Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Unification of Ullman and Kharasch Coupling: Acid promoted CuI catalysed C-N coupling protocols under Ligand, Base and Solvent free conditions

Charu Sharma, Avinash K. Srivastava, Deepak Sharma, Raj K. Joshi*

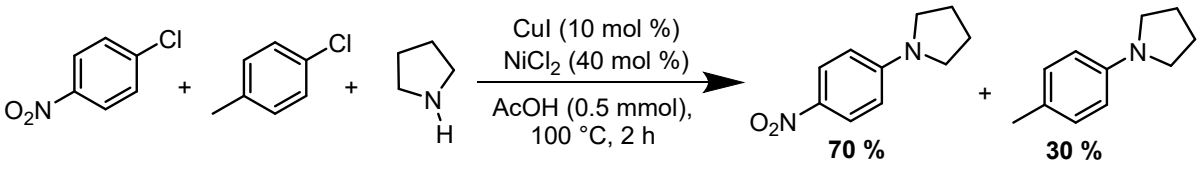
Department of Chemistry, Malaviya National Institute of Technology, Jaipur - 302017, Rajasthan, INDIA, E-mail: rkjoshi.chy@mnit.ac.in

Experimental Details: The ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra were recorded using JEOL ECS-400 spectrometer (operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C). High-Resolution Electron Impact Mass Spectra (HR-EIMS) were obtained with Xevo G2-S Q-Tof (Waters, USA).

Chemicals and reagents: Reactants, reagents, chemicals and solvents available commercially within the country were used.

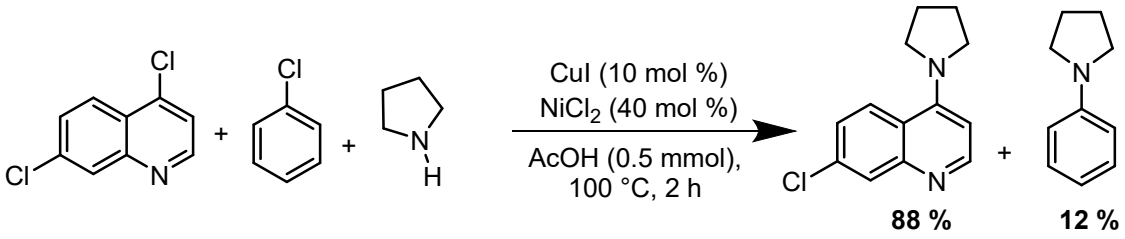
Control Experiments

In order to get a sequence of reactivity towards various amines and halides a series of intermolecular competitive experiments were performed. The very first reaction in this sequence was between p-nitrochlorobenzene and p-methylchlorobenzene and pyrrolidine, which demonstrates a strong preference for the electron withdrawing functionality (Scheme S1).



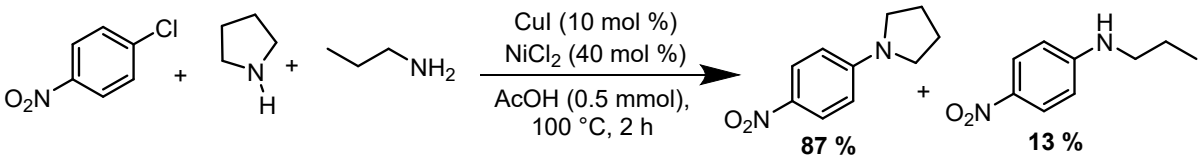
Scheme S1. Selectivity with donating/withdrawing arylchlorides.

After that we check the reactivity of aryl chloride & heterocyclic chloride with pyrrolodine and found that reaction is completely favorable towards heterocyclic chloride (Scheme S2).

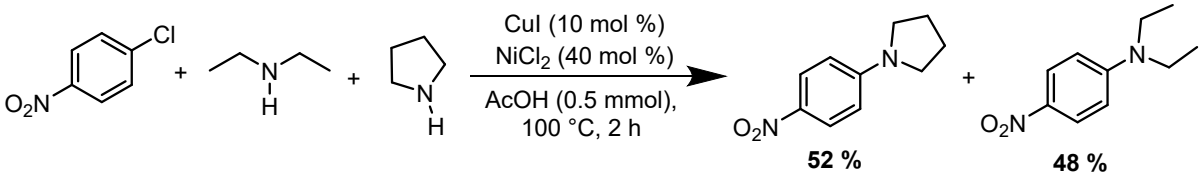


Scheme S2. Selectivity with aryl/heterochlorides.

Another reaction of pyrrolidine & propylamine with 4-nitro chlorobenzene shows the utmost selectivity of the reaction toward pyrrolidine, while the competitive reaction between pyrrolidine & diethylamine transformed comparable yield, with both pyrrolidine & diethylamine as products (Scheme S3 and S4)

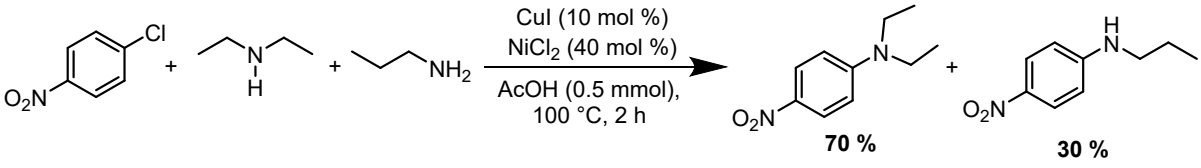


Scheme S3. Selectivity with pyrrolidine or propylamine



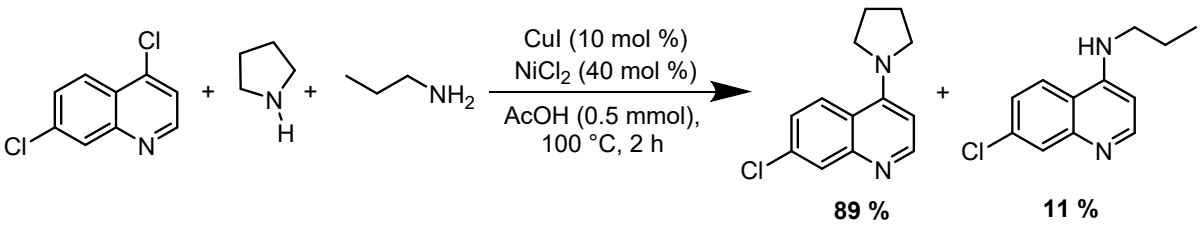
Scheme S4. Selectivity with pyrrolidine or diethyl amine

Among Diethylamine and propylamine, good selectivity was obtained with diethyl amine (Scheme S5)

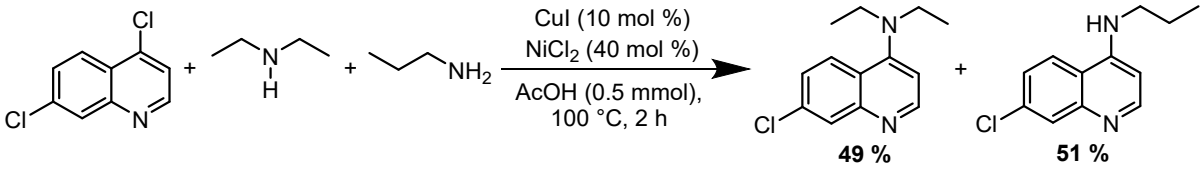


Scheme S5. Selectivity with propyl amine or diethyl amine

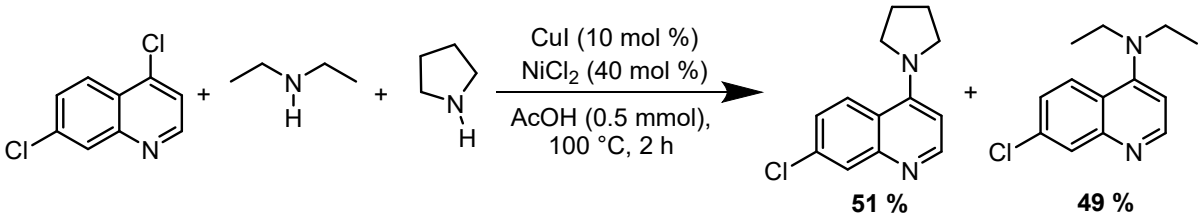
After aryl chloride we also checked the order of reactivity of amines towards heterocyclic halides and we found same pattern of reactivity as in case of aryl chloride. (Scheme S6-S8)



Scheme S6. Selectivity with pyrrolidine or propylamine

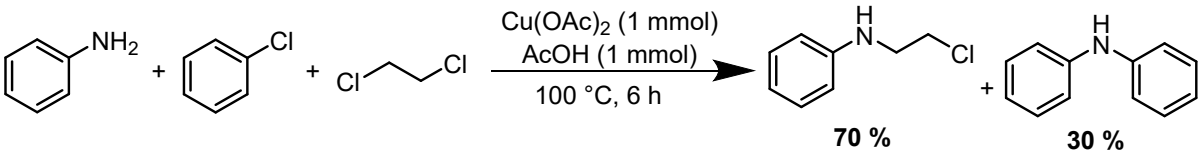


Scheme S7. Selectivity with pyrrolidine or propylamine



Scheme S8. Selectivity with pyrrolidine or Diethylamine

At last we also performed a competitive experiment between aliphatic chloride and aryl chloride with aniline and found that reaction was more favorable towards aliphatic halide. (Scheme S9)



Scheme S9. Selectivity with aliphatic and aryl chloride

Experimental

Kinetic Study

For the kinetic study experiments, the reaction of pyrolidine and 4-chloronitrobenzene was performed by taking an equimolar ratio with varying catalyst loading from 10 to 30 mol% and keeping other parameters constant. Various batch reactions were analyzed by stopping the reaction at different time intervals of 30, 60, 90, 120, and 150 minutes and transferring the

reaction mixture to ethyl acetate. The product was collected and purified after column chromatography, and yield was noted by simply weighing.

Catalyst loading (mol%)	First order rate constant (k)	Correlation Coefficient (R^2)
10	0.0037	0.992
15	0.0084	0.994
20	0.0113	0.990
25	0.0116	0.980
30	0.0118	0.983

Table S1: First order rate constant with respect to catalyst loading.

Plausible Mechanism

Catalysis initiated with the oxidative addition of aryl halide and CuI to produce a ArXCuI intermediate. This intermediate undergo ligand exchange with acetic acid to form another intermediate with maintaining Cu(III) state. Intermediate 3 interacted with amine and formed intermediate 4 by eliminating or regenerating the AcOH in the reaction. Finally, aryl/alkyl amine reductively eliminate from intermediate 4 with bringing the CuX back into the system.

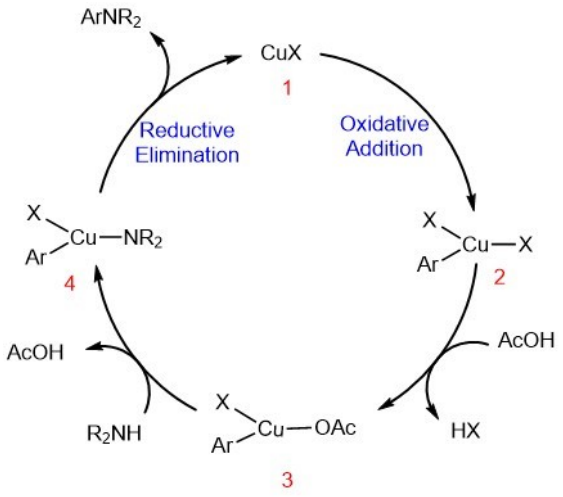


Figure 1. Plausible mechanism for CuI and AcOH catalysed C-N coupling reaction

Here, aryl halide undergo oxidative addition reaction with CuI to form intermediate 2, simultaneously, the $NiCl_2$ interact with acetic acid and form an activated ArNH-Ni(OAc). This activated intermediate react with ArXCuI and undergoes transmetalation reaction via the formation of intermediate 3. Might be this exchange improves the accessibility of the activated reactants and thereby reduced the time of reaction and also improve the yield of coupling product.

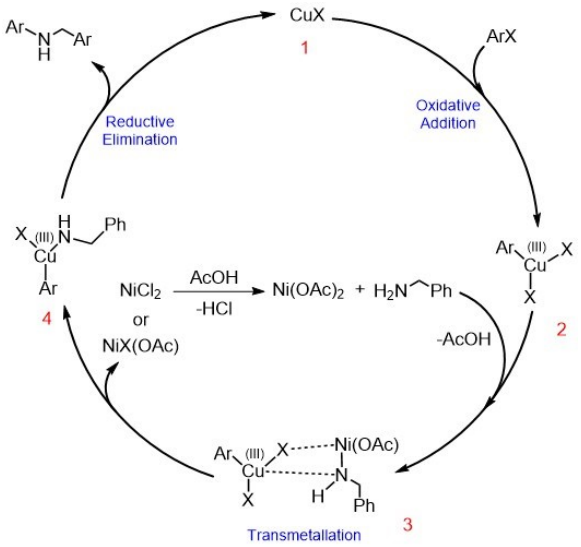


Figure S2. Plausible mechanism showing coupling in presence of CuI, $NiCl_2$ and AcOH

Here, the $Cu(OAc)_2$ first disproportionate into Cu(OAc) and $(Cu(OAc)_3$, the reaction was further proceed by the formation of activated ArNHCu complex by the interaction of $ArNH_2$ and Cu(OAc), this complex undergo the oxidative addition with aryl halide to form ArNHCu(Ar)(X) intermediate. Finally, the intermediate reductively eliminate the desired CN coupling product and regenerate the CuX in the system.

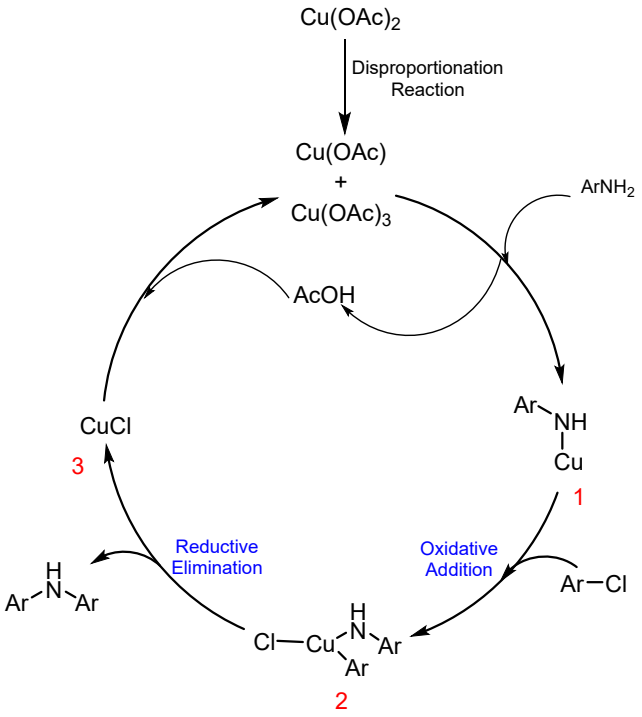
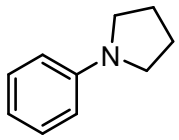
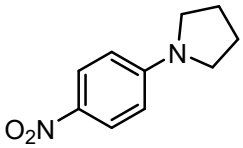
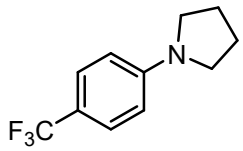
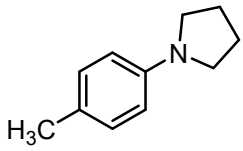
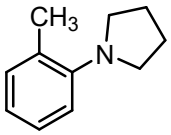
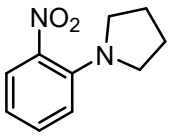
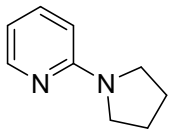
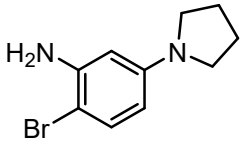
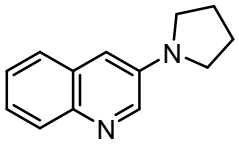
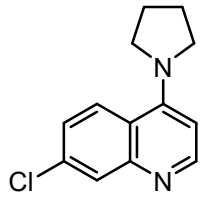
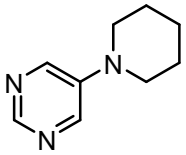
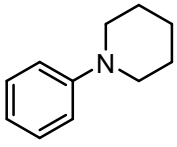


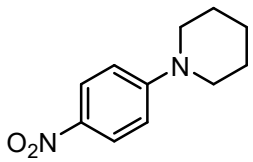
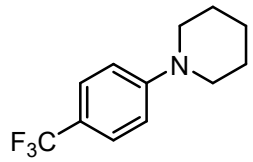
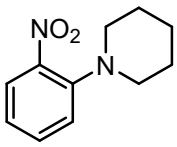
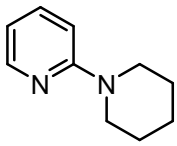
Figure S3. Plausible mechanism for coupling of anilines

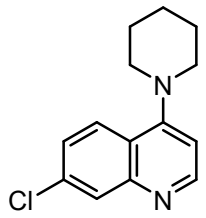
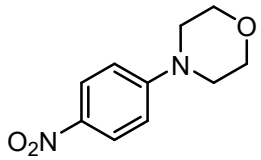
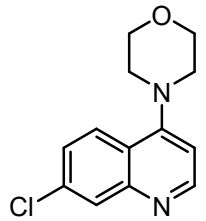
Characterisation Data

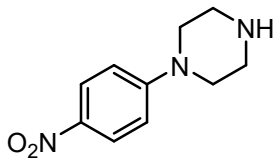
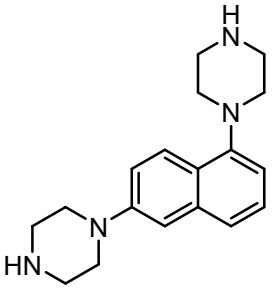
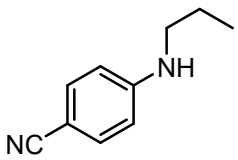
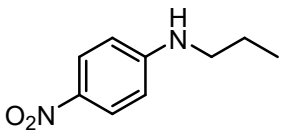
1.		**1-phenyl pyrrolidine[1]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.24-7.21 (m, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J*=8.0 Hz, 2H), 3.28-3.24 (m, 4H), 1.99-1.95 (m, 4H) **13C NMR (101 MHz, $CDCl_3$) δ** 148.07, 129.23, 115.43, 111.72, 47.65, 25.57.
2.		**1-(4-nitro phenyl) pyrrolidine[2]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.08 (dd, *J* = 9.4, 1.1 Hz, 2H), 6.43 (dd, *J* = 9.3, 1.1 Hz, 2H), 3.40 – 3.33 (m, 4H), 2.05-2.02 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 151.77, 136.47, 126.31, 110.35, 47.85, 25.38
3.		**1-[(4-triflouro methyl) phenyl] pyrrolidine[3]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.43 – 7.29 (m, 2H), 6.48 (dd, *J* = 8.8, 1.9 Hz, 2H), 3.42-3.08 (m, 4H), 2.02 – 1.88 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 149.80, 126.808, 126.45 (q, *J* = 3.8 Hz), 125.47 (q, *J* = 268.6 Hz), 116.67 (q, *J* = 32.4 Hz) 110.88, 47.56, 25.54 **19F NMR (400 MHz, $CDCl_3$)** δ -61.00
4.		**1-(4-methyl phenyl) pyrrolidine[1]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.41 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.33 (q, *J* = 4.4 Hz, 4H), 2.63 (s, 3H), 2.38-2.34 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 144.58, 128.11, 122.93, 110.28, 46.32, 23.88, 18.76

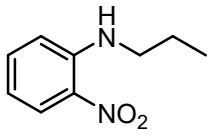
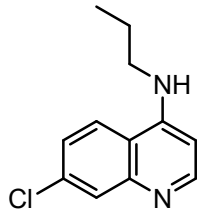
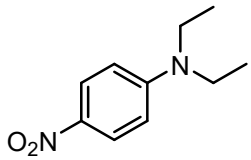
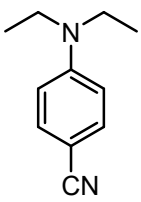
5.		**1-(2-methyl phenyl) pyrrolidine[1]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.34 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 5.2 Hz, 2H), 3.52-3.49 (m, 4H), 2.55 (s, 1H), 2.24 – 2.00 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 147.79, 138.52, 128.73, 116.08, 112.10, 108.62, 47.32, 25.17, 21.59
6.		**1-(2-nitro phenyl) pyrrolidine[4]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.75-7.72 (m, 1H), 7.38-7.34 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 3.22 – 3.19 (m, 4H), 2.00-1.96 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 142.92, 137.20, 133.14, 126.89, 116.05, 115.61, 50.53, 25.89
7.		**2-(pyrrolidin-1-yl) pyridine[3]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.02-8.00 (m, 1H), 7.34-7.22 (m, 1H), 6.36-6.32 (m, 1H), 6.18-6.15 (m, 1H), 3.38 – 3.25 (m, 4H), 1.85-1.79 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 157.25, 148.11, 136.83, 110.98, 106.45, 46.57, 25.51
8.		**2-bromo-5-(pyrrolidin-1-yl) aniline** **1H NMR (400 MHz, $CDCl_3$) δ** 6.95-6.91 (d, 1H), 5.98-5.94 (d, 1H), 5.84-5.83 (s, 1H), 3.21-3.13 (m, 4H), 3.00 (s, 2H), 1.93-1.85 (m, 4H) **13C NMR (101 MHz, $CDCl_3$) δ** 149.62, 147.88, 130.48, 103.82, 103.58, 99.13, 48.12, 25.57 **HRMS (CH_3CN) $[M + H]^+$ (m/z)** Calc. Value: 240.0262, observed: 240.0263

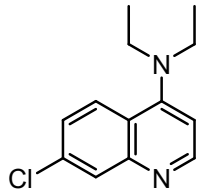
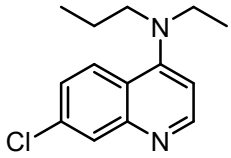
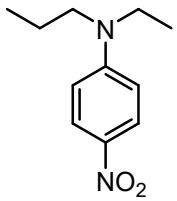
9.		**3-(pyrrolidin-1-yl) quinoline[5]** **1H NMR (400 MHz, $CDCl_3$) δ** δ 8.45 (d, *J* = 2.8 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.54-7.52 (m, 1H), 7.34 – 7.28 (m, 2H), 6.87 (d, *J* = 2.8 Hz, 1H), 3.35-3.32 (m, 4H), 2.00-1.97 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 141.93, 141.43, 143.04, 129.34, 127.35, 126.32, 124.86, 111.55, 48.15, 25.97
10.		**7-chloro-4-(pyrrolidin-1-yl) quinoline[6]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.39 (s, 1H), 8.09-8.05 (m, 1H), 7.89-7.85 (m, 1H), 7.21-7.17 (m, 2H), 6.36-6.34 (m, 1H), 3.62-3.59 (m, 4H), 2.00-1.98 (m, 4H) (**13C NMR (101 MHz, $CDCl_3$) δ** 151.45, 149.99, 149.88, 133.87, 127.40, 126.54, 122.60, 101.90, 51.20, 25.00
11.		**5-(piperidin-1-yl) pyrimidine[7]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.00 (s, 2H), 3.32 – 3.26 (m, 4H), 2.06 – 1.94 (m, 4H), 1.77 (dd, *J* = 6.7, 1.1 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 160.77, 145.59, 138.61, 47.26, 46.27, 24.65
12.		**1-phenylpiperidine[7]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.24-7.20 (m, 2H), 6.93-6.90 (m, 2H), 6.81-6.77 (m, 1H), 3.12 (t, *J* = 5.6 Hz, 4H), 1.71-1.65 (m, 4H), 1.57-1.52 (m, 2H) **13C NMR (101 MHz, $CDCl_3$) δ** 152.34, 129.09, 119.31, 116.66, 50.79, 25.94, 24.38

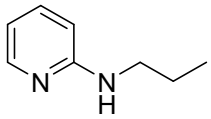
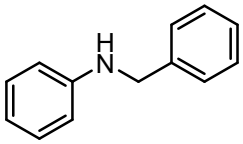
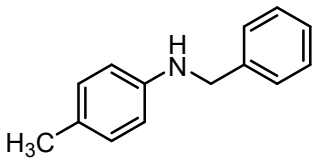
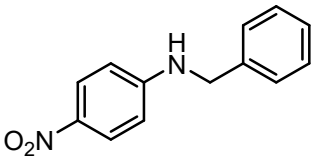
13.		**1-(4-nitro phenyl) piperidine[4]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.11 (d, *J* = 9.5 Hz, 2H), 6.80 (d, *J* = 9.5 Hz, 2H), 3.47-3.44 (m, 4H), 1.76 – 1.66 (m, 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 154.45, 137.27, 126.02, 112.16, 48.24, 25.14, 24.10
14.		**1-[(4-triflouro methyl)phenyl]piperidine[9]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.41 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.26 – 3.19 (m, 4H), 1.65 (dd, *J* = 7.1, 3.7 Hz, 4H), 1.62 – 1.53 (m, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 153.79, 126.33 (q, *J*= 3.7 Hz), 124.67, (q, *J*= 261.1 Hz), 119.52 (q, *J* = 32.5 Hz), 114.58, 49.31, 25.42, 24.28. **19F NMR (400 MHz, $CDCl_3$)** δ -61.45
15.		**1-(2-nitro phenyl) piperidine[8]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.75 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.99 – 6.92 (m, 1H), 3.06 – 2.98 (m, 4H), 1.75-1.70 (m, 4H), 1.61 (q, J = 5.8 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 146.74, 142.31, 133.13, 125.70, 120.58, 120.30, 52.64, 25.67, 23.74
16.		**2-(piperidin-1-yl) pyridine[3]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.15 (d, *J* = 5.2 Hz, 1H), 7.45-7.41 (m, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 6.58 – 6.50 (m, 1H), 3.52 – 3.49 (m, 4H), 1.64-1.62 (m, 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 159.76, 147.92, 137.48, 112.48, 107.27, 46.44, 25.60, 24.80

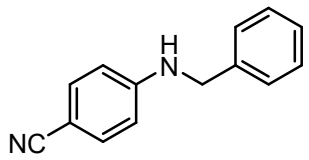
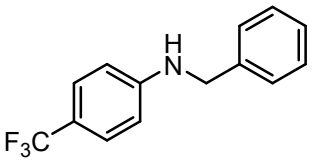
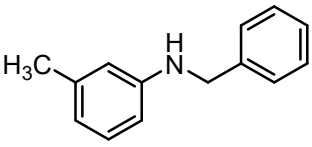
17.		**7-chloro-4-(piperidin-1-yl) quinoline[10]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.95 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.34-7.31 (m, 1H), 6.72 (d, *J* = 5.2 Hz, 1H), 3.10 (t, *J* = 5.2 Hz, 4H), 1.80-1.74 (m, 4H), 1.66 – 1.60 (m, 2H). **13C NMR (101 MHz, $CDCl_3$)** 157.82, 151.29, 149,57, 134.49, 128.18, 125.54, 125.18, 121.74, 108.40, 53.28, 25.69, 24.02
18.		**4-(4-nitrophenyl) morpholine[11a]** **^{1}H NMR (400MHz, $CDCl_3$) δ** 8.11 (dd, *J* = 7.2, 2 Hz, 2H), 6.81 (dd, J = 7.2, 1.6 Hz, 2H), 3.83 (t, *J* = 4.8 Hz, 4H), 3.36-3.33 (m, 4H) **^{13}C NMR (100MHz, $CDCl_3$) δ** 154.71, 138.82, 125.64, 112.45, 66.10, 46.92
19.		**4-(7-chloroquinolin-4-yl) morpholine[10]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.67 (s, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 11.2 Hz, 1H), 6.80 (d, *J* = 4.8 Hz, 1H), 3.92 (t, *J* = 4.4 Hz, 4H), 3.18 (t, *J* = 4.4 Hz, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 157.22, 151.64, 149.82, 135.50, 128.77, 126.64, 125.20, 121.78, 108.94, 66.95, 52.77

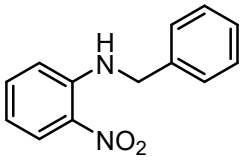
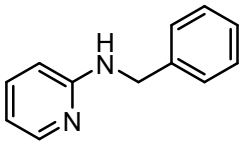
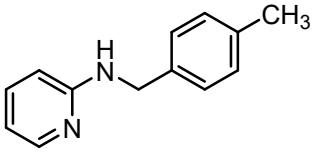
20.		**1-(4-nitrophenyl) piperazine[12]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.59 (d, *J* = 9.2 Hz, 2H), 7.28 (d, *J* = 9.2 Hz, 2H), 3.98-3.84 (m, 4H), 3.51 – 3.49 (m, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 154.61, 137.82, 125.37, 112.03, 50.32, 47.50, 46.45, 45.07
21.		**1,1'-(naphthalene-1,6-diyl)dipiperazine** **1H NMR (400 MHz, $CDCl_3$) δ** 8.80 (s, 2H), 8.06 (s, 1H), 7.96 – 7.92 (m, 1H), 7.44 – 7.41 (m, 2H), 6.84 (s, 1H), 3.86 (t, *J* = 5.2 Hz, 2H), 3.74-3.71 (m, 2H), 3.20-3.14 (m, 6H), 2.15-2.11 (m, 6H) , 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 169.44, 156.70, 135.44, 128.75, 126.83, 124.94, 52.30, 52.08, 46.31, 41.44 , 21.49
22.		**4-(propylamino)benzonitrile[11a]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.90-7.87 (m, 2H), 7.57-7.54 (m, 2H), 6.57 (s, 1H), 3.60-3.55 (m, 2H), 1.85-1.76 (m, 2H), 1.15 (t, *J* = 7.2, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 166.48, 137.39, 133.08, 128.65, 128.24, 41.76, 22.77, 11.35
23.		**4-nitro-N-propylaniline[8]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.01 (dd, *J* = 7.6, 2 Hz, 2H), 6.45 (d, *J* = 6.0 Hz, 2H), 4.44 (s, 1H), 3.13 – 3.09 (m, 2H), 1.62 (q, *J* = 14.4 Hz, 2H), 0.954 (t, J = 7.6 Hz, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 152.76, 137.11, 125.81, 110.23, 44.47, 21.69, 10.81

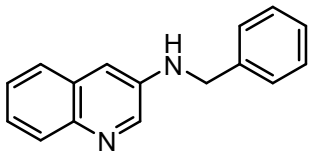
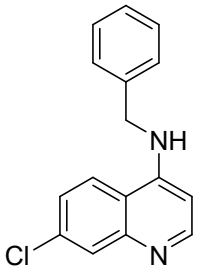
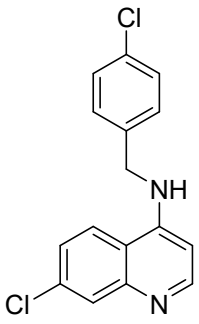
24.		**2-nitro-N-propylaniline[8]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.16-8.13 (m, 1H), 8.06 (s, 1H), 7.43-7.39 (m, 1H), 6.83 (dd, *J* = 8.7, 1.3 Hz, 1H), 6.63-6.59 (m, 1H), 3.28-3.23 (m, 2H), 1.75 (q, J = 7.6 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). **13C NMR (101 MHz, $CDCl_3$)** δ 145.76, 136.29, 127.00, 115.13, 113.88, 44.85, 22.32, 11.68
25.		**7-chloro-N-propylquinolin-4-amine[11b]** **1H NMR (400 MHz, $CDCl_3$)** δ 8.52 (s, 1H), 8.01 (s, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.39 (d, 10.8 Hz, 1H), 6.46 (d, *J* = 5.3 Hz, 1H), 3.38-3.33 (m, 2H), 1.89-1.82 (m, 2H), 1.15-1.11 (m, 3H). **13C NMR (101 MHz, $CDCl_3$)** 156.37, 150.78, 150.13, 135.02, 128.32, 125.86, 125.69, 122.77, 110.06, 47.88, 20.20, 11.66.
26.		**N, N-diethyl-4-nitroaniline[8]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.11 (dd, J = 7.2, 1.6 Hz, 2H), 6.58 (dd, J = 7.2, 1.6 Hz, 2H), 3.46 (q, *J* = 14.4 Hz, 4H), 1.23 (t, *J* = 7.2 Hz, 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 151.79, 135.85, 126.12, 109.40, 44.55, 12.00
27.		**4-(diethylamino)benzonitrile[13]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.37 – 7.34 (m, 2H), 7.31 – 7.28 (m, 2H), 3.37 (d, *J* = 116.8 Hz, 4H), 1.23 – 1.09 (m, 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 170.32, 135.68, 135.23, 128.78, 127.92, 43.41, 39.47, 14.31, 12.95

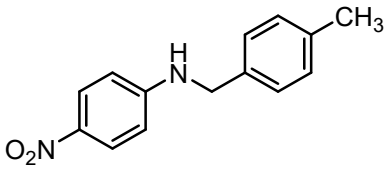
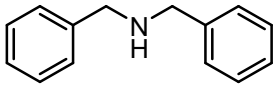
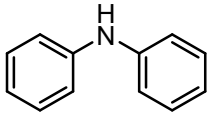
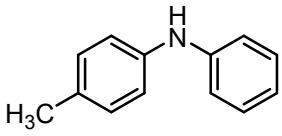
28.		**7-chloro-N, N-diethylquinolin-4-amine** **1H NMR (400 MHz, $CDCl_3$) δ** 8.56 (s, 1H), 7.94 (t, J = 2.4 Hz, 1H), 7.91-7.87 (m, 1H), 7.31-7.29 (m, 1H), 6.74-6.72 (m, 1H), 3.31-3.25 (m, 4H), 1.19-1.06 (m, 6H). **13C NMR (101 MHz, $CDCl_3$) δ** 155.97, 151.09, 150.37, 134.73, 128.50, 125.77, 125.55, 122.89, 110.22, 46.48, 12.12 **HRMS (CH_3CN) $[M + H]^+$ (m/z)** Calc. Value: 235.0997, observed: 235.0994
29.		**N-ethyl-N-propylquinolin-4-amine** **1H NMR (400 MHz, $CDCl_3$) δ** 8.56 (s, 1H), 7.97 (d, *J* = 2.4 Hz, 1H), 7.90 (dd, *J* = 9.0, 1.2 Hz, 1H), 7.33-7.30 (m, 1H), 6.74 (dd, *J* = 5.6, 1.2 Hz, 1H), 3.35-3.29 (m, 2H), 3.21-3.17 (m, 2H), 1.60-1.50 (m, 2H), 1.12-1.08 (m, 3H), 0.85-0.81 (m, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 155.71, 150.12, 149.47, 134.37, 127.66, 125.00, 125.03, 122.11, 109.40, 52.84, 47.22, 19.55, 11.62, 11.00. **HRMS (CH_3CN) $[M + H]^+$ (m/z)** Calc. Value: 249.1153, observed: 249.1155
30.		**N-ethyl-4-nitro-N-propylaniline** **1H NMR (400 MHz, $CDCl_3$ δ** 8.08 (dd, *J* = 7.6, 2.0 Hz, 2H), 6.55 (dd, *J* = 2.4 Hz, 2H), 3.45 (q, *J* = 14.4 Hz, 2H), 3.34 – 3.29 (m, 2H), 1.70 – 1.64 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.96 (t, J = 7.6 Hz, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 126.56, 109.98, 52.47, 45.61, 20.64, 12.25, 11.43

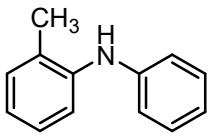
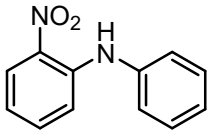
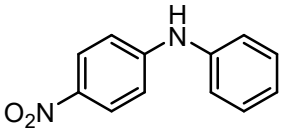
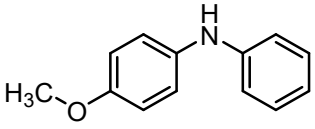
31.		**N-propylpyridin-2-amine**[14] **1H NMR (400MHz, $CDCl_3$) δ** 8.06 (d, J = 7.2 Hz, 1H), 7.38-7.38 (m, 1H), 6.54-6.50 (m, 1H), 6.37-6.35 (m, 1H), 5.07 (s, 1H), 3.22 – 3.17 (m, 2H), 1.65-1.58 (m, 2H), 0.99-0.92 (m, 3H). **13C NMR (100MHz, $CDCl_3$) δ** 159.11, 148.04, 137.41, 112.38, 106.38, 44.03, 22.71, 11.59.
32.		**N-benzylaniline**[15] **1H NMR (400 MHz, $CDCl_3$) δ** 7.37 – 7.24 (m, 5H), 7.19 – 7.14 (m, 2H), 6.73-6.69 (m, 1H), 6.63 – 6.61 (m, 2H), 4.31 (s, 2H), 4.00 (s, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 147.97, 139.26, 129.11, 128.28, 127.35, 117.38, 112.66, 48.13
33.		**N-benzyl-4-methylaniline**[16] **1H NMR (400 MHz, $CDCl_3$) δ** 7.49 – 7.39 (m, 3H), 7.39 – 7.28 (m, 2H), 7.08 – 7.00 (m, 2H), 6.65 – 6.57 (m, 2H), 4.34 (s, 2H), 3.79 (s, 1H), 2.30 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 146.05-139.81, 129.92, 128.77,, 127.67, 113.17, 48.76, 20.59
34.		**N-benzyl-4-nitroaniline**[17] **1H NMR (400 MHz, $CDCl_3$) δ** 8.05-8.02 (m, 2H), 7.33 – 7.30 (m, 5H), 6.54 – 6.51 (m, 2H), 4.86 (s, 1H), 4.39 (d, *J* = 5.5 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 151.73, 136.02, 127.64, 126.54, 126.02, 125.10, 110.00, 98.58, 46.30

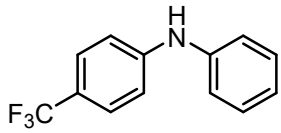
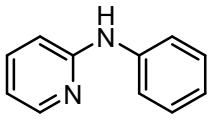
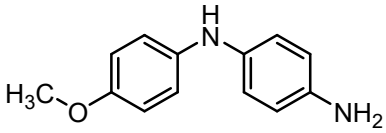
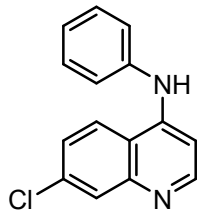
35.		**4-(benzylamino)benzonitrile[17]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.73 – 7.71 (m, 2H), 7.40 – 7.38 (m, 2H), 7.36 – 7.28 (m, 5H), 6.40 (s, 1H), 4.63 (d, *J* = 5.6 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 166.11, 137.74, 137.65, 132.54, 128.70, 128.24, 127.81, 127.60, 44.09
36.		**N-benzyl-4-(trifluoromethyl)aniline[18]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.36 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.59 (d, *J* = 8.6 Hz, 2H), 4.35 (s, 1H), 4.33 (s, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 150.20, 138.19, 127.27, 127.10, 126.36 (q, $J_{C\text{-}F}$ = 3.7 Hz), 126.07, 124.72 (q, $J_{C\text{-}F}$ = 269 Hz) 118.71 (q, $J_{C\text{-}F}$ = 32.5 Hz), 111.70, 47.50 **19F NMR (400 MHz, $CDCl_3$)** δ -60.82
37.		**N-benzyl-3-methylaniline[16]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.14 (d, *J* = 9.2 Hz, 2H), 7.30 – 7.18 (m, 4H), 6.61 (d, *J* = 9.2 Hz, 2H), 4.86 (s, 1H), 4.43 (d, *J* = 5.3 Hz, 2H), 2.41 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 139.72, 139.08, 129.16, 128.66, 127.57, 127.23, 118.53, 113.68, 110.01, 48.30, 21.64.

