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# Supporting Information

## Substrate selective synthesis of pyrazolo[1, 5-a]pyridines through [3+2] cycloaddition of *N*-aminopyridines and *β*-nitro styrenes

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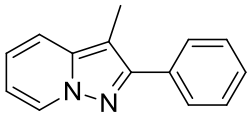
**General Experimental Section:** All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 500, and 125 MHz, respectively. The spectra were recorded in $CDCl_3$as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of $^{1}H$ NMR (7.26), and $^{13}C$ NMR (77.0) are correspond to deuterated solvent chloroform respectively. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent unless otherwise indicated.

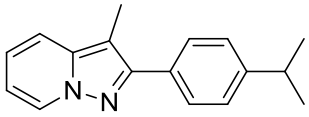
**Typical general procedure for the synthesis of Pyrazol [1,5-a]pyridine (3a):** To a reaction tube without cap equipped with a magnetic stir bar was added 1-aminopyridinium iodide **1a** , (0.3 mmol), (Z)-(2-nitroprop-1-en-1-yl)benzene **2a** (0.2 mmol), and 1.0 mL of NMP. The mixture was at room temperature under an open air in 24h. Reaction was monitored by TLC, after completion of the reaction. Then the mixture was poured into 20 mL of Hypo solution. The product was extracted with EtOAc (15 mL X 3) and dried with anhydrous $Na_2SO_4$. Removal of the solvent under reduced pressure the left out residue was purified by column chromatography using silica gel (10% EtOAc/hexane) to afford **3a**.




(Eluent: 5% EtOAc/hexane); 83% yield (36mg); White solid; M.p.92-97°C; $^{1}H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J$ = 6.5.0 Hz, 1H), 7.84 (d, $J$ = 7.0 Hz, 2H), 7.52-7.42 (m, 4H), 7.08 (t, $J$ = 7.5 Hz, 1H). 6.72 (t, $J$ = 6.5 Hz, 1H), 2.47 (s, 3H).$^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$

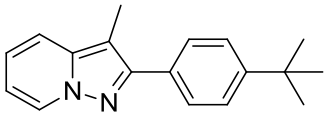
151.7, 140.6, 133.8, 128.5, 128.4, 128.2, 127.8, 122.0, 116.7, 111.4, 103.1, 8.8. HRMS calcd for $C_{14}$ $H_{13}$ $N_2$: 209.1079. Found: 209.1070.

**2-(4-Isopropylphenyl)-3-methylpyrazolo[1,5-a]pyridine (3b)**



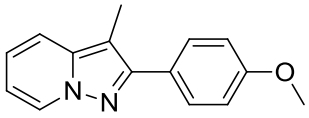
(Eluent: 5% EtOAc/hexane); 75% yield (32.7 mg); White solid; M.p.102-107°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.73 (d, $J$ = 8.0 Hz, 2H), 7.43 (d, $J$ = 8.5 Hz, 1H), 7.34 (t, $J$ = 8.0 Hz, 2H), 7.05(t, $J$ = 6.5 Hz, 1H), 6.68 (t, $J$ = 6.5 Hz, 1H), 2.97 (sep, $J$ = 7.0 Hz, 1H), 2.44 (s, 3H), 1.30 (d, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148,4, 139.8, 131.2, 128.2, 128.1, 126.5, 121.8, 116.5, 11.0, 102.8, 33.8, 23.8, 8.7. HRMS calcd for $C_{17}$ $H_{19}$ $N_2$: 251.1548. Found: 251.1559.

**2-(4-(Tert-butyl)phenyl)-3-methylpyrazolo[1,5-a]pyridine (3c)**



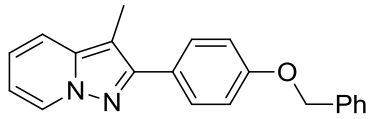
(Eluent: 10% EtOAc/hexane); 70% yield (32.9 mg); White solid; M.p.86-91°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.74 (d, $J$ = 7.0 Hz, 2H), 7.50-7.41 (m, 3H), 7.05-7.02 (m, 1H), 6.68 (t, $J$ = 6.5 Hz, 1H), 2.44 (s, 3H), 1.37 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 15.6, 15.7, 139.9, 130.9, 128.2, 128.0, 125.4, 121.8, 116.6, 111.1, 102.9, 34.6, 31,3, 8.8. HRMS calcd for $C_{18}$ $H_{21}$ $N_2$: 265.1705. Found: 265.1701.

**2-(4-Methoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3d)**



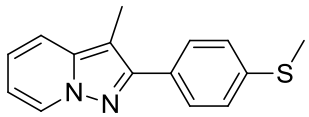
(Eluent: 5% EtOAc/hexane); 58% yield (27.5 mg); White solid; M.p.74-80°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 7.0 Hz, 1H), 7.74 (d, $J$ = 8.5 Hz, 2H), 7.41 (d, $J$ = 6.0 Hz, 1H), 7.04-7.01 (m, 3H), 6.66 (t, $J$ = 6.5 Hz, 1H), 3.86 (s, 3H), 2.41 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.3, 151.5, 139.9, 129.5, 128.1, 126.4, 121.9, 116.5, 113.9, 111.1, 102.6, 35.2, 8.8. HRMS calcd for $C_{15}H_{15}N_2O$: 239.1184. Found: 239.1189.

**2-(4-(Benzyloxy)phenyl)-3-methylpyrazolo[1,5-a]pyridine (3e)**



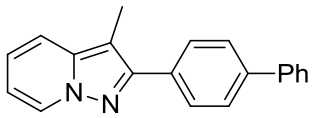

(Eluent: 5% EtOAc/hexane); 65% yield (40.8 mg); White solid; M.p.94-98°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (d, $J$ = 7.0 Hz, 1H), 7.74 (d, $J$ = 8.5 Hz, 2H), 7.47 (d, $J$ = 7.0 Hz, 2H), 7.42-7.38(m, 3H), 7.33 (t, J = 7.5 Hz, 1H), 7.09 (d, $J$ = 8.0 Hz, 2H), 7.04 (t, $J$ = 7.5 Hz, 1H), , 6.67 (t, $J$ = 6.5 Hz, 1H), 5.1 (s, 2H), 2.42 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.5, 151.4, 139.9, 136.9, 129.5, 128.5, 128.1, 127.9, 127.5, 126.5, 121.9, 116.5, 114.9, 111.1, 102.6, 70.6, 8.8. HRMS calcd for $C_{21}H_{19}N_2O$: 315.1497. Found: 315.1511.

**3-Methyl-2-(4-(methylthio)phenyl)pyrazolo[1,5-a]pyridine (3f)**



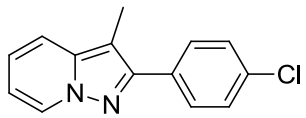

**(**Eluent: 5% EtOAc/hexane); 77% yield (39.4 mg); White solid; M.p.93-98°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 6.5 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 2H), 7.43 (d, $J$ = 9.0 Hz, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.06 (t, $J$ = 8.5 Hz, 1H), 6.69 (t, $J$ = 6.5 Hz, 1H), 2.53 (s, 3H), 2.43 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.1, 140.0, 1381.1, 130.6, 128.6, 128.1, 1265, 122.0, 116.6, 111.3, 103.0, 15.7, 8.8. HRMS calcd for $C_{15}H_{15}N_2S$: 255.0956. Found: 255.0975.

**Biphenyl]-4-yl)-3-methylpyrazolo[1,5-a]pyridine (3g)**



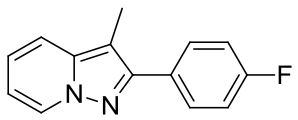

(Eluent: 5% EtOAc/hexane); 71% yield (37.6 mg); White solid; M.p.134-139°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.45 (d, $J$ = 7.5 Hz, 1H), 7.90 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.5 Hz, 2H), 7.67 (d, $J$ = 8.0 Hz, 2H), 7.46 (t, $J$ = 7.0 Hz, 3H), 7.36 (t, $J$ = 7.5 Hz, 1H), 7.07 (t, $J$ = 7.5 Hz, 1H), , 6.71 (t, $J$ = 6.5 Hz, 1H), 2.49 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 1151.3, 151.2, 140.8, 140.5, 140.0, 132.8, 128.79, 128.71, 128.2, 127.2, 127.0, 122.0, 116.7, 111.4, 103.2, 23.5, 8.9. HRMS calcd for $C_{20}H_{17}N_2$ : 285.1392. Found: 285.1388.

**2-(4-Chlorophenyl)-3-methylpyrazolo[1,5-a]pyridine (3h)**




(Eluent: 5% EtOAc/hexane); 68% yield (32.6 mg); White solid; M.p.110-115°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (d, $J$ = 7.0 Hz, 1H), 7.74 (d, $J$ = 8.5 Hz, 2H), 7.44-7.41(m, 3H), 7.06 (t, $J$ = 7.0 Hz, 1H), 6.70 (t, $J$ = 6.5 Hz, 1H), 2.41 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 150.4, 140.0, 133.7, 132.3, 129.5, 128.7, 128.1, 122.1, 116.7, 111.6, 103.2, 8.8. HRMS calcd for $C_{14}H_{12}N_2Cl$ : 243.0689. Found: 243.0693.

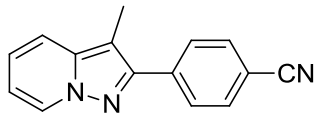
**2-(4-Fluorophenyl)-3-methylpyrazolo[1,5-a]pyridine (3i)**




(Eluent: 5% EtOAc/hexane); 72% yield (32.7 mg); White solid; M.p.88-93°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 7.0 Hz, 1H), 7.77-7.50 (m, 2H), 7.42 (d, $J$ = 7.0 Hz, 1H), 7.15 (t,

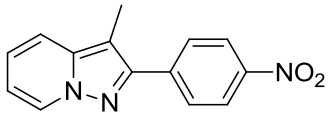
*J* = 8.0 Hz, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.69 (t, *J* = 7.0 Hz, 1H), 2.40 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 163.5, 161.6, 150.7, 140.0, 130.08, 130.02, 129.1, 122.1, 116.0, 115.5, 115.3, 111.4, 102.9, 8.7. HRMS calcd for $C_{14}H_{12}N_2F$: 227.0565. Found: 227.0582.

**4-(3-Methylpyrazolo[1,5-a]pyridin-2-yl)benzonitrile (3j)**



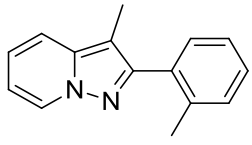

(Eluent: 5% EtOAc/hexane); 80% yield (39 mg); White solid; M.p.194-199°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, *J* = 7.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 2H), 7.75 (d, J= 8.5 Hz, 2H) 7.47 (d, J = 9.0 Hz, 1H), 7.10 (d, 6.5 Hz, 1H), 6.76 (m, 6.5 Hz, 1H), 2,45(s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.2, 140.1, 138.5, 132.2, 128.5, 128.1, 122,4, 118.9, 116.9, 111,1, 103.9, 8.8. HRMS calcd for $C_{15}H_{12}N_3$: 234.1031. Found: 234.1038.

**3-Methyl-2-(4-nitrophenyl)pyrazolo[1,5-a]pyridine (3k)**



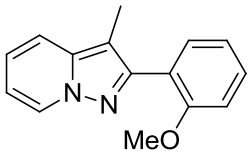

(Eluent: 5% EtOAc/hexane); 77% yield (39.2 mg); White solid; M.p.162-167°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.44 (d, *J* = 7.0 Hz, 1H), 8.34(d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.12 (t, *J* = 8.5 Hz, 1H), 6.79 (t, *J* = 7.0 Hz, 1H), 2.50 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.0, 147.1, 140.5, 140.3, 128.7, 128.2, 123.8, 122.5, 117.0, 112.4, 104.3, 9.0. HRMS calcd for $C_{14}H_{12}N_3O_2$: 254.0930. Found: 254.0925.

**3-Methyl-2-(o-tolyl)pyrazolo[1,5-a]pyridine (3m)**



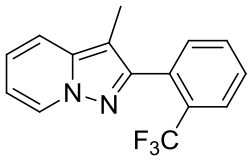
(Eluent: 5% EtOAc/hexane); 60% yield (26 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (d, $J$ = 6.5 Hz, 1H), 7.43(d, $J$ = 9.0 Hz, 1H), 7.34-7.25(m, 4H), 7.05 (t, $J$ = 7.5 Hz, 1H), 6.68 (t, $J$ = 79.0 Hz, 1H), 2.27(s, 3H), 2.17 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 153.0, 138.9, 137.3, 132.9, 130.5, 130.0, 128.19, 128.13, 125.3, 121.9, 116.5, 111.0. 104.2, 19.8, 7.9. HRMS calcd for $C_{15}$ $H_{15}$ $N_2$ : 223.1235. Found: 223.1255.

**2-(2-Methoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3n)**



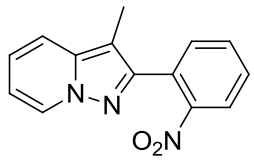

(Eluent: 5% EtOAc/hexane); 64% yield (30.5 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.44 (d, $J$ = 6.5 Hz, 1H), 7.46-7.40(m, 3H), 7.06-7.01(m, 3H), 6.66 (t, $J$ = 7.0 Hz, 1H), 3.84(s,3H), 2.21 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 157.2, 150.2, 139.1, 131.9, 129.6, 128.2, 122.6, 121.8, 120.5, 116.7, 110.98, 110.90, 105.3, 55.4, 8.3. HRMS calcd for $C_{15}$ $H_{15}$ $N_2$ $O_2$: 239.1184. Found: 239.1183.

**3-Methyl-2-(2-(trifluoromethyl)phenyl)pyrazolo[1,5-a]pyridine (3o)**



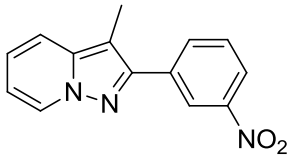

(Eluent: 5% EtOAc/hexane); 79% yield (41 mg); White solid; M.p.88-94°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 7.0 Hz, 1H), 7.80(d, $J$ = 8.0 Hz, 1H), 7.59 (t, $J$ = 7.5 Hz, 1H), 7.53 (t, $J$ = 7.5 Hz, 1H), 7.43 (d, $J$ = 8.5 Hz, 2H), 7.07(t $J$ = 7.0 Hz, 1H), 6.71 (t, $J$ = 7.0 Hz, 1H), 2.13 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 150.7, 138.6, 132.6, 131.1, 130.1, 129.9, 128.4, 126.15, 126.11, 122.1, 116.7, 111.4, 105.1, 7.5. HRMS calcd for $C_{15}$ $H_{12}$ $N_2F_3$ : 277.0953. Found: 277.0943.

**3-Methyl-2-(2-nitrophenyl)pyrazolo[1,5-a]pyridine (3p)**



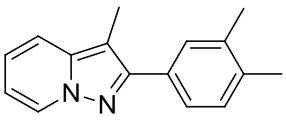
(Eluent: 5% EtOAc/hexane); 87% yield (43.9 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.31 (d, $J$ = 7.0 Hz, 1H), 7.91(d, $J$ = 8.5 Hz, 1H), 7.60 (t, $J$ = 7.0 Hz, 1H), 7.55 (d, $J$ = 7.5 Hz, 1H), 7.50-7.46(m,1H), 7.37 (d, $J$ = 8.5 Hz, 1H), 7.01 (t, $J$ = 8.0 Hz, 1H), 6.66 (t, $J$ = 8.0 Hz, 1H), 2.13 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.7, 148.4, 139.2, 132.7, 132.3, 129.0,128.0, 128.2, 124.2, 122.4, 116.9, 11.7, 104.6, 7.7. HRMS calcd for $C_{14}$ $H_{12}$ $N_3O_2$ : 254.0930. Found: 254.0939.

**3-Methyl-2-(3-nitrophenyl)pyrazolo[1,5-a]pyridine (3q)**



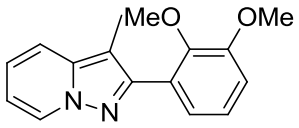
(Eluent: 5% EtOAc/hexane); 90% yield (45.3 mg); White solid; M.p.136-141°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.69 (s, 1H), 8.44 (d, $J$ = 7.0 Hz, 1H), 8.25(d, J = 7.0 Hz, 1H), 7.18 (d, $J$ = 7.5 Hz, 1H), 7.65 (t, $J$ = 8.0 Hz, 1H), 7.50 (d, $J$ = 9.0 Hz, 1H), 7.12(t, J = 9.0 Hz, 1H), 6.78 (t, $J$ = 7.0 Hz, 1H), 2.50 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 167.3, 149.0, 148.4, 135.7, 134.0, 129.4, 128.2, 123.0, 122.5, 117.0,112.2, 103.7, 8.8. HRMS calcd for $C_{14}$ $H_{12}$ $N_3O_2$ : 254.0930. Found: 254.0934.

**2-(3,4-Dimethylphenyl)-3-methylpyrazolo[1,5-a]pyridine (3r)**



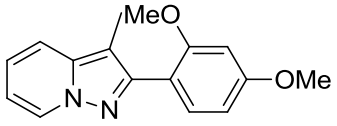
(Eluent: 5% EtOAc/hexane); 58% yield (27.3 mg); White solid; M.p.78-83°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.60(s, 1H), 7.51(d, J = 7.5 Hz, 1H), 7.42 (d, $J$ = 9.0 Hz, 1H), 7.24 (t, $J$ = 7.5 Hz, 1H), 7.03 (t, $J$ = 7.0 Hz, 1H), 6.67 (t, $J$ = 7.0 Hz, 1H), 2.43(s,3H0, 2.34(s, 3H), 2.32 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.8, 149.9, 136.7, 136.3, 131.3, 129.7, 129.5, 128.1, 125.8, 121.9, 116.6, 111.1, 102.9, 19.8, 19.6, 8.8. HRMS calcd for $C_{16}$ $H_{17}$ $N_2$ : 237.1392. Found: 237.1383.

**2-(2,3-Dimethoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine(3s)**



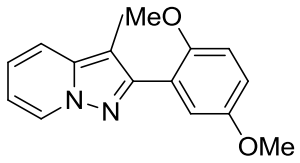

(Eluent: 5% EtOAc/hexane); 63% yield (34.1 mg); White solid; M.p.125-130°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 7.0 Hz, 1H), 7.45(d, $J$ = 8.5 Hz, 1H), 7.14 (t, $J$ = 8.0 Hz, 1H), 7.09-7.04(m, 2H), 7.00-6.98(m, 1H), 6.69(t, $J$ = 7.0 Hz, 1H), 3.92(s, 3H), 3.60(s, 3H), 2.25(s, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.6, 148.9, 146.4, 137.8, 127.0, 126.9, 122.6, 122.4, 120.5, 115.6, 111.1, 109.8, 104.3, 59.8, 54.6, 7.09. HRMS calcd for $C_{16}$ $H_{17}$ $N_2O_3$ : 269.1290. Found: 269.1292.

**2-(2,4-Dimethoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3t)**



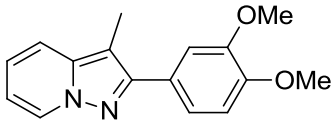

(Eluent: 5% EtOAc/hexane); 62% yield (33.2 mg); White solid; M.p.89-95°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (d, $J$ = 7.0 Hz, 1H), 7.41-7.37(m, 2H), 7.02(t, $J$ = 7.0 Hz, 1H), 6.64 (t, $J$ = 7.5 Hz, 1H), 6.61-6.58(m,2H), 3.86(s,3H), 3.81(s, 3H), 2.20(s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 161.4, 158.6, 150.4, 139.3, 132.6, 128.4, 121.9, 116.8, 115.6, 111.0, 105.4, 104.7, 98.9, 55.7, 55.6, 8.5. HRMS calcd for $C_{16}$ $H_{17}$ $N_2O_2$ : 269.1290. Found: 269.1297.

**2-(2,5-Dimethoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3u)**



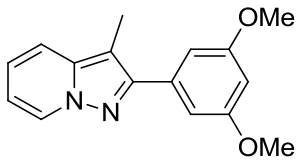

(Eluent: 5% EtOAc/hexane); 61% yield (33 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.43(d, $J$ = 9.0 Hz, 1H), 7.05-7.02(m, 2H), 6.949s, 2H), 6,64 (t, $J$ = 7.0 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.22 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 153.6, 151.8, 150.3, 139.3, 128.4, 123.5, 112.1, 117.6, 116.9, 115.3, 113.5, 111.2, 105.6, 56.3, 56.0, 8.5. HRMS calcd for $C_{16}$ $H_{17}$ $N_2O_2$ : 269.1290 Found: 269.1273.

**2-(3,4-Dimethoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3v)**



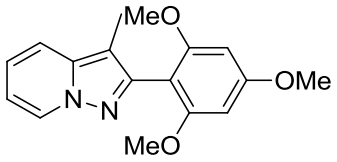

(Eluent: 5% EtOAc/hexane); 60% yield (32 mg); White solid; M.p.88-93°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.43-39 (m, 2H), 7.34-7.31 (m, 1H), 7.05 (t, $J$ = 9.0 Hz, 1H), 6.99 (t, $J$ = 7.0 Hz, 1H), 6.69(t $J$ = 7.0 Hz, 1H), 3.97 (s, 3H), 3.94(s, 3H), 2.44 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.5, 148.9, 148.5, 140.6, 128.1, 126.6, 122.0, 120.9, 116.5, 111.4, 111.2, 111.0, 102.7, 55.9, 8.9. HRMS calcd for $C_{16}$ $H_{17}$ $N_2O_2$ : 269.1290 Found: 269.1290.

**2-(3,5-Dimethoxyphenyl)-3-methylpyrazolo[1,5-a]pyridine (3w)**



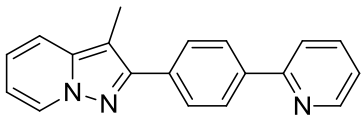
. (Eluent: 5% EtOAc/hexane); 71% yield (37.6 mg); White solid; M.p.64-69°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.43(d, $J$ = 9.0 Hz, 1H), 7.04 (t, $J$ = 9.0 Hz, 1H), 6.96(s, 1H), 6.70-6.68(m,1H), 6.51 (t, $J$ = 7.0 Hz, 1H), 3.86(s, 6H), 2.44 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.7, 151.4, 139.9, 135.6, 128.1, 122.0, 116.7, 111.4, 106.3, 103.2, 100.2, 55.3, 8.8. HRMS calcd for $C_{16}H_{17}N_2O_2$ : 269.1290. Found: 269.1270.

**3-Methyl-2-(2,4,6-trimethoxyphenyl)pyrazolo[1,5-a]pyridine (3x)**



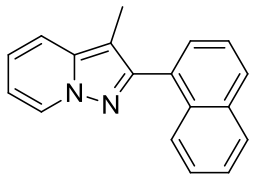

(Eluent: 5% EtOAc/hexane); 38% yield (22.7 mg); White solid; M.p.88-93°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.41(d, $J$ = 4.0 Hz, 1H), 7.05-6,98(m, 1H), 6.63-6.61(m,1H), 6.24(s, 2H0, 3.87(s, 3H), 3.74(s, 6H), 2.10(s,3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.4, 158.4, 145.5, 137.5, 127.2, 120.1, 115.5, 109.2, 105.5, 102.4, 89.4, 54.7, 54.1, 6.7. HRMS calcd for $C_{17}H_{19}N_2O_3$ : 299.1396. Found: 299.1415.

**3-Methyl-2-(4-(pyridin-2-yl)phenyl)pyrazolo[1,5-a]pyridine (3y)**



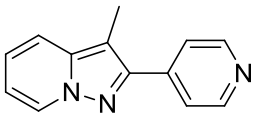

(Eluent: 5% EtOAc/hexane); 38% yield (20.5 mg); White solid; M.p.116-121°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.72 (d, $J$ = 6.5 Hz, 1H), 7.45(d, $J$ = 7.0 Hz, 1H), 8.12 (d, $J$ = 8.0 Hz, 2H), 7.94 (d, $J$ = 8.0 Hz, 2H), 7.80-7.77(m,2H), 7.46 (d, $J$ = 9.0 Hz, 1H), 7.26-7.23(m,1H), 7.07(t, $J$ = 7.0 Hz, 1H), 6.50 (t, $J$ = 7.0 Hz, 1H), 2.48 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 17.0, 151.0, 149.6, 140.0, 138.6, 136.7, 134.4, 128.6, 128.1, 127.0, 122.1, 120.5, 116.7, 111.5, 103.5, 8.9. HRMS calcd for $C_{19}H_{16}N_3$ : 286.1344. Found: 286.1335.

**3-Methyl-2-(naphthalen-1-yl)pyrazolo[1,5-a]pyridine (3z)**



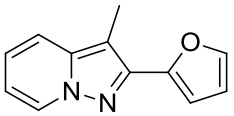
(Eluent: 5% EtOAc/hexane); 55% yield (28.3 mg); White solid; M.p.140-145°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.52 (d, $J$ = 7.0 Hz, 1H), 7.95-7.92(m,3H), 7.62-7.57(m, 2H), 7.52-7.45(m,3H), 7.13(t, $J$ = 8.5 Hz, 1H), 6.77 (t, $J$ = 7.0 Hz, 1H), 2.21 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.8, 139.2, 133.6, 132.2, 131.1, 128.5, 128.3, 128.1, 126.2, 125.7, 125.1, 122.1, 116.7, 111.3, 105.3, 8.2. HRMS calcd for $C_{18}H_{15}N_2$ : 259.1235. Found: 259.1245.

**3-Methyl-2-(pyridin-4-yl)pyrazolo[1,5-a]pyridine (3ab)**



(Eluent: 5% EtOAc/hexane); 51% yield (22 mg); White solid; M.p.79-84°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.70 (d, $J$ = 4.5 Hz, 2H), 8.42(d, $J$ = 7.0 Hz, 1H), 7.75-7.39(m, 2H), 7.47 (d, $J$ = 9.0 Hz, 1H), 7.09 (t, $J$ = 9.0 Hz, 1H), 6.75 (t, $J$ = 7.0 Hz, 1H), 2.47 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.7, 147.2, 140.3, 138.9, 126,9, 121,2, 121.1, 115.7, 111.1, 7.6. HRMS calcd for $C_{13}H_{12}N_3$ : 210.1031. Found: 21046.

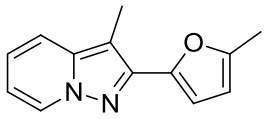
**2-(Furan-2-yl)-3-methylpyrazolo[1,5-a]pyridine (3ac)**



(Eluent: 5% EtOAc/hexane); 83% yield (32.9 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 7.0 Hz, 1H), 7.55(s,1H), 7.40(d, $J$ = 8.5 Hz, 1H), 7.04(d, J = 8.5 Hz,1H), 7.04-

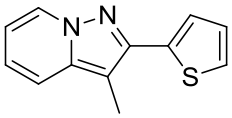
7.01(m, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.53-6.52 (m, 1H), 2.44 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 148.8, 143.2, 142.3, 139.6, 1282, 122.2, 116.5, 111.6, 111.2, 1.8.1, 102.8, 8.4. HRMS calcd for $C_{12}H_{11}N_2O$ : 210.1031. Found: 21046.

**3-Methyl-2-(5-methylfuran-2-yl)pyrazolo[1,5-a]pyridine (3ad)**



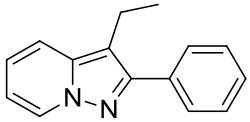

(Eluent: 5% EtOAc/hexane); 61% yield (25.9 mg); White solid; M.p.58-63°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, *J* = 7.0 Hz, 1H), 7.38(d, *J* = 9.0 Hz, 1H), 7.02 (t, *J* = 6.5 Hz, 1H), 6.66-6.63(m, 2H), 6.11(d, *J* = 3.0 Hz, 1H), 2.41(S, 3h), 2.40 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 152.4, 146.9, 143.5, 139.6, 128.2, 122.2, 116.3, 111.3, 109.4, 107.3, 102.3, 13.7, 8.5. HRMS calcd for $C_{13}H_{13}N_2O$ : 213.1028. Found: 213.1022.

**3-Methyl-2-(thiophen-2-yl)pyrazolo[1,5-a]pyridine (3ae)**



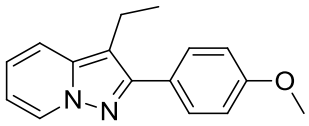

(Eluent: 5% EtOAc/hexane); 52% yield (22.2 mg); White solid; M.p.68-73°C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.39 (d, *J* = 7.0 Hz, 1H), 7.48(d, *J* = 3.5 Hz, 1H), 7.40-7.35(m, 2H), 7.15-7.13(M, 1h), 7.03 (T, *J* = 7.0 Hz, 1H), 6,67 (t, *J* = 7.0 Hz, 1H), 2.46 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 146.3, 140.0, 136.3, 128.0, 127.5, 125.4, 122.2, 116.5, 111.5, 102.8, 8.8. HRMS calcd for $C_{12}H_{11}N_2S$ : 215.0643. Found: 215.0633.

**3-Ethyl-2-phenylpyrazolo[1,5-a]pyridine (3af)**



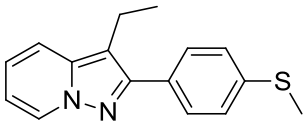
(Eluent: 5% EtOAc/hexane); 89% yield (39.4 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 7.0 Hz, 1H), 7.76(d, $J$ = 7.0 Hz, 2H), 7.49-7.46(m, 3H), 7.40 (t, $J$ = 7.5 Hz, 1H), 7.05 (t, $J$ = 7.0 Hz, 1H), 6.70 (d, $J$ = 6.5 Hz, 1H), 2.91(q $J$ = 7.0 Hz, 2H), 1.27 (t, $J$ = 7.0 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.4, 139.4, 133.8, 128.4, 128.2, 127.8, 122.0, 116.7, 111.4, 110.1, 16.5, 15.5. HRMS calcd for $C_{15}H_{15}N_2$ : 223.1235. Found: 223.1229.

**3-Ethyl-2-(4-methoxyphenyl)pyrazolo[1,5-a]pyridine (3ag)**



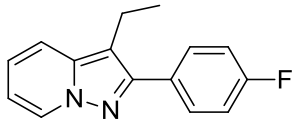

(Eluent: 5% EtOAc/hexane); 66% yield (33.2 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 7.0 Hz, 1H), 7.769(d, $J$ = 9.0 Hz, 2H), 7.56(d, J = 9.0 Hz, 1H), 7.05-7.00(m, 3H), 6.68 (t, $J$ = 7.0 Hz, 1H), 3.86(s, 3H), 2.88(q $J$ = 7.5 Hz, 2H), 1.25 (t, $J$ = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 159.4, 151.2, 139.4, 129.6, 128.2, 126.3, 122.0, 116.6, 133.9, 111.2, 109.7, 51.2, 16.6, 15.4. HRMS calcd for $C_{16}H_{17}N_2O$ : 253.1341. Found: 253.1358.

**3-Ethyl-2-(4-(methylthio)phenyl)pyrazolo[1,5-a]pyridine (3ah)**



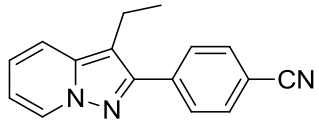

(Eluent: 5% EtOAc/hexane); 69% yield (37 mg); yellow solid; M.p.90-95°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 6.5 Hz, 1H), 7.47 (d, $J$ = 8.5 Hz, 1H), 7,36 (d, $J$ = 8.0 Hz, 2H), 7.06 (t, $J$ = 8.0 Hz, 1H), 6,71 (t, $J$ = 6.5 Hz, 1H), 2.89(q $J$ = 7.5 Hz, 2H), 2.53 (s, 3H), 1.27-1.24 (m, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 150.8, 139.5, 12., 128.2, 126.4, 122.1, 116.7, 111.4, 110.0, 16.7, 15.7, 15.5. HRMS calcd for $C_{16}H_{17}N_2S$ : 269.1112. Found: 269.1106.

**3-Ethyl-2-(4-fluorophenyl)pyrazolo[1,5-a]pyridine (3ai)**



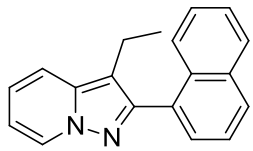

(Eluent: 5% EtOAc/hexane); 63% yield (30.1 mg); Liquid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 7.0 Hz, 1H), 7.72-7.69 (m, 2H), 7.47(d, $J$ = 9.0 Hz, 2H), 7.15(t, $J$ = 8.5 Hz, 1H),7.06 (t, $J$ = 8.5 Hz, 1H), 2.87(q , $J$ = 7.5 Hz, 2H), 1.25 (t, $J$ = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 163.6, 161.6, 150.5, 139.4, 130.17, 130.11, 130.0, 128.2, 122.2, 116.7, 115.5, 115.3, 111.5, 109.5, 16.6, 15.4. HRMS calcd for $C_{15}$ $H_{14}$ $N_2F$ : 241.1141. Found: 241.1137

**4-(3-Ethylpyrazolo[1,5-a]pyridin-2-yl)benzonitrile (3aj)**




(Eluent: 5% EtOAc/hexane); 78% yield (38.5 mg); White solid; M.p.113-118°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 7.0 Hz, 1H), 7.89(d, $J$ = 8.0 Hz, 2H), 7.75(d, J = 8.5 Hz, 2H), 7.51 (d, $J$ = 9.0 Hz, 1H), 7.10 (t, $J$ = 6.5 Hz, 1H), 6.77 (t, $J$ = 6.5 Hz, 1H), 2.91(q $J$ = 7.5 Hz, 2H), 1.27 (t, $J$ = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.0, 139.6, 138.6, 132.2, 128.7, 128.2, 122.5, 118.9, 117.0, 112.3, 111.2, 110.9, 16.6, 15.4. HRMS calcd for $C_{16}$ $H_{14}N_3$ : 248.1188. Found: 248.1176.

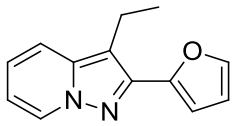
**3-Ethyl-2-(naphthalen-1-yl)pyrazolo[1,5-a]pyridine (3ak)**




(Eluent: 5% EtOAc/hexane); 76% yield (41.1 mg); White solid; M.p.55-61°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.52 (d, $J$ = 7.0 Hz, 1H), 7.96-7.87(m, 3H), 7.60-7.45(m, 5H), 7.12(t, $J$ = 7.0

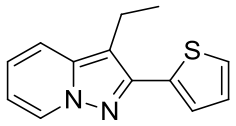
Hz, 1H), 6.77(t, J = 7.0 Hz, 1H), 2.69(q *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.3, 138.7, 133.5, 132.5, 131.3, 128.5, 128.4, 128.1, 128.0, 126.2, 126.1, 125.7, 125.0, 124.2, 124.1, 123.7, 123.0, 122.1, 166.8, 112.2, 111.3, 16.6, 15.4. HRMS calcd for $C_{19}$ $H_{17}N_2$ : 273.1392. Found: 273.1391.

**3-Ethyl-2-(furan-2-yl)pyrazolo[1,5-a]pyridine (3al)**



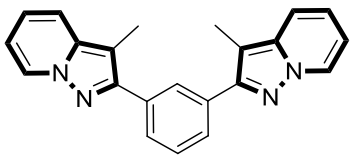

(Eluent: 5% EtOAc/hexane); 75% yield (31.9 mg); Liquid; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.44 (d, *J* = 6.5 Hz, 1H), 7.569s, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.04(t, J = 9.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.70 (t, *J* = 8.5 Hz, 1H), 6.53 (t, *J* = 6.5 Hz, 1H), 2.95(q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 1148.6, 142.5, 142.3, 142.2, 139.2, 128.5, 128.2, 122.3. 116.5, 11.7, 111.2, 109.9, 108.0, 16.6, 15.1. HRMS calcd for $C_{16}$ $H_{17}N_2O$ : 253.1341. Found: 253.1358.

**3-Ethyl-2-(thiophen-2-yl)pyrazolo[1,5-a]pyridine (3am)**




(Eluent: 5% EtOAc/hexane); 63% yield (28.8 mg); Liquid; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (d, *J* = 6.5 Hz, 1H), 7.47(d, *J* = 3.5 Hz, 1H), 7.43(d, J = 9.0 Hz, 1H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.44 (t, *J* = 4.5 Hz, 1H), 7.04 (t, *J* = 7.0 Hz, 1H), 6.69 (t, *J* = 7.0 Hz, 1H), 2.95(q *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 145.7, 139.6, 136.0, 128.1, 127.6, 125.6, 125.3, 124.4, 116.5, 111.6, 109.8, 16.8, 15.1. HRMS calcd for $C_{13}$ $H_{13}N_2S$ : 229.0797. Found: 229.0797.

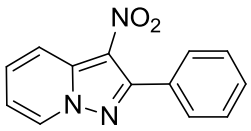
**1,3-Bis(3-methylpyrazolo[1,5-a]pyridin-2-yl)benzene (3an)**



(Eluent: 5% EtOAc/hexane); 57% yield (38.2 mg); White solid; M.p.90-95°C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.45 (d, *J* = 6.5 Hz, 2H), 8.20(s, 1H), 7.85(d, *J* = 7.0 Hz, 2H), 7.59(t, J = 6.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.0Hz, 2H), 6.71(s, 2H), 2.50 (s, 6H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.6, 139.9, 132.0, 128.8, 128.5, 128.2, 127.9, 122.0, 116.7, 111.3, 103.2, 8.9. HRMS calcd for $C_{22}H_{19}N_4$ : 339.1610. Found: 339.1623.

**Typical general procedure for the synthesis of 3-Nitro-2-phenylpyrazolo[1,5-a]pyridine (5a):**

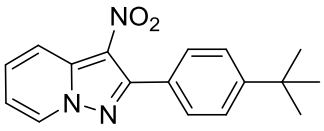
To a reaction tube without cap equipped with a magnetic stir bar was added 1-aminopyridinium iodide **1a** , (0.4 mmol), (Z)-(2-nitroprop-1-en-1-yl)benzene **2a** (0.2 mmol), and 1.0 mL of NMP. The mixture was at 60 $^{o}$C under an open air in 24h. Reaction was monitored by TLC, after completion of the reaction. Then the mixture was poured into 20 mL of Hypo solution. The product was extracted with EtOAc (15 mL X 3) and dried with anhydrous $Na_2SO_4$. Removal of the solvent under reduced pressure the left out residue was purified by column chromatography using silica gel (20% EtOAc/hexane) to afford **5a**.



