

**Copper-mediated radical cross-coupling reaction of
2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) with phenols
or thiophenols**

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Support Information

Table of Contents

1, General Information	S2
2, Experimental Procedure and Characterization	S3
3, ¹⁹F, ¹H and ¹³C NMR spectra for new compounds	S18
4, Reference	S69

1, General Information

All reactions were carried out under the N₂ atmosphere, DMF and DMSO were distilled prior to use. Reagents were purchased at the commercial quality and used without further purification.

¹H NMR spectra were recorded at the Bruker 400 MHz or Varian 300 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS as a reference (CDCl₃ = 7.26 ppm). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

¹⁹F NMR spectra were recorded at the Bruker 300 MHz or Varian 300 MHz spectrometer without proton decoupling. Chemical shifts are reported in ppm relative to CFCl₃.

¹³C NMR spectra were recorded on a Bruker 100 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to TMS as a reference (CDCl₃ = 77.0 ppm).

IR spectra were collected on a Nicolet IN10 FT-IR spectrometer, are reported in terms of frequency of absorption (cm⁻¹).

EI-MS spectra were recorded on an Aligent 5973N MSD.

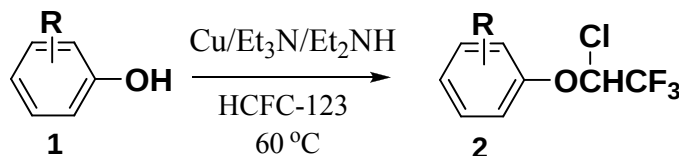
EI-HRMS spectra were recorded on a Waters Micromass GCT Premie.

ESI-MS spectra were recorded on an Aligent LC/MSD SL.

ESI-HRMS spectra were recorded on an APEXIII 7.0 TESLA FTMS.

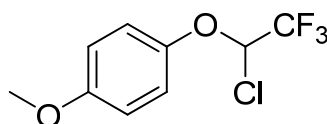
2, Experimental Procedure and Characterization

1) General procedure for Copper-mediated radical cross-coupling between HCFC-123 and phenols.



A 20 mL sealed tube was charged with Cu powder (10 mmol, 0.64 g) and filled with N₂. HCFC-123 (10 mL), *p*-MeOPhOH (1a, 5 mmol, 0.620 g), Et₃N (6.25 mmol, 627 mg) and Et₂NH (10 mmol, 0.731 g) were added into this sealed tube. The solution in the sealed tube was stirred at 60 °C for 3 h. After the solution was cool, the mixture was poured into Et₂O (50 mL). The precipitation was removed with filtration. The solvent was removed and the residue was purified by flash chromatography on a silica gel column using PE:DCM = 5:1 as the eluent. 2a was obtained as the colorless oil (1.14 g, 95% yield).

1-(1-chloro-2,2,2-trifluoroethoxy)-4-methoxybenzene (2a)



Colorless oil

¹⁹F NMR (282 MHz, CDCl₃): -80.0(d, *J* = 4 Hz);

¹H NMR (400 MHz, CDCl₃): 7.06(d, *J* = 9 Hz, 2H), 6.90(d, *J* = 9 Hz, 2H), 6.02(q, *J* = 4 Hz, 1H), 3.80(s, 3H);

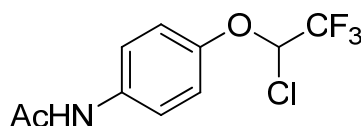
¹³C NMR (100 MHz, CDCl₃): 156.8, 148.6, 120.2(q, *J* = 280 Hz), 118.6, 114.9, 86.9 (q, *J* = 39 Hz, 55.5 Hz);

MS (EI): 240(M⁺, 15.71), 123(100), 95(20.29), 240(15.71), 77(11.73), 92(10.33);

HRMS (EI) M⁺ calcd for C₉H₈F₃O₂Cl: 240.0165, found 240.0164;

IR (KBr) ν/cm⁻¹: 2958, 1749, 1507, 1383, 1289, 1249, 1208, 1147, 1094, 1034.

N-(4-(1-chloro-2,2,2-trifluoroethoxy)phenyl)acetamide (2b)



White solid

m.p.: 102.7-103.5 °C

^{19}F NMR (282 MHz, DMSO): -80.0(d, $J = 4$ Hz);

^1H NMR (400 MHz, DMSO): 9.96(s, 1H), 7.58(d, $J = 9$ Hz, 2H), 7.29(q, $J = 4$ Hz, 1H),

7.13(d, $J = 9$ Hz, 2H), 2.00(s, 3H);

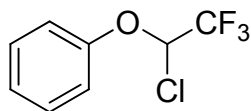
^{13}C NMR (100 MHz, DMSO): 168.6, 149.3, 136.5, 124.0, 120.8, 120.7(q, $J = 280$ Hz), 85.7(q, $J = 38$ Hz), 24.3.

MS (ESI): 268(M+1) $^+$;

HRMS (ESI) (M+Na) $^+$ calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NO}_2\text{Cl}$: 290.0166, found 290.0165;

IR (KBr) ν/cm^{-1} : 3295, 3134, 3050, 1666, 1604, 1537, 1513, 1407, 1376, 1214, 1146, 1085.

(1-chloro-2,2,2-trifluoroethoxy)benzene (2c)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -80.8(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.37-7.40(m, 2H), 7.19(t, $J = 8$ Hz, 1H), 7.12(d, $J = 8$ Hz, 2H),

6.12(q, $J = 4$ Hz, 1H);

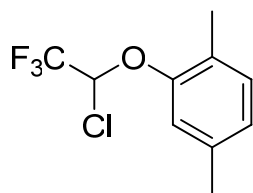
^{13}C NMR (100 MHz, CDCl_3): 154.6, 129.9, 124.7, 120.2(q, $J = 279$ Hz), 116.6, 85.4(q, $J = 40$ Hz);

MS (EI): 210(M $^+$, 74.72), 77(100), 65(74.37), 175(59.61), 93(59.27), 141(31.26);

HRMS (EI) M $^+$ calcd for $\text{C}_8\text{H}_6\text{F}_3\text{OCl}$: 210.0059, found 210.0060

IR (KBr) ν/cm^{-1} : 3074, 2960, 1749, 1595, 1493, 1382, 1289, 1265, 1215, 1149, 1098.

2-(1-chloro-2,2,2-trifluoroethoxy)-1,4-dimethylbenzene (2d)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -80.3(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.09(d, $J = 8$ Hz, 1H), 6.89-6.92(m, 2H), 6.11(q, $J = 4$ Hz, 1H), 2.36(s, 3H), 2.24(s, 3H);

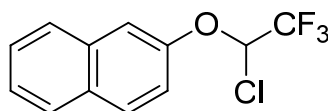
^{13}C NMR (100 MHz, CDCl_3): 153.0, 137.2, 131.3, 125.5, 125.2, 120.9(q, $J = 279$ Hz), 115.4, 86.0(q, $J = 40$ Hz), 21.1, 15.3;

MS (EI): 238(M^+ , 47.17), 121(100), 77(49.90), 91(41.25), 105(30.24), 203(17.06);

HRMS (EI) ($\text{M}-\text{H}$) $^+$ calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{OCl}$: 238.0372, found 238.0373;

IR (KBr) ν/cm^{-1} : 2929, 1749, 1623, 1511, 1308, 1265, 1246, 1194, 1145, 1089.

1-(1-chloro-2,2,2-trifluoroethoxy)naphthalene (2e)



White solid

m.p.: 46.1-47.0°C

^{19}F NMR (282 MHz, CDCl_3): -79.9(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 8.17-8.19(m, 1H), 7.84-7.86(m, 1H), 7.66(d, $J = 8$ Hz, 1H), 7.54-7.56(m, 2H), 7.41-7.45(m, 1H), 7.18(d, $J = 8$ Hz, 1H), 6.31(q, $J = 4$ Hz, 1H);

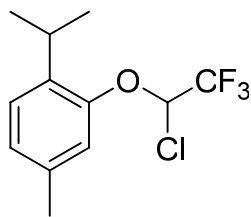
^{13}C NMR (100 MHz, CDCl_3): 150.5, 149.1, 134.6, 127.6, 127.0, 125.6, 125.1, 124.5, 121.3, 120.5(q, $J = 280$ Hz), 109.3, 85.5(q, $J = 39$ Hz);

MS (EI): 260(M^+ , 26.23), 115(100), 145(87.05), 127(32.09), 126(12.55), 116(10.75);

HRMS (EI) M^+ calcd for $\text{C}_{12}\text{H}_8\text{F}_3\text{OCl}$: 260.0216, found 260.0215;

IR (KBr) ν/cm^{-1} : 3072, 2955, 1635, 1599, 1577, 1508, 1464, 1294, 1261, 1236, 1193, 1153, 1125.

2-(1-chloro-2,2,2-trifluoroethoxy)-1-isopropyl-4-methylbenzene (2f)



White solid

m.p.:32.9-33.6°C

^{19}F NMR (282 MHz, CDCl_3): -80.0(d, $J = 4$ Hz);

^1H NMR(400 MHz, CDCl_3):7.18(d, $J = 8$ Hz,1H), 6.96(d, $J = 8$ Hz,1H), 6.68(s,1H), 6.16(q, $J = 4$ Hz,1H), 3.24-3.21(m,1H), 2.36(s,3H), 1.19-1.23(m,6H).

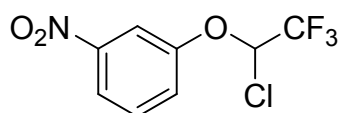
^{13}C NMR (100 MHz, CDCl_3):151.7, 136.9, 135.8, 126.9, 125.3, 120.9(q, $J = 279\text{Hz}$), 85.5(q, $J = 40$ Hz), 26.4, 22.8, 21.1.

MS (EI):266(M^+ , 30.41), 251(100), 134(56.51), 91(48.26), 115(41.31),117(39.33);

HRMS (EI) M^+ calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{OCl}$:266.0685, found 266.0687;

IR (KBr) ν/cm^{-1} :2969, 1892, 1617, 1578, 1508, 1389, 1296, 1281, 1264, 1242, 1191, 1157.

1-(1-chloro-2,2,2-trifluoroethoxy)-3-nitrobenzene (2g)



Yellow solid

m.p.:32.8-33.3°C

^{19}F NMR (282 MHz, CDCl_3): -80.0(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3):8.05(d, $J = 8$ Hz,1H), 7.97(s, 1H), 7.58(t, $J=8$ Hz,1H), 7.44-7.46(m,1H), 6.19(q, $J = 4$ Hz,1H);

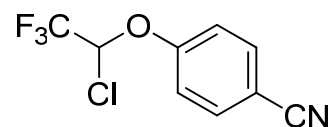
^{13}C NMR (100 MHz, CDCl_3):154.6, 149.1, 130.8, 121.8, 120.8(q, $J = 280$ Hz), 119.5, 111.7, 84.5(q, $J=40$ Hz);

MS (EI):255(M^+ , 59.70), 92(100), 76(42.01), 64(40.64), 63(35.18),50(28.29);

HRMS (EI) M^+ calcd for $\text{C}_8\text{H}_5\text{F}_3\text{O}_3\text{NCl}$:254.9910, found 254.9908;

IR (KBr) ν/cm^{-1} : 3089, 2980, 1533, 1478, 1354, 1228, 1197, 1152, 1111, 1085.

4-(1-chloro-2,2,2-trifluoroethoxy)benzonitrile (2h)



Light yellow oil

^{19}F NMR (282 MHz, CDCl_3): -80.2(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.68(d, $J = 9$ Hz, 2H), 7.19(d, $J = 9$ Hz, 2H), 6.18(q, $J = 4$ Hz, 1H);

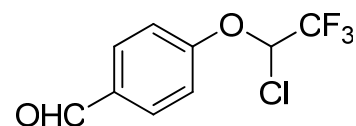
^{13}C NMR (100 MHz, CDCl_3): 157.1, 134.3, 120.5(q, $J = 280$ Hz), 118.0, 117.2, 108.4, 83.7(q, $J = 40$ Hz);

MS (EI): 235(M^+ , 100), 102(78.80), 90(65.30), 200(59.52), 166(58.19);

HRMS (EI) ($\text{M}-\text{H}$) $^+$ calcd for $\text{C}_9\text{H}_5\text{F}_3\text{ONCl}$: 235.0012, found 235.0009;

IR (KBr) ν/cm^{-1} : 2231, 1606, 1507, 1385, 1288, 1231, 1153, 1088.

4-(1-chloro-2,2,2-trifluoroethoxy)benzaldehyde (2i)



Light yellow oil

^{19}F NMR (282 MHz, CDCl_3): -80.1(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 9.94 (s, 1H), 7.91(d, $J = 8$ Hz, 2H), 7.23(d, $J = 8$ Hz, 2H), 6.22(q, $J = 4$ Hz, 1H);

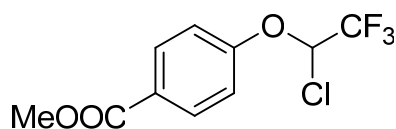
^{13}C NMR (100 MHz, CDCl_3): 190.4, 158.6, 132.9, 131.9, 120.5(q, $J = 280$ Hz), 116.7, 83.9(q, $J = 40$ Hz);

MS (EI): 238(M^+ , 67.60), 237(100), 239(38.94), 65(25.56), 105(25.09), 77(23.09);

HRMS (EI) ($\text{M}-\text{H}$) $^+$ calcd for $\text{C}_9\text{H}_5\text{F}_3\text{O}_2\text{Cl}$: 236.9930, found 236.9934;

IR (KBr) ν/cm^{-1} : 3077, 2835, 2744, 1698, 1602, 1589, 1507, 1387, 1225, 1153, 1089.

methyl 4-(1-chloro-2,2,2-trifluoroethoxy)benzoate (2j)



White solid

m.p.:51.2-52.2°C

^{19}F NMR (282 MHz, CDCl_3):-80.1(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3):8.05(d, $J = 8$ Hz,2H), 7.12(d, $J = 8$ Hz,2H), 6.18(q, $J = 4$ Hz,1H), 3.88(s,3H);

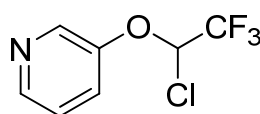
^{13}C NMR (100 MHz, CDCl_3):166.0, 157.6, 131.8, 126.5, 120.6(q, $J = 280$ Hz), 116.4, 84.1(q, $J = 39$ Hz), 52.1;

MS (EI):268(M^+ , 30.77), 237(100), 239(32.31), 92(30.13), 121(19.16),76(18.43);

HRMS (EI) M^+ calcd for $\text{C}_{10}\text{H}_8\text{F}_3\text{O}_3\text{Cl}$:268.0114, found 268.0117;

IR (KBr) v/cm^{-1} :2983, 1707, 1608, 1509, 1292, 1227, 1151, 1091.

3-(1-chloro-2,2,2-trifluoroethoxy)pyridine (2k)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3):-79.9(d, $J = 4\text{Hz}$);

^1H NMR (400 MHz, CDCl_3):8.44-8.99(d, $J = 8$ Hz,2H), 7.32-7.44(m,2H), 6.14(q, $J = 4$ Hz,1H);

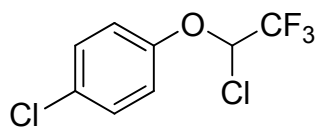
^{13}C NMR (100 MHz, CDCl_3):151.1, 146.0, 139.6, 124.2, 124.1, 120.5(q, $J = 280$ Hz), 85.3(q, $J = 40$ Hz);

MS (EI):211(M^+ , 14.55), 142(100), 211(71.48), 78(62.94), 91(58.15),66(56.64);

HRMS (EI) M^+ calcd for $\text{C}_7\text{H}_5\text{F}_3\text{NOCl}$:211.0012, found 211.0009;

IR (KBr) v/cm^{-1} :3066, 2953, 1732, 1578, 1477, 1432, 1292, 1257, 1190. 1153..

1-chloro-4-(1-chloro-2,2,2-trifluoroethoxy)benzene (2l)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -80.9(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.34(d, $J = 9$ Hz, 2H), 7.05(d, $J = 9$ Hz, 2H), 6.05(q, $J = 4$ Hz, 1H);

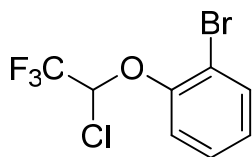
^{13}C NMR (100 MHz, CDCl_3): 151.1, 130.1, 129.9, 120.6(q, $J = 280$ Hz), 118.3, 85.4(q, $J = 40$ Hz);

MS (EI): 244(M^+ , 28.00), 127(100), 99(57.20), 111(42.98), 75(33.25), 129(31.91);

HRMS (EI) M^+ calcd for $\text{C}_8\text{H}_5\text{F}_3\text{OCl}_2$: 243.9670, found 243.9672;

IR (KBr) ν/cm^{-1} : 2959, 1749, 1589, 1490, 1383, 1289, 1267, 1222, 1174, 1095.

1-bromo-2-(1-chloro-2,2,2-trifluoroethoxy)benzene (2m)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -80.3(d, $J = 4$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.61(d, $J = 8$ Hz, 1H), 7.34(t, $J = 8$ Hz, 1H), 7.18(d, $J = 8$ Hz, 1H), 7.08(t, $J = 8$ Hz, 1H), 6.13(q, $J = 4$ Hz, 1H);

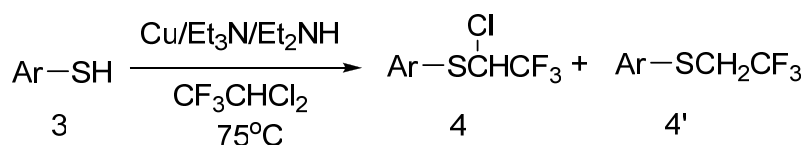
^{13}C NMR (100 MHz, CDCl_3): 151.1, 134.2, 128.6, 126.3, 120.6(q, $J = 280$ Hz), 118.4, 113.9, 85.9(q, $J = 40$ Hz);

MS (EI): 290(M^+ , 100), 171(95.71), 173(93.70), 288(76.16), 143(68.10);

HRMS (EI) ($\text{M}-\text{H}$) $^+$ calcd for $\text{C}_8\text{H}_5\text{F}_3\text{OBrCl}$: 287.9164, found 287.9168;

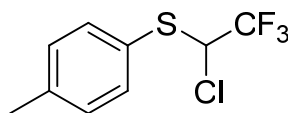
IR (KBr) ν/cm^{-1} : 3071, 2963, 1579, 1477, 1445, 1381, 1292, 1263, 1231, 1194, 1150.

2) General procedure for Copper-mediated radical cross-coupling between HCFC-123 and thiophenols.



A 20 mL sealed tube was charged with Cu powder (8.5 mmol, 0.544 g) and filled with N₂. HCFC-123(10 mL), *p*-tolSH (3a, 5 mmol, 0.620 g), Et₃N (6.25 mmol, 627 mg) and Et₂NH (15 mmol, 1.096 g) were added into this sealed tube. The solution in the sealed tube was stirred at 75 °C for 24 h. After the solution was cool, the mixture was poured into Et₂O (50 mL). The precipitation was removed with filtration. The solvent was removed and the residue was purified by flash chromatography on a silica gel column using PE:DCM = 20:1 as the eluent. **4a** was obtained as the colorless oil (0.948 g, 79% yield).

(1-chloro-2,2,2-trifluoroethyl)(p-tolyl)sulfane¹ (4a)

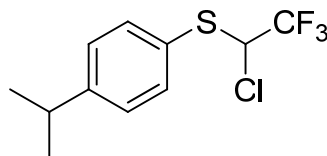


Colorless oil

¹⁹FNMR (282 MHz, CDCl₃): -72.4(d, *J* = 6.6 Hz);

¹HNMR (400 MHz, CDCl₃): 2.37(s, 3H), 5.21(q, *J* = 6.4 Hz, 1H), 7.20(d, *J* = 8 Hz, 2H), 7.50(d, *J* = 8 Hz, 2H).

(1-chloro-2,2,2-trifluoroethyl)(4-isopropylphenyl)sulfane (4b)



Colorless oil

¹⁹FNMR (282 MHz, CDCl₃): -72.5(d, *J* = 7 Hz);

¹HNMR (400 MHz, CDCl₃): 7.53(d, *J* = 8.4 Hz, 2H), 7.25(d, *J* = 8.4 Hz, 2H), 5.22(q, *J* = 6.3 Hz, 1H), 2.87-2.97(m, 1H), 1.25(d, *J* = 7 Hz, 6H);

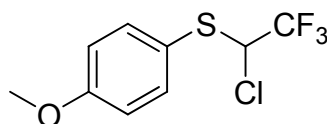
¹³CNMR (100 MHz, CDCl₃): 151.3, 135.1, 127.6, 126.2, 122.8(q, *J* = 280 Hz), 65.8 (q, *J* = 35 Hz), 33.9, 23.6;

MS (EI):268(M^+ , 49.46), 253(100), 255(38.31), 136(26.69), 270(18.83), 135(15.19);

HRMS (EI) M^+ calcd for $C_{11}H_{12}F_3SCl$:268.0296, found 268.0304;

IR (KBr) ν/cm^{-1} :2965, 2932, 2873, 1595, 1488, 1460, 1303, 1254, 1171, 1115.

(1-chloro-2,2,2-trifluoroethyl)(4-methoxyphenyl)sulfane (4c)



Colorless oil

^{19}F NMR (282 MHz, $CDCl_3$):-72.3(d, $J = 5$ Hz);

1H NMR (400 MHz, $CDCl_3$):7.56(d, $J = 8.4$ Hz,2H), 6.92(d, $J = 8.4$ Hz,2H), 5.15(q, $J = 6.6$ Hz,1H), 3.83(s, 3H)

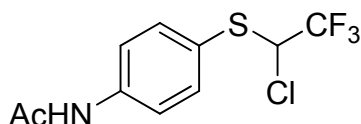
^{13}C NMR (100 MHz, $CDCl_3$):160.4, 136.4, 121.8(q, $J = 279$ Hz), 118.3, 113.9, 64.6(m), 54.3;

MS (EI):256(M^+ , 53.63), 139(100), 258(20.90), 95(16.50), 140(16.43), 96(15.52);

HRMS (EI) M^+ calcd for $C_9H_8F_3SOCl$:255.9936, found 255.9939;

IR (KBr) ν/cm^{-1} :2967, 2840, 1593, 1495, 1304, 1292, 1250, 1173, 1115.

N-(4-(1-chloro-2,2,2-trifluoroethylthio)phenyl)acetamide (4d)



White solid

^{19}F NMR (282 MHz, $CDCl_3$):-72.3(d, $J = 6$ Hz);

1H NMR (400 MHz, $CDCl_3$):7.55(br, 4H), 7.46(br, 1H), 5.17(q, $J = 6.4$ Hz,1H), 2.17(s, 3H);

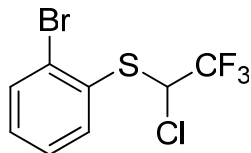
^{13}C NMR (100 MHz, DMSO):169.2, 141.6, 136.2, 123.6(q, $J = 279$ Hz), 121.1, 120.0, 64.0(q, $J = 34$ Hz), 24.5;

MS (EI):283(M^+ , 4.51), 79(100), 124(92.30), 78(61.15), 51(47.37), 52(34.64);

HRMS (EI) M^+ calcd for $C_{10}H_9NOF_3SCl$:283.0045, found 283.0046;

IR (KBr) ν/cm^{-1} : 3318, 1678, 1592, 1537, 1495, 1396, 1304, 1257, 1106.

(2-bromophenyl)(1-chloro-2,2,2-trifluoroethyl)sulfane (4e)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -72.6(d, $J = 5.7$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.69-7.71(m, 2H), 7.27-7.39(m, 2H), 5.42(q, $J = 6.2$ Hz, 1H);

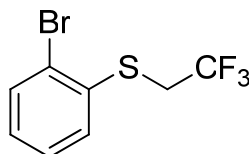
^{13}C NMR (100 MHz, CDCl_3): 136.2, 133.9, 131.3, 130.8, 129.0, 128.3, 125.6(q, $J = 280$ Hz), 63.9(m);

MS (EI): 306(M^+ , 49.00), 108(100), 190(55.46), 304(36.23), 189(30.45), 269(28.85);

HRMS (EI) M^+ calcd for $\text{C}_8\text{H}_5\text{F}_3\text{SBrCl}$: 303.8936, found 303.8941;

IR (KBr) ν/cm^{-1} : 3063, 2970, 1449, 1305, 1252, 1172, 1115, 1022, 809, 745.

(2-bromophenyl)(2,2,2-trifluoroethyl)sulfane (4'e)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -66.1(t, $J = 9.3$ Hz);

^1H NMR (400 MHz, CDCl_3): 7.43-7.52(m, 2H), 7.06-7.21(m, 2H), 3.38(q, $J = 9.8$ Hz, 2H);

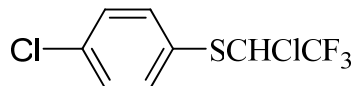
^{13}C NMR (100 MHz, CDCl_3): 134.1, 133.5, 133.0, 129.3, 128.0, 126.7, 125.4(q, $J = 275$ Hz), 36.6(q, $J = 33$ Hz);

MS (EI): 272(M^+ , 100), 270(93.01), 122(92.25), 108(79.36), 203(33.73), 201(33.58);

HRMS (EI) M^+ calcd for $\text{C}_8\text{H}_6\text{F}_3\text{SBr}$: 269.9326, found 269.9329;

IR (KBr) ν/cm^{-1} : 3062, 2947, 1450, 1309, 1269, 1240, 1130, 1080, 750.

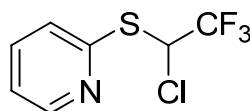
(4-chlorophenyl)(2,2,2-trifluoroethyl)sulfane (4f)¹



¹⁹FNMR (282 MHz, CDCl₃): -72.2(d, *J* = 8 Hz);

¹HNMR (300 MHz, CDCl₃): 7.56(d, *J* = 8 Hz, 2H), 7.38(d, *J* = 8 Hz, 2H), 5.22(q, *J* = 6.4 Hz, 1H);

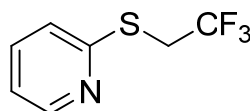
2-(1-chloro-2,2,2-trifluoroethylthio)pyridine (4g)¹



¹⁹FNMR (282 MHz, CDCl₃): -72.5(d, *J* = 6 Hz)

¹HNMR (300 MHz, CDCl₃): 8.52(d, *J* = 5 Hz, 1H), 7.59-7.68(m, 1H), 7.15-7.27(m, 2H), 6.41(q, *J* = 7 Hz, 1H).

2-(2,2,2-trifluoroethylthio)pyridine (4'g)



¹⁹FNMR (282 MHz, CDCl₃): -66.1(t, *J* = 9.3 Hz);

¹HNMR (400 MHz, CDCl₃): 8.46(d, *J* = 4.5 Hz, 1H), 7.53-7.57(m, 1H), 7.24-7.27(m, 1H), 7.06-7.09(m, 1H), 4.06(q, *J* = 9.8 Hz, 2H);

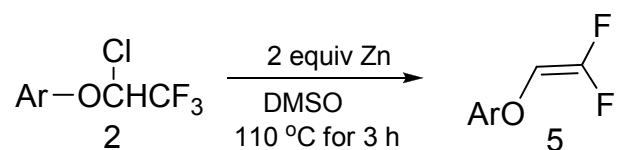
¹³CNMR (100 MHz, CDCl₃): 154.5, 149.3, 136.5, 125.3(q, *J* = 275 Hz), 122.3, 120.5, 31.1(q, *J* = 33 Hz);

MS (EI): 193(M⁺, 87.38), 79(100), 122(92.25), 124(77.64), 173(74.18), 78(51.22);

HRMS (EI) M⁺ calcd for C₇H₆F₃SN: 193.0173, found 193.0172;

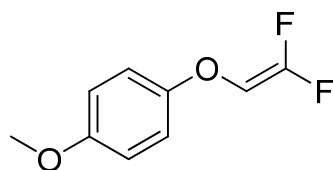
IR (KBr) ν/cm^{-1} : 3052, 3000, 2946, 1580, 1560, 1456, 1418, 1308, 1273, 1243, 1119.

3) Synthesis of difluoroviny aryl ether from 2



A 10mL schlenk tube was charged with Zn (10 mmol, 0.650 g) and filled with N₂, then nitrogen purged solvent DMSO (10 mL) and **2e** (5 mmol, 1.305 g) was added. The mixture was stirred at 110 °C for about 3 h detected by TLC. After the reaction was over, the mixture was poured into Et₂O (50 mL). The resulted solution was washed with water and dried over Na₂SO₄. The solvent was removed and the residue was purified by flash chromatography on a silica gel column using PE as the eluent. **5e** was obtained as colorless oil (0.948 g, 92% yield).

1-(2,2-difluorovinyl)-4-methoxybenzene (**5a**)



Colorless oil

¹⁹F NMR (282 MHz, CDCl₃): -100.8(dd, *J* = 72, 14 Hz, 1F), -118.7(d, *J* = 72 Hz, 1F);

¹H NMR (400 MHz, CDCl₃): 6.93(d, *J* = 9 Hz, 2H), 6.83(d, *J* = 8 Hz, 2H), 6.00(dd, *J* = 14, 3 Hz, 1H), 3.76(s, 3H);

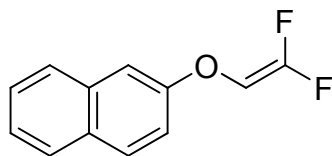
¹³C NMR (100 MHz, CDCl₃): 156.6(dd, *J* = 290, 278 Hz), 155.4, 151.1, 116.4, 114.7, 105.3(dd, *J* = 55, 15 Hz), 55.6.

MS (EI): 186(M⁺, 100), 171(44.14), 157(39.51), 123(37.87), 77(24.12);

HRMS (EI) M⁺ calcd for C₉H₈F₂O₂: 186.0492, found 186.0494;

IR (KBr) ν/cm⁻¹: 3058, 3005, 2838, 1770, 1507, 1348, 1241, 1226, 1134, 1036.

1-(2,2-difluorovinyl) naphthalene (**5e**)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -97.7(dd, $J = 68, 14$ Hz, 1F), -115.6(d, $J = 68$ Hz, 1F);

^1H NMR (400 MHz, CDCl_3): 8.27-8.29(m, 1H),

7.83-7.86(m, 1H), 7.53-7.58(m, 3H), 7.39(t, $J = 8$ Hz, 1H), 6.97(d, $J = 8$ Hz, 1H), 6.24(dd, $J = 15, 5$ Hz, 1H);

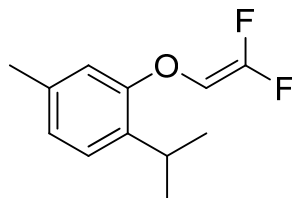
^{13}C NMR (CDCl_3): 156.9(dd, $J = 291, 279$ Hz), 153.0, 134.0, 127.5, 126.8, 125.9, 125.4, 125.0, 122.7, 121.6, 107.1, 104.6(dd, $J = 56, 15$ Hz);

MS (EI): 206(M^+ , 100), 127(58.31), 177(57.25), 186(23.03), 126(21.92), 128(17.13);

HRMS (EI) M^+ calcd for $\text{C}_{12}\text{H}_8\text{F}_2\text{O}$: 206.0543, found 206.0542;

IR (KBr) ν/cm^{-1} : 3060, 1769, 1597, 1579, 1511, 1463, 1395, 1342, 1246, 1185.

