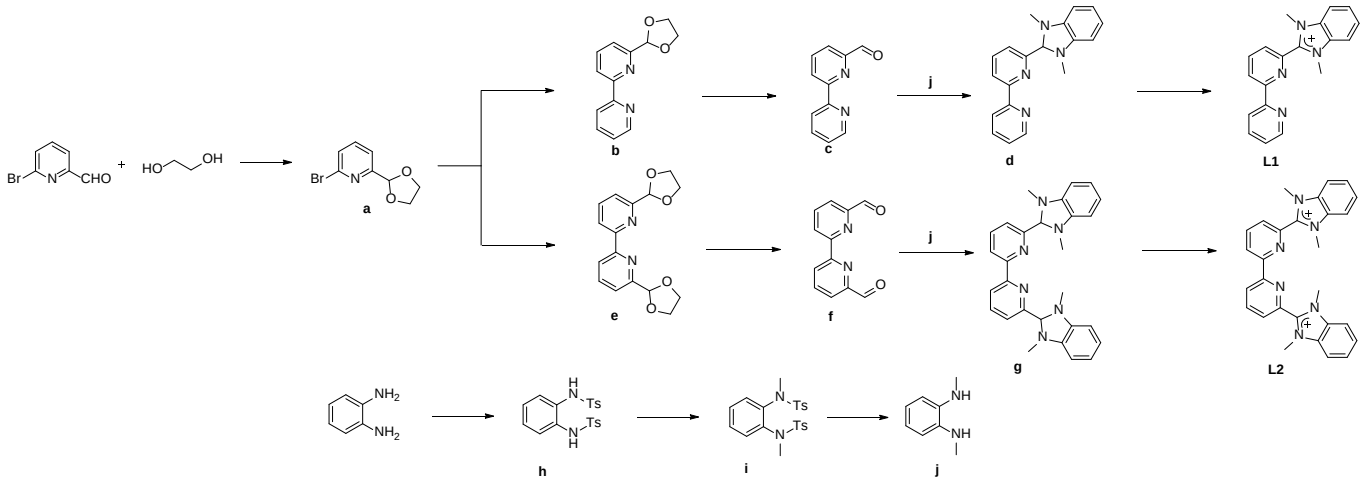
Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Rhodium Catalysts with Cofactor Mimics for Biomimetic Reduction of C=N Bonds

Jie Tang, Wenjin Dong, Fushan Chen, Li Deng* and Mo Xian*

Table of Contents

1. Synthesis of **L1**, **L2, C1** and Substrates



Scheme S1. Synthesis of Ligands **L1** and **L2**

Synthesis of **a**

a was synthesized according to a previously reported procedure.[1] 6-Bromopyridine-2-carbaldehyde (1.86 g, 10.0 mmol, 1.0 eq), *p*-Toluenesulfonic acid (0.084 g, 0.50 mmol, 0.05 eq)，Ethylene glycol (1.1 mL, 20.0 mmol, 2.0 eq) were dissoved in dry benzene (40 mL) and heated with stirring at reflux for 24 h. The reaction mixture was cooled to rt and 1% w/v Na_2CO_3 was added. Then the mixture was extracted with dichloromethane three times and tried with anhydrous Na_2SO_4. And then the dichloromethane was removed *in vacuo* to give the pale yellow oil product. Yield: 85 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 2H), 5.81 (s, 1H), 4.19 – 4.04 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.52 , 141.68 , 139.08 , 128.51 , 119.41 , 102.77 , 65.63.

Synthesis of **b**

b was synthesized according to a previously reported procedure.[2] A 250 mL round-bottom flask was charged with $NiCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol) and DMF (20 mL). the resulting solution was stirred and heated to 40 ℃, and then **a** (0.46 g, 2 mmol), anhydrous LiCl (0.084 g, 2 mmol), and zinc dust (0.157 g, 2.4 mmol) was added. When the temperature rose to 50 ℃, a grain of iodine crystal and two drops of acetic acid were added to the mixture. An immediate rise in temperature and color change to black was caused, indicating the reaction was triggered. The solution of the remaining 2-bromopyridine and **a** in 20 mL of DMF was added dropwise into the mixture at 60-70 ℃ over a period of 3 h. The mixture was stirred at 60-70 ℃ for an additional of 3 h until complete conversion of **a** (monitored by TLC). The cooled reaction mixture was filtrated with a pad of celite and aqueous ammonia (25 %) added. Then the mixture was taken up with dichloromethane two times. The organic layers were collected, dried over anhydrous Na_2CO_3, and concentrated. The crude material was purified by flash chromatography to give the desired pale oil product **b**. Yield: 15 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, J = 4.0 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 7.9 Hz, 1H), 7.87 (t, J = 7.8 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.30 (dd, J = 8.0, 5.4 Hz, 1H), 5.96 (s, 1H), 4.25 – 4.09 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.63, 155.84, 155.72, 149.07, 137.71, 136.84, 123.79, 121.44, 121.27, 120.46, 104.04, 65.66. HR-ESI-MS m/z: [**b**]$^+$, Calcd for $C_{13}H_{12}N_2O_2^+$ 228.0899; found 228.0852.

Synthesis of **c**

c was synthesized according to a previously reported procedure. [3] **b** was dissolved in THF (5 mL). then HCl (1 mL) and H_2O (5 mL). The solvent was heated to 50 ℃ and stirred overnight under Ar atmosphere. After the reaction, the mixture was neutralized with $NaHCO_3$ (sa, aq) until pH=7. Then the mixture was extracted with dichloromethane three times

and tried with anhydrous Na_2SO_4. The crude material was purified by flash chromatography to give the desired white solid **c**. Yield: 80 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 1H), 8.66 (dd, *J* = 6.7, 2.0 Hz, 1H), 8.56 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.88 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 (dd, *J* = 7.5, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.71, 156.70, 155.00, 152.33, 149.34, 137.95, 137.11, 125.17, 124.33, 121.43, 121.29. HR-ESI-MS m/z: [**c**]$^+$, Calcd for $C_{11}H_8N_2O^+$ 184.0637; found 184.0655.

Synthesis of **d**

Compound **c** (184 mg, 1 mmol), **j** (272 mg, 2 mmol) and molecular sieves (five grains) were added to toluene (10 mL).The reaction mixture was stirred at 100 ℃ overnight under Ar atmosphere. Next the cooled mixture was filtered and purified by flash chromatography to give the desired product as a yellow solid **d**. Yield: 64 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, J = 5.5 Hz, 1H), 8.51 (d, J = 7.7 Hz, 1H), 8.43 (d, J = 7.6 Hz, 1H), 7.96 – 7.80 (m, 3H), 7.37 – 7.29 (m, 1H), 6.74 (dd, J = 5.0, 3.2 Hz, 2H), 6.47 (dd, J = 5.1, 3.3 Hz, 2H), 5.23 (s, 1H), 2.72 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.12 , 149.22 , 142.19 , 138.04 , 136.91 , 123.74 , 122.21 , 121.23 , 120.99 , 119.36 , 105.84 , 94.24 , 46.29 , 33.77 , 11.68. HR-ESI-MS m/z: [**d**]$^+$, Calcd for $C_{19}H_{18}N_4^+$ 302.1531; found 302.1588.

Synthesis of **e**

e was synthesized according to a previously reported procedure.[2] A 250 mL round-bottom flask was charged with $NiCl_2{\cdot}6H_2O$ (0.12 g, 0.5 mmol) and DMF (20 mL). the resulting solution was stirred and heated to 40 ℃, and then **a** (0.46 g, 2 mmol), anhydrous LiCl (0.084 g, 2 mmol), and zinc dust (0.157 g, 2.4 mmol) were added. When the temperature rose to 50 ℃, a grain of iodine crystal and two drops of acetic acid were added to the mixture. An immediate rise in temperature and color change to black was caused, indicating the reaction was triggered. The mixture was stirred at 55-60 ℃ for 3 h until complete conversion of **a** (monitored by TLC). The cooled reaction mixture was filtrated with a pad of celite and aqueous ammonia (25 %) added. Then the mixture was taken up with dichloromethane two times. The organic layers were collected, dried over anhydrous Na_2CO_3, and concentrated. The crude material was purified by flash chromatography to give the desired pale oil product **e**. Yield: 55 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (dd, J = 7.9, 1.0 Hz, 2H), 7.85 (t, J = 7.8 Hz, 2H), 7.55 (dd, J = 7.7, 0.9 Hz, 2H), 5.95 (s, 2H), 4.24 – 4.11 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.50 , 155.35 , 137.63 , 121.62 , 120.56 , 104.03 , 65.65. HR-ESI-MS m/z: [**e**]$^+$, Calcd for $C_{16}H_{16}N_2O_4^+$ 300.1110; found 300.1121.

Synthesis of **f**

f was synthesized according to a previously reported procedure.[3] **e** was dissolved in THF (5 mL). Then HCl (1 mL) and H_2O (5 mL). The solvent was heated to 50 ℃ and stirred overnight under Ar atmosphere. After the reaction, the mixture was neutralized with $NaHCO_3$ (sa, aq) until pH=7. Then the mixture was extracted with dichloromethane three times and tried with anhydrous Na_2SO_4. The crude material was purified by flash chromatography to give the desired white soild **f**. Yield: 73 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.01 (s, 2H), 7.93 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.78 – 7.72 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.69 , 153.48 , 142.58 , 139.36 , 132.69 , 120.35. HR-ESI-MS m/z: [**f**]$^+$, Calcd for $C_{12}H_8N_2O_2^+$ 212.0586; found 212.0531.

Synthesis of **g**

Compound **f** (212 mg, 1 mmol), **j** (272 mg, 2 mmol) and molecular sieves (five grains) were added to toluene (10 mL) . The reaction mixture was stirred at 100 ℃ overnight under Ar atmosphere. Next the cooled mixture was filtered and purified by flash chromatography to give the desired product **g** as a yellow solid. Yield: 52 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.73 (dd, *J* = 5.4, 3.2 Hz, 4H), 6.45 (dd, *J* = 5.4, 3.2 Hz, 4H), 5.12 (s, 2H), 2.67 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.54 , 141.85 ,

140.90 , 139.46 , 128.13 , 121.40 , 119.56 , 105.97 , 93.37 , 33.83. HR-ESI-MS m/z: [**g**]$^+$, Calcd for $C_{28}H_{28}N_6^+$ 448.2375, found 448.2389.

Synthesis of **h**

h was synthesized according to a previously reported procedure.[4] *o*-Phenylenediamine (1.0 eq) was added slowly to a solution of p-toluenesulfonyl choride (2.0 eq) in pyridine 50 mL which was cooled to 0 ℃ in an ice bath. The resulting mixture was stirred at room temperature for 18 h. After slow addition of 15 % aqueous HCl, a precipitate was formed. The solids was filtered by sucking filtration. The soild was recrystallized from ethanol. After recrystallized, compound **h** was obtained as a pale soild. Yield: 78 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.2 Hz, 4H), 7.22 (d, *J* = 8.2 Hz, 4H), 7.03 (dd, *J* = 6.0, 3.4 Hz, 2H), 6.96 (dd, *J* = 5.9, 3.6 Hz, 2H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.18 , 135.49 , 130.88 , 129.62 , 127.54 , 127.35 , 126.22 , 21.61. HR-ESI-MS m/z: [**h**]$^+$, Calcd for $C_{20}H_{20}N_2O_4S_2^+$ 416.0864; found 416.0855.

Synthesis of **i**

i was synthesized according to a previously reported procedure.[5] Compound **h** (12.5 g, 30 mmol), K_2CO_3 (16.8 g, 120 mmol) were dissolved in 80 mL MeCN. After stirred for 1 h , MeI (5.6 mL, 90 mmol) was added dropwise at 0 ℃ in an ice bath. The ice bath was removed and the mixture was refluxing overnight. The reaction mixture was cooled to room temperature and filtered by a pad of celite. The reaction was quenched with water and the product precipitated. The product was filtered off, washed with water and dried under vacuum. The product **i** was isolated as an white soild and used without futher purification. Yield: 64 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.26 – 7.23 (m, 2H), 6.91 (dd, *J* = 5.8, 3.6 Hz, 2H), 3.21 (s, 6H), 2.46 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.69 , 141.14 , 134.87 , 129.56 , 128.92 , 128.40 , 128.35 , 38.73 , 21.60. HR-ESI-MS m/z: [**i**]$^+$, Calcd for $C_{22}H_{24}N_2O_4S_2^+$ 444.1177; found 444.1103.

Synthesis of **j**

j was synthesized according to a previously reported procedure.[6] Compound **i** (5.5 g) was dissolved in 90 % aq. H_2SO_4 (5.5 mL) and the mixture was stirred at 100 ℃ for 8 h. Then the solution was poured into ice and NaOH was added until pH~11 was reached. After stirring for 1 h, the product was extracted with Et_2O. The organic layer was dried with anhydrous Na_2SO_4 and concentration *in vacuo* gave the desired product **j** in satisfactory purity as a brown oil. Yield: 85 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (dd, J = 5.7, 3.4 Hz, 2H), 6.67 (dd, J = 5.7, 3.5 Hz, 2H), 2.85 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.35 , 119.08 , 110.51 , 31.08. HR-ESI-MS m/z: [**j**]$^+$, Calcd for $C_8H_{12}N_2^+$ 136.1000; found 136.1013.

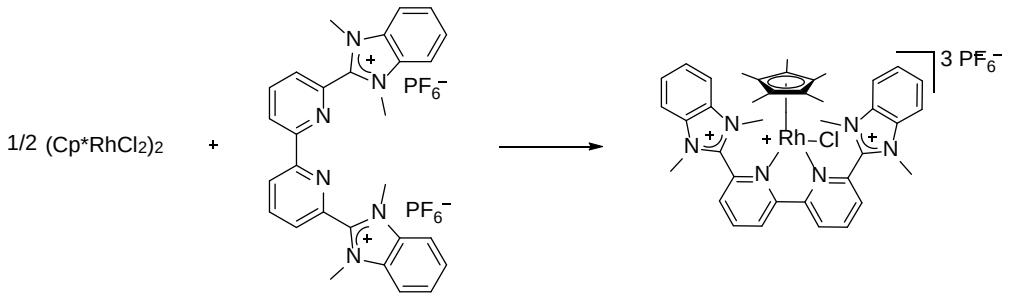
Synthesis of **L1**

Compound **d** (30.2 mg, 0.1 mmol) was dissolved in 2 mL MeOH and then HPF_6 (2.0 eq) was added to the solution. Next the mixture was stirred for 24 h until complete conversion of **d** (monitored by TLC). After the reaction, the Et_2O was added to the mixture to participate the brown soild **L1**. Yield: 74 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79 (t, J = 5.9 Hz, 2H), 8.49 – 8.39 (m, 2H), 8.28 – 8.16 (m, 3H), 8.03 (t, J = 7.5 Hz, 1H), 7.83 (dd, J = 6.2, 3.0 Hz, 2H), 7.61 – 7.53 (m, 1H), 4.15 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.94, 154.17, 150.14, 147.70, 140.85, 139.98, 138.21, 132.20, 128.80, 127.69, 125.68, 124.17, 121.56, 114.18, 33.75. HR-ESI-MS m/z: [**L1**]$^+$, Calcd for $C_{19}H_{17}F_6N_4P^+$ 446.1101; found 446.1113. Elemental analysis: calcd (%) for $C_{19}H_{17}F_6N_4P$ (446.34): C 51.13, H 3.84, N 12.55; found: C 51.23, H 3.75, N 12.43.

Synthesis of **L2**

Compound **g** (44.8 mg, 0.1 mmol) was dissolved in 2 mL MeOH and then HPF_6 (2.0 eq) was added to the solution. Next the mixture was stirred for 24 h until complete conversion of **g** (monitored by TLC). After the reaction, the Et_2O was added to the mixture to participate the pale green soild **L2**. Yield: 71 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (d, *J* = 8.0 Hz, 2H), 8.49 (t, *J* = 7.9 Hz, 2H), 8.34 (d, *J* = 7.6 Hz, 2H), 8.23 (dd, *J* = 6.1, 3.0 Hz, 4H), 7.85 (dd, *J* = 6.1, 2.9 Hz, 4H), 4.17 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.49, 144.49, 141.13, 140.41, 132.23, 129.69, 127.81, 124.75, 114.23, 33.78. HR-ESI-MS m/z: [**L2**]$^+$, Calcd for $C_{28}H_{26}F_{12}N_6P_2^+$ 736.1503; found 736.1522. Elemental analysis: calcd (%) for $C_{28}H_{26}F_{12}N_6P_2$ (736.49): C 45.66, H 3.56, N 11.41; found: C 45.62, H 3.63, N 11.50.

Synthesis of **C1**



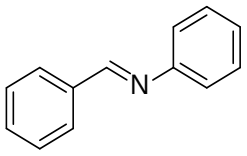
L2 **C1**

Scheme S2. Synthesis of **C1**

Ligand **L2** (44.8 mg, 0.1 mmol), Pentamethylcyclopentadienylrhodium(III) chloride dimer (30.9 mg, 0.05 mmol) were dissolved in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature overnight. After that the solvent was removed under reduced pressure and the resulting residue taken up in the minimum methanol and NH_4PF_6 was added to precipitate the brown soild **C1**. Yield: 85 %. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.82 (d, J = 8.1 Hz, 2H), 8.38 (t, J = 7.9 Hz, 2H), 8.09 (d, J = 7.7 Hz, 2H), 8.00 (dd, J = 6.2, 3.1 Hz, 4H), 7.83 (dd, J = 6.2, 3.1 Hz, 4H), 4.12 (s, 12H), 1.63 (s, 15H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 156.38 , 147.90 , 141.26 , 140.40 , 132.74 , 129.52 , 128.23 , 125.07 , 113.99 , 33.82 , 8.95. Elemental analysis: calcd (%) for $C_{38}H_{41}ClF_{18}N_6P_3Rh$: C 39.52, H 3.58, N 7.28; found: C 39.74, H 3.71, N 7.09.

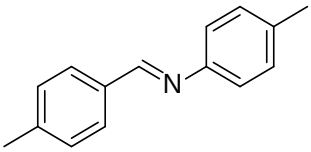
Synthesis of substrates

Unless otherwise specified, substrates preparations were performed in air. Flash chromatography was carried out on 60-200 μm silica gel. Imines were synthesized by refluxing appropriate aldehyde or ketone and appropriate equivats of amine in toluene with a catalytic amount of *p*-toluenesulfonic acid using a Dean-stark apparatus overnight. Removing the solvent *in vacuo* and purified by flash chromatography if necessary to give the products.



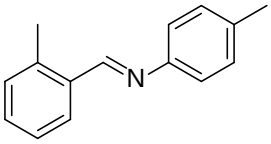
1a

White soild. Yield: 95 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.91 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.48 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.16 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.43 , 152.09 , 136.22 , 131.39 , 129.15 , 128.81 , 128.78 , 125.94 , 120.87 .



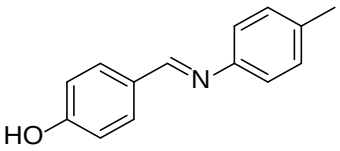
2a

White soild. Yield: 97 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.28 (s, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.39 (d, *J* = 18.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.60 , 149.64 , 141.66 , 135.57 , 133.79 , 129.73 , 129.48 , 128.71 , 120.79 , 21.62 , 21.00 .



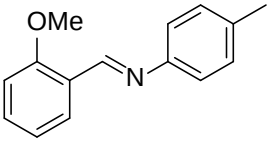
3a

Pale soild. Yield: 98 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 7.75 (s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.40 (d, *J* = 20.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89, 155.40, 142.84, 142.60, 142.28, 133.18, 129.63, 129.07, 127.68, 126.35, 126.27, 120.99, 21.69.



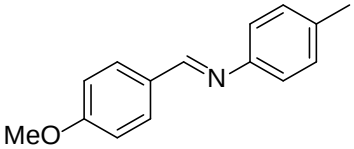
4a

White soild. Yield: 98 %.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.53, 159.59, 149.86, 134.94, 130.99, 130.07, 127.69, 121.24, 116.19, 21.02.



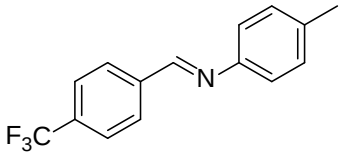
5a

Brown soild. Yield: 94 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.14 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.17 (q, *J* = 8.4 Hz, 4H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.43 , 155.73 , 150.16 , 135.47 , 132.49 , 129.66 , 127.48 , 121.01 , 120.89 , 111.10 , 55.57 , 21.01 .



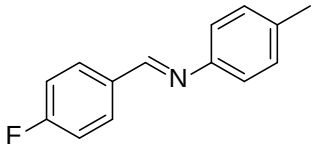
6a

Brown soild. Yield: 92 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.11 , 158.98 , 149.76 , 135.35 , 130.39 , 129.72 , 129.40 , 120.77 , 114.16 , 55.43 , 20.99 .



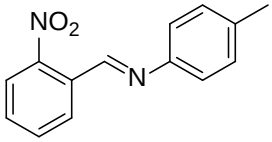
7a

Pale yellow soild. Yield: 98 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.77 .^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.64 , 148.71 , 139.42 , 136.61 , 132.72 , 132.40 , 129.87 , 128.84 , 125.69 (q, J_{FC} = 3.7 Hz), 120.87 , 21.06 .



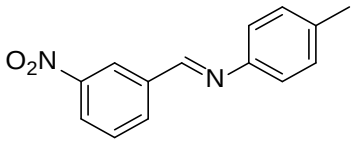
8a

Pale yellow soild. Yield: 98 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.89 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.23 – 7.10 (m, 6H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.42 (p, *J* = 8.4 Hz). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.35 , 158.03 , 149.21 , 135.91 , 132.72 , 130.65 (d, J_{FC} = 8.8 Hz), 129.79 , 120.77 , 115.89 (d, J_{FC} = 22.0 Hz), 21.01 .



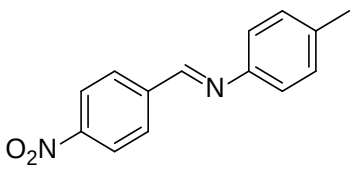
9a

Pale yellow soild. Yield: 93 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.56 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.22, 148.71, 148.23, 138.06, 136.96, 133.95, 129.94, 129.75, 125.39, 123.42, 120.93, 21.09.



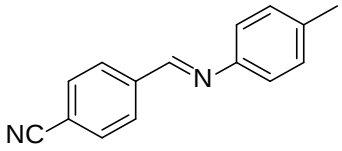
10a

Pale yellow soild. Yield: 89 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.56 (s, 1H), 8.32 (dd, *J* = 9.8, 1.6 Hz, 1H), 8.25 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.22, 148.71, 148.23, 138.06, 136.96, 133.95, 129.94, 129.75, 125.39, 123.43, 120.93, 21.08.



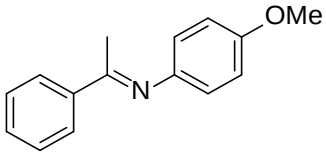
11a

Yellow soild. Yield: 88 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.34 , 148.27 , 141.78 , 137.25 , 129.96 , 129.27 , 124.01 , 121.08 , 120.99 , 21.11 .



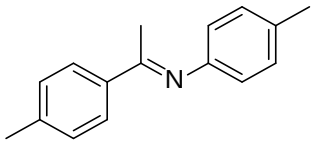
12a

Pale yellow soild. Yield: 89 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.87 , 148.36 , 140.14 , 137.04 , 132.52 , 129.93 , 128.99 , 120.93 , 118.51 , 114.20 , 21.09 .



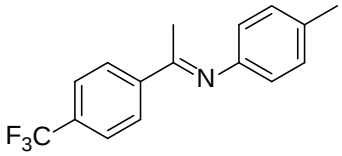
13a

Pale yellow oil. Yield: 79 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.44 (dd, *J* = 5.4, 1.8 Hz, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.77, 155.94, 144.81, 139.77, 130.32, 128.34, 127.11, 120.75, 114.25, 55.50, 17.34.



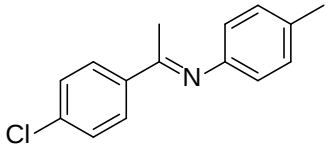
14a

Pale yellow oil. Yield: 75 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.89, 134.73, 129.75, 129.24, 128.45, 127.81, 127.11, 119.46, 115.26, 26.55, 21.65, 20.45.



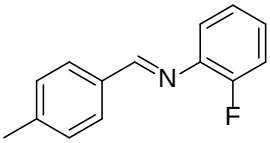
15a

Pale yellow oil. Yield: 60 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H), 2.26 (s, 3H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.71 . ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.29 , 148.48 , 133.13 , 129.59 , 127.48 , 125.29 (q, J_{FC} = 3.8 Hz), 119.23 , 115.27 , 20.88 , 17.38 .



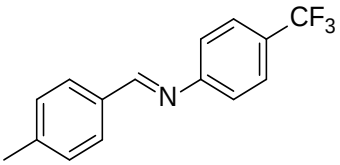
16a

Pale yellow oil. Yield: 81 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.26, 148.72, 138.06, 136.48, 132.84, 129.54, 128.51, 119.33, 20.87, 17.20.



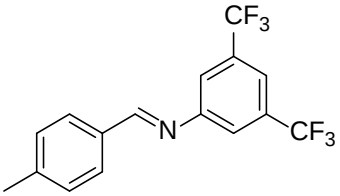
17a

Pale yellow soild. Yield: 85 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.17 – 7.09 (m, 4H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -126.87 (dd, *J* = 8.0, 4.5 Hz).^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.87, 142.32 , 133.46 , 129.52 , 129.00 , 126.49 , 126.42 , 124.45 (d, J_{FC} = 3.9 Hz), 122.01 (d, J_{FC} = 1.9 Hz), 116.30 , 116.10 , 21.68 .



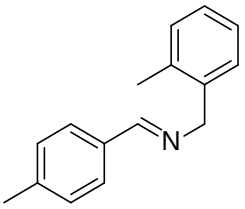
18a

Pale yellow soild. Yield: 79 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.96 .^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.91 , 149.54 , 138.52 , 136.29 , 135.73 , 132.08 , 129.75 , 128.74 (d, J_{FC} = 23.2 Hz), 126.34 , 120.80 , 21.17 (d, J_{FC} = 30.3 Hz).



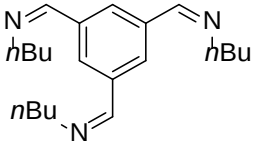
19a

Pale yellow soild. Yield: 88 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.72 (s, 1H), 7.60 (s, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.86 . ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.02 , 153.59 , 143.20 , 132.76 , 132.67 , 132.34 , 129.74 , 129.28 , 121.15, 118.94 (t, J_{FC} = 3.9 Hz), 21.74 .



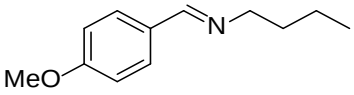
20a

White soild. Yield: 97 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 6H), 4.79 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.79, 140.99, 137.60, 136.20, 133.67, 130.12, 129.32, 128.44, 128.21, 127.06, 126.06, 62.61, 21.52, 19.31.



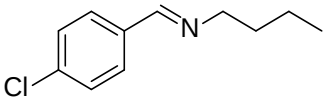
21a

Pale oil. Yield: 67 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 3H), 8.13 (s, 3H), 3.63 (t, *J* = 7.0 Hz, 6H), 1.73 – 1.67 (m, 6H), 1.38 (dt, *J* = 14.7, 7.4 Hz, 6H), 0.95 (t, *J* = 7.4 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.85 , 137.20 , 129.21 , 61.46 , 32.89 , 20.42 , 13.87 .



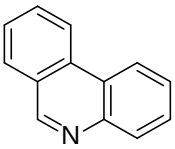
22a

Pale oil. Yield: 78 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.57 (t, *J* = 7.6 Hz, 2H), 1.67 (s, 2H), 1.42 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.45 , 160.06 , 129.52 , 129.34 , 113.95 , 61.39 , 55.35 , 33.13 , 20.47 , 13.92 .



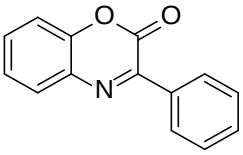
23a

Pale oil. Yield: 73 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 3.60 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.42 – 1.34 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.37 , 136.35 , 134.83 , 129.19 , 128.84 , 61.43 , 32.95 , 20.46 , 13.89 .



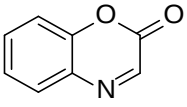
24a

White soild. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 8.64 – 8.57 (m, 2H), 8.20 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.78 – 7.67 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.59, 144.49, 132.58, 131.02, 130.17, 128.78, 128.70, 127.51, 127.10, 126.41, 124.12, 122.23, 121.89.



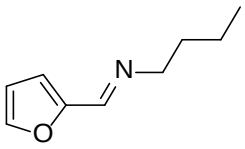
25a

Pale soild. Yield: 57 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55 – 7.48 (m, 4H), 7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.31, 150.90, 146.49, 134.15, 131.69, 131.44, 131.15, 129.47, 129.45, 128.40, 125.59, 116.19.



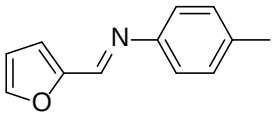
26a

Pale soild. Yield: 53 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.40 (td, *J* = 7.7, 1.3 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.34, 146.35, 146.27, 132.10, 131.22, 129.65, 125.68, 116.84.



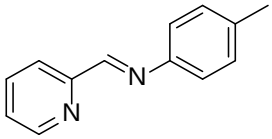
27a

Pale yellow oil. Yield: 89 %.[1]H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.50 (d, *J* = 1.4 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.58 (t, *J* = 7.5 Hz, 2H), 1.70 (dt, *J* = 14.8, 7.2 Hz, 2H), 1.42 – 1.33 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 151.63 , 149.38 , 144.52 , 113.52 , 111.49 , 61.56 , 32.90 , 20.41 , 13.85 .



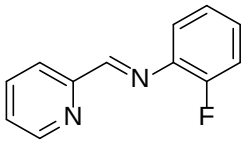
28a

Pale yellow soild. Yield: 92 %.[1]H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.61 (d, *J* = 1.3 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 4H), 6.93 (d, *J* = 3.4 Hz, 1H), 6.55 (dd, *J* = 3.4, 1.7 Hz, 1H), 2.37 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 152.22, 148.76, 146.93, 145.49, 136.18, 129.80, 120.94, 115.92, 112.11, 21.03.



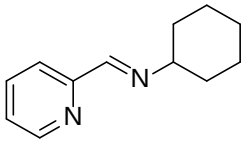
29a

Pale yellow soild. Yield: 82 %. [1]H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.62 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.81 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.23 (s, 4H), 2.39 (s, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 159.70, 154.74, 149.67, 148.34, 136.79, 136.65, 129.87, 124.99, 121.80, 121.11, 21.08.



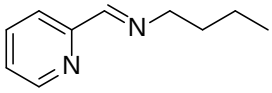
30a

Pale yellow soild. Yield: 83 %.[1]H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 5.3 Hz, 1H), 8.67 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.83 (td, *J* = 7.6, 1.3 Hz, 1H), 7.39 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.20 (tdd, *J* = 10.7, 6.7, 4.2 Hz, 4H). [19]F NMR (376 MHz, Chloroform-*d*) δ -125.82 (ddd, *J* = 10.8, 7.4, 4.9 Hz). [13]C NMR (101 MHz, Chloroform-*d*) δ 163.11 (d, *J* = 2.8 Hz), 156.64 , 154.37 , 149.71 , 138.98 (d, *J* = 10.3 Hz), 136.72 , 127.59 (d, J_{FC} = 7.7 Hz), 125.44 , 124.59 (d, J_{FC} = 3.9 Hz), 121.99 , 121.78 (d, J_{FC} = 1.5 Hz), 116.39 (d, J_{FC} = 20.1 Hz).



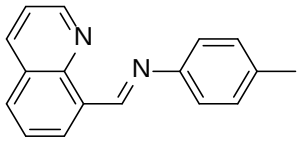
31a

Pale yellow oil. Yield: 72 %.[1]H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 4.8 Hz, 1H), 8.40 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.73 (td, *J* = 7.7, 1.6 Hz, 1H), 7.30 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.30 (ddd, *J* = 14.6, 9.4, 4.1 Hz, 1H), 1.87 – 1.71 (m, 5H), 1.63 – 1.53 (m, 2H), 1.42 – 1.25 (m, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 159.52, 154.92, 149.37, 136.50, 124.50, 121.39, 69.66, 34.18, 25.62, 24.71.



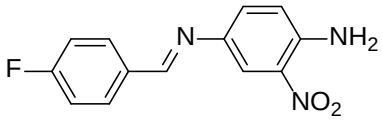
32a

Pale oil. Yield: 67 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 5.4 Hz, 1H), 8.38 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.74 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 3.68 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.66 (m, 2H), 1.39 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.69, 154.66, 149.39, 136.54, 124.59, 121.18, 61.26, 32.77, 20.43, 13.87.



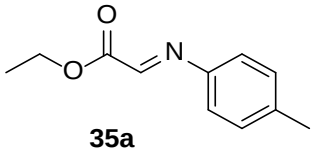
33a

Yellow oil. Yield: 43 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.98 (d, *J* = 5.6 Hz, 1H), 8.64 (d, *J* = 7.3 Hz, 1H), 8.22 (d, *J* = 9.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.30, 150.20, 149.85, 147.02, 136.35, 135.91, 133.28, 130.85, 129.70, 128.31, 127.76, 126.57, 121.39, 121.33, 21.07.



34a

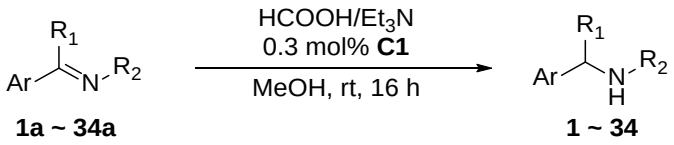
Yellow soild. Yield: 98 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.05 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.43 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.11 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.77 (m).^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.50 , 143.17 , 141.34 , 132.33 (d, J_{FC} = 3.1 Hz), 130.91 , 130.77 , 130.68 , 119.44 , 116.55 , 116.14 , 115.92 .



35a

Yellow oil. Yield: 57 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.23 (s, 4H), 4.42 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 150.0, 146.3, 139.0, 130.0, 121.6, 62.0, 21.2, 14.2.

2. General Methods of the catalytic hydrogenation of imines



1a ~ 34a **1 ~ 34**

Scheme S3. Catalytic C=N bonds hydrogenation by **C1**

Imine (0.05 mmol), HCOOH/Et_3N (2.0 eq) , **C1** (0.3 mol%), MeOH (2 mL) and a magnetic stir were placed in Schlenk Tube. Then the mixture was stirred for 16 h under the atmosphere of Ar. After the reaction, the reaction mixture (200 μL) was sampled and dried in the vacuum for 3 h. Then the residue was taken up with $CDCl_3$. For **35a**, no amine formation was detected. The yield was determined by ^1H NMR according to the following equation:

Yield of amine = mole of amine / (mole of amine + mole of imine)

Yield of amine = integration of peak of amine / (integration of peak of amine + integration of peak of imine)

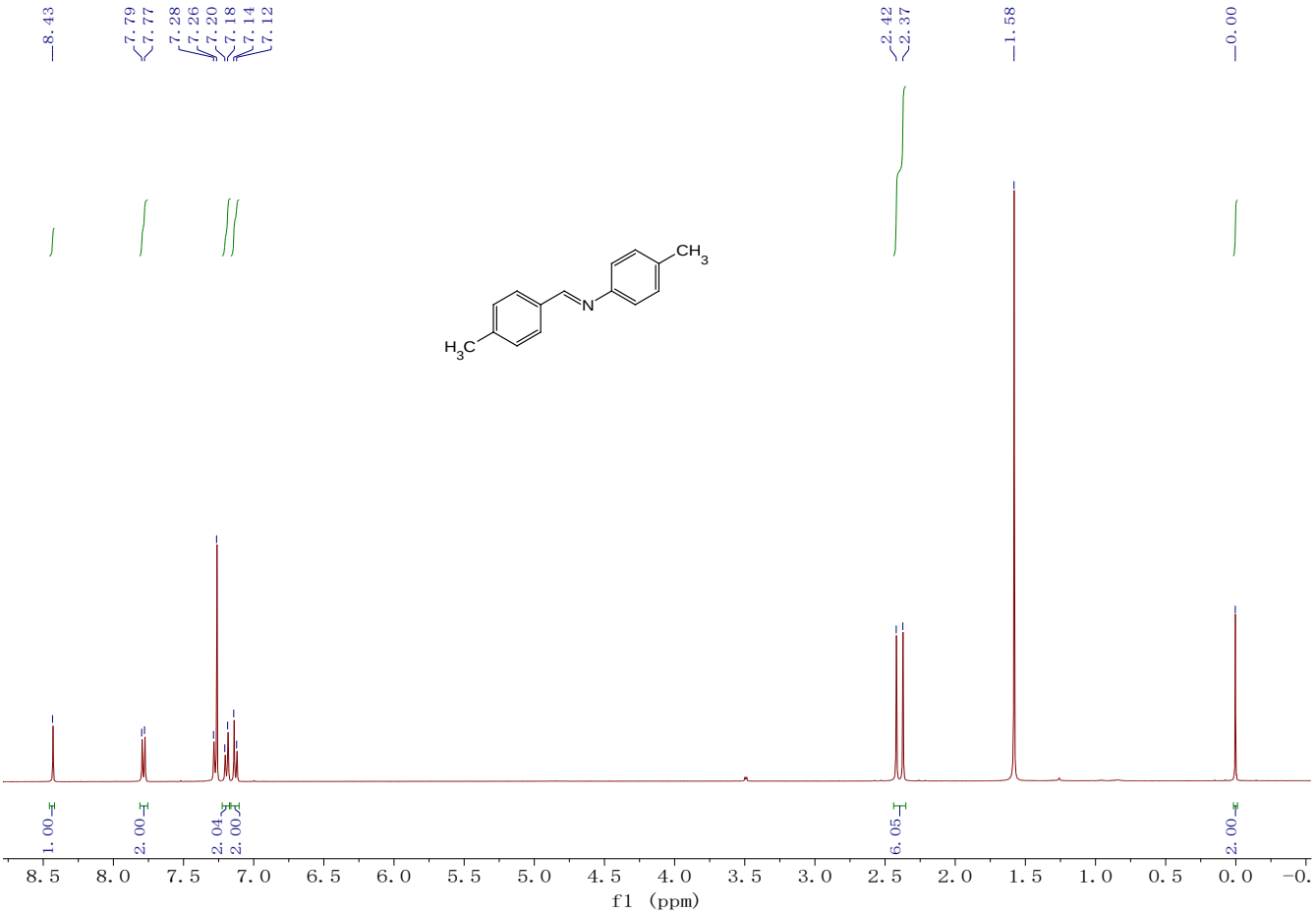


Figure S1. ^1H NMR Spectra of substrate Imine **2a**

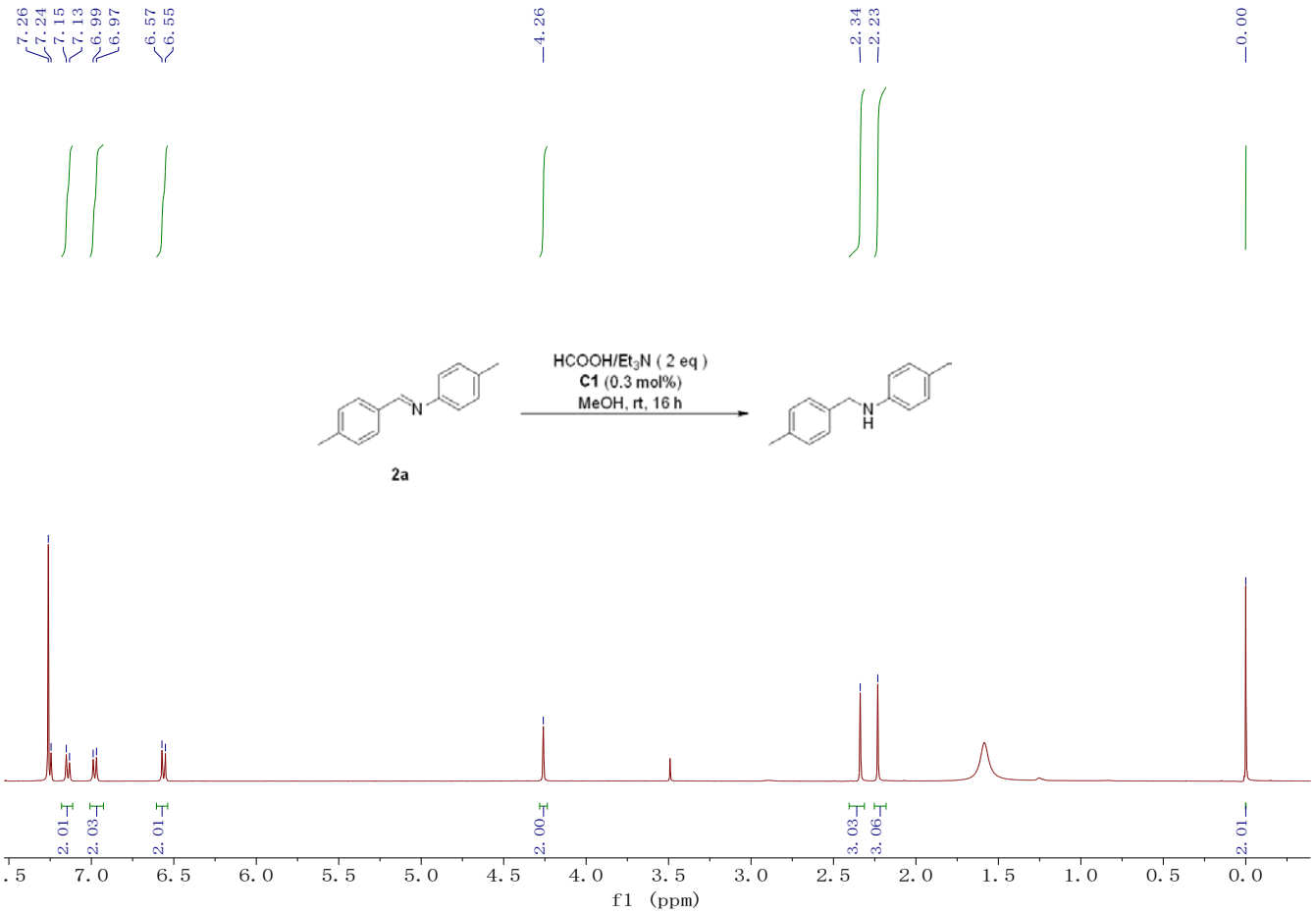
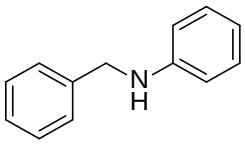
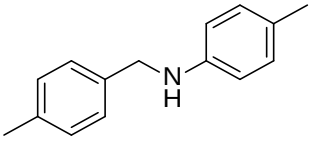


Figure S2. ^{1}H NMR Spectra of the reaction mixture after 16 h



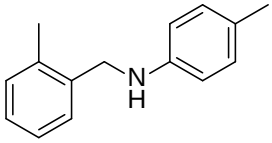
1

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.03 (br s, 1H), 4.33 (s, 2H), 6.64 (d, J = 7.5 Hz, 2H), 6.73 (t, J = 6.8 Hz, 1H), 7.17 (t, J = 7.1 Hz, 1H), 7.24-7.42 (m, 5H).



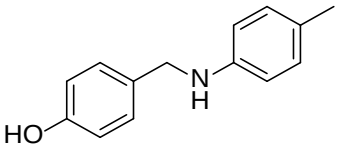
2

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, J=7.8Hz, 2H), 7.06 (d, J=7.9Hz, 2H), 6.95-6.84 (m, 2H), 6.51-6.46 (m, 3H), 4.18 (s, 2H), 2.26 (s, 3H), 2.16 (s, 3H)



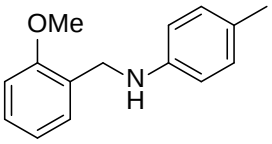
3

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (dt, *J* = 14.1, 7.5 Hz, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.26 (s, 2H), 2.35 (s, 3H), 2.24 (s, 3H).



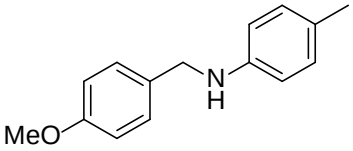
4

NMR yield: 94 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H),6.60 (d, J = 8.4 Hz, 2H), 4.23 (s, 2H), 2.27 (s, 3H)



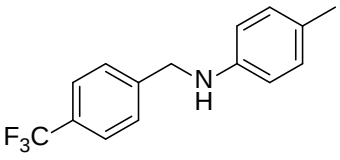
5

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 9.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.94 – 6.85 (m, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.31 (s, 2H), 3.86 (s, 3H), 2.23 (s, 3H).



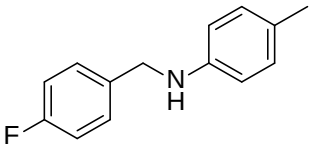
6

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.23 (s, 2H), 3.80 (s, 3H), 2.23 (s, 3H).



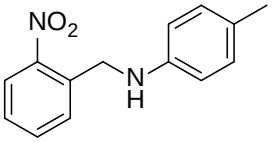
7

NMR yield: 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ: 7.57 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.37 (s, 2H), 3.99 (br s, 1H), 2.23 (s, 3H).



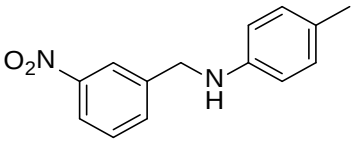
8

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 2H), 7.11 – 6.87 (m, 4H), 6.54 (d, *J* = 7.1 Hz, 2H), 4.28 (s, 2H), 2.23 (s, 3H).



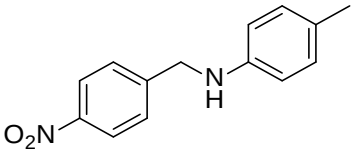
9

NMR yield: 60 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.41 (td, *J* = 7.8, 7.2, 1.4 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.56 – 6.42 (m, 2H), 4.71 (s, 2H), 2.22 (s, 3H).



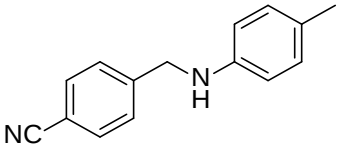
10

NMR yield: 83 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 4.44 (s, 2H), 2.23 (s, 3H).



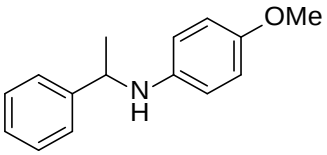
11

NMR yield: 42 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.50 (d, *J* = 8.3 Hz, 2H), 4.46 (s, 2H), 2.23 (s, 3H).



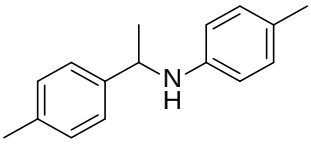
12

NMR yield: 56 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 4.41 (d, J = 5.6 Hz, 2H), 2.23 (s, 3H).



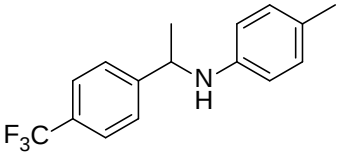
13

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m,4H), 7.25 – 7.19 (m, 1H), 6.72 – 6.66 (m, 2H), 6.51 – 6.44 (m, 2H), 4.41 (q, J = 6.7 Hz,1H), 3.69 (s, 3H), 1.50 (d, J = 6.7 Hz, 3H)



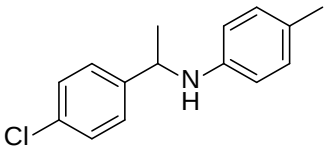
14

NMR yield: 90 %.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 6.43 (d, J = 8.4 Hz, 2H), 4.42 (q, J = 6.7 Hz, 1H), 2.31 (s, 3H), 2.18 (s, 3H), 1.48 (d, J = 6.7 Hz, 3H).



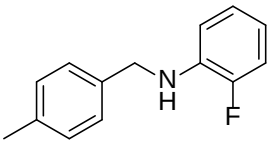
15

NMR yield: 50 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.44 (d, J = 8.5 Hz, 2H), 4.52 (q, J = 6.5 Hz, 1H), 2.21 (s, 3H), 1.54 (d, J = 6.5 Hz, 3H)



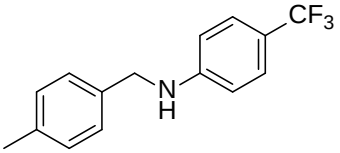
16

NMR yield: 55 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43−7.30 (m, 4H), 7.00 (d, J = 8.2 Hz, 2H), 6.49 (d, J = 8.4 Hz, 2H), 4.50 (q, J = 6.7 Hz, 1H), 3.96 (s, 1H), 2.29 (s, 3H), 1.55 (d, J = 6.7 Hz, 3H)



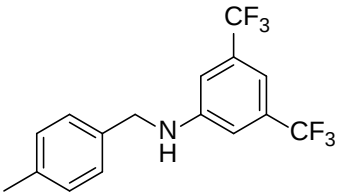
17

NMR yield: 90 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 5.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.88 (m, 2H), 6.74 – 6.56 (m, 2H), 4.40 – 4.29 (m, 2H), 2.35 (s, 3H).



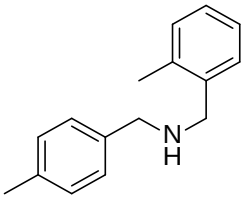
18

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.09 (m, 4H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.33 (s, 2H), 2.35 (s, 3H).



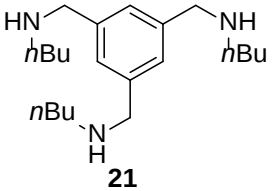
19

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.13 (m, 5H), 6.96 (s, 2H), 4.32 (d, *J* = 5.3 Hz, 2H), 2.36 (s, 3H).



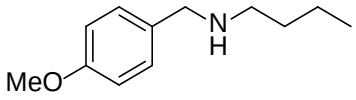
20

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 5.2 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 4H), 3.85 (s, 2H), 3.45 (s, 2H), 2.27 (d, *J* = 36.7 Hz, 6H).



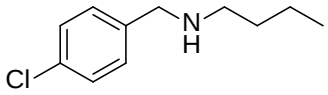
21

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (s, 3H), 3.82 (s, 6H), 2.82 – 2.64 (m, 6H), 1.59 (p, *J* = 7.5 Hz, 6H), 1.40 – 1.31 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H).



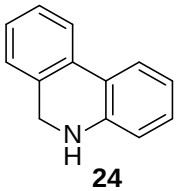
22

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 2H), 3.75 (s, 3H), 2.72 – 2.65 (m, 2H), 1.57 (p, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).



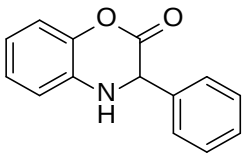
23

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 2H), 2.84 – 2.51 (m, 2H), 1.71 – 1.49 (m, 2H), 1.29 (dq, *J* = 15.1, 7.4 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).



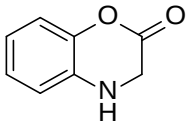
24

NMR yield: 54 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73-7.67 (m, 2 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.22 (t, J = 8.1 Hz, 1H), 7.12 (t, J = 6.7 Hz, 2 H), 6.86 (d, J = 7.9 Hz, 1 H), 6.67 (d, J = 7.9 Hz, 1 H), 4.40 (s, 2 H).



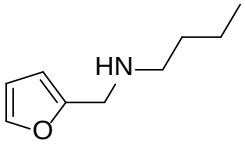
25

NMR yield: 40%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43–7.35 (m, 5H), 7.06–7.01 (m, 2H), 6.87 (td, J = 7.0, 1.6 Hz, 1H), 6.82 (dd, J = 7.6,1.6 Hz, 1H), 5.07 (s, 1H), 4.26 (s, 1H).



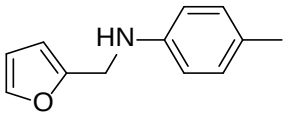
26

NMR yield: 54 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.74 (td, *J* = 7.6, 1.4 Hz, 1H), 6.62 – 6.56 (m, 1H), 6.48 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.93 (s, 2H).



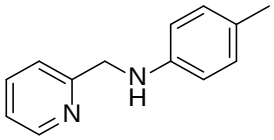
27

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (s, 1H), 6.34 (s, 2H), 3.94 (s, 2H), 2.75 – 2.69 (m, 2H), 1.61 – 1.55 (m, 2H), 1.38 – 1.32 (m, 2H), 0.90 (d, *J* = 7.3 Hz, 3H).



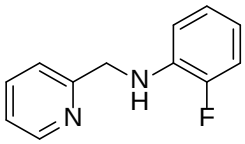
28

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 8.2 Hz, 2H), 6.31 (s, 1H), 6.21 (s, 1H), 4.29 (s, 2H), 2.24 (s, 3H).



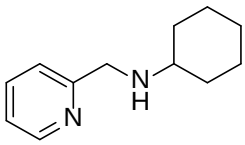
29

NMR yield: 75 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.3 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.15 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.45 (s, 2H), 2.24 (s, 3H).



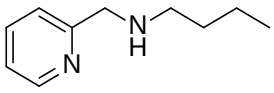
30

NMR yield: 65 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 4.9 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.01 – 6.92 (m, 2H), 6.68 – 6.57 (m, 2H), 4.50 (s, 2H).



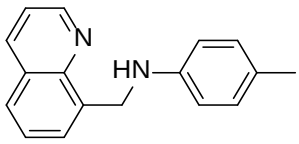
31

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.7 Hz, 1H), 8.45 (s, 1H), 7.69 (t, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 4.16 (s, 2H), 2.04 (d, *J* = 10.5 Hz, 2H), 1.80 (d, *J* = 10.1 Hz, 2H), 1.64 (s, 1H), 1.30 (dt, *J* = 47.0, 9.8 Hz, 6H).



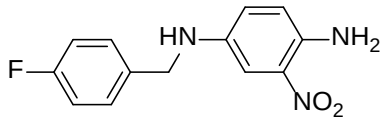
32

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.9 Hz, 1H), 8.44 (s, 1H), 7.76 – 7.70 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 4.21 (s, 2H), 2.95 – 2.88 (m, 2H), 1.71 (dt, *J* = 15.3, 7.1 Hz, 2H), 1.43 – 1.37 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).



33

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.51 – 7.40 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 4.96 (s, 2H), 2.21 (s, 3H).



34

NMR yield: 99 %. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 3H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.85 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 1H), 4.26 (s, 2H).

3. Control experiments and mechanisms study

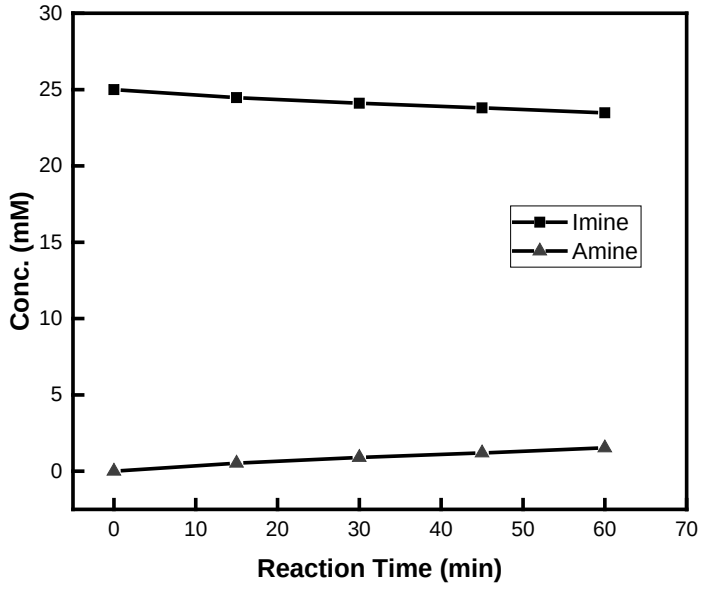


Figure S3. Relationship between concentration and reaction time

Reaction conditions: a mixture of imine **11a** (25 mM), HCOOH/Et_3N (50 mM), **C1** (75 μM) and MeOH (2 mL) was stirred under the atmosphere of Ar at room temperature.

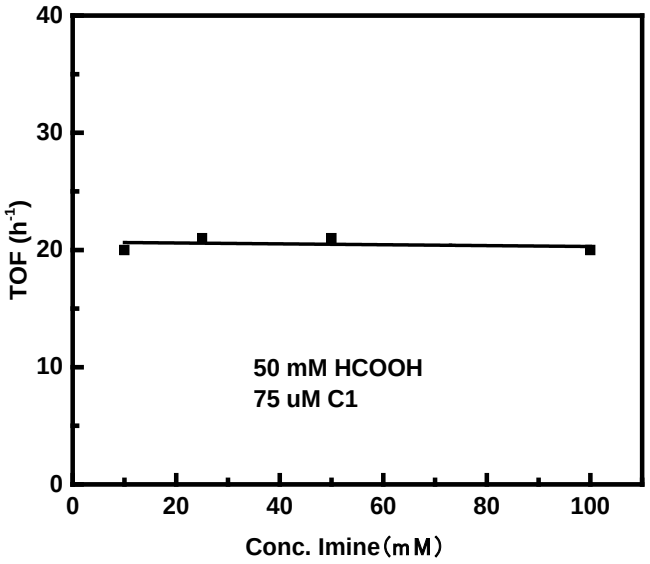


Figure S4. Relationship between TOF and concentration of imine

Reaction conditions: A mixture of Imine **11a** (different concentrations), HCOOH/Et_3N (50 mM), **C1** (75 μM) and MeOH (2 mL) was stirred for 1 h under the atmosphere of Ar at room temperature.

The TOF was calculated according to the following equation:

TOF = mole of amine / (mole of catalyst × reaction time)

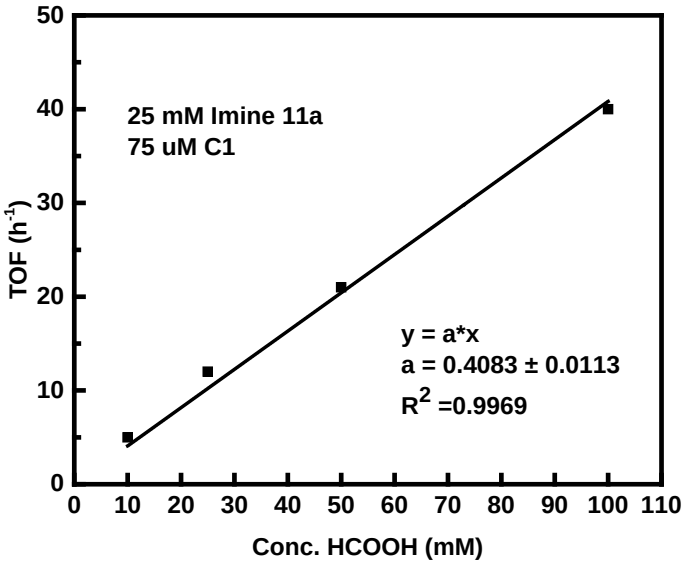
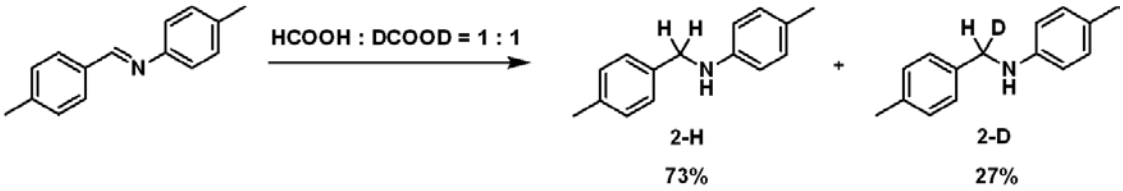


Figure S5. Relationship between TOF and Concentration of HCOOH

Reaction conditions: A mixture of Imine **11a** (25 mM), HCOOH/Et_3N (different concentrations), **C1** (75 μM), MeOH (2 mL) was stirred for 2 h under the atmosphere of Ar at room temperature.



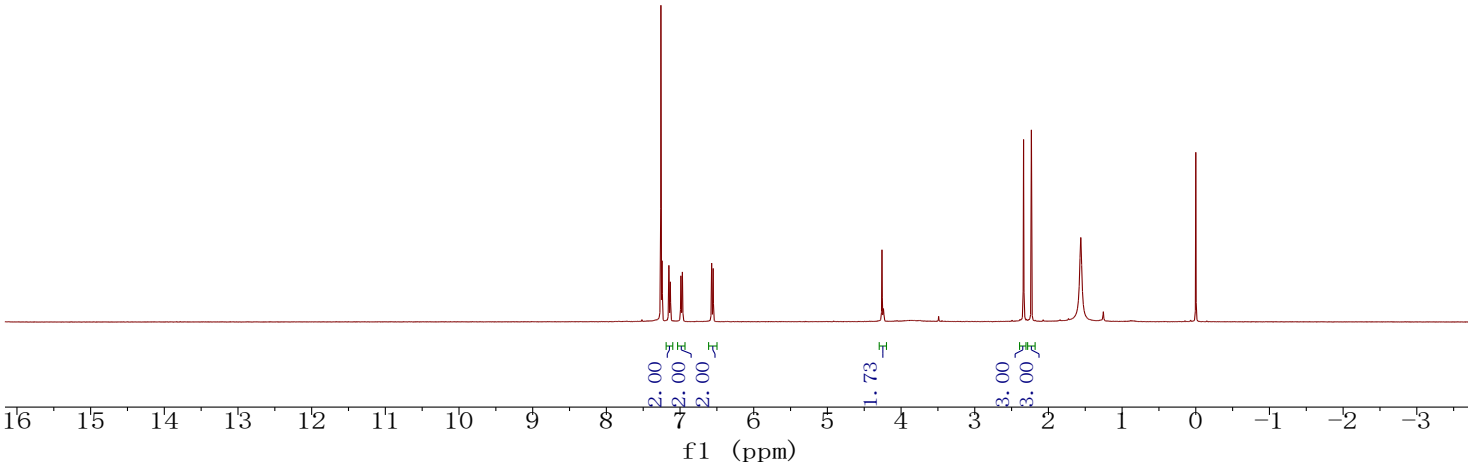


Figure S6. The catalytic imine reduction using HCOOH : DCOOD =1 : 1 as reductant by **C1**

Reaction conditions: a mixture of imine **2a** (25 mM), HCOOH : DCOOD=1 : 1 (50 mM : 50 mM), **C1** (75 μM) and MeOH (2 mL) was stirred for 16 h under the atmosphere of Ar. After that, the reaction mixture (200 μL) was sampled and dried in vacuum for 3 h. The yield was determined by ^{1}H NMR.

The kinetic isotope effect was calculated as the following equation:

$$\frac{\mathrm{d}C_A}{\mathrm{dt}} = kC_{HCOOH}$$

where C_A is the concentration of generated amine; C_{HCOOH} is the concentration of formate; t is reaction time.

$$C_{HCOOH} = C_0 - C_A$$

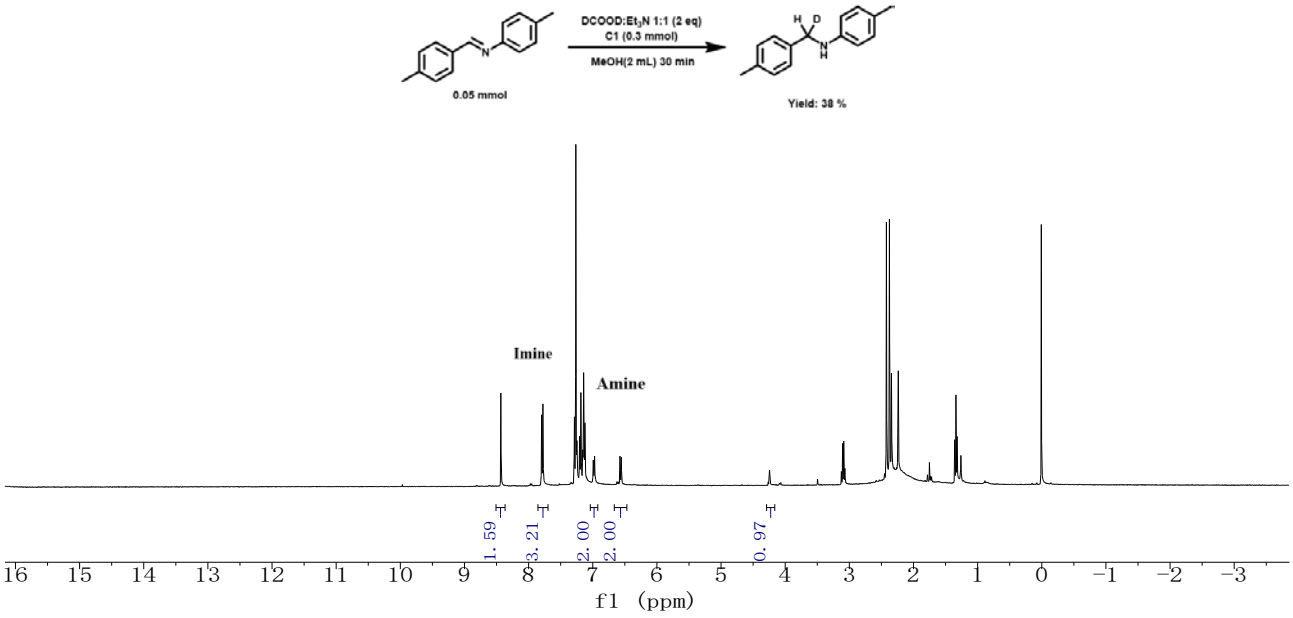
where C_0 is the initial concentration of formate.

$$\frac{\mathrm{d}C_A}{\mathrm{dt}} = k(C_0 - C_A)$$

$$k\mathrm{dt} = \frac{1}{C_0 - C_A}\mathrm{d}C_A$$

$$k\mathrm{t} = \ln C_0 - \ln(C_0 - C_A)$$

$$KIE = \frac{k_H}{k_D} = \frac{\ln C_0 - \ln(C_0 - C_{A(H)})}{\ln C_0 - \ln(C_0 - C_{A(D)})} = \frac{\ln \frac{C_0}{C_0 - C_{A(H)}}}{\ln \frac{C_0}{C_0 - C_{A(D)}}} = \frac{\ln \frac{50}{50 - 25\times 73\%}}{\ln \frac{50}{50 - 25\times 27\%}} = 3.13$$



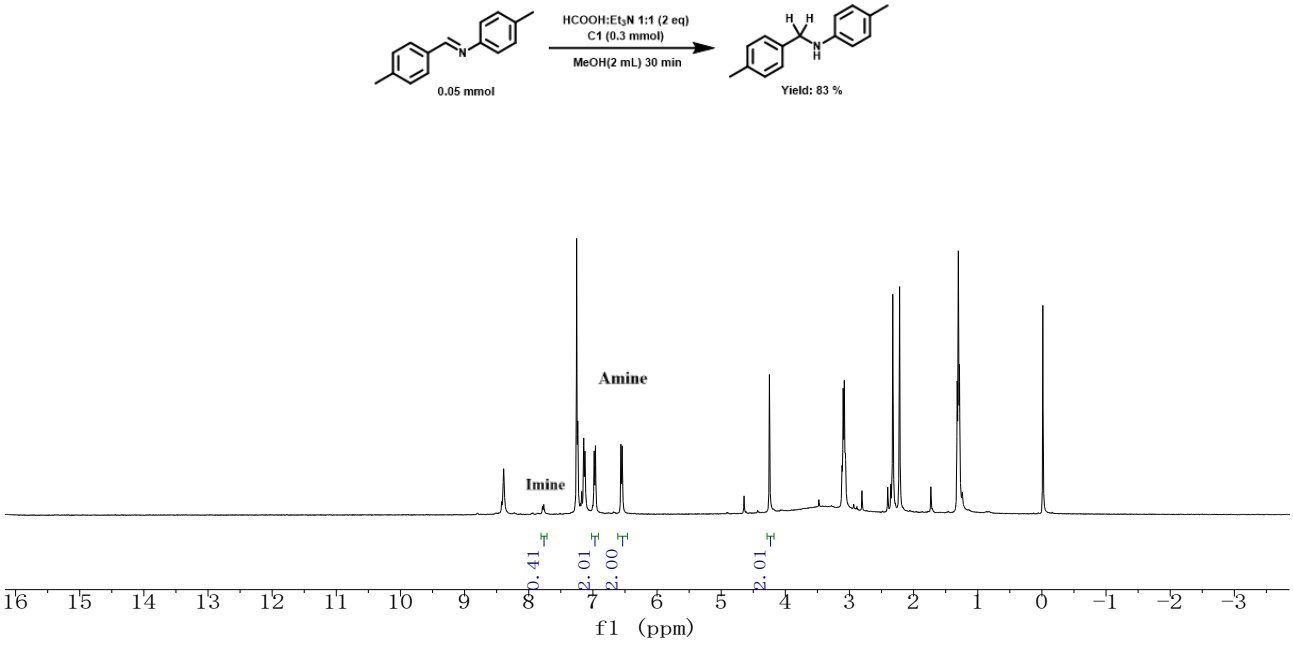


Figure S7. Isotope experiments performed in parallel reactions

Reaction conditions: a mixture of imine **2a** (25 mM), H(D)COOH(D) : Et_3N=1 : 1 (50 mM) , **C1** (75 μM) and MeOH (2 mL) was stirred for 0.5 h under the atmosphere of Ar. After that, the reaction mixture (200 μL) was sampled and dried in vacuum. The yield was determined by ^1H NMR.

$$KIE = \frac{k_H}{k_D} = \frac{\ln C_0 - \ln (C_0 - C_{A(H)})}{\ln C_0 - \ln (C_0 - C_{A(D)})} = \frac{\ln \dfrac{C_0}{C_0 - C_{A(H)}}}{\ln \dfrac{C_0}{C_0 - C_{A(D)}}} = \frac{\ln \dfrac{50}{50 - 25\times 83\%}}{\ln \dfrac{50}{50 - 25\times 38\%}} = 2.55$$

In order to explore the reaction mechanism, the NMR Experiments were performed. We added 1 eq. formate to the NMR tube which containing **C1**. Within 10 minutes, formate gave rise to new peaks at 6.3-6.7 ppm and at 5.1 ppm in the ^{1}H NMR spectrum of **C1**, which were attributed to the formation of dihydrobenzoimidazole. Then we added 1 eq. imine **2a** into the NMR tube. After addition of imine **2a** within 10 minutes, the singals of reduced cofactor mimics (H_1~H_5, 6.3-6.7 ppm, 5.1 ppm) disappeared and amine **2** was detected.

