Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Difluoromethyl and Deuterium-labeled Difluoromethyl Thioethers from Aliphatic Electrophiles

Tianqi Ding, Lvqi Jiang, and Wenbin Yi**

School of Chemical Engineering, Nanjing University of Science and Technology,
Nanjing 210094, China

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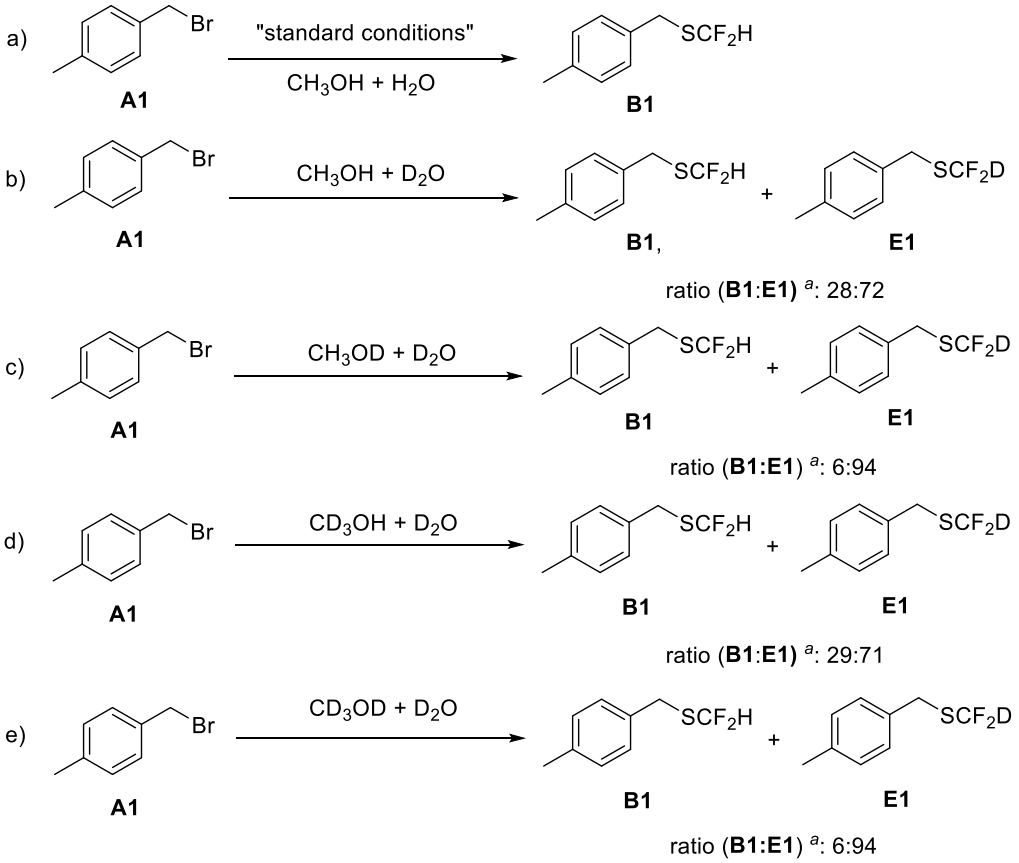
General information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 500 MHz Bruker DRX 500 and data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet), coupling constants (Hz), and assignment. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. GC-MS data was recorded on a ISQ LT Single Quadrupole Mass Spectrometer, coupled with a Trace 1300 Gas Chromatograph (Thermo Fisher Scientific). High resolution mass spectral data were acquired on Waters Micromass GCT Premier spectrometer (electrospray ionization: EI).

Control experiments

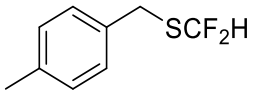


Scheme S1 Exploration of H/D source, the ratio of B1:E1 was determined by ^{19}F NMR

General procedure for one-pot difluoromethylthiolation of aliphatic electrophiles

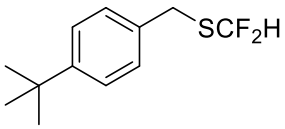
A mixture of aliphatic electrophiles **A** (0.25 mmol) and thiourea (38.1 mg, 0.5 mmol) in CH_3OH (1.0 mL) was refluxed in an oven-dried 20 mL crimp cap vessel for 2 h. Then a solution of NaOH (0.1 g. 2.5 mmol) in H_2O (1.0 mL) was added and the mixture was stirred at 50 ^oC for 0.5 h. Diethyl bromodifluoromethylphosphonate ($BrCF_2P(O)(OEt)_2$) (133.5 mg, 0.5 mmol), I_2 (12.7 mg, 0.05 mmol) and DCM (1.0 mL) were then added and the mixture was stirred at room temperature for 2 h. Upon completion, EtOAc (10 mL) was added, and the mixture was washed with water (20 X 3mL), dried with Na_2SO_4 and concentrated under vacuum to give the crude product. Further column chromatography on silica gel (ethyl acetate/petroleum ether) was needed to afford the pure desired product **B**.

(difluoromethyl)(4-methylbenzyl)sulfane B1



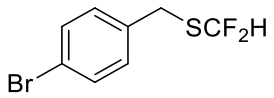
Colorless oil, yield 81% (38.1 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.73 (t, *J* = 56.7 Hz, 1H), 4.00 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.52 (s), 134.19 (s), 130.57 (s), 129.88 (s), 121.42 (t, *J* = 273.4 Hz), 32.63 (t, *J* = 3.4 Hz), 22.20 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.64 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 188.0471, $C_9H_{10}F_2S$, found 188.0475.

(4-(*tert*-butyl)benzyl)(difluoromethyl)sulfane B2 [1]



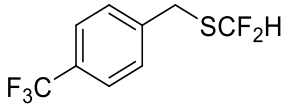
Colorless oil, yield 85% (48.9 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.74 (t, *J* = 56.7 Hz, 1H), 4.00 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.79 (s), 134.13 (s), 129.67 (s), 126.83 (s), 121.43 (t, *J* = 273.4 Hz), 35.64 (s), 32.48 (t, *J* = 3.6 Hz), 32.39 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.69 (d, *J* = 56.4 Hz, 2F).

(4-bromobenzyl)(difluoromethyl)sulfane B3 [1]



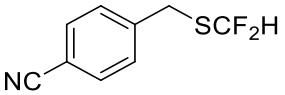
Yellow oil, yield 77% (48.5 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.74 (t, *J* = 56.3 Hz, 1H), 3.97 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.56 (s), 133.01 (s), 131.66 (s), 122.70 (s), 121.09 (t, *J* = 274.1 Hz), 32.07 (t, *J* = 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.39 (d, *J* = 56.4 Hz, 2F).

(difluoromethyl)(4-(trifluoromethyl)benzyl)sulfane B4



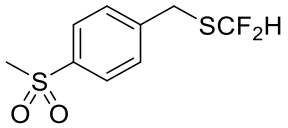
Yellow oil, yield 71% (43.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.77 (t, *J* = 56.1 Hz, 1H), 4.08 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.77 (s), 131.02 (q, *J* = 32.8 Hz), 130.32 (s), 126.84 (q, *J* = 3.8 Hz), 125.08 (q, *J* = 272.6 Hz), 120.96 (t, *J* = 274.7 Hz), 32.08 (t, *J* = 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.78 (s), -93.22 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 242.0189, $C_9H_7F_5S$, found 242.0197.

4-(((difluoromethyl)thio)methyl)benzonitrile B5



Yellow oil, yield 74% (36.8 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 55.8 Hz, 1H), 4.03 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.36 (s), 133.64 (s), 130.72 (s), 120.81 (t, *J* = 275.3 Hz), 119.58 (s), 112.68 (s), 32.11 (t, *J* = 3.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.91 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 199.0267, $C_9H_7F_2NS$, found 199.0270.

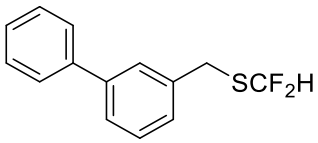
(difluoromethyl)(4-(methylsulfonyl)benzyl)sulfane B6



White solid, yield 68% (42.8 mg). Eluent: ethyl acetate/ petroleum ether (1:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 55.9 Hz, 1H), 4.10 (s, 2H), 3.06

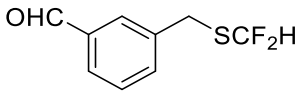
(s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.33 (s), 140.93 (s), 130.93 (s), 129.01 (s), 120.85 (t, *J* = 274.7 Hz), 45.60 (s), 31.93 (t, *J* = 3.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.67 (d, *J* = 56.4 Hz,2F); HR-MS (EI) Calcd. For 252.0090, $C_9H_{10}F_2O_2S_2$, found 252.0100.

([1,1'-biphenyl]-3-ylmethyl)(difluoromethyl)sulfane B7



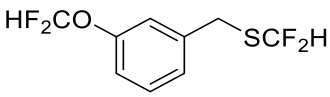
Colorless oil, yield 76% (47.5 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 3H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.44 (dt, *J* = 17.6, 7.6 Hz, 3H), 7.40 – 7.32 (m, 2H), 6.78 (t, *J* = 56.5 Hz, 1H), 4.10 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.95 (s), 141.74 (s), 137.86 (s), 130.33 (s), 129.92 (s), 128.83 (s), 128.63 (s), 128.26 (s), 127.60 (s), 121.32 (t, *J* = 273.4 Hz), 32.86 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.53 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 250.0628, $C_{14}H_{12}F_2S$, found 250.0636.

3-(((difluoromethyl)thio)methyl)benzaldehyde B8



Colorless oil, yield 62% (31.3 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.89 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 56.0 Hz, 1H), 4.11 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.91 (s), 138.98 (s), 137.98 (s), 135.92 (s), 130.89 (s), 130.63 (s), 130.24 (s), 121.00 (t, *J* = 274.1 Hz), 32.08 (t, *J* = 3.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.90 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 202.0264, $C_9H_8F_2OS$, found 202.0271.

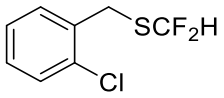
(3-(difluoromethoxy)benzyl)(difluoromethyl)sulfane B9



Colorless oil, yield 80% (48.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 56.3 Hz, 1H), 6.52 (t, *J* = 73.7 Hz, 1H), 4.02 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.50 (s),

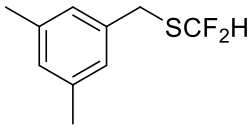
139.80 (s), 131.26 (s), 126.93 (s), 121.10 (s), 121.08 (t, J = 274.1 Hz), 119.75 (s), 116.89 (t, J = 260.6 Hz), 32.23 (t, J = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.04 (dd, J = 75.2, 4.7 Hz, 2F), -94.37 (dd, J = 56.4, 4.7 Hz, 2F); HR-MS (EI) Calcd. For 240.0232, $C_9H_8F_4OS$, found 240.0241.

(2-chlorobenzyl)(difluoromethyl)sulfane B10 [1]



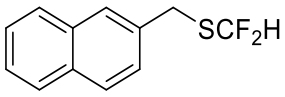
Colorless oil, yield 78% (40.6 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.27 – 7.23 (m, 2H), 6.82 (t, J = 56.3 Hz, 1H), 4.14 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.66 (s), 135.22 (s), 131.95 (s), 130.98 (s), 130.25 (s), 128.21 (s), 121.38 (t, J = 274.1 Hz), 30.54 (t, J = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.05 (d, J = 56.4 Hz, 2F).

(difluoromethyl)(3,5-dimethylbenzyl)sulfane B11



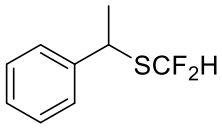
Colorless oil, yield 82% (41.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.92 (s, 1H), 6.74 (t, J = 56.7 Hz, 1H), 3.95 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.52 (s), 137.00 (s), 130.43 (s), 127.76 (s), 121.42 (t, J = 272.8 Hz), 32.78 (t, J = 3.5 Hz), 22.30 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.70 (d, J = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 202.0628, $C_{10}H_{12}F_2S$, found 202.0621.

(difluoromethyl)(naphthalen-2-ylmethyl)sulfane B12



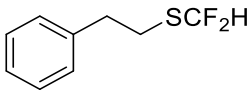
Yellow oil, yield 73% (40.9 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 3H), 7.79 (s, 1H), 7.53 – 7.48 (m, 3H), 6.76 (t, J = 56.6 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.67 (s), 134.38 (s), 133.82 (s), 129.85 (s), 128.82 (s), 128.74 (s), 127.80 (s), 127.54 (s), 127.30 (s), 121.37 (t, J = 274.1 Hz), 33.23 (t, J = 3.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.37 (d, J = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 224.0471, $C_{12}H_{10}F_2S$, found 224.0474.

(difluoromethyl)(1-phenylethyl)sulfane B13 [1]



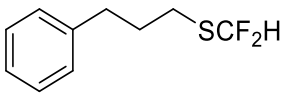
Colorless oil, yield 52% (24.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.32 – 7.28 (m, 1H), 6.57 (dd, *J* = 59.0, 55.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.27 (s), 129.90 (s), 128.86 (s), 128.16 (s), 121.92 (dd, *J* = 275.1, 269.9 Hz), 43.49 (t, *J* = 2.5 Hz), 24.24 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.52 (dd, *J* = 253.8, 56.4 Hz, 1F), δ -96.00 (dd, *J* = 253.8, 56.4 Hz, 1F).

(difluoromethyl)(phenethyl)sulfane B14 [2]



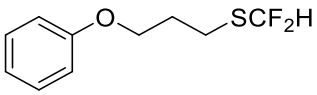
Colorless oil, yield 60% (28.2 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.22 (m, 3H), 6.79 (t, *J* = 56.3 Hz, 1H), 3.10 – 3.05 (m, 2H), 3.02 – 2.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.62 (s), 129.71 (s), 129.64 (s), 127.82 (s), 121.71 (t, *J* = 273.4 Hz), 37.84 (s), 29.65 (t, *J* = 3.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.90 (d, *J* = 56.4 Hz, 2F).

(difluoromethyl)(3-phenylpropyl)sulfane B15 [3]



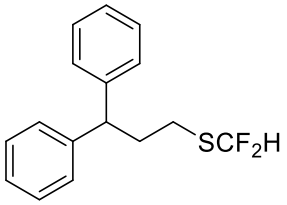
Colorless oil, yield 64% (32.3 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 14.5, 7.3 Hz, 3H), 6.81 (t, *J* = 56.3 Hz, 1H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.06 – 1.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.91 (s), 129.58 (s), 129.54 (s), 127.21 (s), 121.80 (t, *J* = 273.4 Hz), 35.65 (s), 32.76 (s), 27.68 (t, *J* = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.52 (d, *J* = 56.4 Hz, 2F).

(difluoromethyl)(3-phenoxypropyl)sulfane B16



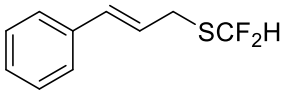
Colorless oil, yield 72% (39.2 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.83 (t, *J* = 56.3 Hz, 1H), 4.09 (t, *J* = 5.9 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.22 – 2.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.77 (s), 130.59 (s), 122.00 (s), 121.82 (t, *J* = 273.4 Hz), 115.58 (s), 66.59 (s), 31.14 (s), 25.09 (t, *J* = 3.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.77 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 218.0577, $C_{10}H_{12}F_2OS$, found 218.0580.

(difluoromethyl)(3,3-diphenylpropyl)sulfane B17



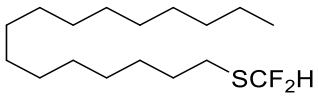
Colorless oil, yield 41% (28.5 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 4H), 7.25 (d, *J* = 7.1 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 6.78 (t, *J* = 56.3 Hz, 1H), 4.09 (t, *J* = 7.8 Hz, 1H), 2.77 – 2.71 (m, 2H), 2.44 (dd, *J* = 15.1, 7.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.70 (s), 129.74 (s), 128.89 (s), 127.61 (s), 121.79 (t, *J* = 273.4 Hz), 51.05 (s), 37.14 (s), 26.81 (t, *J* = 2.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.54 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 278.0941, $C_{16}H_{16}F_2S$, found 278.0939.

cinnamyl(difluoromethyl)sulfane B18



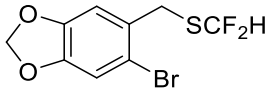
Colorless oil, yield 65% (32.5 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 6.83 (t, *J* = 56.3 Hz, 1H), 6.58 (d, *J* = 15.7 Hz, 1H), 6.30 – 6.21 (m, 1H), 3.64 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.30 (s), 134.60 (s), 129.74 (s), 129.08 (s), 127.55 (s), 125.24 (s), 121.65 (t, *J* = 273.4 Hz), 31.54 (t, *J* = 3.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.35 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 200.0471, $C_{10}H_{10}F_2S$, found 200.0473.

(difluoromethyl)(hexadecyl)sulfane B19



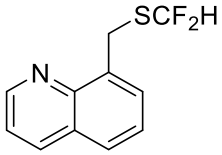
Yellow oil, yield 31% (23.9 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (t, *J* = 56.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.64 (m, 2H), 1.43 – 1.23 (m, 26H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 121.87 (t, *J* = 272.8 Hz), 33.01 (s), 31.18 (s), 30.78 (s), 30.77 (s), 30.74 (s), 30.71 (s), 30.64 (s), 30.53 (s), 30.45 (s), 30.12 (s), 29.78 (s), 28.31 (t, *J* = 3.1 Hz), 23.78 (s), 15.19 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.65 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 308.2349, $C_{17}H_{34}F_2S$, found 308.2347.

5-bromo-6-(((difluoromethyl)thio)methyl)benzo[*d*][1,3]dioxole B20



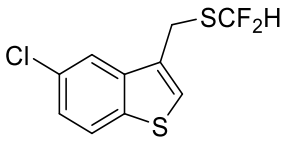
White solid, yield 61% (45.1 mg). Eluent: ethyl acetate/ petroleum ether (1:25). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.89 (s, 1H), 6.83 (t, *J* = 56.3 Hz, 1H), 5.99 (s, 2H), 4.07 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.17 (s), 148.67 (s), 130.20 (s), 121.33 (t, *J* = 274.1 Hz), 116.11 (s), 114.05 (s), 111.45 (s), 103.05 (s), 33.28 (t, *J* = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.41 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 295.9318, $C_9H_7BrF_2O_2S$, found 295.9326.

8-(((difluoromethyl)thio)methyl)quinoline B21



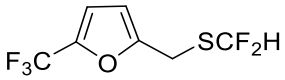
Colorless oil, yield 68% (38.3 mg). Eluent: ethyl acetate/ petroleum ether (1:25). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.18 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.77 (dd, *J* = 16.9, 7.9 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.00 (t, *J* = 56.9 Hz, 1H), 4.66 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.88 (s), 150.81 (s), 137.61 (s), 130.83 (s), 129.67 (s), 129.02 (s), 127.45 (s), 127.41 (s), 122.53 (s), 122.35 (t, *J* = 273.4 Hz), 28.94 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.88 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 225.0424, $C_{11}H_9F_2NS$, found 225.0420.

5-chloro-3-(((difluoromethyl)thio)methyl)benzo[*b*]thiophene B22



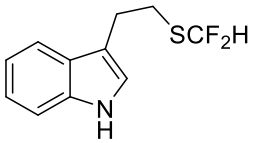
Yellow oil, yield 70% (46.2 mg). Eluent: ethyl acetate/ petroleum ether (1:25). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.7 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.46 (s, 1H), 7.36 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.80 (t, *J* = 56.2 Hz, 1H), 4.25 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.86 (s), 139.81 (s), 131.94 (s), 130.77 (s), 128.22 (s), 126.36 (s), 125.10 (s), 122.61 (s), 121.21 (t, *J* = 274.1 Hz), 25.71 (t, *J* = 4.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.81 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 263.9646, $C_{10}H_7ClF_2S_2$, found 263.9641.

2-(((difluoromethyl)thio)methyl)-5-(trifluoromethyl)furan B23



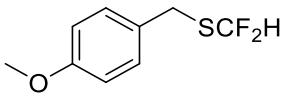
Colorless oil, yield 50% (29.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (t, *J* = 56.1 Hz, 1H), 6.74 (d, *J* = 2.3 Hz, 1H), 6.36 (d, *J* = 3.3 Hz, 1H), 4.05 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.36 (s), 142.62 (s), 120.88 (t, *J* = 274.7 Hz), 119.94 (q, *J* = 267.2 Hz), 113.68 (q, *J* = 2.9 Hz), 110.08 (s), 24.55 (t, *J* = 4.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.14 (s, 3F), -94.41 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 231.9981, $C_7H_5F_5OS$, found 231.9984.

3-(2-((difluoromethyl)thio)ethyl)-1*H*-indole B24



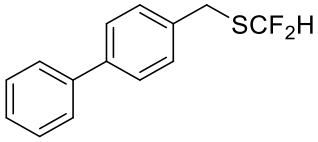
Brown oil, yield 74% (42.0 mg). Eluent: ethyl acetate/ petroleum ether (1:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.07 (s, 1H), 6.82 (t, *J* = 56.4 Hz, 1H), 3.15 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.37 (s), 128.08 (s), 123.34 (s), 123.06 (s), 121.93 (t, *J* = 273.4 Hz), 120.66 (s), 119.69 (s), 115.18 (s), 112.35 (s), 29.04 (t, *J* = 2.7 Hz), 27.71 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.62 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 227.0580, $C_{11}H_{11}F_2NS$, found 227.0586.

(difluoromethyl)(4-methoxybenzyl)sulfane B25 [1]



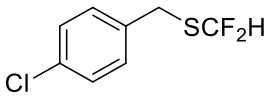
Yellow oil, yield 84% (42.8 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.73 (t, *J* = 56.7 Hz, 1H), 4.00 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.18 (s), 131.15 (s), 129.14 (s), 121.44 (t, *J* = 273.4 Hz), 115.29 (s), 56.39 (s), 32.38 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.44 (d, *J* = 56.4 Hz, 2F).

([1,1'-biphenyl]-4-ylmethyl)(difluoromethyl)sulfane B26 [4]



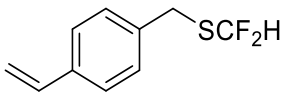
White solid, yield 83% (51.9 mg). Eluent: ethyl acetate/ petroleum ether (1:50).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.3 Hz, 4H), 7.45 (dd, *J* = 15.2, 7.7 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.79 (t, *J* = 56.5 Hz, 1H), 4.08 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.74 (s), 141.63 (s), 136.36 (s), 130.43 (s), 129.91 (s), 128.62 (s), 128.55 (s), 128.16 (s), 121.34 (t, *J* = 273.4 Hz), 32.54 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.29 (d, *J* = 56.4 Hz, 2F).

(4-chlorobenzyl)(difluoromethyl)sulfane B27 [4]



Yellow oil, yield 78% (40.6 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (q, *J* = 8.5 Hz, 4H), 6.75 (t, *J* = 56.3 Hz, 1H), 4.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.03 (s), 134.63 (s), 131.32 (s), 130.05 (s), 121.12 (t, *J* = 274.1 Hz), 32.03 (t, *J* = 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.17 (d, *J* = 56.4 Hz, 2F).

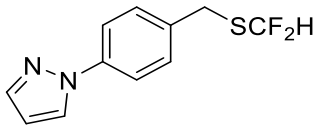
(difluoromethyl)(4-vinylbenzyl)sulfane B28



Colorless oil, yield 76% (38.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 56.5 Hz, 1H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 4.02 (s, 2H); ^{13}C NMR (126

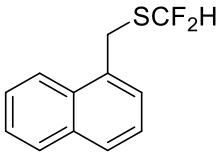
MHz, $CDCl_3$) δ 138.16 (s), 137.32 (s), 136.83 (s), 130.17 (s), 127.69 (s), 121.31 (t, *J* = 273.4 Hz), 115.32 (s), 32.62 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.33 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 200.0471, $C_{10}H_{10}F_2S$, found 200.0478.

1-(4-(((difluoromethyl)thio)methyl)phenyl)-1*H*-pyrazole B29



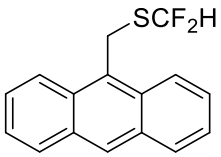
White solid, yield 69% (41.4 mg). Eluent: ethyl acetate/ petroleum ether (1:8). ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.3 Hz, 1H), 7.74 (d, *J* = 1.1 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.77 (t, *J* = 56.4 Hz, 1H), 6.50 – 6.46 (m, 1H), 4.06 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.29 (s), 140.65 (s), 135.66 (s), 131.08 (s), 127.81 (s), 121.21 (t, *J* = 274.1 Hz), 120.55 (s), 108.85 (s), 32.21 (t, *J* = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.16 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 240.0533, $C_{11}H_{10}F_2N_2S$, found 240.0541.

(difluoromethyl)(naphthalen-1-ylmethyl)sulfane B30



Yellow oil, yield 72% (40.3 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H), 7.76 (s, 1H), 7.49 – 7.44 (m, 3H), 6.73 (t, *J* = 56.6 Hz, 1H), 4.17 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.67 (s), 134.37 (s), 133.81 (s), 129.85 (s), 128.81 (s), 128.73 (s), 127.80 (s), 127.54 (s), 127.30 (s), 121.35 (t, *J* = 274.1 Hz), 33.23 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.61 (d, *J* = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 224.0471, $C_{12}H_{10}F_2S$, found 224.0474.

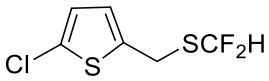
(anthracen-9-ylmethyl)(difluoromethyl)sulfane B31



Yellow solid, yield 61% (41.8 mg). Eluent: ethyl acetate/ petroleum ether (1:20).^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.31 (d, *J* = 8.9 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.55 –

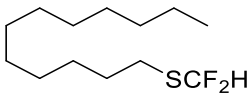
7.49 (m, 2H), 6.93 (t, J = 55.9 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.58 (s), 131.14 (s), 130.45 (s), 129.45 (s), 127.81 (s), 126.82 (s), 126.30 (s), 124.66 (s), 121.56 (t, J = 274.1 Hz), 24.81 (t, J = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.48 (d, J = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 274.0628, $C_{16}H_{12}F_2S$, found 274.0636.

2-chloro-5-(((difluoromethyl)thio)methyl)thiophene B32



Colorless oil, yield 73% (39.1 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (t, J = 56.4 Hz, 1H), 6.79 (d, J = 4.0 Hz, 1H), 6.75 (d, J = 3.5 Hz, 1H), 4.15 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.15 (s), 131.06 (s), 127.42 (s), 127.03 (s), 121.00 (t, J = 274.7 Hz), 27.58 (t, J = 4.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.62 (d, J = 56.4 Hz, 2F); HR-MS (EI) Calcd. For 213.9489, $C_6H_5ClF_2S_2$, found 213.9488.

(difluoromethyl)(dodecyl)sulfane B33 [5]



Colorless oil, yield 43% (27.1 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (t, J = 56.4 Hz, 1H), 2.80 (t, J = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.42 – 1.24 (m, 18H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 121.88 (t, J = 272.8 Hz), 33.01 (s), 31.19 (s), 30.71 (s), 30.65 (s), 30.54 (s), 30.43 (s), 30.34 (s), 30.13 (s), 29.79 (s), 28.31 (t, J = 3.1 Hz), 23.78 (s), 15.21 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.72 (d, J = 56.4 Hz, 2F).

Gram-scale synthesis of compound B2

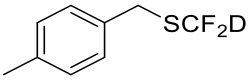
A mixture of 1-(bromomethyl)-4-(*tert*-butyl)benzene **A2** (2.26 g, 10 mmol) and thiourea (1.52 g, 20 mmol) in CH_3OH (20 mL) was refluxed in an oven-dried 100 mL crimp cap vessel for 2 h. Then a solution of NaOH (4.0 g) in H_2O (20 mL) was added and the mixture was stirred at 50 ^{o}C for 0.5 h. Diethyl bromodifluoromethylphosphonate ($BrCF_2P(O)(OEt)_2$) (4.0 g, 15 mmol), I_2 (0.51 g, 2 mmol) and DCM (20 mL) were then added and the mixture was stirred at room temperature for 2 h. Upon completion, EtOAc (100mL) was added, and the mixture was washed with water (100 X 3mL), dried with Na_2SO_4 and concentrated under vacuum to give the crude product. Further column

chromatography on silica gel (ethyl acetate/petroleum ether) was needed to afford the pure desired product **B2** (1.63 g) with 71% yield.

General procedure for one-pot deuterated difluoromethylthiolation of aliphatic electrophiles

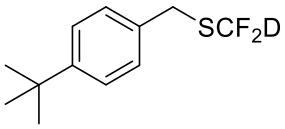
A mixture of aliphatic electrophiles **A** (0.5 mmol) and thiourea (76.1 mg, 1.0 mmol) in CD_3OD (2.0 mL) was refluxed in an oven-dried 20 mL crimp cap vessel for 2 h. Then a solution of NaOH (0.2 g, 5.0 mmol) in D_2O (2.0 mL) was added and the mixture was stirred at 50 °C for 0.5 h. Diethyl bromodifluoromethylphosphonate ($BrCF_2P(O)(OEt)_2$) (267 mg, 1.0 mmol), I_2 (25.4 mg, 0.1 mmol) and DCM (2.0 mL) were then added and the mixture was stirred at room temperature for 2 h. Upon completion, EtOAc (10 mL) was added, and the mixture was washed with water (20 X 3mL), dried with Na_2SO_4 and concentrated under vacuum to give the crude product. Further column chromatography on silica gel (ethyl acetate/petroleum ether) was needed to afford the pure desired product **E**.

(difluoromethyl-*d*)(4-methylbenzyl)sulfane E1



Colorless oil, yield 84% (79.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.02 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.53 (s), 134.23 (s), 130.59 (s), 129.90 (s), 121.15 (tt, *J* = 272.0, 31.1 Hz), 32.61 (t, *J* = 3.6 Hz), 22.21 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.16 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 189.0534, $C_9H_9DF_2S$, found 189.0542.

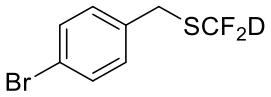
(4-(*tert*-butyl)benzyl)(difluoromethyl-*d*)sulfane E2



Colorless oil, yield 86% (99.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.02 (s, 2H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.80 (s), 134.16 (s), 129.68 (s), 126.84 (s), 121.14 (tt, *J* = 272.2, 31.1 Hz), 35.65 (s),

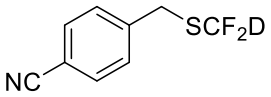
32.46 (t, J = 3.7 Hz), 32.40 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.15 (t, J = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 231.1004, $C_{12}H_{15}DF_2S$, found 231.1001.

(4-bromobenzyl)(difluoromethyl-*d*)sulfane E3



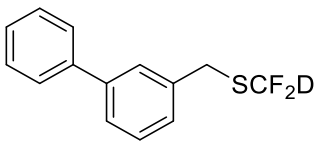
Yellow oil, yield 79% (100.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.98 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.61 (s), 133.02 (s), 131.67 (s), 122.71 (s), 120.85 (tt, J = 272.9, 31.1 Hz), 32.07 (t, J = 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.82 (t, J = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 252.9483, $C_8H_6DBrF_2S$, found 252.9477.

4-(((difluoromethyl-*d*)thio)methyl)benzonitrile E4



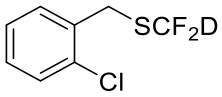
Yellow oil, yield 79% (79.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 4.05 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.46 (s), 133.62 (s), 130.73 (s), 120.65 (tt, J = 273.5, 31.2 Hz), 119.62 (s), 112.59 (s), 32.12 (t, J = 3.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.44 (t, J = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 200.0330, $C_9H_6DF_2NS$, found 200.0331.

([1,1'-biphenyl]-3-ylmethyl)(difluoromethyl-*d*)sulfane E5



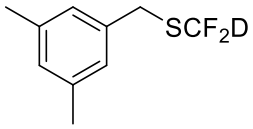
Yellow oil, yield 80% (100.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 3H), 7.57 (d, J = 7.7 Hz, 1H), 7.53 – 7.37 (m, 5H), 4.13 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.99 (s), 141.78 (s), 137.93 (s), 130.37 (s), 129.97 (s), 128.88 (s), 128.86 (s), 128.68 (s), 128.31 (s), 127.64 (s), 121.09 (tt, J = 272.5, 31.1 Hz), 32.87 (t, J = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.90 (t, J = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 251.0691, $C_{14}H_{11}DF_2S$, found 251.0690.

(2-chlorobenzyl)(difluoromethyl-*d*)sulfane E6



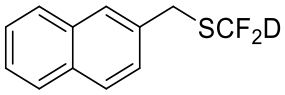
Colorless oil, yield 75% (78.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.28 – 7.24 (m, 2H), 4.15 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.69 (s), 135.22 (s), 131.96 (s), 130.99 (s), 130.26 (s), 128.24 (s), 121.12 (tt, *J* = 272.9, 31.1 Hz), 30.53 (t, *J* = 3.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.55 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 208.9988, $C_8H_6DClF_2S$, found 208.9980.

(difluoromethyl-*d*)(3,5-dimethylbenzyl)sulfane E7



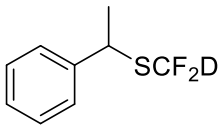
Colorless oil, yield 85% (86.2 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 2H), 6.97 (s, 1H), 3.99 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.54 (s), 137.06 (s), 130.46 (s), 127.80 (s), 121.18 (tt, *J* = 272.0, 31.1 Hz), 32.78 (t, *J* = 3.5 Hz), 22.30 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.15 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 203.0691, $C_{10}H_{11}DF_2S$, found 203.0695.

(difluoromethyl-*d*)(naphthalen-2-ylmethyl)sulfane E8



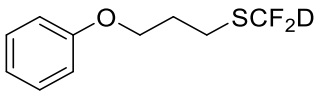
Yellow oil, yield 74% (83.2 mg). Eluent: ethyl acetate/ petroleum ether (1:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (t, *J* = 10.6 Hz, 3H), 7.81 (s, 1H), 7.52 (dd, *J* = 8.9, 6.6 Hz, 3H), 4.21 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.73 (s), 134.42 (s), 133.86 (s), 129.88 (s), 128.86 (s), 128.77 (s), 127.84 (s), 127.58 (s), 127.34 (s), 121.13 (tt, *J* = 272.5, 31.1 Hz), 33.22 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.07 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 225.0534, $C_{12}H_9DF_2S$, found 225.0525.

(difluoromethyl-*d*)(1-phenylethyl)sulfane E9



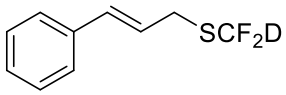
Colorless oil, yield 54% (51.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.31 – 7.28 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.27 (s), 129.90 (s), 128.86 (s), 128.15 (s), 121.61 (tt, *J* = 271.4, 33.6 Hz), 43.45 (t, *J* = 2.5 Hz), 24.24 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.28 (dt, *J* = 249.1, 9.4 Hz, 1F), δ -96.77 (dt, *J* = 249.1, 9.4 Hz, 1F); HR-MS (EI) Calcd. For 189.0534, $C_9H_9DF_2S$, found 189.0540.

(difluoromethyl-*d*)(3-phenoxypropyl)sulfane E10



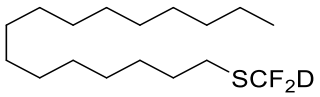
Colorless oil, yield 72% (78.8 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 7.4 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 2H), 4.10 (t, *J* = 5.9 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.23 – 2.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.79 (s), 130.62 (s), 122.03 (s), 121.55 (tt, *J* = 272.1, 30.9 Hz), 115.60 (s), 66.61 (s), 31.16 (s), 25.07 (t, *J* = 3.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.29 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 219.0640, $C_{10}H_{11}DF_2OS$, found 219.0642.

cinnamyl(difluoromethyl-*d*)sulfane E11



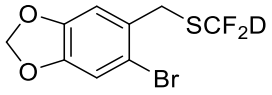
Colorless oil, yield 70% (70.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.26 (m, 1H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.31 – 6.22 (m, 1H), 3.64 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.30 (s), 134.59 (s), 129.76 (s), 129.09 (s), 127.57 (s), 125.26 (s), 121.36 (tt, *J* = 272.3, 31.2 Hz), 31.52 (t, *J* = 3.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.90 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 201.0534, $C_{10}H_9DF_2S$, found 201.0541.

(difluoromethyl-*d*)(hexadecyl)sulfane E12



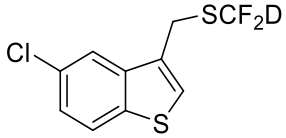
Yellow oil, yield 33% (51.1 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.80 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.64 (m, 2H), 1.44 – 1.22 (m, 26H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 121.57 (tt, *J* = 271.4, 30.8 Hz), 33.02 (s), 31.19 (s), 30.79 (s), 30.78 (s), 30.75 (s), 30.71 (s), 30.64 (s), 30.54 (s), 30.45 (s), 30.12 (s), 29.79 (s), 28.28 (t, *J* = 3.2 Hz), 23.78 (s), 15.20 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.48 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 309.2412, $C_{17}H_{33}DF_2S$, found 309.2408.

5-bromo-6-(((difluoromethyl-*d*)thio)methyl)benzo[*d*][1,3]dioxole E13



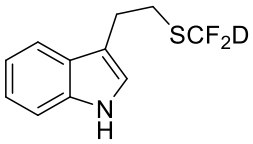
White solid, yield 67% (99.4 mg). Eluent: ethyl acetate/ petroleum ether (1:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.89 (s, 1H), 5.99 (s, 2H), 4.07 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.17 (s), 148.67 (s), 130.20 (s), 121.05 (tt, *J* = 273.0, 31.0 Hz), 116.11 (s), 114.05 (s), 111.45 (s), 103.07 (s), 33.25 (t, *J* = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.19 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 296.9381, $C_9H_6DBrF_2O_2S$, found 296.9386.

5-chloro-3-(((difluoromethyl-*d*)thio)methyl)benzo[b]thiophene E14



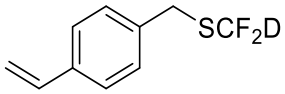
Yellow oil, yield 74% (98.0 mg). Eluent: ethyl acetate/ petroleum ether (1:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.8 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.46 (s, 1H), 7.36 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.25 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.87 (s), 139.82 (s), 131.95 (s), 130.80 (s), 128.22 (s), 126.36 (s), 125.10 (s), 122.61 (s), 120.94 (tt, *J* = 272.8, 31.2 Hz), 25.68 (t, *J* = 4.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.30 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 264.9709, $C_{10}H_6DClF_2S_2$, found 264.9710.

3-(2-((difluoromethyl-*d*)thio)ethyl)-1*H*-indole E15



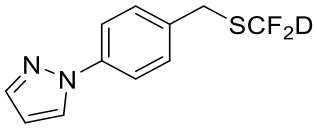
Brown oil, yield 76% (86.6 mg). Eluent: ethyl acetate/ petroleum ether (1:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 8.3 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 3.18 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.39 (s), 128.10 (s), 123.35 (s), 123.10 (s), 121.67 (tt, *J* = 272.2, 30.9 Hz), 120.67 (s), 119.70 (s), 115.16 (s), 112.39 (s), 29.03 (t, *J* = 2.6 Hz), 27.71 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.10 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 228.0643, $C_{11}H_{10}DF_2NS$, found 228.0647.

(difluoromethyl-*d*)(4-vinylbenzyl)sulfane E16



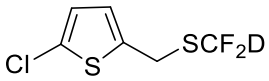
Colorless oil, yield 77% (77.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H), 4.03 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.17 (s), 137.35 (s), 136.89 (s), 130.21 (s), 127.73 (s), 121.07 (tt, *J* = 272.3, 31.1 Hz), 115.35 (s), 32.61 (t, *J* = 3.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.04 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 201.0534, $C_{10}H_9DF_2S$, found 201.0537.

1-(4-(((difluoromethyl-*d*)thio)methyl)phenyl)-1*H*-pyrazole E17



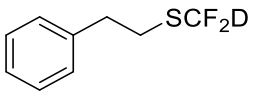
White solid, yield 71% (85.6 mg). Eluent: ethyl acetate/ petroleum ether (1:8). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 1.1 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.49 – 6.46 (m, 1H), 4.05 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.30 (s), 140.66 (s), 135.63 (s), 131.07 (s), 127.79 (s), 120.95 (tt, *J* = 272.5, 30.9 Hz), 120.50 (s), 108.86 (s), 32.18 (t, *J* = 3.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.82 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 241.0596, $C_{11}H_9DF_2N_2S$, found 241.0593.

2-chloro-5-(((difluoromethyl-*d*)thio)methyl)thiophene E18



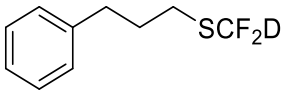
Colorless oil, yield 69% (74.2 mg). Eluent: ethyl acetate/ petroleum ether (1:20). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (d, *J* = 3.8 Hz, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 4.14 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.20 (s), 131.04 (s), 127.41 (s), 127.04 (s), 120.73 (tt, *J* = 273.4, 31.2 Hz), 27.56 (t, *J* = 4.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.30 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 214.9552, $C_6H_4DClF_2S_2$, found 214.9555.

(difluoromethyl-*d*)(phenethyl)sulfane E19



Colorless oil, yield 67% (63.4 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.24 (d, *J* = 7.1 Hz, 2H), 3.11 – 3.06 (m, 2H), 3.04 – 2.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.63 (s), 129.72 (s), 129.65 (s), 127.83 (s), 121.41 (tt, *J* = 272.2, 30.9 Hz), 37.85 (s), 29.62 (t, *J* = 2.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.43 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 189.0534, $C_9H_9DF_2S$, found 189.0532.

(difluoromethyl-*d*)(3-phenylpropyl)sulfane E20



Colorless oil, yield 72% (73.0 mg). Eluent: ethyl acetate/ petroleum ether (1:50). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.24 (dd, *J* = 14.6, 7.3 Hz, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.10 – 2.01 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.95 (s), 129.61 (s), 129.57 (s), 127.24 (s), 121.54 (tt, *J* = 272.0, 30.9 Hz), 35.67 (s), 32.80 (s), 27.67 (t, *J* = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.21 (t, *J* = 9.4 Hz, 2F); HR-MS (EI) Calcd. For 203.0691, $C_{10}H_{11}DF_2S$, found 203.0697.

References

1. X. Y. Deng, J. H. Lin, J. Zheng, J. C. Xiao, *Chem. Commun.* **2015**, *51*, 8805.
2. Y. Ran, Q. Y. Lin, X. H. Xu, F. L. Qing, *J. Org. Chem.* **2017**, *82*, 7373.
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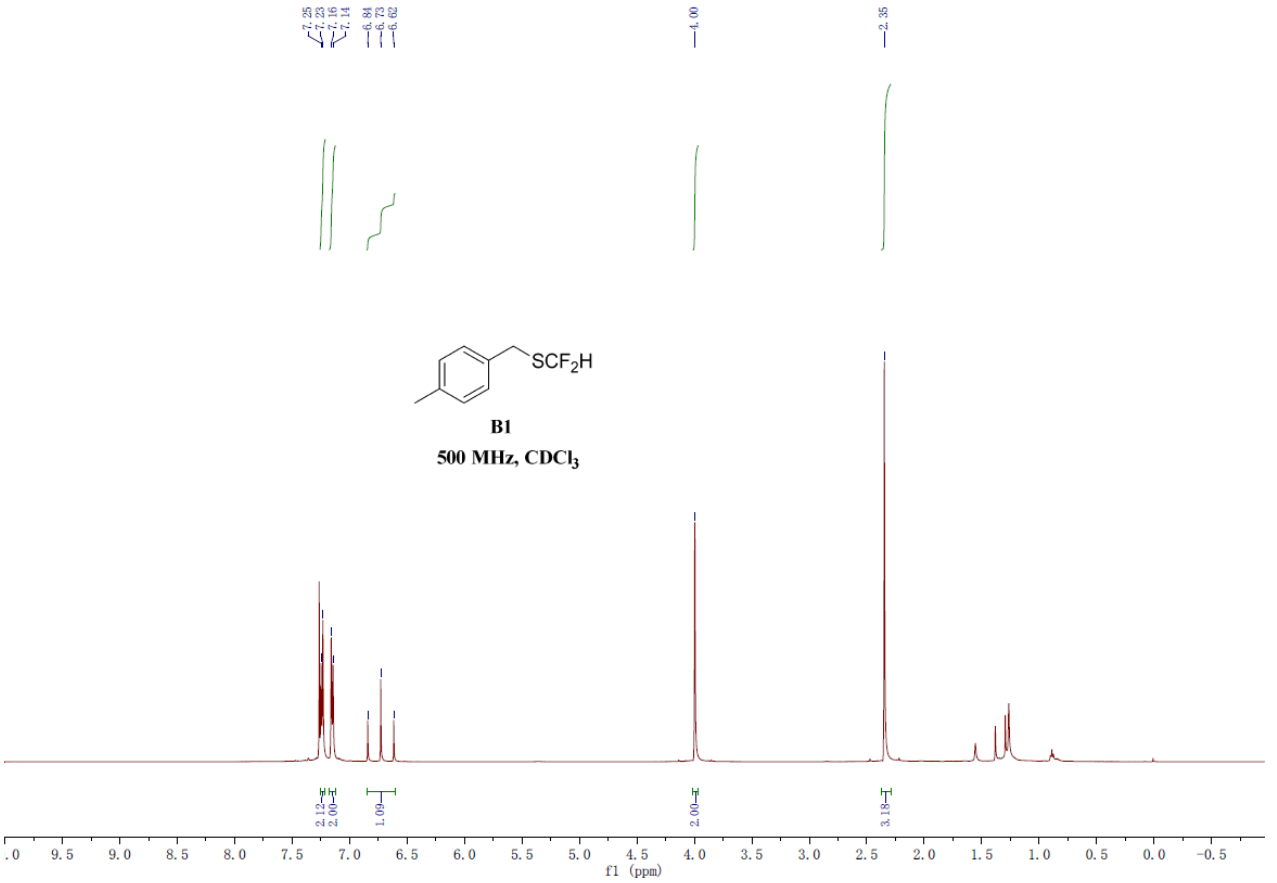
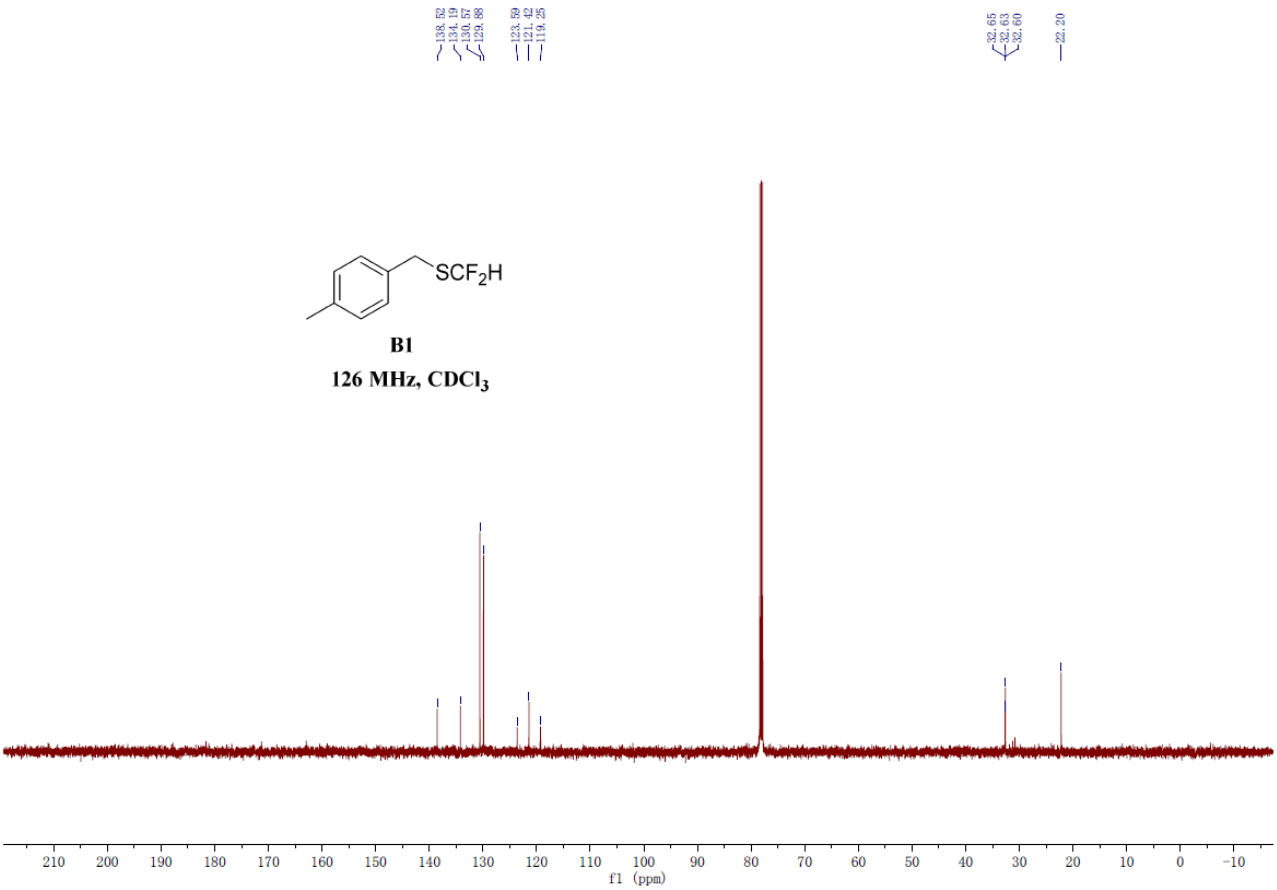
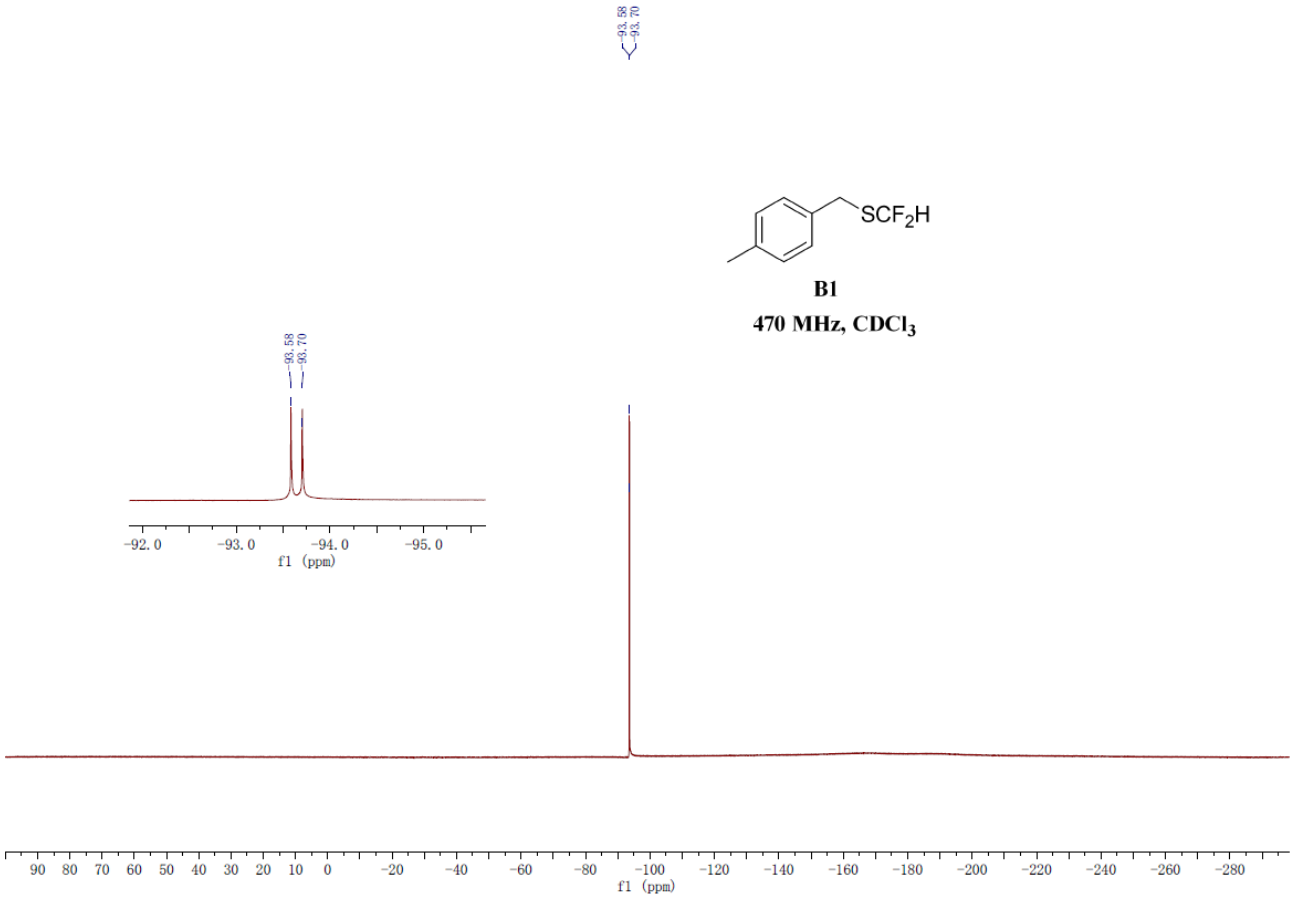
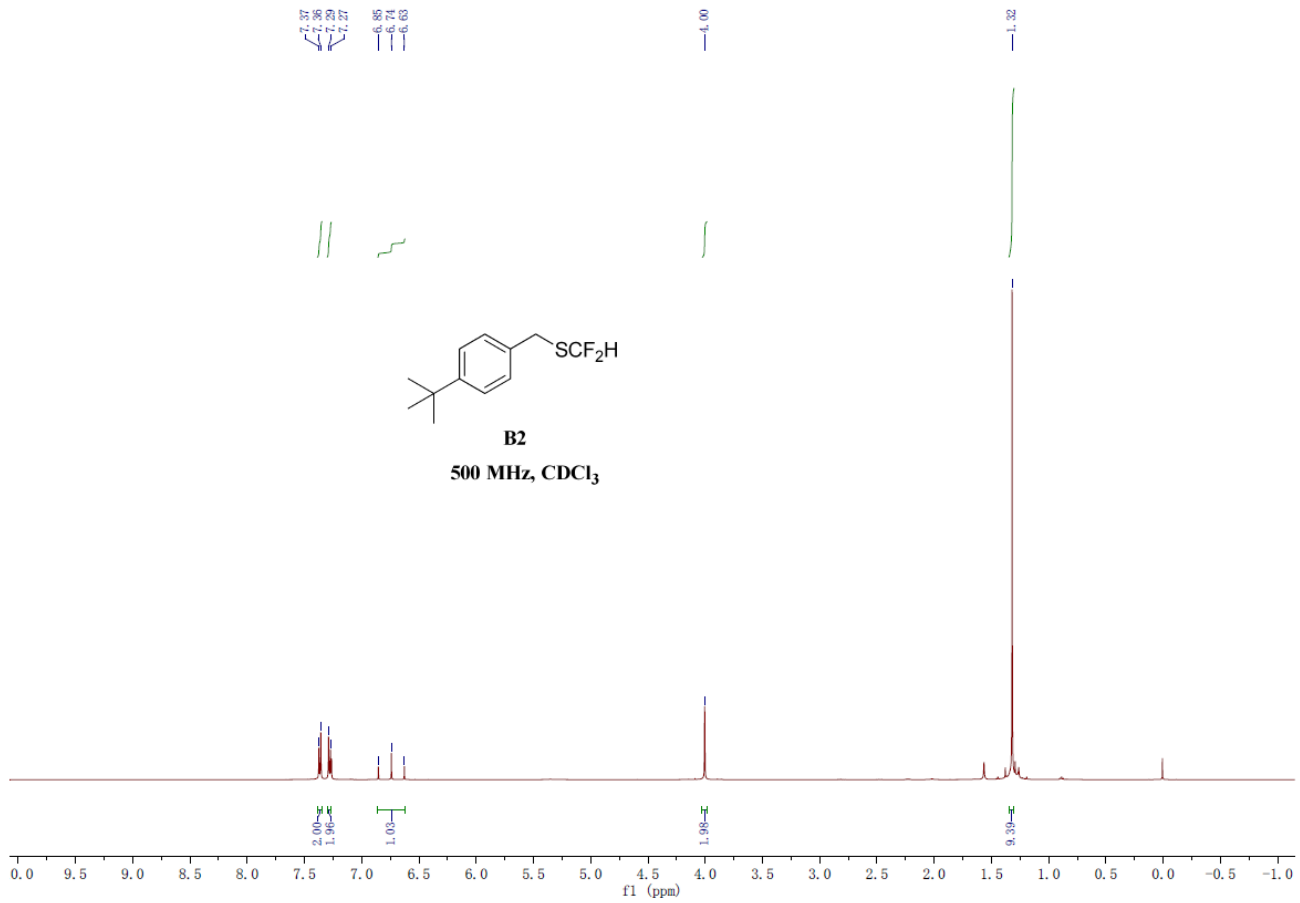
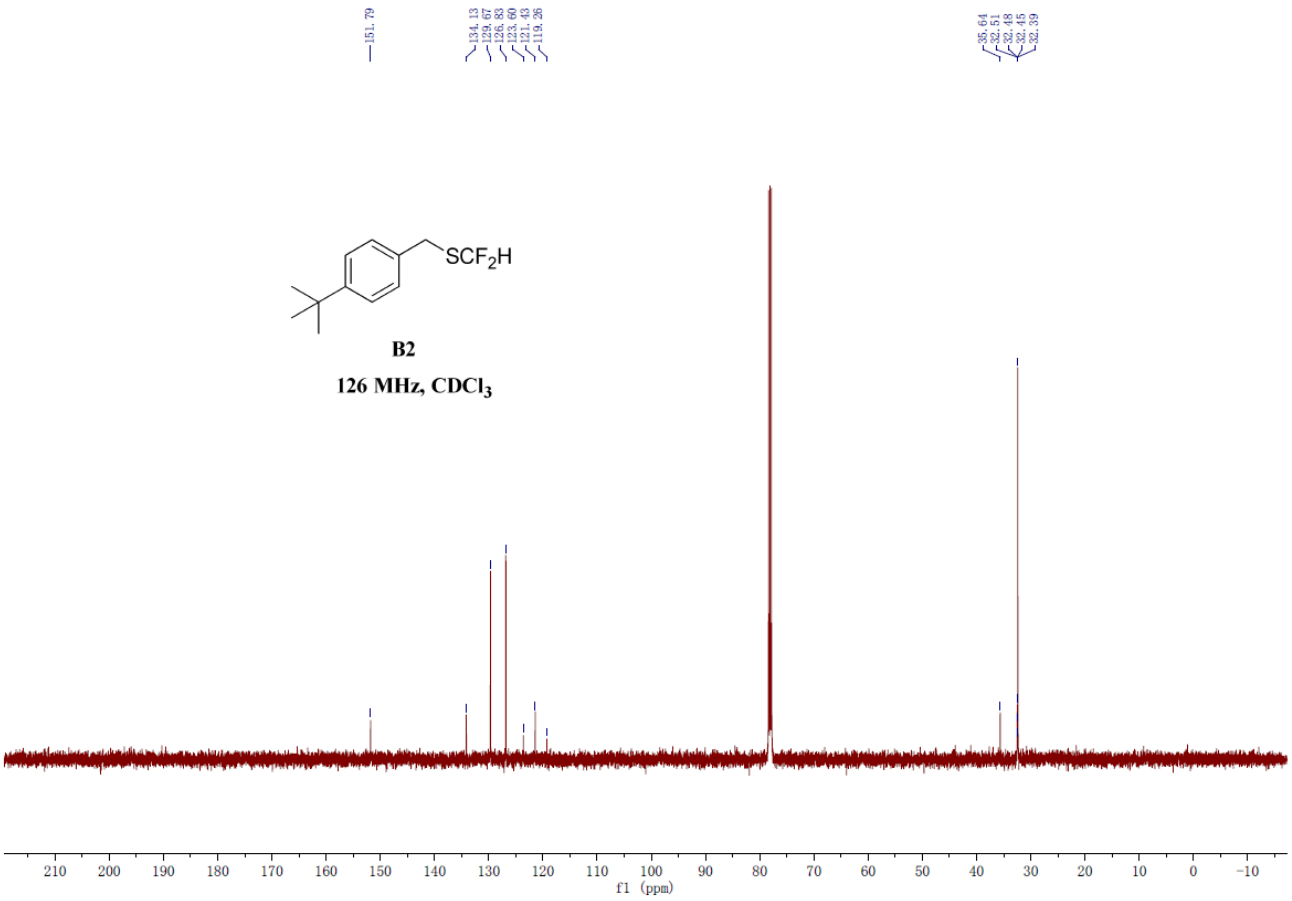
NMR spectra

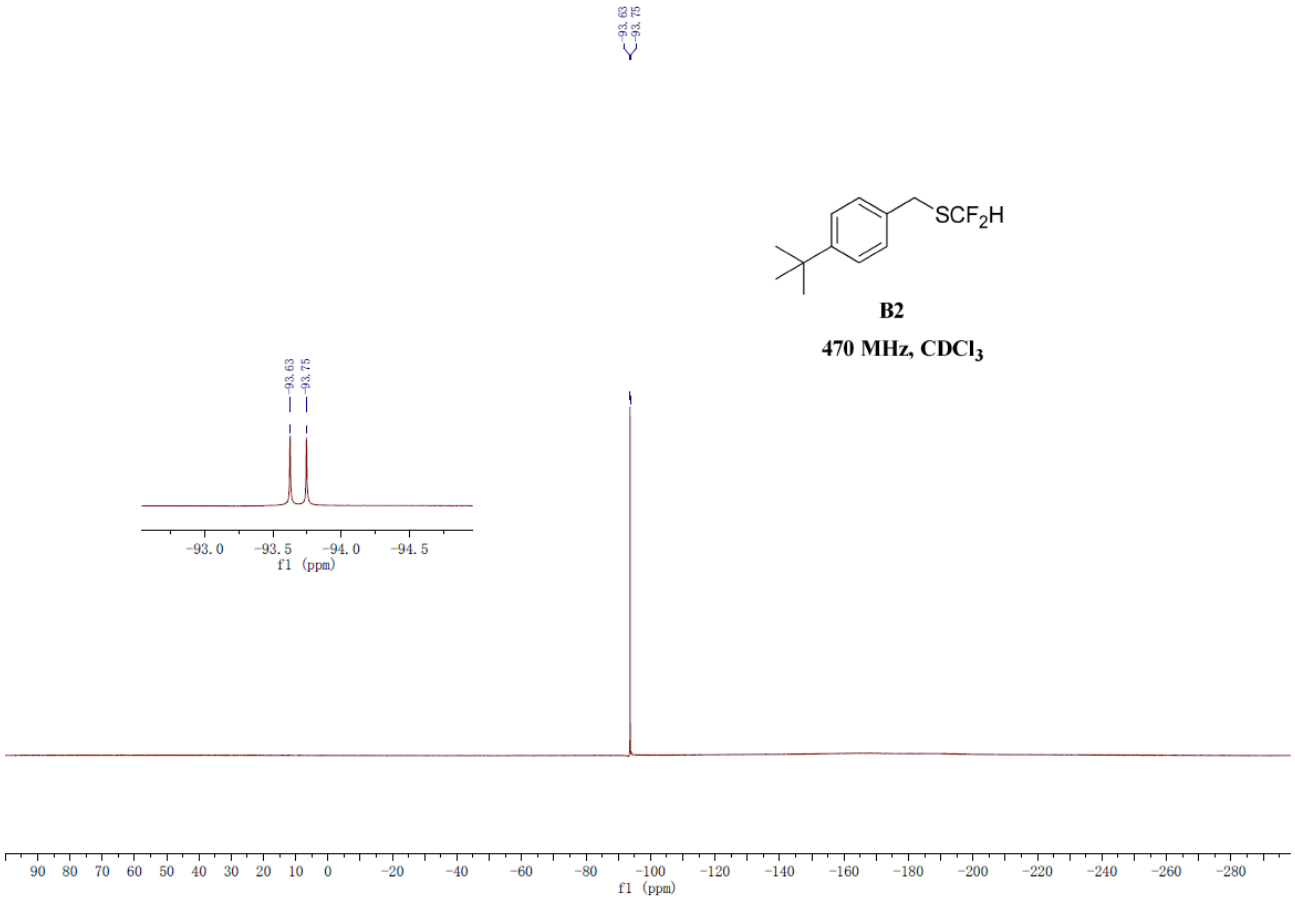

7.25
7.23
7.16
7.14
6.84
6.73
6.62
4.00
2.35
SCF2H
B1
500 MHz, CDCl3
2.12
2.00
1.09
2.00
3.18
f1 (ppm)

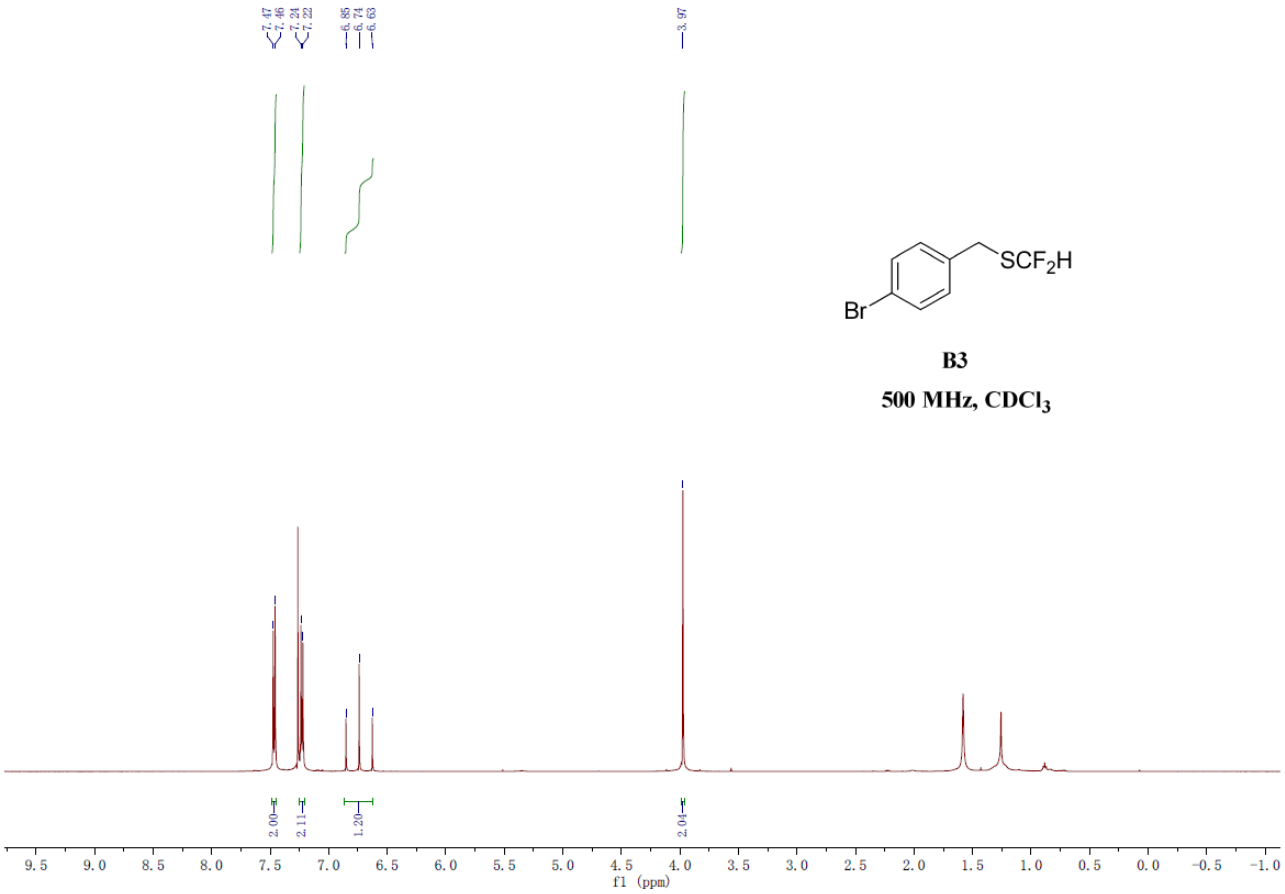

138.52
134.19
130.57
129.88
123.59
121.42
119.25
32.65
32.63
32.60
22.20
SCF2H
B1
126 MHz, CDCl3
f1 (ppm)


-93.58
-93.70
SCF2H
B1
470 MHz, CDCl3
-92.0
-93.0
-94.0
-95.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


7.37
7.36
7.29
7.27
6.85
6.74
6.63
4.00
1.32
SCF2H
B2
500 MHz, CDCl3
2.00
1.96
1.03
1.98
9.39
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

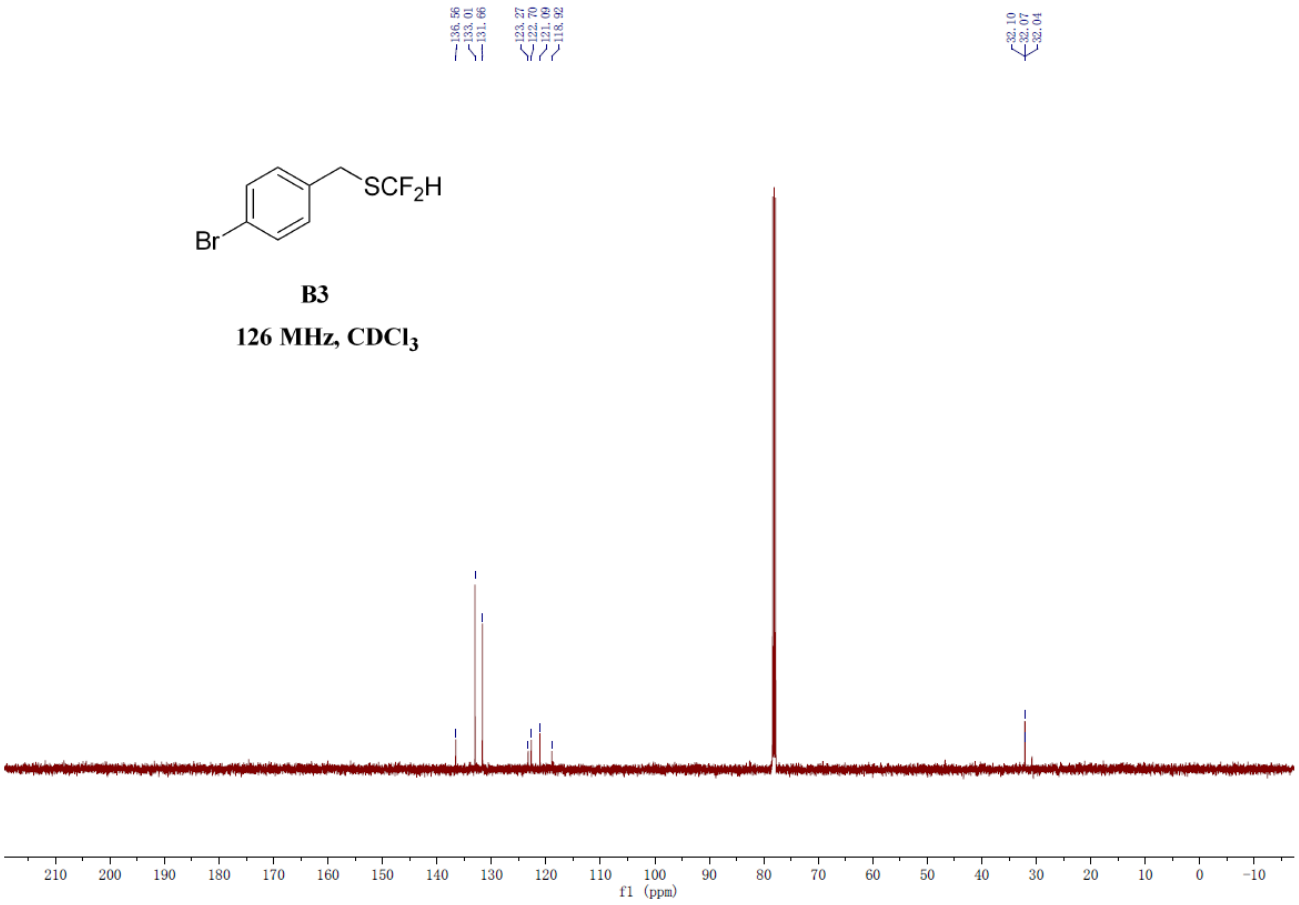

151.79
134.13
129.67
126.83
123.60
121.43
119.26
35.64
32.51
32.48
32.45
32.39
SCF2H
B2
126 MHz, CDCl3
f1 (ppm)


-93.63
-93.75
SCF2H
B2
470 MHz, CDCl3
f1 (ppm)



