Supplementary Information

Pd and photoredox dual catalysis assisted decarboxylative *ortho*-benzoylation of *N*-phenyl-7-azaindoles

Shruti Rajput, Ramandeep Kaur and Nidhi Jain*

Table of contents

1. LED emission spectra

The measurement was recorded using Open Spectrophotometer Ava Light-DH-S-BAL Avantes. The light source used for illuminating the reaction vessel is 10 W blue LEDs (λ_{max} = 457 nm).

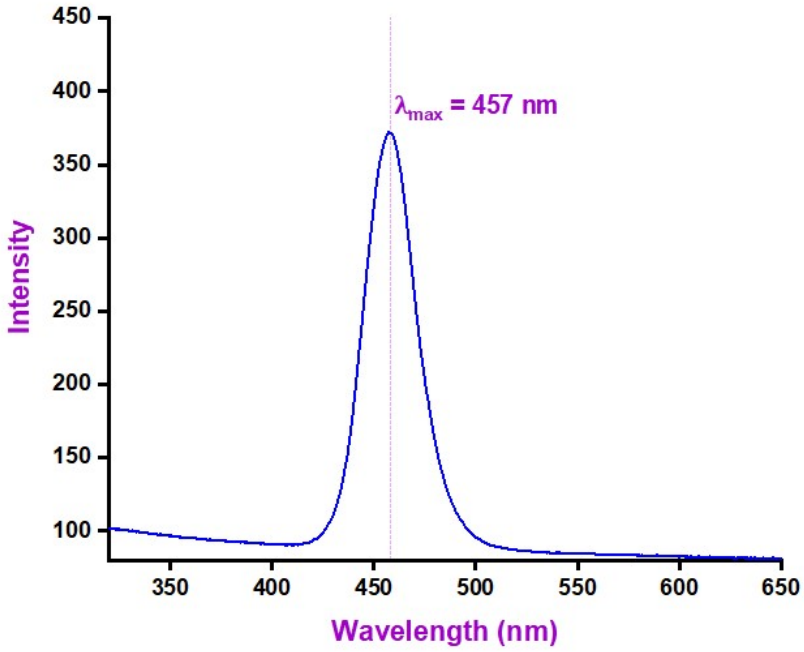
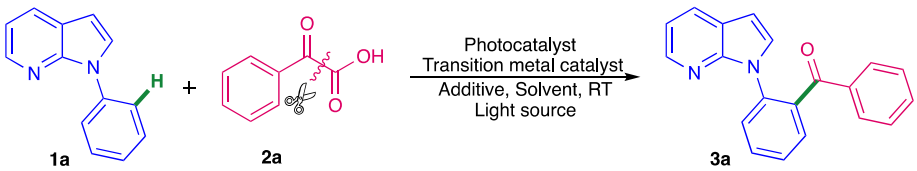


Figure S1. The emission spectra of 10 W blue LED

Figure S2. Reaction Set-up

2. Optimization of the reaction conditions[a] (Table S1)



S.No.	Photocatalyst	Metal Catalyst	Additive	Solvent	Light Source	Yield[b] (%)

1	Eosin Y	$Pd(OAc)_2$	-	PhCl	10 W Green LED	44
2	Eosin Y	$Cu(OAc)_2$/ Cu(OAc)	-	PhCl	10 W Green LED	NR
3	Eosin Y	$Ni(acac)_2$	-	PhCl	10 W Green LED	NR
4	Eosin Y	$Pd(OAc)_2$	-	DCE	10 W Green LED	Traces
5	Eosin Y	$Pd(OAc)_2$	-	1,4-dioxane	10 W Green LED	NR
6	Eosin Y	$Pd(OAc)_2$	-	DMF	10 W Green LED	37
7	Eosin Y	$Pd(OAc)_2$	-	Toluene	10 W Green LED	Traces
8	Eosin Y	$Pd(OAc)_2$	-	DMSO	10 W Green LED	42
9	Eosin Y	$Pd(OAc)_2$	-	MeOH/ *t*-BuOH	10 W Green LED	NR
10	Eosin Y	$Pd(OAc)_2$	-	ACN	10 W Green LED	47
11	Eosin Y	$Pd(OAc)_2$	-	DCM	10 W Green LED	NR
12	Eosin Y	$Pd(OAc)_2$	-	THF	10 W Green LED	39
13	Eosin Y	$Pd(OAc)_2$	-	ACN	10 W blue LED	53
14	Eosin Y	$Pd(OAc)_2$	-	ACN	50 W blue LED	37
15	Eosin Y	$Pd(OAc)_2$	-	ACN	10 W blue LED	51[c], 48[d], 49[e], Traces[f]
16	Eosin Y	$Pd(OAc)_2$	NaOAc	ACN	10 W blue LED	Traces
17	Eosin Y	$Pd(OAc)_2$	K_2CO_3/ Pyridine	ACN	10 W blue LED	NR
18	Eosin Y	$Pd(OAc)_2$	AgOAc	ACN	10 W blue LED	66
19	Eosin Y	$Pd(OAc)_2$	AgF	ACN	10 W blue LED	58
20	Eosin Y	$Pd(OAc)_2$	CF_3SO_3Ag	ACN	10 W blue LED	55
21	Eosin Y	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	75, 73[g], Traces[h]
22	Eosin Y	$Pd(OAc)_2$	$K_2S_2O_8$	ACN	10 W blue LED	Traces
23	Eosin Y	$Pd(OAc)_2$	$KHSO_4$	ACN	10 W blue LED	NR
24	Eosin Y	$Pd(OAc)_2$	$AgNO_3$ + $K_2S_2O_8$	ACN	10 W blue LED	NR
25	Eosin Y	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	72[i], 69[j]
26	Rose Bengal	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	49
27	$Ru(bpy)_3Cl_2$	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	52
28	$(Mes\text{-}Acr)ClO_4$	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	58
29	Eosin Y	$PdCl_2$	$AgNO_3$	ACN	10 W blue LED	56
30	Eosin Y	$Pd(CH_3CN)Cl_2$	$AgNO_3$	ACN	10 W blue LED	57
31	Eosin Y	$Pd(dppf)Cl_2$	$AgNO_3$	ACN	10 W blue LED	NR

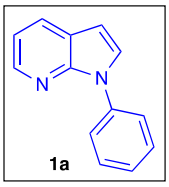
32	Eosin Y	$Pd_2(dba)_3$	$AgNO_3$	ACN	10 W blue LED	63
33	-	$Pd(OAc)_2$	$AgNO_3$	ACN	10 W blue LED	Traces[k]
34	Eosin Y	-	$AgNO_3$	ACN	10 W blue LED	0[l]
35	Eosin Y	$Pd(OAc)_2$	$AgNO_3$	ACN	-	0[m, n]

[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), Transition-metal (10 mol%), Photocatalyst (3.0 mol%), solvent (3.0 mL), Additives (1 eq.), O_2, 40 h, rt, [b]Isolated yield, NR = no reaction. [c]Eosin Y (5 mol%), [d]$Pd(OAc)_2$ (5 mol%), [e]$Pd(OAc)_2$ (15 mol%), [f]Eosin Y (10 mol%), [g]open air atmosphere, [h]nitrogen atmosphere, [i]$AgNO_3$ (2 eq.), [j]$AgNO_3$ (3 eq.), [k]without Eosin Y, [l] Without $Pd(OAc)_2$, [m]without light, [n]80 [o]C in dark.

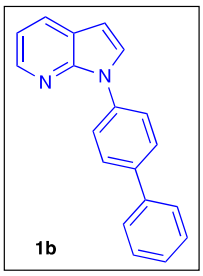
3. Synthesis and characterization of starting materials:

1-phenyl-1H-pyrrolo[2,3-b] pyridine (1a) (procedure B)[1]:

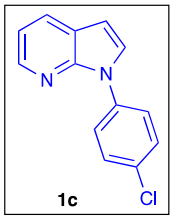
7-azaindole (0.75 g, 6.34 mmol), copper iodide (9.65 mg, 0.05 mmol), potassium phosphate (1.78 g, 8.38 mmol), racemic *trans*-1,2-diaminocyclohexane (45 µL, 0.37 mmol), and iodobenzene (0.46 mL, 4.19 mmol) in anhydrous 1,4-dioxane (7.0 mL) were stirred at 110 [o]C under N_2 atmosphere for 24 h. Upon completion of the reaction (indicated by TLC), the resulting mixture was filtered through a short pad of silica gel and washed with EtOAc. The filtrate was evaporated under vacuum to give a brown oil and purified by column chromatography on silica gel (EtOAc/hexane = 2:98) to afford **1a** (0.71 g, 88%) as yellow viscous liquid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.38 (dd, J = 4.7, 1.3 Hz, 1H), 7.97 (dd, J = 7.8, 1.4 Hz, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.52 (dd, J = 8.5, 5.8 Hz, 3H), 7.34 (t, J = 7.4 Hz, 1H), 7.13 (dd, J = 7.8, 4.7 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H) ppm.



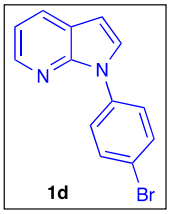
1-([1,1'-biphenyl]-4-yl)-1H-pyrrolo[2,3-b] pyridine (1b)[1]**:** Synthesized following procedure B with 4-iodobiphenyl (1.17 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1b** (0.92 g, 82%) as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.41 (d, J = 4.5 Hz, 1H), 8.26 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 3H), 7.54 (t, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.36-7.31 (m, 2H), 7.20 (dd, J = 8.0, 4.5 Hz, 1H) ppm.



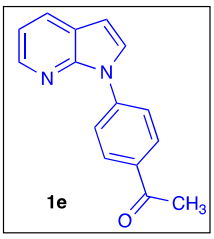
1-(4-chlorophenyl)-1H-pyrrolo[2,3-b]pyridine (1c)[1]**:** Synthesized following procedure B with 1-chloro-4-iodobenzene (0.99 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1c** (0.83 g, 87%) as white solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.38 (dd, J = 4.8, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.4 Hz, 1H), 7.72-7.69 (m, 2H), 7.48-7.37 (m, 3H), 7.13 (dd, J = 7.8, 4.7 Hz, 1H), 6.61 (d, J = 3.4 Hz, 1H) ppm.



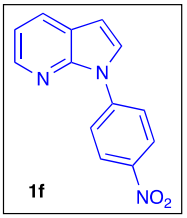
1-(4-bromophenyl)-1H-pyrrolo[2,3-b]pyridine (1d)[1]**:** Synthesized following procedure B with 1-bromo-4-iodobenzene (1.18 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1d** (0.93 g, 82%)as yellow viscous liquid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.36 (dd, J = 4.8, 1.2 Hz, 1H), 7.96 (dd, J = 7.8, 1.4 Hz, 1H), 7.68-7.61 (m, 4H), 7.48 (d, J = 3.0 Hz, 1H), 7.15-7.12 (m, 1H), 6.63-6.62 (m, 1H) ppm.



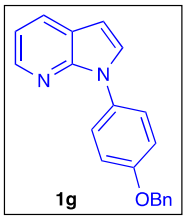
1-(4-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)ethan-1-one (1e)[1]**:** Synthesized following procedure B with 4-iodoacetophenone (1.03 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 4:96) to afford **1e** (0.69 g, 70%) as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.39 (dd, J = 4.8, 1.2 Hz, 1H), 8.12-8.09 (m, 2H), 7.99-7.96 (m, 3H), 7.57 (d, J = 4.0 Hz, 1H), 7.16 (dd, J = 7.8, 4.7 Hz, 1H), 6.67 (d, J = 3.7 Hz, 1H), 2.63 (s, 3H) ppm.



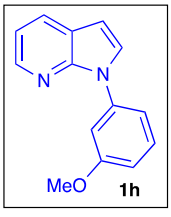
1-(4-nitrophenyl)-1H-pyrrolo[2,3-b]pyridine (1f)[1]**:** Synthesized following procedure B with 1-iodo-4-nitro benzene (1.04 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 6:94) to afford **1f** (0.61 g, 61%) as yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.39 (ddd, J = 9.6, 6.4, 1.6 Hz, 3H), 8.15-8.12 (m, 2H), 7.99 (dd, J = 7.6, 1.6 Hz, 1H), 7.60 (d, J = 3.6 Hz, 1H), 7.21 (dd, J = 8.0, 4.8 Hz, 1H), 6.73 (d, J = 3.6 Hz, 1H) ppm.



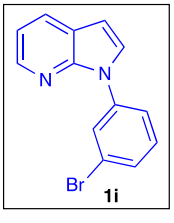
1-(4-(benzyloxy)phenyl)-1H-pyrrolo[2,3-b]pyridine (1g)[1,2]**:** Synthesized following procedure B with 1-(Benzyloxy)-4-iodobenzene (1.30 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 4:96) to afford **1g** (0.90 g, 72%) as yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.35 (d, J = 4.4 Hz, 1H), 7.95 (dd, J = 7.6, 1.2 Hz, 1H), 7.65-7.56 (m, 2H), 7.48-7.37 (m, 5H), 7.33 (t, J = 7.2 Hz, 1H), 7.14-7.06 (m, 3H), 6.59 (d, J = 3.6 Hz, 1H), 5.11 (s, 2H) ppm.



1-(3-methoxyphenyl)-1H-pyrrolo[2,3-b]pyridine (1h)[1]**:** Synthesized following procedure B with 3-iodoanisole (0.98 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1h** (0.61 g, 65 %) as yellow viscous liquid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.37 (dd, J = 4.7, 1.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.6 Hz, 1H), 7.51 (d, J = 3.6 Hz, 1H), 7.42 (t, J = 8.1 Hz, 1H), 7.37 (t, J = 2.2 Hz, 1H), 7.34-7.32 (m, 1H), 7.13 (dd, J = 7.8, 4.7 Hz, 1H), 6.89-6.87 (m, 1H), 6.62 (d, J = 3.6 Hz, 1H), 3.87 (s, 3H) ppm.

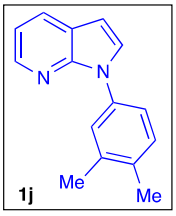


1-(3-bromophenyl)-1H-pyrrolo[2,3-b]pyridine (1i): Synthesized following procedure B with 1-bromo-3-iodobenzene (1.18 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol),

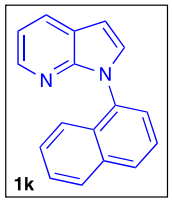


purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1i** (0.76 g, 67 %) as yellow liquid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.35 (dd, J = 4.7, 1.5 Hz, 1H), 7.95 (t, J = 2.0 Hz, 1H), 7.90 (dd, J = 7.8, 1.4 Hz, 1H), 7.72-7.70 (m, 1H), 7.40-7.38 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.09 (dd, J = 7.8, 4.7 Hz, 1H), 6.56 (d, J = 3.7 Hz, 1H) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ 147.2, 143.5, 139.5, 130.3, 129.0, 128.8, 127.0, 126.3, 122.5, 121.9, 121.5, 116.8, 102.2. HRMS (ESI, Q-TOF) m/z: calcd for $C_{13}H_{10}N_2Br$ $[M+H]^+$ 273.0022; found 273.0034.

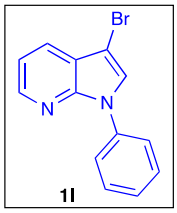
1-(3,4-dimethylphenyl)-1H-pyrrolo[2,3-b] pyridine (1j): Synthesized following procedure B with 1-iodo-3,4-dimethylbenzene (0.97 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1j** (0.69 g, 75%) as a yellow viscous liquid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.43 (d, J = 4.6 Hz, 1H), 8.00 (dd, J = 7.8, 0.8 Hz, 1H), 7.54-7.48 (m, 3H), 7.32 (d, J = 8.0 Hz, 1H), 7.15 (dd, J = 7.8, 4.7 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ:** 147.5, 143.3, 137.4, 136.1, 134.8, 130.2, 128.7, 128.0, 125.4, 121.6, 121.2, 116.2, 100.9, 19.8, 19.2 ppm. HRMS (ESI, Q-TOF) m/z: calcd for $C_{15}H_{15}N_2$ $[M+H]^+$ 223.1230; found 223.1253.



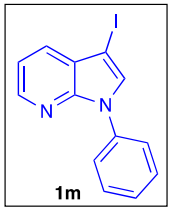
1-(naphthalen-1-yl)-1H-pyrrolo[2,3-b]pyridine (1k)[1,3]**:** Synthesized following procedure B with 1-iodonaphthalene (1.06 g, 4.19 mmol) and 7-azaindole (0.75 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 3:97) to afford **1k** (0.59 g, 58 %) as brown liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.31 (dd, J = 4.7 Hz, 1.5 Hz, 1H), 8.06 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.59-7.66 (m, 2H), 7.61-7.64 (m, 2H), 7.50-7.56 (m, 1H), 7.46 (d, J = 3.6 Hz, 1H), 7.38-7.42 (m, 2H), 7.15 (dd, J = 7.8 Hz, 4.5 Hz, 1H), 6.73 (d, J = 3.5 Hz, 1H) ppm.



3-bromo-1-phenyl-1H-pyrrolo[2,3-b] pyridine (1l)[1]**:** A mixture of 1-phenyl-1H-pyrrolo[2,3-b] pyridine (0.97 g, 5.0 mmol), NBS (0.97 g, 5.50 mmol) and KOH (0.84 g, 15.0 mmol) was stirred in CH_3CN (5.0 mL) at room temperature for 11 h. The succinimide was filtered off, washed with CH_2Cl_2 and the filtrate and was evaporated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/hexane = 2:98) to give **1l** (1.07 g, 85 %) as pale white liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.40 (dd, J = 4.7, 1.5 Hz, 1H), 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.71-7.69 (m, 2H), 7.53-7.48 (m, 3H), 7.36-7.21 (m, 1H), 7.20 (dd, J = 7.9, 4.7 Hz, 1H) ppm.

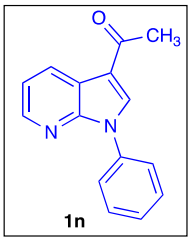


3-iodo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1m)[1]**:** A mixture of 1-phenyl-1H-pyrrolo[2,3-b] pyridine (0.97 g, 5.0 mmol), NIS (1.24 g, 5.50 mmol) and KOH (0.84 g, 15.0 mmol) was stirred in CH_3CN (5.0 mL) at room temperature for 11 h. The succinimide was

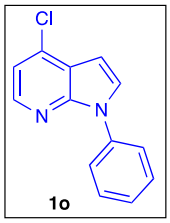


filtered off, washed with CH_2Cl_2 and the filtrate was evaporated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/hexane = 1:99) to give **1m** (1.26 g, 79 %) as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.39 (dd, J = 4.8, 1.2 Hz, 1H), 7.80 (dd, J = 8.0, 1.6 Hz, 1H), 7.72-7.70 (m, 2H), 7.62 (s, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.22 (dd, J = 8.0, 4.4 Hz, 1H) ppm.

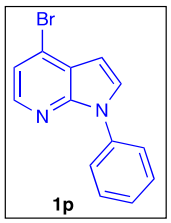
1-(1-phenyl-1H-pyrrolo[2,3-b]pyridin-3-yl)ethan-1-one (1n)[1]**:** 1-phenyl-1H-pyrrolo[2,3-b] pyridine (0.39 g, 2.0 mmol) was added to a stirred suspension of $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (48 mL). After the mixture was stirred at room temperature for 1 h, acetyl chloride (0.78 g, 10 mmol) was added dropwise, and the resulting mixture was stirred for 6 h. The reaction was quenched with MeOH (10 mL) and the solvents were removed under vacuum. The residue was purified by silica gel column chromatography (EtOAc/hexane = 3:97) to afford **1n** (0.38 g, 81 %) as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.64 (dd, J = 8.0, 1.6 Hz, 1H), 8.36 (dd, J = 4.4, 1.6 Hz, 1H), 8.03 (s, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 (dd, J = 7.6, 4.8 Hz, 1H), 2.51 (s, 3H) ppm.



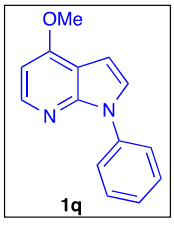
4-chloro-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1o)[1]**:** Synthesized following procedure B with iodobenzene (0.46 mL, 4.19 mmol) and 4-chloro-7-azaindole (0.96 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 2:98) to afford **1o** as yellow solid (0.89 g, 93%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, J = 5.0 Hz, 1H), 7.70 (dd, J = 8.3, 1.0 Hz, 2H), 7.53-7.50 (m, 3H), 7.35 (t, J = 7.0 Hz, 1H), 7.14 (d, J = 5.0 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H) ppm.



4-bromo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1p): Synthesized following procedure B with iodobenzene (0.46 mL, 4.19 mmol) and 4-bromo-7-azaindole (1.24 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 4:96) to afford **1p** (1.01 g, 92 %) as yellow liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.15 (d, J = 5.2 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.52-7.47 (m, 3H), 7.36-7.29 (m, 2H), 6.65 (d, J = 3.6 Hz, 1H) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ 147.1, 143.6, 138.0, 129.3, 128.4, 126.7, 125.2, 124.0, 122.9, 119.8, 101.5 ppm. HRMS (ESI, Q-TOF) m/z: calcd for $C_{13}H_{10}N_2Br$ $[M+H]^+$ 273.0022; found 273.0035.

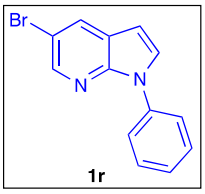


4-methoxy-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1q)[1]**:** A suspension of 4-chloro-1-phenyl-1H-pyrrolo[2,3-b]pyridine (0.23 g, 1.0 mmol) in a 90% methanolic sodium hydroxide solution (0.21 g, 5.25 mmol in 2.0 mL) was heated in a sealed tube at 150 °C for 23 h. After cooling, the reaction mixture was poured into crushed ice (about 20 g). The solid

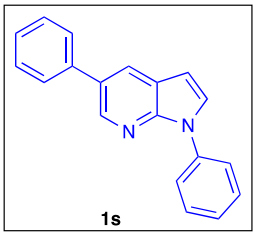


which precipitated was collected by filtration and purified by silica gel column chromatography (EtOAc/hexane = 4:96) to give **1q** (0.15 g, 68%) as white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.26 (d, J = 5.6 Hz, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.36-7.28 (m, 2H), 6.71 (d, J = 3.6 Hz, 1H), 6.60 (d, J = 5.6 Hz, 1H), 4.02 (s, 3H) ppm.

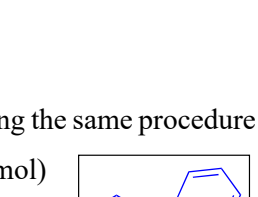
5-bromo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1r)[1]**:** Synthesized following procedure B with iodobenzene (0.46 mL, 4.19 mmol)) and 5-bromo-7-azaindole (1.24 g, 6.34 mmol), purified by column chromatography on silica gel (EtOAc/hexane = 4:96) to afford **1r** (1.01 g, 89%) as yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.43-8.00 (m, 2H), 7.64-7.62 (m, 2H), 7.47-7.39 (m, 3H), 7.29 (t, J = 7.6 Hz, 1H), 6.49 (dd, J = 8.0, 3.6 Hz, 1H) ppm.



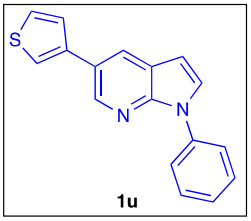
1,5-diphenyl-1H-pyrrolo[2,3-b]pyridine (1s)[1]**:** A solution of 5-bromo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (0.38 g, 1.40 mmol), phenylboronic acid (0.21 g, 1.80 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), dppf (27.7 mg, 0.05 mmol) and Cs_2CO_3 (0.91 g, 2.80 mmol) in 1,4-dioxane/water (5.0 mL, 3:1 mixture) was heated to 60 °C for 26 h under N_2 atmosphere. The reaction was allowed to cool to room temperature, diluted with EtOAc (30 mL) filtered through celite and was concentrated under vacuum. The residue product was purified by silica gel column chromatography (EtOAc/hexane = 5:95) to give **1s** (0.23 g, 63%) as yellowish solid. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.62 (d, J = 2.5 Hz, 1H), 8.15 (d, J = 3.0 Hz, 1H), 7.80-7.77 (m, 2H), 7.65-7.63 (m, 2H), 7.55-7.52 (m, 3H), 7.47 (t, J = 8.0 Hz, 2H), 7.40-7.34 (m, 2H), 6.68 (d, J = 4.5 Hz, 1H) ppm.



4-(dibenzo[b,d]furan-4-yl)-1-phenyl-1H-pyrrolo[2,3-b]pyridine (1t): Following the same procedure used for **1s** with 4-bromo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (0.38 g, 1.40 mmol) and dibenzofuran-4-boronic acid (0.38 g, 1.80 mmol). After reacted at 60 °C for 26 h under N_2 atmosphere, purified by column chromatography on silica gel (EtOAc/hexane = 5:95) to afford **1t** (0.37 g, 75 %) as white solid; M.P.: 146-149 °C; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.53 (d, J = 5.0 Hz, 1H), 8.03-7.99 (m, 2H), 7.79-7.74 (m, 3H), 7.57-7.51 (m, 5H), 7.49-7.3 (m, 2H), 7.35 (dd, J = 17.0, 7.5 Hz, 2H), 6.70 (d, J = 3.5 Hz, 1H) ppm. **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$):** δ 156.1, 153.3, 148.1, 143.6, 138.5, 137.3, 129.3, 128.1, 127.9, 127.4, 126.3, 125.1,124.1, 124.0, 123.1, 123.0, 122.9, 120.7, 120.6, 120.1, 117.32, 111.8, 101.6 ppm. HRMS (ESI, Q-TOF) m/z: calcd for $C_{25}H_{17}N_2O$ $[M+H]^+$ 361.1335; found 361.1343.



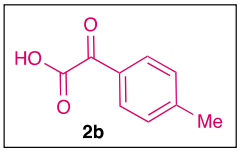
1-phenyl-5-(thiophen-3-yl)-1H-pyrrolo[2,3-b]pyridine (1u)[1,4]**:** Following the same procedure used for **1s** with 5-bromo-1-phenyl-1H-pyrrolo[2,3-b]pyridine (0.38 g, 1.40 mmol) and thiophene-3-broronic acid (0.43 g, 1.80 mmol). After reacted for 24 h at



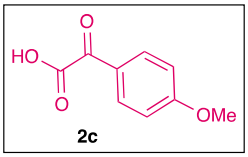
110 °C, purified by column chromatography on silica gel (EtOAc/hexane = 4:96) to afford **1u** (0.25 g, 65%) as off-white solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.65 (d, J = 2.0 Hz, 1H), 8.14 (d, J = 2.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H) 7.55-7.51 (m, 3H), 7.47-7.43 (m, 3H), 7.35 (t, J = 7.2 Hz, 1H), 6.65 (d, J = 3.6 Hz, 1H) ppm.

The *α*-oxocarboxylic acids were prepared from oxidation of corresponding aryl methyl ketones by SeO_2 according to the reported procedure.[5]

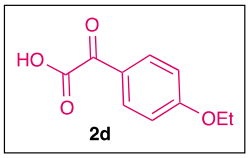
2-oxo-2-(p-tolyl)acetic acid (2b): Synthesized following the reported procedure[5] using 4-methyl acetophenone (1.0 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as light brown solid **2b** (1.02 g, 85%). **^{1}H NMR (400 MHz, DMSO-d_6):** δ 7.83 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H) ppm.



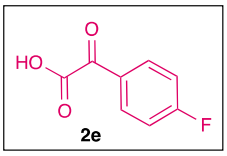
2-(4-methoxyphenyl)-2-oxoacetic acid (2c): Synthesized following the reported procedure[5] using 4-methoxyacetophenone (1.10 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as brown solid **2c** (1.10 g, 83%). **^{1}H NMR (400 MHz, DMSO-d_6):** δ 7.56-7.49 (m, 2H), 7.41 (s, 1H), 7.34 (dd, J = 7.6, 1.2 Hz, 1H), 3.83 (s, 3H) ppm.



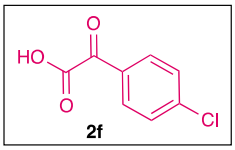
2-(4-ethoxyphenyl)-2-oxoacetic acid (2d): Synthesized following the reported procedure[5] using 4-ethoxyacetophenone (1.20 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as light brown solid **2d** (1.10 g, 79%). **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.88 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 4.16 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H) ppm.



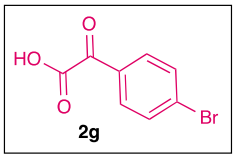
2-(4-fluorophenyl)-2-oxoacetic acid (2e): Synthesized following the reported procedure[5] using 4-fluoroacetophenone (1.0 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as brown solid **2e** (0.98 g, 87%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.44-8.40 (m, 2H), 7.22 (t, J = 8.4 Hz, 2H) ppm.



2-(4-chlorophenyl)-2-oxoacetic acid (2f): Synthesized following the reported procedure[5] using 4-chloroacetophenone (1.10 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as off-white solid **2f** (1.18 g, 82%). Yield: 0.162 g in 89%. **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.34 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H) ppm.

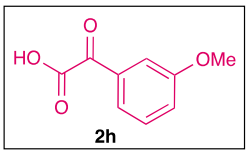


2-(4-bromophenyl)-2-oxoacetic acid (2g): Synthesized following the reported procedure[5] using 4-bromoacetophenone (1.47 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The

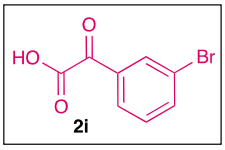


product was isolated as white solid **2g** (1.47 g, 87%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.23 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H) ppm.

2-(3-methoxyphenyl)-2-oxoacetic acid (2h): Synthesized following the reported procedure[5] using 3-methoxyacetophenone (1.11 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as dark brown viscous liquid **2h** (1.11 g, 84%). **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.56-7.49 (m, 2H), 7.41 (s, 1H), 7.35 (dd, J = 8.0, 2.5 Hz, 1H), 3.84 (s, 3H) ppm.



2-(3-bromophenyl)-2-oxoacetic acid (2i): Synthesized following the reported procedure[5] using 3-bromoacetophenone (1.47 g, 7.4 mmol) and SeO_2 (1.65 g, 14.9 mmol). The product was isolated as light-yellow solid **2i** (1.44 g, 85%). **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.63-7.57 (m, 2H), 7.45 (s, 1H), 7.30 (dd, J = 8.0, 2.5 Hz, 1H) ppm.



4. Gram scale Synthesis

To an oven dried 100 mL round bottom flask, *N*-phenyl-7-azaindole **1a** (1.0 g, 5.15 mmol), phenylglyoxylic acid **2a** (1.16 g, 7.72 mmol), Eosin Y (100.0 mg, 3.0 mol%), $Pd(OAc)_2$ (115.6 mg, 10 mol%), $AgNO_3$ (0.87 g, 5.15 mmol) were dissolved in acetonitrile (60 mL) in an oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar, and irradiated using 10 W Blue LED at room temperature under O_2 atmosphere for 60 h. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated $NaHCO_3$, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel/neutral alumina (EtOAc/hexane = 3:97) to give desired product **3a** in 53% yield.

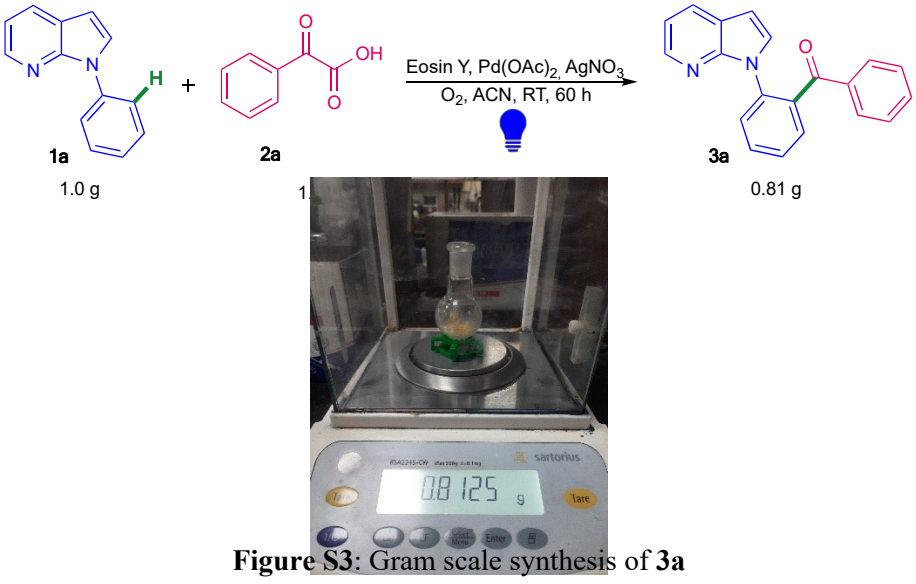


Figure S3: Gram scale synthesis of **3a**

5. Crystallographic Description of compound 3r

The crystal was grown by dissolving 10 mg of **3r** in 0.5ml of chloroform. The clear solution was covered and kept at room temperature for 72 h.

