Supporting Information

I_2/NaH_2PO_2-Mediated Deoxyamination of Cyclic Ethers for the Synthesis of *N*-Aryl-Substituted Azacycles

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S1. General Method

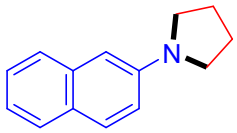
All experiments were carried out under air atmosphere using standard Schlenk techniques or in a dry glovebox. All heating (heating module) and stirring were conducted on the IKA (Model: RCT B S025). Solvents were dried over Na metal or CaH_2, and were distilled under nitrogen prior to use. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. Column chromatography was performed using Silica Gel 60 (200–300 mesh). The reactions were monitored by GC and GC-MS, GC-MS data were recorded on GC-MS QP 2010 plus, and GC analysis was performed on GC 2014. ^{1}H NMR (400MHz) spectra were recorded on Bruker ADVANCE III spectrometers in $CDCl_3$ [using $(CH_3)_4Si$ (for ^{1}H, $\delta = 0.00$) as internal standard]. $^{13}C\{^1H\}$ NMR (100MHz) spectra on Bruker ADVANCE III spectrometers in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as an internal standard]. The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiple), td (triplet of doublets). Chemical shifts (δ) are in parts per million relatives to $CDCl_3$ at 7.26 ppm for ^{1}H and at 77.16 ppm for $^{13}C\{^1H\}$, ^{19}F NMR spectra were recorded using the F-H decoupled pulse sequence from the Varian program library. Melting points were measured using a melting point instrument and are uncorrected. All solvents, reagents and acid were purchased from Energy Chemical, Alfa Aesar and Aladdin.

S2. Experimental Section

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, naphthalen-2-amine (**1a**) (0.2 mmol, 1.0 equiv) and tetrahydrofuran (**2a)** (2.0 mL), NaH_2PO_2 (0.4 mmol, 2 equiv), I_2 (0.3 mmol, 1.5 equiv), was vigorously stirred at 160 °C for 11 h. Then the mixture was cooled to room temperature, added water (15 mL), extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the desired product.

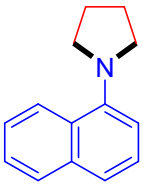
S3. Analysis Data for the Products

1-(naphthalen-2-yl)pyrrolidine[s1] **(3a)**



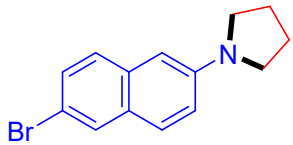
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3a** in 99% (39.0 mg) as a White solid; mp: 90 – 91 °C (literature reported: 91 – 92 °C); R_f = 0.7 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 3H), 7.43 – 7.39 (m, 1H), 7.26 – 7.20 (m, 1H), 7.06 – 7.03 (m, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 3.46 – 3.43 (m, 4H), 2.18 – 1.98 (m, 4H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.0, 135.4, 128.9, 127.7, 126.4, 126.2, 125.9, 121.3, 115.8, 104.8, 47.9, 25.6. Ms (EI): *m/z* = 197.1 $[M]^+$.

1-(naphthalen-1-yl)pyrrolidine[s2] **(3b)**



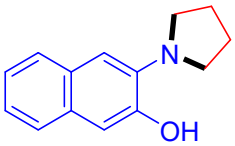
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3b** in 79% (31.2 mg) as a Brown oil; R_f = 0.7 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.18 (m, 1H), 7.85 – 7.78 (m, 1H), 7.49 – 7.42 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 3.39 (t, *J* = 6.2 Hz, 4H), 2.17 – 1.88 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 134.9, 128.2, 128.1, 125.9, 125.5, 124.7, 124.3, 121.3, 111.4, 52.7, 24.7. Ms (EI): *m/z* = 197.1 $[M]^+$.

1-(6-bromonaphthalen-2-yl)pyrrolidine (3c)



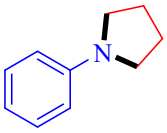
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3c** in 91% (50.1 mg) as a Blue solid; mp: 166–167 °C; R_f = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.3 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.00 – 6.98 (m, 1H), 6.71 (s, 1H), 3.39 (t, *J* = 6.5 Hz, 4H), 2.13 – 1.97 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.0, 133.7, 129.5, 129.3, 127.9, 127.5, 127.3, 116.5, 114.2, 104.7, 47.9, 25.5. Ms (EI): *m/z* = 275.0 $[M]^+$.

3-(pyrrolidin-1-yl)naphthalen-2-ol (3d)



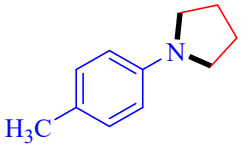
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3d** in 31% (13.2 mg) as a Brown oil; R_f = 0.1 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.69 (s, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.19 – 7.12 (m, 2H), 7.07 (s, 1H), 6.92 (s, 1H), 2.54 – 2.52 (m, 4H), 1.93 – 1.90 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.2, 139.4, 131.7, 129.1, 126.9, 126.2, 125.0, 123.5, 117.1, 108.8, 53.2, 24.5. Ms (EI): m/z = 213.1 $[M]^+$.

1-phenylpyrrolidine[s2] **(3e)**



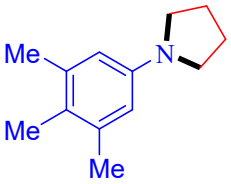
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3e** in 99% (29.1 mg) as a Brown solid; mp: 100 – 101 °C (literature reported: 101 – 102 °C); R_f = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.9 Hz, 2H), 3.26 – 3.29 (m, 4H), 2.10 – 1.85 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 128.1, 114.3, 110.6, 46.5, 24.4. Ms (EI): m/z = 147.1 $[M]^+$.

1-(p-tolyl)pyrrolidine[s2] **(3f)**



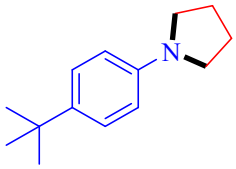
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3f** in 43% (13.9 mg) as a Brown oil; R_f = 0.3 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 3.28 (t, J = 6.6 Hz, 4H), 2.28 (s, 3H), 2.03 – 1.98 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.2, 129.7, 124.5, 111.8, 47.9, 25.4, 20.3. Ms (EI): m/z = 161.1 $[M]^+$.

1-(3,4,5-trimethylphenyl)pyrrolidine (3g)



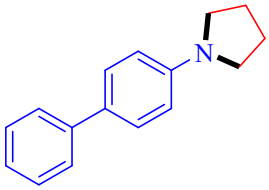
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3g** in 83% (31.4 mg) as a Brown oil; R_f = 0.3 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 2H), 3.25 (t, *J* = 6.5 Hz, 4H), 2.25 (s, 6H), 2.09 (s, 3H), 2.00 – 1.93 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.0, 137.1, 111.6, 48.0, 25.4, 21.0, 14.3. Ms (EI): *m/z* = 189.2 $[M]^+$.

1-(4-(tert-butyl)cyclohepta-1,3,5-trien-1-yl)pyrrolidine[s3] (3h)



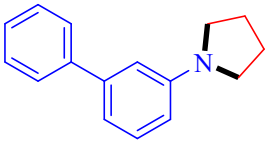
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3h** in 99% (40.2 mg) as a Brown oil; R_f = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.6 Hz, 2H), 3.30 (t, *J* = 6.5 Hz, 4H), 2.11 – 1.87 (m, 4H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.8, 138.0, 125.9, 111.4, 47.7, 33.7, 31.6, 25.4. Ms (EI): *m/z* = 203.1 $[M]^+$.

1-([1,1'-biphenyl]-4-yl)pyrrolidine[s4] (3i)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3i** in 92% (41.0 mg) as a Yellow solid; mp: 128–129 °C; R_f = 0.35 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 4H), 7.42 (dd, *J* = 10.5, 4.9 Hz, 2H), 7.27 (dd, *J* = 8.2, 6.5 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 3.36 (t, *J* = 6.4 Hz, 4H), 2.12 – 1.93 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 141.5, 128.6, 128.1, 127.8, 126.1, 125.7, 111.9, 47.7, 25.5. Ms (EI): *m/z* = 223.1 $[M]^+$.

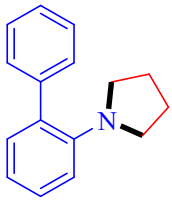
1-([1,1'-biphenyl]-3-yl)pyrrolidine[s4] (3j)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3j** in 71% (31.7 mg) as a Brown oil; R_f = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.70 – 6.68 (m, 1H), 3.45 (t, *J* = 6.5 Hz, 4H), 2.20 – 2.02 (m, 4H). ^{13}C{^{1}H}

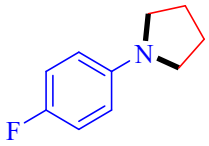
NMR (100 MHz, $CDCl_3$) δ 148.4, 142.5, 142.4, 129.6, 128.7, 127.4, 127.1, 114.8, 110.9, 110.7, 47.8, 25.6. Ms (EI): *m/z* = 223.1 $[M]^+$.

1-([1,1'-biphenyl]-2-yl)pyrrolidine[s4] (3k)



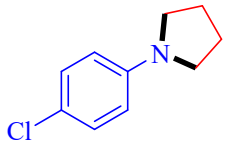
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3k** in 94% (42.0 mg) as a Brown oil; R_f = 0.4 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.89 – 6.84 (m, 2H), 2.90 (s, 4H), 1.74 (t, *J* = 6.0 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.9, 143.3, 132.3, 130.2, 129.1, 127.9, 127.8, 126.1, 118.2, 114.5, 50.9, 25.4. Ms (EI): *m/z* = 223.1 $[M]^+$.

1-(4-fluorophenyl)pyrrolidine[s2] (3l)



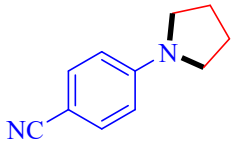
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3l** in 48% (15.8 mg) as a Brown oil; R_f = 0.5 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.89 (m, 2H), 6.55 – 6.44 (m, 2H), 3.25 (t, *J* = 6.6 Hz, 4H), 2.06 – 1.96 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.0 (d, *J* = 231.9 Hz), 144.7, 115.5 (d, *J* = 21.8 Hz), 112.3 (d, *J* = 6.6 Hz), 48.3, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.97. Ms (EI): *m/z* = 165.1 $[M]^+$.

1-(4-chlorophenyl)pyrrolidine[s2] (3m)



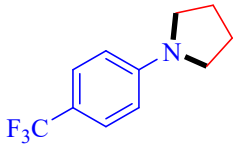
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3m** in 83% (30.1 mg) as a Yellow solid; mp: 83 – 84 °C (literature reported: 85 °C); R_f = 0.5 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 2H), 6.53 – 6.44 (m, 2H), 3.27 (t, *J* = 6.6 Hz, 4H), 2.08 – 1.98 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.6, 128.9, 120.1, 112.7, 47.8, 25.5. Ms (EI): *m/z* = 181.0 $[M]^+$.

4-(pyrrolidin-1-yl)benzonitrile[s5] (3n)



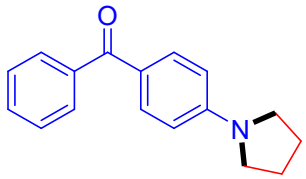
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3n** in 46% (15.8 mg) as a Yellow solid; mp: 88 – 89 °C (literature reported: 88 – 90 °C); R_f = 0.3 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 3.39 – 3.28 (m, 4H), 2.11 – 1.98 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 133.5, 121.1, 111.5, 96.5, 47.5, 25.4. Ms (EI): *m/z* = 172.1 $[M]^+$.

1-(4-(trifluoromethyl)phenyl)pyrrolidine[s6] (3o)



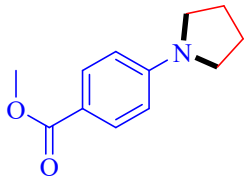
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3o** in 69% (29.7 mg) as a White solid; mp: 95 – 96 °C (literature reported: 96 – 97 °C); R_f = 0.8 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 4H), 2.04 (td, *J* = 6.6, 3.2 Hz, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.7, 125.3 (q, *J* = 37 Hz), 124.3 (q, *J* = 268.2 Hz), 115.6 (q, *J* = 32.2 Hz), 109.8, 46.5, 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.57. Ms (EI): *m/z* = 215.1 $[M]^+$.

phenyl(4-(pyrrolidin-1-yl)phenyl)methanone[s7] (3p)



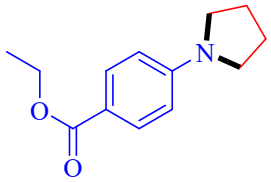
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3p** in 69% (34.6 mg) as a Yellow solid; mp: 148 – 149 °C (literature reported: 138 °C); R_f = 0.2 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.72 – 7.70 (m, 2H), 7.51 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 6.55 – 6.52 (m, 2H), 3.38 – 3.35 (m, 4H), 2.04 – 2.02 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.2, 150.9, 139.5, 133.0, 131.0, 129.4, 128.0, 124.2, 110.6, 47.6, 25.5. Ms (EI): *m/z* = 251.1 $[M]^+$.

methyl 4-(pyrrolidin-1-yl)benzoate[s8] (3q)



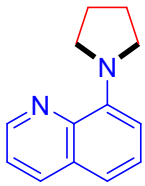
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3q** in 65% (26.7 mg) as a Yellow solid; mp: 130 – 131 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.77 (m, 2H), 6.59 – 6.38 (m, 2H), 3.85 (s, 3H), 3.44 – 3.22 (m, 4H), 2.17 – 1.86 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.7, 150.9, 131.4, 116.2, 110.7, 51.5, 47.5, 25.5. Ms (EI): *m/z* = 205.1 $[M]^+$.

ethyl 4-(pyrrolidin-1-yl)benzoate[s9] (3r)



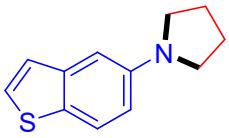
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3r** in 56% (24.5 mg) as a Yellow solid; mp: 112 – 113 °C (literature reported: 114 – 116 °C); R_f = 0.3 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.80 (m, 2H), 6.52 – 6.41 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.32 – 3.29 (m, 4H), 2.08 – 1.83 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.2, 150.8, 131.3, 116.6, 110.6, 60.0, 47.5, 25.5, 14.5. Ms (EI): *m/z* = 219.1 $[M]^+$.

8-(pyrrolidin-1-yl)quinoline (3s)



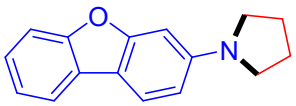
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3s** in 77% (30.5 mg) as a Brown oil; R_f = 0.2 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.75 (m, 1H), 8.04 – 8.02 (m, 1H), 7.41 – 7.27 (m, 2H), 7.17 – 7.15 (m, 1H), 6.85 – 6.82 (m, 1H), 3.75 – 3.71 (m, 4H), 2.07 – 1.93 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.7, 141.5, 135.8, 129.9, 127.0, 120.7, 116.8, 111.1, 52.0, 25.4. Ms (EI): *m/z* = 198.1 $[M]^+$.

1-(benzo[b]thiophen-5-yl)pyrrolidine (3t)



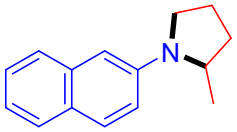
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3t** in 99% (40.3 mg) as a White solid; mp: 76 – 77 °C; R_f = 0.3 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 5.4 Hz, 1H), 7.18 (d, *J* = 5.4 Hz, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.77 – 6.74 (m, 1H), 3.39 – 3.24 (m, 4H), 2.09 – 1.93 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.0, 141.1, 127.1, 126.7, 123.4, 112.7, 112.0, 104.6, 48.2, 25.5. Ms (EI): *m/z* = 203.1 $[M]^+$.

1-(dibenzo[b,d]furan-3-yl)pyrrolidine (3u)



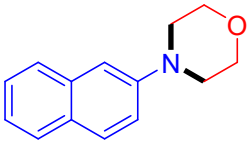
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3u** in 99% (47.0 mg) as a Yellow solid; mp: 148 – 149 °C; R_f = 0.35 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.51 – 7.49 (m, 1H), 7.34 – 7.28 (m, 2H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.65 – 6.63 (m, 1H), 3.43 (t, *J* = 6.6 Hz, 4H), 2.14 – 2.06 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 155.7, 148.4, 125.3, 124.4, 122.4, 120.9, 118.9, 112.7, 110.9, 108.2, 93.6, 48.1, 25.5. Ms (EI): *m/z* = 237.1 $[M]^+$.

2-methyl-1-(naphthalen-2-yl)pyrrolidine (3v)



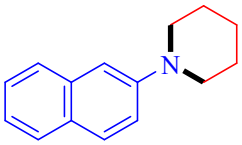
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3v** in 58% (24.5 mg) as a Brown oil; R_f = 0.4 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.52 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.75 (s, 1H), 4.01 (p, *J* = 6.2 Hz, 1H), 3.63 – 3.41 (m, 1H), 3.30 – 3.24 (m, 1H), 2.14 – 1.97 (m, 3H), 1.76 – 1.68 (m, 1H), 1.23 (t, *J* = 8.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 135.4, 128.8, 127.6, 126.2, 126.1, 125.8, 121.2, 116.0, 105.0, 53.8, 48.4, 33.2, 23.3, 19.5. Ms (EI): *m/z* = 211.1 $[M]^+$.

4-(naphthalen-2-yl)morpholine[s1] **(3w)**



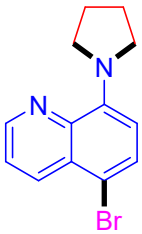
The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **3w** in 77% (32.8 mg) as a Yellow solid; mp: 83 – 84 °C (literature reported: 87 – 88 °C); R_f = 0.4 (petroleum ether/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.14 (d, *J* = 2.1 Hz, 1H), 3.96 – 3.92 (m, 4H), 3.31 – 3.27 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.1, 134.6, 128.9, 128.7, 127.5, 126.8, 126.4, 123.6, 118.9, 110.2, 67.0, 49.9. Ms (EI): *m/z* = 213.1 $[M]^+$.

1-(naphthalen-2-yl)piperidine[s1] **(3x)**



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether) yielded the title compound **3x** in 96% (40.7 mg) as a Brown oil; R_f = 0.5 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 9.7 Hz, 3H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.12 (d, *J* = 2.2 Hz, 1H), 3.26 – 3.24 (m, 4H), 1.79 – 1.73 (m, 4H), 1.64 – 1.59 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 134.7, 128.5, 128.3, 127.4, 126.7, 126.1, 123.1, 120.2, 110.4, 51.1, 25.9, 24.4. Ms (EI): *m/z* = 211.1 $[M]^+$.

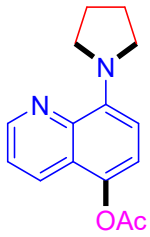
5-bromo-8-(pyrrolidin-1-yl)quinoline (4)



A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, 8-(pyrrolidin-1-yl)quinoline (3s) (0.2 mmol, 1.0 equiv) and tetrahydrofuran (2a) (2.0 mL), *N*-Bromosuccinimide (0.22 mmol, 1.1 equiv), was vigorously stirred at 50 °C for 3 h. Then the mixture was cooled to room temperature, added water (15 mL), extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the desired product.

The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **4** in 65% (36.1 mg) as a Brown oil; R_f = 0.6 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.73 (m, 1H), 8.42 – 8.40 (m, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.38 (m, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 3.76 – 3.65 (m, 4H), 2.05 – 1.96 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 146.1, 141.9, 135.0, 130.6, 128.4, 121.7, 110.8, 107.6, 52.0, 25.5. Ms (EI): *m/z* = 277.9 $[M]^+$.

8-(pyrrolidin-1-yl)quinolin-5-yl acetate (5)



A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, 8-(pyrrolidin-1-yl)quinoline (3s) (0.2 mmol, 1.0 equiv) and AcOH (2.0 mL), $Cu(OAc)_2$ (0.02 mmol, 0.1 equiv), $PhI(OAc)_2$ (0.3 mmol, 1.5 equiv), was vigorously stirred at 45 ^oC for 5 h. Then the mixture was cooled to room temperature, added water (15 mL), extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the desired product.

The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5** in 54% (27.7 mg) as a Brown oil; R_f = 0.6 (petroleum ether/ethyl acetate = 5/1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 – 8.77 (m, 1H), 8.06 – 8.04 (m, 1H), 7.37 – 7.33 (m, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 3.75 – 3.66 (m, 4H), 2.42 (s, 3H), 2.07 – 1.98 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 146.3, 145.9, 141.2, 136.6, 129.3, 123.1, 120.9, 119.0, 109.3, 51.0, 25.4, 21.0. Ms (EI): *m/z* = 256.1 $[M]^+$.

S4. Control Experiment

(a) Radical trapping experiment. A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL) I_2 (76.1 mg, 0.30 mmol), TEMPO (31.2 mg, 0.2 mmol, 1.0 equiv) under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/petroleum ether (1:40, v/v), to afford the product **3a** (yield = 91%).

