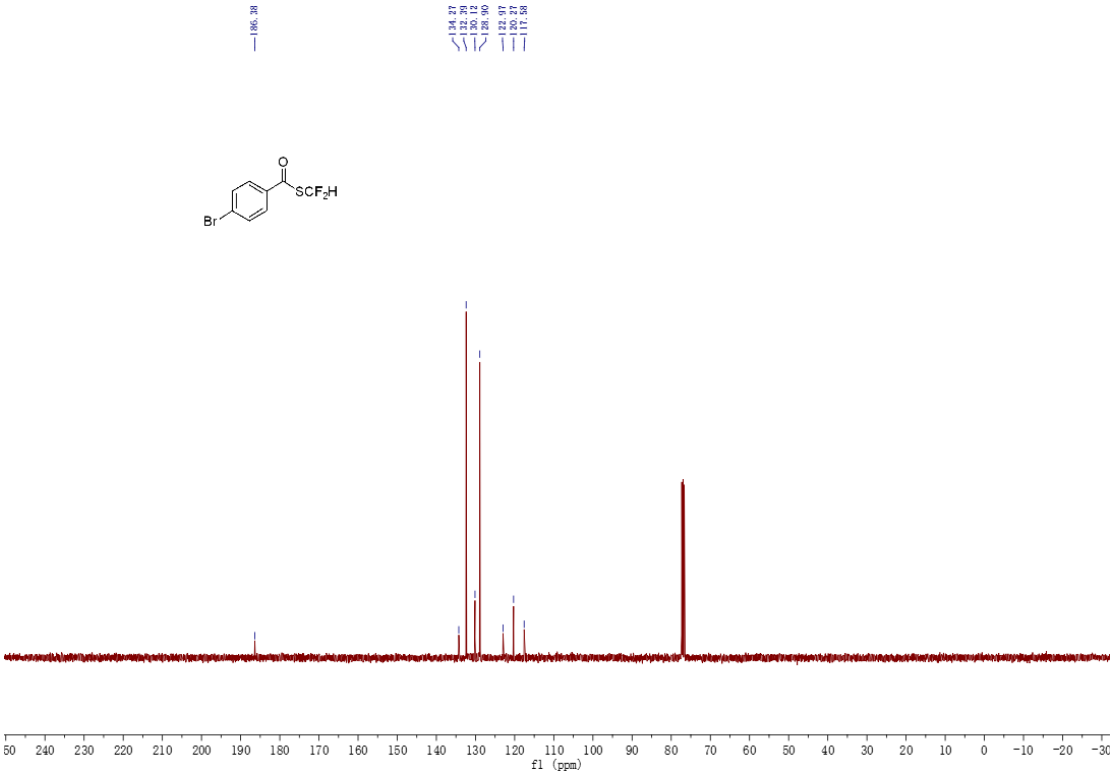
^{1}H NMR spectrum of S-(difluoromethyl)-4-bromobenzothioate 2e



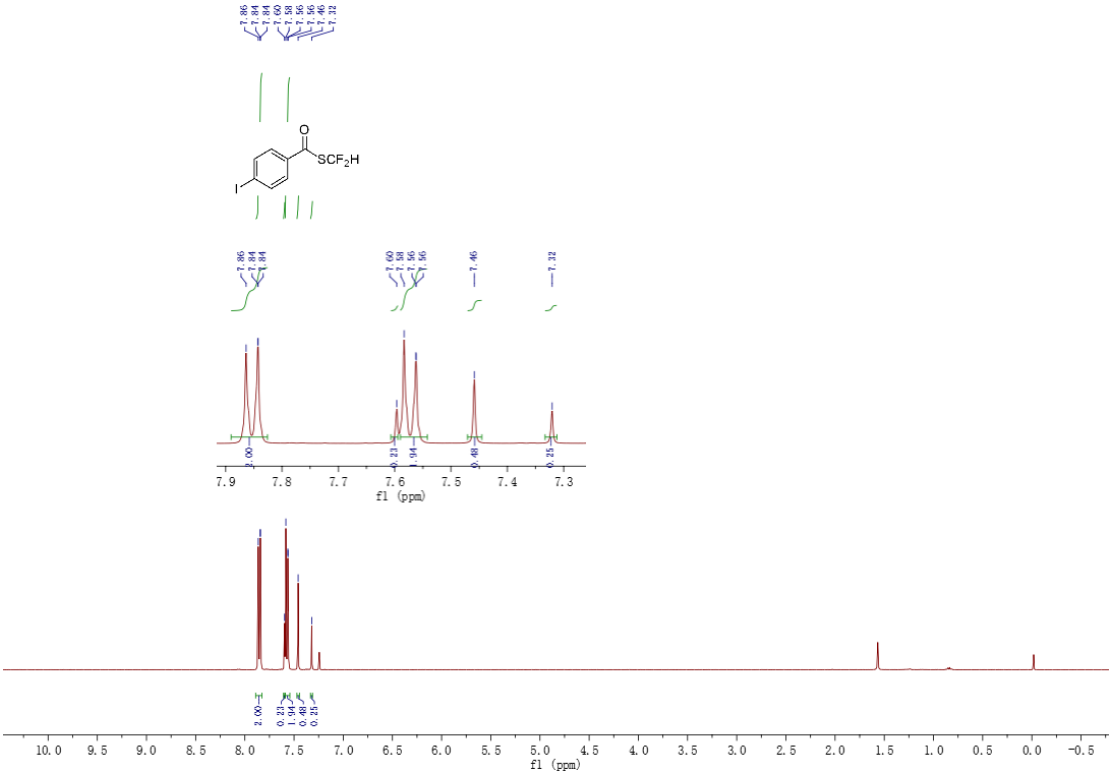
^{19}F NMR spectrum of S-(difluoromethyl)-4-bromobenzothioate 2e



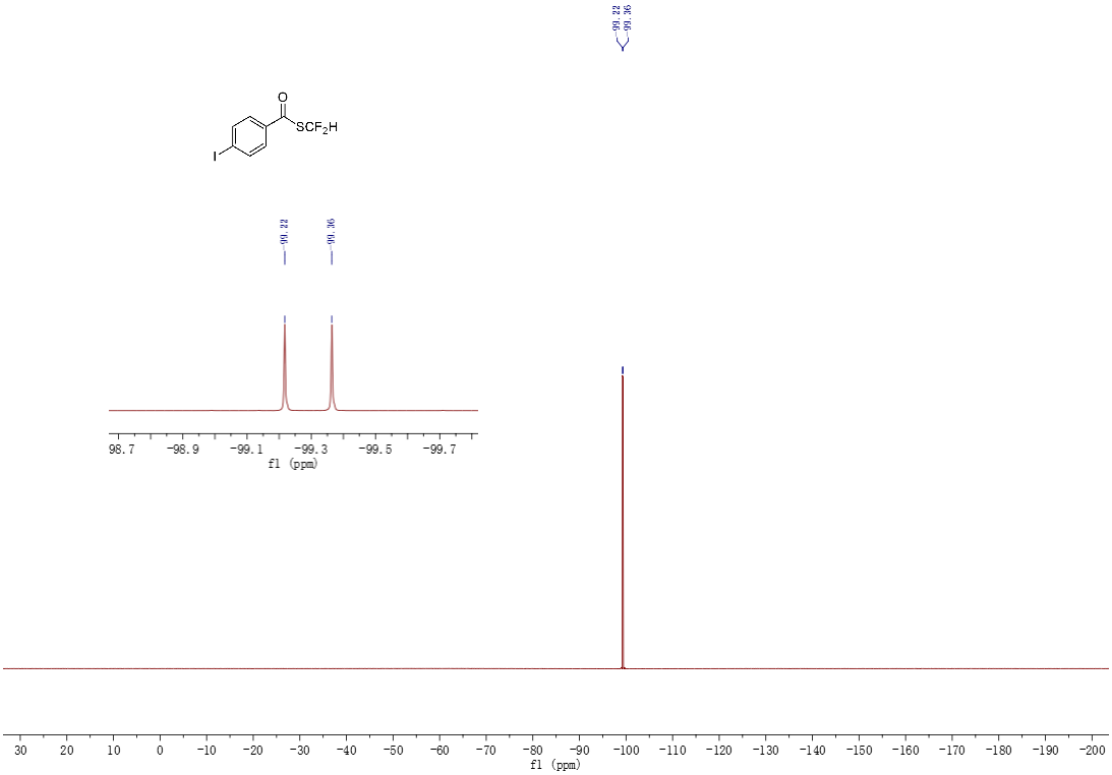
^{13}C NMR spectrum of S-(difluoromethyl)-4-bromobenzothioate 2e



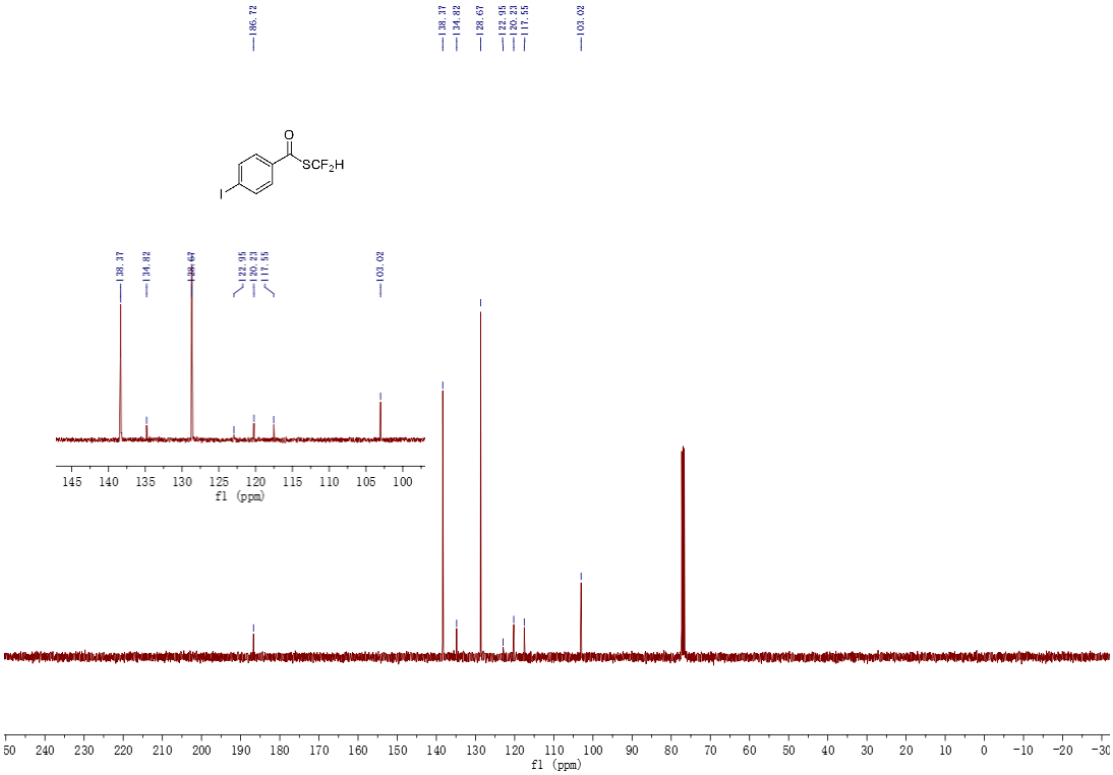
^{1}H NMR spectrum of S-(difluoromethyl)-4-iodobenzothioate 2f



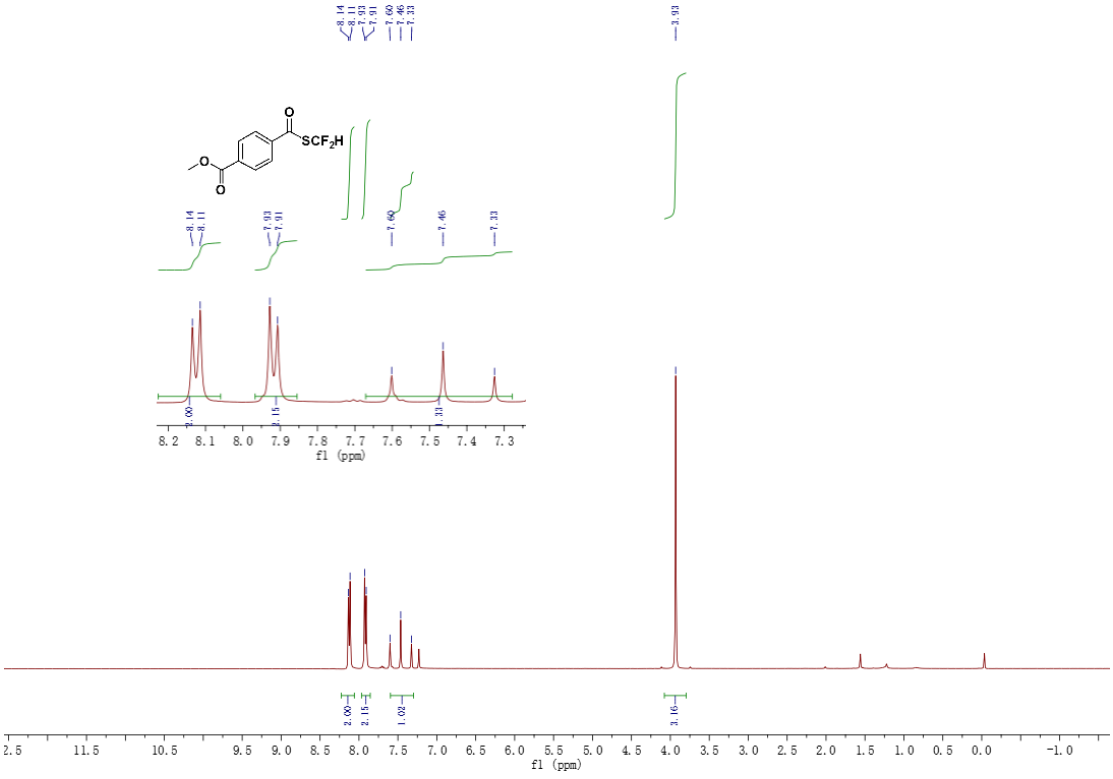
^{19}F NMR spectrum of S-(difluoromethyl)-4-iodobenzothioate 2f



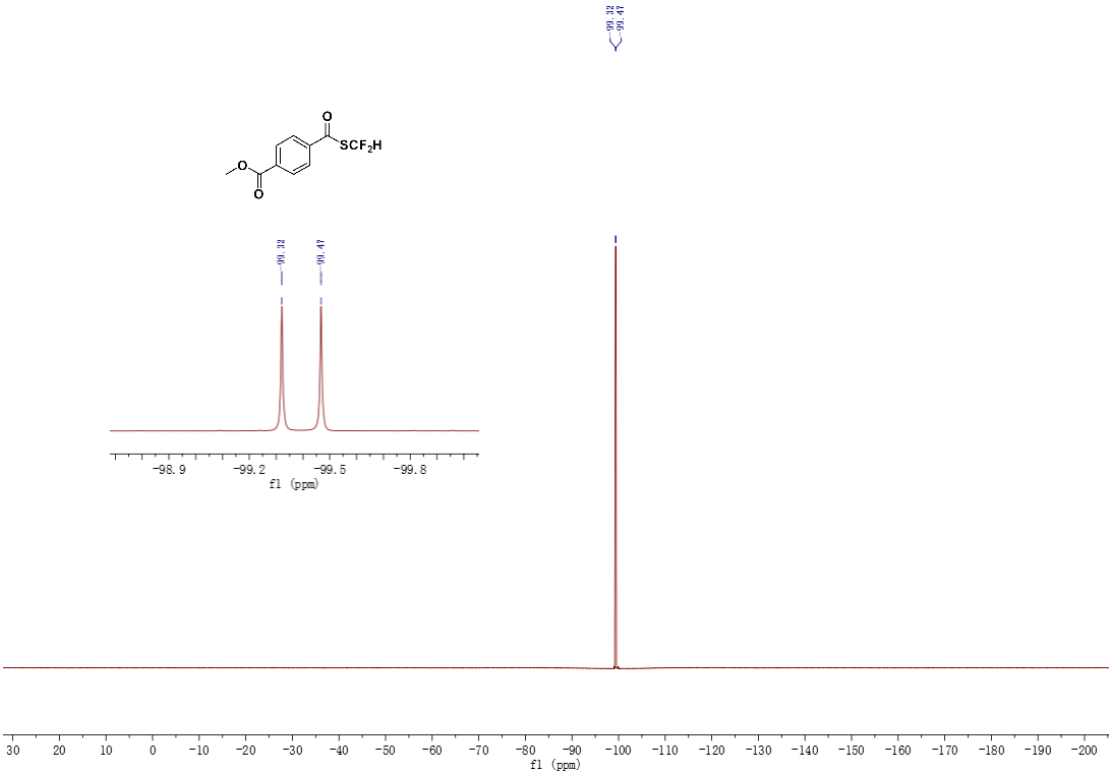
^{13}C NMR spectrum of S-(difluoromethyl)-4-iodobenzothioate 2f



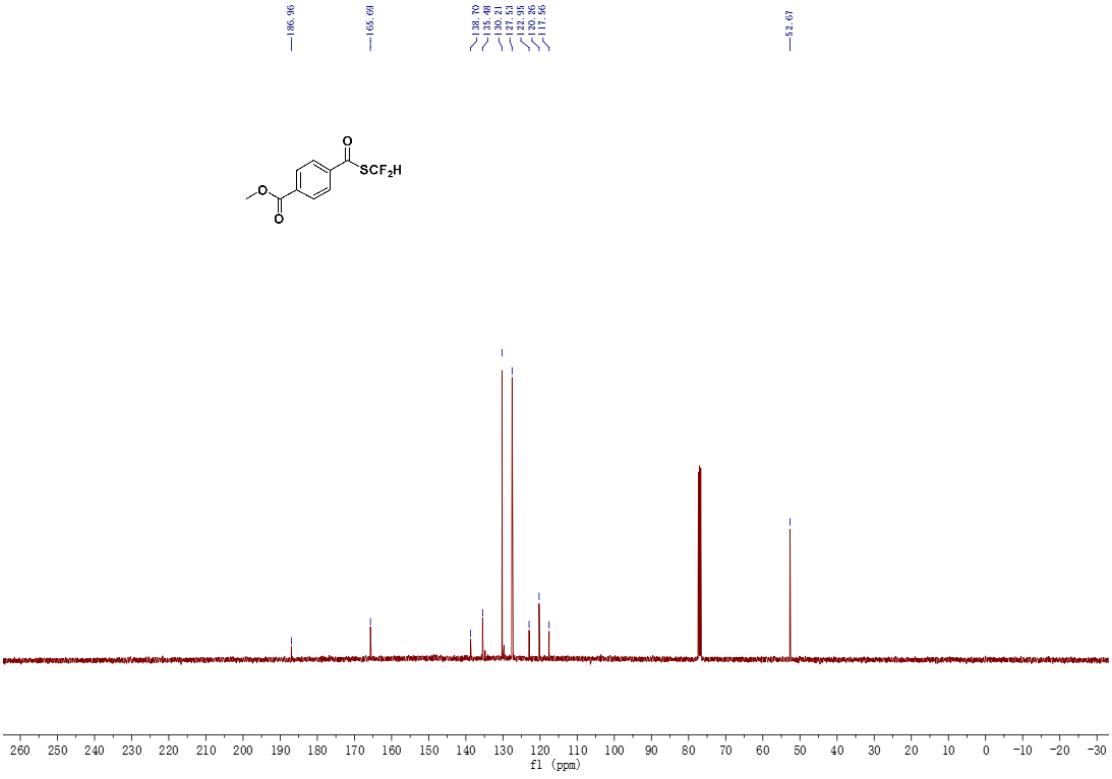
^{1}H NMR spectrum of methyl 4-(((difluoromethyl)thio)carbonyl)benzoate 2g



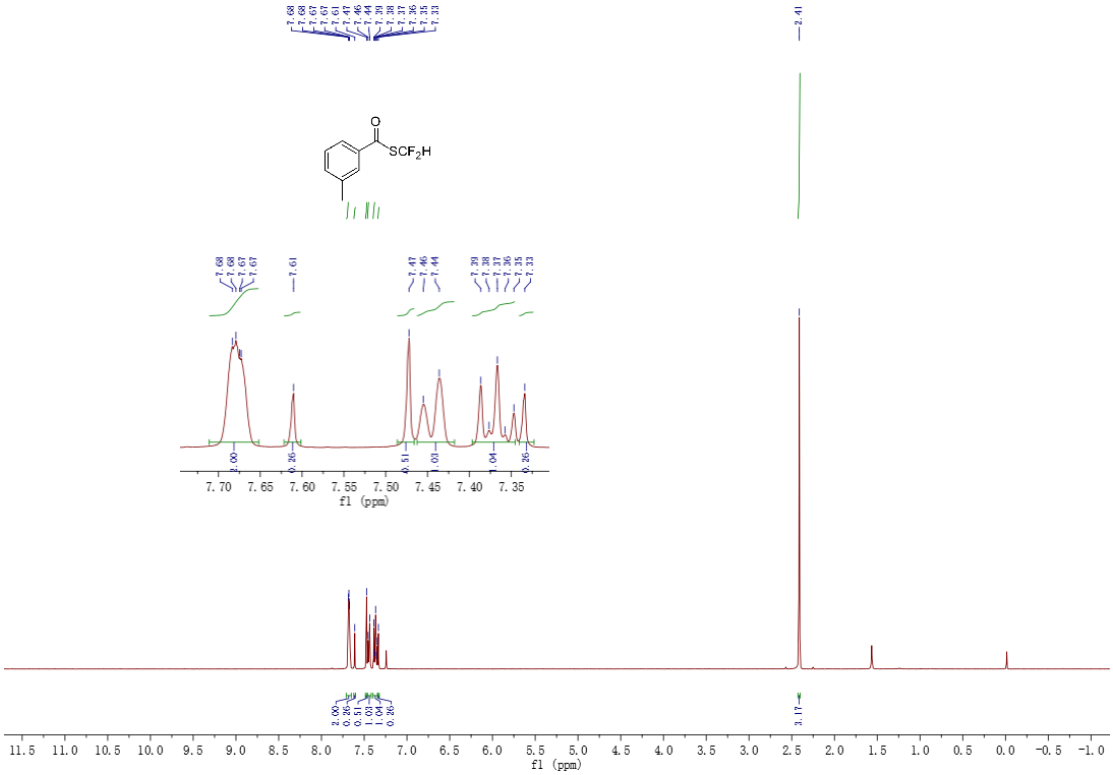
^{19}F NMR spectrum of methyl 4-(((difluoromethyl)thio)carbonyl)benzoate 2g



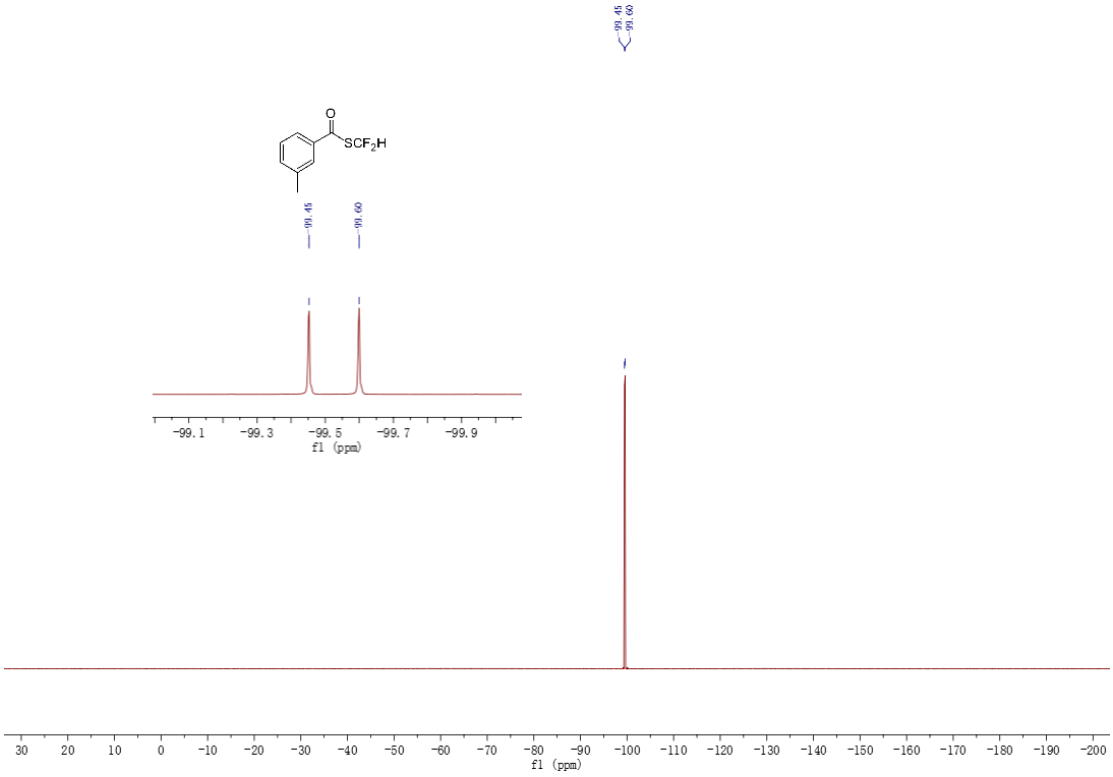
^{13}C NMR spectrum of methyl 4-(((difluoromethyl)thio)carbonyl)benzoate 2g



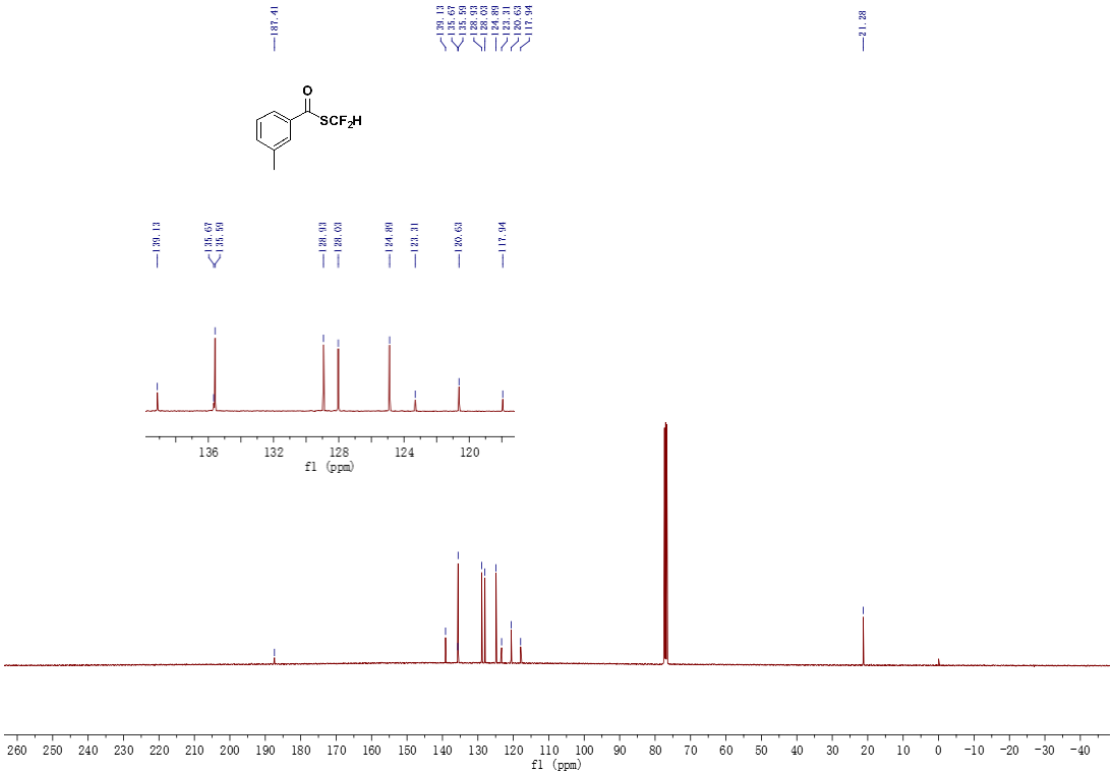
^{1}H NMR spectrum of S-(difluoromethyl)-3-methylbenzothioate 2h



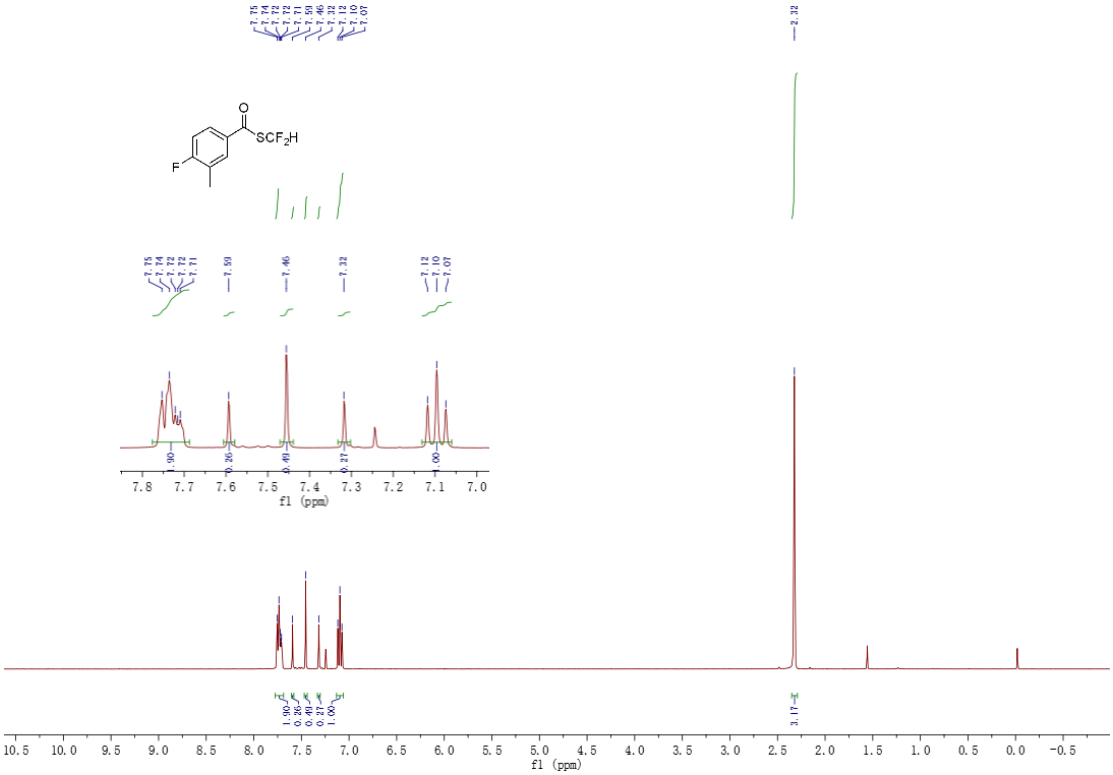
^{19}F NMR spectrum of S-(difluoromethyl)-3-methylbenzothioate 2h



