Cyclometalated iridium complexes for transfer hydrogenation of carbonyl groups in water

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Supporting Information

1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. MeOH was dried over magnesium and distilled prior to use. Dichloromethane (DCM) was dried over CaH_2 and distilled prior to use. Water was distilled water. NMR spectra were recorded on a Bruker 300 or 400 MHz NMR spectrometer with TMS as the internal standard. GC chromatography and GC-MS analysis was carried out on an Agilent 7890A GC with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25 μm) and an Agilent 5975C mass-selective detector (58 psi helium gas, 58 psi hydrogen gas, injector temperature 250 °C, FID detector temperature 300 °C). Imines were prepared according to the literature.[1] The pH values were measured by a Sartorius PB-10 pH meter at 25 ^{o}C.

2. General procedure for preparation of cyclometalated complexes [2, 3, 4]

To $IrCl_3 \cdot 3H_2O$ (0.5 g, 1.35 mmol) in 13 mL methanol was added excess pentamethylcyclopentadiene (0.4 mL), the mixture was refluxed for 36 h. After the mixture was cooled to room temperature, the product $[Cp^*IrCl_2]_2$ was isolated by filtration and washed with cold methanol and dried in *vacuo*.

$[Cp^*IrCl_2]_2$ (1 equiv.), an imine ligand (2.2 equiv.) and NaOAc (10 equiv.) were placed into a Schlenk tube. The tube was then degassed and recharged with argon three times. DCM was then added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered through celite, and dried over Na_2SO_4. Following removal of the solvent under vacuum the resulting solid was washed with diethyl ether/petrol ether to afford cyclometalated iridium complexes.

3. pH effect on transfer hydrogenation of acetophenone with precatalyst 1 and 2 in water

(a) General procedure for transfer hydrogenation of acetopheone at different pH values

Acetophenone (5 mmol), complex **1** or **2** (0.0025 mmol) and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 4 mL HCOOH/HCOONa aqueous solution with the pH value showen in the text (**Scheme 1**). The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 1 h. After cooling to room temperature, the

reaction was quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (7 x 3 mL). The organic layers were washed with brine, and dried over Na_2SO_4. The conversion was determined by an Agilent 7890A GC with a HP-5 MS column (quartz capillary column, 30 m x 0.25 mm x 0.25 μm) and an Agilent 5975C mass-selective detector (58 psi helium gas, 58 psi hydrogen gas, injector temperature 250 °C, FID detector temperature 300 °C). The retention time of acetophenone was 5.80 min, and the 1-phenylethanol was 5.71 min.

(b) Procedure for preparation of HCOOH/HCOONa aqueous solutions of different pH values

The solutions with different pH values used for reactions in **Scheme 1** in the text were prepared by mixing HCOONa, HCOOH (88%, wt) and H_2O in a beaker and the pH values were measured by a pH meter at 25 ^oC.

C^0 = total moles of HCOOH and HCOONa added per liter of H_2O.

For pH 0.5, 2 g HCOONa (29.4 mmol),10.3 mL HCOOH (88%, wt) (240 mmol) and 2.5 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 21 mol/L.

For pH 1.55, 2 g HCOONa (29.4 mmol), 8.3 mL HCOOH (88%, wt) (194 mmol) and 2.8 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 20 mol/L.

For pH 2.0, 2 g HCOONa (29.4 mmol), 5.2 mL HCOOH (88%, wt) (121 mmol) and 2.4 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 20 mol/L.

For pH 3.0, 2 g HCOONa (29.4 mmol), 2.2 mL HCOOH (88%, wt) (51 mmol) and 2.8 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 16 mol/L.

For pH 4.0, 2 g HCOONa (29.4 mmol), 1.1 mL HCOOH (88%, wt) (194 mmol) and 2.8 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 14 mol/L.

For pH 4.5, 2 g HCOONa (29.4 mmol), 0.6 mL HCOOH (88%, wt) (14 mmol) and 2.8 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 13 mol/L.

For pH 5.0, 3 g HCOONa (44.1 mmol), 0.4 mL HCOOH (88%, wt) (9 mmol) and 4.2 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 11 mol/L.

For pH 5.2, 5 g HCOONa (73.5 mmol), 0.3 mL HCOOH (88%, wt) (7 mmol) and 7 mL H_2O were used. The total concentration of HCOONa and HCOOH, C^0 = 11 mol/L.

When C^0 values varied from 11 mol/L to 20 mol/L, the effect of C^0 on conversions at the same pH was less than 20% under the conditions above.

4. General procedure for the reduction of ketones with the precatalyst 3

Ketone (5 mmol), complex **3** (0.0025 mmol) and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 4 mL HCOOH/HCOONa aqueous solution (pH = 2.5, C^0 = 20 mol/L). The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 4 or 12 h. After cooling to room temperature, the reaction was quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (7 x 3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The product was purified by flash chromatography using petroleum ether and ethyl acetate as elute. 2 mL and 1 mL aqueous solution of HCOOH/HCOONa was used for S/C = 1000 and 500, respectively. For products with low boiling points, **7q** and **7r**, the yields were determined by GC. The retention times for ketone **6q** and alcohol **7q** were 5.22 min and 5.90 min respectively. The retention times for ketone **6r** and alcohol **7r** were 6.17 min and 6.65 min respectively.

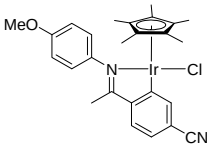
5. General procedure for the reduction of aromatic aldehydes with the precatalyst 3

Aldehyde (2.5 mmol), complex **3** (0.0025 mmol) and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 2 mL HCOOH/HCOONa aqueous solution (pH = 2.5, C^0 = 20 mol/L). The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 12 h. After cooling to room temperature, the reaction was quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (7 x 3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The product was purified by flash chromatography using petroleum ether and ethyl acetate as elute. The volume of HCOOH/HCOONa aqueous solution was 4 mL for S/C = 2000.

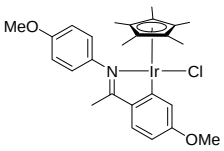
6. Procedure for large scale transfer hydrogenation in water

Acetophenone (50 mmol), complex **3** (0.025 mmol) and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 40 mL HCOOH/HCOONa aqueous solution (pH 2.5, C^0 = 20 mol/L). The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 24 h. After cooling to room temperature, the reaction was quenched with aqueous $NaHCO_3$ solution, and extracted with ethyl acetate (50 x 3 mL). The organic layers were washed with brine, dried over Na_2SO_4, and evaporated. 5.82 g of product was obtained by flash chromatography using petroleum ether and ethyl acetate as elute (97% yield).

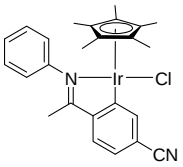
7. Analytic data of catalysts and products



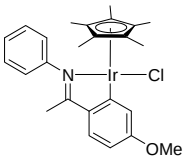
Iridium complex 1[4]**:** Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.97 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 12.9 Hz, 3H), 6.91 (s, 2H), 3.79 (s, 3H), 2.38 (s, 3H), 1.37 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 180. 9, 167.6, 158.2, 151.9, 143.7, 138.3, 128.0, 124.4, 123.8, 119.5, 114.4, 89.9, 55.6, 17.1, 8.5; HRMS (ESI) for $C_{26}H_{28}ClIrN_2O$ $[M\text{-}Cl]^+$: calc.: 577.1831. Found: 577.1818.



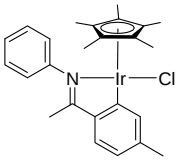
Iridium complex 2[4]**:** Red solid; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.45 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.58 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 2.38 (s, 3H), 1.44 (s, 15H); ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 180.1 , 170.4, 162.1, 157.6, 144.3, 141.3, 130.0, 124.5, 119.2, 112.8, 107.8, 89.0, 55.5, 55.0, 16.8, 8.6; HRMS (ESI) for $C_{26}H_{31}ClIrNO_2$ $[M\text{-}Cl]^+$: calc.: 582.1984. Found: 582.1979.



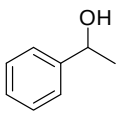
Iridium complex 3: Red solid; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.92 (s, 2H), 7.44-7.36 (m, 3H), 7.19 (dd, *J* = 17.6, 7.7 Hz, 2H), 6.90 (s, 1H), 2.41 (s, 3H), 1.41 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 180.8, 170.5, 150.5, 146.5, 137.4, 129.8, 127.4, 126.5, 124.5, 123.0, 89.4, 17.0, 8.4; HRMS (ESI) for $C_{25}H_{26}ClIrN_2$ $[M\text{-}Cl]^+$: calc.: 547.1725. Found: 547.1711.



Iridium complex 4: Orange solid; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.49-7.35 (m, 4H), 7.23-7.20 (m, 3H), 6.59 (d, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H), 1.42 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 179.8, 170.8, 162.2, 150.9, 141.0, 130.1, 126.0, 119.3, 107.9, 89.0, 55.0, 16.8, 8.5; HRMS (ESI) for $C_{25}H_{29}ClIrNO$ $[M\text{-}Cl]^+$: calc.: 552.1878. Found: 552.1873.

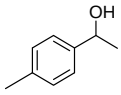


Iridium complex 5: Orange solid; ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.64 (s, 1H), 7.41 (d, *J* = 7.4 Hz, 3H), 7.25-7.21 (m, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H), 1.41 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 180.8, 168.4, 150.8, 145.0, 142.1, 135.8, 128.4, 126.1, 122.6, 89.0, 22.0, 16.8, 8.4; HRMS (ESI) for $C_{25}H_{29}ClIrN$ $[M\text{-}Cl]^+$: calc.: 536.1929. Found: 536.1925.



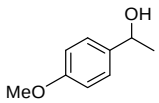
7a

1-Phenylethanol 7a[5]**:** 585mg; 96% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.33-7.31 (m, 5H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.36 (s, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 145.9, 128.5, 127.4, 125.4, 70.3, 25.1; MS(EI) for $C_8H_{10}O$ $[M+H]^+$: 123.



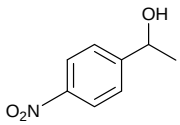
7b

1-(4-Tolyl)ethanol 7b[5]**:** 591mg; 87% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, CDCl3) δ (ppm): 7.19 (d, *J* = 6.0, 2H), 7.10 (d, *J* = 6.0, 2H), 4.4 (q, *J* = 6.4 Hz, 1H), 2.59 (d, *J* = 10.2 Hz, 1H), 2.30 (s, 3H), 1.40 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 143.0, 137.0, 129.1, 125.4, 70.1, 25.1, 21.1; MS (EI) for $C_9H_{12}O$ $[M+H]^+$: 137.



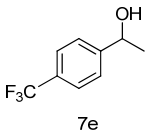
7c

1-(4-Methoxyphenyl)ethanol 7c[6]**:** 60mg; 79% yield (S/C=200); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.27 (d, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 4.80 (q, J = 6.4, 1H), 3.77 (s, 3H), 2.30 (brs, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.0, 138.1, 126.7, 113.9, 69.9, 55.3, 25.0; MS(EI) for $C_9H_{12}O_2$ $[M+H]^+$: 153.



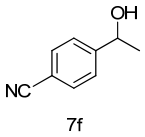
7d

1-(4-Nitrophenyl)ethanol 7d[7]**:** 812mg; 97% yield (S/C=2000); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 4.99 (d, *J* = 6.4 Hz 1H), 3.06 (brs, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 153.4, 147.0, 126.1, 123.6, 69.3, 25.3; HRMS(ESI) for $C_8H_9NO_3$ $[M+Na]^+$, m/z calc.: 190.0480, found: 190.0483.



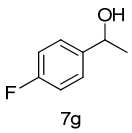
7e

1-(4-(Trifluoromethyl)phenyl)ethanol 7e[6]: 904mg; 95% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 4.87 (d, *J* = 6.4 Hz, 1H), 2.85 (d, *J* = 4.9 Hz, 1H), 1.44 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 149.7, 129.6 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 125.8, 125.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz) 124.3 (q, $^{1}J_{C\text{-}F}$ = 270.0 Hz), 69.7, 25.2; HRMS(ESI) for $C_9H_9F_3O$ $[M\text{-}H]^-$, m/z calc.: 189.0527, found: 189.0539.



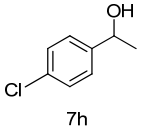
7f

4-(1-Hydroxyethyl)benzonitrile 7f[8]: 333mg; 91% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.62 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 4.95 (d, J = 6.4 Hz, 1H), 2.27 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 151.4, 132.3, 126.1, 118.9, 110.7, 69.4, 25.3; MS(EI) for C_9H_9NO $[M+H]^+$: 148.



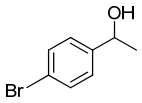
7g

1-(4-Fluorophenyl)ethanol 7g[6]: 623mg; 89% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.29 (d, *J* = 19.5 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 4.87 (d, *J* = 6.0 Hz, 1H), 1.98 (s, 1H), 1.46 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 162.5 (d, $^{1}J_{C\text{-}F}$ = 243.8 Hz), 141.6, 127.1 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 69.6, 25.2; MS(EI) for C_8H_9FO $[M+H]^+$: 141.



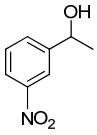
7h

1-(4-Chlorophenyl)ethanol 7h[9]**:** 354mg; 89% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.29 (d, *J* = 5.7 Hz, 4H), 4.86 (q, *J* = 6.0 Hz, 1H), 1.90 (s, 1H), 1.45 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.3, 133.0, 128.5, 126.8, 69.6, 25.2; MS(EI) for C_8H_9ClO $[M+H]^+$: 157.



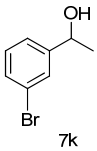
7i

1-(4-Bromophenyl)ethanol 7i[5]**:** 470mg; 94% yield (S/C=1000); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.86 (q, *J* = 6.0 Hz, 1H), 1.88 (s, 1H), 1.46 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.8, 131.5, 127.18, 121.1, 69.6, 25.2; MS(EI) for C_8H_9BrO $[M+H]^+$: 201.



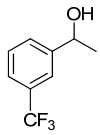
7j

1-(3-Nitrophenyl)ethanol 7j[7]**:** 803mg; 96% yield (S/C=2000); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.21 (s, 1H), 8.07 (d, *J* = 6.8 Hz, 1H), 7.69 (s, 1H), 7.49 (t, *J* = 6.0 Hz, 1H), 4.99 (d, *J* = 6.0 Hz, 1H), 2.90 (brs, 1H), 1.51 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.1, 131.7, 129.4, 122.2, 120.3, 69.2, 25.3; HRMS(ESI) for $C_8H_9NO_3$ $[M+Na]^+$, calc.: 190.0480, found: 190.0485.



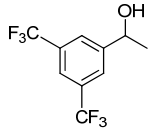
7k

1-(3-Bromophenyl)ethanol 7k[5]**:** 937mg; 93% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.48 (s, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 12.9, 7.4 Hz, 2H), 4.76 (q, *J* = 6.4 Hz, 1H), 2.77 (s, 1H), 1.41 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 148.2, 130.4, 130.1, 128.6, 124.1, 122.6, 69.6, 25.2; MS(EI) for C_8H_9BrO $[M+H]^+$: 201.



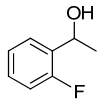
7l

1-(3-(Trifluoromethyl)phenyl)ethanol 7l[9]: 860mg; 91% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.43 (m, 4H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.49 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.8, 130.5 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 128.8, 125.9 (q, $^{1}J_{C\text{-}F}$ = 246.8 Hz), 124.0, 122.2, 69.7, 25.2; MS(EI) for $C_9H_9F_3O$ $[M+H]^+$: 191.



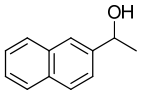
7m

1-(3,5-Bis(trifluoromethyl)phenyl)ethanol 7m[8]: 580mg; 90% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83 (s, *2*H), 7.79 (s, 1H), 5.02 (q, *J* = 6.4 Hz, 1H), 2.30 (s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 148.2, 131.8 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 125.6, 123.2 (q, $^{1}J_{C\text{-}F}$ = 270.0 Hz) , 121.3, 69.2, 25.2; HRMS(ESI) for $C_{10}H_8F_6O$ $[M-H]^-$, m/z calc.: 257.0401, found: 257.0414.



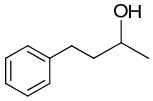
7n

1-(2-fluorophenyl)ethanol 7n[8]: 319mg; 91% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 1H), 7.21 (m, 1H), 7.13 (m, 1H), 7.00 (m, 1H), 5.17 (d, *J* = 6.1 Hz, 1H), 2.32 (s, 1H), 1.48 (d, *J* =6.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 159.7 (d, $^{1}J_{C\text{-}F}$ = 245.2 Hz), 132.7 (d, $^{3}J_{C\text{-}F}$ = 13.3 Hz), 128.7 (d, $^{4}J_{C\text{-}F}$ = 8.2 Hz), 126.6 (d, $^{5}J_{C\text{-}F}$ = 4.6 Hz), 124.3 (d, $^{6}J_{C\text{-}F}$ = 3.4 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 64.4, 24.0; MS(EI) for C_8H_9FO $[M+H]^+$: 141.#



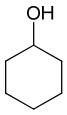
7o

1-(Naphthalen-2-yl)ethanol 7o[5]: 766mg; 89% yield (S/C=2000); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.77– 7.71 (m, 4H), 7.44 – 7.41 (m, 3H), 4.94 (dd, *J* = 12.9, 6.4 Hz, 1H), 2.41 (s, 1H), 1.56 (d, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.29, 133.40, 132.97, 128.30, 127.99, 127.72, 126.15, 125.80, 123.90, 123.85, 70.45, 25.12; MS(EI) for $C_{12}H_{12}O$ $[M+H]^+$: 173.



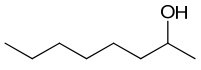
7p

4-Phenylbutan-2-ol 7p[8]: 364mg; 97% yield, (S/C=1000); pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (m, 2H), 7.22 (m, 3H), 3.83 (dt, *J* = 12.3, 6.2 Hz, 1H), 2.73 (m, 2H), 1.80 (m, 3H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ (ppm): 142.1, 128.4, 125.8, 67.5, 40.9, 32.2, 23.6; MS(EI) for $C_{10}H_{14}O$ $[M+H]^+$: 151.



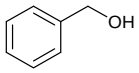
7q

Cyclohexanol 7q[7]: 100% conversion (S/C=2000), GC retention time: 5.90 min; colorless liquid; ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 3.61-3.56 (m, 1H), 2.10-2.09 (m, 1H), 1.86-1.85 (m, 2H), 1.71-1.69 (m, 2H), 1.52-1.51 (m, 1H), 1.25-1.12 (m, 5H); ^{13}C NMR (101 MHz, CDCl3) δ (ppm) 70.3, 35.5, 25.4, 25.1; MS(EI) for $C_6H_{12}O$ $[M+H]^+$: 101.



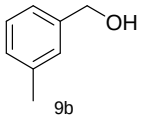
7r

octan-2-ol 7r[10]: 100% conversion (S/C=2000), GC retention time: 6.65 min; colorless liquid; ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 3.77-3.75 (m, 1H), 1.54 (s, 1H), 1.41-1.15 (m, 12H), 0.87-0.84 (m, 3H); ^{13}C NMR (101 MHz, CDCl3) δ (ppm) 68.1, 39.4, 31.8, 29.3, 25.7, 23.4, 22.6, 14.1; MS(EI) for $C_8H_{18}O$ $[M+H]^+$: 131.



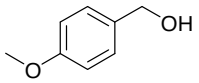
9a

Phenyl methanol 9a[11]**:** 515mg; 95% yield (S/C=2000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.30-7.21 (m, 5H), 4.57 (s, 2H), 2.70 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 141.0, 128.5, 127.5, 127.0, 64.9; MS(EI) for C_7H_8O $[M+H]^+$: 109.



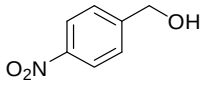
9b

m-Tolylmethanol 9b[11]**:** 240mg; 79% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.23-7.08 (m, 4H), 4.60 (s, 2H), 2.34 (s, 3H), 2.10 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 141.0, 138.2, 128.4, 128.3, 127.8, 124.1, 65.2, 65.1, 21.4; MS(EI) for $C_8H_{10}O$ $[M+H]^+$: 123.



