Supplementary Information

Selective formation of formamidines, carbodiimides and formimidates from isocyanide complexes of Mn(I) mediated by Ag_2O

Javier Ruiz,* Daniel Sol, María A. Mateo and Marilín Vivanco

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain. E-mail: Jruiz@uniovi .es

Contents

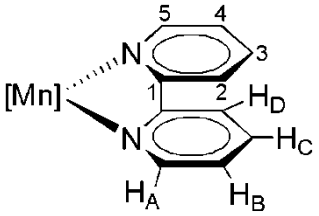
Synthesis and characterization of the new compounds

General Considerations

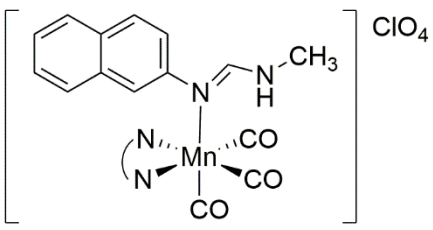
All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer Spectrum 100 and Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. Mass spectra were recorded on Bruker model Impact II (ESI and APCI) and MAT95XP (FAB) apparatus. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts of the NMR spectra were referenced to internal $SiMe_4$ (^1H and ^{13}C) or external H_3PO_4 (^{31}P). Assignments are based on $^1H,^1H$-COSY, $^1H,^{13}C$-HMBC, $^1H,^{13}C$-HSQC and DEPT experiments. All reagents were obtained commercially and used without further purification. Compounds [**3a**]CO_4 and [**3d**]ClO_4 were prepared as described in reference 12b of the manuscript.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of such materials should be prepared and these should be handled with great caution.

For the NMR spectra the atom-labeling in 2,2'-bipyridine ligand is as follows:

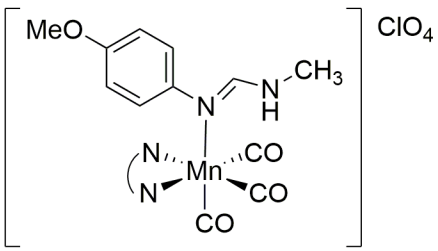


Synthesis of compound [3b]ClO_4. To a solution of *fac*-[Mn{$C(NHC_{10}H_7)(NHCH_3)$}(bipy)$(CO)_3$]ClO_4 ([**2b**]ClO_4, 0.10 g, 0.17 mmol) in CH_2Cl_2 (10 mL)



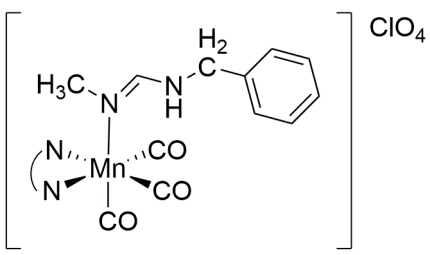
Ag_2O (21 mg, 0.09 mmol) was added, and the resulting mixture stirred for 3 h. The solution was filtered and then concentrated under vacuum to 3 mL. Addition of hexane (10 mL) afforded a yellow solid. Yield: 95 mg (95%). The ^{1}H NMR indicates the presence of two isomers in an approximate ratio 4:1. The major isomer (shown in the figure) corresponds to coordination of the formamidine through the N-Naphthyl group, whereas the minor one features N-Methyl coordination of the corresponding formamidine tautomer. A sample of the major isomer for ^{1}H NMR measurements was obtained by successive recrystallizations in CH_2Cl_2/Et_2O. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2036 (vs), 1946 (s), 1935 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, δ, ppm): Major isomer (80%): δ = 8.99 (d, ^3J(H,H) = 5.2 Hz, 1H, H_A bipy), 8.83 (d, ^3J(H,H) = 5.2 Hz, 1H, H_A bipy), 8.20-8.16 (m, 2H, H_D bipy), 8.11 (t, ^3J(H,H) = 7.6 Hz, 1H, H_C bipy), 8.04 (t, ^3J(H,H) = 7.6 Hz, 1H, H_C bipy), 7.75-7.73 (m, 1H, Naph), 7.59-7.54 (m, 2H, H_B bipy and Naph), 7.48-7.39 (m, 4H, H_B bipy and Naph), 7.19 (d, ^3J(H,H) = 13.0 Hz, 1H, NCHN), 6.35-6.32 (m, 2H, Naph), 4.64 (br, 1H, NH), 2.80 (d, ^3J(H,H) = 4.8 Hz, 3H, NCH_3). Minor isomer (20%): δ = 9.21 (d, ^3J(H,H) = 5.0 Hz, 2H, H_A bipy), 8.36 (d, ^3J(H,H) = 7.9 Hz, 2H, H_D bipy), 8.22 (t, ^3J(H,H) = 8.1 Hz, 2H, H_C bipy), 7.77-7.70 (m, H_B bipy), 7.10-7.08 (m, 2H, Naph), 2.71 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, ppm): Major isomer (80%): δ = 220.1 (s, CO), 218.2 (s, CO), 159.3 (s, NCHN), 156.1 (s, C_1 bipy), 154.0 (s, C_5 bipy), 141.9 (s, C_{ipso} Naph), 140.5, 140.4 (s, C_3 bipy), 134.0, 131.8 (s, C Naph), 130.8, 128.2, 126.9 (s, CH Naph), 127.8, 127.7 (s, C_4 bipy), 123.9, 123.8 (s, C_2 bipy), 122.9, 122.0 (s, CH Naph), 32.9 (s, NCH_3). Minor isomer (20%): 156.2 (s, C_1 bipy), 153.9 (s, C_5 bipy), 140.9 (s, C_3 bipy), 124.5 (s, C_2 bipy), 118.9 (s, CH Naph), 114.0 (s, CH Naph), 39.7 (s, NCH_3). MS (ESI): ***m/z*****:** 479.0901 [M - ClO_4]$^+$

Synthesis of compound [3c]ClO_4. This was similarly prepared starting from *fac*-[Mn{CNH(4-$MeOC_6H_4$)($NHCH_3$)}(bipy)$(CO)_3$]ClO_4 ([**2c**]ClO_4, 0.10 g, 0.18 mmol) and Ag_2O (21 mg, 0.09 mmol). Yield: 93 mg (93%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2036 (vs), 1946 (s), 1938 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): Major isomer (60%): δ = 8.92 (d, ^3J(H,H) = 5.4 Hz, 2H, H_A bipy), 8.27-8.25 (m, 2H, H_D bipy), 8.15 (t, ^3J(H,H) = 7.3 Hz, 2H, H_C bipy), 7.58 (t, ^3J(H,H) = 6.7 Hz, 2H, H_B bipy), 7.11 (d, ^3J(H,H) = 13.1 Hz, 1H,



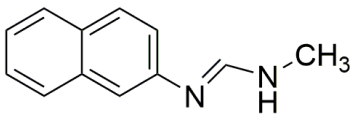
NCHN), 6.55 (d, ^3J(H,H) = 8.7 Hz, 2H, C_6H_4), 5.96 (d, ^3J(H,H) = 8.7 Hz, 2H, C_6H_4), 4.59 (br, 1H, NH), 3.69 (s, 3H, OCH_3), 2.79 (d, ^3J(H,H) = 4.9 Hz, 3H, NCH_3). Minor isomer (40%): δ = 9.18 (d, ^3J(H,H) = 5.4 Hz, 2H, H_A bipy), 8.35 (d, ^3J(H,H) = 8.1 Hz, 2H, H_D bipy), 8.22 (t, ^3J(H,H) = 8.4 Hz, 2H, H_C bipy), 7.72 (t, ^3J(H,H) = 6.5 Hz, 2H, H_B bipy), 6.99 (br, 1H, NH), 6.90 (d, ^3J(H,H) = 10.7 Hz, 1H, NCHN), 6.82 (d, ^3J(H,H) = 8.9 Hz, 2H, C_6H_4), 6.75 (d, ^3J(H,H) = 8.9 Hz, 2H, C_6H_4), 3.75 (s, 3H, OCH_3), 2.60 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): Major isomer (75%): δ = 220.1 (s, CO), 218.0 (s, CO), 158.3 (C_{ipso}), 159.7 (s, NCHN), 156.0 (s, C_1 bipy), 153.9 (s, C_5 bipy), 140.5 (s, C_3 bipy), 137.0 (s, C_{ipso}), 128.0 (s, C_4 bipy), 125.0 (s, C_6H_4), 123.8 (s, C_2 bipy), 115.6 (s, C_6H_4), 56.0 (s, OCH_3), 32.7 (s, NCH_3). Minor isomer (25%): 157.7 (s, C_{ipso}), 156.2 (s, C_1 bipy), 153.8 (s, C_5 bipy), 153.7 (s, NCHN), 140.9 (s, C_3 bipy), 132.0 (s, C_{ipso}), 128.2 (s, C_4 bipy), 124.3 (s, C_2 bipy), 120.5 (s, C_6H_4), 115.4 (s, C_6H_4), 56.0 (s, OCH_3), 39.0 (s, NCH_3). MS (ESI): *m/z*: 459.0863 [$M - ClO_4$]$^+$

Synthesis of compound [3e]ClO_4. This was similarly prepared starting from *fac*-[Mn{$CNH(CH_2C_6H_5)(NHCH_3)$}$(CO)_3$(bipy)]ClO_4 ([**2e**]ClO_4, 0.10 g, 0.18 mmol) and Ag_2O (21 mg, 0.09 mmol), maintaining the reaction mixture at 0 ºC.



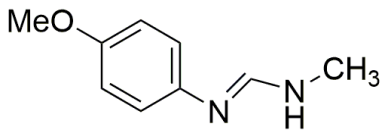
Yield: 63 mg (63%). Crystals of [**3e**]ClO_4 suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound. Yield: 63 mg (63%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2036 (vs), 1943 (s), 1937 (sh). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 9.07 (d, ^3J(H,H) = 4.6 Hz, 2H, H_A bipy), 8.28 (d, ^3J(H,H) = 7.9 Hz, 2H, H_D bipy), 8.14 (t, ^3J(H,H) = 7.6 Hz, 2H, H_C bipy), 7.62 (t, ^3J(H,H) = 6.1 Hz, 2H, H_B bipy), 7.30 (s, 3H, C_6H_5), 7.00 (s, 2H, C_6H_5), 6.42 (d, ^3J(H,H) = 12.0 Hz, 1H, NCHN), 6.06 (br, 1H, NH), 4.19 (d, ^3J(H,H) = 4.6 Hz, 2H, CH_2 Bn), 2.45 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 219.9 (s, CO), 217.6 (s, CO), 157.4 (s, NCHN), 155.8 (s, C_1 bipy), 153.6 (s, C_5 bipy), 140.5 (s, C_3 bipy), 138.3 (s, C_{ipso}), 129.2, 128.2, 127.8 (s, Ph), 127.9 (s, C_4 bipy), 123.9 (s, C_2 bipy), 49.4 (s, CH_2 Bn), 38.5 (s, NCH_3). MS (ESI): *m/z***:** 443.0924 [$M - ClO_4$]$^+$

Liberation of formamidine 4b. A solution of [**3b**]ClO_4 (80 mg, 0.14 mmol) in 15 ml of CH_3CN was heated under reflux for 45 min. The solution was then evaporated to dryness under vacuum. Extraction with diethyl ether (2 x 5 mL) afforded **4b** as a white

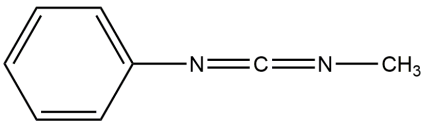


solid. The remaining residue corresponding to *fac*-[Mn(NCMe)(bipy)$(CO)_3$]ClO_4 can be transformed to [**2b**]ClO_4 by reaction with 2-Naphthyl isocyanide. Yield: 21 mg (85%)**.** ^{1}H NMR (400 MHz, CD_2Cl_2, ppm, 298K): δ = 7.79-7.72 (4H, NCHN and Naph), 7.42 (t, ^3J(H,H) = 7.4 Hz, 1H, Naph), 7.33 (t, ^3J(H,H) = 7.2 Hz, 1H, Naph), 7.26 (s, 1H, Naph), 7.21 (d, ^3J(H,H) = 7.6 Hz, 1H, Naph), 4.75 (br, 1H, NH), 3.00 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm, 193K): δ = 151.6 (s, NCHN), 149.3, 133.9, 129.5 (s, C Naph), 128.3, 127.2, 126.6, 125.8, 123.6, 123.0, 115.2 (s, CH Naph), 28.0 (s, NCH_3). MS (APCI): *m/z***:** 185.1078 $[M + H]^+$.

Liberation of formamidine 4c. This was similarly performed from [**3c**]ClO_4 (80 mg, 0.14 mmol). Yield: 19 mg (84%). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm, 298K): δ = 7.61 (s, 1H, NCHN), 6.82 (q, AB, C_6H_4), 4.66 (br, 1H, NH), 3.74 (s, 3H, OCH_3), 2.91 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm, 193K): δ = 154.7 (s, C_{ipso}), 151.0 (s, NCHN), 144.7 (s, C_{ipso}), 121.4, 113.5 (s, C_6H_4), 55.1 (s, OCH_3), 27.9 (s, NCH_3). MS (APCI): *m/z***:** 165.1031 $[M + H]^+$.



Formation of carbodiimide 6a. To a solution of *fac*-[Mn{CNH$(C_6H_5)$$(NHCH_3)$}(bipy)$(CO)_3$]$ClO_4$ ([**2a**]ClO_4, 0.20 g, 0.38 mmol) in CH_2Cl_2 (10 mL) an excess of KOH (0.2 g, 3.56 mmol) was added and the resulting mixture stirred for 45 min. The formation of the deprotonated diaminocarbene (formamidinile) derivative **5a** was monitored by IR spectroscopy. The solution was then filtered and poured into a Schlenk containing Ag_2O (88 mg, 0.38 mmol). The mixture was stirred for 1 h. The solvent was then evaporated to dryness under vacuum and the residue extracted with hexane (2 x 5 mL) and filtered. The solution was evaporated to dryness and the residue chromatographed on a silica gel column. Elution with CH_2Cl_2 gave the carbodiimide **6a** as a colorless oil. Yield: 33 mg (66%). IR (CH_2Cl_2, cm^{-1}): ν(NCN) 2146 (s), 2134 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 7.29 (t, ^3J(H,H) = 7.8 Hz, 2H, *m*-Ph), 7.11 (t, ^3J(H,H) = 7.4 Hz, 1H, *p*-Ph), 7.08 (d, ^3J(H,H) = 7.5 Hz, 2H, *o*-Ph), 3.15 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 141.3 (s, C_{ipso}), 136.7 (s, NCN), 129.9 (s, *m*-Ph), 125.1 (s, *p*-Ph), 124.0 (s, *o*-Ph), 32.9 (s, NCH_3). MS (APCI): *m/z*: 133.0791 $[M + H]^+$.



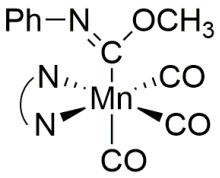
Formation of carbodiimide 6b. This was similarly obtained using *fac*-[Mn{C($NHC_{10}H_7$)($NHCH_3$)}$(CO)_3$(bipy)]ClO_4 ([**2b**]ClO_4, 0.20 g, 0.35 mmol) and Ag_2O (80 mg, 0.35 mmol). Yield: 30 mg (48%). IR (CH_2Cl_2, cm^{-1}): ν(NCN) 2141 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 7.81-7.73 (3H, Naph), 7.49-7.38 (3H, Naph), 7.26 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 2.2 Hz, 1H, Naph), 3.20 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 138.8, 134.7, 131.5 (s, C Naph), 136.6 (s, NCN), 129.7, 128.2, 127.6, 127.1, 125.6, 123.8, 120.8 (s, CH Naph), 33.0 (s, NCH_3). MS (APCI): *m/z*: 183.0918 $[M + H]^+$.

Formation of carbodiimide 6c. This was similarly obtained using *fac*-[Mn{CNH(*p*-$MeOC_6H_4$)($NHCH_3$)}$(CO)_3$(bipy)]ClO_4 ([**2c**]ClO_4, 0.20 g, 0.36 mmol) and Ag_2O (83 mg, 0.36 mmol). Yield: 31 mg (53%). IR (CH_2Cl_2, cm^{-1}): ν(NCN) 2140 (s), 2120 (sh). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 7.01 (d, ^3J(H,H) = 8.7 Hz, 2H, C_6H_4), 6.82 (d, ^3J(H,H) = 8.7 Hz, 2H, C_6H_4), 3.77 (s, 3H, OCH_3), 3.12 (s, 3H, NCH_3). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 157.5, 133.6 (s, C_{ipso}), 137.8 (s, NCN), 124.9 (s, CH C_6H_4), 115.1 (s, CH C_6H_4), 56.0 (s, OCH_3), 33.1 (s, NCH_3). MS (APCI): *m/z*: 163.0868 $[M + H]^+$.

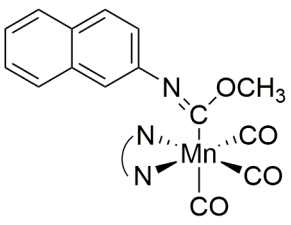
Formation of carbodiimide 6f. This was similarly obtained using *fac*-[Mn{C($NHC_6H_3(CH_3)_2$)($NHCH_3$)}$(CO)_3$(bipy)]ClO_4 ([**2f**]ClO_4, 0.20 g, 0.36 mmol) and Ag_2O (83 mg, 0.36 mmol). Yield: 27 mg (47%). IR (CH_2Cl_2, cm^{-1}): ν(NCN) 2166 (s), 2148 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 7.00 (d, ^3J(H,H) = 7.5 Hz, 2H, *m*-Xylyl), 6.90 (t, ^3J(H,H) = 6.9 Hz, 1H, *p*-Xylyl), 3.08 (s, 3H, NCH_3), 2.31 (s, 6H, CH_3 Xylyl). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 137.6 (s, C_{ipso} Xylyl), 132.7 (s, *o*-Xylyl), 128.6 (s, *m*-Xylyl), 124.6 (s, *p*-Xylyl), 33.1 (s, NCH_3), 19.2 (s, CH_3 Xylyl). MS (APCI): *m/z*: 161.1078 $[M + H]^+$.

Formation of carbodiimide 6g. This was similarly prepared using *fac*-[Mn{C($NHC_6H_3Cl(CH3)$)($NHCH_3$)}$(CO)_3$(bipy)]ClO_4 ([**2g**]ClO_4, 0.20 g, 0.35 mmol) and Ag_2O (80 mg, 0.35 mmol). Yield: 35 mg (56%). IR (CH_2Cl_2, cm^{-1}): ν(NCN) 2162 (s), 2145 (sh). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 7.22 (d, ^3J(H,H)

= 8.0 Hz, 1H, *m*-C_6H_3), 7.07 (d, ^3J(H,H) = 7.6 Hz, 1H, *m*-C_6H_3), 6.93 (t, ^3J(H,H) = 7.8 Hz, 1H, *p*-C_6H_3), 3.13 (s, 3H, NCH_3), 2.30 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 136.8, 134.9, 129.6 (s, C C_6H_3), 129.4 (s, *m*-C_6H_3), 127.7 (s, *m*-C_6H_3), 125.0 (s, *p*-C_6H_3), 32.8 (s, NCH_3), 19.4 (s, CH_3). MS (APCI): *m/z*: 181.0528 [*M + H*]$^+$.



Synthesis of compound 7a. To a solution of *fac*-[Mn(CNPh)$(CO)_3$(bipy)]ClO_4 ([**1a**]ClO_4, 0.10 g, 0.20 mmol) in MeOH (1 mL) a two fold excess of sodium was added (10 mg, 0.43 mmol). The color of the solution instantaneously changed from yellow to red. 15 mL of CH_2Cl_2 were added to the reaction mixture and the resulting solution was then washed with water (3 x 15 mL). The organic phase was dried with Na_2CO_3 and then filtered through diatomaceous earth. The solution was concentrated to 1 mL under vaccum and hexane (5 mL) added to obtain a redish solid. Red crystals of **7a** suitable for X-ray diffraction were formed by slow difussion of hexane into a dichlorometane solution of the compound. Yield: 68 mg (79%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2008 (vs), 1912 (vs), 1906 (sh). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.71 (d, ^3J(H,H) = 5.4 Hz, 2H, H_A bipy), 7.96 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 7.80 (t, ^3J(H,H) = 7.6 Hz, 2H, H_C bipy), 7.11 (t, ^3J(H,H) = 6.4 Hz, 2H, H_B bipy), 6.86 (t, ^3J(H,H) = 7.6 Hz, 2H, *m*-Ph), 6.74 (t, ^3J(H,H) = 7.2 Hz, 1H, *p*-Ph), 6.25 (d, ^3J(H,H) = 7.5 Hz, 2H, *o*-Ph), 3.30 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 224.7 (s, CO), 213.4 (s, CO), 202.7 (s, NCO), 154.8 (s, C_1 bipy), 154.2 (s, C_5 bipy), 152.6 (s, C_{ipso}), 137.0 (s, C_3 bipy), 128.7 (s, *m*-Ph), 124.9 (s, C_4 bipy), 121.7 (s, *o*-Ph), 121.6 (s, C_2 bipy), 120.1 (s, *p*-Ph), 52.9 (s, OCH_3). MS (ESI): *m/z*: 398.0331 [*M – OCH$_3$*]$^+$.



Synthesis of compound 7b. This was prepared in a similar way as **7a** from *fac*-[Mn(CNNaph)$(CO)_3$(bipy)]ClO_4 (([**1b**]ClO_4, 0.10 g, 0.18 mmol), methanol (1 mL) and sodium (10 mg, 0.43 mmol). Yield: 72 mg (83%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2008 (vs), 1914 (vs), 1907 (sh). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.59 (d, ^3J(H,H) = 5.0 Hz, 2H, H_A bipy), 7.92 (d, ^3J(H,H) = 7.9 Hz, 2H, H_D bipy), 7.72-7.68 (m, 3H, H_C bipy and Naph), 7.46 (d, ^3J(H,H) = 8.1 Hz, 1H, Naph), 7.36-7.32 (m, 2H, Naph), 7.27 (t, ^3J(H,H) = 7.3 Hz, 1H, Naph), 6.80 (t, ^3J(H,H) = 6.3 Hz, 2H, H_B bipy), 6.68 (s, 1H, Naph), 6.47 (d, ^3J(H,H) = 7.7. Hz, 1H, Naph), 3.37 (s, 3H, OCH_3).

$^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 224.8 (s, CO), 213.3 (s, CO), 203.3 (s, NCO), 154.9 (s, C_1 bipy), 154.2 (s, C_5 bipy), 150.2, 134.9, 129.5 (s, C Naph), 137.2 (s, C_3 bipy), 128.1, 127.9, 127.3, 126.0, 124.3, 123.3, 116.4 (s, CH Naph), 124.8 (s, C_4 bipy), 121.5 (s, C_2 bipy), 53.1 (s, OCH_3). MS (ESI): *m/z*: 480.0755 $[M + H]^+$.