(20% EtOAc/hexane) 84% yield (40 mg); solid ; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.58 (d, *J* = 7.0 Hz, 1H), 8.46(d, *J* = 8.5 Hz, 1H), 7.82-7.80(m, 2H), 7. 69 (t, *J* = 7.0 Hz, 1H), 7.51-7.50 (m, 3H), 7.17 (t, *J* = 7.0 Hz, 1H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 152.2, 138.2, 130.8, 130.0,

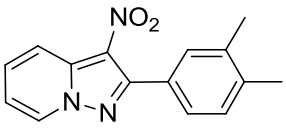
129.9, 129.8, 129.4, 128.2, 119.3, 115.9. HRMS calcd for $C_{13}H_{10}N_3O_2$ : 240.0773. Found: 240.0771

**2-(4-(Tert-butyl)phenyl)-3-nitropyrazolo[1,5-a]pyridine (5b)**



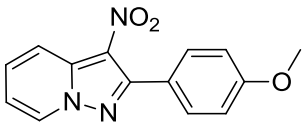

(20% EtOAc/hexane) 63% yield (37 mg); solid ; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.56 (d, $J$ = 7.0 Hz, 1H), 8.43(d, $J$ = 9.0 Hz, 1H), 7. 77 (d, $J$ = 8.5 Hz, 2H), 7.66 (t, $J$ = 7.5 Hz, 2H), (20% EtOAc/hexane) 7.53(d, $J$ = 8.5 Hz, 2H), 7.14 (t, $J$ = 7.0 Hz, 1H), 1.37 (s, 9H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 153.1, 152,1m 138.2, 130.7, 129.5, 129.3, 127.0, 125.1, 119.1, 115.8, 34.8 13.1. HRMS calcd for $C_{17}H_{18}N_3O_2$ : 296.1399. Found: 296.1395

**2-(3,4-Dimethylphenyl)-3-nitropyrazolo[1,5-a]pyridine (5c)**



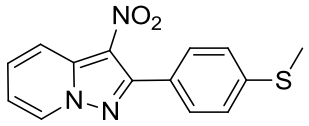

(20% EtOAc/hexane) 62% yield (33 mg); solid; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 7.0 Hz, 1H), 8.35(d, $J$ = 9.0 Hz, 1H), 7. 58 (t, $J$ = 8.5 Hz, 1H), 7.49-7.46 (m, 2H), 7.19 (d, $J$ = 7.5 Hz, 1H), 7.06 (t, $J$ = 7.0 Hz, 1H), 2.20 (s, 6H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 152,6, 139.0, 138.4, 136.7, 130.9, 129.7, 129.6, 127.6, 127.5, 119.4, 116.0, 20.0. HRMS calcd for $C_{15}H_{14}N_3O_2$ : 268.1086. Found: 268.1082

**2-(4-Methoxyphenyl)-3-nitropyrazolo[1,5-a]pyridine (5d)**



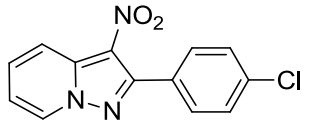
(20% EtOAc/hexane) 51% yield (27.4 mg); solid ; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.55 (d, $J$ = 6.5 Hz, 1H), 8.42 (d, $J$ = 9.0 Hz, 1H), 7. 81 (d, $J$ = 8.5 Hz, 2H), 7.66 (t, $J$ = 7.5 Hz, 1H), 7.14 (t, $J$ = 7.0 Hz, 1H), 7.03 (d $J$ = 8.5 Hz, 2H), 3.88 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 160.9, 151.9, 138.3, 131.3, 130.6, 129.3, 122.1, 119.1, 115.8, 113.6, 55.3. HRMS calcd for $C_{14}H_{12}N_3O_3$ : 270.0879. Found: 270.877

**2-(4-(Methylthio)phenyl)-3-nitropyrazolo[1,5-a]pyridine (5e)**



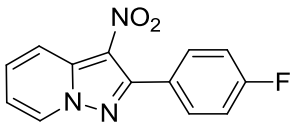

(20% EtOAc/hexane) 54% yield (31 mg); solid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.58 (d, $J$ = 6.5 Hz, 1H), 8.43 (d, $J$ = 9.0 Hz, 1H), 7. 76 (d, $J$ = 8.5 Hz, 2H), 7.68 (t, $J$ = 7.5 Hz, 1H), 7.35 (d, $J$ = 8.5 Hz, 2H), 7.16 (t $J$ = 6.5 Hz, 1H), 2.54 (s, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.6, 141.4, 138.2, 130.8, 130.1, 129.3, 126.2, 125.4, 119.2, 115.9, 15.2. HRMS calcd for $C_{14}H_{12}N_3O_2S$ : 286.0650. Found: 286.0554

**2-(4-Chlorophenyl)-3-nitropyrazolo[1,5-a]pyridine (5f)**



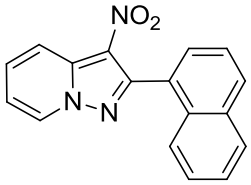

(20% EtOAc/hexane) 77% yield (42 mg); solid ; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.57 (d, $J$ = 6.5 Hz, 1H), 8.45 (d, $J$ = 9.0 Hz, 1H), 7. 77 (d, $J$ = 8.5 Hz, 2H), 7.70 (t, $J$ = 7.5 Hz, 1H), 7.48 (d, $J$ = 8.5 Hz, 2H), 7.19 (t $J$ = 7.5 Hz, 1H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 150.0, 137.2, 135.1, 130.2, 130.0, 128.4, 128.3, 127.4, 126.3, 118.2, 115.1. HRMS calcd for $C_{13}H_9N_3O_2Cl$ : 273.0383. Found: 273.0376

**2-(4-Fluorophenyl)-3-nitropyrazolo[1,5-a]pyridine (5g)**



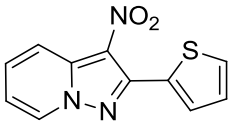

(20% EtOAc/hexane) 51% yield (26.5 mg); solid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.57 (d, $J$ = 6.5 Hz, 1H), 8.45 (d, $J$ = 9.0 Hz, 1H), 7. 82 (d, $J$ = 5.0 Hz, 2H), 7.70 (t, $J$ = 7.5 Hz, 1H), 7.19 (d, $J$ = 8.0Hz, 3H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 164.8, 162.8, 151.2, 138.2, 132.0, 131.9, 130.9, 129.4, 126.0, 119.3, 116.0, 115.4, 115.2. HRMS calcd for $C_{13}$ $H_9$ $N_3O_2$ F : 258.0679. Found: 258.0683

**2-(Naphthalen-1-yl)-3-nitropyrazolo[1,5-a]pyridine (5h)**



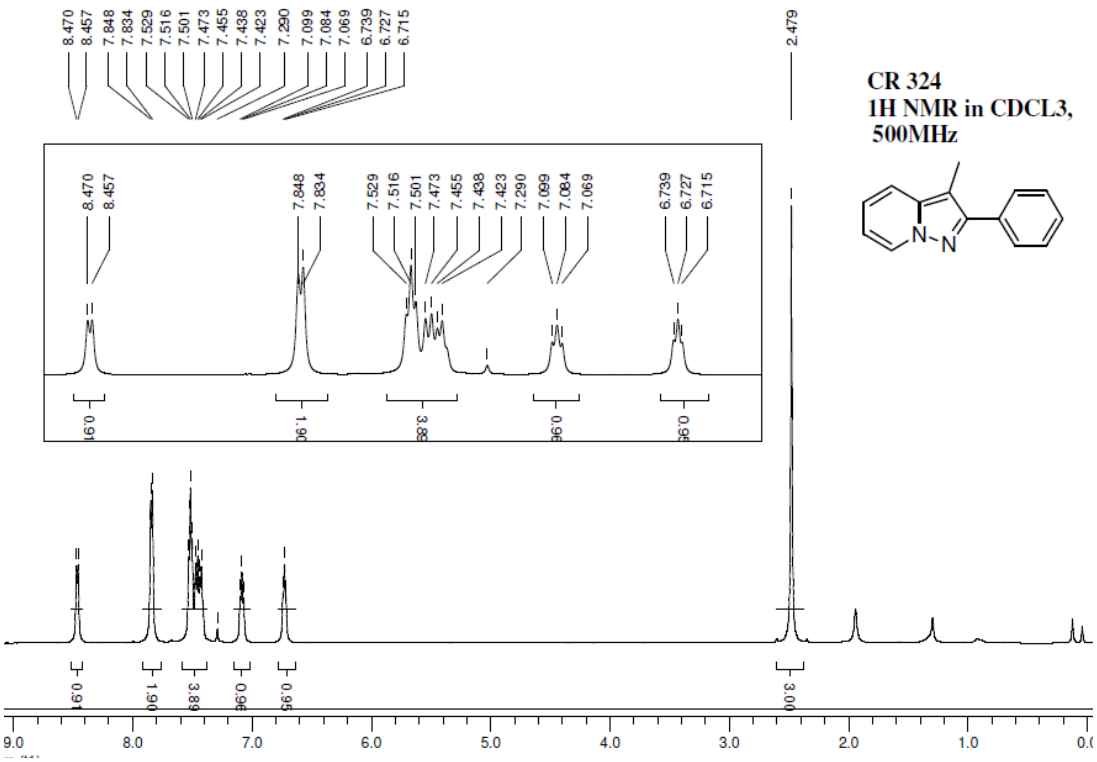

(20% EtOAc/hexane) 51% yield (29.4 mg); solid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.59 (d, $J$ = 7.0 Hz, 1H), 8.47 (d, $J$ = 9.0 Hz, 1H), 8.01 (d, $J$ = 80 Hz, 1H), 7.93 (d, $J$ = 8.5 Hz, 1H), 7.70-7.63 (m, 3H)<, 7.58 (t, $J$ = 8.5 Hz, 1H), 7.50 (t, $J$ = 7.5 Hz, 1H), 7.543 (t, $J$ = 7.5 Hz, 1H), 7.16-7.13 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 151.3, 137.5, 133.2, 131.6, 130.9, 130.1, 129.5, 128.4, 128.1, 128.0, 126.7, 126.0, 124.9, 124.8, 123.7, 118.9. HRMS calcd for $C_{17}$ $H_{12}$ $N_3O_2$ : 290.0930. Found: 290.0928

**3-Nitro-2-(thiophen-2-yl)pyrazolo[1,5-a]pyridine (5i)**

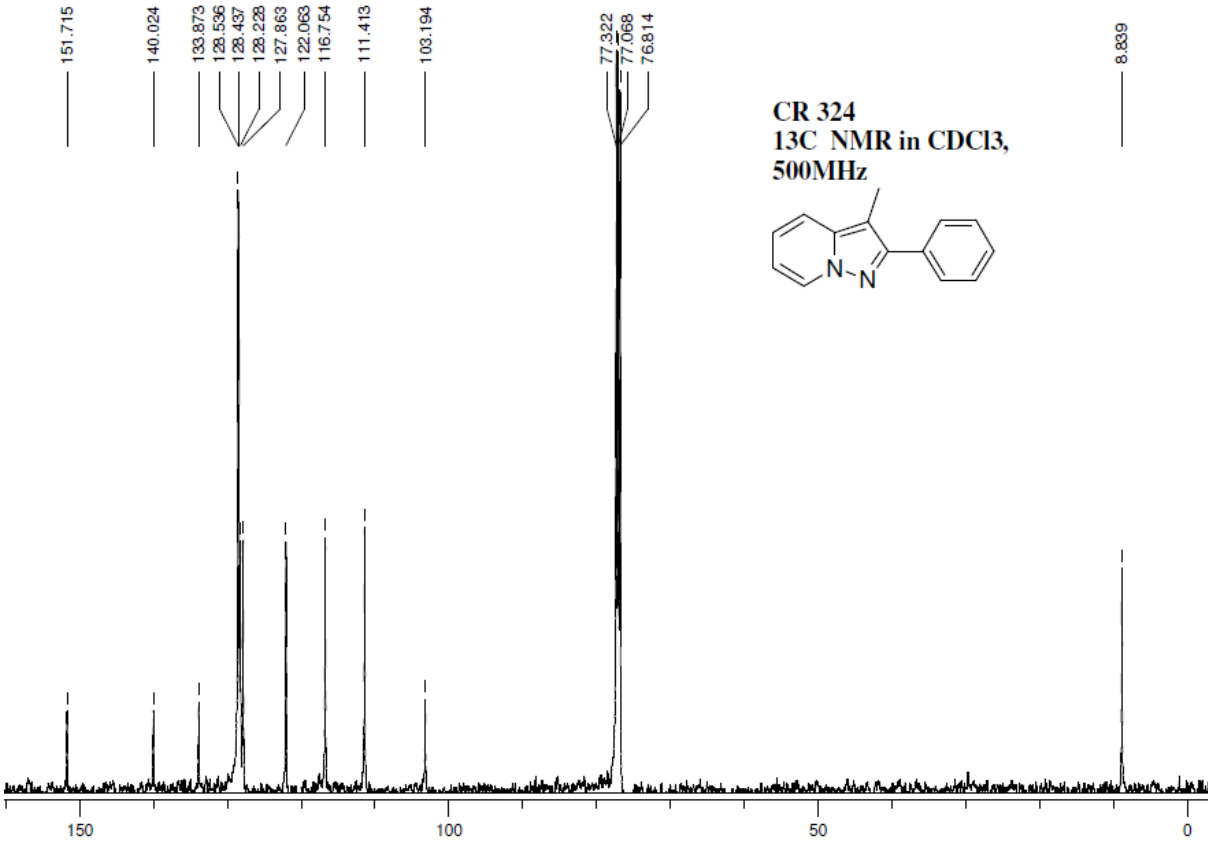



(20% EtOAc/hexane) 69% yield (34 mg); solid; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.58 (d, $J$ = 7.0 Hz, 1H), 8.44 (d, $J$ = 9.0 Hz, 1H), 8.27 (d, $J$ = 3.0 Hz, 1H), 7.66 (t, $J$ = 8.0 Hz, 1H),

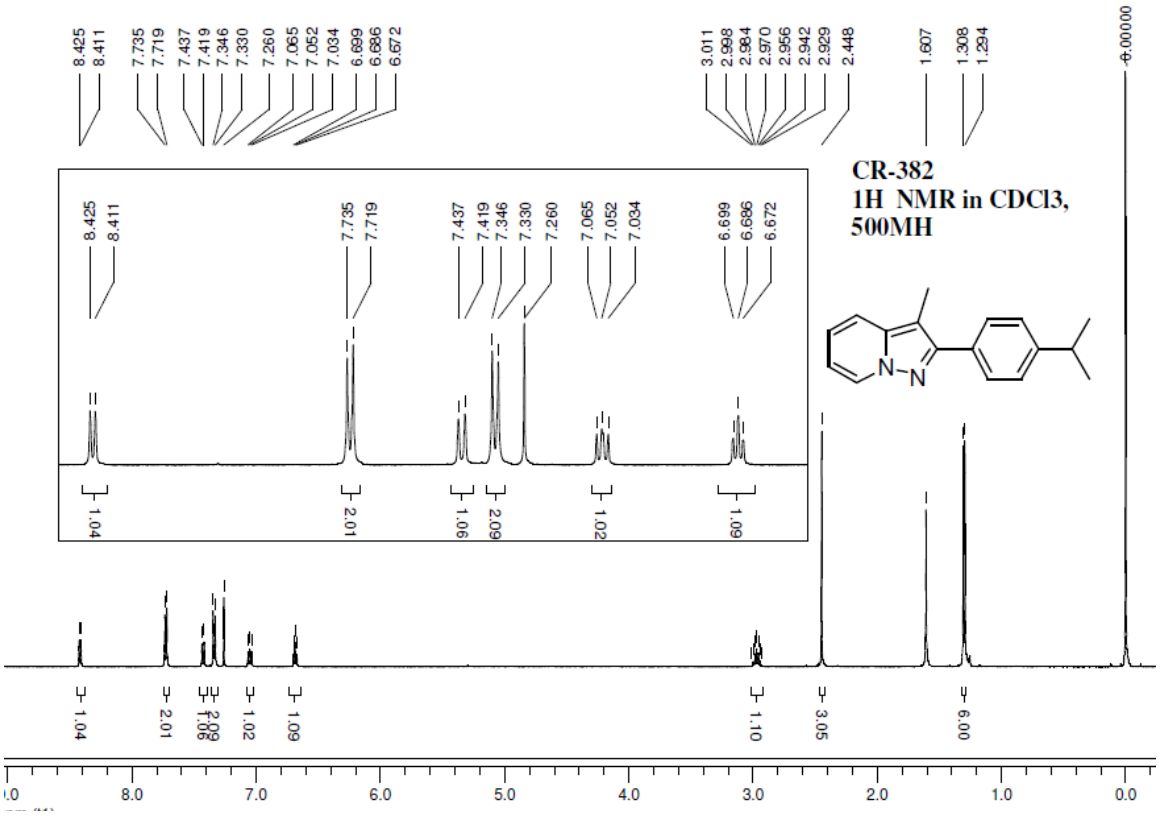
7.55(d, $J$ = 5.0 Hz, 1H), 7.21 (t, $J$ = 4.0 Hz, 1H), 7.17 (t, $J$ = 7.0 Hz, 1H), $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 145.7, 138.4, 131.9, 131.1, 130.7, 128.6, 129.1, 127.8, 119.2, 116.2. HRMS calcd for $C_{11}$ $H_8$ $N_3O_2$ S: 246.0337. Found: 246.0334.