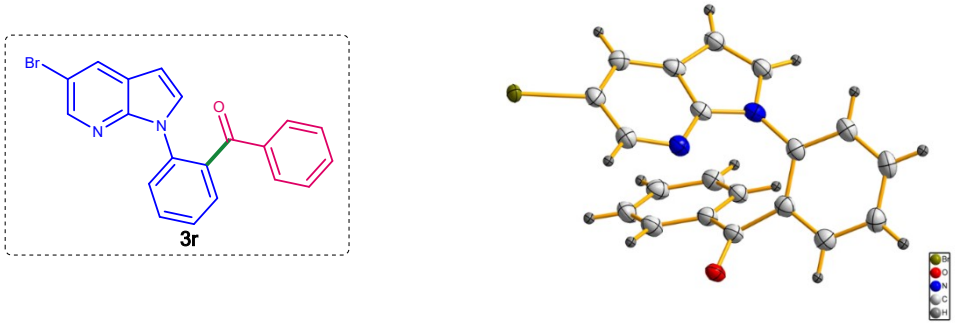


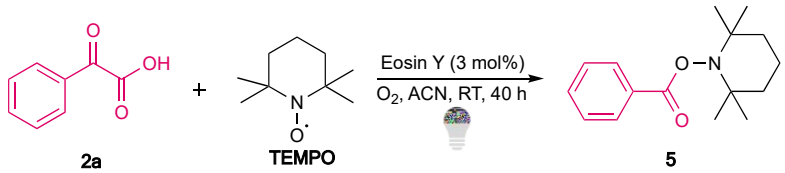
Fig S4. ORTEP diagram of compound **3r** (with 40% probability ellipsoids).

Identification code	st306_0m_a	
Empirical formula	$C_{20}H_{13}BrN_2O$	
Formula weight	377.22	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0295 (5) Å	α = 93.581° (2)
	b = 8.2401 (7) Å	β = 107.210° (2)
	c = 13.3944 (10) Å	γ = 100.420° (2)
Volume	809.45 (11) $Å^3$	
Z	2	
Density (calculated)	1.544 g/cm^3	
Absorption coefficient	2.542	
F_(000)	380.0	
Crystal size	$0.29 \times 0.22 \times 0.11\ mm^3$	
Theta range for data collection	1.637 to 24.999°	
Index ranges	-9<=h<=9 -9<=k<=9 -15<=l<=15	
Reflections collected	2854	
Independent reflections	10899 [R_{int} = 0.1459]	
Completeness to theta = 24.99°	100%	
Absorption correction	Multi-scan	

Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	10899 / 0 / 218
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R_1 = 0.0545 WR_2 = 0.1433
R indices (all data)	R_1 = 0.0694 WR_2 = 0.1564
CCDC	2116278

6. Mechanistic Insights

a) Free radical-trapping experiment



Phenylglyoxylic acid **2a** (30 mg, 0.2 mmol), Eosin Y (3.8 mg, 3.0 mol%), and TEMPO (62.6 mg, 0.4 mmol) were dissolved in acetonitrile (3 mL) in an oven-dried reaction vessel equipped with a magnetic stirring bar, irradiated using 10 W Blue LED at room temperature in O_2 atmosphere for 40 h. The desired adduct **5** was identified by the HRMS of the reaction mixture.

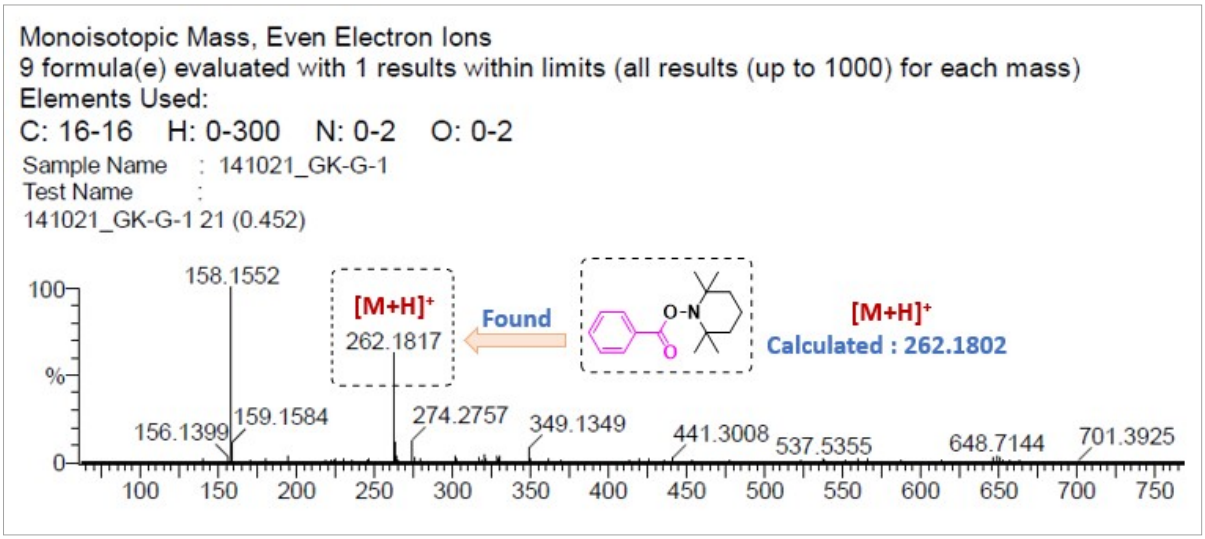


Figure S5: HRMS of the reaction mixture

b) Quantum Yield Determination

The quantum yield was calculated by following the procedure reported by Yoon[6] and modified appropriately. First, the intensity of LED light used in the experiment was calculated using standard ferrioxalate actinometry, and then the quantum yield of the reaction was measured.

A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4 and a buffered solution of phenanthroline was also prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both the solutions were stored in dark.

Determination of photon flux of Blue LED

1 mL of the ferrioxalate solution was irradiated at λ_{max} = 457 nm for 300 seconds. After irradiation, 175 µL of the phenanthroline solution was added immediately and the mixture was allowed to stir in dark for 1 hour to achieve the complete coordination between ferrous ions and phenanthroline. A non-irradiated sample was also prepared and the absorbance of both the solutions was measured at 270 nm. The mol product of Fe^{2+} was calculated using eq 1.

$$mol\ Fe^{2+} = \frac{V.\Delta A}{l.\varepsilon} = 9.60 \times 10^{-8} \quad (1)$$

Where V is the total volume (0.00175 L) of the solution after the addition of phenanthroline, ΔA is the difference in absorbance at 270 nm between the irradiated and non-irradiated solutions (0.164 from Fig S4a), l is the path length (1.0 cm), and ε is the molar absorptivity of 7.5×10^{-5} M ferrioxalate solution at 270 nm. The absorbance of the ferrioxalate solution is 0.224 (Fig S4b) which corresponds to the ε value of 2986.6 $Lmol^{-1}cm^{-1}$ (applying Beer-lambert's law, A= εcl).

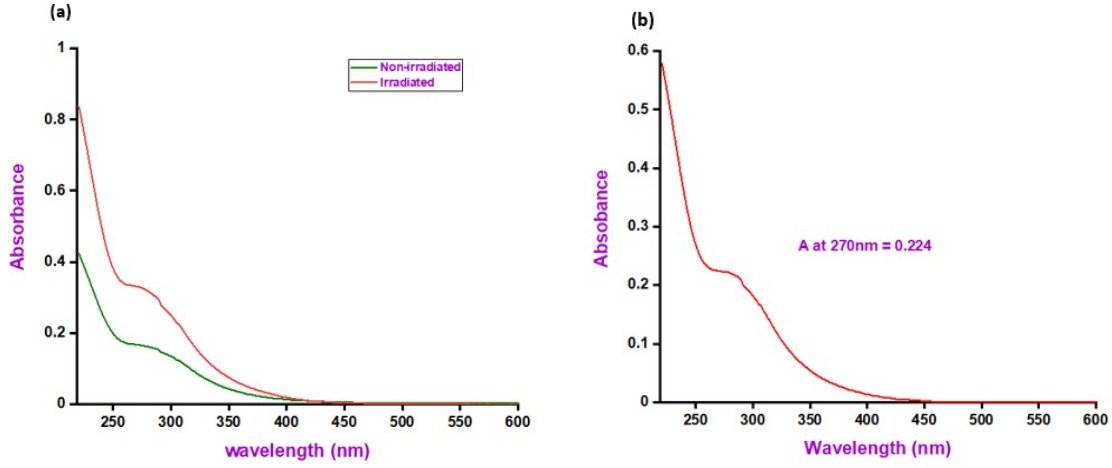


Figure S6: (a) UV-visible spectra of the irradiated and non-irradiated ferrioxalate solution after interacted with buffered solution of phenanthroline; (b) UV-visible spectra of Ferrioxalate solution.

The photon flux can be calculated using eq 2.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\phi.t.f} = 4.09 \times 10^{-10} \quad (2)$$

Where ϕ is the quantum yield for 0.15 M solution of ferrioxalate actinometer (0.92 at λ_{max} = 468 nm)[7], t is the irradiation time (300s), and f is the fraction of light absorbed by 0.15 M ferrioxalate actinometer at λ = 468 nm (0.850)[7]

Determination of the reaction quantum yield (ϕ)

The absorbance of Eosin Y in acetonitrile was measured at the reaction concentration of 1.02 x 10^{-3} M. The absorbance at 468 nm is 0.485, thus f is 0.673 calculated using eq 3.

$$f = 1 - 10^{-A} \quad (3)$$

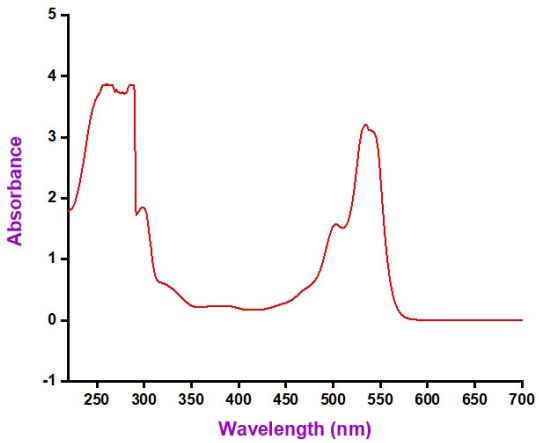


Figure S7: UV-visible spectra of Eosin Y

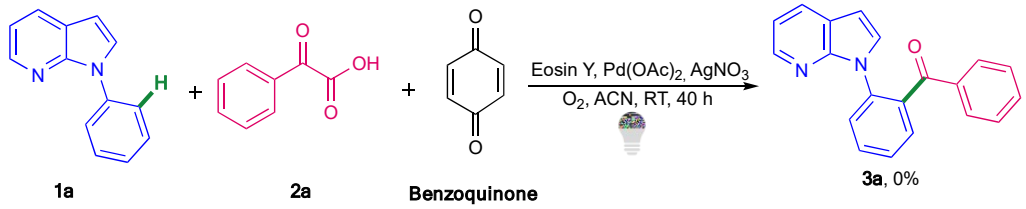
N-phenyl-7-azaindole **1a** (20 mg, 0.1 mmol), phenylglyoxylic acid **2a** (23 mg, 0.15 mmol), Eosin Y (1.9 mg, 3.0 mol%), $Pd(OAc)_2$ (2.2 mg, 10 mol%), $AgNO_3$ (16.9 mg, 0.1 mmol) were dissolved in acetonitrile (3 mL) in an oven-dried reaction vessel equipped with a magnetic stirring bar, irradiated using 10 W Blue LED at room temperature in O_2 atmosphere for 5 h. After irradiation, the reaction was quenched with saturated $NaHCO_3$, and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel/neutral alumina to give the desired product in 17% yield (5.2 mg, 1.7 x 10^{-5} mol). The reaction quantum yield (ϕ) was calculated using eq 4.

$$\phi = \frac{moles\ of\ product\ formed}{photon\ flux.t.f} = 3.43 \quad (4)$$

Where t is the reaction time (18000 s), photon flux is 4.09×10^{-10} einstein s^{-1} and f is the fraction of light absorbed by Eosin Y (0.673).

The experiment above shows the quantum yield of the reaction is >1, indicating the reaction should involve the radical chain process. The involvement of an oxygen atmosphere, which could easily terminate the radical chain process,[8] results in a lower value of quantum yield in comparison to other photoredox reactions.[6]

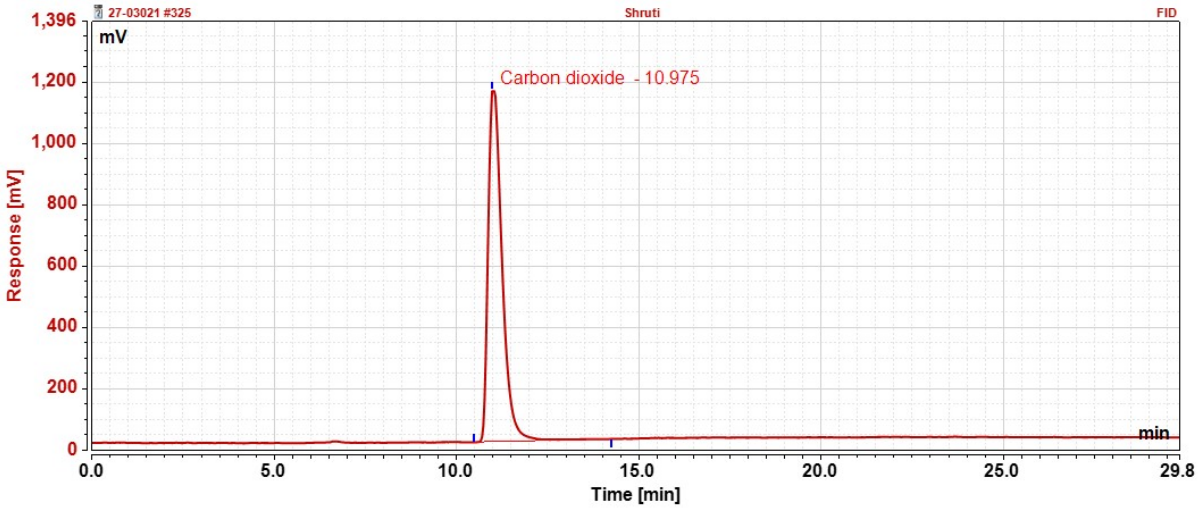
c) Superoxide radical anion trapping experiment



N-phenyl-7-azaindole **1a** (20 mg ,0.1 mmol), phenylglyoxylic acid **2a** (23 mg, 0.15 mmol), Eosin Y (1.9 mg, 3.0 mol%), $Pd(OAc)_2$ (2.2 mg, 10 mol%), $AgNO_3$ (16.9 mg, 0.1 mmol) and Benzoquinone (21.6 mg, 0.2 mmol) were dissolved in acetonitrile (3 mL) in an oven-dried reaction vessel equipped with magnetic stirring bar, irradiated using 10 W Blue LED at room temperature in O_2 atmosphere for 40 h. The reaction was monitored by TLC and the benzoylation product **3a** was not formed which indicated the quenching of superoxide radical anion.

d) Detection of Carbon Dioxide (Monitoring Reaction by HS-GC)

Gas quantification was carried out by gas chromatography (GC trace 1110 Thermo scientific with carboxen column, FID detector). A sealed tube was charged with *N*-phenyl-7-azaindole **1a** (58 mg, 0.3 mmol), phenylglyoxylic acid **2a** (67 mg, 0.45 mmol), Eosin Y (5.8 mg, 3 mol%), $Pd(OAc)_2$ (6.7 mg, 10 mol%), and $AgNO_3$ (51 mg, 0.3 mmol) dissolved in acetonitrile (3 mL). The reaction



mixture was stirred under 10 W blue LED irradiation at RT for 10 h. The gases produced in the reaction mixture were injected into the HS-GC instrument via a 1 mL syringe. A calibration curve was drawn between the retention time (min) of gases and response in mV. A peak obtained at 10.975 min confirmed the liberation of CO_2 in the reaction system.

Figure S8: Calibration Curve for CO_2 estimation

e) Cyclic Voltammetry

The Cyclic voltammetry (CV) and differential pulse voltammograms (DPV) for *N*-phenyl-7-azaindole (**1a**) were recorded using CH Instrument (CHI 760E, CH Instrument, USA). The experiments were carried out in 0.5 mM of **1a** in acetonitrile (5 mL) containing 0.06 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte at 25 °C. A 3mm glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl in saturated KCl was used as reference electrode during measurement. During CV measurement, 100 mV/s scan rate was used and in DPV, peak amplitude 50 mV, pulse width 0.05 sec, pulse period 0.5 sec, and increment E at 4 mV was used.

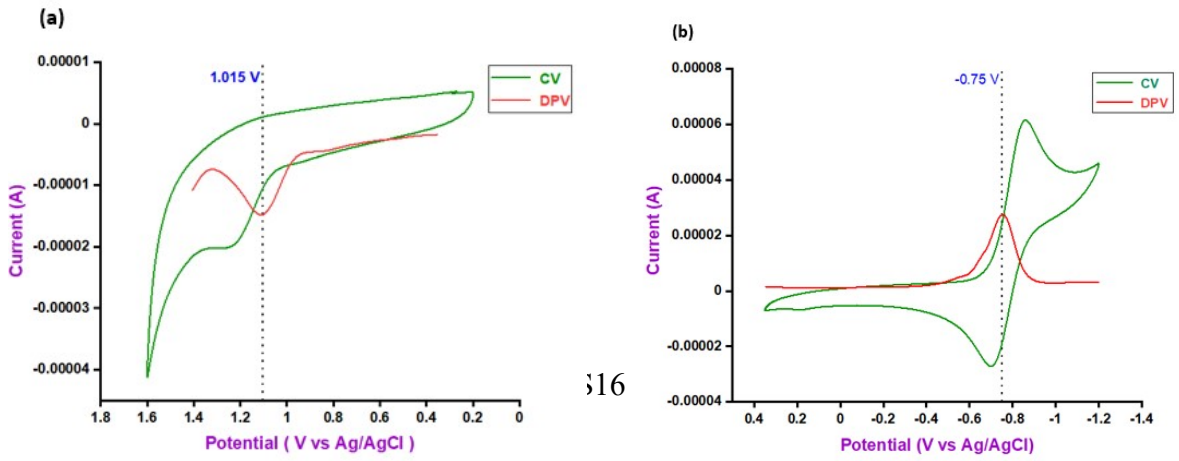
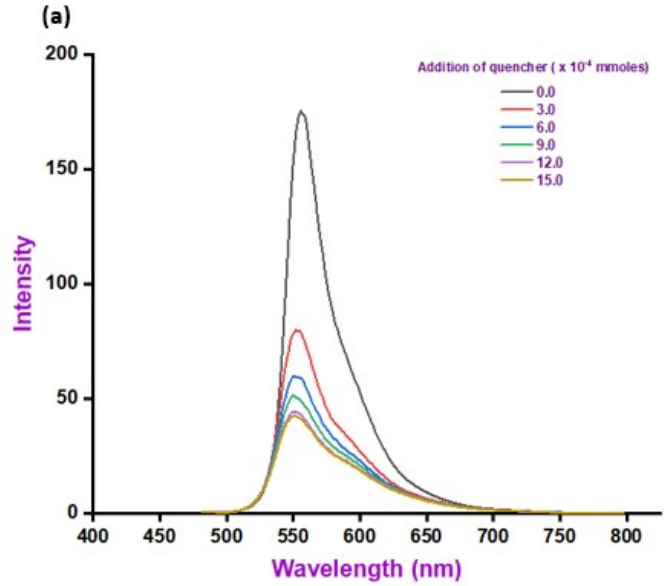


Figure S9: Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) show oxidation (a) and reduction (b) potential values of **1a.**

f) Stern-Volmer Study: Fluorescence Quenching Experiments

All fluorescence measurements were recorded using the F-Varian Cary Eclipse fluorescence spectrophotometer. The experiments were carried out in 2 x 10^{-3} M of Eosin Y in acetonitrile at 25 ^{o}C, excited at 457 nm and the emission intensity was collected at 556 nm. Measurements were recorded with the subsequent addition of phenylglyoxylic acid **2a** and *N*-phenyl-7-azaindole **1a** as quenchers (0.0, 3.0,6.0, 9.0, 12.0, 15.0) x 10^{-4} mmoles.



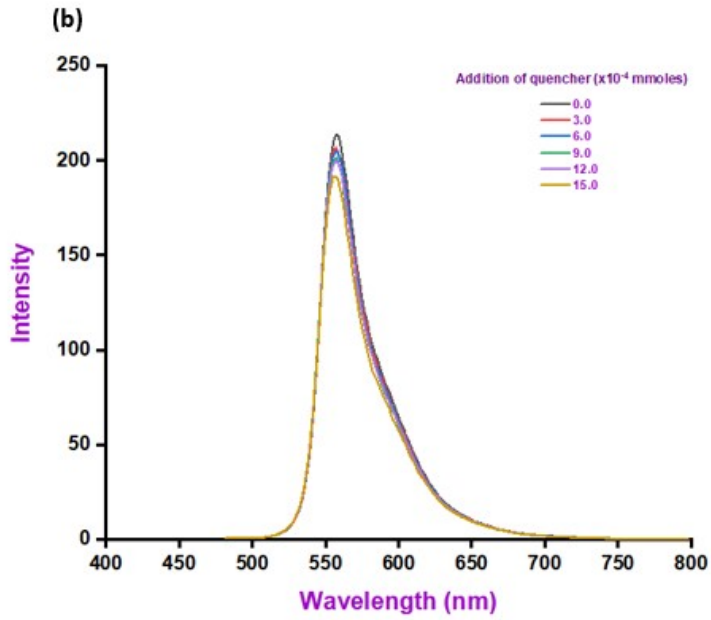


Figure S10: (a) Luminescence quenching of Eosin Y by **2a**; (b) Luminescence quenching of Eosin Y by **1a**.

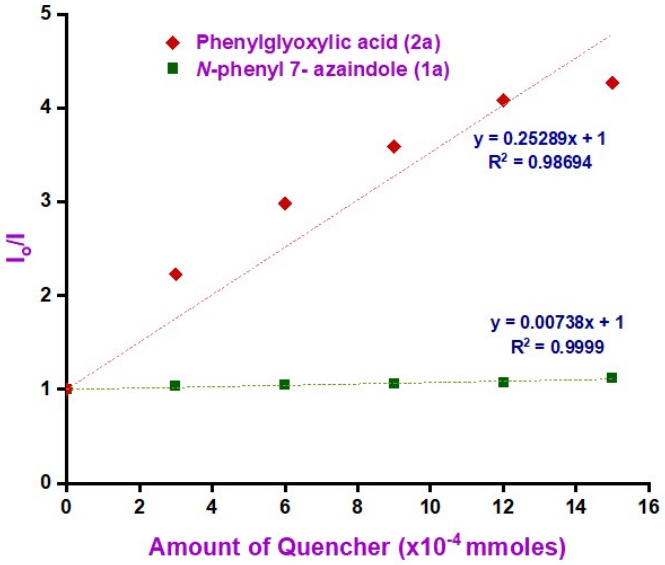


Figure S11: Stern-Volmer plots of Eosin Y quenching with **2a** and **1a.**

g) H_2O_2 Detection Using Hydrogen Peroxide Strips[9]

N-phenyl-7-azaindole **1a** (58 mg ,0.3 mmol), phenylglyoxylic acid **2a** (67 mg, 0.45 mmol), Eosin Y (5.8 mg, 3.0 mol%), $Pd(OAc)_2$ (6.7 mg, 10 mol%), and $AgNO_3$ (51 mg, 0.3 mmol) were dissolved in acetonitrile (3 mL) in an oven-dried reaction vessel equipped with magnetic stirring bar, irradiated using 10 W Blue LED at room temperature in O_2 atmosphere for 40 h. The reaction was monitored by TLC and upon completion, 10µL of the solution was taken into a 1.5 ml centrifuge tube using a pipette. Deionized water and ethyl acetate were added to the centrifuge tube and hydrogen peroxide test strip was dipped into the aqueous layer for 2 seconds and was taken out, left undisturbed for another 10 seconds. The color of the strip was compared with the color chart. On comparing, we found that the hydrogen peroxide concentration in reaction was between 3-10 ppm.

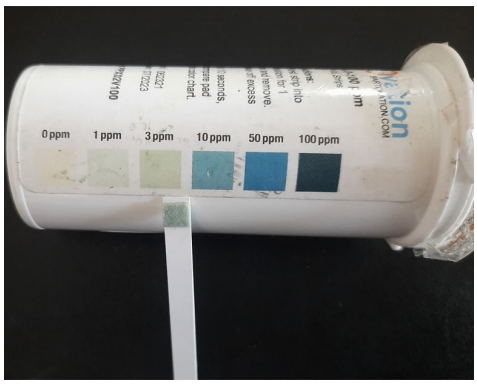


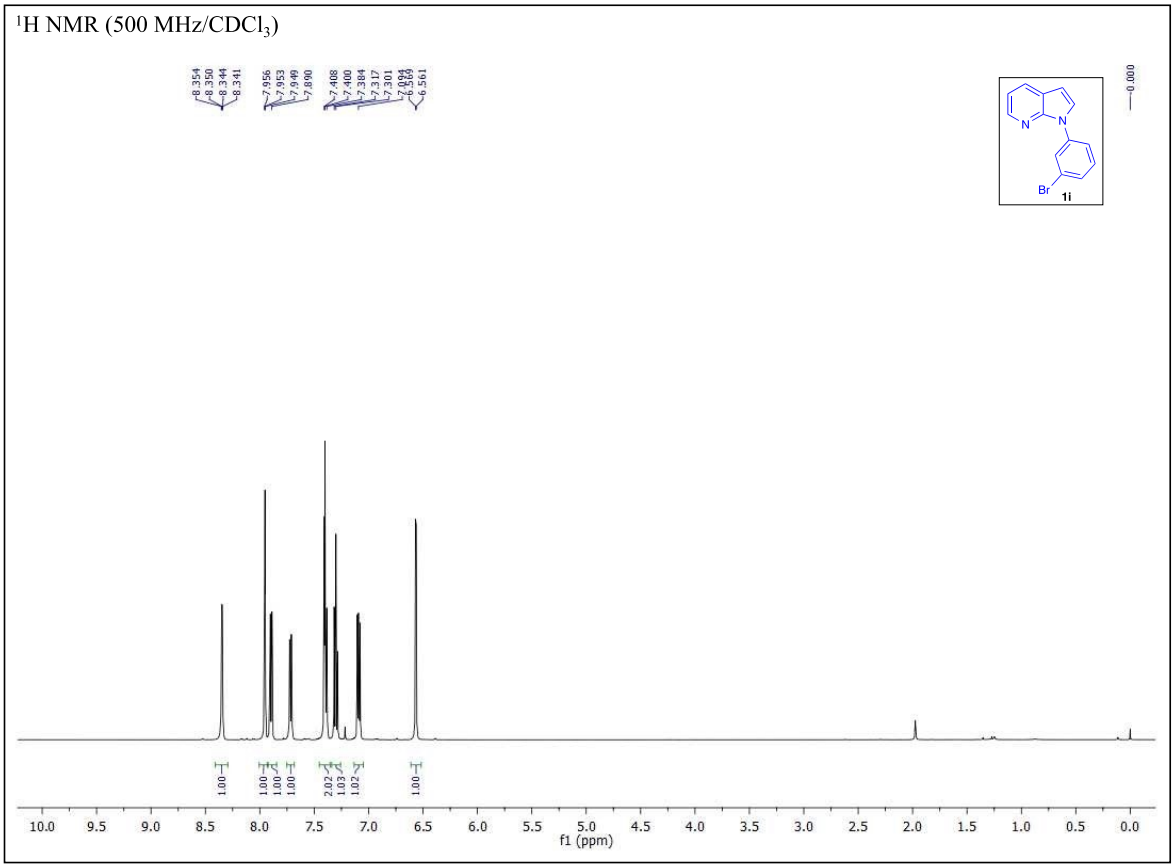
Figure S12: H_2O_2 detection using hydrogen peroxide strips

7. References

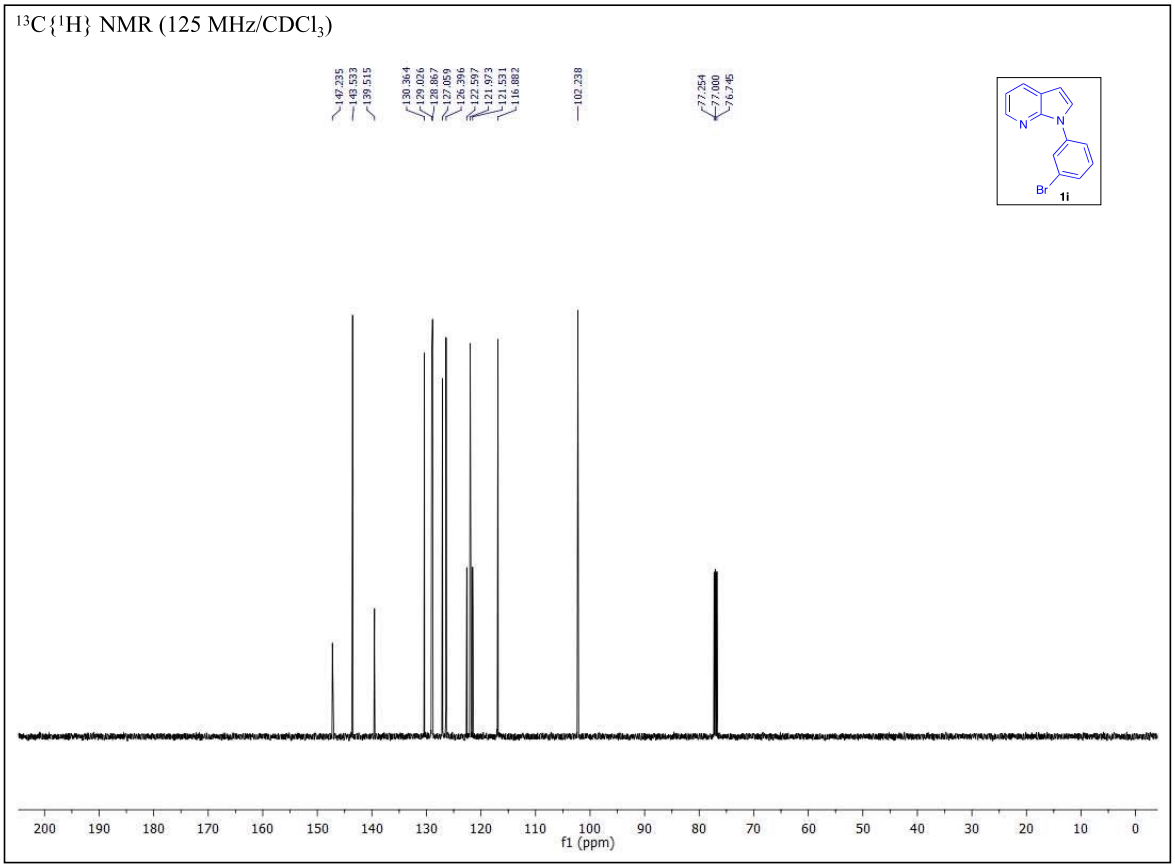
1. G. Qian, X. Hong, B. Liu, H. Mao and B. Xu, *Org. Lett.*, 2014, **16**, 5294.
2. R. J. Davenport, A. J. Ratcliffe, B. Perry, D. J. Phillips and M. W. Jones, US Pat., WO 208/064830 A1, 2007.
3. A. Mishra, T.K. Vats and I. Deb, *J. Org. Chem.*, 2016, **81**, 6525.
4. W. Li, L. Wu, S. Li, C. Liu, G. Zhang and L. Dong, *Chem. Eur. J.*, 2016, **22**, 17926.
5. (a) K. Wadhwa, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434; (b) L. Long, J. Wang, L. Gu, S. Yang, L. Qiao, G. Luo and Z. Chen, *J. Org. Chem.*, 2021, **86**, 12084; (c) E. Johannes, R. Horbert, J. Schlosser, D. Schmidt and C. Peifer, *Tetrahedron Lett.*, 2013, **54**, 4067; (d) H. Inada, M. Shibuya and Y Yamamoto, *J. Org. Chem.*, 2020, **85**, 11047; (e) L. Zhou, S. Qiao, F. Zhou, X. Xuchen, G. Deng, Y. Yang and Y. Liang, *Org. Lett.*, 2021, **23**, 8, 2878.
6. M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426.
7. C. G. Hatchard and C. A. Parker, *C. A. Proc. Roy. Soc. (London)*, 1956, **A235**, 518.
8. Y. Jin, L. Ou, H. Yang and H. Fu, *J. Am. Chem. Soc.*, 2017, **139**, 14237.
9. L. Y. Xie, Y. S. Bai, X. Q. Xu, X. Peng, H. S. Tang, Y. Huang, Y. W. Lin, Z. Cao and W. M. He, *Green Chem.*, 2020, **22**, 1720.

8. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of synthesized compounds

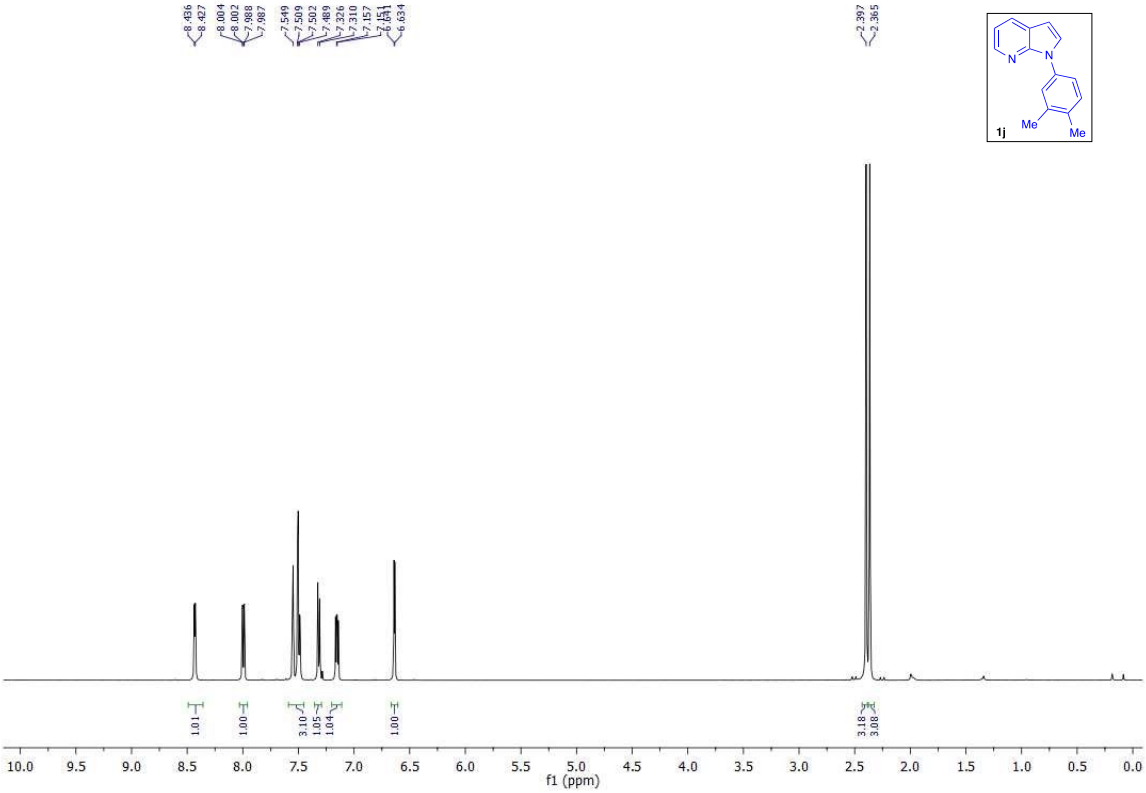
^{1}H NMR (500 MHz/$CDCl_3$)



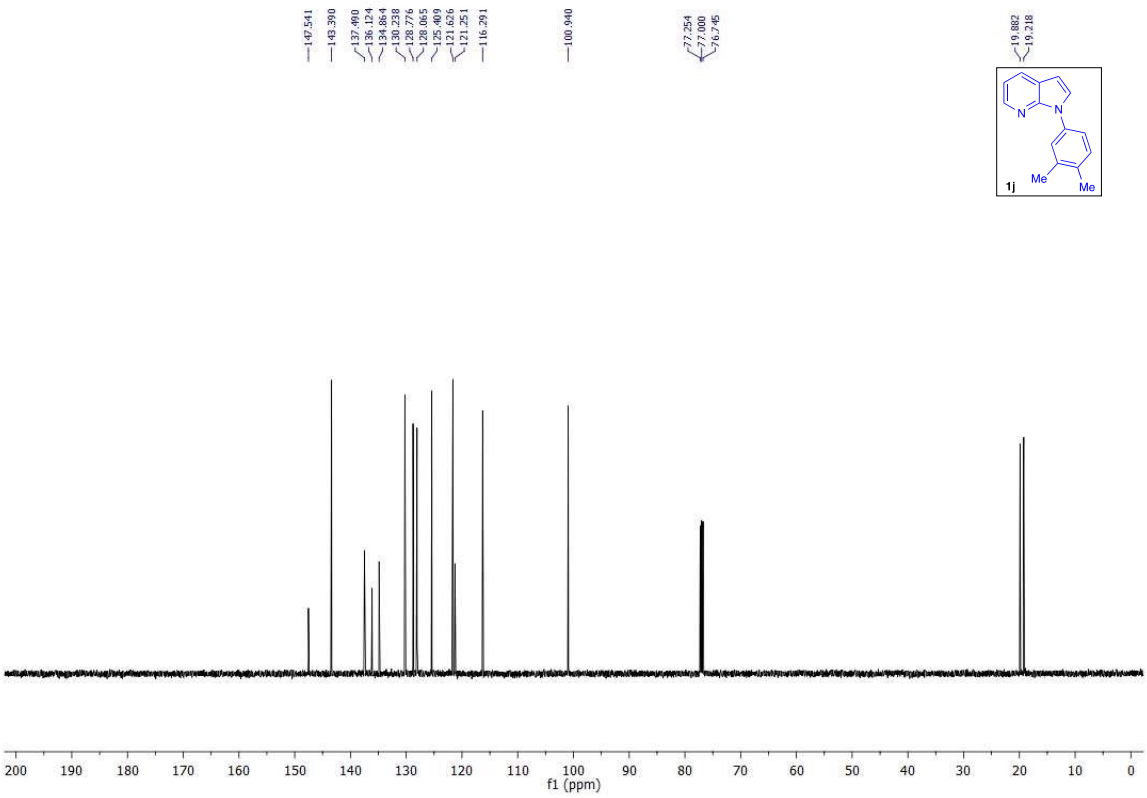
$^{13}C\{^{1}H\}$ NMR (125 MHz/$CDCl_3$)



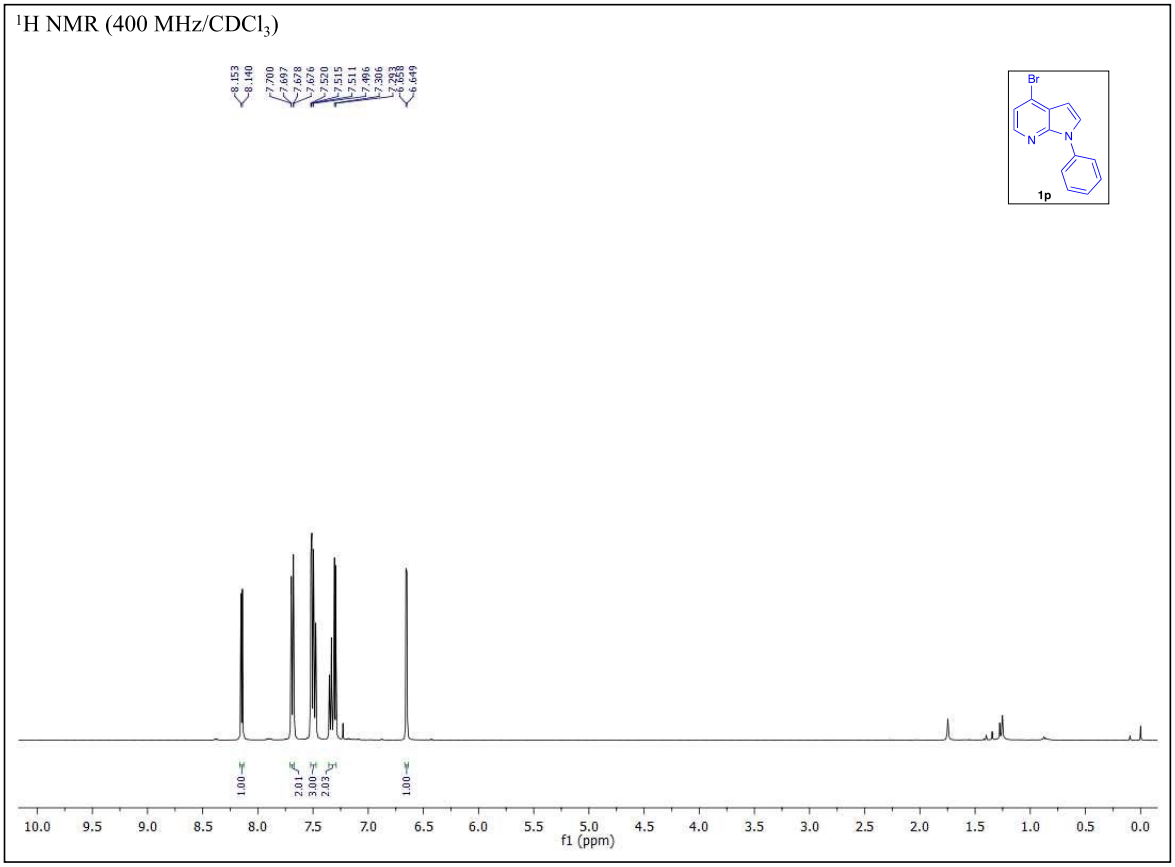
^{1}H NMR (500 MHz/$CDCl_3$)



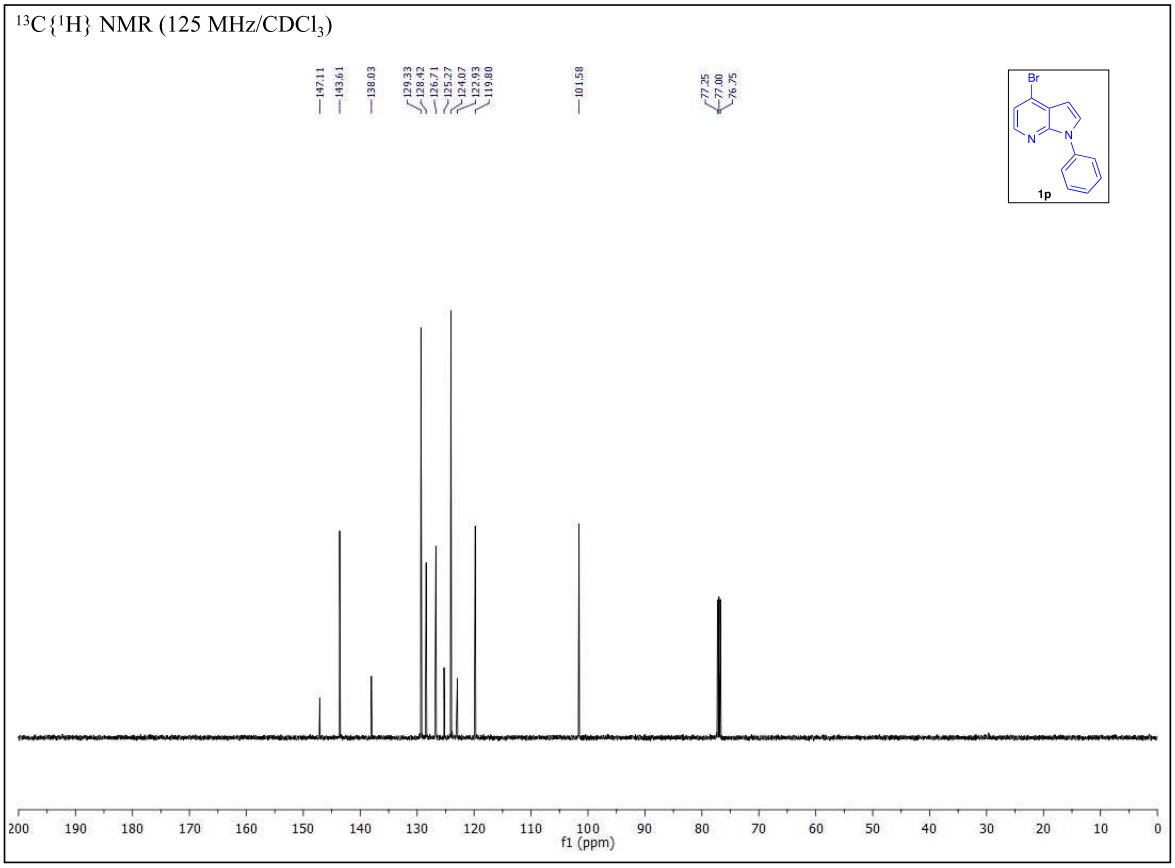
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



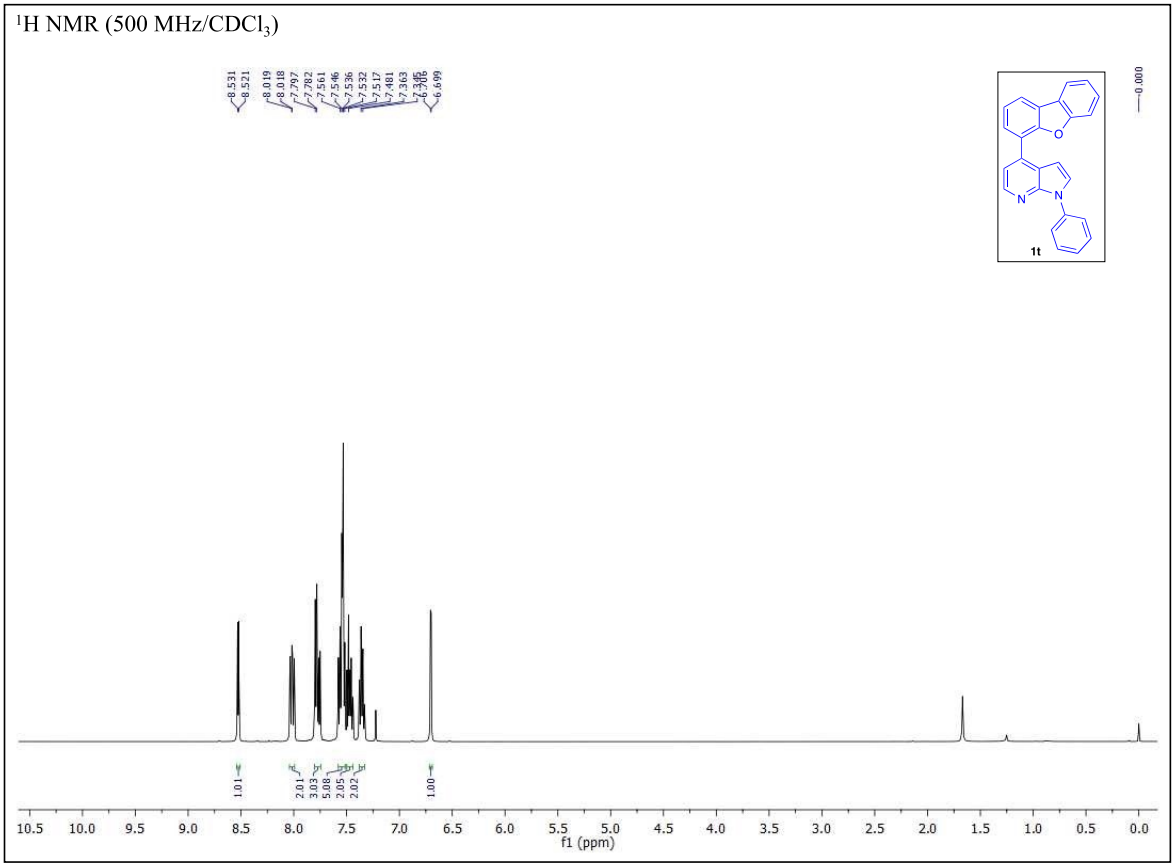
^{1}H NMR (400 MHz/$CDCl_3$)



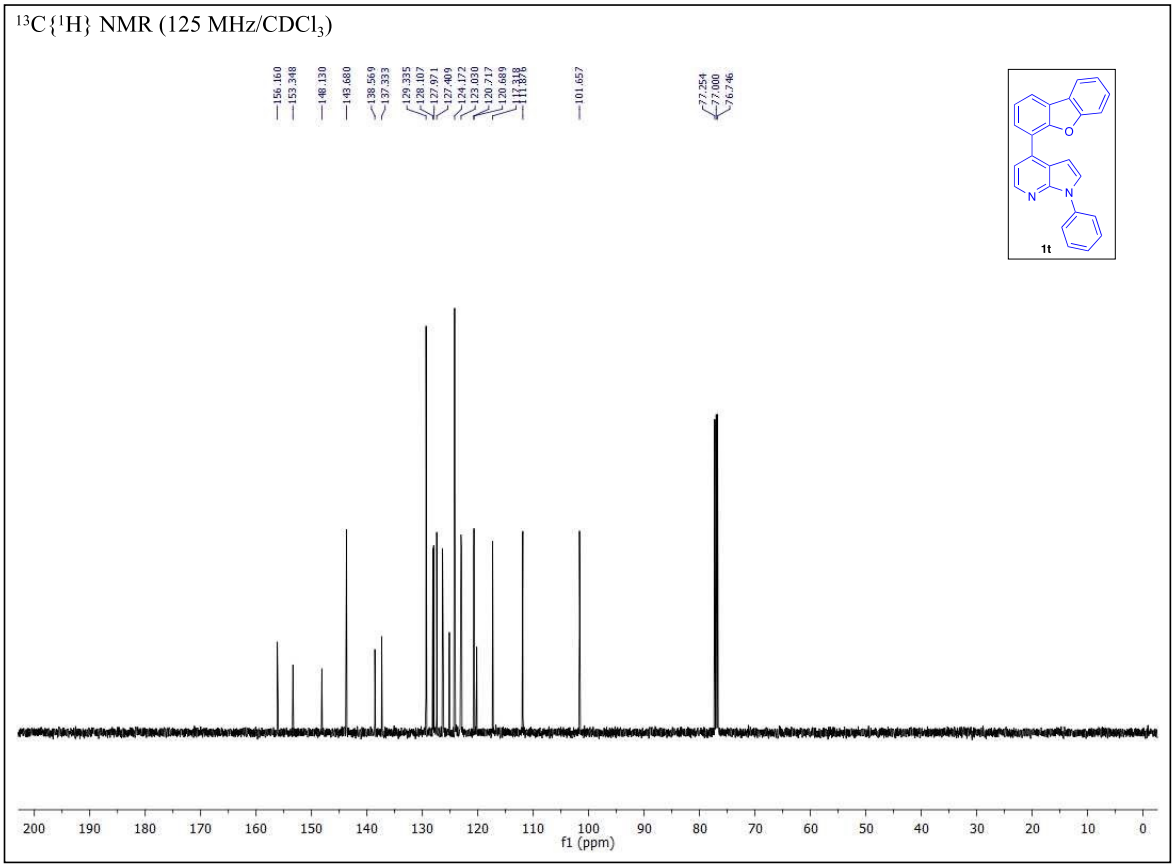
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



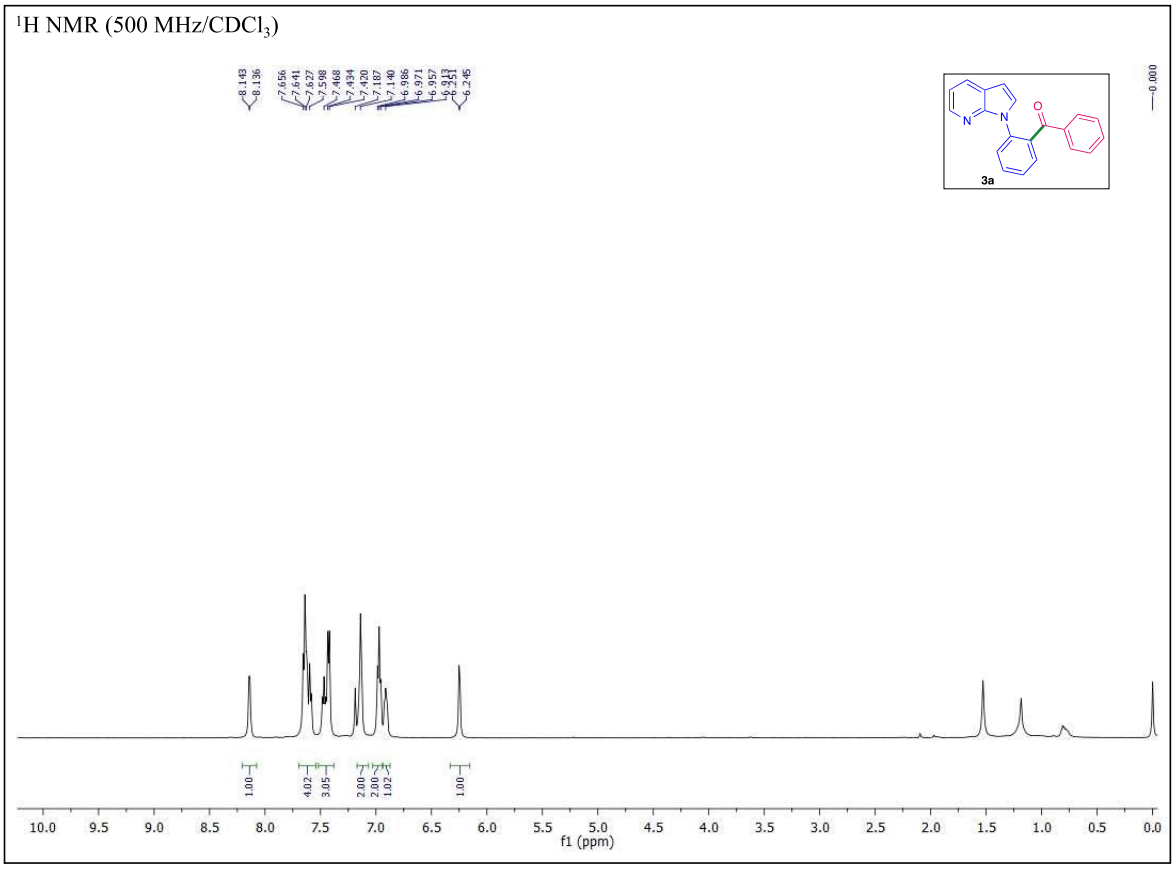
^{1}H NMR (500 MHz/$CDCl_3$)



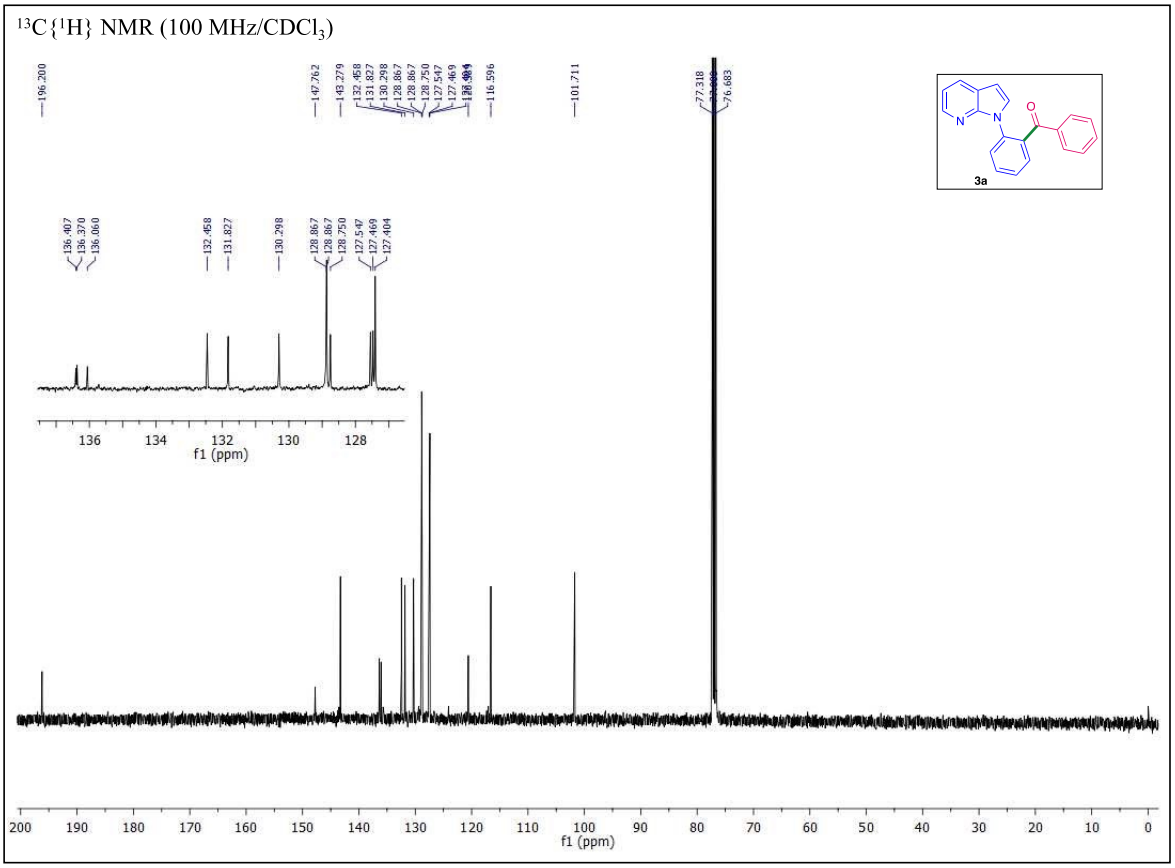
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



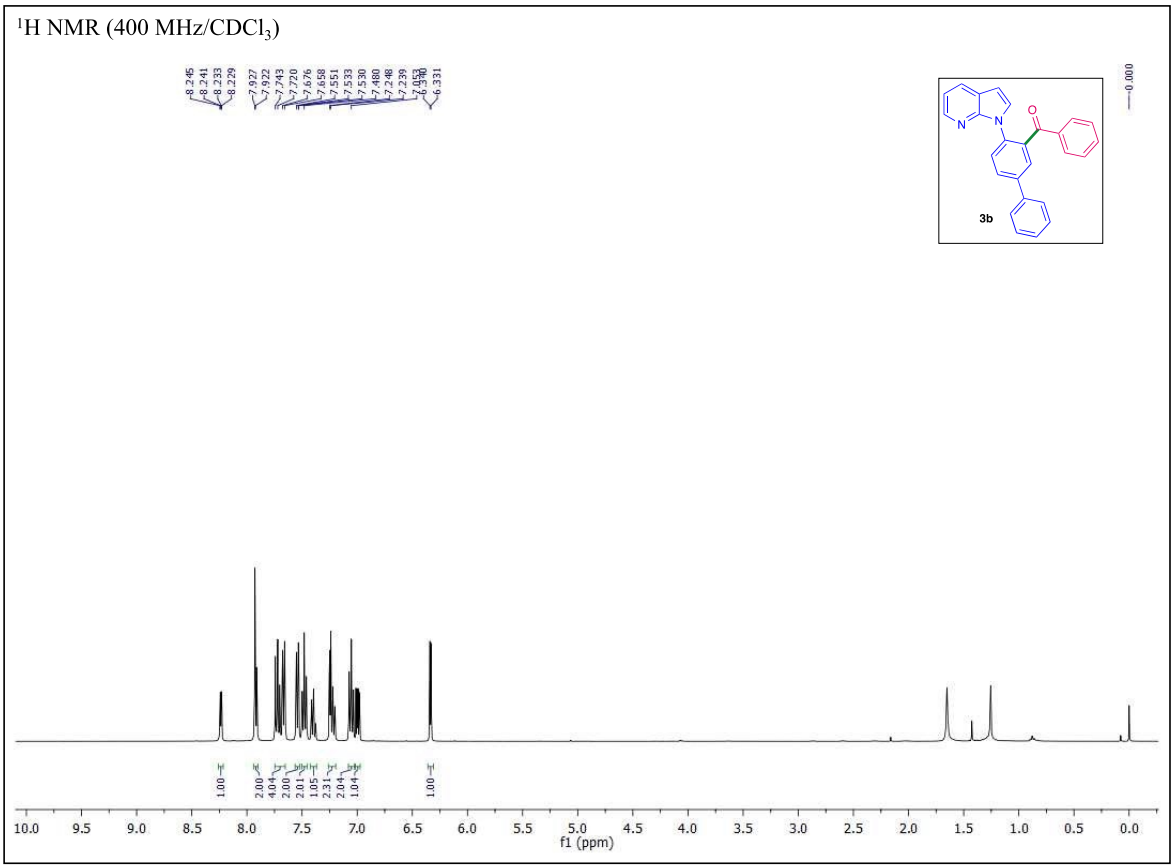
^{1}H NMR (500 MHz/$CDCl_3$)



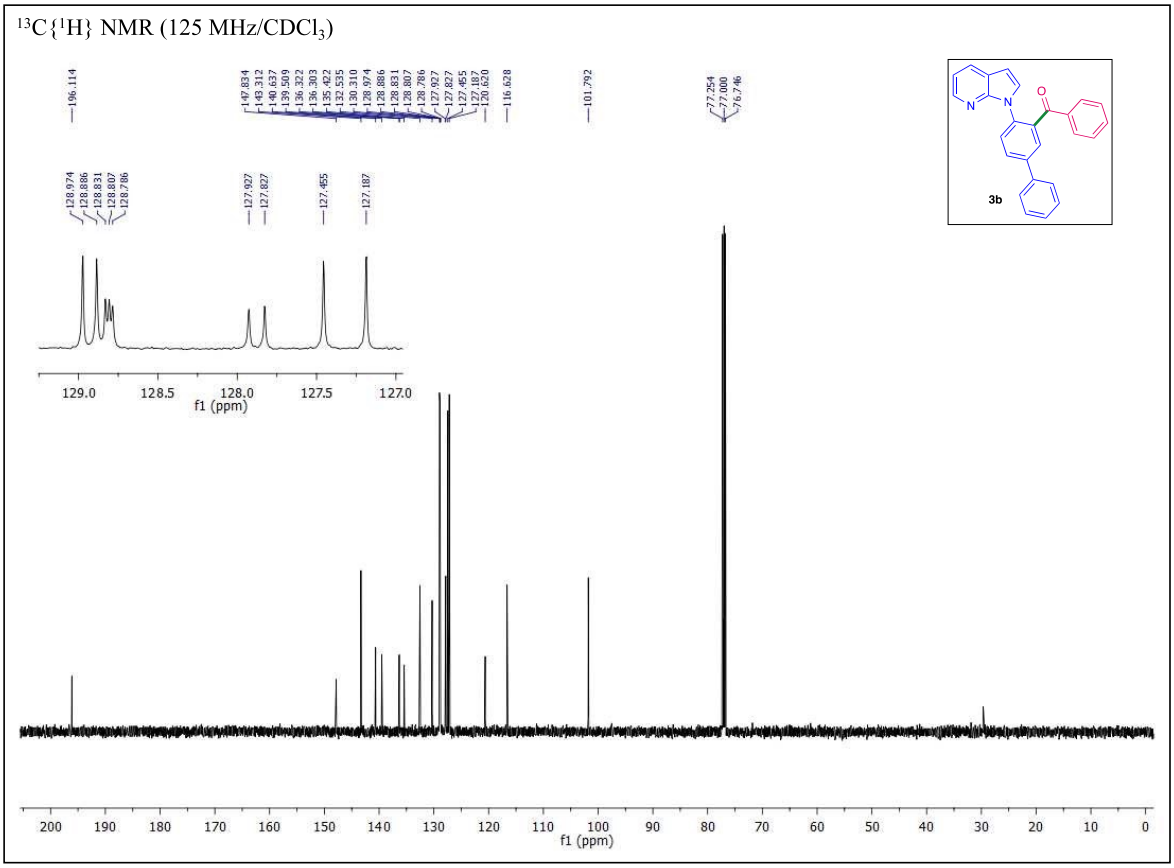
^{13}C{^{1}H} NMR (100 MHz/$CDCl_3$)