^{13}C NMR spectrum of S-(difluoromethyl)-3-methylbenzothioate 2h



^{1}H NMR spectrum of S-(difluoromethyl)-4-fluoro-3-methylbenzothioate 2i



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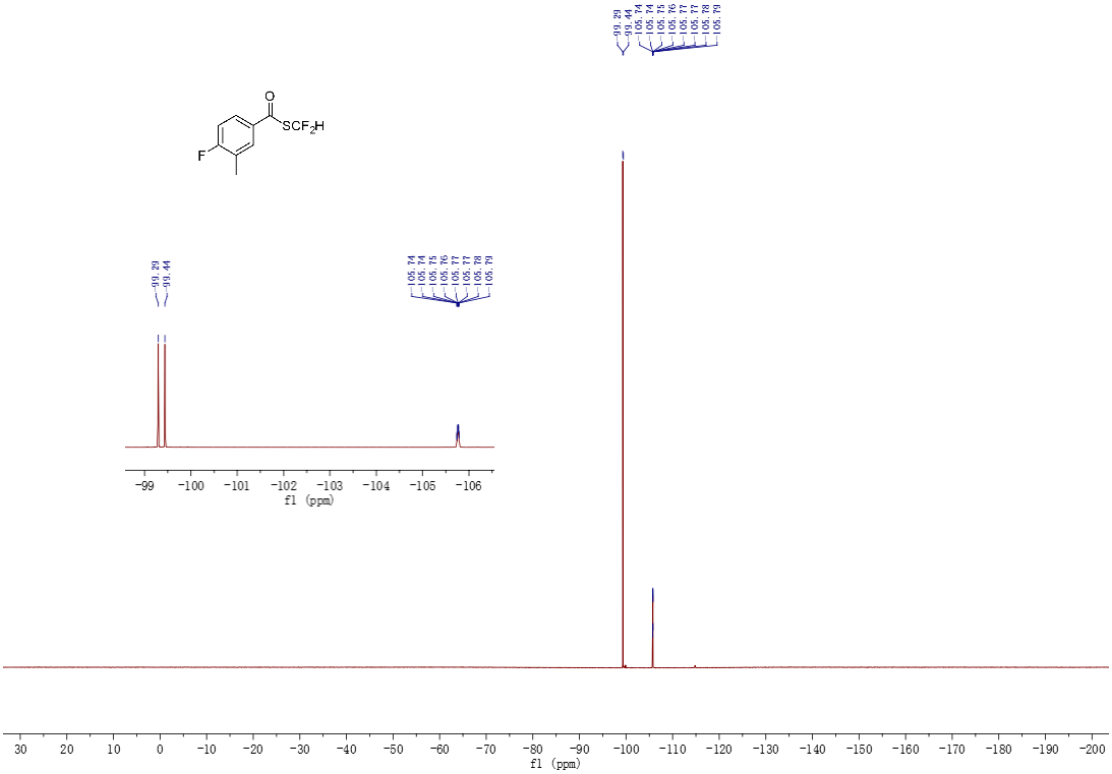
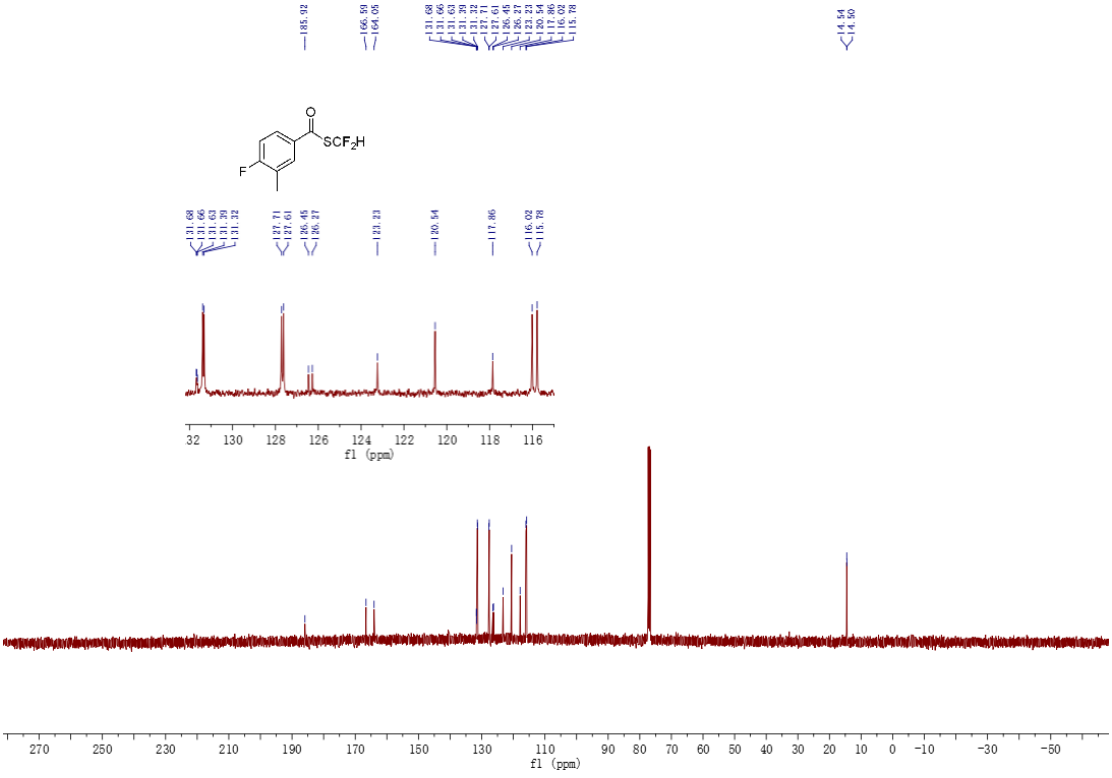
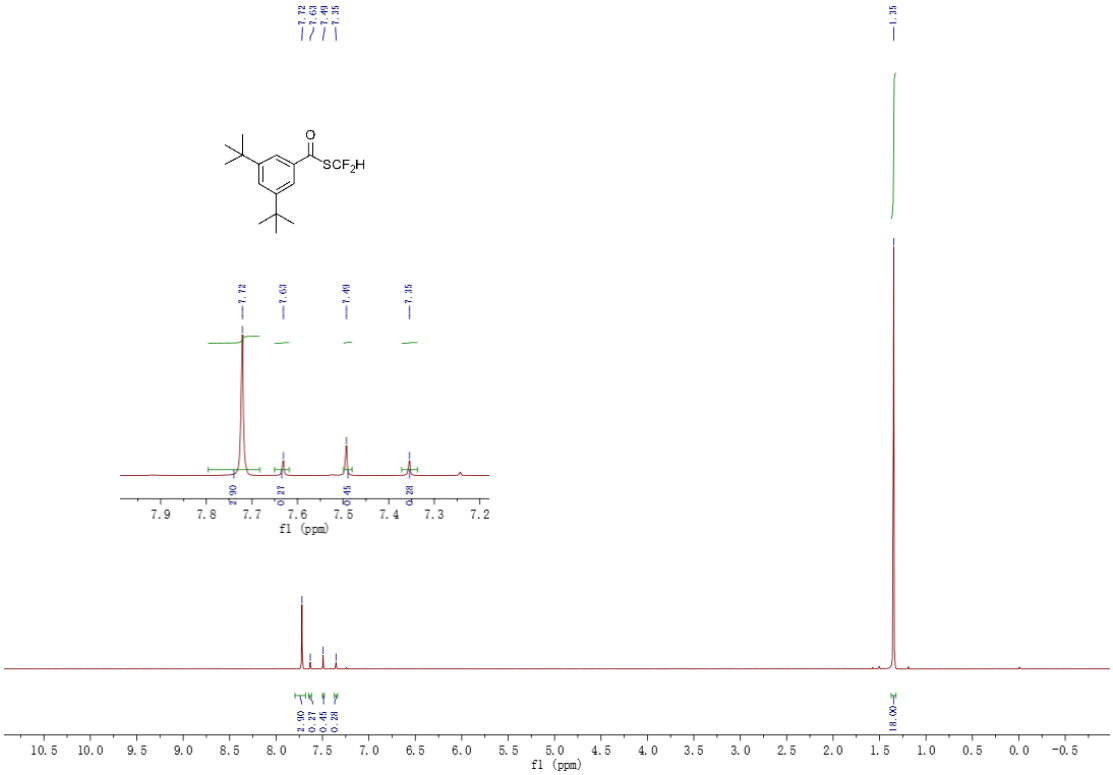


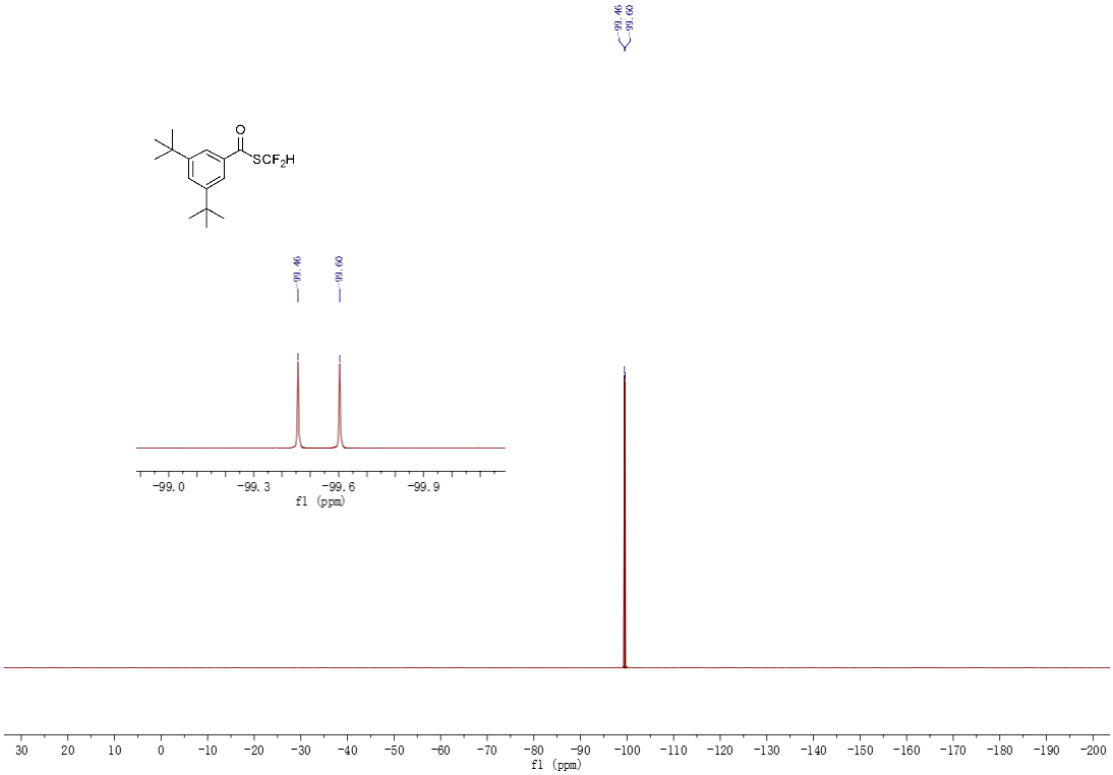
^{13}C NMR spectrum of S-(difluoromethyl)-4-fluoro-3-methylbenzothioate 2i



^{1}H NMR spectrum of S-(difluoromethyl)-3,5-di-*tert*-butylbenzothioate 2j



^{19}F NMR spectrum of S-(difluoromethyl)-3,5-di-*tert*-butylbenzothioate 2j



^{13}C NMR spectrum of
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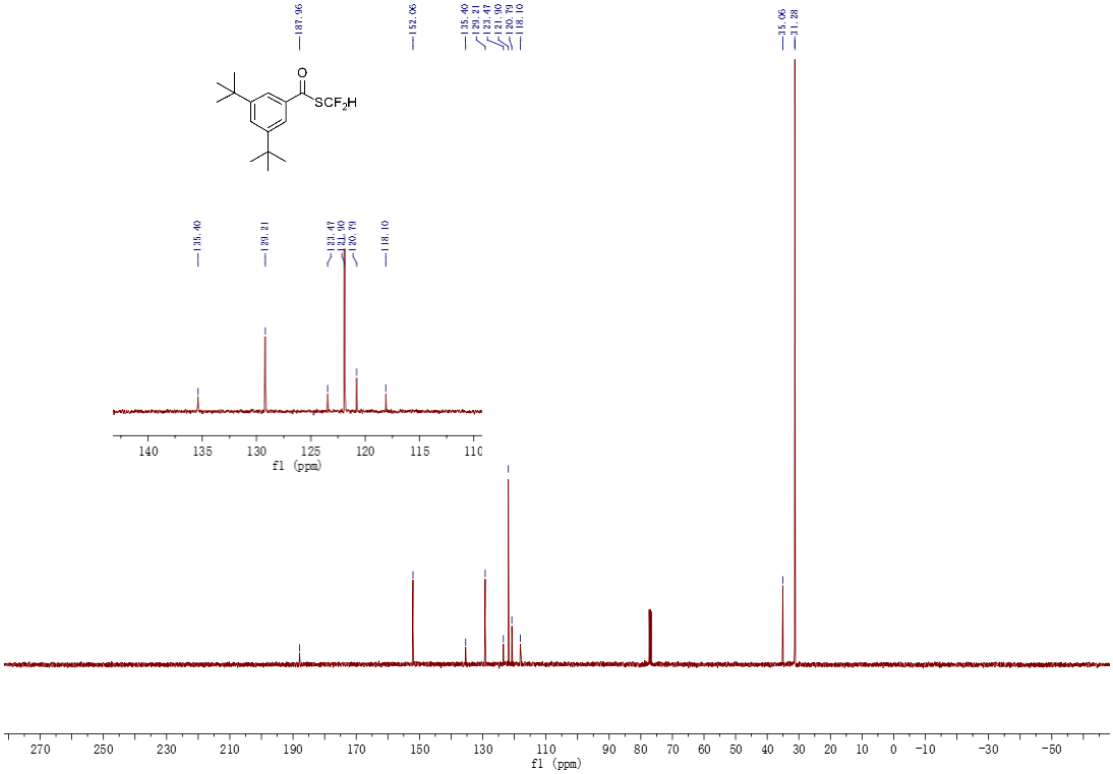
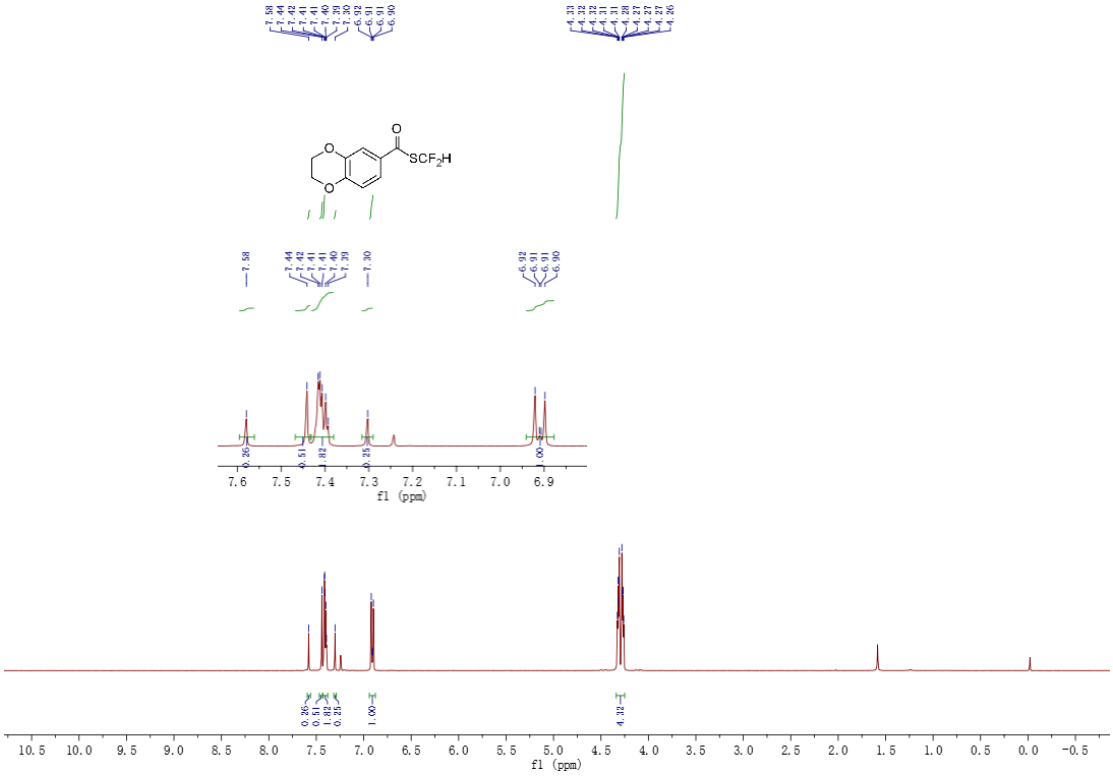
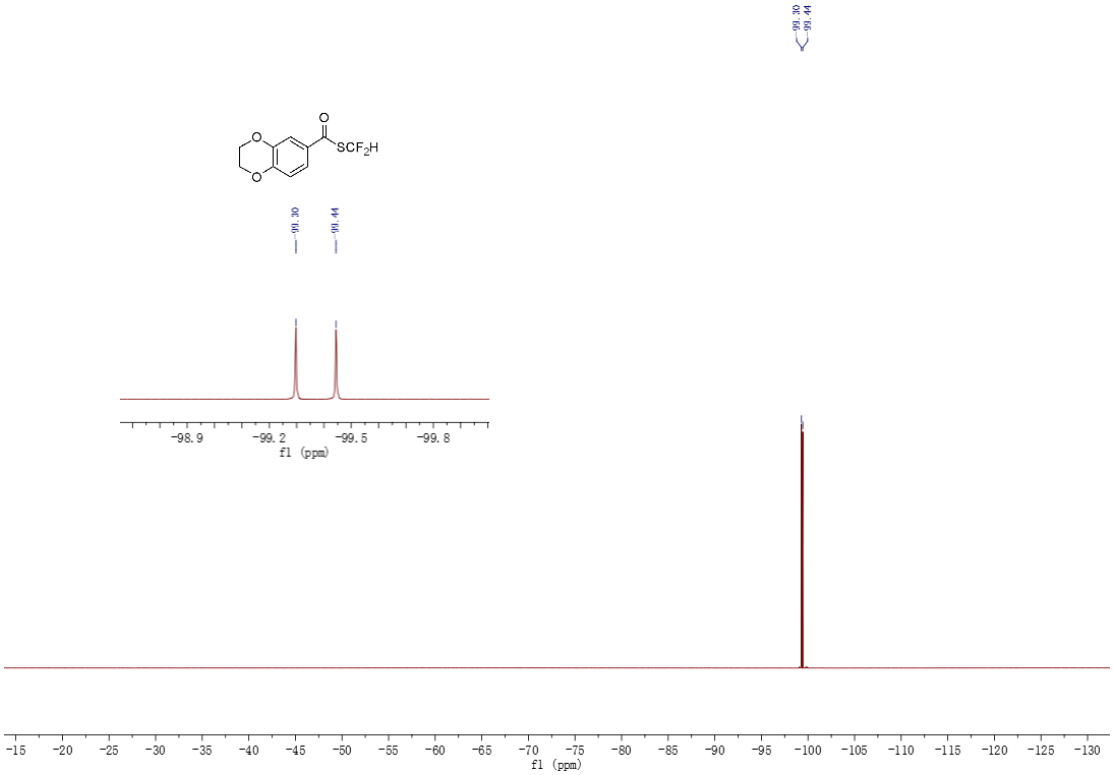


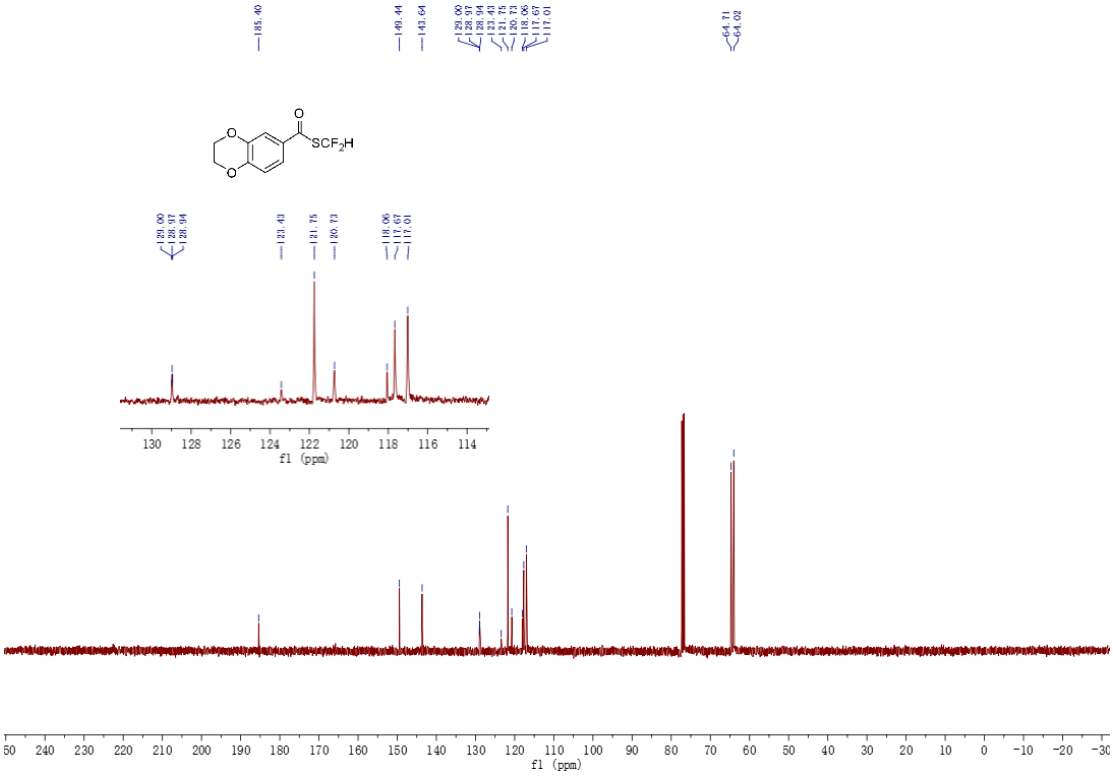
^{1}H NMR spectrum of
S-(difluoromethyl)-2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbothioate 2k



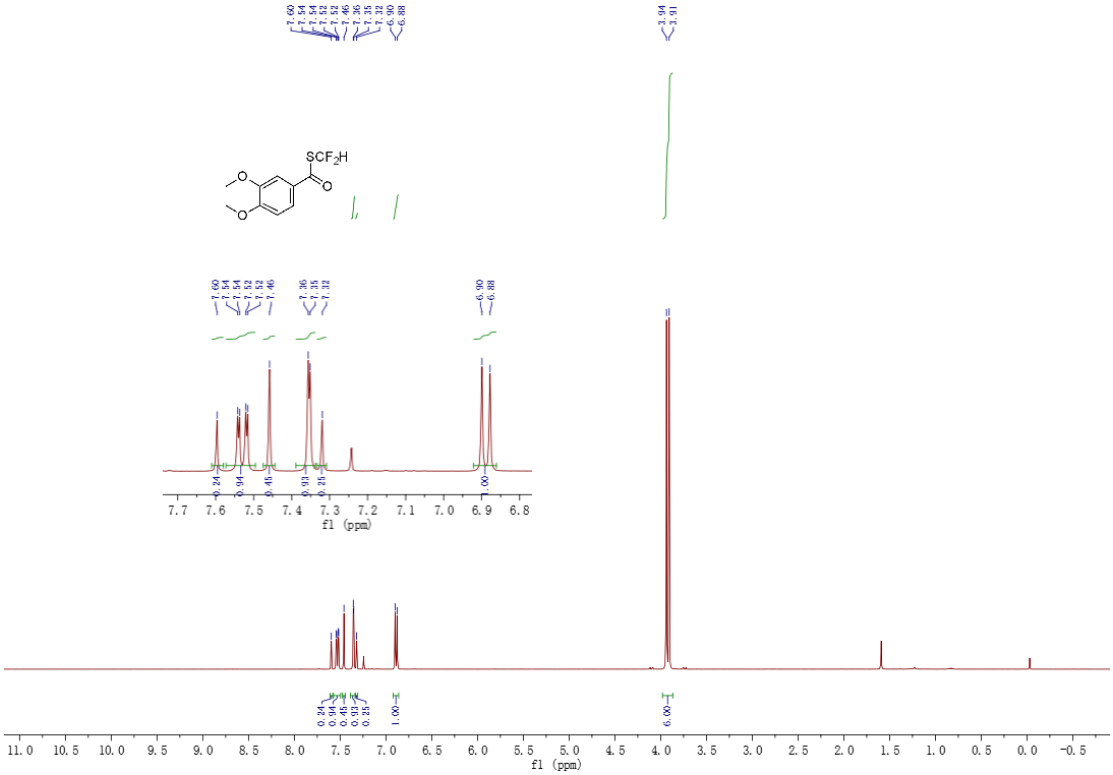
^{19}F NMR spectrum of S-(difluoromethyl)-2,3-dihydrobenzo[*b*](1,4]dioxine-6-carbothioate 2k



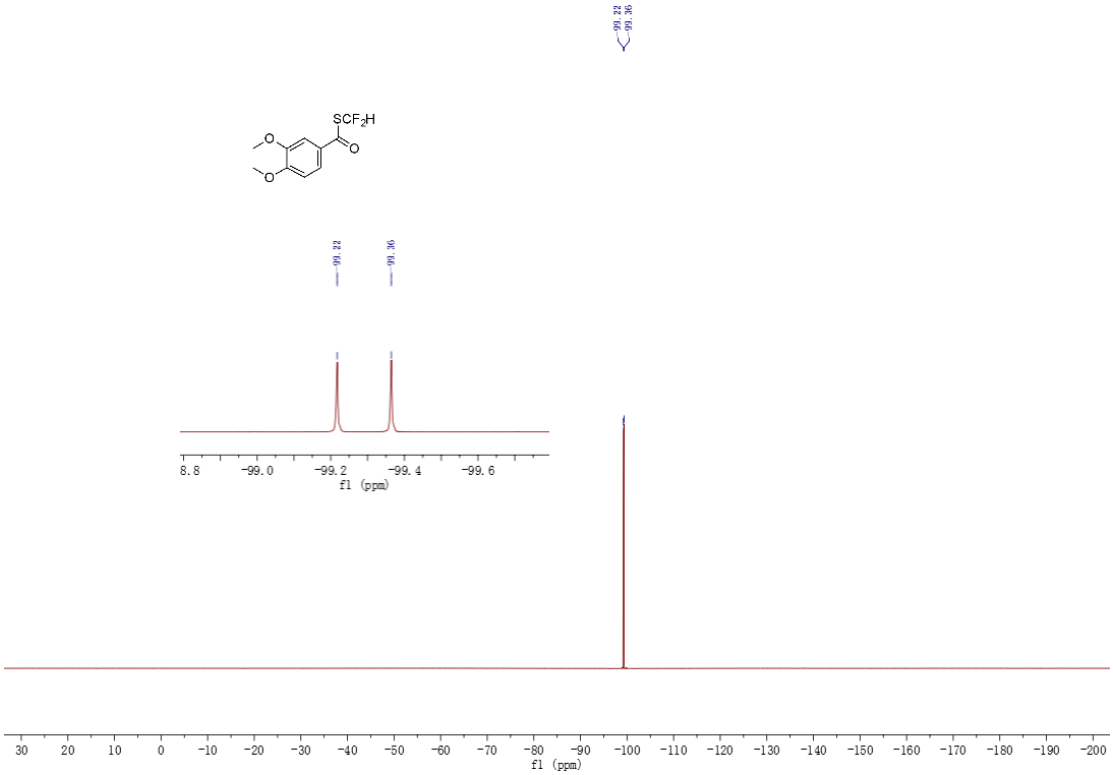
^{13}C NMR spectrum of S-(difluoromethyl)-2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbothioate 2k



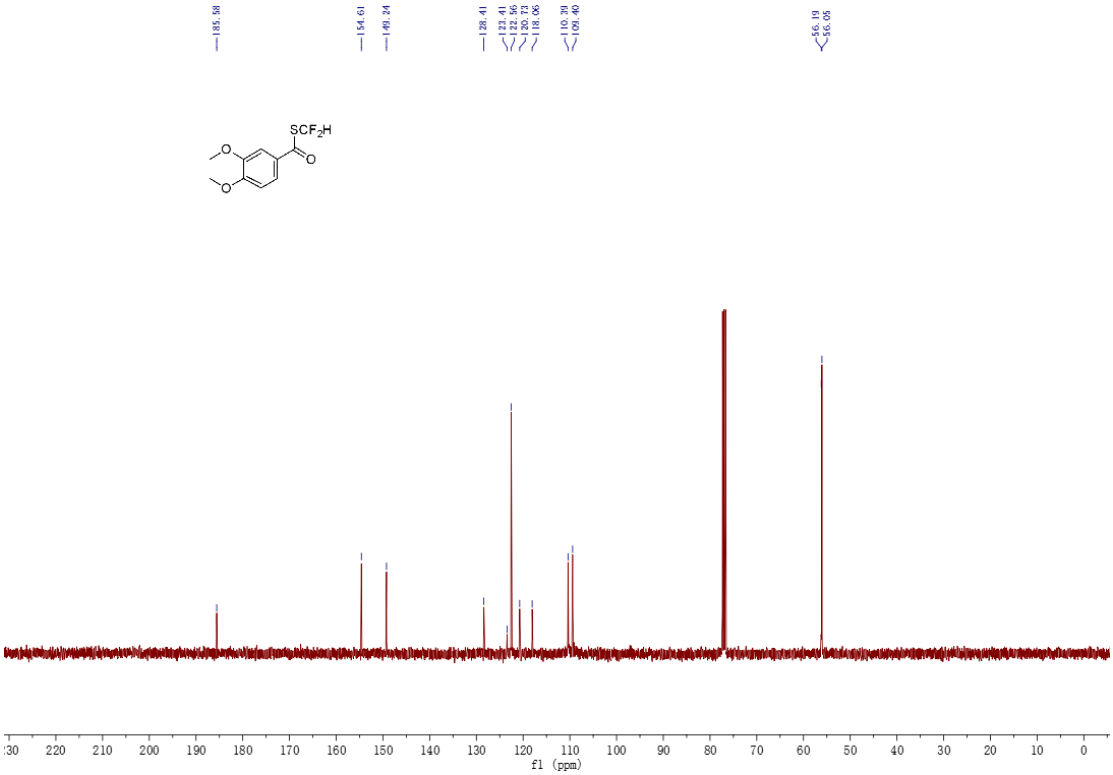
^{1}H NMR spectrum of S-(difluoromethyl)-3,4-dimethoxybenzothioate 2l



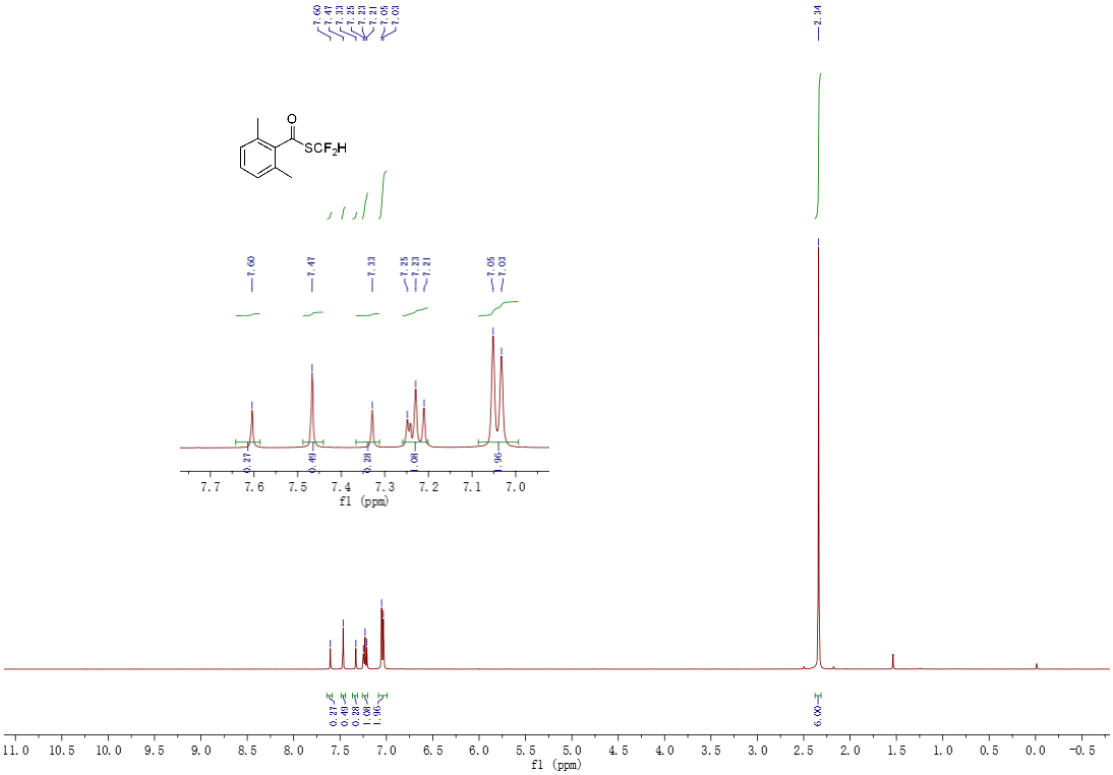
^{19}F NMR spectrum of S-(difluoromethyl)-3,4-dimethoxybenzothioate 2l