Radical trapping experiment. A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL) I_2 (76.1 mg, 0.30 mmol), BHT (44.0 mg, 0.2 mmol, 1.0 equiv) under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/petroleum ether (1:40, v/v), to afford the product **3a** (yield = 93%).

(b) A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL) HI (184.0 μL, 0.80 mmol; 46.0 μL, 0.20 mmol; 4.5 μL, 0.02 mmol) under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/petroleum ether (1:40, v/v), to afford the product **3a** (yield = 65%; 62%; 6%).

(c) Condition A: A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL), HCl (aq) (40.0 μL, 0.4 mmol, 2.0 equiv) under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, it is no react.

Condition B: A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL) KI (66.4 mg, 0.40 mmol), HCl (aq) (40.0 μL, 0.4 mmol, 2.0 equiv) under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/petroleum ether (1:40, v/v), to afford the product **3a** (yield = 59%).

(d) A 25-mL Schlenk tube was charged with **1a** (28.6 mg, 0.20 mmol), **2a** (2.0 mL) 1,4-Diiodobutane (52.8 μL, 0.40 mmol), under standard reaction conditions. Stirred at 160 °C for 11 h. The mixture was then cooled to room temperature, diluted with CH_2Cl_2 (2 mL), filtered through a celite pad, analyzed by GCMS, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/petroleum ether (1:40, v/v), to afford the product **3a** (yield = 99%).

S5. References

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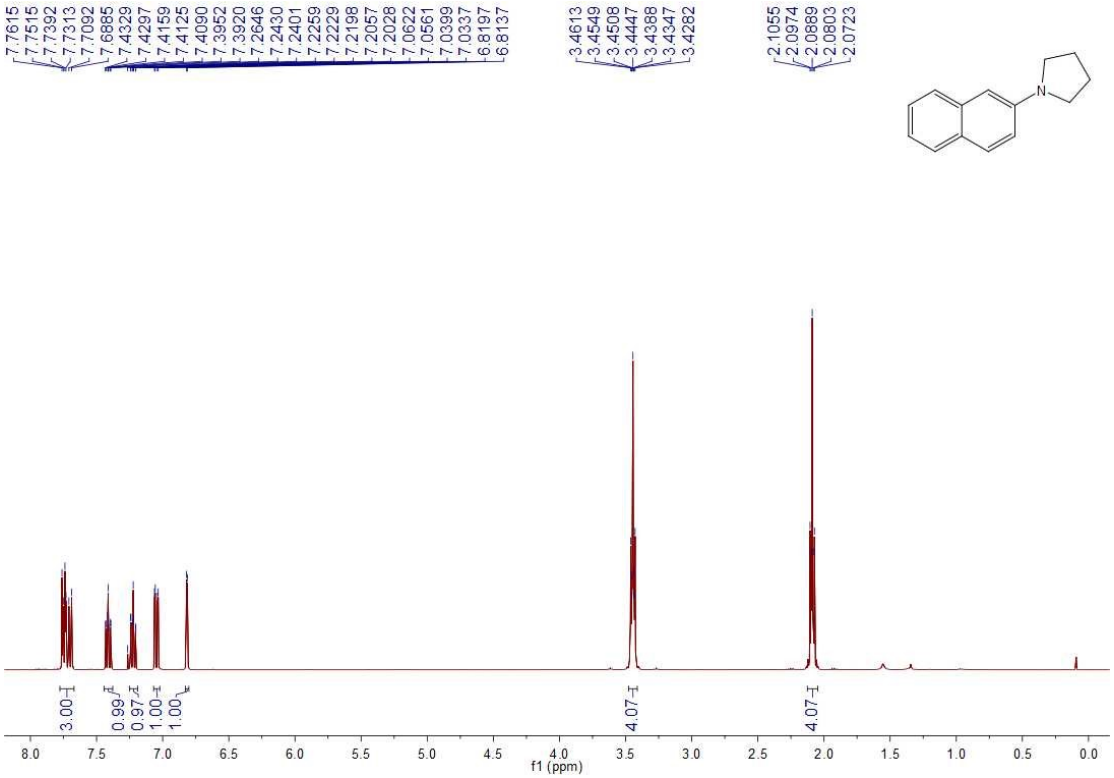
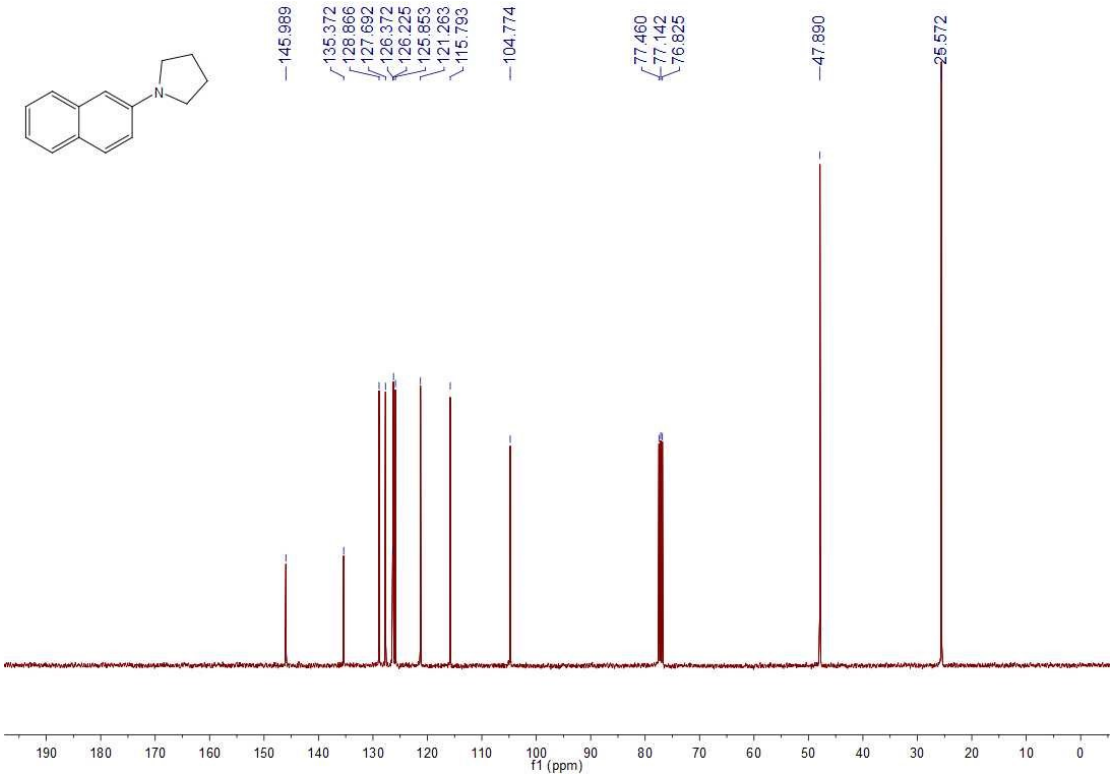
S6. NMR Spectra of All Compounds

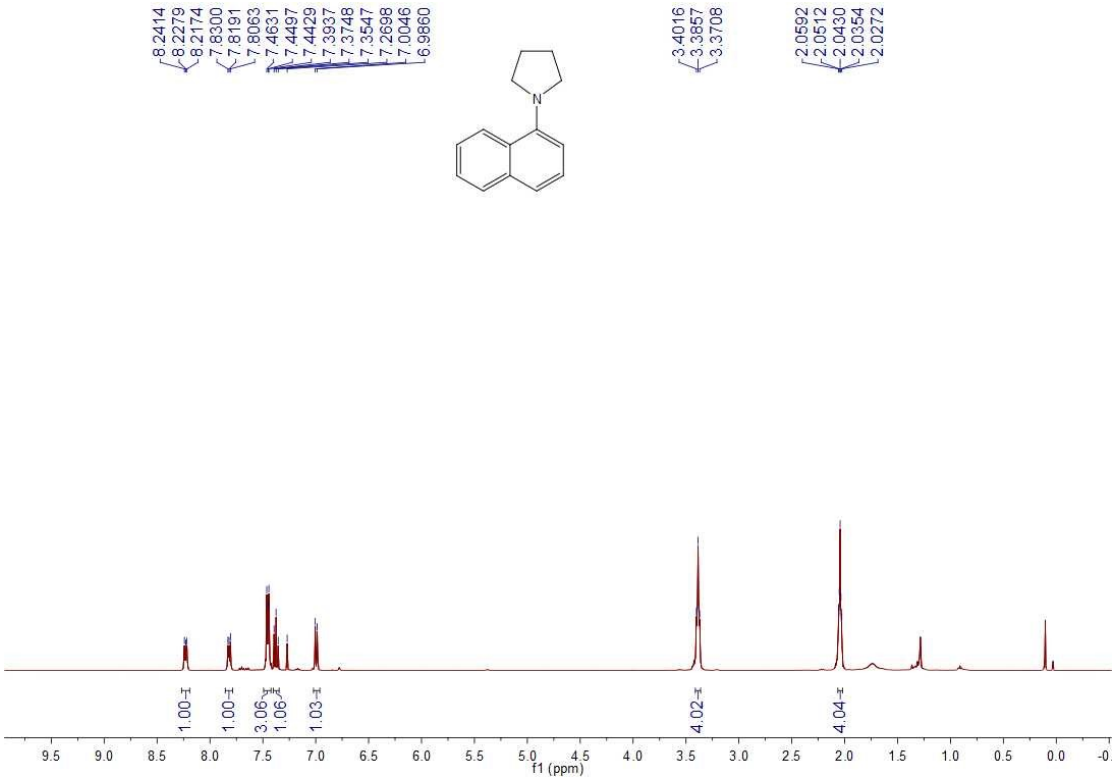
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



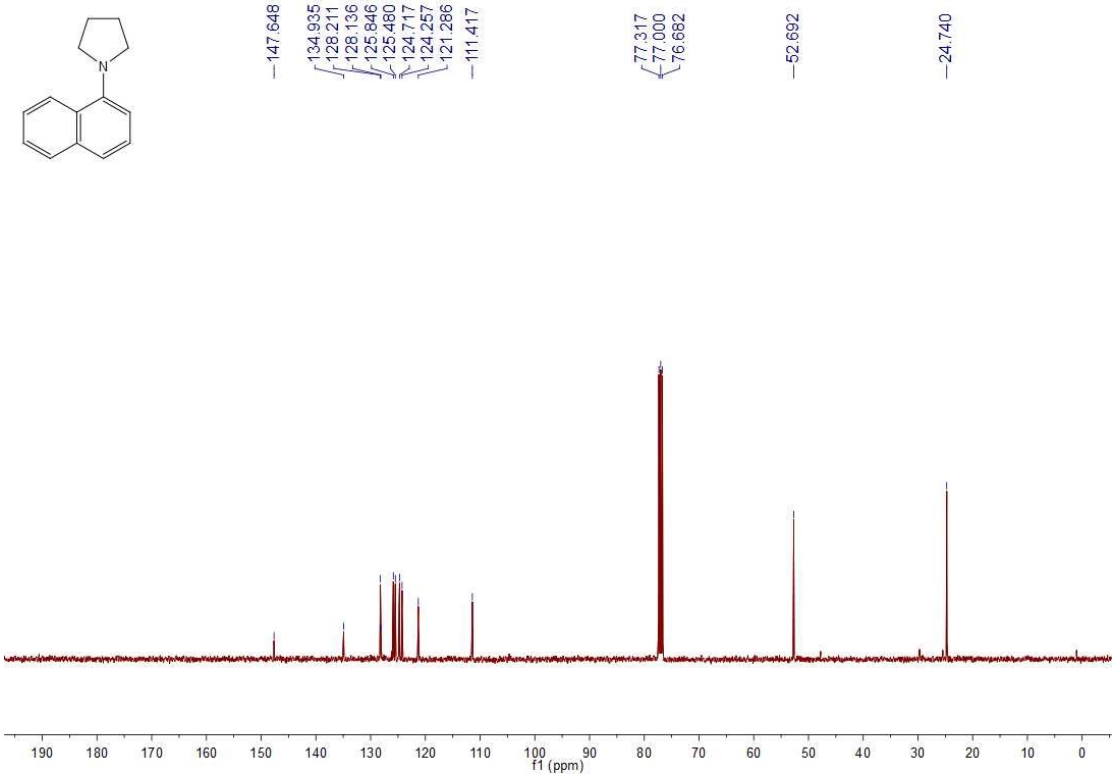
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3a



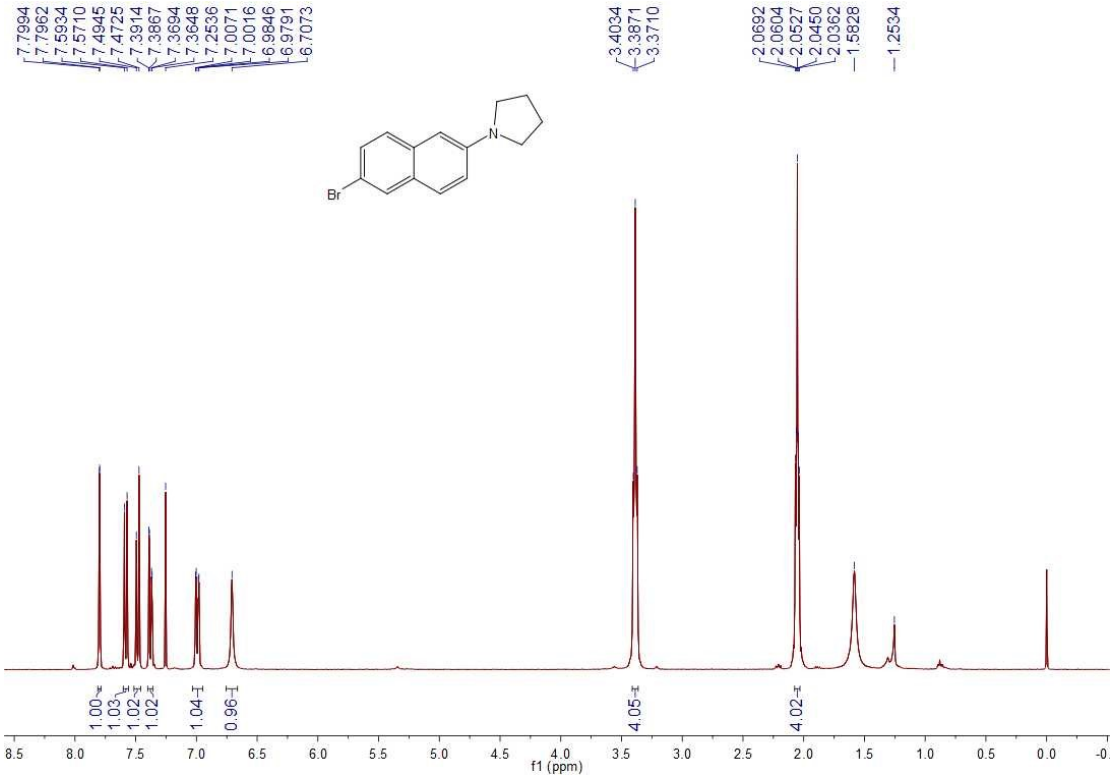
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b



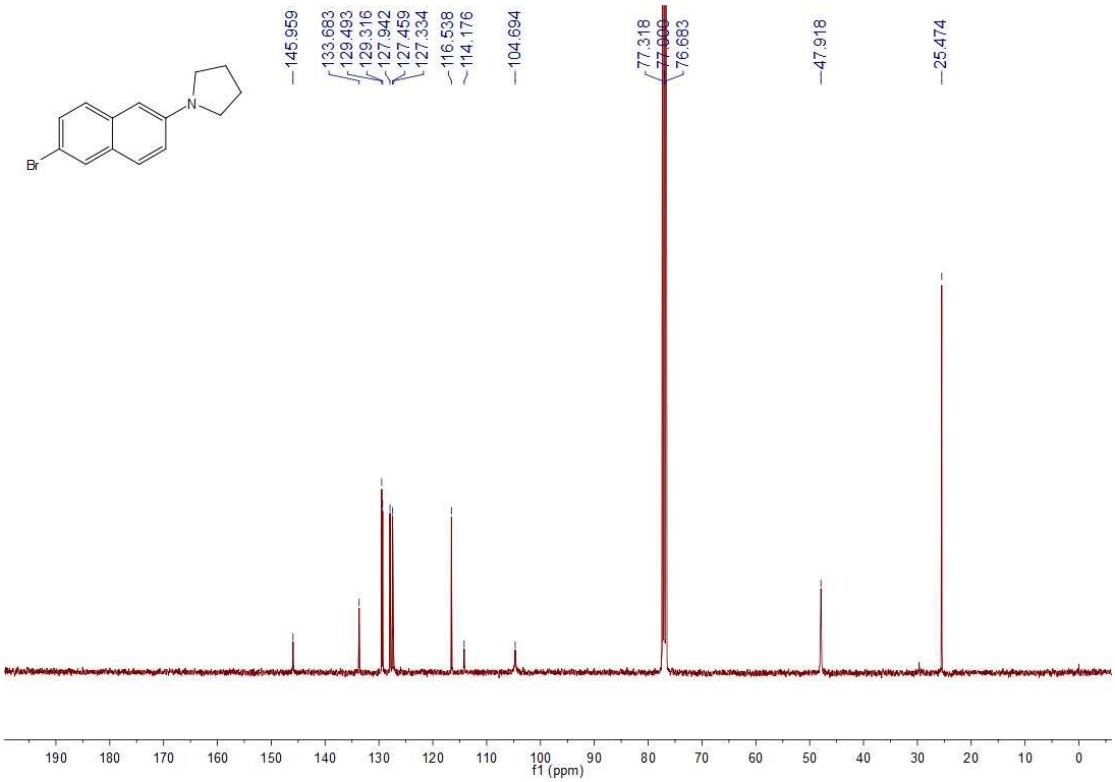
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3b



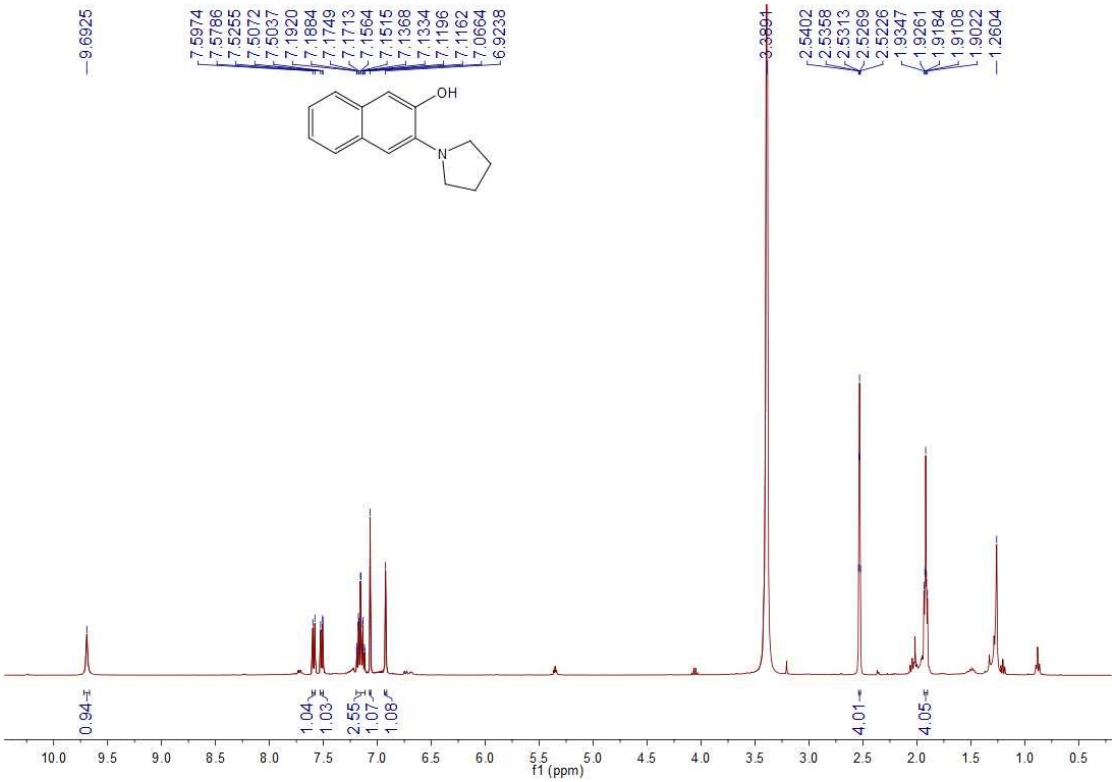
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c