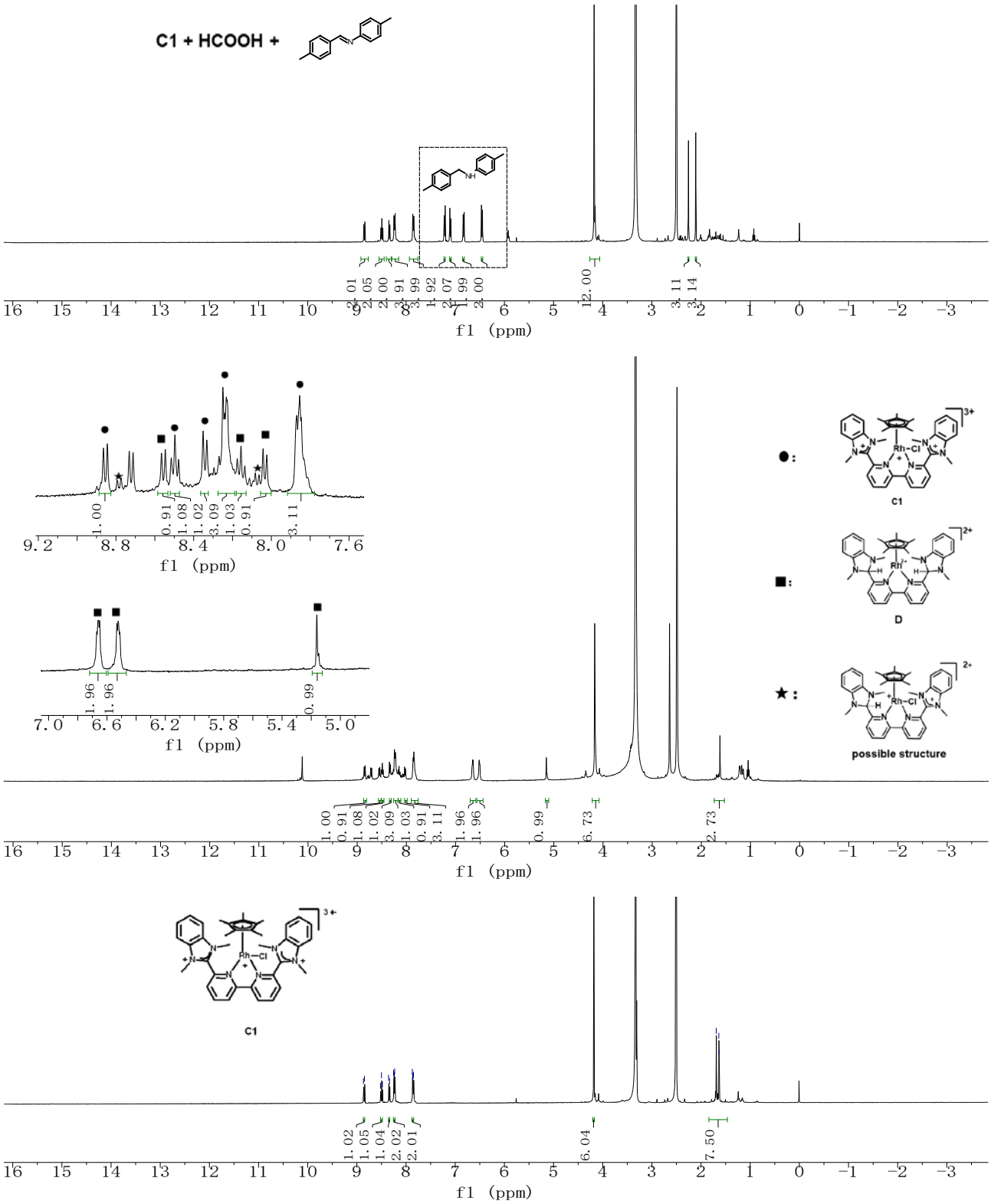


Figure S8. NMR Spectra of **C1** in the presence of formate (**C1** with 1eq. HCOOH; top: to middle sample containing **C1** with 1eq. HCOOH, 1eq. Imine **2a** was added)

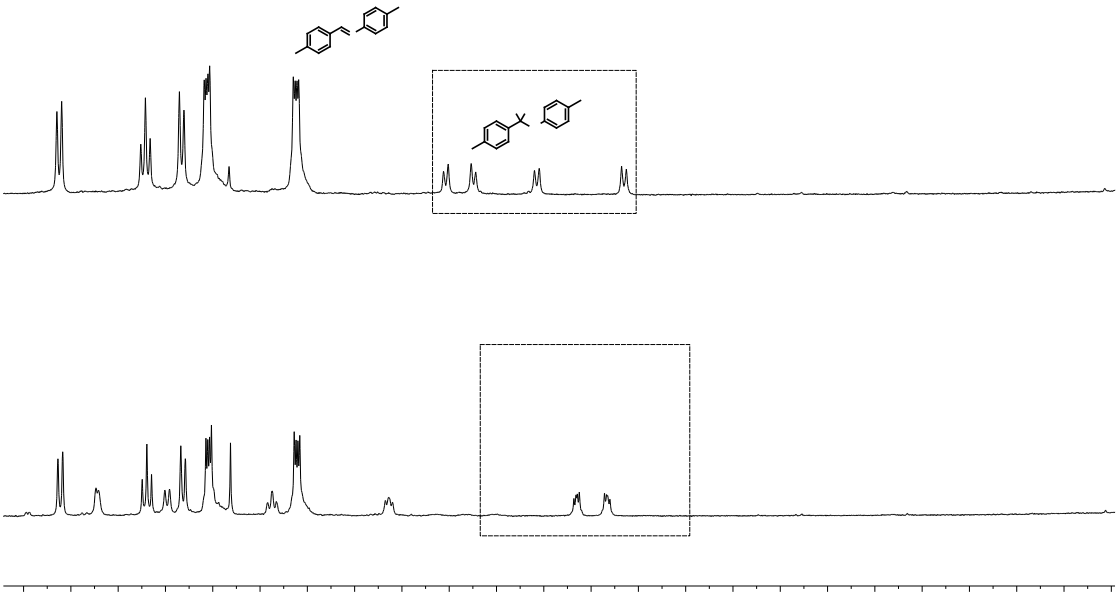


Figure S9. NMR Spectra of **C1** in the presence of DCOOD and imine (bottom: **C1** with DCOOD; top: Imine **2a** was added to bottom sample until H_1-H_4 signals disappeared)

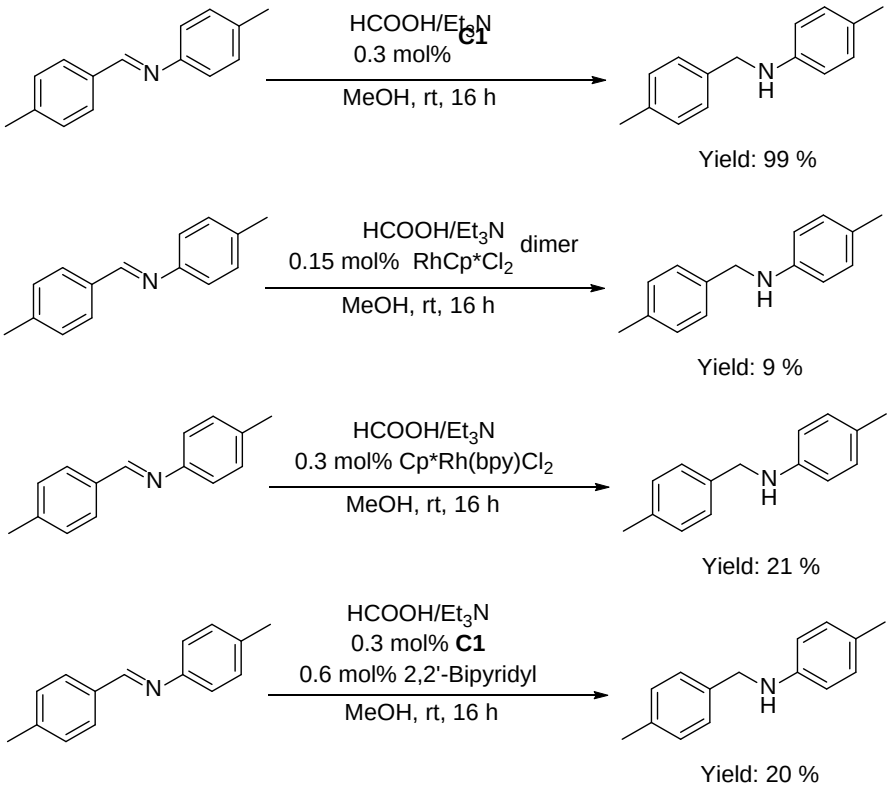
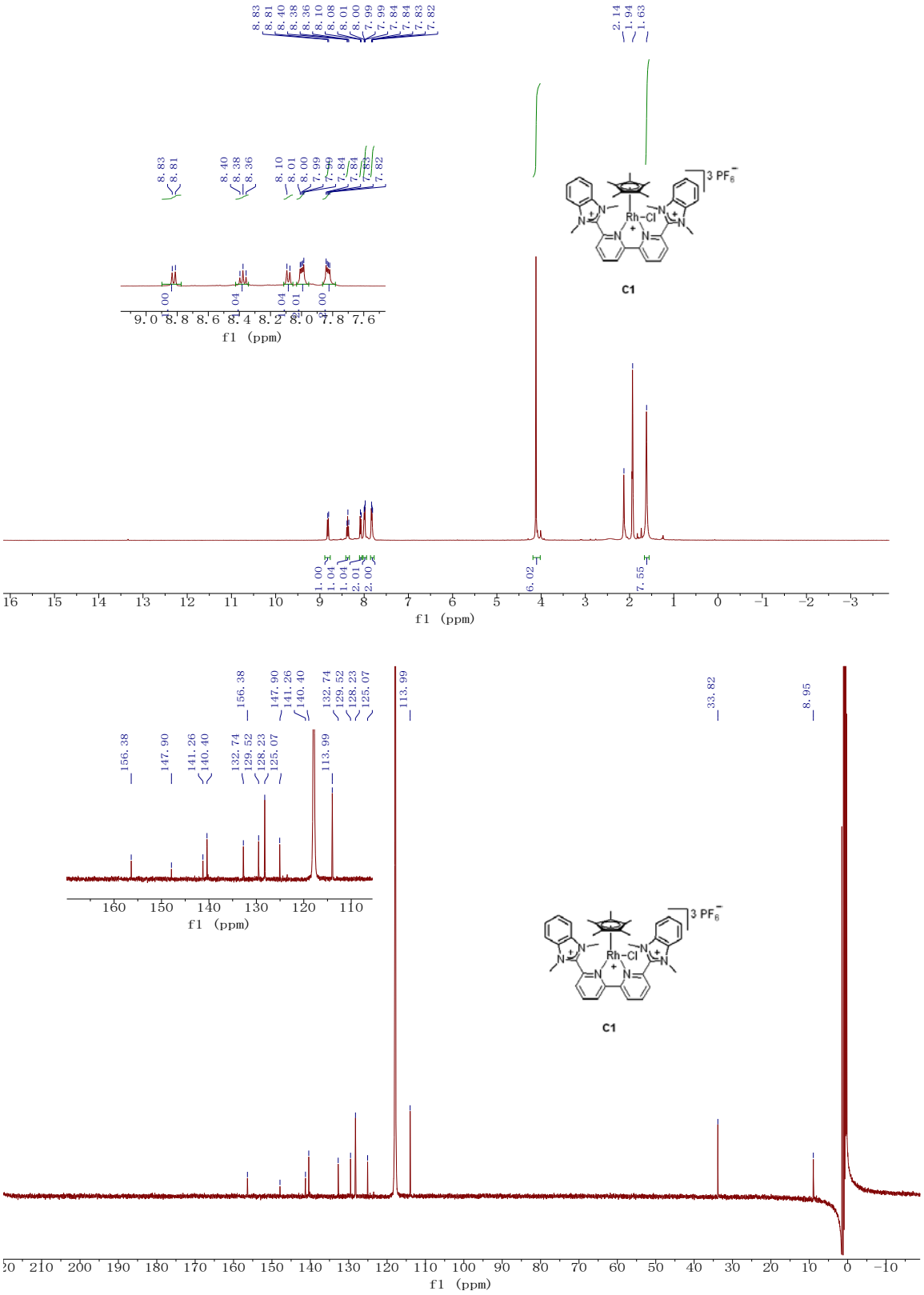
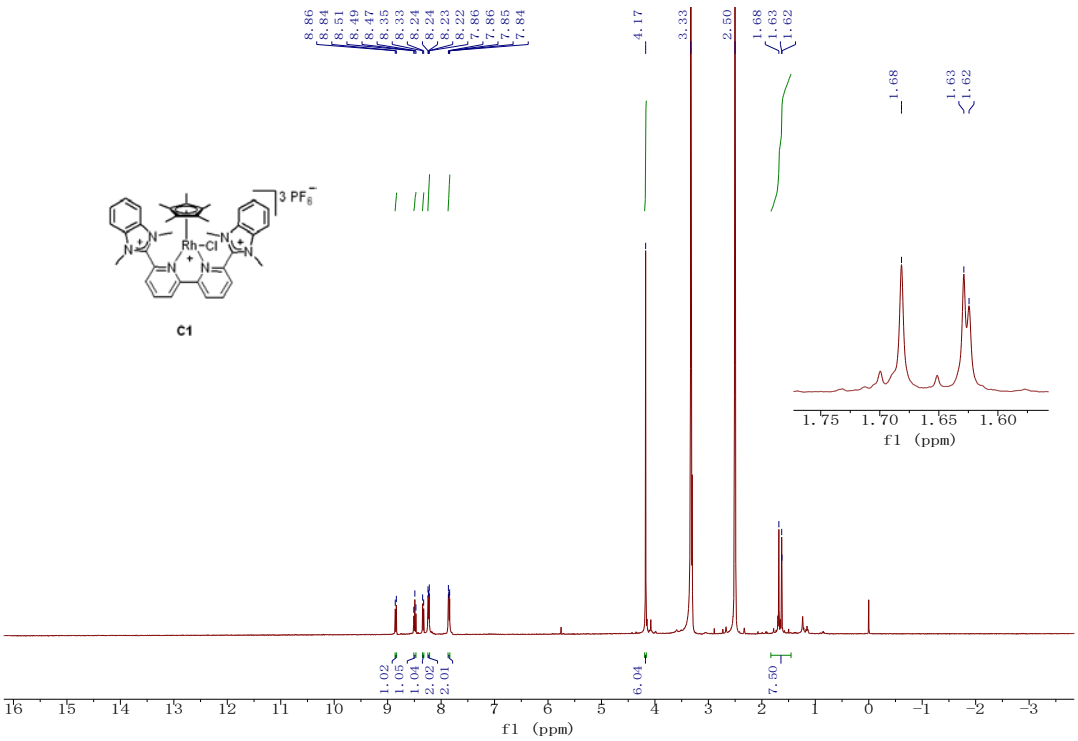


Figure S10. Control experiments of the reduction of imine **2a** to **2**

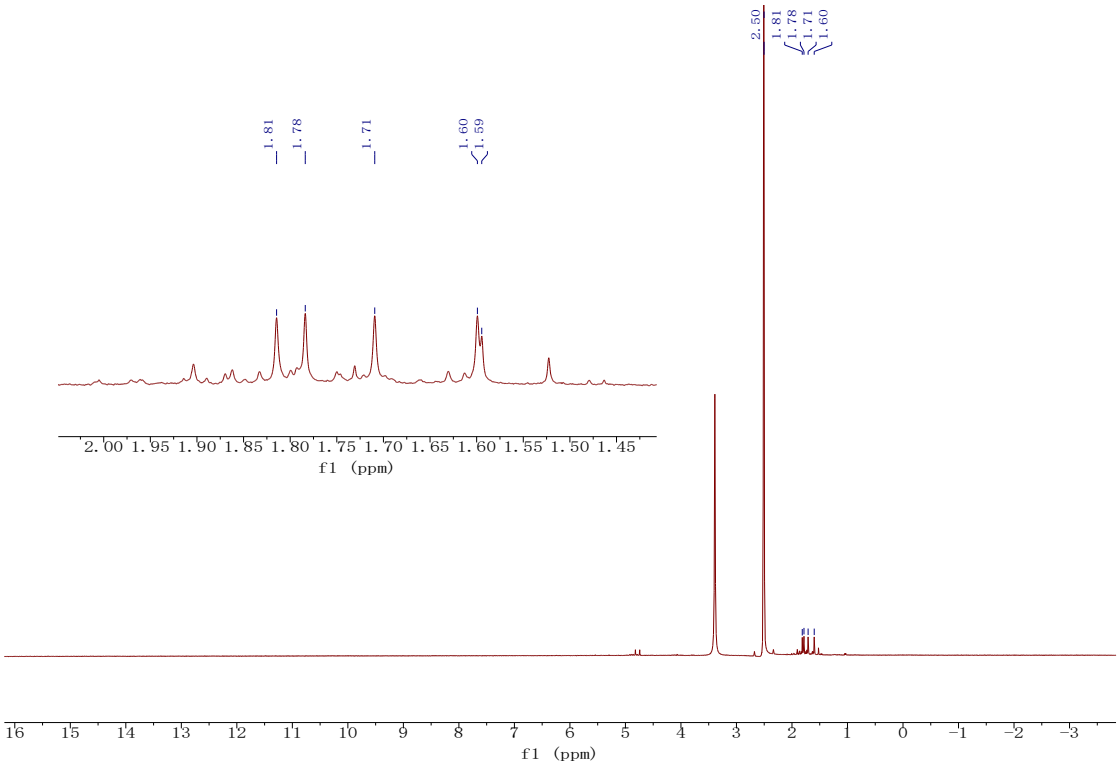
4. ^{1}H NMR and ^{13}C NMR Spectra



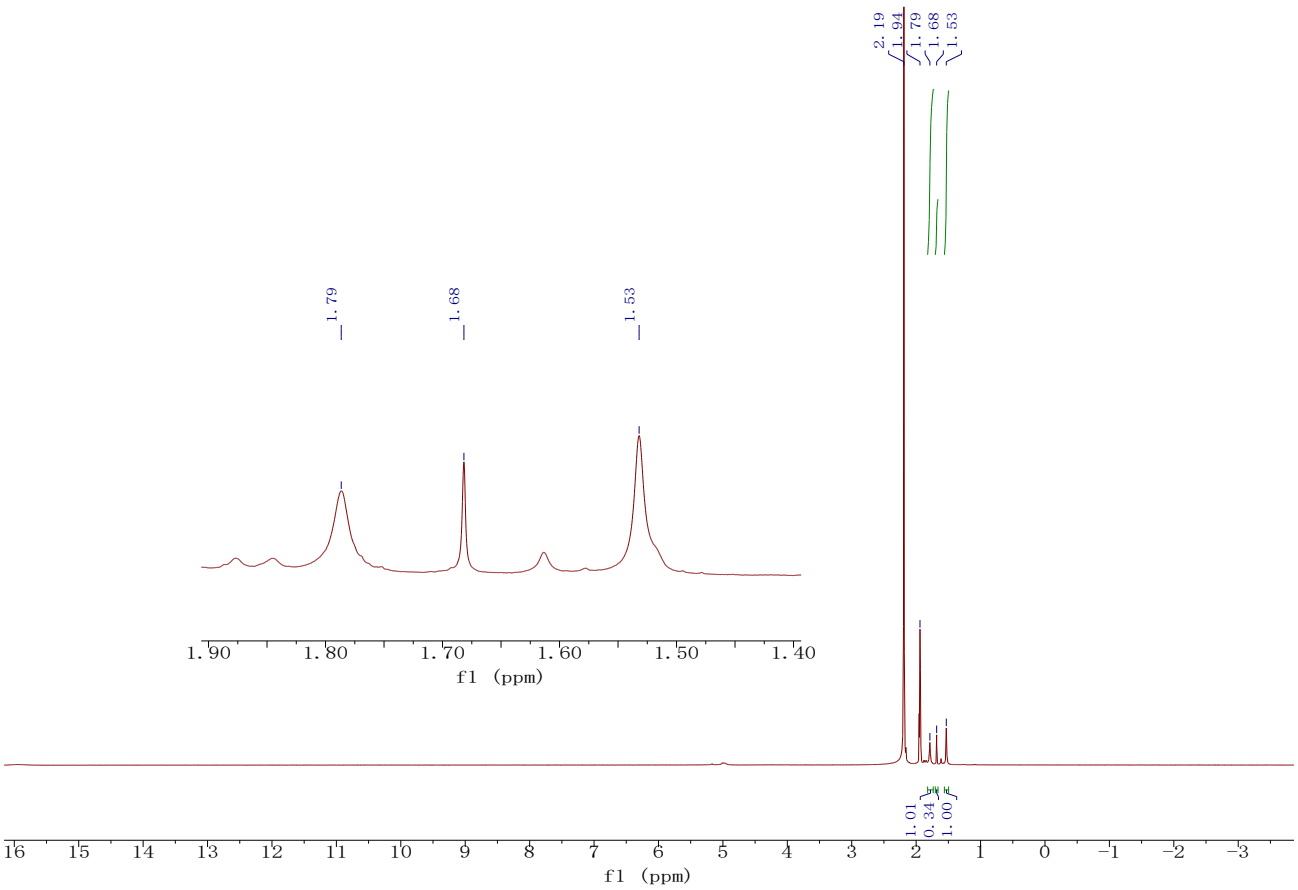
^{1}H and ^{13}C NMR spectra of **C1** in MeCN-d_3



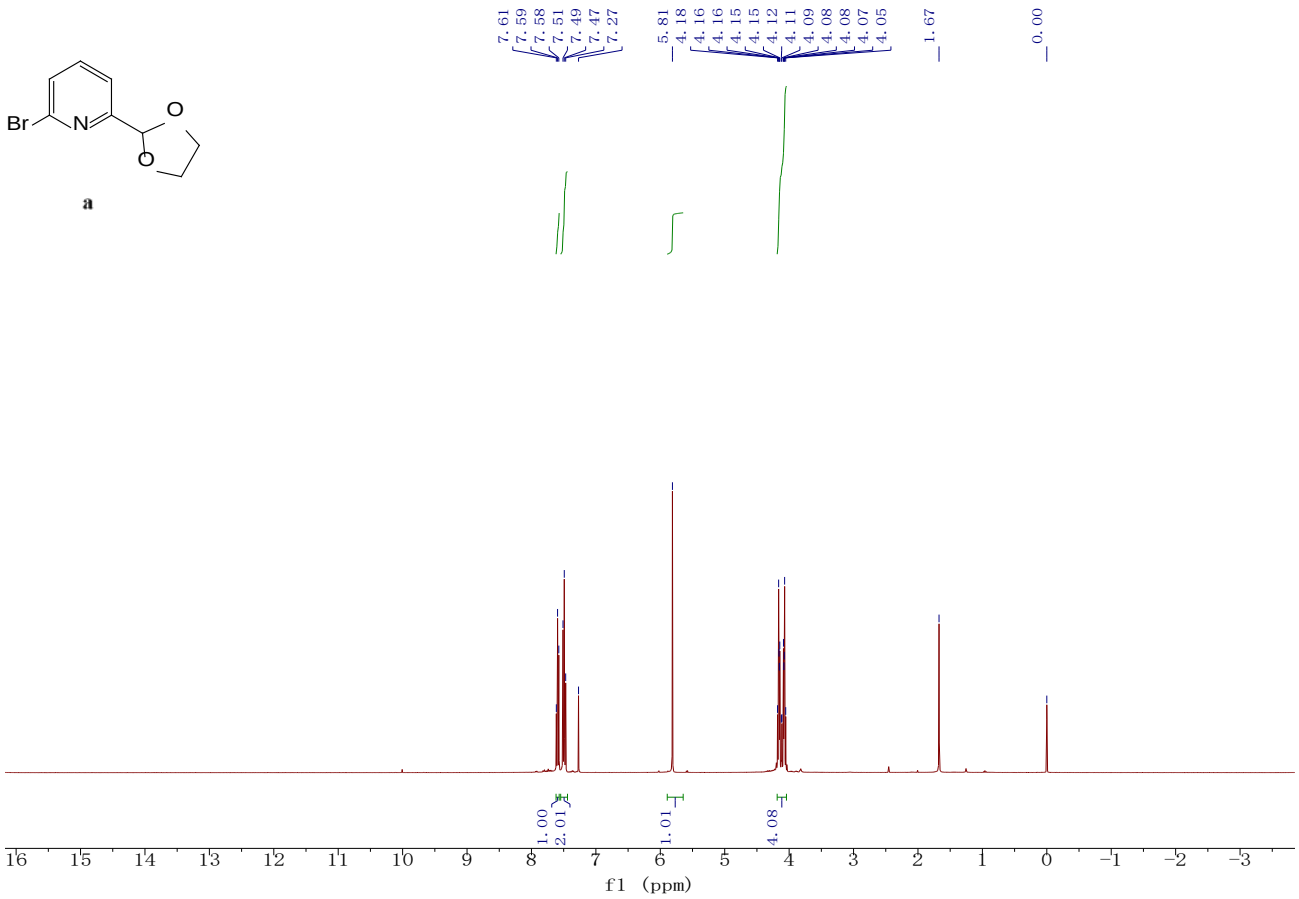
^{1}H NMR spectrum of **C1** in DMSO-d_6

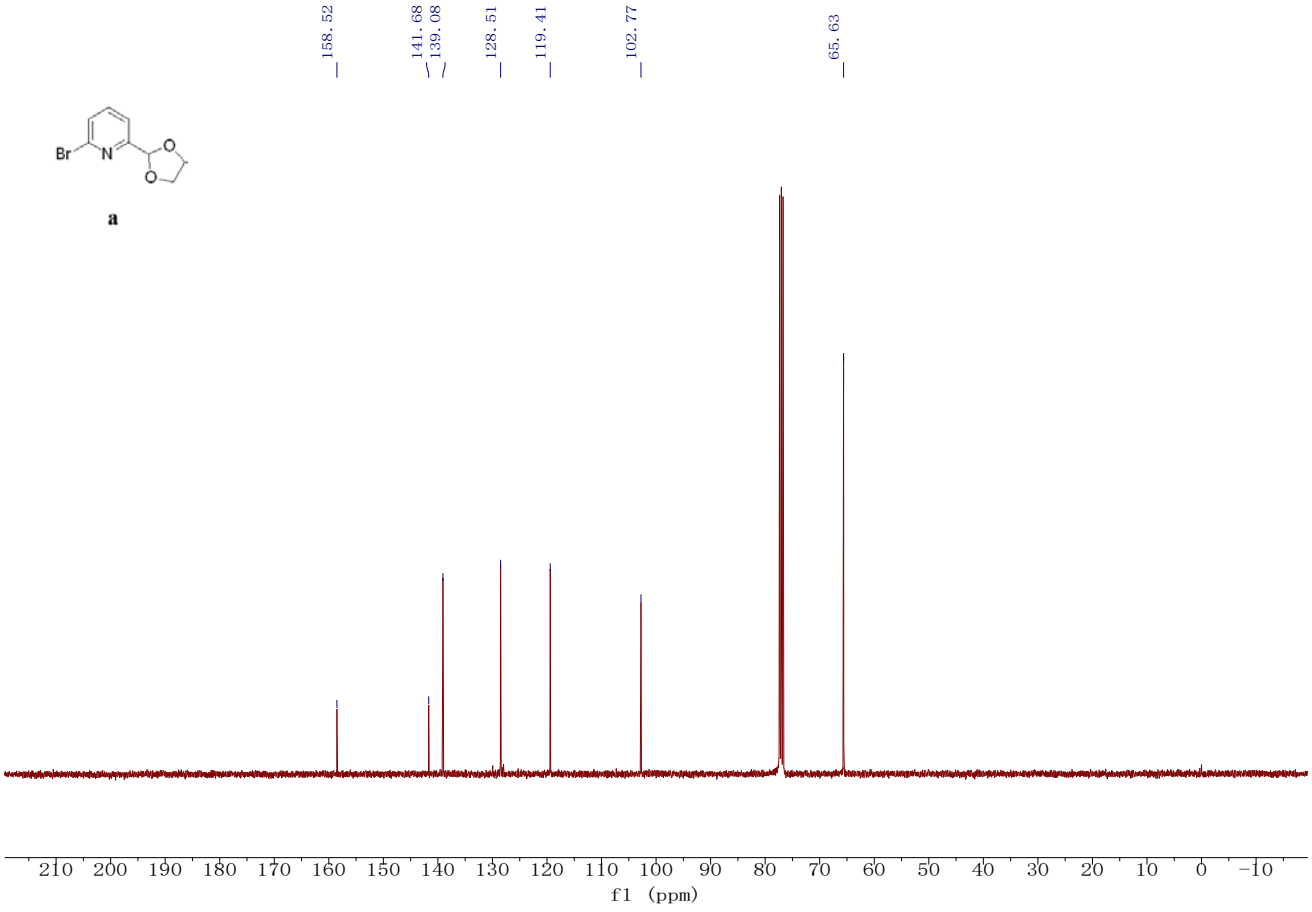


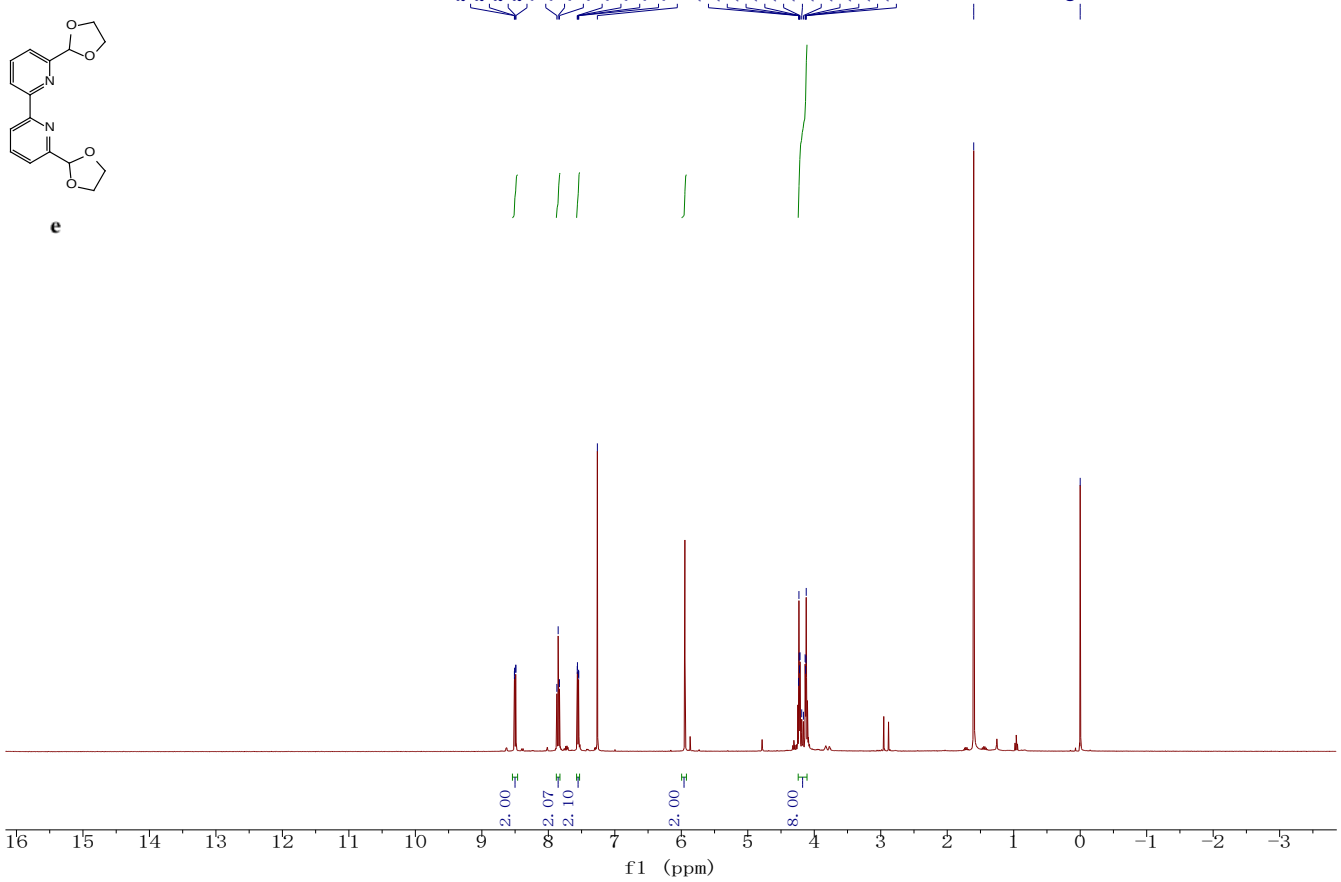
^{1}H NMR spectrum of RhCp*Cl$_2$ dimer in DMSO-d_6



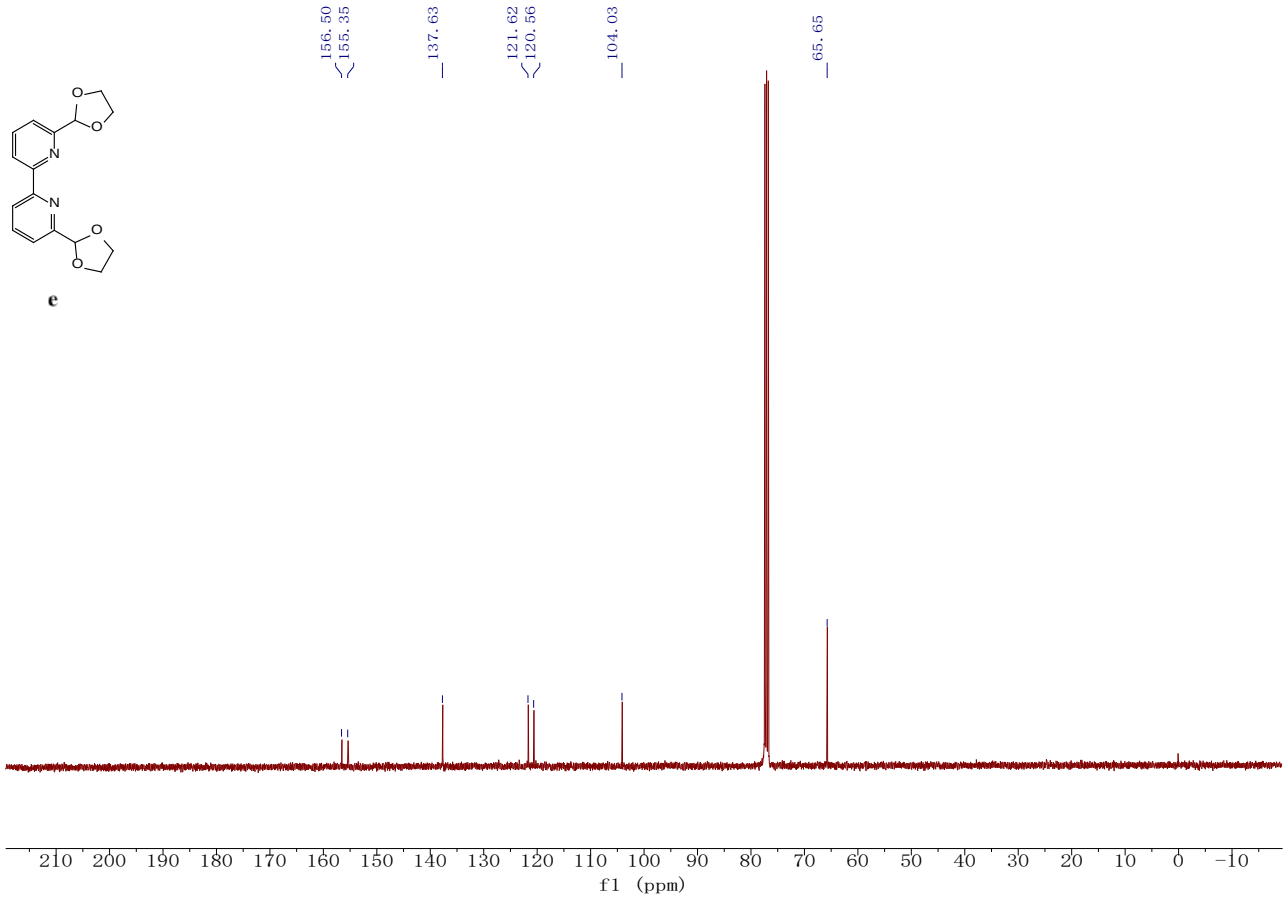
^{1}H NMR spectrum of RhCp*Cl$_2$ dimer in acetonitrile-d_3


Br
N
O
O
a
7.61
7.59
7.58
7.51
7.49
7.47
7.27
5.81
4.18
4.16
4.16
4.15
4.15
4.12
4.11
4.09
4.08
4.08
4.07
4.05
1.67
0.00
1.00
2.01
1.01
4.08
f1 (ppm)

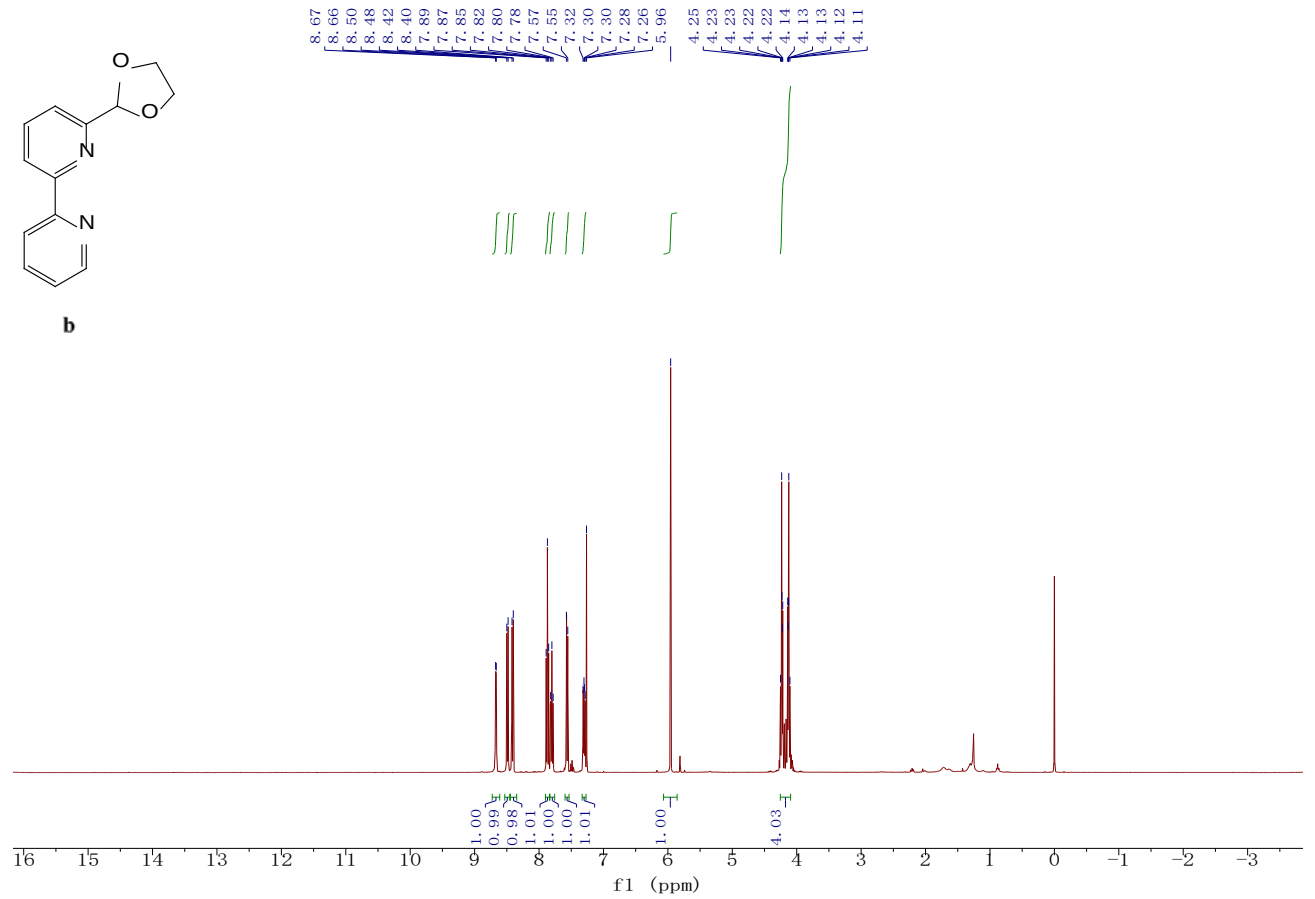

158.52
141.68
139.08
128.51
119.41
102.77
65.63
Br
N
O
O
a
f1 (ppm)

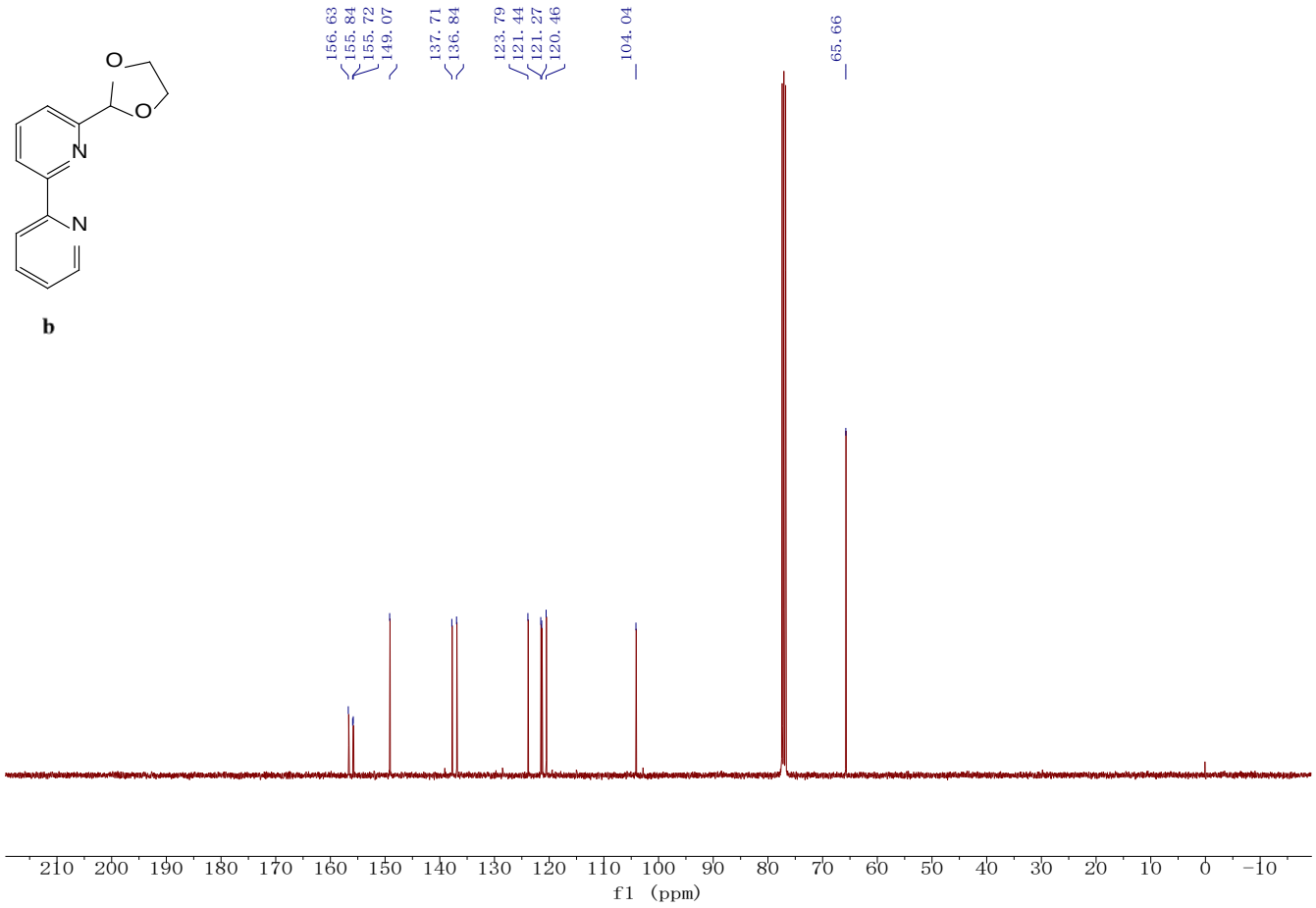

8.51
8.51
8.49
8.49
7.87
7.85
7.83
7.56
7.56
7.55
7.54
7.26
4.24
4.23
4.23
4.22
4.21
4.19
4.16
4.14
4.13
4.12
4.12
1.60
0.00
2.00
2.07
2.10
2.00
8.00
f1 (ppm)

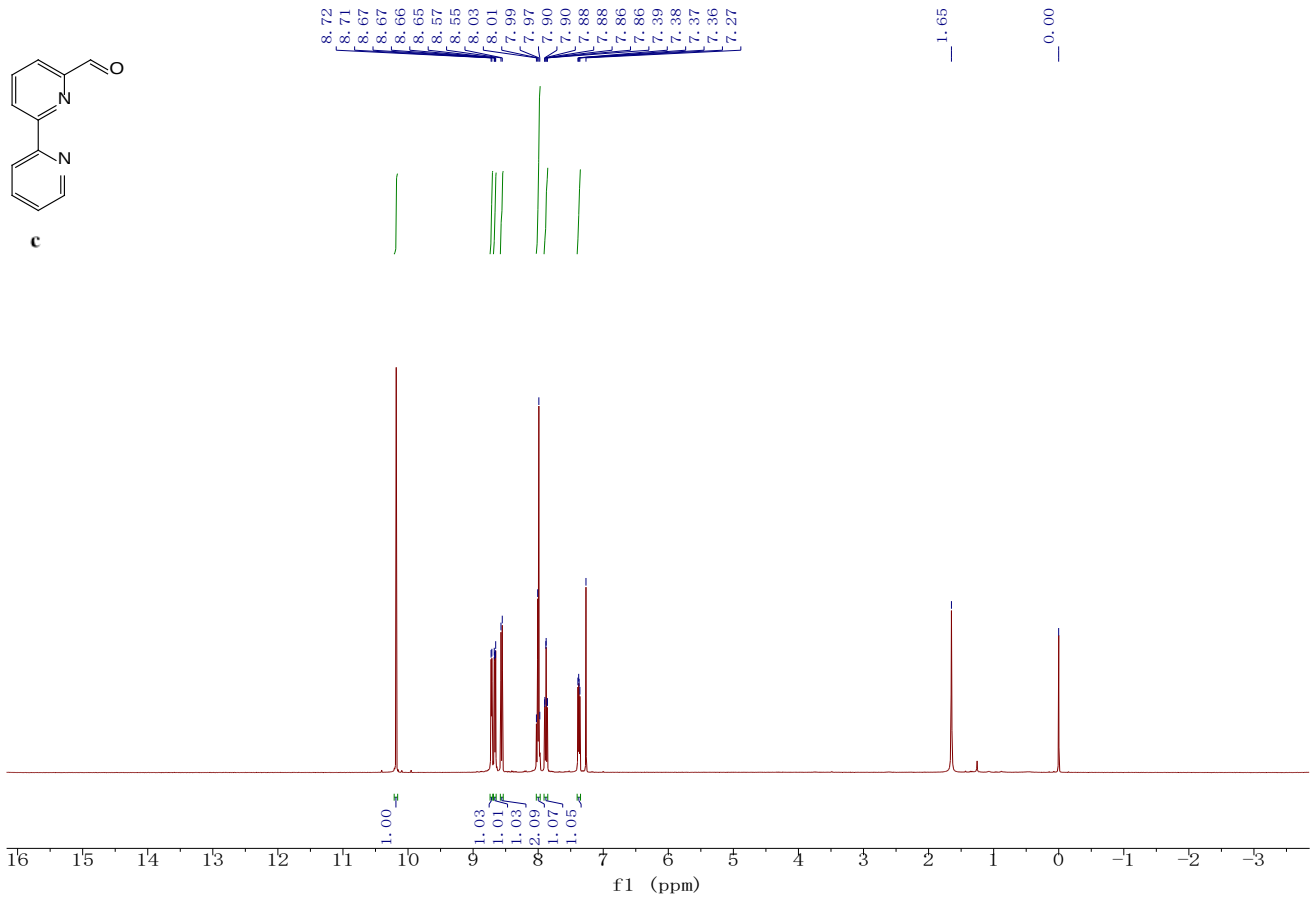
e

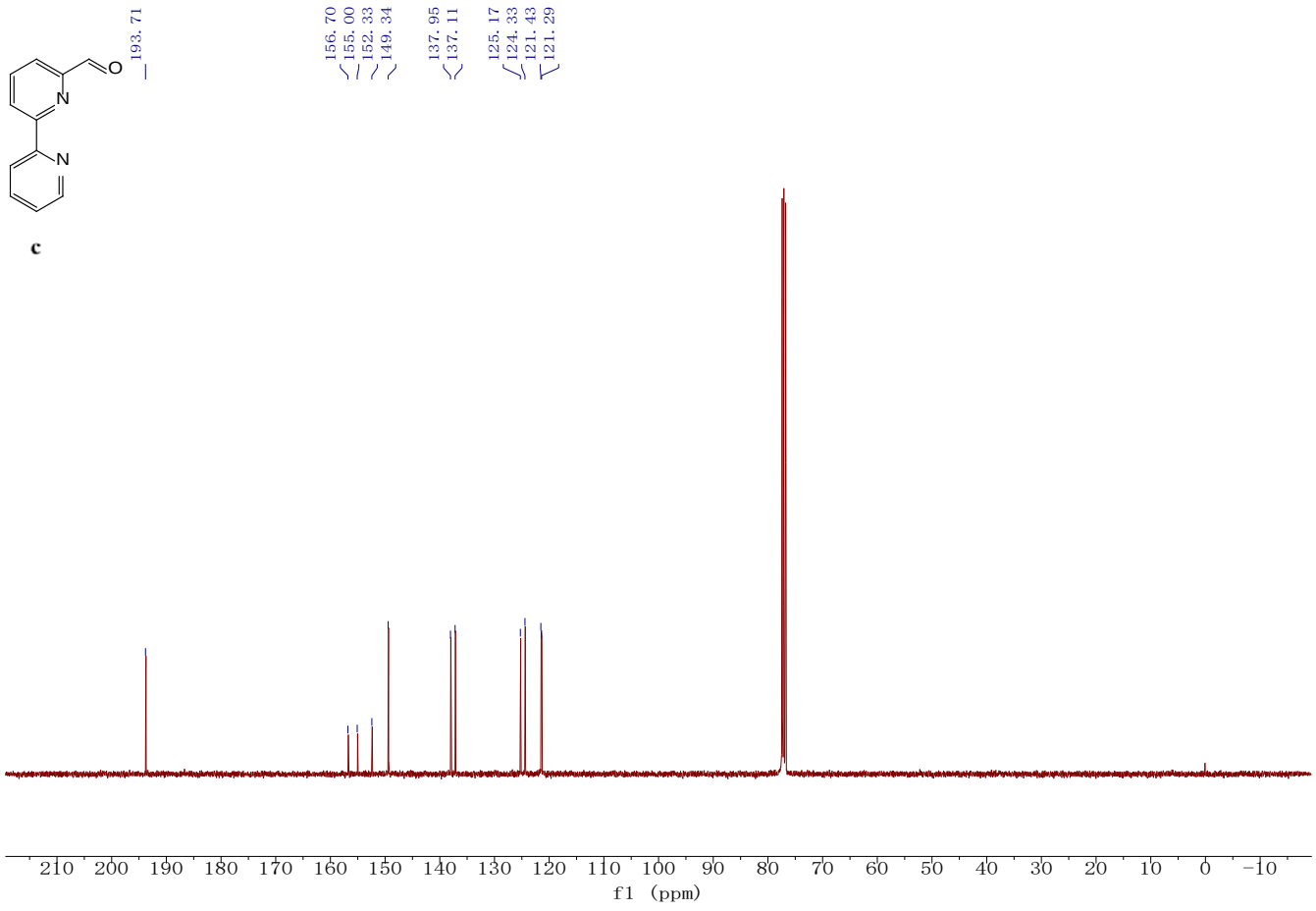

156.50
155.35
137.63
121.62
120.56
104.03
65.65
f1 (ppm)

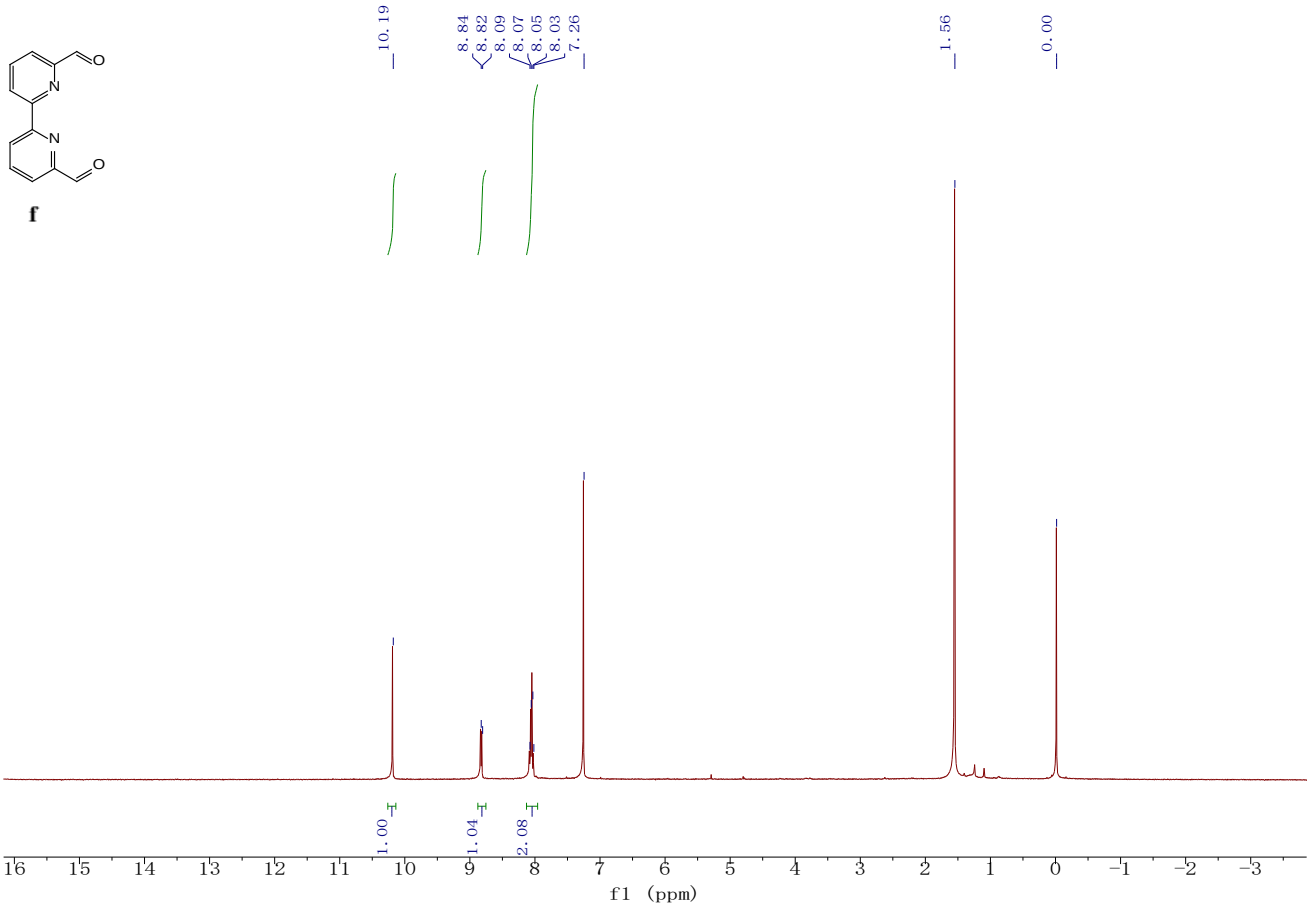
e


8.67
8.66
8.50
8.48
8.42
8.40
7.89
7.87
7.85
7.82
7.80
7.78
7.57
7.55
7.32
7.30
7.30
7.28
7.26
5.96
4.25
4.23
4.23
4.22
4.22
4.14
4.13
4.13
4.12
4.11
O
O
N
N
b
1.00
0.99
0.98
1.01
1.00
1.00
1.01
1.00
4.03
f1 (ppm)

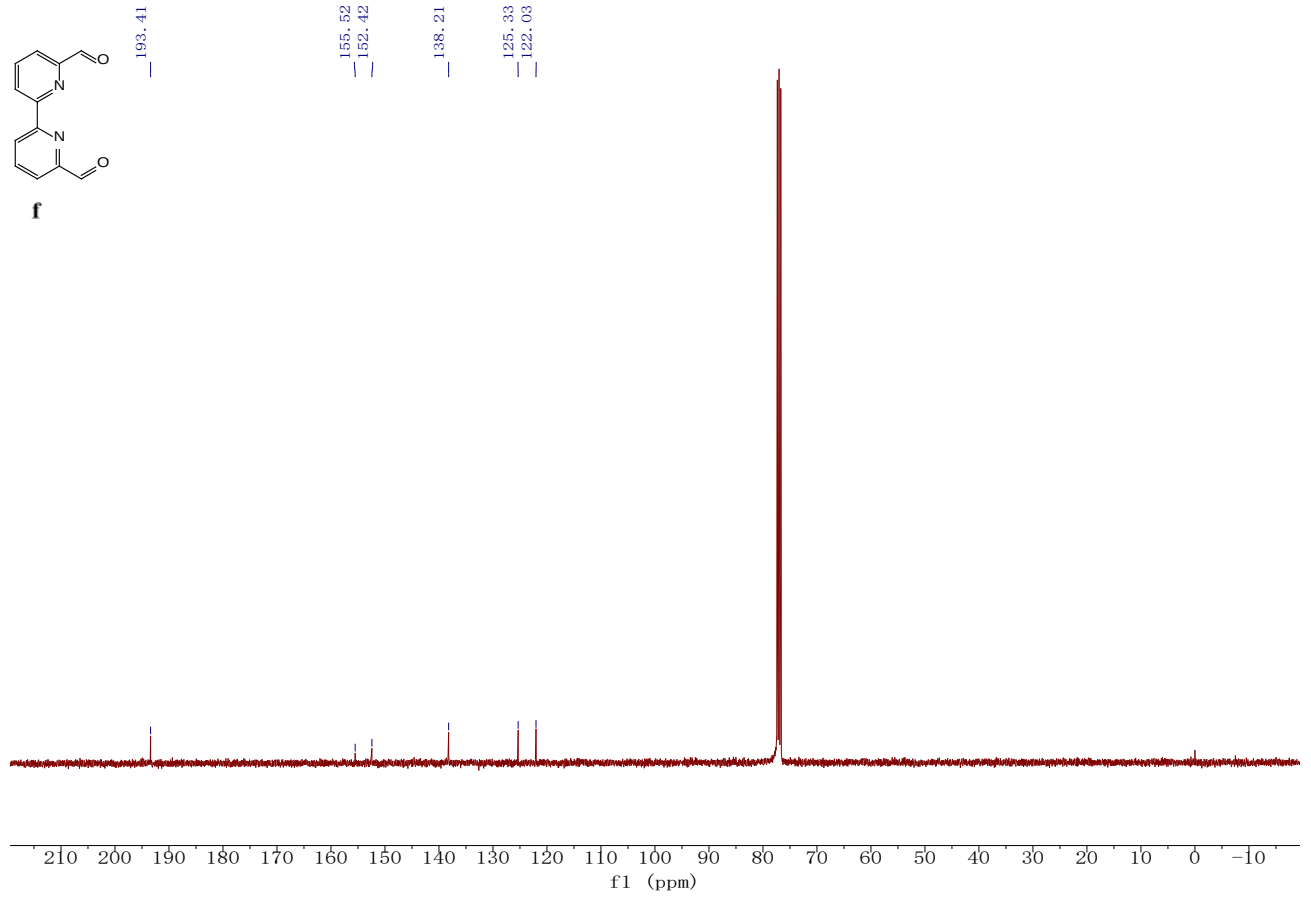

156.63
155.84
155.72
149.07
137.71
136.84
123.79
121.44
121.27
120.46
104.04
65.66
O
O
N
N
b
f1 (ppm)


8.72
8.71
8.67
8.67
8.66
8.65
8.57
8.55
8.03
8.01
7.99
7.97
7.90
7.90
7.88
7.88
7.86
7.86
7.39
7.38
7.37
7.36
7.27
1.65
0.00
O
N
N
c
1.00
1.03
1.01
1.03
2.09
1.07
1.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

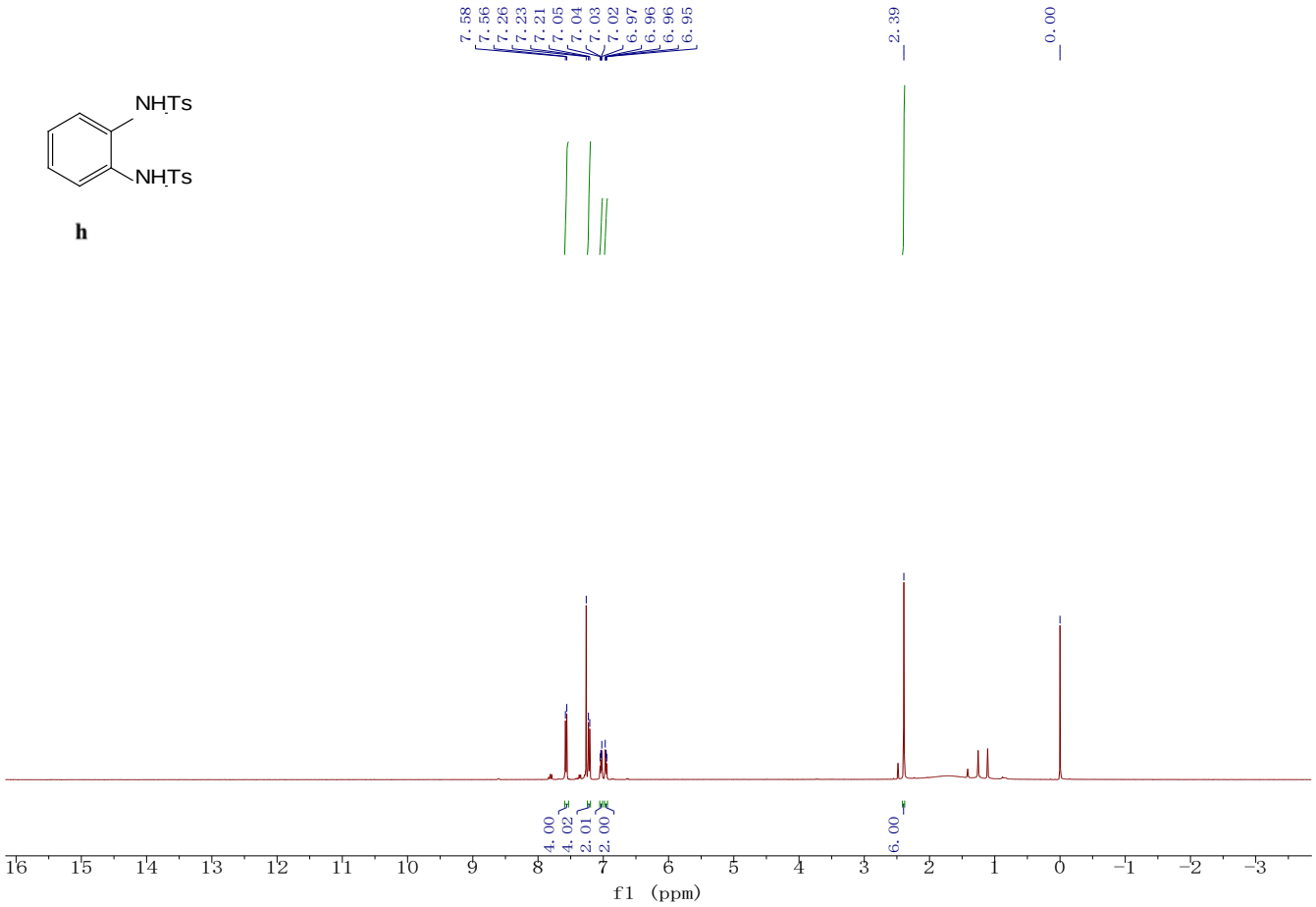

193.71
156.70
155.00
152.33
149.34
137.95
137.11
125.17
124.33
121.43
121.29
O
N
N
c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

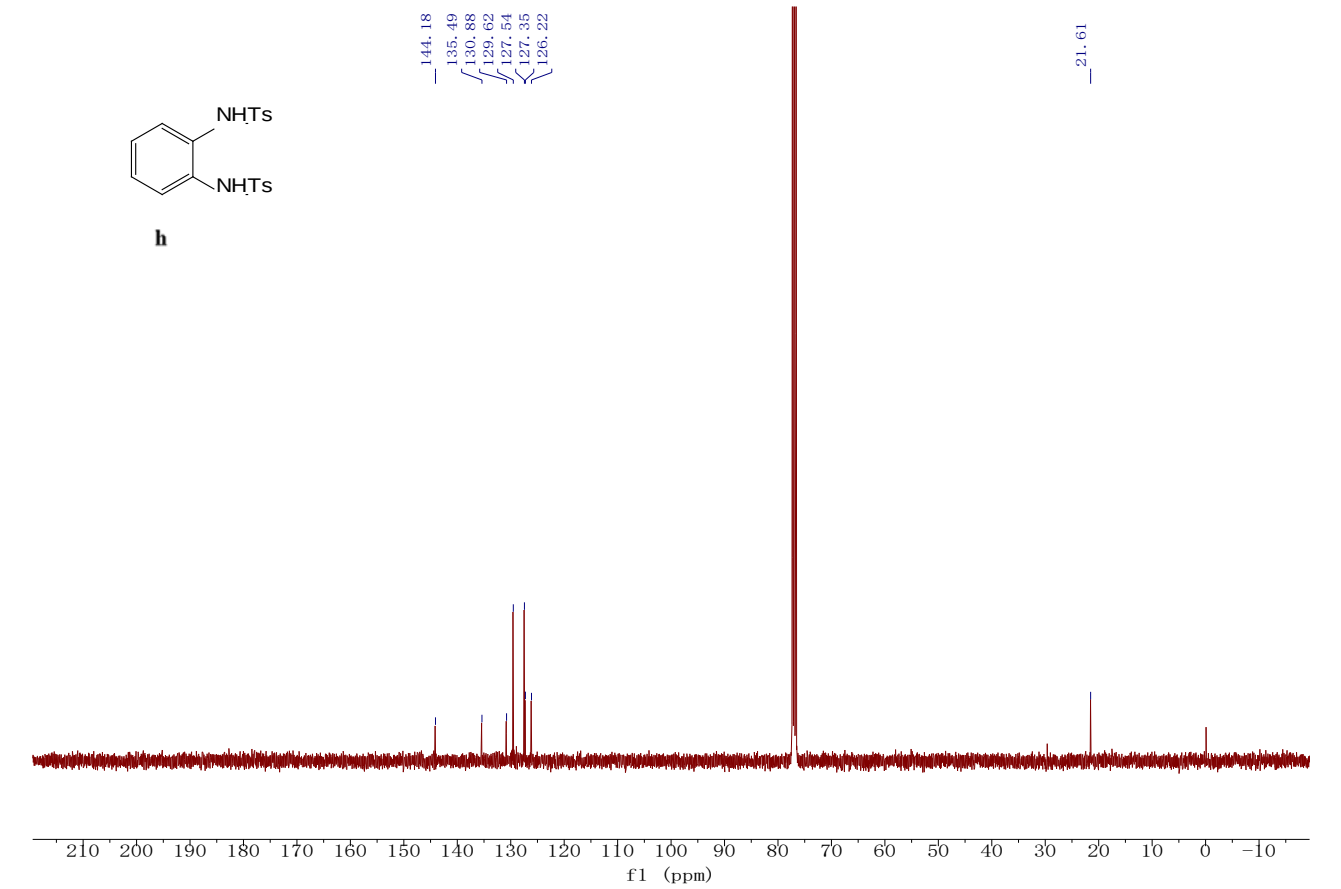

10.19
8.84
8.82
8.09
8.07
8.05
8.03
7.26
1.56
0.00
1.00
1.04
2.08
f1 (ppm)