Synthesis of compound 7a'. This was prepared in a similar way as **7a** from *fac*-[Mn(CNPh)(CO)$_3$(bipy)]ClO_4 (([**1a**]ClO_4, 0.10 g, 0.20 mmol), ethanol (4 mL) and sodium (10 mg, 0.43 mmol). Yield: 59 mg (66%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2007 (vs), 1908 (vs). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.73 (d, ^3J(H,H) = 5.1 Hz, 2H, H_A bipy), 7.98 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 7.81 (t, ^3J(H,H) = 7.7 Hz, 2H, H_C bipy), 7.14 (t, ^3J(H,H) = 6.5 Hz, 2H, H_B bipy), 6.88 (t, ^3J(H,H) = 7.5 Hz, 2H, *m*-Ph), 6.75 (t, ^3J(H,H) = 7.2 Hz, 1H, *p*-Ph), 6.26 (d, ^3J(H,H) = 7.7 Hz, 2H, *o*-Ph), 3.70 (q, ^3J(H,H) = 7.0 Hz, 2H, CH_2), 0.89 (t, ^3J(H,H) = 7.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 224.8 (s, CO), 213.5 (s, CO), 202.0 (s, $C_{carbeno}$), 154.9 (s, C_1 bipy), 154.3 (s, C_5 bipy), 152.9 (s, C_{ipso}), 136.9 (s, C_3 bipy), 128.7 (s, *m*-Ph), 124.9 (s, C_4 bipy), 122.0 (s, *o*-Ph), 121.5 (s, C_2 bipy), 120.2 (s, *p*-Ph), 60.3 (s, CH_2), 14.7 (s, CH_3). MS (ESI): *m/z*: 444.0750 $[M + H]^+$.

Synthesis of compound [8a]BF_4. To a solution of **7a** (70 mg, 0.16 mmol) in 12 mL of CH_2Cl_2 was added $HBF_4{\cdot}OEt_2$ (34 μL, d = 1.18 g/mL, 0.25 mmol). The color of the solution changed instantaneously from red to yellow. The solution was then concentrated to 1 mL and further addition of hexane (5 mL) caused the formation of a yellow solid, which was washed with diethyl ether (2 x 5 mL). The NMR data (see below) show the presence of two isomers in an approximate ratio of 9:1. Slow diffusion of hexane into a dichoromethane solution of the compound afforded yellow crystals suitable for an X-ray analysis. Yield: 81 mg (96%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2033 (vs), 1952 (s), 1930 (s). ^1H NMR (400 MHz, CD_2Cl_2, ppm): Major isomer (90%): δ = 9.75 (br, 1H, NH), 8.59 (d, ^3J(H,H) = 5.1 Hz, 2H, H_A bipy), 8.18 (d, ^3J(H,H) = 7.9 Hz, 2H, H_D bipy), 8.02 (t, ^3J(H,H) = 7.5 Hz, 2H, H_C bipy), 7.42 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-Ph), 7.37-7.32 (m, 4H, H_B bipy and *m*-Ph), 7.10 (d, ^3J(H,H) = 7.4 Hz, 2H, *o*-Ph), 3.77 (s, 3H, OCH_3). Minor isomer (10%): δ = 9.15 (d, ^3J(H,H) = 4.7 Hz, 2H, H_A bipy), 8.51 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 8.24 (br, 2H, H_C bipy), 7.73 (br, 2H, H_D bipy), 7.27-7.20 (m, *m*-Ph and *p*-Ph), 6.80 (d, ^3J(H,H) = 7.9

Hz, 2H, *o*-Ph), 4.24 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): Major isomer (90%): δ = 238.9 (s, $C_{carbene}$), 221.0 (s, CO), 213.8 (s, CO), 155.5 (s, C_1 bipy), 153.9 (s, C_5 bipy), 139.2 (s, C_3 bipy), 137.3 (s, C_{ipso}), 130.1 (s, *m*-Ph), 129.4 (s, *p*-Ph), 128.3 (s, C_4 bipy), 127.0 (s, *o*-Ph), 123.1 (s, C_2 bipy), 57.3 (s, OCH_3). Minor isomer (10%): 154.5 (s, C_5 bipy), 140.8 (s, C_3 bipy), 124.8 (s, *o*-Ph), 62.6 (s, OCH_3). MS (ESI): *m/z*: 430.0594 $[M - BF_4]^+$.

Synthesis of compound [8b]BF_4. This was prepared in a similar way from **7b** (72 mg, 0.13 mmol) and $HBF_4{\cdot}OEt_2$ (31 µL, d = 1.18 g/mL, 0.23 mmol). Yield: 67 mg (81%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2033 (vs), 1953 (vs), 1929 (s). ^1H NMR (400 MHz, CD_2Cl_2, ppm): Major isomer (95%): δ = 9.92 (br, 1H, NH), 8.44 (d, ^3J(H,H) = 4.6 Hz, 2H, H_A bipy), 8.14 (d, ^3J(H,H) = 7.8 Hz, 2H, H_D bipy), 7.91 (br, 3H, H_C bipy and Naph), 7.75 (br, 2H, Naph), 7.61-7.57 (m, 3H, Naph), 7.14 (d, ^3J(H,H) = 7.8 Hz, 1H, Naph), 7.07 (t, ^3J(H,H) = 5.8 Hz, 2H, H_B bipy) 3.82 (s, 3H, OCH_3). Minor isomer (5%): δ = 9.17 (br, 2H, H_A bipy), 4.24 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): Major isomer (95%): δ = 239.2 (s, $C_{carbene}$), 221.2 (s, CO), 213.7 (s, CO), 155.4 (s, C_1 bipy), 153.6 (s, C_5 bipy), 139.1 (s, C_3 bipy), 134.5, 133.6, 133.4 (s, C Naph), 130.0, 128.7, 128.3, 127.9, 127.8, 127.1, 125.5 (s, CH Naph), 126.7 (s, C_4 bipy), 123.1 (s, C_2 bipy), 57.5 (s, OCH_3). Minor isomer (5%): δ = 154.4 (s, C_5 bipy), 140.8 (s, C_3 bipy), 62.7 (s, OCH_3). MS (ESI): *m/z*: 480.0750 $[M - BF_4]^+$.

Synthesis of compound [8a']BF_4. This was prepared in a similar way as **[8a]BF_4** from **7a'** (70 mg, 0.16 mmol) and $HBF_4{\cdot}OEt_2$ (33 µL, d = 1.18 g/mL, 0.24 mmol). Yield: 80 mg (95%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2032 (vs), 1951 (s), 1929 (s). ^1H NMR (400 MHz, CD_2Cl_2, ppm): Major isomer (93%): δ = 9.69 (br, 1H, NH), 8.62 (d, ^3J(H,H) = 5.4 Hz, 2H, H_A bipy), 8.21 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 8.03 (t, ^3J(H,H) = 7.8 Hz, 2H, H_C bipy), 7.44-7.33 (5H, H_B bipy, *m*-Ph and *p*-Ph), 7.13 (d, ^3J(H,H) = 7.5 Hz, 2H, *o*-Ph), 3.96 (q, ^3J(H,H) = 6.8 Hz, 2H, CH_2), 0.99 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3). Minor isomer (7%): δ = 9.16 (br, 2H, H_A bipy), 8.46 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 7.72 (br, 2H, H_B bipy), 7.24-7.17 (m, *m*-Ph and *p*-Ph), 6.81 (d, ^3J(H,H) = 7.7 Hz, 2H, *o*-Ph), 4.55 (q, ^3J(H,H) = 6.9 Hz, 2H, CH_2), 1.20 (t, ^3J(H,H) = 6.9 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): Major isomer (93%): δ = 238.1 (s, $C_{carbeno}$), 221.1 (s, CO), 213.8 (s, CO), 155.7 (s, C_1 bipy),

153.8 (s, C_5 bipy), 139.3 (s, C_3 bipy), 137.5 (s, C_{ipso}), 130.1 (s, *m*-Ph), 129.5 (s, *p*-Ph), 128.5 (s, *o*-Ph), 127.0 (s, C_4 bipy), 123.1 (s, C_2 bipy), 66.3 (s, CH_2), 13.6 (s, CH_3). Minor isomer (7%): δ = 154.4 (s, C_5 bipy), 140.7 (s, C_3 bipy), 124.9 (s, C_2 bipy), 124.6 (s, *o*-Ph), 72.6 (s, CH_2), 15.3 (s, CH_3). MS (ESI): *m/z*: 444.0748 $[M - BF_4]^+$.

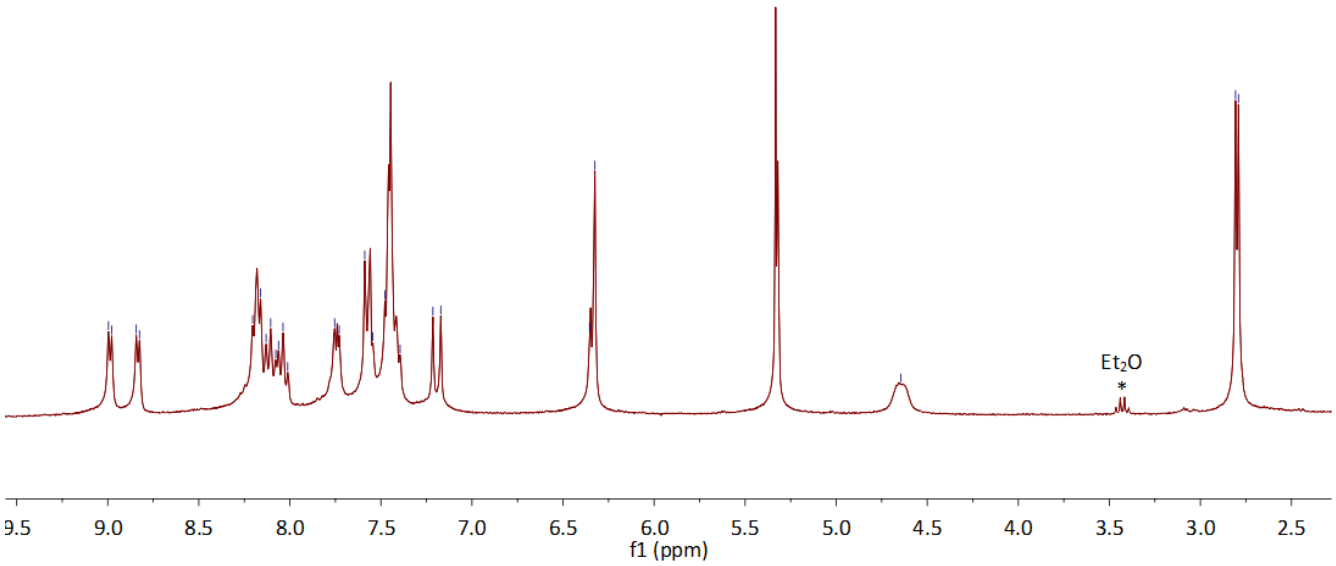
Synthesis of compound [9a]BF_4. To a solution of [**8a**]BF_4 (0.10 g, 0.19 mmol) in CH_2Cl_2 (10 mL) Ag_2O (23 mg, 0.10 mmol) was added and the mixture stirred for 4 h. The solution was then filtered and evaporated to dryness under vacuum. Hexane (5 mL) was added to the residue and the mixture stirred to obtain a yellow solid. Yellow crystals of [**8a**]BF_4 suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 93 mg (93%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2040 (vs), 1950 (s), 1943 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.86 (d, ^3J(H,H) = 5.1 Hz, 2H, H_A bipy), 8.21 (d, ^3J(H,H) = 8.1 Hz, 2H, H_D bipy), 8.08 (t, ^3J(H,H) = 7.9 Hz, 2H, H_C bipy), 7.69 (s, 1H, NCHO), 7.46 (t, ^3J(H,H) = 6.5 Hz, 2H, H_B bipy), 7.04 (t, ^3J(H,H) = 7.4 Hz, 1H, *p*-Ph), 6.96 (t, ^3J(H,H) = 7.6 Hz, 2H, *m*-Ph), 6.24 (d, ^3J(H,H) = 8.0 Hz, 2H, *o*-Ph), 4.07 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2, ppm): δ = 219.4 (br, CO), 169.8 (s, NCHO), 156.0 (s, C_1 bipy), 154.6 (s, C_5 bipy), 145.6 (s, C_{ipso}), 140.5 (s, C_3 bipy), 129.6 (s, *m*-Ph), 127.4 (s, C_4 bipy), 127.2 (s, *p*-Ph), 123.8 (s, *o*-Ph and C_2 bipy), 61.6 (s, OCH_3). MS (ESI): *m/z*: 430.0594 $[M - BF_4]^+$.

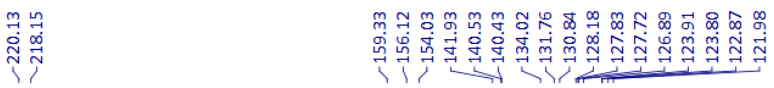
Synthesis of compound [9b]BF_4. This was prepared in a similar way from [**8b**]BF_4 (0.10 g, 0.18 mmol) and Ag_2O (21 mg, 0.09 mmol). Yield: 91 mg (91%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2039 (vs), 1949 (s), 1941 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.83 (br, 2H, H_A bipy), 8.12 (m, 2H, H_D bipy), 7.97 (s, 2H, H_C bipy), 7.79 (br, 1H, NCHN), 7.72 (br, 2H, Naph), 7.51-7.44 (4H, Naph), 7.32 (br, 2H, H_B bipy), 6.58 (d, ^3J(H,H) = 7.8 Hz, 1H, Naph), 6.47 (s, 1H, Naph), 4.08 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 219.8 (s, CO), 218.9 (s, CO), 170.0 (s, NCHO), 156.1 (s, C_1 bipy), 154.7 (s, C_5 bipy), 142.8, 133.4, 131.8 (s, C Naph), 140.4 (s, C_3 bipy), 129.5, 128.1, 127.9, 127.8, 127.0, 122.5, 121.7 (s, CH Naph), 127.2 (s, C_4 bipy), 123.7 (s, C_2 bipy), 61.6 (s, OCH_3). MS (ESI): *m/z*: 480.0751 $[M - BF_4]^+$.

Synthesis of compound [9a']BF_4. This was prepared in a similar way from **[8a']BF_4** (0.10 g, 0.19 mmol) and Ag_2O (23 mg, 0.10 mmol). Yield: 75 mg (75%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2040 (vs), 1947 (s), 1943 (sh). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 8.87 (d, ^3J(H,H) = 4.9 Hz, 2H, H_A bipy), 8.22 (d, ^3J(H,H) = 8.0 Hz, 2H, H_D bipy), 8.09 (t, ^3J(H,H) = 7.5 Hz, 2H, H_C bipy), 7.74 (s, 1H, NCHO), 7.45 (t, ^3J(H,H) = 6.3 Hz, 2H, H_B bipy), 7.05 (t, ^3J(H,H) = 7.0 Hz, 1H, *p*-Ph), 6.96 (t, ^3J(H,H) = 7.4 Hz, 2H, *m*-Ph), 6.24 (d, ^3J(H,H) = 7.4 Hz, 2H, *o*-Ph), 4.36 (q, ^3J(H,H) = 7.0 Hz, 2H, CH_2), 1.49 (t, ^3J(H,H) = 7.0 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm): δ = 219.9 (br, CO), 168.7 (s, NCHO), 156.1 (s, C_1 bipy), 154.6 (s, C_5 bipy), 145.7 (s, C_{ipso}), 140.5 (s, C_3 bipy), 129.6 (s, *m*-Ph), 127.4 (s, C_4 bipy), 127.2 (s, *p*-Ph), 123.9 (s, *o*-Ph and C_2 bipy), 71.9 (s, CH_2), 15.5 (s, CH_3). MS (ESI): *m/z*: 444.0749 $[M - BF_4]^+$.

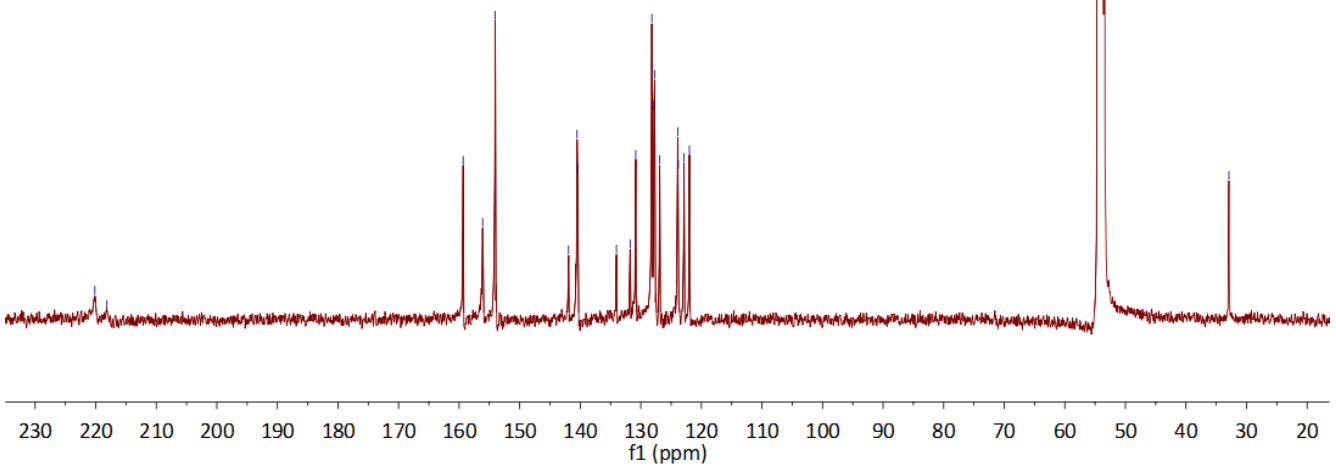
Liberation of formimidate 10b. A solution of [**9b**]BF_4 (80 mg, 0.14 mmol) in acetonitrile (15 mL) was stirred for 2 h at room temperature. The solvent was evaporated to dryness under vacuum and the resulting residue extracted with diethyl ether (2 x 5 mL) and filtered. Evaporation of the solvent afforded an slightly orange oil. Yield: 24 mg (91%). ^1H NMR (400 MHz, CD_2Cl_2, ppm, 298K): δ = 7.87 (s, 1H, NCHO), 7.82-7.72 (m, 3H, Naph), 7.46 (t, ^3J(H,H) = 7.4 Hz, 1H, Naph), 7.40 (t, ^3J(H,H) = 7.2 Hz, 1H, Naph), 7.33 (s, 1H, Naph), 7.20 (d, ^3J(H,H) = 8.6 Hz, 1H, Naph), 3.93 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, ppm, 298K): δ = 156.3 (s, NCHO), 146.4, 134.8, 131.6 (s, C Naph), 129.4, 128.1, 127.8, 126.8, 125.2, 123.0, 117.6 (s, CH Naph), 54.3 (s, OCH_3). MS (APCI): *m/z*: 186.0920 $[M + H]^+$.

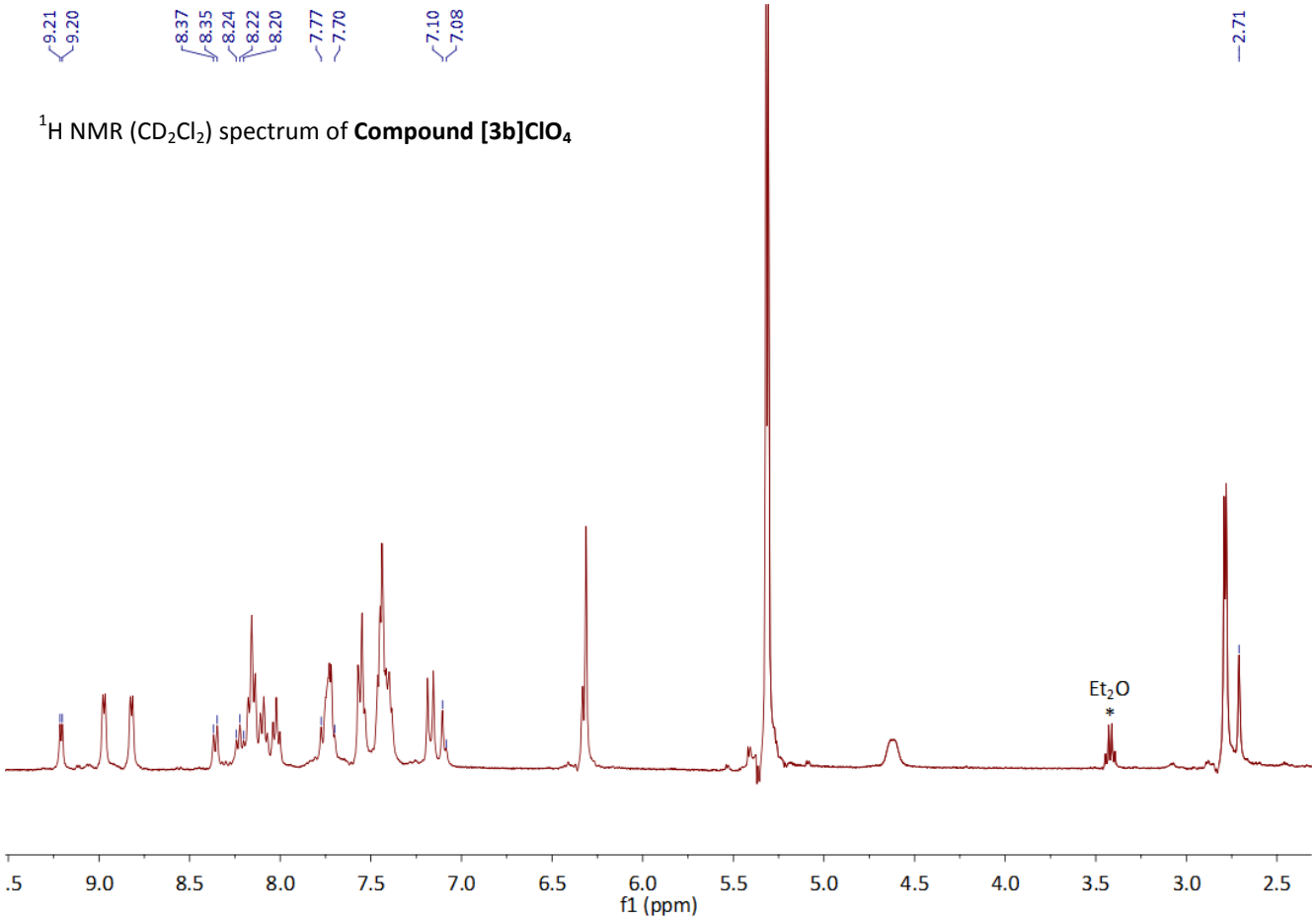
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [3b]ClO_4** (major isomer)