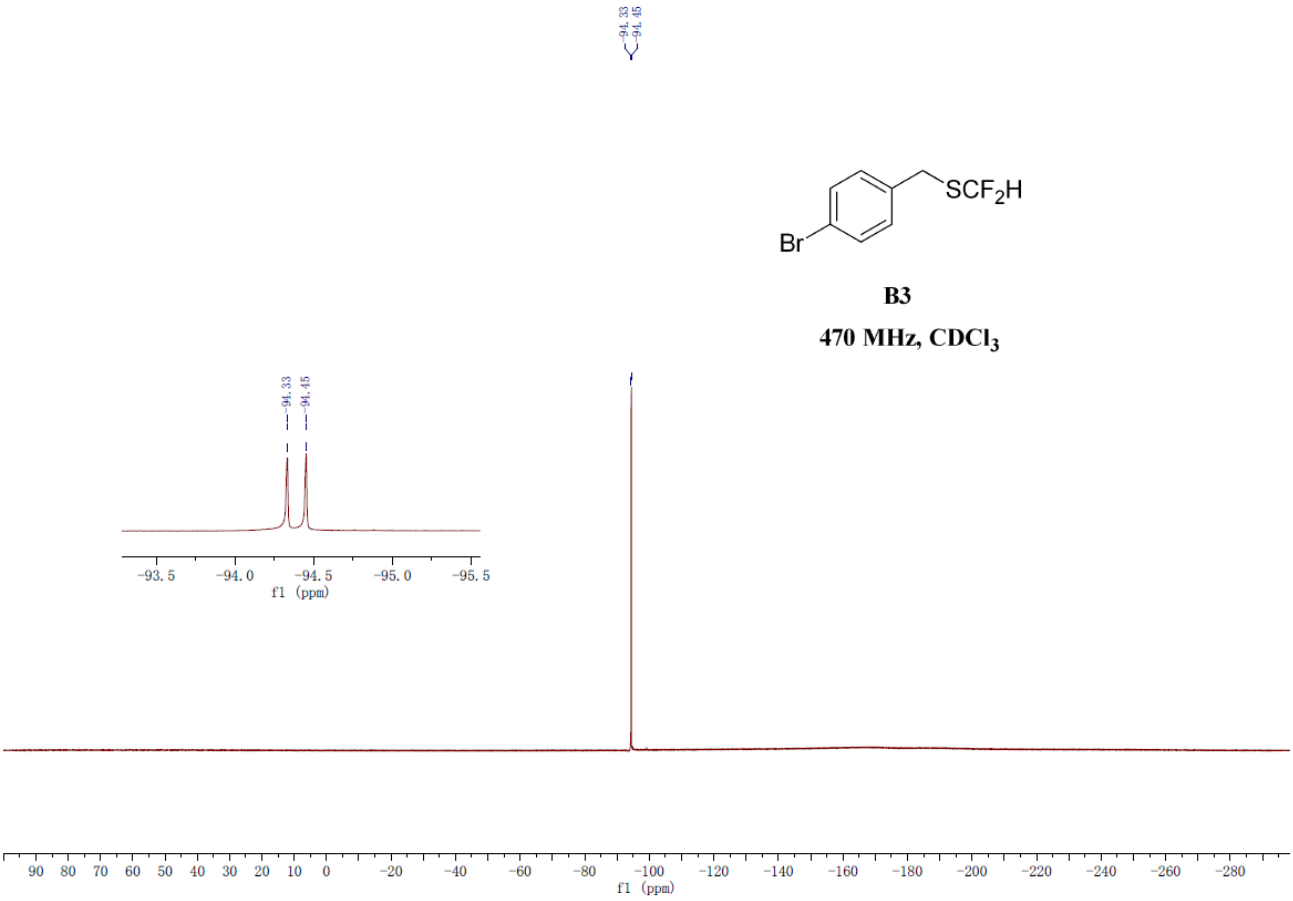
B3

500 MHz, $CDCl_3$



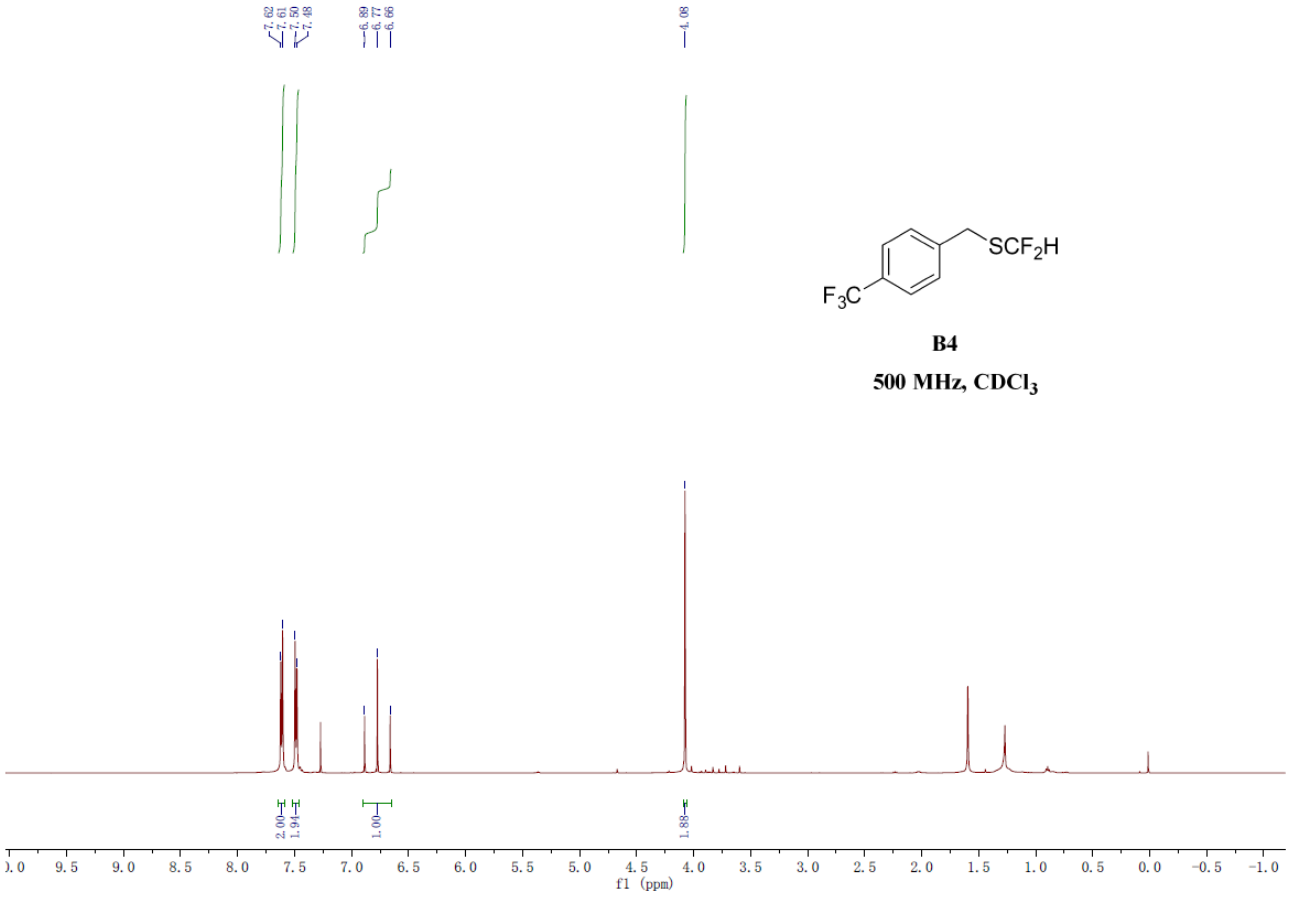
B3

126 MHz, $CDCl_3$



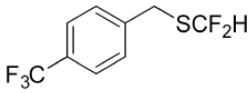
B3

470 MHz, $CDCl_3$



B4

500 MHz, $CDCl_3$

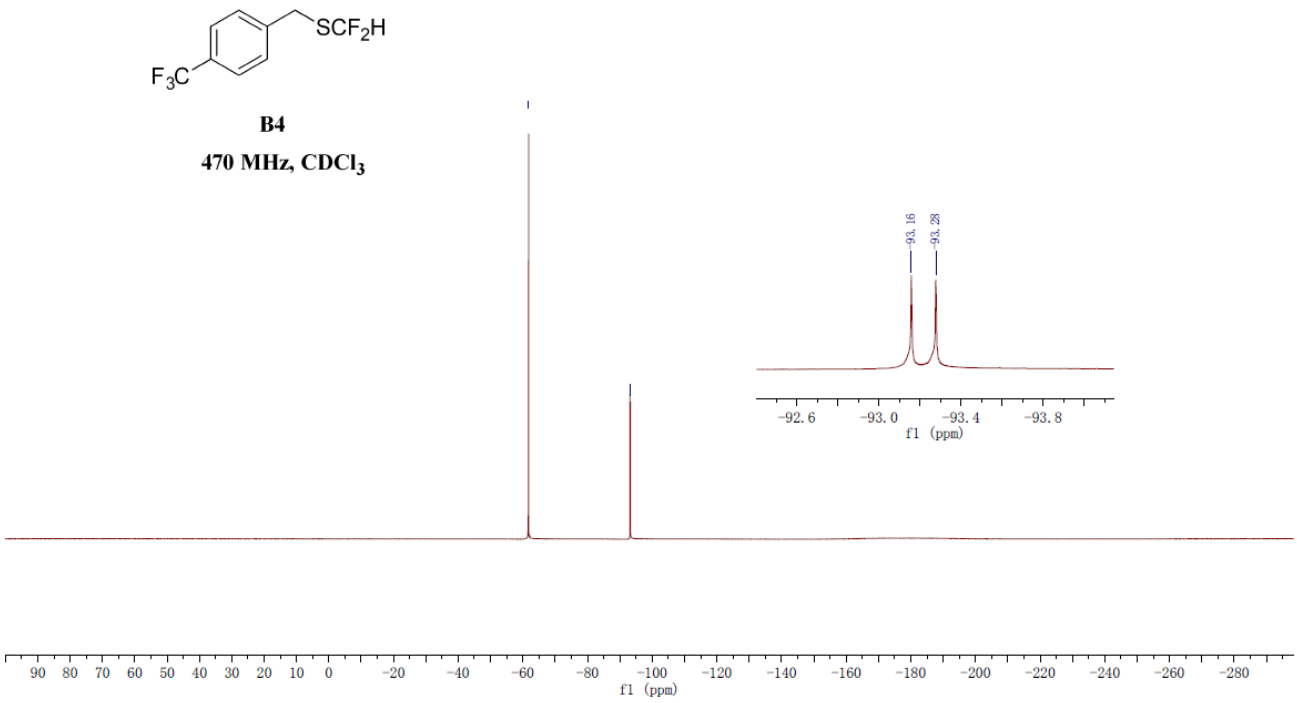


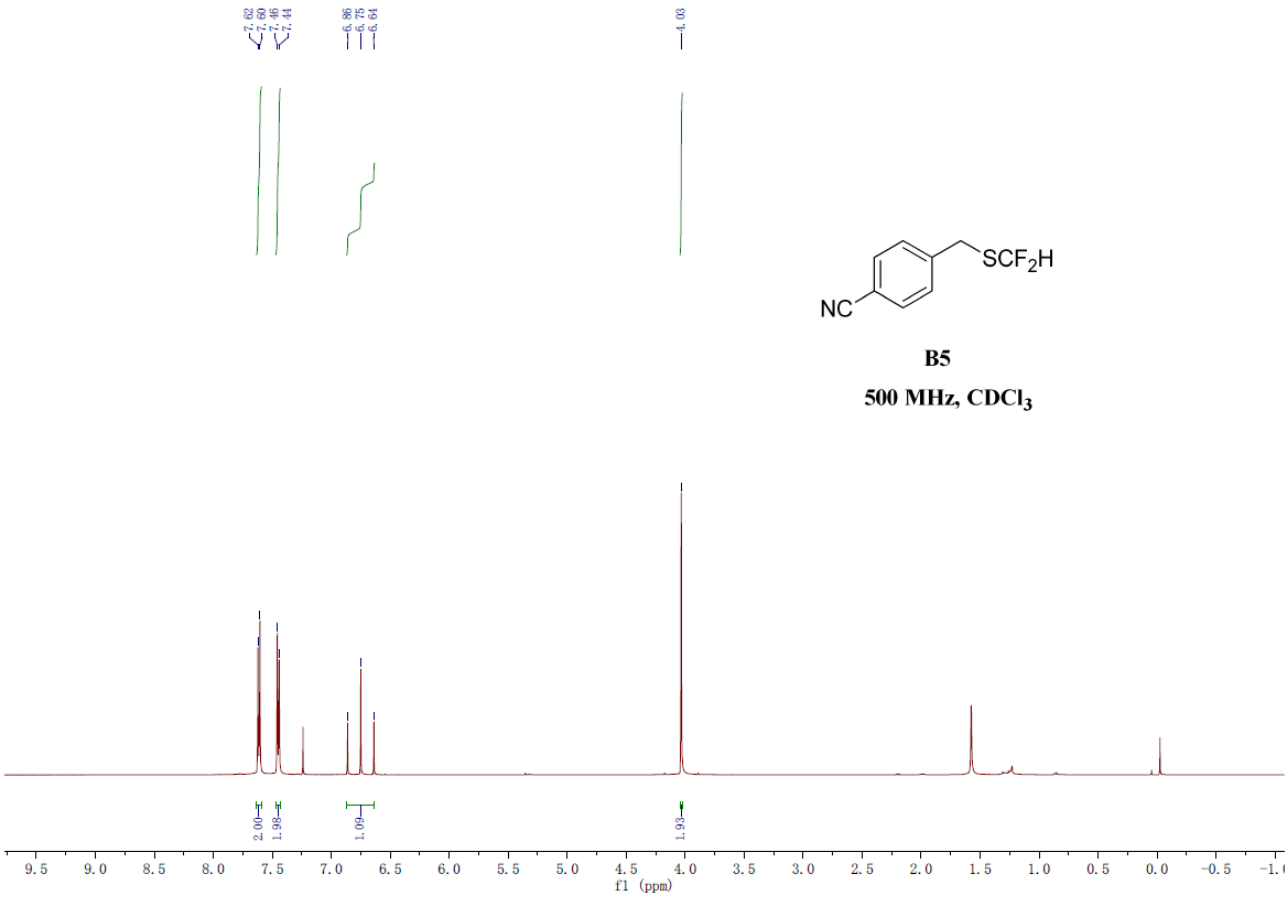
B4

126 MHz, $CDCl_3$

B4

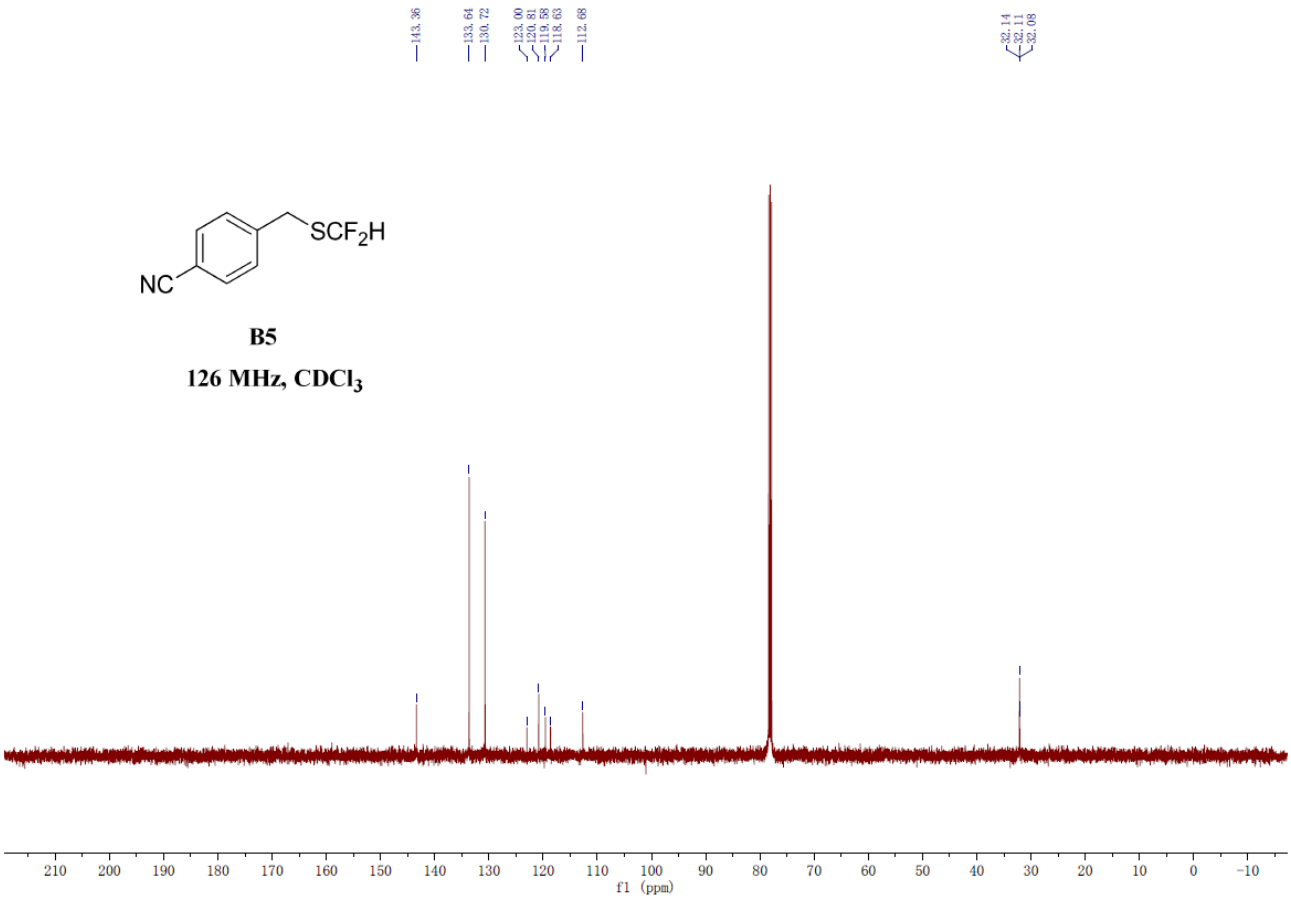
470 MHz, $CDCl_3$





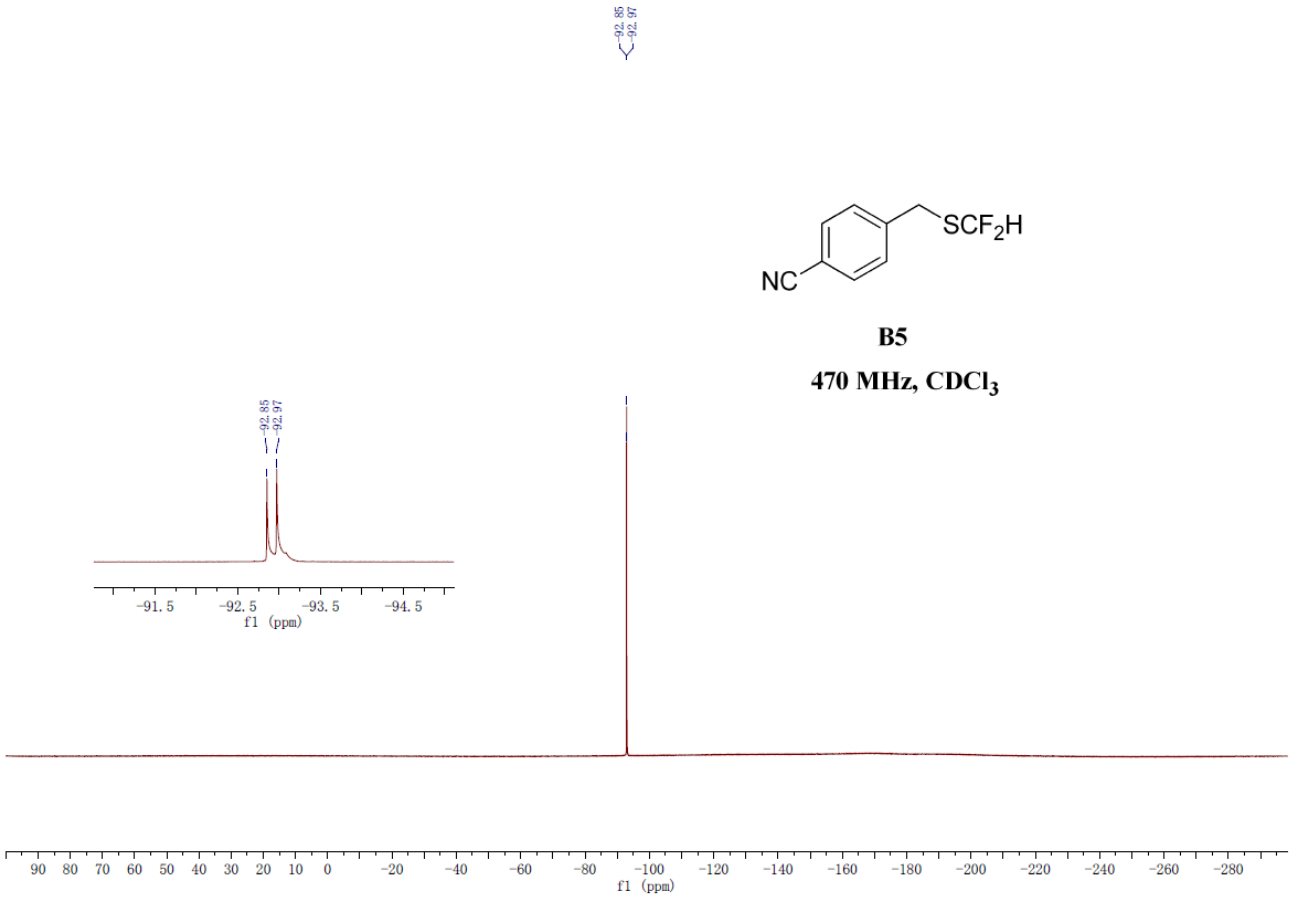
B5

500 MHz, $CDCl_3$



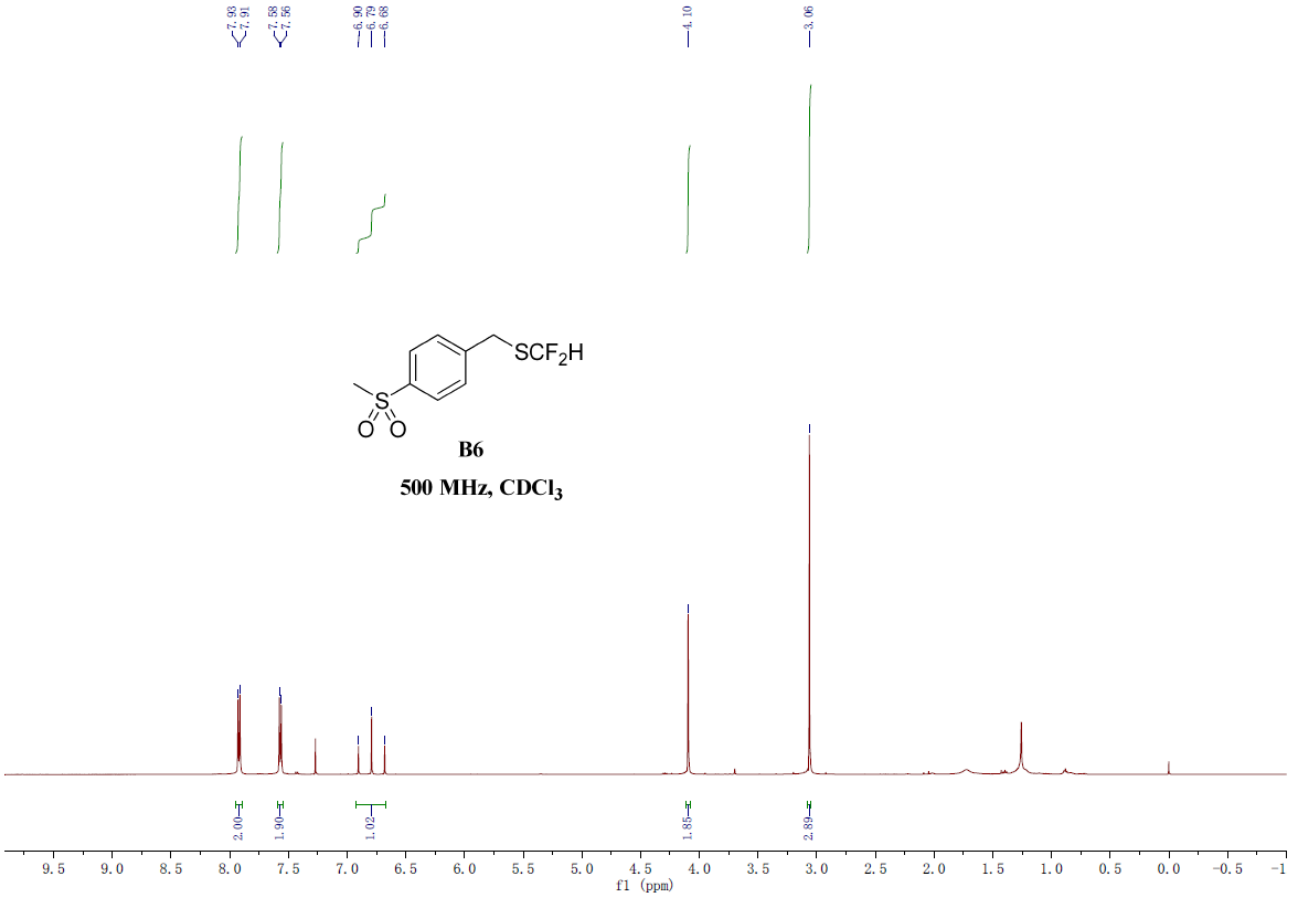
B5

126 MHz, $CDCl_3$



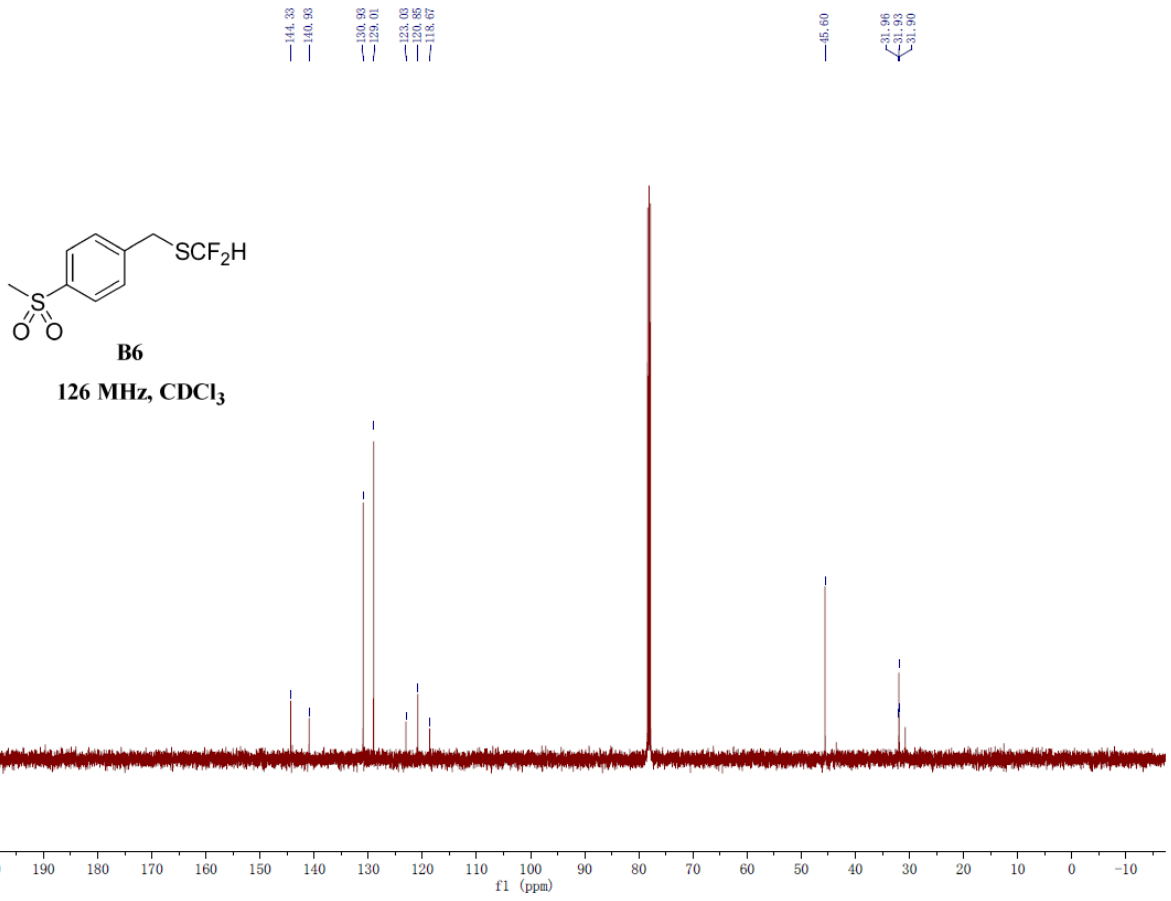
B5

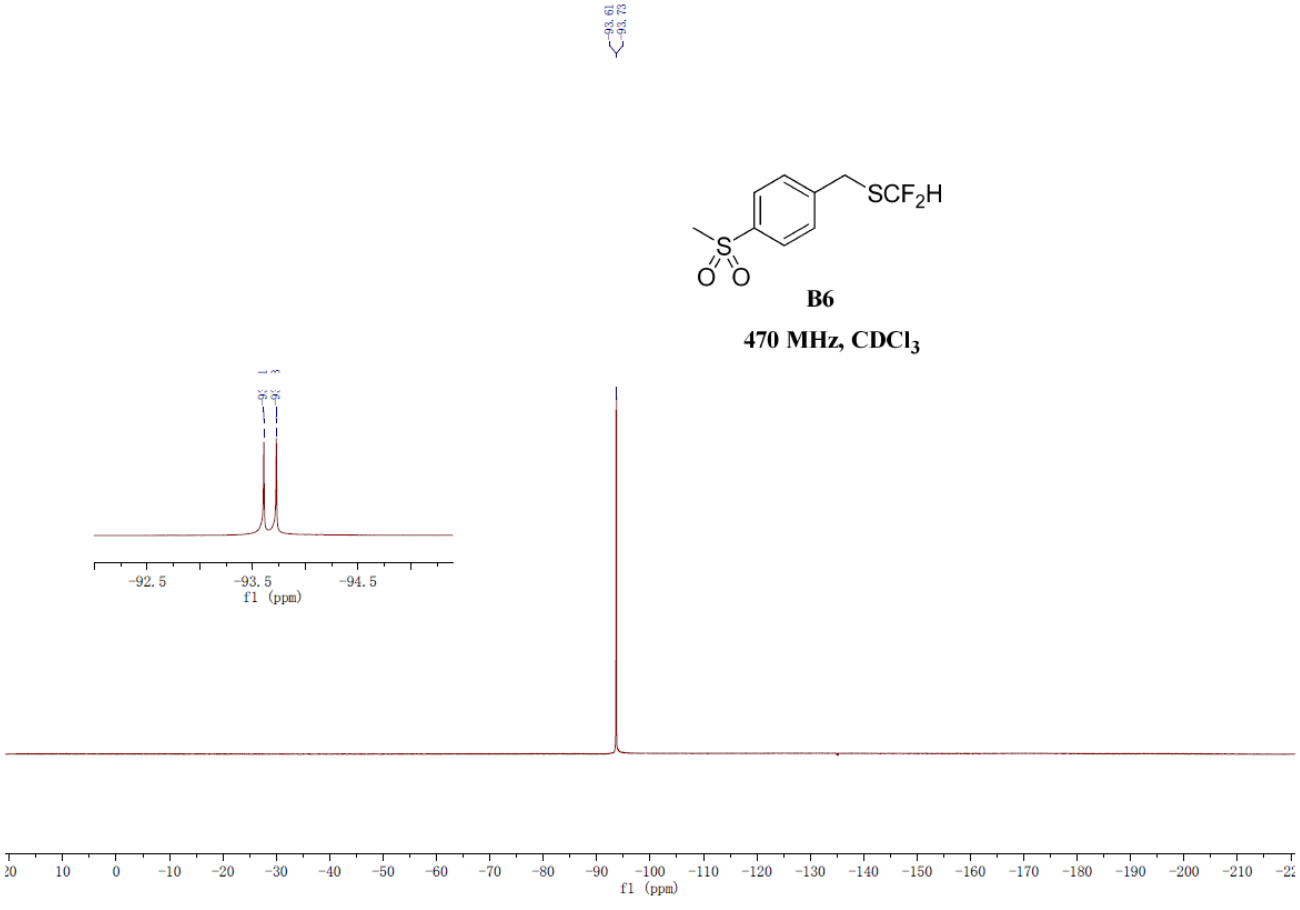
470 MHz, $CDCl_3$

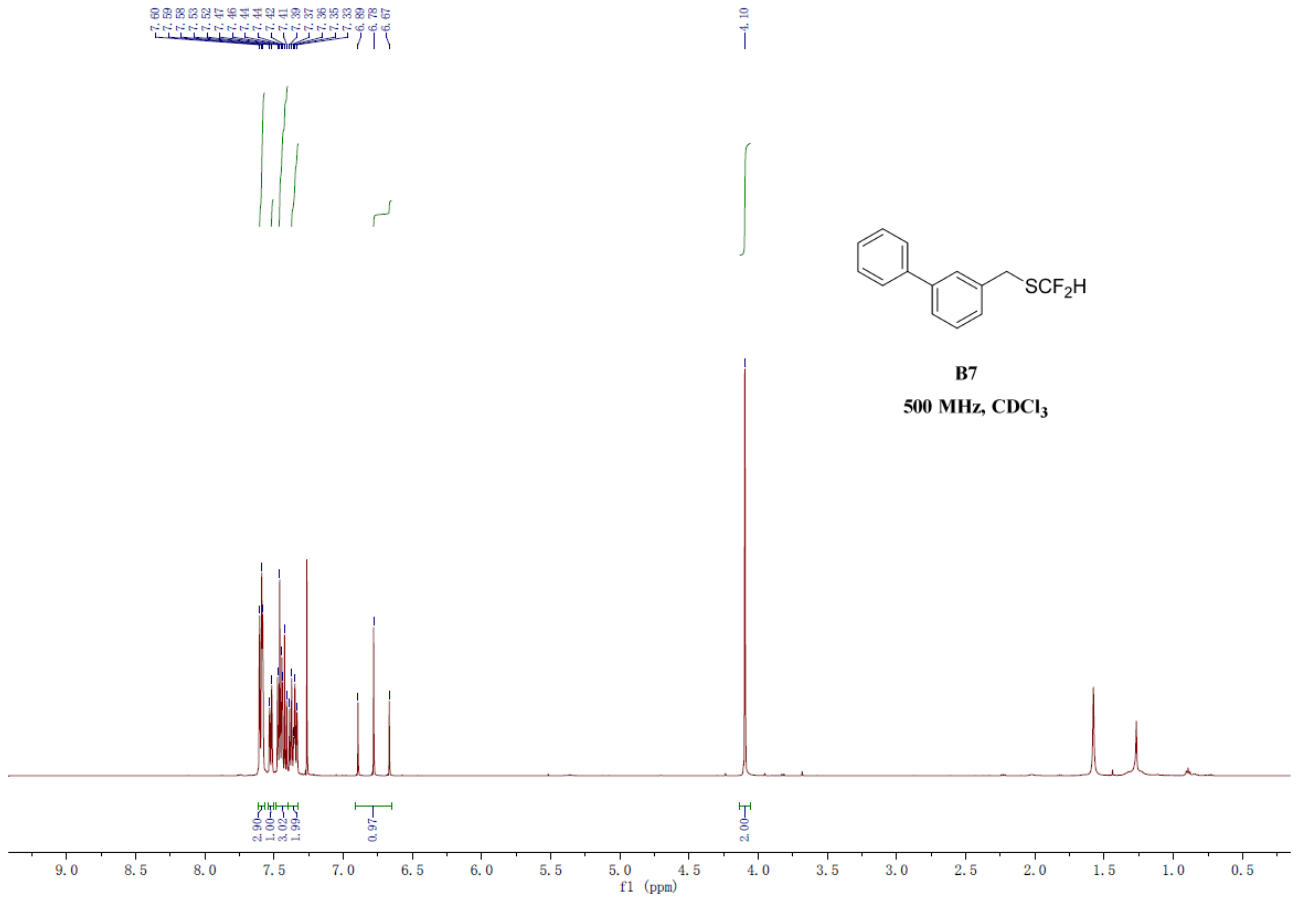


B6

500 MHz, $CDCl_3$

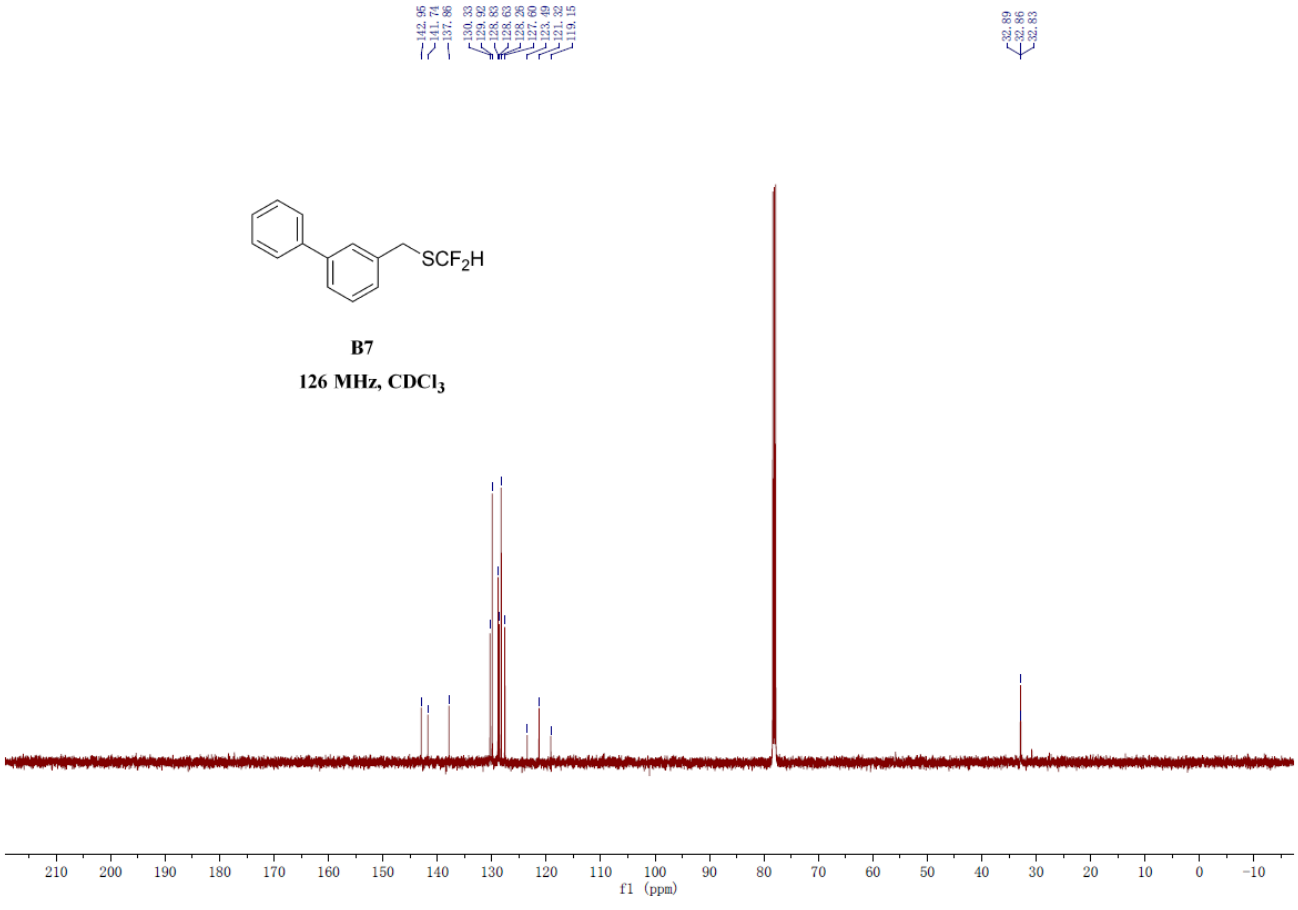

144.33
140.93
130.93
129.01
123.03
120.85
118.67
45.60
31.96
31.93
31.90
SCF2H
B6
126 MHz, CDCl3
f1 (ppm)


-93.61
-93.73
SCF2H
B6
470 MHz, CDCl3
-92.5
-93.5
-94.5
f1 (ppm)
f1 (ppm)



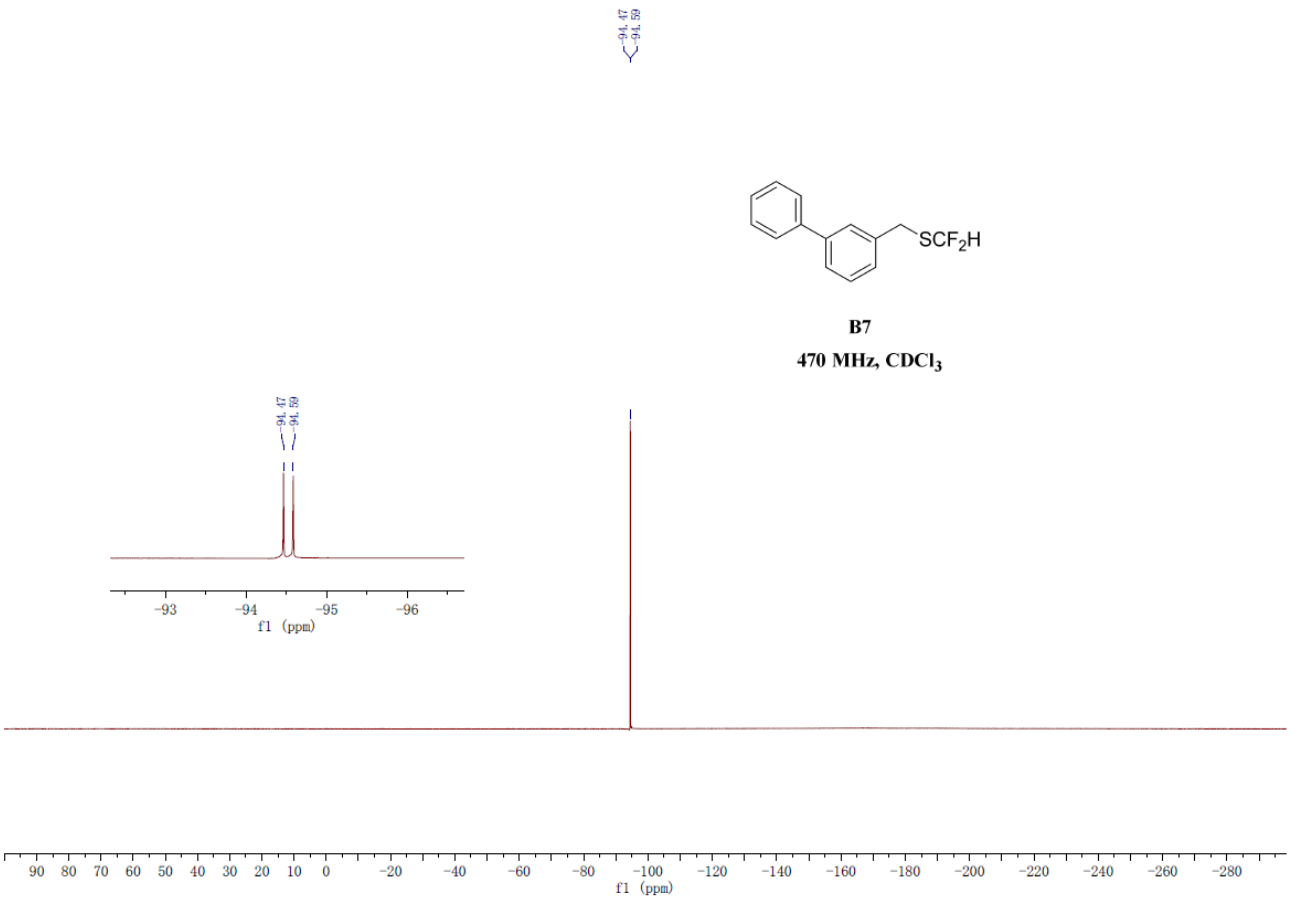
B7

500 MHz, $CDCl_3$



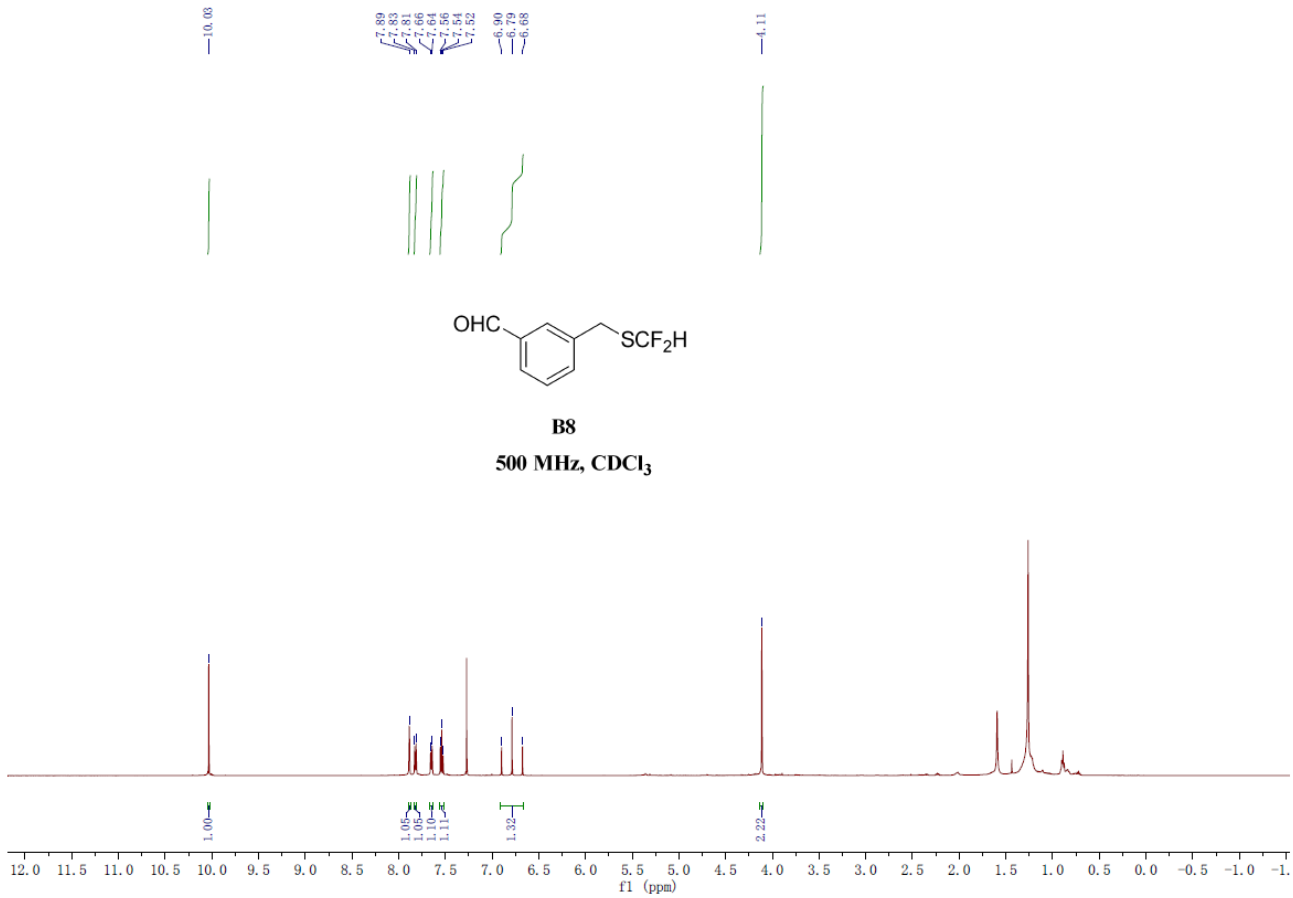
B7

126 MHz, $CDCl_3$



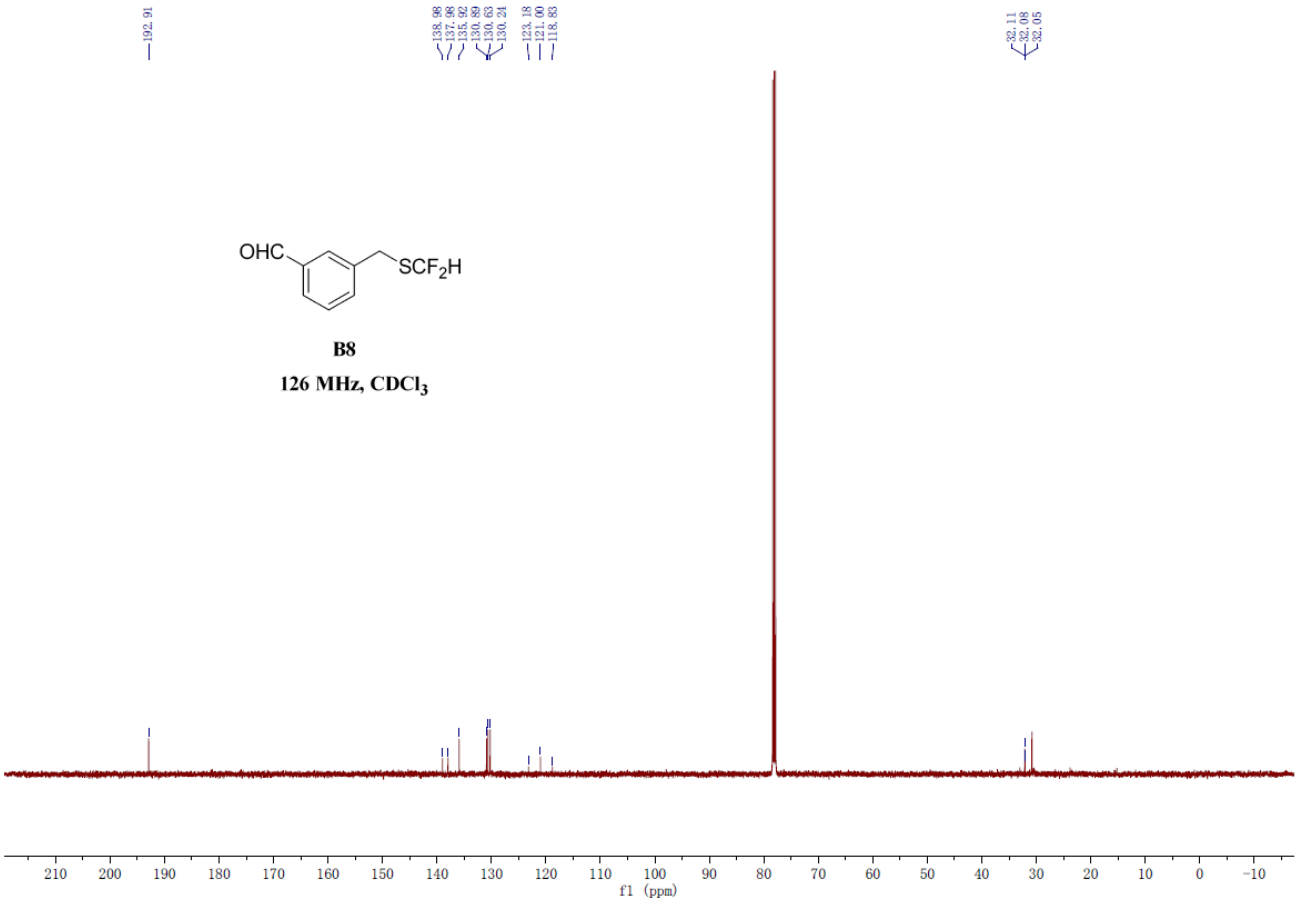
B7

470 MHz, $CDCl_3$



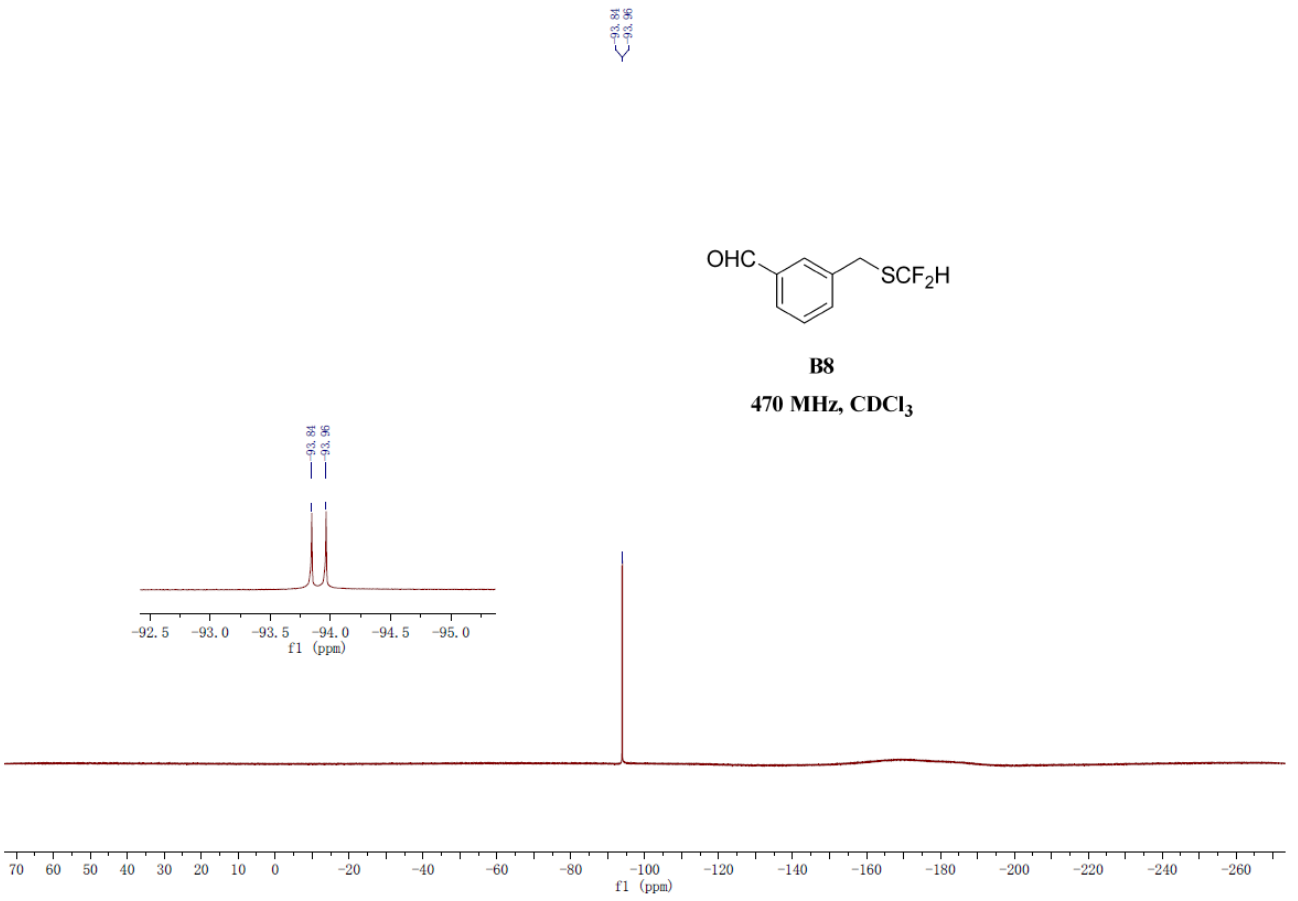
B8

500 MHz, $CDCl_3$



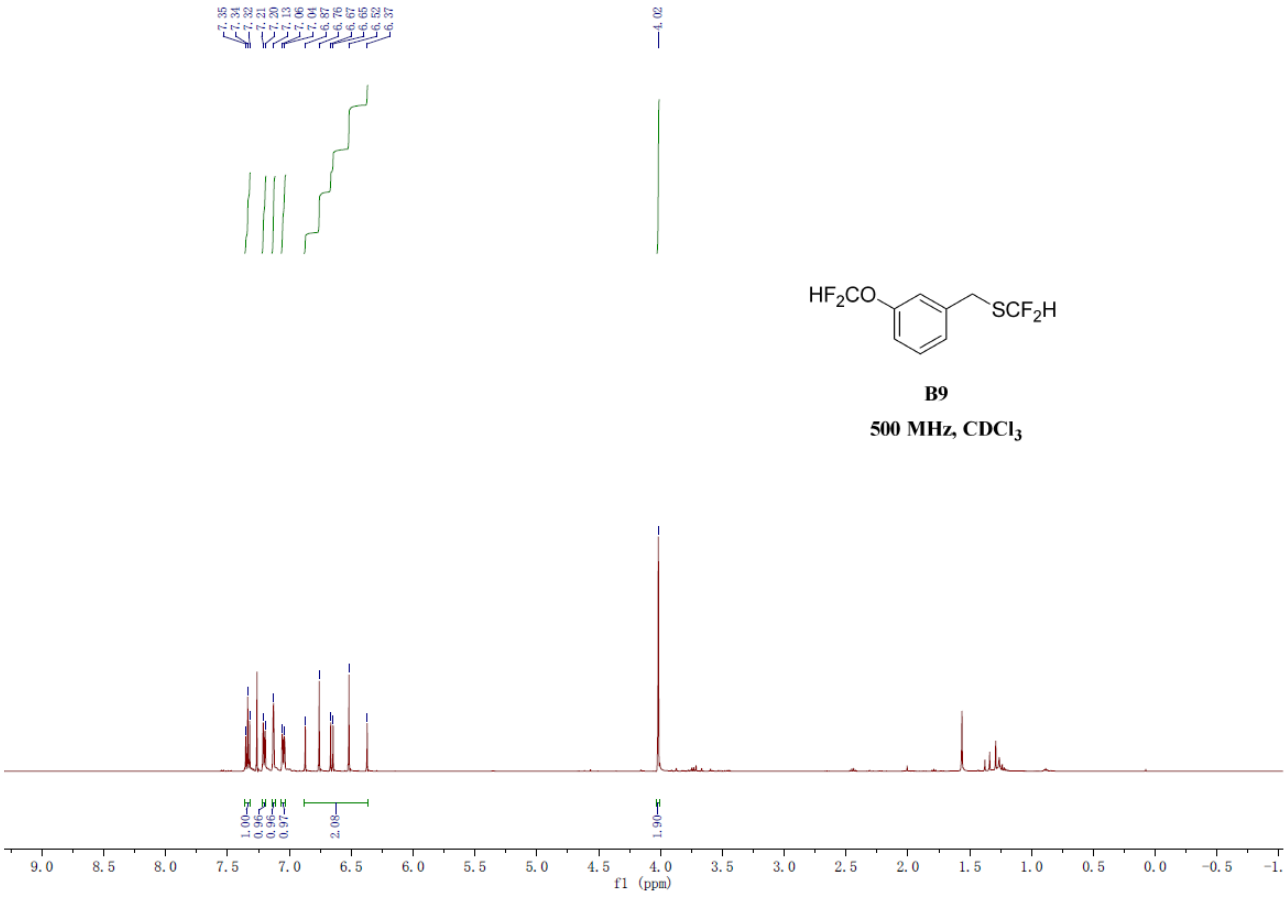
B8

126 MHz, $CDCl_3$



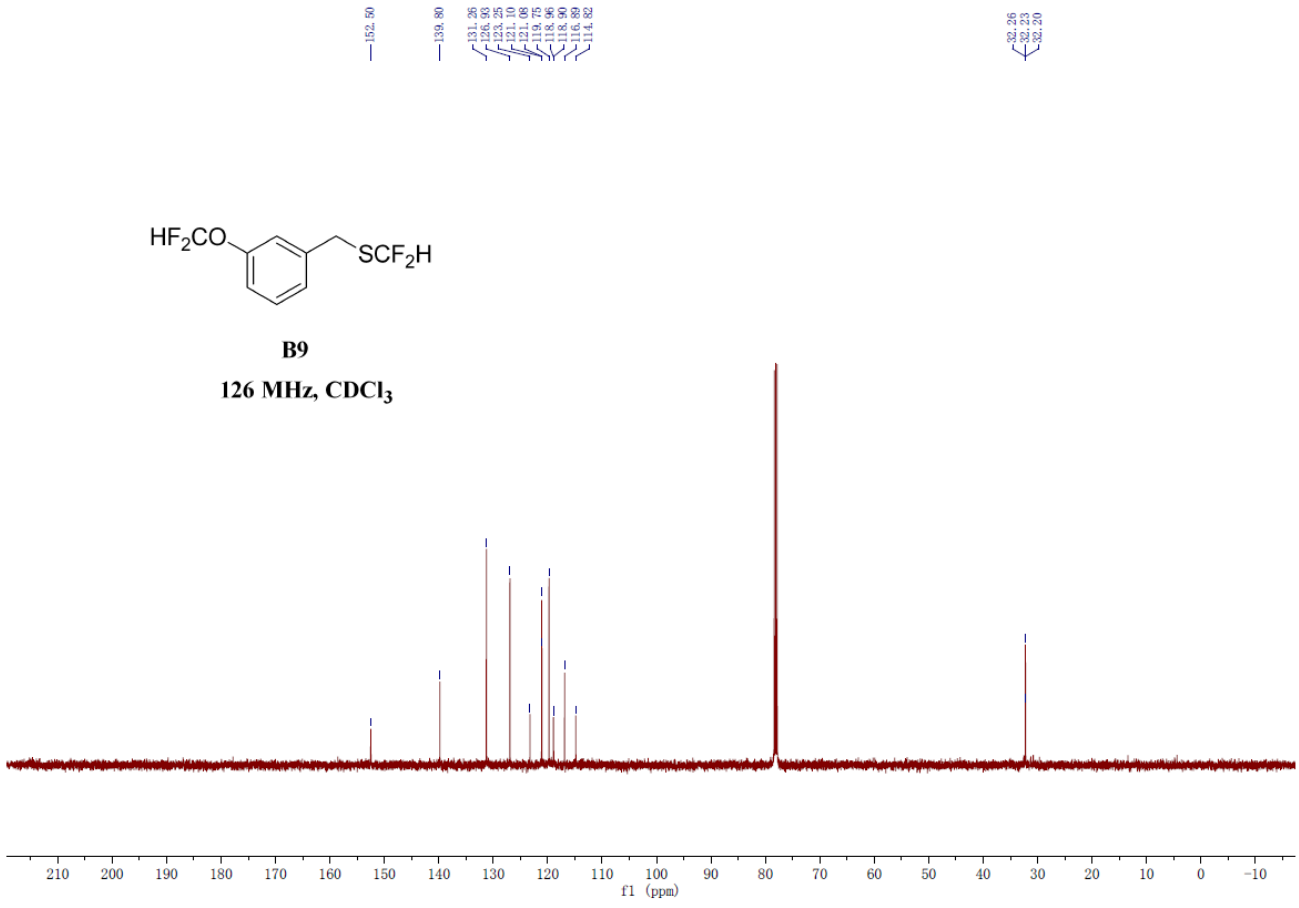
B8

470 MHz, $CDCl_3$



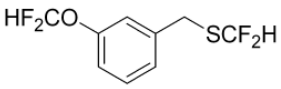
B9

500 MHz, $CDCl_3$



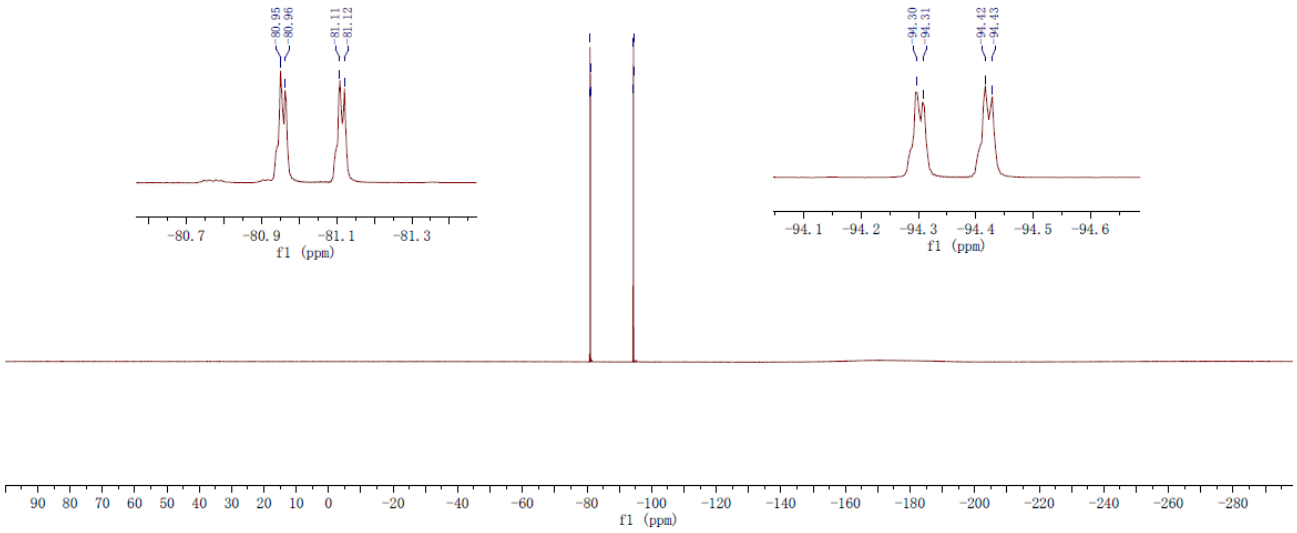
B9

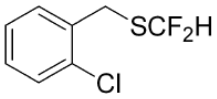
126 MHz, $CDCl_3$



B9

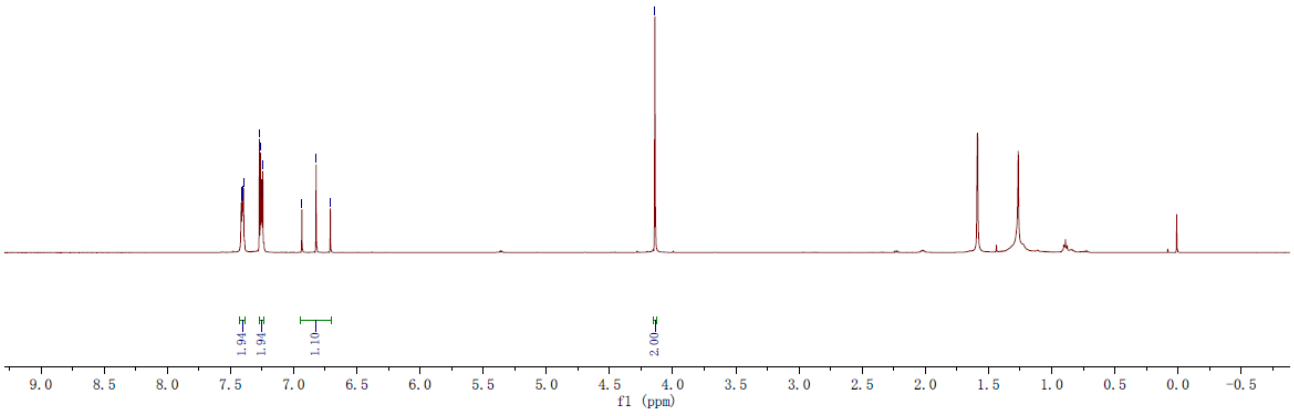
470 MHz, $CDCl_3$

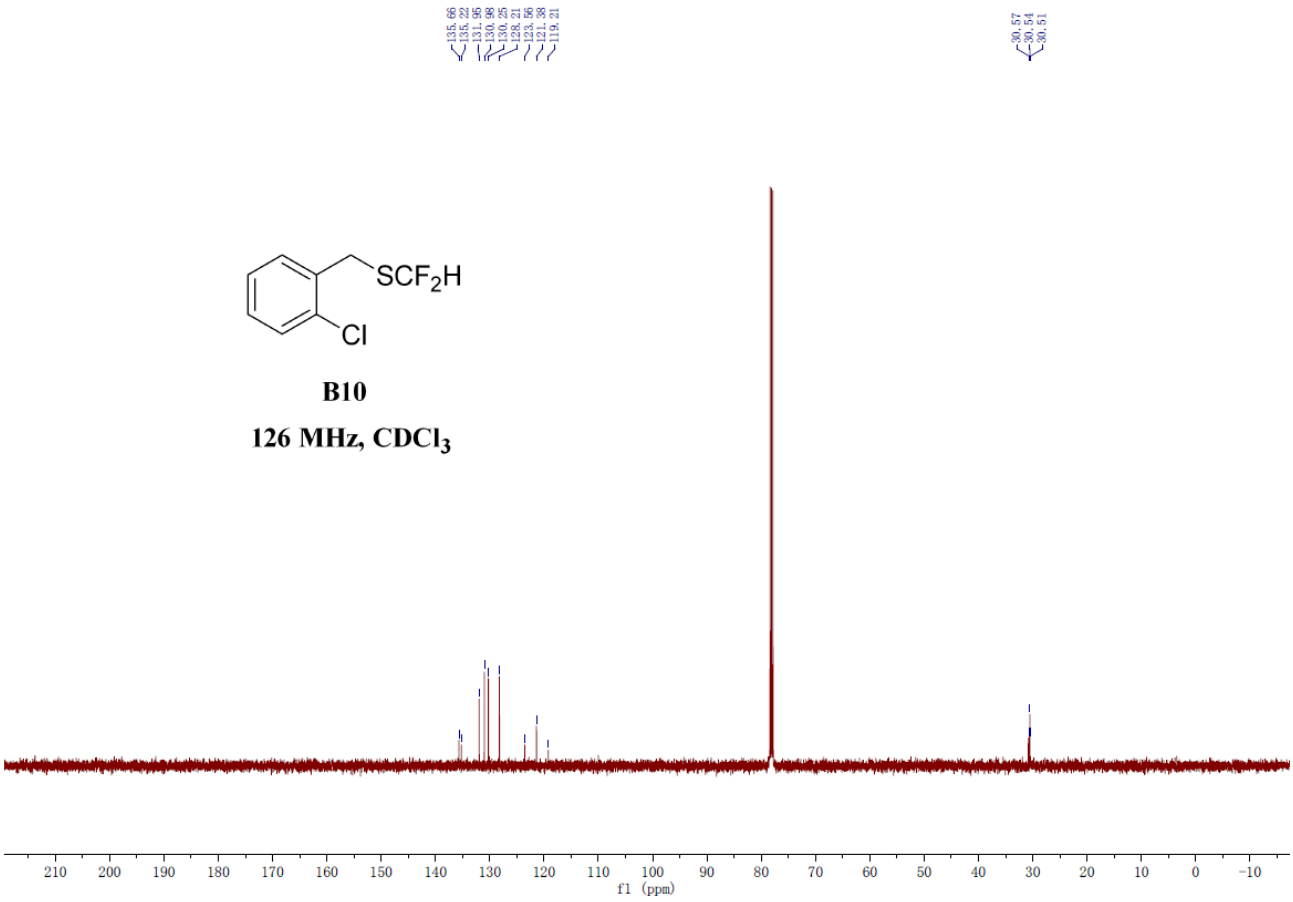


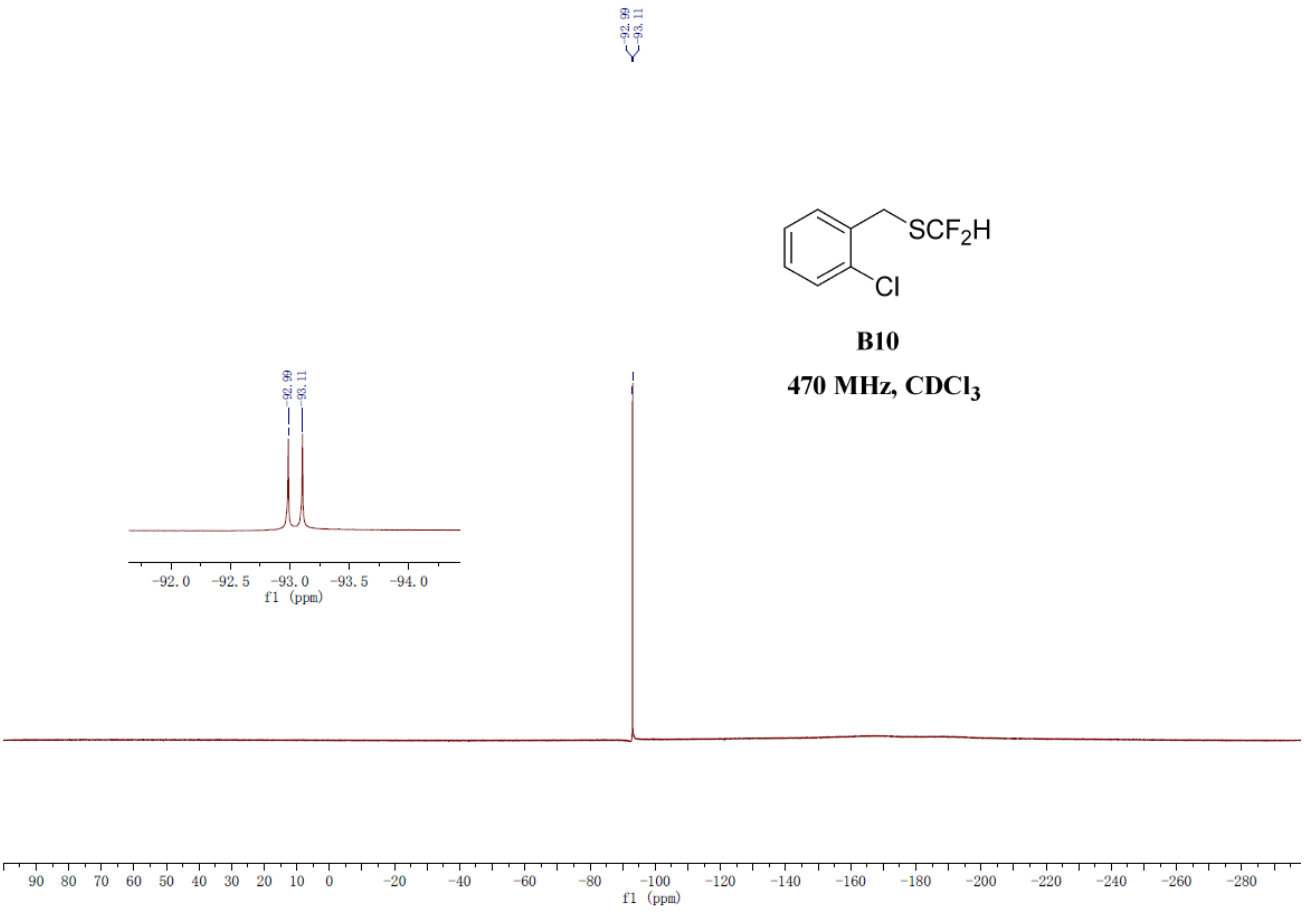


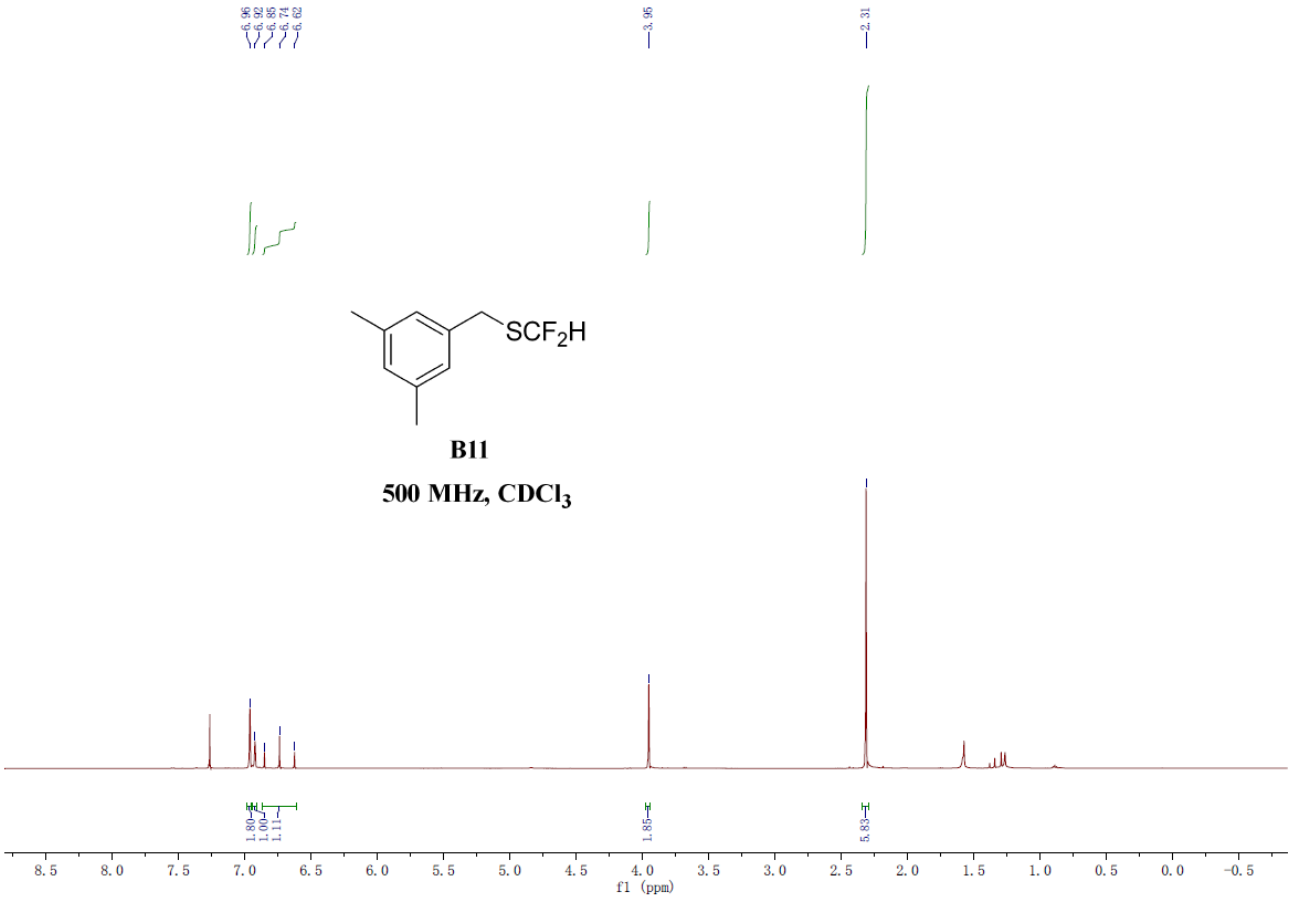
B10

500 MHz, $CDCl_3$



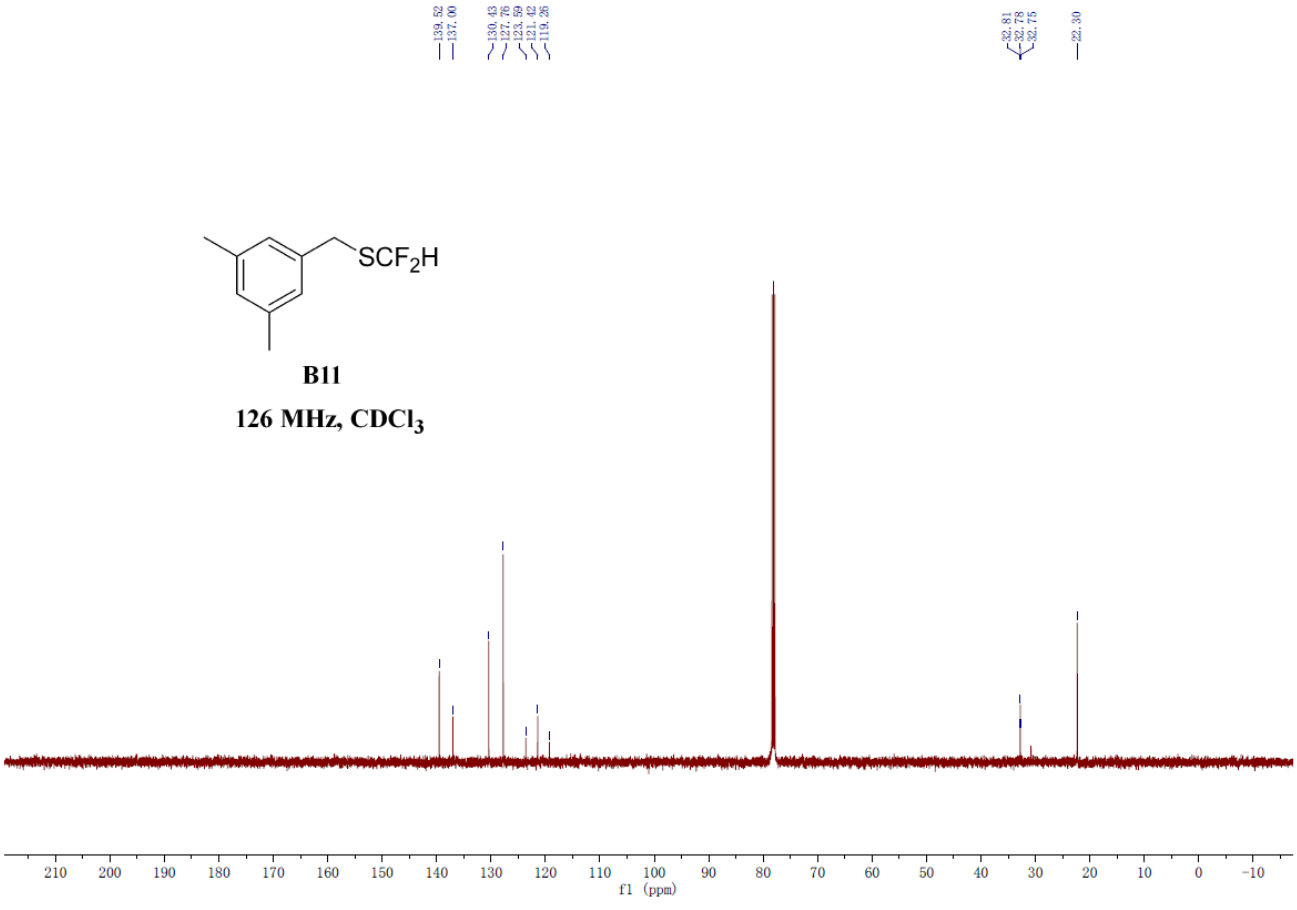

135.66
135.22
131.95
130.68
130.25
128.21
123.56
121.38
119.21
30.57
30.54
30.51
SCF2H
Cl
B10
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-92.99
-93.11
SCF2H
Cl
B10
470 MHz, CDCl3
-92.0 -92.5 -93.0 -93.5 -94.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)



