Copper−Catalyzed Denitrogenative Transannulation Reaction of Pyridotriazoles: Synthesis of Imidazopyridines with Amines and Amino acids

Abhisek Joshi, Darapaneni Chandra Mohan and Subbarayappa Adimurthy*

Academy of Scientific & Innovative Research, CSIR–Central Salt & Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002. Gujarat (INDIA)

E-mail: adimurthy@csmcri.org

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Experimental Section

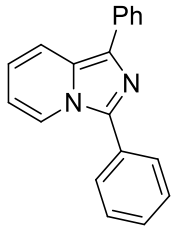
General: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz respectively. The spectra were recorded in $CDCl_3$ and DMSO-d_6 as solvent. Multiplicity was indicated as follows: 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 (7.2), and ^{13}C NMR (77.0) are correspond to deuterated solvent chloroform 1H NMR (2.50) and 13C NMR (39.43) are correspond to deuterated solvent DMSO 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.

General procedure

General procedure for the synthesis of imidazo[1,5-a]pyridine (**3a**): To a reaction tube equipped with a magnetic stir bar, added 3-phenyl-[1,2,3]triazolo[1,5-a]pyridine **1a** (39.0 mg, 0.2 mmol), benzyl amine **2a** (64.2mg, 0.6 mmol), and copper iodide (0.04 mmol/20 mol%) and 1.0 mL of 1,2-dichlorobenzne. The mixture was heated in an oil bath at 150 ^{o}C in a closed tube. Reaction was monitored by TLC, after completion of the reaction, it was allowed to attain room temperature. Then the mixture was poured into 30 mL of sodium chloride 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 (4% EtOAc/hexane) to afford **3a** (44.5 mg; 82% yield).

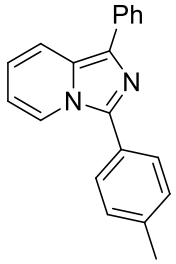
Characterization data

1, 3-diphenylimidazo[1,5-a]pyridine (3a)



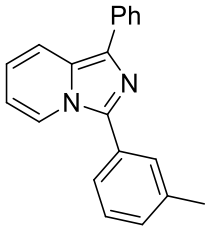
(Eluent: 4% EtOAc/hexane); 82% yield (44.5 mg); solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 5.5 Hz, 1H), 7.94 (d, J = 5.5 Hz, 2H), 7.81 (s, 5H), 7.51 (d, J = 5.5 Hz, 2H), 7.45 (d, J = 5.5 Hz, 2H), 7.29 (s, 1H), 6.75 (s, 1H), 6.53 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 134.9, 131.9, 130.1, 128.9, 128.7, 128.6, 128.2, 127.6, 126.7, 126.4, 121.6, 119.6, 119.0, 113.1. HRMS calcd for $C_{19}H_{15}N_2$ Cl : 271.1235. Found: 271.1240.

1-Phenyl-3-(p-tolyl)imidazo[1,5-a]pyridine (3b)



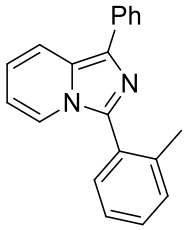
(Eluent: 4% EtOAc/hexane); 78% yield (44.3 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 9.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 6.76-6.73 (m, 1H), 6.54 (t, J = 7.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 138.8, 138.3, 135.0, 131.8, 129.7, 128.7, 128.2, 127.5, 127.2, 126.9, 126.4, 121.8, 119.5, 119.1, 113.0, 21.4. HRMS calcd for C_{20} H_{17} N_2 Cl : 285.1392. Found: 285.1396.

1-Phenyl-3-(m-tolyl)imidazo[1,5-a]pyridine (3c)



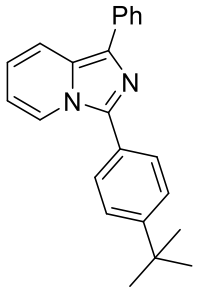
(Eluent: 4% EtOAc/hexane); 62% yield (35.3 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 7.0 Hz, 1H), 7.93 (d, J = 7.0 Hz, 2H), 7.82 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30(t, J = 7.5 Hz, 1H), 6.76-6.73(m, 1H), 6.54 (t, J = 7.0 Hz, 1H), 2.42(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.3, 135.0, 131.8, 129.6, 128.7, 128.2, 127.5, 127.3, 126.8, 126.4, 121.8, 119.5, 119.1, 113.0, 21.4. HRMS calcd for C_{20} H_{17} N_2 Cl : 285.1392. Found: 285.1386.

1-Phenyl-3-(o-tolyl)imidazo[1,5-a]pyridine (3d)



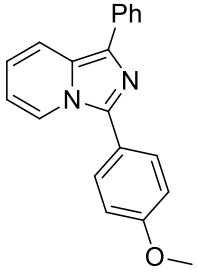
(Eluent: 4% EtOAc/hexane); 92% yield (52.3 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.0 Hz, 2H), 7.85 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 6.5 Hz, 1H), 7.47-7.43 (m, 3H), 7.38 (d J = 10.0 Hz, 2H), 7.32-7.27 (m, 2H), 6.78 (t, J = 7.0 Hz, 1H), 6.51 (t, J = 5.5 Hz, 1H), 2.24(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 137.8, 135.1, 131.1, 130.8, 130.6, 129.6, 129.2, 128.7, 126.6, 126.4, 126.1, 121.9, 119.6, 118.9, 112.9, 19.7. HRMS calcd for C_{20} H_{17} N_2 Cl : 285.1392. Found: 285.1386.

3-(4-(Tert-butyl)phenyl)-1-phenylimidazo[1,5-a]pyridine (3e)



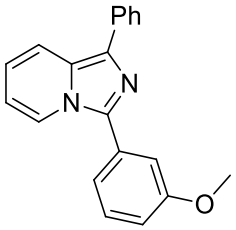
(Eluent: 4% EtOAc/hexane); 68% yield (44.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.37(t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.0 Hz, 1H), 6.66-6.63 (m, 1H), 6.44 (t, J = 6.5 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 135.0, 131.8, 128.7, 127.2, 126.8, 126.4, 125.9, 122.9, 119.5, 119.1, 113.0, 34.8. 31.2. HRMS calcd for $C_{23}H_{22}N_2Cl$: 327.1861. Found: 327.1872.

3-(4-Methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine (3f)



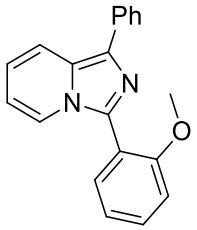
(Eluent: 4% EtOAc/hexane); 83% yield (49.8 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 6.5 Hz, 1H), 7.49-7.43 (m, 3H), 7.28 (m, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H), 6.81-6.78 (m, 1H), 6.54 (t, J = 7.0 Hz, 1H), 3.81(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 136.0, 134.9, 132.8, 131.2, 130.9, 128.6, 127.3, 126.7, 126.3, 123.5, 121.2, 119.5, 118.8, 188.5, 112.1, 111.1, 55.5. HRMS calcd for $C_{20}H_{17}N_2O$:301.1341. Found: 301.1341.

3-(3-Methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine (3g)



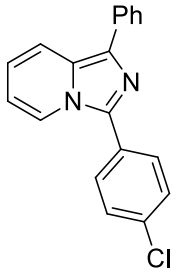
(Eluent: 4% EtOAc/hexane); 65% yield (39.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 7.0 Hz, 1H), 7.84 (d, J =7.5 Hz, 2H), 7.72 (d, J = 9.5 Hz, 1H), 7.37-7.28 (m, 5H), 7.19 (t, J = 7.0 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6,66-6.63 (m, 1H), 6.43 (t, J = 6.5 Hz, 1H), 3,37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 137.8, 134.8, 131.8, 131.2, 129.9, 128.6, 127.6, 126.7, 126.4, 121.8, 120.5, 119.6, 1189, 114.7, 113.6, 113.1, 55.3. HRMS calcd for $C_{20}H_{17}N_2O$: 301.1341. Found: 301.1353.

3-(2-Methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine (3h)



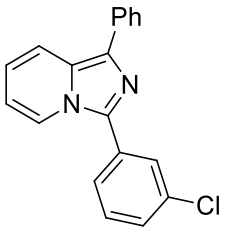
(Eluent: 4% EtOAc/hexane); 45% yield (27.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.21-7.16 (m, 1H), 6.97 (d, J = 9.0 Hz, 2H), 6.67-6.64 (m, 1H), 6.45 (t, J = 7.0 Hz, 1H), 3.78(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 138.0, 135.0, 131.5, 129.7, 128.6, 127.2, 126.7, 126.3, 122.5, 121.6, 119.3, 119.0, 114.4, 112.9, 55.3. HRMS calcd for $C_{20}H_{17}N_2O$: 301.1341. Found: 301.1353.

3-(4-Chlorophenyl)-1-phenylimidazo[1,5-a]pyridine (3i)



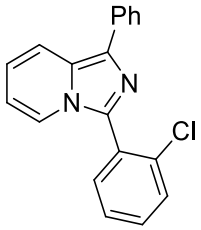
(Eluent: 4% EtOAc/hexane); 60% yield (36.5 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 9.5 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.42-7.36 (m, 4H), 7.23 (t, J = 7.5 Hz, 1H), 6.72-6.69 (m, 1H), 6.51 (t, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 134.7, 134.6, 132.3, 129.4, 129.2, 128.7, 128.6, 127.9, 126.8, 126.7, 121.5, 119.8, 119.2, 113.6. HRMS calcd for $C_{19}H_{14}N_2Cl$: 305.0846. Found: 305.0857.

3-(3-Chlorophenyl)-1-phenylimidazo[1,5-a]pyridine (3j)



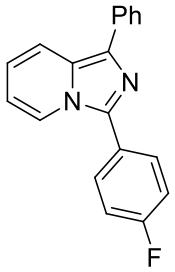
(Eluent: 4% EtOAc/hexane); 84% yield (51.2 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 7.5 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.38-7.29 (m, 5H), 7.23 (t, J 7.5 Hz, 1H), 6.72(t, J = 7.0 Hz, 1H), 6.52 (t, J = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 134.9, 134.5, 132.3, 131.7, 130.1, 128.7, 128.1, 126.7, 1260, 121.4, 119.9, 1191, 113.6. HRMS calcd for $C_{19}H_{14}N_2Cl$: 305.0846. Found: 305.0837

3-(2-Chlorophenyl)-1-phenylimidazo[1,5-a]pyridine (3k)



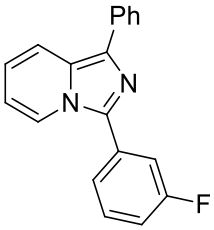
(Eluent: 4% EtOAc/hexane); 82% yield (50.0 g); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 9.5 Hz, 1H), 7.67 (t, J = 5.0 Hz, 1H), 7.59 (d, J = 7.0 Hz, 1H), 7,55 (d, J = 7.5 Hz, 1H), 7.47-7.42 (m, 4H), 7.30-7.24 (m, 1H), 6.84-6.81 (m, 1H), 6.60 (t, J = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 134.8, 134.3, 133.3, 131.5, 130.8, 129.8, 129.2, 128.6, 127.2, 126.6, 126.4, 122.5, 119.8, 118.8. HRMS calcd for C_{19} H_{14} N_2 Cl: 305.0846. Found: 305.0853.

3-(4-Fluorophenyl)-1-phenylimidazo[1,5-a]pyridine (3l)



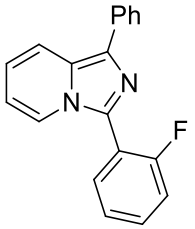
(Eluent: 4% EtOAc/hexane); 87% yield (50.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.74-7.69 (m, 3H), 7.39 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.16-7.11 (m, 2H), 6.70 (t, J = 6.5 Hz, 1H), 6.49 (t, J = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9(d, J = 247.6 Hz), 137.1, 134.8, 132.0, 130.3(d, J = 7.8 Hz,), 128.7, 127.6, 126.7, 126.6, 126.3, 121.4, 119.7, 119.1, 116.2 (d, J = 21.5 Hz), 113.4. HRMS calcd for C_{19} H_{14} N_2 F: 289.1141. Found: 289.1122.

3-(3-Fluorophenyl)-1-phenylimidazo[1,5-a]pyridine (3m)



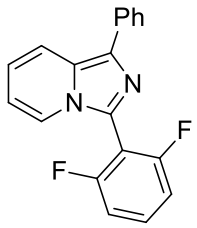
(Eluent: 4% EtOAc/hexane); 85% yield (49.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.10 (m, 1H), 7.82-7.81 (m, 2H), 7.73-7.71 (m, 1H), 7.52-7.50 (m, 1H), 7.48-7.45 (m, 1H), 7.39-7.34 (m, 3H), 7.21-7.18 (m, 1H), 7.04-7.00 (m, 1H), 6.69-666 (m, 1H), 6.49-6.46 (m, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5(d, J = 245 Hz), 136.1, 134.2, 131.8, 131.7, 131.6, 130.1 (d, J = 8.2 Hz), 128.2, 127.5, 126.3, 126.2, 123.1, 121.1, 119.5, 118.7, 115.2 (d, J = 20.8 Hz), 114.8(d, J = 22.6 Hz), 113.1. HRMS calcd for C_{19} H_{14} N_2 F: 289.1141. Found: 289.1141.

3-(2-fluorophenyl)-1-phenylimidazo[1,5-a]pyridine (3n)



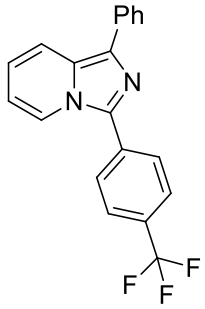
(Eluent: 4% EtOAc/hexane); 70% yield (40.3 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.0 Hz, 2H), 7.85 (d, J = 9.0 Hz, 1H), 7.80-7.78 (m, 1H),7.75 -7.73 (m, 1H), 7,46 (t, J = 7.5 Hz, 3H), 7.32-727 (m, 2H), 7.24-7.21 (m, 1H), 6.82-6.79 (m, 1H), 6,58 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9 (d, J = 248 Hz), 134.8, 133.3, 132.5, 132.2, 131.0 (d, J = 7.8 Hz), 128.6, 127.8, 126.7, 1265, 124.8, 122.6 (d, J = 5.6 Hz), 119.5, 118.7, 118.0 (d, J = 14.3 Hz), 116.1, 115.9, 112.9. HRMS calcd for C_{19} H_{14} N_2 F: 289.1141. Found: 289.1158.

3-(2,6-Difluorophenyl)-1-phenylimidazo[1,5-a]pyridine (3o)



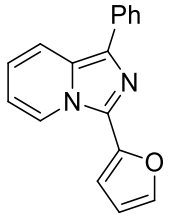
(Eluent: 4% EtOAc/hexane); 90% yield (55.0 mg); semi-solid; 1H NMR (500 MHz, CDCl3) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 6.5 Hz, 1H), 7.55-7.51 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22-7.12 (m, 1H), 6.87-6.84 (m, 1H), 6.64 (t, *J* = 7.0 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 159.8 (d, J = 117.6 Hz), 156.8 (d, J = 243.5 Hz), 134.5, 132.6, 132.3, 128.7, 128.1, 126.7, 122.6 (d, J = 6.8 Hz), 120.1, 119.4- 119.2 (m), 118.8, 118.5, 117.5-117.2 (m), 113.3. HRMS calcd for $C_{19}H_{13}N_2F_2$: 307.1047 Found: 307.1056.

1-phenyl-3-(4-(trifluoromethyl)phenyl)imidazo[1,5-a]pyridine (3p)



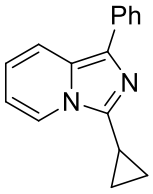
(Eluent: 4% EtOAc/hexane); 67% yield (45.3 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.16 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.75-6.72 (m, 1H), 6.55 (t, *J* = 6.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 136.4, 134.6, 133.6, 132.8, 130.4, 130.2, 128.8, 128.3, 128.2, 126.8, 126.0, 125.1, 121.4, 120.2, 119.3, 113.9. HRMS calcd for $C_{20}H_{14}N_2F_3$: 339.1109. Found: 339.1121.

3-(Furan-2-yl)-1-phenylimidazo[1,5-a]pyridine (3q)



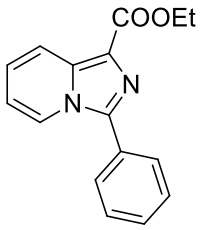
(Eluent: 4% EtOAc/hexane); 72% yield (37.4 g); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 7.24-7.18 (m, 1H), 7.01 (d, J = 3.0 Hz, 1H), 6.75-6.72 (m, 1H), 6.61 (t, J = 7.5 Hz, 1H), 6.53-6.52(m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 142.1, 134.5, 132.3, 130.1, 128.6, 127.3, 126.9, 126.7, 123.2, 119.9, 118.9, 113.8, 111.7, 108.7. HRMS calcd for $C_{16}H_{13}N_2O$: 261.1028. Found: 261.1046.

3-Cyclopropyl-1-phenylimidazo[1,5-a]pyridine (3s)



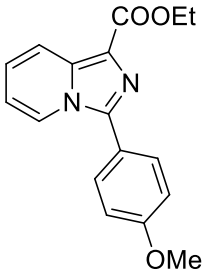
(Eluent: 4% EtOAc/hexane); 51% yield (24.0 g); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.0 Hz, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 6.74-6.71 (m, 1H), 6.59 (t, J = 7.0 Hz, 1H), 2.07-2.01 (m, 1H), 1.14-1.09 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 135.0, 130.9, 129.7, 129.4, 129.0, 128.6, 126.8, 126.6, 126.4, 126.1, 121.1, 119.0, 118.9, 112.3. 6.6, 6.0. HRMS calcd for $C_{16}H_{15}N_2$: 235.1235. Found: 235.1238.

Ethyl 3-phenylimidazo[1,5-a]pyridine-1-carboxylate (3u)



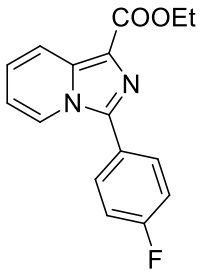
(Eluent: Dichloromethane); 51% yield (27 mg); solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.24 (m, 2H), 7,80 (d, J = 7.0 Hz, 2H), 7.54-7,48 (m, 3H), 7.14-7.11(m,1H), 6.77(t, J = 6.5 Hz, 1H), 4.50 (q, J = 7.0 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 139.1, 135.3, 129.4, 128.9, 128.7, 124.1, 122.4, 120.0, 114.3, 60.3. HRMS calcd for $C_{16}H_{15}N_2O_2$:267.1134. Found: 267.1130.

Ethyl 3-(4-methoxyphenyl)imidazo[1,5-a]pyridine-1-carboxylate(3v)



(Eluent: 20% EtOAc/hexane); 95% yield (35.2 mg); solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (t, J = 8.0 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 2H), 6.75(t, J = 7.0 Hz, 1H), 4,49(q, J = 7.0 Hz, 2H), 3.87(s, 3H), 1.45(t, J = 7.0 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 160.4, 139.1, 135.2, 130.2, 126.3, 123.9, 122.4, 121.4, 119.9, 114.3, 114.1, 60.2, 55.3, 14.6. HRMS calcd for $C_{17}H_{17}N_2O_3$:297.1239. Found: 297.1249.

Ethyl 3-(4-fluorophenyl)imidazo[1,5-a]pyridine-1-carboxylate(3w)

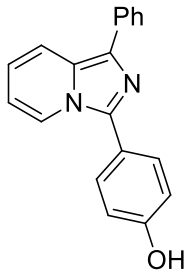


(Eluent: 20% EtOAc/hexane); 47% yield (26.5 mg); solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (t, J = 7.5 Hz, 2H), 7.78-7.75(m, 2H), 7.22 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.0 Hz, 1H), 6,79 (t, J = 6.5 Hz, 1H), 4.50 (q, J = 7.0 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1642. (d, J = 248.8 Hz), 163.4, 138.0, 135.5, 130.7 (d, J = 8.1 Hz), 125.3, 124.1, 122.1, 121.7, 120.0, 116.1 (d, J = 21.7 Hz), 114.4, 60.3, 14.5. HRMS calcd for $C16H_{14}N_2O2F$:285.1039. Found: 285.1032.

General procedure for the synthesis of imidazo[1,5-a]pyridine (5a) from amino acids

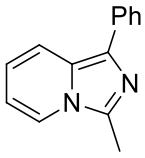
General procedure for the synthesis of imidazo[1,5-a]pyridine (**5a**): To a reaction tube equipped with a magnetic stir bar was added 3-phenyl-[1,2,3]triazolo[1,5-a]pyridine **1a** (39.0mg, 0.2 mmol), D-Phenylglycine **4** (90.6mg, 0.6 mmol), and copper iodide (0.08 mmol, 40 mol%) and 1.0 mL of 1,2-dichlorobenzne. The mixture was heated in an oil bath at 150 ^{o}C in a closed tube. The reaction was monitored by TLC, after completion of the reaction, it was allowed to attain room temperature. Then the mixture was poured into 30 mL of sodium chloride solution. The product was extracted with EtOAc (15 mL X 3) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure the left out crude residue was purified by column chromatography using silica gel (4% EtOAc/hexane) to afford **5a** (43.2 mg; 80% yield).