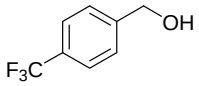
9c

(4-Methoxyphenyl)methanol 9c[11]**:** 250mg; 73% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.27 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.58 (s, 2H), 3.79 (s, 3H), 1.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.2, 133.3, 128.6, 114.0, 64.8, 55.3; MS(EI) for $C_8H_{10}O_2$ $[M+H]^+$: 139.



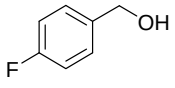
9d

(4-Nitrophenyl)methanol 9d[11]**:** 285mg; 75% yield (S/C=1000); yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 4.84 (d, *J* = 5.4 Hz, 2H), 1.98 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):148.3, 147.3, 127.0, 123.7, 64.0; MS(EI) for $C_7H_7NO_3$ $[M+H]^+$:154.



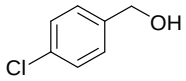
9e

(4-(Trifluoromethyl)phenyl)methanol 9e[11]**:** 408mg; 93% yield (S/C=1000); pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.61 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 4.76 (s, 2H), 1.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 144.7, 129.6 (q, $^{2}J_{C-F}$ = 32.0 Hz), 126.8, 125.4, 124.2 (q, $^{1}J_{C-F}$ = 270.0 Hz), 64.3; HRMS(ESI) for $C_8H_7F_3O$ $[M-H]^-$, m/z calc.: 175.0371, found: 175.0375.



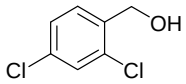
9f

(4-Fluorophenyl)methanol 9f[11]**:** 590mg; 94% yield (S/C=2000); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.31-7.27 (m, 2H), 7.05-6.99 (m, 2H), 4.60 (s, 2H), 2.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 162.3 (d, $^{1}J_{C-F}$ = 243.8 Hz), 128.7 (d, $^{3}J_{C-F}$ = 8.3 Hz), 115.3 (d, $^{2}J_{C-F}$ = 21.8 Hz), 64.5; MS(EI) for C_7H_7FO $[M+H]^+$:127.



9g

(4-Chlorophenyl)methanol 9g[11]**:** 285mg; 80% yield (S/C=1000); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.33-7.26 (m, 4H), 4.64 (s, 2H), 1.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 139.3, 133.3, 128.7, 128.3, 64.4; MS(EI) for C_7H_7ClO $[M+H]^+$: 143.



9h

(2,4-Dichlorophenyl)methanol 9h[12]: 273mg; 62% yield (S/C=1000); pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.35 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 4.72 (s, 2H), 2.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.73, 133.78, 133.11, 129.29, 129.07, 127.21, 61.91; MS(EI) for $C_7H_6Cl_2O$ $[M+H]^+$:177.

8. References

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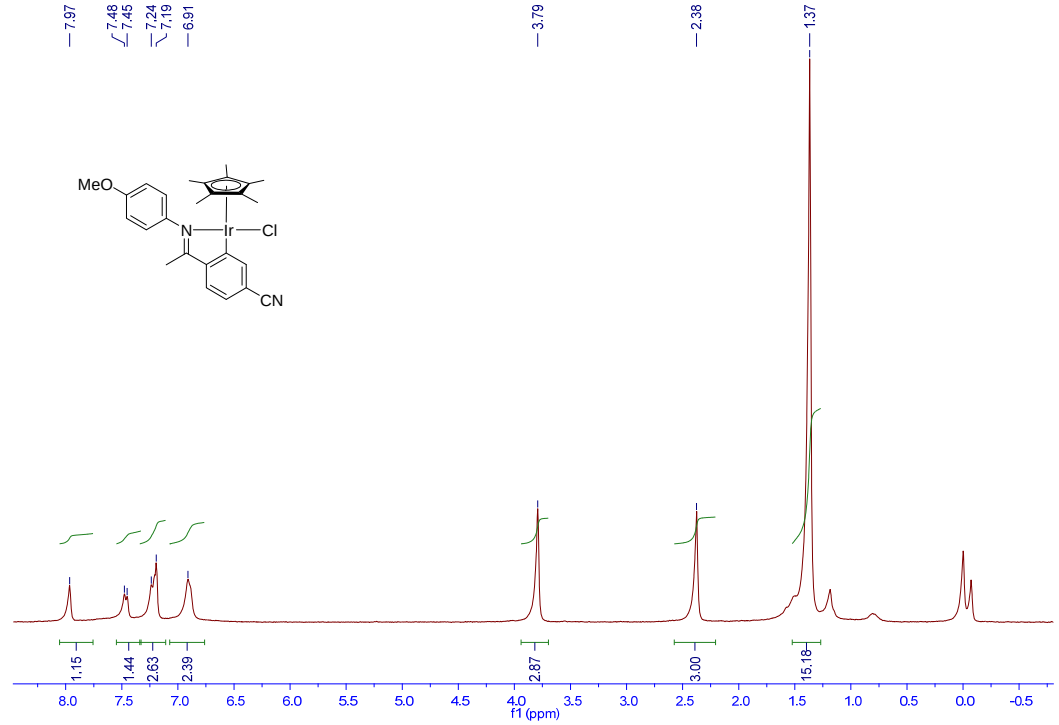
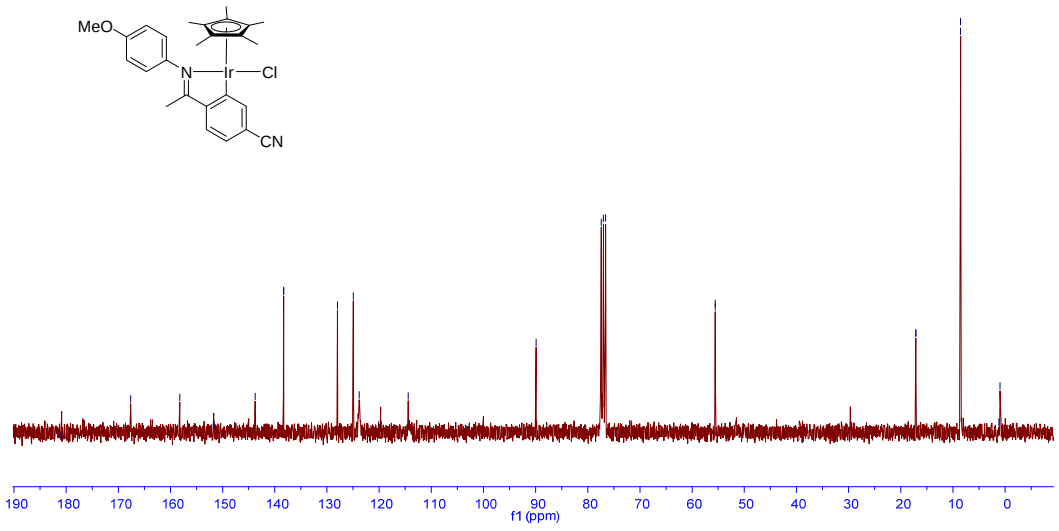
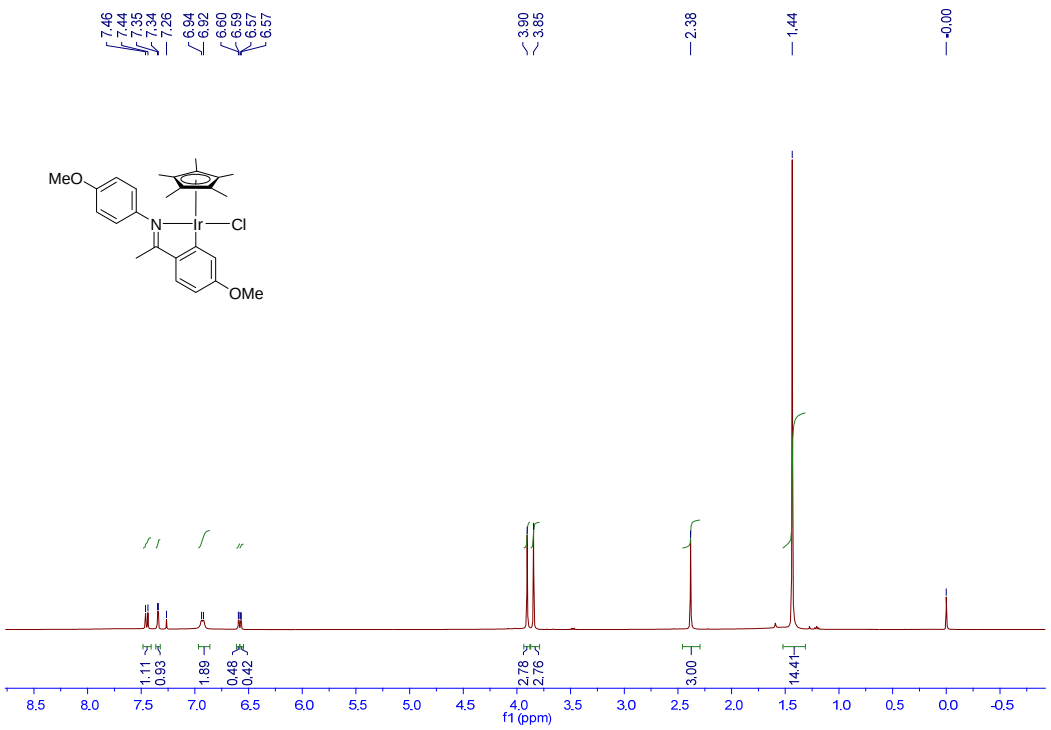
9. Traces of ^{1}H NMR and ^{13}C NMR spectra