^{13}C NMR spectrum of S-(difluoromethyl)-3,4-dimethoxybenzothioate 2l



^{1}H NMR spectrum of S-(difluoromethyl)-2,6-dimethylbenzothioate 2m



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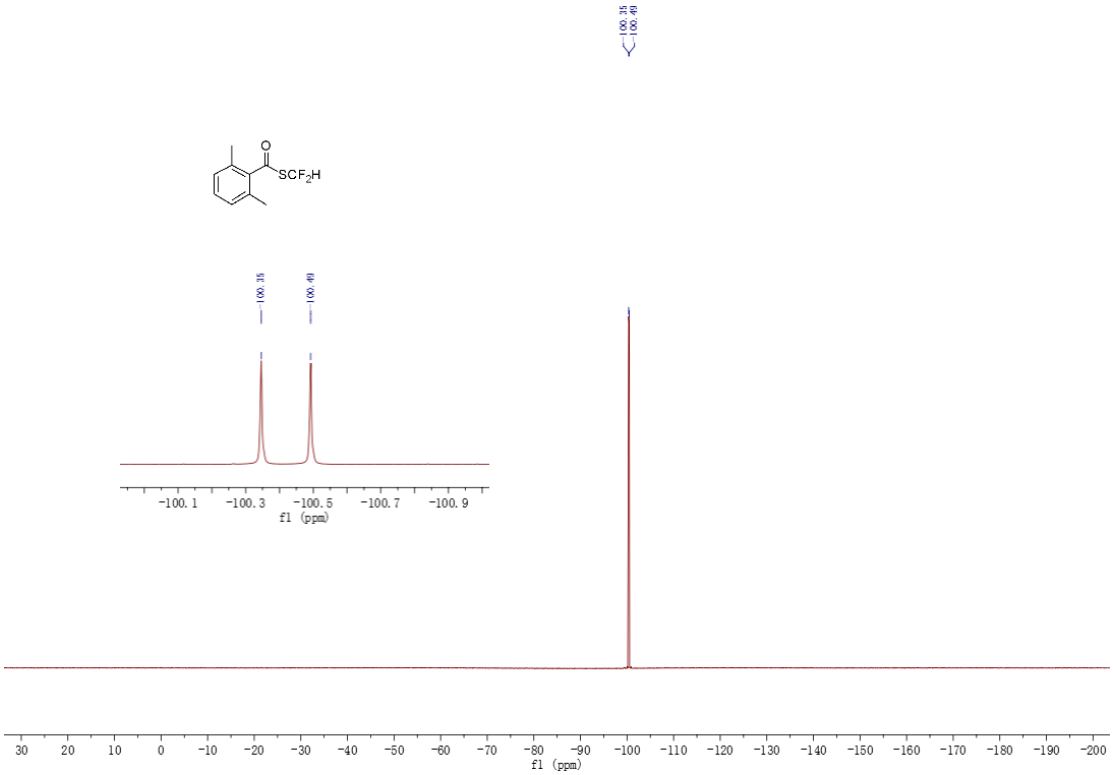

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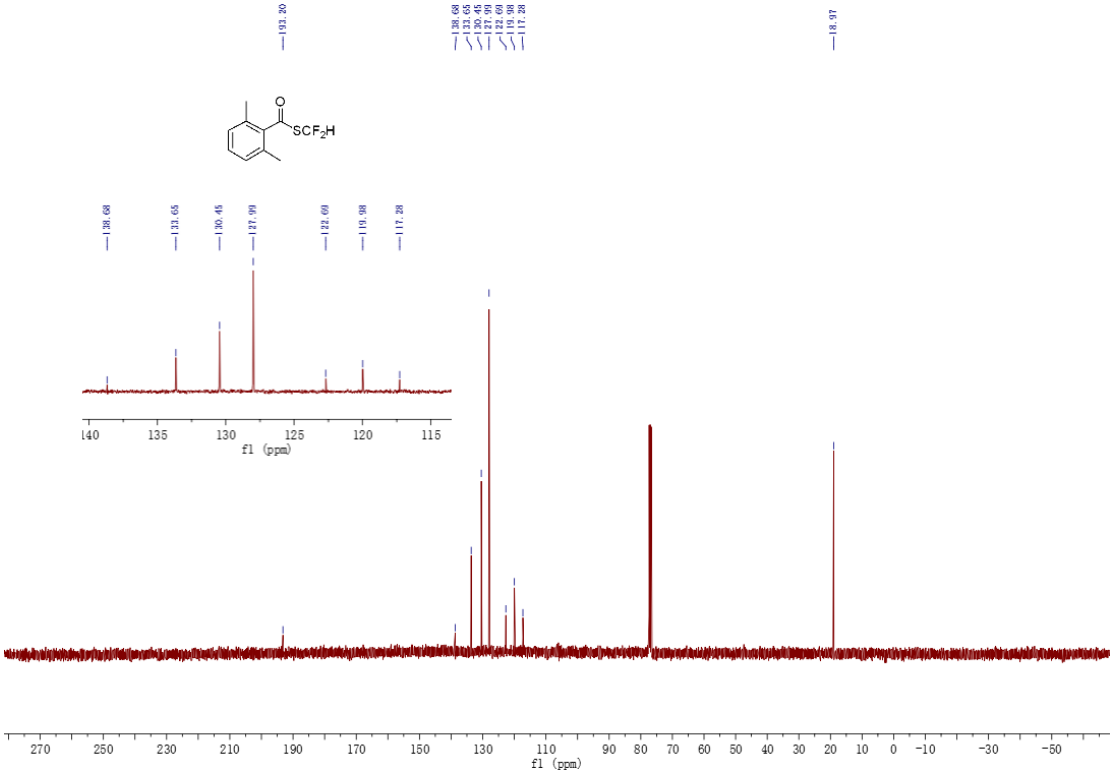
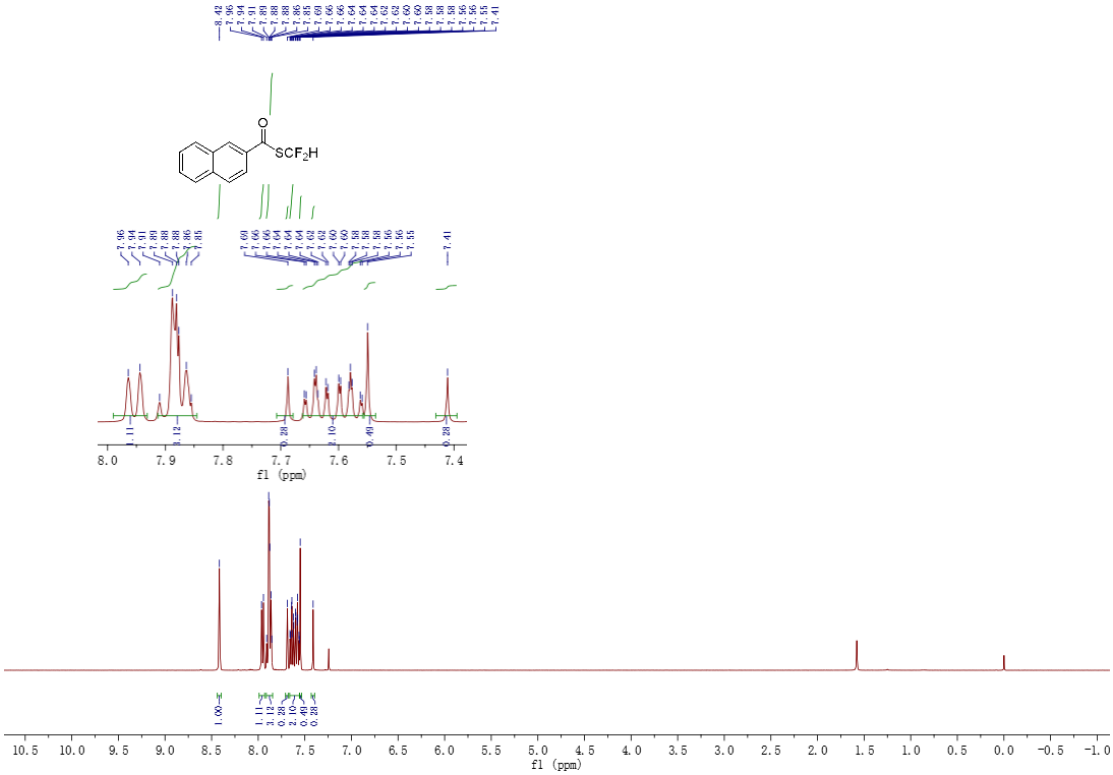


^{1}H NMR spectrum of S-(difluoromethyl)-naphthalene-2-carbothioate 2n



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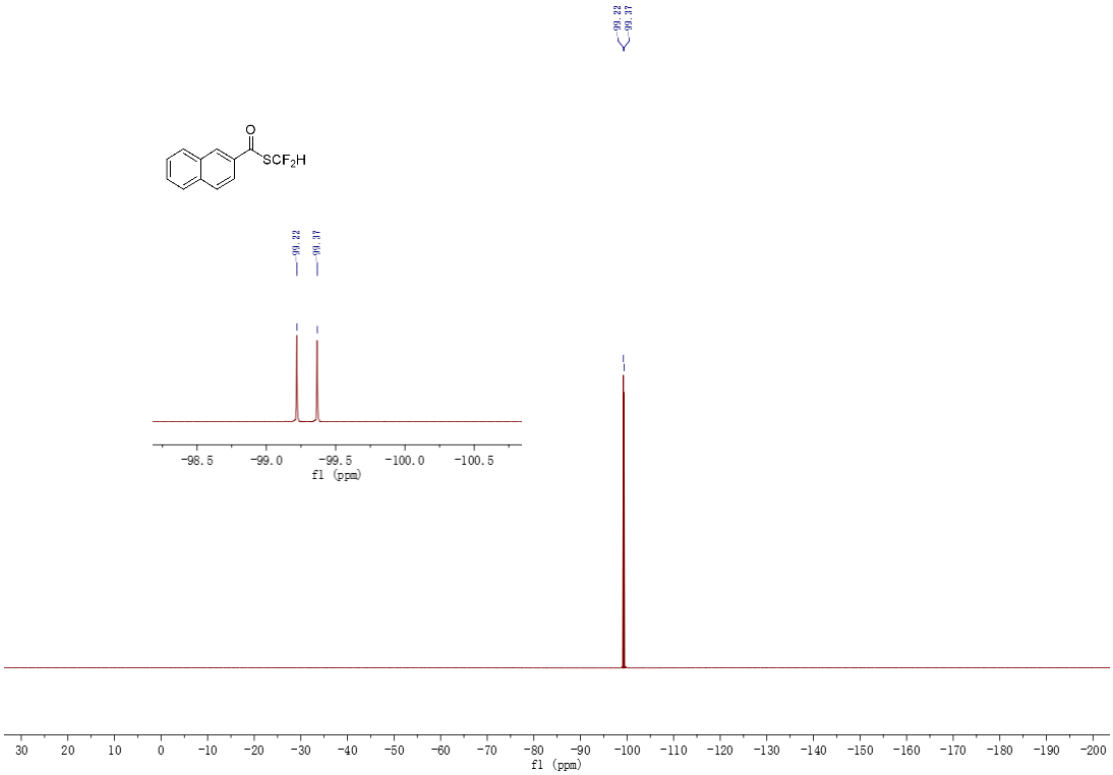

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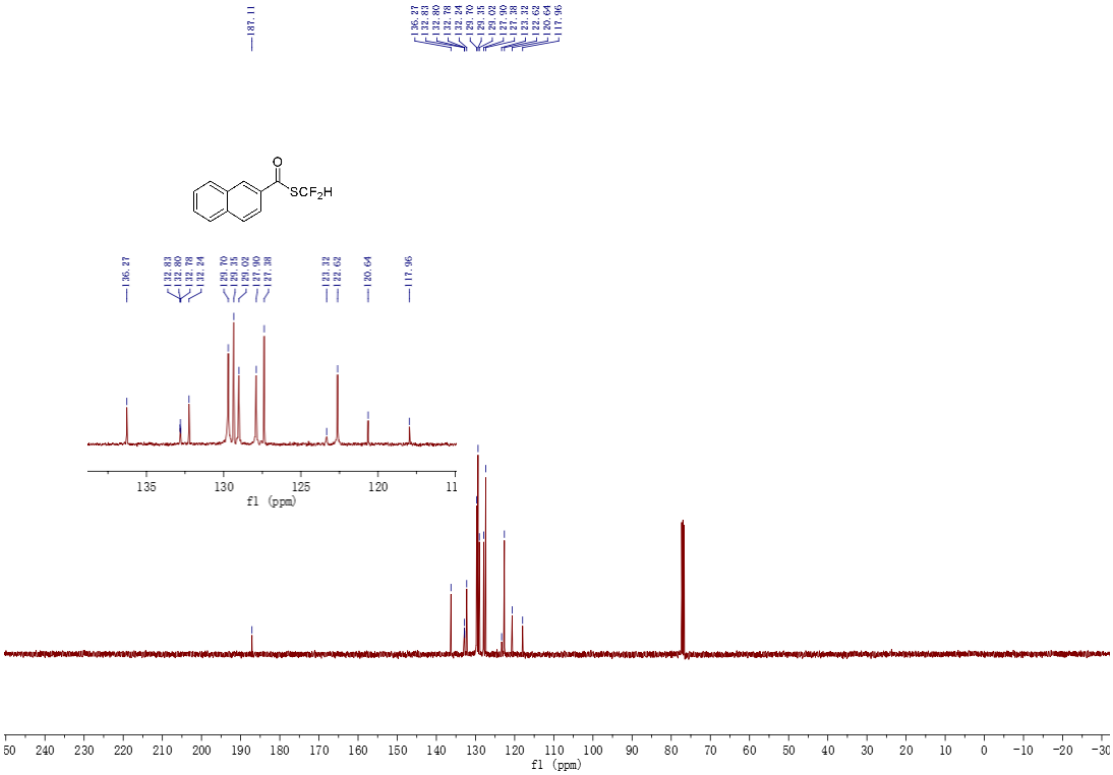
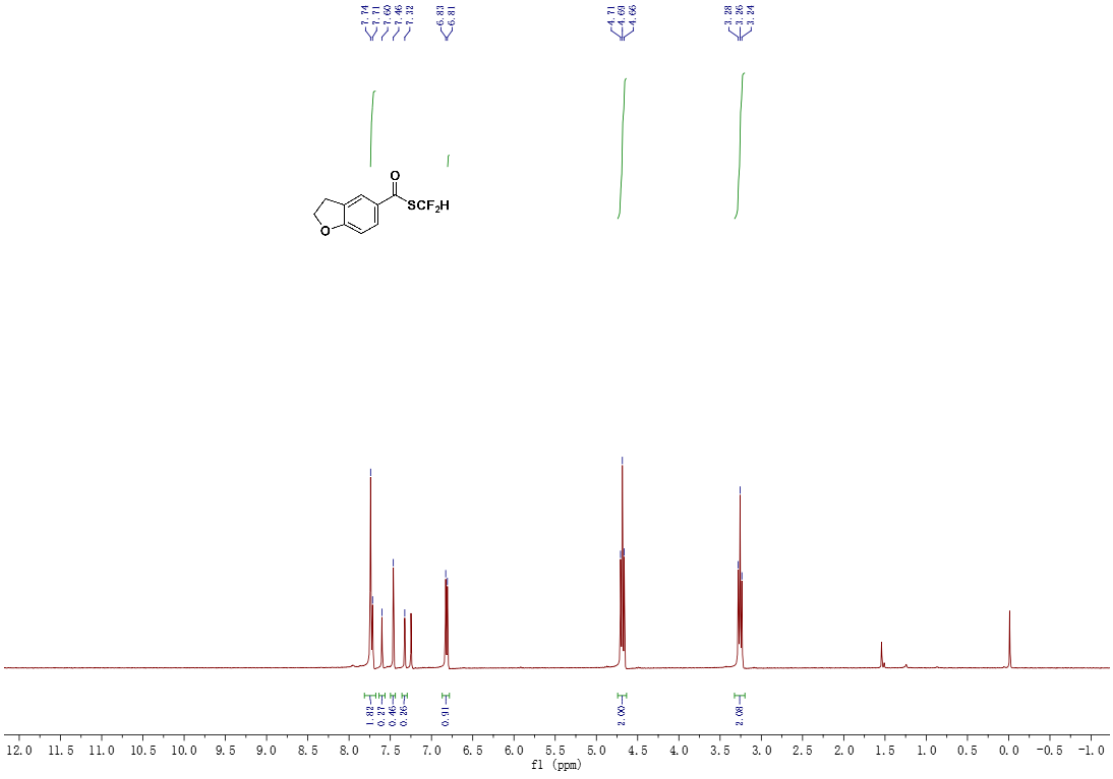
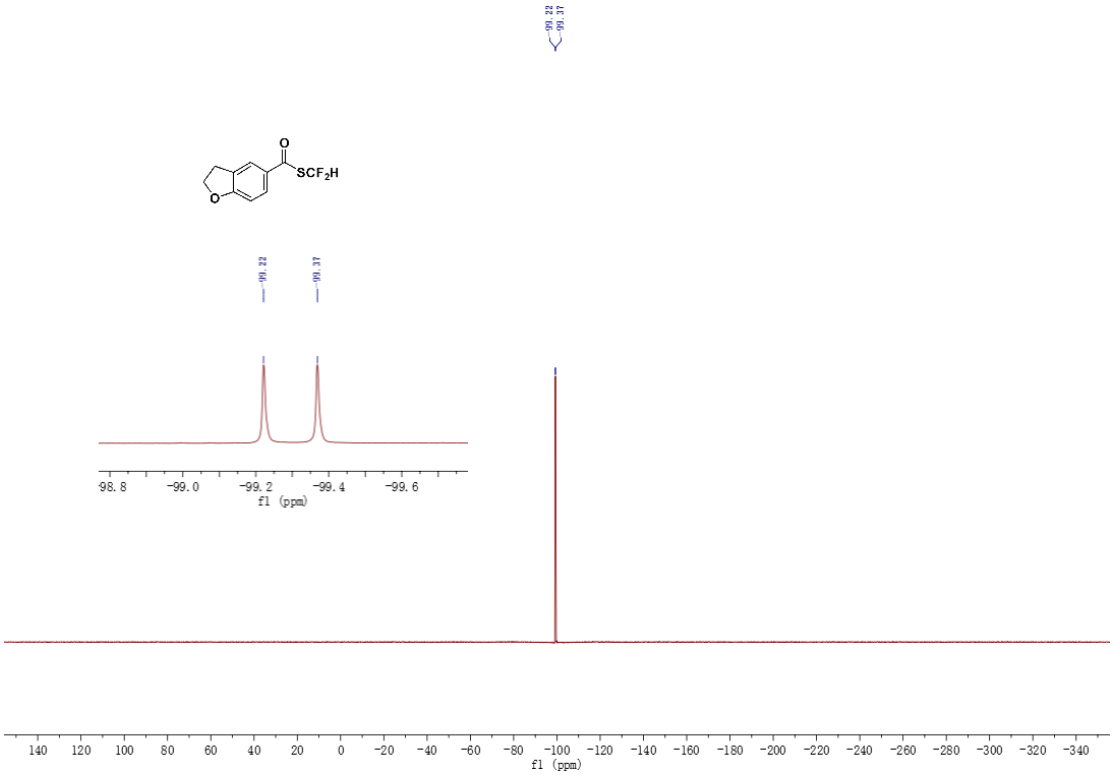


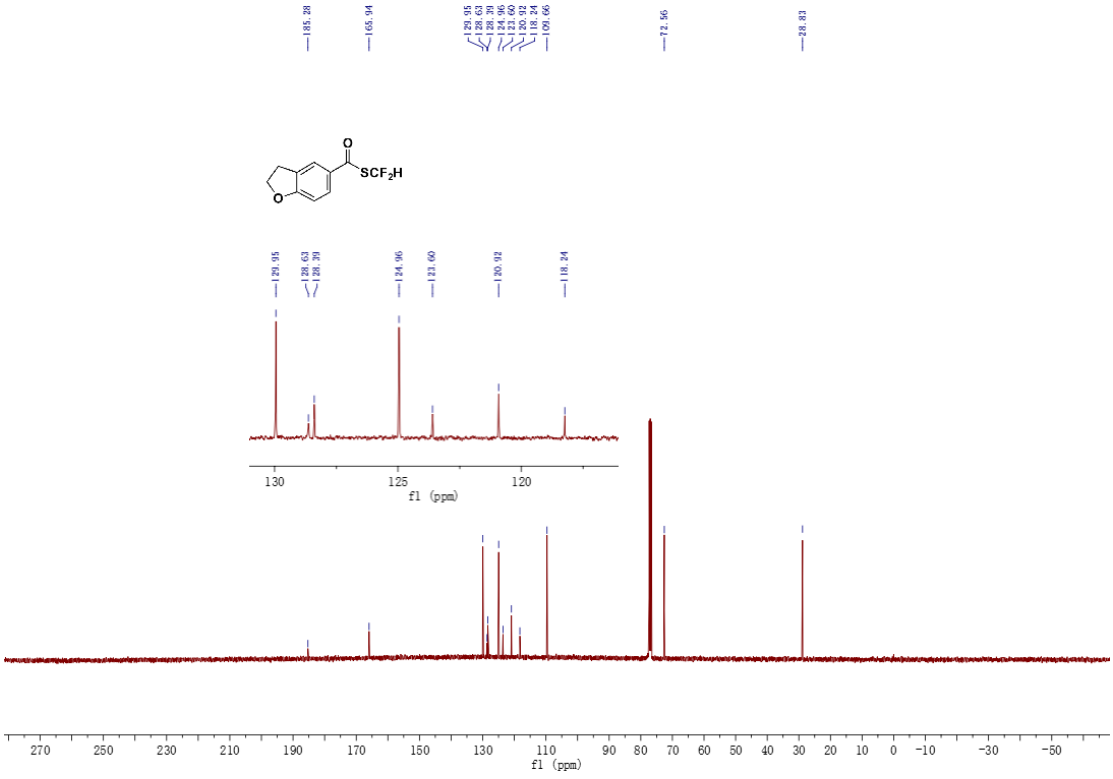
^{1}H NMR spectrum of S-(difluoromethyl)-2,3-dihydrobenzofuran-5-carbothioate 2o



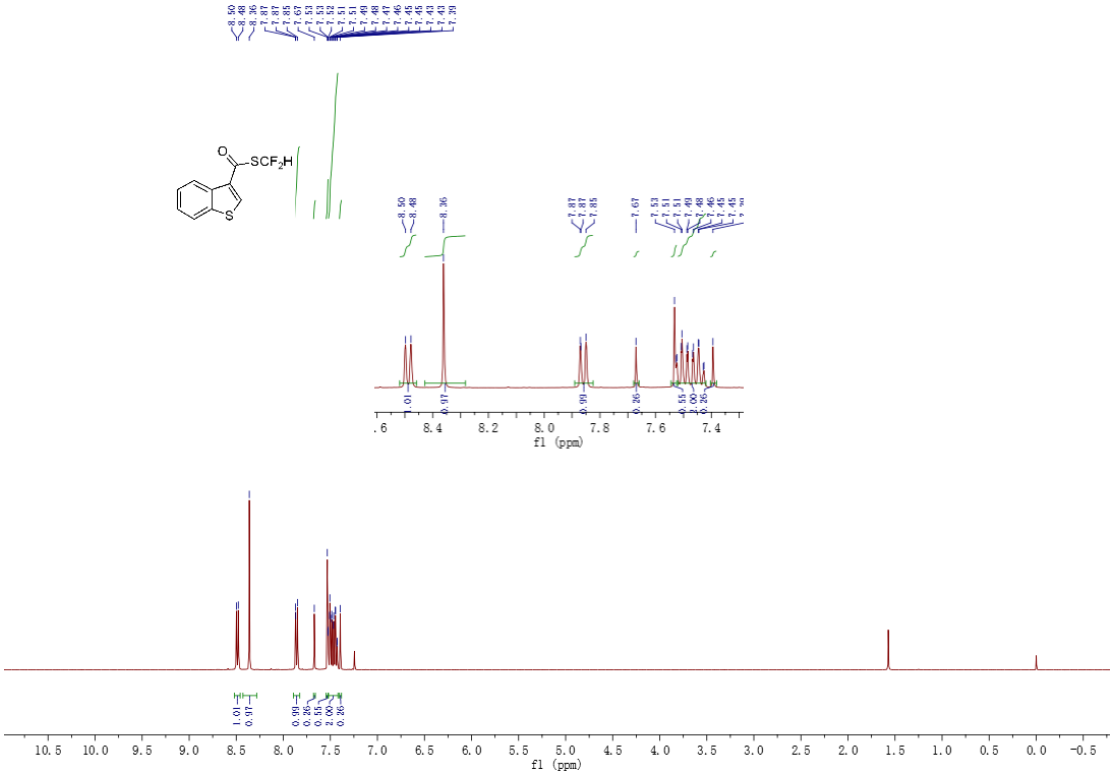
^{19}F NMR spectrum of S-(difluoromethyl)-2,3-dihydrobenzofuran-5-carbothioate 2o



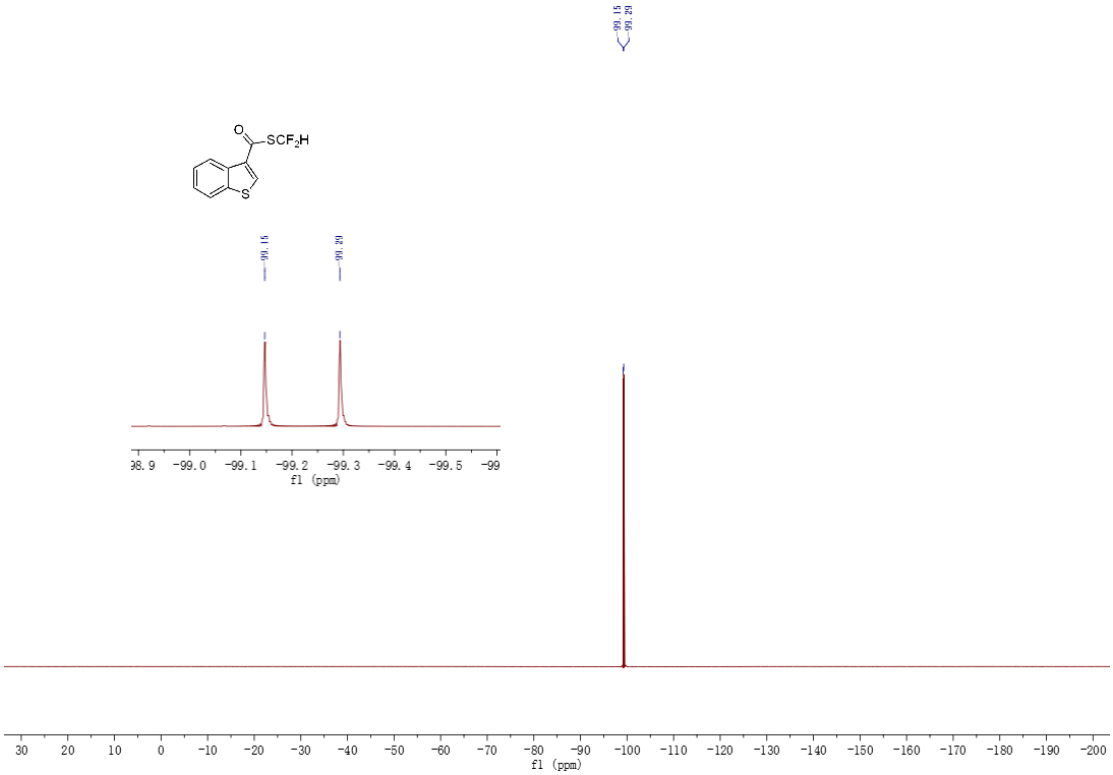
^{13}C NMR spectrum of S-(difluoromethyl)-2,3-dihydrobenzofuran-5-carbothioate 2o



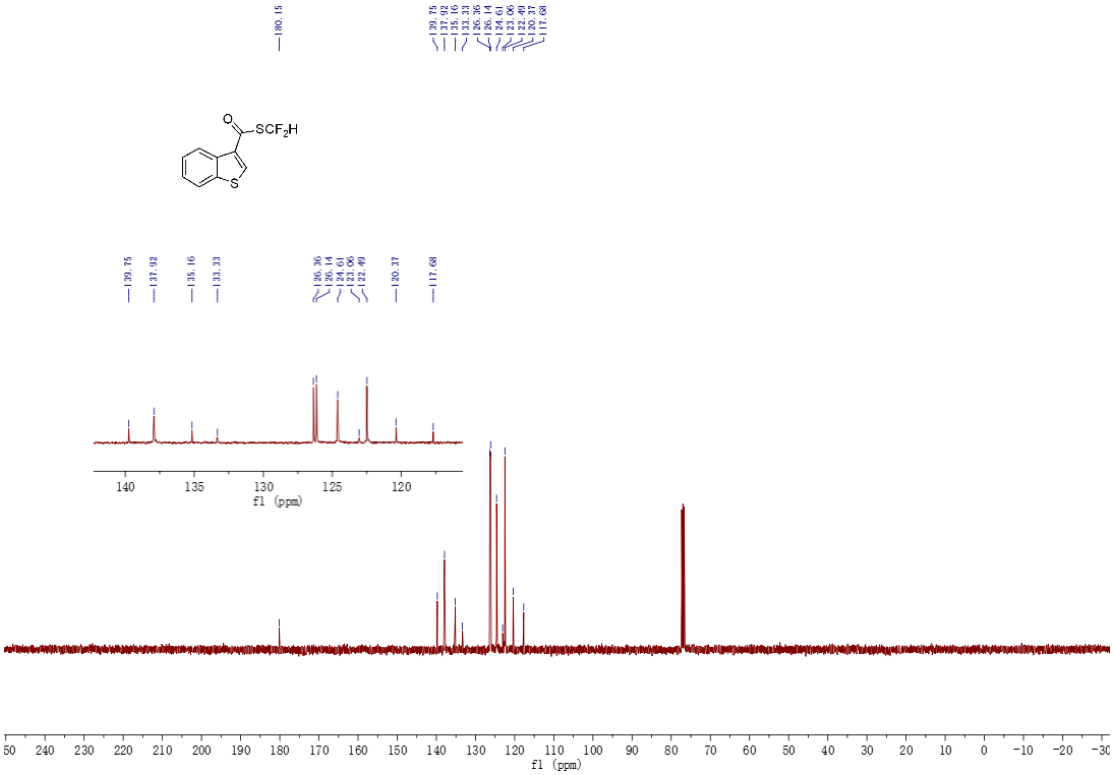
^{1}H NMR spectrum of S-(difluoromethyl)-benzo[b]thiophene-3-carbothioate 2p



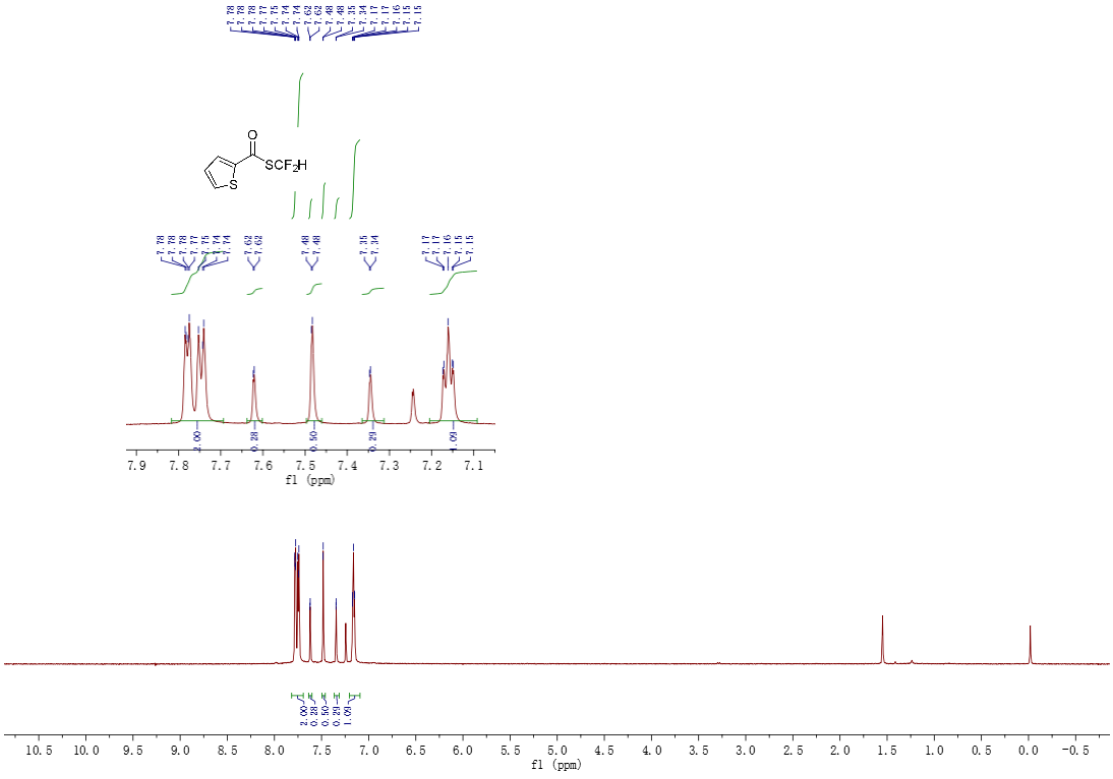
^{19}F NMR spectrum of S-(difluoromethyl)-benzo[b]thiophene-3-carbothioate 2p