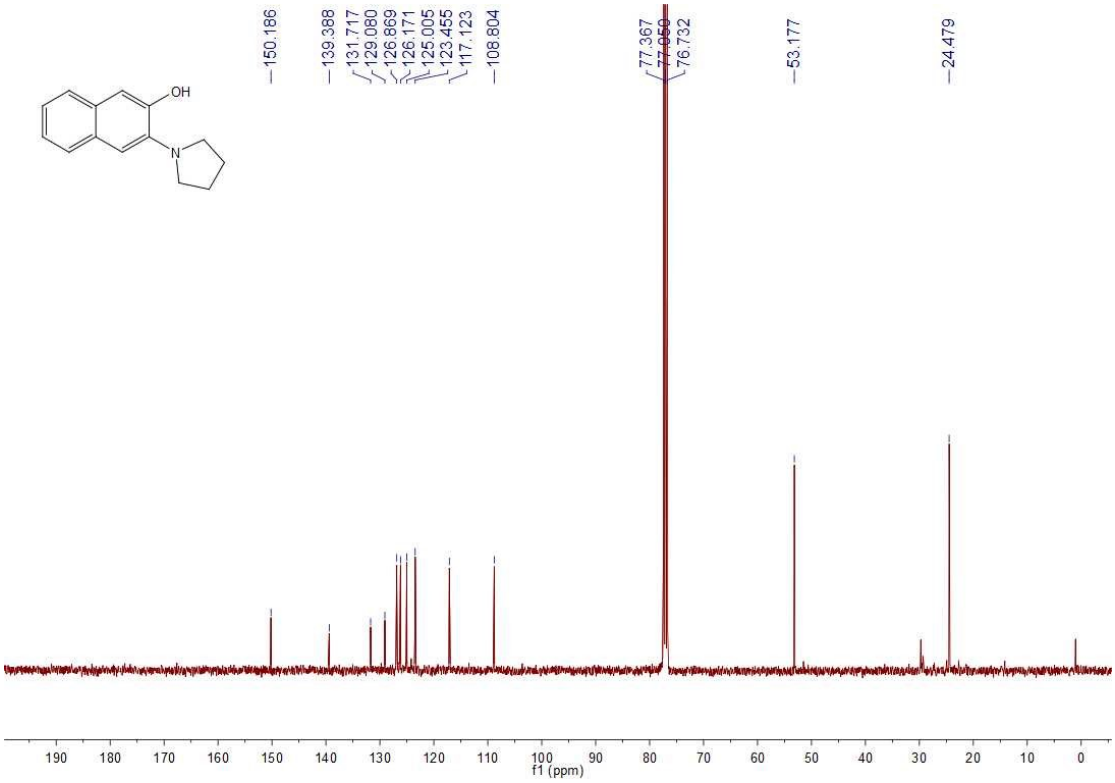
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3c



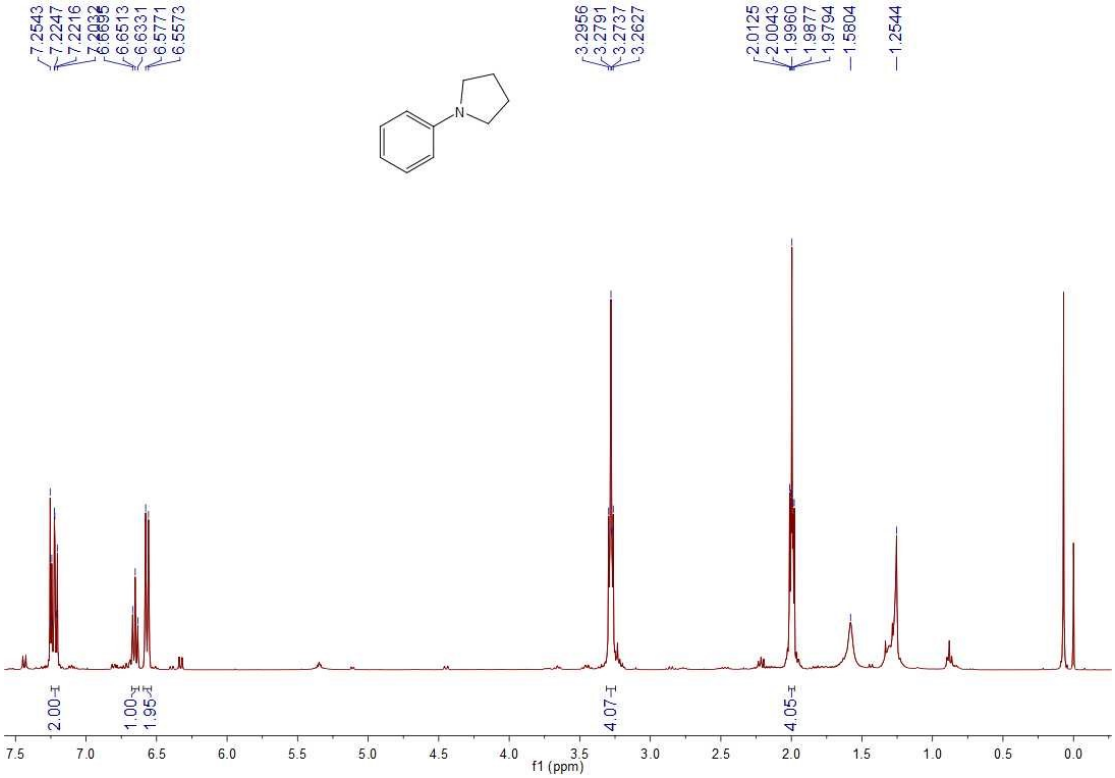
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 3d



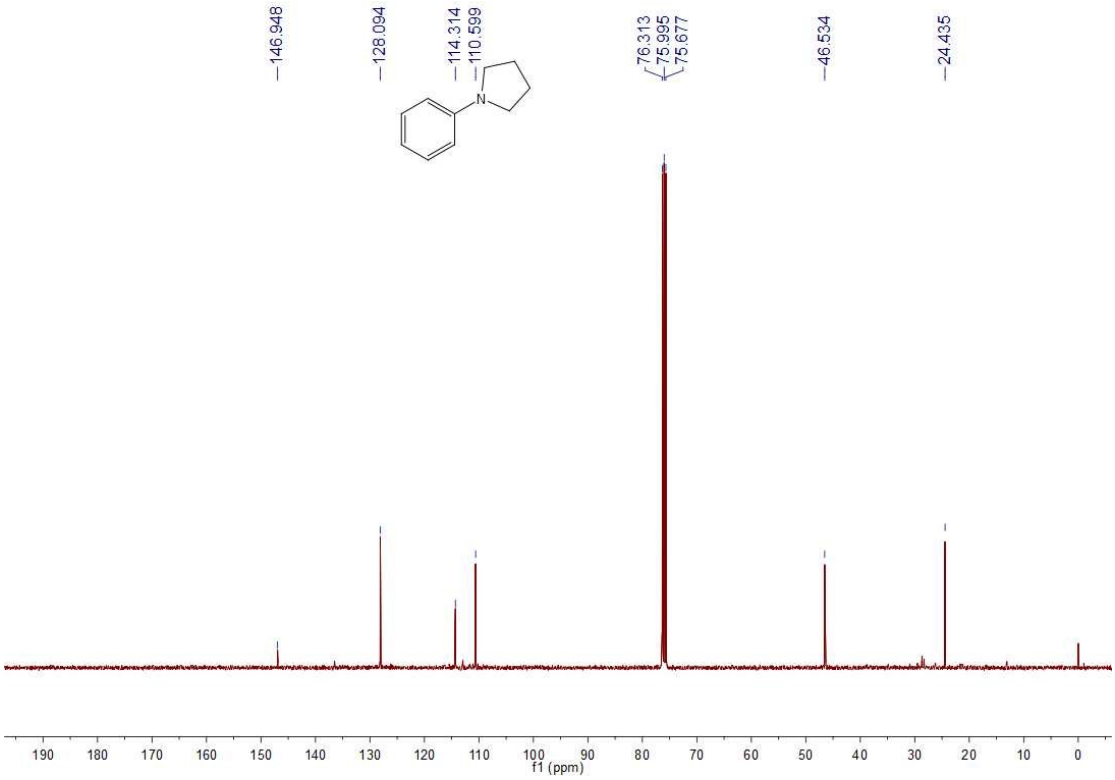
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3d



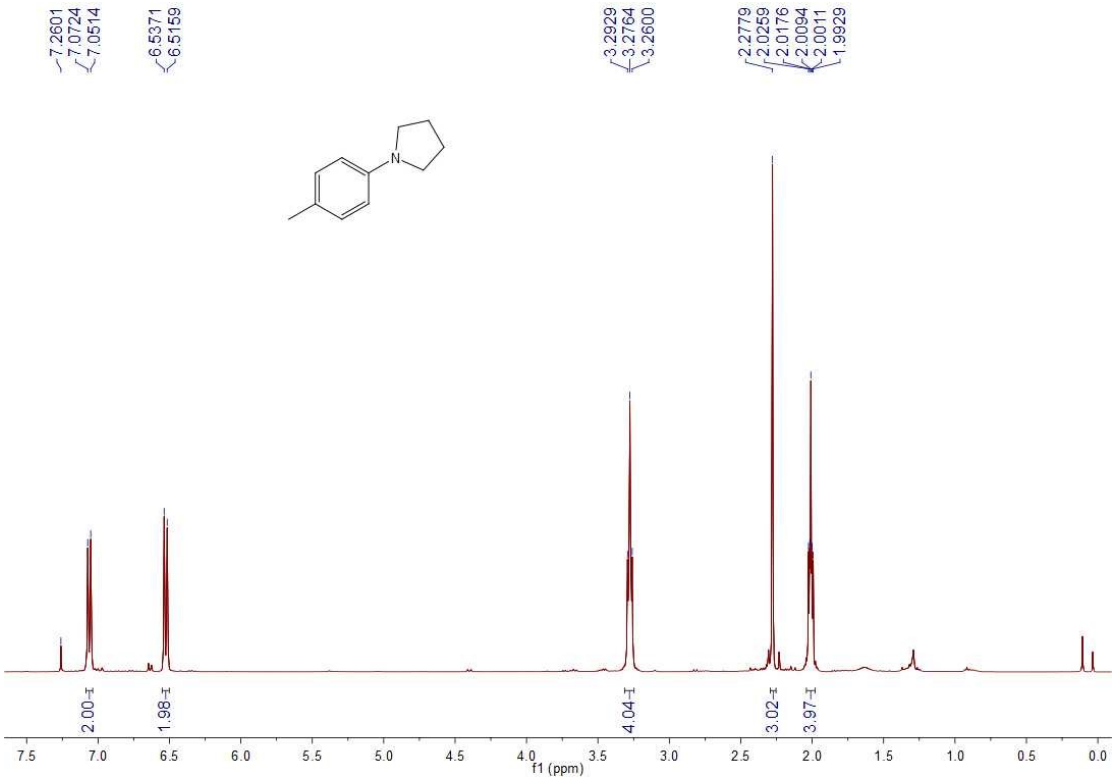
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e



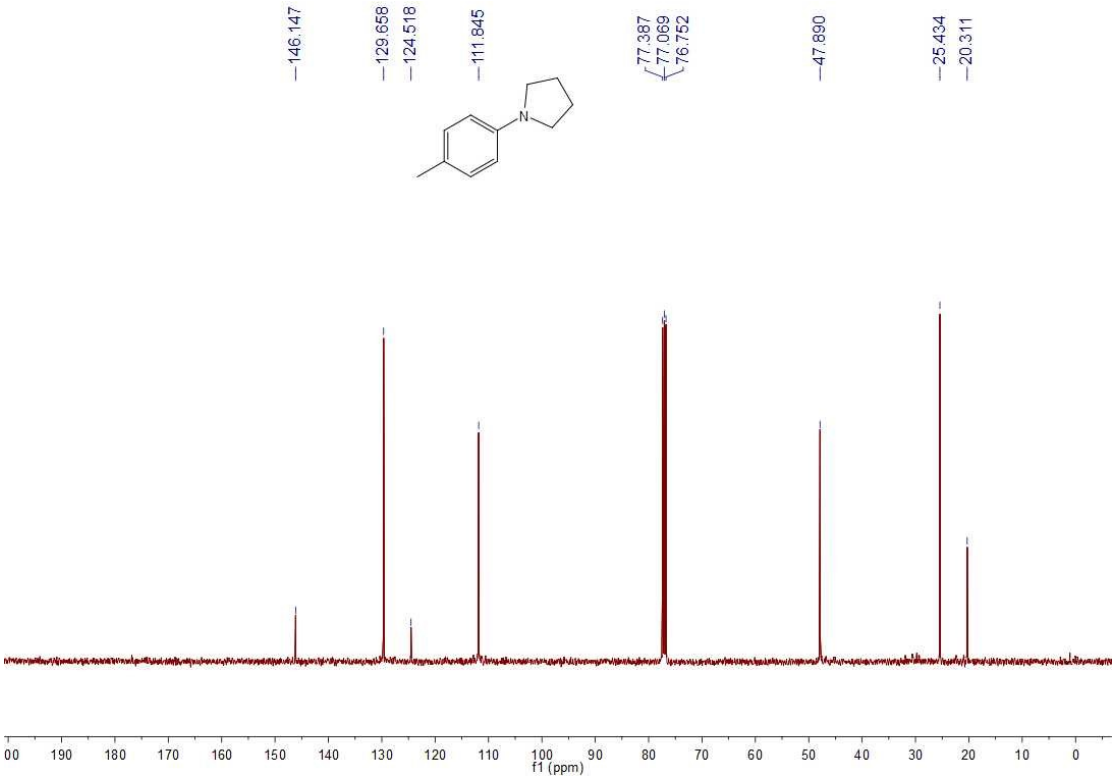
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3e



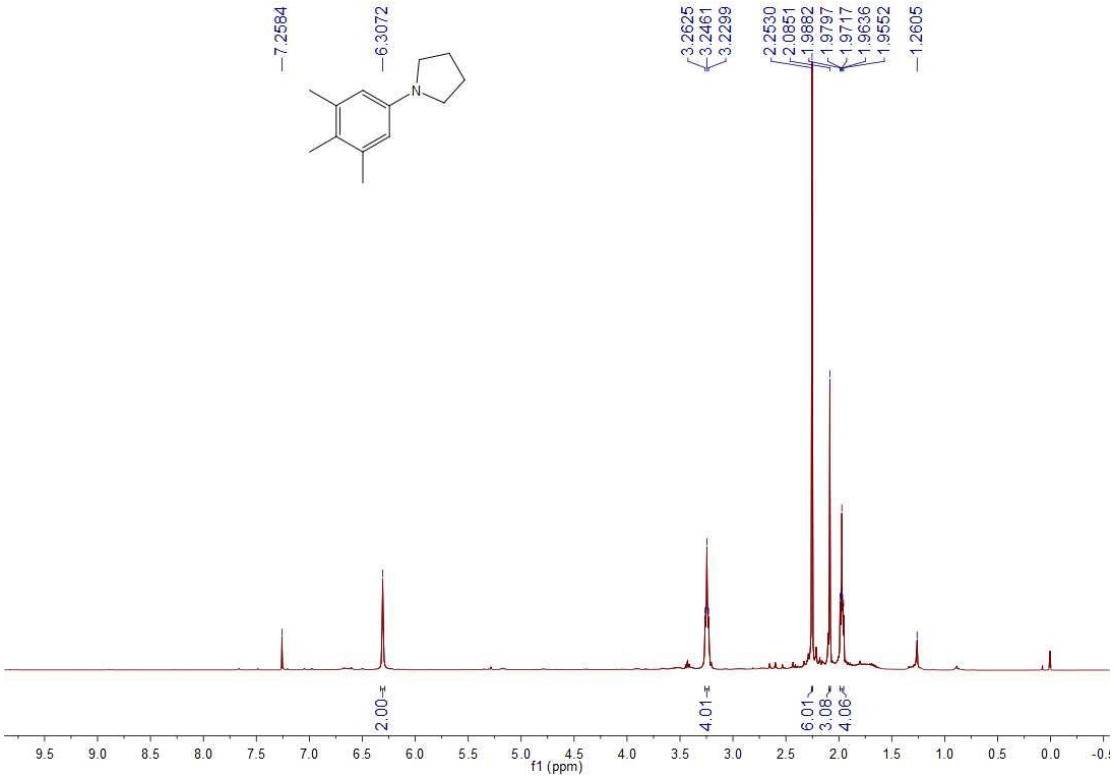
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f



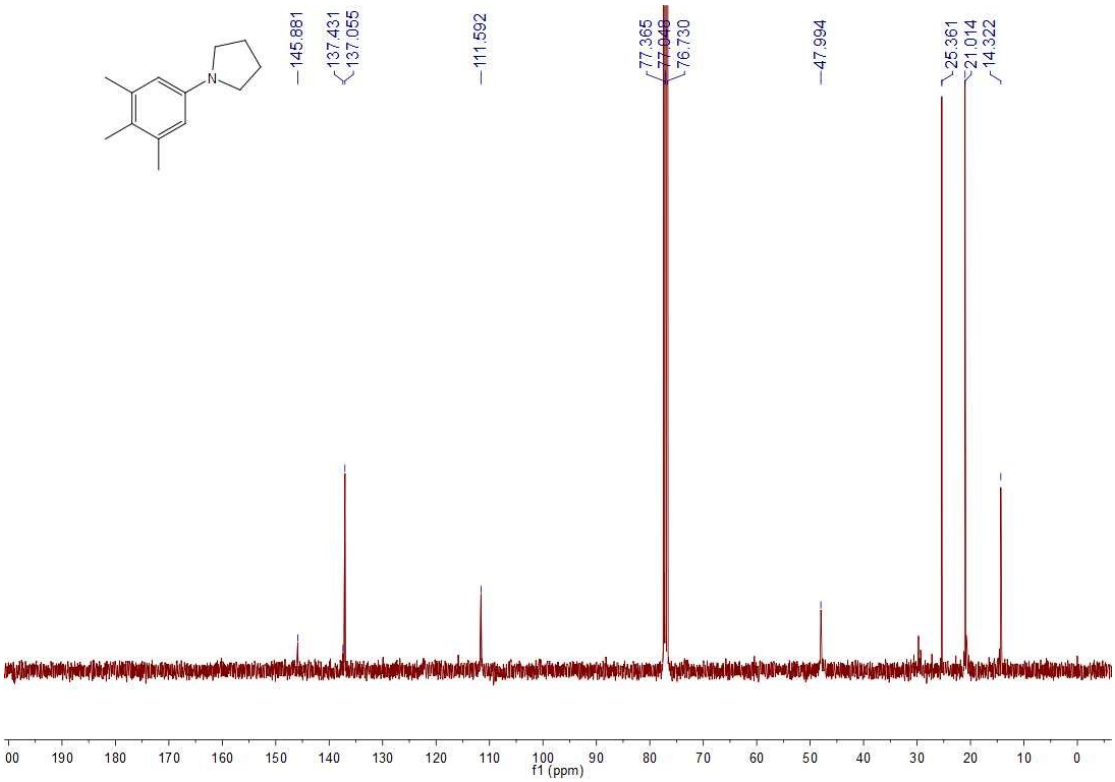
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3f



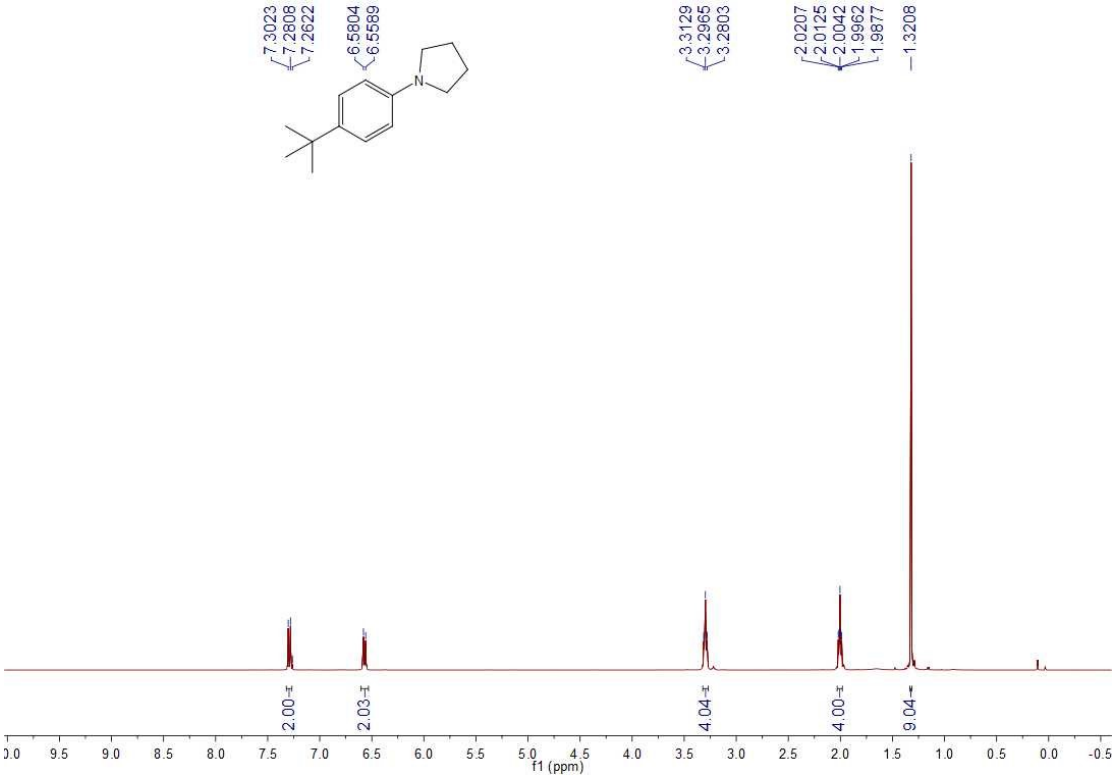
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g



