A Unprecedented Pd-catalyzed Decarboxylative Coupling Reaction of Aromatic Carboxylic Acids in Aqueous Medium under Air: Synthesis of 3-Aryl-imidazo[1,2-a]pyridines from Aryl Chlorides

Bing Mu,[a, b] Yusheng Wu,* [a, c, e] Jingya Li,[c, d] Dapeng Zou,[a] Junbiao, Chang[a] and Yangjie Wu[a]

[a]*The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, PR China.*

[b]*The College of Chemistry and Chemical Engineering, Zhengzhou Normal University, Zhengzhou 450044, PR China.*

[c]*Collaborative Innovation Center of New Drug Research and Safety Evaluation, Henan Province.*

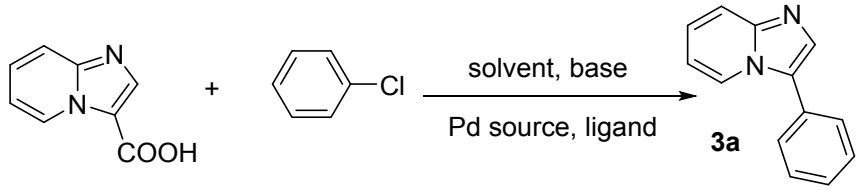
[d]*Tetranov Biopharm, LLC, 75 Daxue Road, Zhengzhou, PR China.*

[e]*Tetranov International, Inc., 100 Jersey Avenue, Suite A340, New Brunswick, NJ 08901, USA.*

E-mail: yusheng.wu@tetranovglobal.com; Fax: +1 732 253 7327; Tel: +1 732 253 7326

Supporting Information

1. Table S1. Optimization of the reaction conditions.[a]



Entry	Pd source	Ligand	Base	Solvent	Temp (°C)	Yield (%) [b]
1 [d, e]	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA	160	91 [c]
2 [e]	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA	160	52
3 [d]	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA	160	61
4	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA	160	70
5	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA	150	26
6	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMF	150	20
7	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMSO	150	Trace
8	$Pd(OAc)_2$	PCy_3	K_2CO_3	Dioxane	110	Trace
9	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA/H_2O (40/1)	150	67
10	$Pd(OAc)_2$	PCy_3	K_2CO_3	DMA/H_2O (3/1)	150	5
11	$Pd(OAc)_2$	PCy_3	K_2CO_3	Xylene/H_2O (1/1)	120	NR
12	$Pd(OAc)_2$	PCy_3	Na_2CO_3	DMA/H_2O (40/1)	150	46
13	$Pd(OAc)_2$	PCy_3	KOAc	DMA/H_2O (40 /1)	150	53
14	$Pd(OAc)_2$	PCy_3	$K_3PO_4 \cdot 7H_2O$	DMA/H_2O (40/1)	150	10
15	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	DMA/H_2O (40/1)	150	6
16	$Pd(OAc)_2$	PCy_3	KO^{t}Bu	DMA/H_2O (40/1)	150	Trace
17	$Pd(OAc_)_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	81
18[f]	$Pd(OAc)_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	100 (96 [c])
19[f]	$Pd(OAc)_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	140	11
20[f]	$Pd(OAc)_2$	X-Phos	K_2CO_3	DMA/H_2O (40/1)	150	59
21[f]	$Pd(OAc)_2$	Ru-Phos	K_2CO_3	DMA/H_2O (40/1)	150	30
22[f]	$PdCl_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	27
23[f]	$Pd_2(dba)_3$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	NR
24[f]	$Pd(acac)_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	61
25[f]	$Pd(CF_3CO_2)_2$	S-Phos	K_2CO_3	DMA/H_2O (40/1)	150	44

[a] Reaction conditions: 0.3 mmol of imdazol[1,2-a]pyridine-3-carboxylic acid, 0.9 mmol of chlorobenzene, 0.9 mmol of base, 5 mol% of cat., 6 mol% of ligand, and 4 mL of solvent under air for 24 h. [b] GC yields. [c] Isolated yields.

[d] 0.15mmol of Cu_2O. [e] 4 mL of dry DMA, 200 mg of 4 Å molecular sieve, under nitrogen. [f] 7.5 mol% of ligand.

2. General Methods.

All reactions were performed in glass reaction tube equipped with a magnetic stir bar under air unless otherwise noted. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard 15 grade). Solvents and the other chemicals were bought from commercial sources and used as received unless otherwise noted. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. The high resolution mass spectrum was received via Agilent Technologies 6540 UHD Accurate-mass Q-Tof LC/MS. TheGC yields were determined using n-dodecane internal standards. GC analyses were carried out using a Shimadzu GC-2010 Plus instrument. Melting point were obtained by XT4A micro Melting-point Measurement Instruments, thermometer was unrevised. NMR spectra were obtained on Bruker DPX 400 systems using $CDCl_3$ as solvent, TMS as internal standard substance, with proton and carbon resonances at 400 and 100 MHz, respectively.

3. Characterization data of compounds.

3-phenylimidazo[1,2-a]pyridine (3a):[1] light yellow solid (56 mg, yield 96%); m.p. 83-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.34 (d, J = 7.2 Hz, 1H), 7.70-7.66 (m, 2H), 7.58-7.50 (m, 4H), 7.44-7.40 (m, 1H), 7.21-7.17 (m, 1H), 6.80 (td, J = 6.8 Hz, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.2, 132.6, 129.4, 129.3, 128.2, 128.1, 125.7, 124.2, 123.4, 118.3, 112.5; MS: 195.1 $[M + H]^+$.

3-(4-methylphenyl)-imidazo[1,2-a]pyridine (3b):[2] White solid (60 mg, yield 96%); m.p. 78-80℃; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.28 (d, J = 6.8 Hz, 1H), 7.65 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.17-7.13 (m, 1H), 6.76 (t, J = 6.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.8, 137.0, 131.1, 128.8, 126.8, 125.2, 124.6, 122.9, 122.2, 117.0, 111.2, 20.2; MS: 209.2 $[M + H]^+$.

3-(3-methylphenyl)-imidazo[1,2-a]pyridine (3c):[3] light yellow oil (62mg, yield 99%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.33 (d, J = 6.4 Hz, 1H), 7.68 (s, 1H), 7.66 (d, J = 10.4 Hz, 1H), 7.42-7.34 (m, 3H), 7.24-7.16 (m, 2H), 6.79 (td, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.9, 137.9, 131.3,

128.0, 127.9, 127.8, 127.5, 124.7, 123.9, 123.0, 122.3, 117.0, 111.3, 20.3; MS: 209.1 $[M + H]^+$.

3-(2-methylphenyl)-imidazo[1,2-a]pyridine (3d):[1] light yellow oil (55 mg, yield 88%); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75 (d, J = 6.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.62 (s, 1H), 7.39-7.31 (m, 4H), 7.22-7.18 (m, 1H), 6.76 (t, J = 6.8 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.3, 137.1, 131.6, 130.0, 129.6, 128.1, 127.0, 125.1, 123.5, 122.9, 122.5, 116.8, 111.2, 18.6; MS: 209.1 $[M + H]^+$.

3-(4-methoxyphenyl)-imidazo[1,2-a]pyridine (3e):[2] light yellow solid (64 mg, yield 95%); m.p. 110-112℃; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22 (d, J = 6.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.61 (s, 1H), 7.45-7.42 (m, 2H), 7.16-7.12 (m, 1H), 7.04-7.00 (m, 2H), 6.75 (td, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.6, 145.8, 132.0, 129.6, 125.5, 123.9, 123.3, 121.5, 118.1, 114.7, 112.3, 55.4; MS: 225.1 $[M + H]^+$.

3-(2-methoxyphenyl)-imidazo[1,2-a]pyridine (3f): light yellow oil (48 mg, yield 71%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83 (d, J = 6.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.66 (s, 1H), 7.47-7.40 (m, 2H), 7.20 (t, J = 1.0 Hz, 1H), 7.10-7.04 (m, 2H), 6.76 (td, J = 6.8 Hz, 0.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.2, 131.8, 130.9, 129.3, 124.3, 123.0, 120.0, 117.0, 116.7, 110.6, 110.2, 54.4; MS: 225.0 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{14}H_{13}N_2O$ $(M + H)^+$ 225.1028, found 225.1026.

N-(4-(imidazo[1,2-a]pyridin-3-yl)phenyl)acetamide (3g): White solid (71mg, yield 94%), m.p. 204-207 °C; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.99 (s, 1H), 8.30 (d, J = 6.8 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H) 7.22-7.18 (m, 1H), 6.81 (td, J = 6.8 Hz, 0.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.0, 144.8, 137.5, 130.9, 127.6, 124.5, 123.5, 123.4, 122.4, 119.5, 116.9, 111.6, 23.4; MS: 252.1 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{15}H_{14}N_3O$ $(M + H)^+$ 252.1137, found 252.1134.

N-(3-(imidazo[1,2-a]pyridin-3-yl)phenyl)acetamide (3h): light yellow solid (55 mg, yield 73%); m.p. 152-154 °C; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.09 (s, 1H), 8.39 (d, J = 6.8 Hz, 1H), 7.84 (s, 1H), 7.67 (s, 1H), 7.63-7.58 (m, 2H), 7.41 (t, J = 8.0 Hz,

1H), 7.26 (d, *J* = 7.6 Hz, 1H) 7.18 (td, *J* = 8.0 Hz, 0.8 Hz, 1H), 6.79 (t, J = 6.6 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.1, 145.0, 138.3, 131.1, 128.7, 128.5, 124.5, 123.6, 122.6, 122.2, 118.5, 118.2, 116.7, 111.7, 23.3; MS: 252.1 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{15}H_{14}N_3O$ $(M + H)^+$ 252.1137, found 252.1135.

N-(2-(imidazo[1,2-a]pyridin-3-yl)phenyl)acetamide (3i): light yellow solid (40mg, yield 53%); m.p. 252-255 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.88 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.54-7.50 (m, 1H), 7.36-7.25 (m, 3H), 7.21-7.14 (m, 2H), 6.83-6.80 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 168.4, 144.8, 135.7, 131.7, 130.4, 129.0, 123.9, 123.3, 120.7, 118.7, 116.3, 111.5, 23.1; MS: 252.1 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{15}H_{14}N_3O$ $(M + H)^+$ 252.1137, found 252.1140.

3-(imidazo[1,2-a]pyridin-3-yl)aniline (3j):[5] light yellow oil (38 mg, yield 61%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.37 (d, *J* = 6.8 Hz, 1H), 7.66 (s, 1H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.20-7.16 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 1.8 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 1H), 6.74-6.72 (m, 1H), 3.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.3, 132.3, 130.3, 130.2, 126.1, 124.3, 123.8, 118.2, 118.1, 115.0, 114.5, 112.5; MS: 210.1 $[M + H]^+$.

3-(imidazo[1,2-a]pyridin-4-yl)aniline (3k): light gray oil (37 mg, yield 59%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.23 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.58 (s, 1H), 7.33-7.29 (m, 2H), 7.16-7.12 (m, 1H), 6.81-6.74 (m, 3H), 3.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.7, 144.5, 130.5, 128.6, 125.0, 122.8, 122.4, 117.9, 117.0, 114.4, 111.2; MS: 210.0 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{13}H_{12}N_3$ $(M + H)^+$ 210.1031, found 210.1029.

3-naphthalen-1-ylimidazo[1,2-a]pyridine (3l):[2] light yellow oil (48 mg, yield 66%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00-7.95 (m, 2H), 7.80 (s, 1H), 7.75-7.05 (m, 2H), 7.60-7.51 (m, 4H), 7.45-7.42 (m, 1H), 7.26-7.20 (m, 1H), 6.70 (td, *J* = 6.8 Hz, 0.8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.8, 132.9, 132.8, 131.0, 128.5, 128.1, 127.7, 125.9, 125.3, 125.2, 124.6, 124.2, 123.2, 123.0, 122.6, 117.0, 111.2; MS: 245.1 $[M + H]^+$.

4-imidazo[1,2-a]pyridin-3-ylacetophenone (3m):[2] light yellow solid (53mg, yield

75%); m.p. 157-159℃; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.41 (d, *J* = 6.4 Hz, 1H), 8.11 (d, *J* = 7.6Hz, 2H), 7.81 (s, 1H), 7.72-7.68 (m, 3H), 7.28-7.24 (m, 1H), 6.89 (td, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.2, 145.8, 135.2, 133.0, 132.7, 128.3, 126.3, 123.8, 123.7, 122.3, 117.5, 112.1, 25.6; MS: 237.1 $[M + H]^+$.

3-(4-nitrophenyl)-imidazo[1,2-a]pyridine (3n):[2] orange solid (50 mg, yield 70%); m.p. 209-211°C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.43 (dd, *J* = 6.8 Hz, 0.8 Hz, 1H), 8.38 (dd, *J* = 7.2 Hz, 2.0 Hz, 2H), 7.86 (s, 1H), 7.78-7.72 (m, 3H), 7.33-7.28 (m, 1H), 6.95 (td, *J* = 6.8 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.3, 145.8, 134.9, 133.7, 126.4, 124.4, 123.7, 122.7, 122.2, 117.7, 112.6; MS: 240.1 $[M + H]^+$.

3-pyridin-4-ylimidazo[1,2-a]pyridine (3o):[4] White solid (55 mg, yield 94%); m.p. 117-119℃; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.69 (dd, *J* = 4.8 Hz, 1.2 Hz, 2H), 8.41 (d, *J* = 6.8 Hz, 1H), 7.82 (s, 1H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.46 (dd, *J* = 4.4 Hz, 1.6 Hz, 2H), 7.26-7.22 (m, 1H), 6.88 (td, *J* = 6.8 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.6, 146.2, 135.9, 133.3, 124.2, 122.3, 122.0, 120.0, 117.5, 112.3; MS: 196.2 $[M + H]^+$.

3-pyridin-3-ylimidazo[1,2-a]pyridine (3p):[4] light gray oil (45 mg, yield 77%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.83 (s, 1H), 8.67 (d, *J* = 4.0 Hz, 1H), 8.30 (d, *J* = 6.8 Hz, 1H), 7.91-7.88 (m, 1H), 7.77 (s, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.28-7.24 (m, 1H), 6.89-6.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.1, 147.7, 145.5, 134.0, 132.3, 124.5, 123.7, 122.8, 121.8, 121.2, 117.4, 112.0; MS: 196.2 $[M + H]^+$.

3, 3'-biimidazo[1,2-a]pyridine (3q): light yellow solid (69 mg, yield 98%); m.p. 220-221 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.90-7.88 (m, 4H), 7.76 (dt, *J* = 9.2 Hz, *J* = 0.8 Hz, 2H), 7.33-7.29 (m, 2H), 6.87 (td, *J* = 6.8 Hz, *J* = 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.8, 134.3, 124.4, 122.8, 117.4, 112.2, 111.7; MS: 235.2 $[M + H]^+$; HRMS (ESI^+) calcd for $C_{14}H_{11}N_4$ $(M + H)^+$ 235.0984, found 235.0981.

2-methyl-3-phenylimidazo[1,2-a]pyridine (3r):[6] Yellow oil (64 mg, yield 98%); ^{1}H

NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 6.8 Hz, 1H), 7.56-7.50 (m, 3H), 7.46-7.39 (m, 3H), 7.13 (t, J = 7.8 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 141.1,129.6, 129.5, 129.3, 128.2, 124.1, 123.1, 121.5, 117.1, 111.9, 14.0; MS: 209.1 $[M + H]^+$.

2, 3-diphenylimidazo[1, 2-a]pyridine (3s):[6] White solid (71 mg, yield 86%), m.p.: 139-140 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 6.8 Hz, 1H), 7.68-7.66 (m, 3H), 7.53-7.45 (m, 5H), 7.28-7.17 (m, 4H), 6.73 (td, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 142.6, 134.3, 130.9, 130.0, 129.6, 129.0, 128.4, 128.2, 127.6, 124.7, 123.4, 121.2, 117.7, 112.3; MS: 271.2 $[M + H]^+$.