4-(1-phenylimidazo[1,5-a]pyridin-3-yl)phenol (5e)



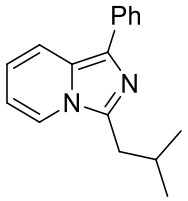
(Eluent: 20% EtOAc/hexane); 26 % yield (14.88 mg); semi-solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.89 (s, 1H), 8.35 (d, *J* = 7.0 Hz, 1H), 7.97-7.92 (m, 3H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.93-6.89 (m, 1H), 6.74 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 137.8, 134.8, 130.5, 129.7, 129.5, 129.3, 128.6, 126.7, 126.0, 125.8, 122.3, 120.4, 120.3, 118.4, 115.7, 114.9, 113.3. HRMS calcd for $C_{19}H_{15}N_2O$: 287.1184. Found: 287.1184.

3-Methyl-1-phenylimidazo[1,5-a]pyridine (5f)



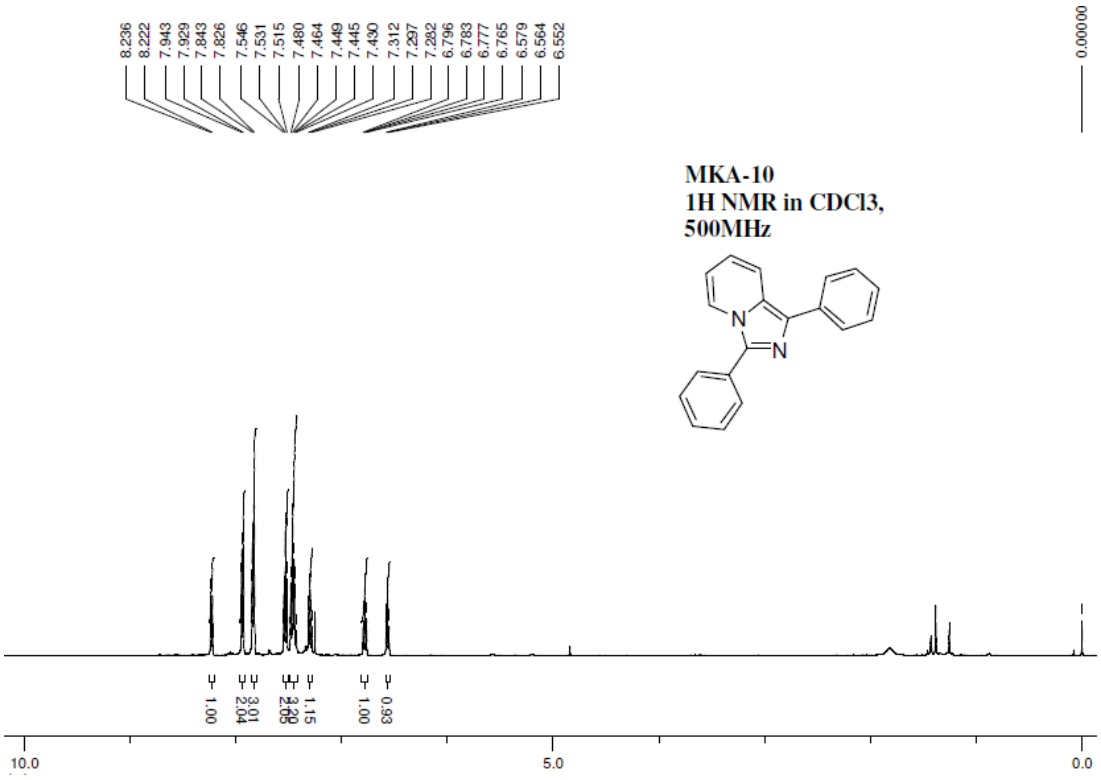
(Eluent: 20% EtOAc/hexane); 65% yield (27.0 mg); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 6.5 Hz, 1H), 6.73-6.70 (m, 1H), 6.58 (t, *J* = 7.0 Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.1, 134.9, 129.8, 128.7, 126.3, 126.1, 121.0, 118.9, 118.6, 112.5, 12.5. HRMS calcd for $C_{14}H_{13}N_2Cl$: 209.1079. Found: 209.1079.

3-isobutyl-1-phenylimidazo[1,5-a]pyridine (5g)

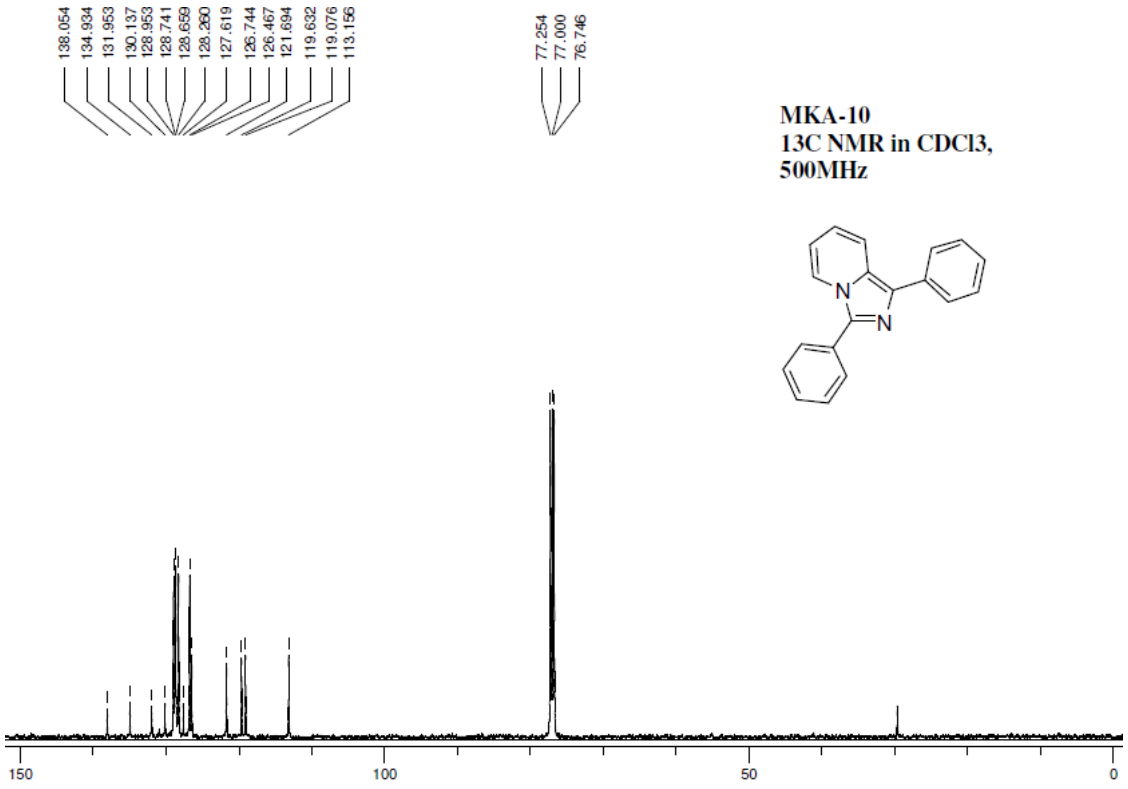


(Eluent: 15% EtOAc/hexane); 59% yield (29.5 g); semi-solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.75 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.0 Hz, 1H), 6.70-6.67 (m, 1H), 6.53 (t, J = 7.0 Hz, 1H), 2.90 (d, J = 7.0 Hz, 2H), 2.25 (septet, J = 7.0 Hz, 1H), 1.02 (d, J = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 135.2, 130.1, 128.6, 126.5, 126.3, 126.0, 121.0, 118.9, 118.4, 112.3, 35.5, 27.8, 22.6. HRMS calcd for C_{17} H_{19} N_2 Cl Na: 251.1548. Found: 251.1555.