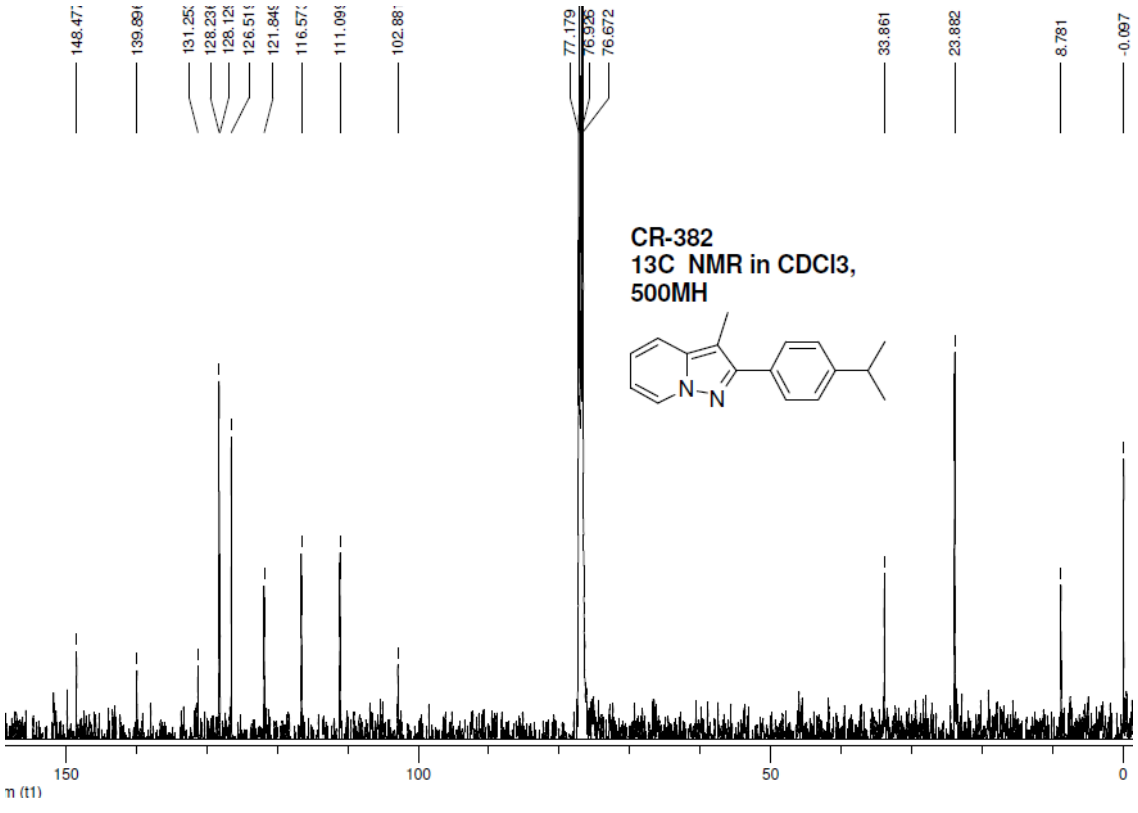

**1H NMR of 3a**



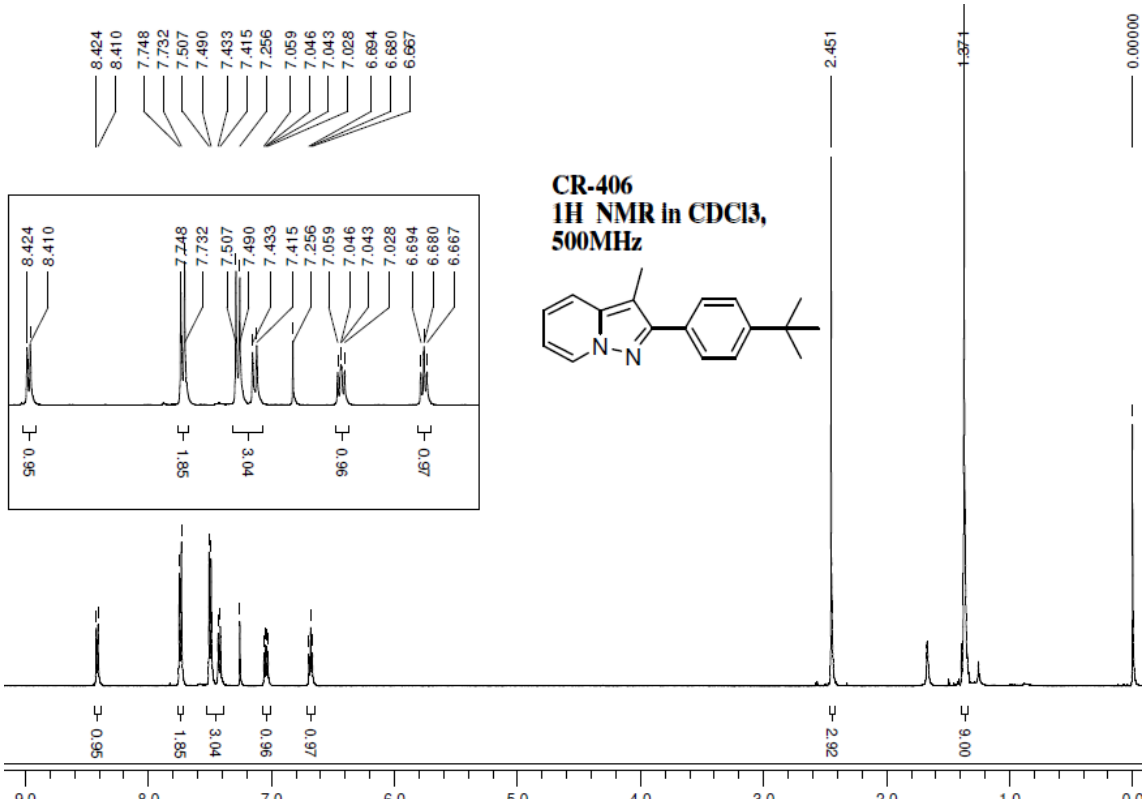

**13C NMR of 3a**



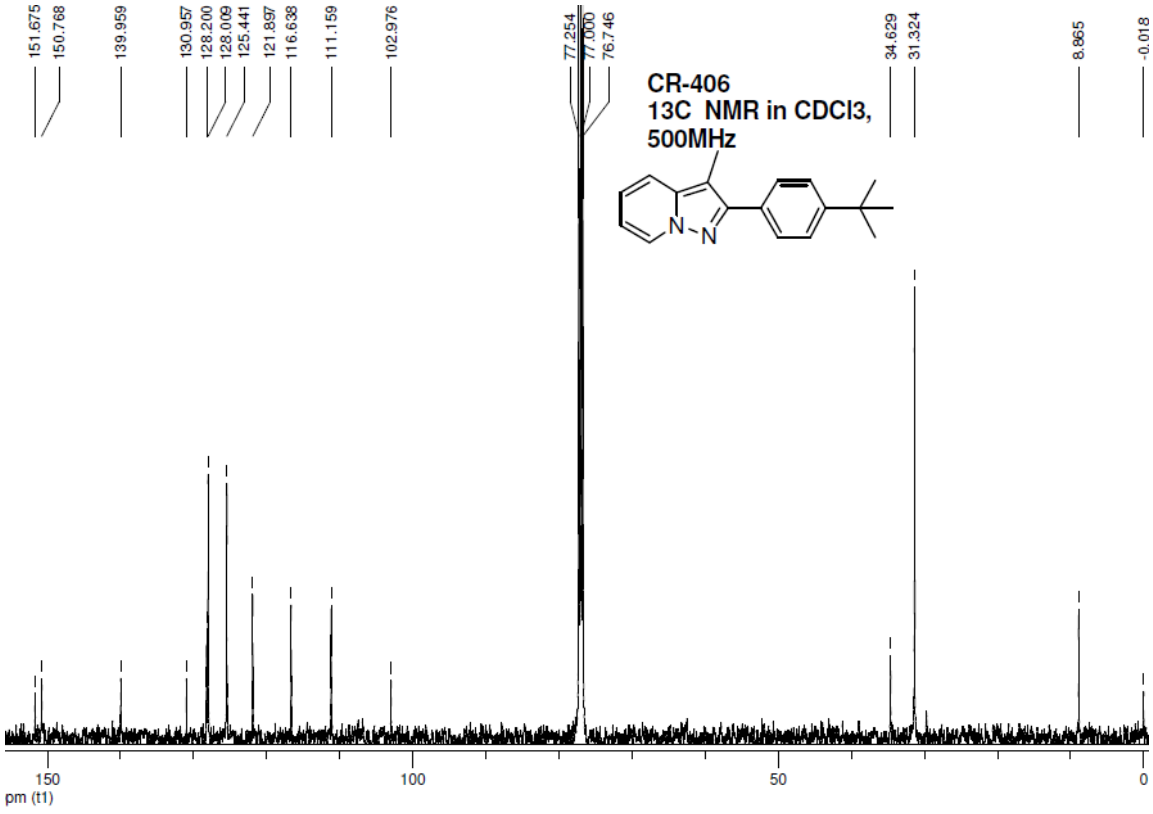

**1H NMR of 3b**



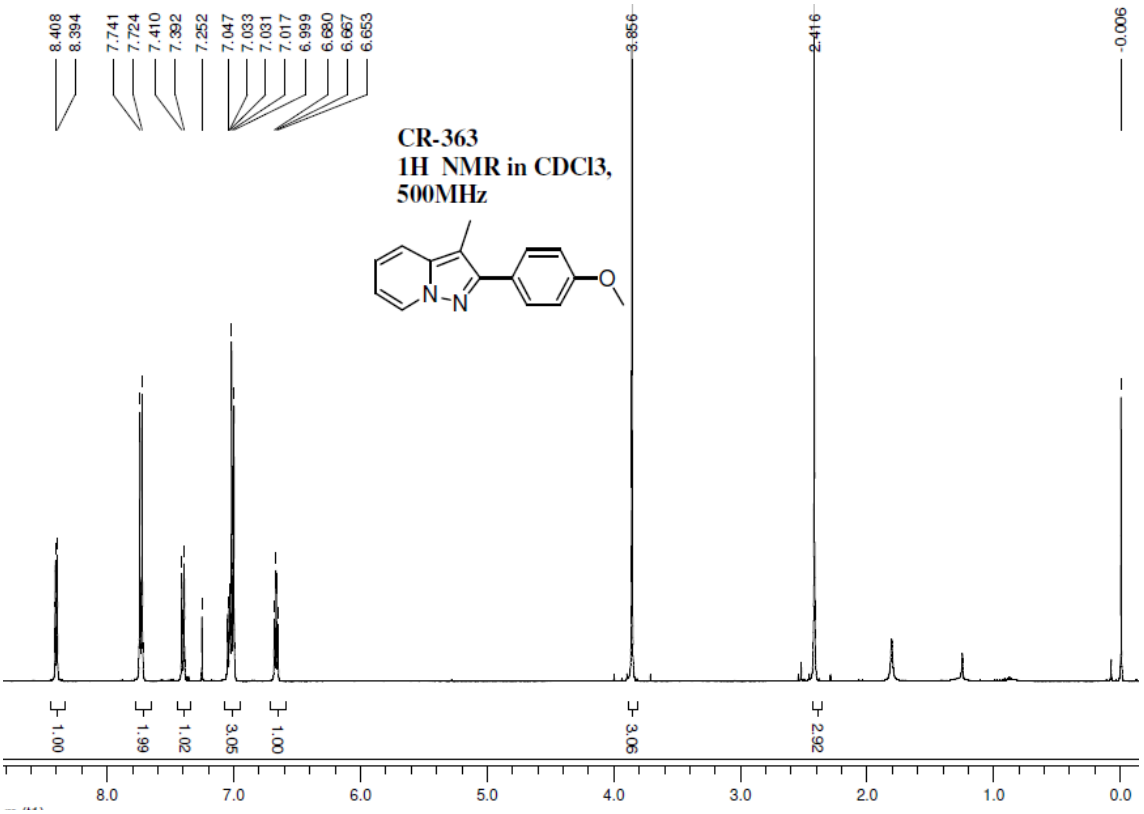

**13C NMR of 3b**



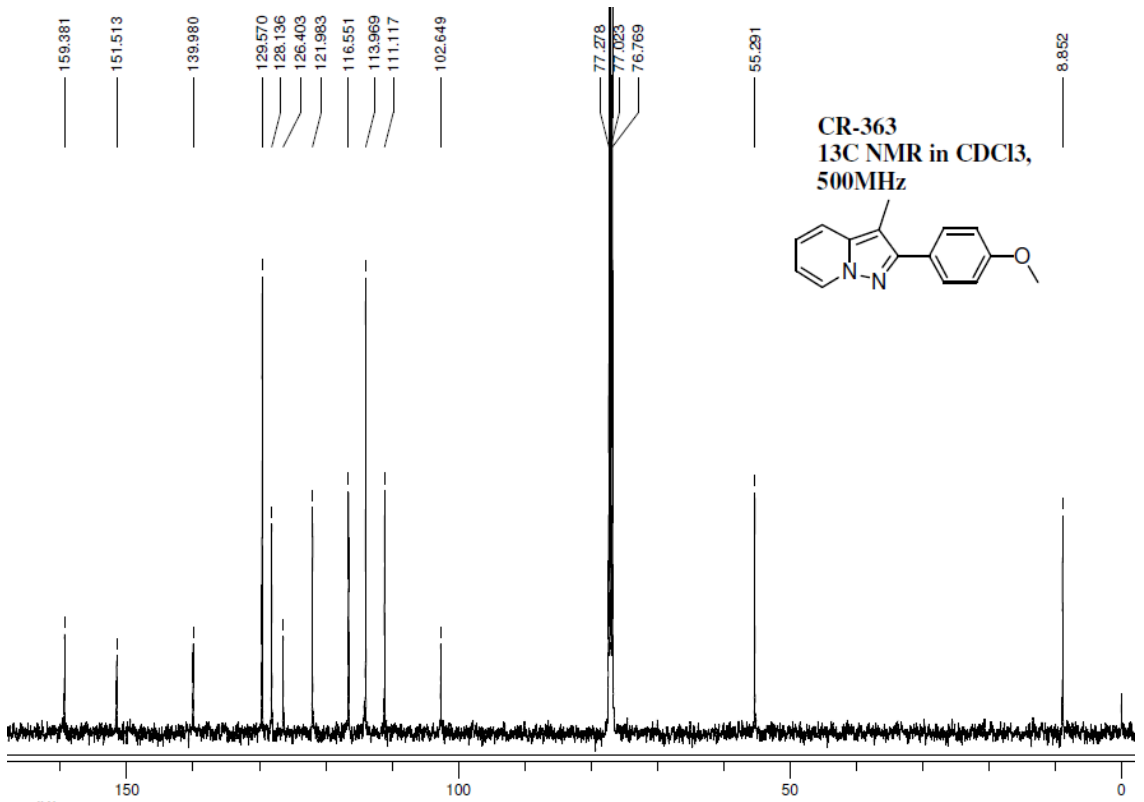

**1H NMR of 3c**



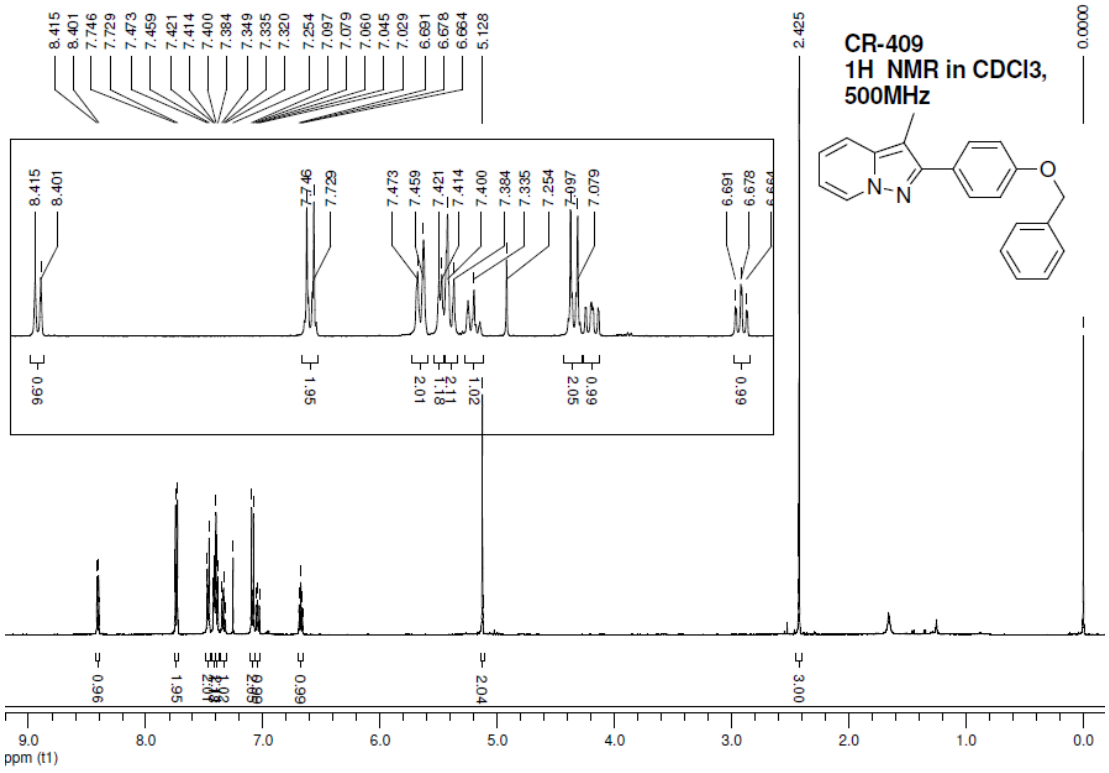

**13C NMR of 3c**



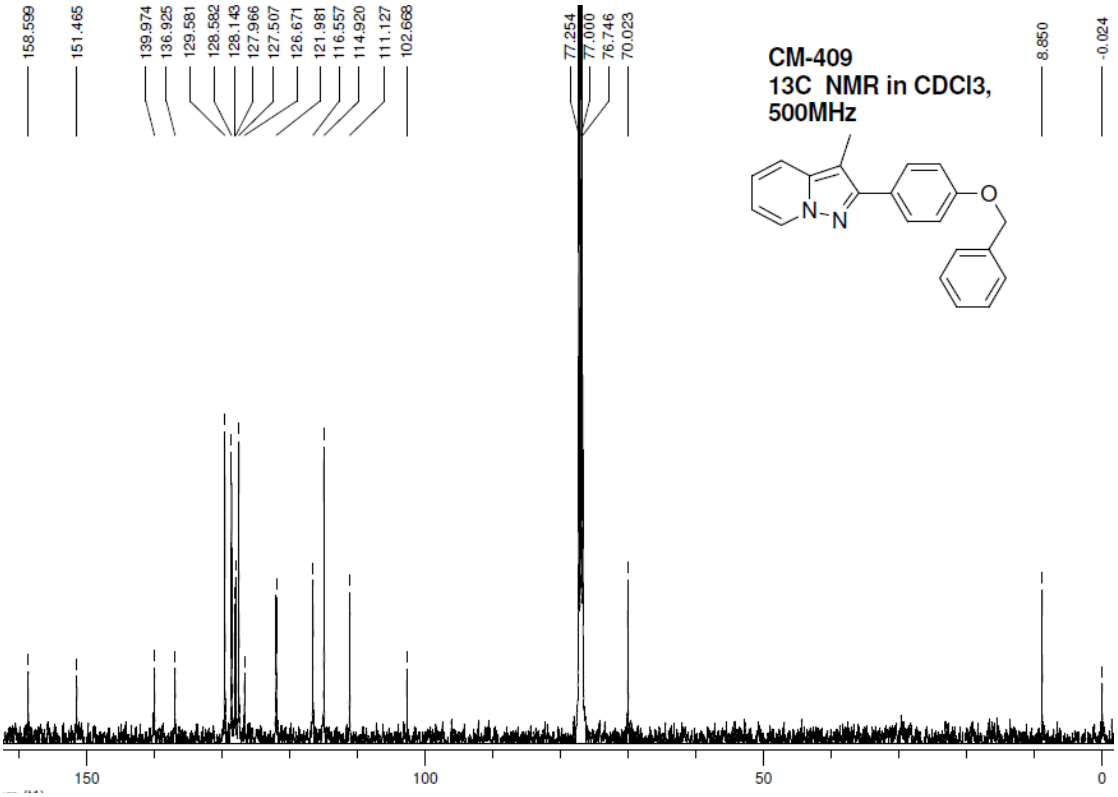

**1H NMR of 3d**



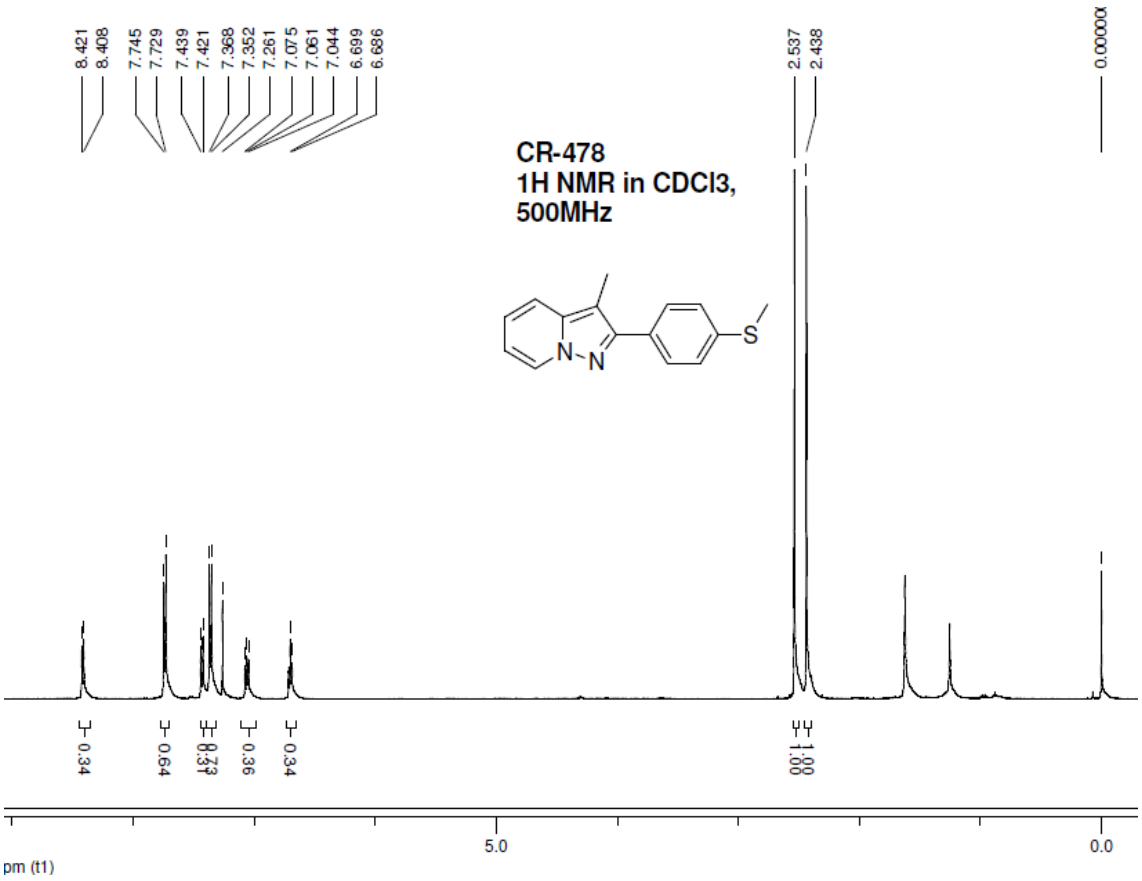

**13C NMR of 3d**



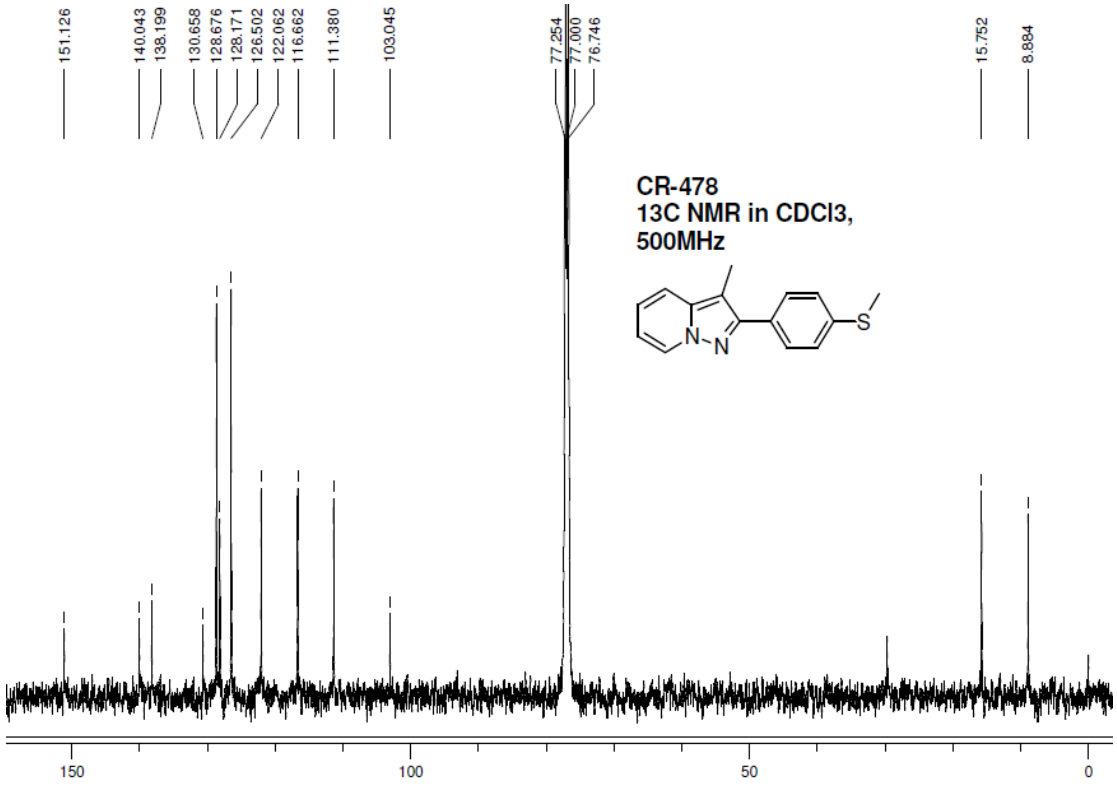

**1H NMR of 3e**



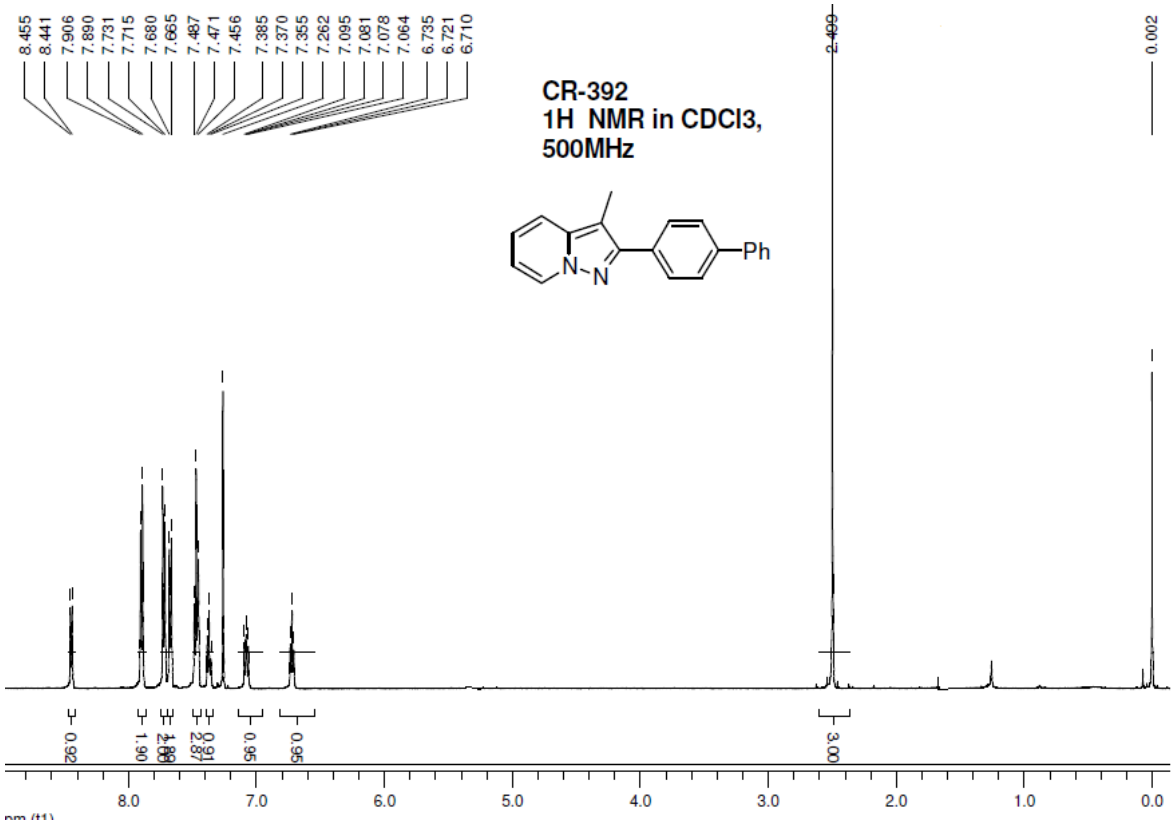

**13C NMR of 3e**



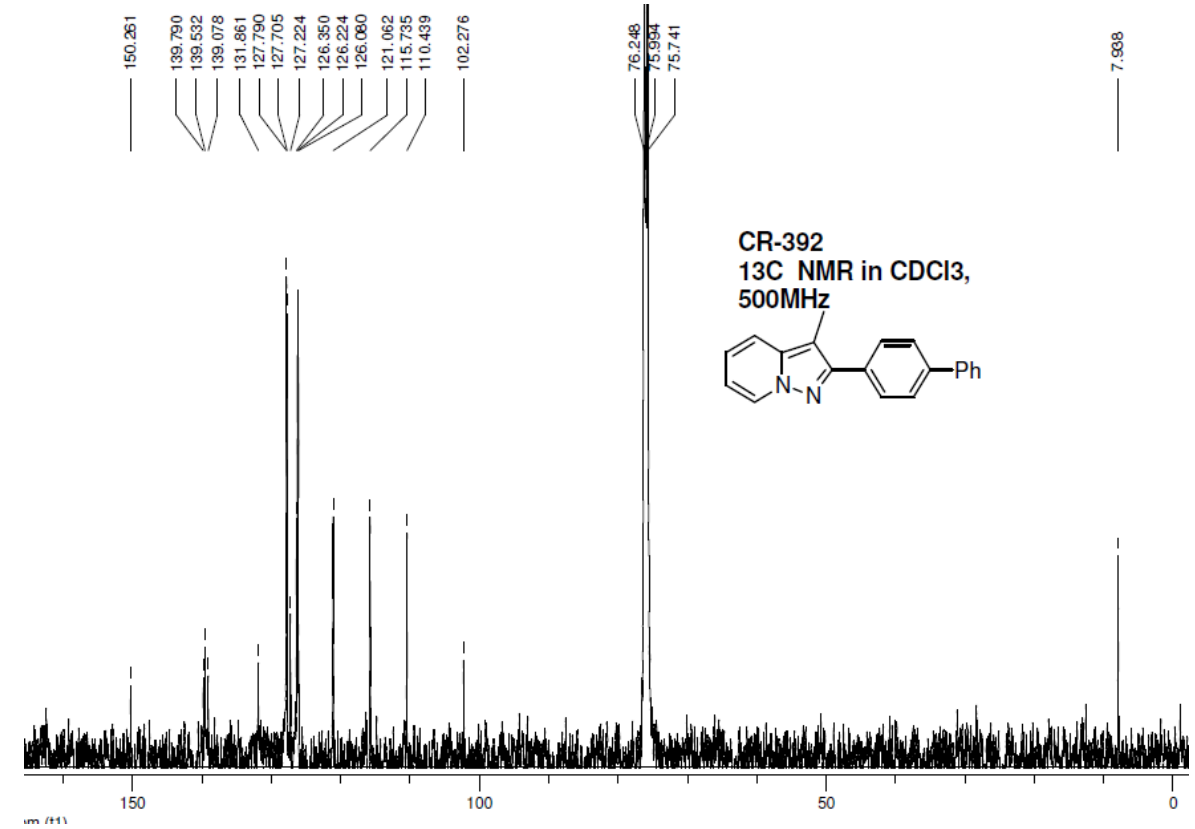

**1H NMR of 3f**



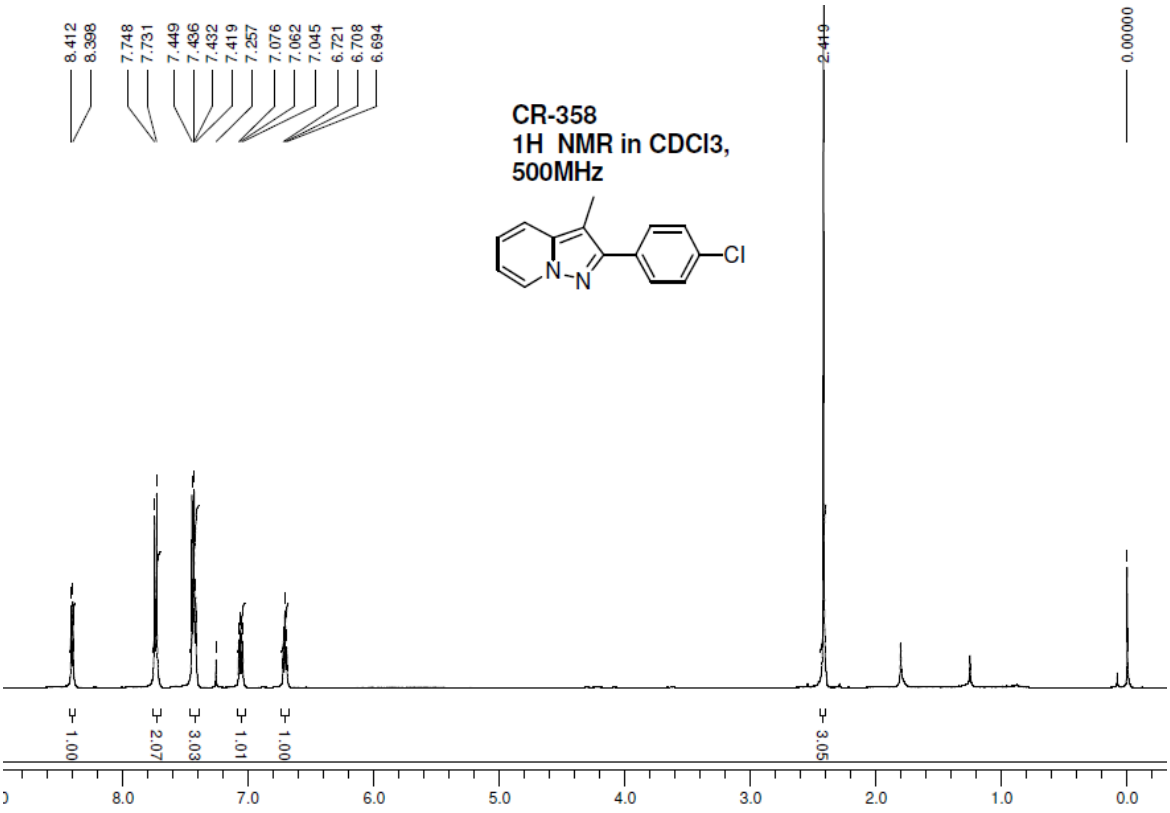

**13C NMR of 3f**



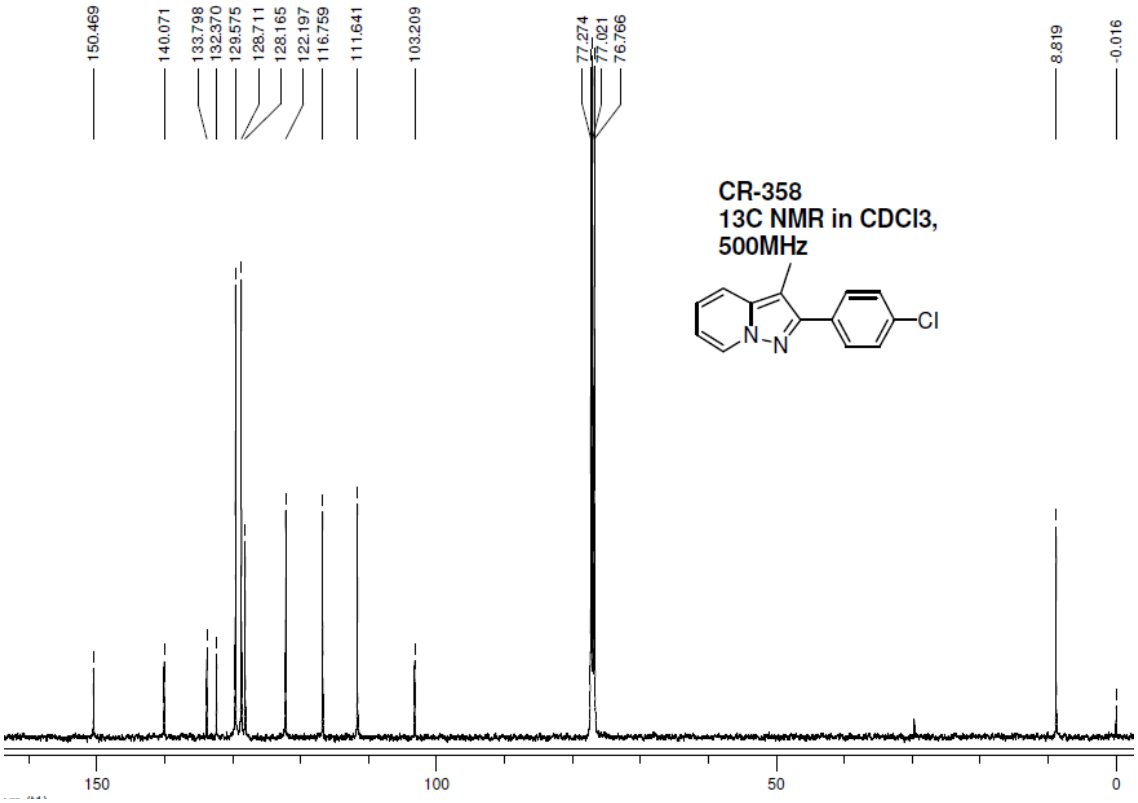

**1H NMR of 3g**



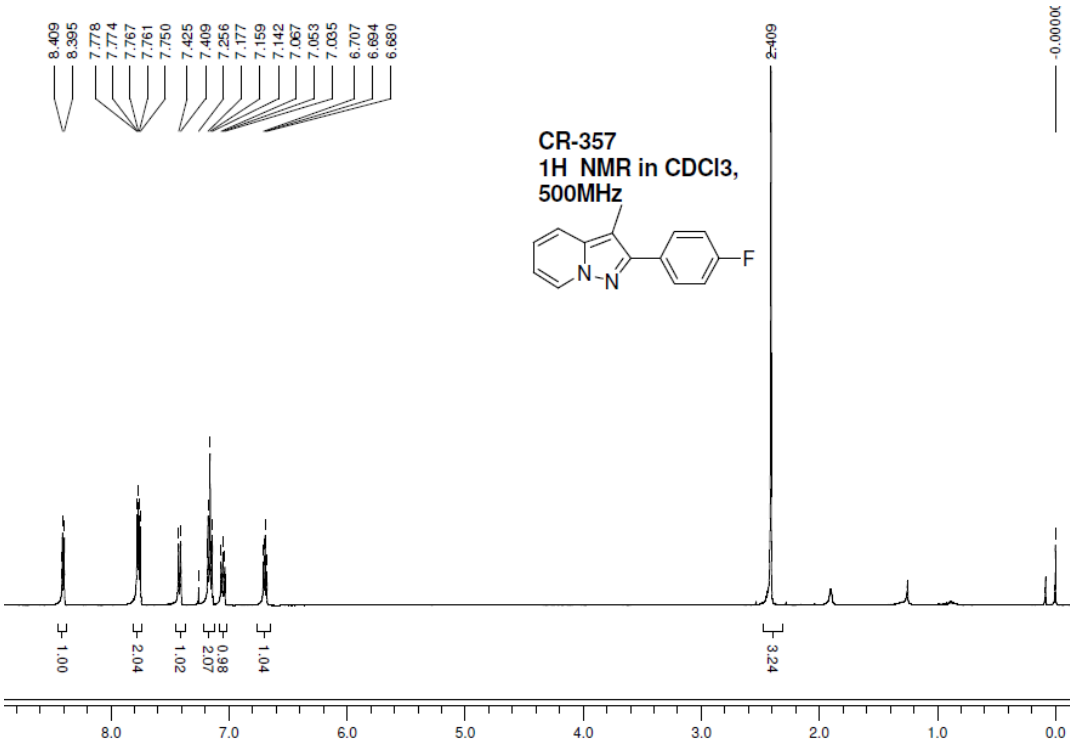

**13C NMR of 3g**



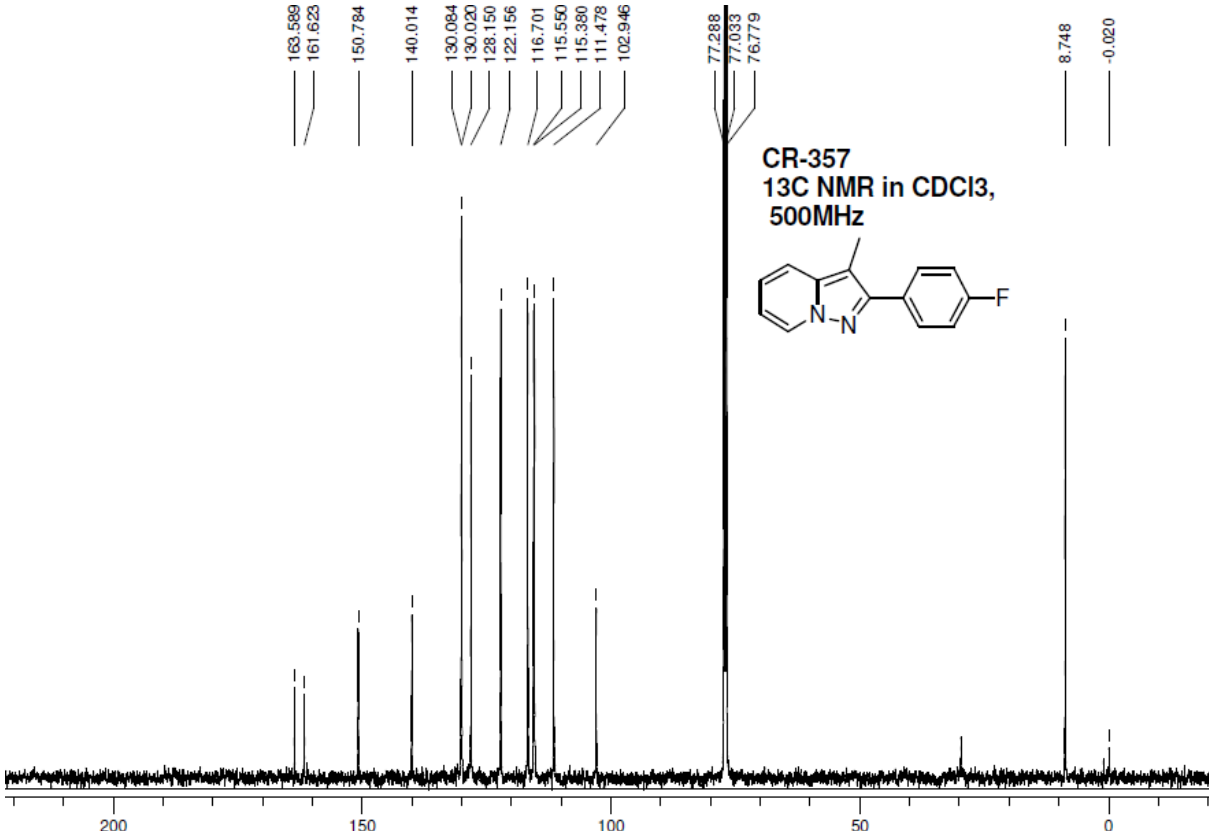

**1H NMR of 3h**



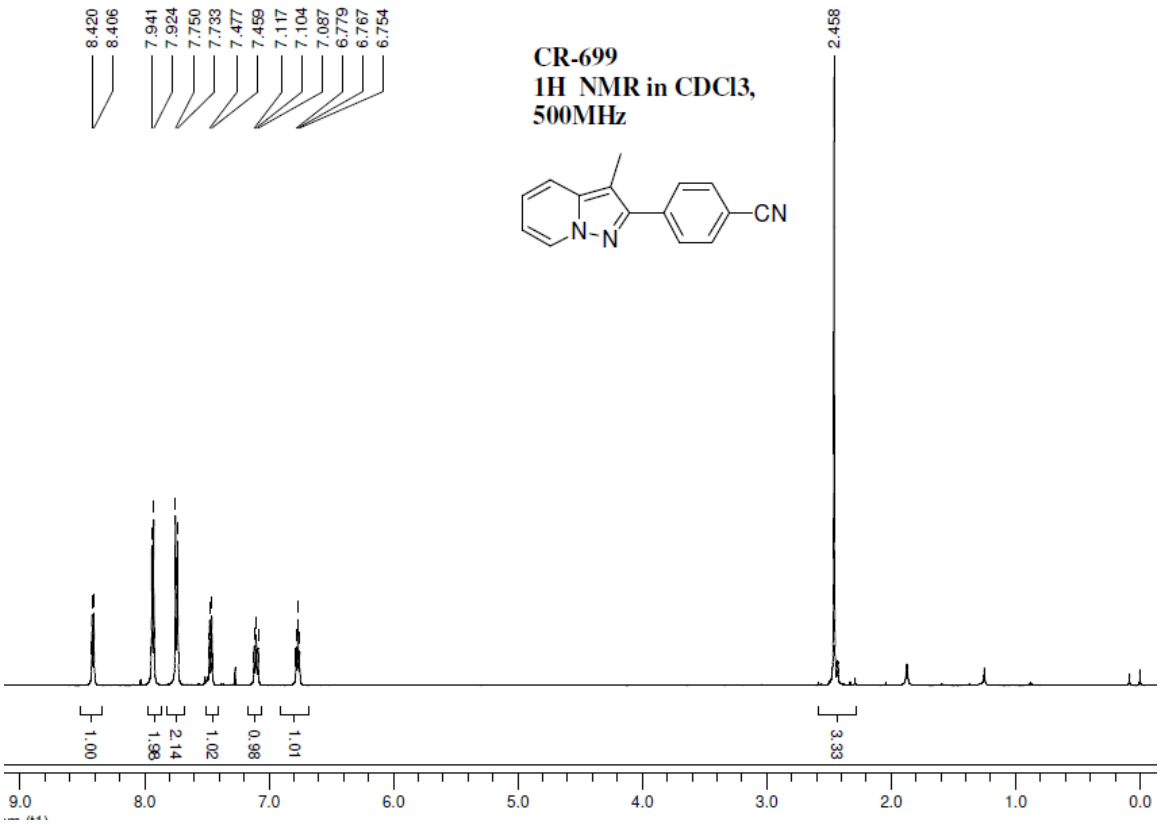

**13C NMR of 3h**




**1H NMR of 3i**




**13C NMR of 3i**

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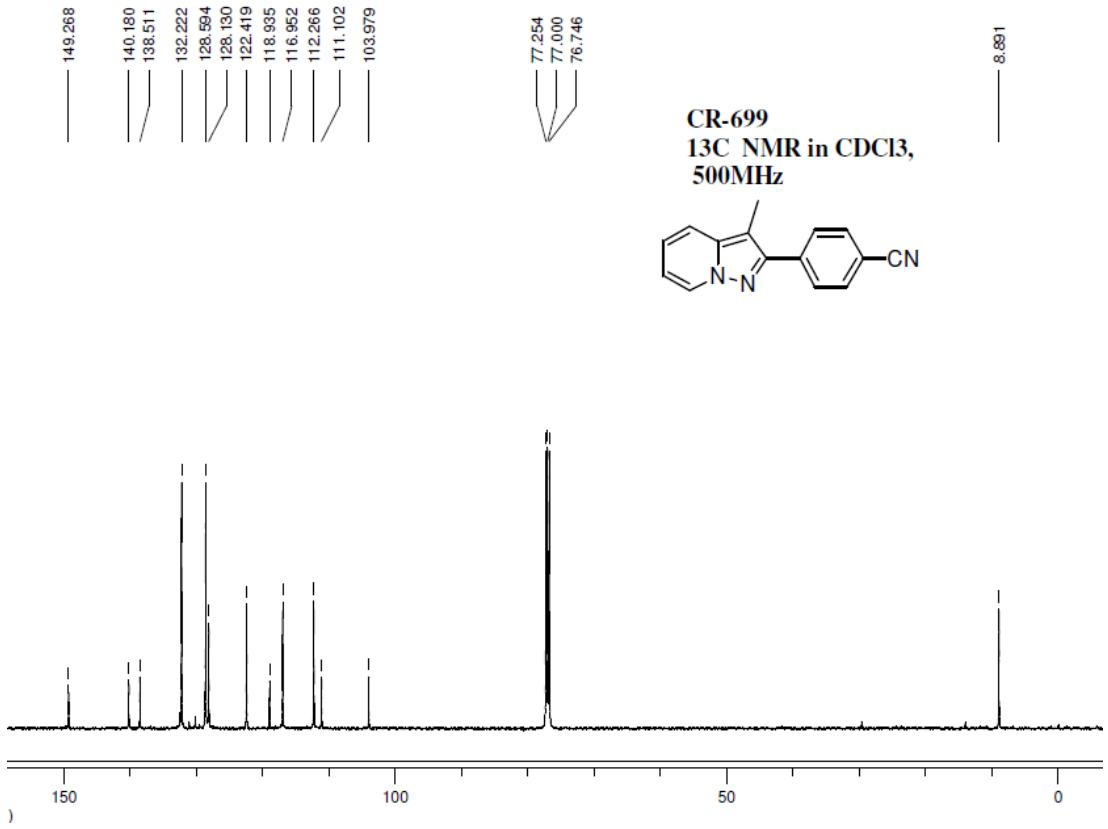


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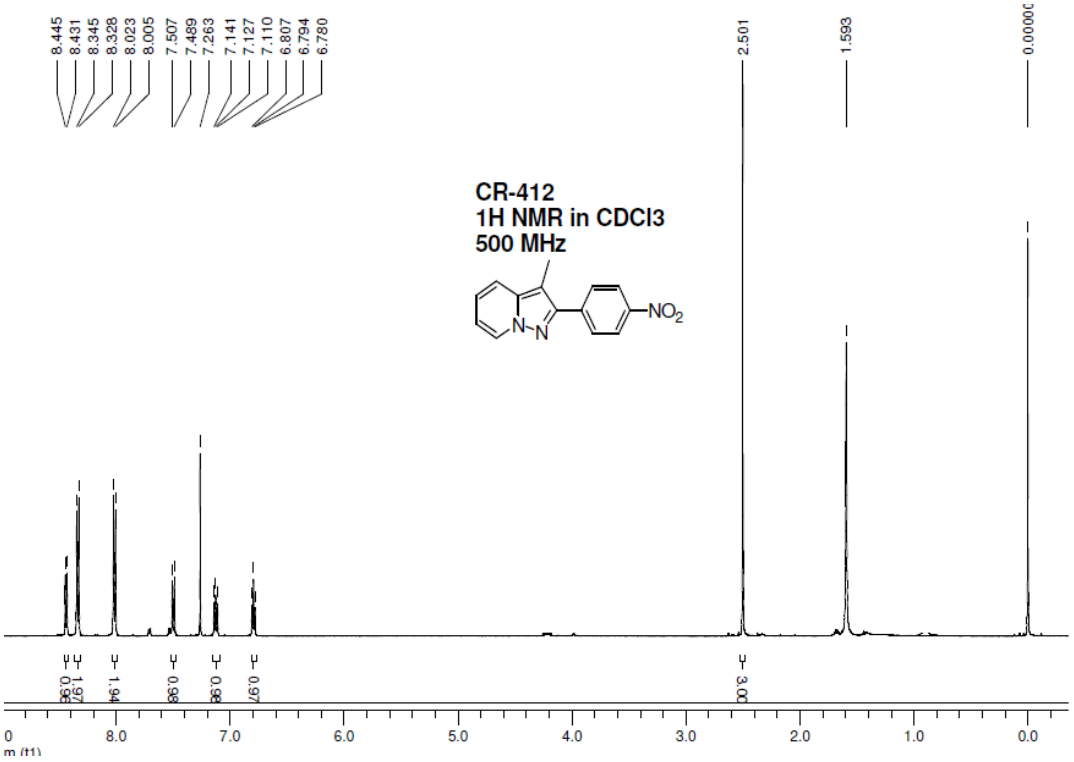
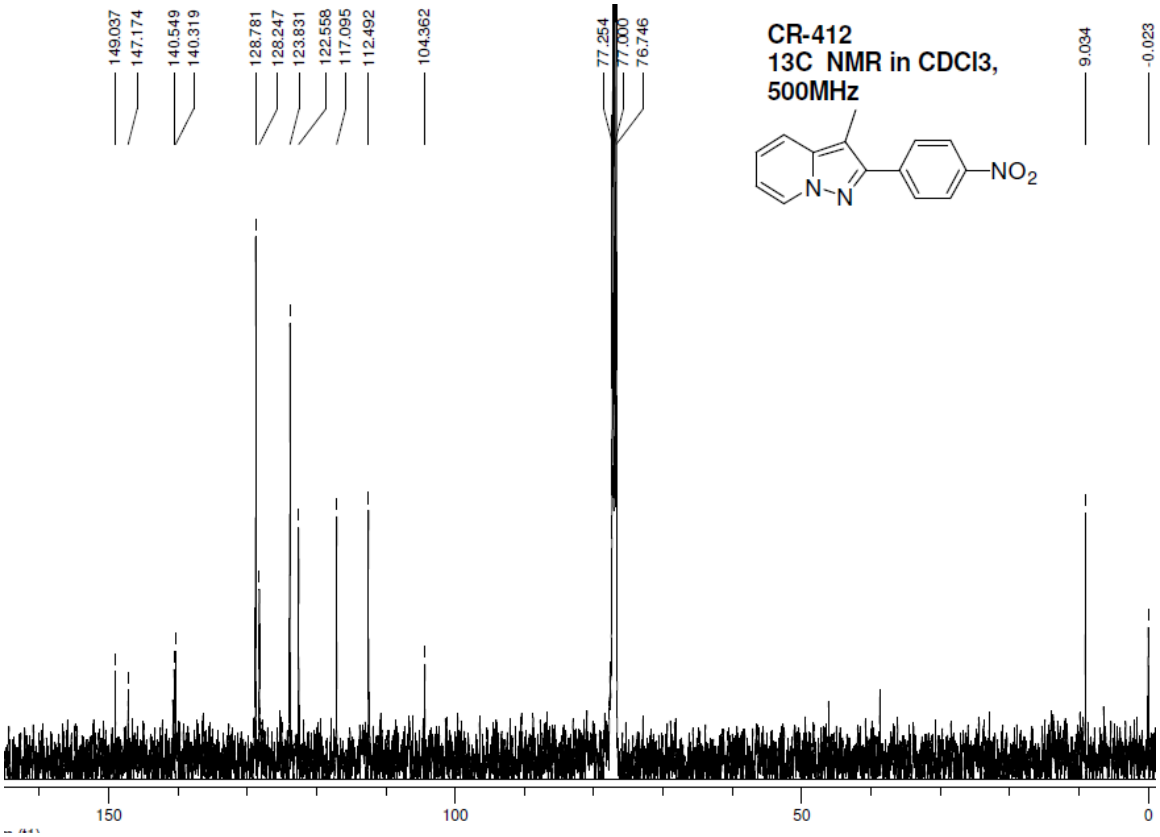



**1H NMR of 3k**

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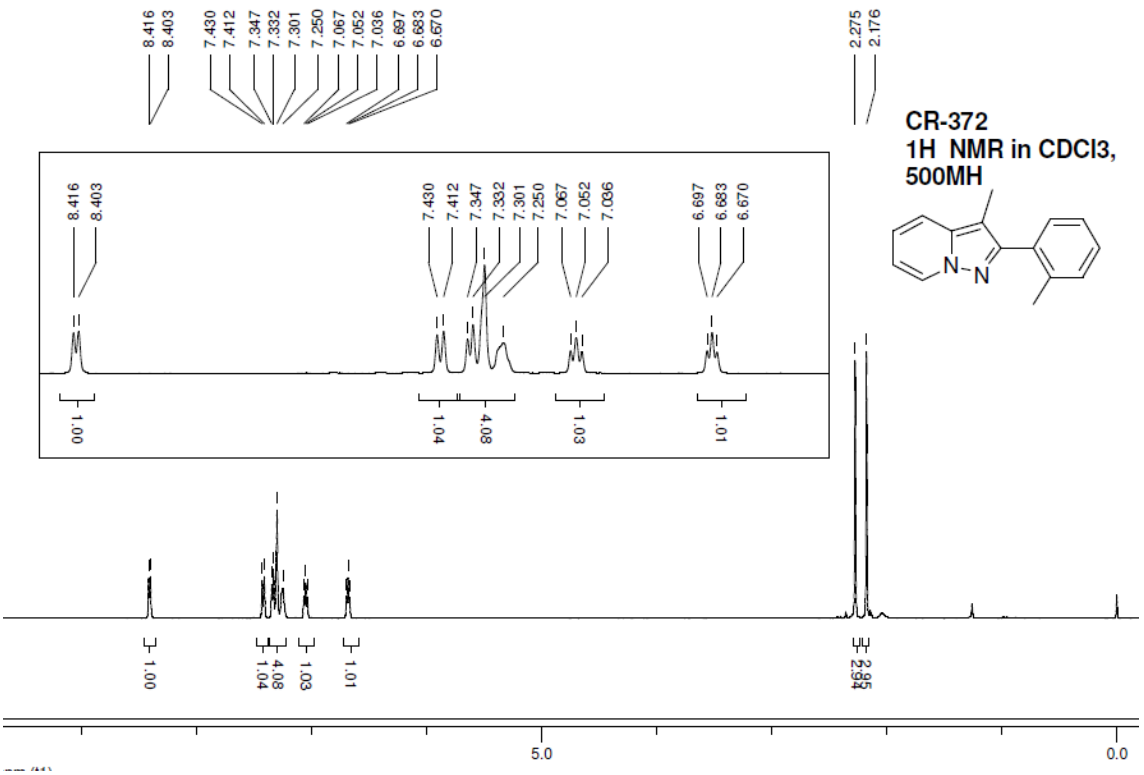


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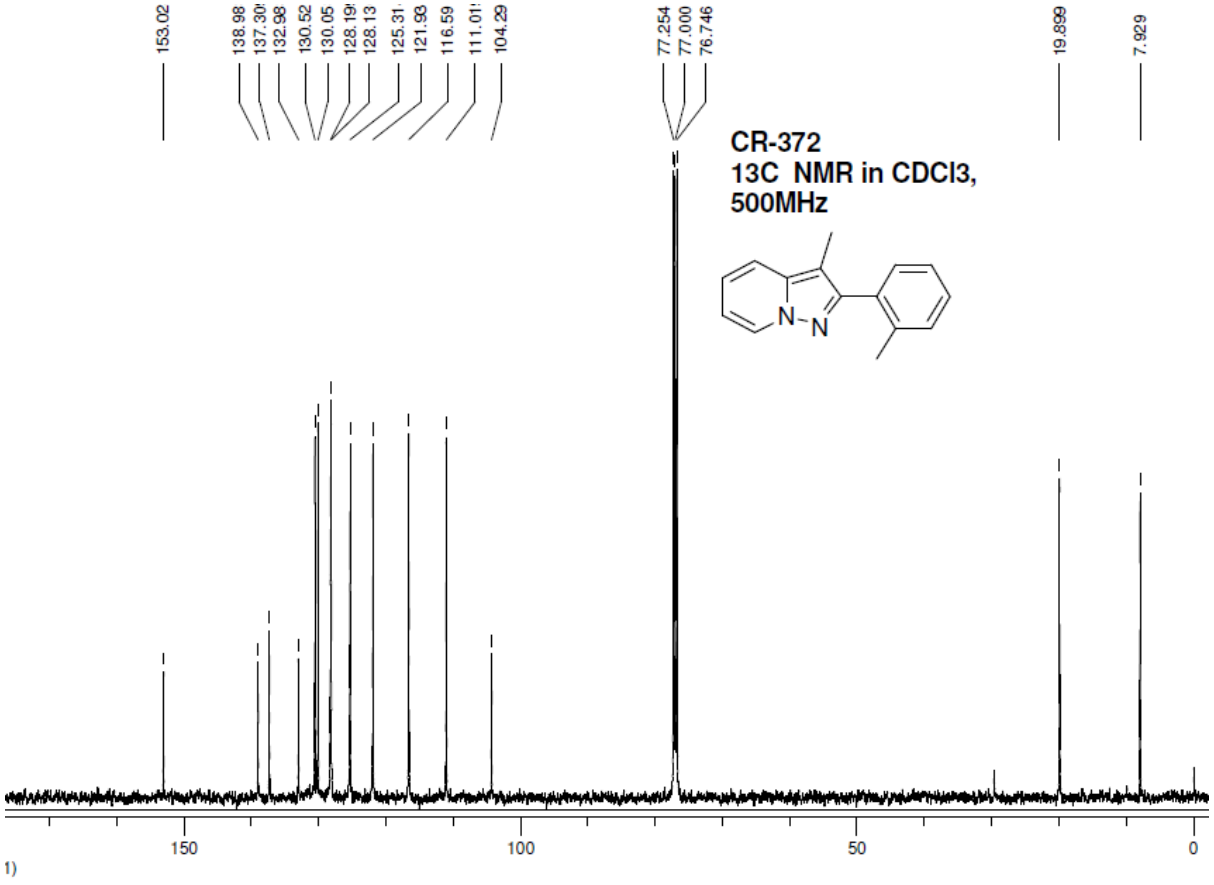
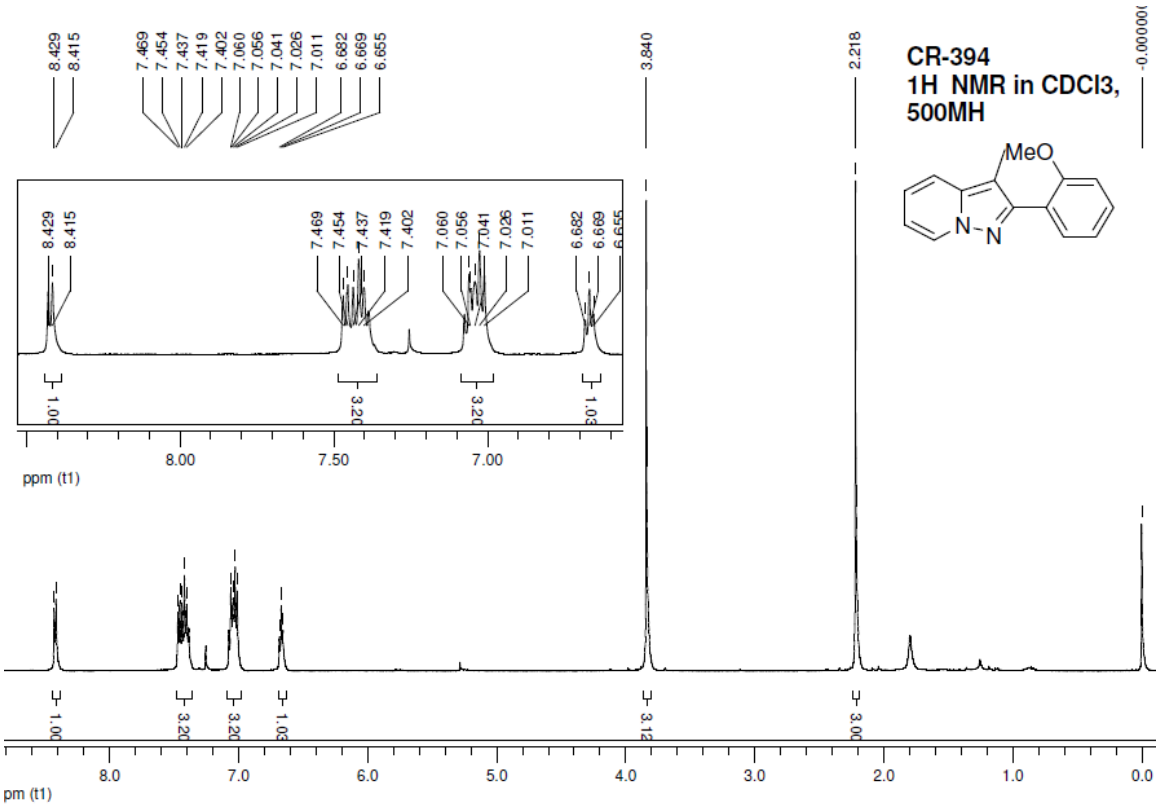
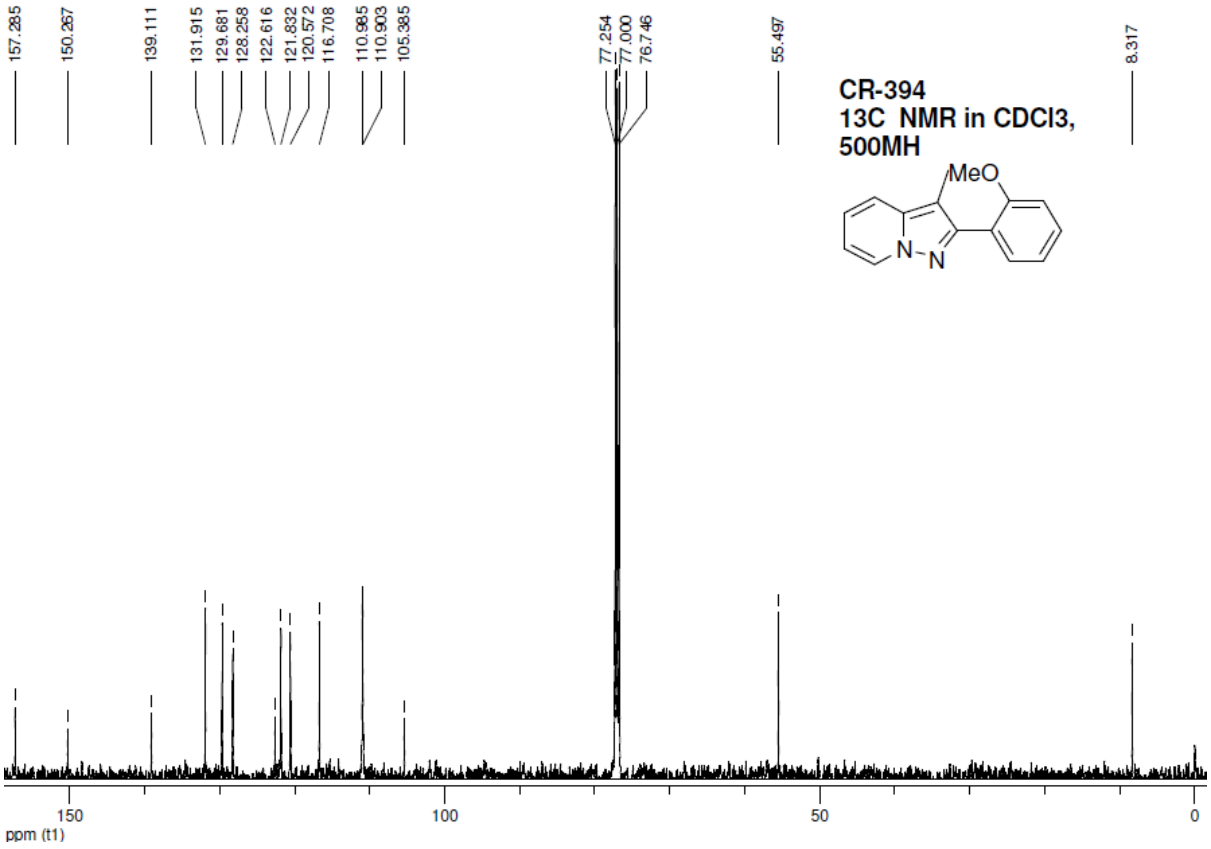