2-(2,2-difluorovinyl)-1-isopropyl-4-methylbenzene (5f)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -99.0(dd, $J = 73, 16$ Hz, 1F), -117.0(d, $J = 73$ Hz, 1F);

^1H NMR (400 MHz, CDCl_3): 7.15(d, $J = 8$ Hz, 1H), 6.88(d, $J = 8$ Hz, 1H), 6.77(s, 1H),

6.05(dd, $J = 15, 3$ Hz, 1H), 3.27-3.34(m, 1H), 3.24(s, 3H), 1.24(d, $J = 7$ Hz, 6H);

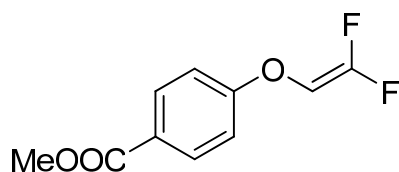
^{13}C NMR (100 MHz, CDCl_3): 156.6(dd, $J = 290, 278$ Hz), 154.3, 136.6, 134.3, 126.5, 123.6, 114.2, 104.8(dd, $J = 55, 15$ Hz), 26.7, 22.7, 21.0;

MS (EI): 212(M^+ , 100), 177(91.04), 197(61.59), 91(56.50), 115(41.24), 105(35.59);

HRMS (EI) M^+ calcd for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}$: 212.1013, found 212.1017;

IR (KBr) ν/cm^{-1} : 2964, 2929, 2872, 1769, 1617, 1507, 1416, 1347, 1420, 1177, 1138.

methyl 4-(2,2-difluorovinyl)oxybenzoate (5j)



White solid

m.p.: 32.2-33.1 °C;

^{19}F NMR (282 MHz, CDCl_3): -96.0(dd, $J = 66, 16$ Hz, 1F), -114.4(d, $J = 66$ Hz, 1F);

^1H NMR (400 MHz, CDCl_3): 8.00(d, $J = 9$ Hz, 2H), 7.01(d, $J = 9$ Hz, 2H), 6.00(dd, $J = 15, 3$ Hz, 1H), 3.87(s, 3H);

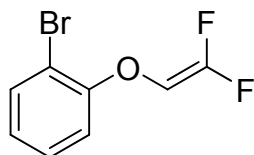
^{13}C NMR (100 MHz, CDCl_3): 166.4, 160.5, 156.7(dd, $J = 291, 279$ Hz), 131.7, 124.8, 114.8, 103.9(dd, $J = 56, 16$ Hz), 52.0;

MS (EI): 214(M^+ , 45.89), 189(100), 127(14.59), 136(11.81), 155(10.56), 184(10.11);

HRMS (EI) M^+ calcd for $\text{C}_{10}\text{H}_8\text{F}_2\text{O}_3$: 214.0442, found 214.0441;

IR (KBr) ν/cm^{-1} : 3067, 2955, 1770, 1722, 1606, 1506, 1436, 1283, 1251, 1168, 1112.

1-bromo-2-(2,2-difluorovinyl)oxybenzene (5m)



Colorless oil

^{19}F NMR (282 MHz, CDCl_3): -97.0(dd, $J = 66, 16$ Hz, 1F), -115.4(d, $J = 66$ Hz, 1F);

^1H NMR (400 MHz, CDCl_3): 8.00(d, $J = 9$ Hz, 2H), 7.01(d, $J = 9$ Hz, 2H), 6.00(dd, $J = 15, 3$ Hz, 1H);

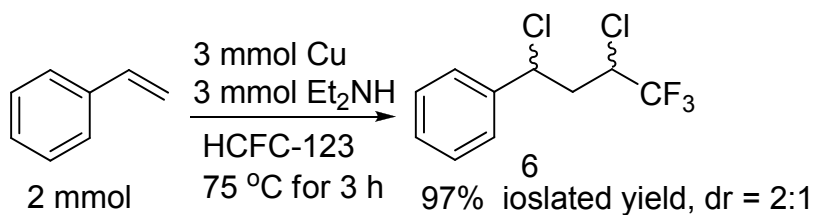
^{13}C NMR (100 MHz, CDCl_3): 156.8(dd, $J = 290, 279$ Hz), 153.7, 133.8, 128.5, 124.2, 114.9, 111.8, 104.6(dd, $J = 57, 16$ Hz);

MS (EI): 234(M^+ , 61.30), 127(100), 155(93.24), 236(61.41), 75(38.97), 76(37.63);

HRMS (EI) M^+ calcd for $\text{C}_8\text{H}_5\text{F}_2\text{OBr}$: 233.9492, found 233.9494;

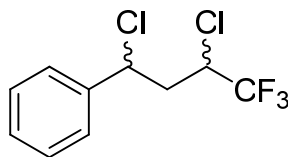
IR (KBr) ν/cm^{-1} : 3066, 1769, 1588, 1506, 1475, 1444, 1351, 1250, 1143, 930.

4) Trapping the radical intermediate with styrene



A 10mL sealed tube with charged with Cu powder (3 mmol, 0.192 g) and filled with N₂. HCFC-123 (4 mL), styrene (2 mmol, 0.208 g) and Et₂NH (10 mmol, 0.731 g) were added into this sealed tube. The solution in the sealed tube was stirred at 75 °C for 3 h. After the solution was cool, the mixture was poured into Et₂O (50 mL). The precipitation was removed with filtration. The solvent was removed and the residue was purified by flash chromatography on a silica gel column using PE as the eluent. **6** was obtained as the colorless oil (0.497 g, 97% yield).

(1,3-dichloro-4,4,4-trifluorobutyl)benzene (**6**)



Colorless oil

¹⁹F NMR (282 MHz, CDCl₃): -74.8(d, *J* = 7.6 Hz, 0.66*3F), -75.0(d, *J* = 6.3 Hz, 0.32*3F);

¹H NMR (400 MHz, CDCl₃): 7.35-7.41(m, 5H), 5.18(dd, *J* = 11.4, 1.8 Hz, 0.66H), 5.10(dd, *J* = 10, 5.3 Hz, 0.32H), 4.59-4.64(m, 0.67H), 3.66-3.70(m, 0.32H), 2.67-2.77(m, 1.4H), 2.29-2.36(m, 0.7H);

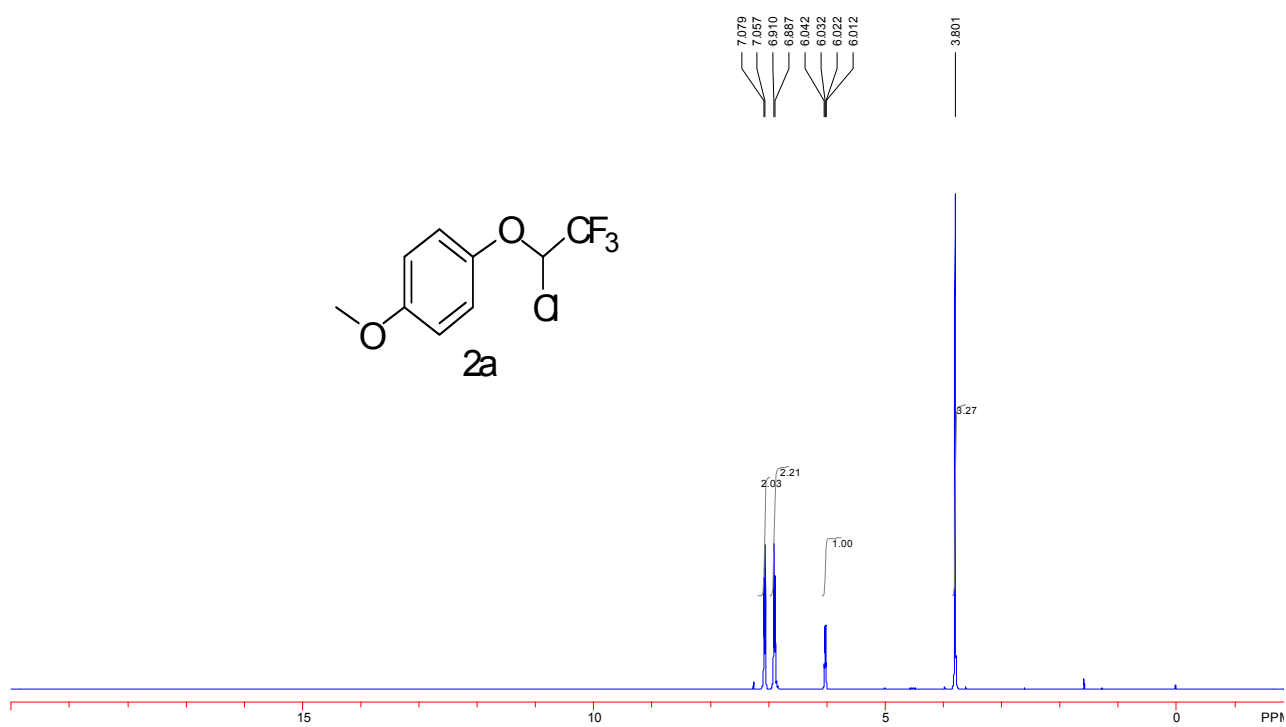
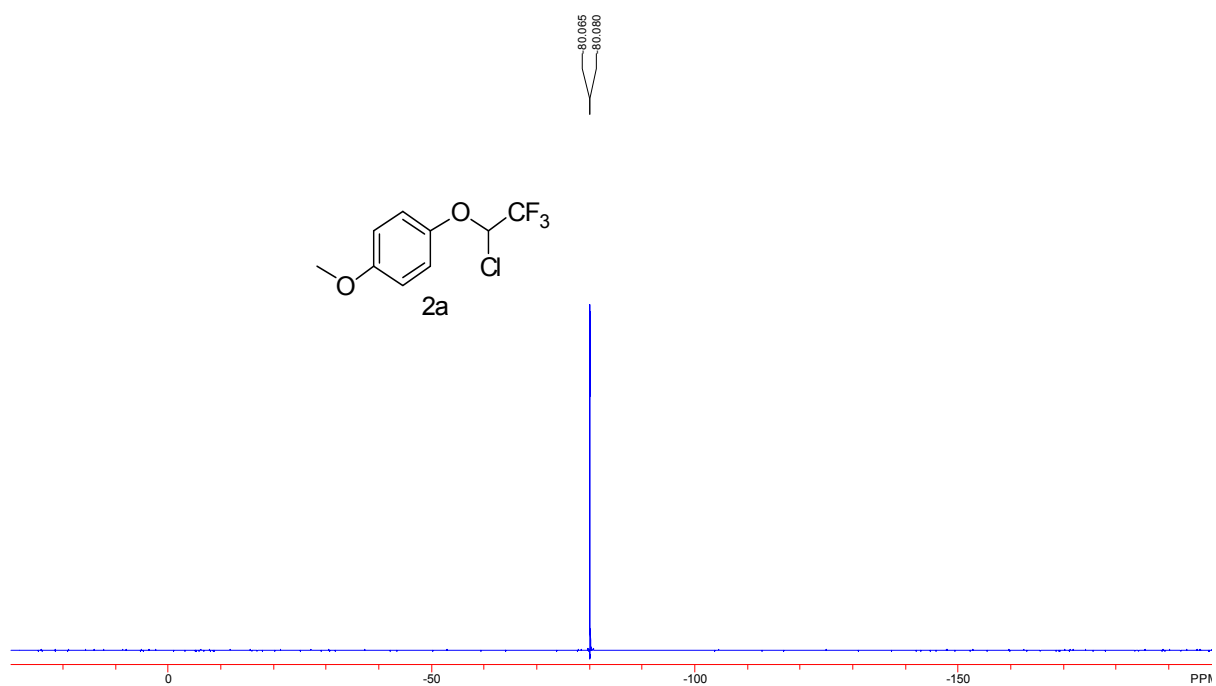
¹³C NMR (100 MHz, CDCl₃): 139.9, 138.3, 129.3, 129.2, 129.0, 128.9, 127.1, 126.8, 123.9(q, *J* = 279 Hz), 123.6(q, *J* = 279 Hz), 59.1, 57.9, 55.4(q, *J* = 34 Hz), 54.5(q, *J* = 34 Hz), 41.4;

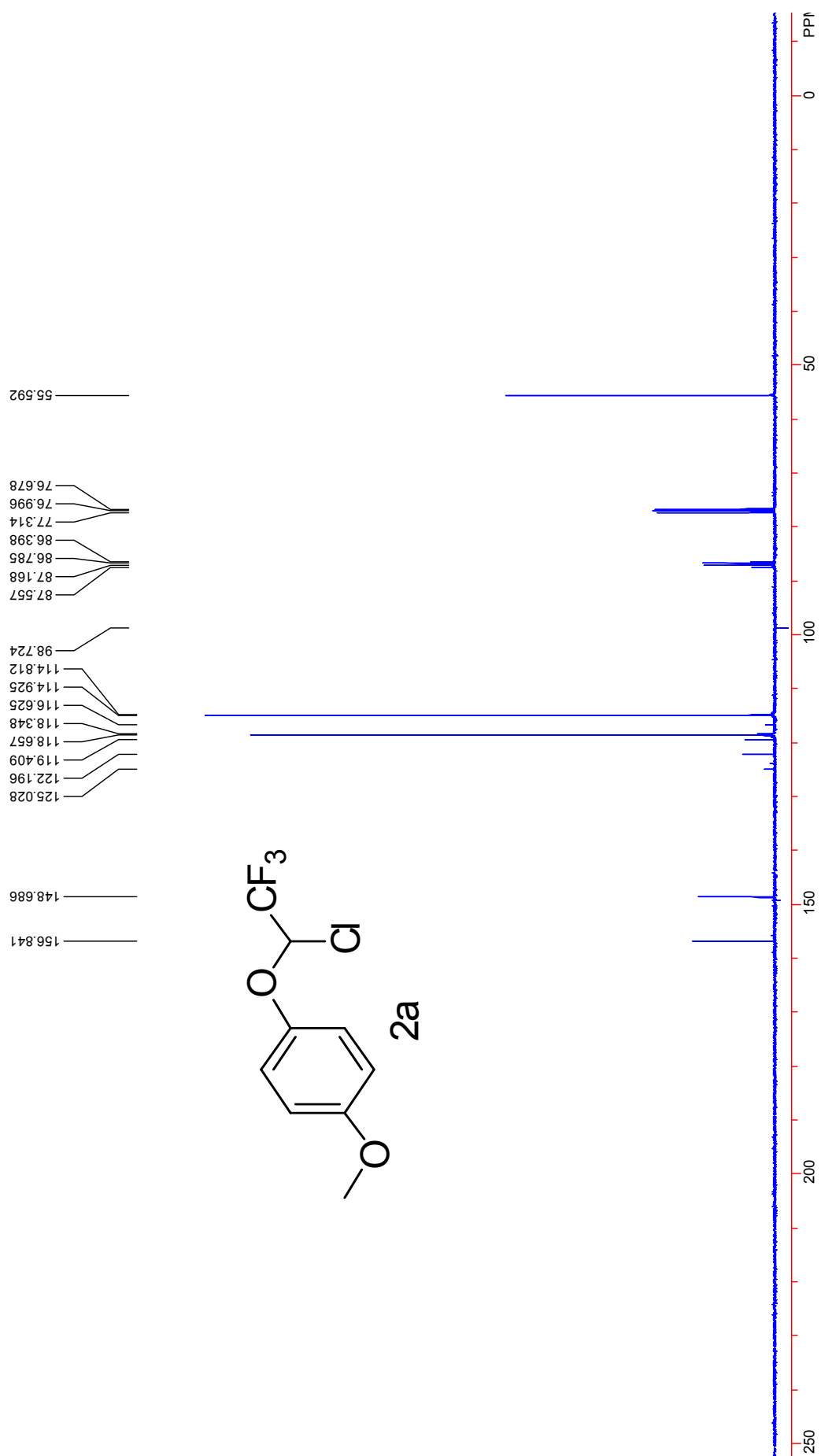
MS (EI): 234(M⁺, 19.70), 221(100), 125(51.08), 91(44.30), 223(36.58), 104(20.30);

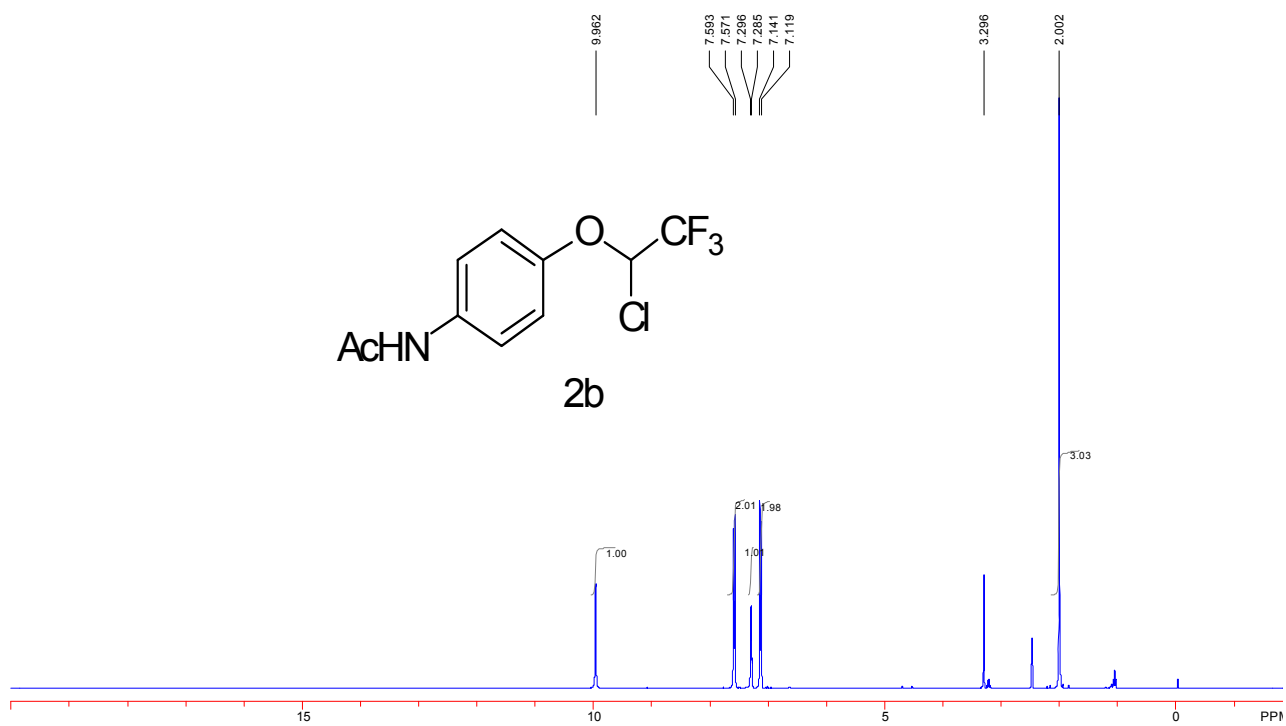
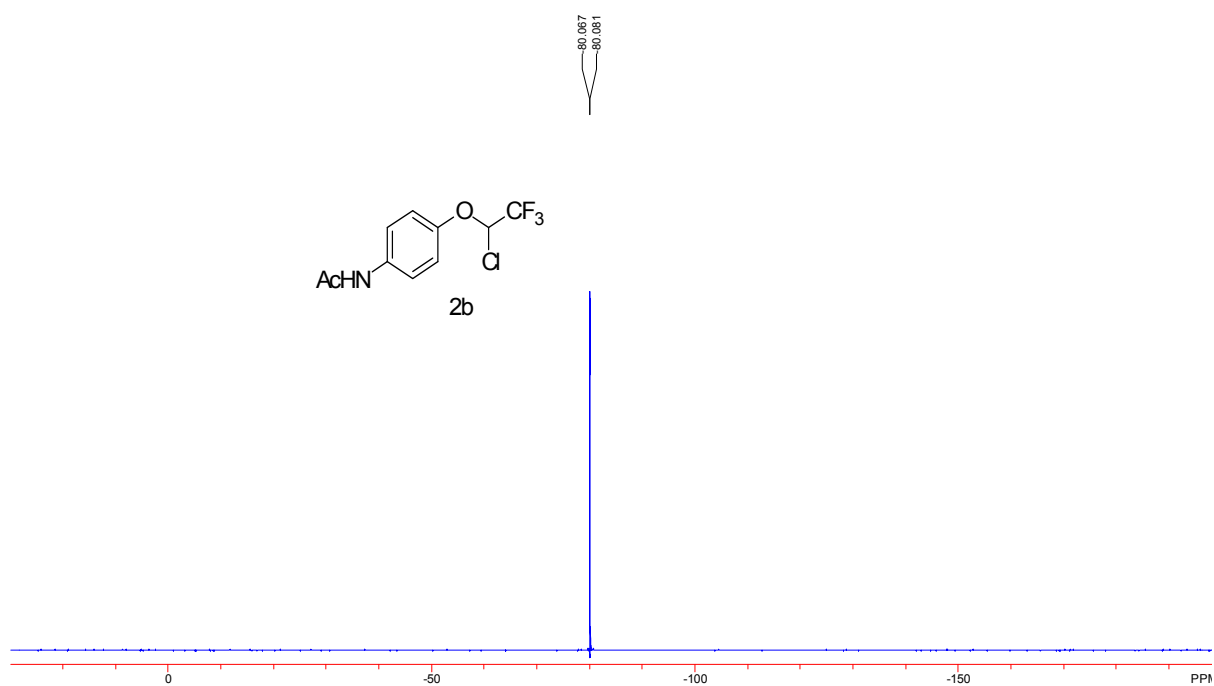
HRMS (EI) M⁺ calcd for C₁₀H₉F₃Cl₂: 256.0033, found 256.0029;

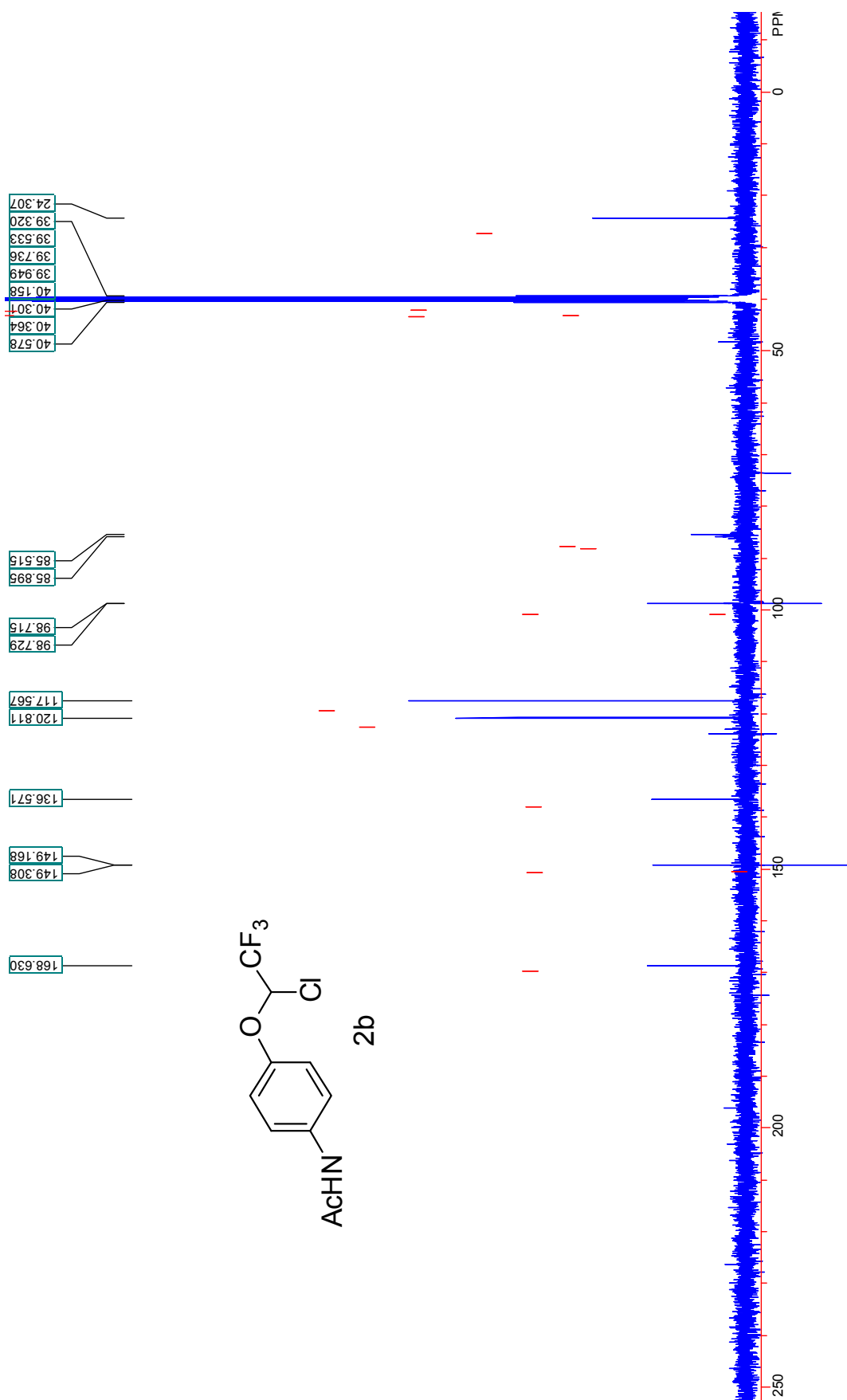
IR (KBr) ν/cm⁻¹: 3035, 2927, 1495, 1456, 1313, 1268, 1189, 1165, 1127, 1025, 939.

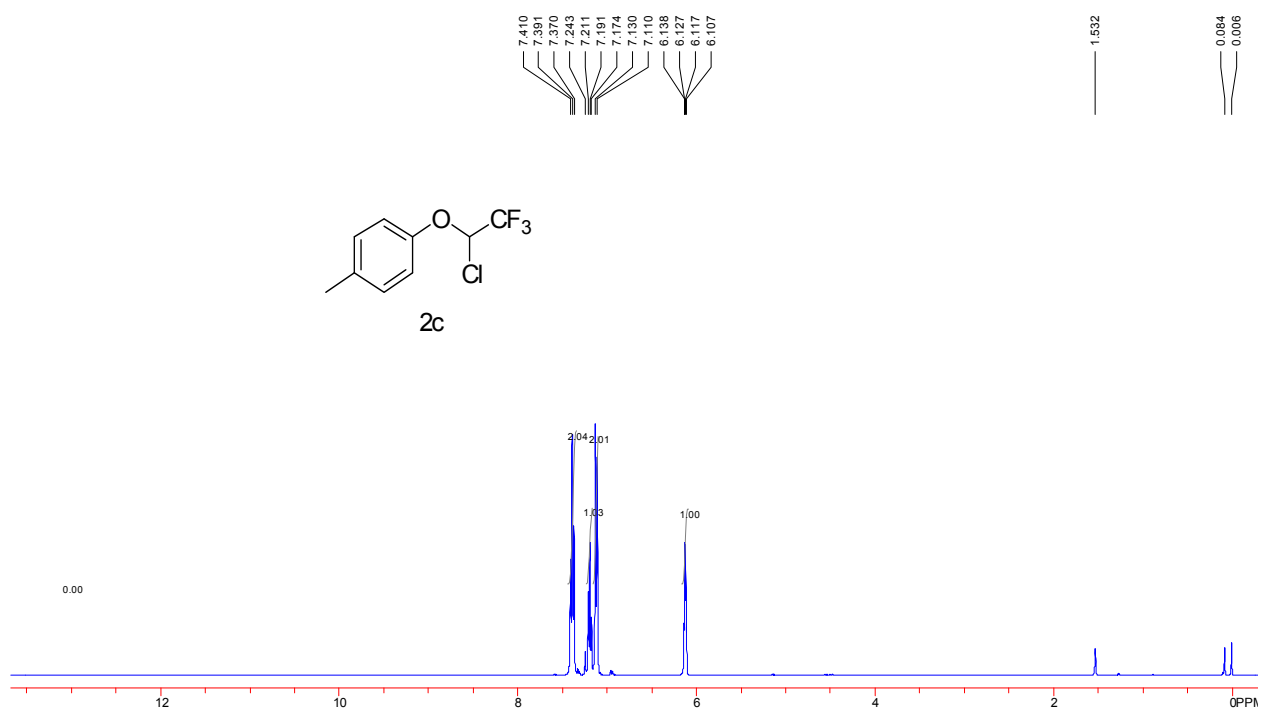
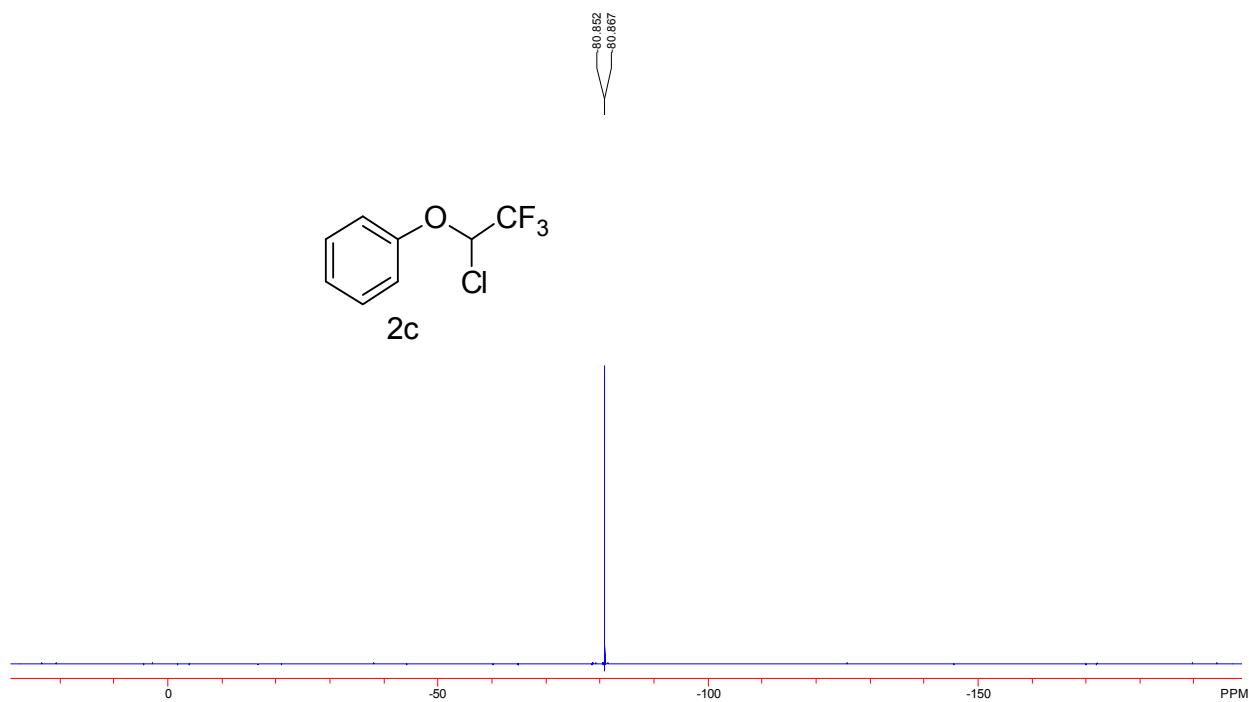
3, ^{19}F , ^1H and ^{13}C NMR spectra for new compounds