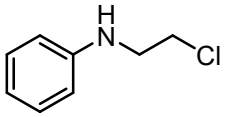
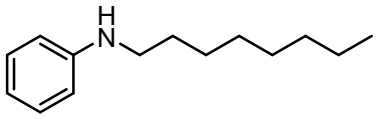
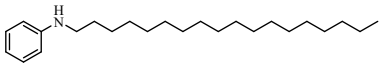
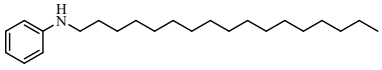
38.		**N-benzyl-2-nitroaniline[17]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.35 (s, 1H), 8.10 (dd, J = 8.5, 1.7 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.26 – 7.15 (m, 2H), 6.72 (d, J = 8.6 Hz, 1H), 6.57 (dd, J = 8.6, 7.0 Hz, 1H), 4.45 (d, J = 5.6 Hz, 2H **13C NMR (101 MHz, $CDCl_3$) δ** 145.22, 137.31, 136.22, 132.17, 128.90, 127.66, 127.00, 126.82, 115.69, 114.17, 47.03
39.		**N-benzylpyridin-2-amine[16]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.08 – 8.02 (m, 1H), 7.40 – 7.26 (m, 5H), 7.26 – 7.19 (m, 1H), 6.56-6.53 (m, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 5.01 (s, 1H), 4.46 (d, *J* = 5.7 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 158.21, 147.78, 138.74, 137.08, 128.22, 126.97, 126.82, 112.73, 106.36, 45.89,
40.		**N-(4-methylbenzyl)pyridin-2-amine[18]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.10 – 8.08 (m, 1H), 7.40 – 7.36 (m, 1H), 7.25 – 7.20 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.58-6.56 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.87 (s, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 2.33 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 158.47, 148.02, 137.26, 136.69, 135.86, 129.12, 127.21, 112.89, 106.55, 45.92, 20.90

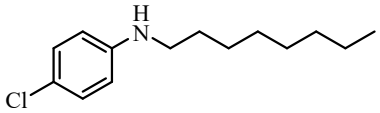
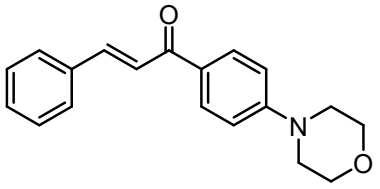
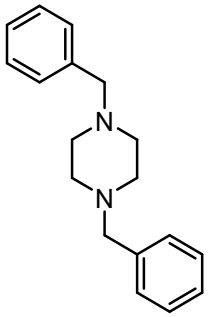
41.		**N-benzylquinolin-3-amine**[19a] **1H NMR (400 MHz, $CDCl_3$) δ** 8.46 (d, *J* = 2.8 Hz, 1H), 7.95-7.92 (m, 1H), 7.57 – 7.54 (m, 1H), 7.41-7.34 (m, 2H), 7.38 – 7.32 (m, 4H), 7.32 – 7.24 (m, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 4.47 (s, 1H), 4.40 (d, *J* = 4.8 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 141.45, 138.03, 131.52, 129.95, 129.44, 128.82,128.37, 127.60, 127.46, 127.10, 126.00, 125.25,124.83, 47.92
42.		**N-benzyl-7-chloroquinolin-4-amine**[19b] **1H NMR (400 MHz, $CDCl_3$) δ** 8.46 (d, *J* = 5.2 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.34 – 7.25 (m, 6H), 6.39 (d, *J* = 5.6 Hz, 1H), 5.28 (s, 1H), 4.46 (d, *J* = 4.8 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 151.03, 148.45, 148.02, 136.14, 133.98, 128.01, 127.87, 126.98, 126.59, 124.52, 119.89, 98.66, 46.58
43.		**7-chloro-N-(4-chlorobenzyl)quinoline-4-amine** **1H NMR (400 MHz, $CDCl_3$) δ** 8.23 (s, 1H), 7.69 (s, 1H), 7.48 – 7.44 (m, 1H), 7.11 – 6.96 (m, 6H), 6.10 (d, *J* = 4.8 Hz, 1H), 5.24 (t, *J* = 5.2 Hz) 1H), 4.22 (d, *J* = 5.2 Hz, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 151.61, 148.93, 135.26, 134.68, 133.32, 128.75, 128.50, 128.36, 125.26, 120.56, 99.41, 46.45 **HRMS (CH_3CN) $[M + H]^+$ (m/z)** Calc. Value: 303.0451, observed: 303.0452

44.		**N-(4-methylbenzyl)-4-nitroaniline** **1H NMR (400 MHz, $CDCl_3$) δ** 8.09 (d, *J* = 9.2 Hz, 2H), 7.25 – 7.18 (m, 4H), 6.57 (d, *J* = 9.2 Hz, 2H), 4.82 (s, 1H), 4.39 (d, *J* = 5.6 Hz, 2H), 2.37 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 152.11, 136.78, 133.34, 128.72, 126.47, 125.50, 121.28, 110.37, 46.54, 20.21 **HRMS (CH_3CN) $[M + H]^+$ (m/z)** Calc. Value: 242.1055, observed: 242.1052
45.		**Dibenzylamine[20]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.26 – 7.20 (m, 4H), 7.18-7.13 (m, 4H), 7.10-7.05 (m, 2H), 4.95 (d, *J* = 2.4 Hz, 1H), 3.40 (d, *J* = 2.4 Hz, 4H). **13C NMR (101 MHz, $CDCl_3$) δ** 139.64, 128.72, 128.20, 126.84, 57.89
46.		**Diphenylamine[13]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.25-7.21 (m, 4H), 7.05 – 7.03 (d, J = 8 Hz, 4H), 6.90 (t, *J* = 7.2 Hz, 2H), 5.66 (s, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 142.73, 128.98, 120.62, 117.42,
47.		**4-methyl-N-phenylaniline[21a]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.17 – 7.13 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.90 (m, 4H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.51 (s, 1H), 2.22 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 142.24, 138.58, 129.22, 128.16, 127.61, 118.59, 117.20, 115.15, 19.00

48.		**2-methyl-N-phenylaniline[21b]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.15 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.84 (m, 4H), 5.34 (s, 1H) 2.22 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 141.71, 138.96, 128.70, 127.07, 126.02, 124.52, 119.73, 118.22, 116.50, 115.20, 15.67
49.		**2-nitro-N-phenylaniline[22]** **1H NMR (400 MHz, $CDCl_3$) δ** 9.50 (s, 1H), 8.21 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.80-6.75 (m, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 143.00, 138.59, 135.60, 129.64, 126.58, 125.57, 124.30, 117.40, 115.93.
50.		**4-nitro-N-phenylaniline[22]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.99 (d, *J* = 9.2 Hz, 2H), 7.26 (t, J = 8 Hz, 2H), 7.09-7.02 (m, 3H), 6.81 (d, J = 8 Hz, 2H), 6.15 (s, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 150.00, 139.67, 139.34, 129.62, 126.11, 124.55, 121.80, 113.55
51.		**4-methoxy-N-phenylaniline[21]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.84 – 7.75 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.99 (s, 1H), 6.96 – 6.88 (m, 1H), 6.86 – 6.72 (m, 4H), 3.72 (s, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 154.95, 144.84, 135.38, 128.99, 121.88, 119.24, 115.30, 114.34, 55.27

52.		**N-phenyl-4-(trifluoromethyl)aniline[21]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.15 – 7.13 (m, 2H), 7.07 – 7.03 (m, 3H), 5.91 (s, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 146.48**,** 140.86, 129.30, 126.44 (q, J_{C-F} = 3.0 Hz), 124.35 (q, J_{C-F} = 269 Hz) 122.67, 121.36 (q, J_{C-F} = 32.6 Hz),119.75, 115.06 **19F NMR (400 MHz, $CDCl_3$)** δ -61.85
53.		**N-phenylpyridin-2-amine[23]** **1H NMR (400 MHz, $CDCl_3$) δ** 8.20 (d, *J* = 4.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.36-7.31 (m, 4H), 7.07-7.03 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.75 – 6.72 (m, 1H), 6.61 (s, 1H). **13C NMR (101 MHz, $CDCl_3$) δ** 155.83, 148.30, 140.30, 137.58, 129.18, 122.71, 120.21, 114.95, 108.09
54.		**N1-(4-methoxyphenyl)benzene-1,4-diamine[24]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.32 (dd, *J* = 6.4, 2.0 Hz, 2H), 6.70 (dd, *J* = 6.8, 2 Hz, 2H), 3.72 (s, 3H), 3.62 (s, 2H) **13C NMR (101 MHz, $CDCl_3$) δ** 168.16, 156.38, 130.85, 121.86, 114.06, 55.40
55.		**7-chloro-N-phenylquinolin-4-amine[6]** **1H NMR (400 MHz, DMSO) δ** 8.57 (s, 1H), 7.99 (s, 1H), 7.38-7.35 (m, 2H), 7.22-7.18 (m, 3H), 6.91-6.87 (m ,2H), 6.48-6.45 (m, 2H)

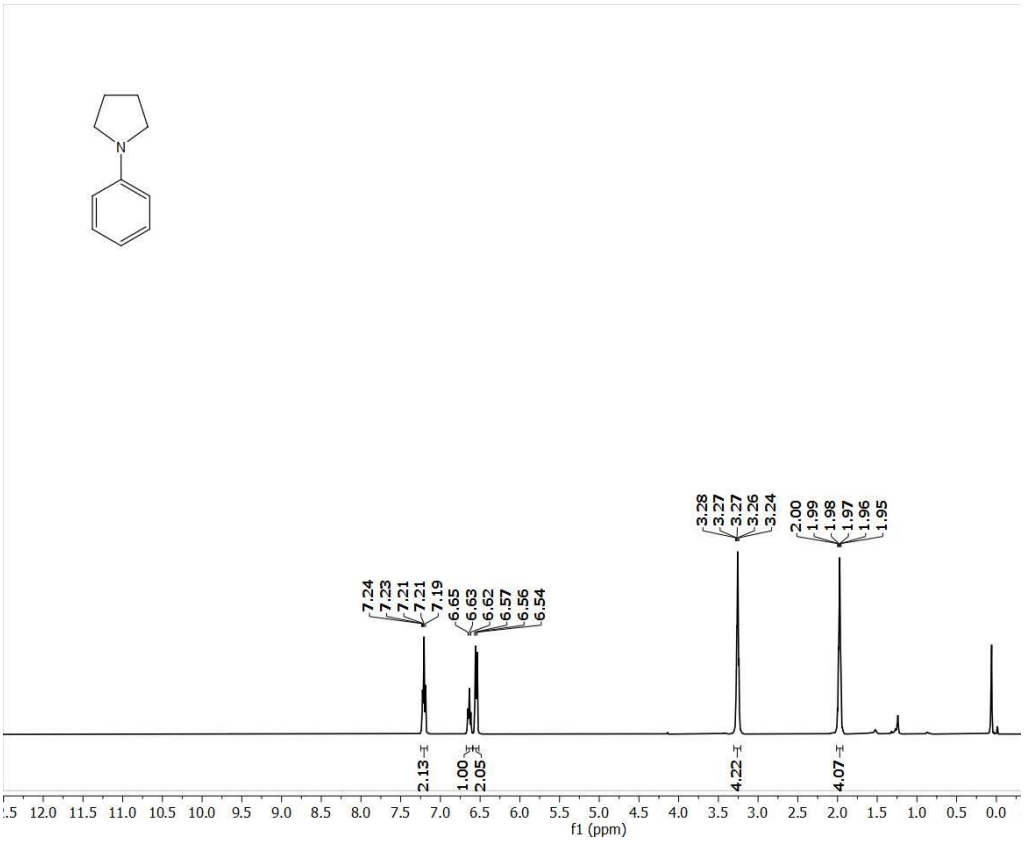
56.		**N-(2-chloroethyl)aniline[25]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.27 – 7.19 (m, 1H), 7.19 – 7.15 (m, 1H), 6.77-6.72 (m, 1H), 6.68 – 6.61 (m, 2H), 4.05 (s, 1H), 3.74 – 3.67 (m, 2H), 3.51-3.48 (m, 2H). **13C NMR (101 MHz, $CDCl_3$) δ** 147.16, 129.52, 118.34, 113.31, 45.51, 43.57
57.		**N-octylaniline[26]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.25-7.17 (m, 2H), 6.73-6.66 (m, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.42 (t, *J* = 7.8 Hz, 2H), 1.39 – 1.31 (m, 8H), 0.92 (t, *J* = 6.5 Hz, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 148.00, 128.69, 128.65, 116.53, 116.49, 112.16, 112.12, 43.49, 43.44, 31.29, 26.69, 26.65, 22.15, 22.12, 13.59, 13.55
58.		**N-octadecylaniline[27]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.19 – 7.12 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.62 – 6.56 (m, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 1.60 (t, *J* = 7.4 Hz, 2H), 1.53 (s, 4H), 1.41 – 1.23 (m, 26H), 0.89 – 0.83 (m, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 129.84, 119.89, 117.17, 113.37, 36.84, 32.54, 30.31, 27.14, 21.62, 14.73
59.		**N-heptadecylaniline[27]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.25-7.24 (d, 2H), 7.20-7.16 (t, 1H), 6.62-6.60 (m, 2H), 6.59-6.57 (s, 1H), 3.24-3.20 (t, 2H), 1.30-1.24 (m, 30H), 0.88-0.85 (t, 3H) **13C NMR (101 MHz, $CDCl_3$) δ** 129..86, 116.66, 116.22, 112.35, 32.62, 30.39, 30.05, 27.91, 23.38, 14.81

60.		**4-chloro-N- octadecylaniline[28]** **1H NMR (400 MHz, $CDCl_3$) δ** 7.09 (dd, *J* = 8.9, 3.9 Hz, 2H), 6.49 (dd, *J* = 8.8, 4.0 Hz, 2H), 3.87 – 3.26 (m, 1H), 3.04 (td, *J* = 7.1, 3.9 Hz, 2H), 1.58 (td, *J* = 7.1, 3.7 Hz, 2H), 1.36 (q, *J* = 7.4, 6.4 Hz, 3H), 1.32 – 1.25 (m, 7H), 0.87 (td, *J* = 6.5, 3.6 Hz, 3H). **13C NMR (101 MHz, $CDCl_3$) δ** 146.50, 128.42, 126.92, 125.00, 120.94, 113.11, 43.53, 31.24, 30.85, 29.77, 29.61, 29.28, 29.13, 28.85, 28.82, 28.67, 28.02, 26.56, 25.34, 22.08, 13.52
61.		**(E)-1-(4-morpholinophenyl)-3-phenylprop-2-en-1-one[29]** **1H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.72(m, 2H), 7.52 (dd, J = 15.6 Hz, 1H), 7.33 – 7.29 (m, 4H), 7.26-7.22 (m, 2H), 6.66-6.63 (m, 2H), 3.63-3.59 (m, 4H), 3.03-3.00 (m, 4H). **13C NMR (101 MHz, $CDCl_3$)** δ 191.26 159.22, 145.15, 132.51, 130.24, 128.62, 128.47, 128.39, 118.83, 114.73, 66.73, 48.08.
62.		**1,4-dibenzylpiperazine[30]** **1H NMR (400 MHz, $CDCl_3$)** δ 7.07-7.04 (m, 8H), 7.02-6.98 (m, 2H), 3.28 (s, 4H), 2.28 (s, 8H) **13C NMR (101 MHz, $CDCl_3$)** δ 136.69, 128.22, 127.15, 125.98, 62.02, 52.00

References

1. T. Hou, C. Zhang, Y. Wang, Z. Liu, Z. Zhang, F. Wang, *Catal. Commun.* 2017, **94**, 56-59
2. D. Dehe, I. Munstein, A. Reis, W. R. Thiel, *J. Org. Chem.* 2011, **76**, 1151–1154
3. G. Manolikakes, A. Gavryushin, P. Knochel, *J. Org. Chem.* 2008, **73**, 1429-1434
4. G. Toma, R. Yamaguchi, *Eur. J. Org. Chem.* 2010, 6404–6408
5. S. Vandekerckhove, S. Van Herreweghe, J. Willems, B. Danneels, T. Desmet, C. de Kock, P. J. Smith, K. Chibale, M. D'hooghe, *Eur. J. Med. Chem.* 2015, **92**, 91-102
6. R. Sánchez-Martín, J. M. Campos, A. Conejo-García, O. Cruz-López, M. Báñez-Coronel, A. Rodríguez-González, M. A. Gallo, C. Juan, A. Espinosa, J. Med. Chem. 2005, **48**, 3354–3363
7. Z. Zhang, J. Mao, D. Zhu, F. Chen, H. Wu. B. Wan, *Tetrahedron,* 2006, **62**, 4435–4436
8. X. Yang, C. Xi, *Synth. Commun.*, 2007, **37**, 3381-3392
9. I. Geukens, J. Fransaer, D. E. De Vos, *ChemCatChem* 2011, **3**, 1431 – 1434
10. M. M. Shaikh, P. L. Bhutiya, K. H. Chikhalia, *ChemistrySelect,* 2017, **2**, 2677 –2680
11. (a) T. Tu, W. Fang, J. Jiang, *Chem. Commun.*, 2011, **47**, 12358-12360. (b) T. E. D'Ambra, K. G. Estep, M. R. Bell, M. A. Eissenstat, K. A. Josef, S. J. Ward, D. A. Haycock, E. R. Baizman, F. M. Casiano, N. C. Beglin, S. M. Chippari, J. D. Grego, R. K. Kullnig, G. T. Daley, *J. Med. Chem.*, 1992, **35**, 124-135
12. S. W. Kim, J. G. Lee, E. J. Lee, H. Y. P. Choo, C. Y. Yoo, D. Y. Lee, K. R. Roh, E. K. Kim, *J. Comb. Chem.* 2004, **6**, 851–854
13. Z. Yan, H. Tian, D. Zhao, H. Jin, W. Tian, Chinese Chem. *Lett*. 2016, **27**, 96-98
14. A. T. Londregan, S. Jennings, L. Wei, *Org. Lett.* 2010, **12**, 5254–5257
15. D. Gartner, A. Welther, B. R. Rad, R. Wolf, A. J. Von Wangelin, *Angew. Chem. Int. Ed.* 2014, **53**, 3722 –3726
16. M. Huang, Y. Li, J. Liu, S. Shu, Y. Liu, Z. Ke, *Chem. Commun.*, 2019, **55**, 6213 – 6216
17. P. R. Likhar, R. Arundhathi, M. L. Kantam, P. S. Prathima, *Eur. J. Org. Chem.*, 2009, 5383–5389
18. B. Blank, M. Madalska, R. Kempe, *Adv. Synth. Catal.* 2008, **350**, 749– 758
19. (a) H. Hikawa, R. Tan, A. Tazawa, S. Kikkawa, I. Azumaya, *Eur. J. Org. Chem.*, 2020, 539–547. (b) W. Villarreal, L. Colina-Vegas, C. R. de Oliveira, J. C. Tenorio, J. Ellena, F. C. Gozzo, M. R. Cominetti, A. G. Ferreira, M. A. B. Ferreira, M. Navarro, A. A. Batista, *Inorg. Chem.,* 2015, **54**, 11709−11720
20. P. Pandey, P. Daw, N. U. D. Reshi, K. R. Ehmann, M. Holscher, W. Leitner, J. K. Bera, *Organometallics*, 2020, **39**, 3849-3863

21. (a) P. S. Hanley, T. P. Clark, A. Krasovskiy, M. S. Ober, J. P. O'Brien, T. S. Staton, *ACS Catal.* 2016, **6**, 3515–3519; (b) B. Lin, M. Liu, Z. Ye, J. Ding, H. Wu, J. Cheng, *Org. Biomol. Chem.* 2009, **7**, 869-873
22. H. Rao, H. Fu, Y. Jiang, Y. Zhao, *J. Org. Chem.*, 2005, **70**, 8107-8109
23. R. J. Lundgren, A. S. Kumankumah, M. Stradiotto, *Chem. Eur. J.*, 2010, **16**, 1983 – 1991
24. R. J. Lundgren, B. D. Peters, P. G. Alsabeh, M. Stradiotto, *Angew. Chem. Int. Ed.*, 2010, **49**, 4071 –4074
25. G. Li, C. Wang, Y. Li, K. Shao, G. Yu, S. Wang, X. Guo, W. Zhao, H. Nakamura, *Chem. Commun*. 2020, **56**, 7333-7336
26. A. Bismuto, T. Delcaillau, P. Miiller, B. Morandi, *ACS Catal*. 2020, **10**, 4630-4639
27. A. Afanasenko, S. Elangovan, M. C. A. Stuart, G. Bonura, F. Frusteri, K. Barta, *Catal. Sci. Technol*., 2018, **8**, 5496
28. T. Ogata, J. F. Hartwig, *J. Am. Chem. Soc*., 2008, **130**, 13848-13849
29. M. Gopalakrishnan, J. Thanusu, V. Kanagarajan, R. Govindaraju, *Med Chem Res,* 2009, **18**, 341–350
30. M. Caproiu, C. Florea, C. Galli, A. Petride, H. Petride, *Eur. J. Org. Chem.* 2000,1037 – 1043



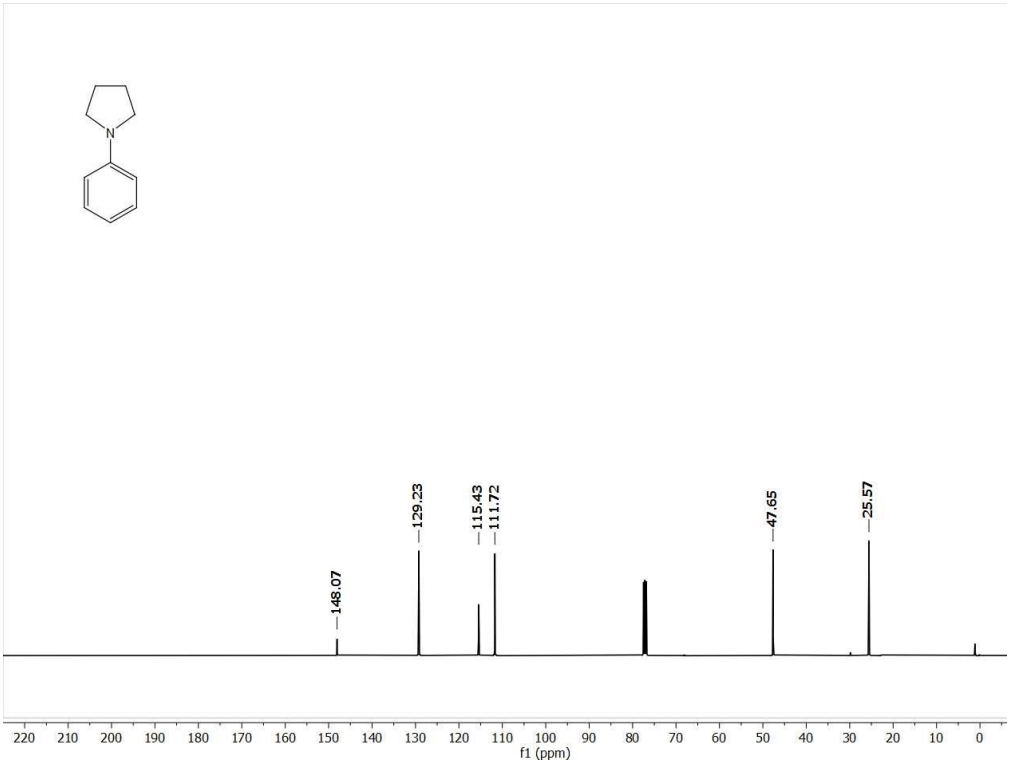
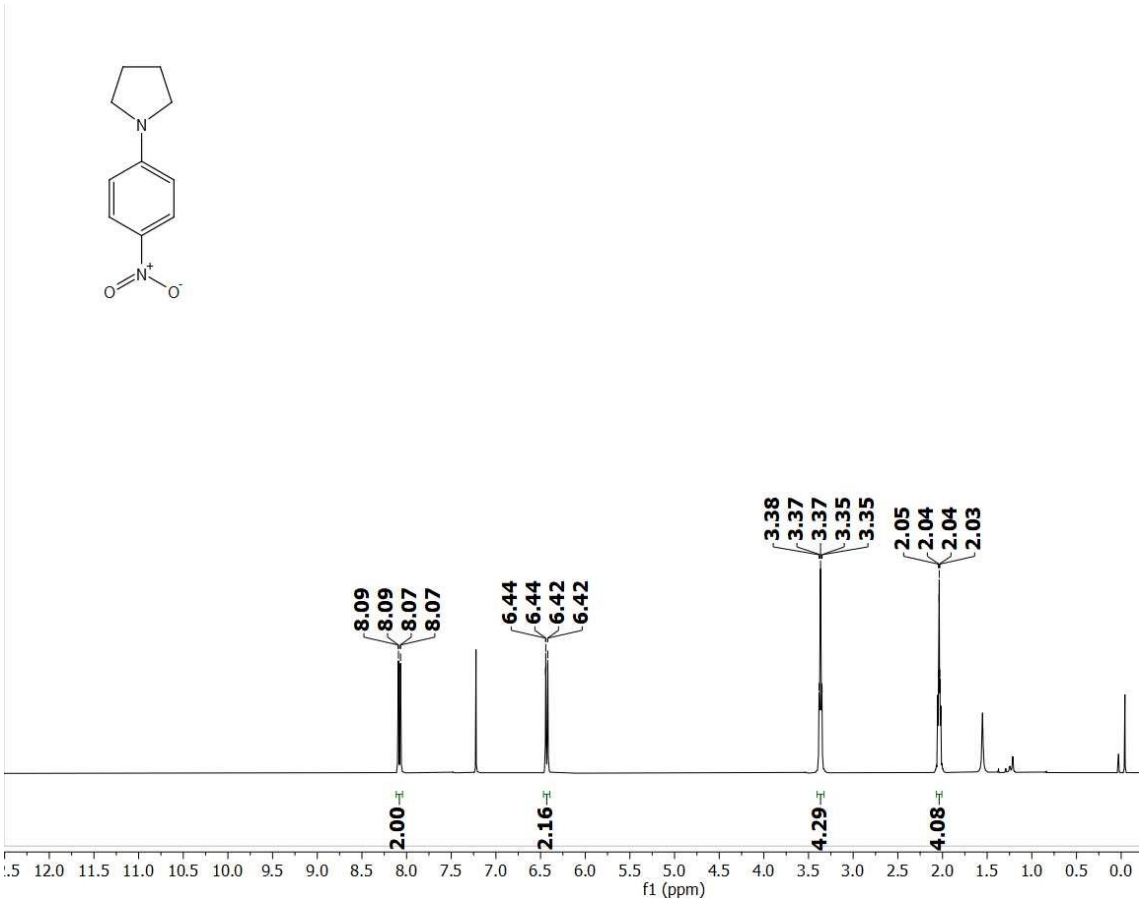


Figure 1: ^{1}H & ^{13}C NMR Spectra of representative compound



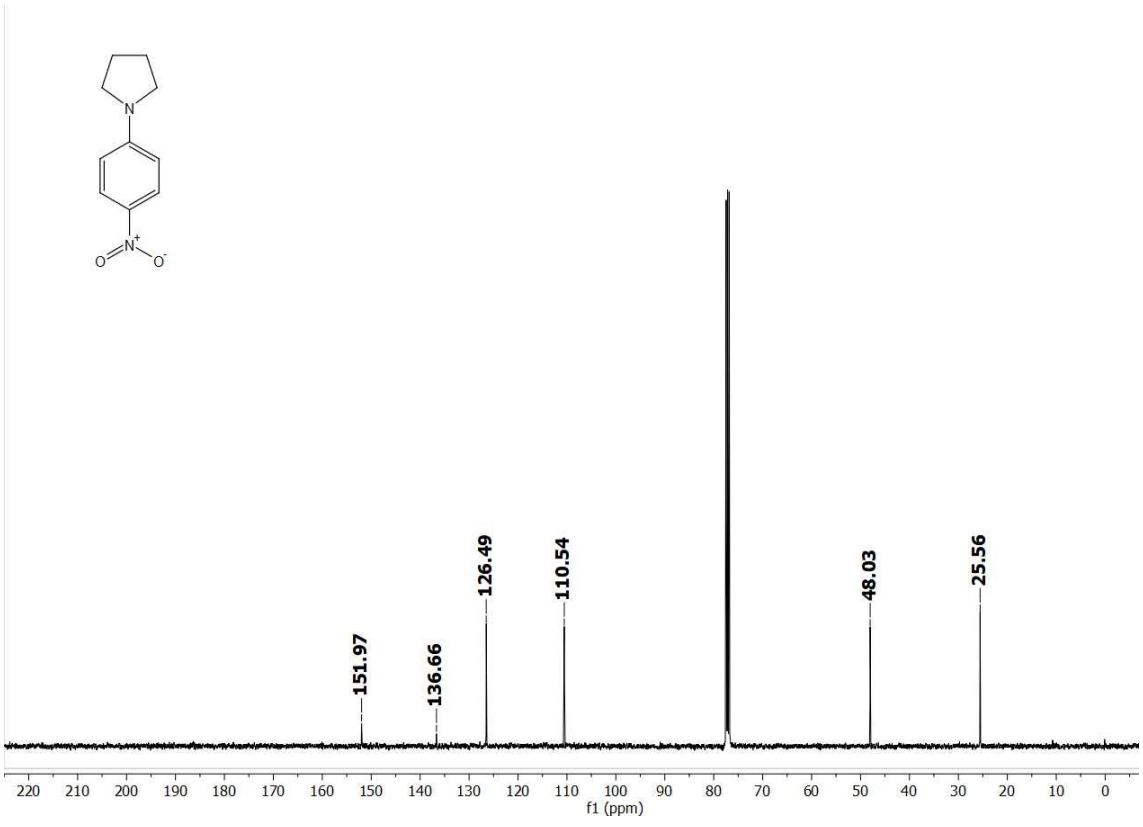


Figure 2: ^{1}H & ^{13}C NMR Spectra of representative compound

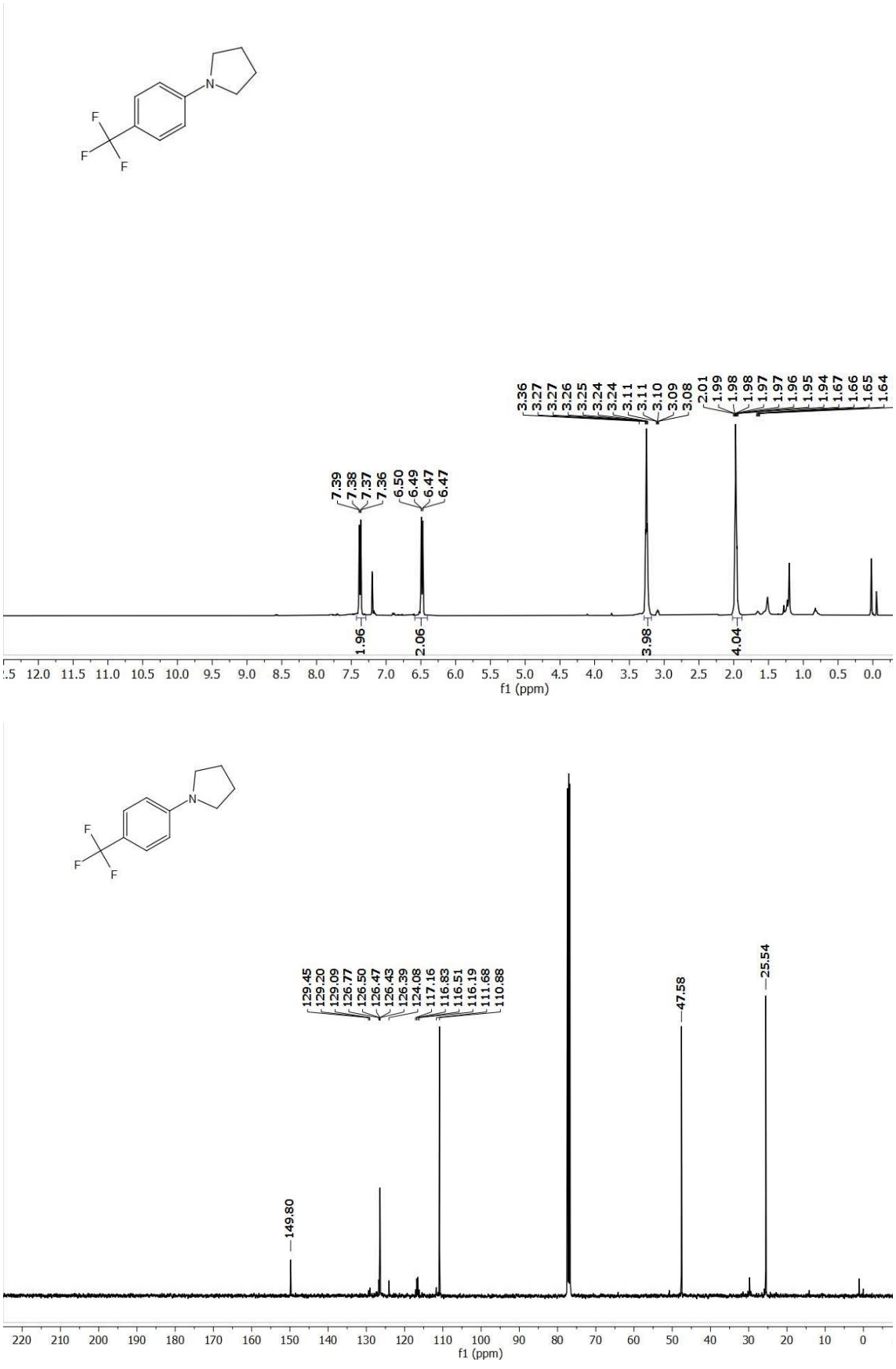
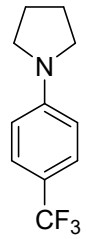