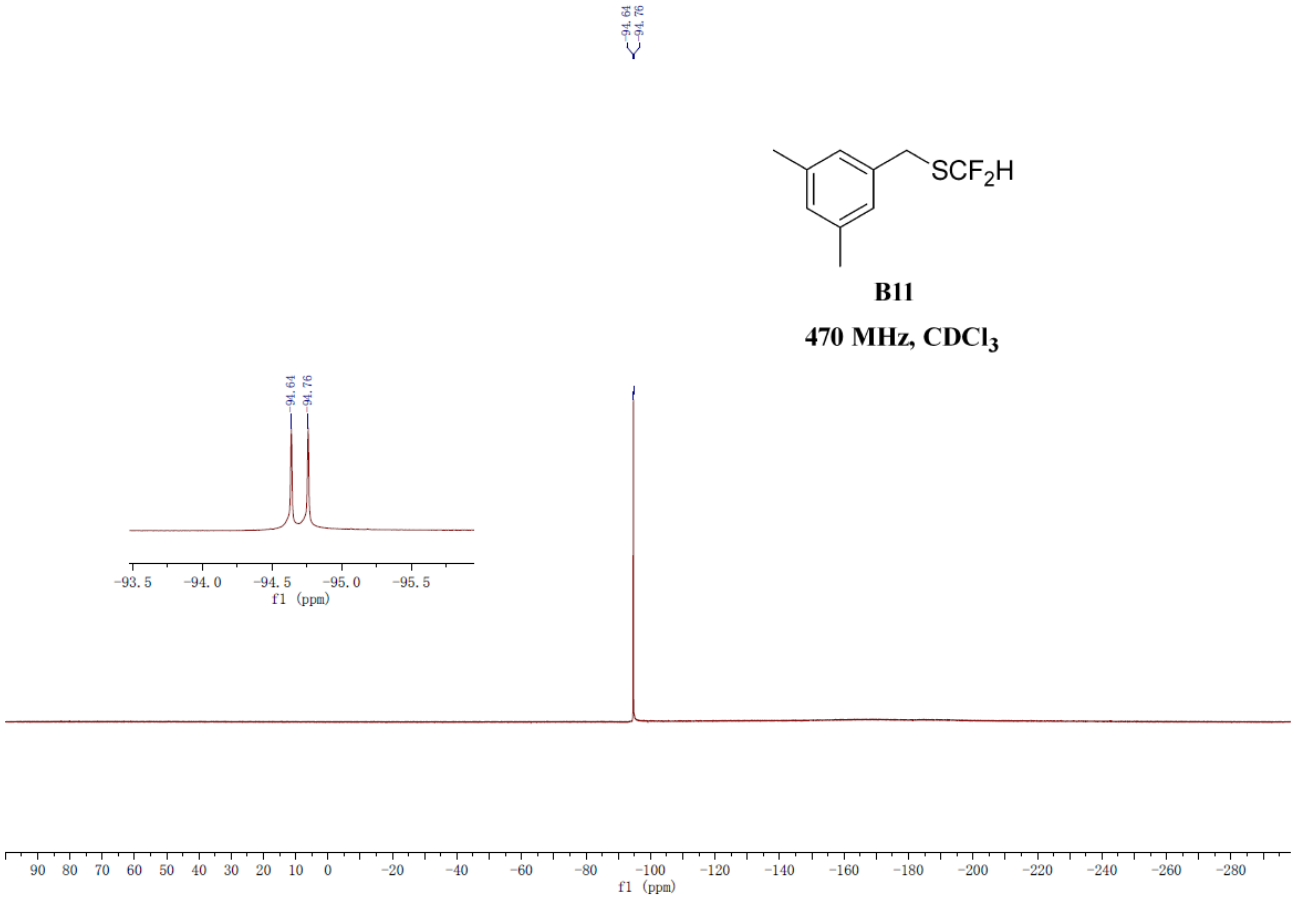
B11

500 MHz, $CDCl_3$



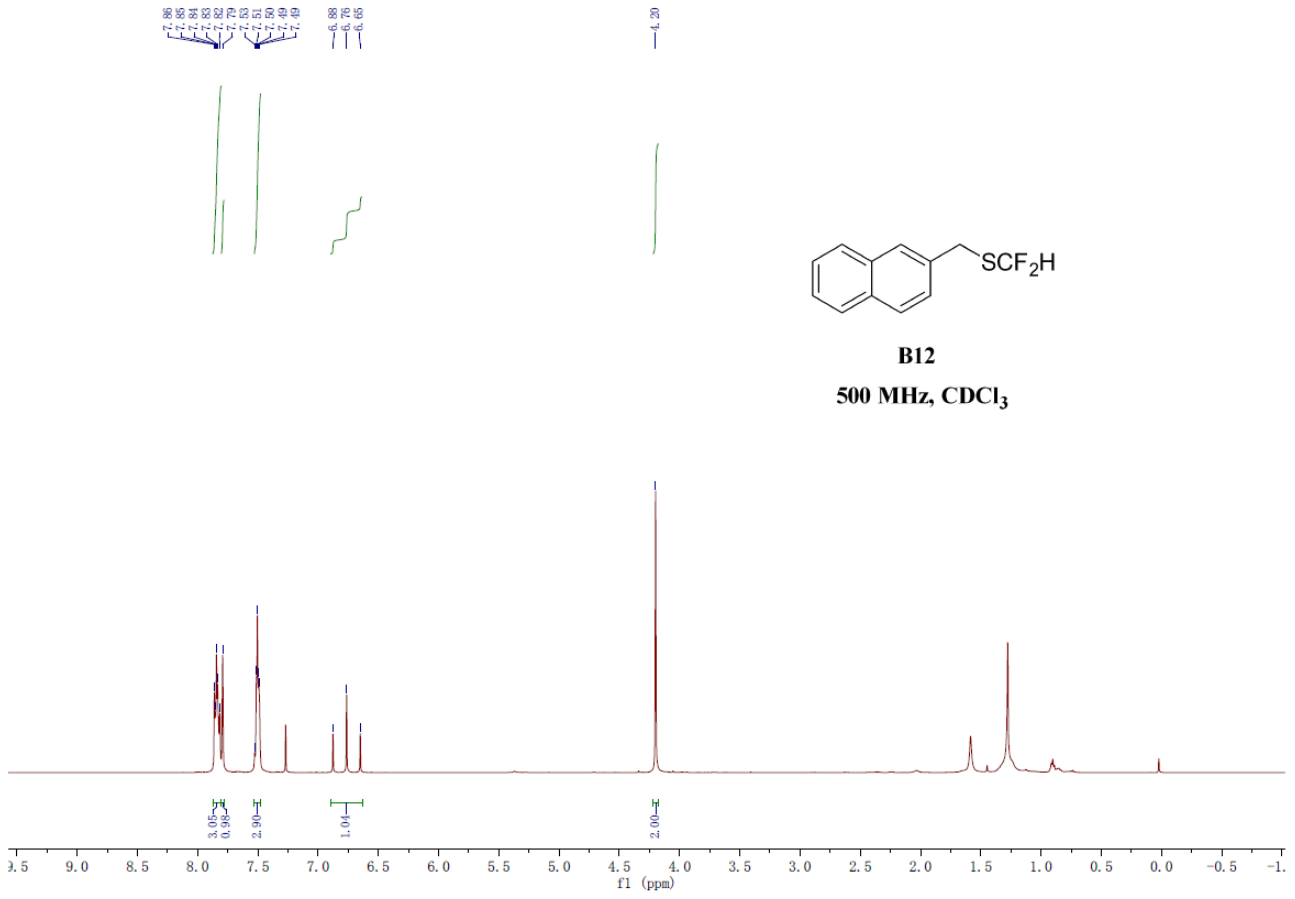
B11

126 MHz, $CDCl_3$



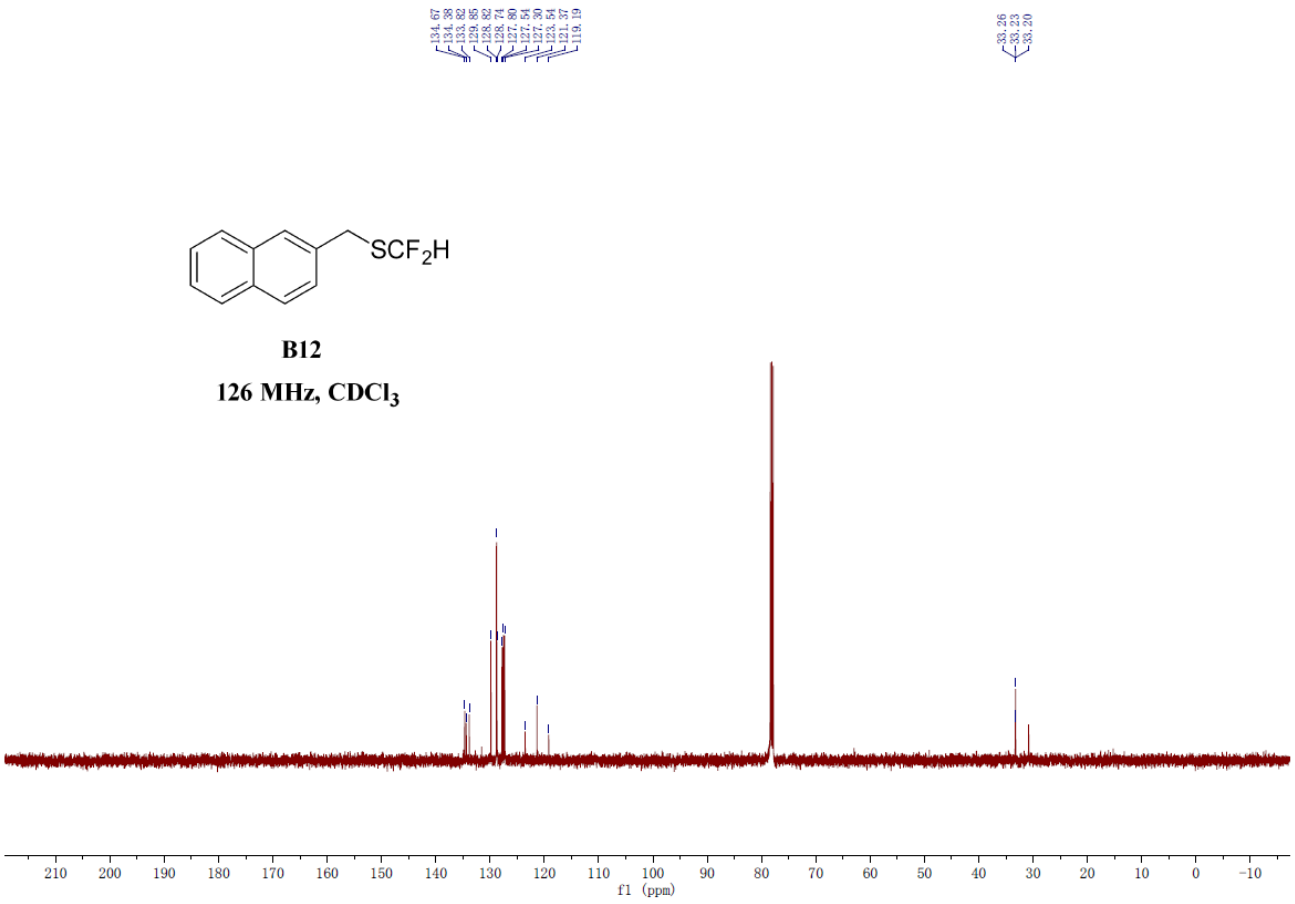
B11

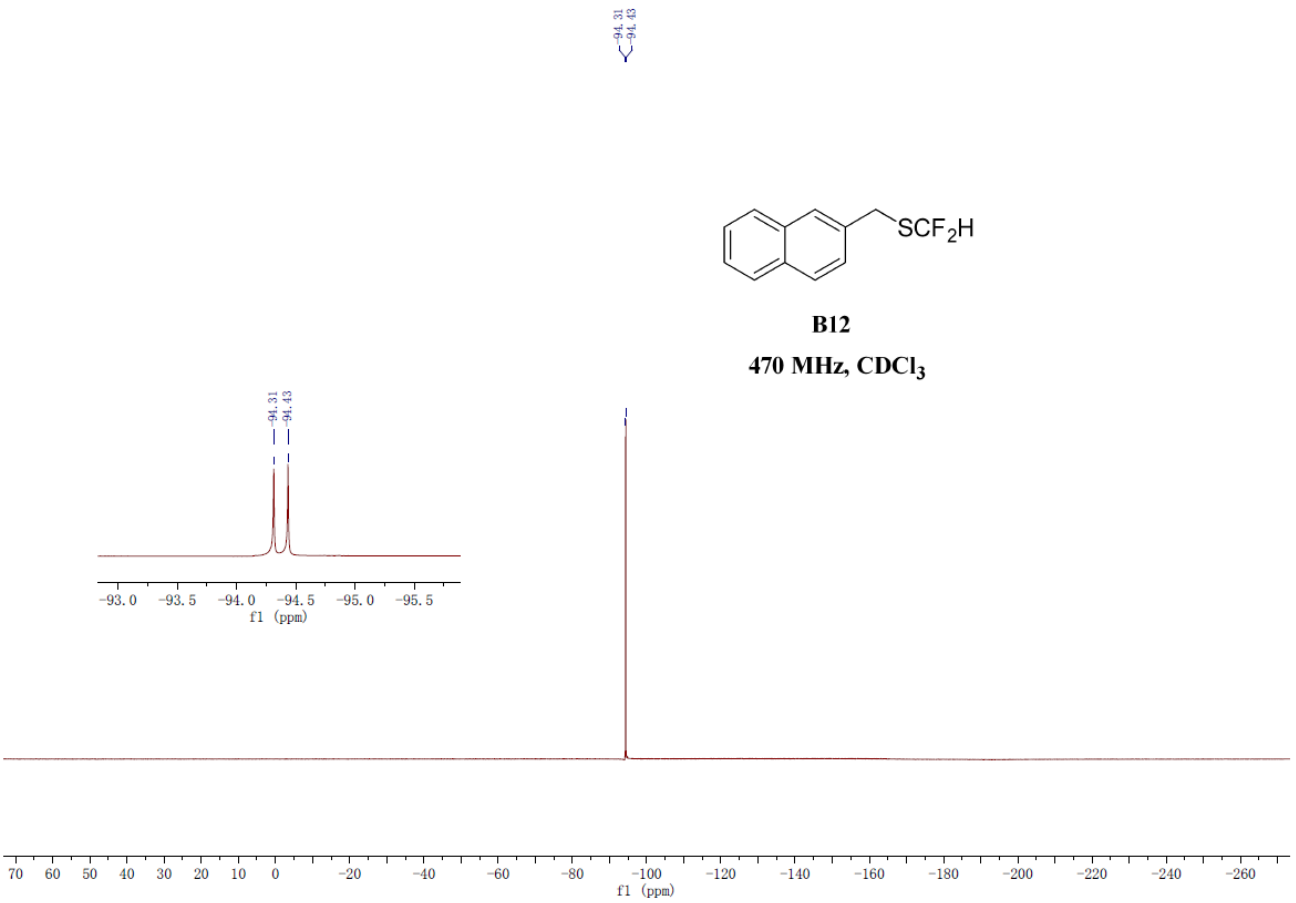
470 MHz, $CDCl_3$

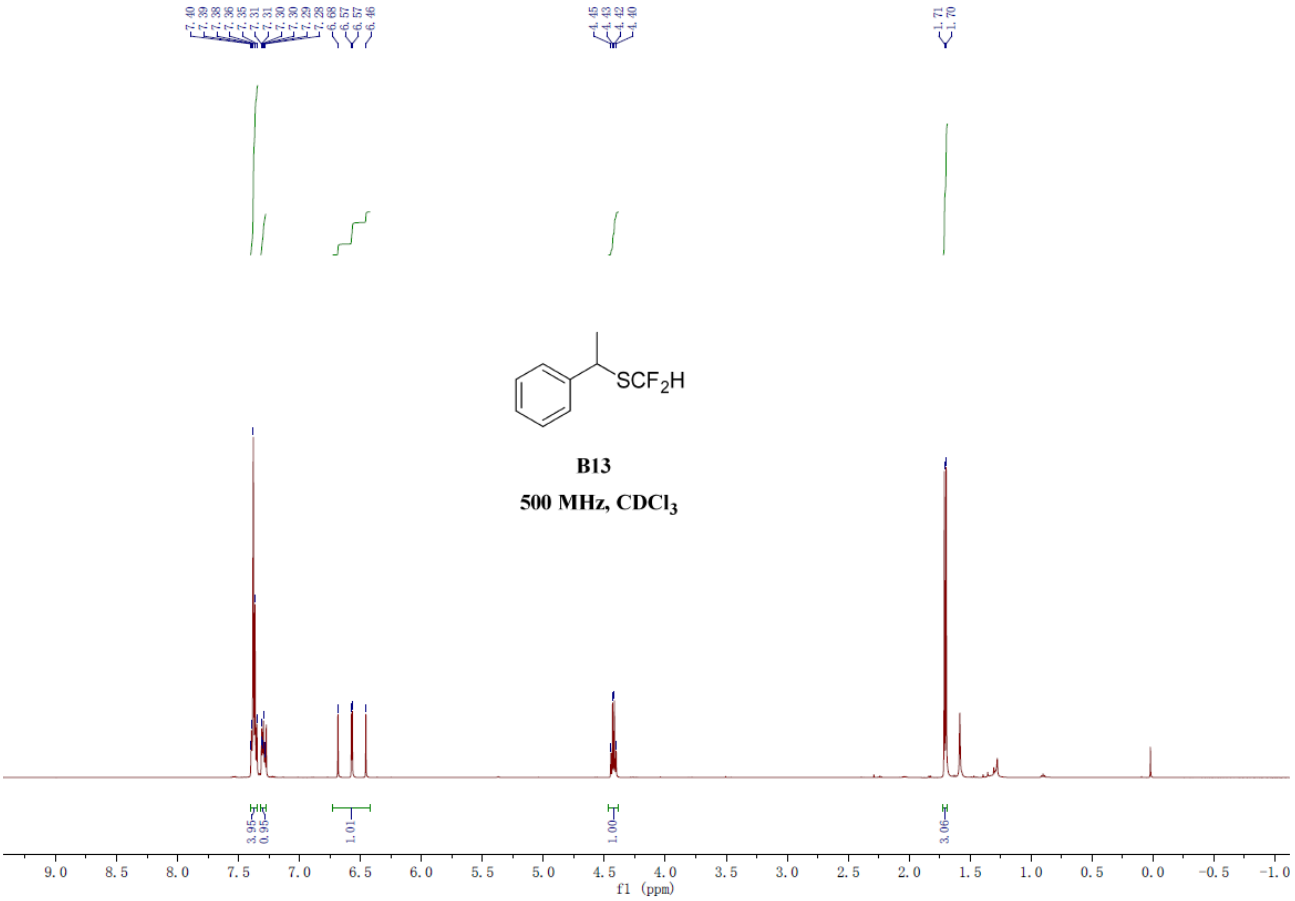


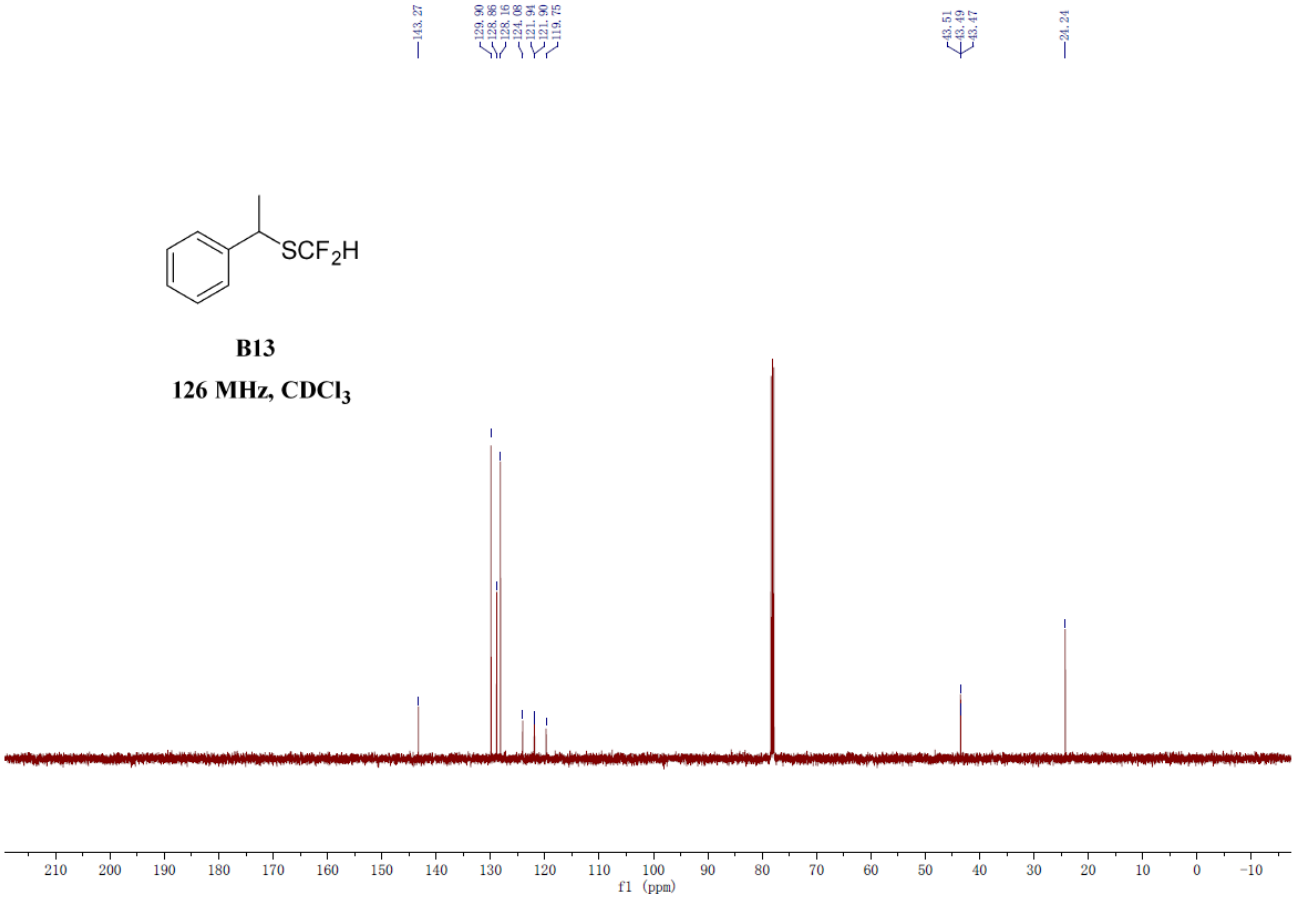
B12

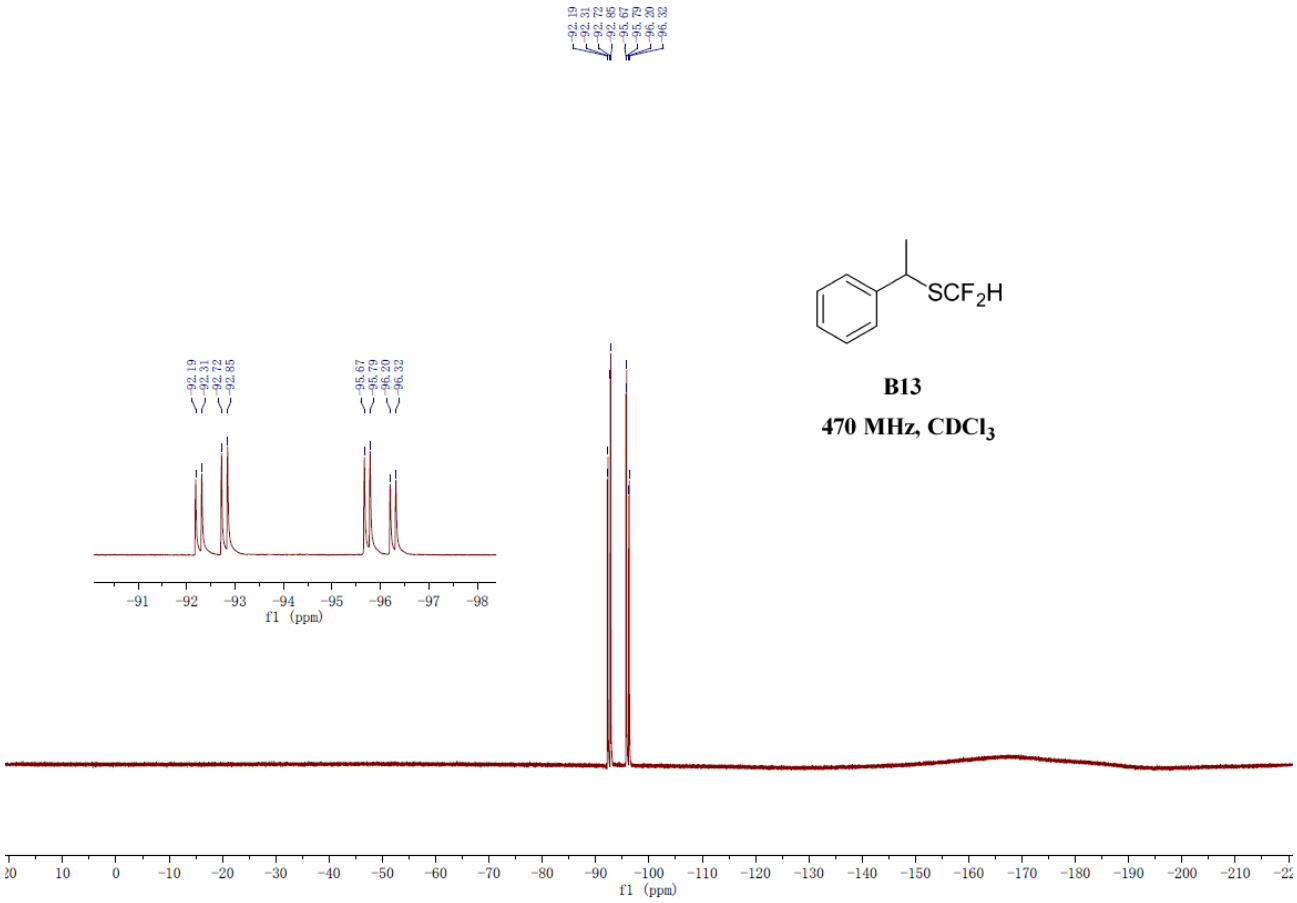
500 MHz, $CDCl_3$


134.67
134.38
133.82
129.95
128.82
128.74
127.80
127.54
127.30
123.54
121.37
119.19
33.26
33.23
33.20
SCF2H
B12
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-94.31
-94.43
SCF2H
B12
470 MHz, CDCl3
-93.0 -93.5 -94.0 -94.5 -95.0 -95.5
f1 (ppm)
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

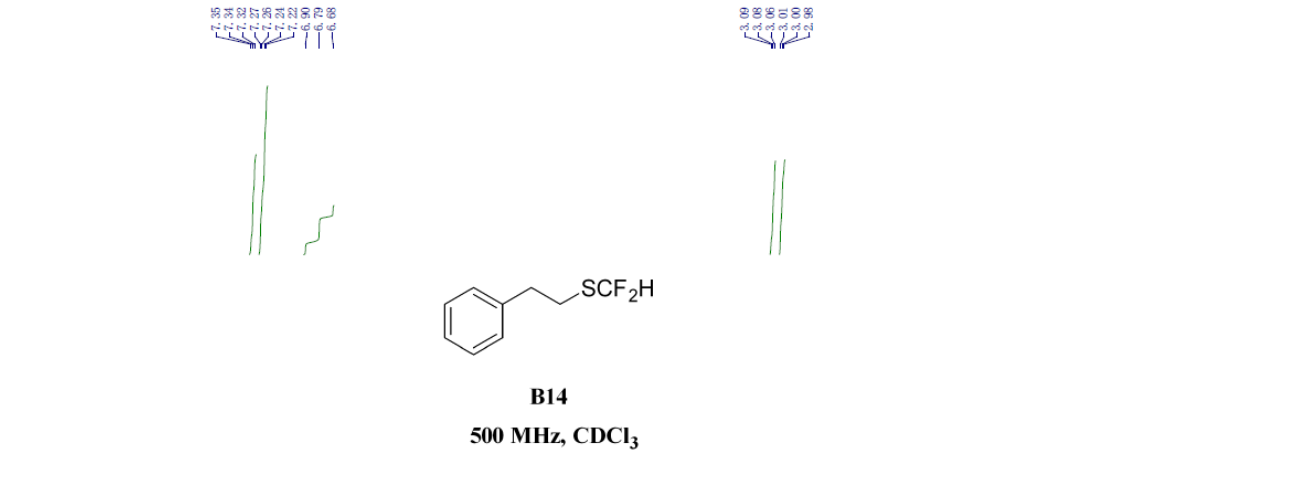

SCF2H
B13
500 MHz, CDCl3
f1 (ppm)


SCF2H
B13
126 MHz, CDCl3
f1 (ppm)



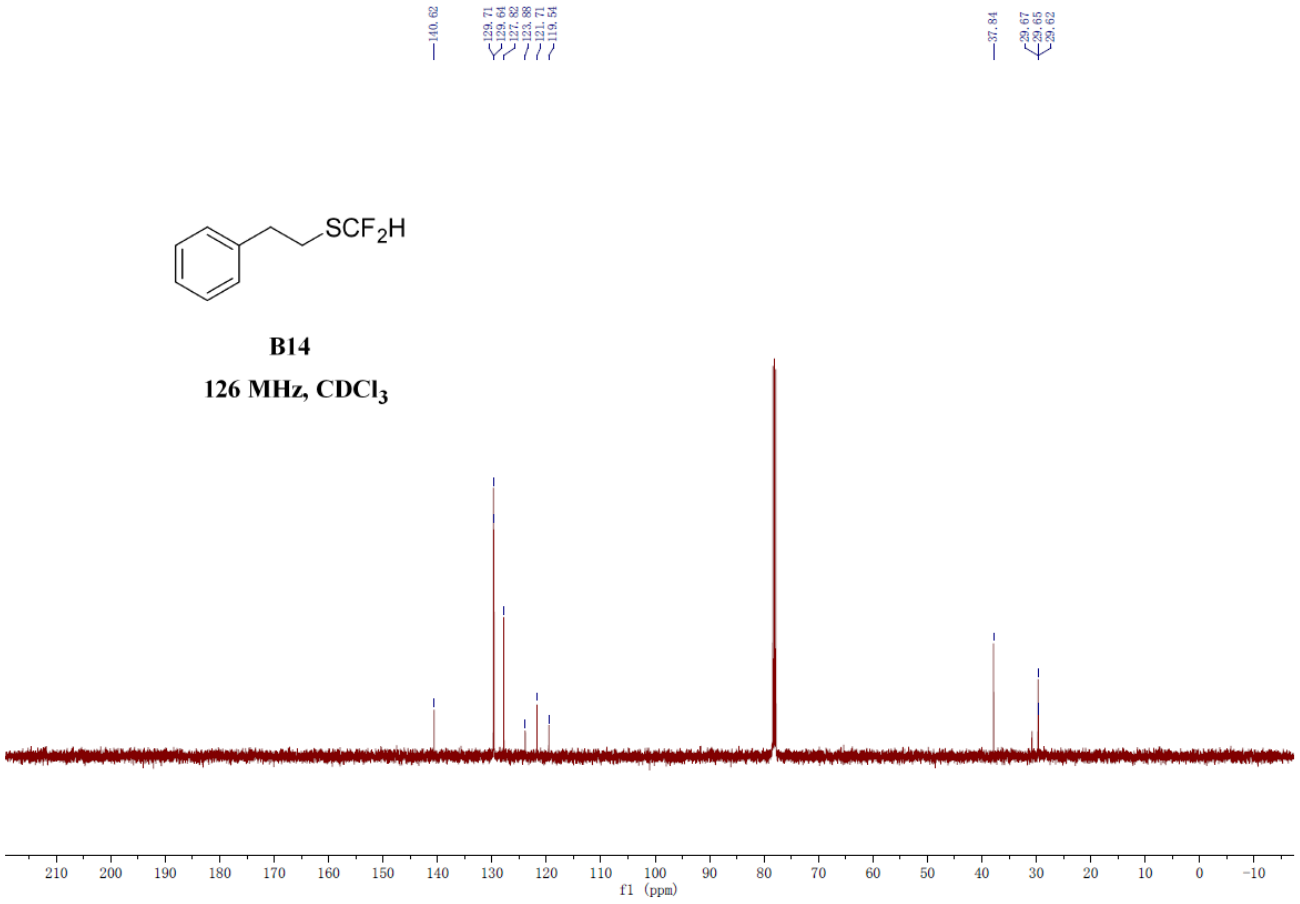
B13

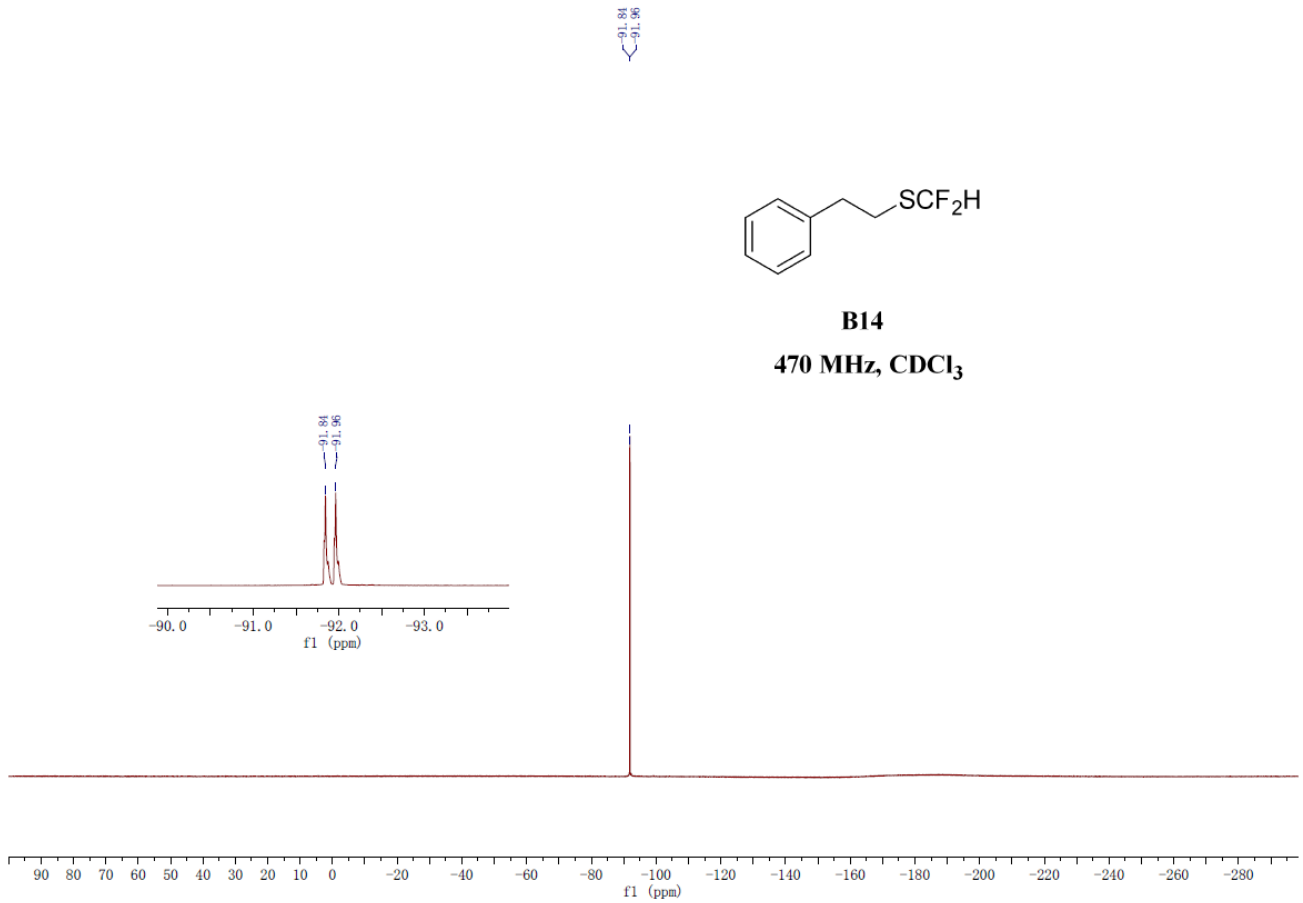
470 MHz, $CDCl_3$

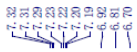


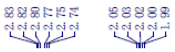
B14

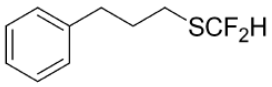
500 MHz, $CDCl_3$


140.62
129.71
129.64
127.82
123.88
121.71
119.64
37.84
29.67
29.65
29.62
SCF2H
B14
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-91.84
-91.96
SCF2H
B14
470 MHz, CDCl3
-90.0 -91.0 -92.0 -93.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

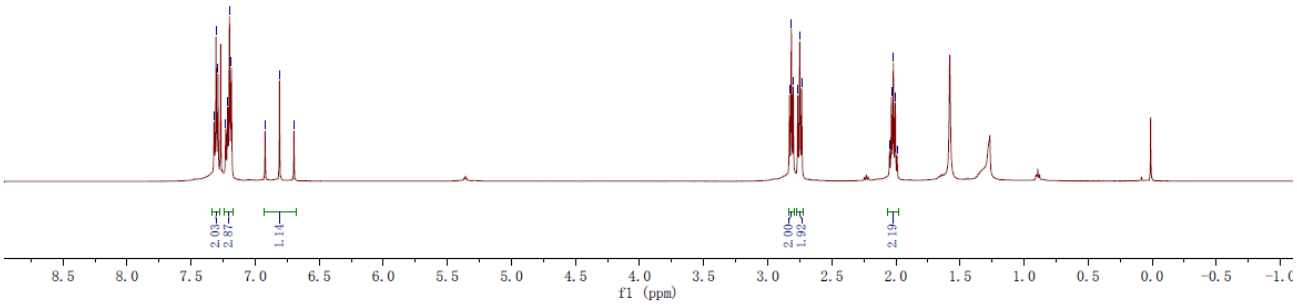


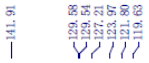


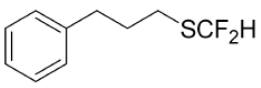


B15

500 MHz, $CDCl_3$

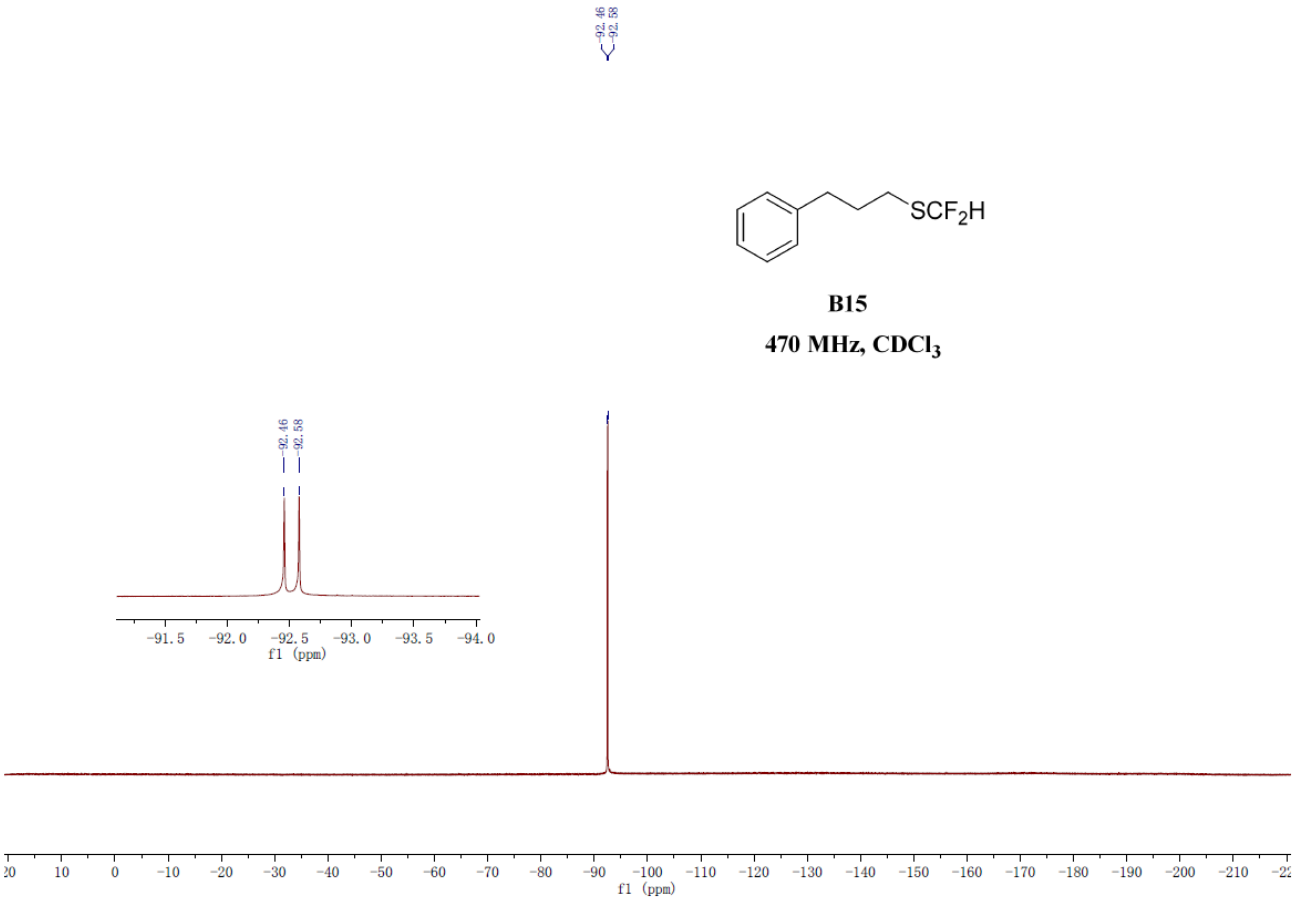






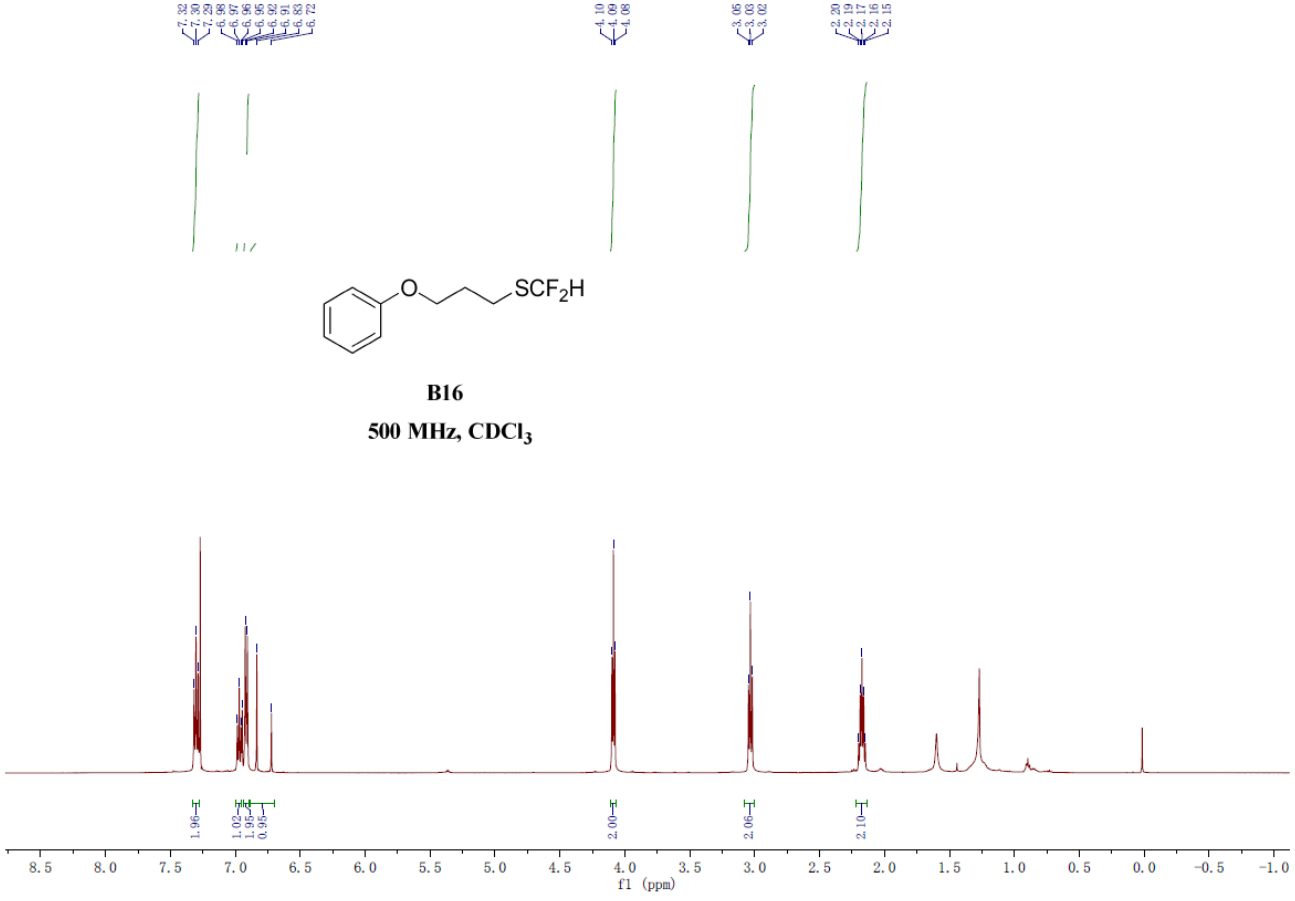
B15

126 MHz, $CDCl_3$



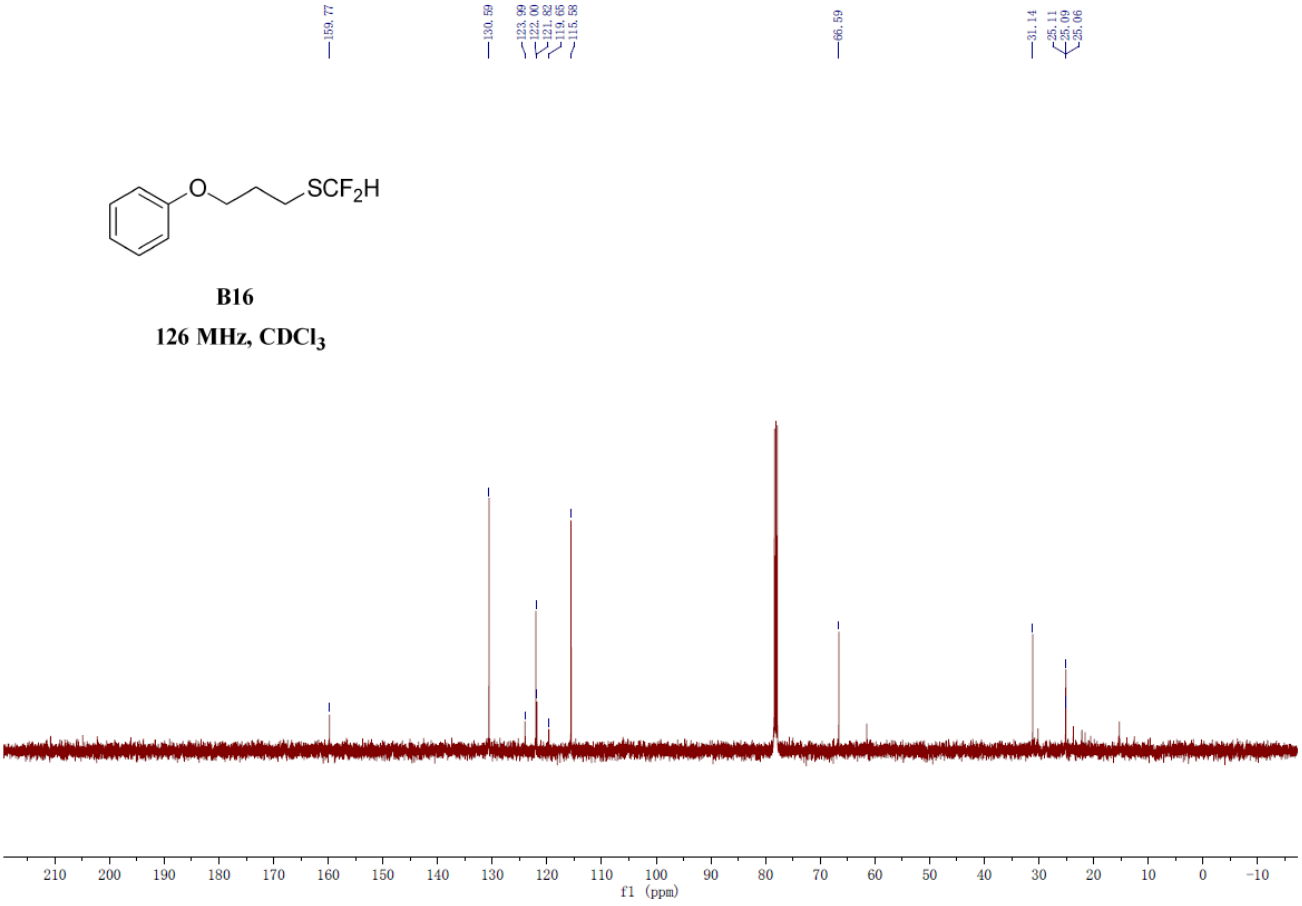
B15

470 MHz, $CDCl_3$



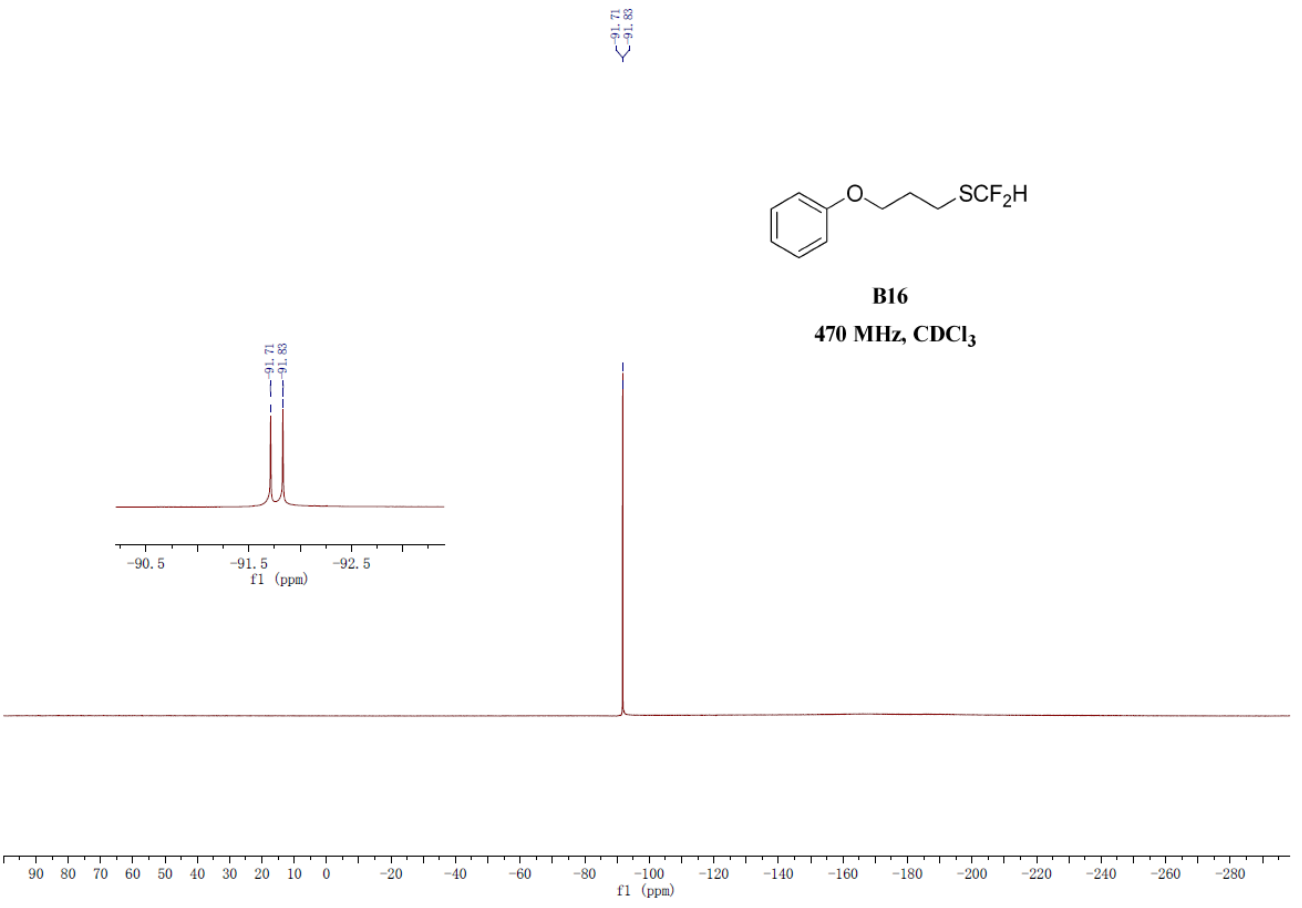
B16

500 MHz, $CDCl_3$



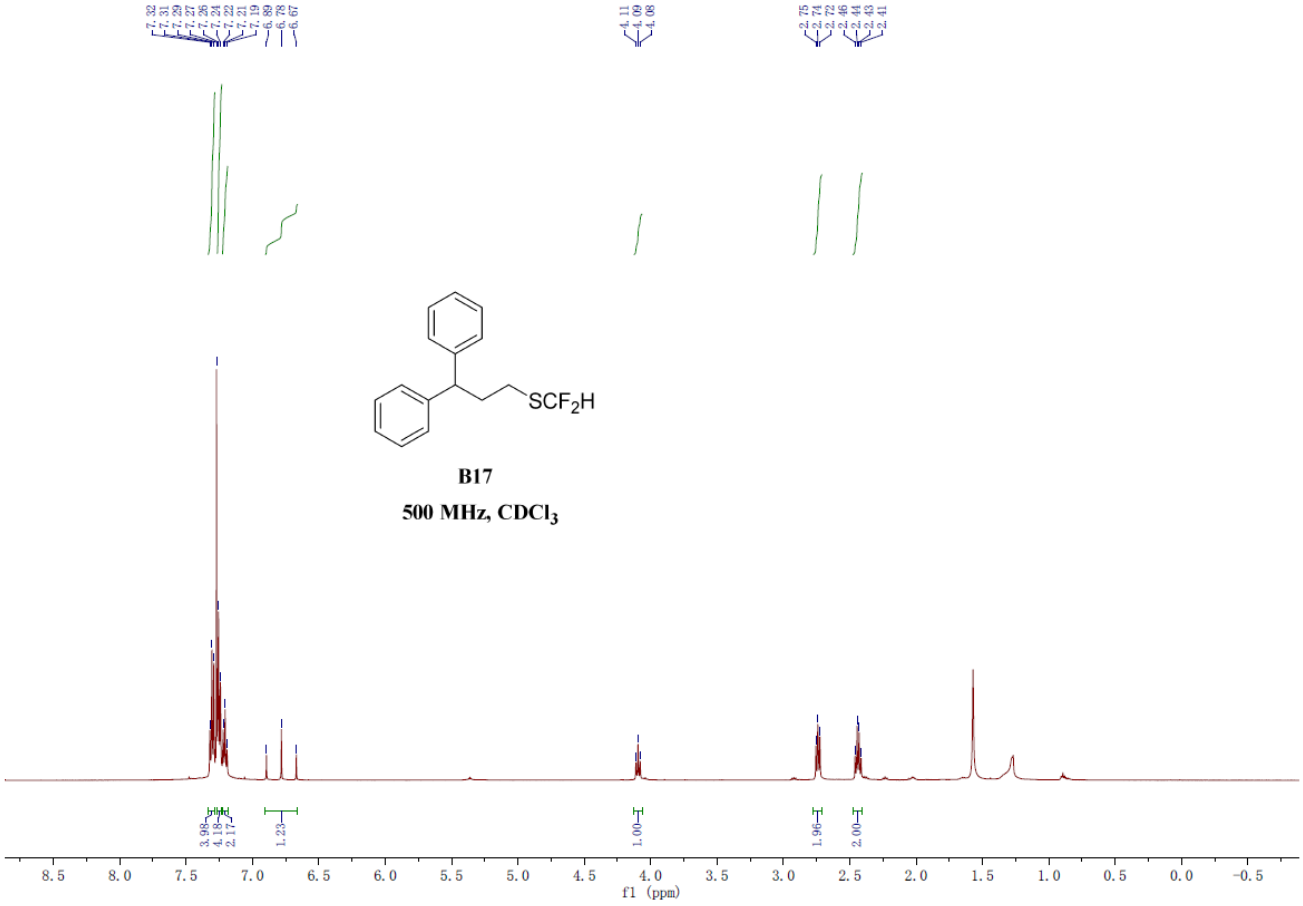
B16

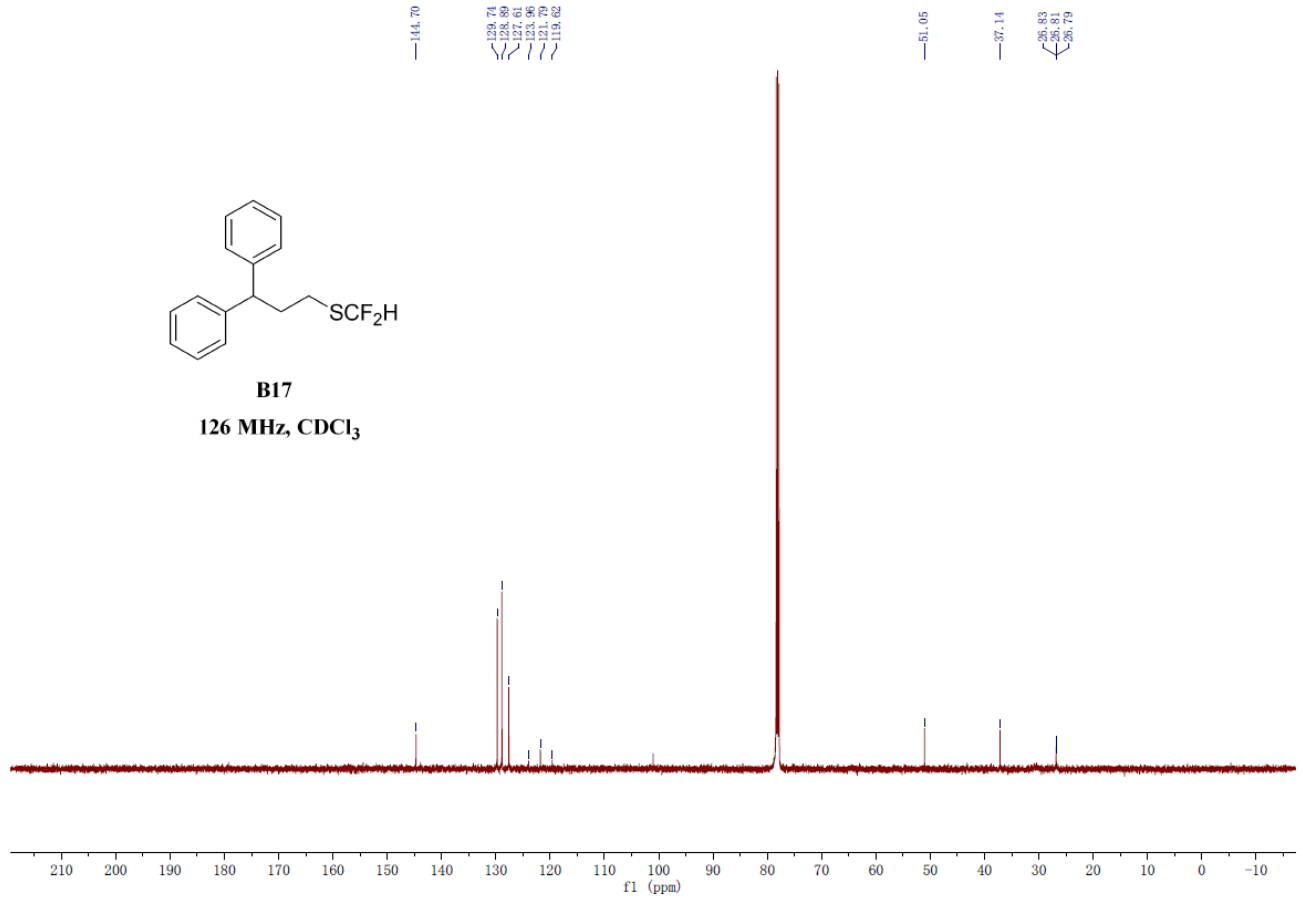
126 MHz, $CDCl_3$

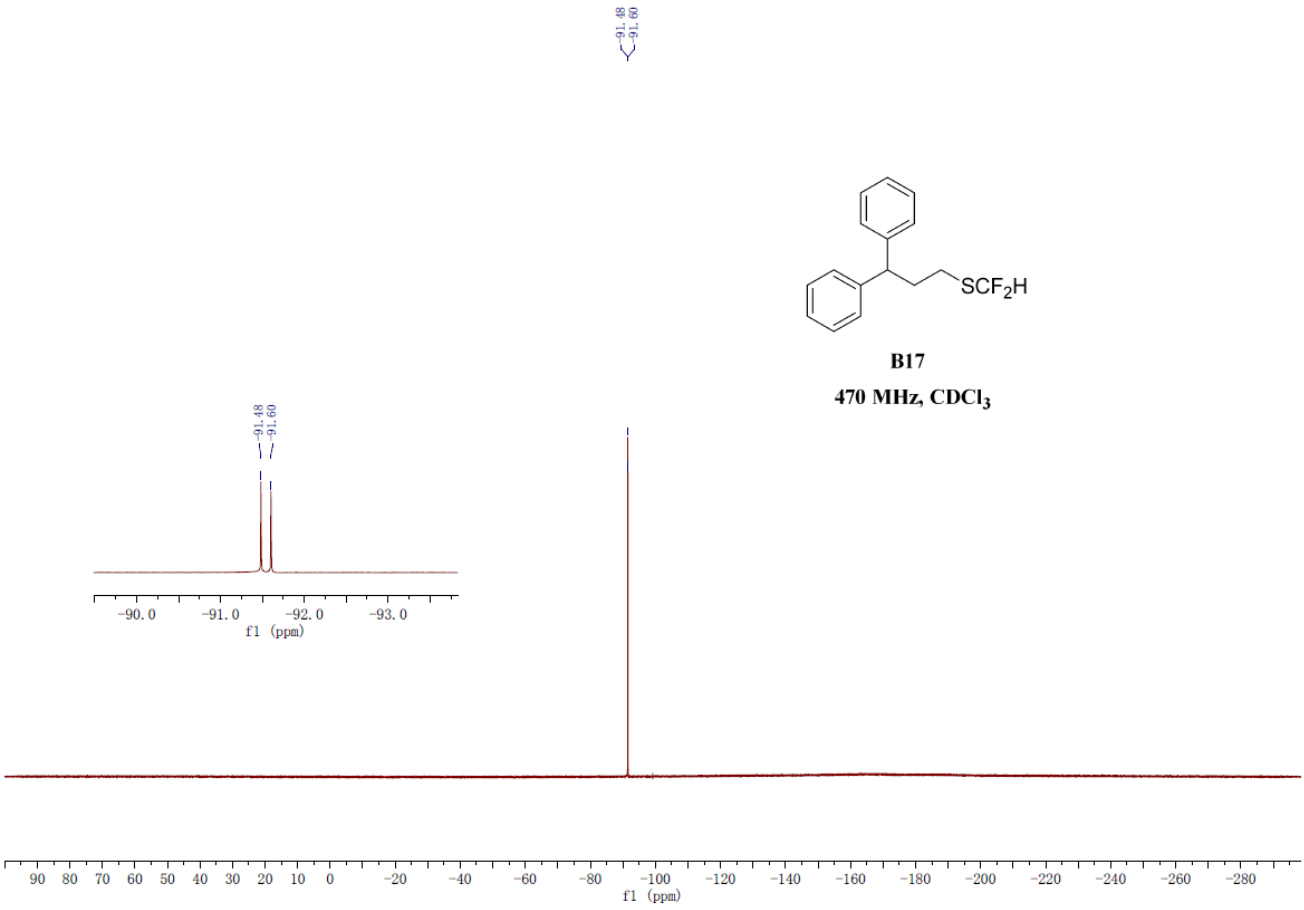


B16

470 MHz, $CDCl_3$

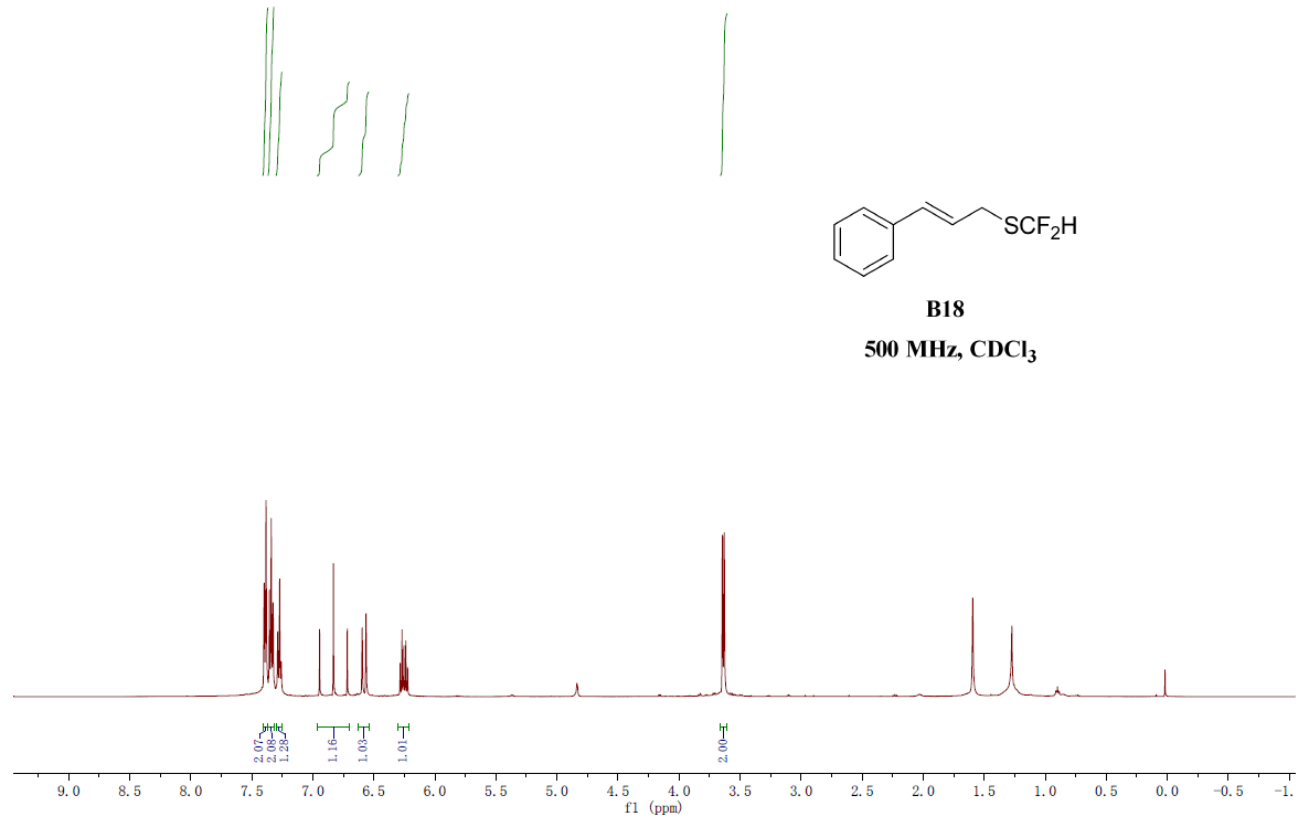

SCF2H
B17
500 MHz, CDCl3
f1 (ppm)


SCF2H
B17
126 MHz, CDCl3
f1 (ppm)



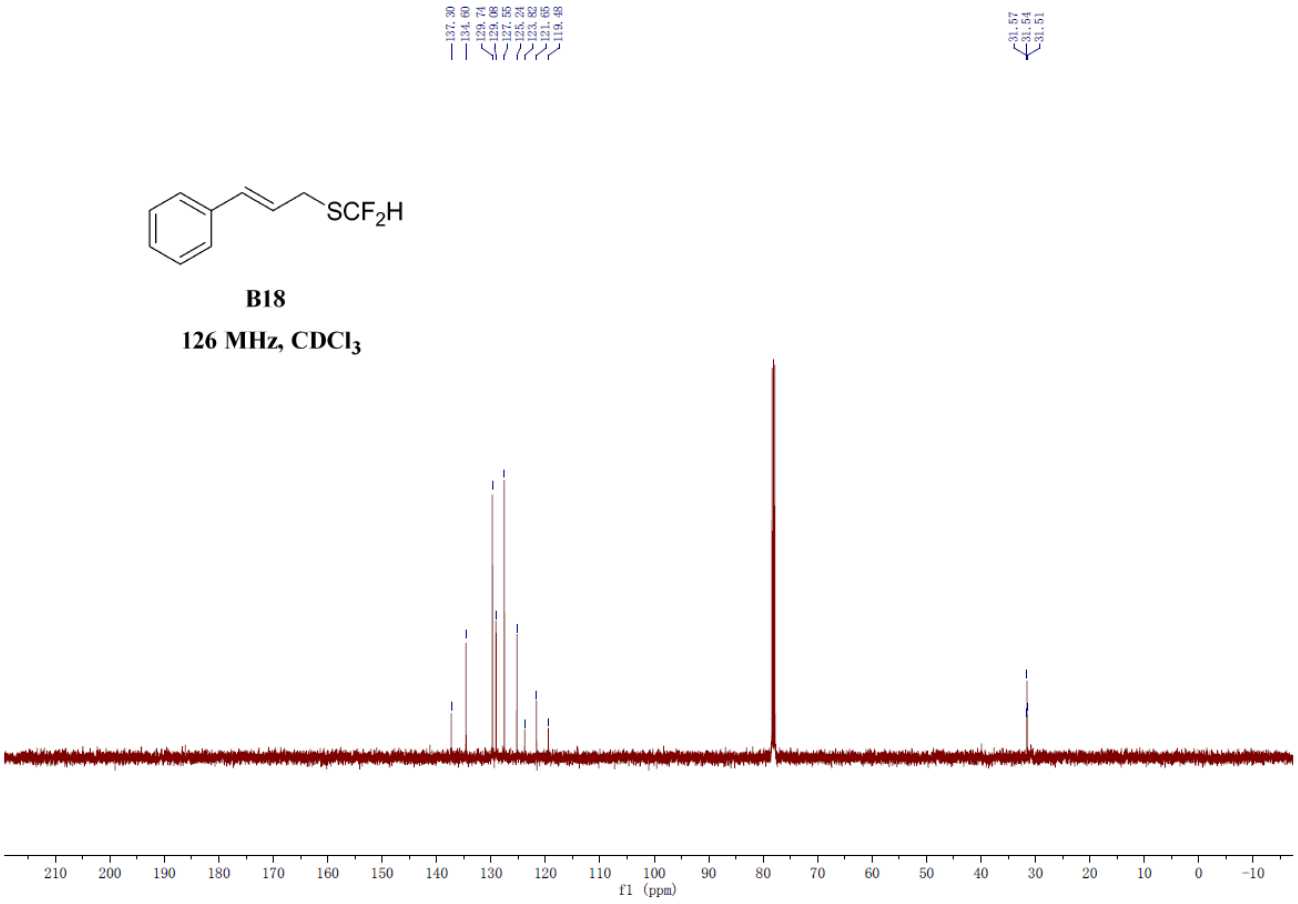
B17

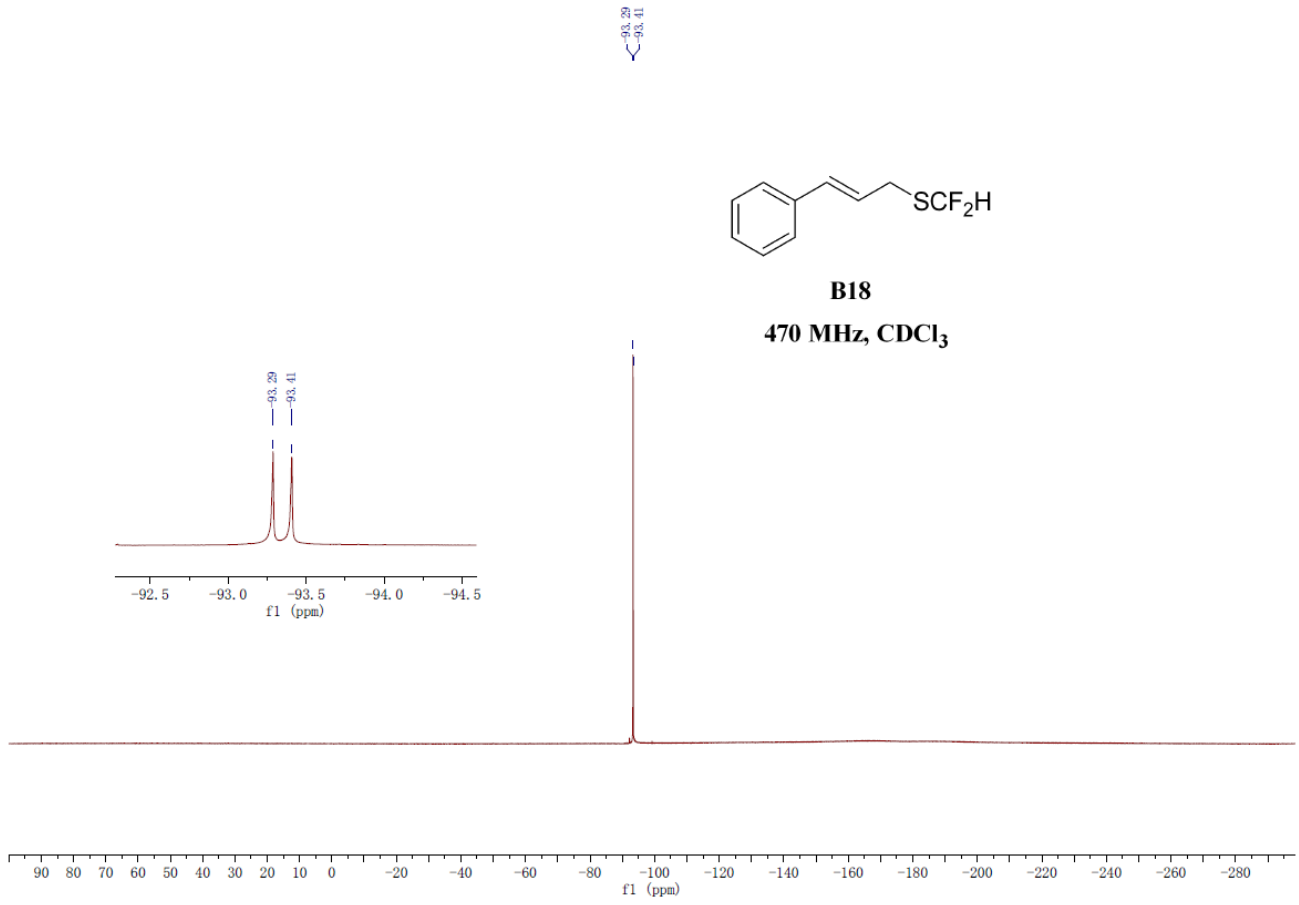
470 MHz, $CDCl_3$

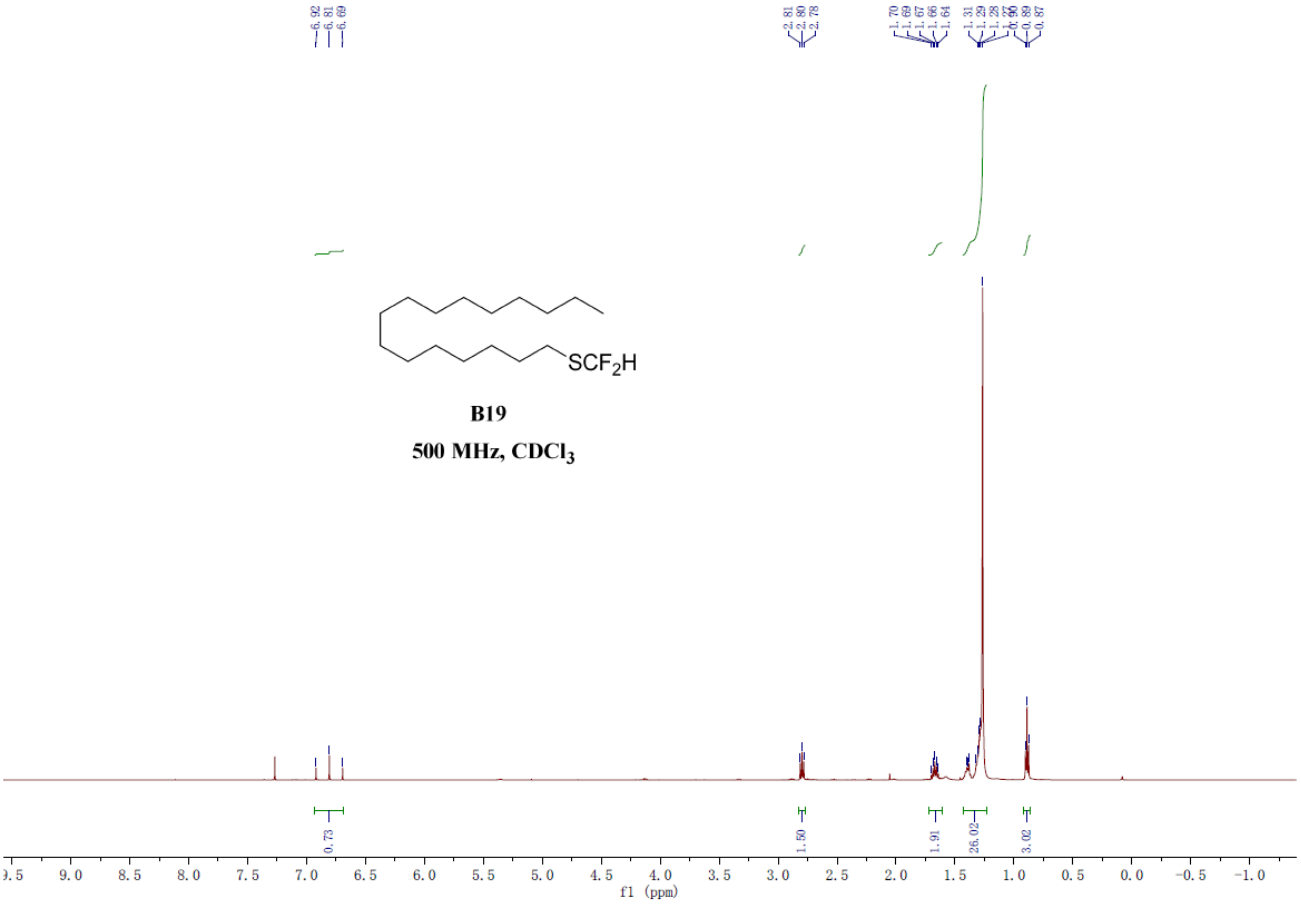


B18

500 MHz, $CDCl_3$

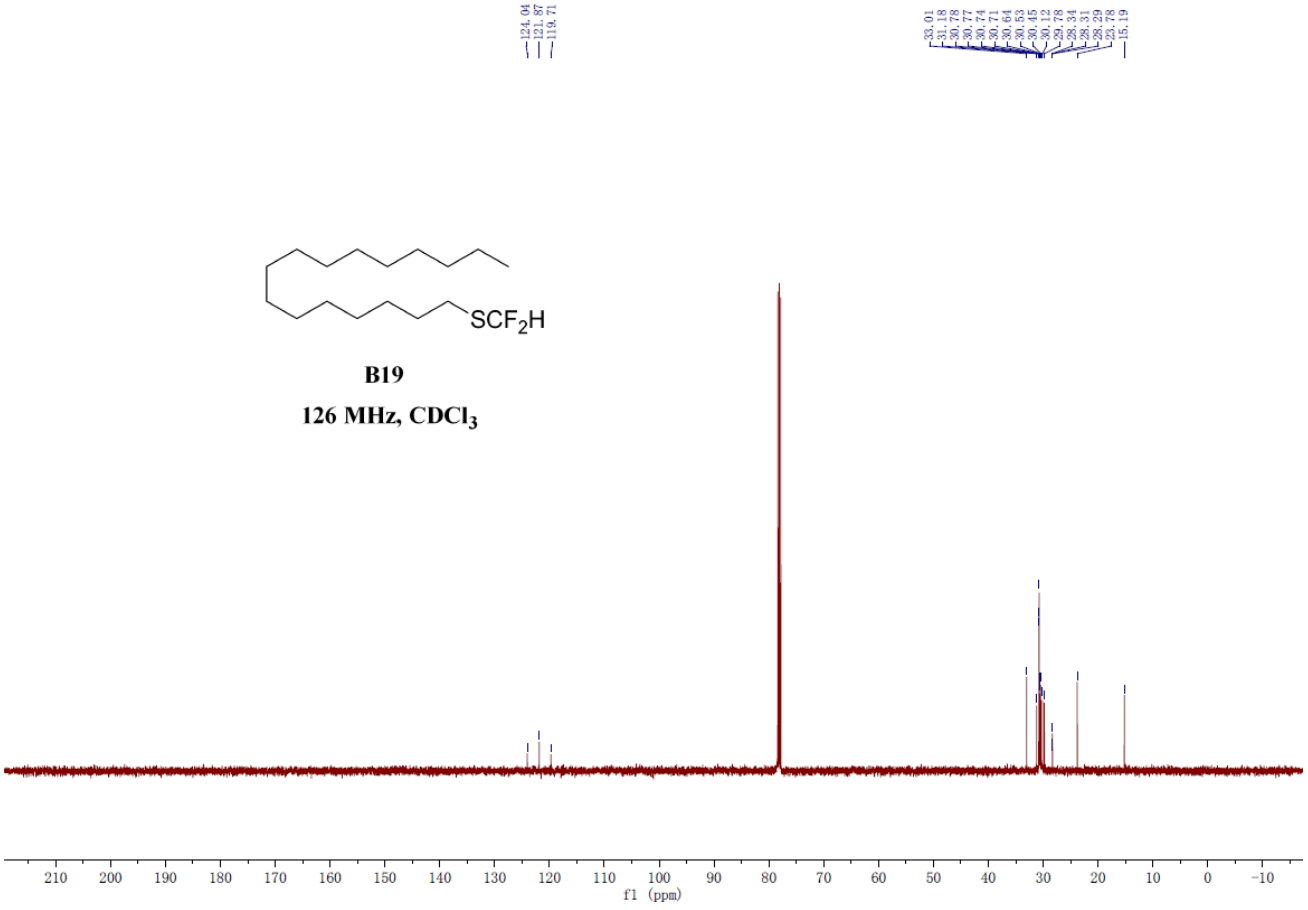

137.30
134.60
129.74
129.08
127.55
125.24
123.82
121.65
119.48
31.57
31.54
31.51
SCF2H
B18
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-93.29
-93.41
SCF2H
B18
470 MHz, CDCl3
-92.5 -93.0 -93.5 -94.0 -94.5
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)