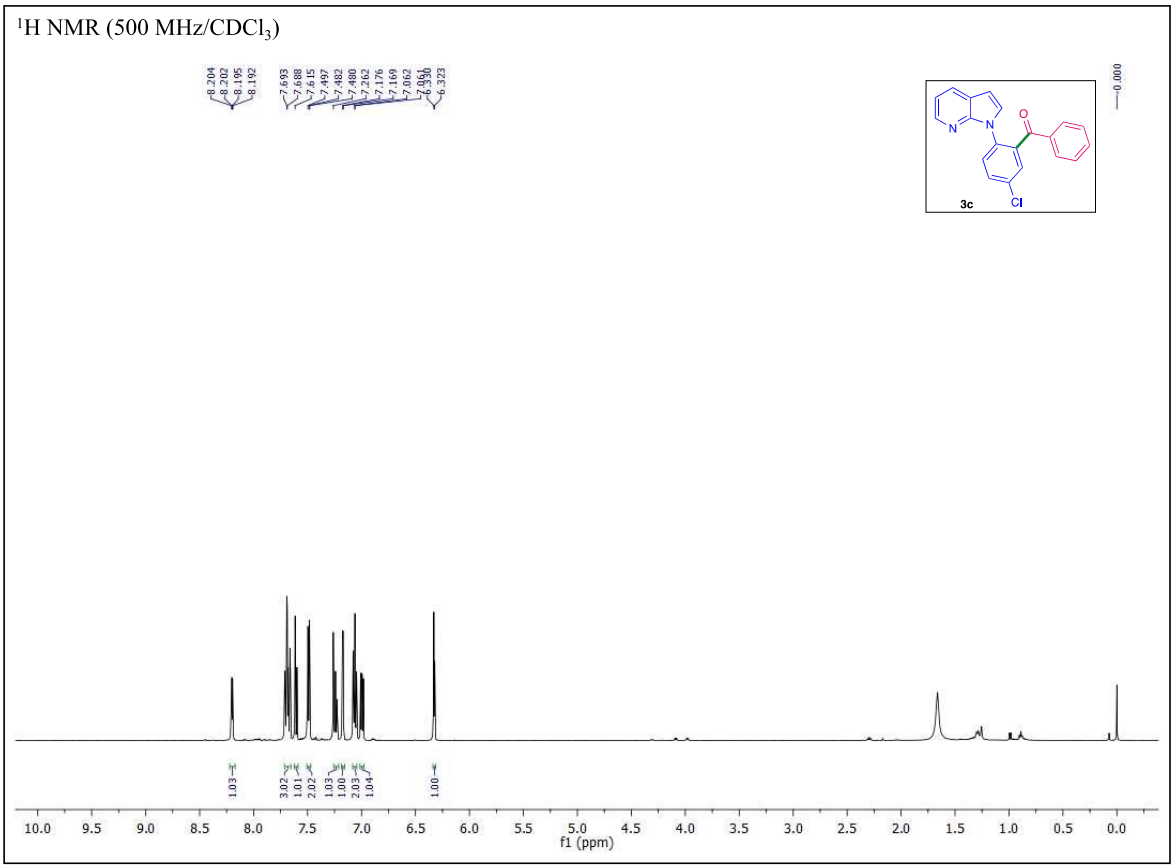
^{1}H NMR (400 MHz/$CDCl_3$)



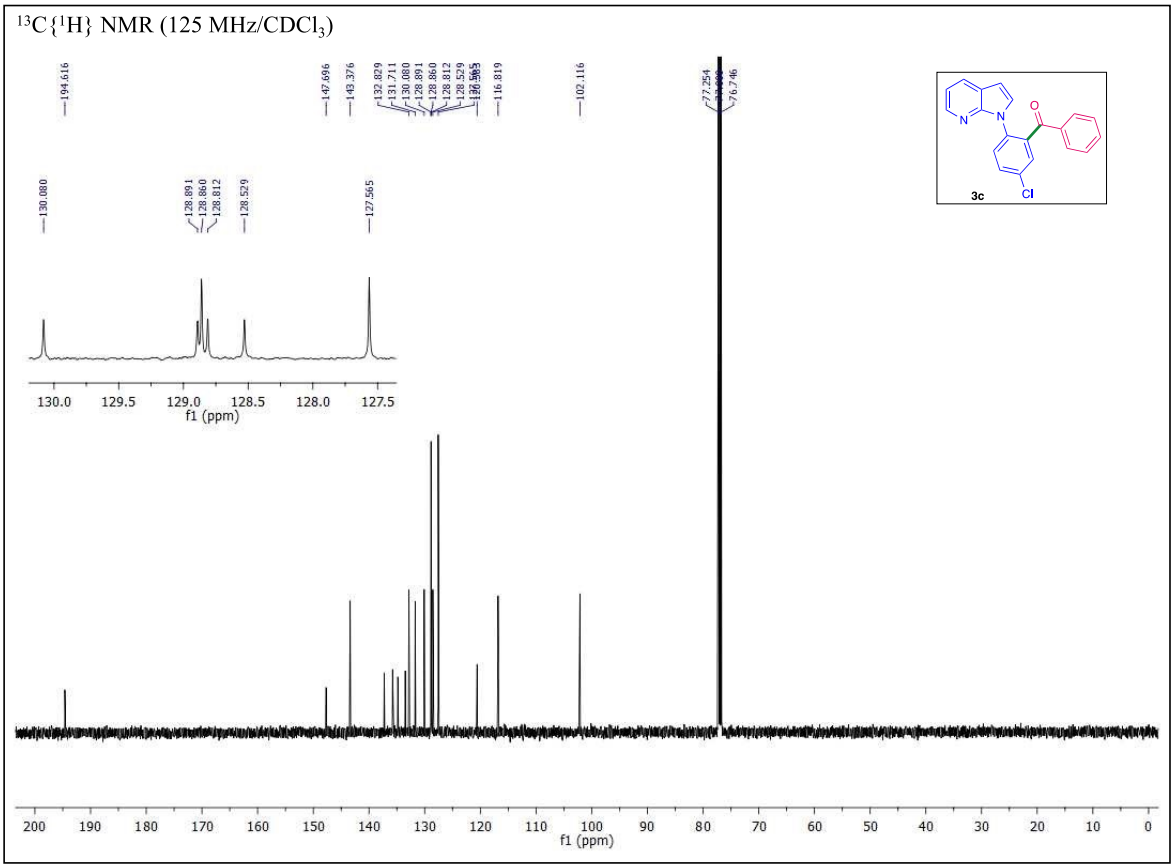
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



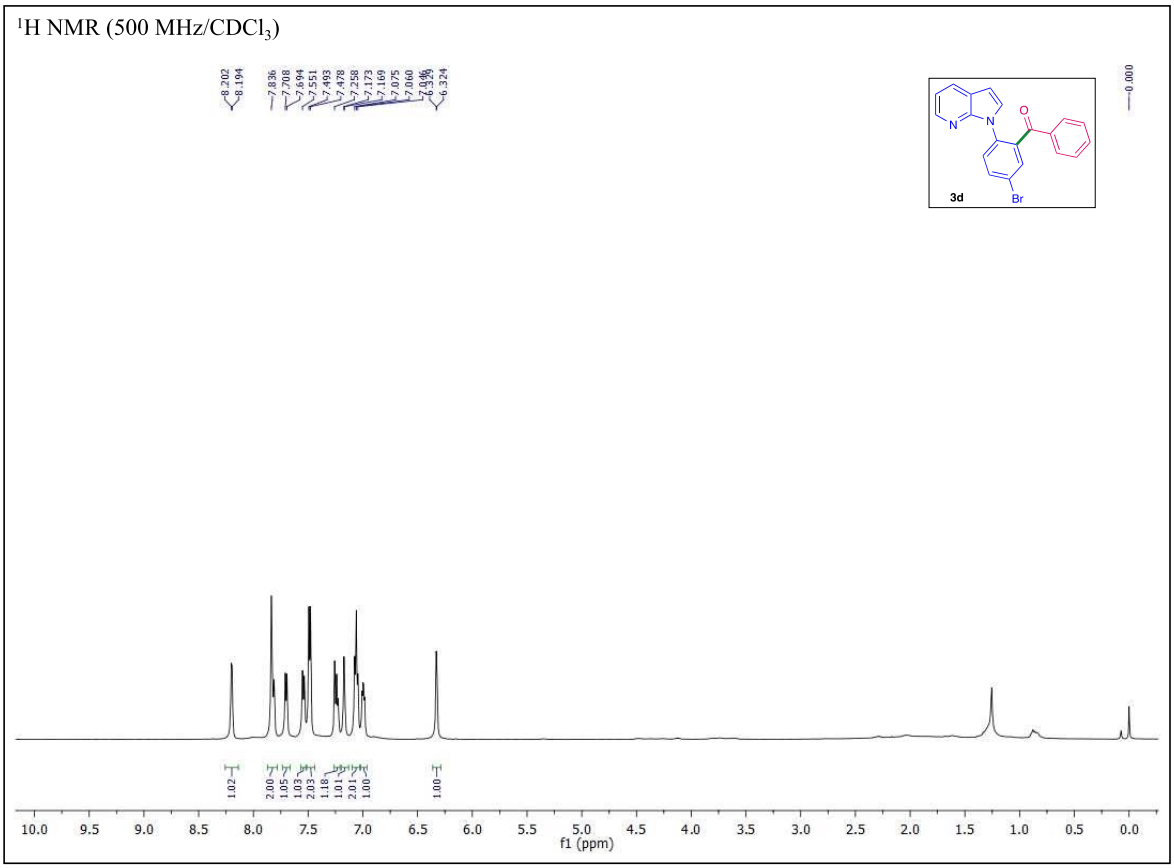
^{1}H NMR (500 MHz/$CDCl_3$)



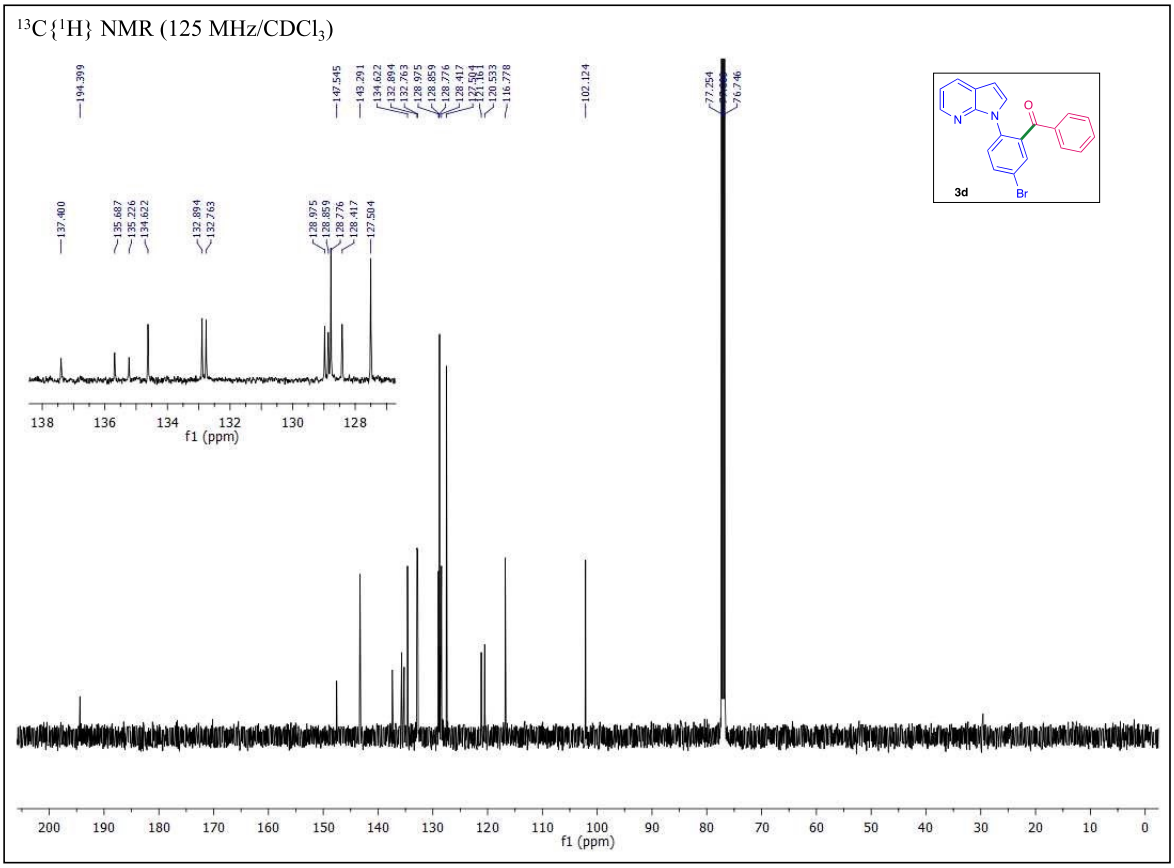
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



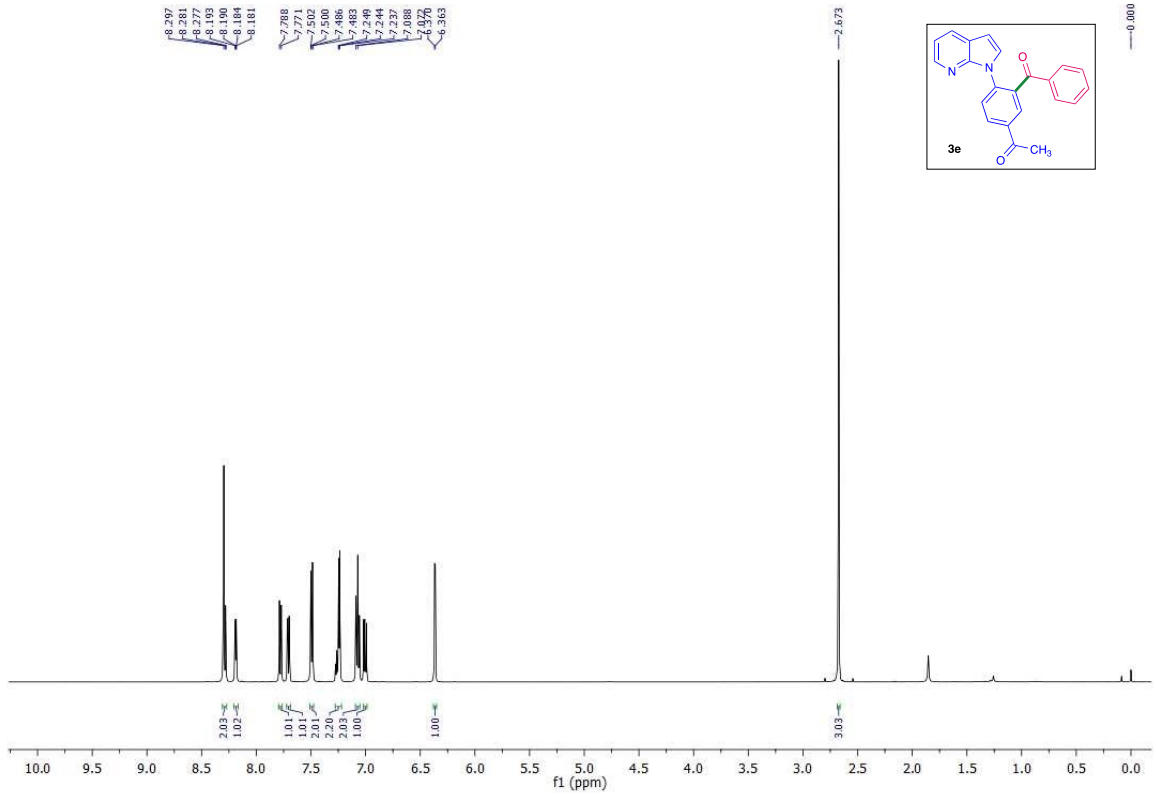
^{1}H NMR (500 MHz/CDCl$_3$)



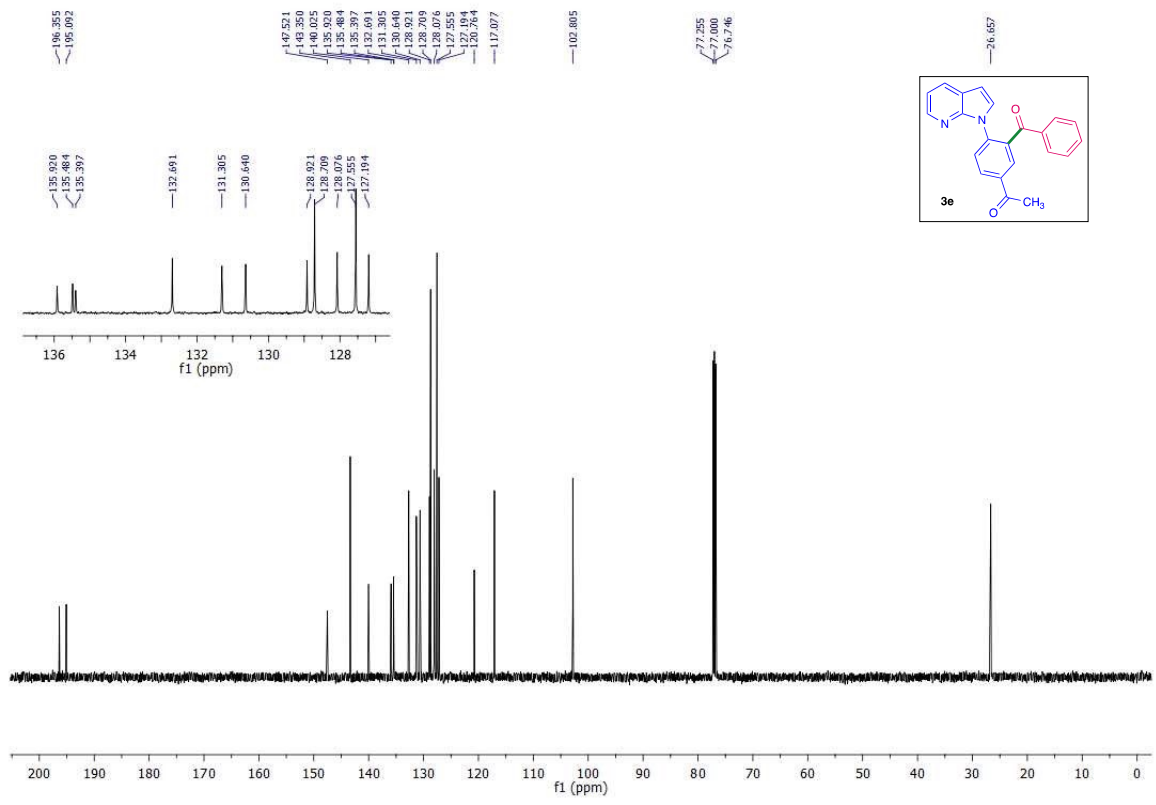
^{13}C{^{1}H} NMR (125 MHz/CDCl$_3$)



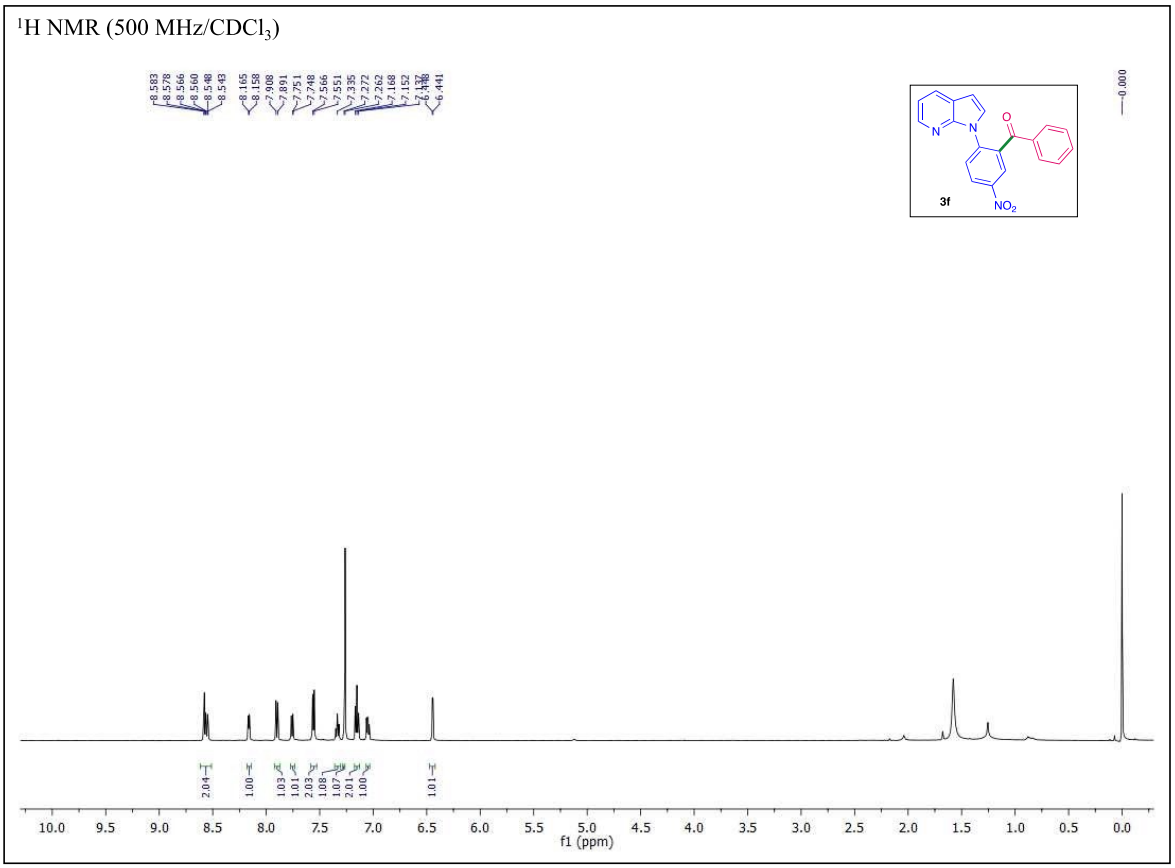
^{1}H NMR (500 MHz/$CDCl_3$)



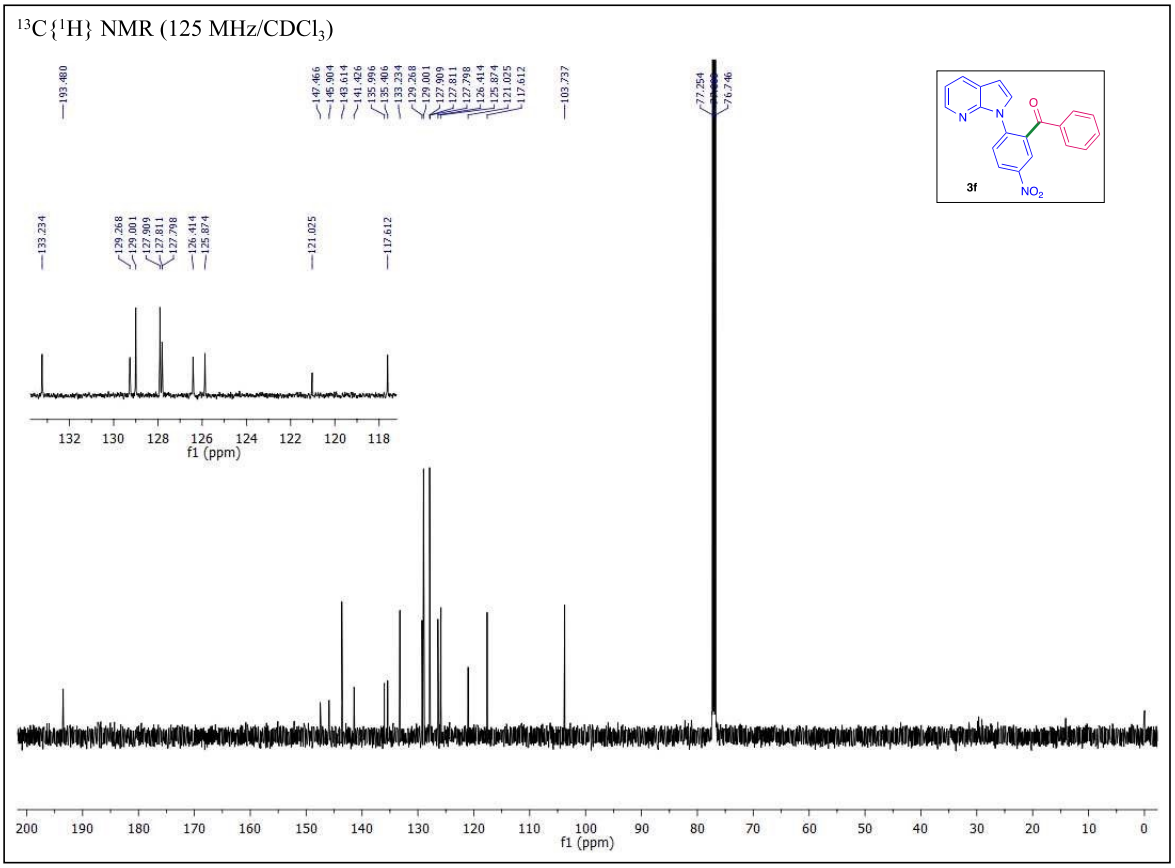
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



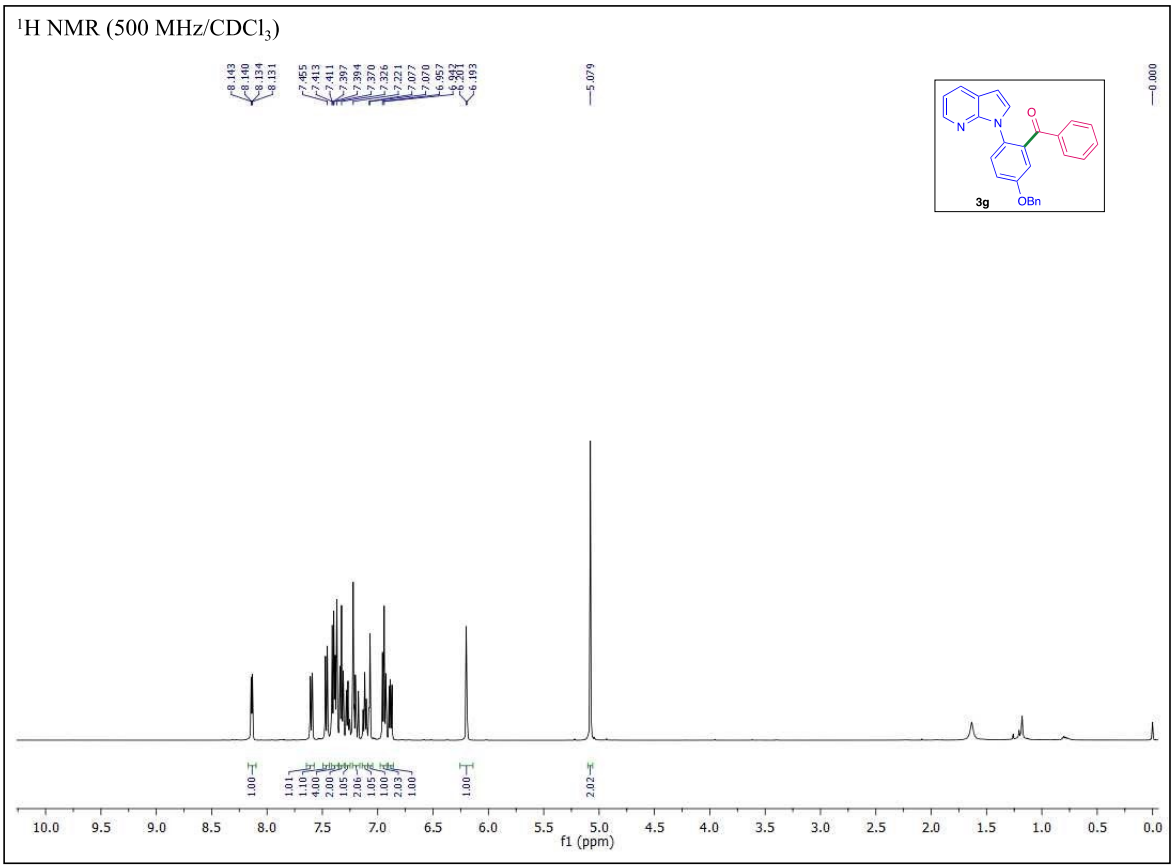
^{1}H NMR (500 MHz/$CDCl_3$)



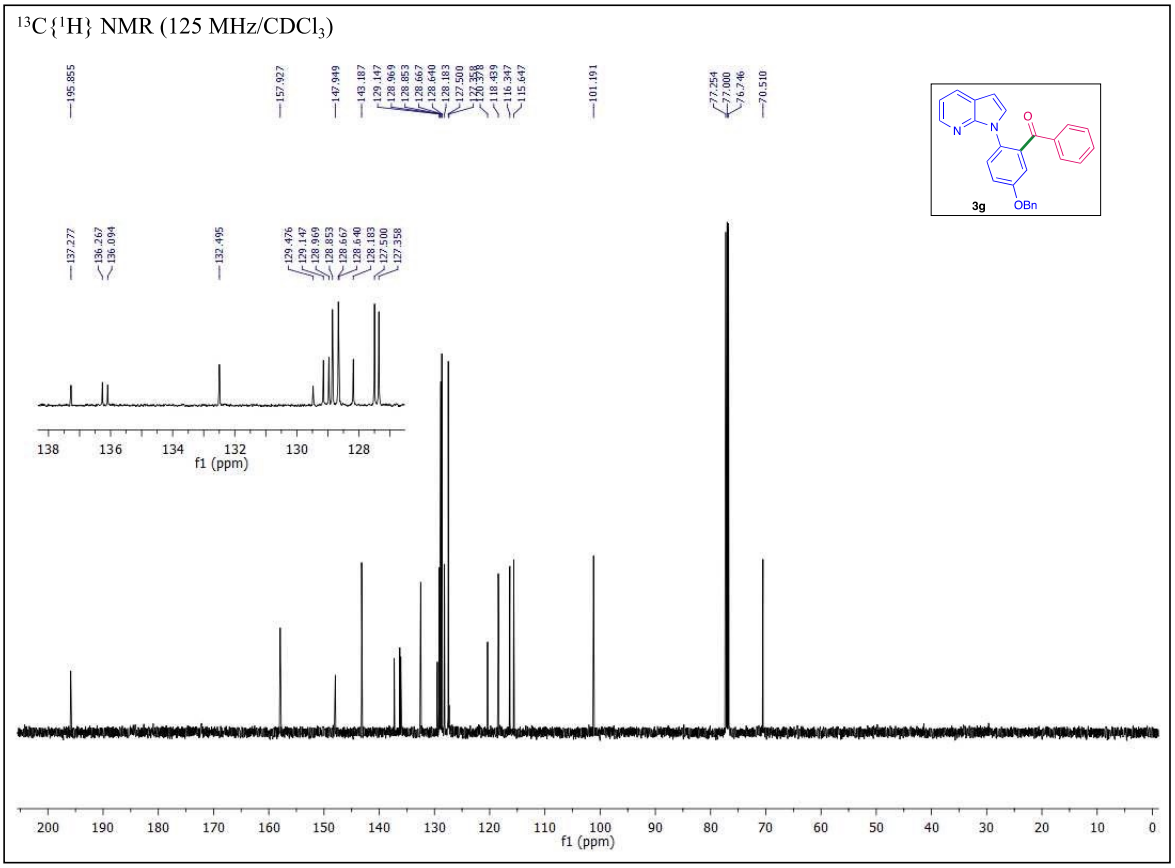
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



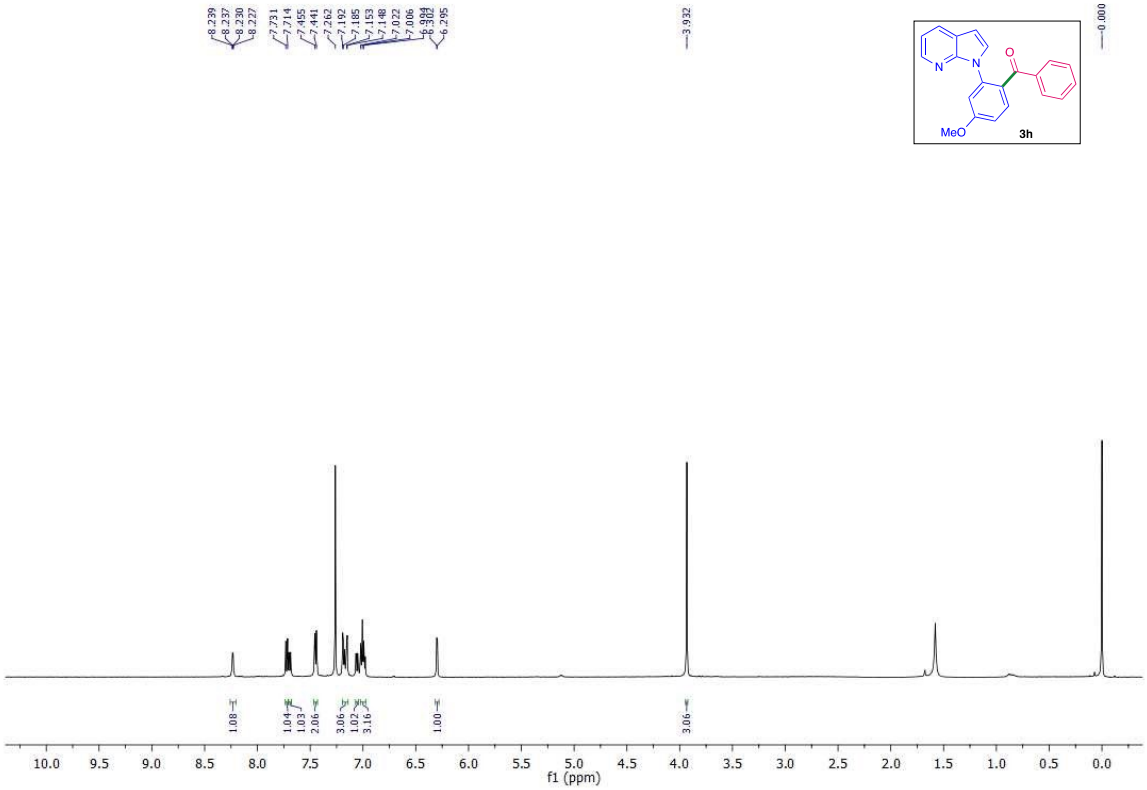
^{1}H NMR (500 MHz/$CDCl_3$)