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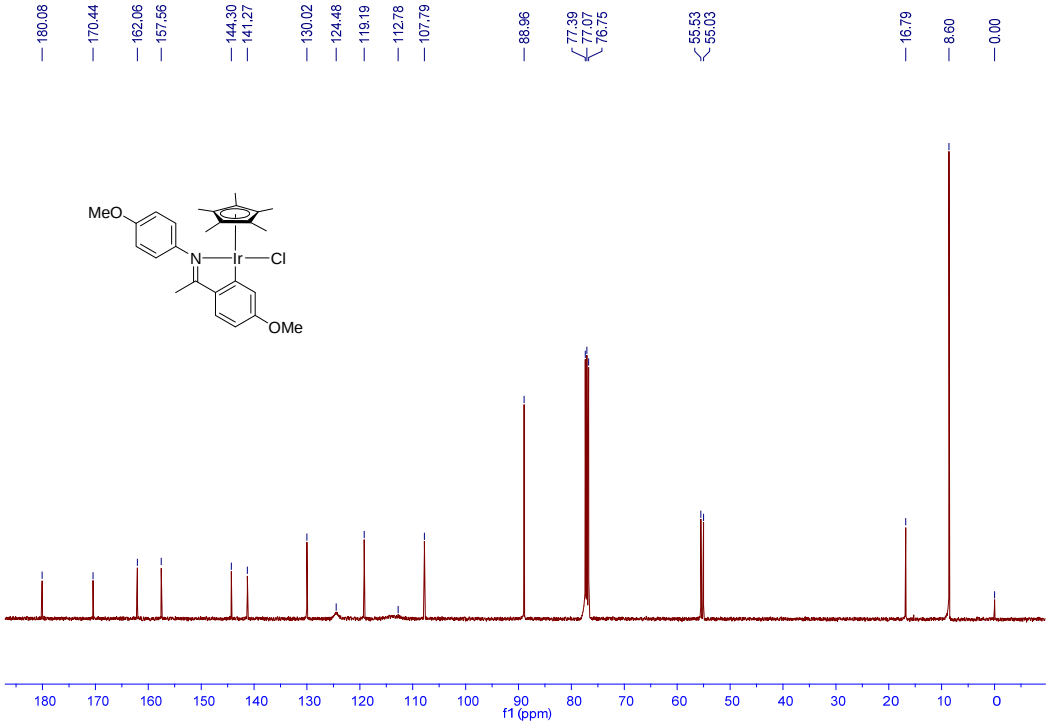
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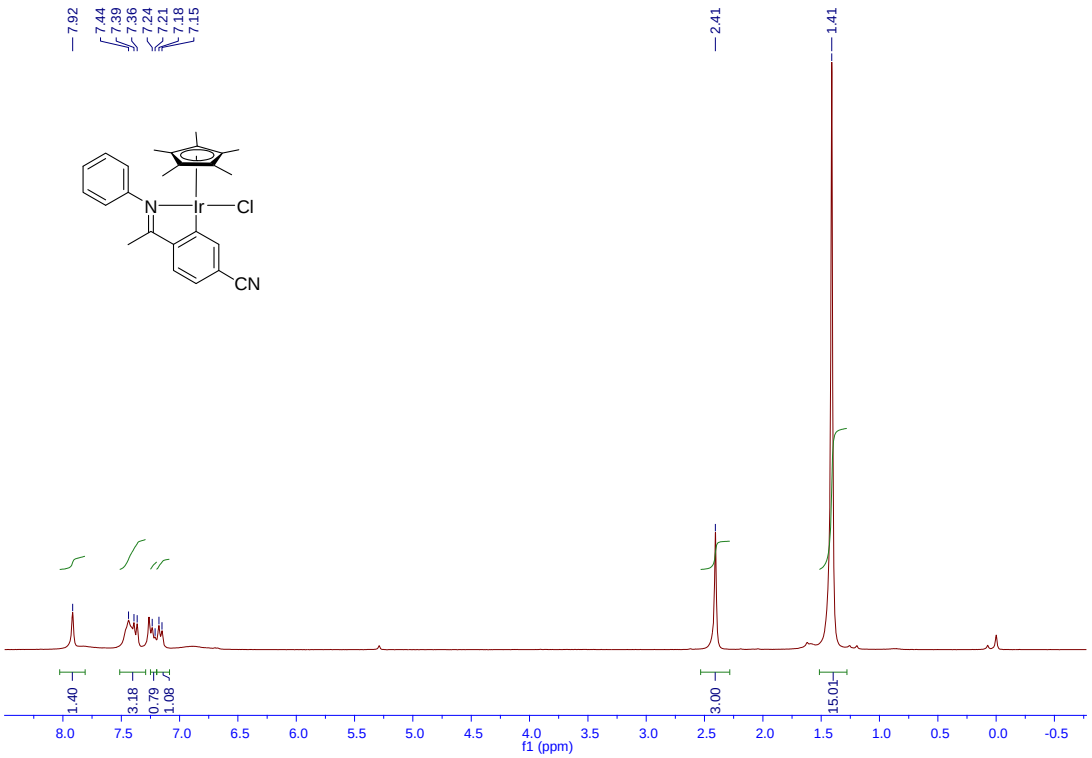
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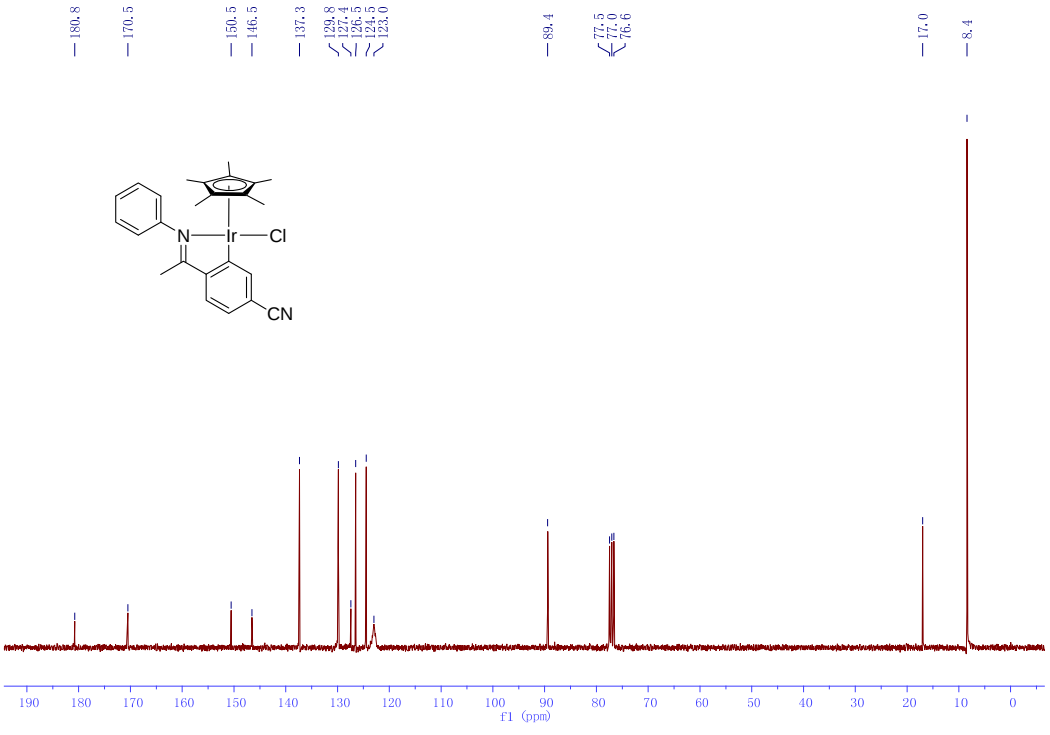
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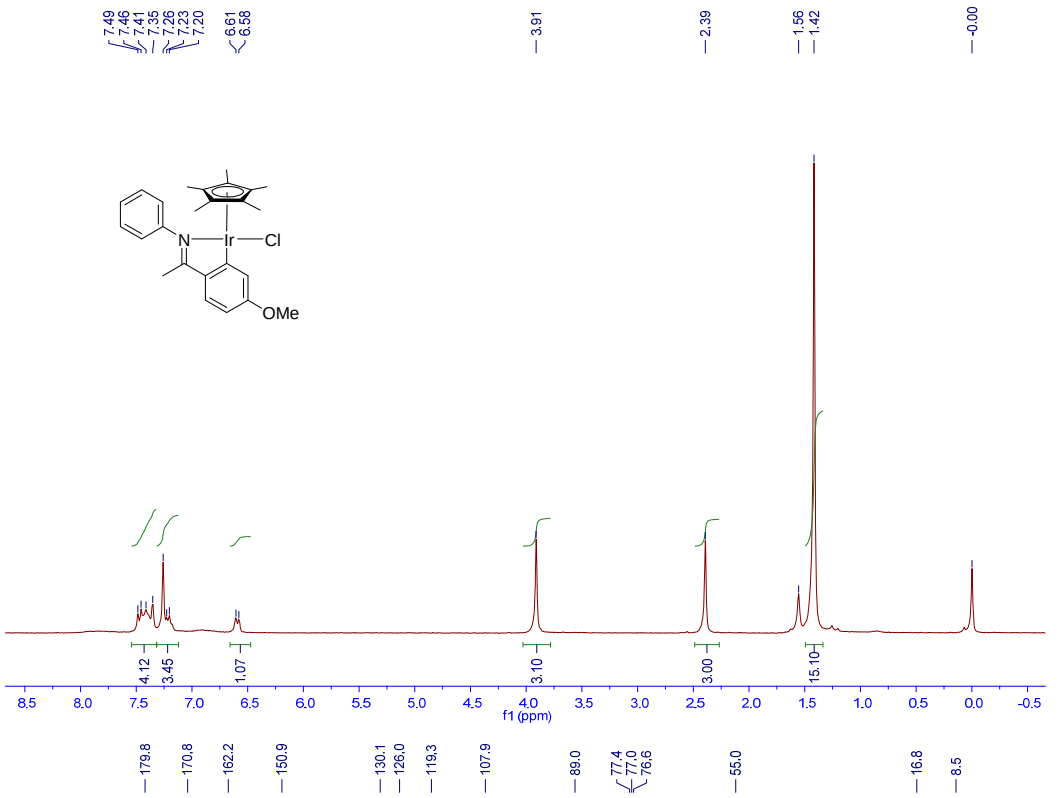
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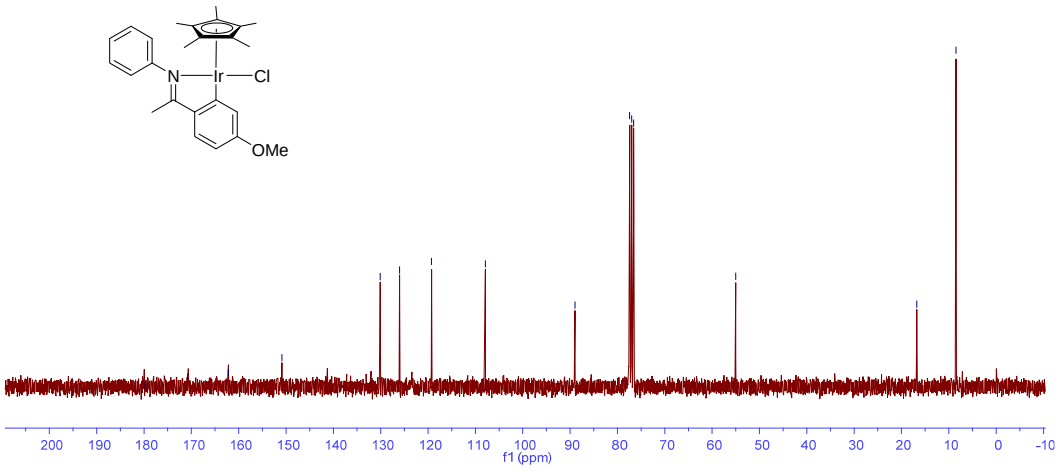
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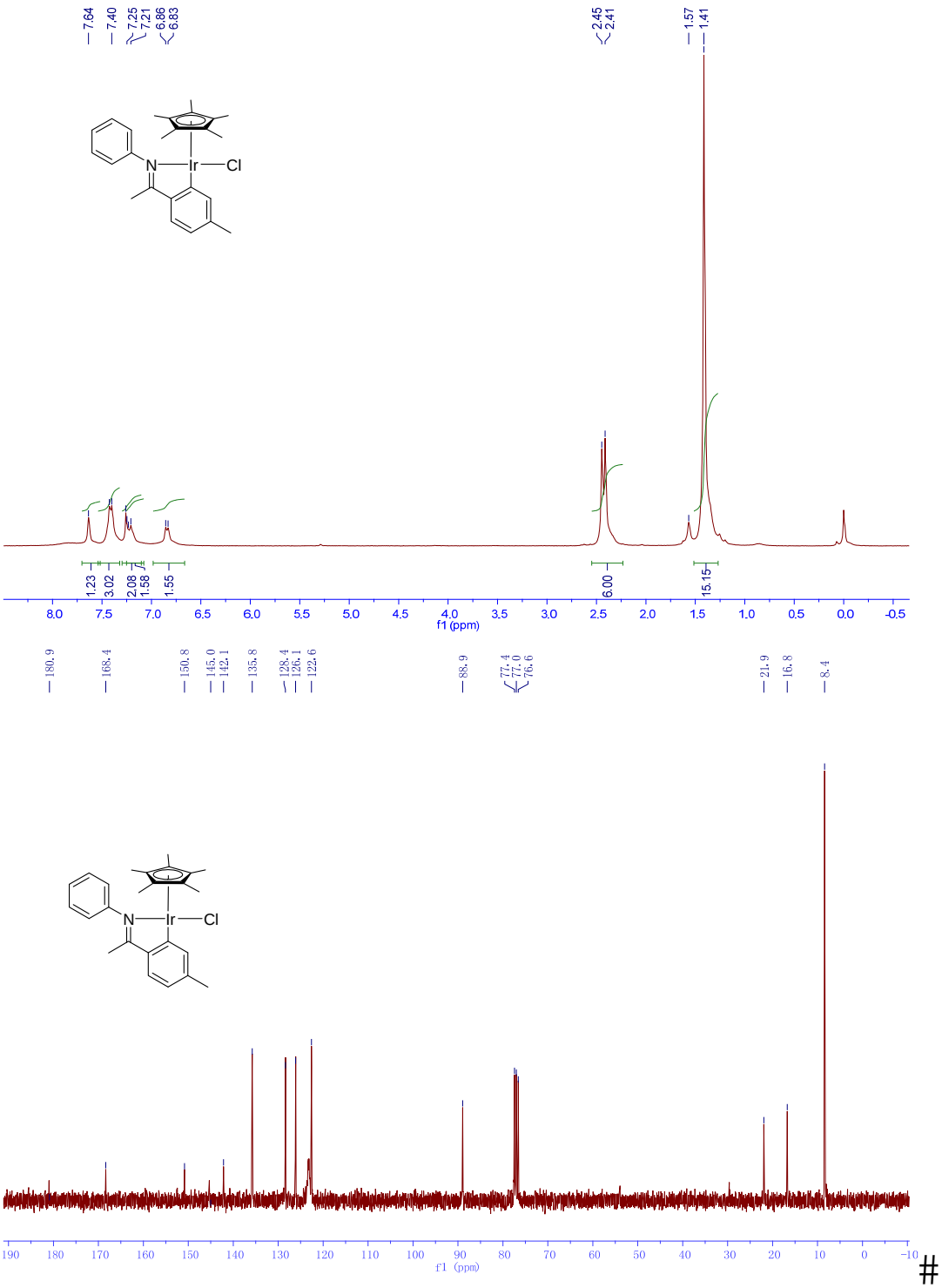
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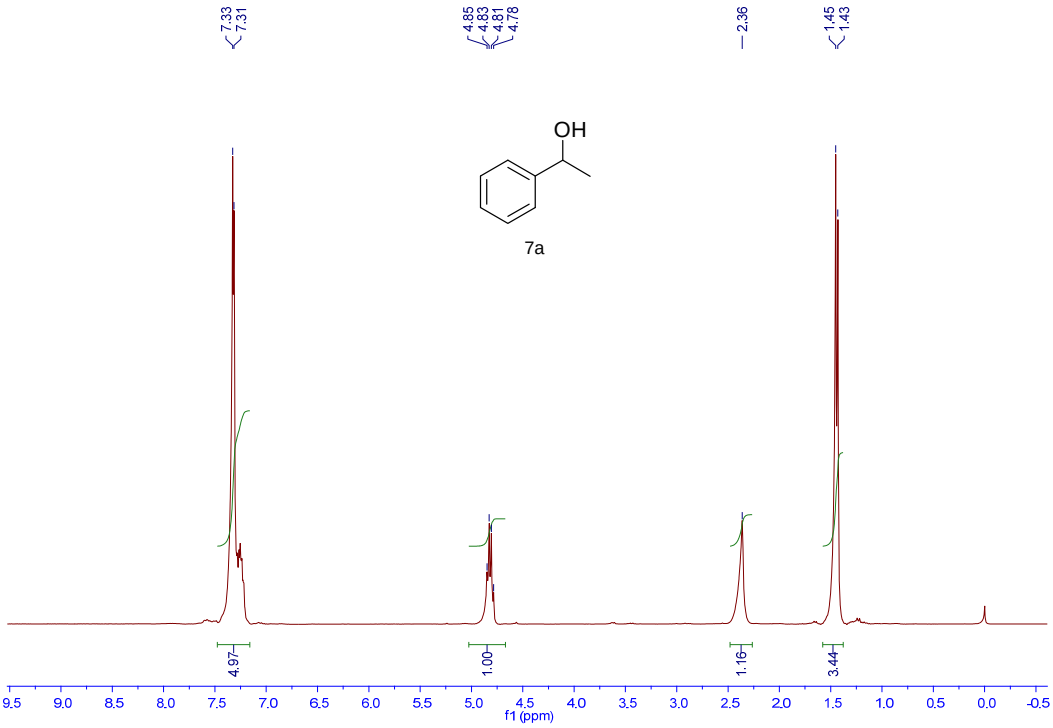
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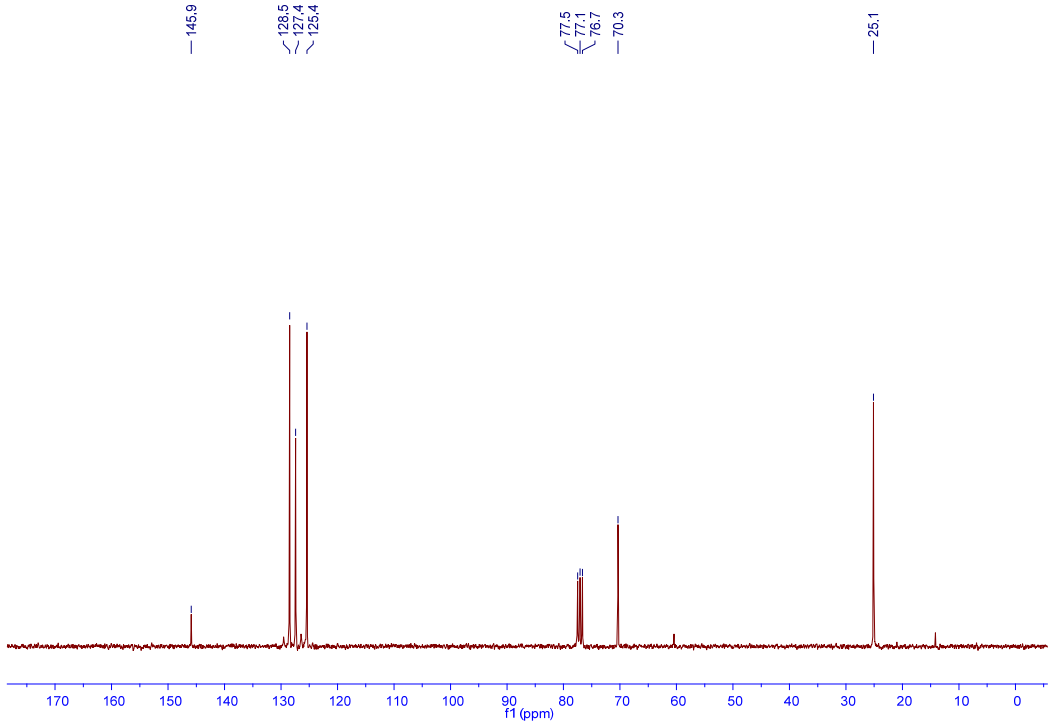
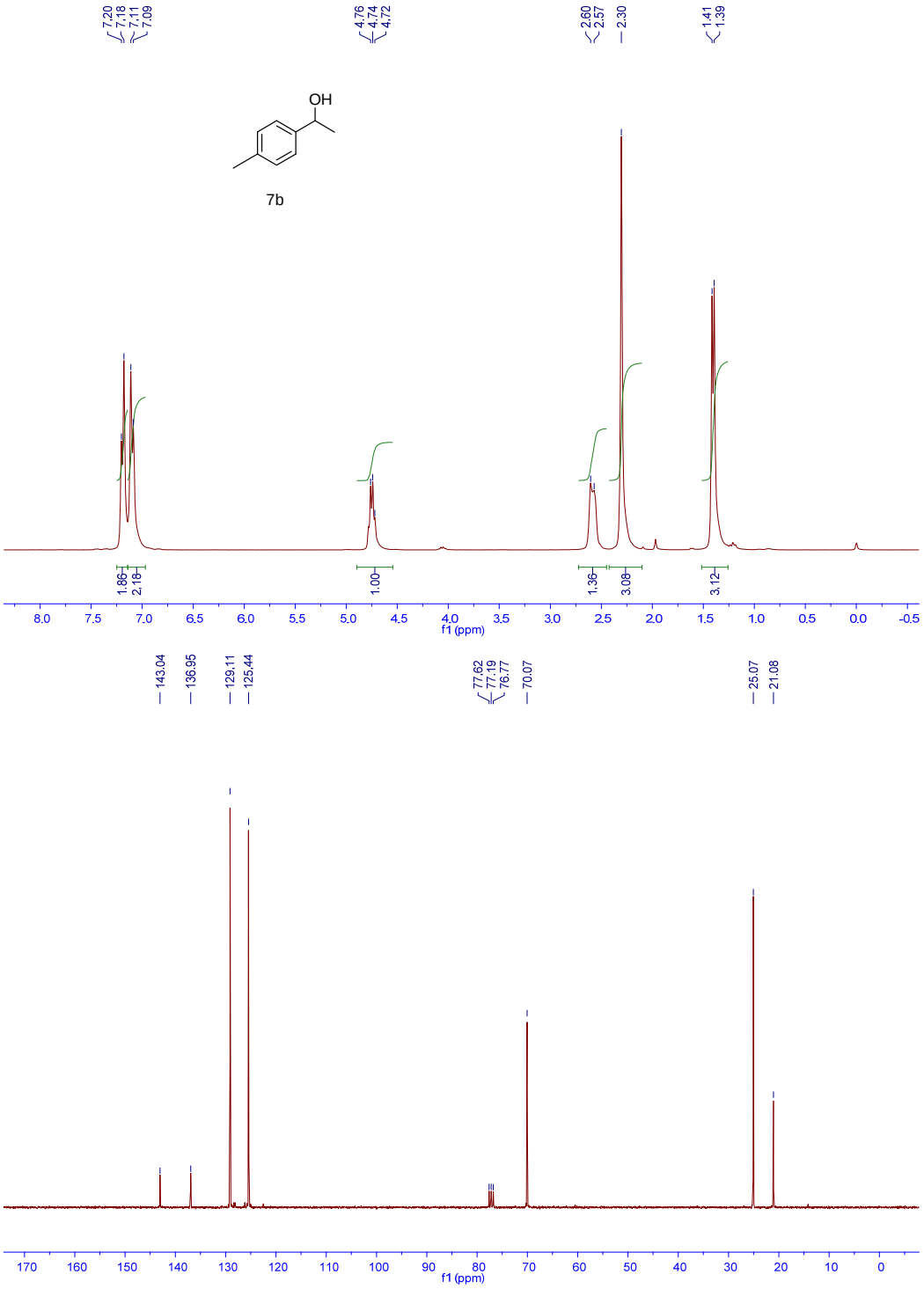
1.16
3.44
f1 (ppm)


145.9
128.5
127.4
125.4
77.5
77.1
76.7
70.3
25.1
f1 (ppm)