Figure 3: ^{1}H & ^{13}C NMR Spectra of representative compound



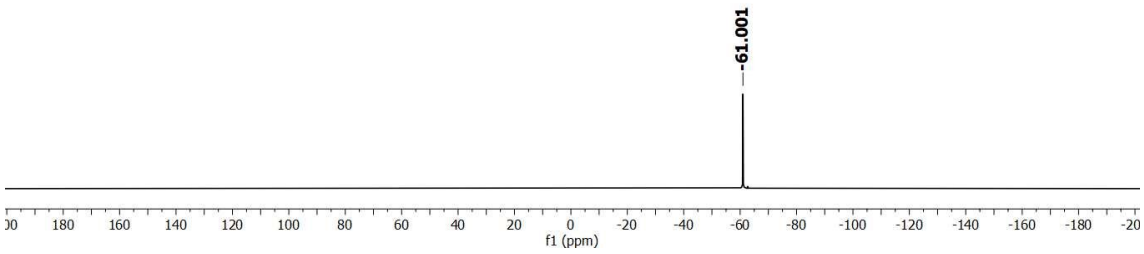


Figure 4: ^{19}F NMR Spectra of representative compound

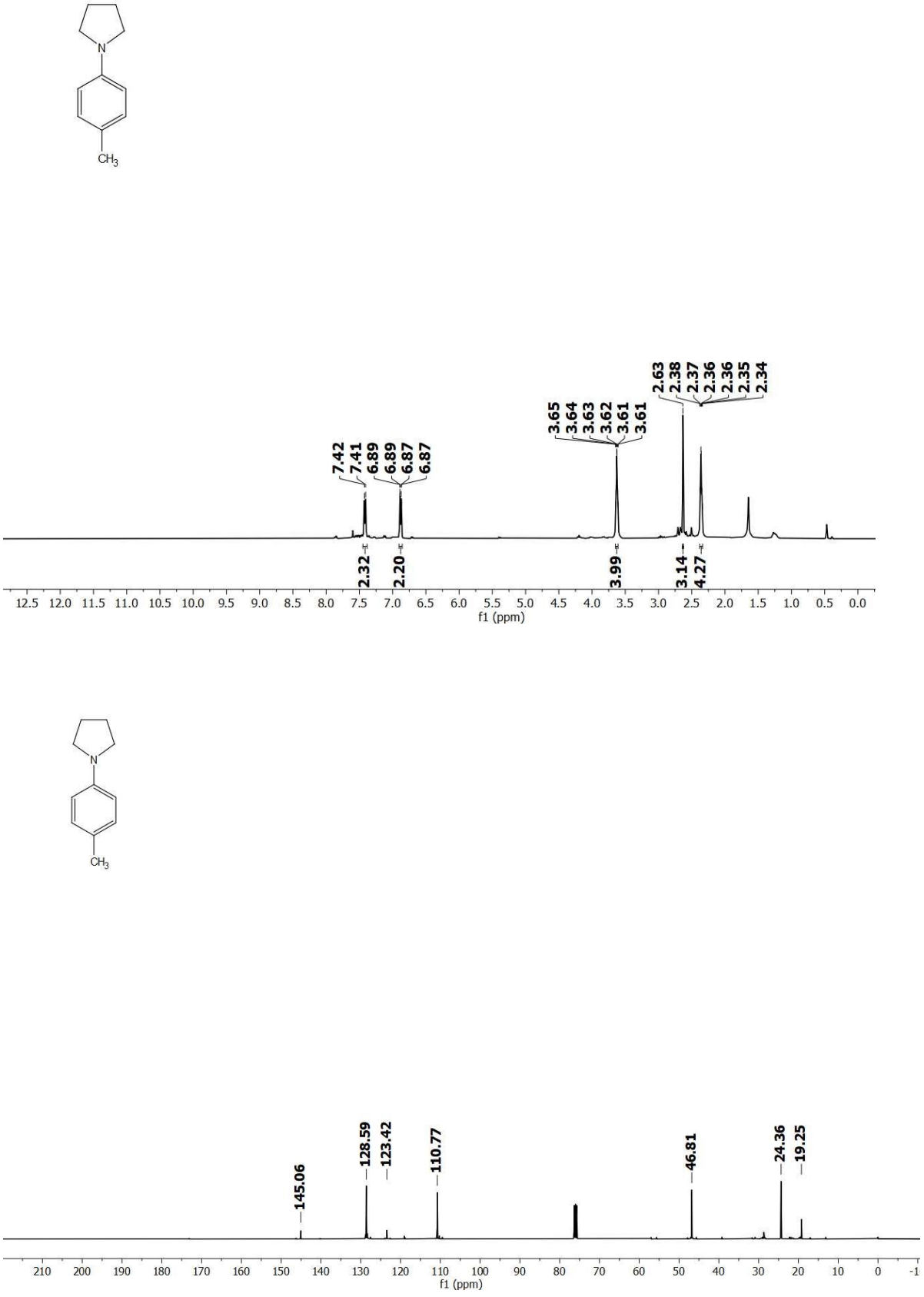


Figure 5: ^{1}H & ^{13}C NMR Spectra of representative compound

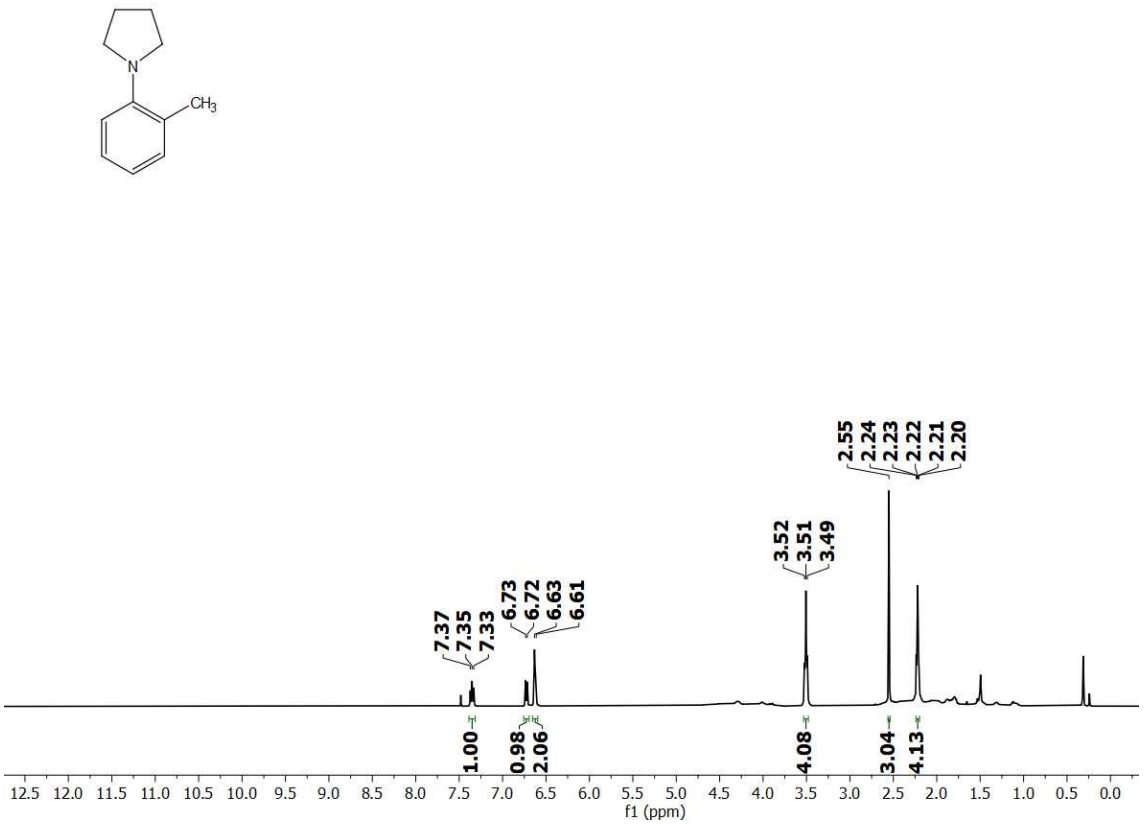
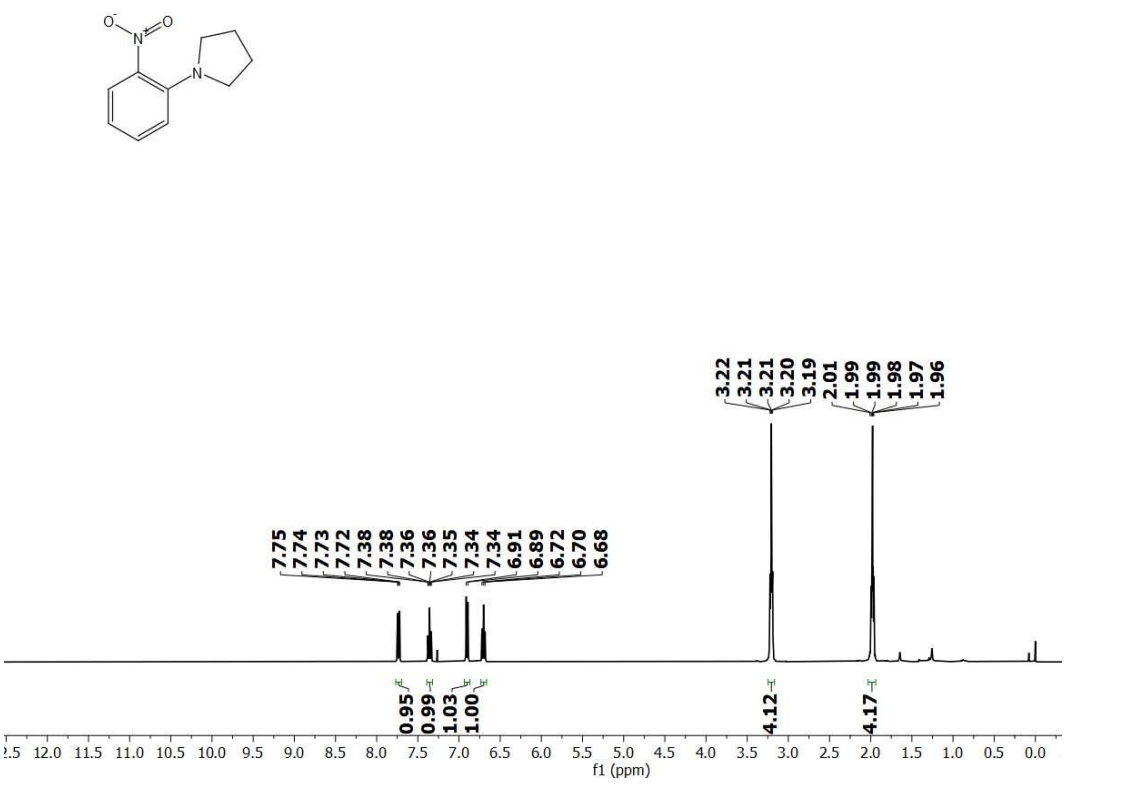


Figure 6: ^{1}H & ^{13}C NMR Spectra of representative compound



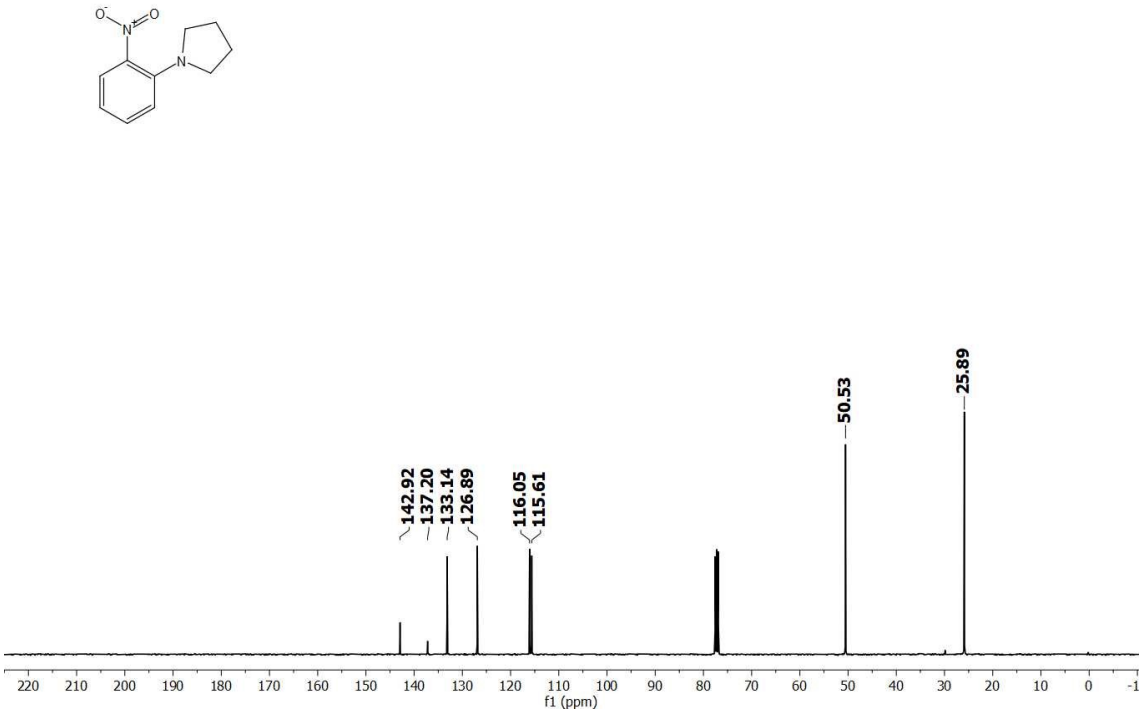
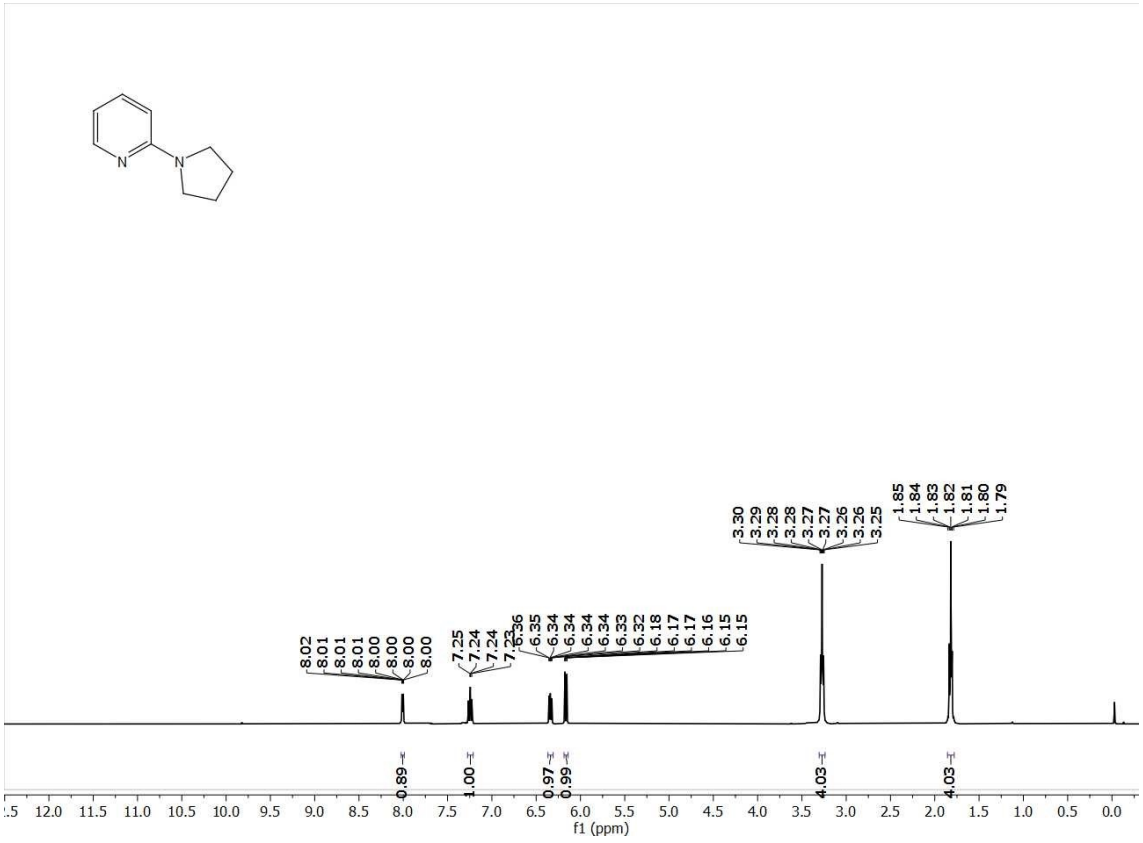


Figure 7: ^{1}H & ^{13}C NMR Spectra of representative compound



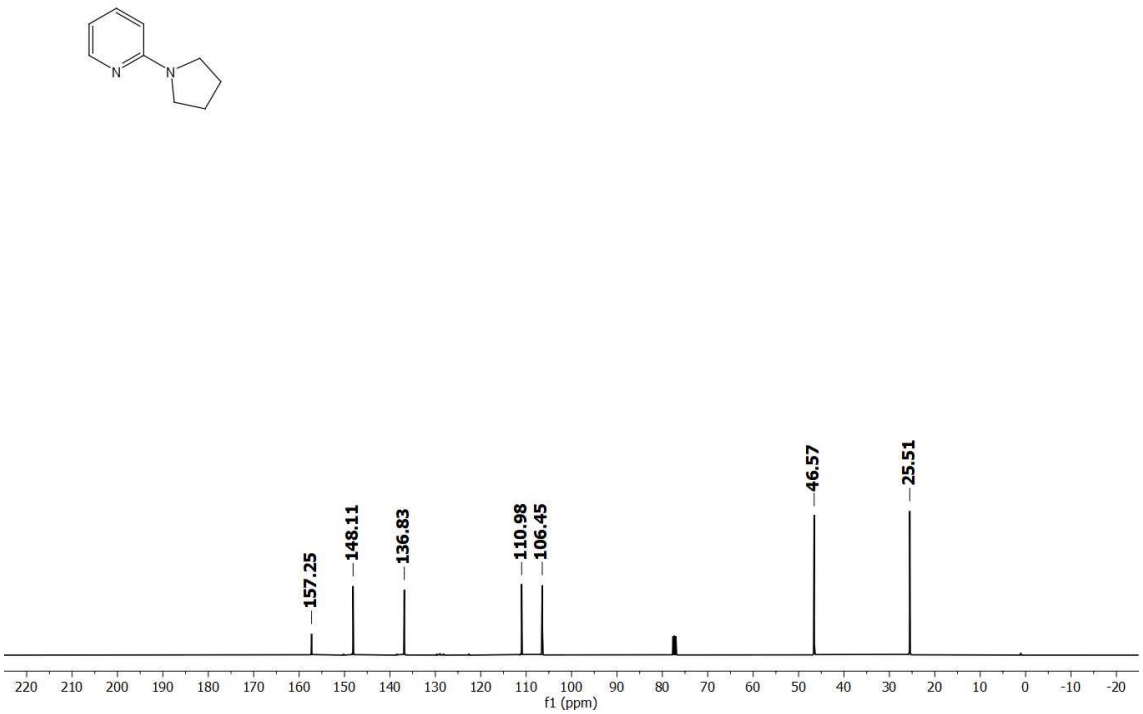


Figure 8: ^{1}H & ^{13}C NMR Spectra of representative compound

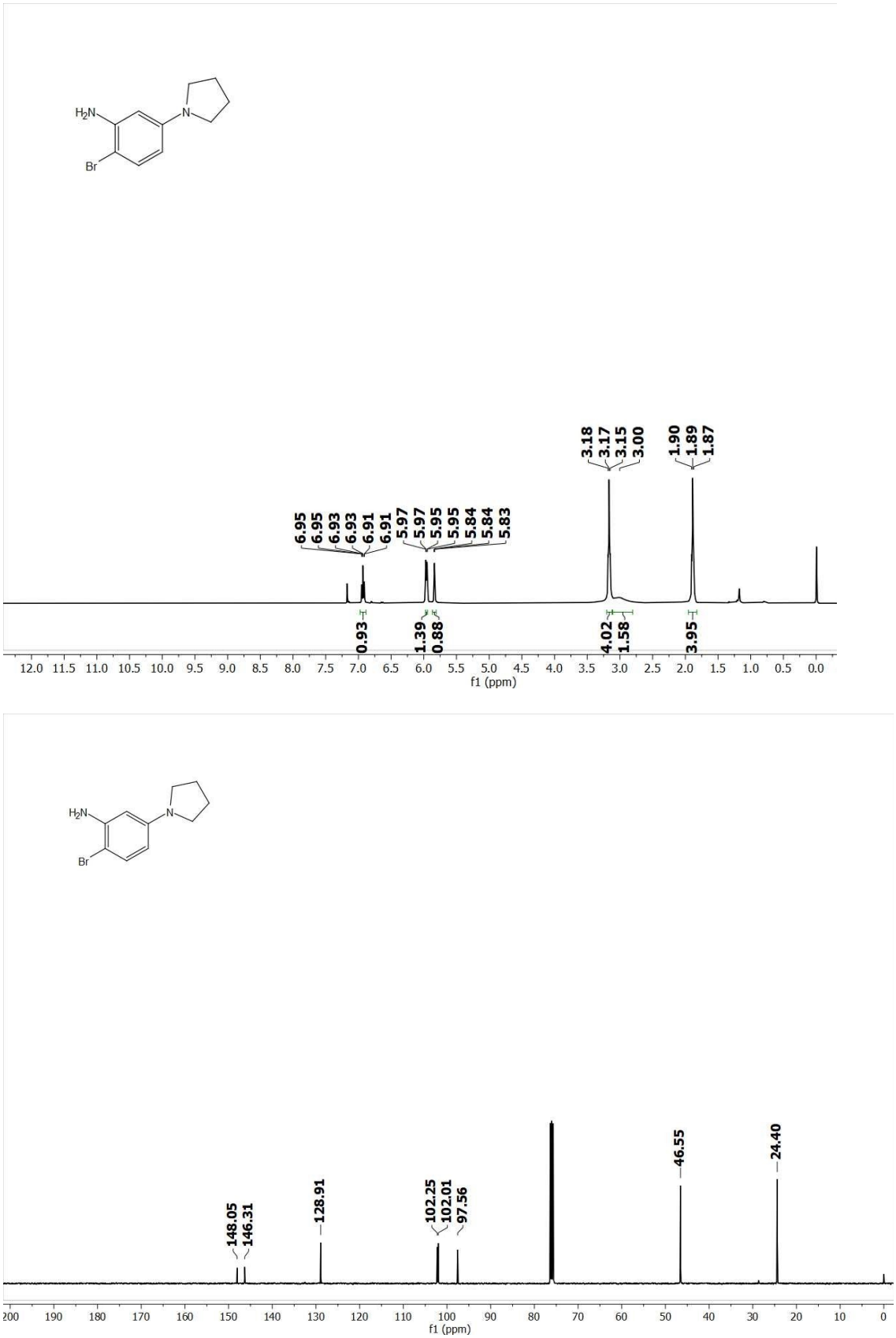


Figure 9: ^{1}H & ^{13}C NMR Spectra of representative compound

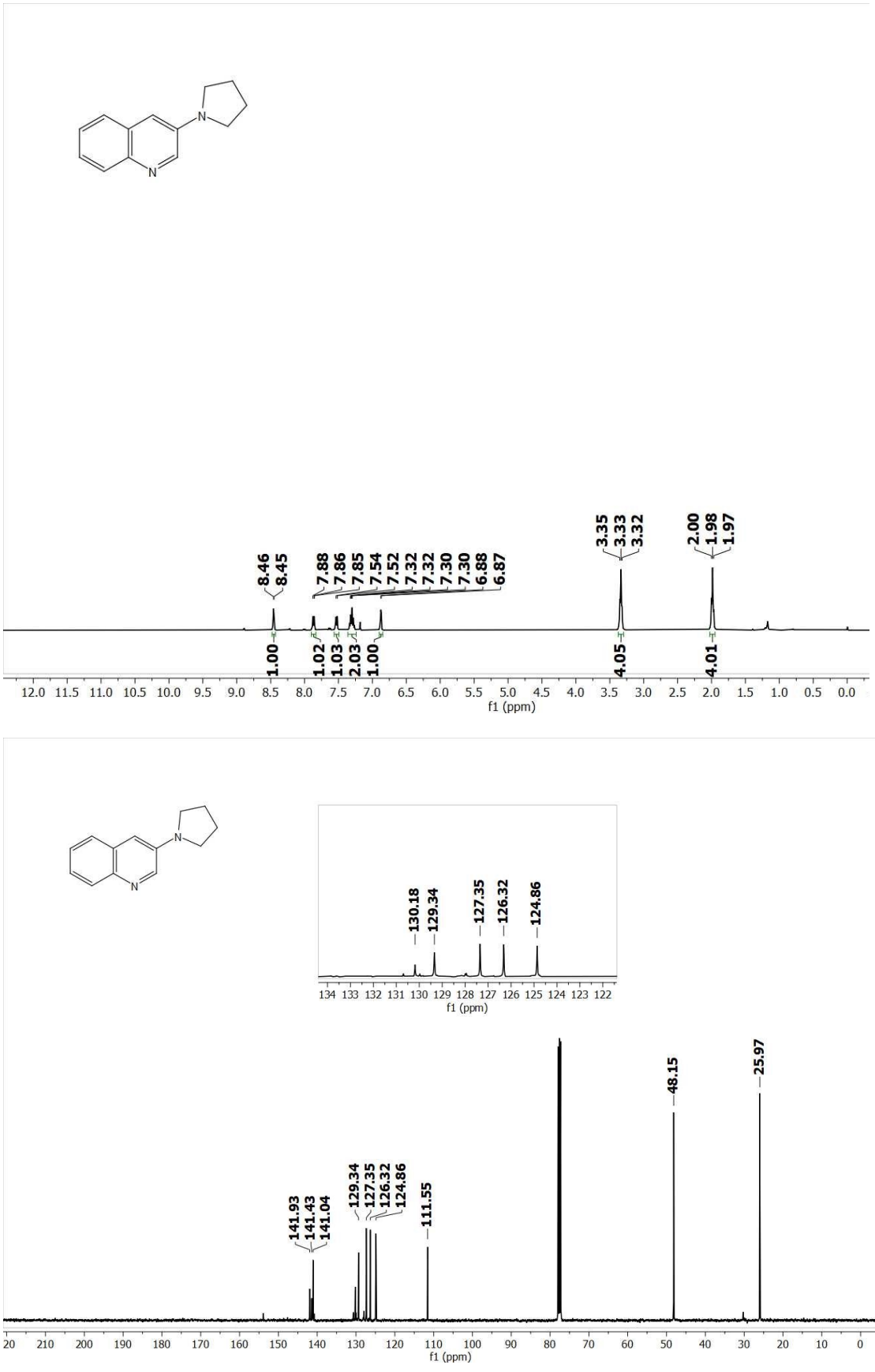


Figure 10: ^{1}H & ^{13}C NMR Spectra of representative compound

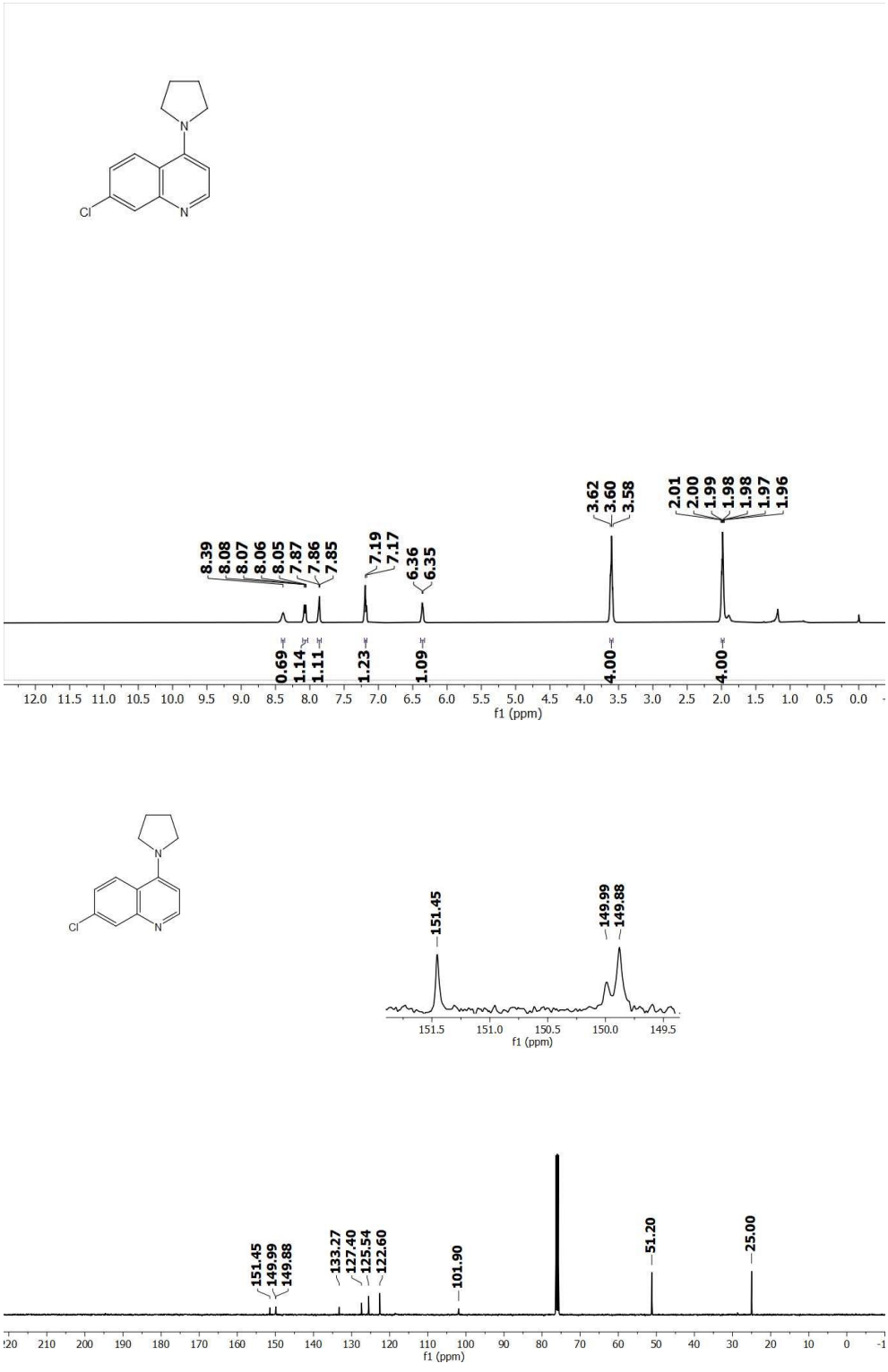


Figure 11: ^{1}H & ^{13}C NMR Spectra of representative compound

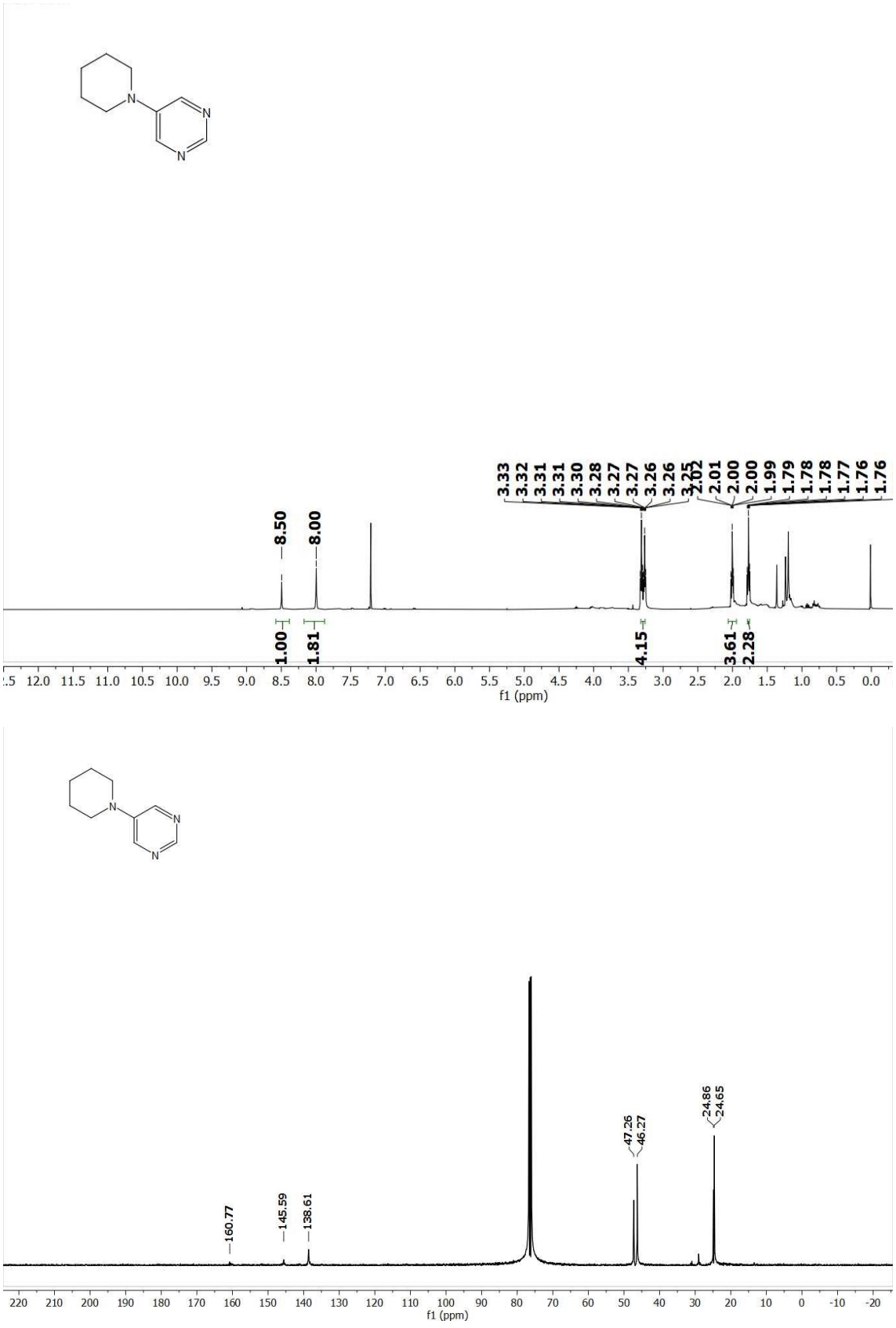


Figure 12: ^{1}H & ^{13}C NMR Spectra of representative compound

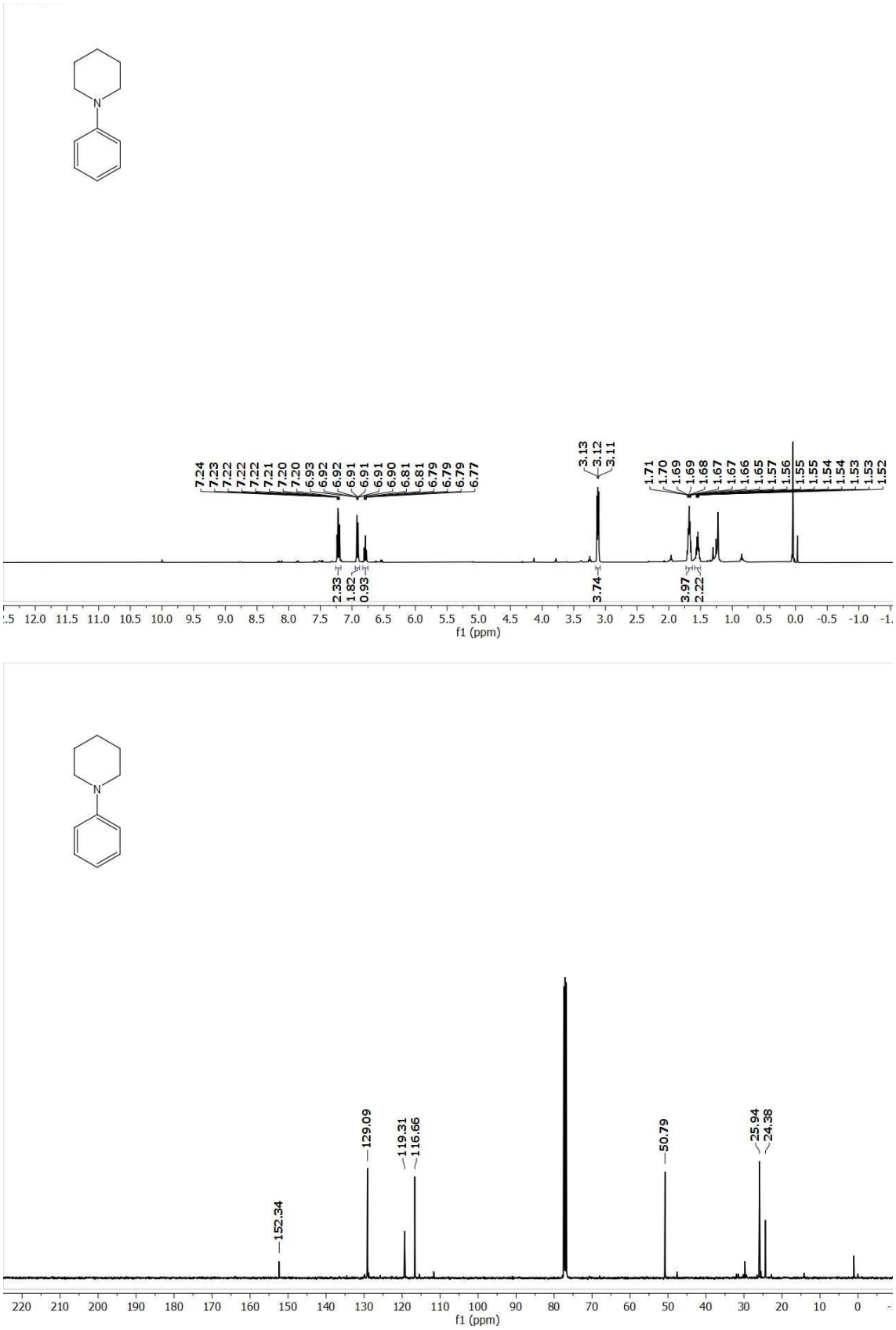


Figure 13: ^{1}H & ^{13}C NMR Spectra of representative compound

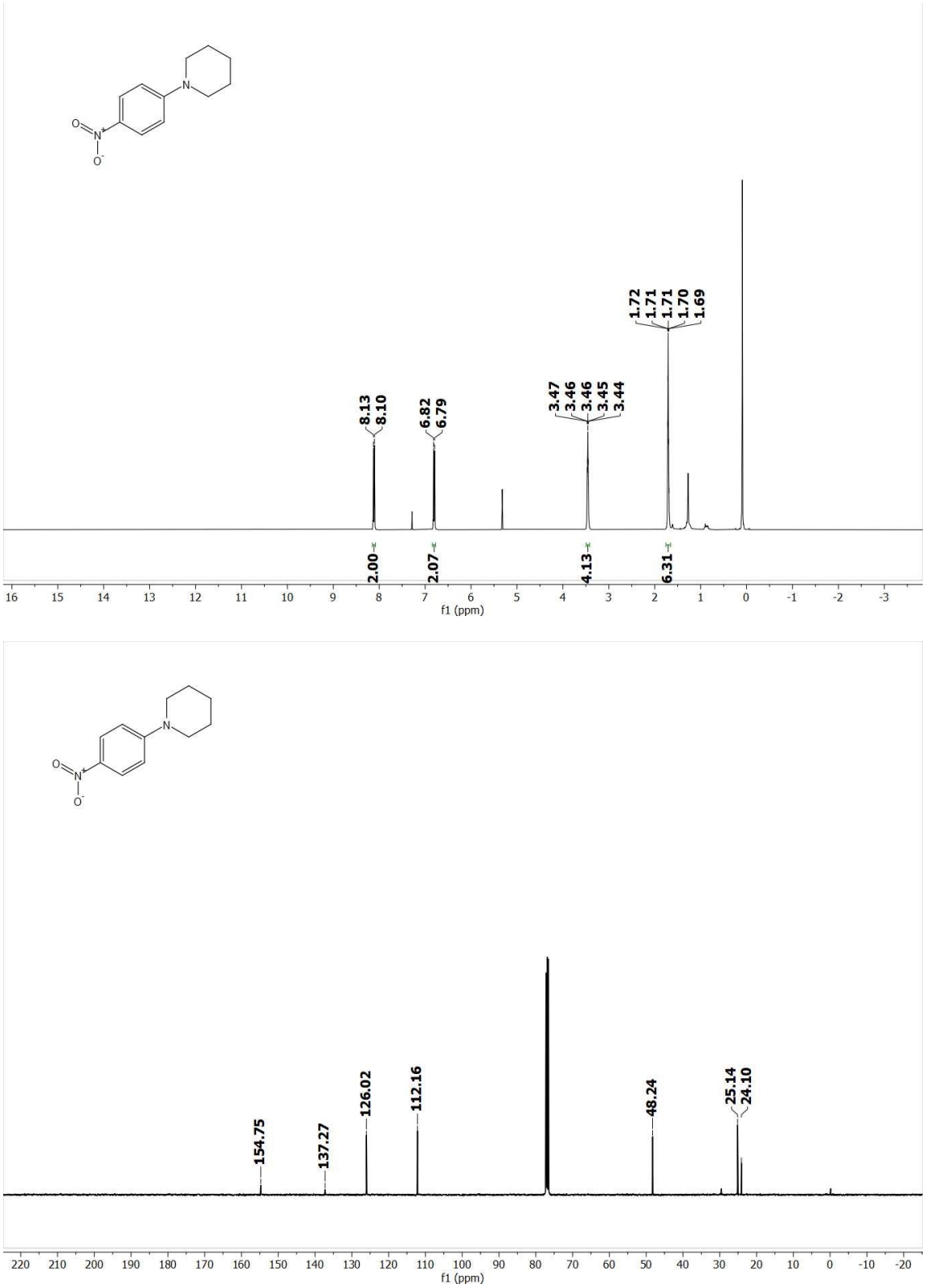


Figure 14: ^{1}H & ^{13}C NMR Spectra of representative compound

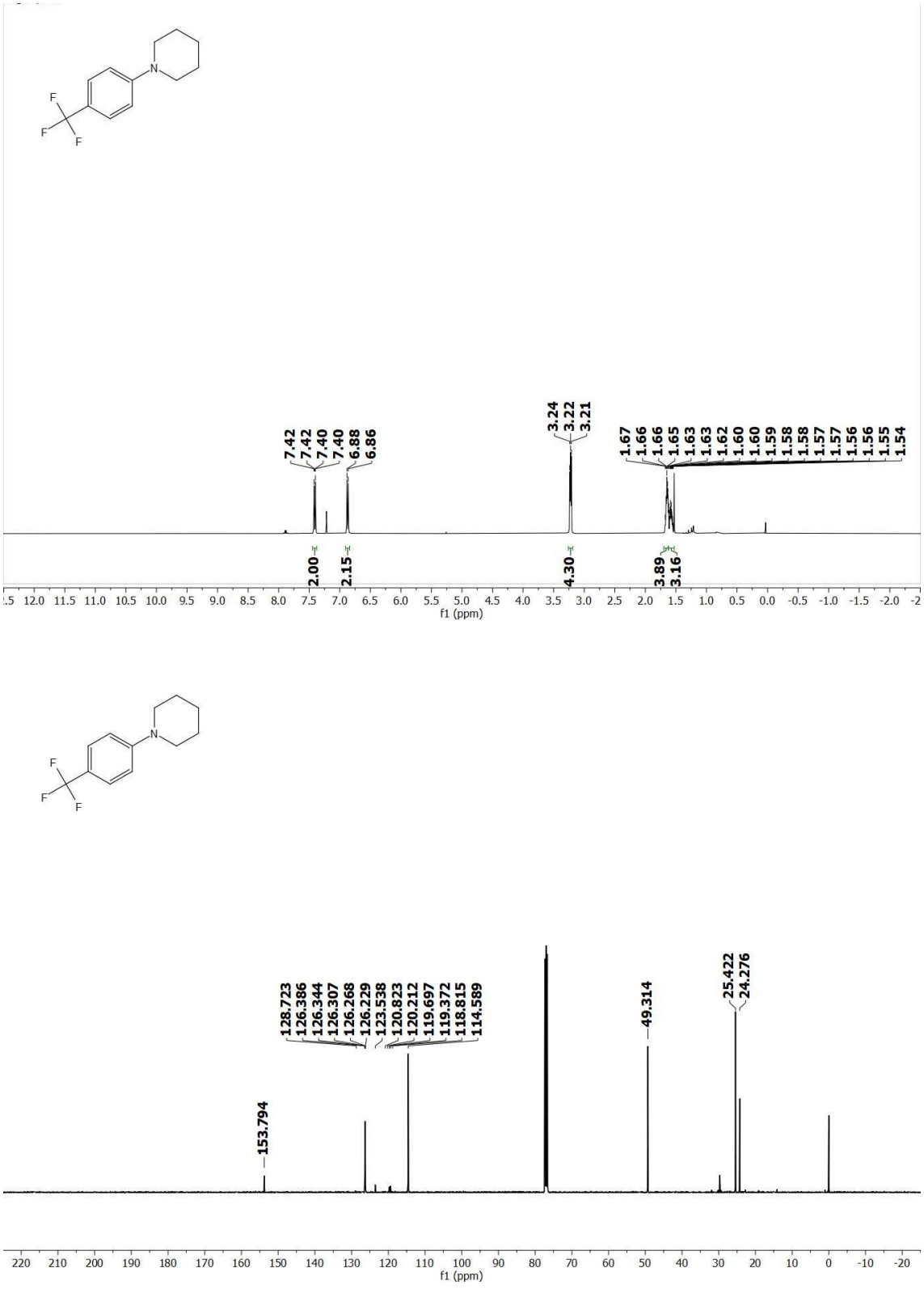
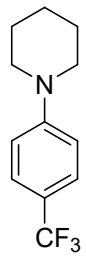