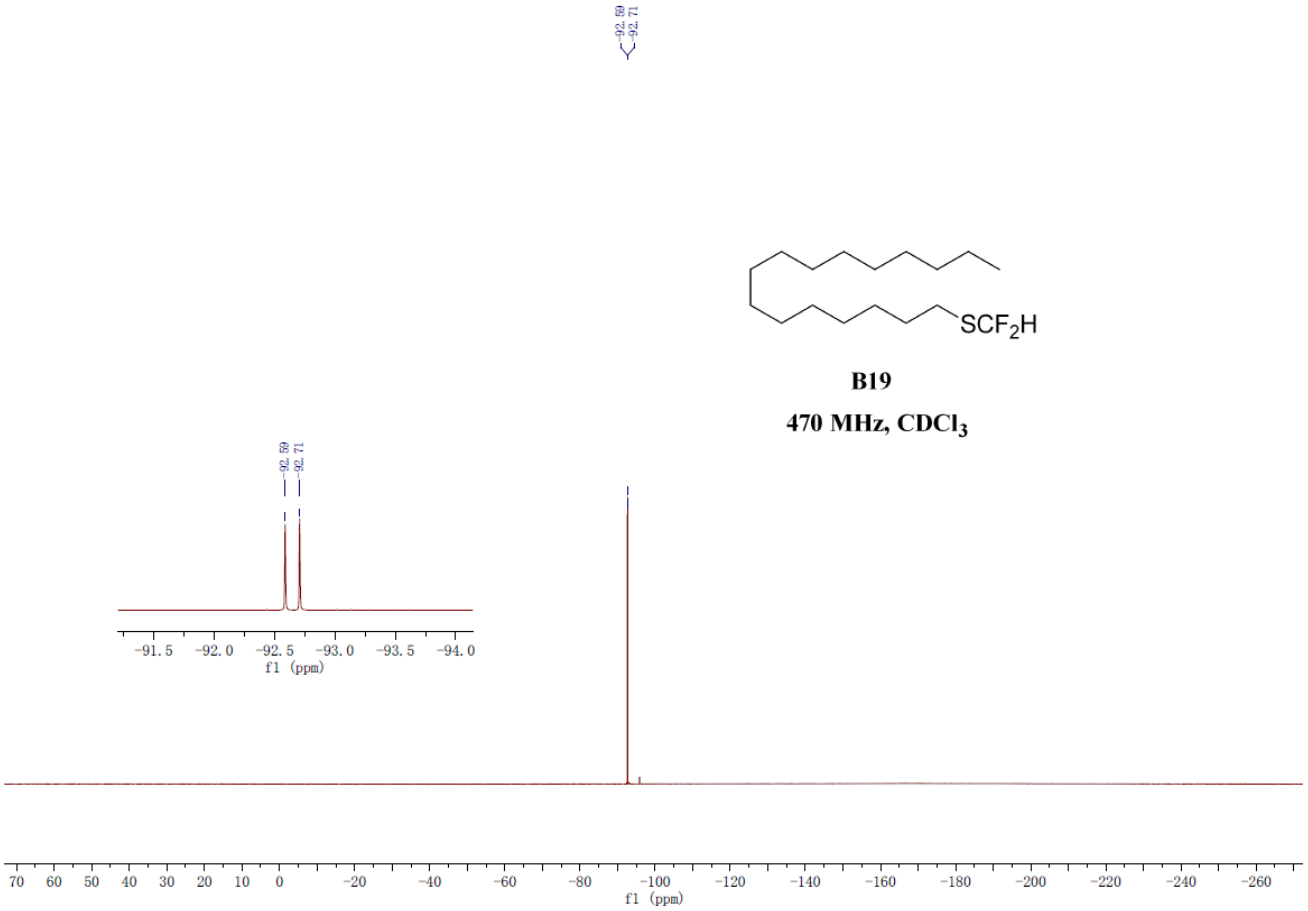
B19

500 MHz, $CDCl_3$



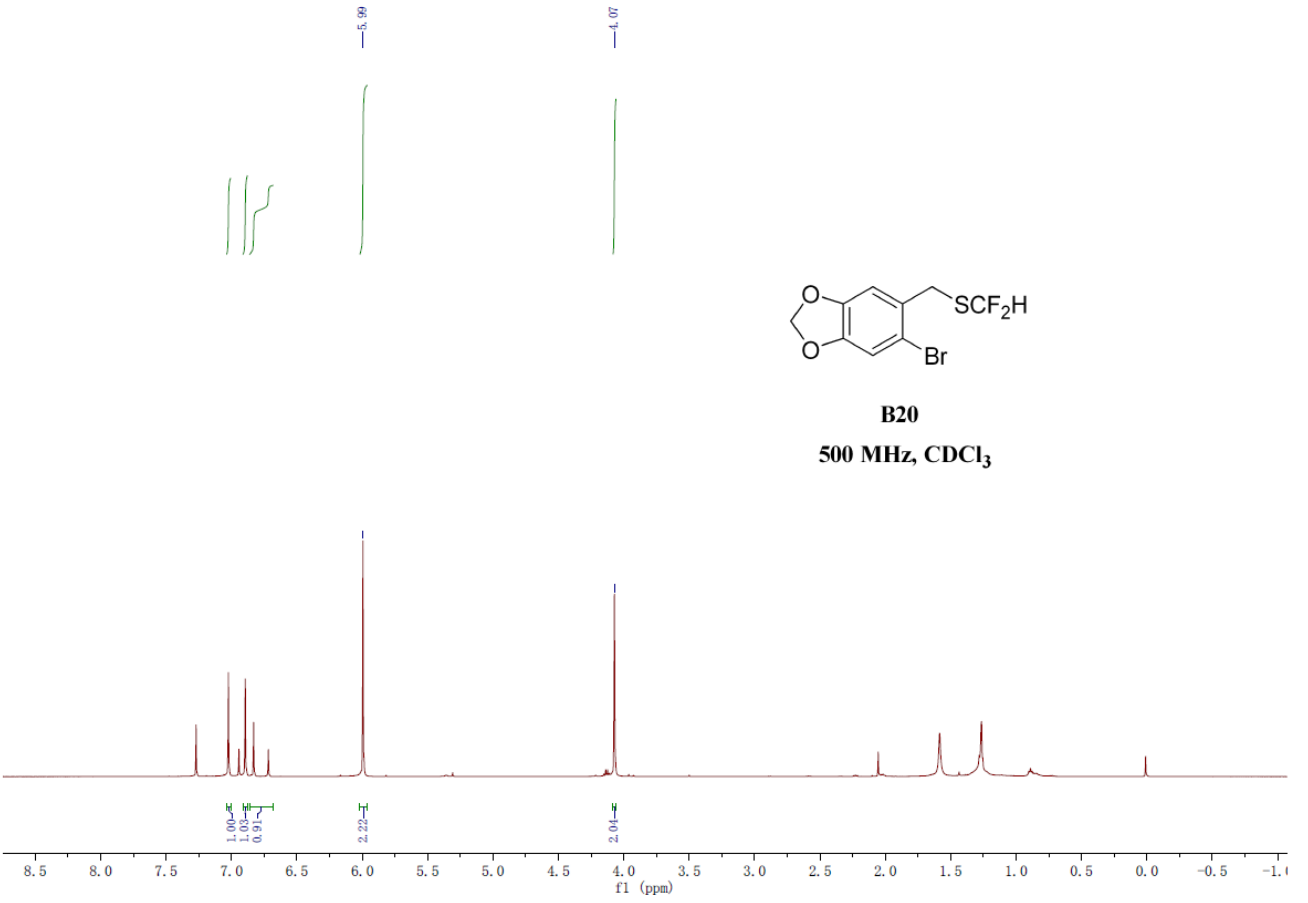
B19

126 MHz, $CDCl_3$



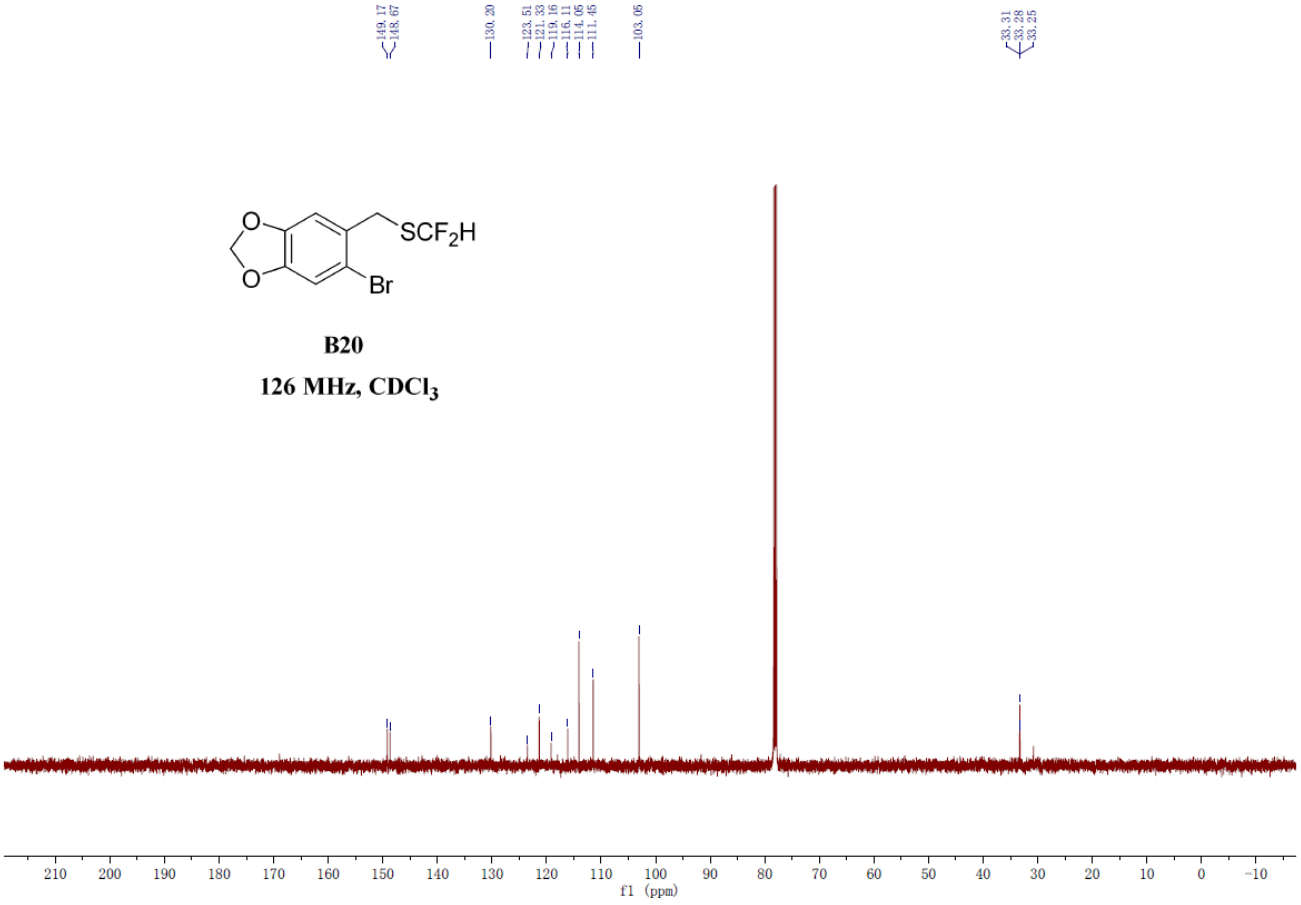
B19

470 MHz, $CDCl_3$



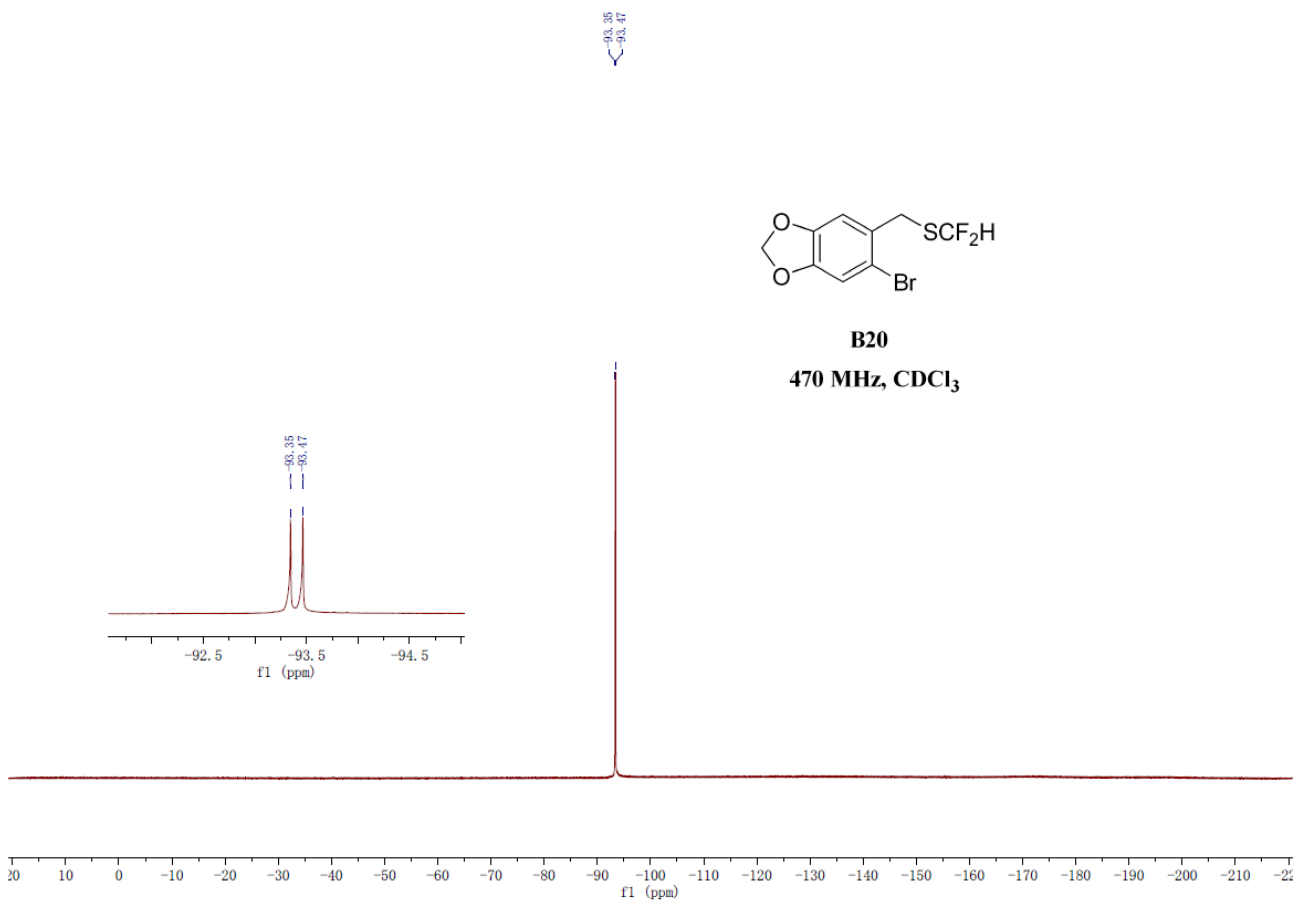
B20

500 MHz, $CDCl_3$



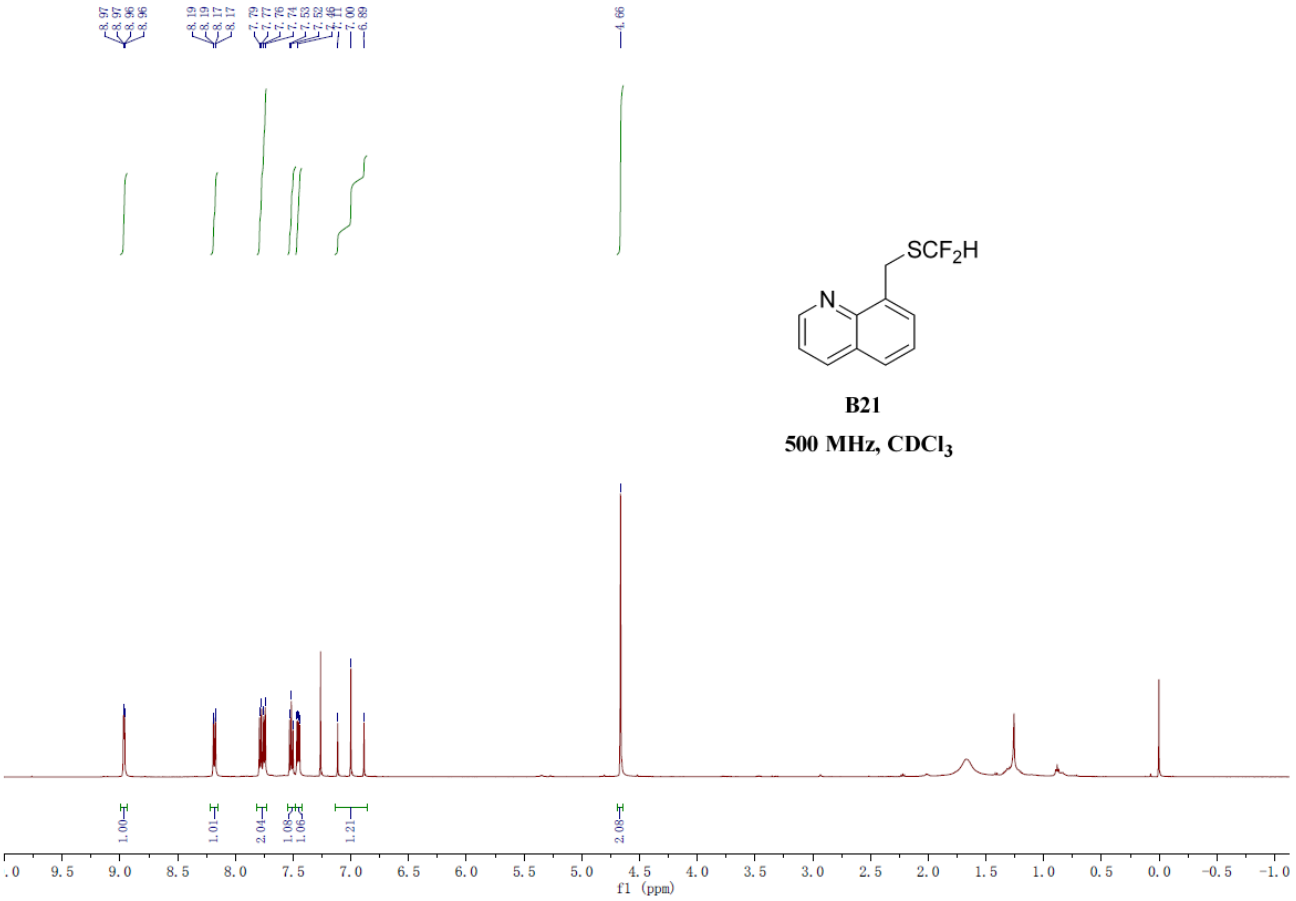
B20

126 MHz, $CDCl_3$



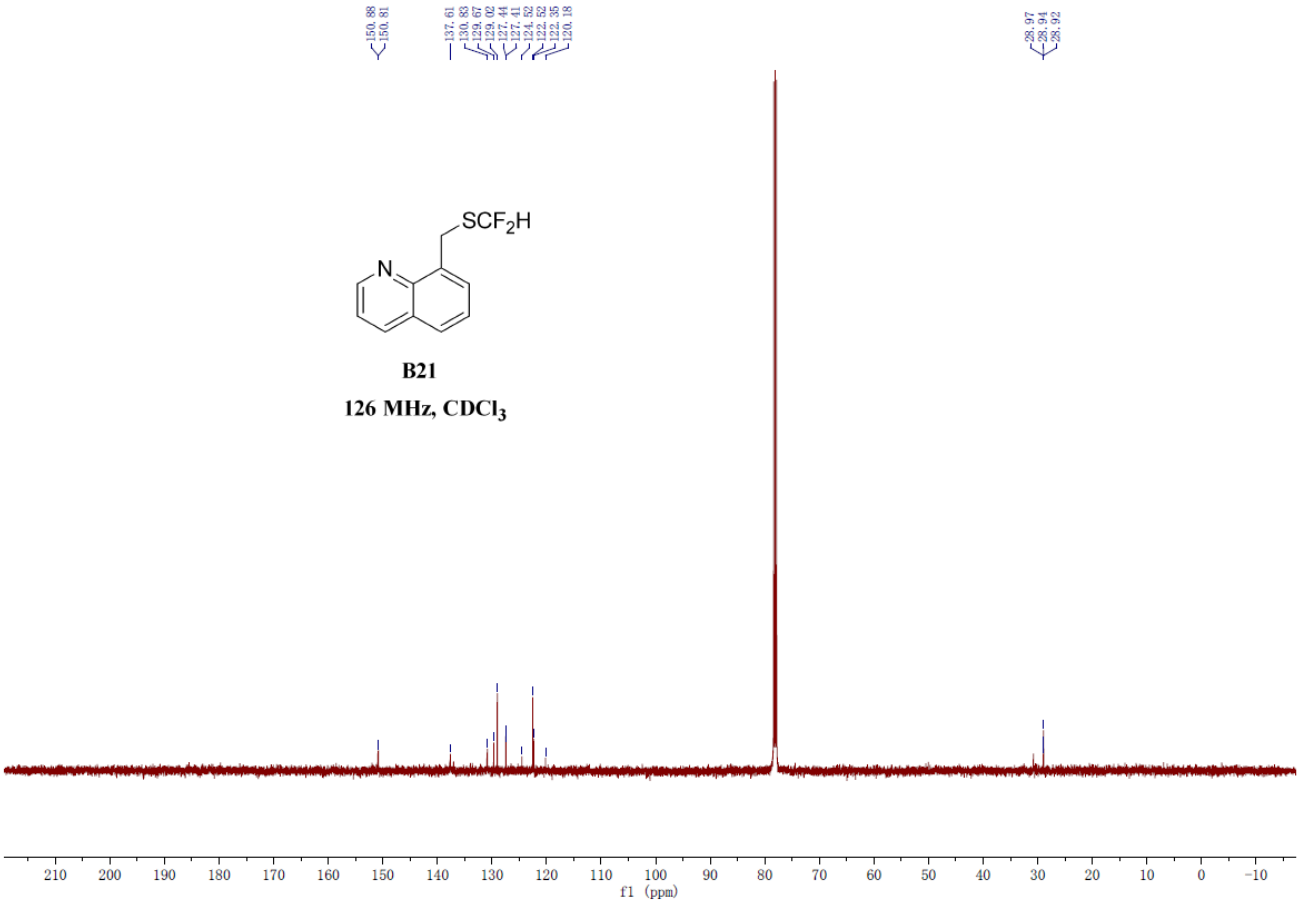
B20

470 MHz, $CDCl_3$



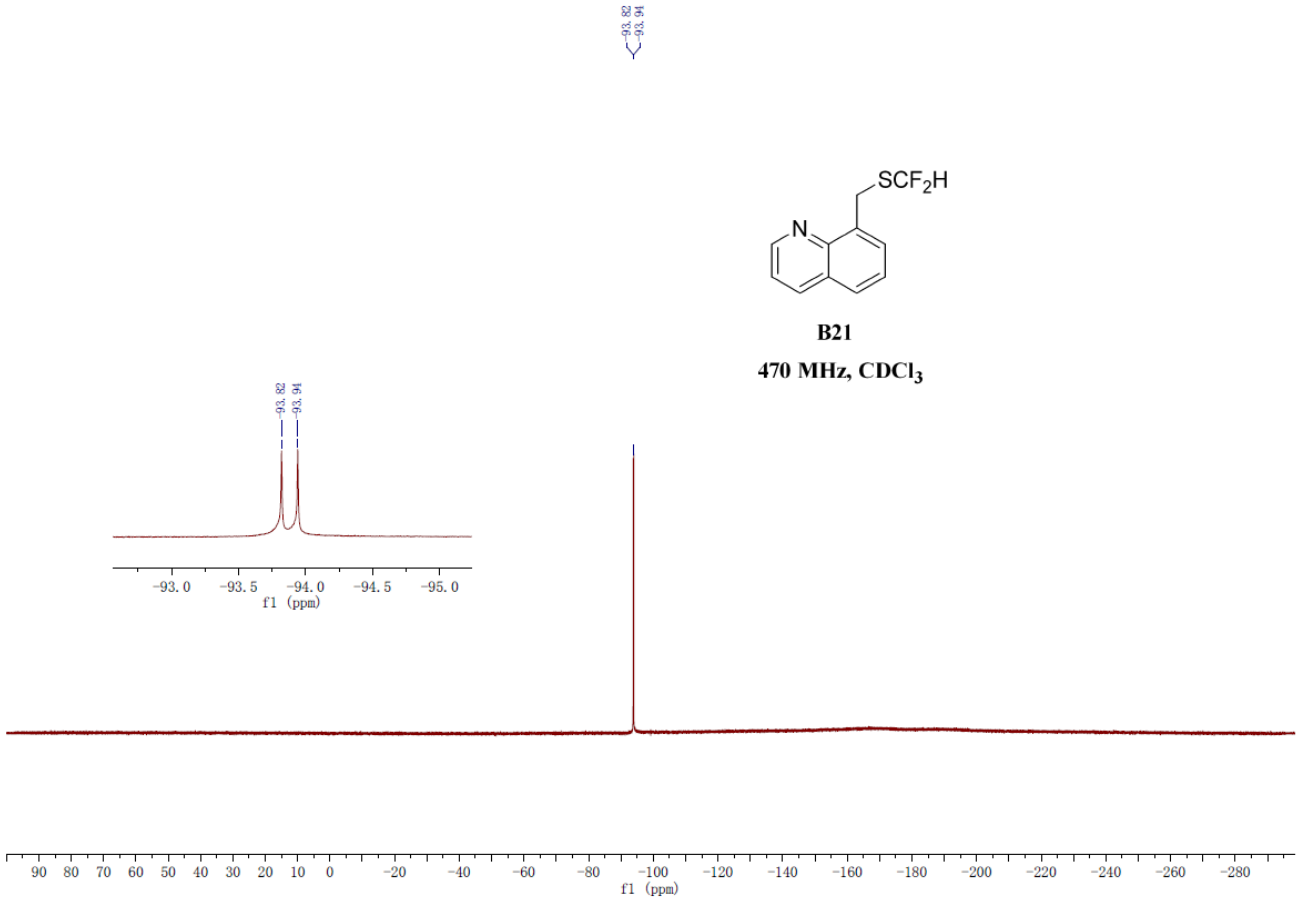
B21

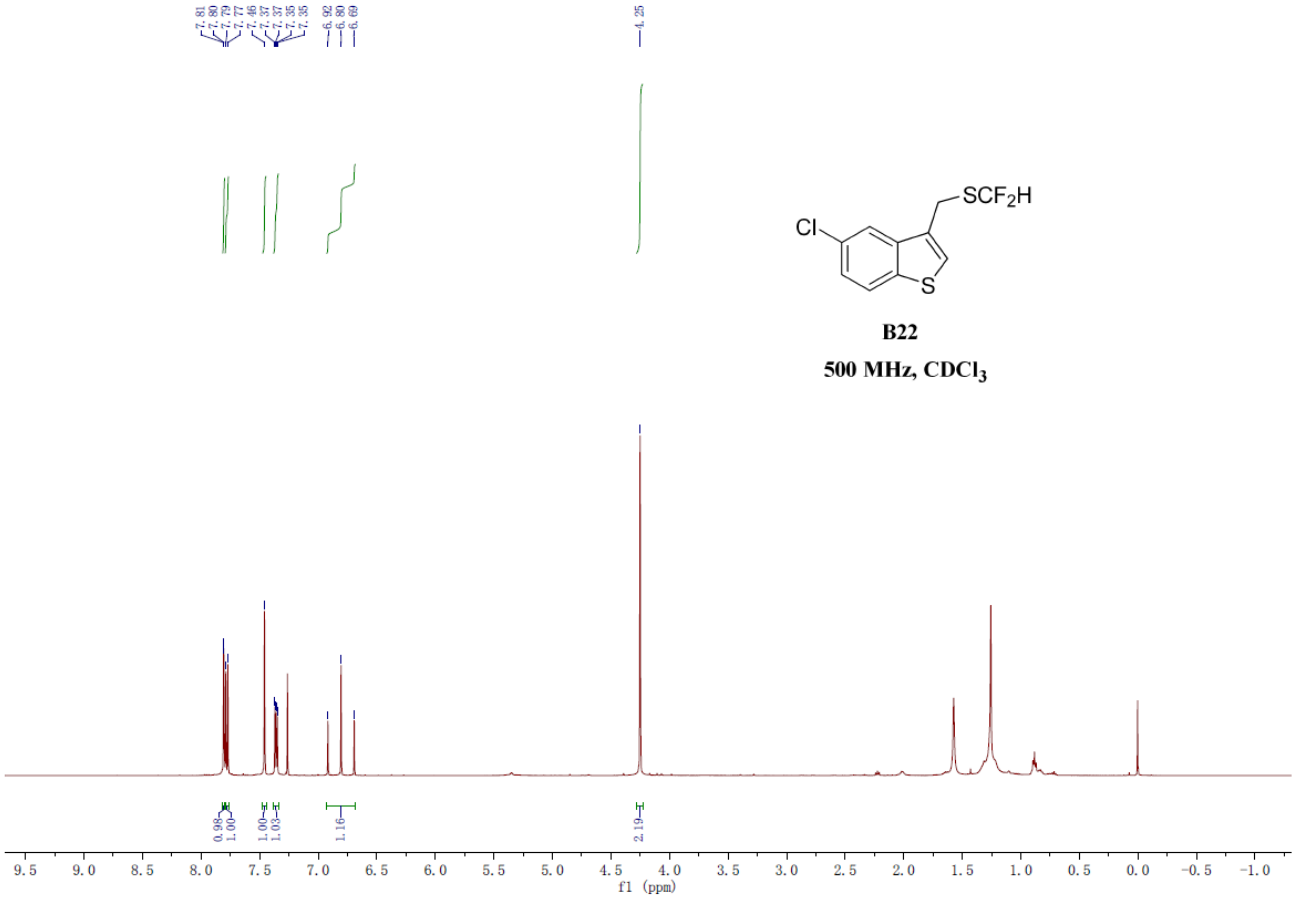
500 MHz, $CDCl_3$

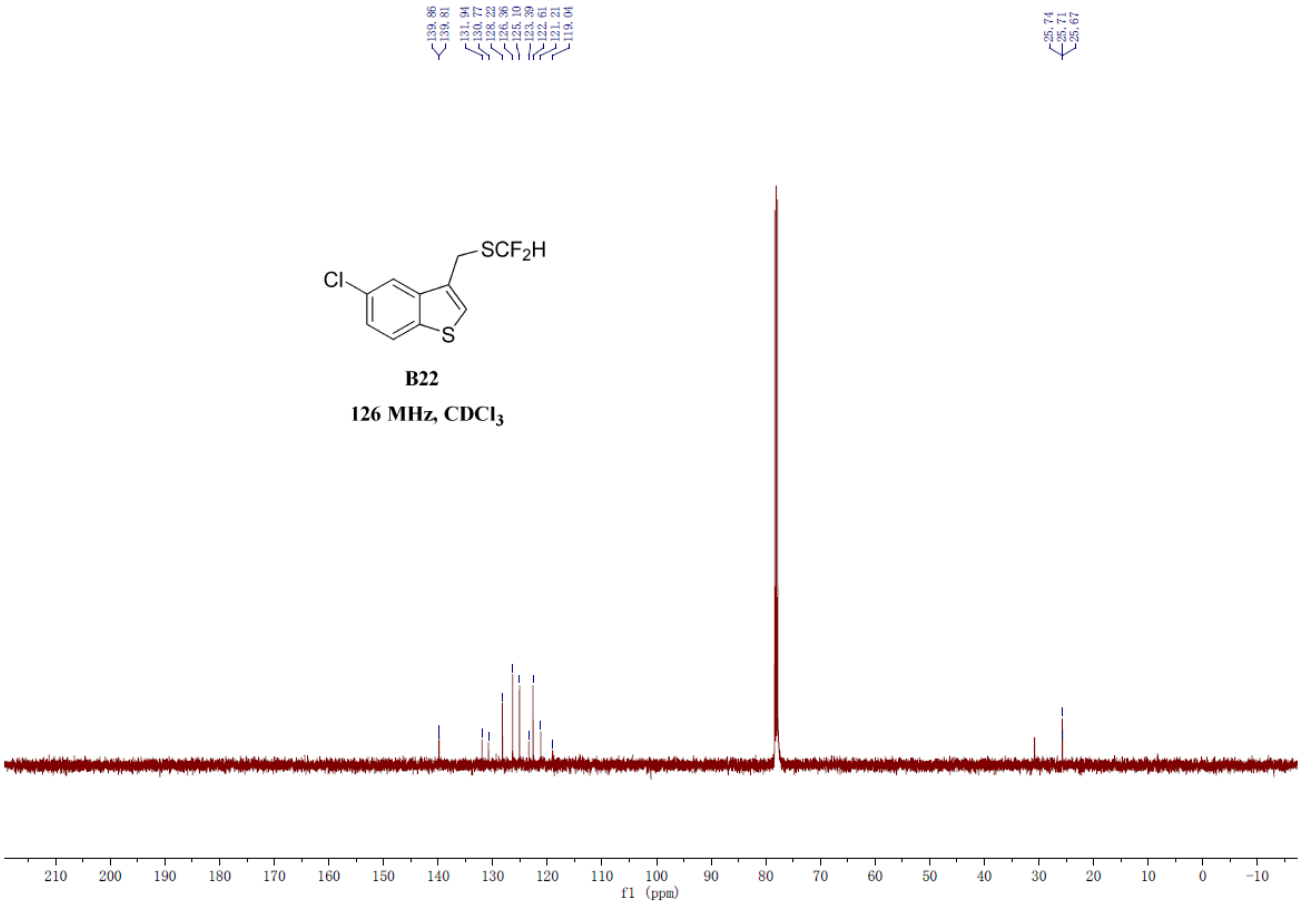


B21

126 MHz, $CDCl_3$

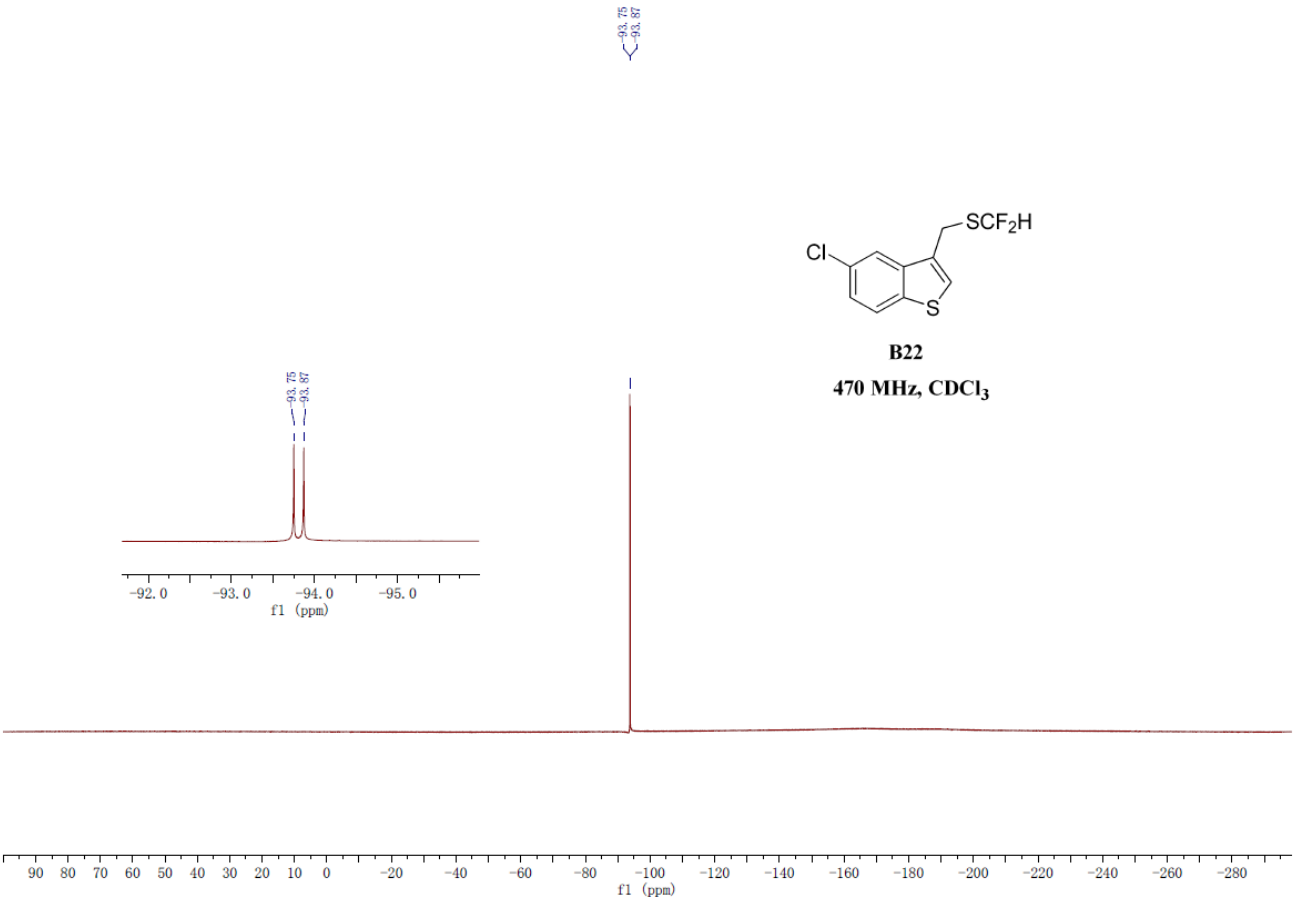

-93.82
-93.94
SCF2H
N
B21
470 MHz, CDCl3
-93.0
-93.5
-94.0
-94.5
-95.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


7.81
7.80
7.79
7.77
7.46
7.37
7.37
7.35
7.35
6.92
6.88
6.69
4.25
SCF2H
Cl
S
B22
500 MHz, CDCl3
0.98
1.00
1.00
1.03
1.16
2.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



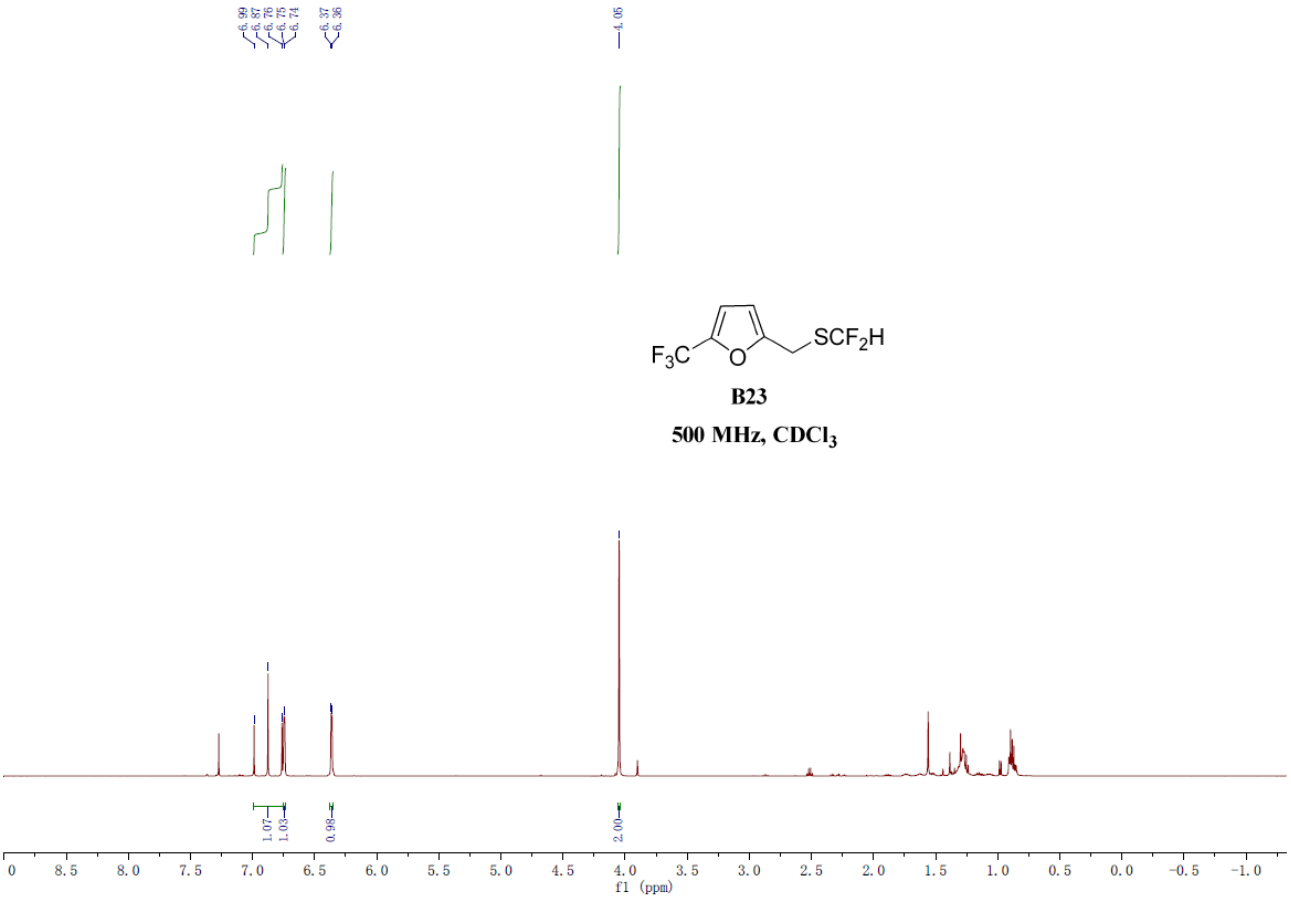
B22

126 MHz, $CDCl_3$



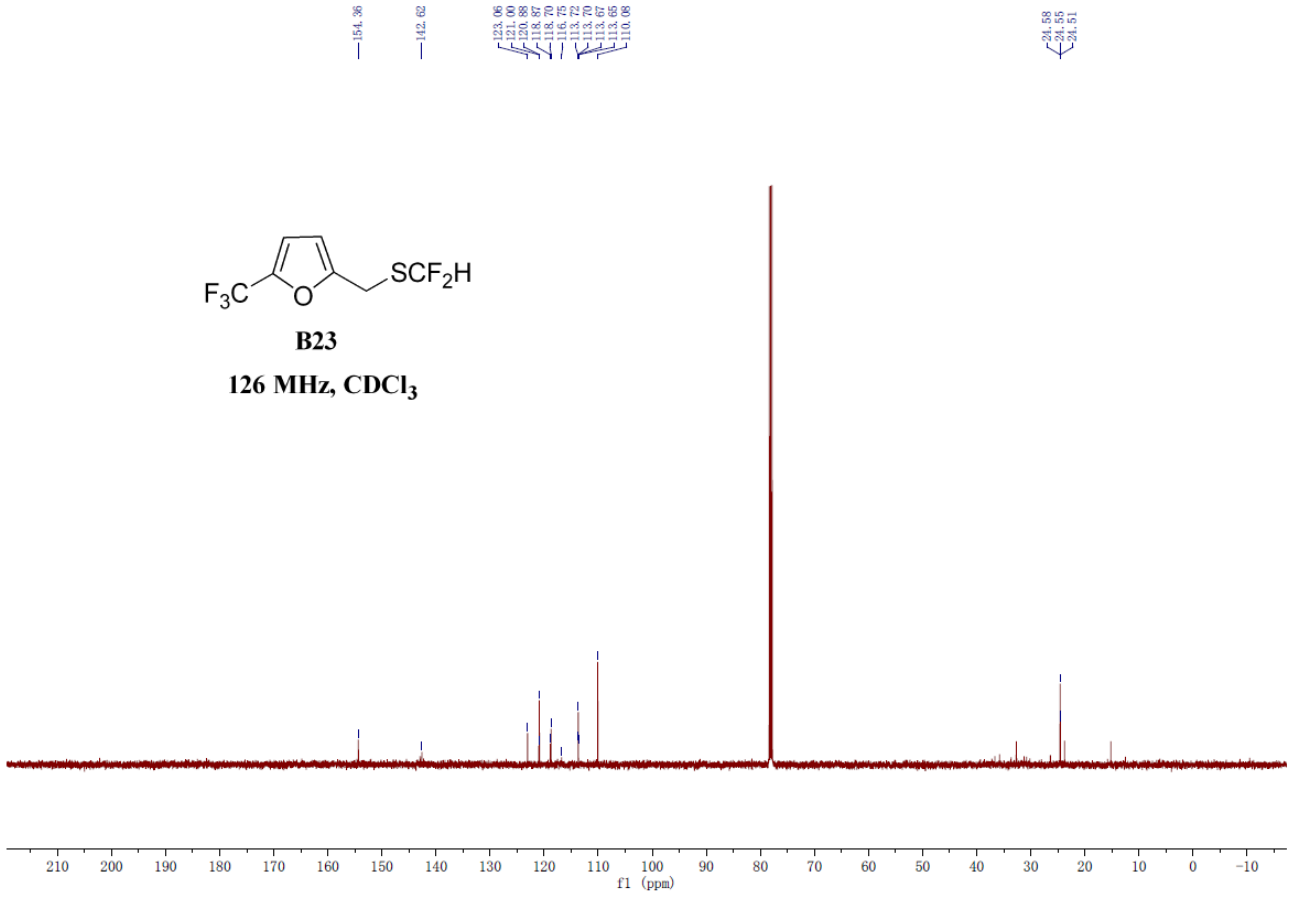
B22

470 MHz, $CDCl_3$



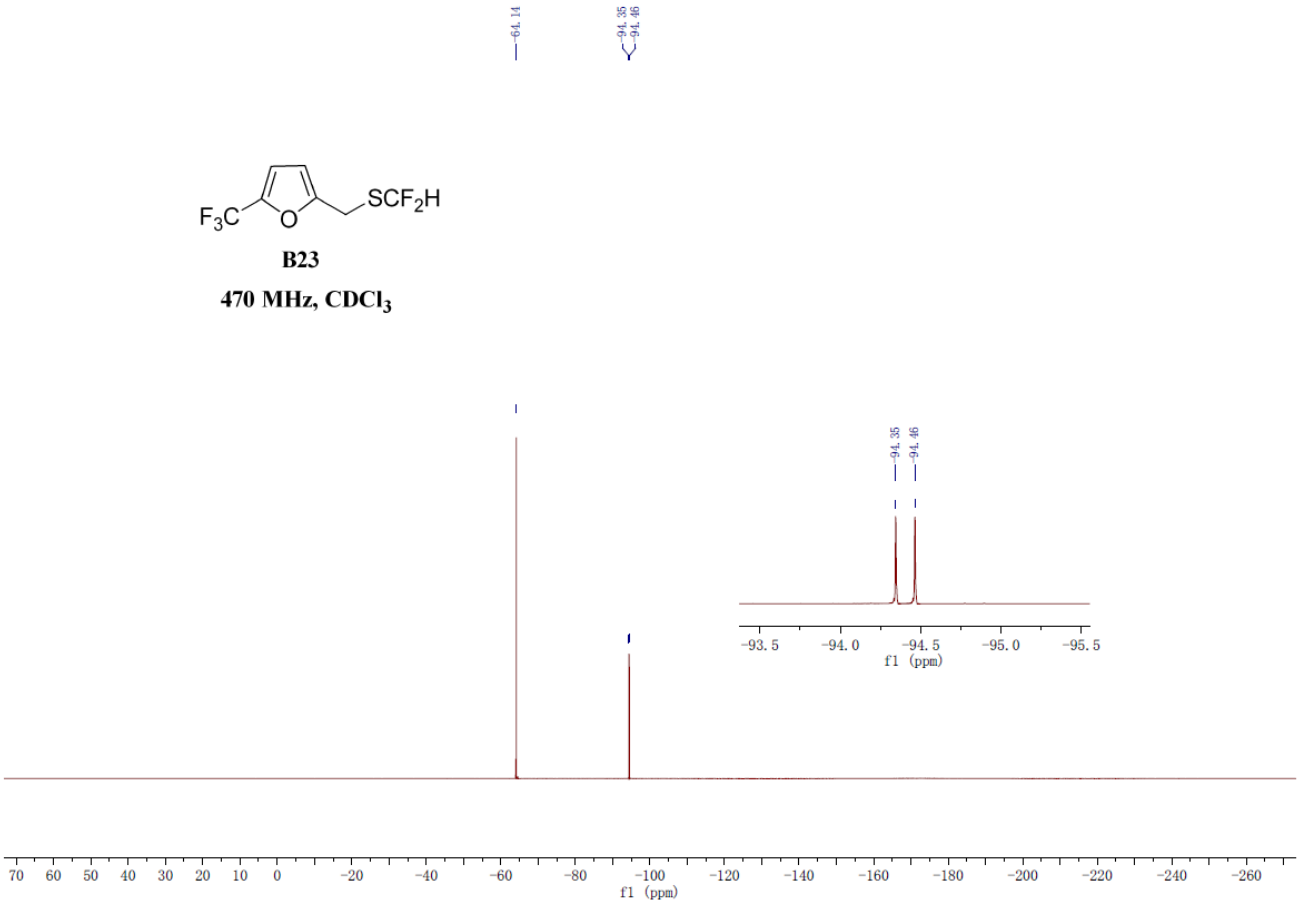
B23

500 MHz, $CDCl_3$



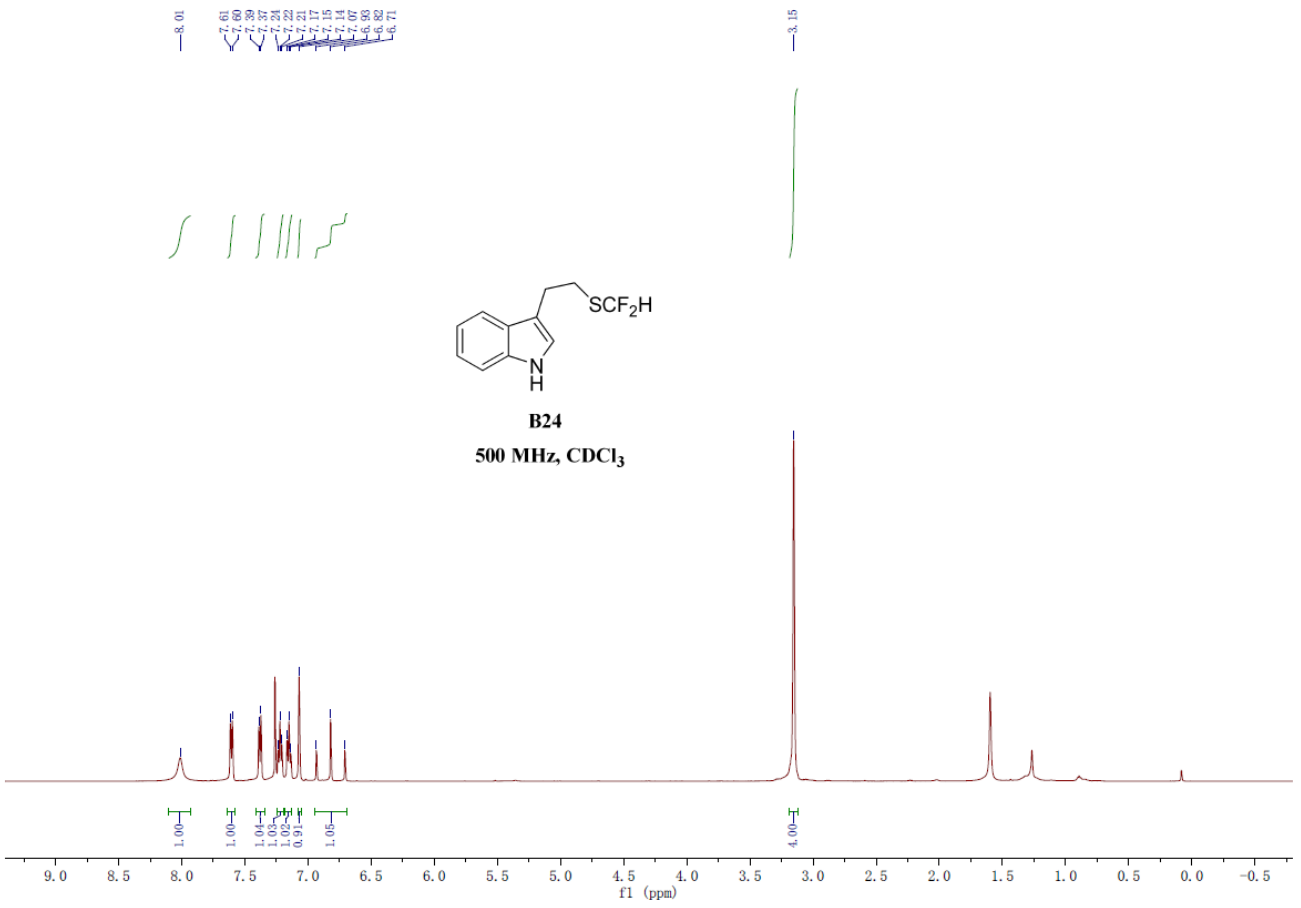
B23

126 MHz, $CDCl_3$



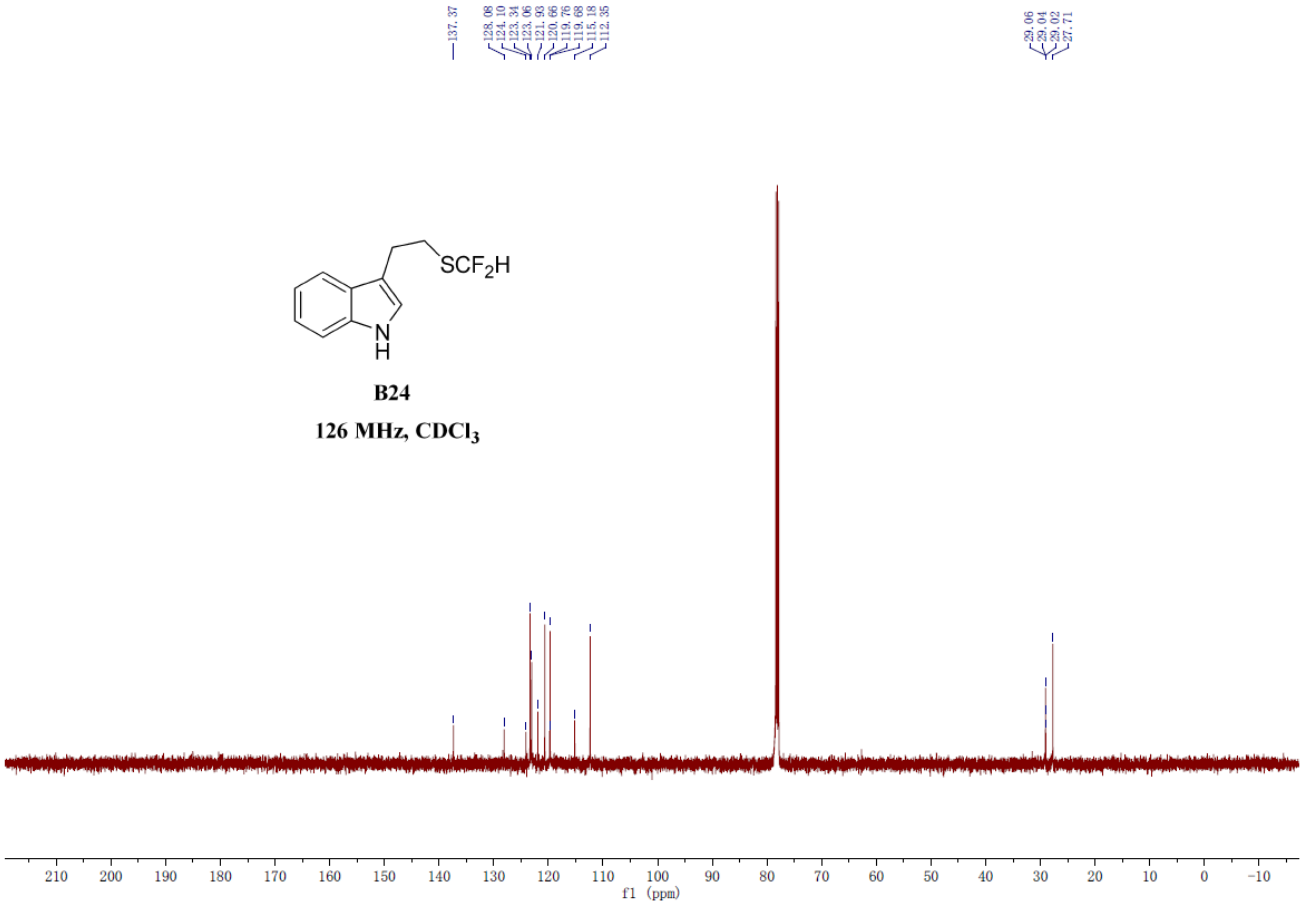
B23

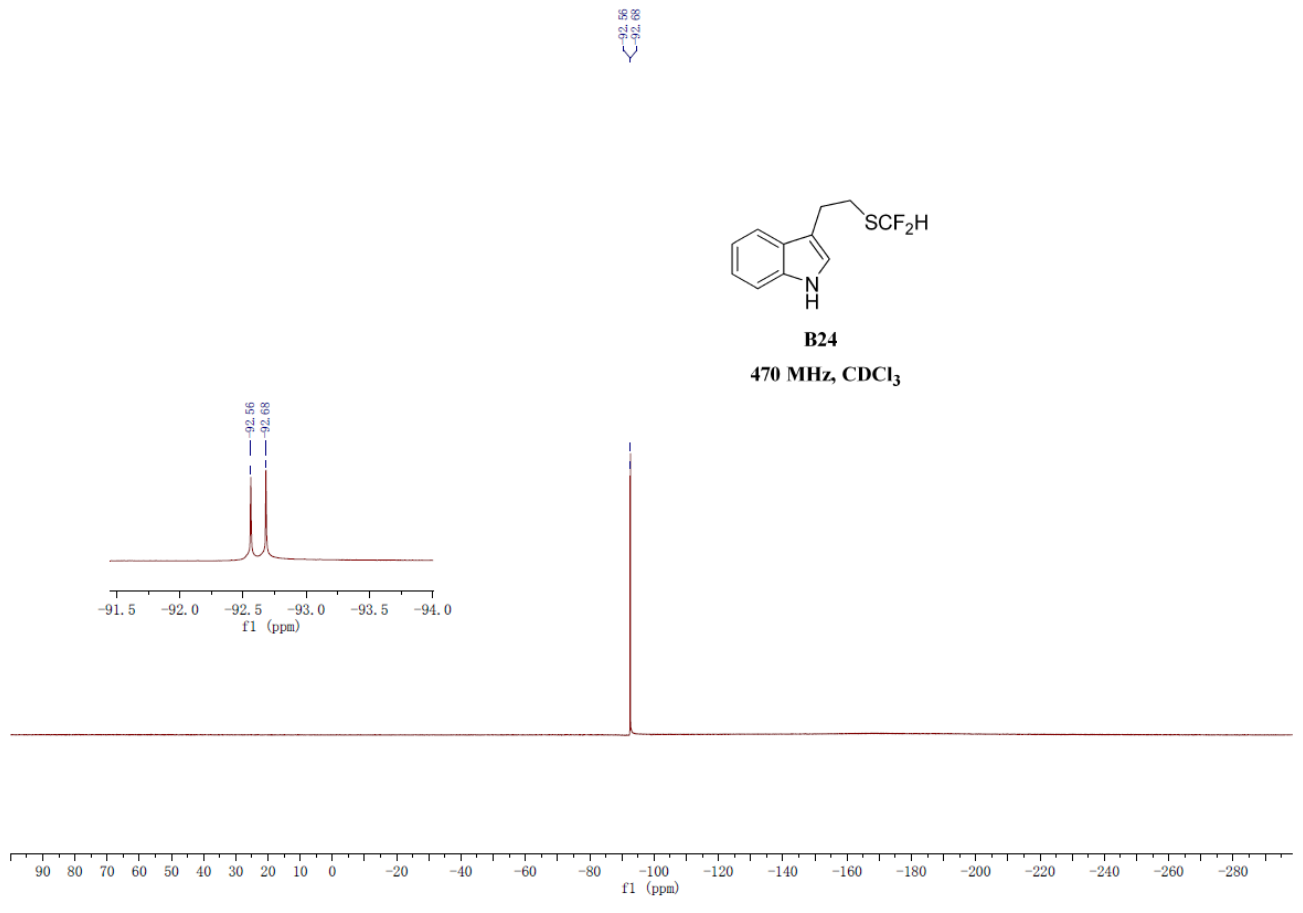
470 MHz, $CDCl_3$

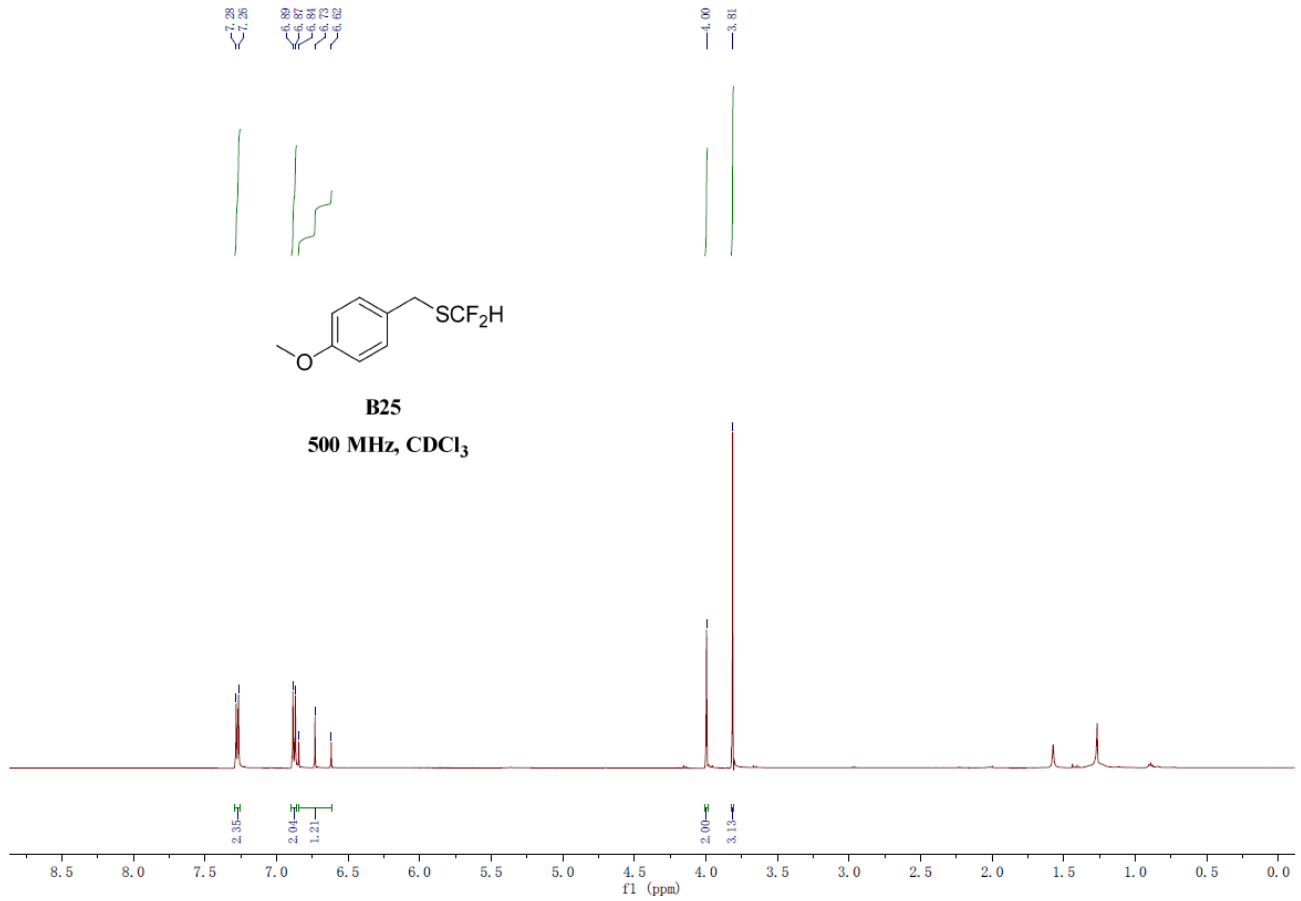


B24

500 MHz, $CDCl_3$

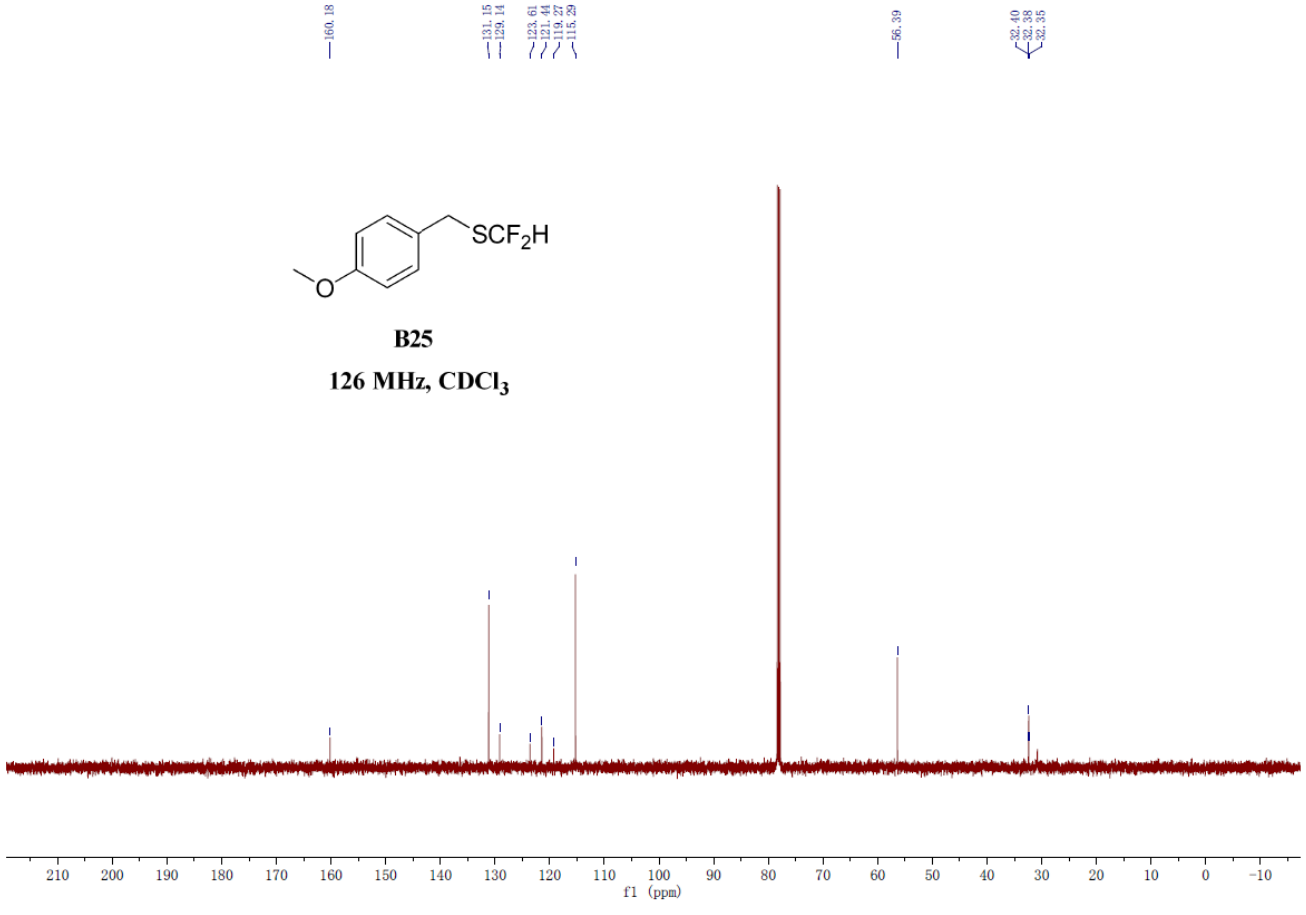

137.37
128.08
124.10
123.34
123.06
121.93
120.66
119.76
119.68
115.18
112.35
29.06
29.04
29.02
27.71
SCF2H
N
H
B24
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-92.56
-92.68
SCF2H
N
H
B24
470 MHz, CDCl3
-92.56
-92.68
-91.5 -92.0 -92.5 -93.0 -93.5 -94.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)