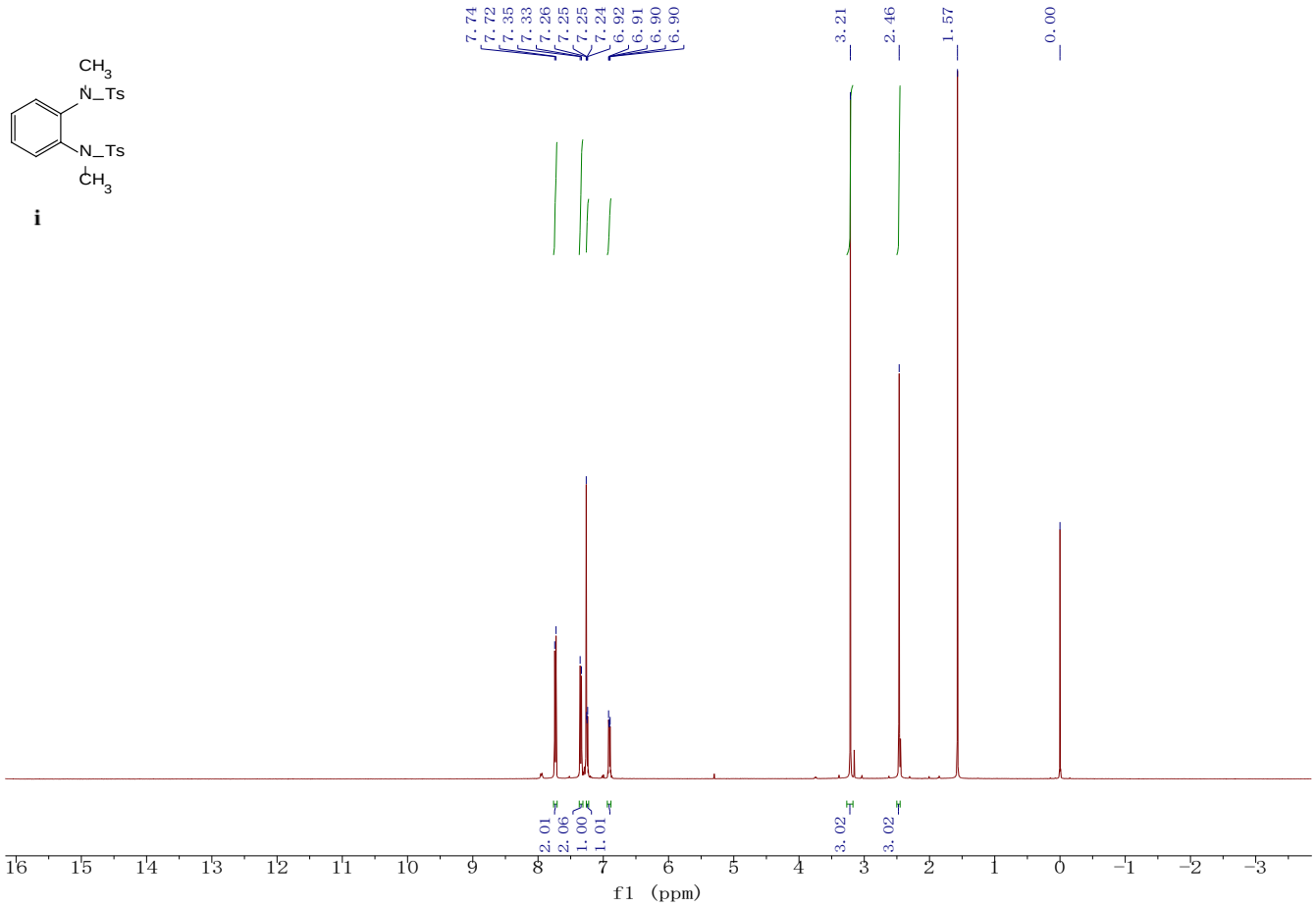
f

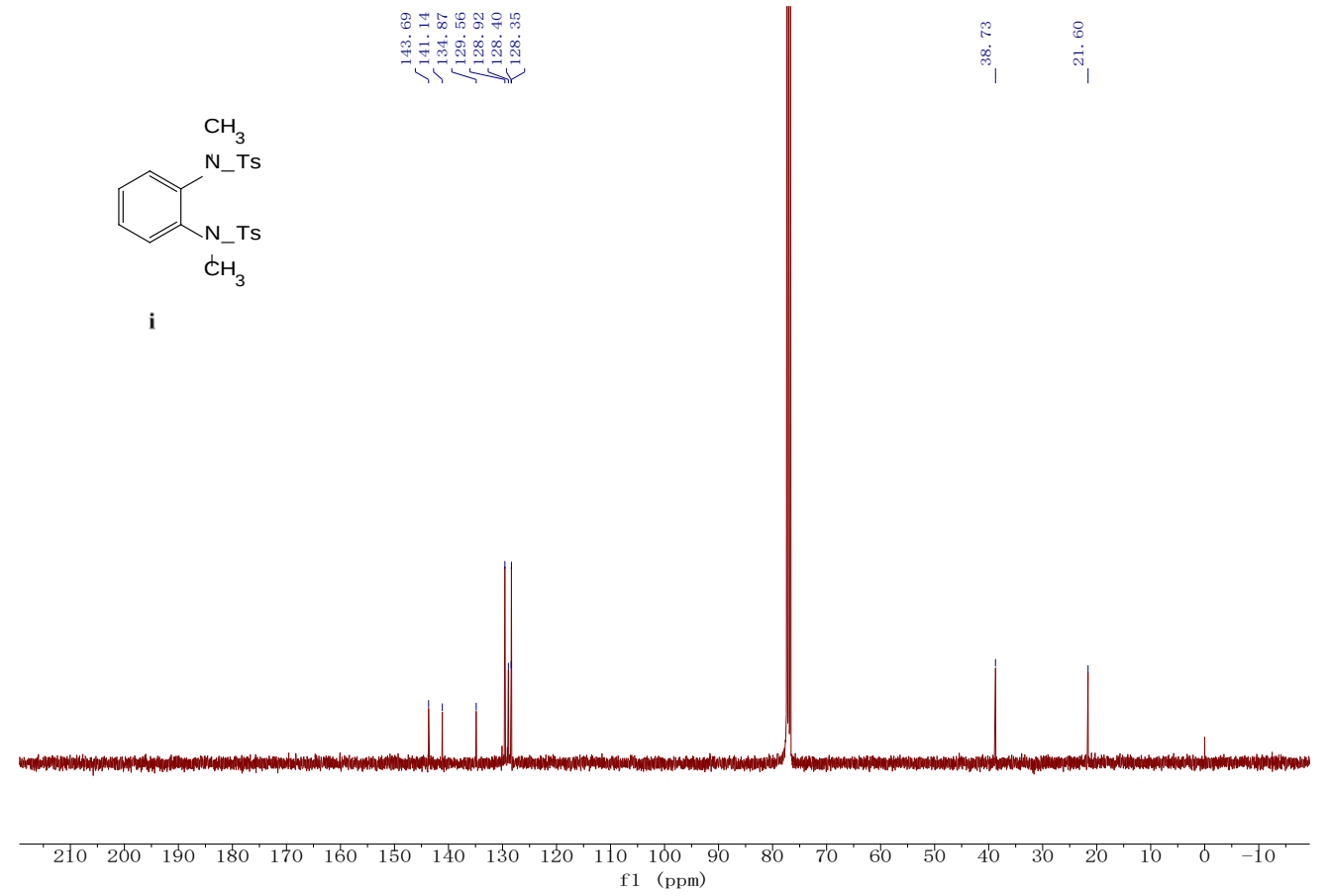

193.41
155.52
152.42
138.21
125.33
122.03
f1 (ppm)

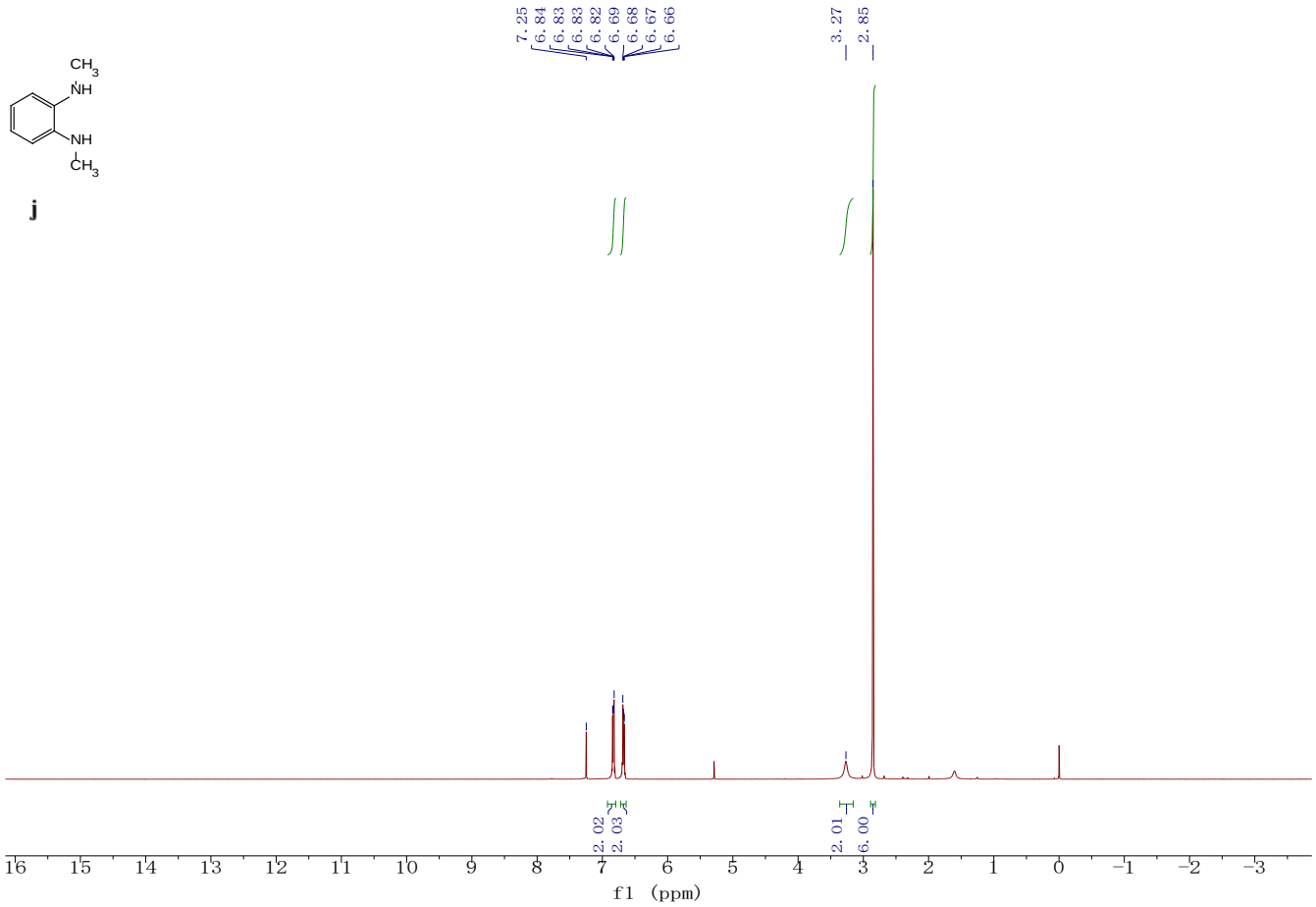
f

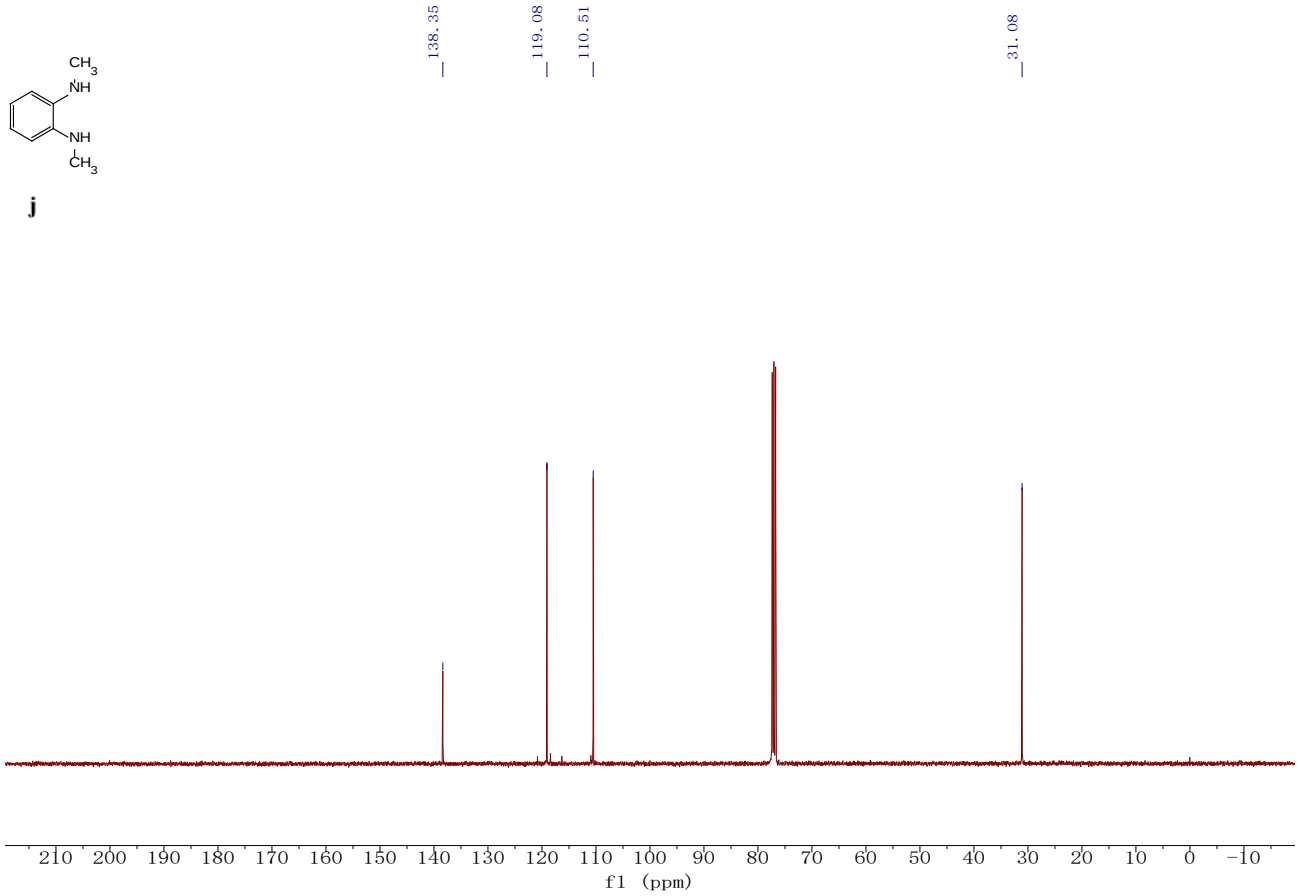

7.58
7.56
7.26
7.23
7.21
7.05
7.04
7.03
7.02
6.97
6.96
6.96
6.95
2.39
0.00
NHTs
NHTs
h
4.00
4.02
2.01
2.00
6.00
f1 (ppm)

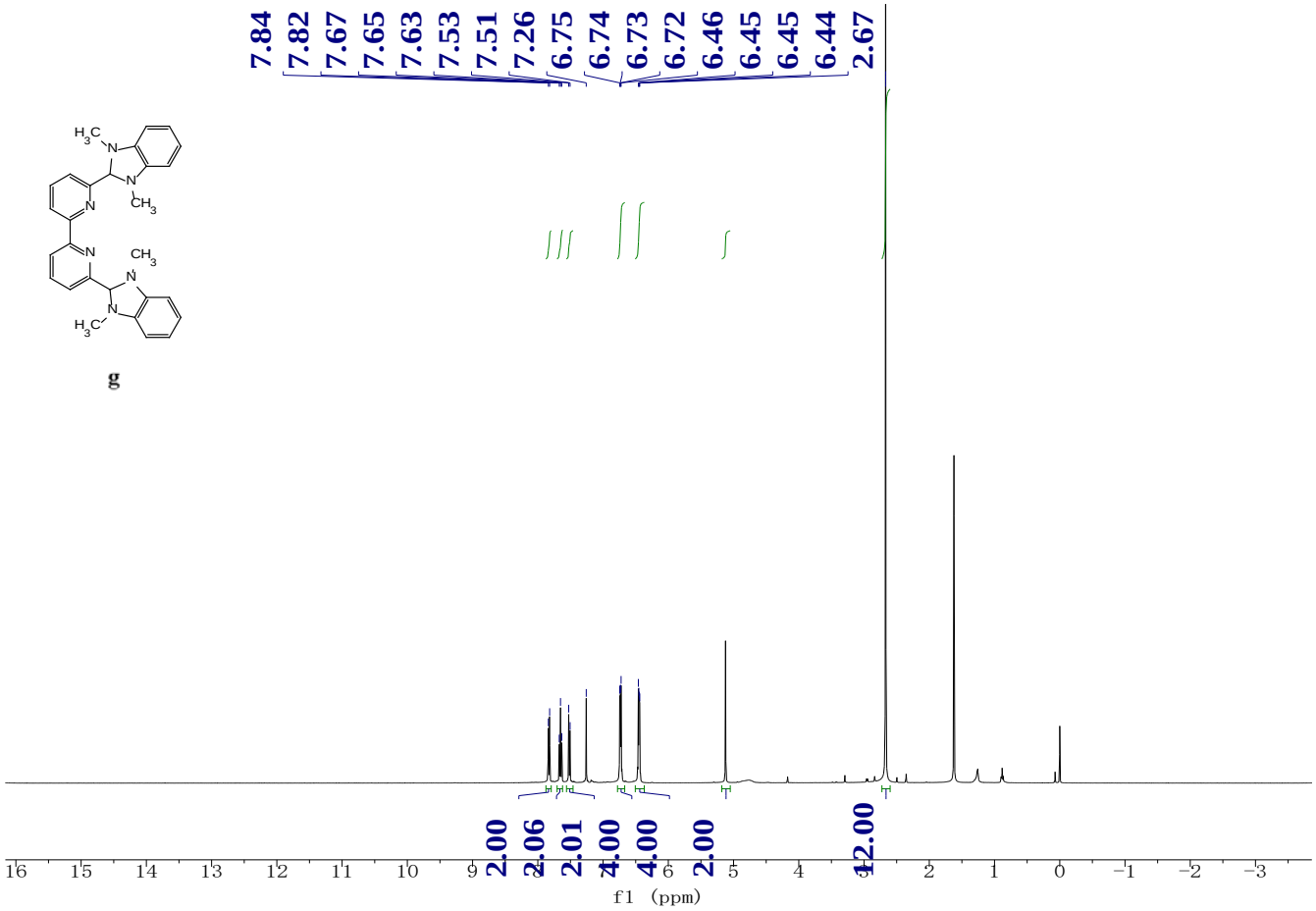

144.18
135.49
130.88
129.62
127.54
127.35
126.22
21.61
NHTs
NHTs
h
f1 (ppm)


CH3
N_Ts
N_Ts
CH3
i
7.74
7.72
7.35
7.33
7.26
7.25
7.25
7.24
6.92
6.91
6.90
6.90
3.21
2.46
1.57
0.00
2.01
2.06
1.00
1.01
3.02
3.02
f1 (ppm)

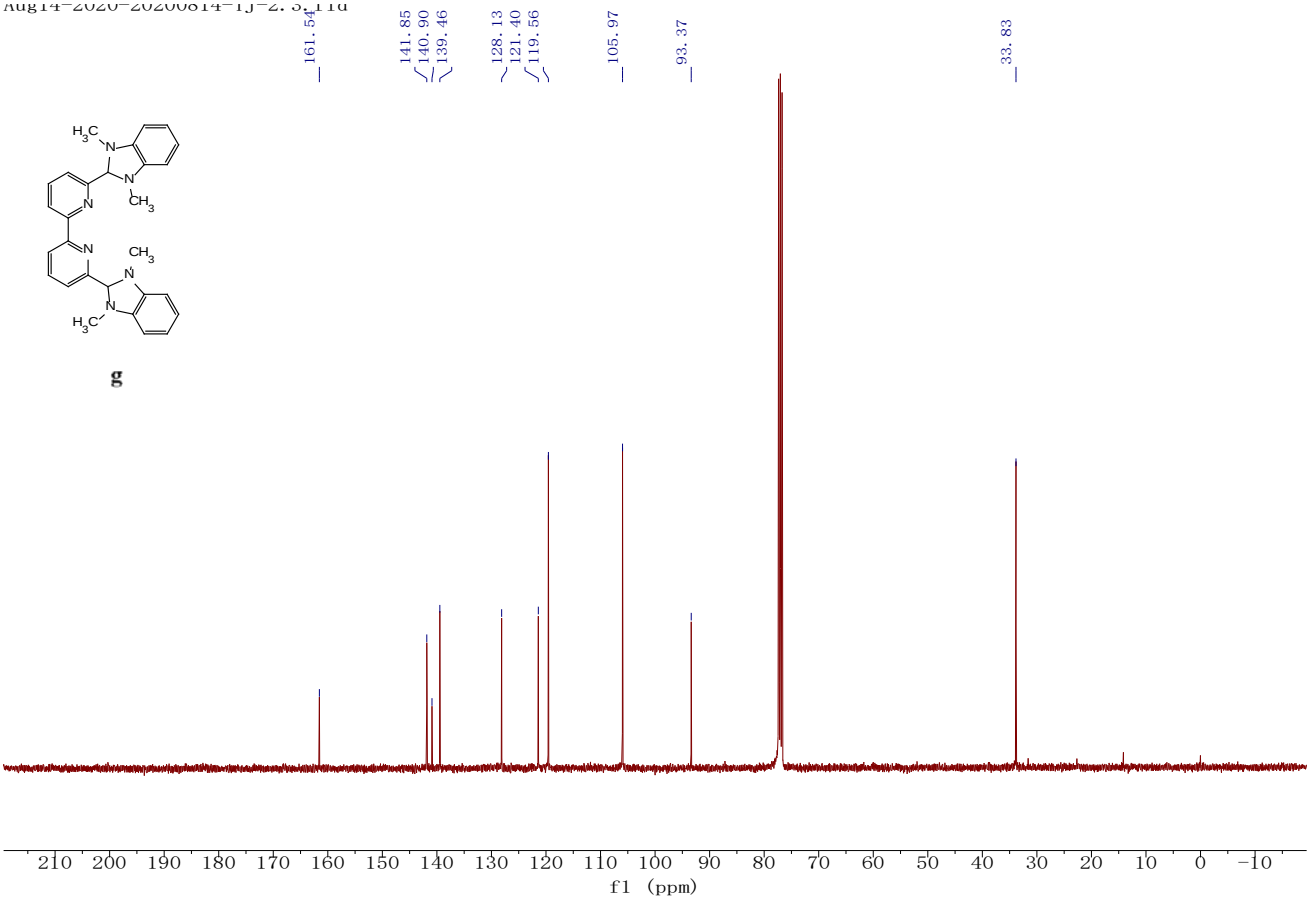

CH3
N_Ts
N_Ts
CH3
i
143.69
141.14
134.87
129.56
128.92
128.40
128.35
38.73
21.60
f1 (ppm)


7.25
6.84
6.83
6.83
6.82
6.69
6.68
6.67
6.66
3.27
2.85
CH3
NH
NH
CH3
j
2.02
2.03
2.01
6.00
f1 (ppm)

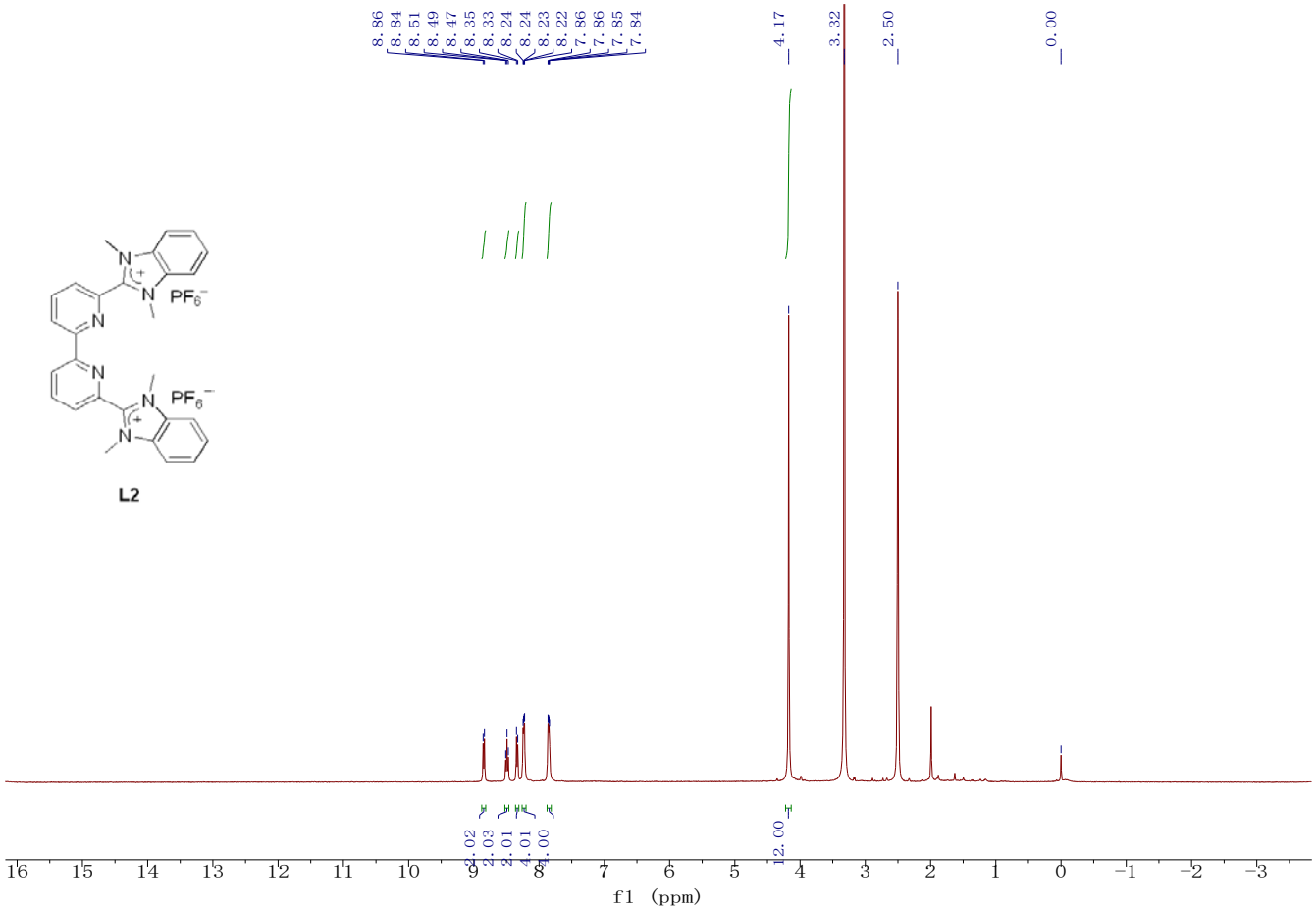

138.35
119.08
110.51
31.08
CH3
NH
NH
CH3
j
f1 (ppm)


7.84
7.82
7.67
7.65
7.63
7.53
7.51
7.26
6.75
6.74
6.73
6.72
6.46
6.45
6.45
6.44
2.67
2.00
2.06
2.01
4.00
4.00
2.00
12.00
f1 (ppm)

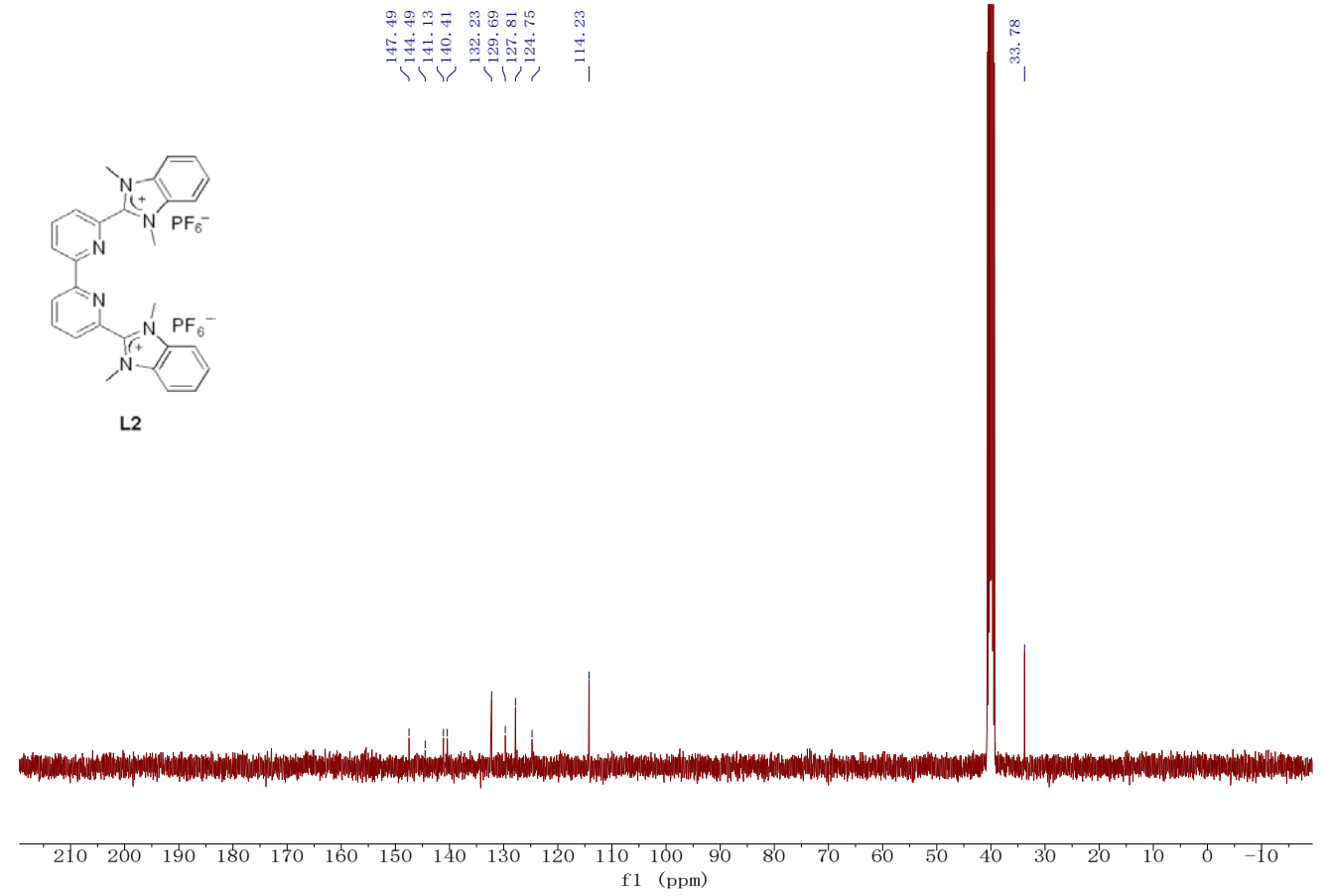
g


161.54
141.85
140.90
139.46
128.13
121.40
119.56
105.97
93.37
33.83
f1 (ppm)

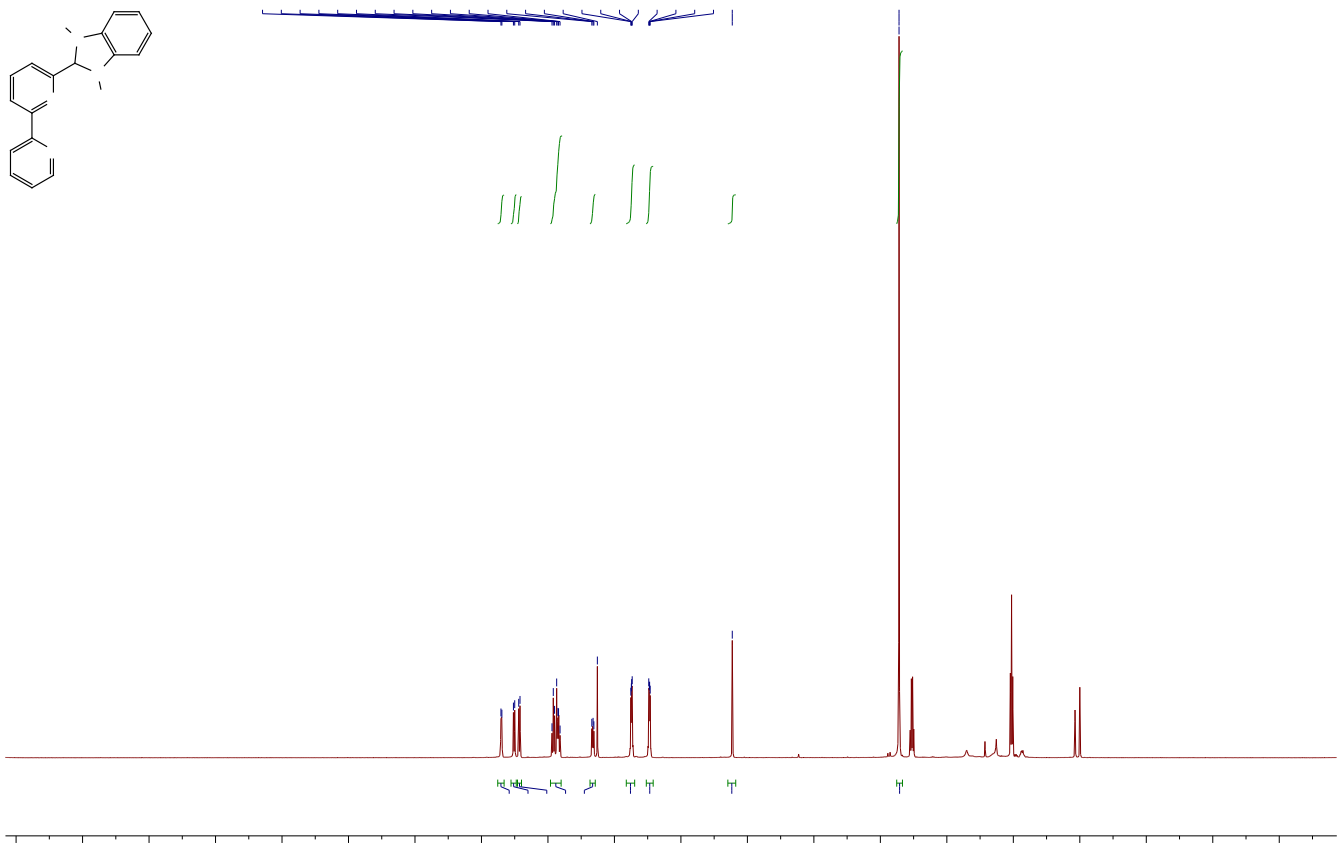
g

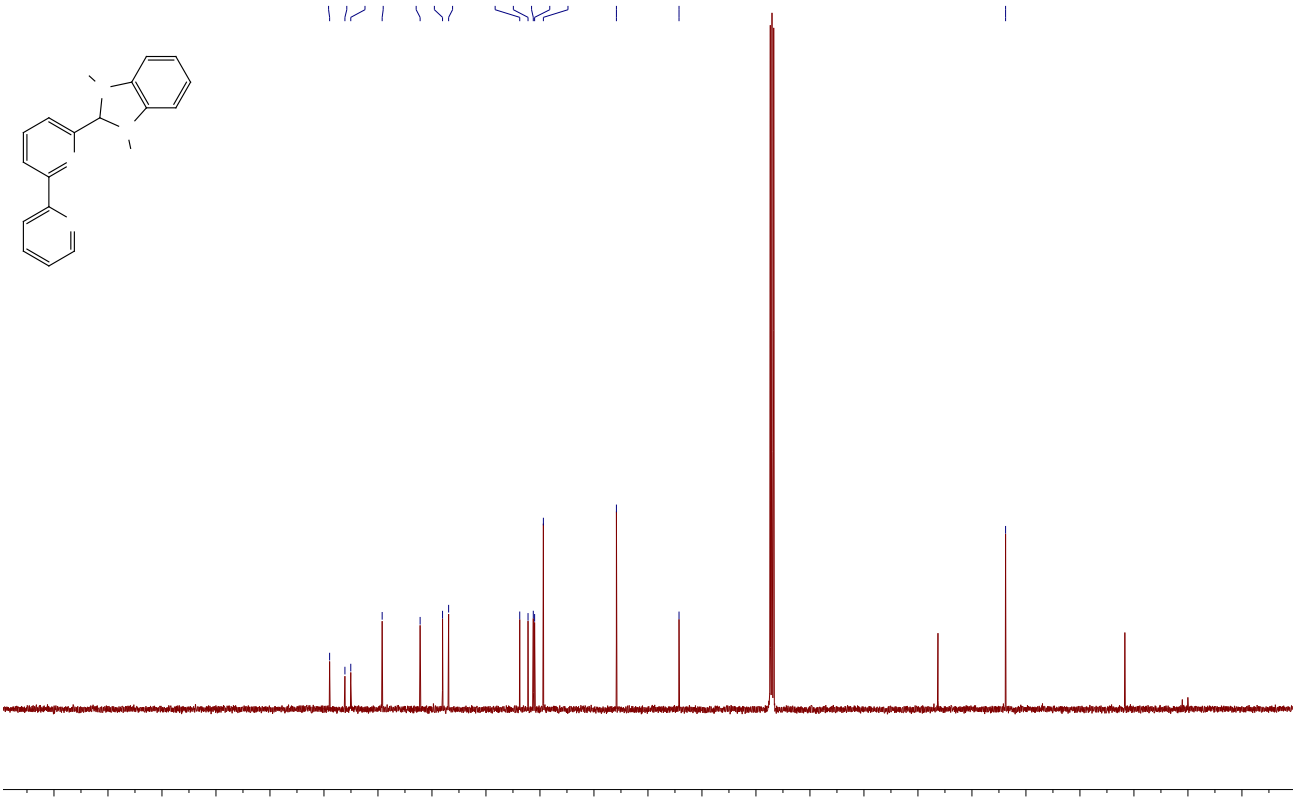

8.86
8.84
8.51
8.49
8.47
8.35
8.33
8.24
8.24
8.23
8.22
7.86
7.86
7.85
7.84
4.17
3.32
2.50
0.00
PF6−
PF6−
2.02
2.03
2.01
4.01
4.00
12.00
f1 (ppm)

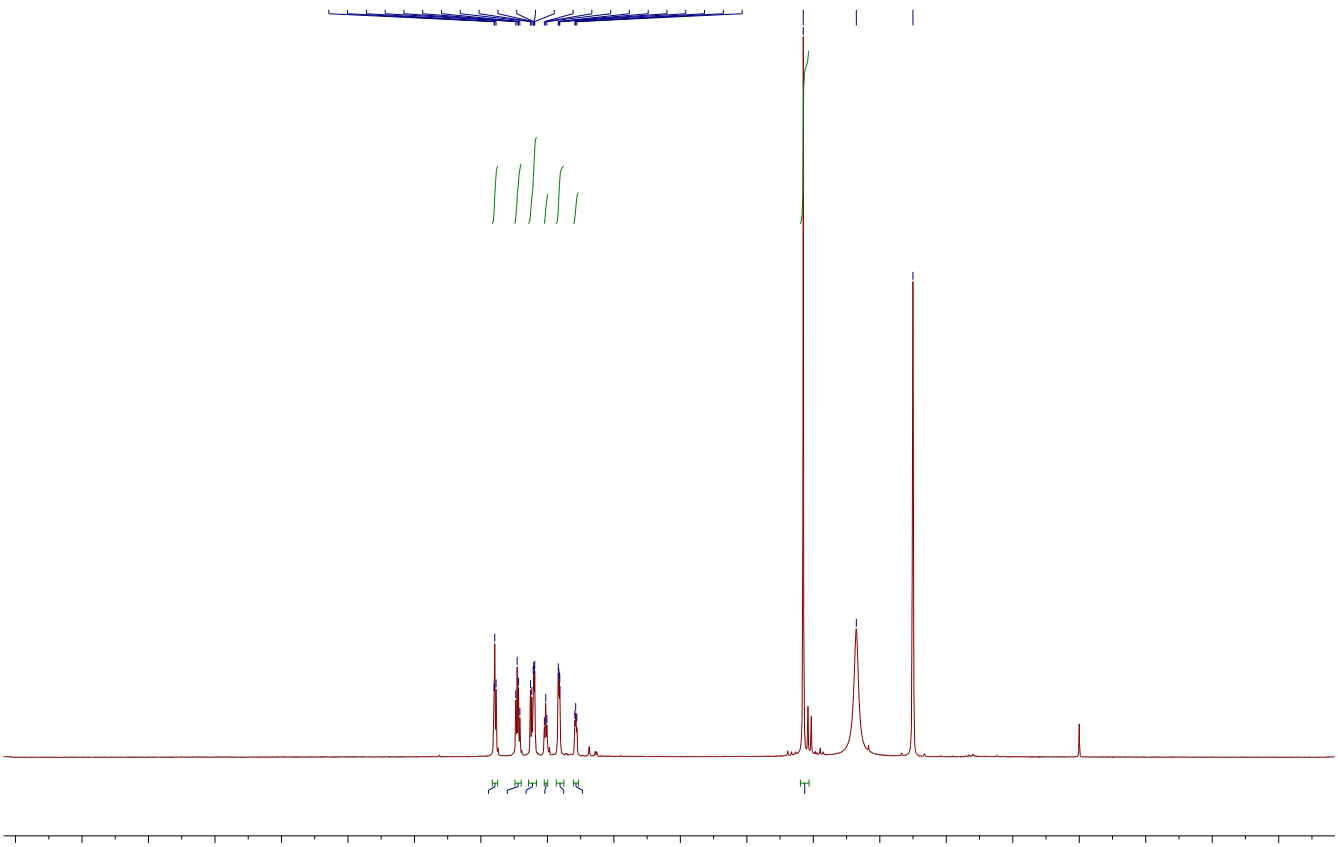
L2

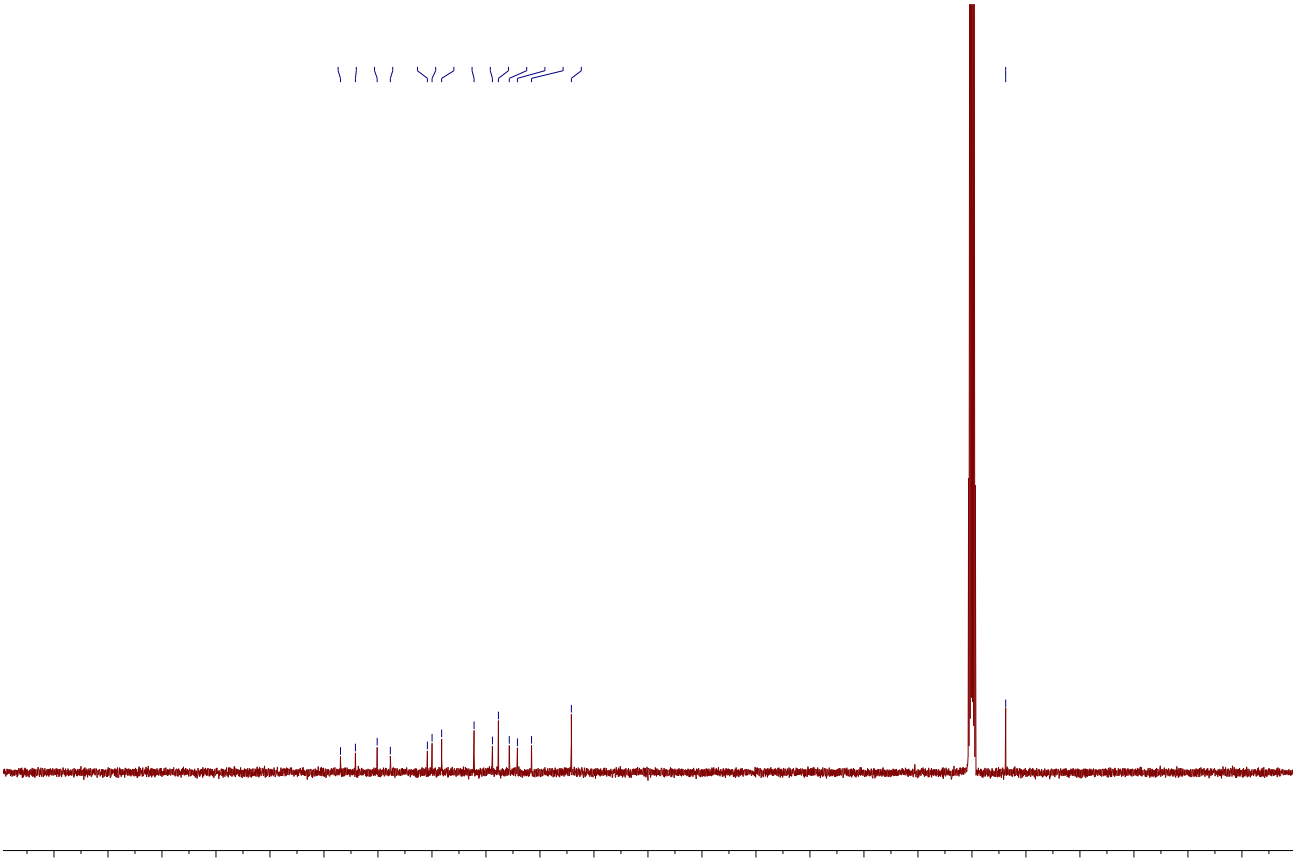

147.49
144.49
141.13
140.41
132.23
129.69
127.81
124.75
114.23
33.78
PF6−
PF6−
f1 (ppm)