2,8-dimethyl-3-phenylimidazo[1,2-a]pyridine (3t): [7] Yellow oil (61 mg, yield 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 6.8, 1H), 7.53-7.49 (m, 2H), 7.45-7.40 (m, 3H), 6.94 (d, J = 6.8 Hz, 1H), 6.62 (t, J = 6.8 Hz, 1H), 2.63 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 140.3, 129.9, 129.7, 129.2, 128.1, 126.8, 123.1, 122.0, 1201.1, 112.0, 17.2, 14.0; MS: 223.3 $[M + H]^+$.

6-fluoro-3-phenylimidazo[1,2-a]pyridine (3u): [8] Yellow oil (31 mg, yield 49%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, J_1 = 4.4 Hz, J_2 = 2.4 Hz, 1H), 7.74 (s, 1H), 7.68-7.65 (m, 1H), 7.55-7.53 (m, 4H), 7.46-7.44 (m, 1H), 7.13 (td, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 152.6, 133.8, 129.5, 129.0, 128.7, 128.0, 127.2, 118.9, 118.8, 116.6, 116.3, 110.4, 110.0; MS: 213.2 $[M + H]^+$.

4. References

[1] S. K. Lee and J.K. Park, *J. Org. Chem*., 2015, 80, 3723.

[2] J. Lee, J. Chung, S. M. Byun, B. M. Kim and C. Lee, Tetrahedron, 2013, 69, 5660.

[3] P. Y. Choy, K. C. Luk, Y. N. Wu, C. M. So, L. L. Wang and F. Y. Kwong, *J. Org. Chem*., 2015, 80, 1457.

[4] H. Y. Fu, L. Chen and H. Doucet, *J. Org. Chem*., 2012, 77, 4473.

[5] G. Saxty, V. Berdini, D. R. Newell, O. Callaghan, M. G. Carr, M. S. Congreve, A. L. Gill, A. Madin, C. W. Murray, US 8131527, 2012.

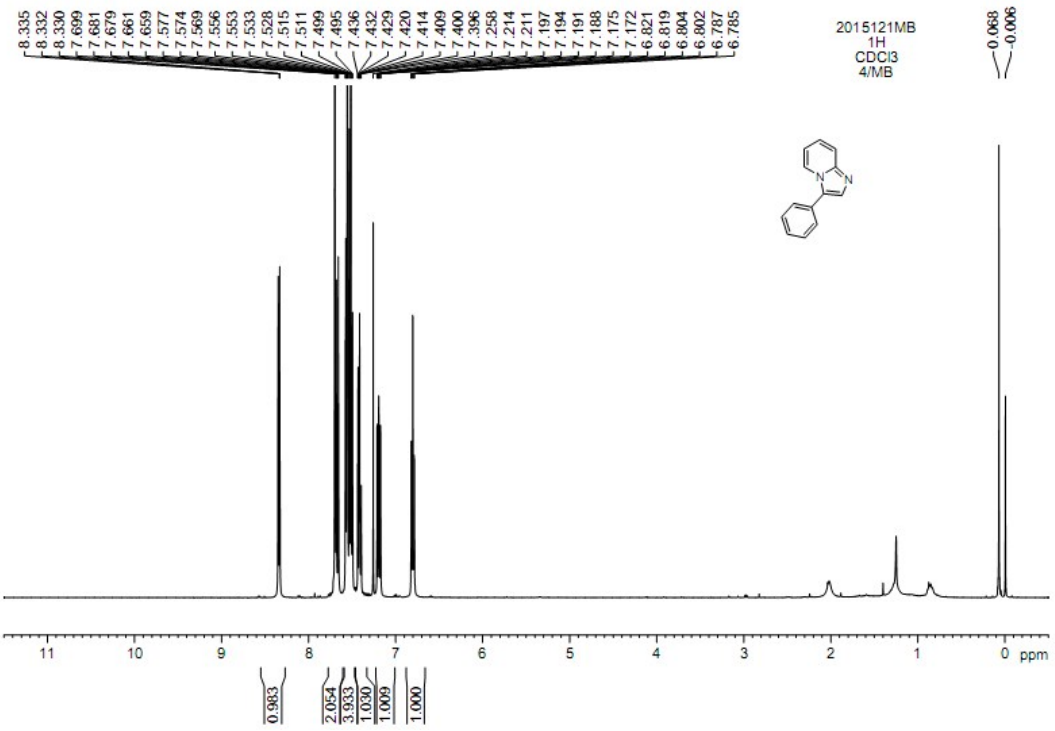
[6] H. Cao, Y. G. Lin, H. Y. Zhan, Z. D. Du, X. L. Lin, Q. M. Liang and H. Zhang, *RSC Adv*., 2012, **2**, 5972.

[7] S. H. Wang, W. J. Liu, J. H. Cen, J. Q. Liao, J. P. Huang and H. Y. Zhan, Tetrahedron Lett., 2014, 55, 1589.

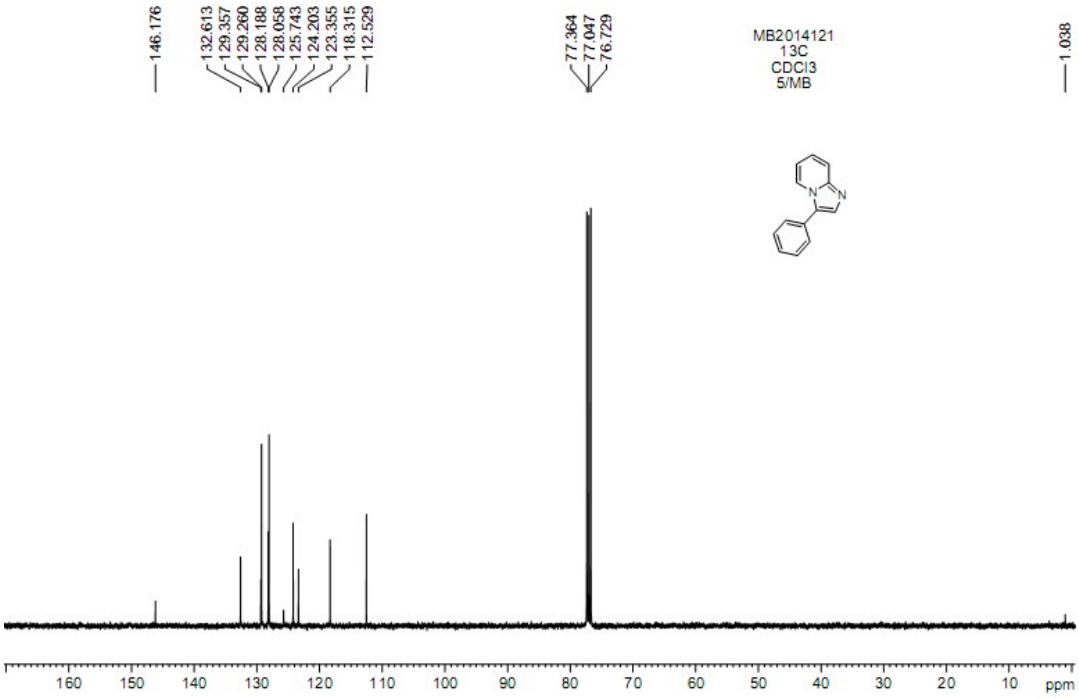
[8] Z. Wu, Y. Pan and X. Zhou, Synthesis, 2011, 14, 2255.