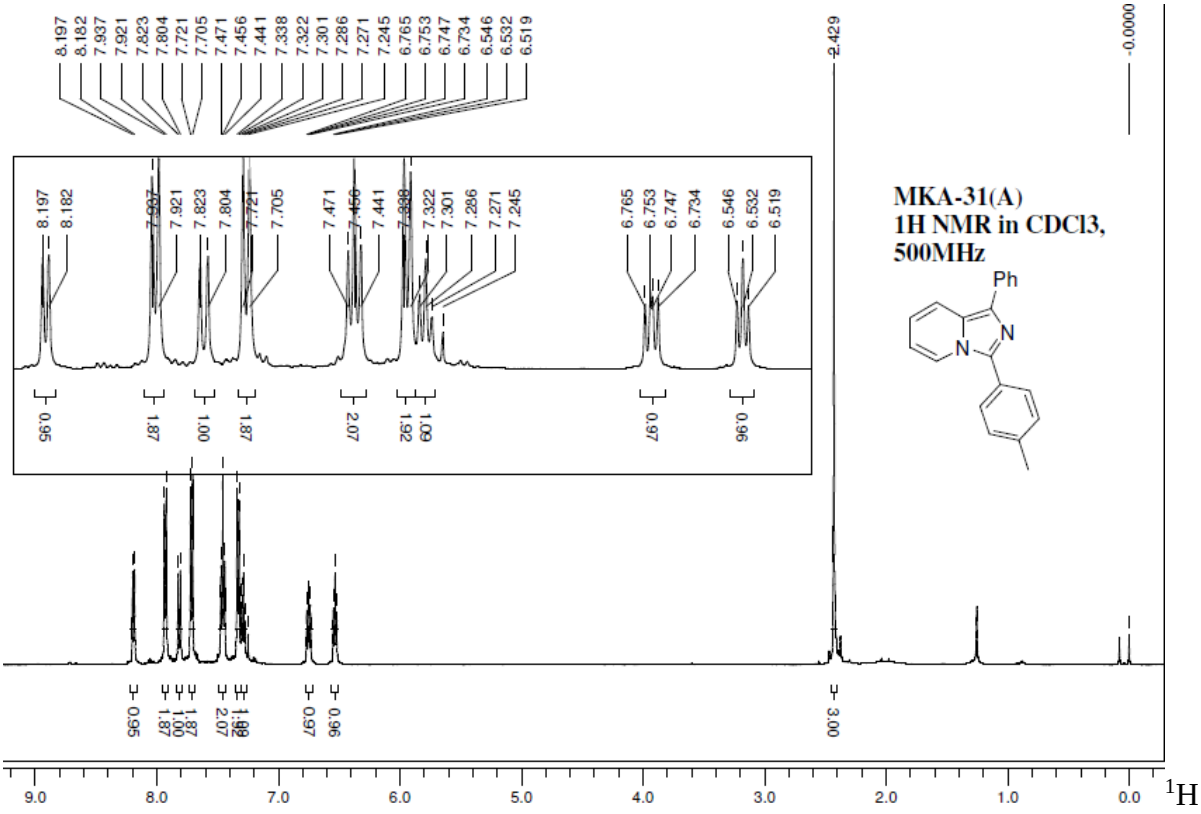
Copies of ^{1}H & ^{13}C NMR spectra



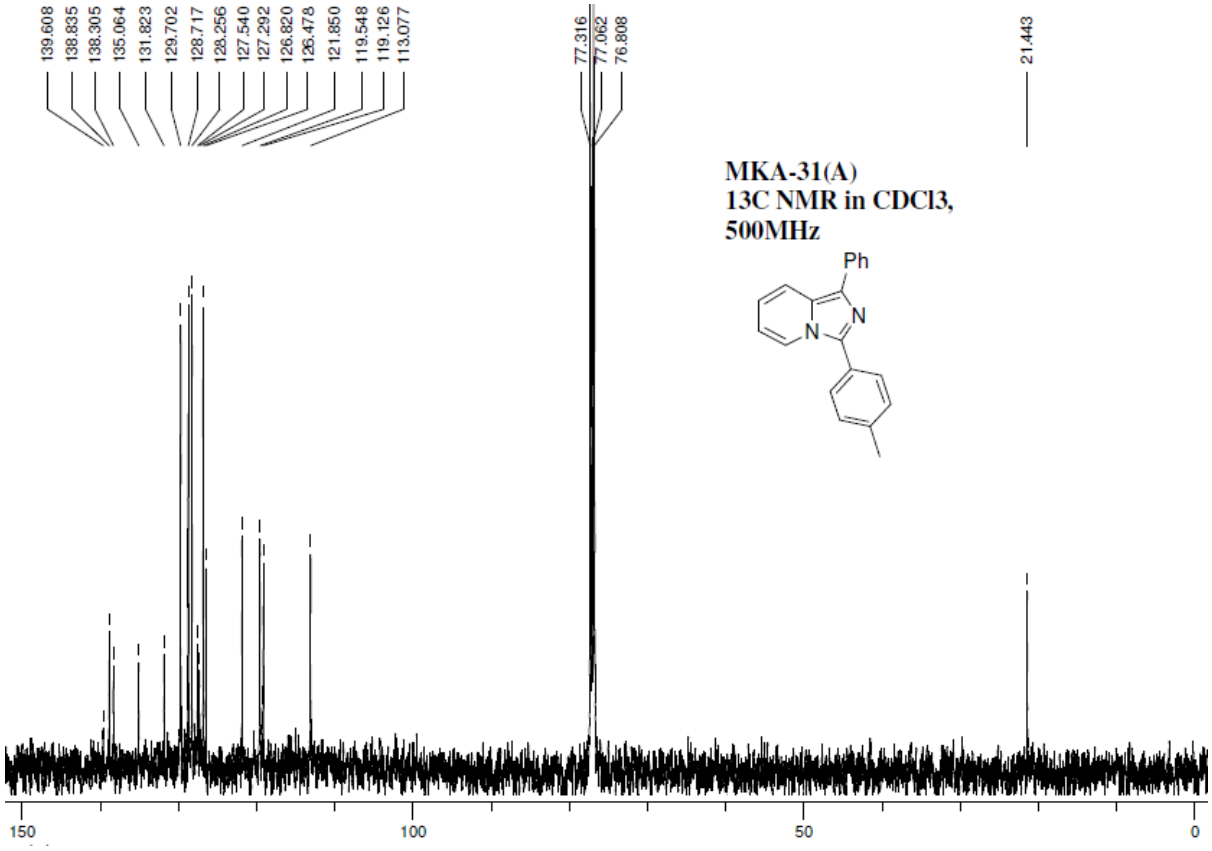
^{1}H NMR of **3a**



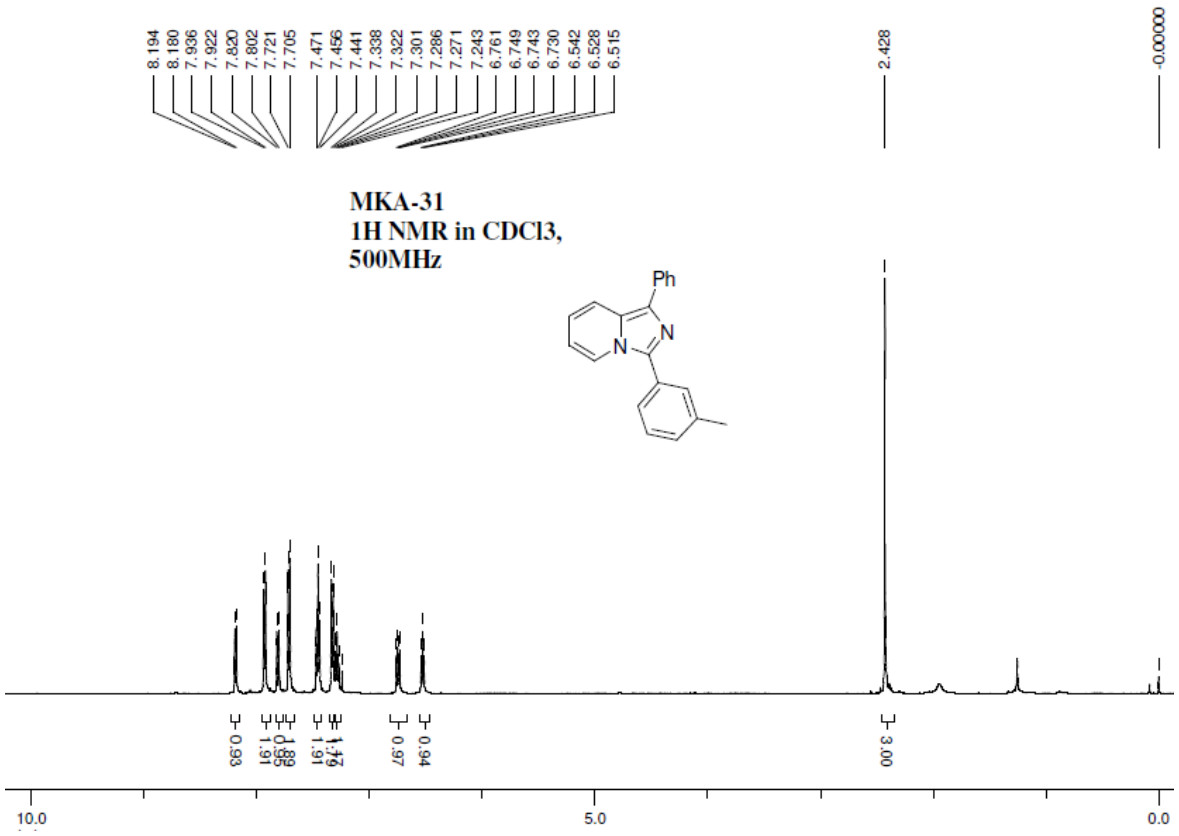
^{13}C NMR of **3a**



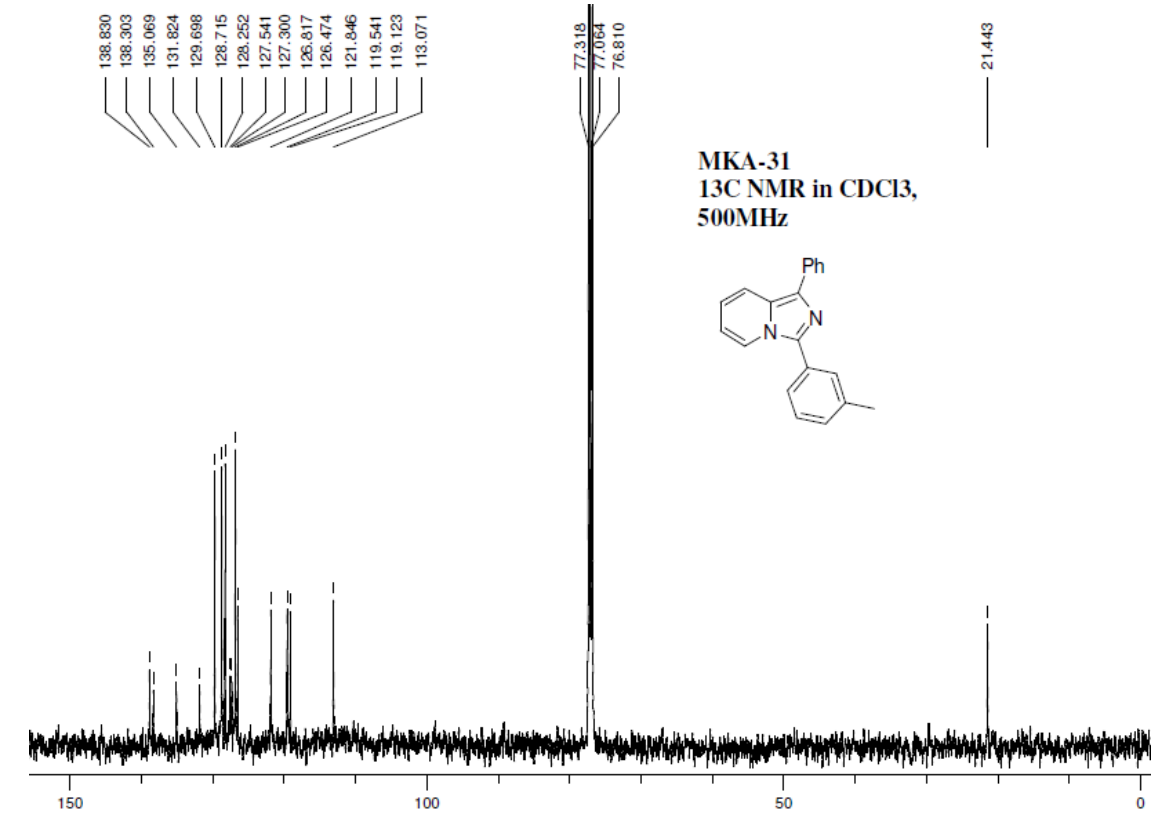
NMR of **3b**



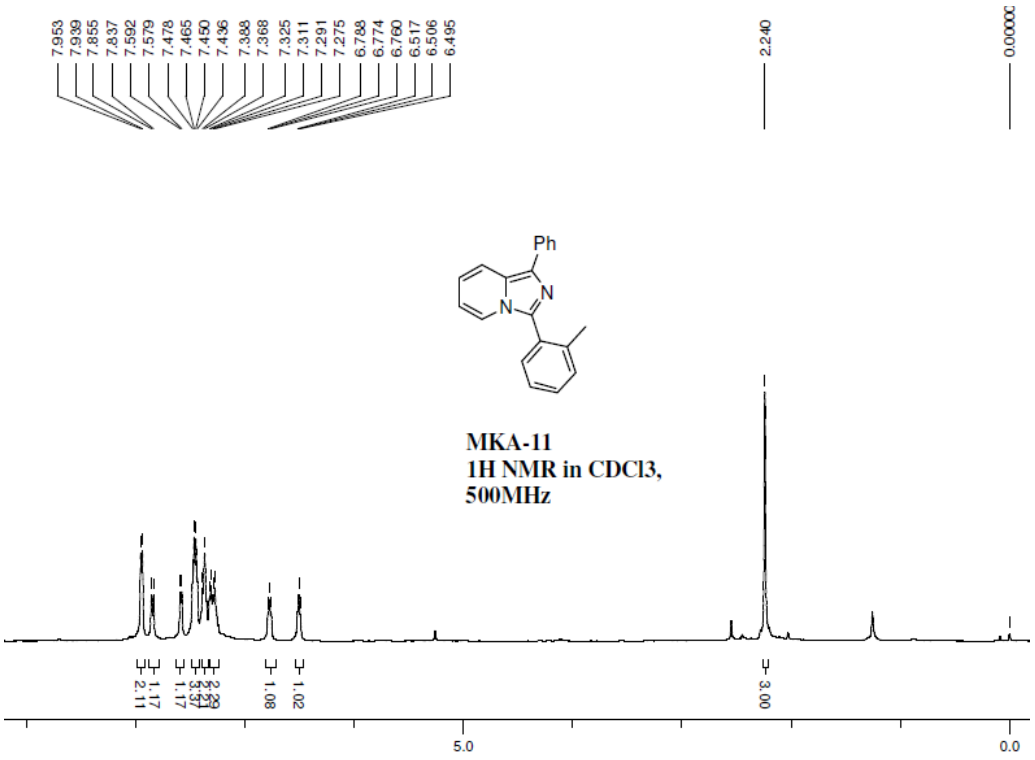
^{13}C NMR of **3b**



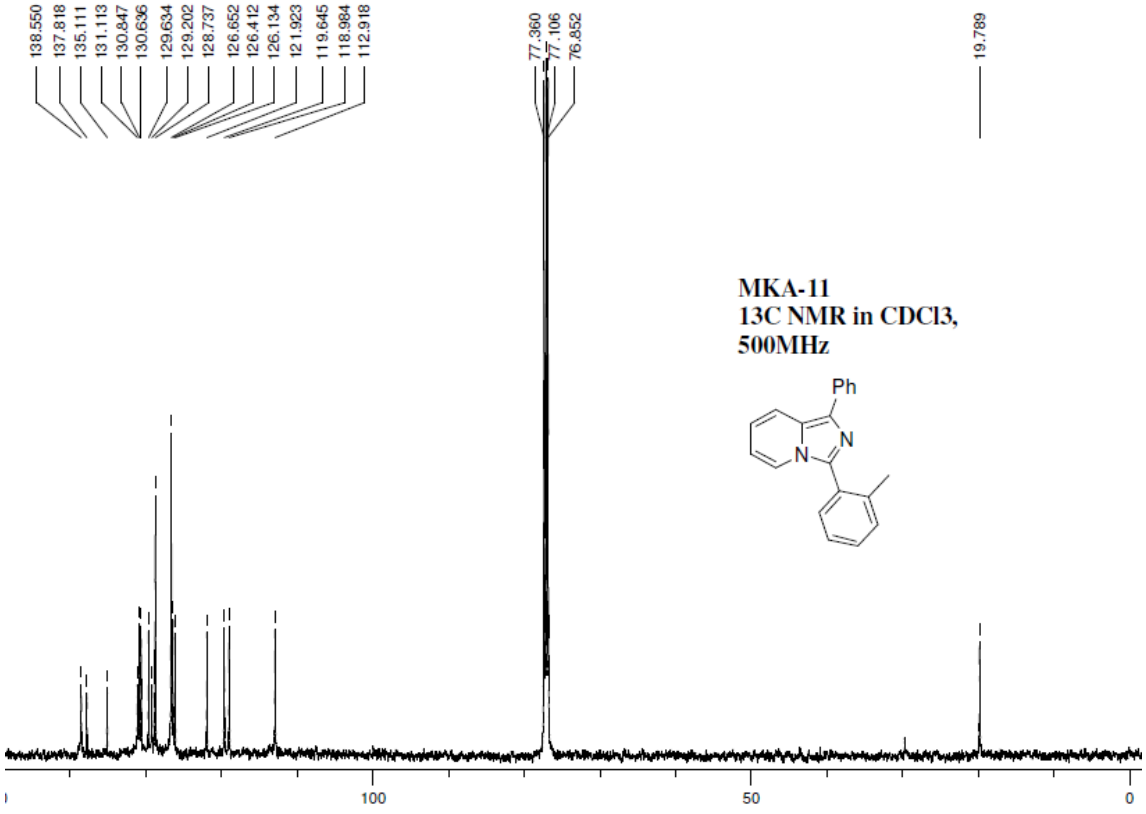
^{1}H NMR of **3c**



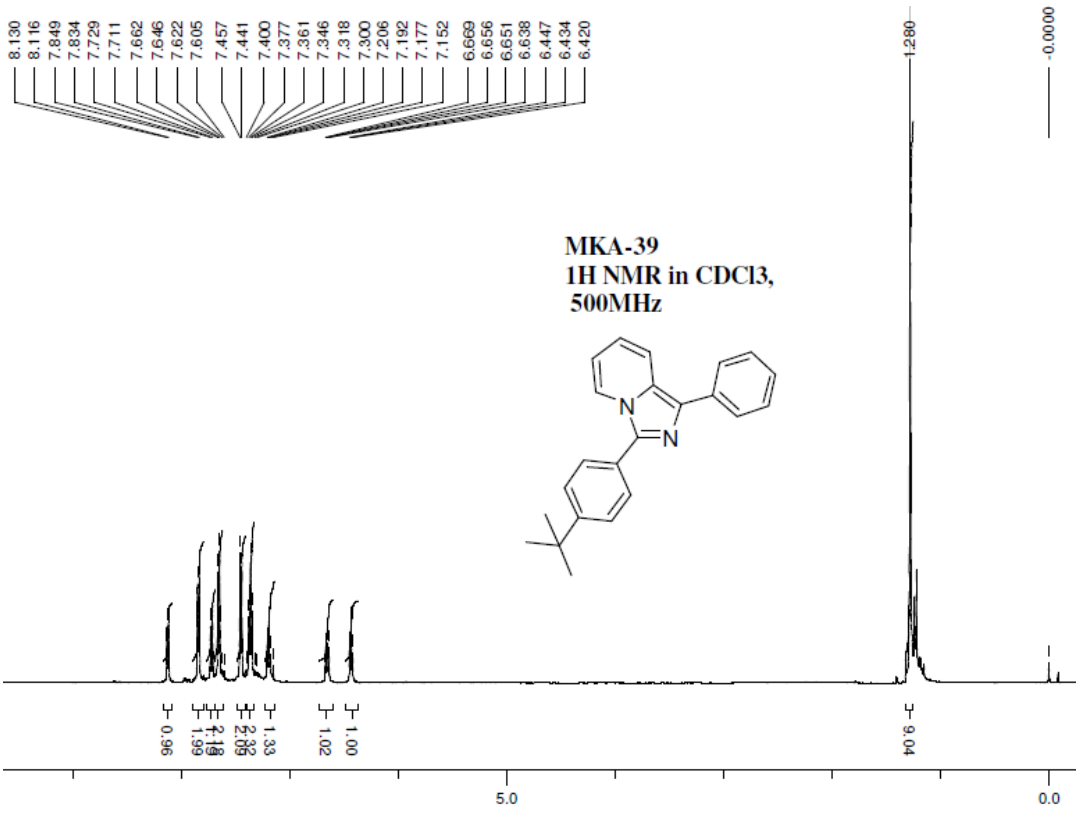
^{13}C NMR of **3c**



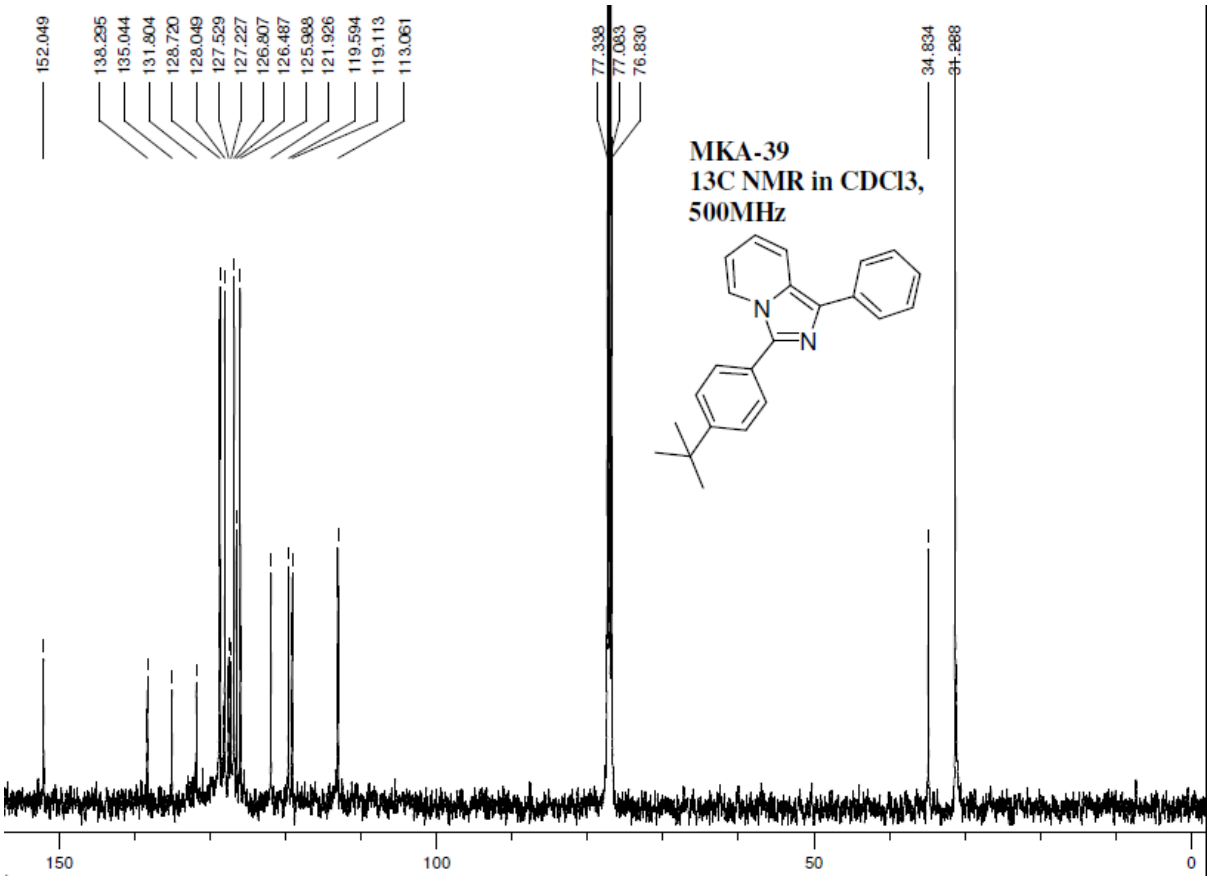