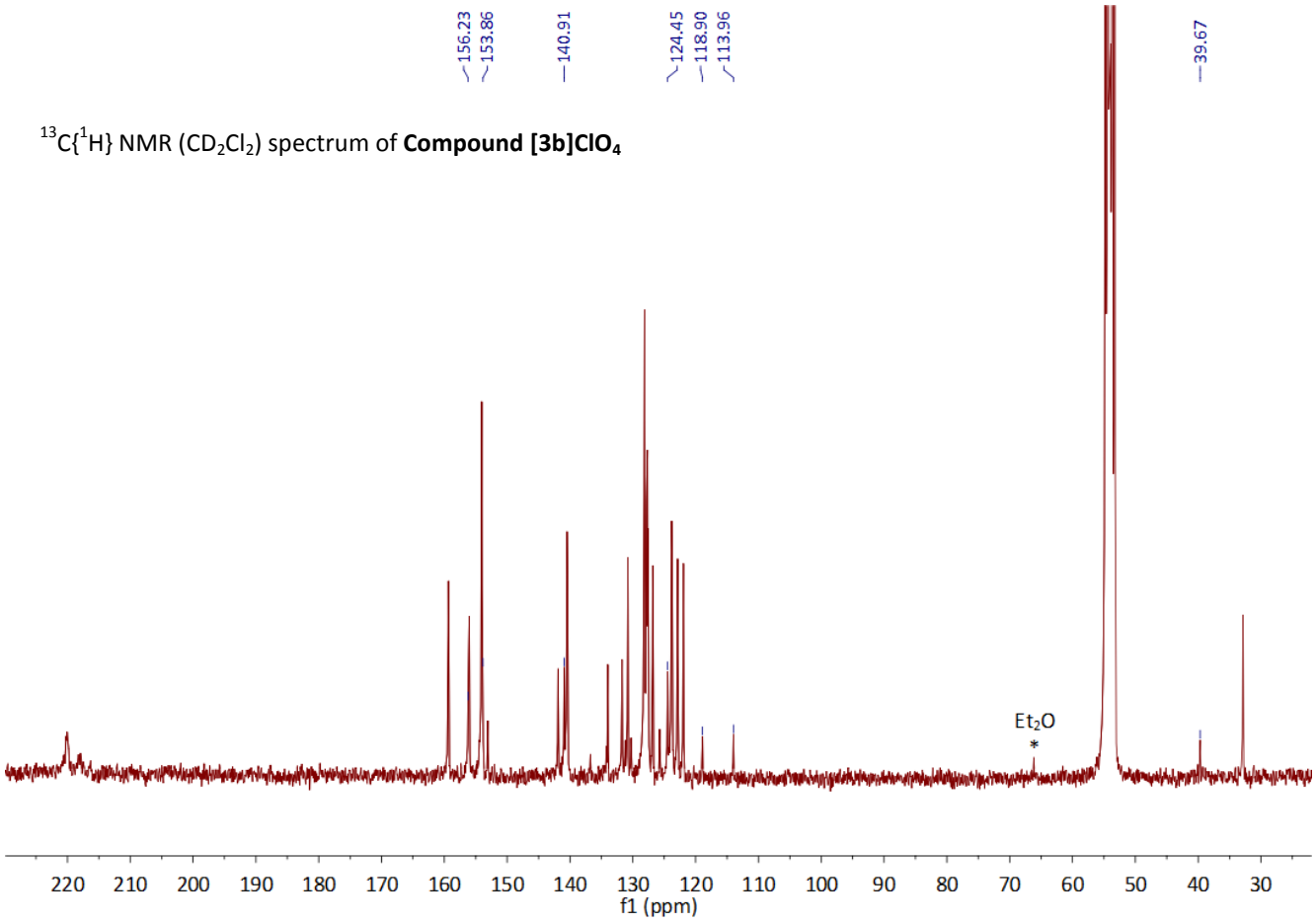


^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [3b]ClO_4** (major isomer)

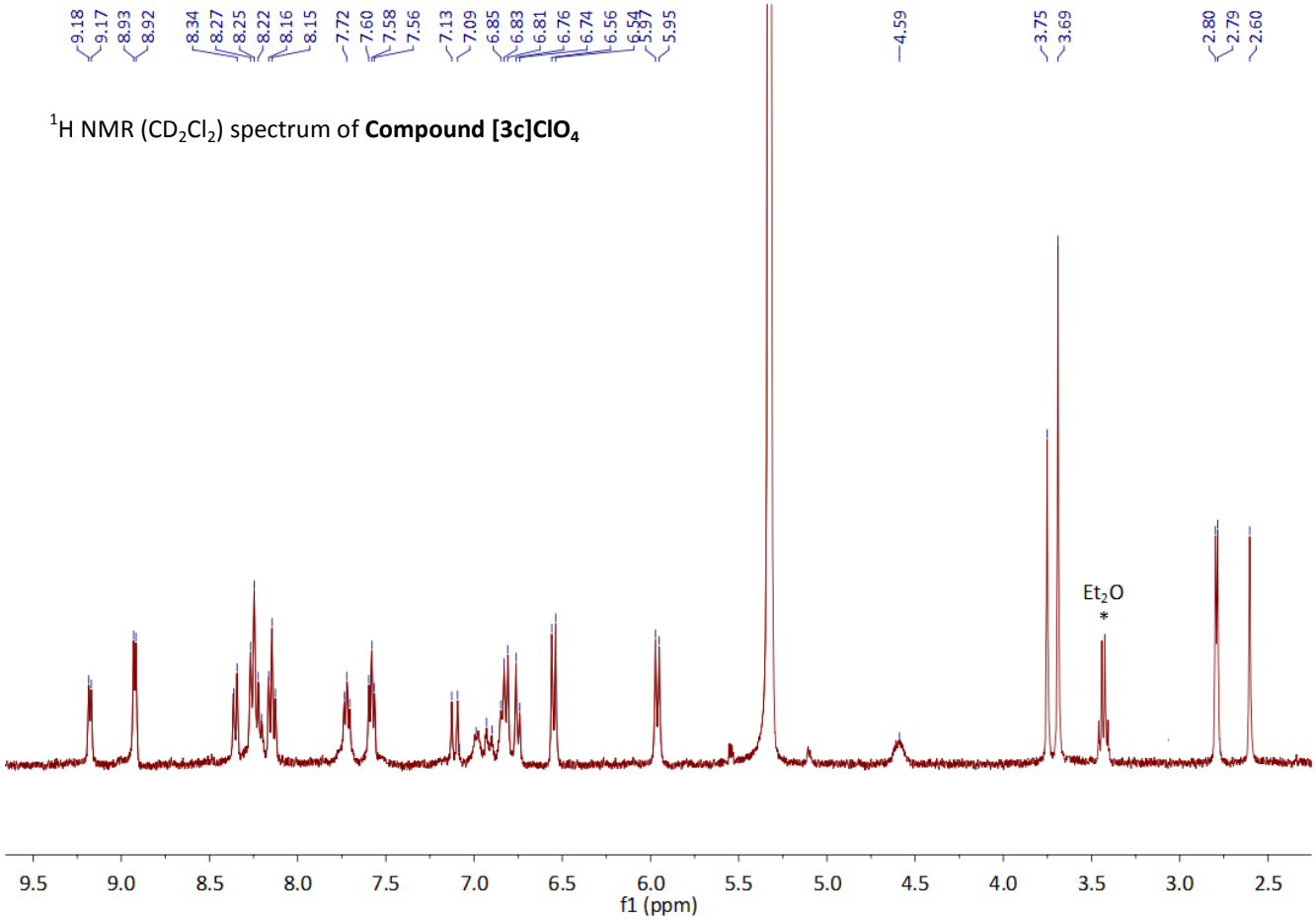




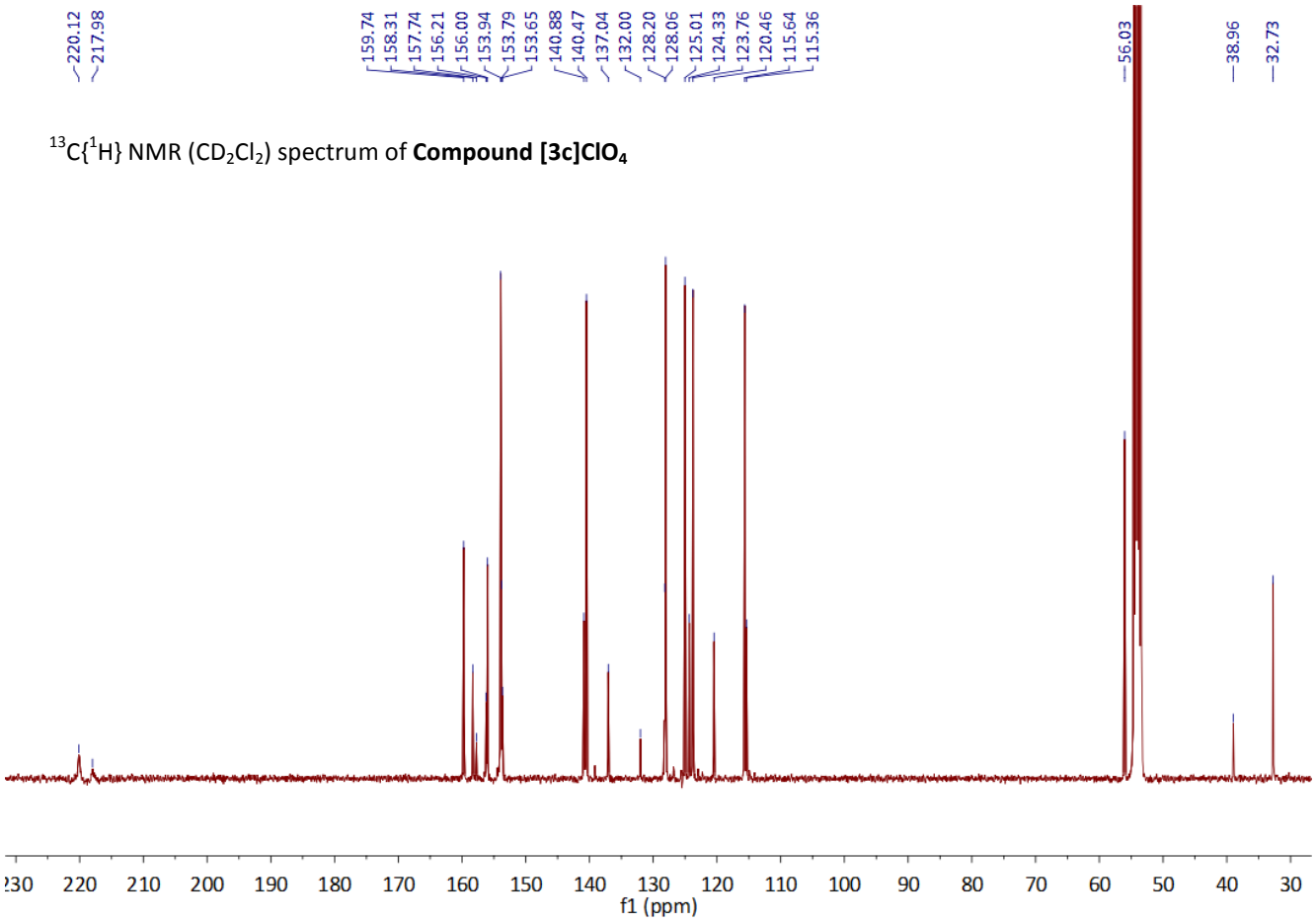
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [3b]ClO_4**



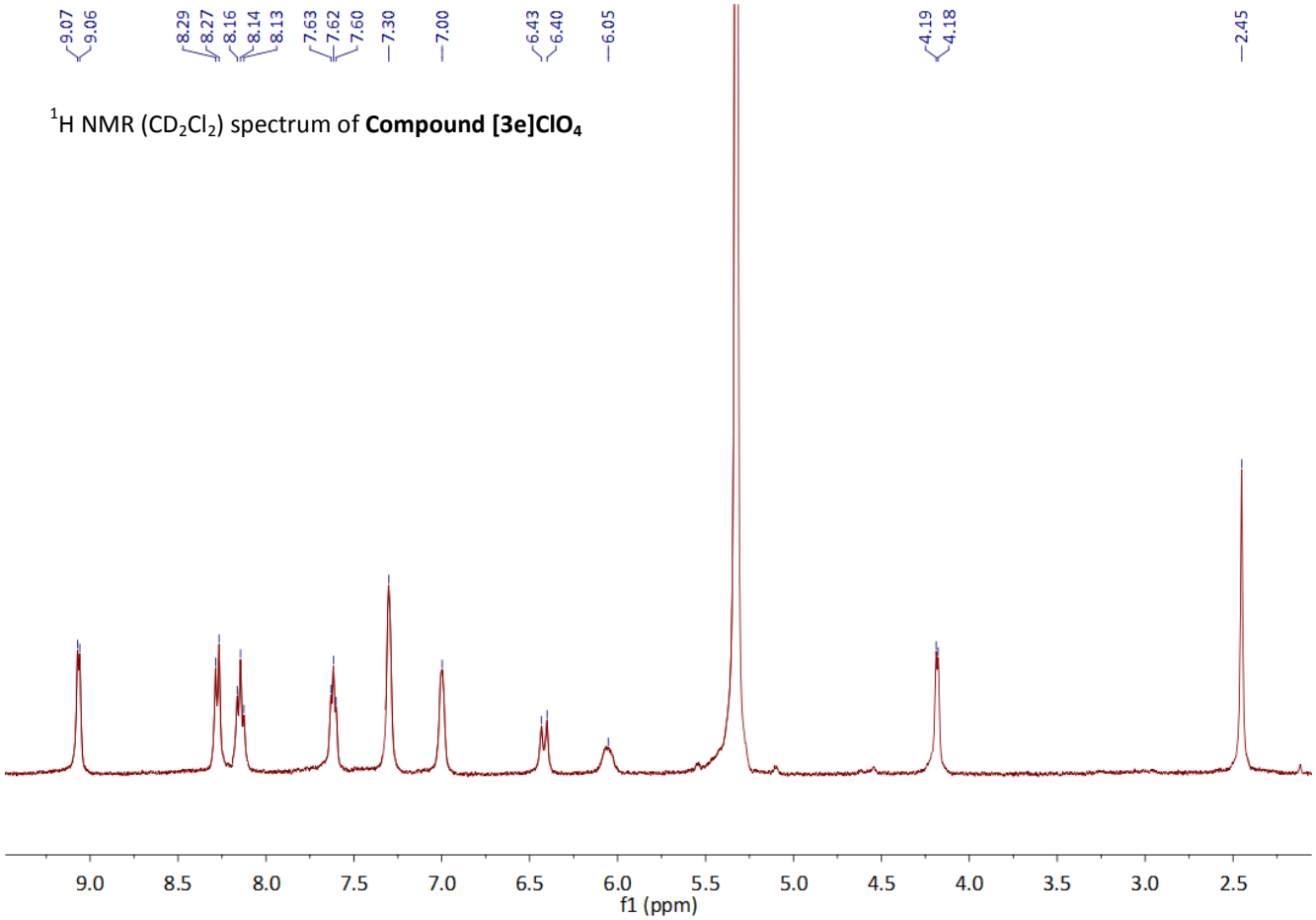
$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of **Compound [3b]ClO_4**



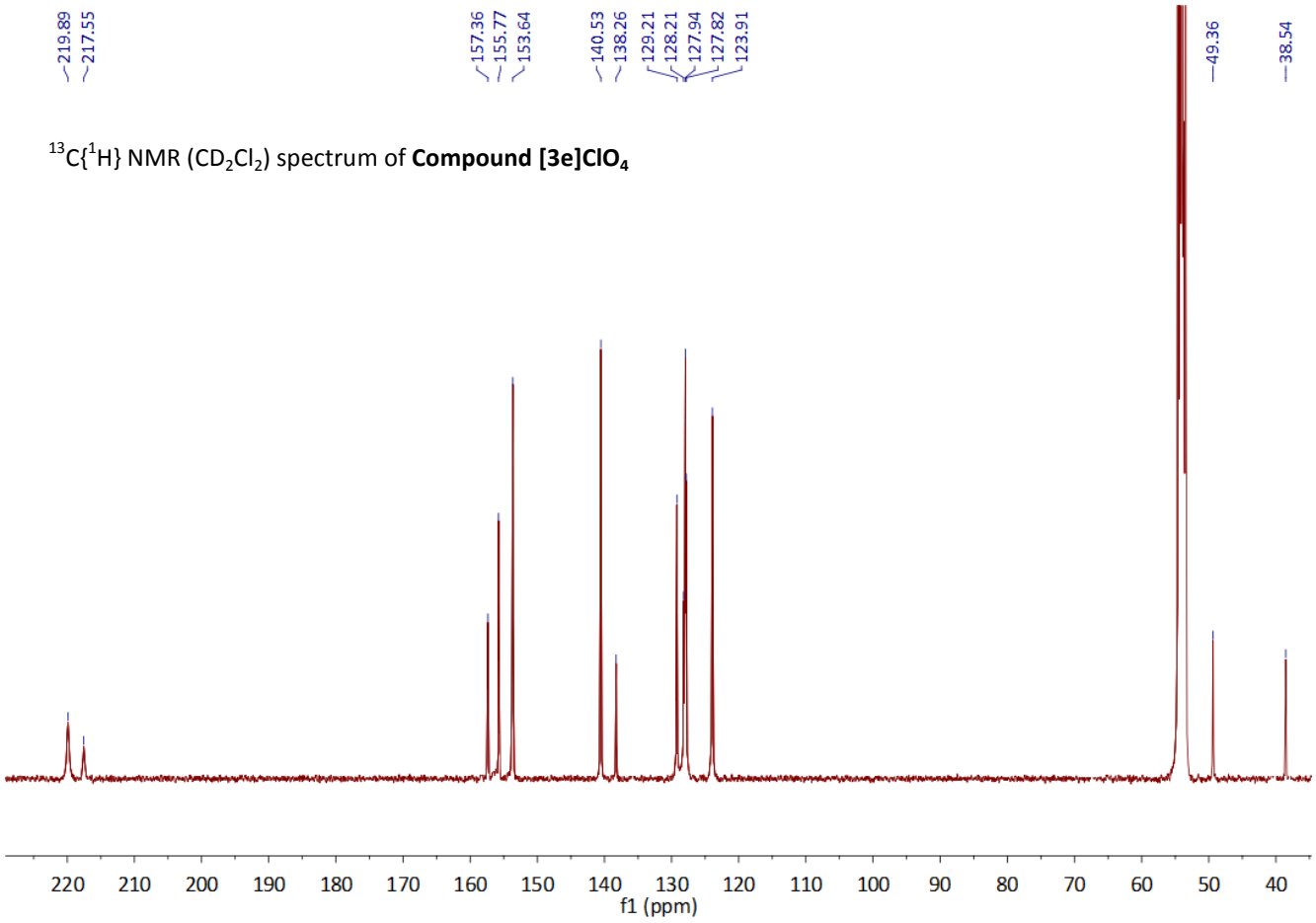
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [3c]ClO$_4$**



^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [3c]ClO$_4$**

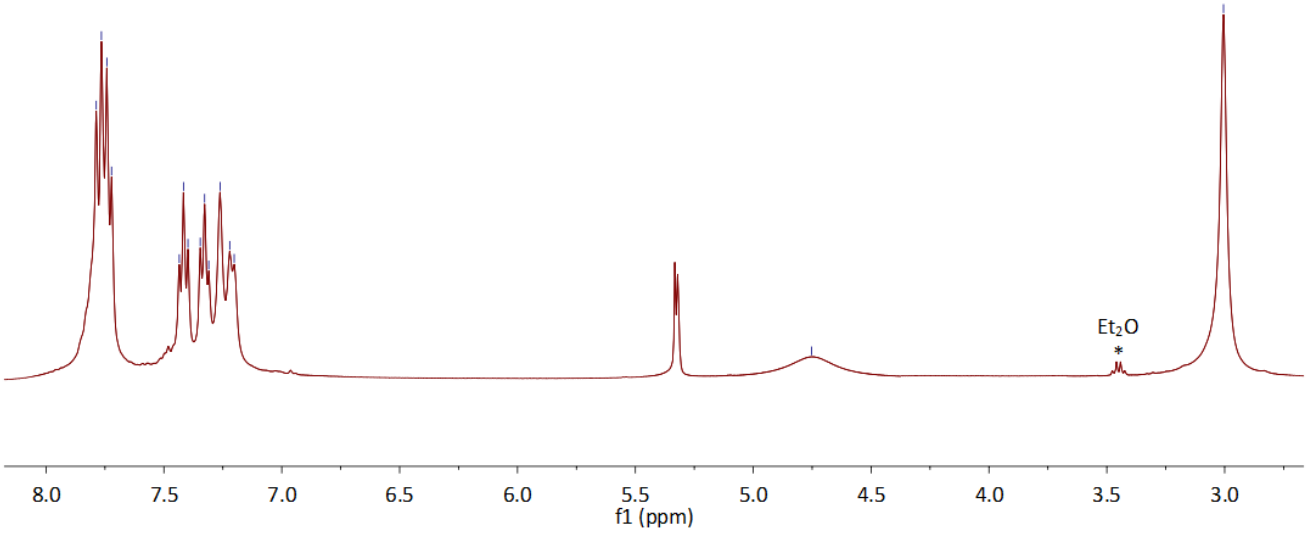


^{1}H NMR (CD_2Cl_2) spectrum of **Compound [3e]ClO_4**



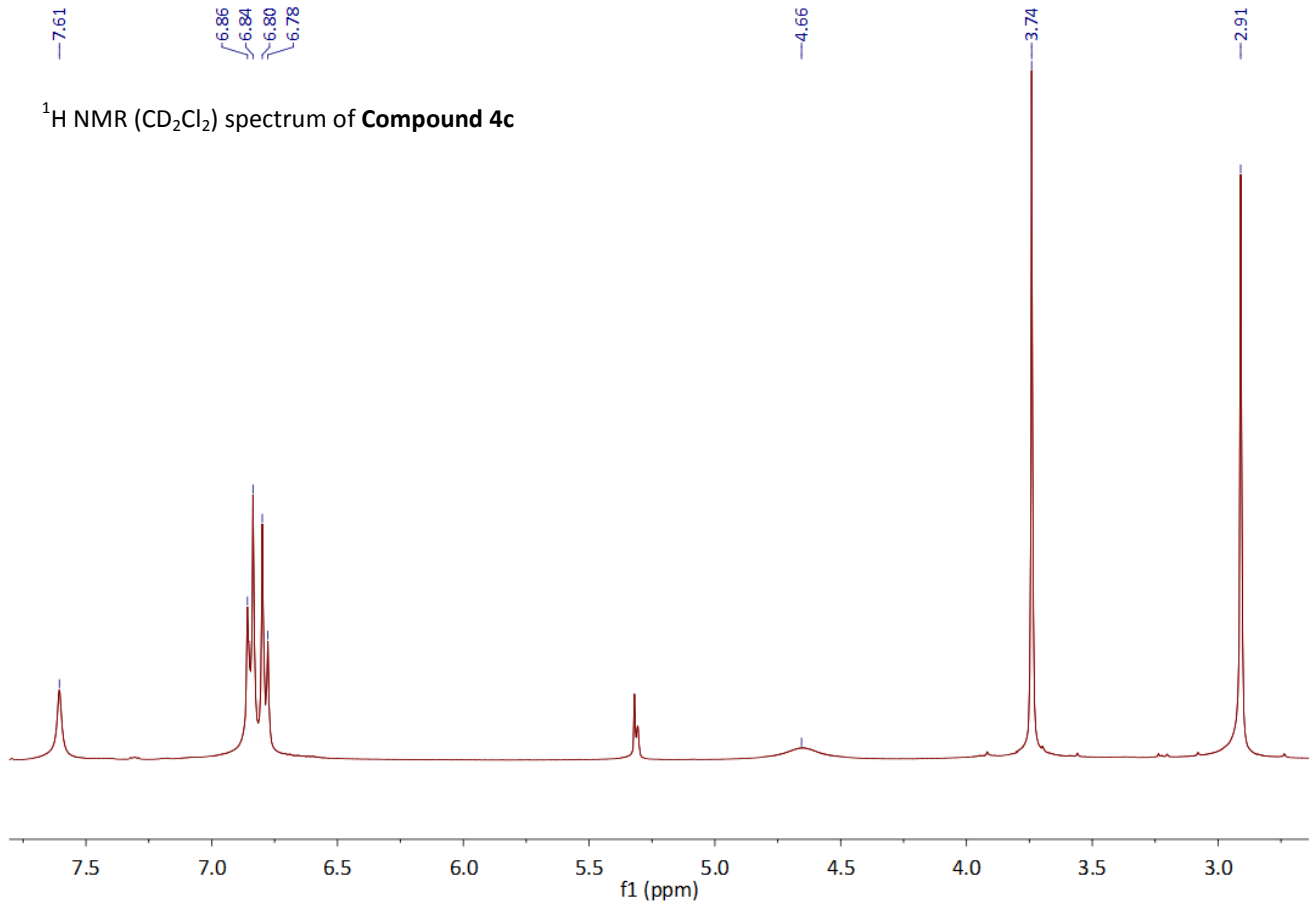
$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of **Compound [3e]ClO_4**