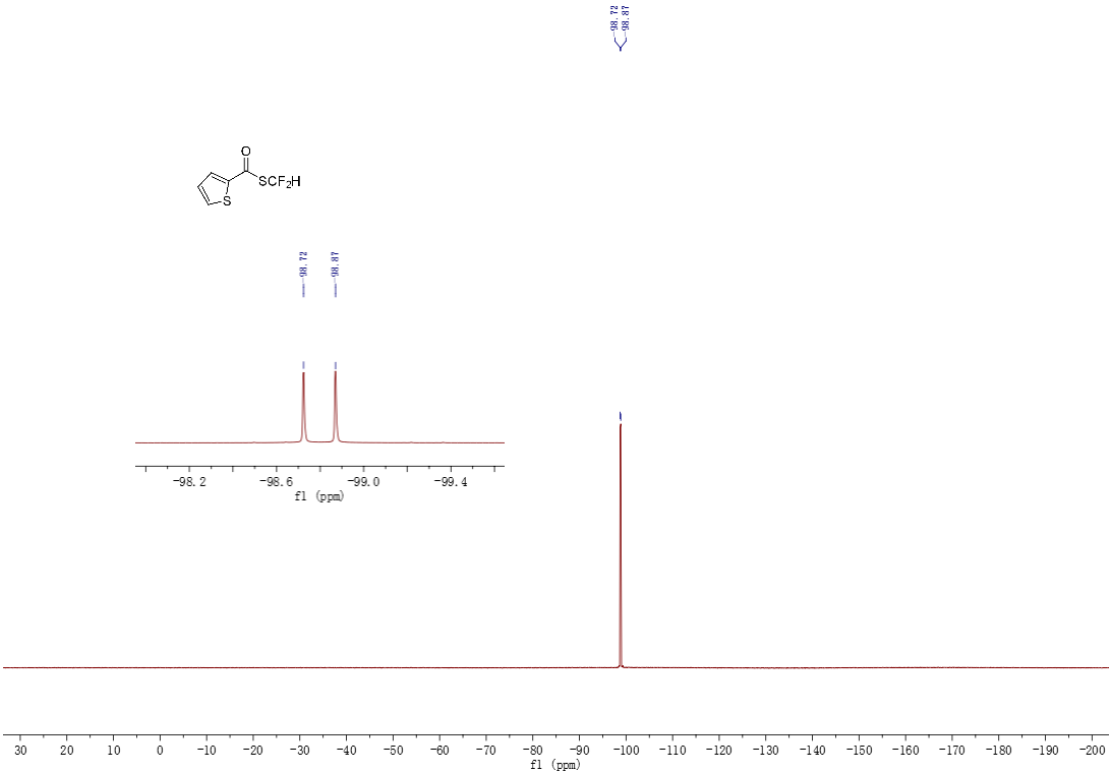
^{13}C NMR spectrum of S-(difluoromethyl)-benzo[b]thiophene-3-carbothioate 2p



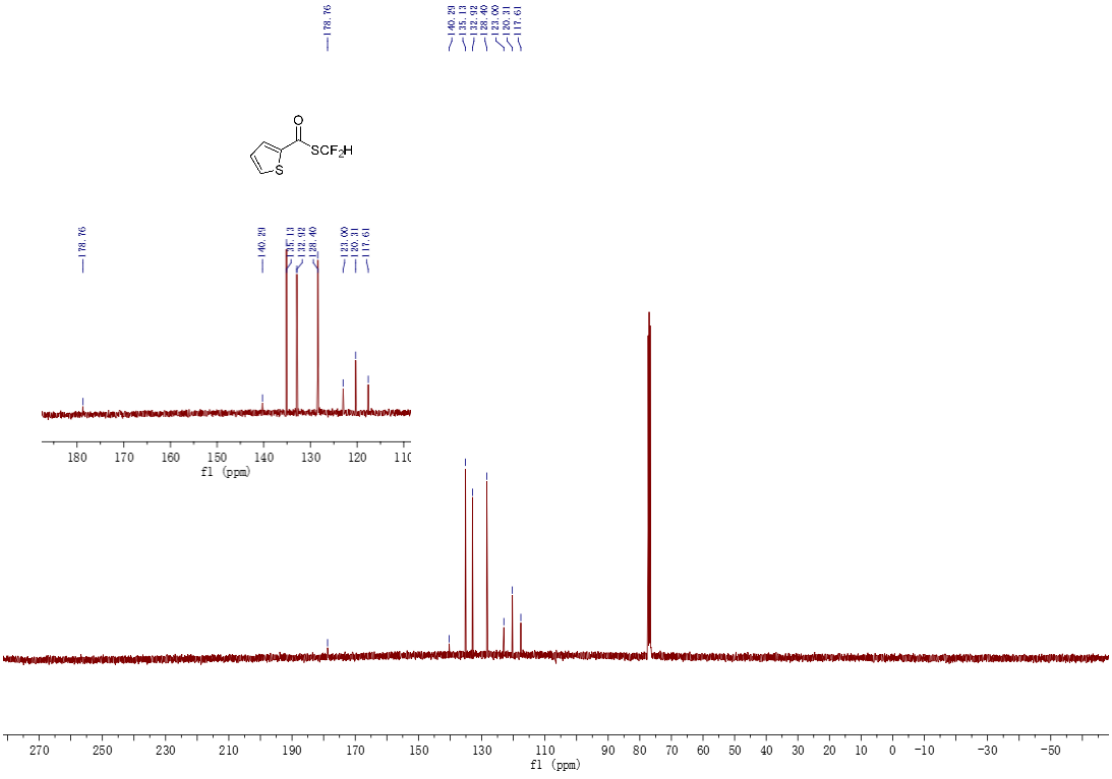
^{1}H NMR spectrum of S-(difluoromethyl)-thiophene-2-carbothioate 2q



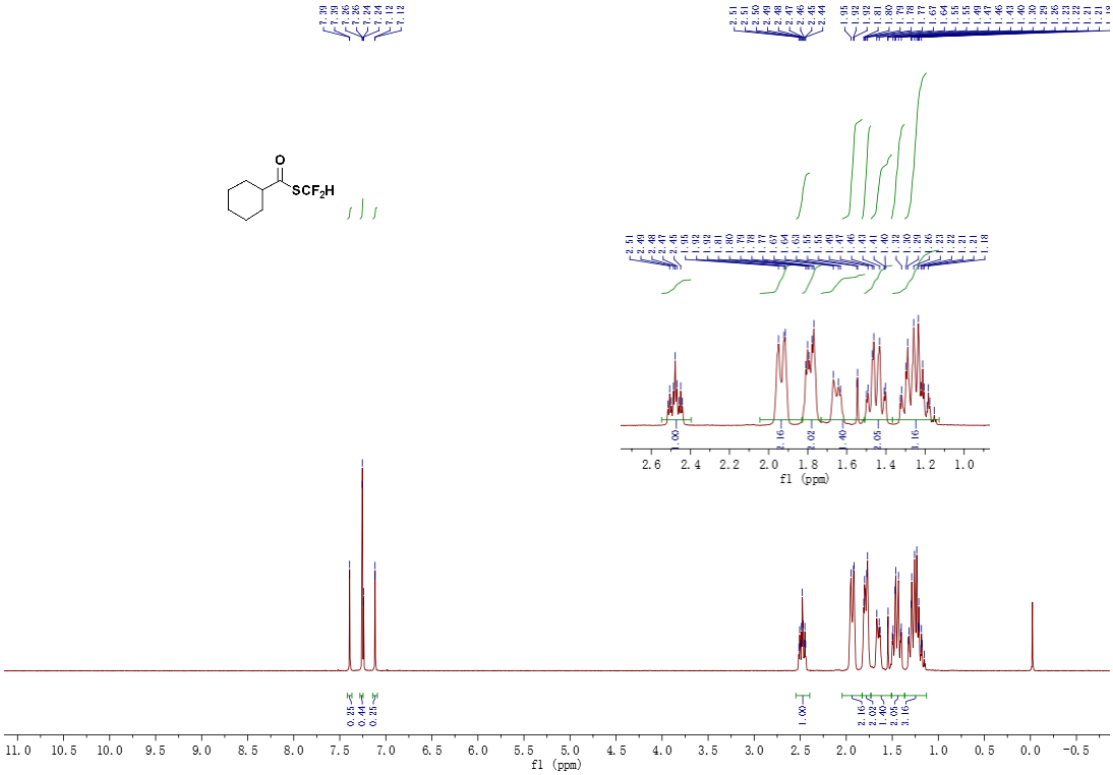
^{19}F NMR spectrum of S-(difluoromethyl)-thiophene-2-carbothioate 2q



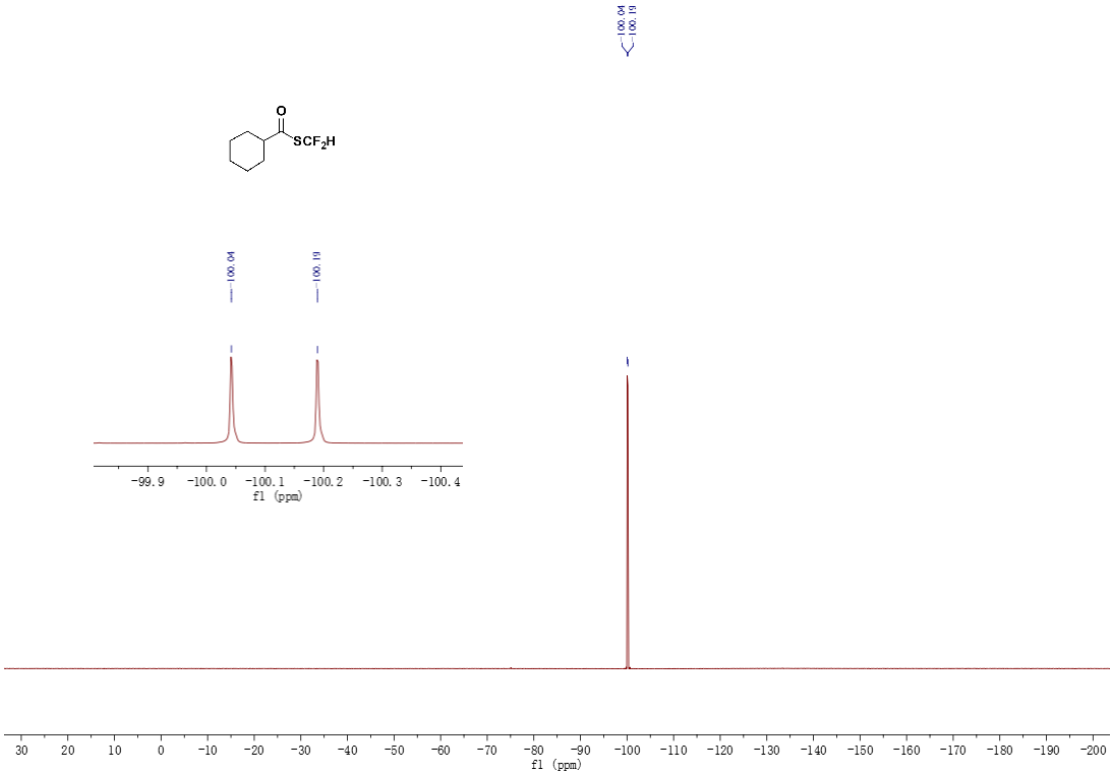
^{13}C NMR spectrum of S-(difluoromethyl)-thiophene-2-carbothioate 2q



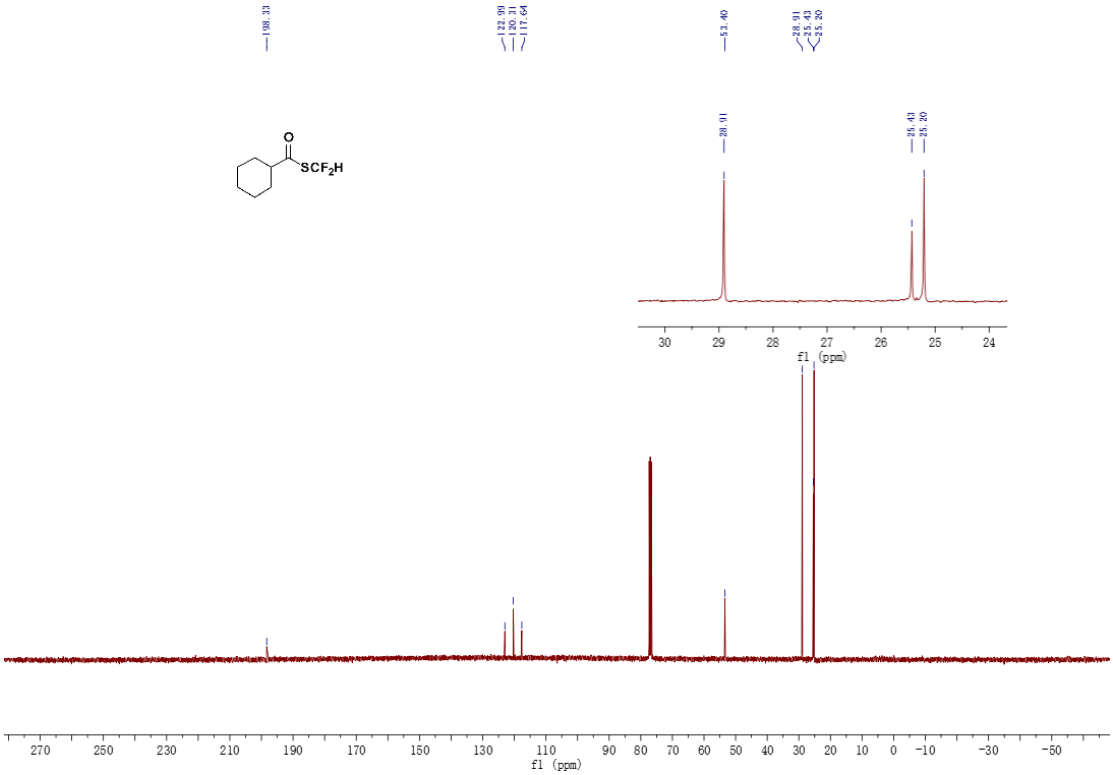
^{1}H NMR spectrum of S-(difluoromethyl)-cyclohexanecarbothioate 2r



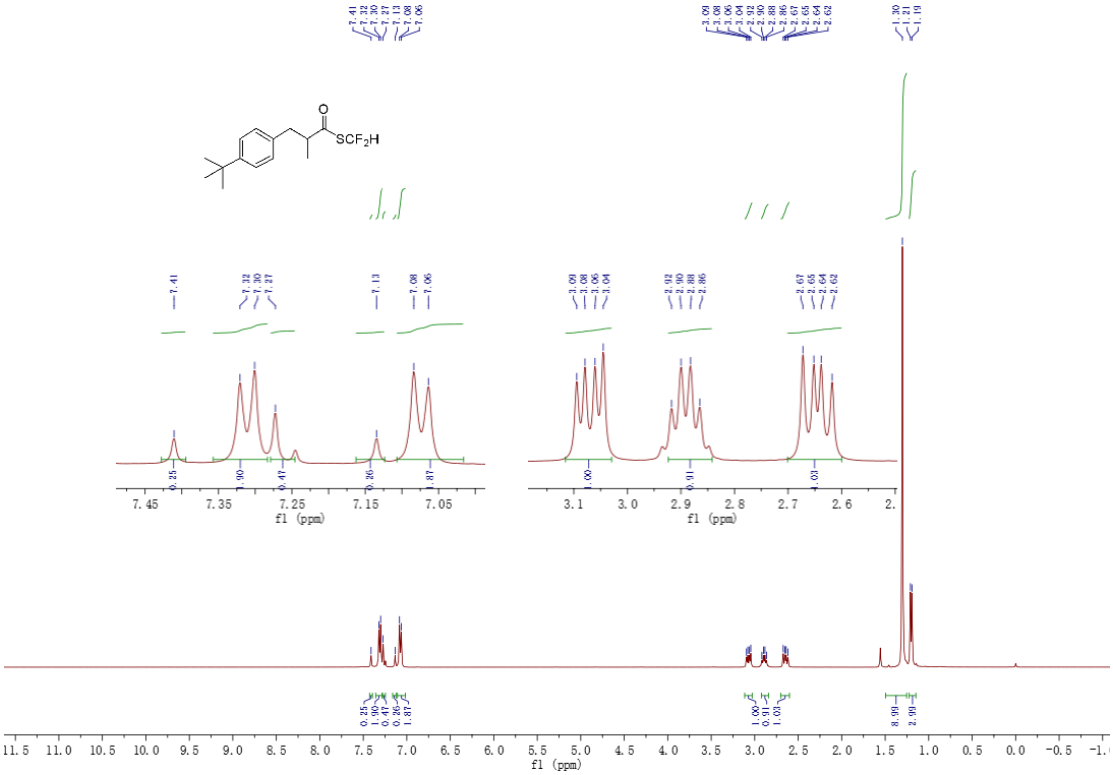
^{19}F NMR spectrum of S-(difluoromethyl)-cyclohexanecarbothioate 2r



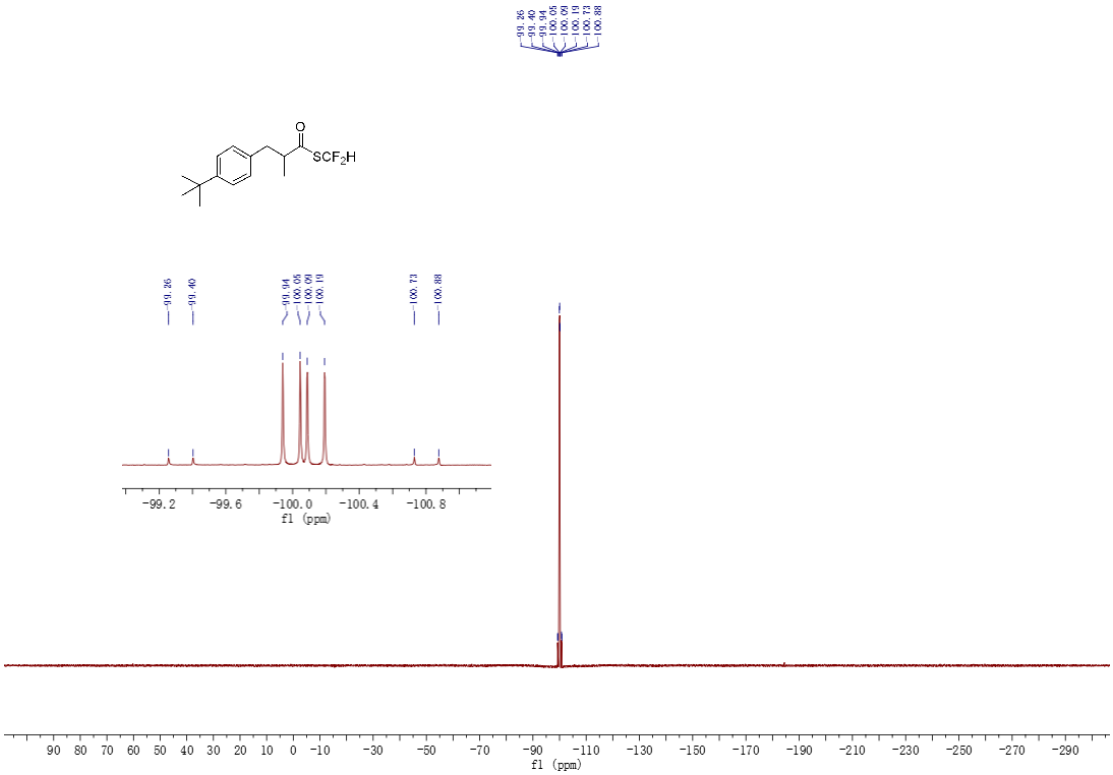
^{13}C NMR spectrum of
S-(difluoromethyl)-cyclohexanecarbothioate 2r



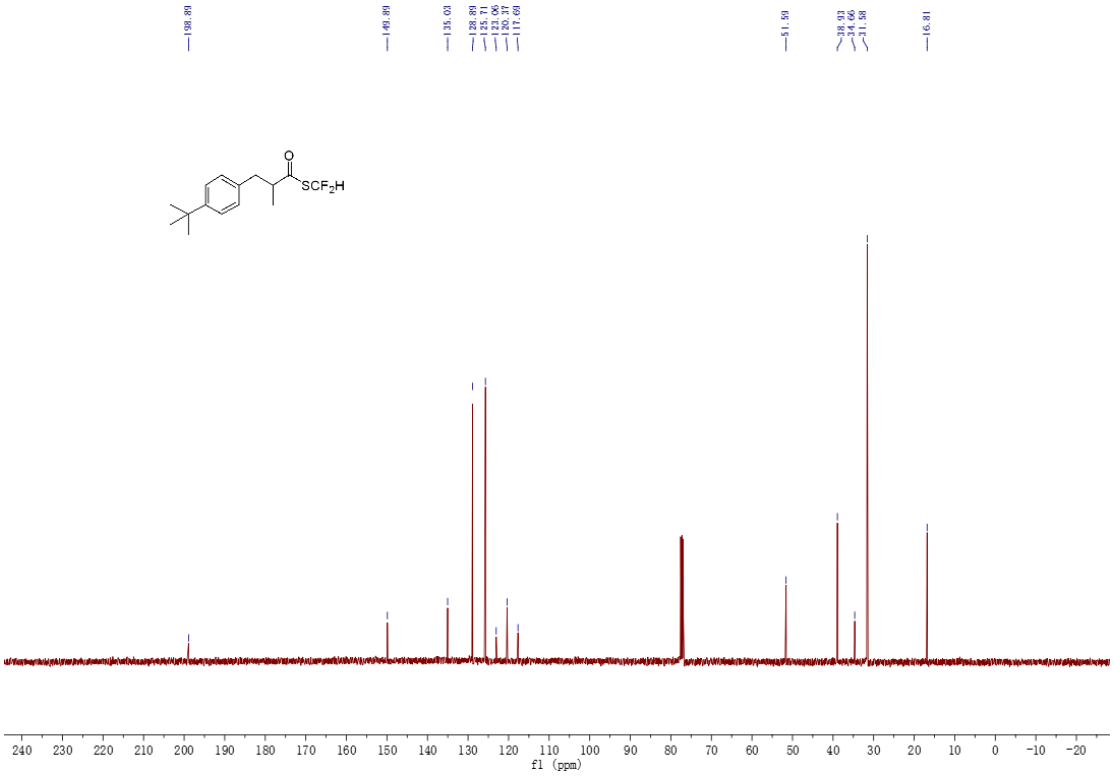
^{1}H NMR spectrum of
S-(difluoromethyl) 3-(4-(*tert*-butyl)phenyl)-2-methylpropanethioate 2s



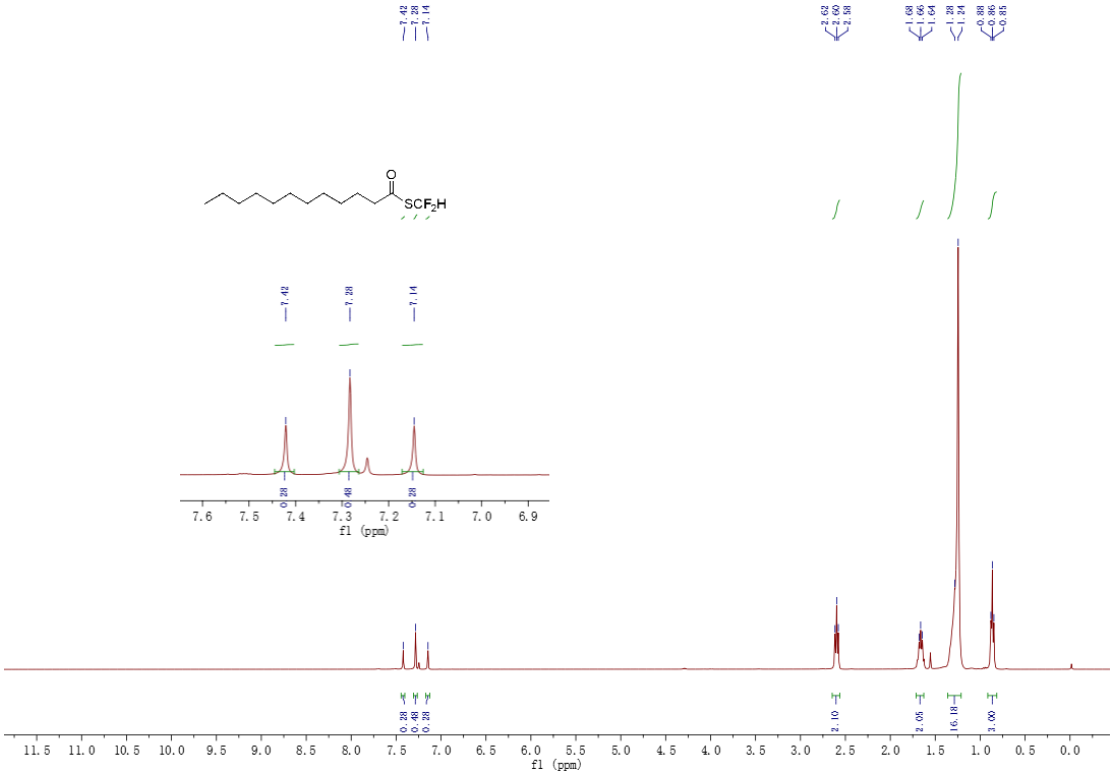
^{19}F NMR spectrum of S-(difluoromethyl) 3-(4-(*tert*-butyl)phenyl)-2-methylpropanethioate 2s



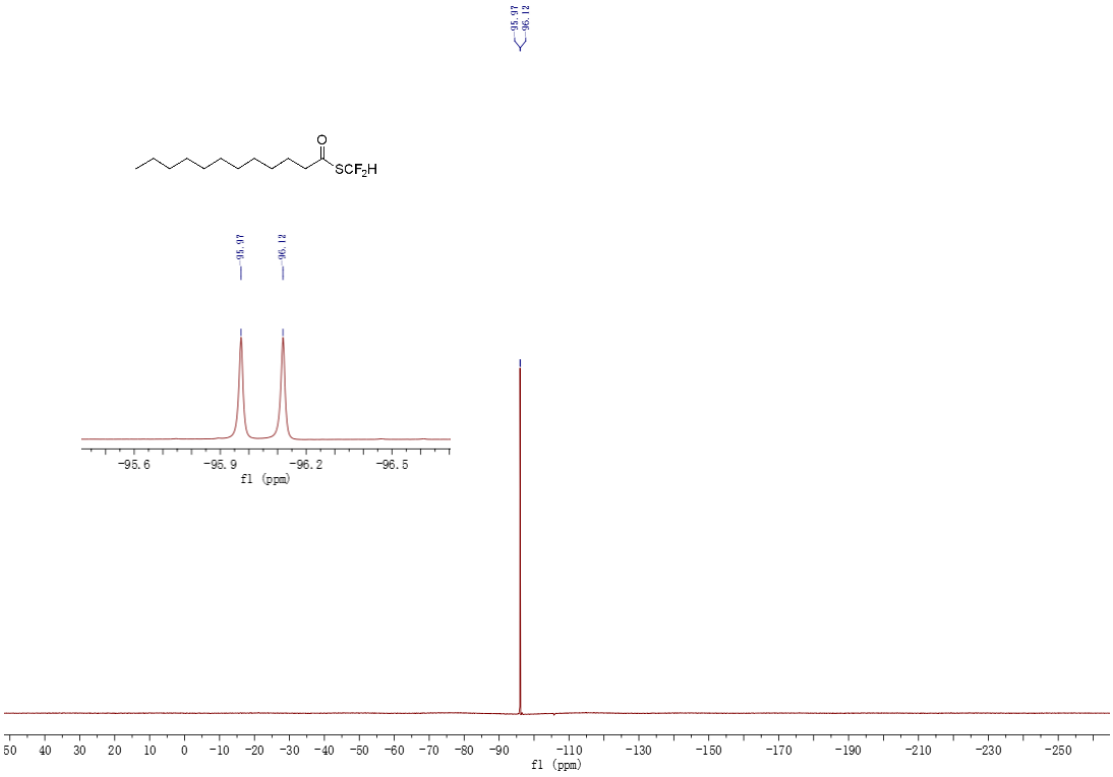
^{13}C NMR spectrum of S-(difluoromethyl) 3-(4-(*tert*-butyl)phenyl)-2-methylpropanethioate 2s



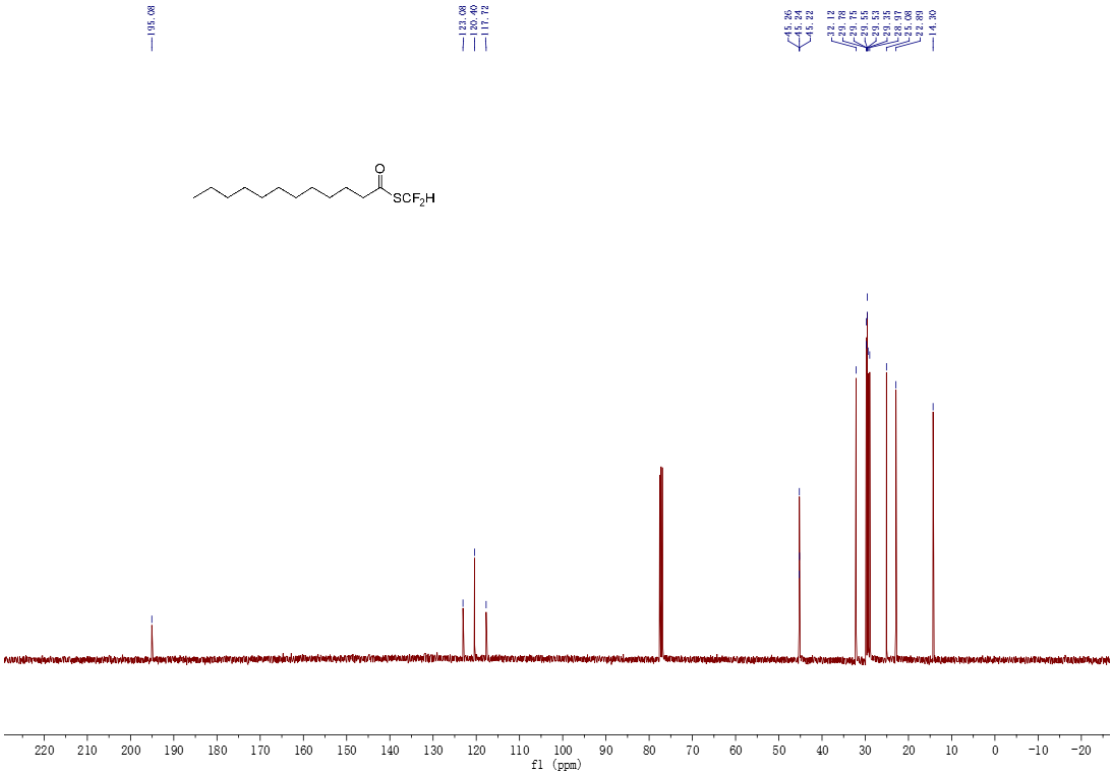
^{1}H NMR spectrum of S-(difluoromethyl) dodecanethioate 2t



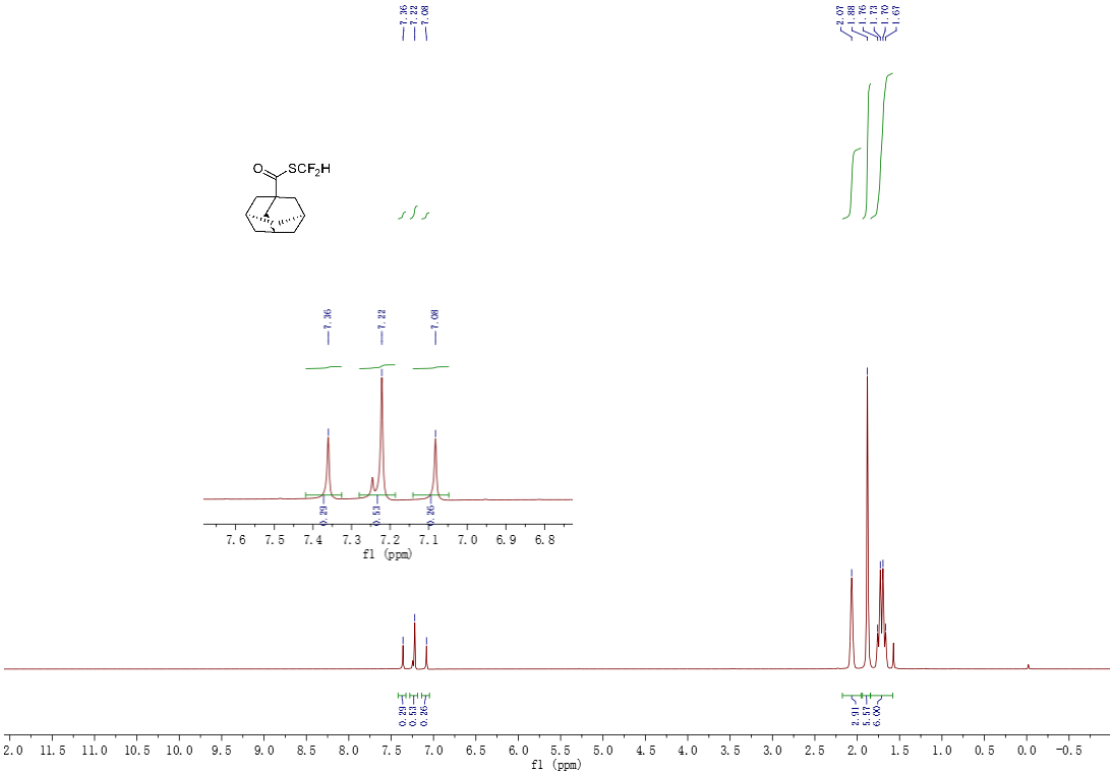
^{19}F NMR spectrum of S-(difluoromethyl) dodecanethioate 2t