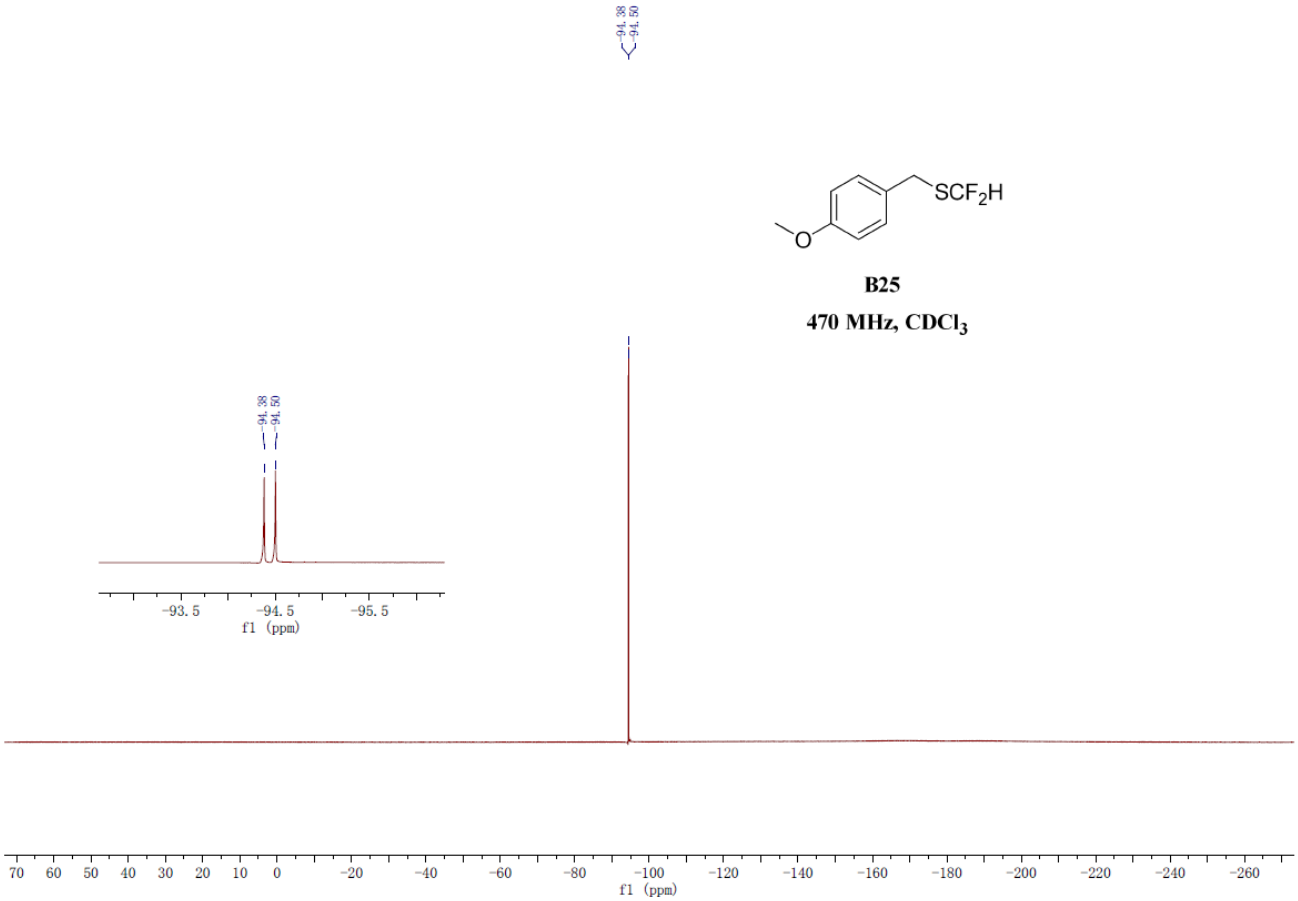
B25

500 MHz, $CDCl_3$



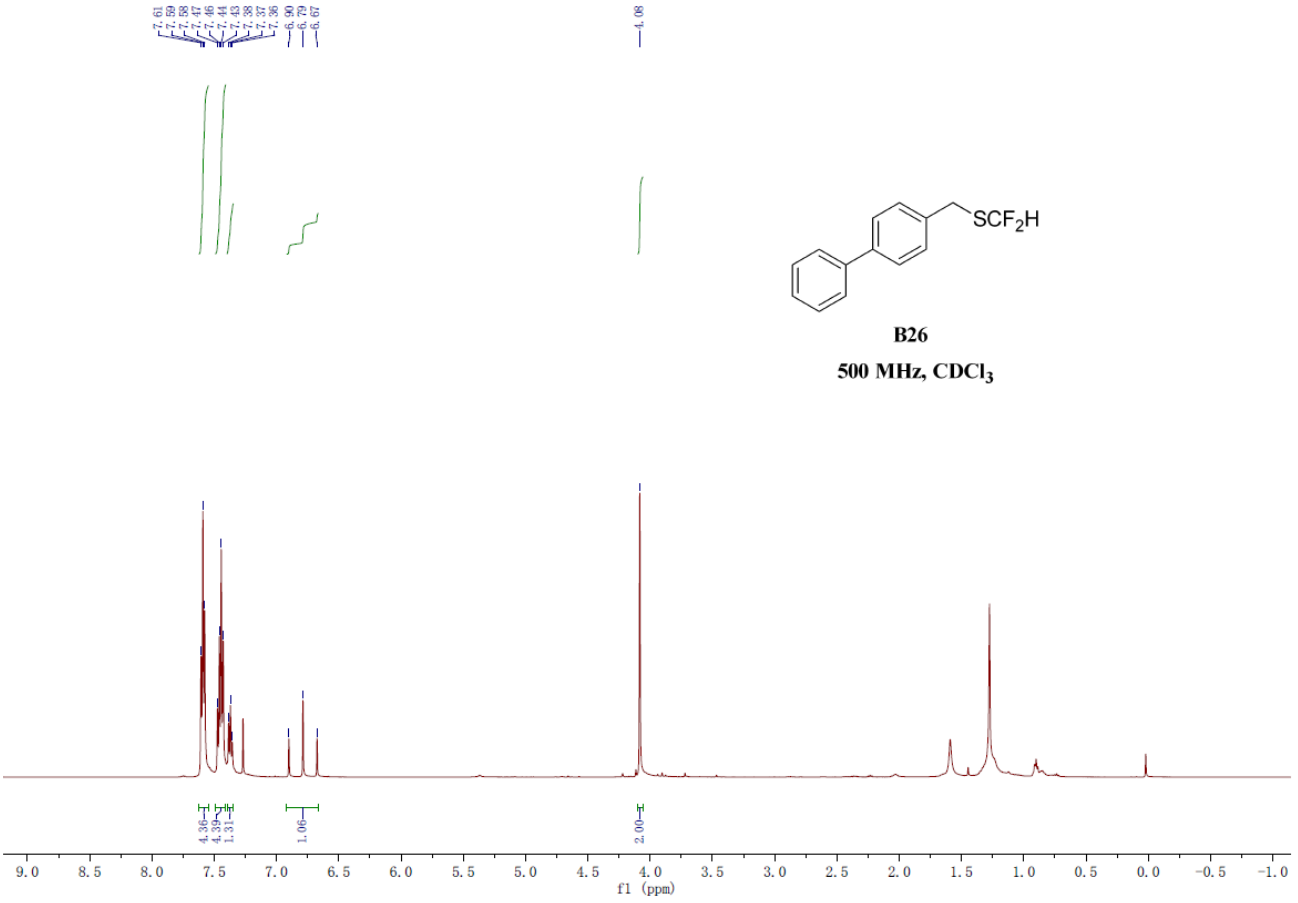
B25

126 MHz, $CDCl_3$



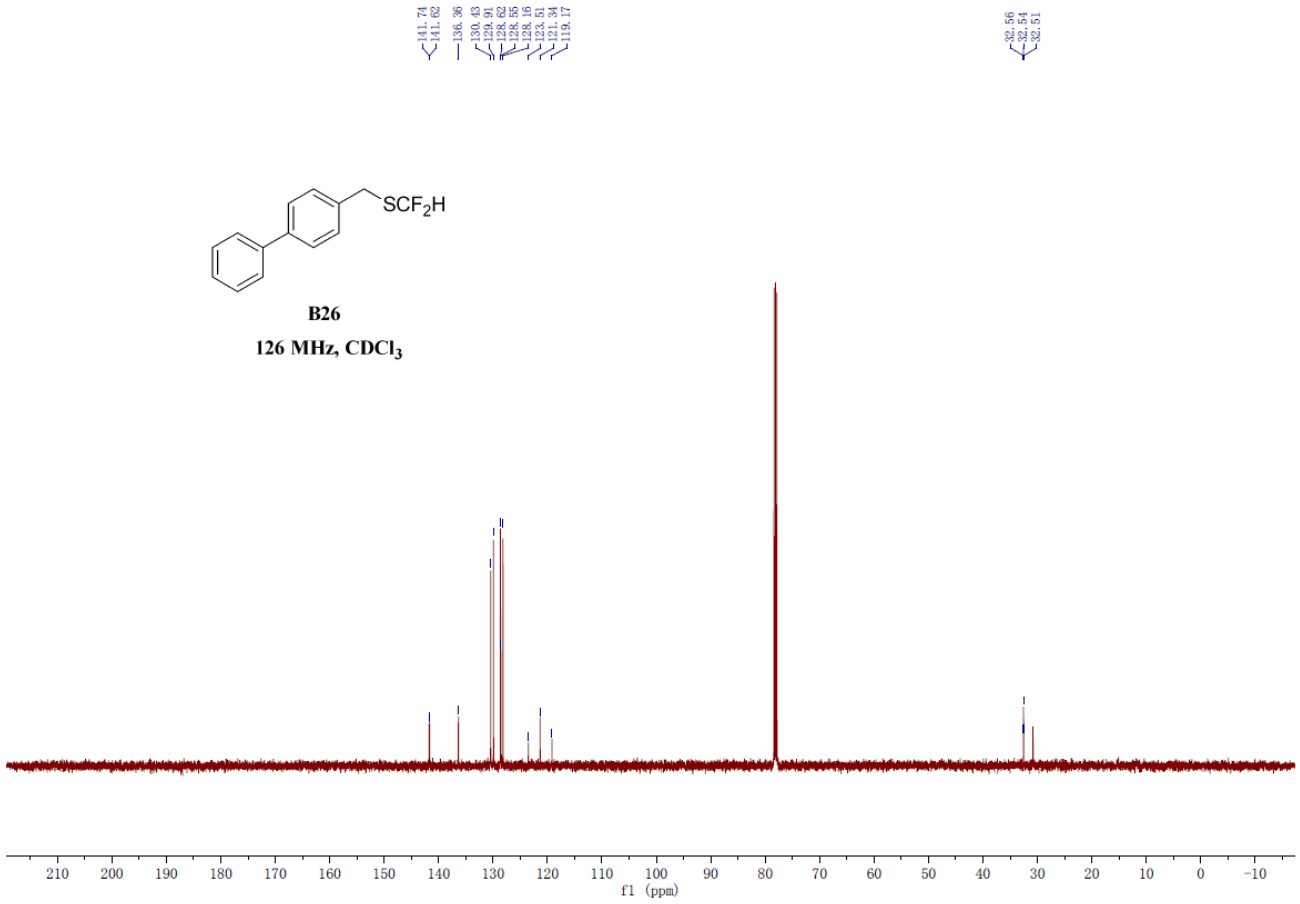
B25

470 MHz, $CDCl_3$



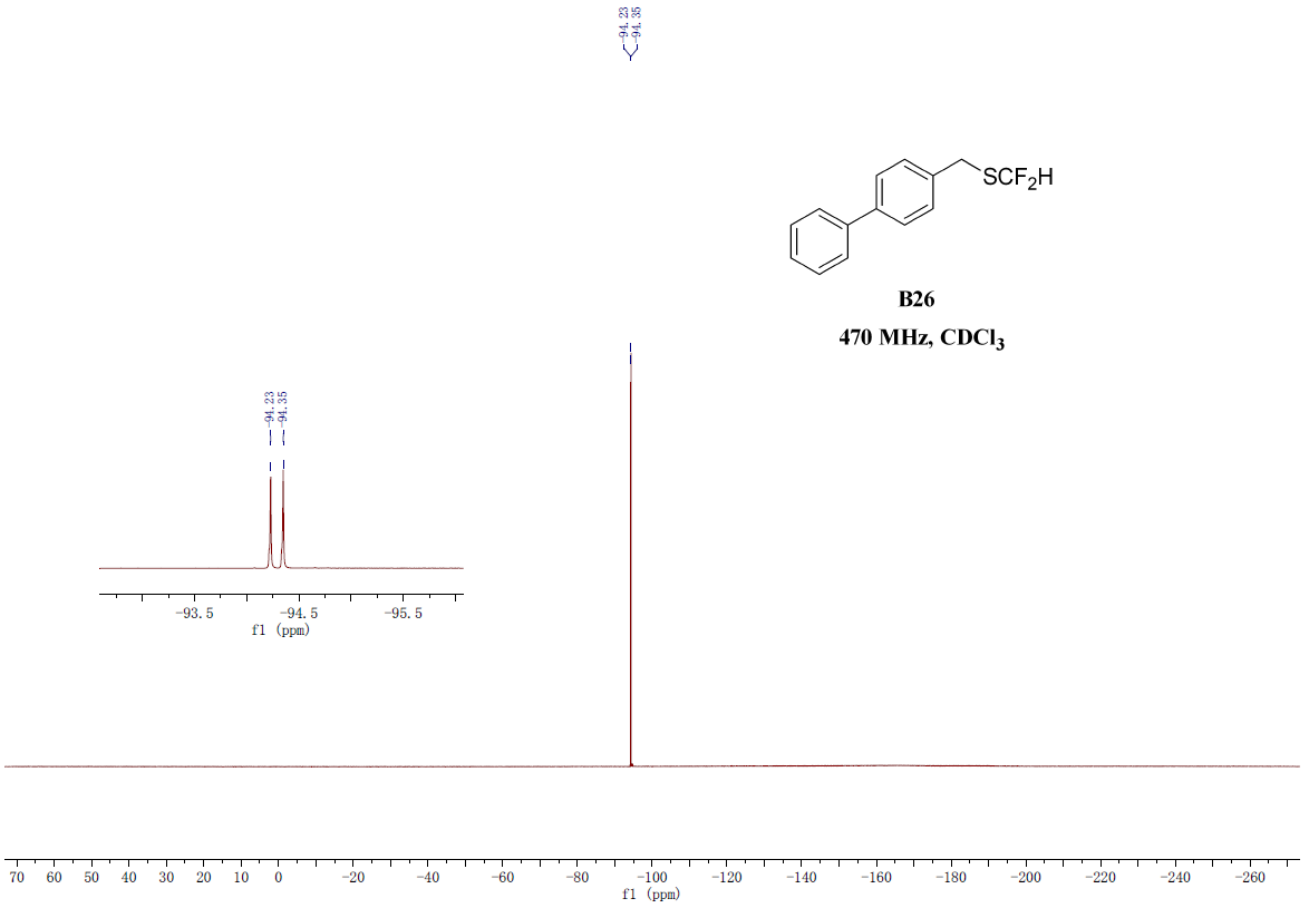
B26

500 MHz, $CDCl_3$



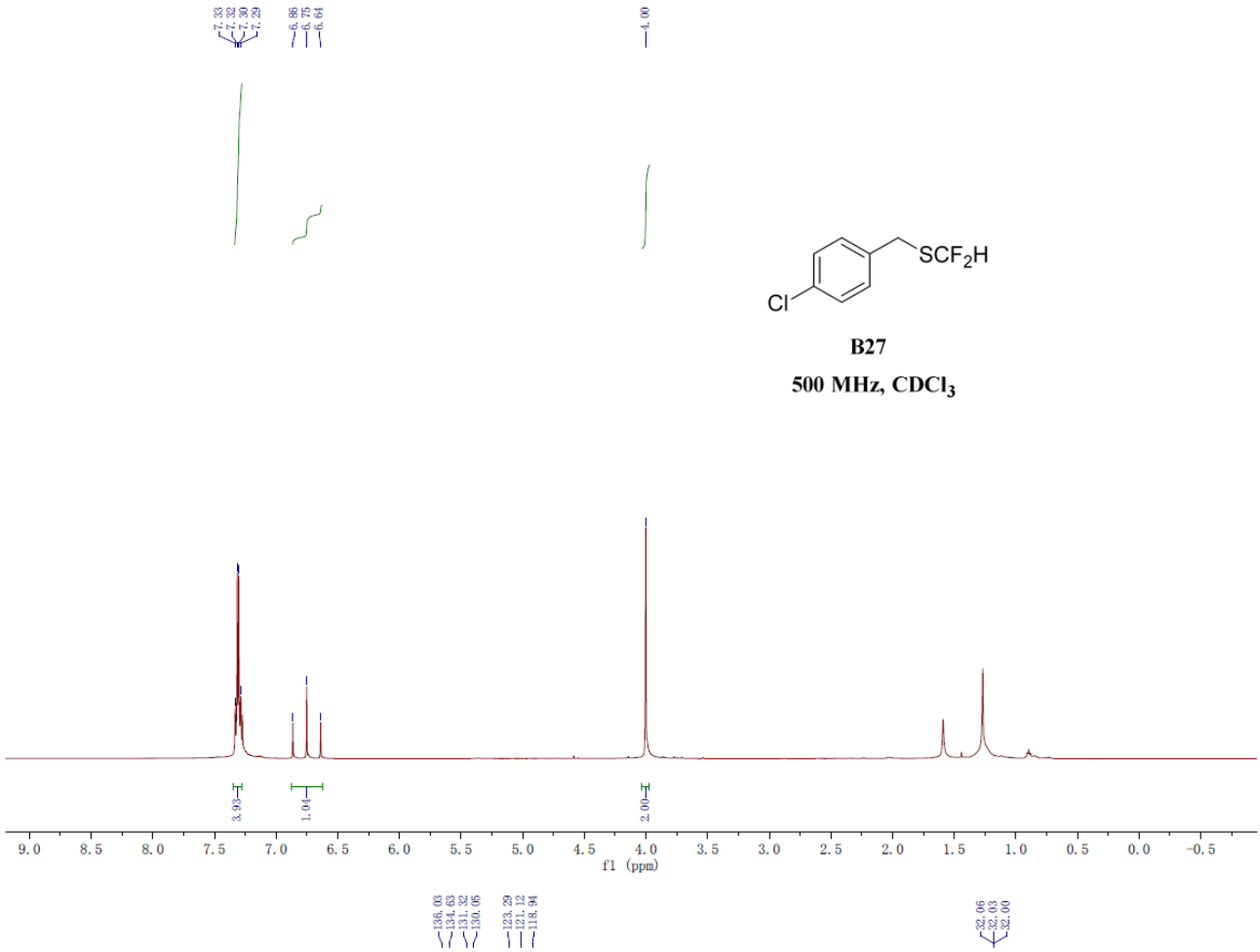
B26

126 MHz, $CDCl_3$



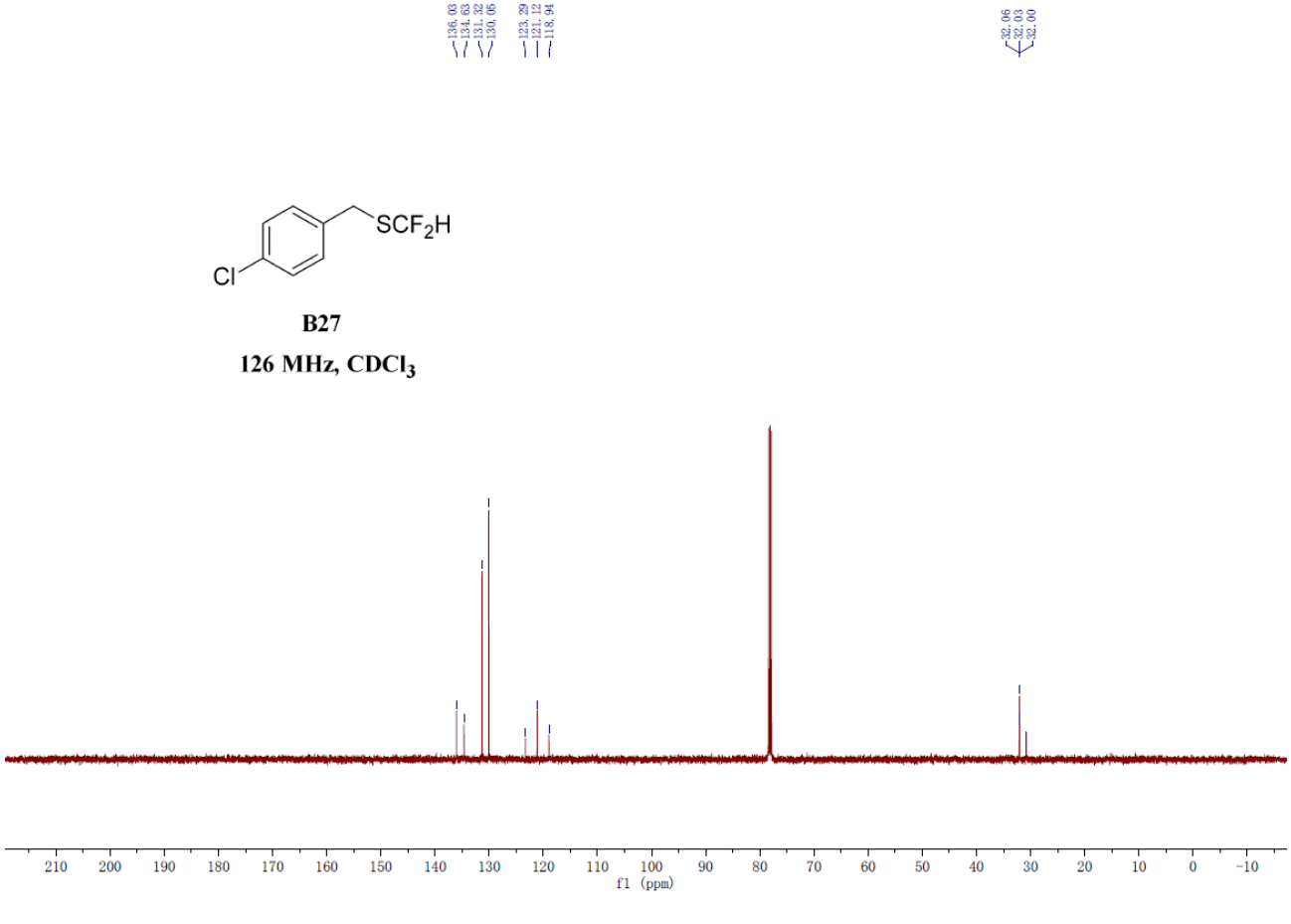
B26

470 MHz, $CDCl_3$



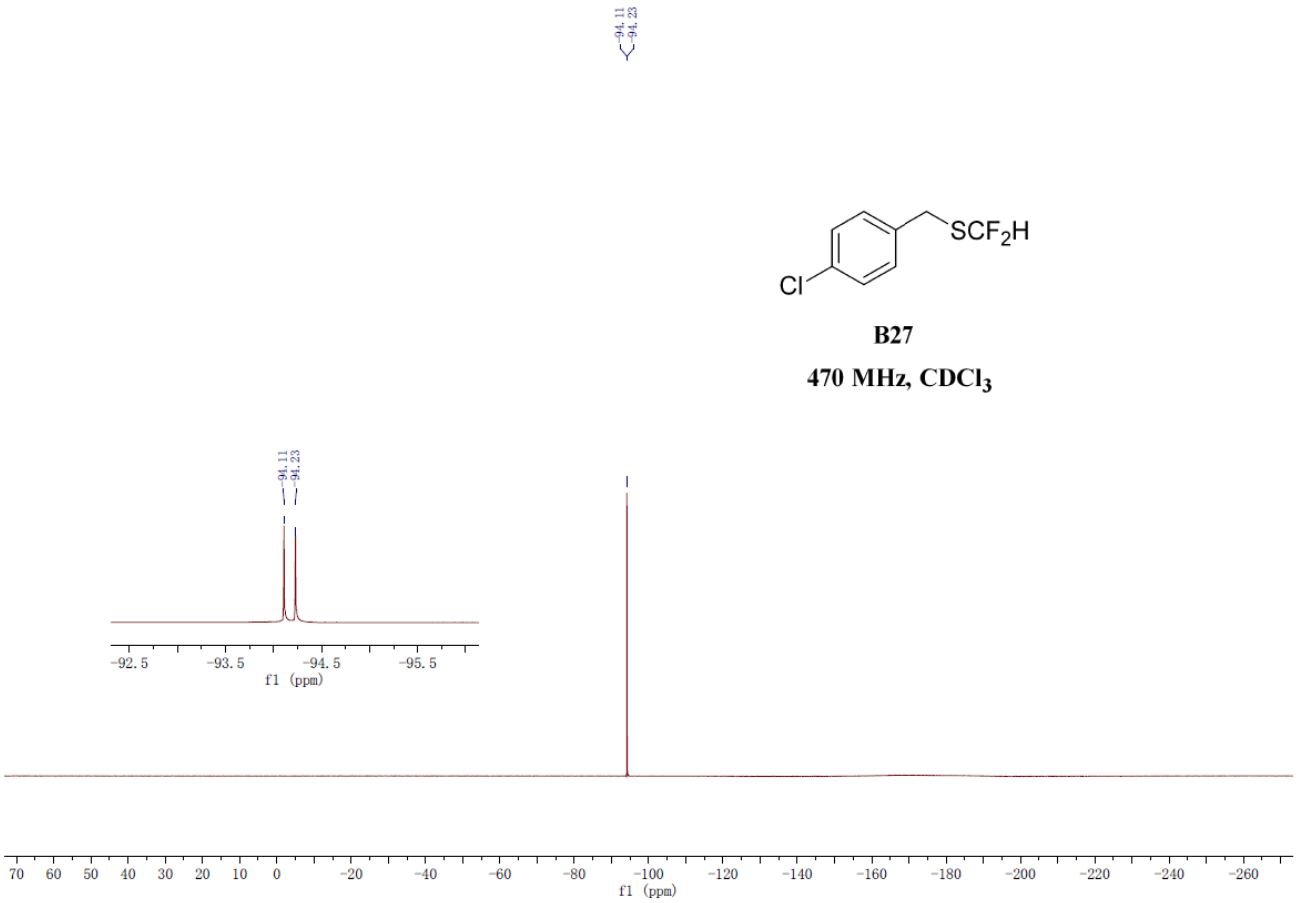
B27

500 MHz, $CDCl_3$



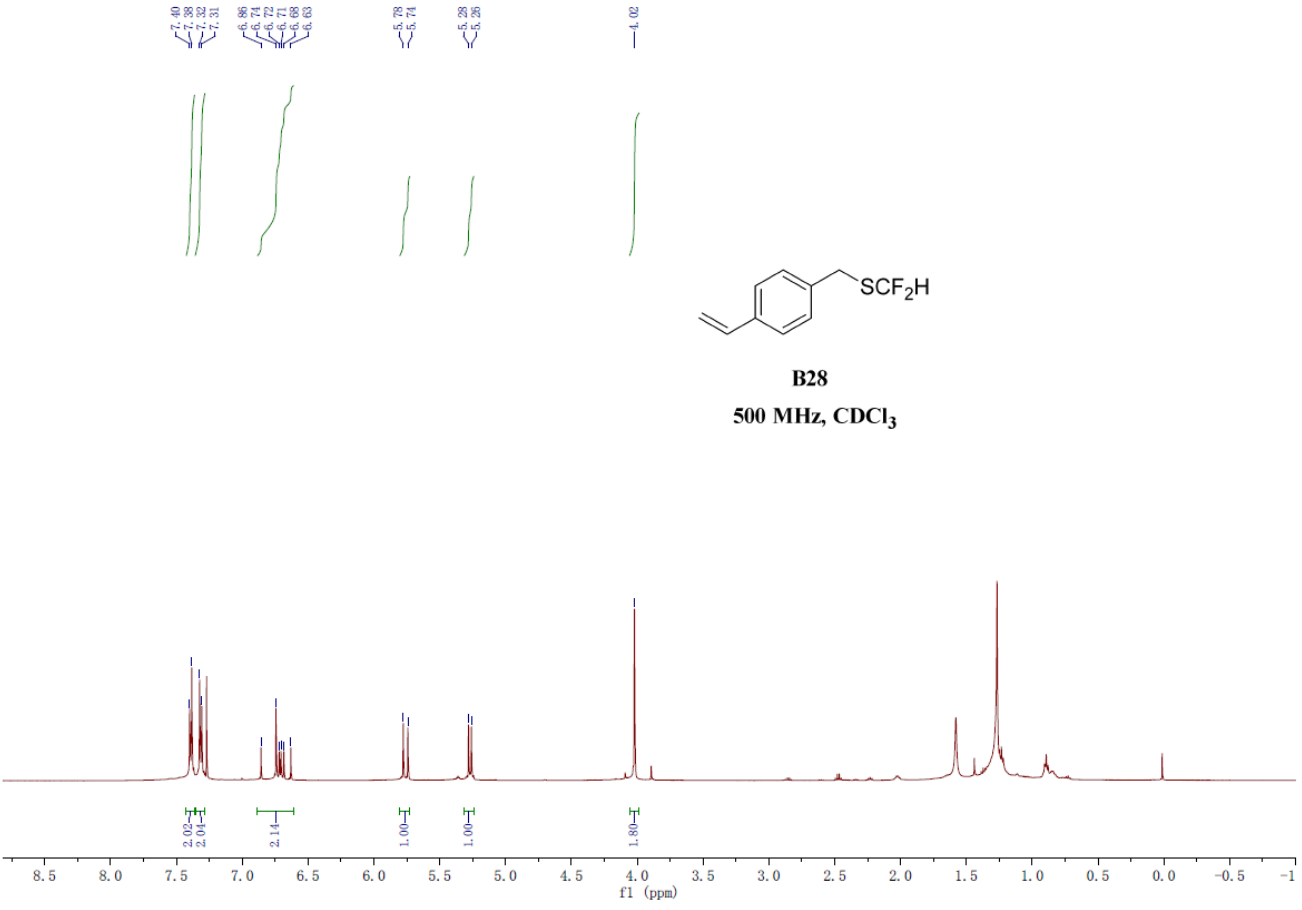
B27

126 MHz, $CDCl_3$



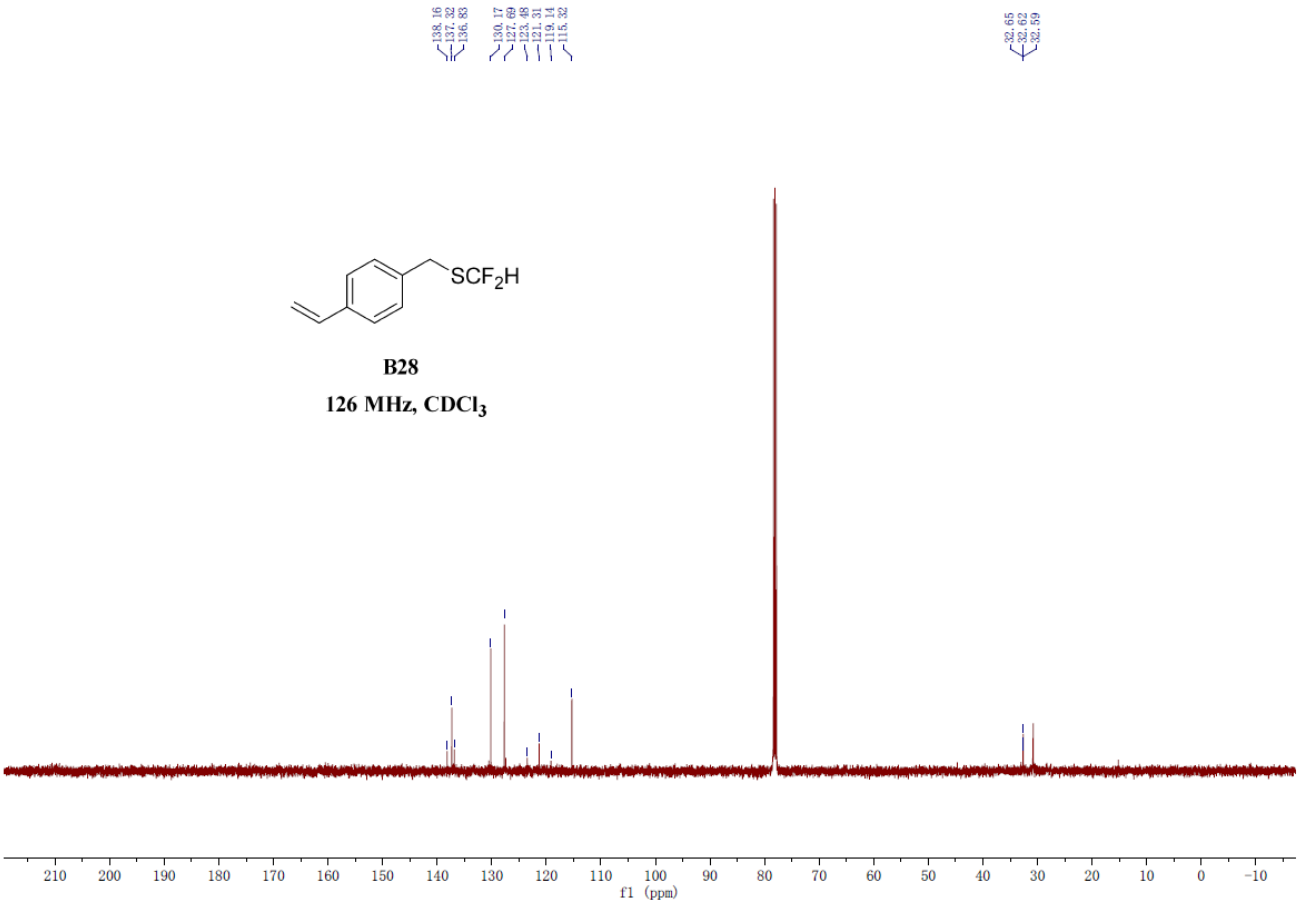
B27

470 MHz, $CDCl_3$



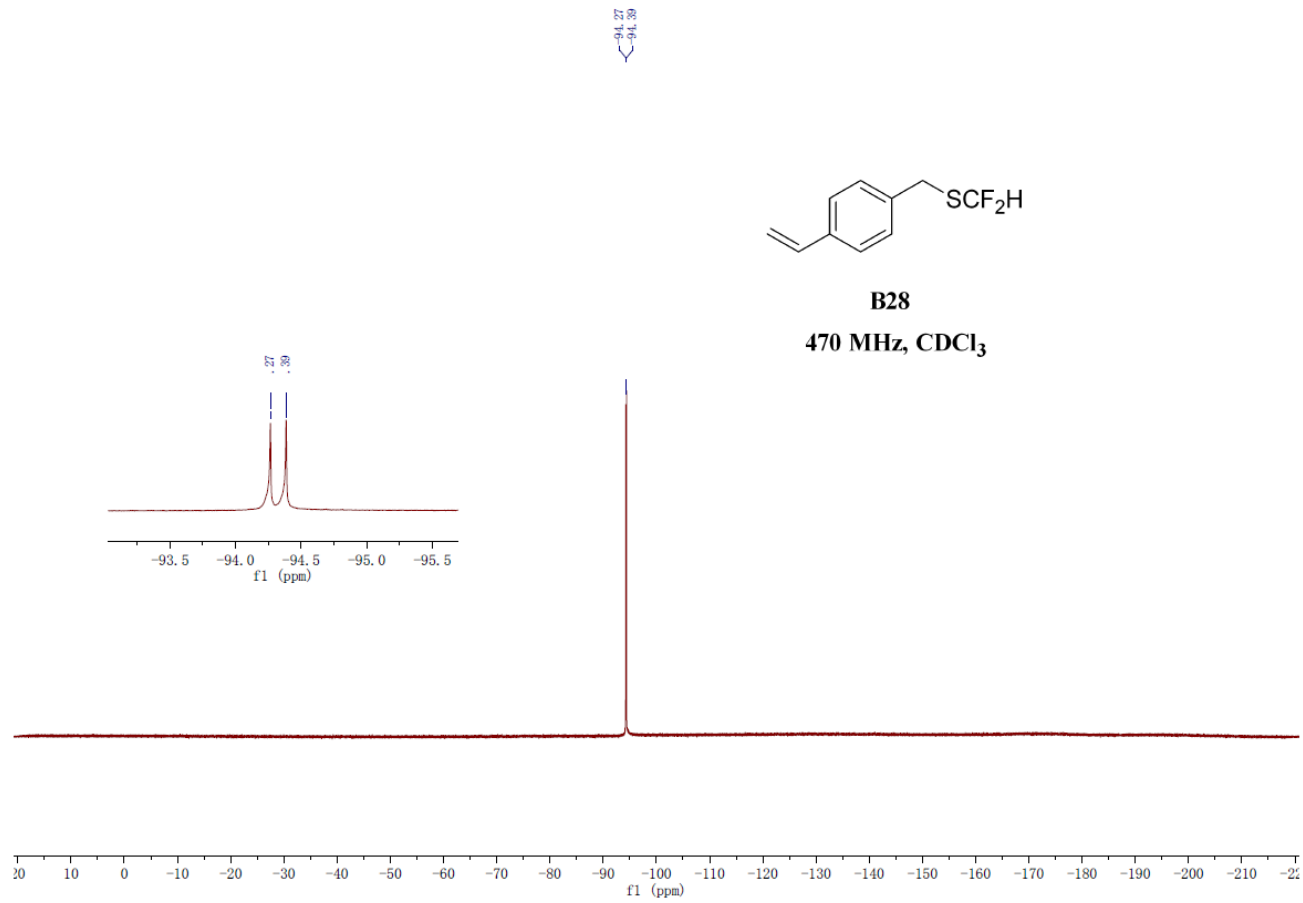
B28

500 MHz, $CDCl_3$



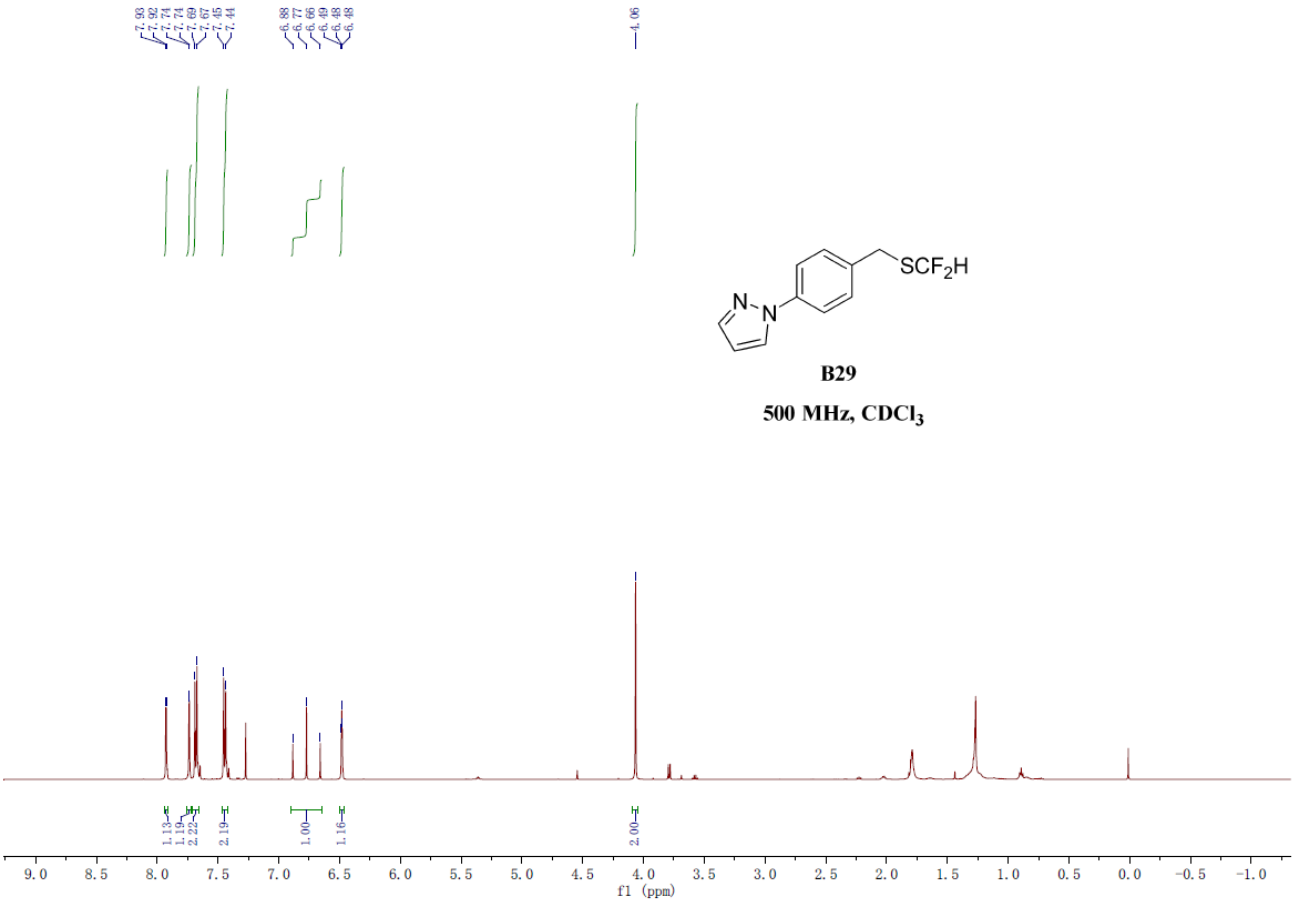
B28

126 MHz, $CDCl_3$



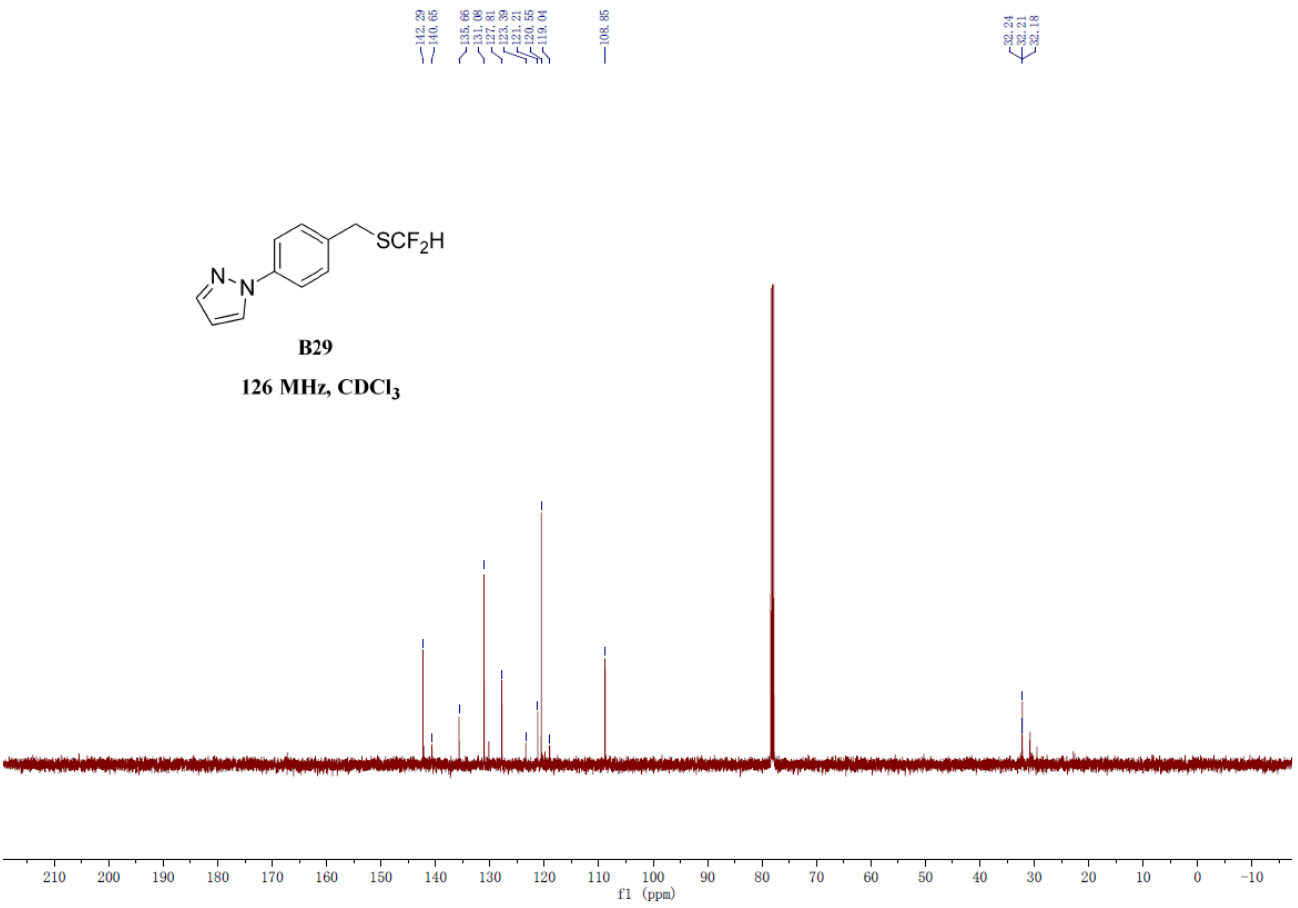
B28

470 MHz, $CDCl_3$



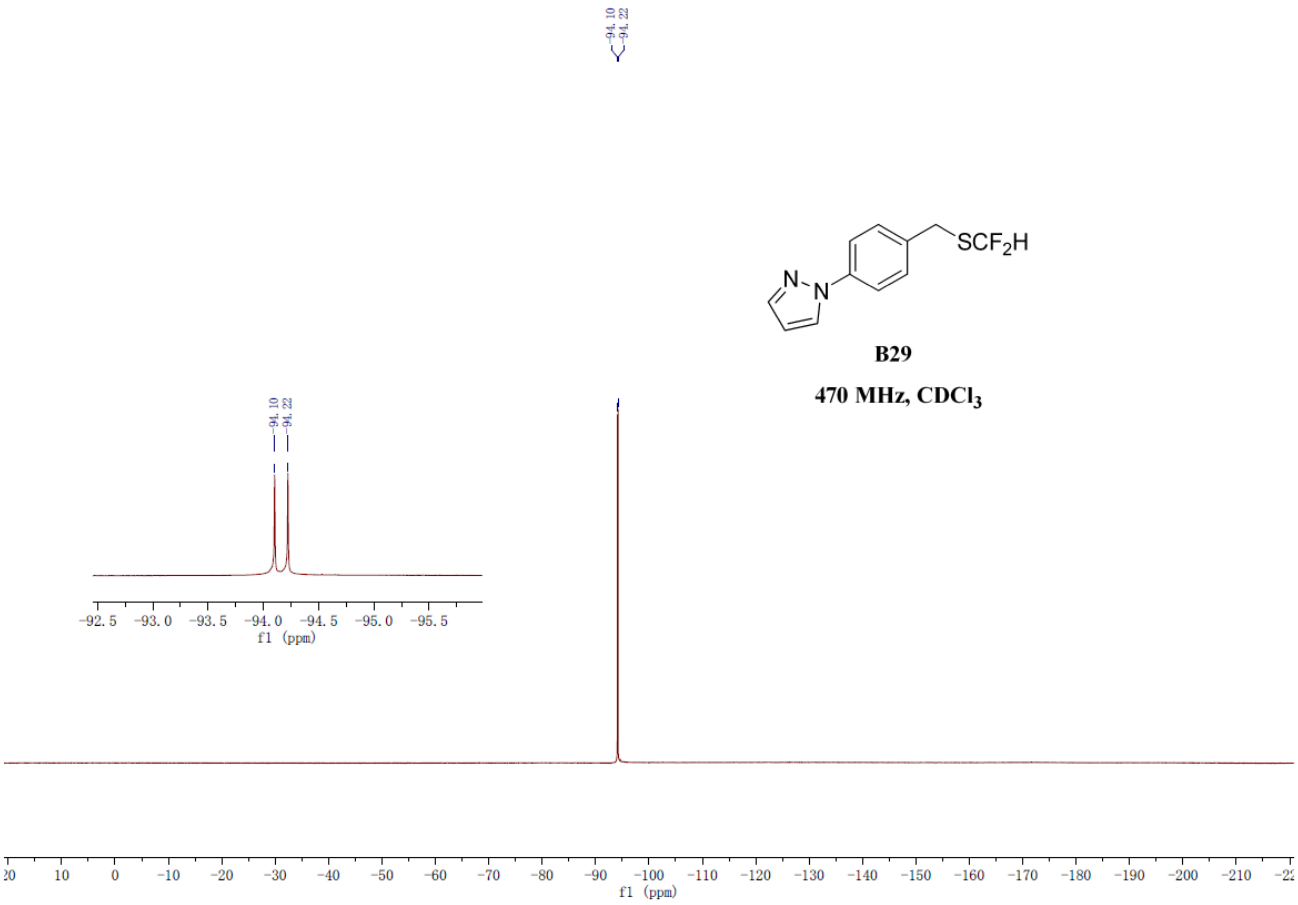
B29

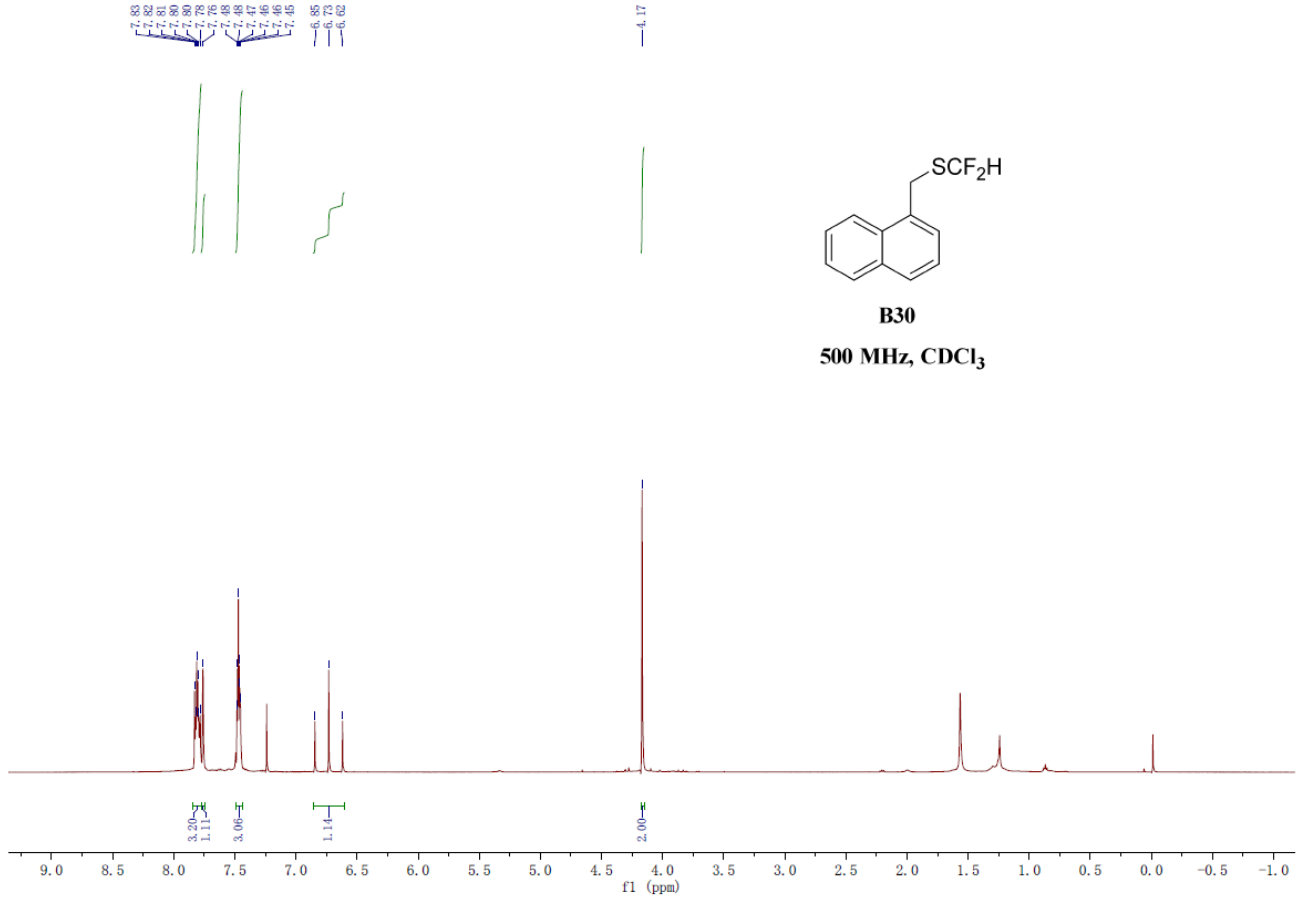
500 MHz, $CDCl_3$

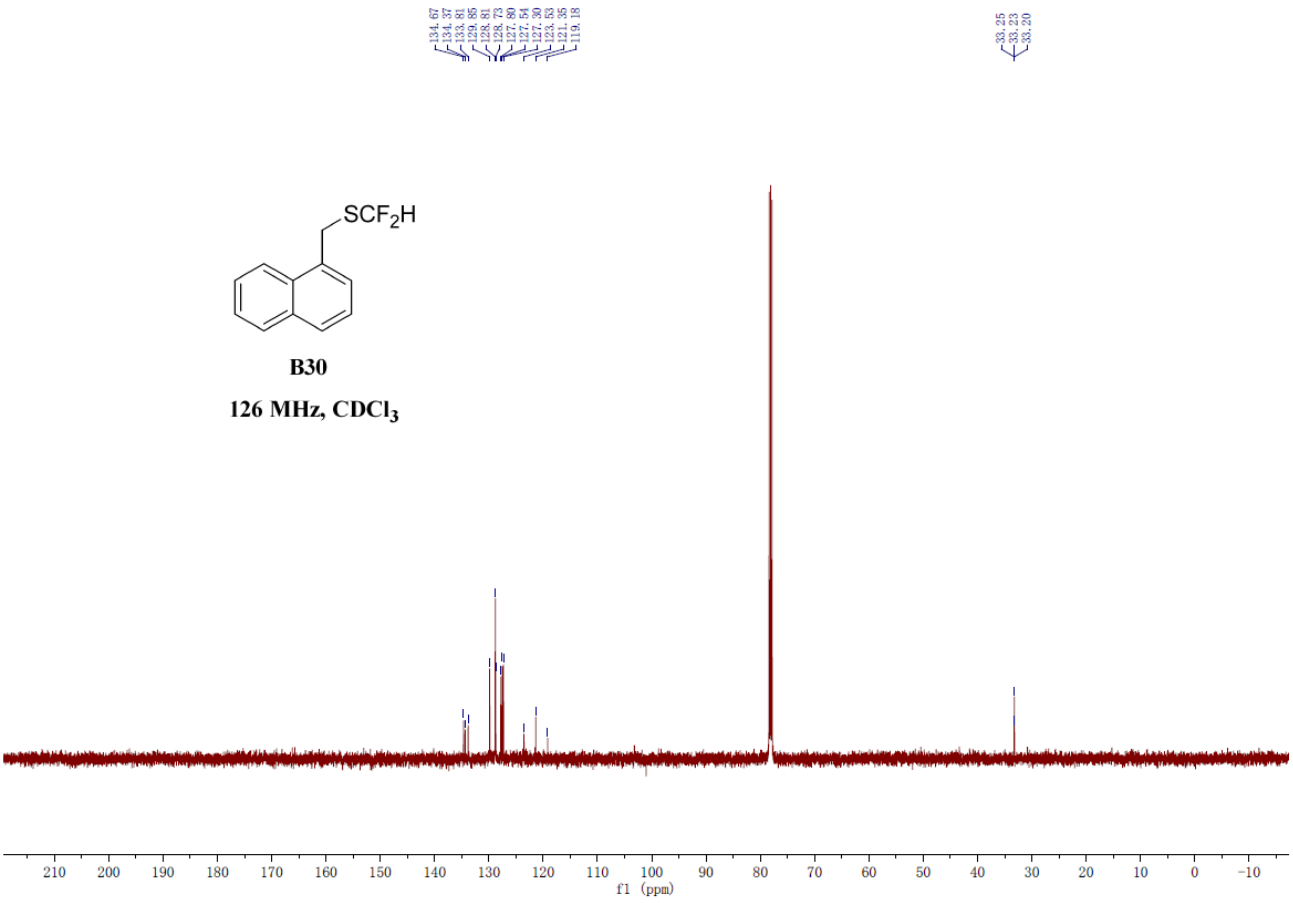


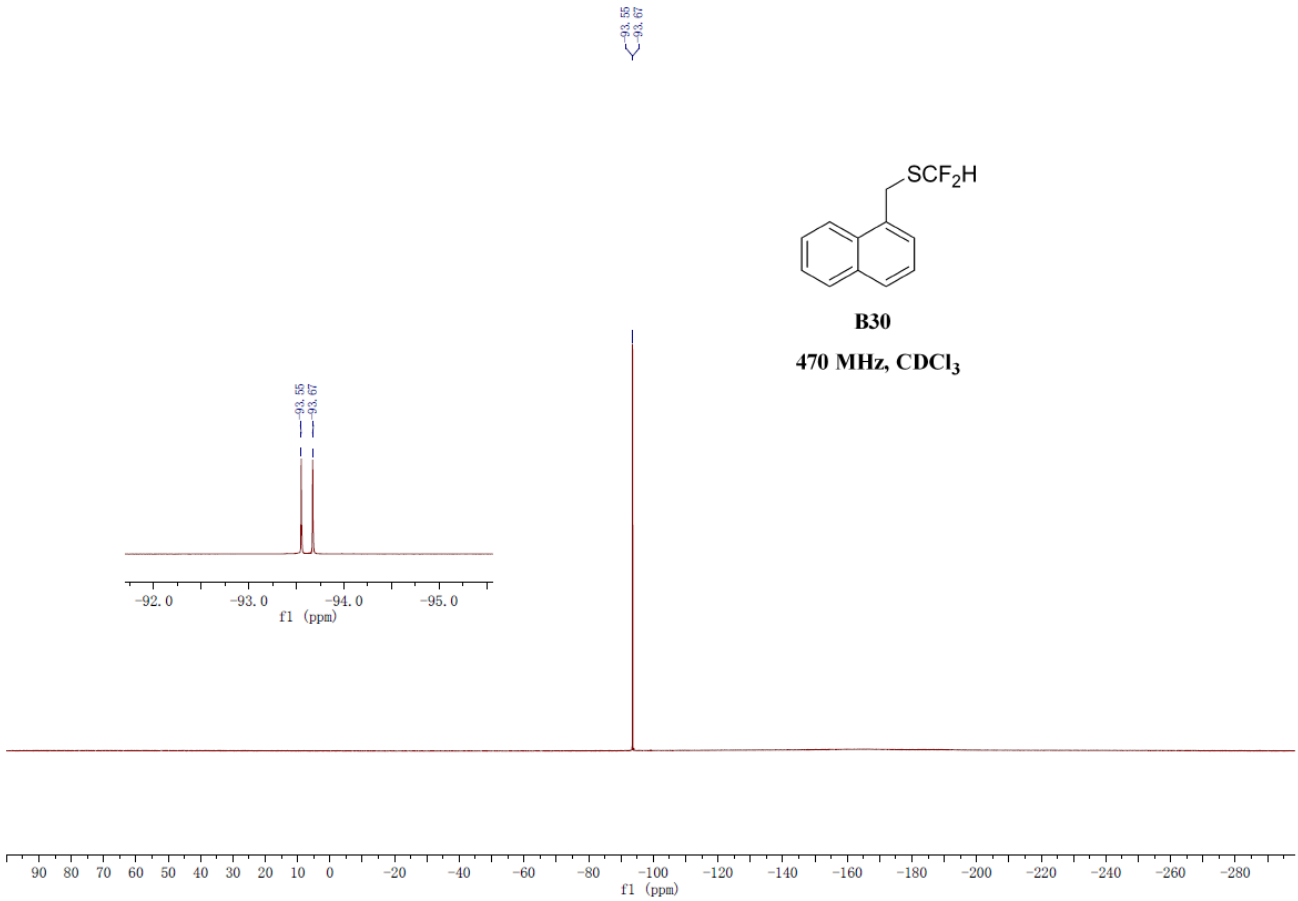
B29

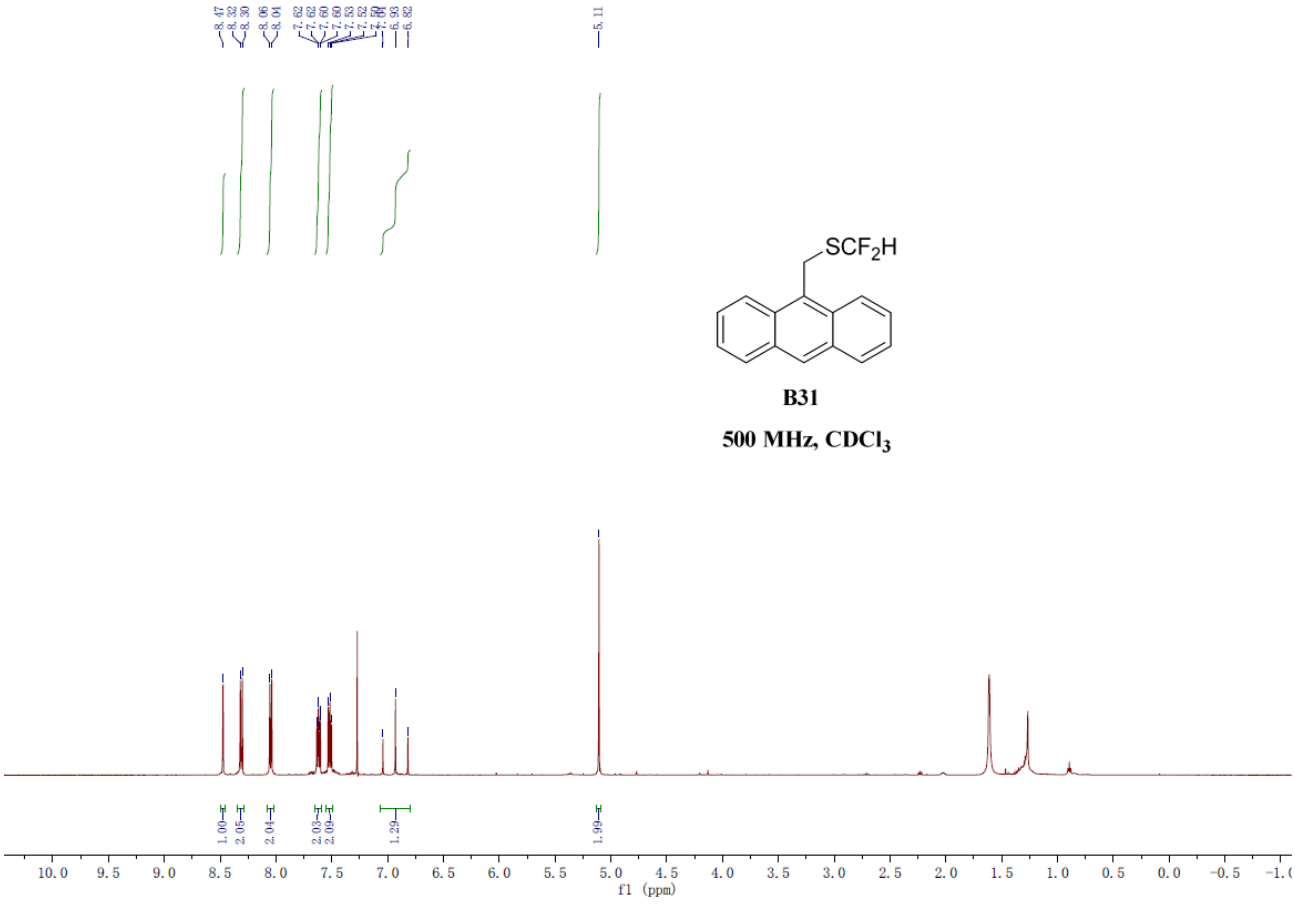
126 MHz, $CDCl_3$


-94.10
-94.22
SCF2H
N
N
B29
470 MHz, CDCl3
-92.5 -93.0 -93.5 -94.0 -94.5 -95.0 -95.5
f1 (ppm)
f1 (ppm)


7.83
7.82
7.81
7.80
7.79
7.78
7.76
7.48
7.47
7.46
7.46
7.45
6.85
6.73
6.62
4.17
SCF2H
B30
500 MHz, CDCl3
3.20
1.11
3.06
1.14
2.00
f1 (ppm)

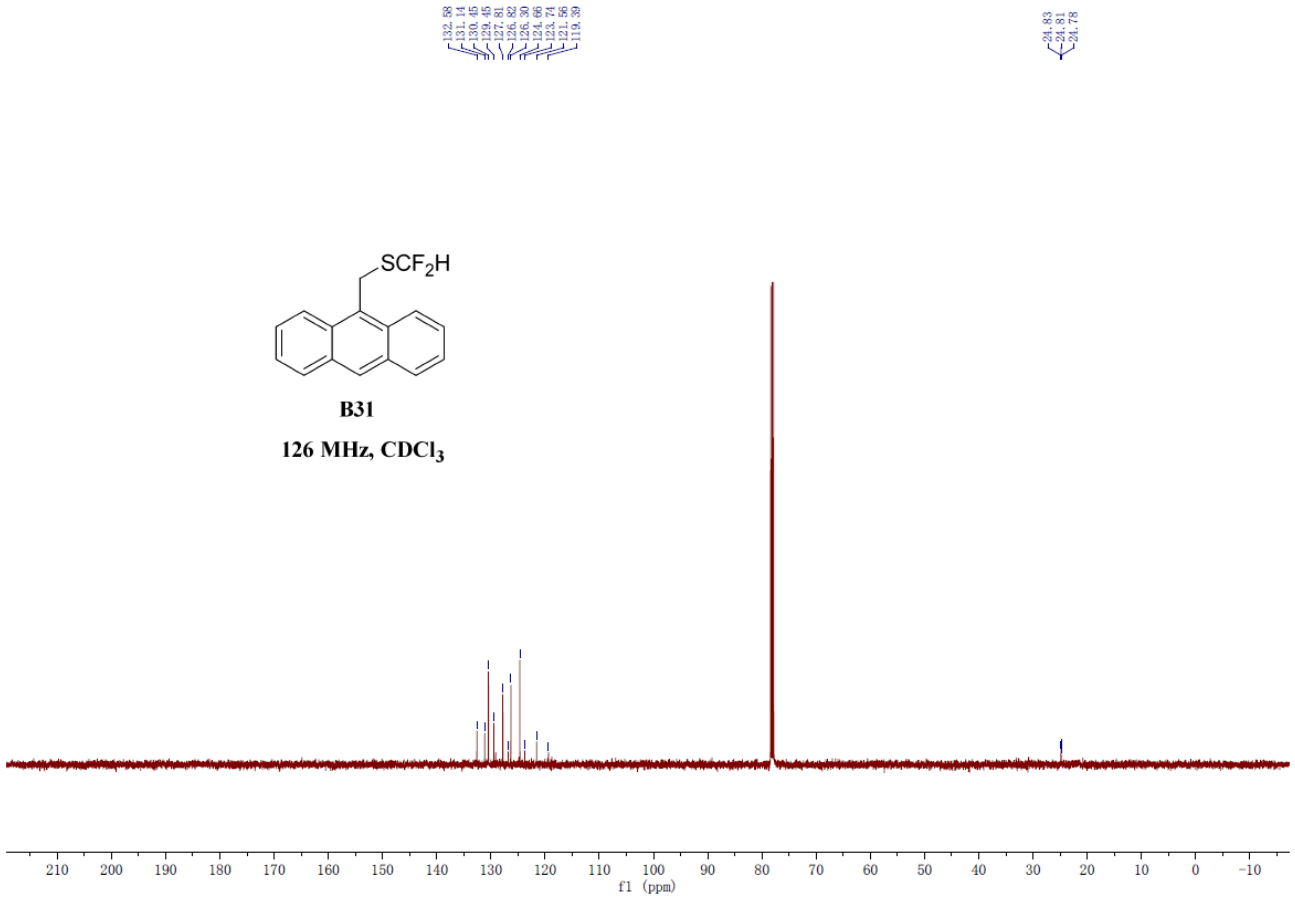

134.67
134.37
133.81
129.85
128.81
128.73
127.80
127.54
127.30
123.53
121.95
119.18
33.25
33.23
33.20
SCF2H
B30
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-93.55
-93.67
SCF2H
B30
470 MHz, CDCl3
-92.0 -93.0 -94.0 -95.0
f1 (ppm)
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)