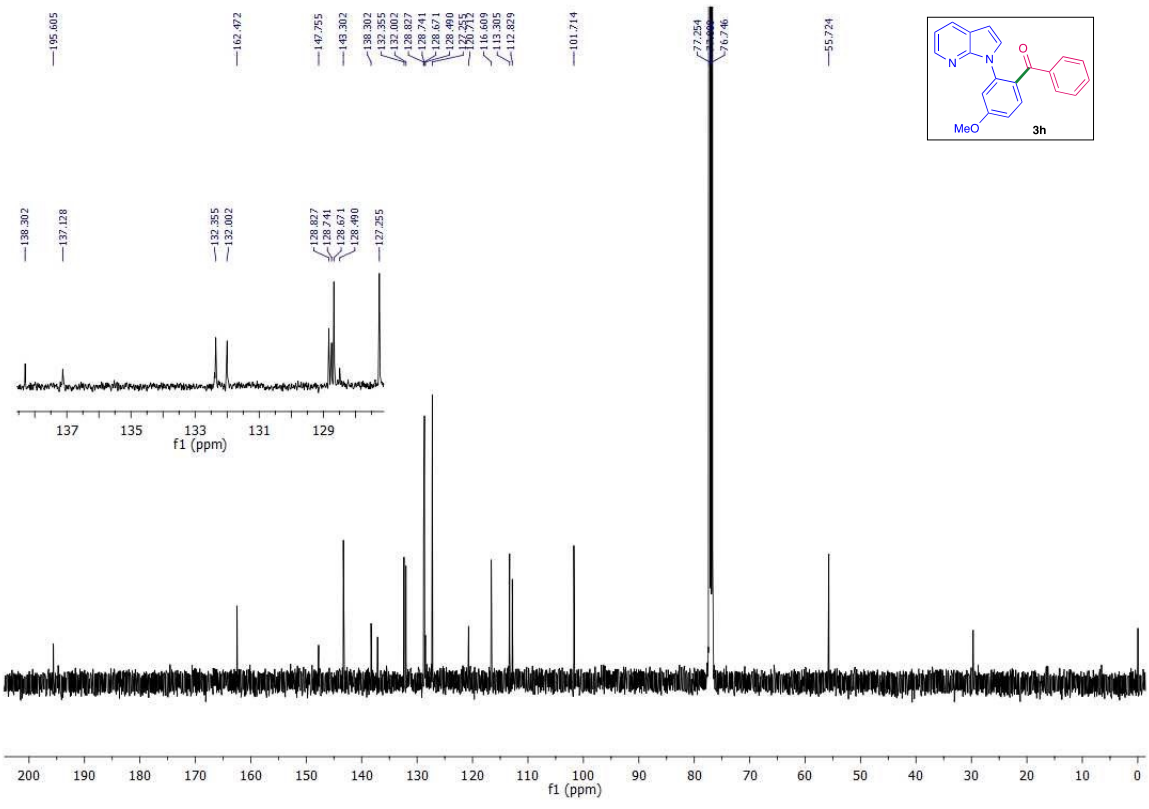
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



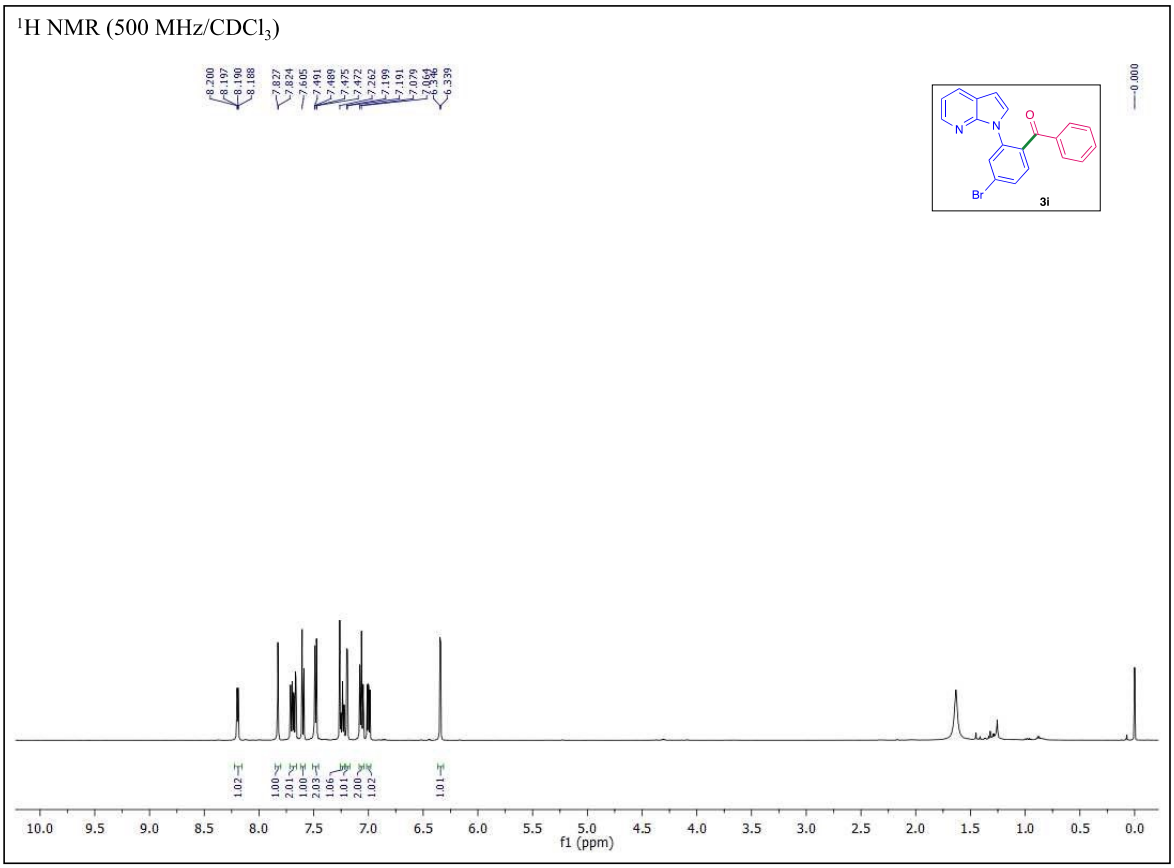
^{1}H NMR (500 MHz/$CDCl_3$)



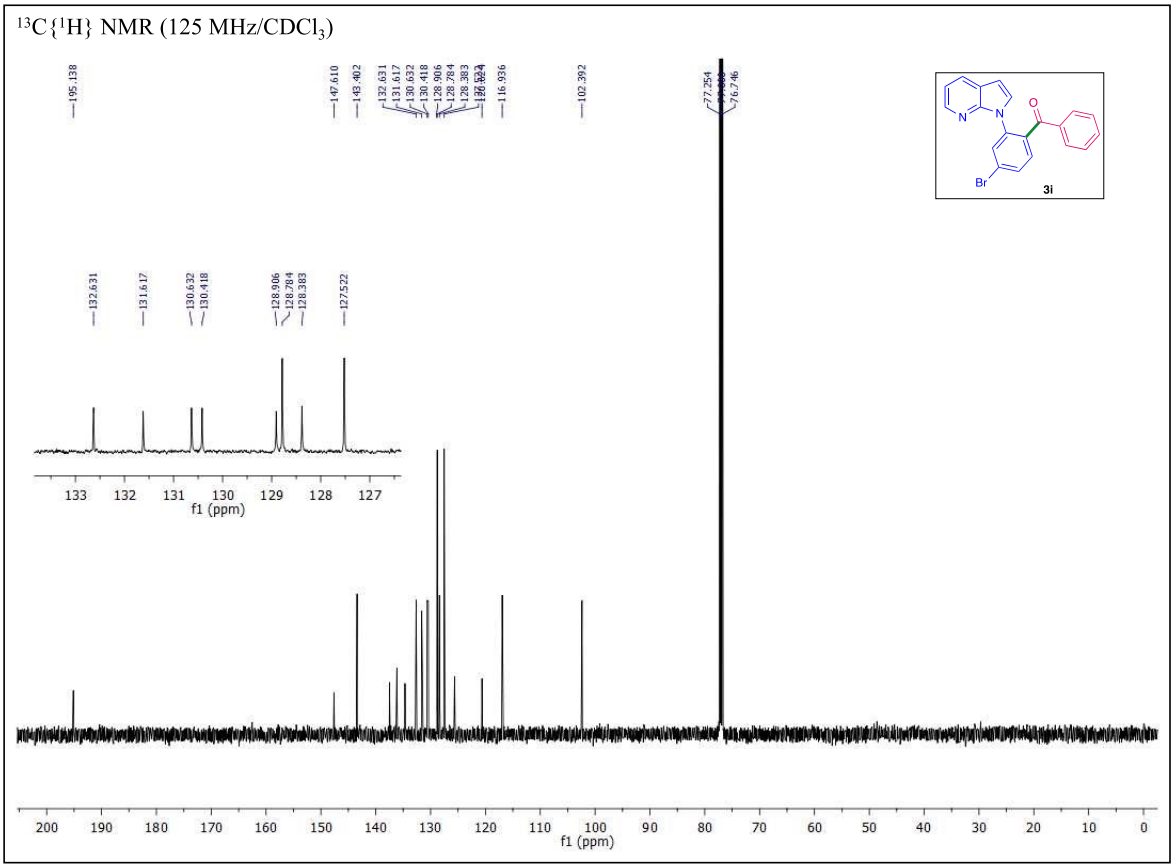
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



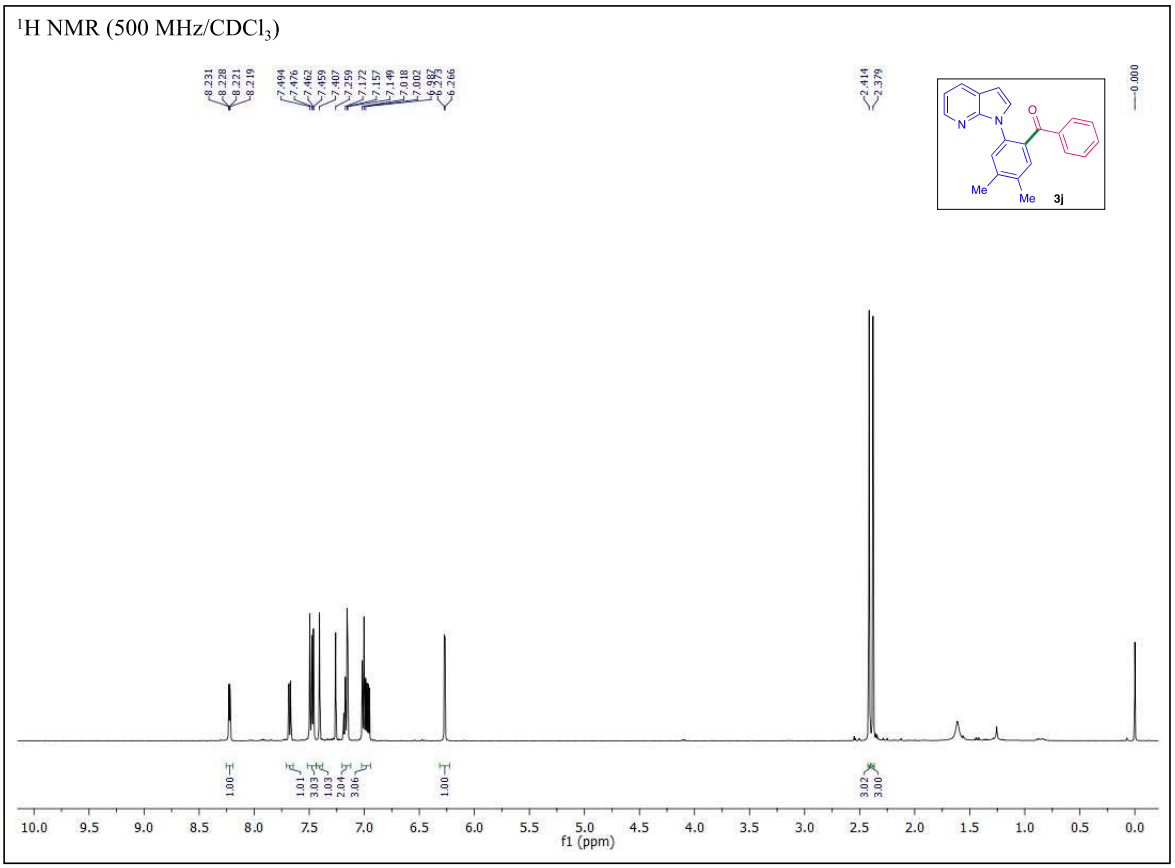
^{1}H NMR (500 MHz/$CDCl_3$)



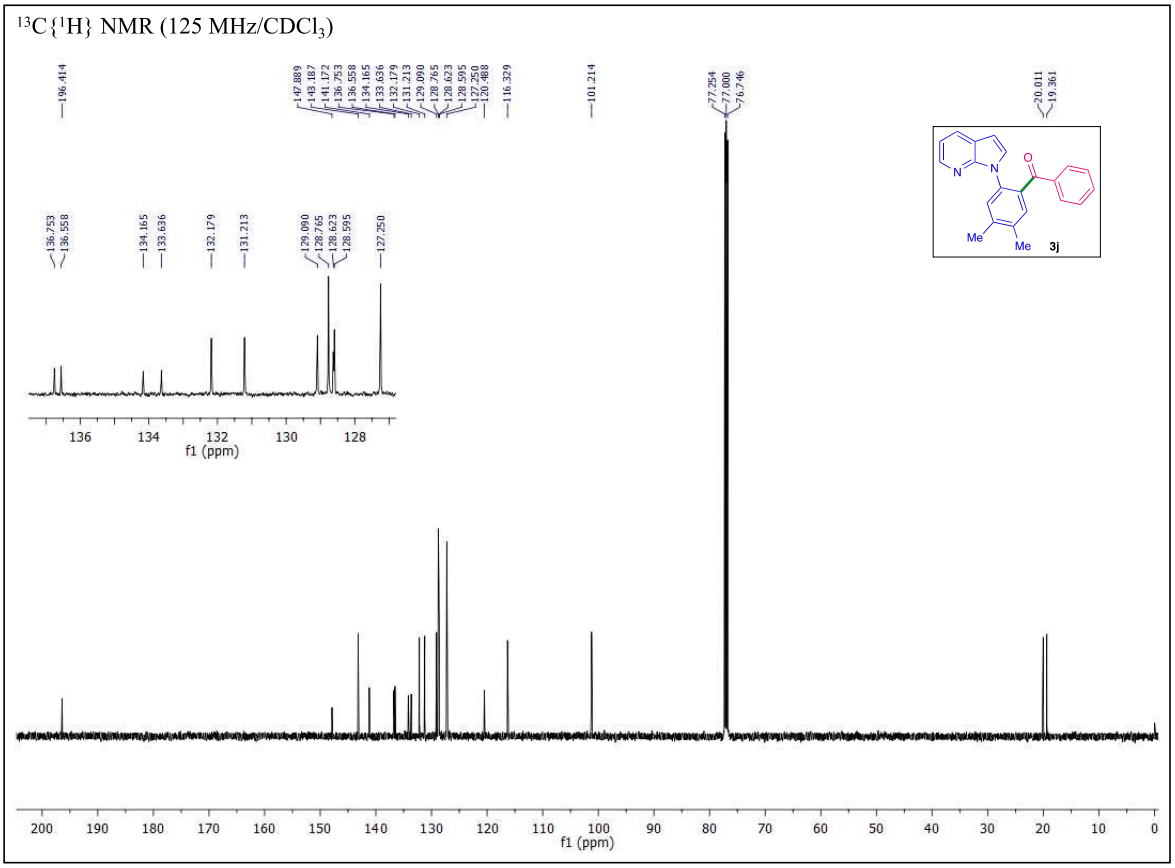
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



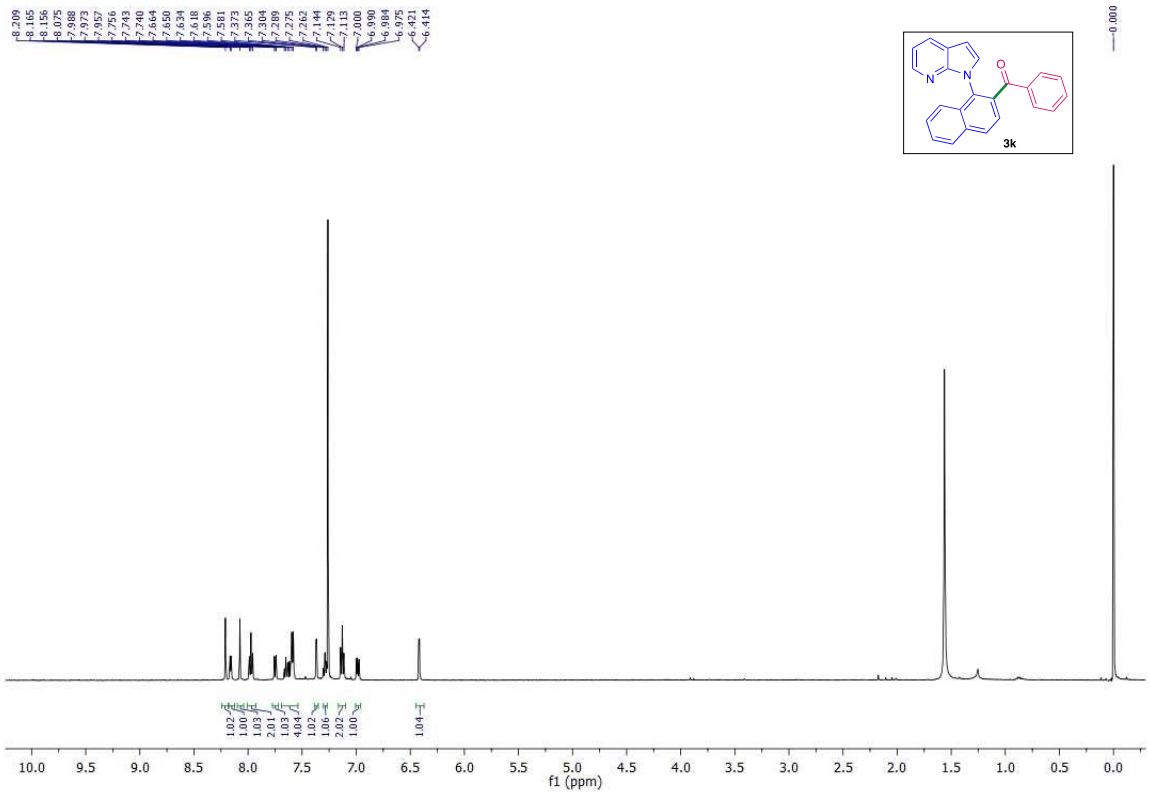
^{1}H NMR (500 MHz/$CDCl_3$)



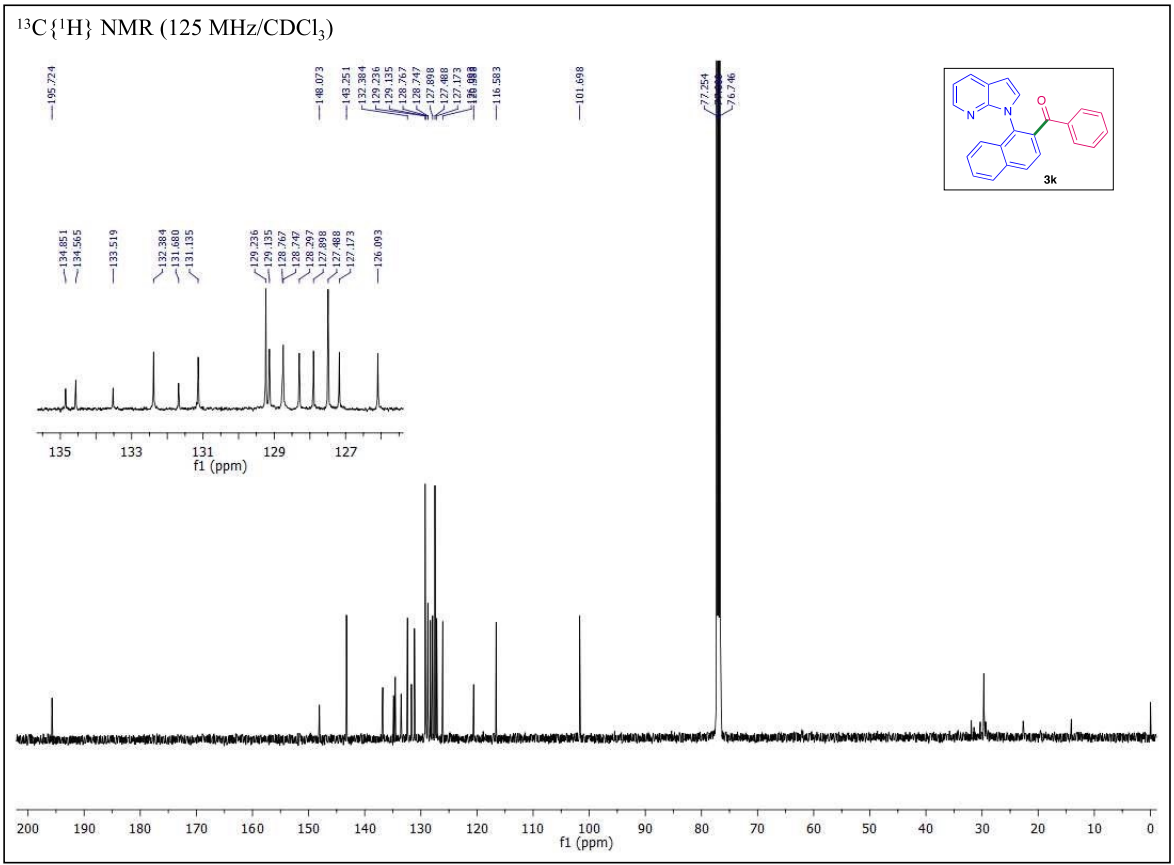
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



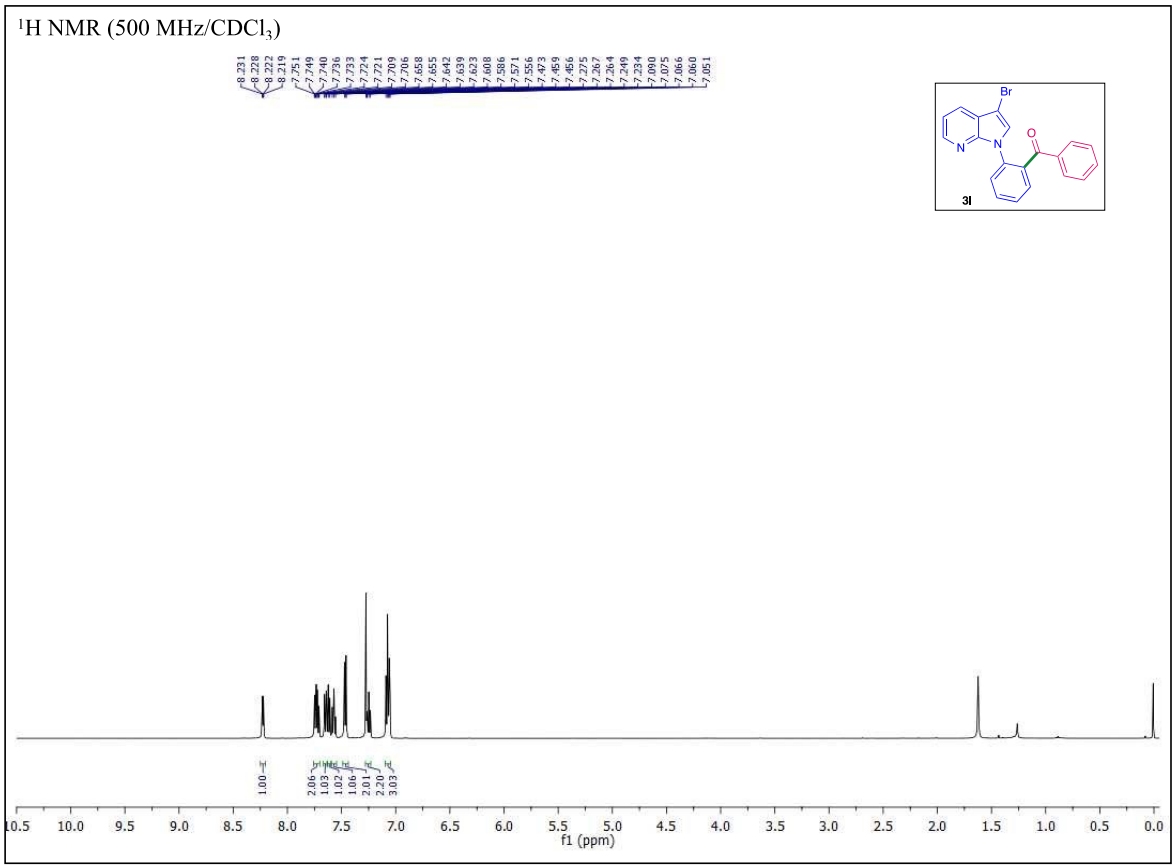
^{1}H NMR (500MHz/$CDCl_3$)



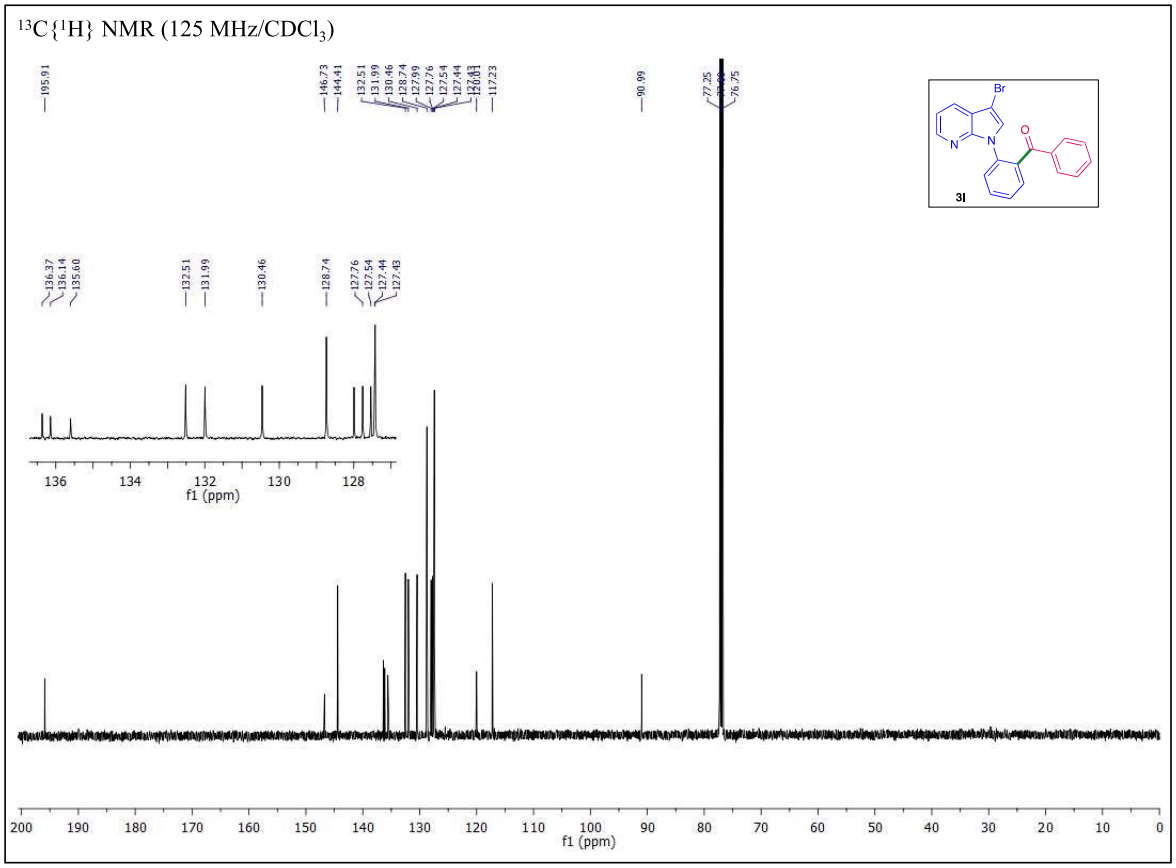
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



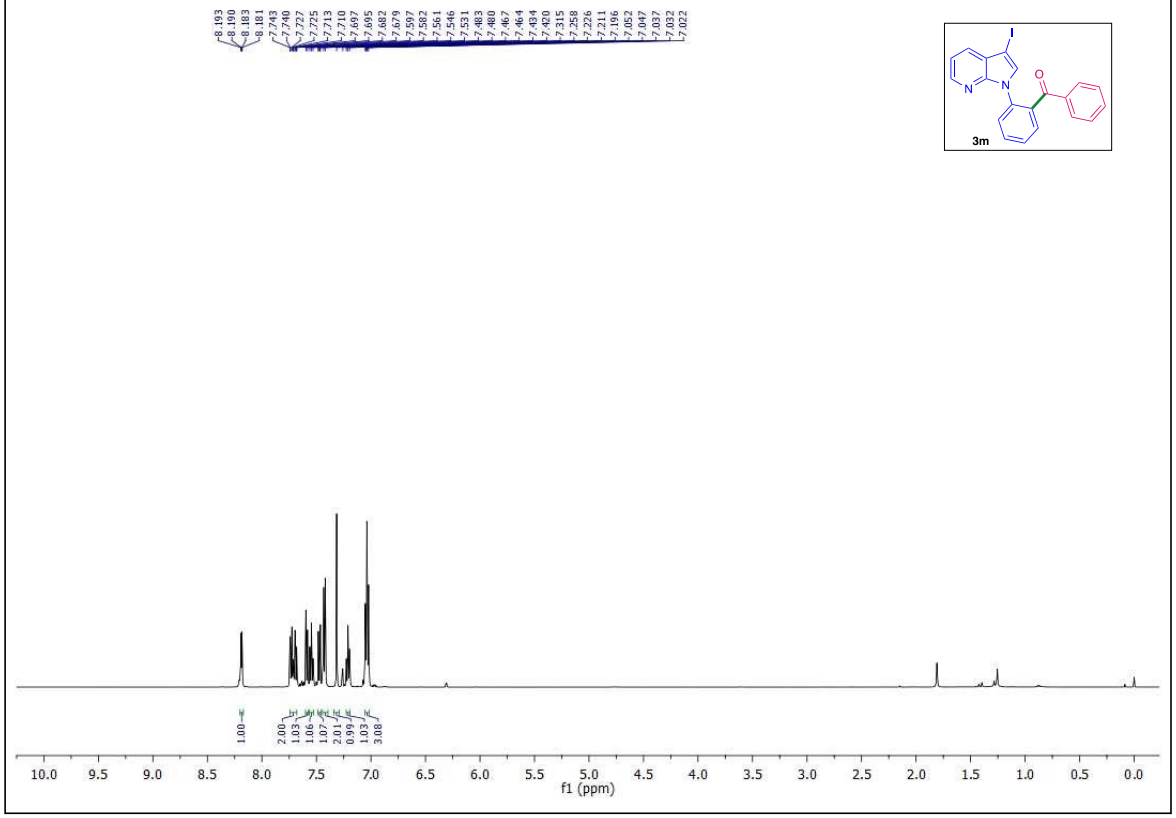
^{1}H NMR (500 MHz/$CDCl_3$)