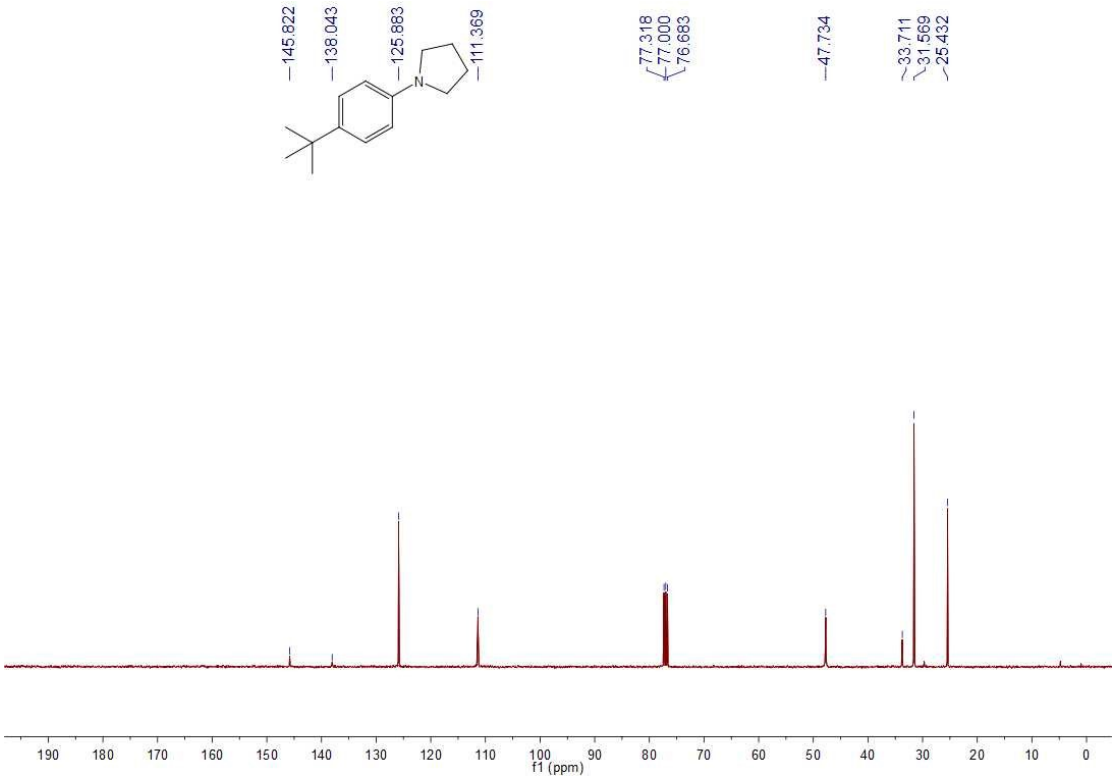
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3g



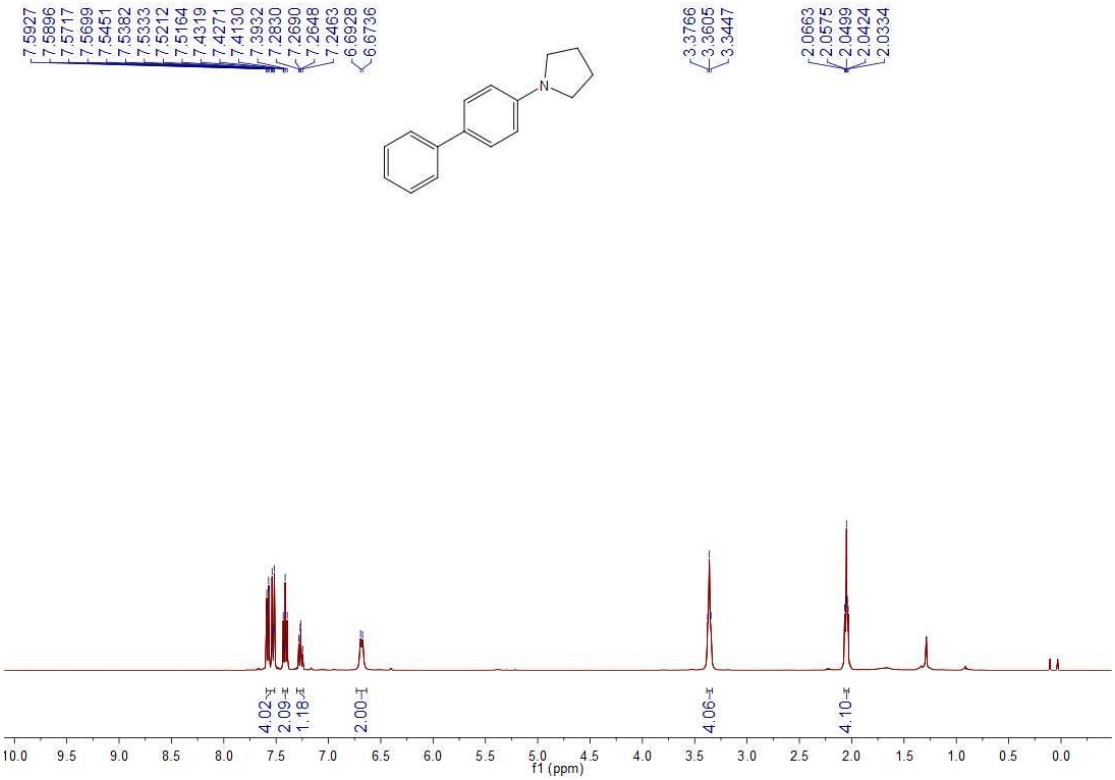
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



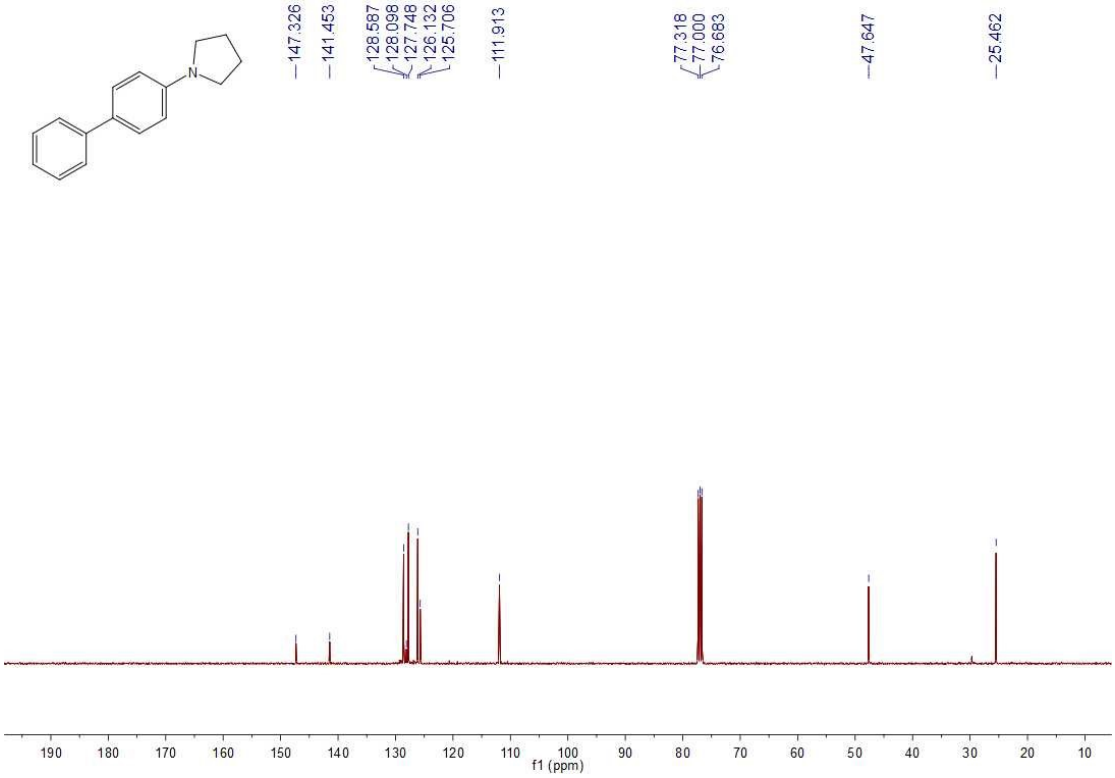
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3h



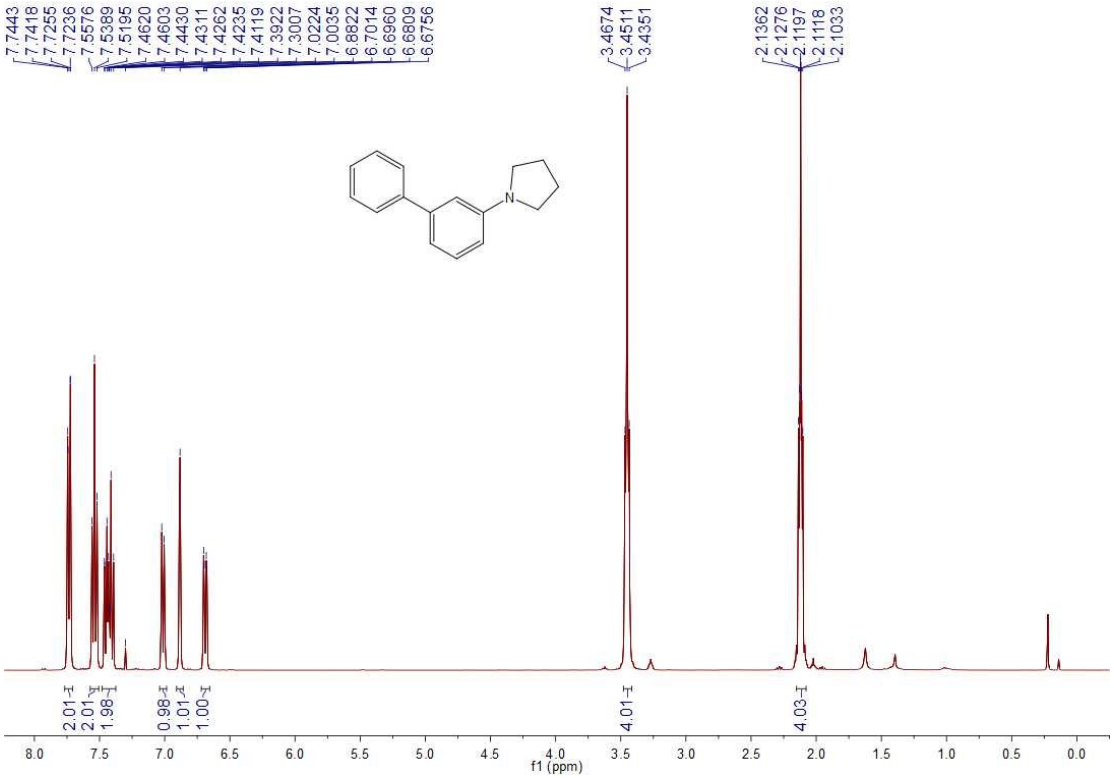
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i



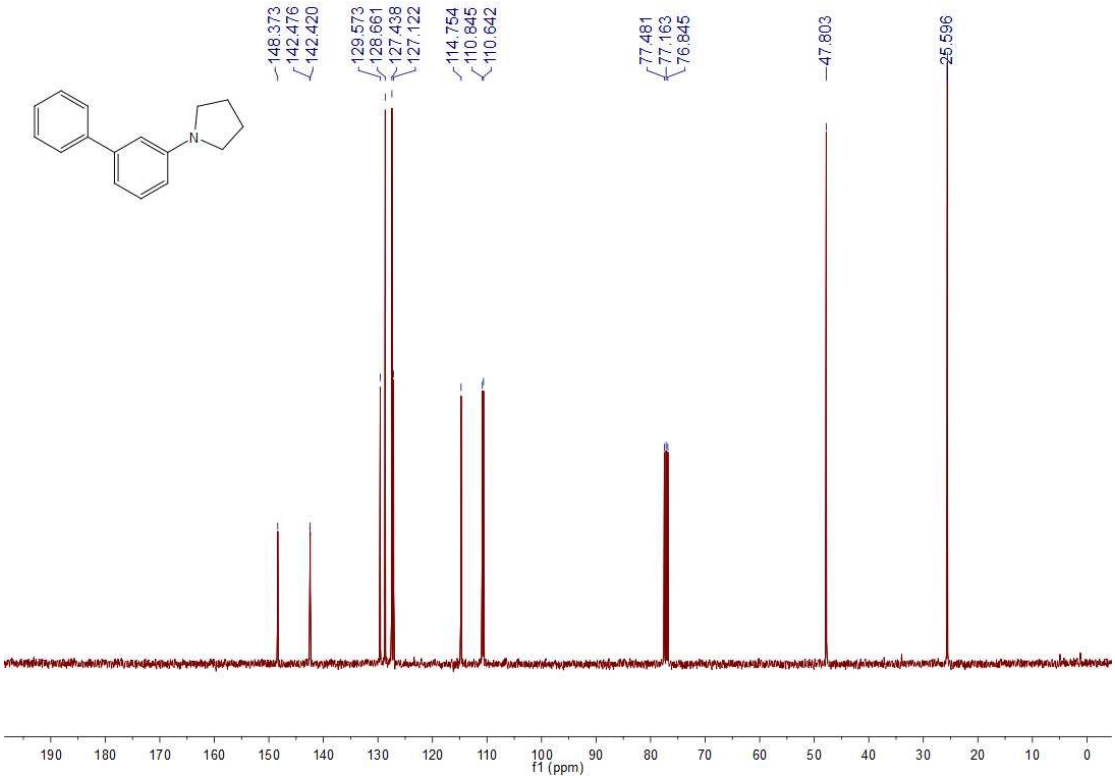
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3i



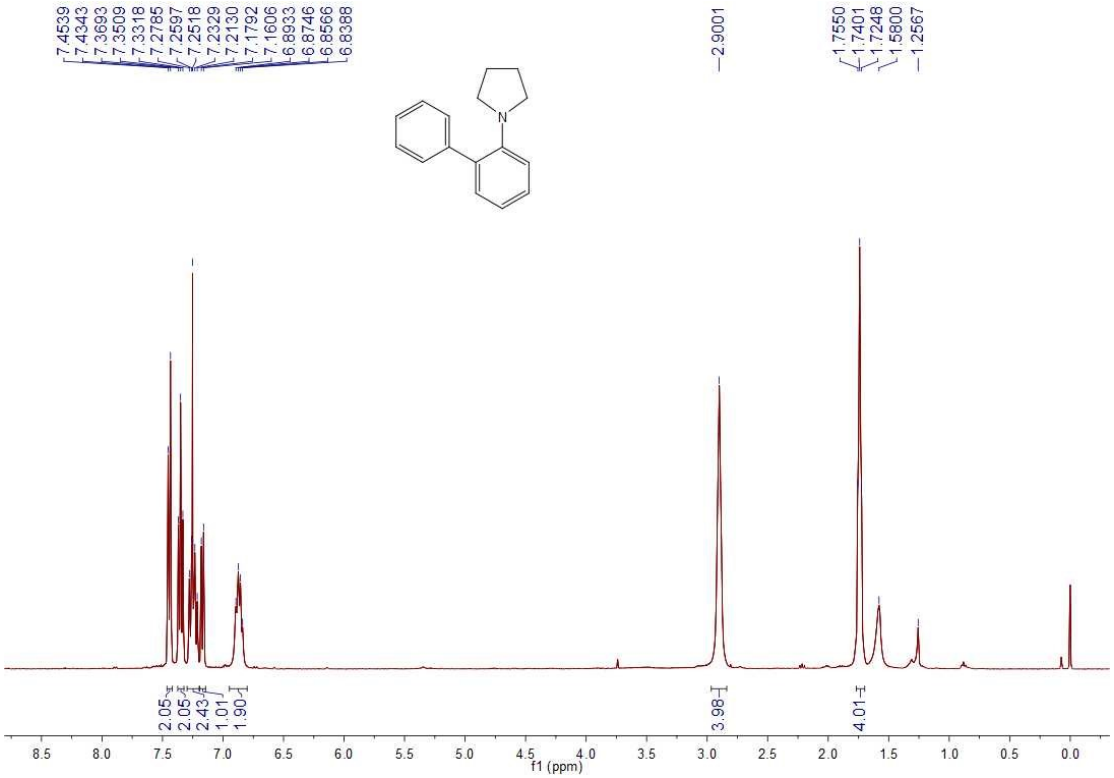
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j



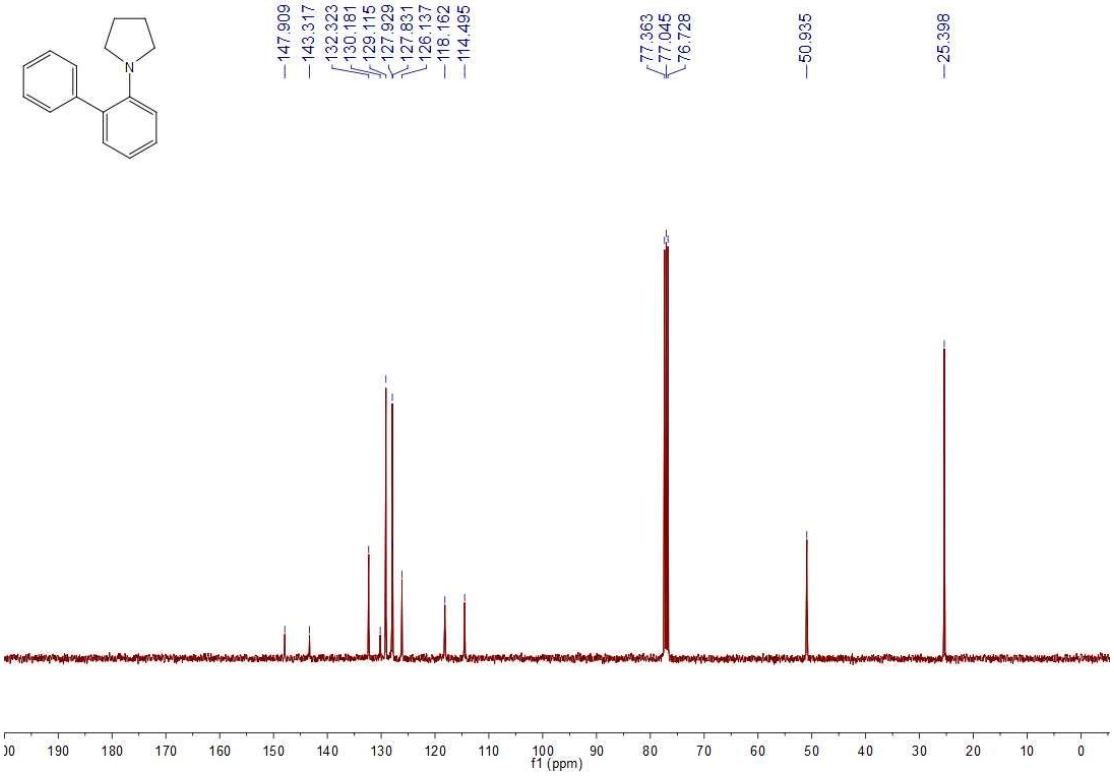
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3j