^{1}H NMR of **3d**



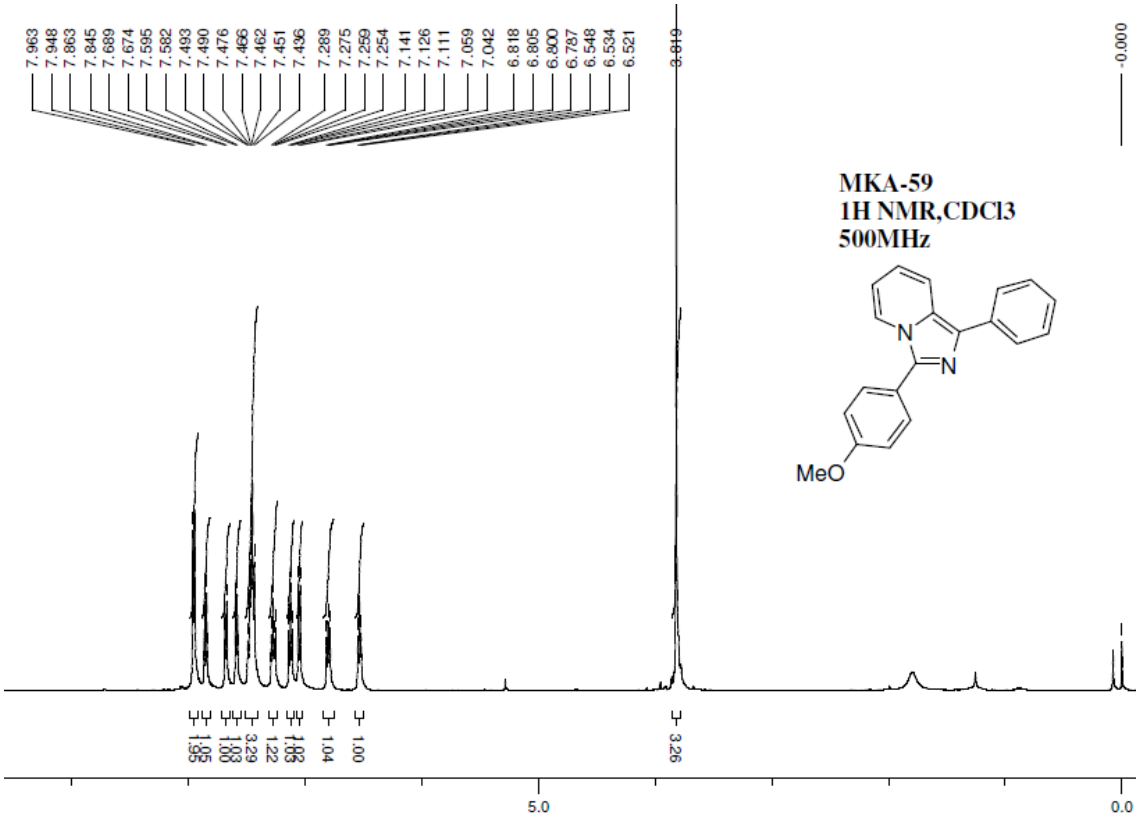
^{13}C NMR of **3d**



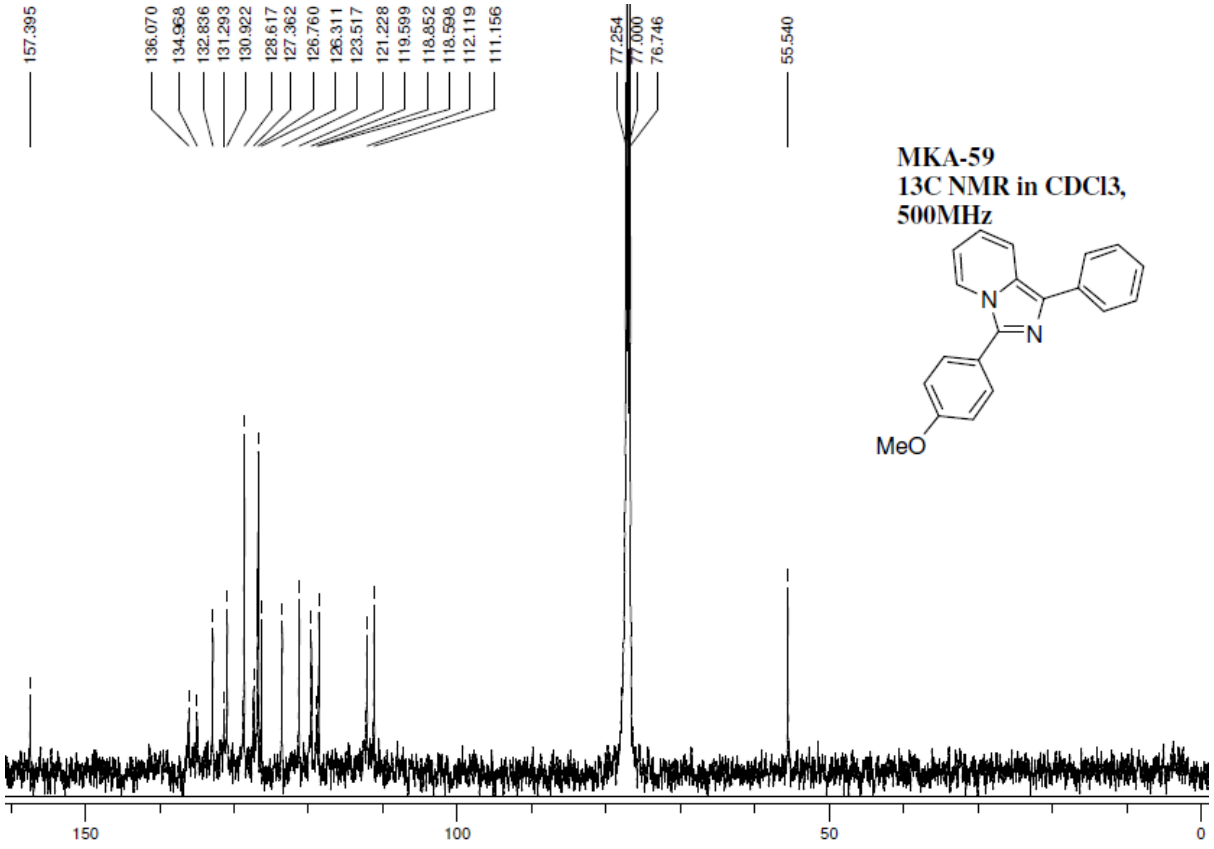
^{1}H NMR of **3e**



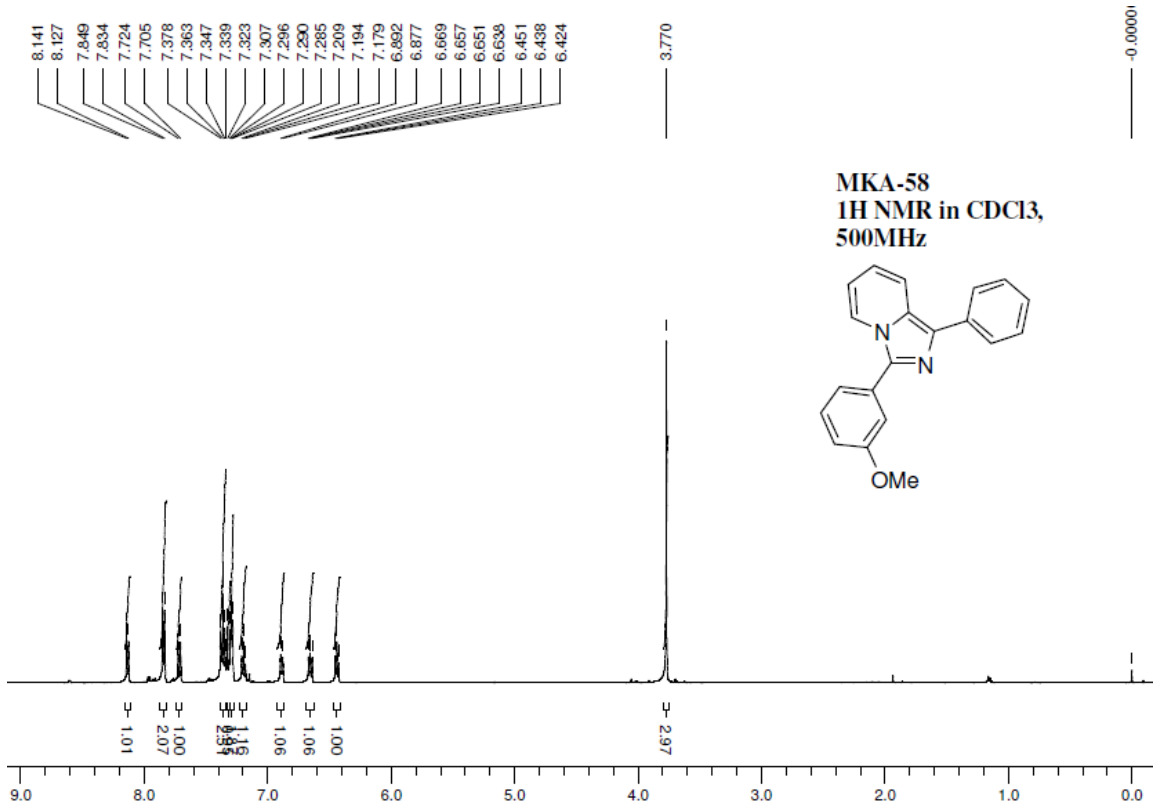
^{13}C NMR of **3e**



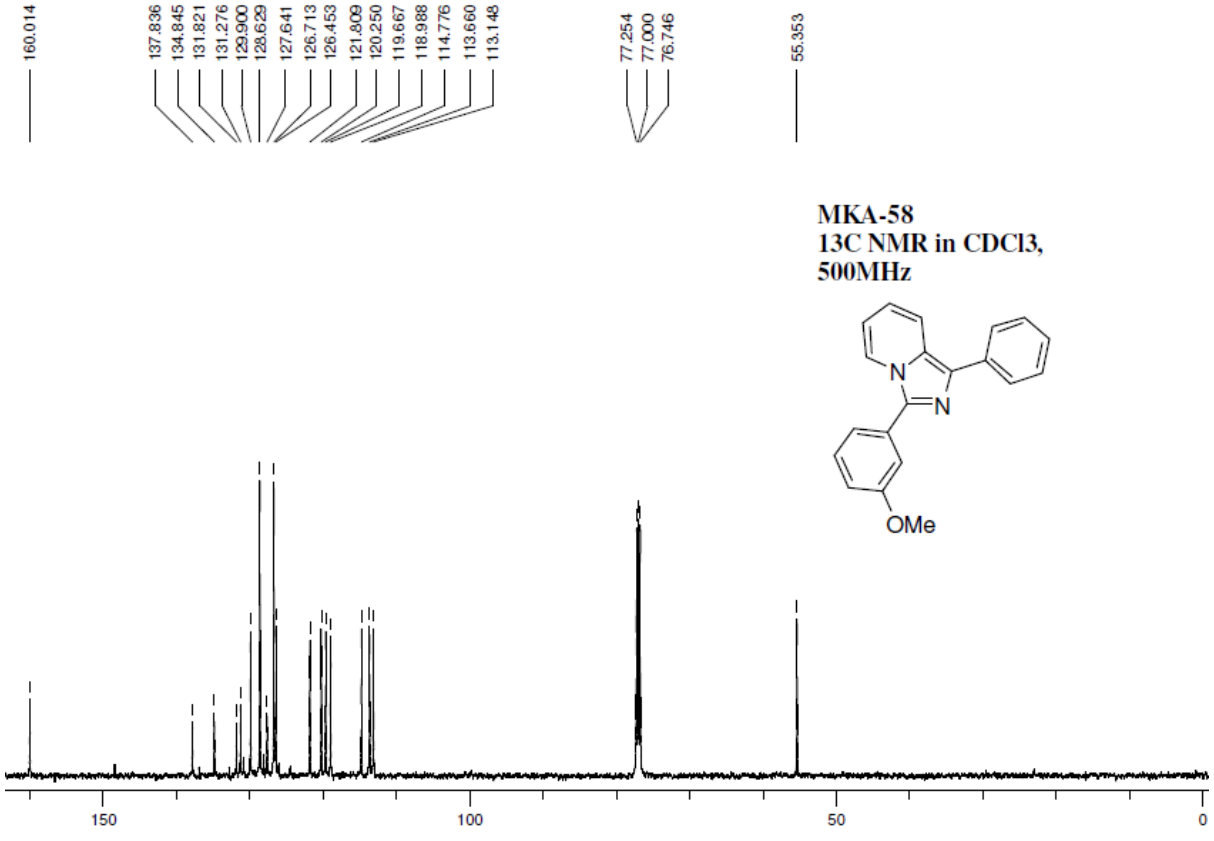
^{1}H NMR of **3f**



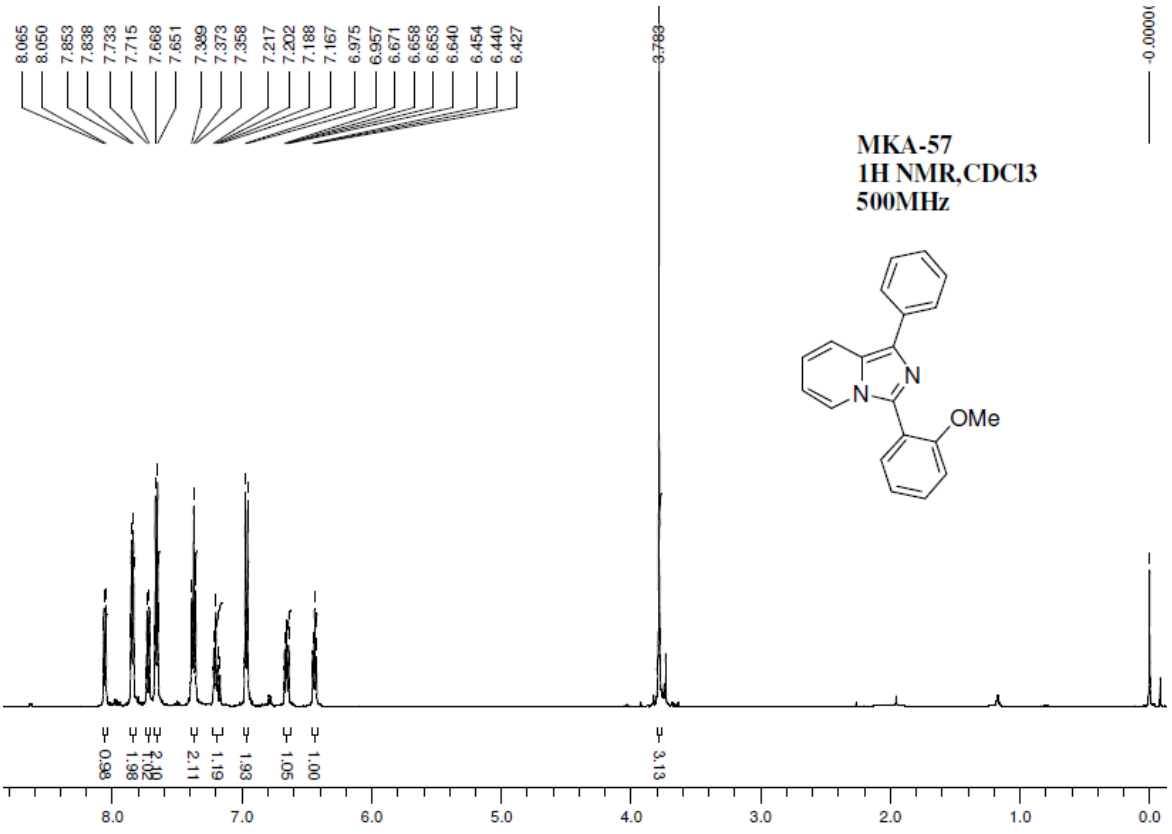
^{13}C NMR of **3f**



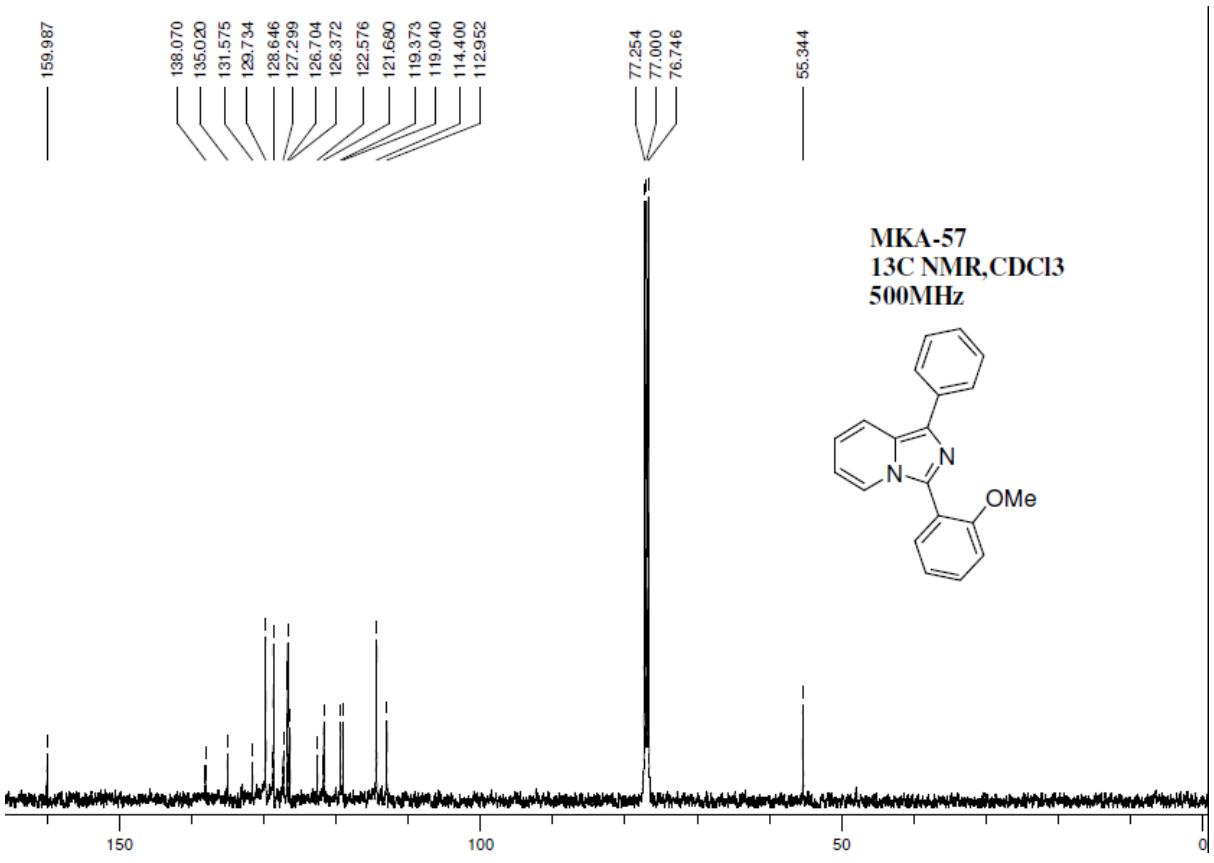
^{1}H NMR of **3g**



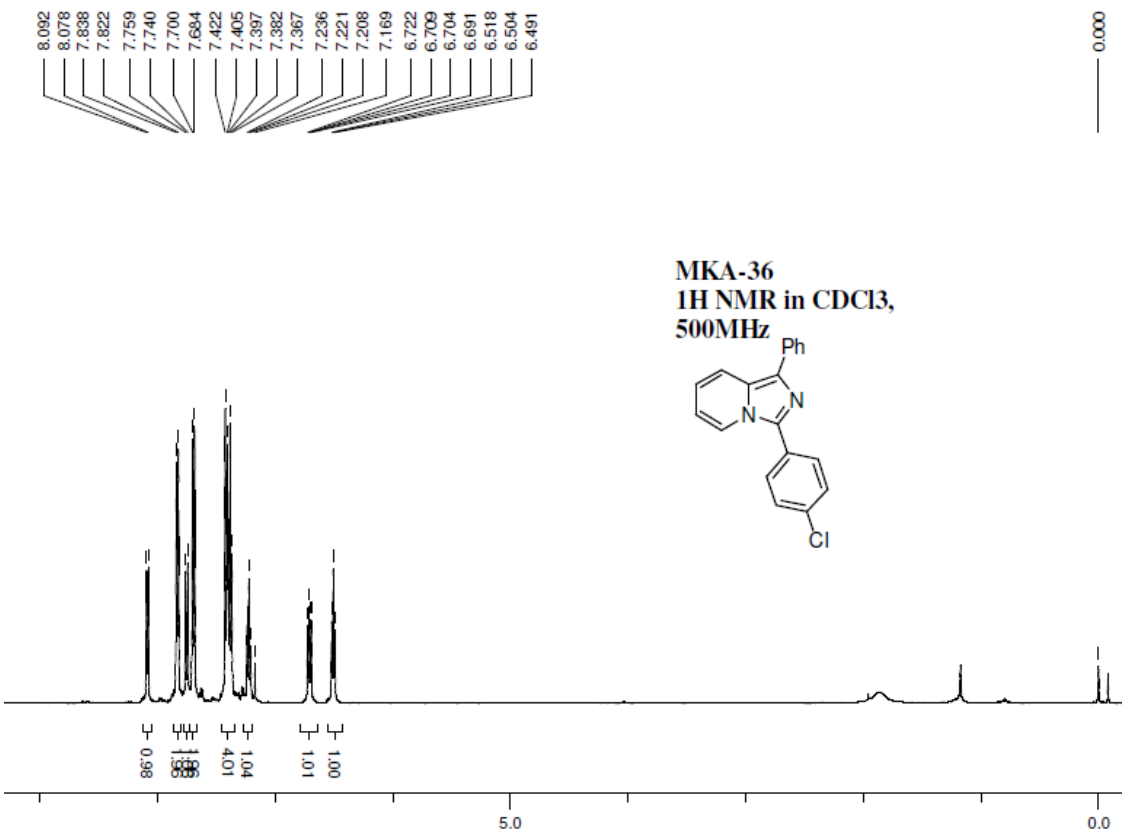
^{13}C NMR of **3g**



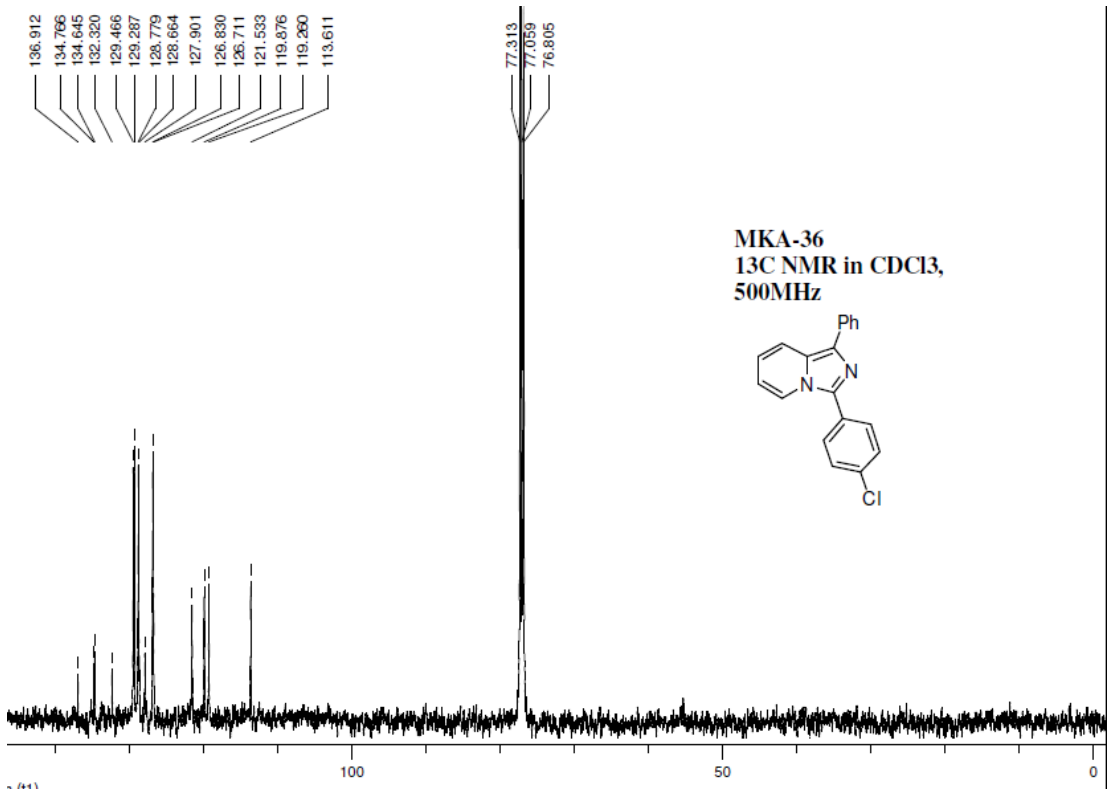