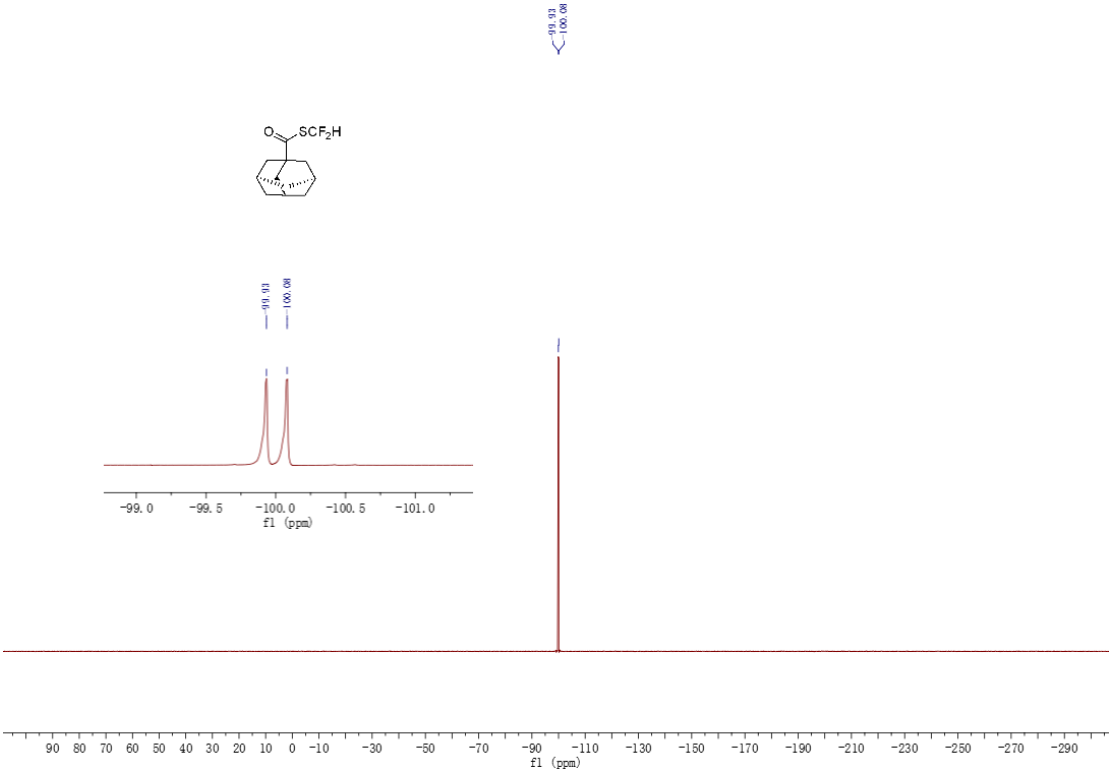
^{13}C NMR spectrum of S-(difluoromethyl) dodecanethioate 2t



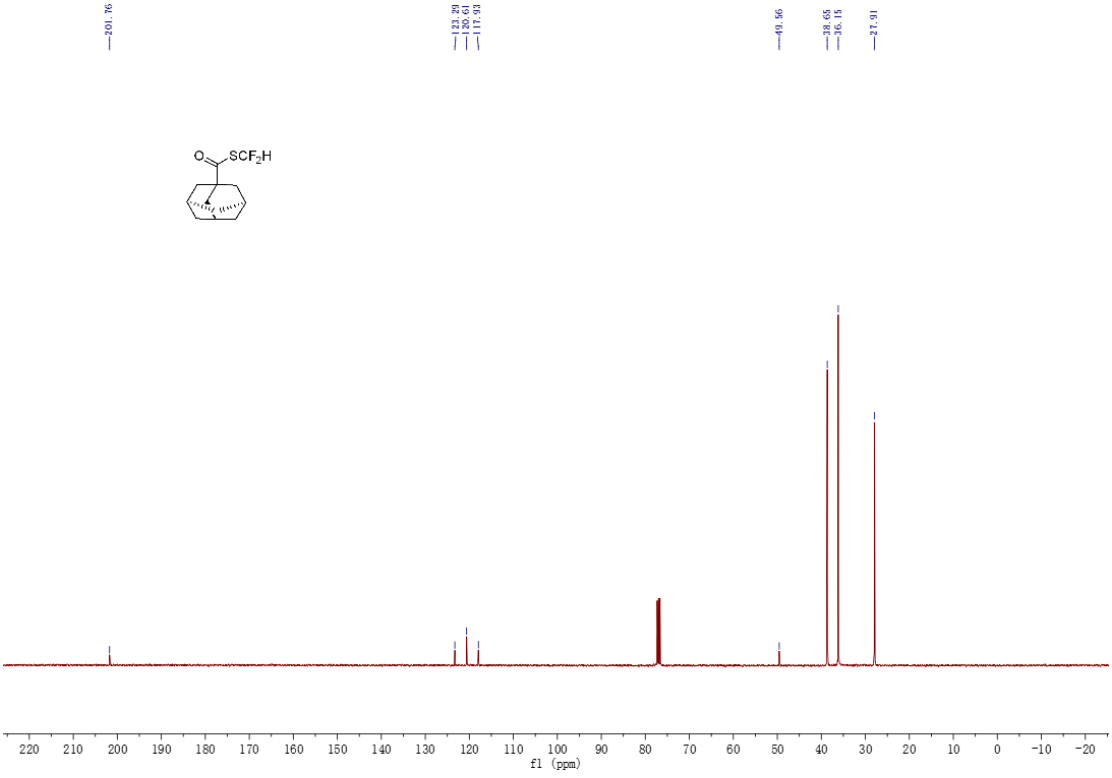
^{1}H NMR spectrum of S-(difluoromethyl) (*3r,5r,7r*)-adamantane-1-carbothioate 2u



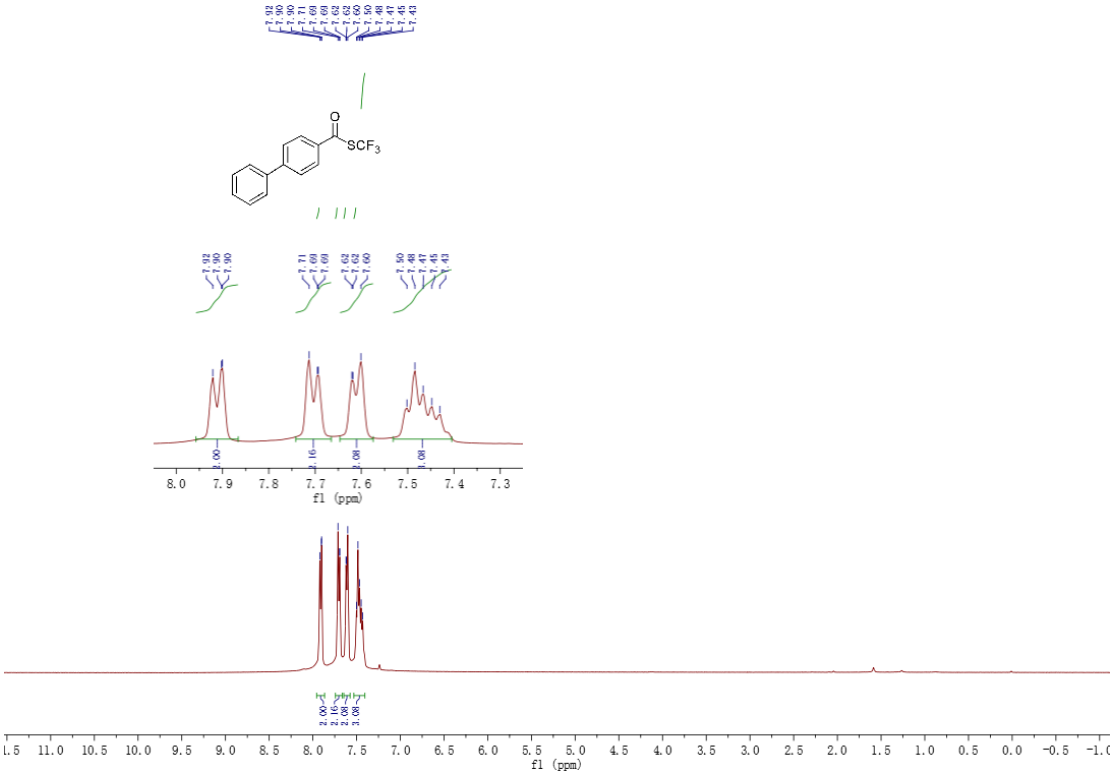
^{19}F NMR spectrum of
S-(difluoromethyl) (*3r,5r,7r*)-adamantane-1-carbothioate 2u



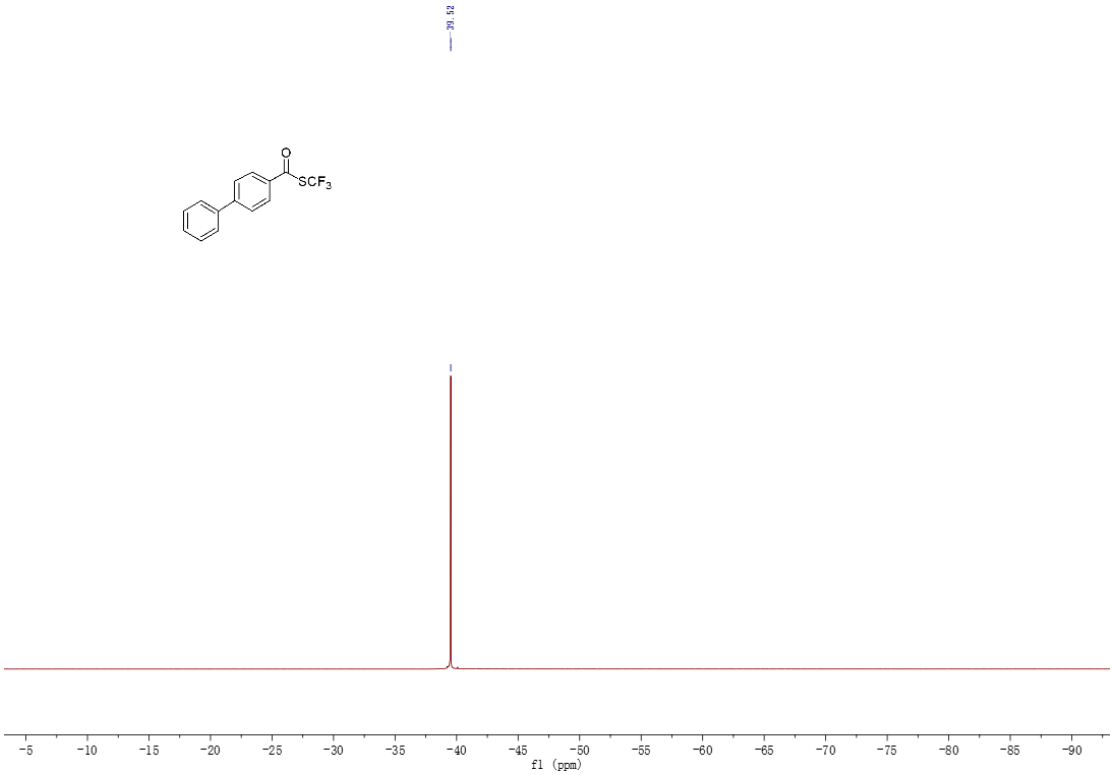
^{13}C NMR spectrum of
S-(difluoromethyl) (*3r,5r,7r*)-adamantane-1-carbothioate 2u



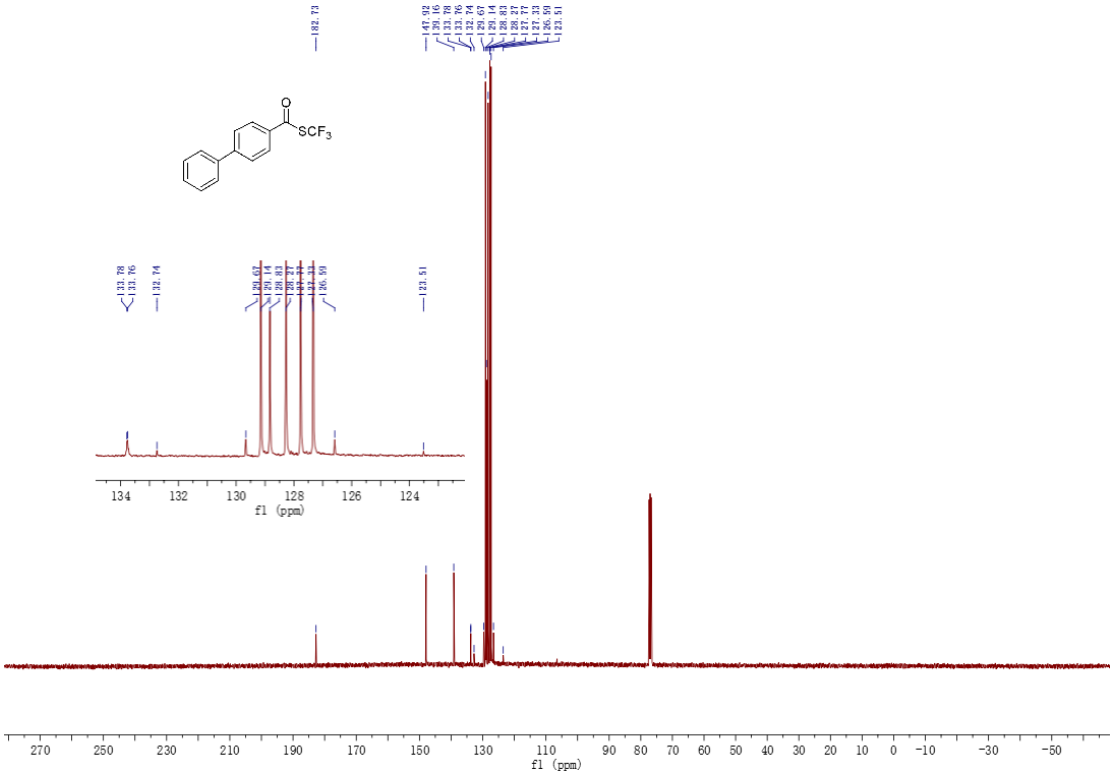
^{1}H NMR spectrum of S-(trifluoromethyl)(1,1'-biphenyl)-4-carbothioate 3a



^{19}F NMR spectrum of S-(trifluoromethyl)(1,1'-biphenyl)-4-carbothioate 3a



^{13}C NMR spectrum of
S-(trifluoromethyl)(1,1'-biphenyl)-4-carbothioate 3a



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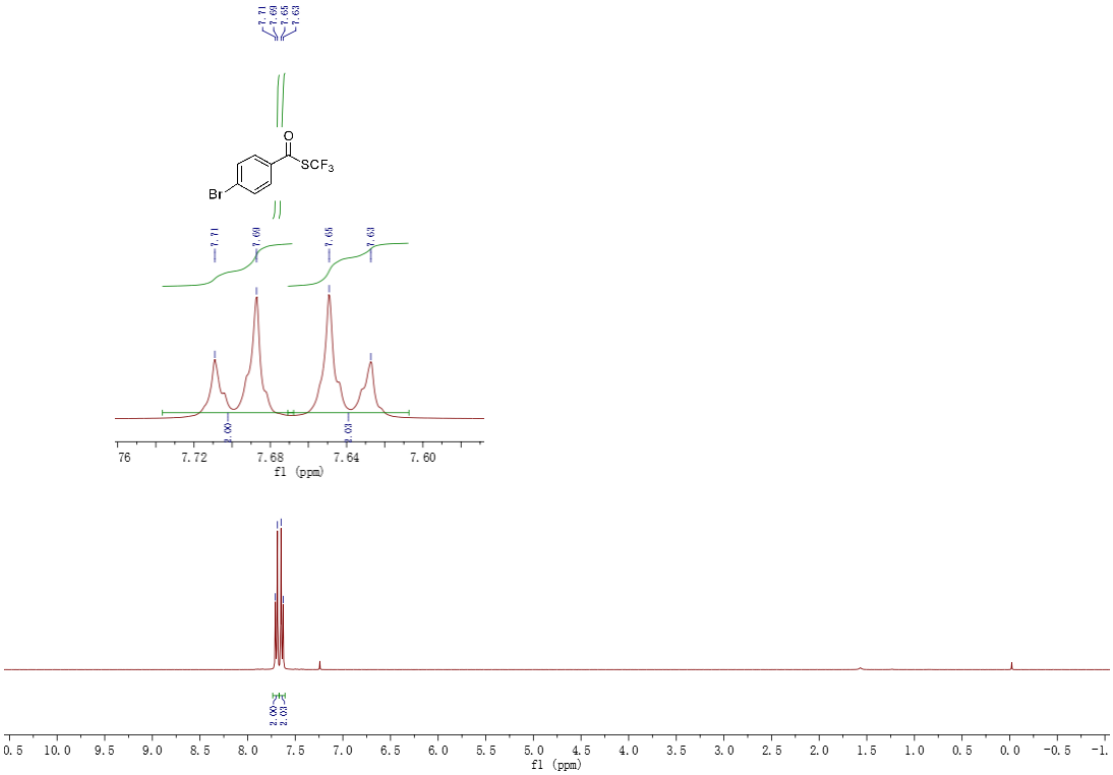
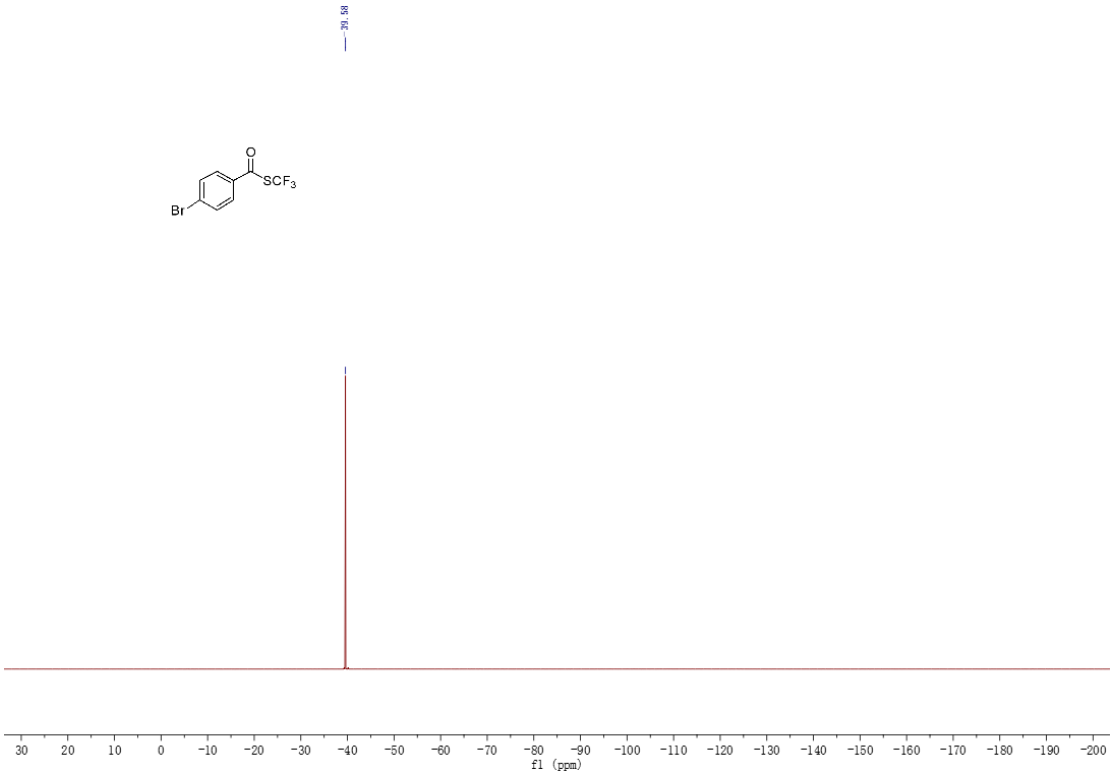
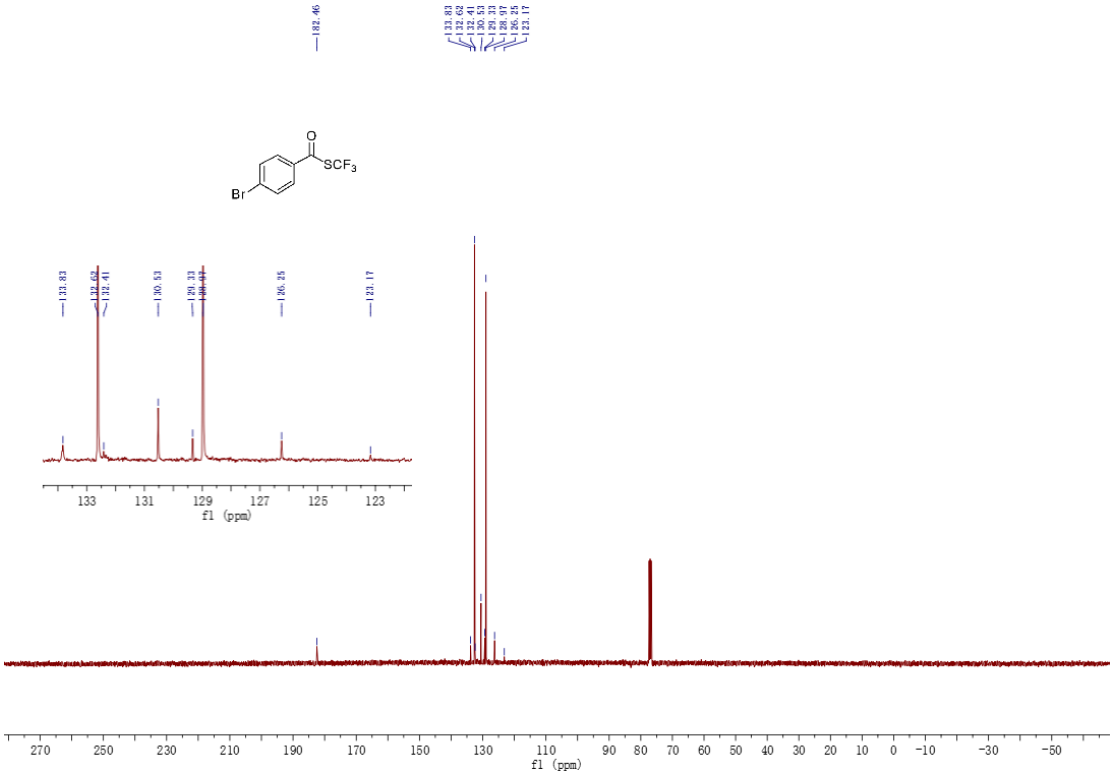
S-(trifluoromethyl)-4-bromobenzothioate 3b



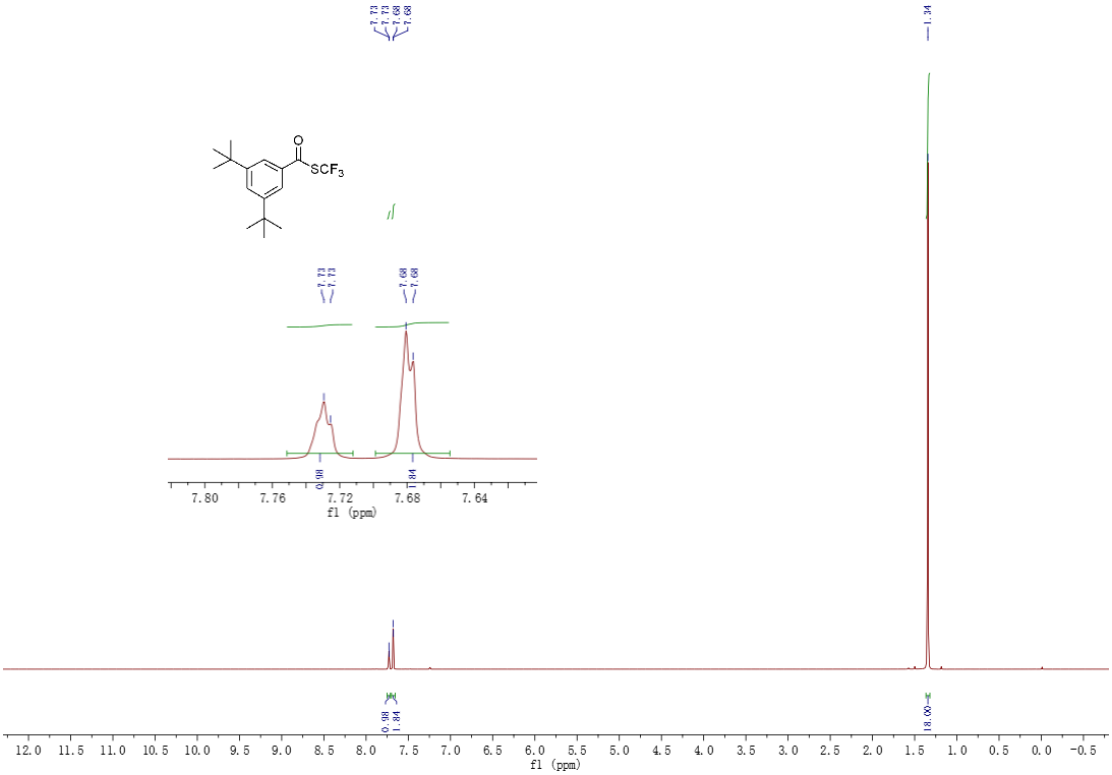
^{19}F NMR spectrum of S-(trifluoromethyl)-4-bromobenzothioate 3b



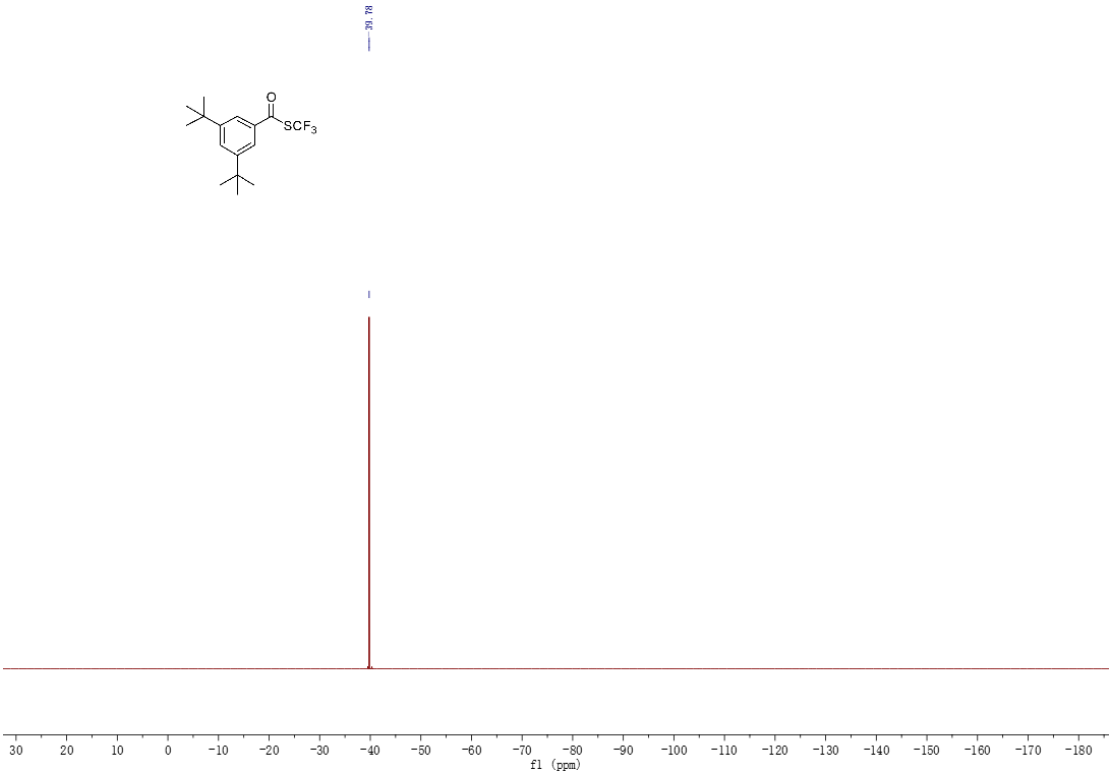
^{13}C NMR spectrum of S-(trifluoromethyl)-4-bromobenzothioate 3b



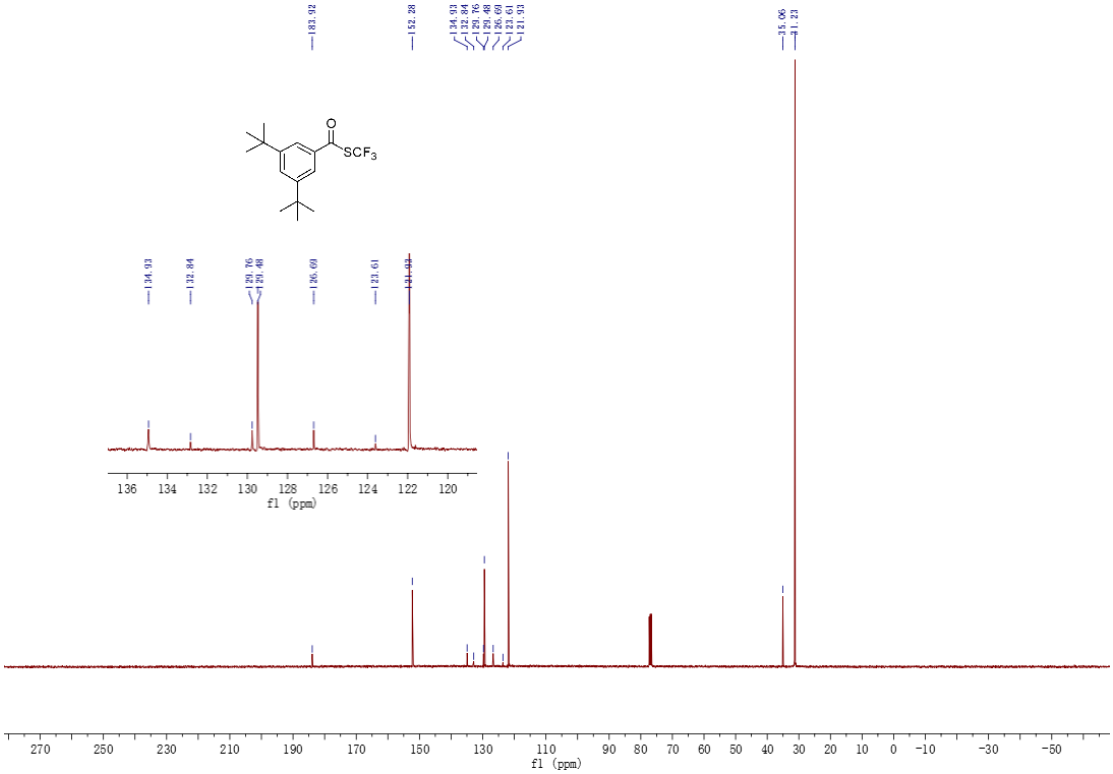
^{1}H NMR spectrum of S-(trifluoromethyl)-3,5-di-*tert*-butylbenzothioate 3c