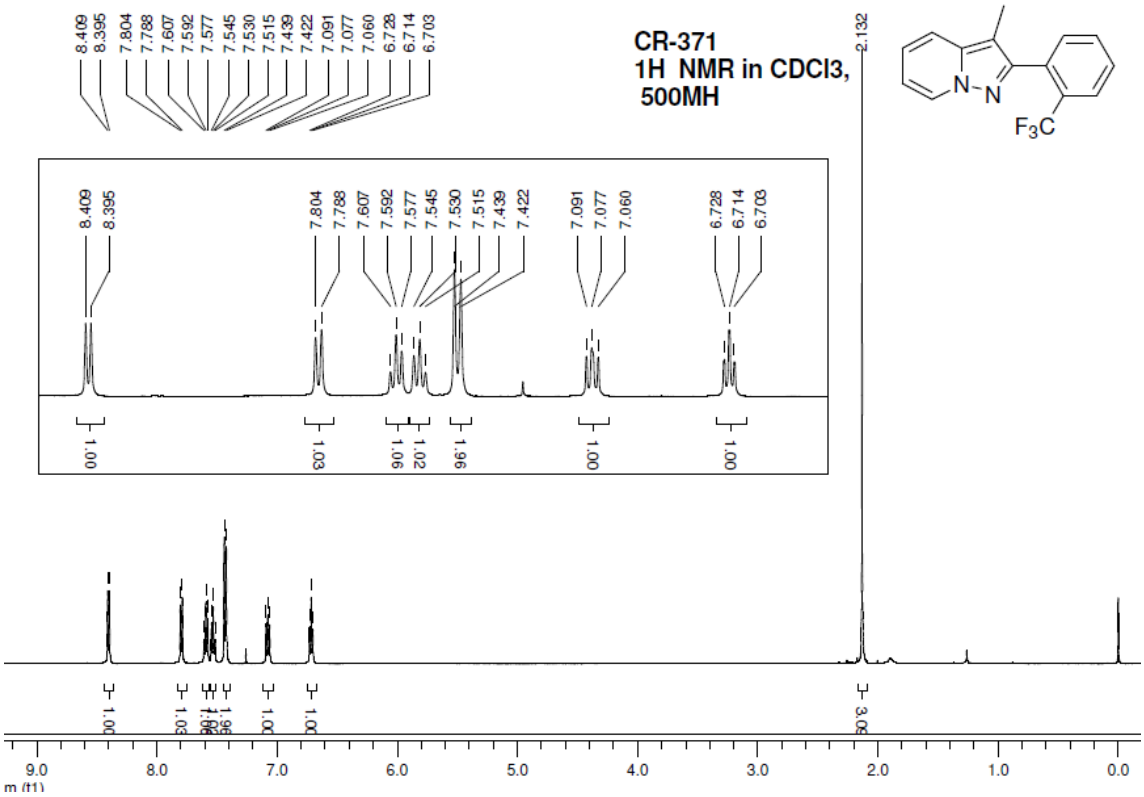

**13C NMR of 3m**



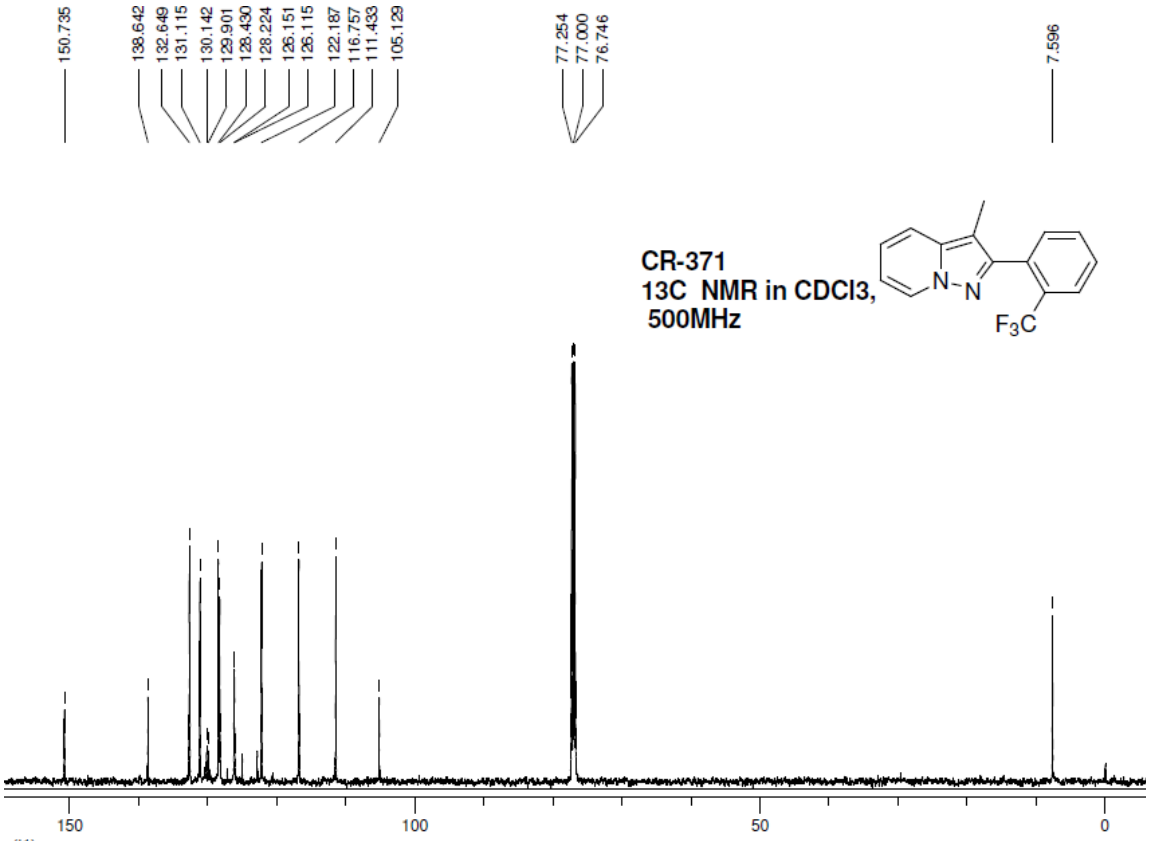

**1H NMR of 3n**



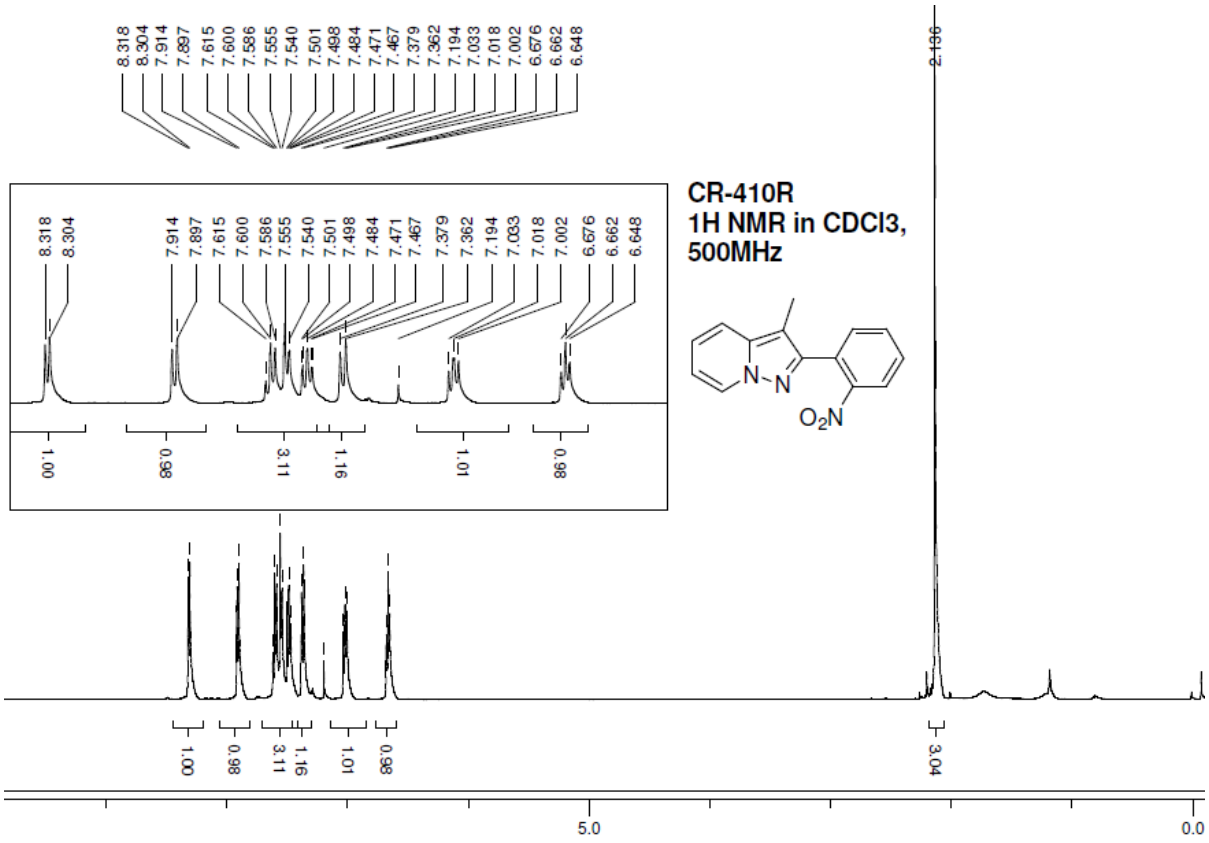

**13C NMR of 3n**



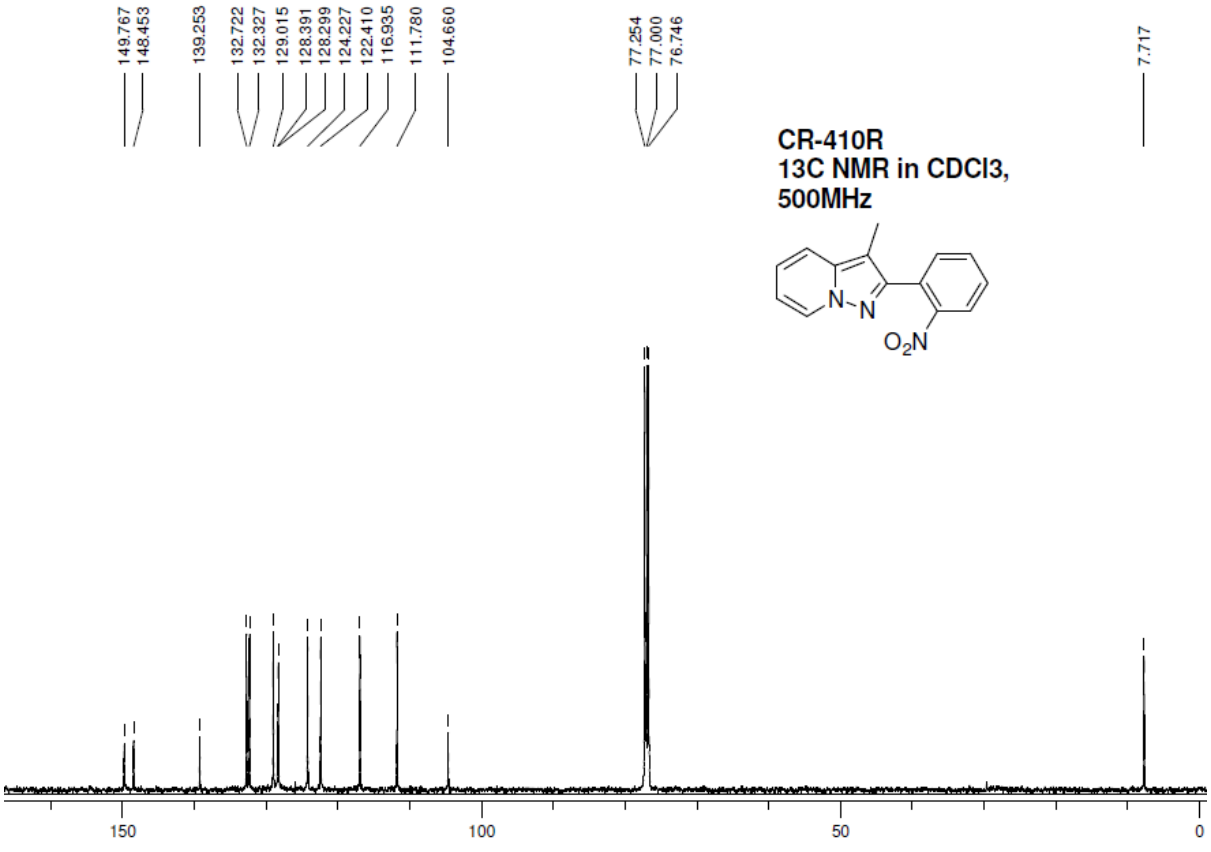

**1H NMR of 3o**




**13C NMR of 3o**




**1H NMR of 3p**

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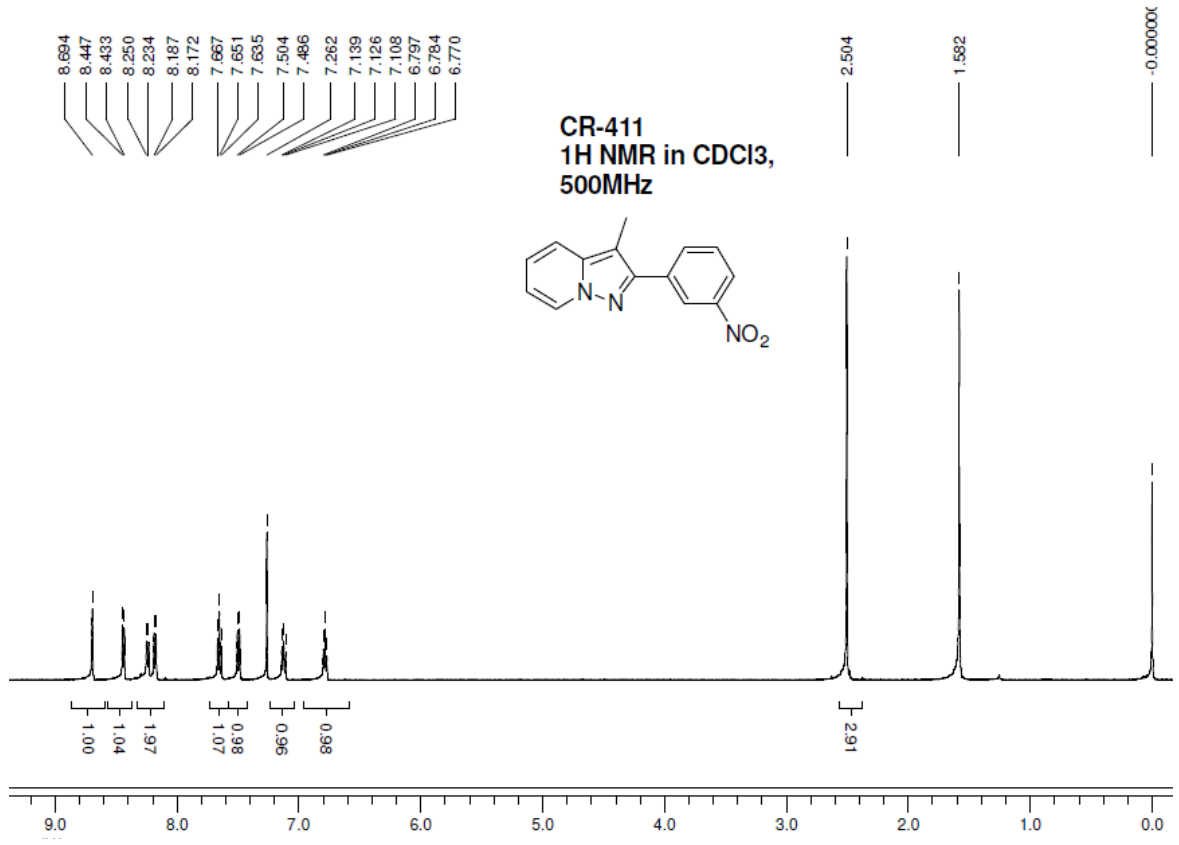


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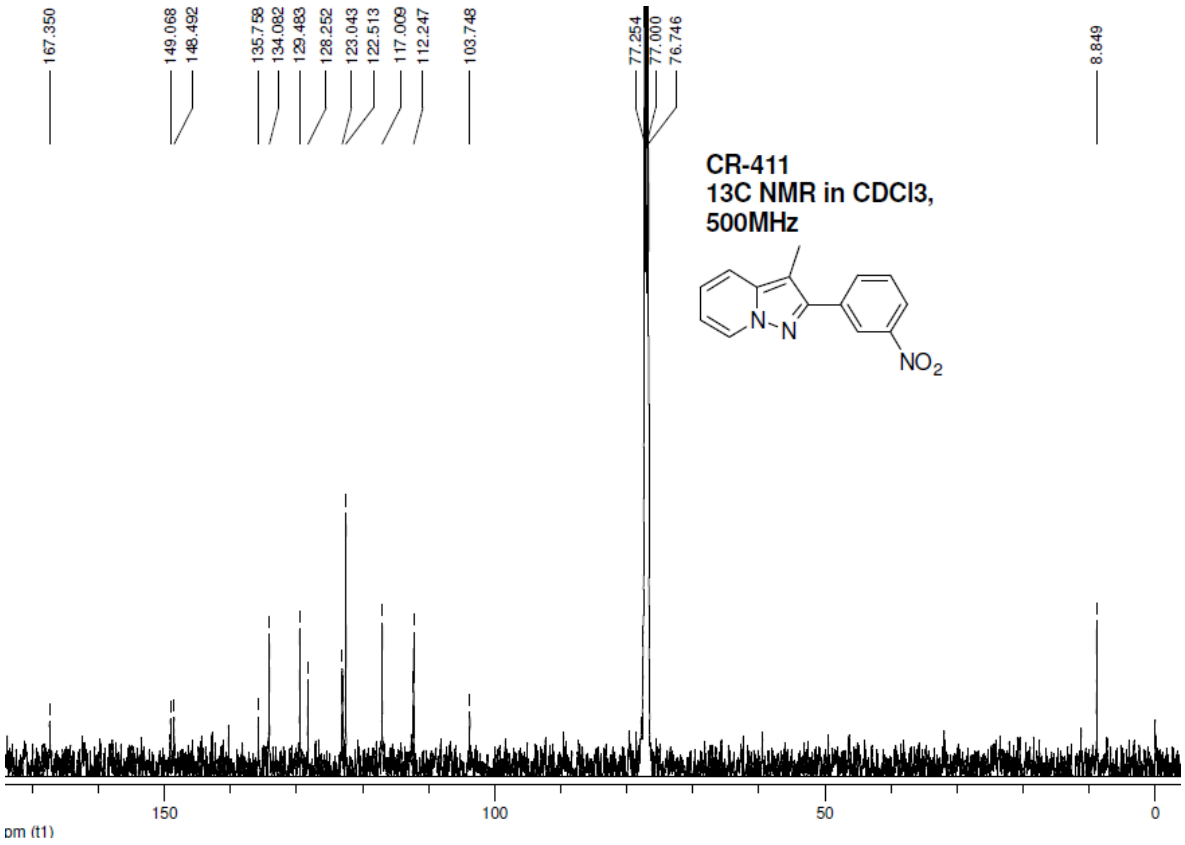


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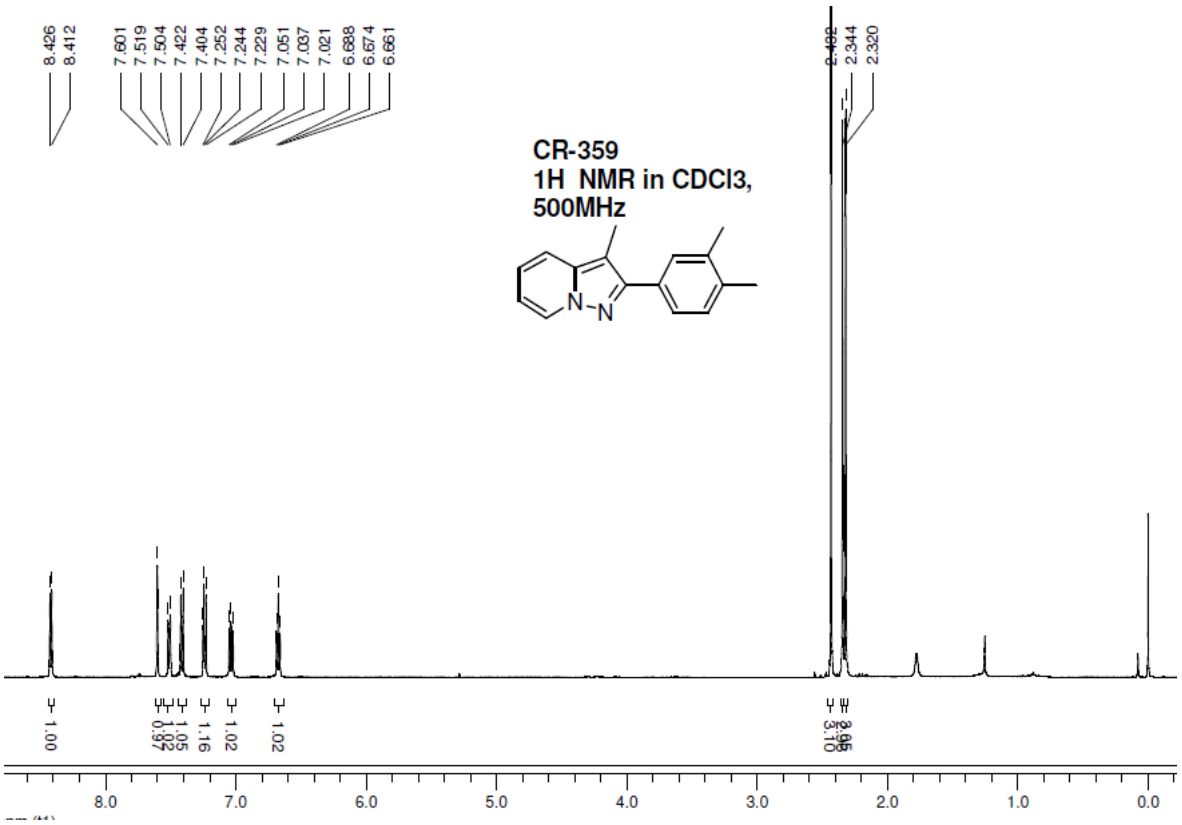
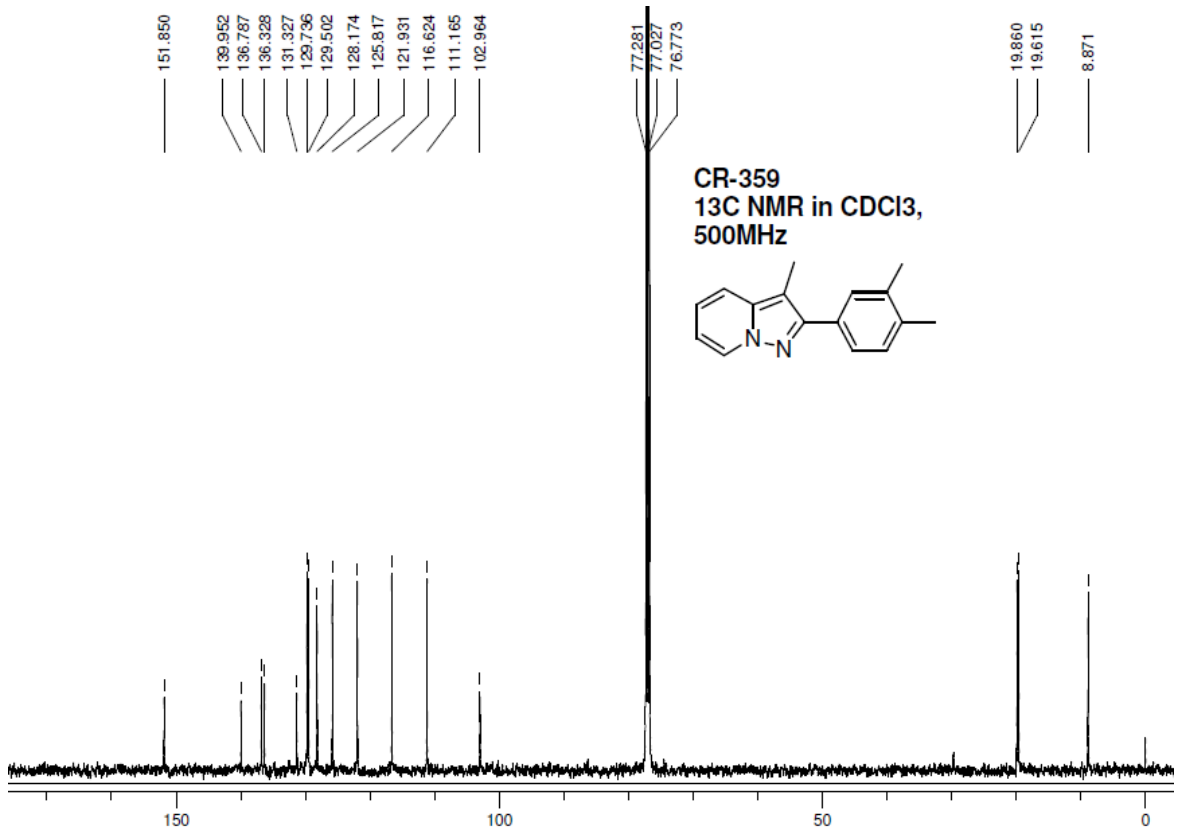
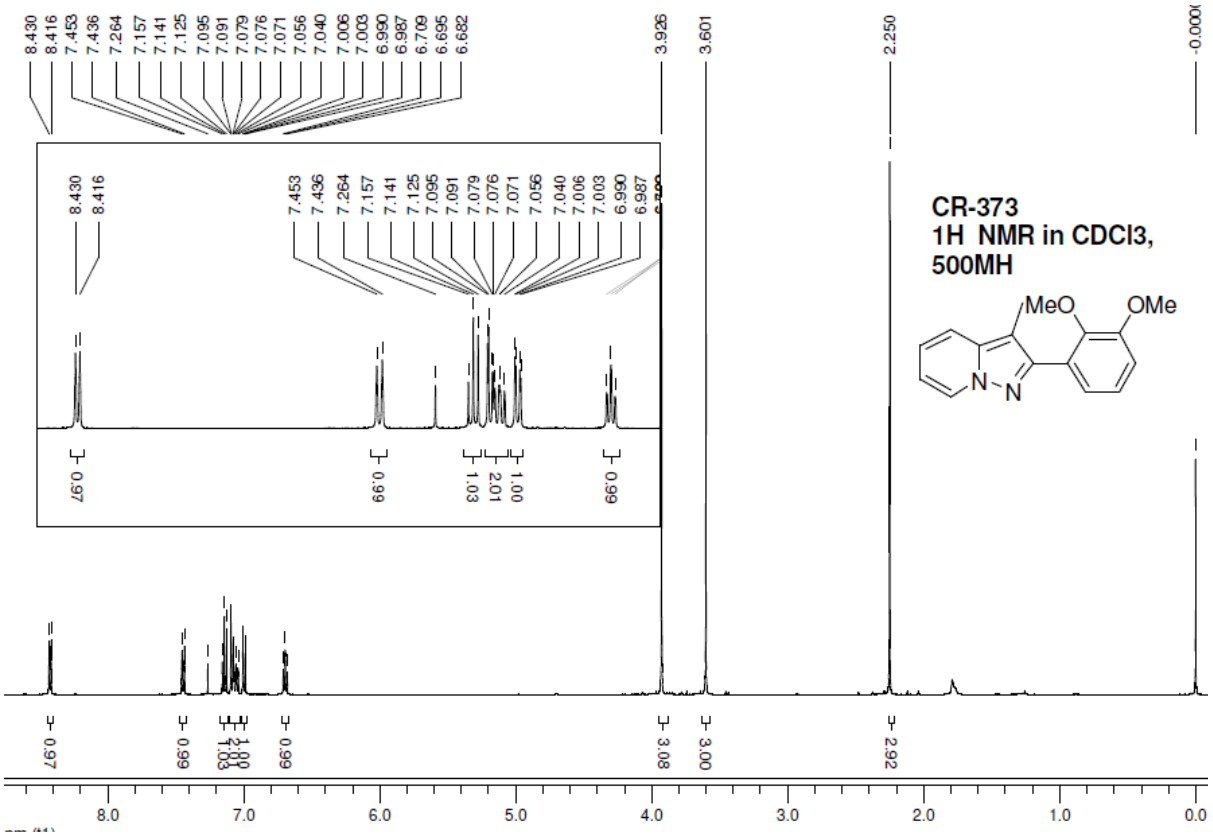


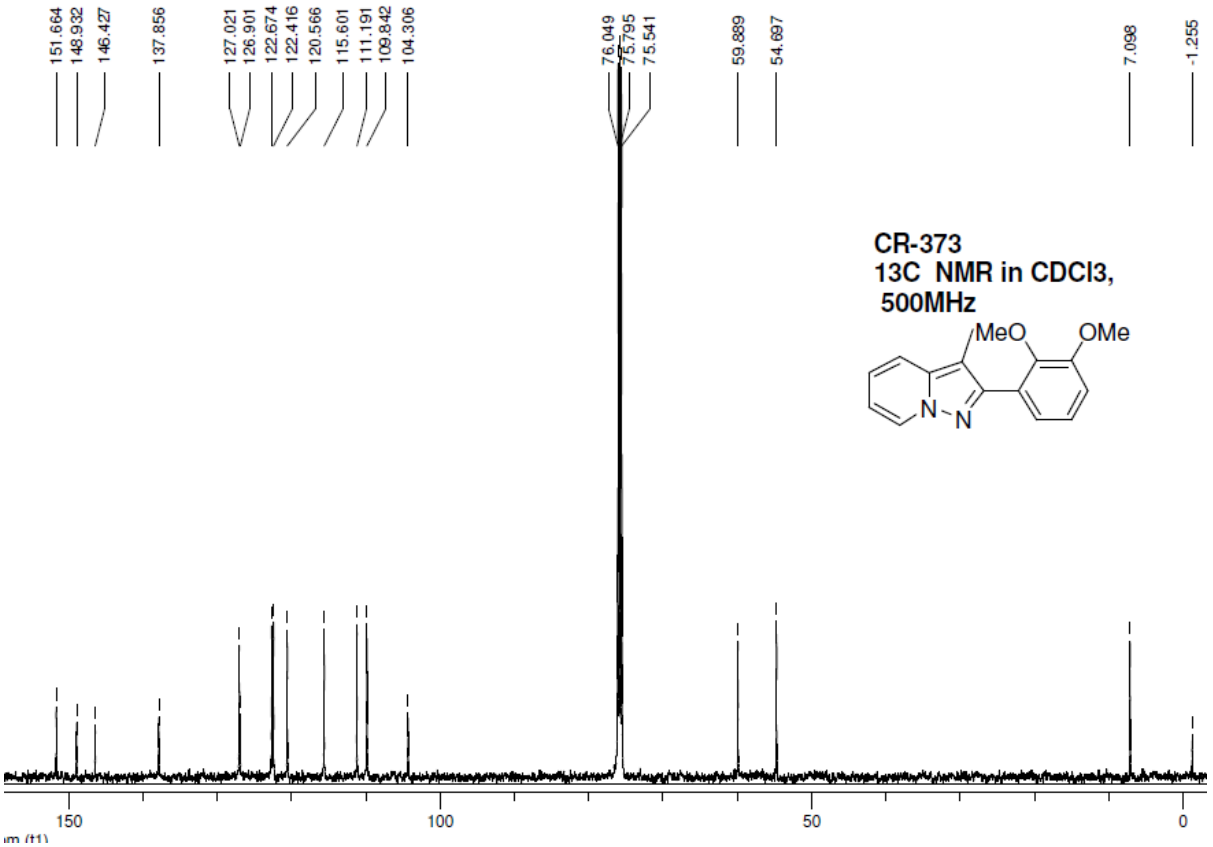

**1H NMR of 3r**



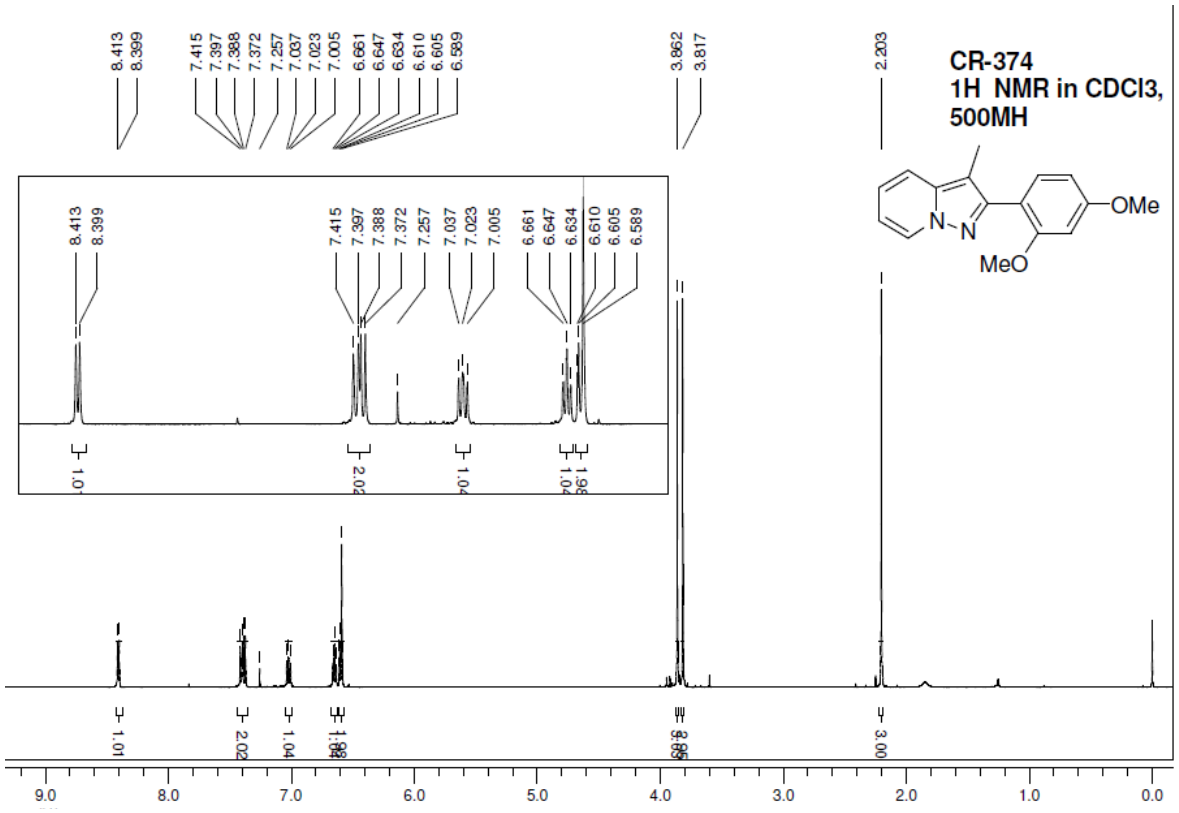

**13C NMR of 3r**




**1H NMR of 3s**




**13C NMR of 3s**

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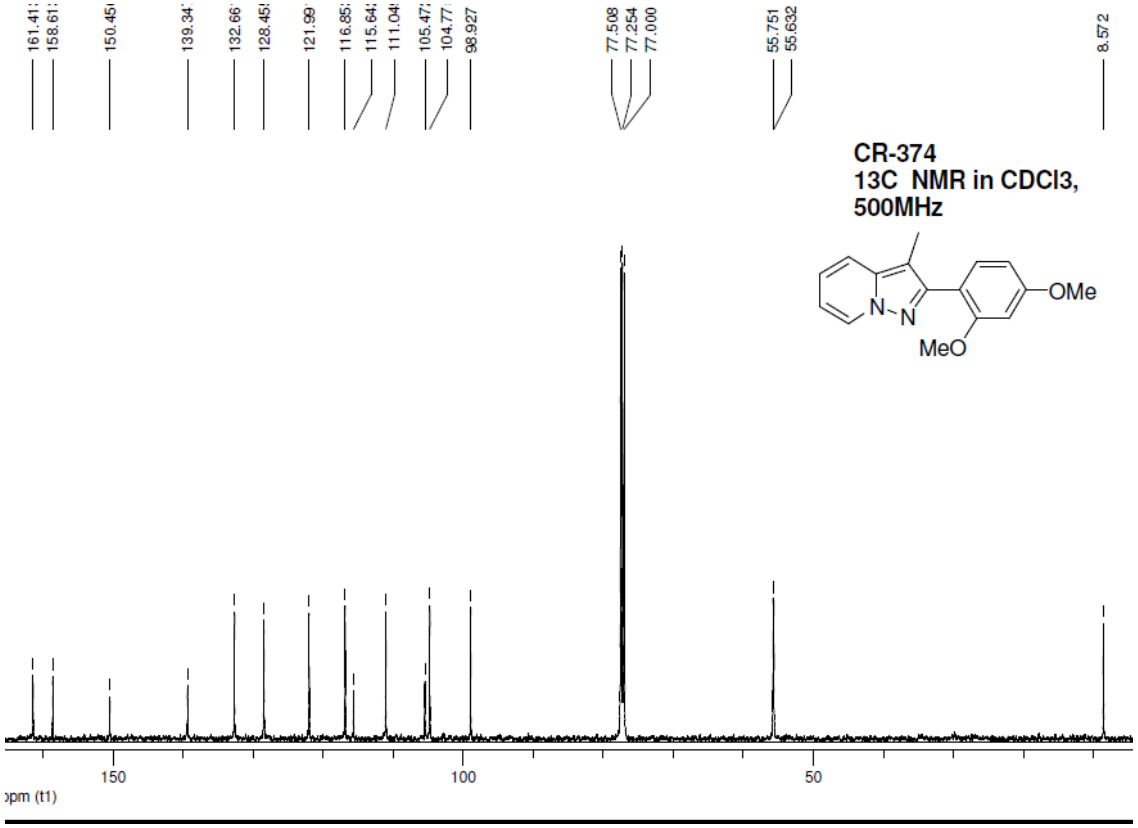


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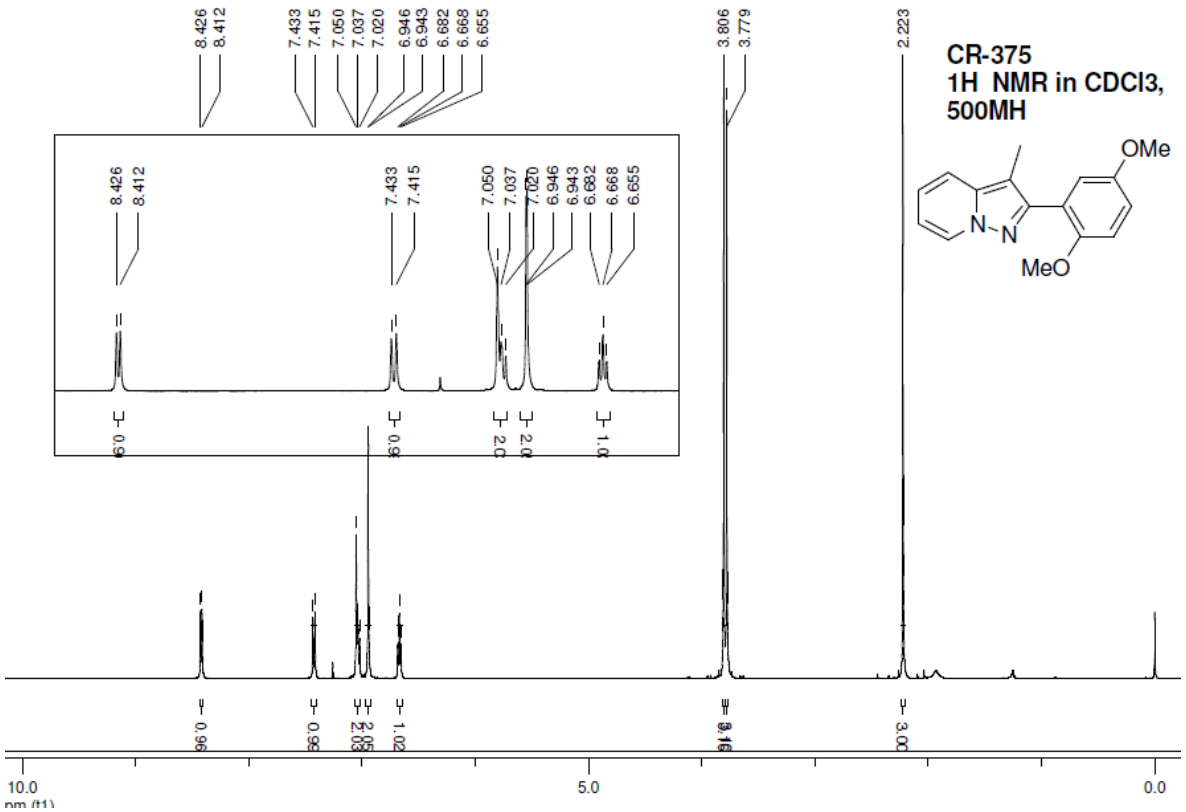


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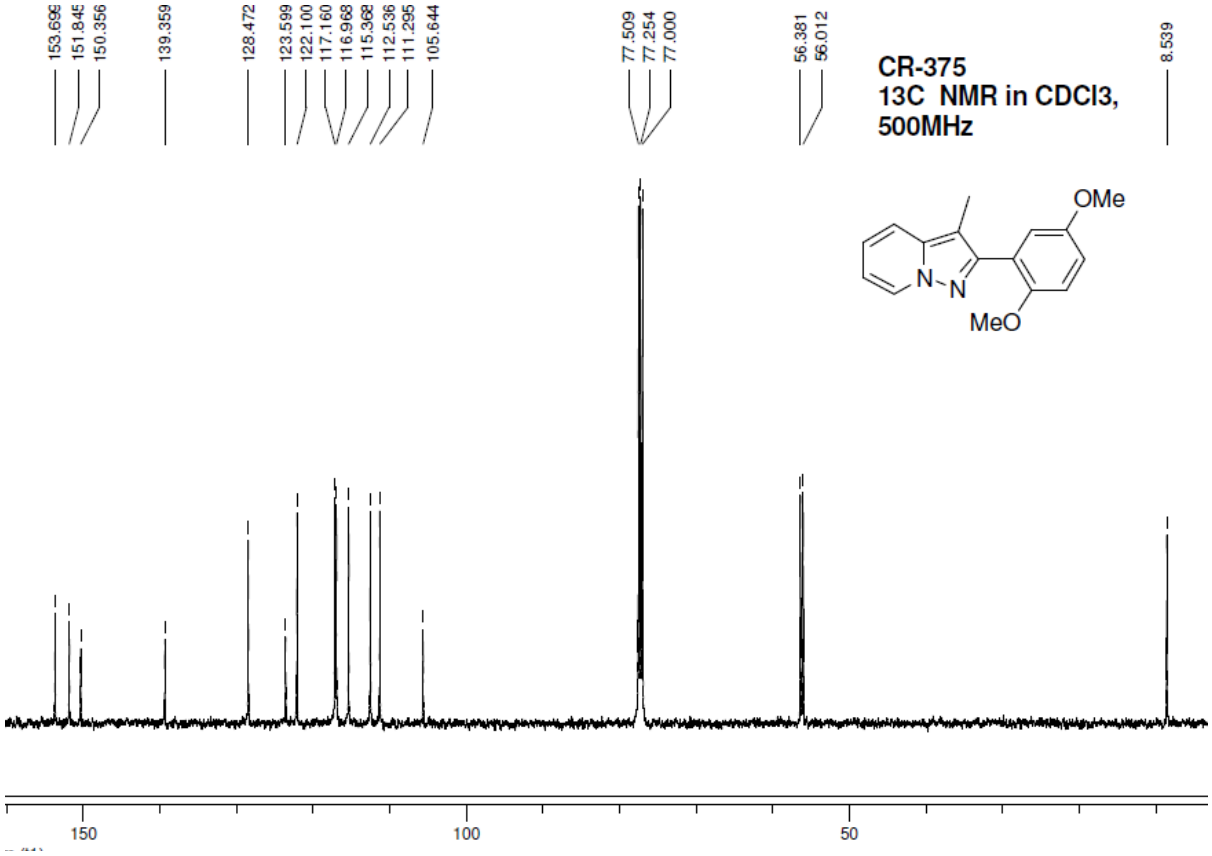