^{1}H NMR of **3h**



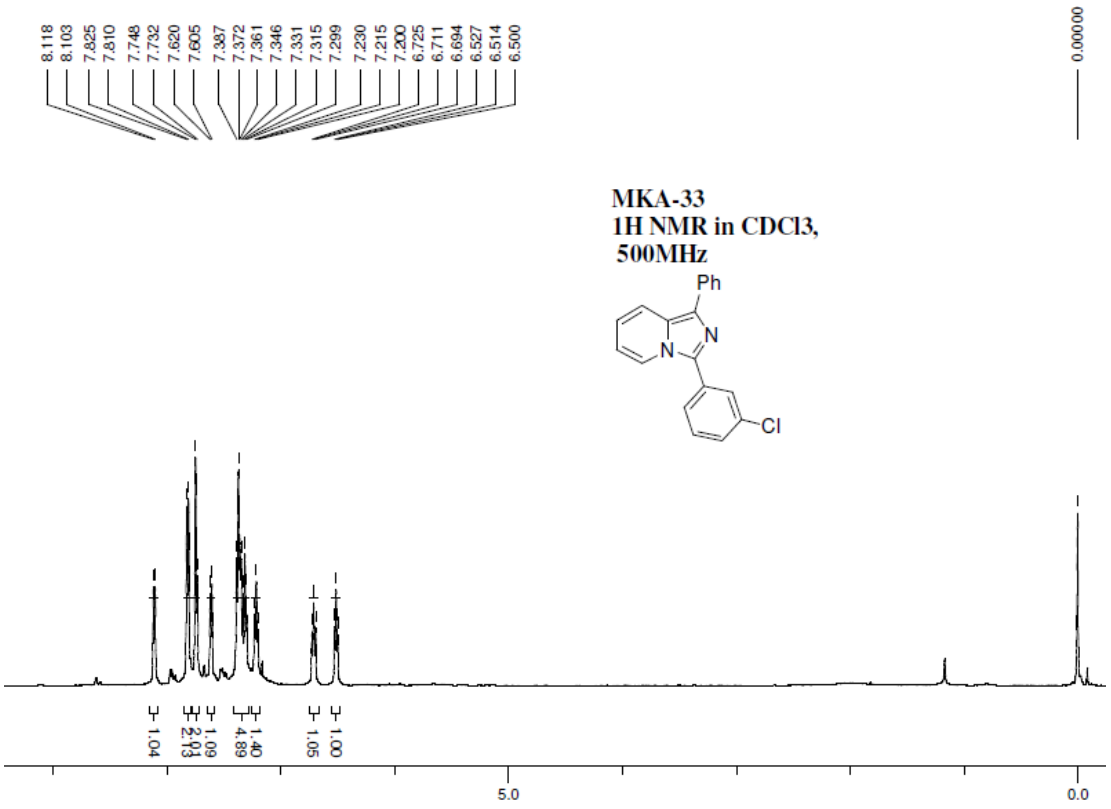
^{13}C NMR of **3h**



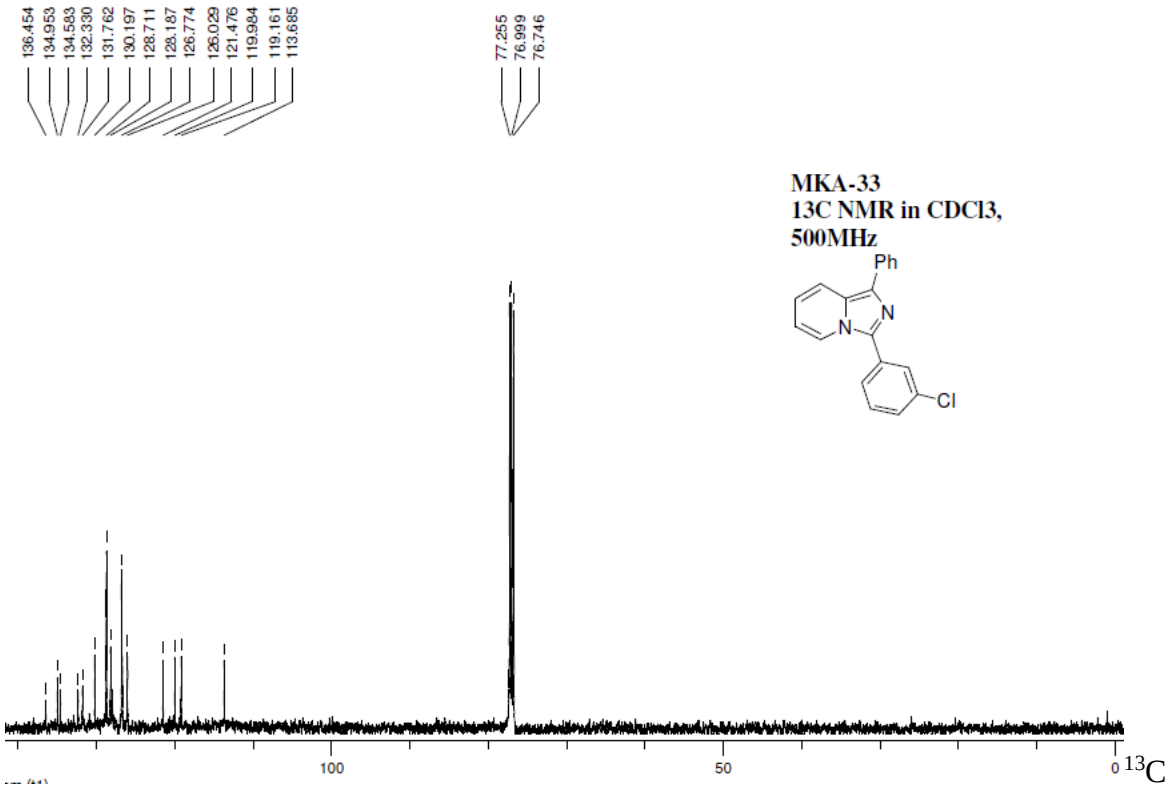
^{1}H NMR of **3i**



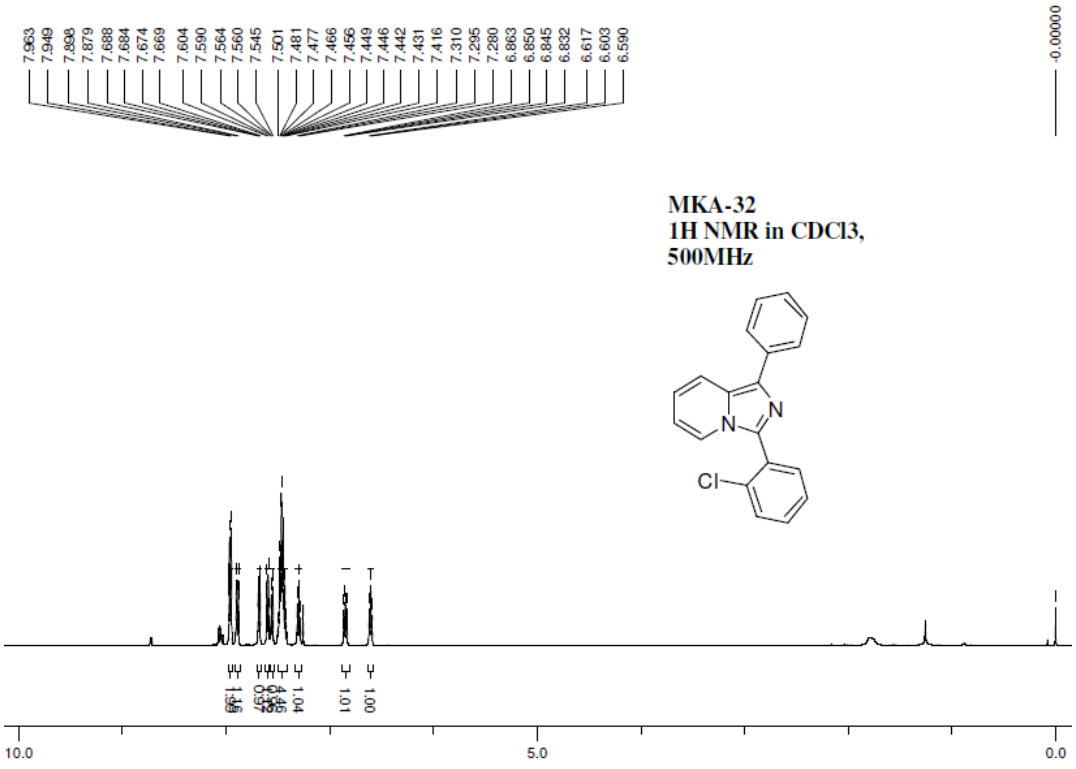
^{13}C NMR of **3i**



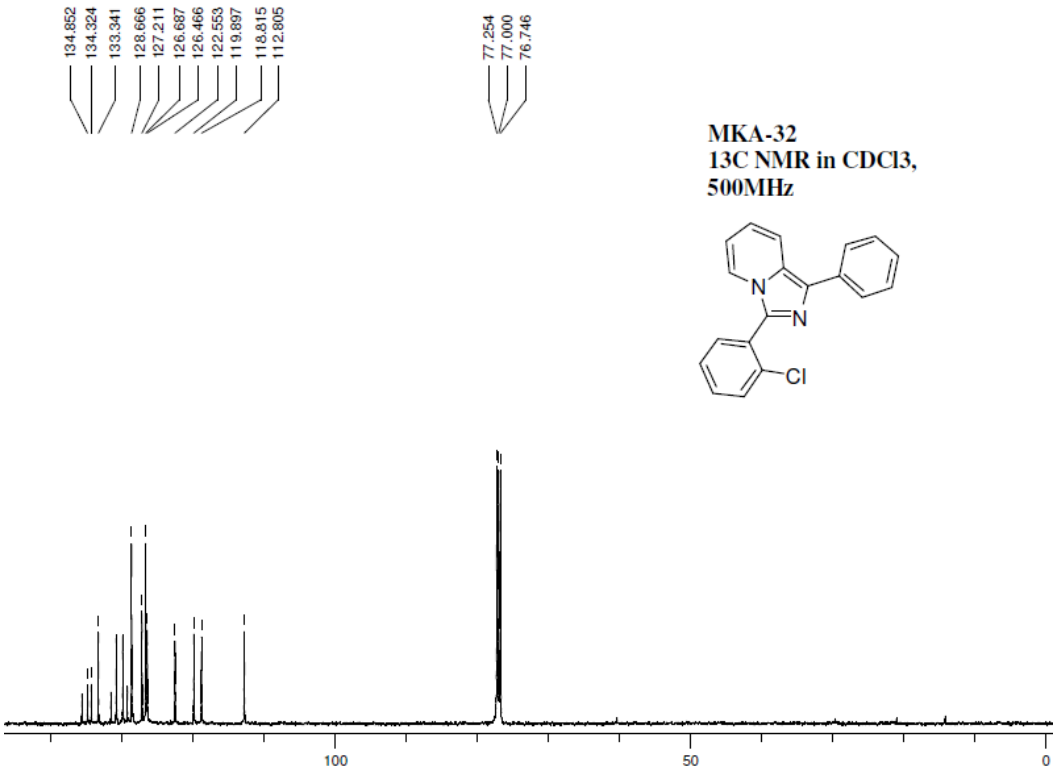
^{1}H NMR of **3j**



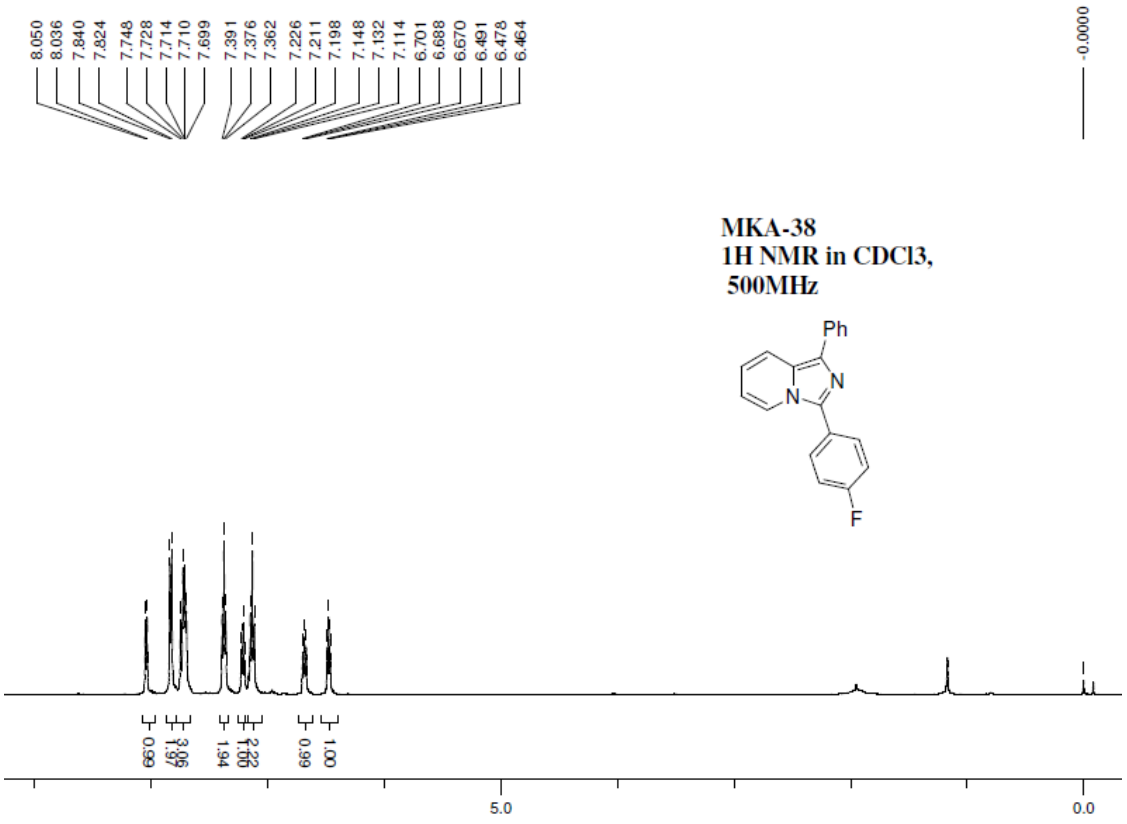
NMR of **3j**



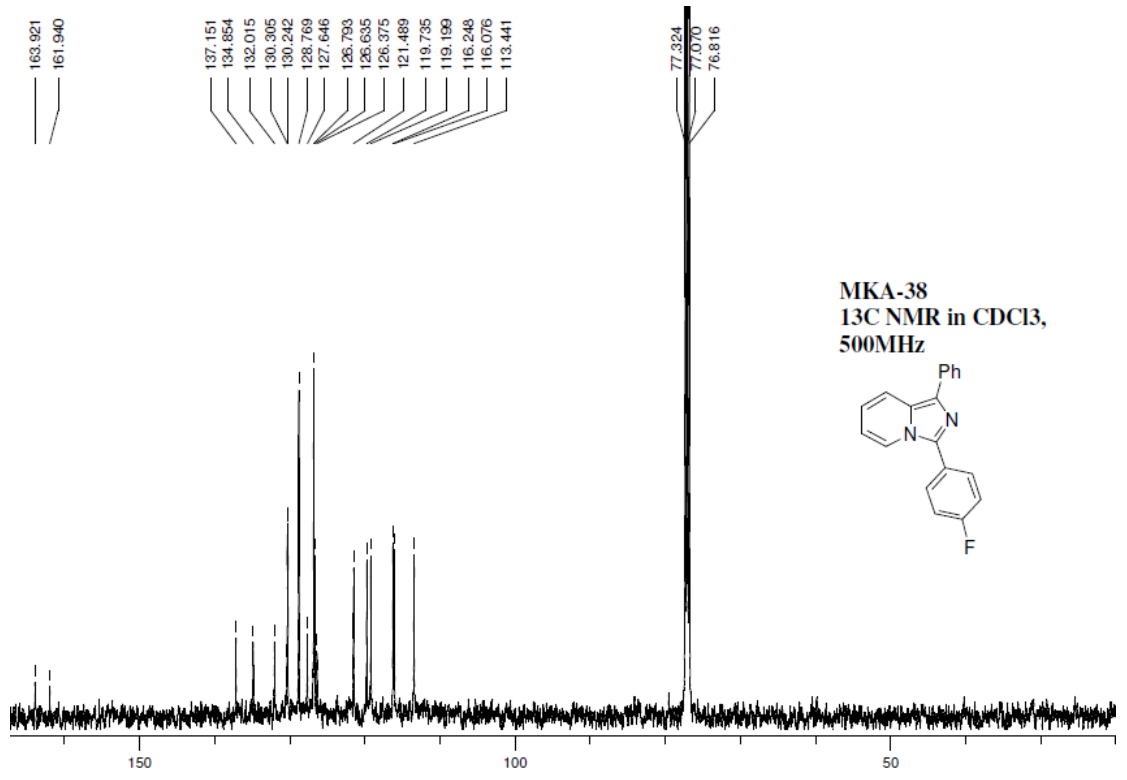
^{1}H NMR of **3k**



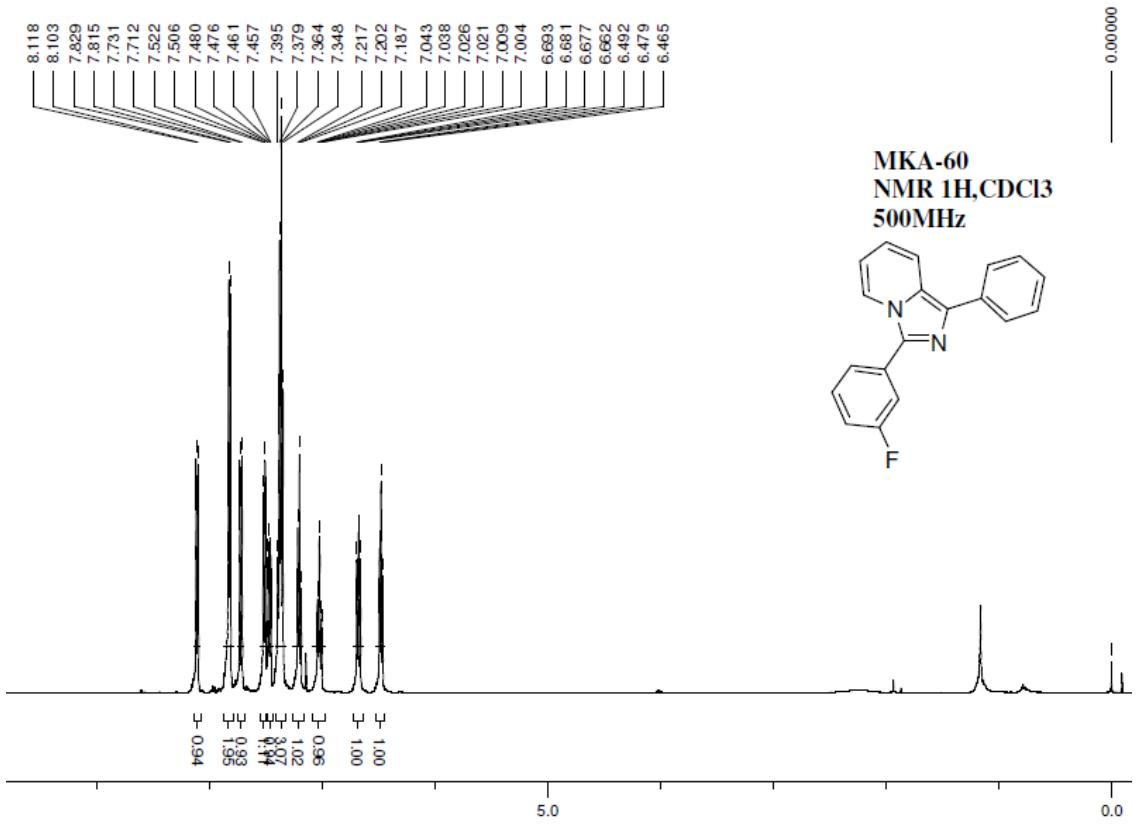
^{13}C NMR of **3k**



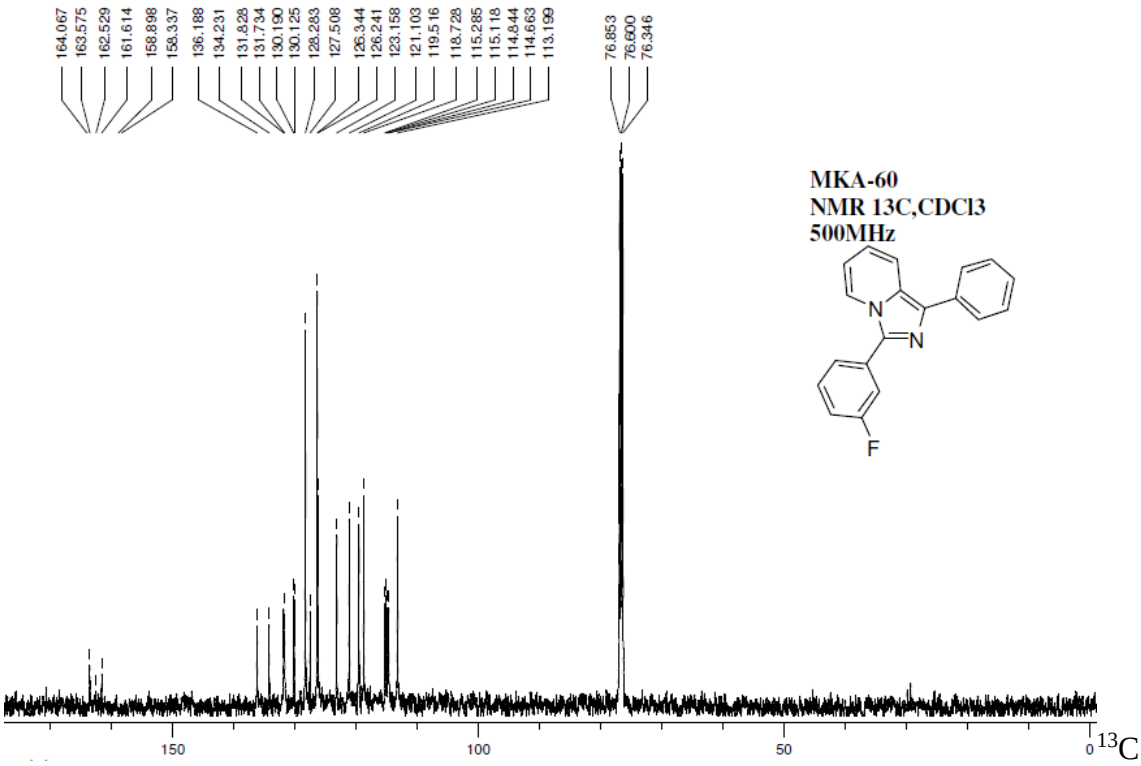