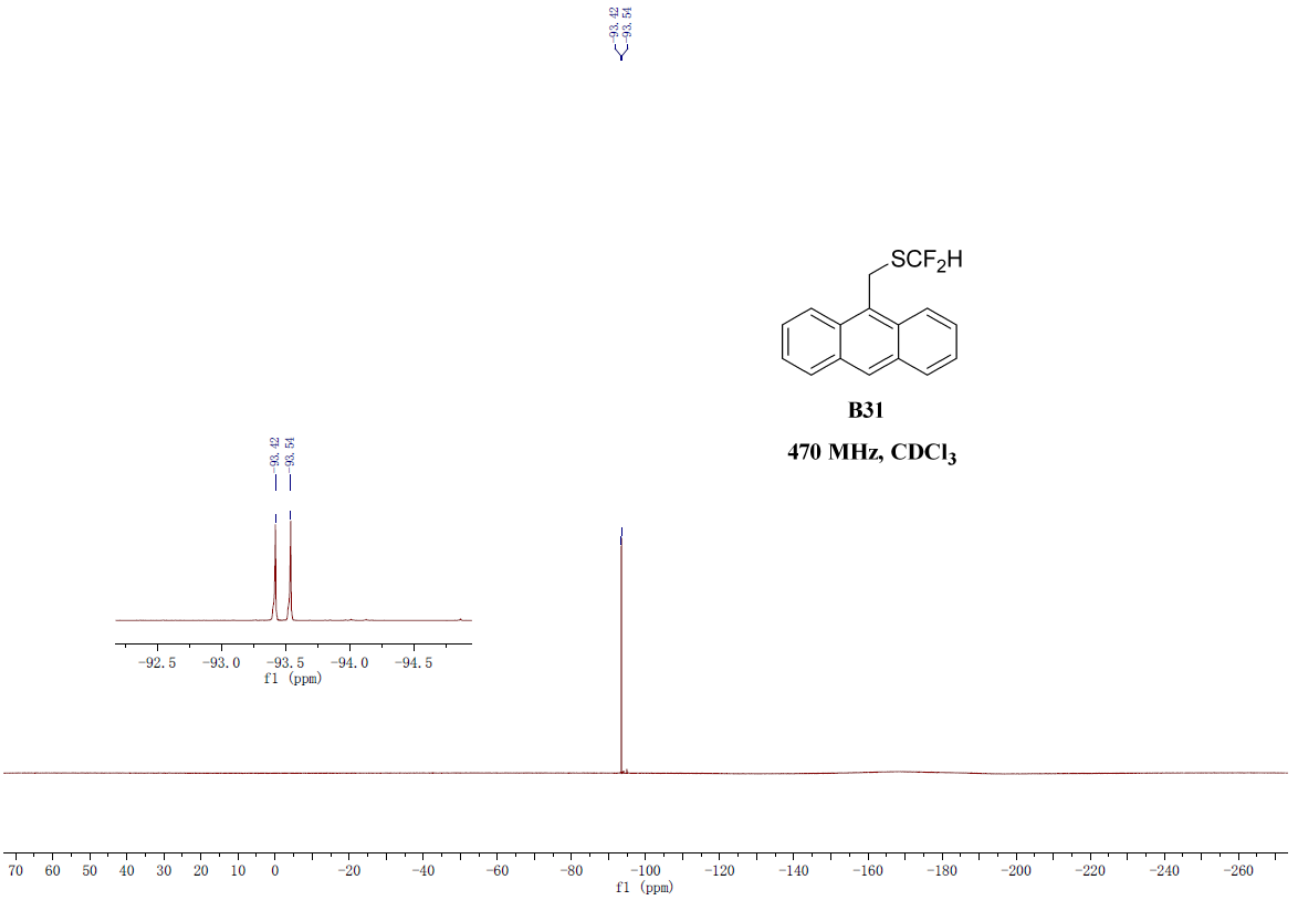
B31

500 MHz, $CDCl_3$



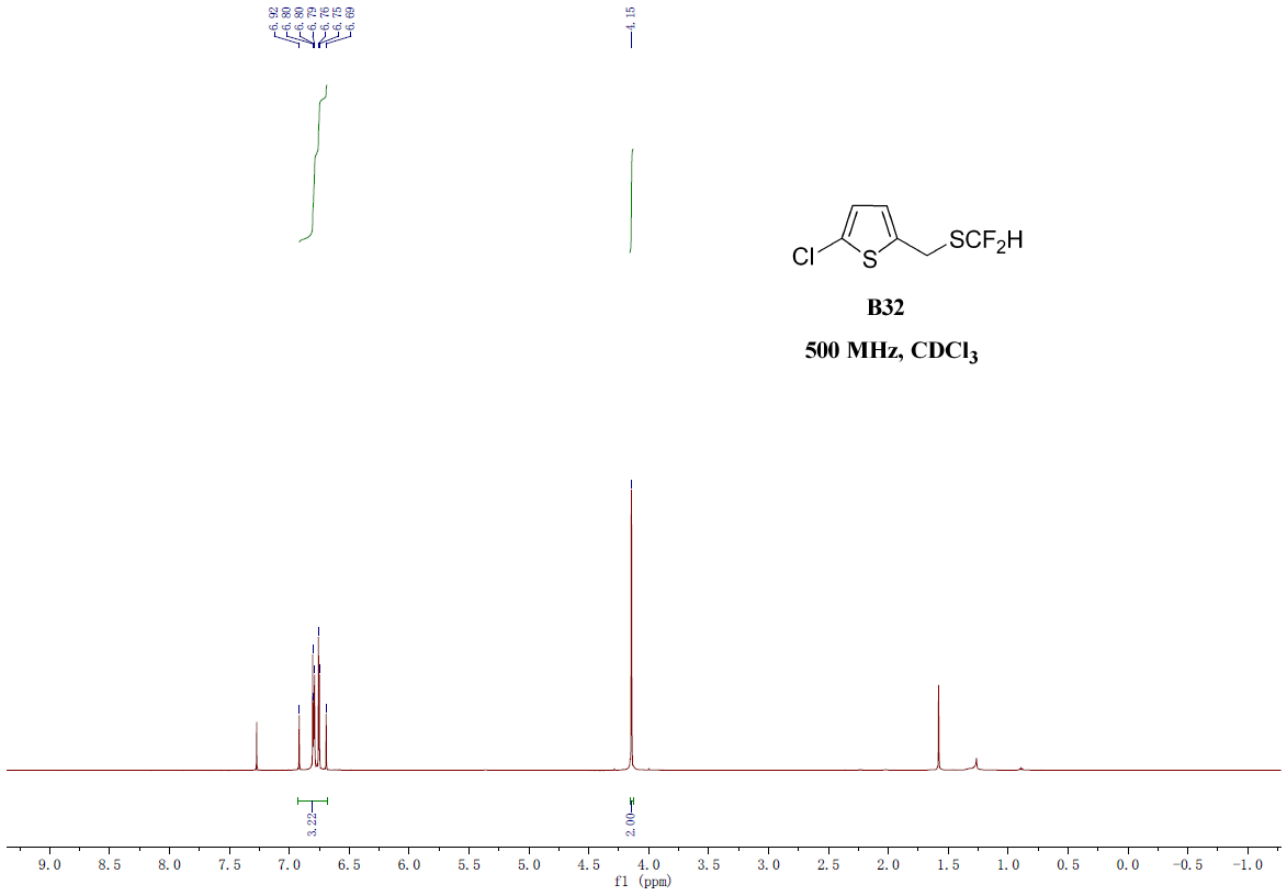
B31

126 MHz, $CDCl_3$



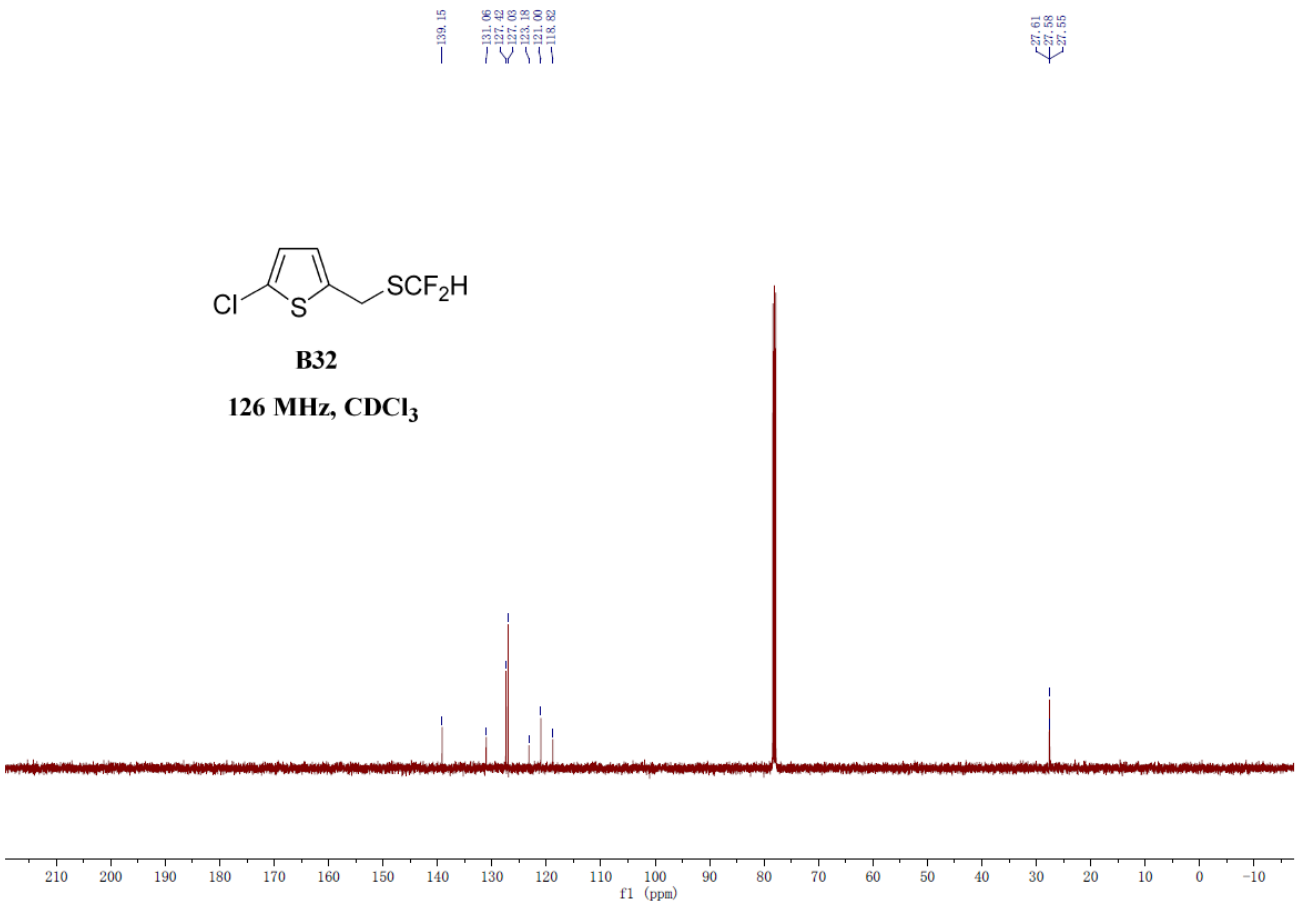
B31

470 MHz, $CDCl_3$



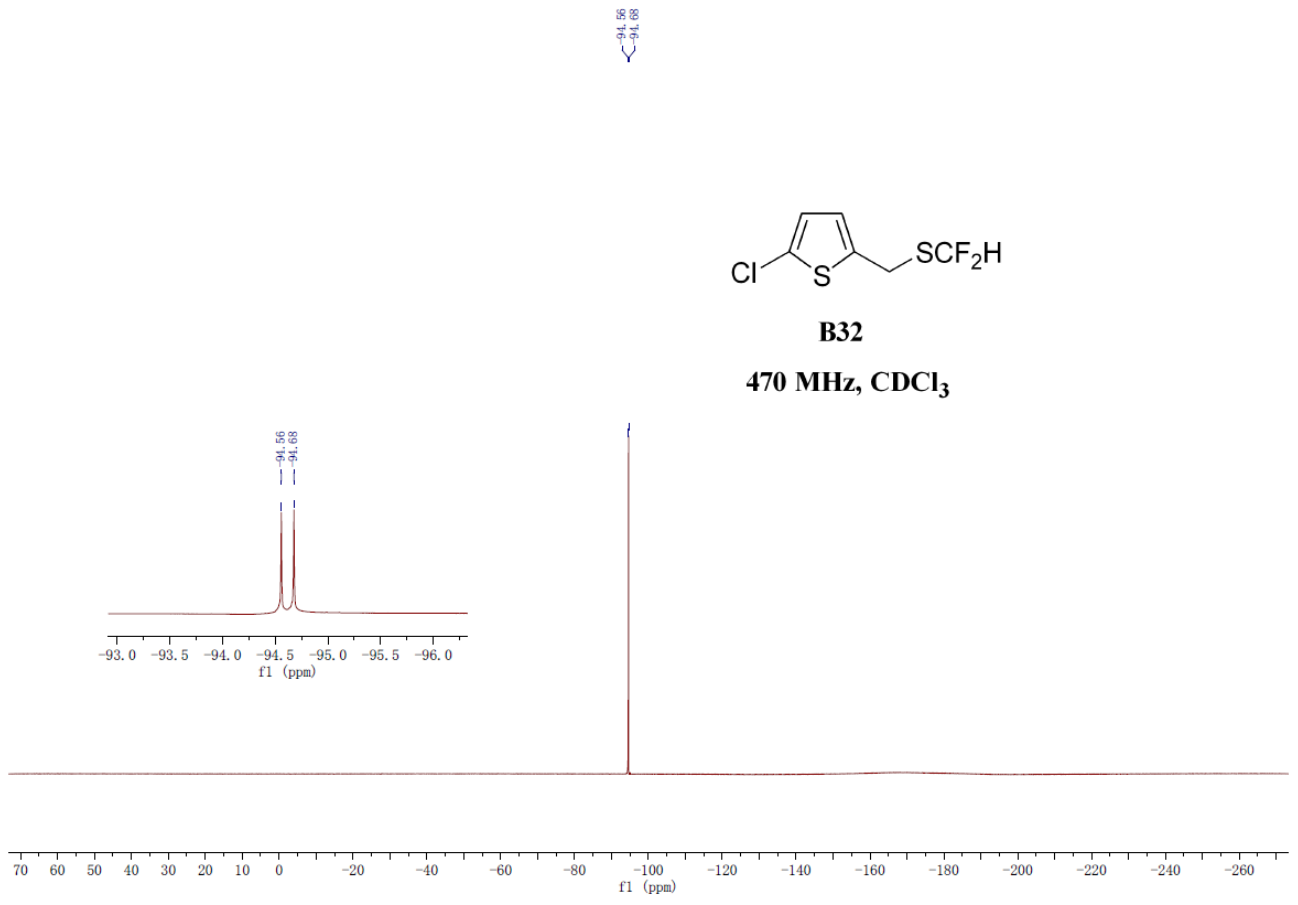
B32

500 MHz, $CDCl_3$



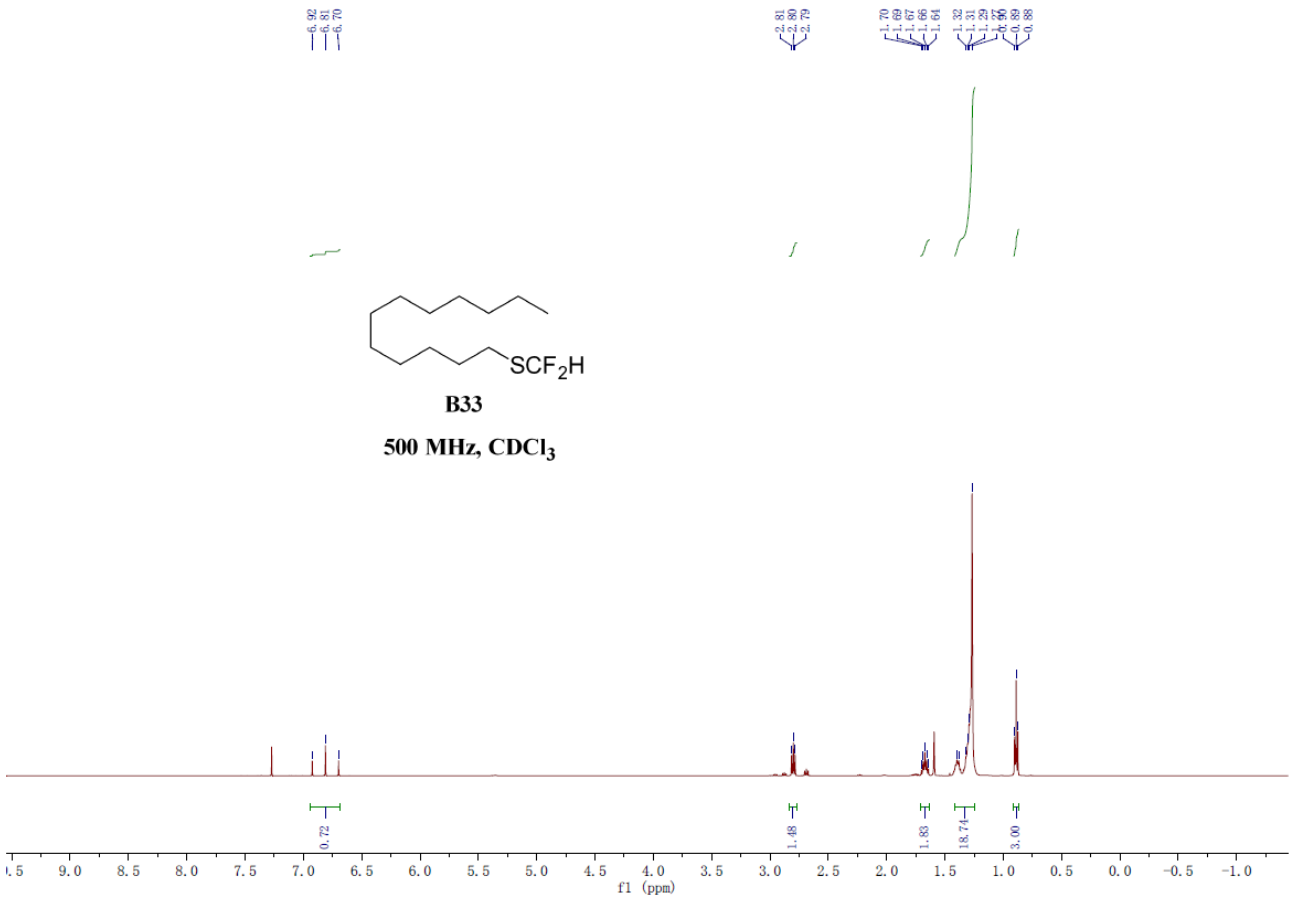
B32

126 MHz, $CDCl_3$



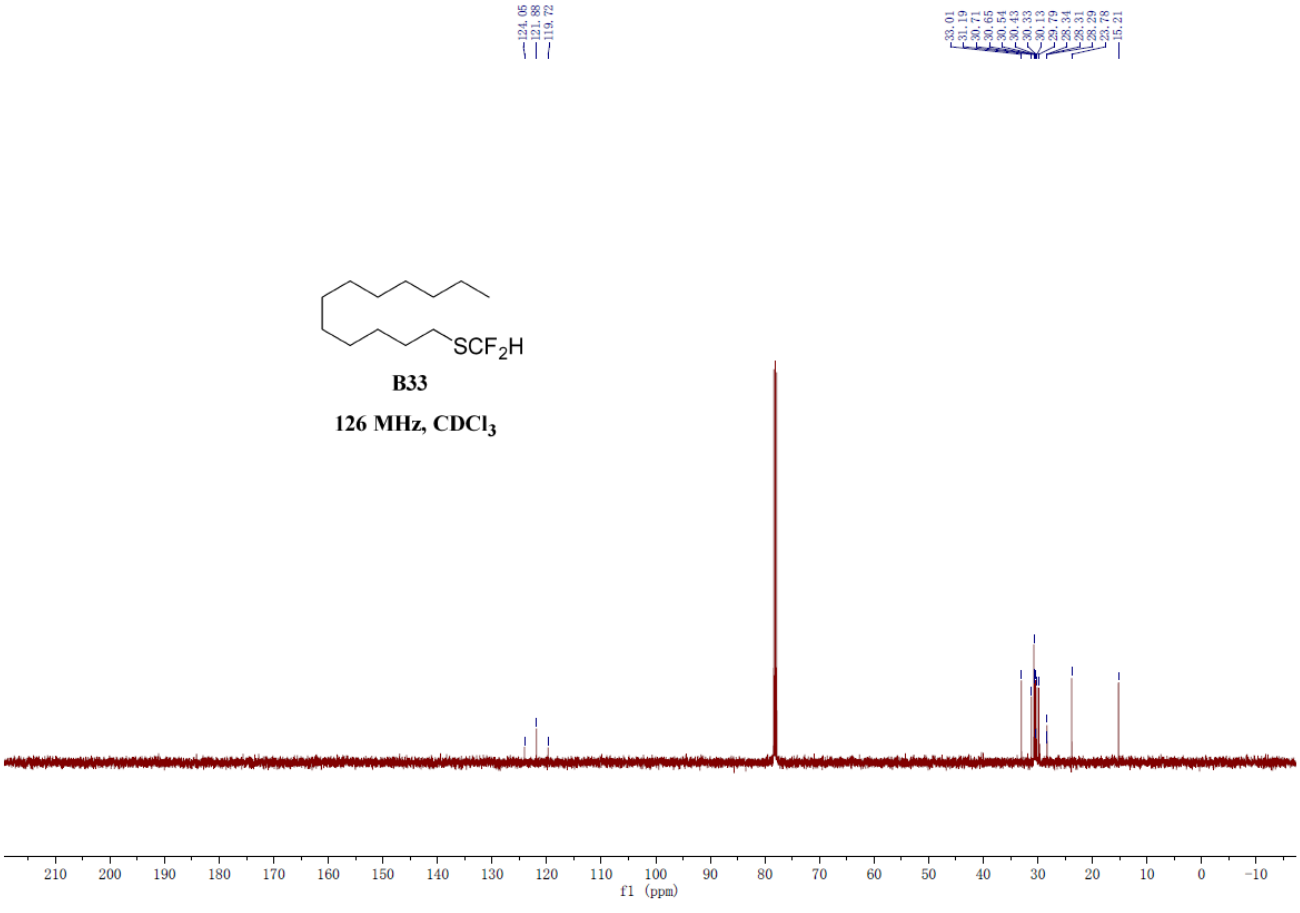
B32

470 MHz, $CDCl_3$



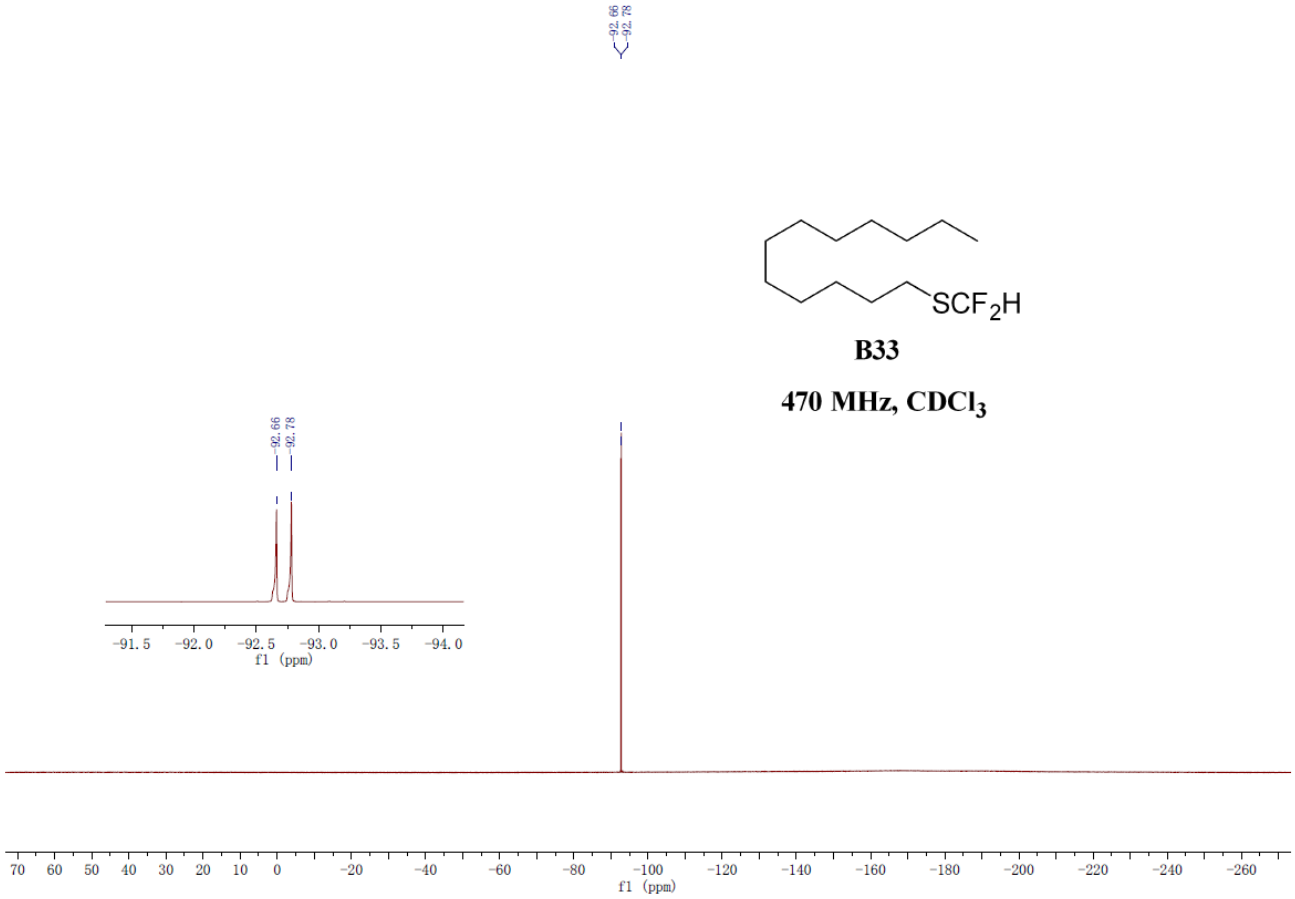
B33

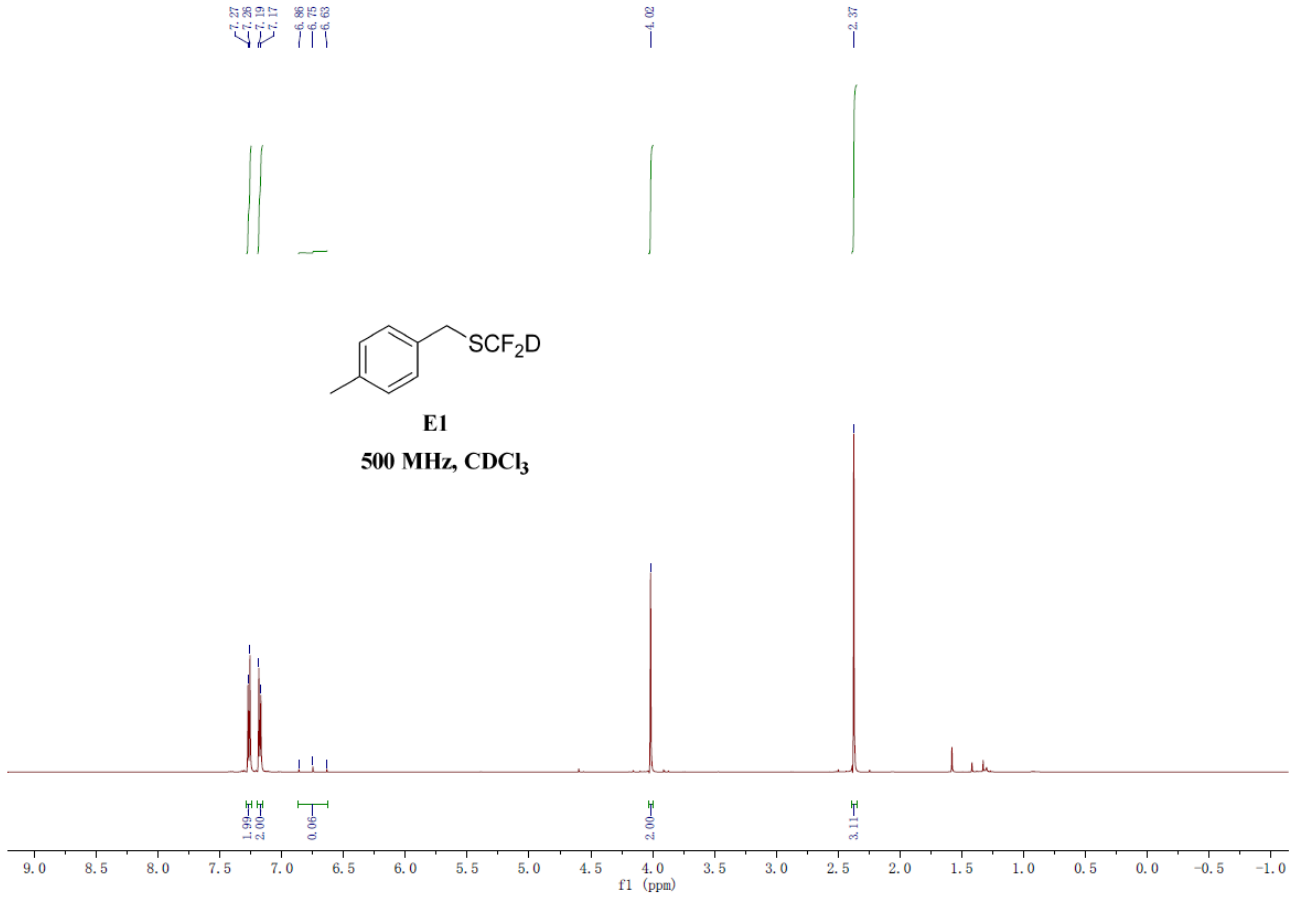
500 MHz, $CDCl_3$

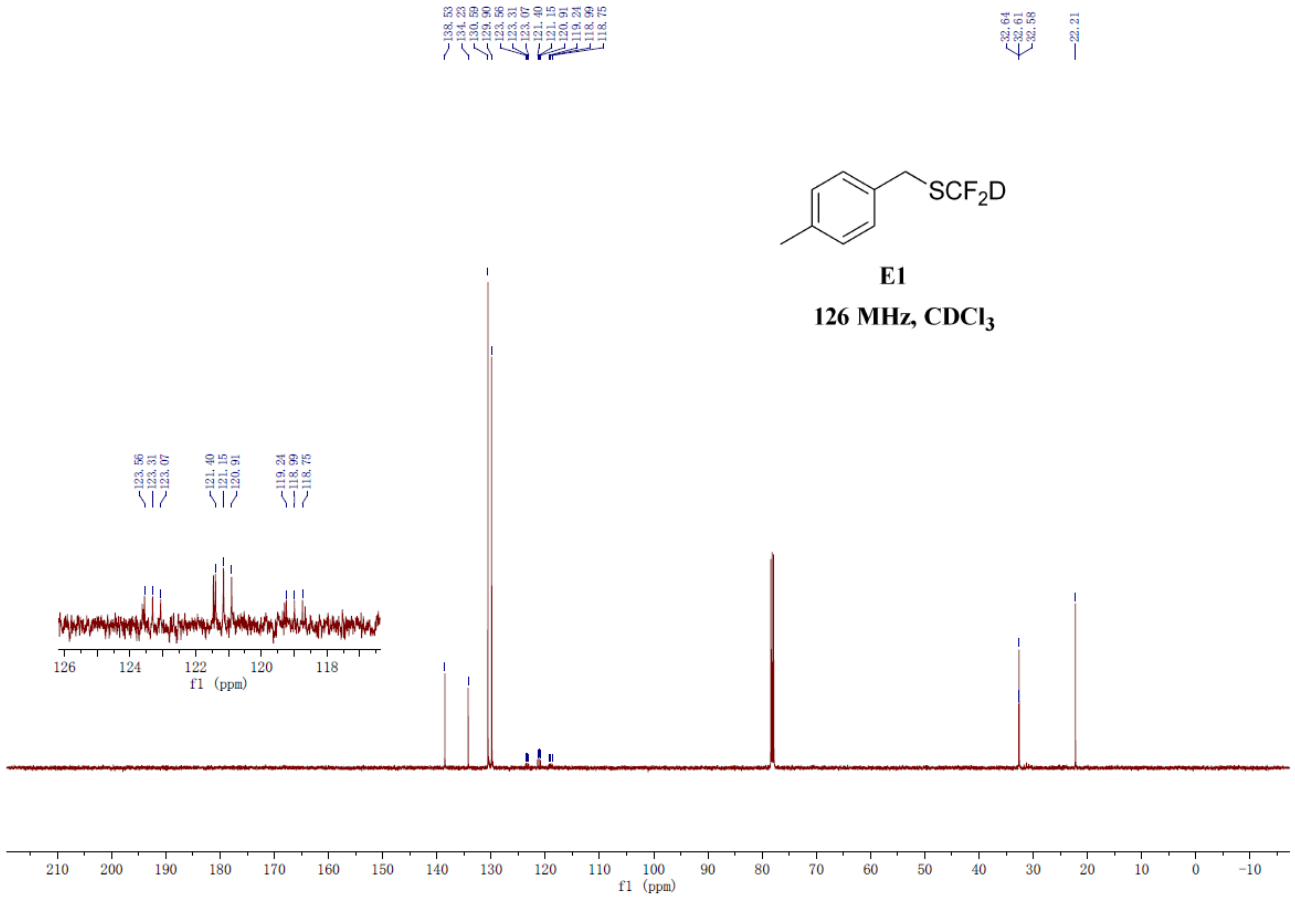


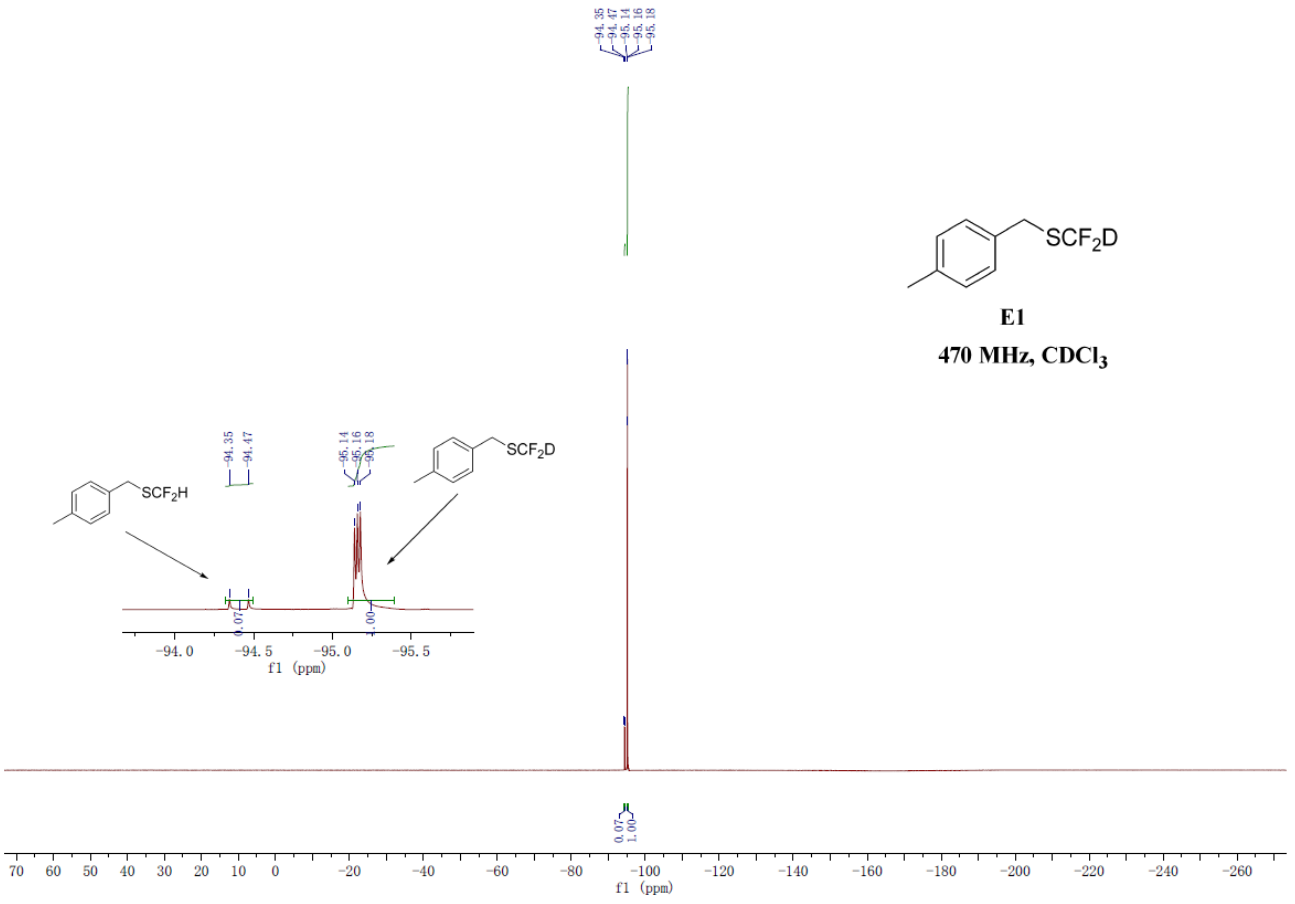
B33

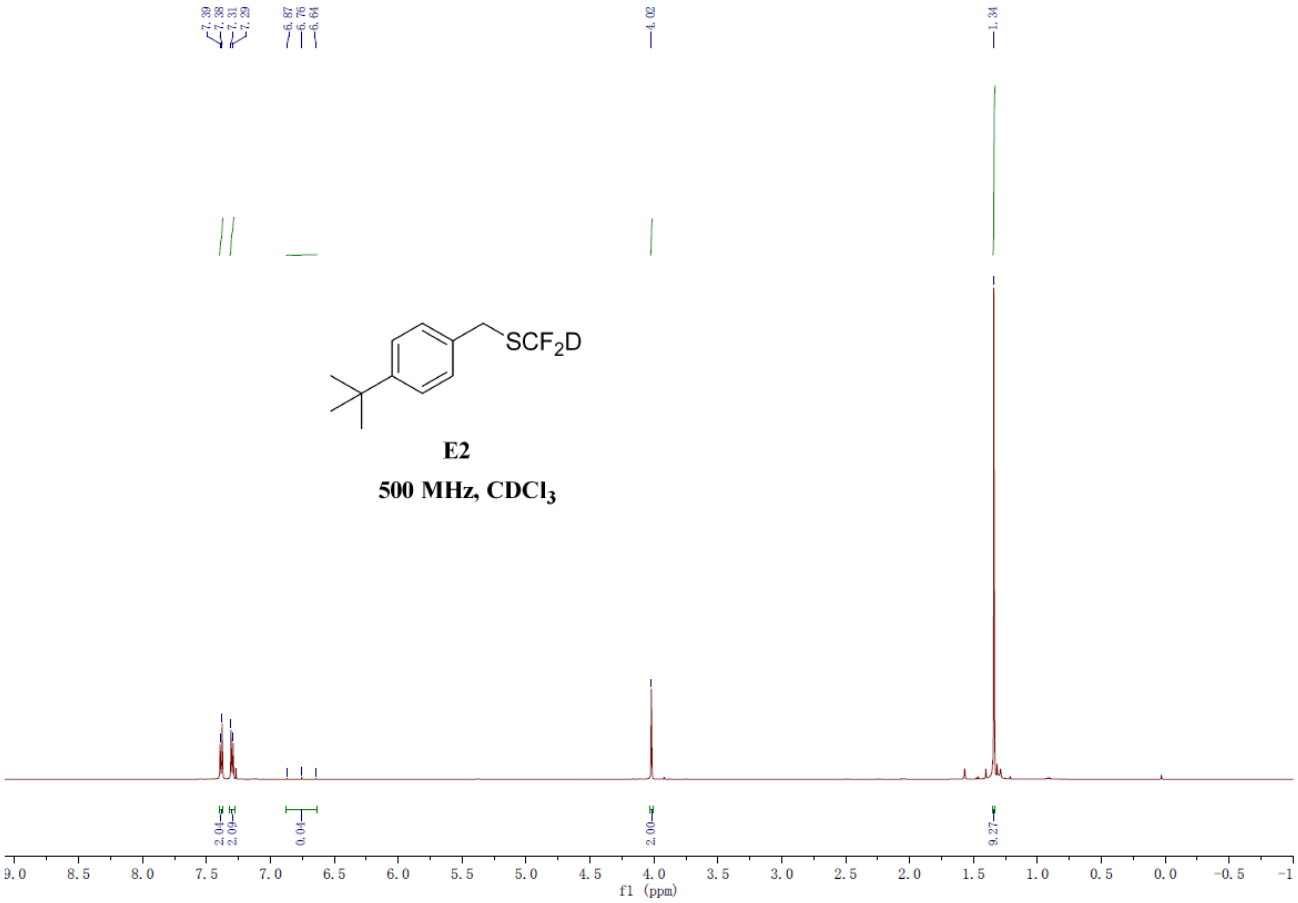
126 MHz, $CDCl_3$


-92.66
-92.78
SCF2H
B33
470 MHz, CDCl3
-91.5 -92.0 -92.5 -93.0 -93.5 -94.0
f1 (ppm)
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)


7.27
7.26
7.19
7.17
6.86
6.75
6.63
4.02
2.37
SCF2D
E1
500 MHz, CDCl3
1.99
2.00
0.06
2.00
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

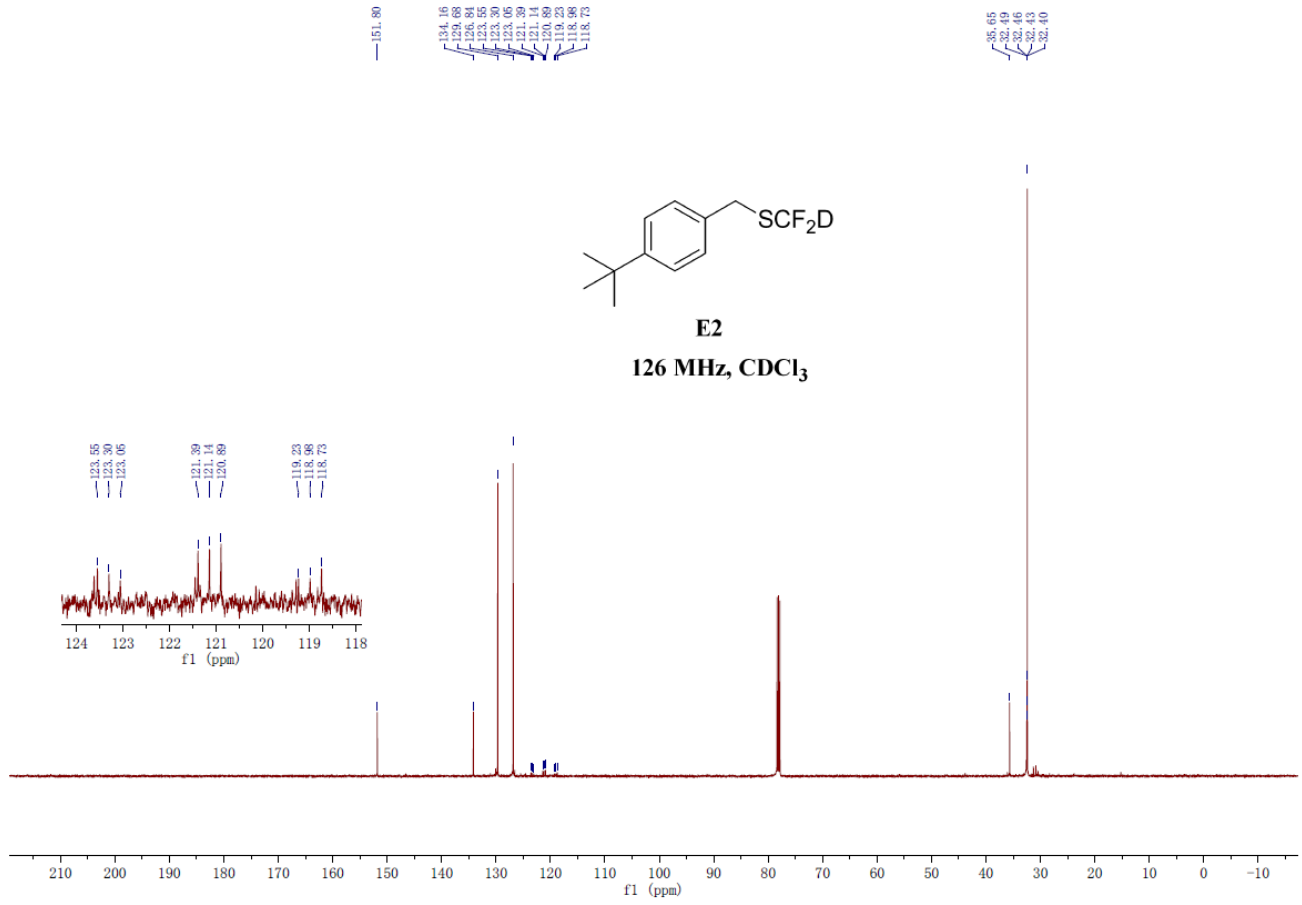

SCF2D
E1
126 MHz, CDCl3
f1 (ppm)


SCF2D
E1
470 MHz, CDCl3
SCF2H
f1 (ppm)



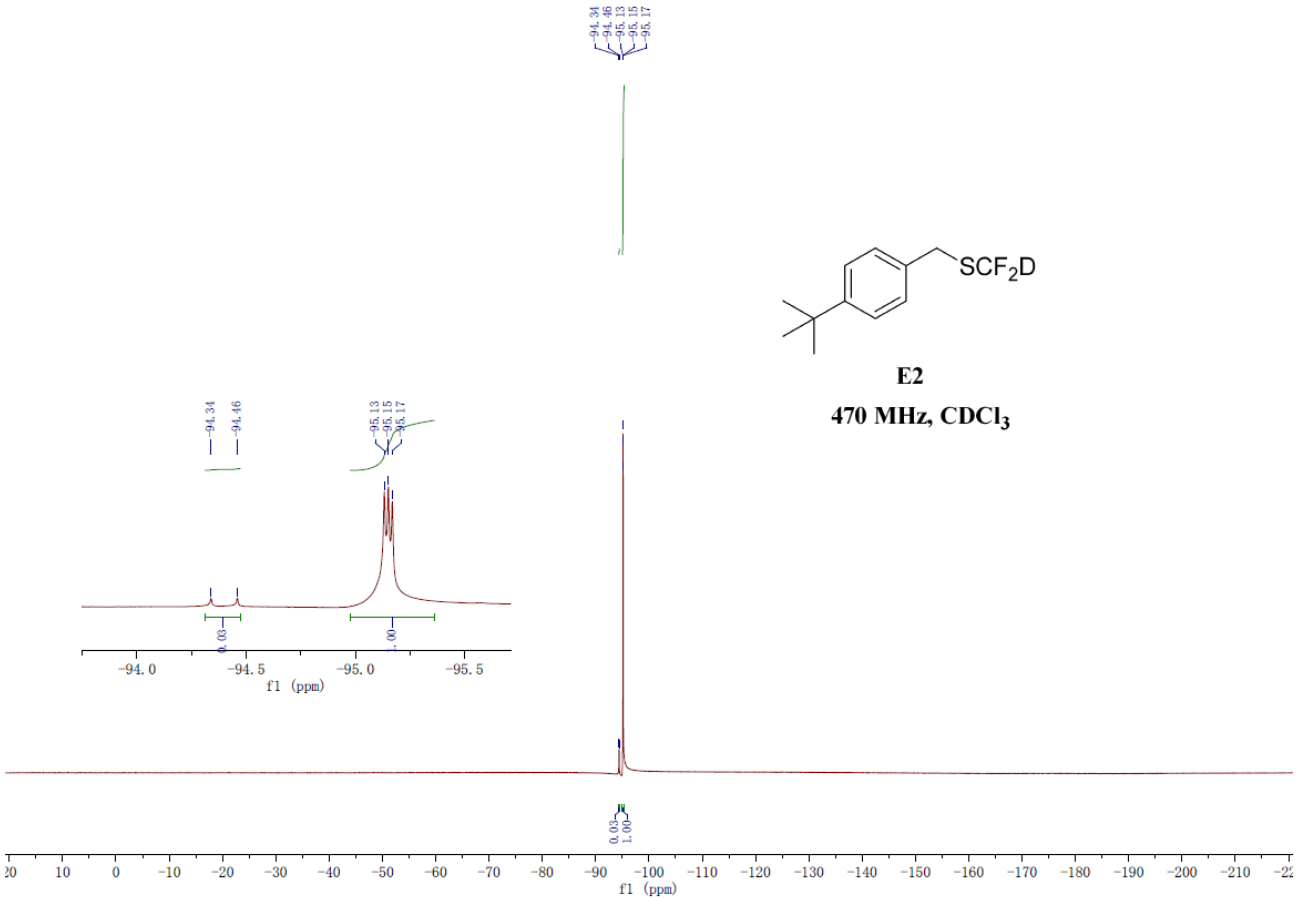
E2

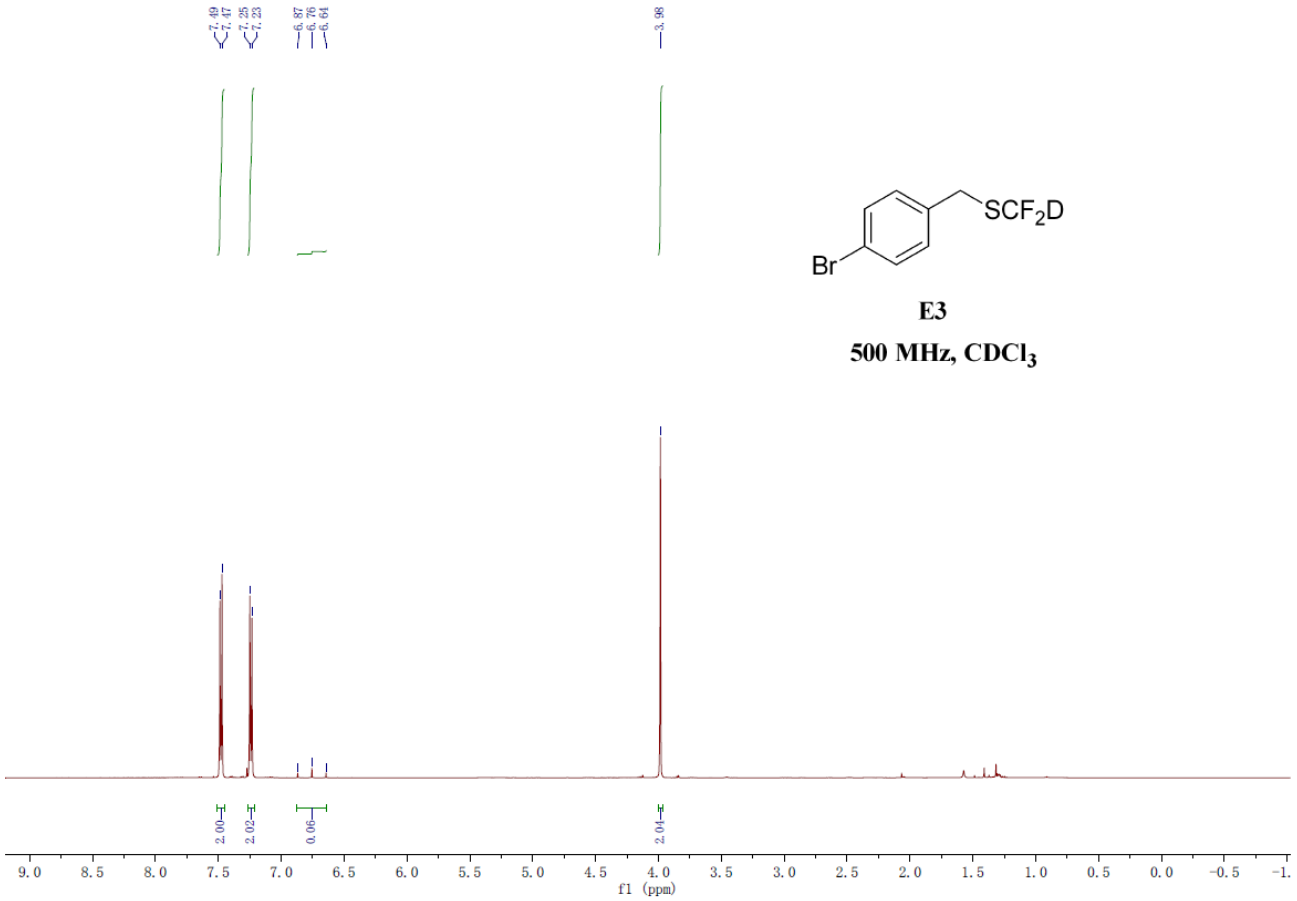
500 MHz, $CDCl_3$

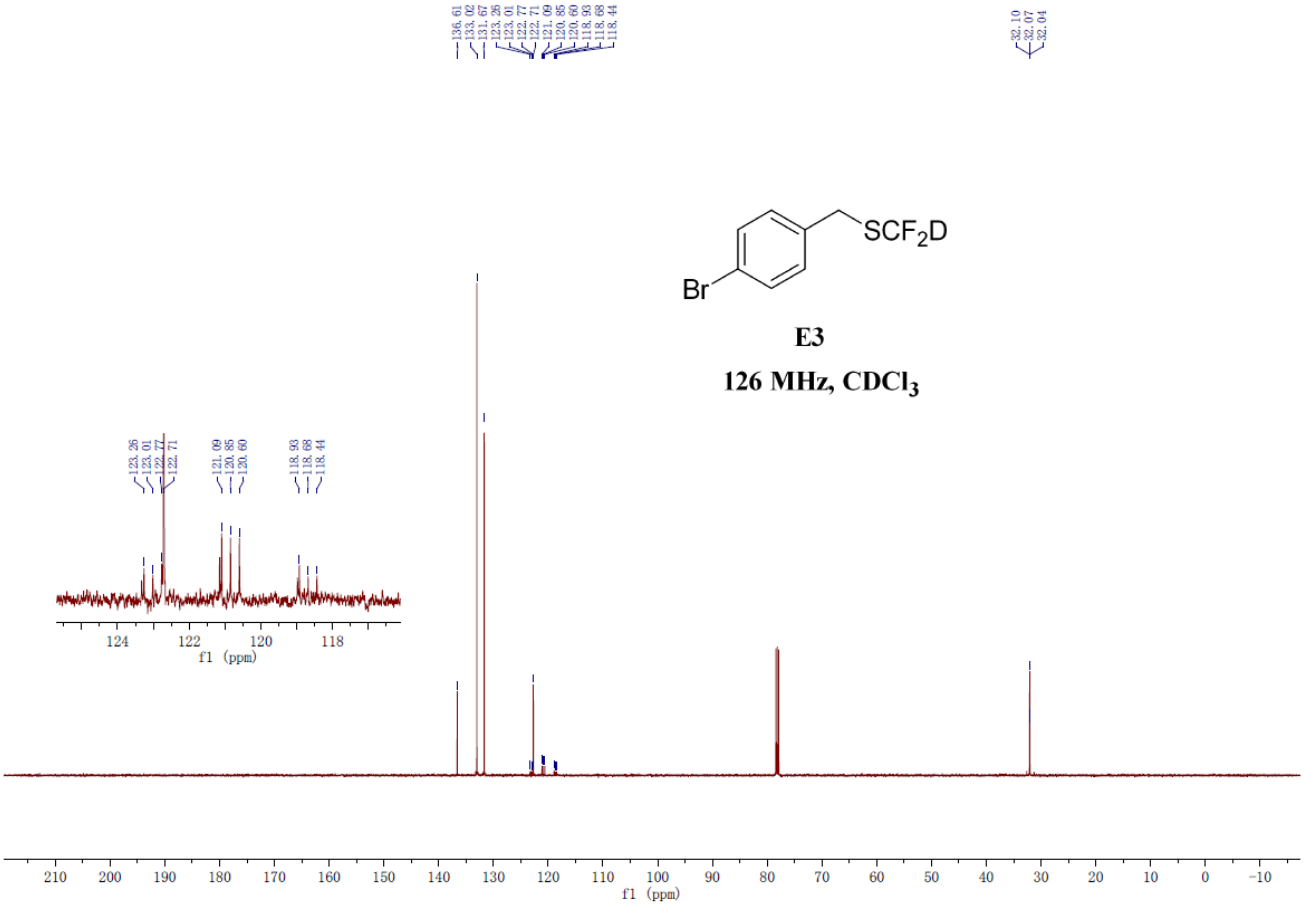


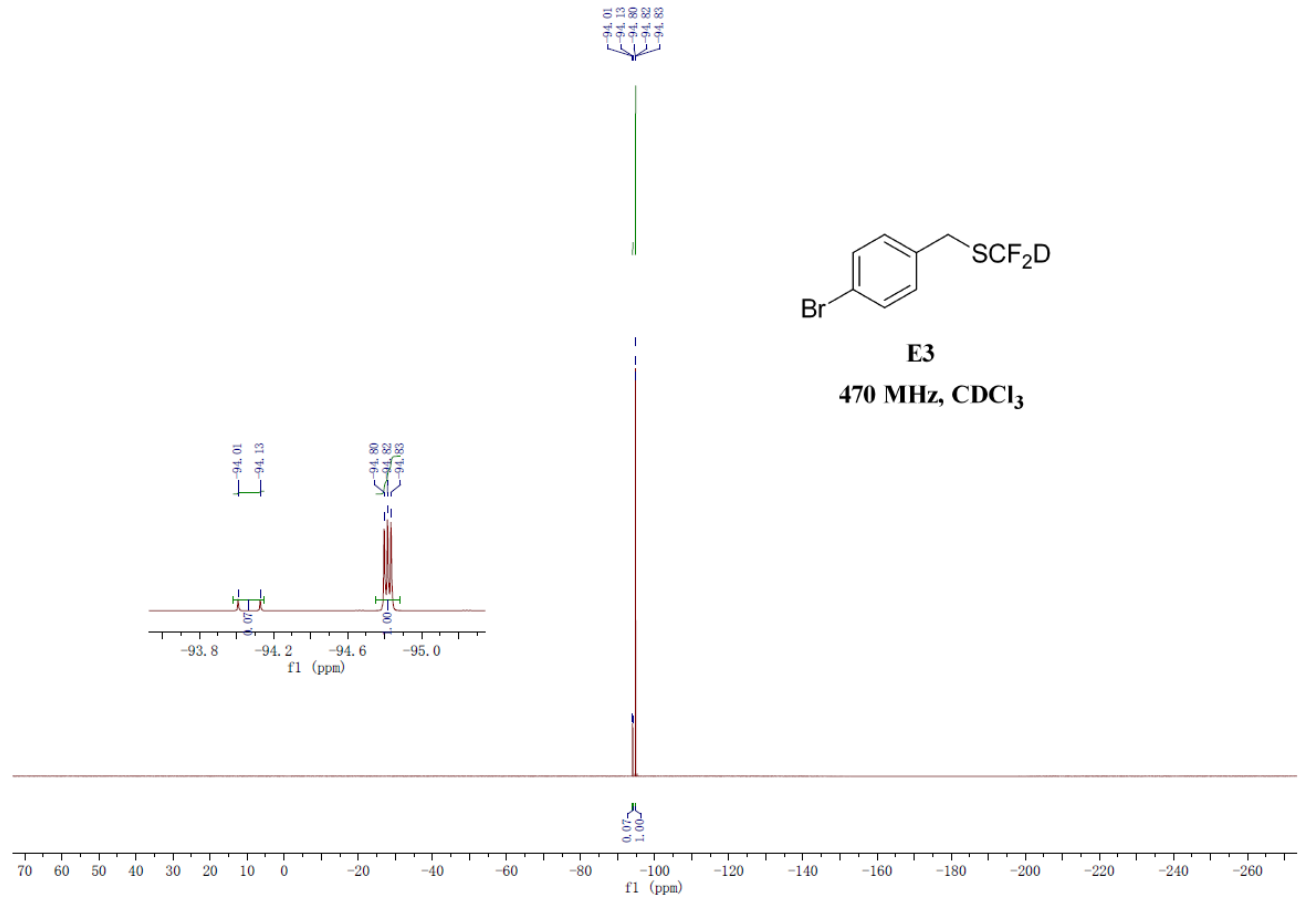
E2

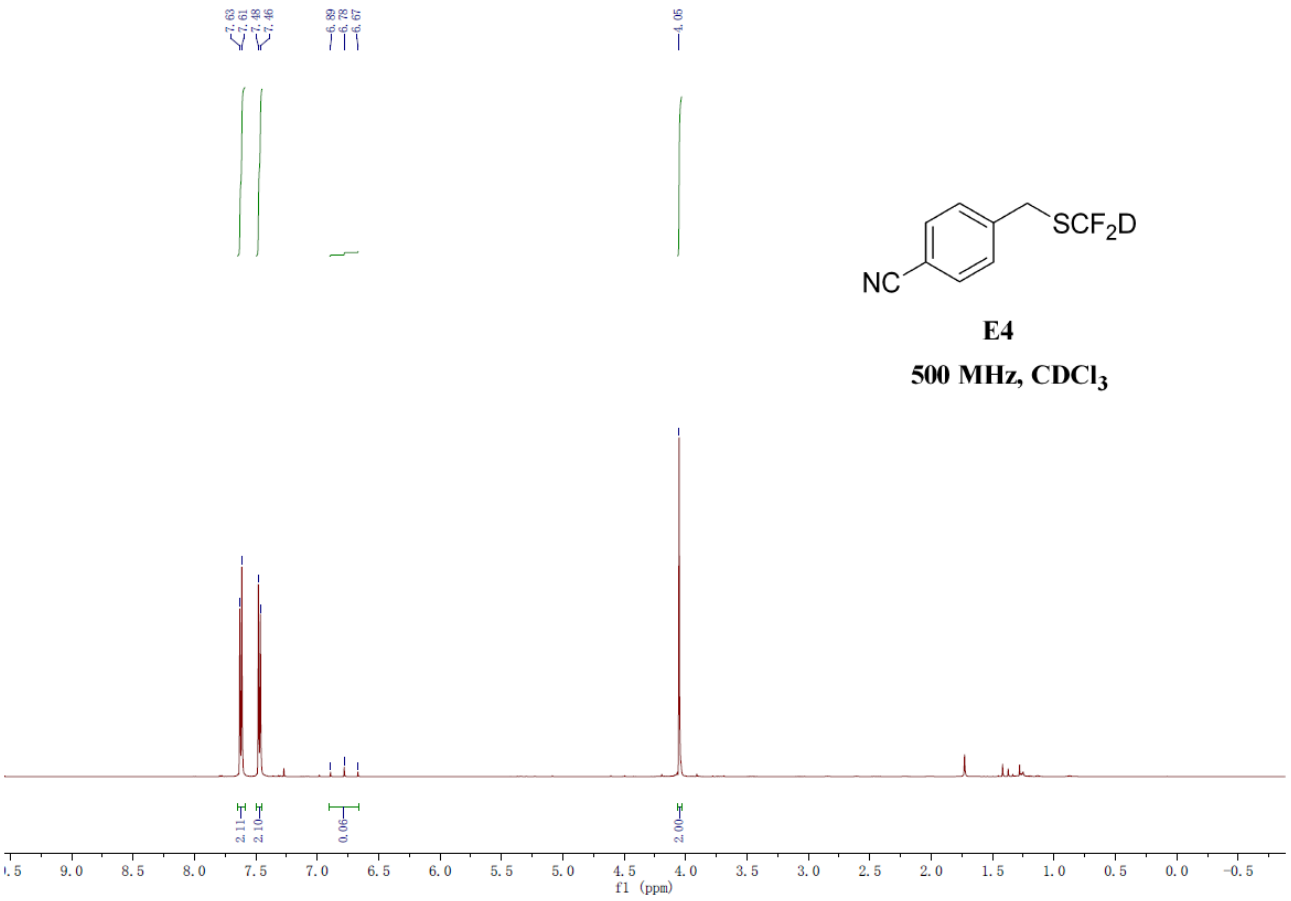
126 MHz, $CDCl_3$


-94.34
-94.46
-95.13
-95.15
-95.17
SCF2D
E2
470 MHz, CDCl3
0.03
1.00
-94.0
-94.5
-95.0
-95.5
f1 (ppm)
f1 (ppm)


7.49
7.47
7.25
7.23
6.87
6.76
6.64
3.98
SCF2D
Br
E3
500 MHz, CDCl3
2.00
2.02
0.06
2.04
f1 (ppm)

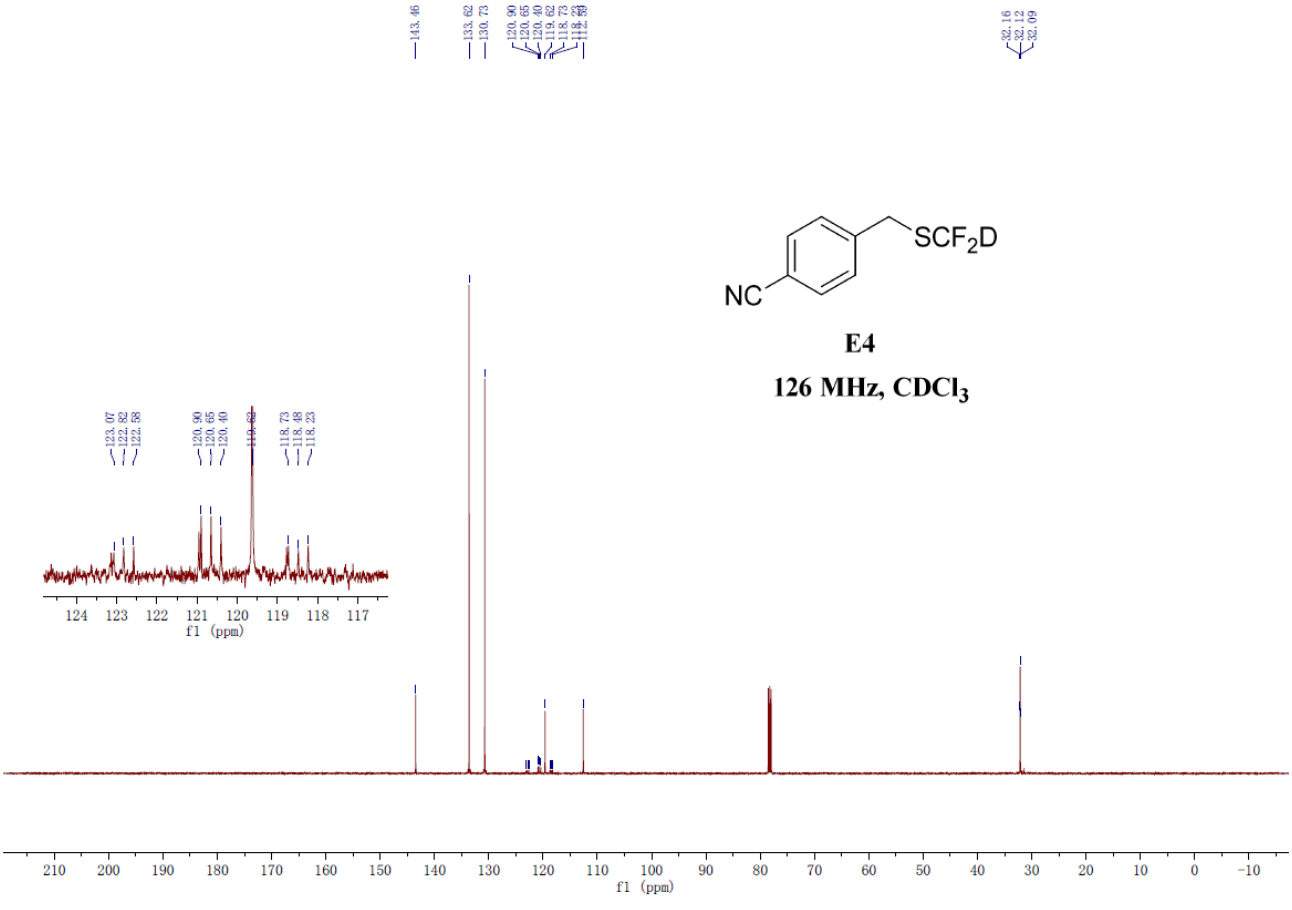

136.61
133.62
131.67
131.26
123.01
122.77
122.71
121.09
120.85
120.60
118.93
118.68
118.44
32.19
32.07
32.04
SCF2D
Br
E3
126 MHz, CDCl3
123.26
123.01
122.77
122.71
121.09
120.85
120.60
118.93
118.68
118.44
124
122
120
118
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-94.01
-94.13
-94.80
-94.82
-94.83
SCF2D
Br
E3
470 MHz, CDCl3
-94.01
-94.13
-94.80
-94.82
-94.83
0.07
1.00
-93.8
-94.2
-94.6
-95.0
f1 (ppm)
0.07
1.00
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)



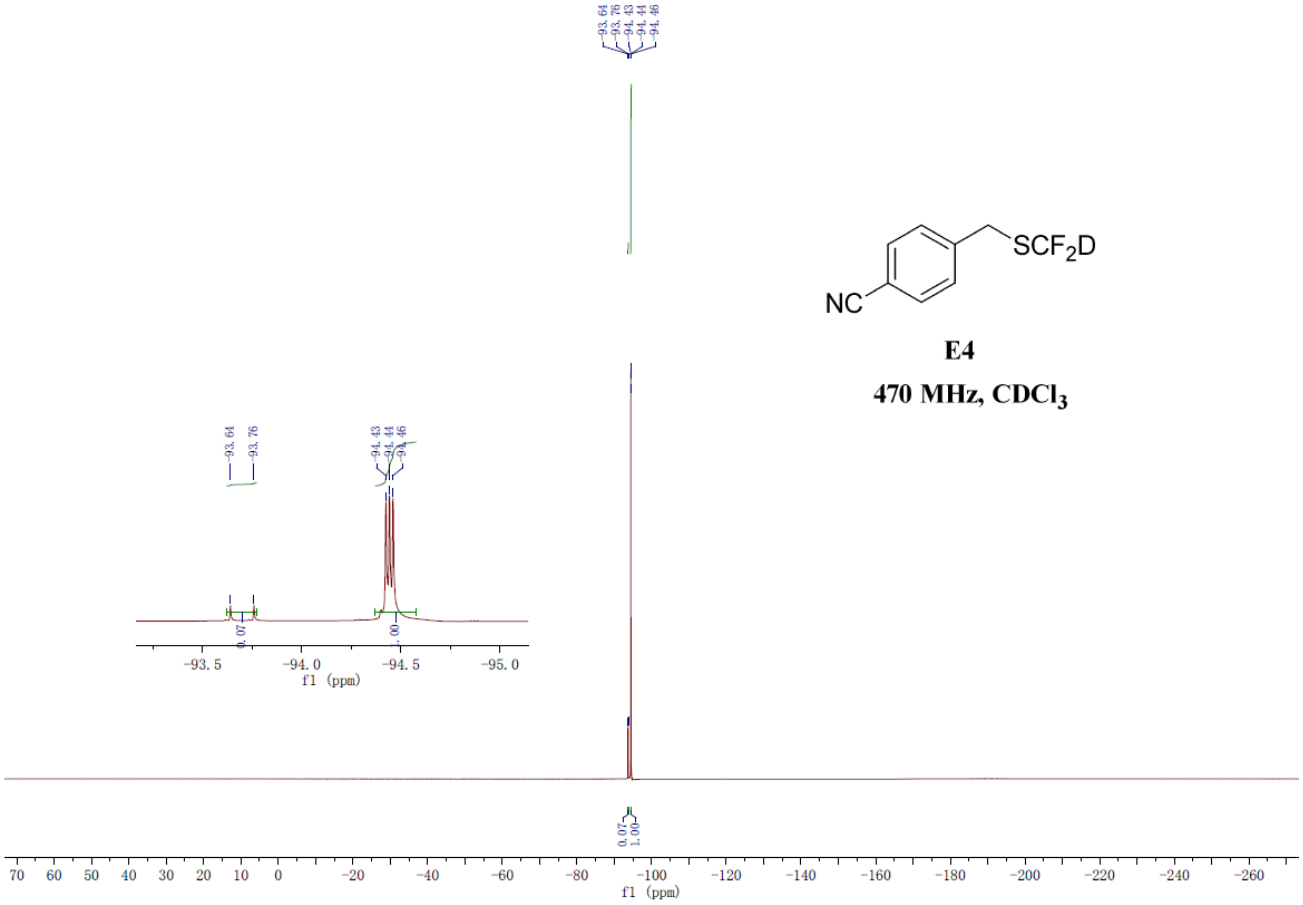
E4

500 MHz, $CDCl_3$



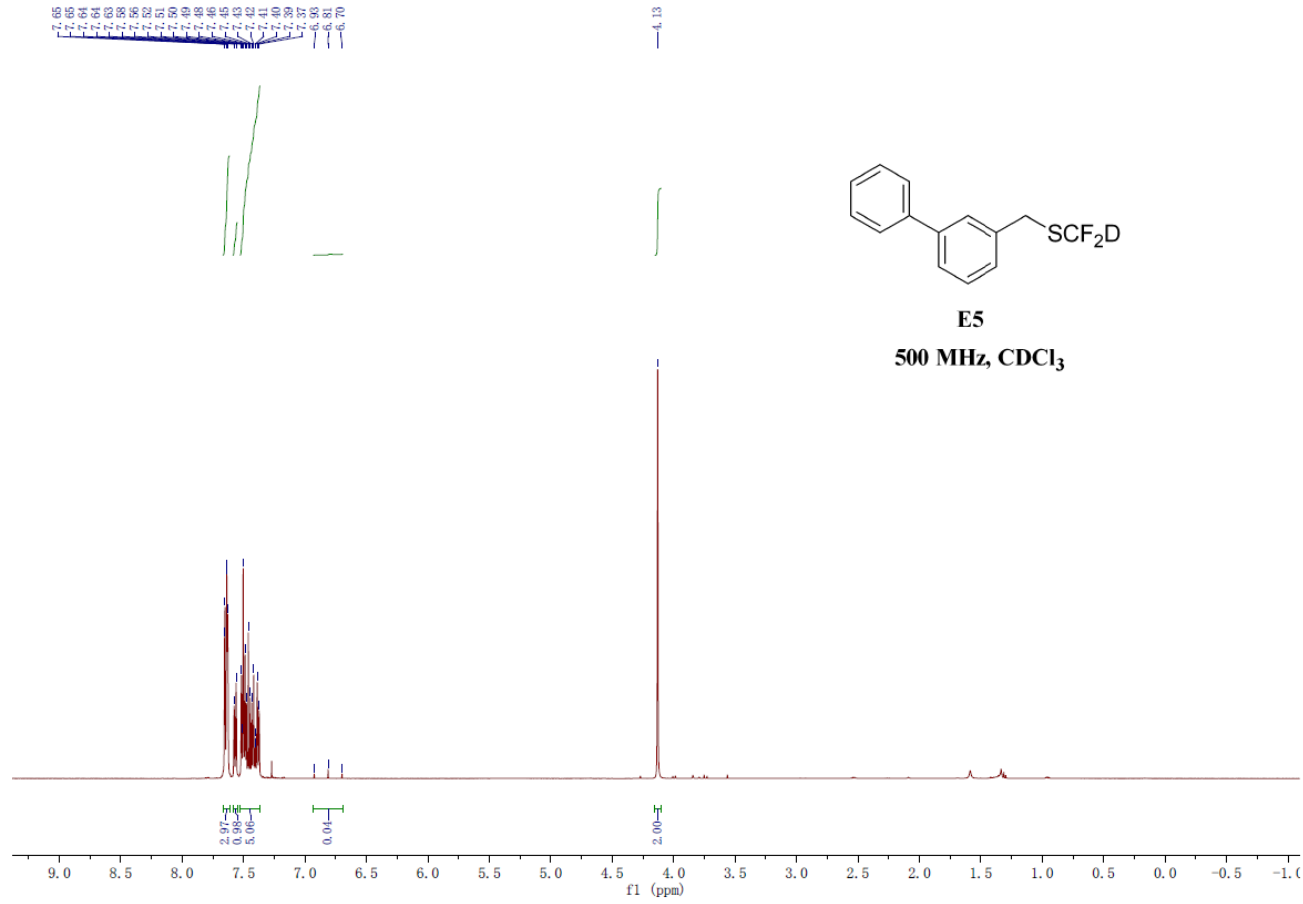
E4

126 MHz, $CDCl_3$



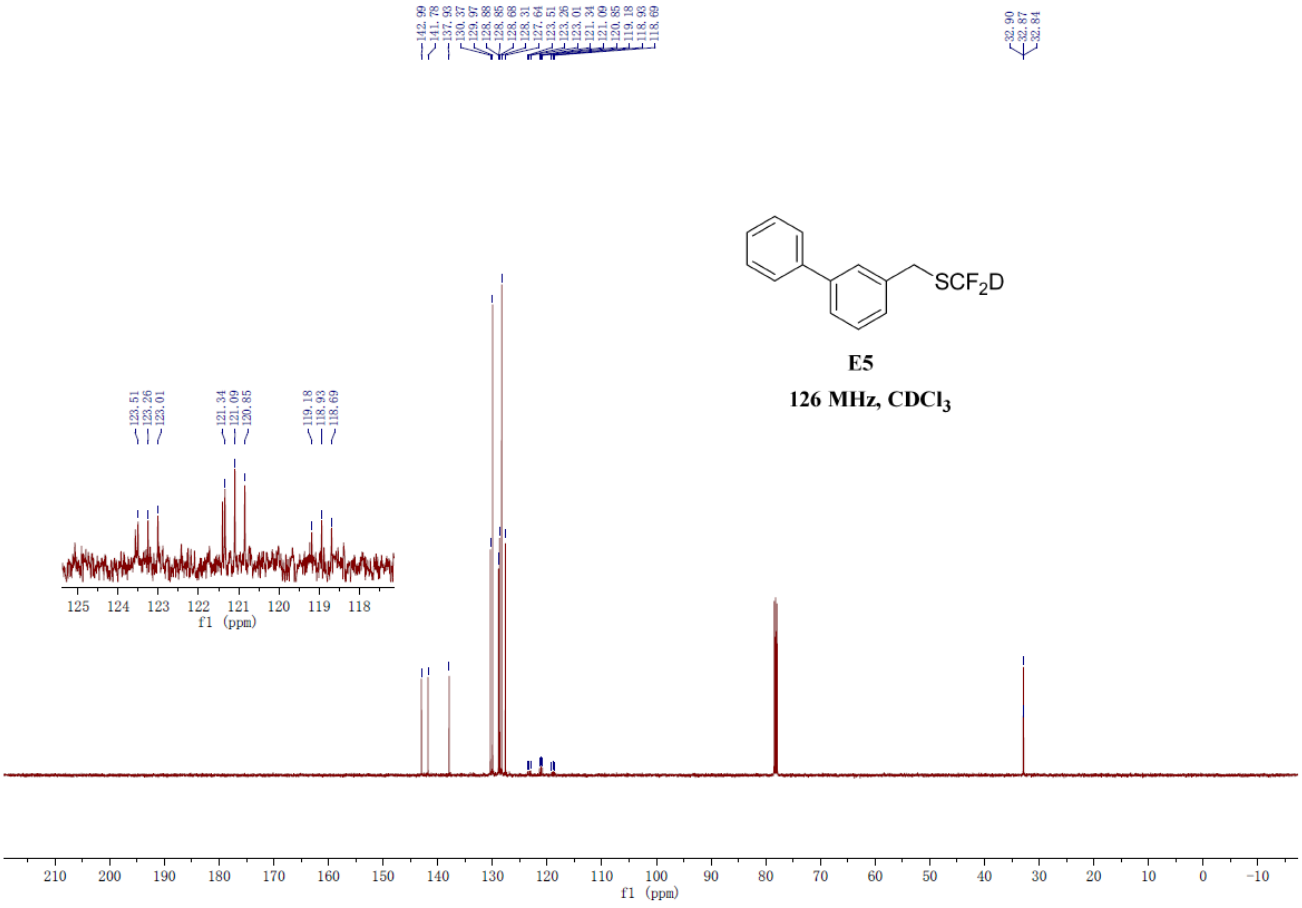
E4

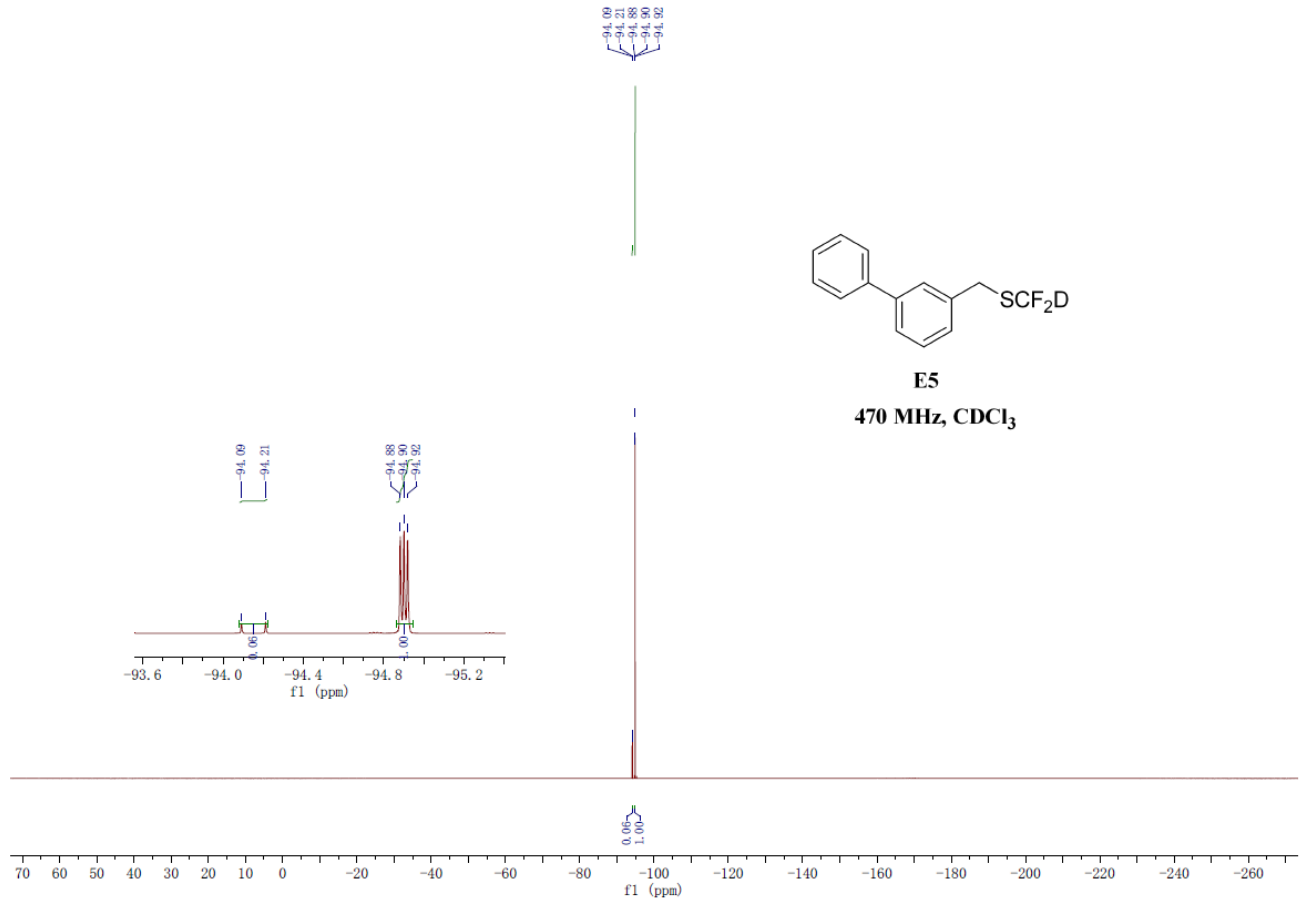
470 MHz, $CDCl_3$

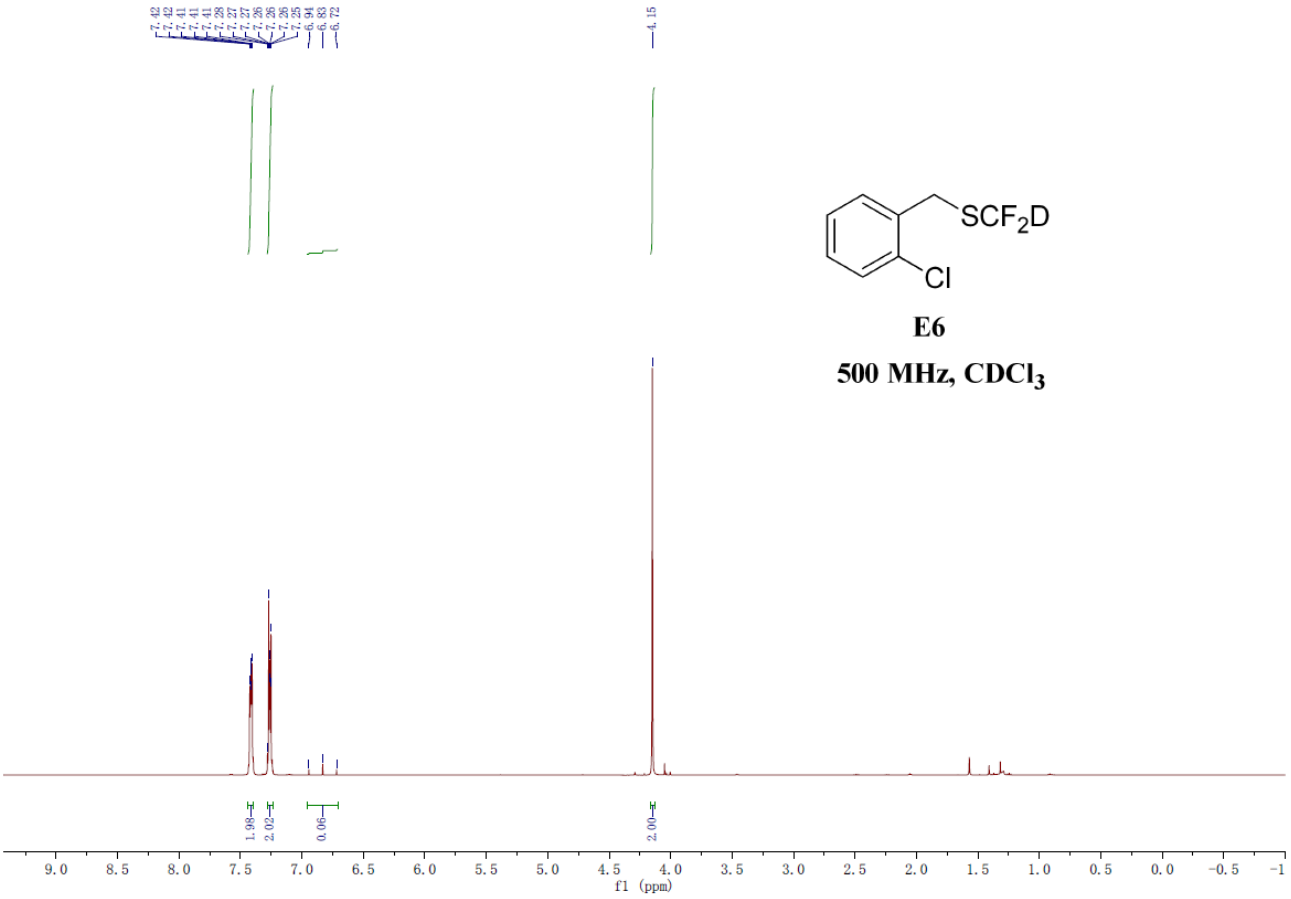


E5

500 MHz, $CDCl_3$

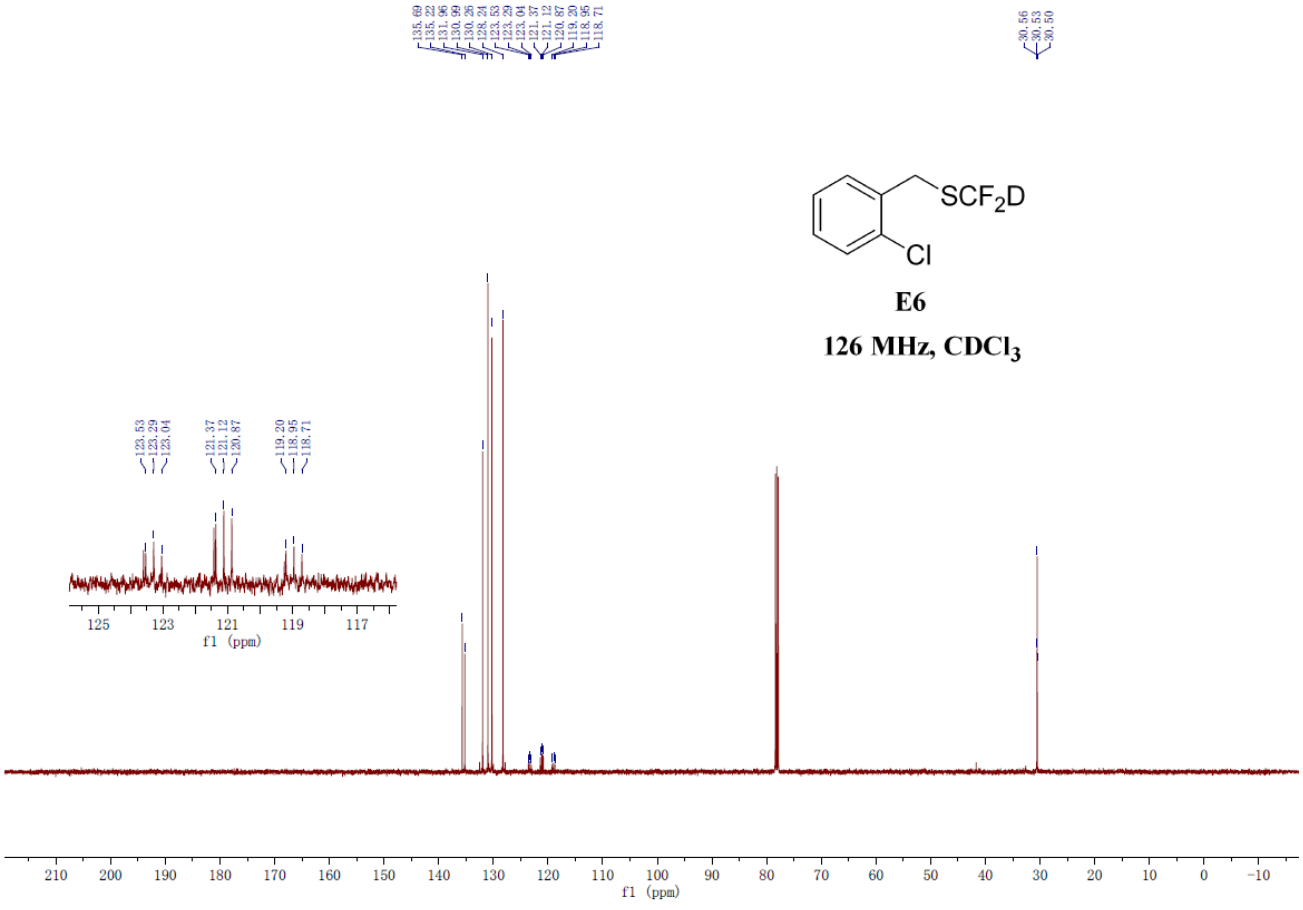

142.99
141.78
137.93
130.57
129.97
128.88
128.85
128.68
128.31
127.64
123.51
123.26
123.01
121.34
121.09
120.85
119.18
118.93
118.69
32.90
32.87
32.84
SCF2D
E5
126 MHz, CDCl3
f1 (ppm)


-94.09
-94.21
-94.88
-94.90
-94.92
SCF2D
E5
470 MHz, CDCl3
0.06
1.00
f1 (ppm)