7.20
7.18
7.11
7.09
4.76
4.74
4.72
2.60
2.57
2.30
1.41
1.39
OH
7b
1.86
2.18
1.00
1.36
3.08
3.12
f1 (ppm)
143.04
136.95
129.11
125.44
77.62
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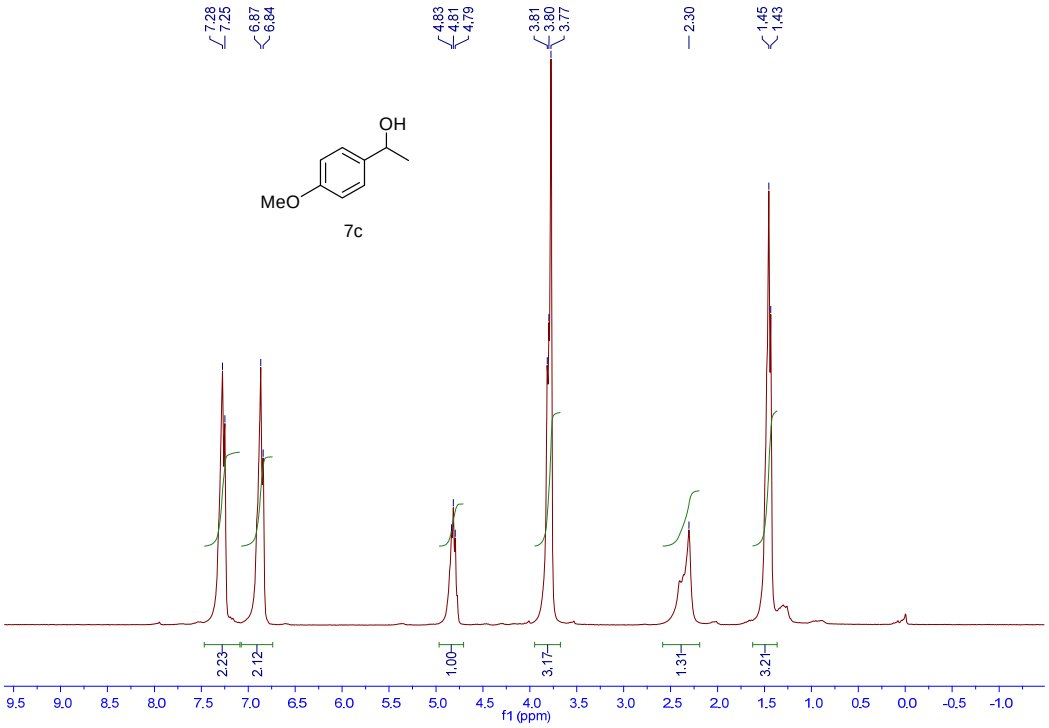
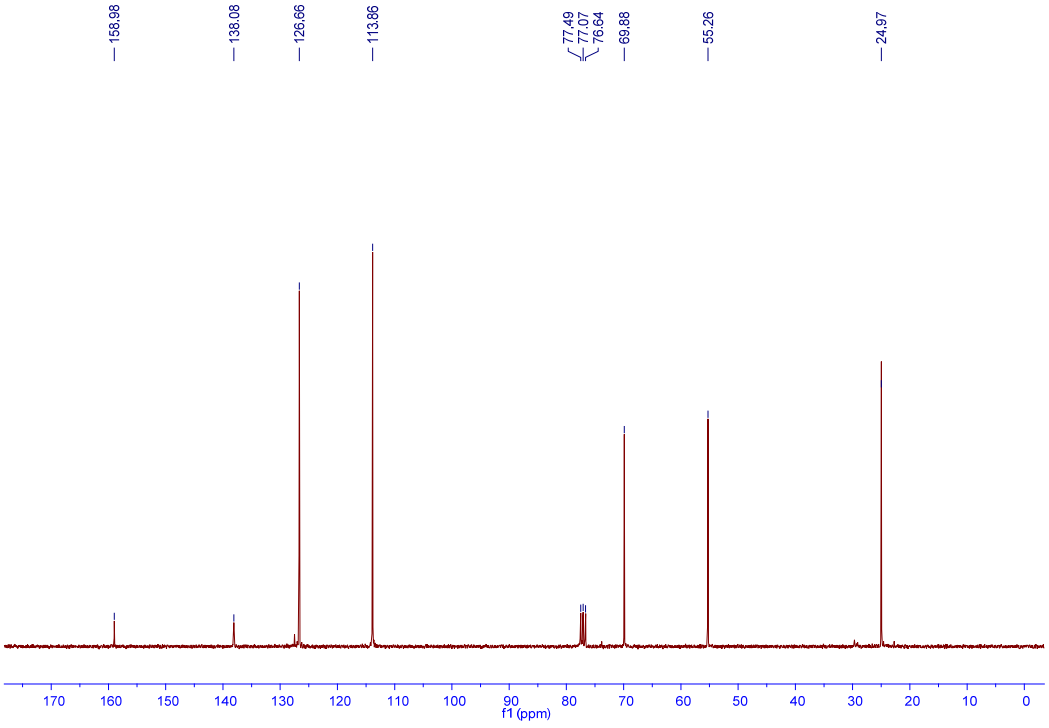
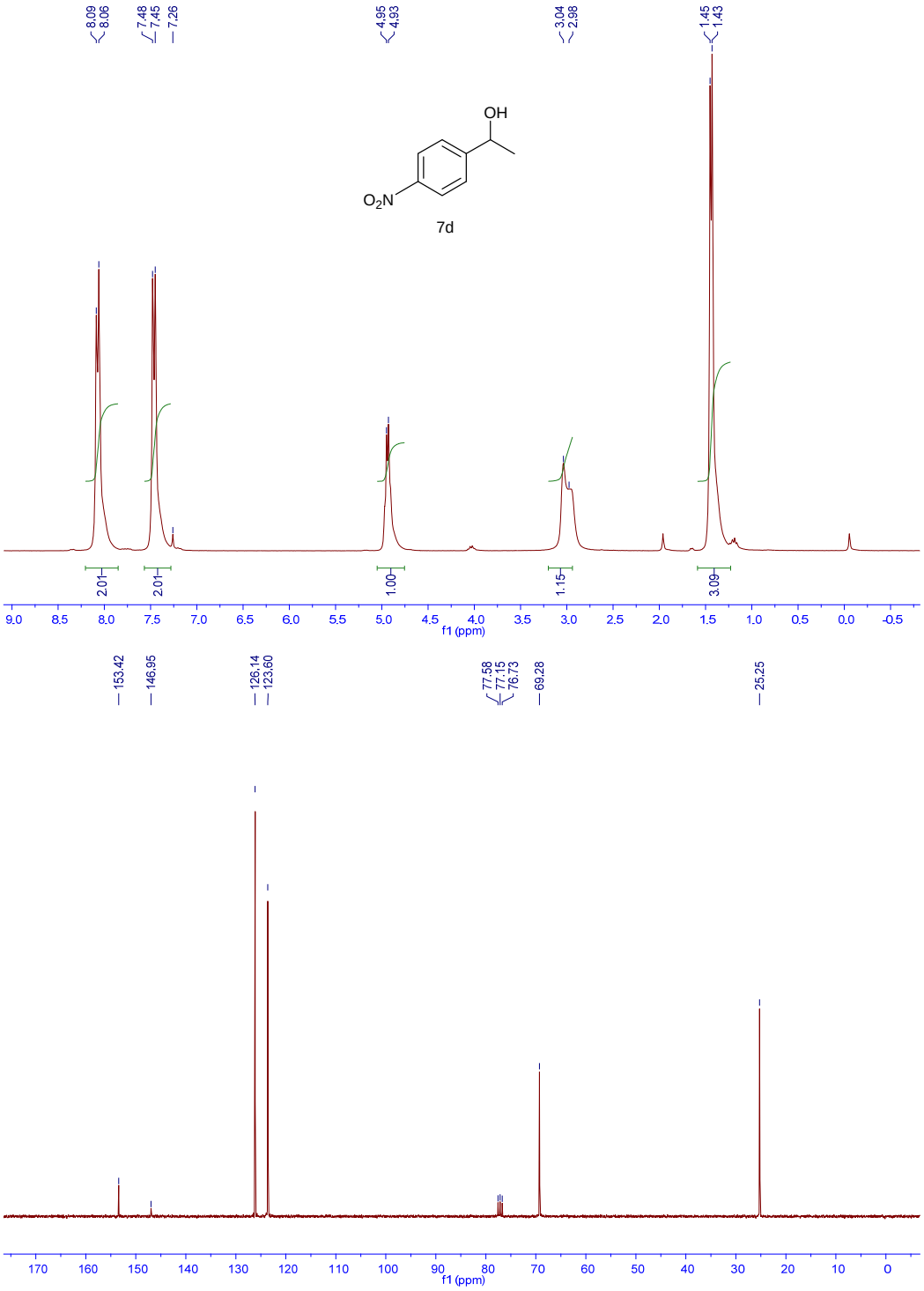
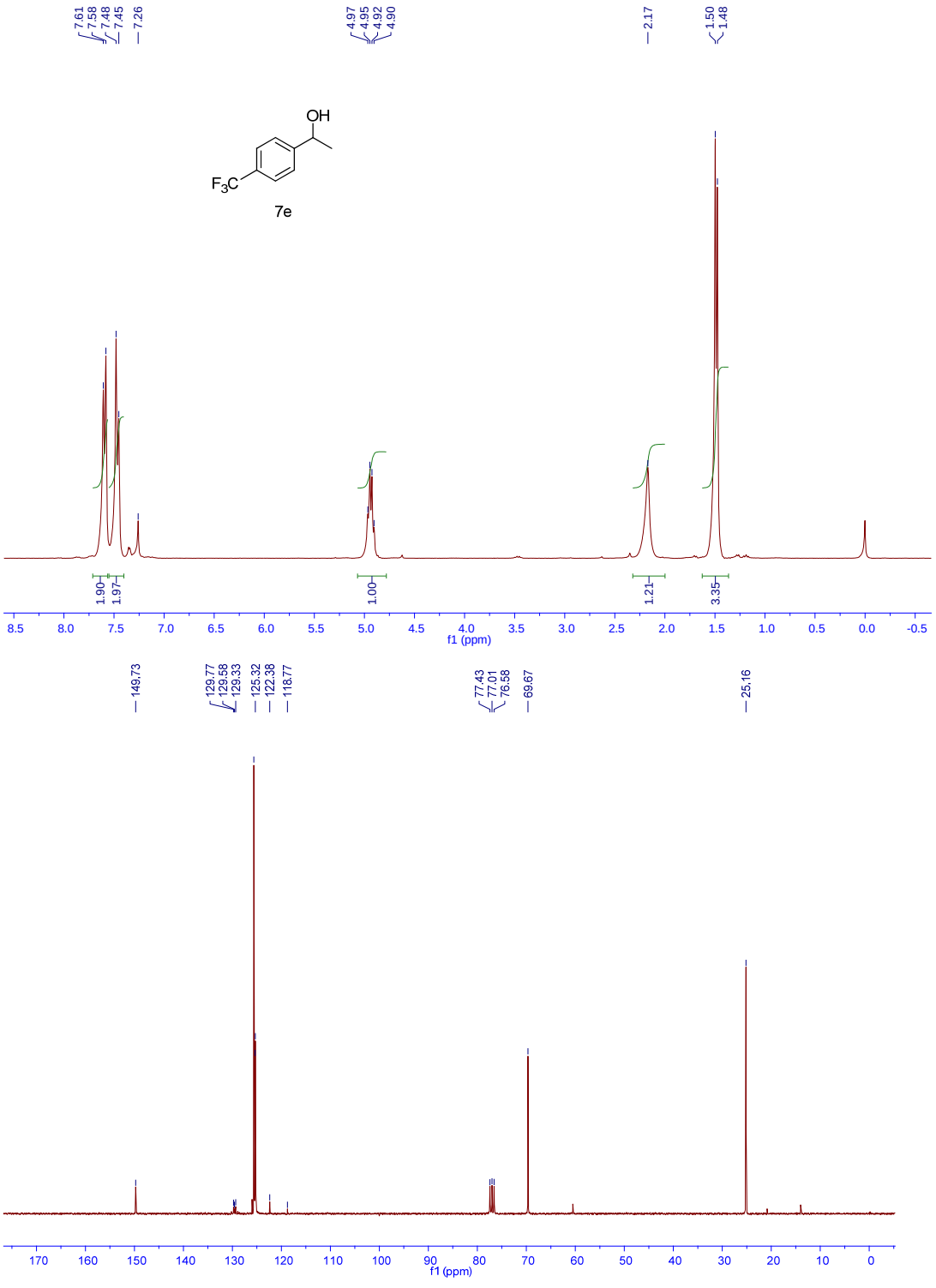
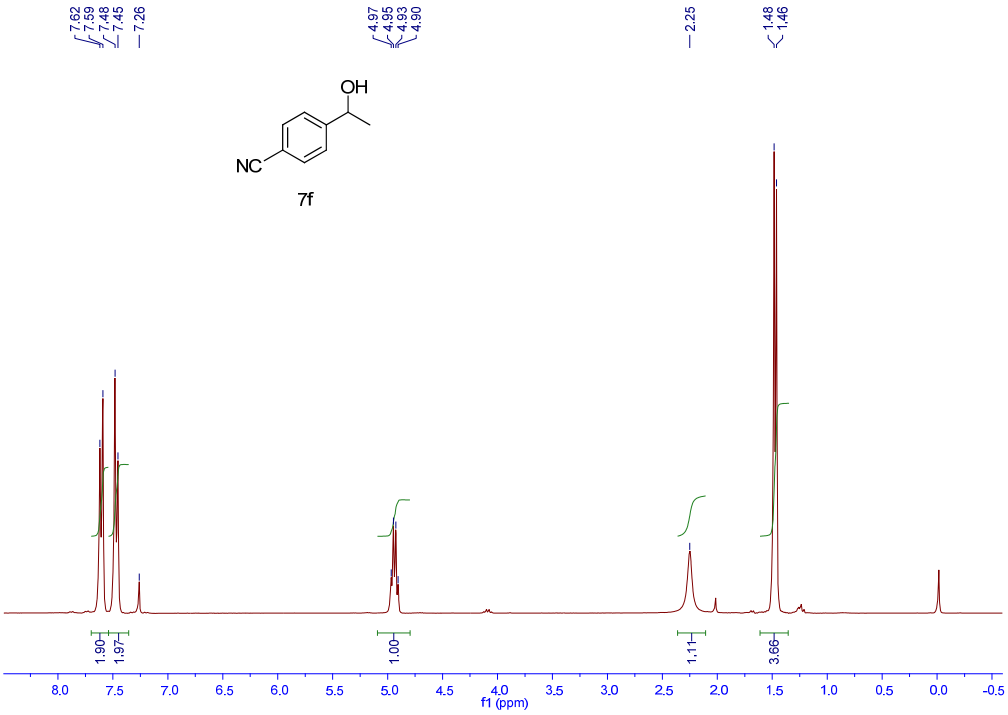
76.77
70.07
25.07
21.08
f1 (ppm)