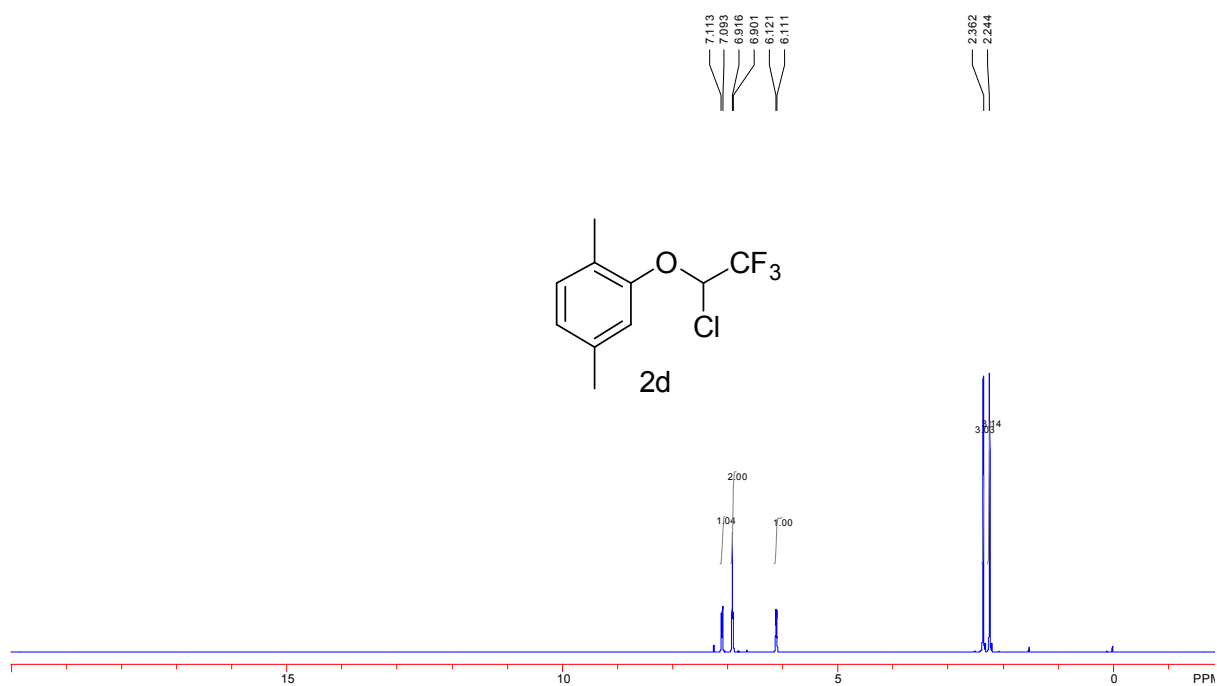
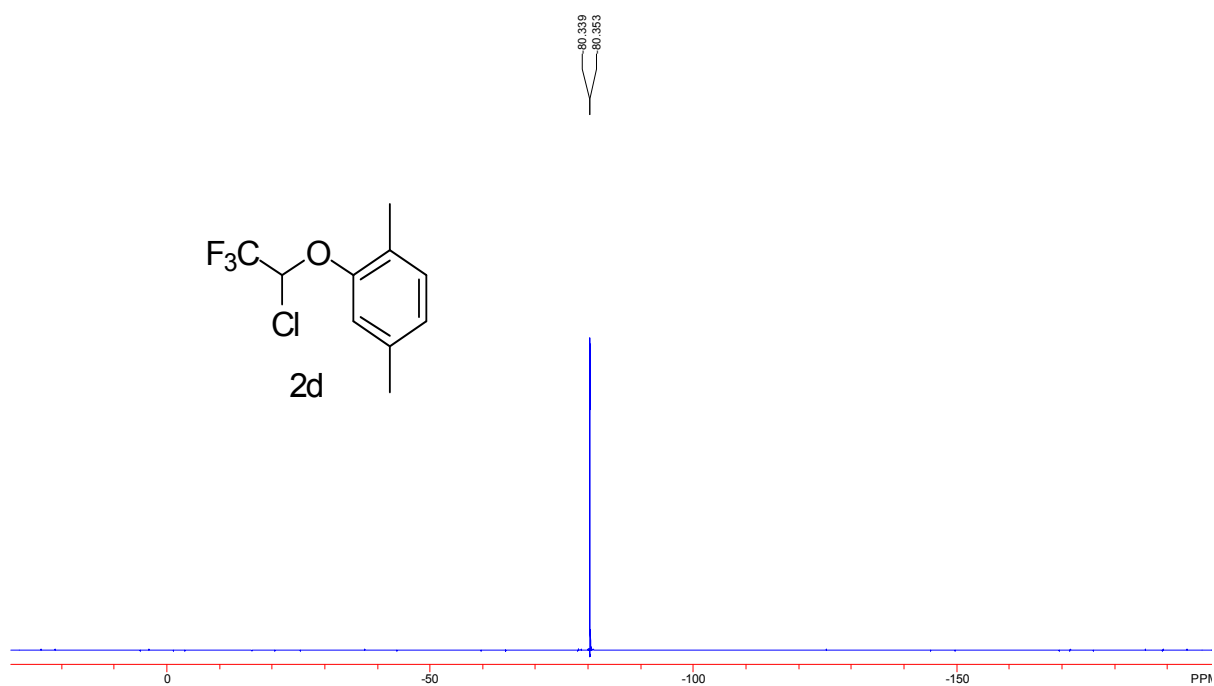




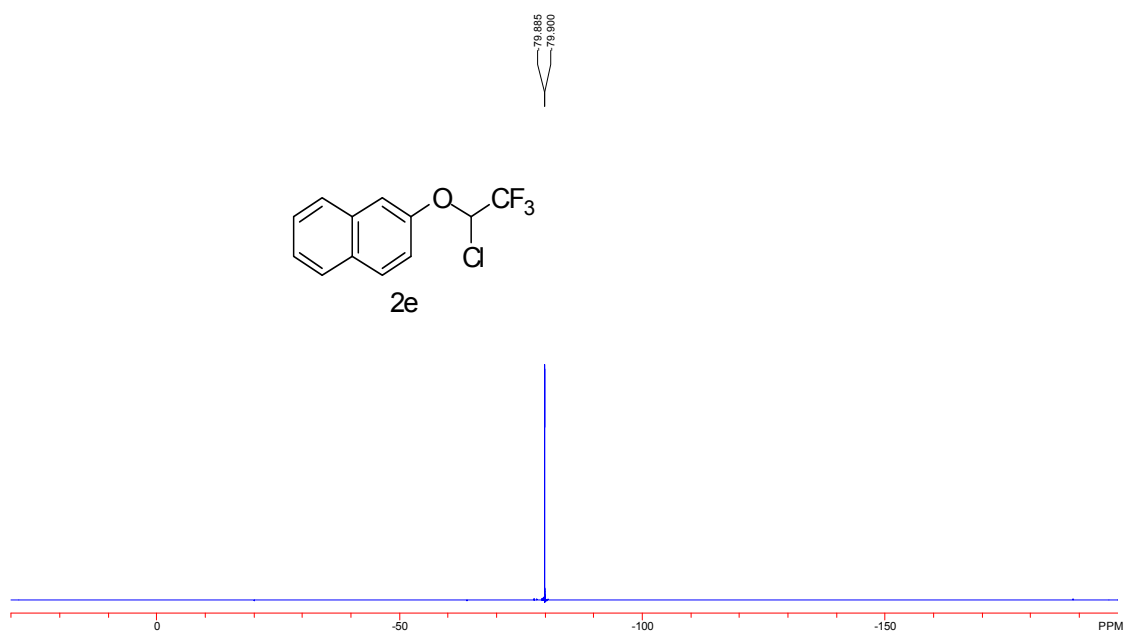
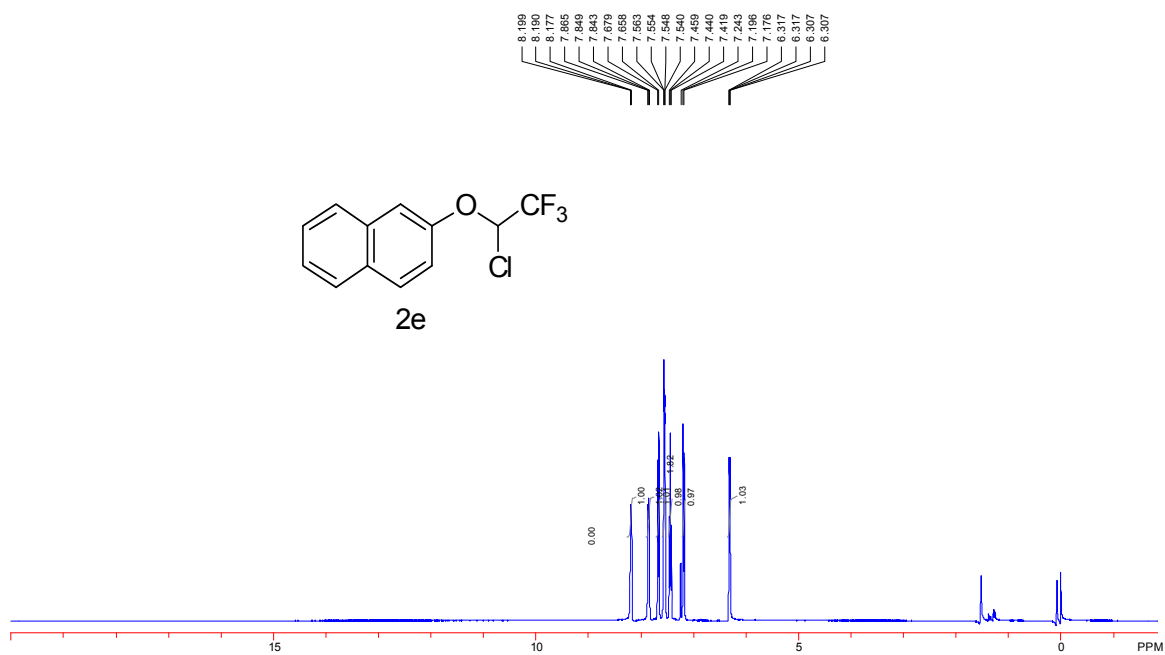


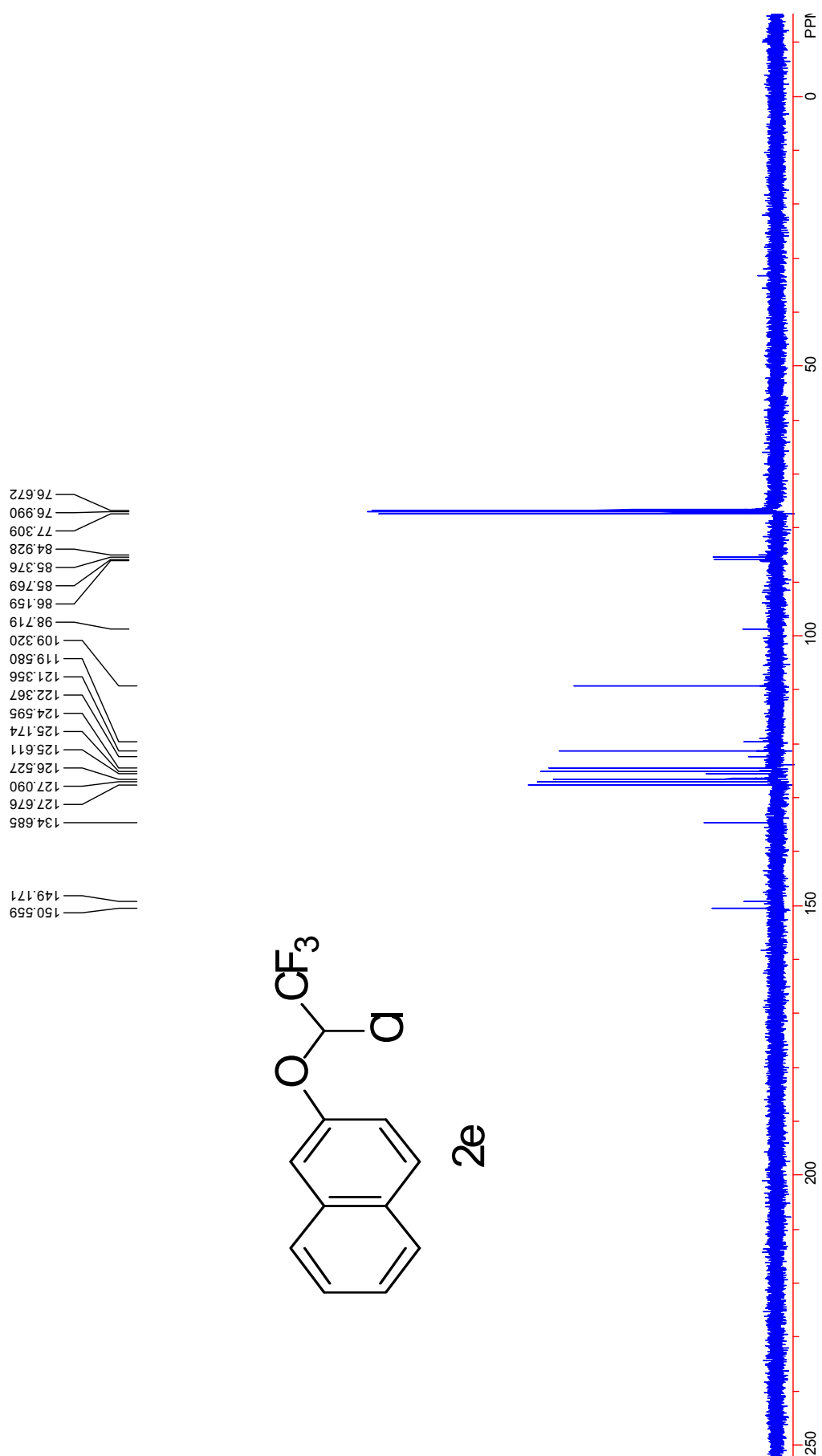


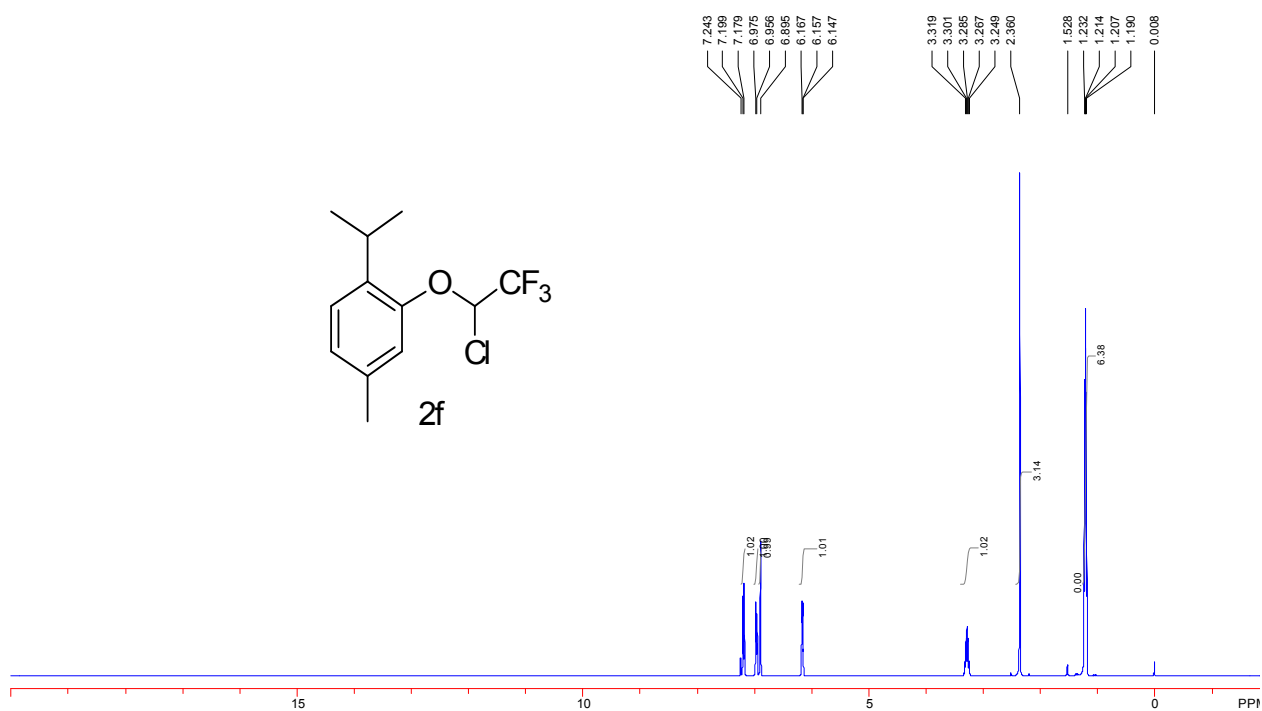
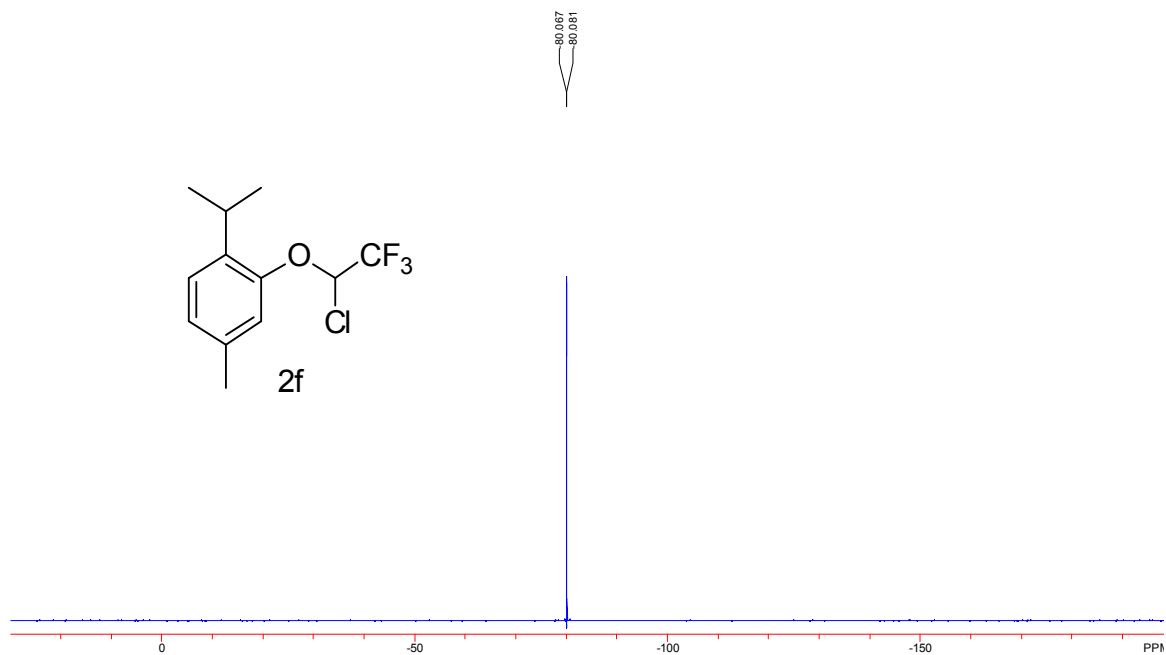


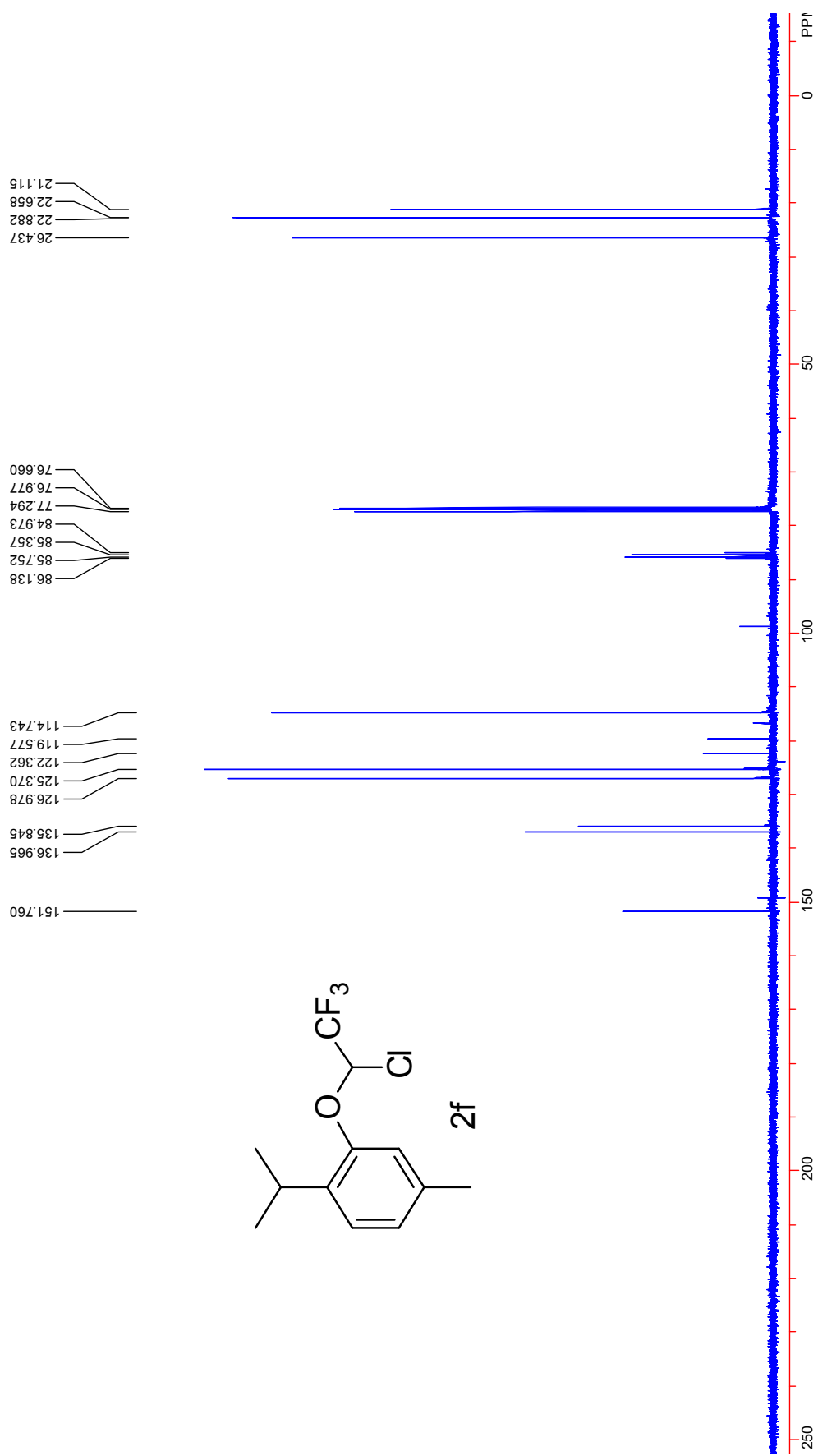


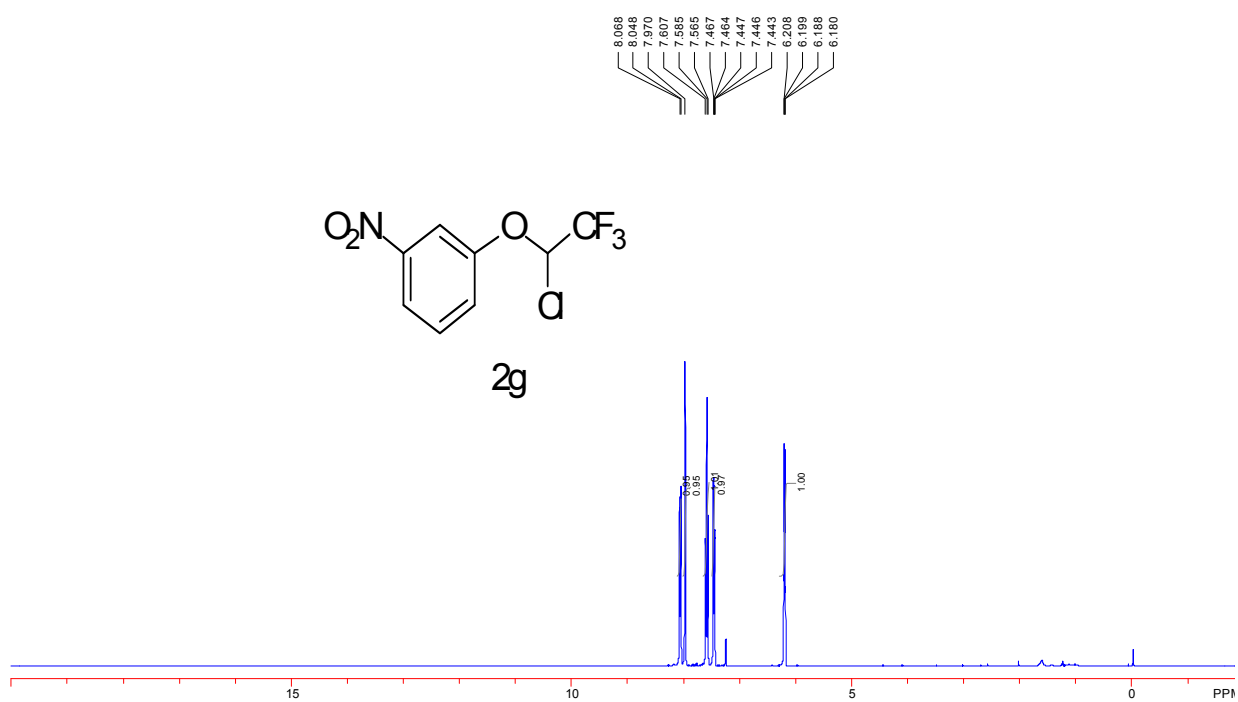


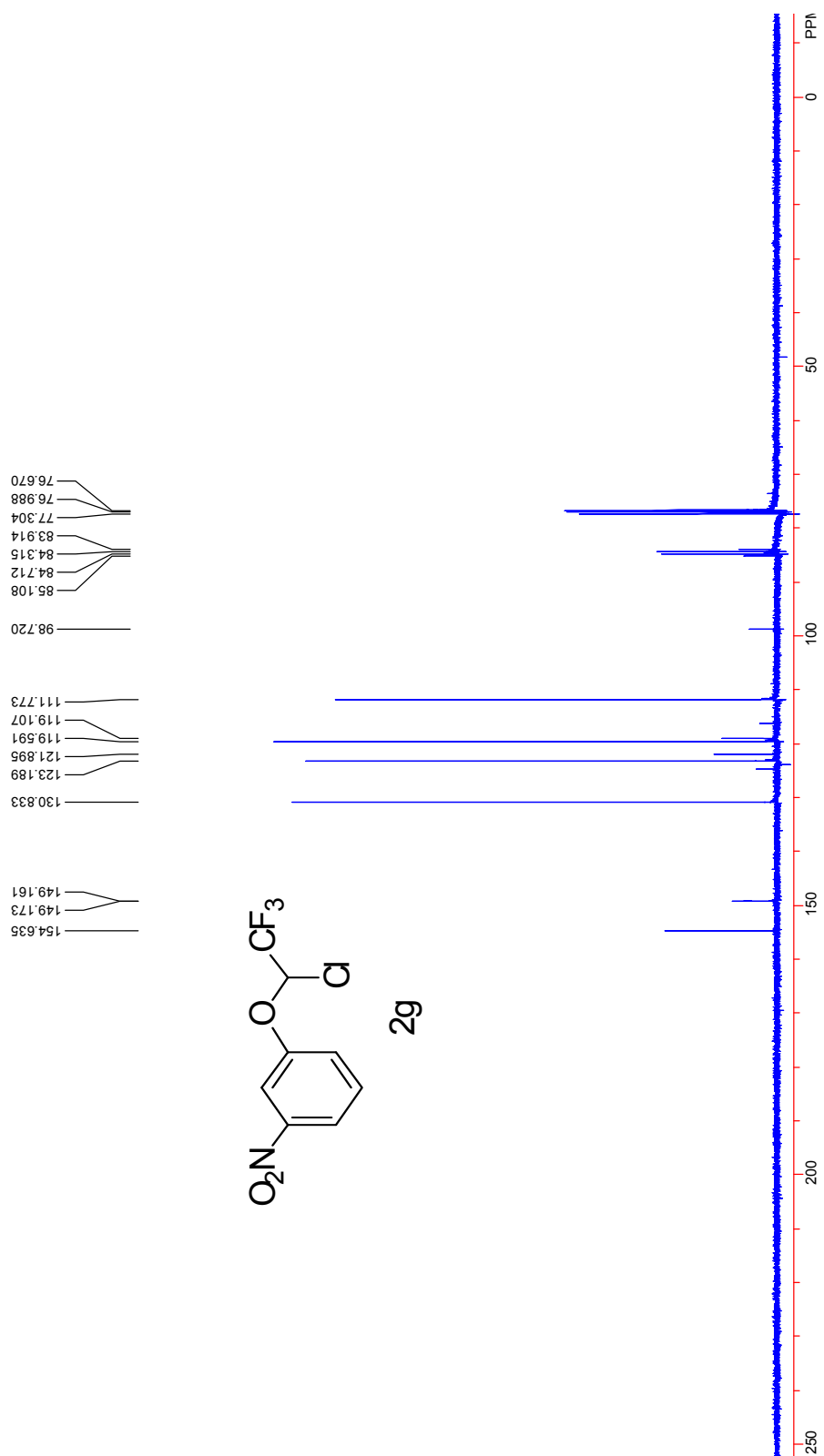


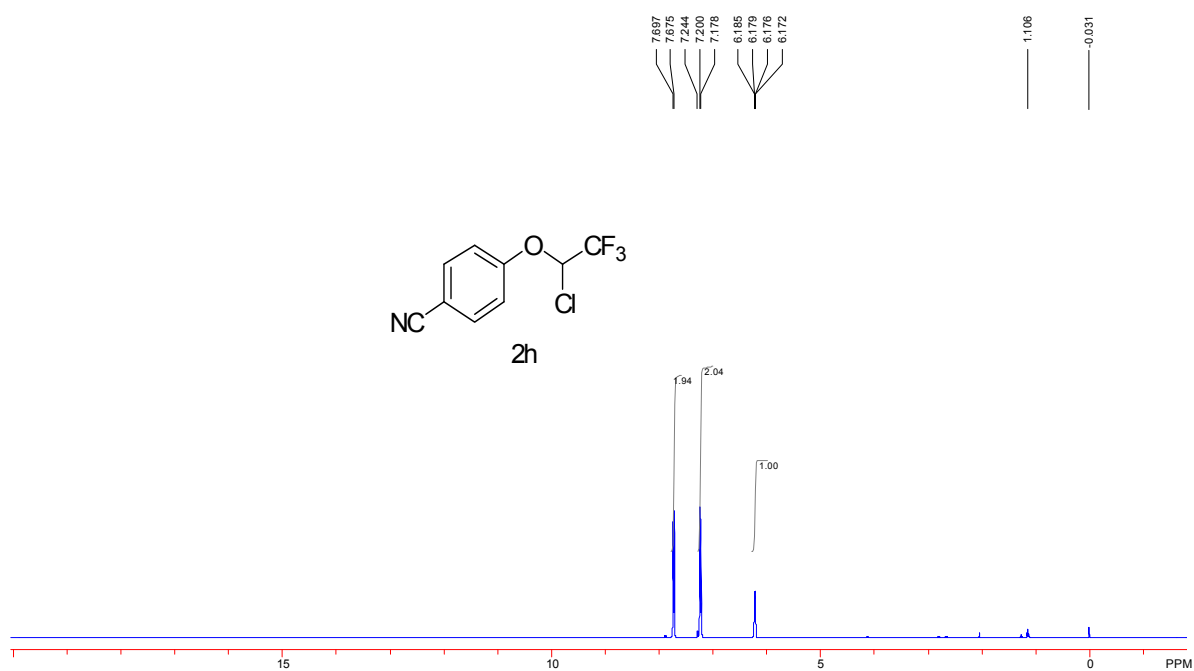
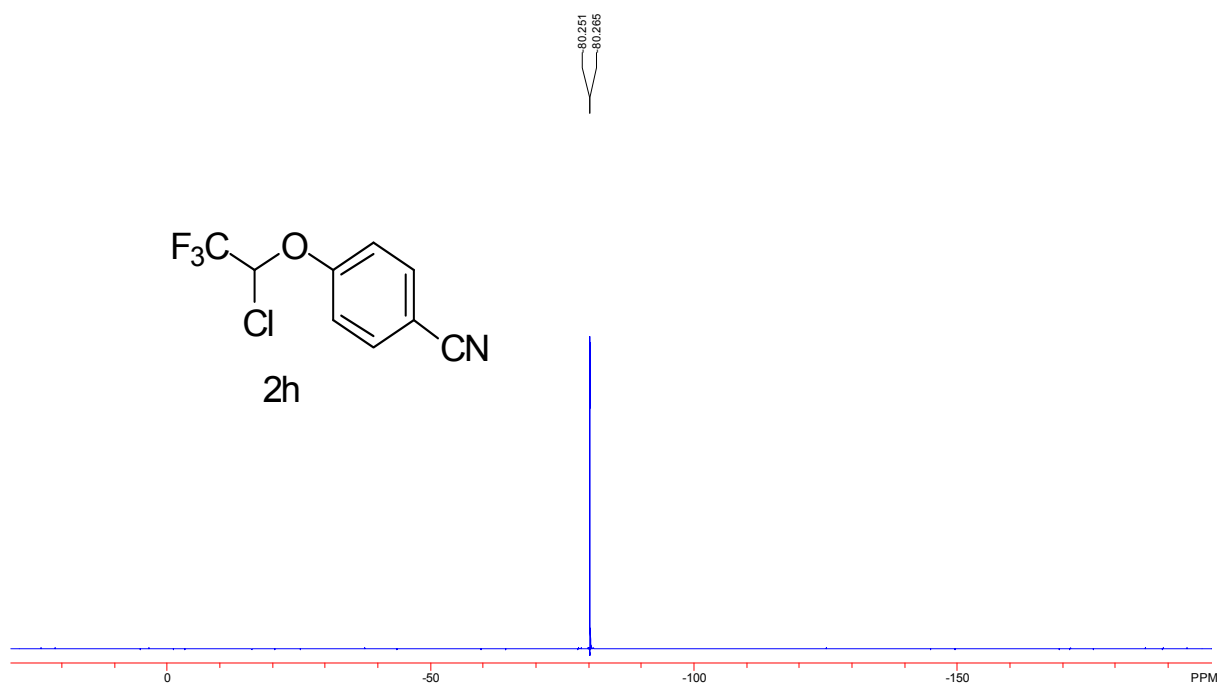