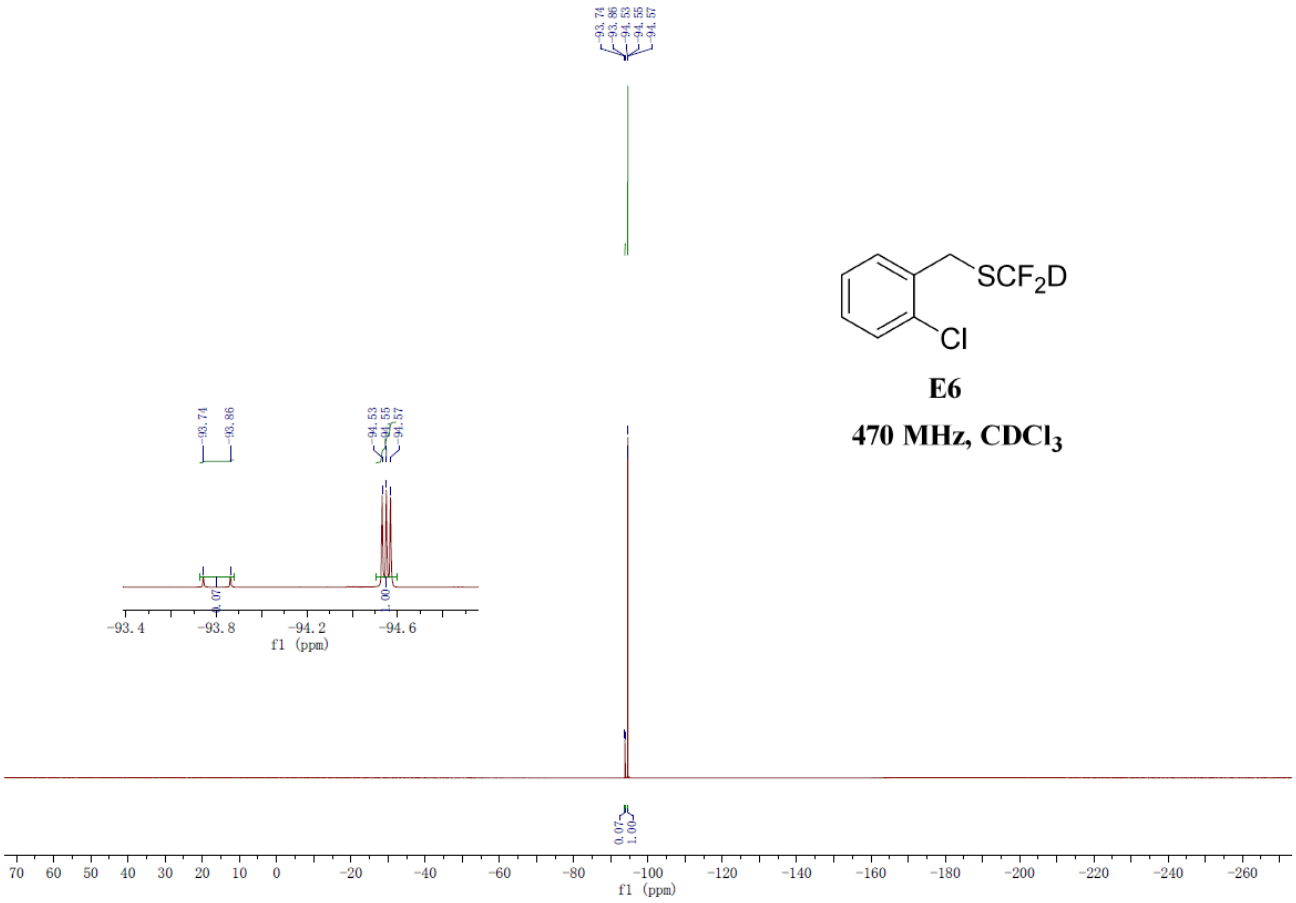
E6

500 MHz, $CDCl_3$



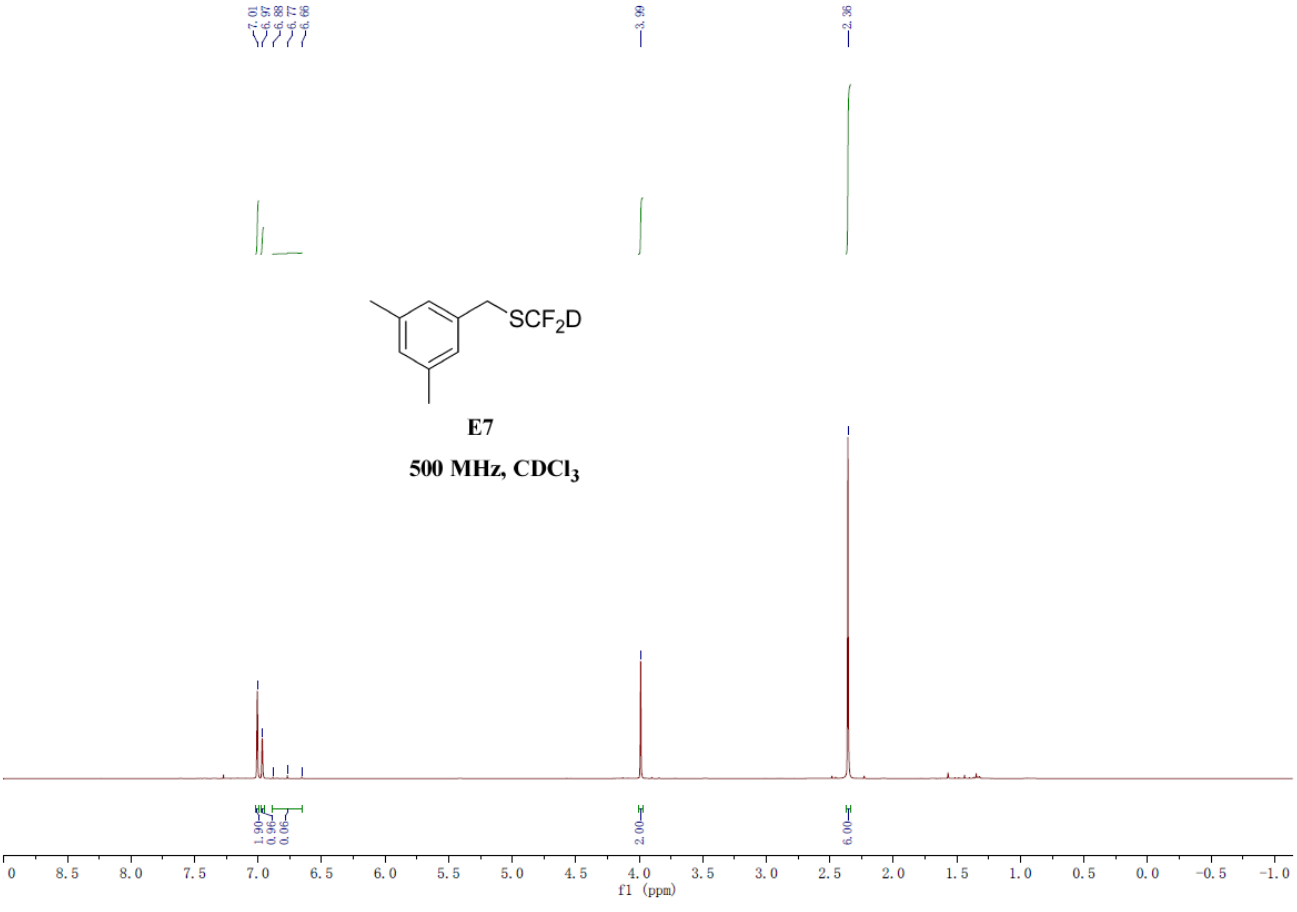
E6

126 MHz, $CDCl_3$



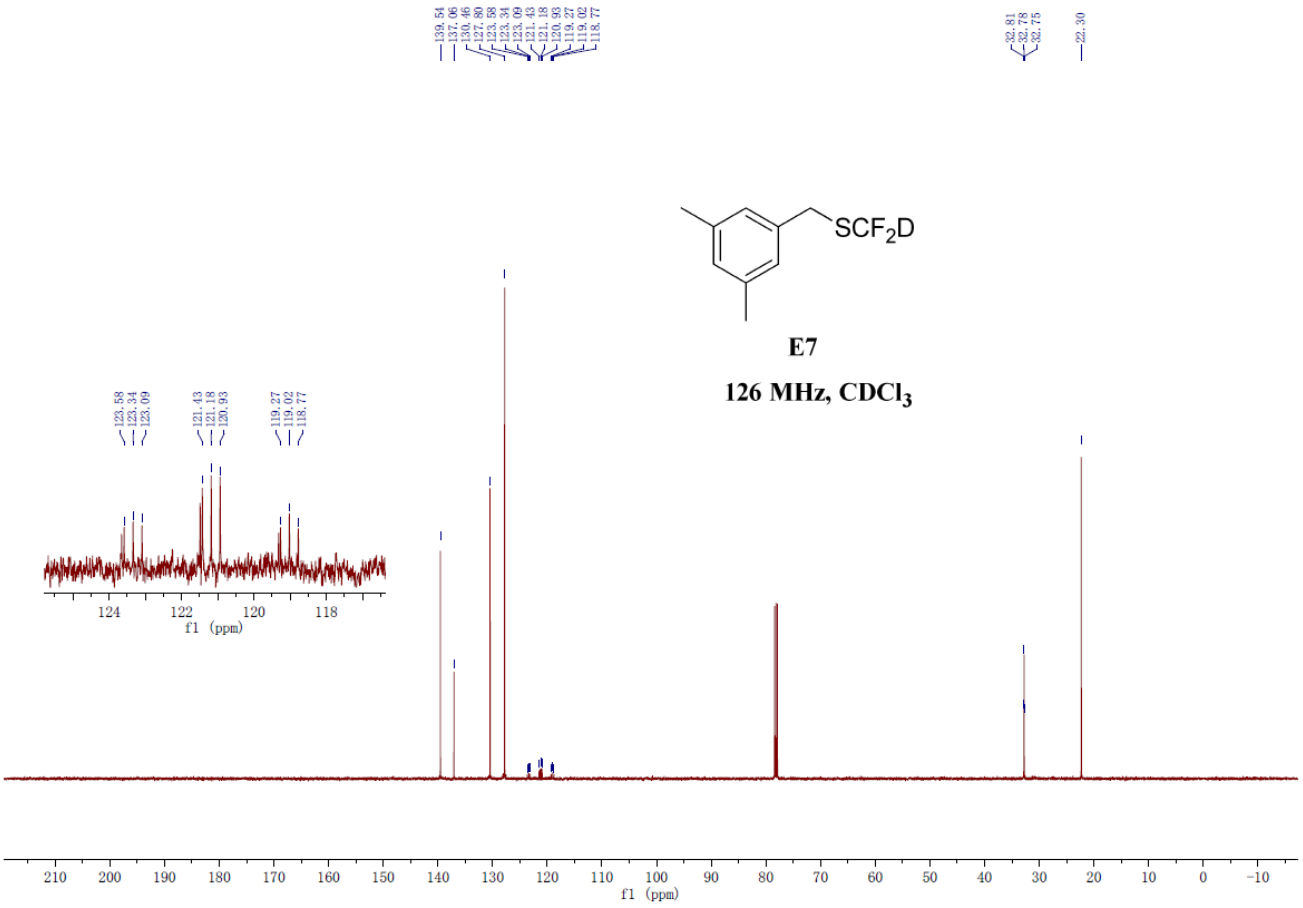
E6

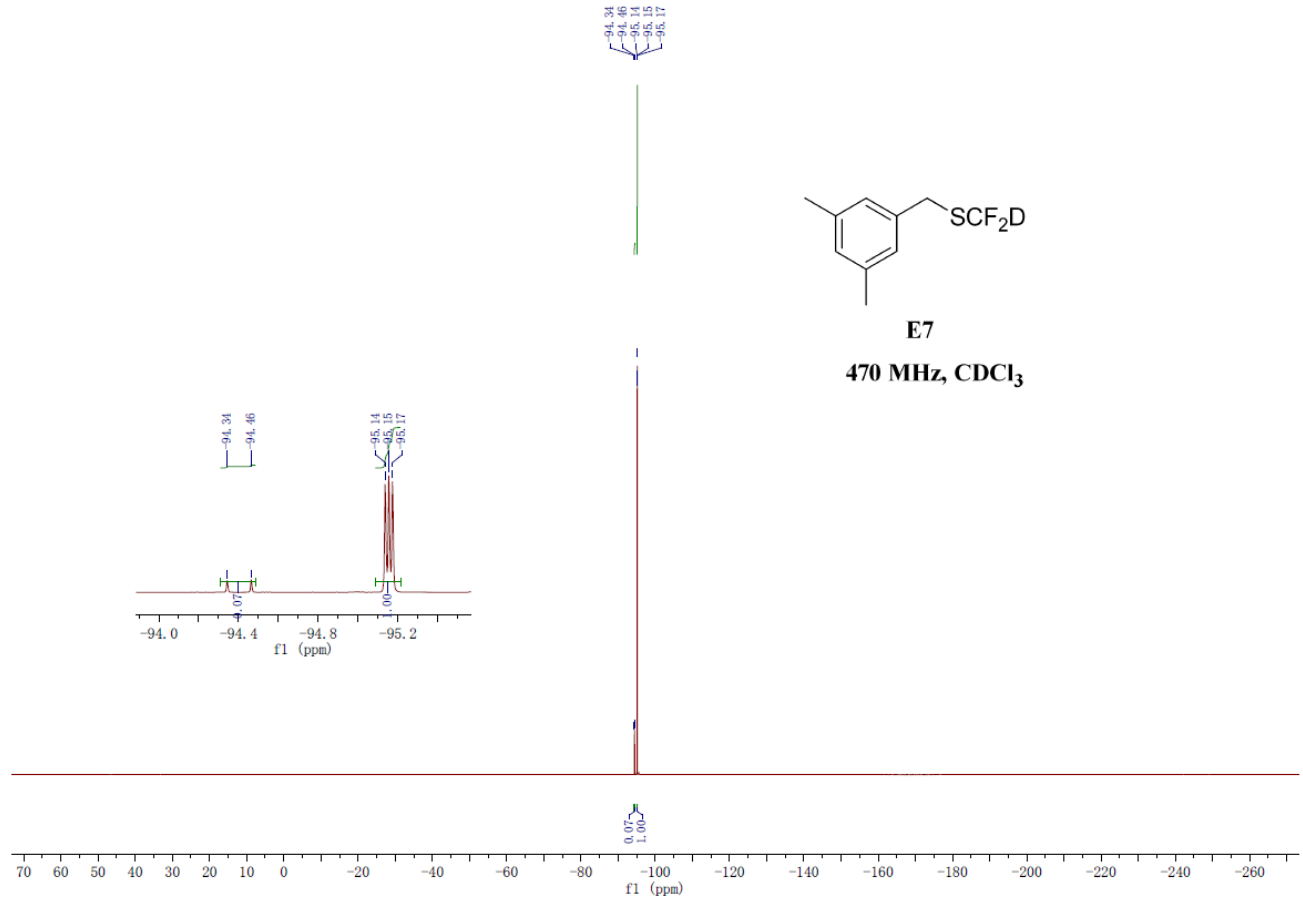
470 MHz, $CDCl_3$

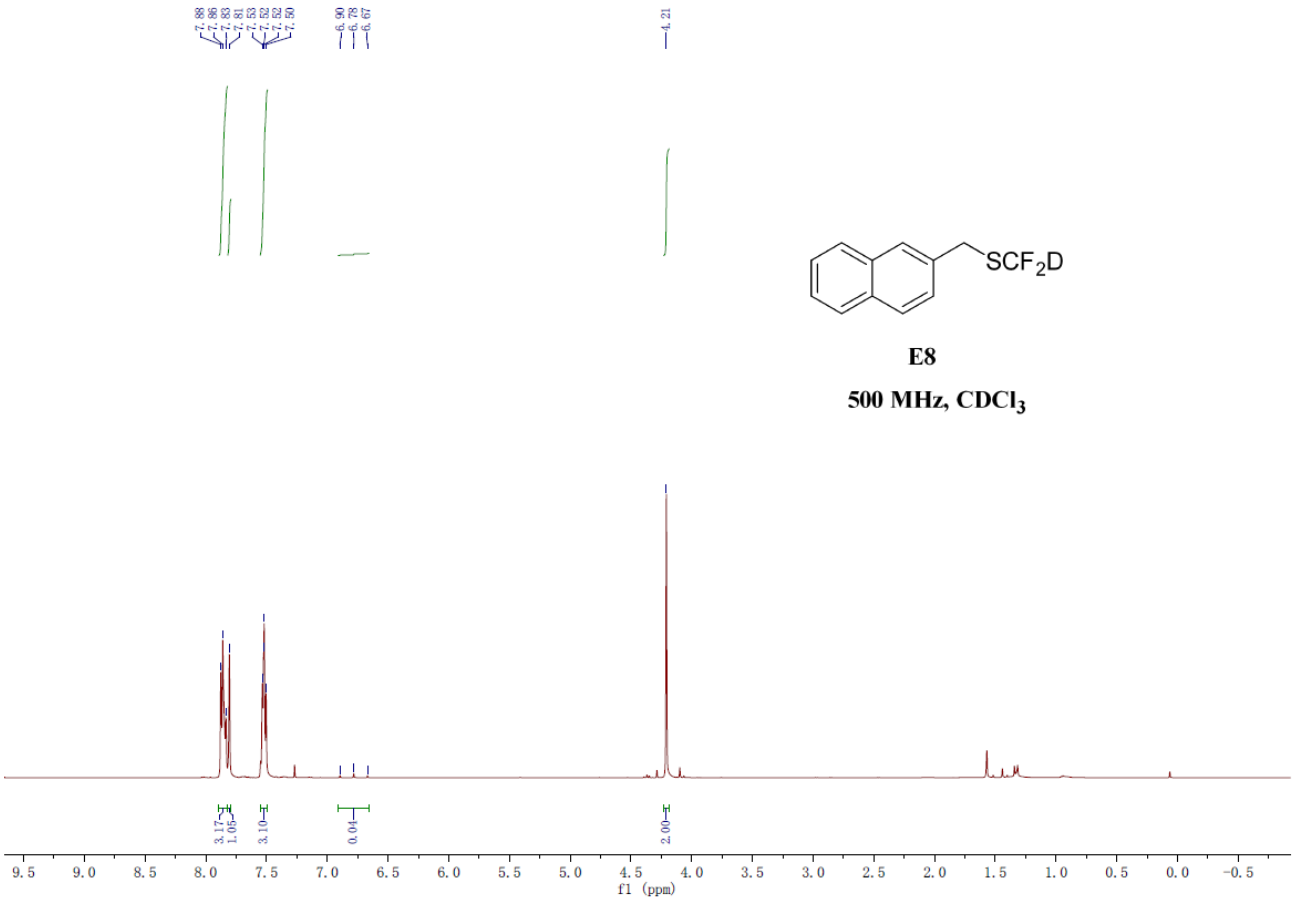


E7

500 MHz, $CDCl_3$

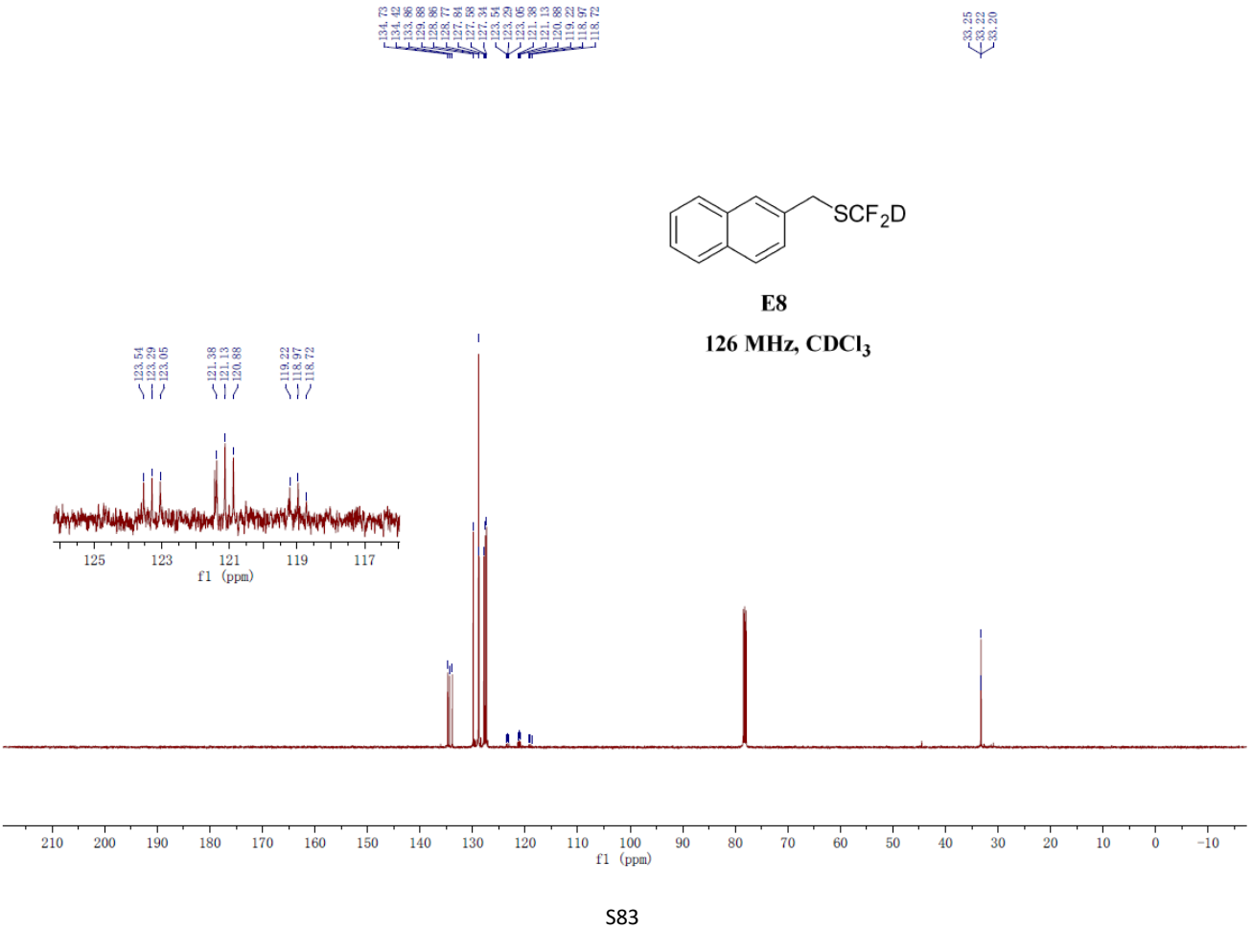

139.54
137.06
130.46
127.80
123.58
123.34
123.09
121.43
121.18
120.93
119.27
119.02
118.77
32.81
32.78
32.75
22.30
SCF2D
E7
126 MHz, CDCl3
123.58
123.34
123.09
121.43
121.18
120.93
119.27
119.02
118.77
124
122
120
118
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-94.34
-94.46
-95.14
-95.15
-95.17
SCF2D
E7
470 MHz, CDCl3
-94.34
-94.46
-95.14
-95.15
-95.17
4.07
1.00
-94.0
-94.4
-94.8
-95.2
f1 (ppm)
0.07
1.00
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)



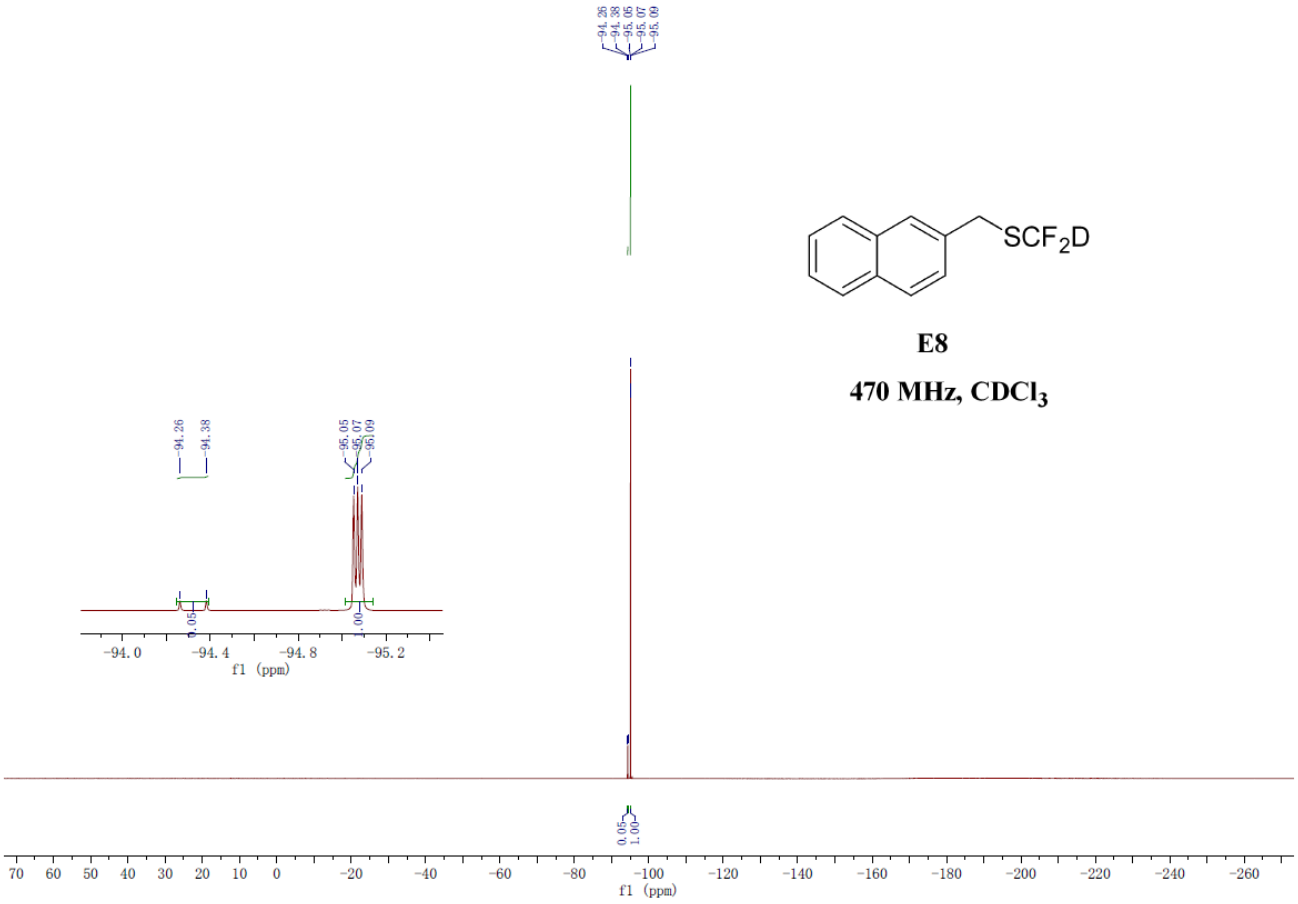
E8

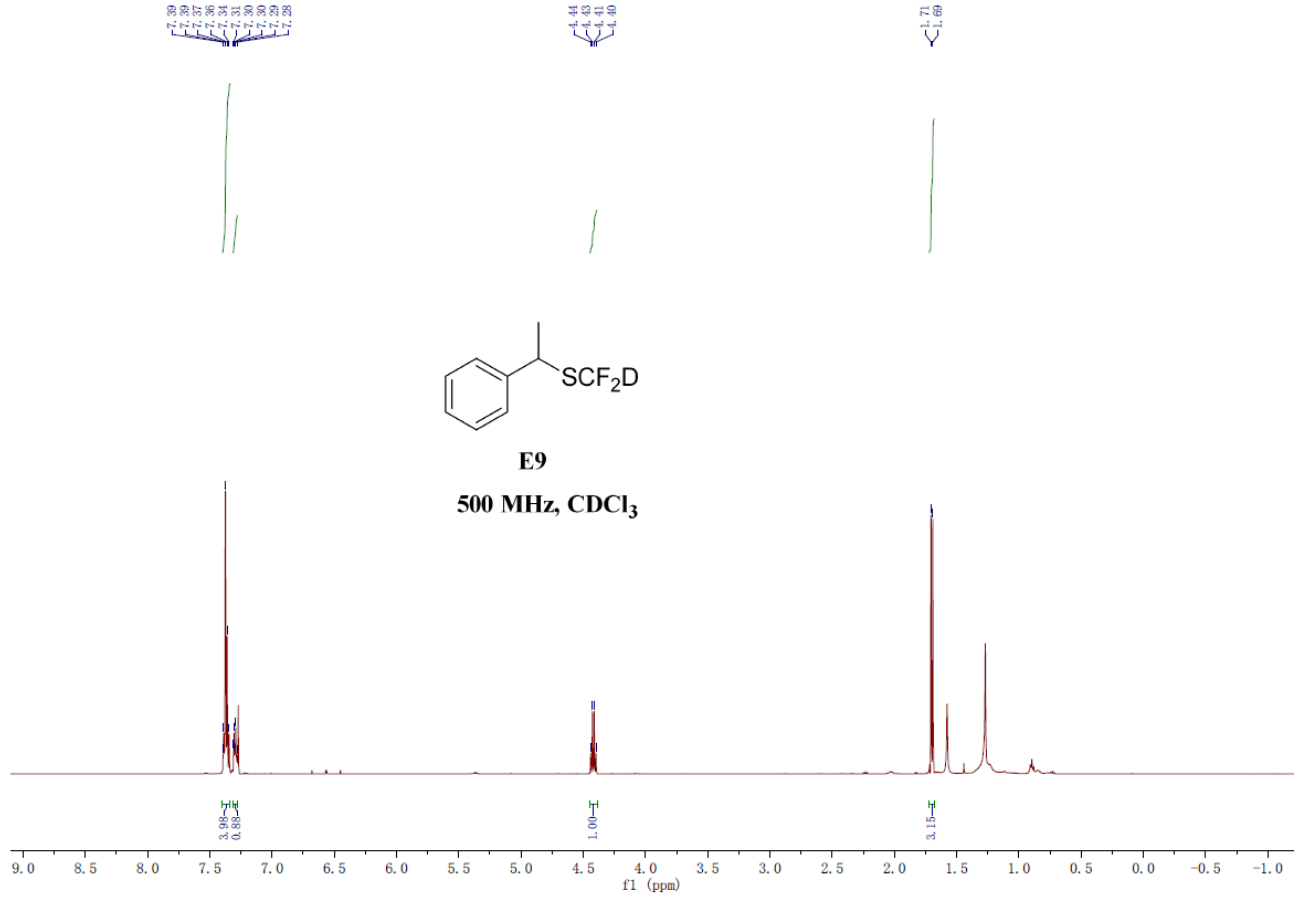
500 MHz, $CDCl_3$

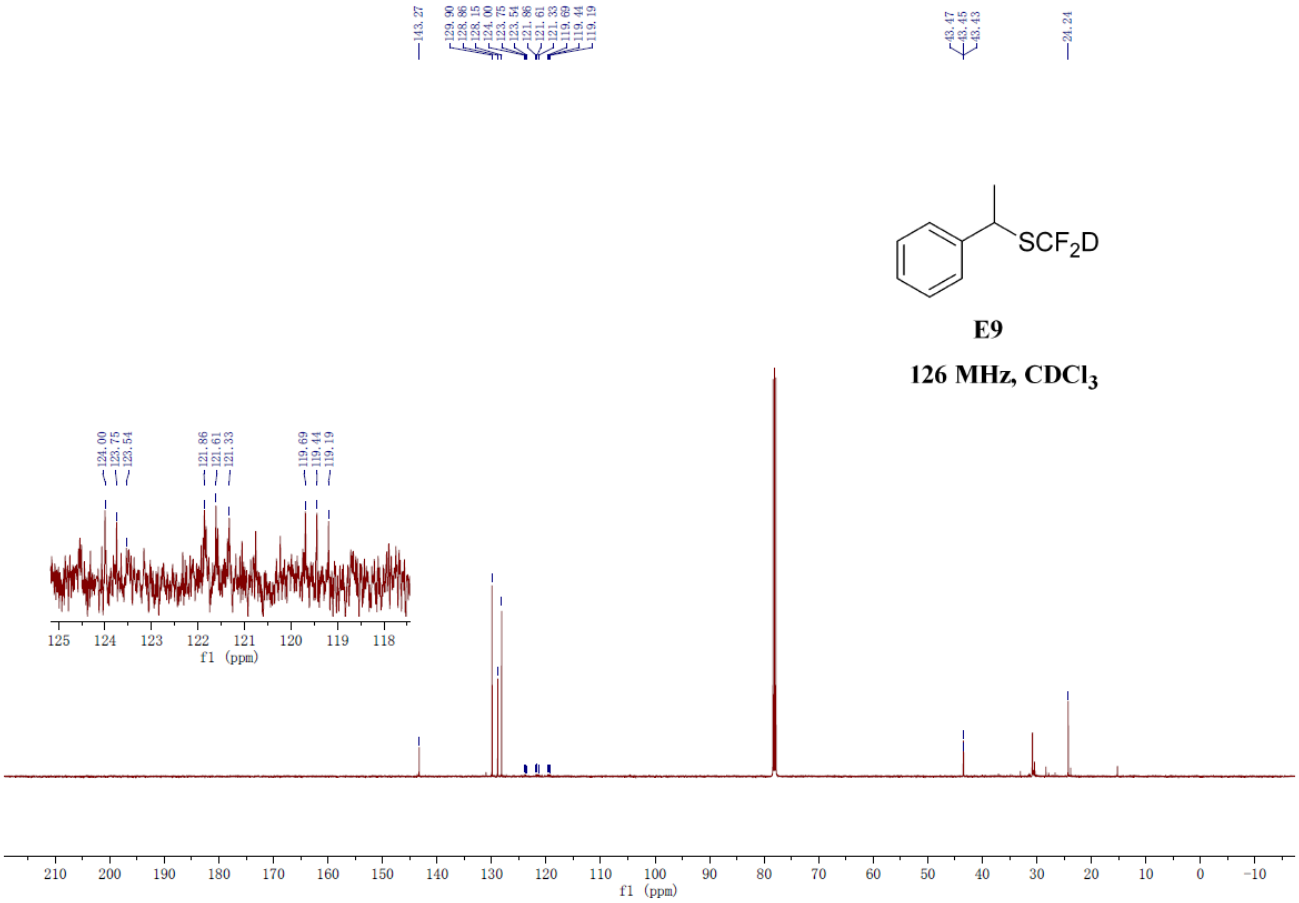


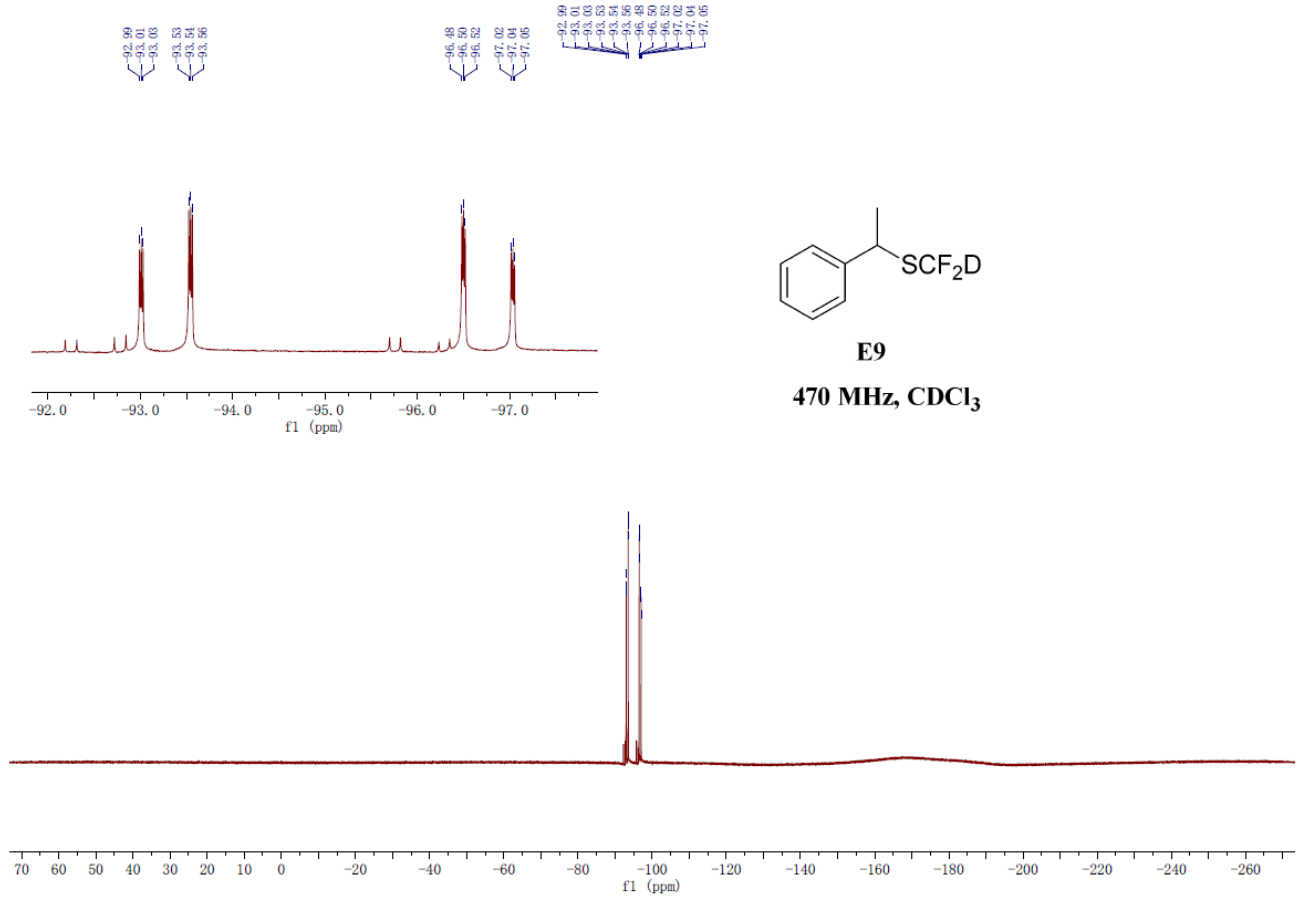
E8

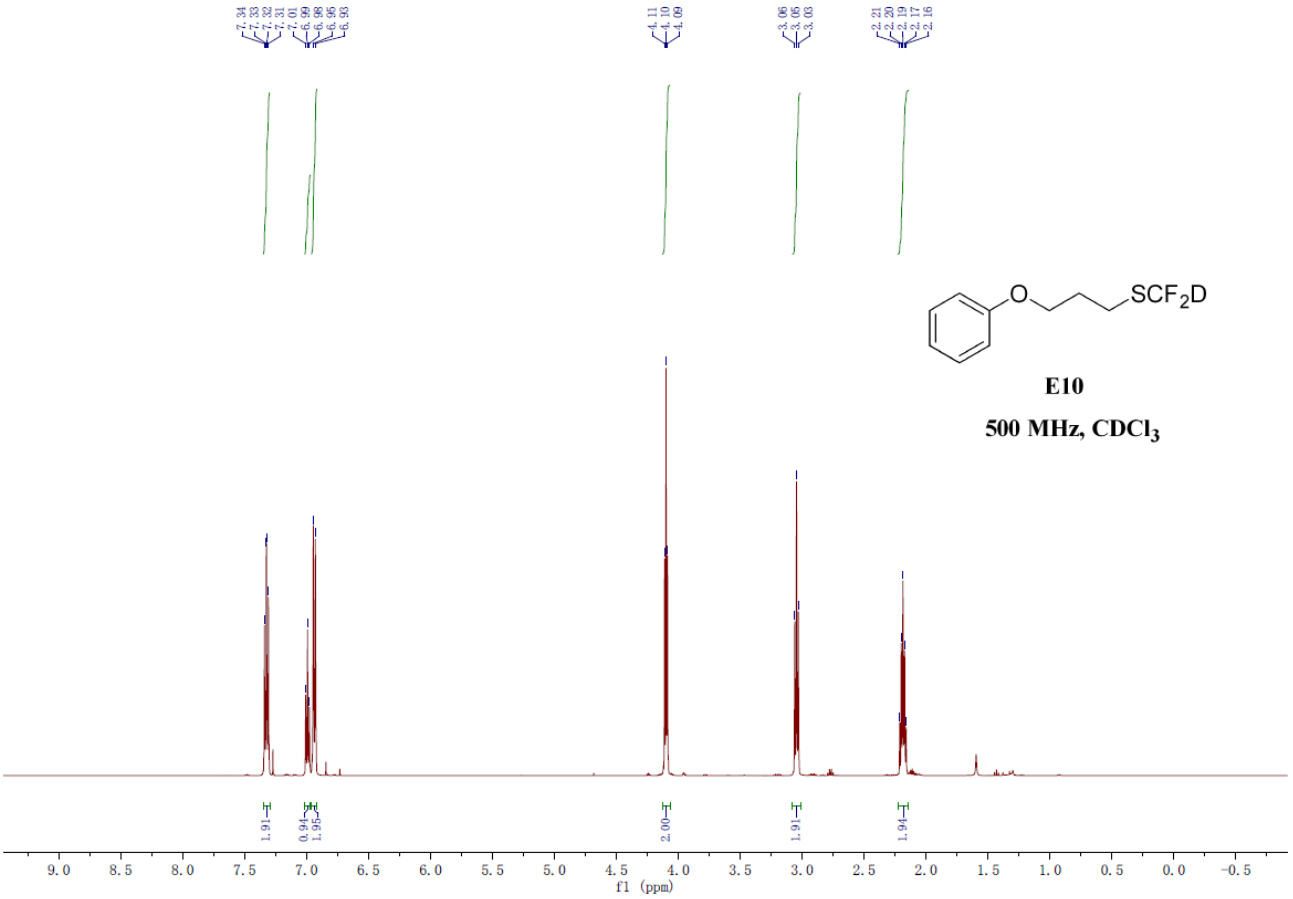
126 MHz, $CDCl_3$

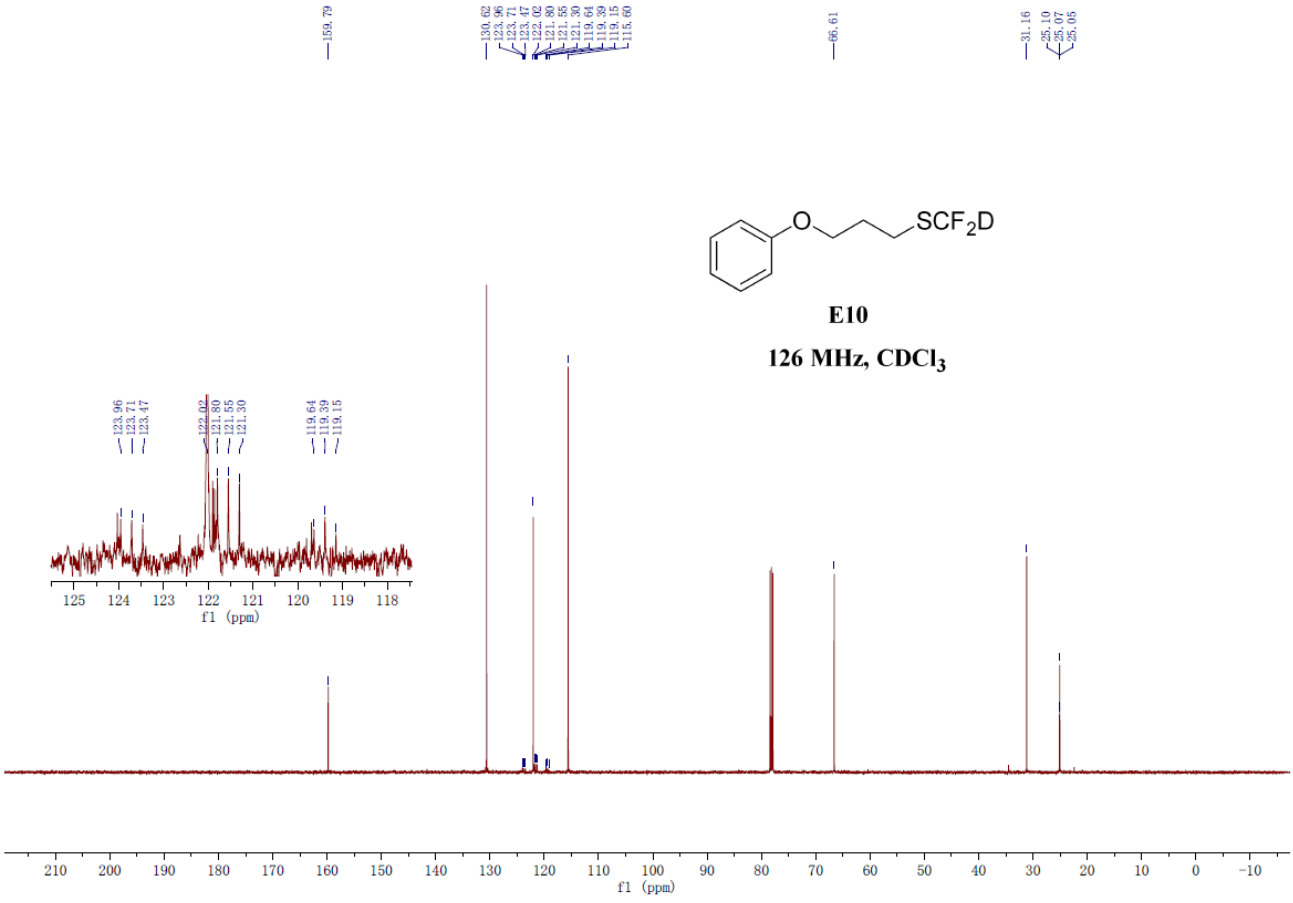

-94.26
-94.38
-95.05
-95.07
-95.09
SCF2D
E8
470 MHz, CDCl3
-94.26
-94.38
-95.05
-95.07
-95.09
0.05
1.00
-94.0
-94.4
-94.8
-95.2
f1 (ppm)
0.05
1.00
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

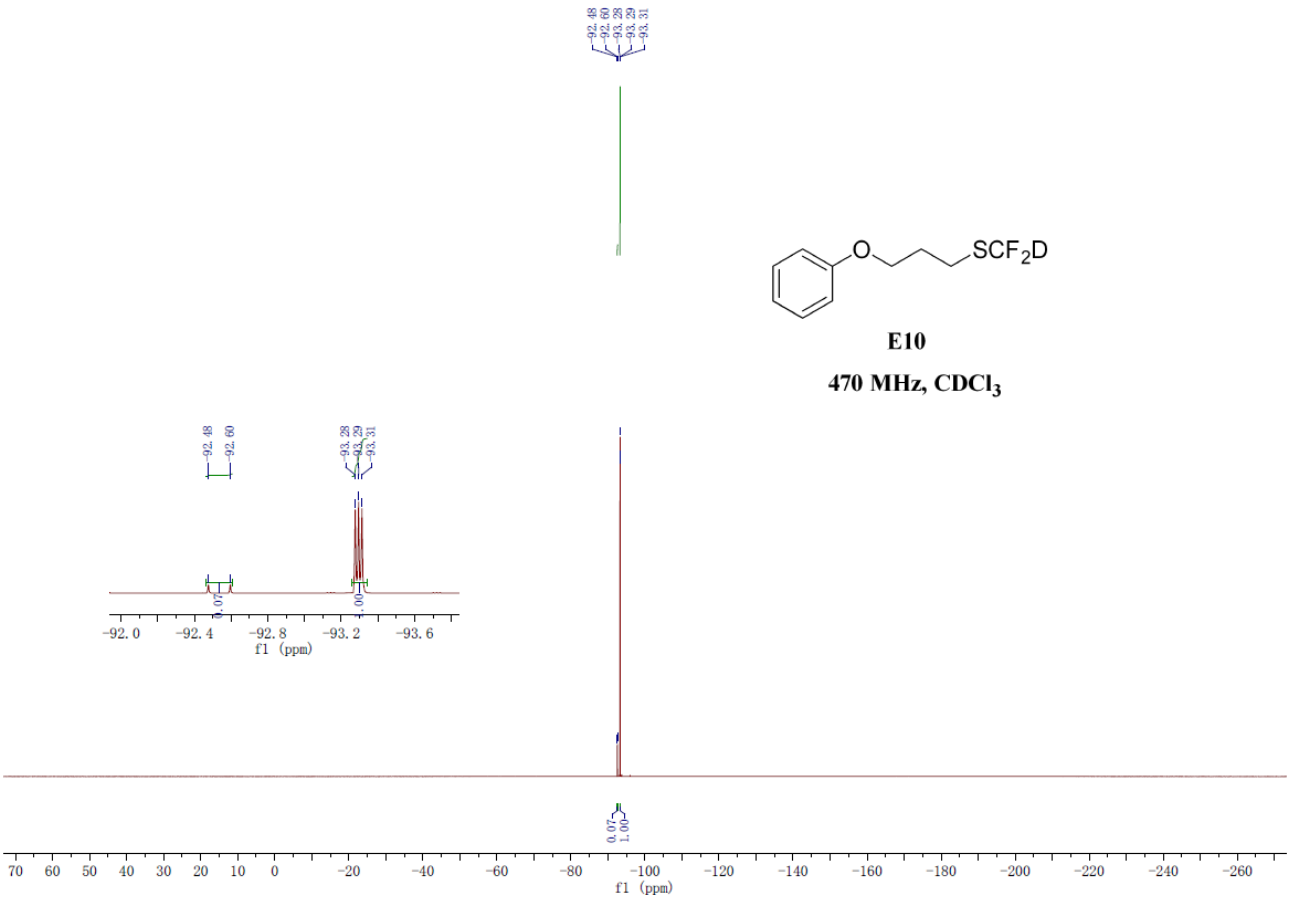

7.39
7.39
7.37
7.36
7.34
7.31
7.30
7.30
7.29
7.28
4.44
4.43
4.41
4.40
1.71
1.69
SCF2D
E9
500 MHz, CDCl3
3.98
0.88
1.00
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


143.27
129.90
128.86
128.15
124.00
123.75
123.54
121.86
121.61
121.33
119.69
119.44
119.19
43.47
43.45
43.43
24.24
SCF2D
E9
126 MHz, CDCl3
f1 (ppm)


-92.99
-93.01
-93.03
-93.53
-93.54
-93.56
-96.48
-96.50
-96.52
-97.02
-97.04
-97.05
SCF2D
E9
470 MHz, CDCl3
f1 (ppm)

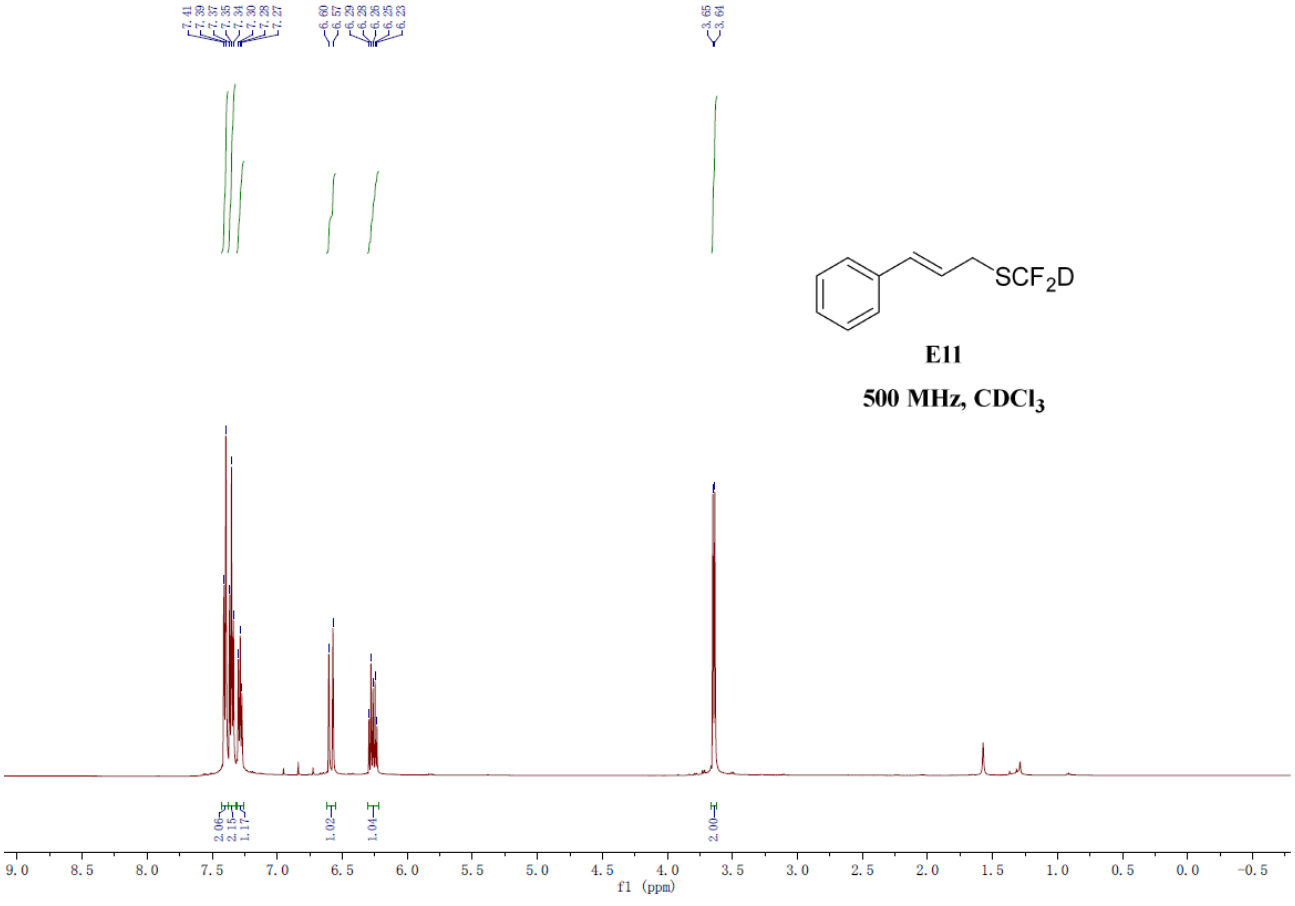

7.34
7.33
7.32
7.31
7.01
6.99
6.88
6.95
6.93
4.11
4.10
4.09
3.06
3.05
3.03
2.21
2.20
2.19
2.17
2.16
O
SCF2D
E10
500 MHz, CDCl3
1.91
0.94
1.95
2.00
1.91
1.94
f1 (ppm)


159.79
130.62
123.96
123.71
123.47
122.02
121.80
121.55
121.30
119.64
119.39
119.15
115.60
66.61
31.16
25.10
25.07
25.05
O
SCF2D
E10
126 MHz, CDCl3
123.96
123.71
123.47
122.02
121.80
121.55
121.30
119.64
119.39
119.15
f1 (ppm)
f1 (ppm)



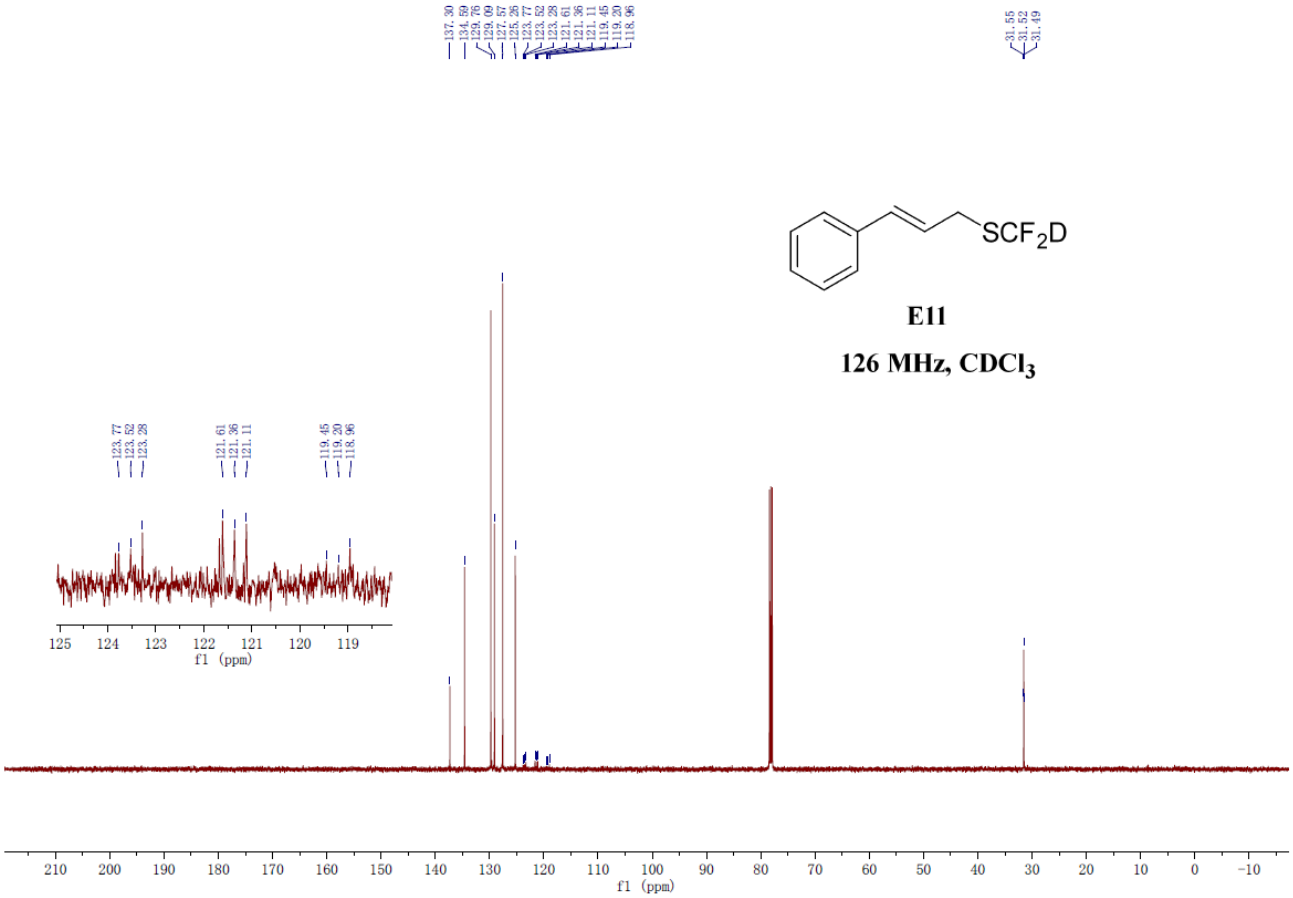
E10

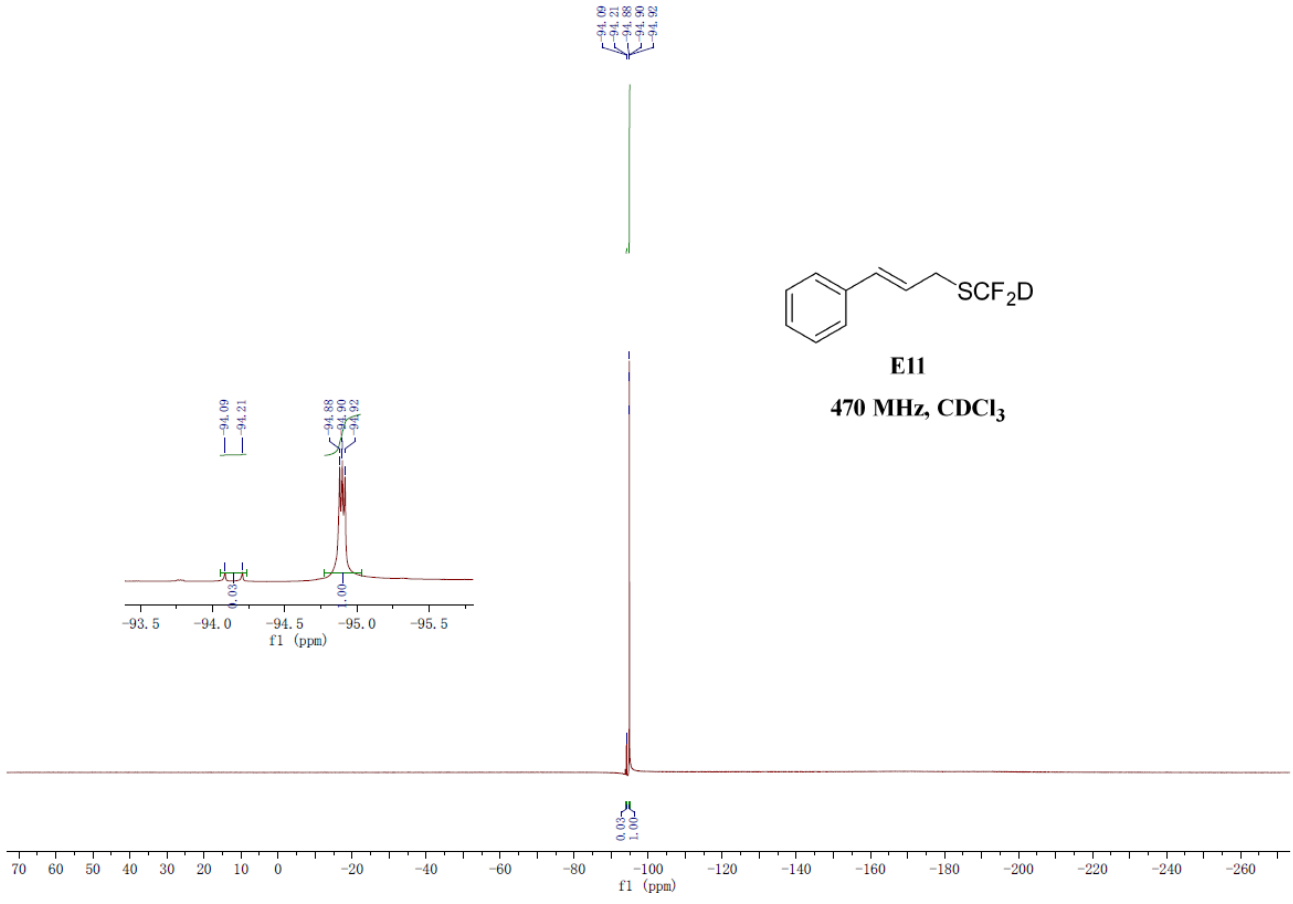
470 MHz, $CDCl_3$

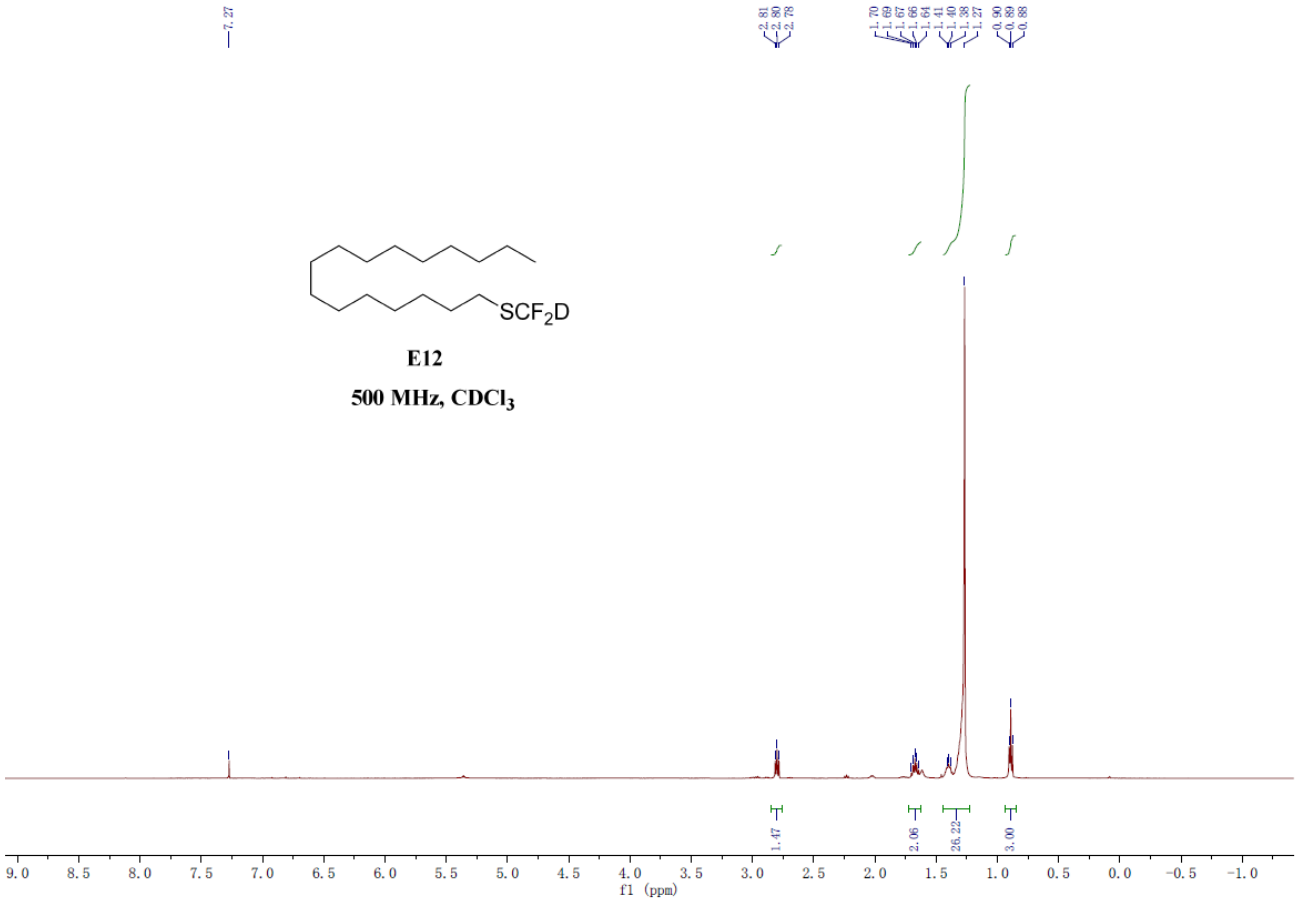


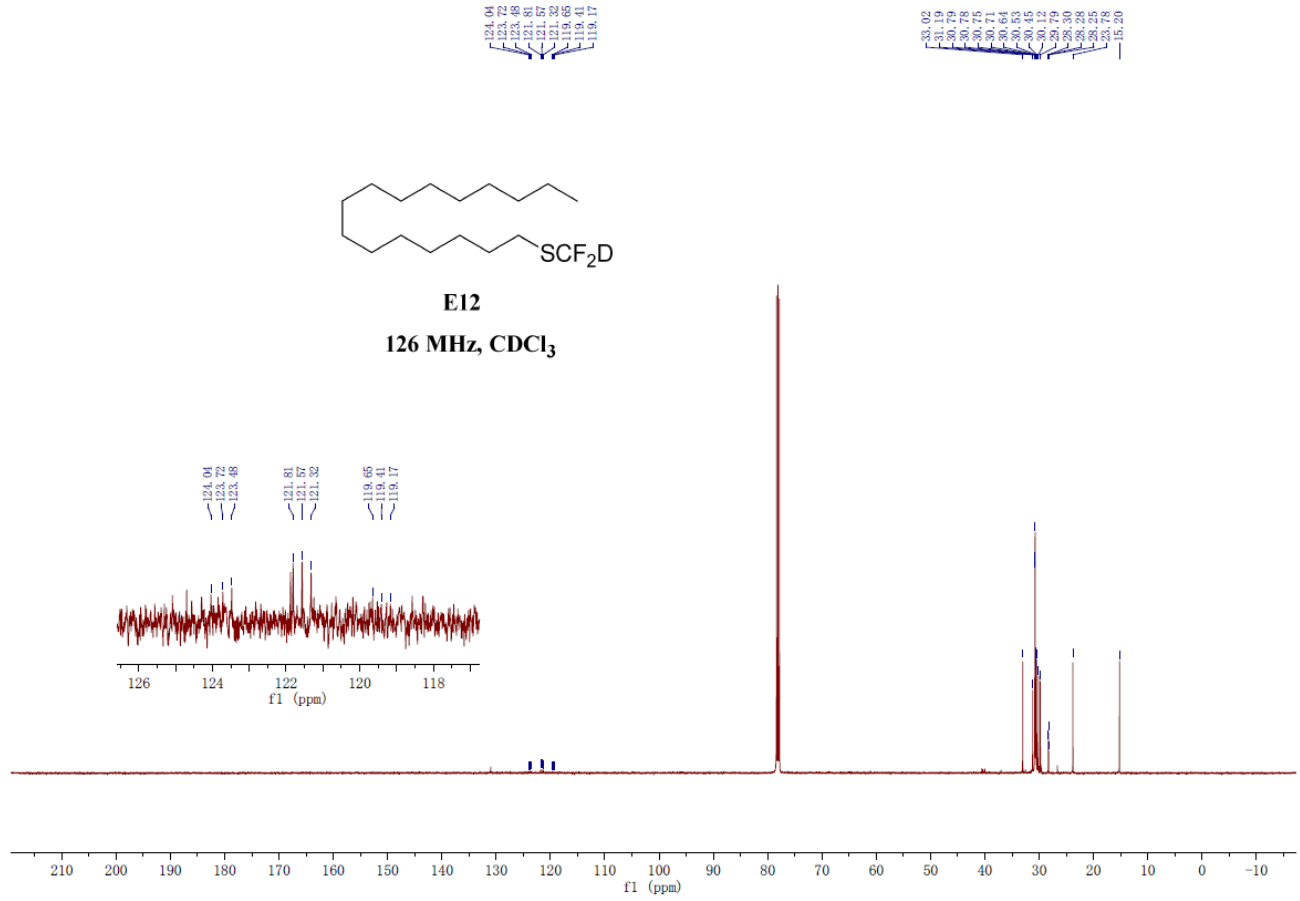
E11

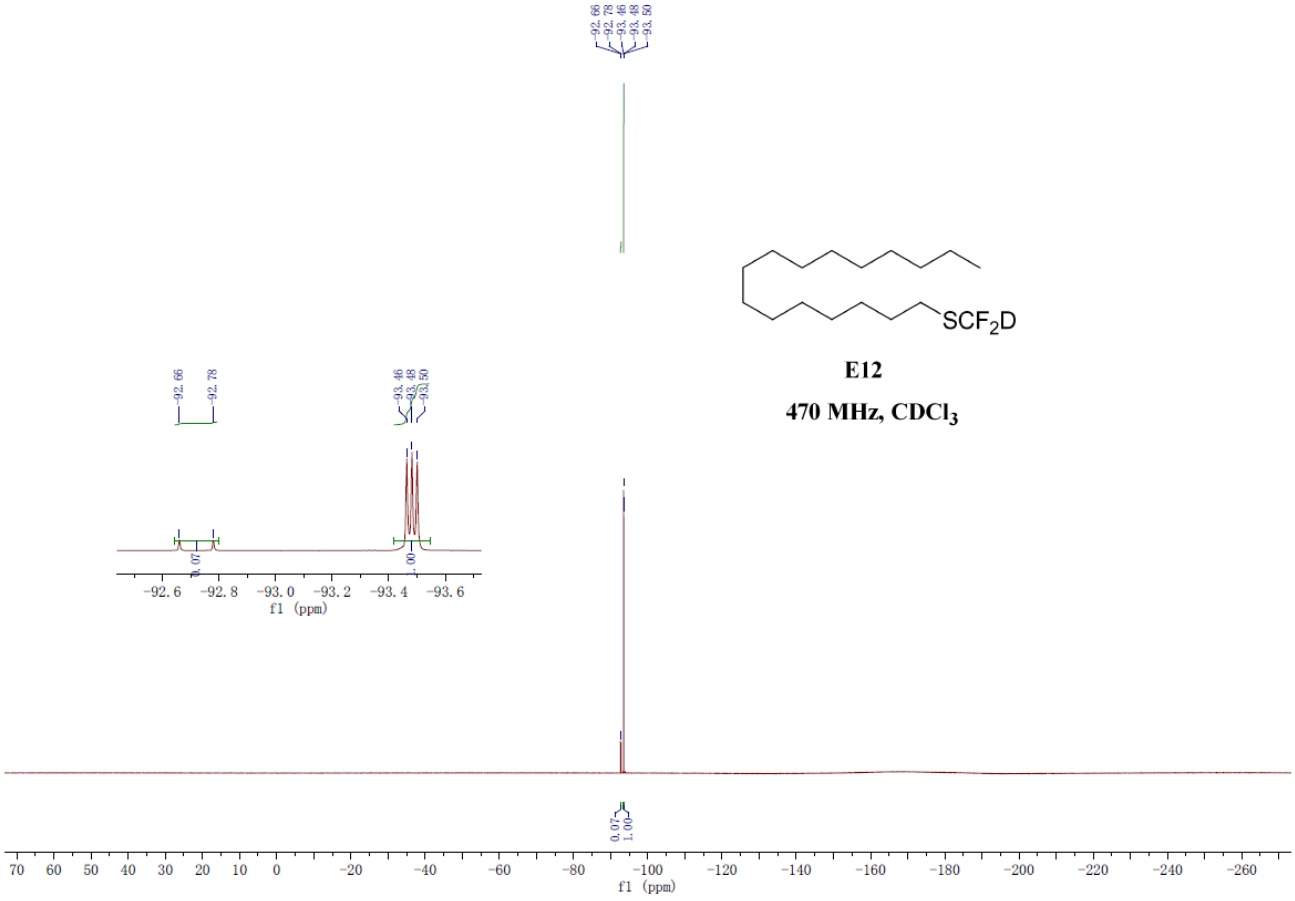
500 MHz, $CDCl_3$

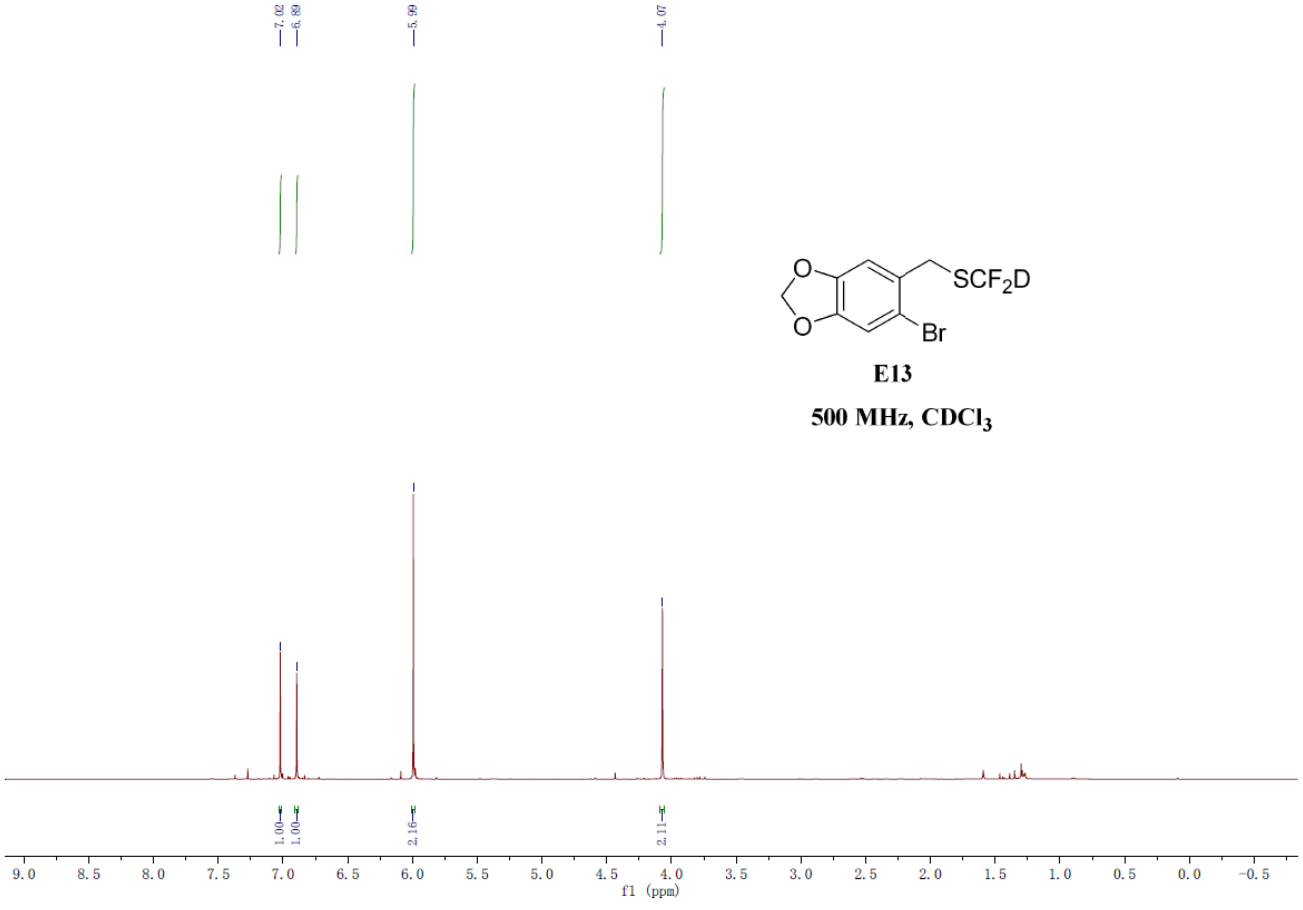

137.30
134.59
129.76
129.09
127.67
125.25
123.77
123.52
123.28
121.61
121.36
121.11
119.45
119.20
118.96
31.55
31.52
31.49
SCF2D
E11
126 MHz, CDCl3
123.77
123.52
123.28
121.61
121.36
121.11
119.45
119.20
118.96
125 124 123 122 121 120 119
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

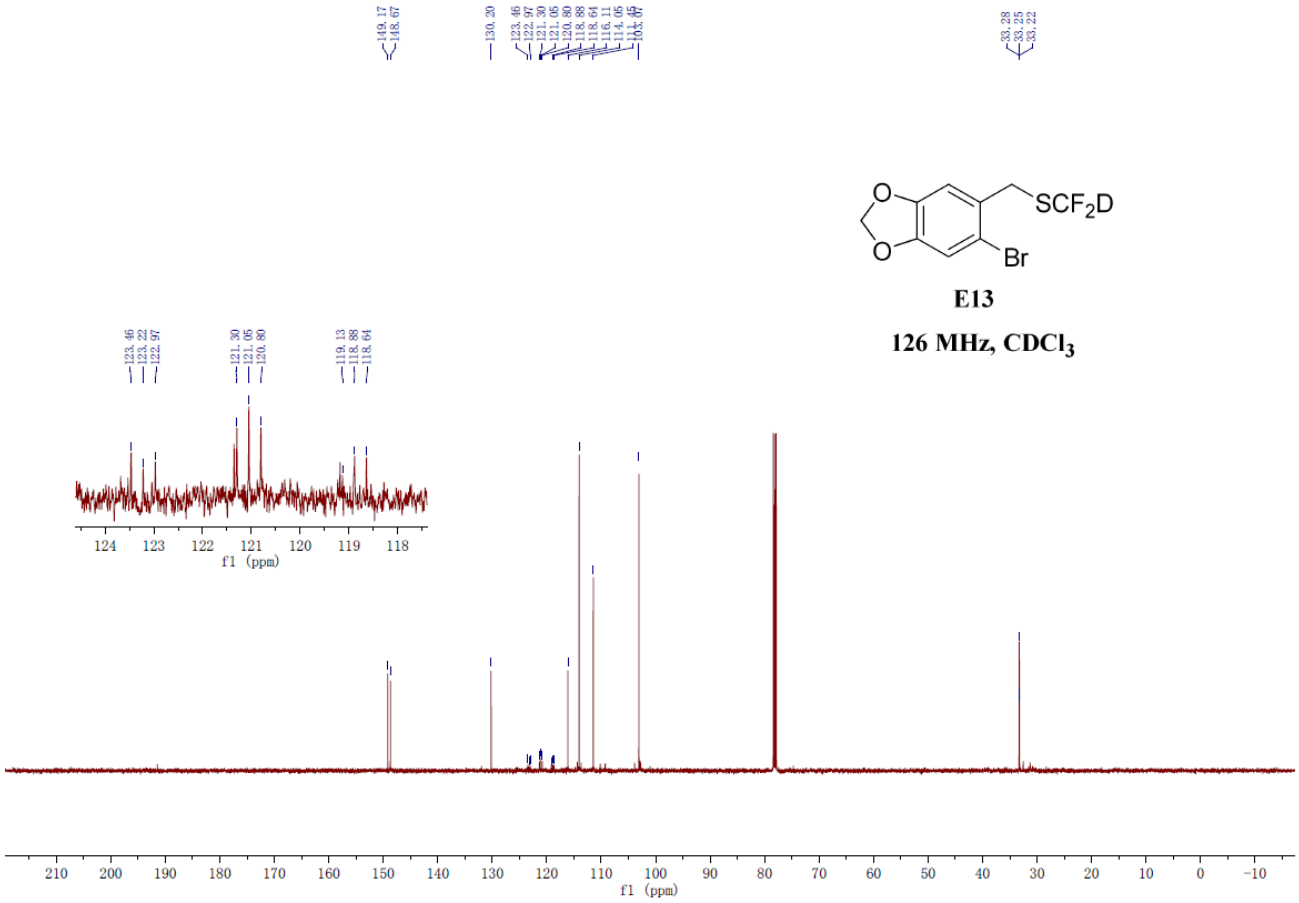

-94.09
-94.21
-94.88
-94.90
-94.92
SCF2D
E11
470 MHz, CDCl3
-94.09
-94.21
-94.88
-94.90
-94.92
0.03
1.00
-93.5 -94.0 -94.5 -95.0 -95.5
f1 (ppm)
0.03
1.00
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

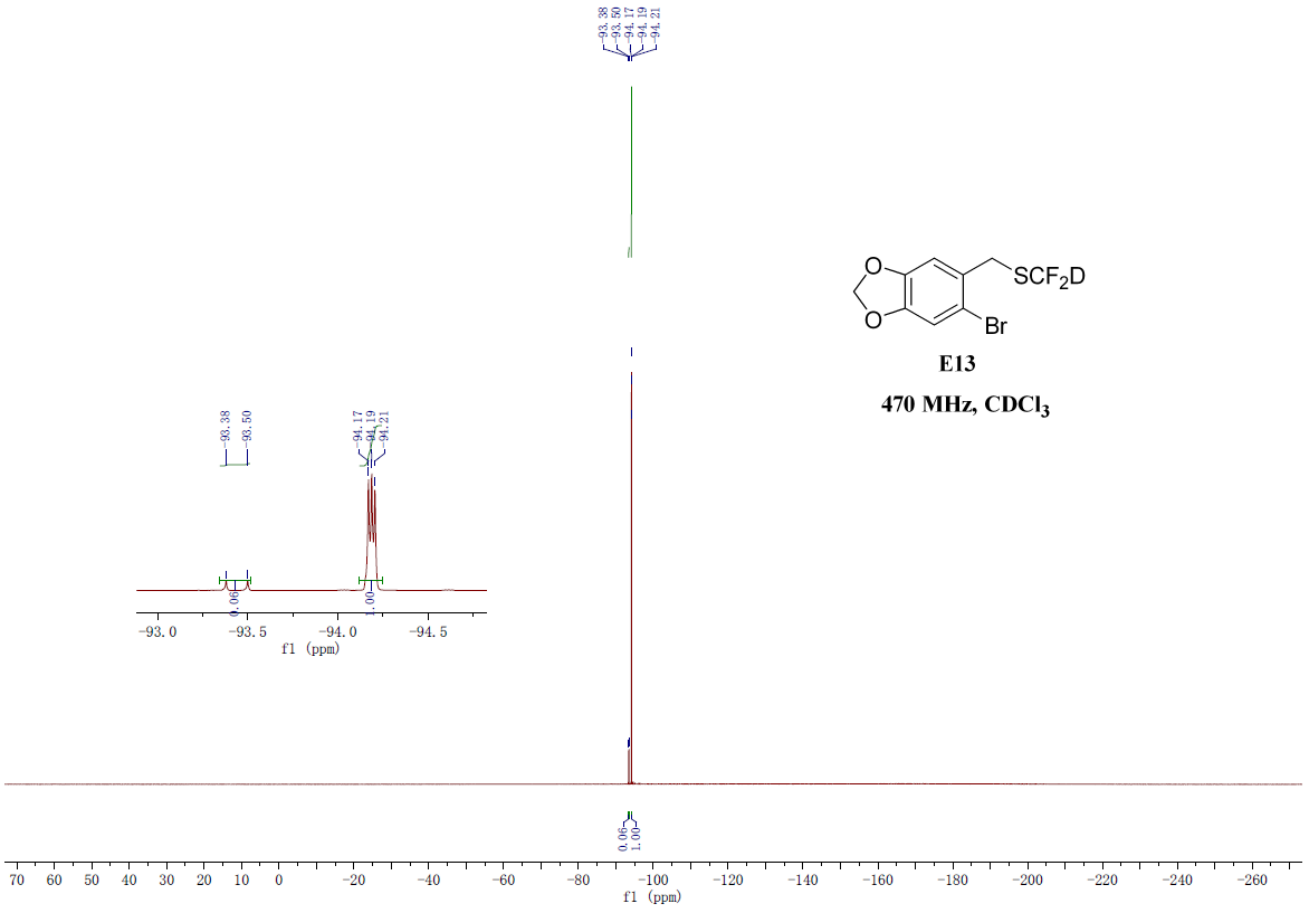

7.27
2.81
2.80
2.78
1.70
1.69
1.67
1.66
1.64
1.41
1.40
1.38
1.27
0.90
0.89
0.88
SCF2D
E12
500 MHz, CDCl3
1.47
2.06
26.22
3.00
f1 (ppm)

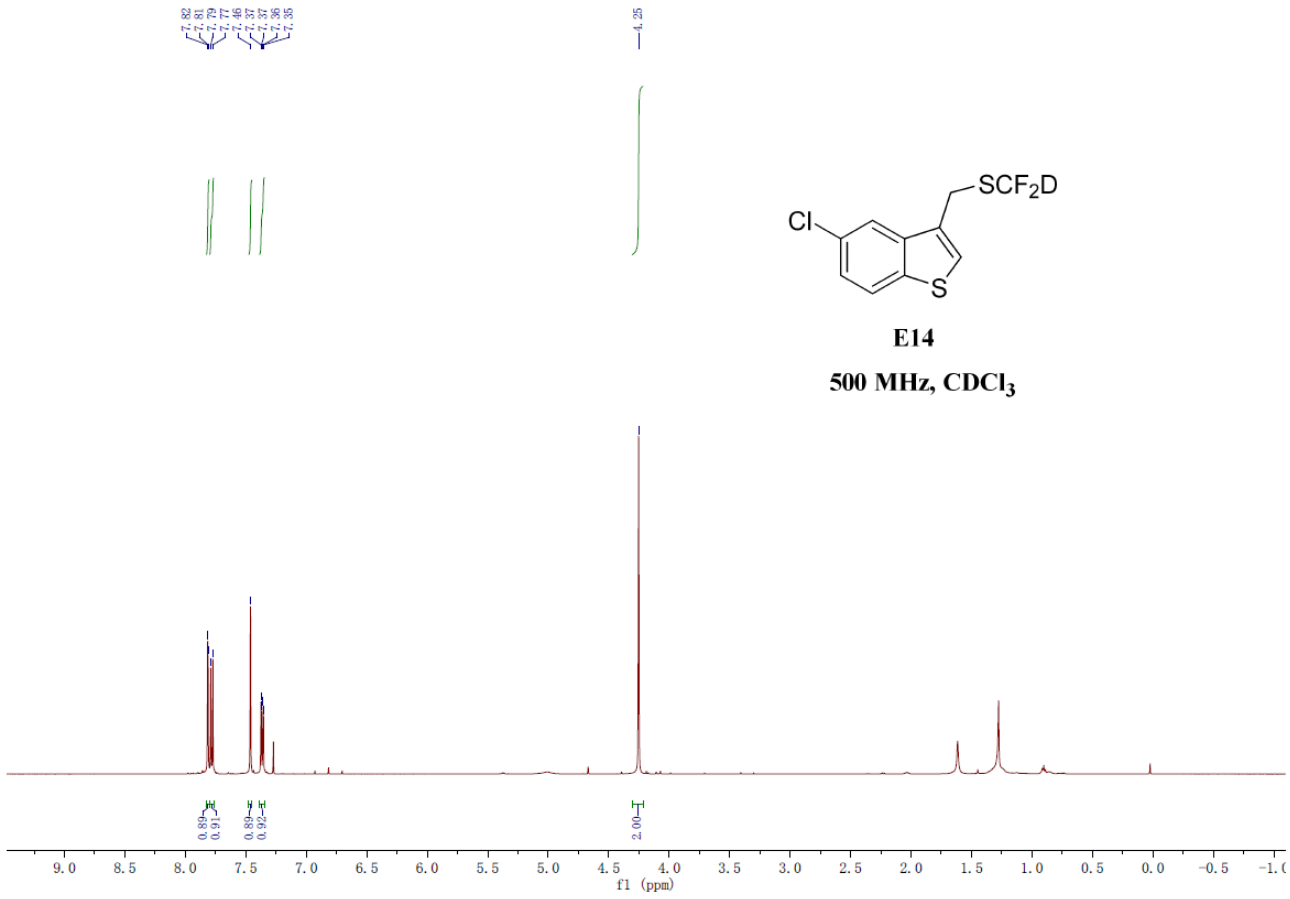

124.04
123.72
123.48
121.81
121.57
121.32
119.65
119.41
119.17
53.02
31.19
30.79
30.78
30.75
30.71
30.64
30.53
30.45
30.12
29.79
29.50
28.28
28.25
23.78
15.20
SCF2D
E12
126 MHz, CDCl3
f1 (ppm)