^{1}H NMR (CD_2Cl_2) spectrum of **Compound 4b**

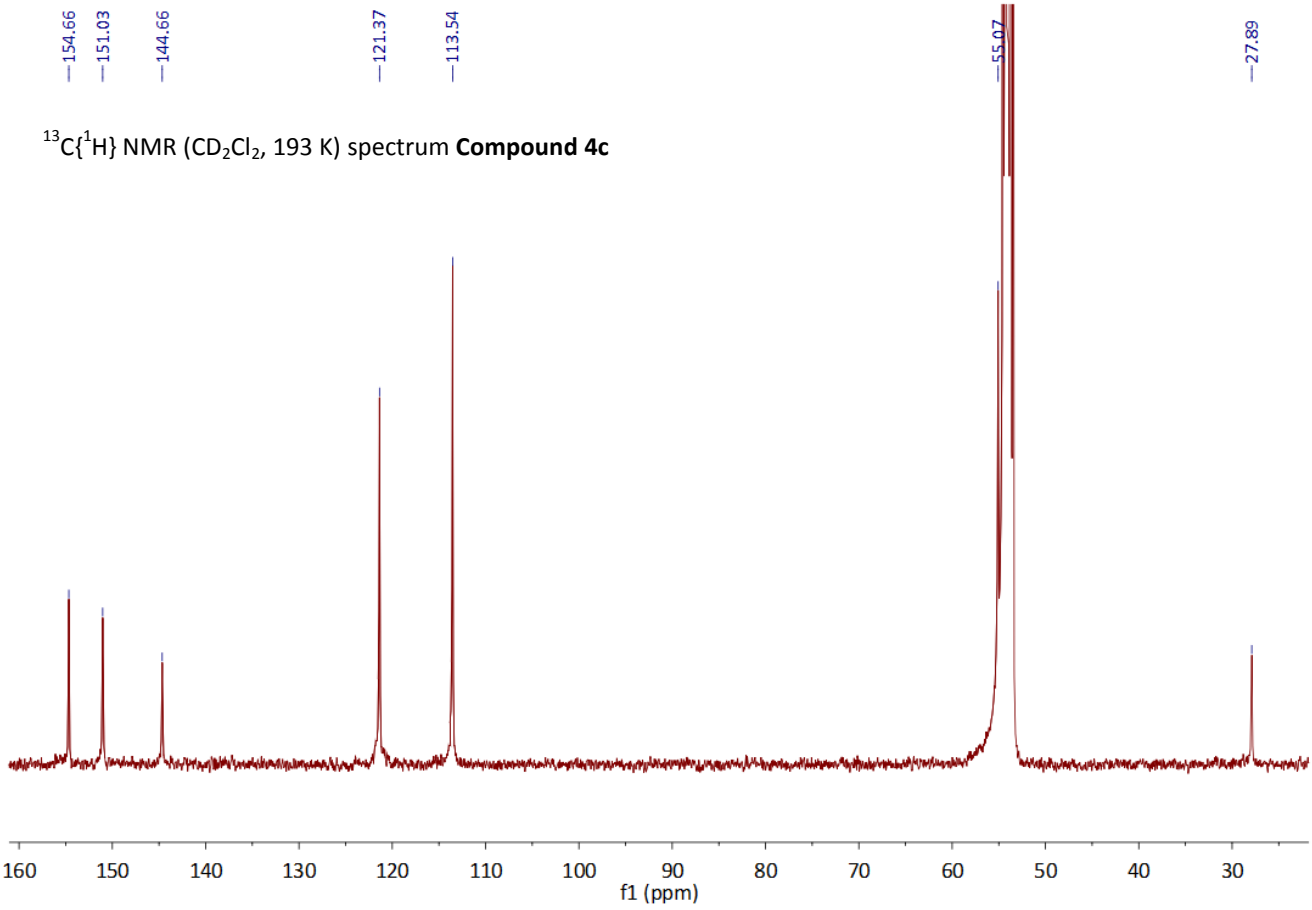


^{13}C{^{1}H} NMR (CD_2Cl_2, 193 K) spectrum of **Compound 4b**

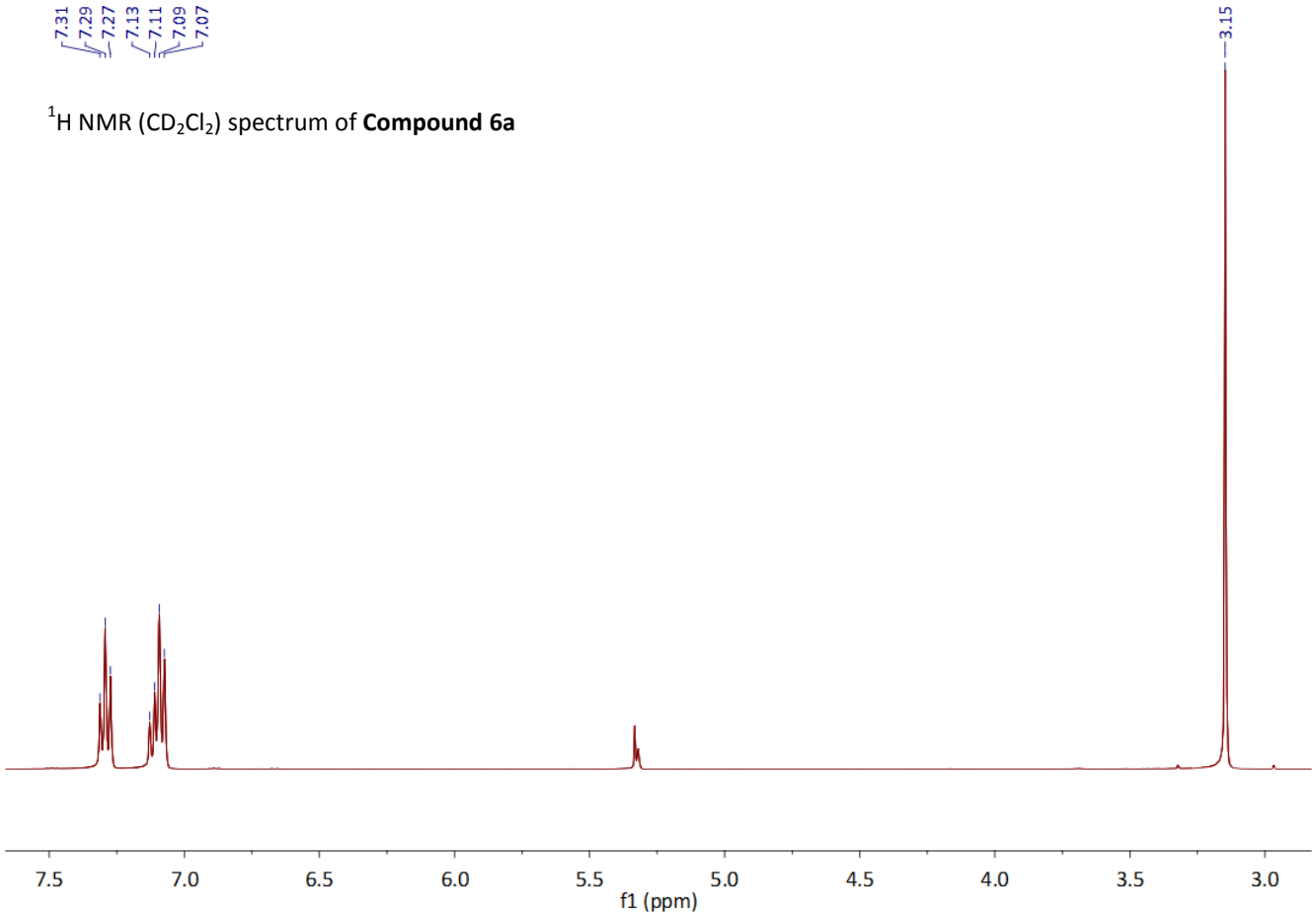
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 4c**



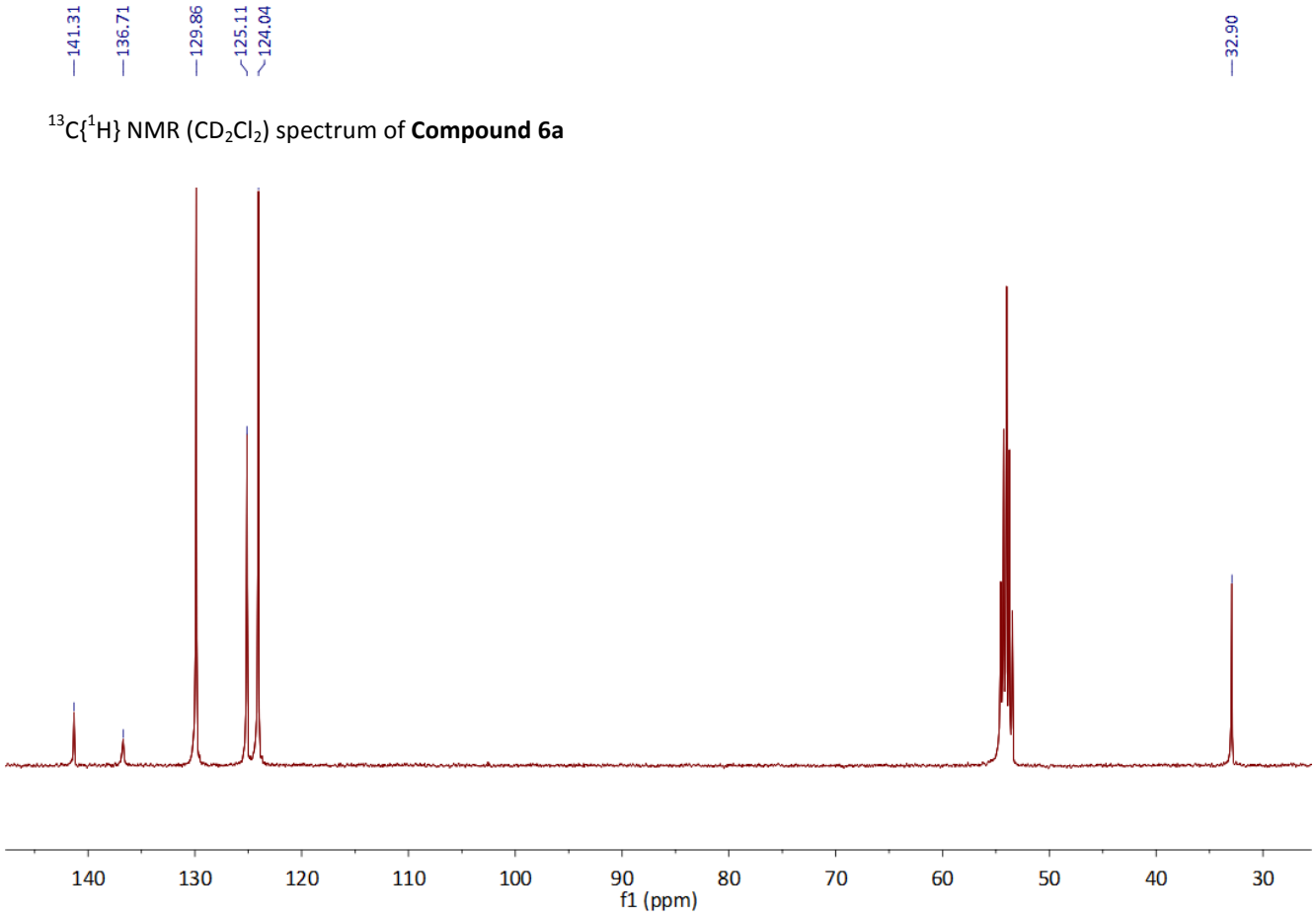
^{13}C{^{1}H} NMR (CD_2Cl_2, 193 K) spectrum **Compound 4c**