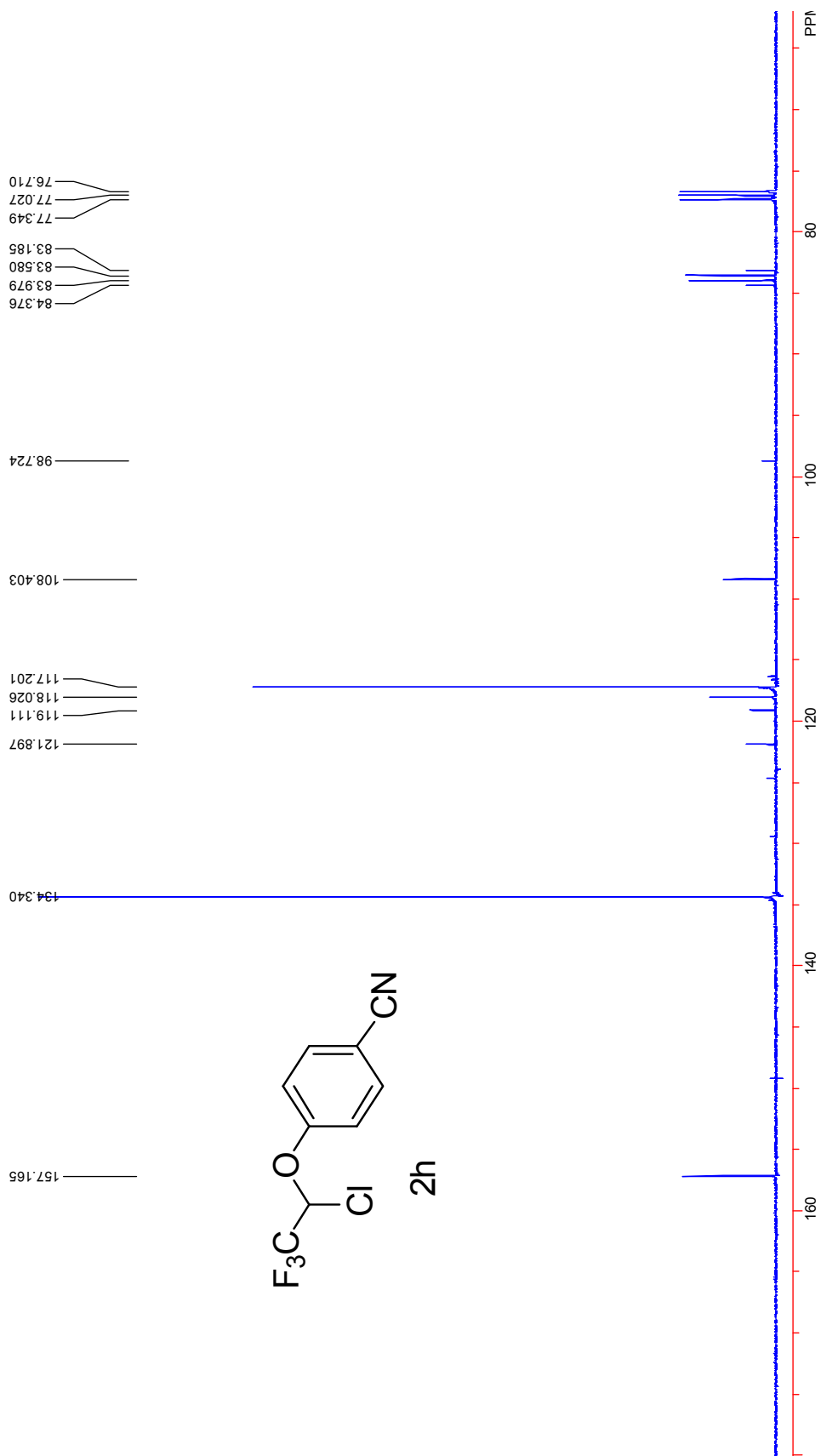


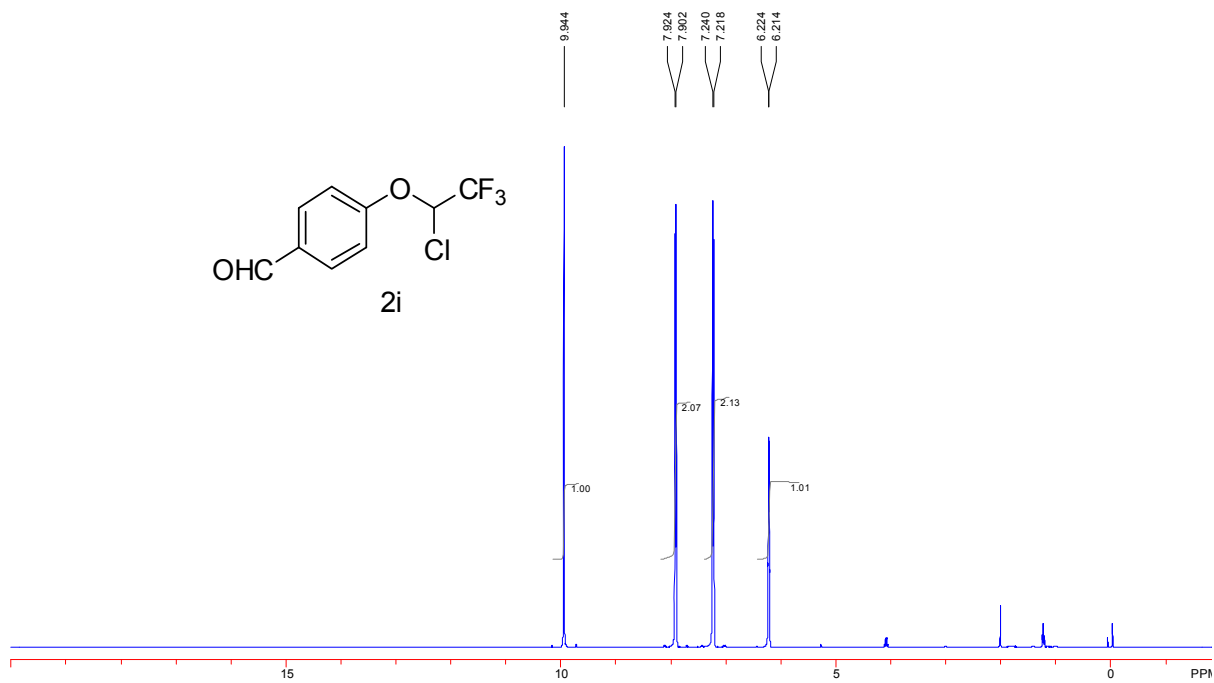
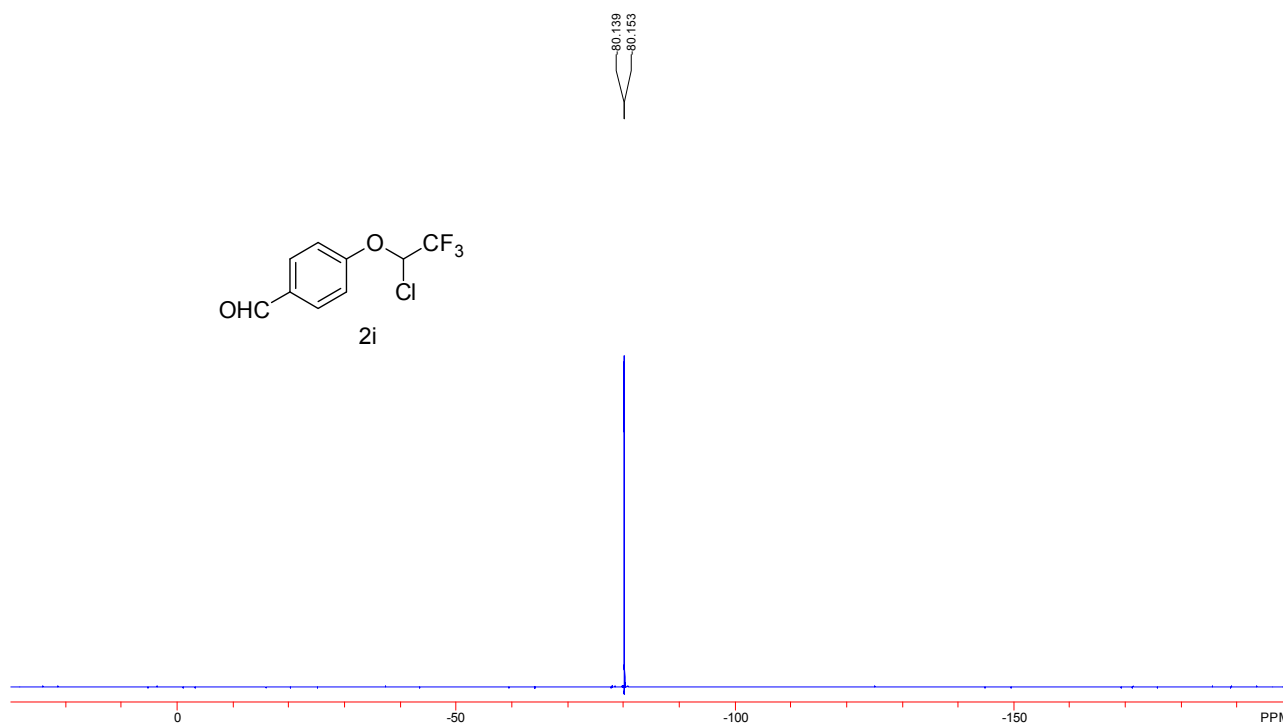


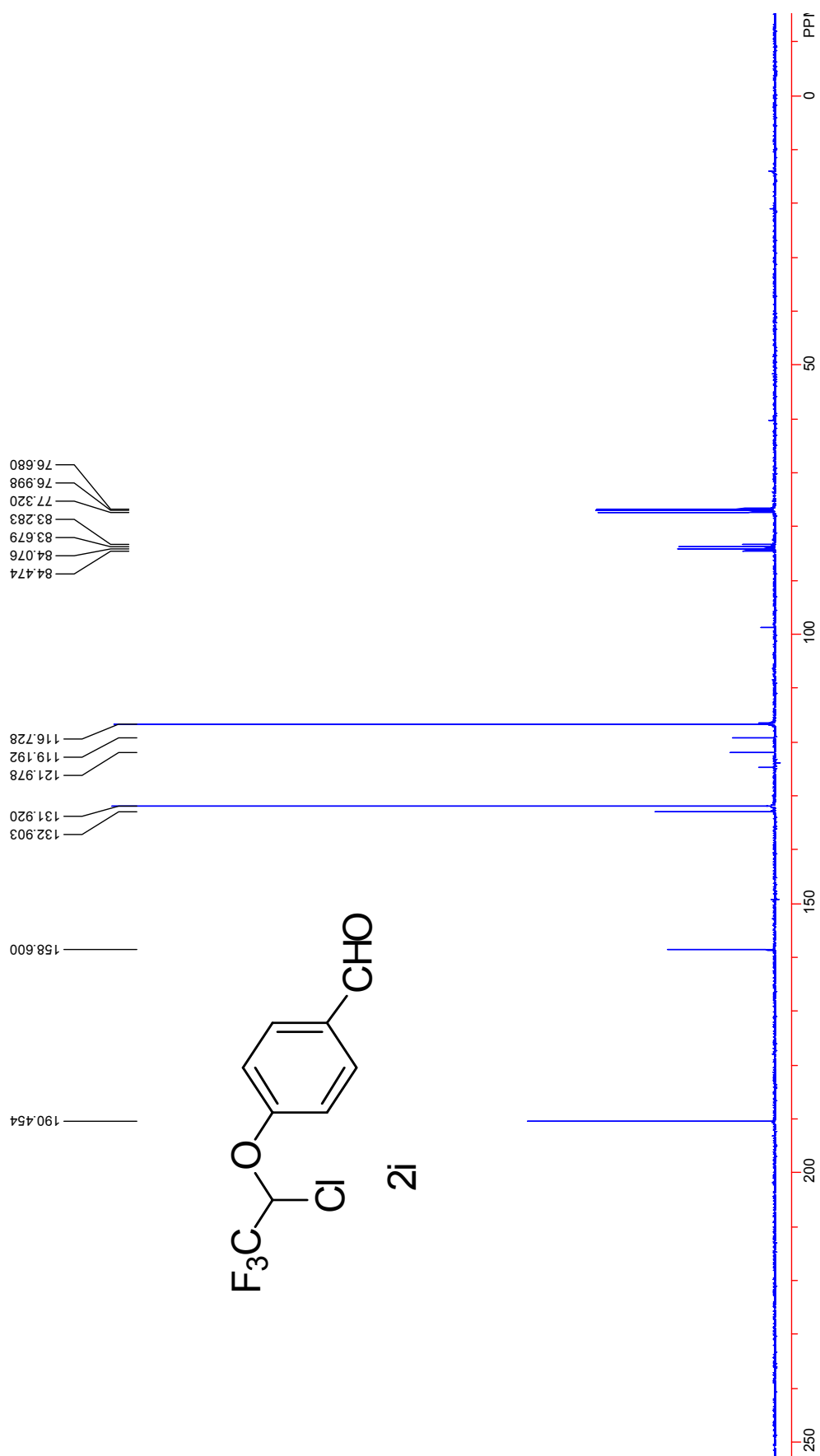


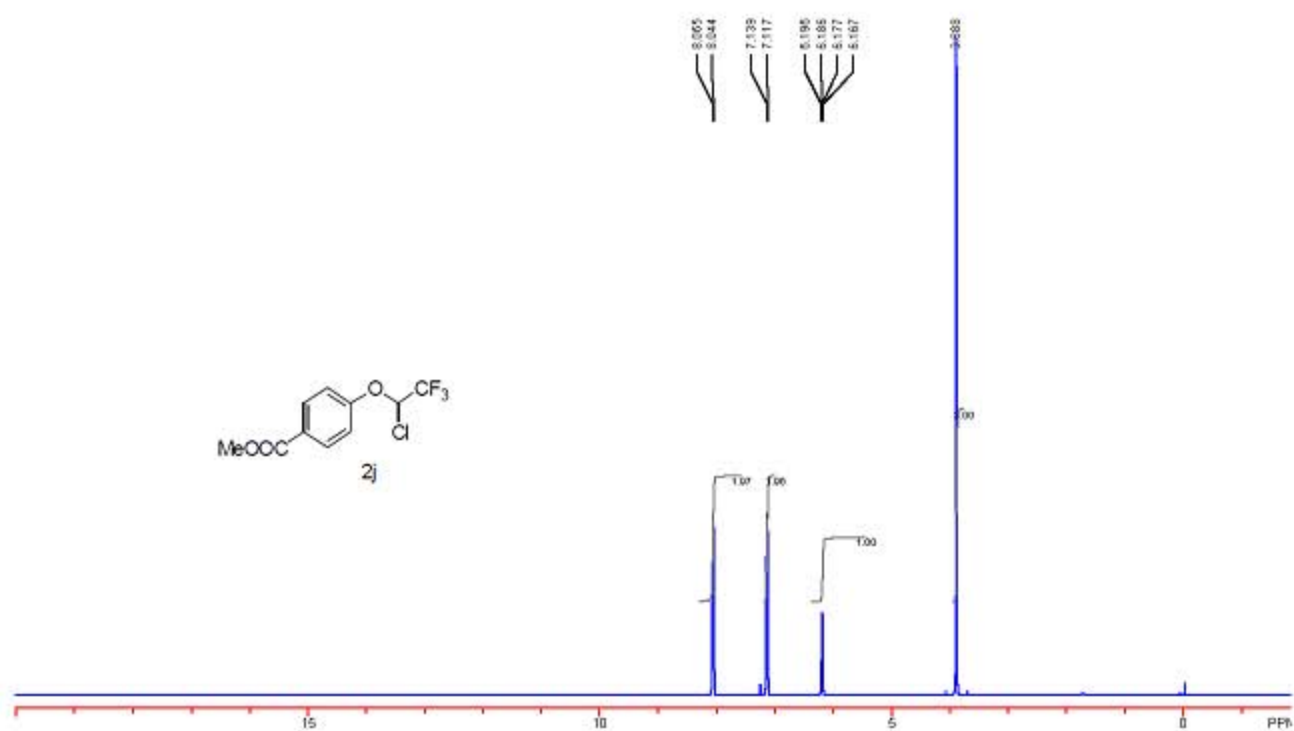
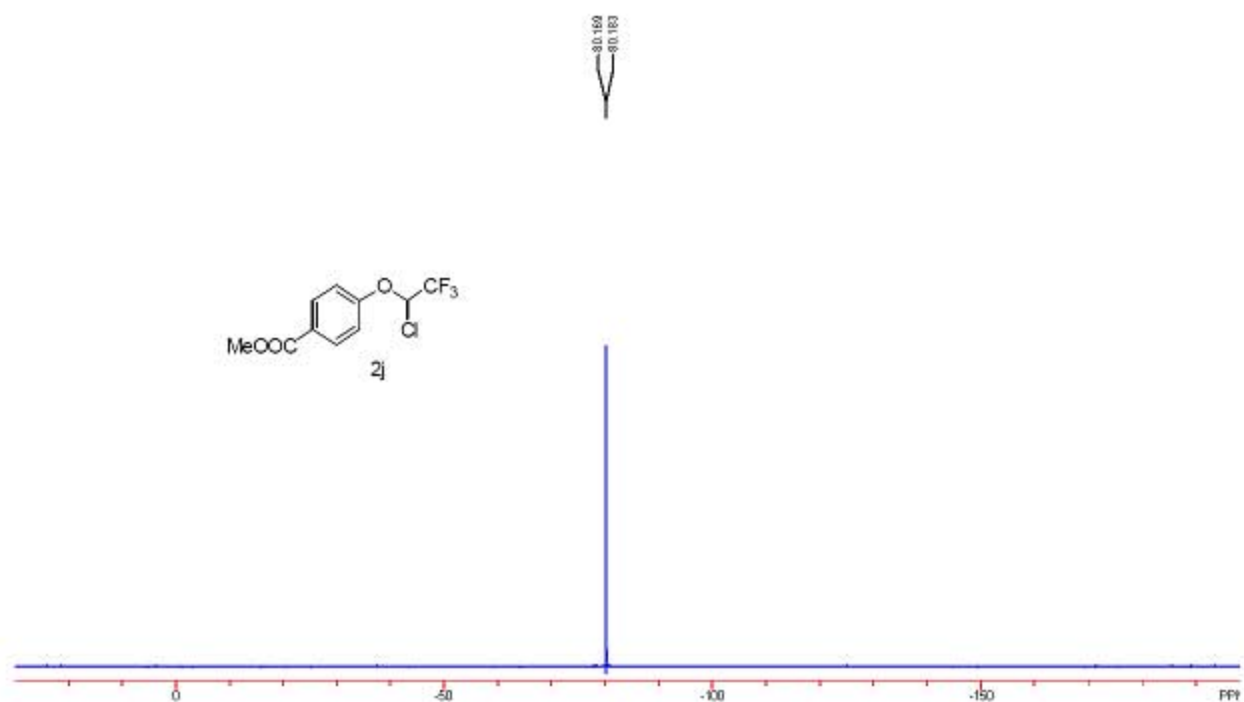


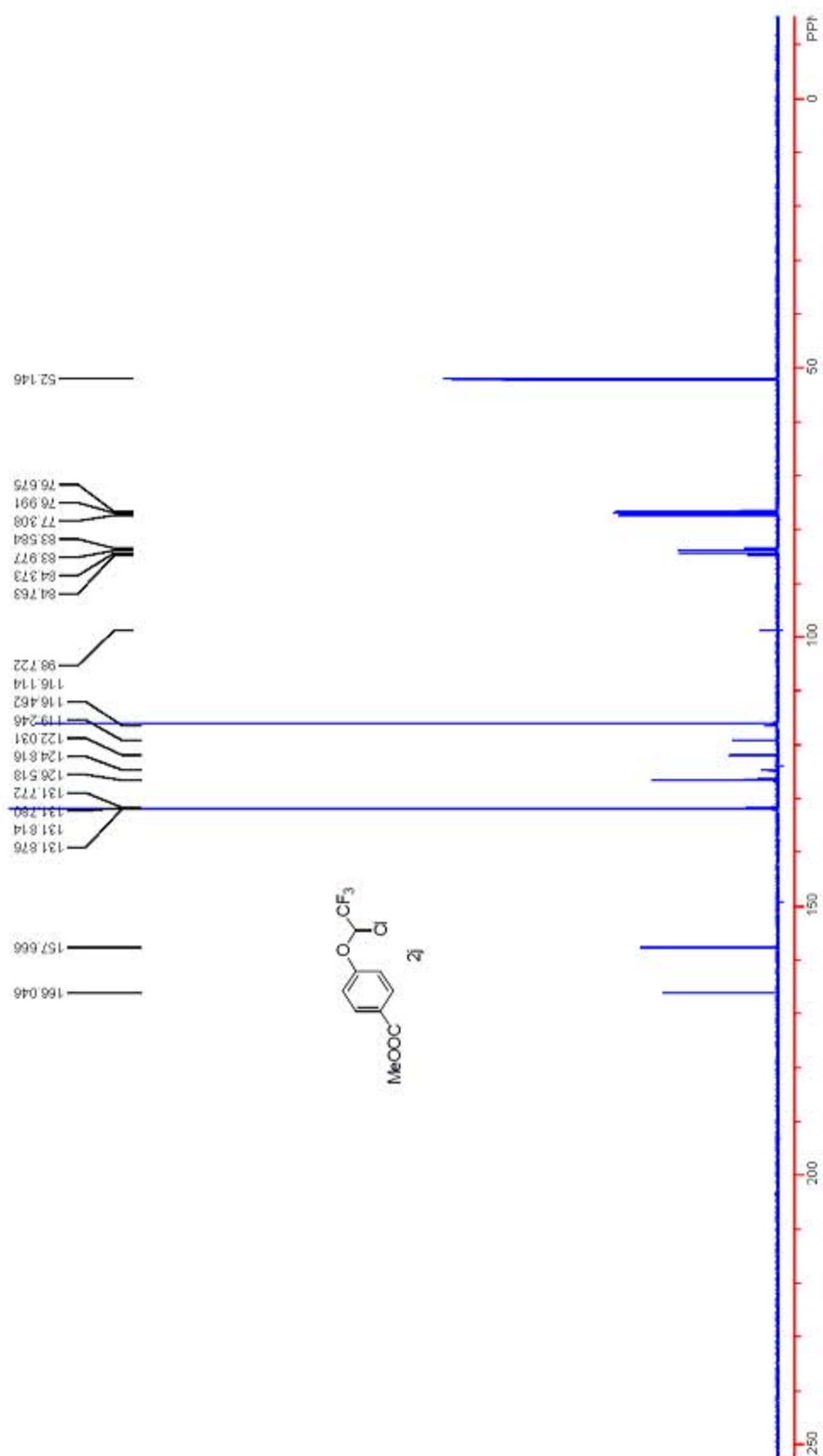


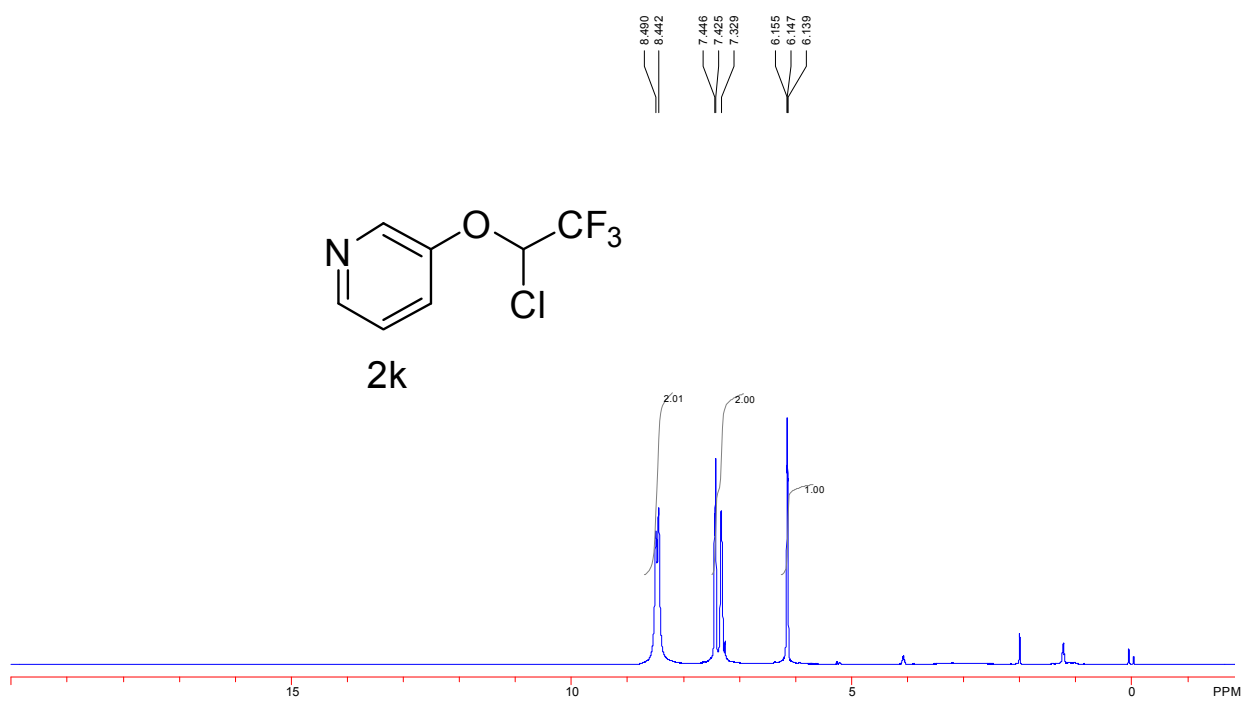
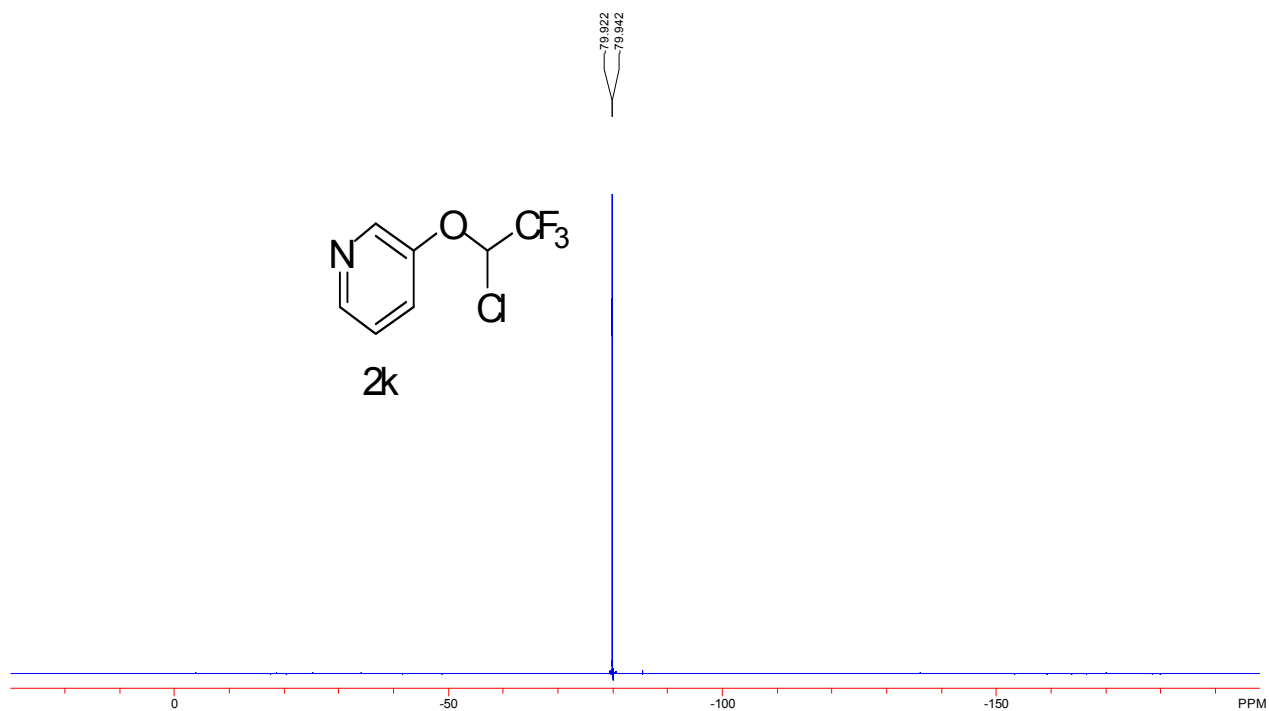