5. Copies of NMR spectra.

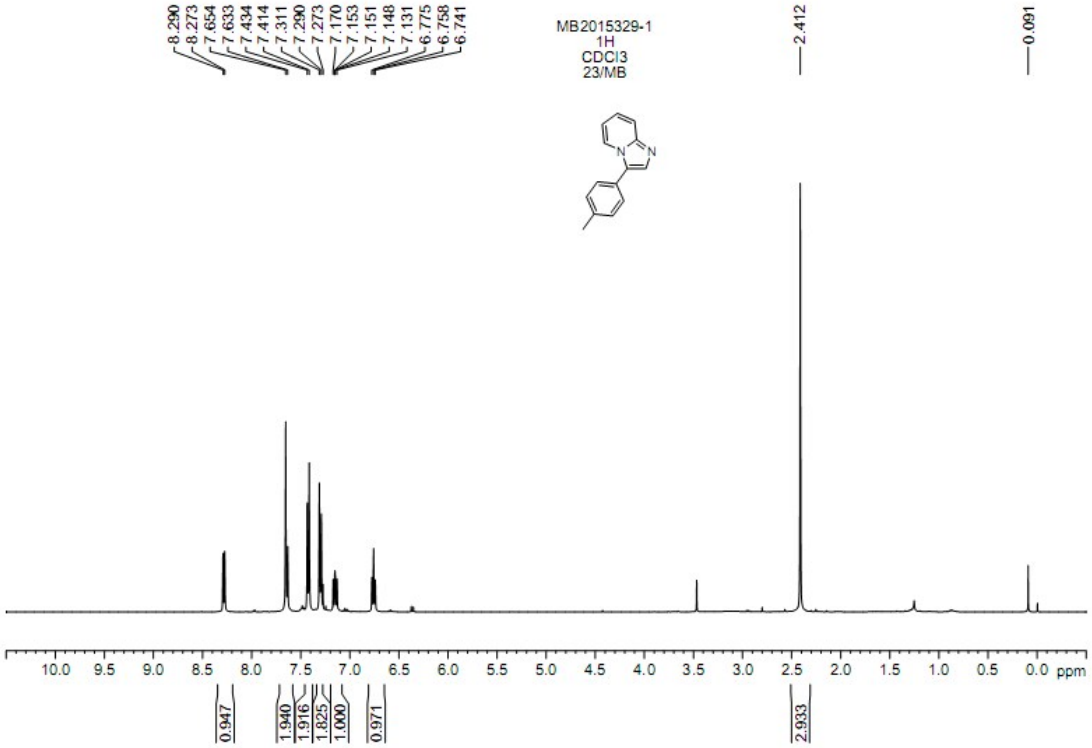
^{1}H NMR of Compound 3a



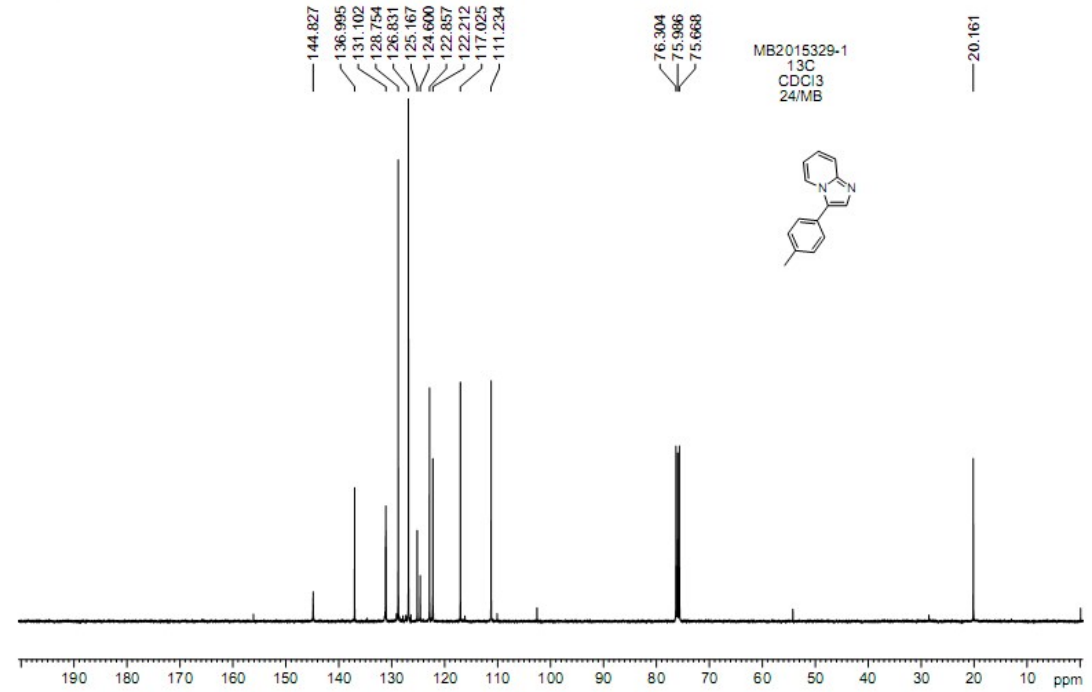
^{13}C NMR of Compound 3a



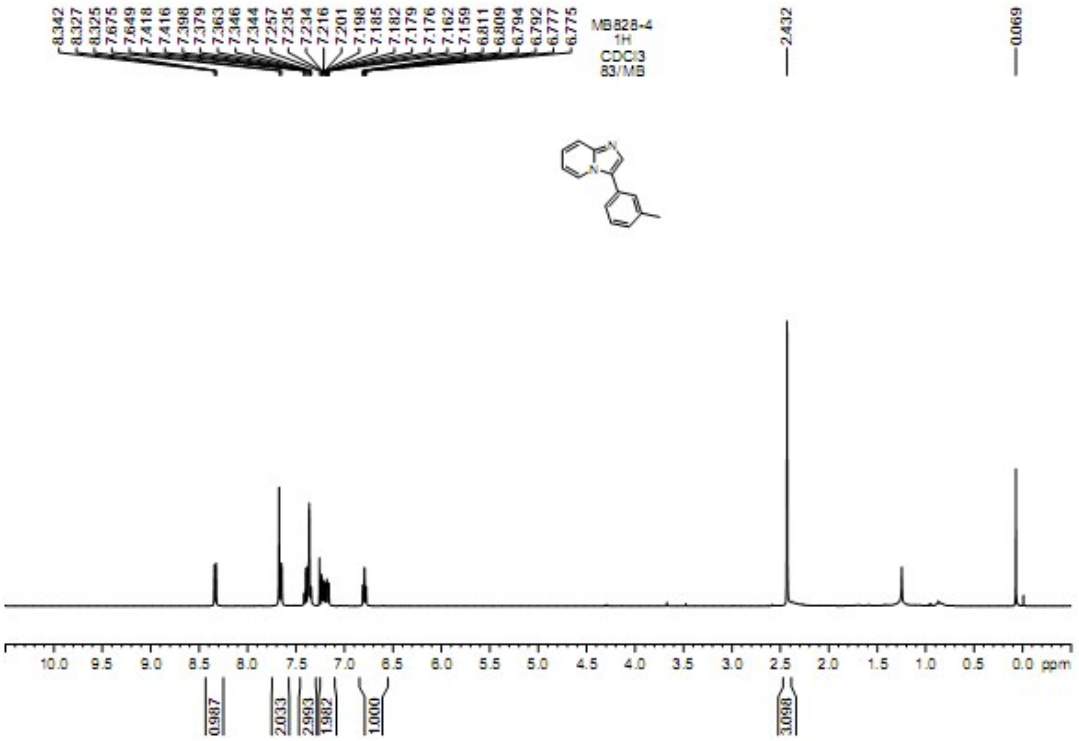
^{1}H NMR of Compound 3b



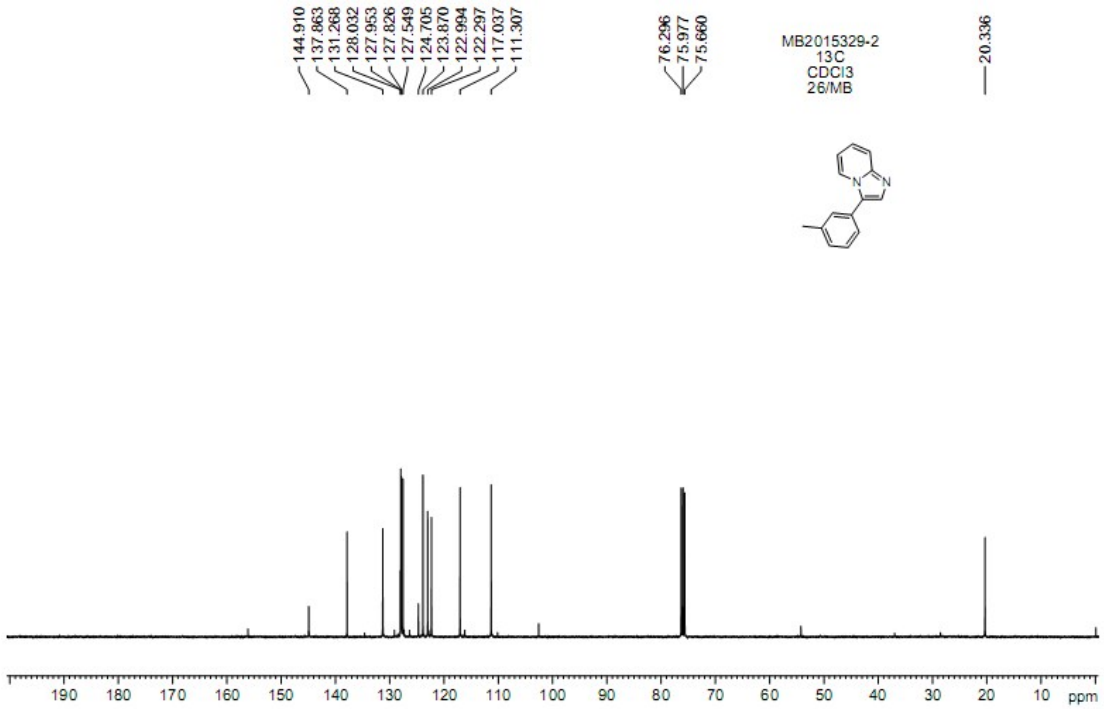
^{13}C NMR of Compound 3b



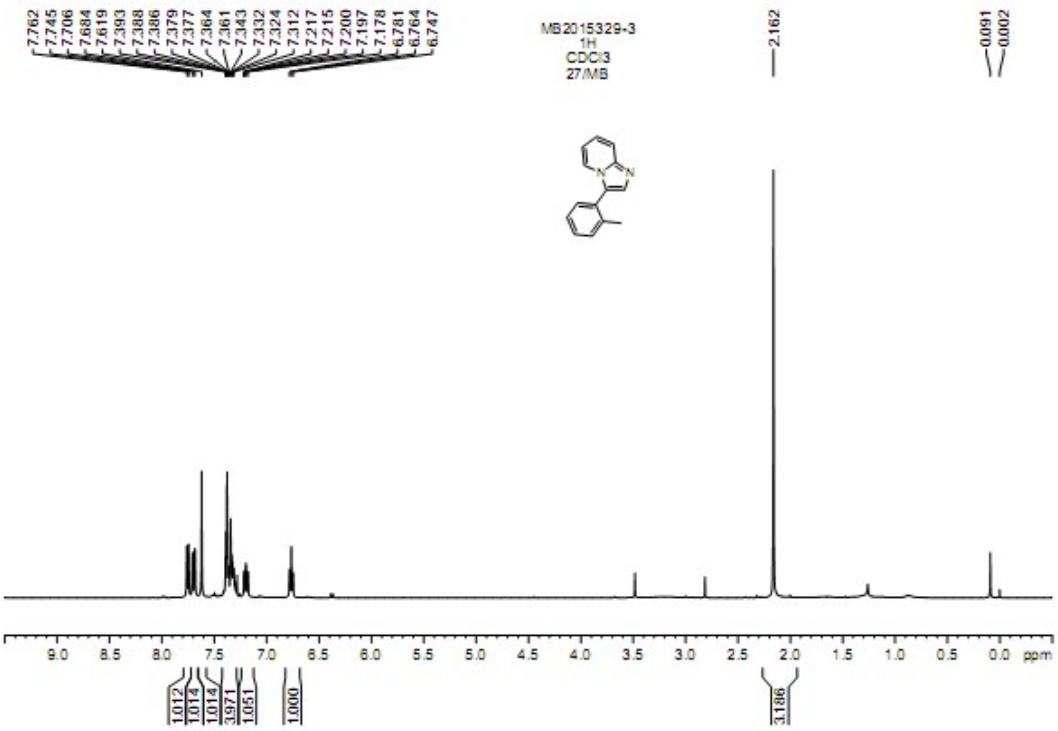
^{1}H NMR of Compound 3c



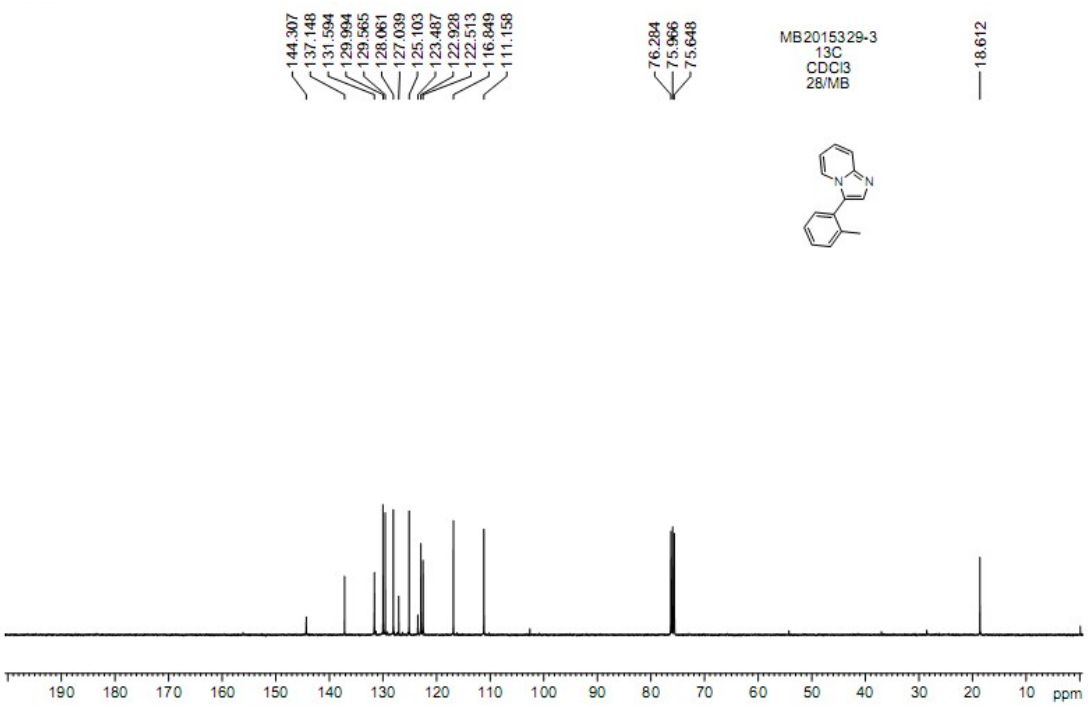
^{13}C NMR of Compound 3c



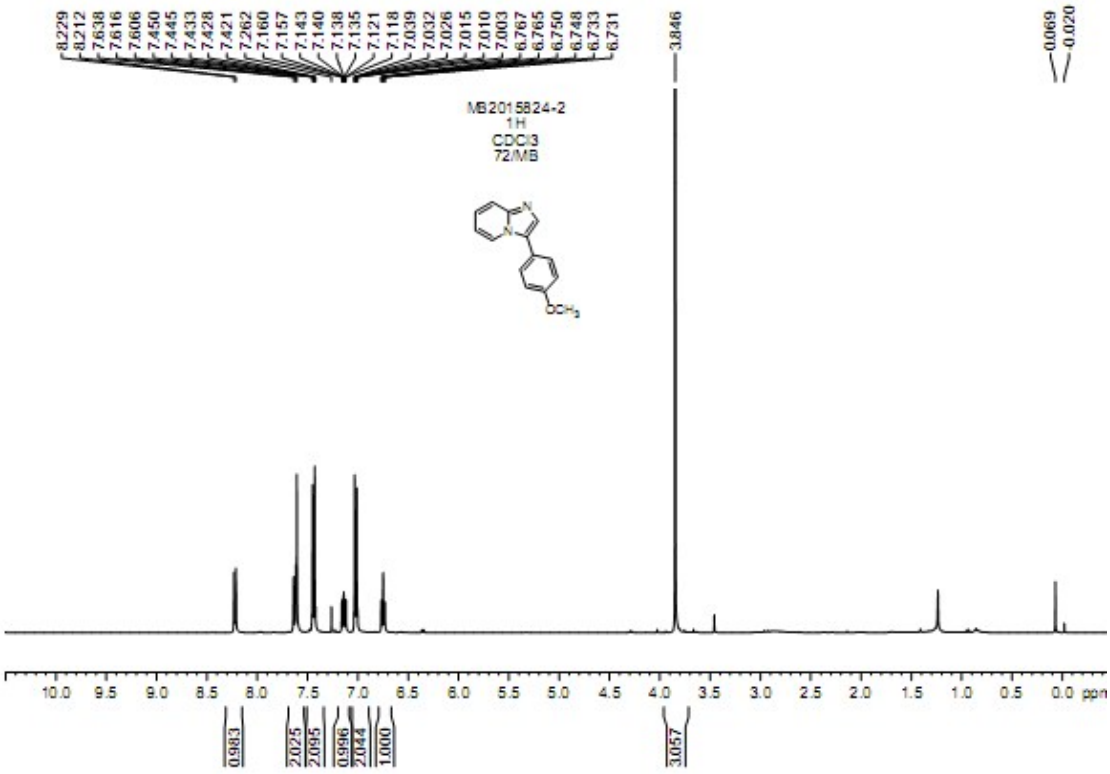
^{1}H NMR of Compound 3d