1H NMR of **3l**



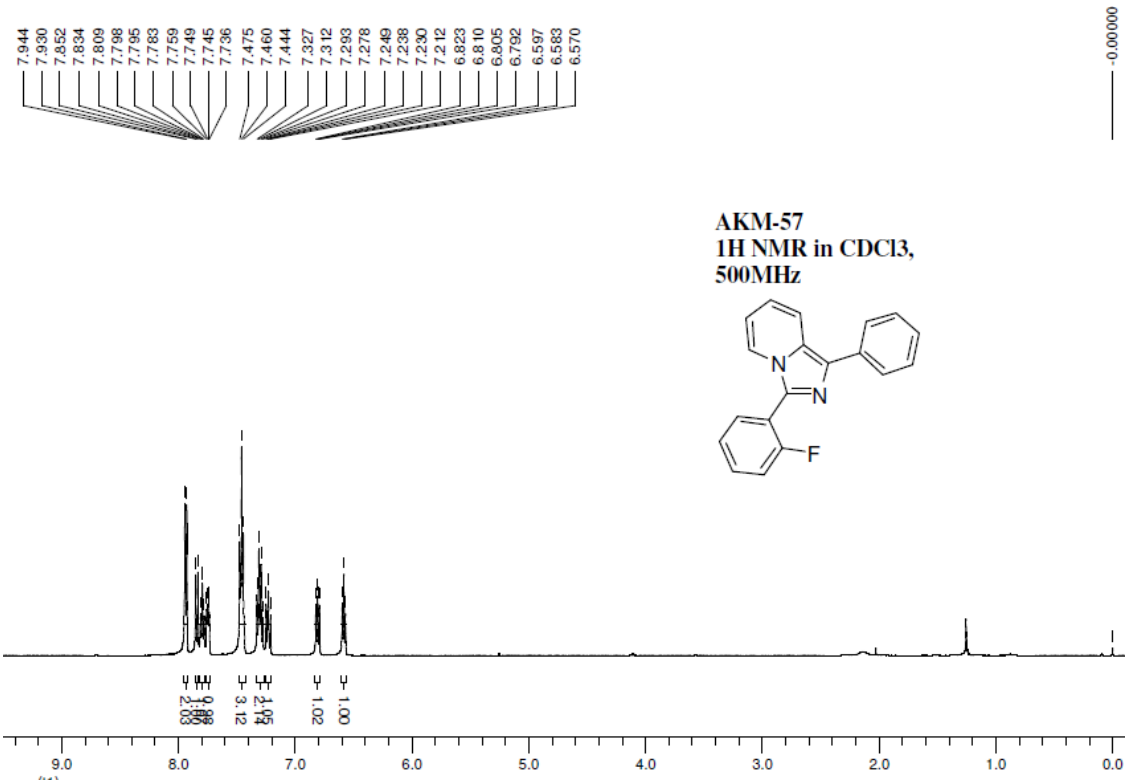
^{13}C NMR of **3l**



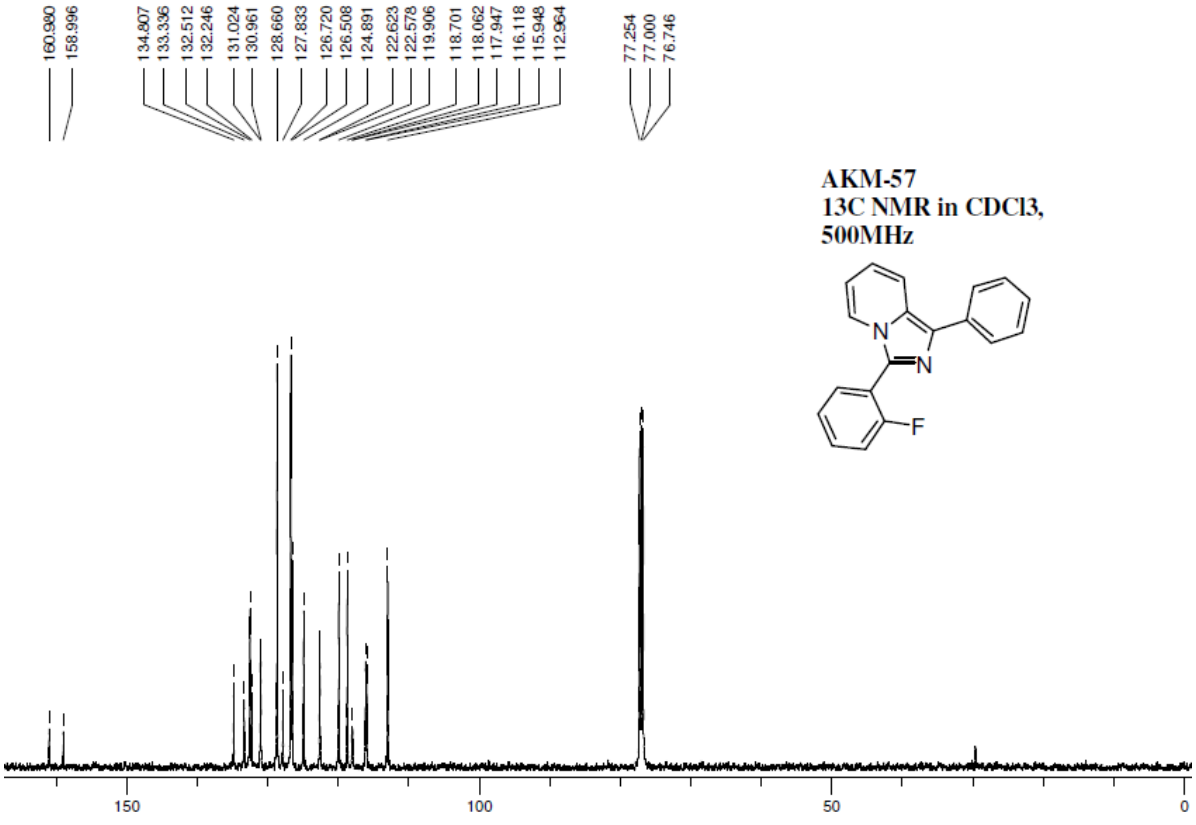
^{1}H NMR of **3m**



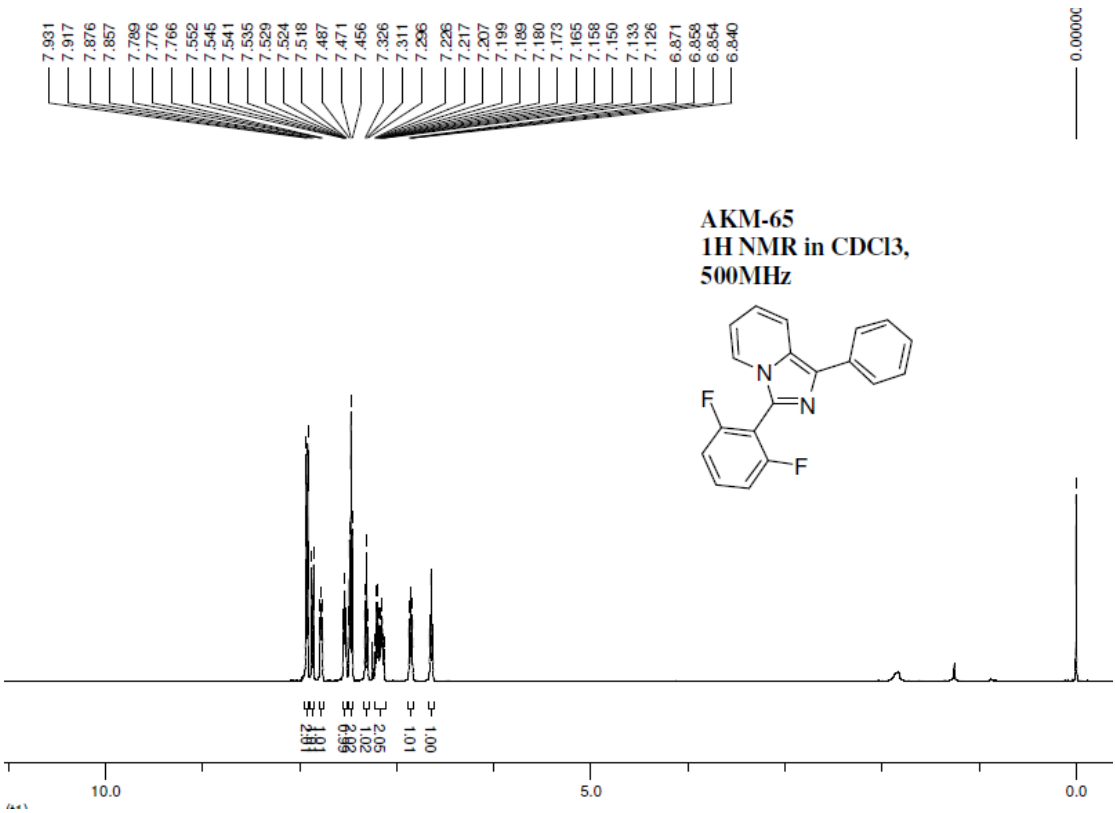
NMR of **3m**



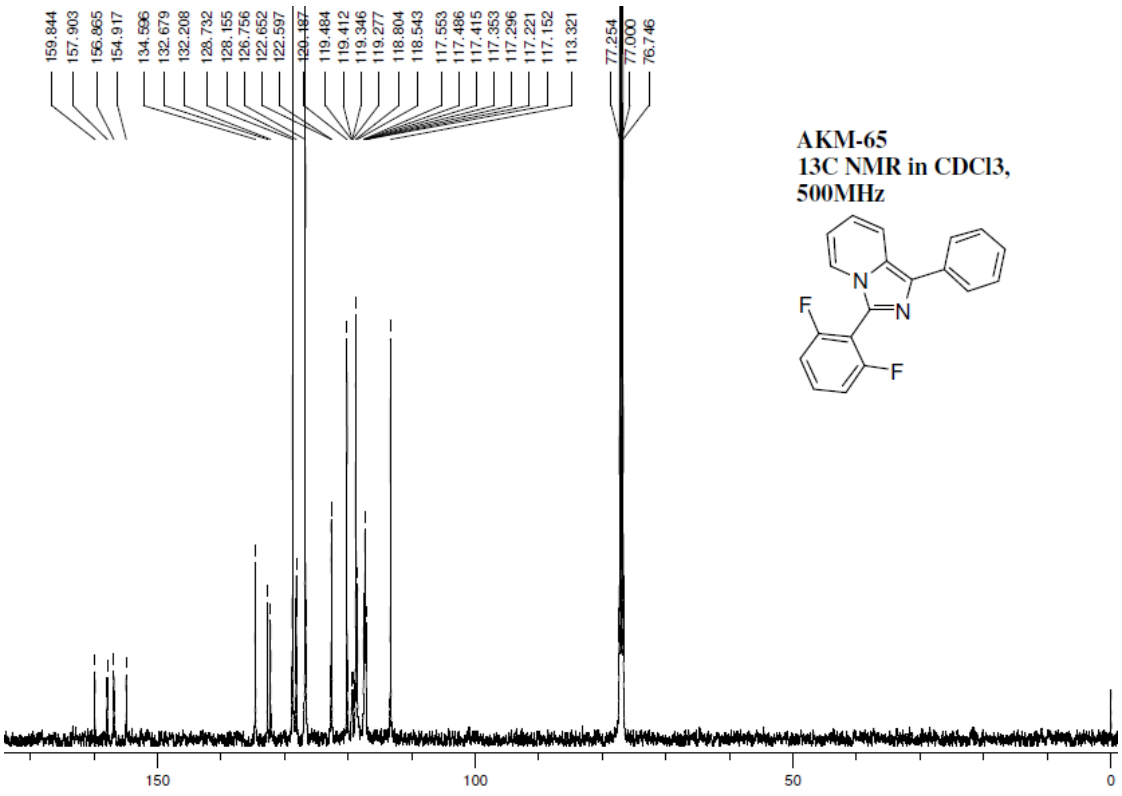
^{1}H NMR of **3n**



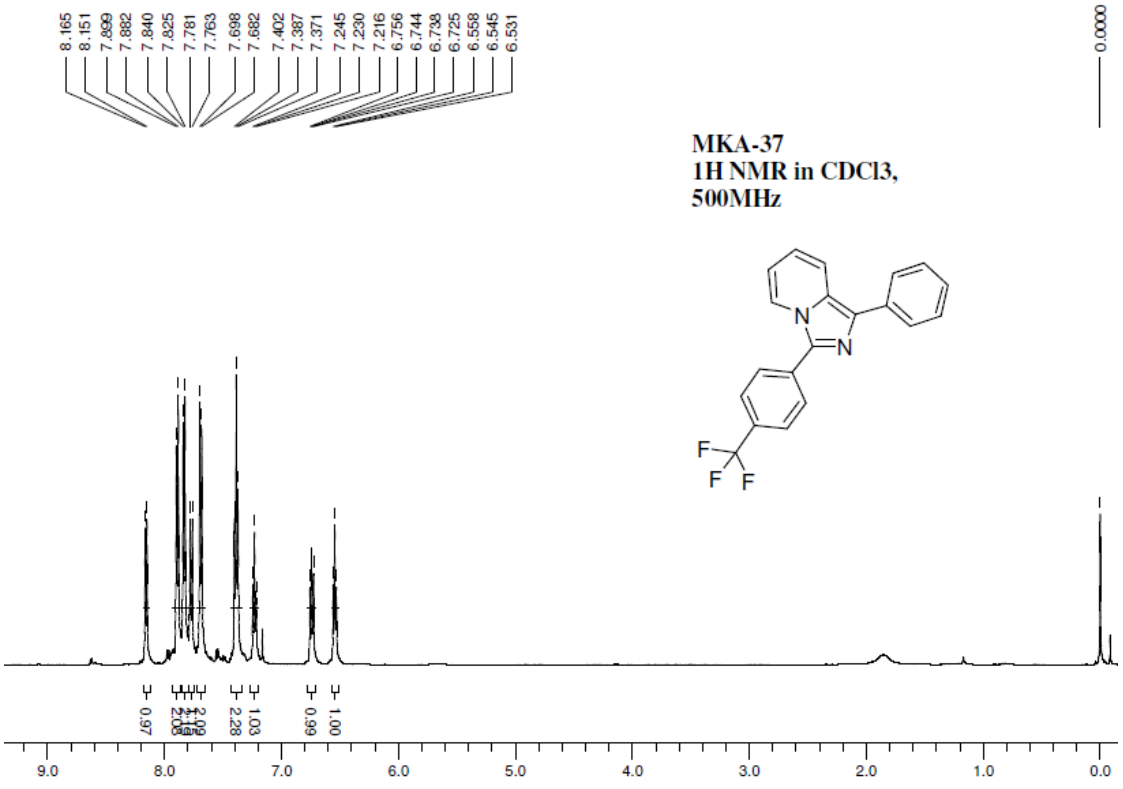
^{13}C NMR of **3n**



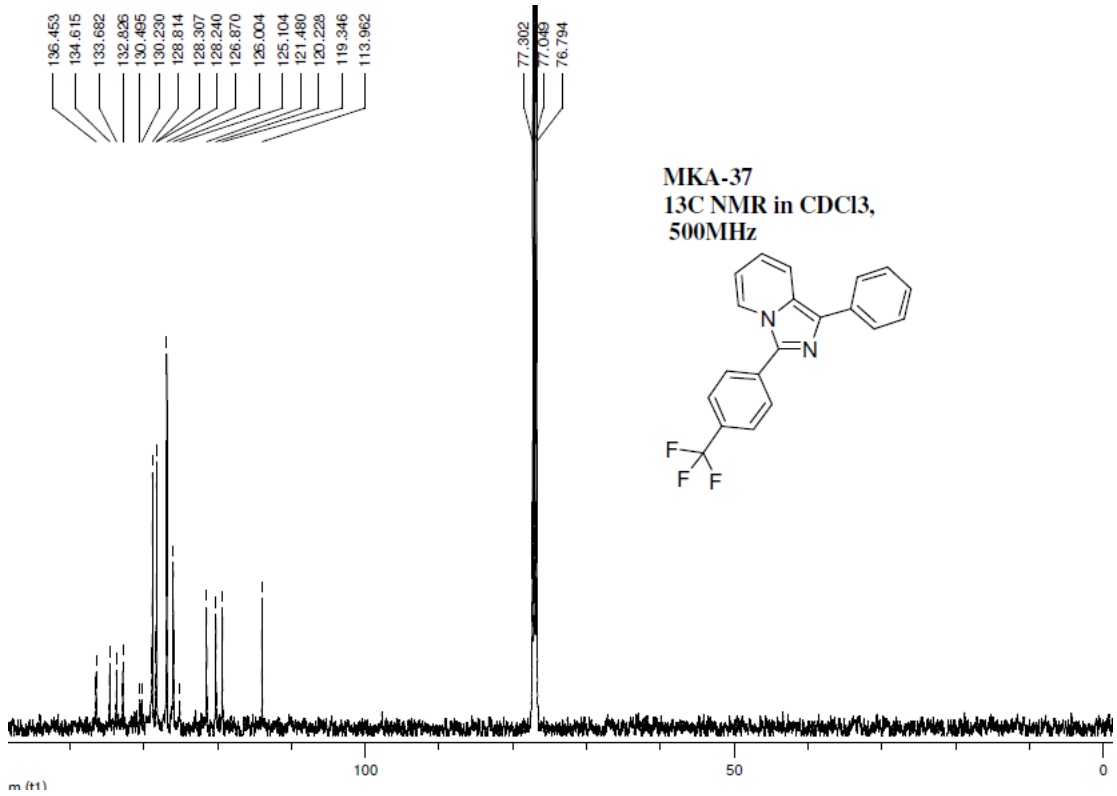
^{1}H NMR of **3o**



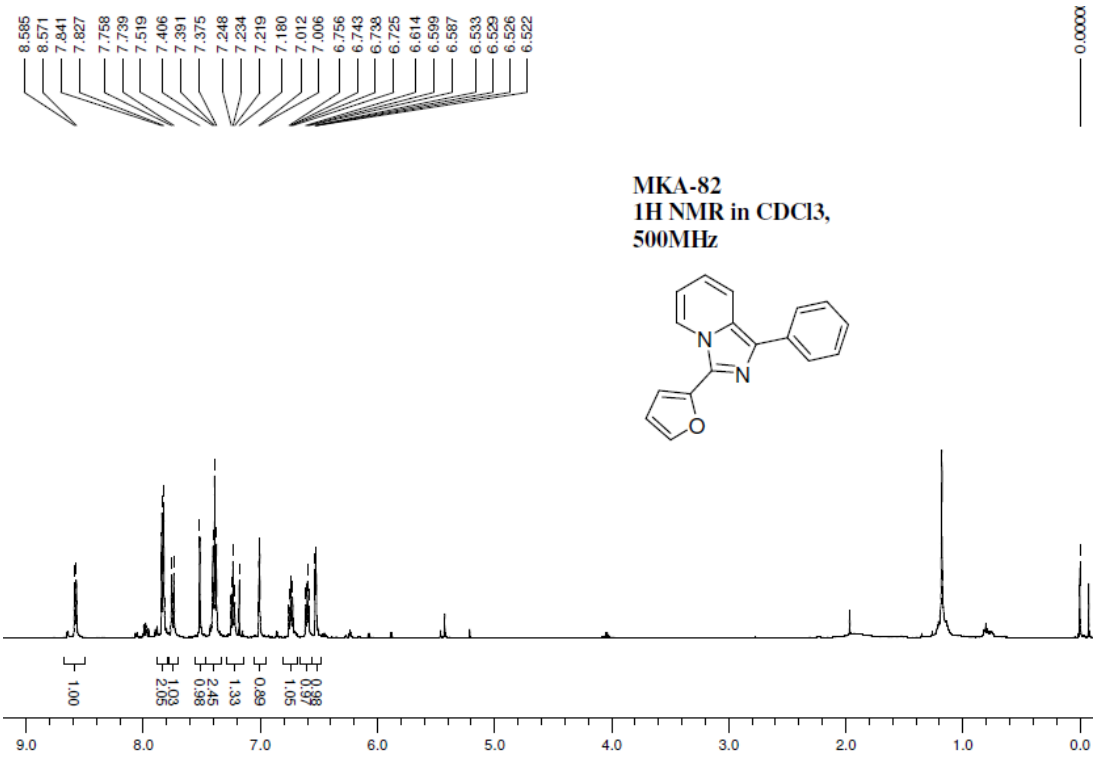
^{13}C NMR of **3o**



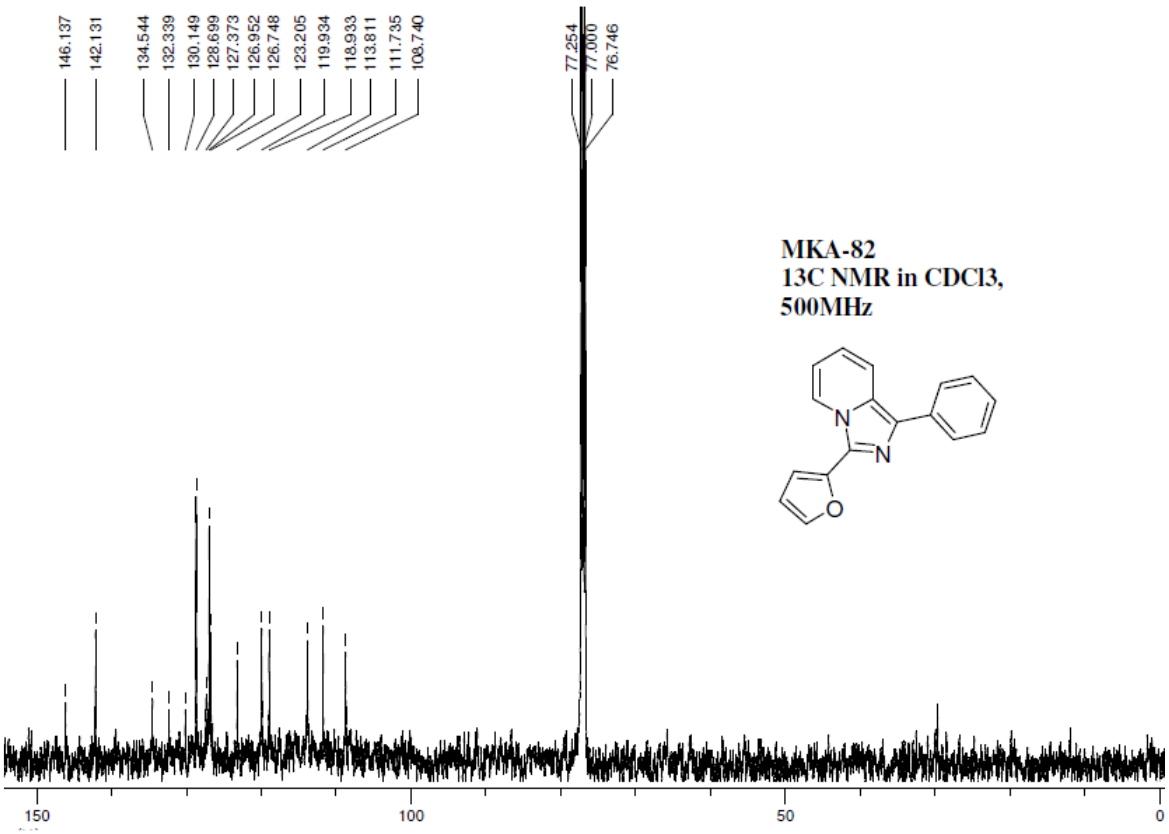