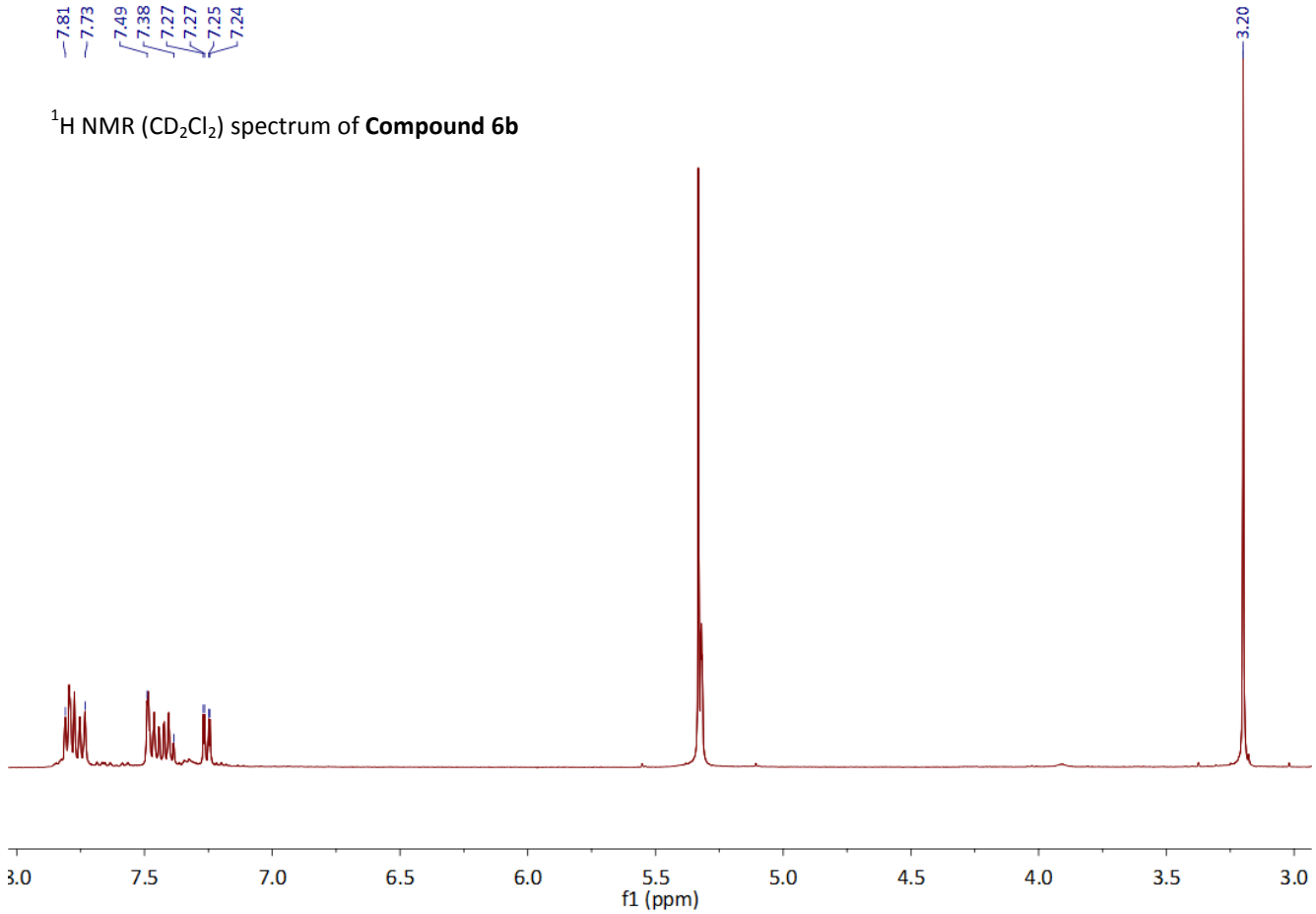


^{1}H NMR (CD_2Cl_2) spectrum of **Compound 6a**

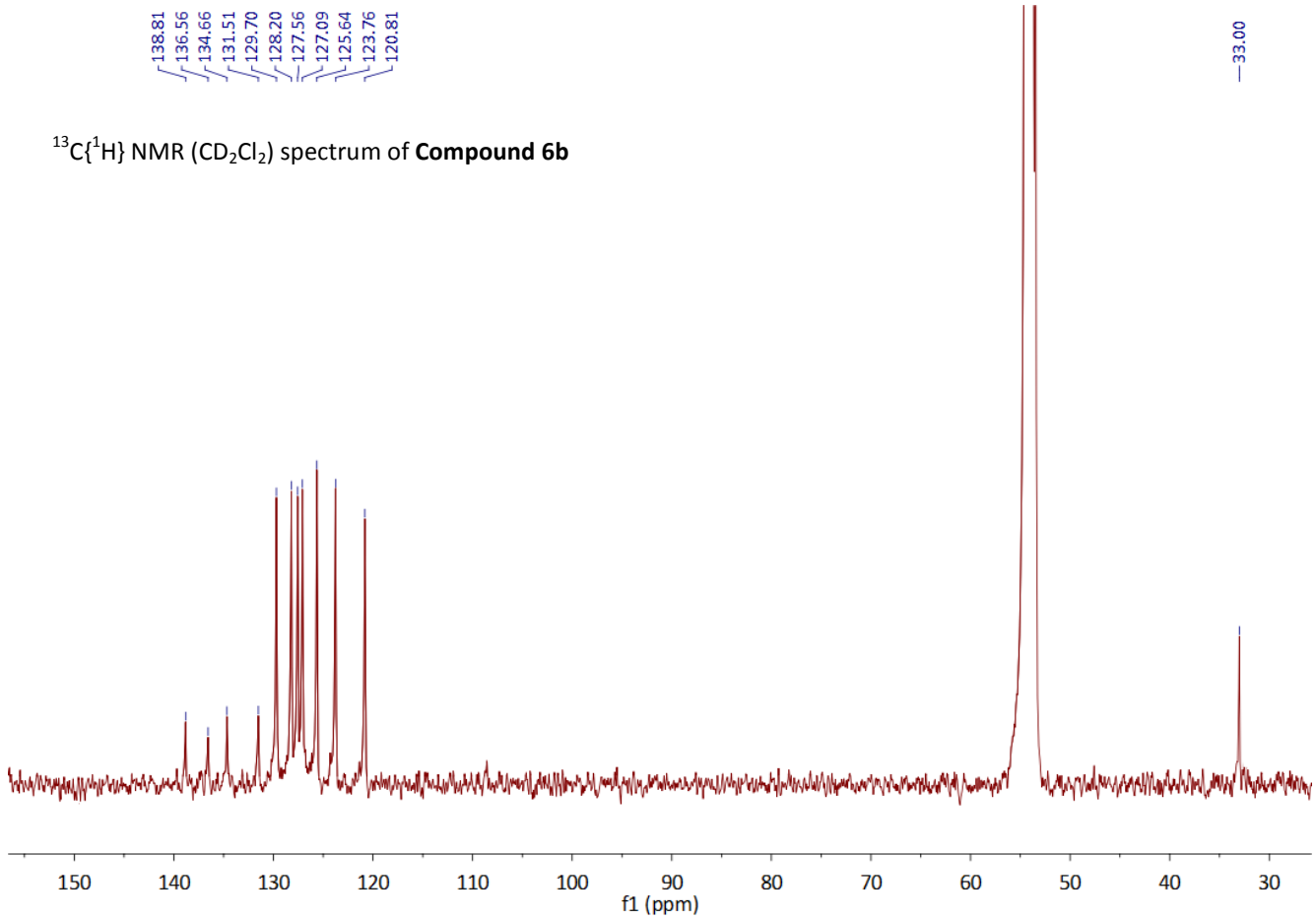


^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 6a**



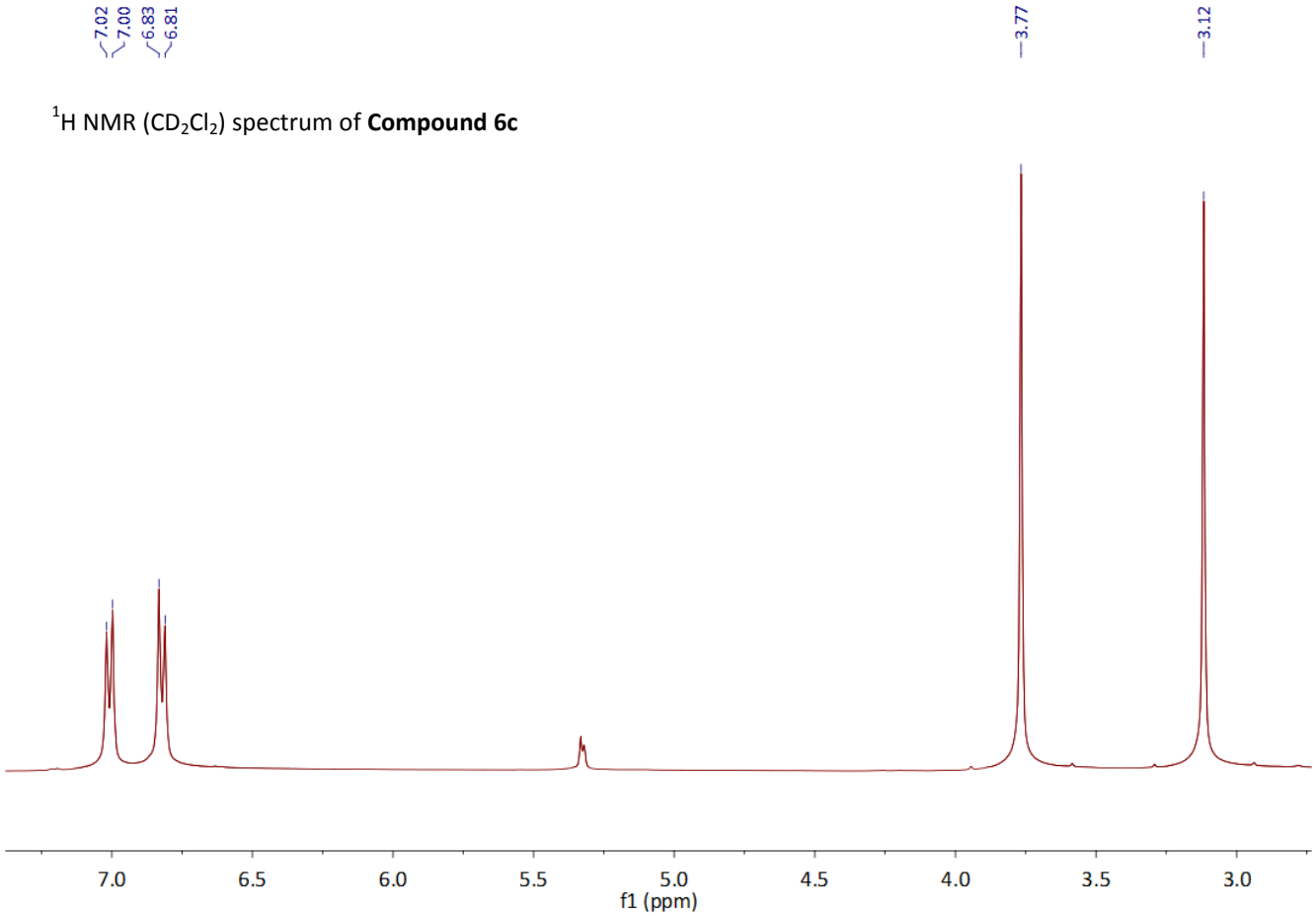


^{1}H NMR (CD_2Cl_2) spectrum of **Compound 6b**

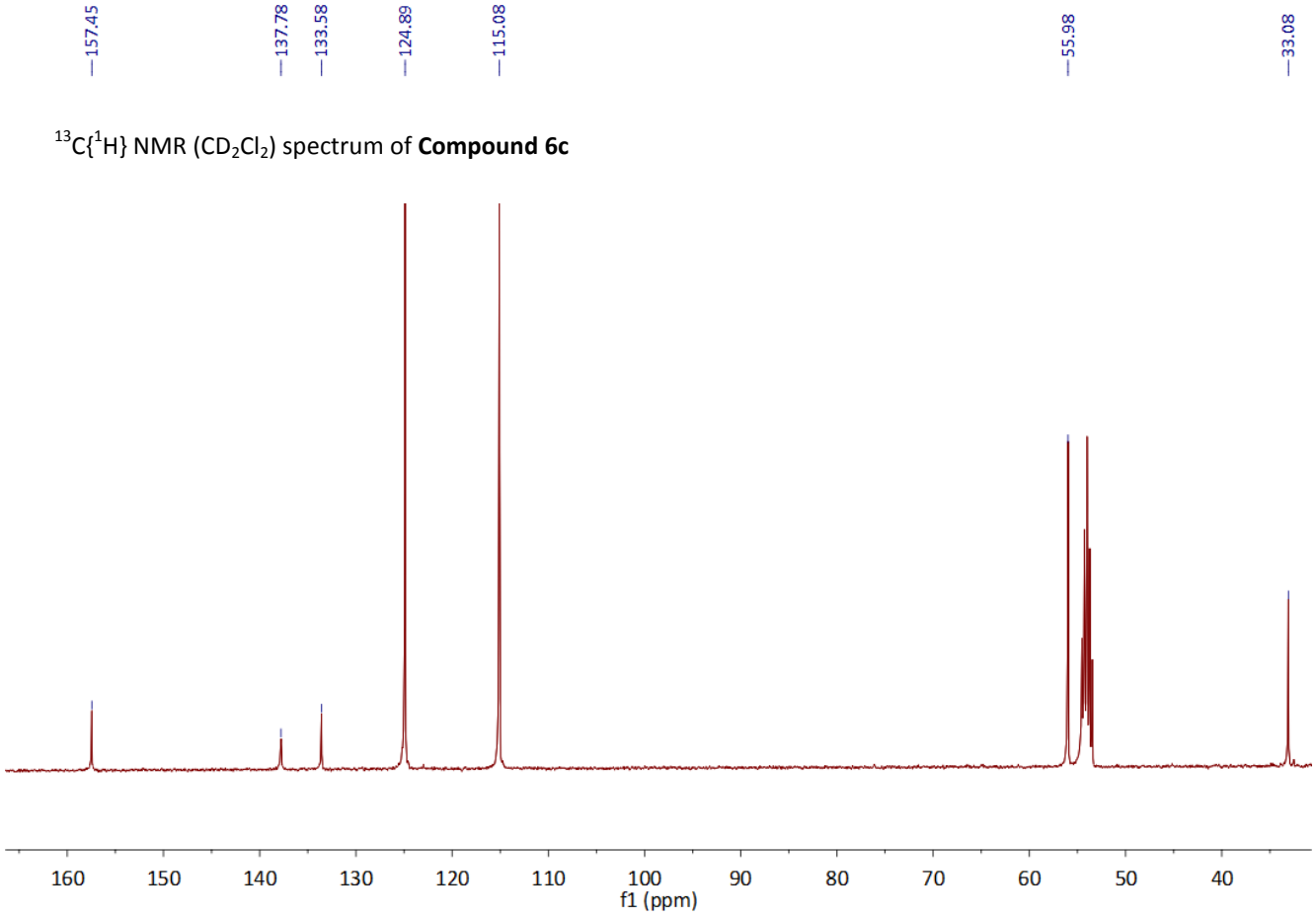


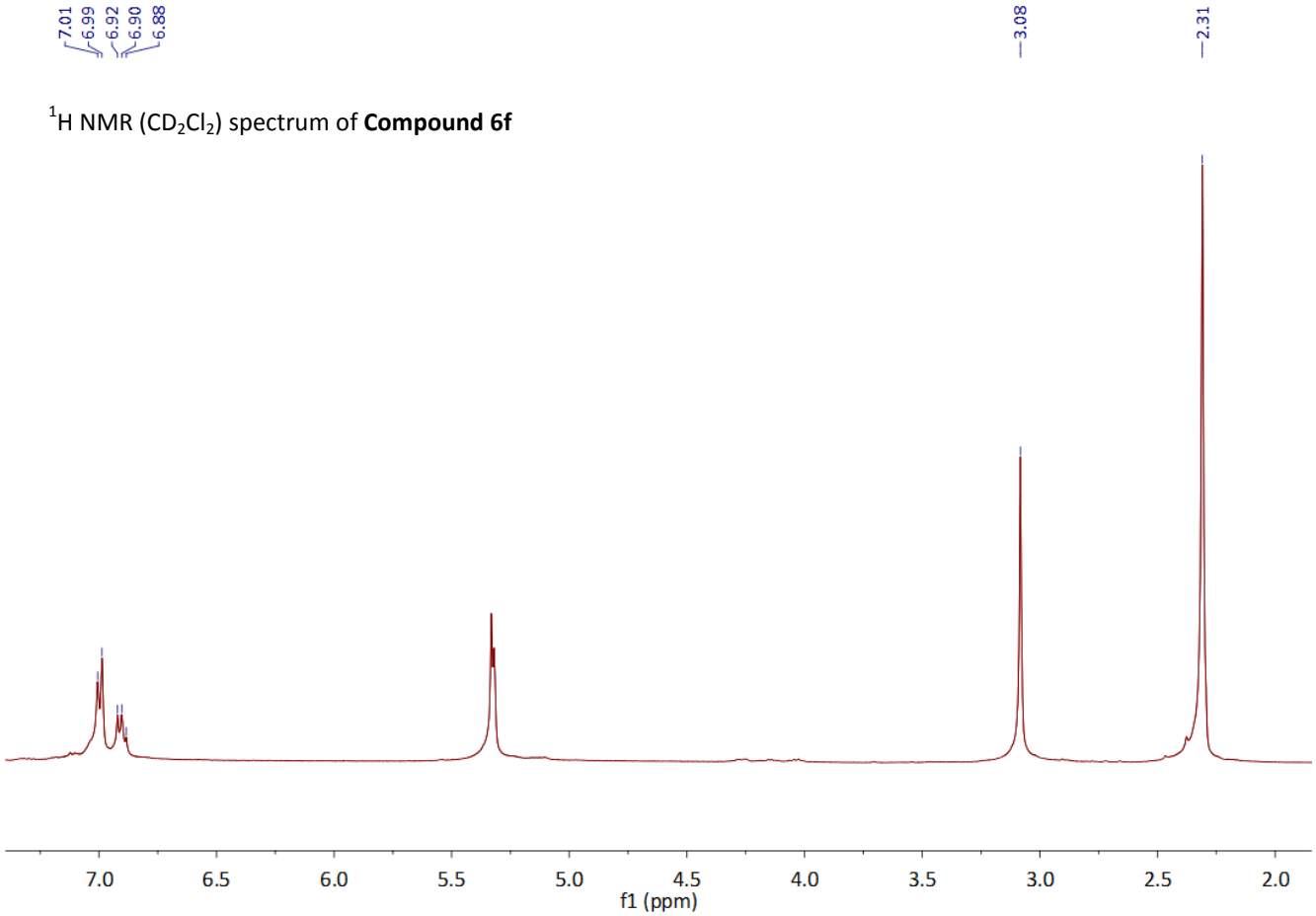
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 6b**

^{1}H NMR (CD_2Cl_2) spectrum of **Compound 6c**

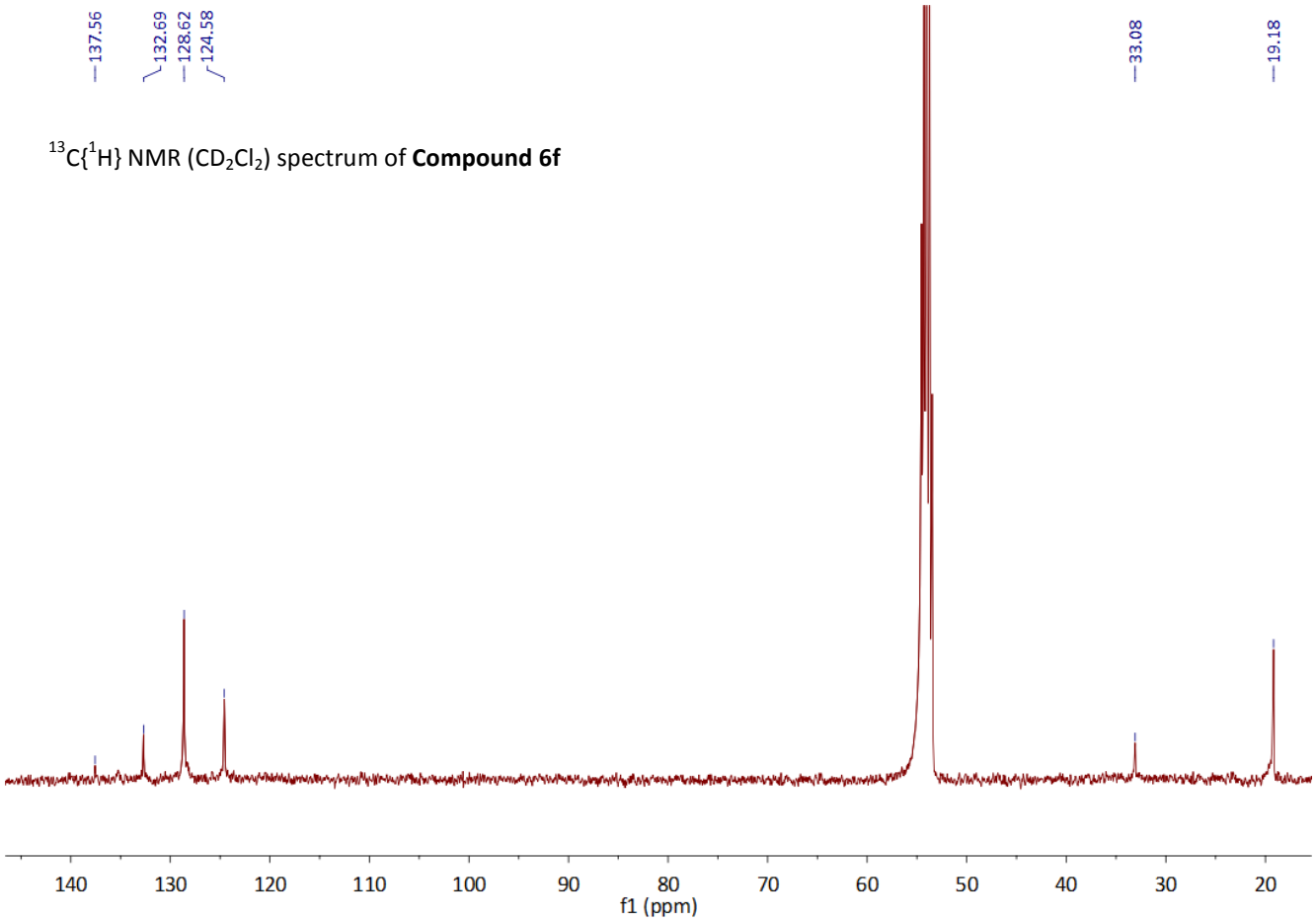


^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 6c**

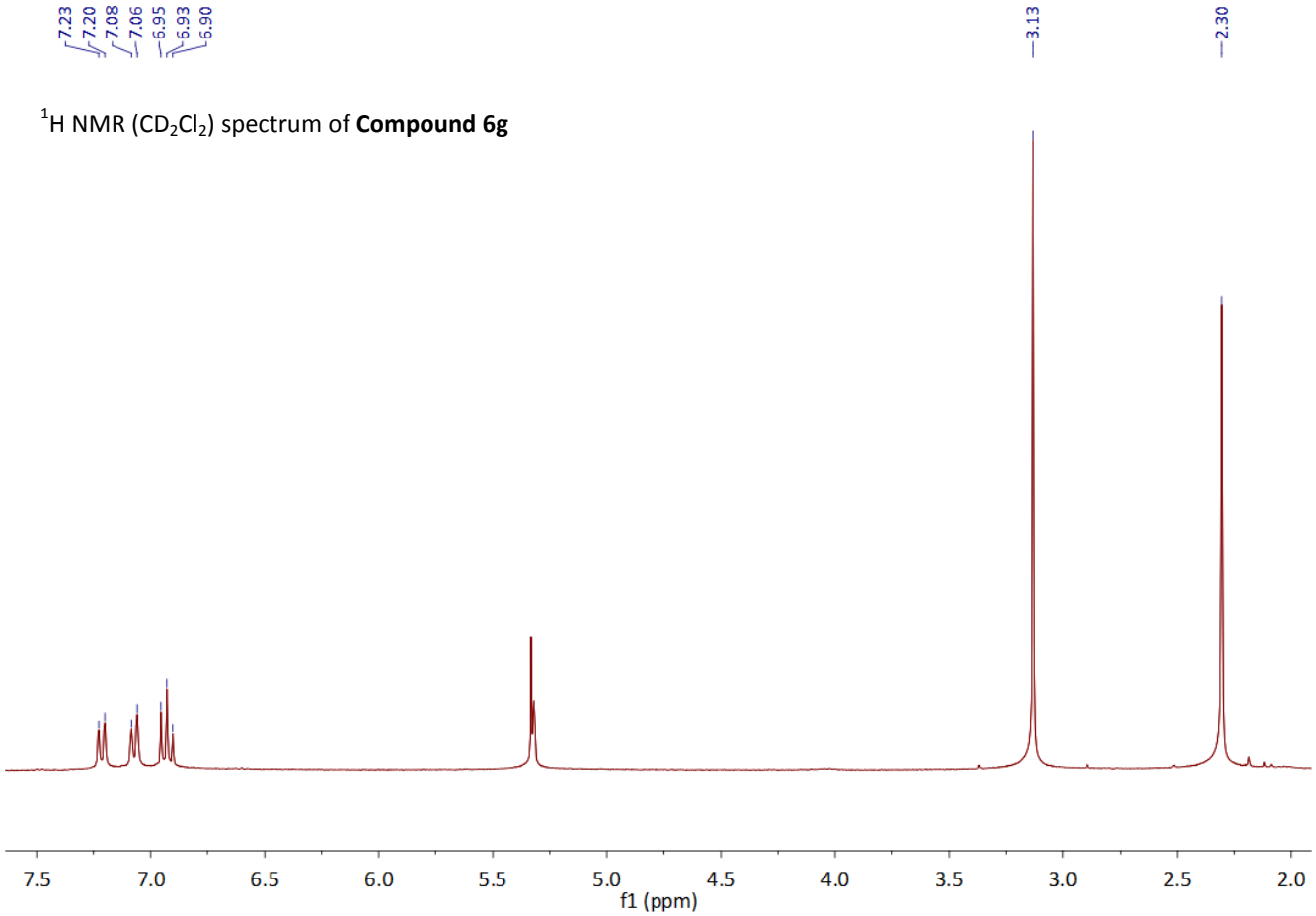




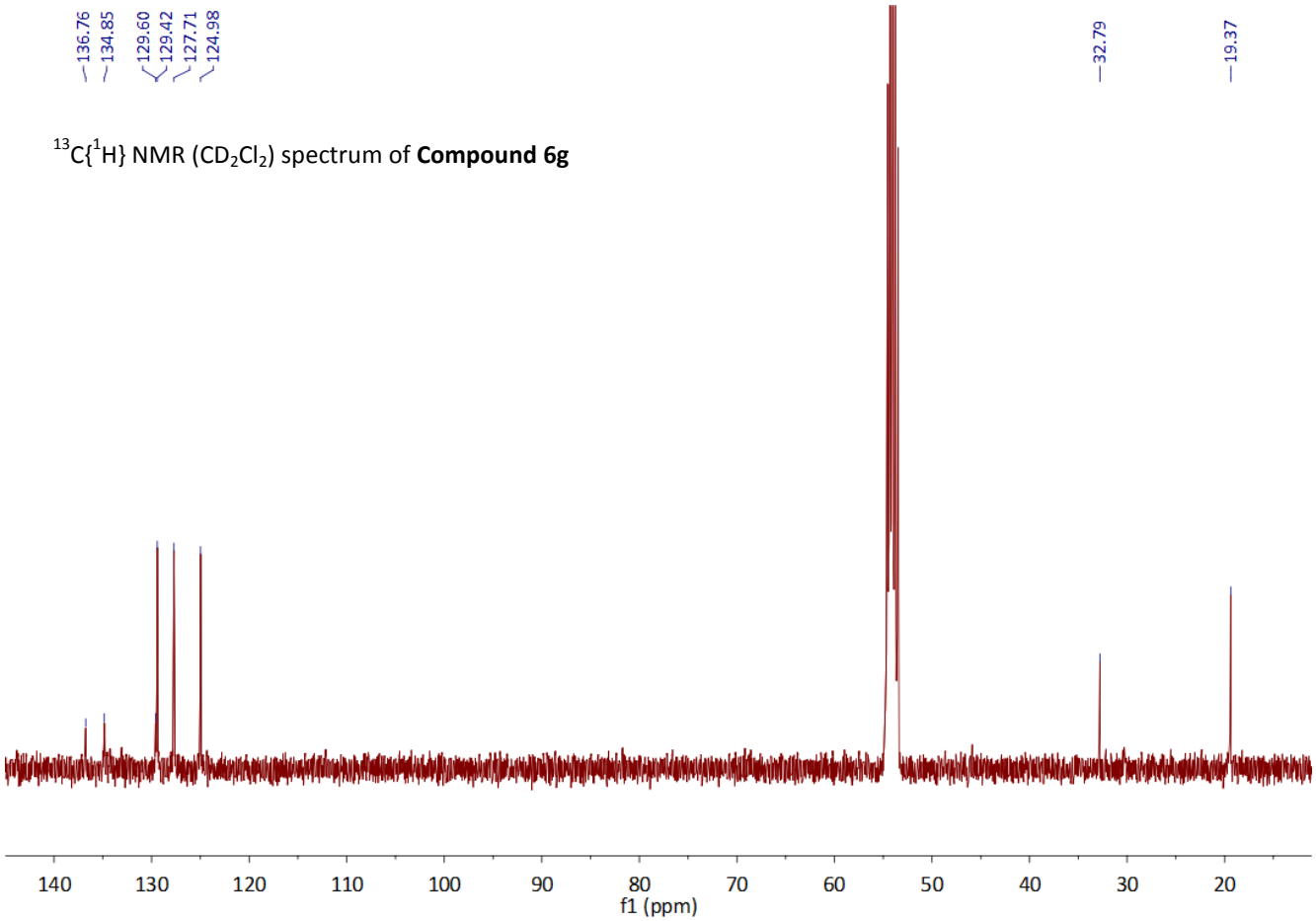
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 6f**



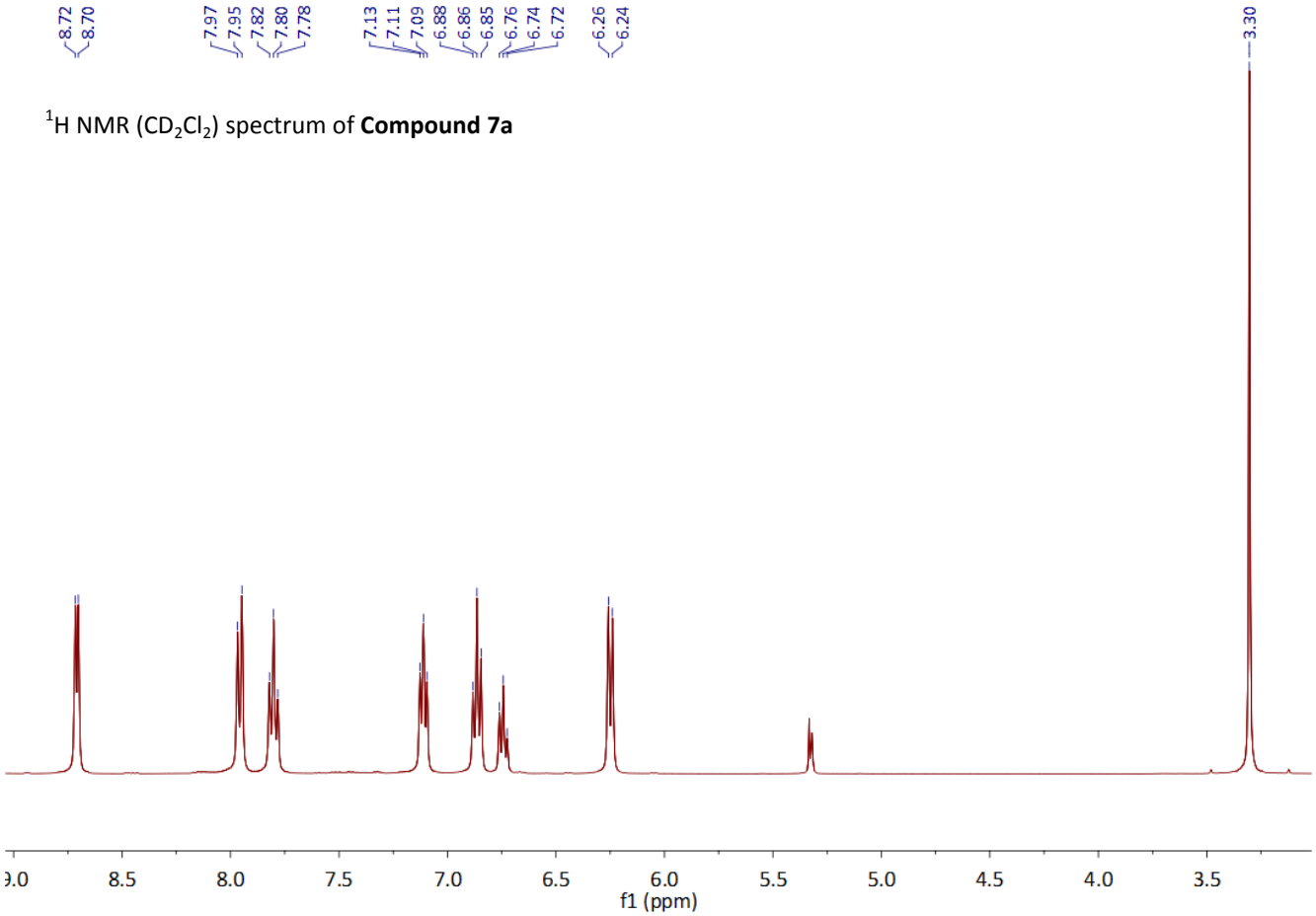
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 6f**