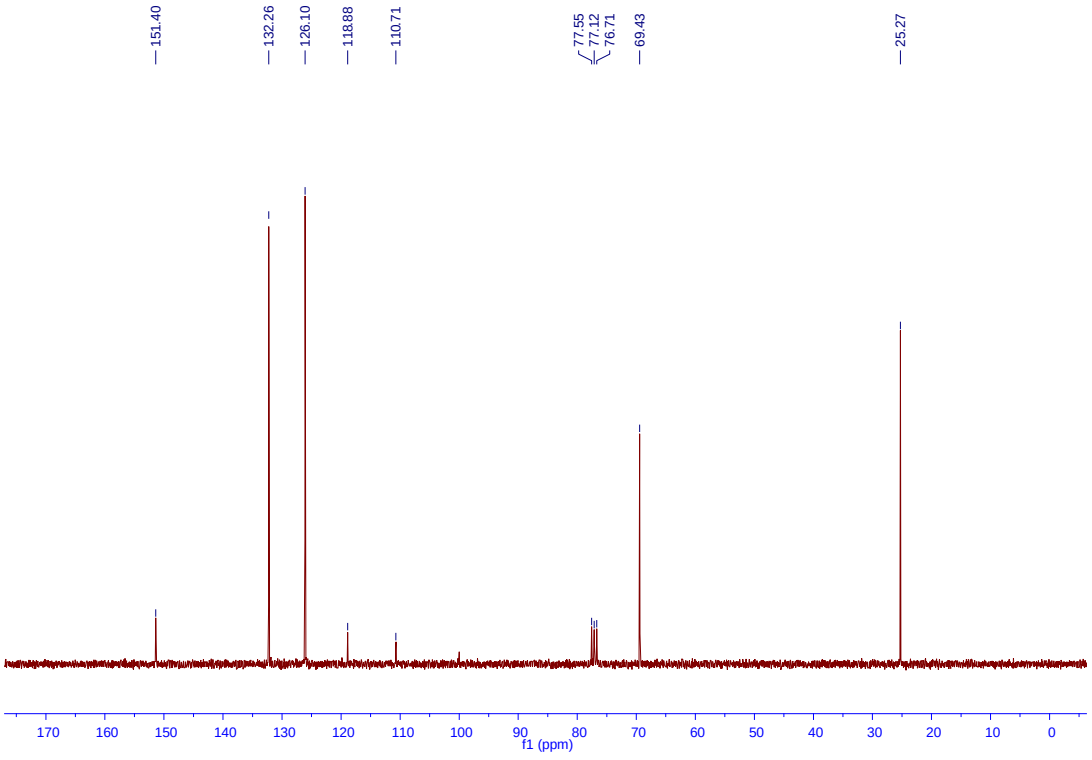


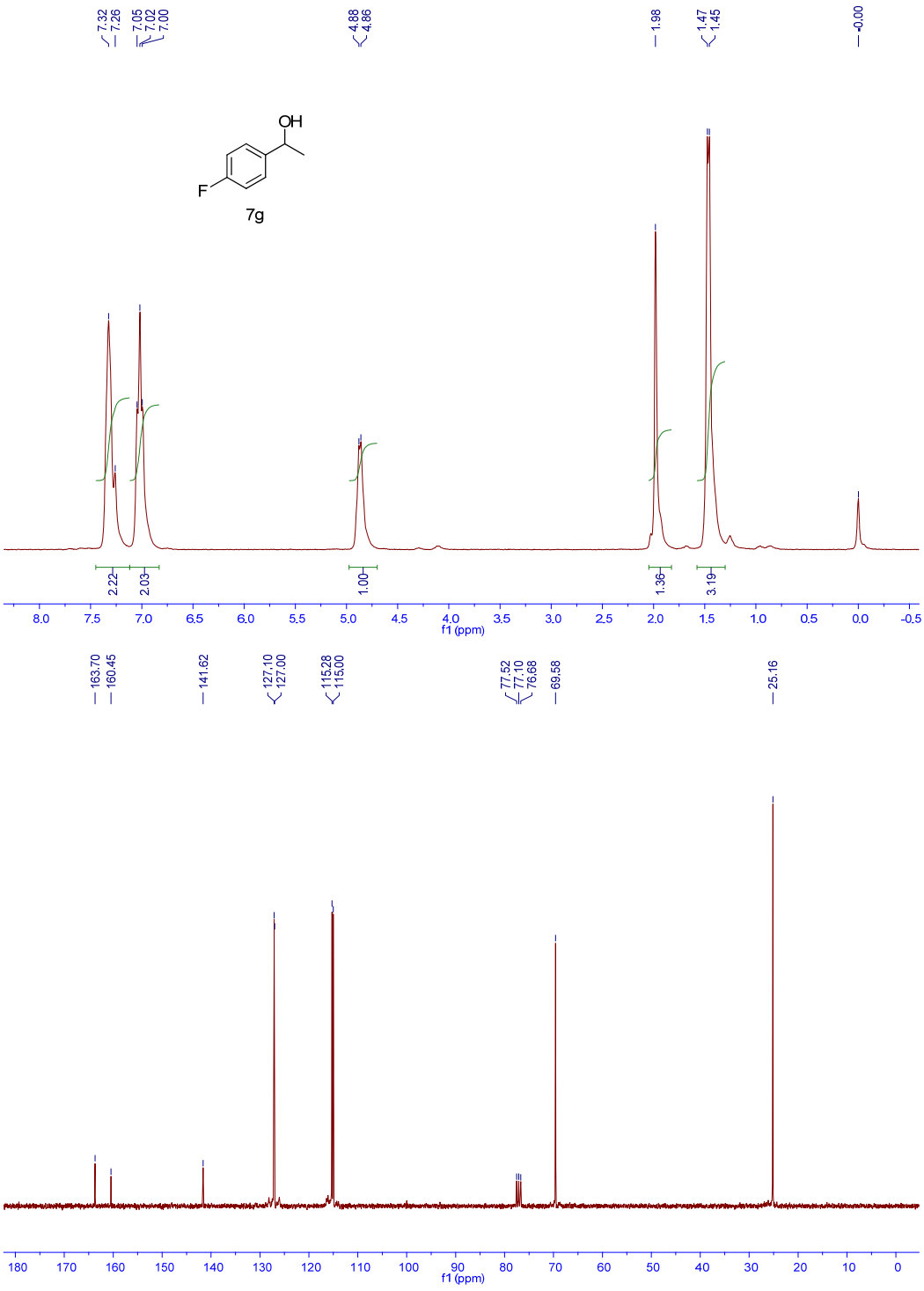


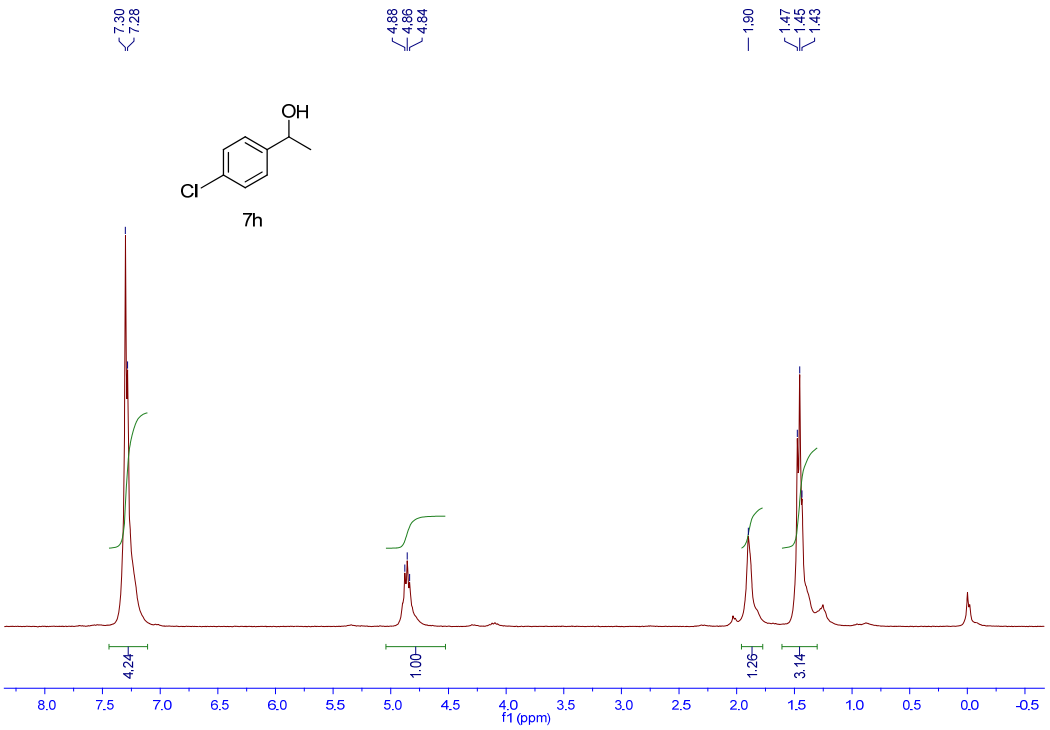


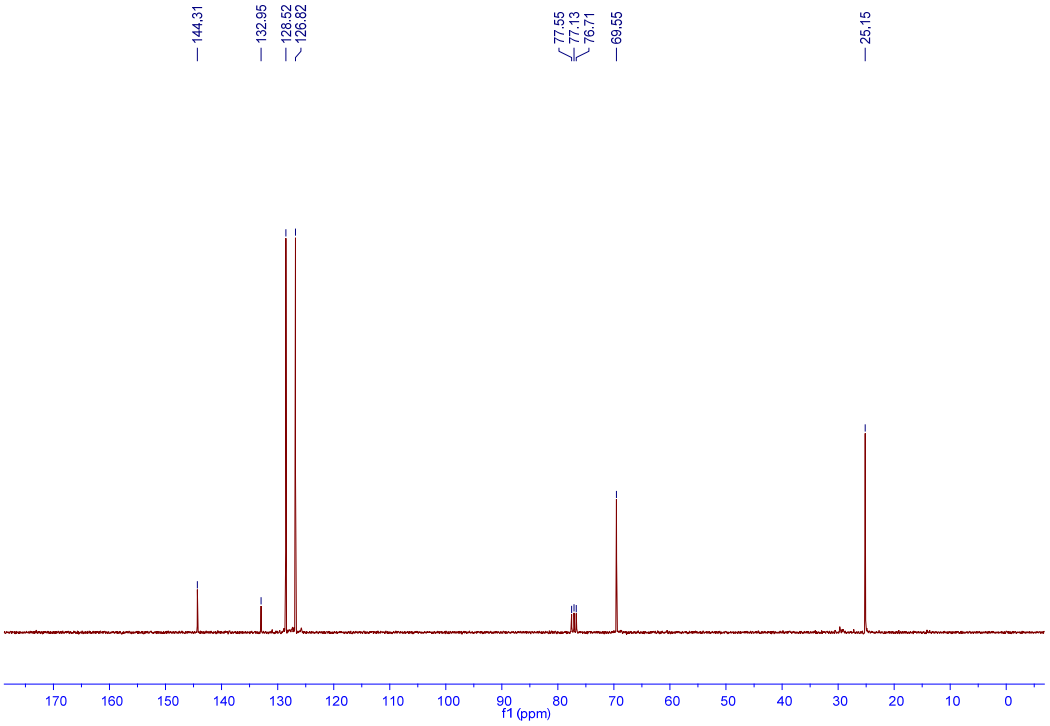


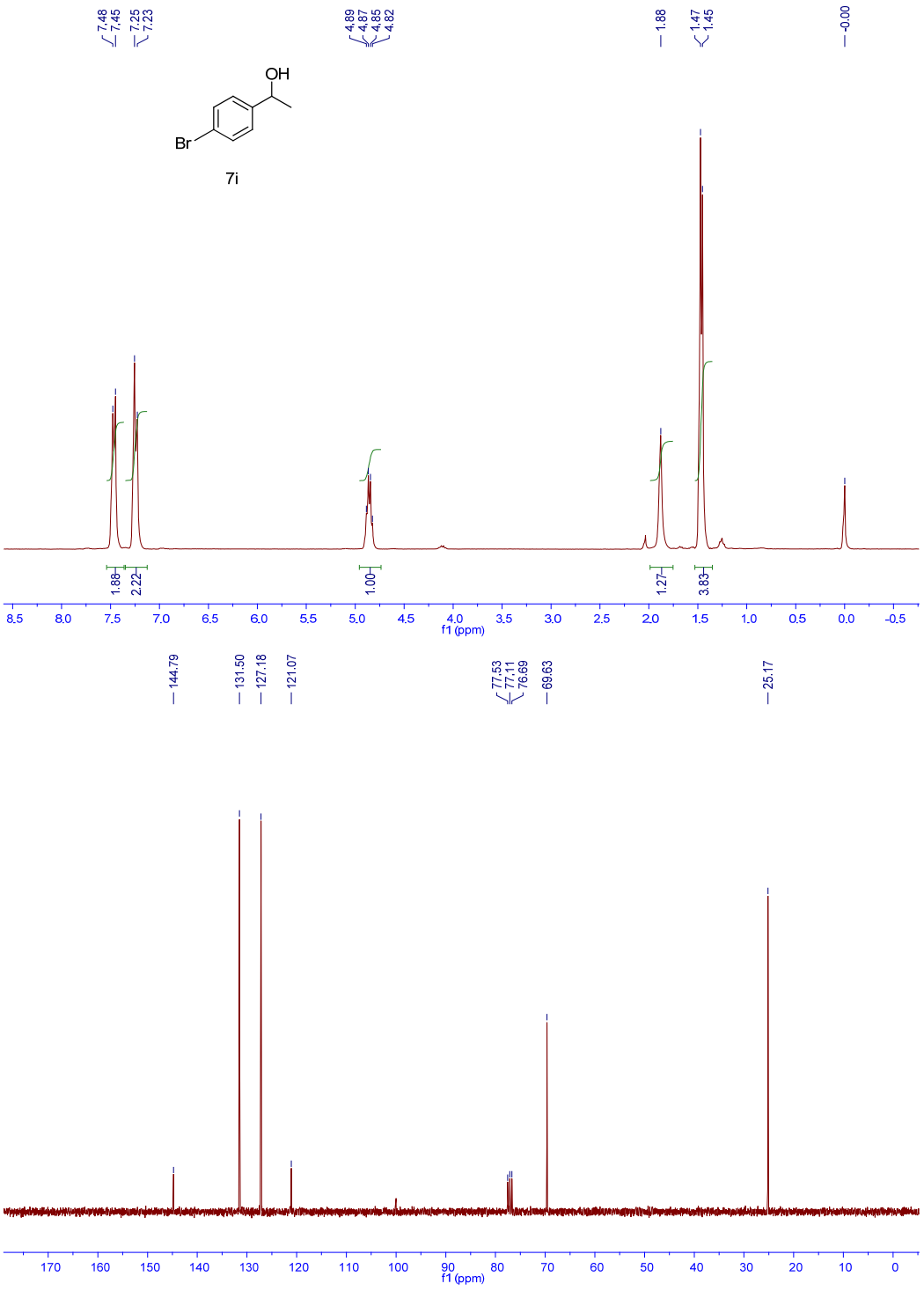

7.62
7.59
7.48
7.45
7.26
4.97
4.95
4.93
4.90
2.25
1.48
1.46
OH
NC
7f
1.90
1.97
1.00
1.11
3.66
f1 (ppm)

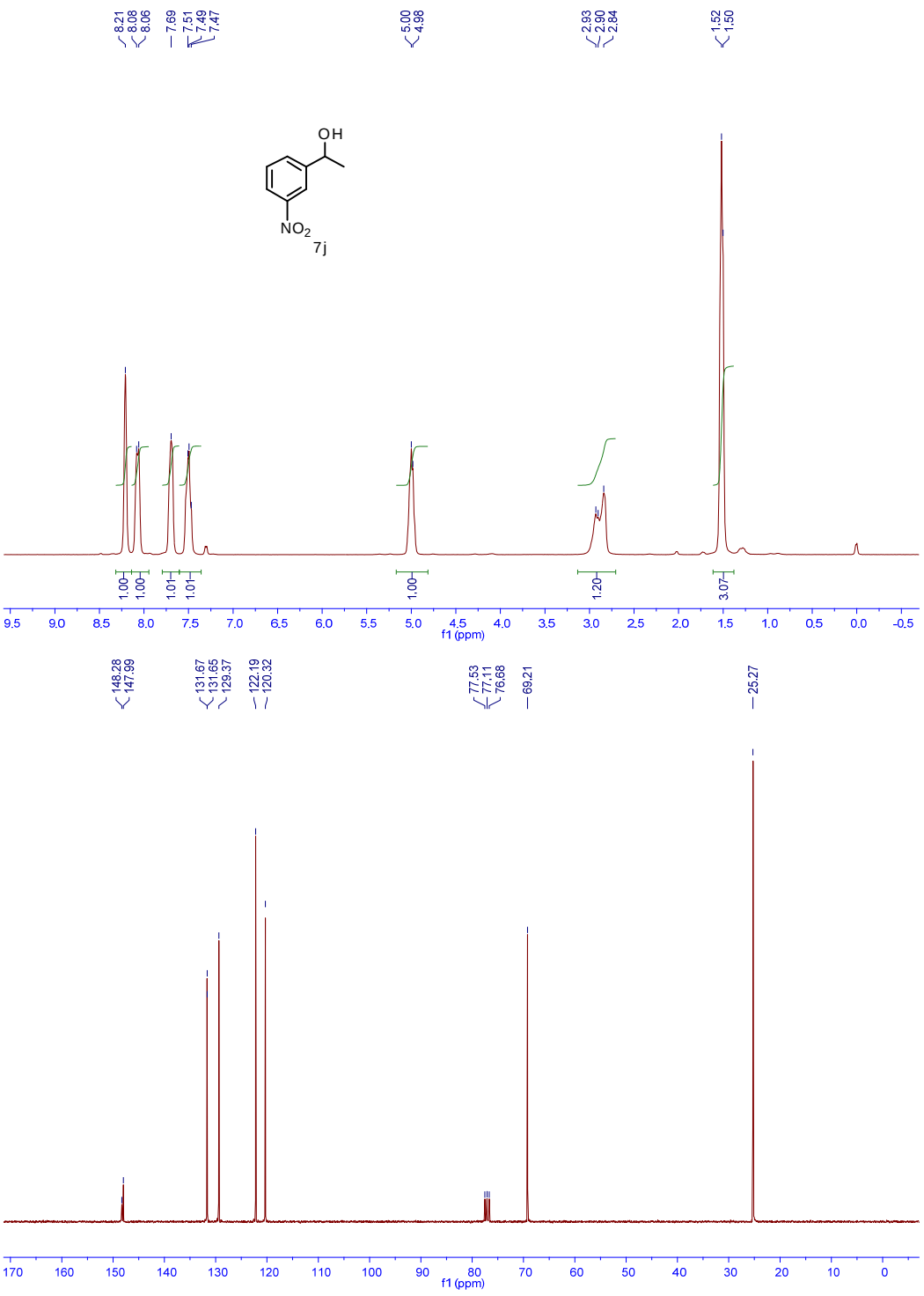

151.40
132.26
126.10
118.88
110.71
77.55
77.12
76.71
69.43
25.27
f1 (ppm)

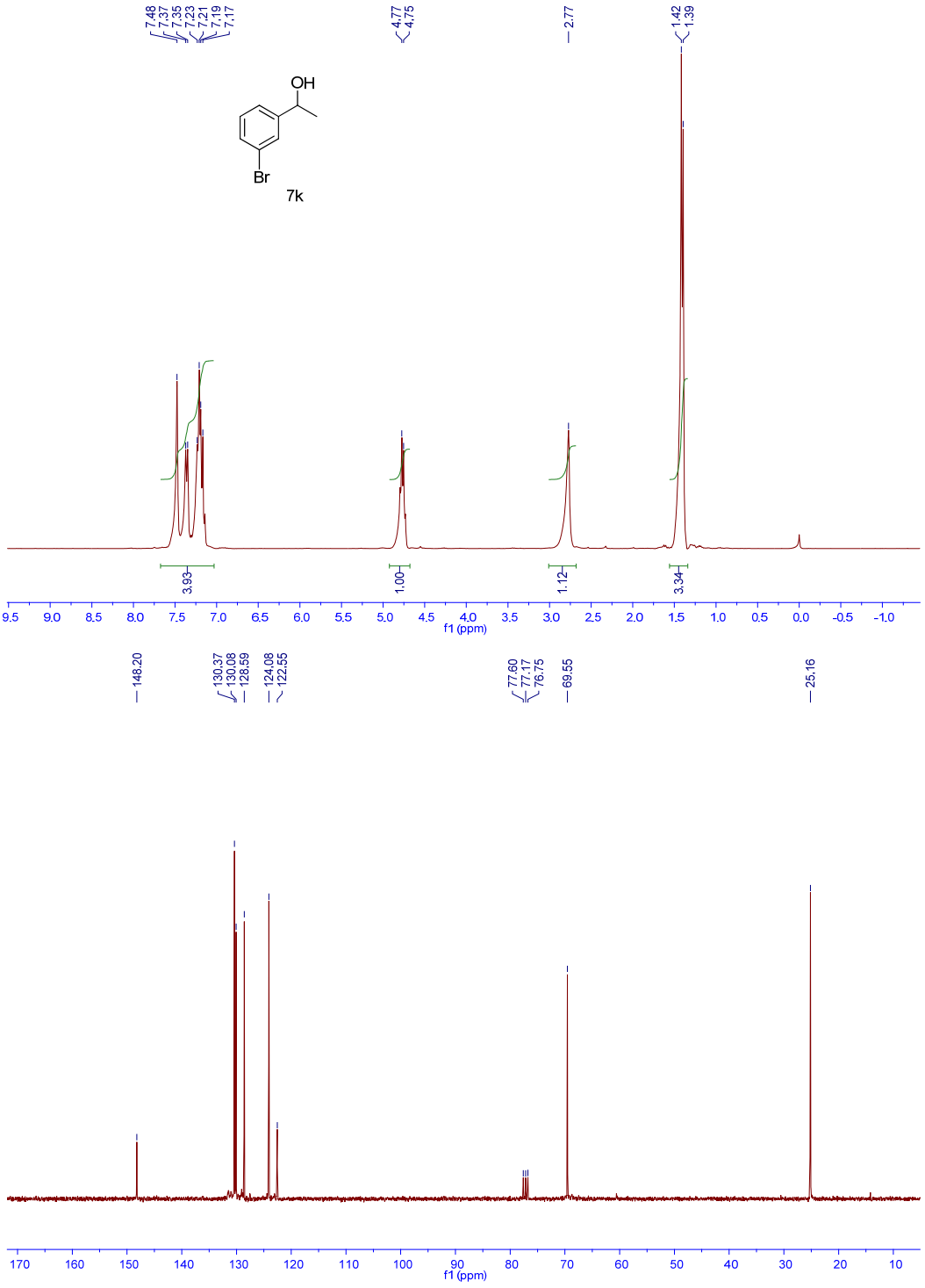

7.32
7.26
7.05
7.02
7.00
4.88
4.86
1.98
1.47
1.45
0.00
OH
F
7g
2.22
2.03
1.00
1.36
3.19
f1 (ppm)
163.70
160.45
141.62
127.10
127.00
115.28
115.00
77.52
77.10
76.68
69.58
25.16
f1 (ppm)

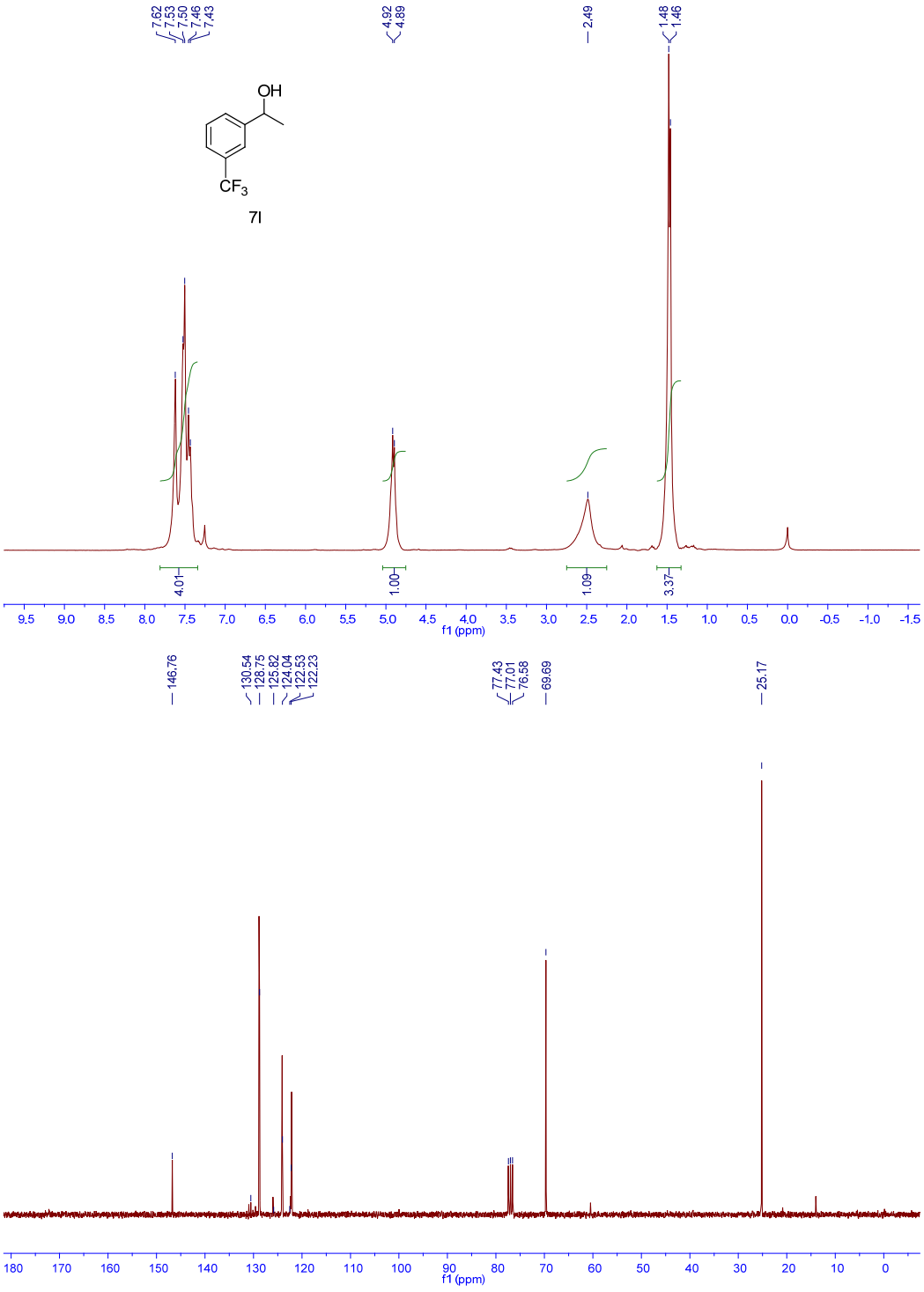


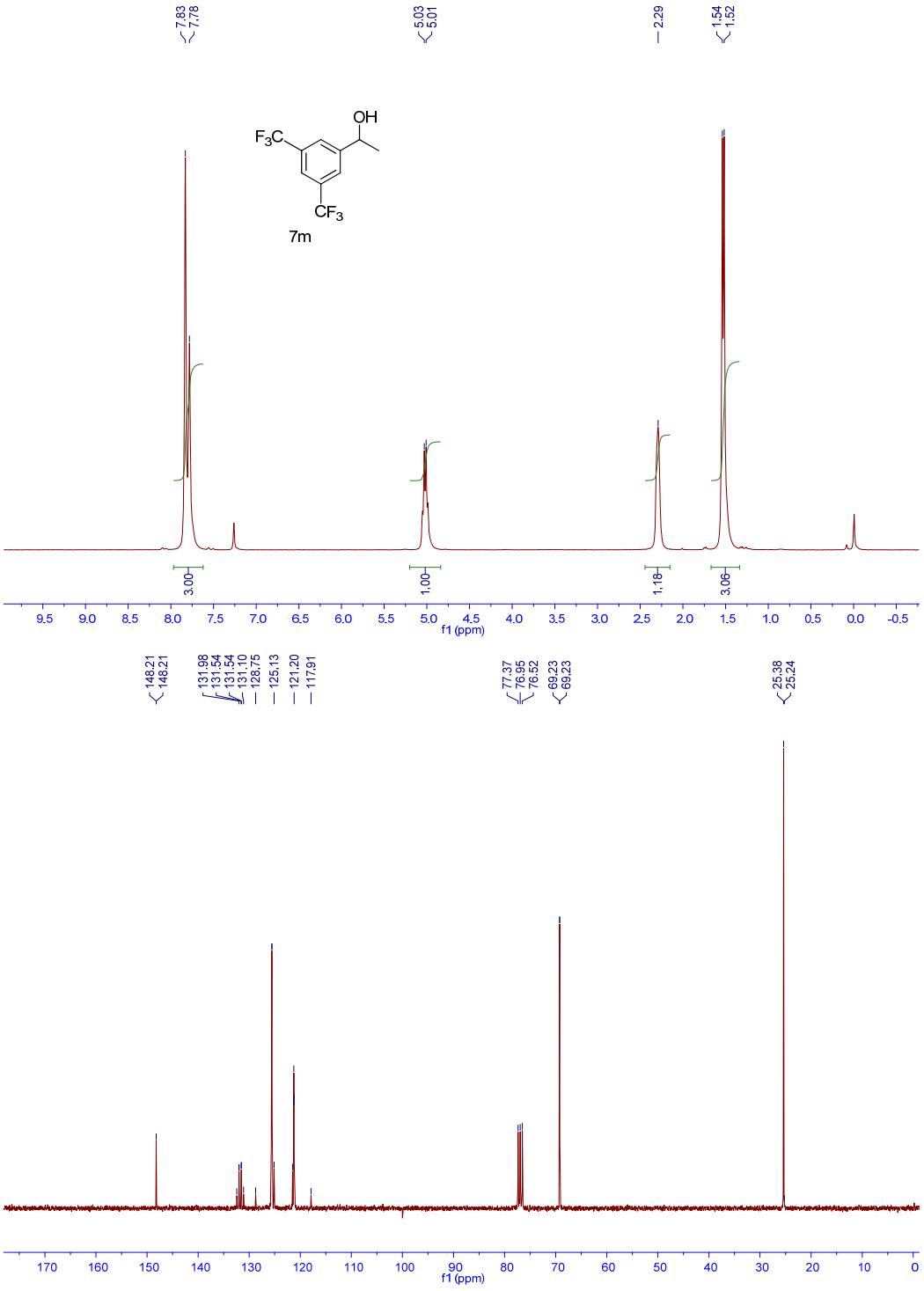




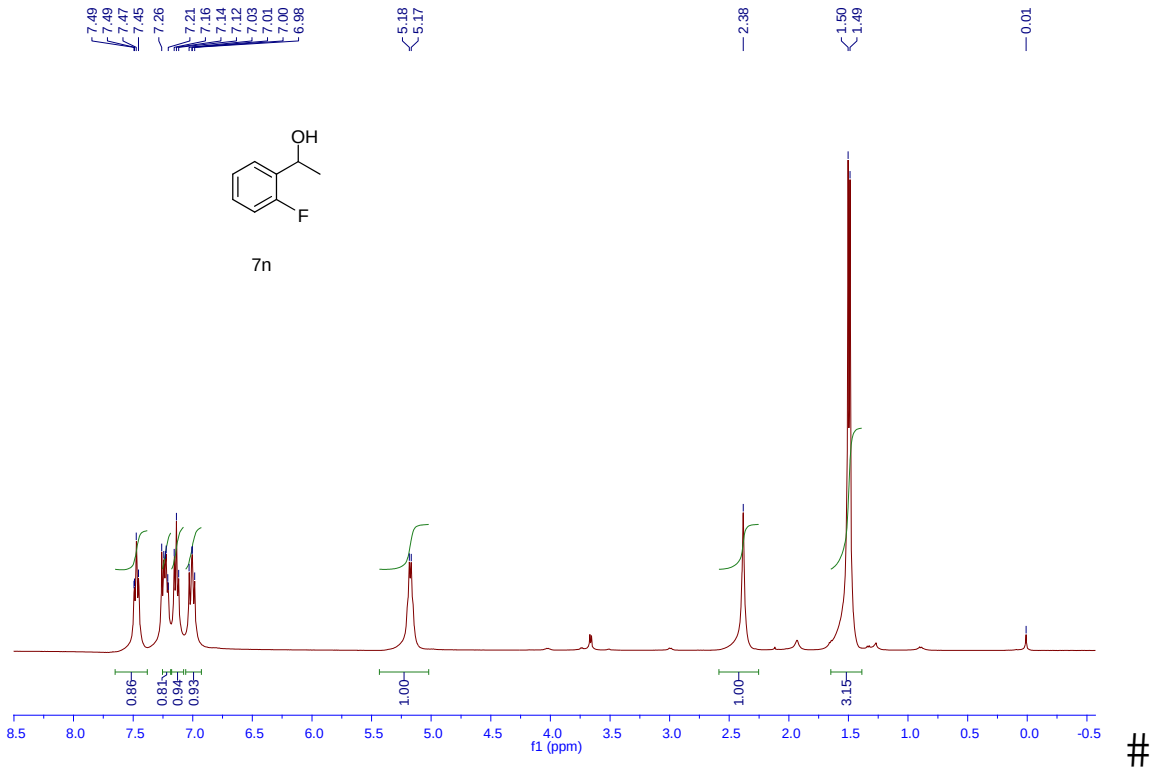



7.48
7.37
7.35
7.23
7.21
7.19
7.17
4.77
4.75
2.77
1.42
1.39
OH
Br
7k
3.93
1.00
1.12
3.34
f1 (ppm)
148.20
130.37
130.08
128.59
124.08
122.55
77.60
77.17
76.75
69.55
25.16
f1 (ppm)