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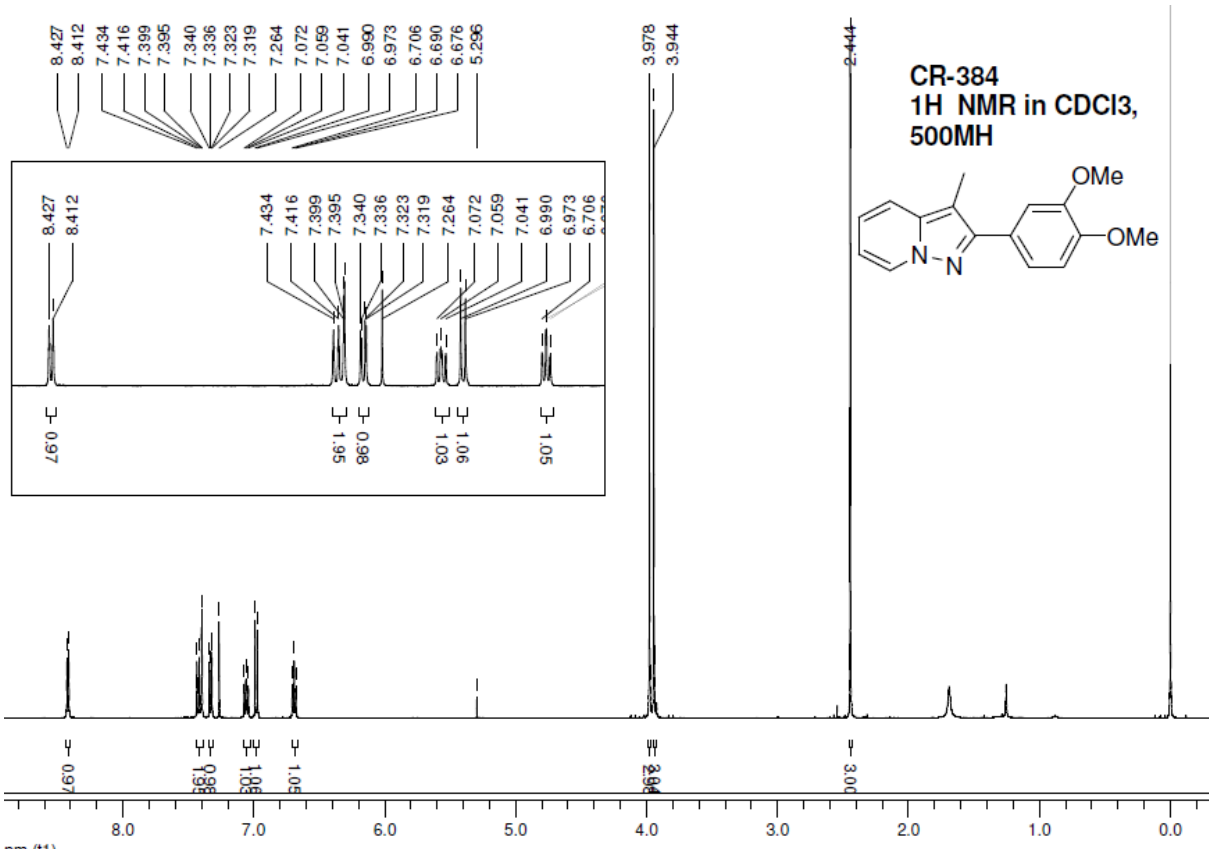


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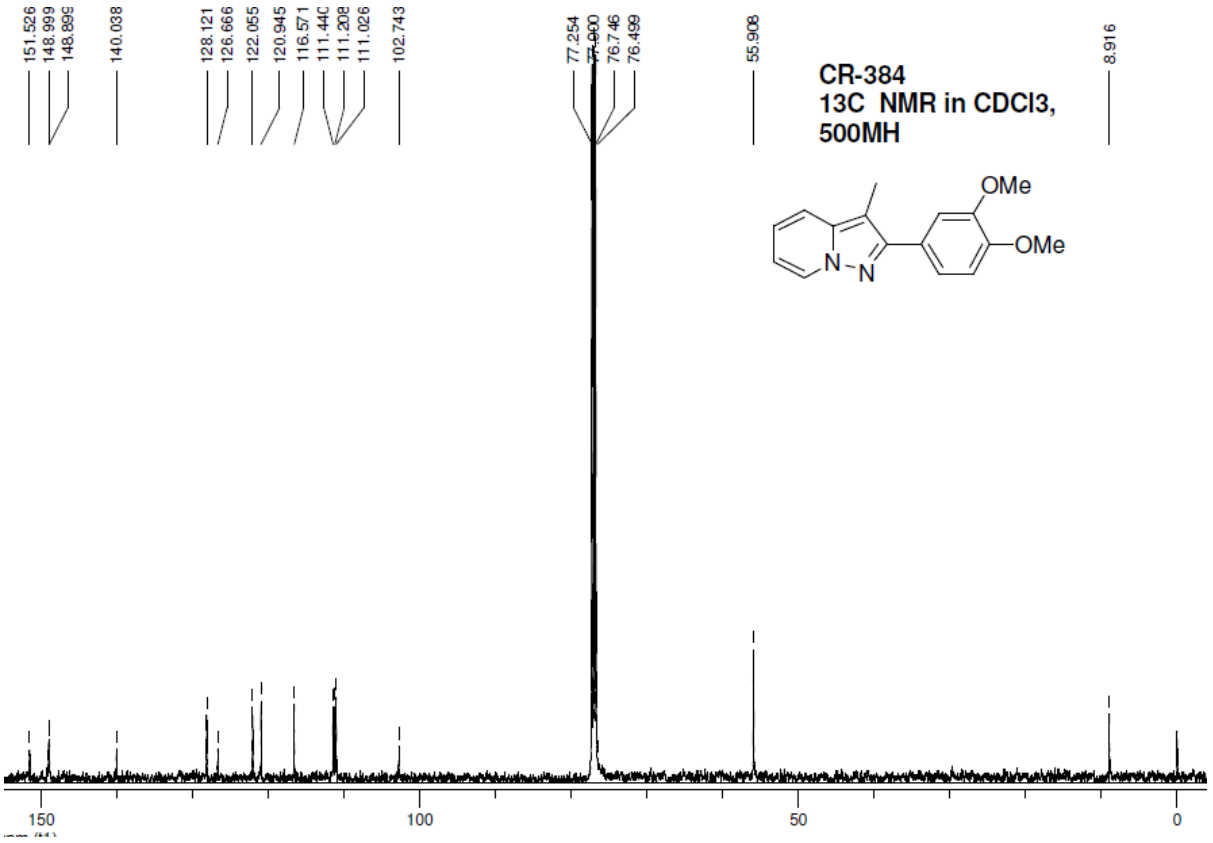
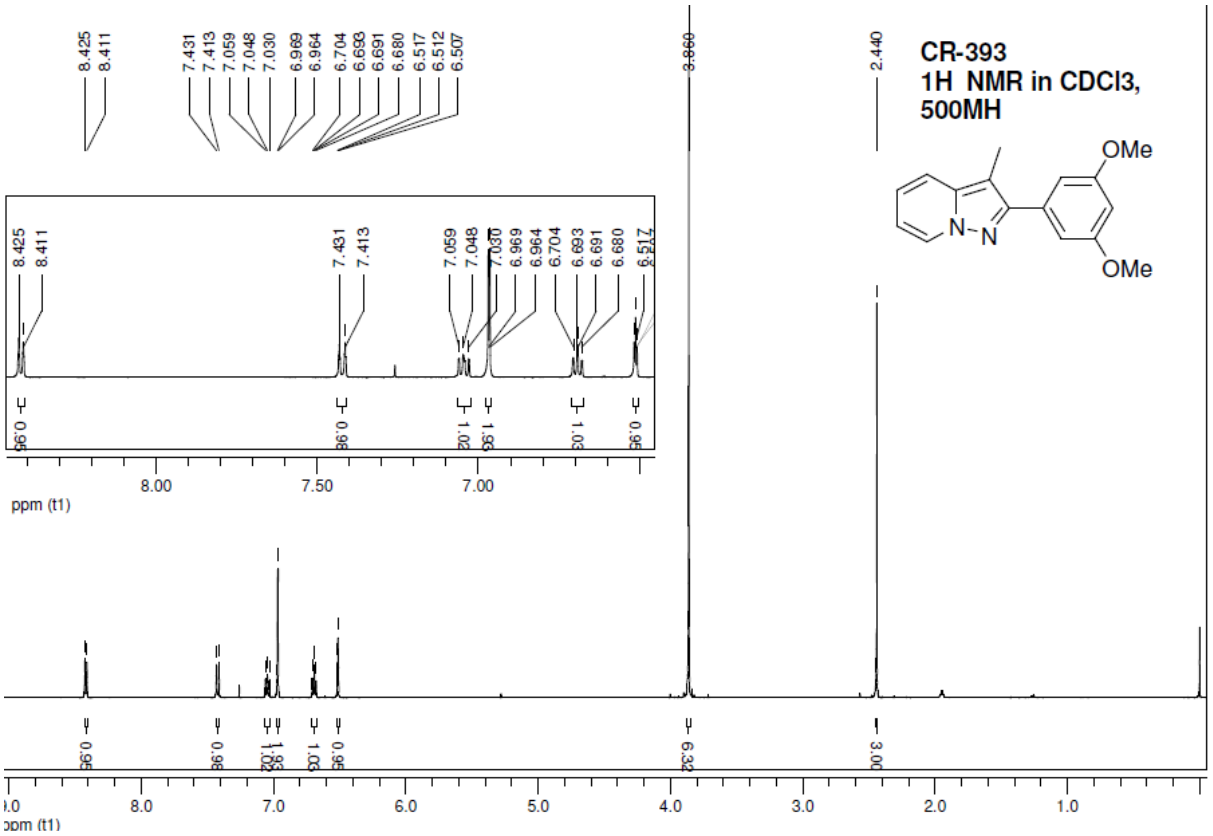



**13C NMR of 3v**

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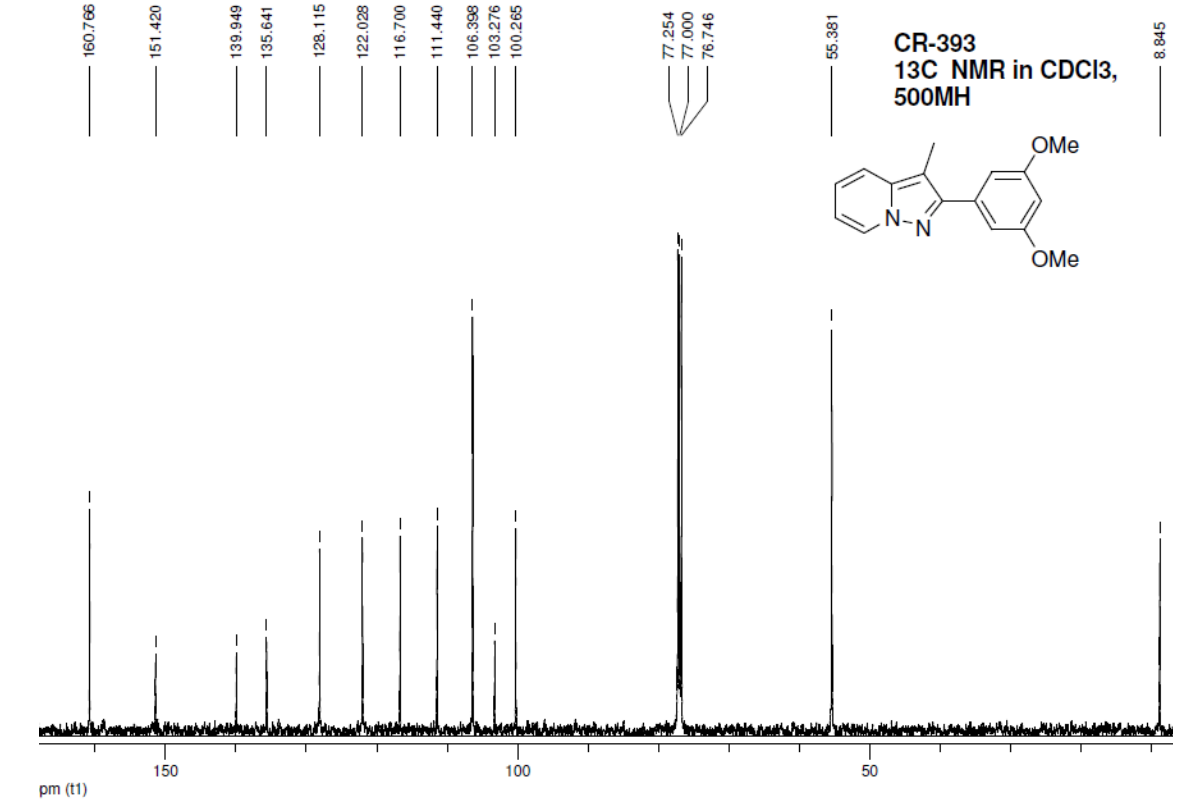
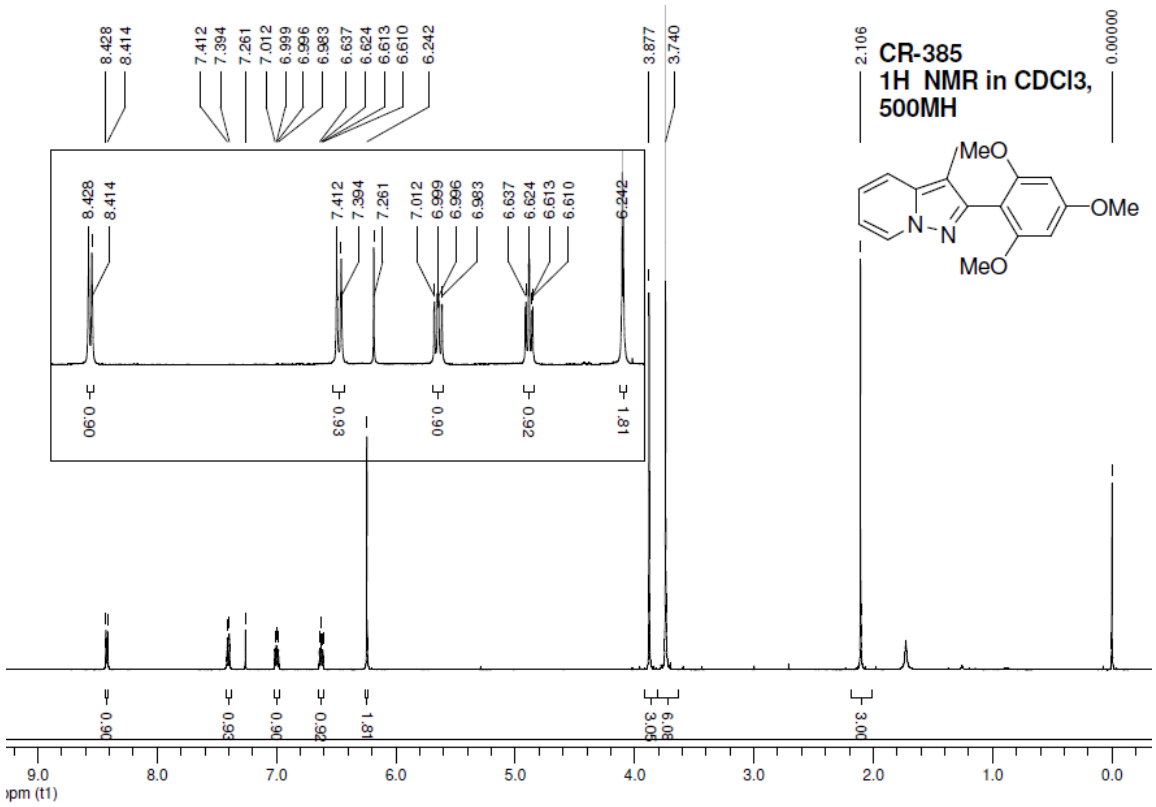



**13C NMR of 3w**

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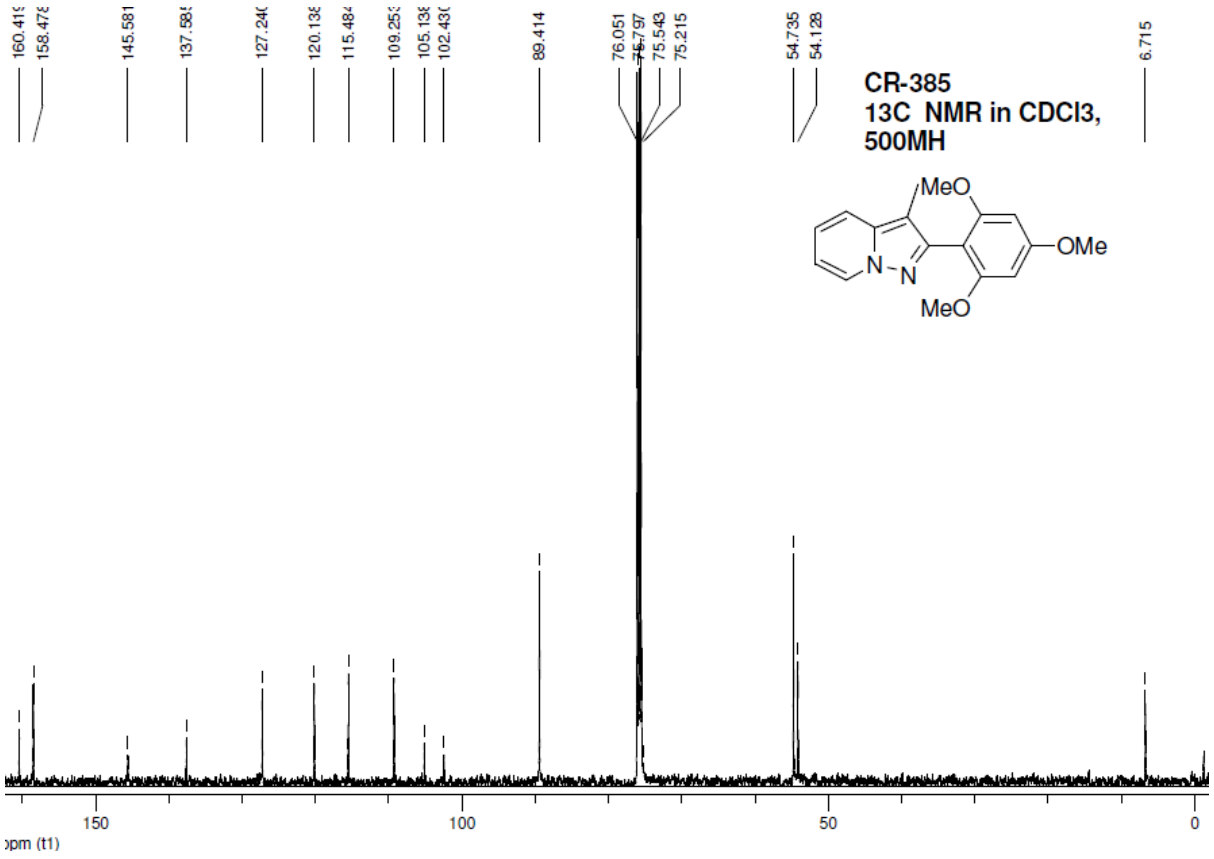


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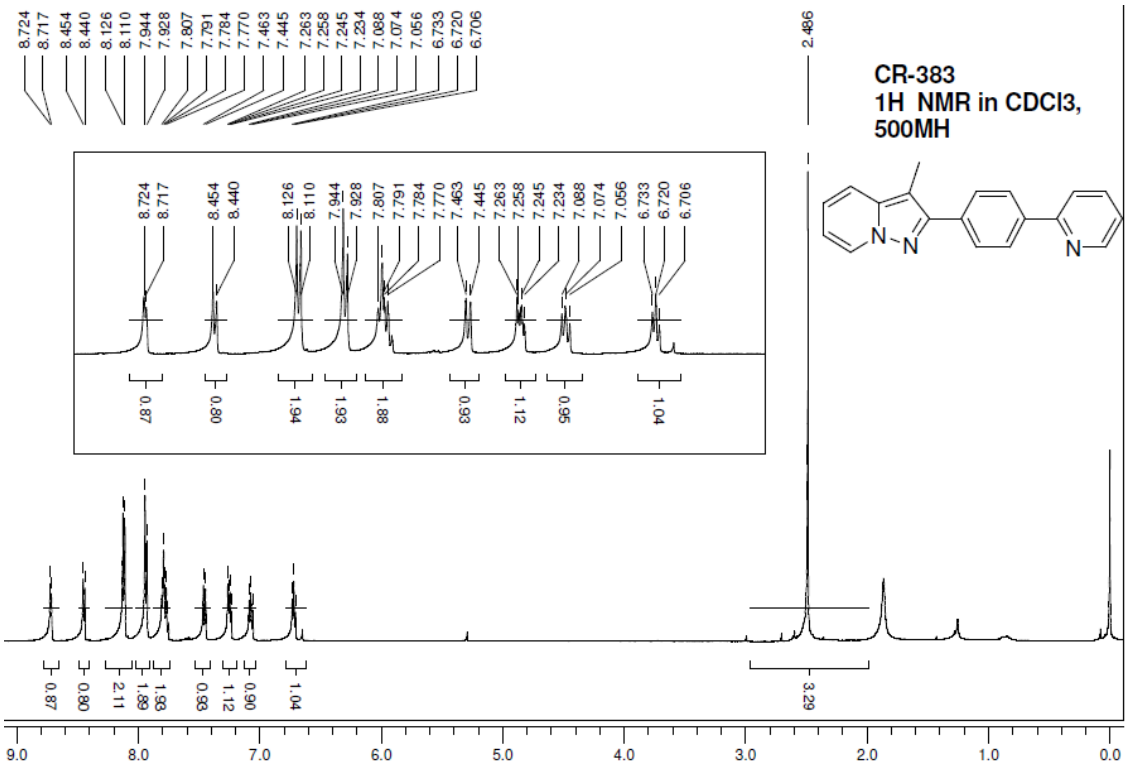


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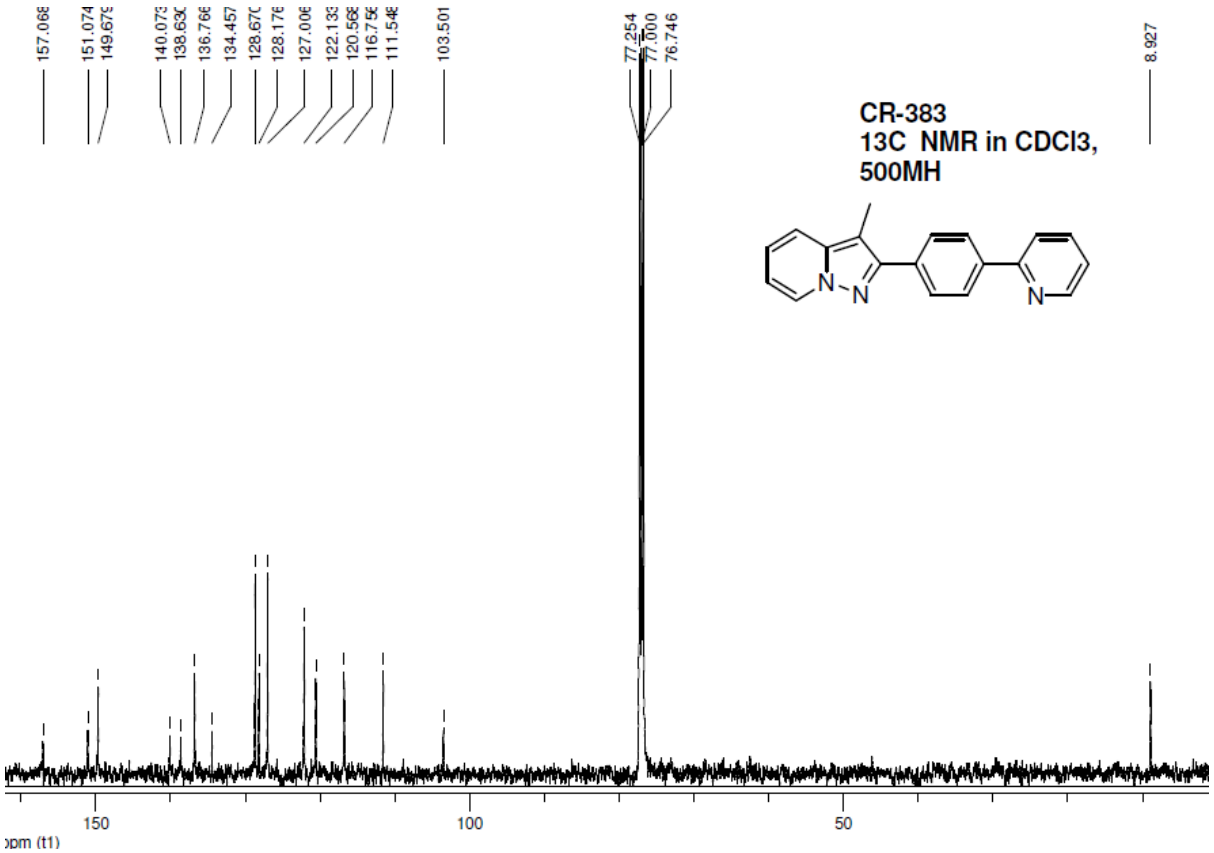


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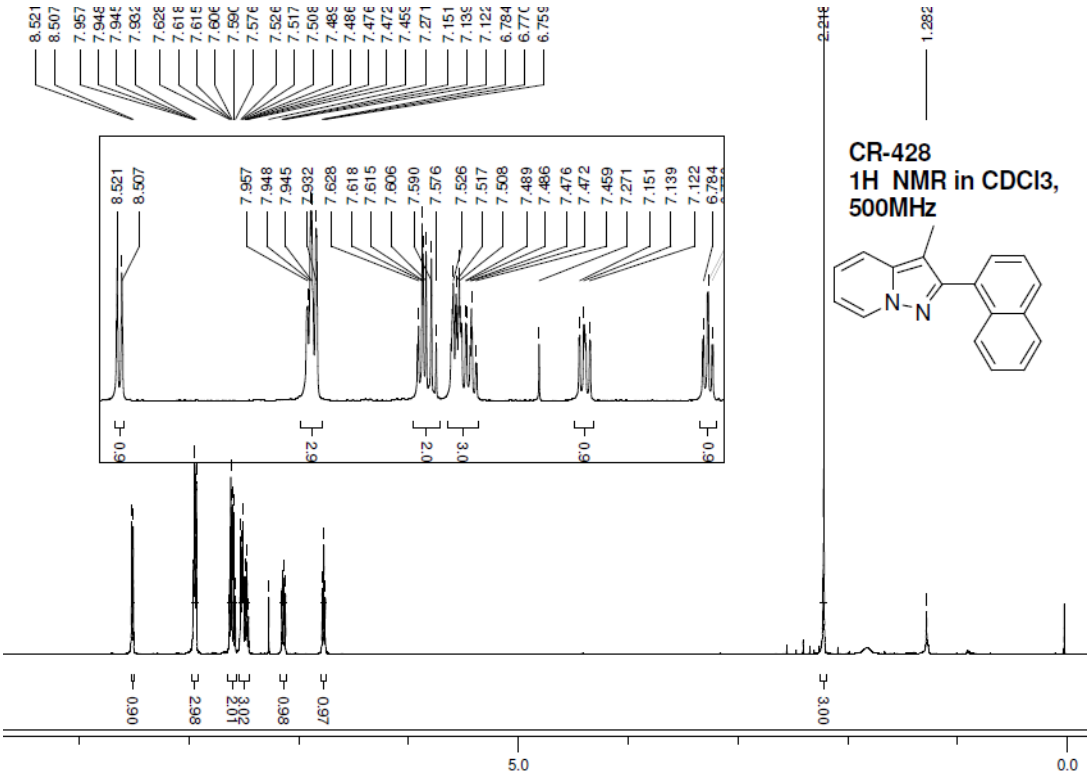


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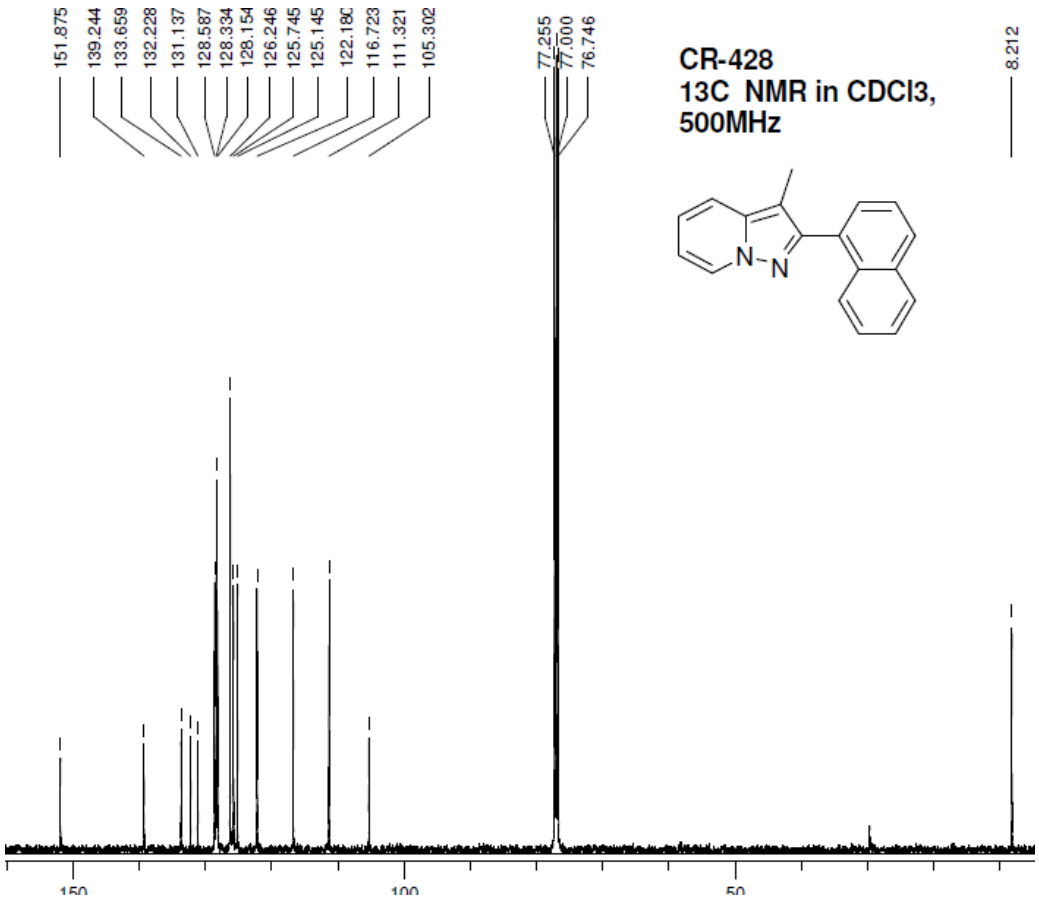


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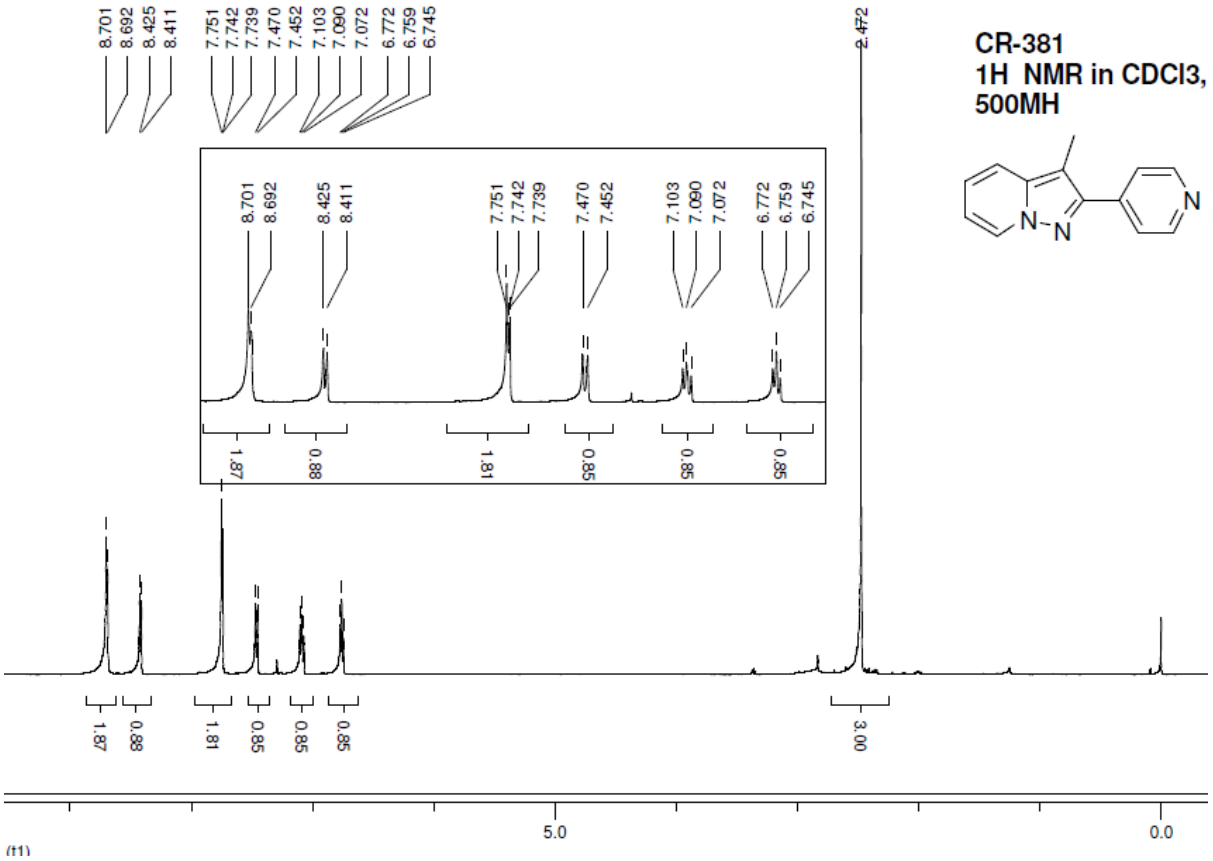


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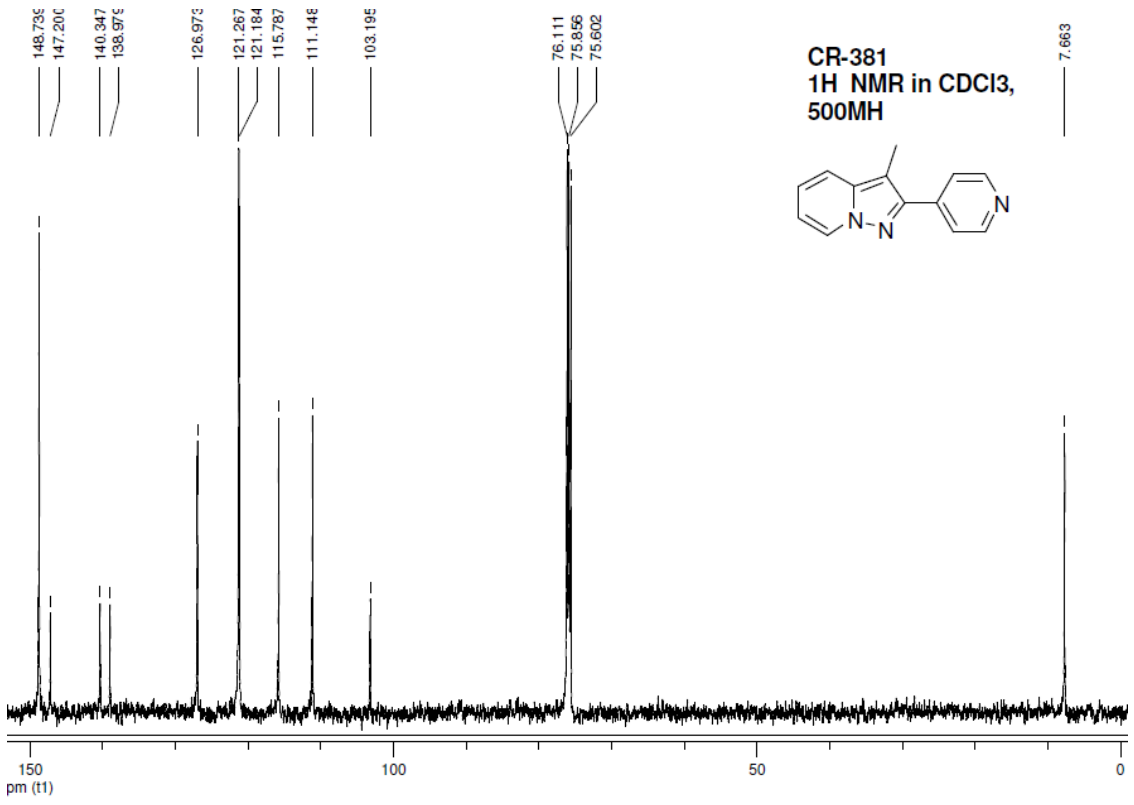
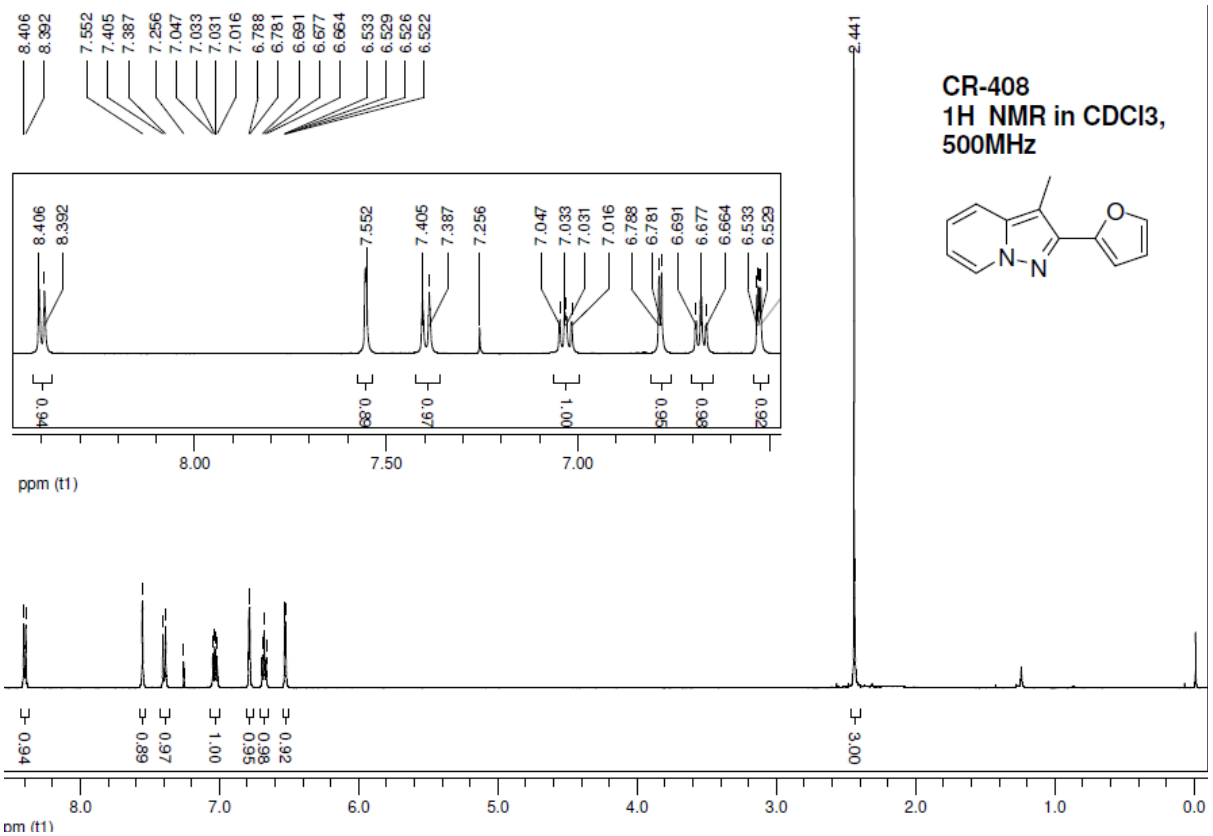



**13C NMR of 3ab**

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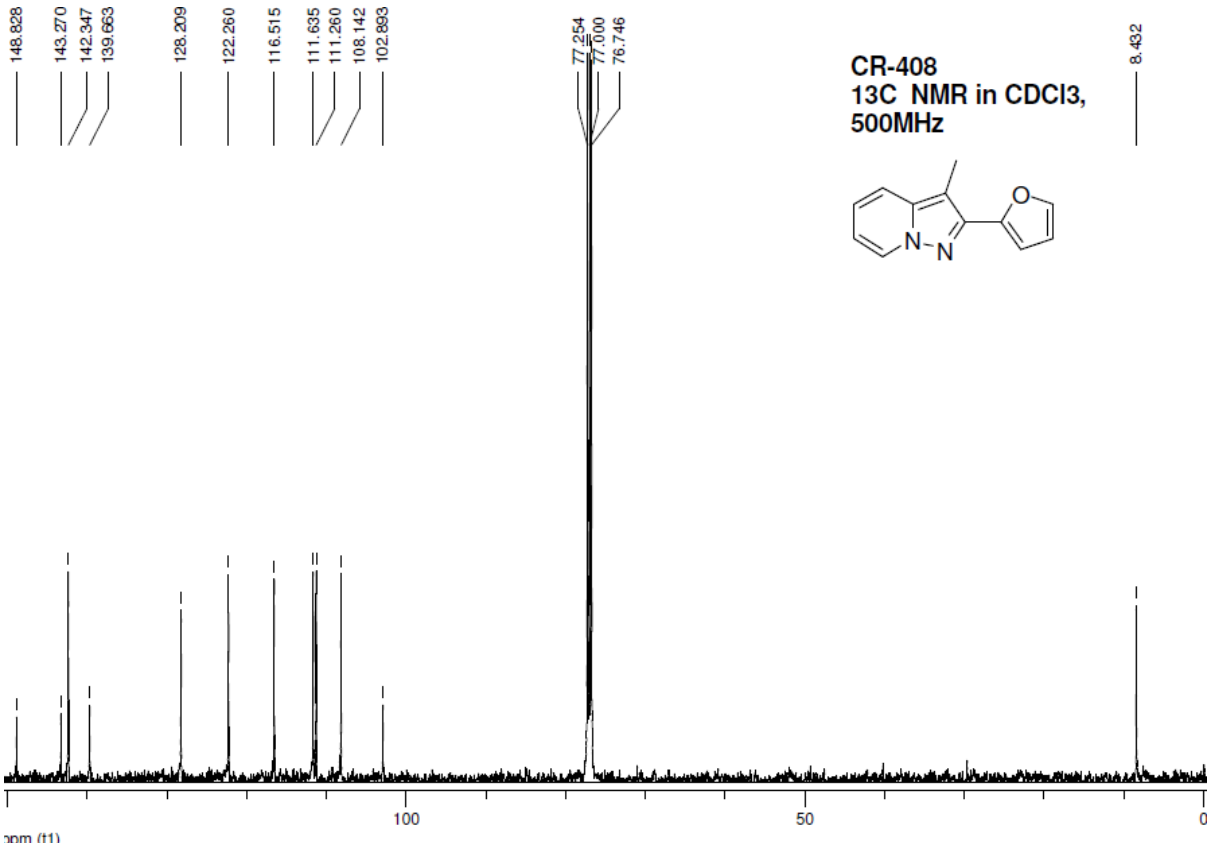