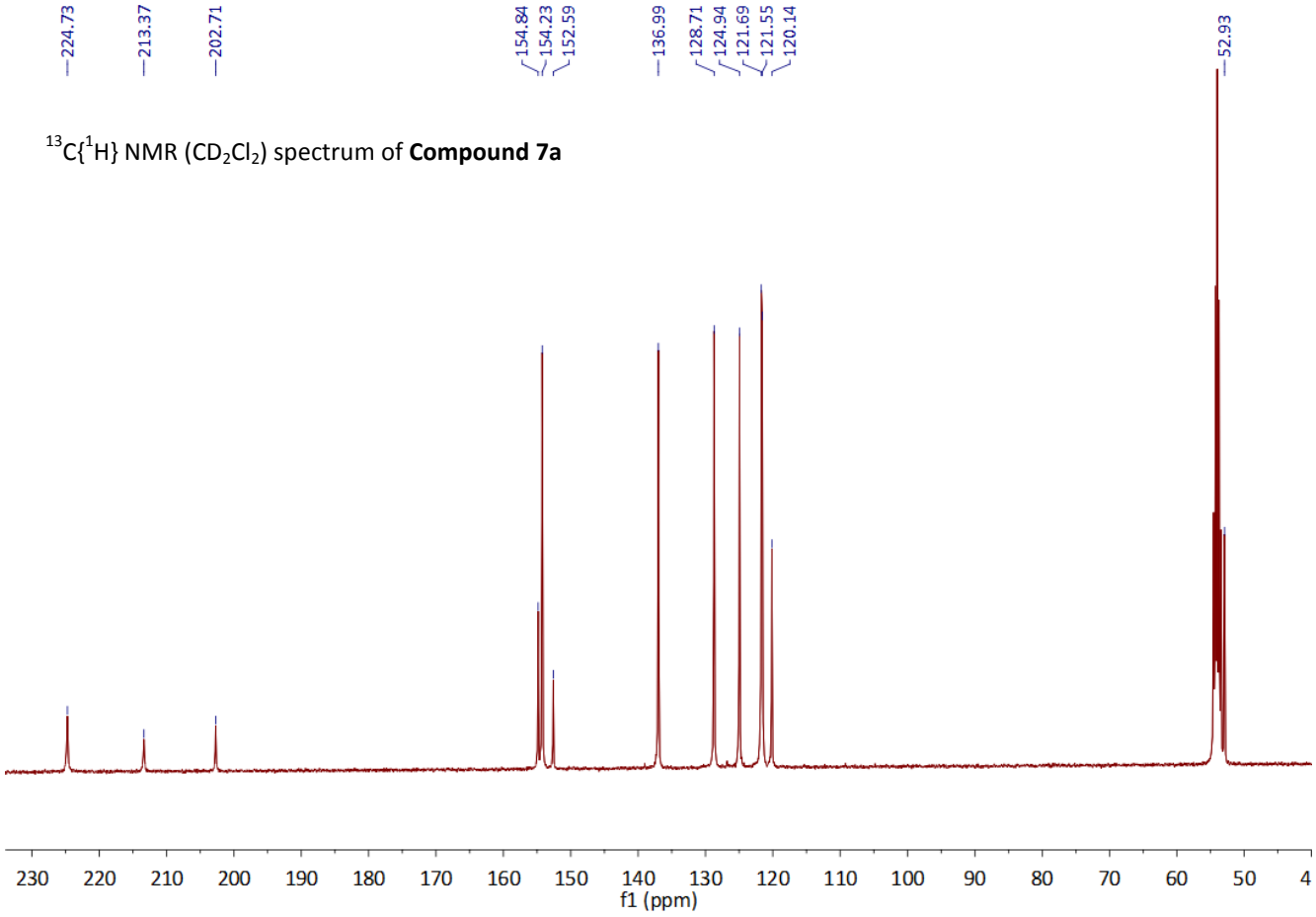
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 6g**



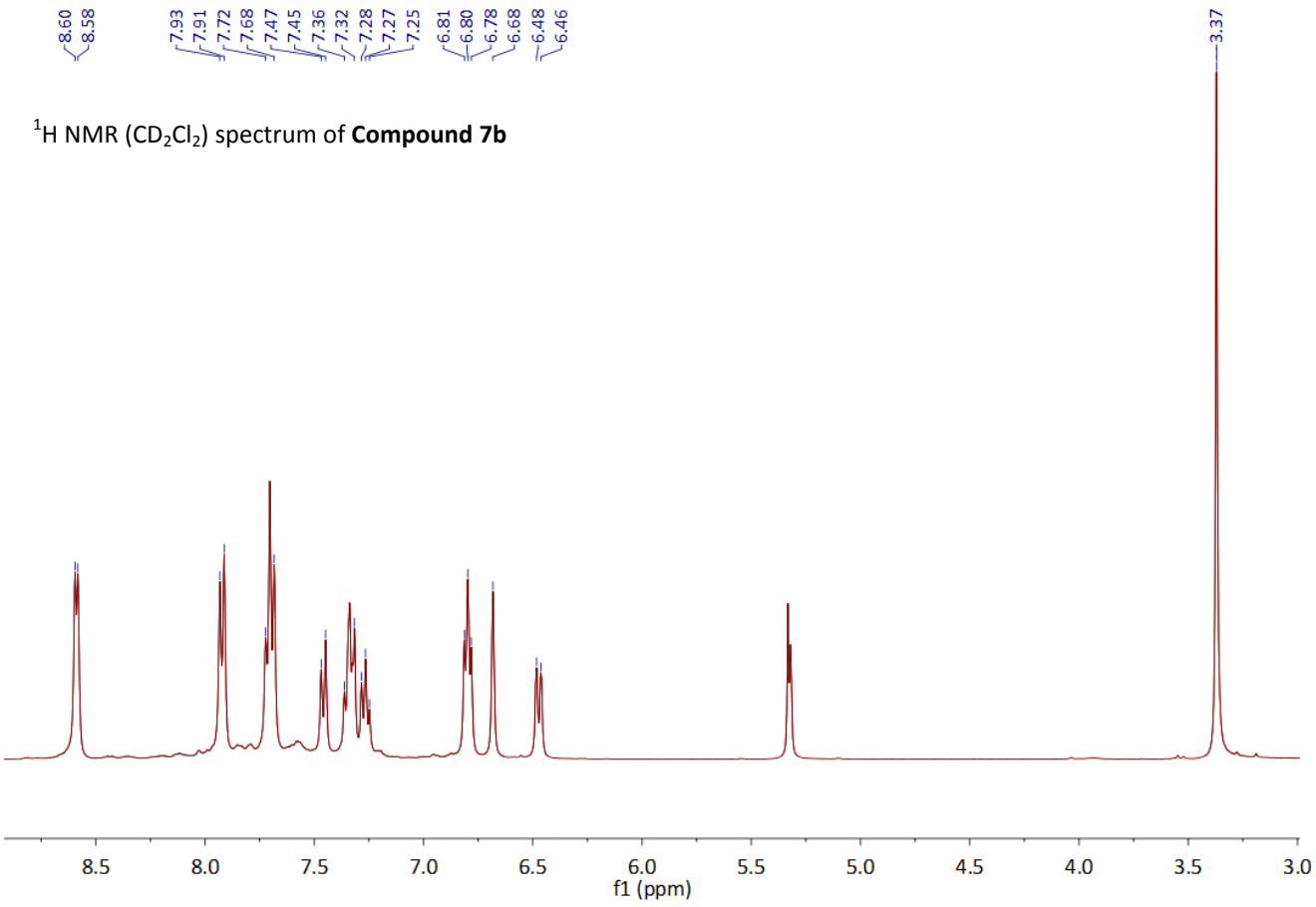
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 6g**



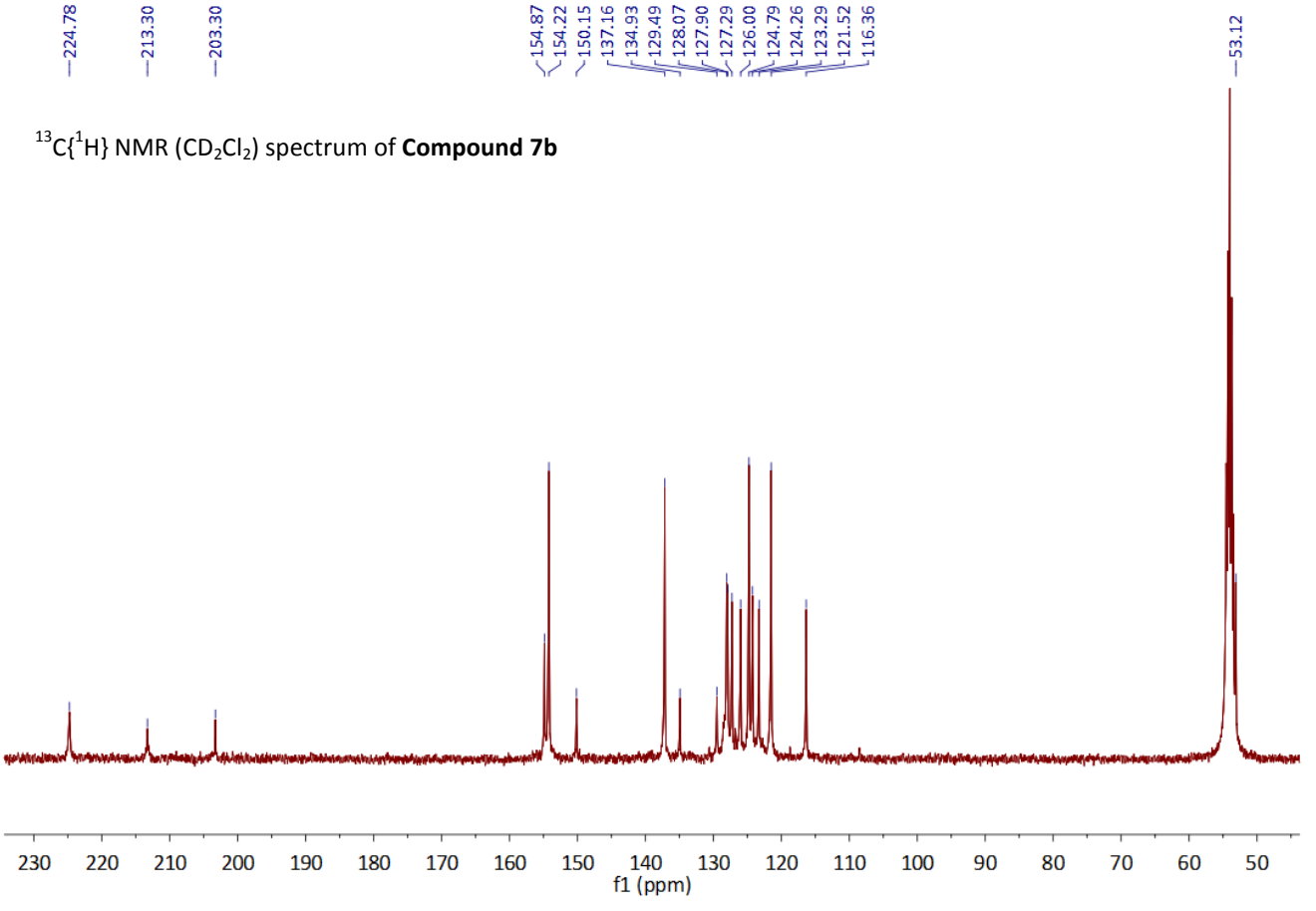
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 7a**



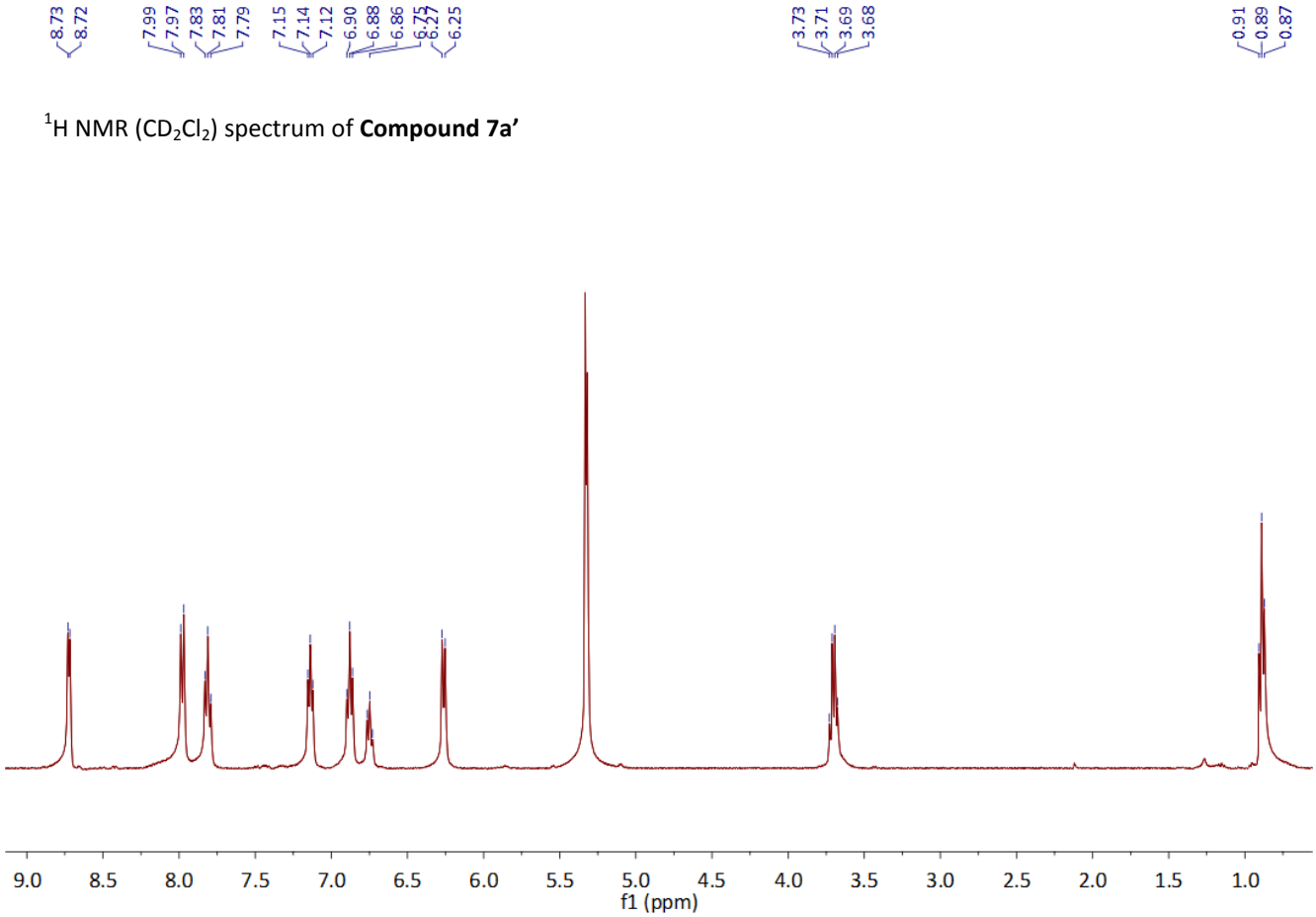
$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of **Compound 7a**



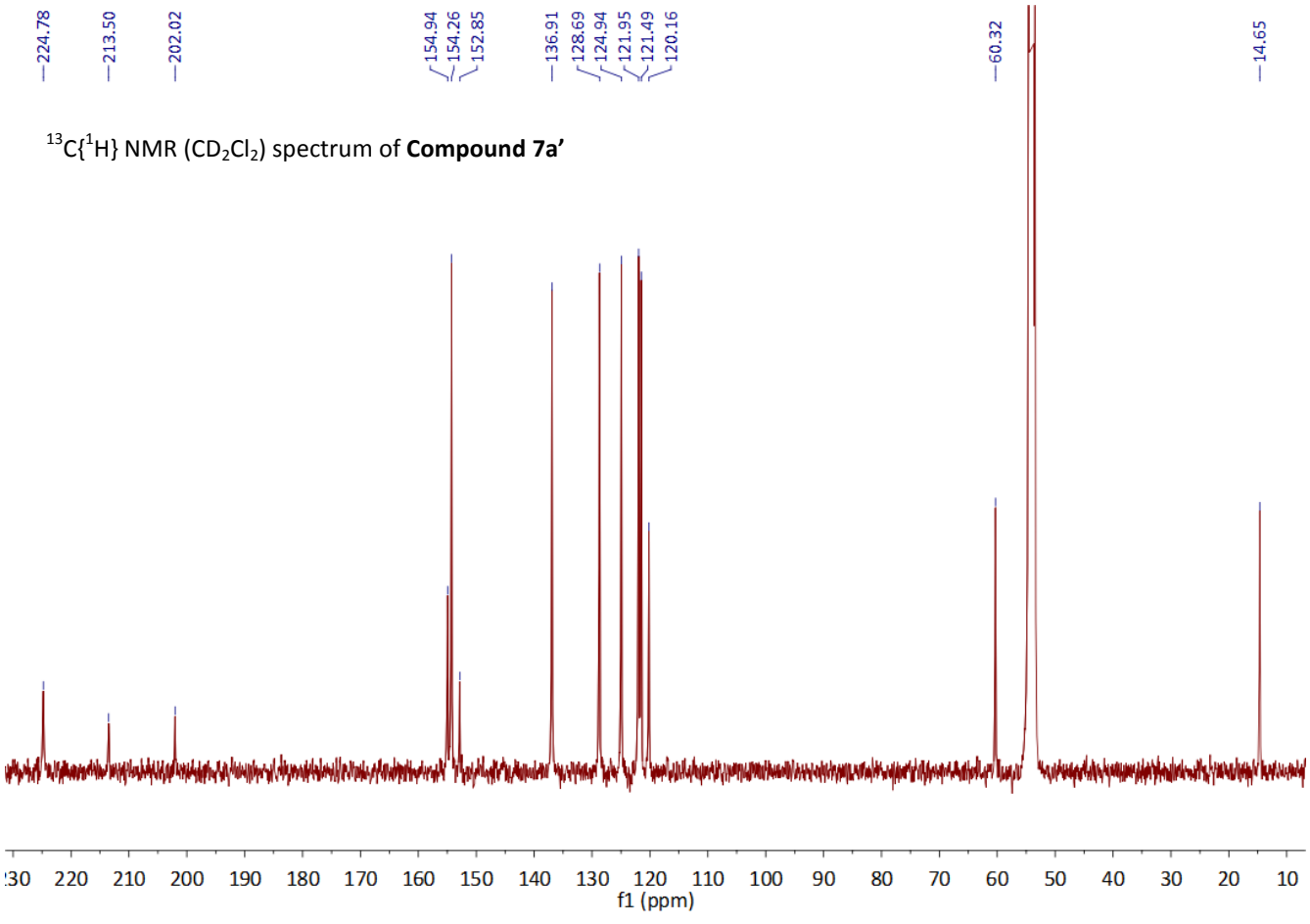
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 7b**



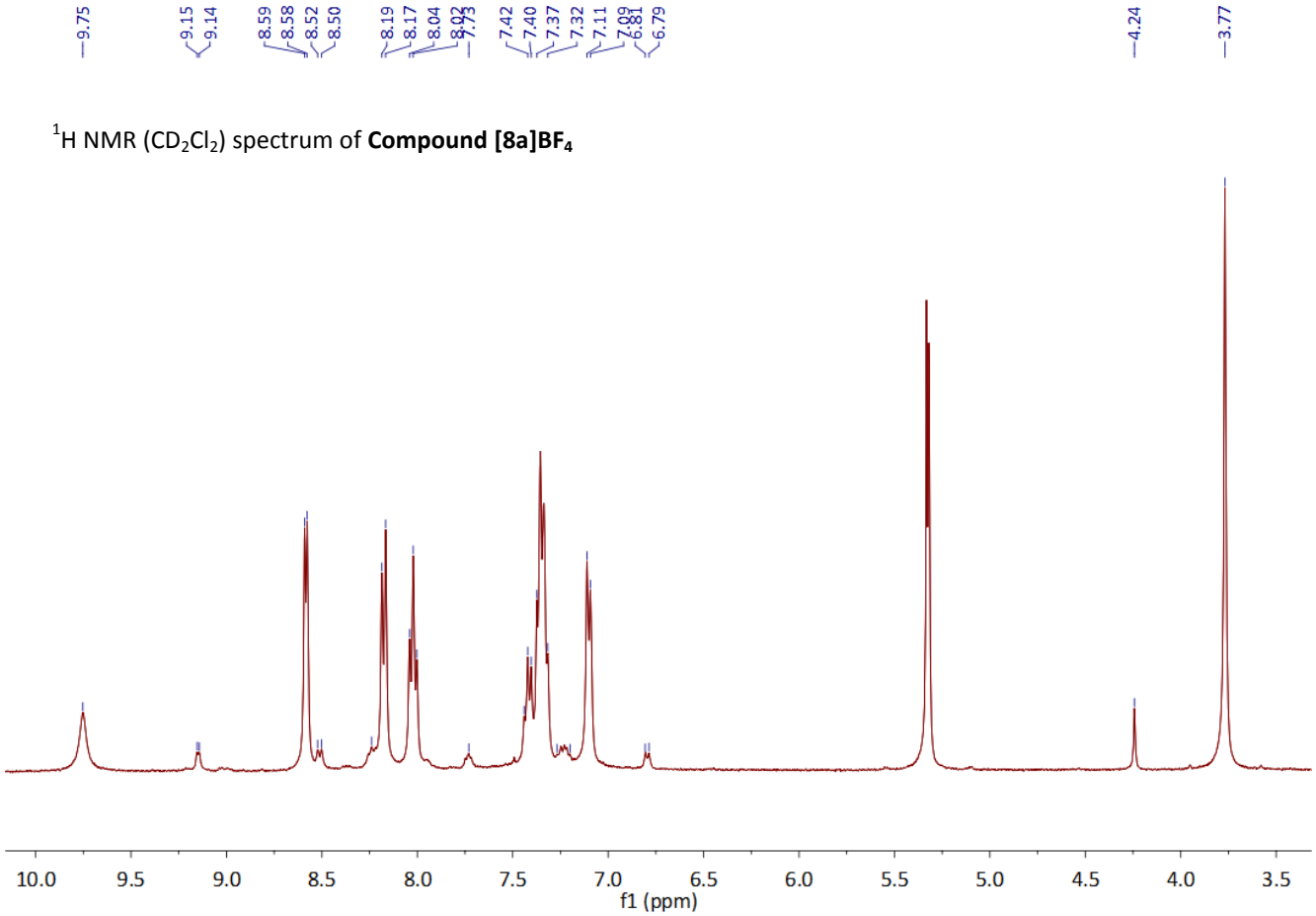
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 7b**