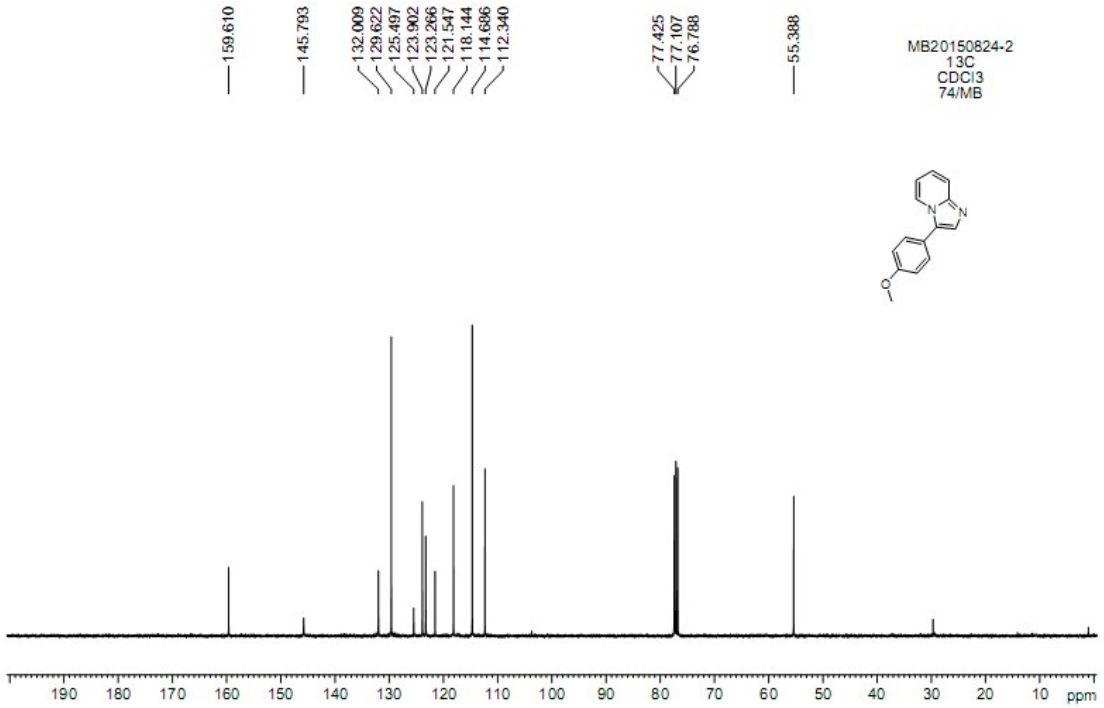
^{13}C NMR of Compound 3d



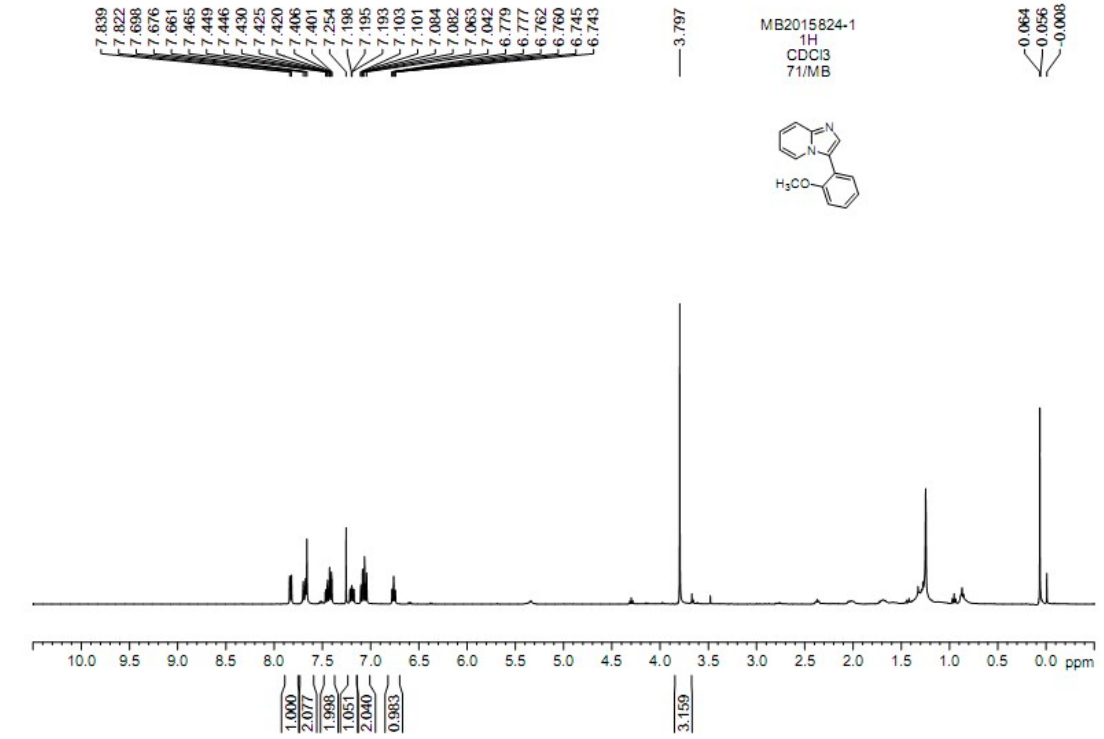
^{1}H NMR of Compound 3e



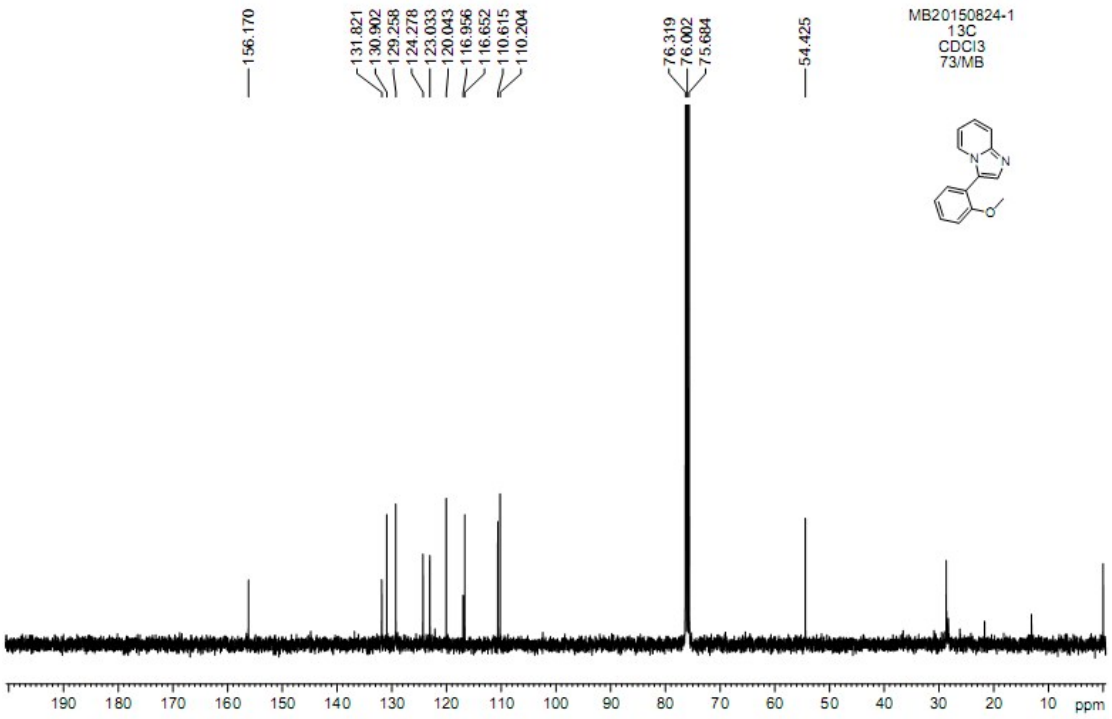
^{13}C NMR of Compound 3e



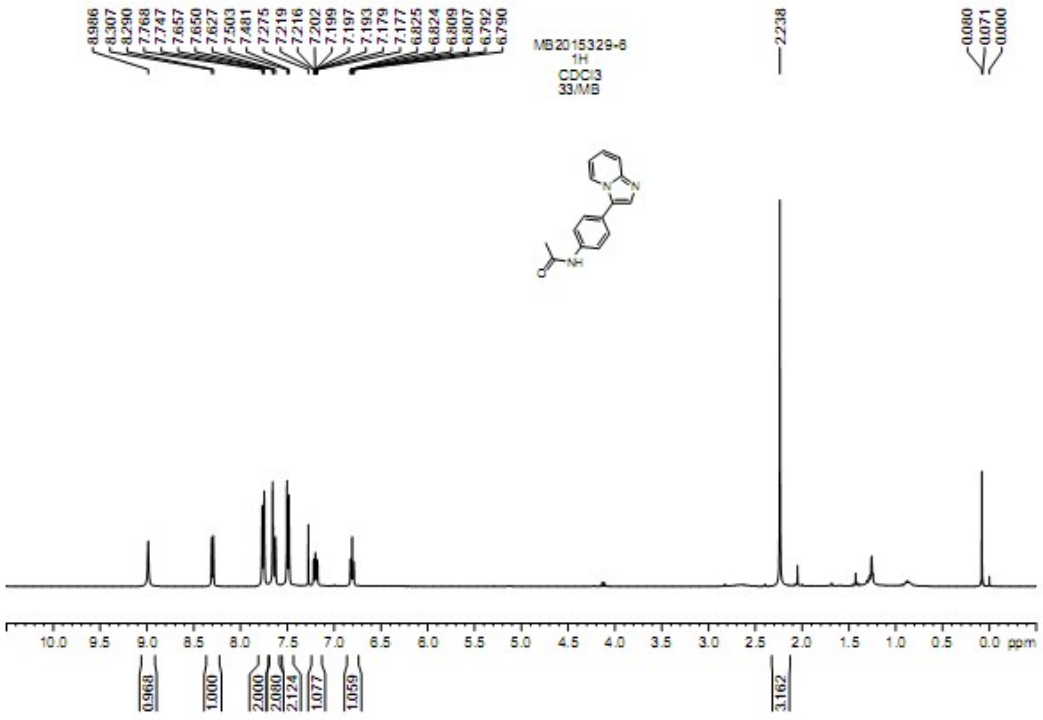
^{1}H NMR of Compound 3f



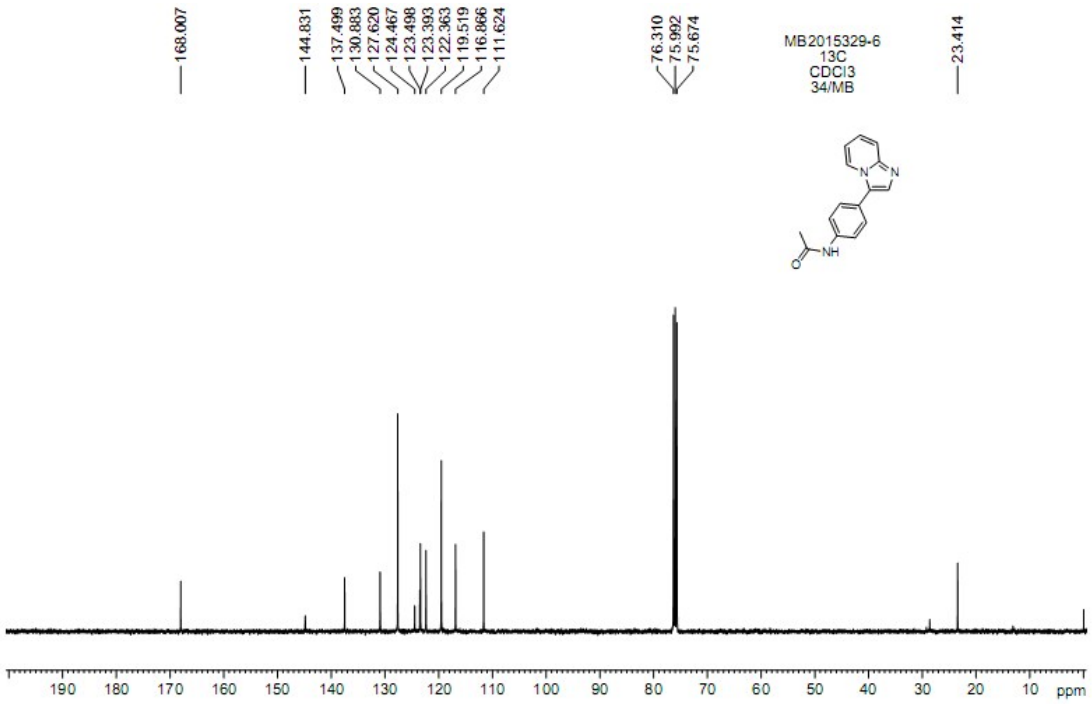
^{13}C NMR of Compound 3f



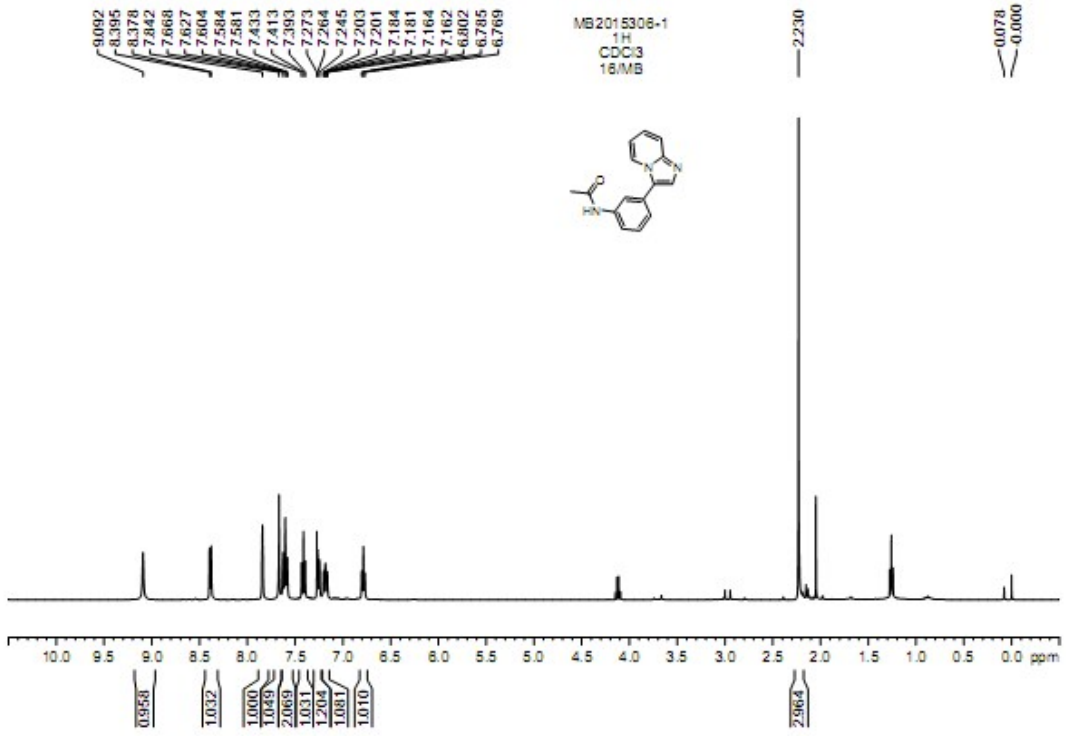
[1]H NMR of Compound 3g



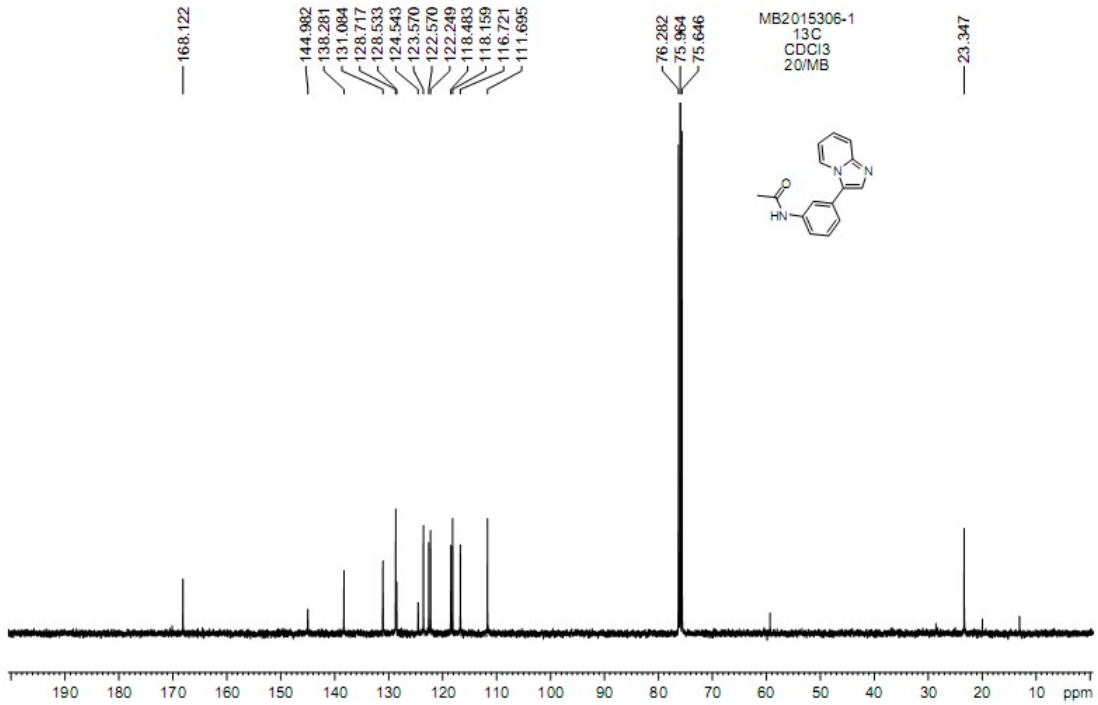
[13]C NMR of Compound 3g



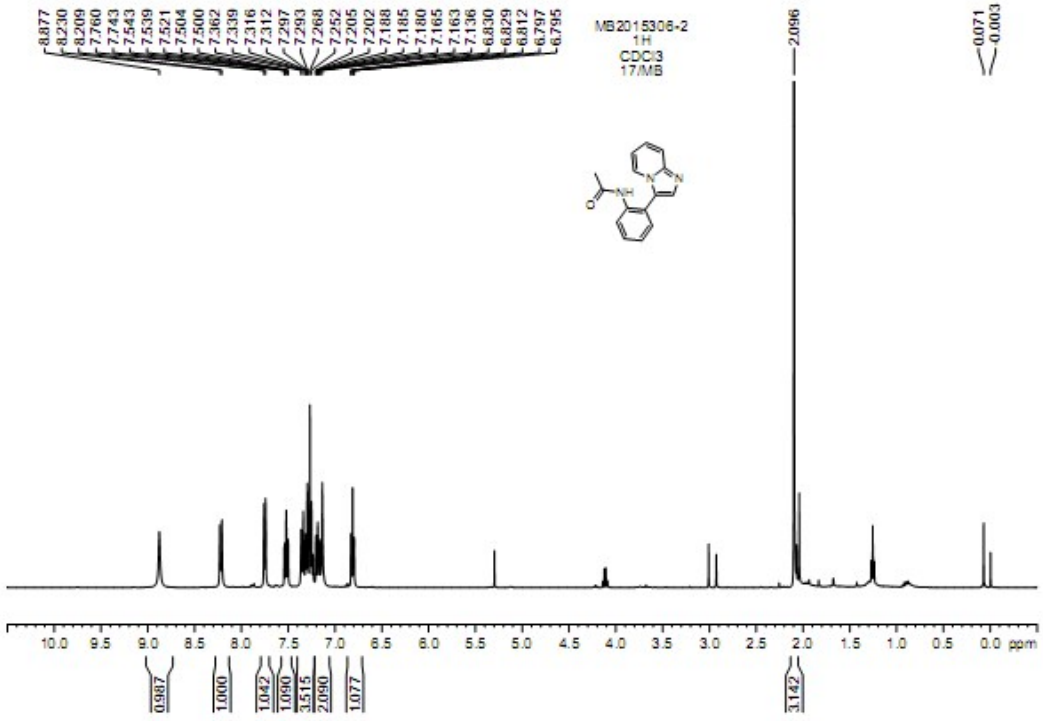