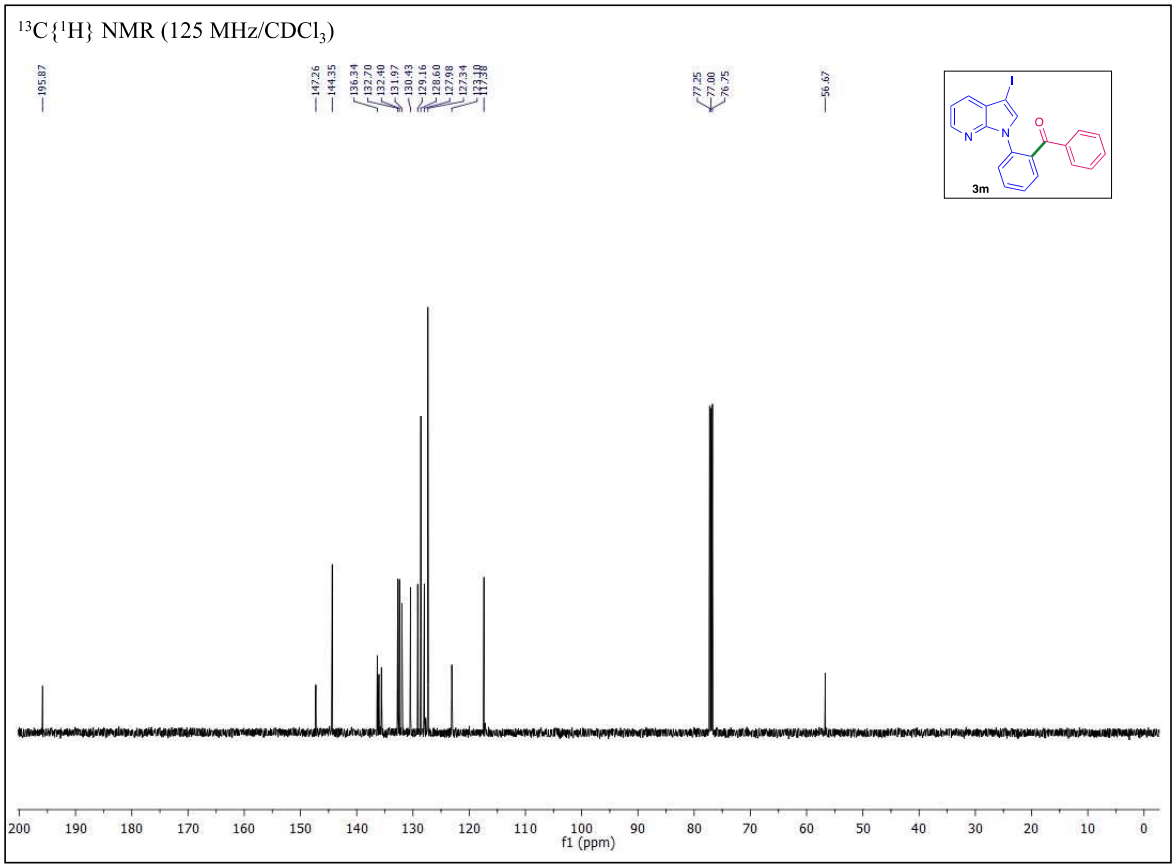
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



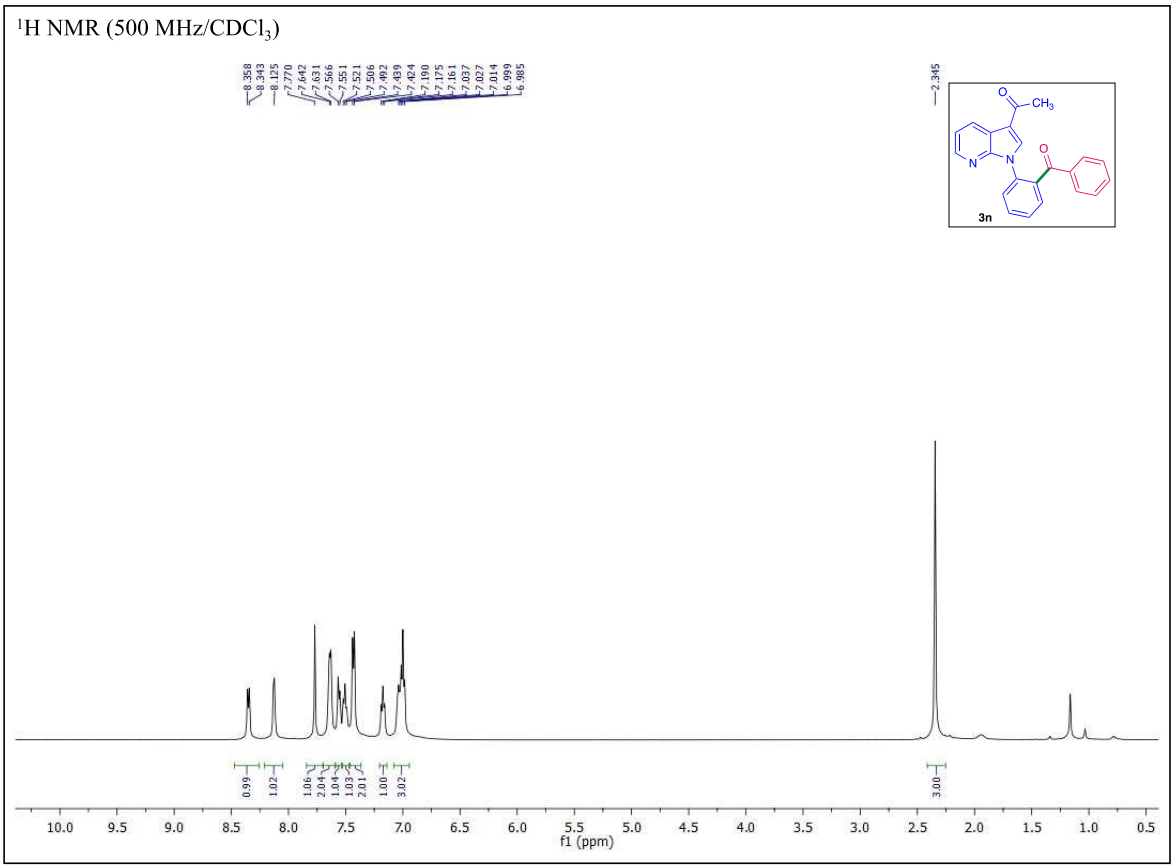
^{1}H NMR (500 MHz/$CDCl_3$)



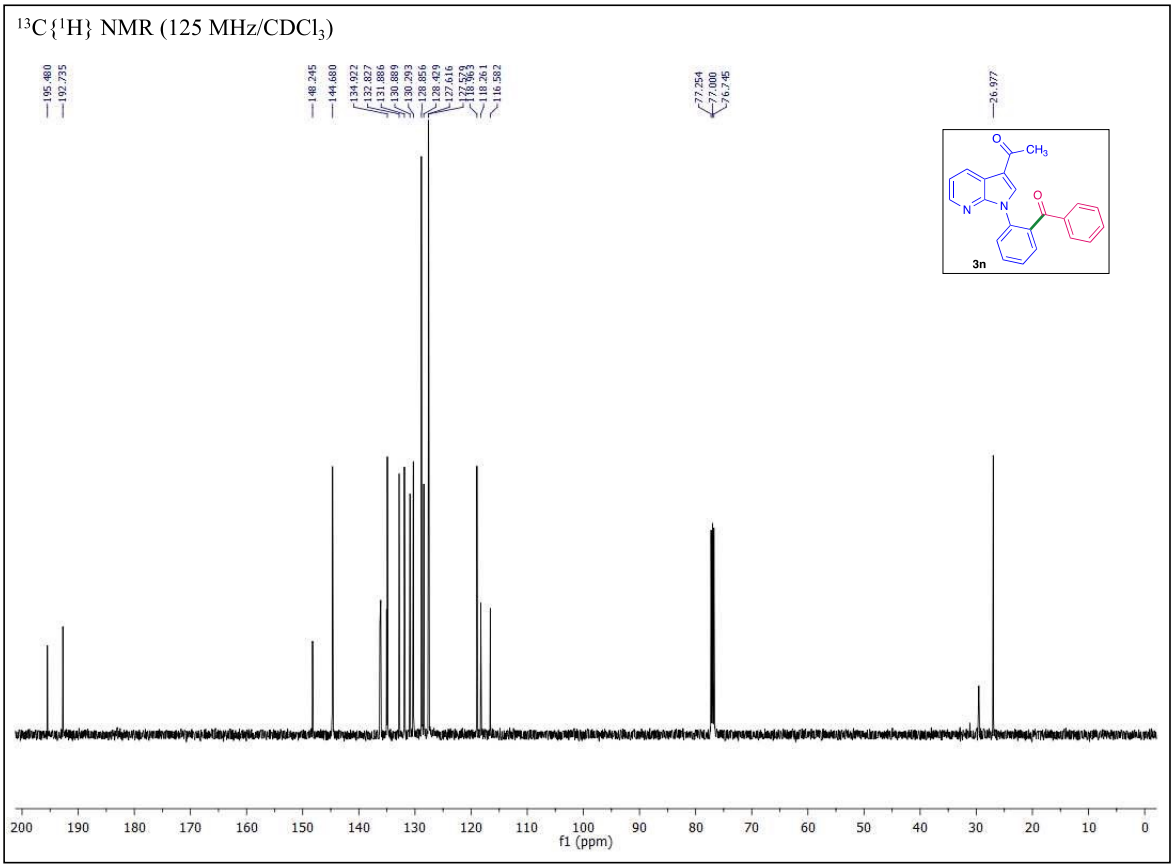
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



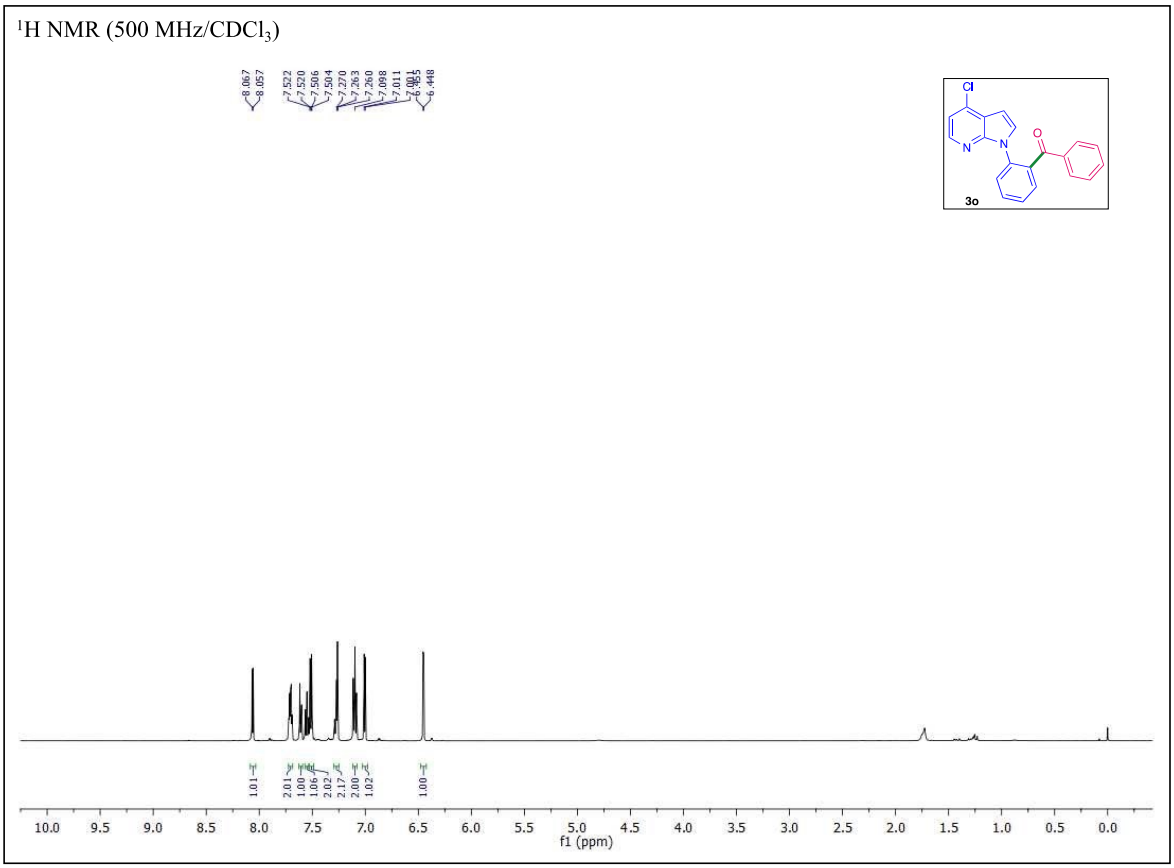
^{1}H NMR (500 MHz/$CDCl_3$)



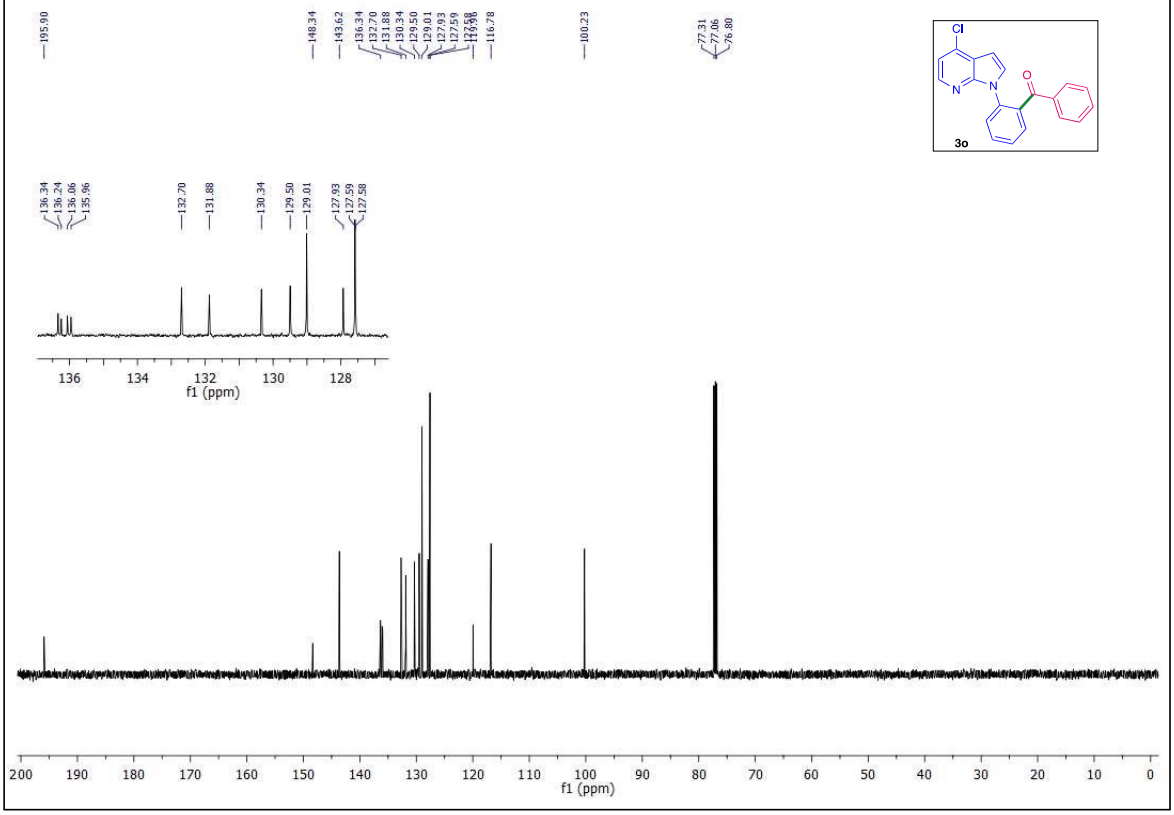
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



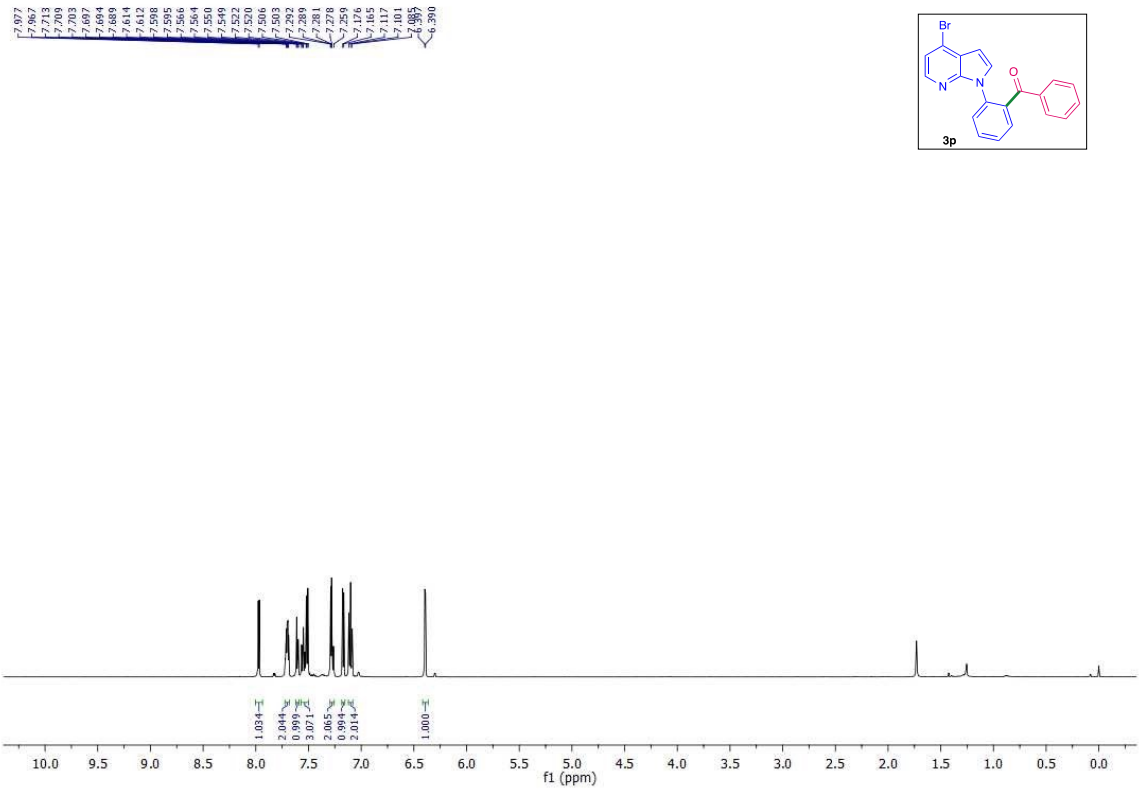
^{1}H NMR (500 MHz/$CDCl_3$)



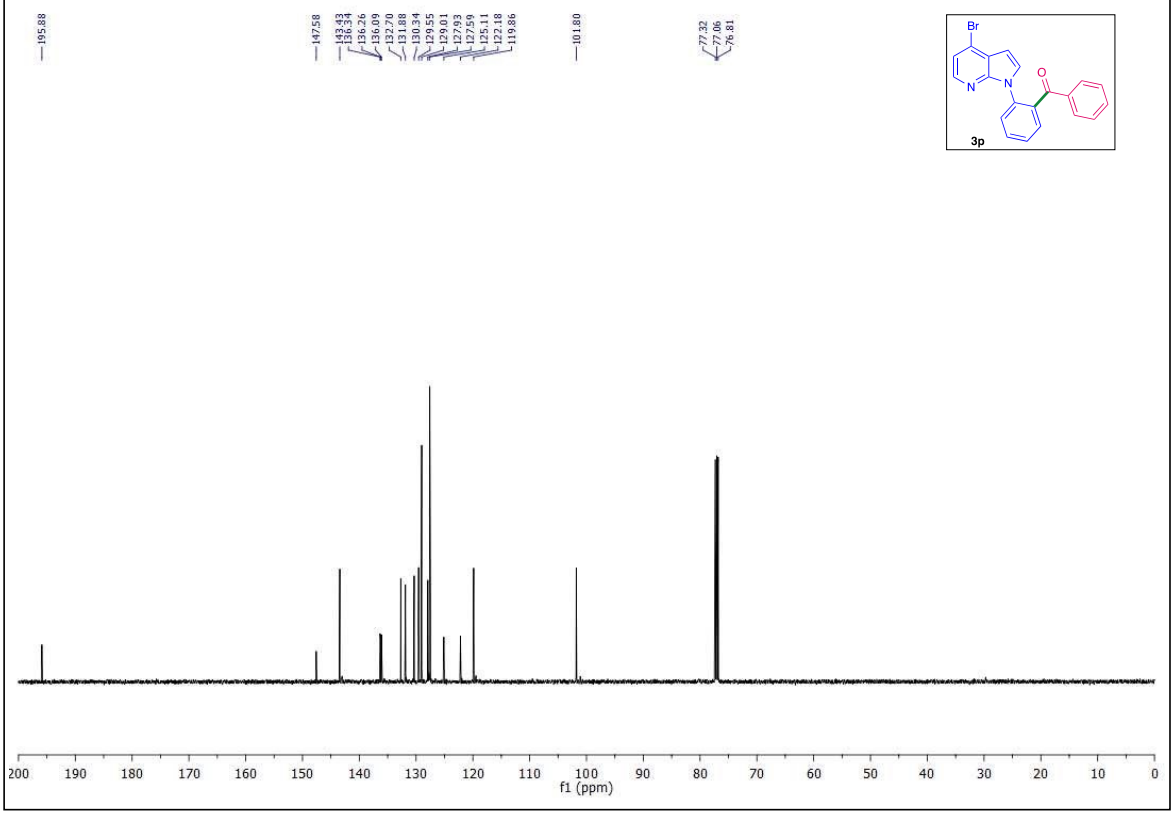
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



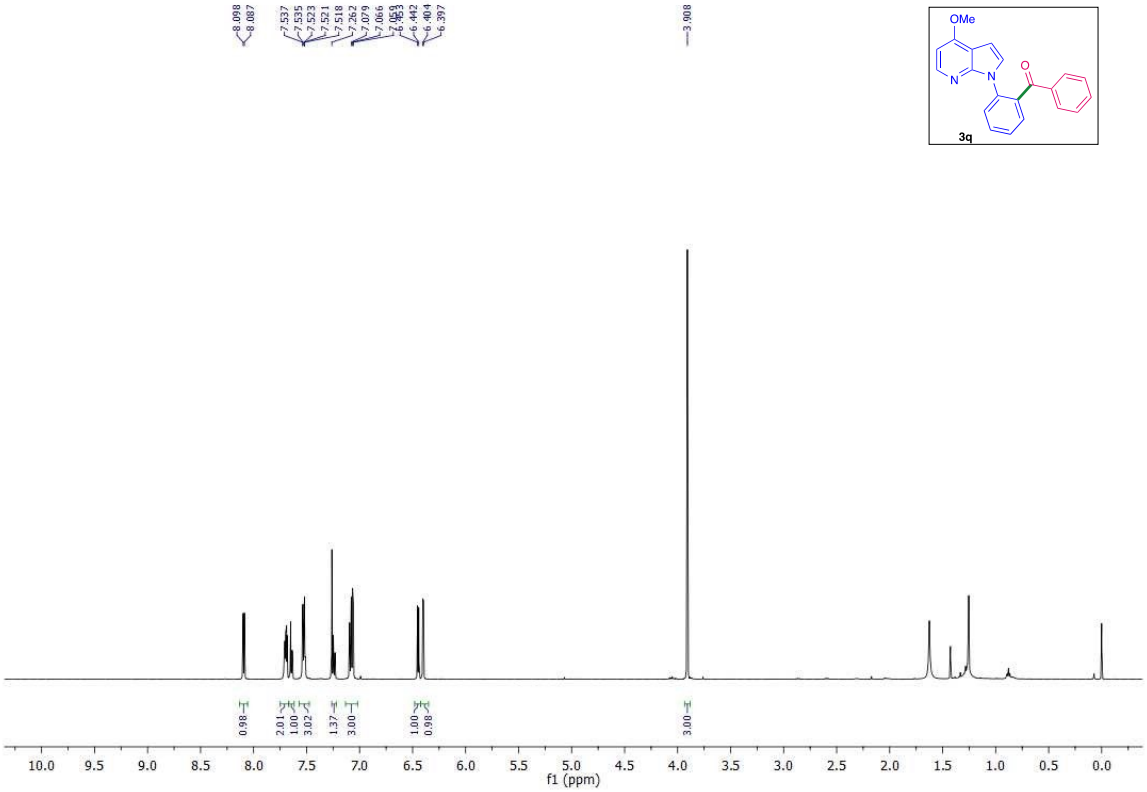
^{1}H NMR (500 MHz/$CDCl_3$)



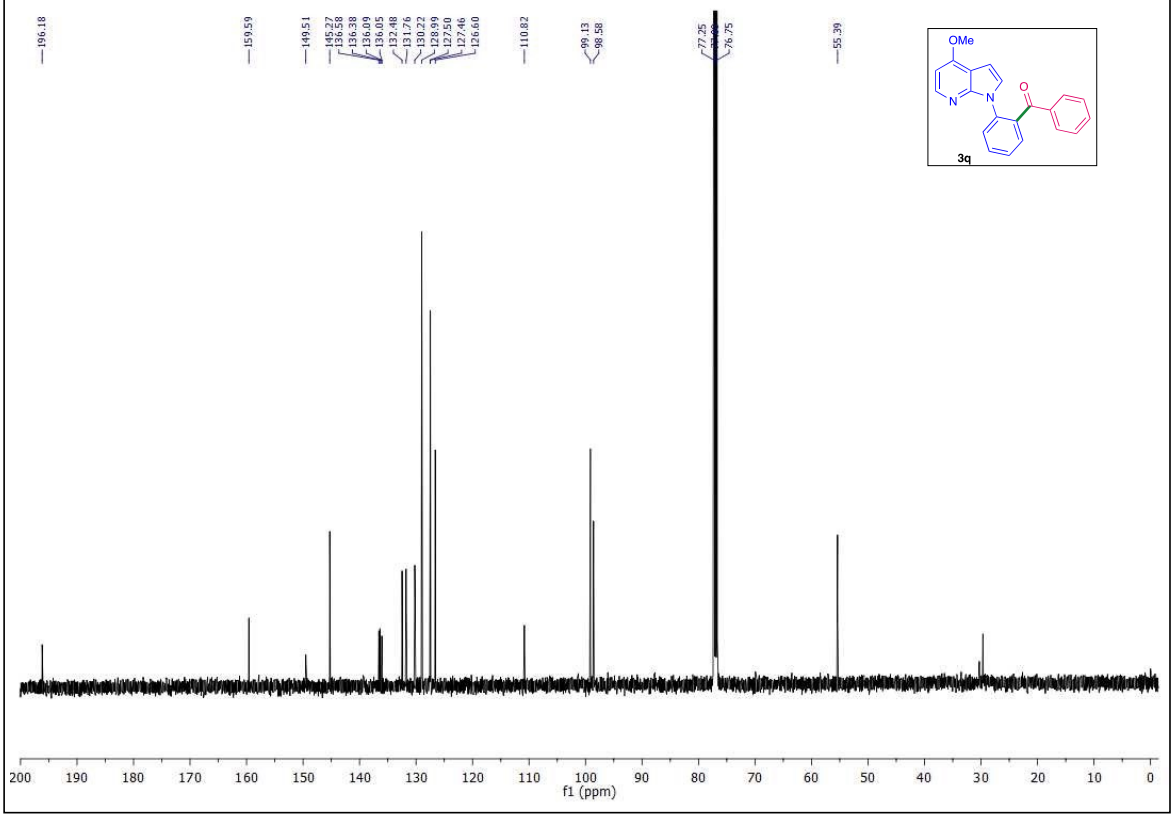
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



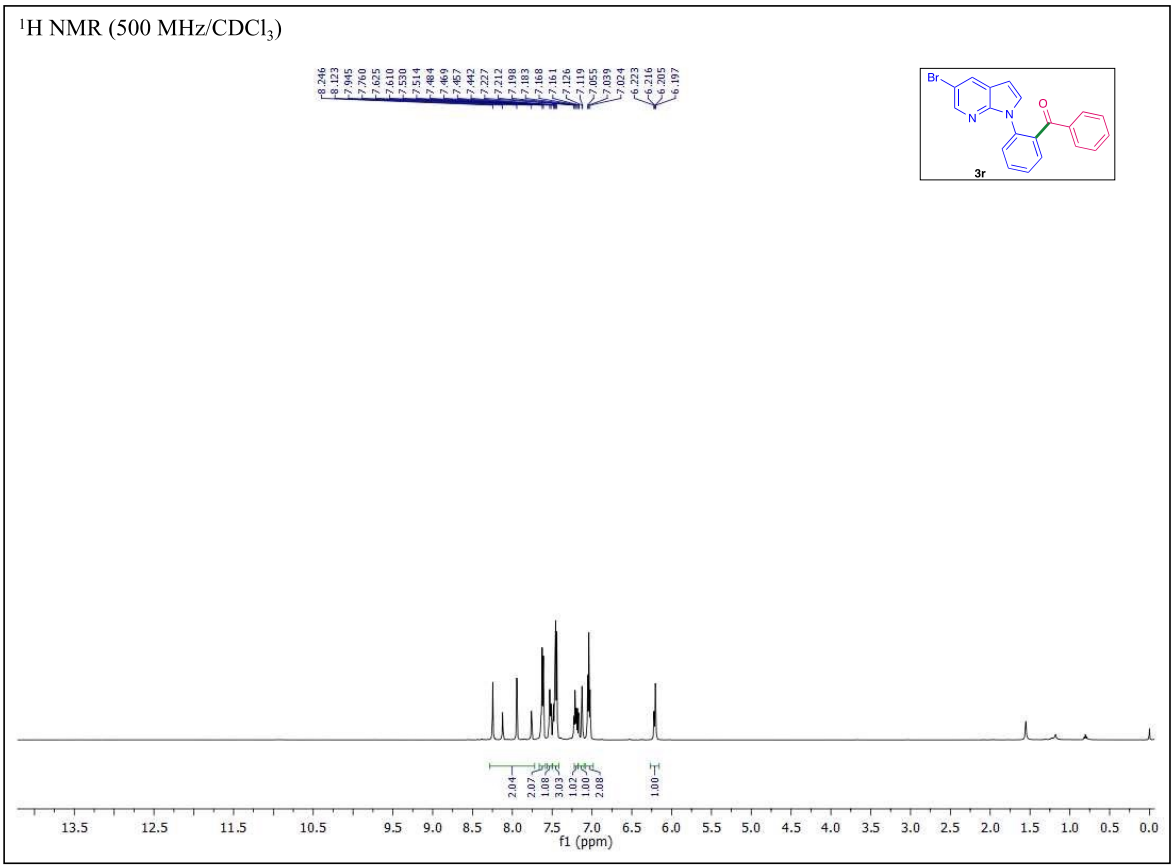
^{1}H NMR (500 MHz/$CDCl_3$)



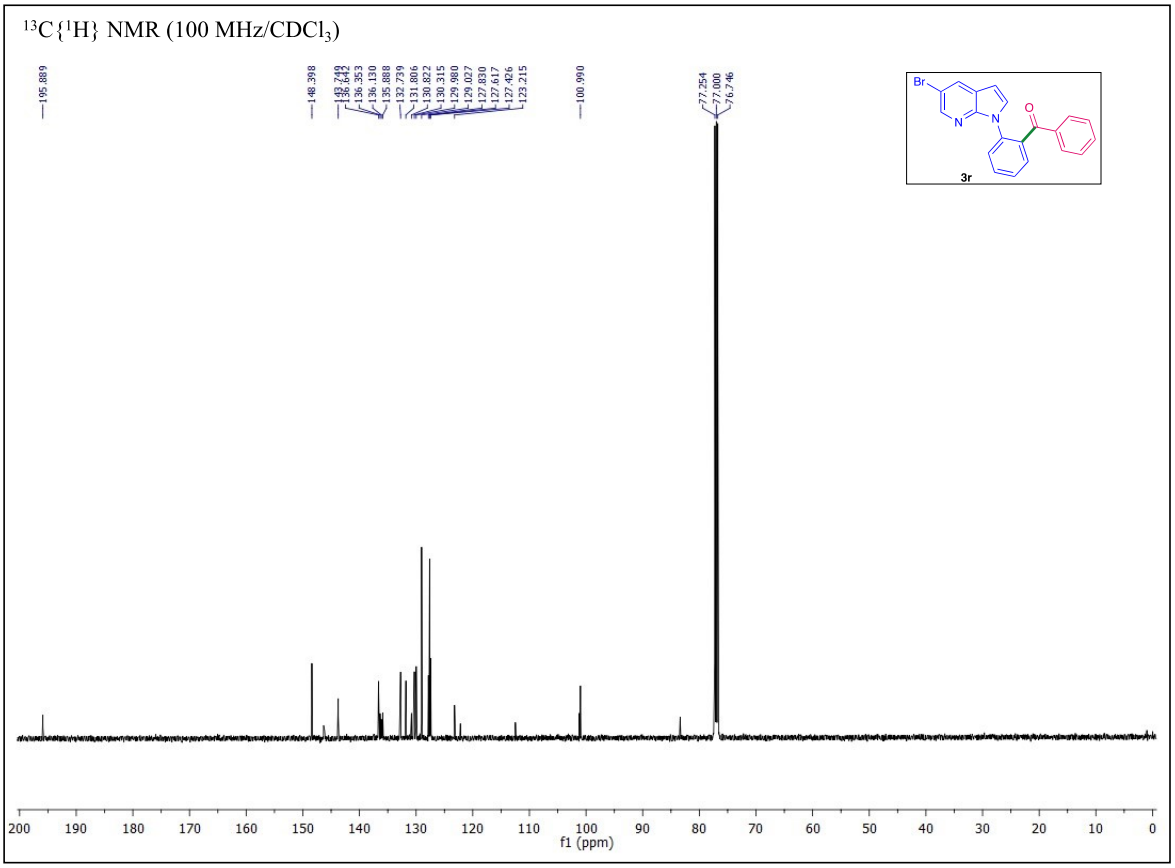
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