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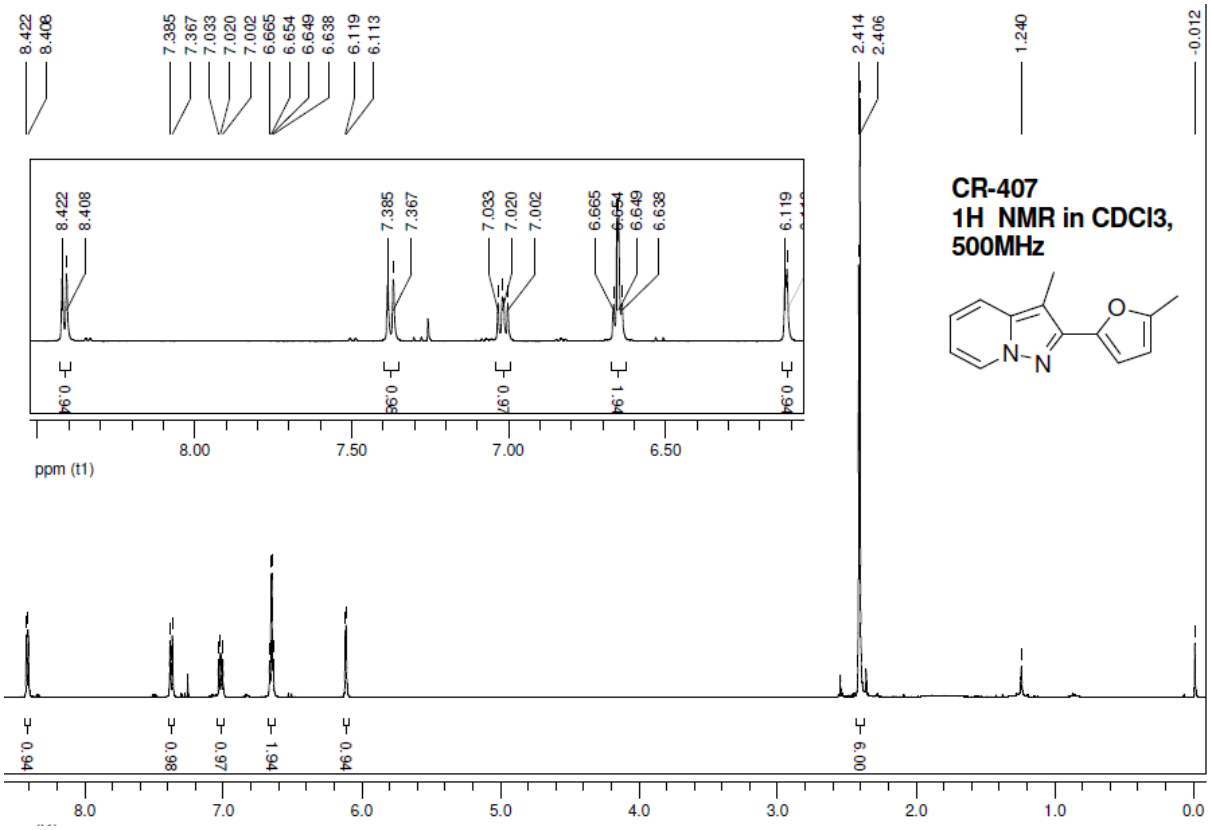


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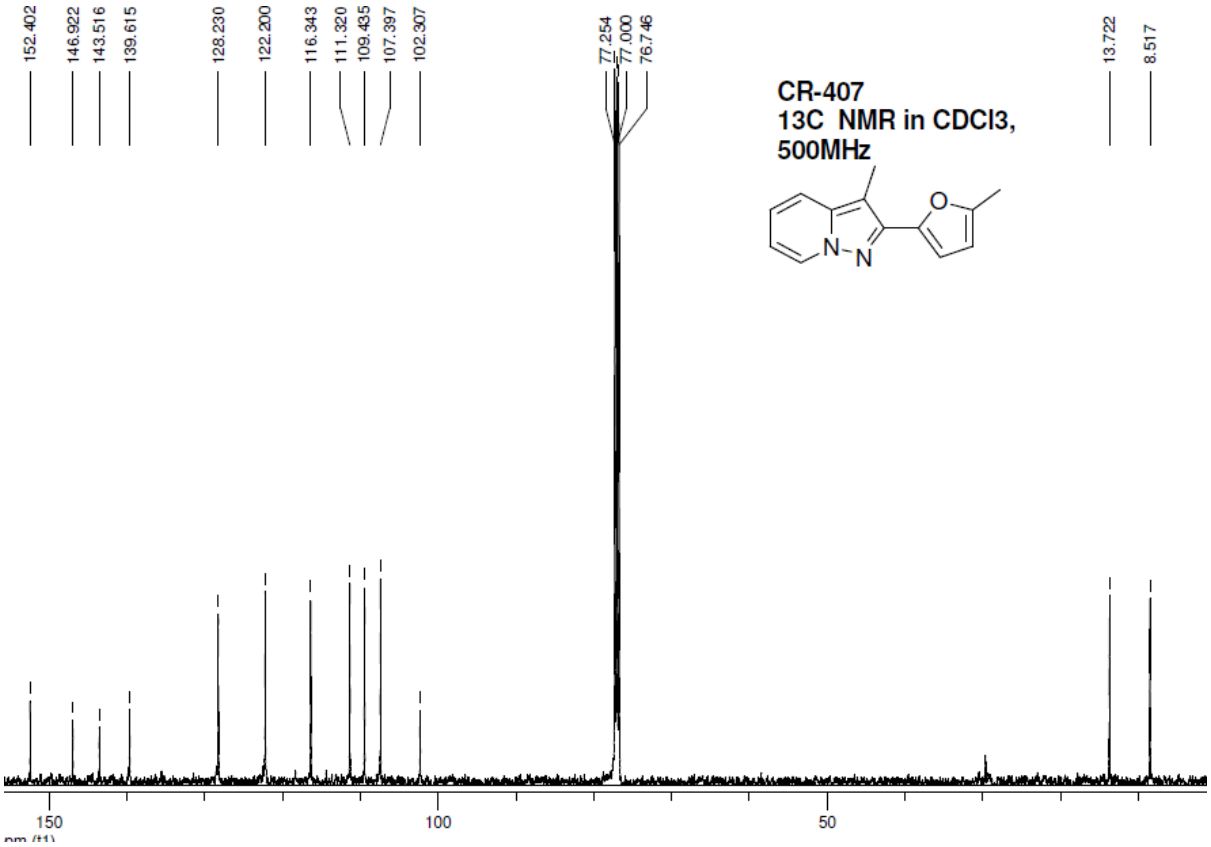


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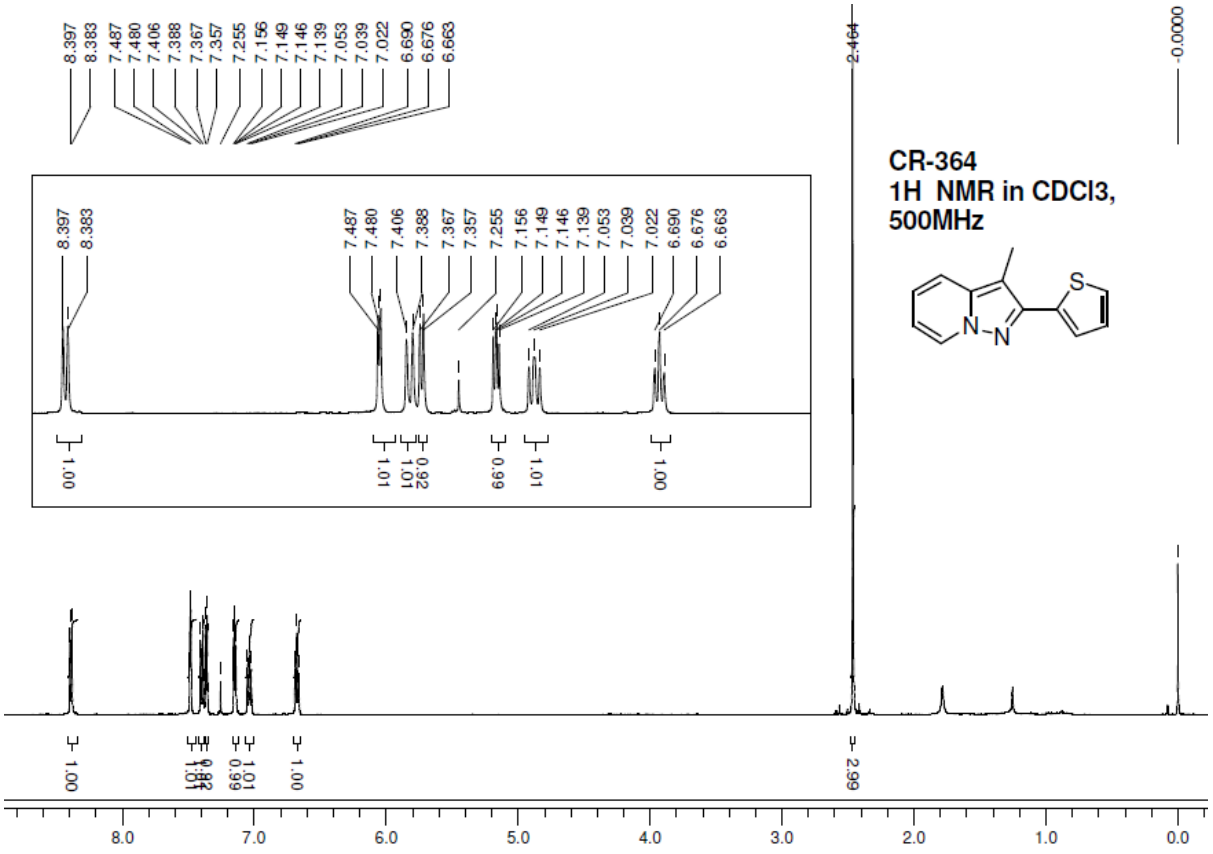


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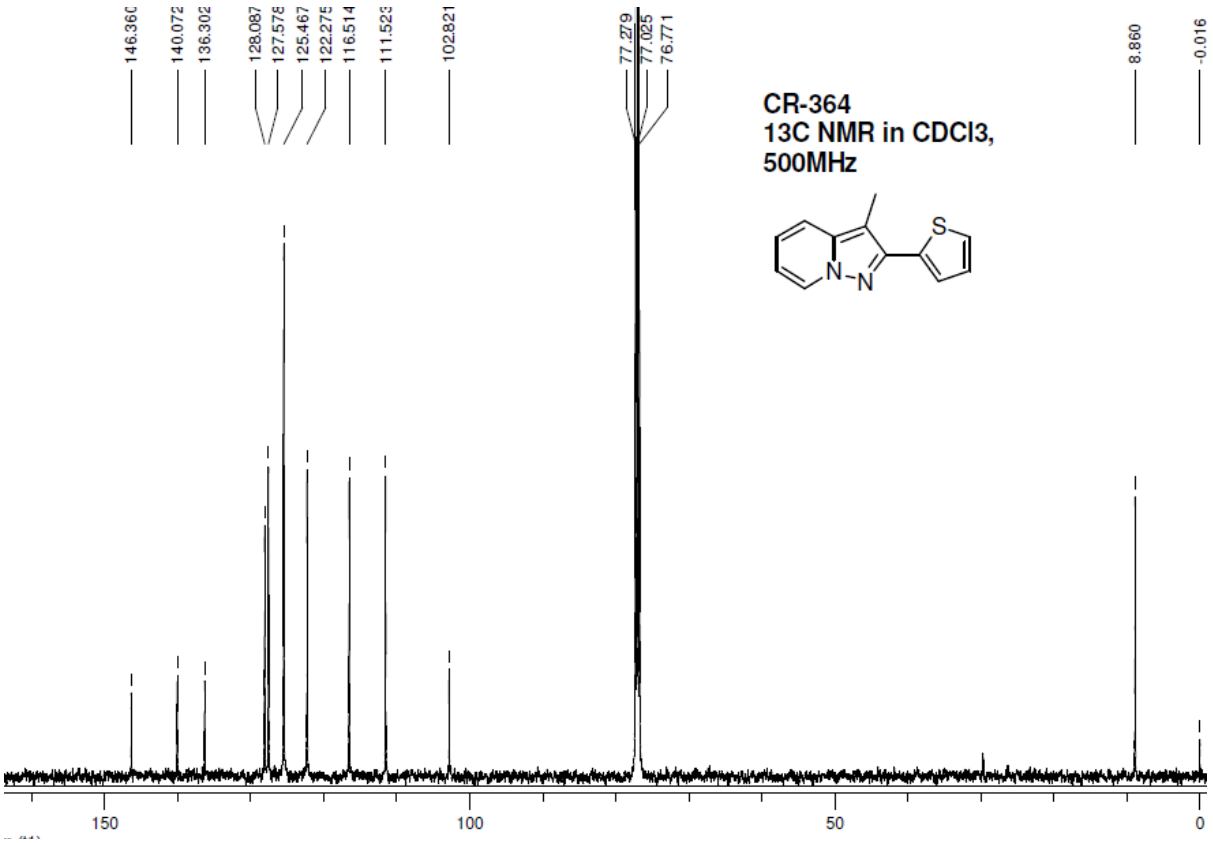


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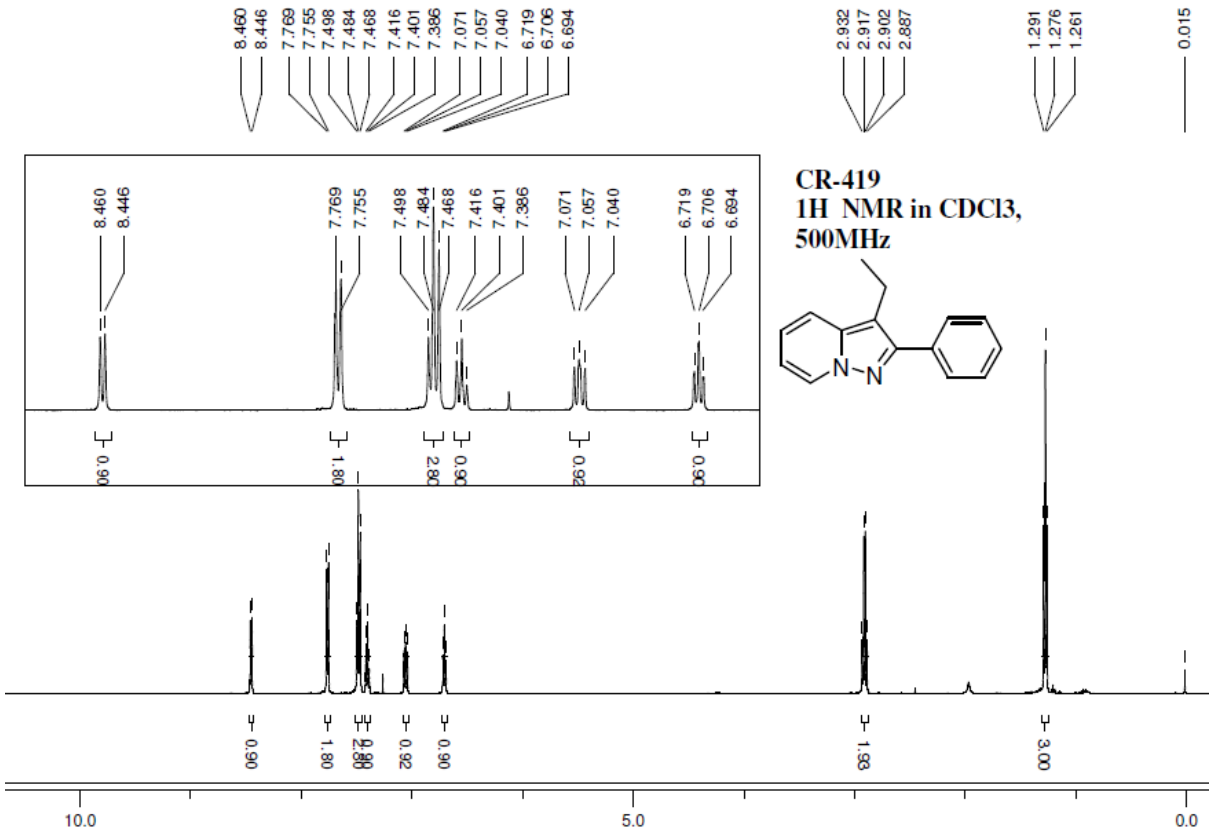


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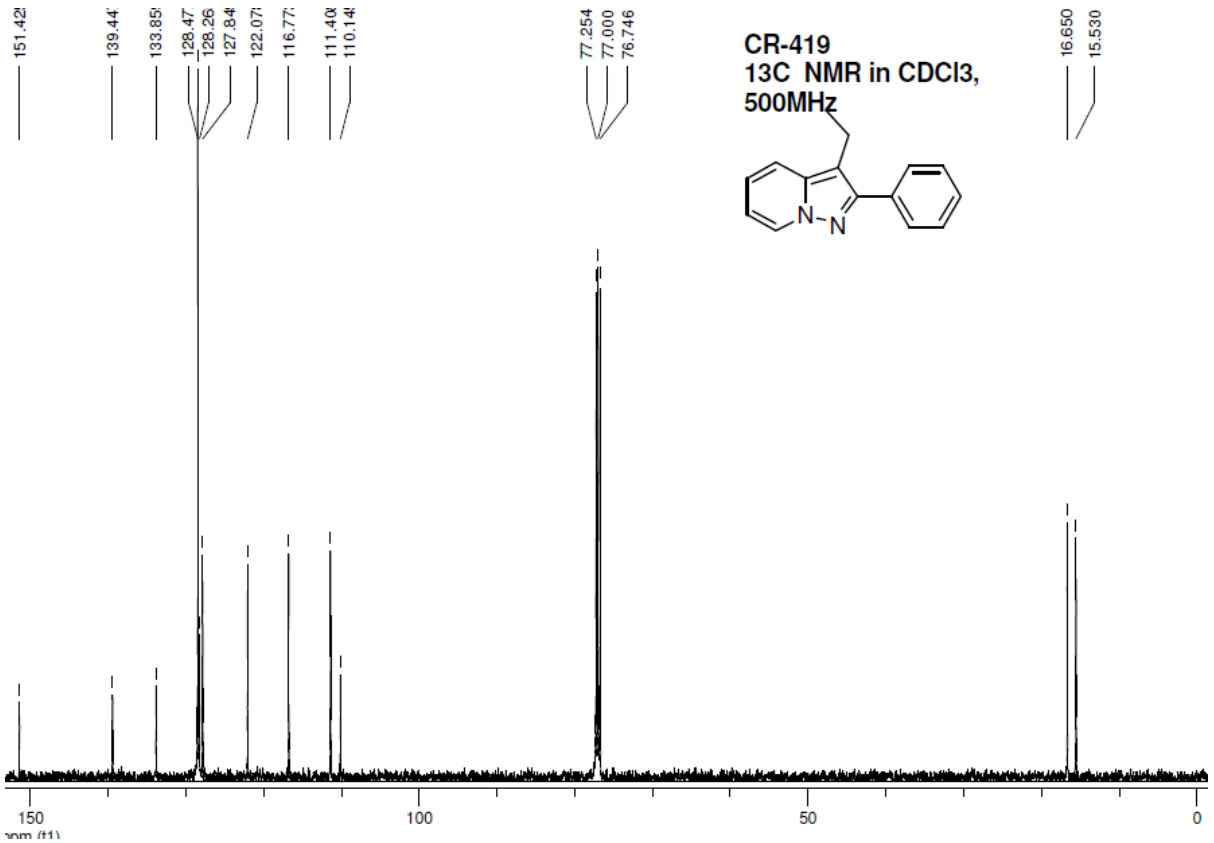


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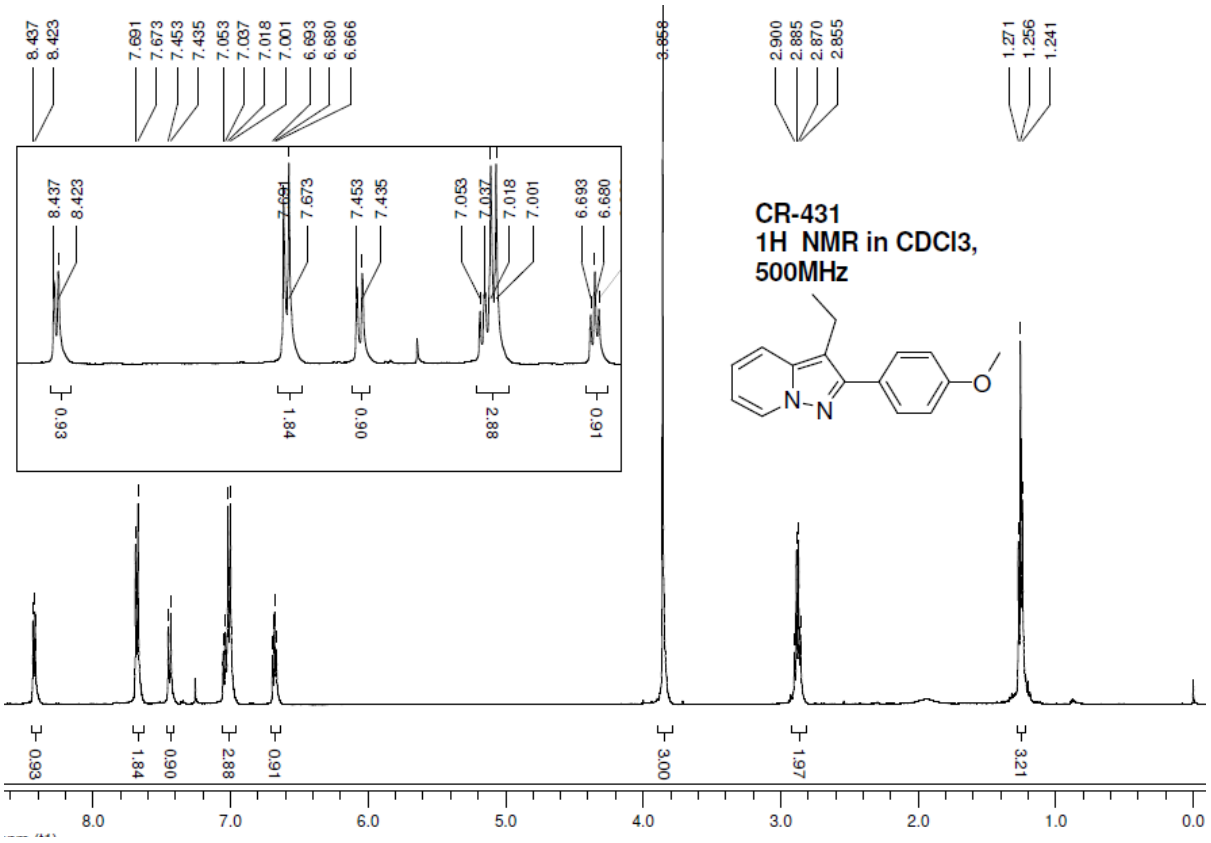
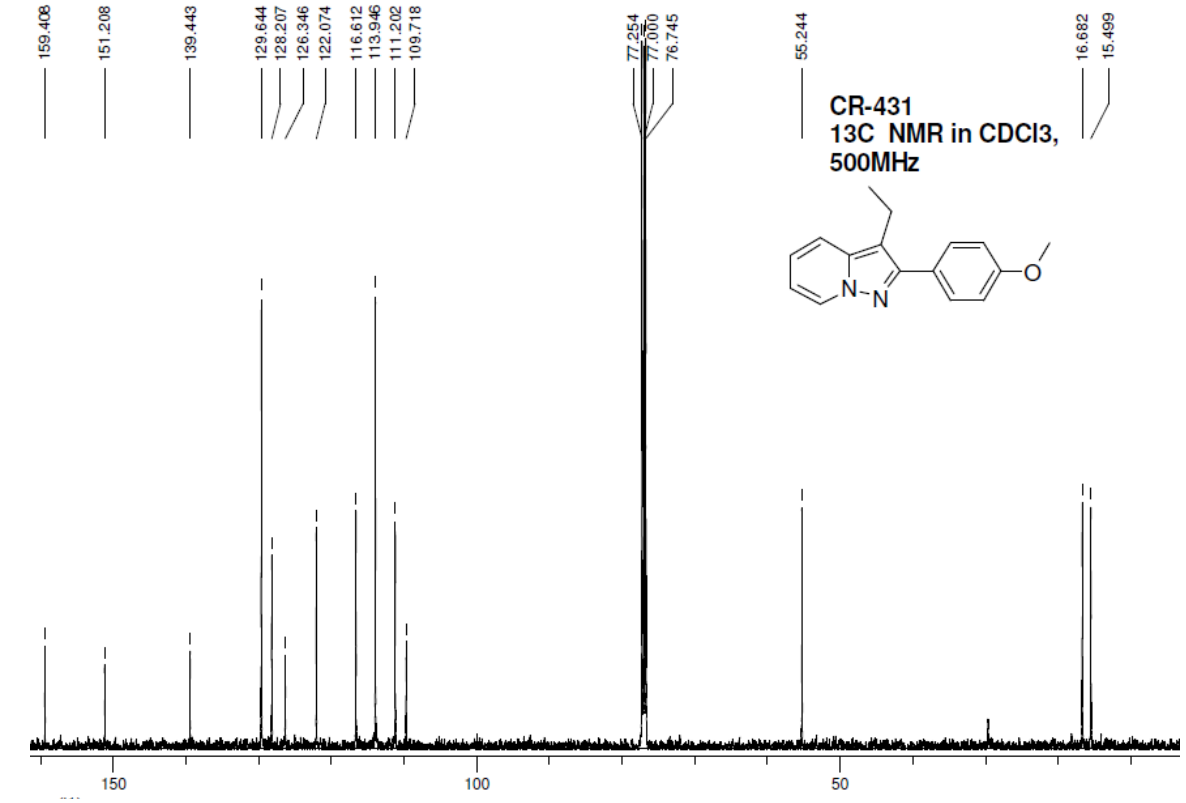
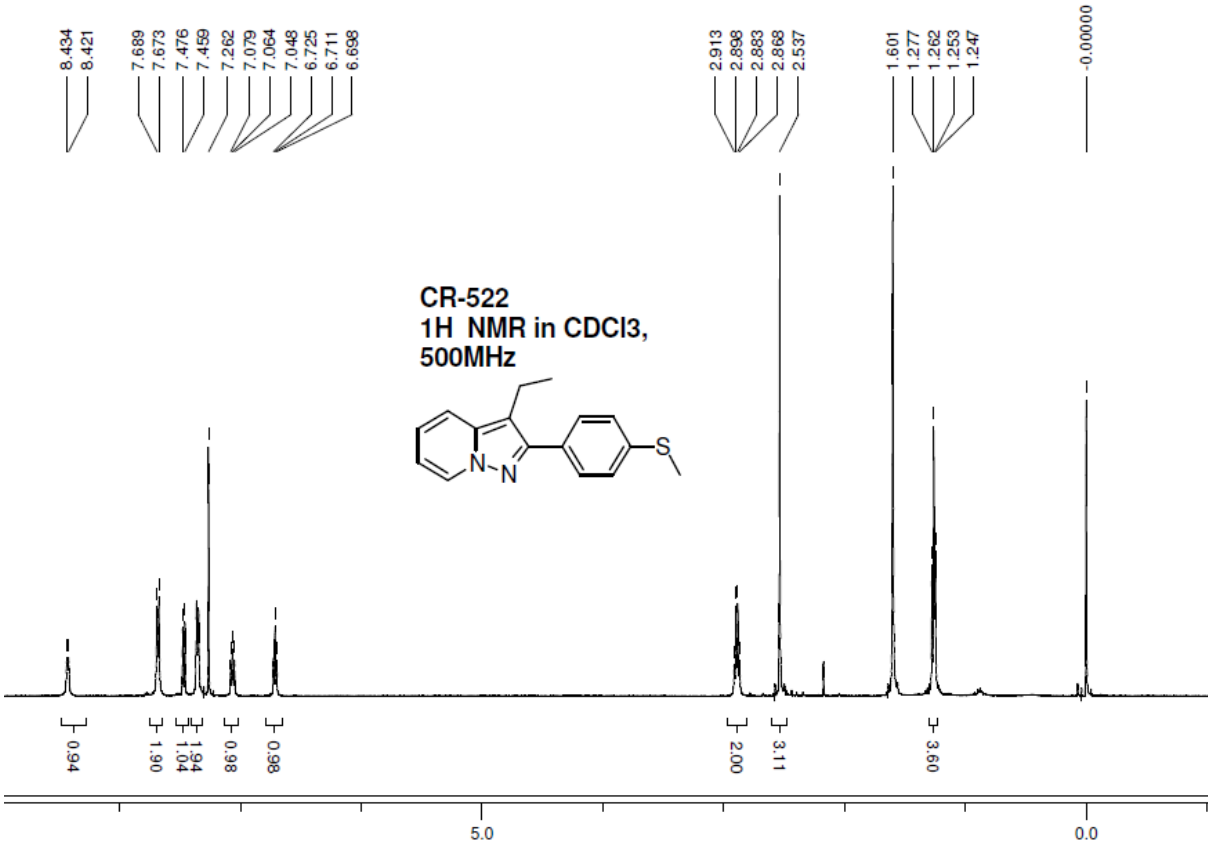



**1H NMR of 3ag**




**13C NMR of 3ag**

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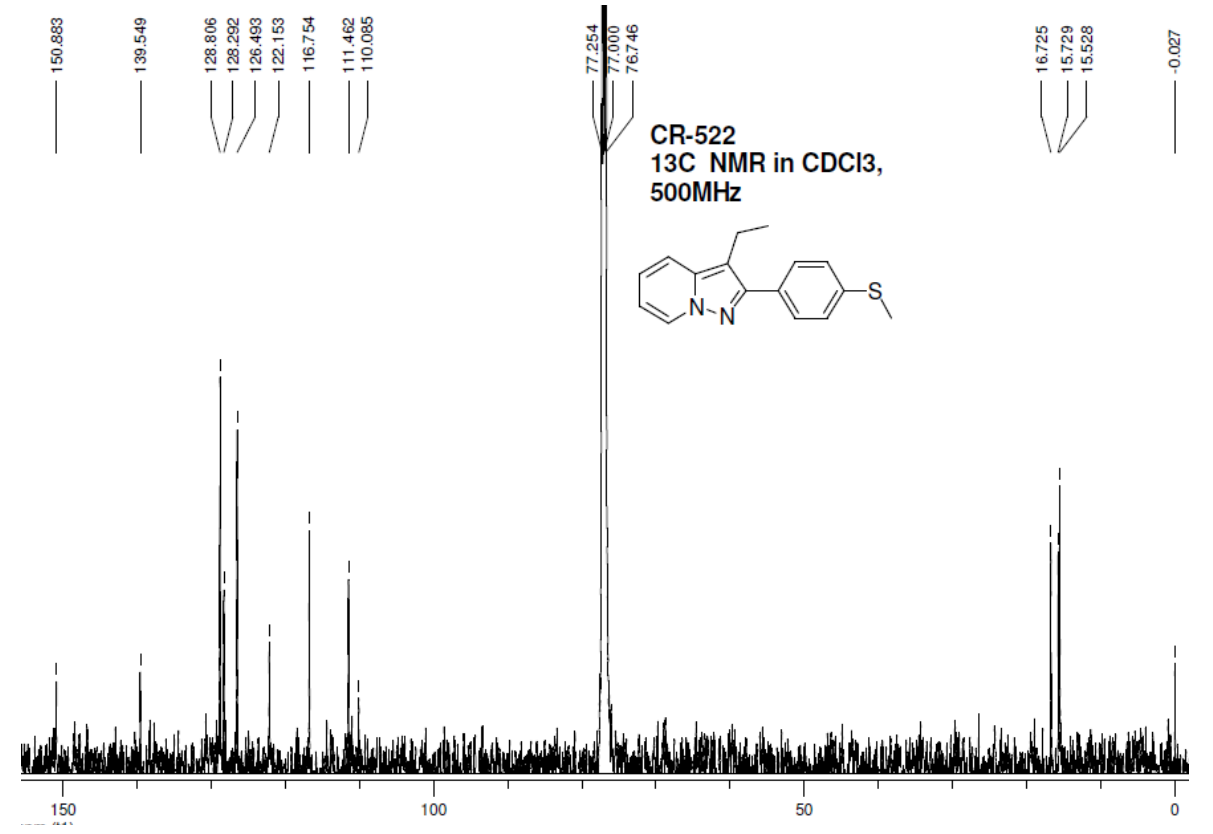


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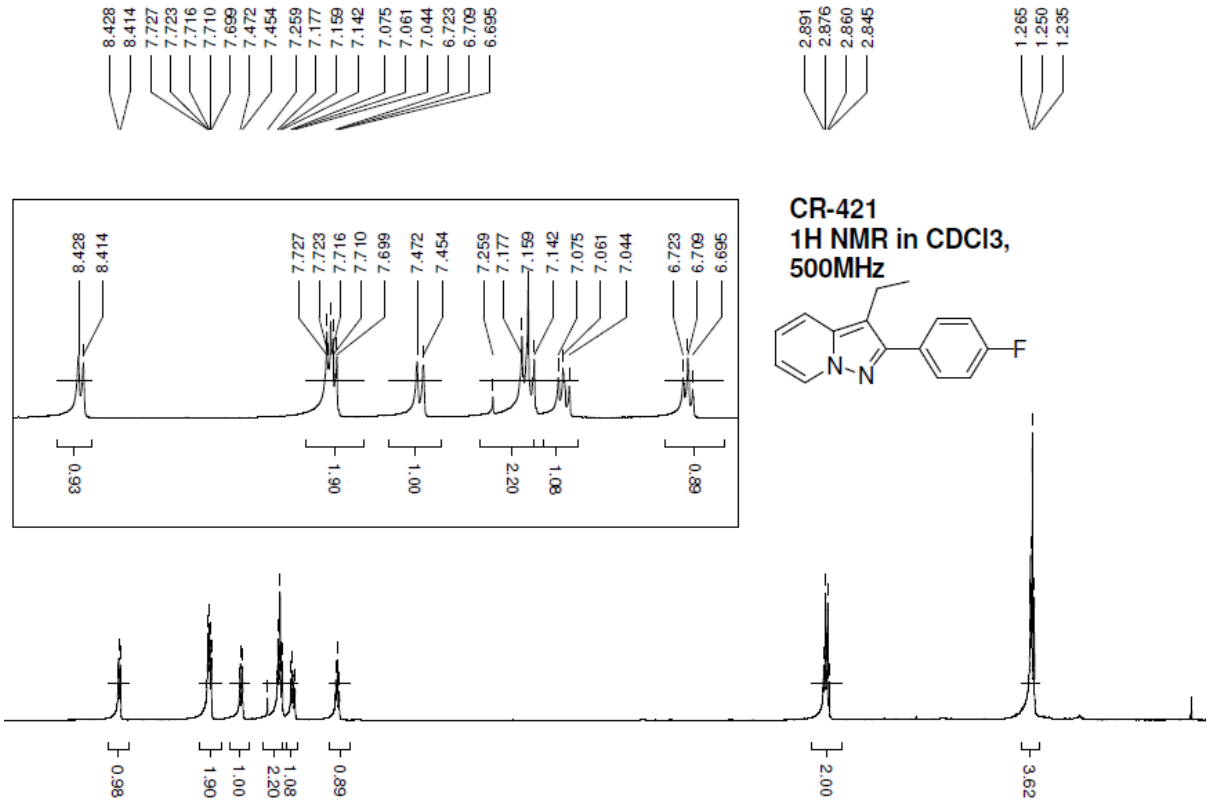


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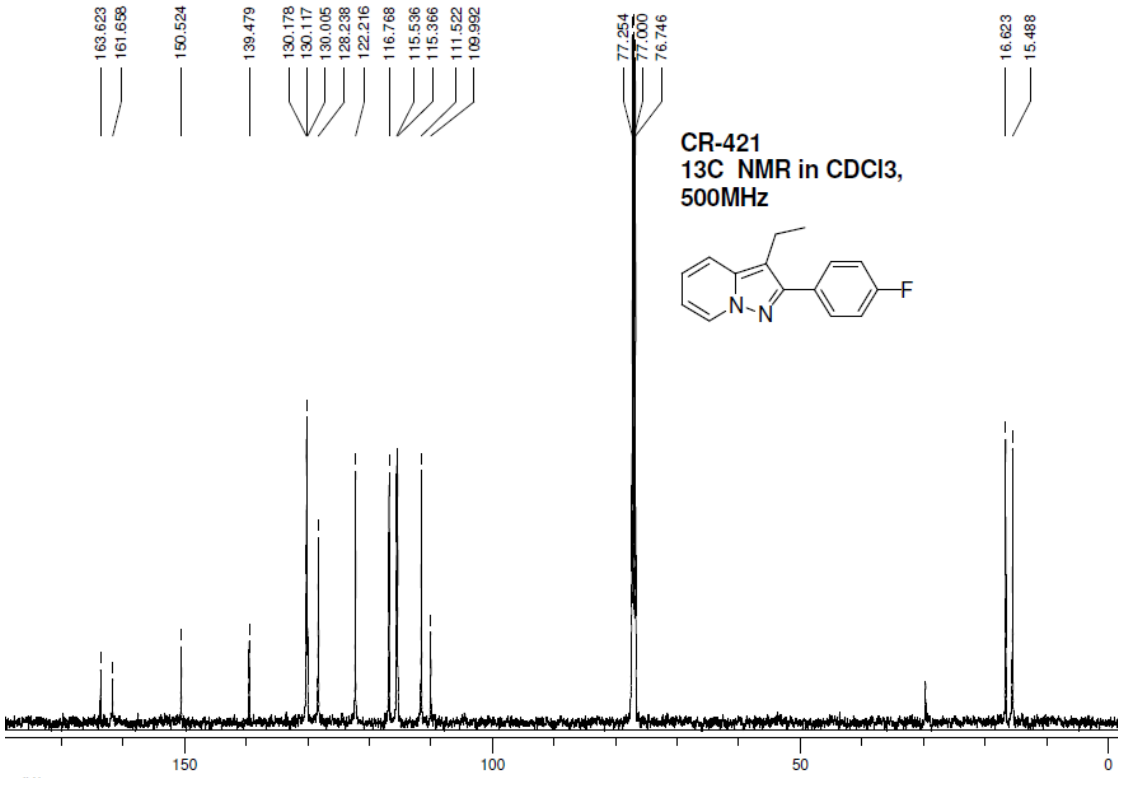


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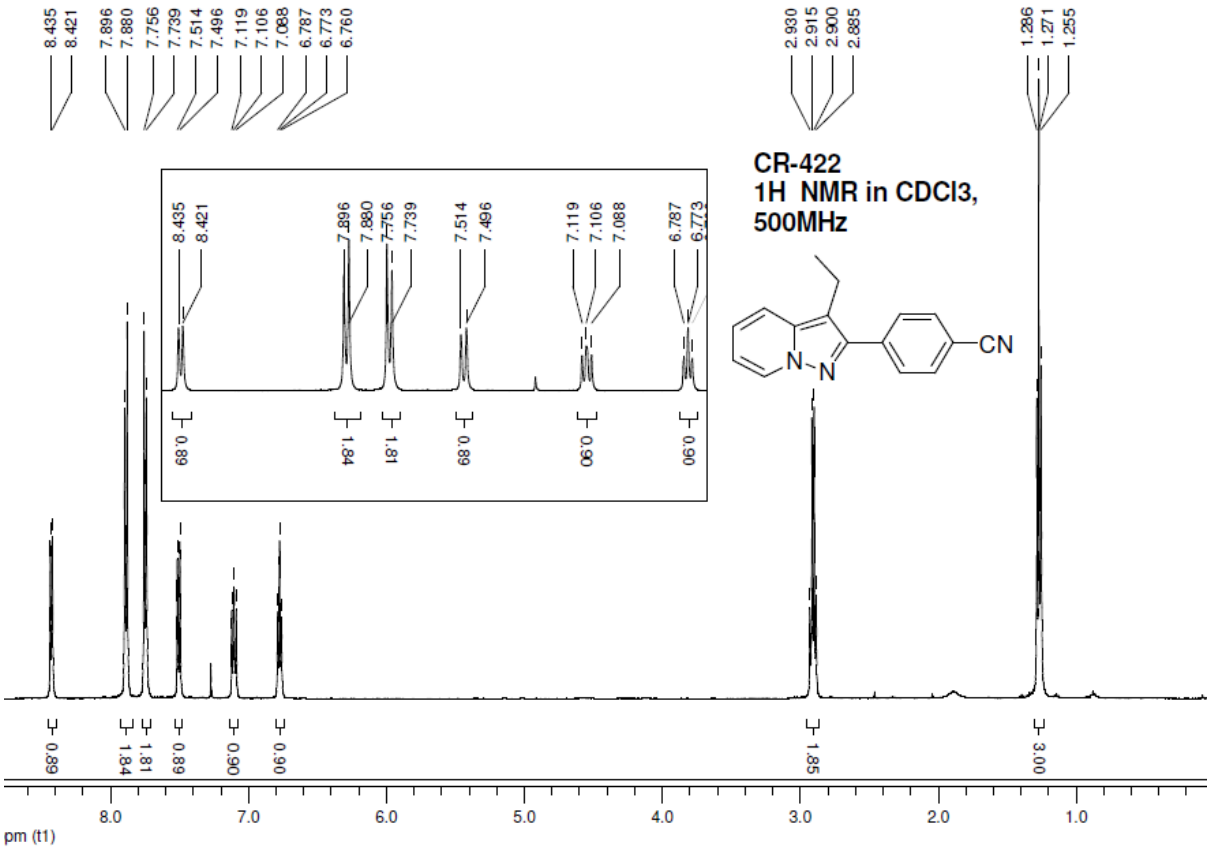