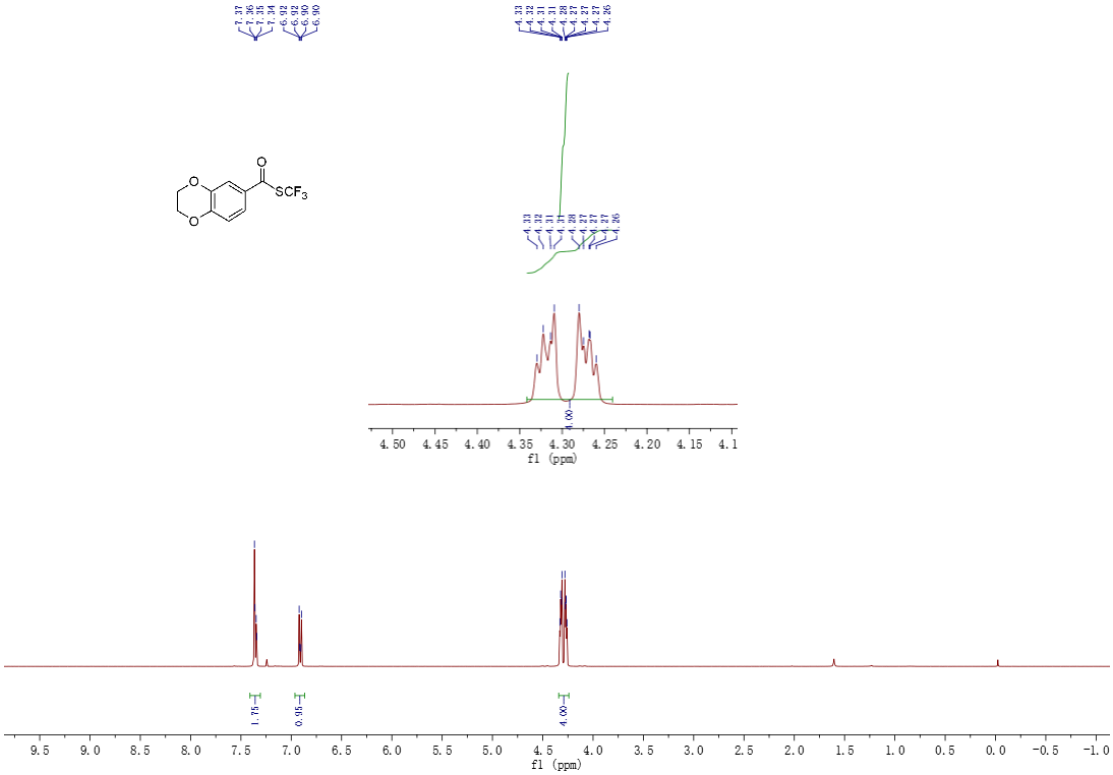
^{19}F NMR spectrum of S-(trifluoromethyl)-3,5-di-*tert*-butylbenzothioate 3c



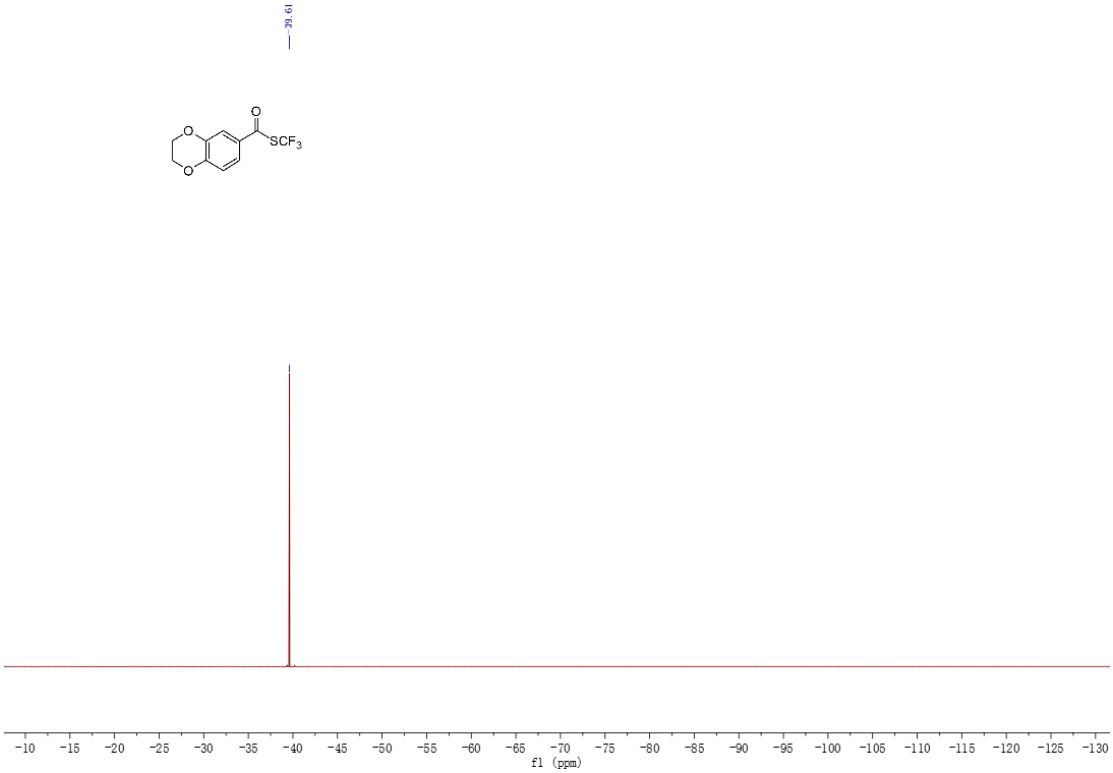
^{13}C NMR spectrum of
S-(trifluoromethyl)-3,5-di-*tert*-butylbenzothioate 3c



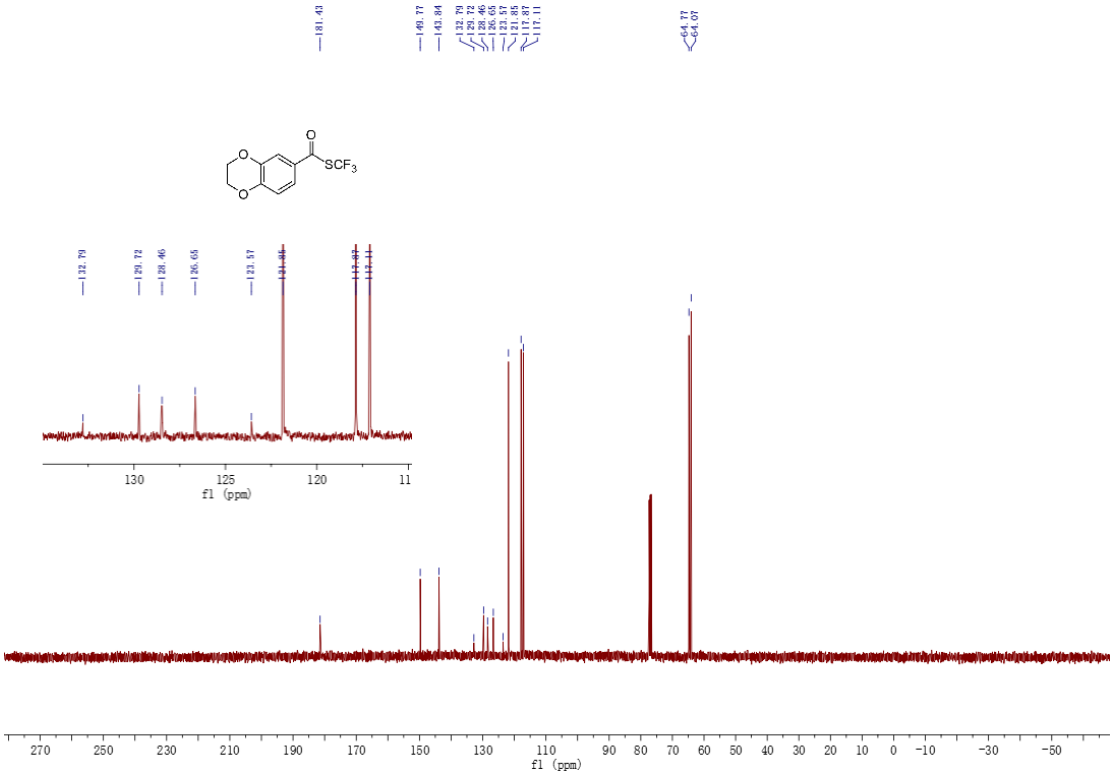
^{1}H NMR spectrum of
S-(trifluoromethyl)-2,3-dihydrobenzo[*b*](1,4]dioxine-6-carbothioate 3d



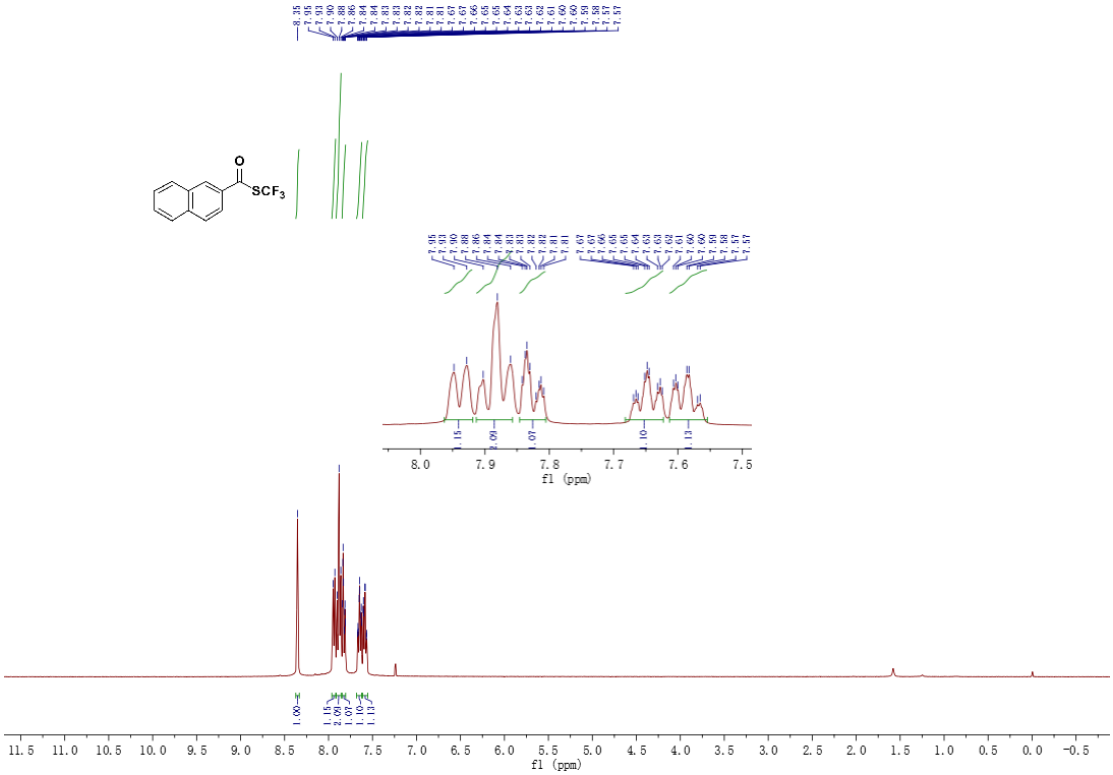
^{19}F NMR spectrum of S-(trifluoromethyl)-2,3-dihydrobenzo[*b*](1,4)dioxine-6-carbothioate 3d



^{13}C NMR spectrum of S-(trifluoromethyl)-2,3-dihydrobenzo[*b*](1,4]dioxine-6-carbothioate 3d



^{1}H NMR spectrum of S-(trifluoromethyl)-naphthalene-2-carbothioate 3e



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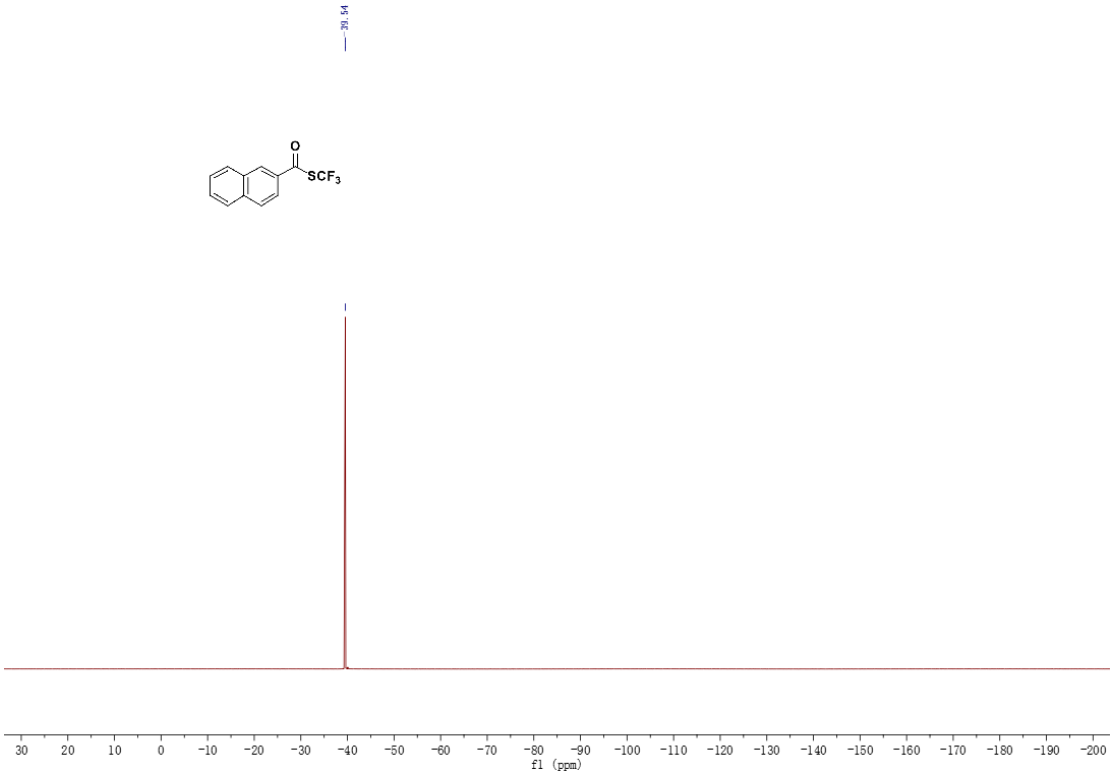
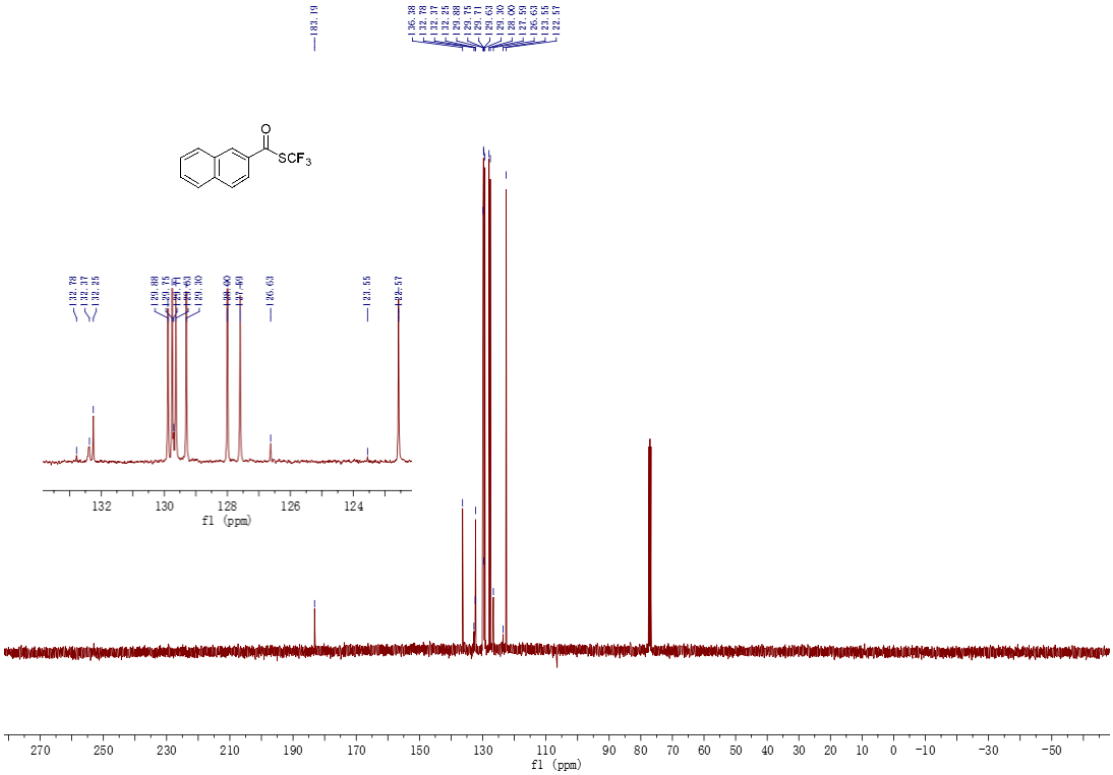
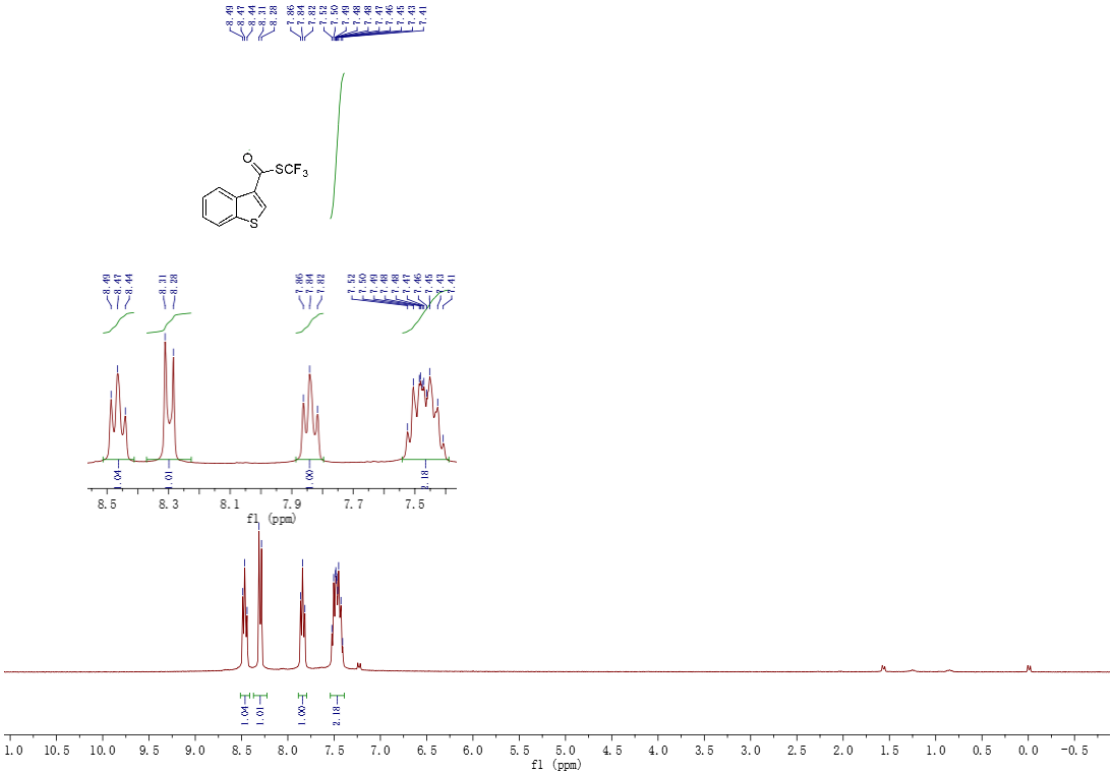


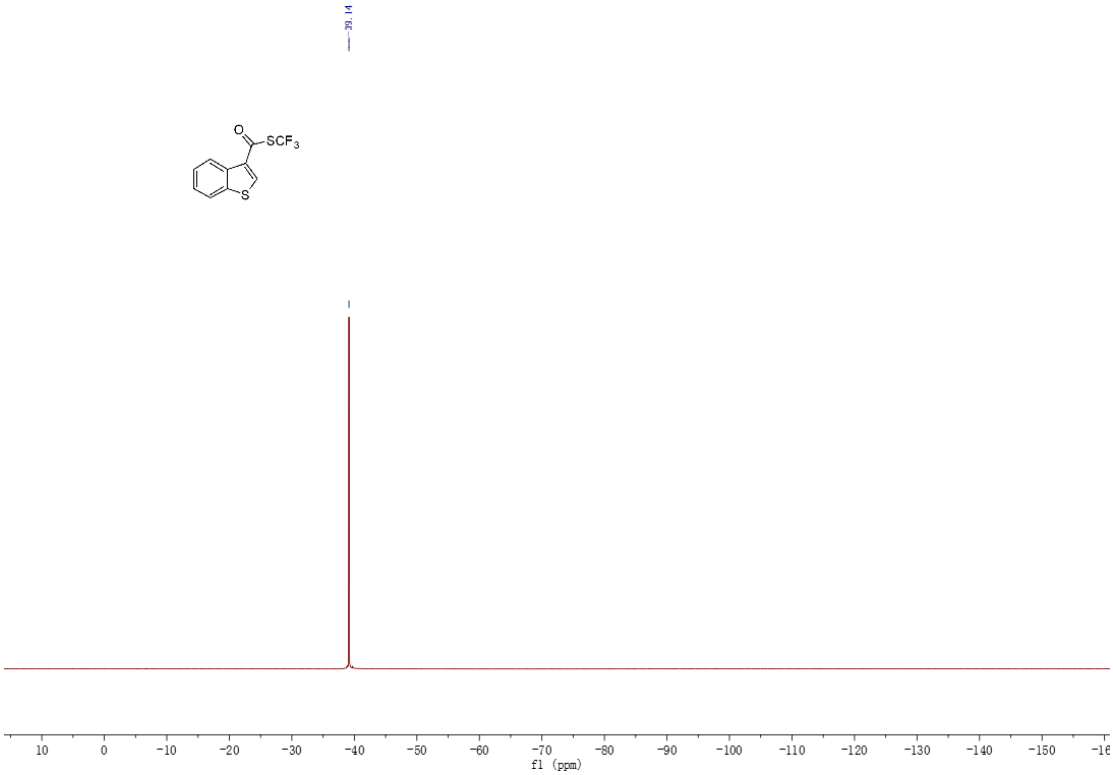
^{13}C NMR spectrum of
S-(trifluoromethyl)-naphthalene-2-carbothioate 3e



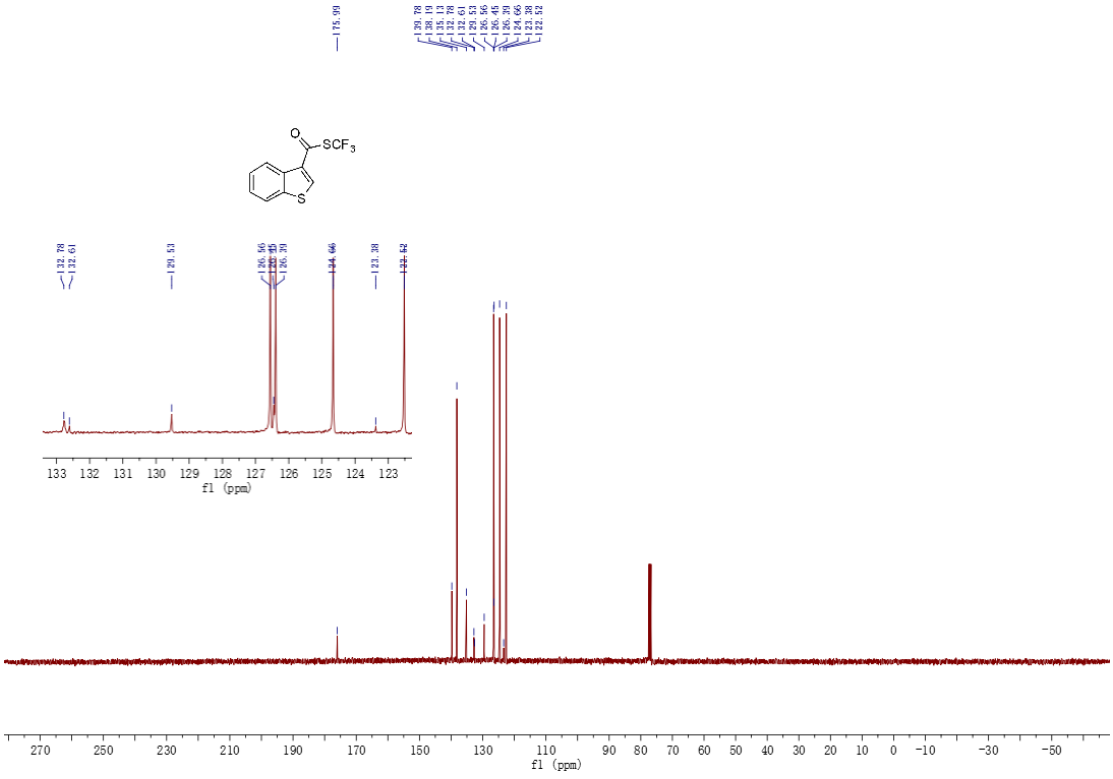
^{1}H NMR spectrum of
S-(trifluoromethyl)-benzo[*b*]thiophene-3-carbothioate 3f



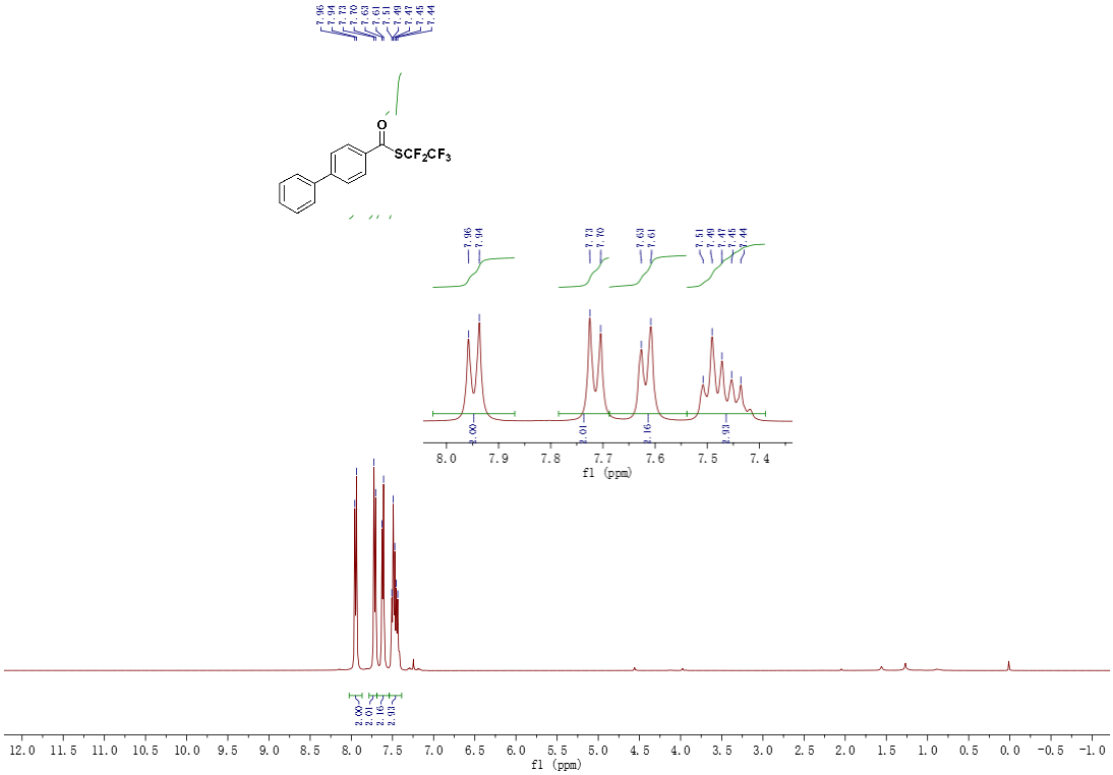
^{19}F NMR spectrum of S-(trifluoromethyl)-benzo[*b*]thiophene-3-carbothioate 3f



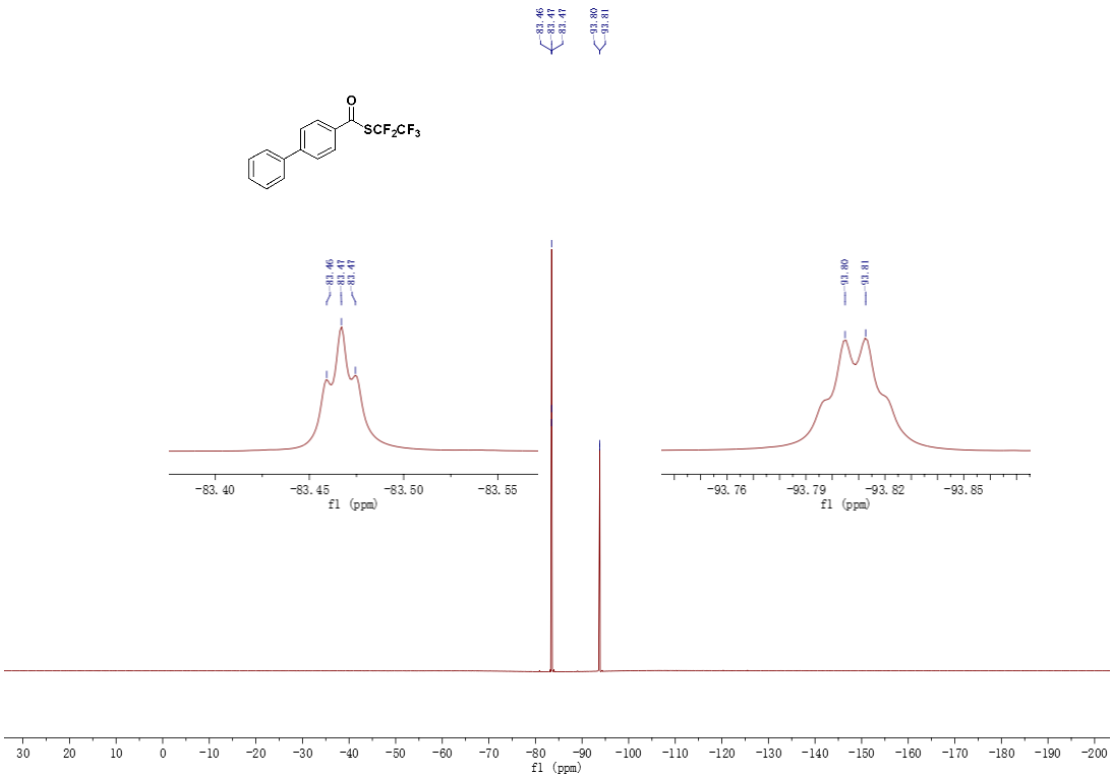
^{13}C NMR spectrum of S-(trifluoromethyl)benzo[*b*]thiophene-3-carbothioate 3f



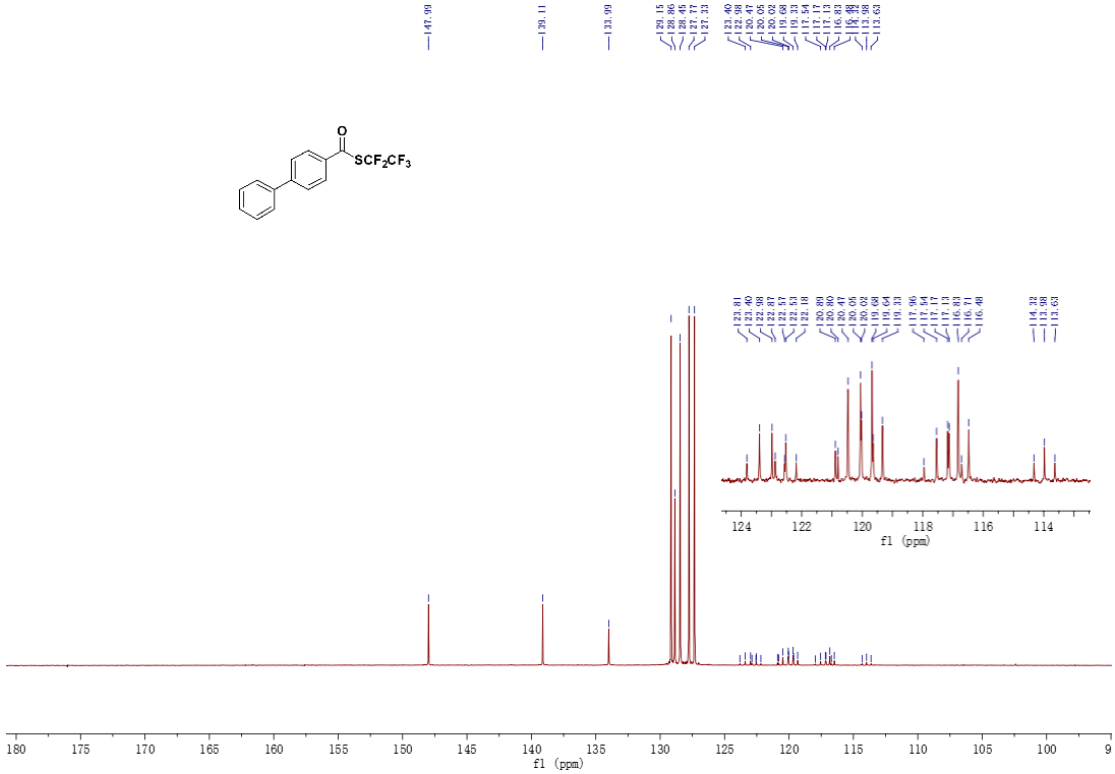
^{1}H NMR spectrum of S-(pentafluoroethyl)(1,1'-biphenyl)-4-carbothioate 4a