^{1}H NMR of **3p**



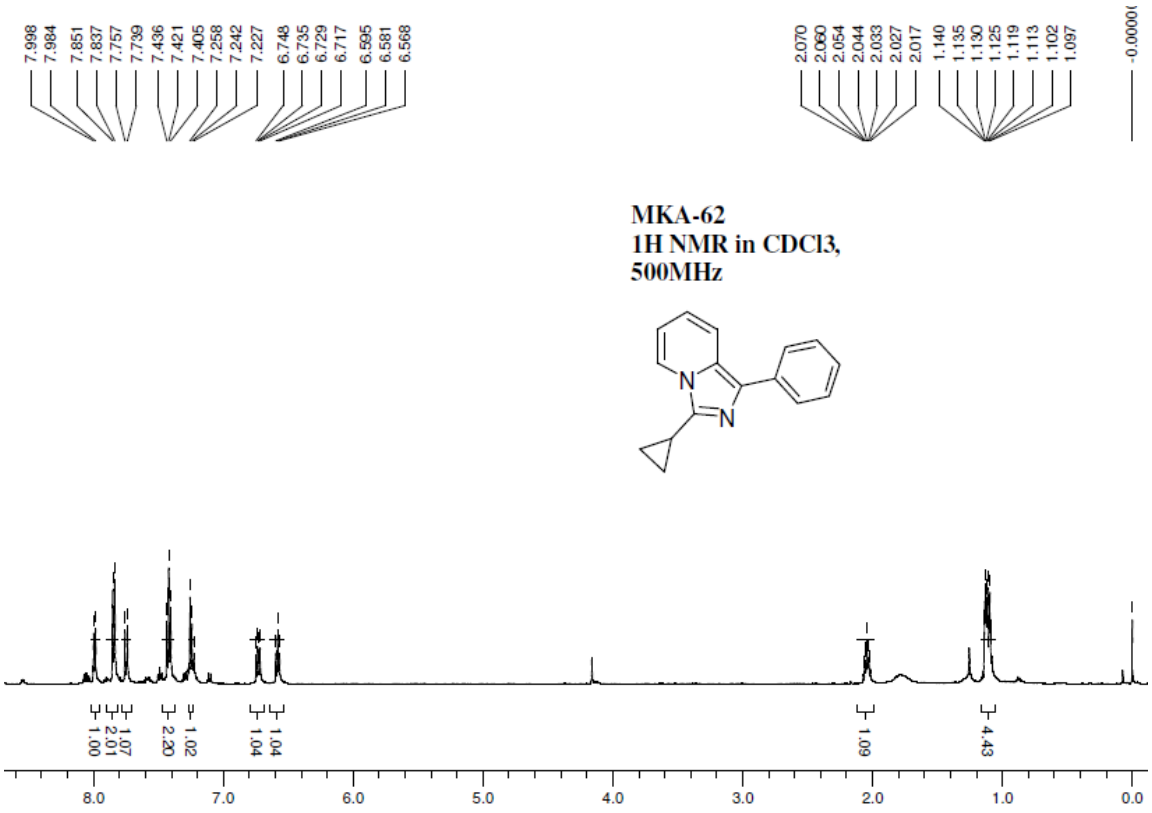
^{13}C NMR of **3p**



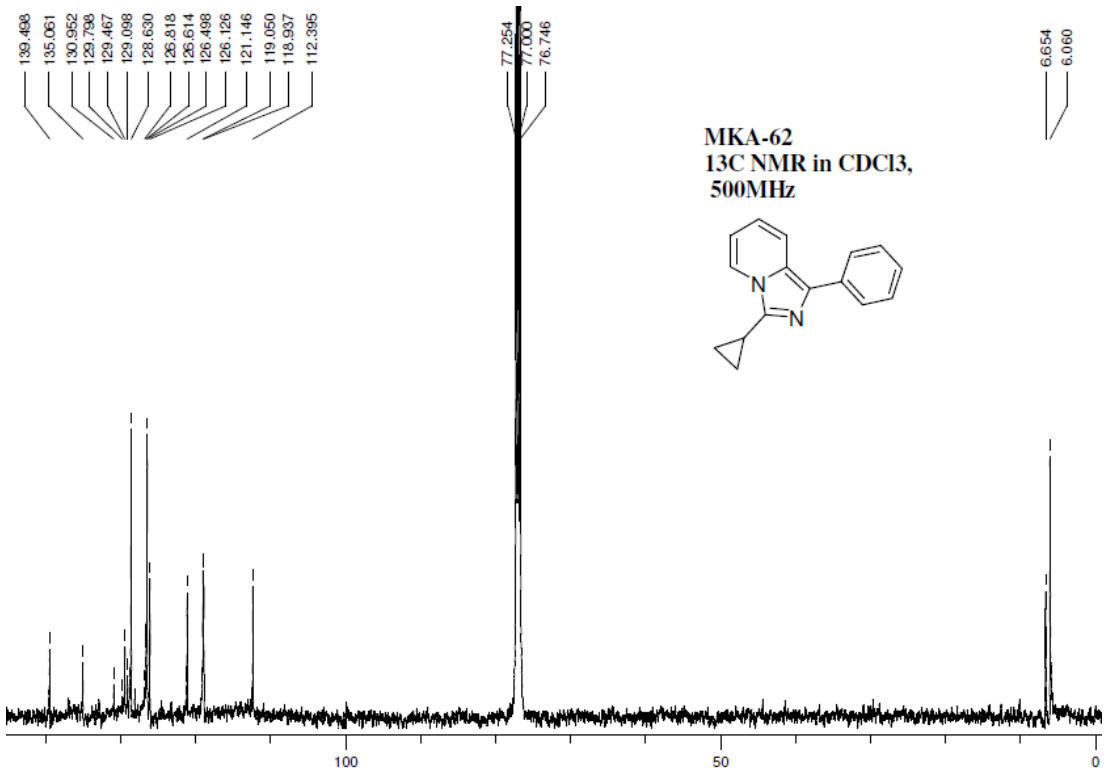
^{1}H NMR of **3q**



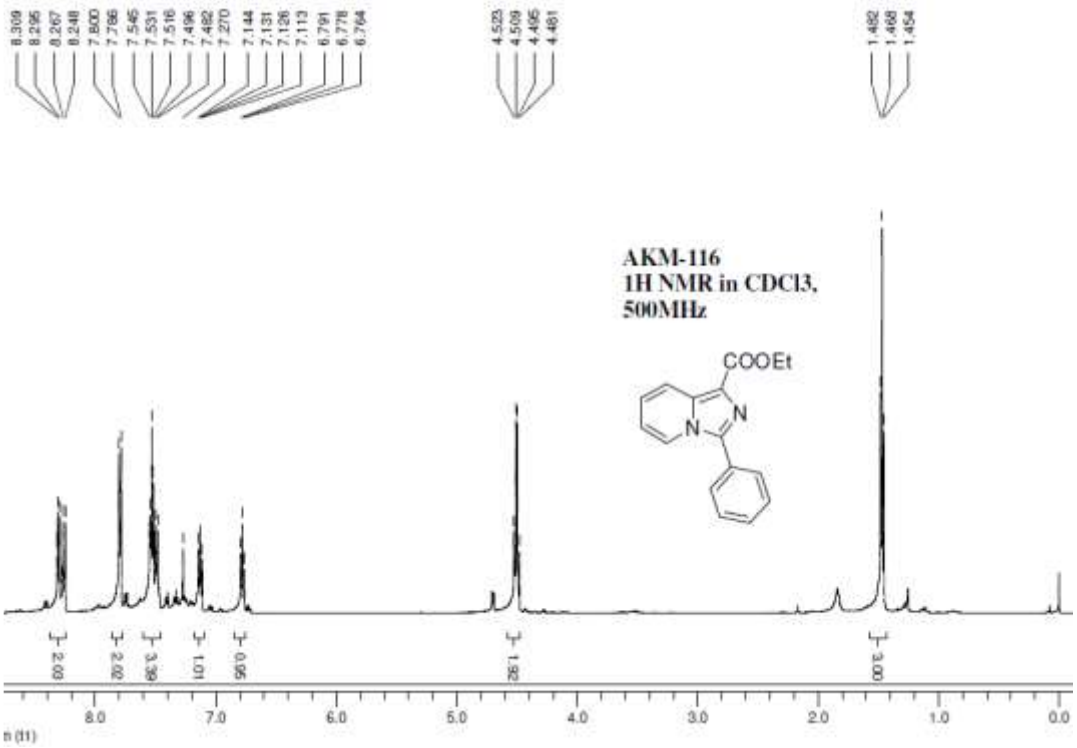
^{13}C NMR of **3q**



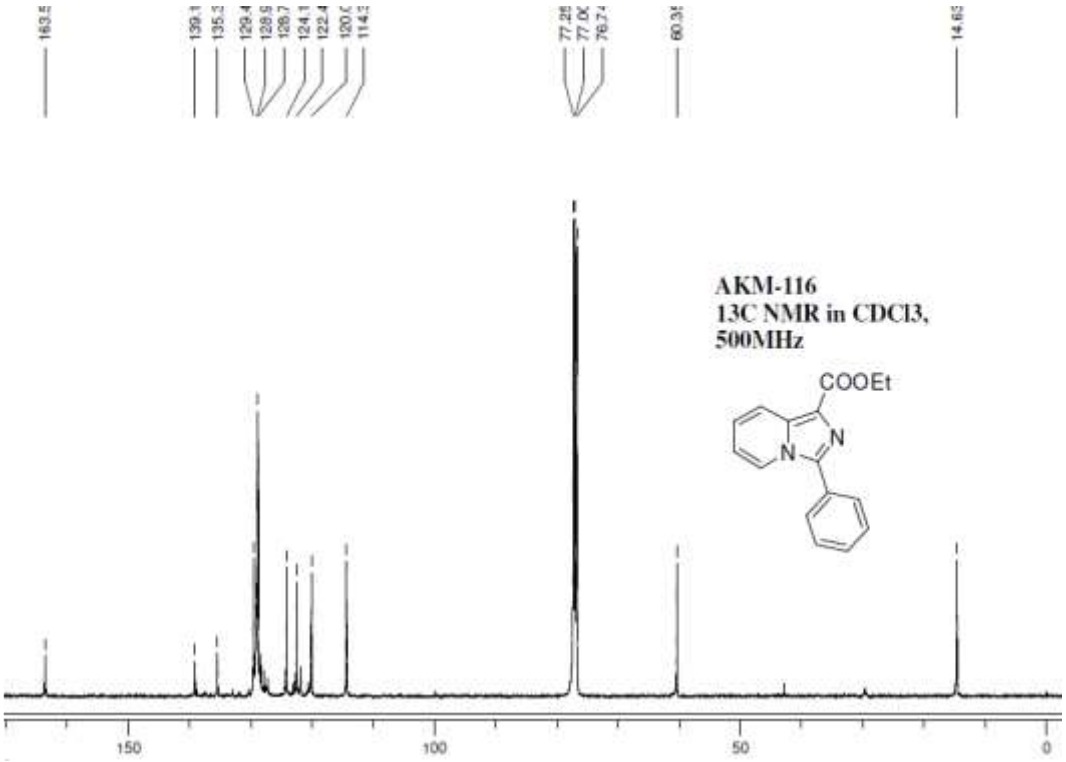
^{1}H NMR of **3s**



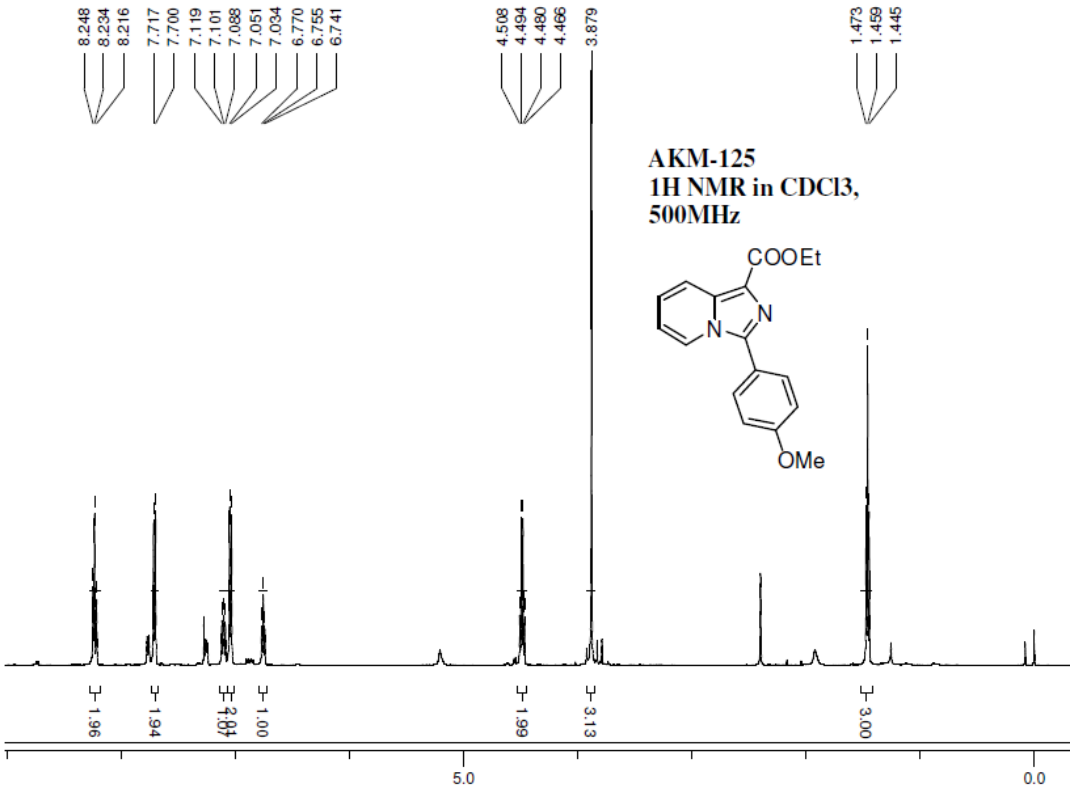
^{13}C NMR of **3s**



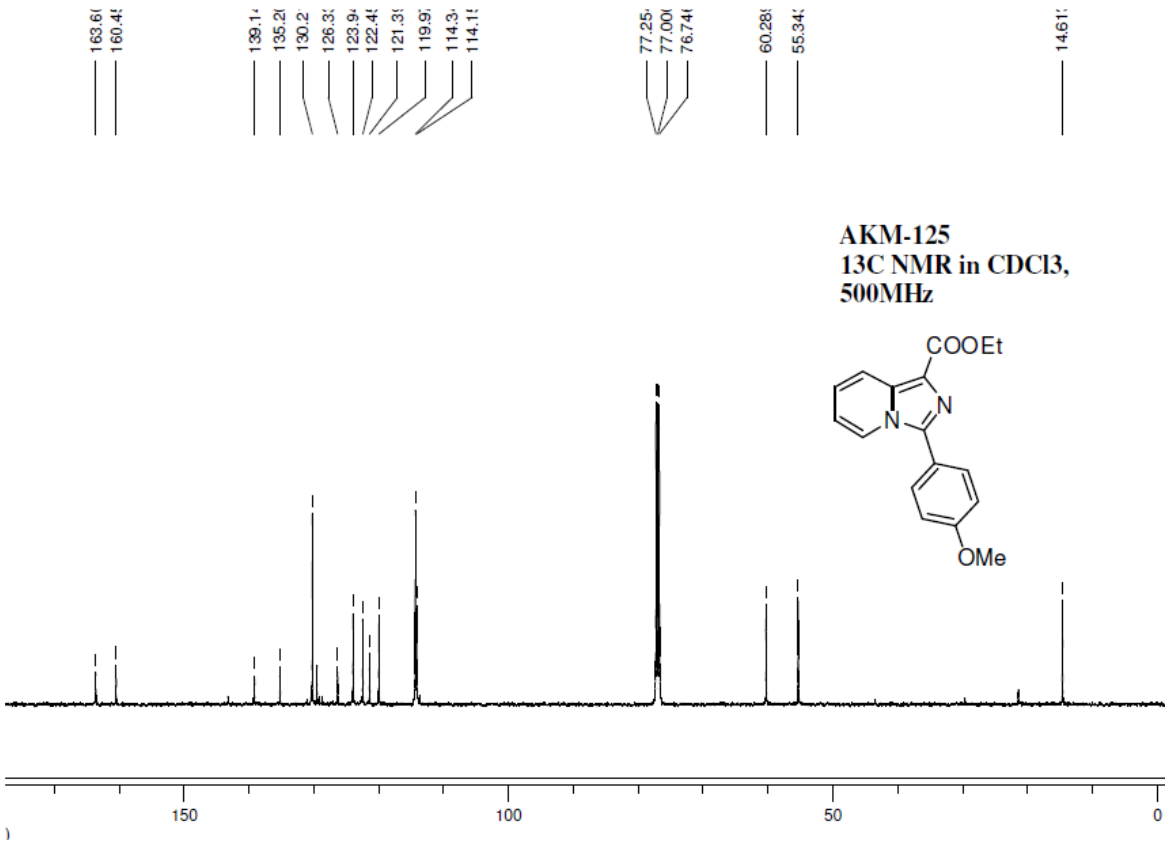
^{1}H NMR of **3u**



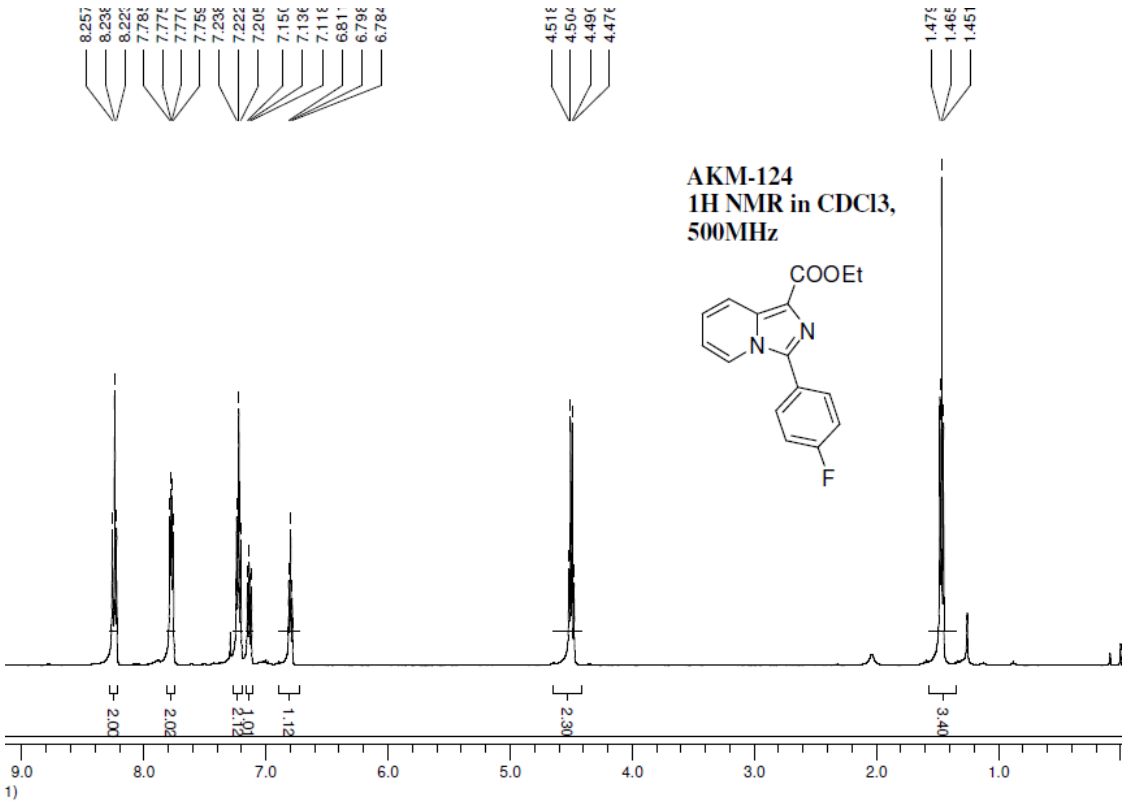
^{13}C NMR of **3u**