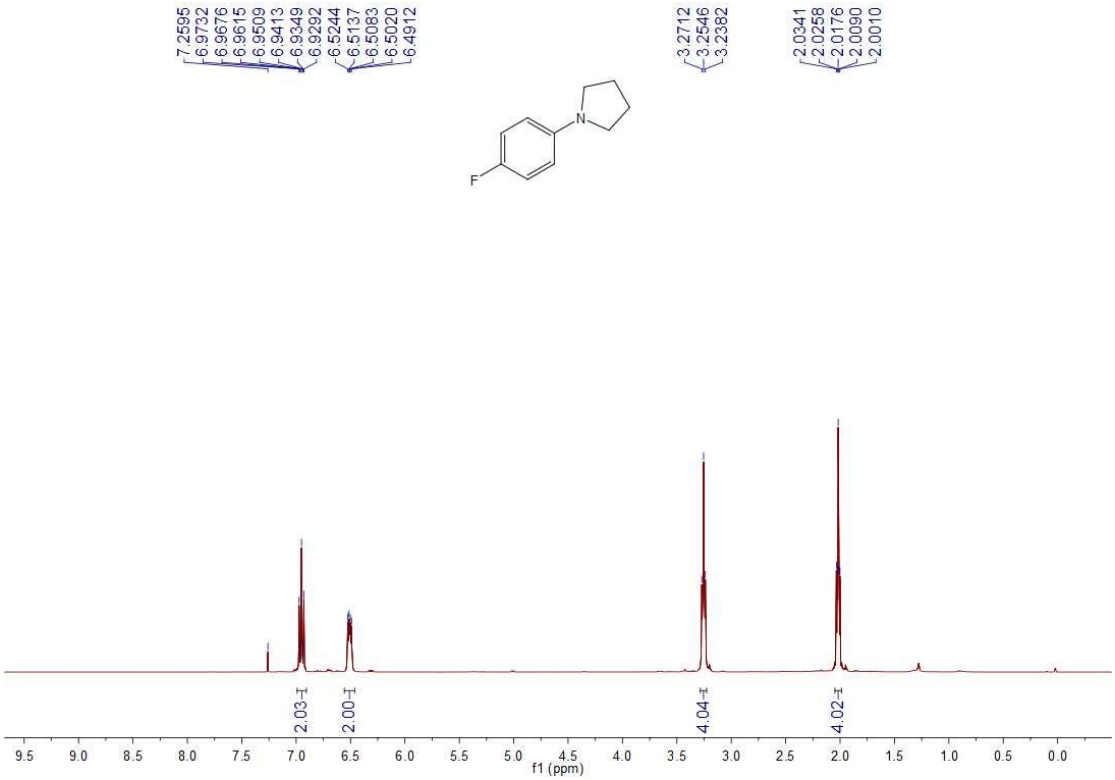
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3k



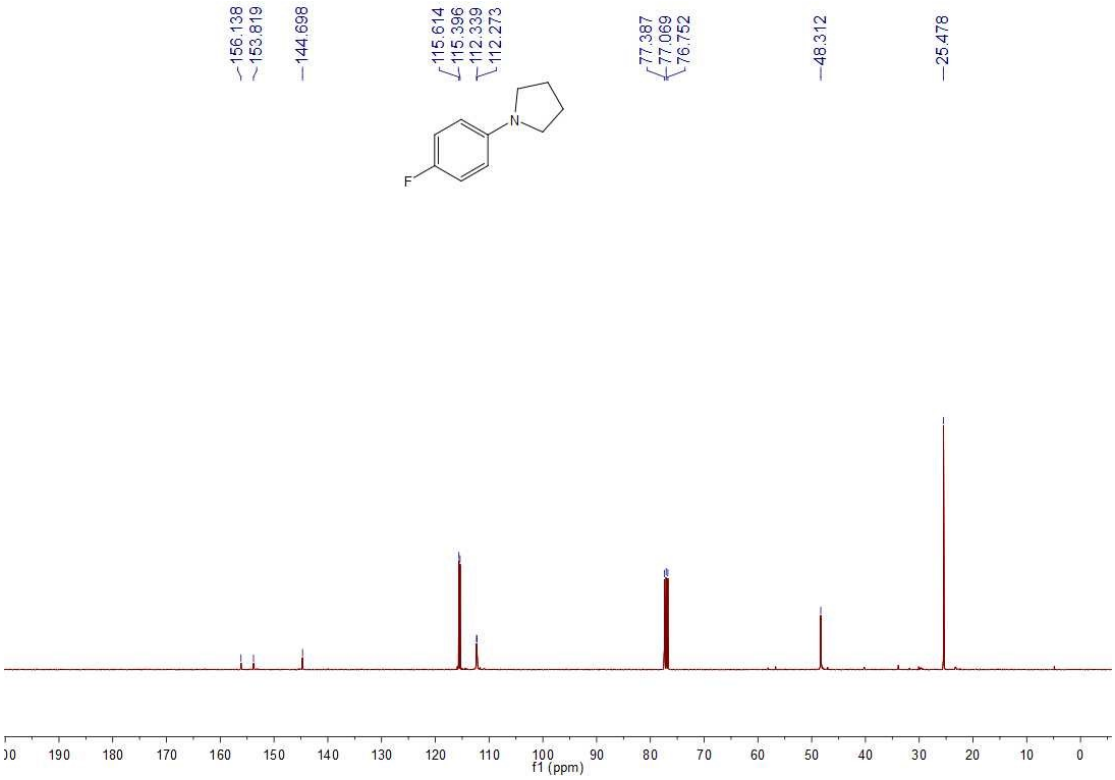
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3k



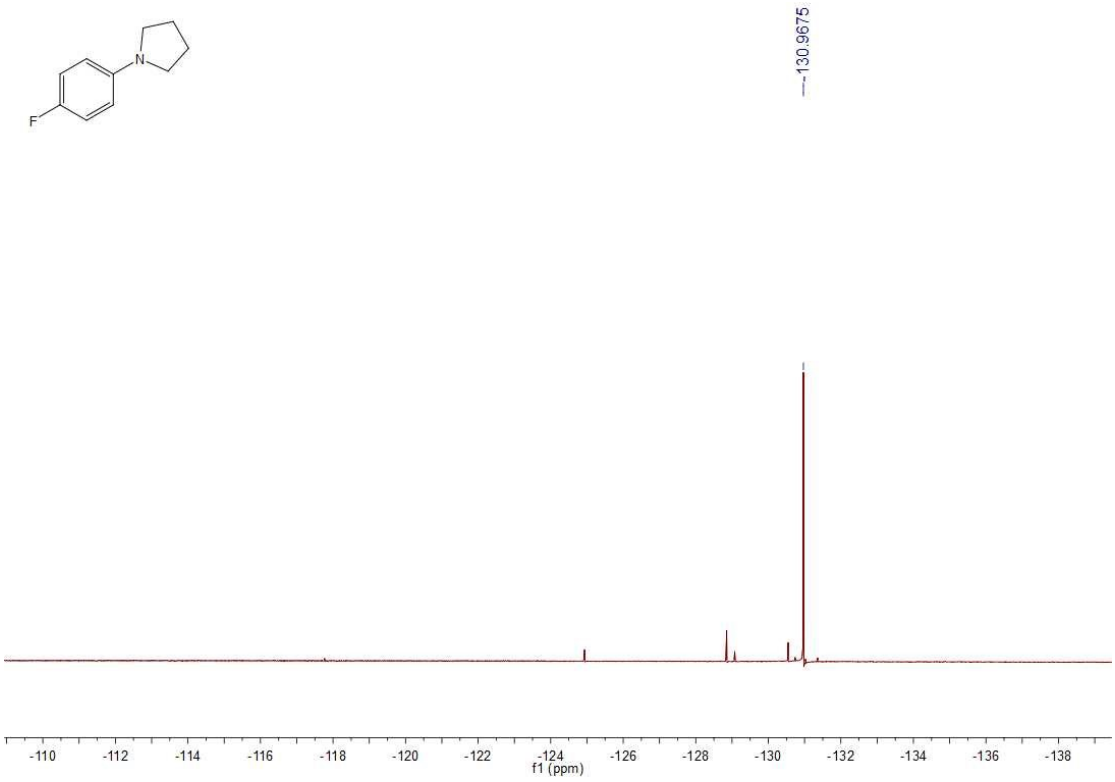
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l



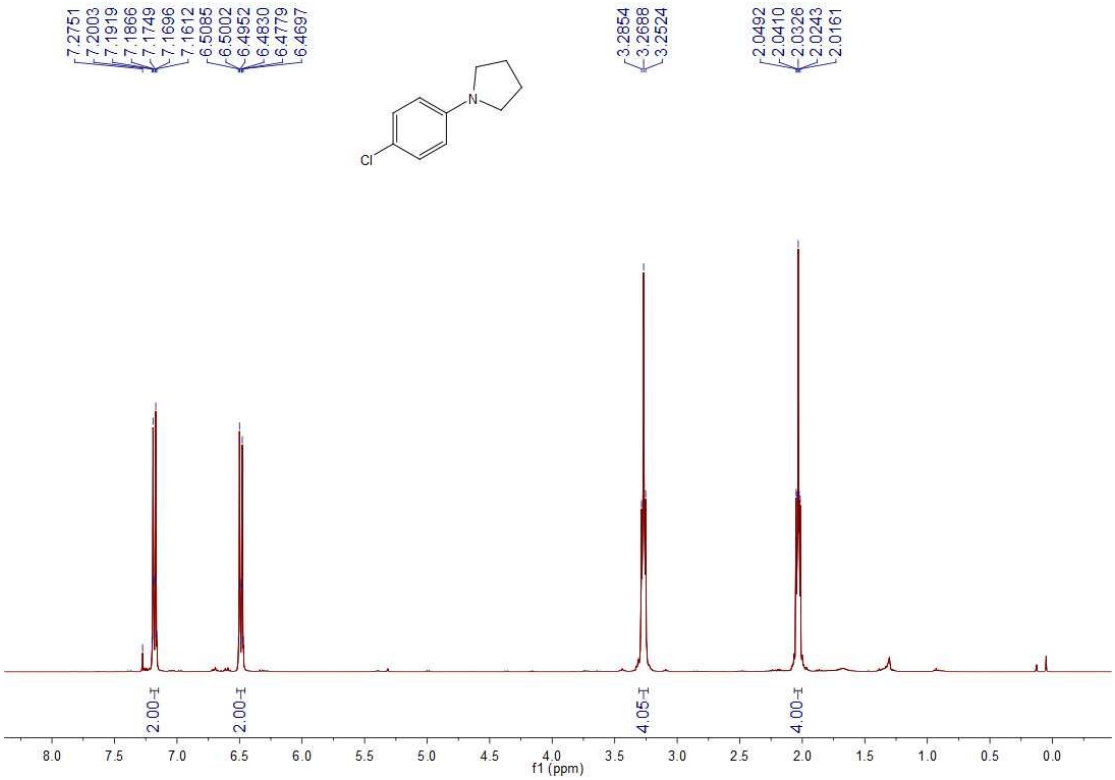
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3l



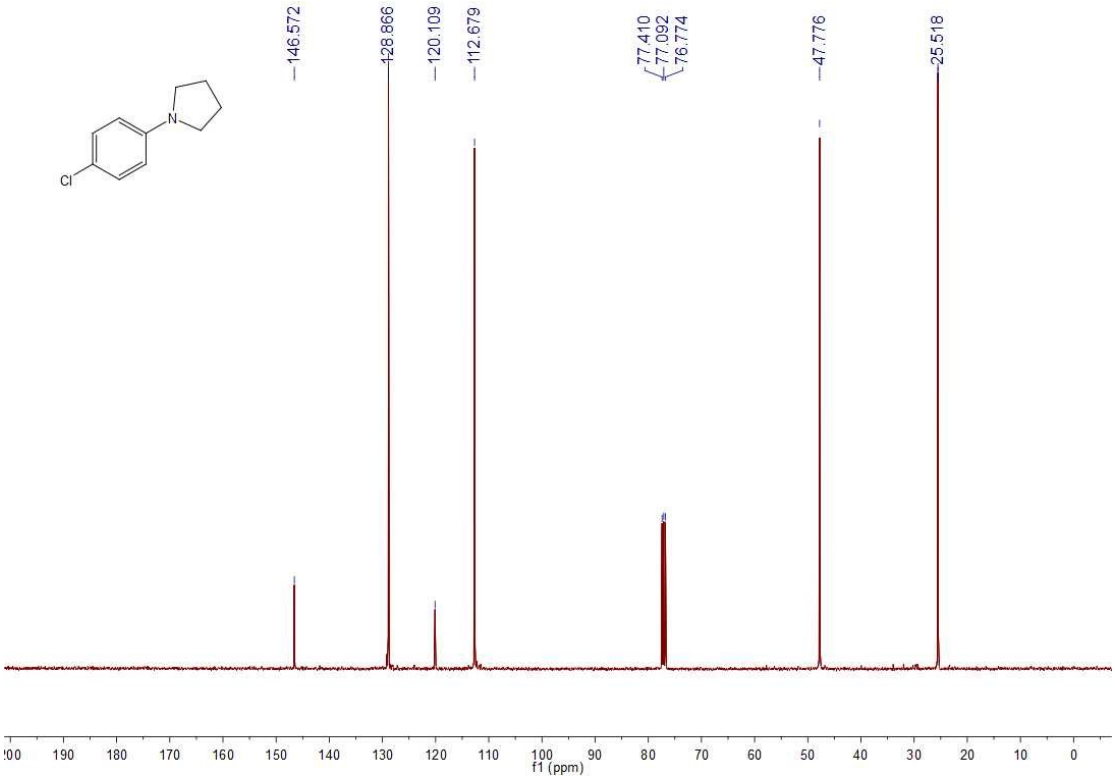
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3l



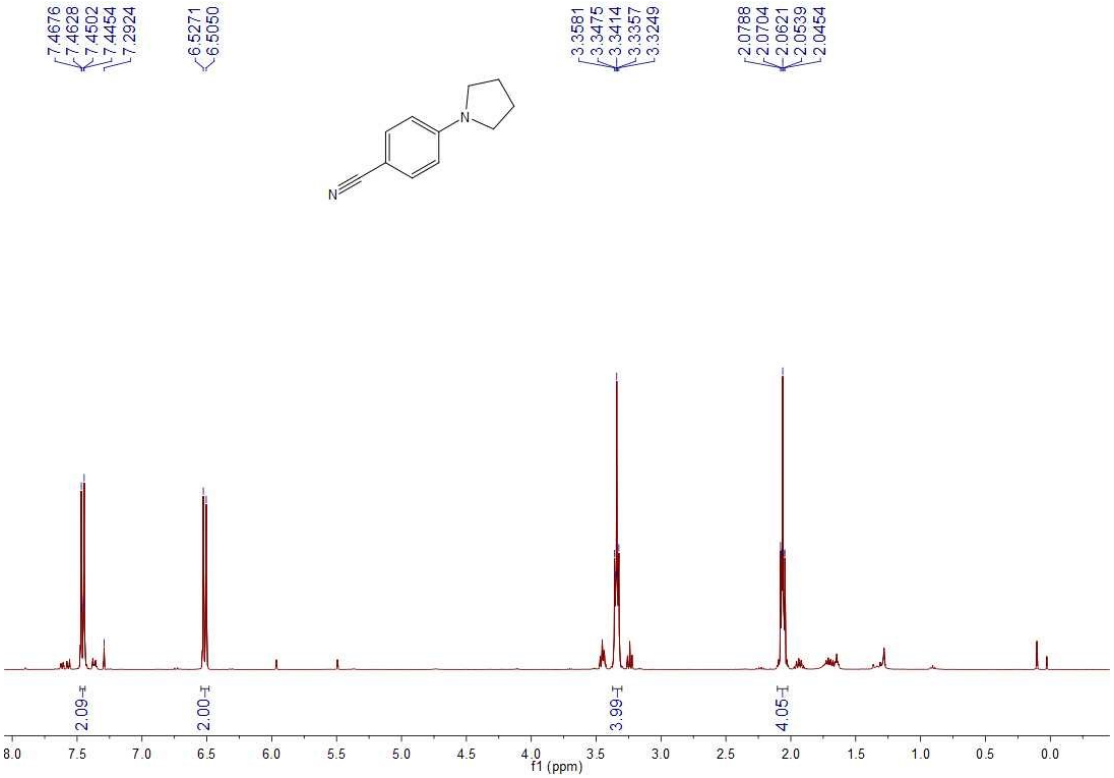
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3m



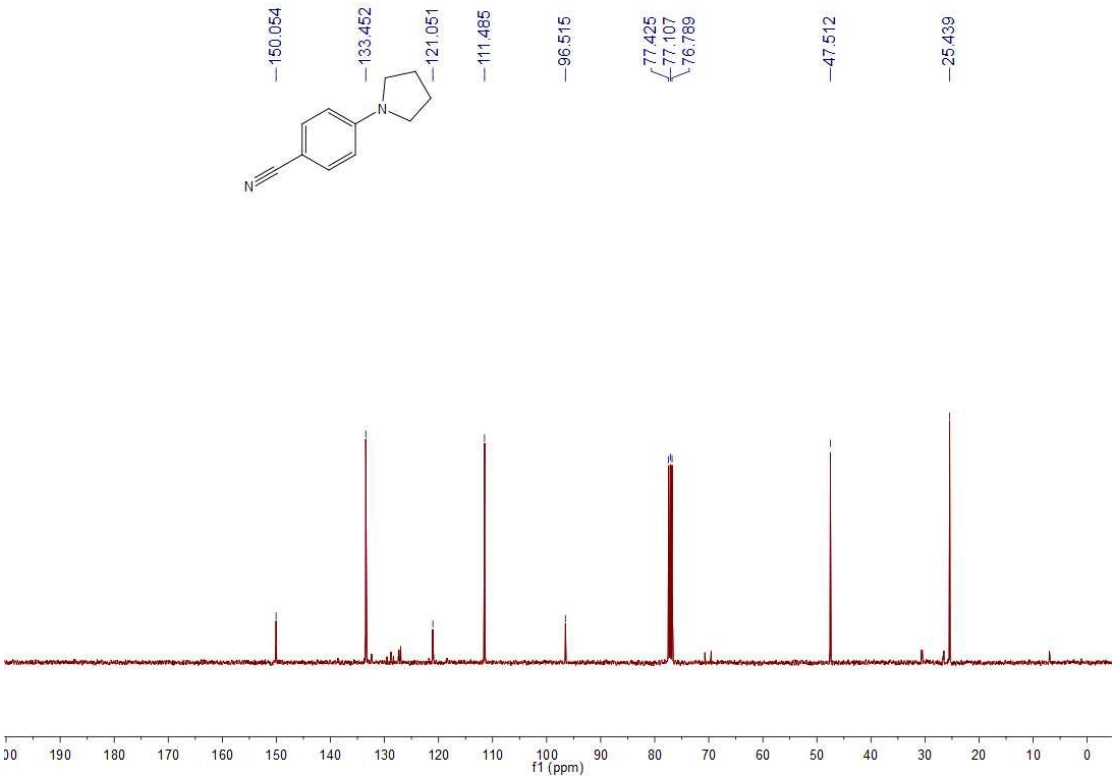
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3m



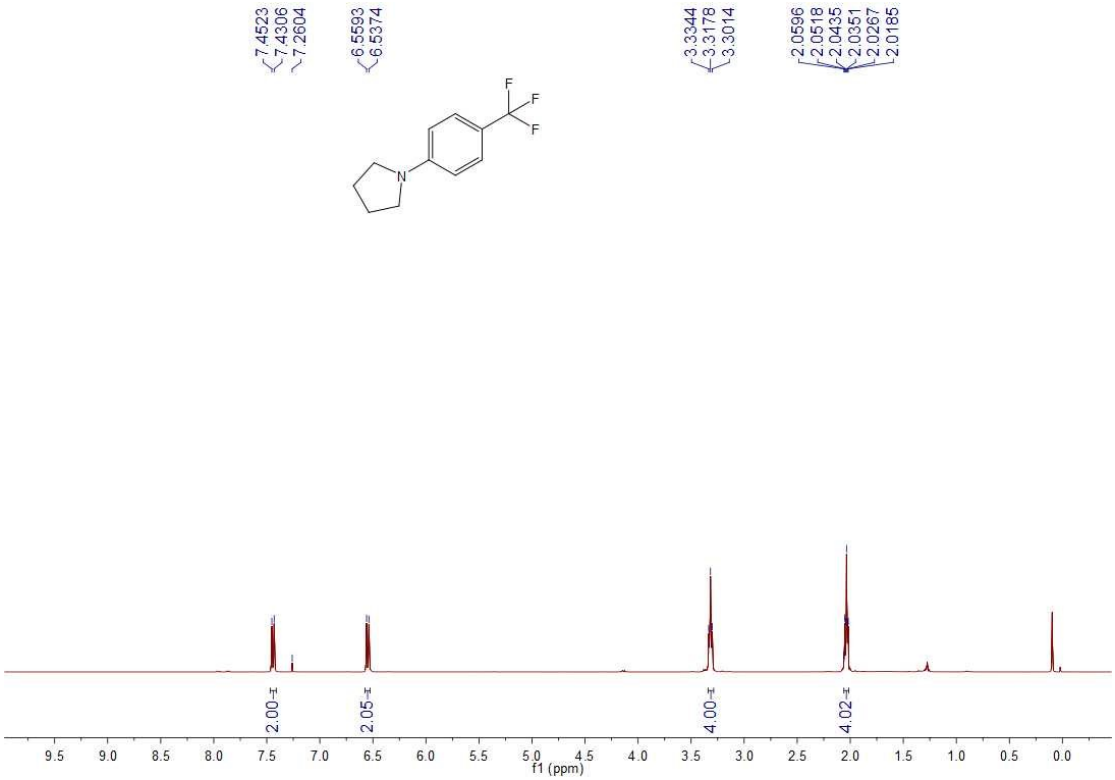
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3n