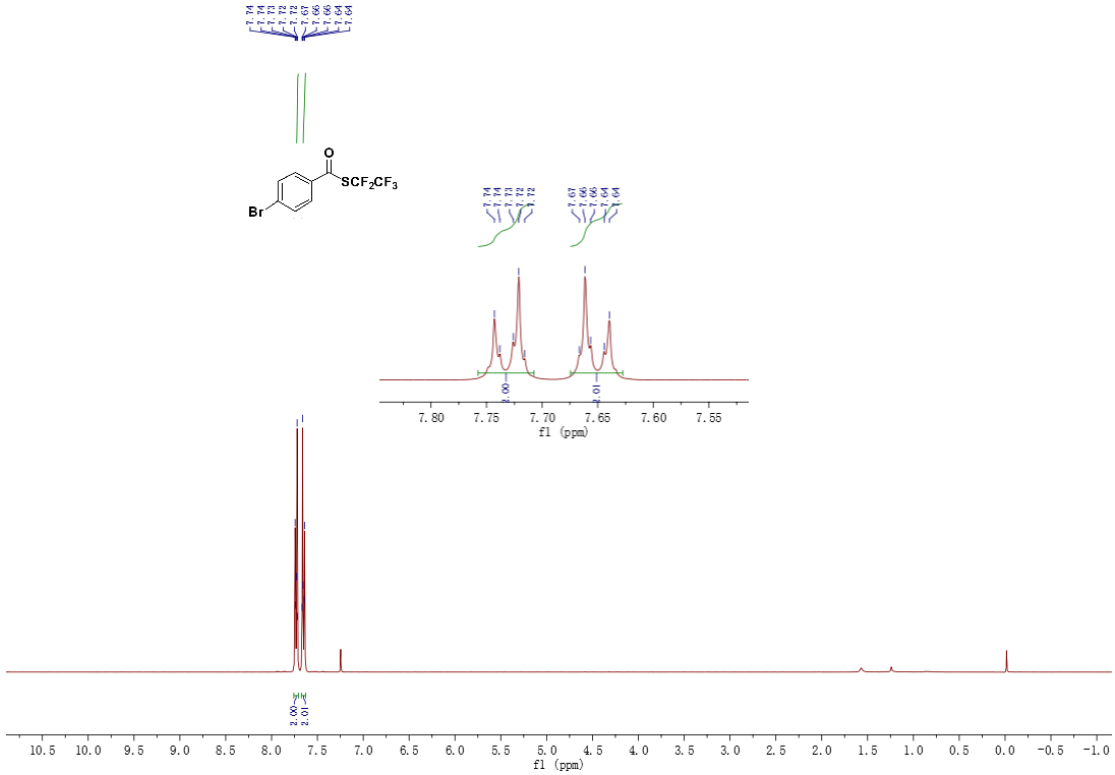
^{19}F NMR spectrum of S-(pentafluoroethyl)(1,1'-biphenyl)-4-carbothioate 4a



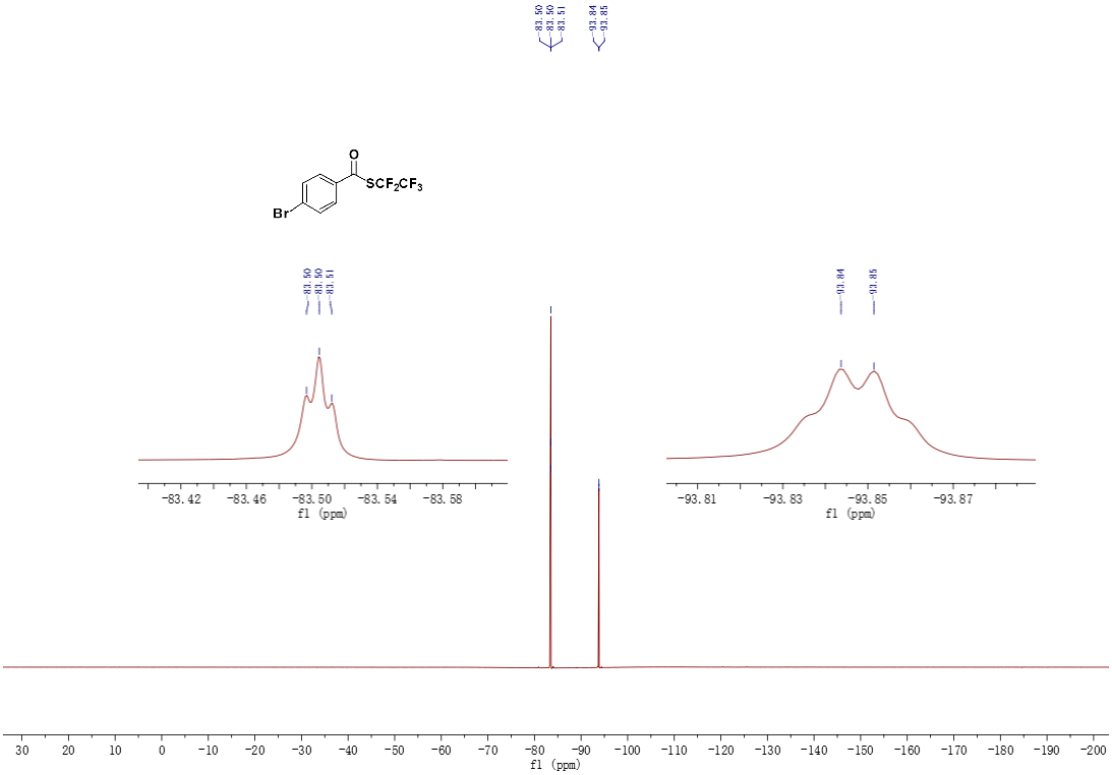
^{13}C NMR spectrum of S-(pentafluoroethyl)(1,1'-biphenyl)-4-carbothioate 4a



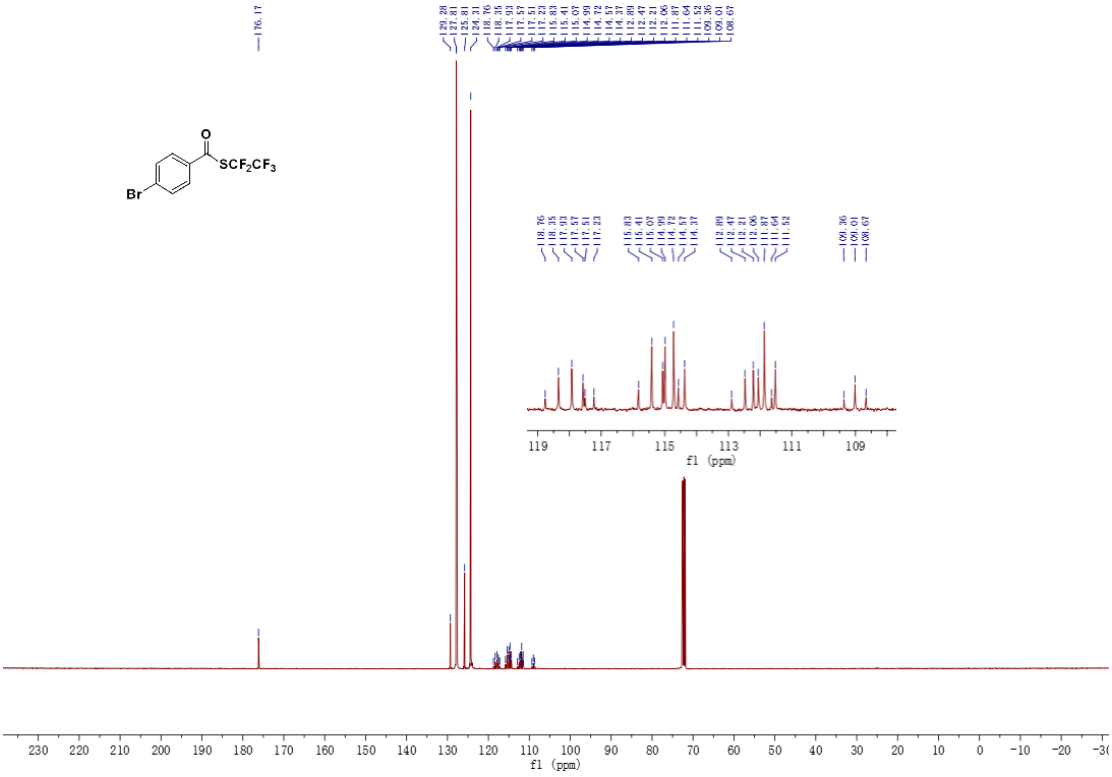
^{1}H NMR spectrum of S-(pentafluoroethyl)-4-bromobenzothioate 4b



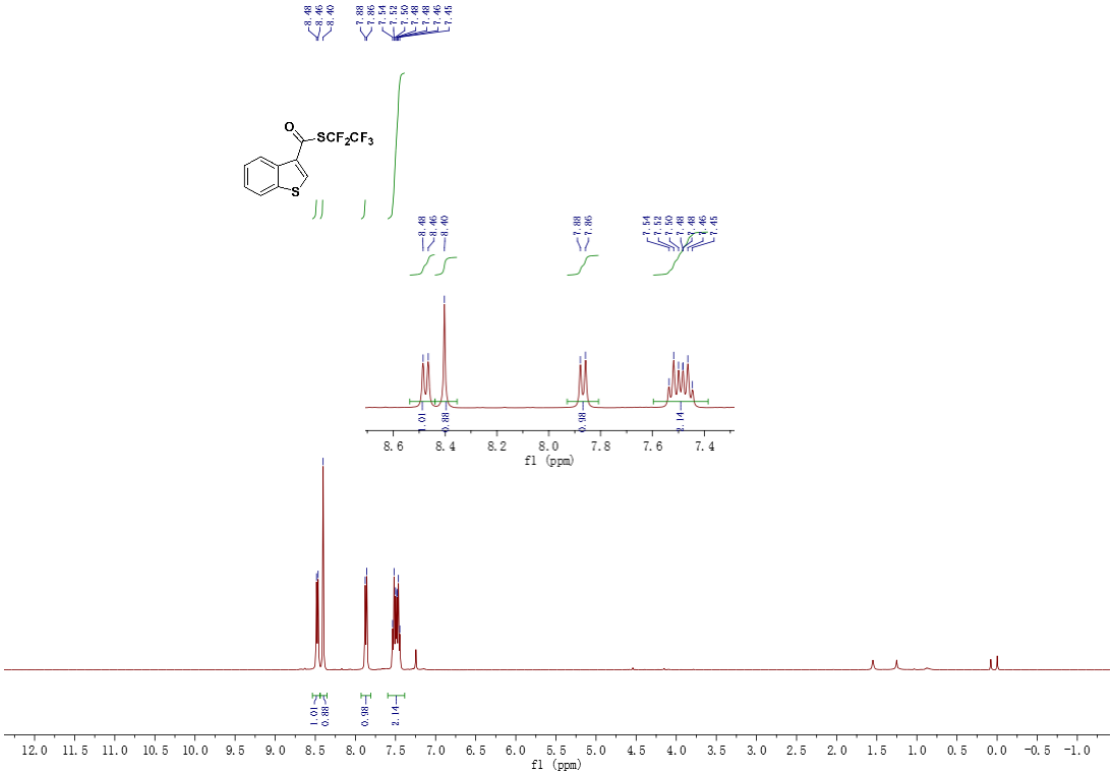
^{19}F NMR spectrum of S-(pentafluoroethyl)-4-bromobenzothioate 4b



^{13}C NMR spectrum of S-(pentafluoroethyl)-4-bromobenzothioate 4b



^{1}H NMR spectrum of
S-(pentafluoroethyl)-benzo[*b*]thiophene-3-carbothioate 4c



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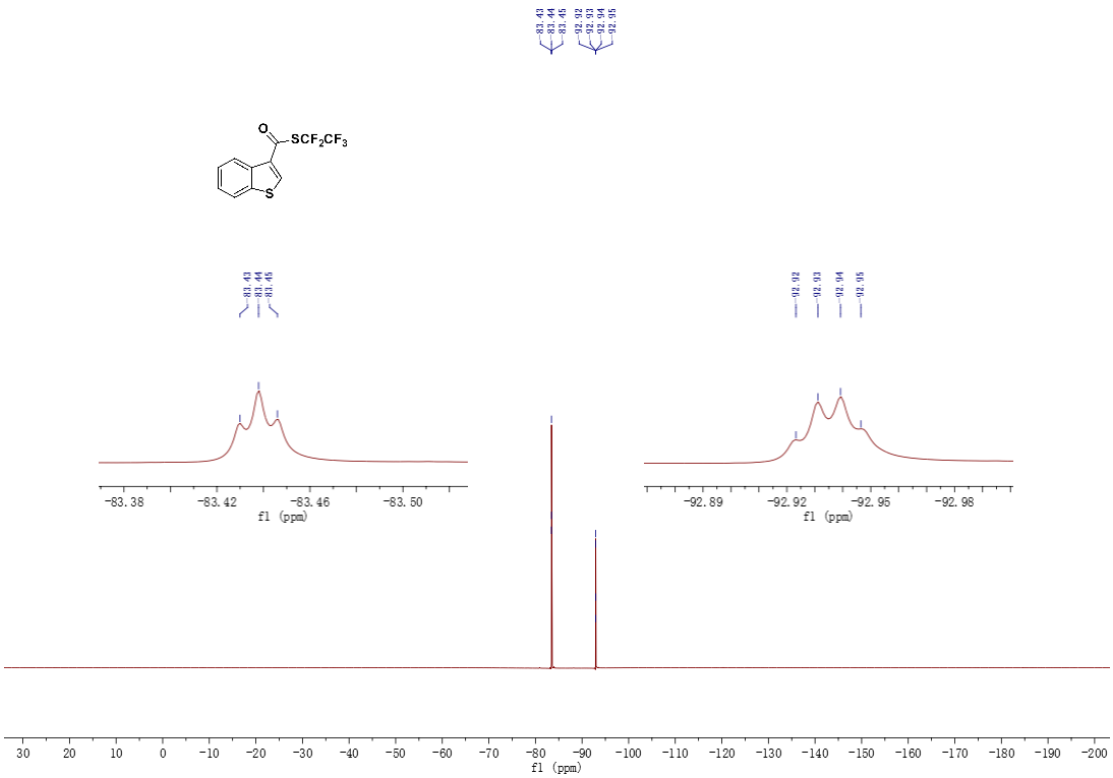
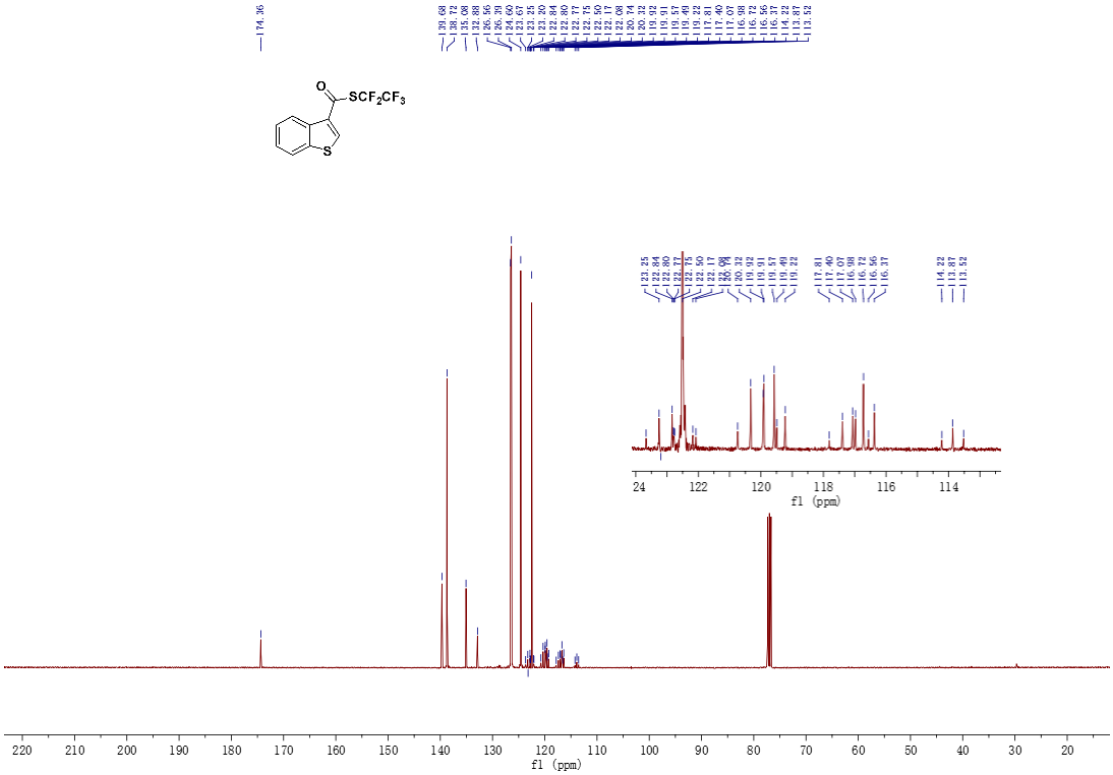
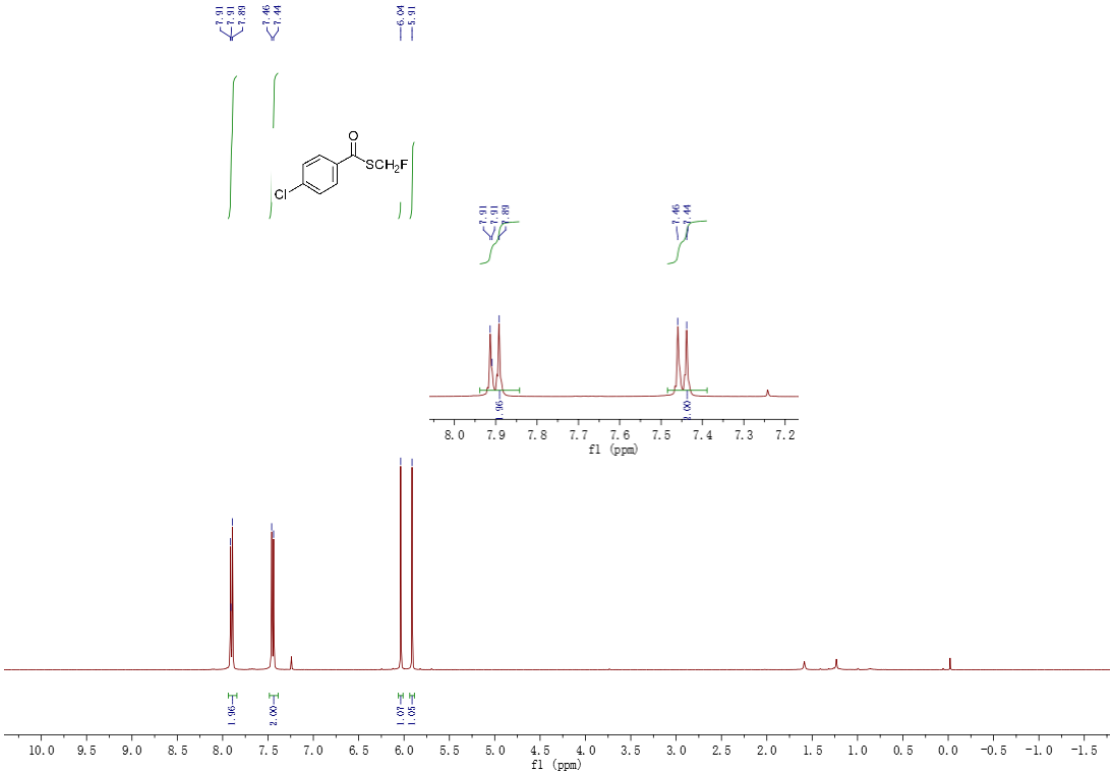


^{13}C NMR spectrum of S-(pentafluoroethyl)-benzo[*b*]thiophene-3-carbothioate 4c



^{1}H NMR spectrum of S-(fluoromethyl)-4-chlorobenzothioate 5a



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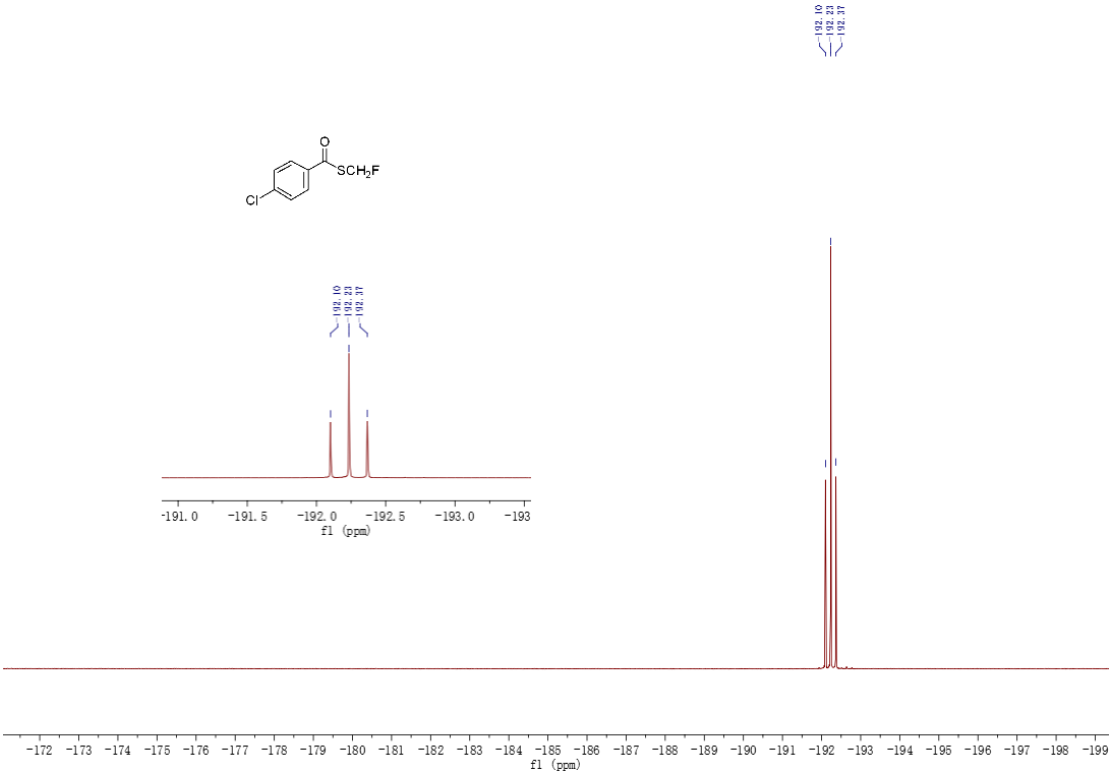
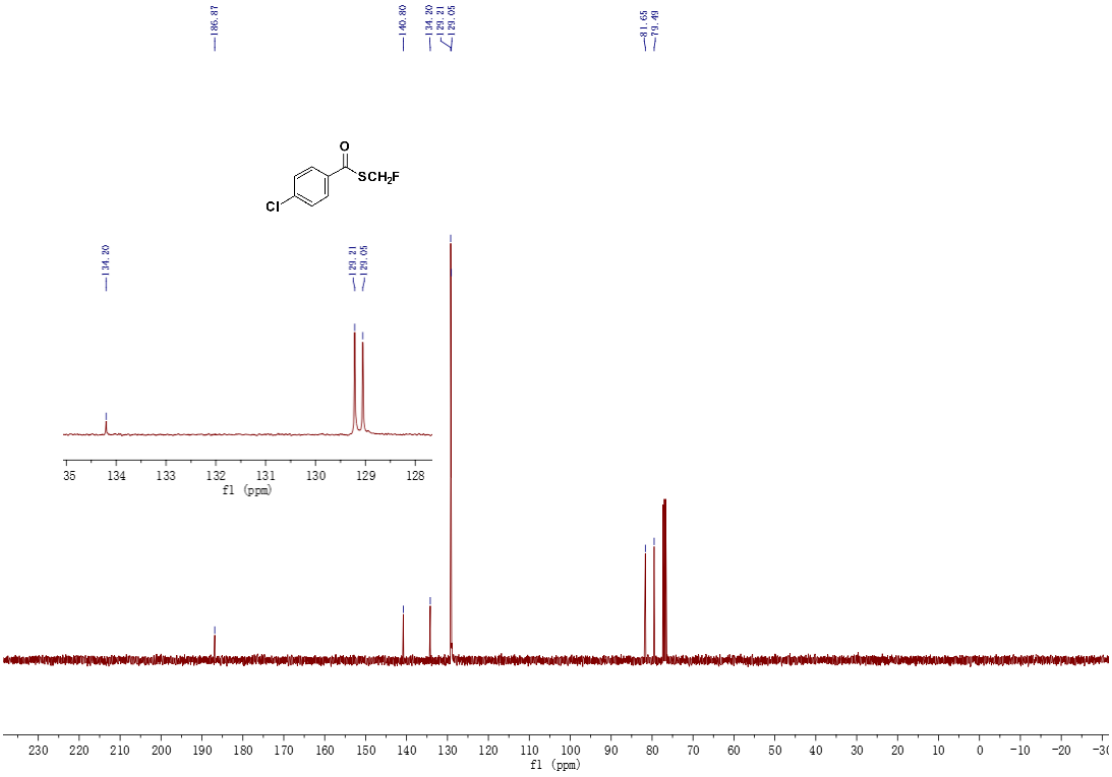
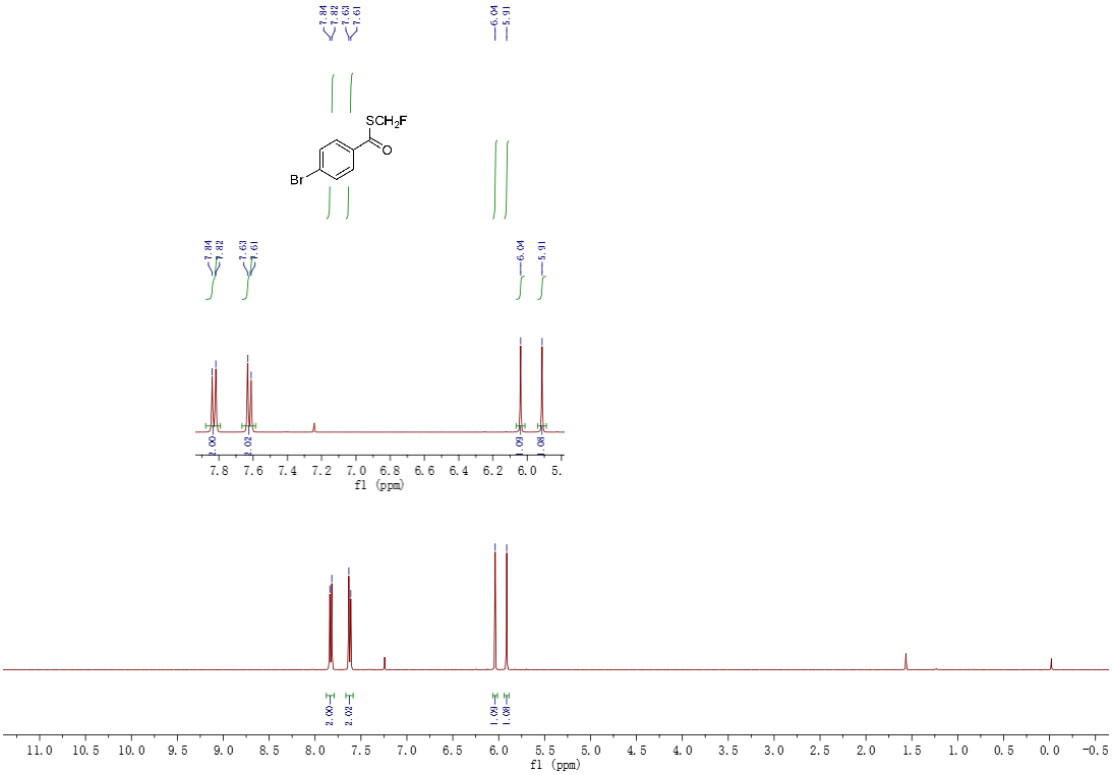


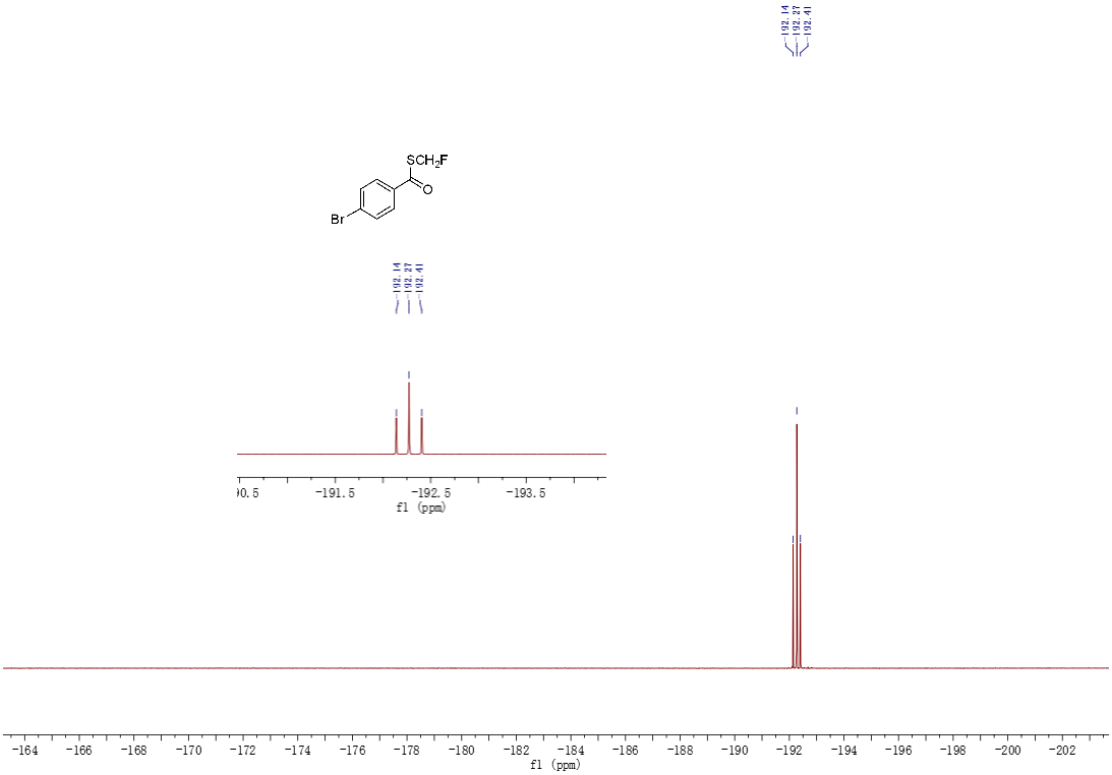
^{13}C NMR spectrum of S-(fluoromethyl)-4-chlorobenzothioate 5a