^{1}H NMR of Compound 3h



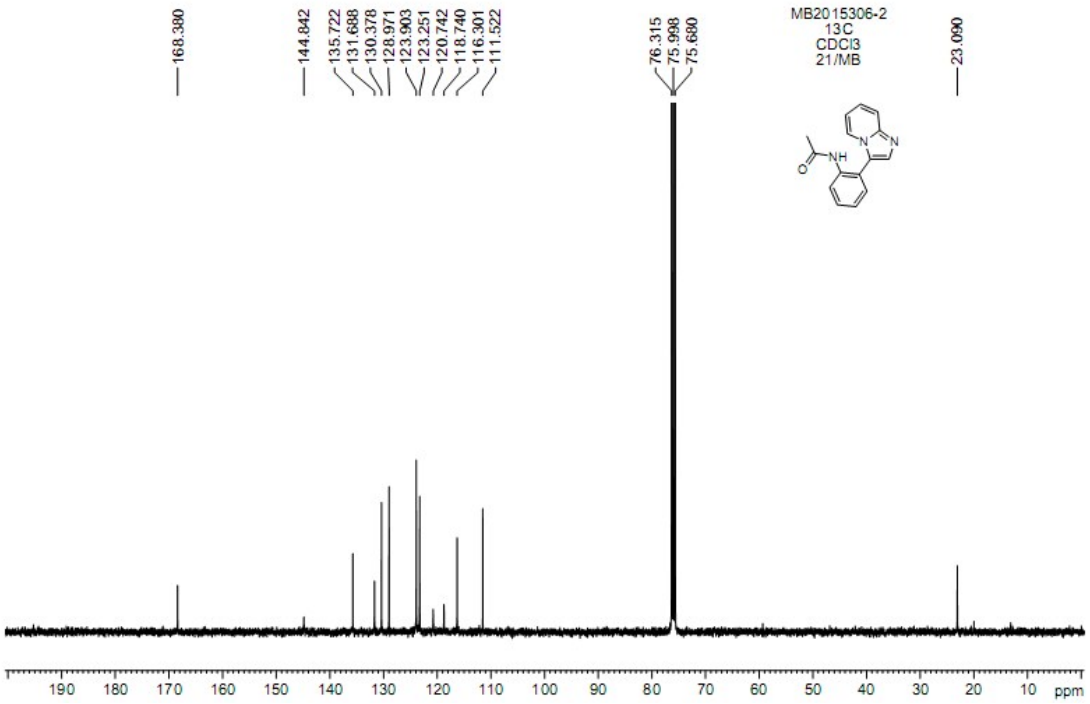
^{13}C NMR of Compound 3h



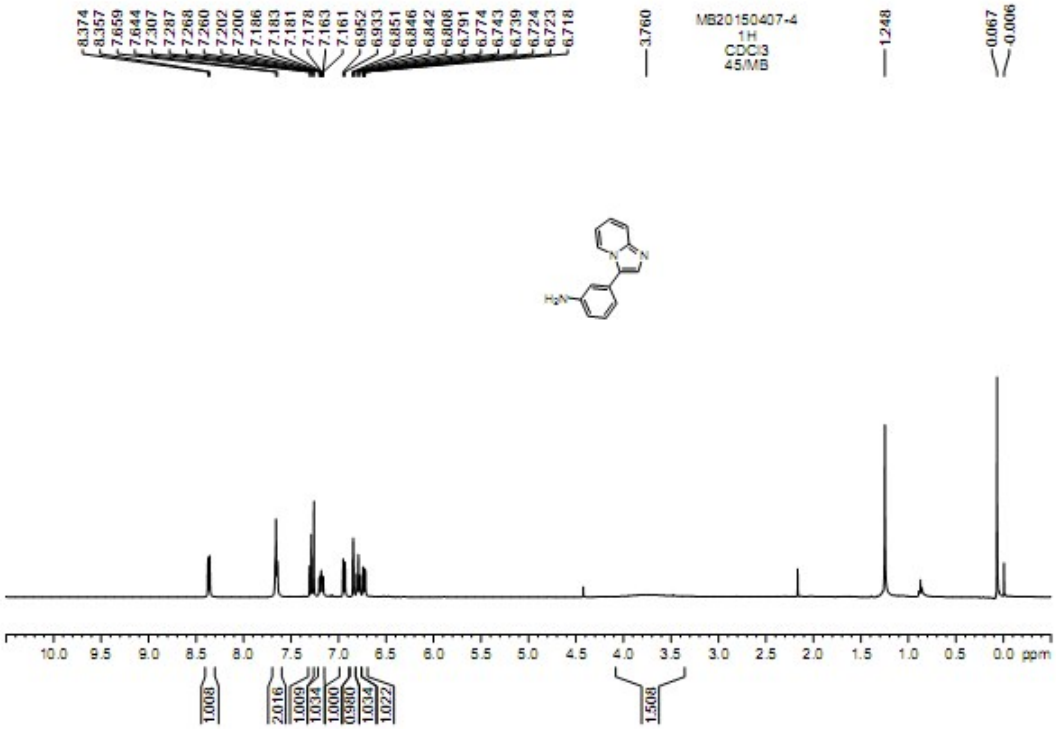
^{1}H NMR of Compound 3i



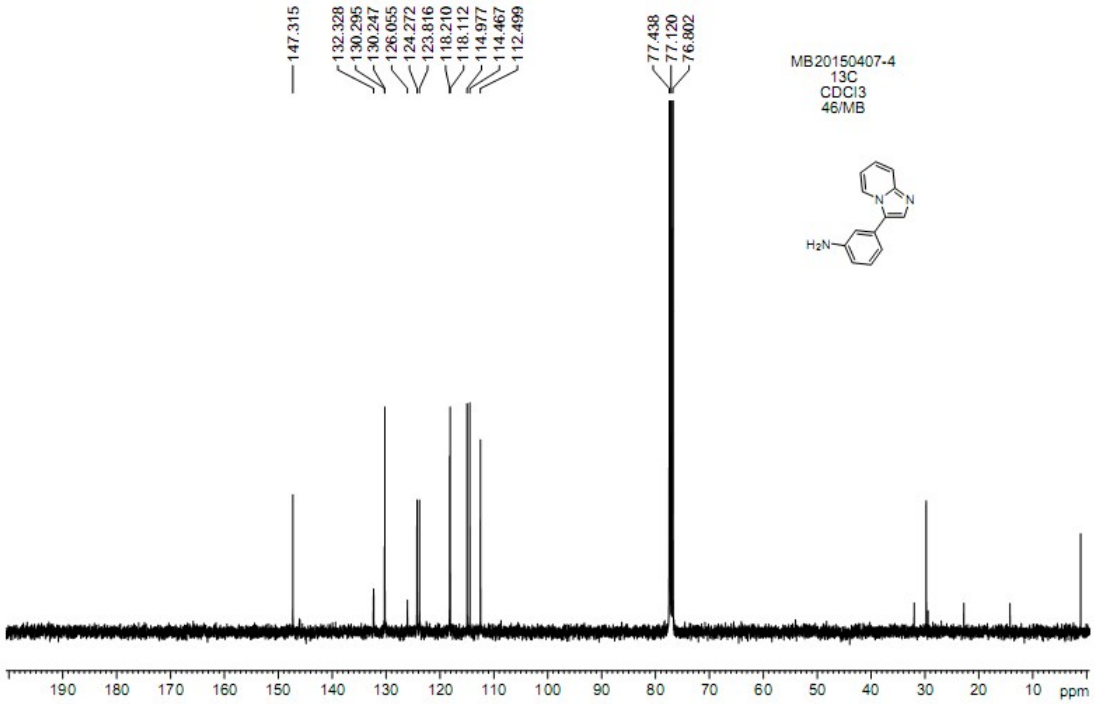
^{13}C NMR of Compound 3i



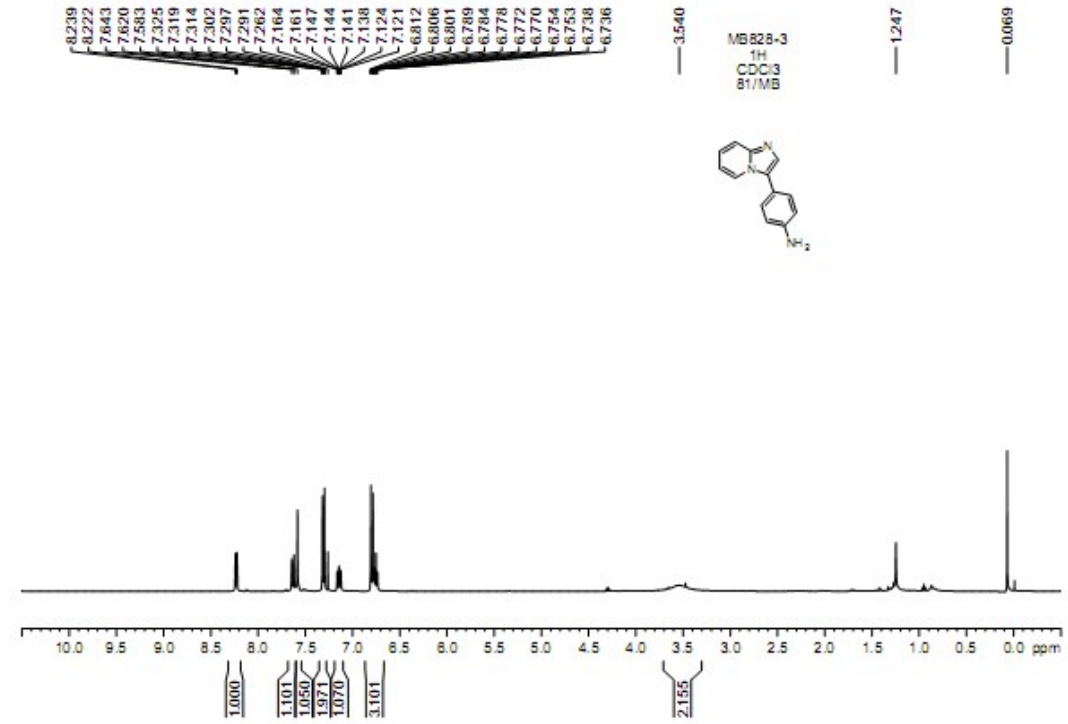
^{1}H NMR of Compound 3j



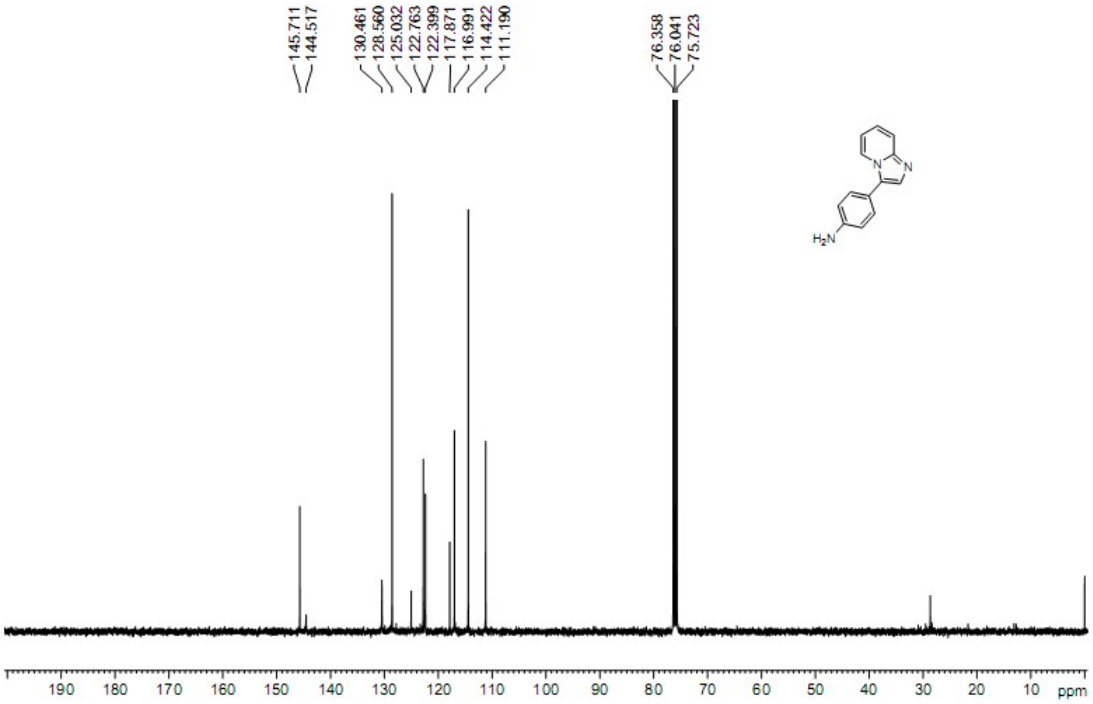
^{13}C NMR of Compound 3j



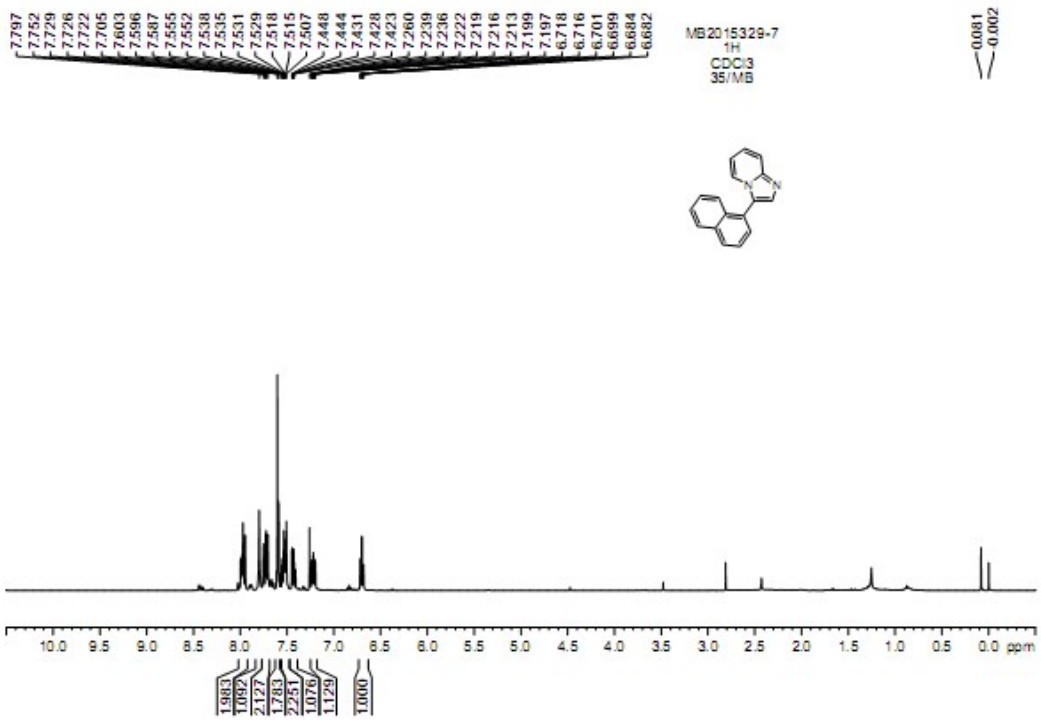
^{1}H NMR of Compound 3k



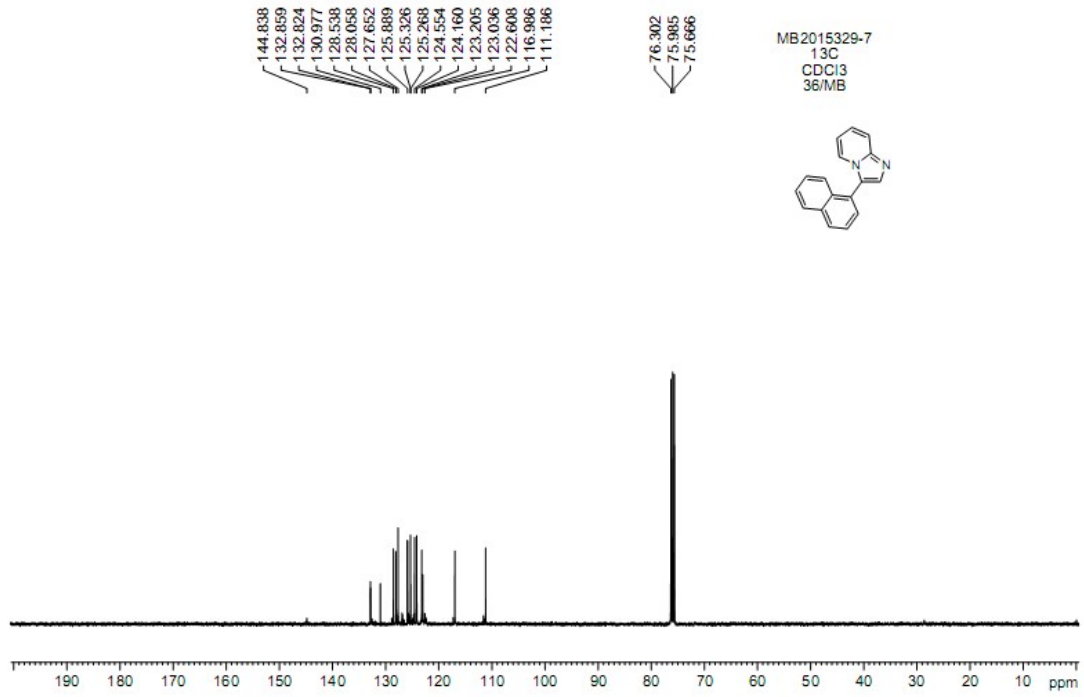