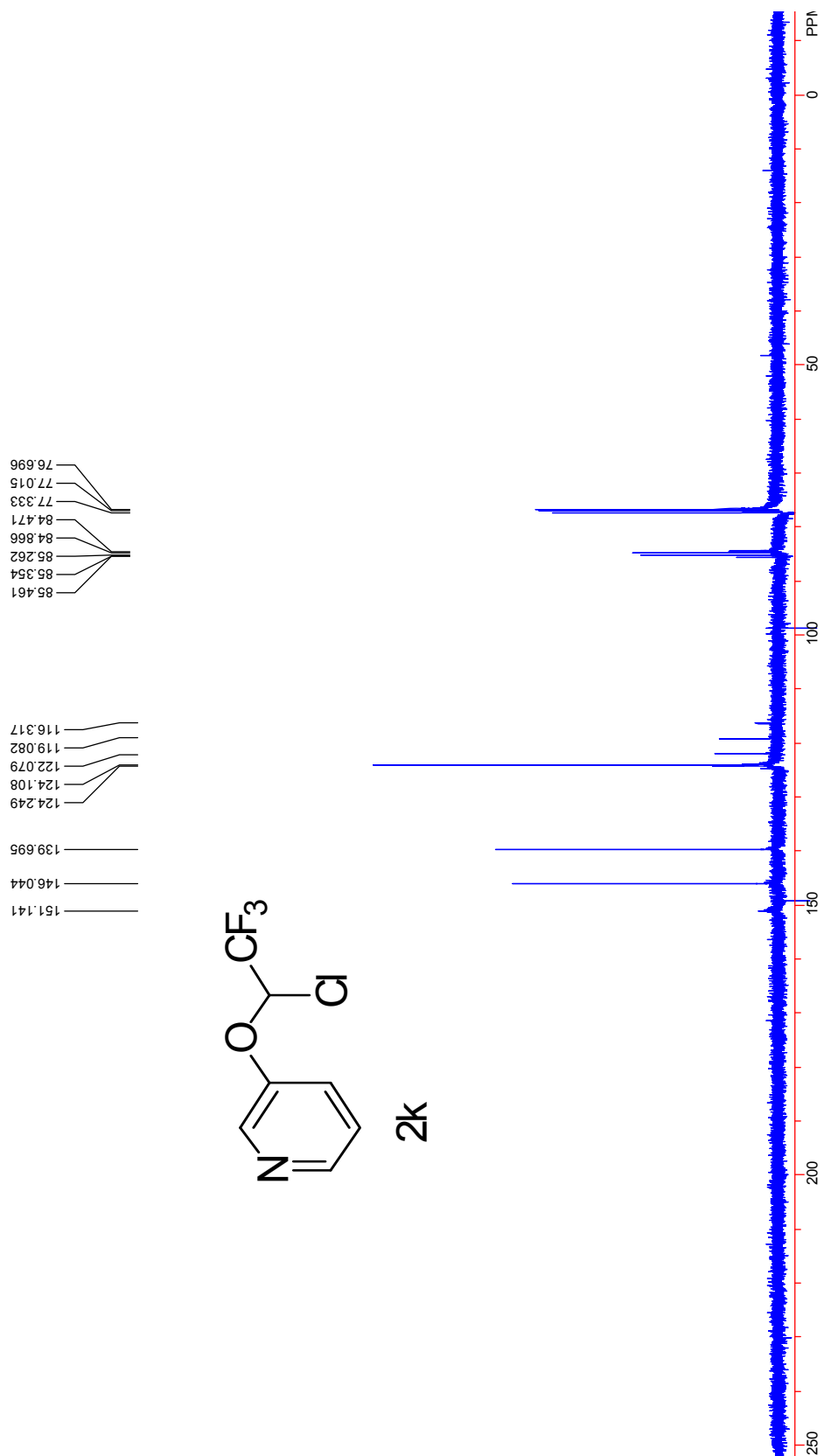


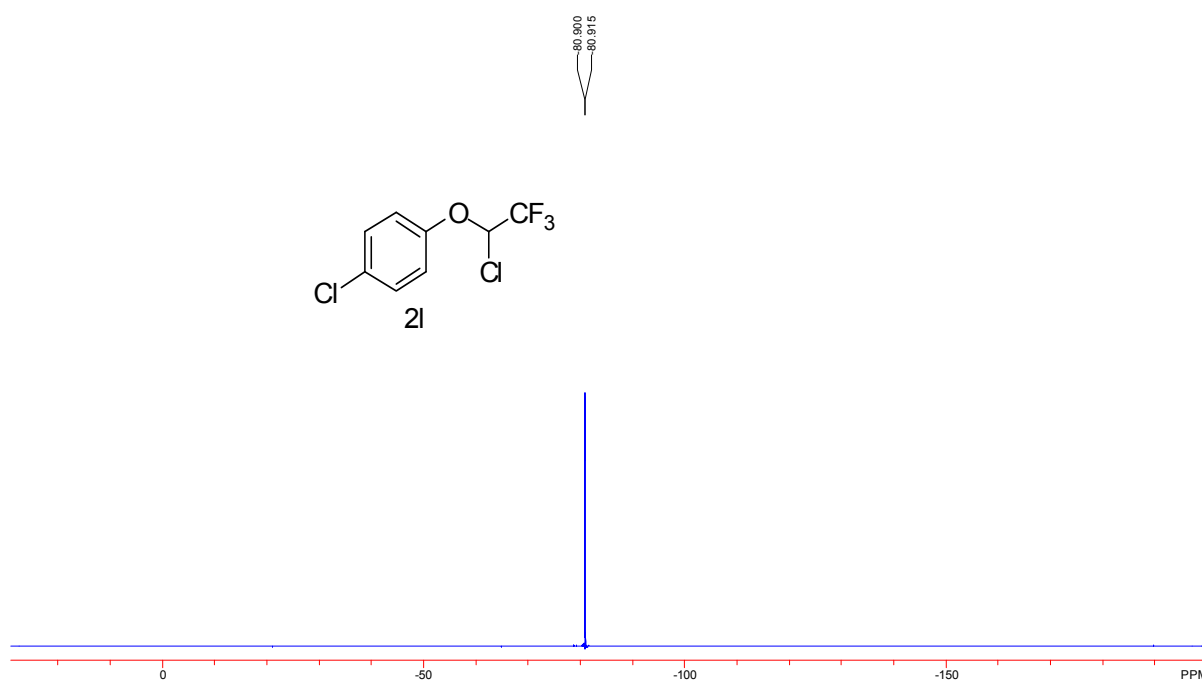
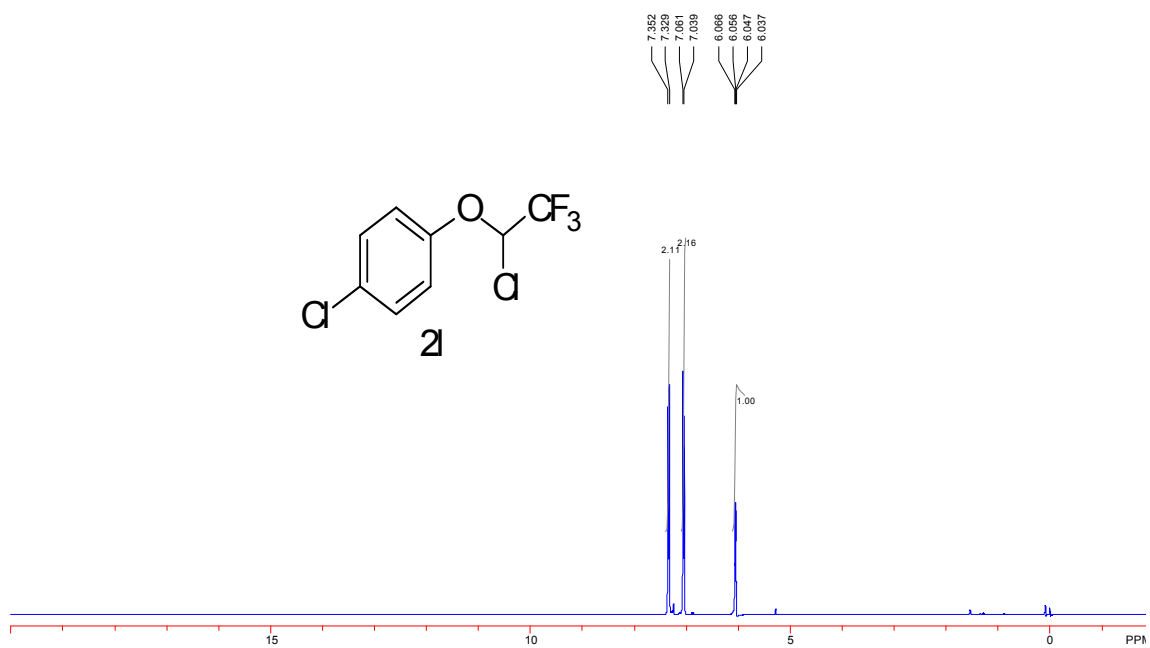


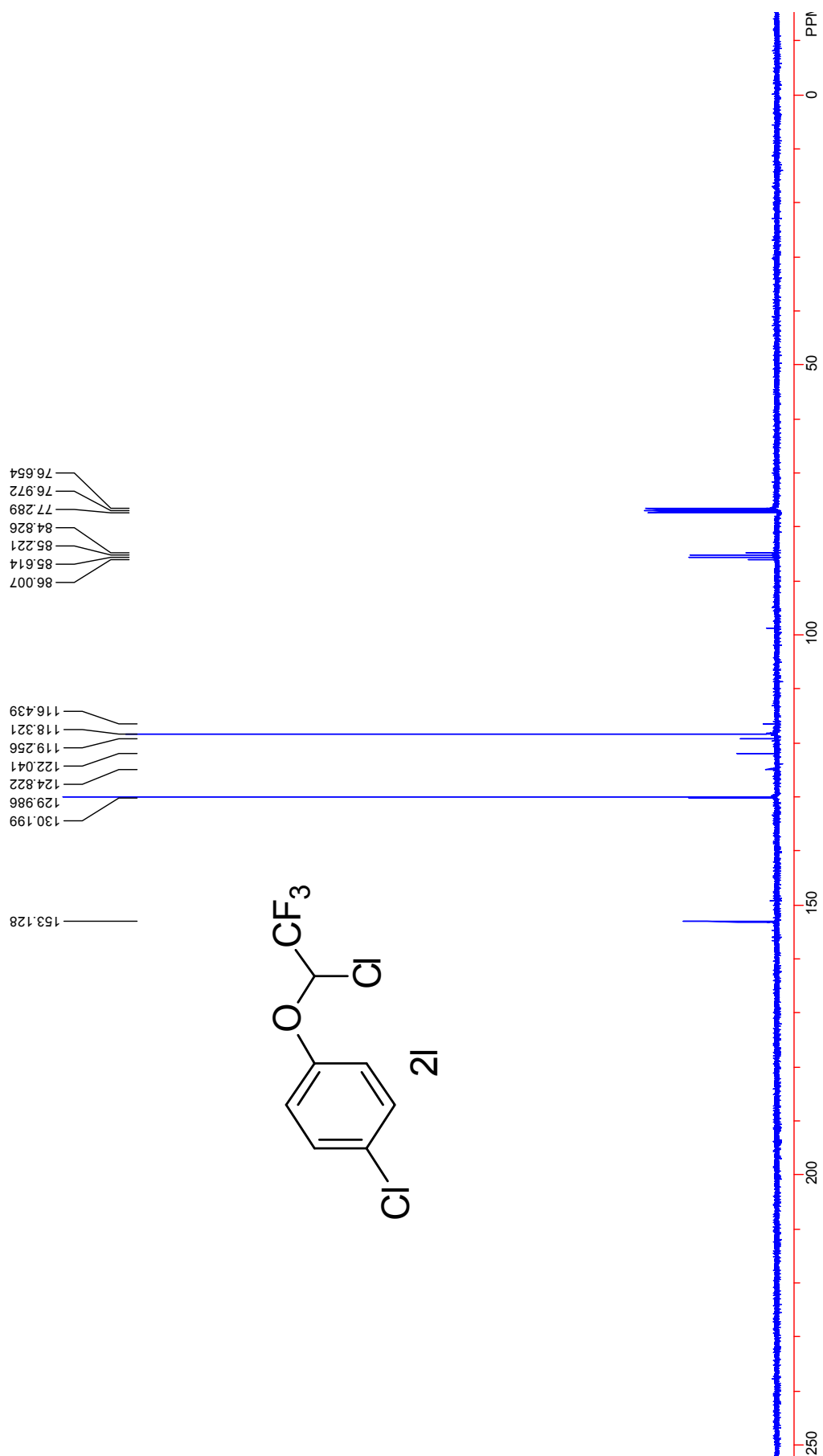


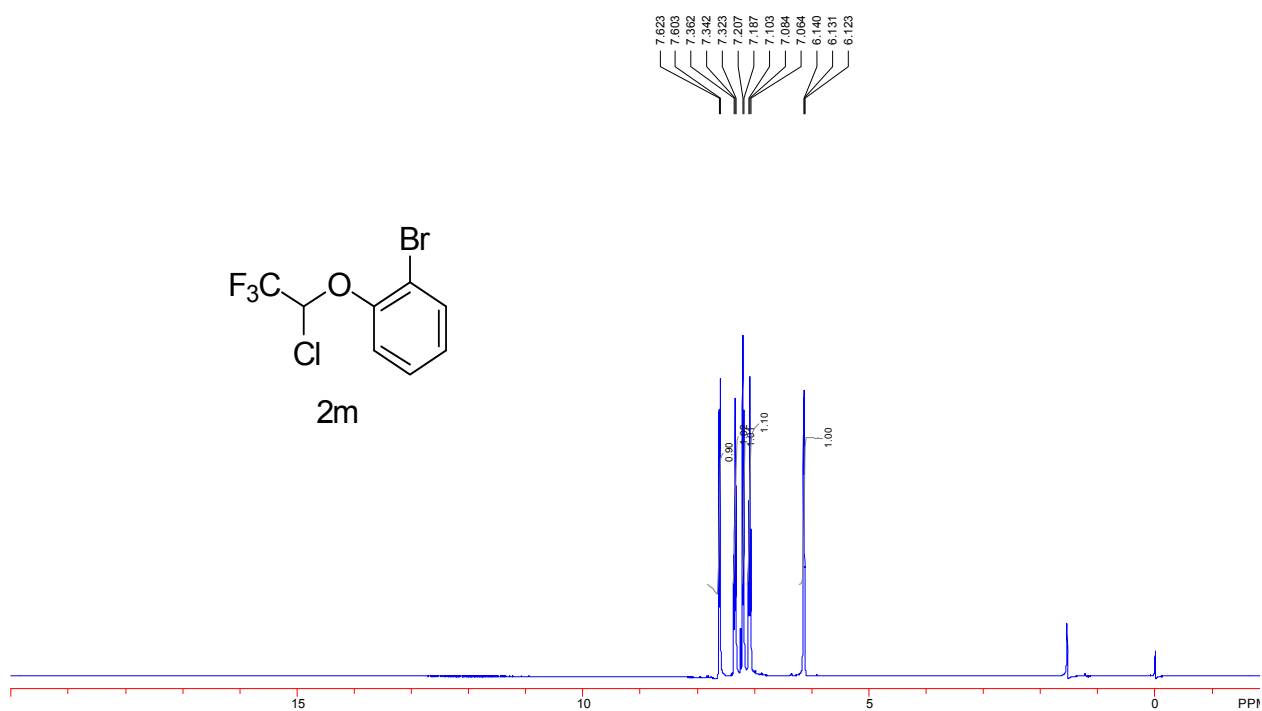
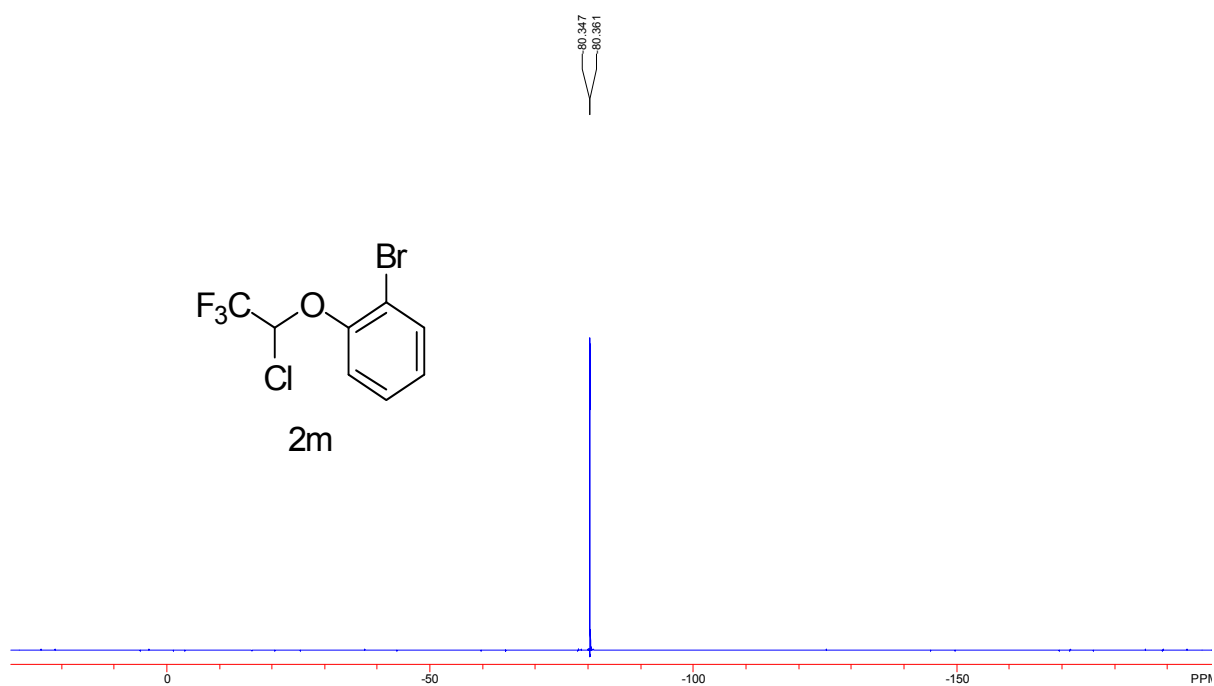


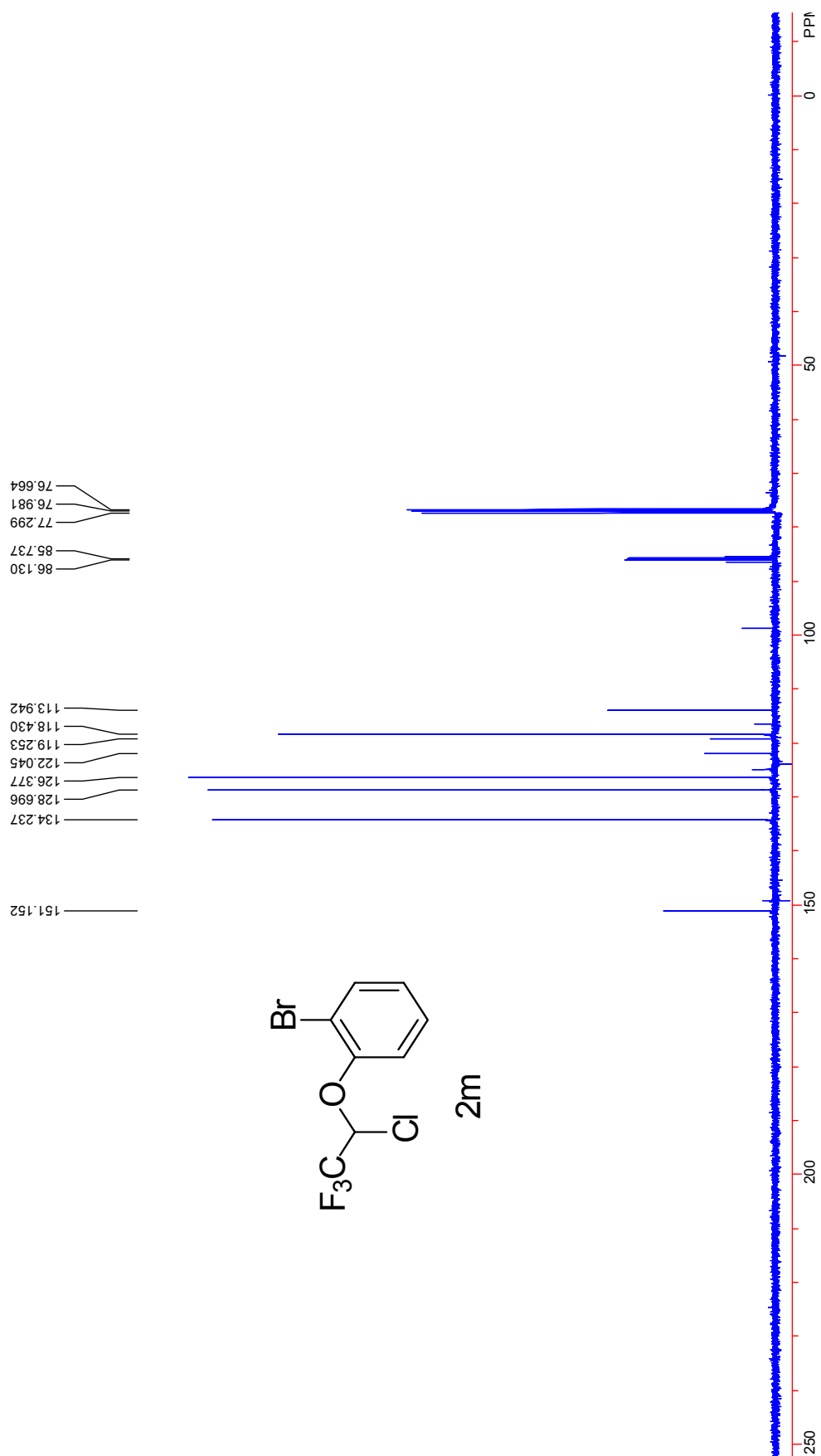


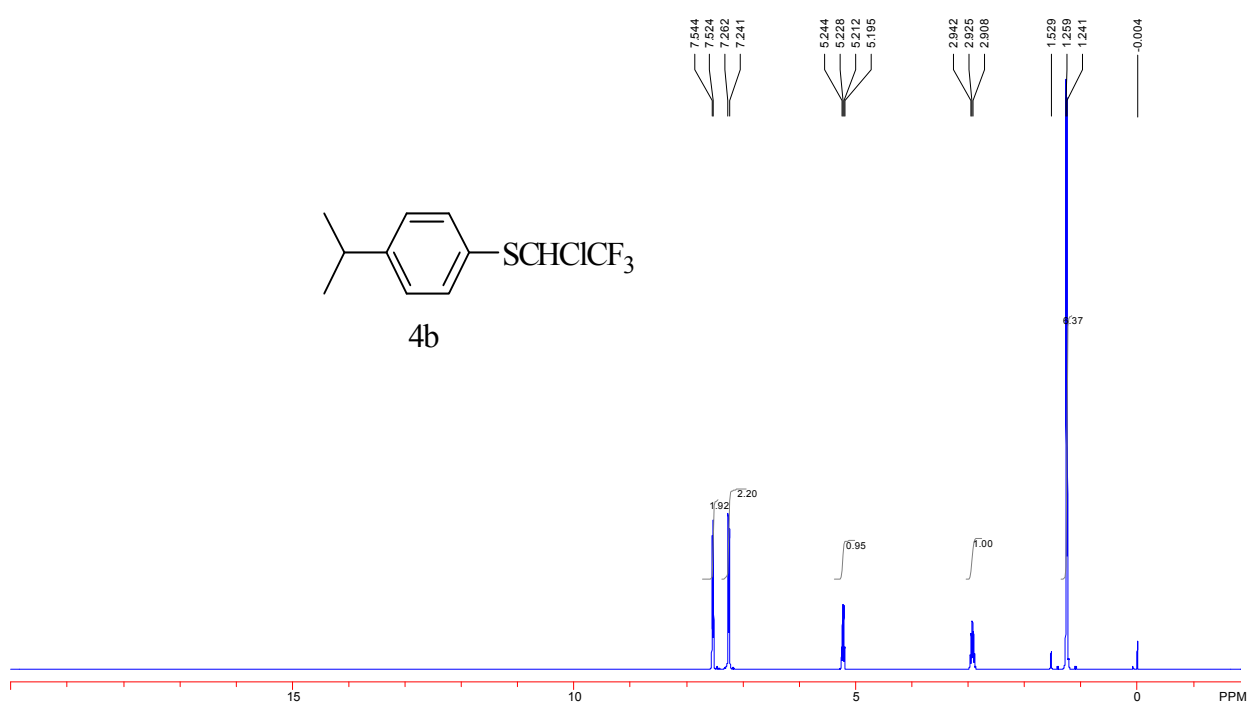
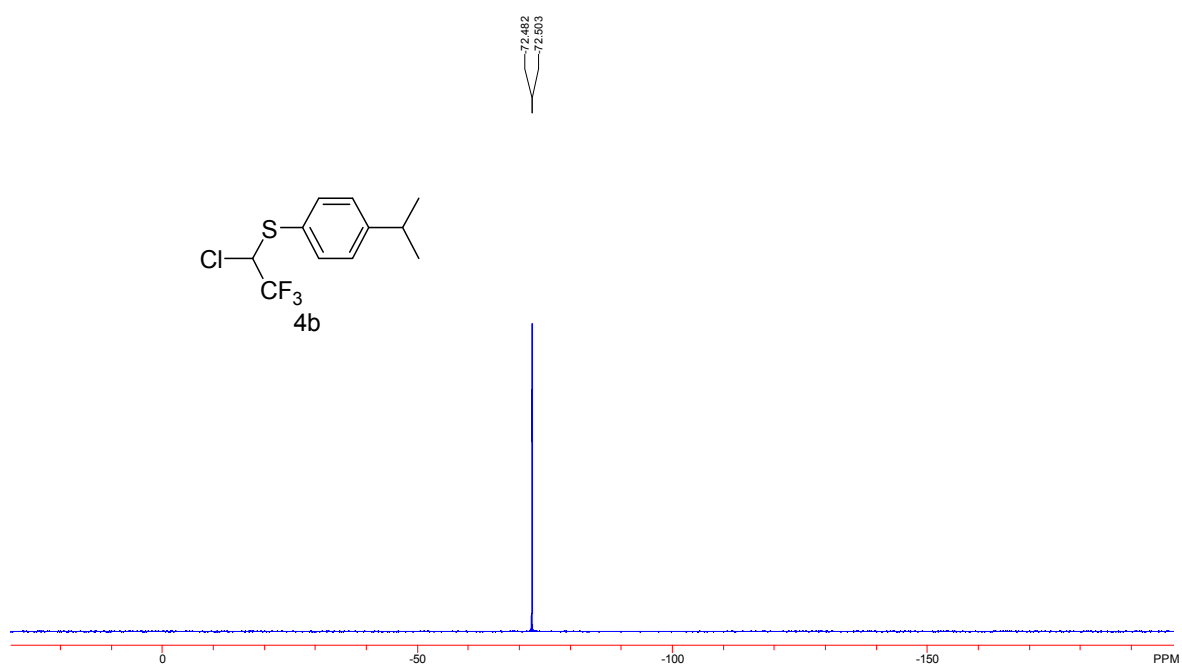


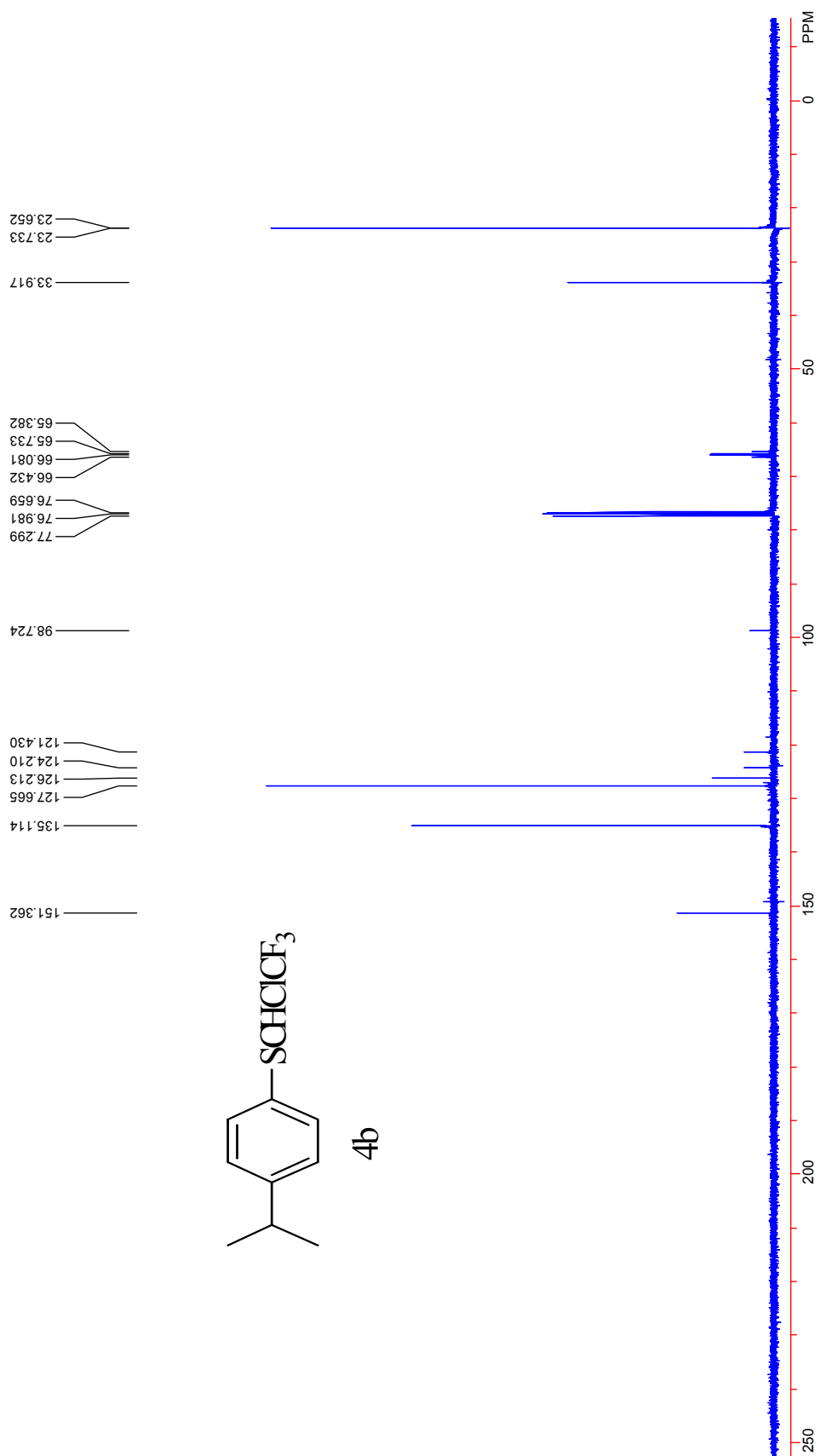


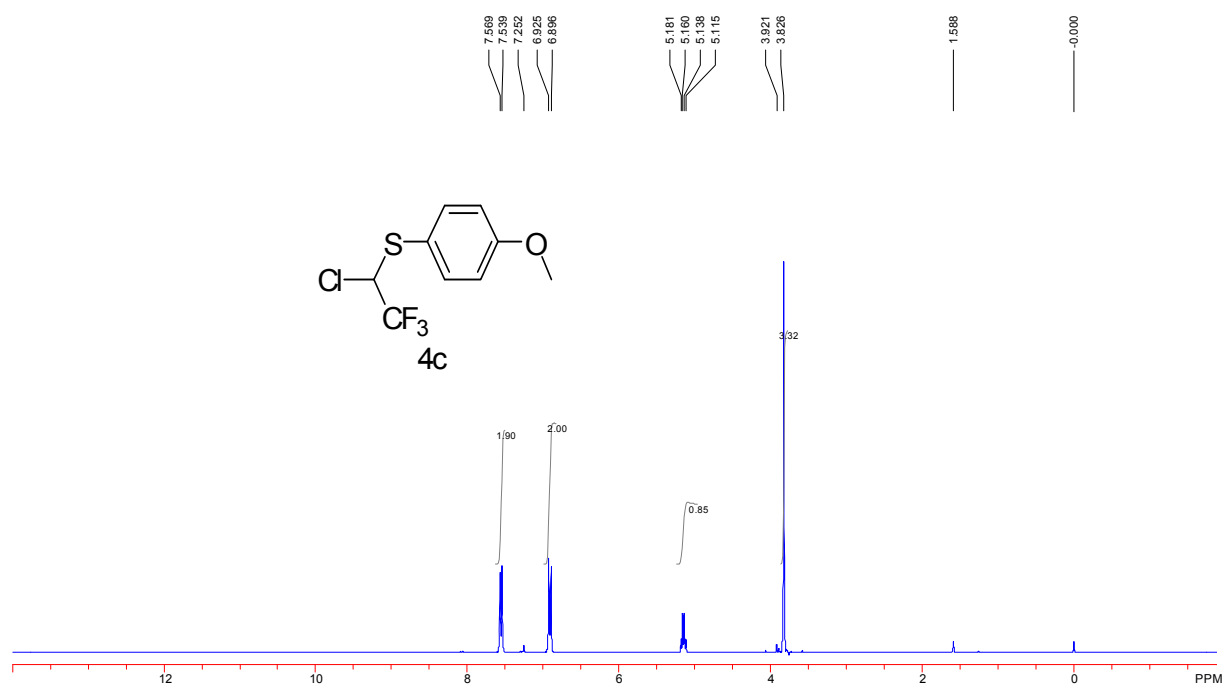
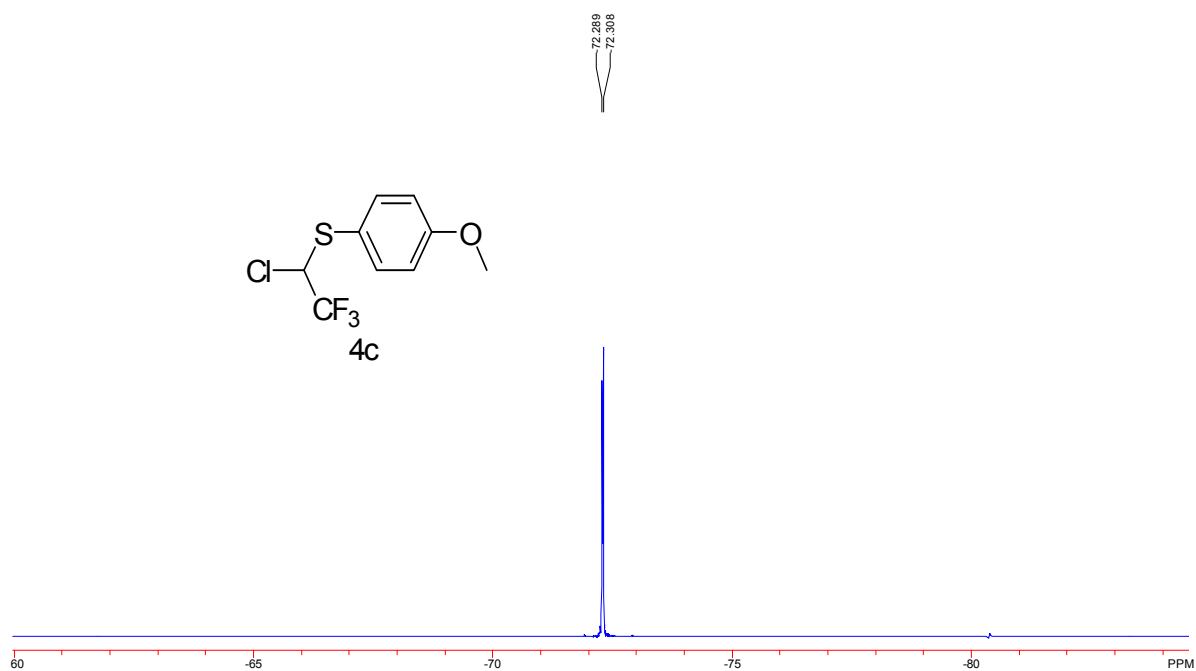