Figure 15: ^{1}H & ^{13}C NMR Spectra of representative compound



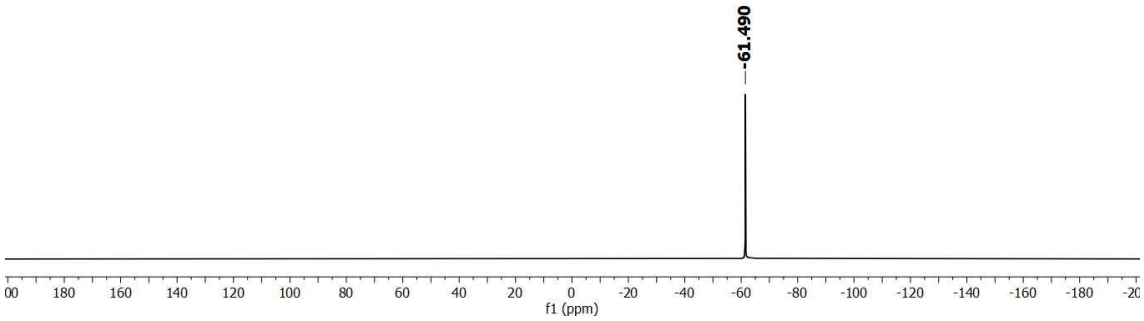
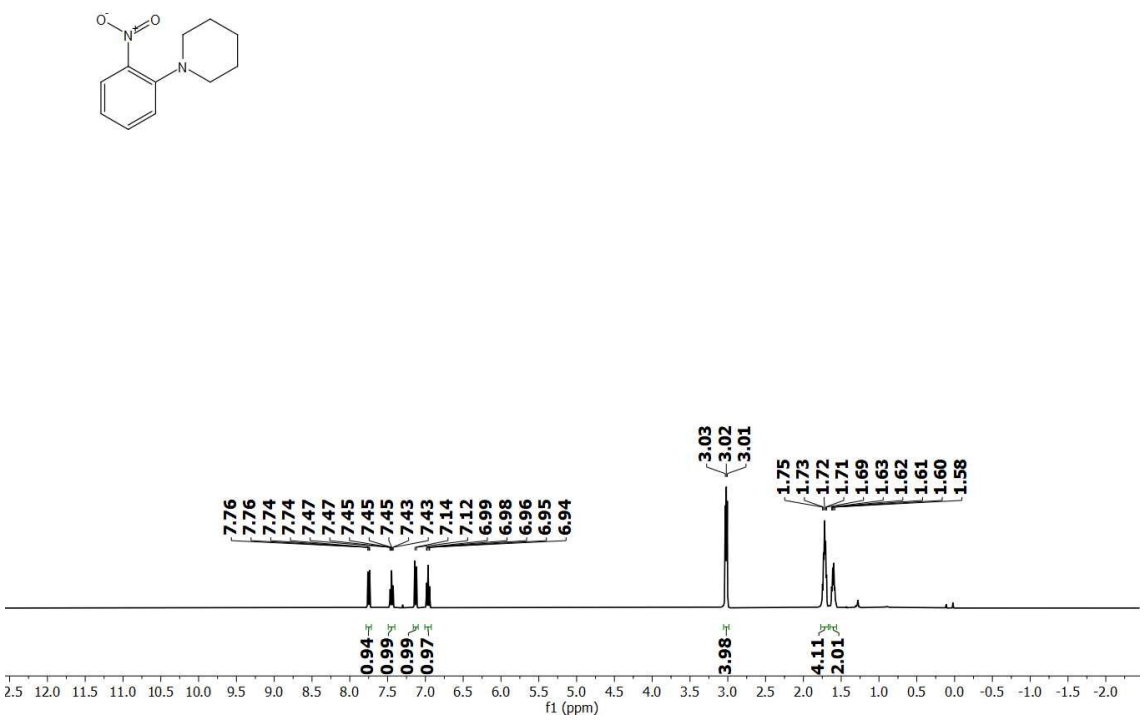


Figure 16: ^{19}F NMR Spectra of representative compound



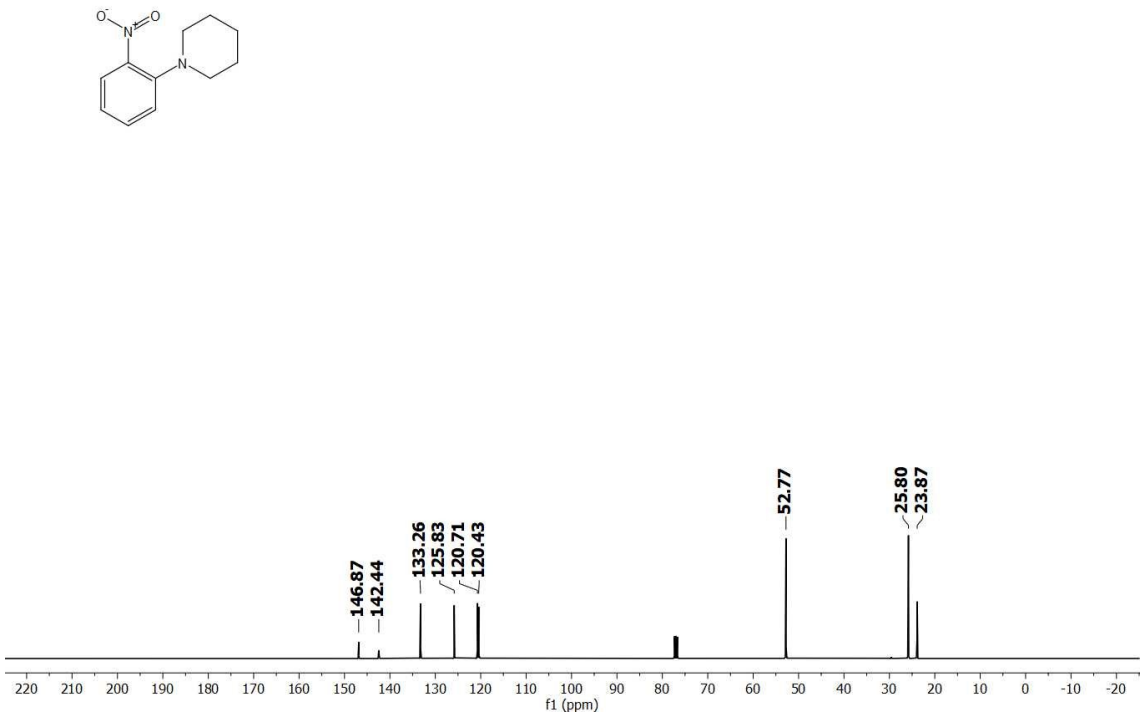
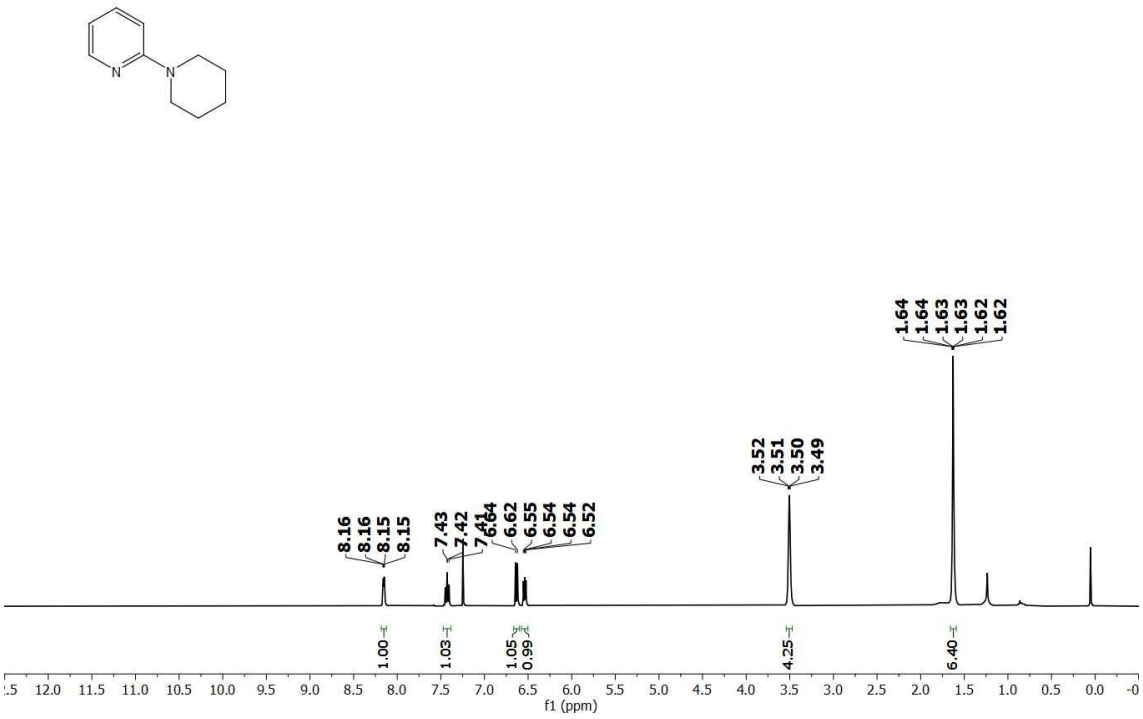


Figure 17: ^{1}H & ^{13}C NMR Spectra of representative compound



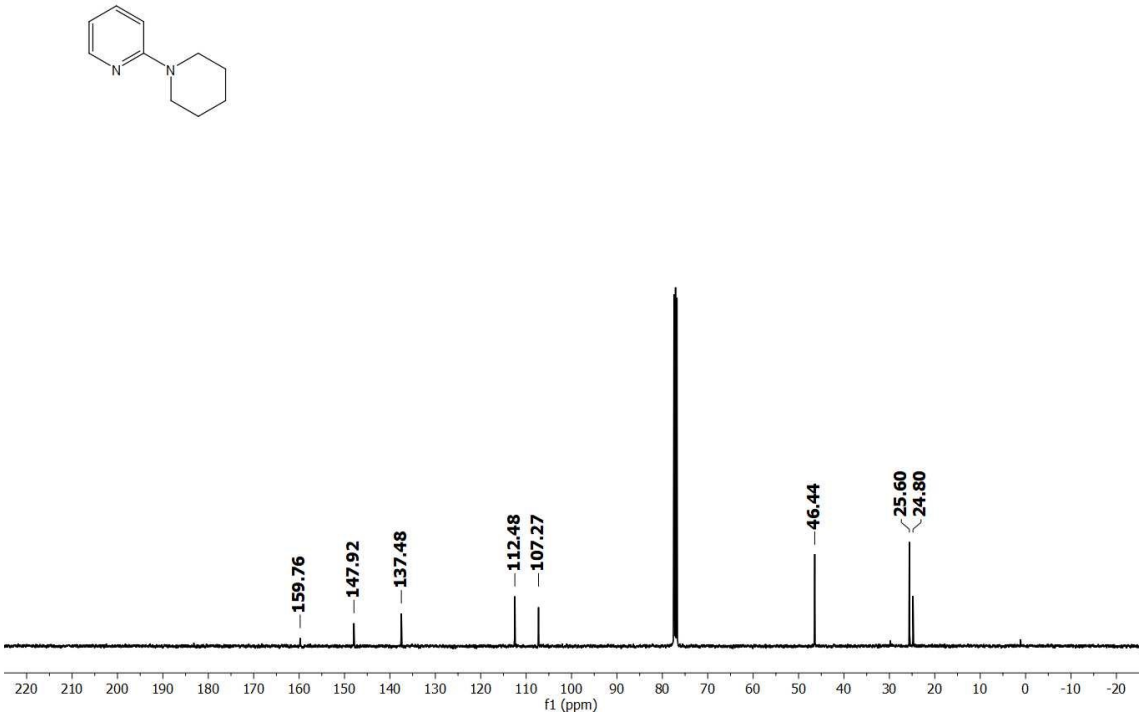


Figure 18: ^{1}H & ^{13}C NMR Spectra of representative compound

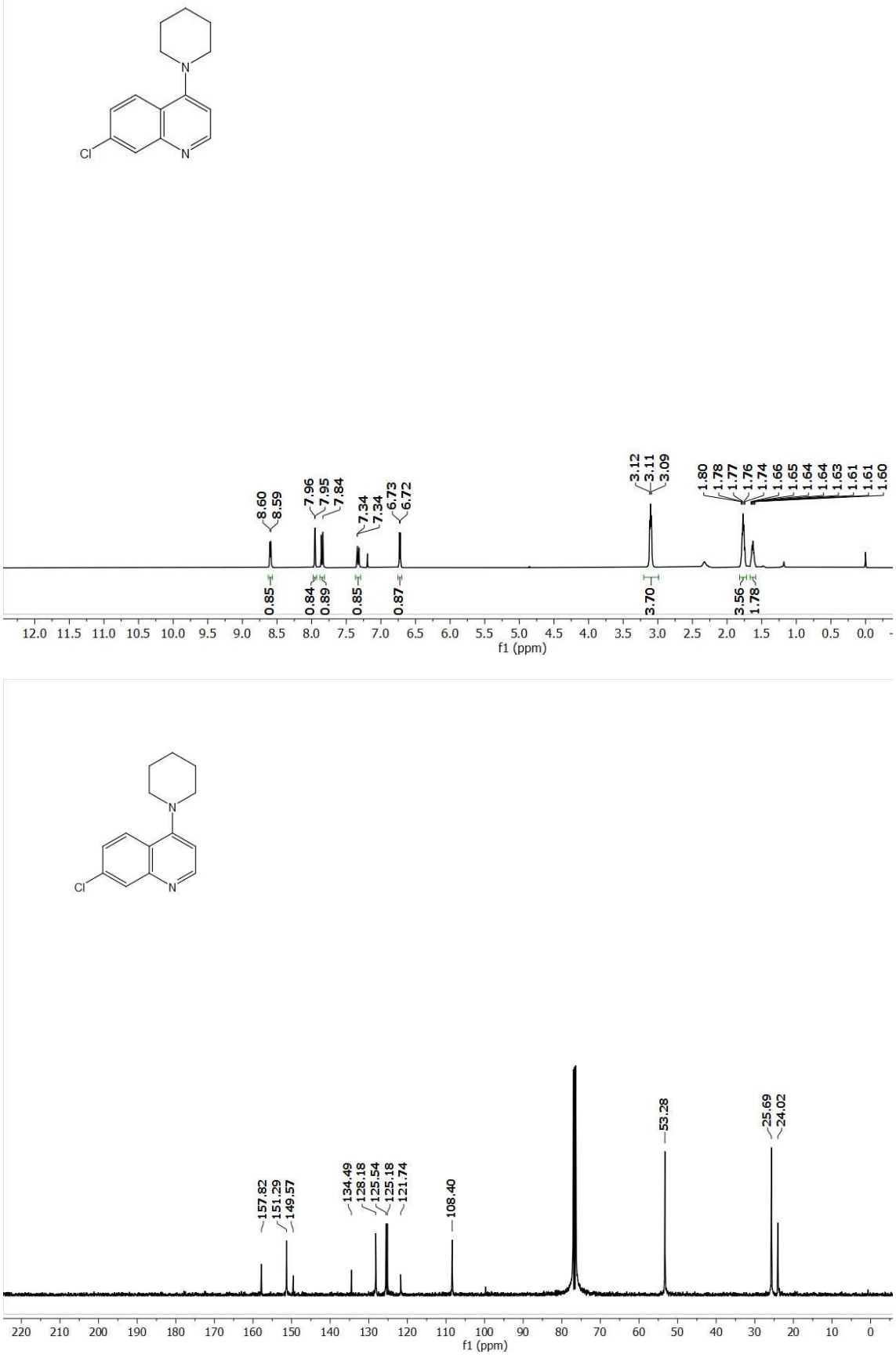


Figure 19: ^{1}H & ^{13}C NMR Spectra of representative compound

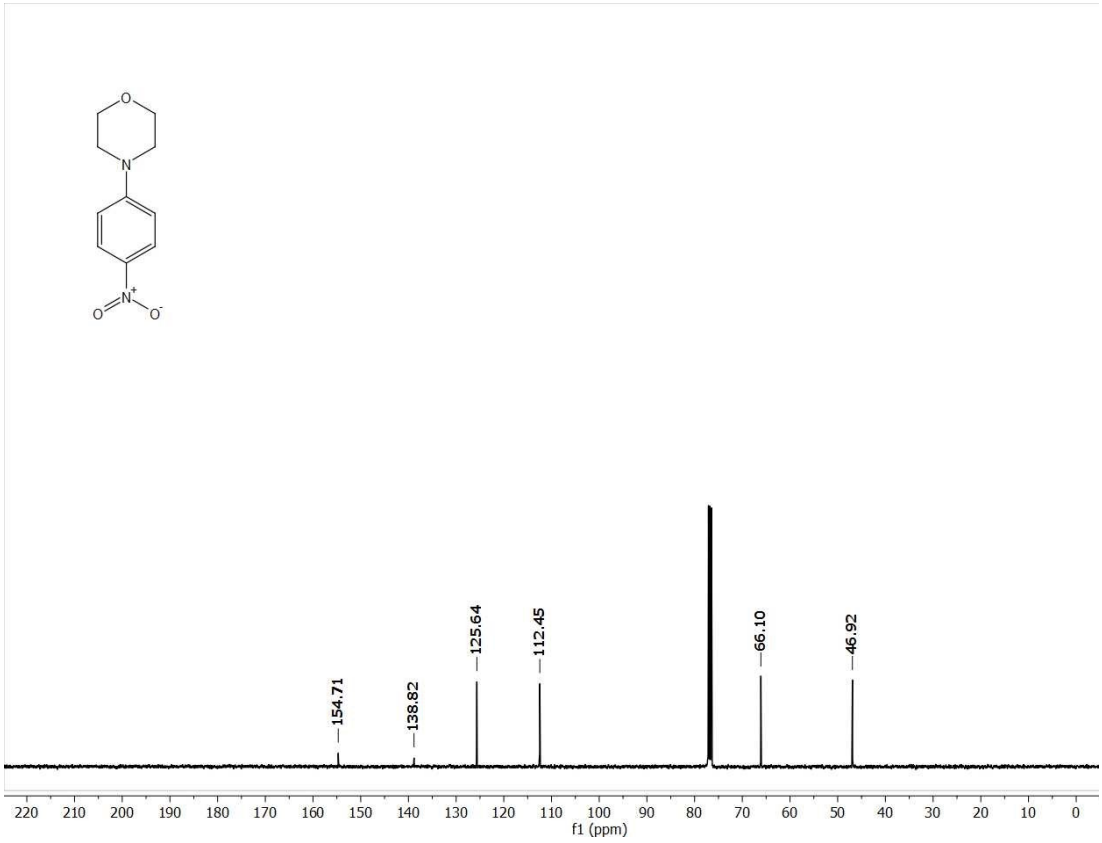


Figure 20: ^{1}H & ^{13}C NMR Spectra of representative compound

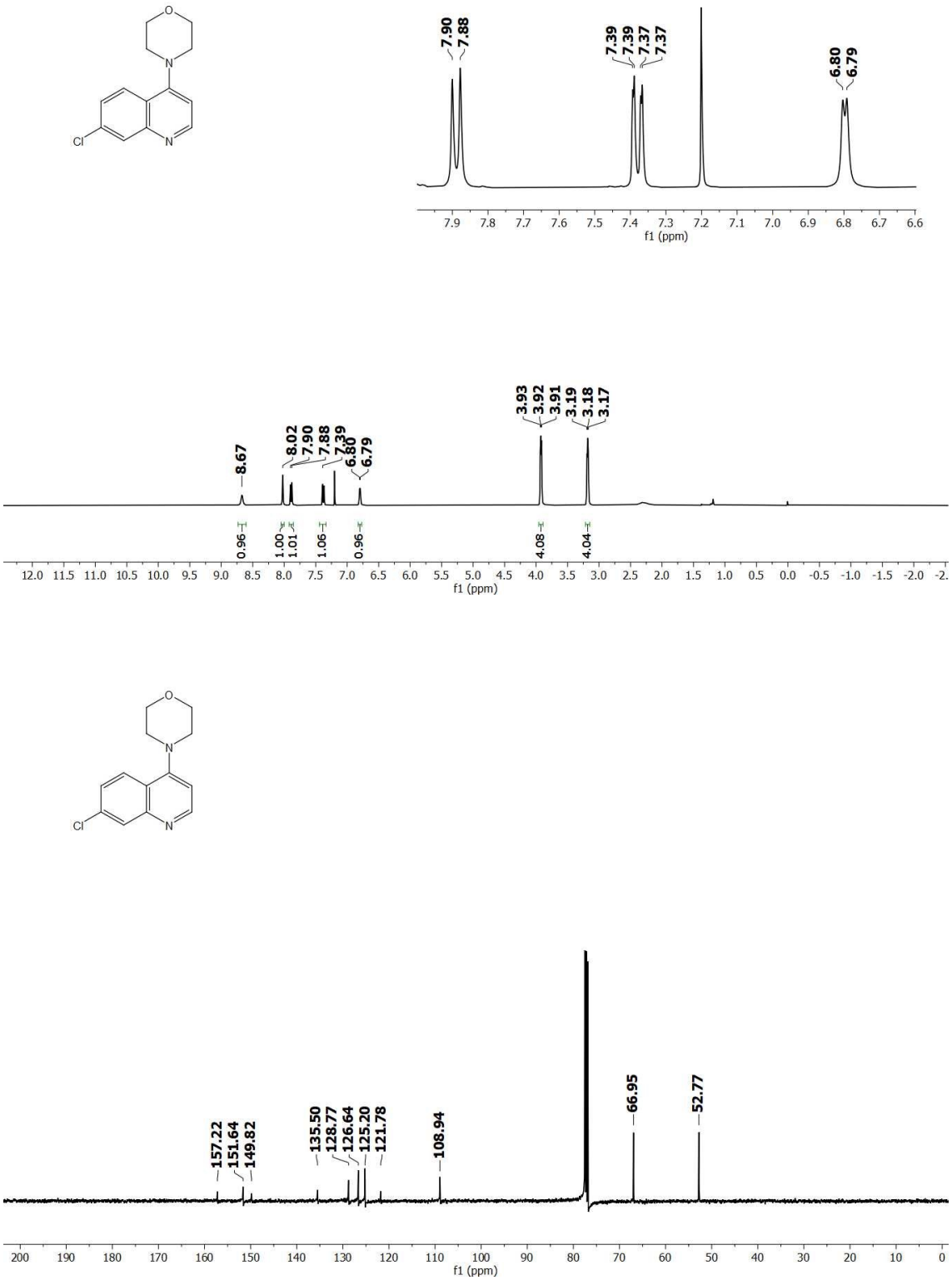
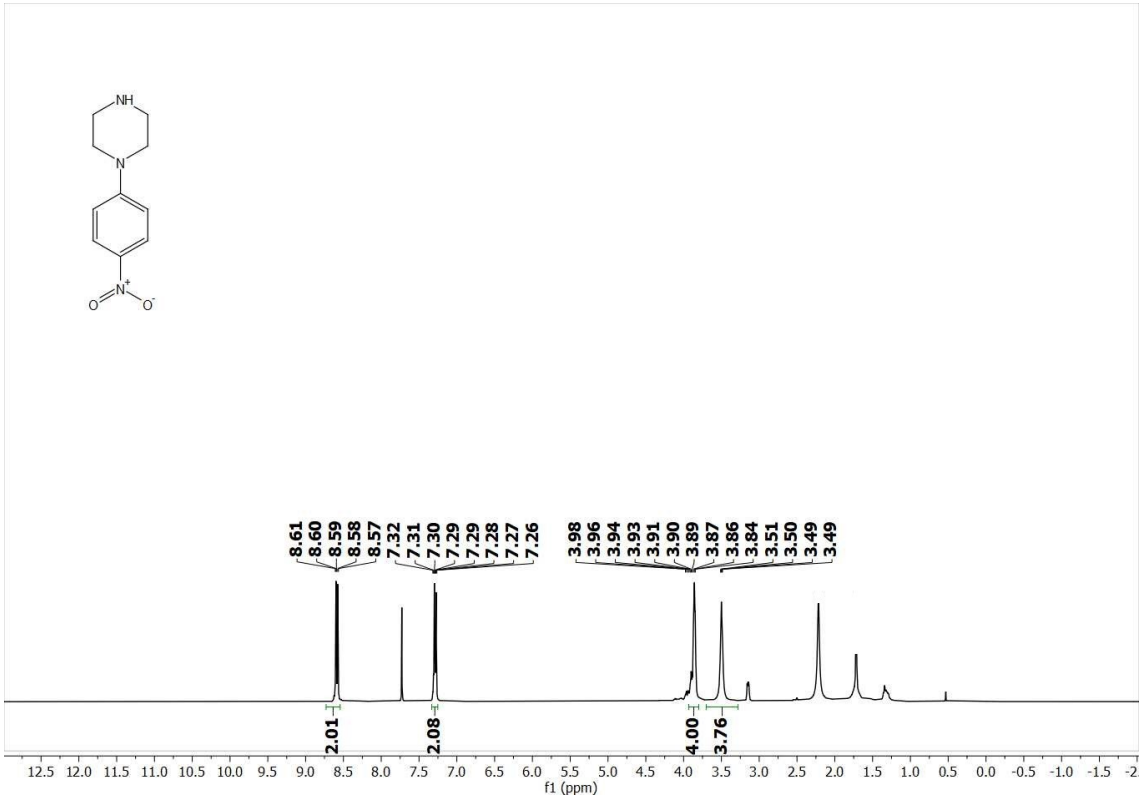


Figure 21: ^{1}H & ^{13}C NMR Spectra of representative compound



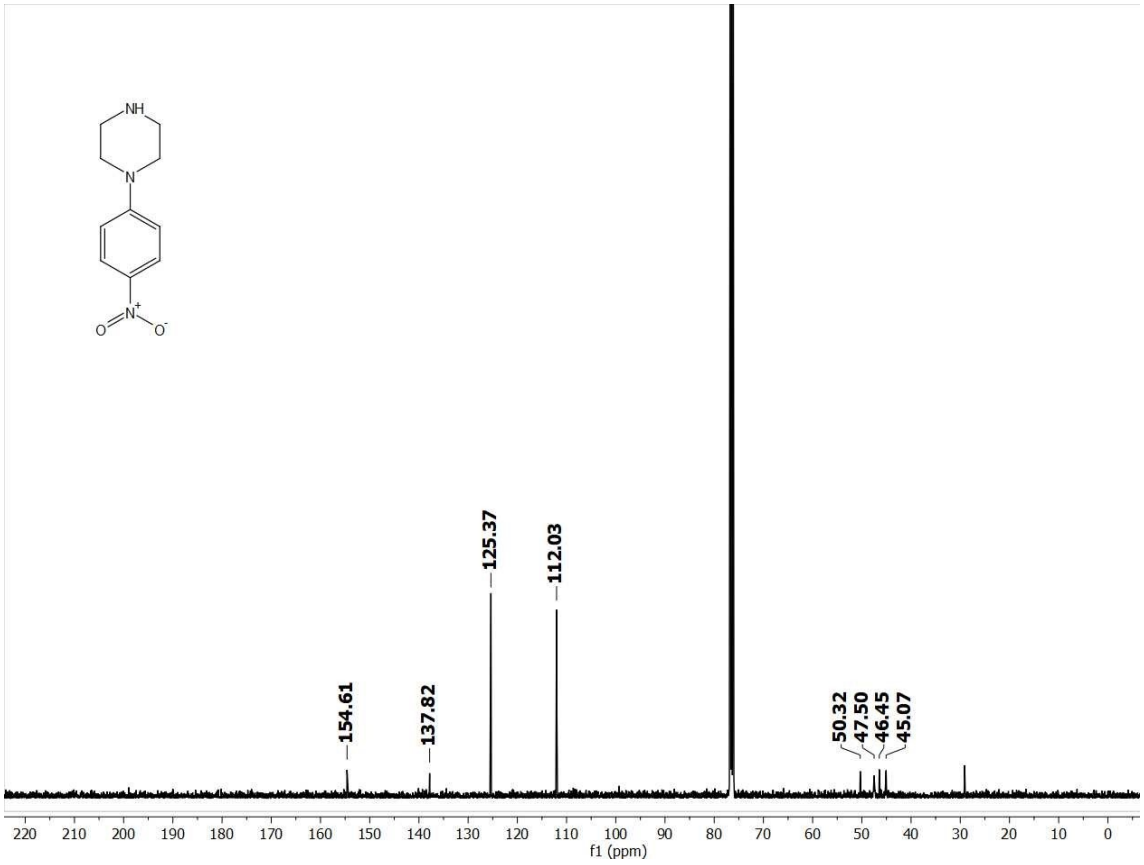
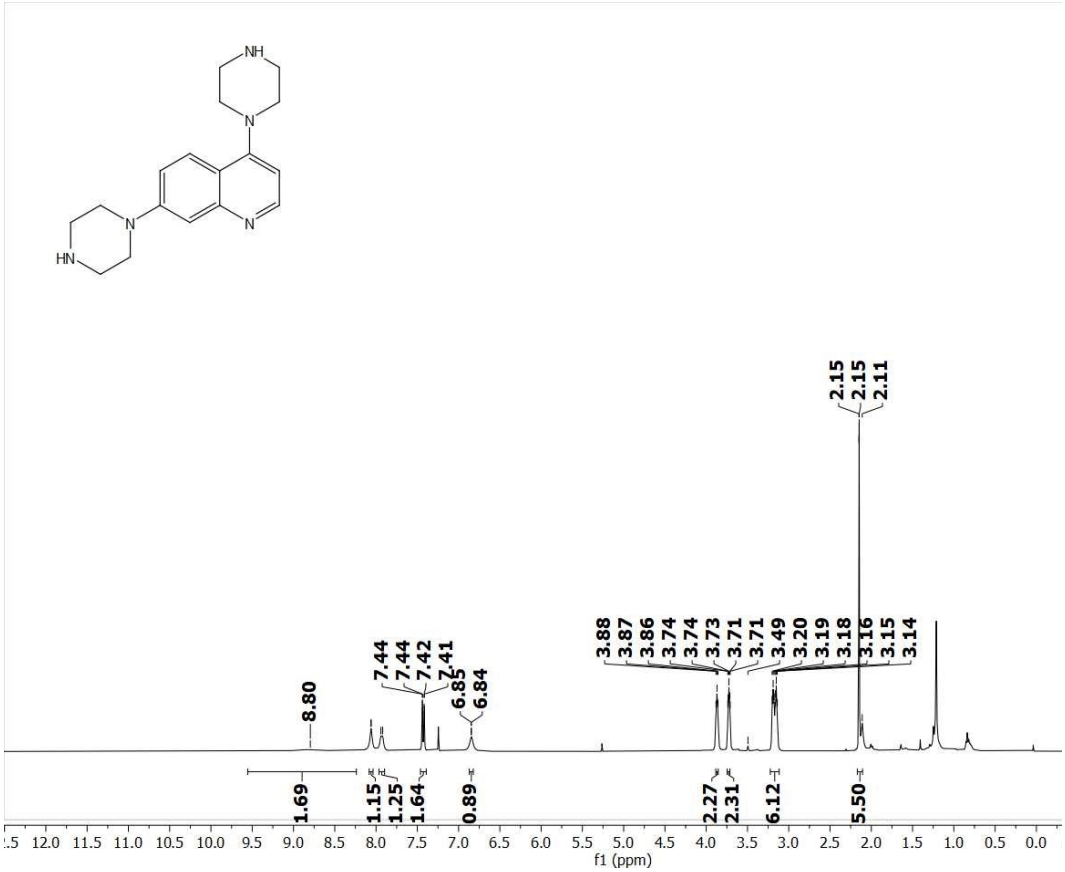