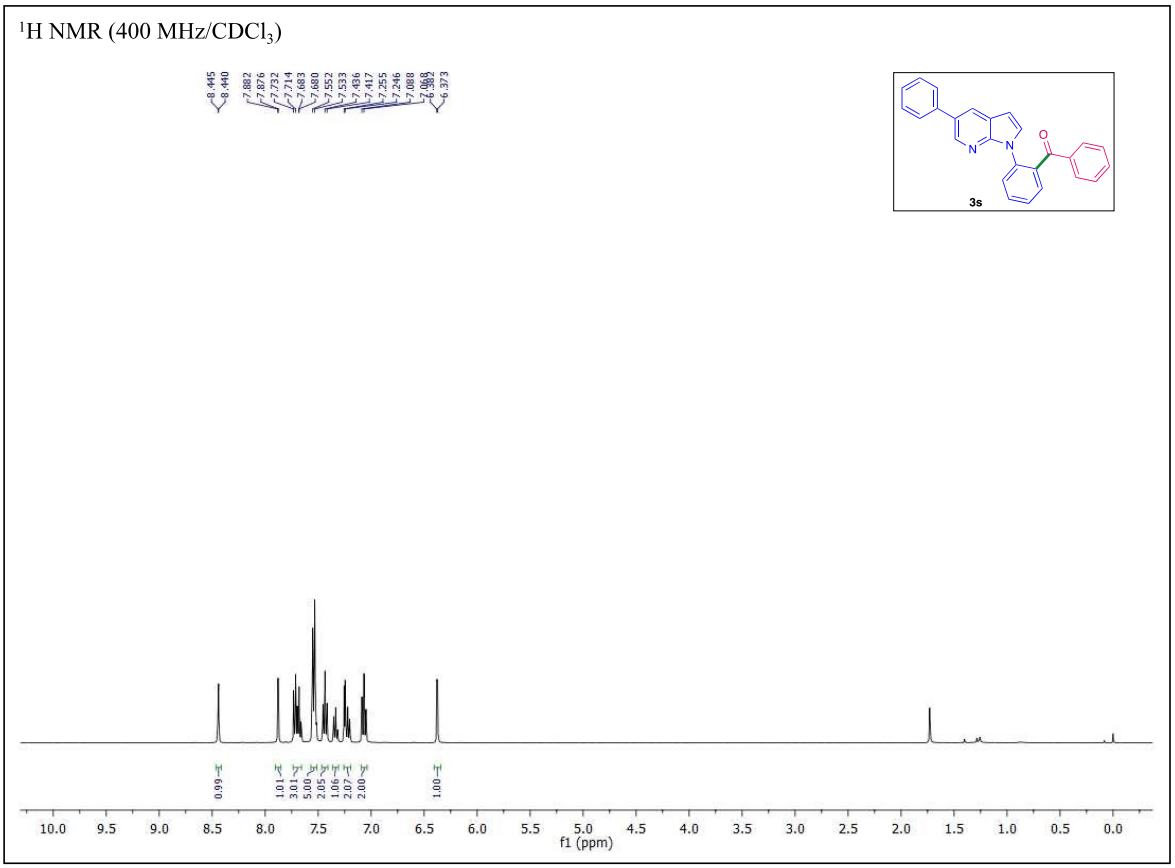
^{1}H NMR (500 MHz/$CDCl_3$)



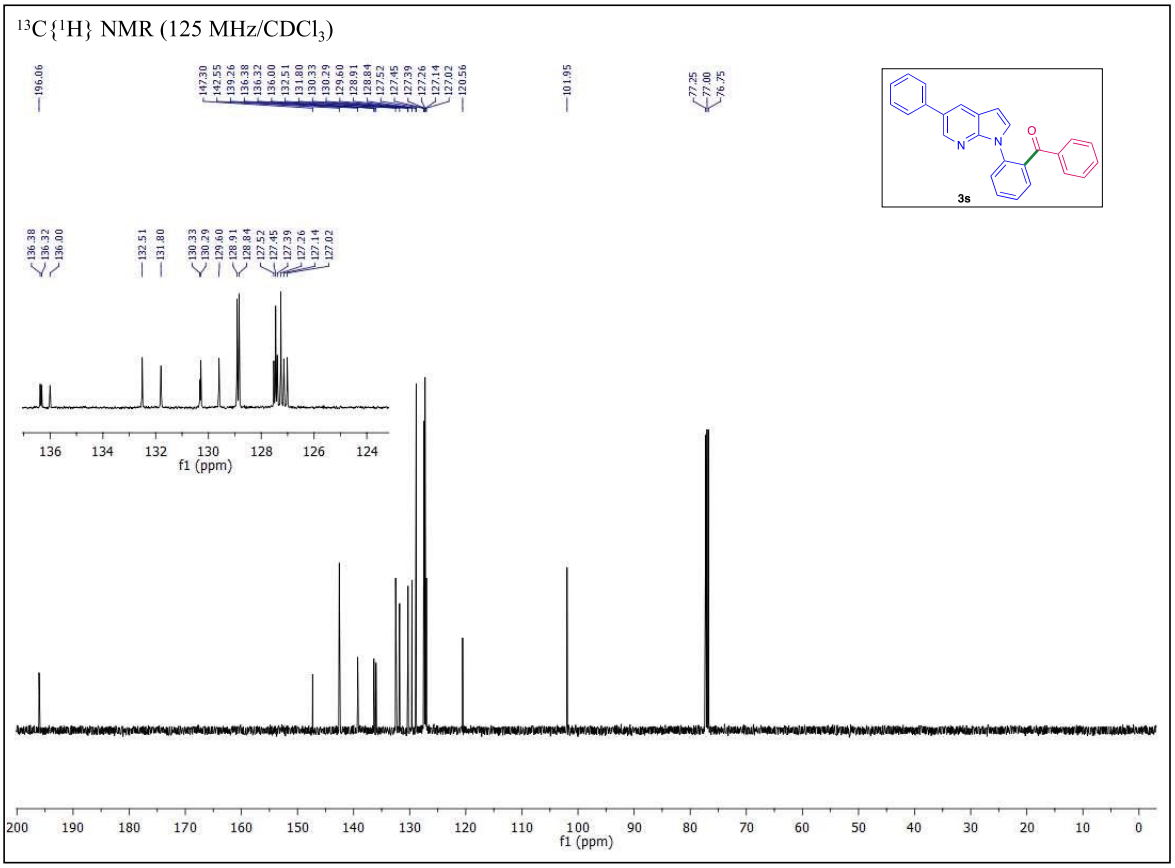
^{13}C{^{1}H} NMR (100 MHz/$CDCl_3$)



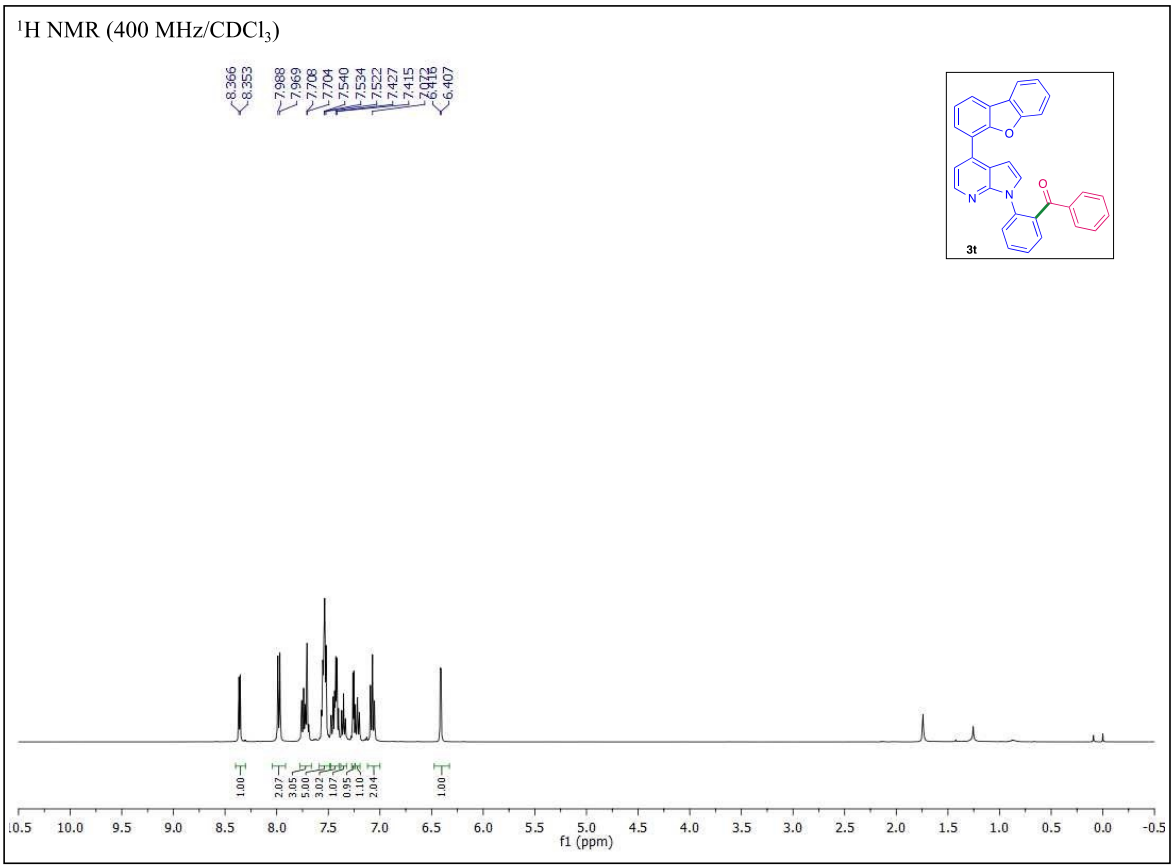
^{1}H NMR (400 MHz/$CDCl_3$)



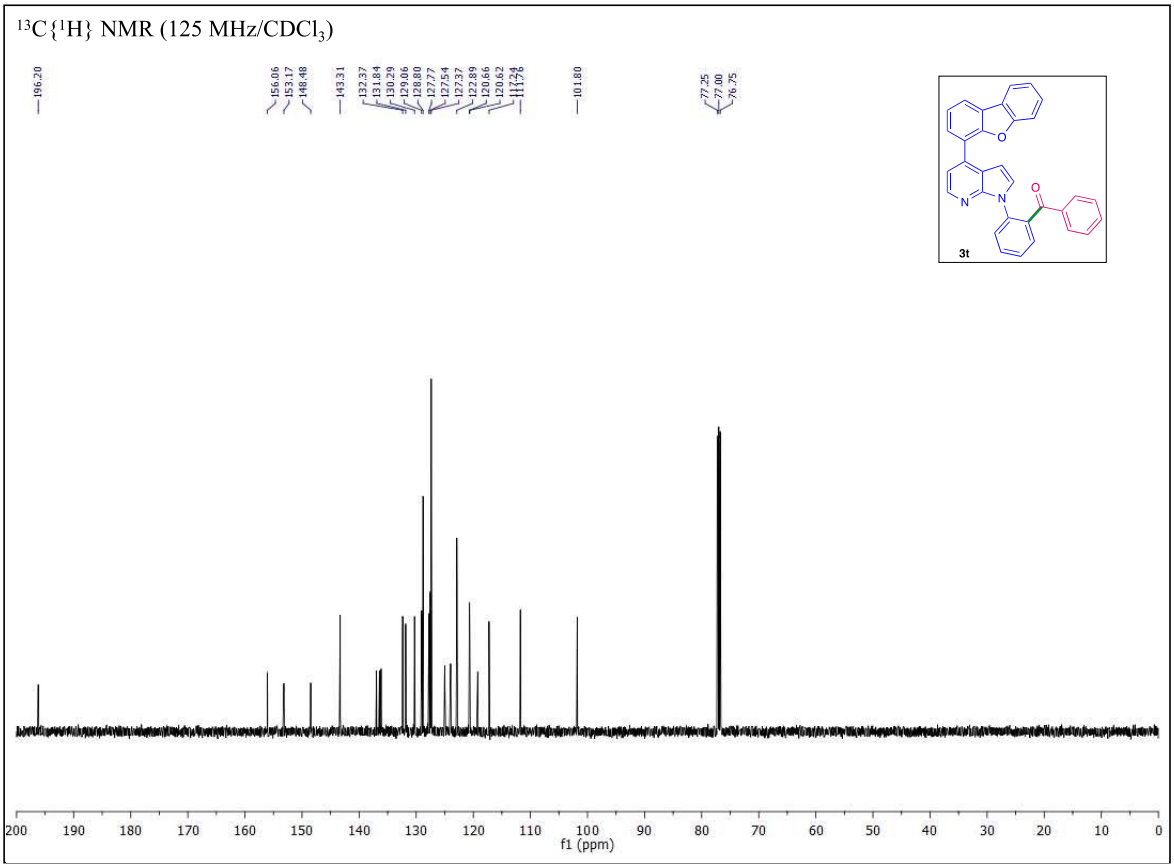
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



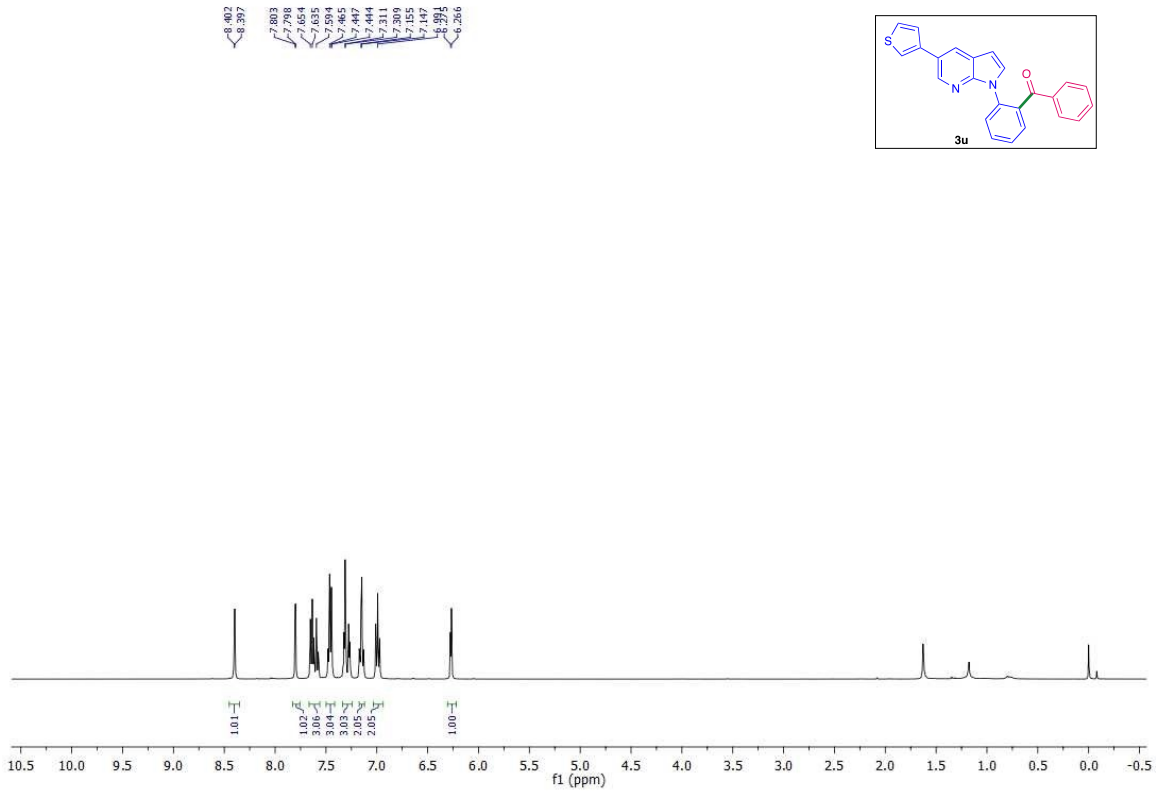
^{1}H NMR (400 MHz/$CDCl_3$)



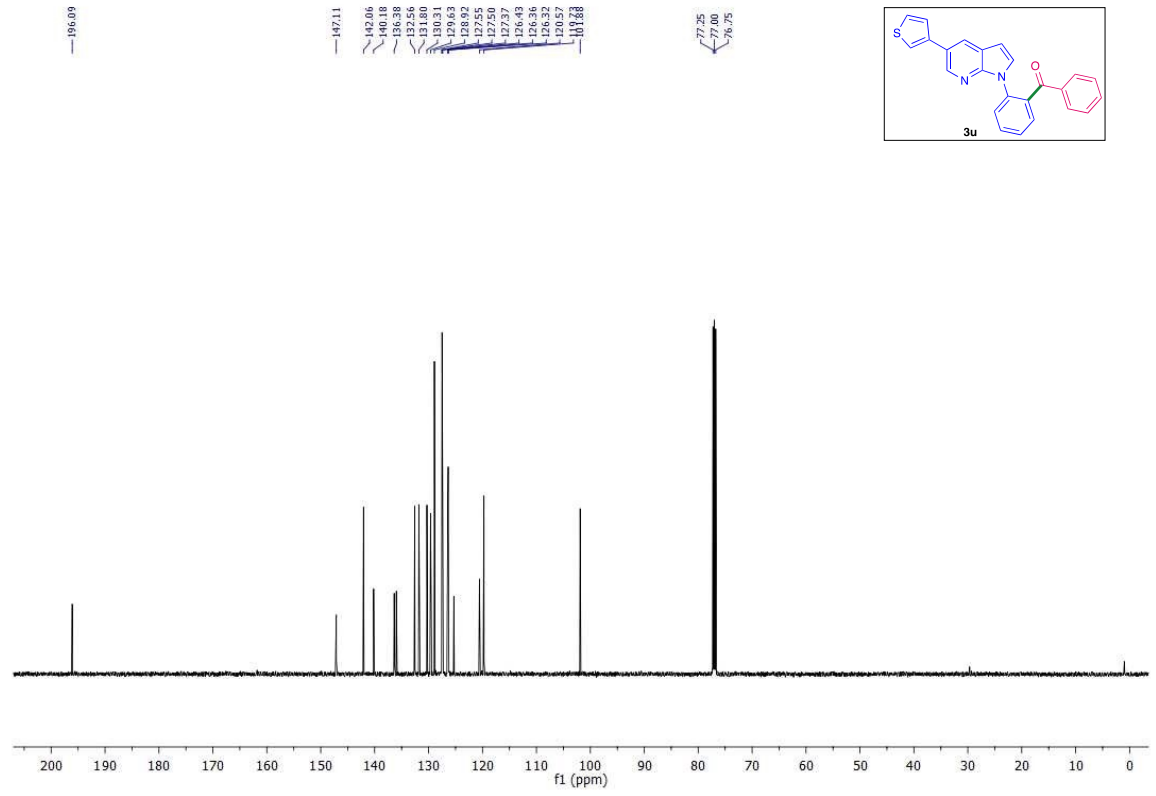
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



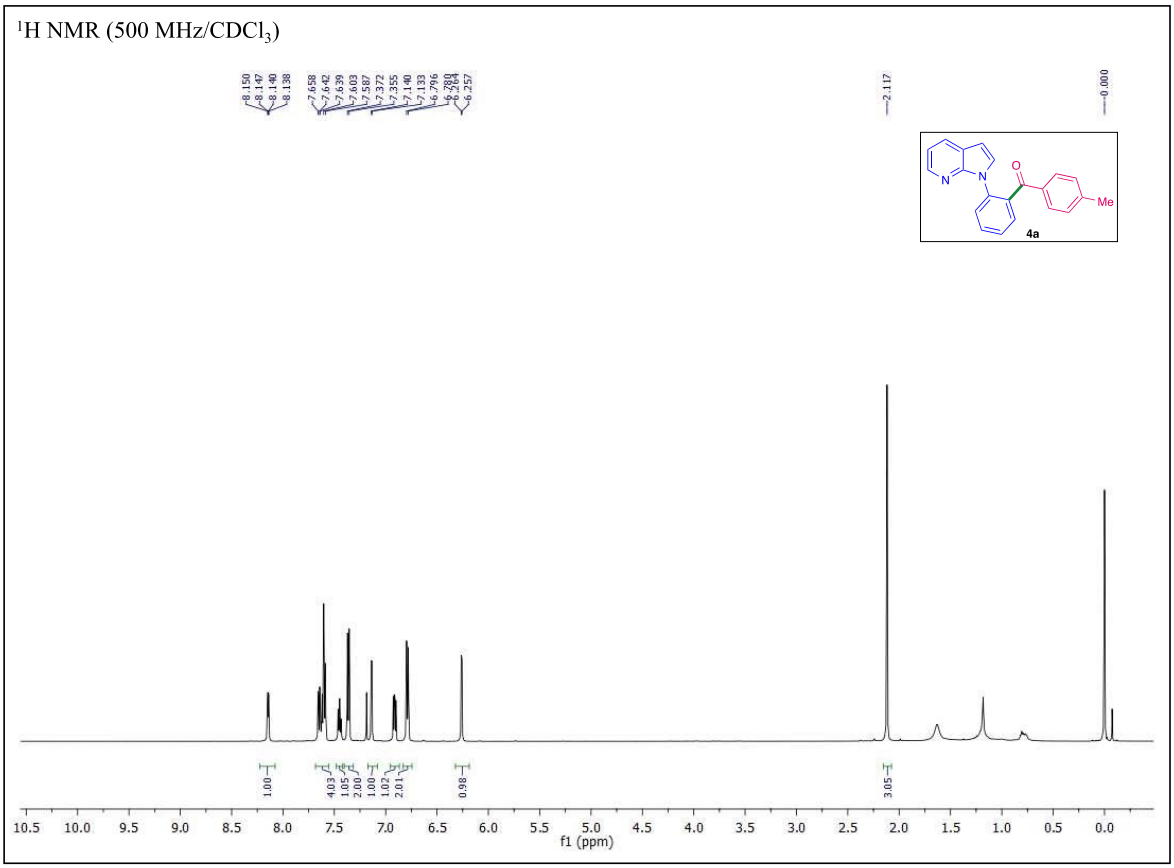
^{1}H NMR (400 MHz/$CDCl_3$)



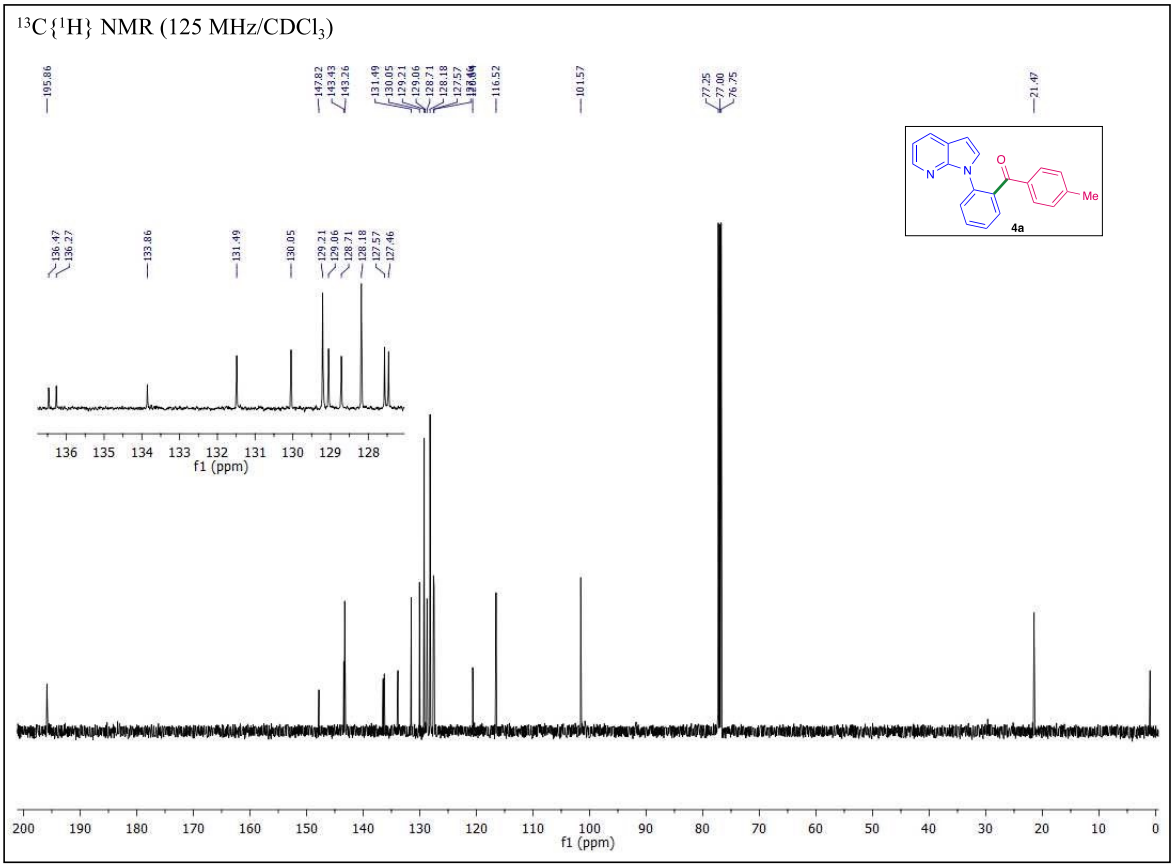
^{13}C{^{1}H} NMR (100 MHz/$CDCl_3$)



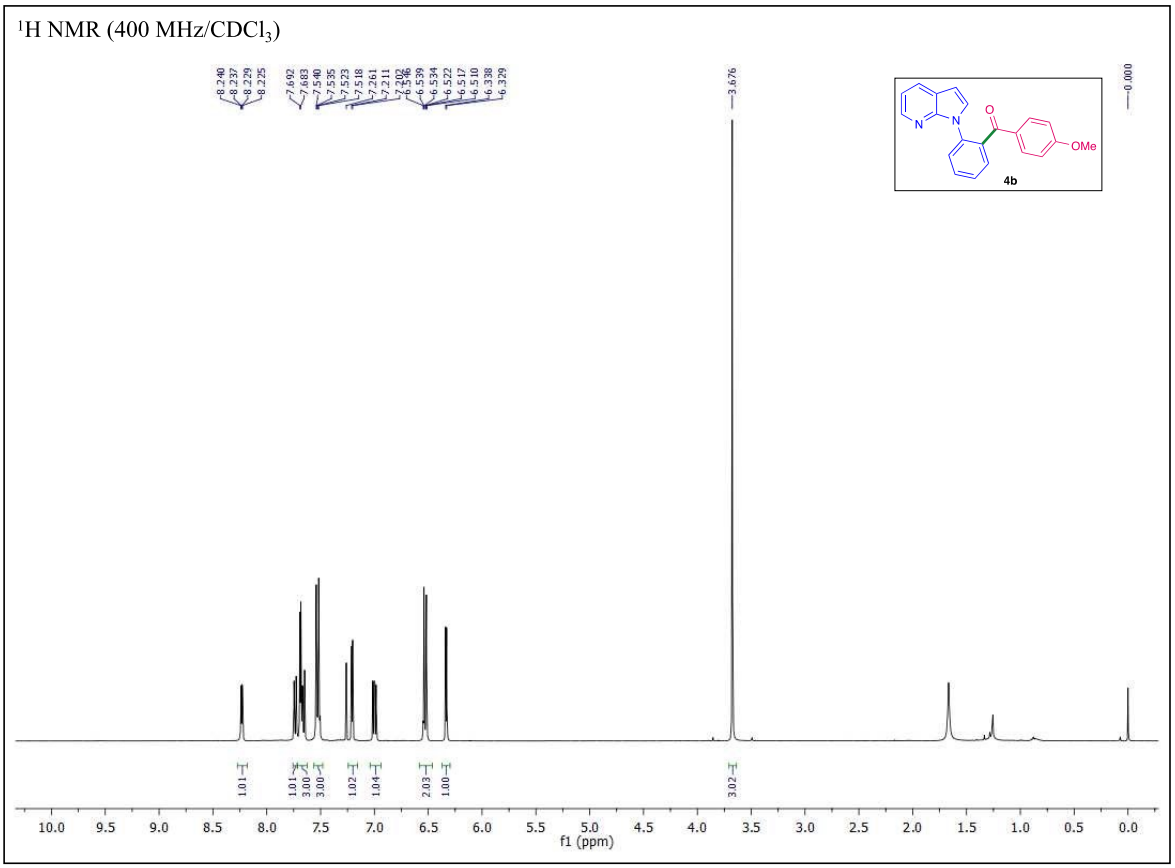
^{1}H NMR (500 MHz/$CDCl_3$)



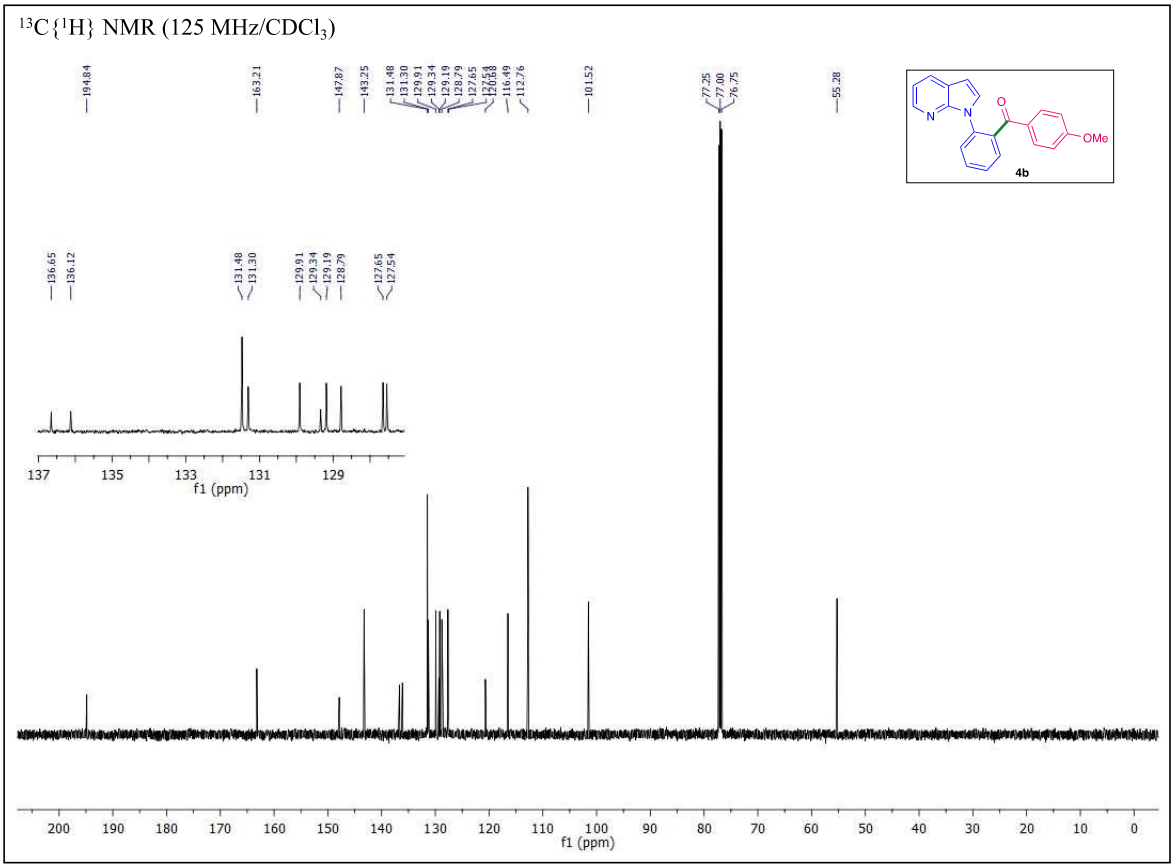
$^{13}C\{^{1}H\}$ NMR (125 MHz/$CDCl_3$)