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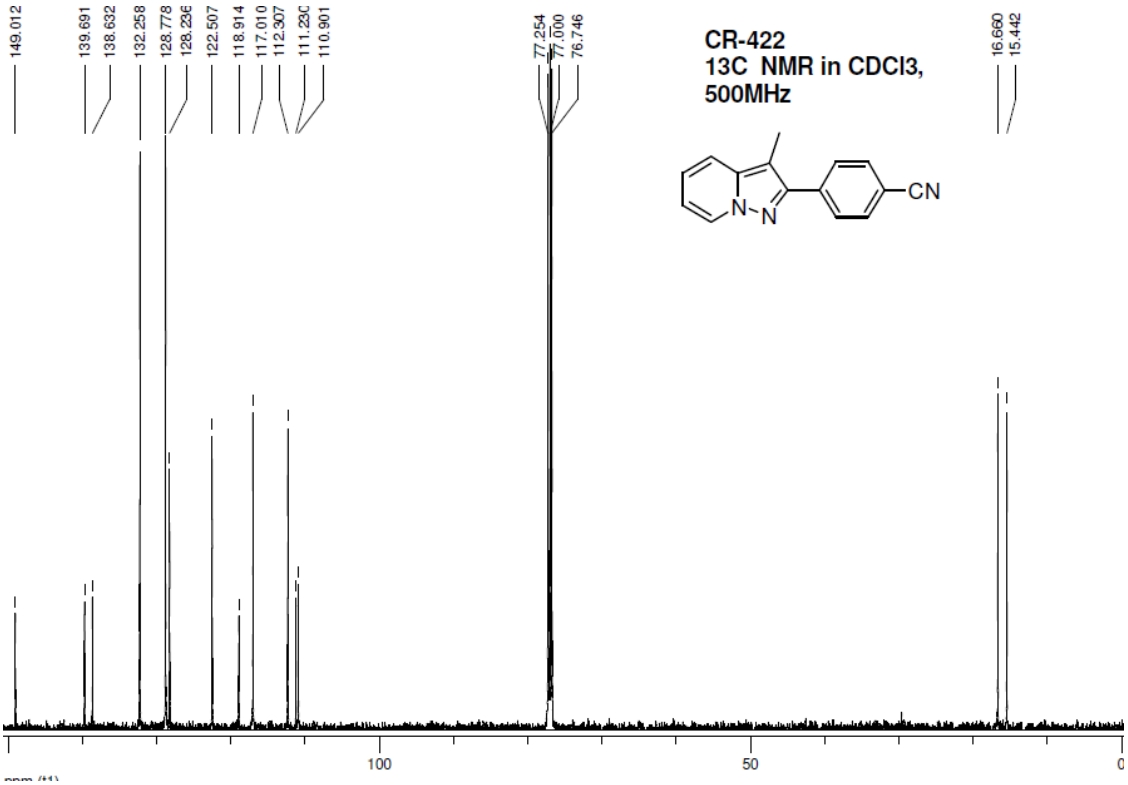


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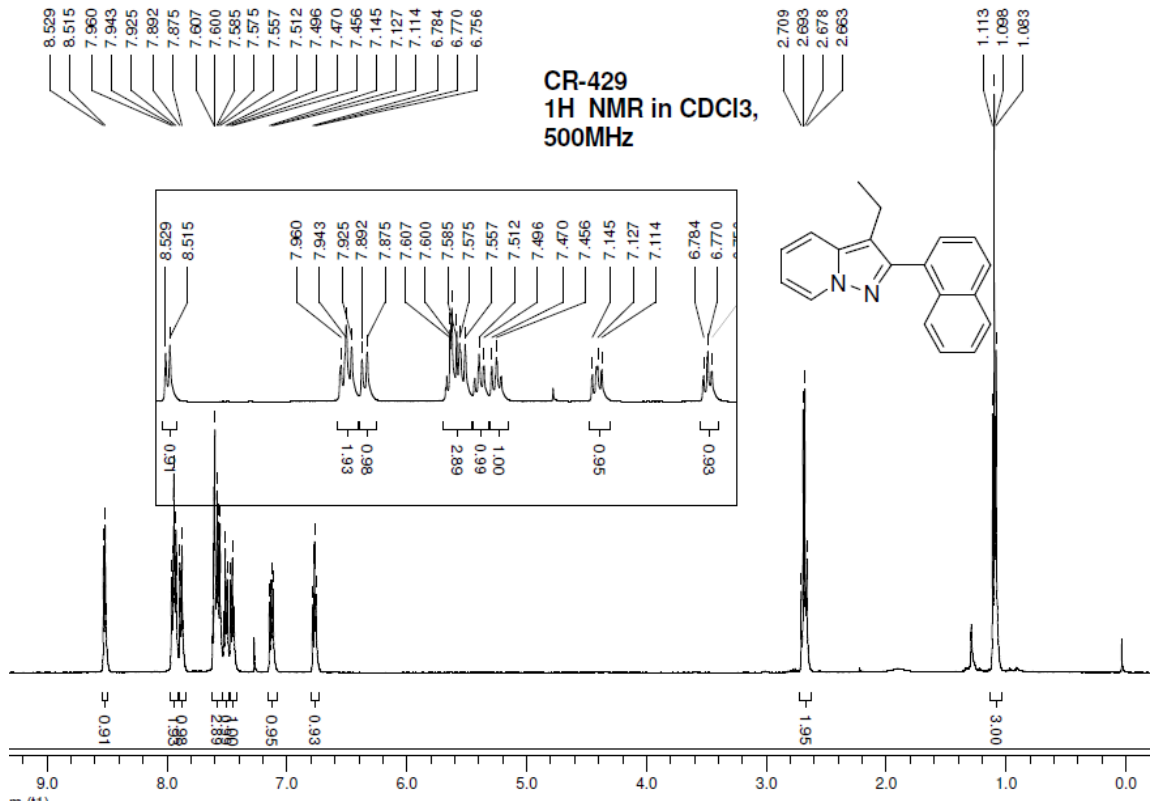


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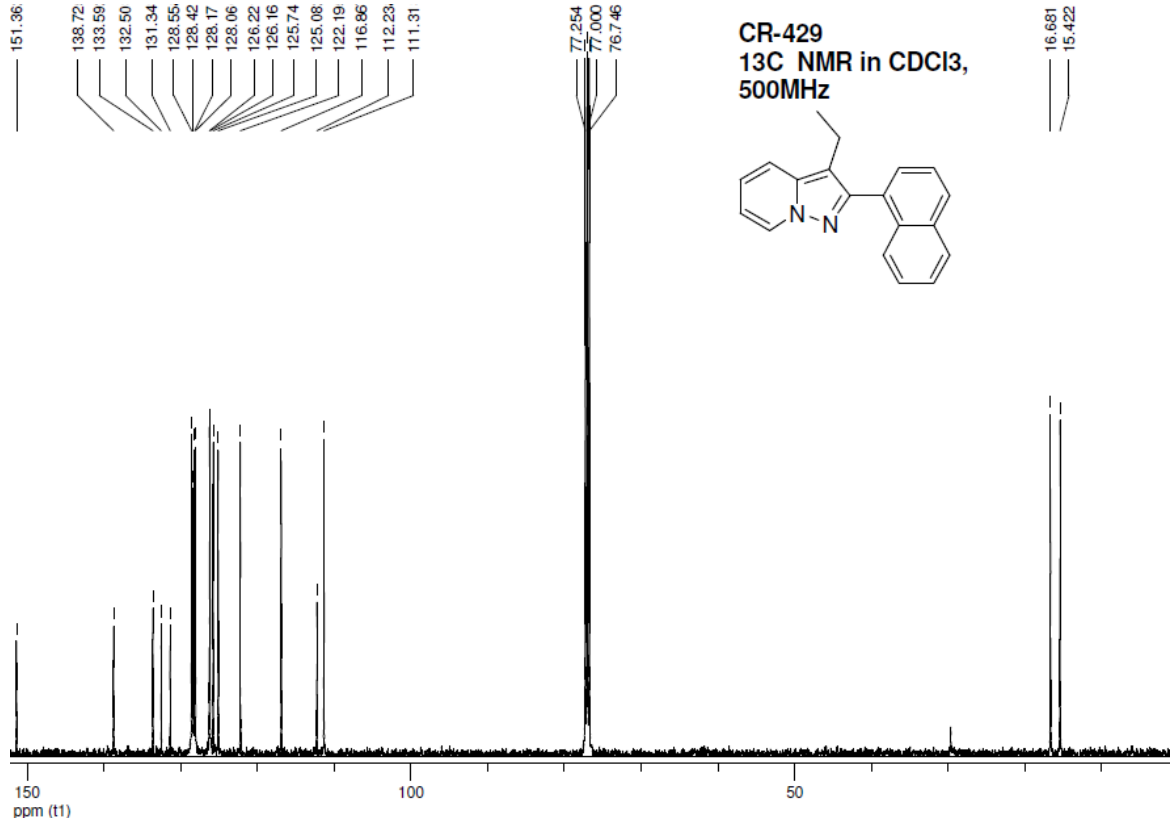


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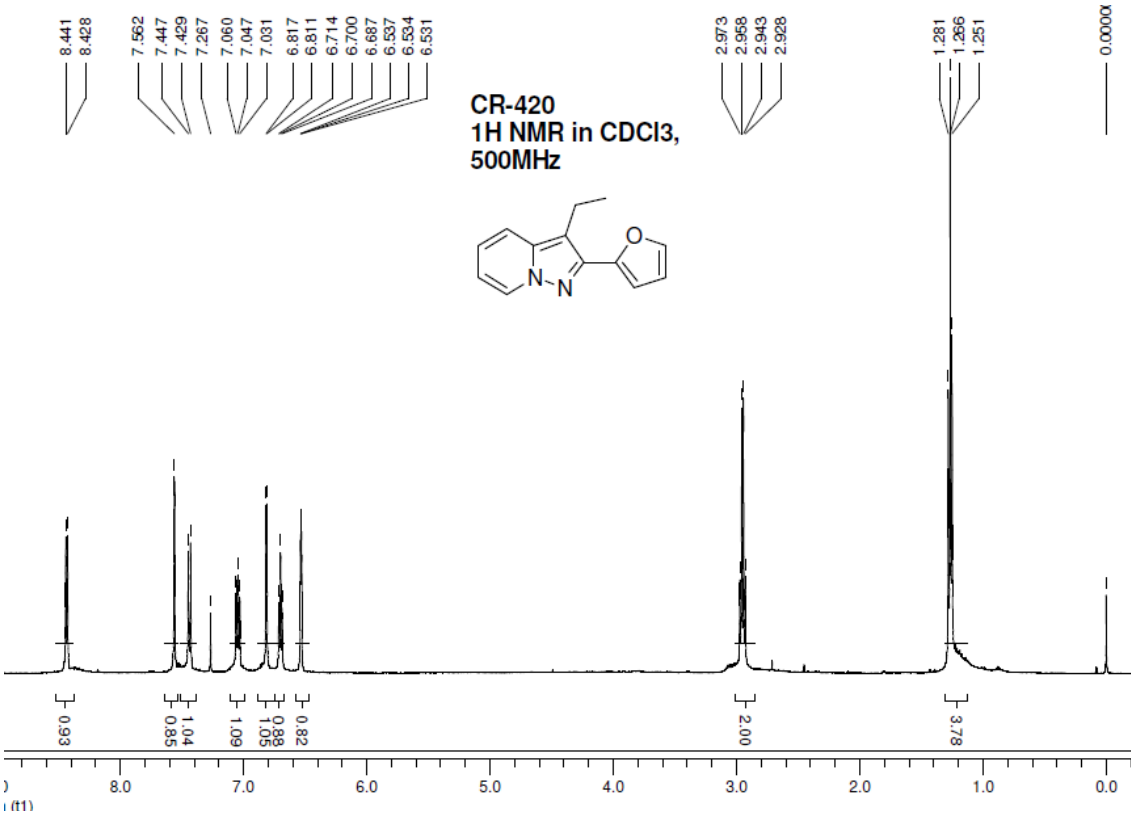


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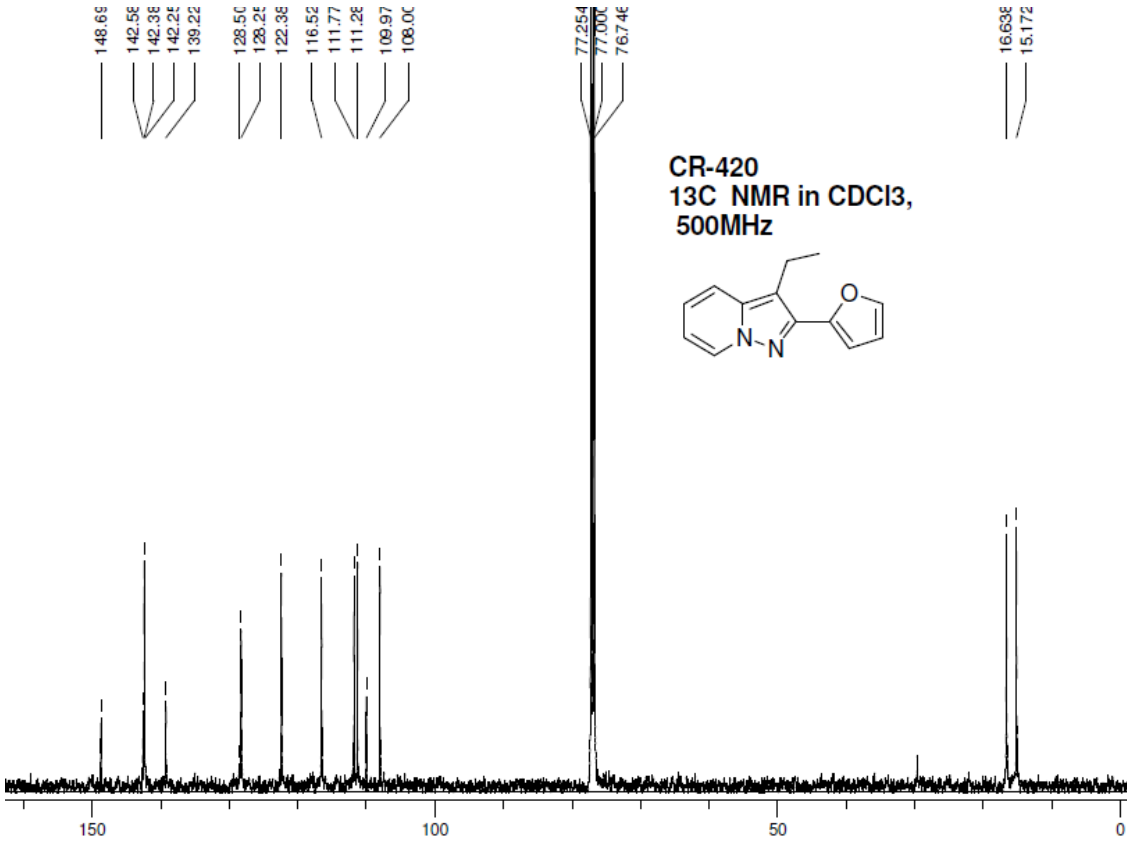


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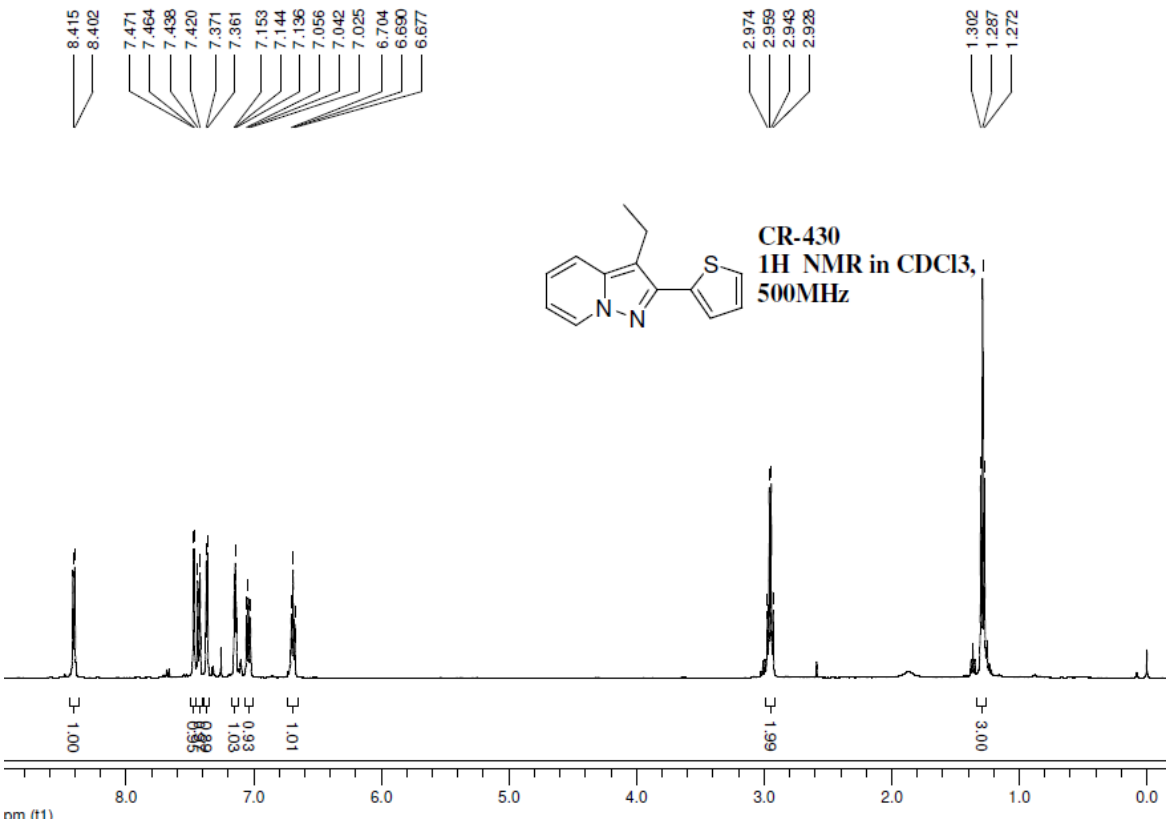


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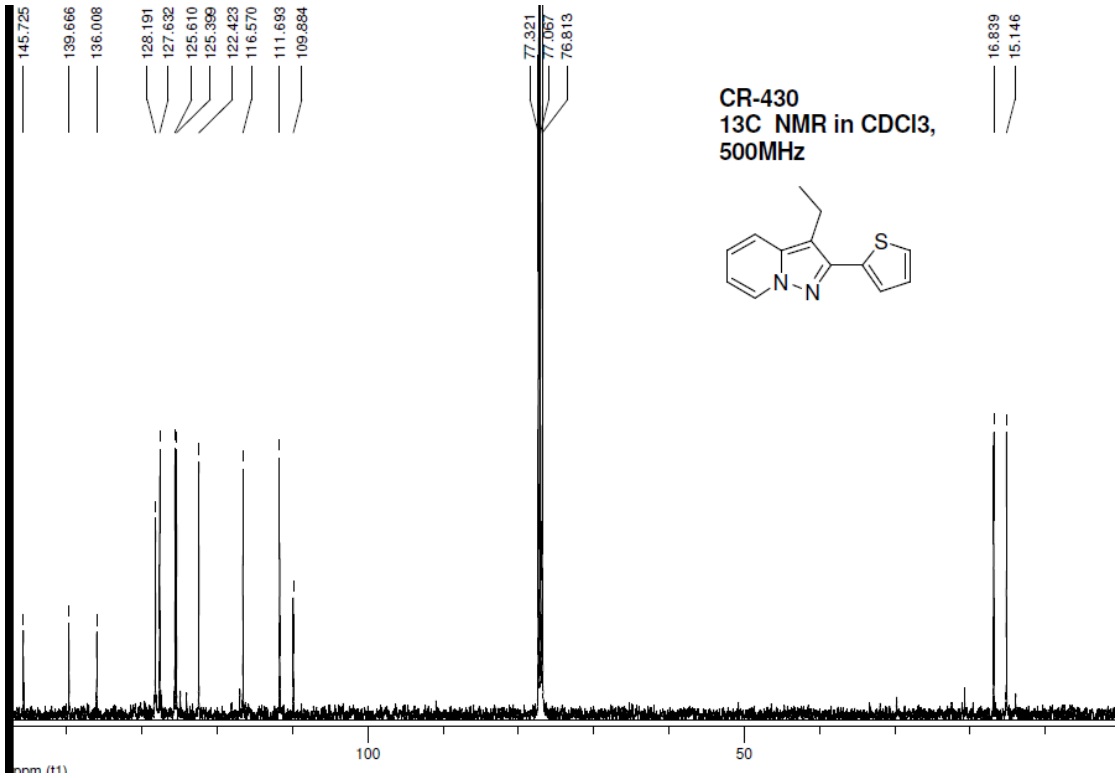
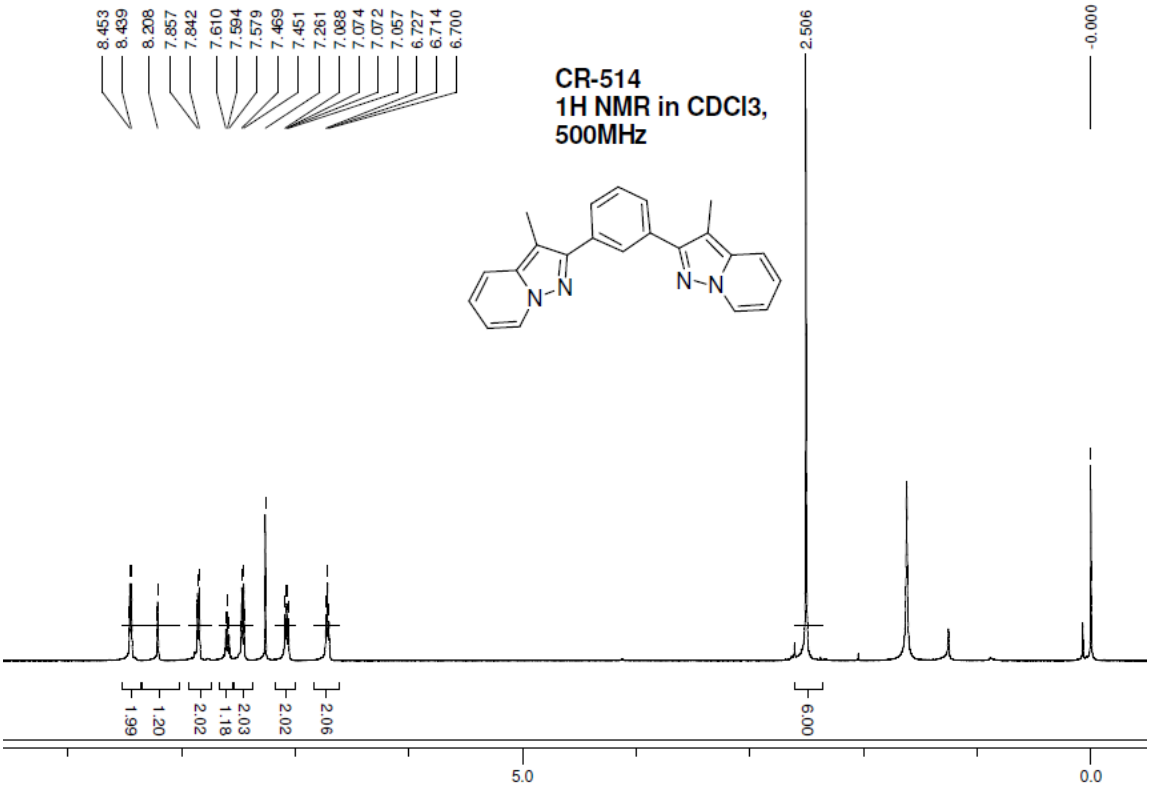
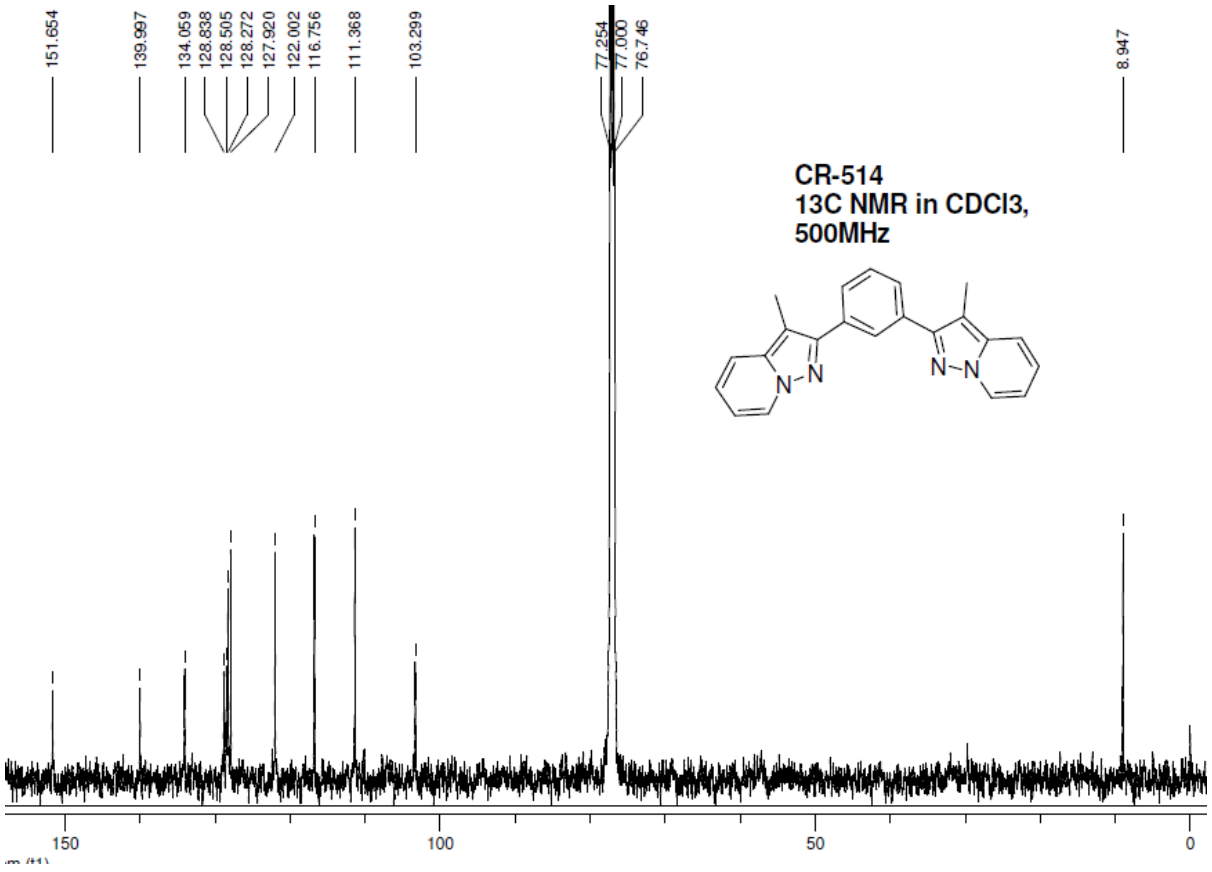