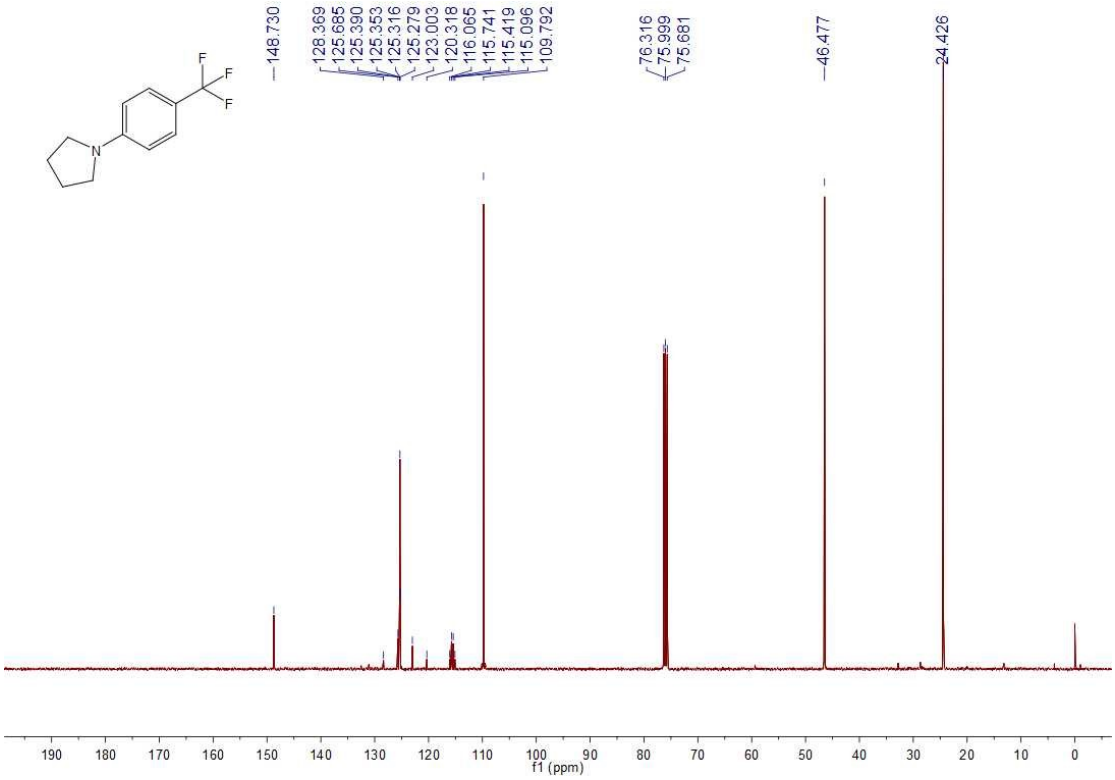
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3n



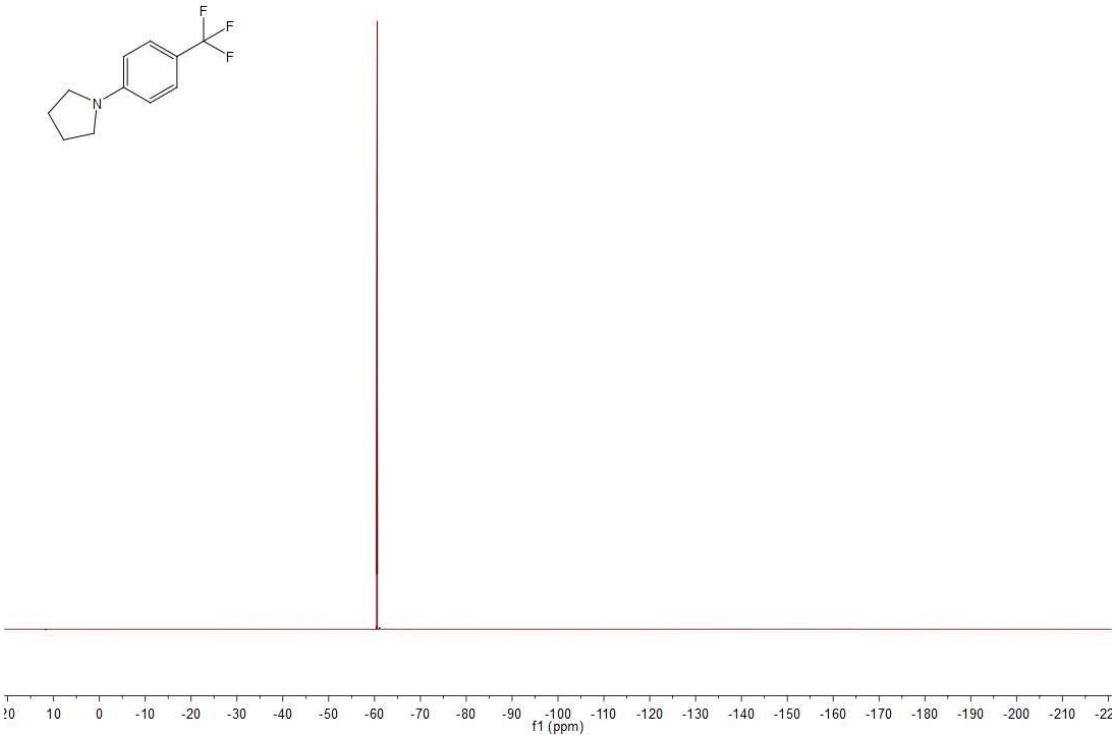
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3o



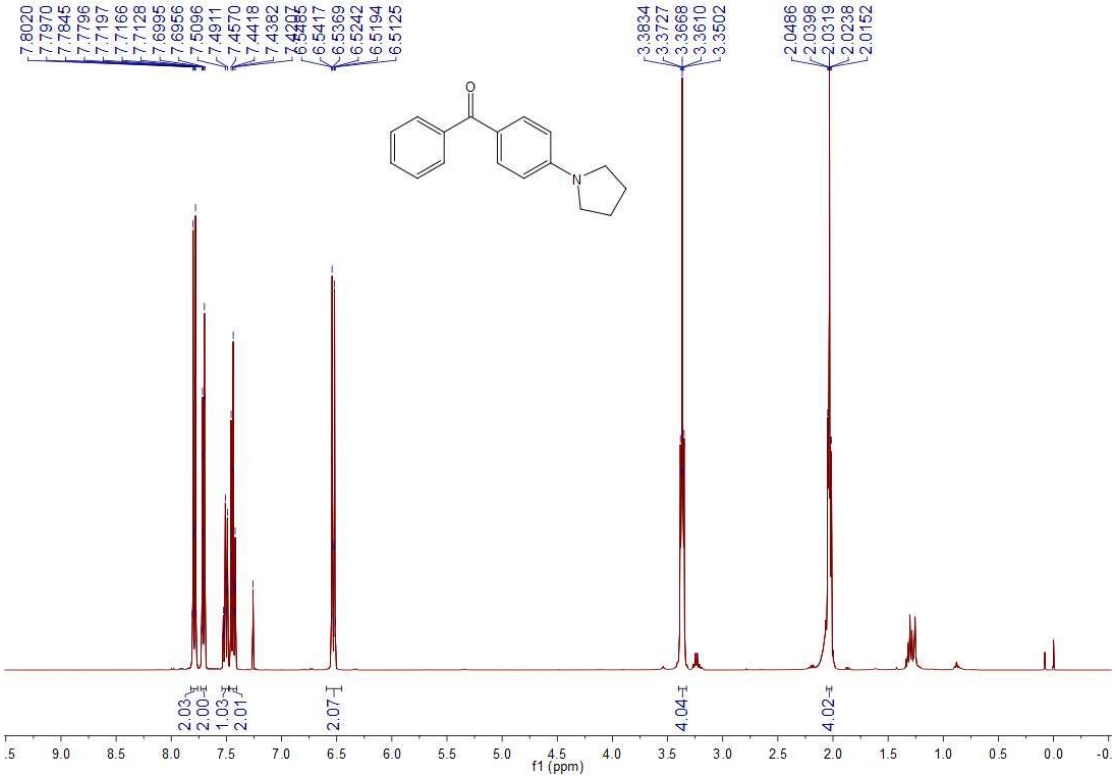
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3o



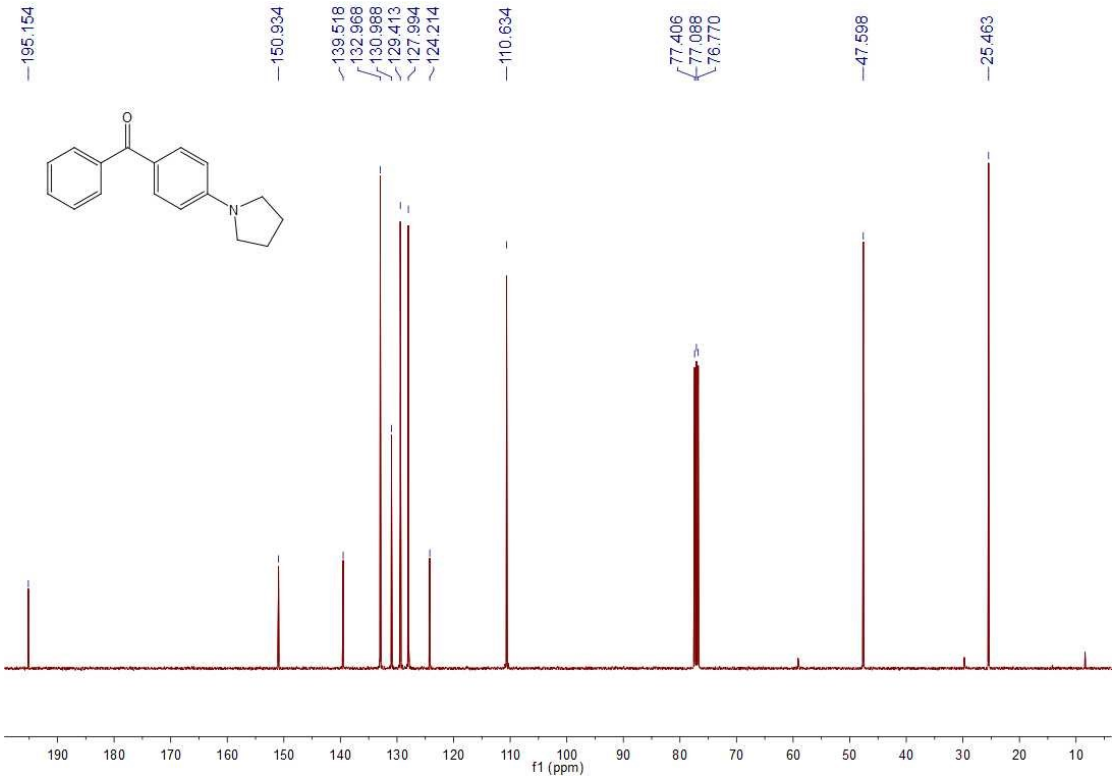
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3o



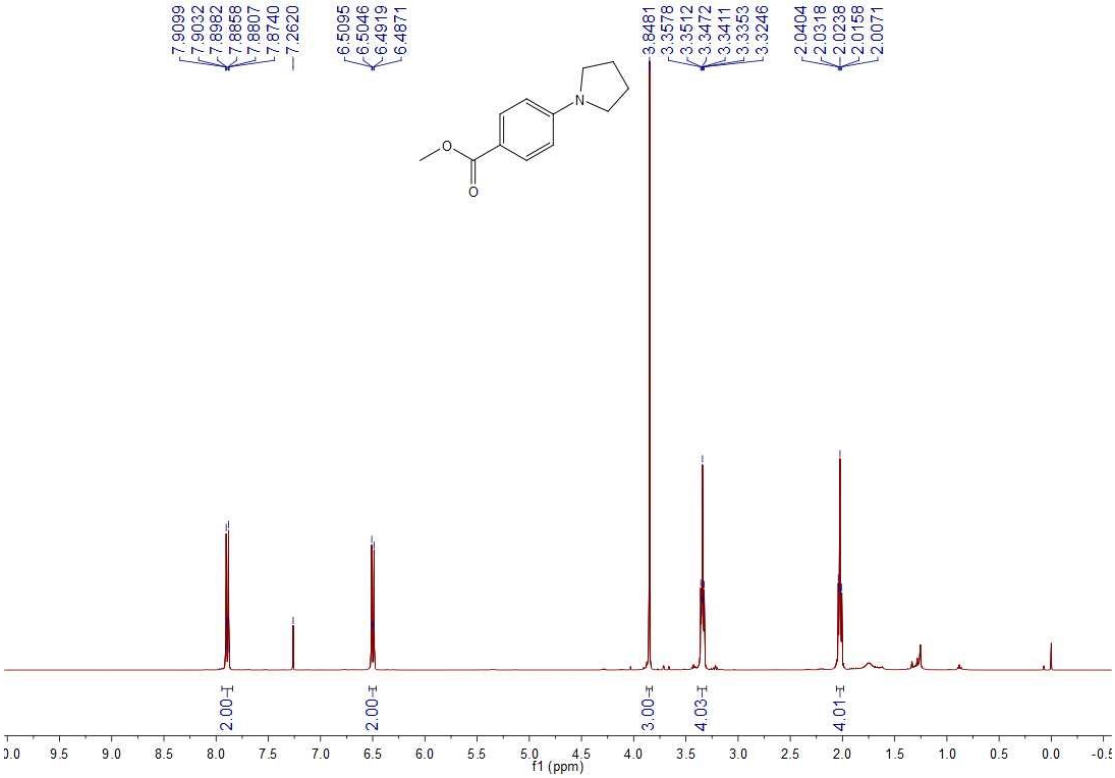
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3p



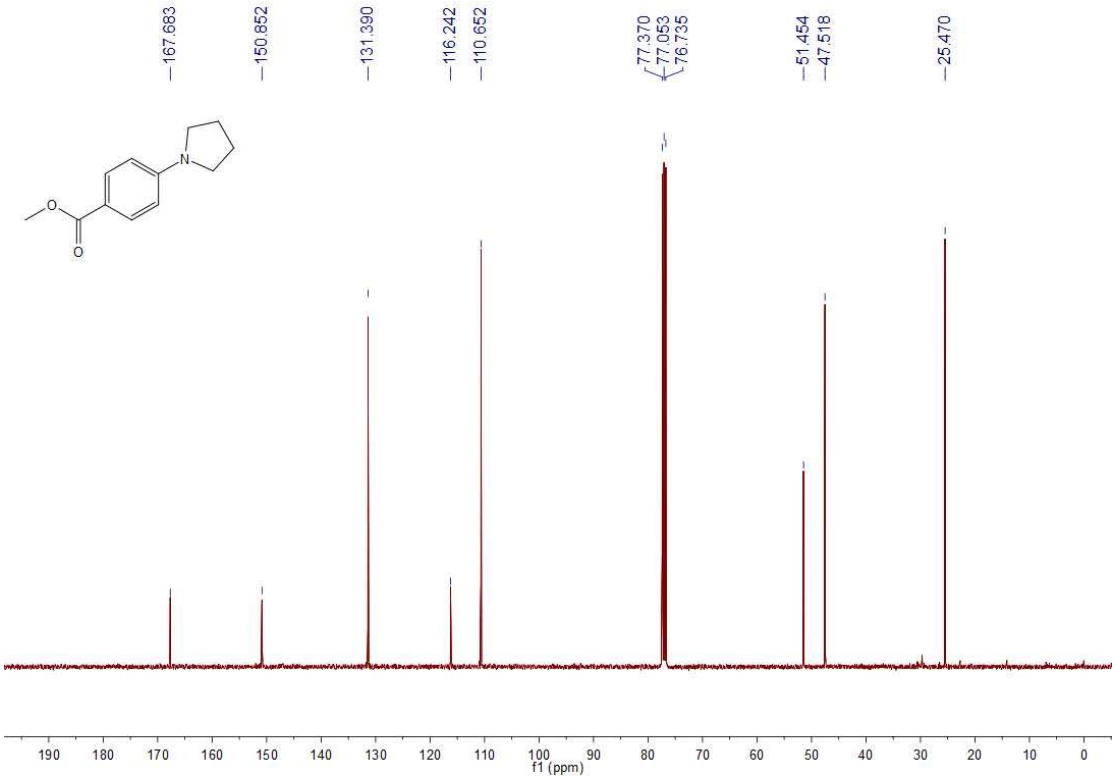
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3p



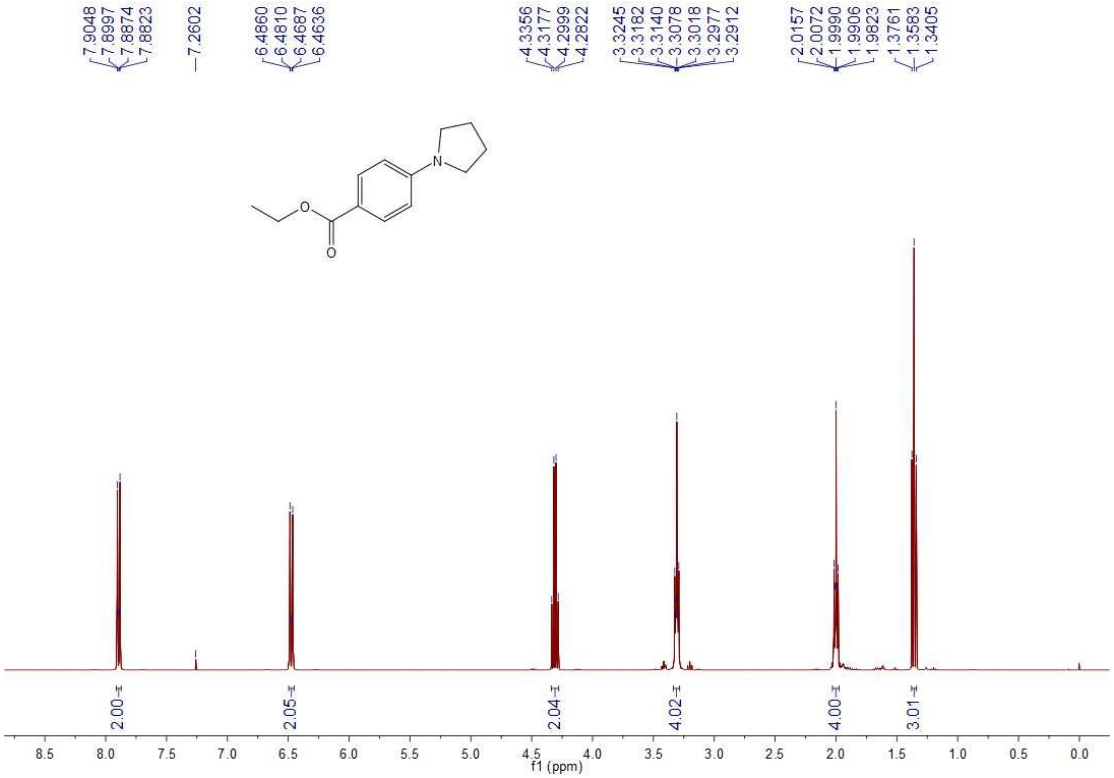
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3q



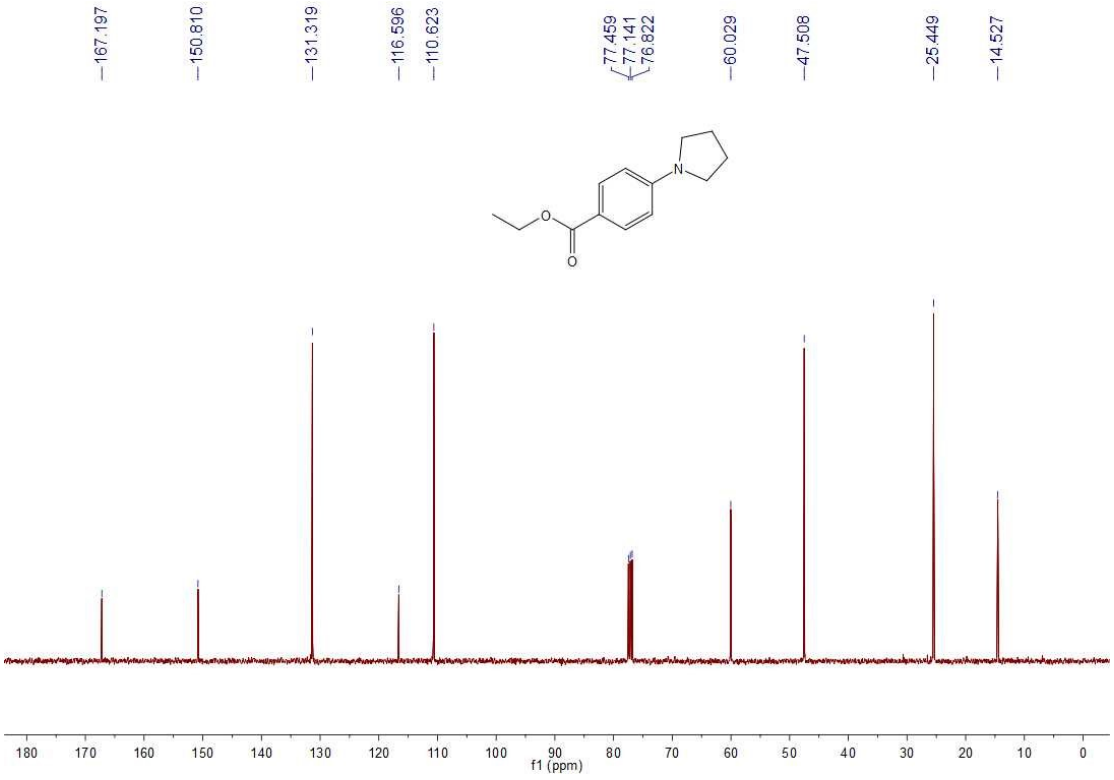
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3q