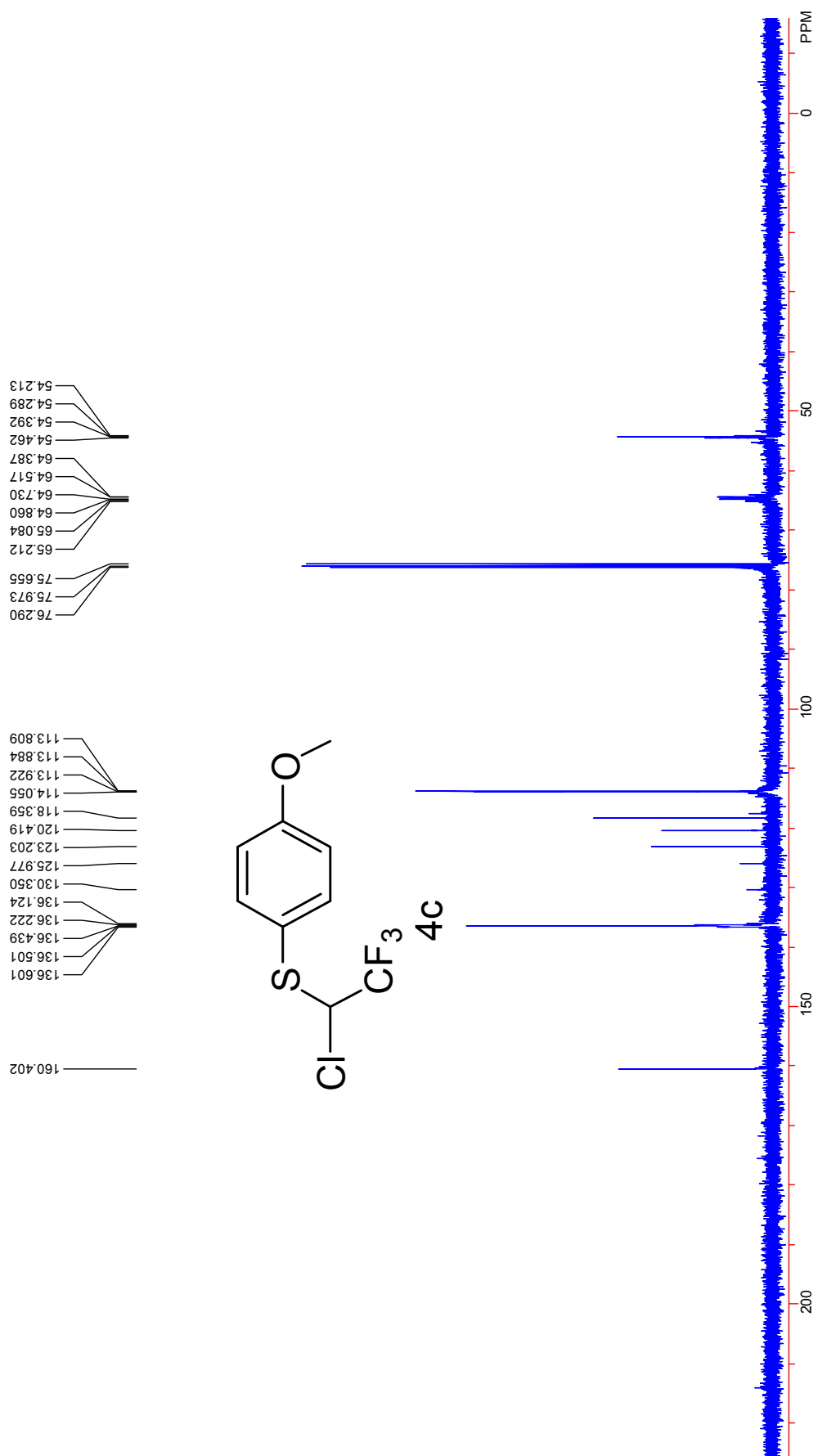


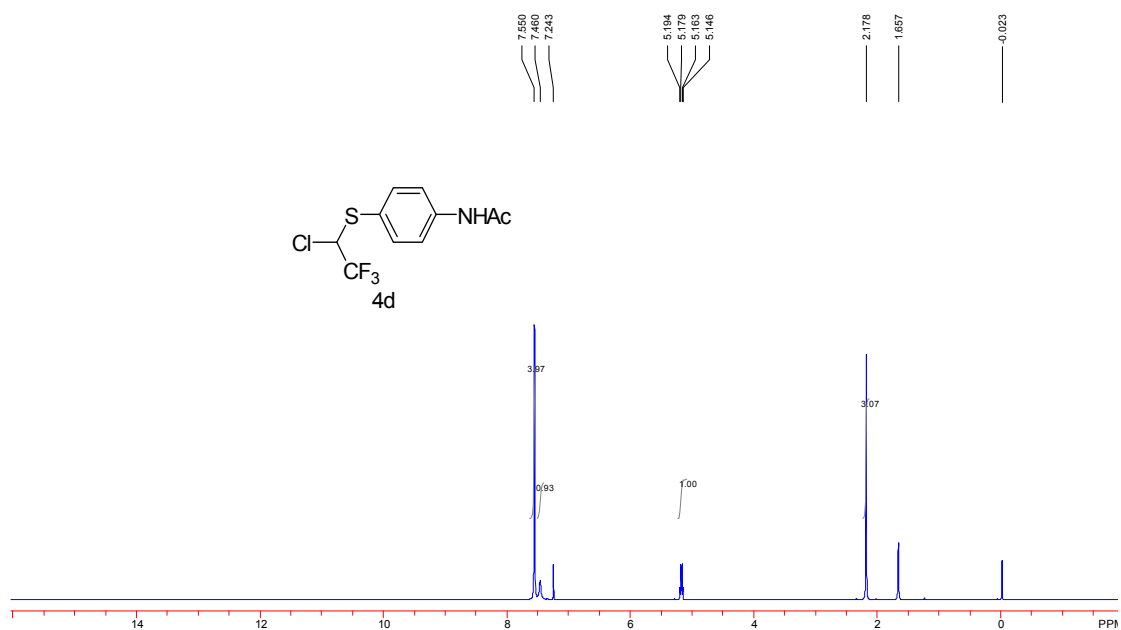
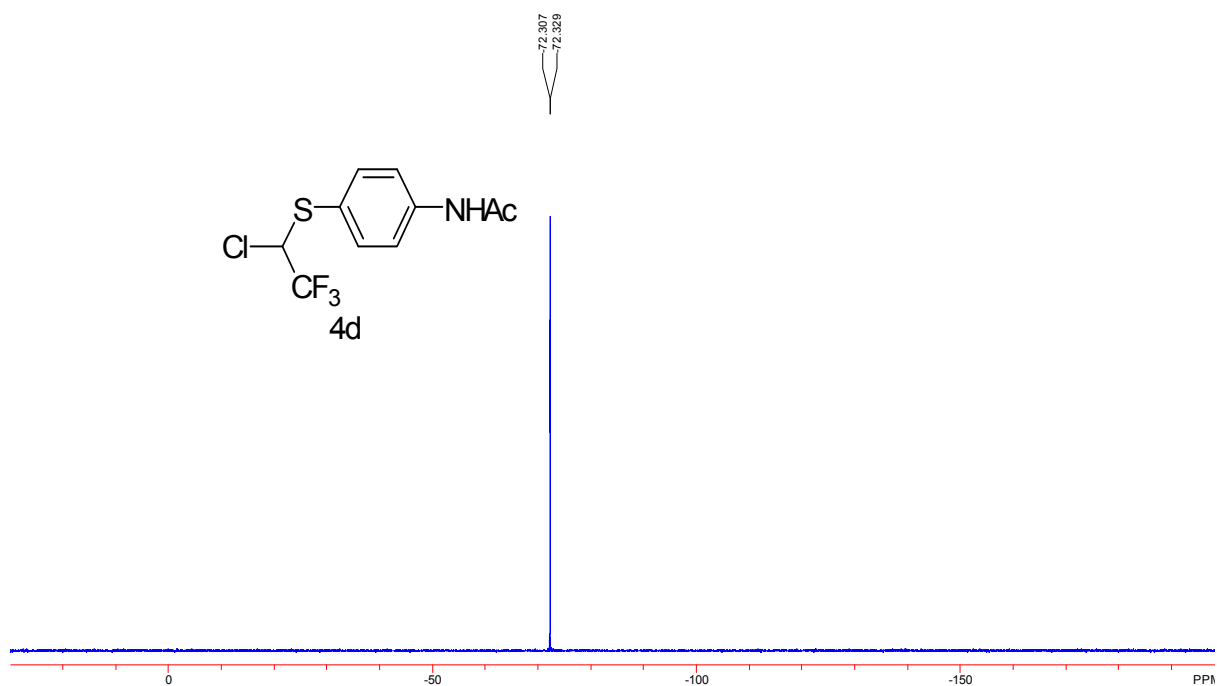


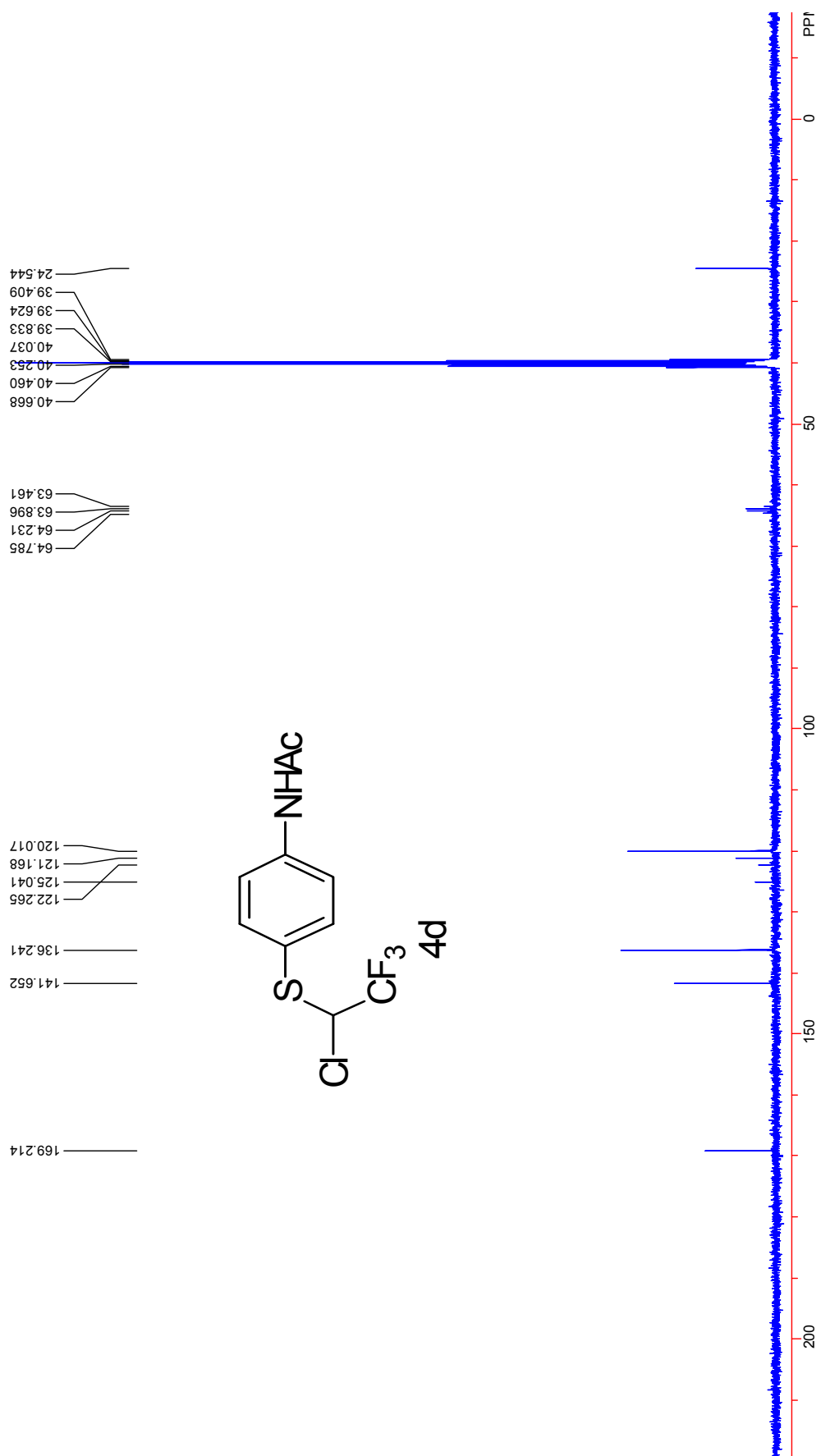


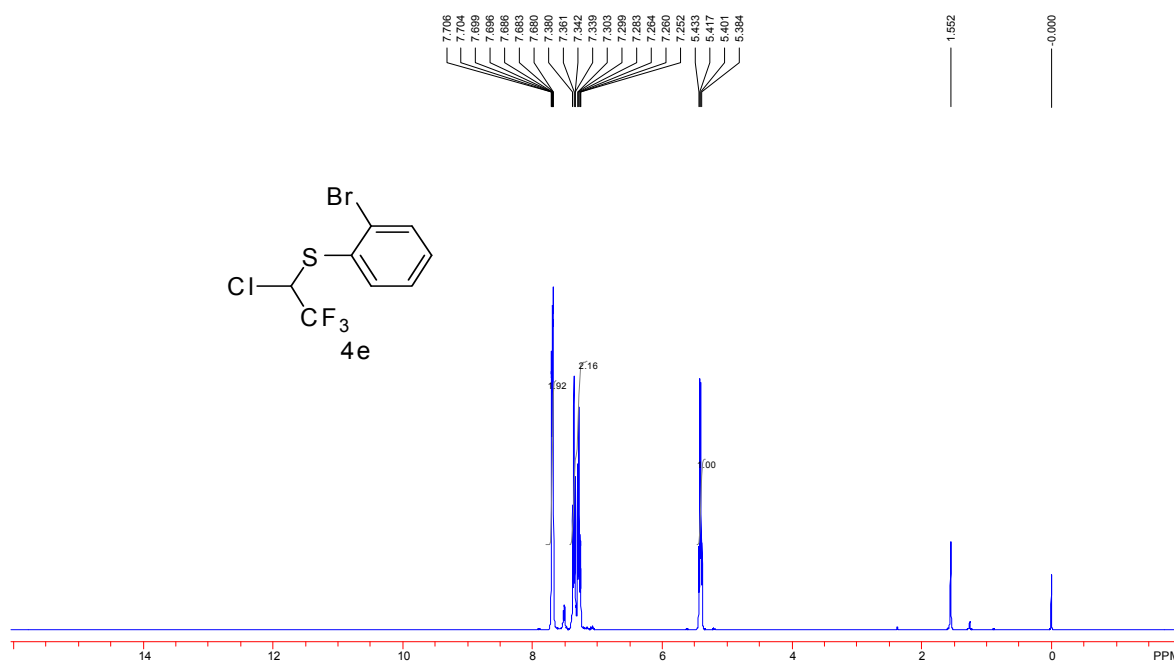
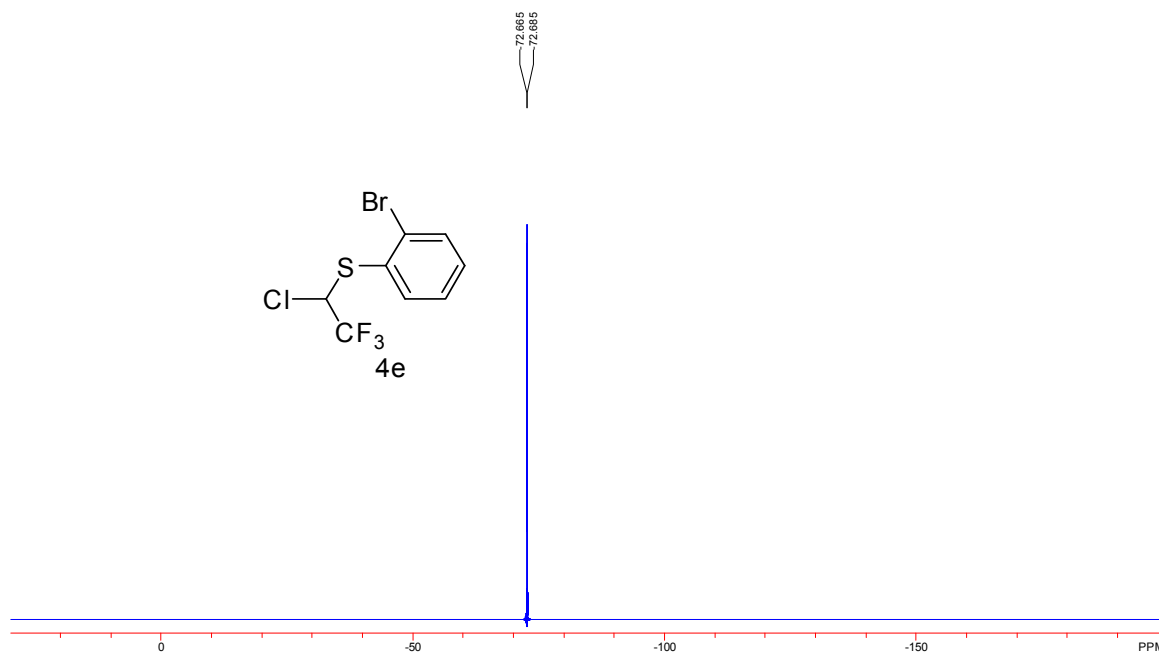


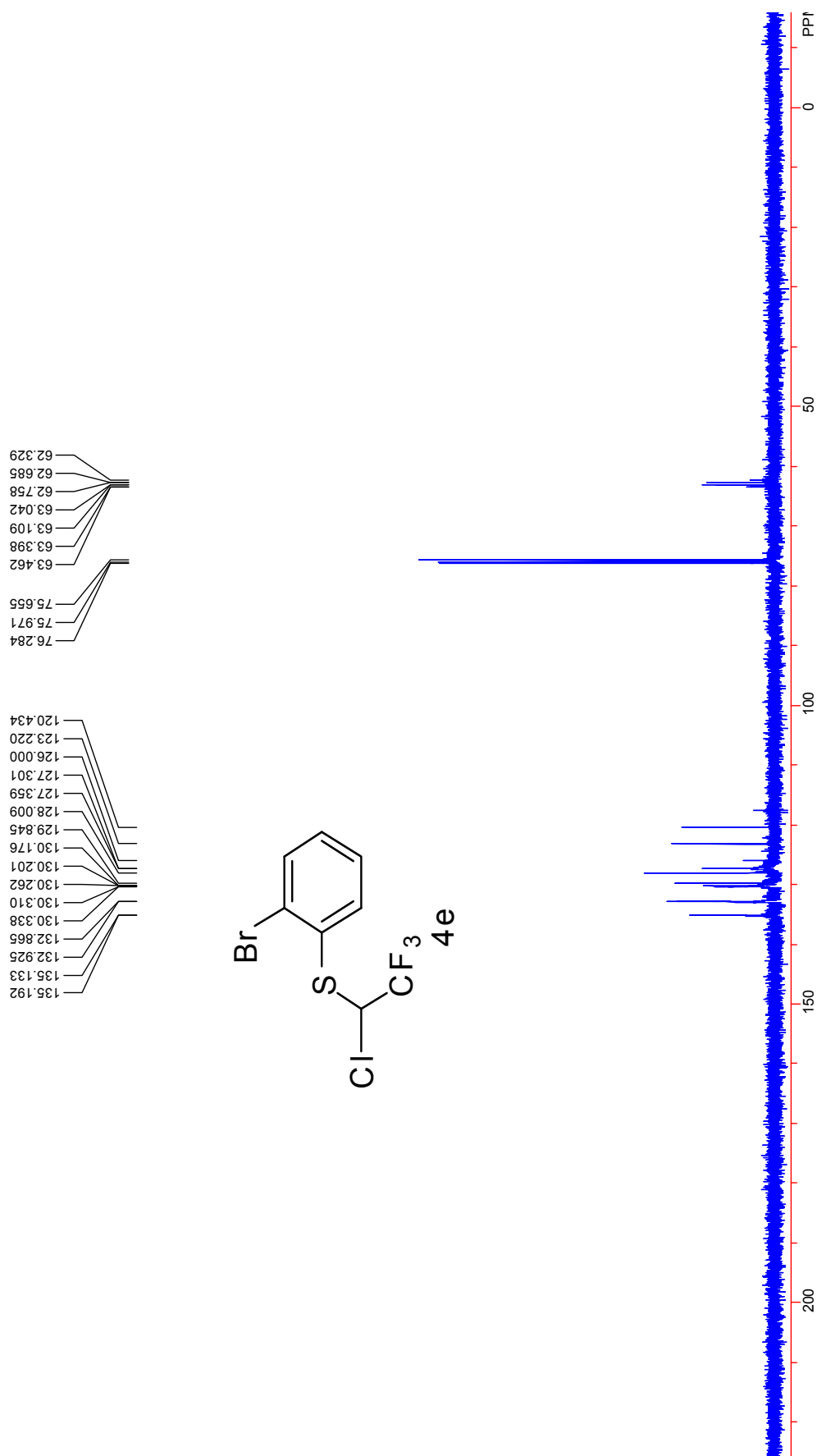
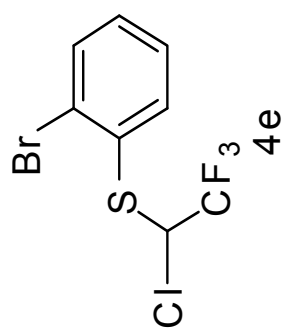


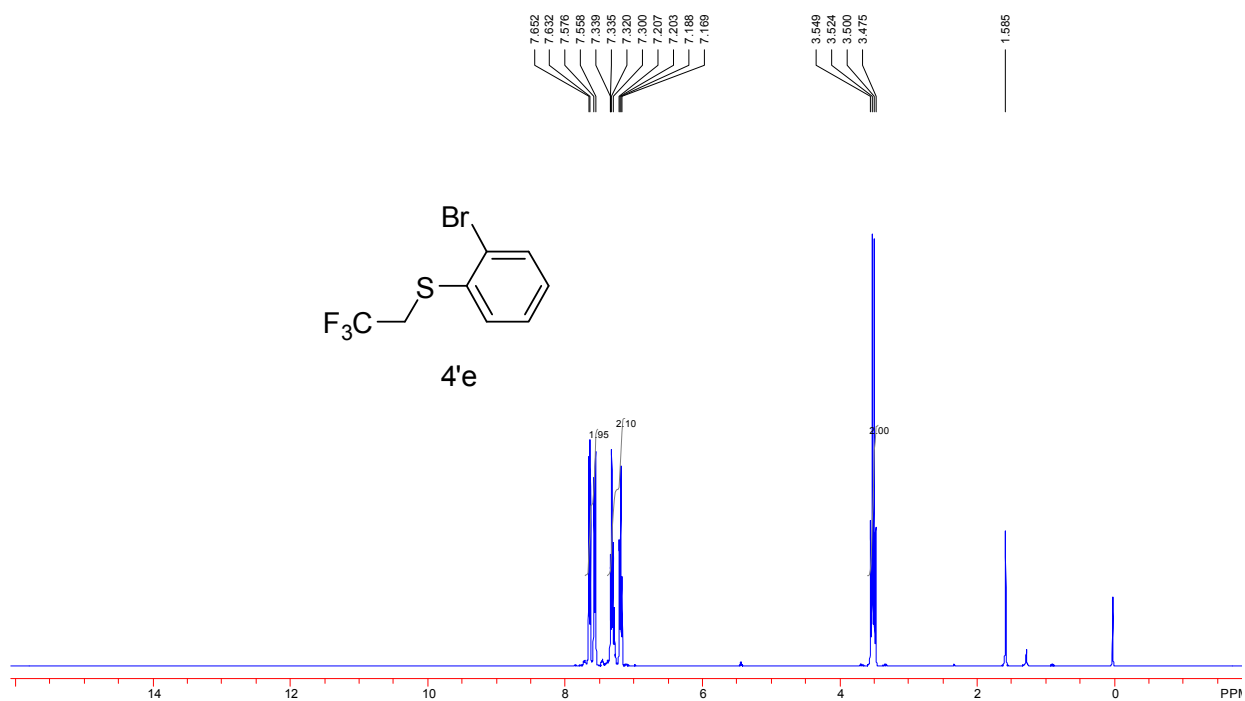
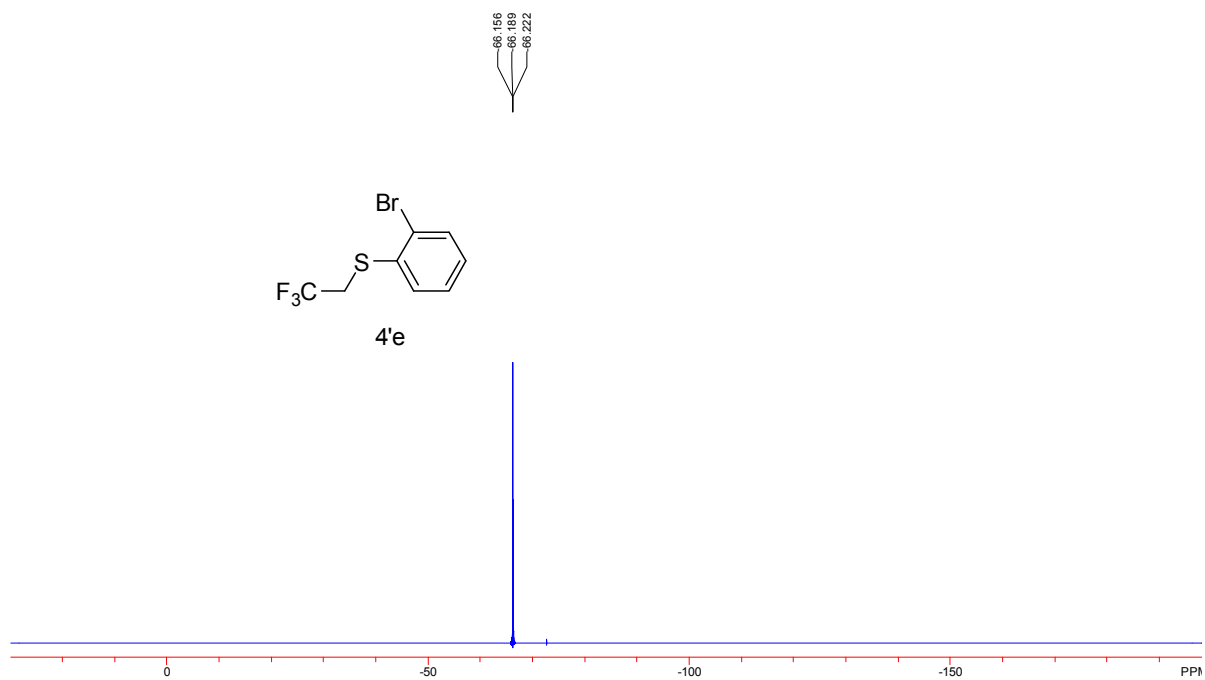