7.62
7.53
7.50
7.46
7.43
4.92
4.89
2.49
1.48
1.46
OH
CF3
7l
4.01
1.00
1.09
3.37
f1 (ppm)
146.76
130.54
128.75
125.82
124.04
122.53
122.23
77.43
77.01
76.58
69.69
25.17
f1 (ppm)


7.83
7.78
5.03
5.01
2.29
1.54
1.52
OH
F3C
CF3
7m
3.00
1.00
1.18
3.06
f1 (ppm)
148.21
148.21
131.98
131.54
131.54
131.10
128.75
125.13
121.20
117.91
77.37
76.95
76.52
69.23
69.23
25.38
25.24
f1 (ppm)

#



7n

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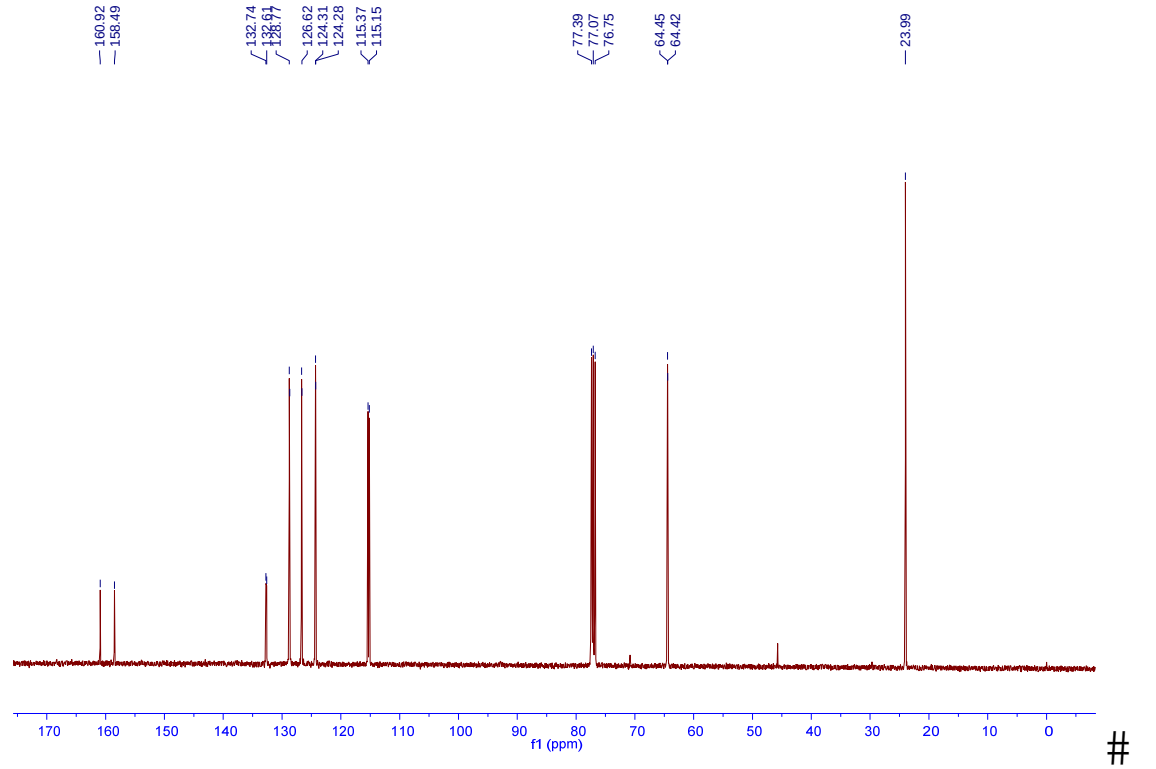

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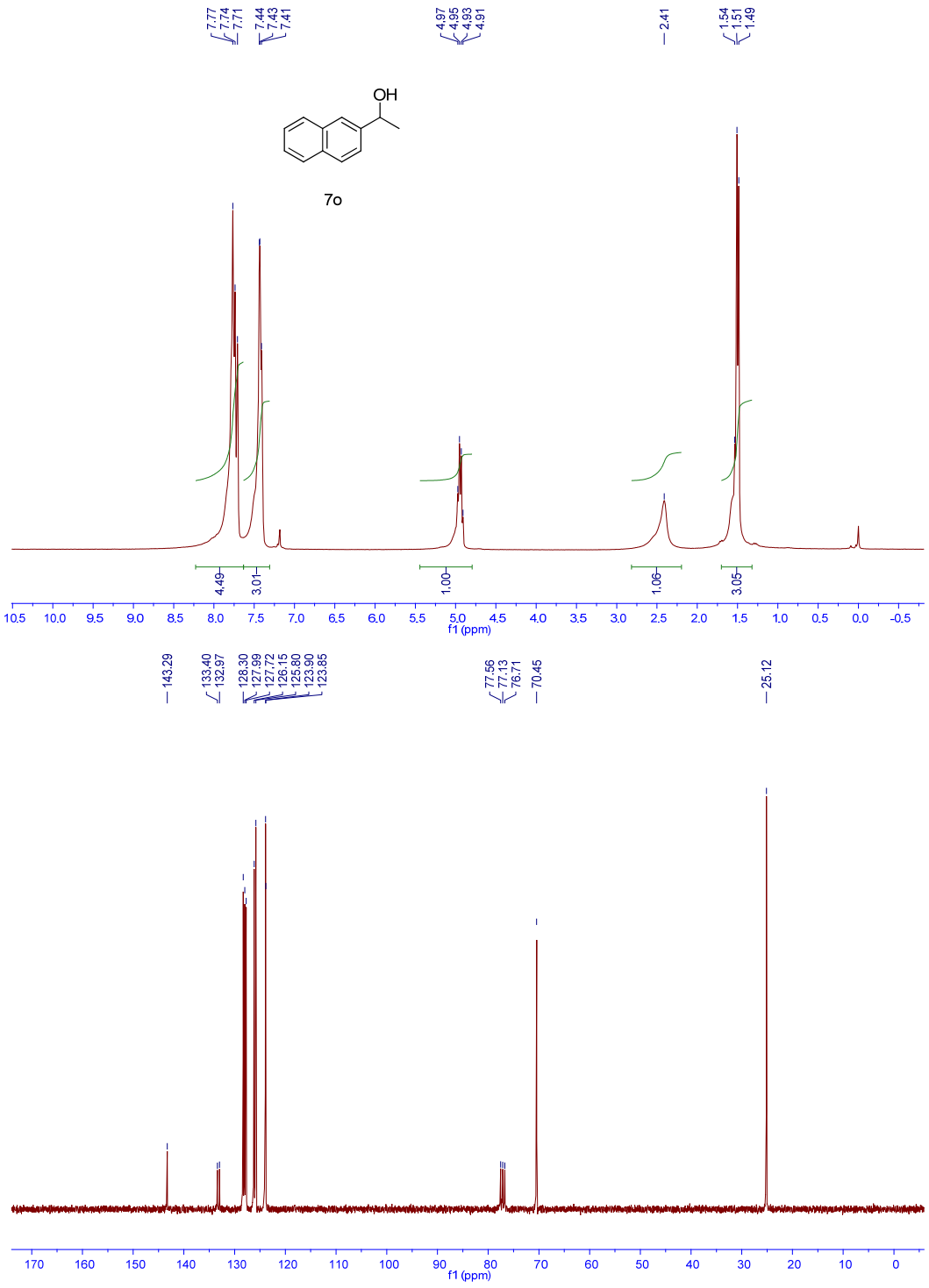
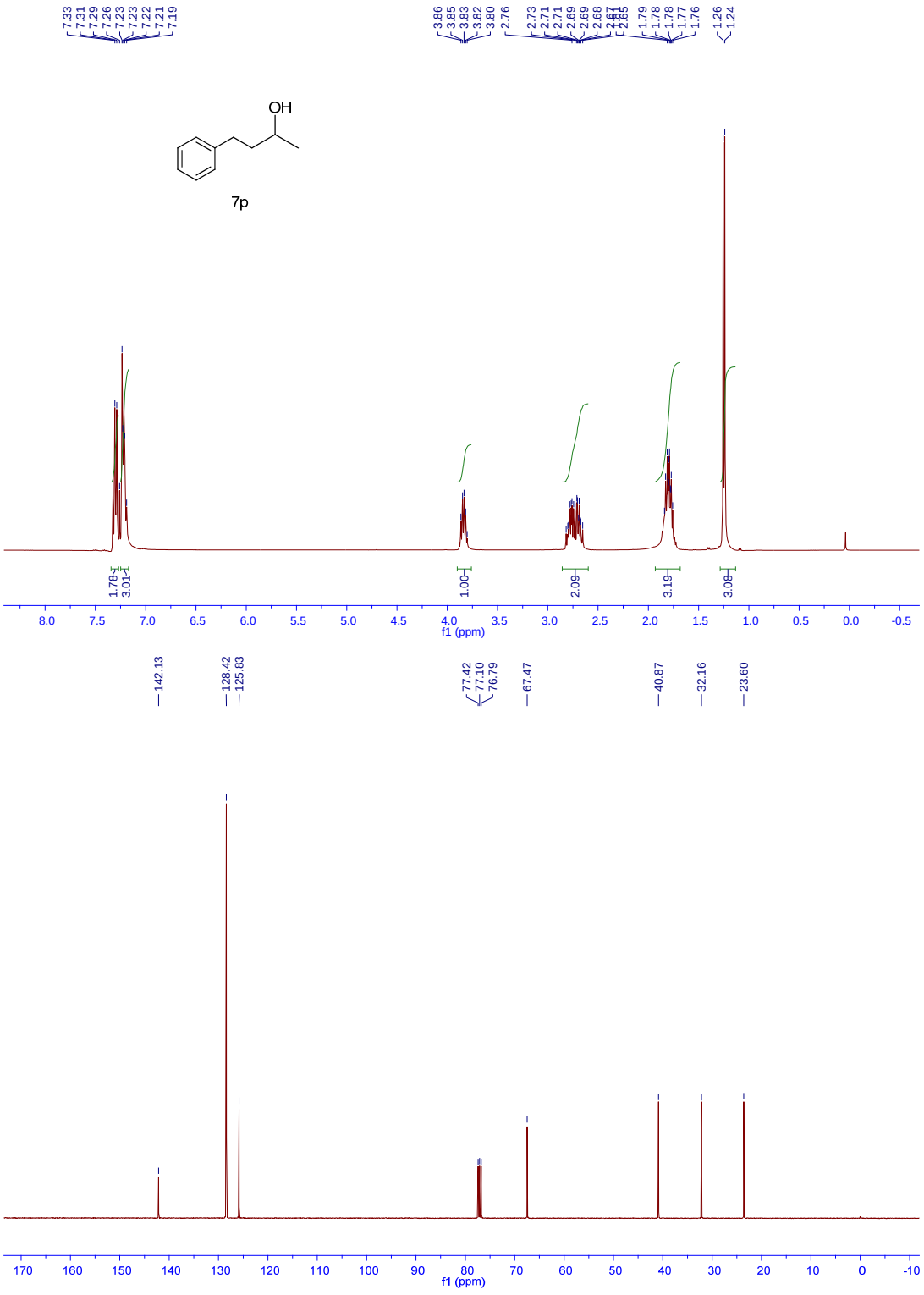
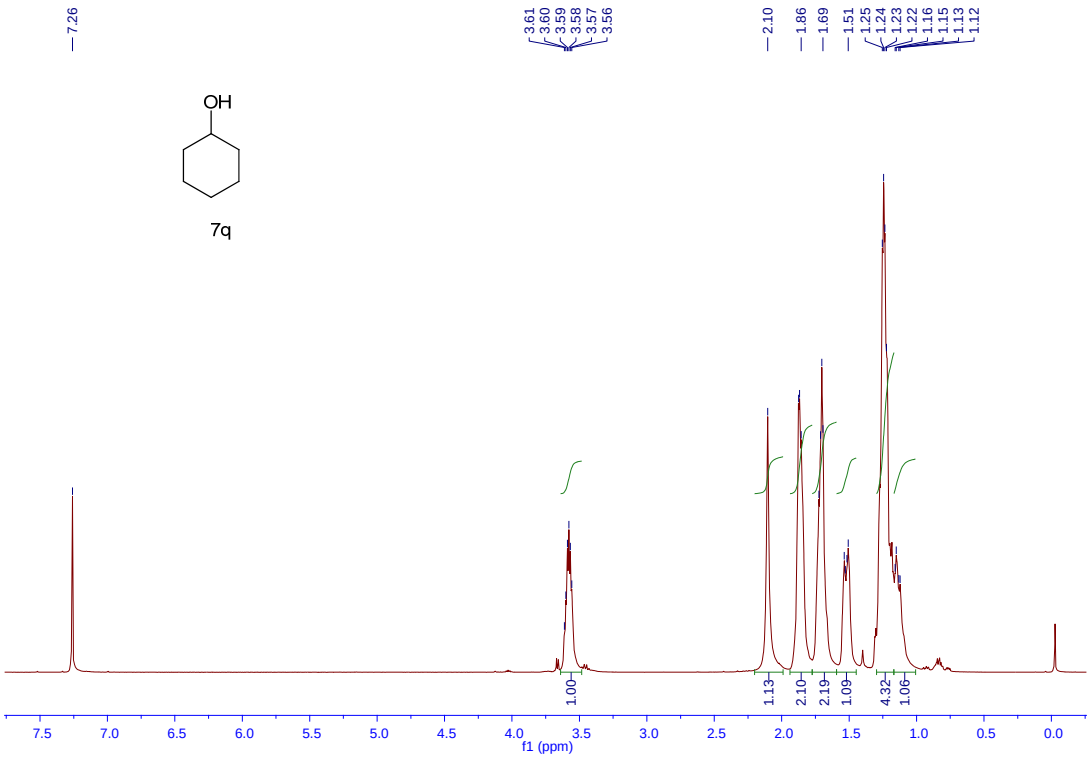
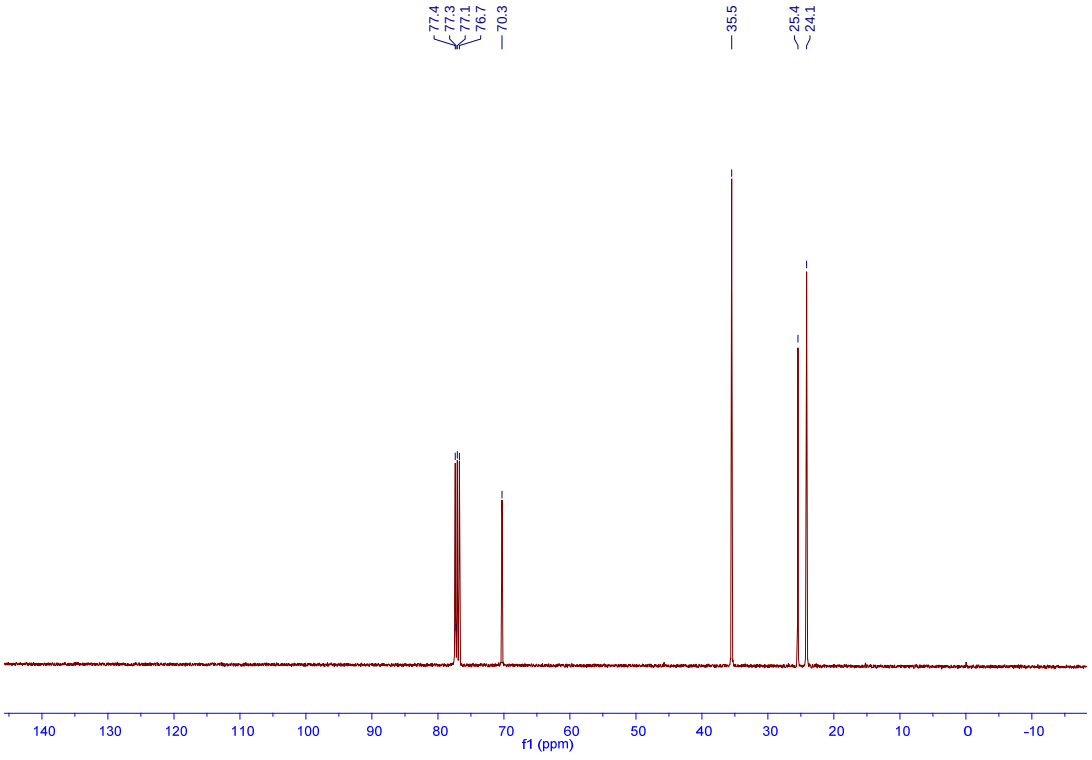
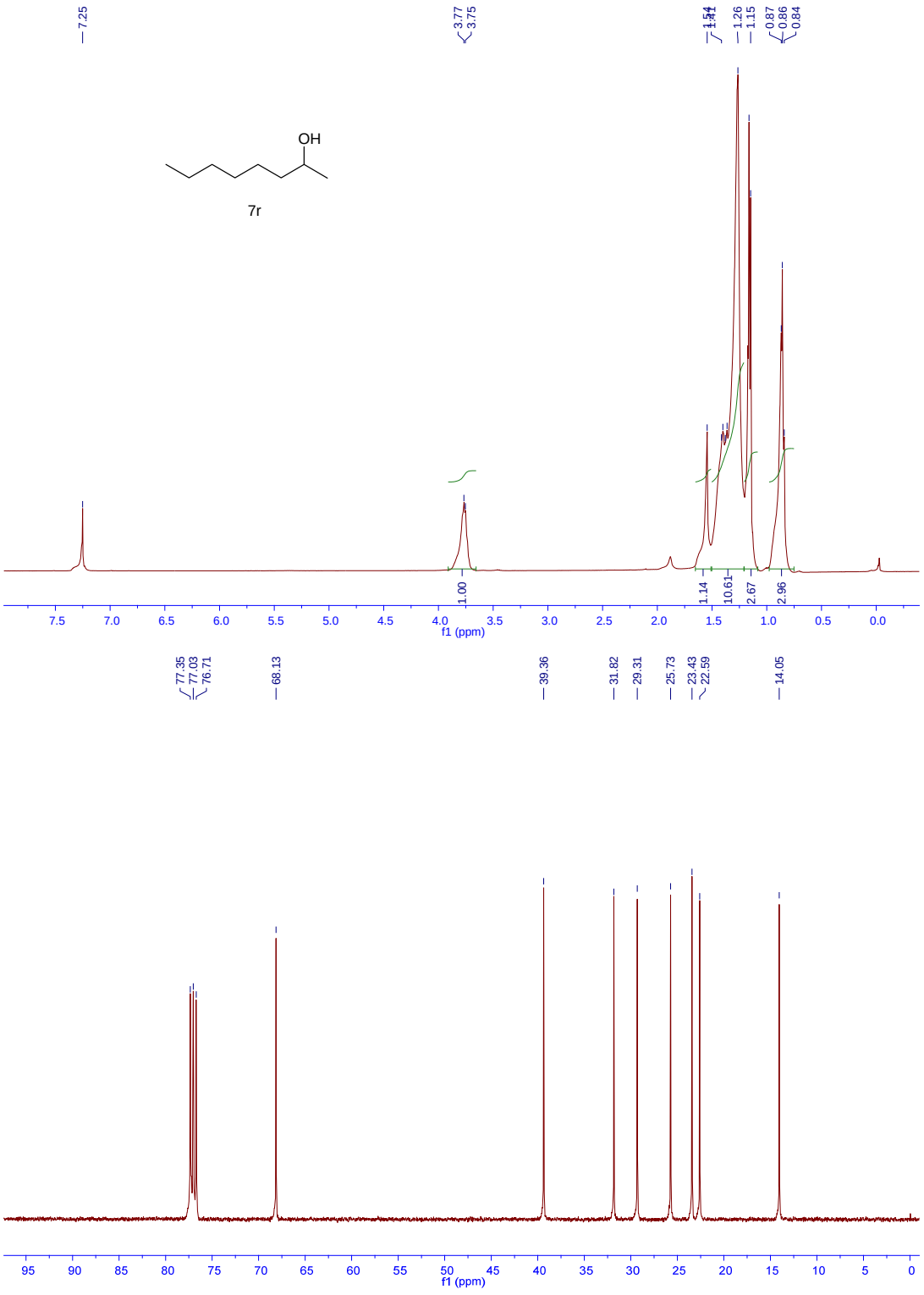
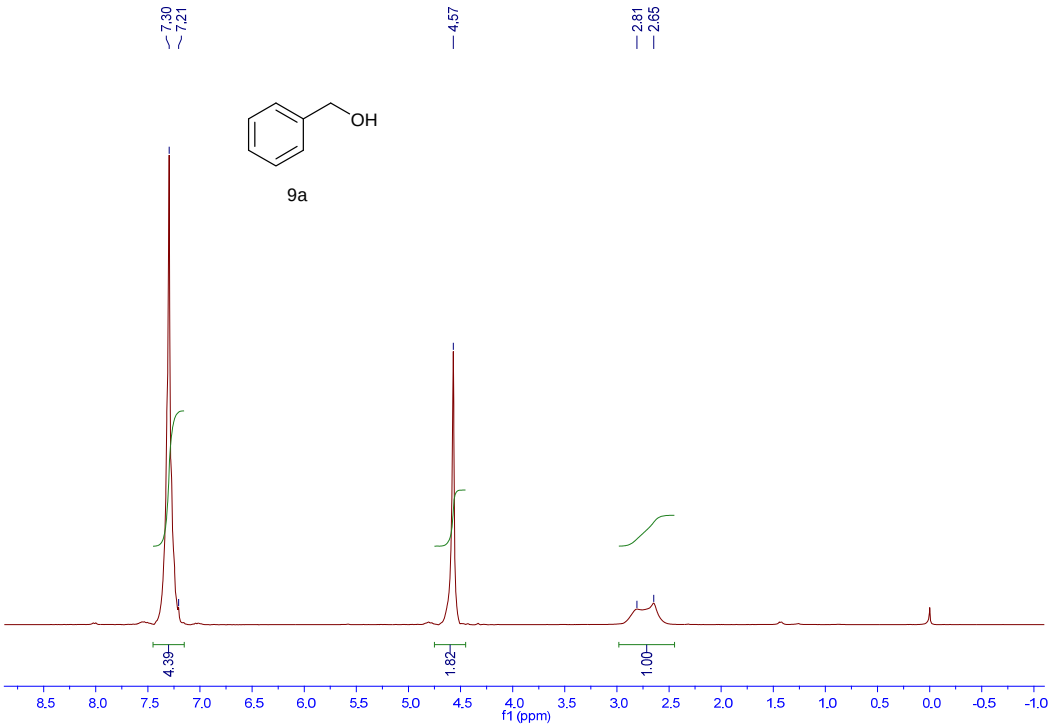