-92.66
-92.78
-93.46
-93.48
-93.50
SCF2D
E12
470 MHz, CDCl3
0.07
1.00
f1 (ppm)


7.02
6.89
5.99
4.07
SCF2D
Br
E13
500 MHz, CDCl3
1.00
1.00
2.16
2.11
f1 (ppm)

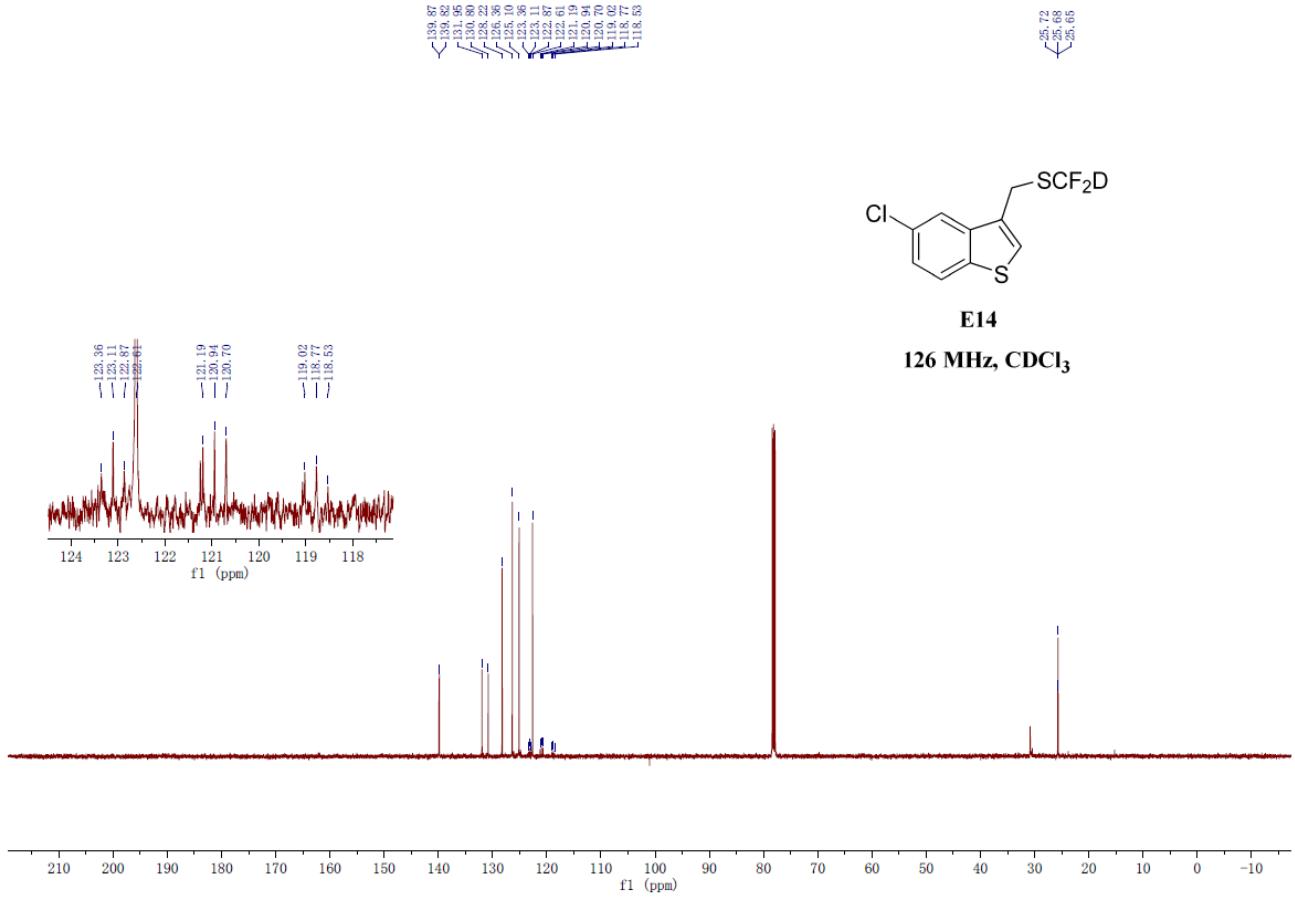

149.17
148.67
130.20
123.46
122.97
121.30
121.05
120.80
118.88
118.64
114.06
103.07
33.28
33.25
33.22
123.46
123.22
122.97
121.30
121.05
120.80
119.13
118.88
118.64
124
123
122
121
120
119
118
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
SCF2D
Br
E13
126 MHz, CDCl3


-93.38
-93.50
-94.17
-94.19
-94.21
-93.38
-93.50
-94.17
-94.19
-94.21
0.06
1.00
-93.0
-93.5
-94.0
-94.5
f1 (ppm)
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)
SCF2D
Br
E13
470 MHz, CDCl3



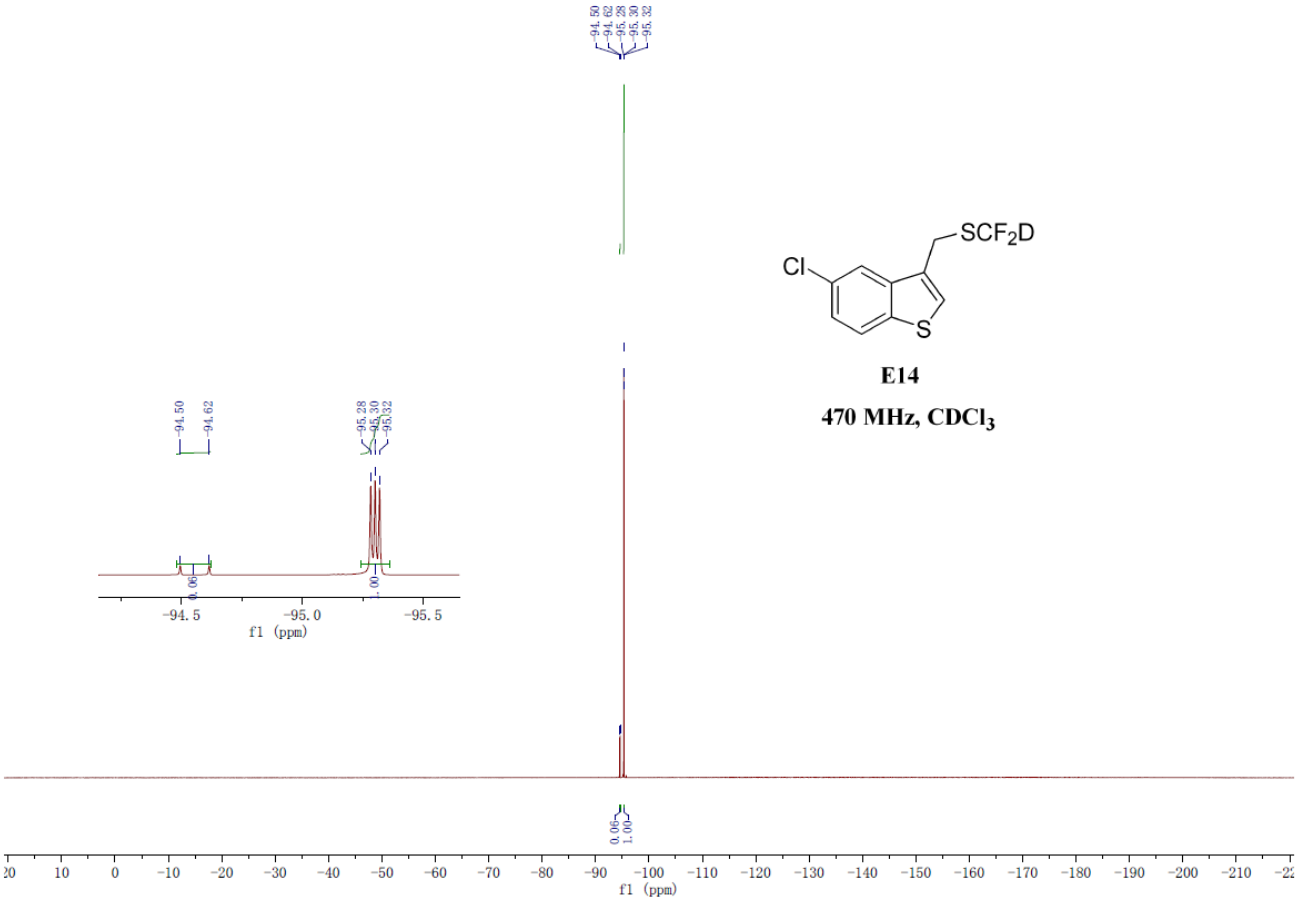
E14

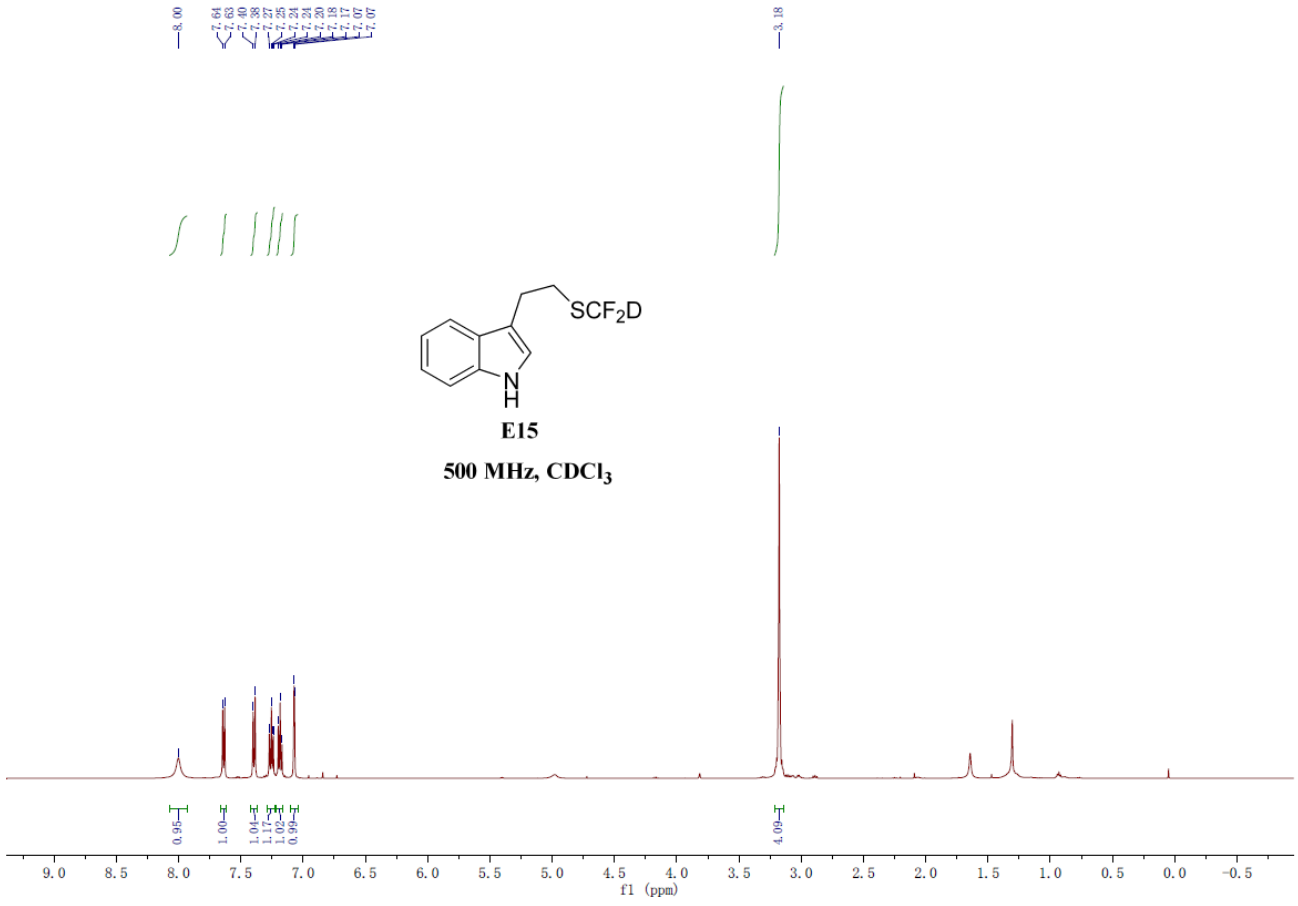
500 MHz, $CDCl_3$

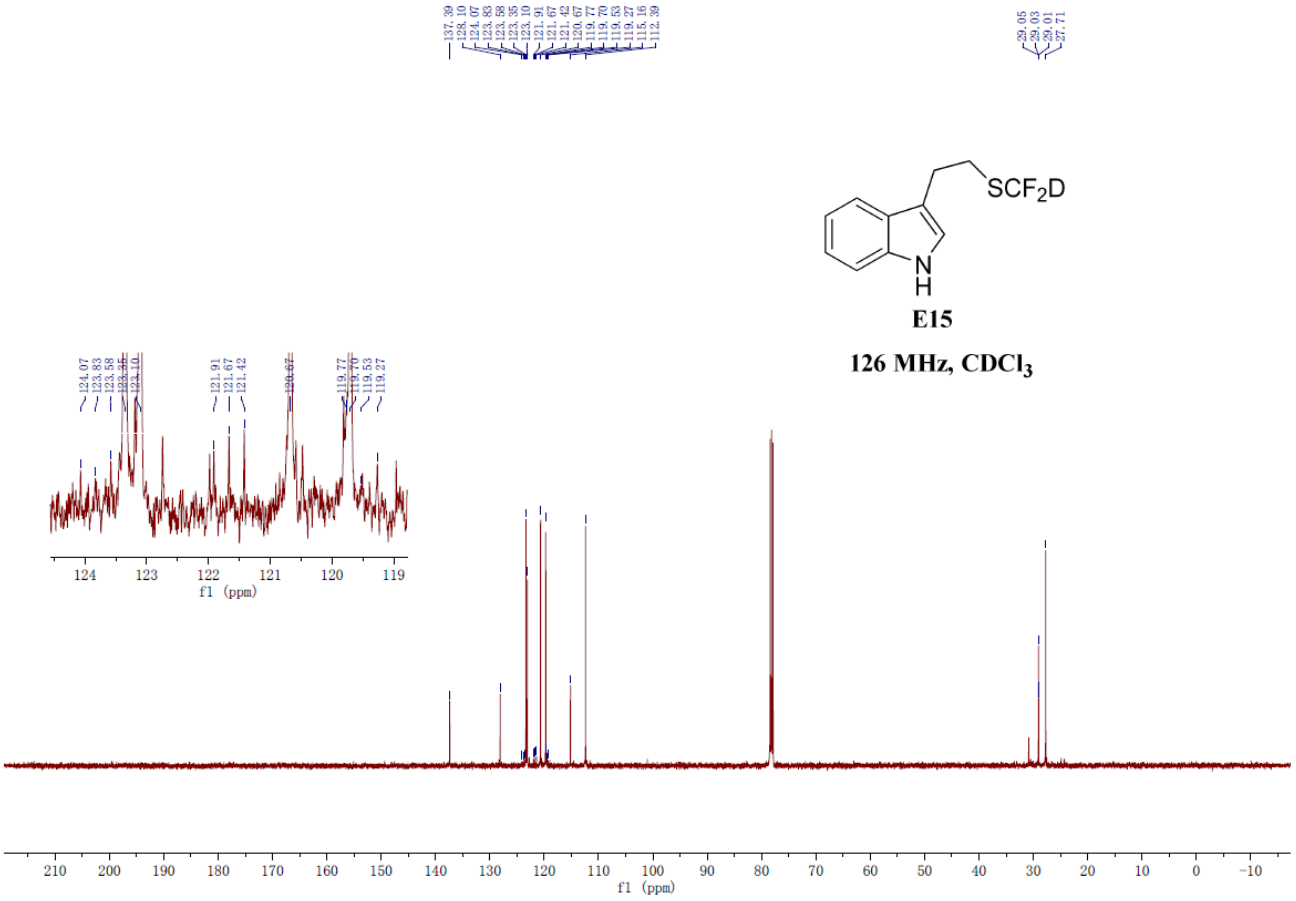


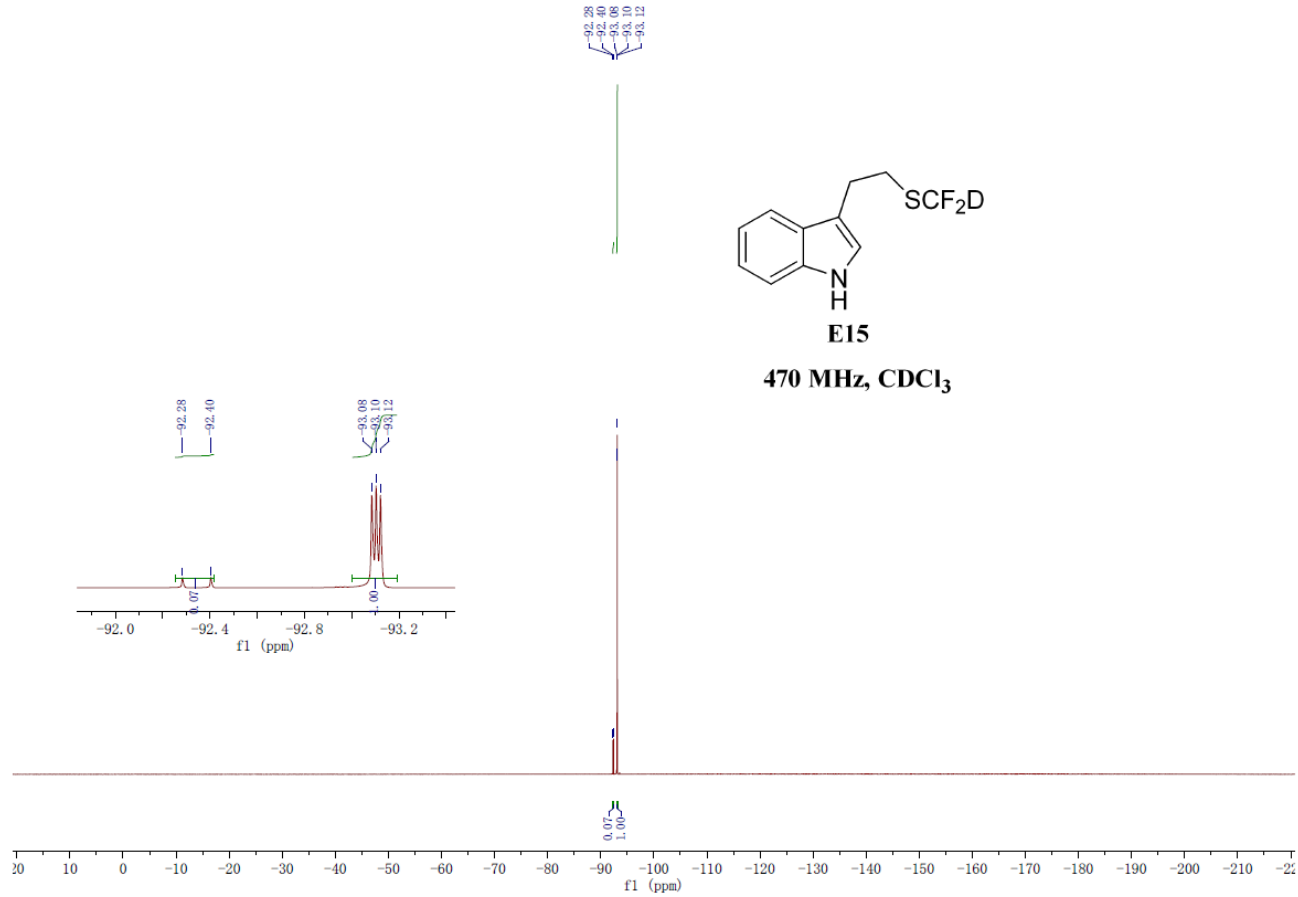
E14

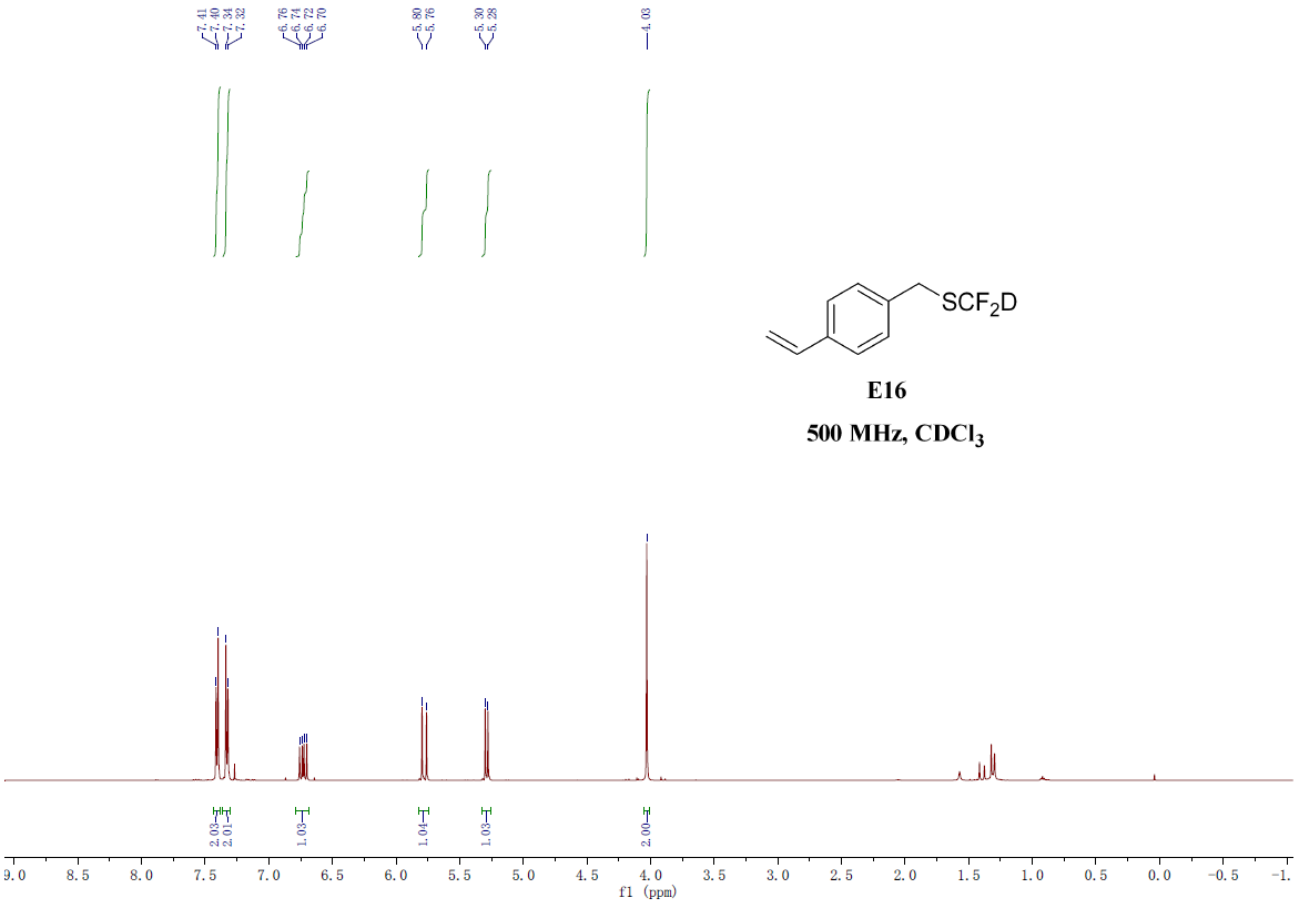
126 MHz, $CDCl_3$


-94.50
-94.62
-95.28
-95.30
-95.32
Cl
SCF2D
S
E14
470 MHz, CDCl3
f1 (ppm)


8.00
7.64
7.63
7.40
7.38
7.27
7.25
7.24
7.24
7.20
7.18
7.17
7.07
7.07
3.18
SCF2D
N
H
E15
500 MHz, CDCl3
f1 (ppm)

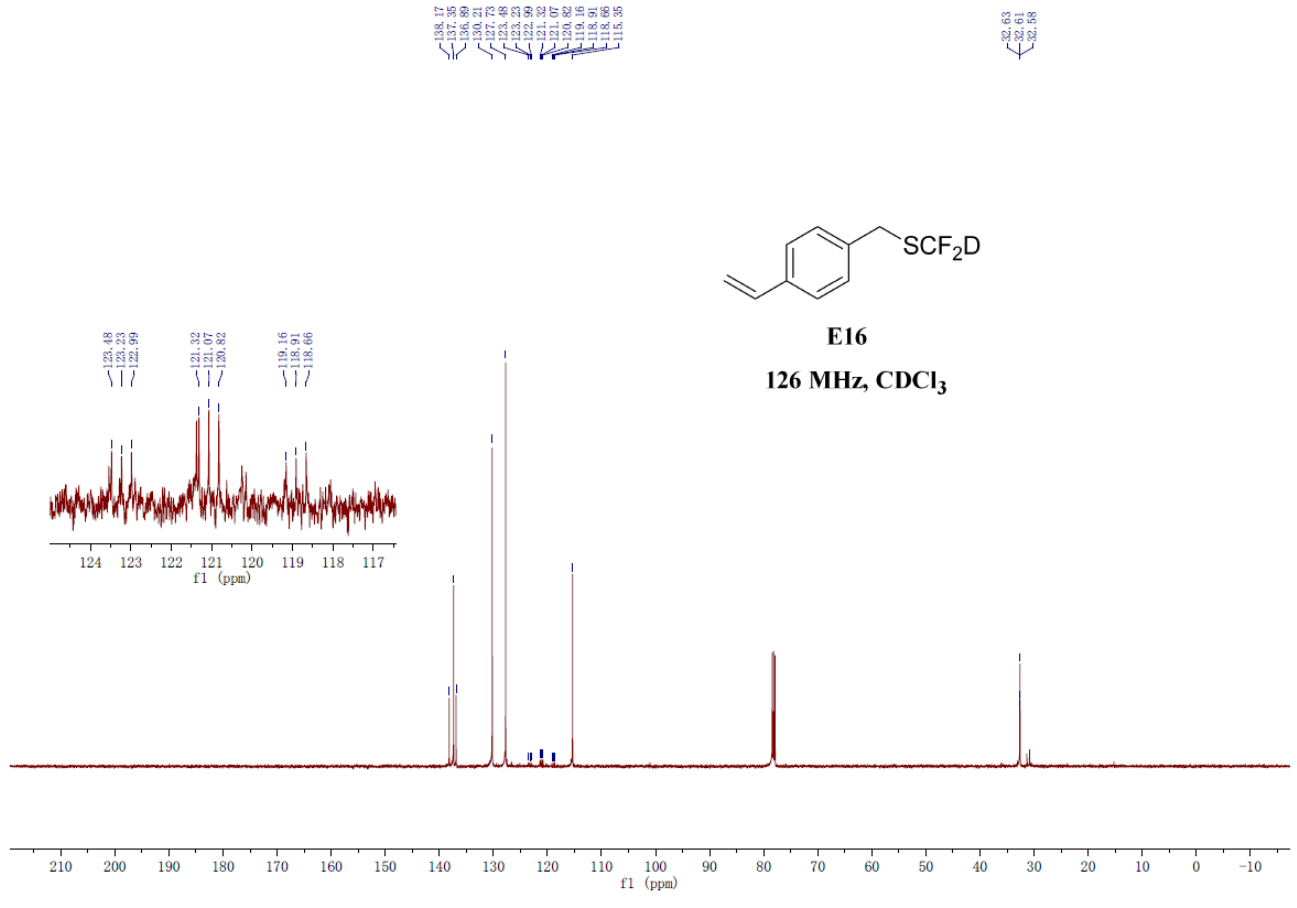

SCF2D
N
H
E15
126 MHz, CDCl3
f1 (ppm)


SCF2D
N
H
E15
470 MHz, CDCl3
f1 (ppm)



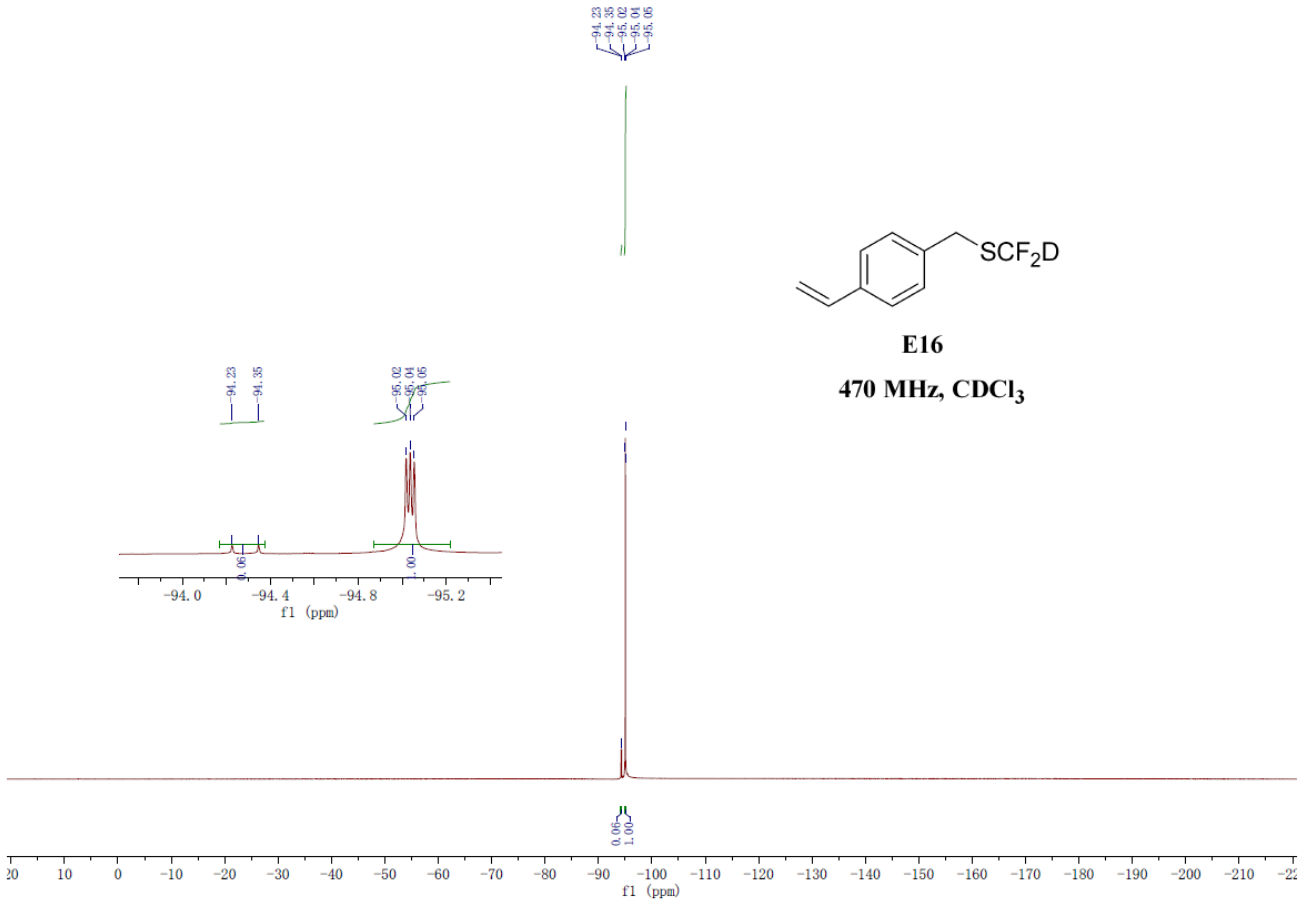
E16

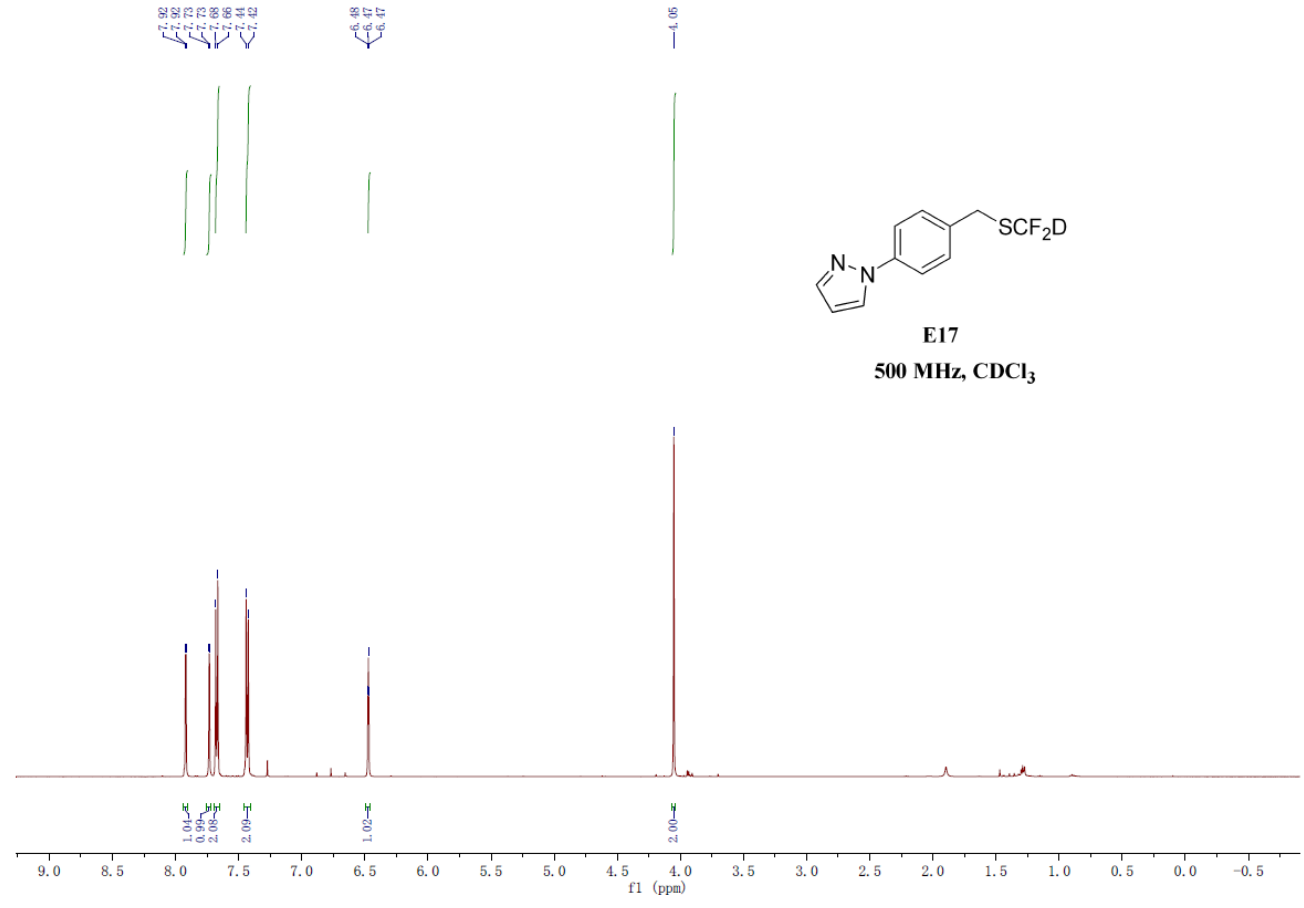
500 MHz, $CDCl_3$

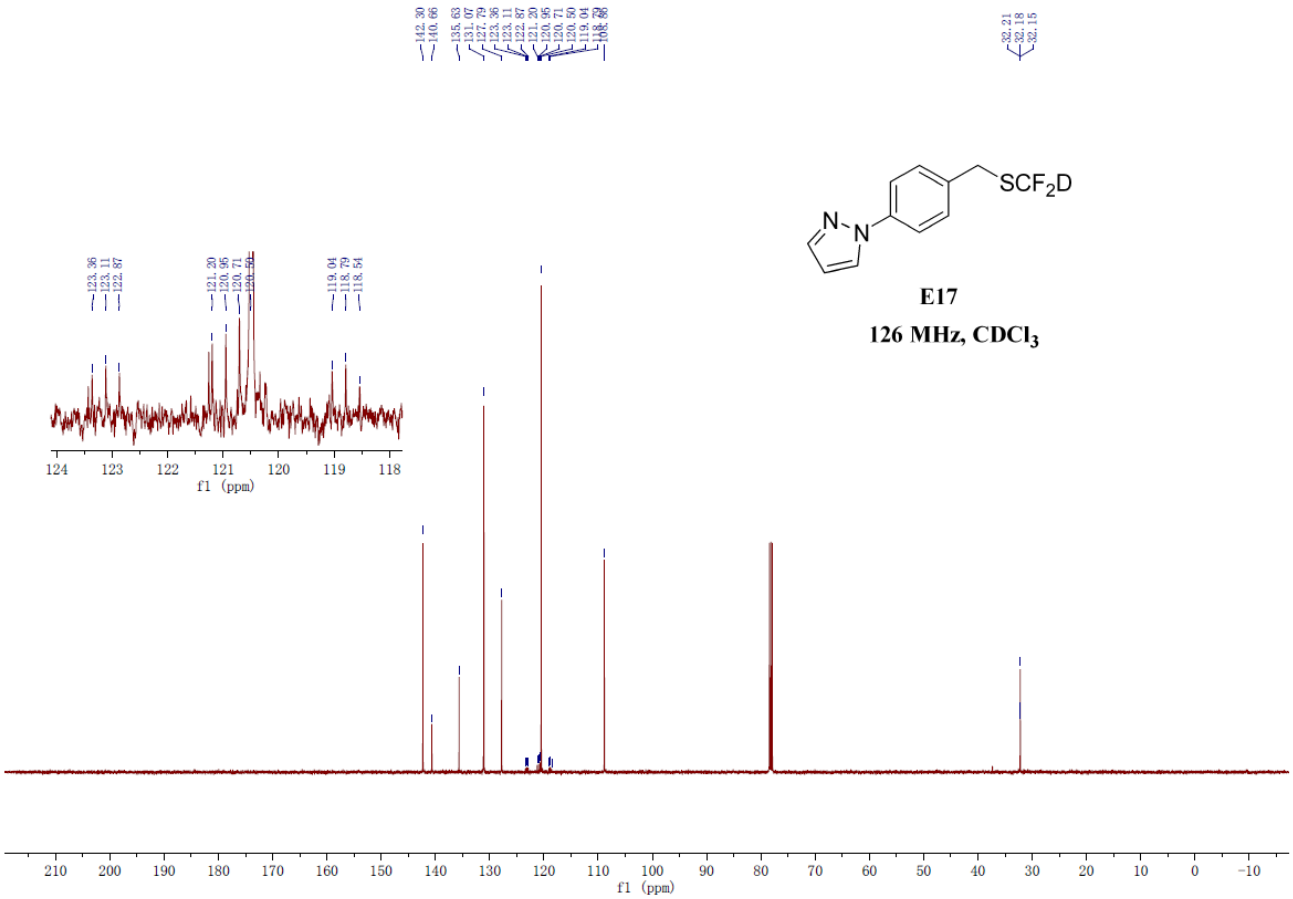


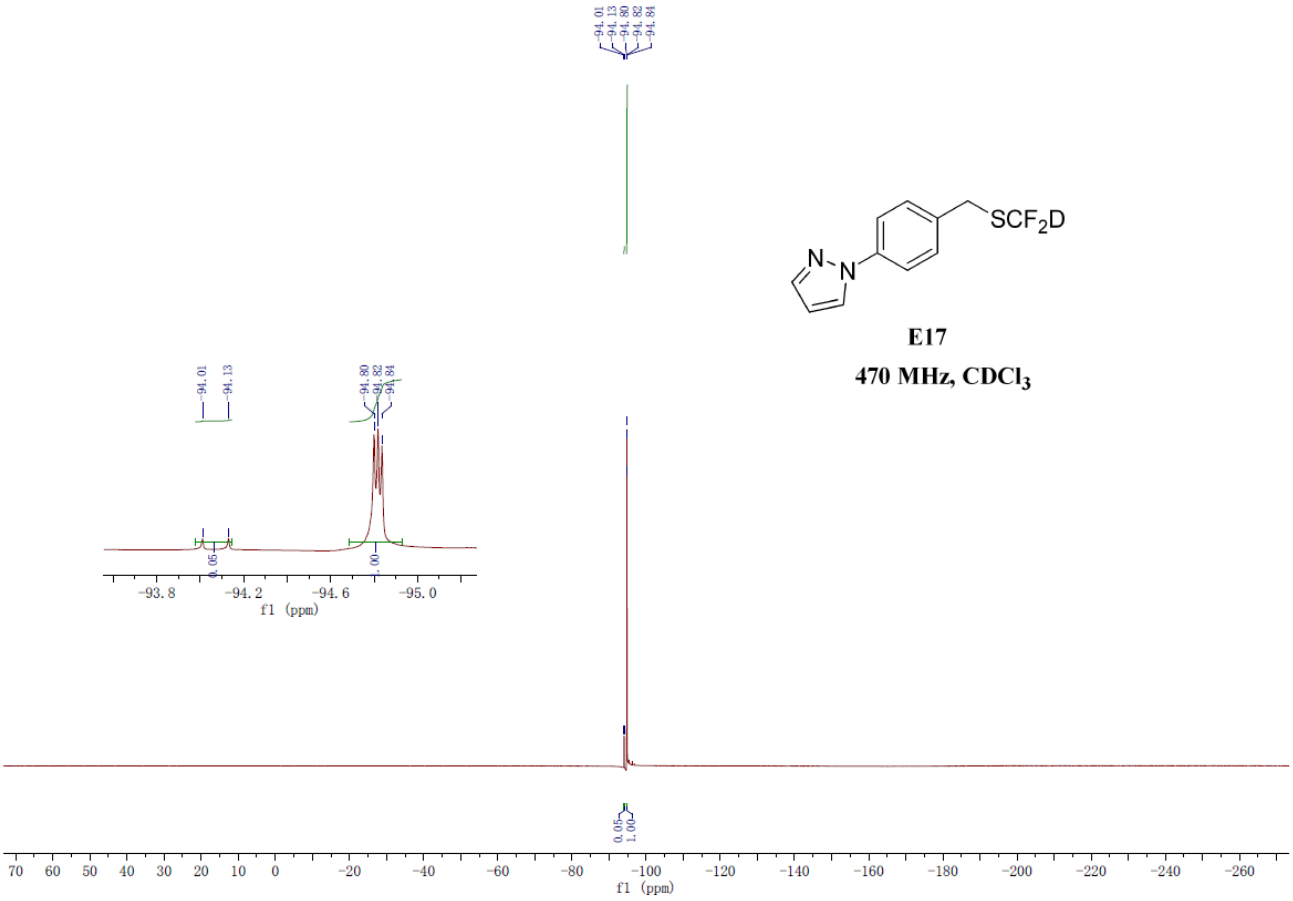
E16

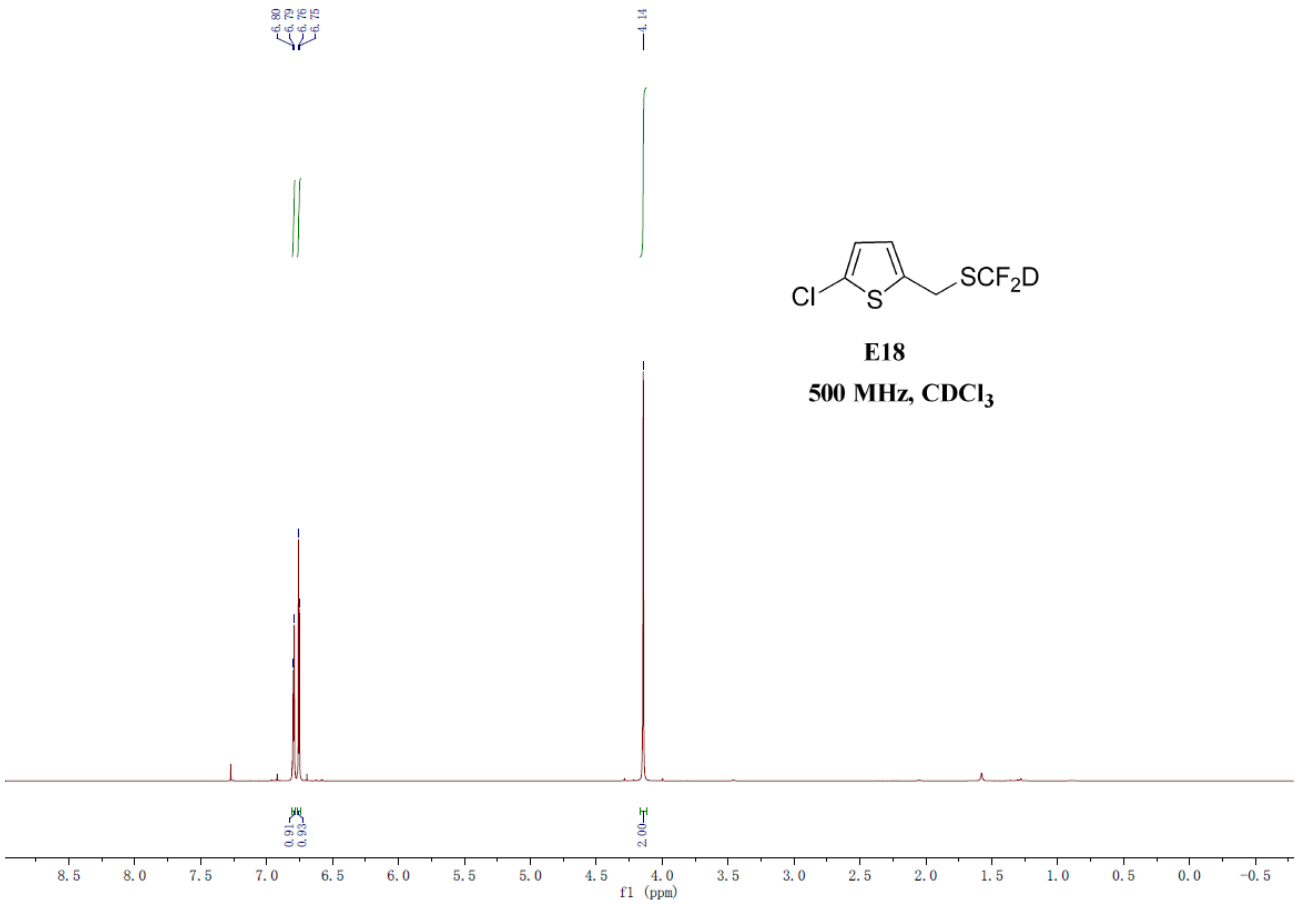
126 MHz, $CDCl_3$


SCF2D
E16
470 MHz, CDCl3
f1 (ppm)


SCF2D
E17
500 MHz, CDCl3
f1 (ppm)

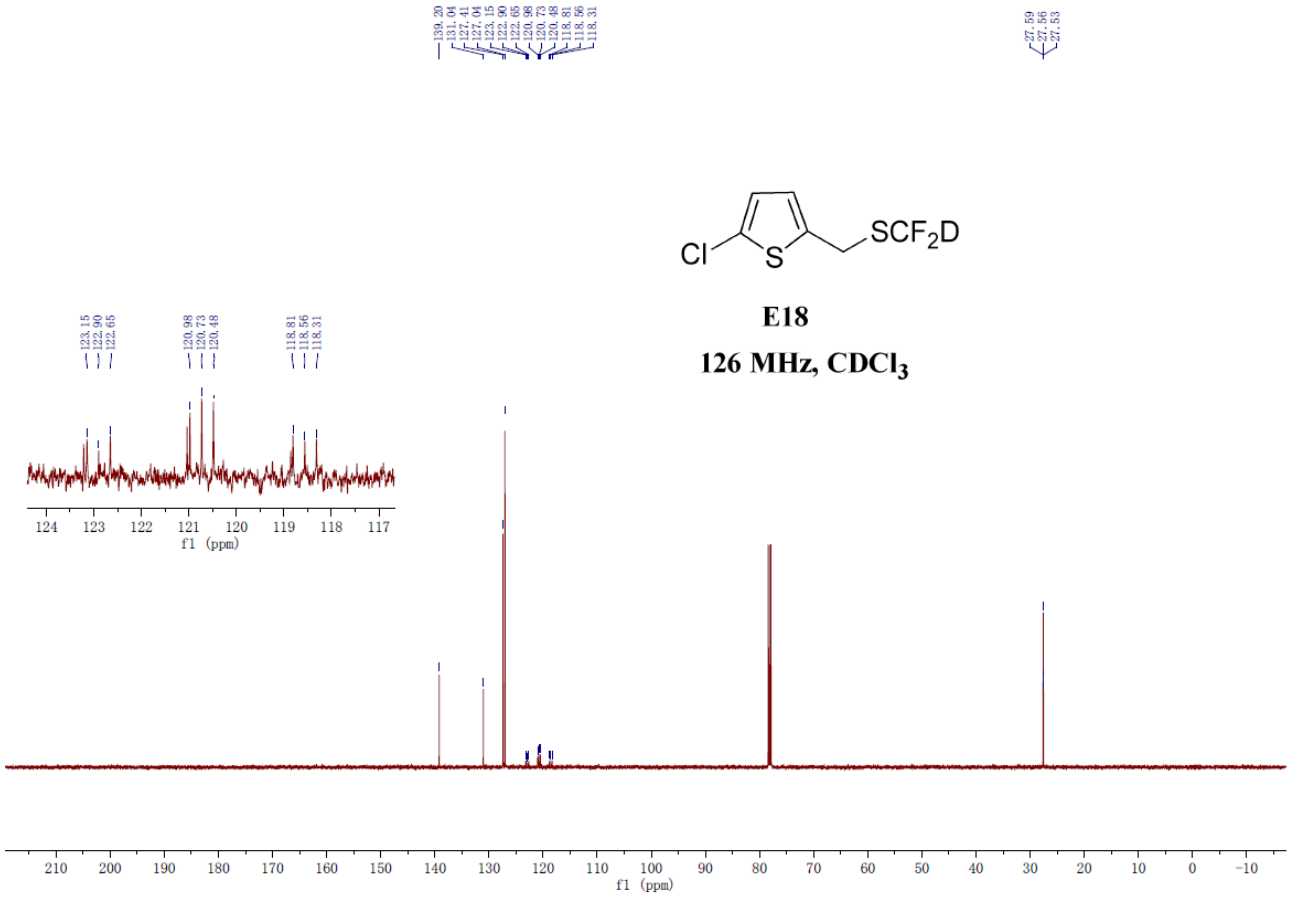

142.30
140.66
135.63
131.07
127.79
123.36
123.11
122.87
121.20
120.95
120.71
120.59
119.04
118.79
118.54
32.21
32.18
32.15
SCF2D
N
N
E17
126 MHz, CDCl3
123.36
123.11
122.87
121.20
120.95
120.71
120.59
119.04
118.79
118.54
124
123
122
121
120
119
118
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-94.01
-94.13
-94.80
-94.82
-94.84
SCF2D
N
N
E17
470 MHz, CDCl3
-94.01
-94.13
-94.80
-94.82
-94.84
0.05
1.00
-93.8
-94.2
-94.6
-95.0
f1 (ppm)
0.05
1.00
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
f1 (ppm)



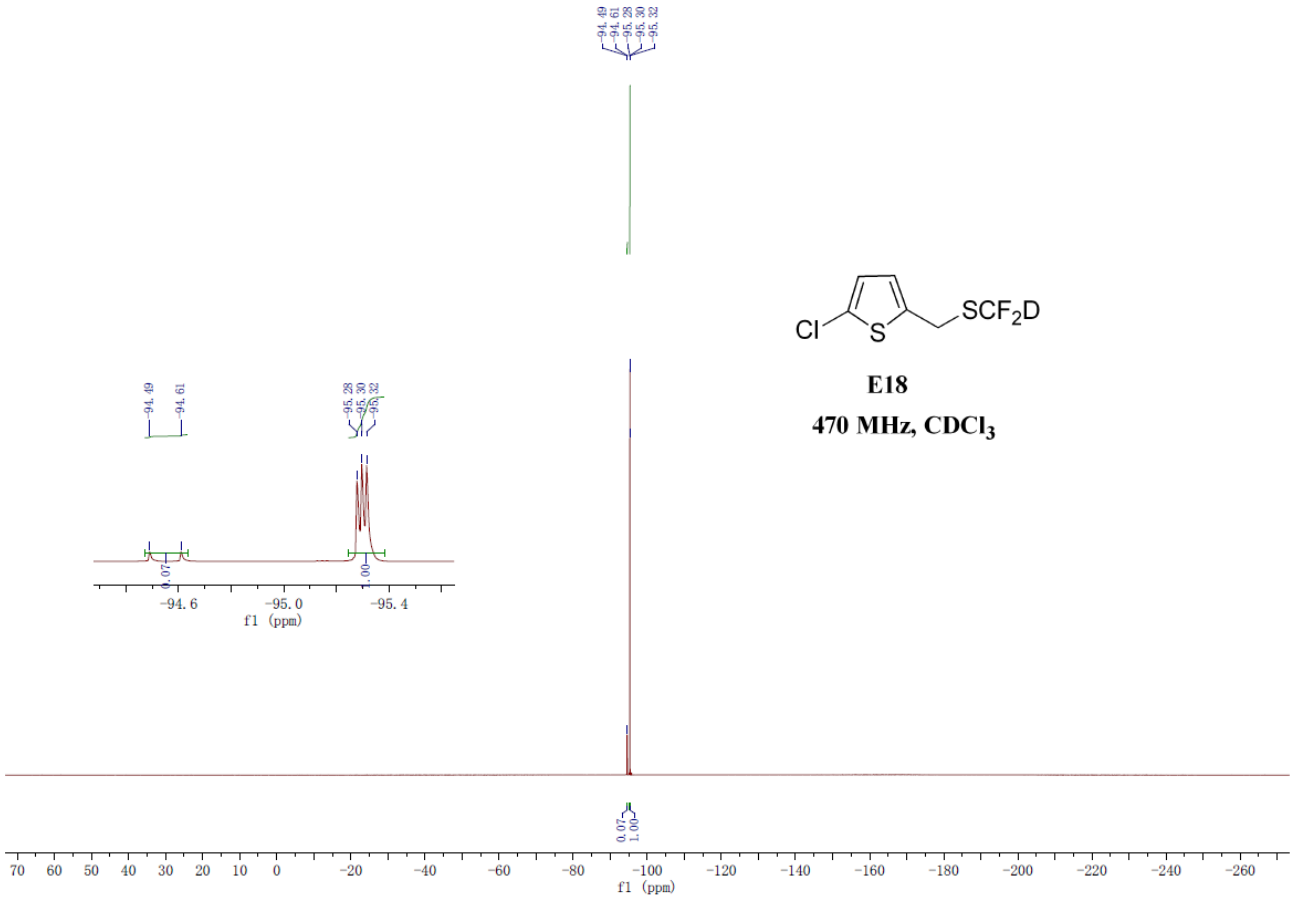
E18

500 MHz, $CDCl_3$



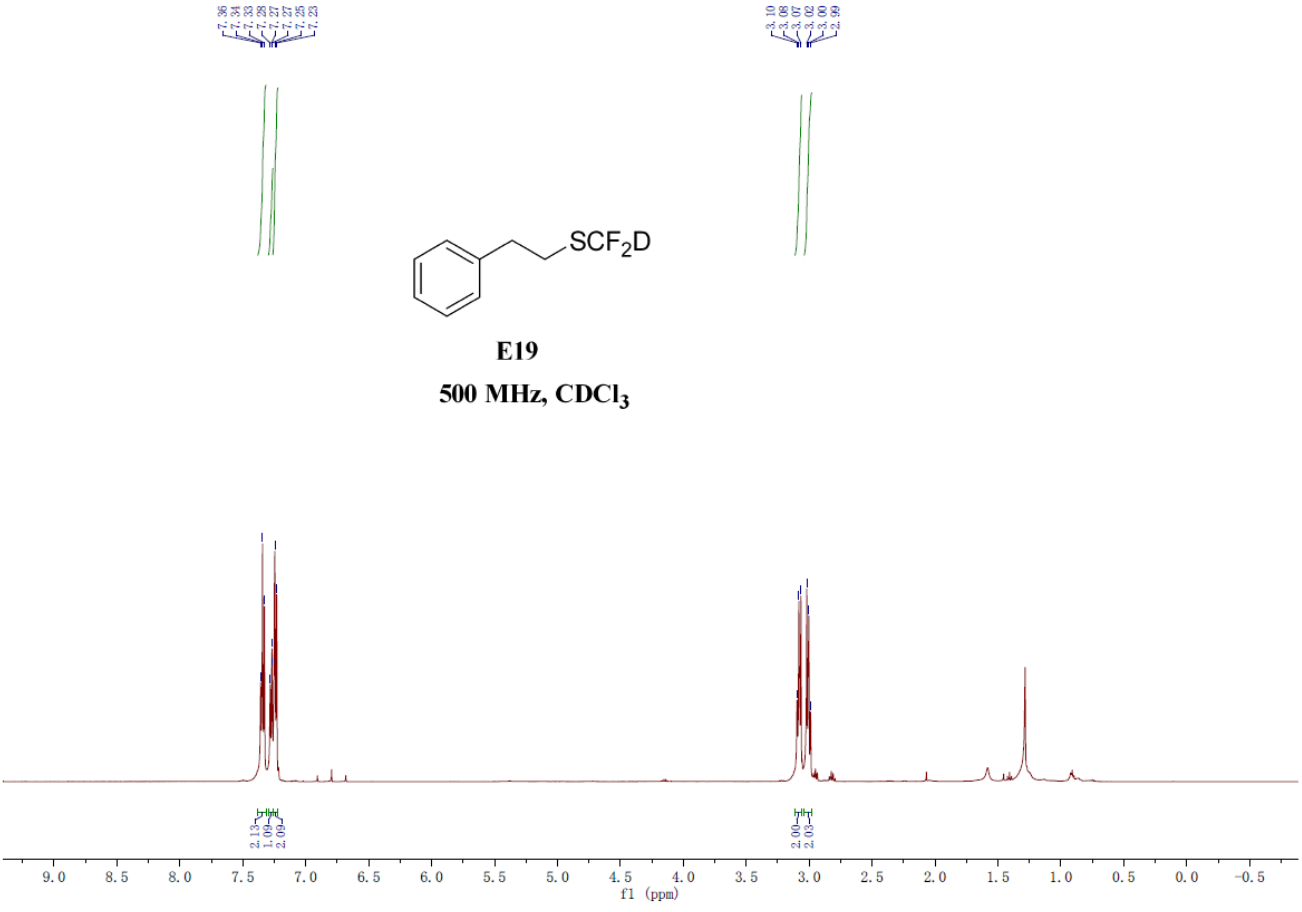
E18

126 MHz, $CDCl_3$



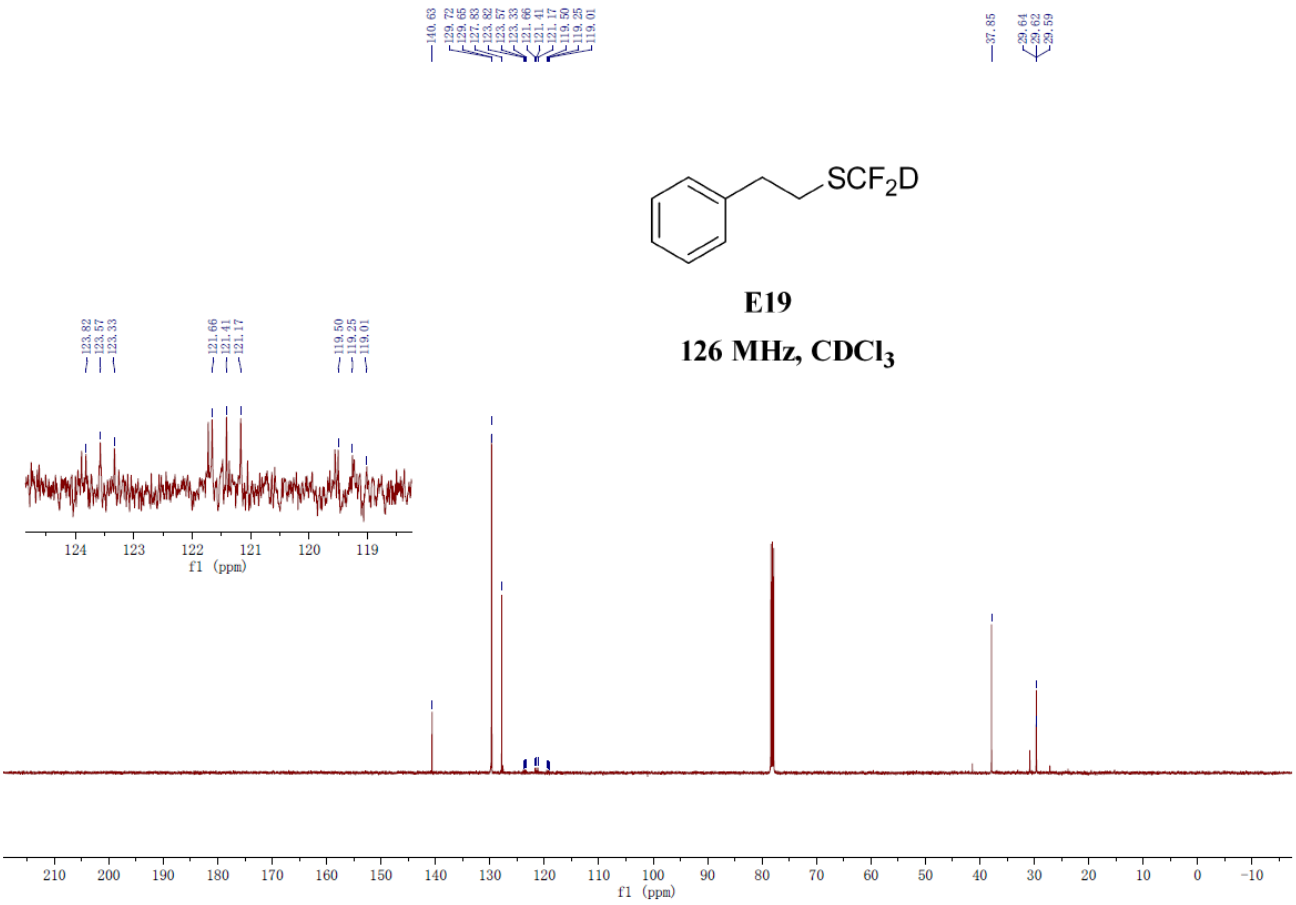
E18

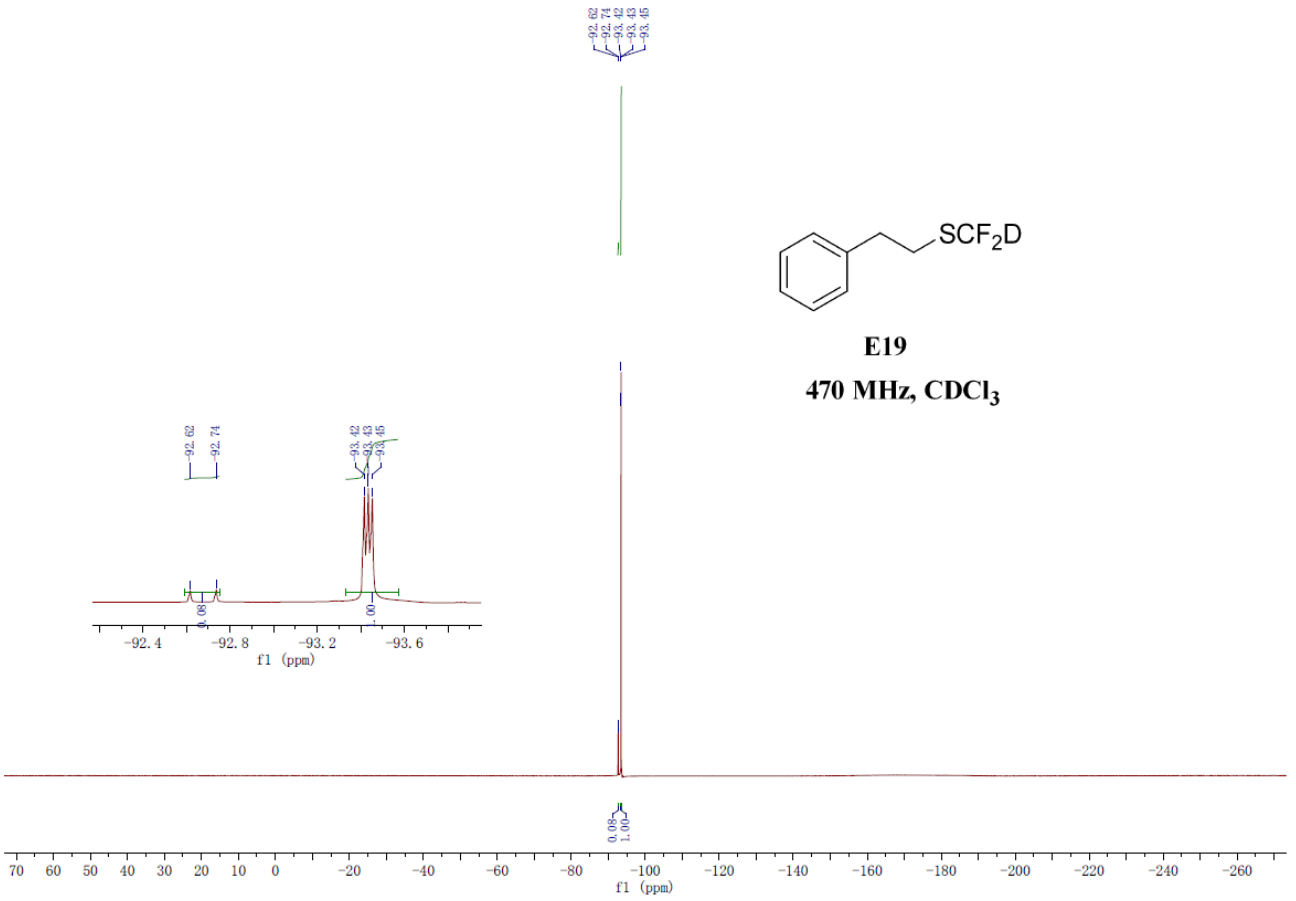
470 MHz, $CDCl_3$

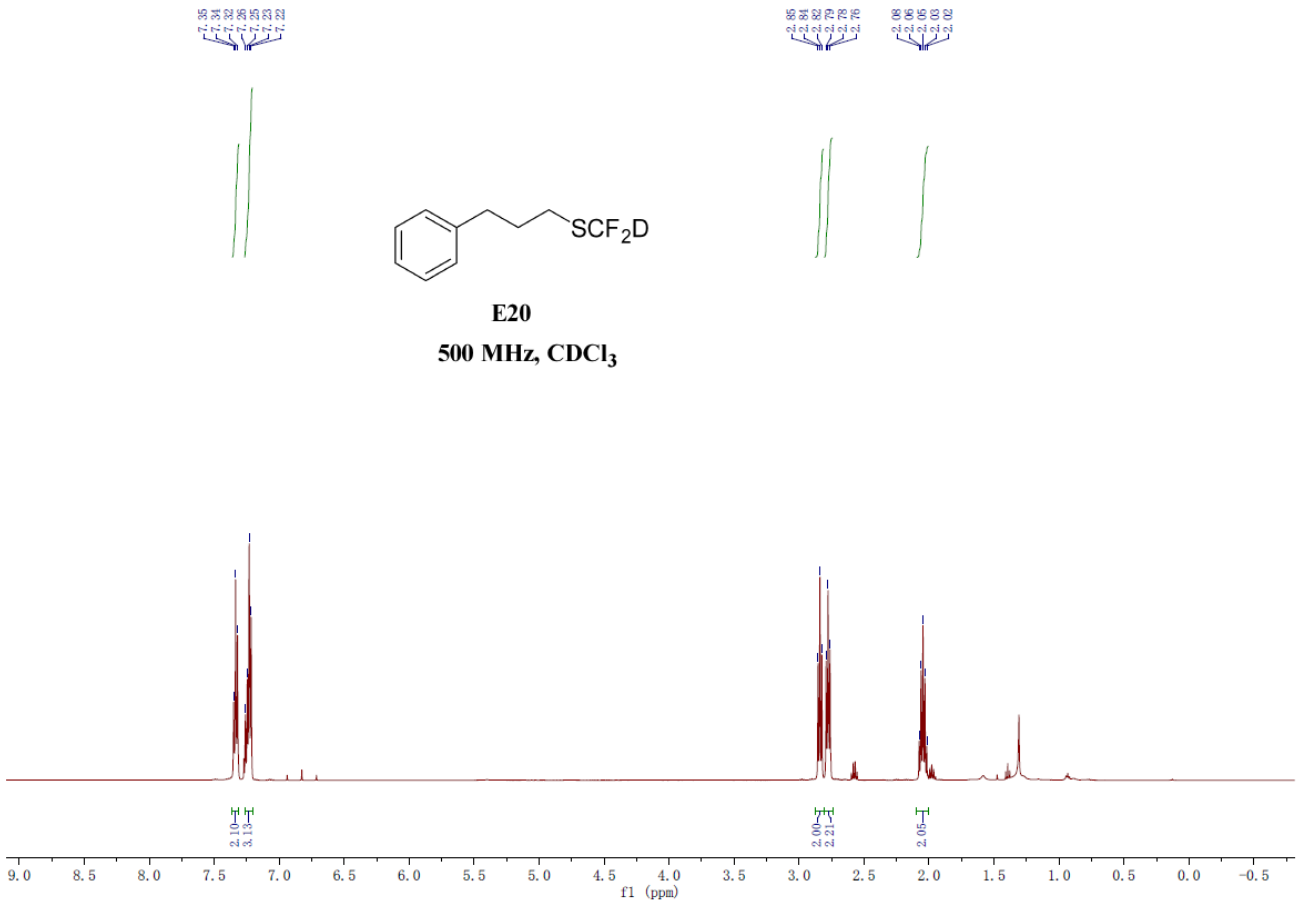


E19

500 MHz, $CDCl_3$

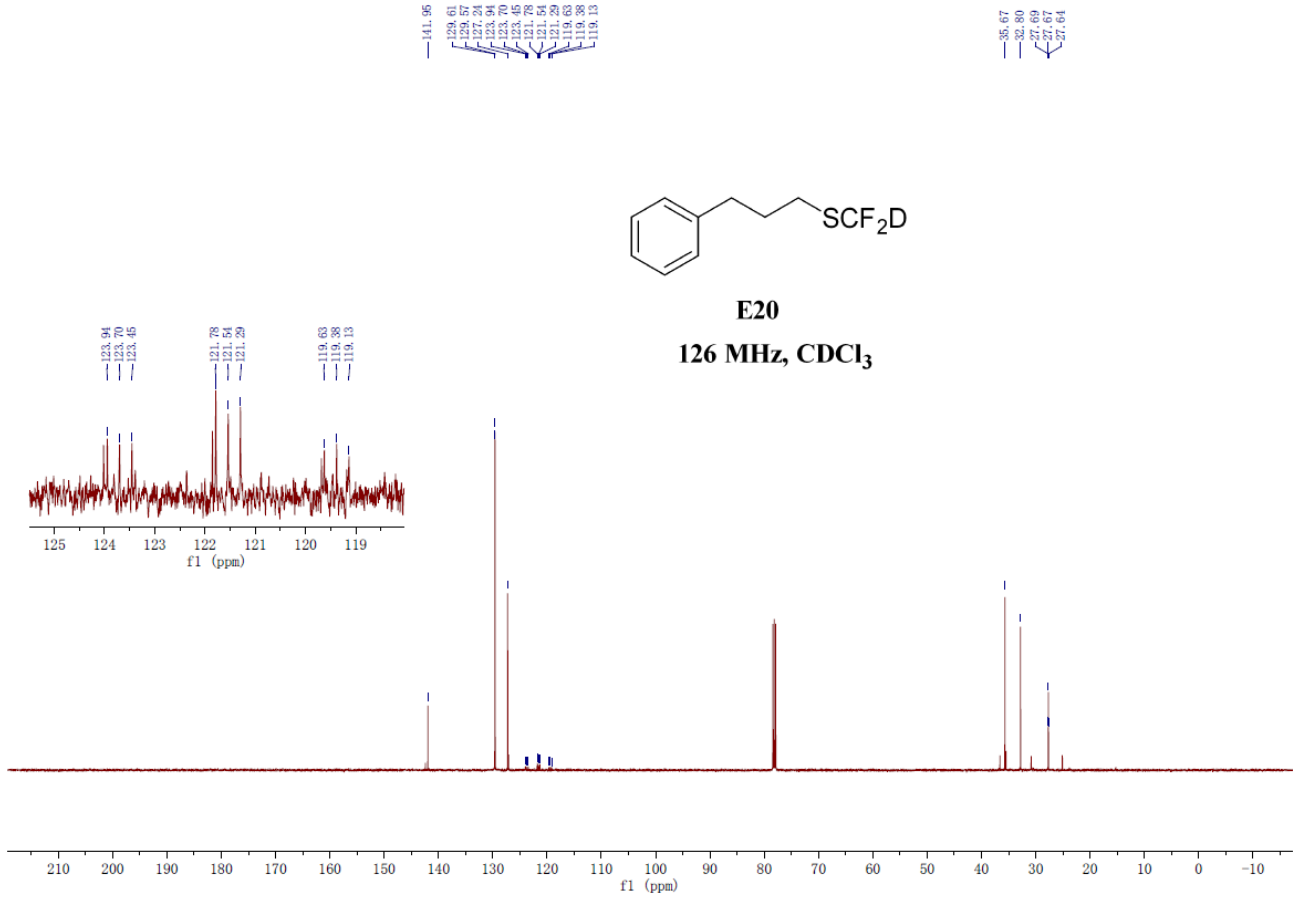

SCF2D
E19
126 MHz, CDCl3
f1 (ppm)


SCF2D
E19
470 MHz, CDCl3
f1 (ppm)



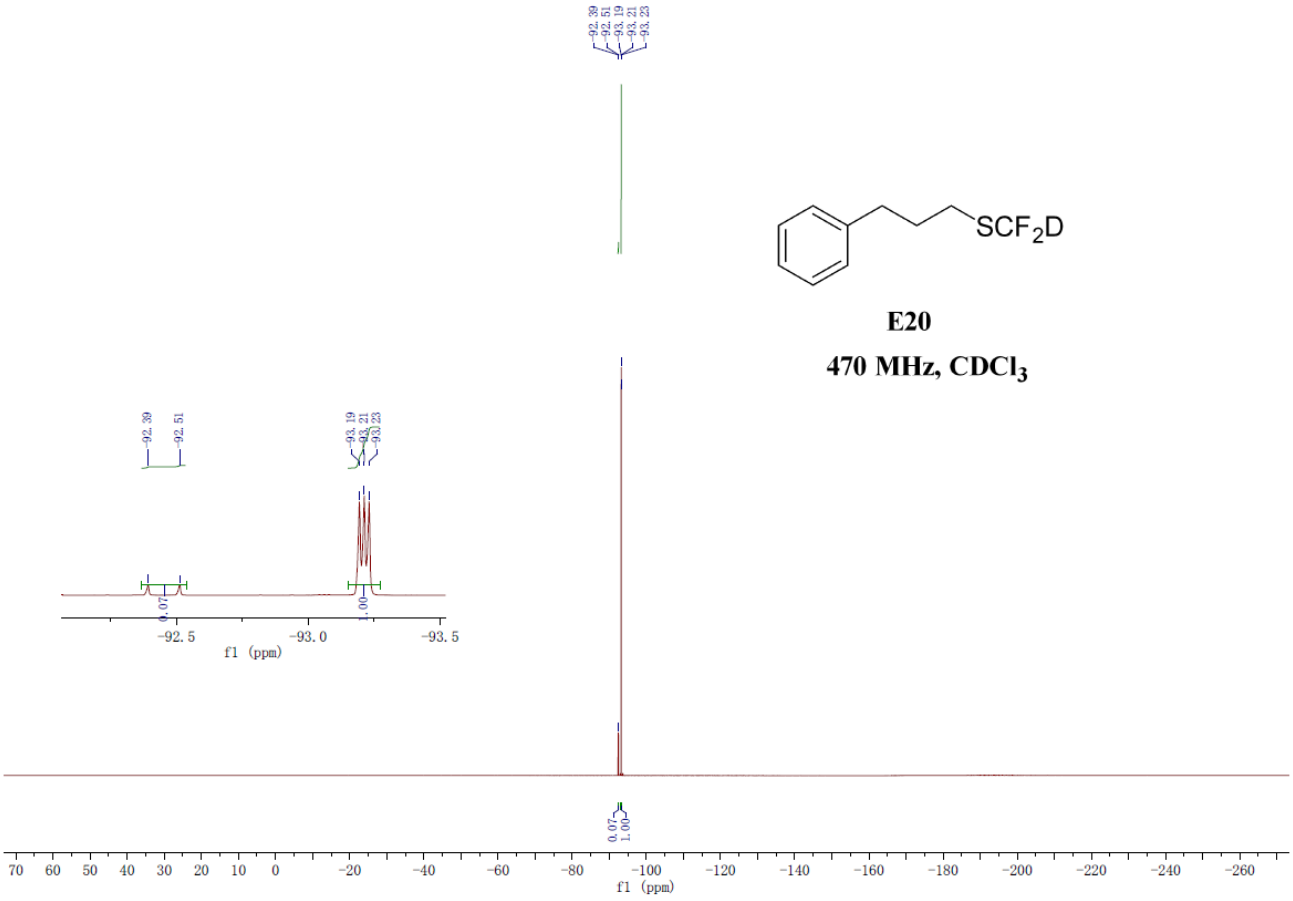
E20

500 MHz, $CDCl_3$



E20

126 MHz, $CDCl_3$


-92.39
-92.51
-93.19
-93.21
-93.23
SCF2D
E20
470 MHz, CDCl3
0.07
1.00
f1 (ppm)