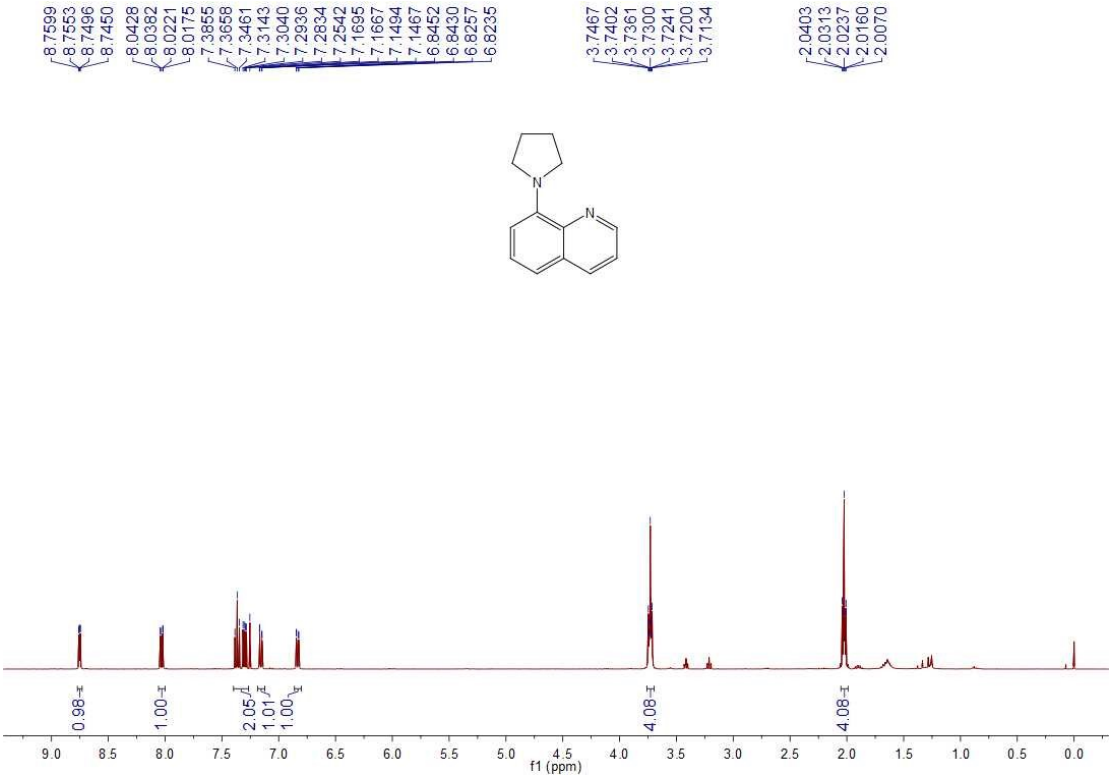
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3r



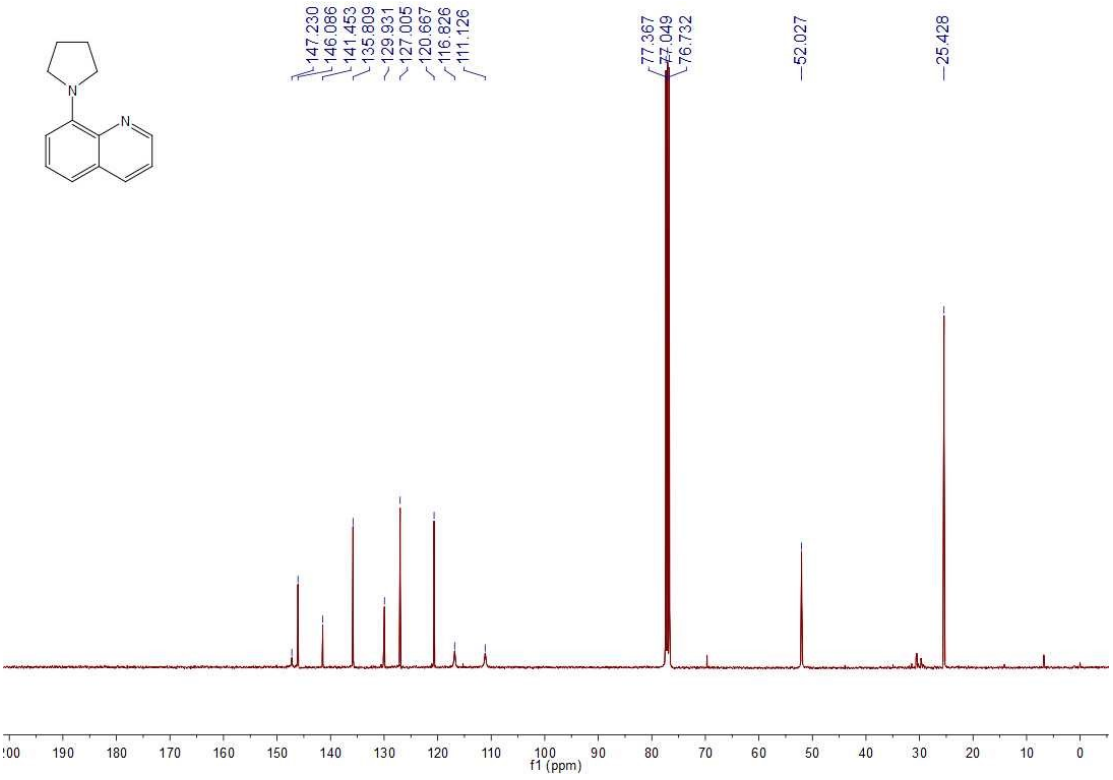
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3r



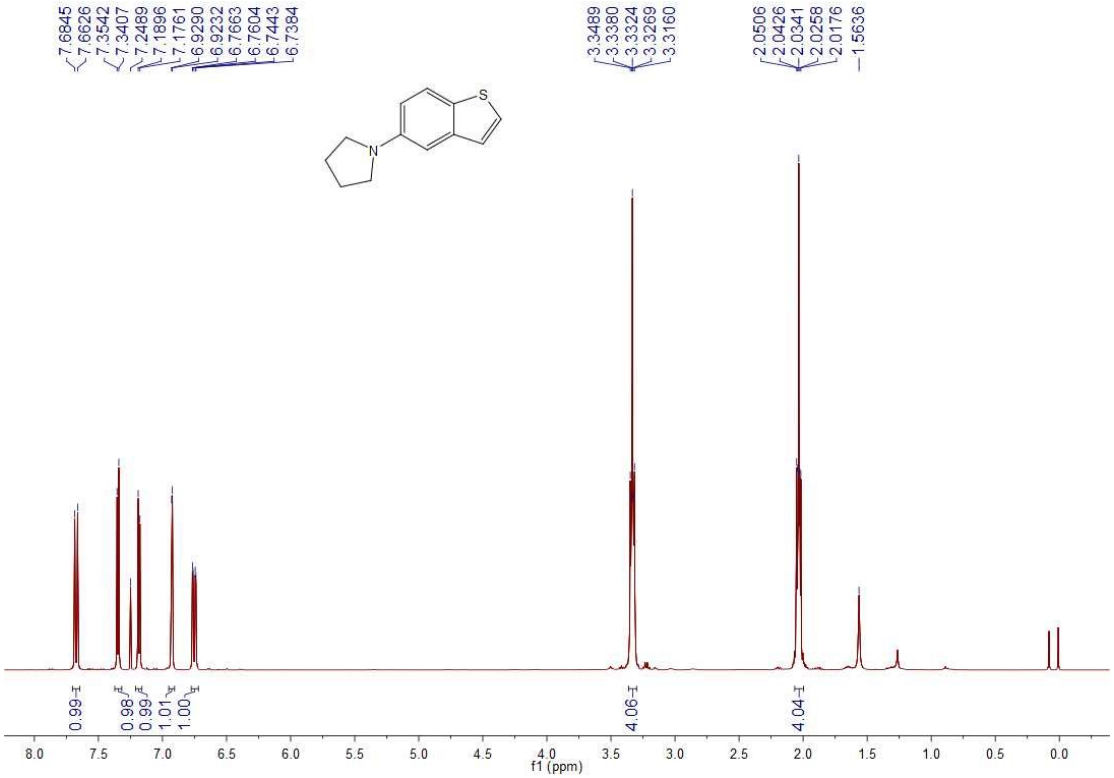
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3s



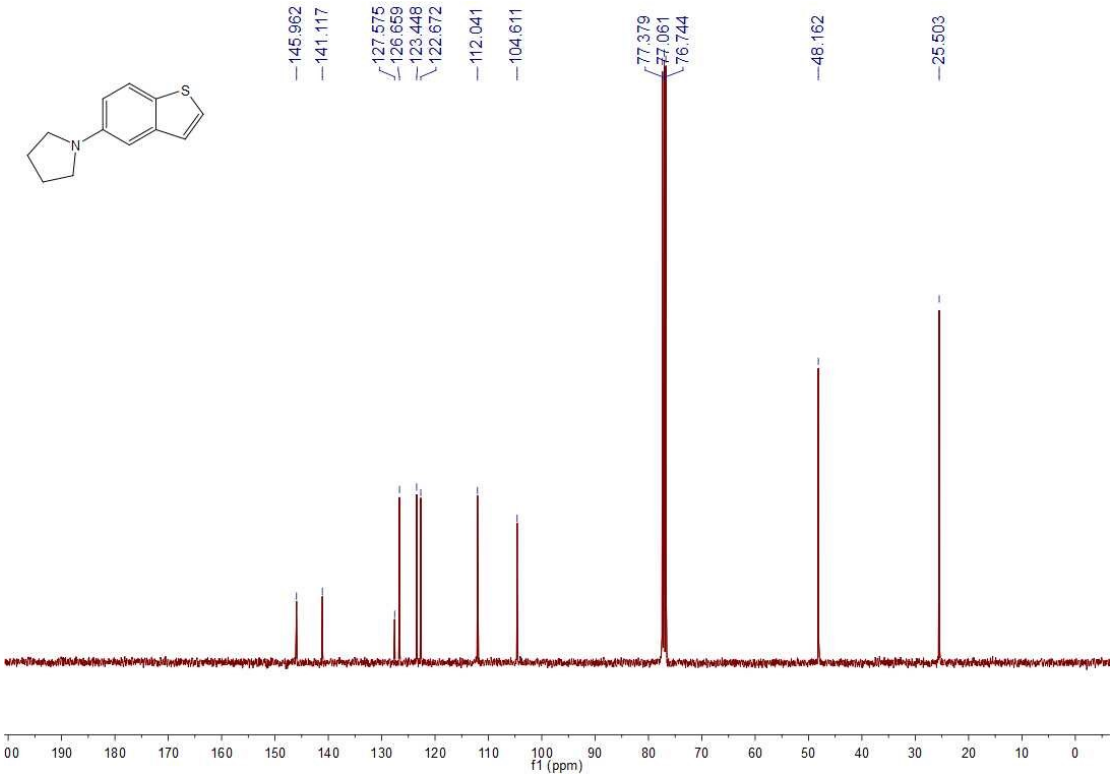
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3s



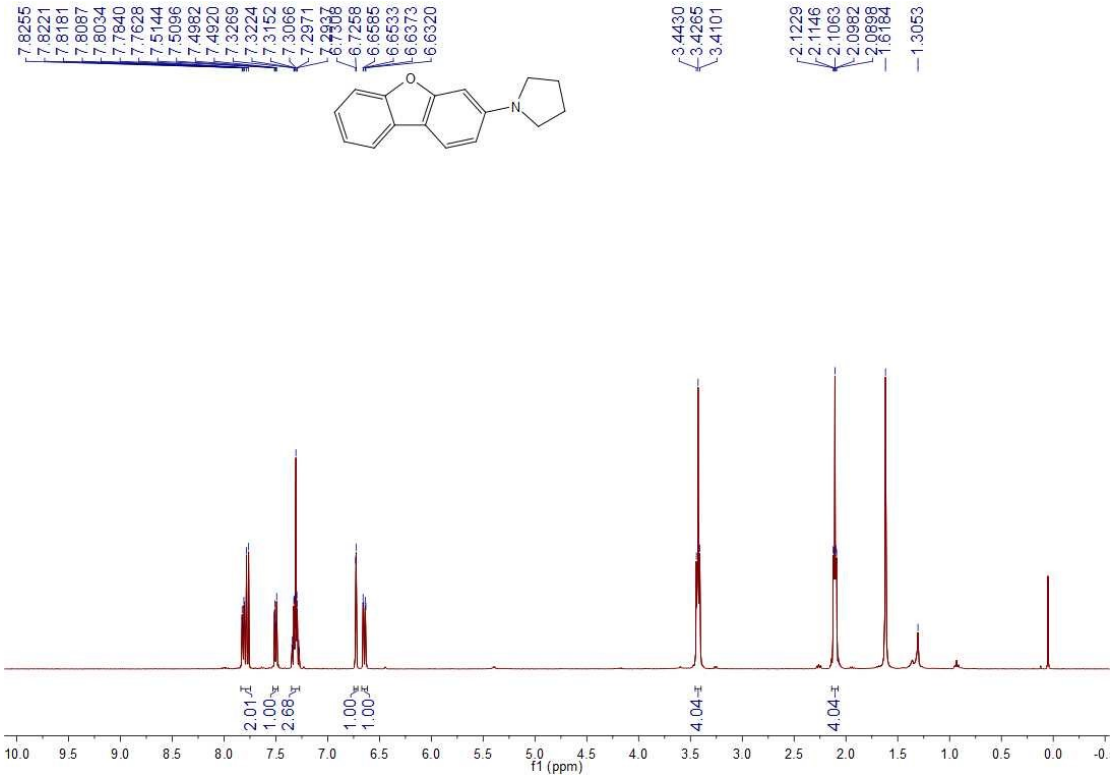
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3t



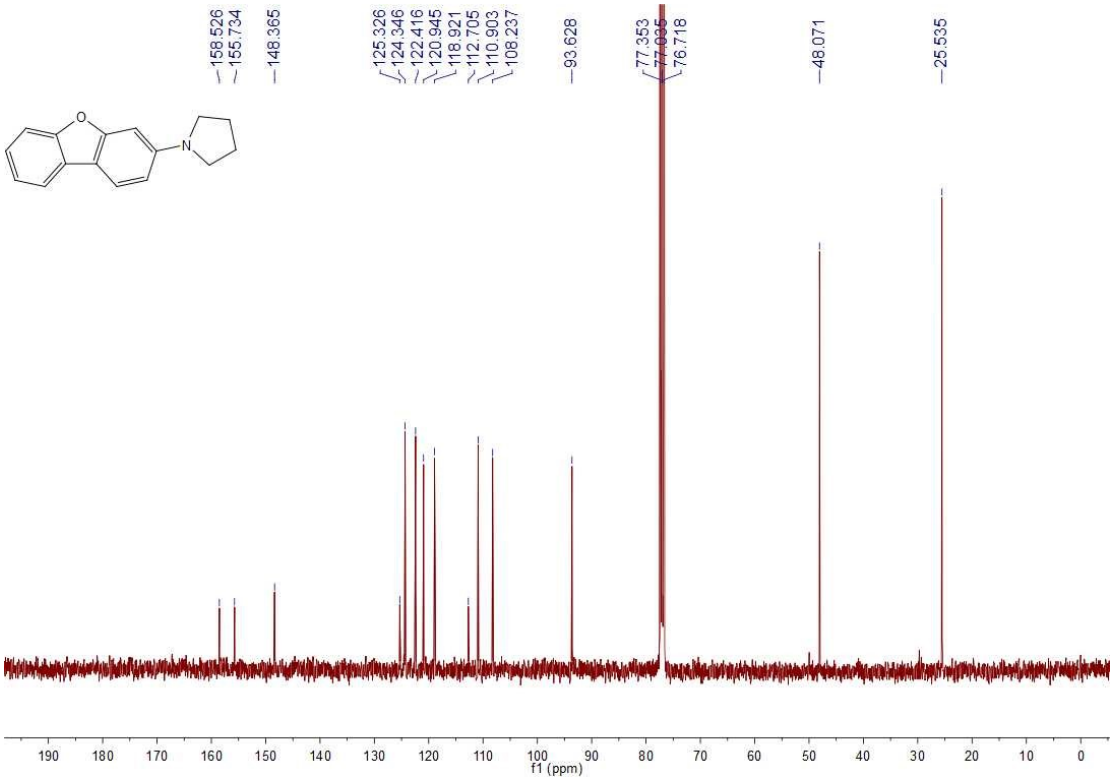
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3t



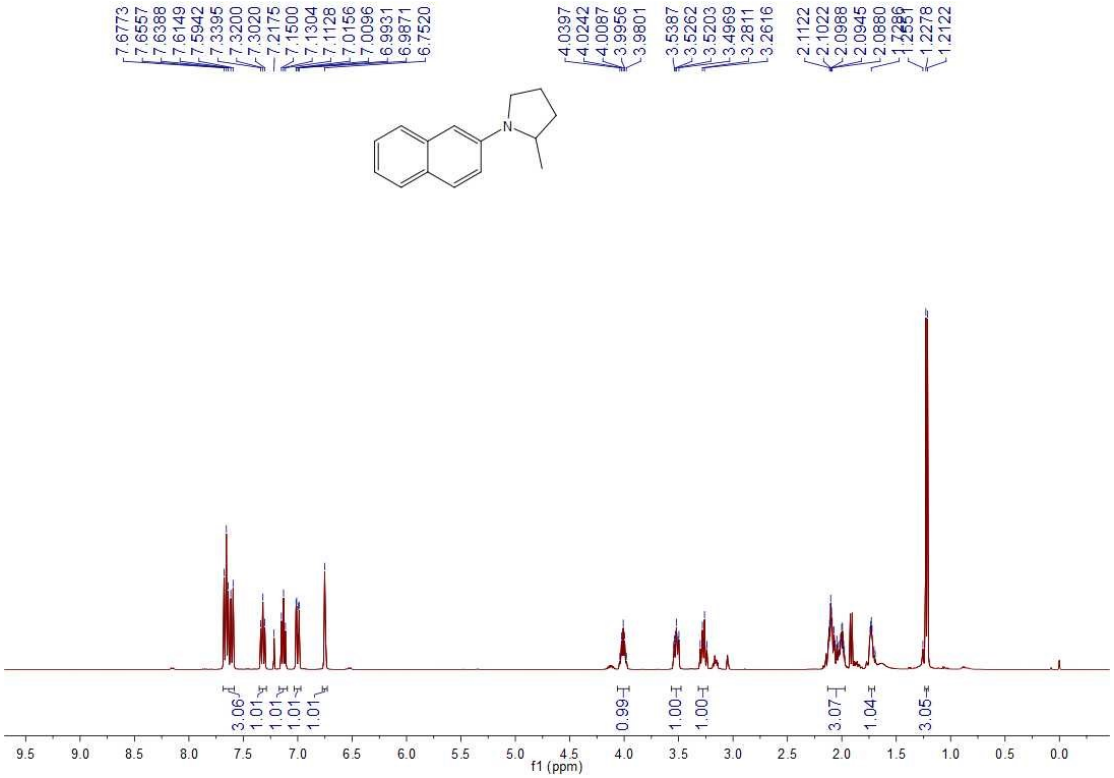
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3u