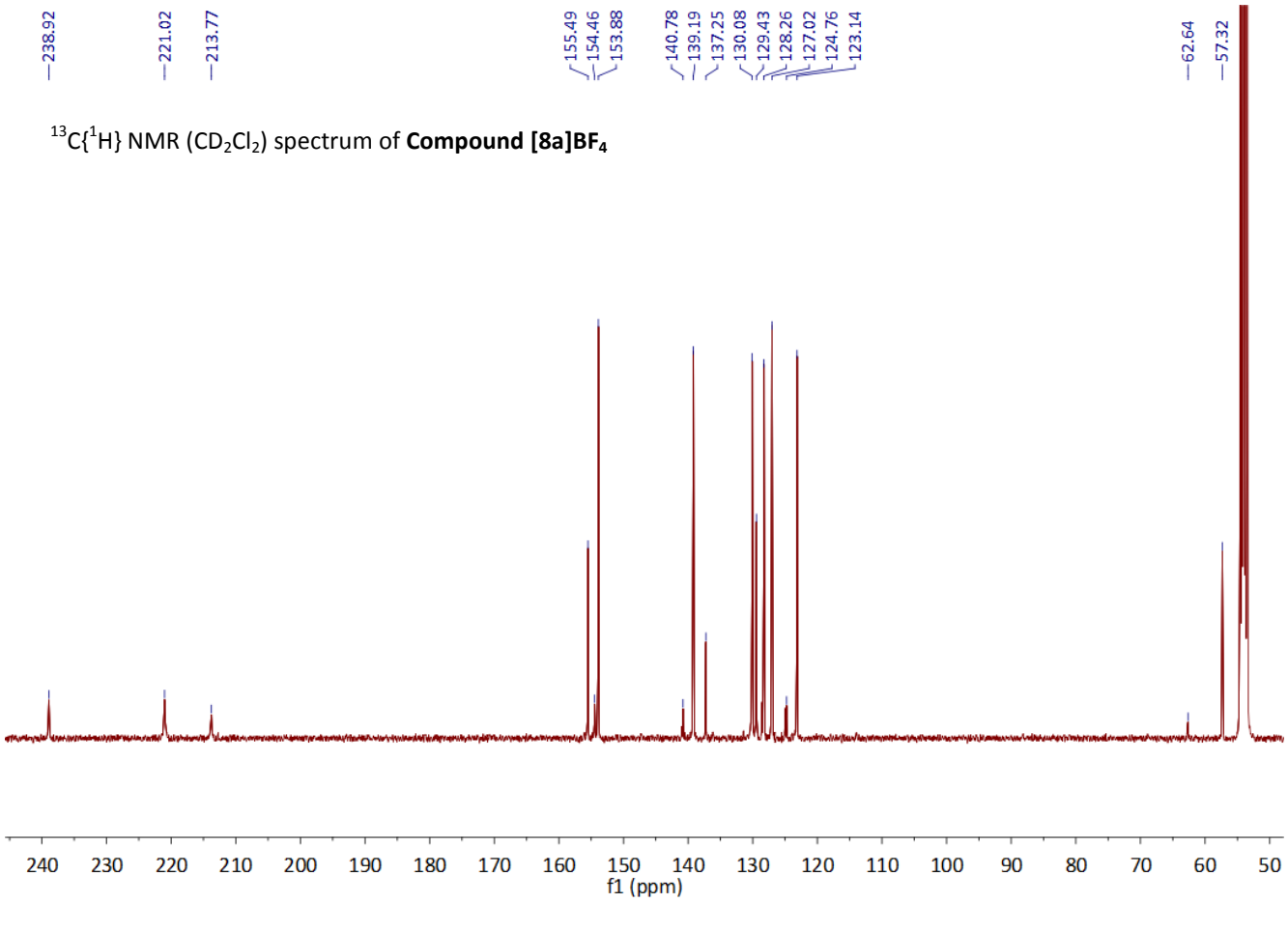
^{1}H NMR (CD_2Cl_2) spectrum of **Compound 7a'**



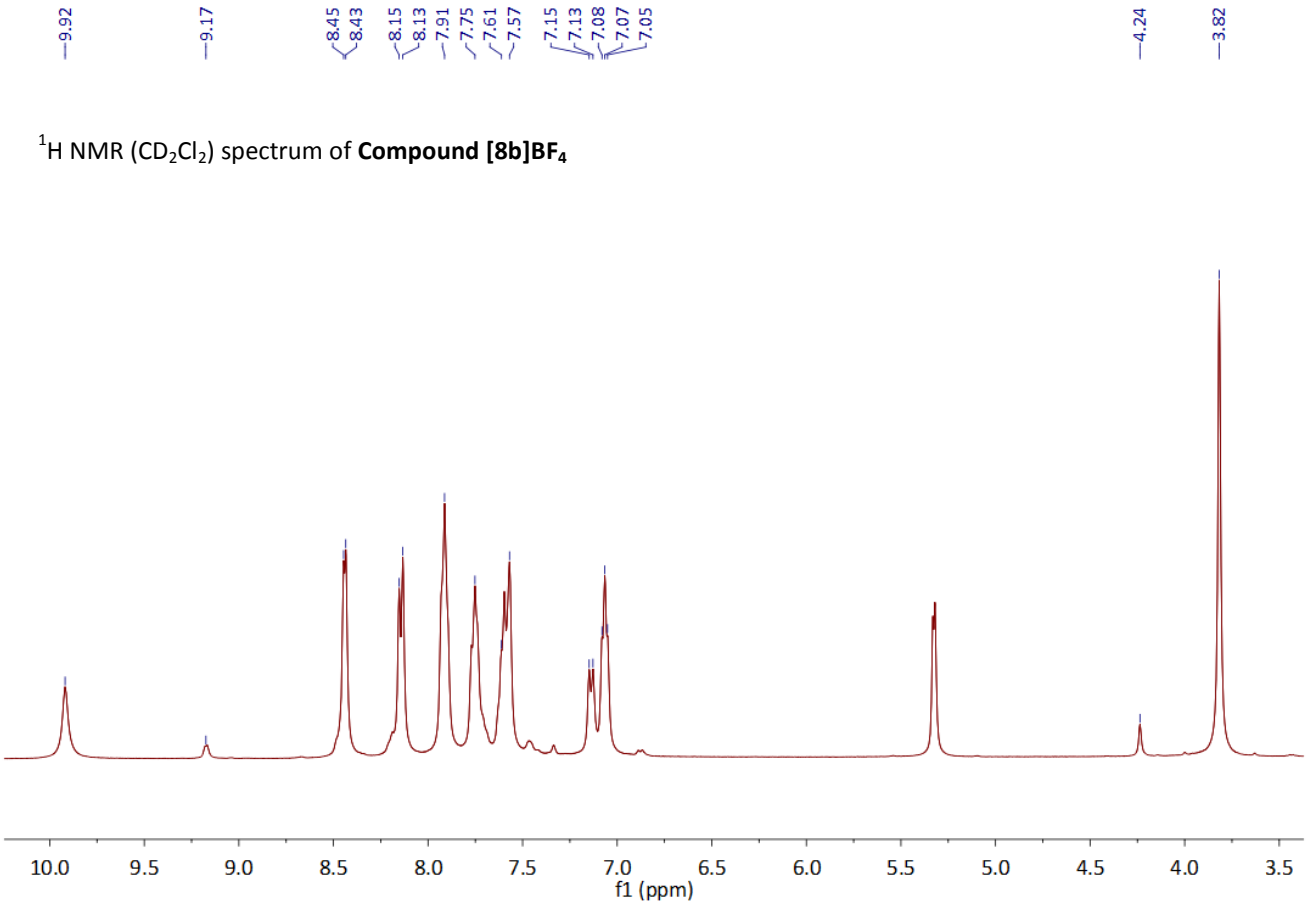
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 7a'**



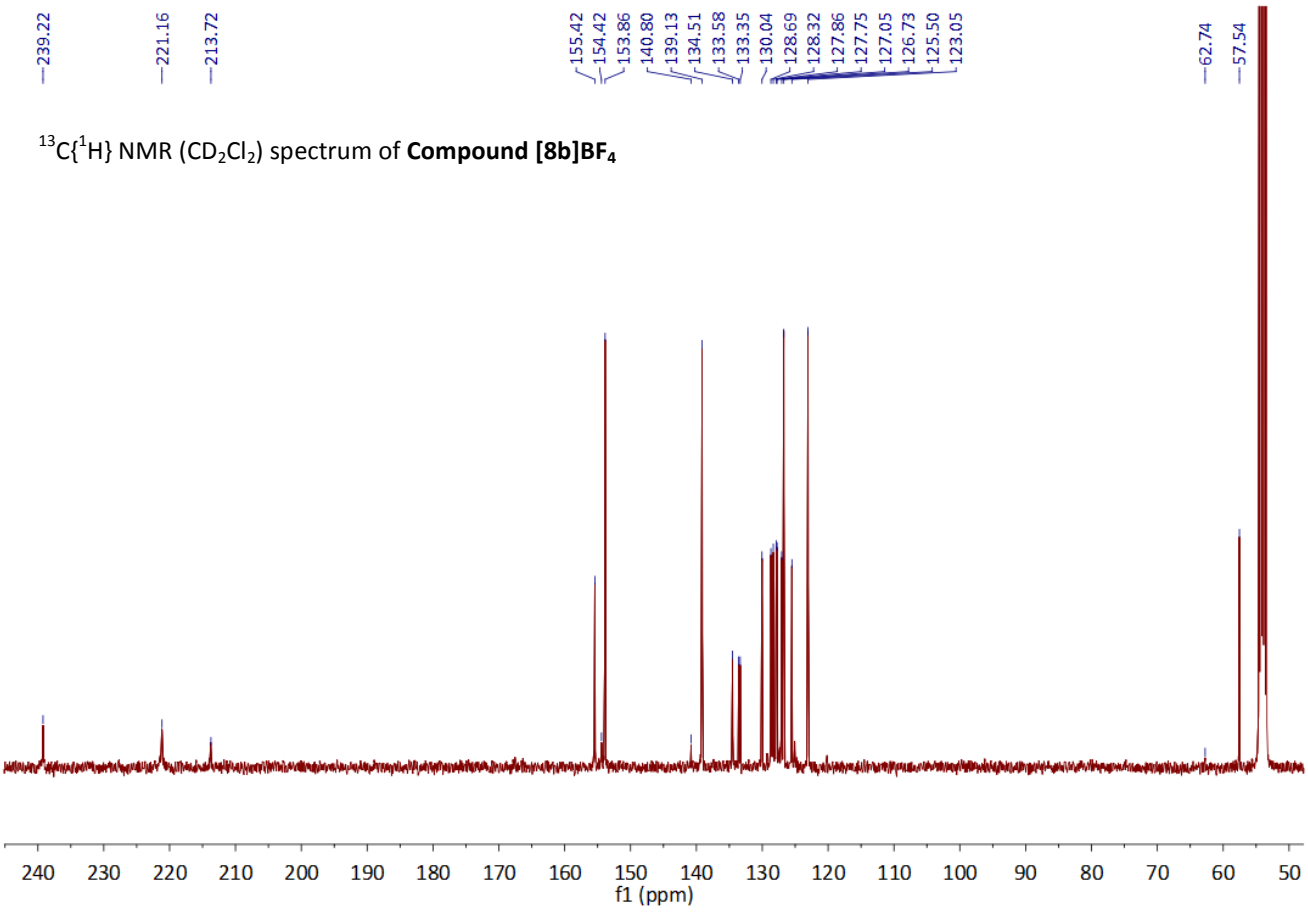
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [8a]BF_4**



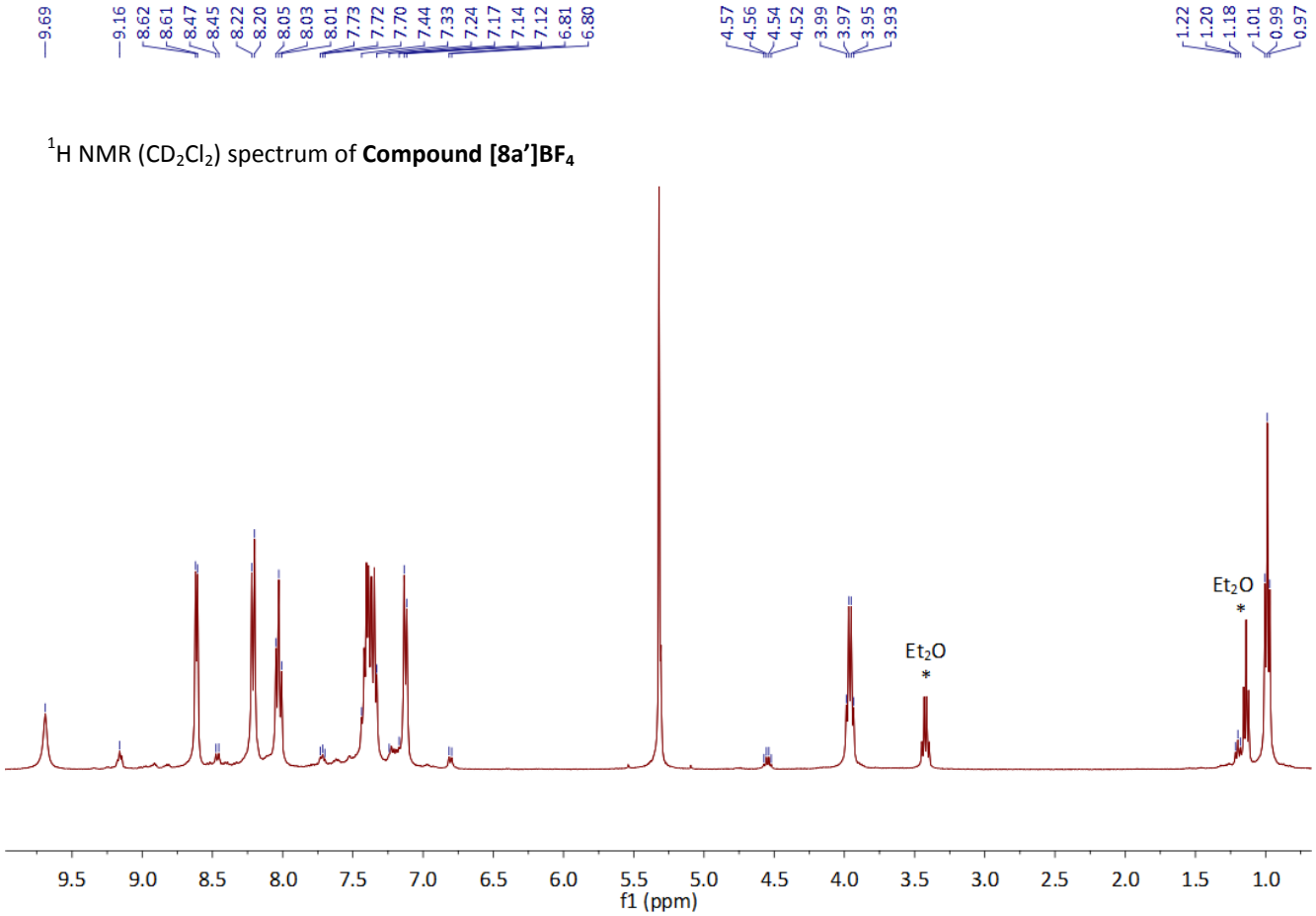
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [8a]BF_4**



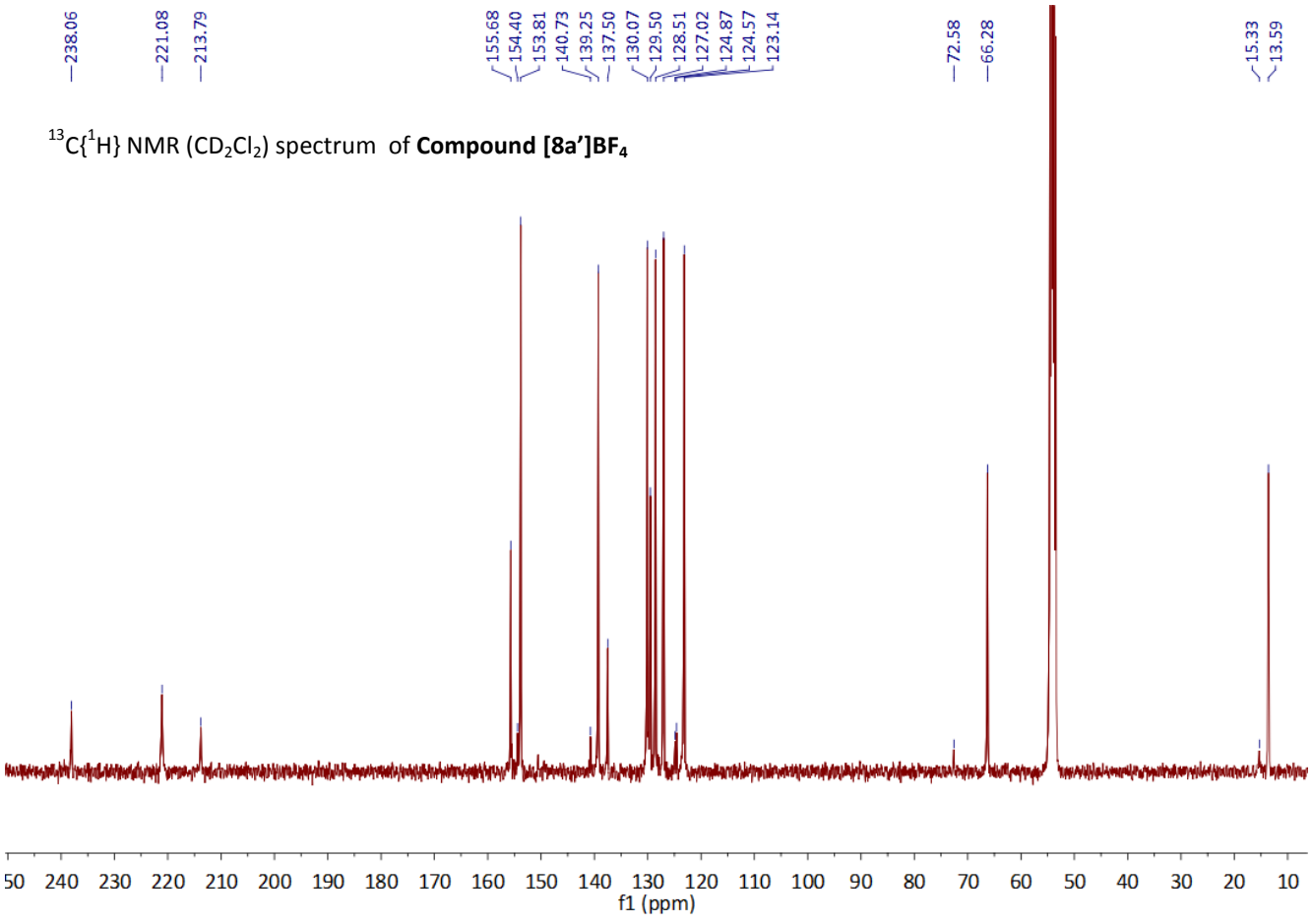
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [8b]BF_4**