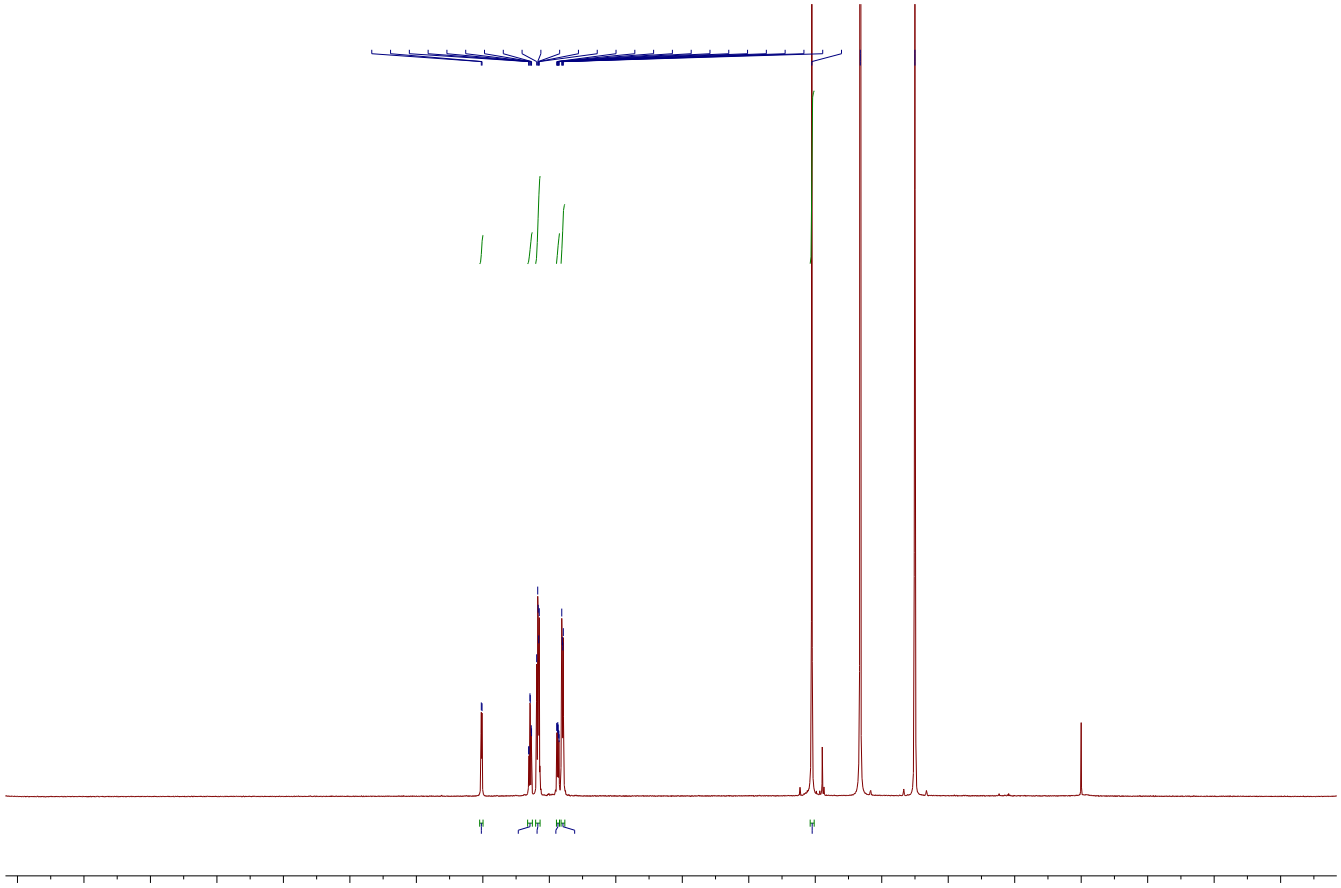
L2

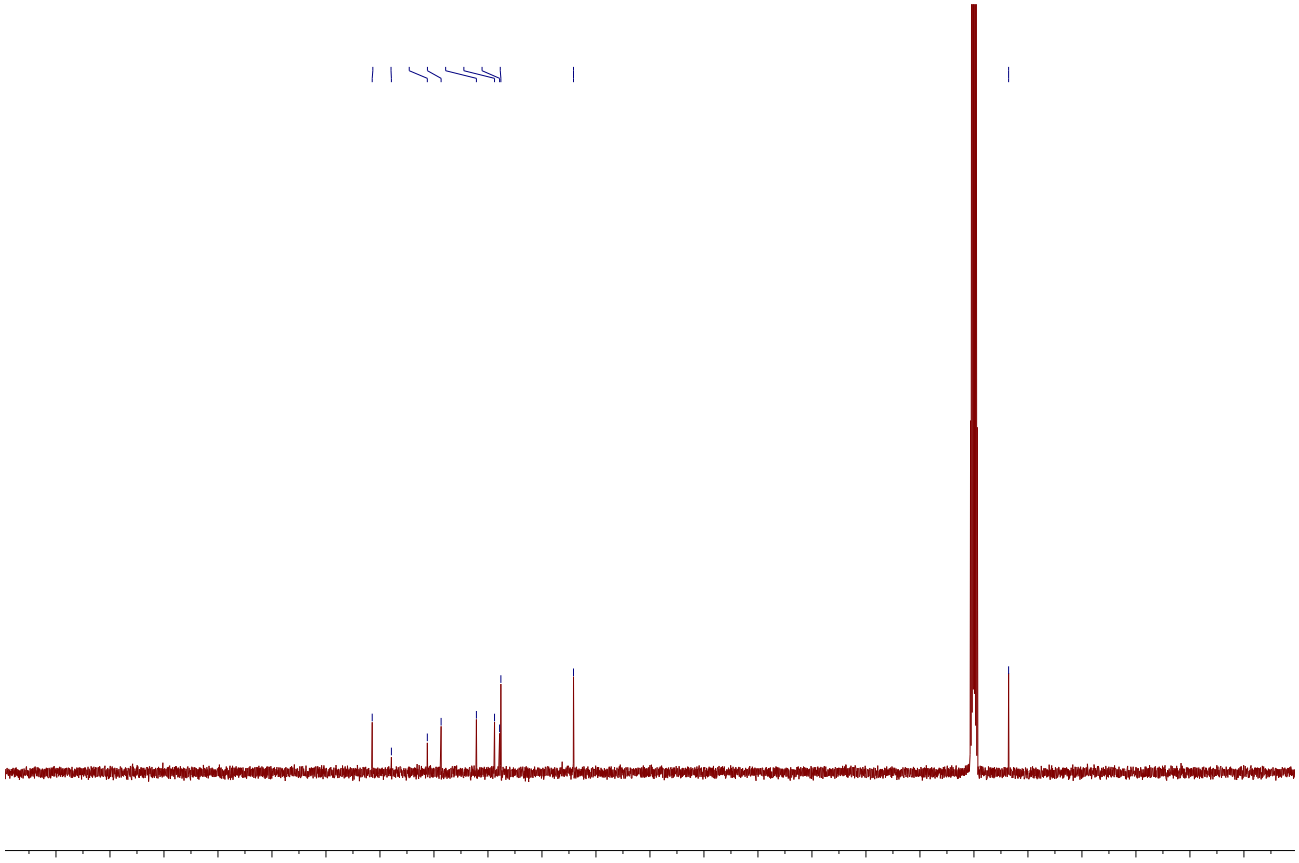


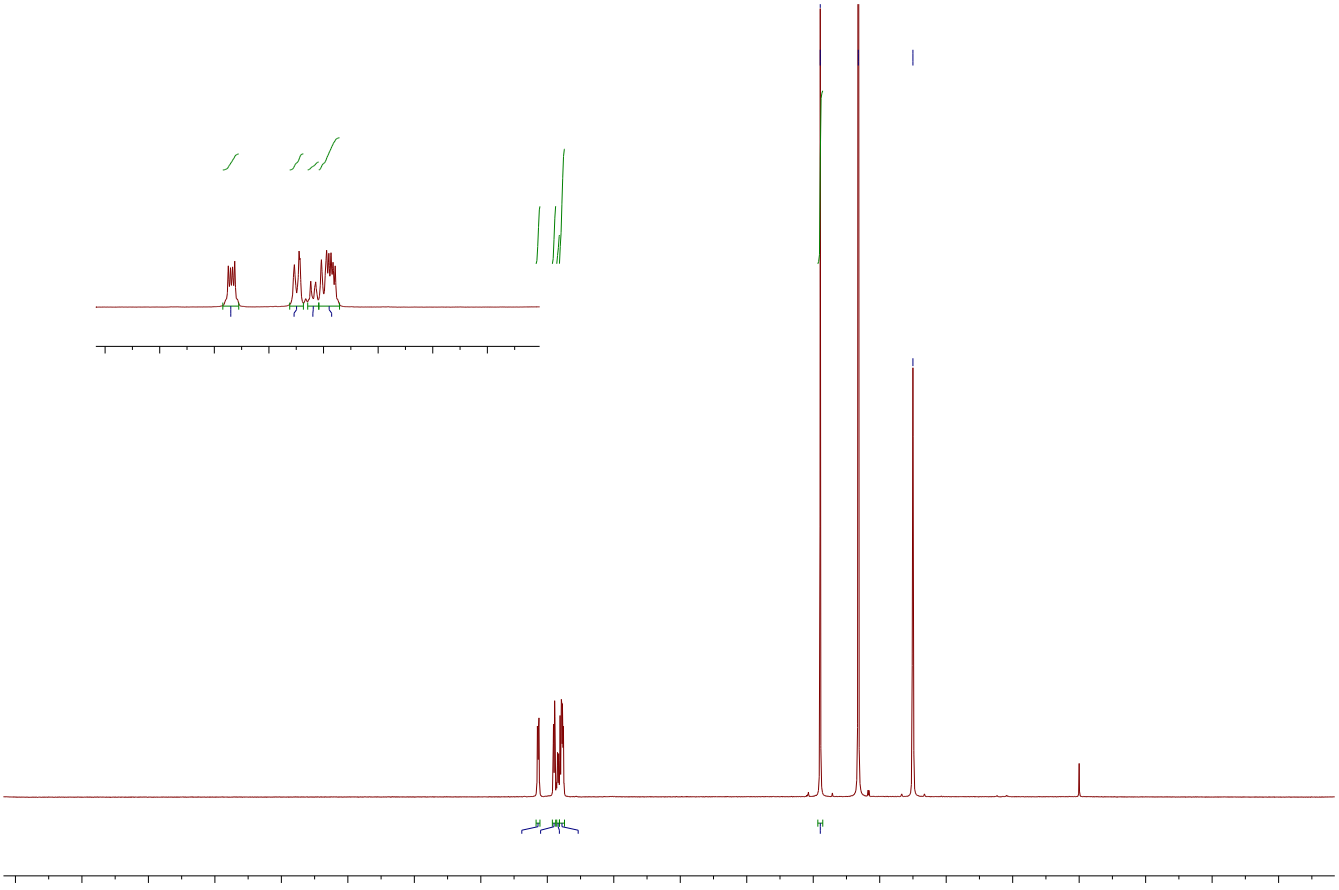


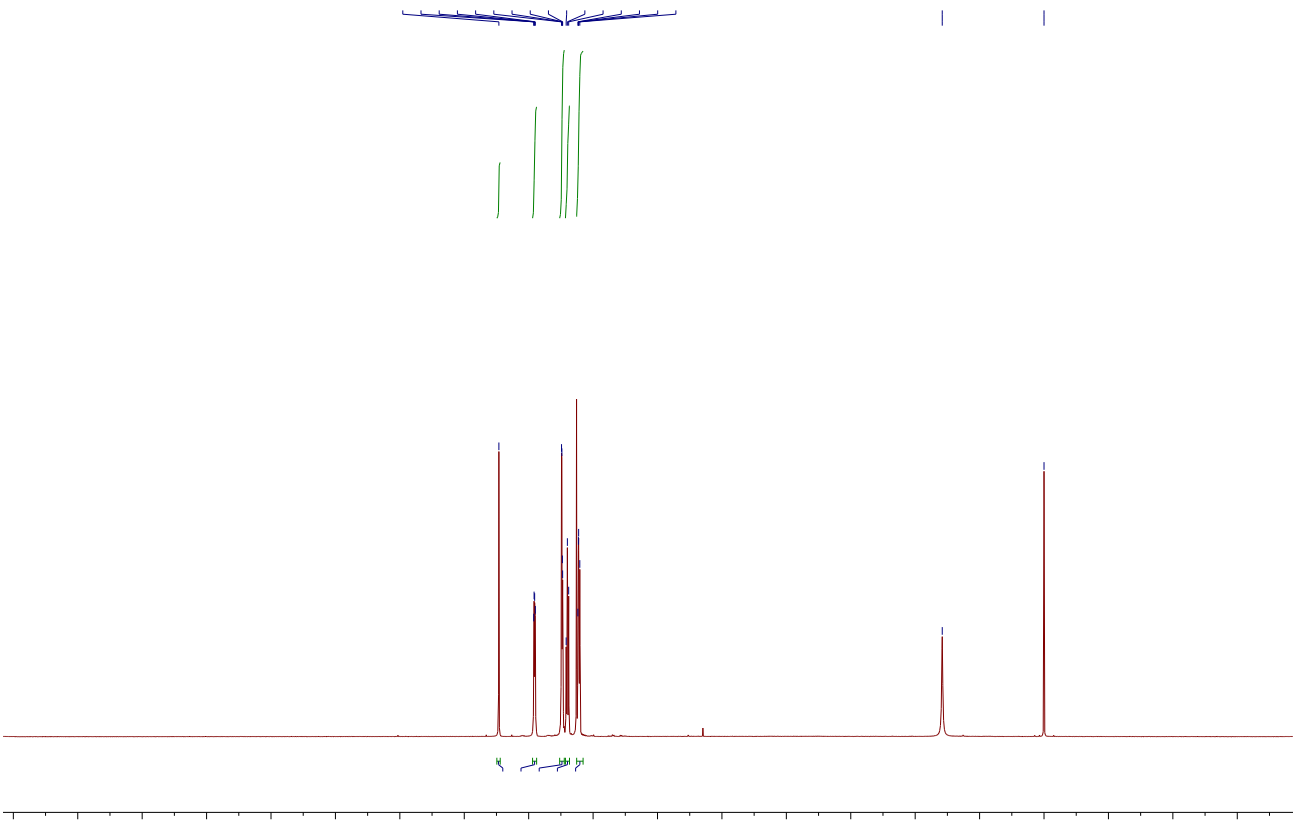


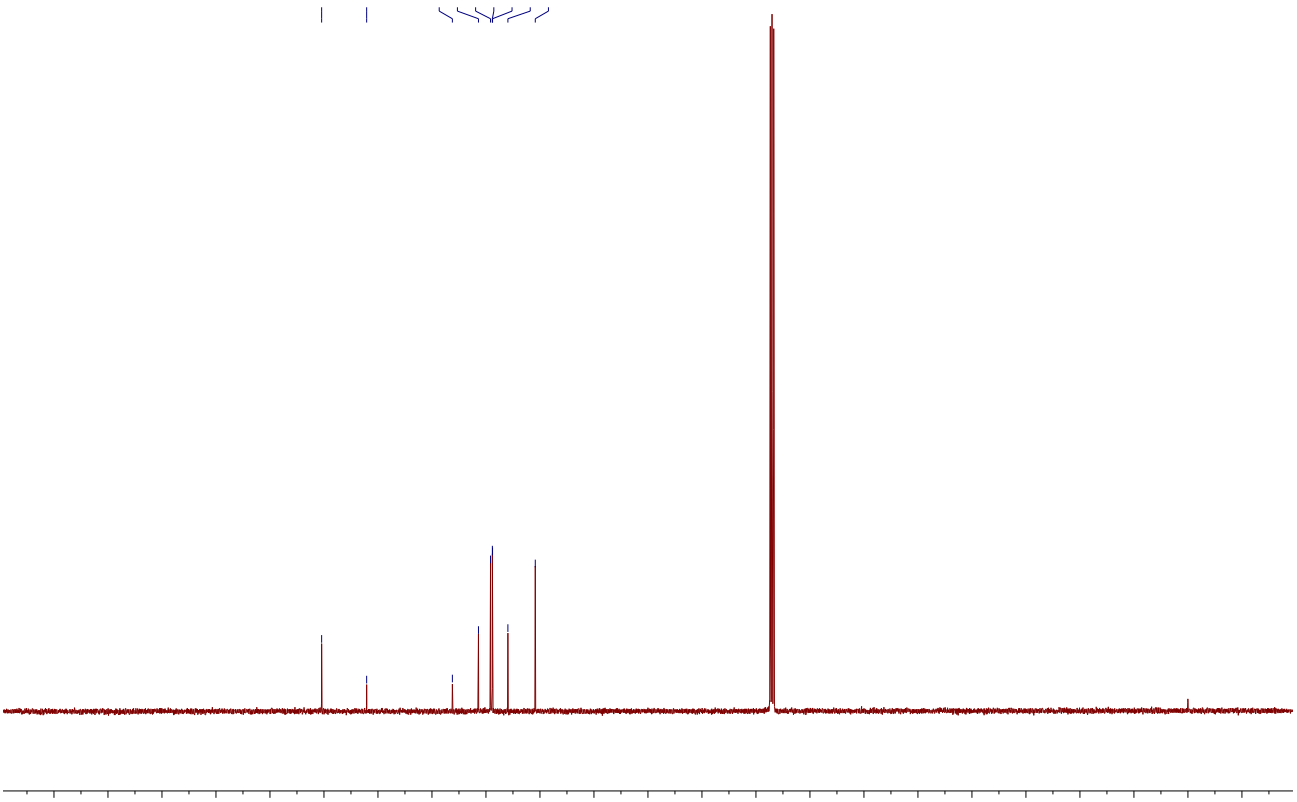


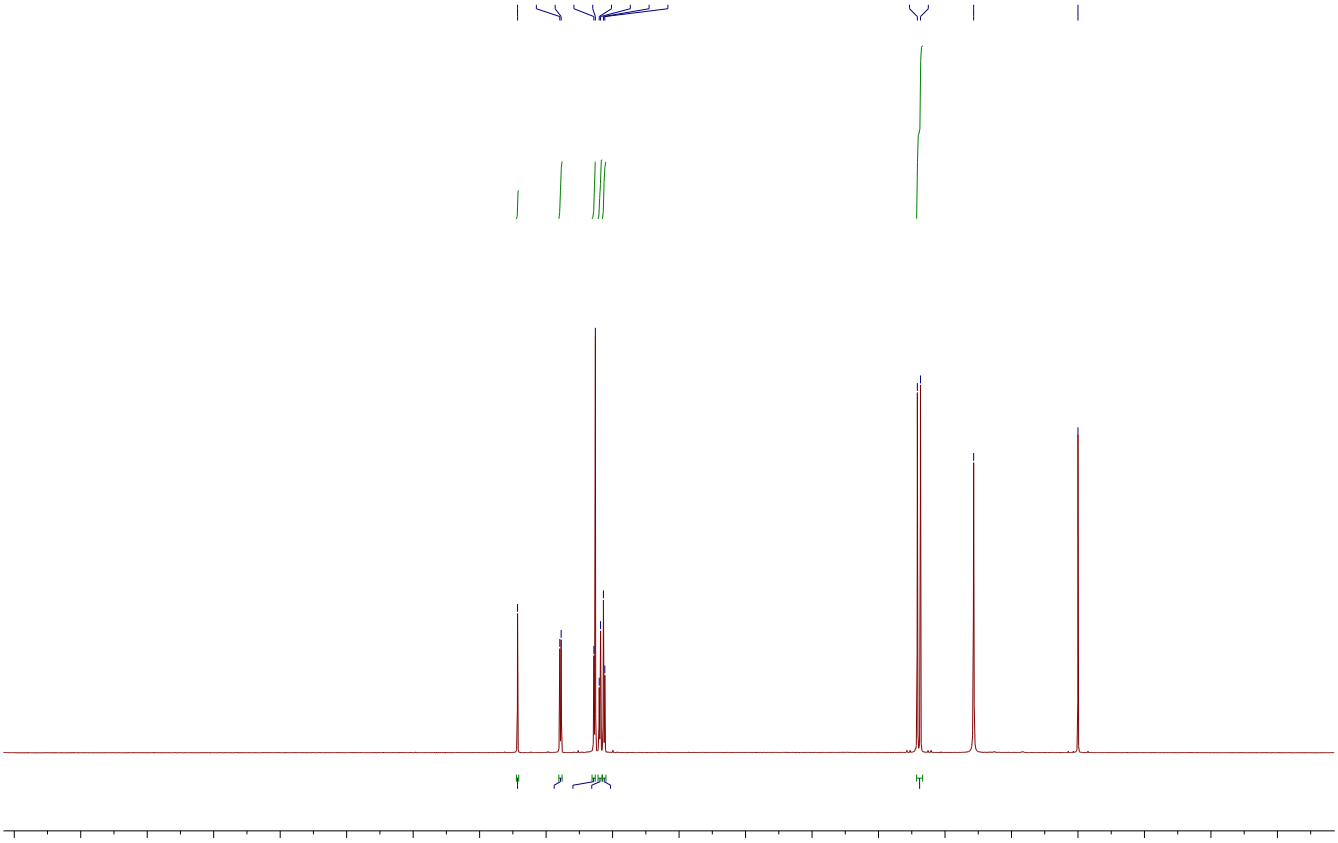


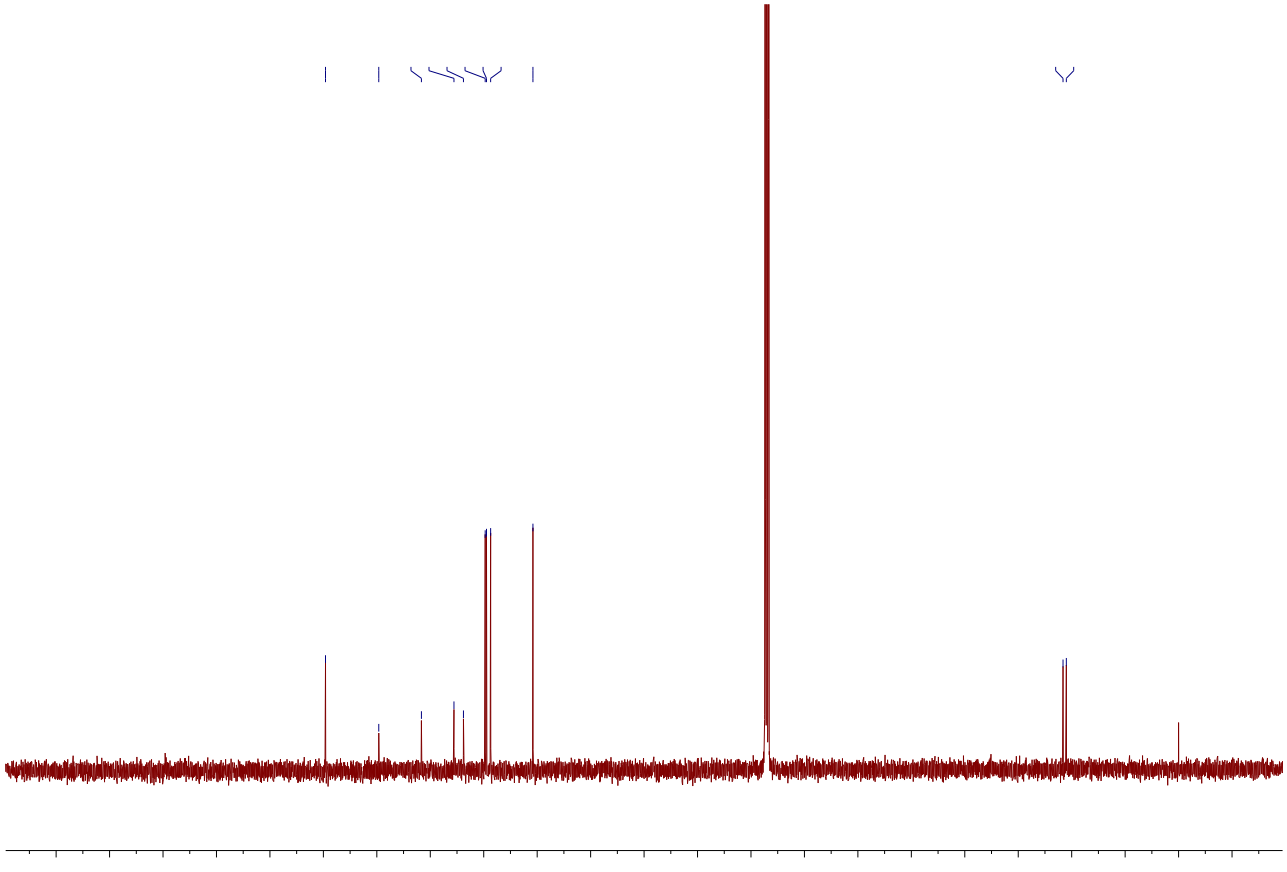


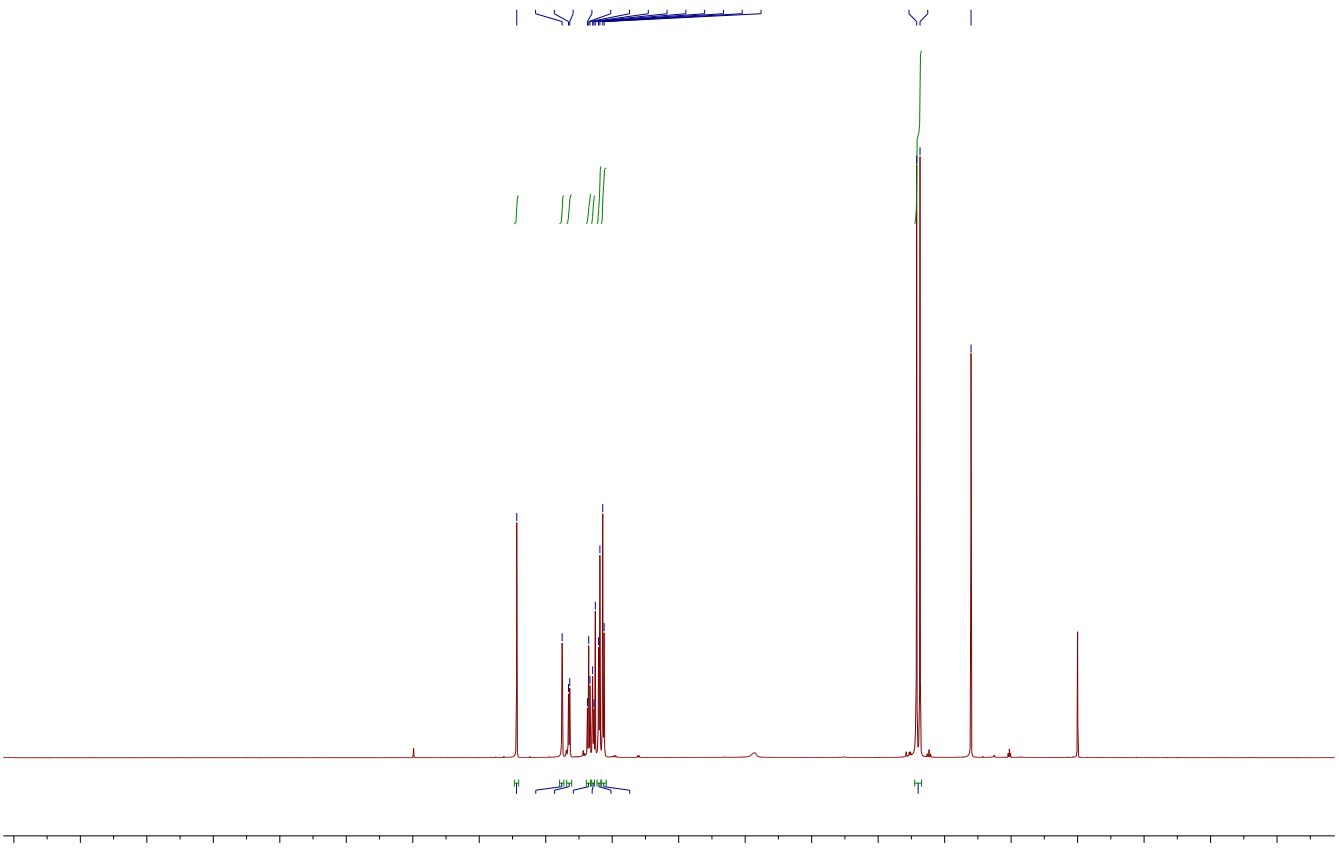


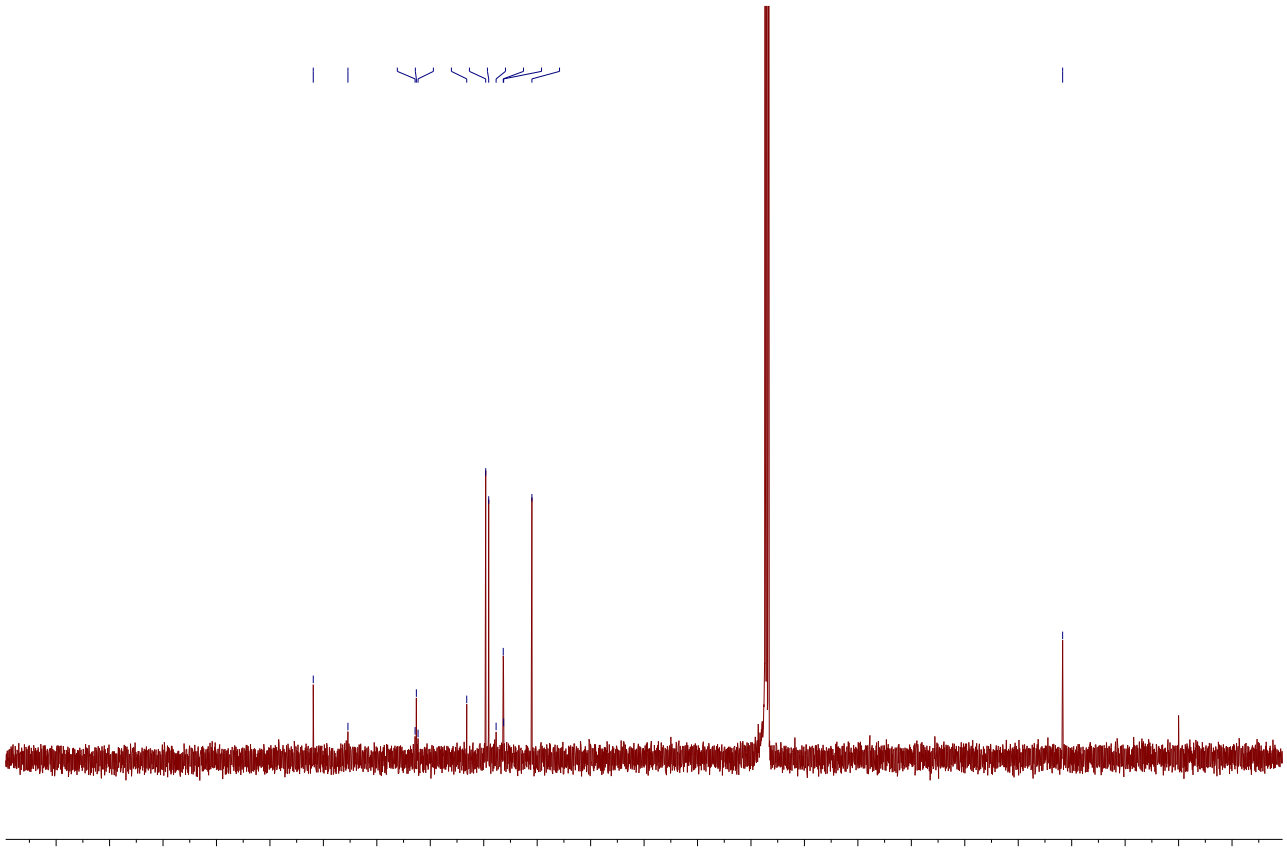


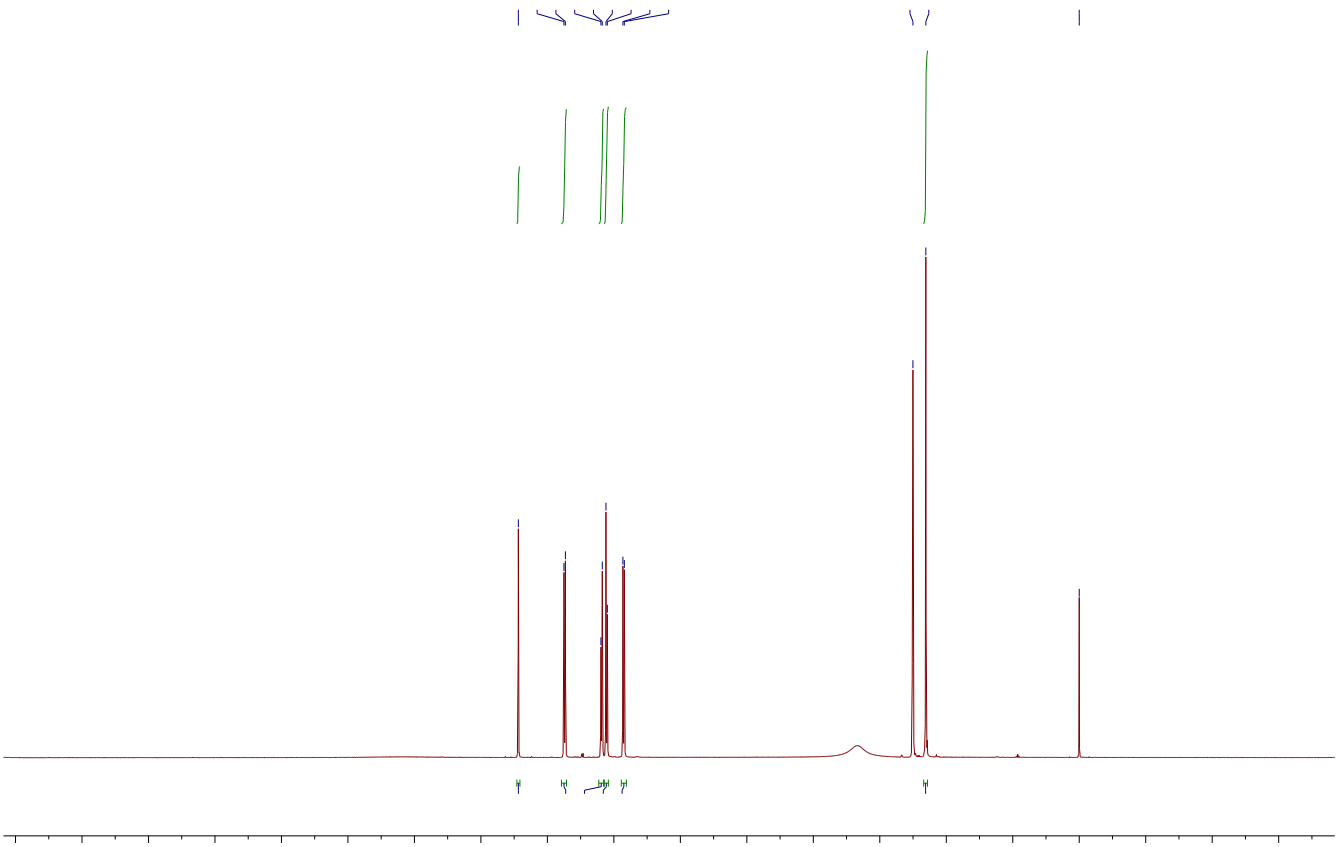


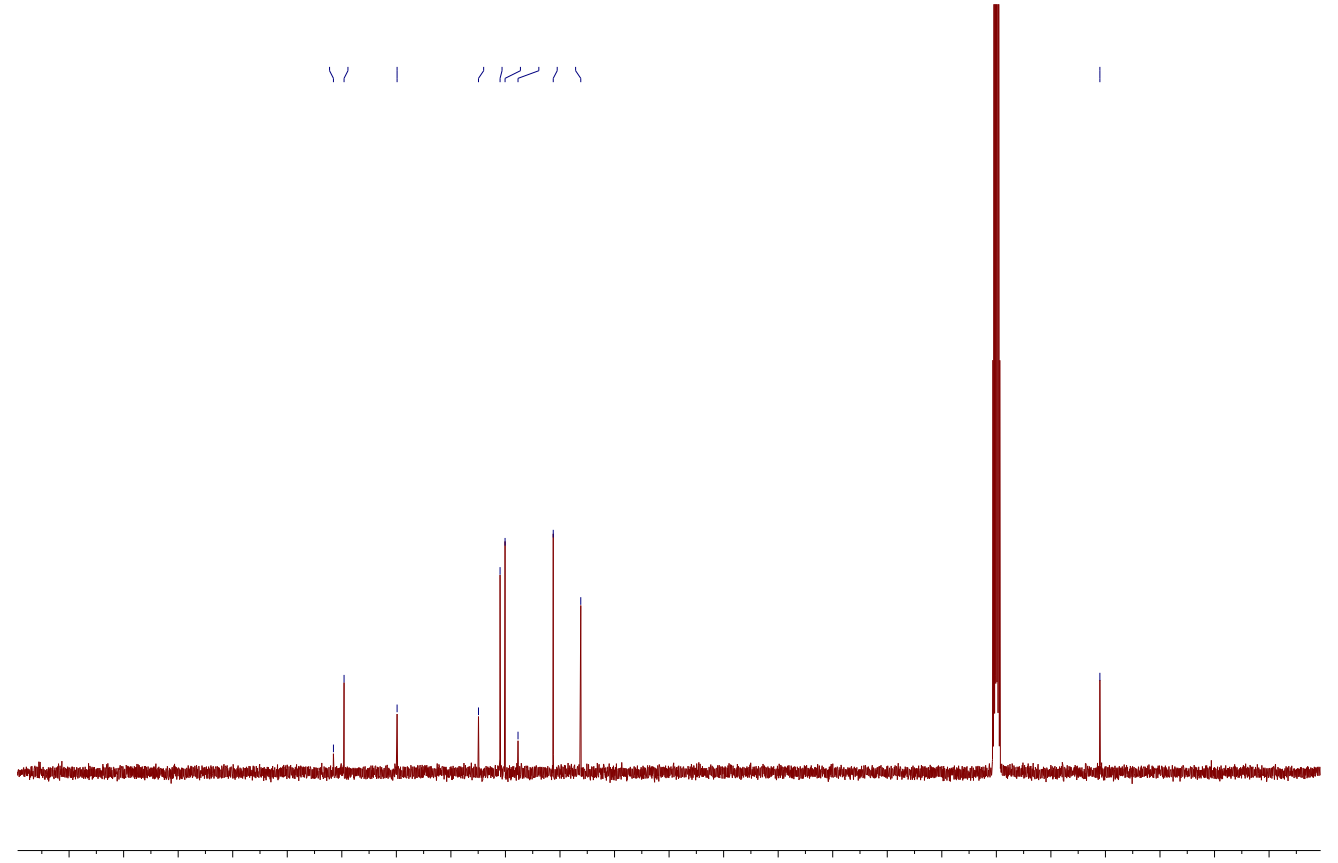


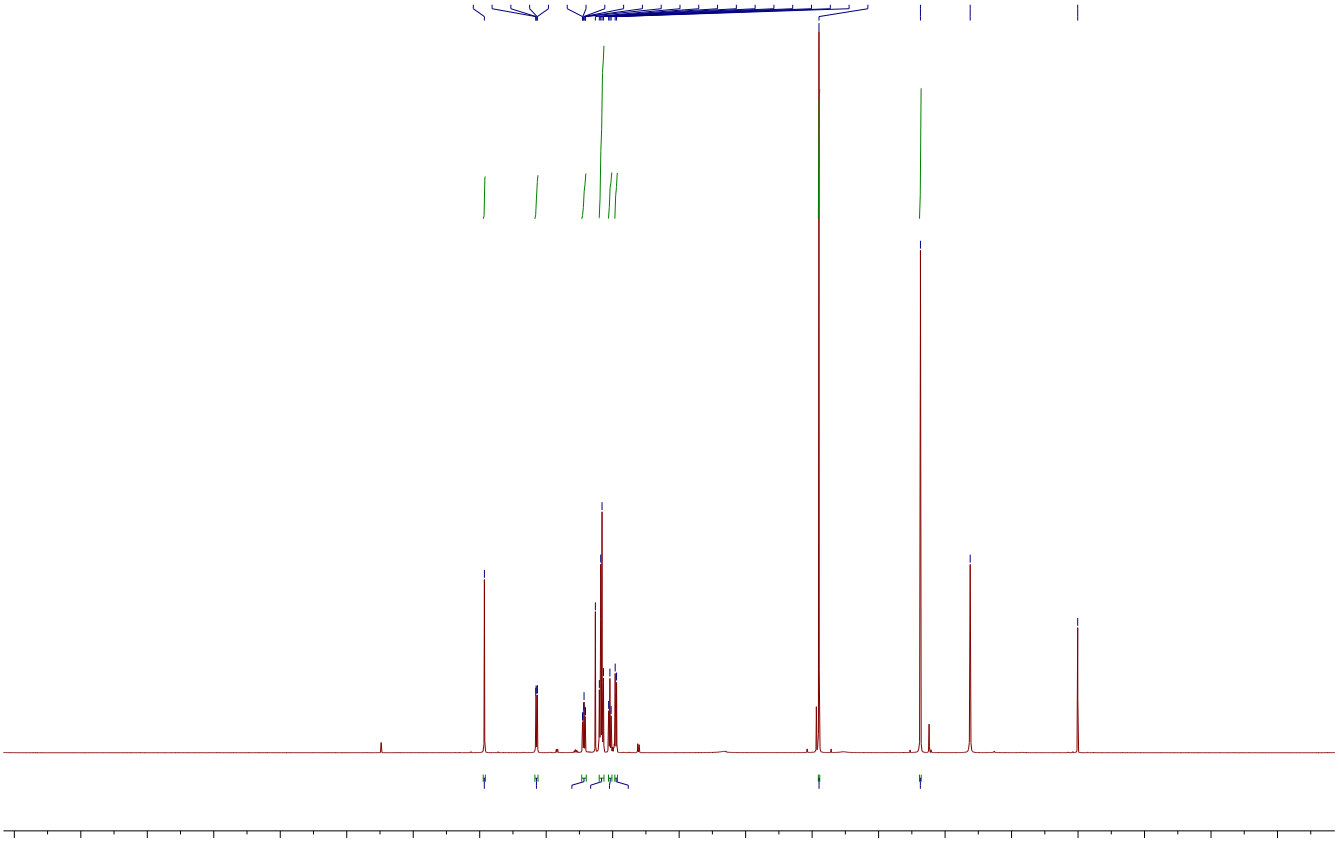


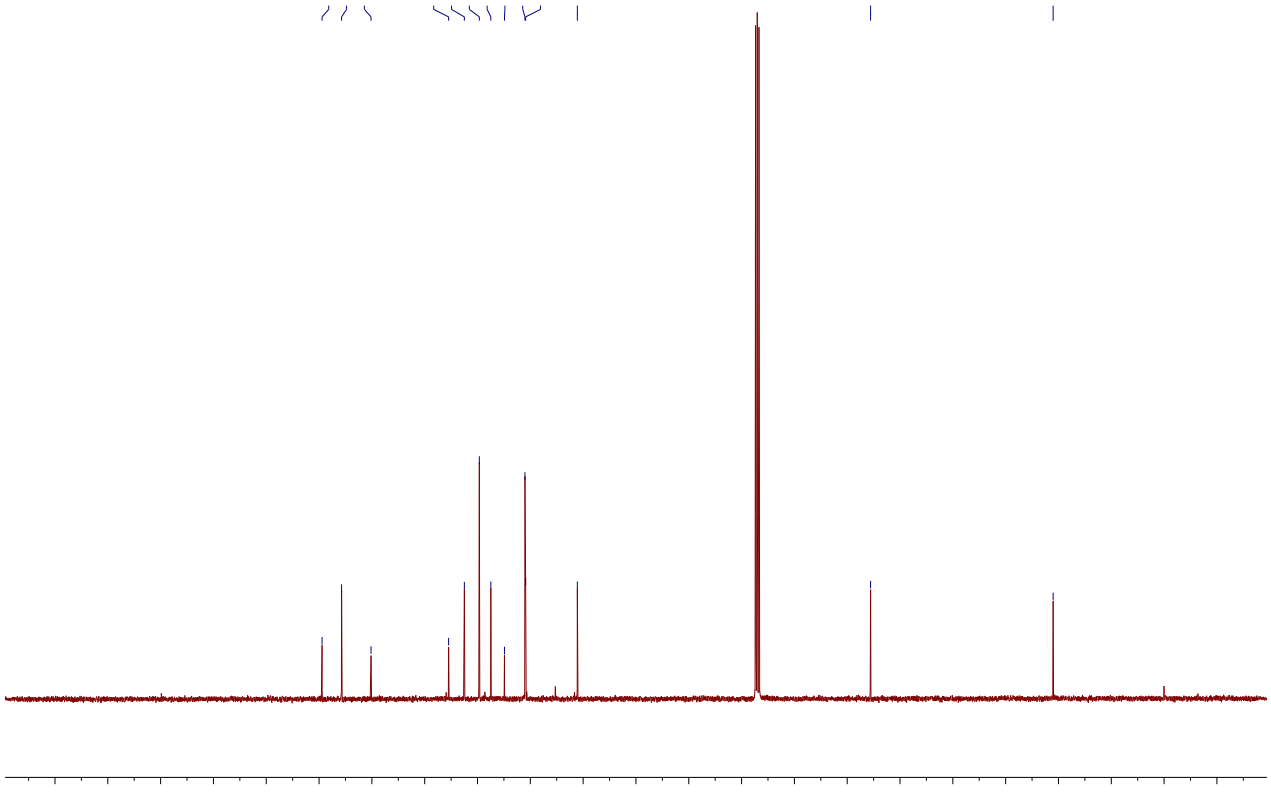


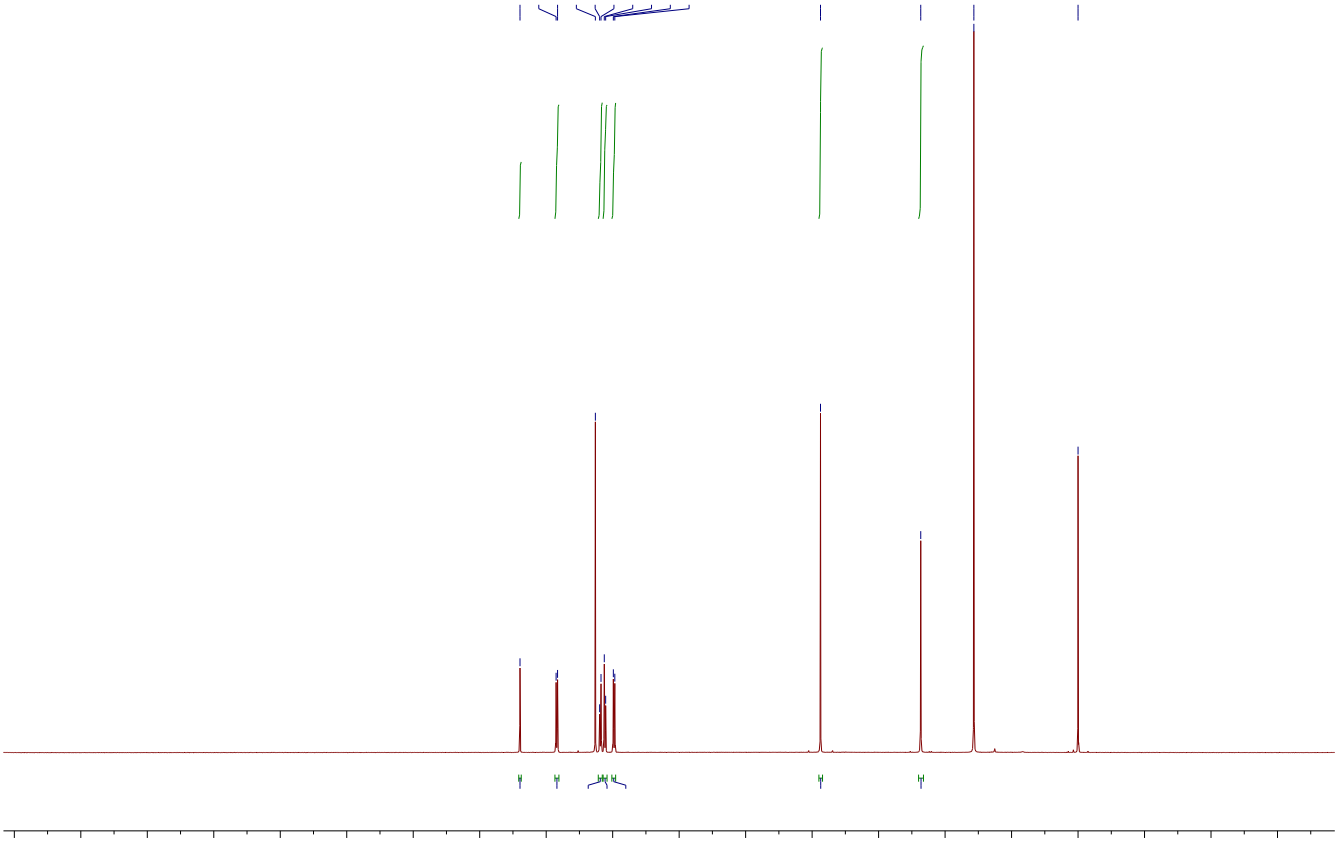


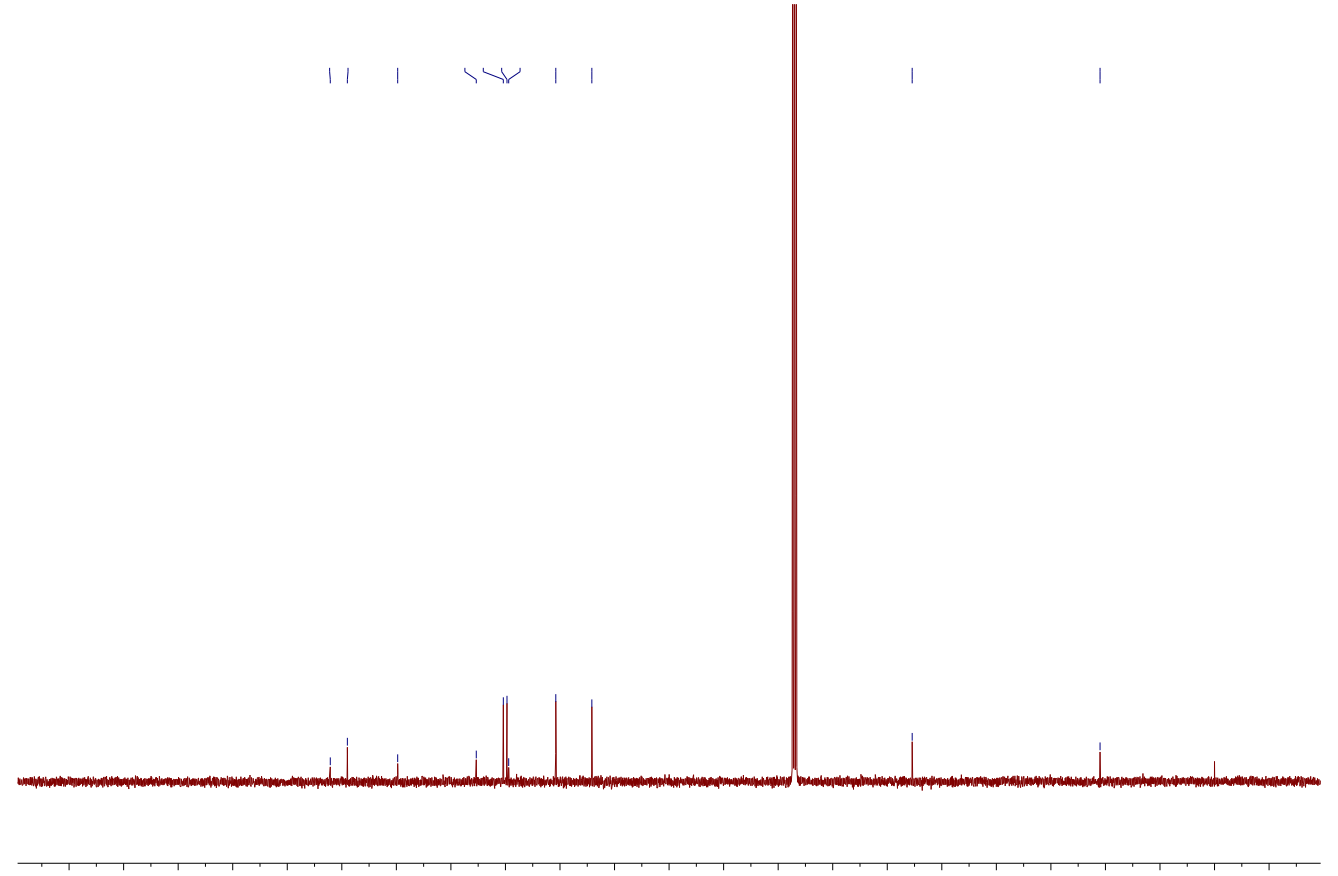


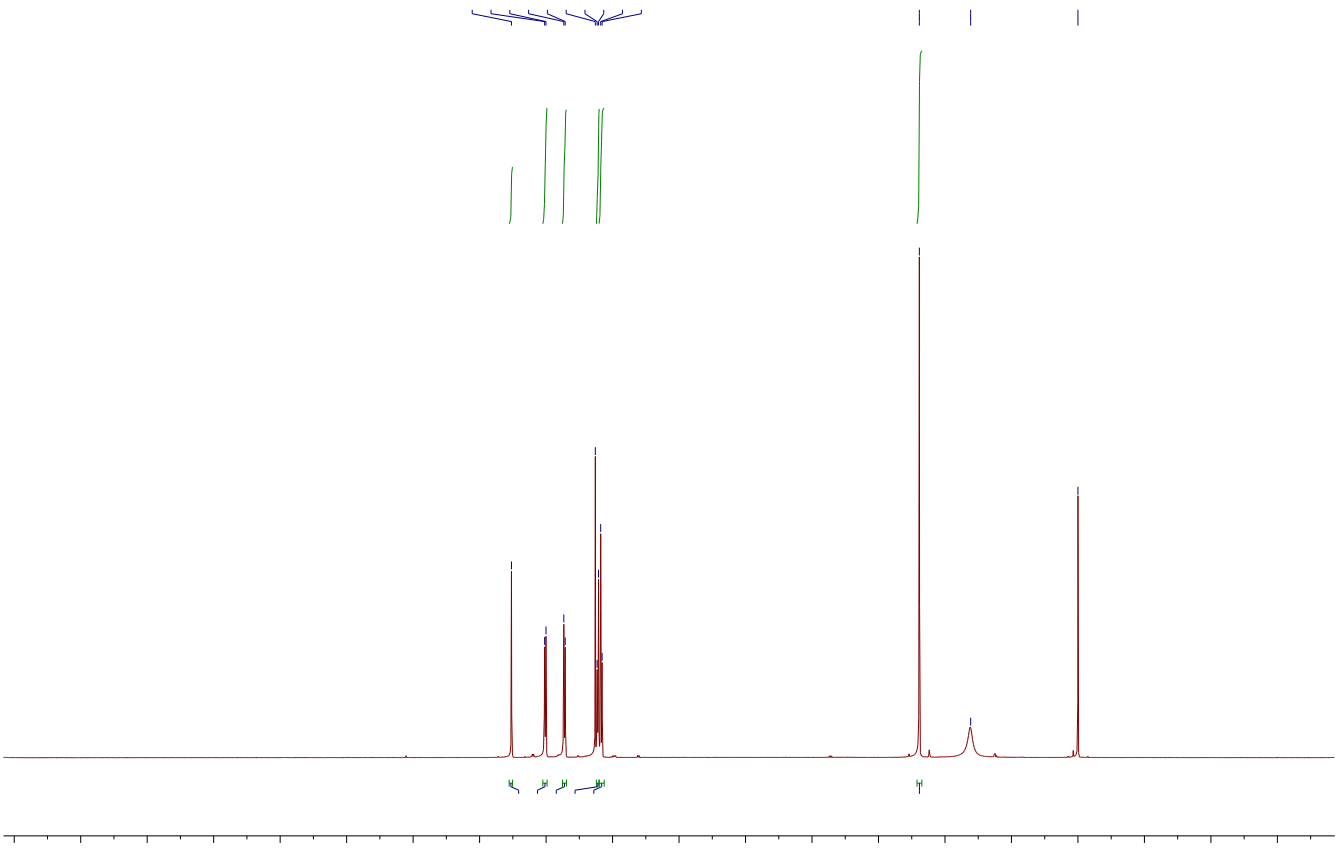


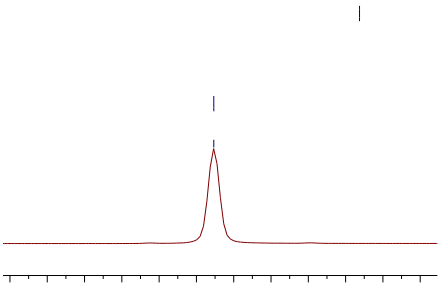


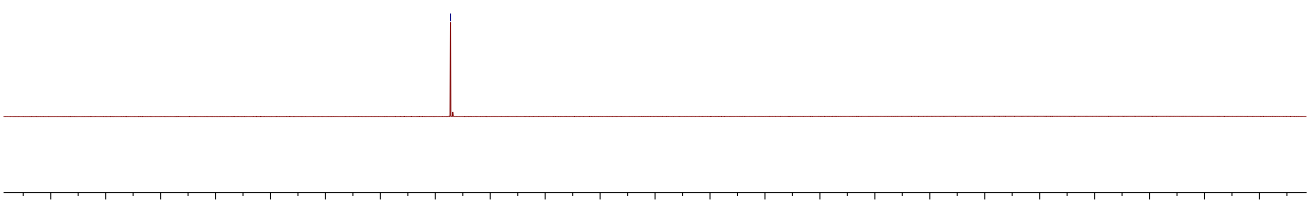


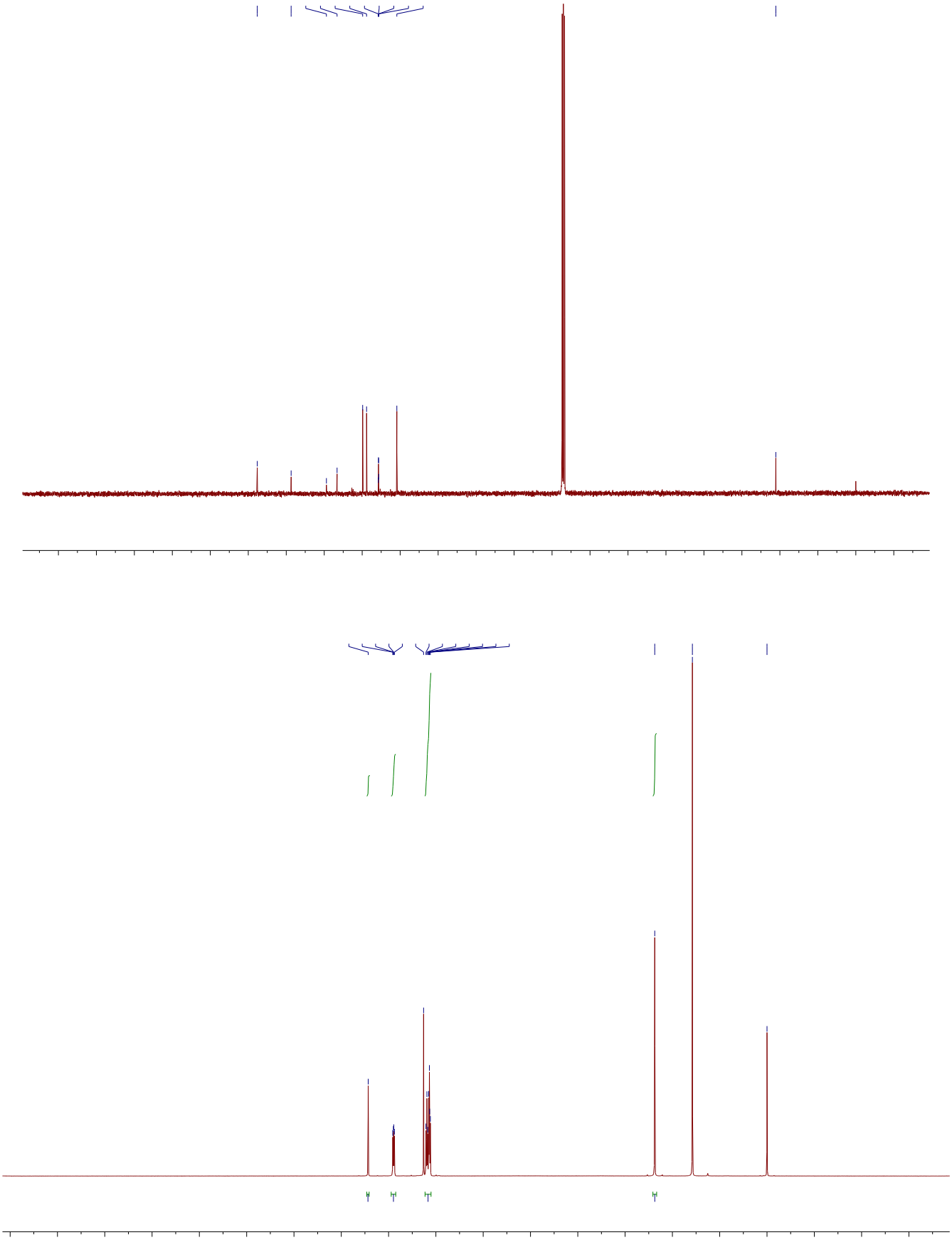


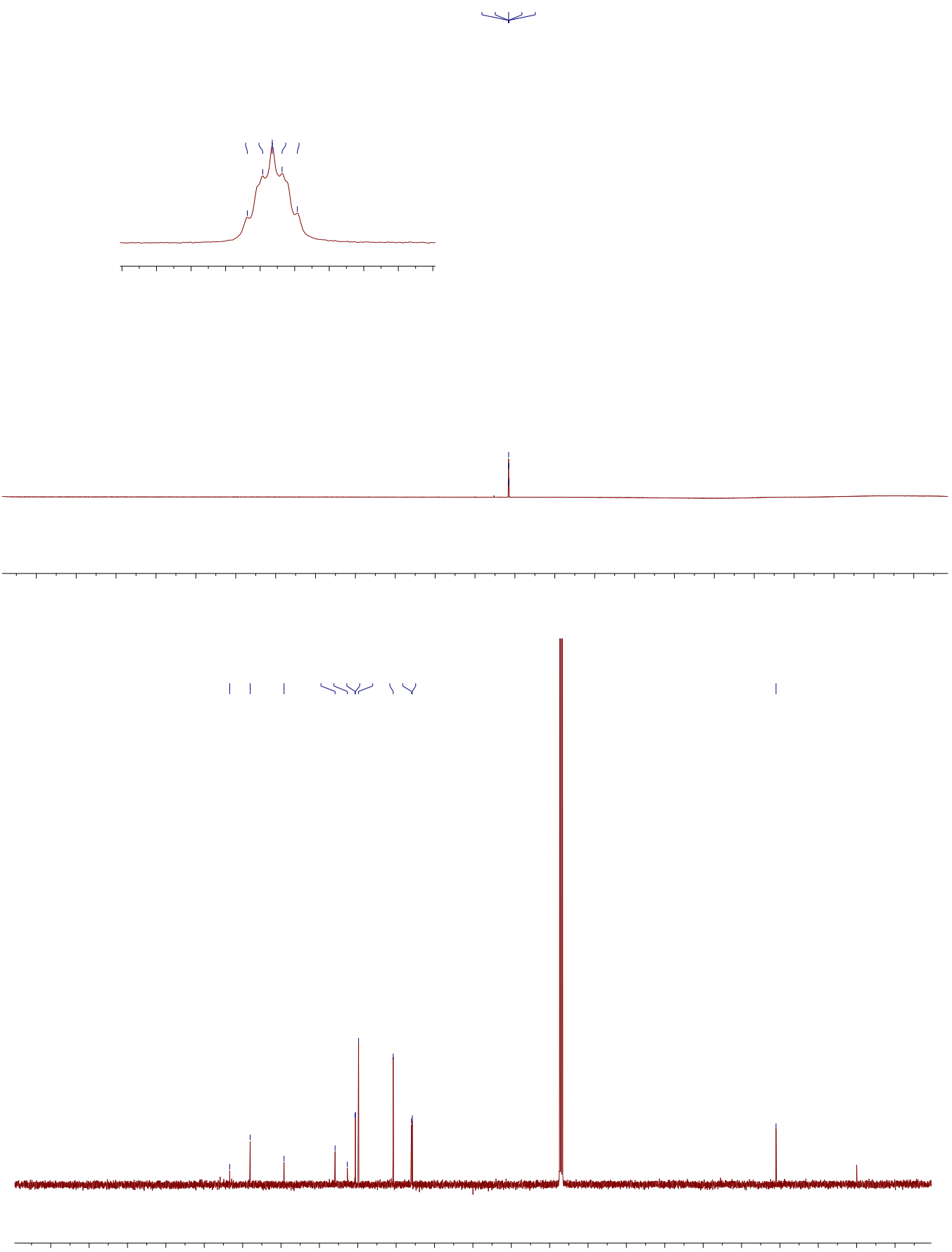


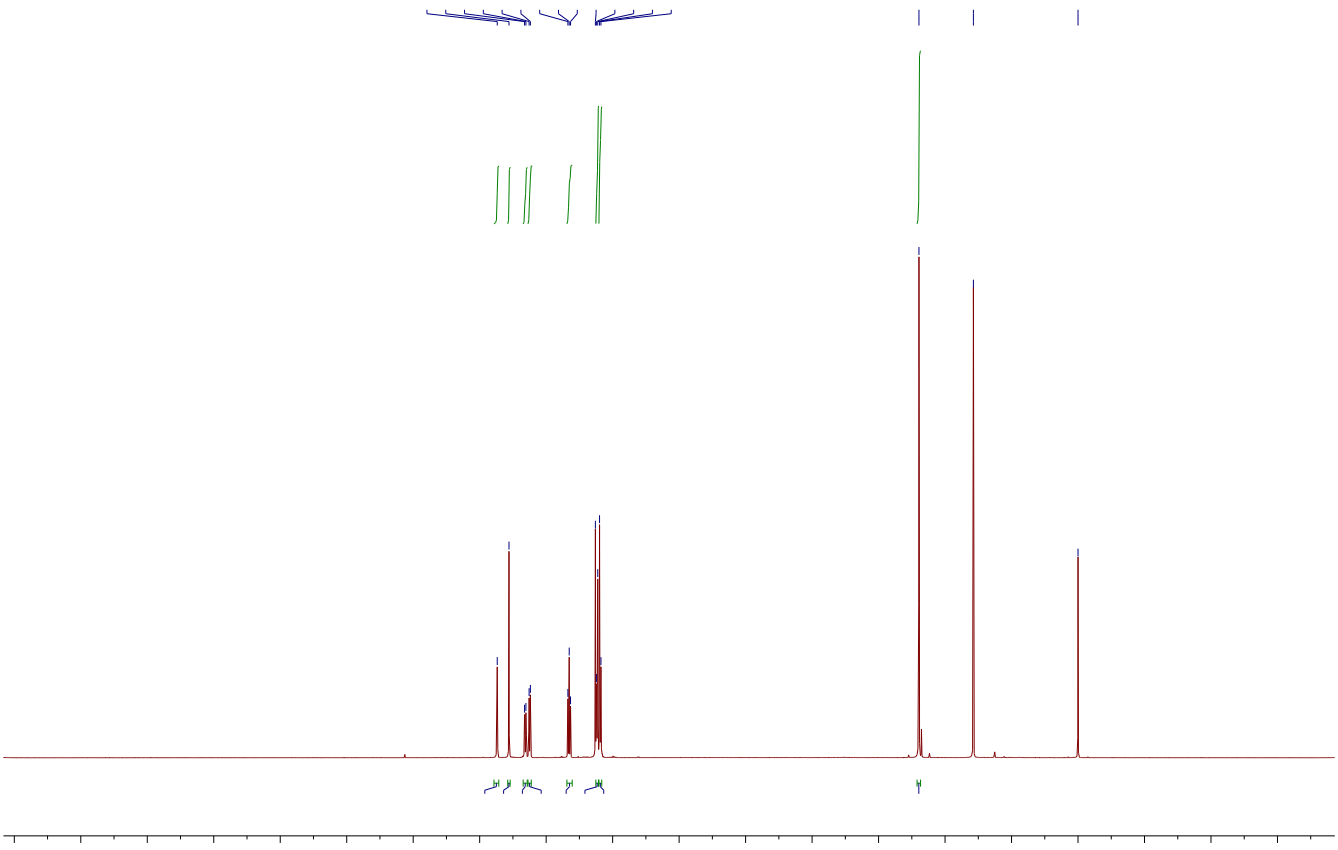


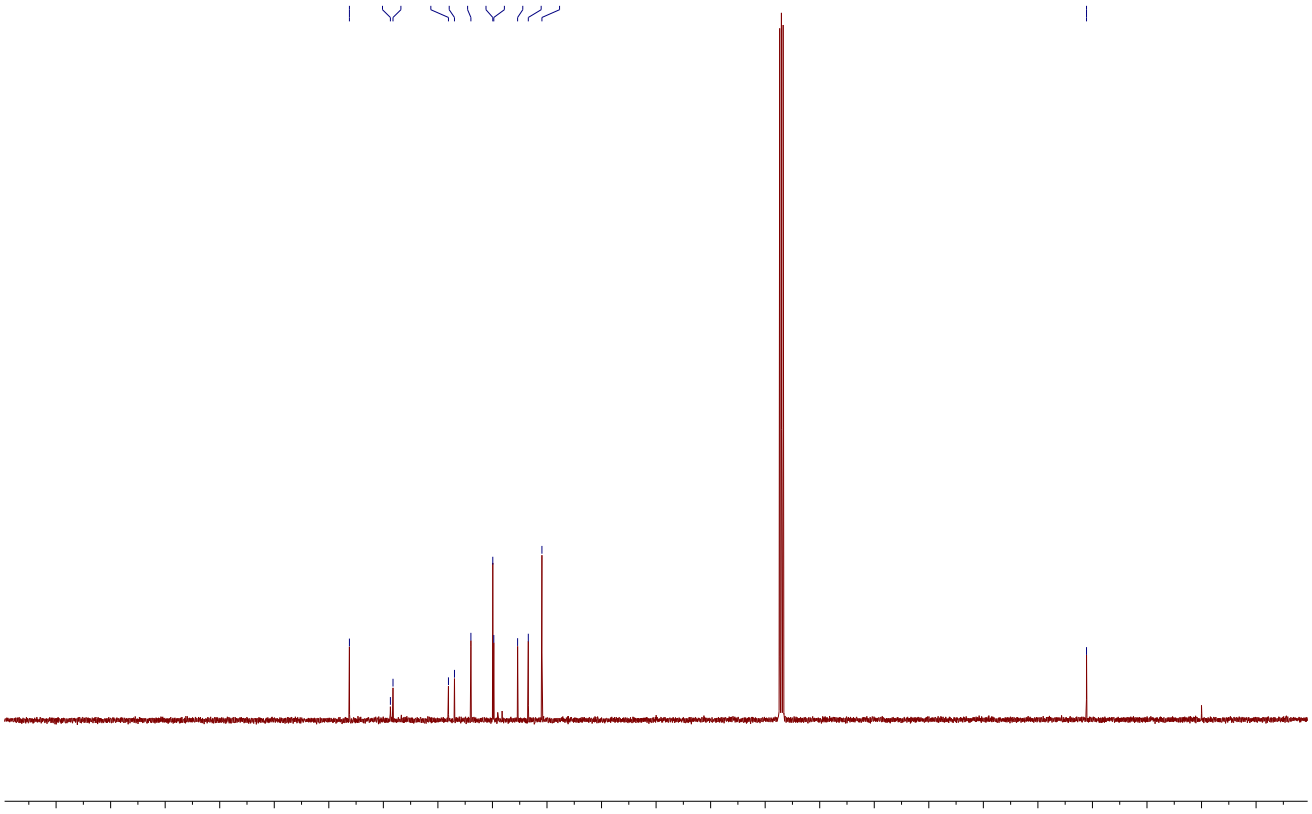


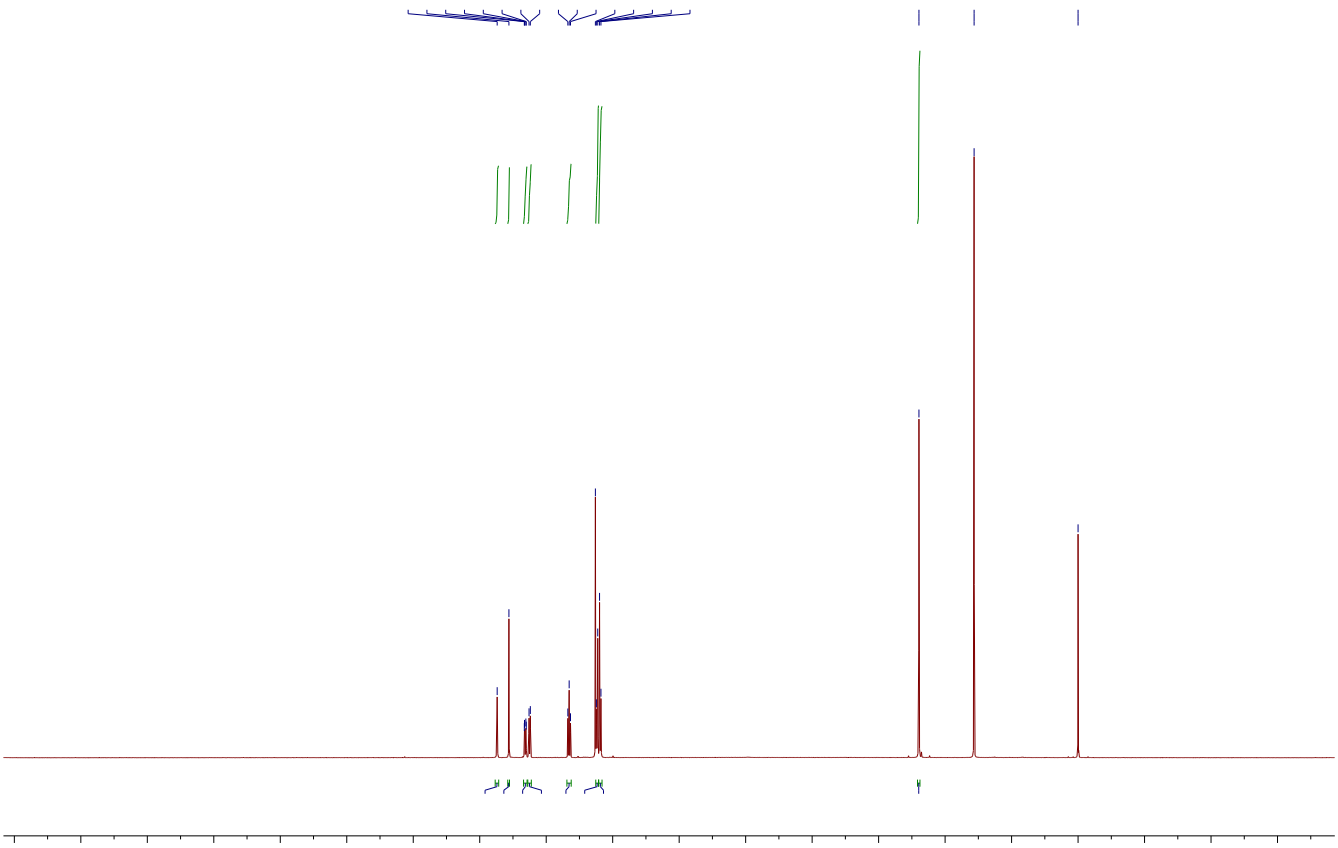


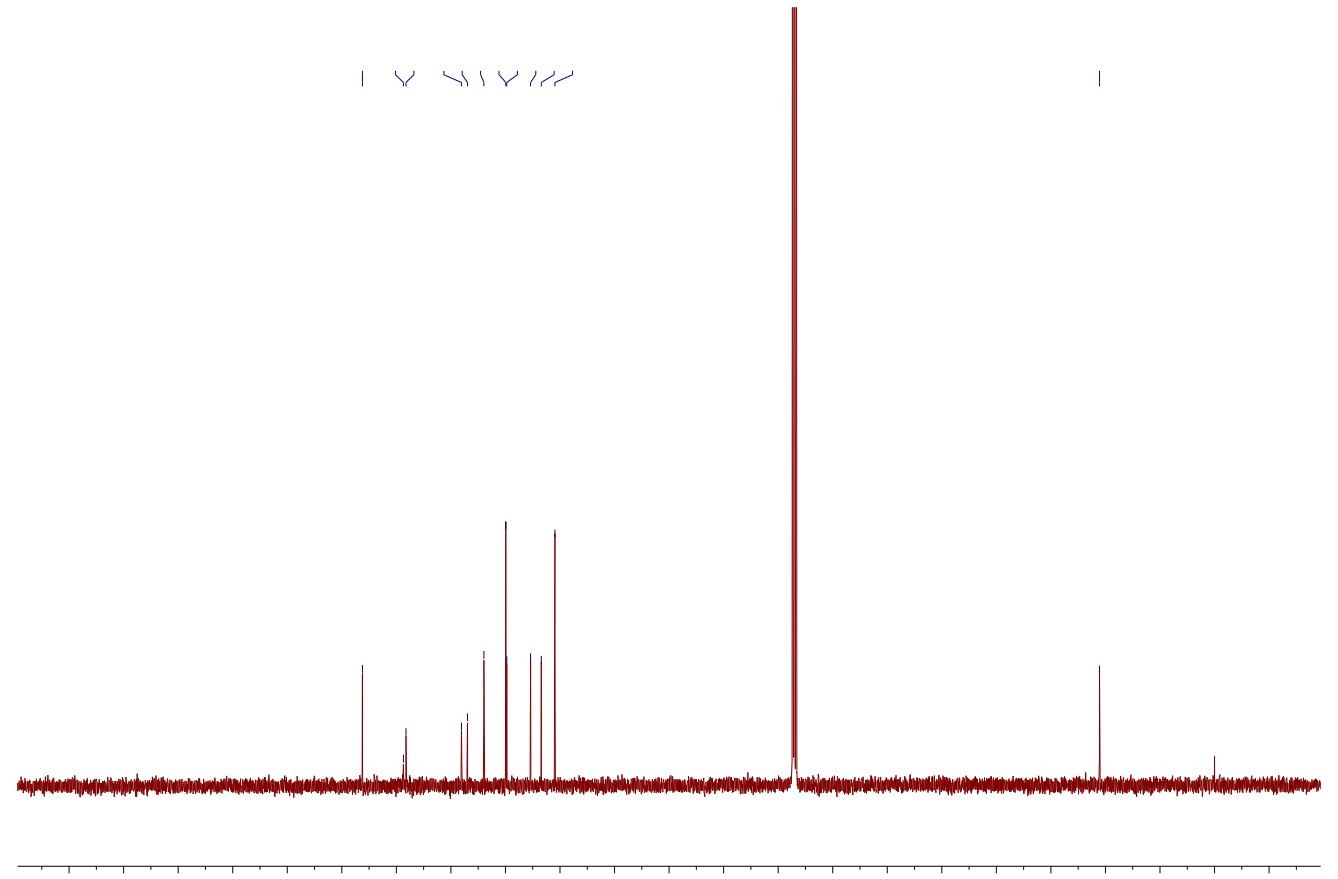


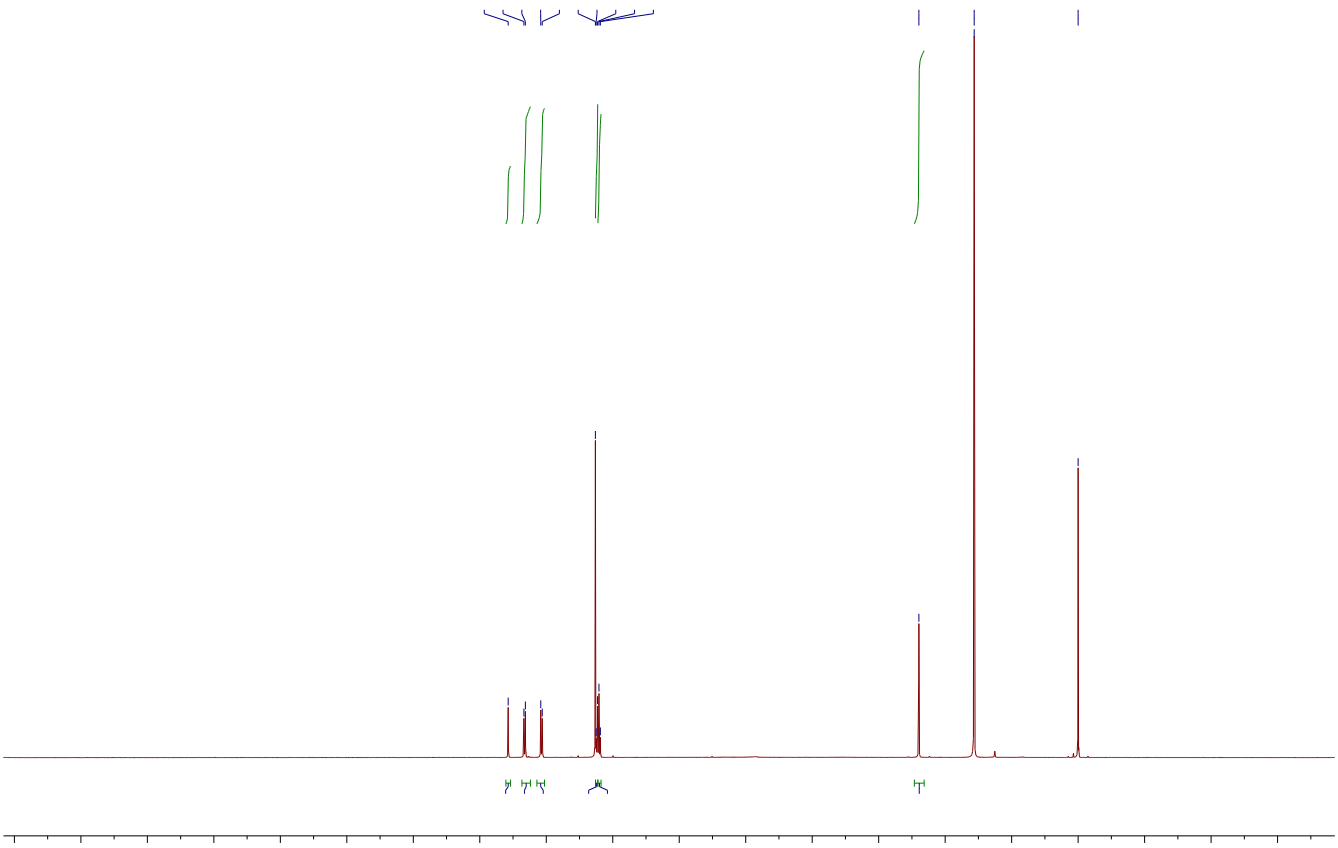


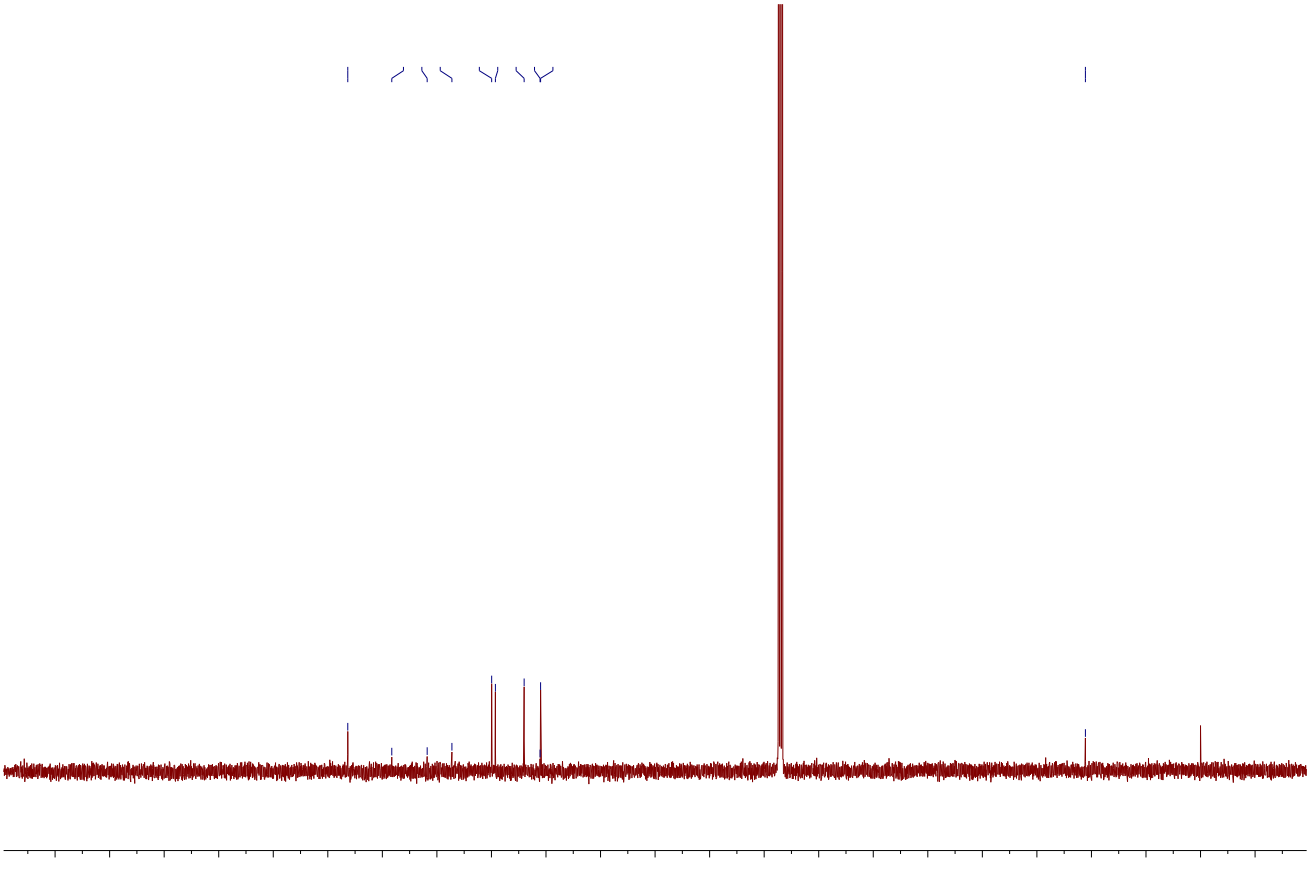


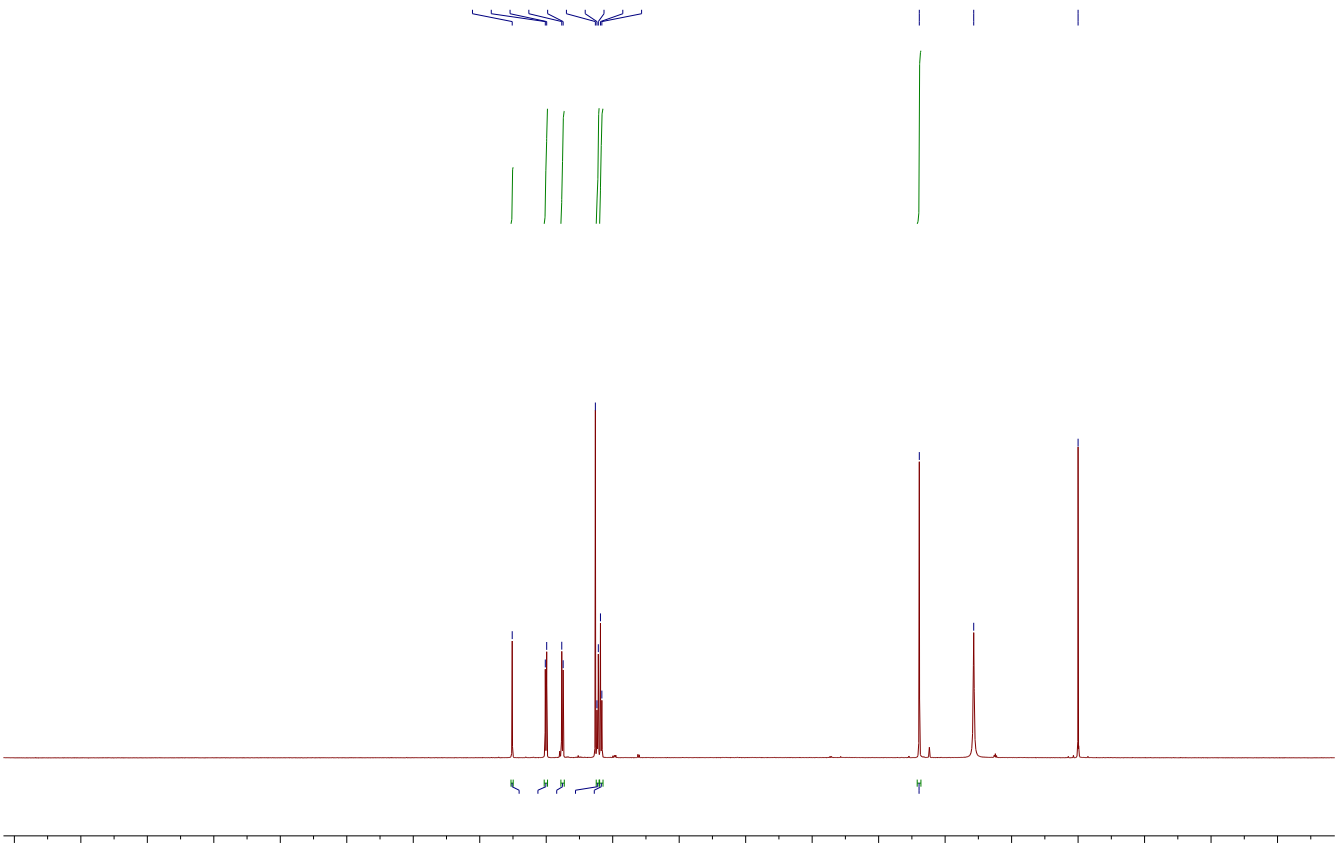


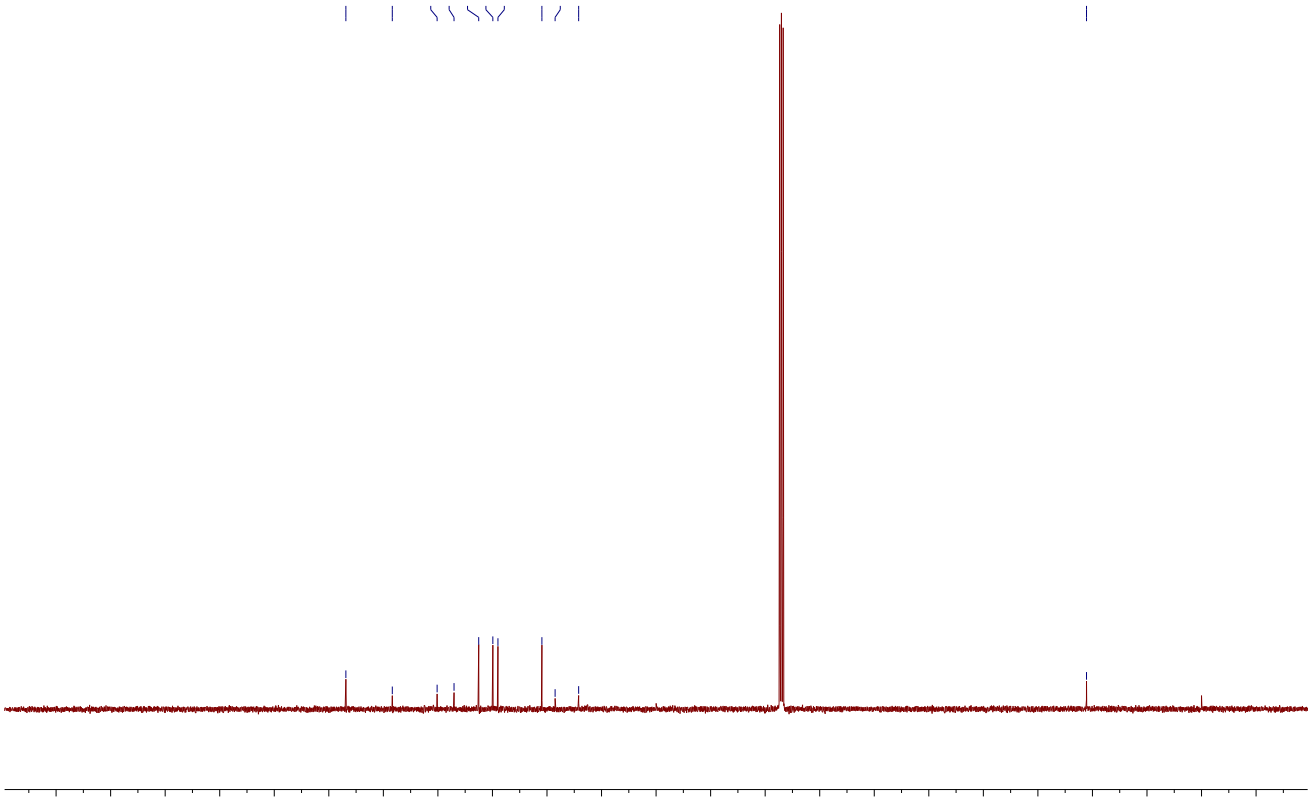


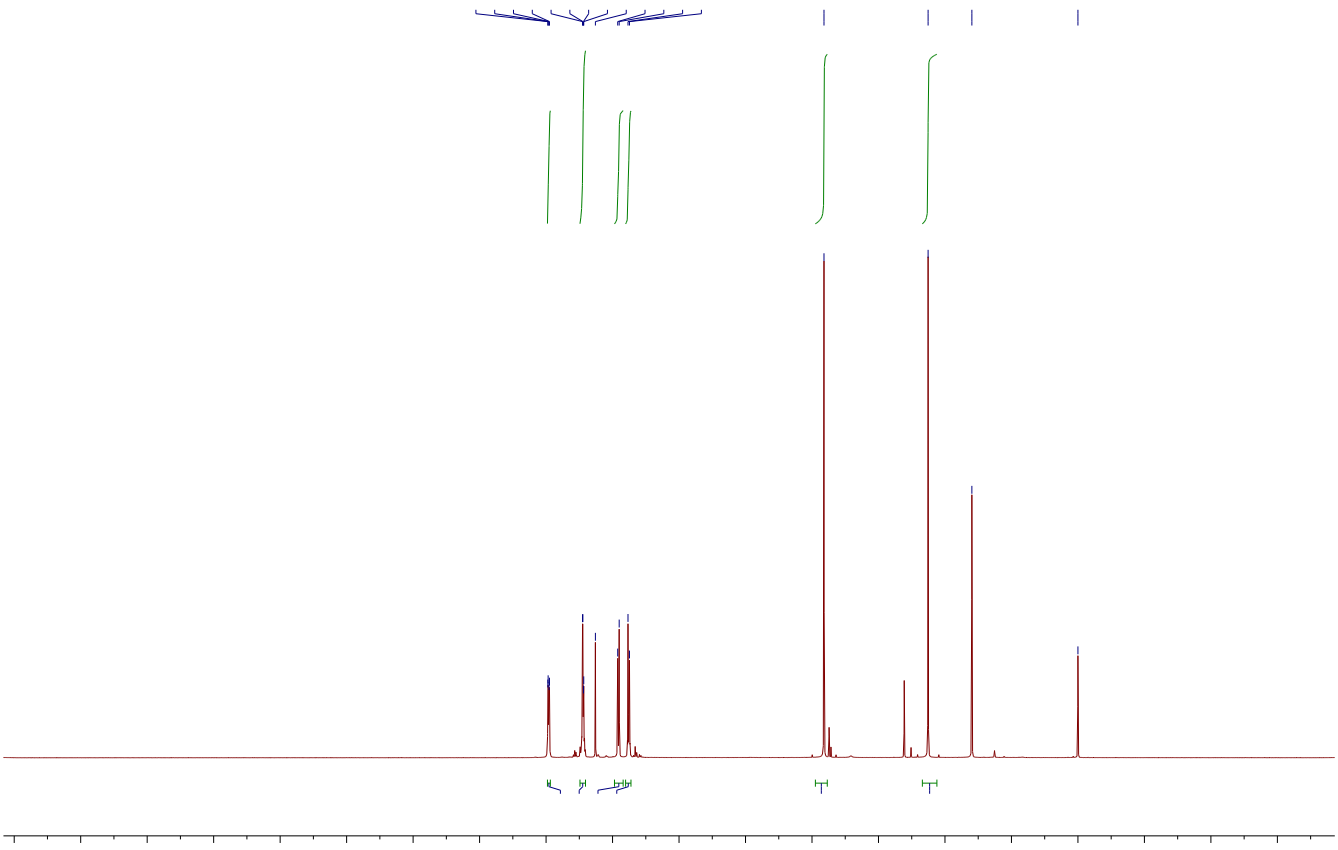


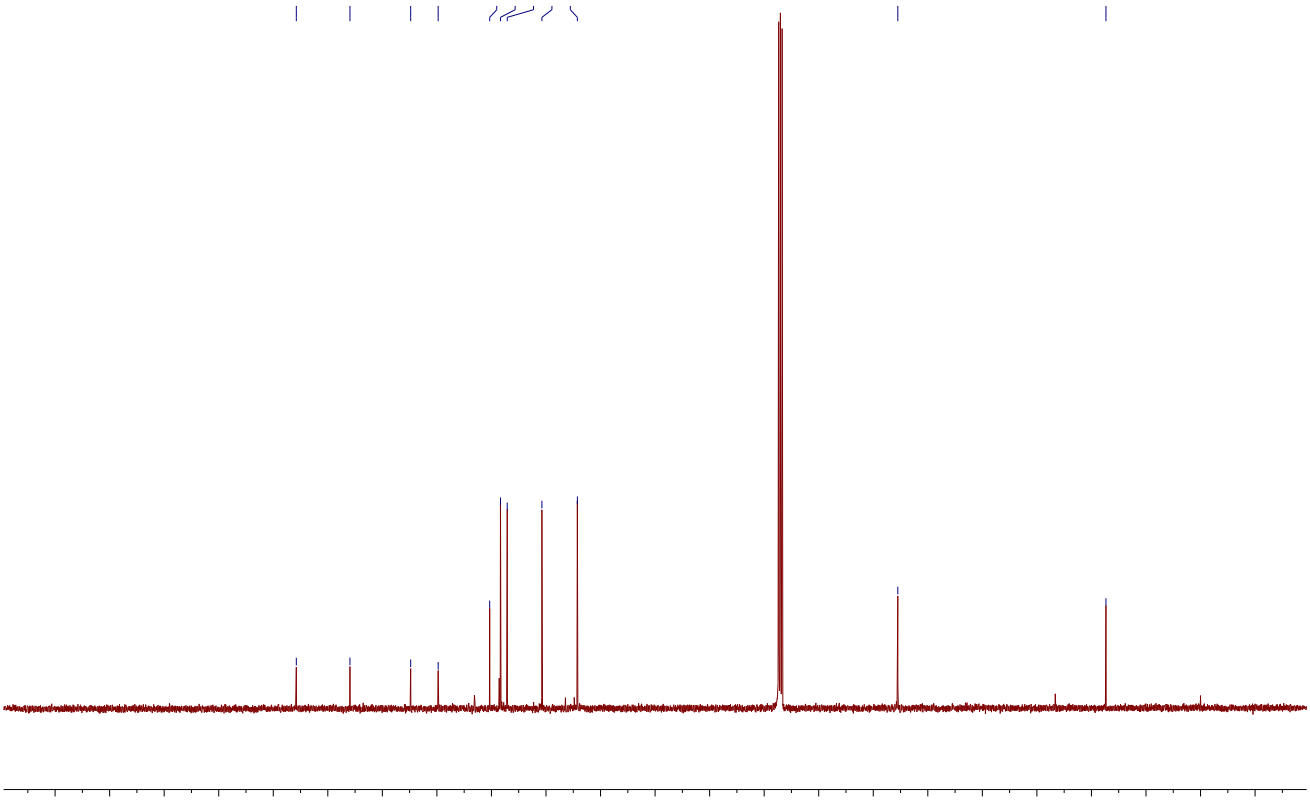


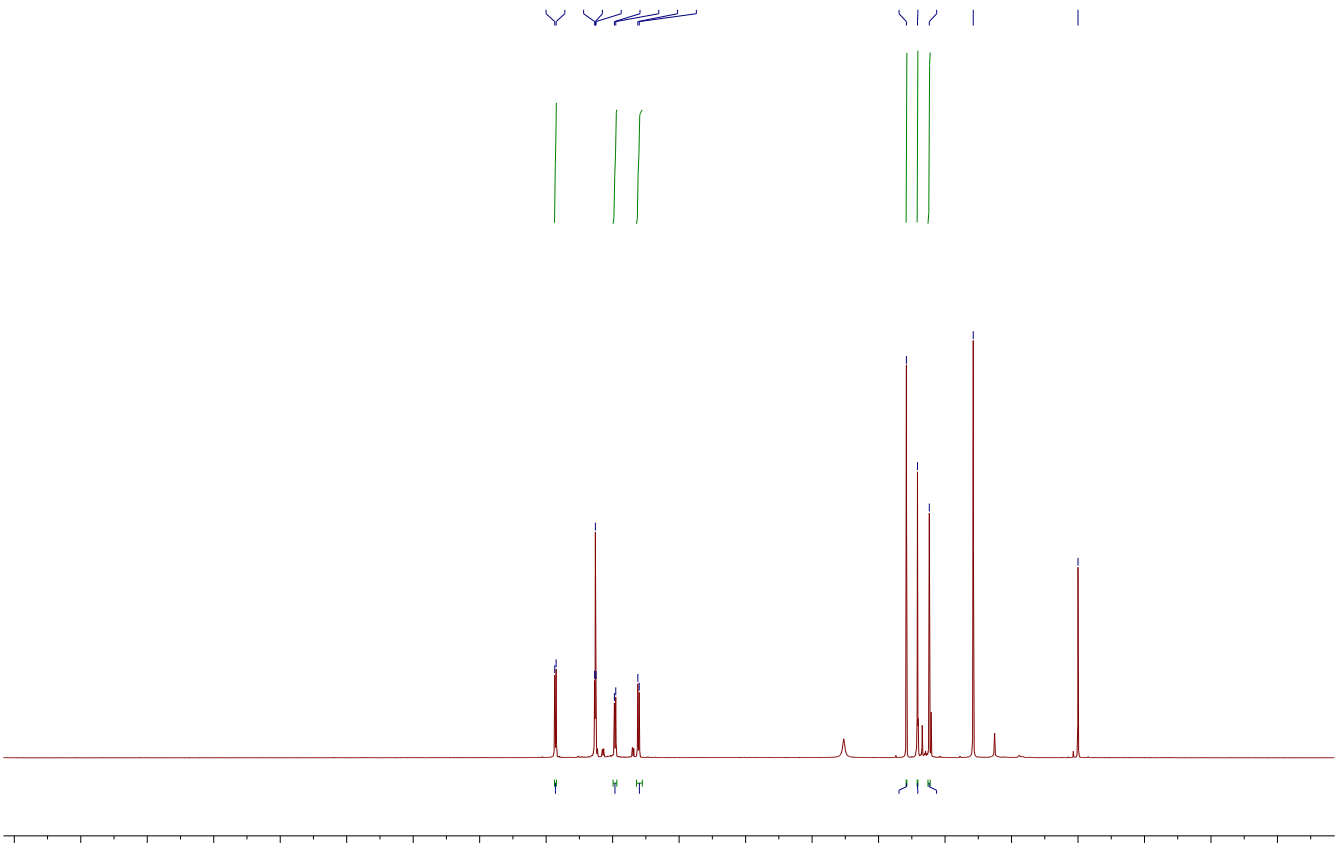


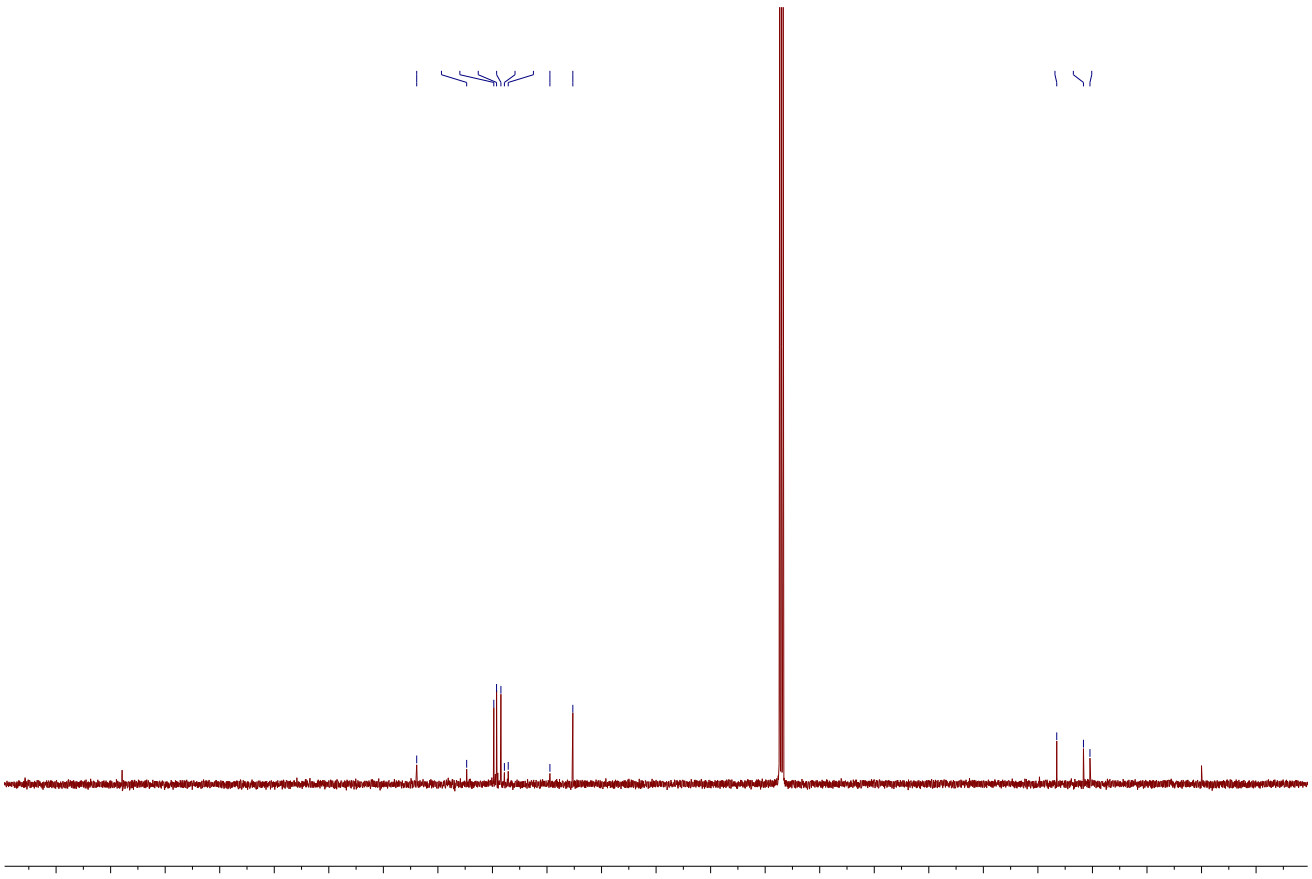


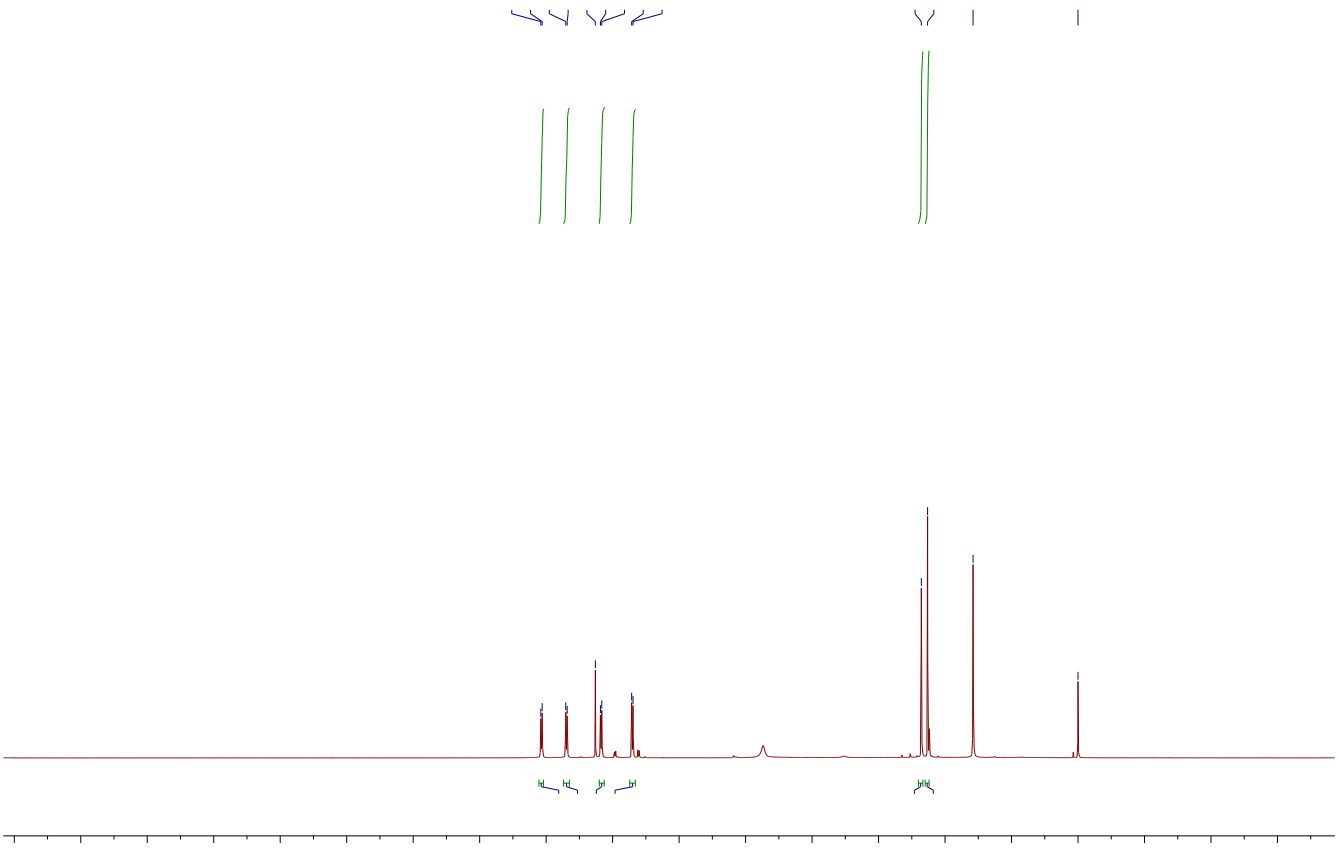


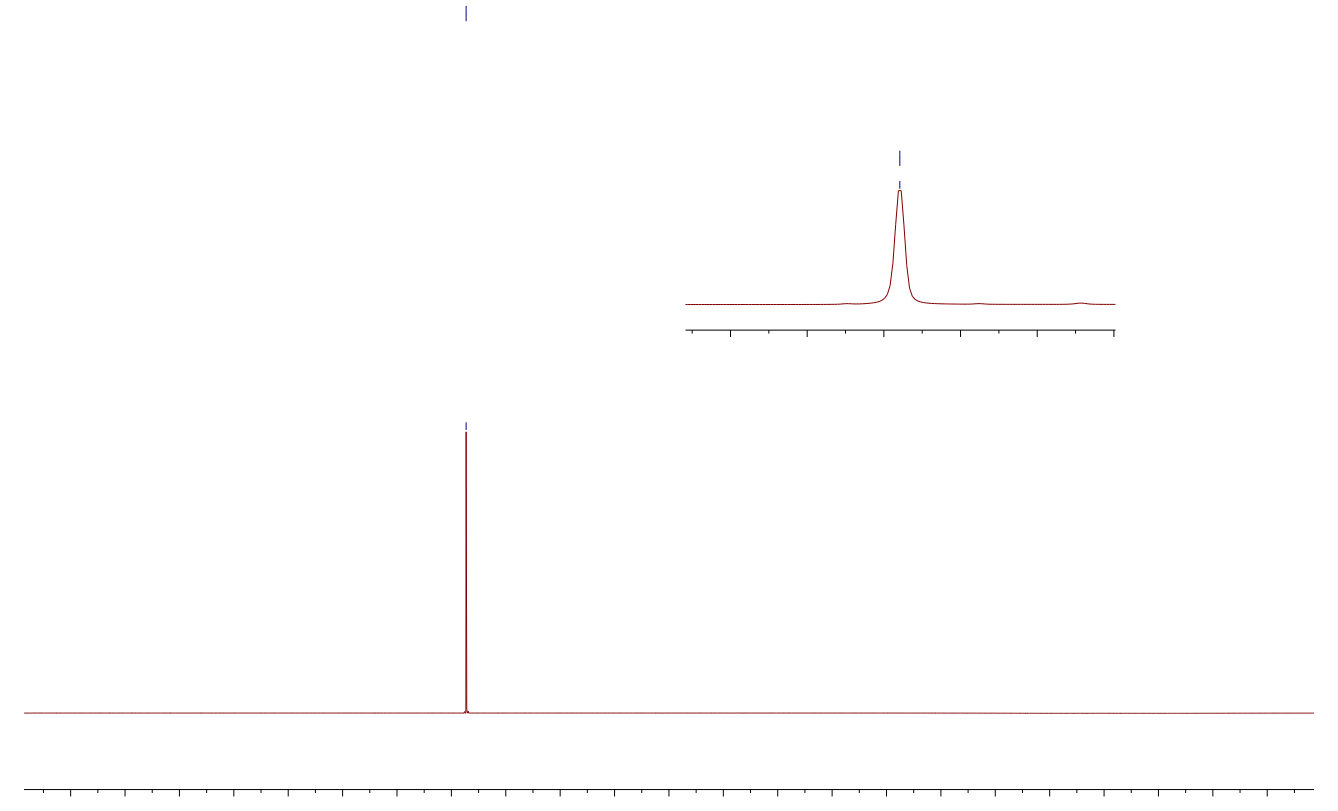


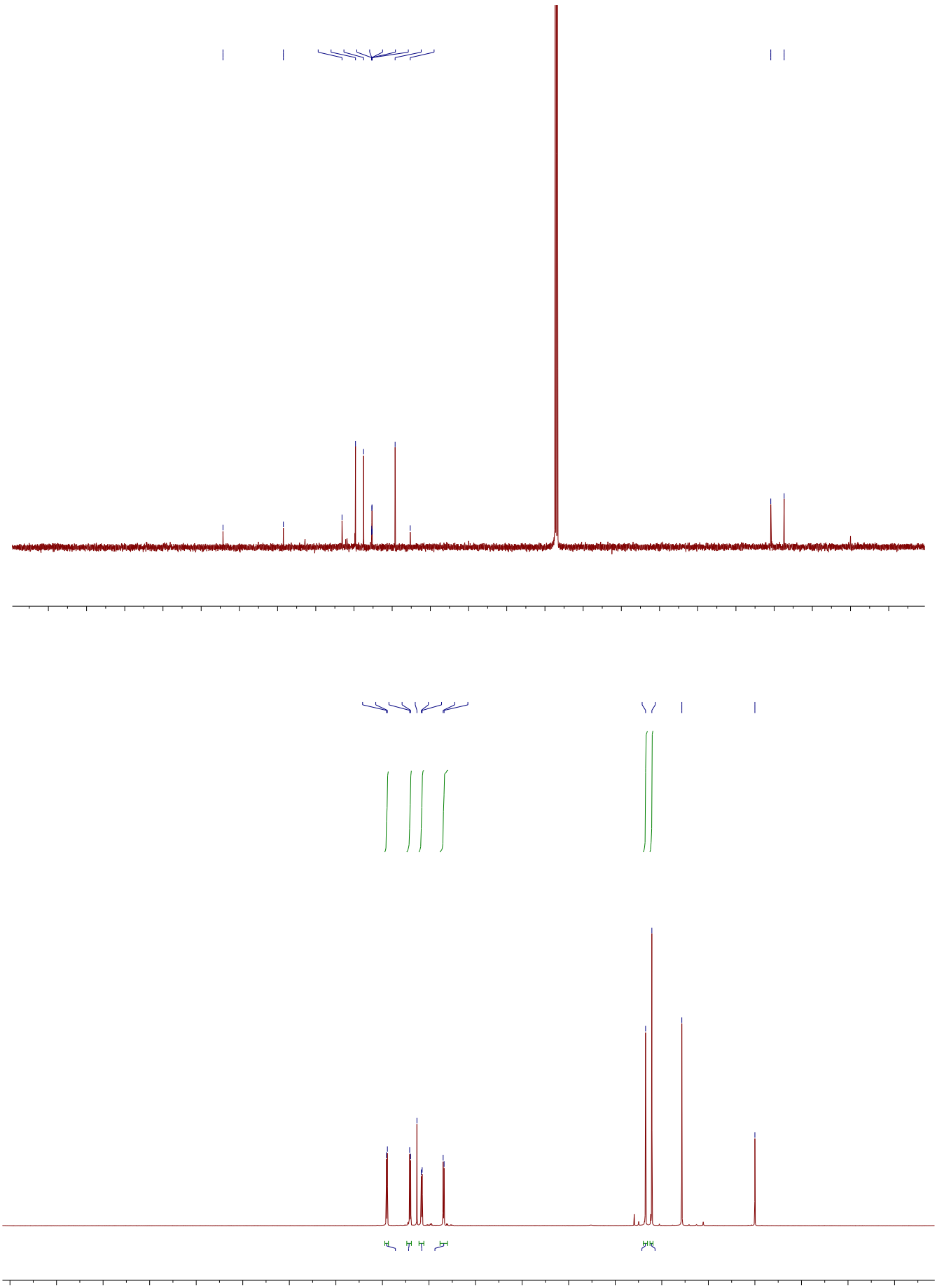


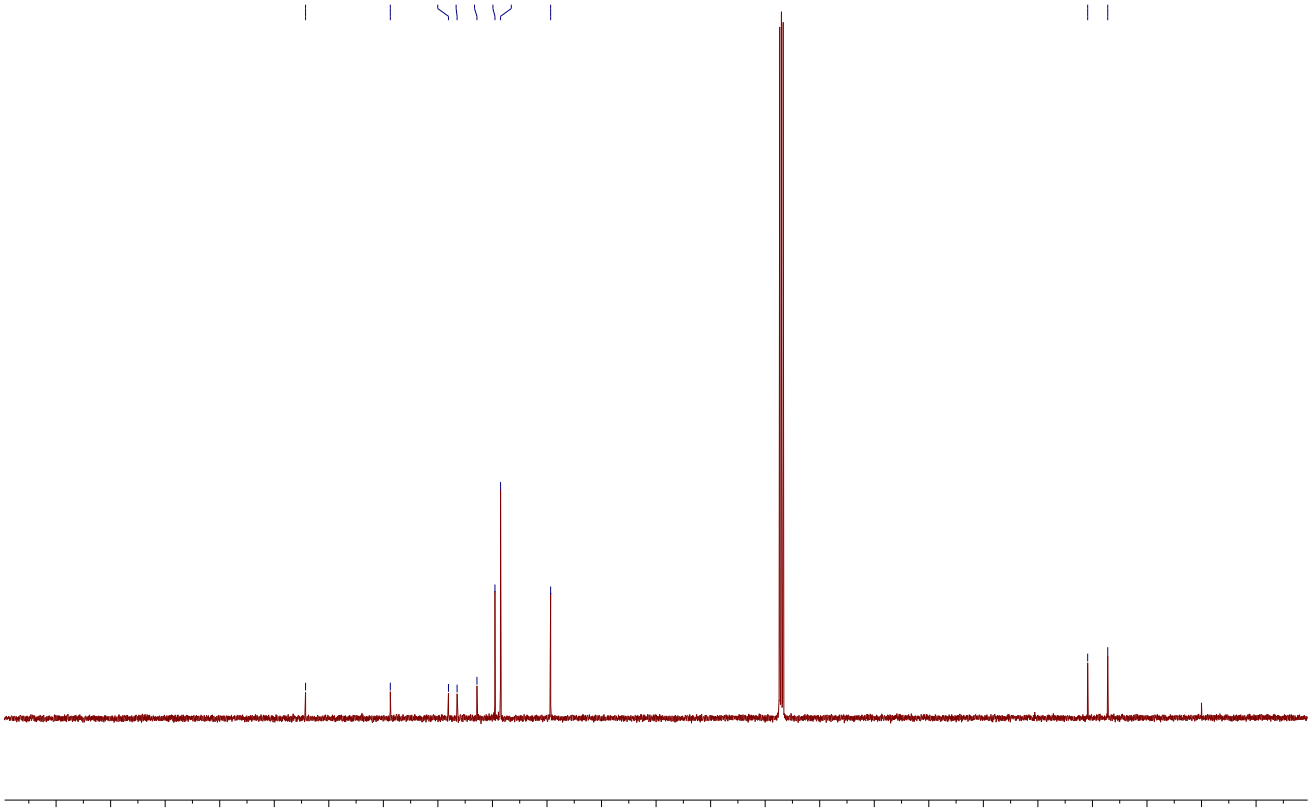


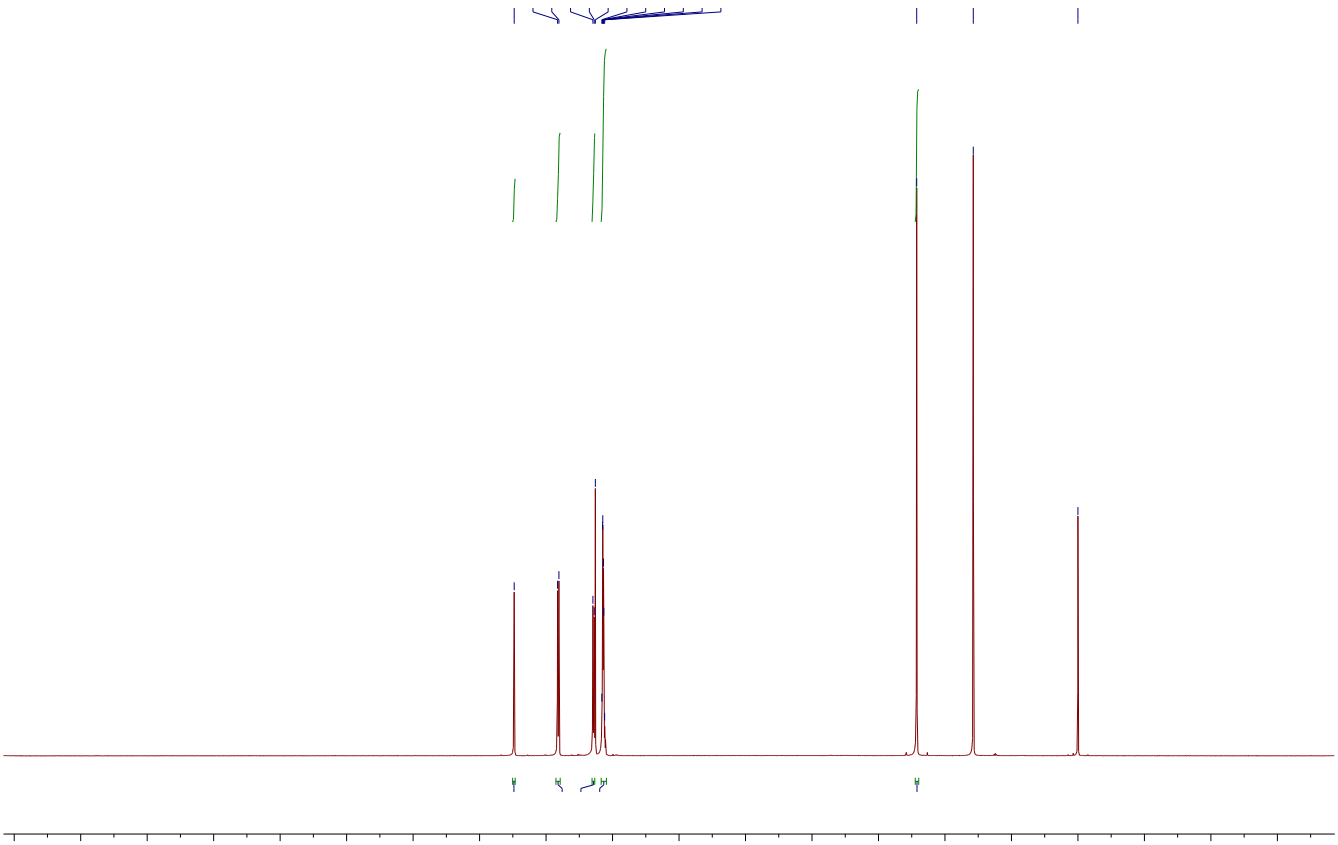


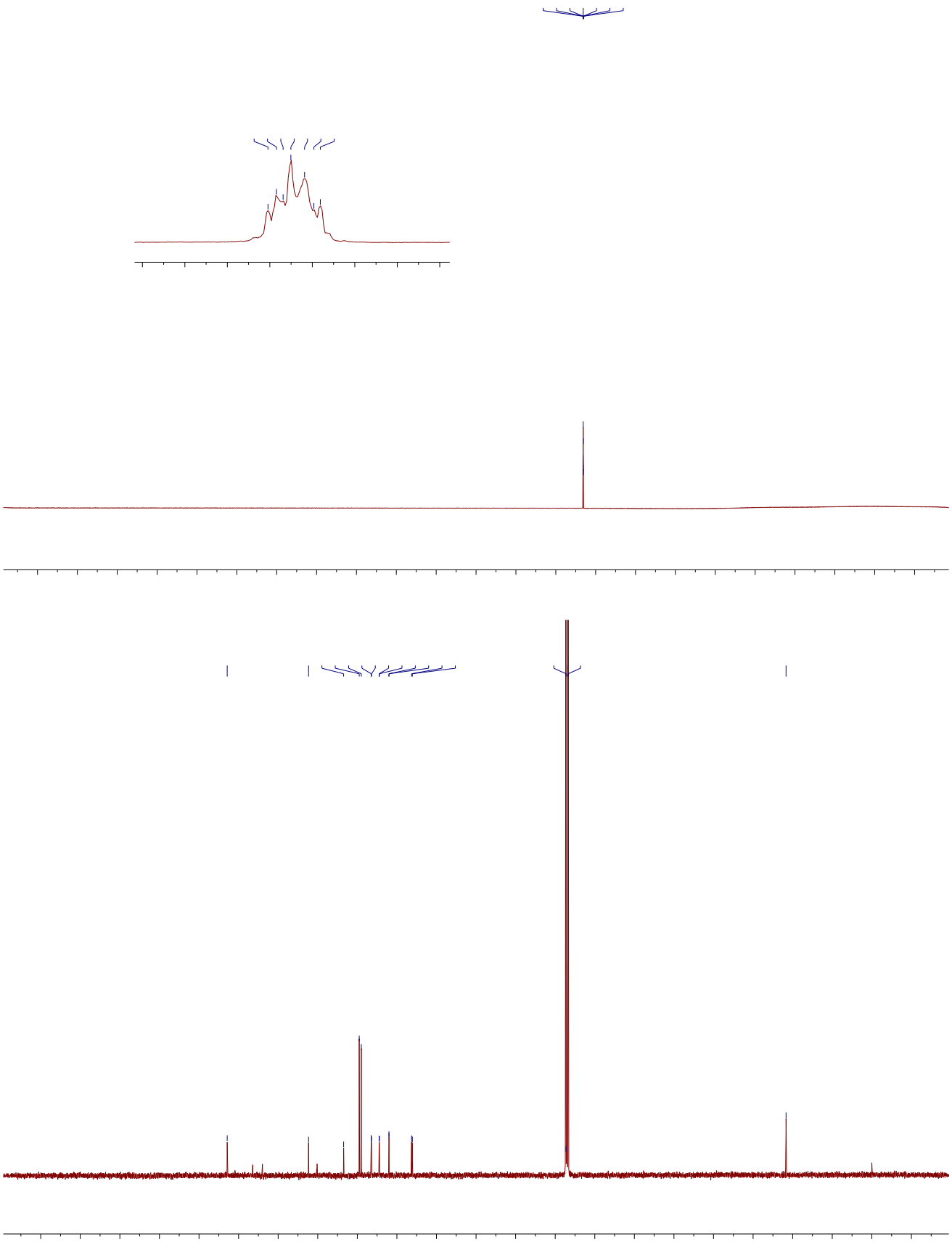


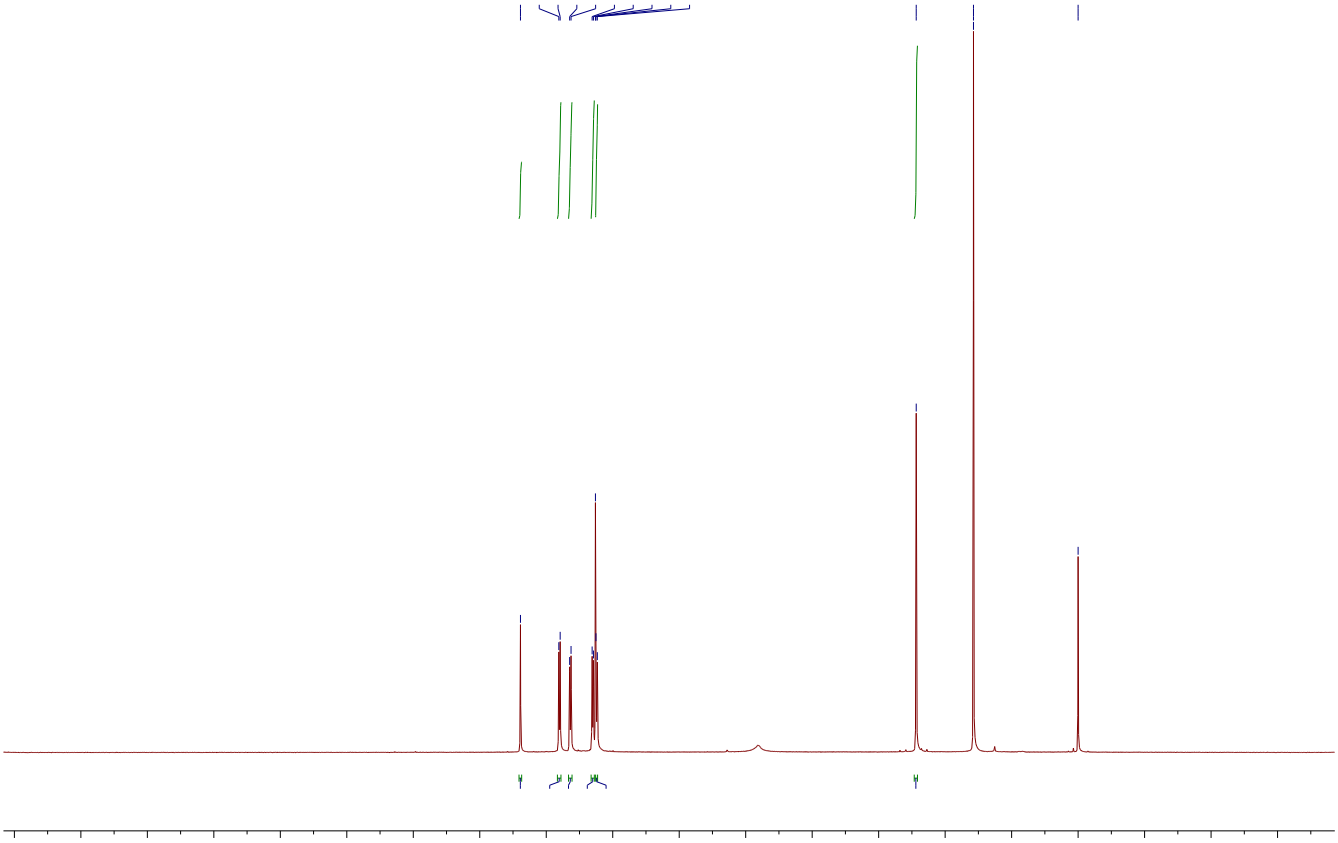


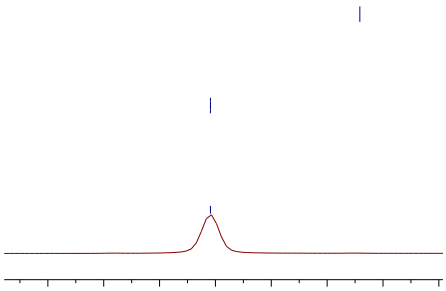


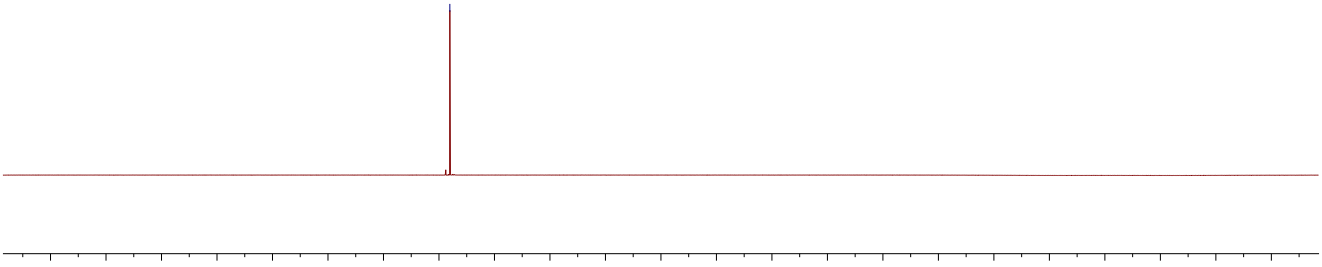


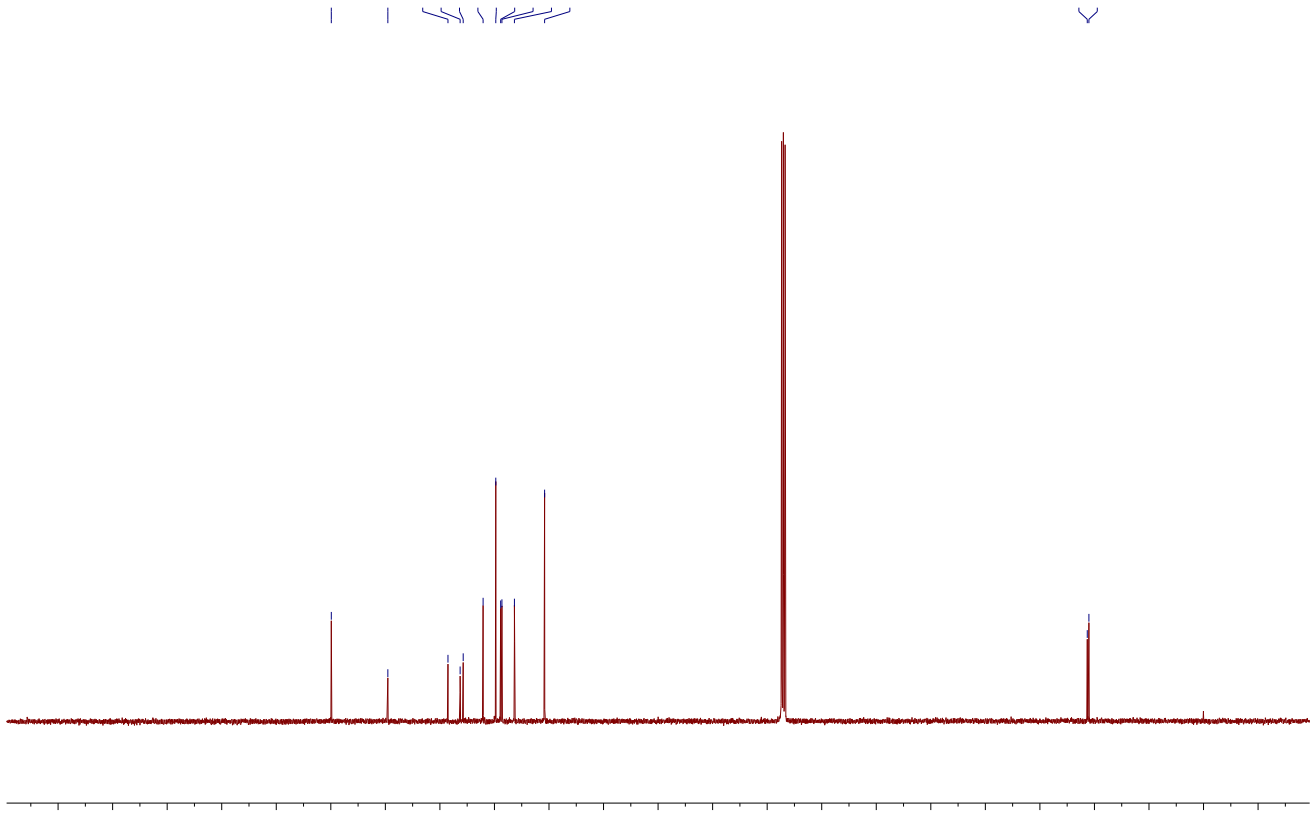


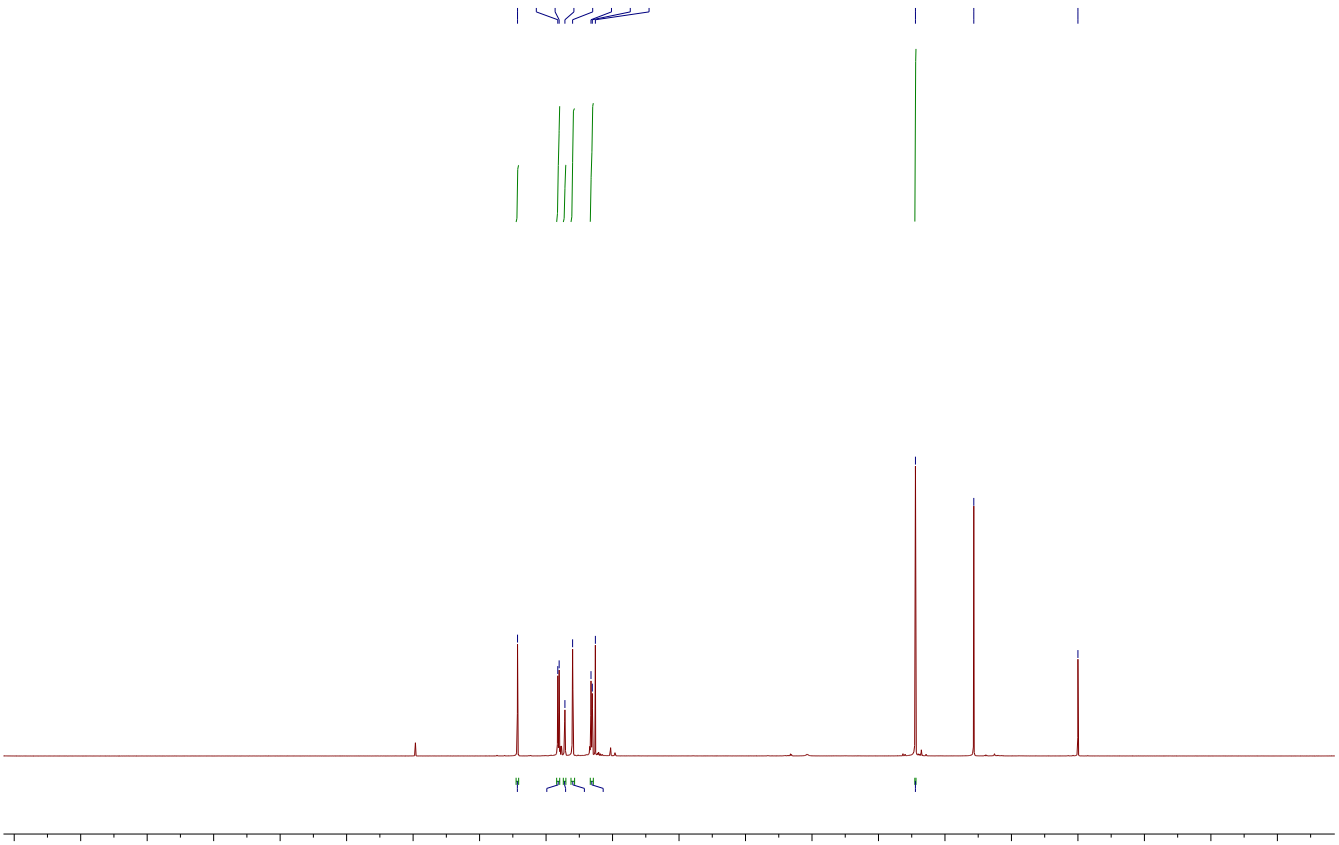


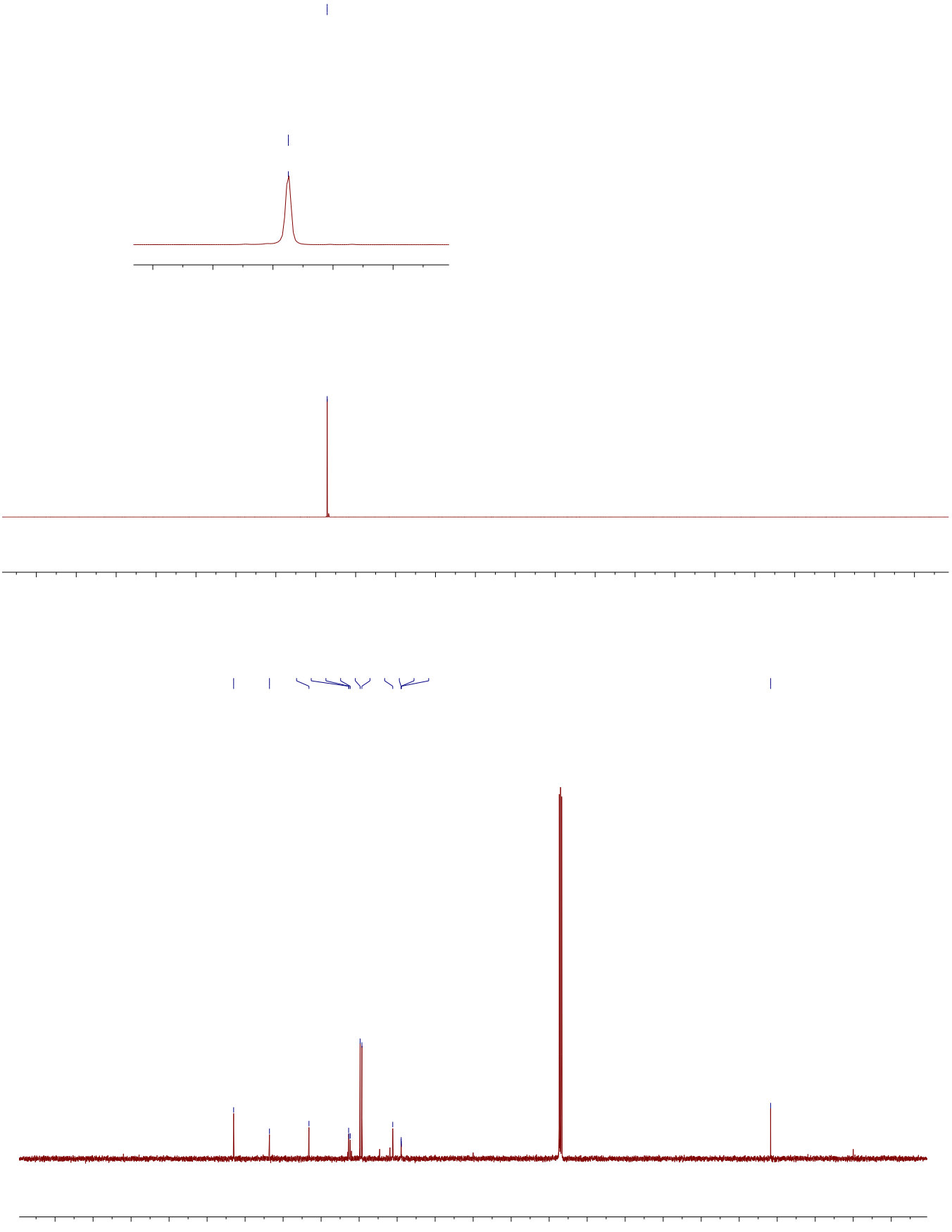


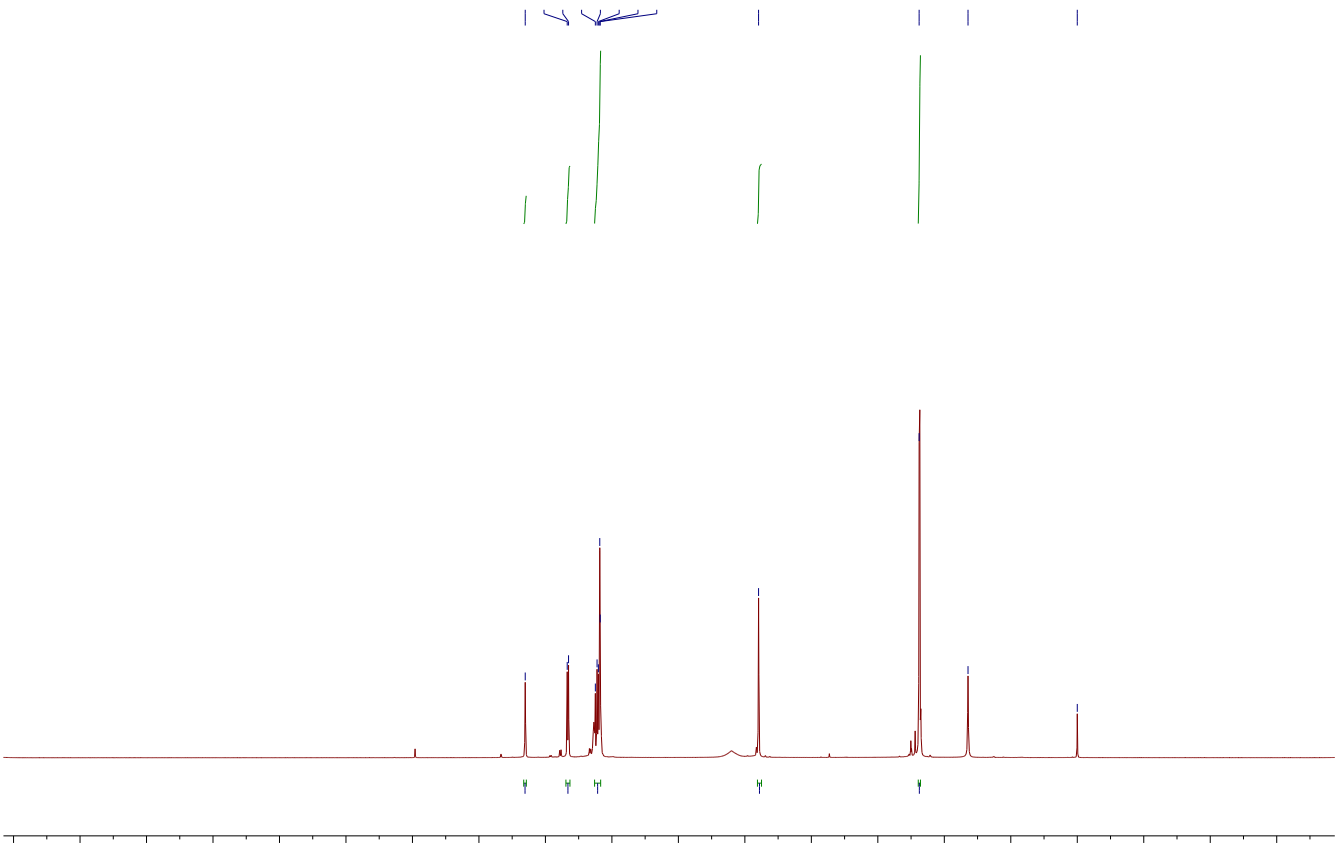


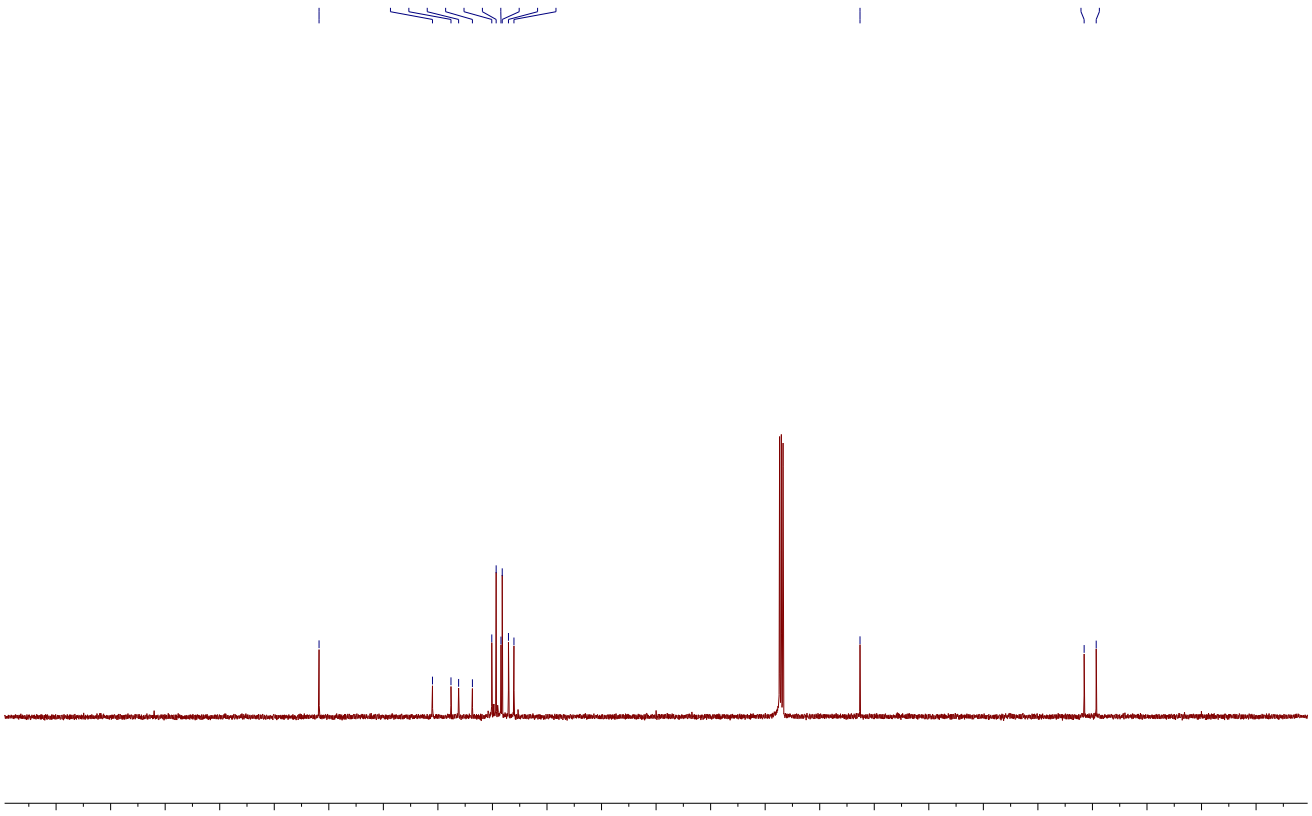


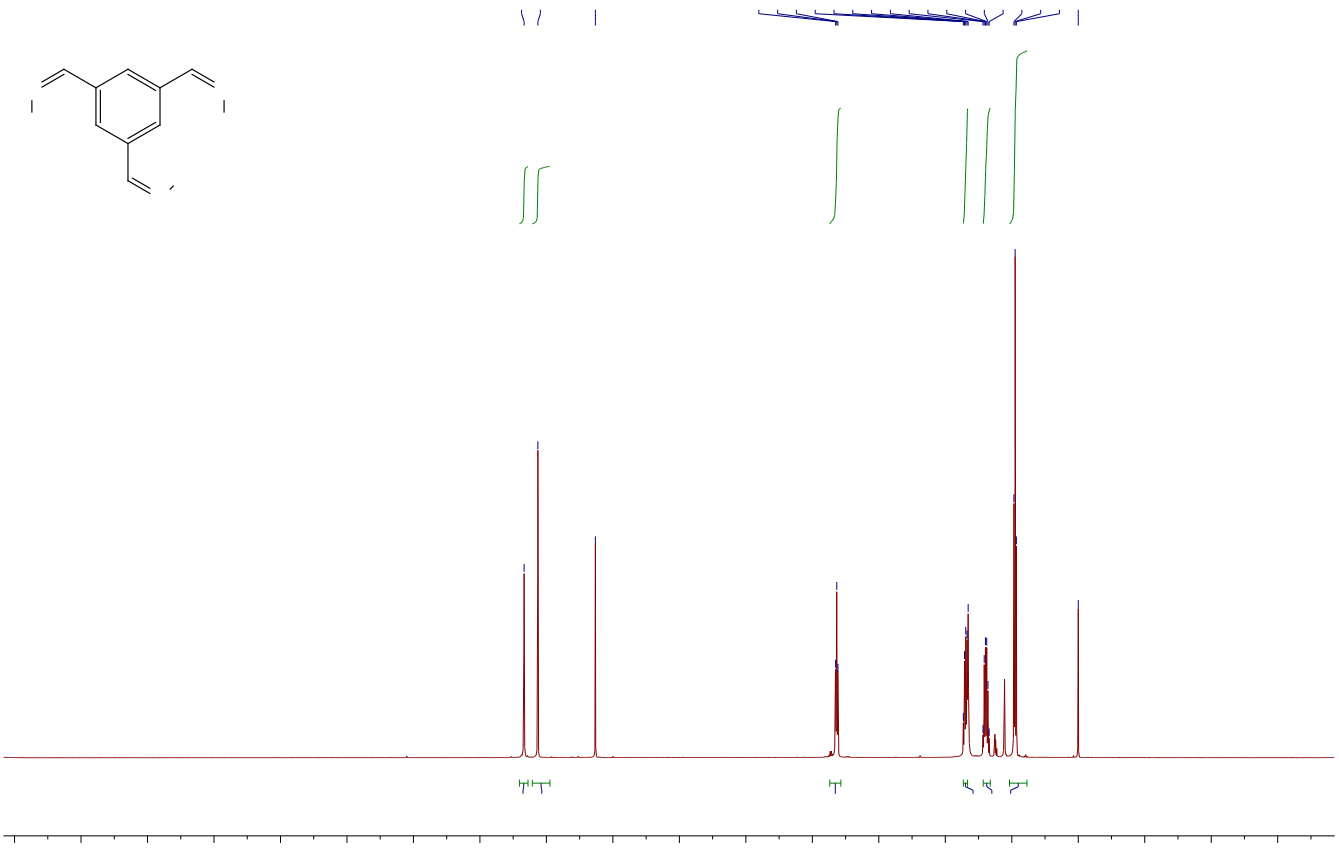


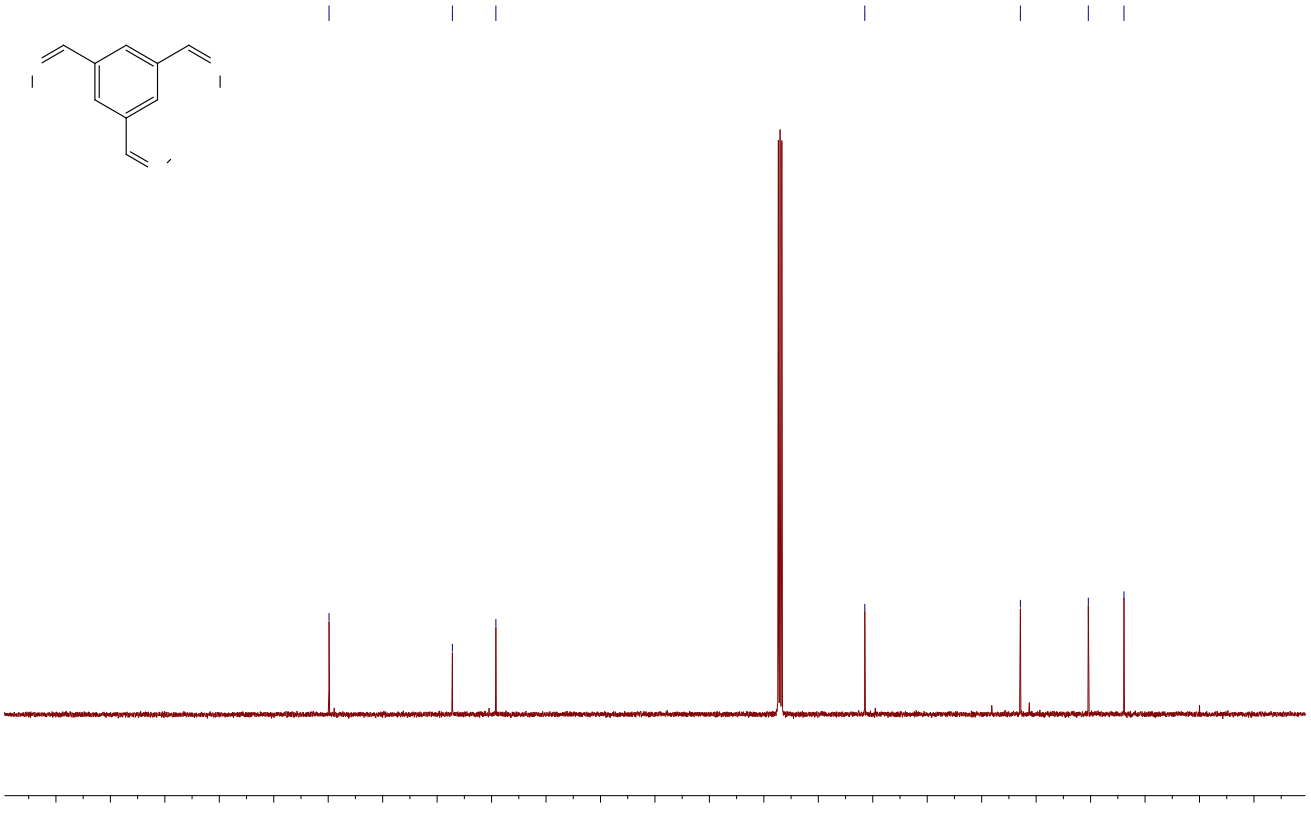


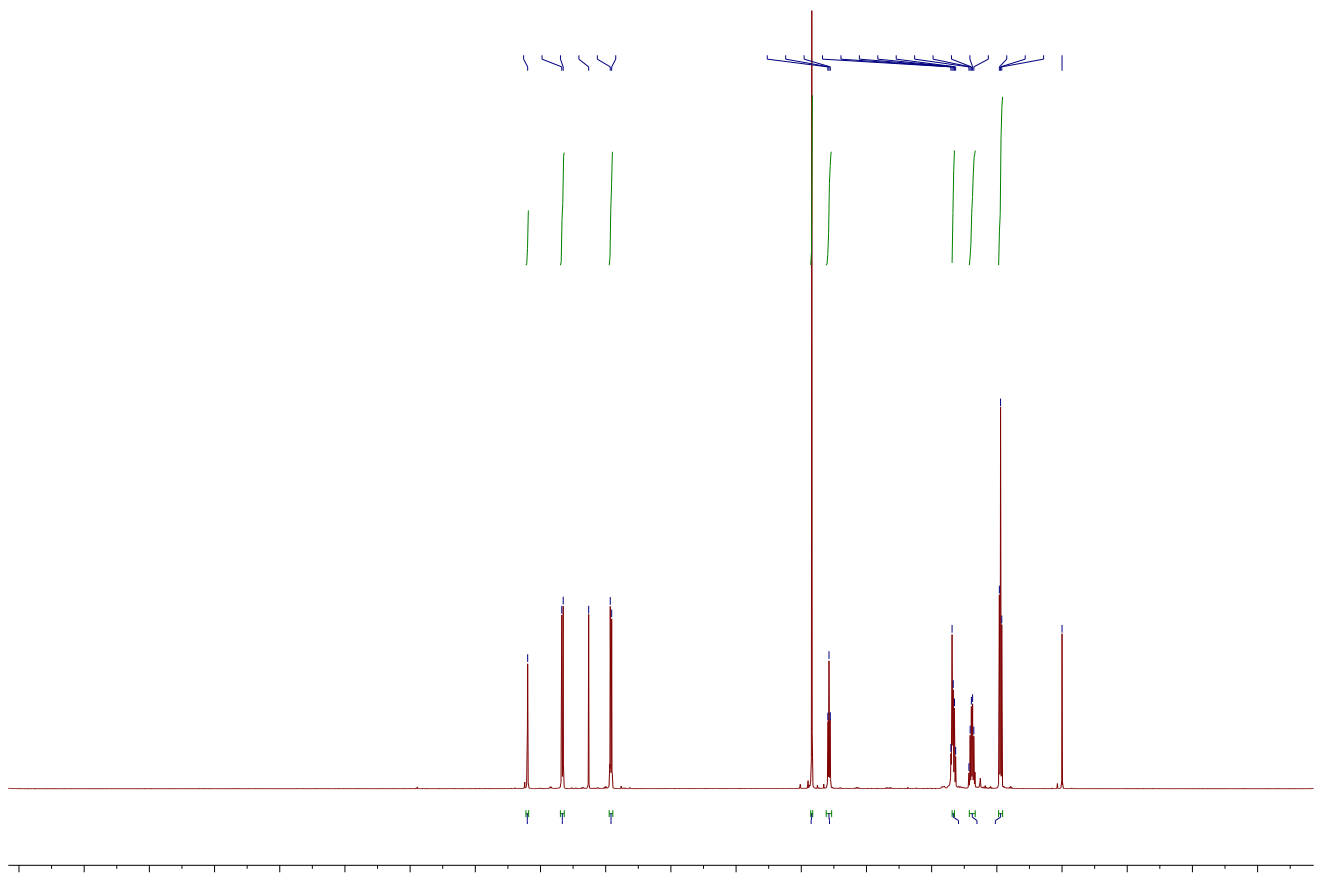


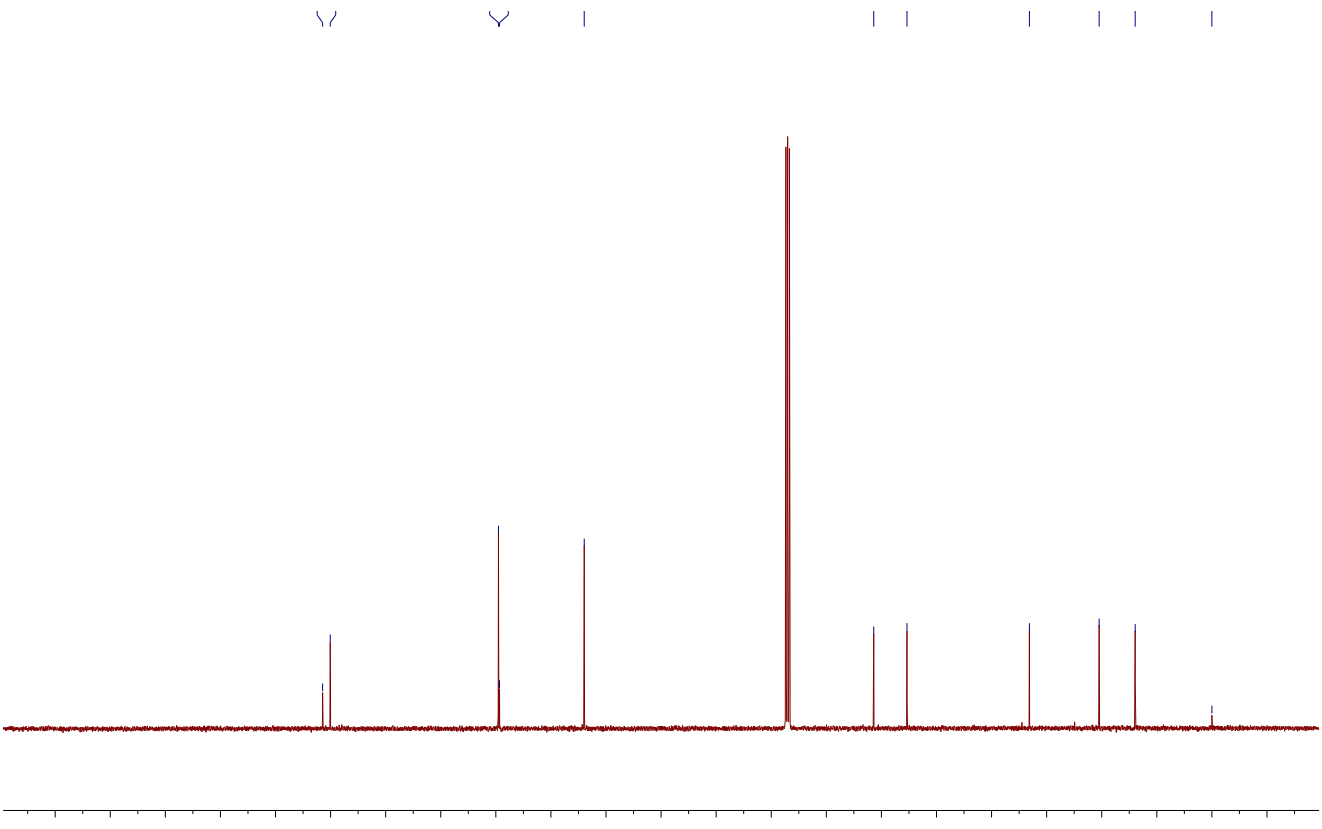


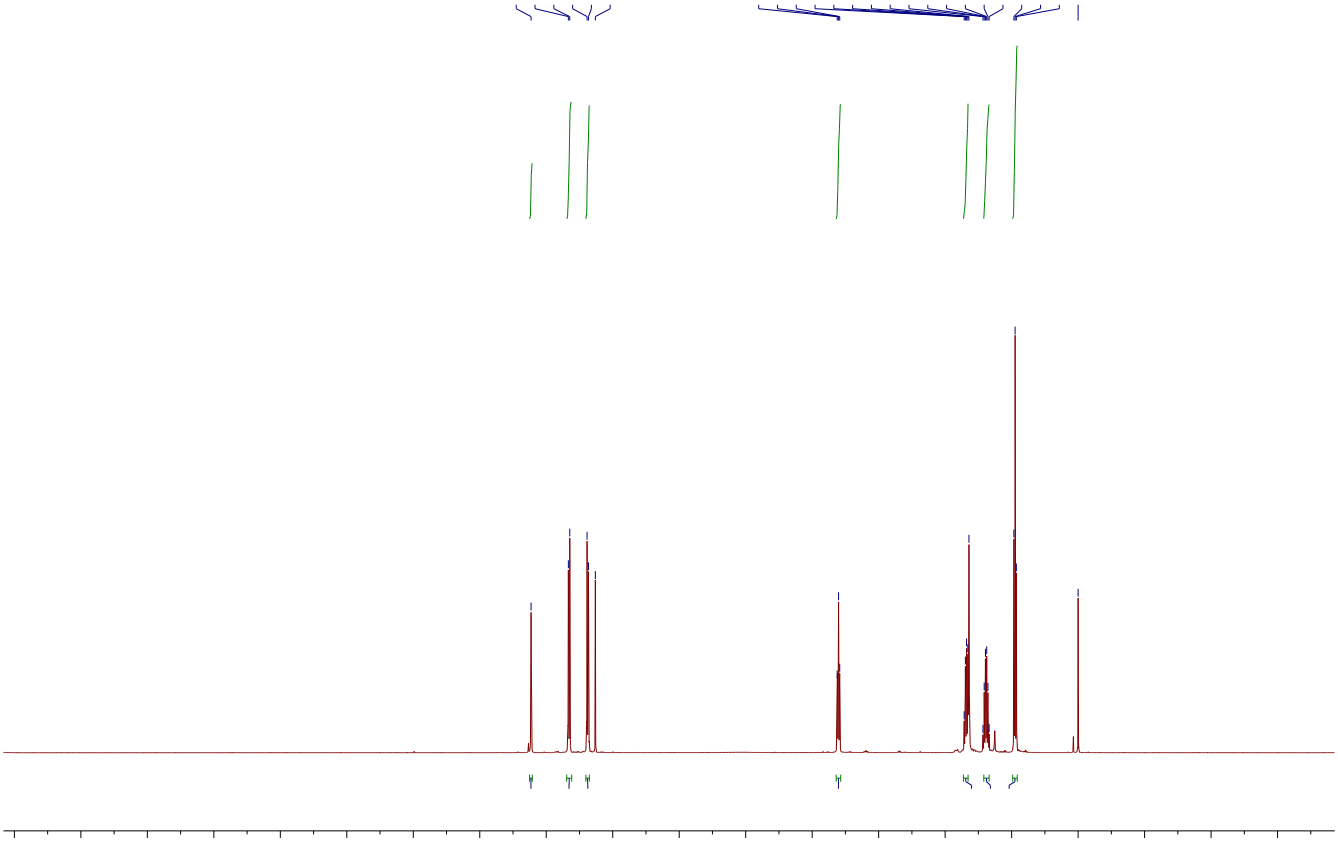


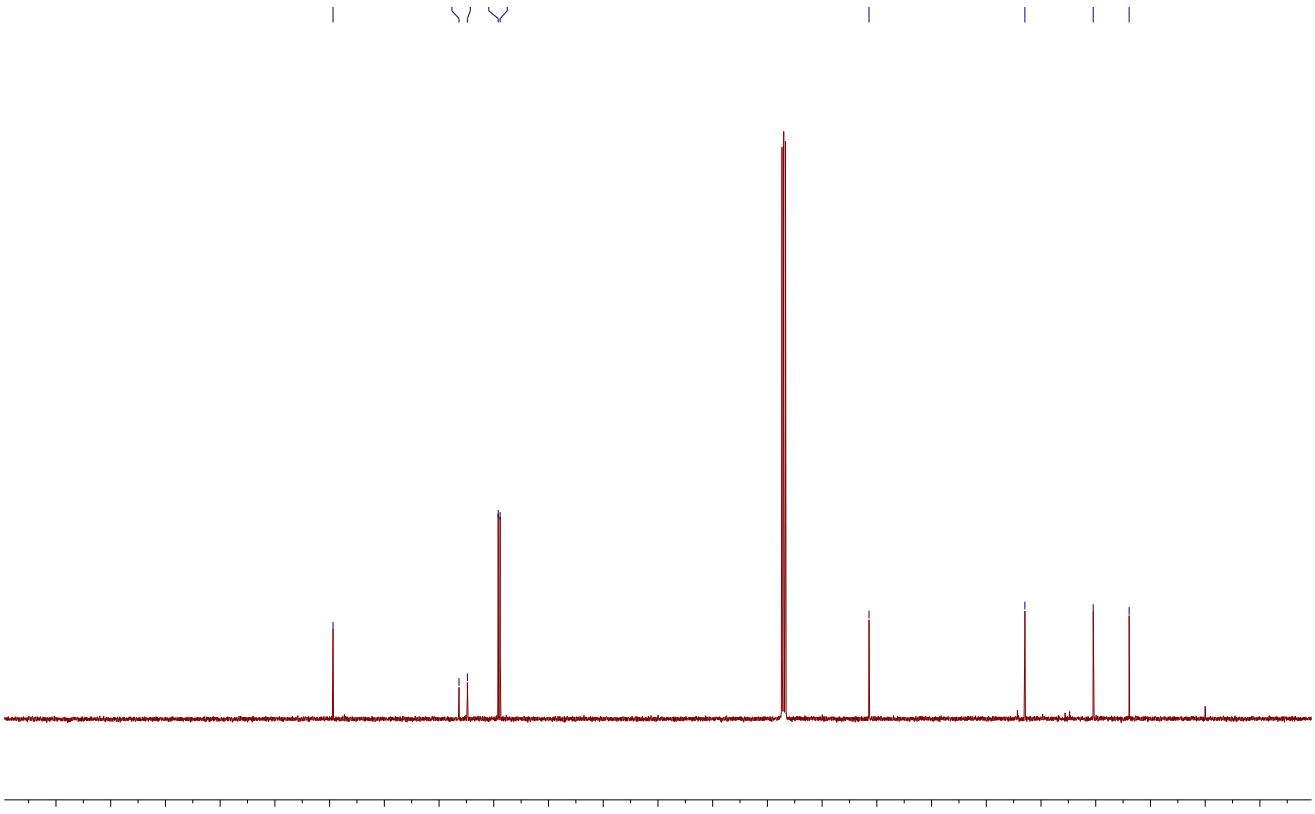


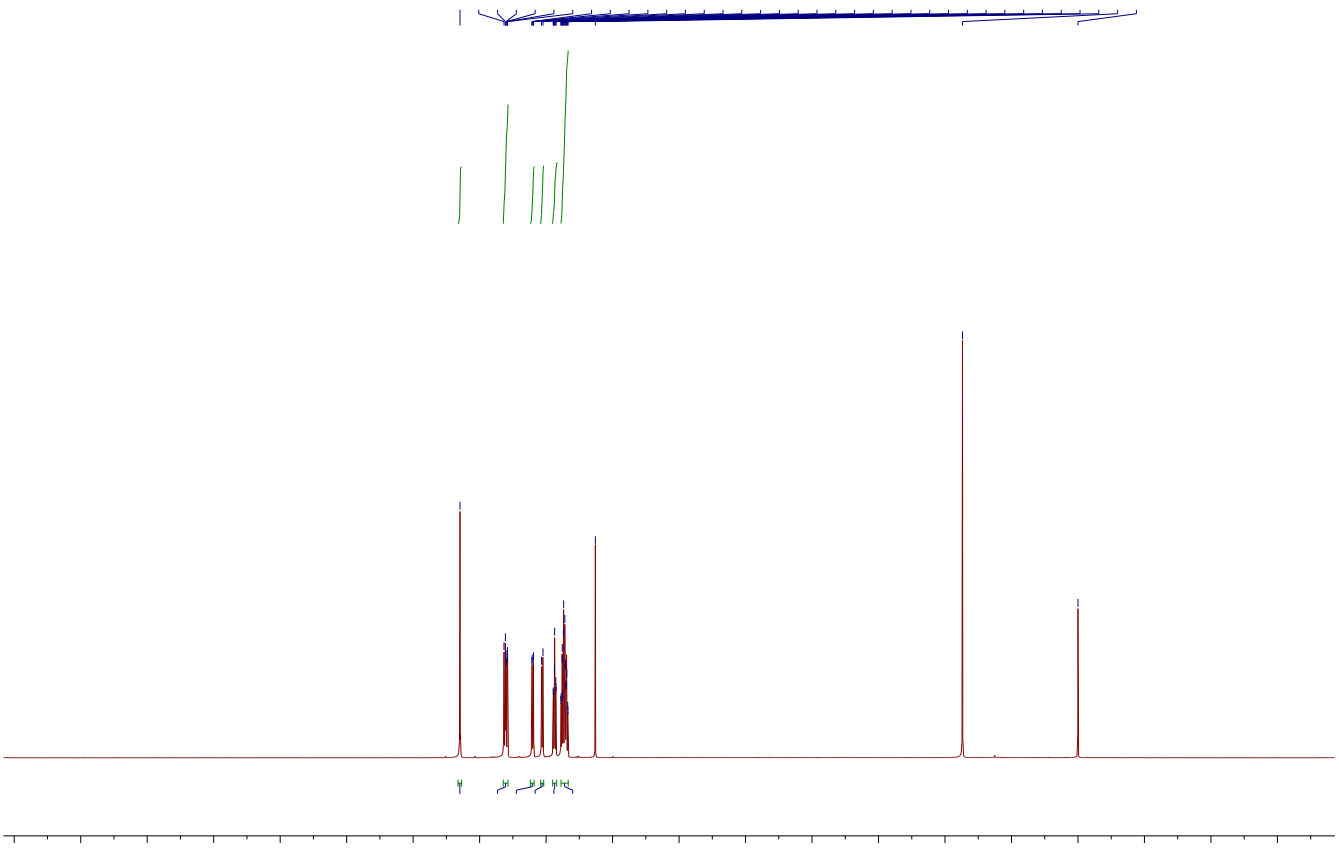


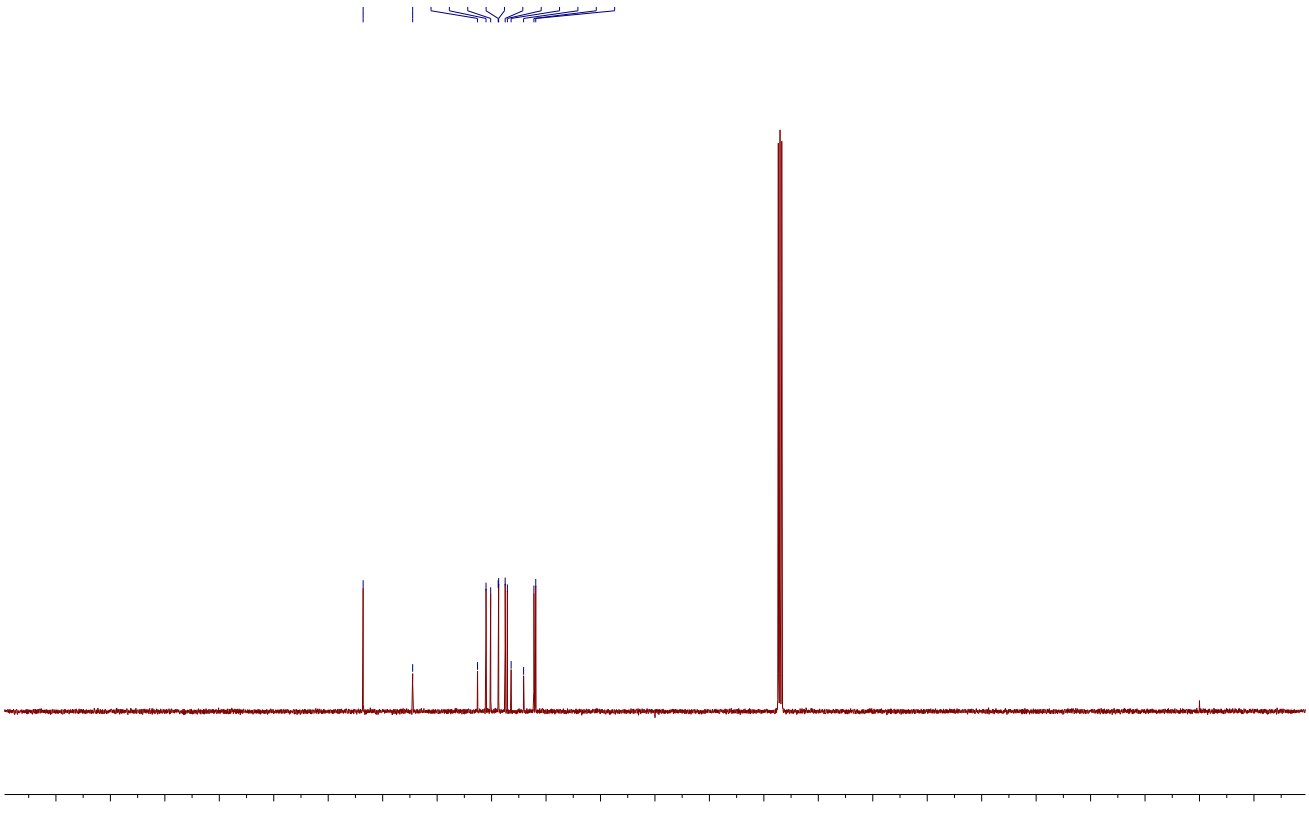


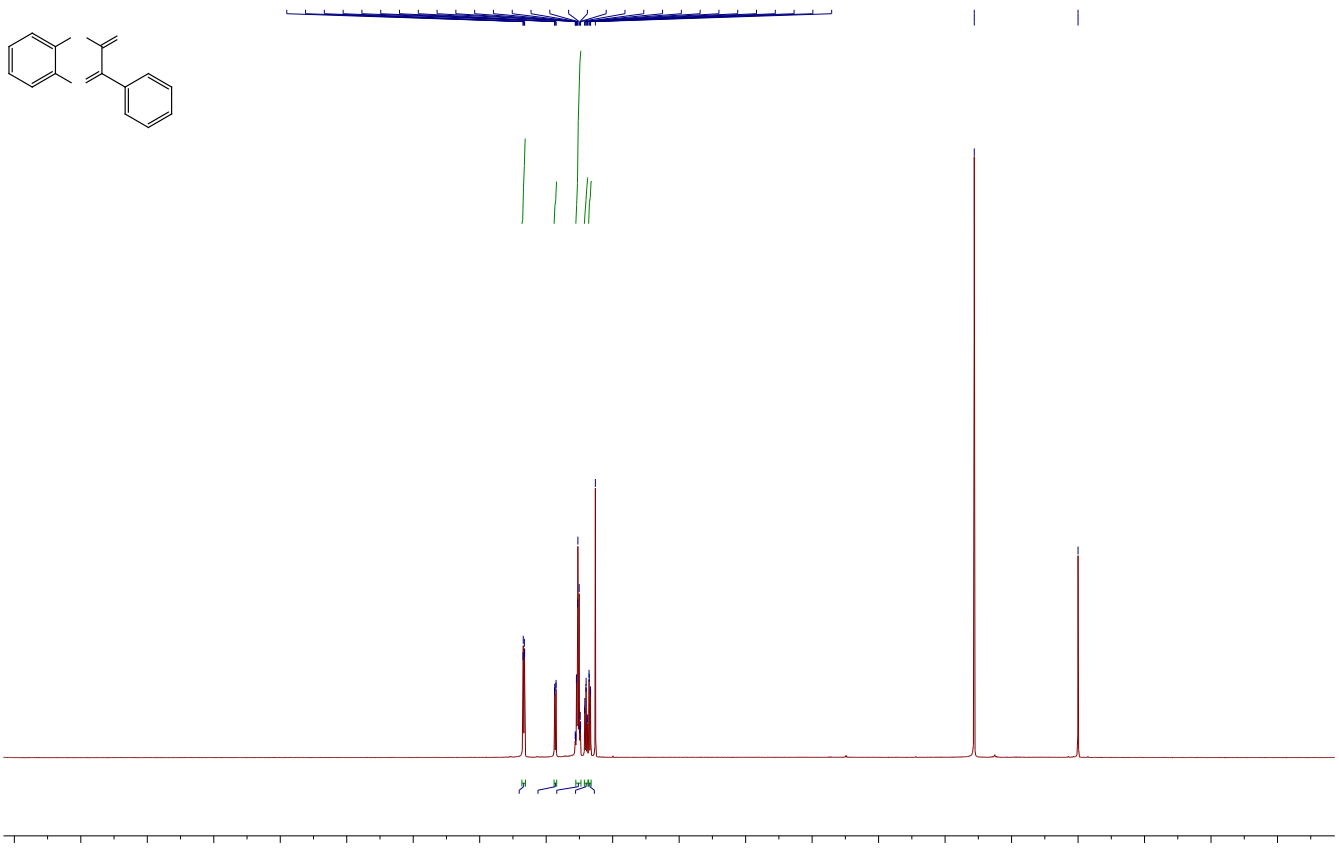


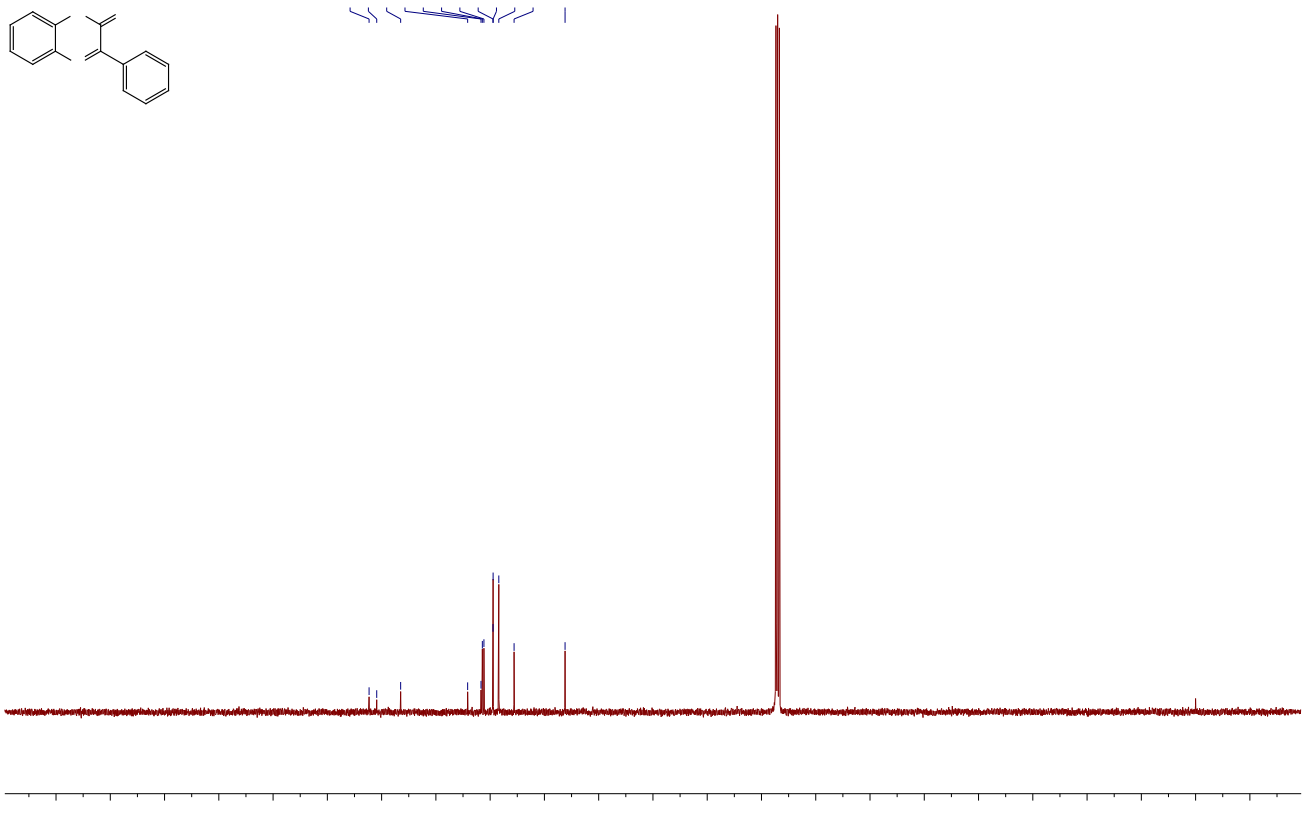


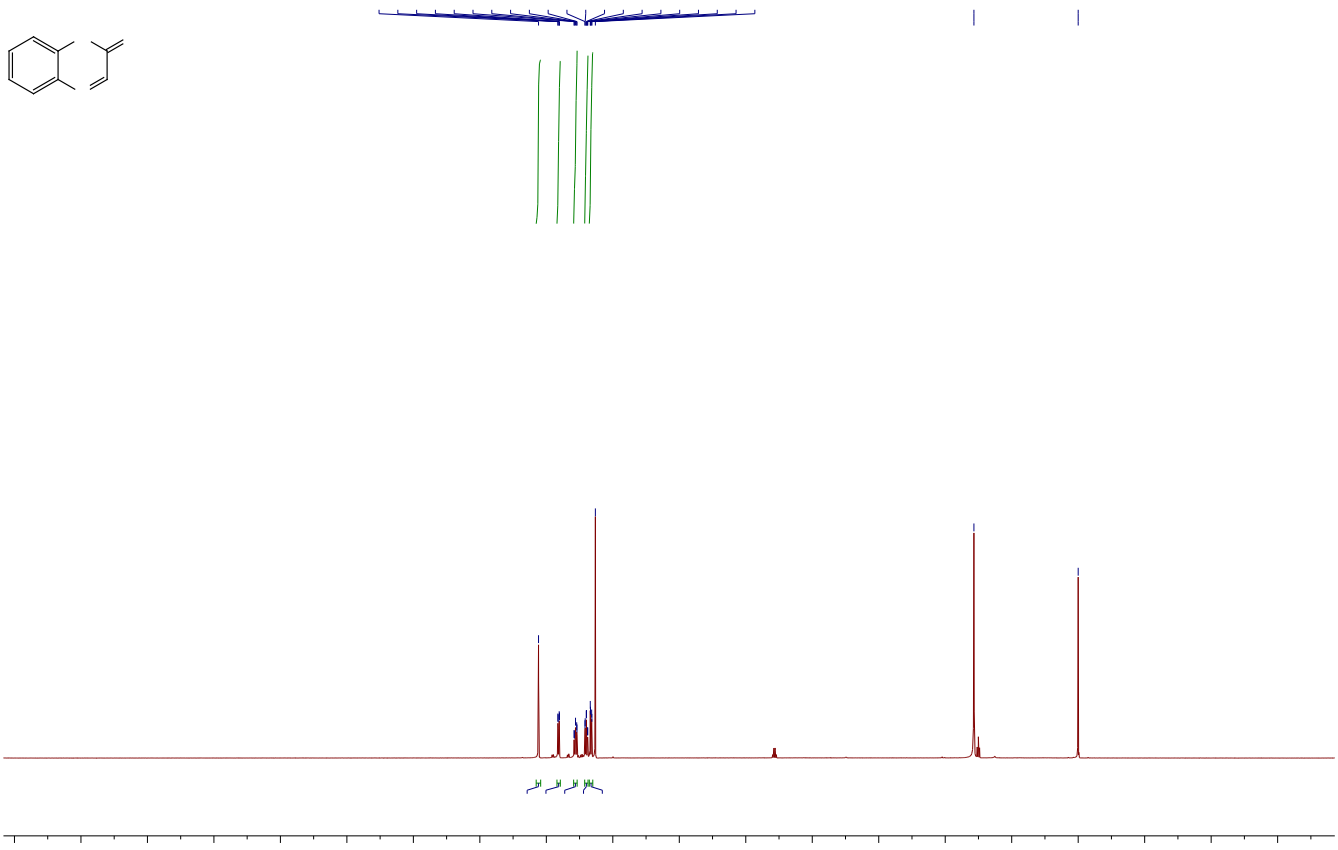


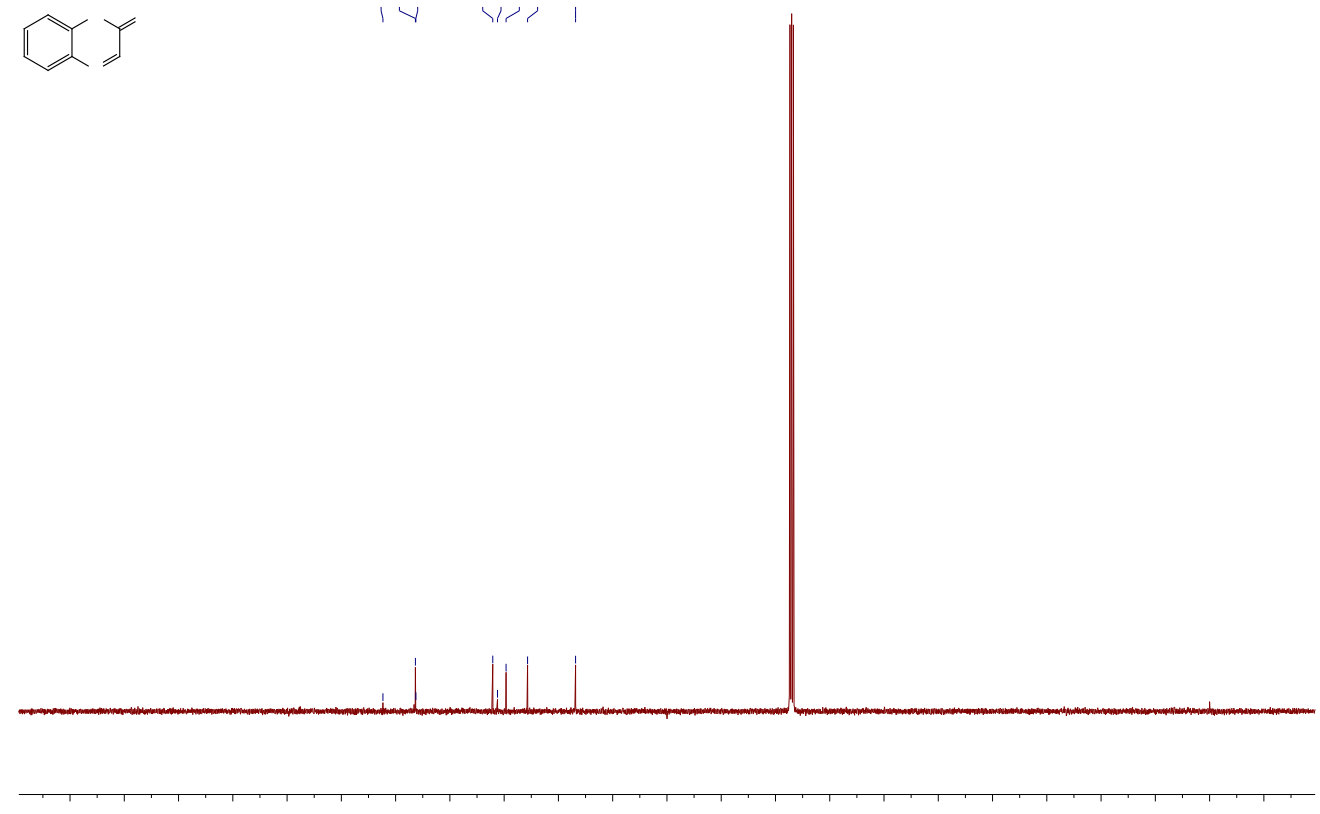


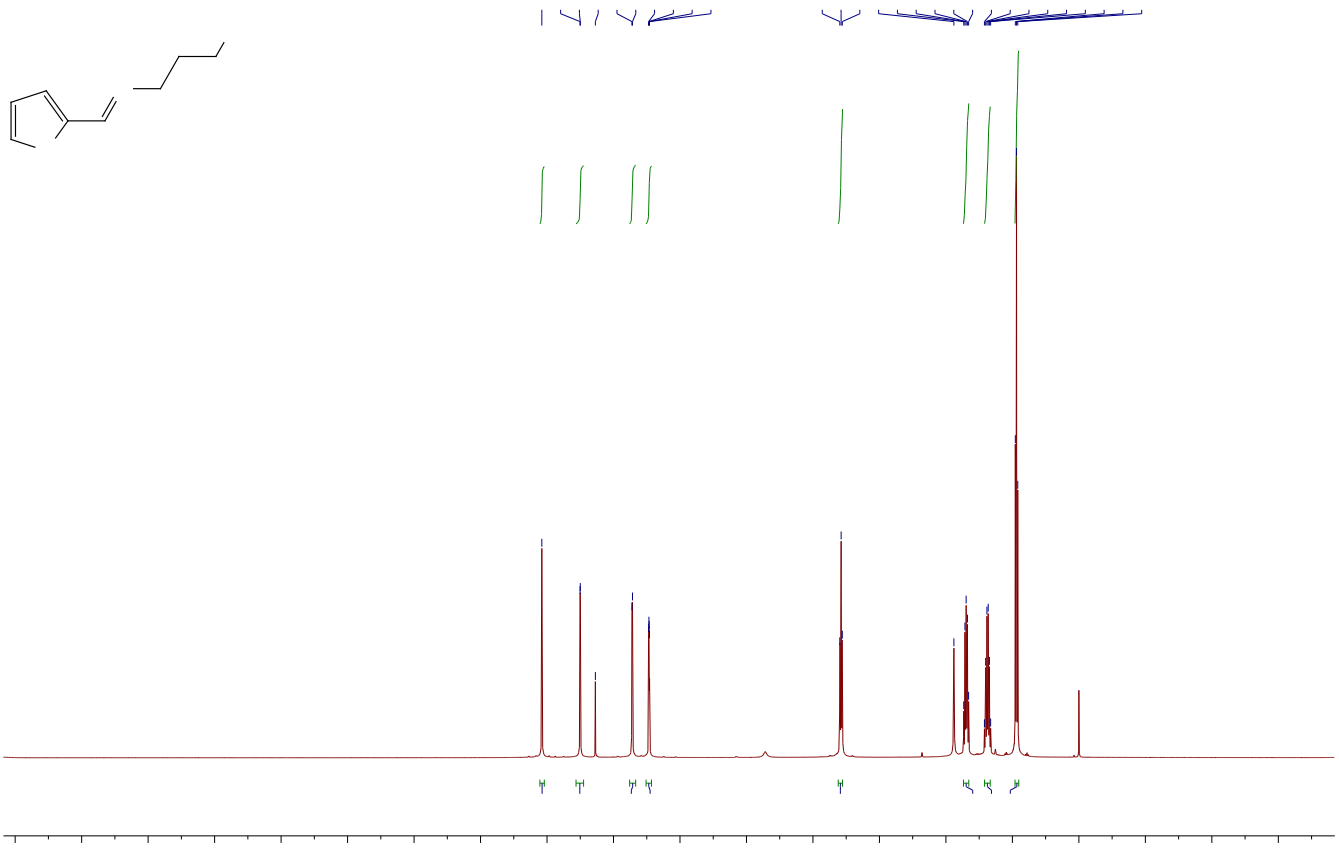


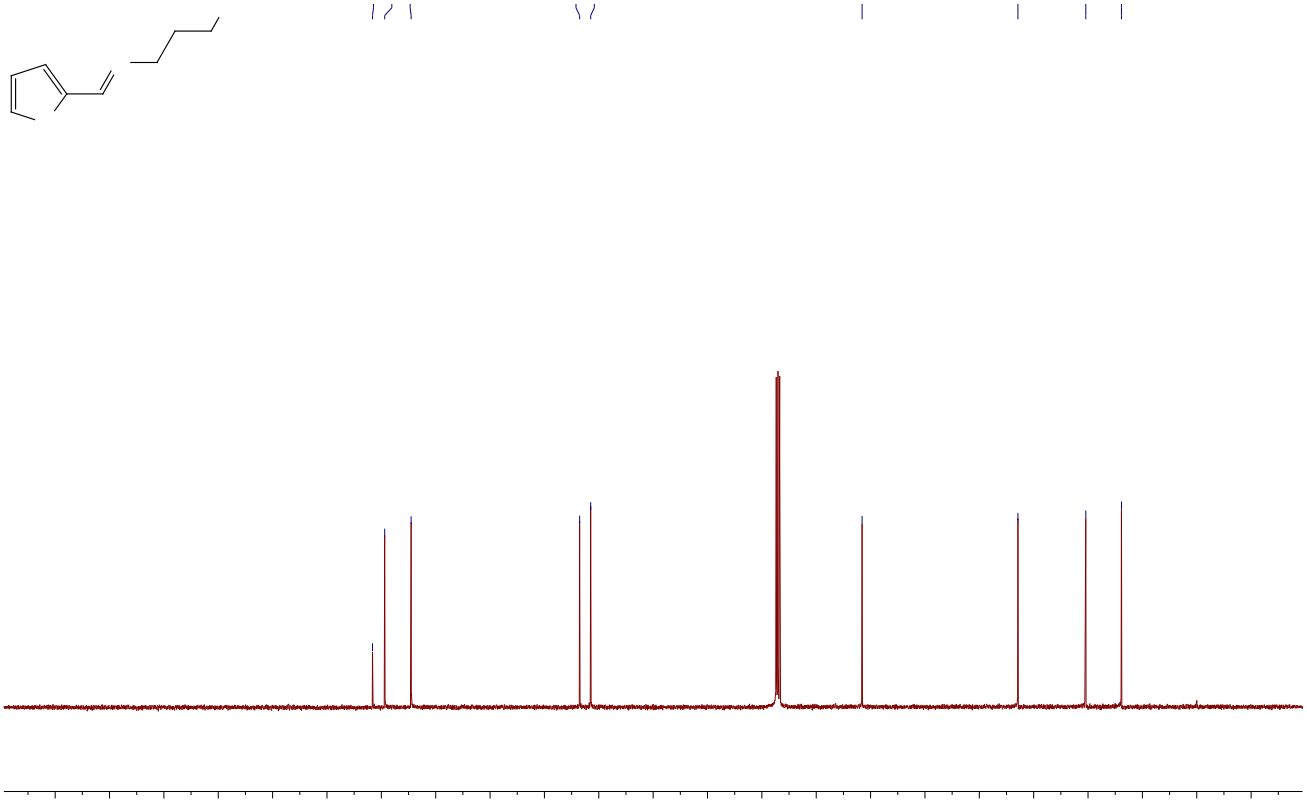


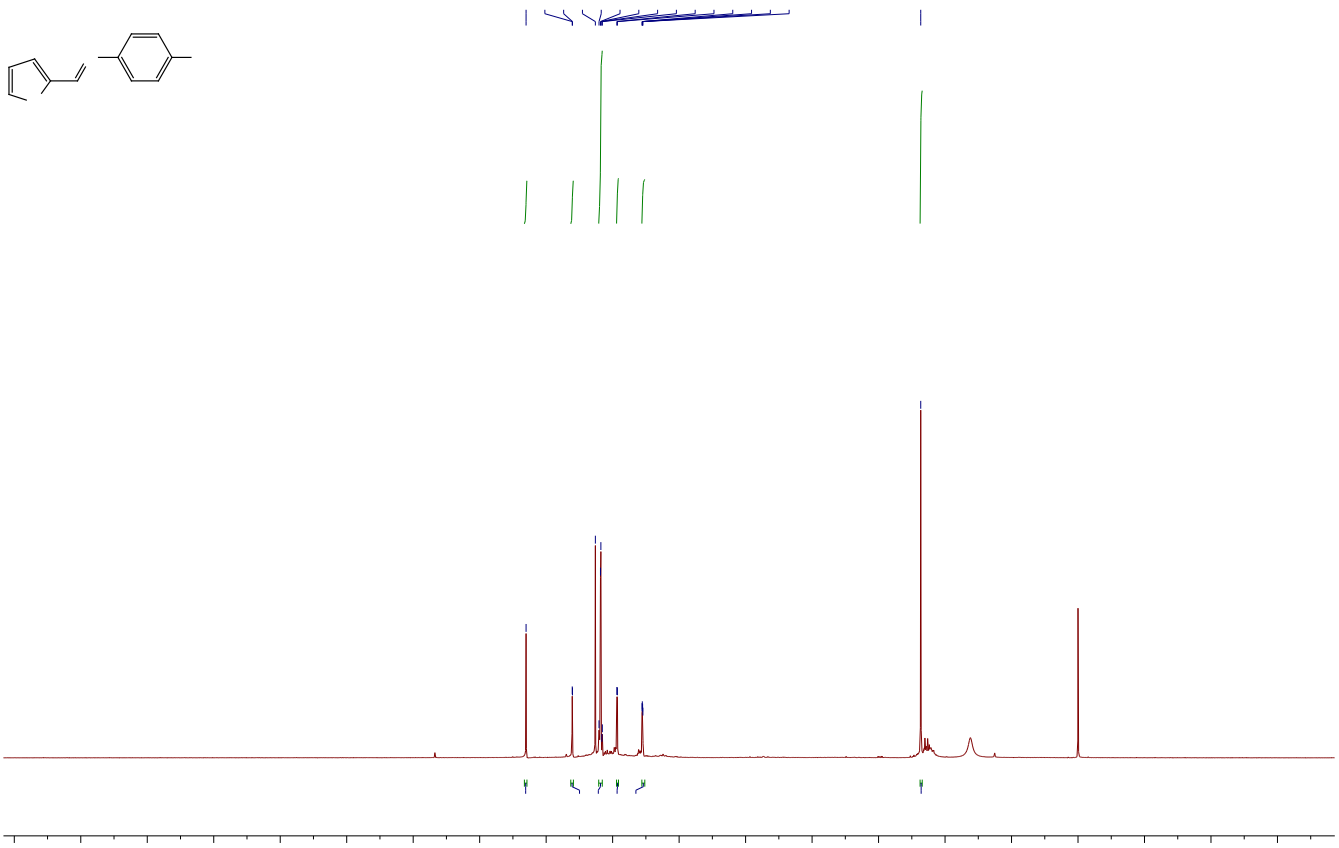


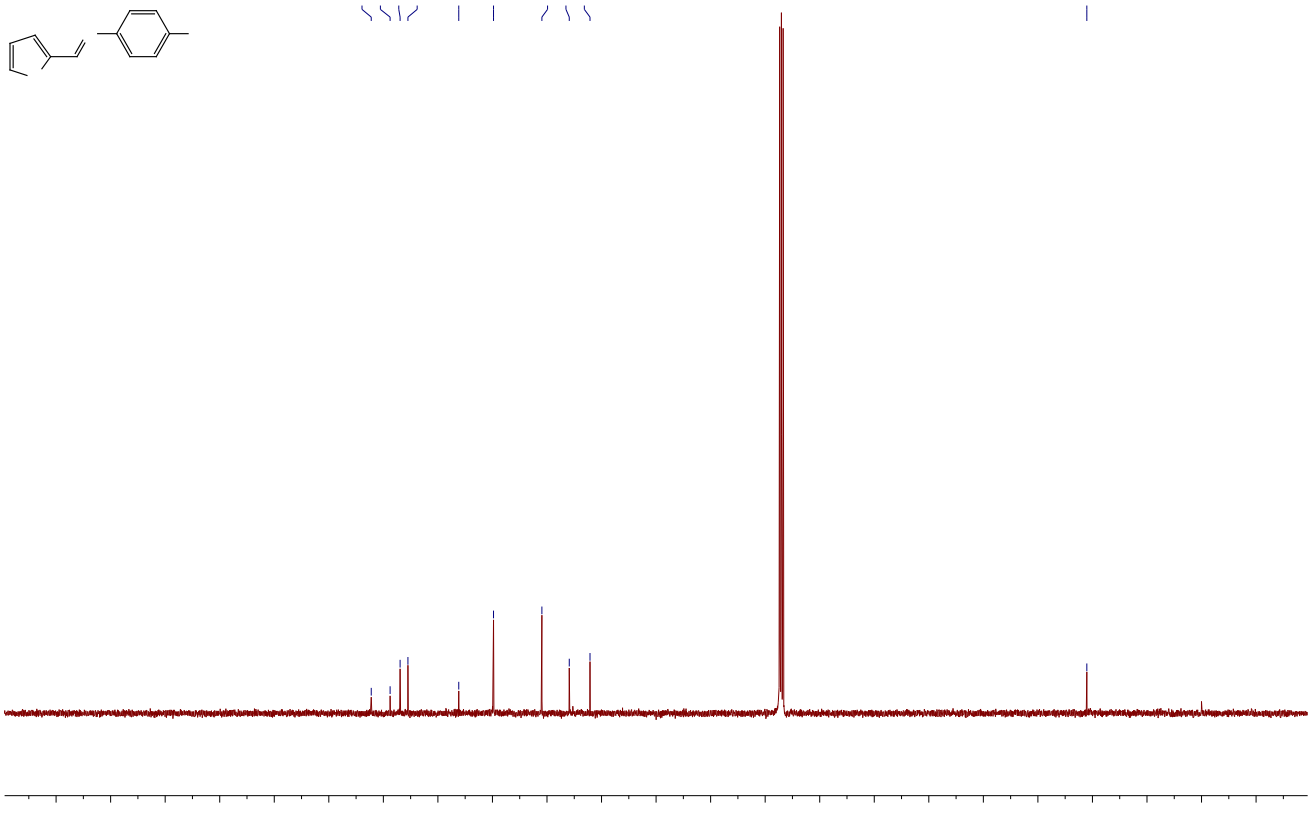


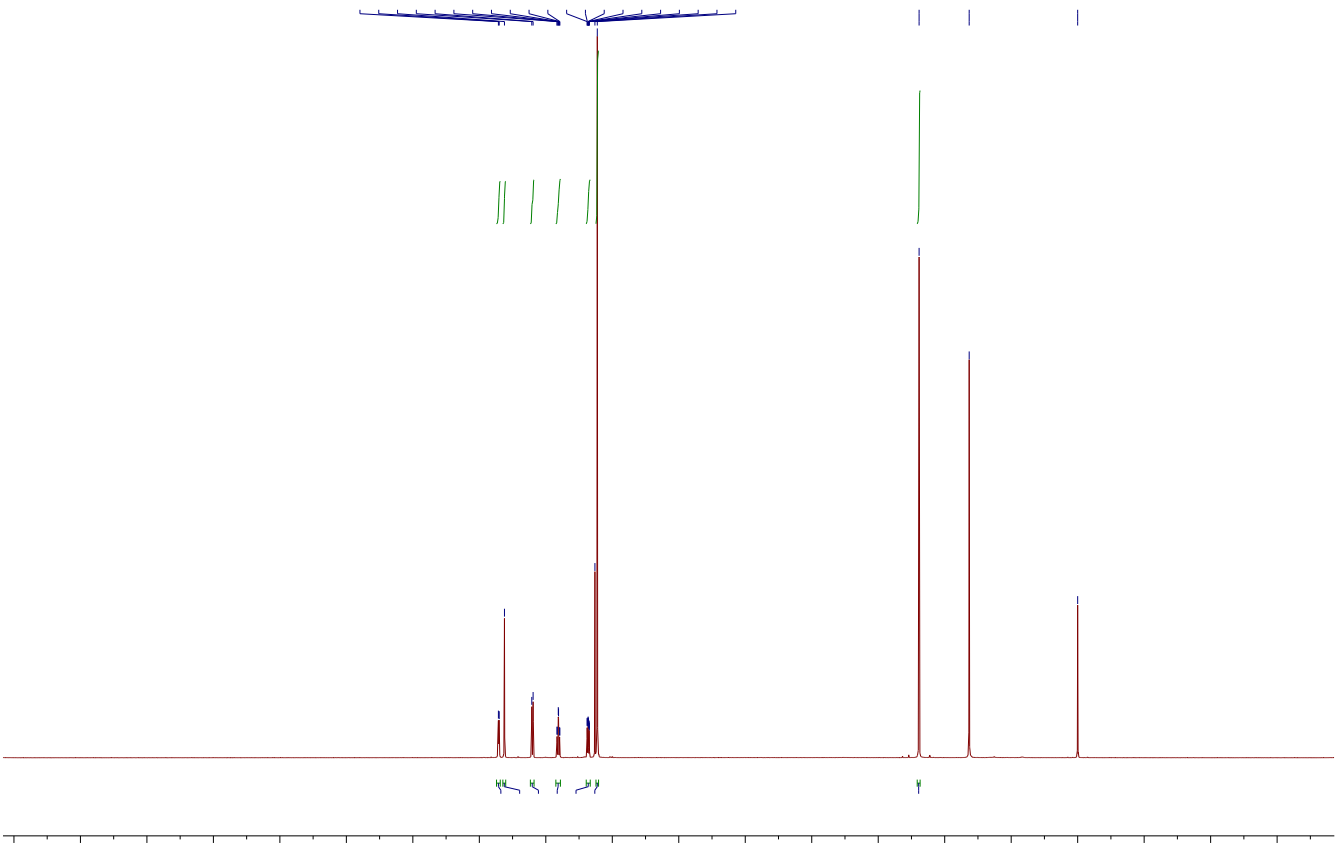


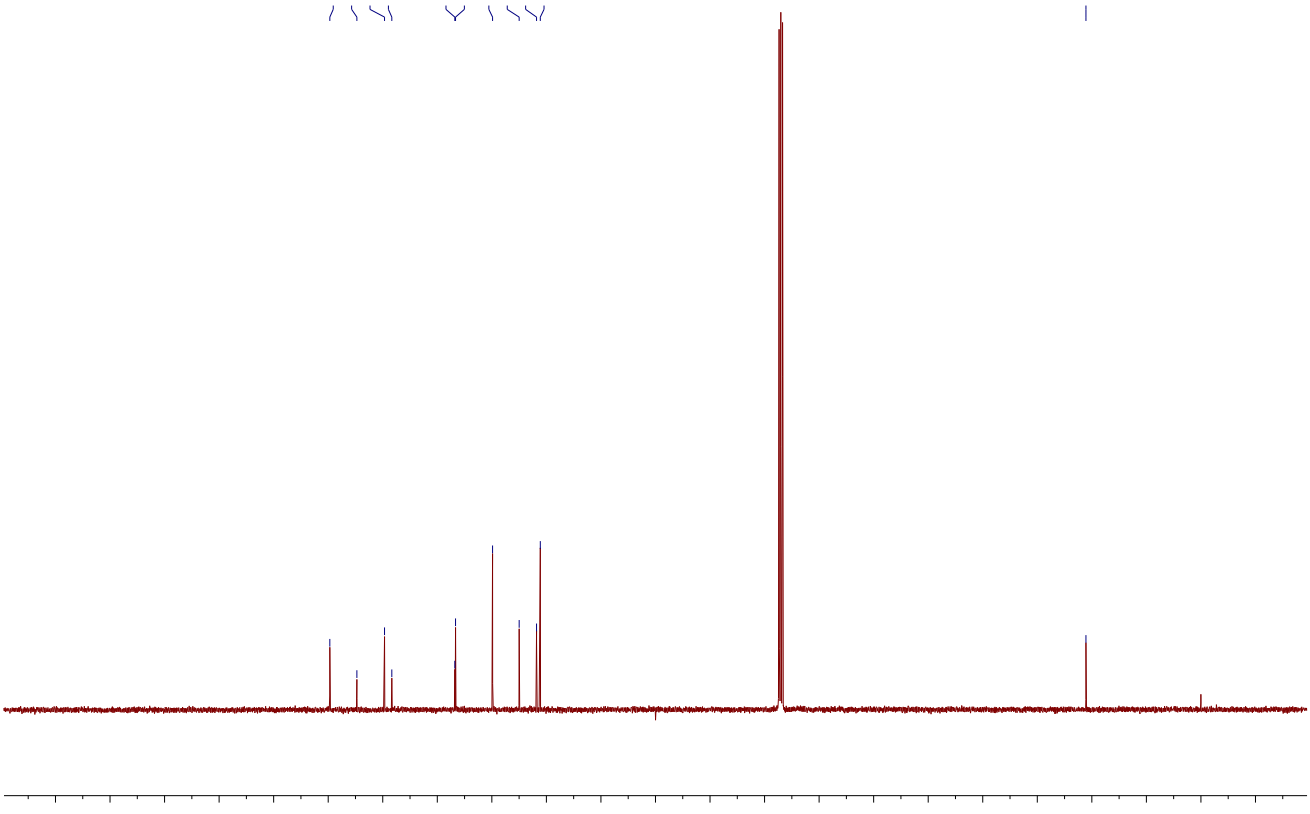


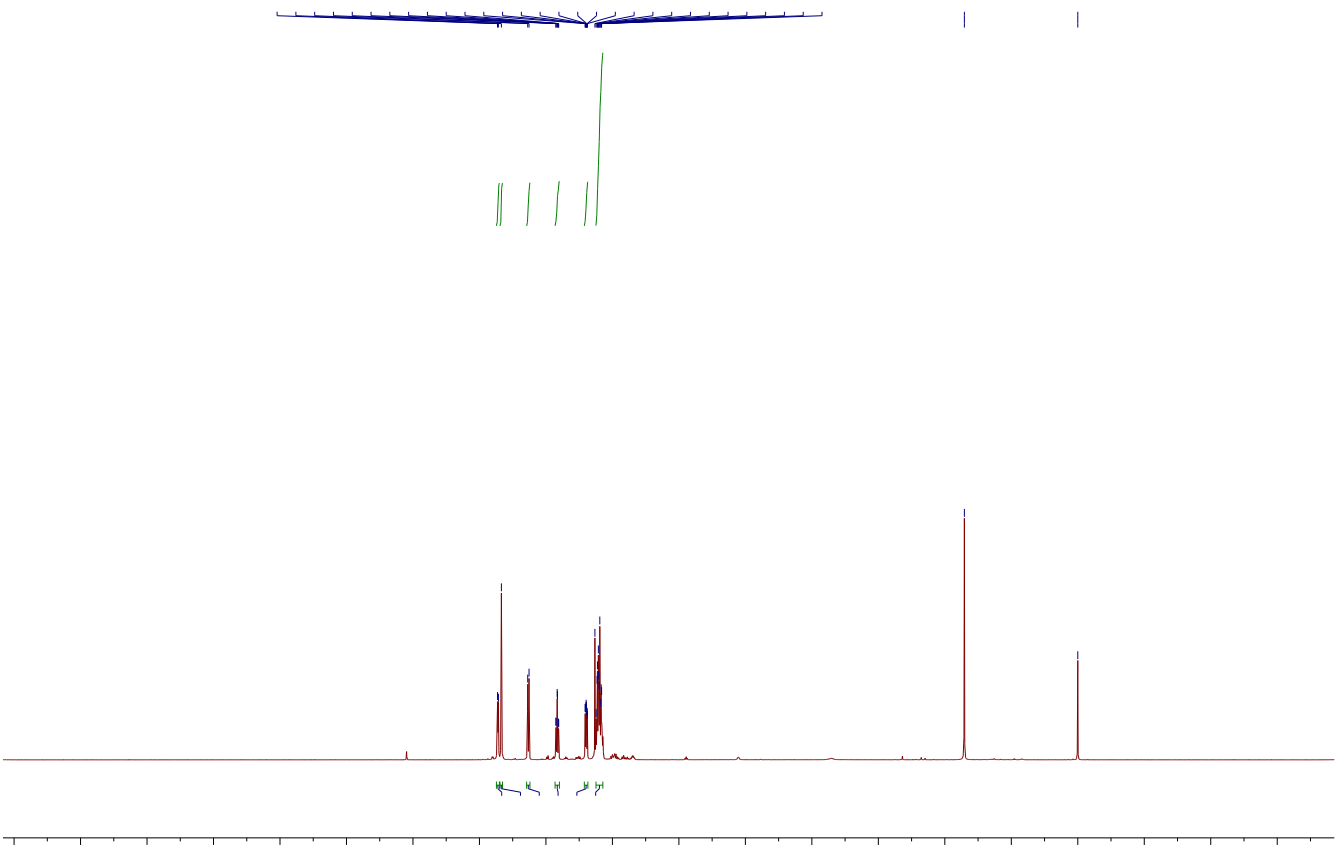


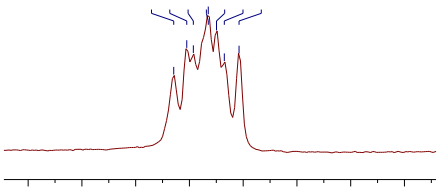


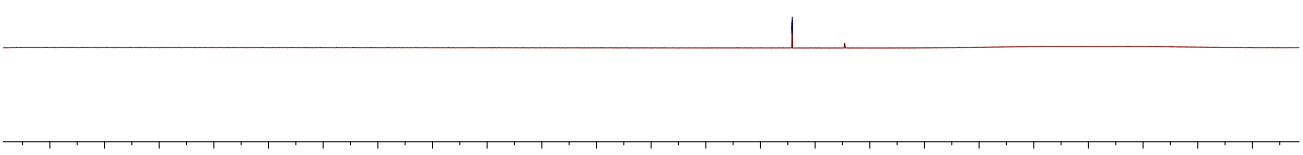


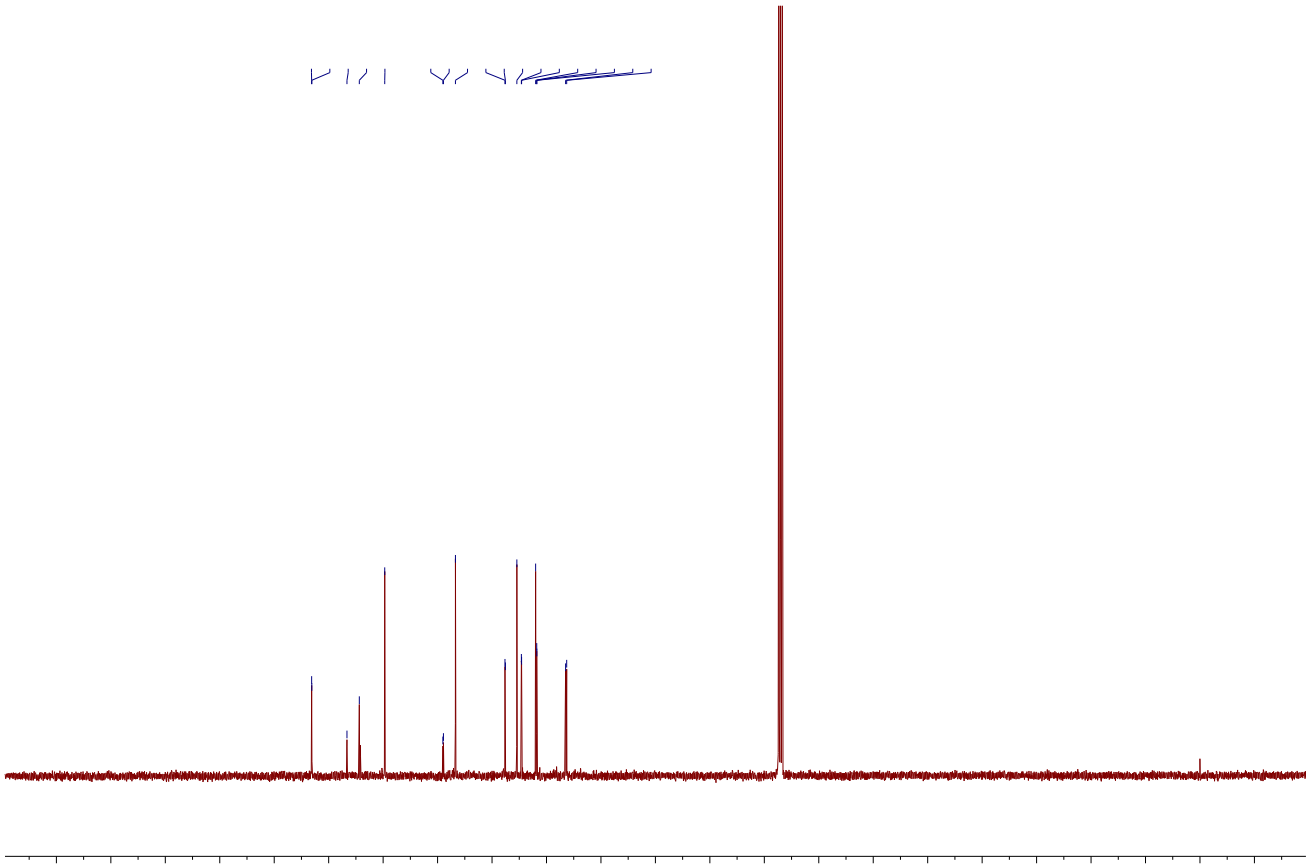


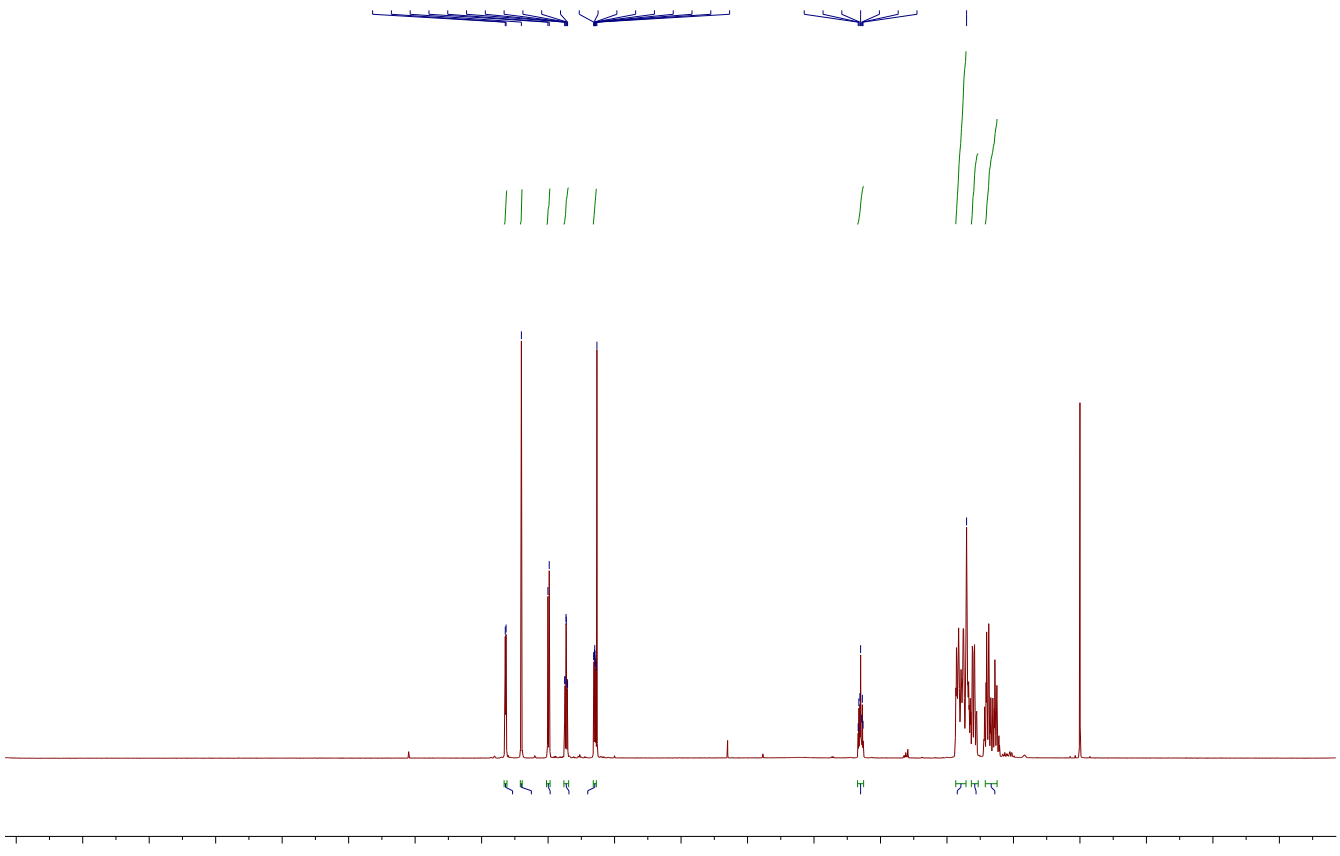


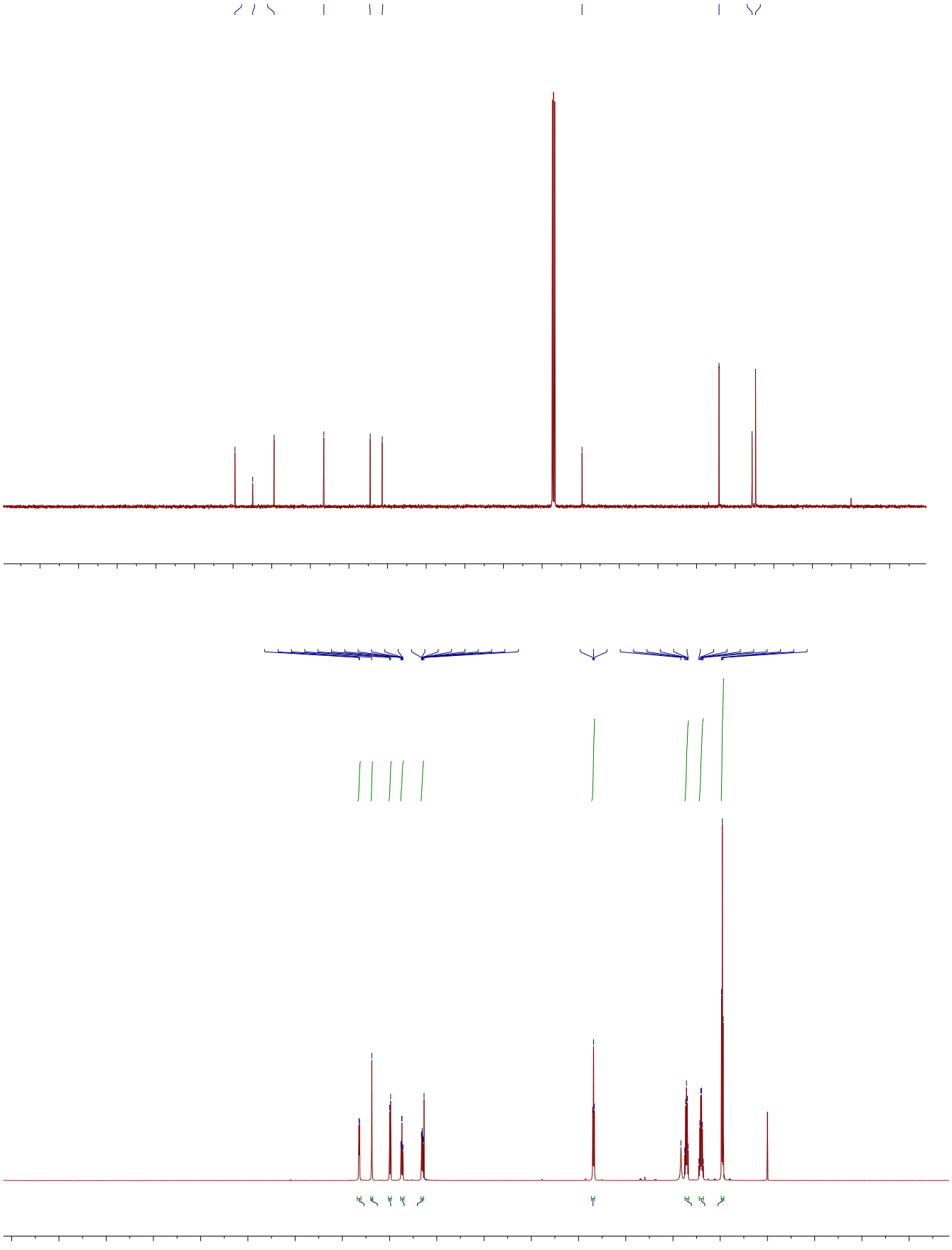


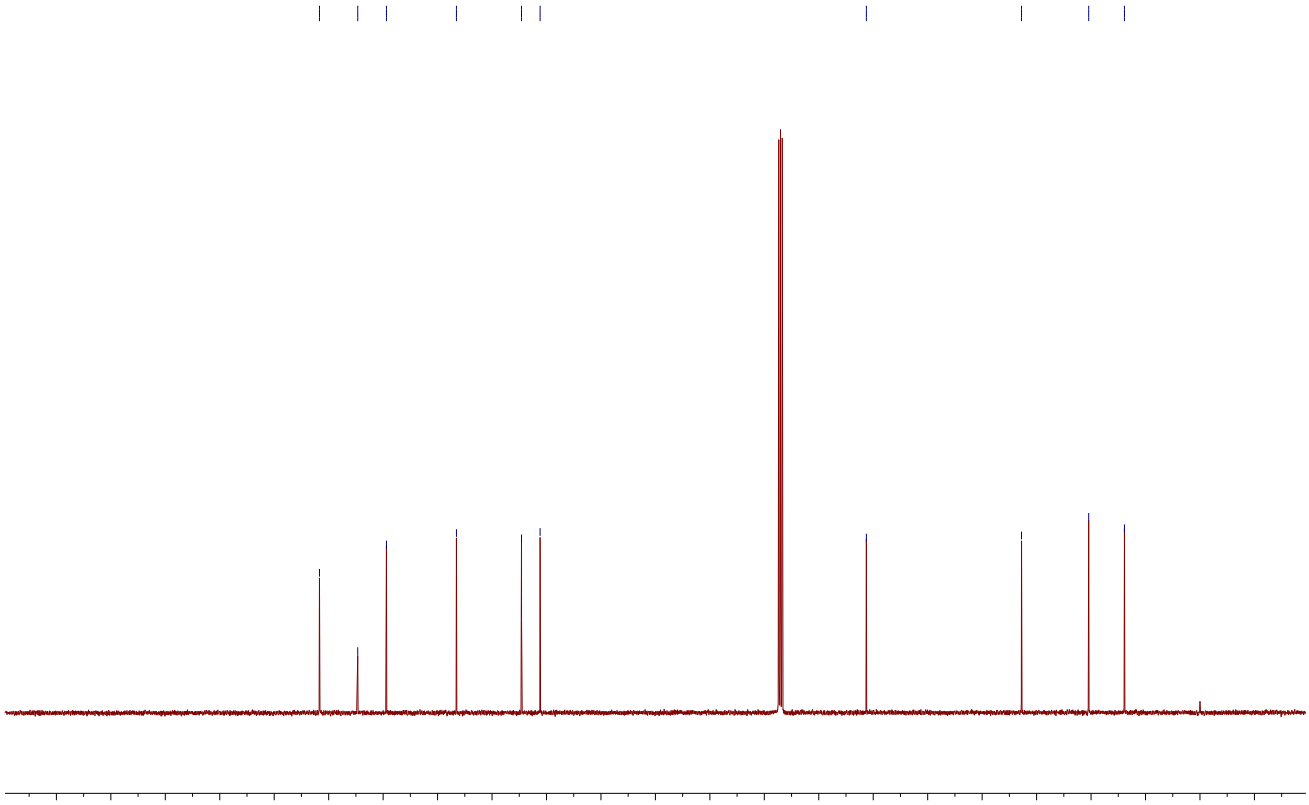


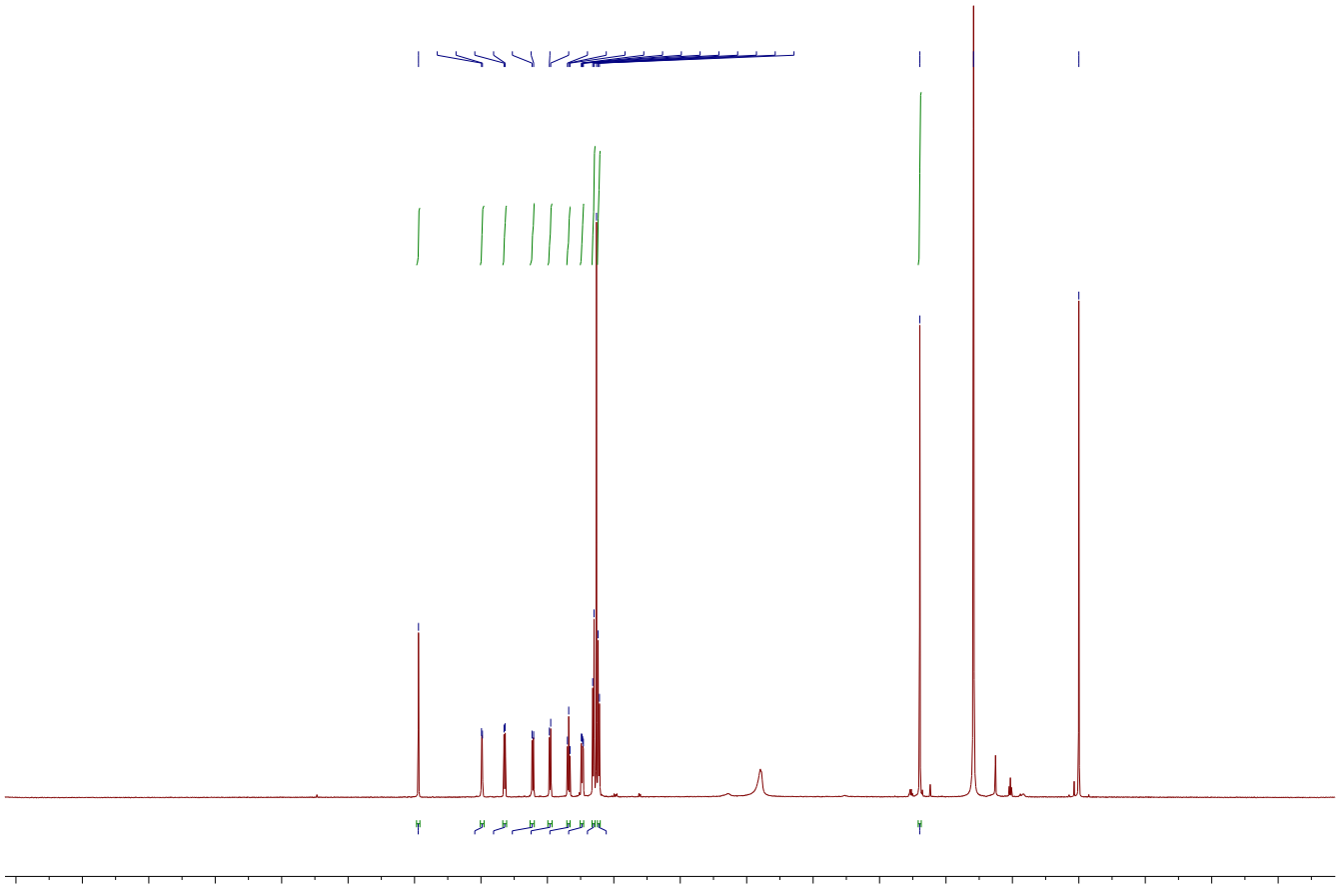


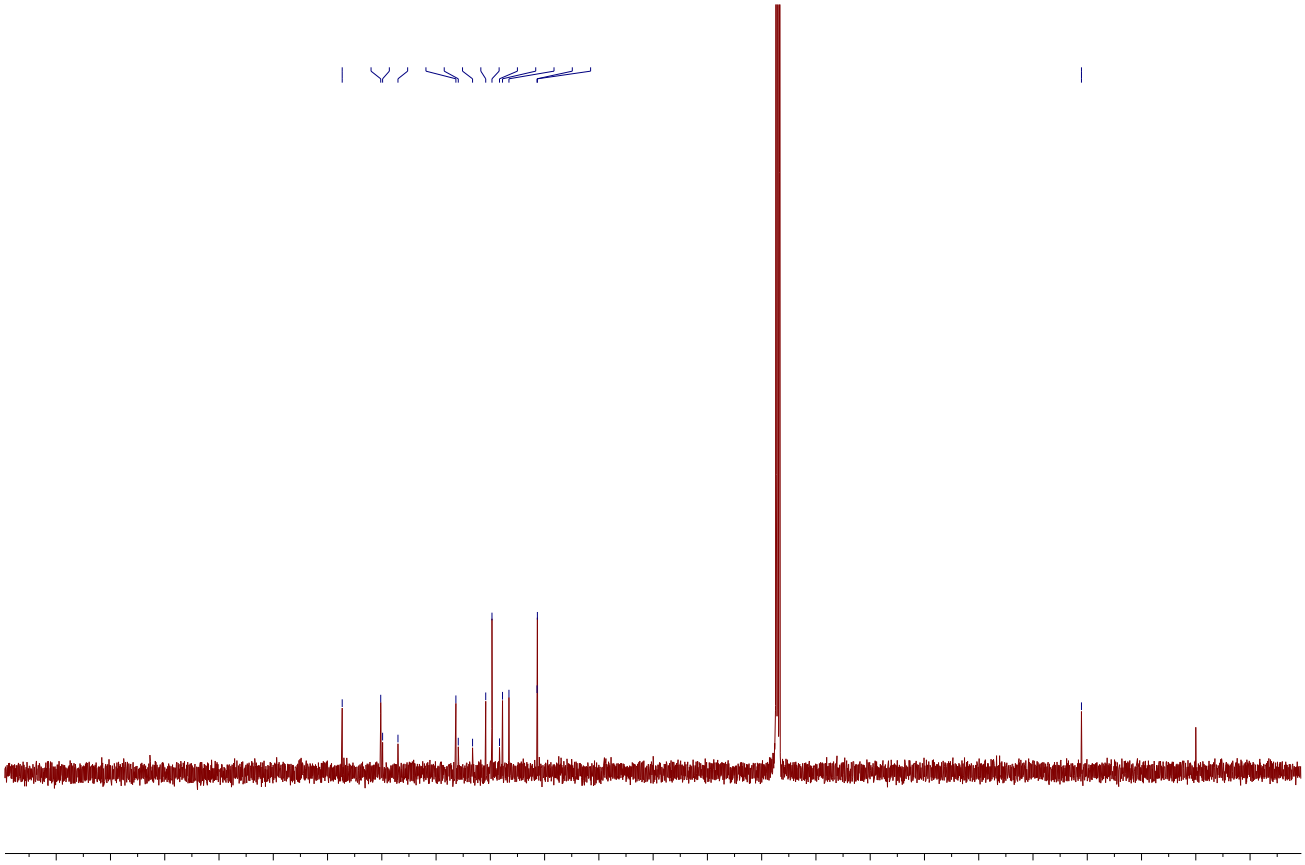


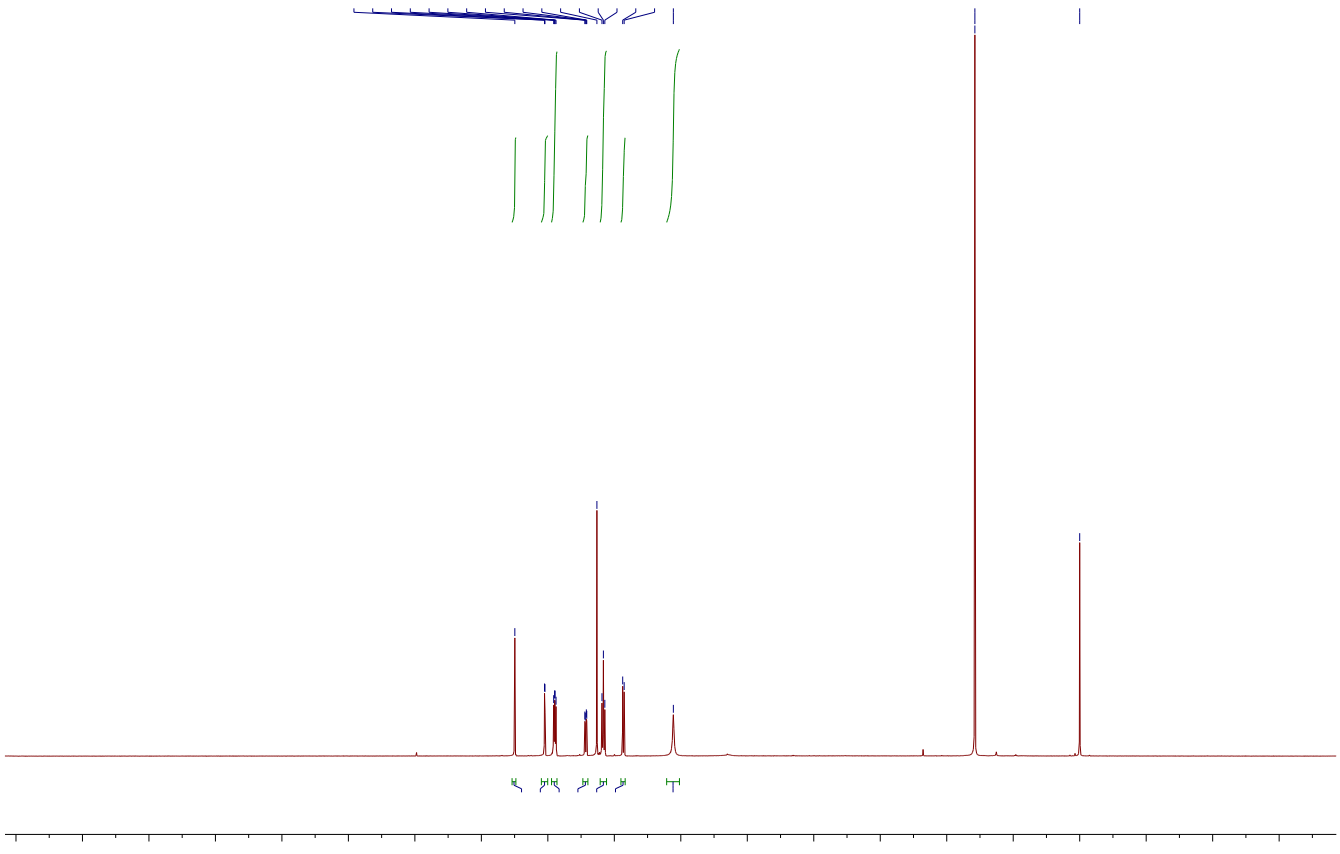


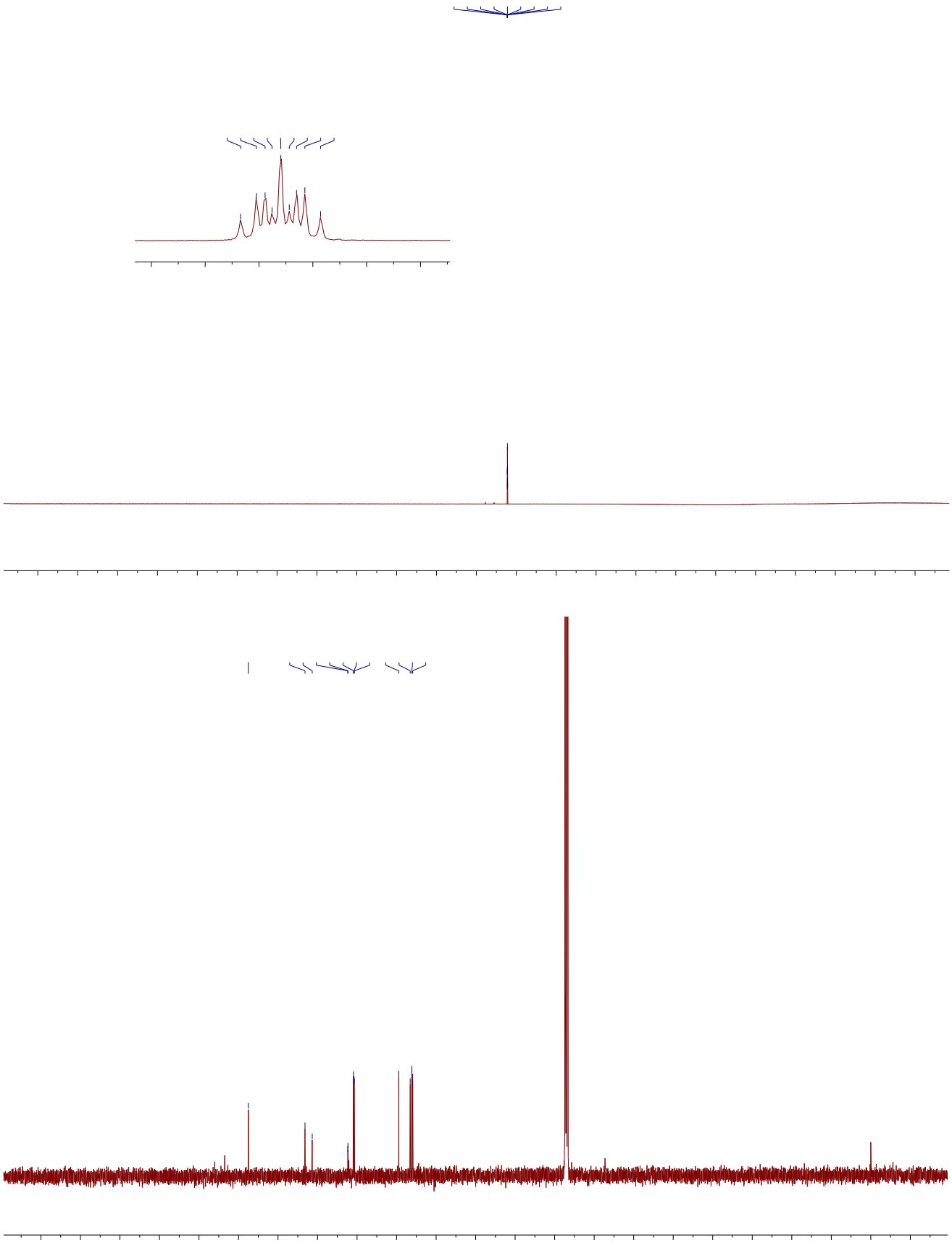


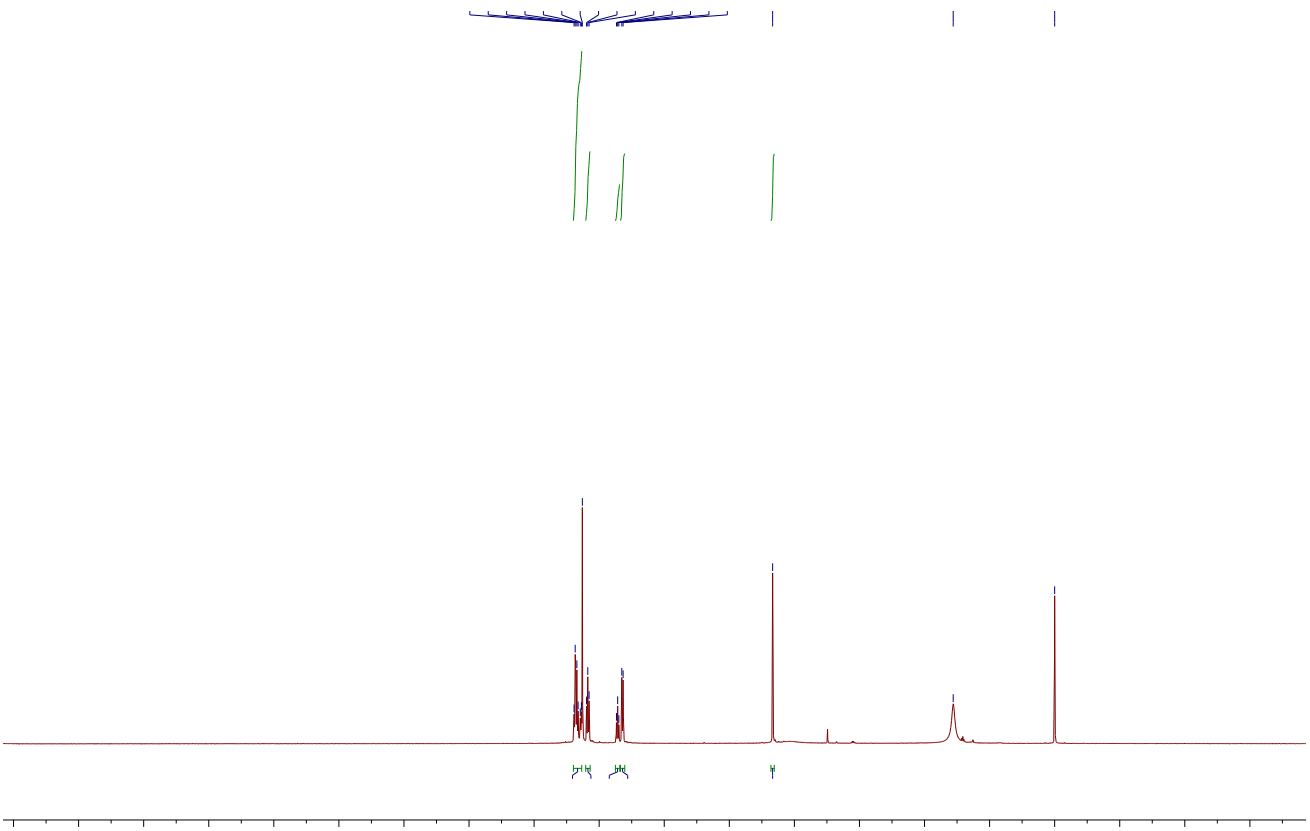


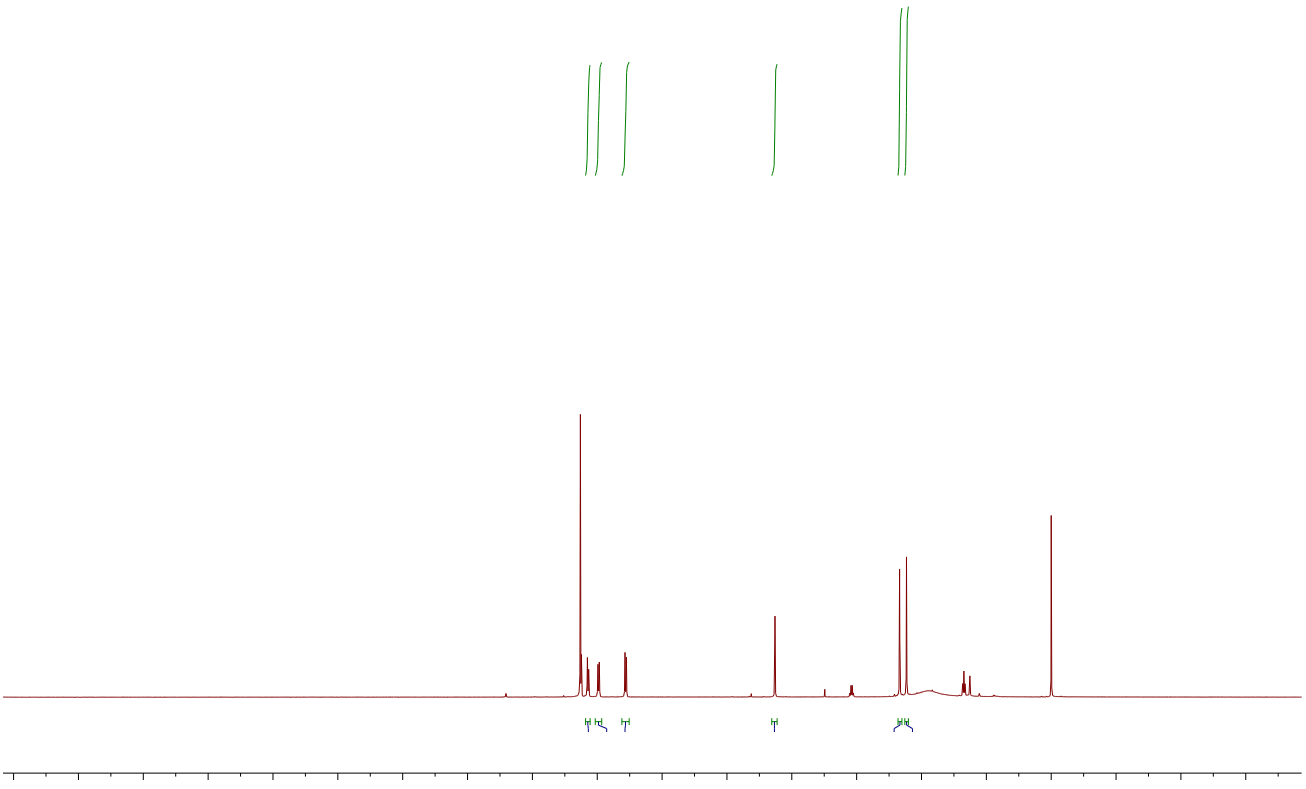


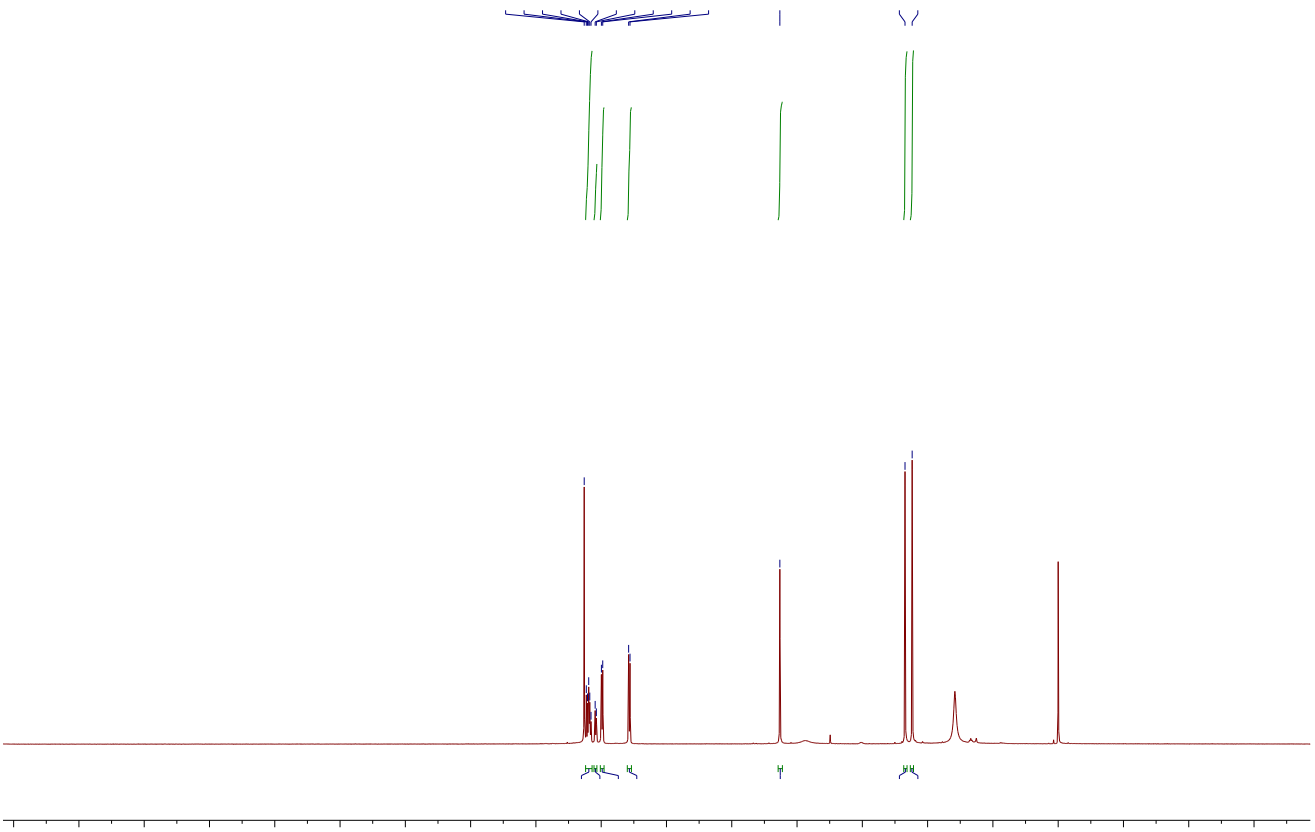


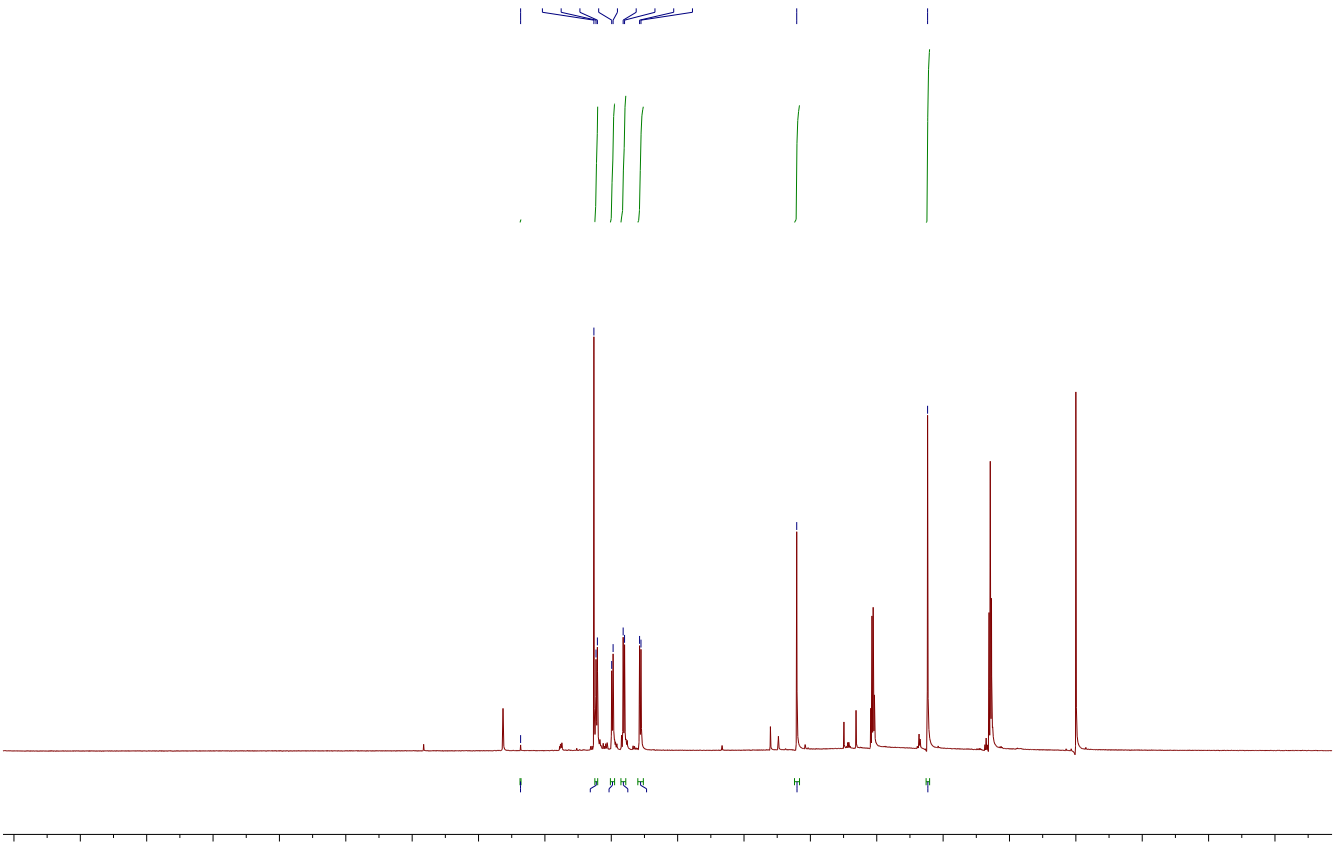


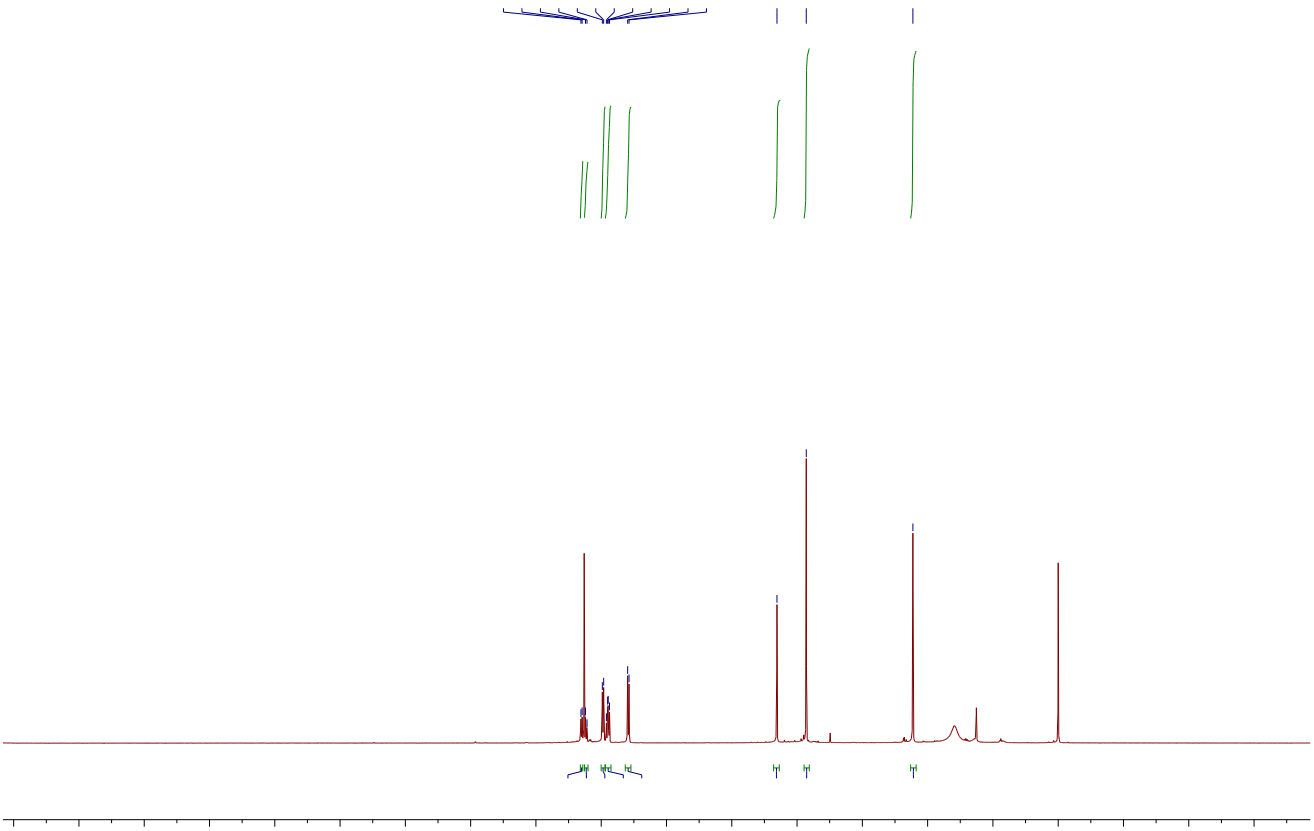


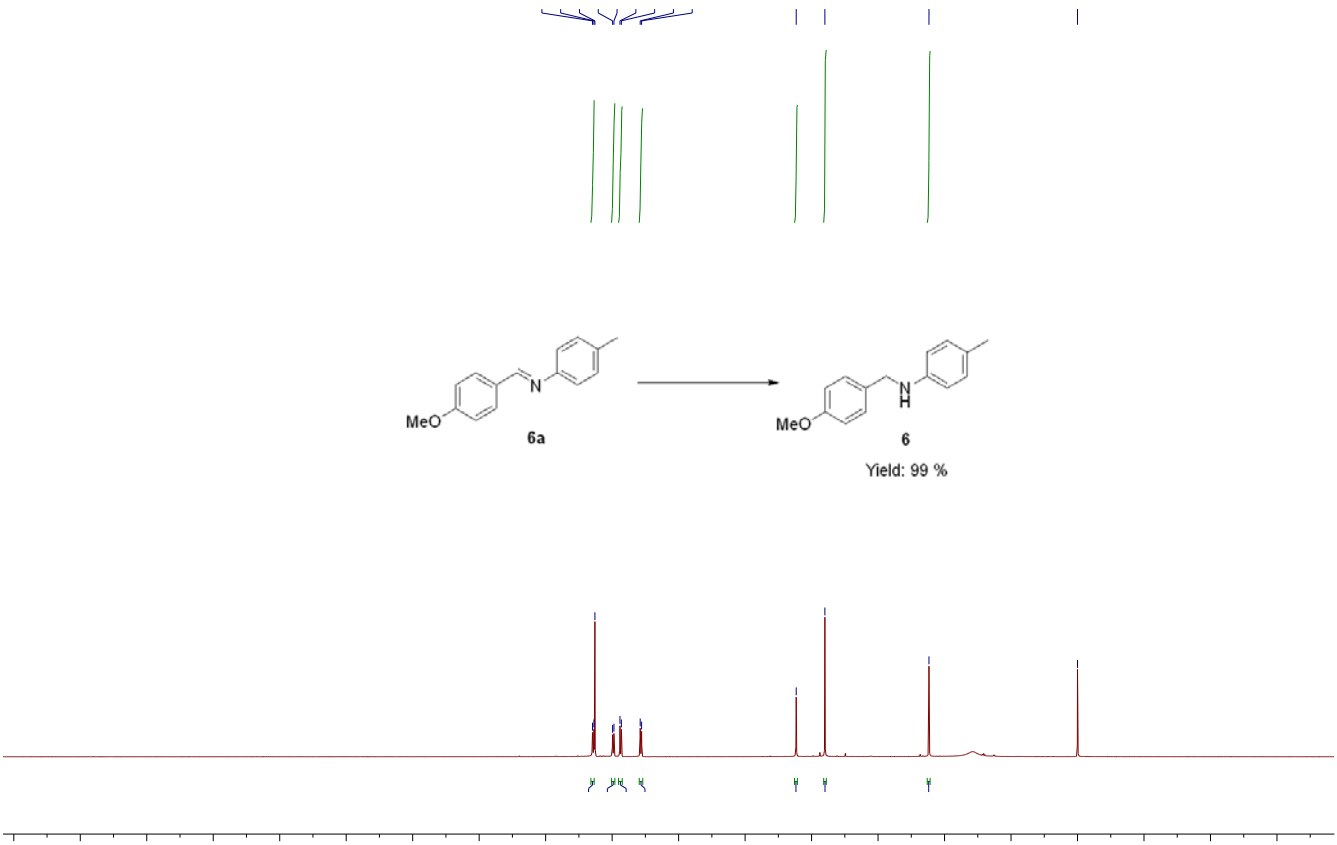


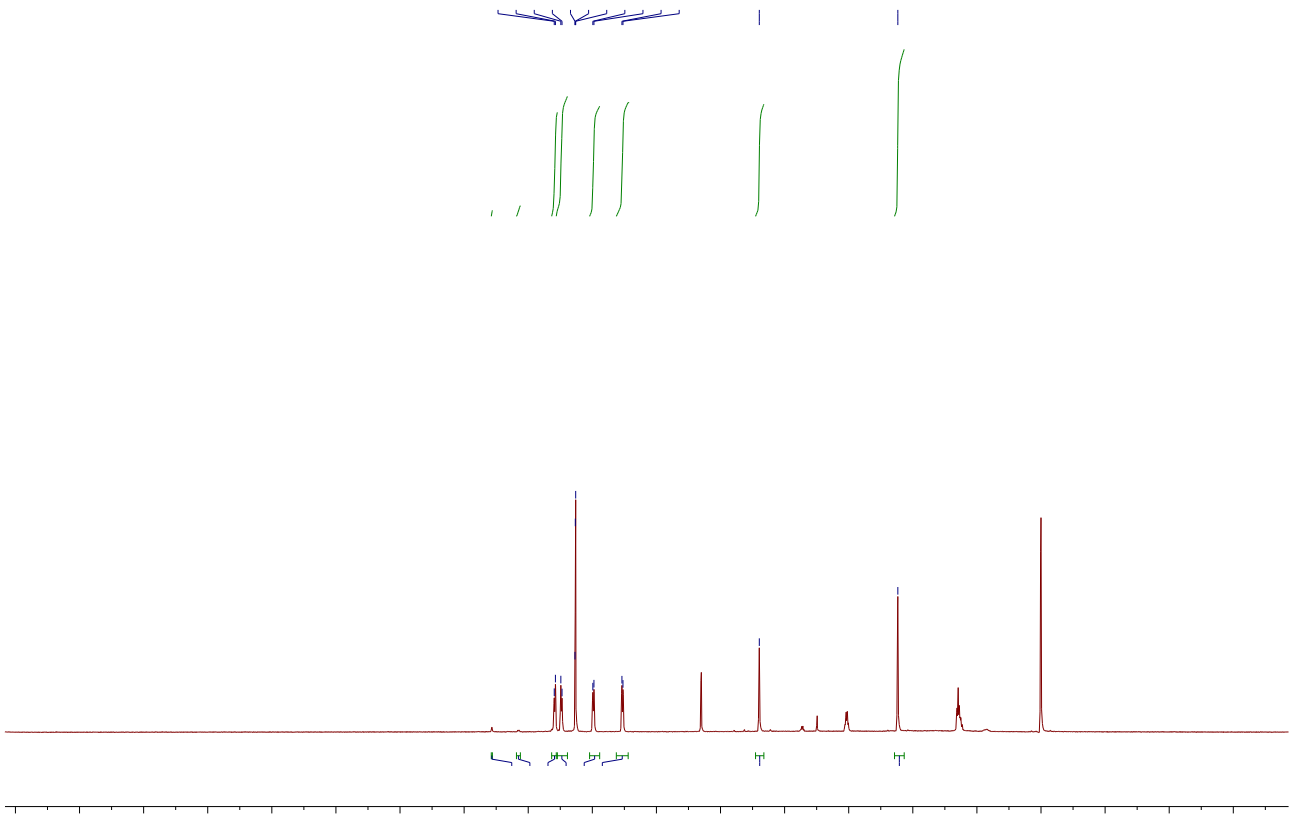


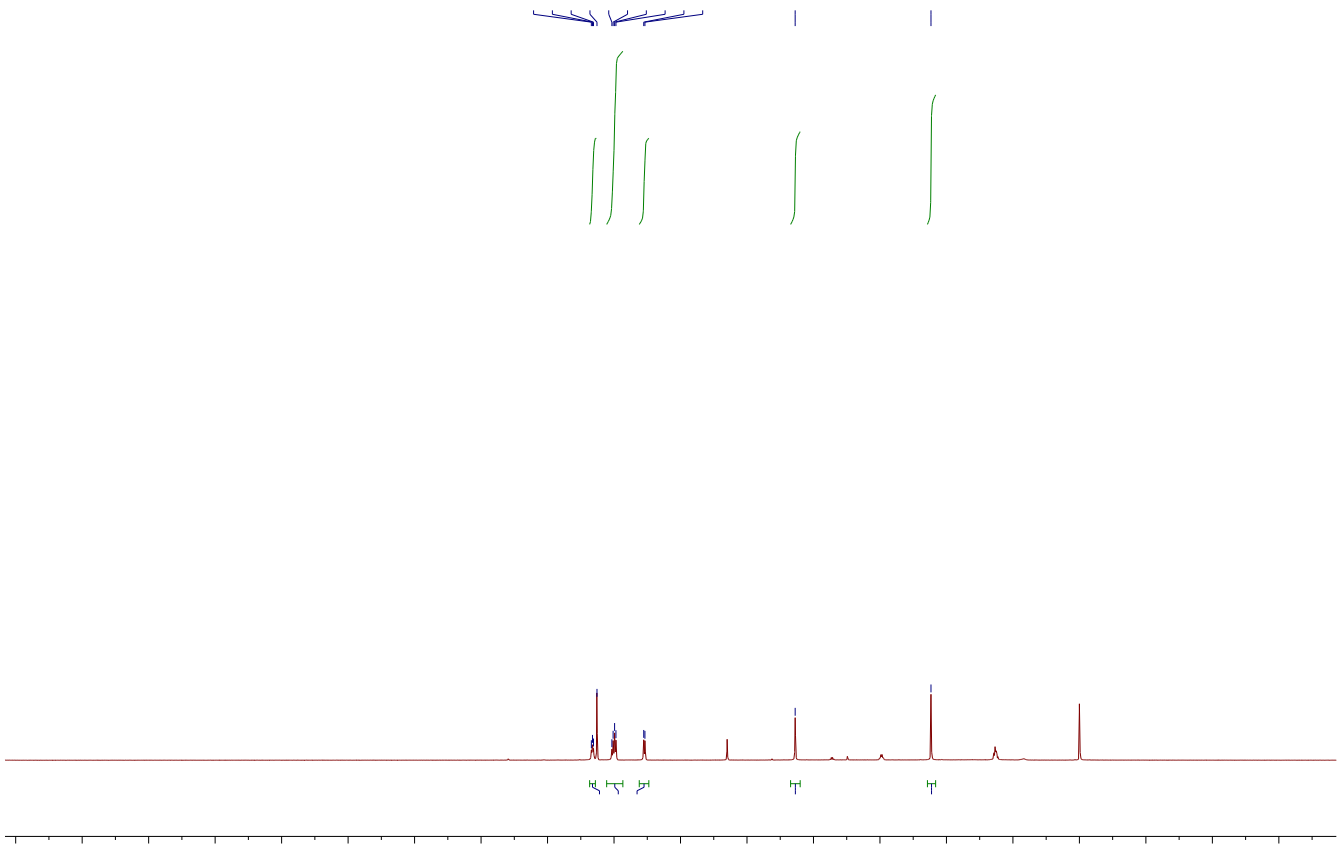


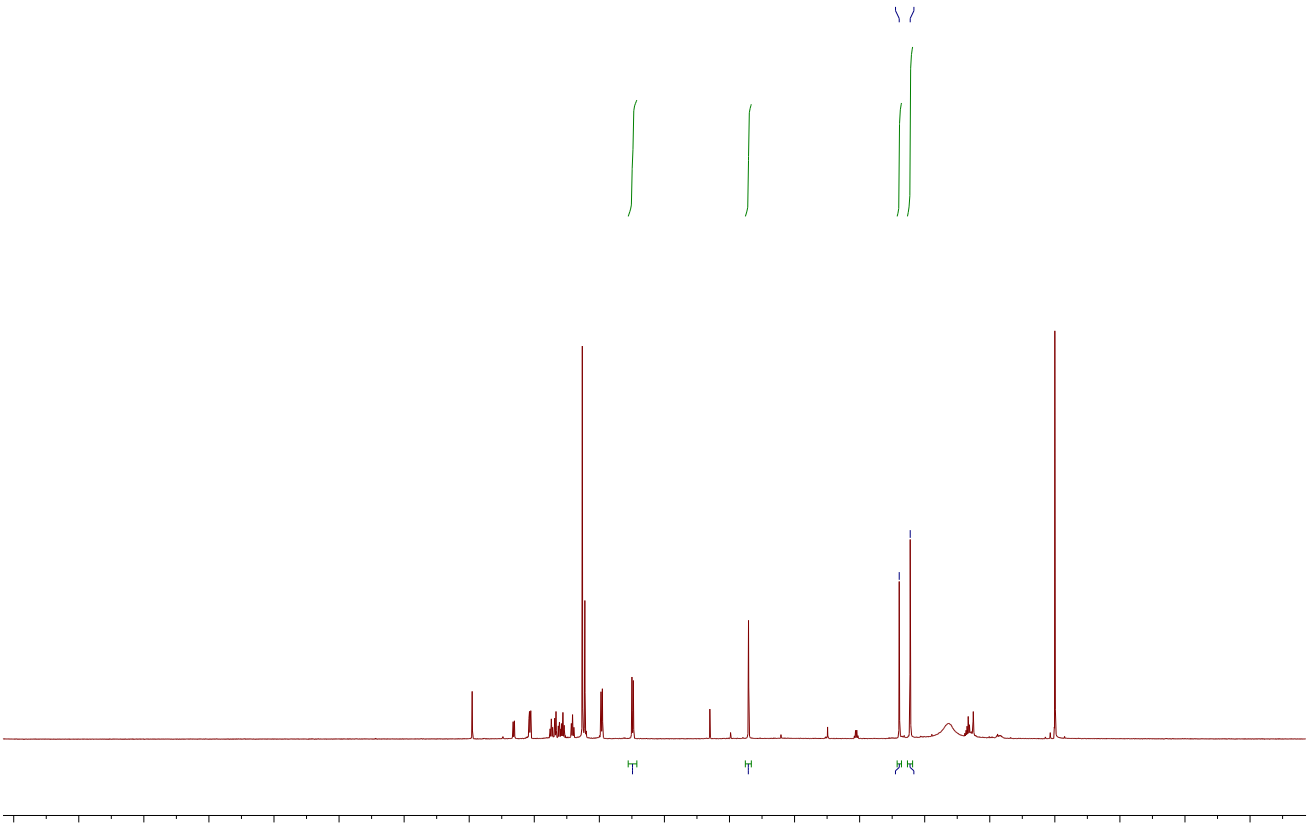


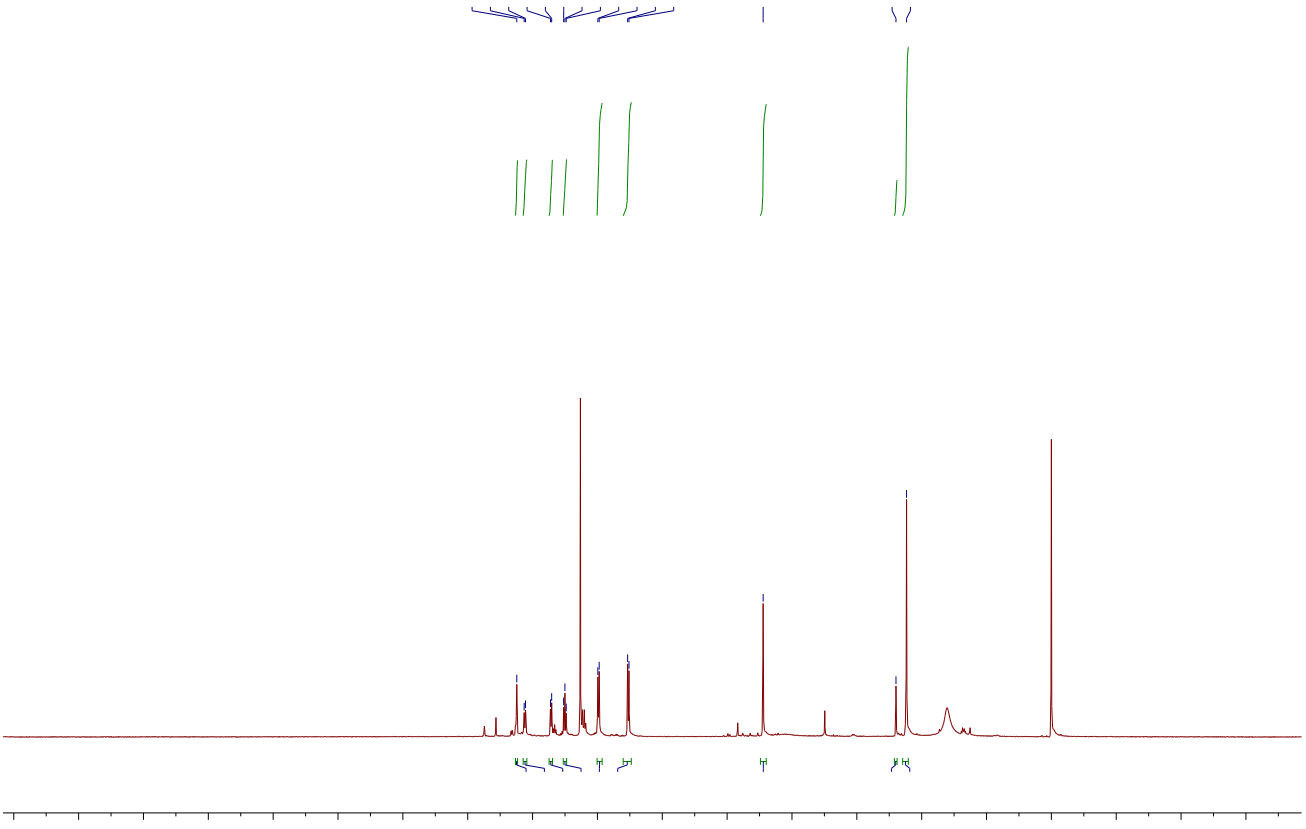


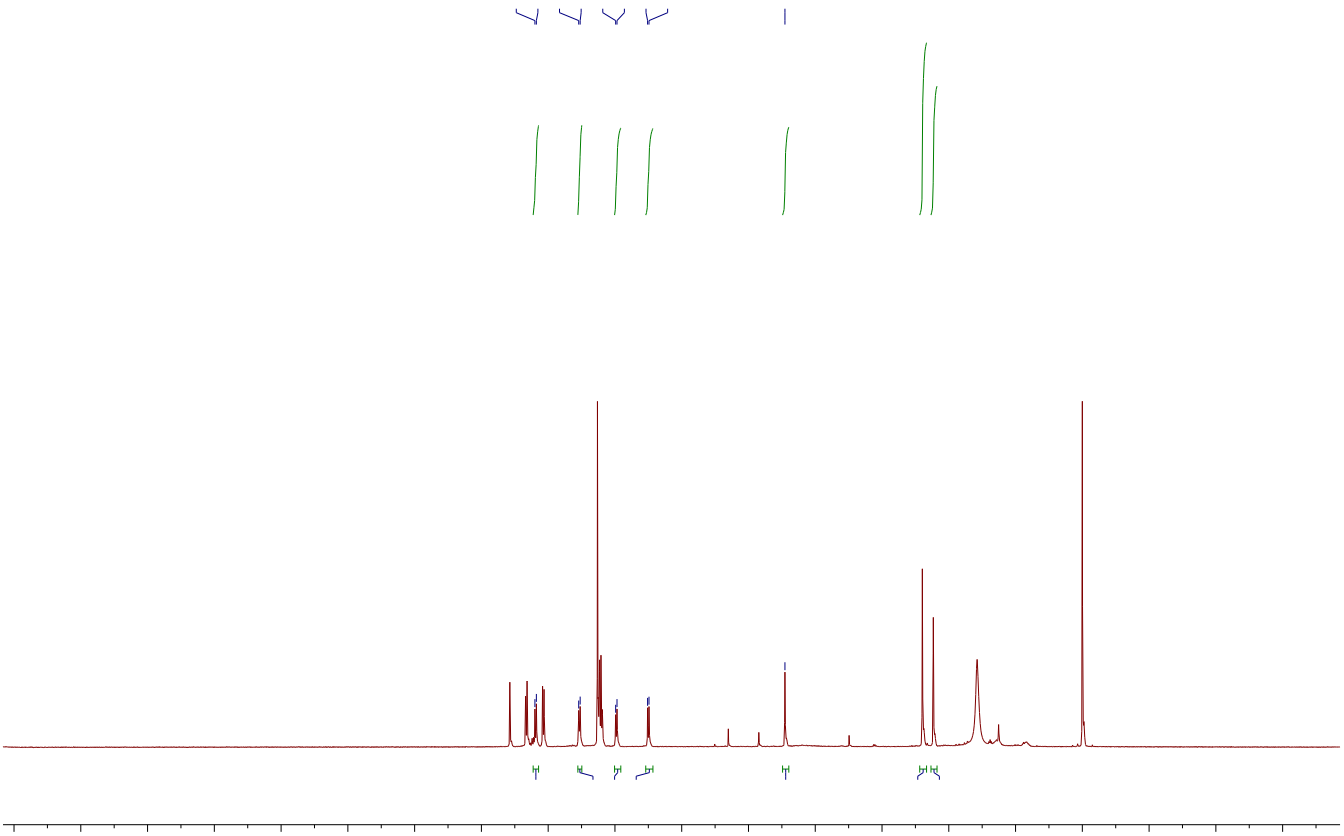

MeO
N
6a
MeO
N
H
6
Yield: 99 %

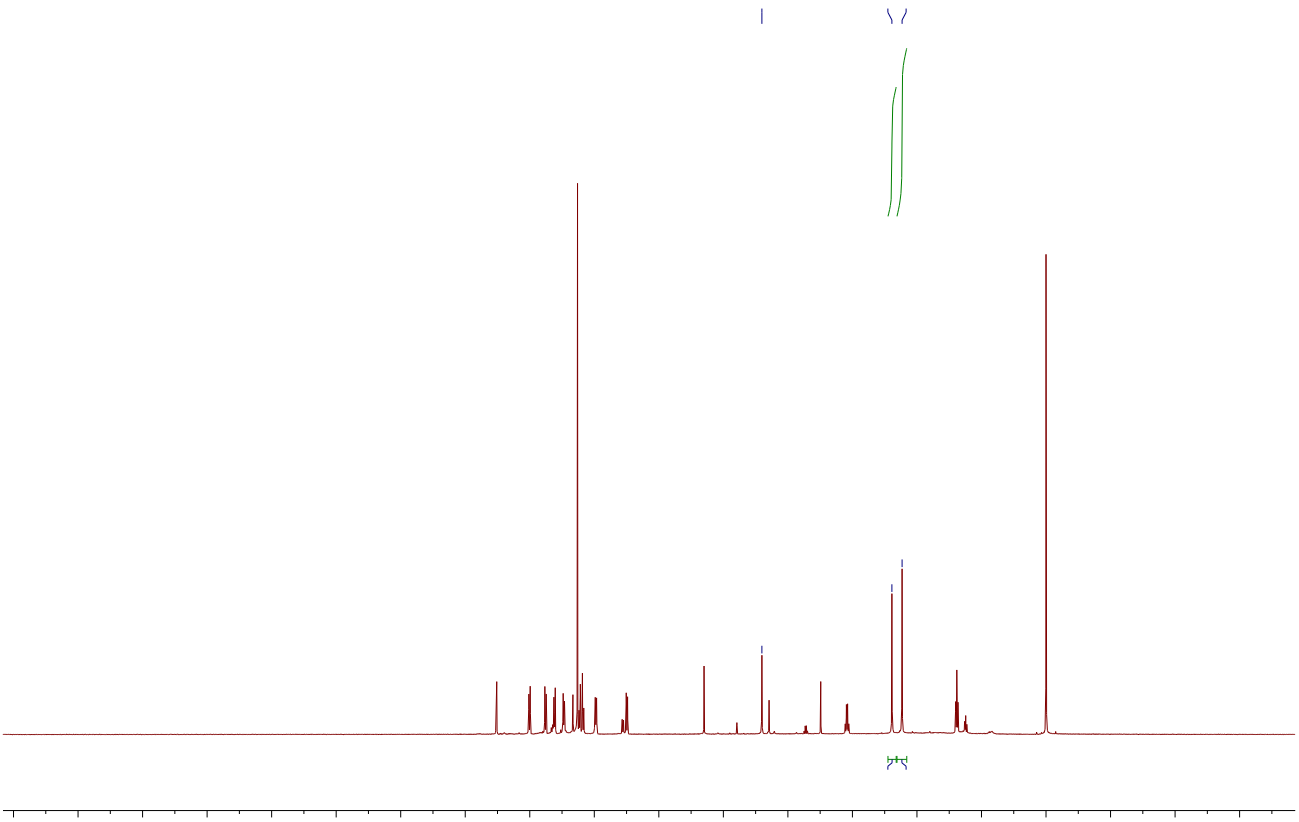


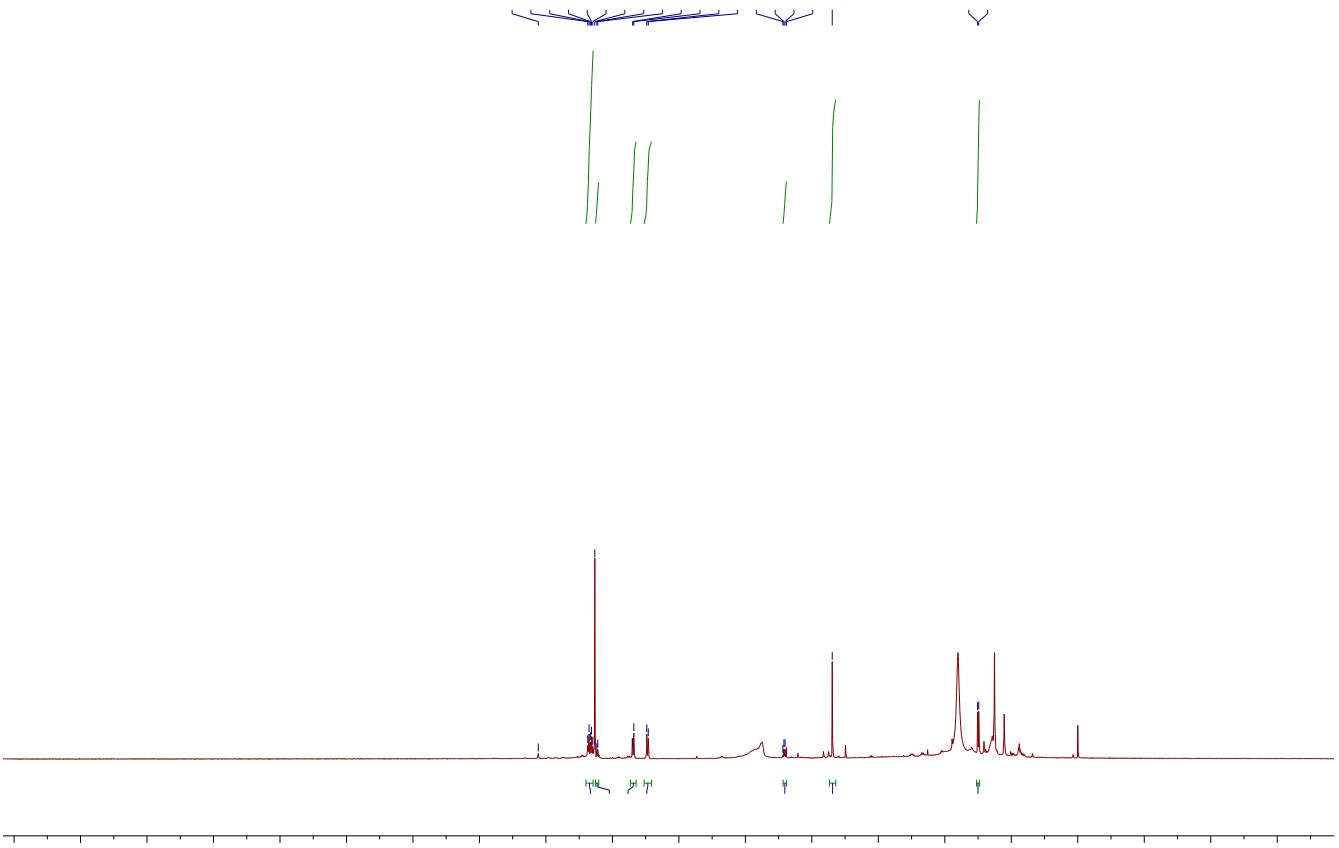


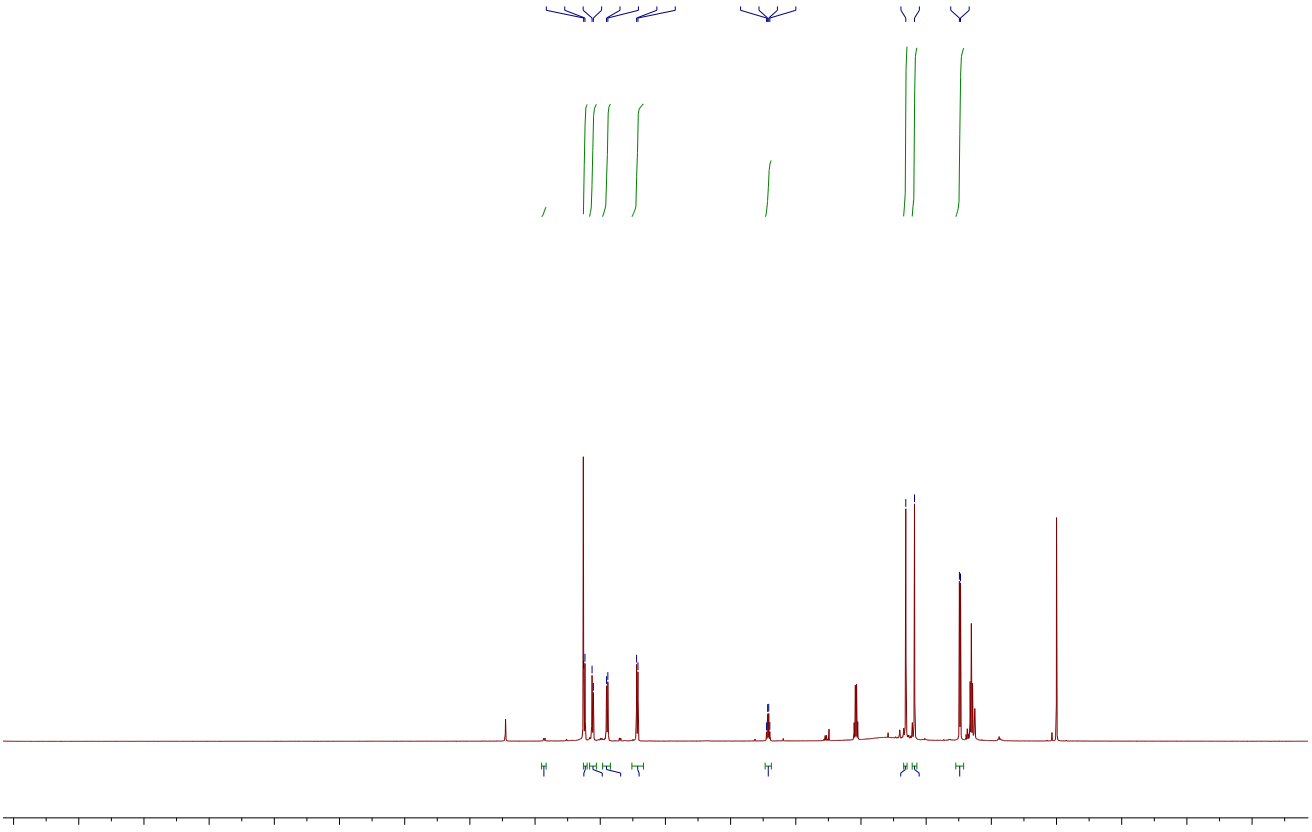


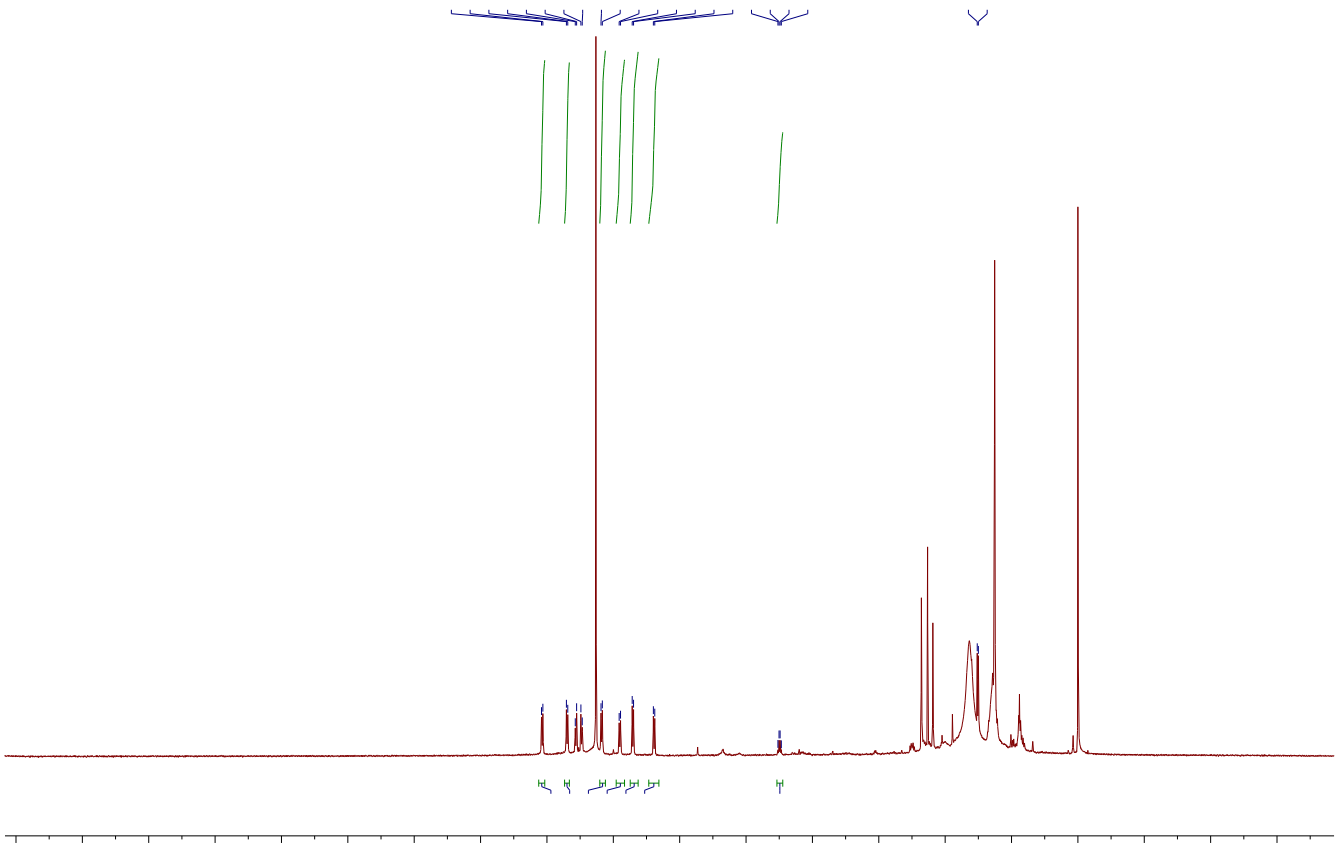


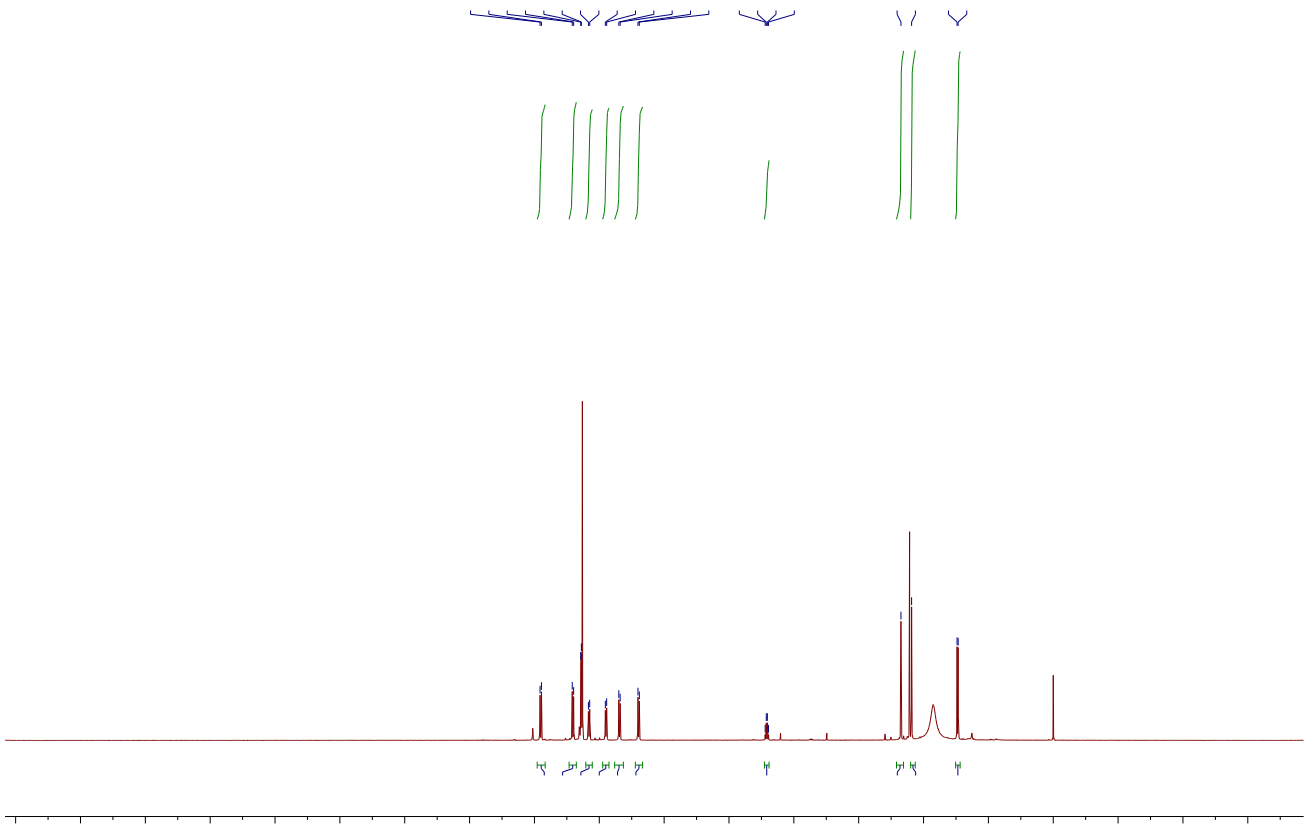


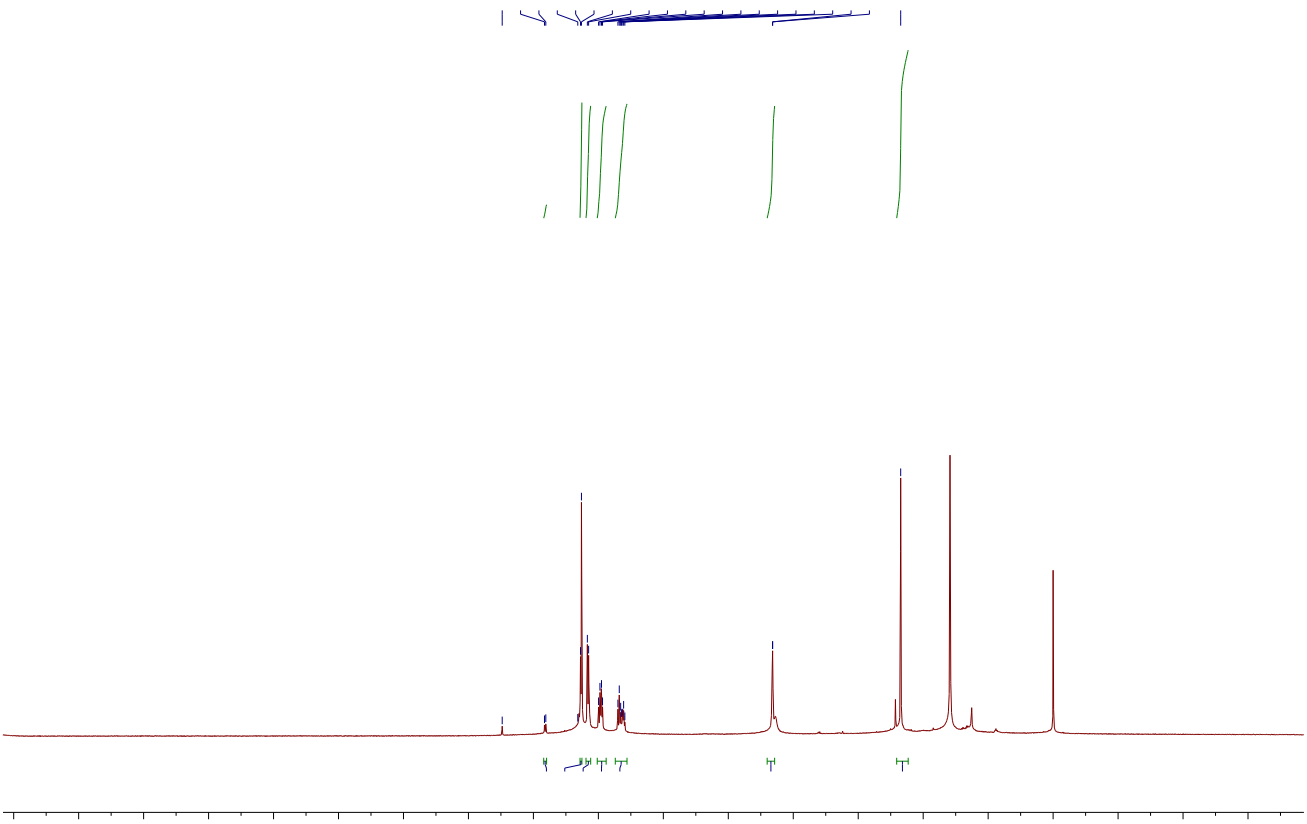


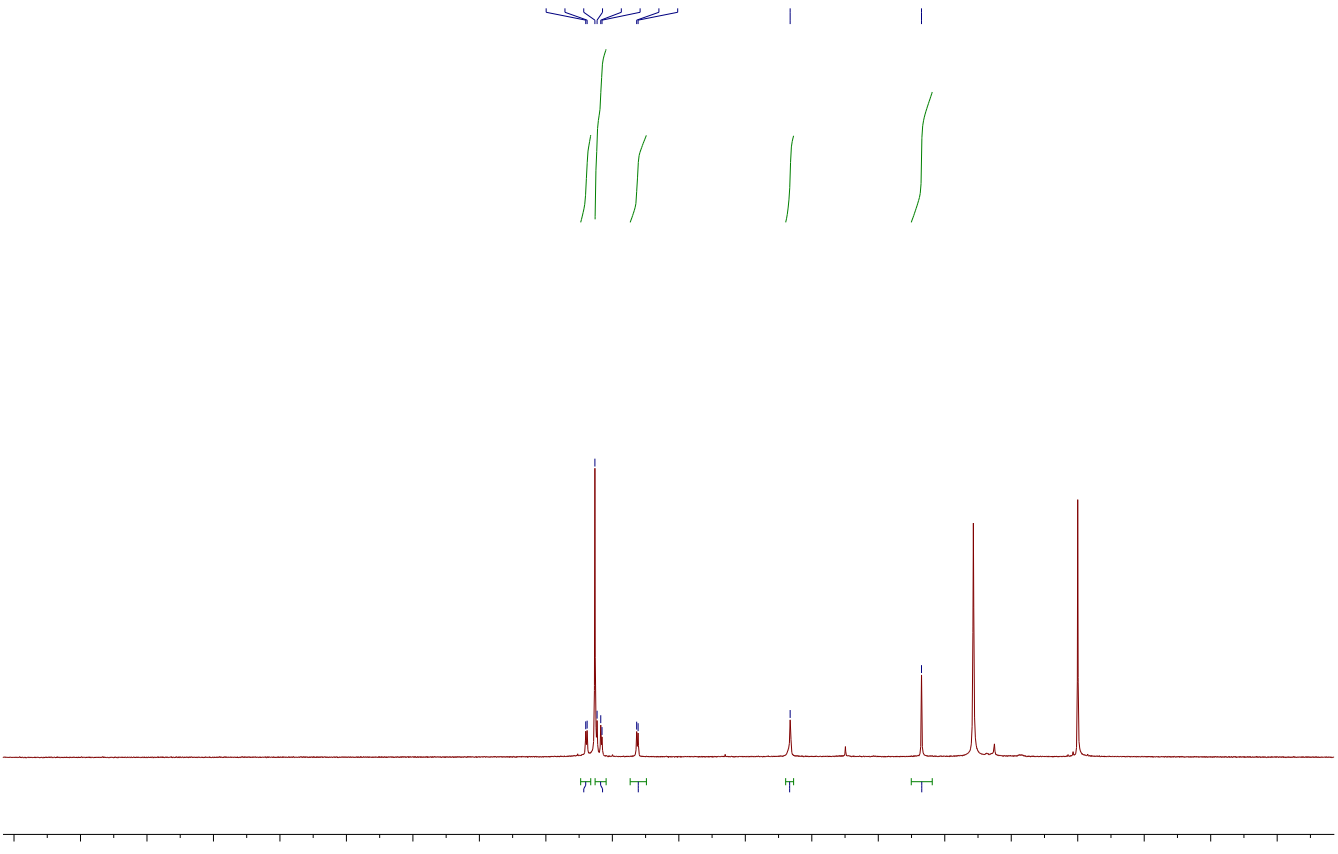


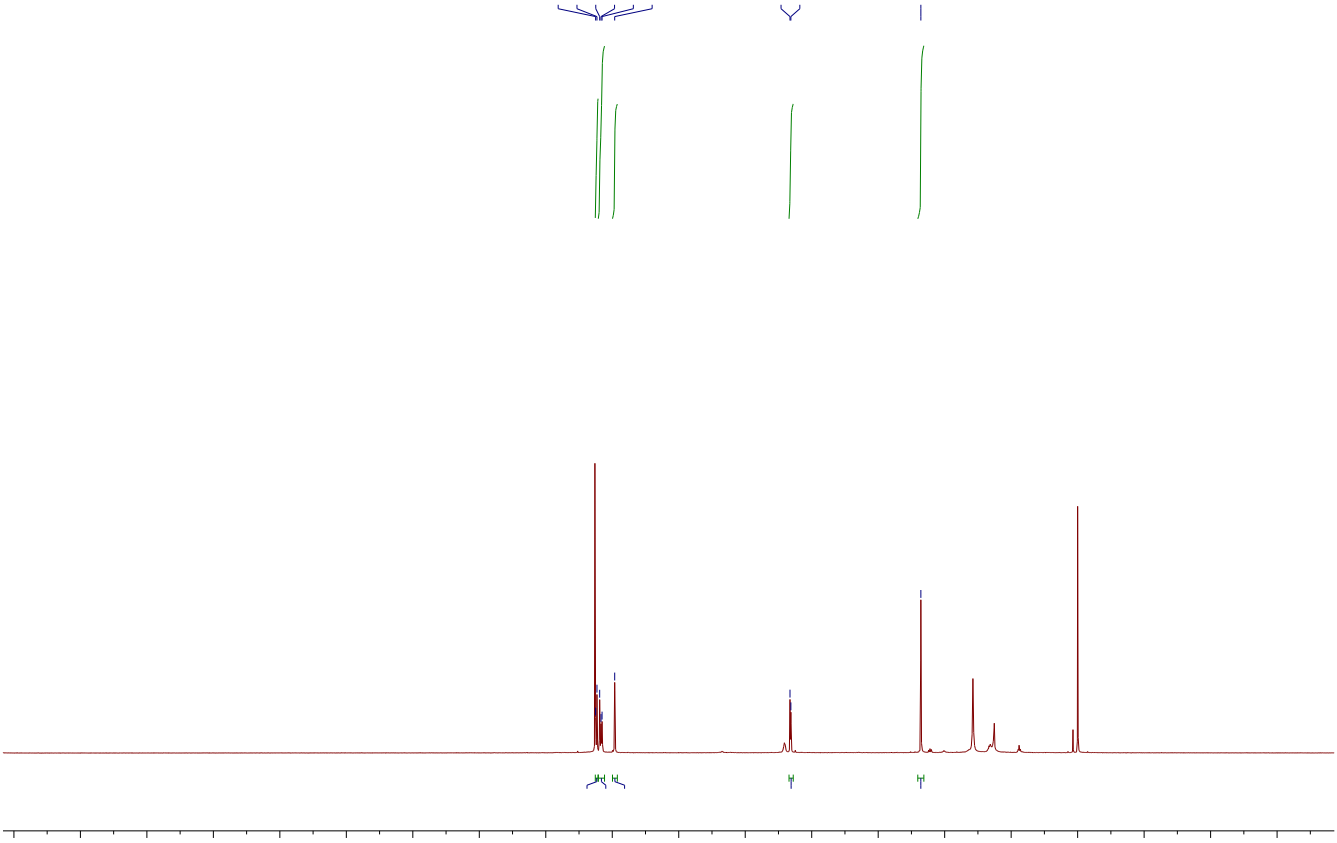


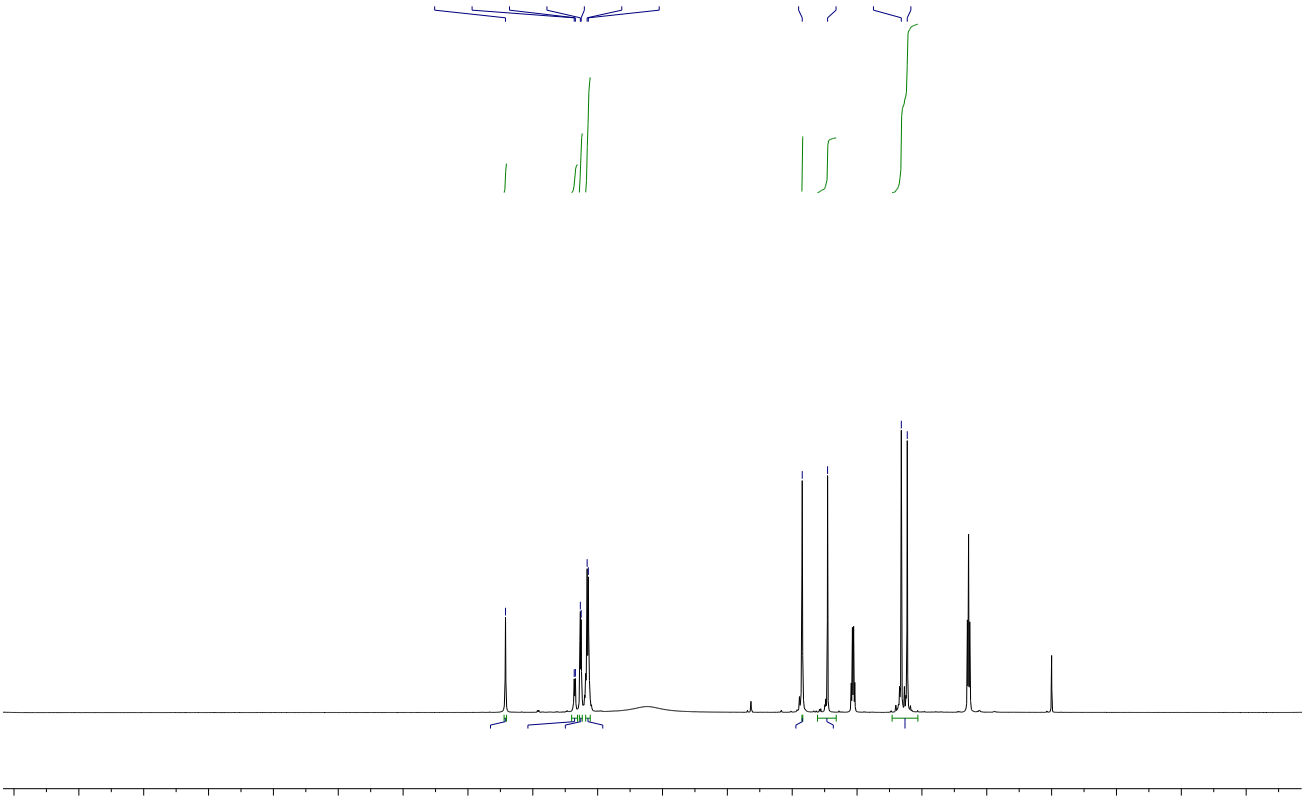


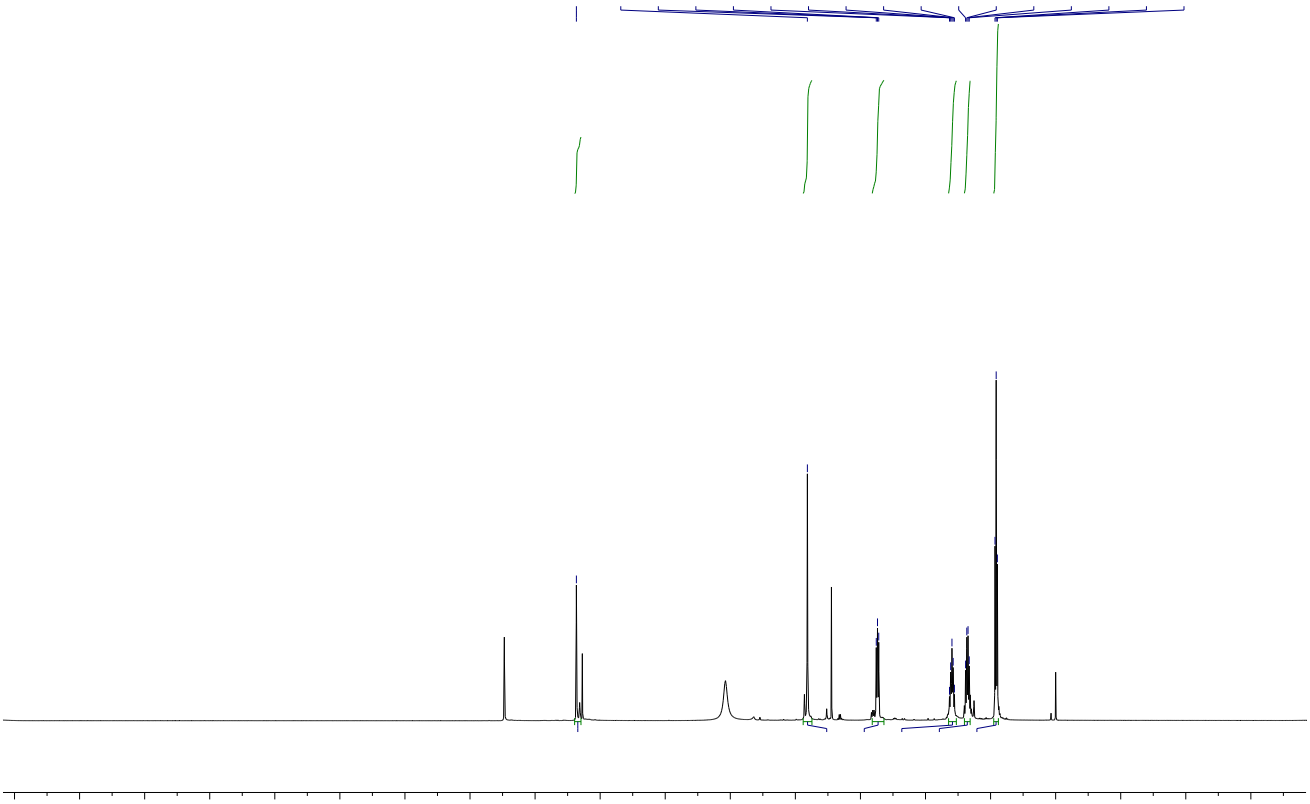


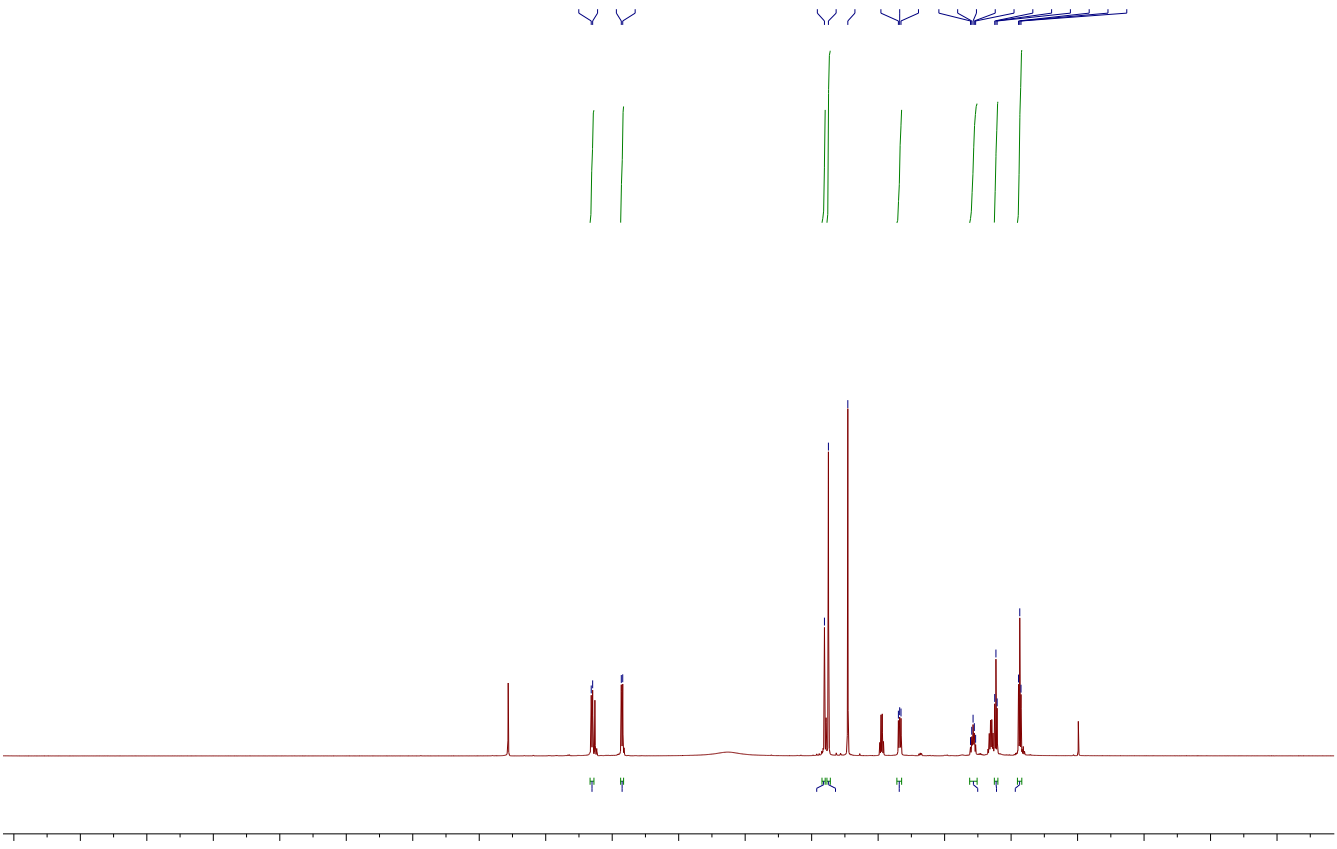


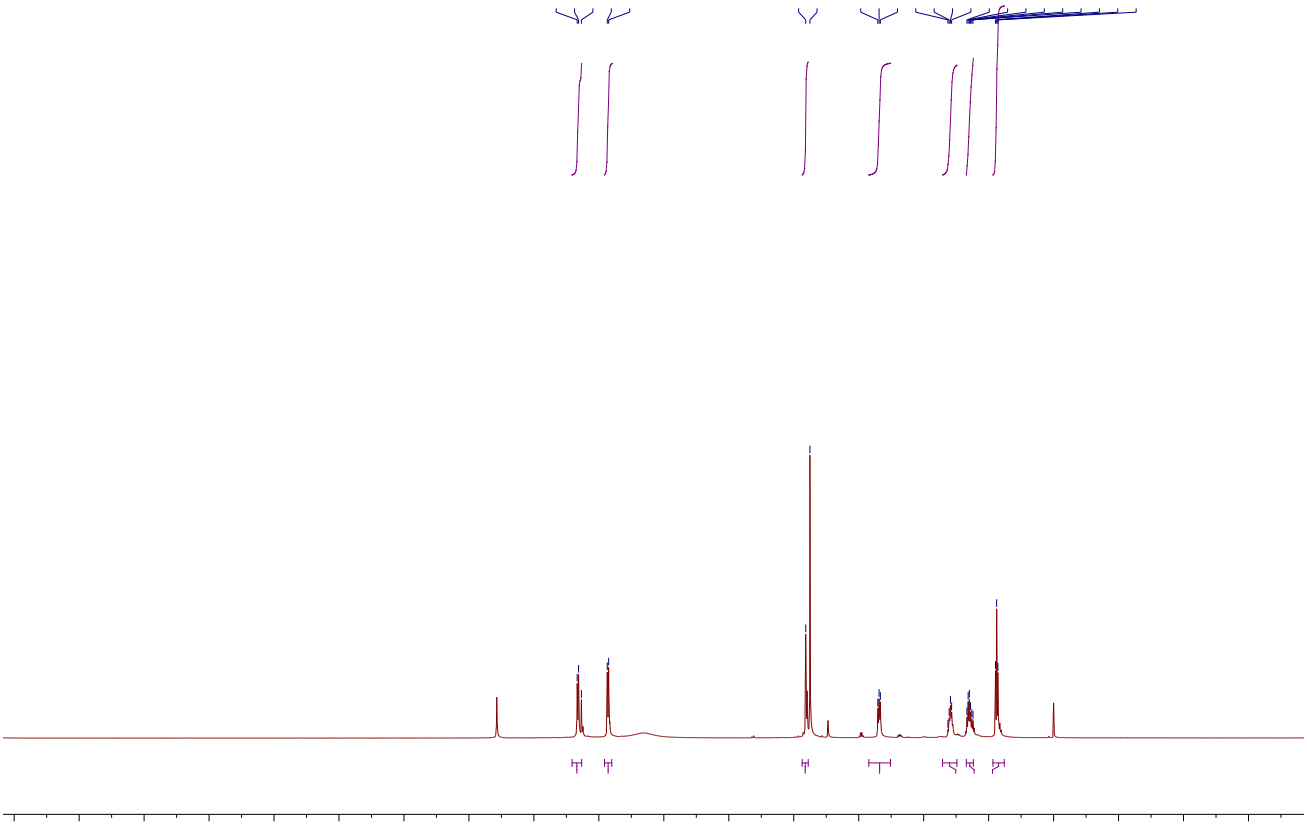