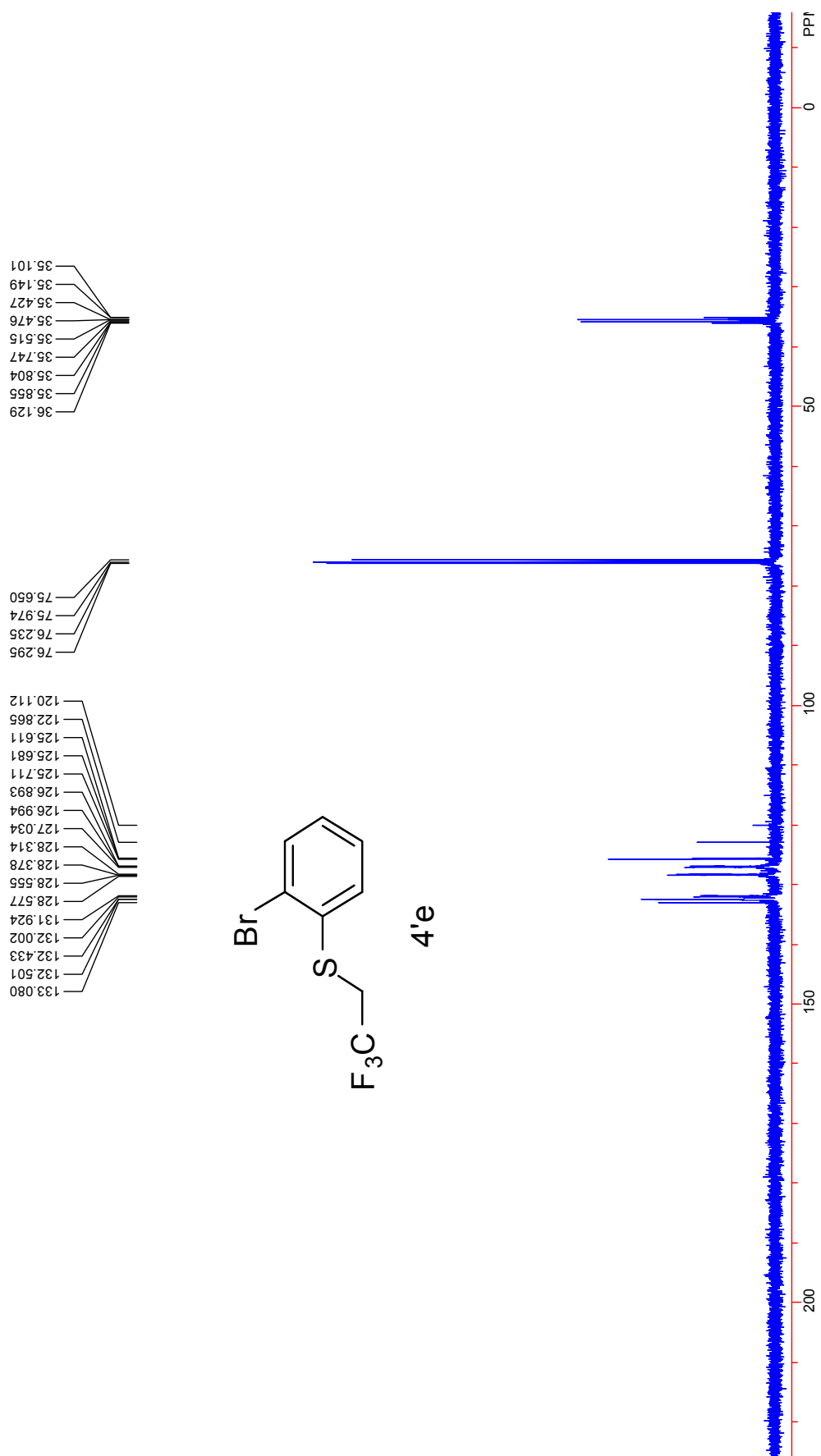


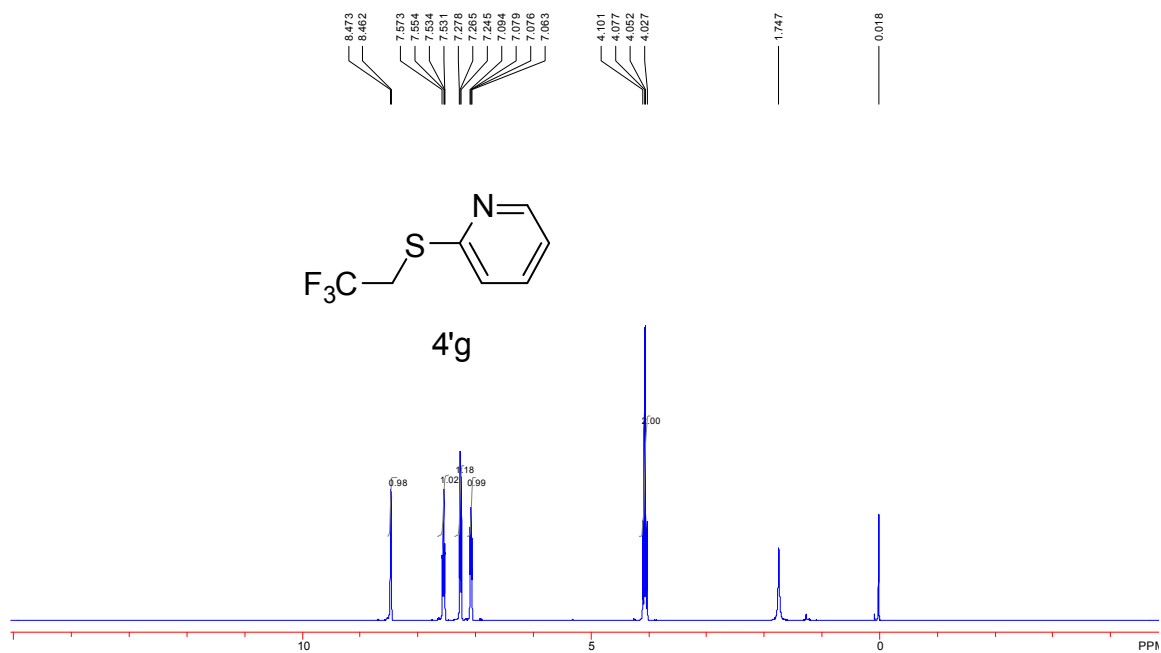
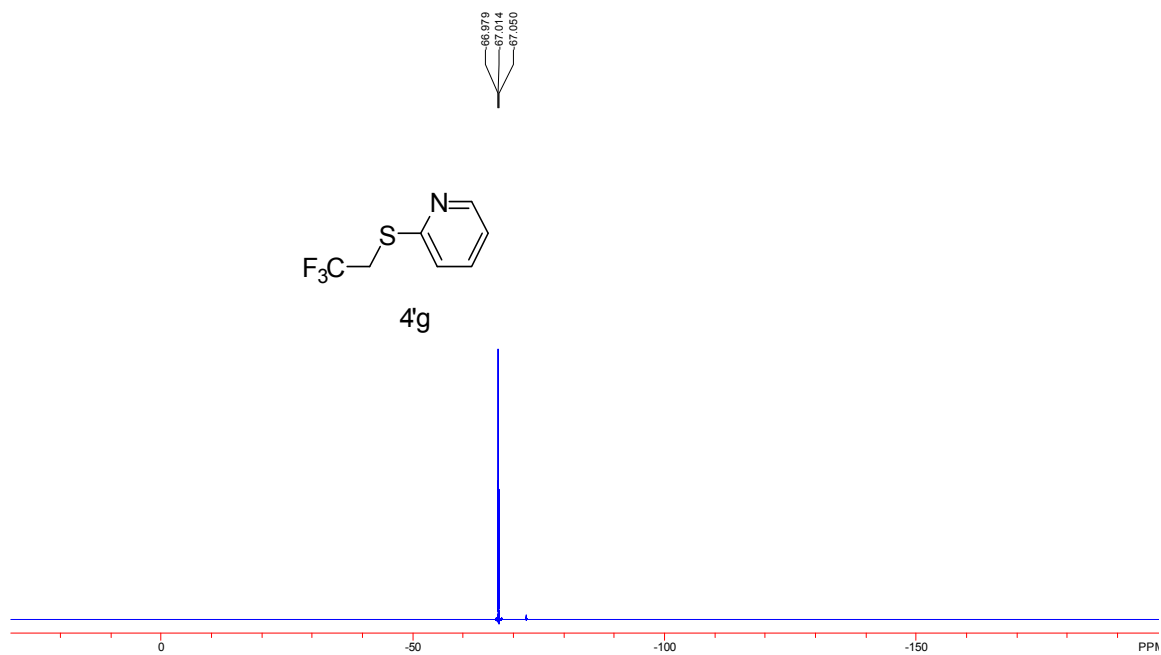


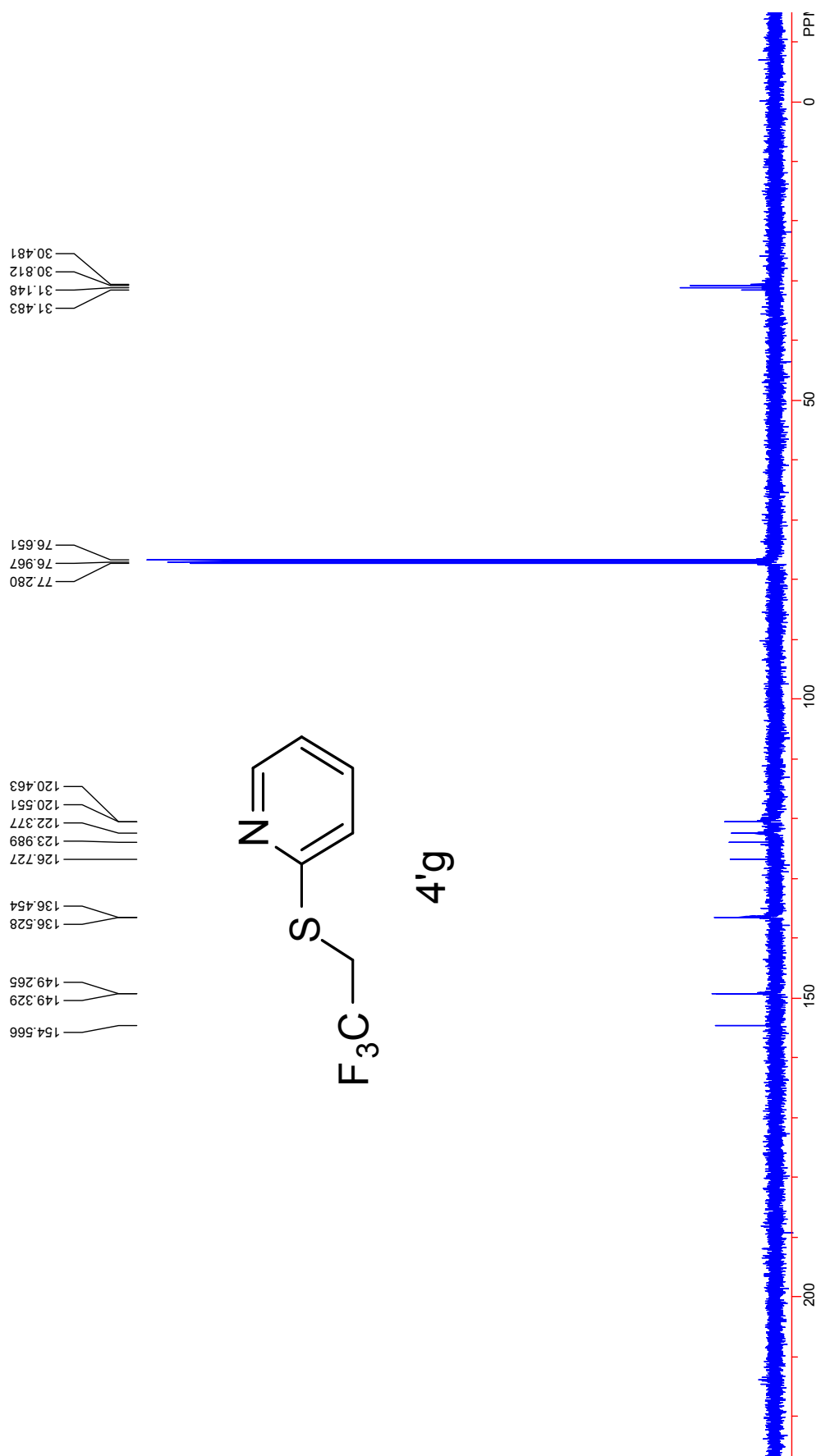


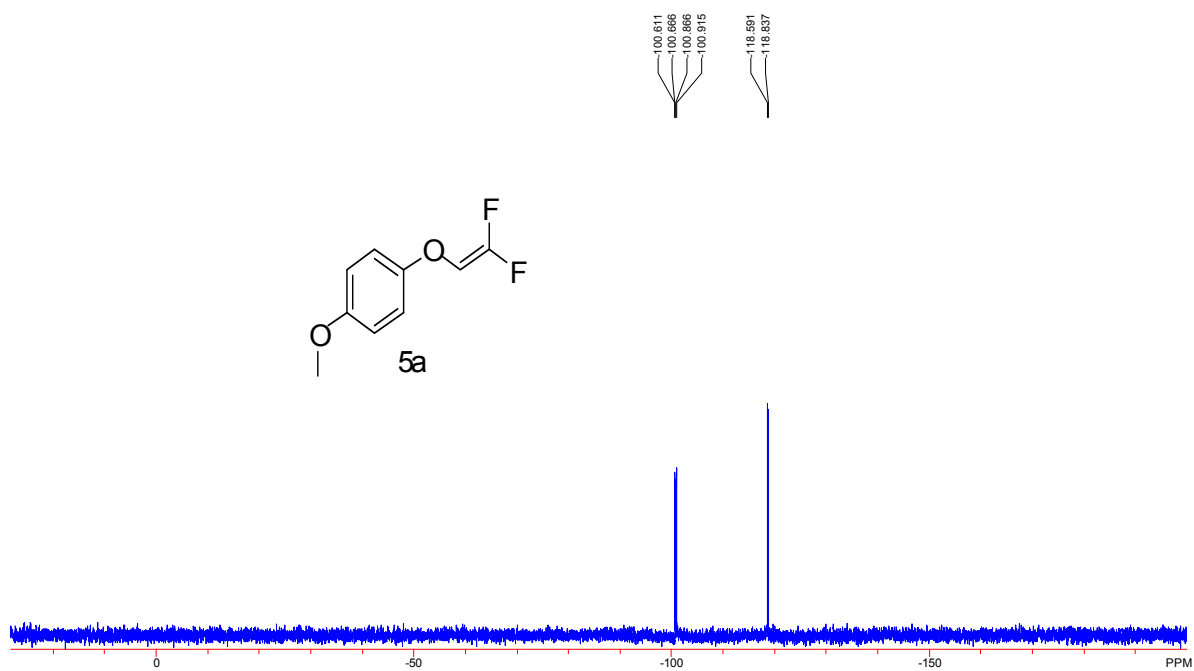
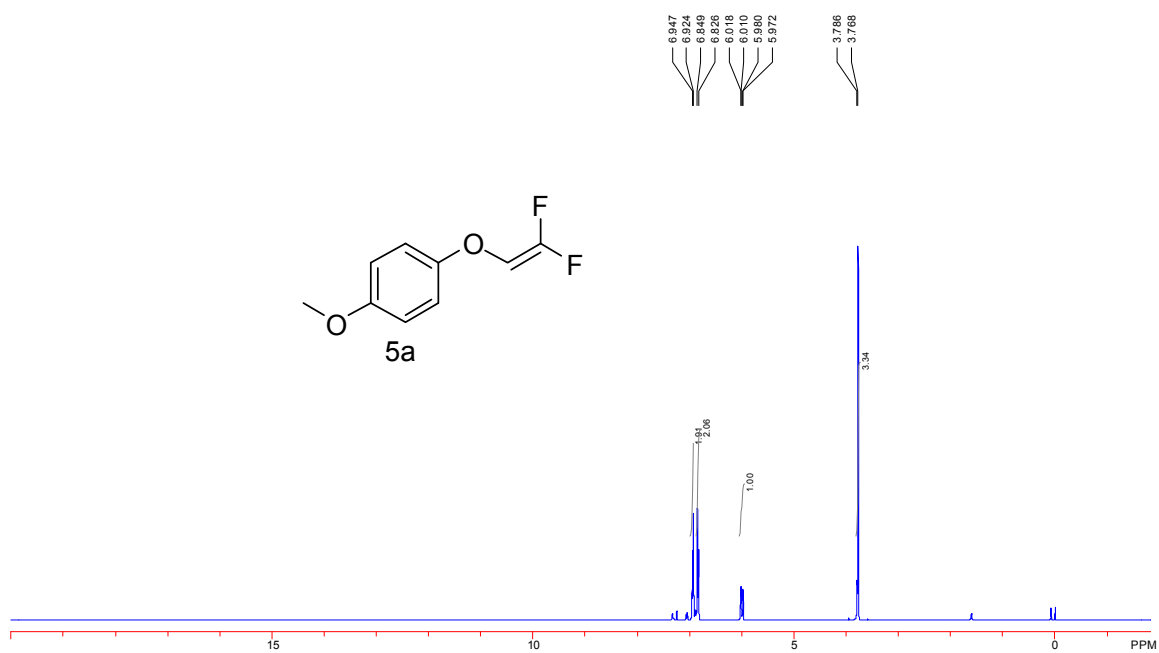


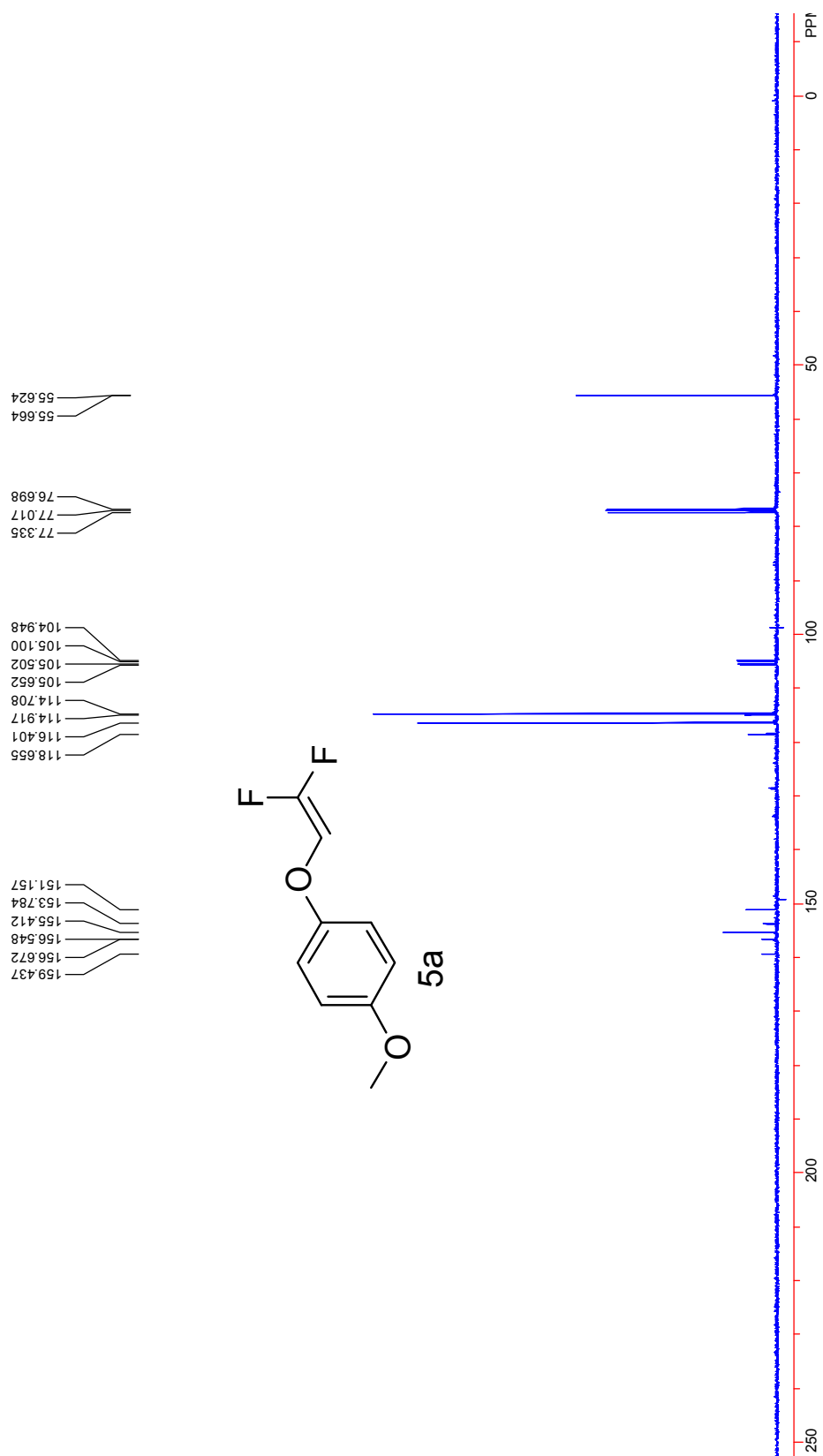


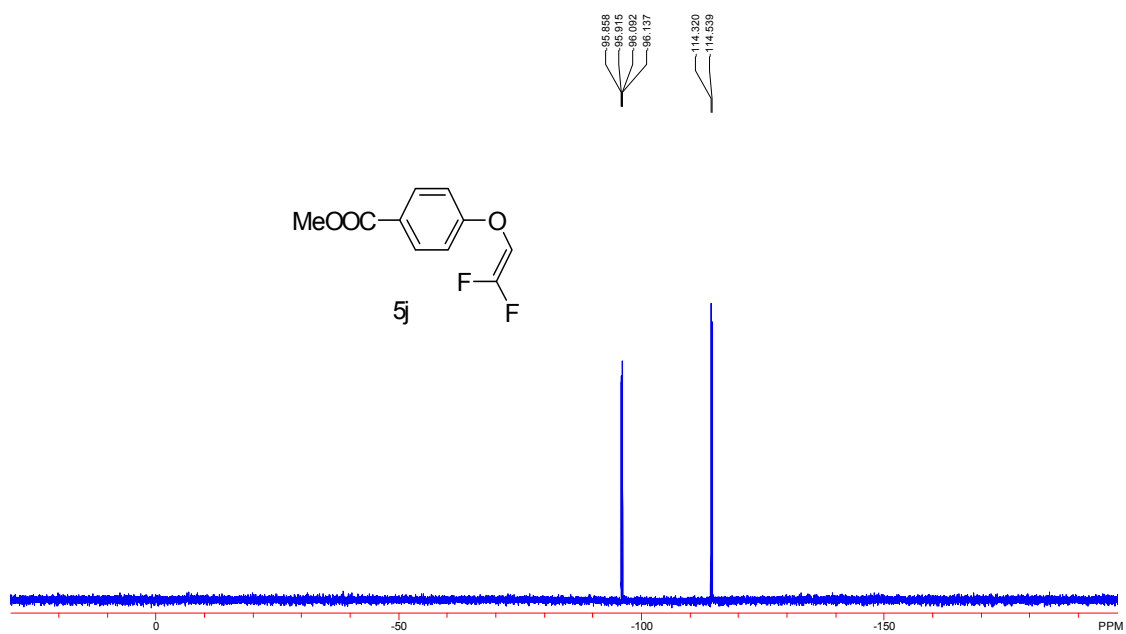
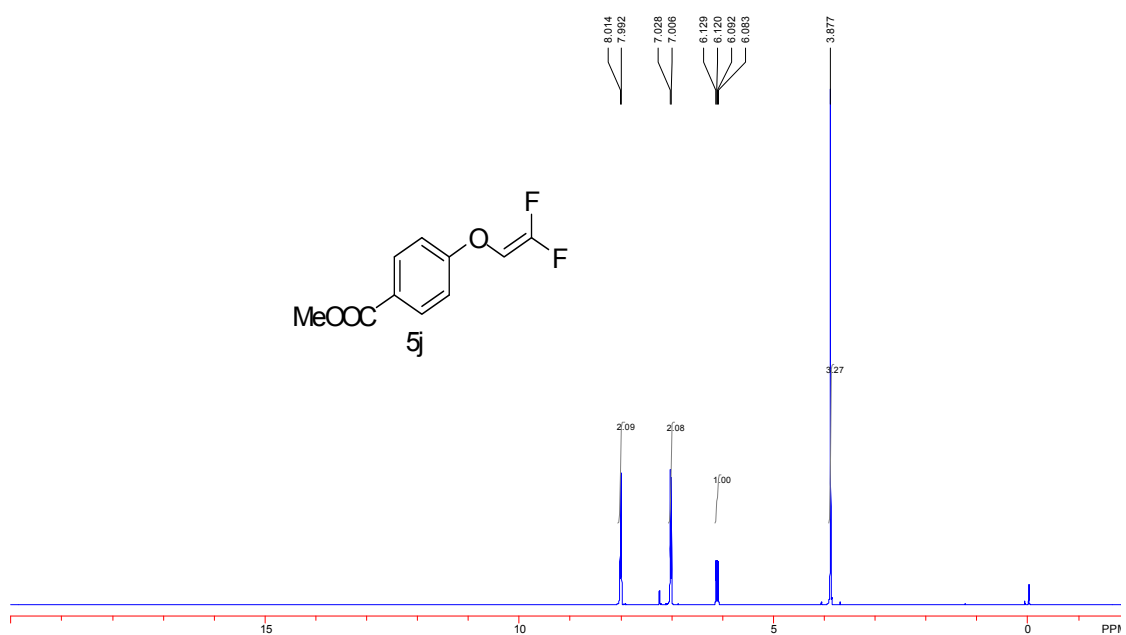


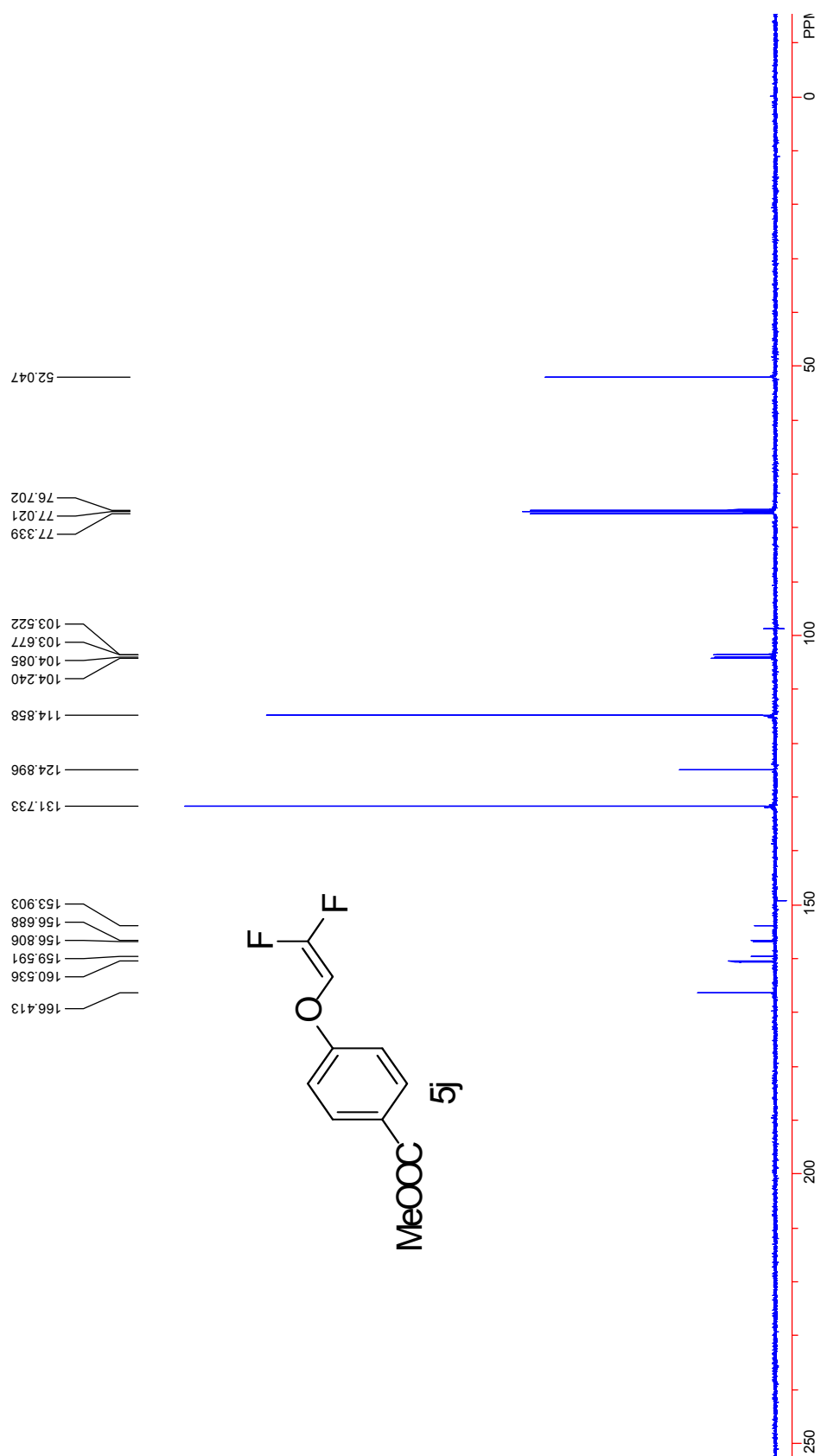


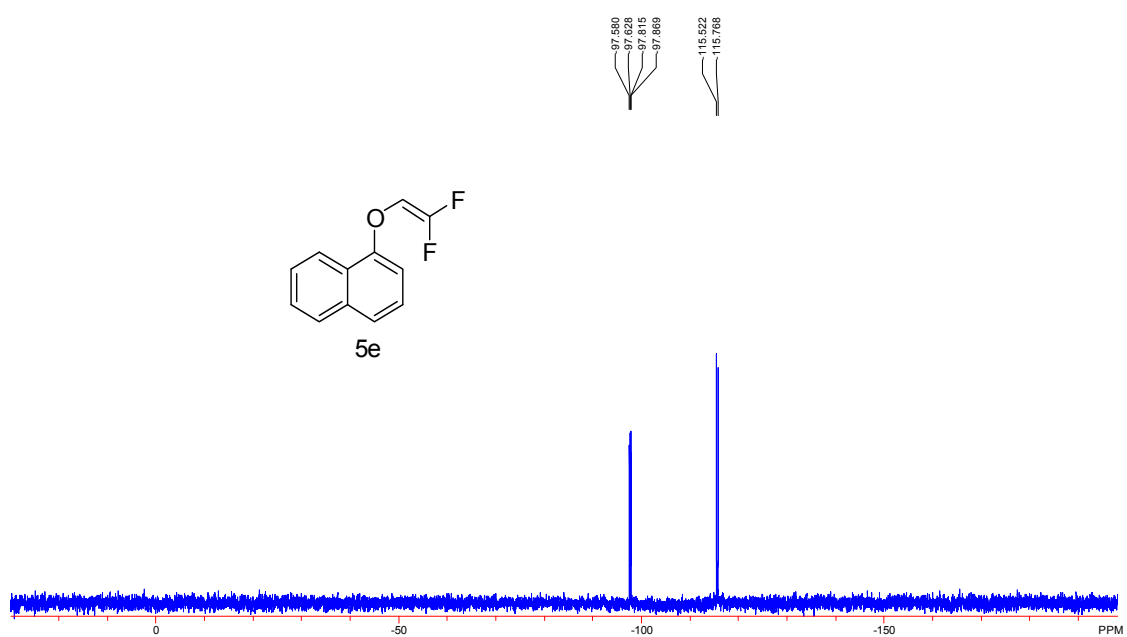
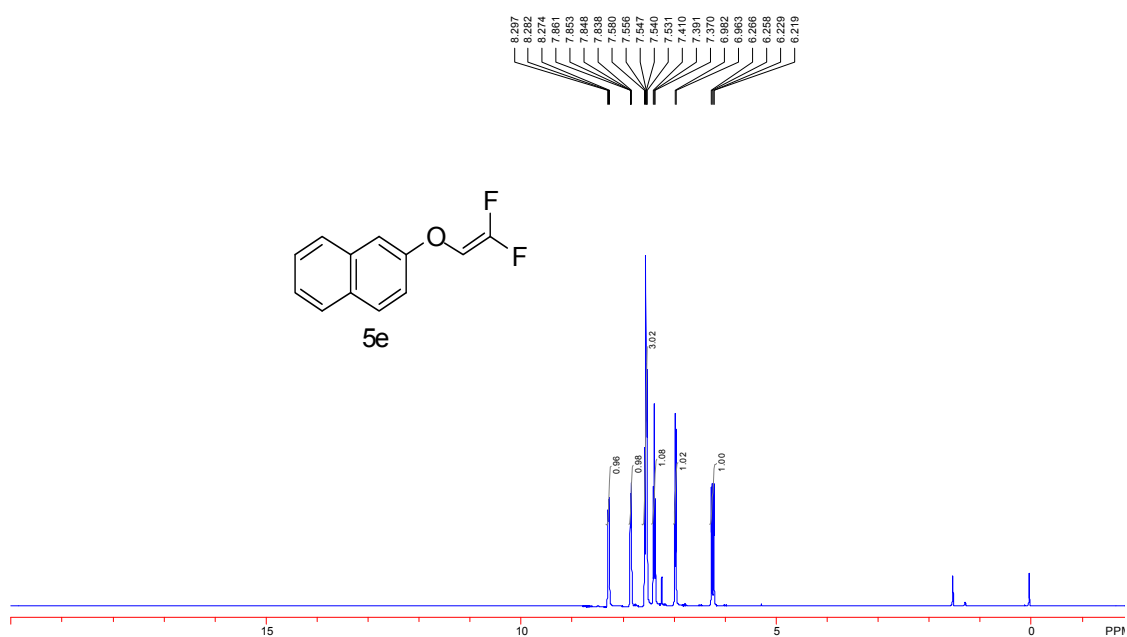