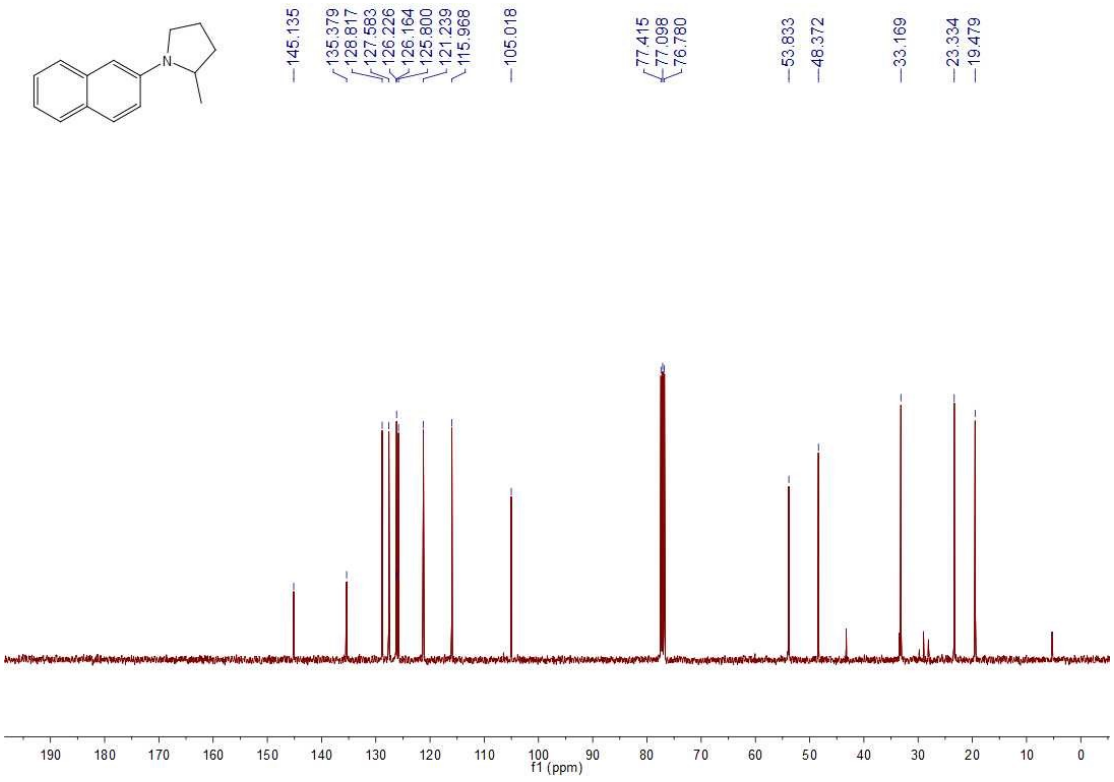
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3u



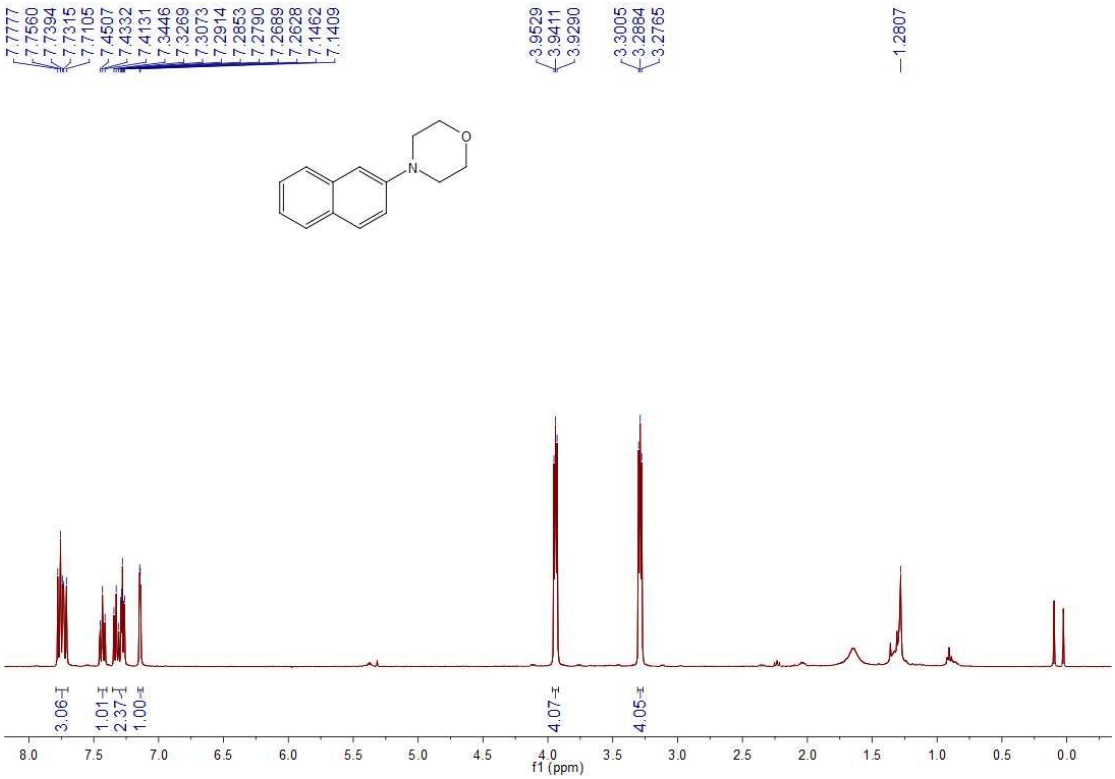
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3v



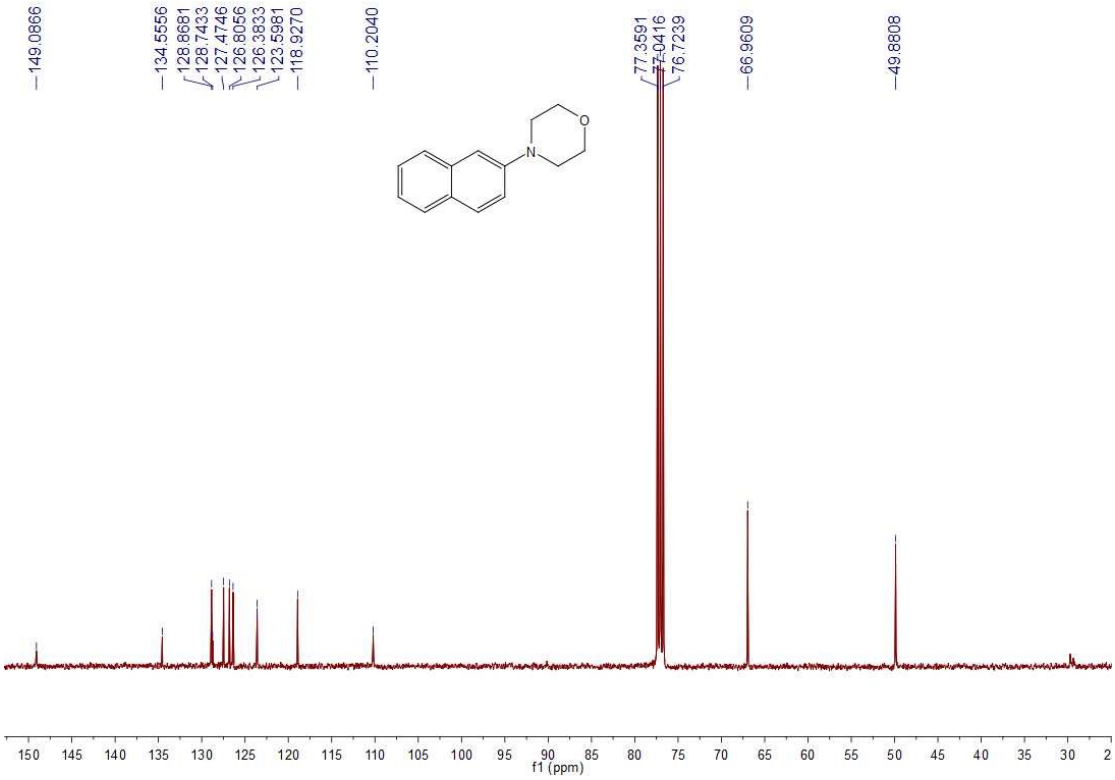
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3v



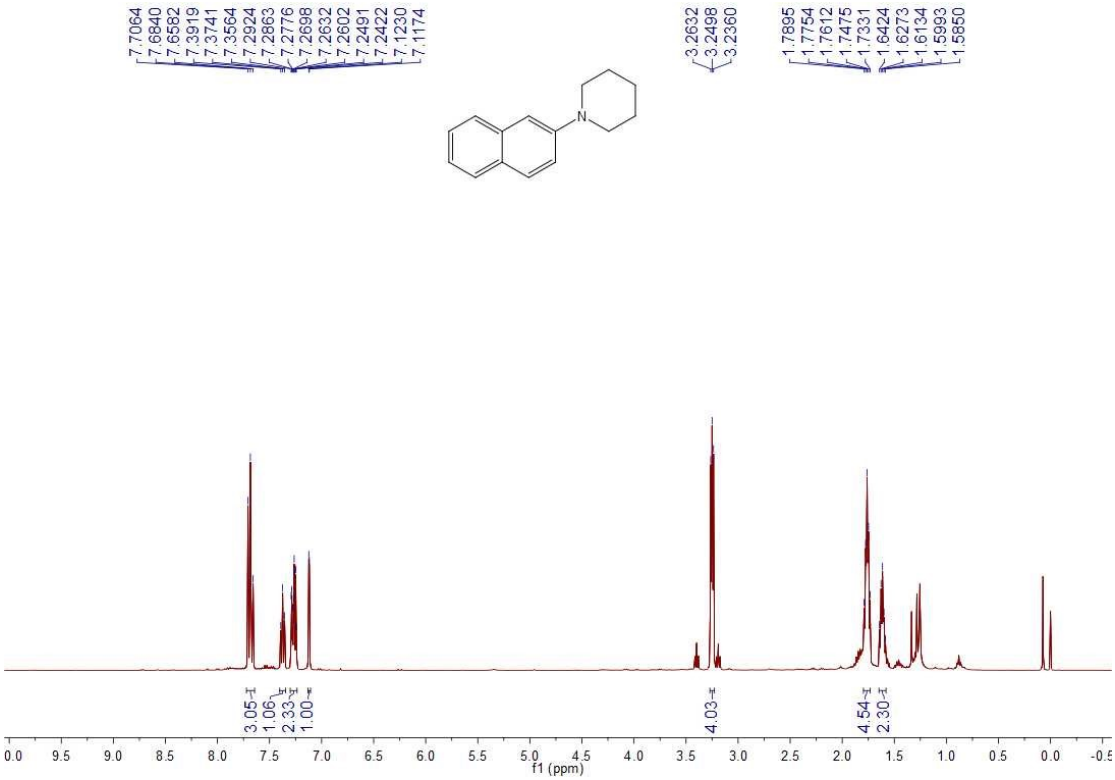
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3w



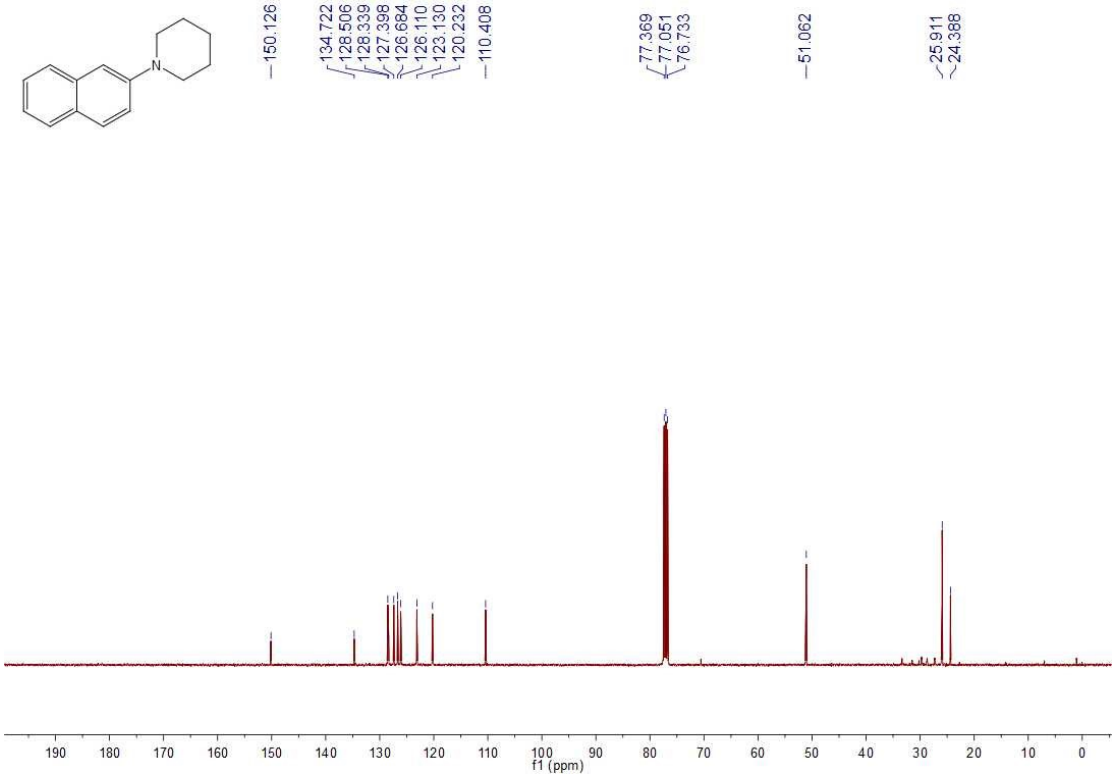
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 3w



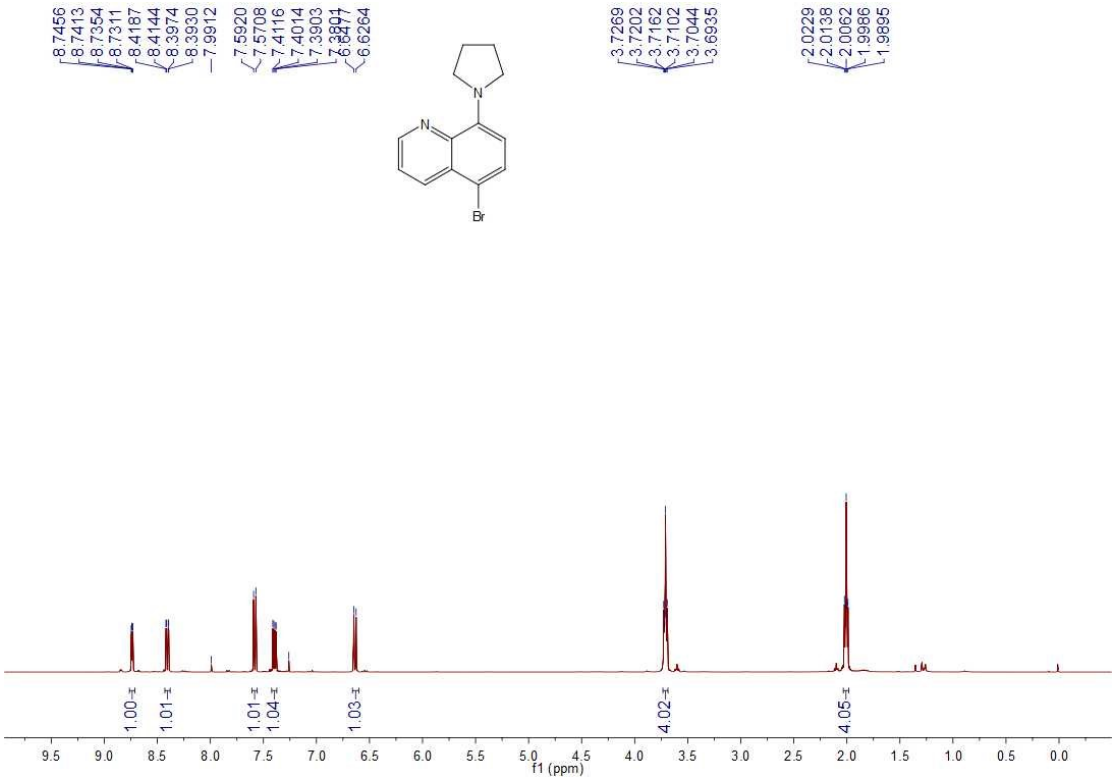
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3x



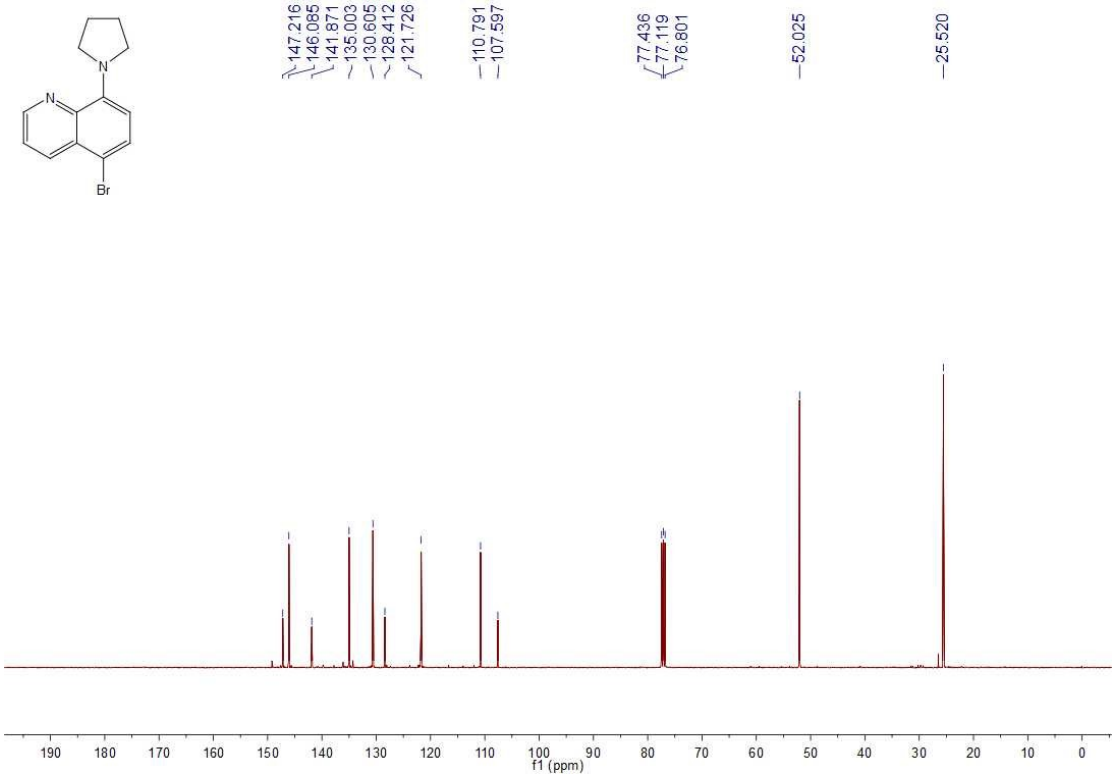
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 3x



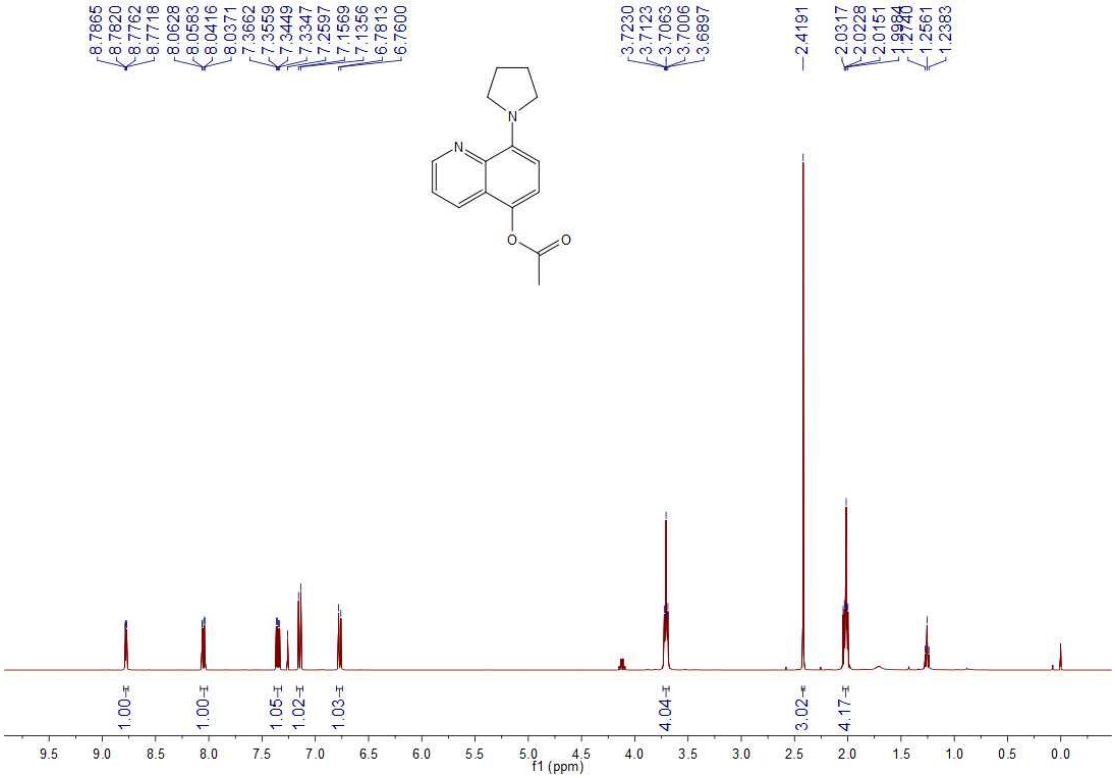
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 4



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 5