^{13}C NMR of Compound 3k



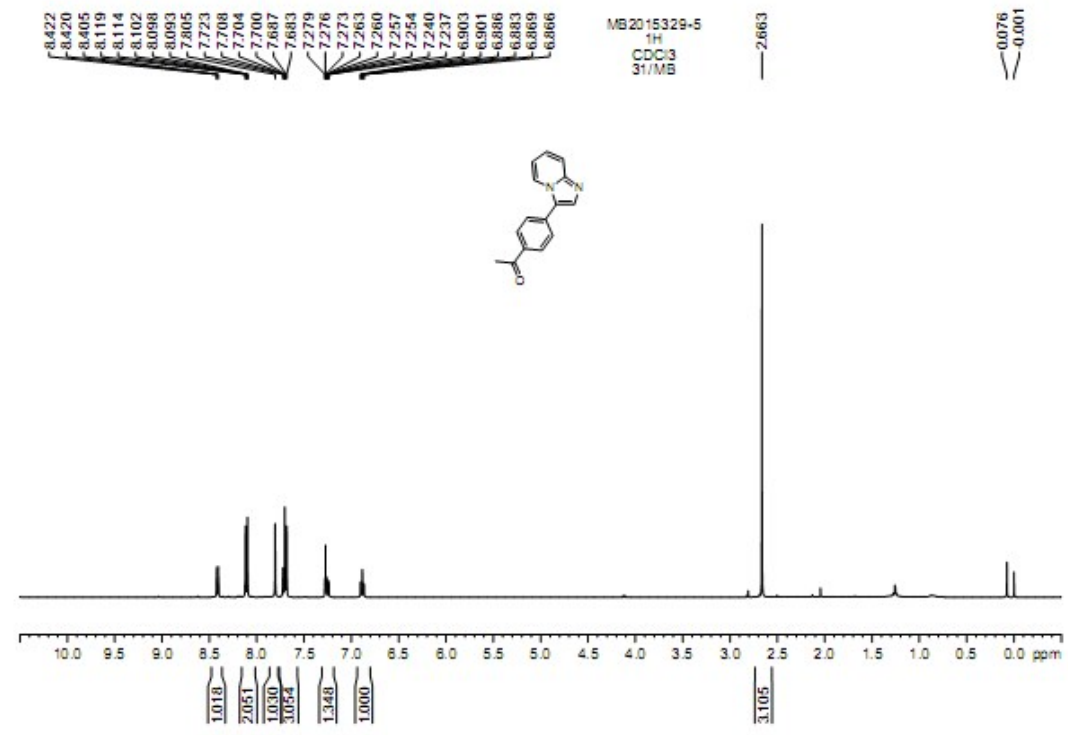
^{1}H NMR of Compound 3l



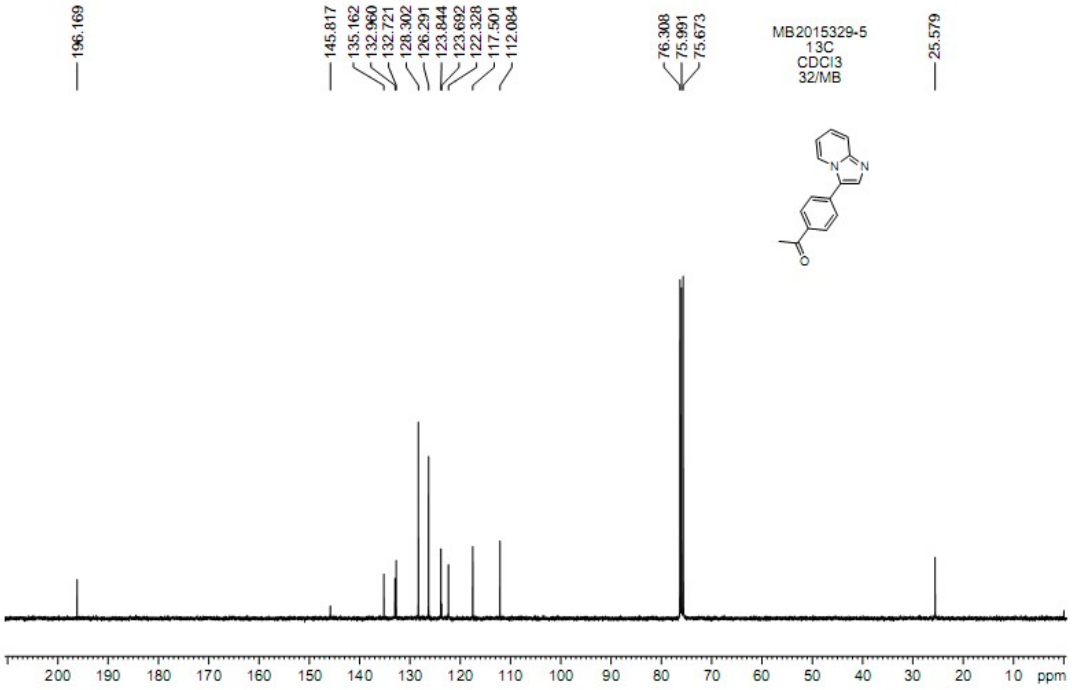
^{13}C NMR of Compound 3l



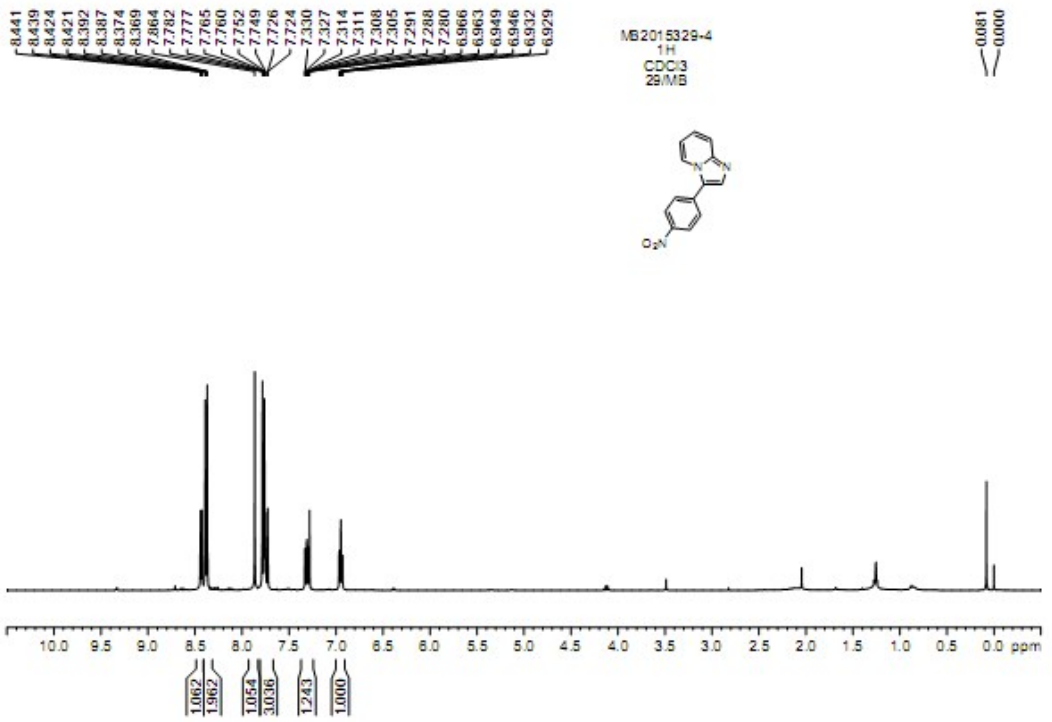
^{1}H NMR of Compound 3m



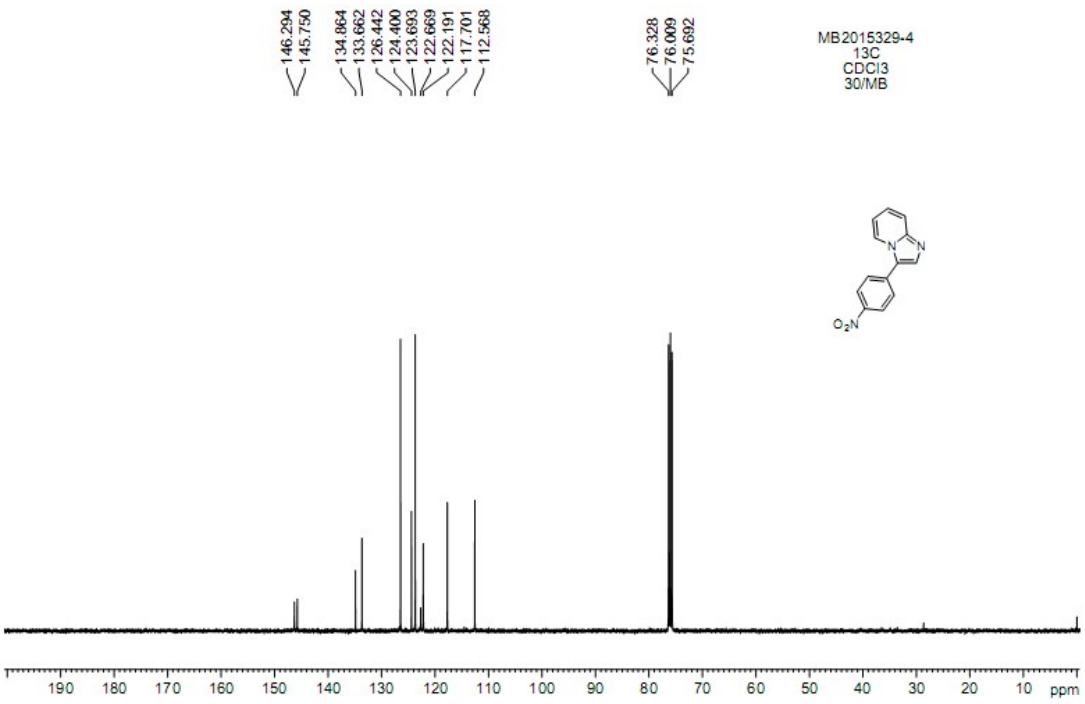
^{13}C NMR of Compound 3m



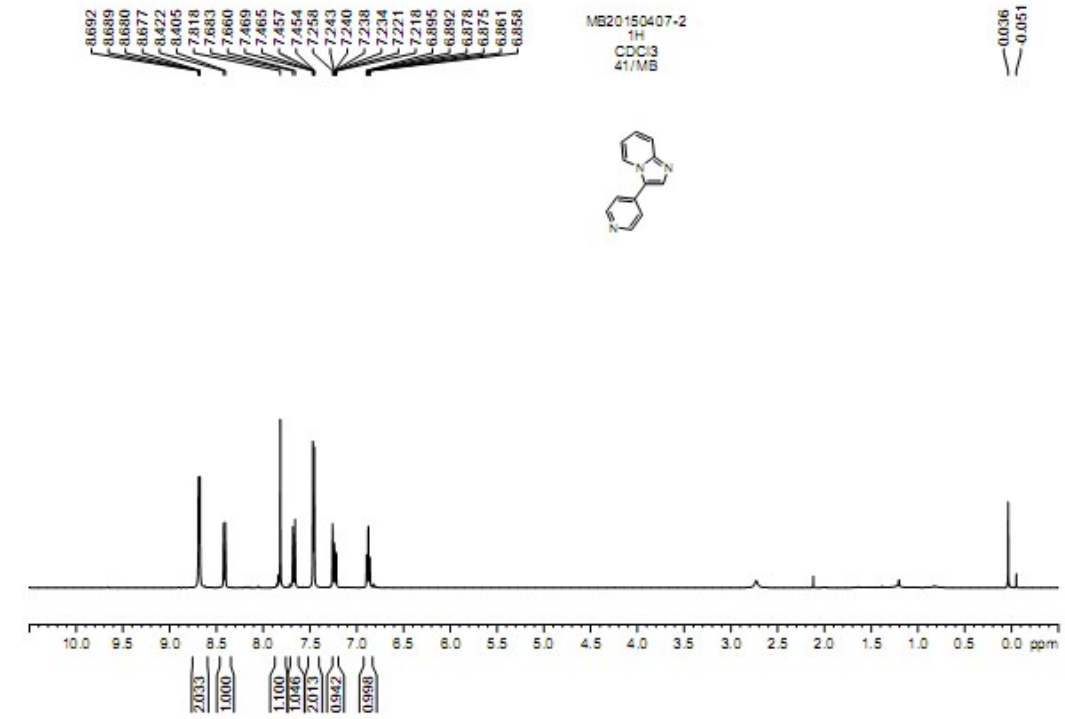
^{1}H NMR of Compound 3n



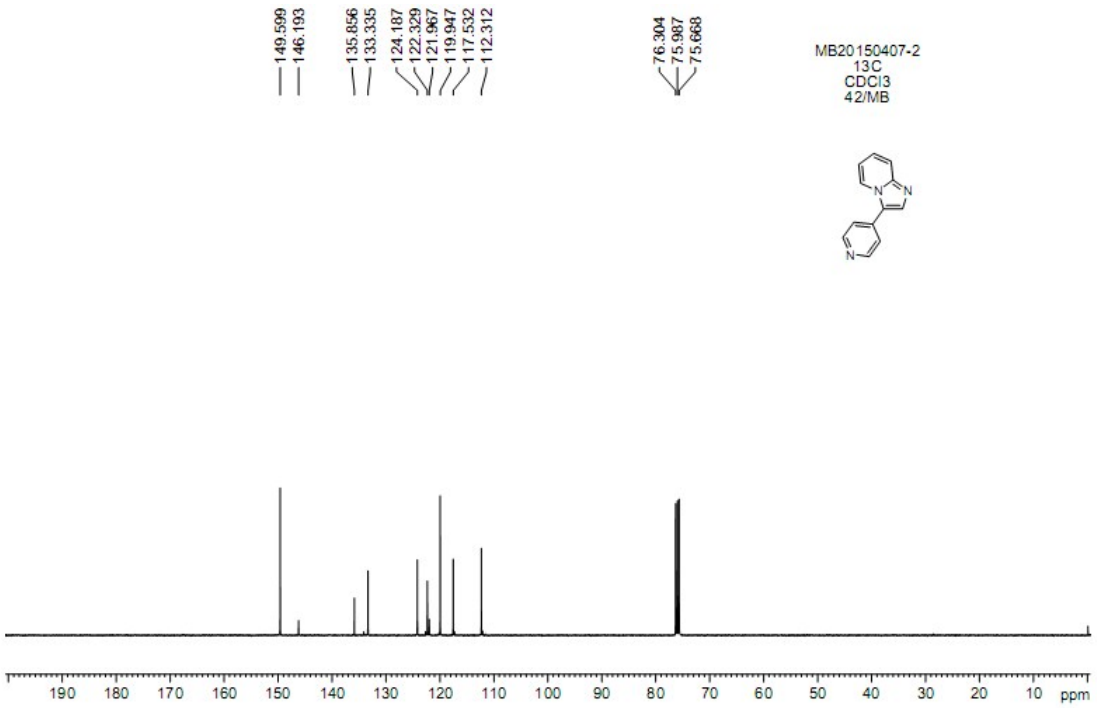
^{13}C NMR of Compound 3n



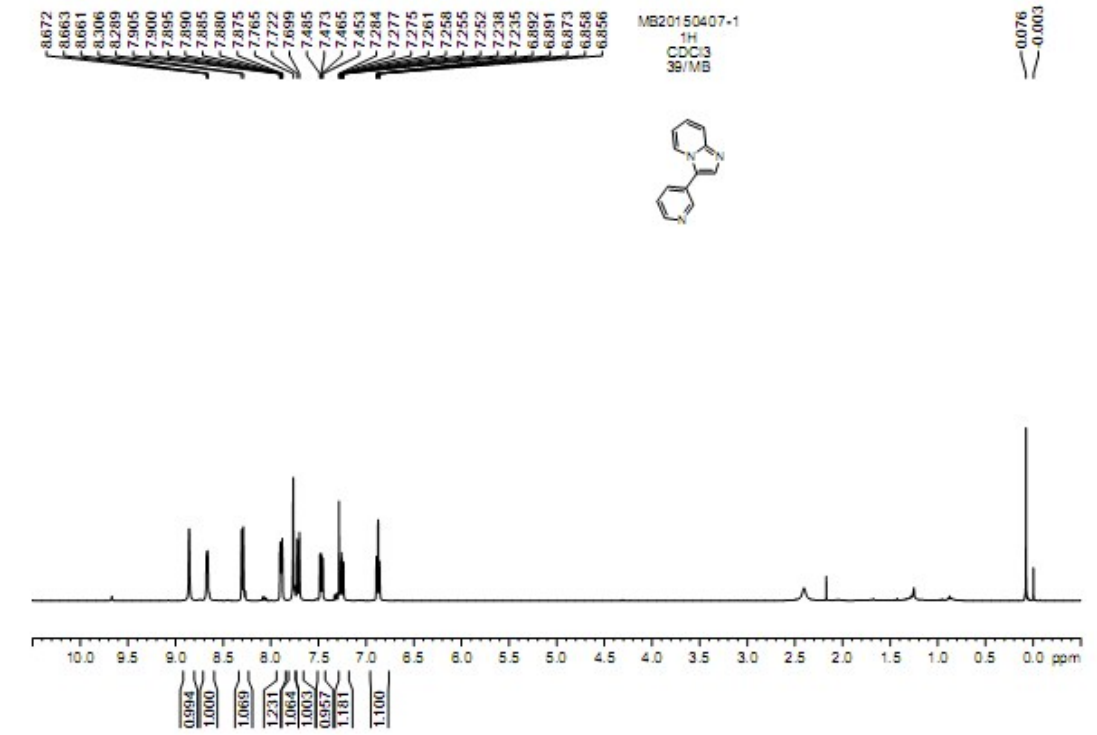
[1]H NMR of Compound 3o