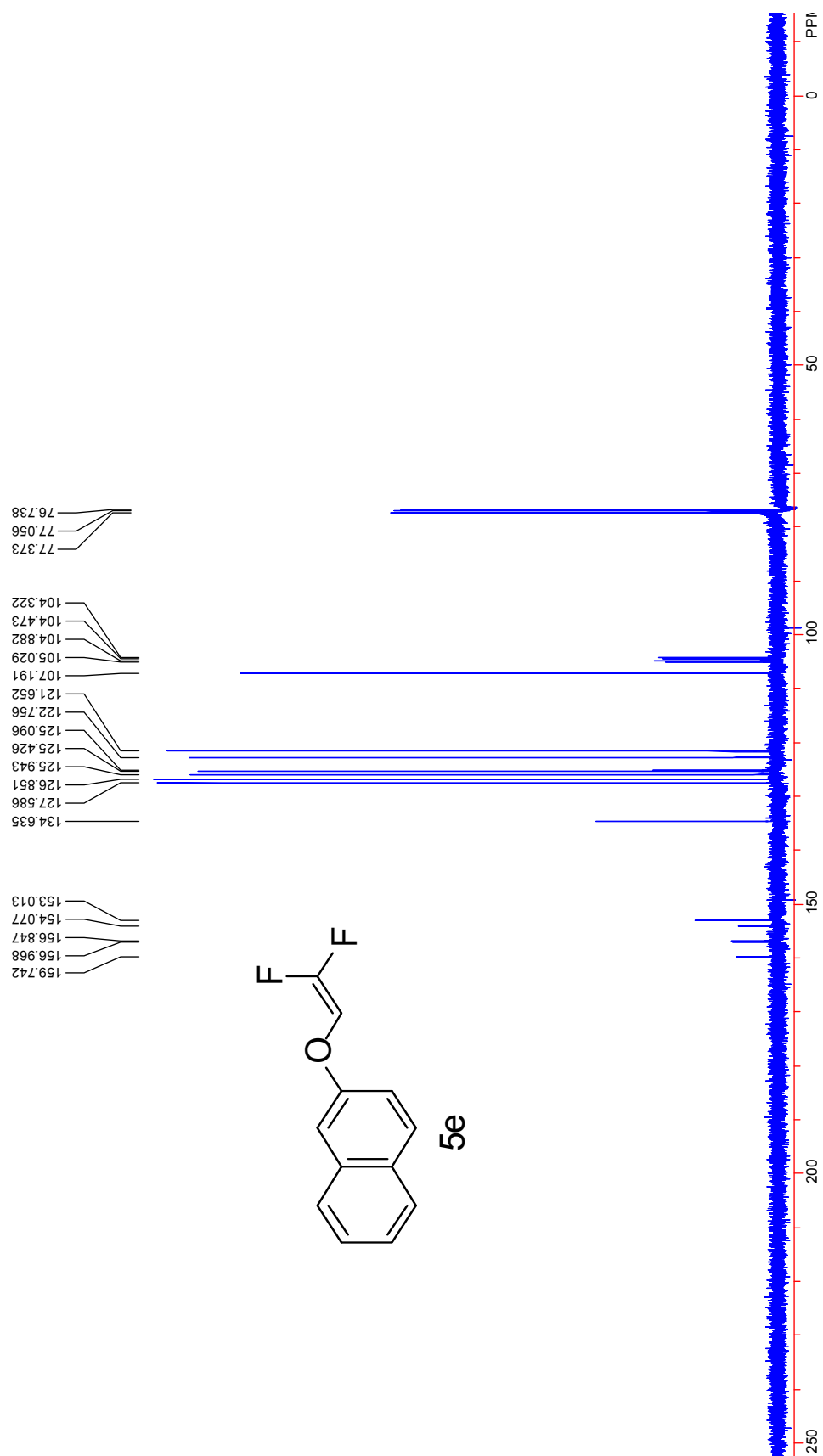


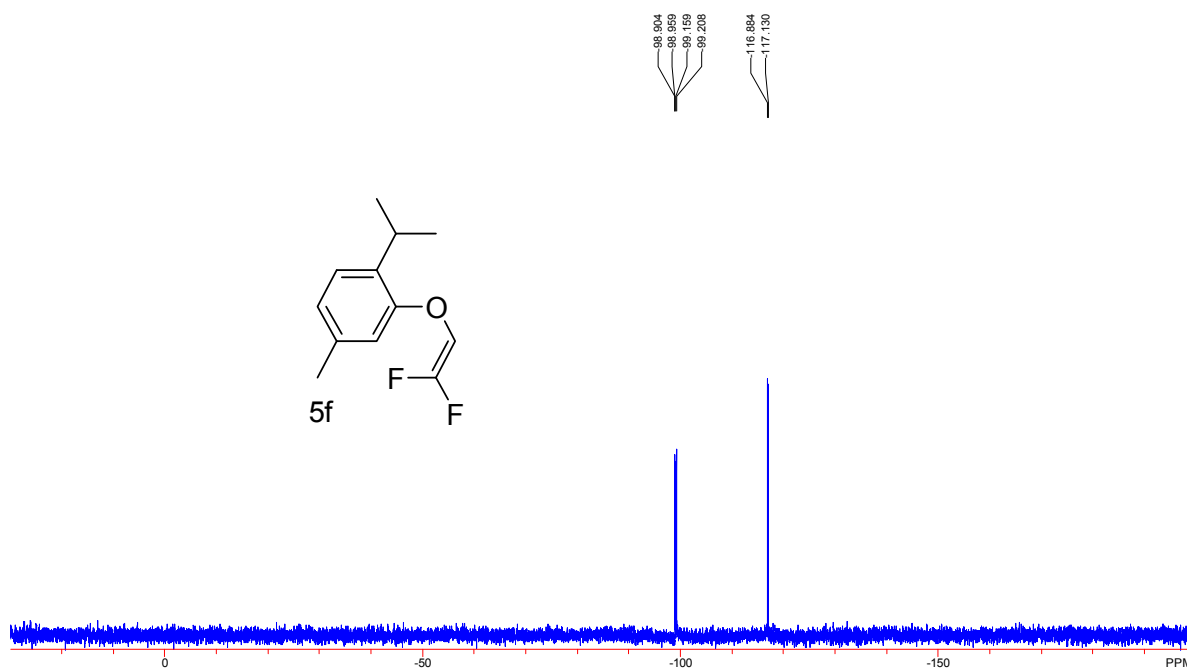
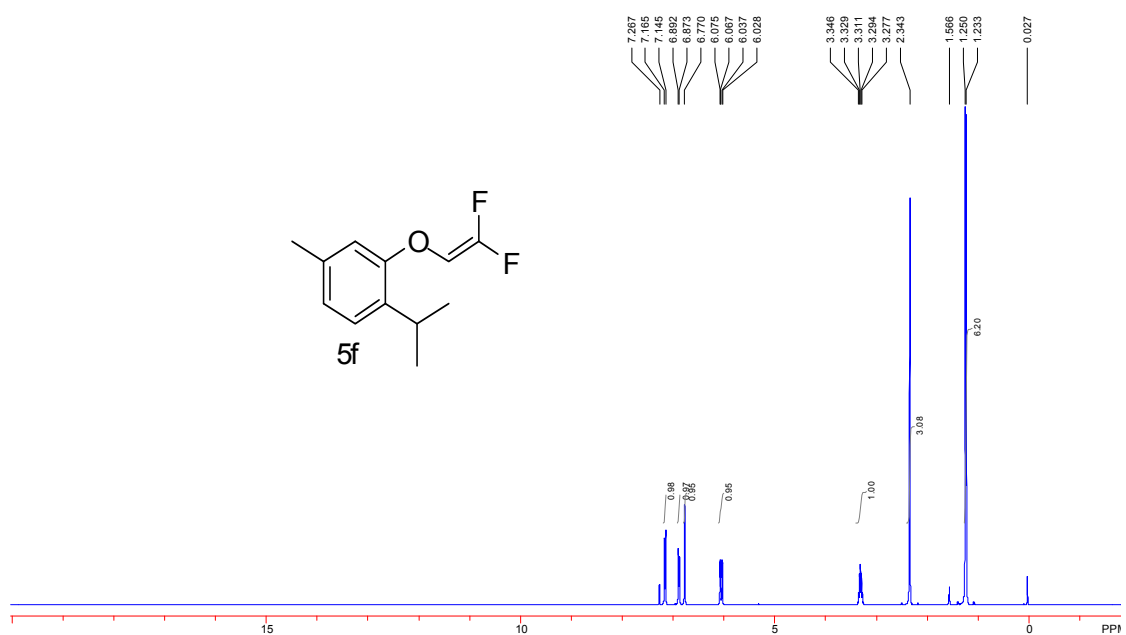


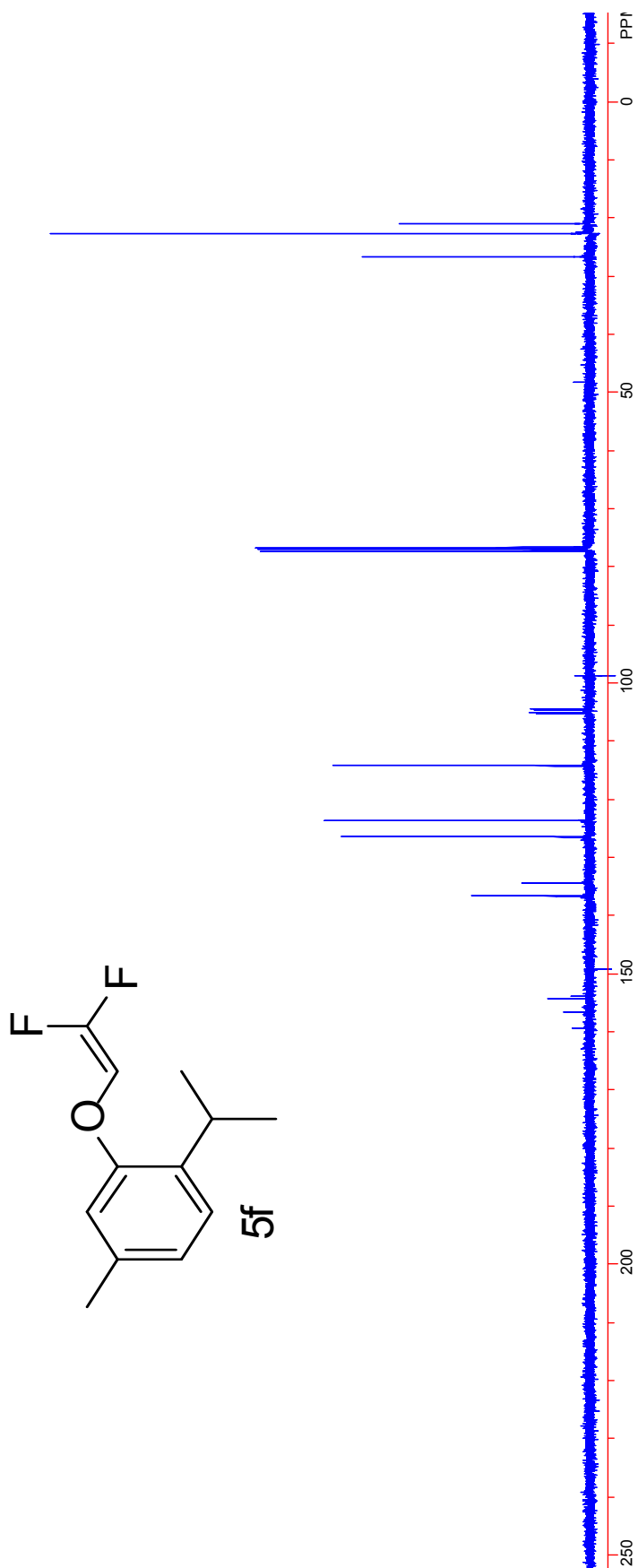


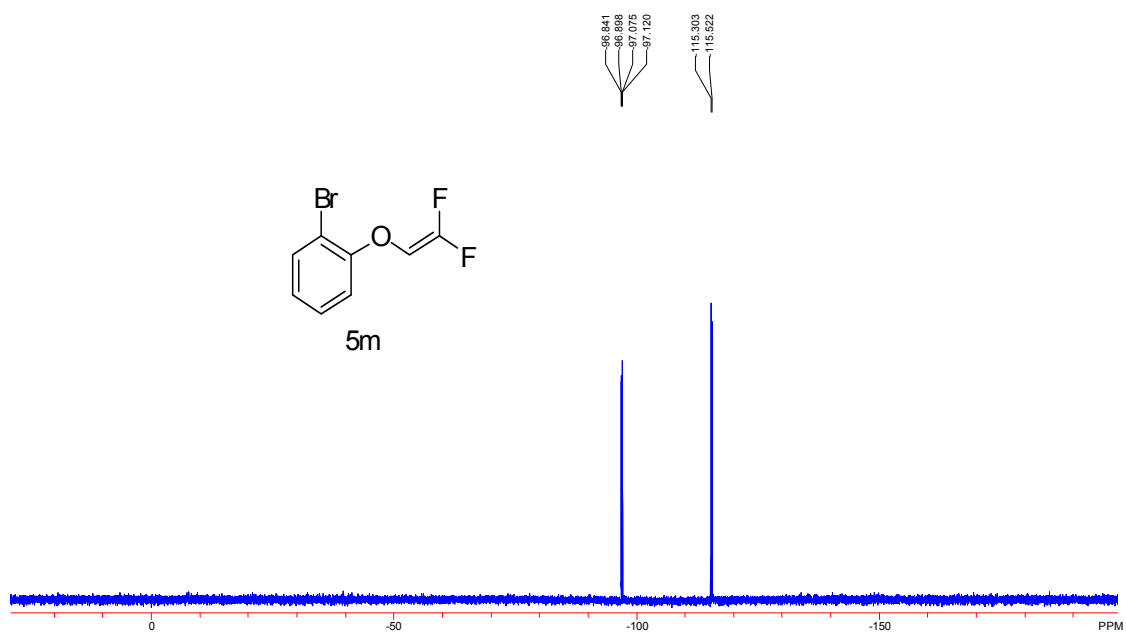
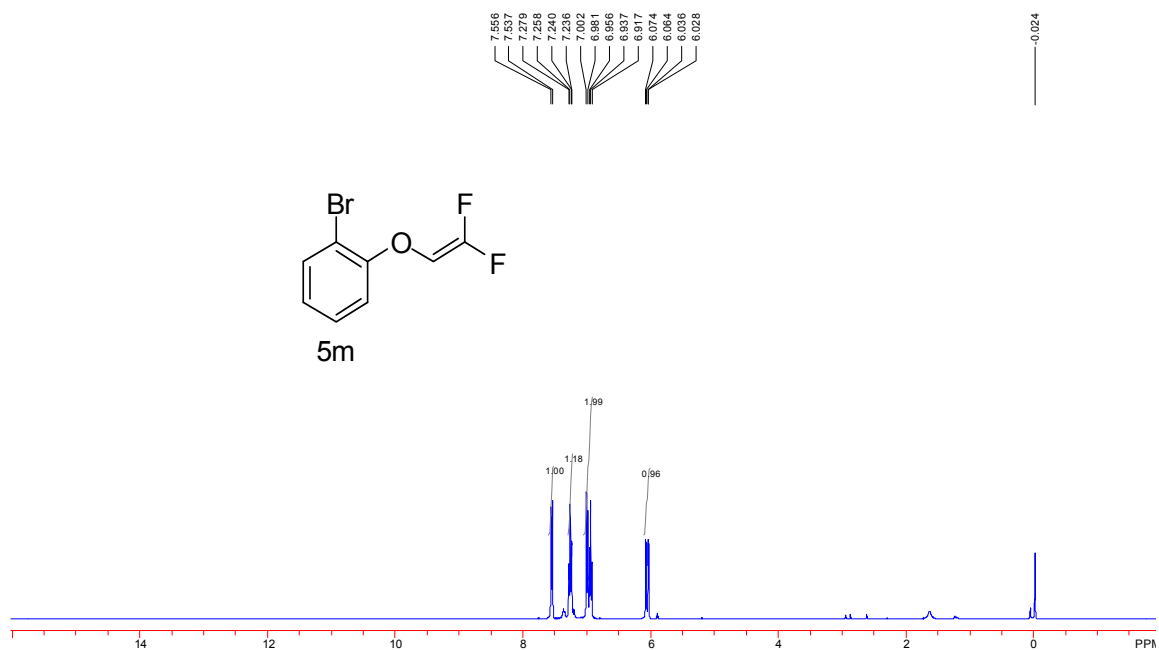


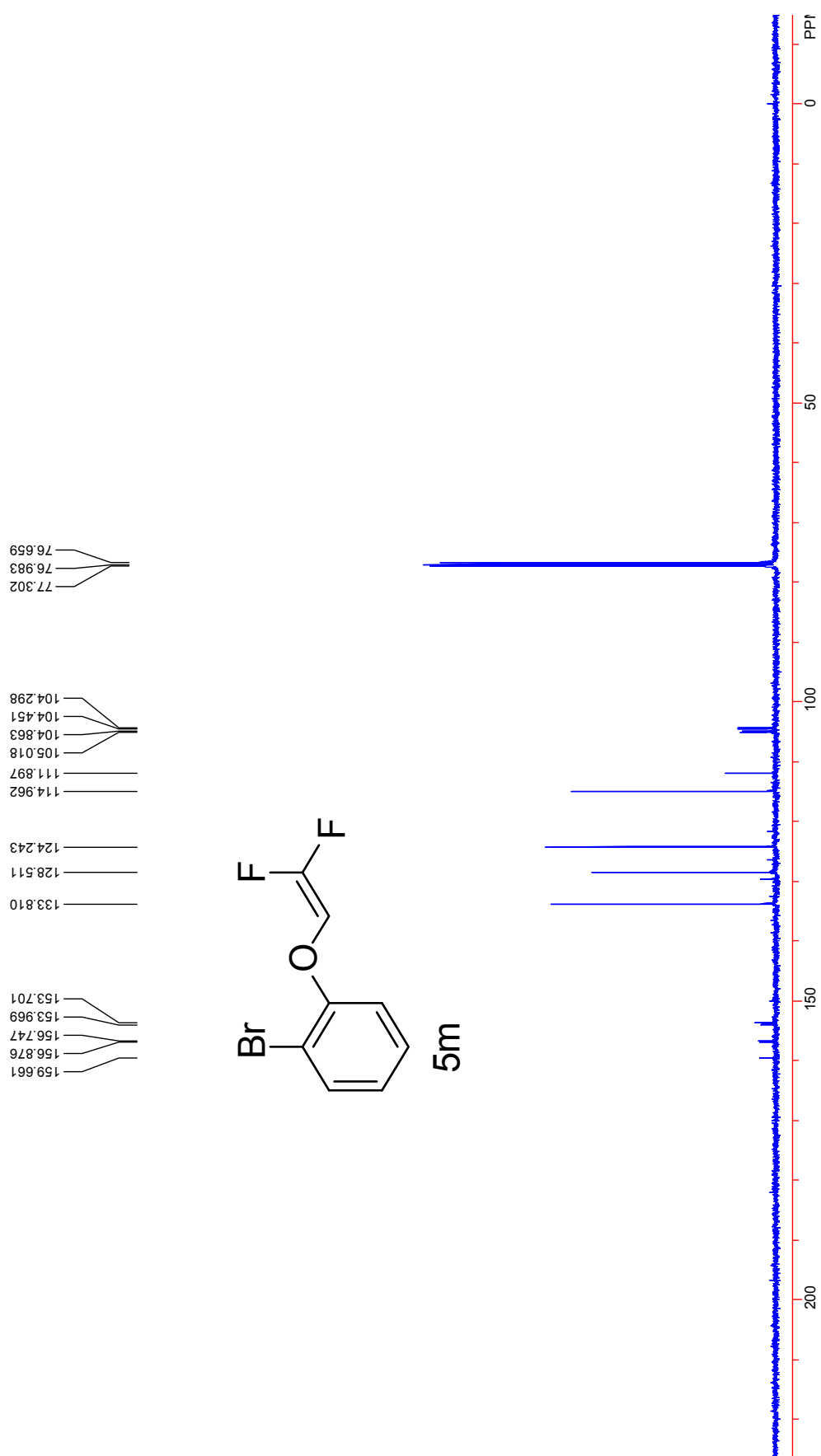


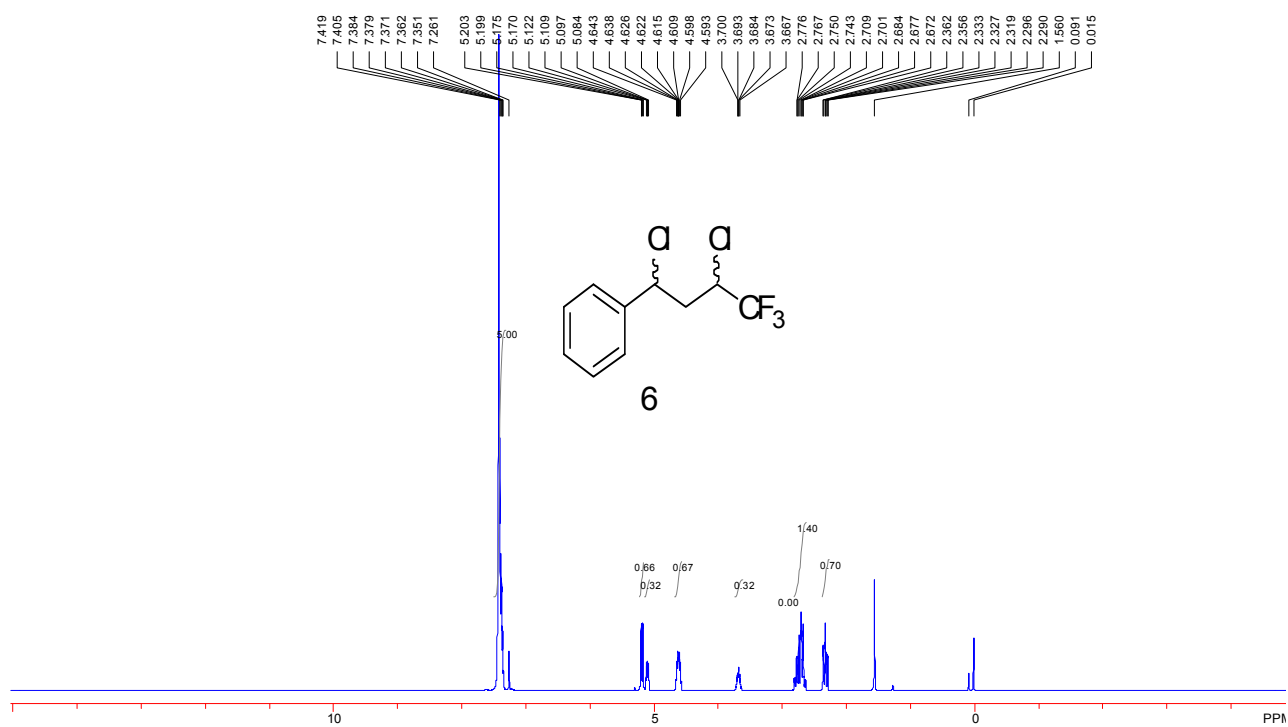
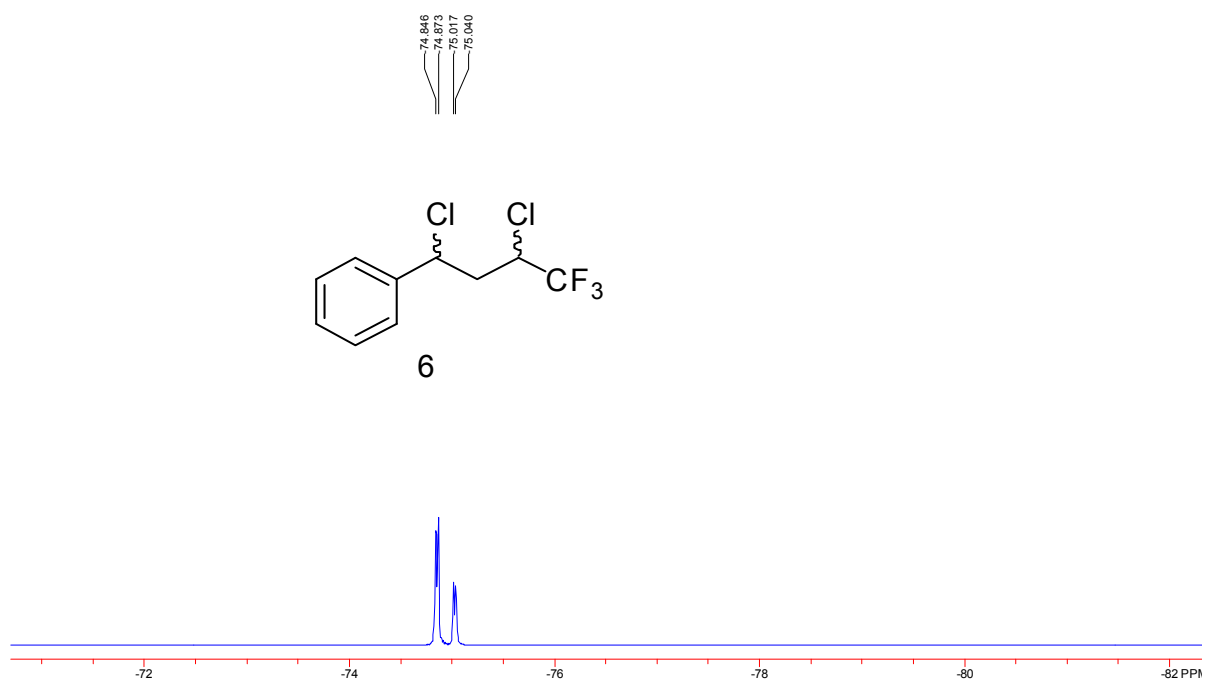


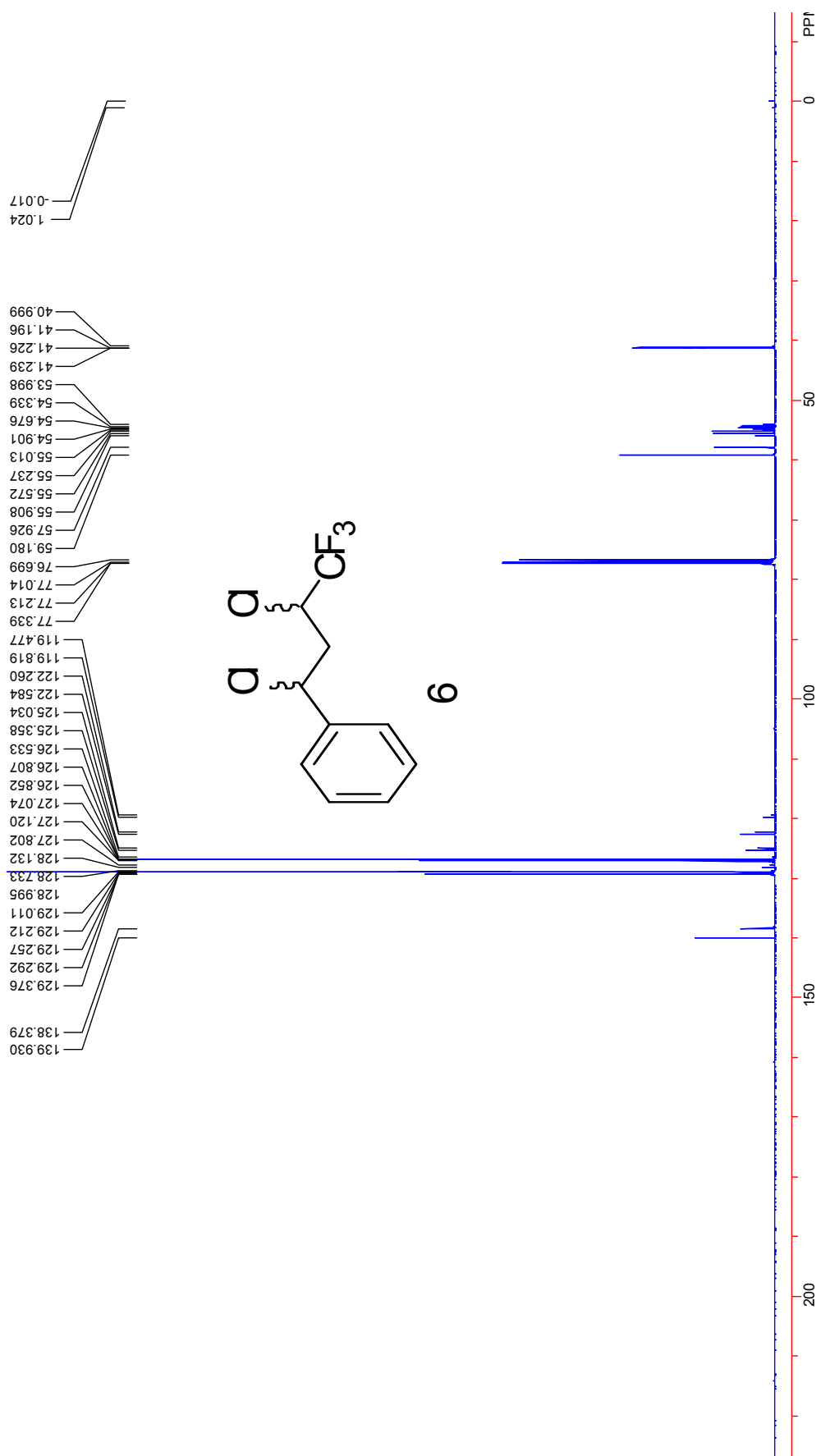












4, Reference

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