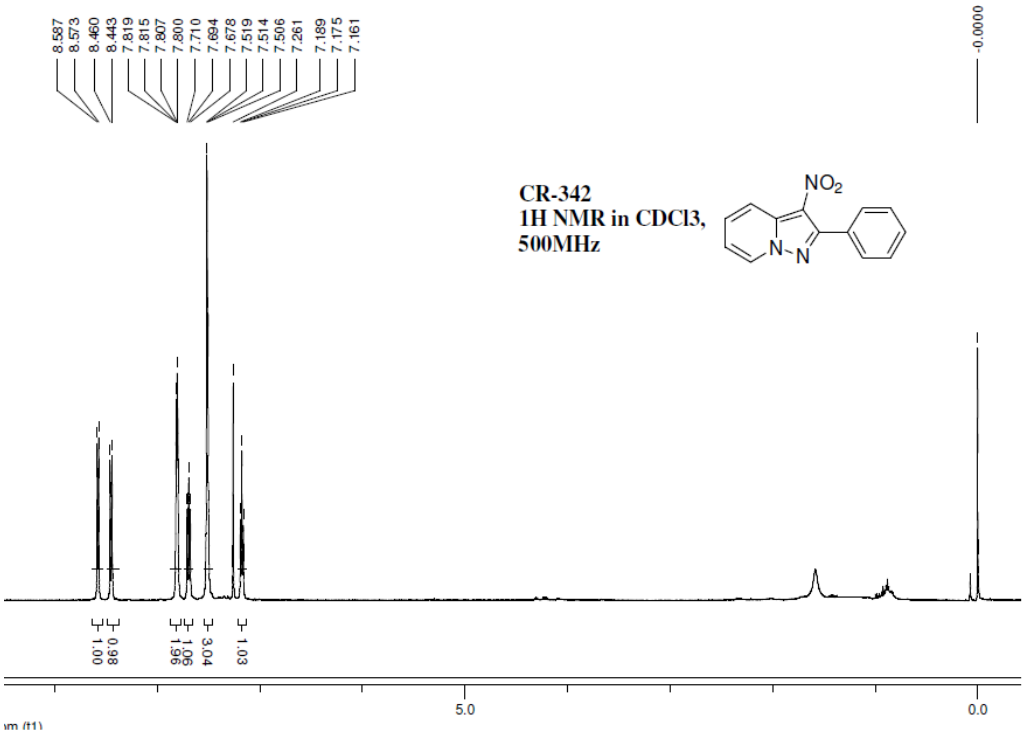

**13C NMR of 3am**



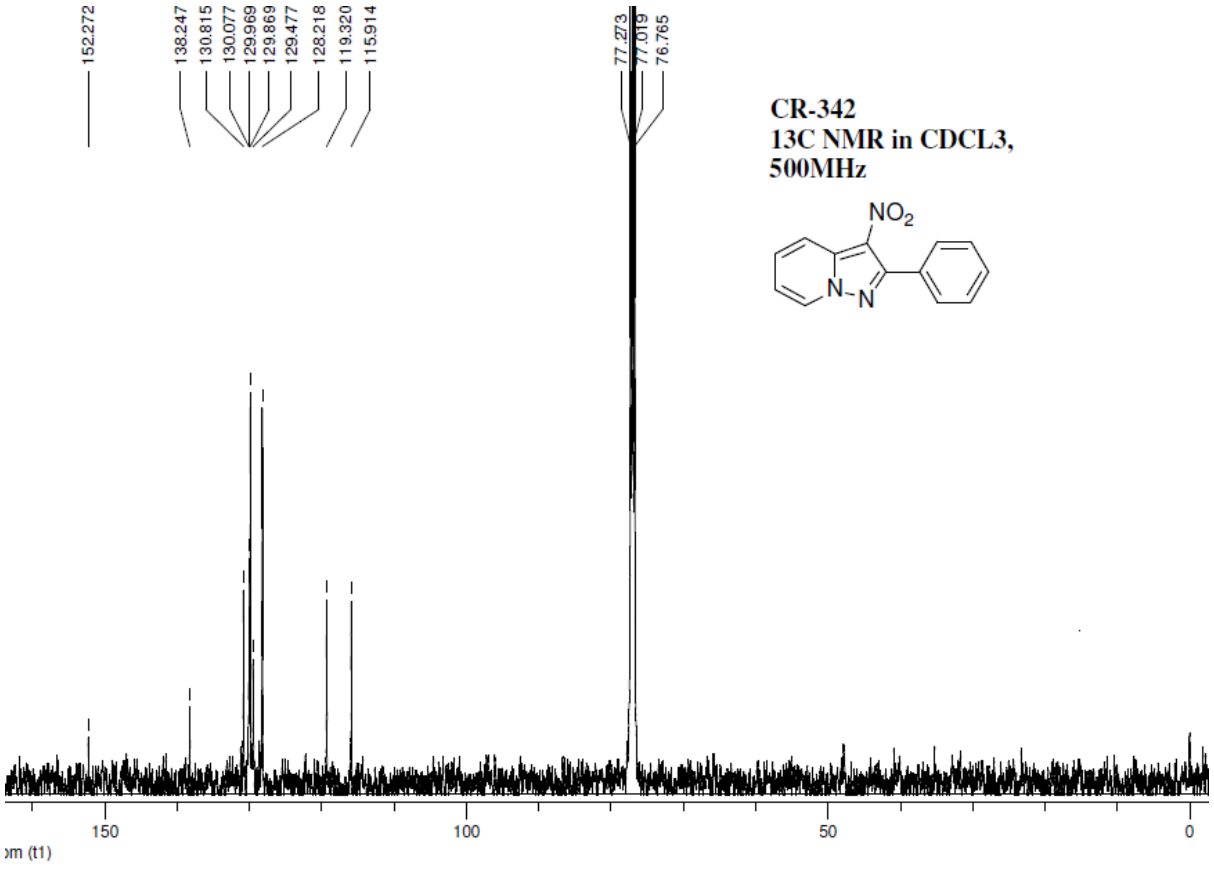

**1H NMR of 3an**



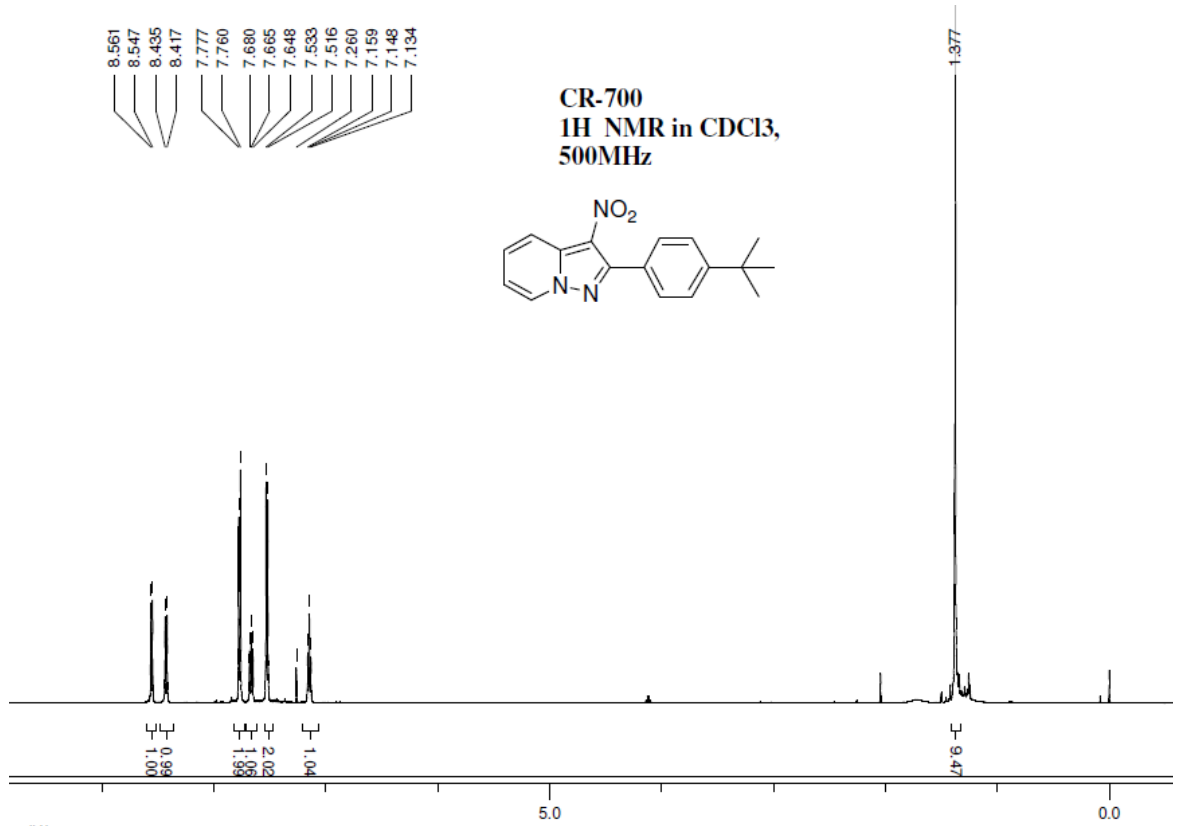

**13C NMR of 3an**



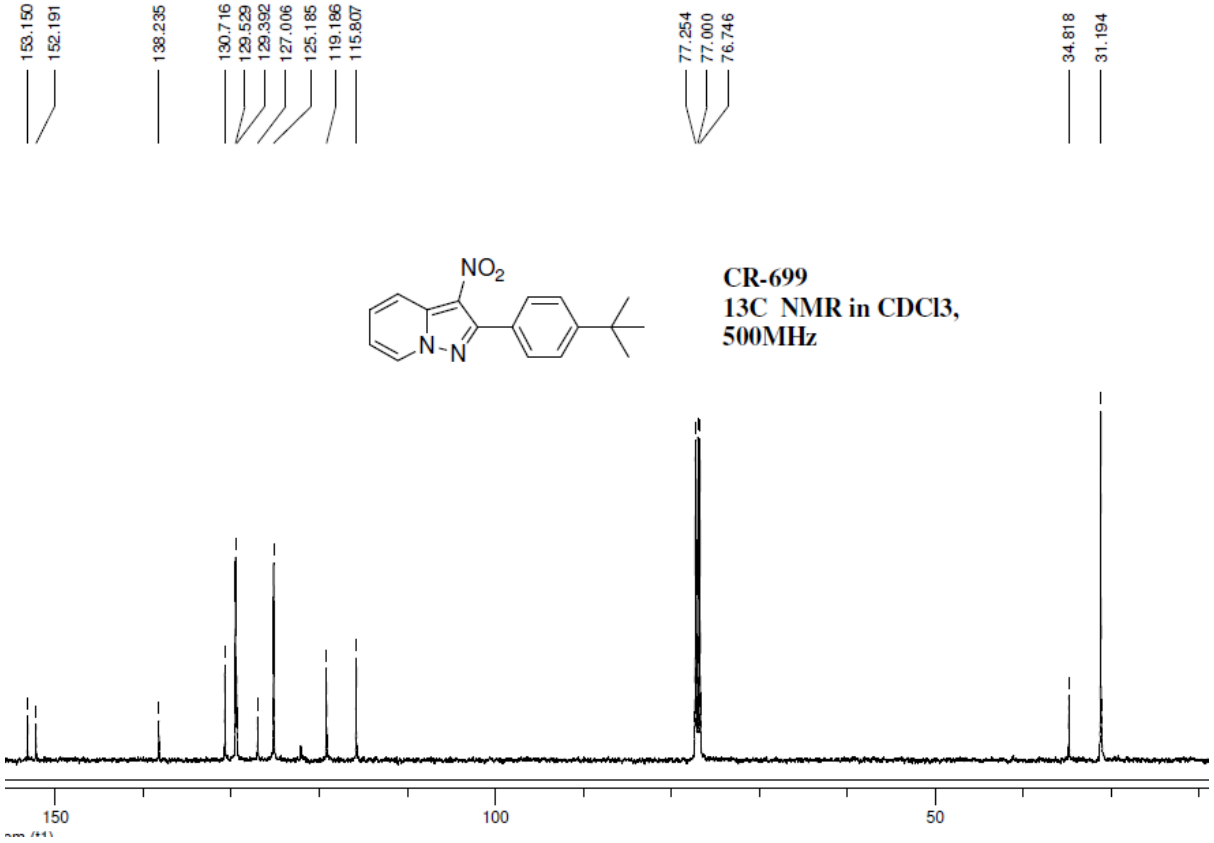

**1H NMR of 5a**




**13C NMR of 5a**




**1H NMR of 5b**

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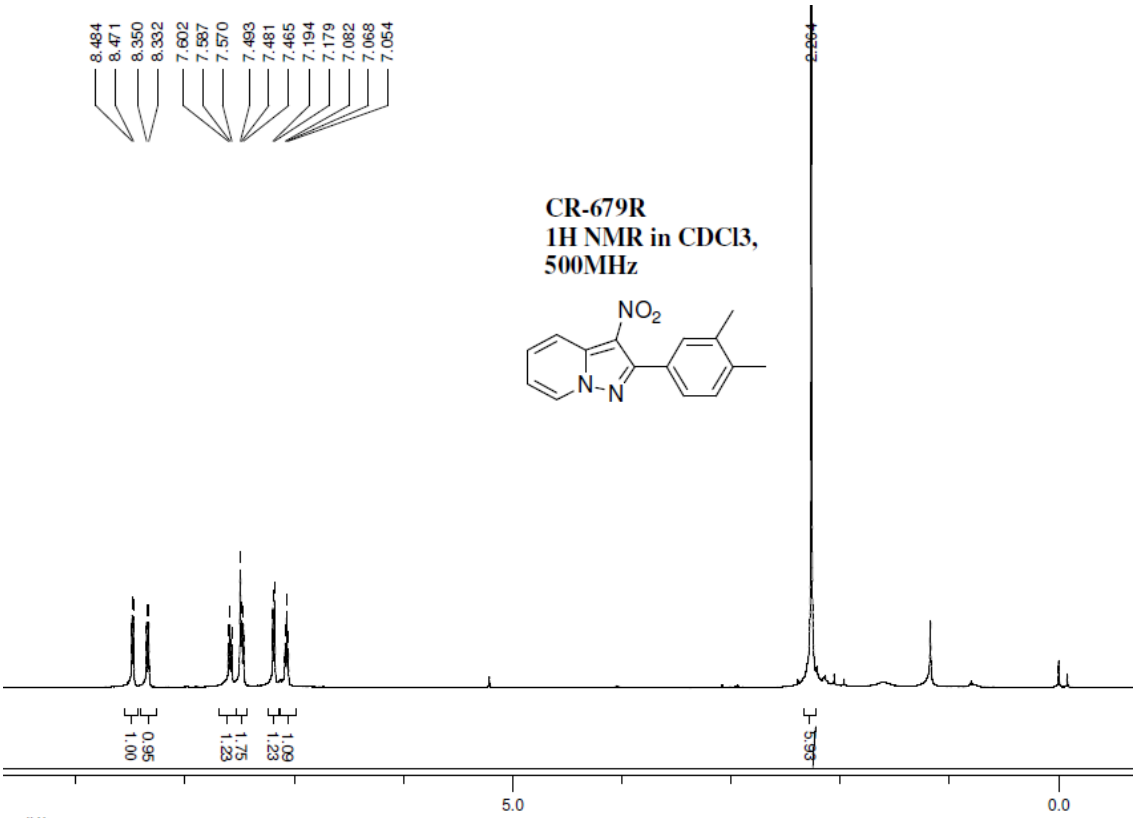
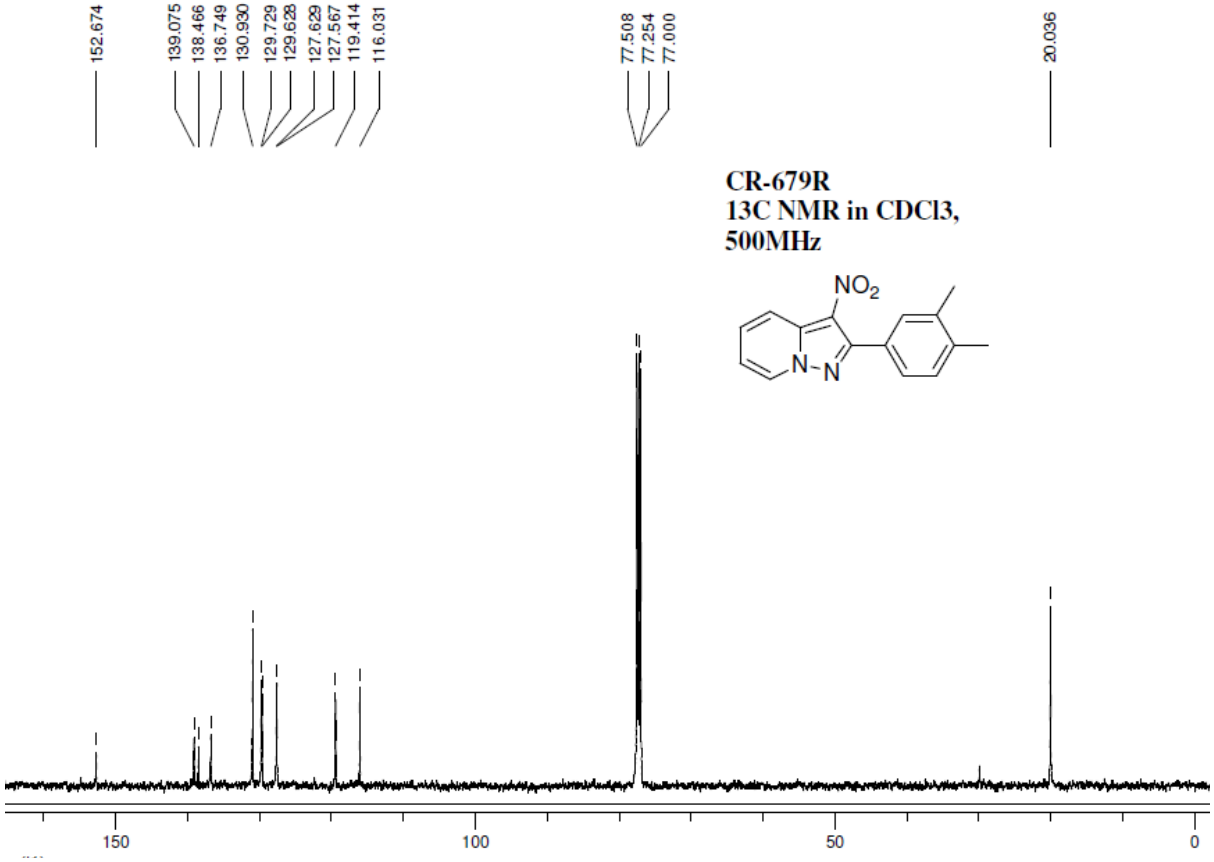
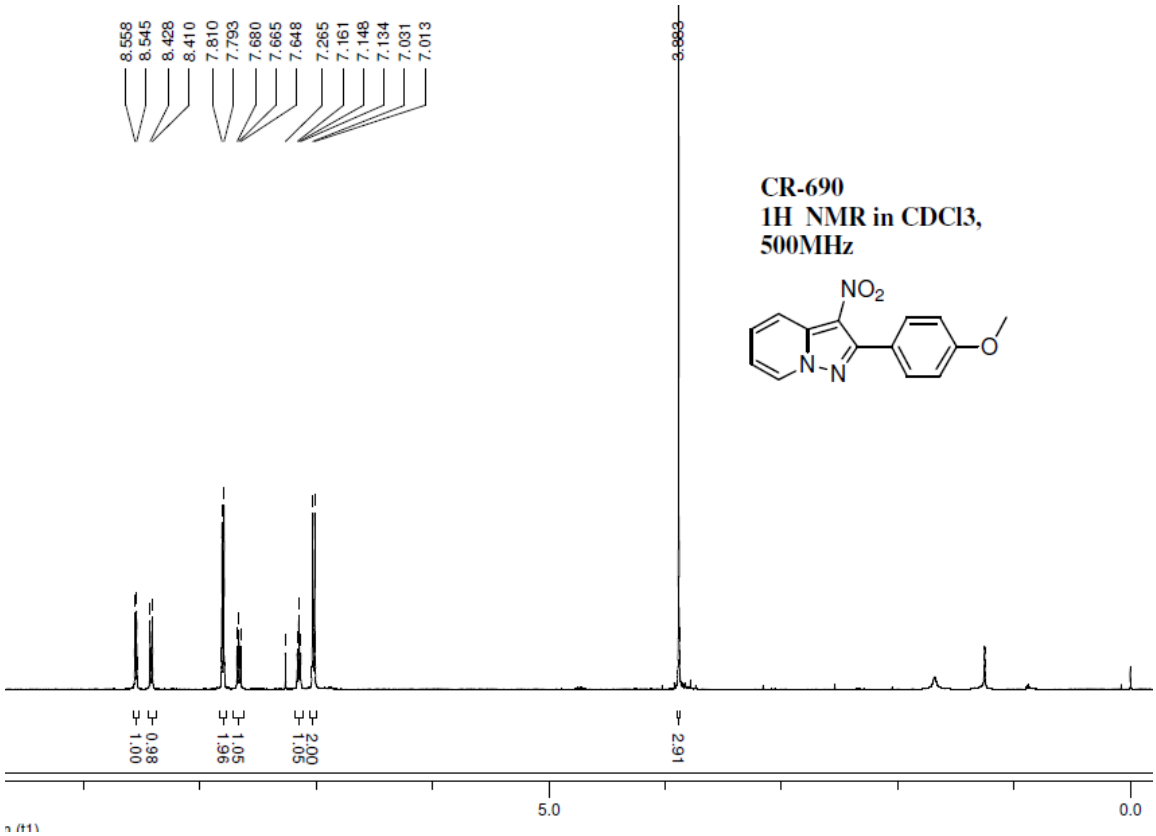


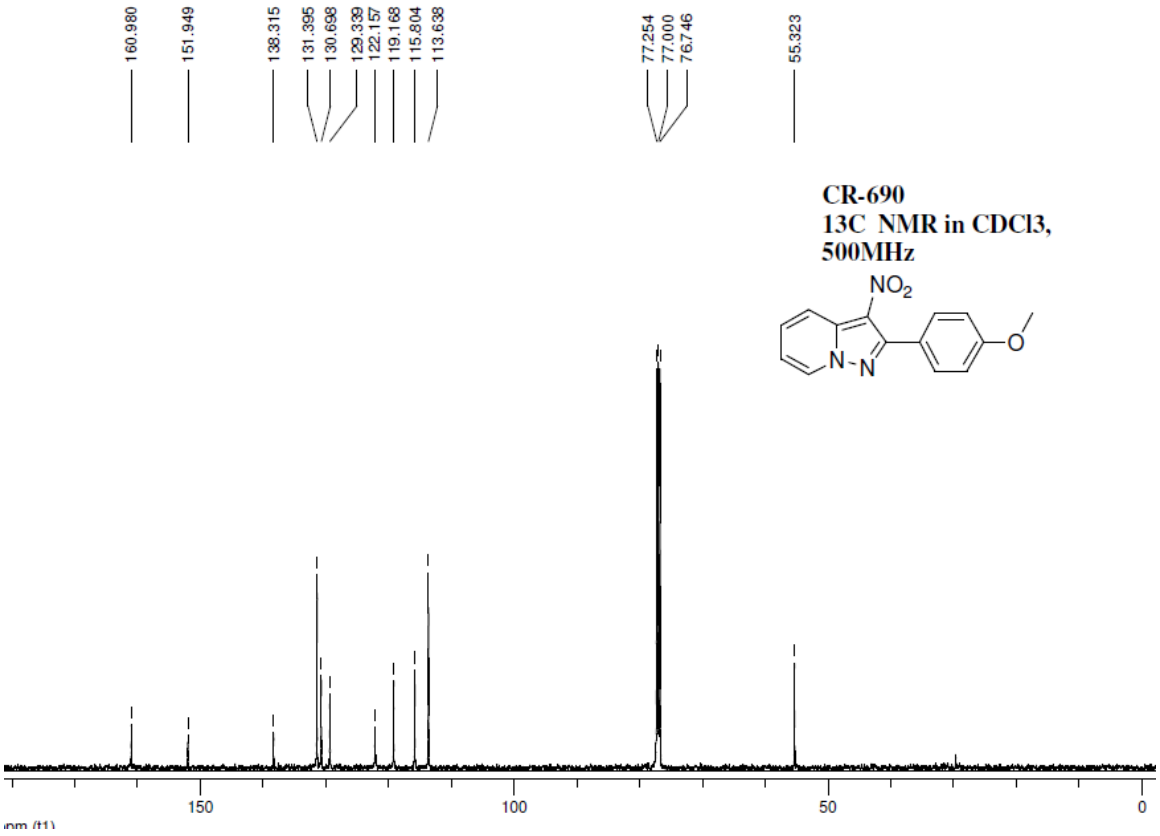

**1H NMR of 5c**



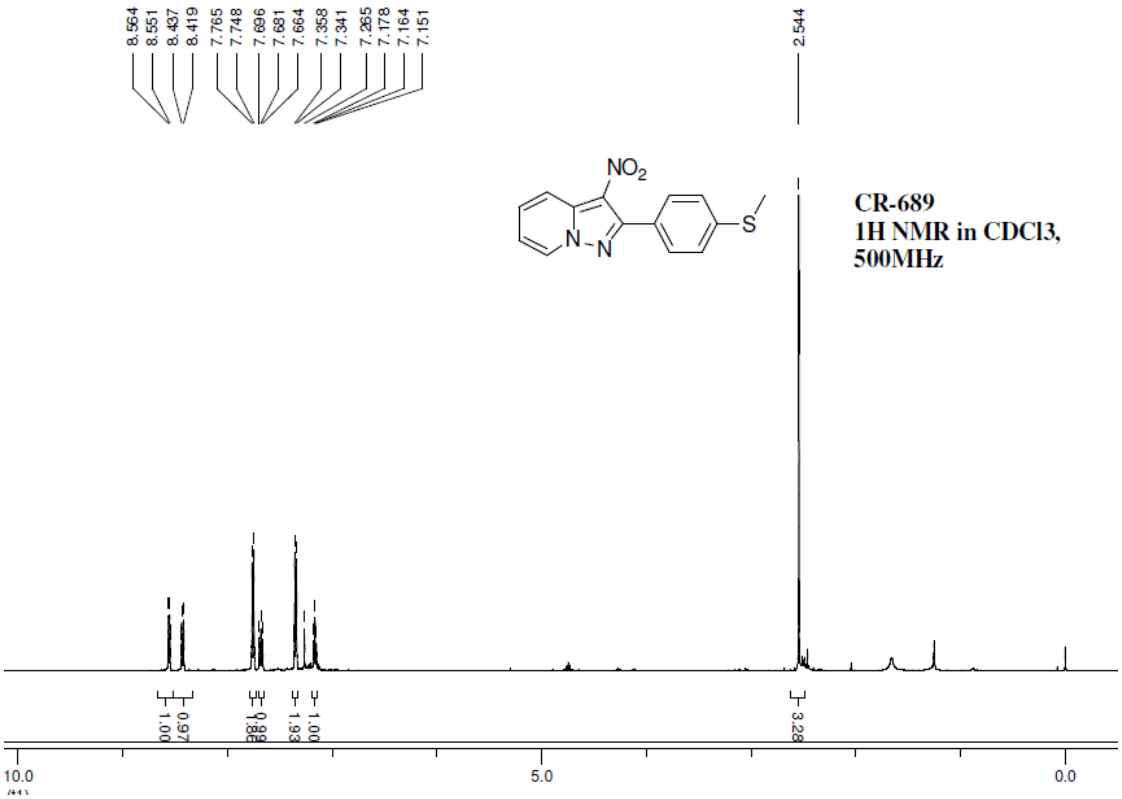

**13C NMR of 5c**



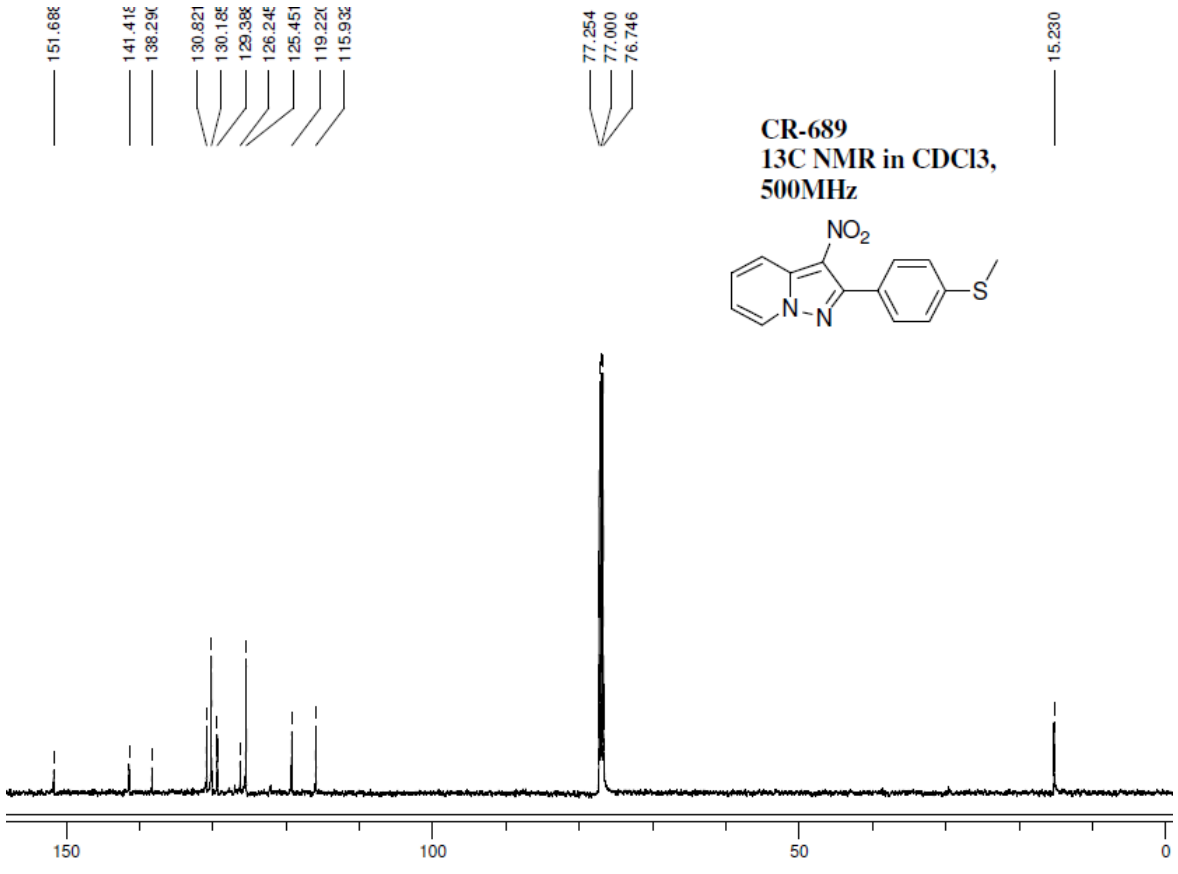

**1H NMR of 5d**




**13C NMR of 5d**




**1H NMR of 5e**

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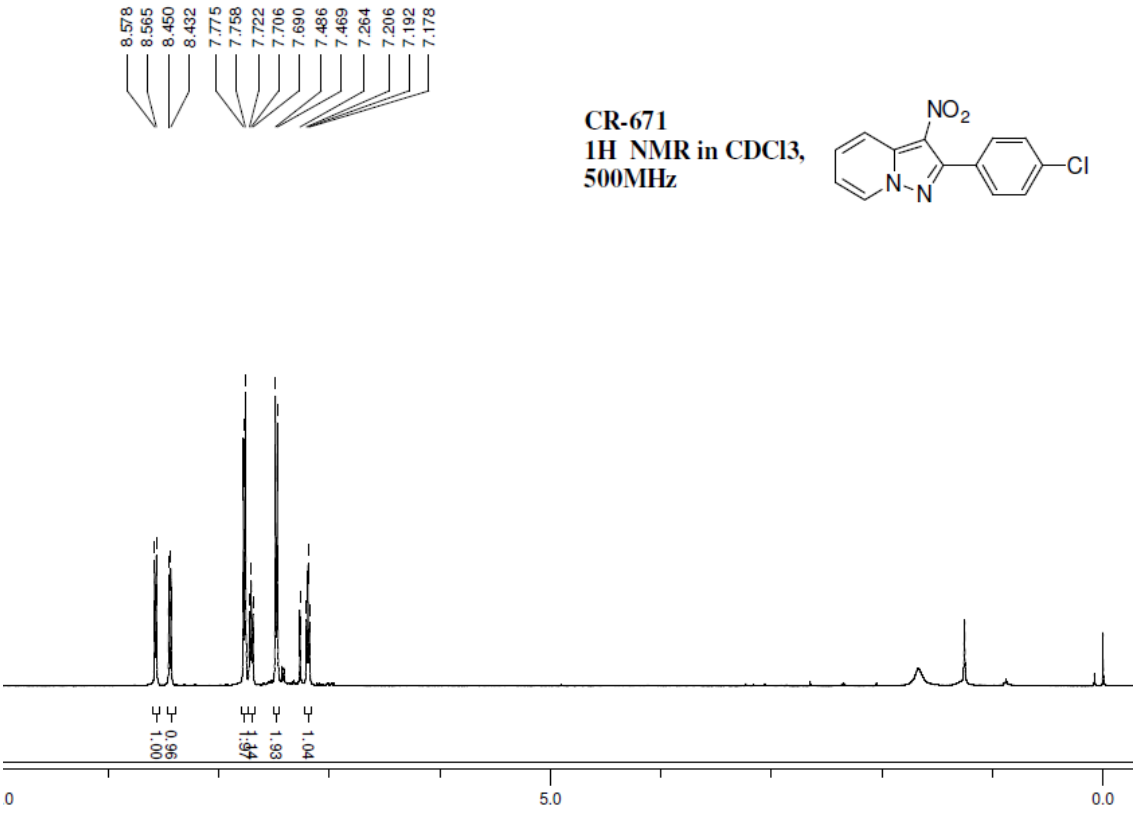
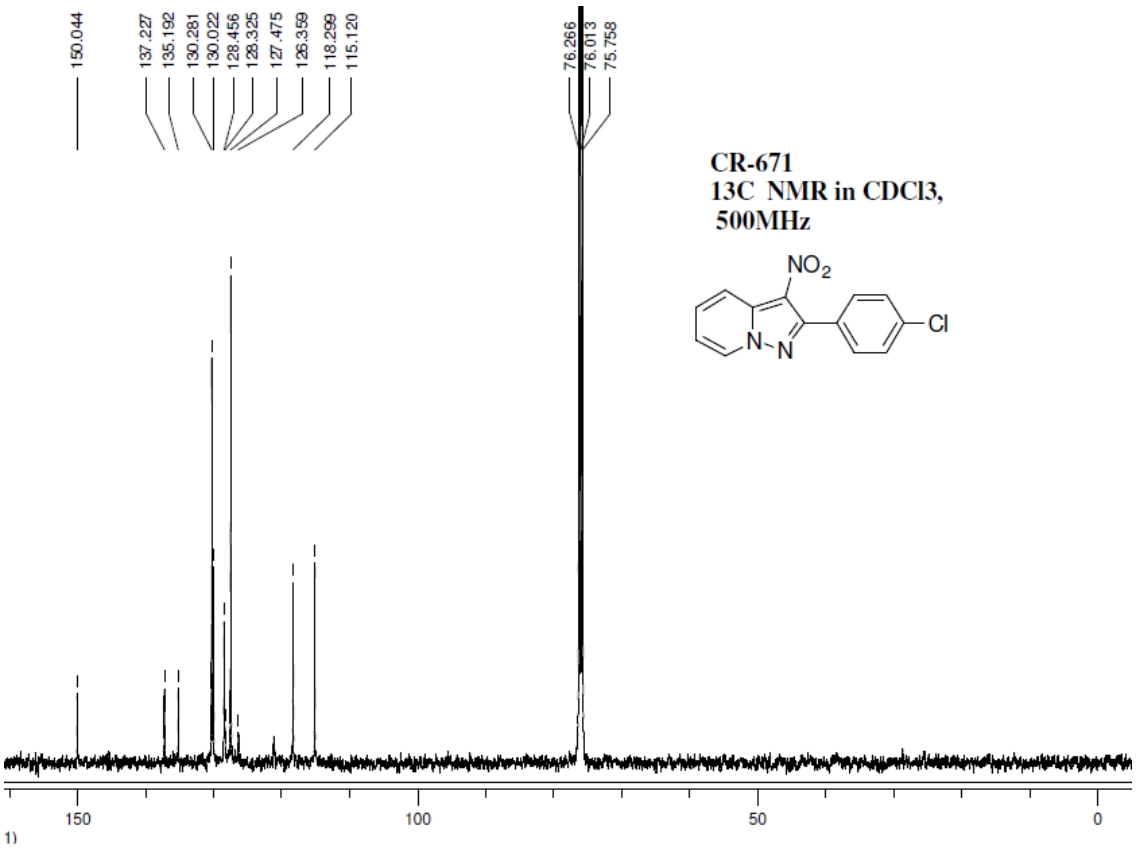
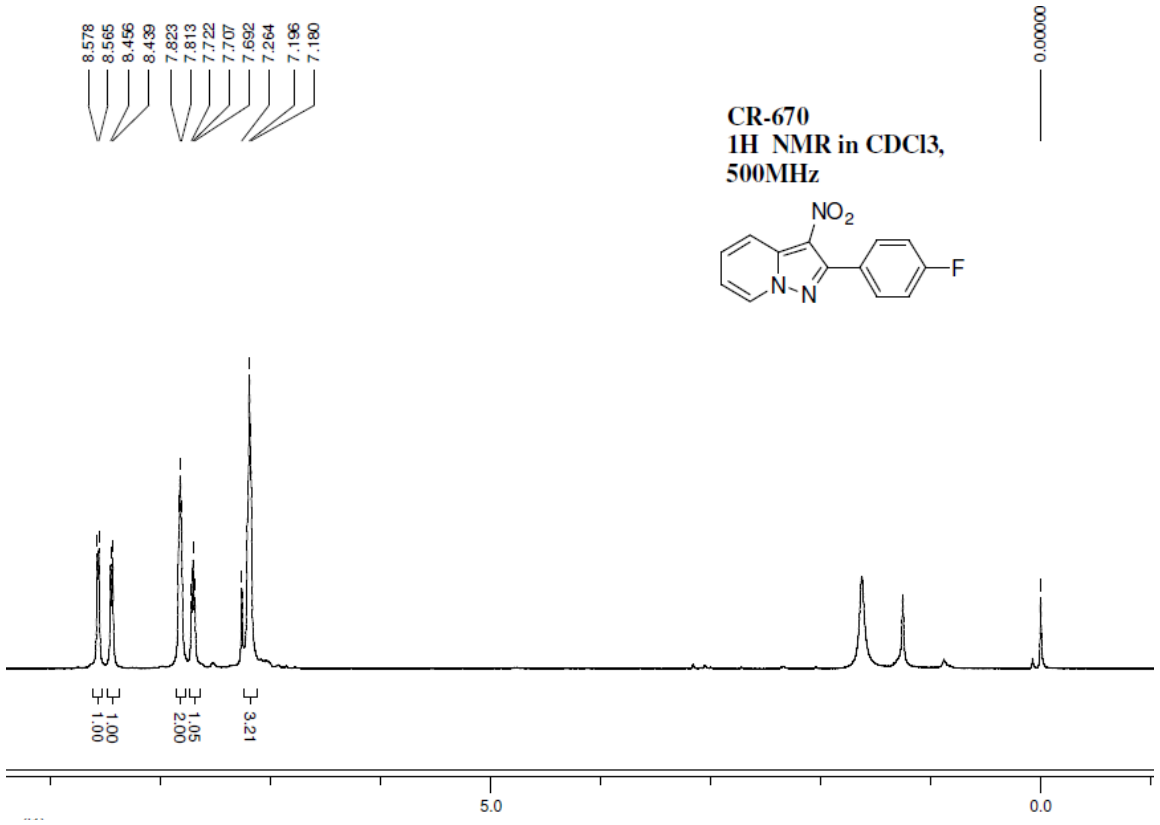


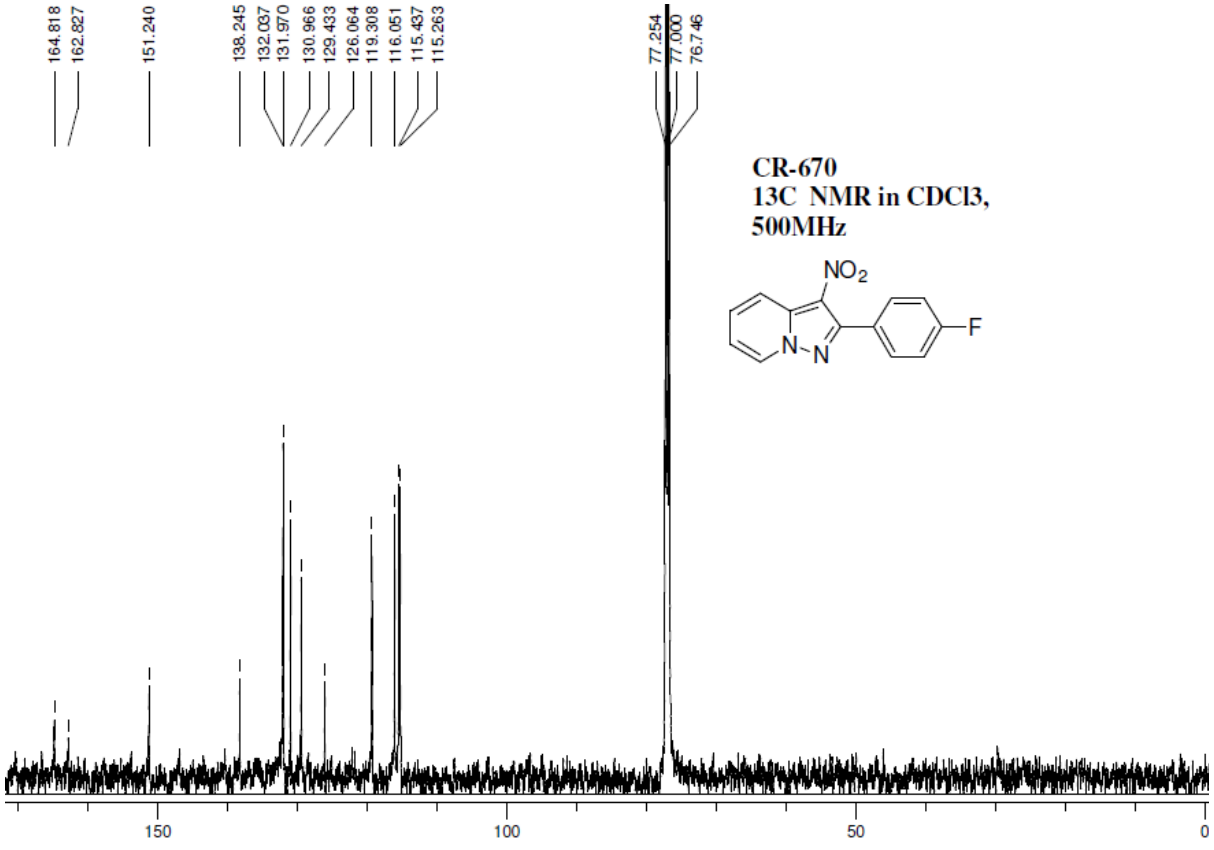

**1H NMR of 5f**



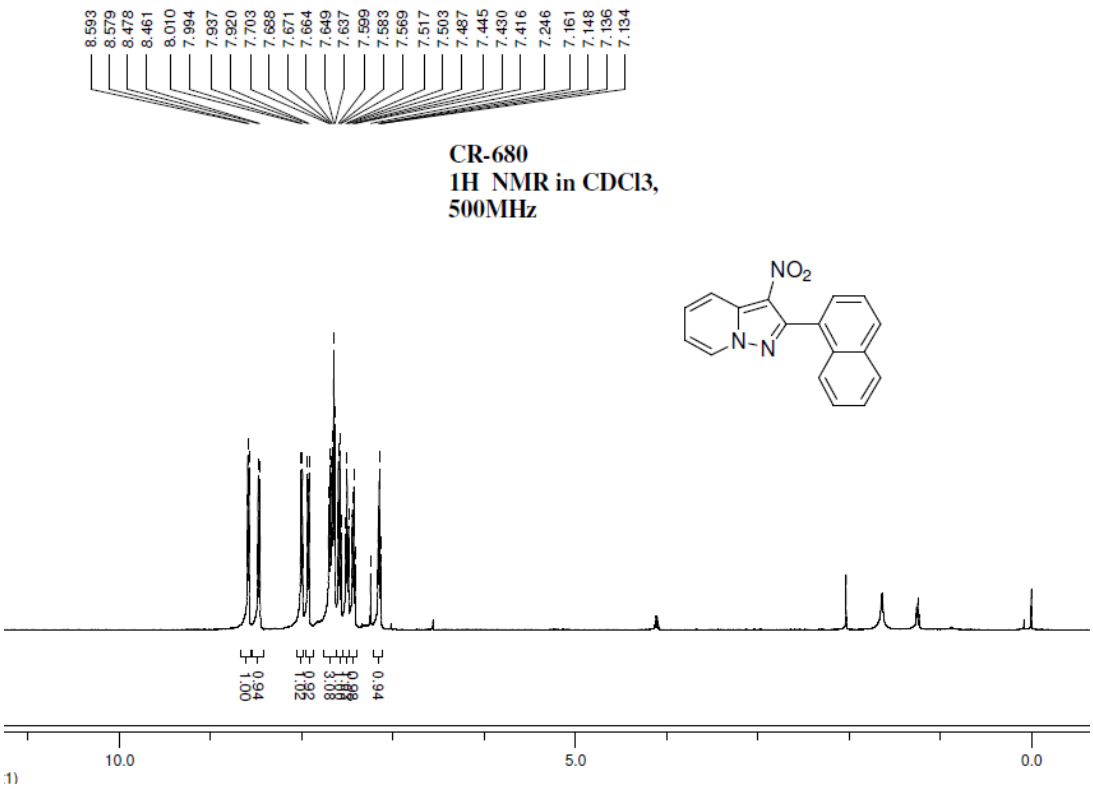

**13C NMR of 5f**



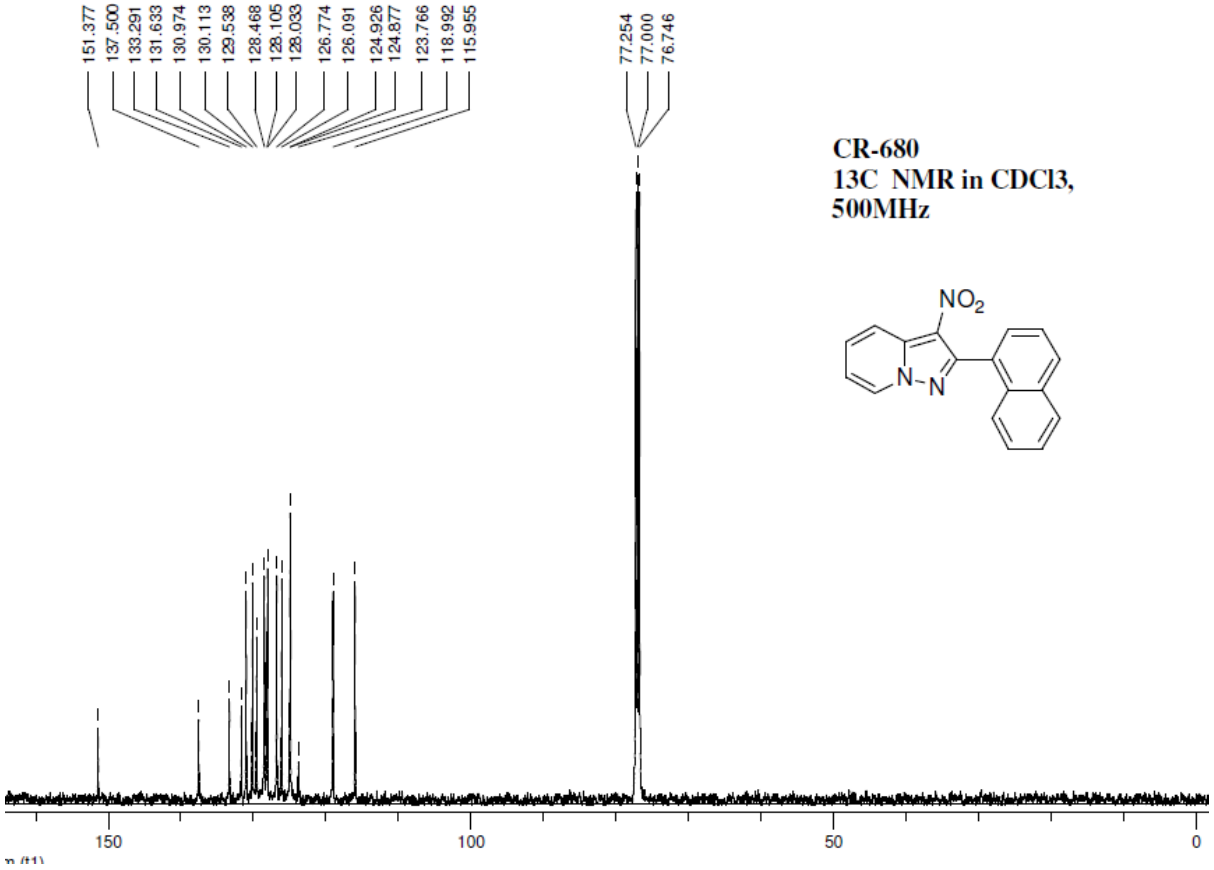

**1H NMR of 5g**



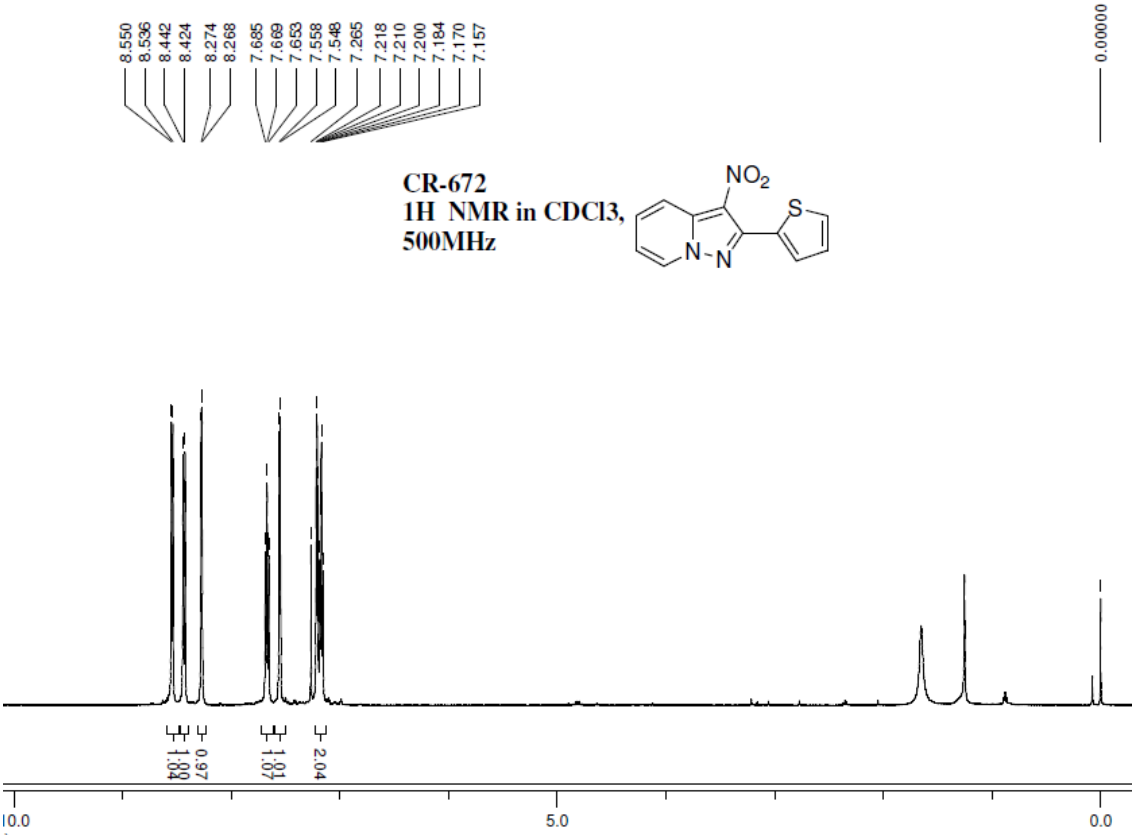

**13C NMR of 5g**



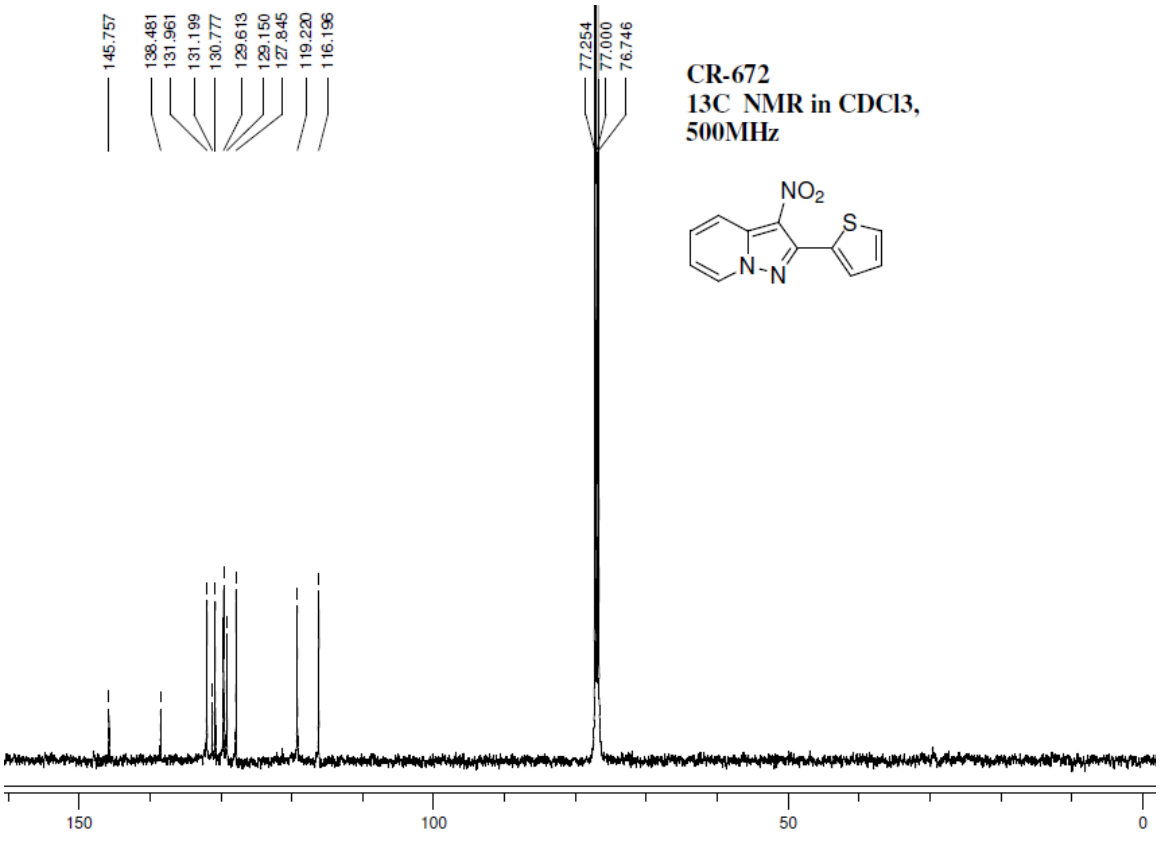

**1H NMR of 5h**




**13C NMR of 5g**




**1H NMR of 5h**




**13C NMR of 5h**