7.77
7.74
7.71
7.44
7.43
7.41
4.97
4.95
4.93
4.91
2.41
1.54
1.51
1.49
OH
7o
4.49
3.01
1.00
1.06
3.05
f1 (ppm)
143.29
133.40
132.97
128.30
127.99
127.72
126.15
125.80
123.90
123.85
77.56
77.13
76.71
70.45
25.12
f1 (ppm)

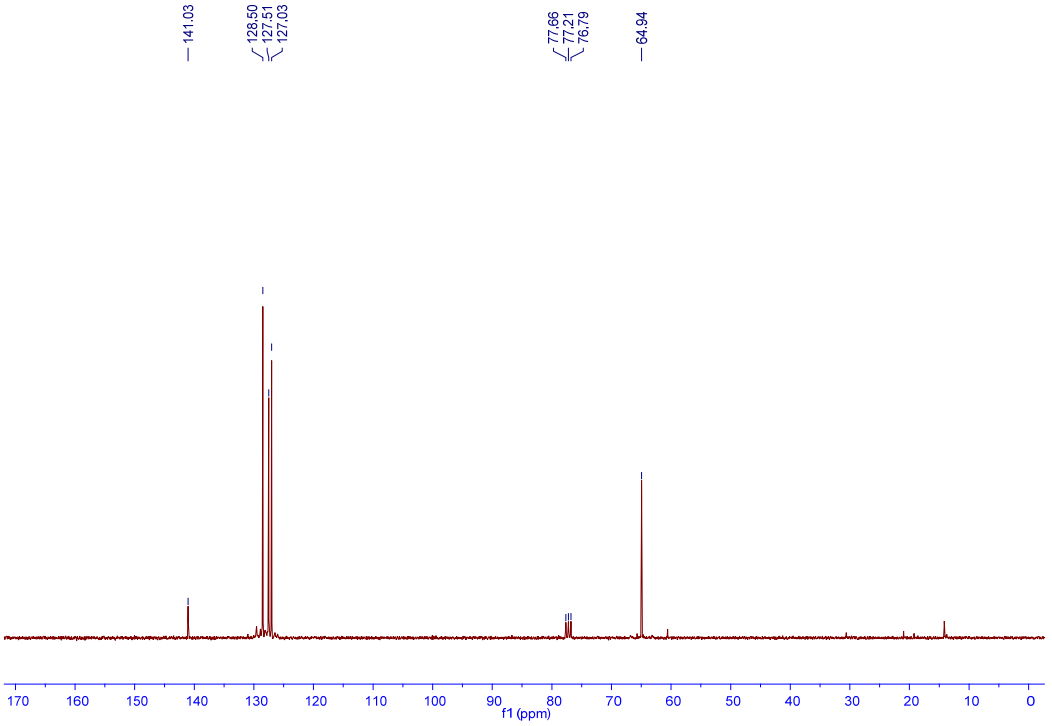

7.33
7.31
7.29
7.26
7.23
7.23
7.22
7.21
7.19
3.86
3.85
3.83
3.82
3.80
2.76
2.73
2.71
2.71
2.69
2.69
2.68
1.79
1.78
1.78
1.77
1.76
1.26
1.24
OH
7p
1.78
3.01
1.00
2.09
3.19
3.08
f1 (ppm)
142.13
128.42
125.83
77.42
77.10
76.79
67.47
40.87
32.16
23.60
f1 (ppm)

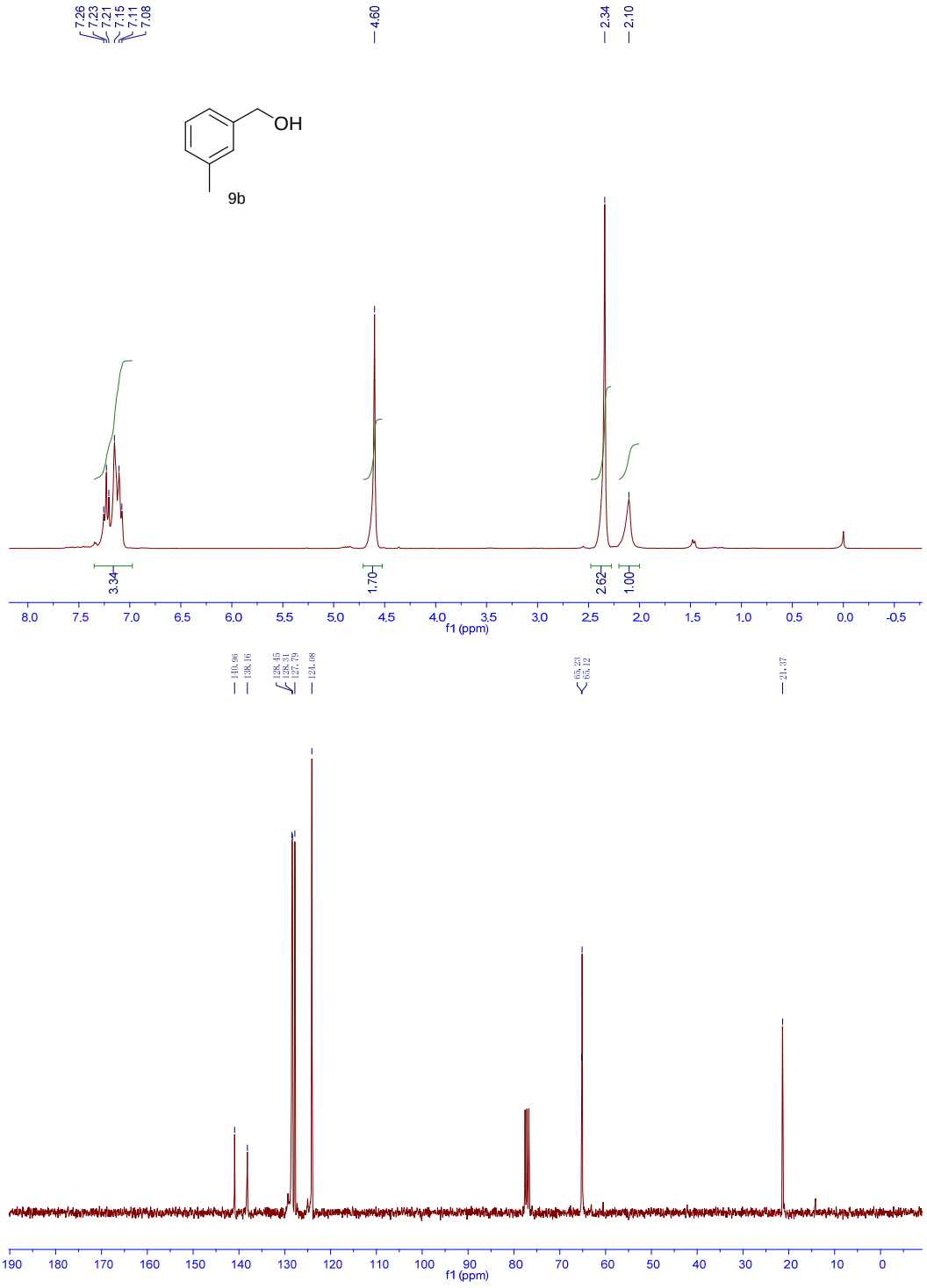

7.26
3.61
3.60
3.59
3.58
3.57
3.56
2.10
1.86
1.69
1.51
1.25
1.24
1.23
1.22
1.16
1.15
1.13
1.12
OH
7q
1.00
1.13
2.10
2.19
1.09
4.32
1.06
f1 (ppm)

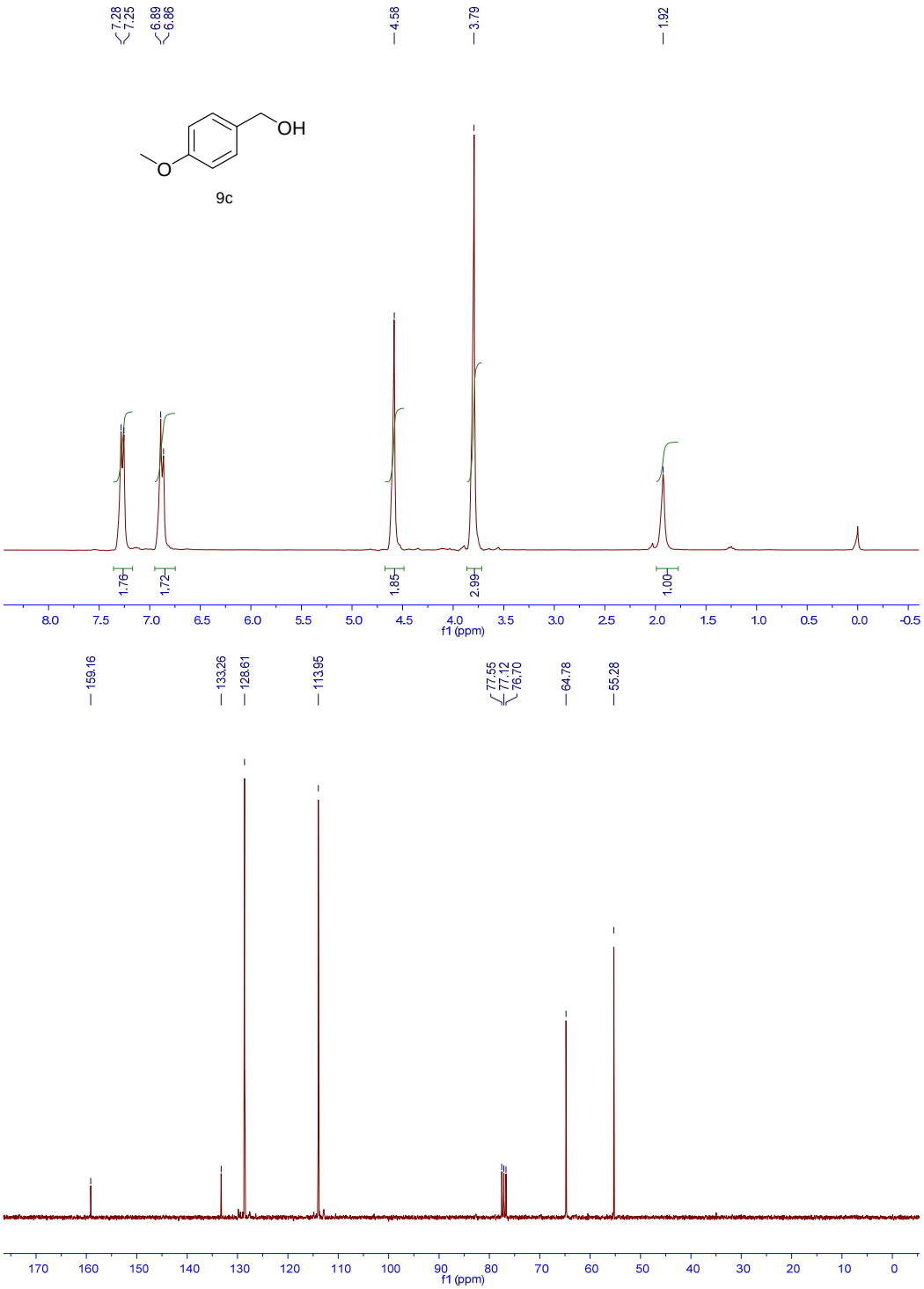

77.4
77.3
77.1
76.7
70.3
35.5
25.4
24.1
f1 (ppm)

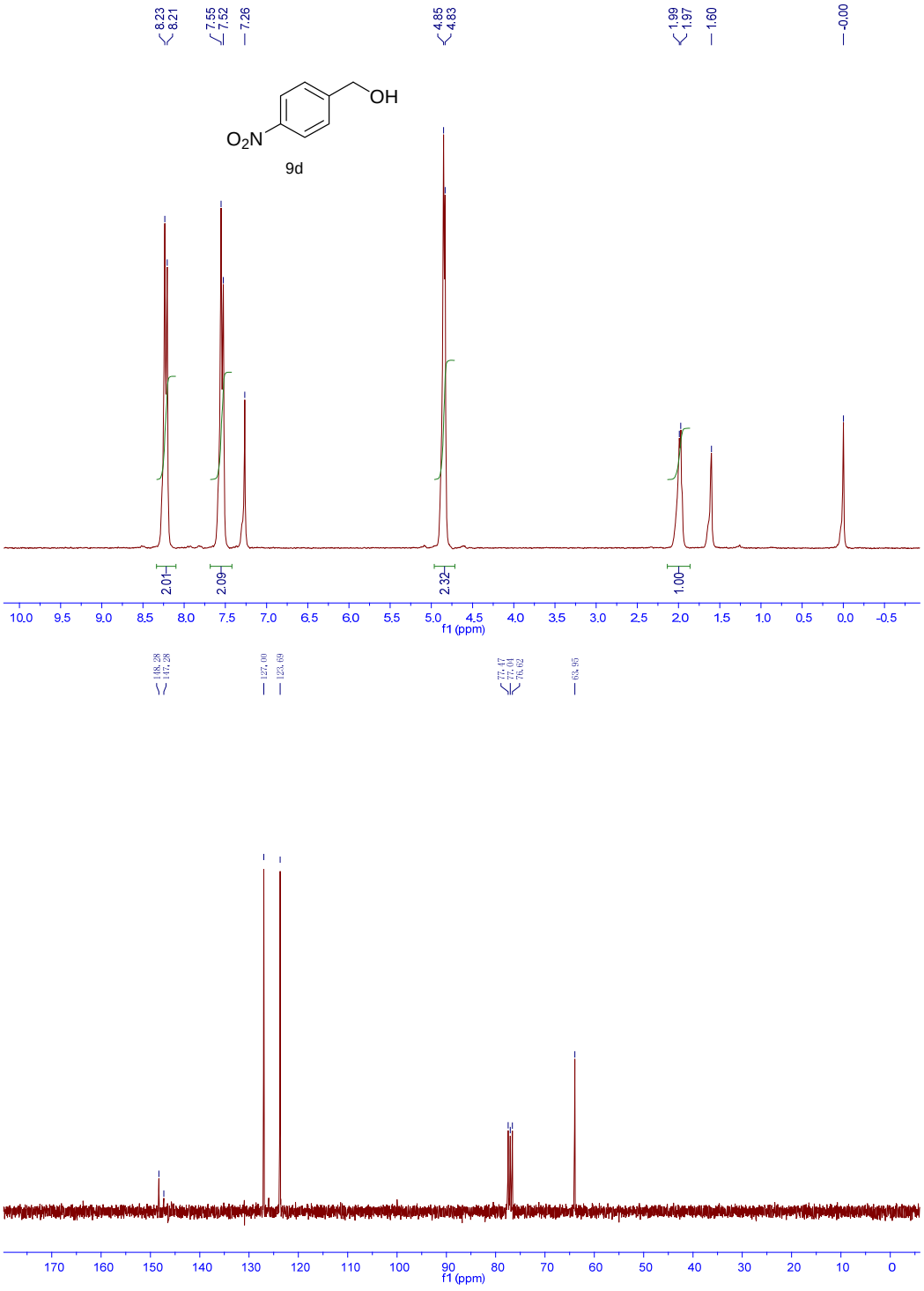

7.25
3.77
3.75
1.54
1.41
1.26
1.15
0.87
0.86
0.84
OH
7r
1.00
1.14
10.61
2.67
2.96
f1 (ppm)
77.35
77.03
76.71
68.13
39.36
31.82
29.31
25.73
23.43
22.59
14.05
f1 (ppm)