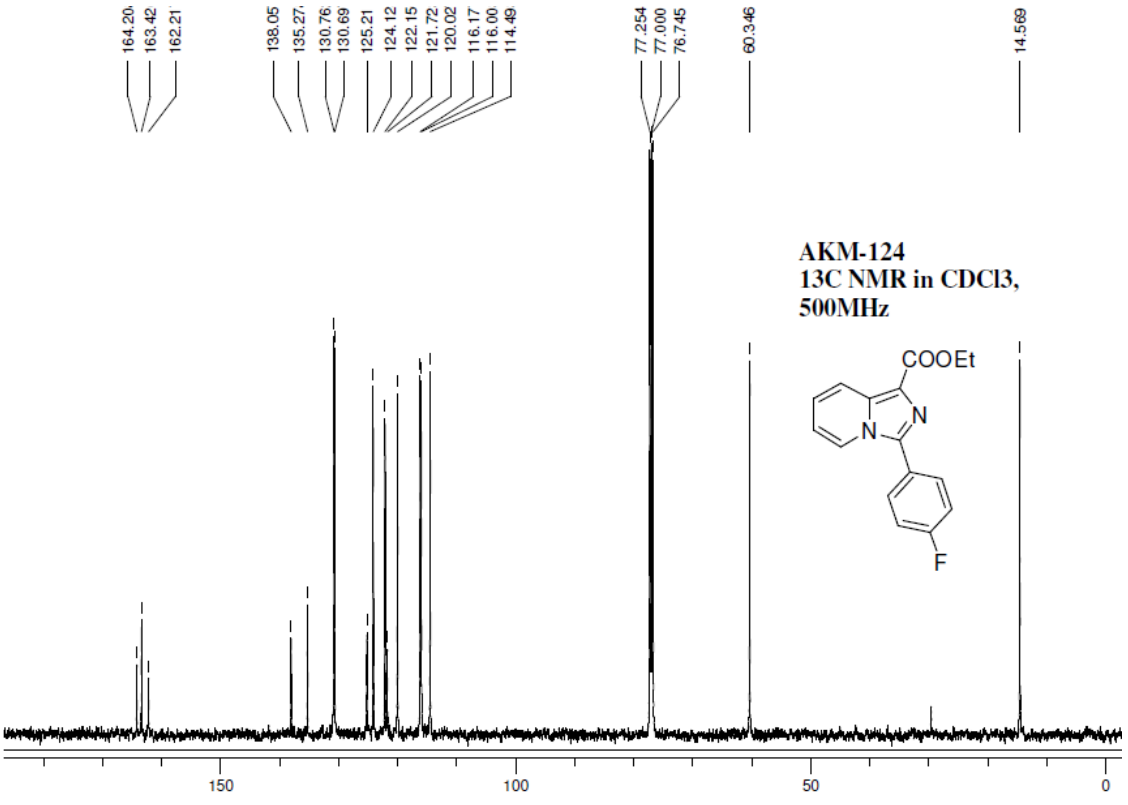
^{1}H NMR of **3v**



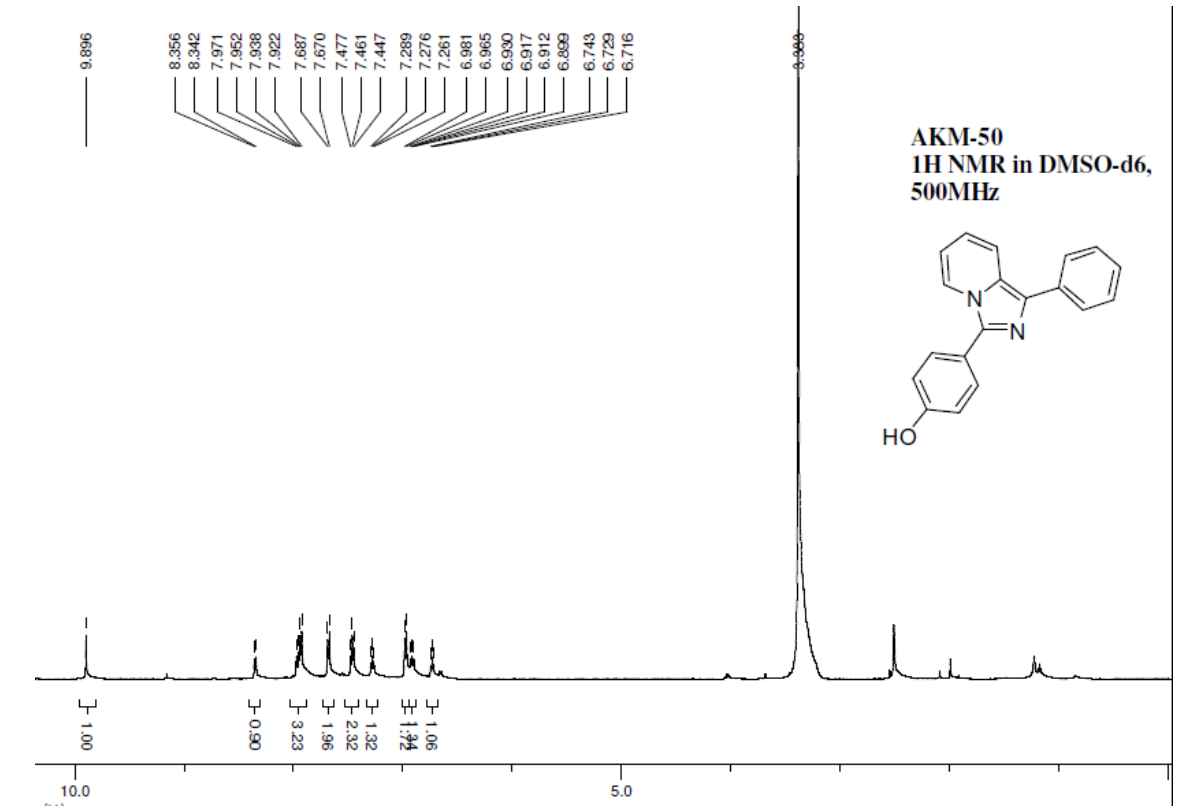
^{13}C NMR of **3v**



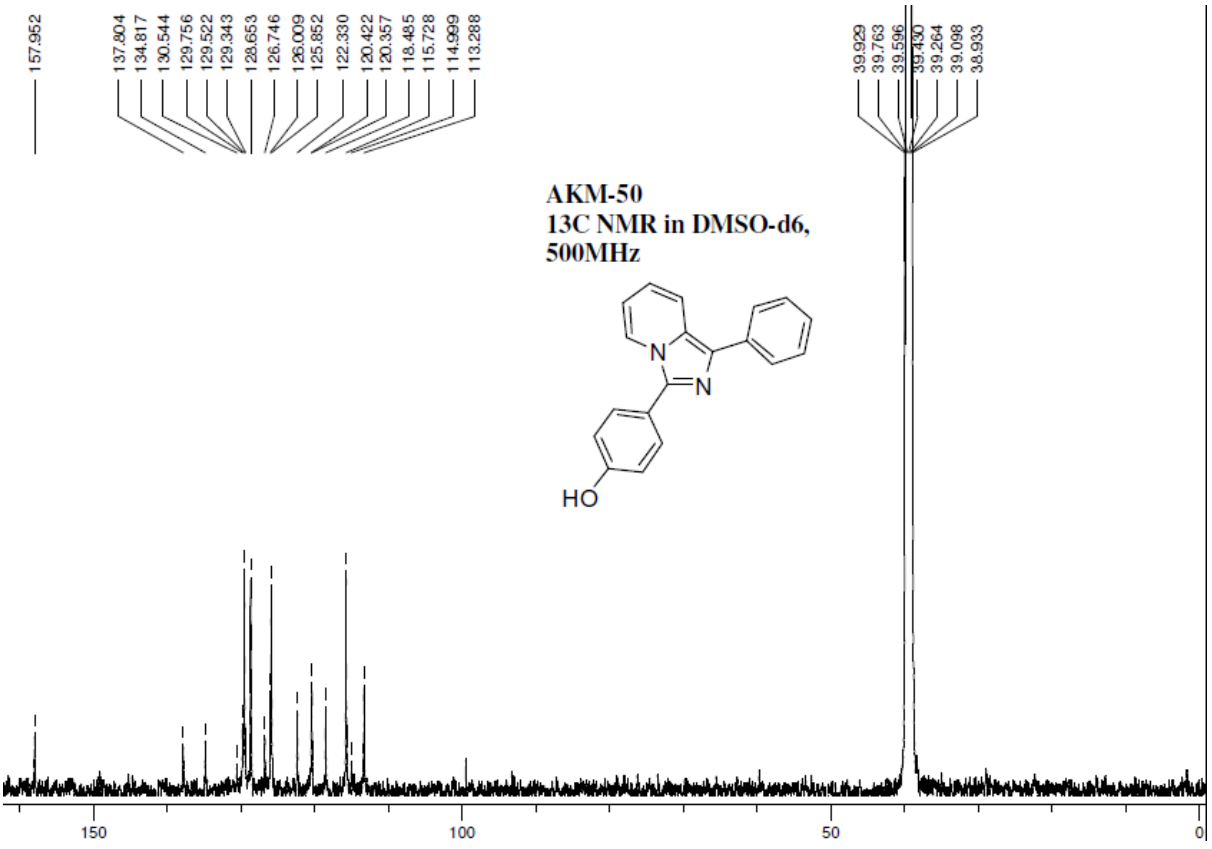
^{1}H NMR of **3w**



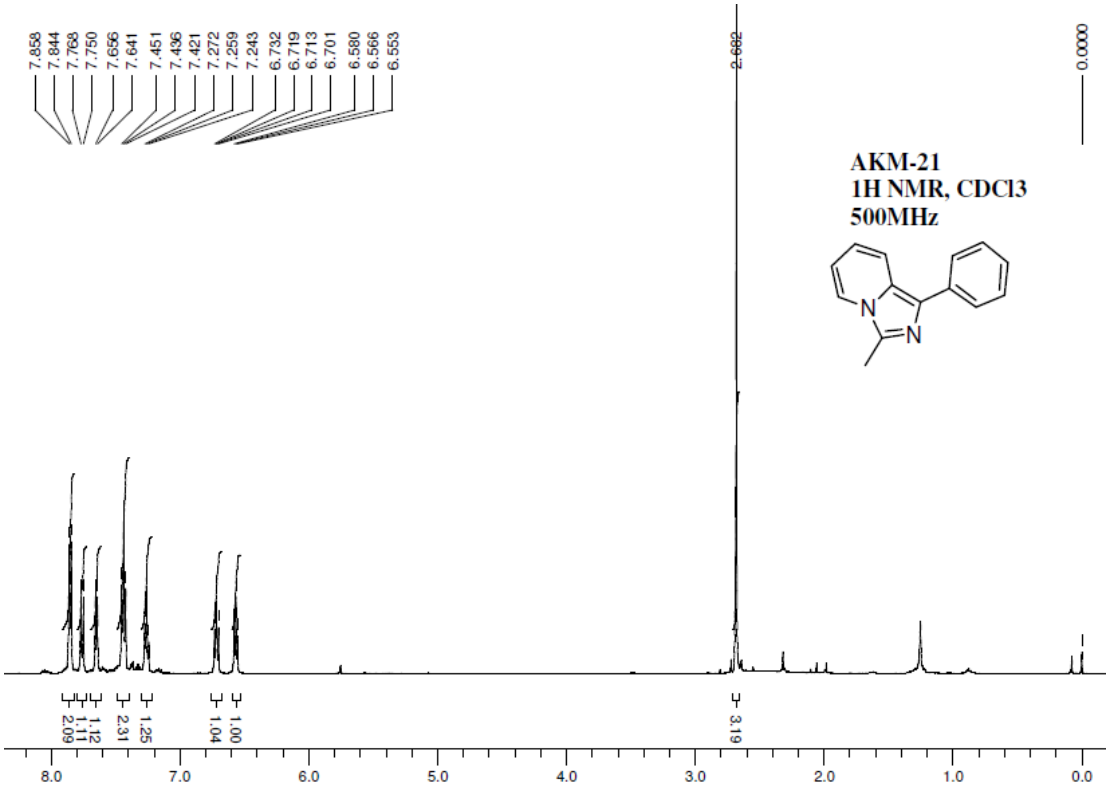
^{13}C NMR of **3w**



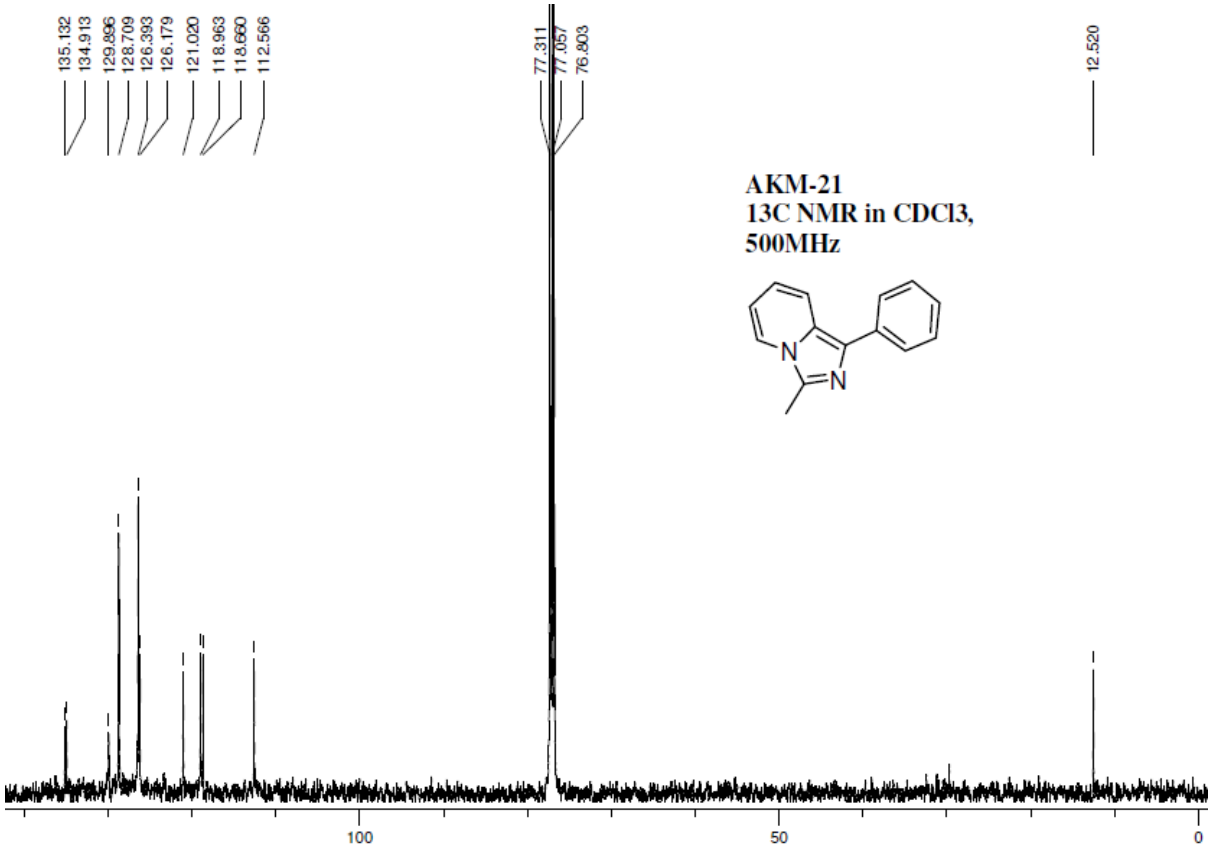
^{1}H NMR of **5e**



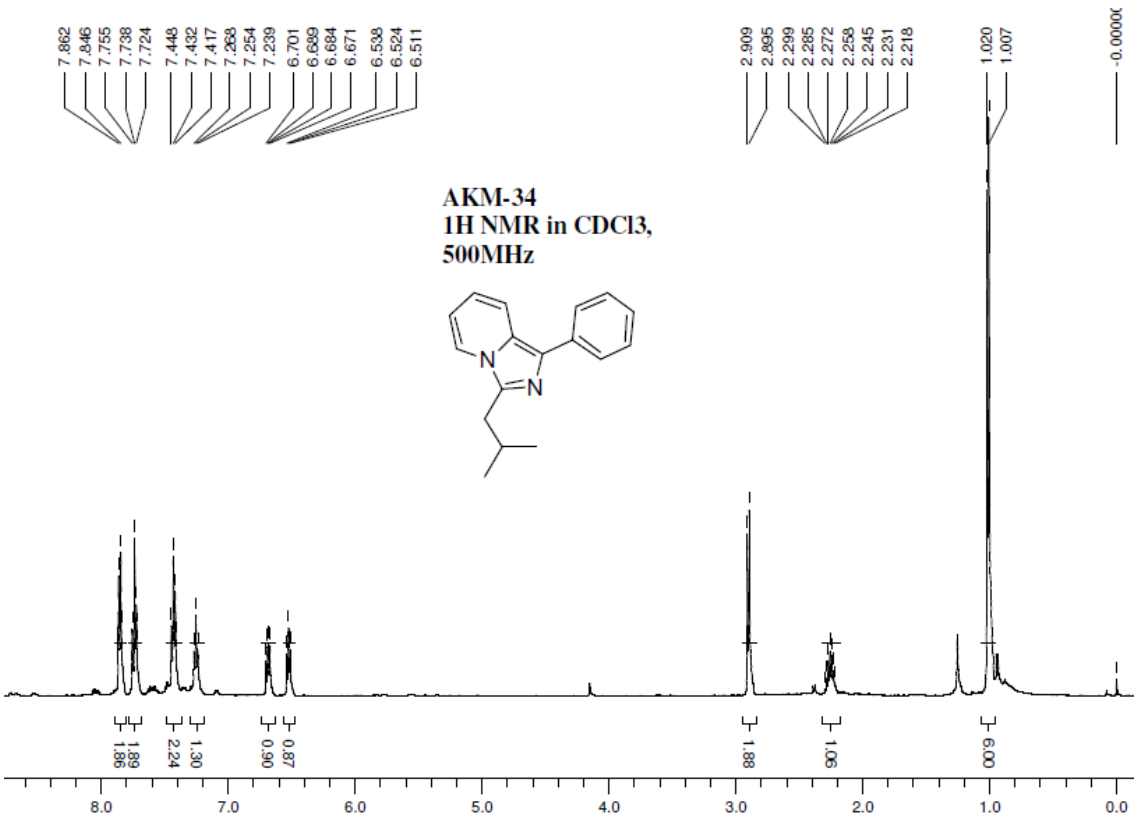
^{13}C NMR of **5e**



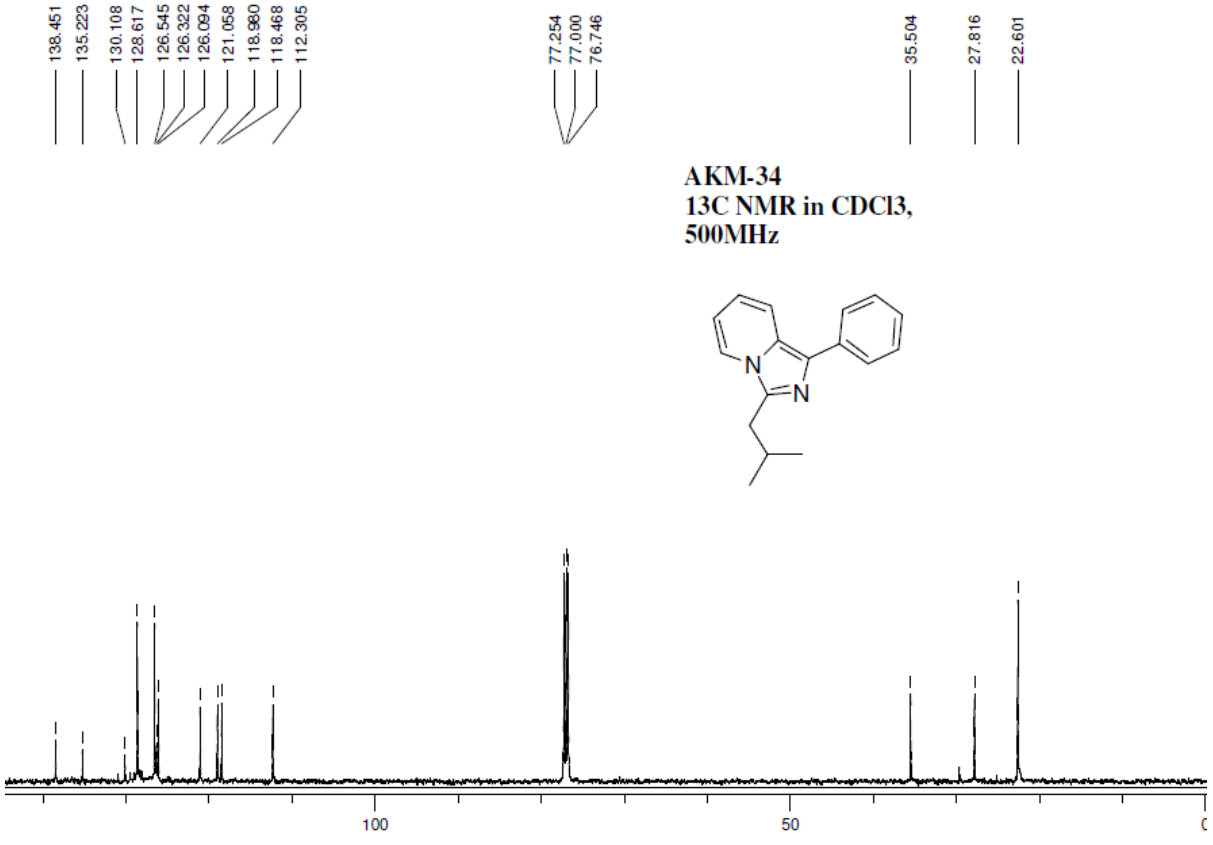
^{1}H NMR of **5f**



^{13}C NMR of **5f**



^{1}H NMR of **5g**



^{13}C NMR of **5g**