^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [8b]BF_4**

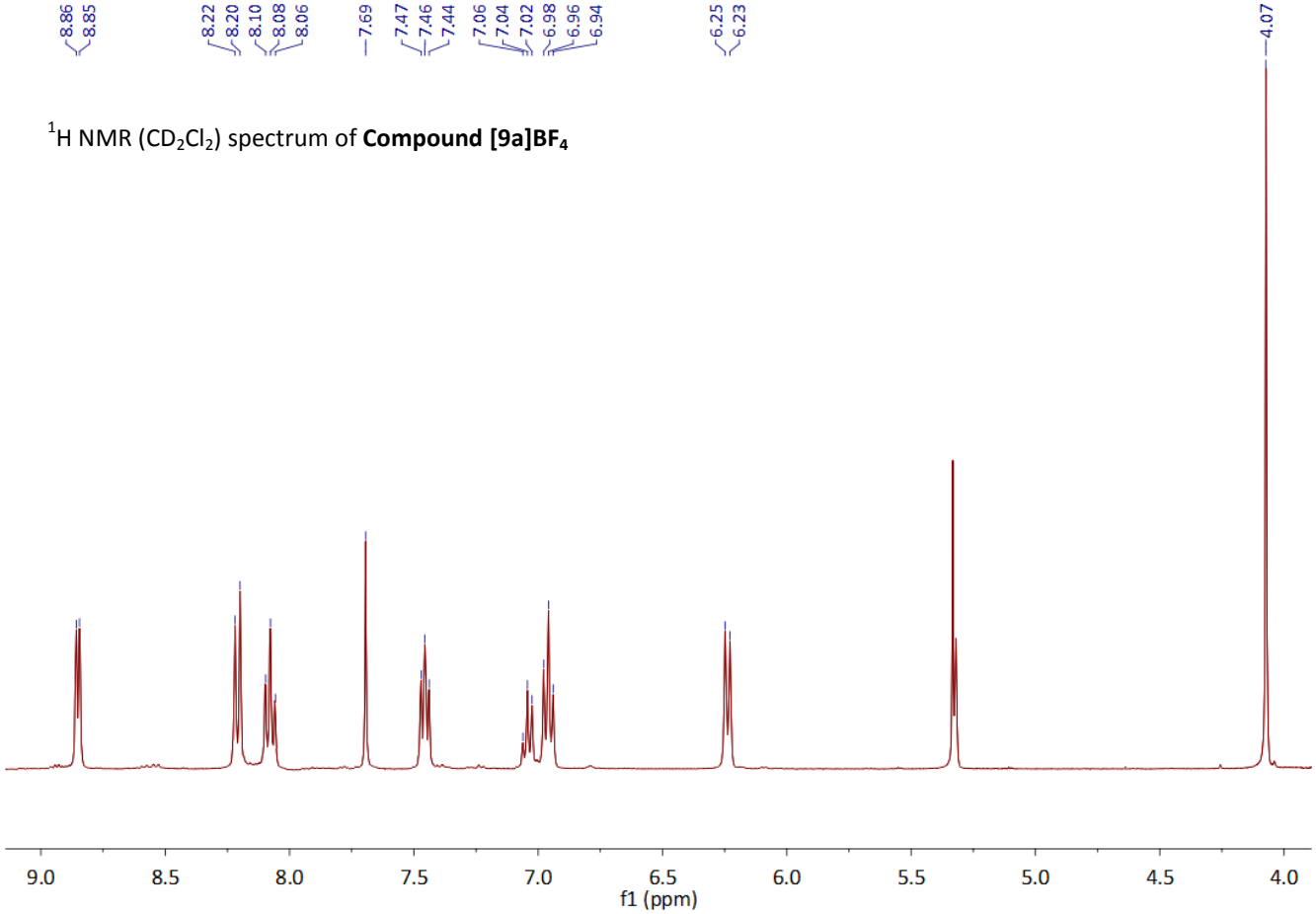


^{1}H NMR (CD_2Cl_2) spectrum of **Compound [8a']BF_4**

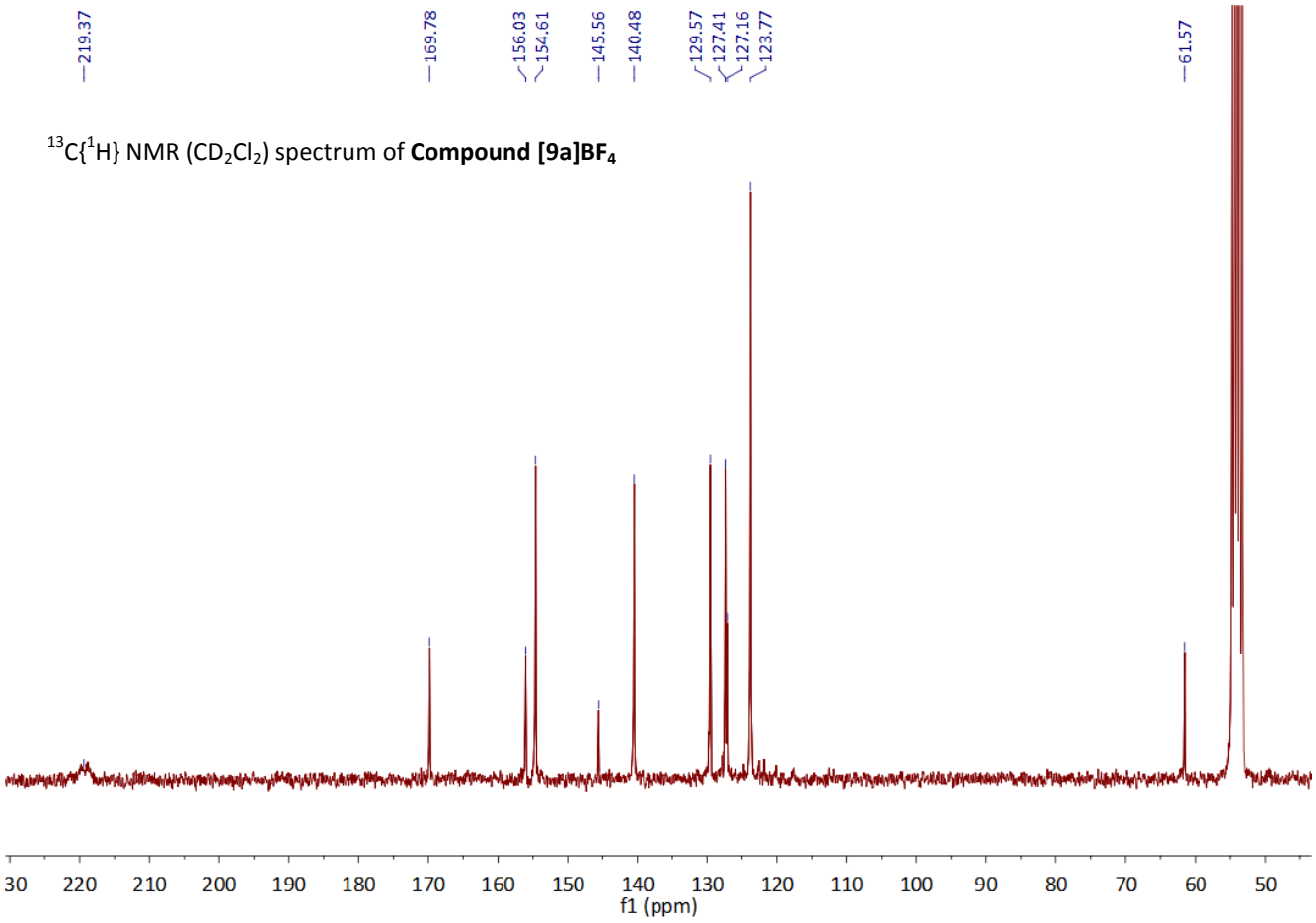


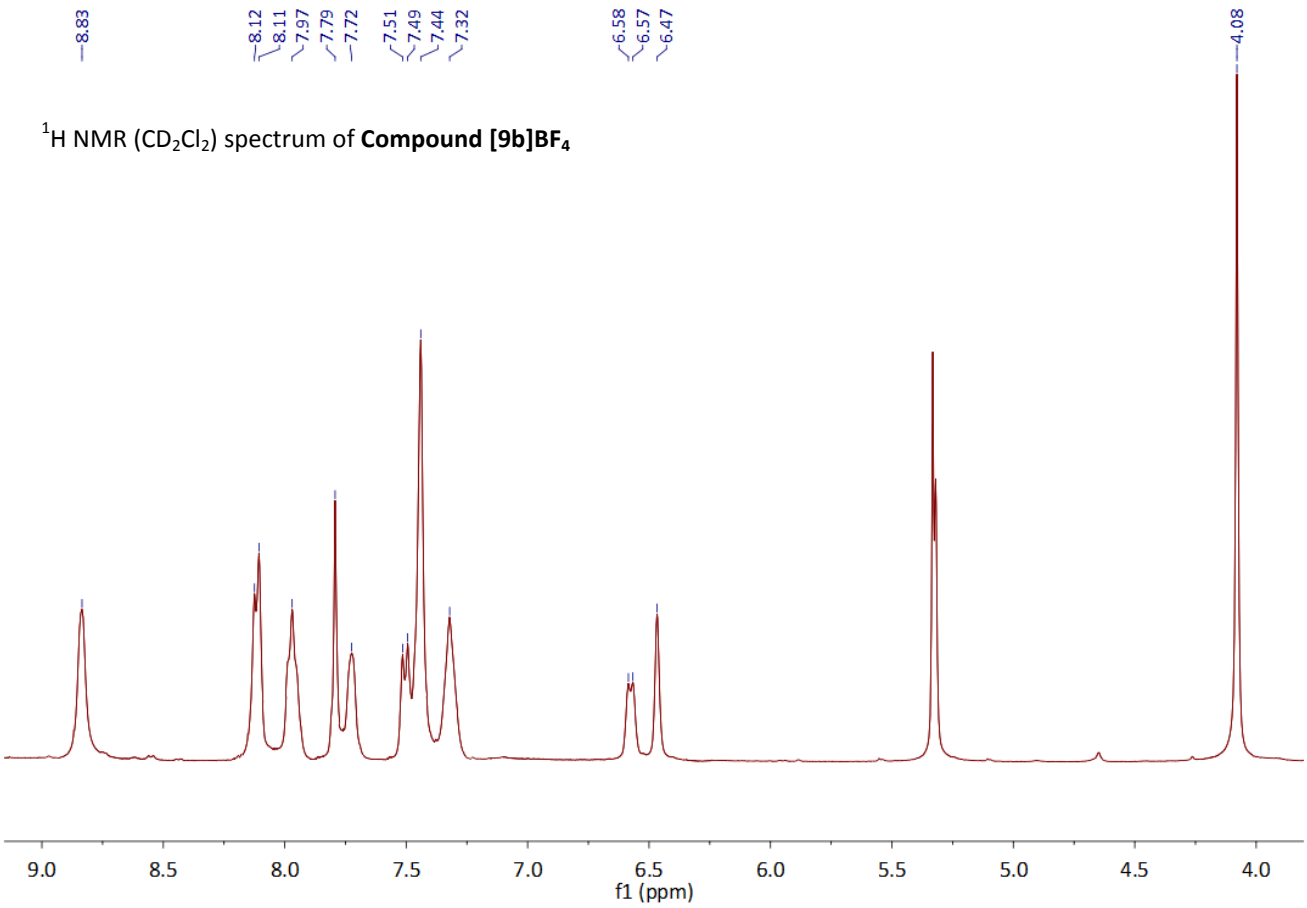
^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [8a']BF_4**

^{1}H NMR (CD_2Cl_2) spectrum of **Compound [9a]BF_4**

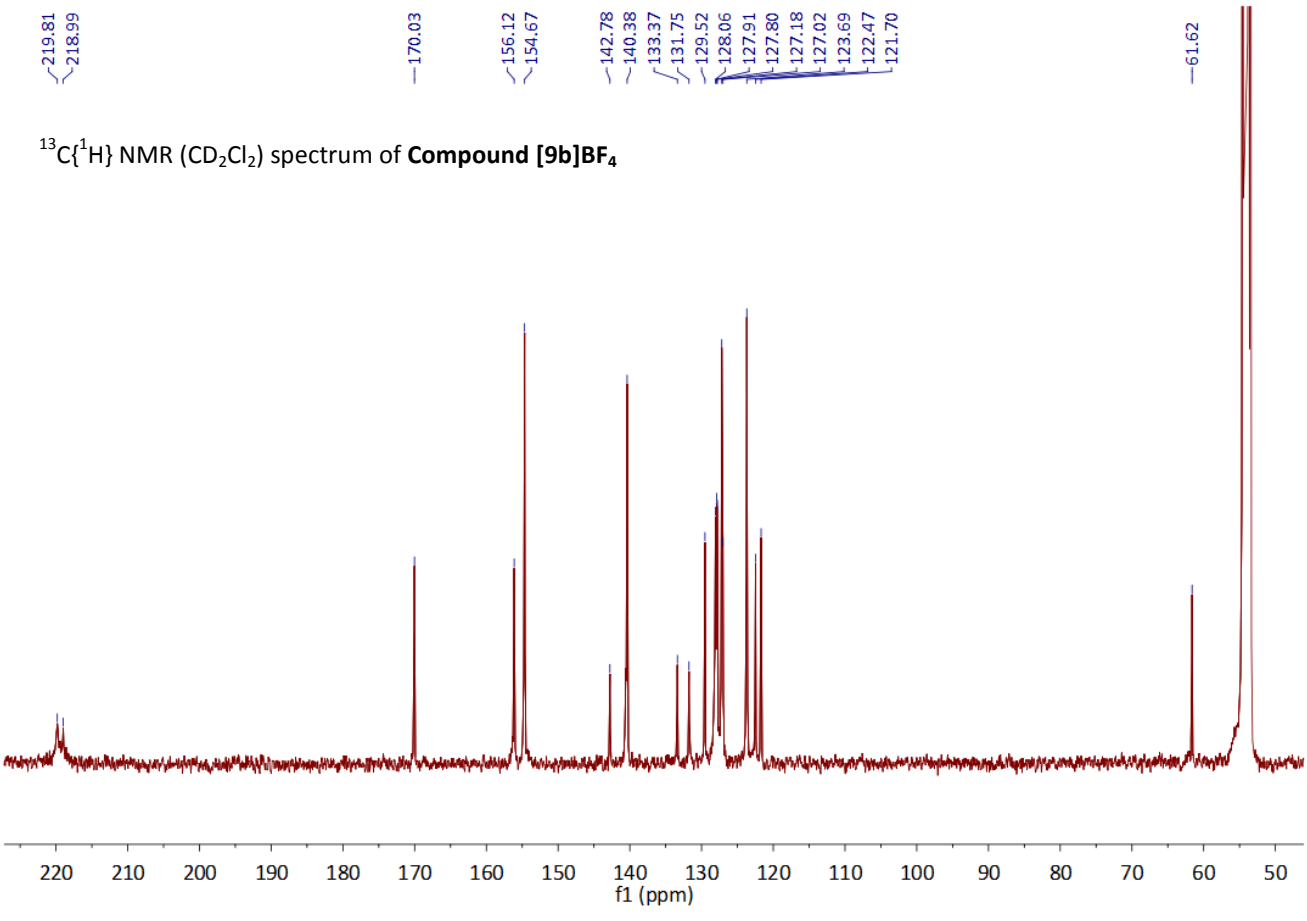


^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [9a]BF_4**

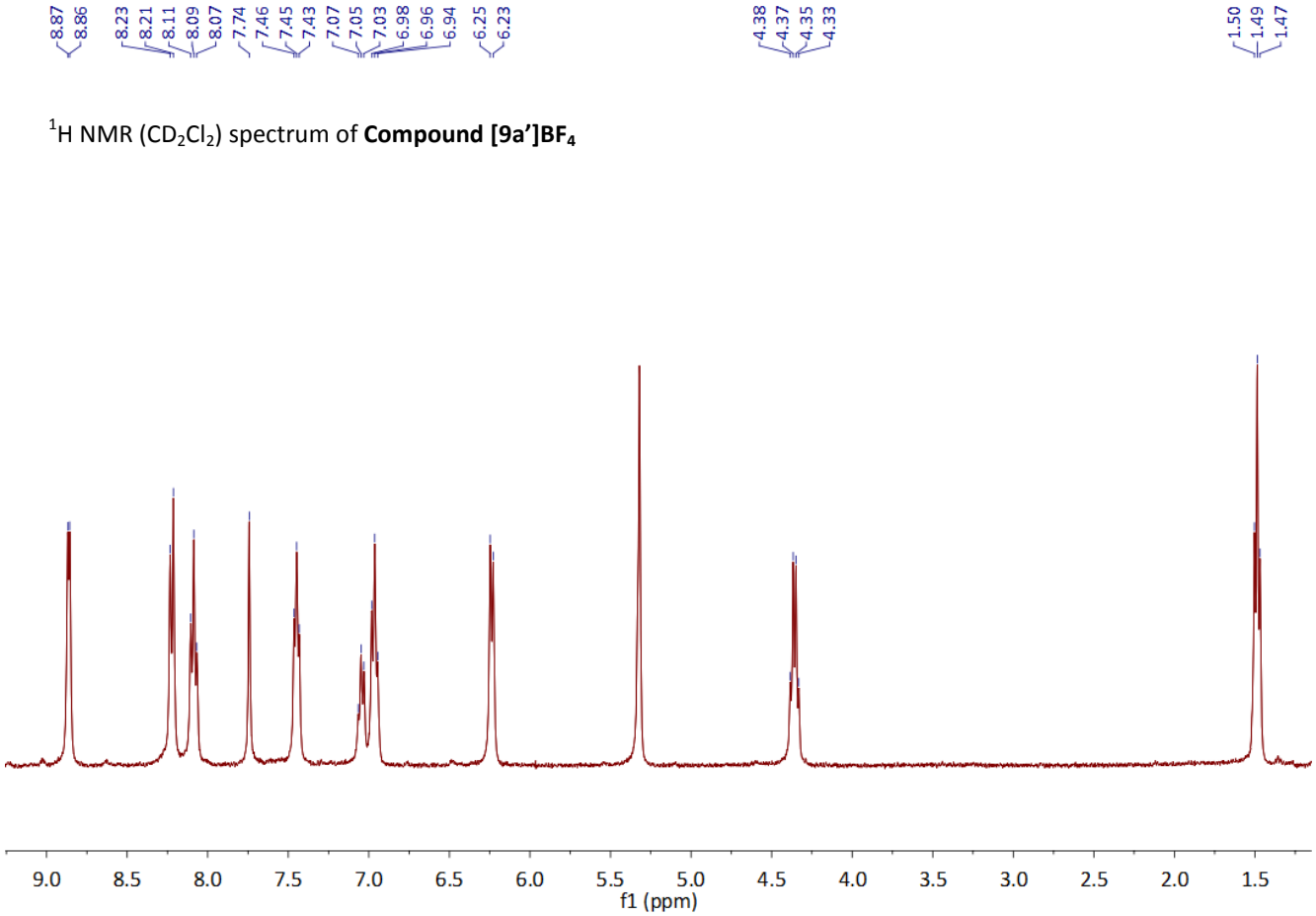




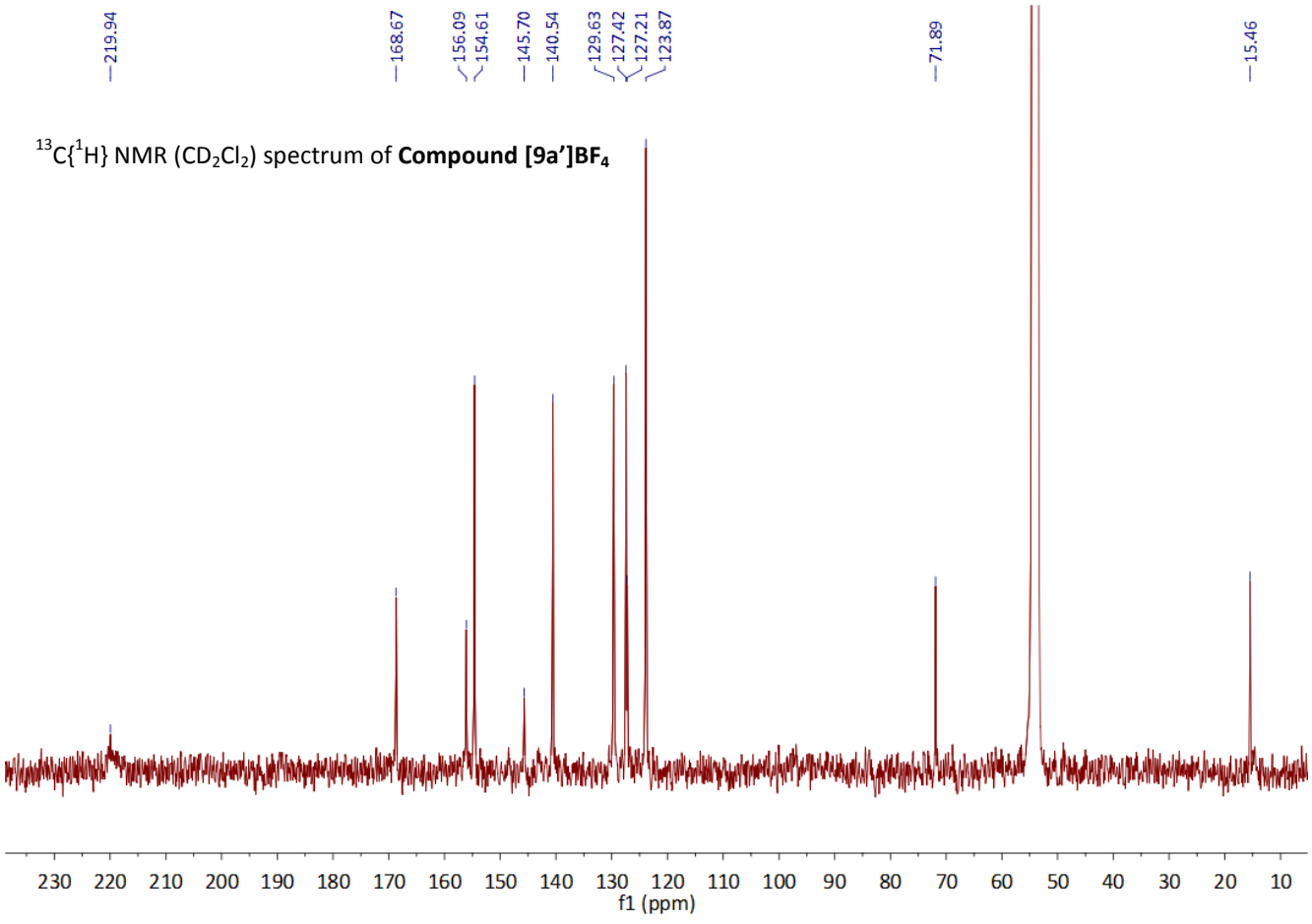
^{1}H NMR (CD_2Cl_2) spectrum of **Compound [9b]BF_4**



^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [9b]BF_4**

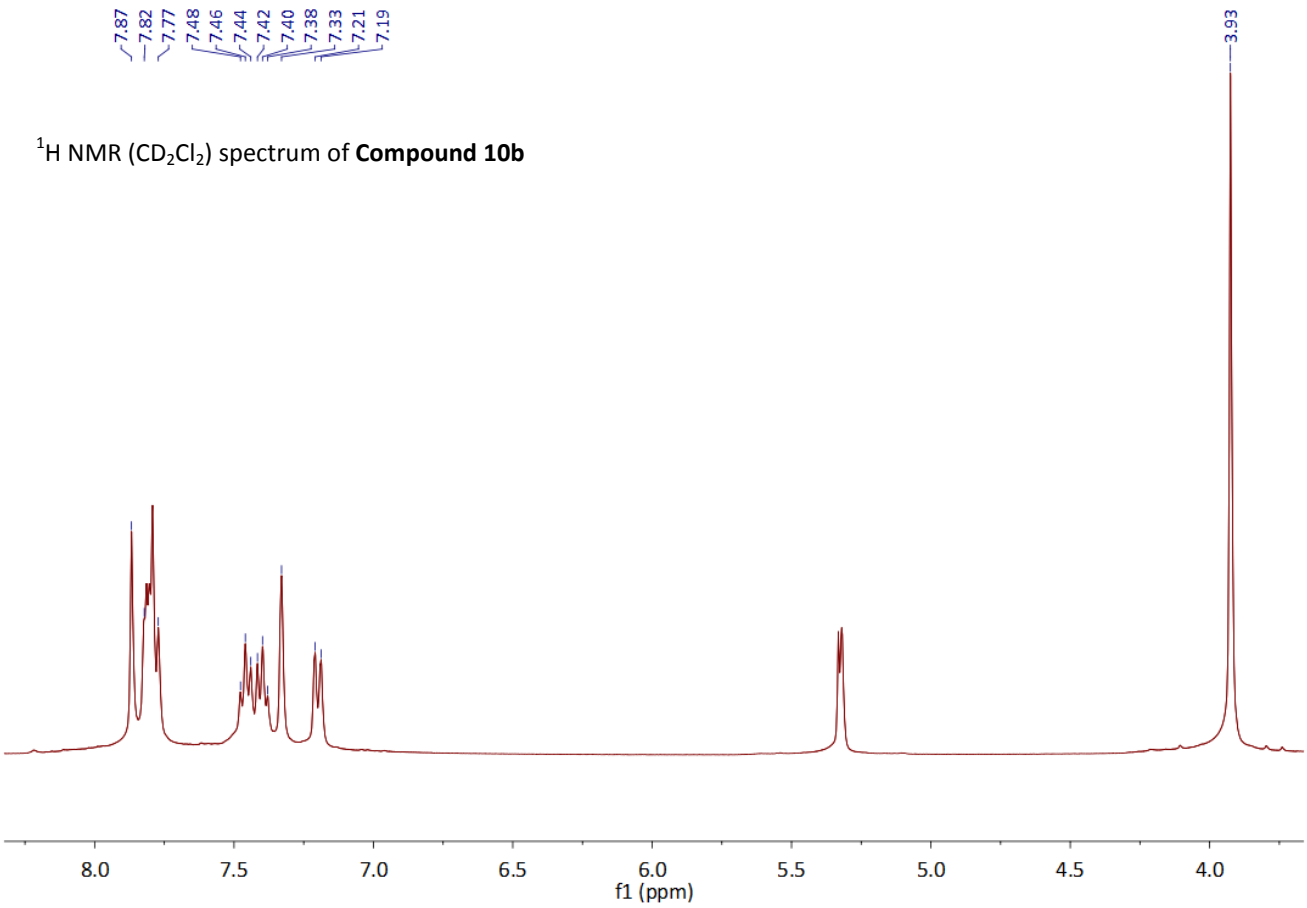


^{1}H NMR (CD_2Cl_2) spectrum of **Compound [9a']BF_4**



^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound [9a']BF_4**

^{1}H NMR (CD_2Cl_2) spectrum of **Compound 10b**



^{13}C{^{1}H} NMR (CD_2Cl_2) spectrum of **Compound 10b**