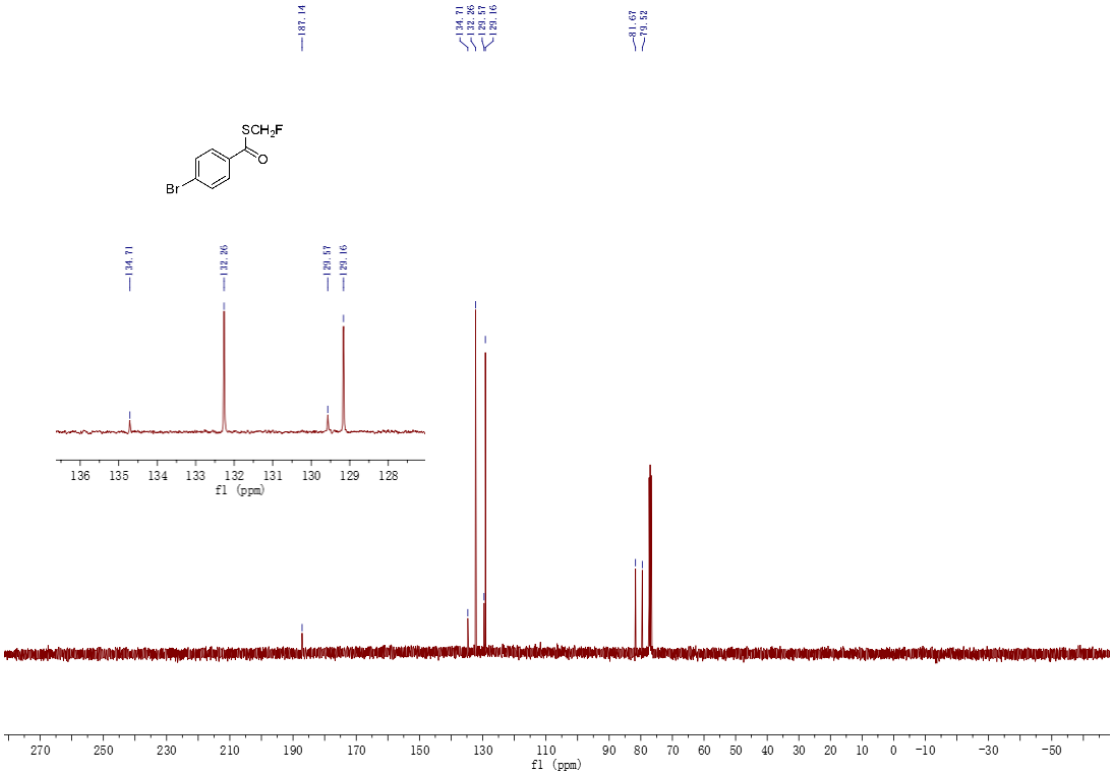
^{1}H NMR spectrum of S-(fluoromethyl)-4-bromobenzothioate 5b



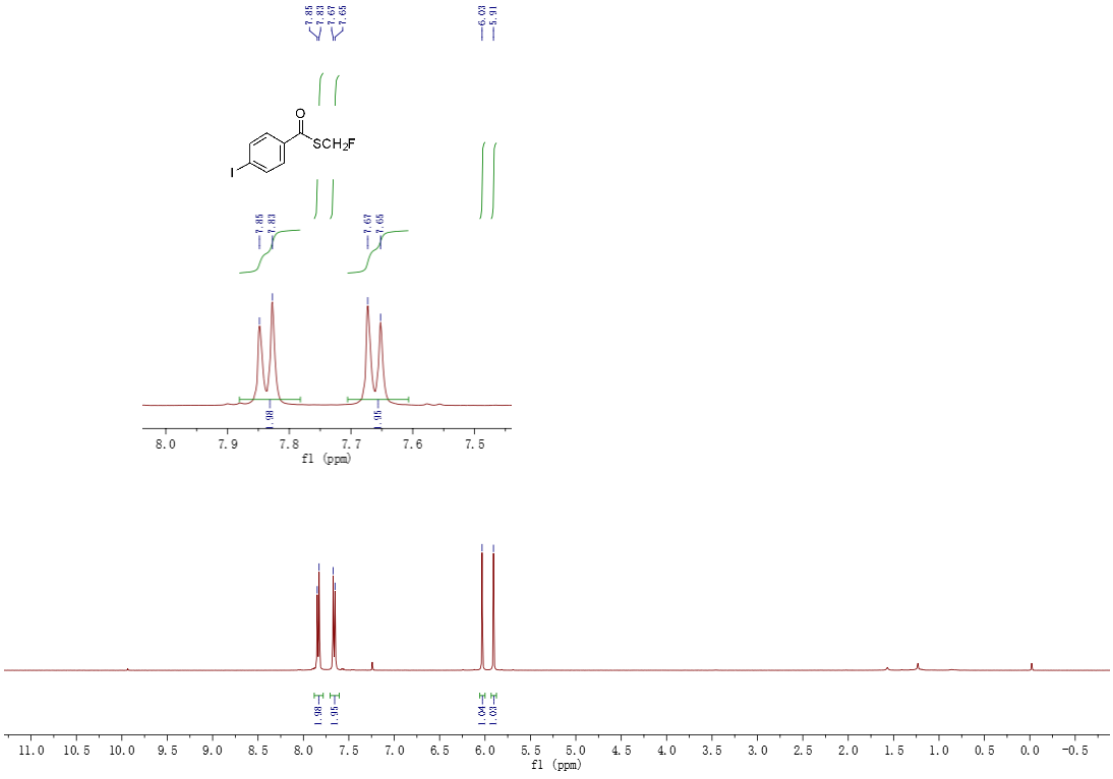
^{19}F NMR spectrum of S-(fluoromethyl)-4-bromobenzothioate 5b



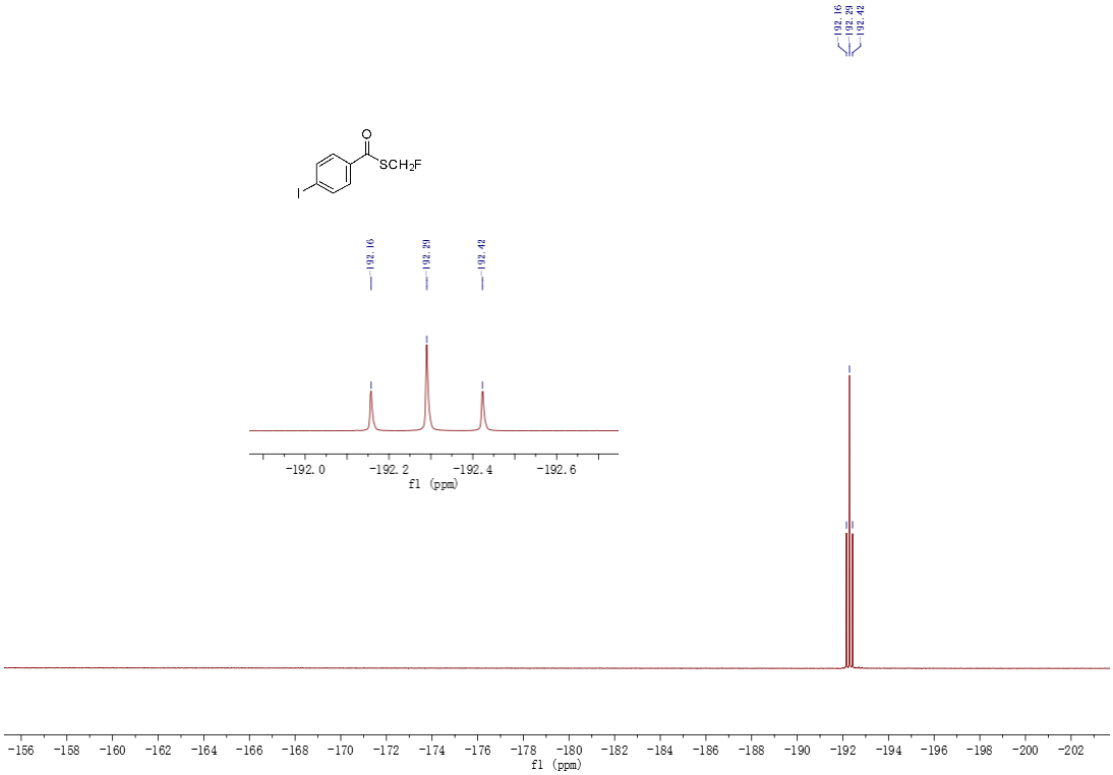
^{13}C NMR spectrum of S-(fluoromethyl)-4-bromobenzothioate 5b



^{1}H NMR spectrum of S-(fluoromethyl)-4-iodobenzothioate 5c



^{19}F NMR spectrum of S-(fluoromethyl)-4-iodobenzothioate 5c



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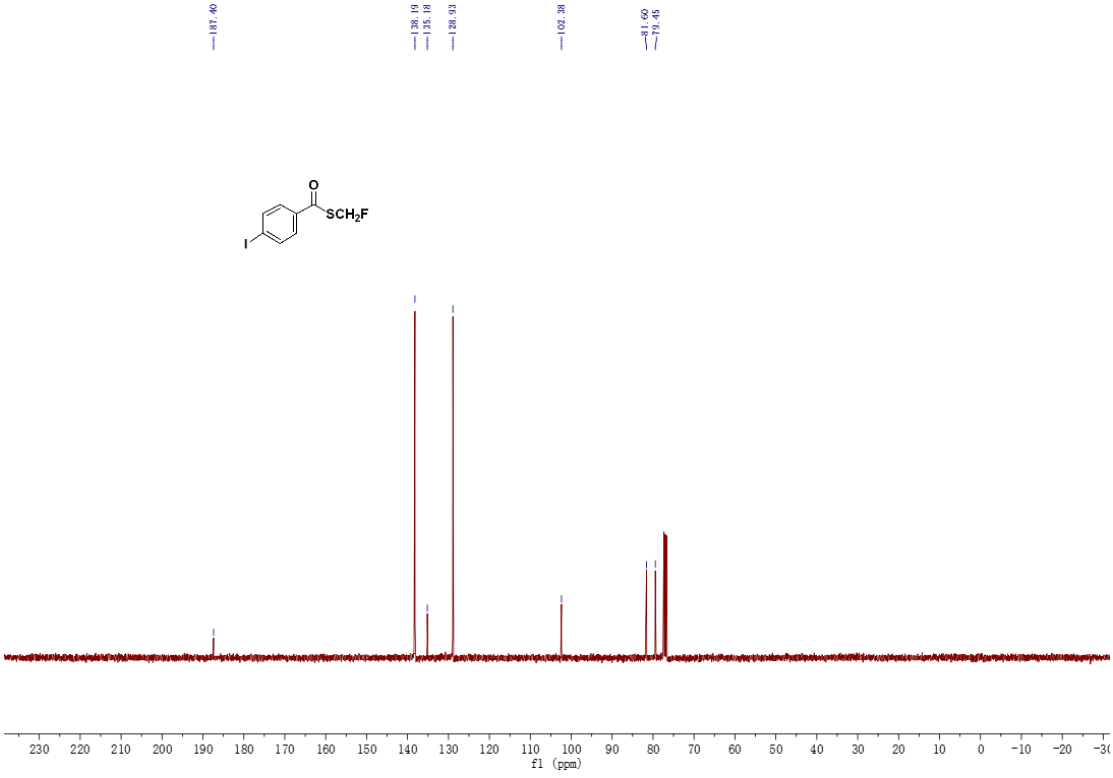
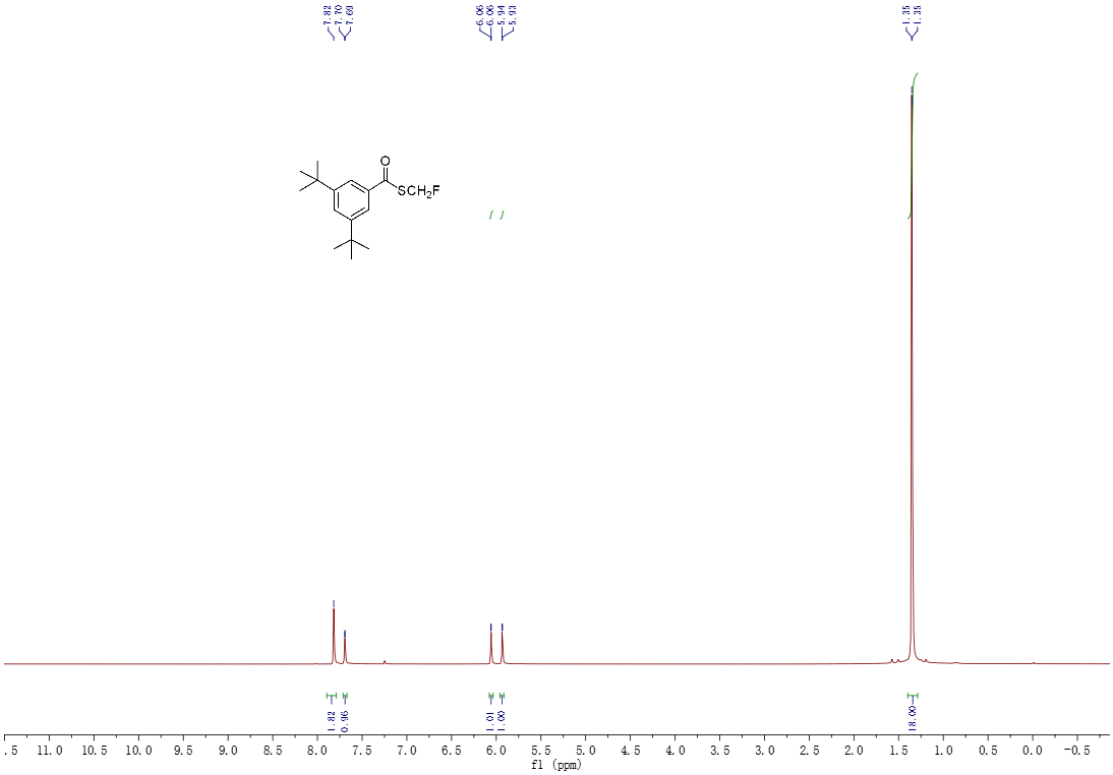
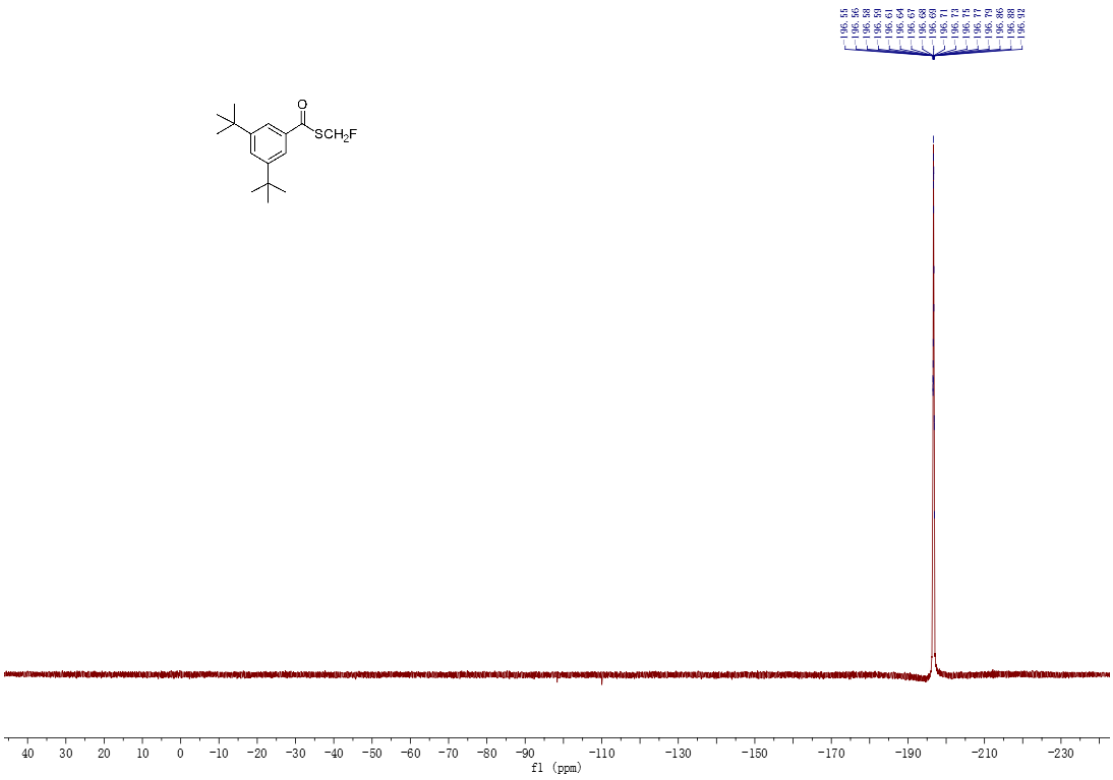


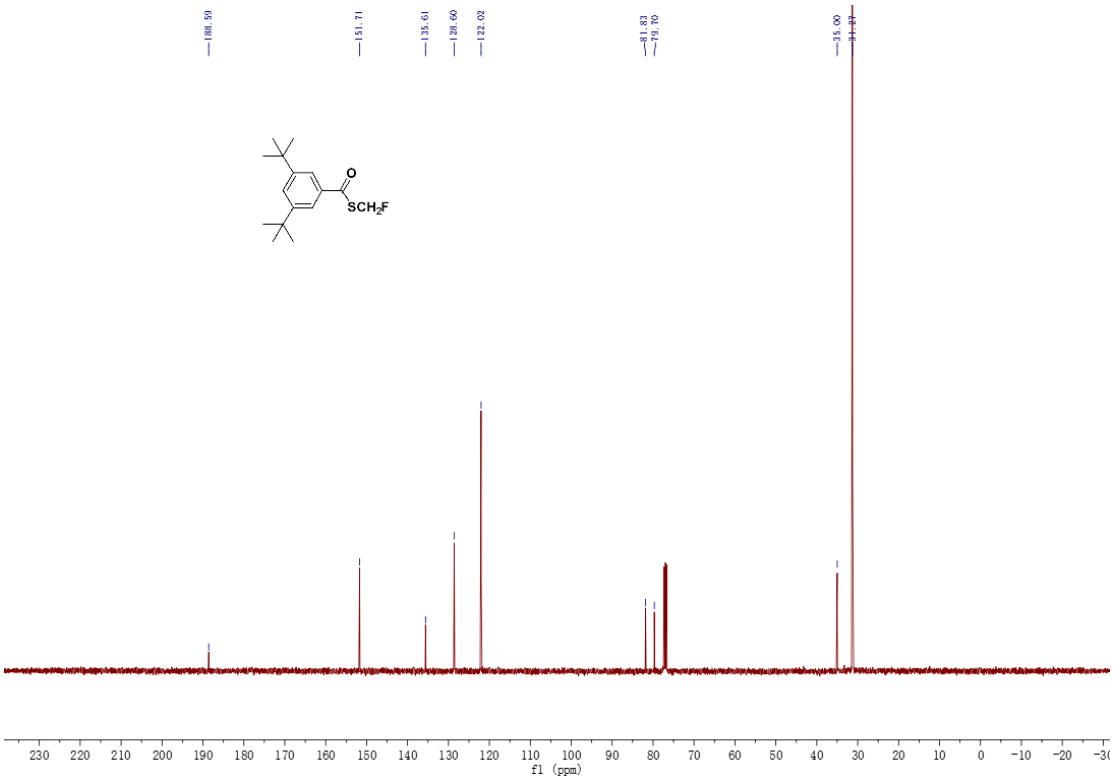
^{1}H NMR spectrum of S-(fluoromethyl)-3,5-di-*tert*-butylbenzothioate 5d



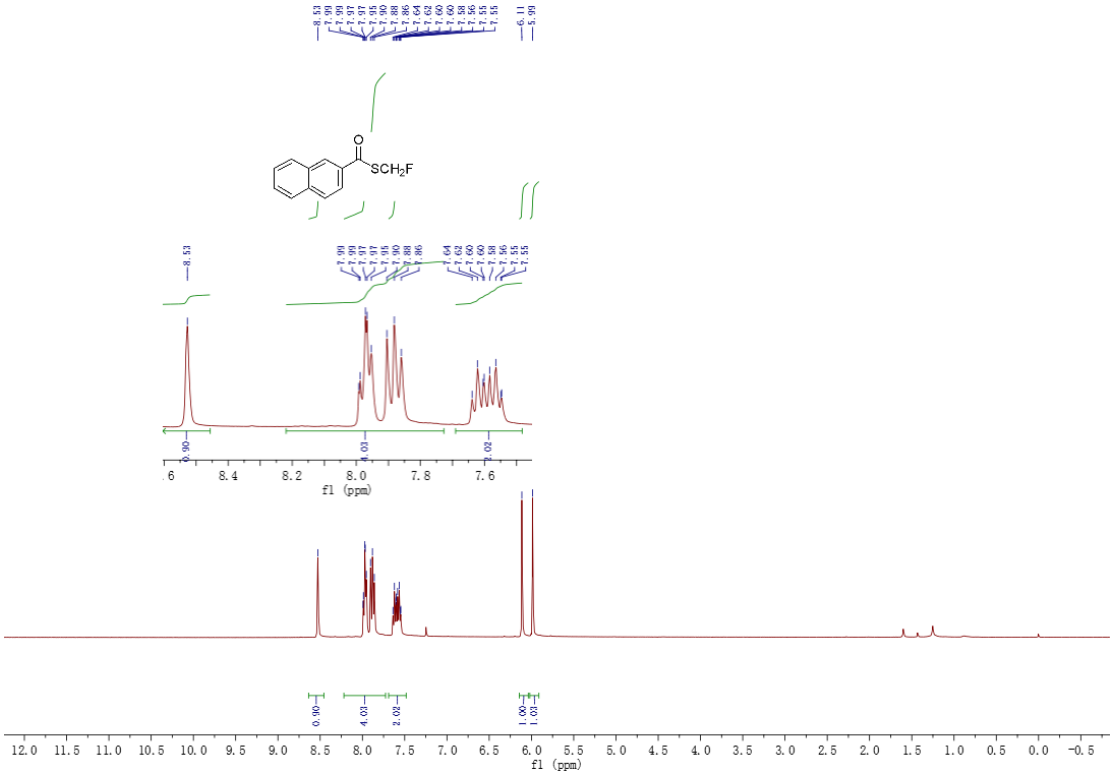
^{19}F NMR spectrum of S-(fluoromethyl)-3,5-di-*tert*-butylbenzothioate 5d



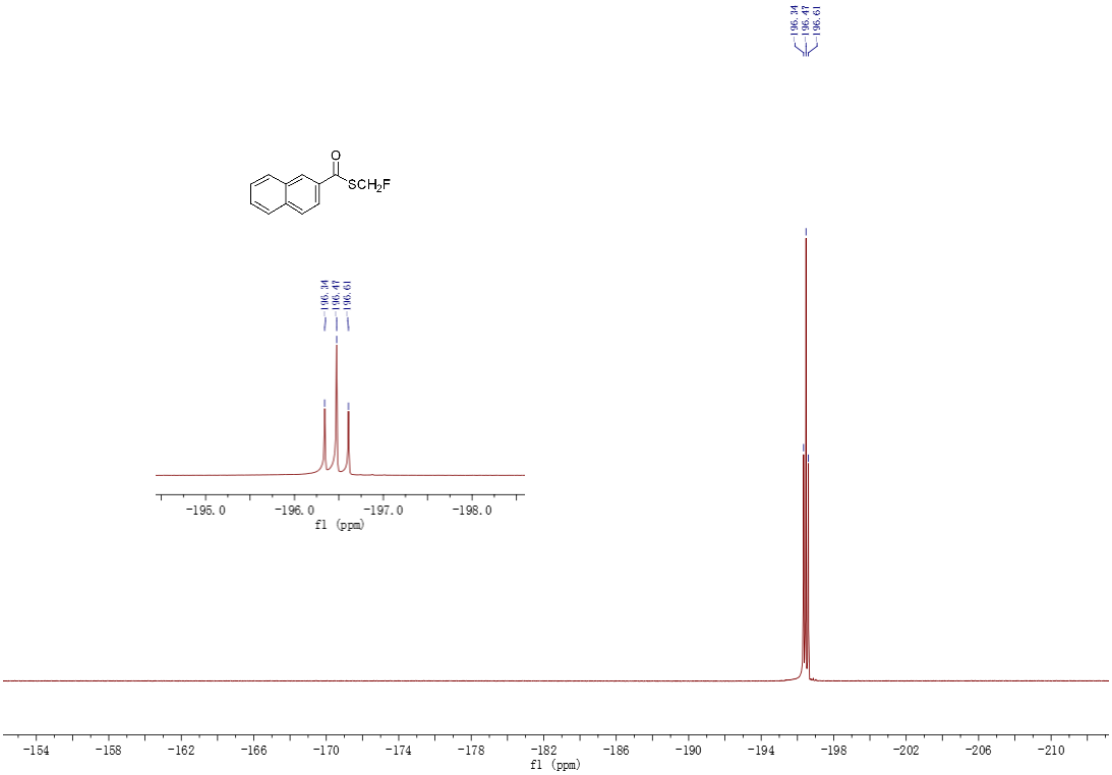
^{13}C NMR spectrum of S-(fluoromethyl)-3,5-di-*tert*-butylbenzothioate 5d



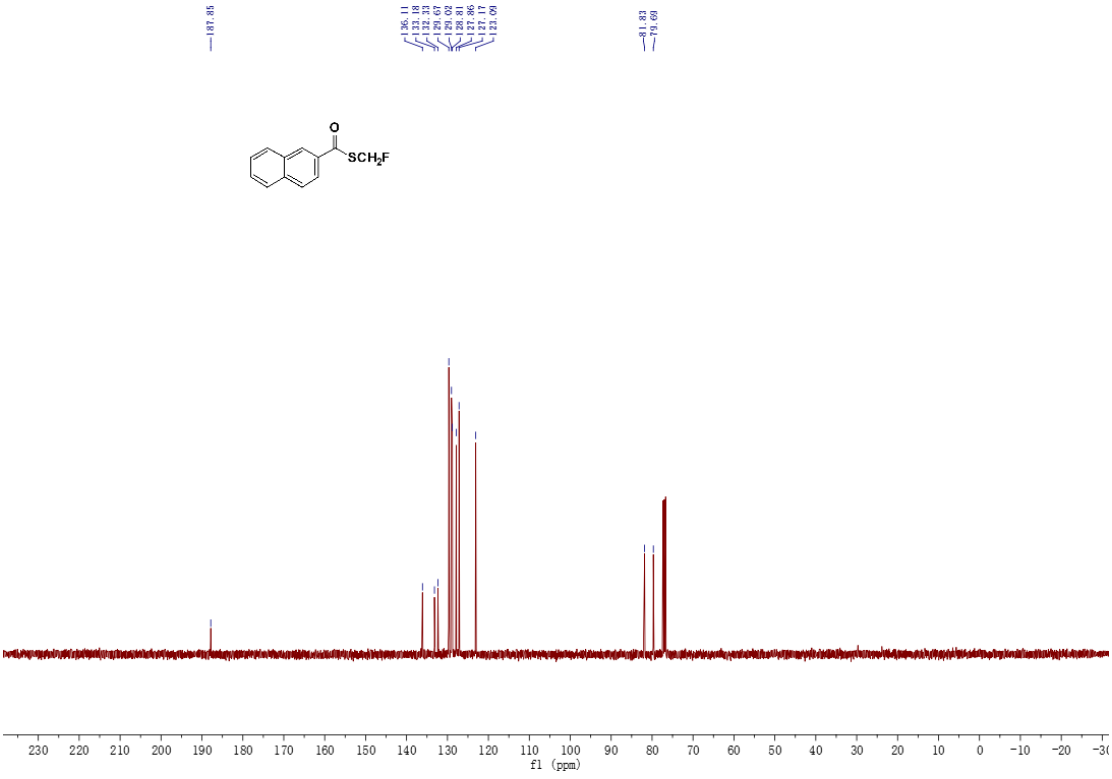
^{1}H NMR spectrum of S-(fluoromethyl)-naphthalene-2-carbothioate 5e



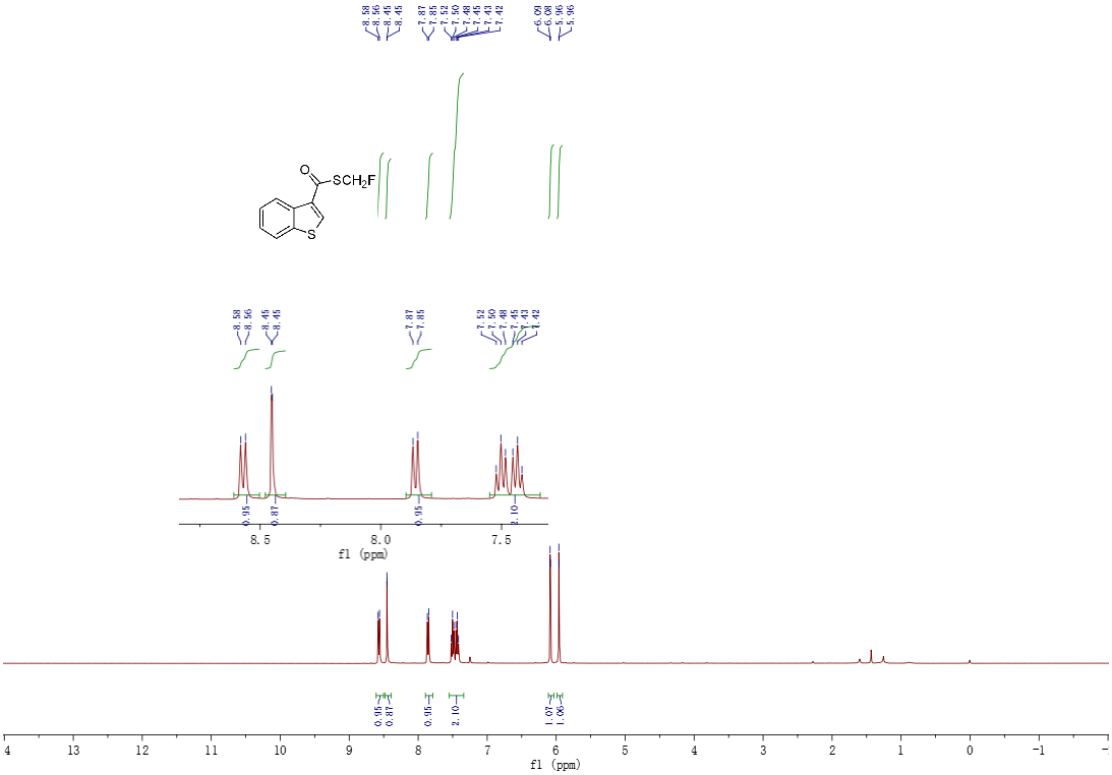
^{19}F NMR spectrum of S-(fluoromethyl)-naphthalene-2-carbothioate 5e



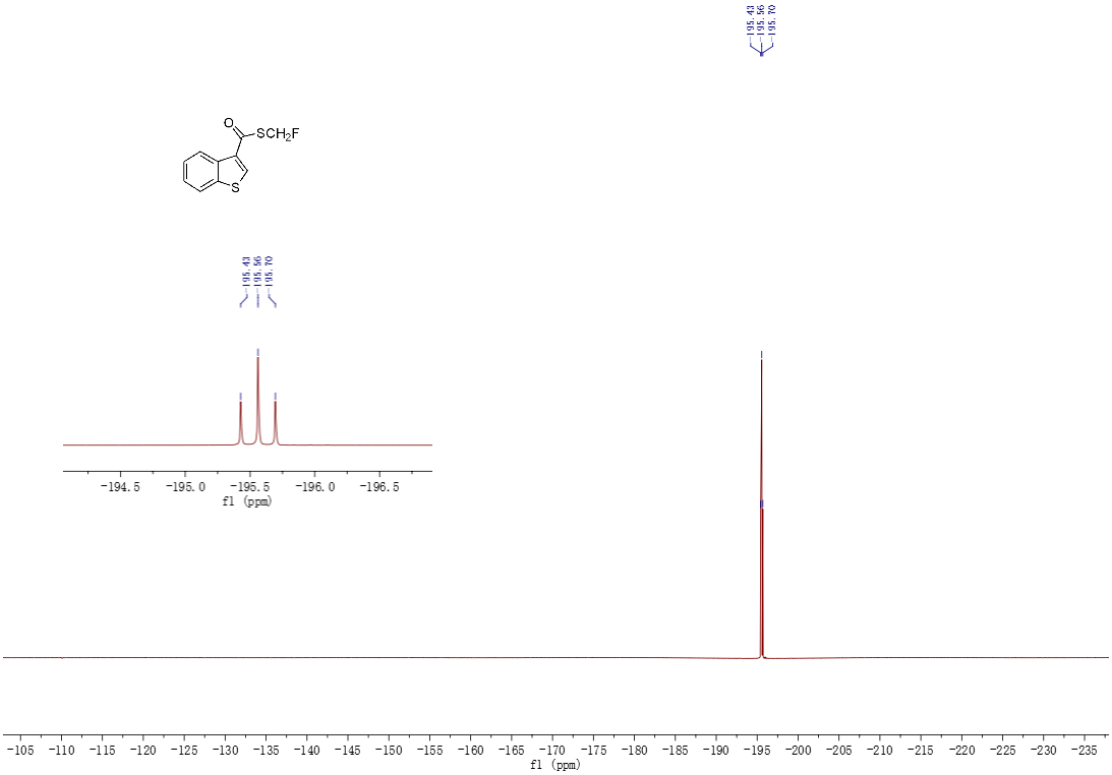
^{13}C NMR spectrum of S-(fluoromethyl)-naphthalene-2-carbothioate 5e



^{1}H NMR spectrum of S-(fluoromethyl)-benzo[*b*]thiophene-3-carbothioate 5f



^{19}F NMR spectrum of S-(fluoromethyl)-benzo[*b*]thiophene-3-carbothioate 5f



^{13}C NMR spectrum of
S-(fluoromethyl)-benzo[*b*]thiophene-3-carbothioate 5f