Figure 22: ^{1}H & ^{13}C NMR Spectra of representative compound



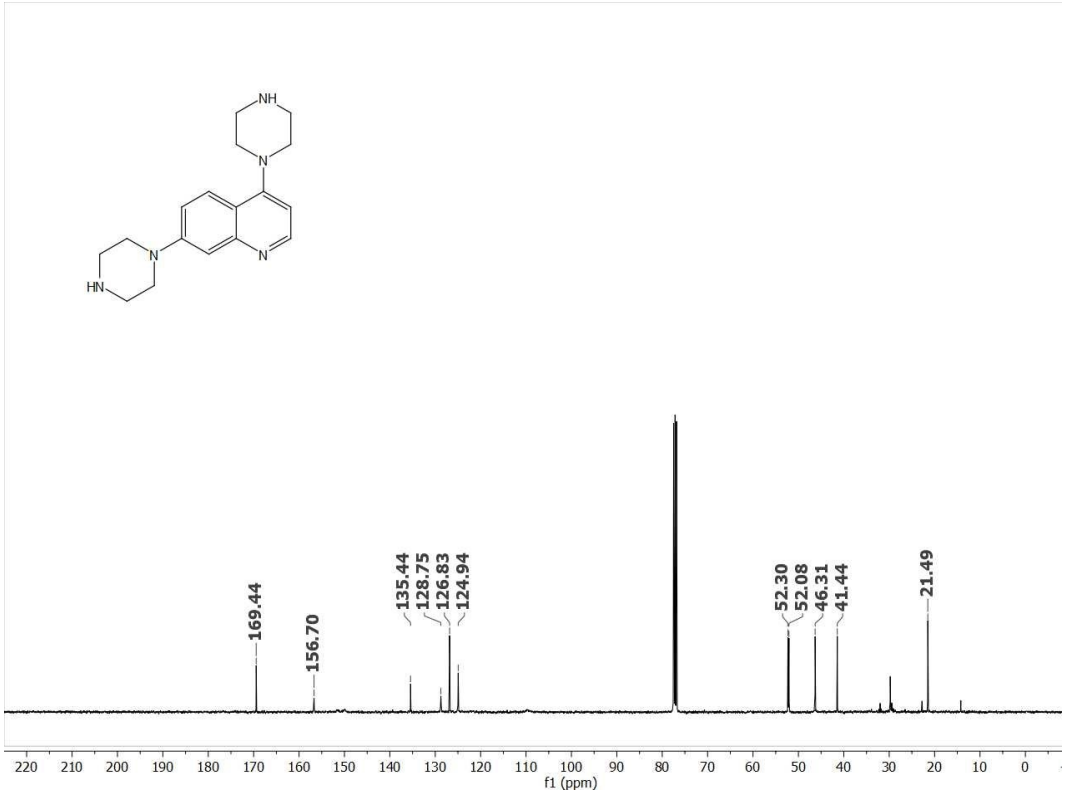


Figure 23: ^{1}H & ^{13}C NMR Spectra of representative compound

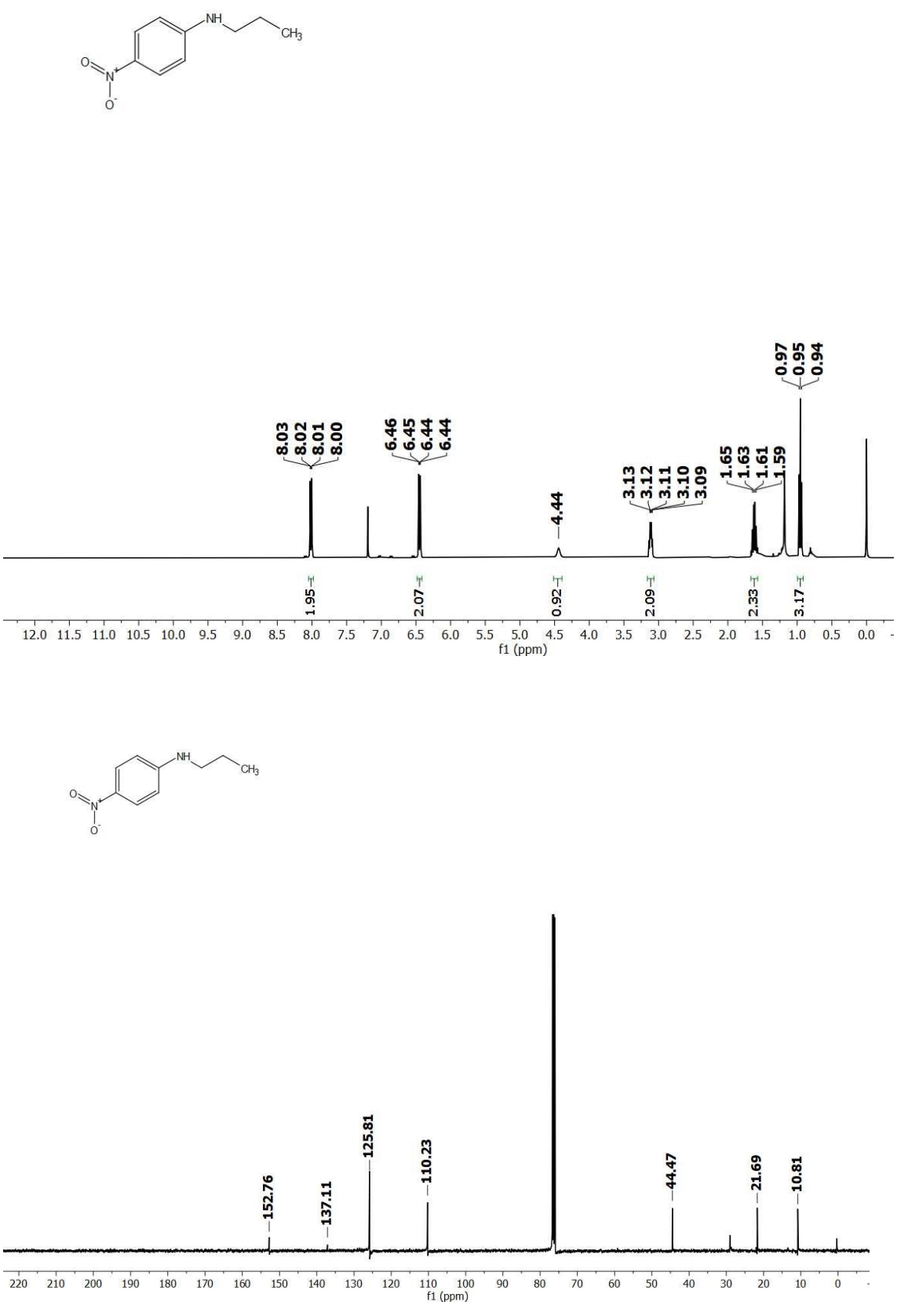


Figure 24: ^{1}H & ^{13}C NMR Spectra of representative compound

Figure 25: ^{1}H & ^{13}C NMR Spectra of representative compound

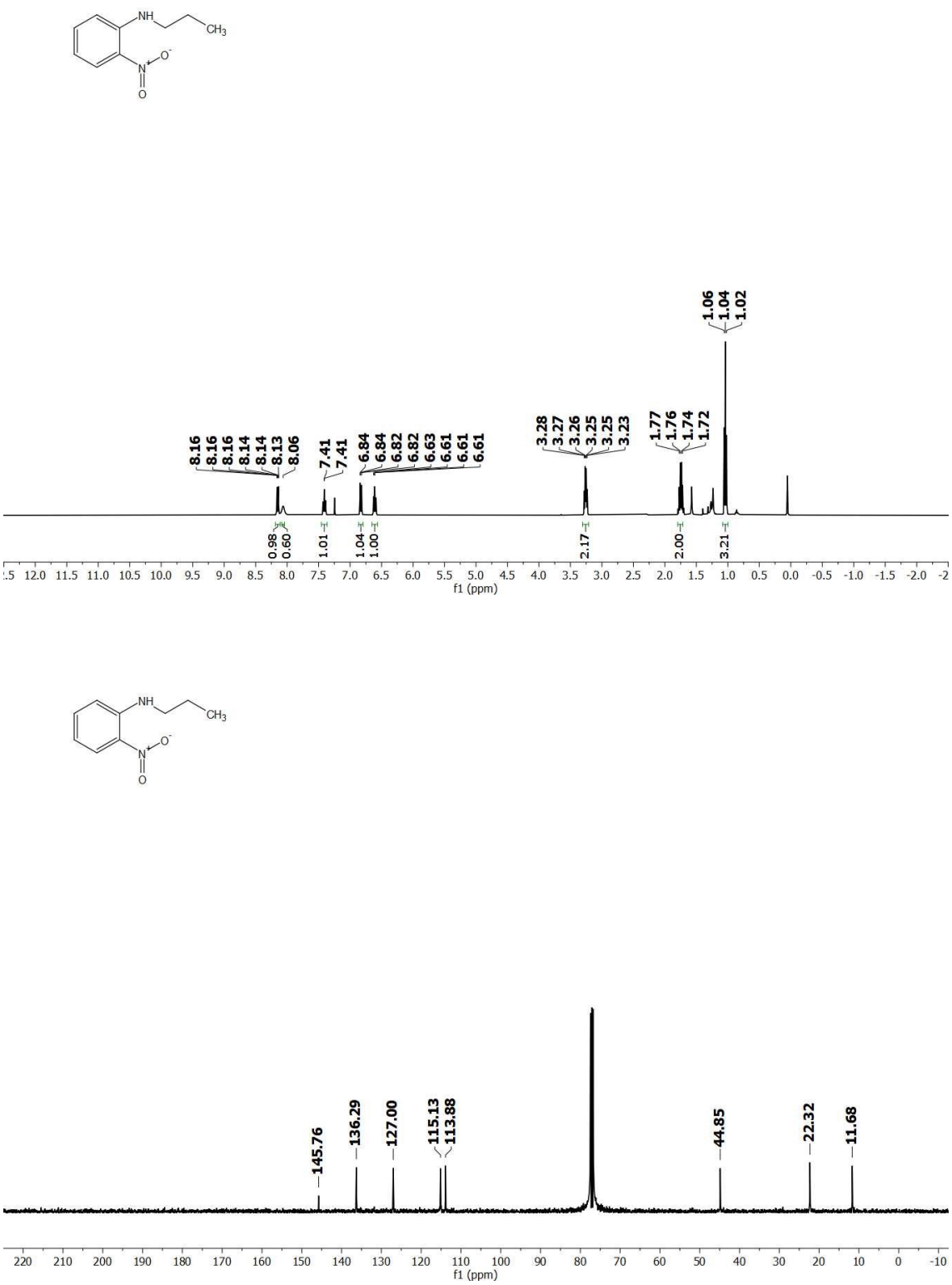


Figure 26: ^{1}H & ^{13}C NMR Spectra of representative compound

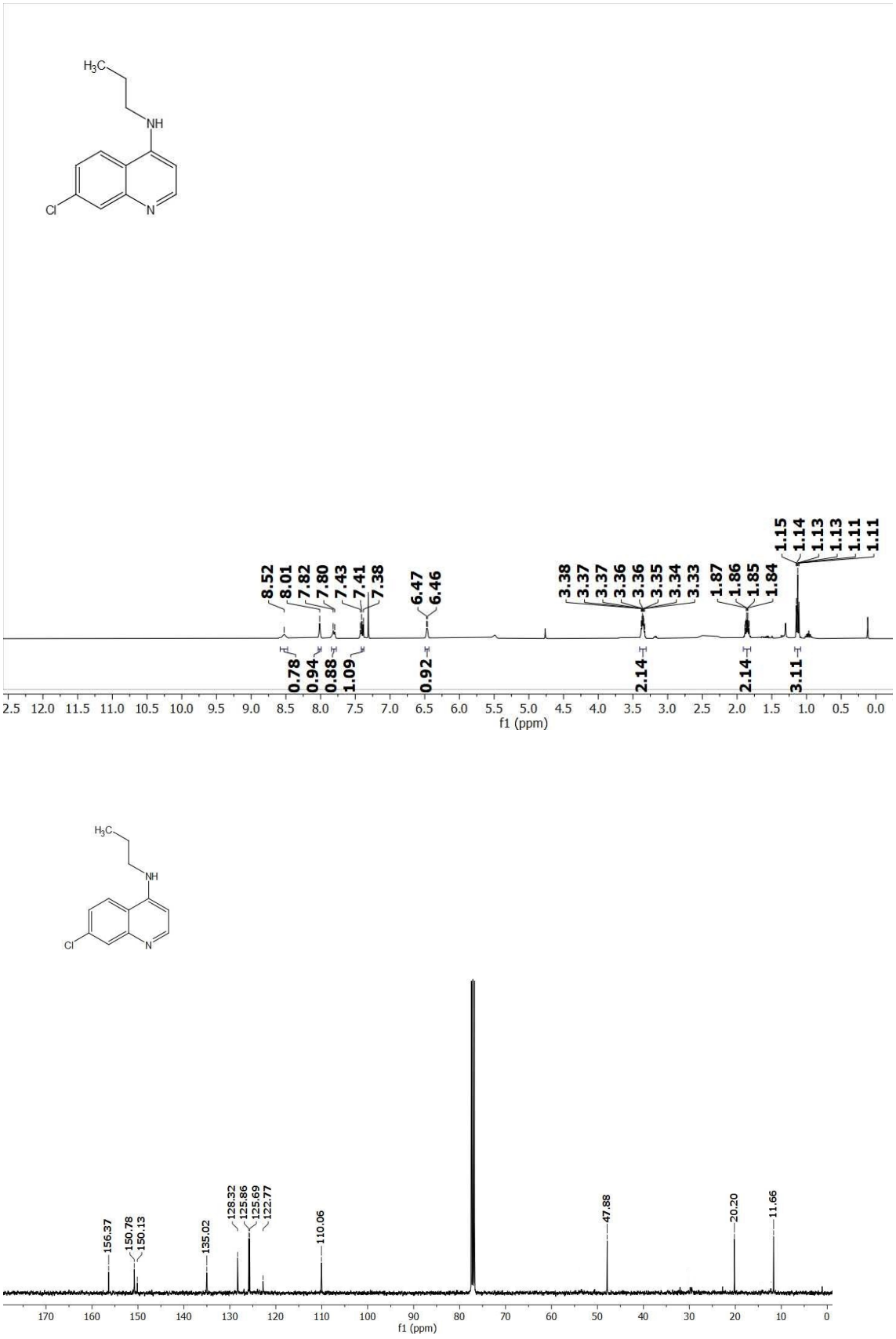
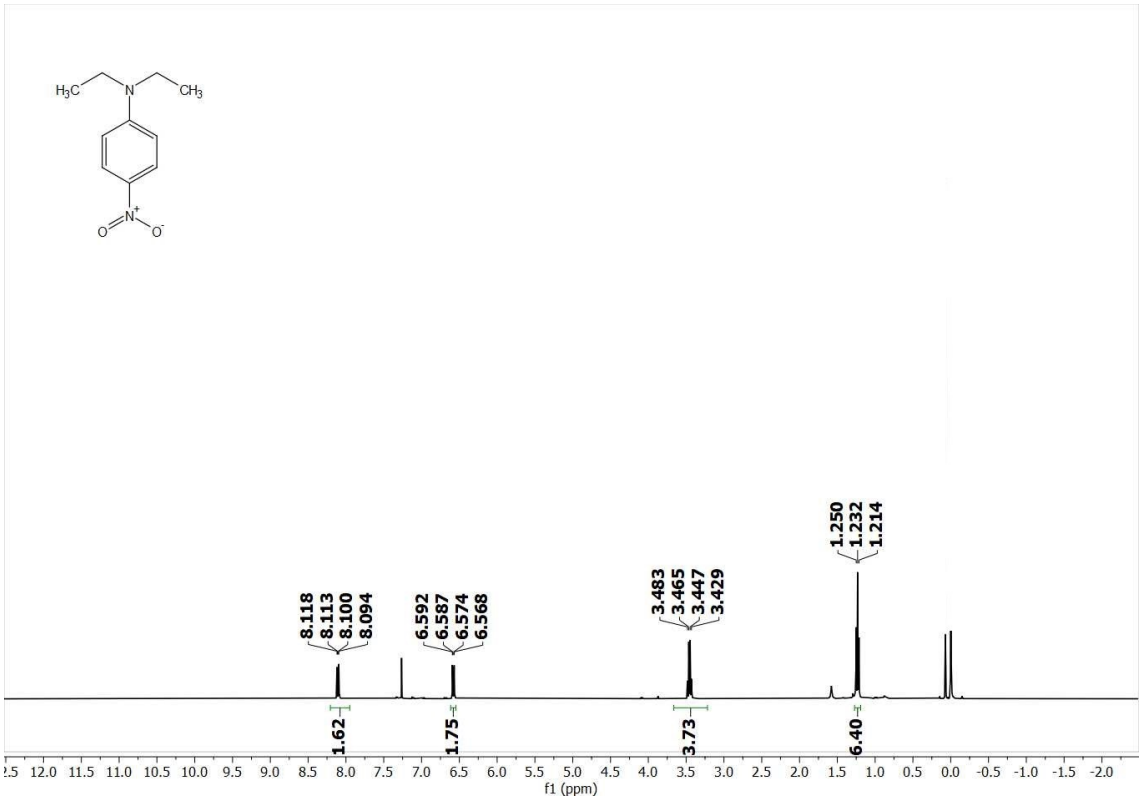


Figure 27: ^{1}H & ^{13}C NMR Spectra of representative compound



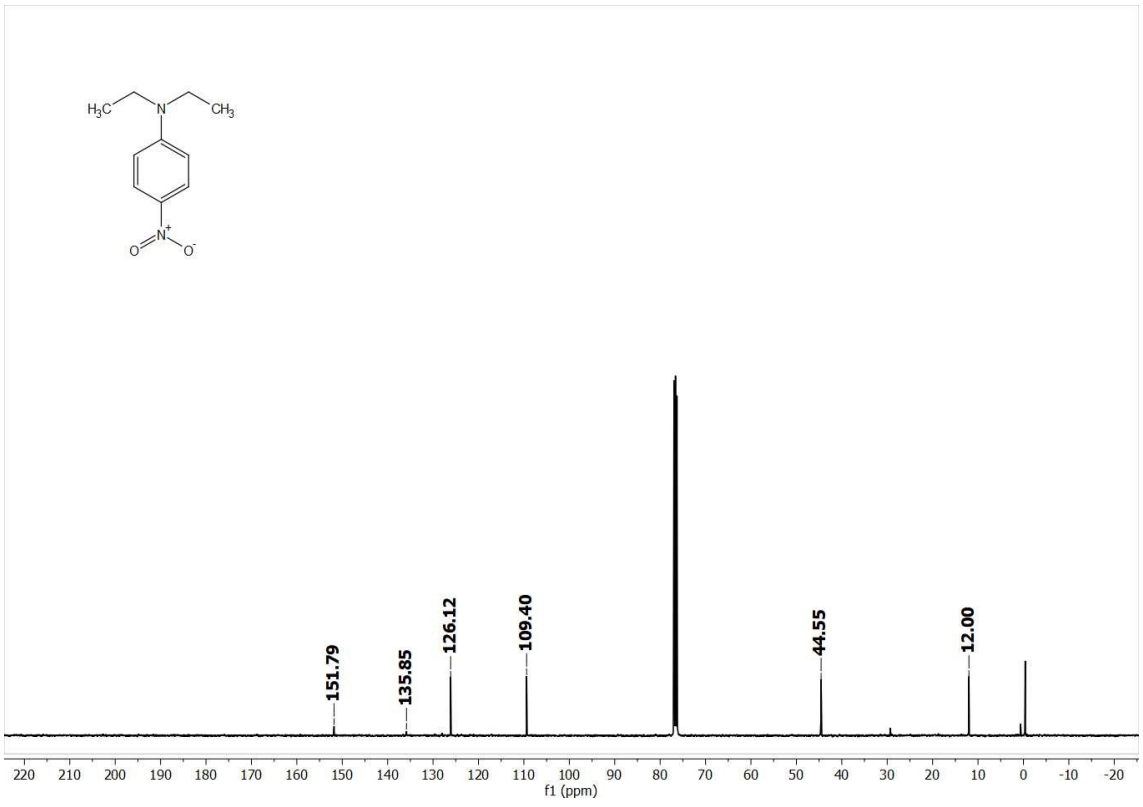


Figure 28: ^{1}H & ^{13}C NMR Spectra of representative compound

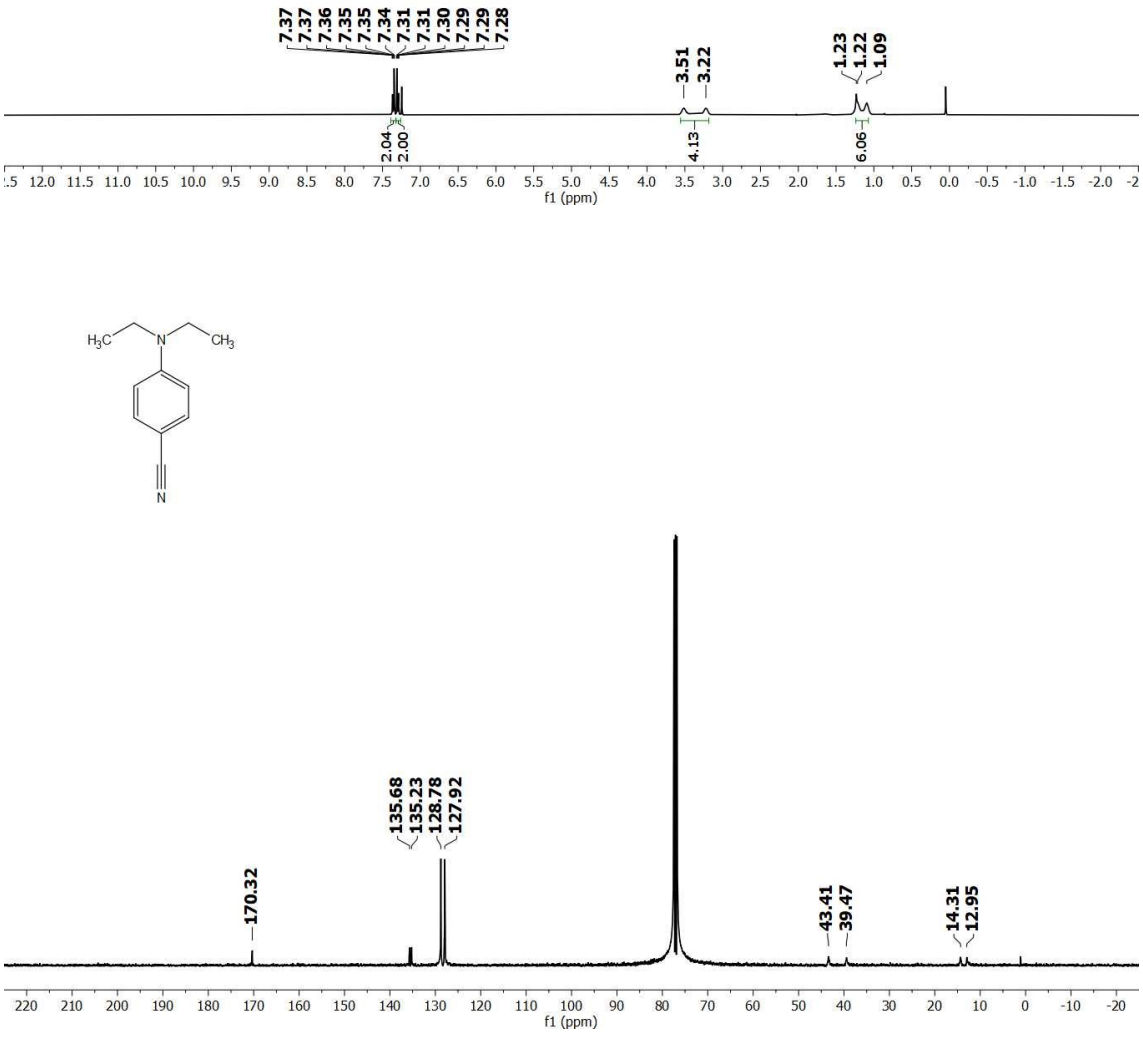


Figure 29: ^{1}H & ^{13}C NMR Spectra of representative compound

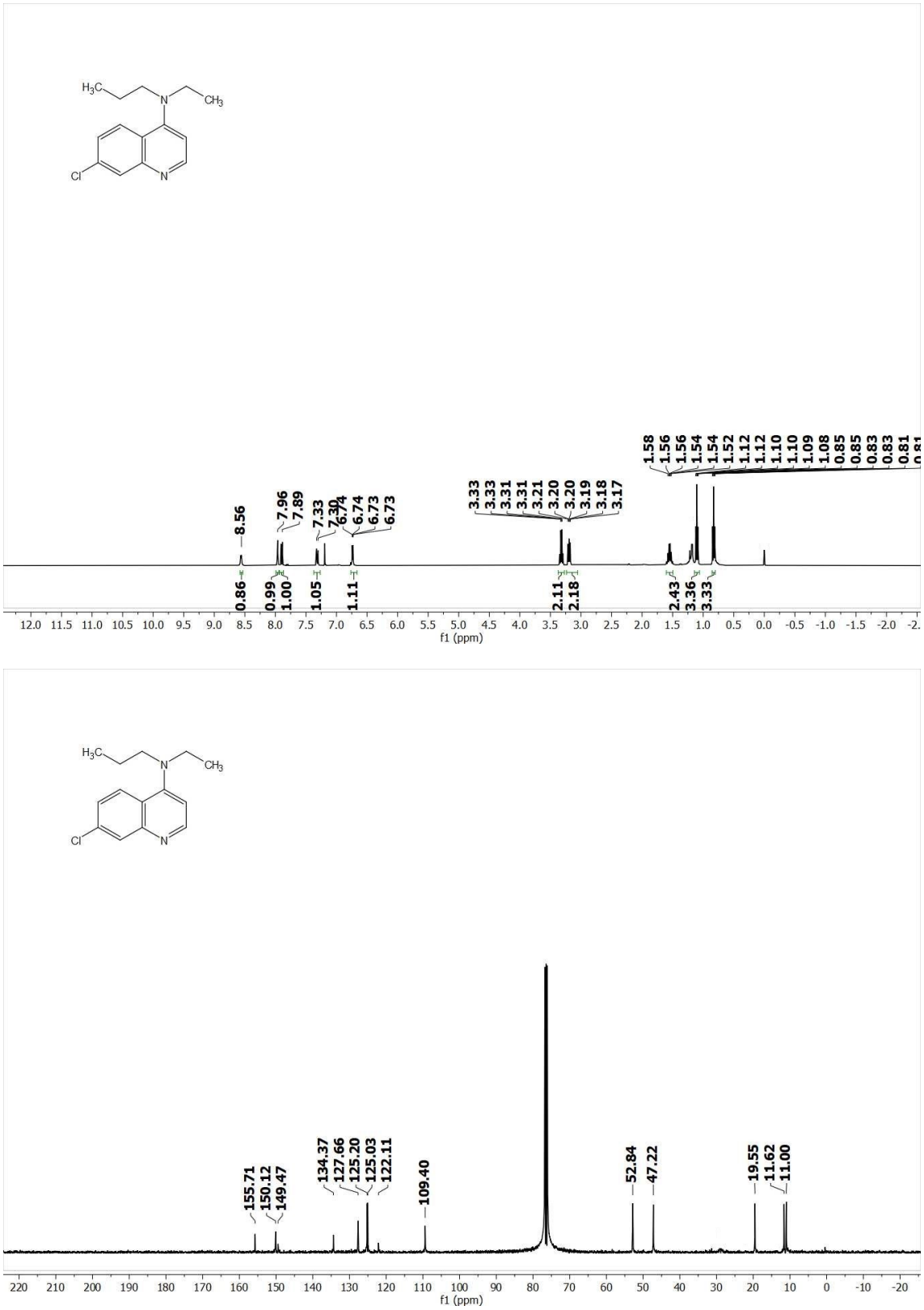


Figure 30: ^{1}H & ^{13}C NMR Spectra of representative compound

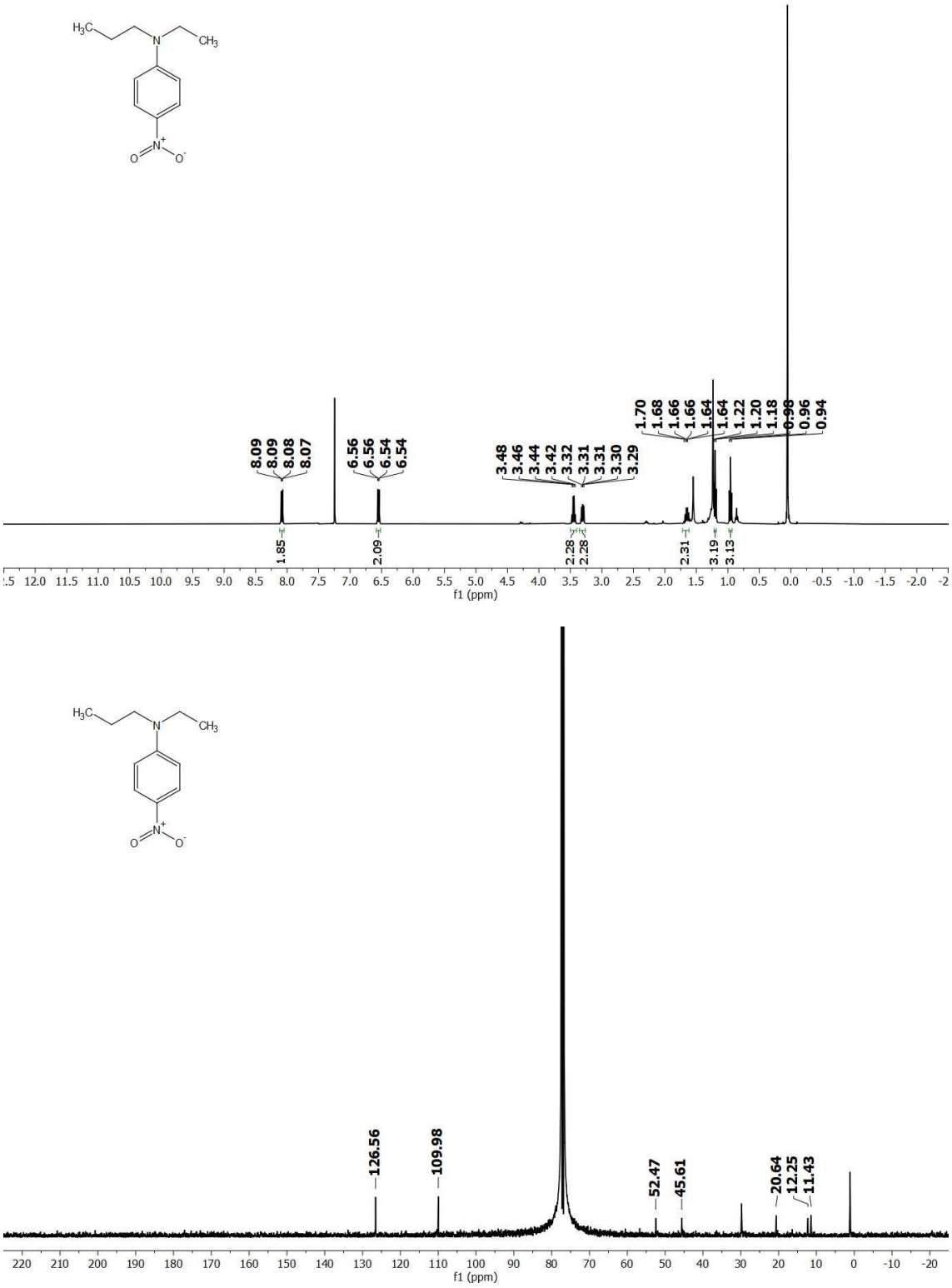


Figure 31: ^{1}H & ^{13}C NMR Spectra of representative compound

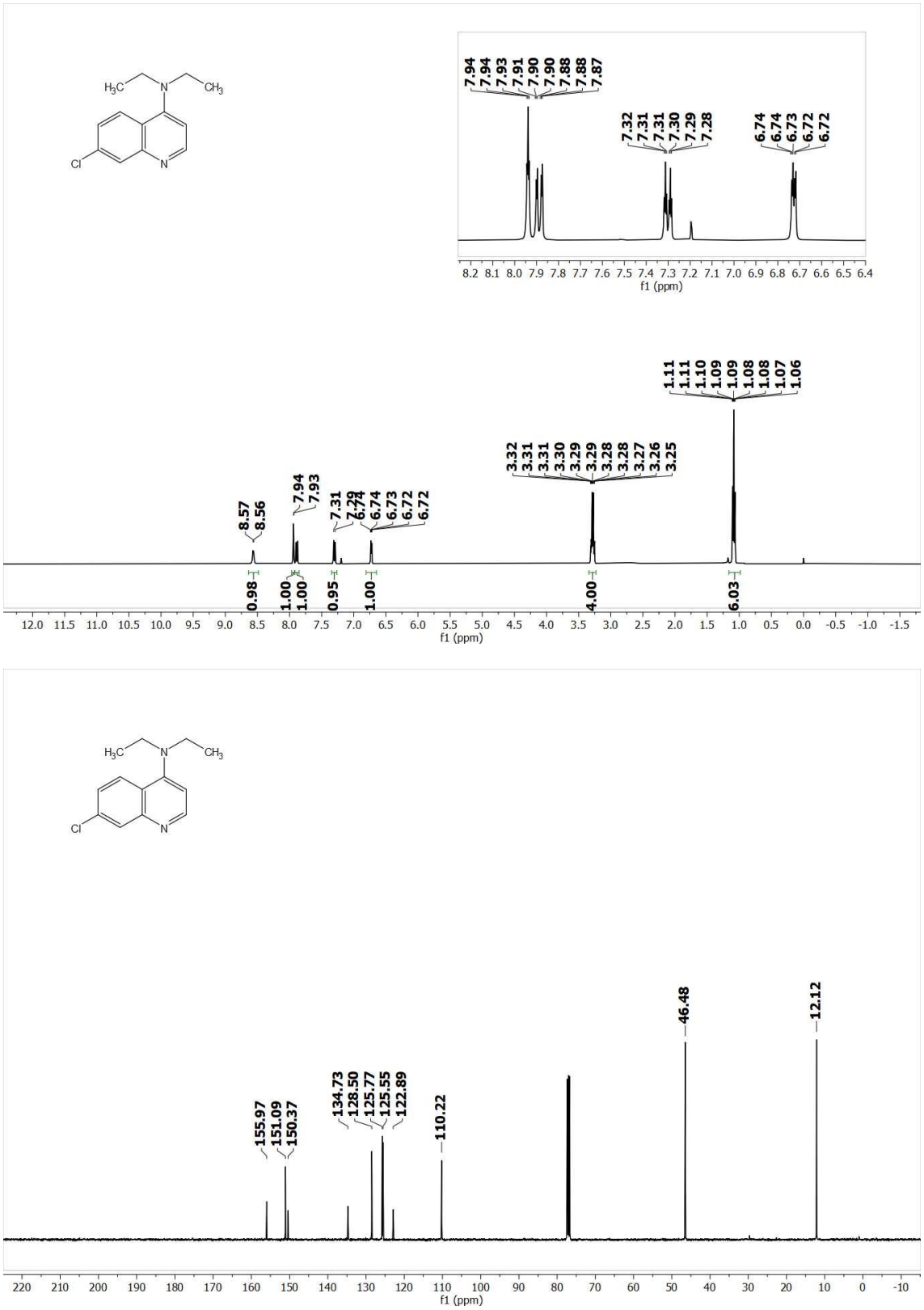


Figure 32: ^{1}H & ^{13}C NMR Spectra of representative compound

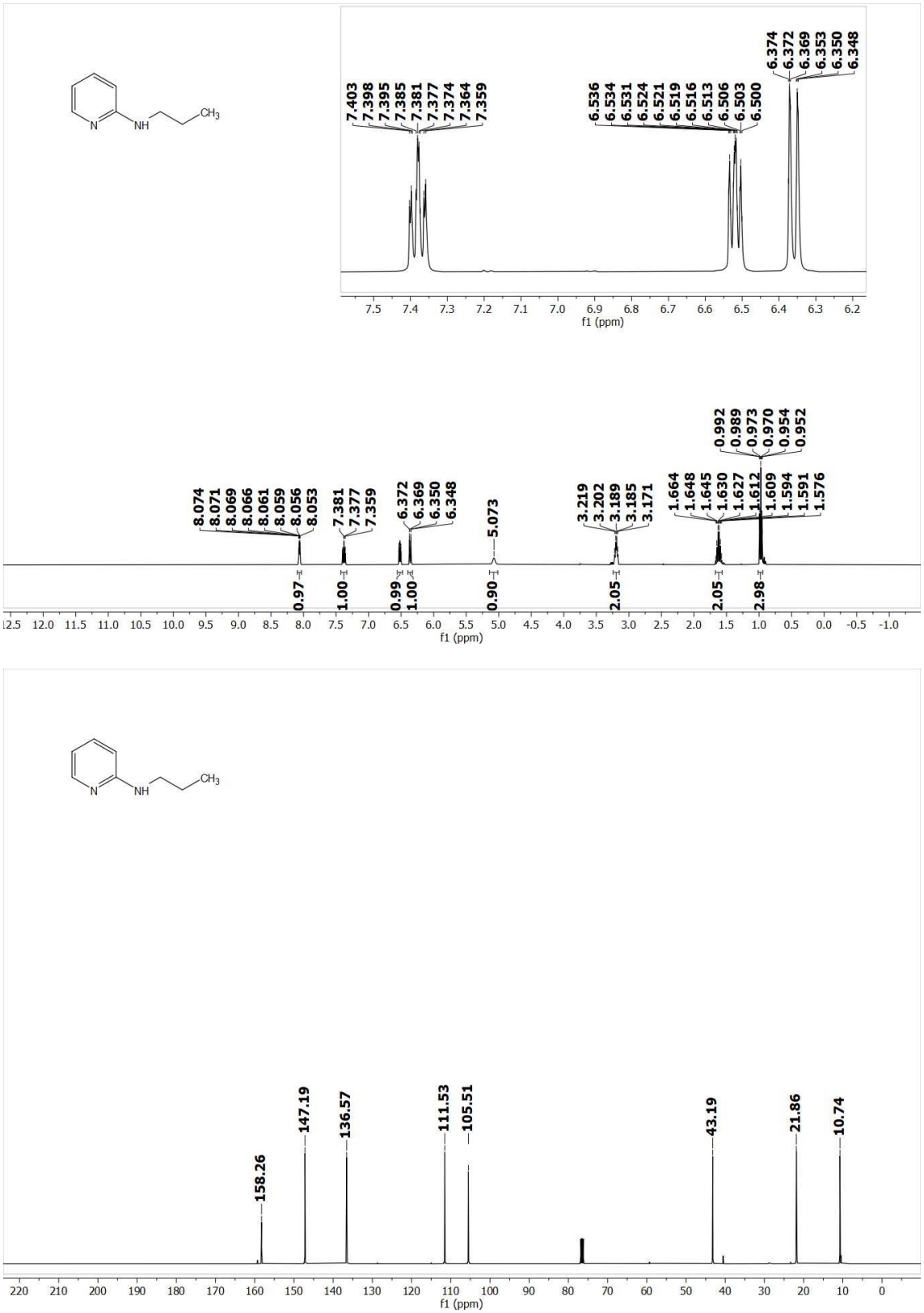
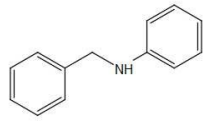
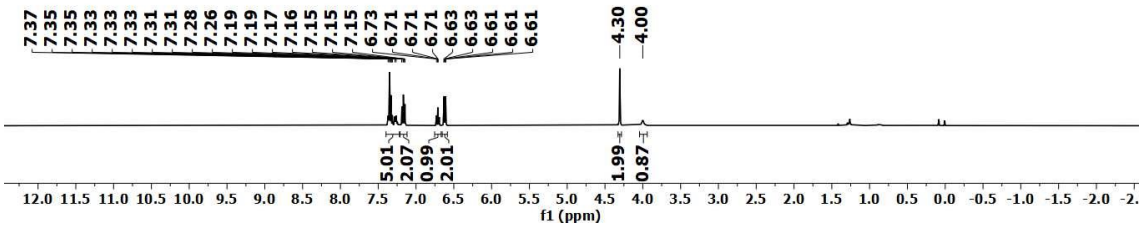
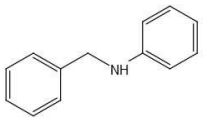