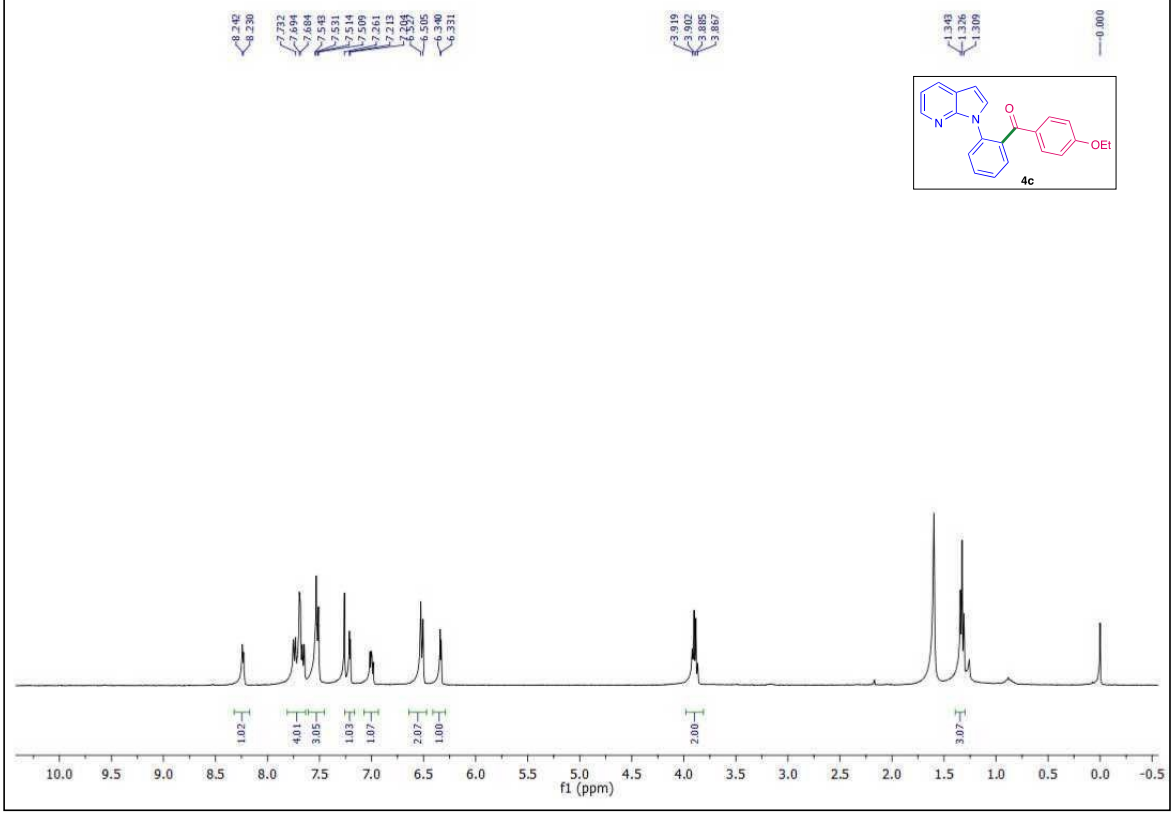
^{1}H NMR (400 MHz/$CDCl_3$)



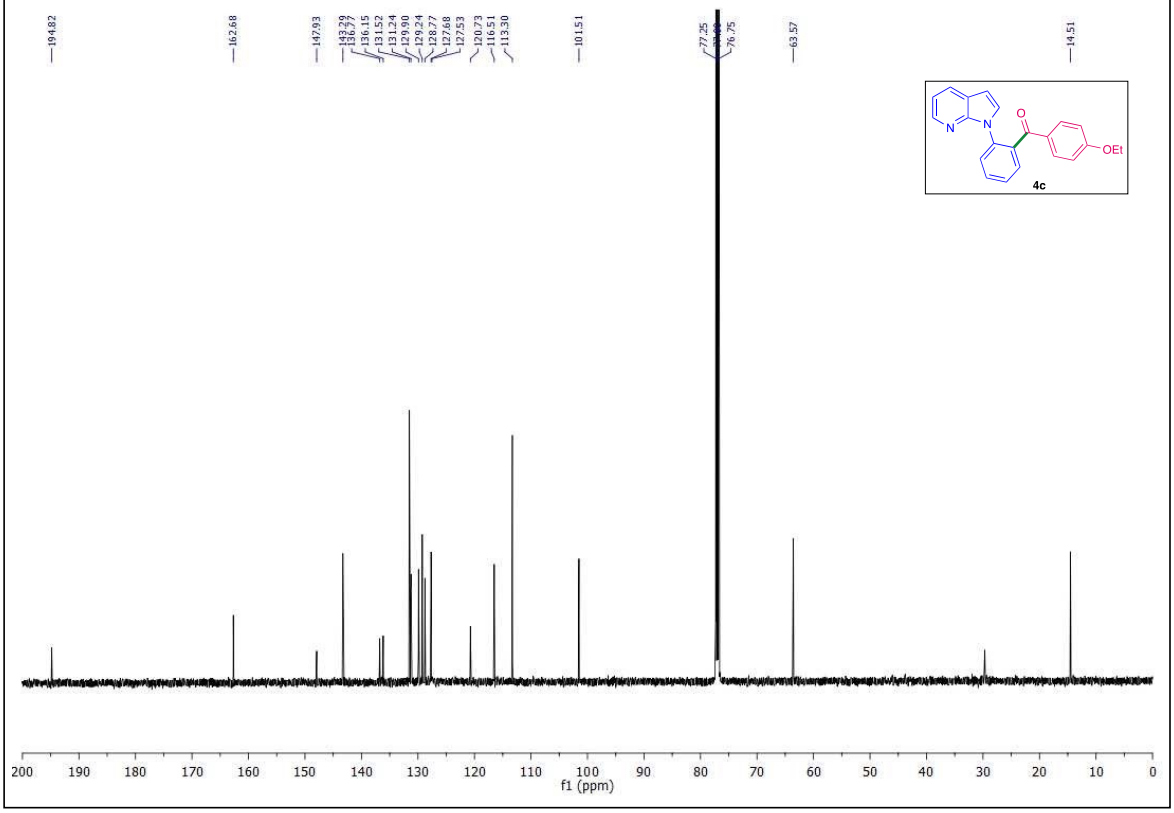
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



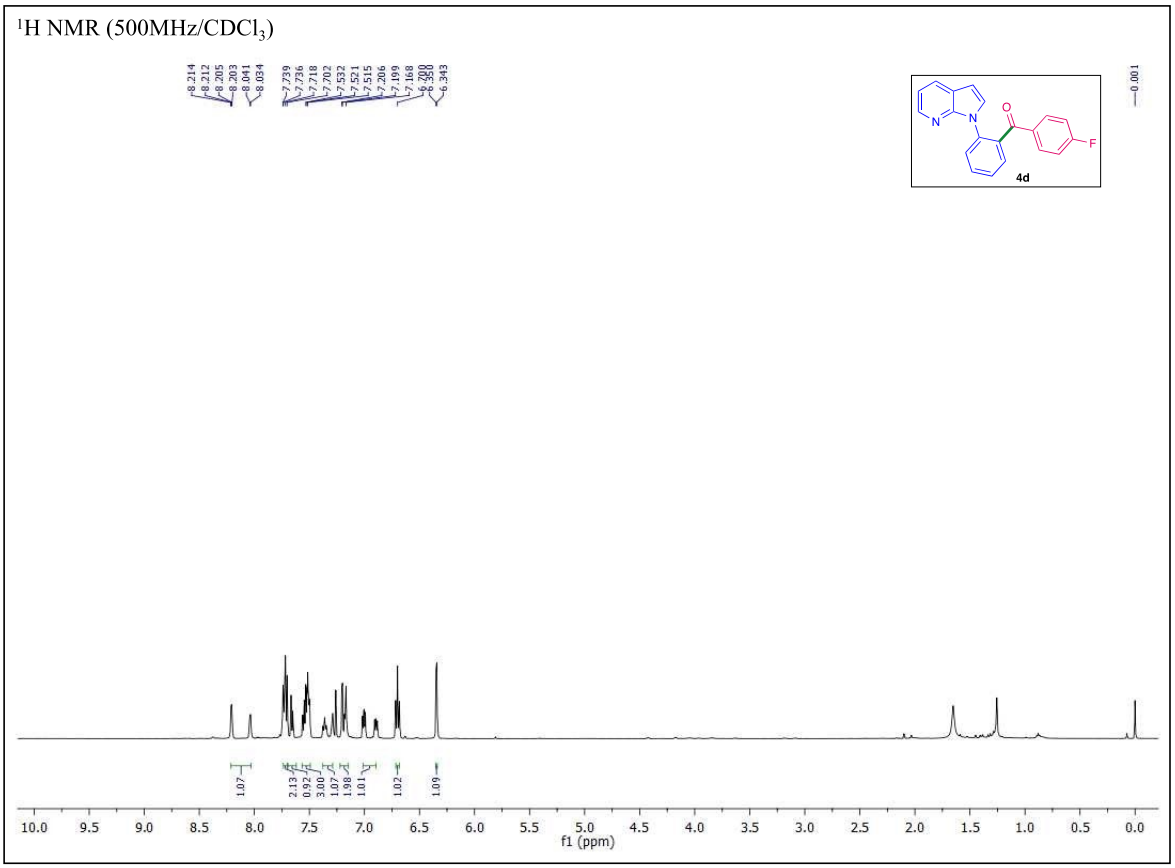
^{1}H NMR (400 MHz/$CDCl_3$)



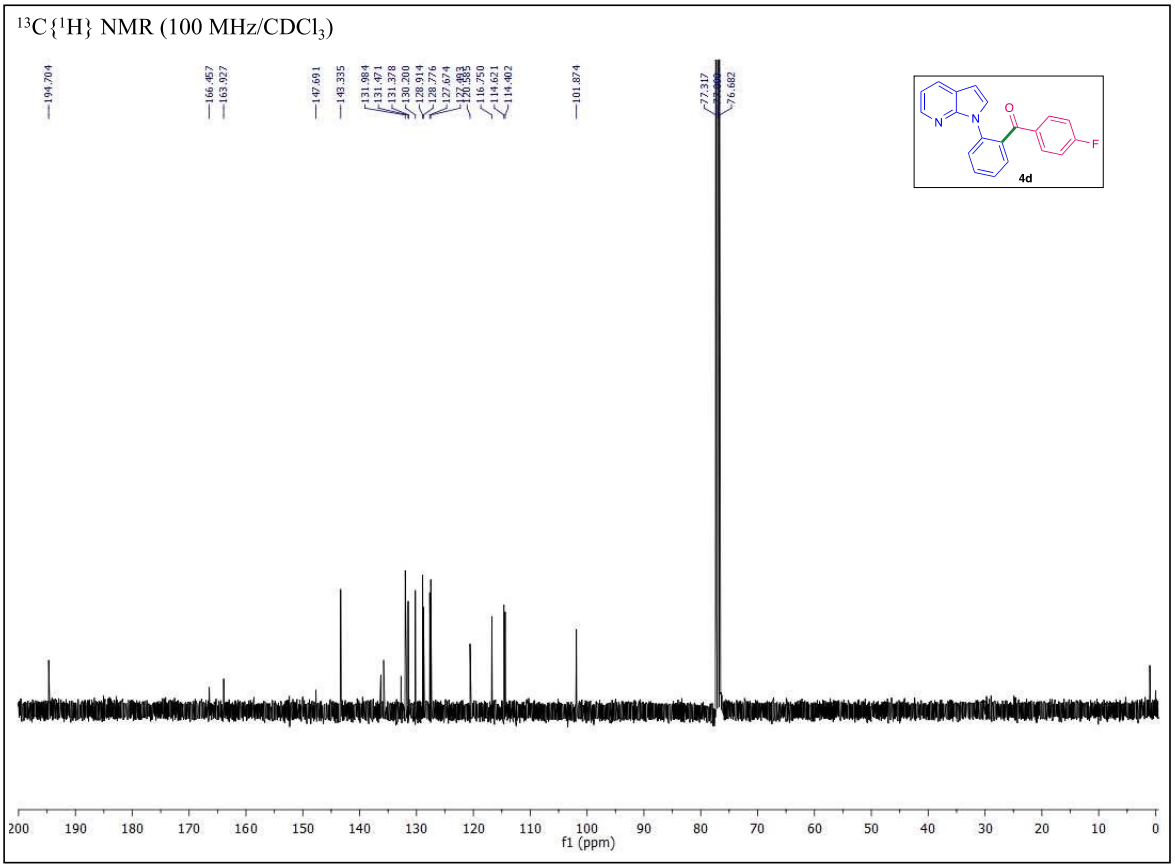
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



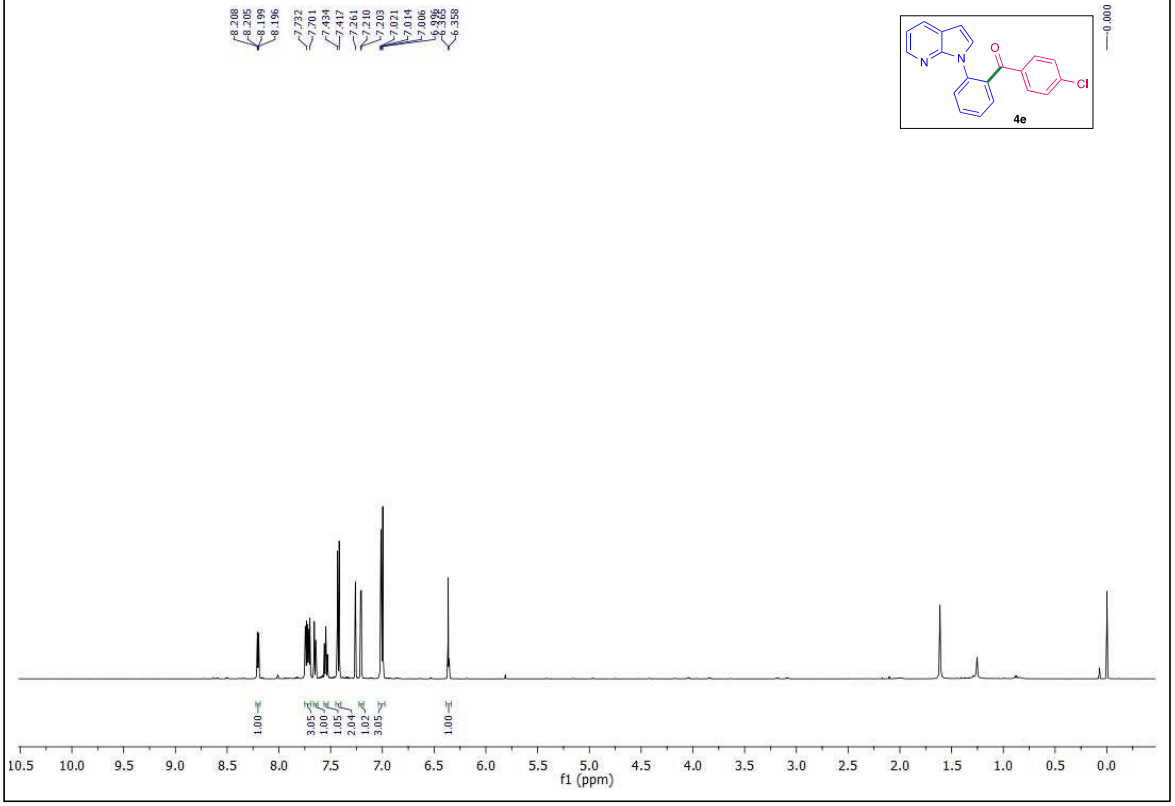
^{1}H NMR (500MHz/$CDCl_3$)



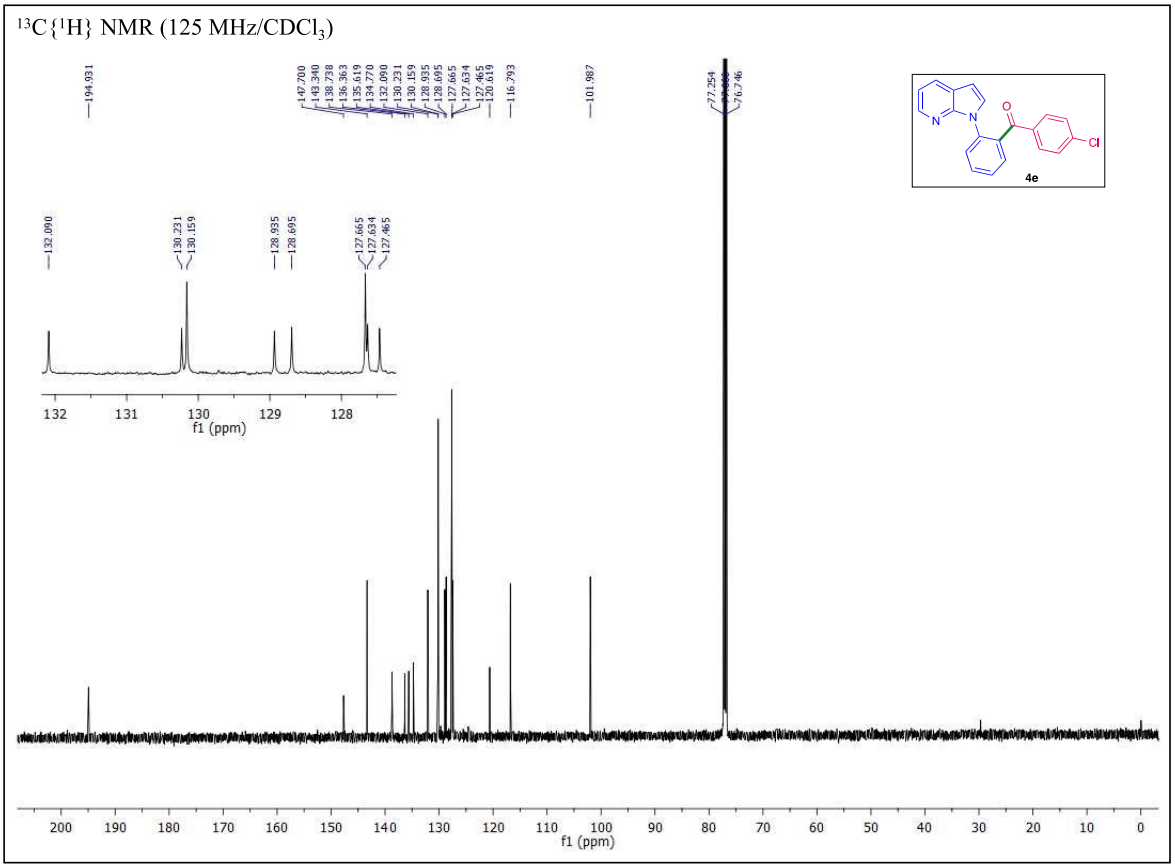
^{13}C{^{1}H} NMR (100 MHz/$CDCl_3$)



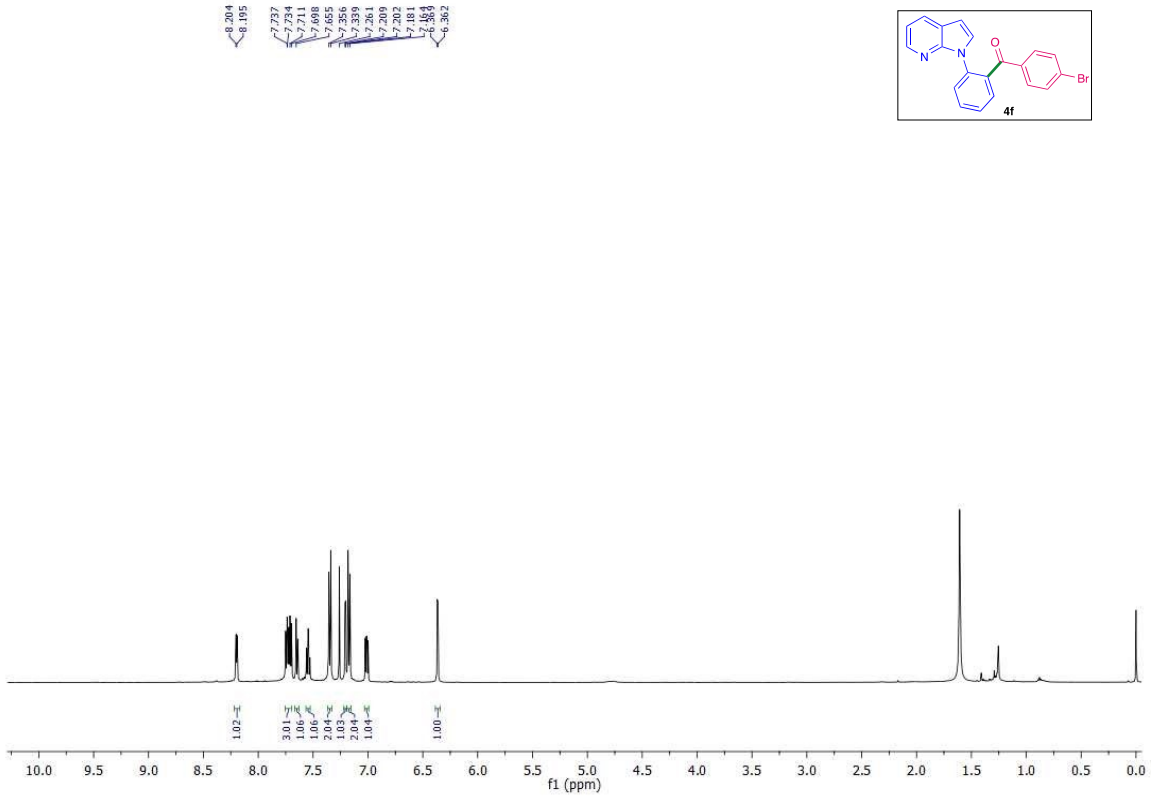
^{1}H NMR (500MHz/$CDCl_3$)



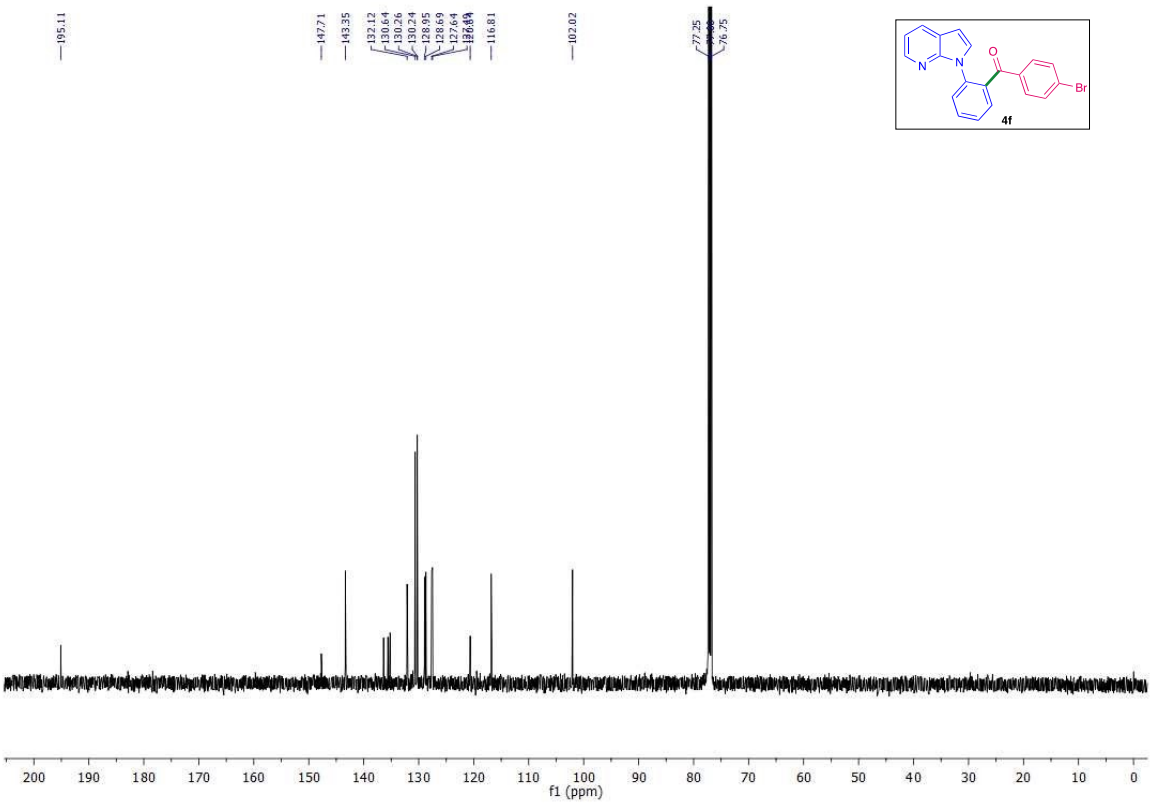
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



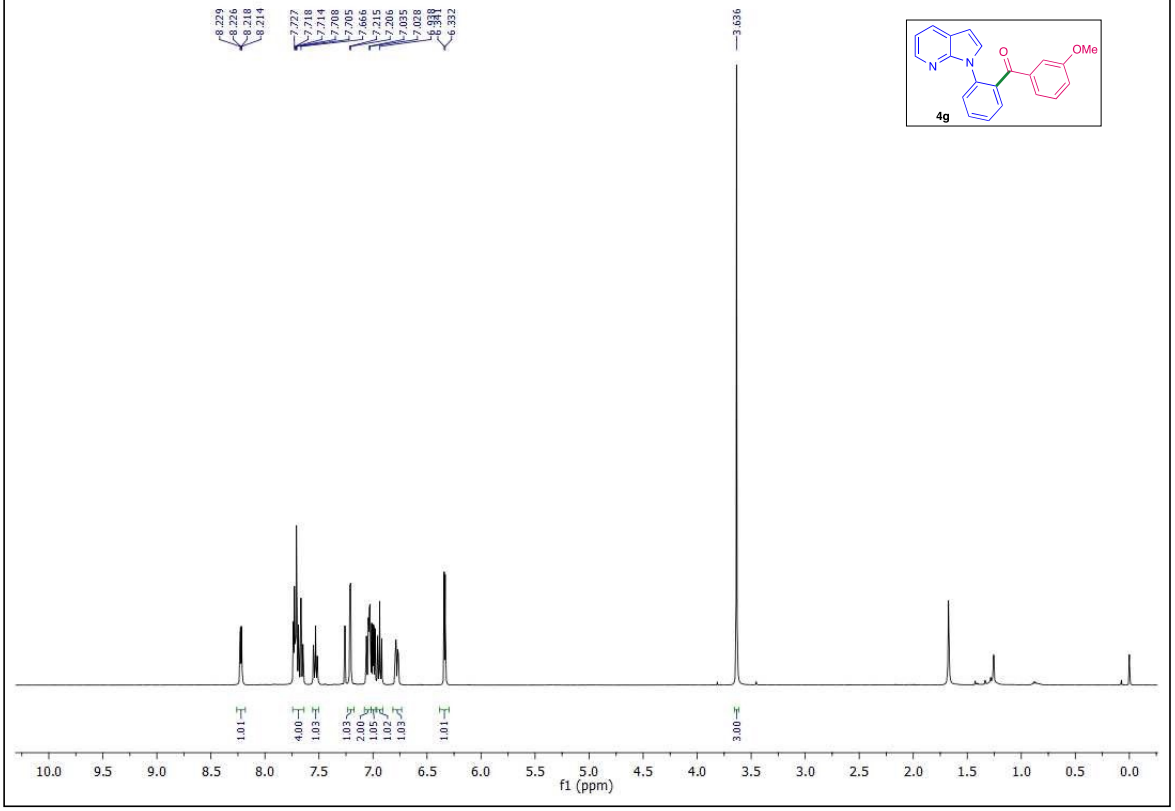
^{1}H NMR (500 MHz/$CDCl_3$)



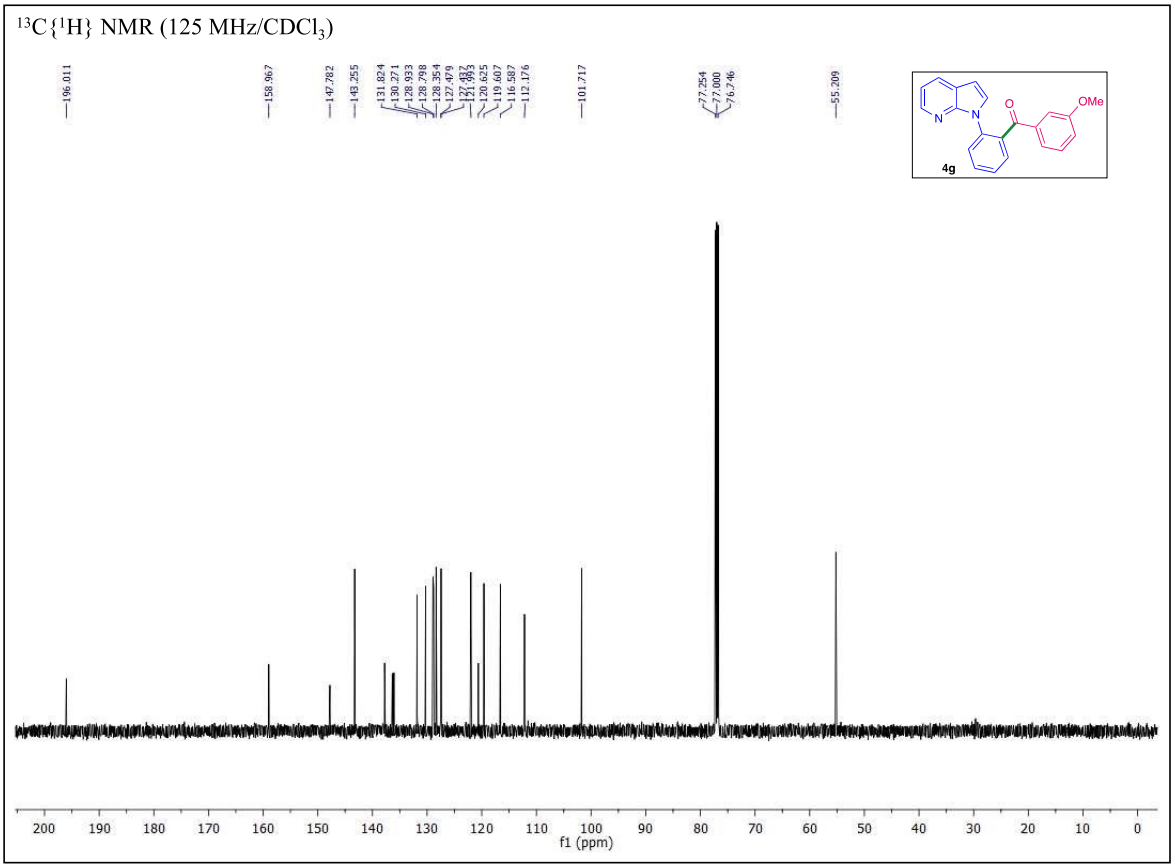
^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



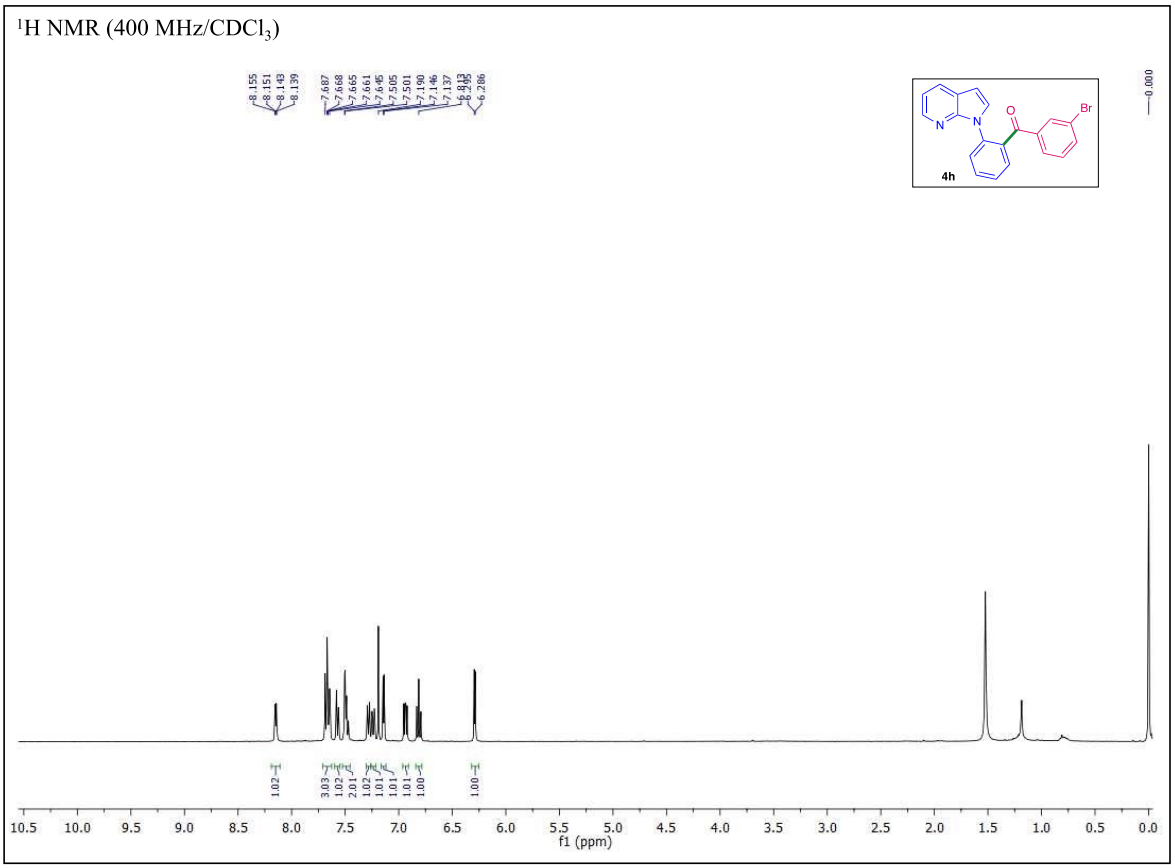
^{1}H NMR (400 MHz/$CDCl_3$)



^{13}C{^{1}H} NMR (125 MHz/$CDCl_3$)



^{1}H NMR (400 MHz/$CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (125 MHz/$CDCl_3$)