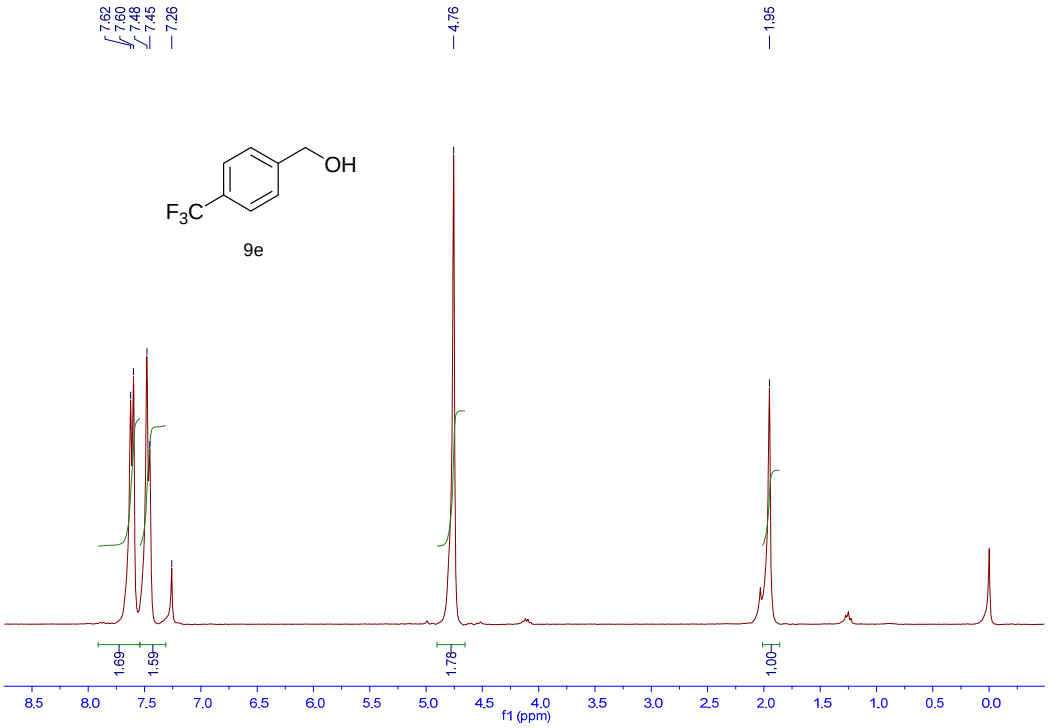

7.30
7.21
4.57
2.81
2.65
OH
9a
4.39
1.82
1.00
f1 (ppm)

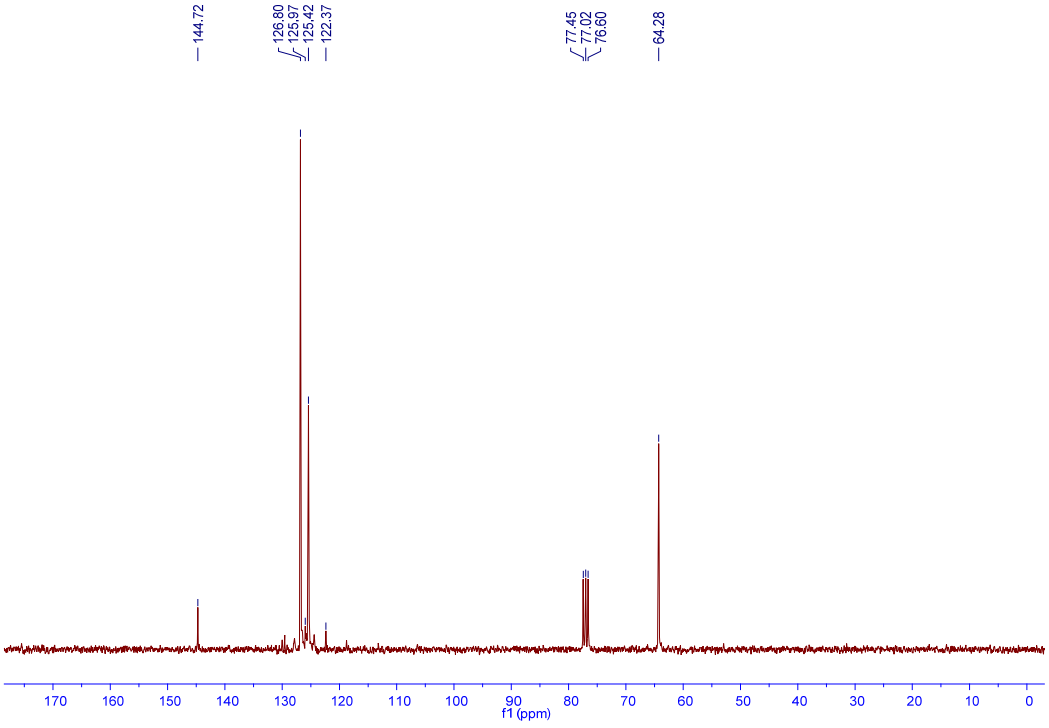

141.03
128.50
127.51
127.03
77.66
77.21
76.79
64.94
f1 (ppm)

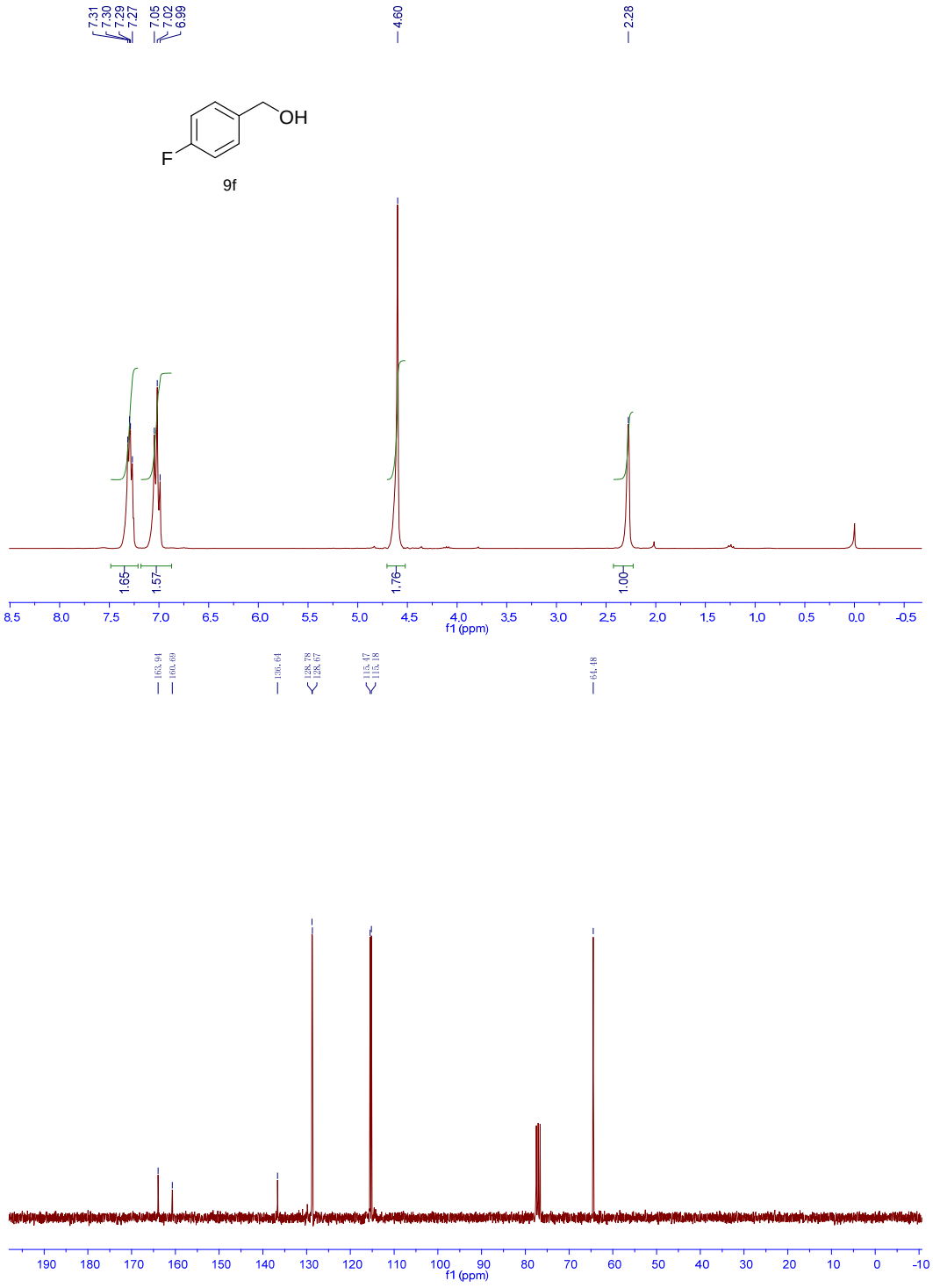

7.26
7.23
7.21
7.15
7.11
7.08
4.60
2.34
2.10
OH
9b
3.34
1.70
2.62
1.00
f1 (ppm)
140.96
138.16
128.45
128.31
127.79
124.08
65.23
65.12
21.37
f1 (ppm)

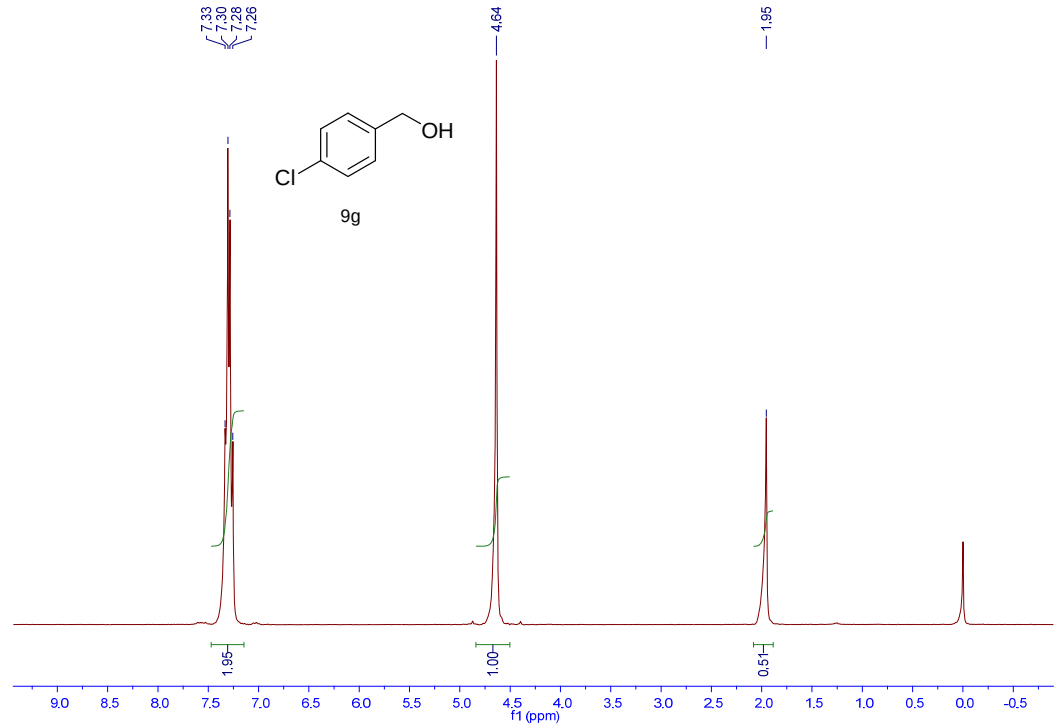



8.23
8.21
7.55
7.52
7.26
4.85
4.83
1.99
1.97
1.60
-0.00
OH
O2N
9d
2.01
2.09
2.32
1.00
f1 (ppm)
148.28
147.28
127.00
123.69
77.47
77.04
76.62
63.95
f1 (ppm)






7.31
7.30
7.29
7.27
7.05
7.02
6.99
4.60
2.28
OH
F
9f
1.65
1.57
1.76
1.00
f1 (ppm)
163.94
160.69
136.64
128.78
128.67
115.47
115.18
64.48
f1 (ppm)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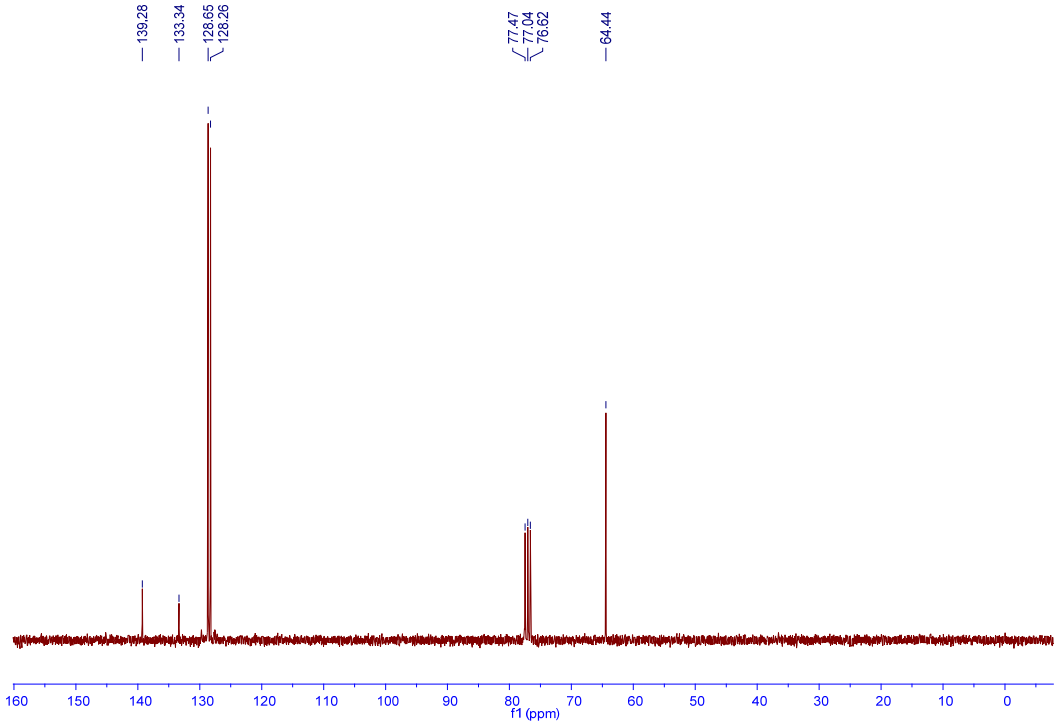
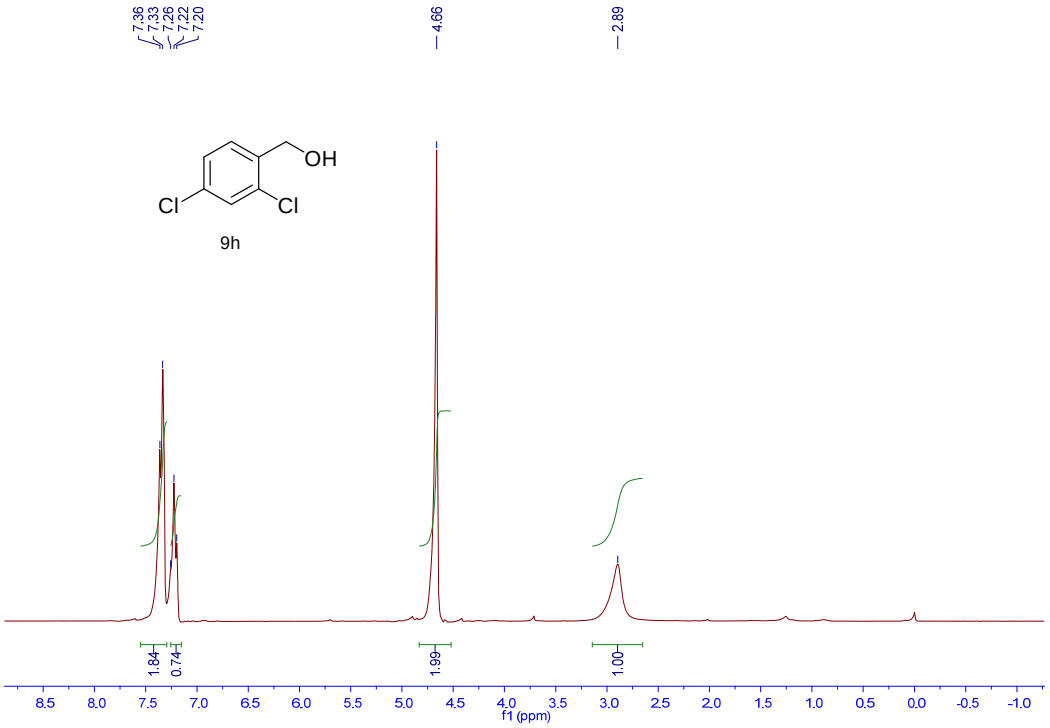
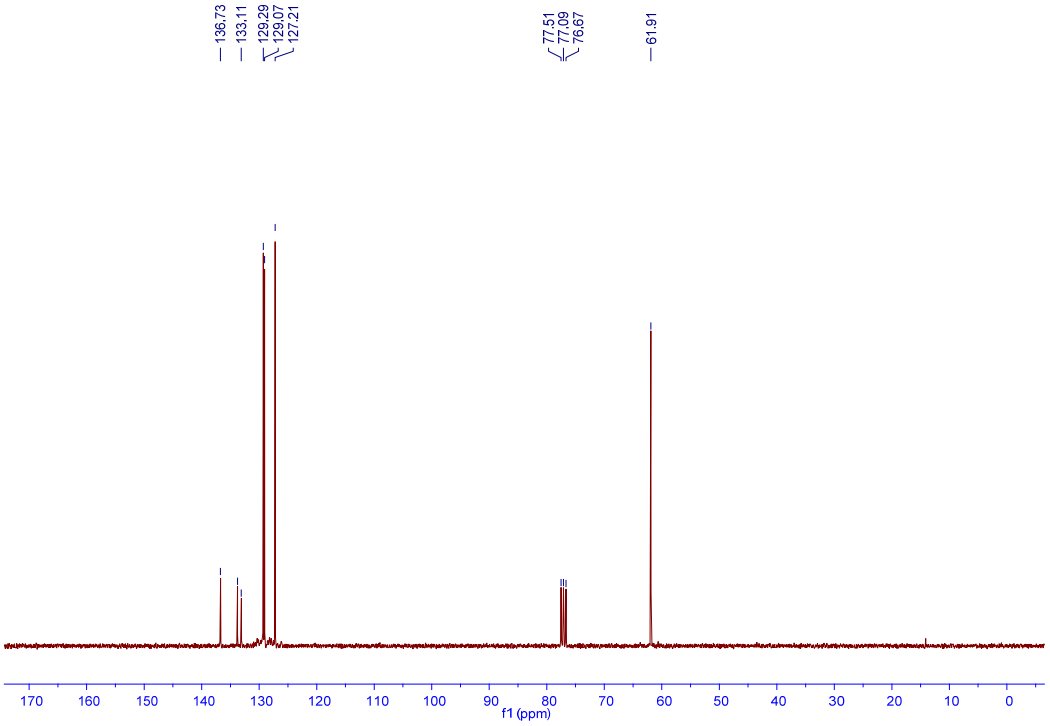
7.30
7.28
7.26
4.64
1.95
OH
Cl
9g
1.95
1.00
0.51
f1 (ppm)


139.28
133.34
128.65
128.26
77.47
77.04
76.62
64.44
f1 (ppm)


7.36
7.33
7.26
7.22
7.20
4.66
2.89
OH
Cl
Cl
9h
1.84
0.74
1.99
1.00
f1 (ppm)


136.73
133.11
129.29
129.07
127.21
77.51
77.09
76.67
61.91
f1 (ppm)