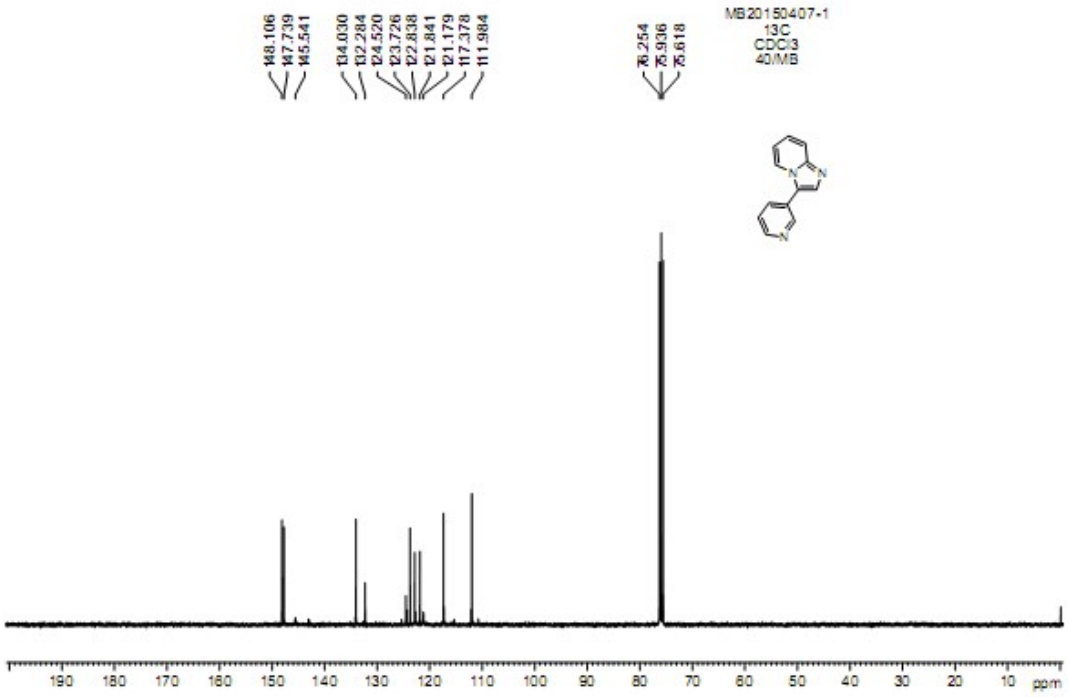
[13]C NMR of Compound 3o



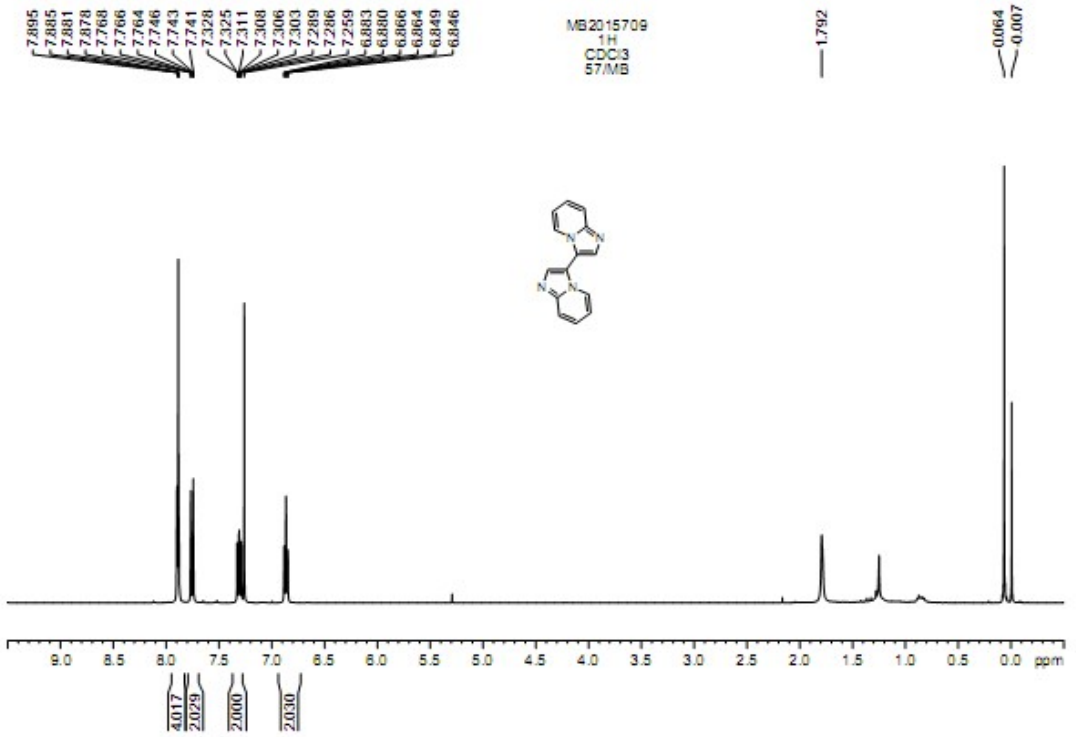
^{1}H NMR of Compound 3p



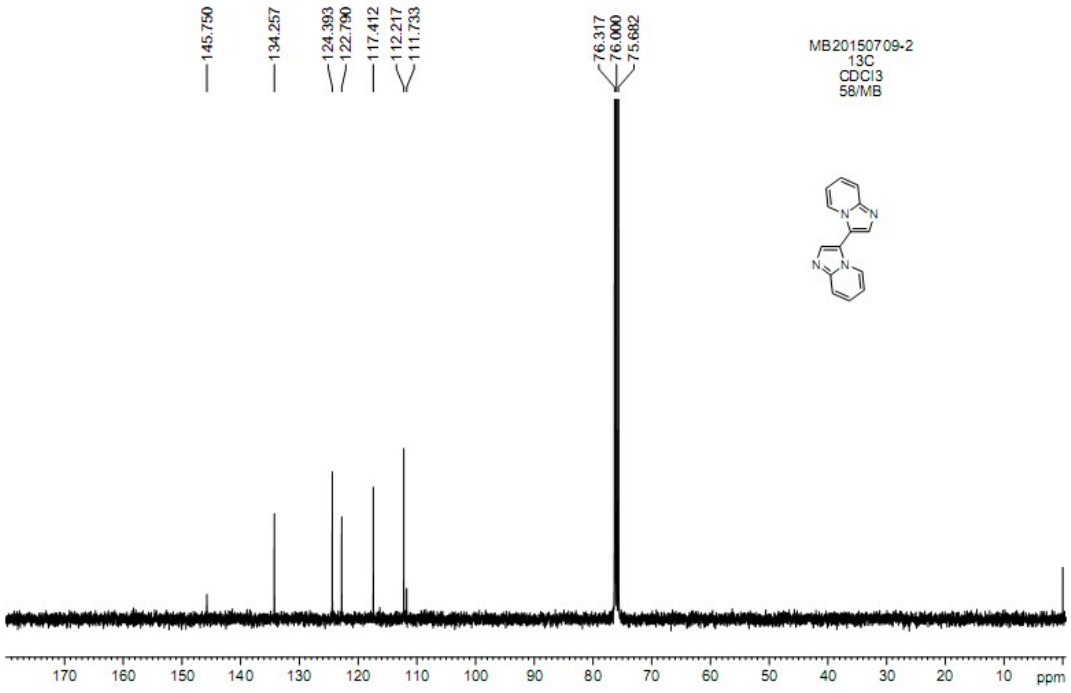
^{13}C NMR of Compound 3p



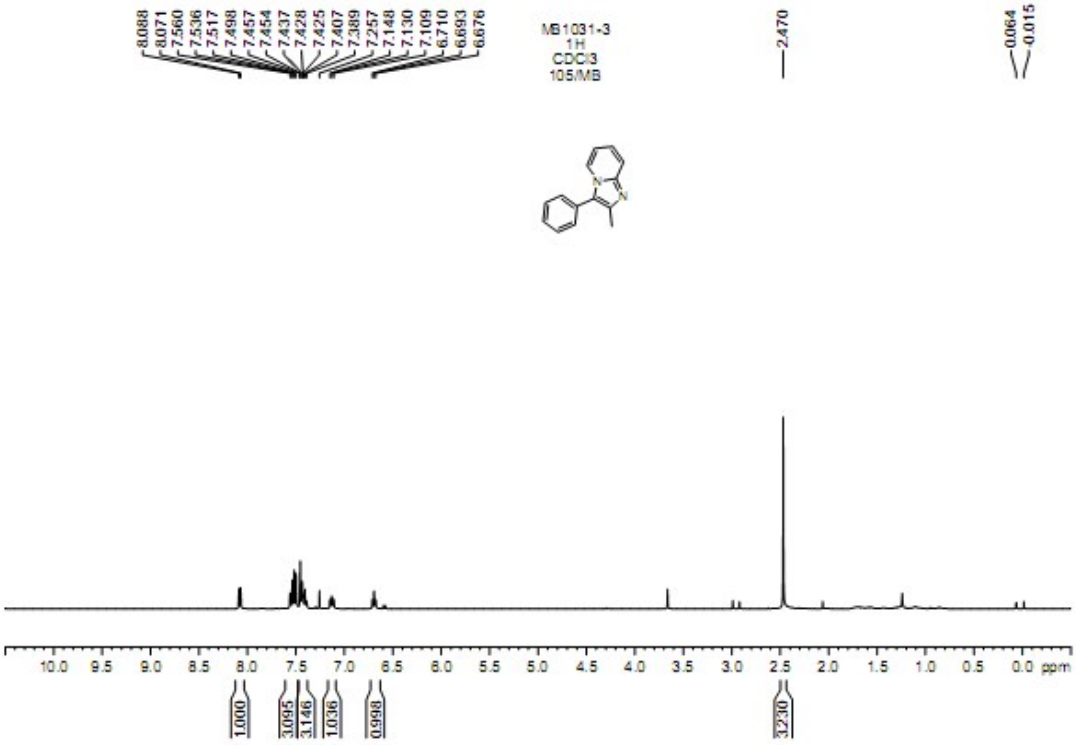
[1]H NMR of Compound 3q



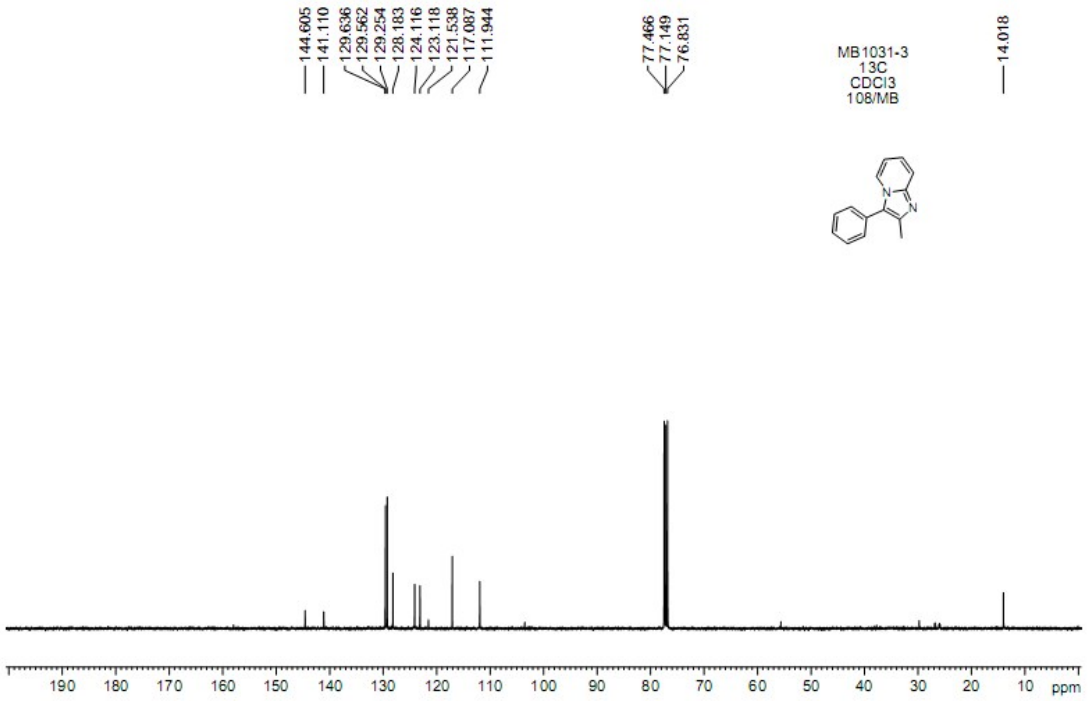
[13]C NMR of Compound 3q



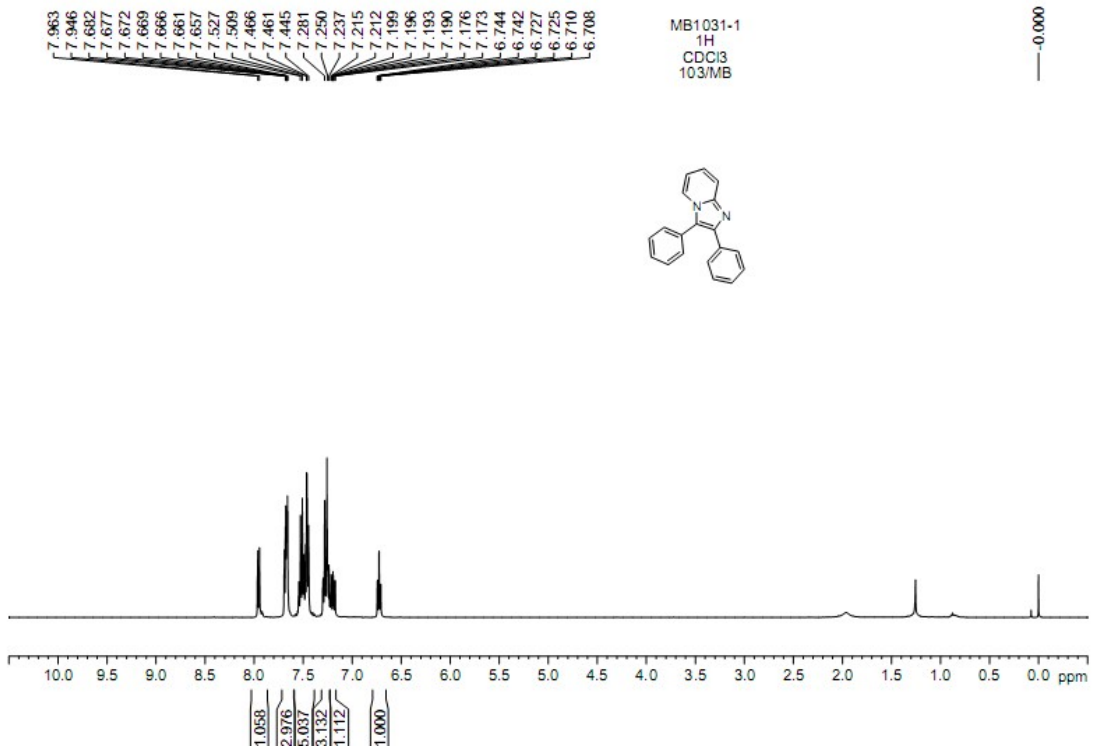
[1]H NMR of Compound 3r



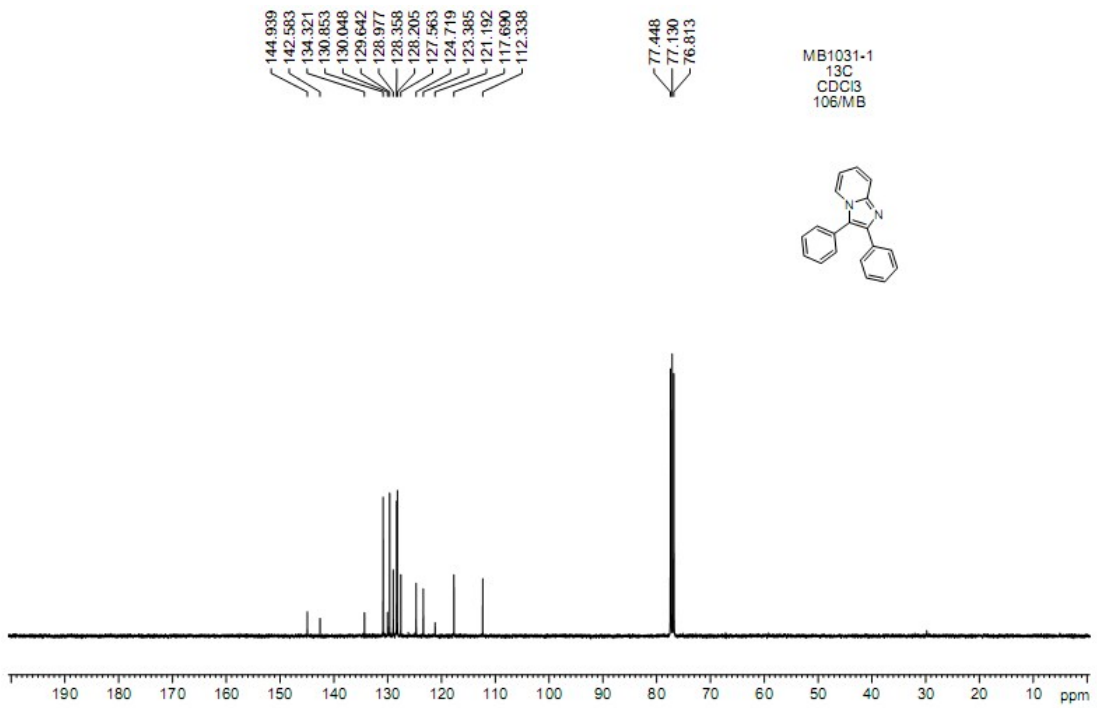
[13]C NMR of Compound 3r



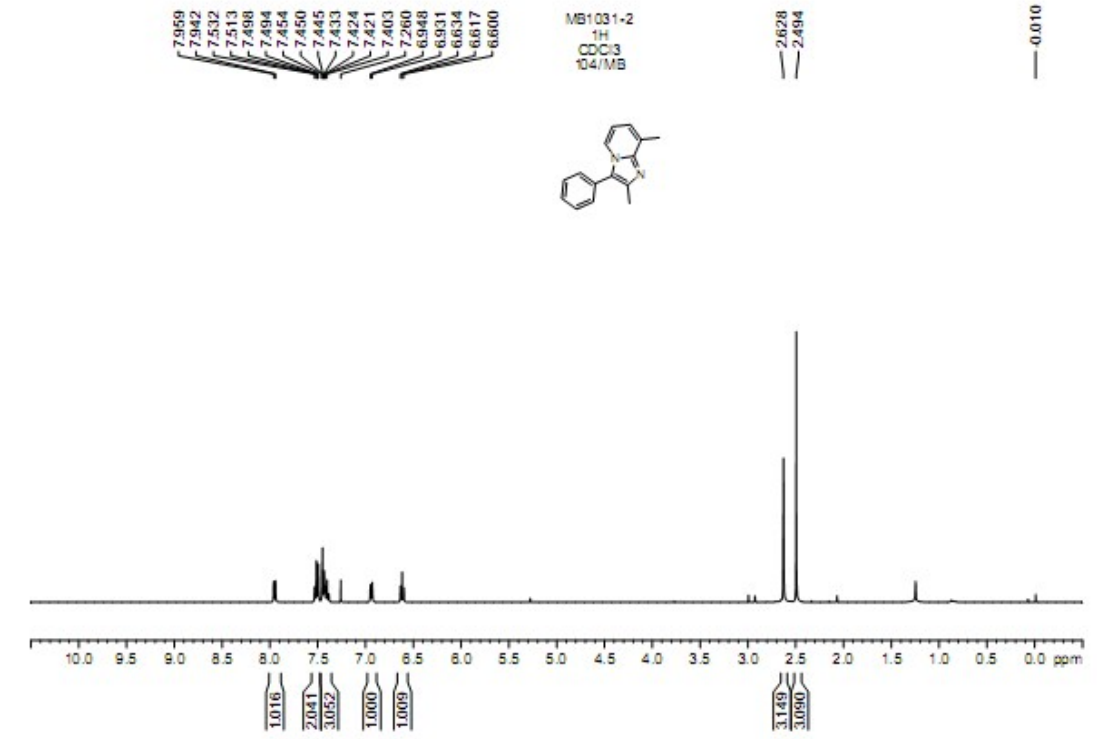