Figure 33: ^{1}H & ^{13}C NMR Spectra of representative compound







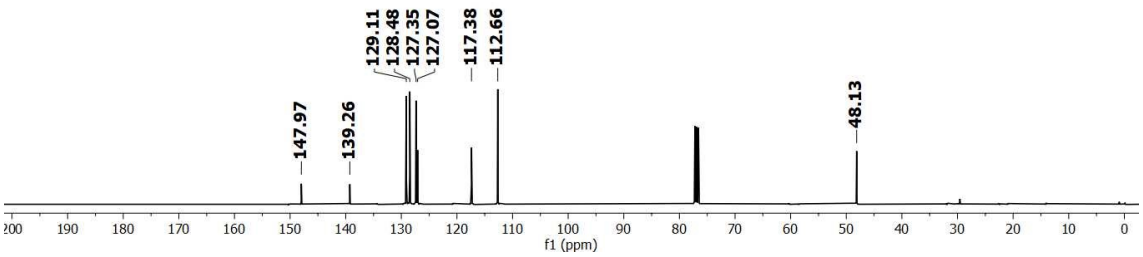


Figure 34: ^{1}H & ^{13}C NMR Spectra of representative compound

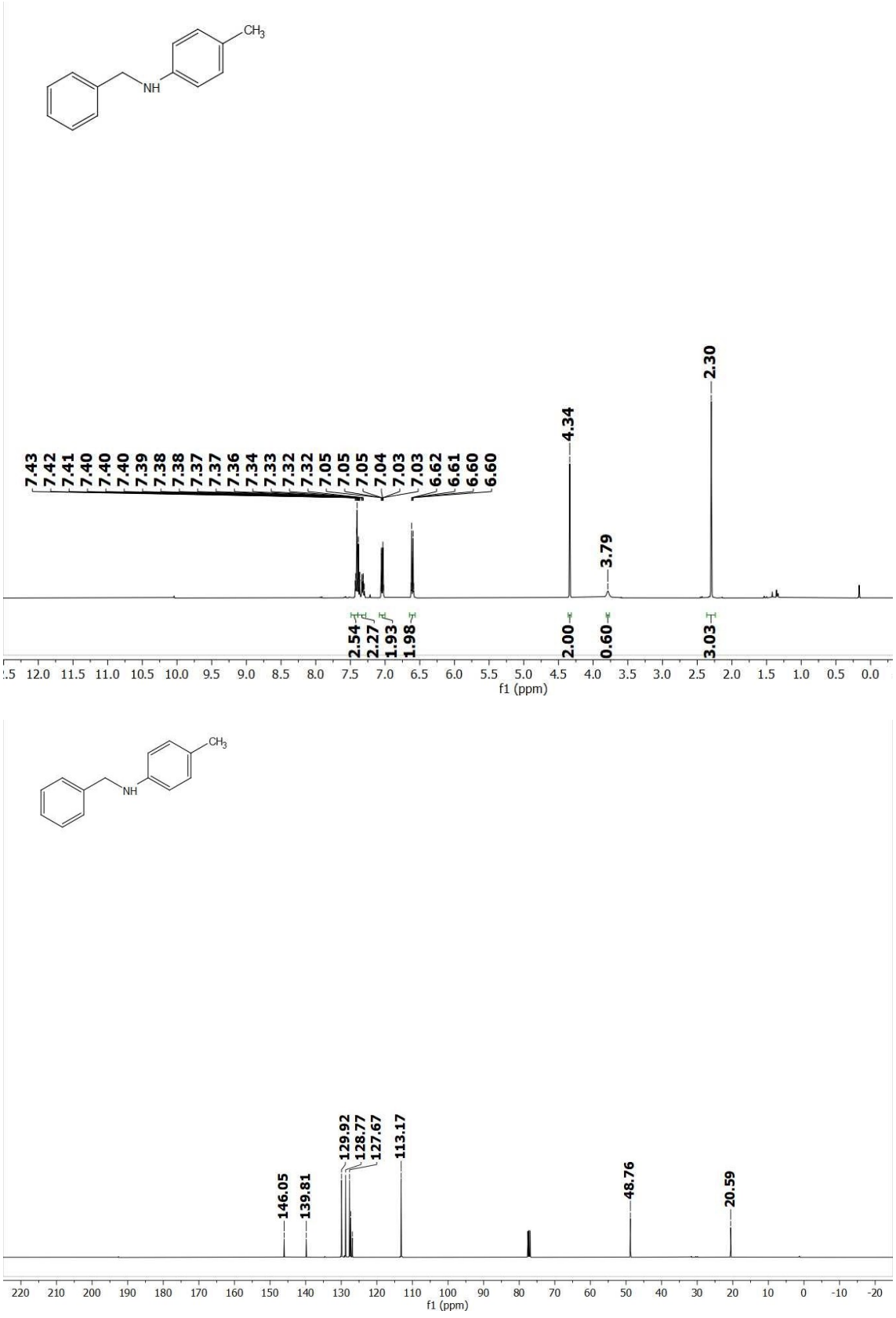


Figure 35: ^{1}H & ^{13}C NMR Spectra of representative compound

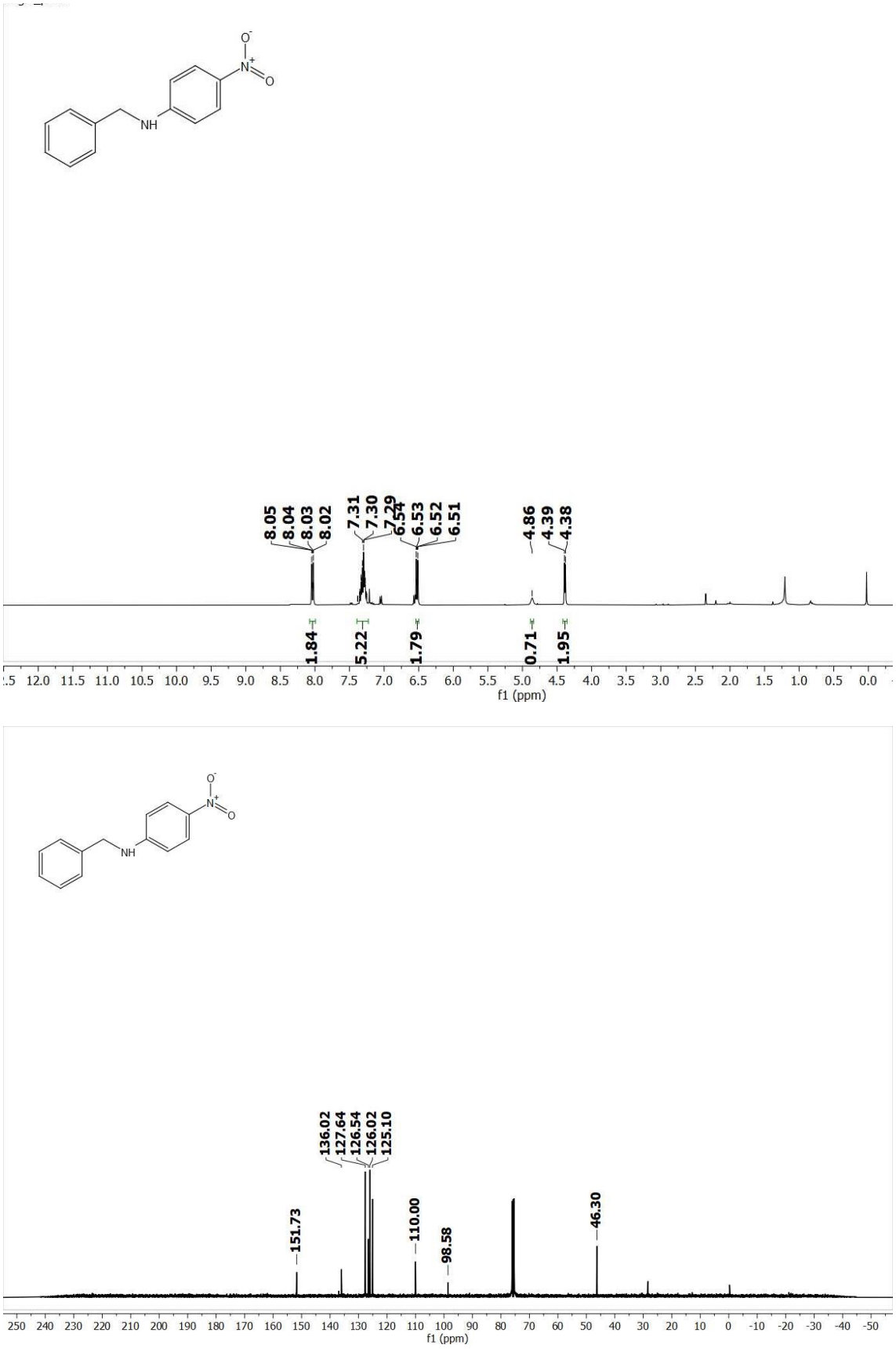


Figure 36: ^{1}H & ^{13}C NMR Spectra of representative compound

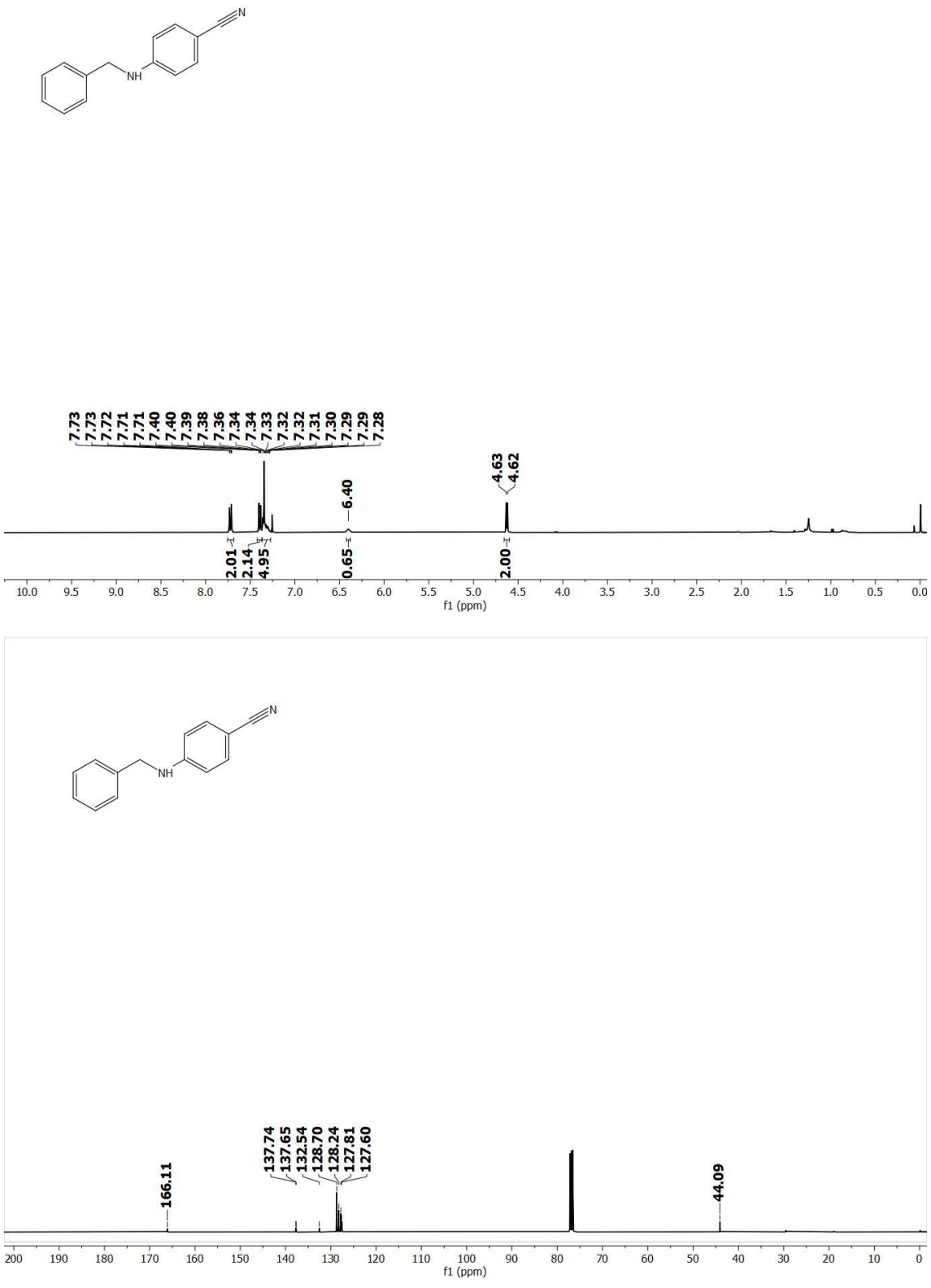


Figure 37: ^{1}H & ^{13}C NMR Spectra of representative compound

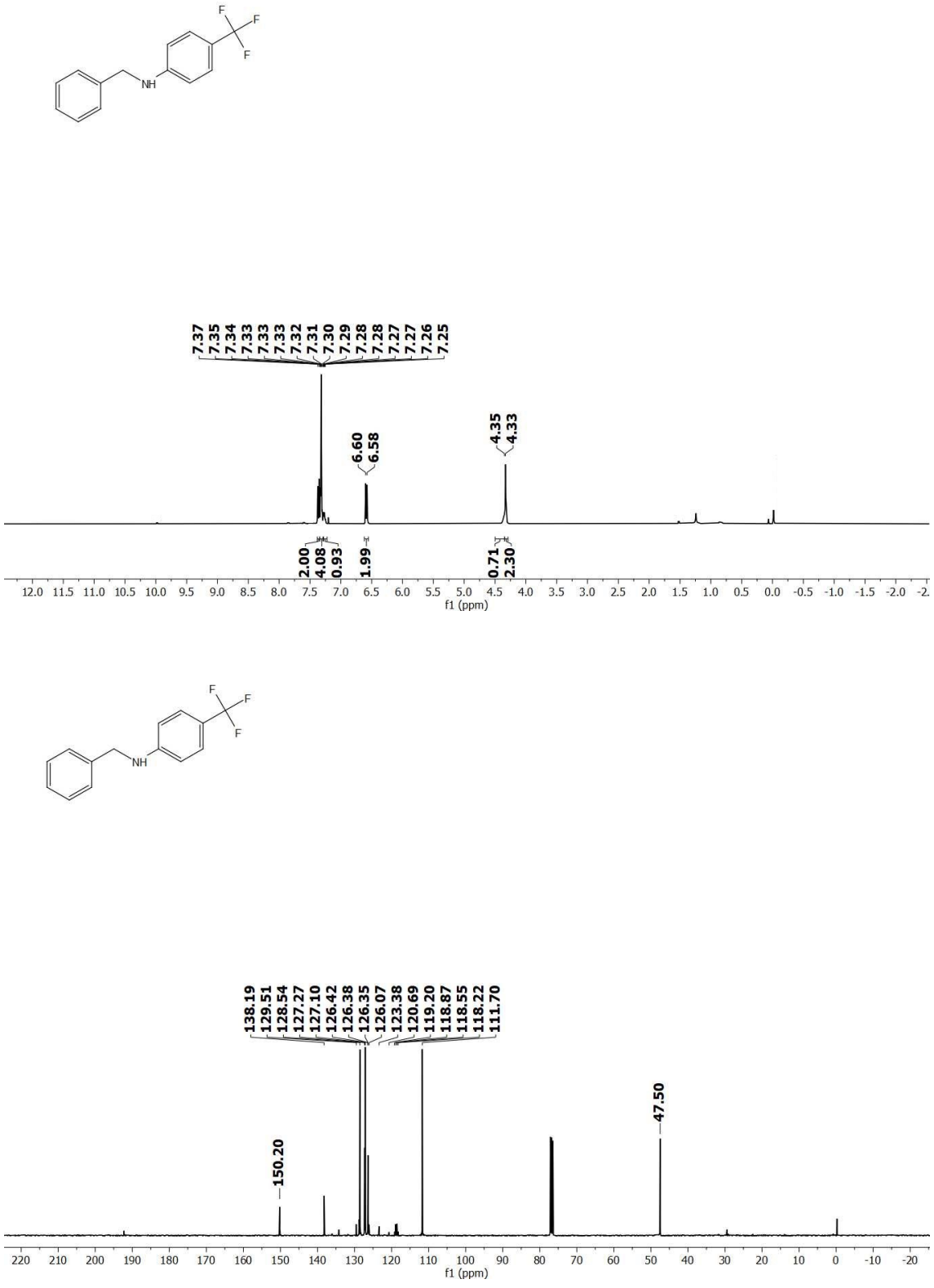
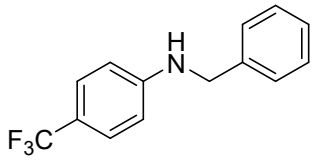


Figure 38: ^{1}H & ^{13}C NMR Spectra of representative compound



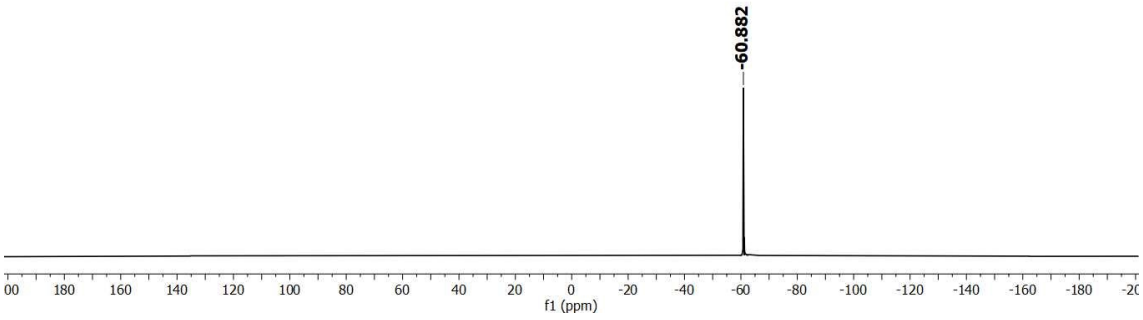


Figure 39: ^{19}FNMR Spectra of representative compound

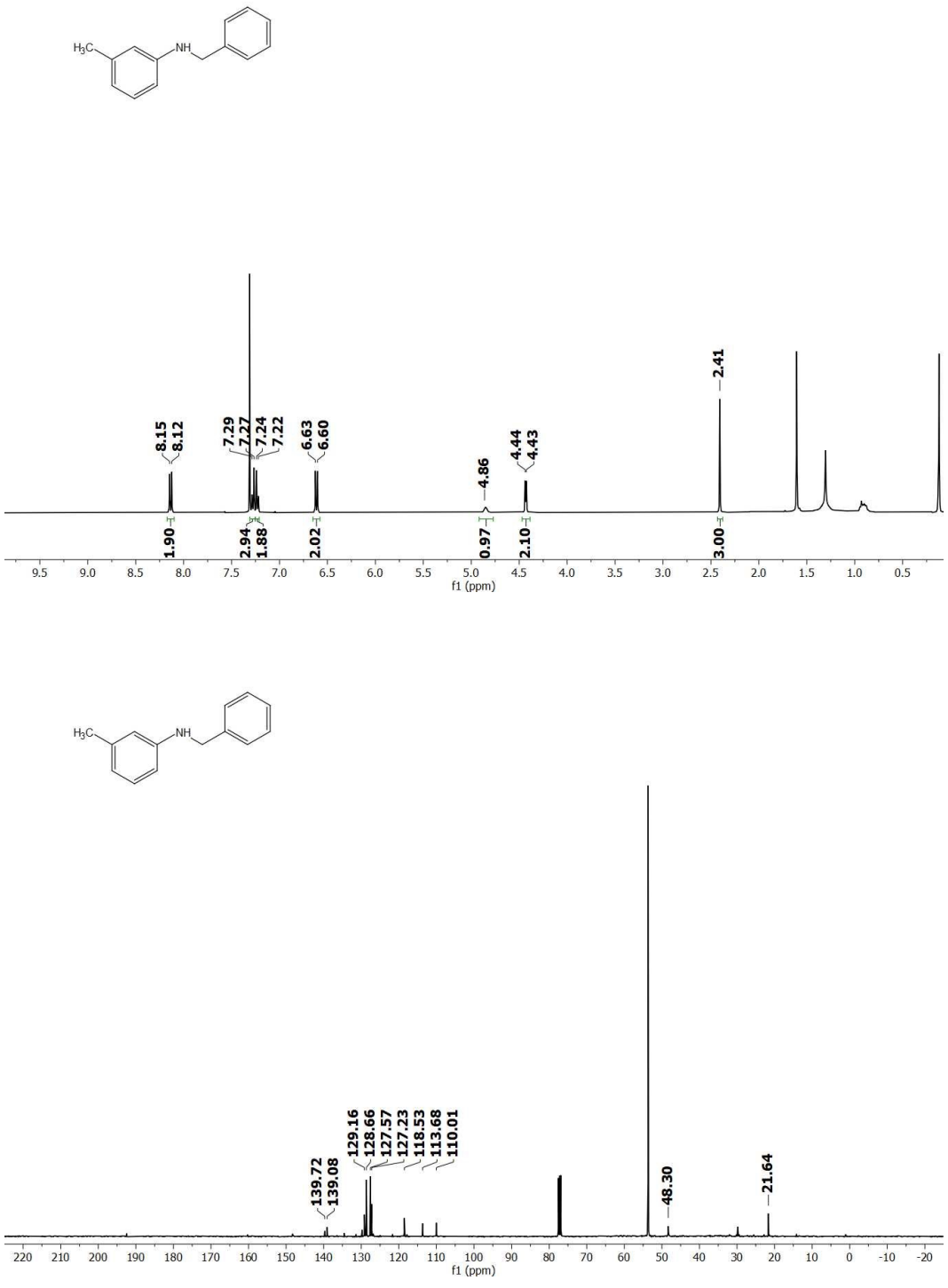


Figure 40: ^{1}H & ^{13}C NMR Spectra of representative compound

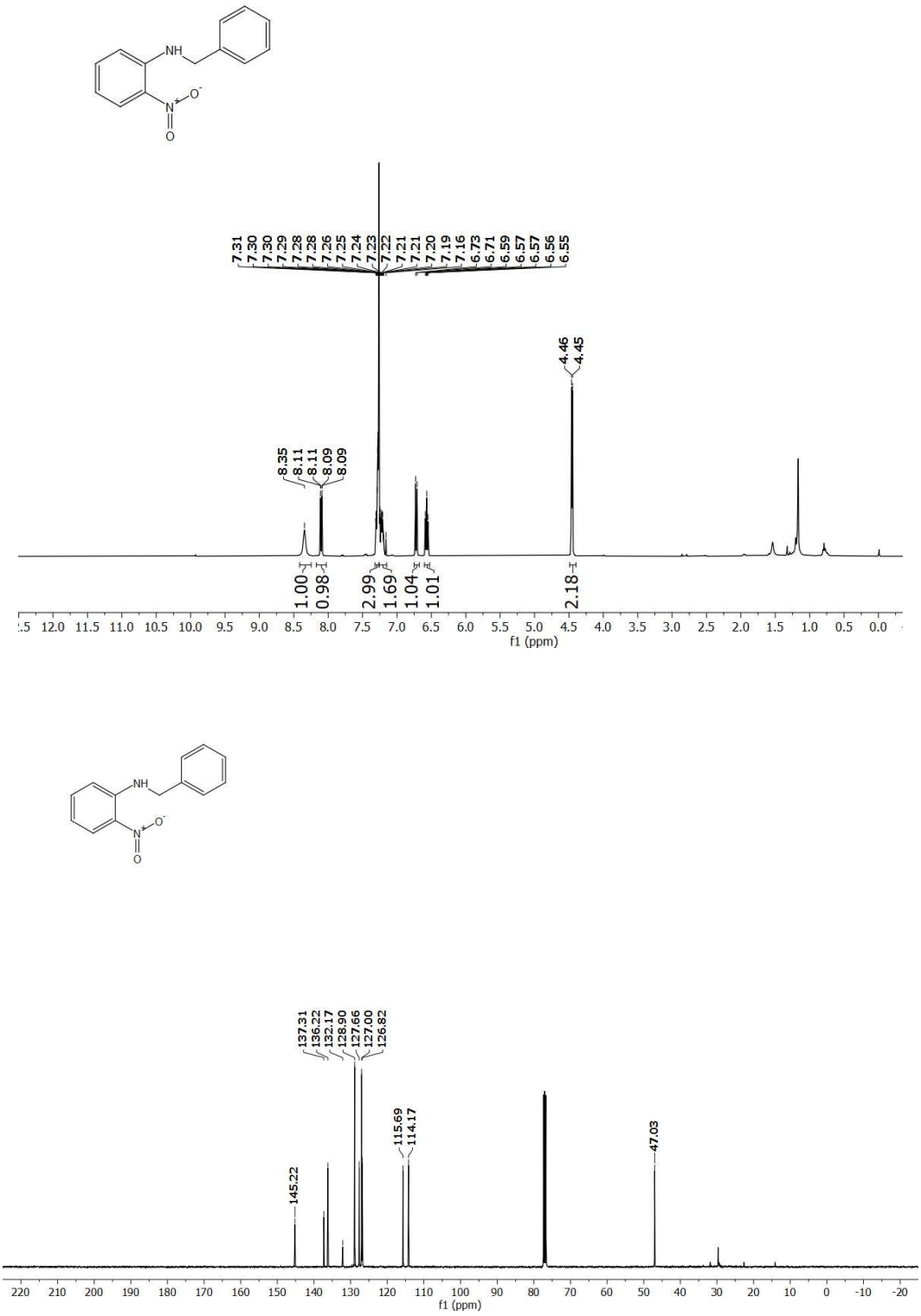
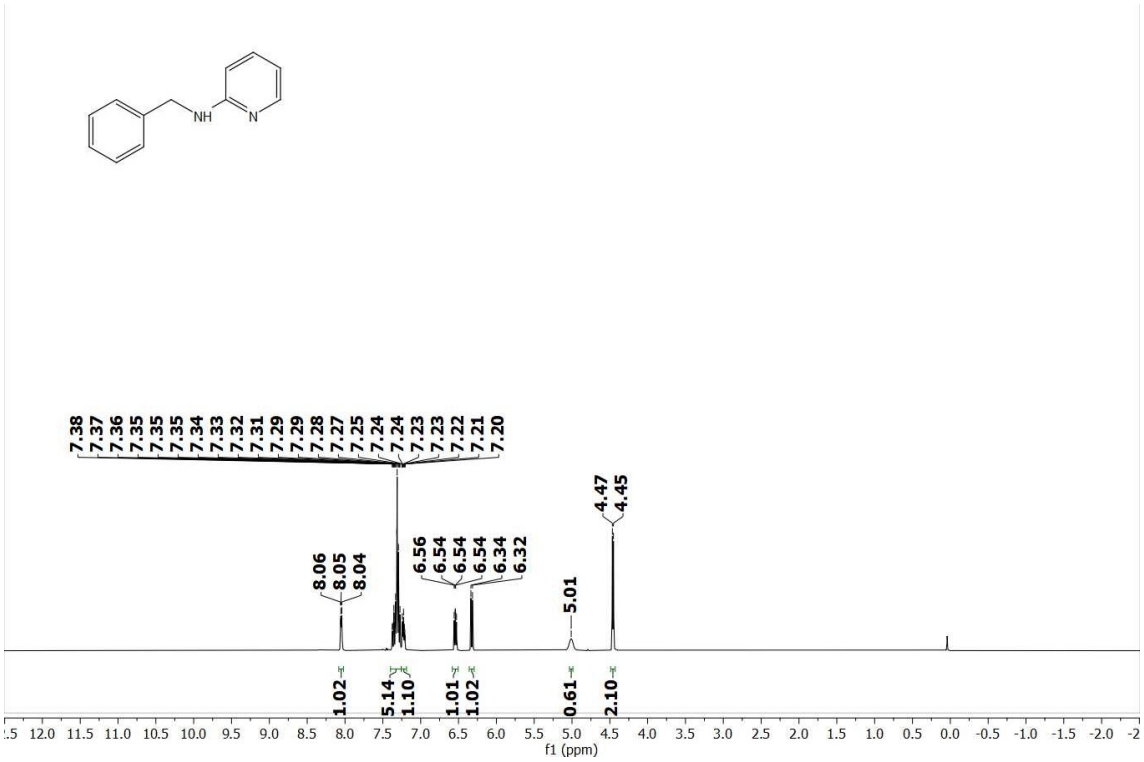


Figure 41: ^{1}H & ^{13}C NMR Spectra of representative compound



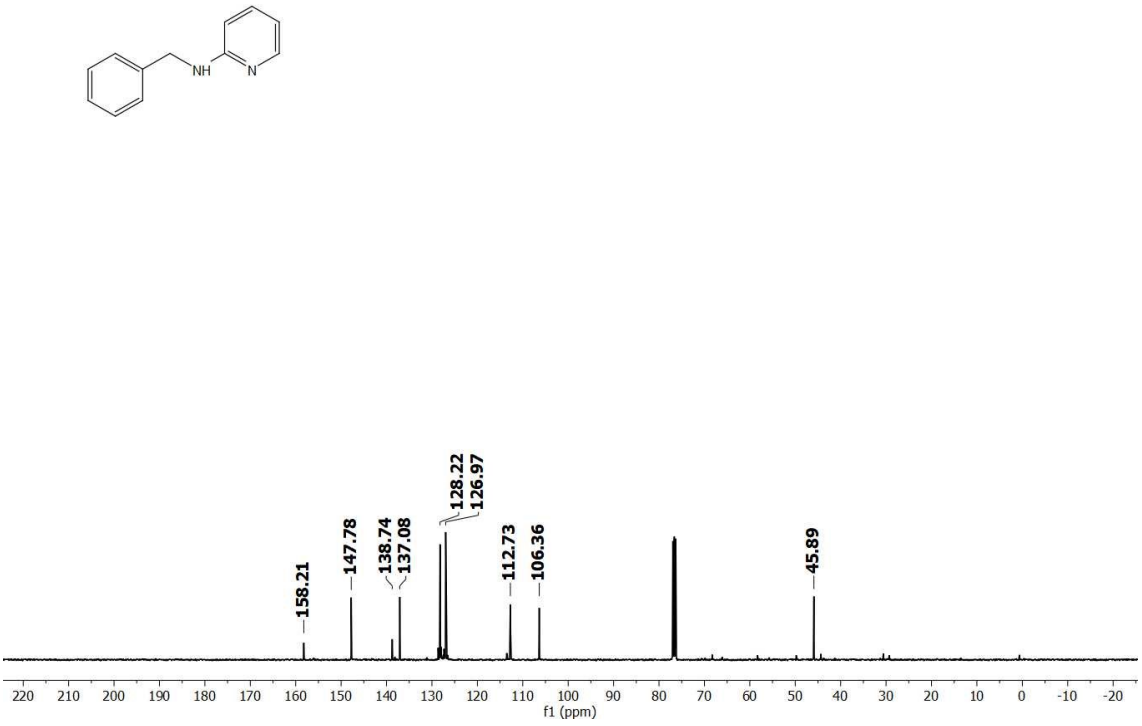


Figure 42: ^{1}H & ^{13}C NMR Spectra of representative compound

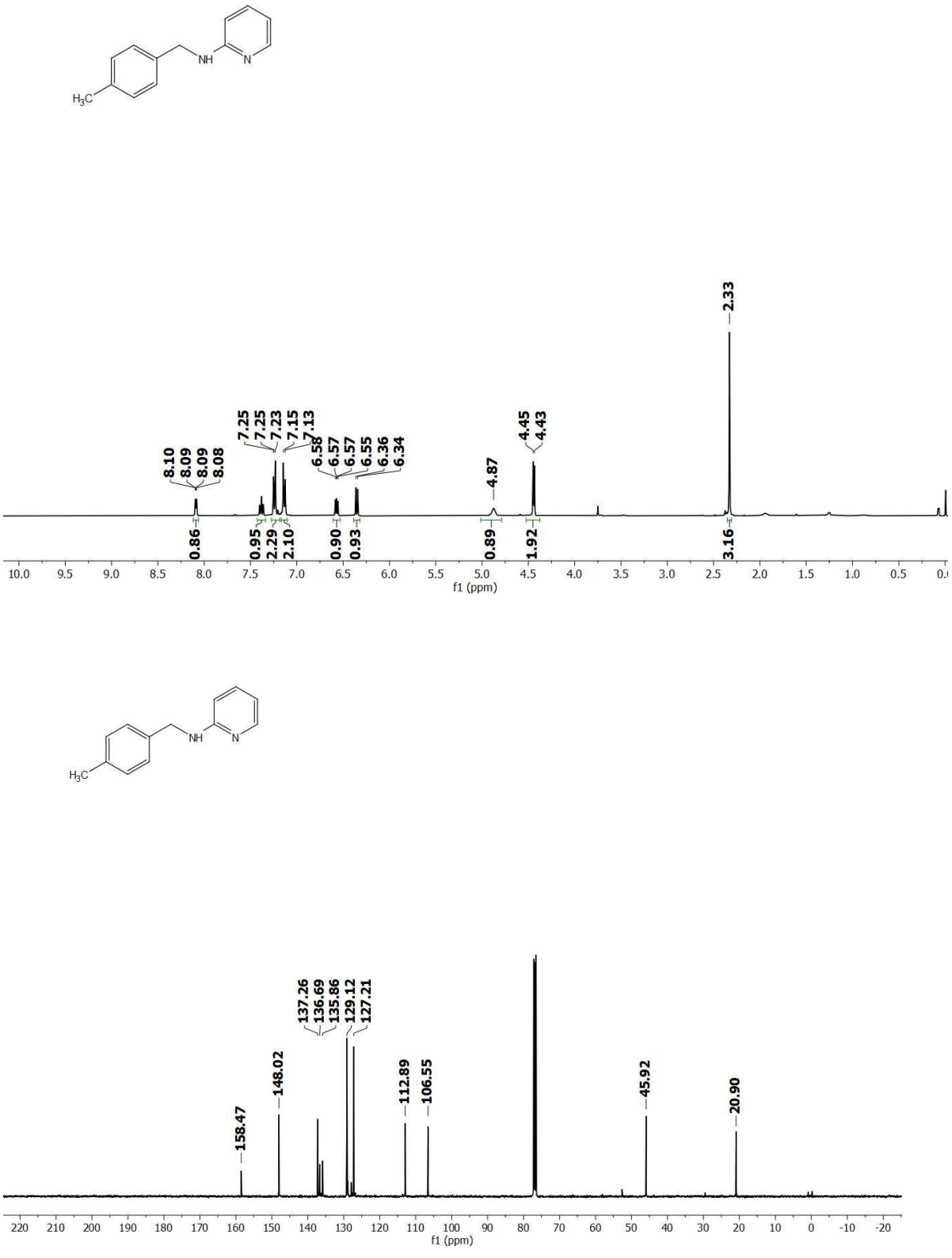


Figure 43: ^{1}H & ^{13}C NMR Spectra of representative compound

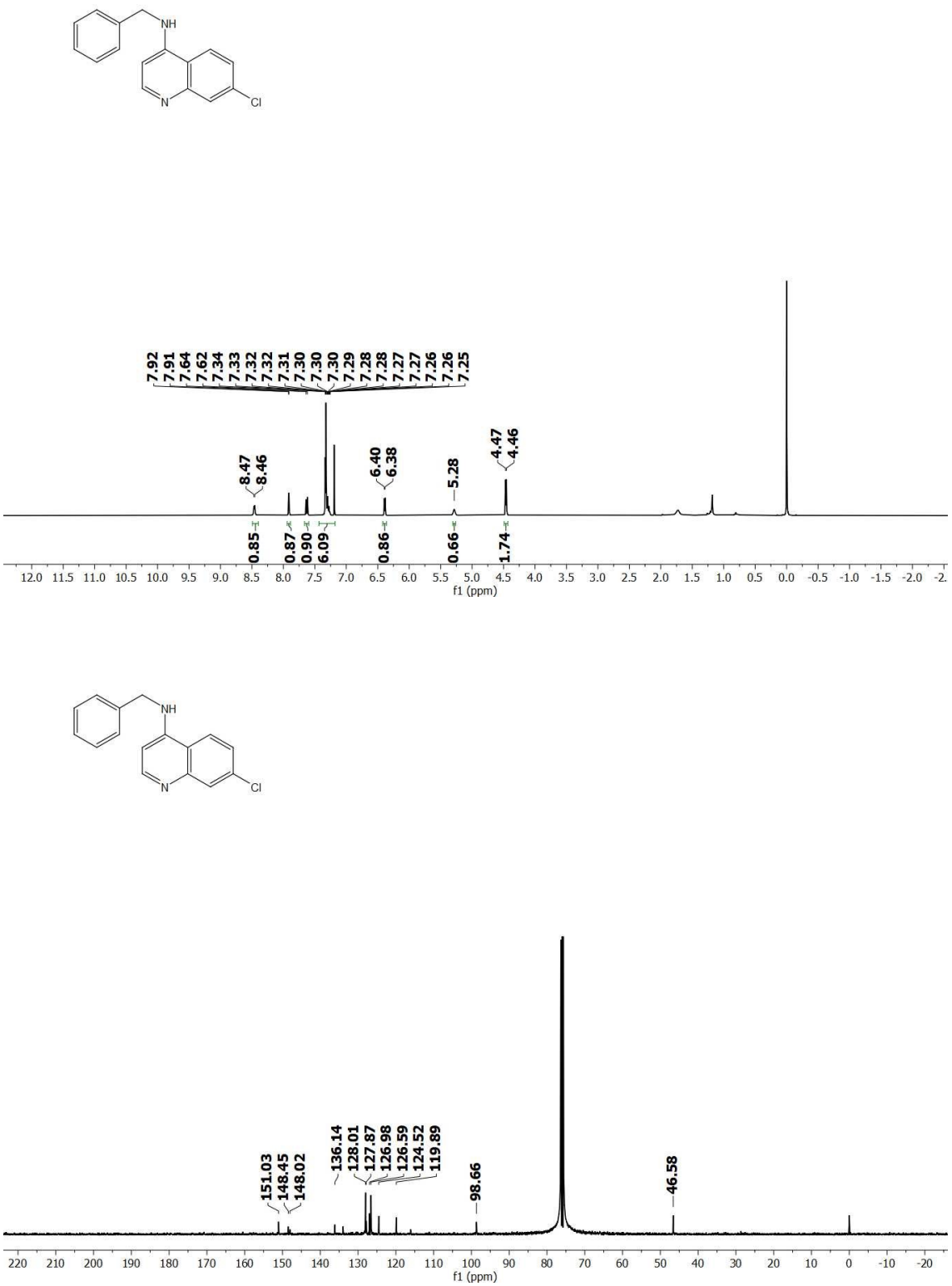


Figure 44: ^{1}H & ^{13}C NMR Spectra of representative compound

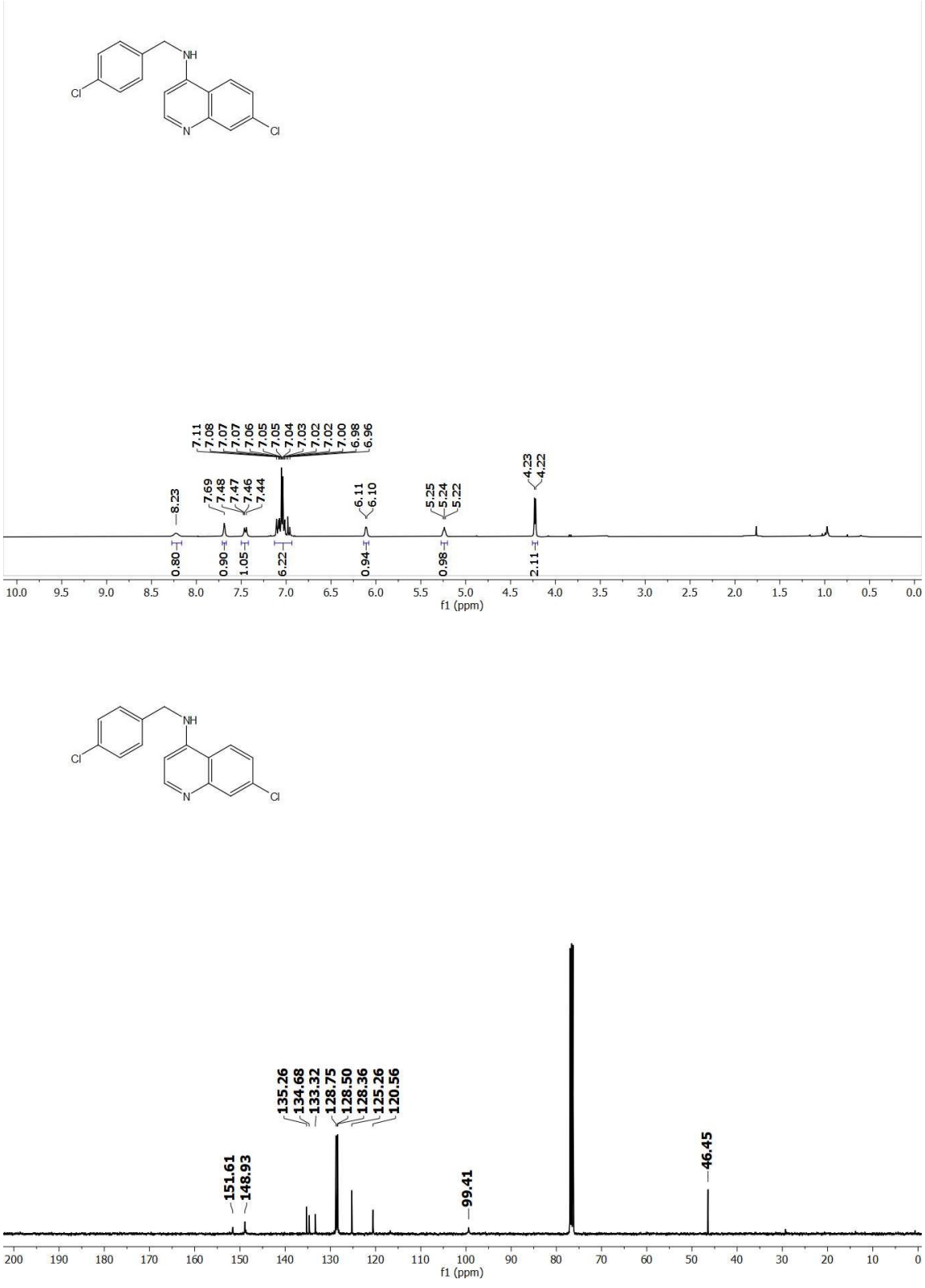


Figure 45: ^{1}H & ^{13}C NMR Spectra of representative compound

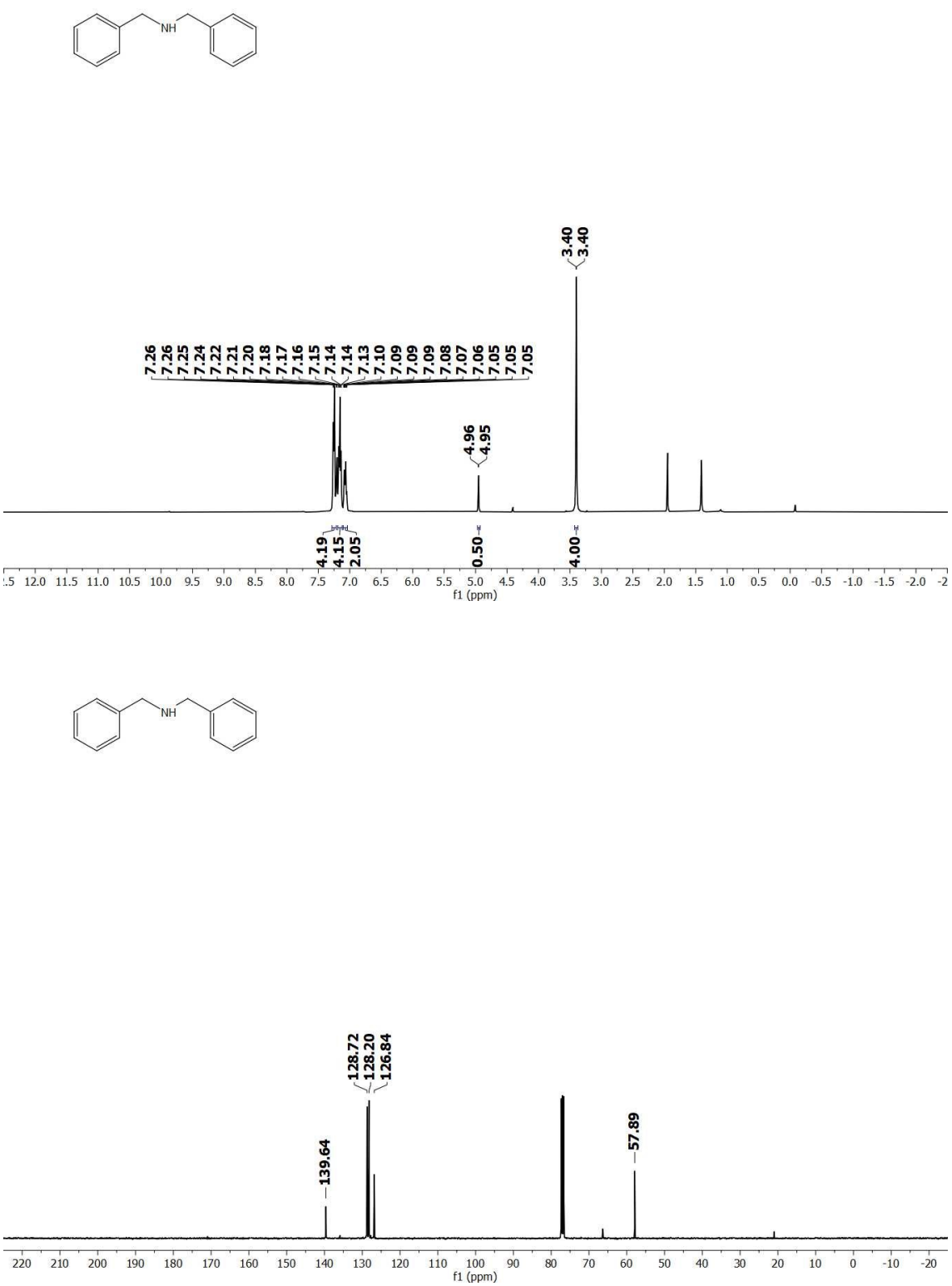
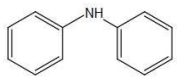
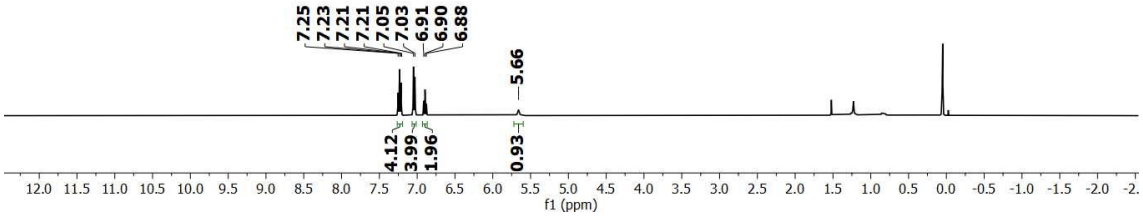
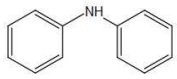


Figure 46: ^{1}H & ^{13}C NMR Spectra of representative compound







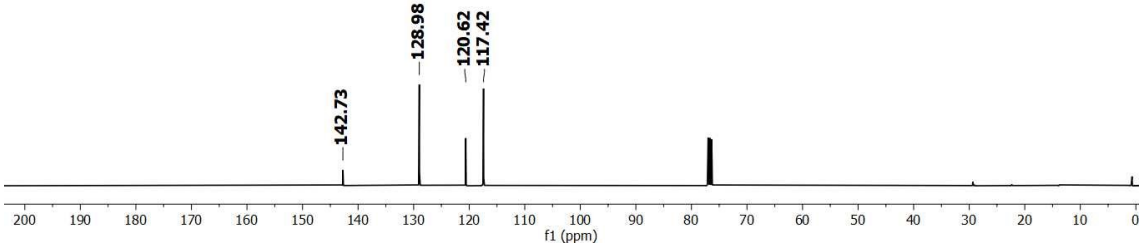


Figure 47: ^{1}H & ^{13}C NMR Spectra of representative compound

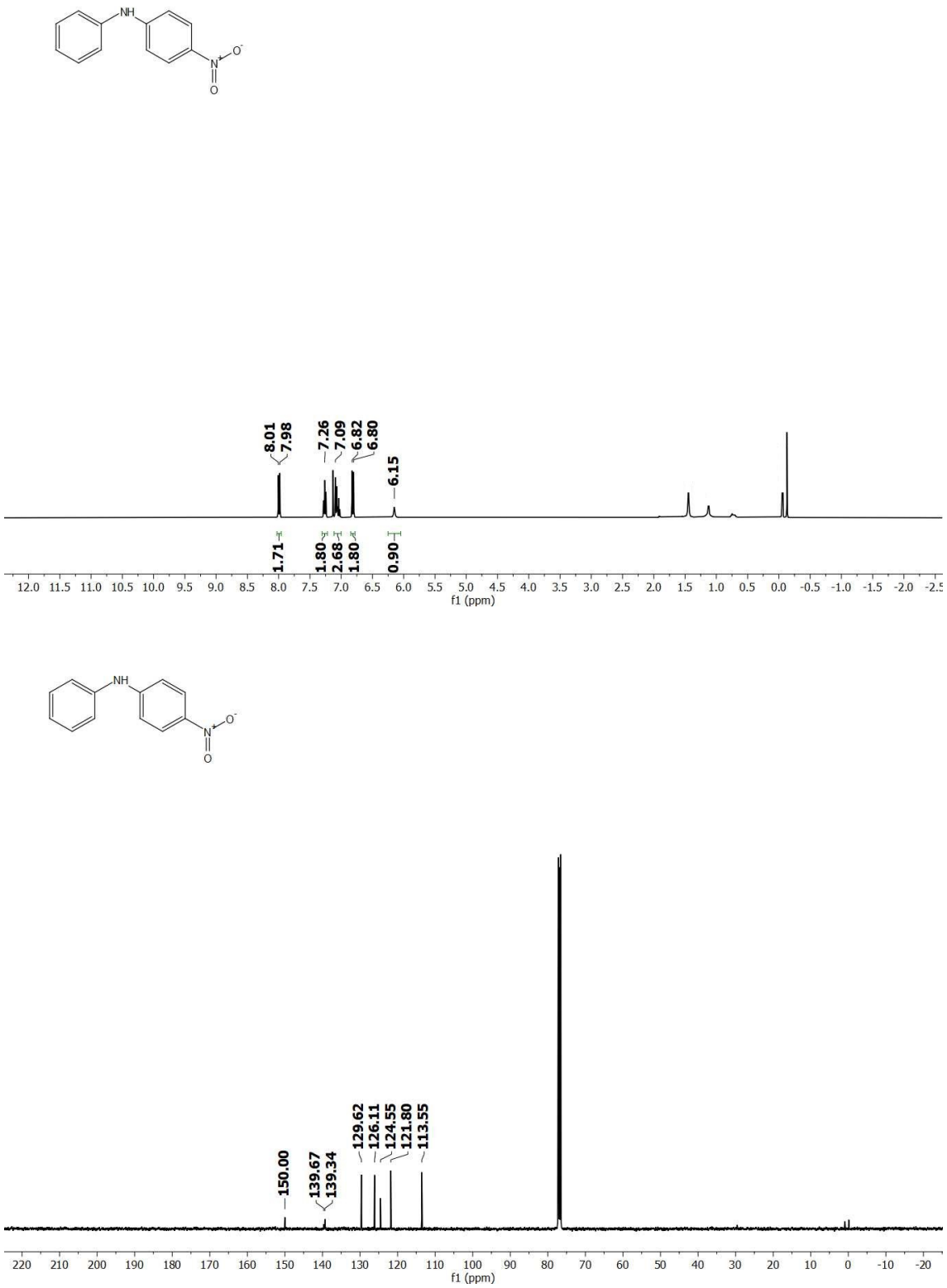
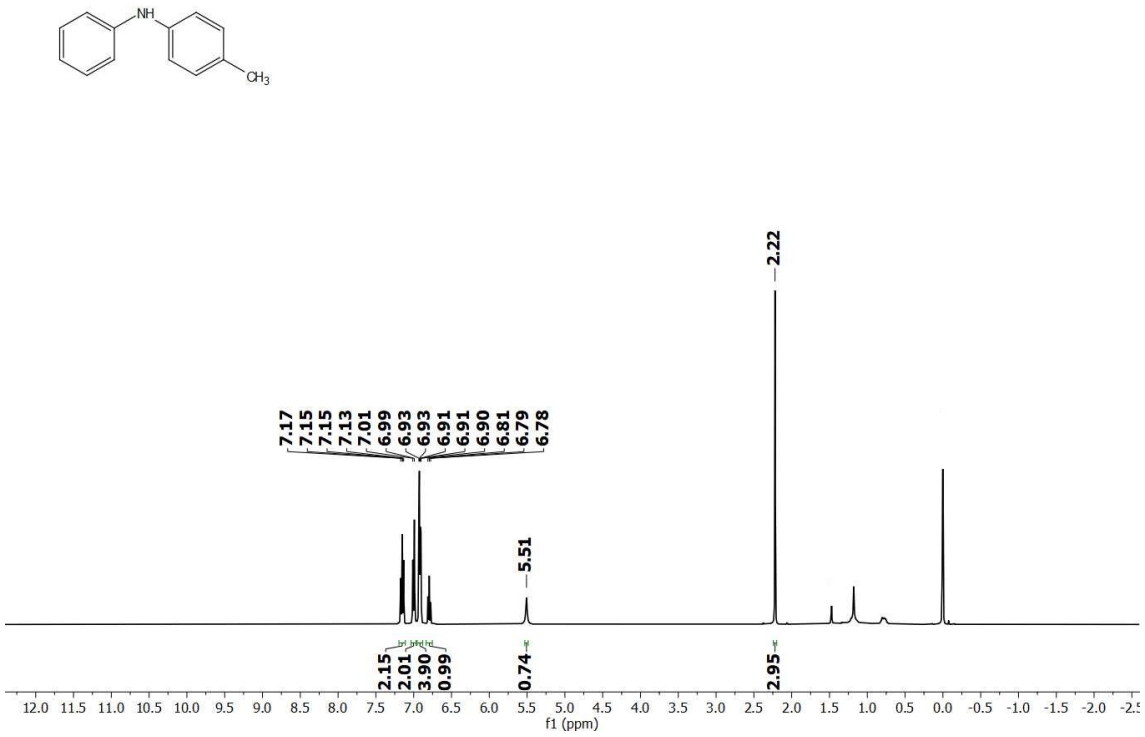


Figure 48: ^{1}H & ^{13}C NMR Spectra of representative compound



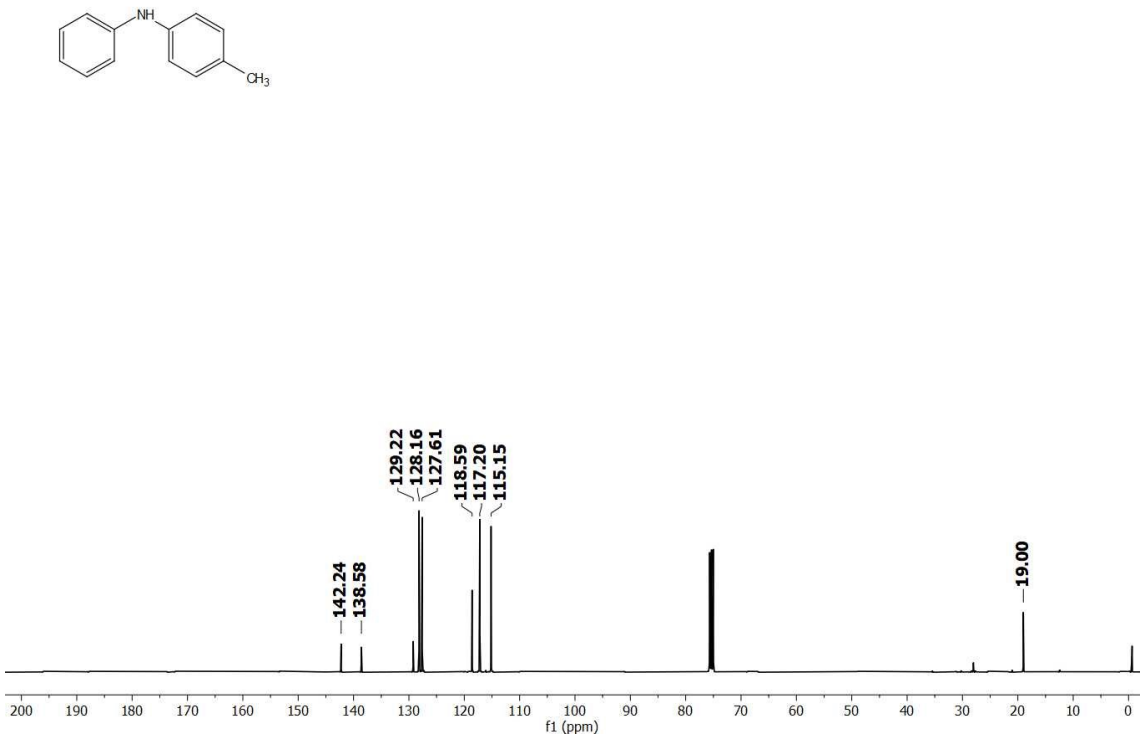


Figure 49: ^{1}H & ^{13}C NMR Spectra of representative compound

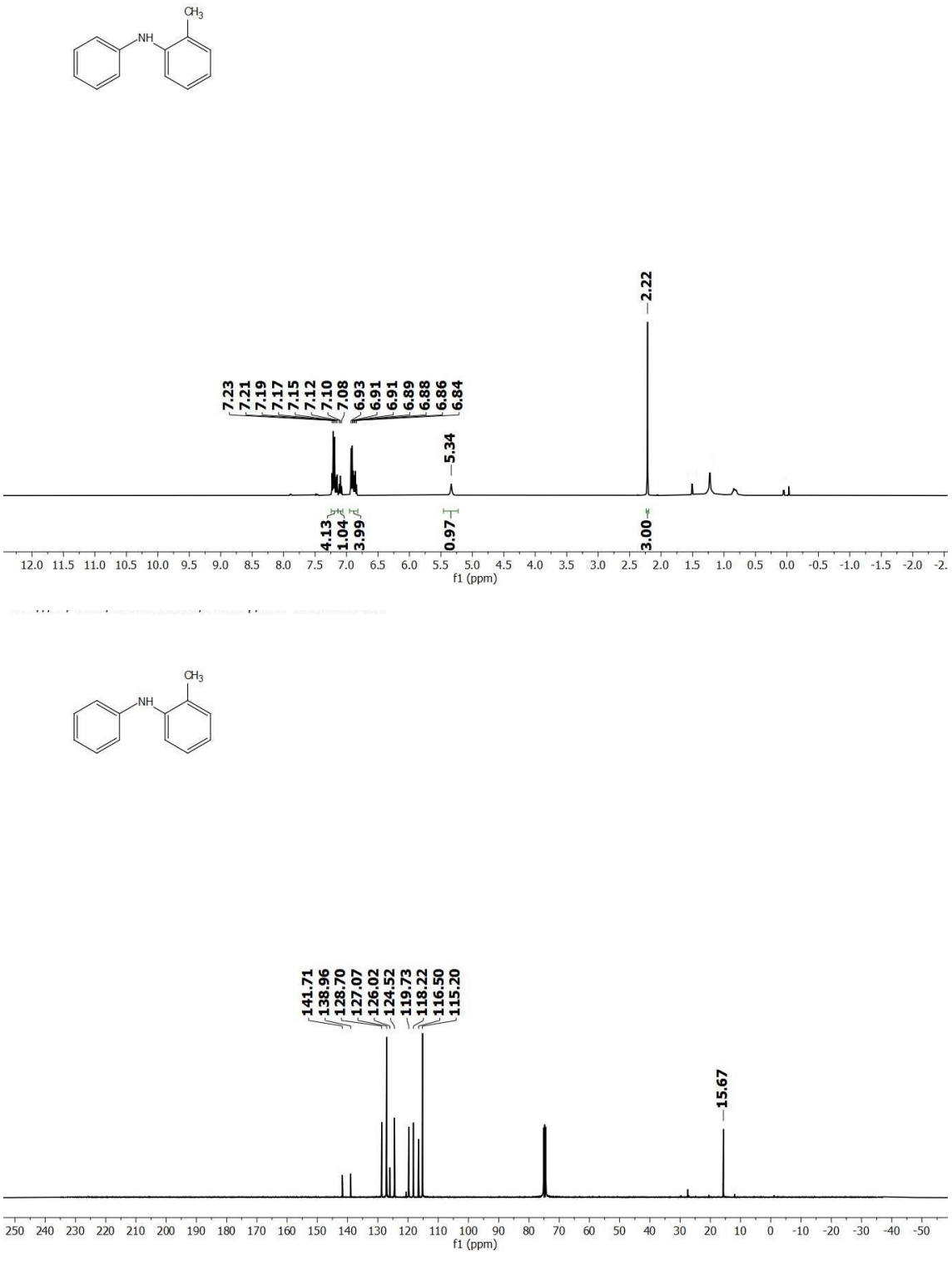


Figure 50: ^{1}H & ^{13}C NMR Spectra of representative compound

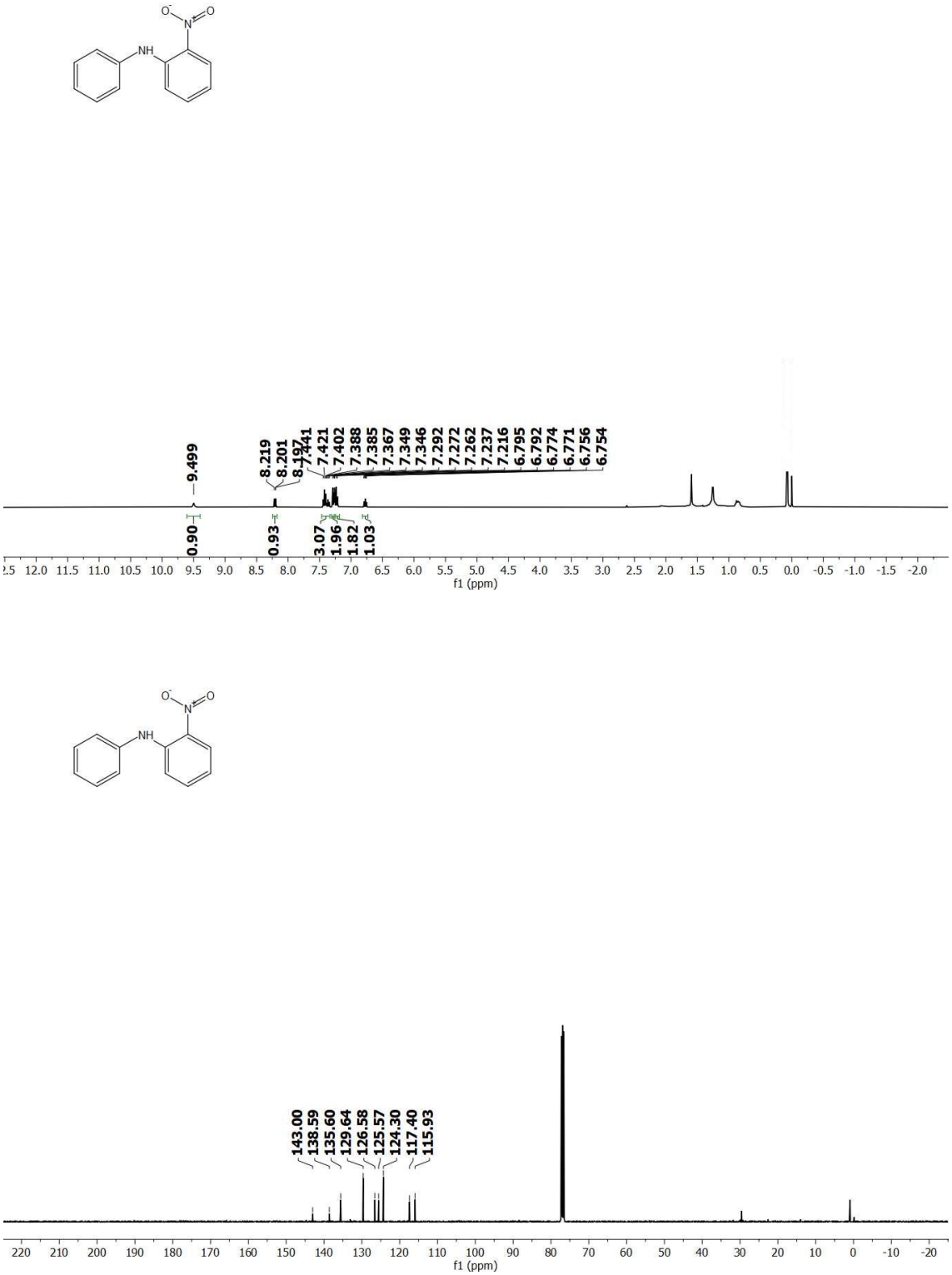
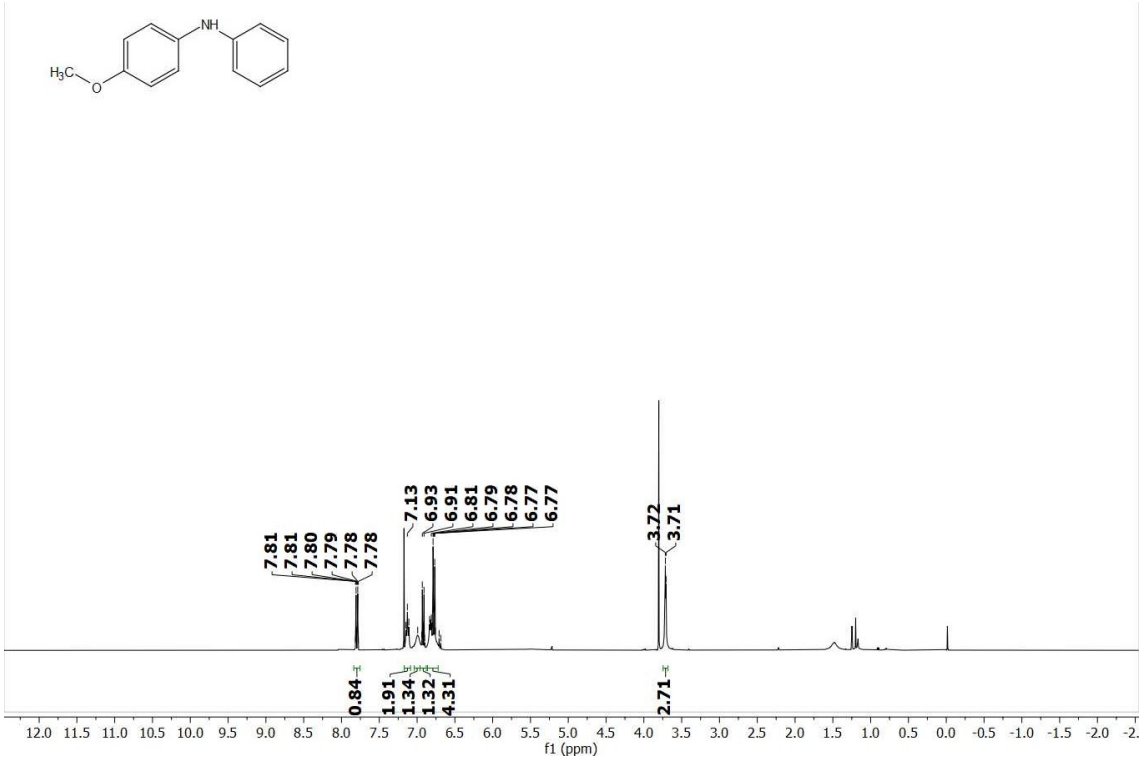


Figure 51: ^{1}H & ^{13}C NMR Spectra of representative compound



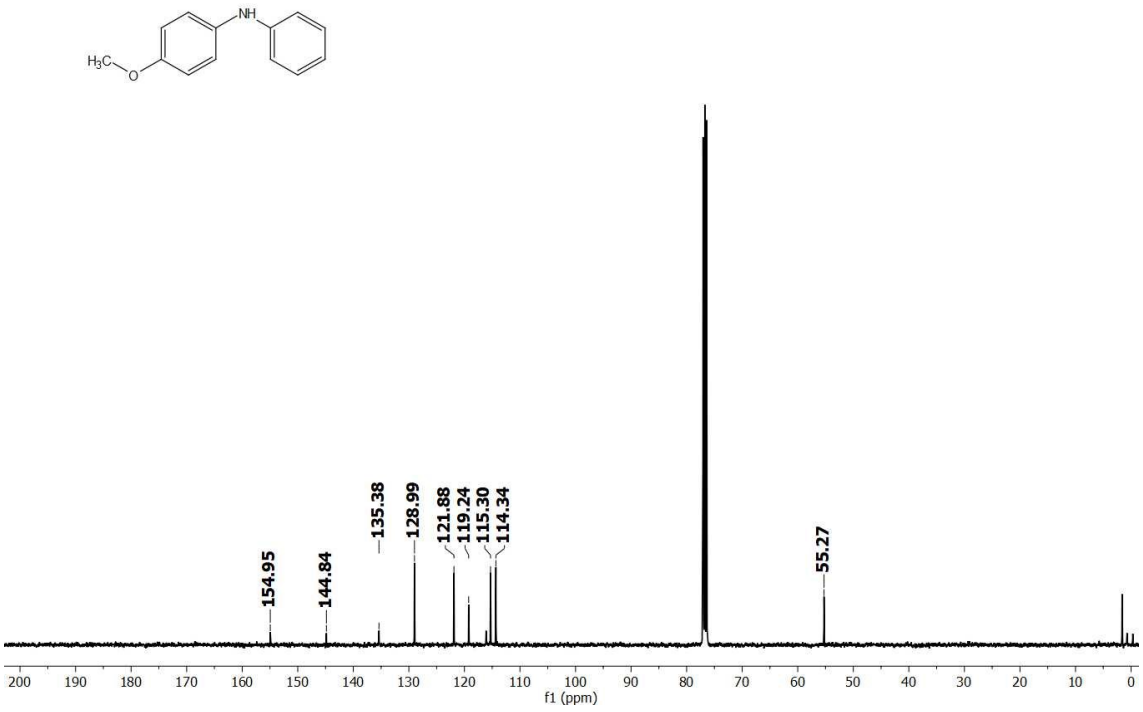


Figure 52: ^{1}H & ^{13}C NMR Spectra of representative compound

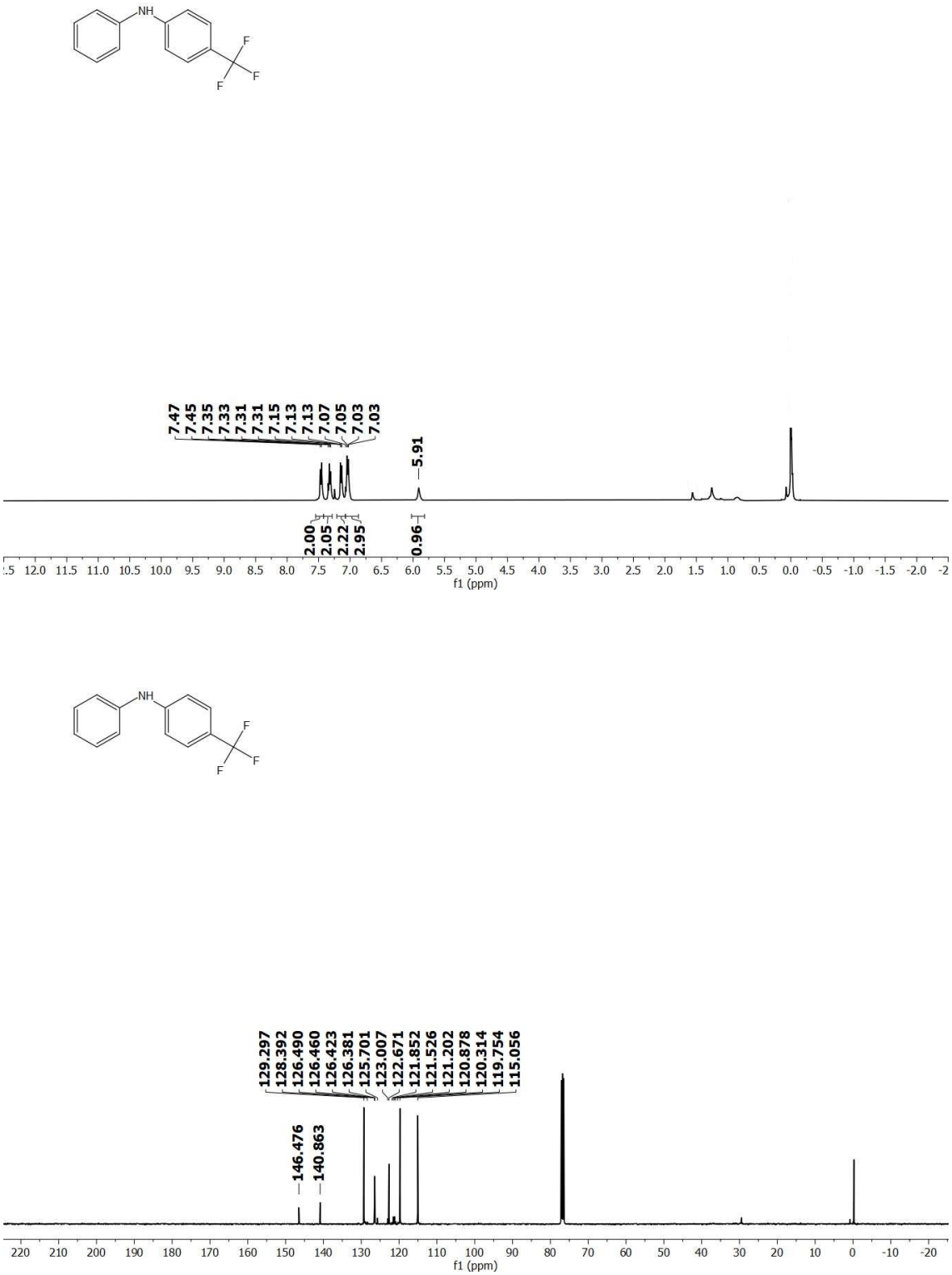
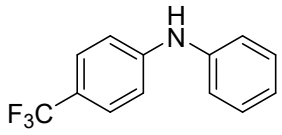


Figure 53: ^{1}H & ^{13}C NMR Spectra of representative compound



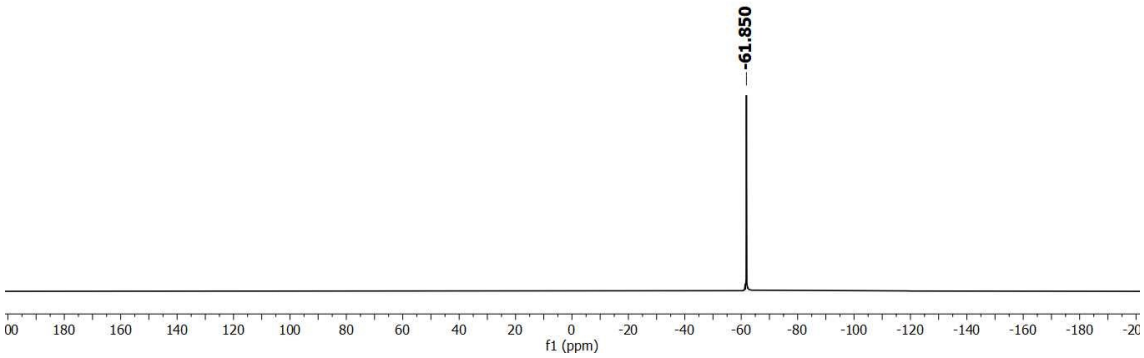


Figure 54: ^{19}F Spectra of representative compound

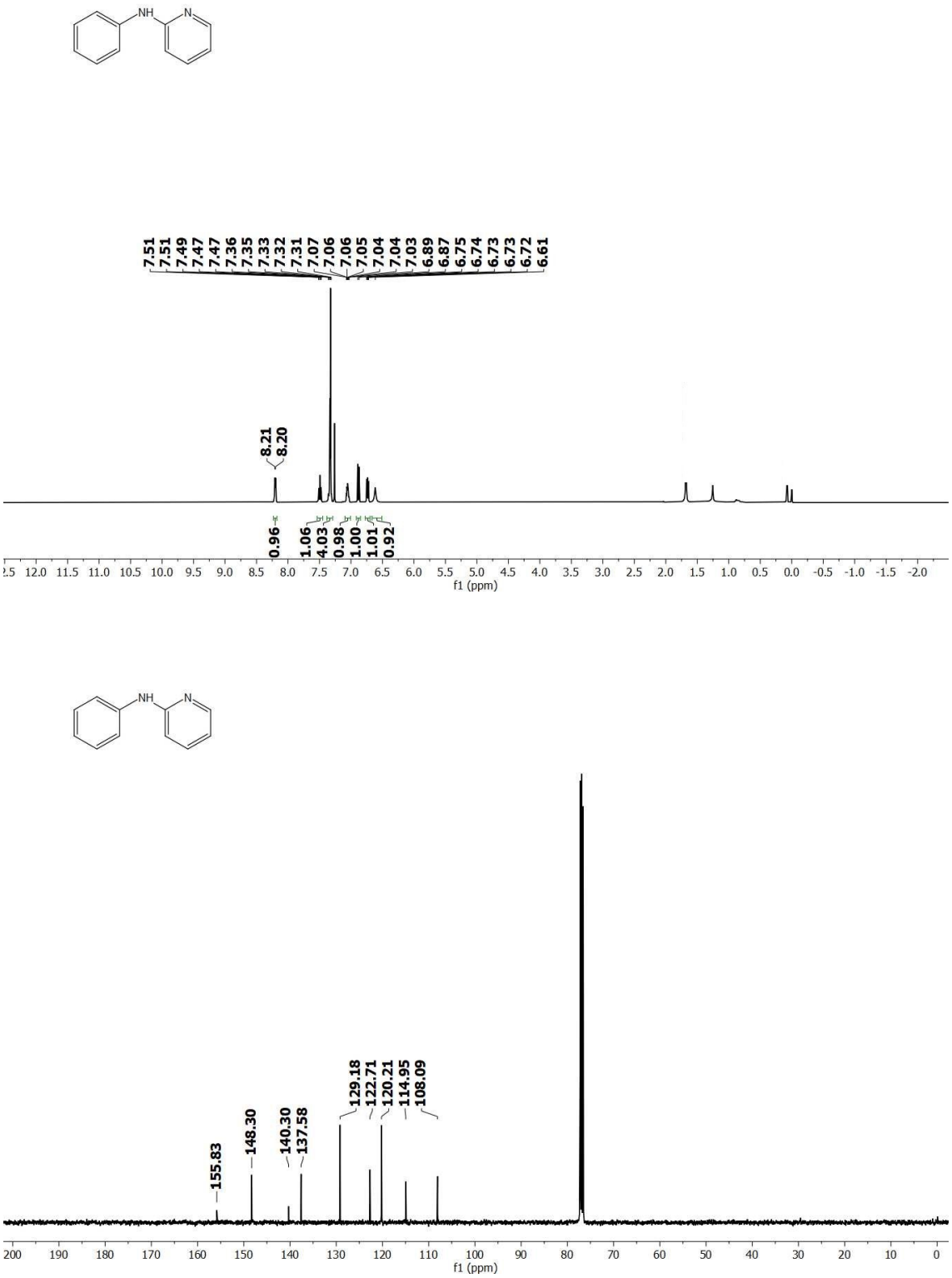
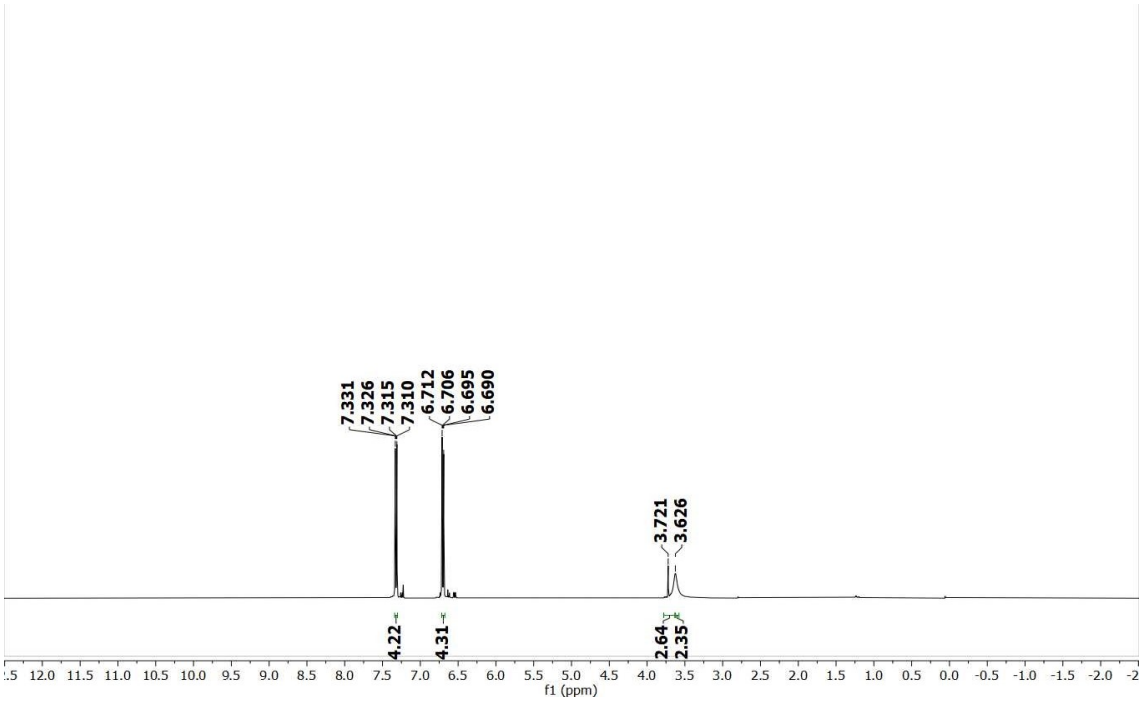
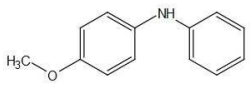


Figure 55: ^{1}H & ^{13}C NMR Spectra of representative compound





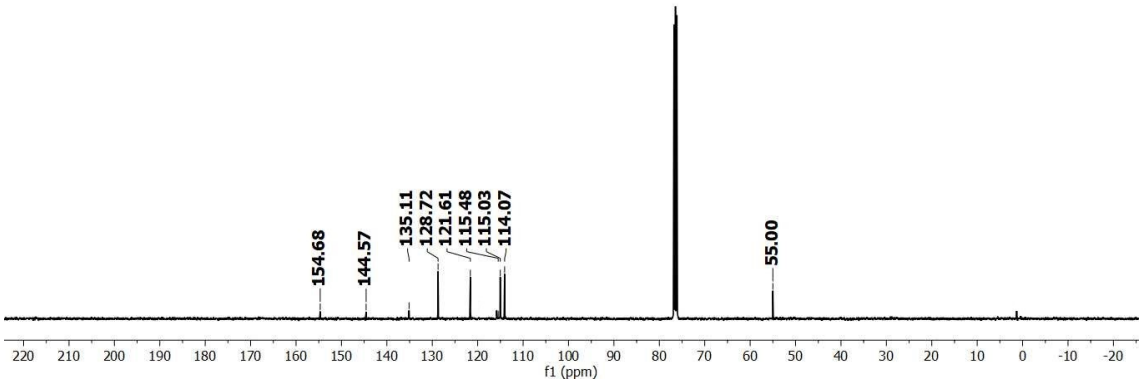


Figure 56: ^{1}H & ^{13}C NMR Spectra of representative compound

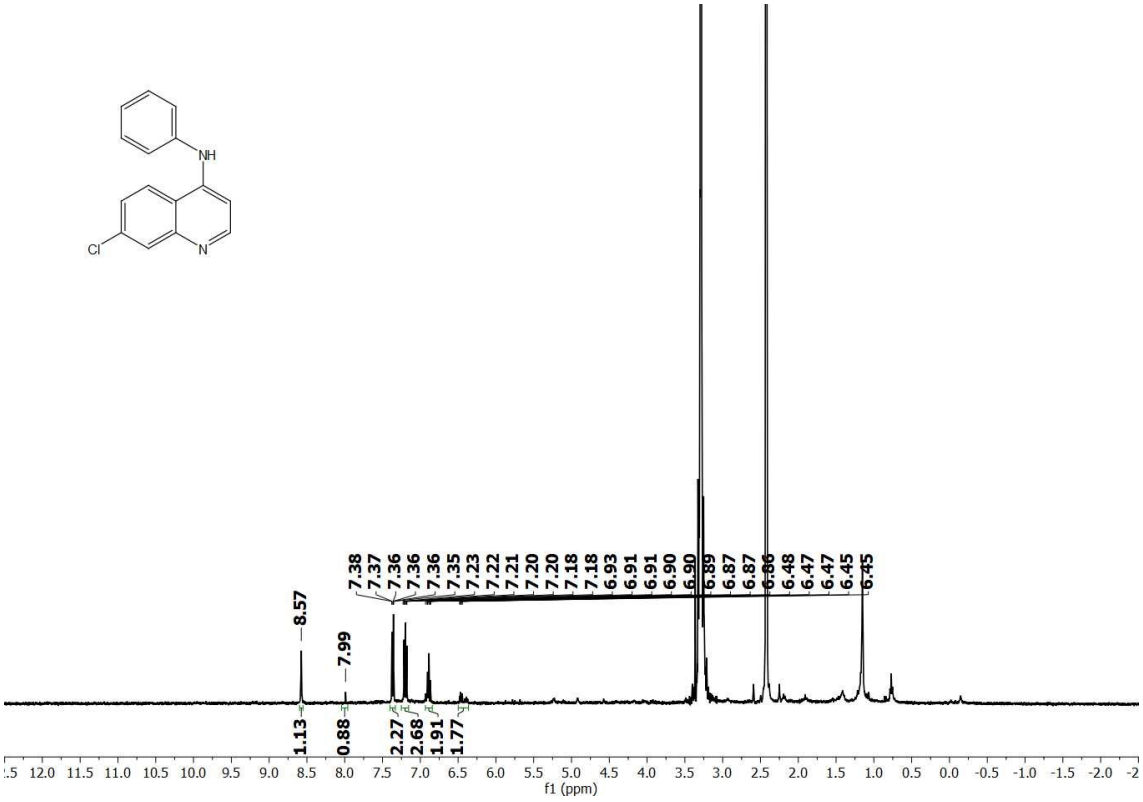
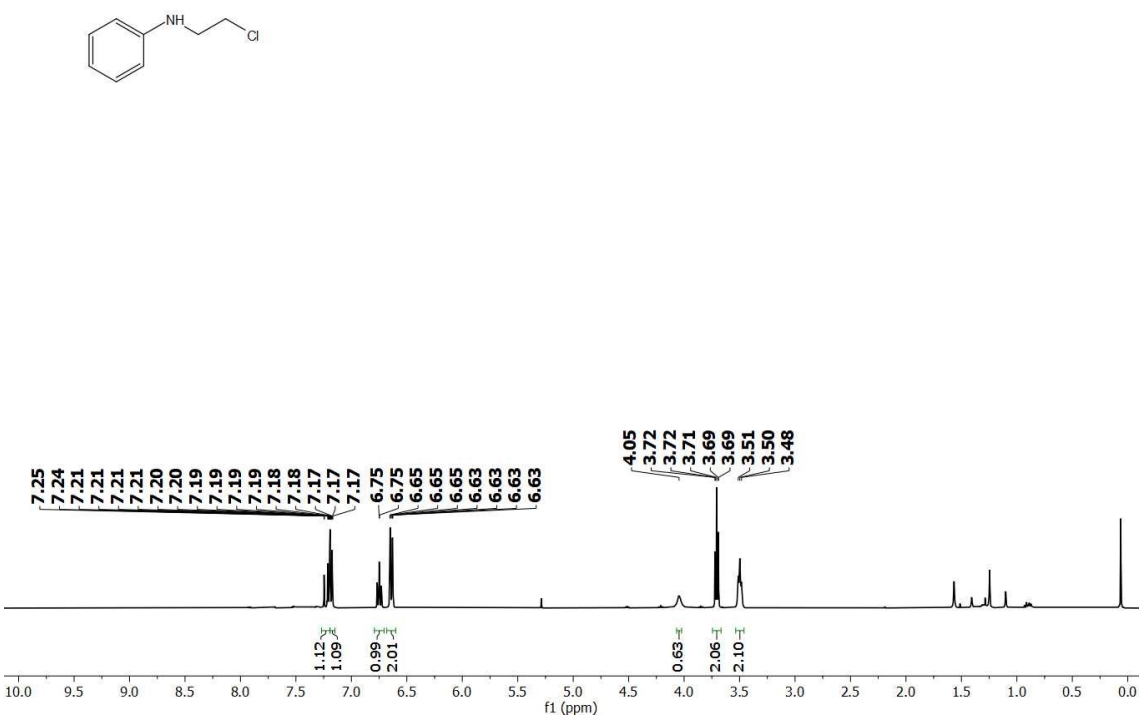


Figure 57: ^{1}H Spectra of representative compound



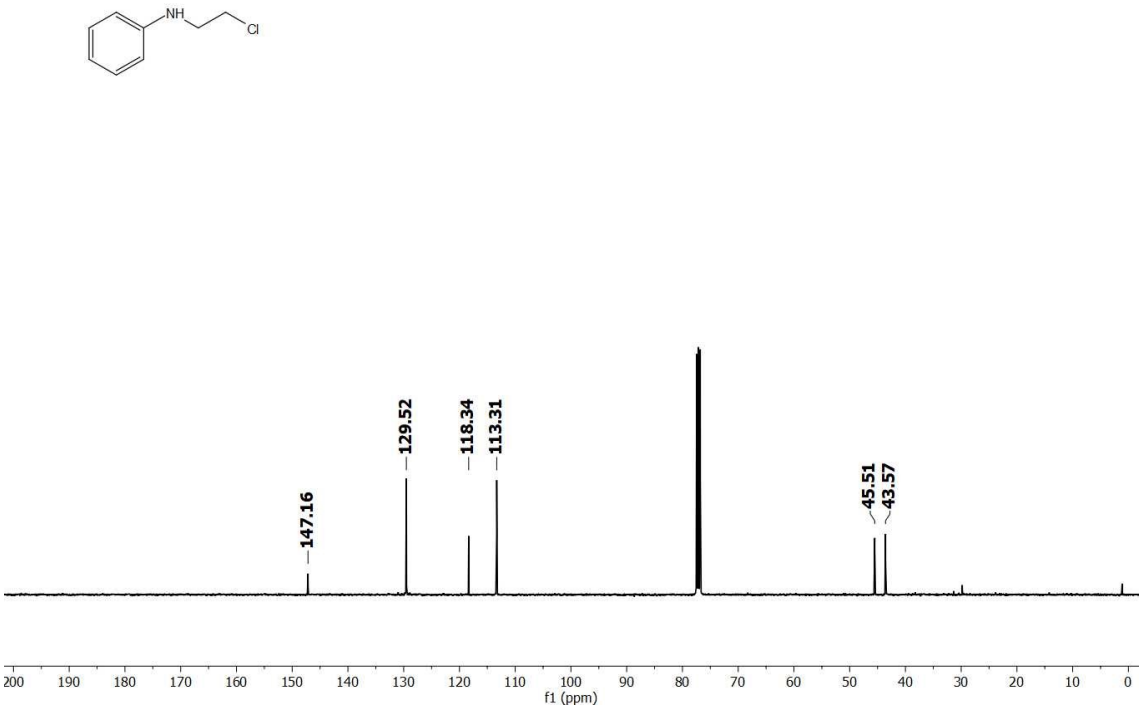
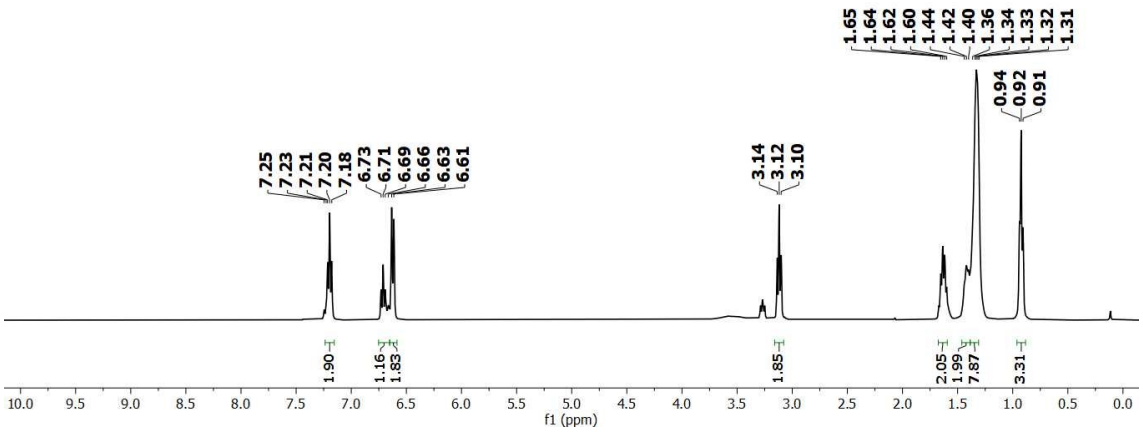
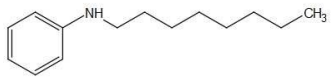


Figure 58: ^{1}H & ^{13}C NMR Spectra of representative compound





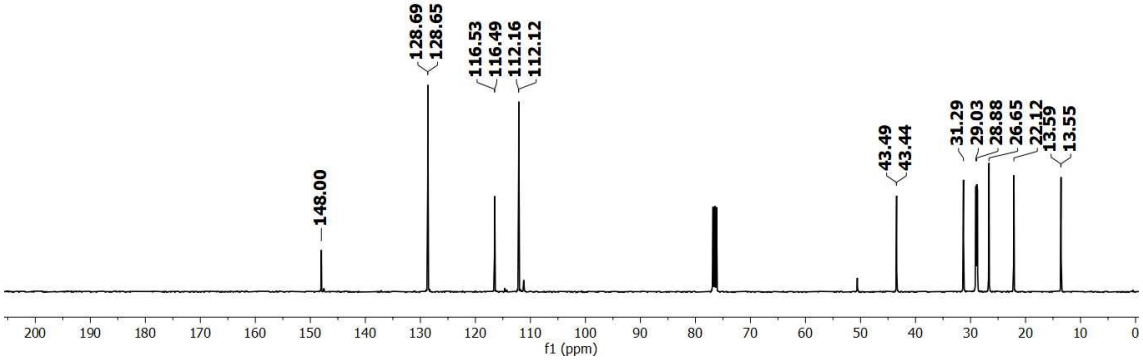


Figure 59: ^{1}H & ^{13}C NMR Spectra of representative compound

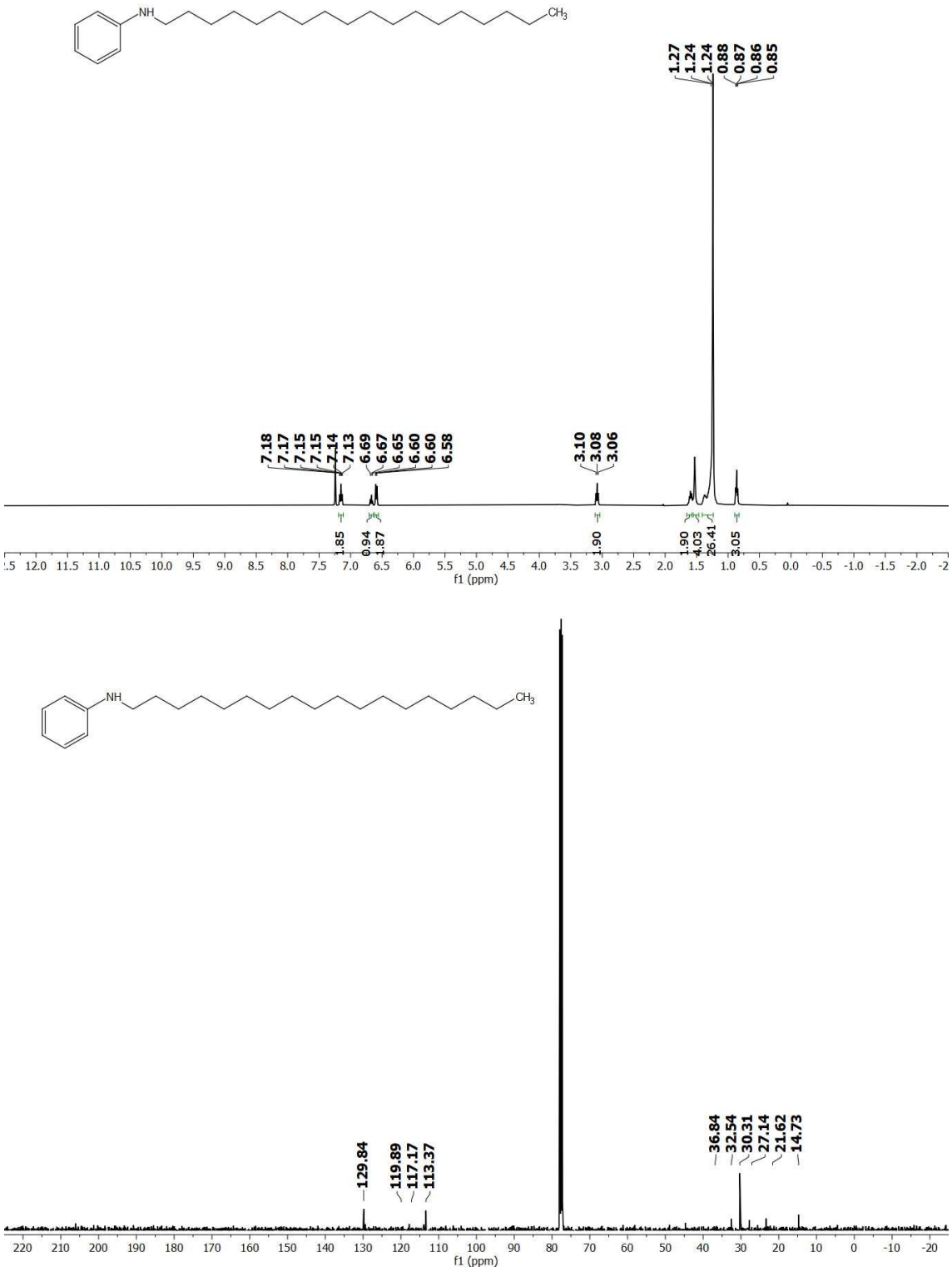
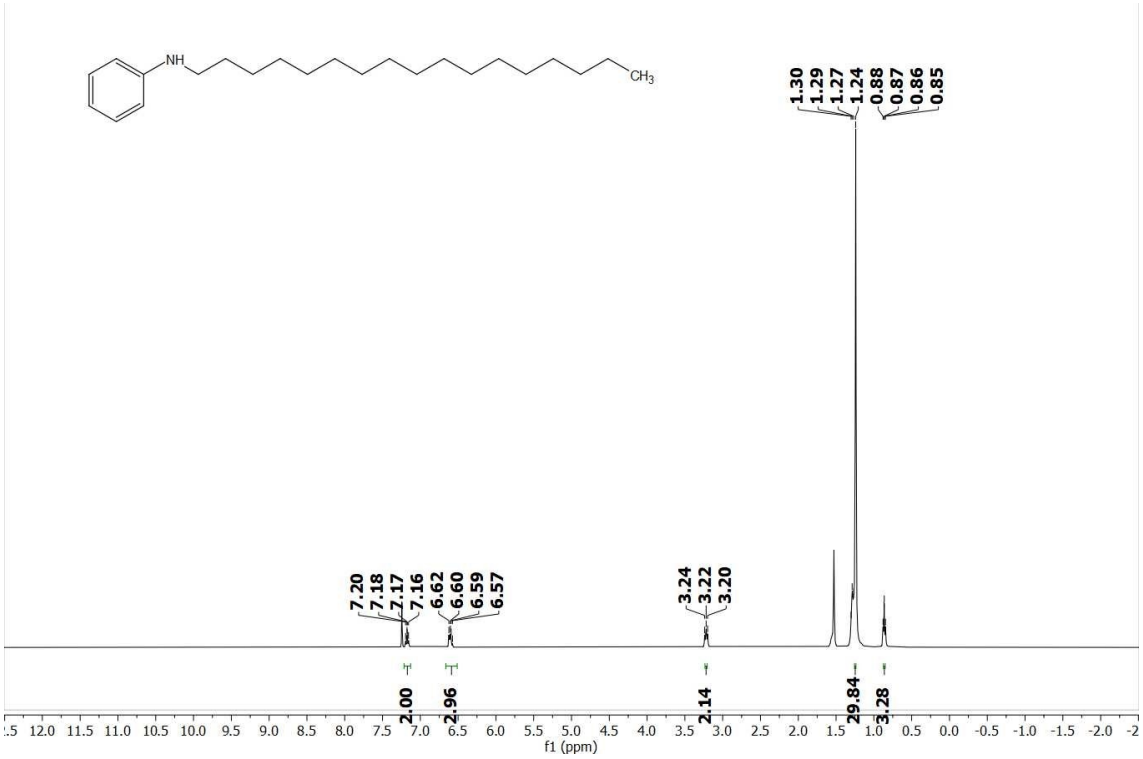


Figure 60: ^{1}H & ^{13}C NMR Spectra of representative compound



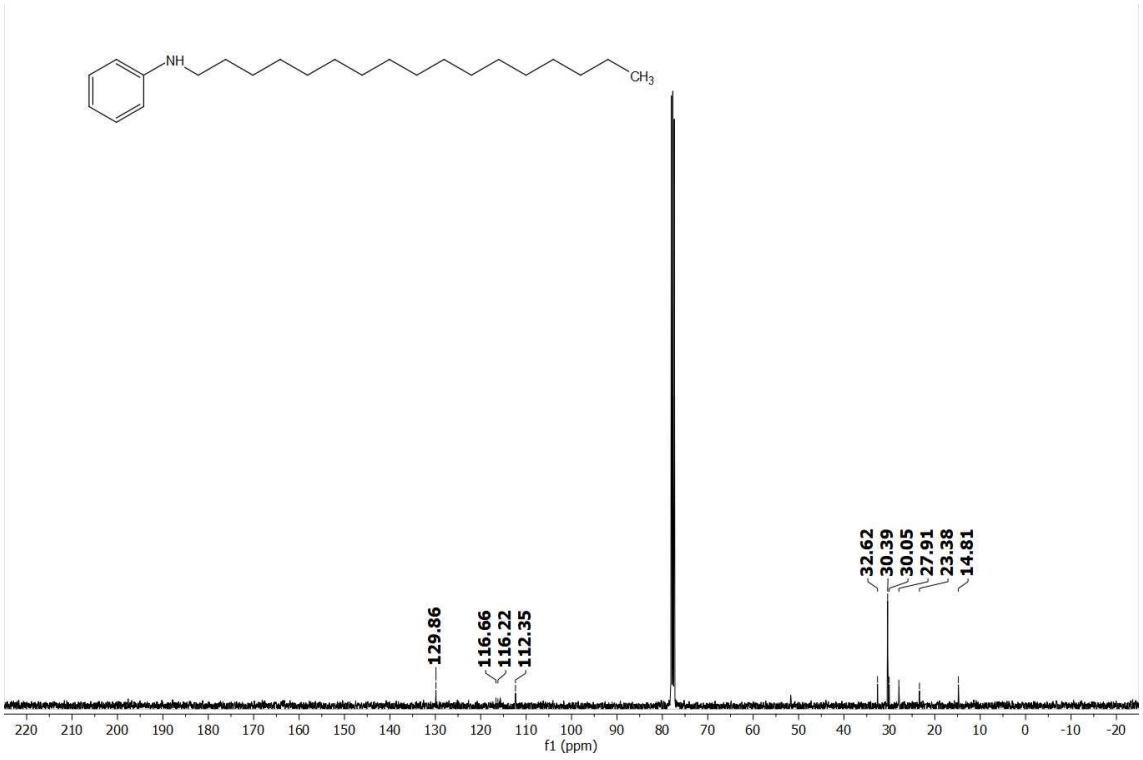
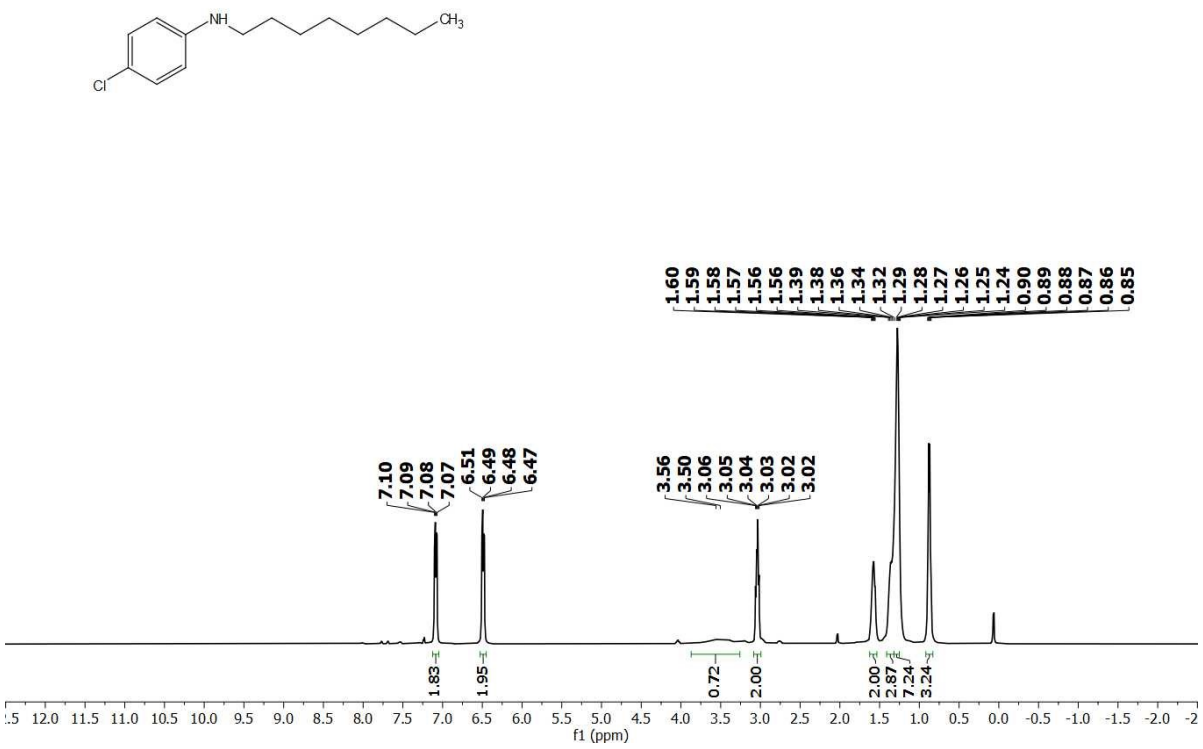


Figure 61: ^{1}H & ^{13}C NMR Spectra of representative compound



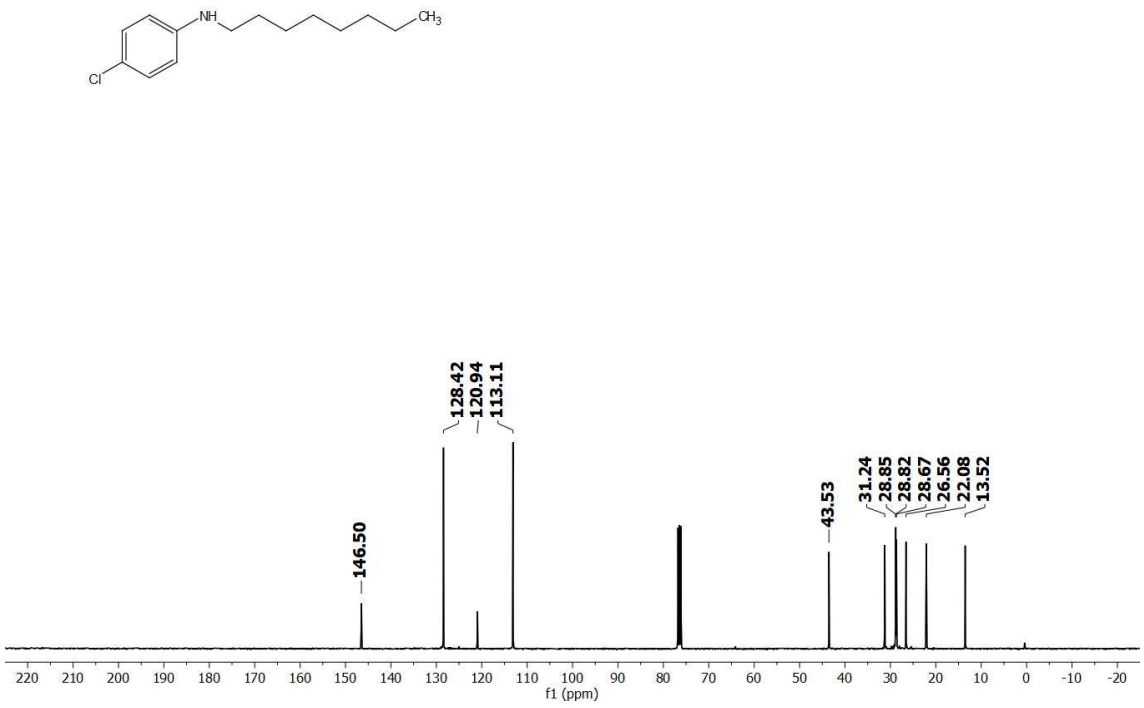
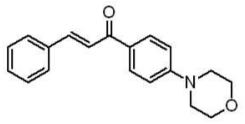
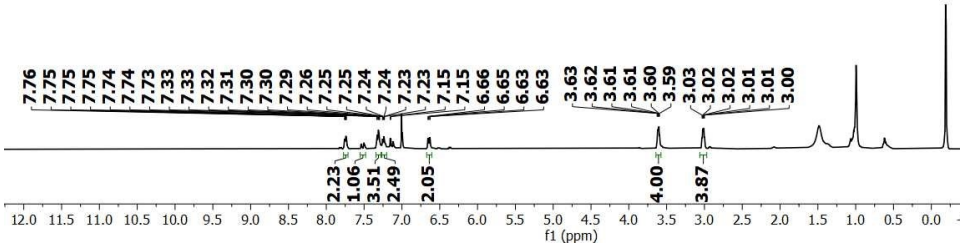


Figure 62: ^{1}H & ^{13}C NMR Spectra of representative compound





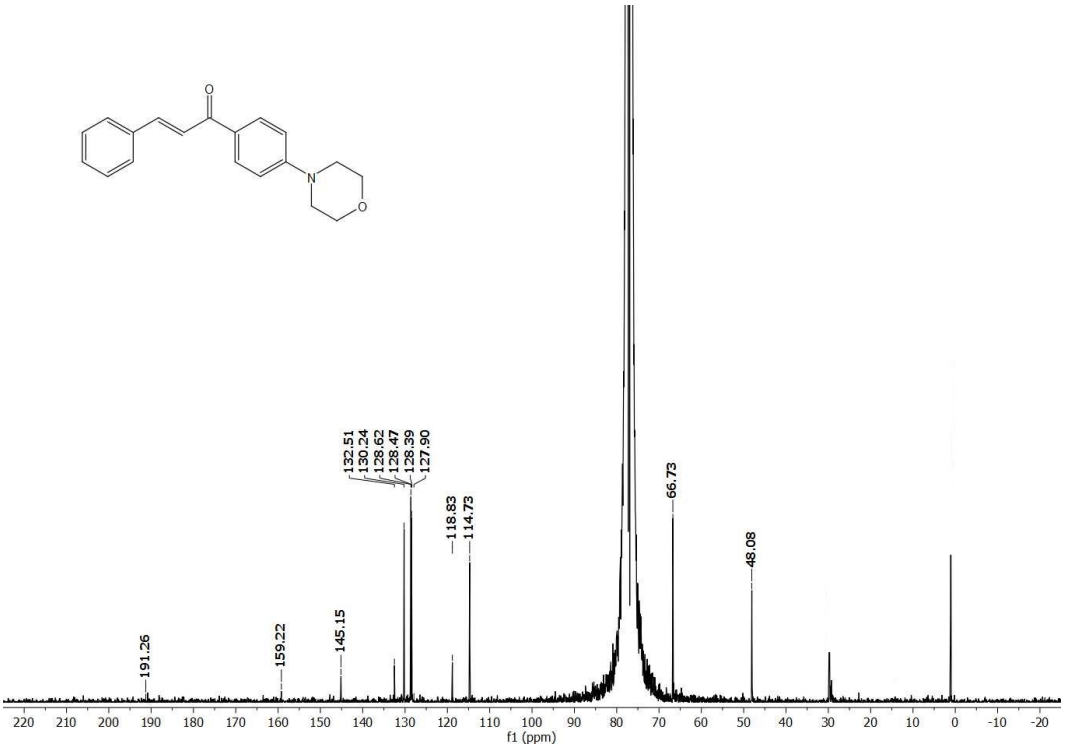


Figure 63: ^{1}H & ^{13}C NMR Spectra of representative compound

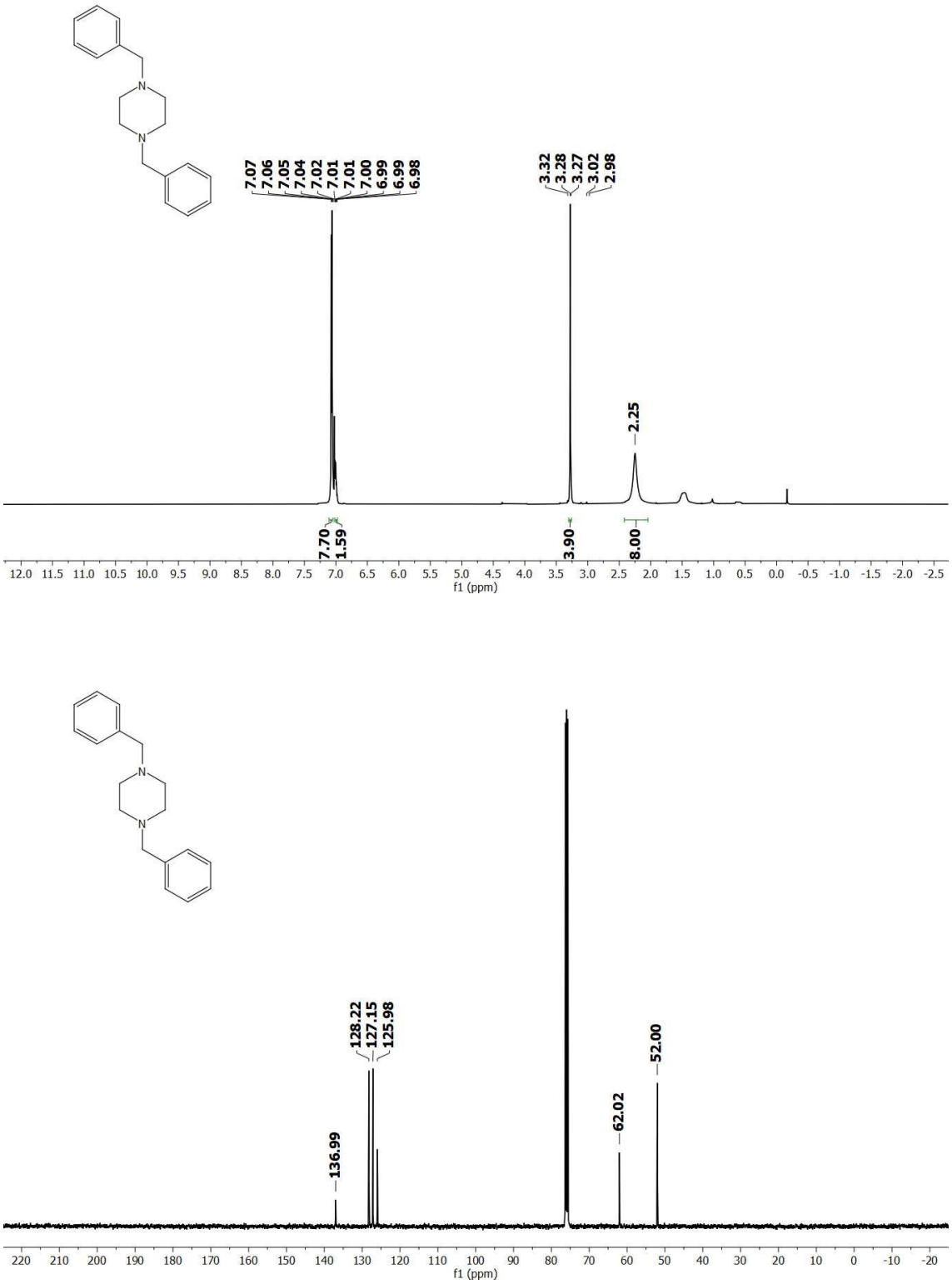


Figure 64: ^{1}H & ^{13}C NMR Spectra of representative compound