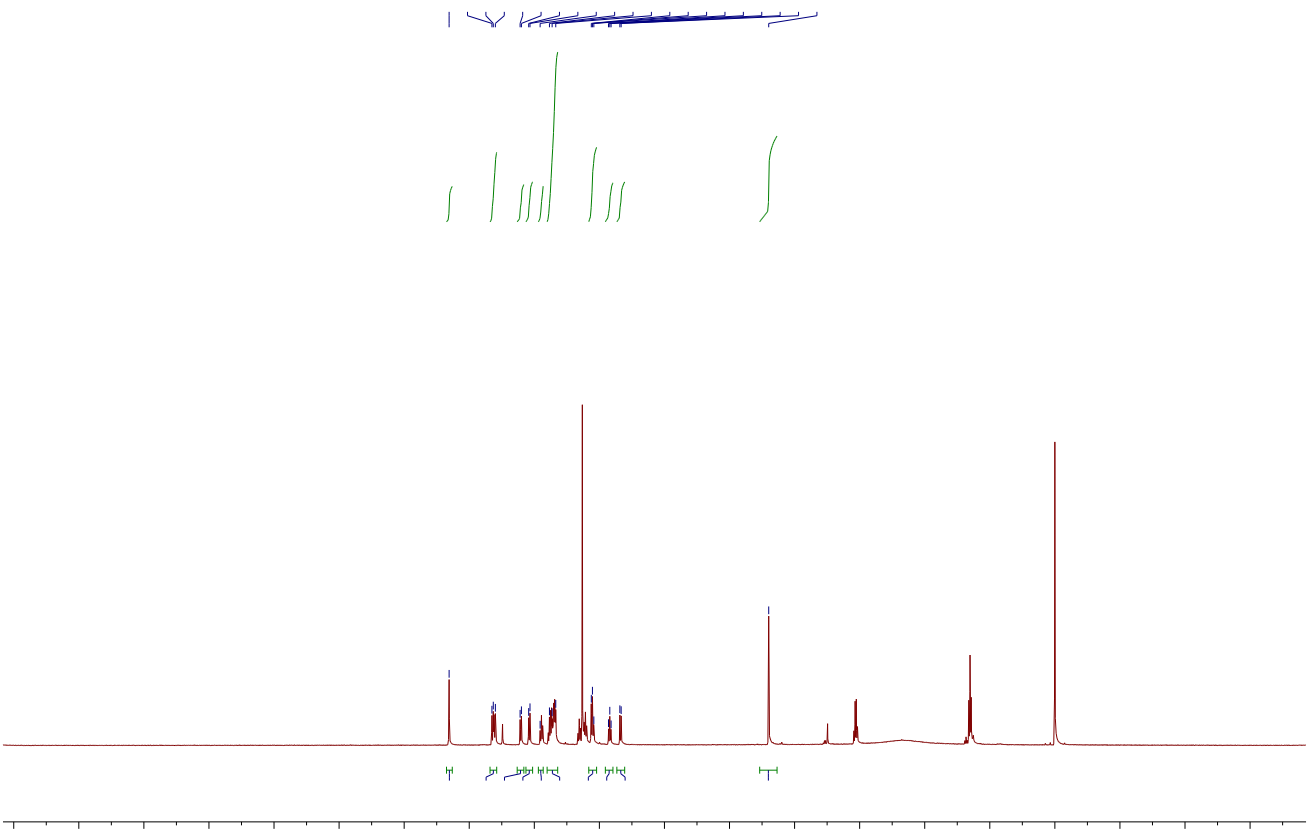


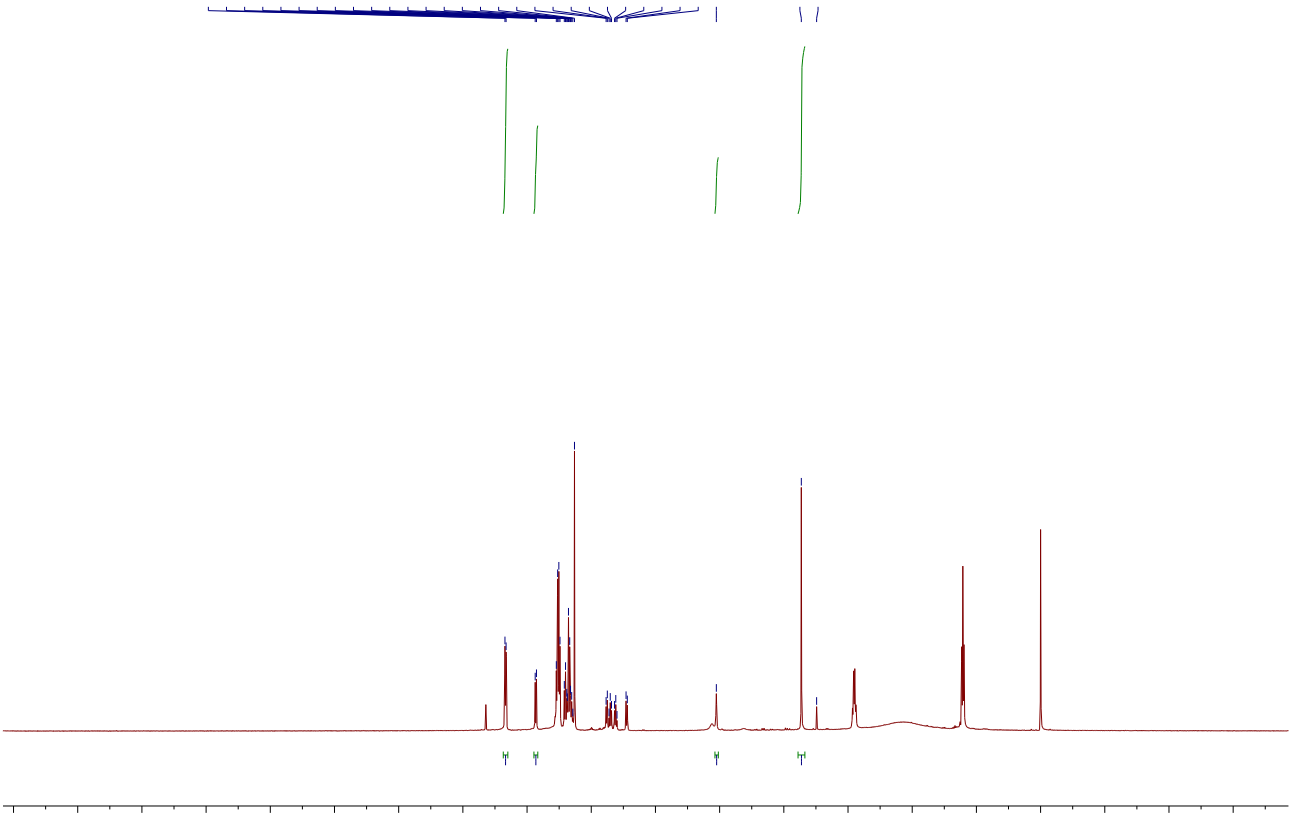


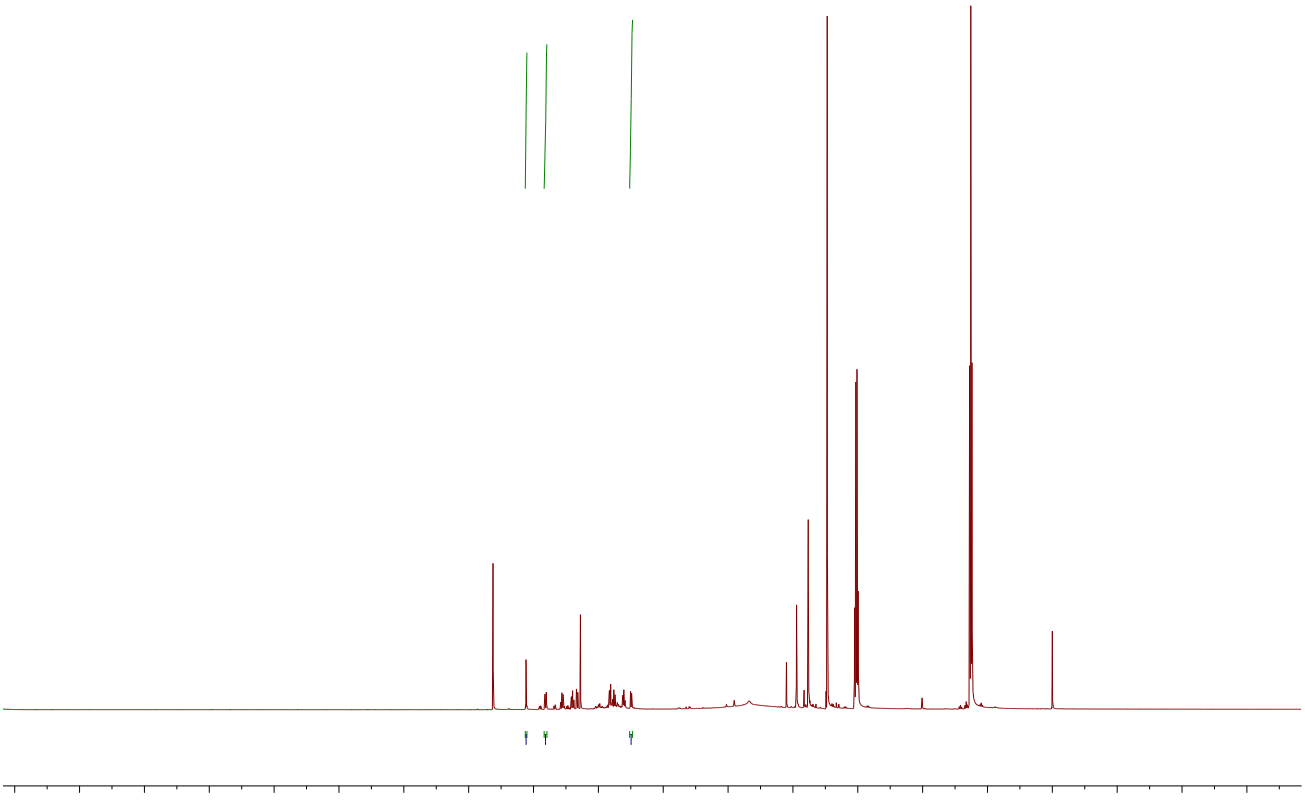


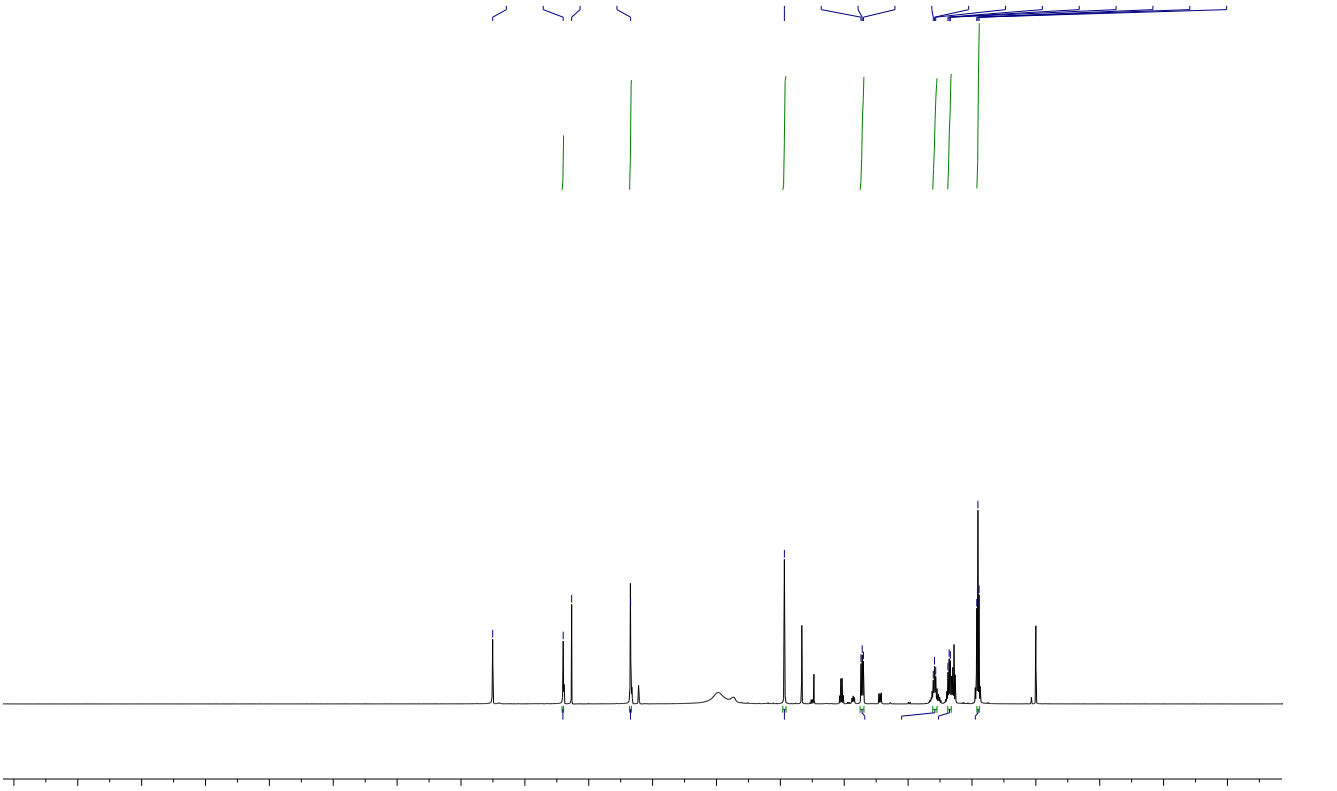


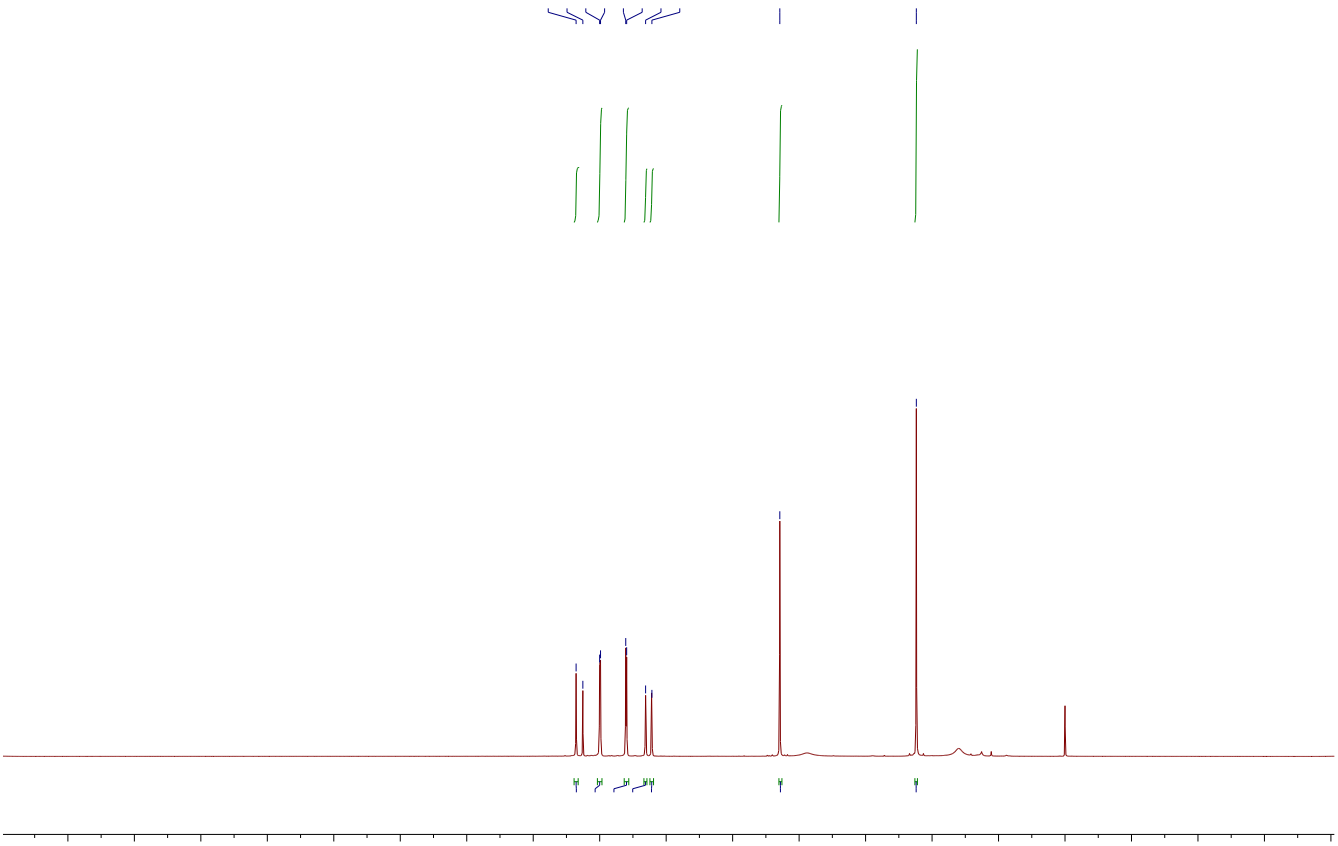


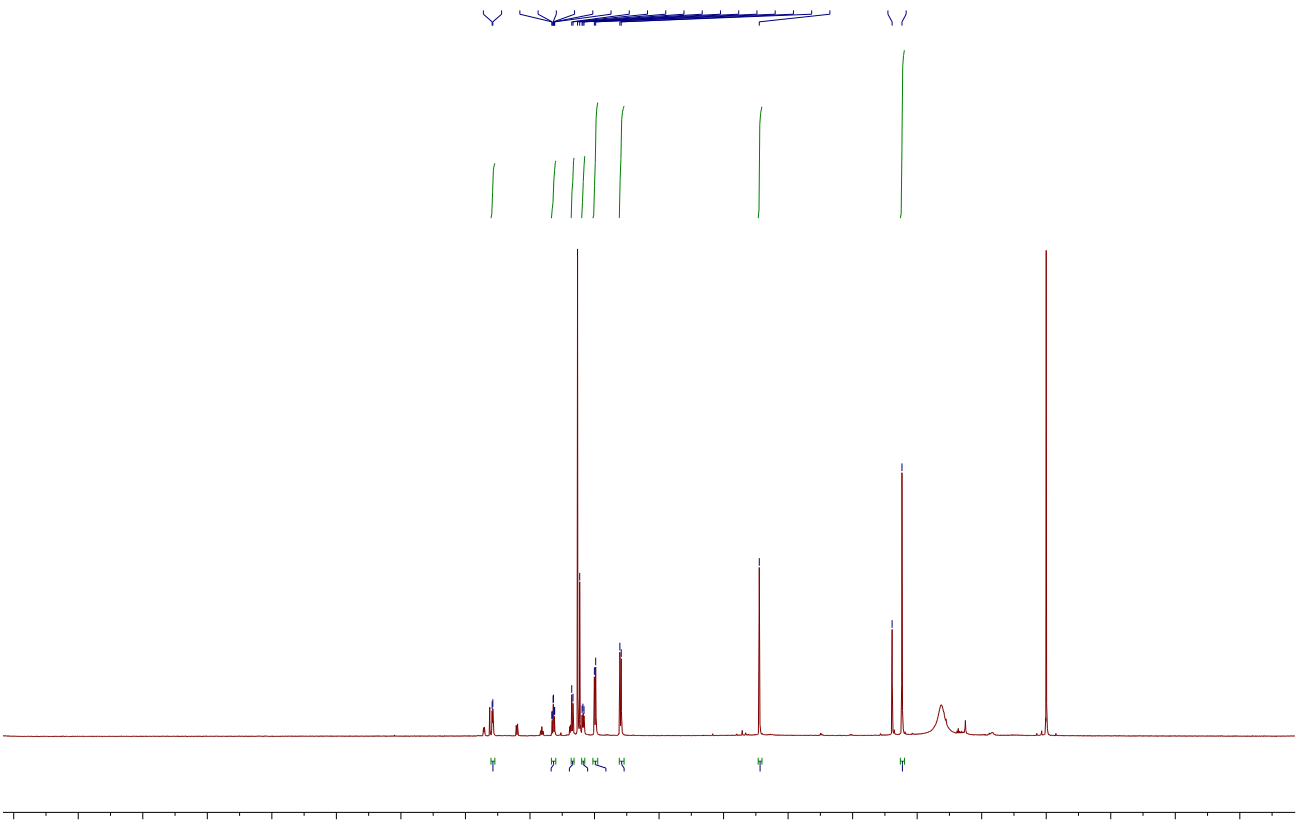


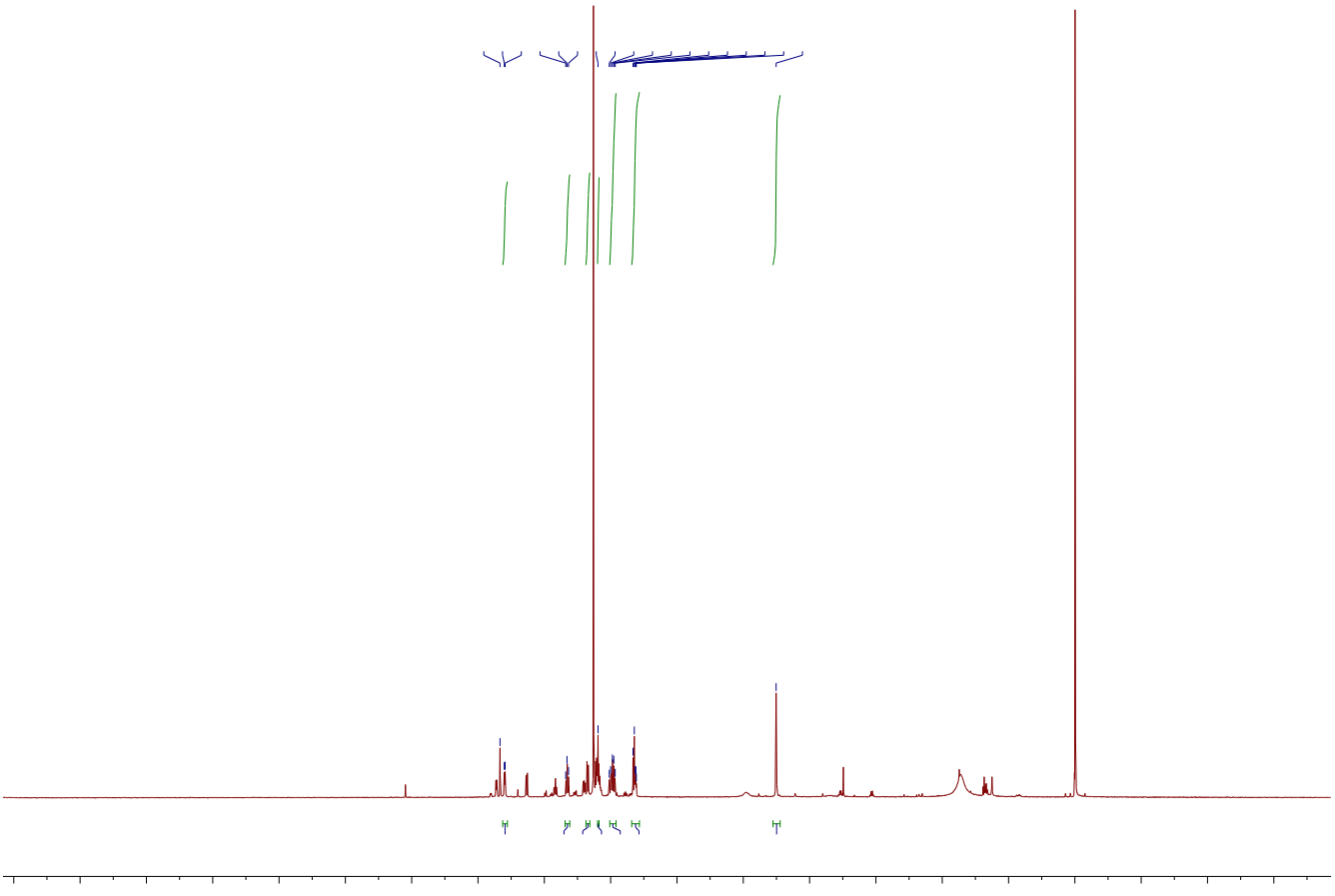


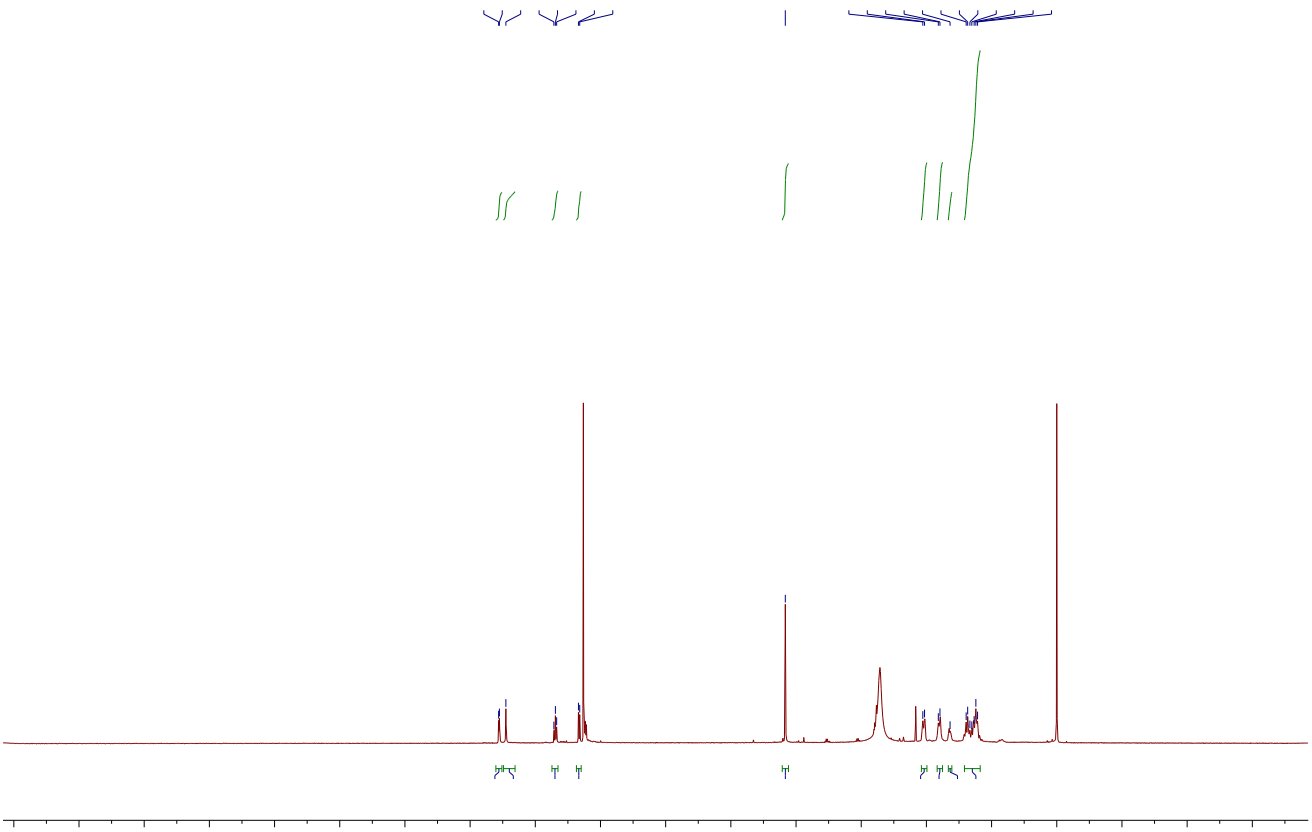


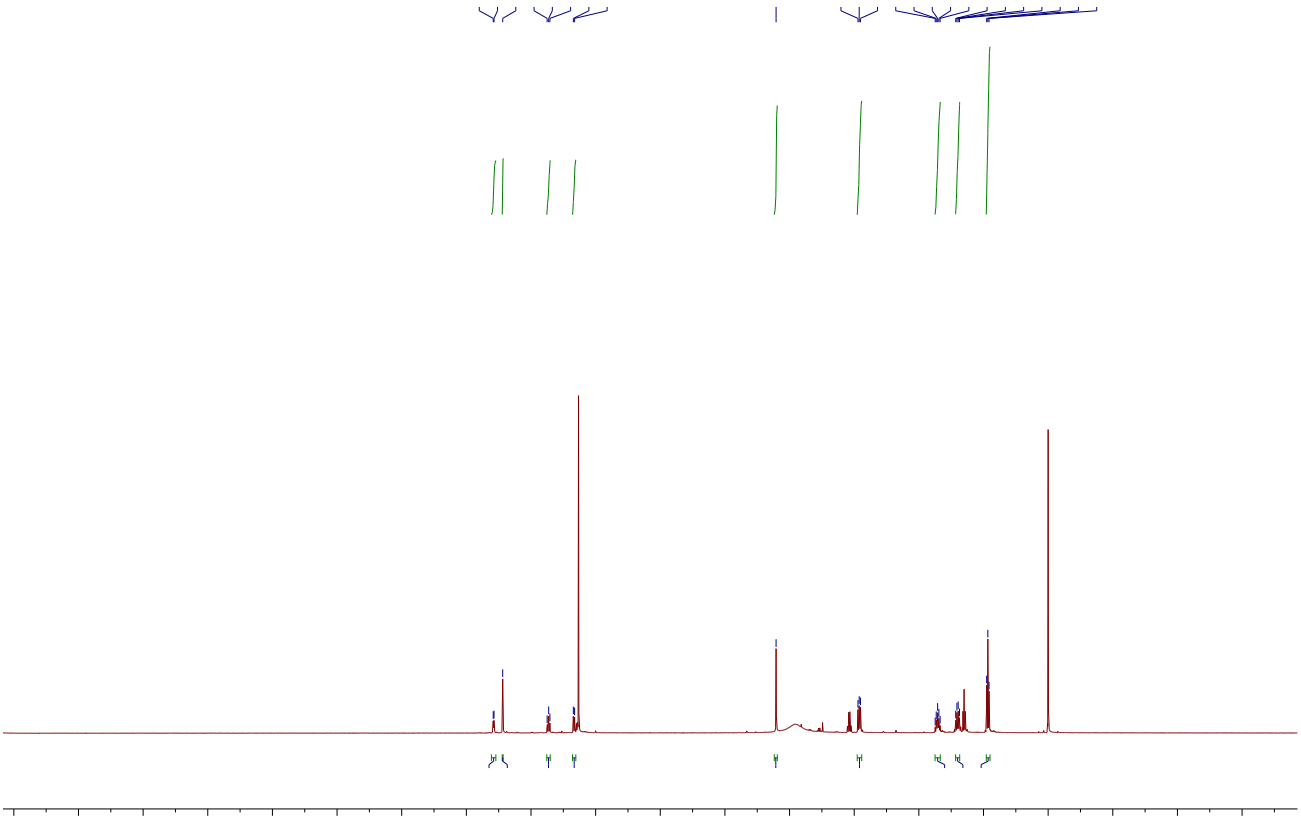


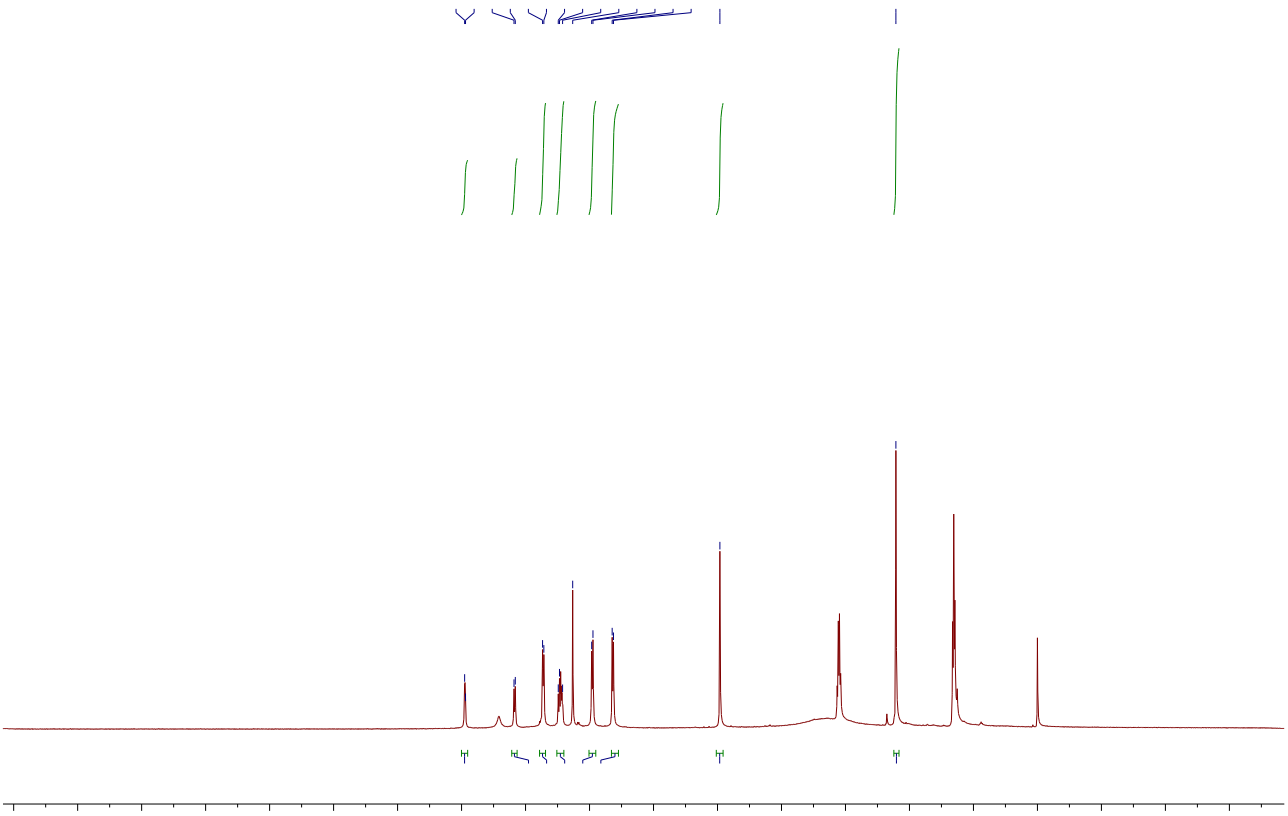


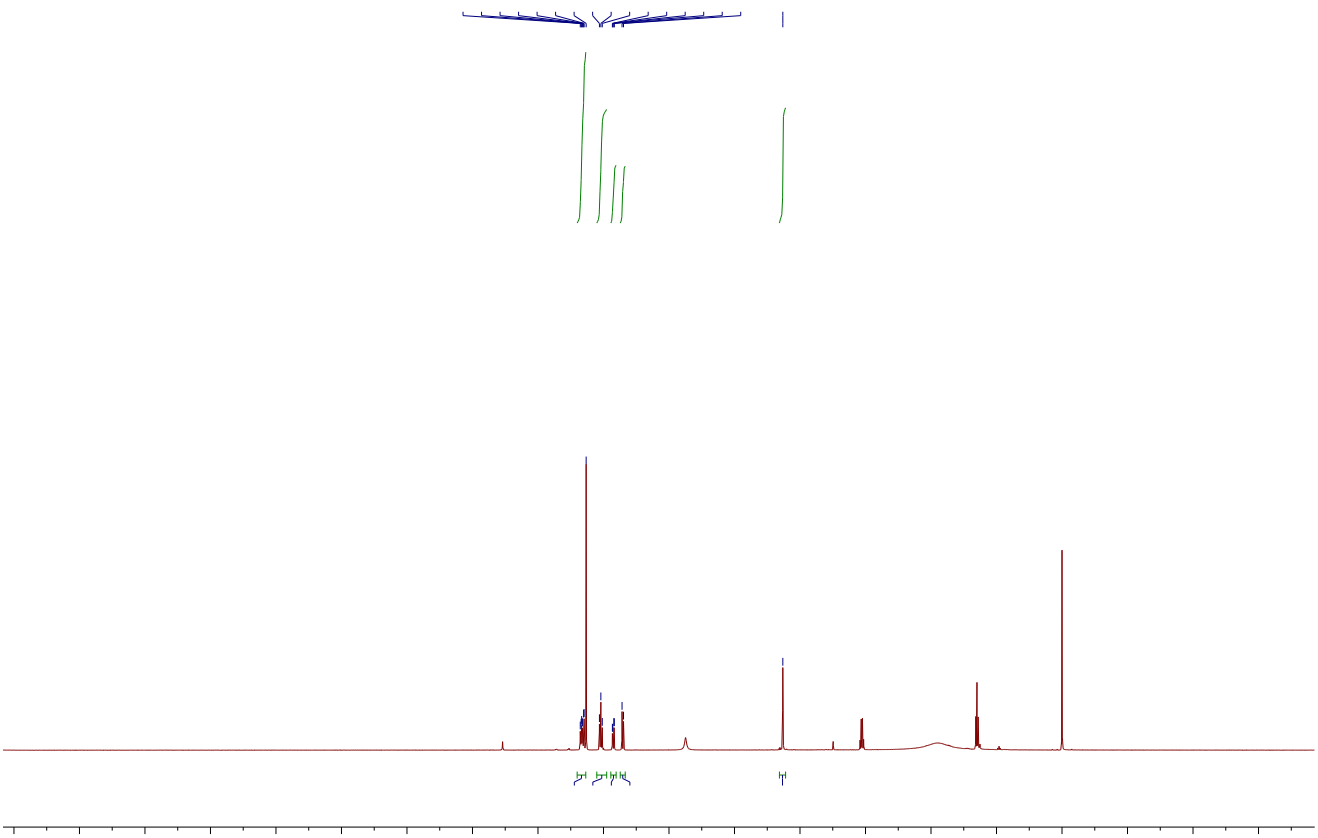












5. References

1. Rizeq. N, Georgiades. S. N, Eur. *J. Org. Chem*. **2016,** 122-131
2. Liao. L. Y, Kong. X. R, Duan. *X. F, J. Org. Chem.* **2013,** 777-782.
3. Harnying. W, Berkessel. A, *Chem. Eur. J.* **2015**, 6057-6061..
4. Rombouts. J. A, Ravensbergen. J, Frese. R. N, Kennis. J. T. M, Ehlers. A. W, Slootweg. J. C, Ruijter. E, Lammertsma, *Chem. Eur. J.* **2014,** 10285-10291.
5. Tomohito. I, Eiji. T, Hajime. I, Eietsu. H, *Tetrahedron Lett.* **2013**, 6874-6877.
6. Vlaar. T, Cioc. R. C, Mampuys. P, *Angew. Chem. Int. Ed.* **2012**, 13058-13061.