^{1}H NMR of Compound 3s



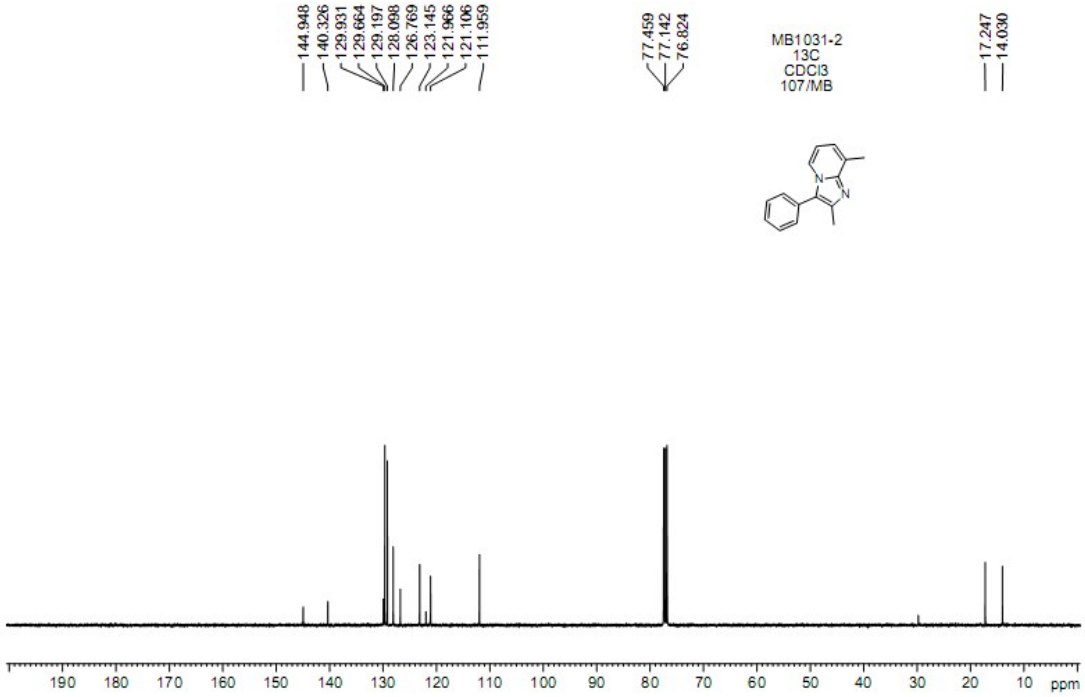
^{13}C NMR of Compound 3s



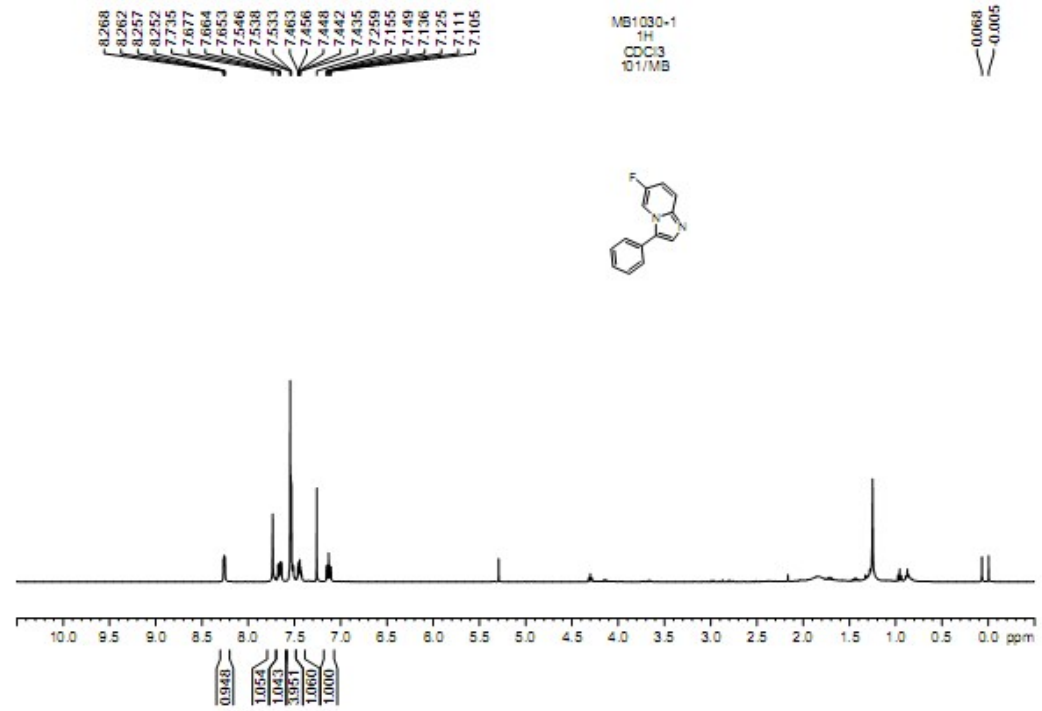
^{1}H NMR of Compound 3t



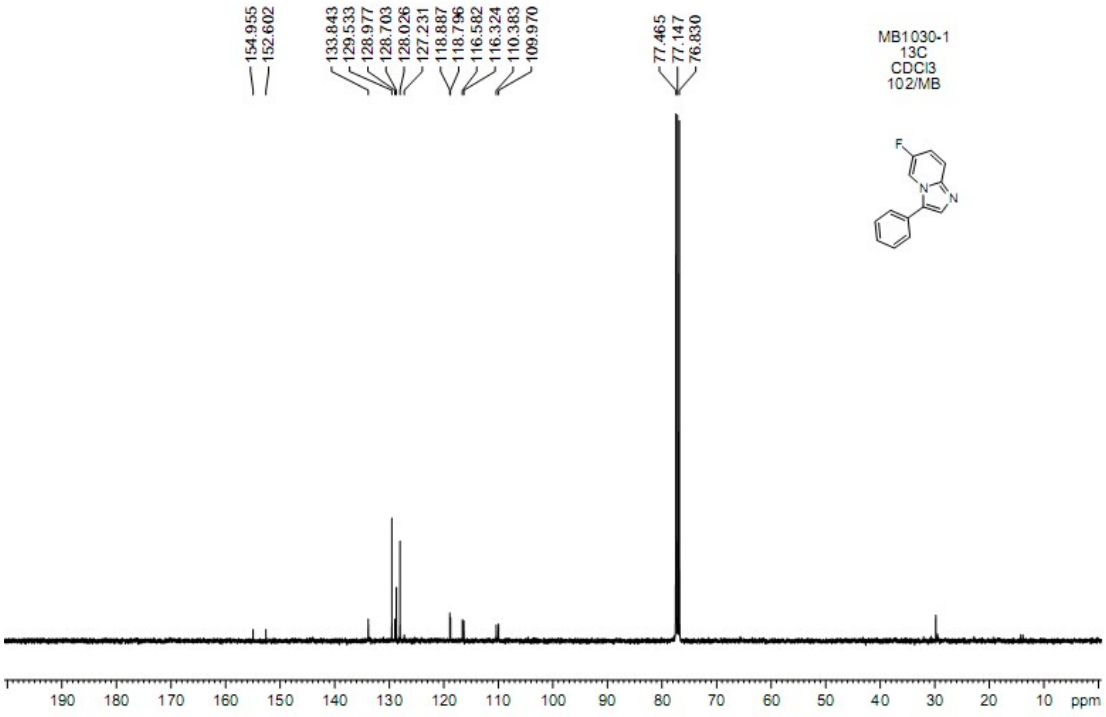
^{13}C NMR of Compound 3t



^{1}H NMR of Compound 3u



^{13}C NMR of Compound 3u


154.955
152.602
133.843
129.533
128.977
128.703
128.026
127.231
118.887
118.796
116.582
116.324
110.383
109.970
77.465
77.147
76.830
MB1030-1
13C
CDCl3
102/MB
F
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm