Electronic Supplementary Material (ESI) for Chemical Communications.

A solvent controlled regioselective synthesis of 2- and 4-substituted α-carbolines under palladium catalysis

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1. **General Information:** All solvents were distilled prior to use. Petroleum ether refers to fraction boiling in the range 60−80 °C. Dichloromethane was dried over phosphorous pentoxide, distilled, and stored over 3 Å molecular sieves in a sealed container. 1,4-Dioxane was distilled over sodium and benzophenone. Commercial grade dry DMF (Dimethylformamide), DMA (Dimethylacetamide), NMA (*N*-Methylacetamide) and DME (1,2-Dimethoxyethane) were used as a solvent. All the reactions were carried out under an argon atmosphere and anhydrous conditions unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum TLC sheets. Visualization of the developed chromatogram was performed by UV absorbance or iodine exposure. For purification, column chromatography was performed using 100−200 mesh silica gel. ^{1}H and ^{13}C NMR spectra were recorded on a 300, 400 or 600 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are given from TMS (δ = 0.00) in parts per million (ppm) with reference to the residual nuclei of the deuterated solvent used [$CDCl_3$: ^{1}H NMR δ = 7.260 ppm (s); ^{13}C NMR δ = 77.160 ppm]. Coupling constants (*J*) are expressed in hertz (Hz), and spin multiplicities are given as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet) and m (multiplet). All ^{13}C NMR spectra were obtained with complete proton decoupling. Mass spectra were performed using ESI-TOF or EI mode. Some compounds were purified using preparative TLC. Reactions that require heating, oil bath containing of silicon oil is use as a heat source. The starting materials **7** are commercially available (except **7d**, **7h** and **7n**).

2. Structures of α-carbolines (1) and few biologically active α-carbolines 2-5 (as reported in the introduction of the manuscript).

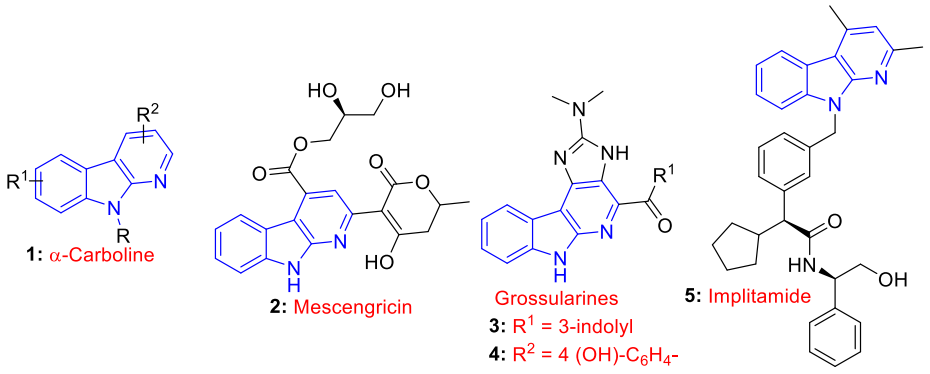
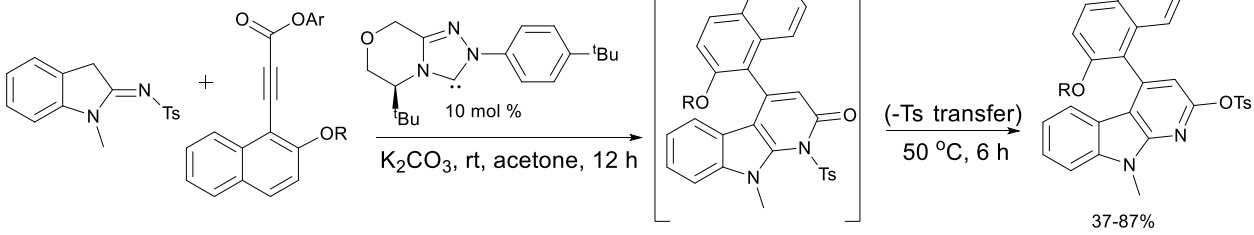


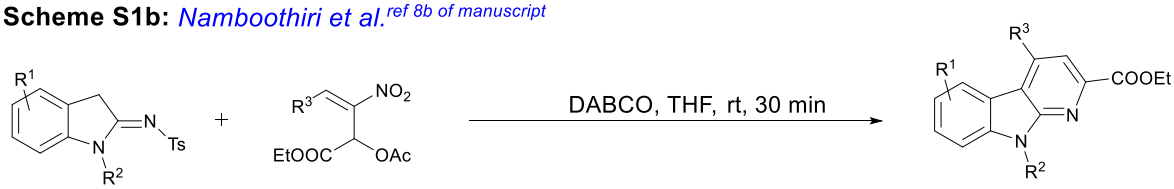
Figure S1. Few biologically active α-carbolines **2-5**.

3. Previous works on the synthesis of α-carbolines using tosyliminoindoline as substrate (as reported in the introduction of the manuscript)

Scheme S1a: *Du et al.*[ref 8a of manuscript]



Scheme S1b: *Namboothiri et al.*[ref 8b of manuscript]



Scheme S1: Previous works

4. X-Ray Crystallographic Information of products 1bn and 1bu:

Single crystal of products **1bn** and **1bu** were obtained through slow evaporation (at room temperature) of a solution in dichloromethane-petroleum ether. A single crystal of **1bn** and **1bu** were attached to a glass fiber with epoxy glue and transferred to X-ray diffractometer, equipped with a graphite-monochromator. Diffraction data of products **1bn** and **1bu** were measured with MoKα radiation (λ = 1.54178 Å) at 106K. The structure was solved by direct methods using the SHELXS-97 program.[1] Refinements were carried out with a full matrix least squares method against F 2 using SHELXL-97.[2] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Important crystal data and ORTEP diagram (drawn at 50% probability level) of product **1bn** and **1bu** are given below.

5. Important crystal data of product 1bn

Empirical formula:	$C_{18}H_{13}N_3O_2$
Formula weight:	303.31
Temperature:	106.00K
Wavelength:	1.54178
Crystal system:	triclinic
Space group:	P-1
Unit cell dimensions:	a=6.9020(6), α= 66.241(4) b= 13.8797(12), β= 89.878(3) c= 13.3061(14), Ɣ= 76.826(3)
Volume:	1385.0(2) $Å^3$
Z:	4
Density (calculated):	1.455 g/cm^3
Absorption coefficient (μ):	0.795 mm^{-1}
F(000):	632.0
Theta range for data collection:	5.952-137.64
Index ranges:	$-7 \le h \le 8$, $-16 \le k \le 16$, $-19 \le l \le 19$
Reflection collected:	12890
Independent reflections:	4911 [R_{int} = 0.0536]
Completeness of theta:	95.6%
Absorption correction:	multi scan
Max. and min. transmissions:	0.753 and 0.558
Refinement method:	Full-matrix least- squares on F^2
Data/ restrains/ parameters:	4911/0/417
Goodness-of-fit on F^2:	1.141
Final R indices [I>2sigma(I)]:	R_1 = 0.0959, wR_2= 0.2987
R indices (all data):	R_1 = 0.1010, wR_2= 0.3005
Largest diff. peak and hole:	0.47 & -0.45 e $Å^{-3}$

The single crystal of compound **1bn** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **1bn** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2308710.**

6. Important crystal data of product 1bu

Empirical formula:	$C_{19}H_{16}N_2$
Formula weight:	272.34
Temperature:	106.00K
Wavelength:	1.54178
Crystal system:	monoclinic
Space group:	$P2_1/n$
Unit cell dimensions:	a=13.4739(4), α= 90 b= 7.1393(2), β= 101.5760(10) c= 14.6043(5), Y= 90
Volume:	1376.27(7)$Å^3$
Z:	4
Density (calculated):	1.314 g/cm^3
Absorption coefficient (μ):	0.600 mm^{-1}
F(000):	576.0
Theta range for data collection:	13.416-133.722
Index ranges:	-15≤ h ≤ 16, -8≤ k ≤ 8, -17≤ l ≤ 17
Reflection collected:	20579
Independent reflections:	2336 [R_{int} = 0.0648]
Completeness of theta:	95.5%
Absorption correction:	multi scan
Max. and min. transmissions:	0.753and 0.432
Refinement method:	Full-matrix least- squares on F^2
Data/ restrains/ parameters:	2336/0/193
Goodness-of-fit on F^2:	1.060
Final R indices [I>2sigma(I)]:	R_1 = 0.0424, wR_2= 0.1092
R indices (all data):	R_1 = 0.0429, wR_2= 0.1097
Largest diff. peak and hole:	0.19 & -0.20e $Å^{-3}$

The single crystal of compound **1bu** suitable for X-ray crystallographic determination was obtained by recrystallizing from a solution containing petroleum ether and dichloromethane at room temperature. The crystal data of product **1bu** has already been deposited at Cambridge Crystallographic Data Centre. The CCDC reference number is **2308711.**

7. ORTEP Diagrams of the product 1bn

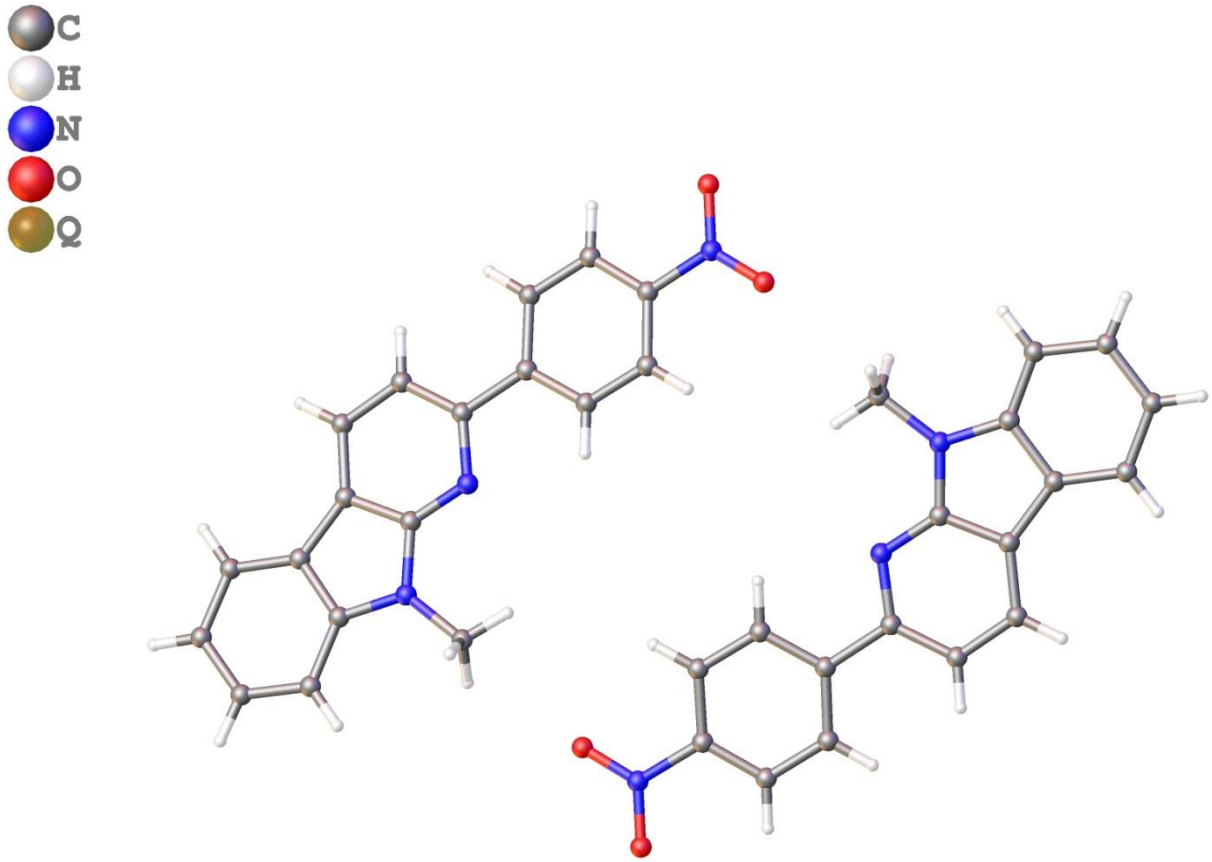


Figure S2. ORTEP Diagram (thermal ellipsoid plot) of product **1bn** (drawn at 50% probability level.

8. ORTEP Diagrams of the products 1bu

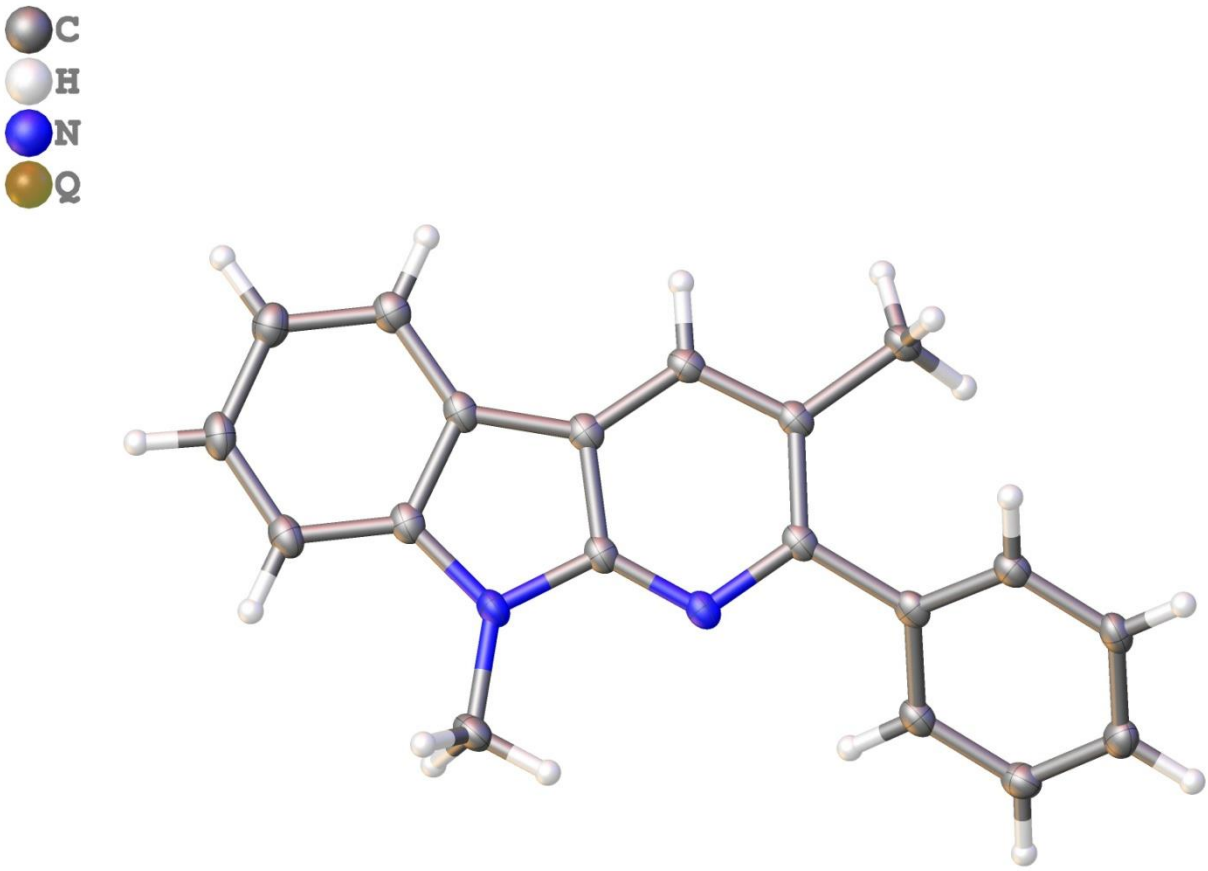
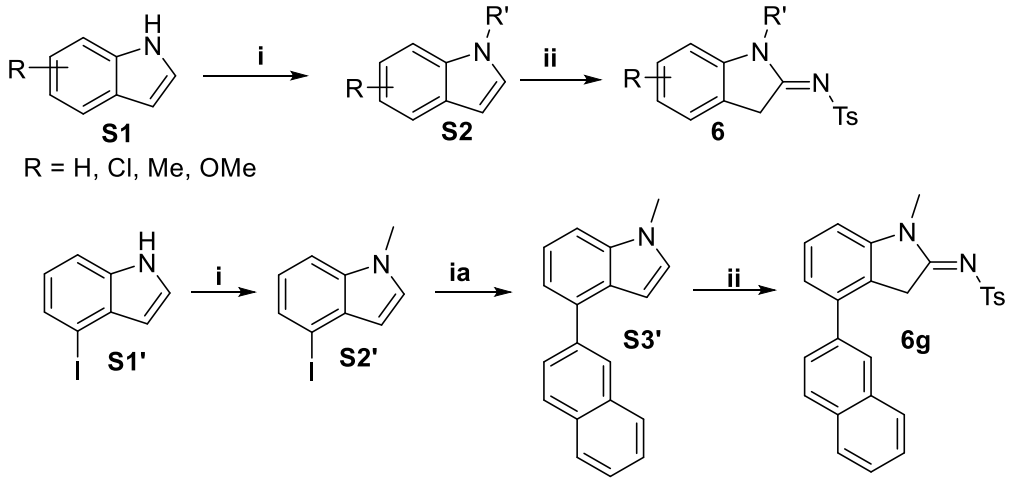


Figure S3. ORTEP Diagram (thermal ellipsoid plot) of product **1bu** (drawn at 50% probability level)

9. Schematic representation and procedure for preparation of starting materials 6:

The requisite substrates **6** were synthesized in two steps starting from commercially available indoles as shown in Scheme **S1**. Thus intermediates **S2** can be achieved by simple *N*-alkylation of indoles **S1**. Next, (*Z*)-4-Methyl-*N*-(1-methylindolin-2-ylidene)benzenesulfonamide **6** could easily be achieved by treatment of **S2** with TsN_3 in 1,4-dioxane. However, naphthyl analog **S3'** was synthesized in three steps starting from commercially available 4-iodo indole **S1'** as shown below.



Scheme S2. Synthesis of benzenesulfonamide substrates **6**. Reagent and Conditions: (i) NaH, R'I, DMF, 0 ^oC- rt, 6 h, 87-90%; (ii) TsN_3, 1,4 Dioxane, 80 ^oC, 24 h, 55-60%. (ia) 2-Naphthyl boronic acid, $Pd(PPh_3)_4$, Na_2CO_3 (2 molar solution in water), 1,4 Dioxane, 110^oC, 12 h, 65%.

10. Procedure for the preparation of starting substrate 6.

*Procedure for the synthesis[3] of 1-Methyl-1H-indole (**S2**) (of Scheme S2)*

To a well stirred solution of **S1** (4.27 mmol, 1 equiv.) in dry DMF (5 mL) NaH (6.4 mmol, 1.5 equiv.) was added into under ice-cold conditions and the stirring was continued for 20 minutes under argon atmosphere. Next, alkyl iodide (5.5 mmol, 1.3 equiv.) was added dropwise and the reaction mixture was allowed to attain room temperature over a period of 2h and the whole reaction mixture was stirred at room temperature for another 6 h. After completion (TLC) of the reaction, the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (3 x 40 mL) and brine (3 x10 mL), respectively. The organic layer was then dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) using 2-5% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product N-methyl indole **S2** in 87-90% yield.

General Procedure for the synthesis[4a] of 1-methyl-4-(naphthalen-2-yl)-1H-indole **S3'** *(Scheme S2):*

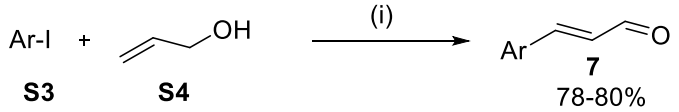
To a solution of compound **S2'** in 1,4-dioxane at room temperature was subsequently added $Pd(Ph_3P)_4$ (0.1 equiv), Na_2CO_3 (3 equiv, 2 M), and 2-naphthyl boronic acid (1.5 equiv). The resulting mixture was then heated to 110 ^oC for 12 h under argon atmosphere. After completion of the reaction (TLC) the reaction mixture was filtered through celite, solvent was removed and the crude residue obtained was purified through column chromatography using 5% EtOAc in petroleum ether (v/v) as eluent to furnish the desired compounds **S3'** with 65% yield.

*General Procedure for the synthesis[4b] of (Z)-4-methyl-N-(1-methylindolin-2-ylidene)benzenesulfonamide **6**. (Scheme S2):*

An oven-dried round-bottomed flask (25 mL) was charged with N-alkyl indole **S2** (1.53 mmol, 1 equiv.) and *p*-toluenesulfonyl azide (2.13 mmol, 1.4 equiv) in dry 1,4-dioxane (3 mL) under argon atmosphere. The mixture was heated at 80 °C for about 24 h. After the completion of the reaction (TLC), cold ethanol (25 mL) was added which led to the precipitation of product, i.e., 2-sulfonamidoindoline **6**. Then the precipitated was further purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (75:25 to 70:30) as eluent to obtain 2-sulfonamidoindole **6** in 55-60% yields.

11. Schematic representation and procedure for the preparation of starting materials 7:

The substrates **7** were synthesized in one steps starting from commercially available aryl iodide **S3** and allyl alcohol **S4** as shown in Scheme **S3**



Scheme S3. Synthesis of α, β unsaturated aldehyde substrates **7**. Reagent and Conditions: (i) $Pd(OAc)_2$, O_2, $Bu_4N^+Cl^-$, $NaHCO_3$, DMSO:DMF (1:1, v/v), 12 h.

12. Procedure for the synthesis[5a] of starting materials 7d and 7h (scheme S3):

To a well-stirred solution of aryl iodide **S3** (0.38 mmol) in a mixture of DMF and DMSO (1:1, v/v), allyl alcohol **S4** (0.57 mmol, 1.5 equiv.), $Pd(OAc)_2$ (0.076 mmol, 20 mol%), tertrabutylammonium chloride (0.38 mmol, 1 equiv.), sodium bicarbonate (0.95 mmol, 2.5 equiv.) were added successively. The whole reaction mixture was then heated at 60 ºC for overnight under oxygen atmosphere. After completion (TLC) of the reaction, the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (3 x 40 mL) and brine (3 x10 mL), respectively. The organic layer was then dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography over silica gel (100-200 mesh) to give the desired product **7**.

*Procedure for the synthesis (E)-3-(p-tolyl)acrylaldehyde (**7d**):*

A dry round-bottomed flask (10 mL) was charged with 1-iodo-4-methylbenzene (0.46 mmol, 1 equiv.) and allyl alcohol **S4** (0.64 mmol, 1.4 equiv.) in a mixture of DMSO and DMF (1:1, v/v) (2 mL) under atmospheric oxygen. Next, $Pd(OAc)_2$ (20.69 mg, 0.092 mmol), tertrabutylammonium chloride (128.0 mg, 0.46 mmol), sodium bicarbonate (96.77 mg, 1.15 mmol) were added successively and the whole reaction mixture was heated at 60 °C for 12 h. Aftercompletion of the reaction (TLC), the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (3 x 40 mL) and brine (3 x10 mL), respectively. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography over silica gel (100-200 mesh) using 5% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product (*E*)-3-(*p*-tolyl)acrylaldehyde in 80% yield.

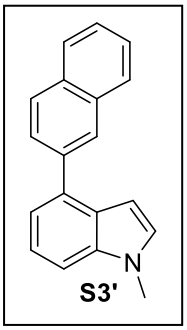
*General Procedure for the synthesis of Methyl (E)-4-(3-oxoprop-1-en-1-yl)benzoate (**7h**):*

A dry round-bottomed flask (10 mL) was charged with 1-iodo-4-methylbenzene (0.38 mmol, 1 equiv.) and allyl alcohol **S4** (0.53 mmol, 1.4 equiv.) in a mixture of DMSO and DMF (1:1, v/v) (2 mL) under atmospheric oxygen. Then, $Pd(OAc)_2$ (17.13 mg, 0.076 mmol), tertrabutylammonium chloride (122.07mg, 0.38 mmol), sodium bicarbonate (80.15 mg, 0.95 mmol) were added successively and the whole reaction mixture was heated at 60 °C for 12 h. After the completion of the reaction (TLC), the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (3 x 40 mL) and brine (3 x10 mL), respectively. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography over silica gel (100-200 mesh) using 5% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product methyl (*E*)-4-(3-oxoprop-1-en-1-yl)benzoate in 78% yield.

*General Procedure for the synthesis of acrylaldehyde (**7n**):* Acryaldehyde has been prepared from commercially available allyl alcohol following the reported[5b] oxidation protocol.

13. Spectral data of substrates S3':

1-methyl-4-(naphthalen-2-yl)-1H-indole (S3')

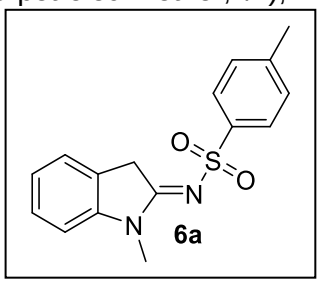


Colourless liquid (195.0 mg, 65% yield); (5% ethyl acetate-petroleum ether,v/v);^{1}H NMR ($CDCl_3$, 400 MHz) 8.17 – 8.15 (m, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.91 (tt, *J* = 6.1, 2.6 Hz, 2H), 7.87 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.38 – 7.35 (m, 2H), 7.32 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.14 (d, *J* = 3.1 Hz, 1H), 6.73 (d, *J* = 3.1 Hz, 1H), 3.87 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 138.9, 137.3, 134.6, 133.8, 132.6, 129.4, 128.3, 128.0, 127.8, 127.5, 127.4, 127.0, 126.2, 125.8, 122.0, 119.8, 108.6, 100.6, 33.2; HRMS (EI^+) m/z calculated for $C_{19}H_{15}N$ $[M]^+$ 257.1204 found 257.1203.

14. Spectral data of substrates 6:

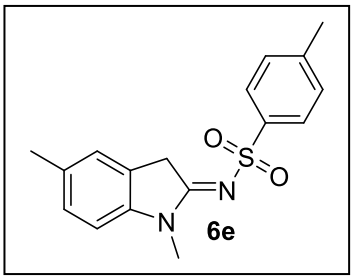
(*E*)-4-Methyl-*N*-(1-methylindolin-2-ylidene)benzenesulfonamide (6a)

Brown solid (251.90 mg, 55% yield); mp. 152-154^{o}C; (25% ethyl acetate-petroleum ether,v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.88 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.33-7.27 (m, 4H), 7.13-7.09 (m, 1H), 6.94 (d, *J* = 8 Hz ,1H), 4.21 (s, 2H), 3.35 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 169.8, 144.0, 142.8, 139.5, 129.4, 128.2, 126.8, 126.4, 124.5, 123.8, 109.3, 36.3, 28.6, 21.6; HRMS (EI$^+$) m/z calculated for $C_{16}H_{16}N_2O_2S$ $[M]^+$ 300.0932, found 300.0925



(*E*)-*N*-(1,5-dimethylindolin-2-ylidene)-4-methylbenzenesulfonamide (6e):

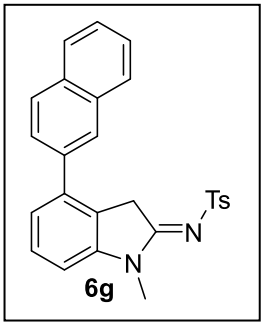
Brown solid (259.5 mg, 60% yield); mp. 177- 179 ^{o}C; (30% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.88 (d, *J* = 8, 2H), 7.28 (d, *J* = 8, 2H), 7.15 (d, *J* = 7, 1H), 7.04-6.96 (m, 2H), 4.17 (s, 2H), 3.63 (s, 3H), 2.58 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 170.6, 142.8, 139.7, 129.4, 127.0, 126.8, 126.4, 123.7, 122.4, 121.0, 115.6, 36.1, 32.2, 21.6, 19.4; HRMS (EI$^+$) m/z calculated for $C_{17}H_{18}N_2O_2S$ $[M]^+$ 314.1089, found 314.1085



The synthesis tosyliminoindolines **6b, 6c**[4e]**, 6d**, **6f, 6g** and **6h** has been prepared following the reported[4] method.

(*E*)-4-methyl-*N*-(1-methyl-4-(naphthalen-2-yl)indolin-2-ylidene)benzenesulfonamide (6g):

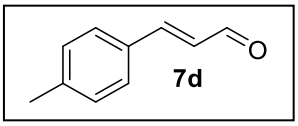
Brown solid (187.47 mg, 58% yield); (20% ethyl acetate-petroleum ether,v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.95 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.87 – 7.83 (m, 2H), 7.58 – 7.53 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.26 – 7.25 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 4.35 (s, 2H), 3.41 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 142.8, 139.5, 138.9, 136.4, 133.5, 129.4, 128.83, 128.82, 128.3, 127.9, 127.3, 126.8, 126.7, 126.6, 124.7, 124.3, 108.3, 100.0, 36.3, 28.8, 21.6; HRMS (EI$^+$) m/z calculated for $C_{26}H_{22}N_2O_2S$ $[M]^+$ 426.1402, found 426.1395.



15. Spectral data of substrates unsaturated aldehyde

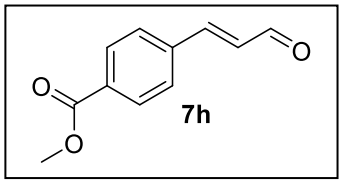
(*E*)-3-(*p*-Tolyl)acrylaldehyde (7d):

Yellow solid (53.82 mg, 80% yield); mp. 45-47 ^{o}C; (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.67 (d, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 3H), 7.25 (d, *J* = 8 Hz ,2H), 6.71-6.65 (m, 1H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 193.9, 153.07, 142.09, 131.4, 129.9, 128.6, 127.8, 21.6; HRMS (EI^{+}) m/z calculated for $C_{10}H_{10}O$ $[M]^{+}$ 146.0732, found 146.0735.



Methyl (*E*)-4-(3-oxoprop-1-en-1-yl) benzoate (7h):

White solid (56.0 mg, 78% yield); mp. 100-102^{o}C; (10% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H), 9.74 (d, *J* = 7.6 Hz ,1H), 8.08 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.63(dt, *J* = 8, 2 Hz, 2H), 7.50 (d, *J* = 16 Hz ,1H), 6.80-6.75 (m, 1H), 3.94(s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 193.4, 166.4, 151.0, 138.2, 132.3, 130.5, 130.4, 128.4, 52.5; HRMS (EI^{+}) m/z calculated for $C_{11}H_{10}O_3$ $[M]^{+}$ 190.0630, found 190.0629.



16. General Procedure for the Synthesis of Products 1a:

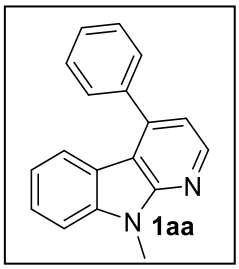
To a well-stirred solution of tosyliminoindoline **6a** (0.067 mmol, 1 equiv.) in dry DMF (3.0 mL), sodium acetate (21.86 mg, 4 equiv.) was added and the whole reaction mixture was heated at 80 ^{o}C for 10 min under argon atmosphere. Next, Pd(bpy)Cl_2 (2.23 mg, 0.006 mmol, 10 mol %) and α,β-unsaturated aldehyde **7** (0.08 mmol, 1.2 equiv.) were added successively and the whole reaction mixture was heated at 80 ^{o}C for 10 h until completion of the reaction (TLC). Thereafter, the reaction mixture was quenched by water (10 mL) and extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified through silica gel (100-200 mesh) column chromatography using 5-10% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product **1a** in 59-79% yield.

17. Gram scale synthesis of the Product 1aa:

To a well-stirred solution of tosyliminoindoline **6a** (1g, 3.33 mmol, 1 equiv.) in dry DMF (25.0 mL), sodium acetate (1.120 g, 4 equiv.) was added, and the whole reaction mixture was heated at 80 ^{o}C for 10 min under argon atmosphere. Next, Pd(bpy)Cl_2 (111 mg, 0.33 mmol, 10 mol %) and α,β-unsaturated aldehyde **7a** (4.00 mmol, 1.2 equiv.) were added successively. The whole reaction mixture was then heated at 80 ^{o}C for 10 h until completion of the reaction (TLC). Thereafter, the reaction mixture was diluted by water (50 mL) and extracted with ethyl acetate (3x20 mL). The combined organic extracts were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified through silica gel (100-200 mesh) column chromatography using 5% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product **1aa** (0.56 gm) in 65% yield.

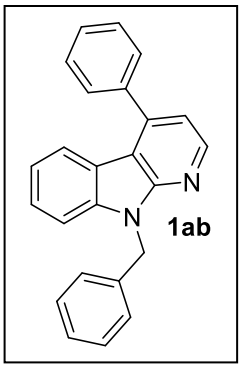
18. Spectral data of products 1aa-1ap:

9-Methyl-4-phenyl-9*H*-pyrido[2,3-*b*]indole (1aa):



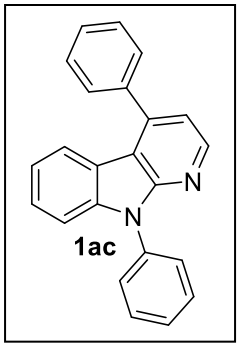
Orange viscous liquid (9.67 mg, 74% yield); (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.52 (d, *J* = 7.6 Hz, 1H), 7.67 (dt, *J* = 8, 1.2 Hz, 3H), 7.59-7.52 (m, 3H), 7.49-7.45 (m, 2H),), 7.08 (d, *J* = 5.2 Hz, 2H), 4.02 (s, 3H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 145.6, 145.4, 140.5, 139.1, 128.8, 128.7, 126.7, 122.8, 120.2, 119.6, 116.4 109.0, 28.0; HRMS (EI$^+$) m/z calculated for $C_{18}H_{14}N_2$ [M]$^+$ 258.1157, found 258.1152

9-benzyl-4-phenyl-9H-pyrido[2,3-b]indole (1ab):



White solid (12.61 mg, 71% yield); mp. 116-118 ^{o}C; (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.58 (d, *J* = 4.6 Hz, 1H), 8.51 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.38 (q, *J* = 7.0 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.14 (dd, *J* = 9.1, 5.8 Hz, 2H), 7.10 (t, *J* = 7.1 Hz, 2H), 6.55 (d, *J* = 7.2 Hz, 2H), 5.17 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 142.7, 141.4, 137.6, 137.1, 131.5, 130.1, 129.5, 129.2, 128.32, 128.29, 128.2, 127.1, 122.5, 121.2, 120.6, 109.9, 48.08; HRMS (EI$^+$) m/z calculated for $C_{24}H_{18}N_2$ [M]$^+$ 334.1470, found 334.1477.

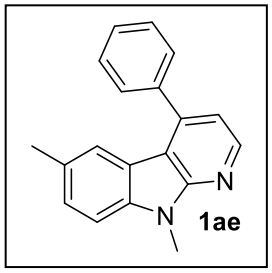
4,9-diphenyl-9H-pyrido[2,3-b]indole (1ac):



Brown solid (11.49 mg, 65% yield); mp. 78-80 ^{o}C; (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H δ 8.58 – 8.51 (m, 1H), 8.18 – 8.13 (m, 2H), 7.80 – 7.74 (m, 2H), 7.64 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.55 – 7.50 (m, 3H), 7.51 – 7.49 (m, 2H), 7.43 – 7.37 (m, 2H).^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 151.0, 142.5, 142.0, 140.6, 137.2, 133.6, 130.2, 128.8, 128.2, 128.0, 127.8, 127.2, 126.9, 123.0, 121.4, 118.0, 117.4, 110.2; HRMS (EI$^+$) m/z calculated for $C_{23}H_{16}N_2$ [M]$^+$ 320.1313, found 320.1303.

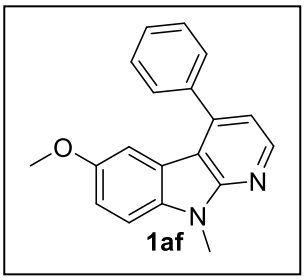
6,9-dimethyl-4-phenyl-9H-pyrido[2,3-b]indole (1ae):

Orange viscous liquid (14.03 mg, 81% yield); (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.37 – 8.32 (m, 1H), 8.18 – 8.13 (m, 2H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.50 (ddd, *J* = 7.9, 6.7, 1.1 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.27 (dt, *J* = 6.3, 0.9 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.14 (s, 3H), 2.88 (s, 3H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 149.9, 142.0, 141.1, 140.7, 134.3, 130.8, 128.8, 128.0, 127.1, 123.4, 120.9, 119.3, 117.7, 116.1, 32.5, 20.4; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2$ [M]$^+$ 272.1313, found 272.1317.



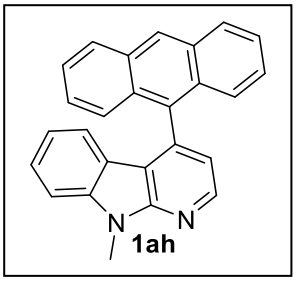
6-methoxy-9-methyl-4-phenyl-9H-pyrido[2,3-b]indole (1af):

Yellow viscous liquid (14.66 mg, 84% yield); (7% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.49 (d, *J* = 5.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 3H), 7.56 – 7.51 (m, 3H), 7.34 (s, 1H), 7.14 (d, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 3.98 (s, 3H), 3.67 (s, 3H).;^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.7, 145.8, 139.0, 135.4, 132.2, 128.9, 128.7, 120.5, 115.9, 115.5, 109.6, 106.3, 100.0, 55.9, 28.0; 145.6, HRMS (EI$^+$) m/z calculated for $C_{18}H_{16}N_2O$ [M]$^+$ 288.1263, found 288.1256.



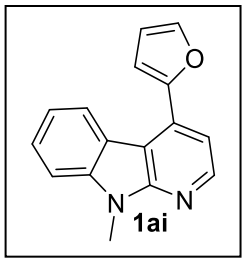
4-(Anthracen-9-yl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1ah):

Yellow solid (16.94 mg, 71% yield); mp. 182-184^{o}C; (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.57 (s, 1H), 8.53 (d, *J* = 8 Hz, 1H), 8.21(d, *J* = 7.6 Hz, 1H) 8.08(d, *J* = 7.6 Hz, 2H), 7.71(d, *J* = 8.8 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8 Hz, 2H), 7.41-7.35 (m, 4H), 3.99 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 154.5, 152.0, 140.7, 136.1, 131.6, 130.5, 128.5, 128.2, 127.5, 126.9, 126.6, 125.7, 125.2, 121.1, 120.4, 120.1, 118.4, 114.71, 114.70, 109.3, 28.1; HRMS (EI$^+$) m/z calculated for $C_{26}H_{18}N_2$ [M]$^+$ 358.1470, found 358.1467.



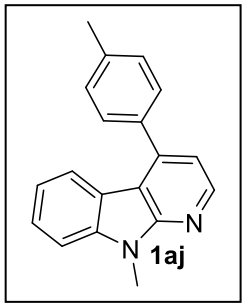
4-(Furan-2-yl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1ai):

Brown solid (9.75 mg, 60% yield); mp.110-112°C; (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.32 (d, *J* = 8.0 Hz, 1H), 8.05 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.54 – 7.50 (m, 1H), 7.46 – 7.43 (m, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.16 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.57 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.00 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 154.9, 146.0, 143.2, 128.65, 128.64, 126.6, 120.8, 120.0, 114.8, 112.2, 110.6, 109.1, 108.3, 27.7; HRMS (EI$^+$) m/z calculated for $C_{16}H_{12}N_2O$ $[M]^+$ 248.0950, found 248.0924.



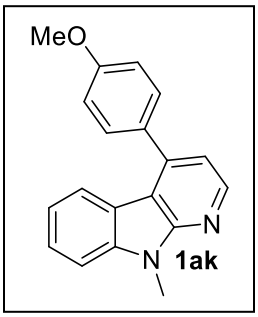
9-Methyl-4-(*p*-tolyl)-9*H*-pyrido[2,3-*b*]indole (1aj):

Brown solid (12.69 mg, 70% yield); mp. 132-134°C; (6% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 8.53 (d, *J* = 8.0 Hz, 1H), 8.17 – 8.15 (m, 1H), 8.15 – 8.11 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.49 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.51-7.47 (m, 1H), 3.94 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 145.4, 140.5, 138.6, 136.3, 129.5, 128.7, 126.7, 122.9, 120.3, 119.6, 116.5, 109.0, 29.8, 21.5; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2$ $[M]^+$ 272.1313, found 272.1323



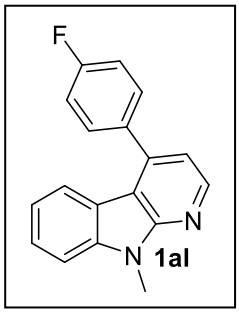
4-(4-Methoxyphenyl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1ak):

White solid (12.86 mg, 67% yield); mp. 128-130°C; (8% ethyl acetate-petroleum ether, v/v); ^{1}H NMR (DMSO-d_6, 600 MHz) δ_H 8.51 (d, *J* = 8.1 Hz, 1H), 8.21 – 8.16 (m, 2H), 8.14 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.50-7.46 (m, 1H), 7.25-7.21 (m, 1H), 7.08 – 7.02 (m, 2H), 3.93 (s, 3H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (DMSO-d_6, 150 MHz) δ_C 160.5, 153.2, 151.7, 140.7, 132.3, 129.8, 128.6, 121.5, 120.3, 114.6, 113.8, 111.6, 110.1, 99.9, 55.7, 27.9; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2O$ $[M]^+$ 288.1263, found 288.1250.



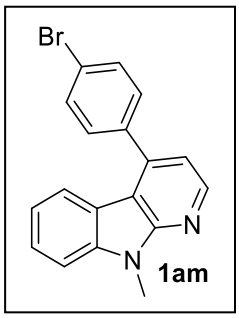
4-(4-Fluorophenyl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1al):

Yellow solid (13.80 mg, 75% yield); mp.94-96^{o}C; (10% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.52 (d, J = 4.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.64-7.63(m, 1H), 7.50-7.47(m, 2H), 7.29-7.27 (m, 1H), 7.25-7.22 (m, 1H), 7.12-7.07 (m, 1H), 7.04 (d, J = 5.2 Hz, 1H), 4.01 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 163.1 (d, $J_{C\text{-}F}$ = 247.0 Hz), 152.3, 145.8, 144.2, 140.5, 135.1 (d, $J_{C\text{-}F}$ = 2 Hz), 130.6 (d, $J_{C\text{-}F}$ = 8 Hz), 126.8, 122.6, 119.7, 116.3, 115.9 (d, $J_{C\text{-}F}$ = 22 Hz), 109.1, 100.0, 27.9;^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ – 113.09 HRMS (EI^{+}) m/z calculated for $C_{18}H_{13}N_2F$ $[M]^{+}$ 276.1063, found 276.1071.



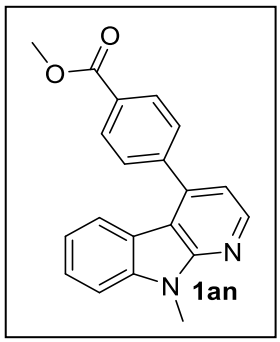
4-(4-Bromophenyl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1am):

Yellow solid(15.68 mg, 70% yield); mp. 118-120^{o}C; (8% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.53 (d, J = 5.2 Hz, 1H), 7.71 (dt, J = 8.8, 2 Hz, 2H), 7.66 (dt, J = 7.6, 0.8 Hz, 1H), 7.55 (dt, J = 8.4, 2 Hz, 2H), 7.52-7.48 (m, 2H), 7.13-7.09 (m 1H), 7.05 (d, J = 4.8 Hz, 1H), 4.03 (s, 3H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 149.7, 149.5, 139.3, 132.1, 130.5, 128.9, 127.1, 122.7, 119.9, 116.1, 113.8, 112.4, 109.2, 100.4, 29.8; HRMS (EI^{+}) m/z calculated for $C_{18}H_{13}N_2Br$ $[M]^{+}$ 336.0262, found 336.0253.



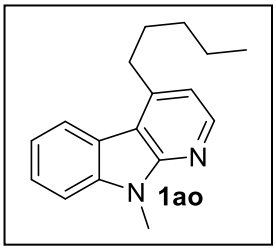
Methyl 4-(9-methyl-9*H*-pyrido[2,3-*b*]indol-4-yl)benzoate (1an):

Pale yellow solid (16.64 mg, 79% yield); mp. 96-98^{o}C; (10% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.54 (d, J = 5.2 Hz, 1H), 8.24 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.52-7.46 (m, 2H), 7.08-7.05 (m, 2H), 4.02 (s, 3H), 4.00 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 167.0, 152.2, 145.8, 144.05, 143.8, 140.6, 130.4, 130.1, 128.9, 127.0, 122.7, 119.9, 119.8, 116.0, 109.2, 52.4, 27.9; HRMS (EI^{+}) m/z calculated for $C_{20}H_{16}N_2O_2$ $[M]^{+}$ 316.1212, found 316.1214.



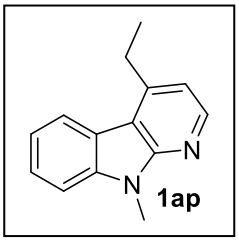
9-Methyl-4-pentyl-9*H*-pyrido[2,3-*b*]indole (1ao):

Pale yellow liquid (12.05 mg, 68% yield); (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.22 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.44-7.42 (m, 1H), 7.29-7.28 (m, 1H), 7.03 (d, *J* = 8 Hz, 1H), 3.98 (s, 3H), 2.96(t, *J* = 7.6 Hz, 2H), 1.87-1.80(m, 2H), 1.42-1.38(m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 149.3, 147.3, 140.6, 139.2, 127.5, 125.3, 119.6, 113.2, 109.1, 108.1, 30.8, 29.1, 28.8, 21.7, 13.2 ; HRMS (EI$^+$) m/z calculated for $C_{17}H_{20}N_2$ $[M]^+$ 252.1626, found 252.1637.



4-Ethyl-9-methyl-9*H*-pyrido[2,3-*b*]indole (1ap):

Pale yellow liquid (8.68 mg, 62% yield); (3% ethyl acetate-petroleum ether, v/v); δ_H 8.22 (d, *J* = 7.6 Hz, 1H), 8.04-7.995 (m, 2H), 7.49-7.47 (m, 1H), 7.44-7.42 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 2.98 (q, *J* = 7.6, 2H), 1.40 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 140.5, 140.3 126.1, 125.0 120.6, 119.7, 113.5, 109.0, 100.0, 29.8, 22.8, 14.5; HRMS (EI$^+$) m/z calculated for $C_{14}H_{14}N_2$ $[M]^+$ 210.1157, found 210.1154



19. General Procedure for the Synthesis of Products 1b:

To a well-stirred solution of tosyliminoindoline **6** (0.067 mmol, 1 equiv.) in dry NMA (3.0 mL), sodium acetate (21.86 mg, 4 equiv.) was added and the whole reaction mixture was heated at 80 ^{o}C for 10 min under argon atmosphere. Next, Pd(bpy)Cl_2 (2.23 mg, 0.0067 mmol, 10 mol %) and α,β unsaturated aldehyde **7** (0.08 mmol, 1.2 equiv.) were added successively and the whole reaction mixture was heated at 80 ^{o}C for 10 h until completion of the reaction (TLC). Thereafter, the reaction mixture was quenched by water (10 mL) and extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified through silica gel (100-200 mesh) column chromatography using 1-12% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product **1b** in 53-88% yield.

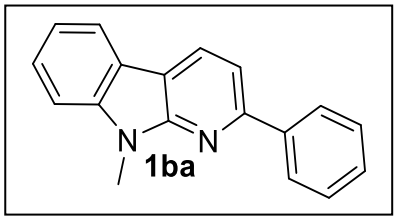
20. Gram scale synthesis of the Product 1ba:

To a well-stirred solution of tosyliminoindoline **6a** (1g, 3.33 mmol, 1 equiv.) in dry NMA (25.0 mL), sodium acetate (1.120 g, 4 equiv.) was added and the whole reaction mixture was heated at 80 ^{o}C for 10 min under argon atmosphere. Next, Pd(bpy)Cl_2 (111 mg, 0.33 mmol, 10 mol %) and α,β-unsaturated aldehyde **7a** (4.00 mmol, 1.2 equiv.) were added successively and the whole reaction mixture was heated at 80 ^{o}C for 10 h until completion of the reaction (TLC). Thereafter, the reaction mixture was quenched by water (50 mL) and extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified through silica gel (100-200 mesh) column chromatography using 5% ethyl acetate-petroleum ether (v/v) as eluent to afford the desired product **1ba** (0.60 g) in 70% yield.

21. spectral data of products 1ba-1bw:

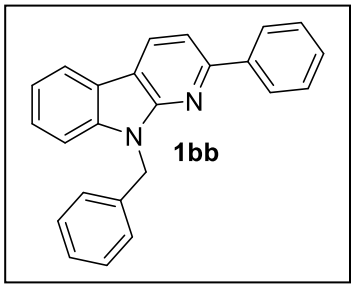
9-methyl-2-phenyl-9*H*-pyrido[2,3-*b*]indole (1ba):

Pale yellow liquid (13.07 mg, 76% yield); (1% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.36 (d, *J* = 7.6 Hz, 1H), 8.22-8.19 (m, 2H), 8.08 (dt, *J* = 8, 1.2 Hz, 1H), 7.66 (d, *J* = 8 Hz, 1H), 7.53-7.48 (m, 4H), 7.44-7.39 (m, 1H),), 7.31-7.27 (m, 1H), 4.04 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 154.1, 140.9, 140.3, 130.6, 128.8, 128.7, 127.3, 126.6, 121.0, 119.9, 114.6, 112.2, 109.1, 100.0, 27.7 HRMS (EI$^+$) m/z calculated for $C_{18}H_{14}N_2$ [M]$^+$ 258.1157, found 258.1143.



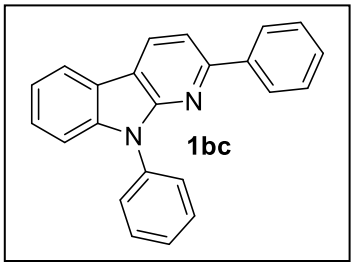
9-benzyl-2-phenyl-9H-pyrido[2,3-b]indole (1bb):

Yellow viscous liquid (13.85 mg, 78% yield); (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.39 (d, *J* = 8.0 Hz, 1H), 8.23 – 8.20 (m, 2H), 8.08 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.44 – 7.40 (m, 2H), 7.39 – 7.34 (m, 3H), 7.31 – 7.26 (m, 3H), 7.25 – 7.23 (m, 1H), 5.79 (s, 2H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 154.1, 152.0, 140.1, 137.8, 128.84, 128.82, 128.77, 127.5, 127.2, 126.6, 121.0, 120.9, 120.1, 114.6, 112.5, 110.0, 45.1; HRMS (EI$^+$) m/z calculated for $C_{24}H_{18}N_2$ [M]$^+$ 334.1470, found 334.1471.



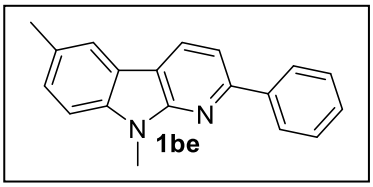
2,9-diphenyl-9H-pyrido[2,3-b]indole(1bc):

Brown solid (10.96 mg, 62% yield); mp. 113-115 ^{o}C; (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.43 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 6.9 Hz, 3H), 7.77 (dd, *J* = 9.9, 8.2 Hz, 3H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.46 (q, *J* = 7.7 Hz, 4H), 7.39 – 7.33 (m, 2H).;^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 151.2, 136.3, 133.0, 132.2, 131.8, 129.4, 128.9, 128.8, 127.4, 127.3, 127.2, 126.8, 126.6, 126.2, 125.9, 121.0, 102.9, 100.0; HRMS (EI$^+$) m/z calculated for $C_{23}H_{16}N_2$ [M]$^+$ 320.1313, found 320.1324.



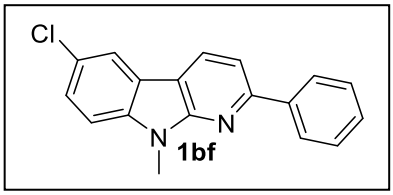
6,9-dimethyl-2-phenyl-9H-pyrido[2,3-b]indole (1be):

Orange liquid (10.96 mg, 76% yield); (1% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.32 (d, *J* = 8 Hz, 1H), 8.21-8.19 (m, 2H), 7.93-7.90 (m, 1H), 7.64 (d, *J* = 8 Hz, 1H), 7.52-7.48 (m, 2H), 7.43-7.39 (m, 2H), 7.17-7.15 (m, 1H), 4.34 (s, 3H), 2.90 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.8, 140.3, 139.6, 130.4, 129.5, 128.8, 128.6, 128.4, 127.2, 121.2, 119.9, 118.8, 114.7, 112.2, 30.7, 20.1; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2$ [M]$^+$ 272.1313, found 272.1311.



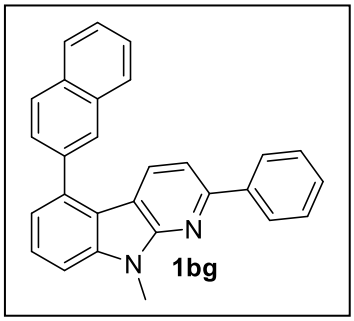
6-chloro-9-methyl-2-phenyl-9H-pyrido[2,3-b]indole (1bf):

Yellow viscous liquid (11.18 mg, 64% yield); (5% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.15-8.12 (m, 2H), 7.87-7.84 (m, 1H), 7.79-7.77 (m, 1H), 7.54-7.50 (m, 4H), 7.43-7.41 (m, 1H), 7.38-7.35 (m, 1H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 141.5, 140.6, 139.0, 135.2, 134.4, 129.2, 128.0, 127.9, 127.8, 125.8, 122.9, 120.6, 114.2, 110.0, 29.3; HRMS (EI$^+$) m/z calculated for $C_{18}H_{13}ClN_2$ [M]$^+$ 292.0767, found 292.0766



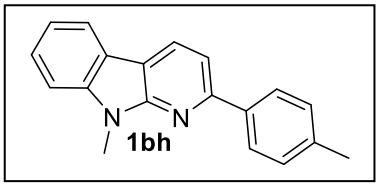
9-methyl-5-(naphthalen-2-yl)-2-phenyl-9H-pyrido[2,3-b]indole (**1bg):**

Colourless viscous liquid (10.12 mg, 60% yield);(2% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.16 – 8.11 (m, 3H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (dd, *J* = 5.4, 4.1 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.84 – 7.79 (m, 2H), 7.64 – 7.56 (m, 3H), 7.52 – 7.46 (m, 3H), 7.41 – 7.37 (m, 2H), 7.29 (dd, *J* = 7.4, 1.0 Hz, 1H), 4.10 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.8, 141.3, 140.1, 138.5, 138.0, 133.7, 133.0, 130.5, 128.8, 128.7, 128.3, 128.2, 128.0, 127.8, 127.6, 127.2, 126.5, 126.3, 121.6, 118.4, 114.4, 111.9, 108.2, 100.0, 27.8; HRMS (EI$^+$) m/z calculated for $C_{28}H_{20}N_2$ [M]$^+$ 384.1626, found 384.1625.



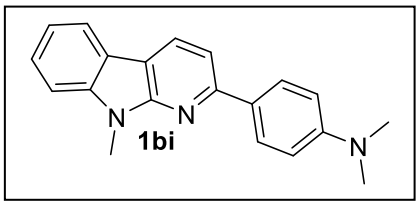
9-Methyl-2-(*p*-tolyl)-9*H*-pyrido[2,3-*b*]indole (1bh):

White solid (13.23 mg, 73% yield); mp. 118-120°C; (2% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.34 (d, *J* = 5.2 Hz, 1H), 8.10 (d, *J* = 5.2 Hz, 2H), 8.07 (d, *J* = 5.2 Hz, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.52 (t, *J* = 4.8 Hz, 1H), 7.47-7.45 (m, 1H), 7.32-7.27 (m, 3H), 4.03 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100MHz) δ_C 154.1, 140.8, 138.7, 137.49, 129.5, 128.7, 127.1, 126.5, 120.9, 120.6, 119.8, 114.4, 111.9, 109.1, 27.7, 21.4; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2$ $[M]^+$ 272.1313, found 272.1315.



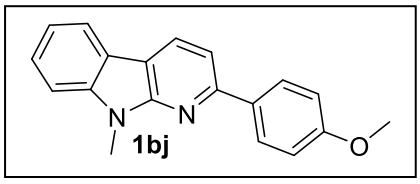
***N,N*-Dimethyl-4-(9-methyl-9*H*-pyrido[2,3-*b*]indol-2-yl)aniline (1bi):**

White powder (13.64 mg, 68% yield); mp. 105-107°C; (6%ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.28 (d, *J* = 8 Hz, 1H), 8.12 (dt, *J* = 9.2, 2.8 Hz, 2H), 8.03 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.57(d, *J* = 8 Hz, 1H), 7.49-7.47 (m, 1H), 7.45-7.42 (m, 1H), 7.28-7.262 (m, 1H), 6.85 (dt, *J* = 8.8, 2.8 1 Hz, 2H), 4.02 (s, 3H), 3.04 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 152.2, 148.5, 140.6, 130.4, 128.6, 128.1, 126.0, 120.8, 120.6, 119.6, 113.3, 111.0, 109.0, 40.7, 27.6.; HRMS (EI$^+$) m/z calculated for $C_{20}H_{19}N_3$ $[M]^+$ 301.1579, found 301.1584



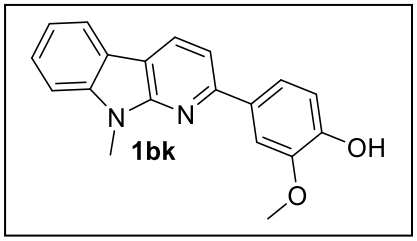
2-(4-Methoxyphenyl)-9-methyl-9*H*-pyrido[2,3-*b*]indole (1bj):

Yellowish white solid (13.82 mg, 72% yield); mp. 136-138°C; (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.32 (d, *J* = 8 Hz, 1H), 8.15 (dt, *J* = 8.8, 2 Hz, 2H), 8.07-8.04 (m, 1H), 7.58 (d, *J* = 8 Hz, 1H), 7.54-7.49 (m, 1H), 7.46-7.44 (m, 1H), 7.30-7.26 (m, 1H), 7.04 (dt, *J* = 8.8, 2 Hz, 2H), 4.03 (s, 3H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ_C 160.4, 153.8, 140.7, 132.8, 128.8, 128.5, 126.4, 120.8, 120.6, 119.8, 114.2, 114.1, 111.5, 109.1, 55.5, 27.7 ; HRMS (EI$^+$) m/z calculated for $C_{19}H_{16}N_2O$ $[M]^+$ 288.1263, found 288.1250.



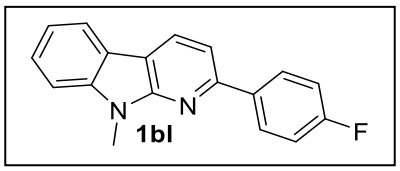
2-Methoxy-4-(9-methyl-9H-pyrido[2,3-b]indol-2-yl)phenol (1bk):

White solid (14.38 mg, 71% yield); mp. 148-150°C; (12% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.33 (d, *J* = 8 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 2 Hz, 1H), 7.67 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.58 (d, *J* = 8 Hz, 1H), 7.54-7.50 (m, 1H), 7.47-7.45 (m, 1H), 7.30-7.28 (m, 1H), 7.04 (d, *J* = 8.4 Hz, 1H) 4.05 (s, 3H), 4.07 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 153.8, 146.9, 146.7, 128.9, 126.5, 120.8, 120.7, 120.0, 114.6, 111.7, 109.9, 109.1, 100.0, 56.2, 29.8 ; HRMS (EI+) m/z calculated for $C_{19}H_{16}N_2O_2$ $[M]^+$ 304.1212, found 304.1205.



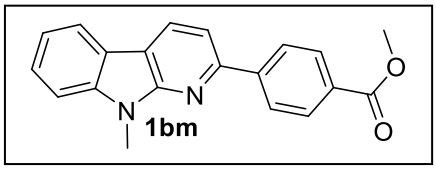
2-(4-Fluorophenyl)-9-methyl-9H-pyrido[2,3-b]indole (1bl):

Yellowish brown solid (14.90 mg, 81% yield); mp. 123-125°C; (6% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.35 (d, *J* = 8 Hz, 1H), 8.21-8.15 (m, 2H), 8.07(dt, *J* = 8, 0.8 Hz, 1H) 7.59(d, *J* = 8 Hz, 1H), 7.55-7.52(m, 1H), 7.46 (dt, *J* = 8, 0.8 Hz, 1H), 7.31-7.27 (m, 1H), 7.21-7.17 (m, 2H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 163.7 (d, $J_{C\text{-}F}$ = 247.0 Hz), 153.2, 152.3, 141.1, 136.6 (d, $J_{C\text{-}F}$ = 3 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8 Hz), 129.0, 126.9, 121.2, 120.7, 120.2, 115.9 (d, $J_{C\text{-}F}$ = 22 Hz), 114.8, 112.0, 109.4, 27.9; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ – 113.73; HRMS (EI$^+$) m/z calculated for $C_{18}H_{13}N_2F$ $[M]^+$ 276.1063, found 276.1056.



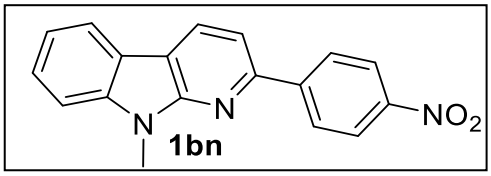
Methyl 4-(9-methyl-9H-pyrido[2,3-b]indol-2-yl)benzoate (1bm):

Yellow solid (16.64 mg, 85 % yield); mp. 136-138°C; (6% ethyl acetate-petroleum ether, v/v); ^{1}H NMR($CDCl_3$, 400 MHz) δ_H 8.38 (d, *J* = 8 Hz, 1H), 8.28 (dt, *J* = 8.4, 0.8 Hz, 2H), 8.18-8.15 (m, 2H), 8.09 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H), 7.57-7.53 (m, 1H), 7.49-7.47 (m, 1H), 7.32-7.28 (m, 1H), 4.04 (s, 3H), 3.96 (s, 3H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 167.2, 152.5, 152.0, 144.4, 141.1, 130.1, 128.7, 127.0, 121.2, 120.1, 115.4, 112.6, 109.2, 100.0, 52.3, 27.7; HRMS (EI$^+$) m/z calculated for $C_{20}H_{16}N_2O_2$ $[M]^+$ 316.1212, found 316.1220.



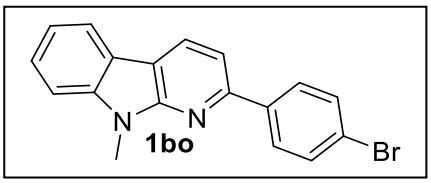
9-Methyl-2-(4-nitrophenyl)-9H-pyrido[2,3-b]indole (1bn):

Yellowish green solid (17.76 mg, 88% yield); mp. 180-182 ^{o}C; (10% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.40 (d, *J* = 8 Hz, 1H), 8.39-8.33 (m, 4H), 8.10 (dt, *J* = 8, 0.8 Hz, 1H), 7.72 (d, *J* = 8 Hz, 1H), 7.59-7,56 (m, 1H), 7.50-7.48 (m, 1H), 7.34-7.30 (m, 1H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 152.0, 150.9, 148.8, 146.2, 141.3, 128.8, 127.8, 127.4, 124.1, 121.4, 120.3, 120.2, 116.1, 112.7, 109.3, 27.7; HRMS (EI^{+}) m/z calculated for $C_{18}H_{13}N_3O_2[M]^{+}$ 303.1008, found 303.1016



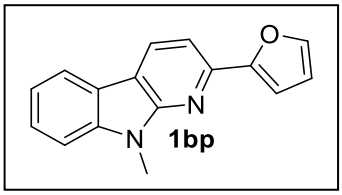
2-(4-Bromophenyl)-9-methyl-9H-pyrido[2,3-b]indole (1bo):

White powder (15.68 mg, 70% yield); mp.168-170^{o}C; (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.36 (d, *J* = 8 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 3H), 7.64-7.62 (m, 3H), 7.545 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 4.03 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C, 152.7, 152.0, 141.0, 139.1, 131.9, 128.9, 126.8, 123.1, 121.1, 120.4, 120.0, 115.0, 111.9, 109.2, 27.8; HRMS (EI+) m/z calculated for$C_{18}H_{13}N_2Br$ [M]$^{+}$ 336.0262, found 336.0263.

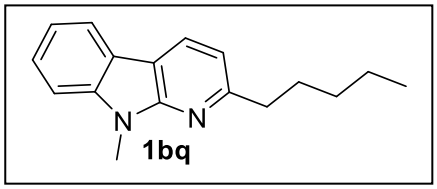


2-(furan-2-yl)-9-methyl-9H-pyrido[2,3-b]indole (1bp):

Brown solid (10.25 mg, 62% yield); mp. 86-88 ^{o}C; (3% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.83 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 15.1, 3.8 Hz, 1H), 6.57 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 146.0, 142.7, 142.3, 137.9, 126.2, 120.1, 116.8, 116.2, 113.0, 112.2, 108.9, 29.8; HRMS (EI^{+}) m/z calculated for $C_{16}H_{12}N_2O$ [M]$^{+}$ 248.0950, found 248.0956.

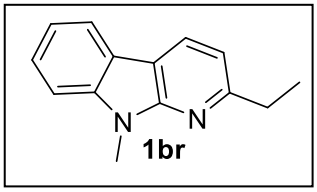


9-Methyl-2-pentyl-9H-pyrido[2,3-b]indole (1bq):



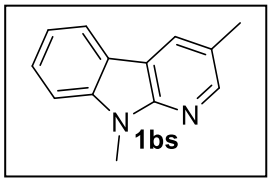
Colorless viscous liquid (9.39 mg, 53% yield); (1% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.15 (d, *J* = 8 Hz, 1H), 7.72 (s, 1H), 7.64-7.59 (m, 1H), 7.53-7.51 (m, 1H), 7.37- 7.33 (m, 2H), 4.03 (s, 3H) 3.27 (t, *J* = 7.6 Hz, 2H), 1.89-1.82 (m, 2H), 1.57-1.48 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H);^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 152.2. 148.8, 147.5, 142.0, 127.8, 123.9, 120.6, 120.0, 118.1, 114.7, 109.4, 33.5, 31.1, 27.9, 22.9, 14.1; HRMS (EI$^+$) m/z calculated for $C_{17}H_{20}N_2$ [M]$^+$ 252.1626, found 252.1629.

2-Ethyl-9-methyl-9H-pyrido[2,3-b]indole (1br):



Orange viscous liquid(7.70 mg, 55% yield); (1% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.20 (d, *J* = 8 Hz, 1H), 8.03 (dt, *J* = 7.2, 0.8 Hz, 1H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 1H), 7.25-7.23(m, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 2.94-2.90 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 140.2, 128.3, 126.1, 120.7, 120.64, 119.6, 114.3, 109.0, 29.8, 23.6, 14.1; HRMS (EI$^+$) m/z calculated for $C_{14}H_{14}N_2$ [M]$^+$ 210.1157, found 210.1160

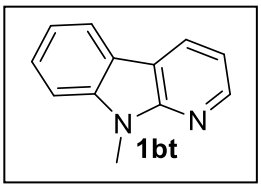
3,9-Dimethyl-9H-pyrido[2,3-b]indole (1bs):



Colorless liquid (8.75 mg, 67% yield); (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.34-8.33 (m, 1H), 8.14-8.13 (m, 1H), 8.03 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.54-7.49 (m, 1H), 7.45-7.42 (m, 1H), 7.26-7.25 (m, 1H), 3.94 (s, 3H), 2.51(s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 146.6, 140.6, 128.6, 126.6, 124.0, 121.0, 120.3, 119.6, 109.0, 27.7, 18.6;HRMS (EI$^+$) m/z calculated for $C_{13}H_{12}N_2$ [M]$^+$ 196.1000, found 196.0984.

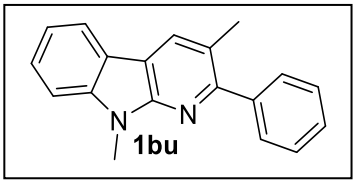
9-Methyl-9H-pyrido[2,3-b]indole (1bt):

Pale yellow viscous liquid (7.52 mg, 62% yield); (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.51 (dd, *J* = 3.2, 1.6 Hz, 1H), 8.33 (dd, *J* = 6, 1.6 Hz, 1H), 8.09-8.07 (m, 1H), 7.57-7.52 (m, 1H), 7.48-7.45 (m, 1H), 7.31-7.27 (m, 1H), 7.18-7.15 (m, 1H), 3.98 (s, 3H);$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 145.9, 140.3, 128.3, 126.8, 121.1, 119.9, 115.0, 109.1, 27.1; HRMS (EI^+) m/z calculated for $C_{12}H_{10}N_2$ $[M]^+$ 182.0844, found 182.0836.



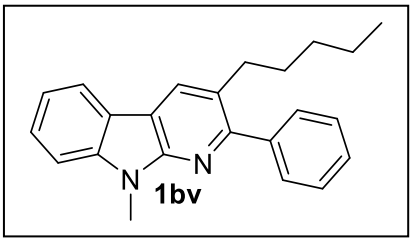
3,9-Dimethyl-2-phenyl-9H-pyrido[2,3-b]indole (1bu):

White powder (12.23 mg, 73% yield); mp. 121-123°C; (4% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.21 (d, *J* = 0.4 Hz, 1H), 8.07 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.67-7.64 (m, 2H), 7.54-7.47(m, 3H),7.48-7.43 (m, 2H), 7.42-7.39 (m, 1H), 3.97 (s, 3H), 2.51(s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 141.2, 130.7, 129.8, 128.4, 128.1, 126.8, 122.06, 121.2, 120.4, 119.8, 115.0, 109.3, 28.1, 20.8; HRMS (EI^+) m/z calculated for $C_{19}H_{16}N_2$ $[M]^+$ 272.1313, found 272.1304.

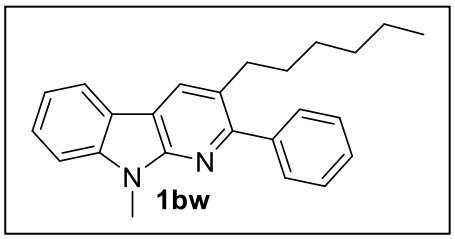


9-Methyl-3-pentyl-2-phenyl-9H-pyrido[2,3-b]indole (1bv):

Pale brown solid (15.75 mg, 72% yield); mp. 80-82°C; (5% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.25 (s, 1H), 8.09 (d, *J* = 7.6, 1.2 Hz, 1H), 7.59-7.57 (m, 2H), 7.53-7.42(m, 5H), 7.30-7.28 (m, 1H), 3.98 (s, 3H), 2.80-2.76(m, 2H), 1.25-1.22 (m, 6H), 0.84-0.81 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 154.3, 153.9, 141.0, 129.5, 128.2, 127.9, 126.7, 121.06, 120.2, 119.8, 109.1, 100.0, 32.7, 31.7, 31.6, 29.8, 22.5, 14.1; HRMS (EI^+) m/z calculated for $C_{23}H_{24}N_2$ $[M]^+$ 328.1939, found 328.1930.



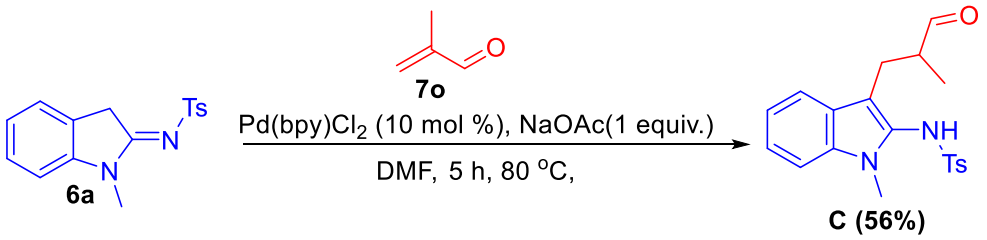
3-Hexyl-9-methyl-2-phenyl-9H-pyrido[2,3-b]indole (1bw):



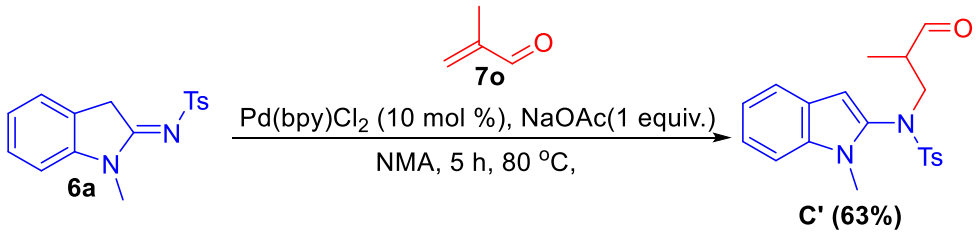
White powder (17.10 mg, 75% yield); mp. 80-82^{o}C; (3% ethyl acetate-petroleum ether, v/v);^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.23 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.60-7.57 (m, 2H), 7.54-7.53 (m, 1H), 7.50-7.49 (m, 1H), 7.48-7.47 (m, 1H), 7.44 (d, *J* = 4.8 Hz, 1H), 7.43-7.40 (m, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 2.78(t, *J* = 8 Hz, 2H), 1.25(s, 6H), 1.22-1.20(m, 2H), 0.84(t, *J* = 8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz) δ_C 151.54, 151.53,141.0, 131.4, 129.5, 128.2, 121.0, 120.2, 109.1, 36.4, 32.7, 31.9, 31.6, 29.1, 22.6, 14.2; HRMS (EI^{+}) m/z calculated for $C_{24}H_{26}N_2$ $[M]^{+}$ 342.2096, found 342.20.

22. Control experiment to support the mechanism:

As per the mechanism (Scheme 4 of manuscript), the base (i.e., NaOAc) has played a significant role in forming the products **1a/1b.** To isolate the acyclic intermediate **C** and **C'** as proposed in Scheme 4, we carried out two control experiments (Schemes S4 and S5) where tosyliminoindoline **6a** was allowed to react with methacrolein (**7o**) under the optimized reaction conditions except that one equivalent of the base was used instead of four equivalents employed in optimized reaction conditions. From these experiments, we were able to isolate the desired C3 alkylated products **C** and N-alkylated product **C'** in DMF and NMA, respectively. These results support the formation of the said acyclic intermediates for the formations of products **1a** and **1b** as proposed in Scheme 4.



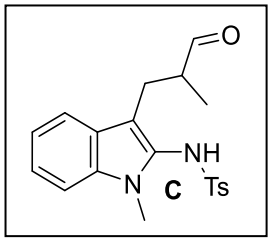
Scheme S4: control experiment in DMF solvent



Scheme S5: control experiment in NMA solvent

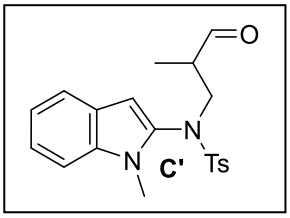
23. Spectral data of intermediate C and C'.

4-methyl-N-(1-methyl-3-(2-methyl-3-oxopropyl)-1H-indol-2-yl)benzenesulfonamide (C):



Colourless liquid (13.81 mg, 56% yield); (30% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.51 (d, *J* = 3.4 Hz, 1H), 8.84 (d, *J* = 3.8 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 3H), 7.21 – 7.17 (m, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.33 (s, 3H), 2.45 (s, 3H), 2.43 (d, *J* = 9.3 Hz, 1H), 1.89 (dd, *J* = 14.4, 5.3 Hz, 2H), 1.05 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) δ_C 204.6, 143.5 , 142.5 , 140.9 , 132.5 , 129.8 , 129.4 , 126.31 , 126.29 , 124.3 , 122.8 , 109.8 , 55.9 , 43.6 , 39.5 , 21.6 , 15.0 .; HRMS (EI$^+$) m/z calculated for $C_{20}H_{22}N_2O_3S$ $[M]^+$ 370.1351, found 370.1344.

4-methyl-N-(1-methyl-1H-indol-2-yl)-N-(2-methyl-3-oxopropyl)benzenesulfonamide (C'):



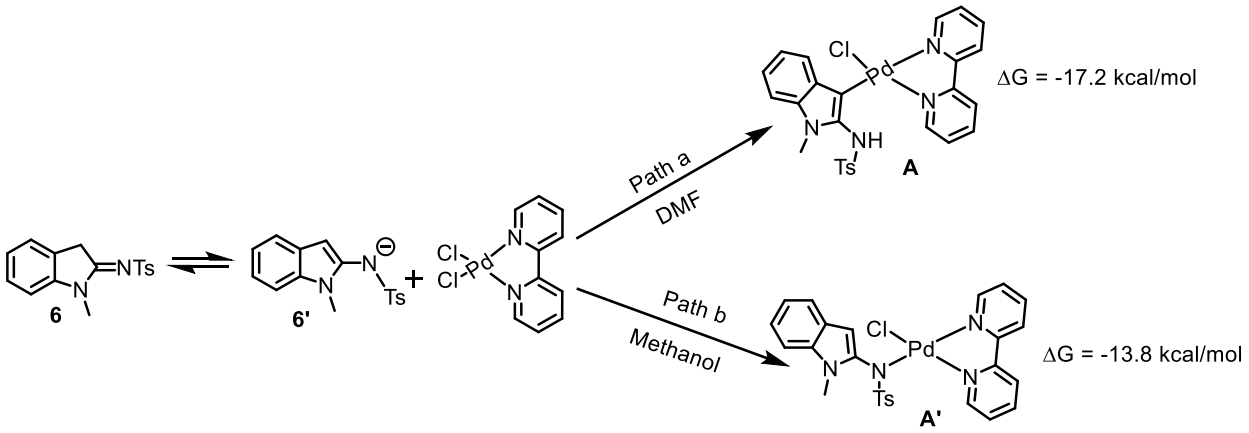
Orange liquid (15.54 mg, 63% yield);(25% ethyl acetate-petroleum ether, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.42 (s, 1H), 7.63 – 7.58 (m, 2H), 7.37 – 7.34 (m, 1H), 7.29 (dt, *J* = 8.3, 1.0 Hz, 2H), 7.22 (dt, *J* = 8.2, 0.9 Hz, 3H), 7.08 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 3.73 (s, 3H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.70 – 2.55 (m, 1H), 2.42 (s, 3H), 1.99 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.05 (d, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ_C 205.9, 144.1, 136.4, 135.3, 129.6, 129.3, 128.6, 127.7, 126.4, 125.7, 122.3, 119.4, 118.5, 110.0, 107.4, 47.5, 29.8, 22.5, 21.6, 14.4; HRMS (EI$^+$) m/z calculated for $C_{20}H_{22}N_2O_3S$ $[M]^+$ 370.1351 found 370.1341.

Rational for the selectivity of product formation (1a and 1b) based on the dieletric constant of the solvent used:

The selectivity of product formation could perhaps be ascribed to the dielectric constants of the solvents used. Thus, in DMF having lower dielectric constant compared to NMA (35.05 vs 169.70 at 35 ^{o}C; *J. Am. Chem. Soc*. 1951, **73**, 5731-5733), tight ion pair formation (*Org Lett.*, 2004,**6**, 3199-3202) of substrate **6** may take place leading to the sodiated salt **6'** (Scheme 4) rendering the nitrogen atom (of NHTs) less nucleophilic to undergo aminopalladation. This instead forms the palladated species **A** (Scheme 4) which undergoes Heck type reaction with **7** to produce **1a**. A more polar solvent like NMA could break the ion pair of **6'** through hydrogen bonding, facilitating aminopalladation to generate the transient species **A**' (Scheme 4) which delivers **1b** after few more transformation

24. DFT calculations for reaction feasibility in different solvents:

We have calculated the Gibbs free energy for the path a and path b as well. In path a (DMF) involves C paladation (C-Pd) while in path b (in MeOH) it involves N-paladation (N-Pd). It has been found that, palladation in both the cases give negative ΔG value. We have done the DFT calculation in methanol (MeOH) in place of NMA as NMA is not listed in Gaussian 09 as a solvent. Besides, the reaction carried out in methanol produced α-carboline **1ba** in good yield (61%), close to the yield (76%) obtained from the reaction carried out in NMA. In path a, the palladation on C3 of indole moiety resulting in intermediate **A** (as proposed in Scheme 4) provides the Gibbs free energy value of -17.2 kcal/ mol, while in path b, the palladation on NTs group of indole moiety resulting in intermediate **A'** (as proposed in Scheme 4) also provides comparable negative free energy value, i.e. -13.8 kcal/mol. This proves that both the reaction pathways are thermodynamically favourable in the respective Condition.

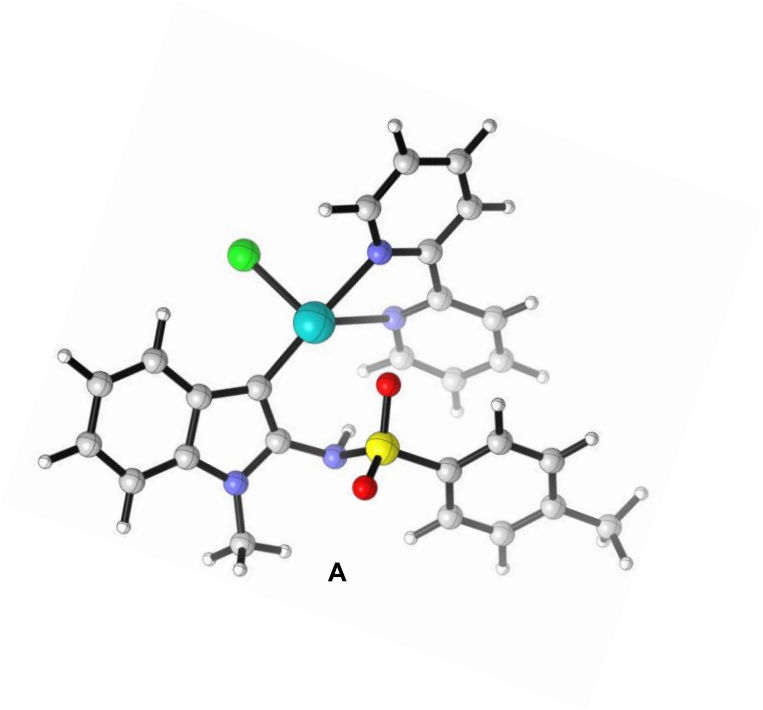


Method of DFT Study:

Geometry optimization of all the reactants and Pd−complexes was carried out in vacuum with density functional theory (DFT) using, B3LYP,[6a] with the addition of Grimme's empirical D3 dispersion correction,[6b] 6-31++(d)g** basis set is used for C, N, H,O, S and Cl atoms and LanL2DZ for the Pd atom. Harmonic vibrational frequencies at the same level of theory were computed to characterize the structures as minimum (all real frequencies) at 353.15 K temperature.Thermo-chemical information like zero-point corrections (ZPC) and thermal correction to enthalpy (Hcorr) were taken from frequency calculations. Single point total energies were computed, based on optimized geometry at the same level of theoryemploying CPCM solvation model[6c-e] to compute the free energy change (ΔG) of solvation, using DMF and methanol as a solvent. For solvent phase free energy changes the solvent phase entropies of entities were used. The solvent phase entropies were derived from empirical scaling of the corresponding gas phase entropies by a factor of 0.5.[6f-g] Binding energies (ΔG) at 353.15 K

were calculated using the equation S1. All DFT optimizations, frequency calculations and solvent-phase single point calculations were conducted by using the Gaussian 09 suite of programs.[6h] The 3D structures were generated with CYL view package.[6i]

$$\Delta G = G_{reactant} - G_{product} \qquad (Eq.S1)$$



A

Fig. S4. Optimized Structure of C-palladated intemedite **A**

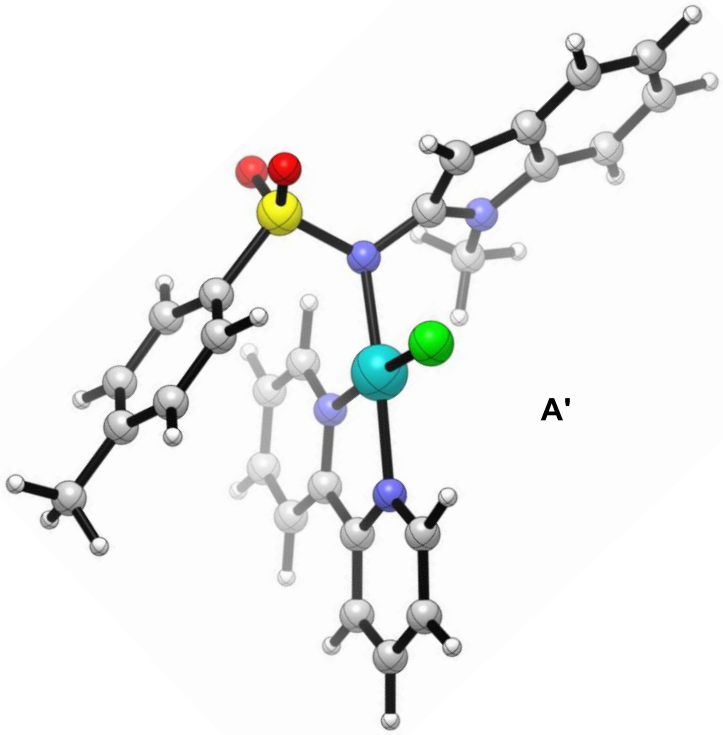


Fig. S5. Optimized Structure of N-palladated intemedite **A‘**

25. UV-Vis and Fluorescence study:

(a) Materials and Apparatus:

All the starting materials such as Quinine Sulphate, Tries-HCL buffer were procured from Sigma-Aldrich and used as received. The solvent like acetonitrile (MeCN) was of analytical grade and dried before use by applying standard procedure. The UV-Vis absorption spectra, emission spectra have been monitored by utilizing the instruments of same model described in our previous work.[7a]

(b) Preparation of Stock Solution of α-carbolines:

Mili-Q-Millipore water was used in every experimental study even in the preparation of stock solutions of various compounds. The stock solution of the series **1a** and series **1b** with concentration 1.0×10^{-3} mL^{-1} was prepared in CH_3CN. All the photophysical studies were performed in 10 mM Tries-HCL buffer at pH 7.0 by taking 2 ml Tries-HCL buffer at pH 7.0 in the cuvette and mixing 10 µL of 10^{-3} M ligands in MeCN to get resulting concentration of the α-carbolines 5 x 10^{-6} M.

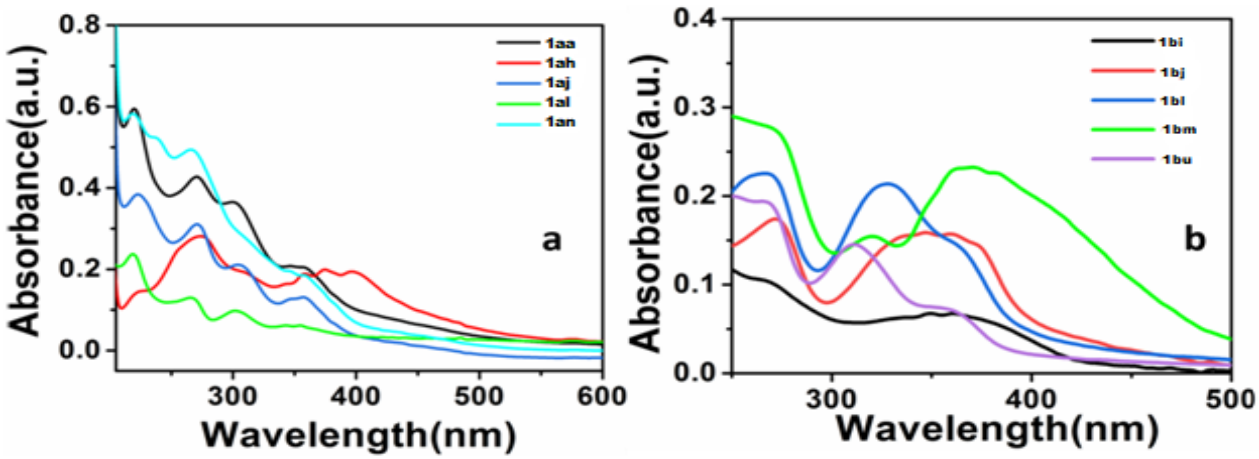


Figure S6. (a) Absorption spectra of the compounds **1a** in Tries-HCL buffer; and (b) absorption spectra of compounds **1b** in Tries-HCL buffer.

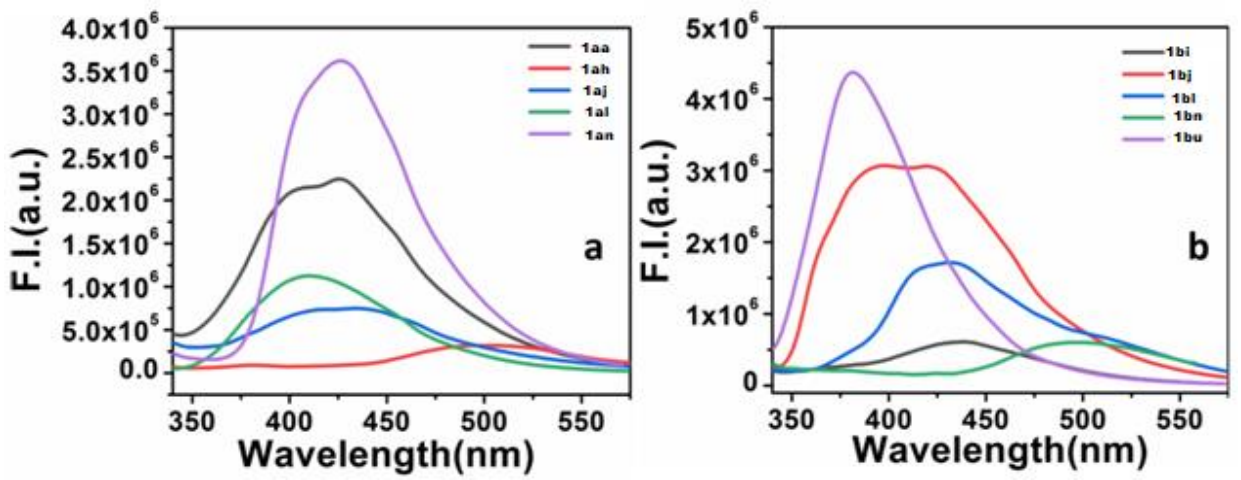


Figure S7. (a) Emission spectra of compounds **1a** in Tries-HCL buffer; (b) Emission spectra of compounds **1b** in Tries-HCL buffer.

(c) Quantum Yield:

Fluorescence quantum yields (Φ) of series (i) and series (ii) were calculated with the help of eqn. S2[7b]

$$\Phi_{sample} = (OD_{std} \times A_{sample})/(OD_{sample} \times A_{std}) \times \Phi_{std} \quad \text{.....(S2)}$$

Where, the respective areas under the fluorescence spectral curves of the standard and sample are symbolized as $A_{std}$and A_{sample} respectively. The optical densities of the standard and the sample are represented by OD_{std} and OD_{sample} respectively. Here, aqueous acidic solution of quinine sulfate was used as the standard with $\Phi_{std} = 0.54$

Table S1: Photophysical properties of few 4- and 2-substituted α-carbolines (**1a** and **1b**)

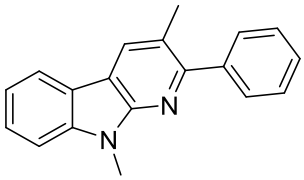
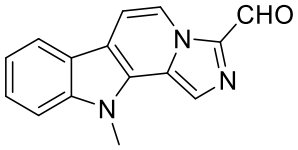
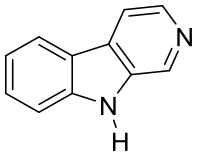
1a/1b	λ^{a}_{abs} (nm)	$\epsilon_{(Abs)} \times 10^{-3}$ ($M^{-1}cm^{-1}$)	λ_{ex} (nm)	λ^{b}_{em} (nm)	Φ^{c}
1aa	219,271, 300, 357	59.3,85.5, 73.0, 41.0	357	426	0.192
1ah	222,276, 307, 357	14.2,56.0, 20.9, 37.7	357	520	0.045
1aj	223,307, 347, 360	38.4,41.9, 25.4, 25.7	360	428	0.060
1al	219,266, 301, 355	23.7,26.0, 19.5, 12.3	355	410	0.091
1an	219,237, 265, 358	58.2,52.4, 98.7, 37.0	358	426	0.097
1bi	268, 371	10.3, 12.5	371	439	0.048
1bj	273, 347	34.7, 31.8	347	409	0.086
1bl	267, 329, 356	45.1,42.7, 15.2	356	432	0.038
1bn	269, 320, 371	54.5, 15.4, 46.5	371	508	0.016
1bu	267,311, 356	38.7, 26.1, 14.7	356	382	0.39

[a]Absorption maxima in CH_3CN (5 x 10^{-6} mL^{-1}). [b]Emission maxima in CH_3CN (5 x 10^{-6} mL^{-1}). [c]Determined with aqueous acidic solution of quinine sulfate as a standard.

Comparison between present data and standard data of Known compound:

The fluorosecene property of carboline and carbazole derivatives are well known[8a-c]. In particular, carboline derivatives are used in various field of material sciences.[8d] However, of four isomeric carboline compounds (α, β, γ, δ), the photo physical properties of β-carboline are well explored[8e] where the β-carboline **BC** (Table S1) in acidic solution shows higher quantum yield (i.e., **0.60**) compared to its fused derivative FC using acidic quinine sulphate as standard.[8e] Nevertheless, in our experiments, the quantum yield **1bu** was estimated to be 0.39 using acidic QS as standard which is comparable to the value of **FC** as shown in Table S1.Thus **1bu** shows promise to be used in various applications of material sciences. More studies in this regard are currently underway in our laboratory.

Table S2: Comparison of the fluorescence quantum yield value (φ) of synthesized compounds with others

Compound	Structure	quantum yield (φ)
1bu		**0.39**
FC		**0.384**
BC (β-carboline)		**0.60**
QS (standard compound)	Quinine sulphate in H_2SO_4	**0.54**

26. references:

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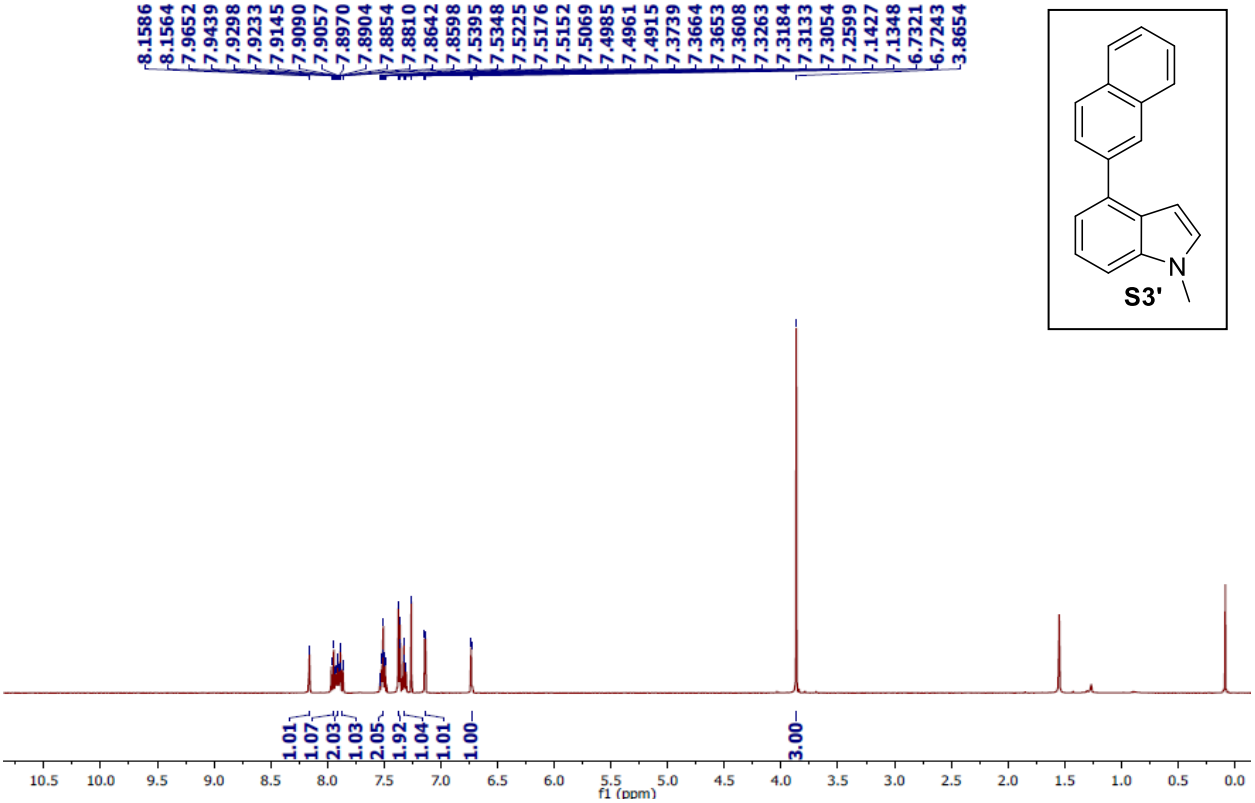
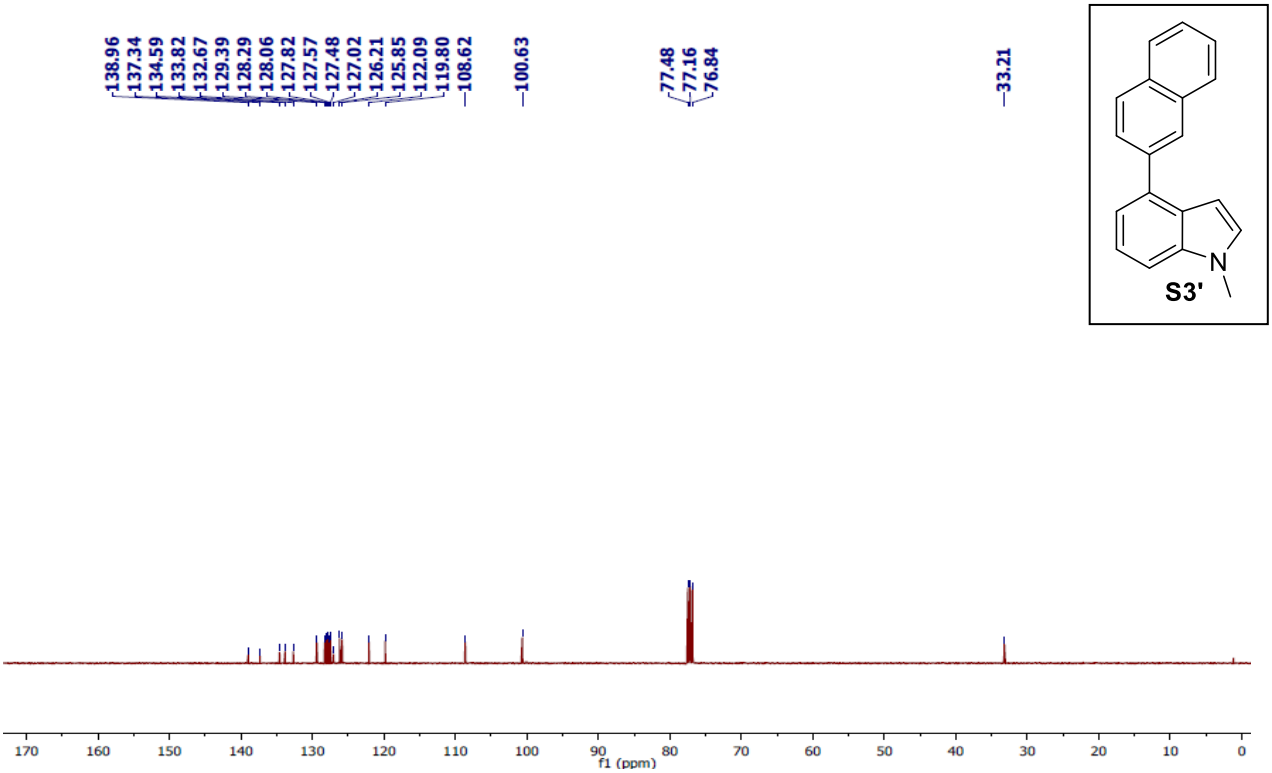
27. NMR spectra of starting material S3'

^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **S3'**

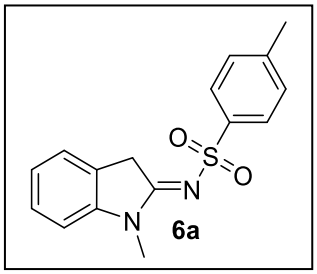


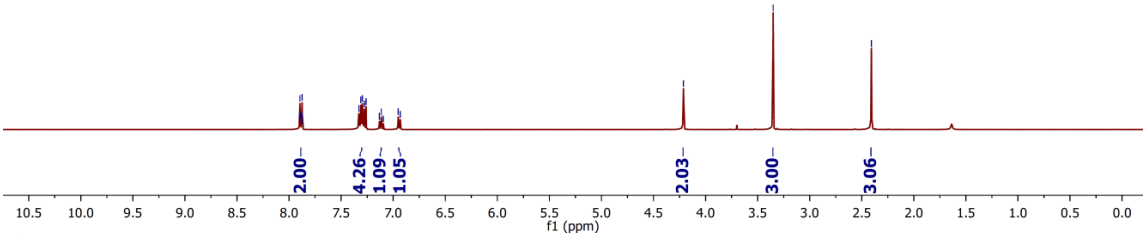
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **S3'**



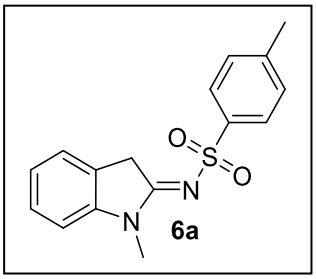
28. NMR spectra of starting material 6a,6e & 6g:

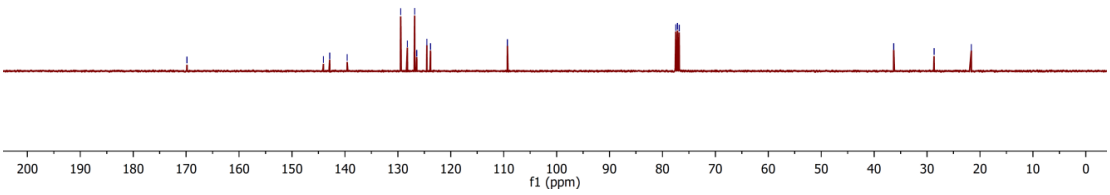
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **6a:**



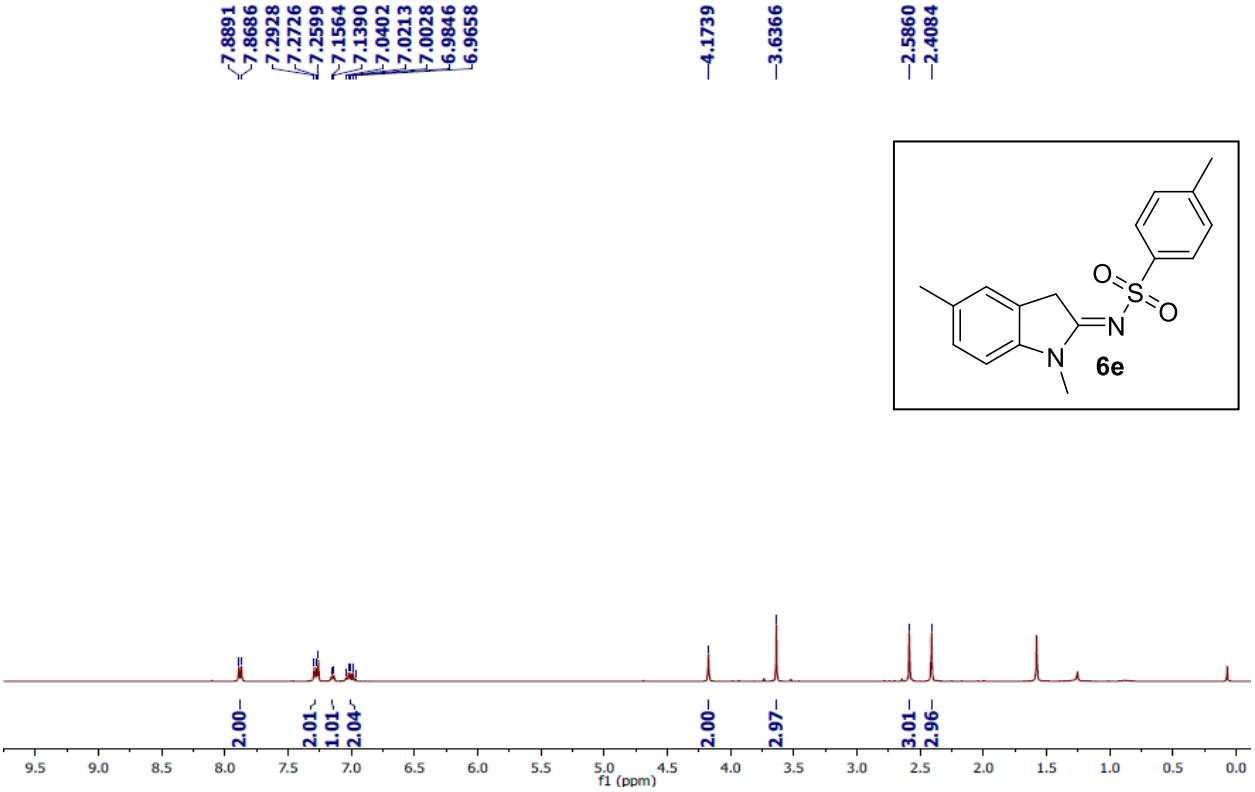


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **6a**:

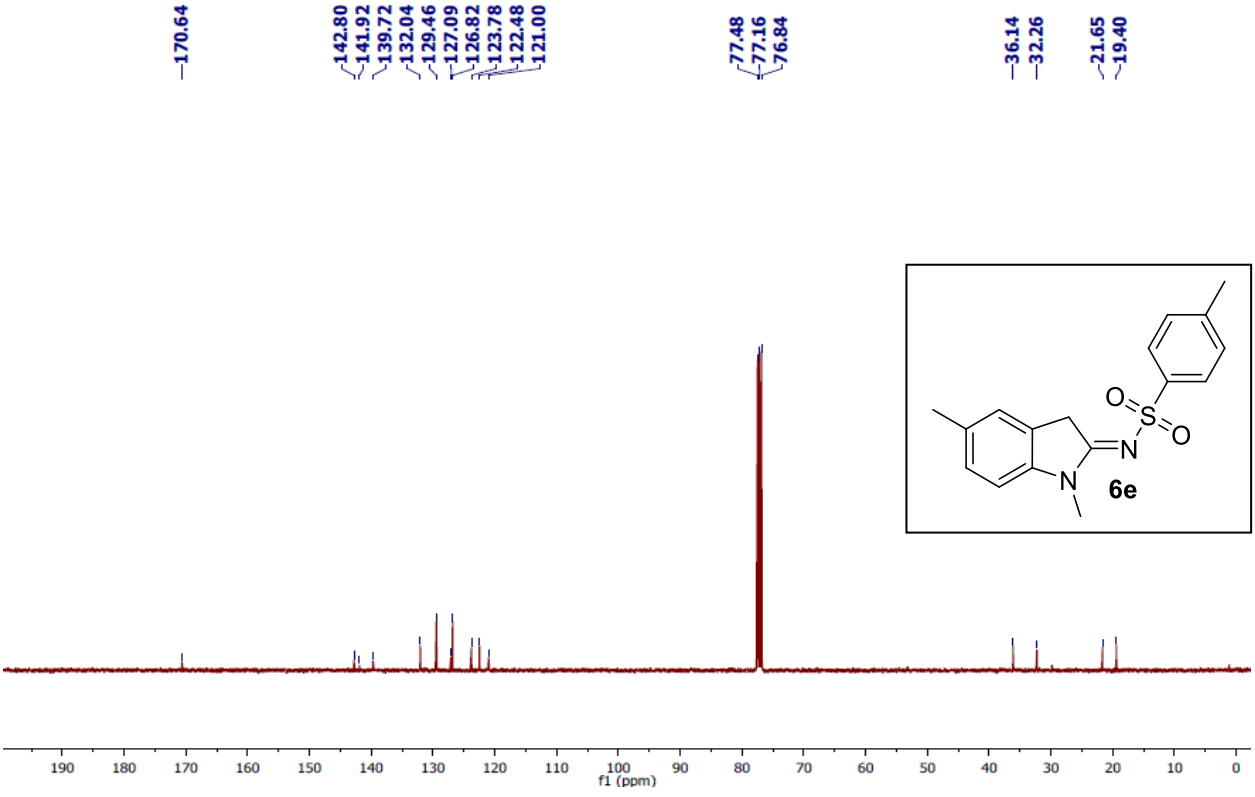




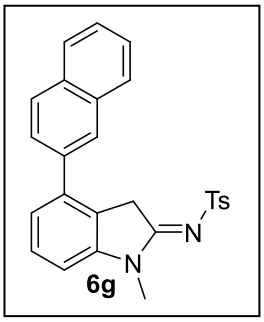
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **6e:**



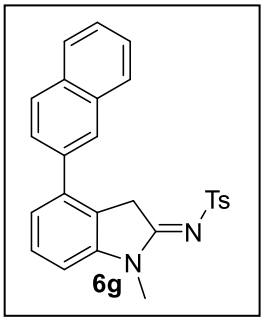
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **6e**:



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **6g:**

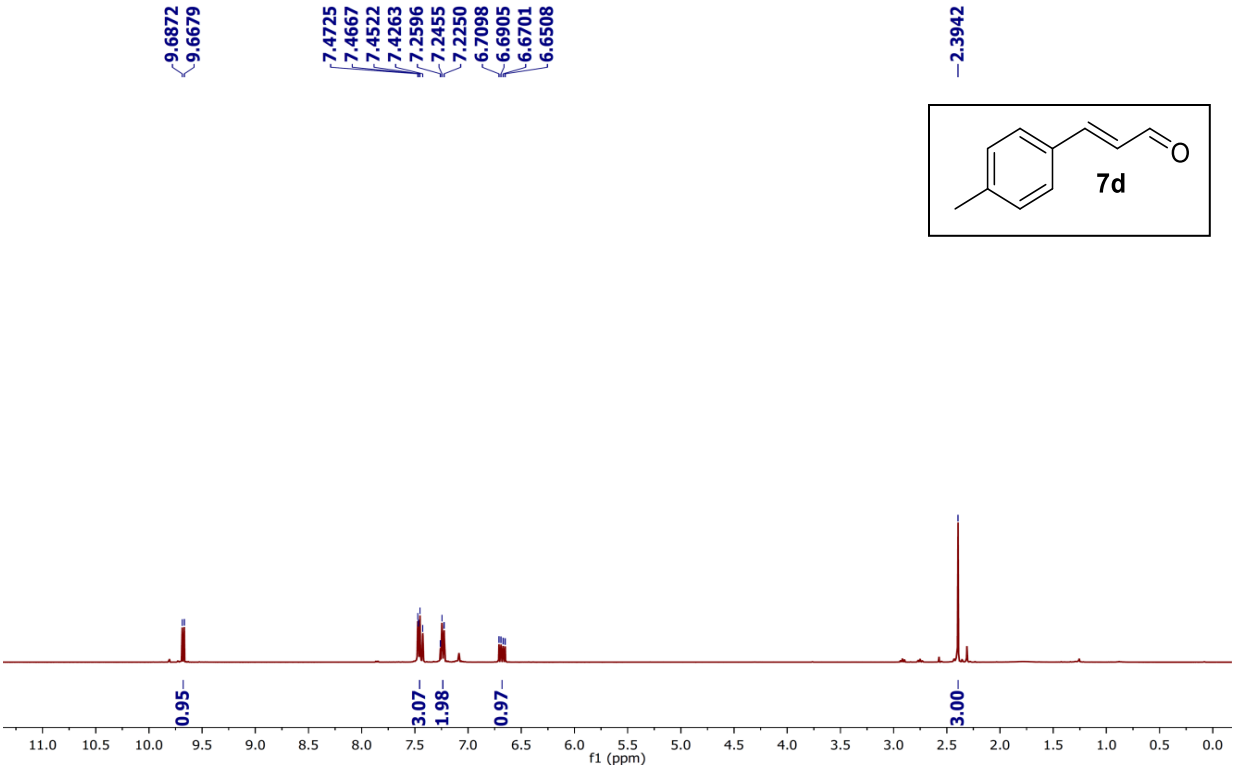


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **6g**:

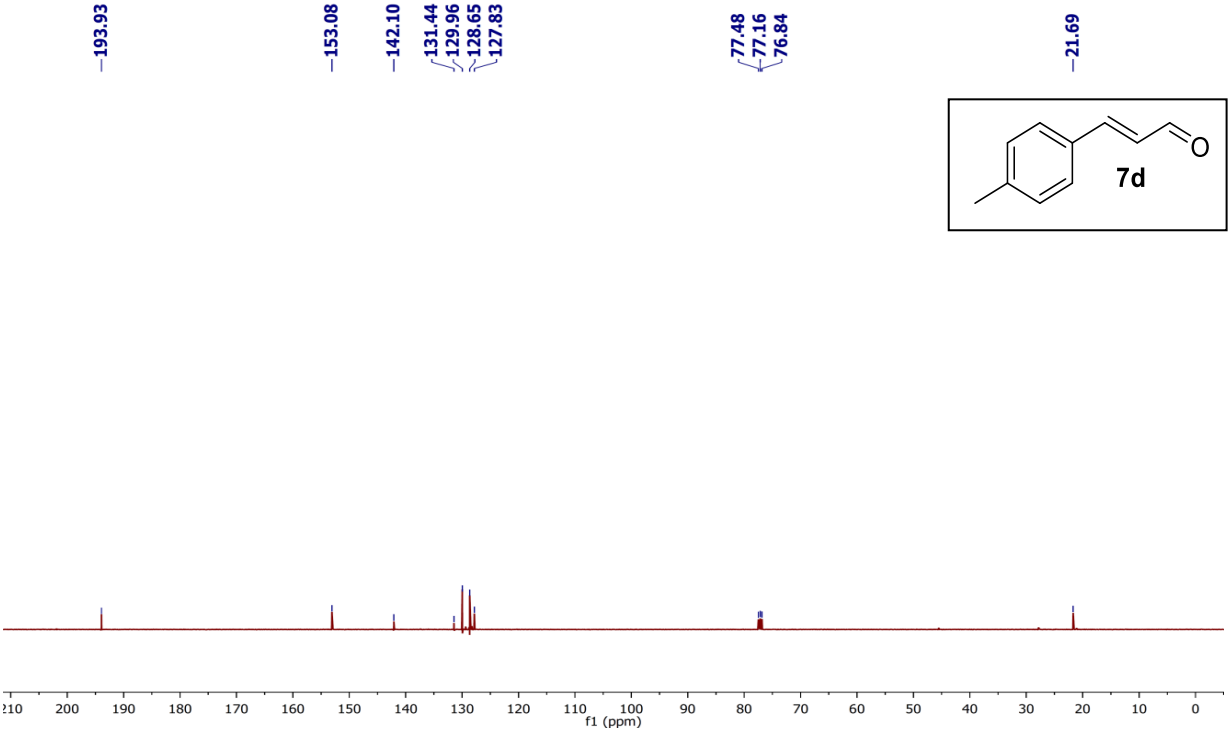


29. NMR spectra of starting materials 7d and 7h:

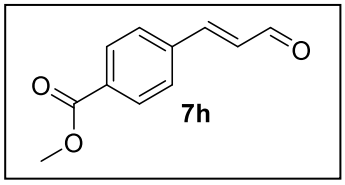
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7d:**

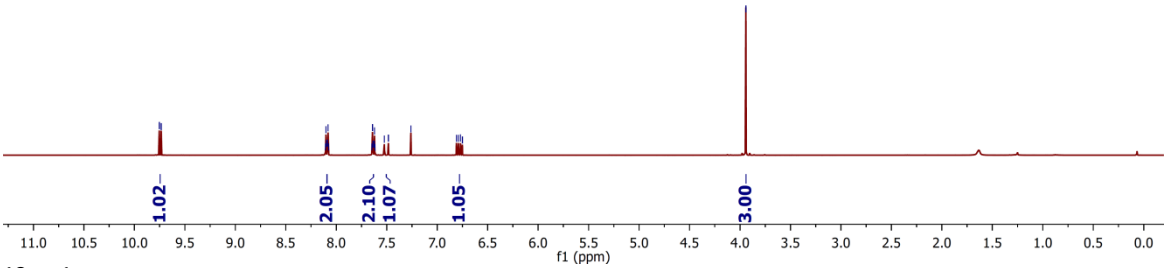


^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) spectrum of compound **7d**:

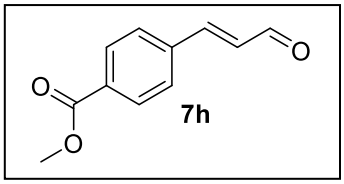


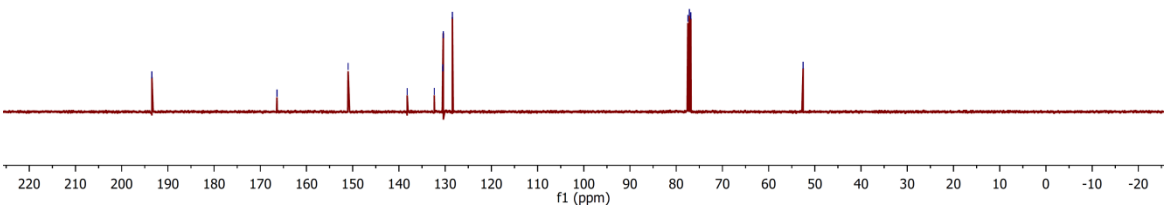
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7h:**





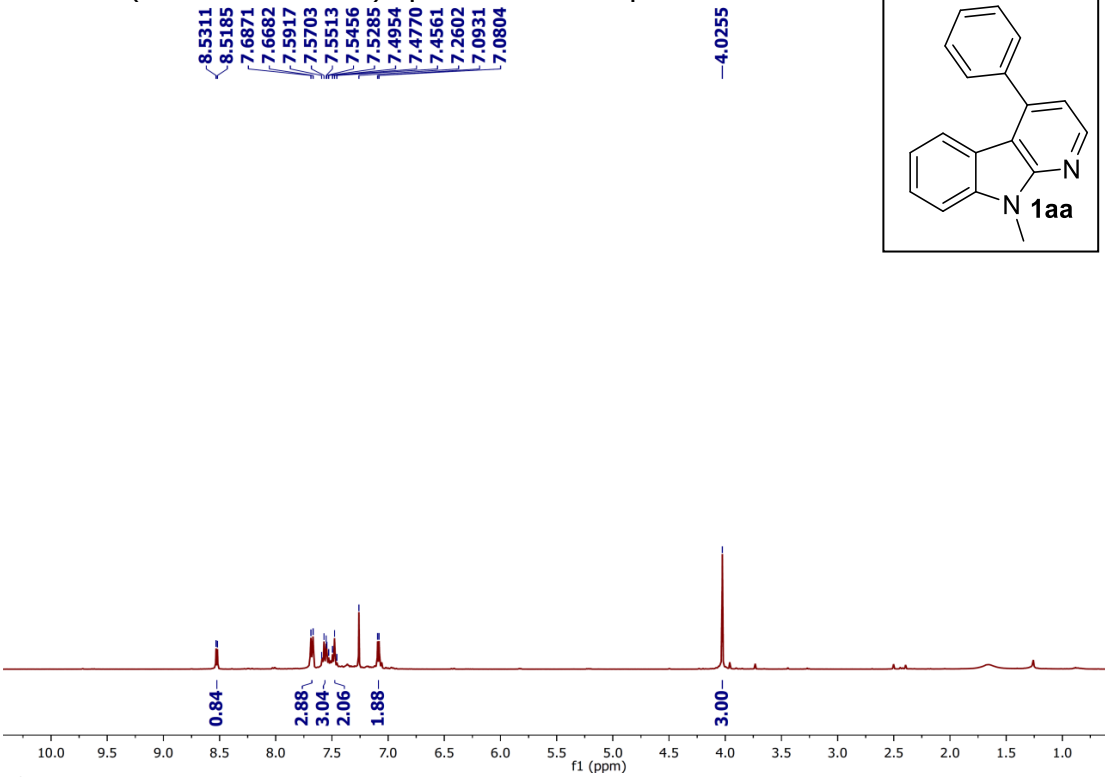
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **7h**:



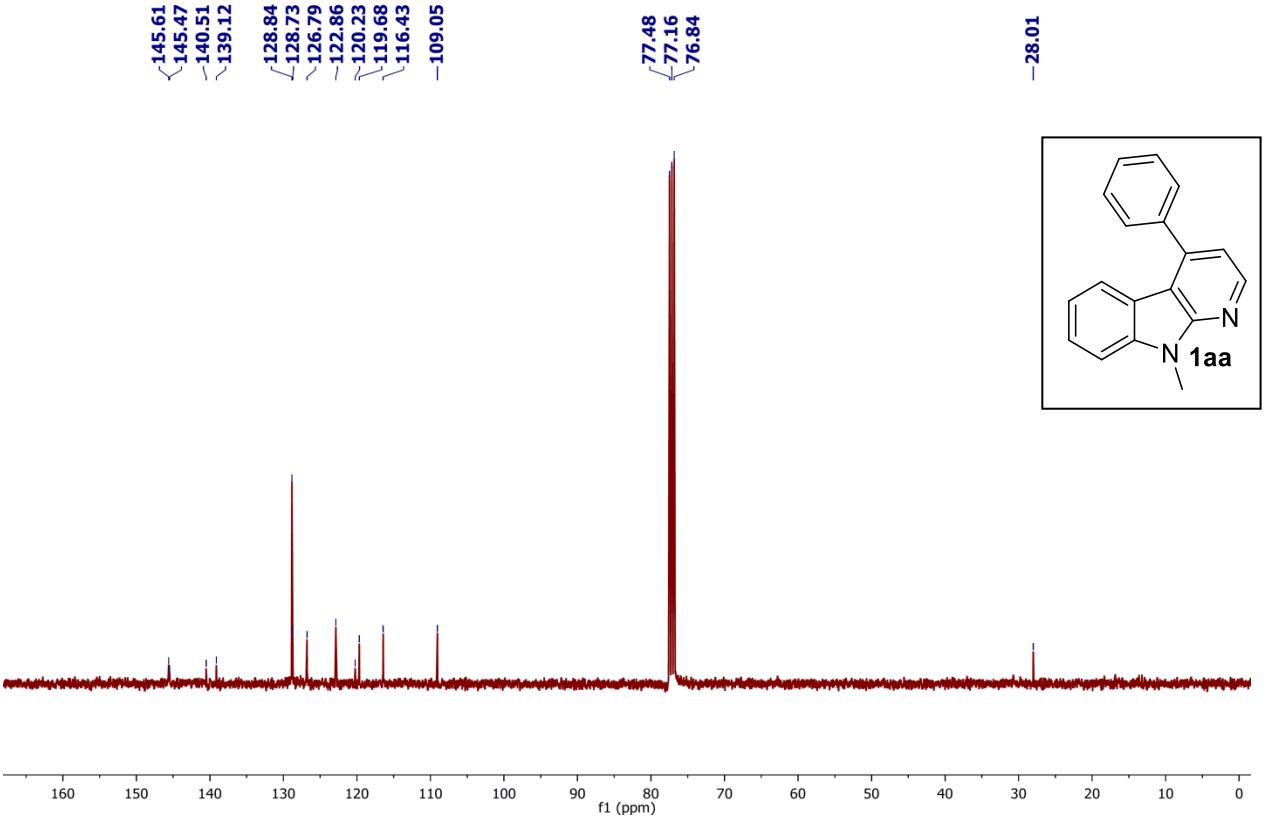


30. NMR spectra of products 1aa-1ap:

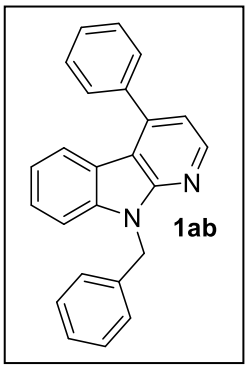
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1aa**

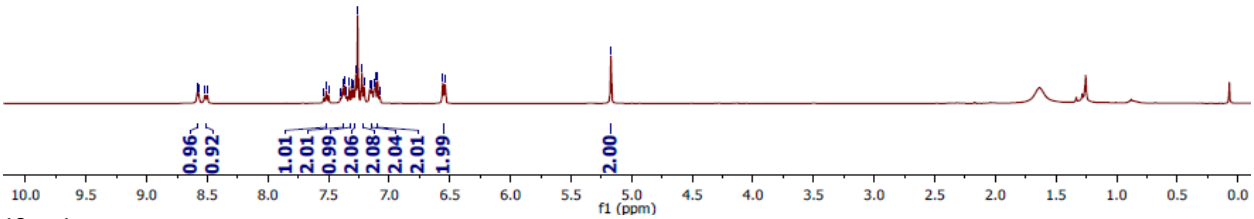


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1aa**:

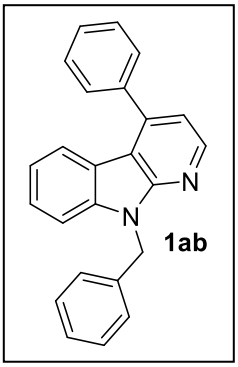


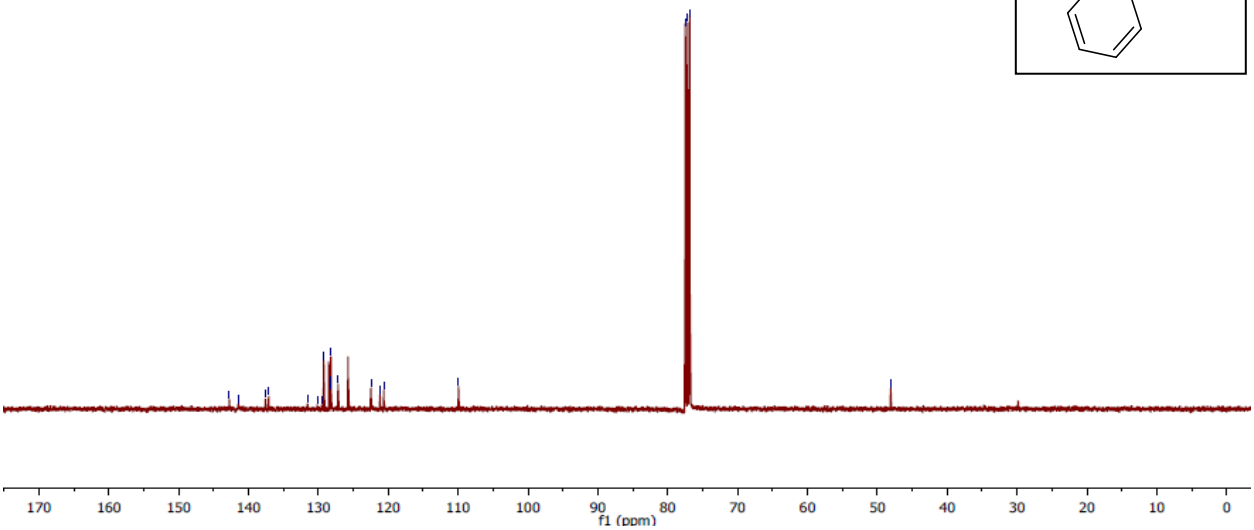
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ab**:



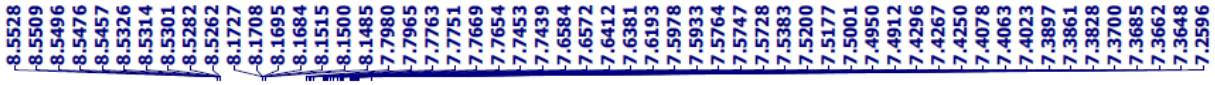


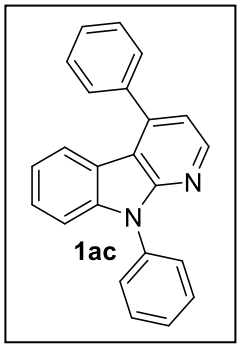
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ab**:

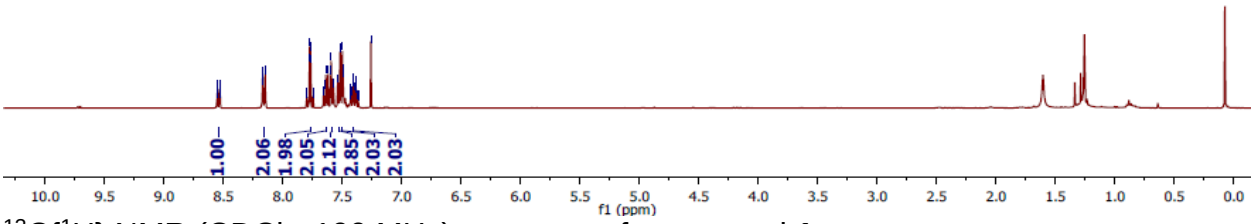




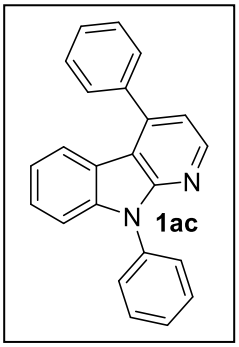
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ac**:

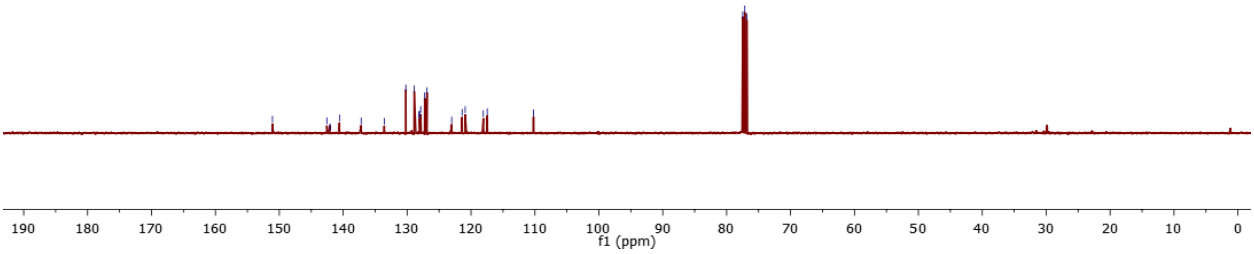




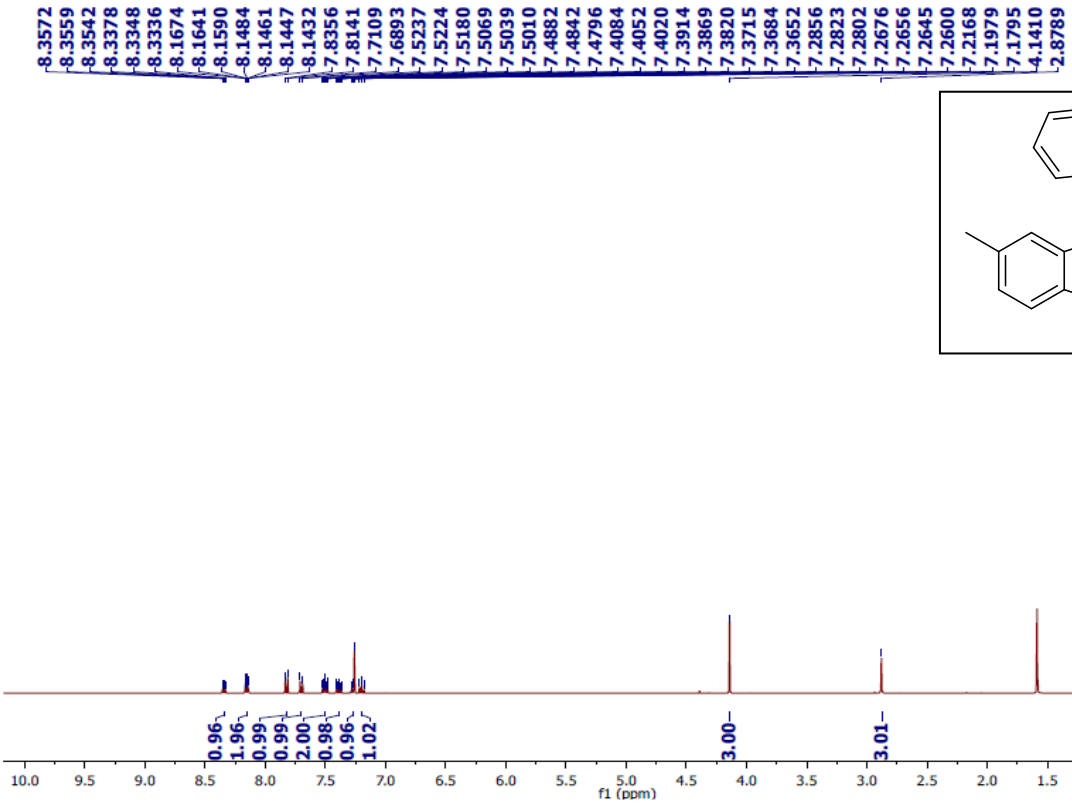


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ac**:

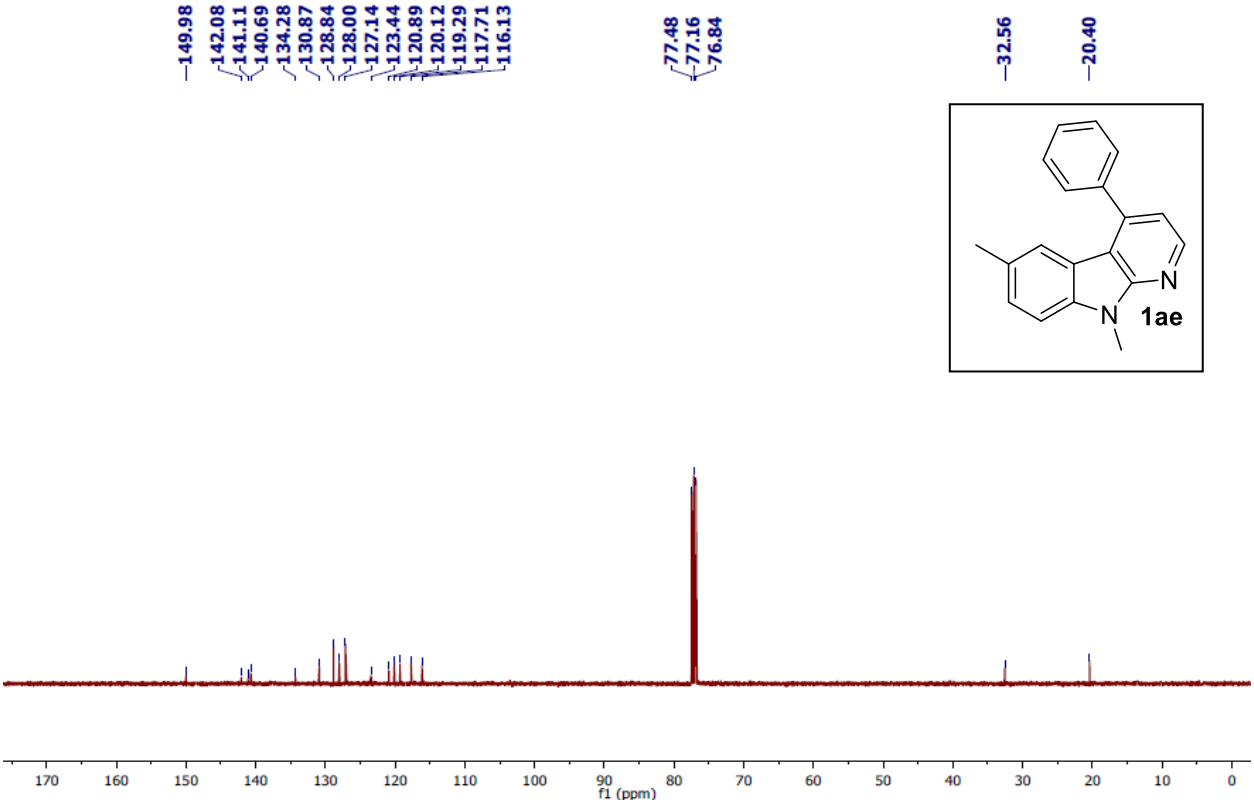




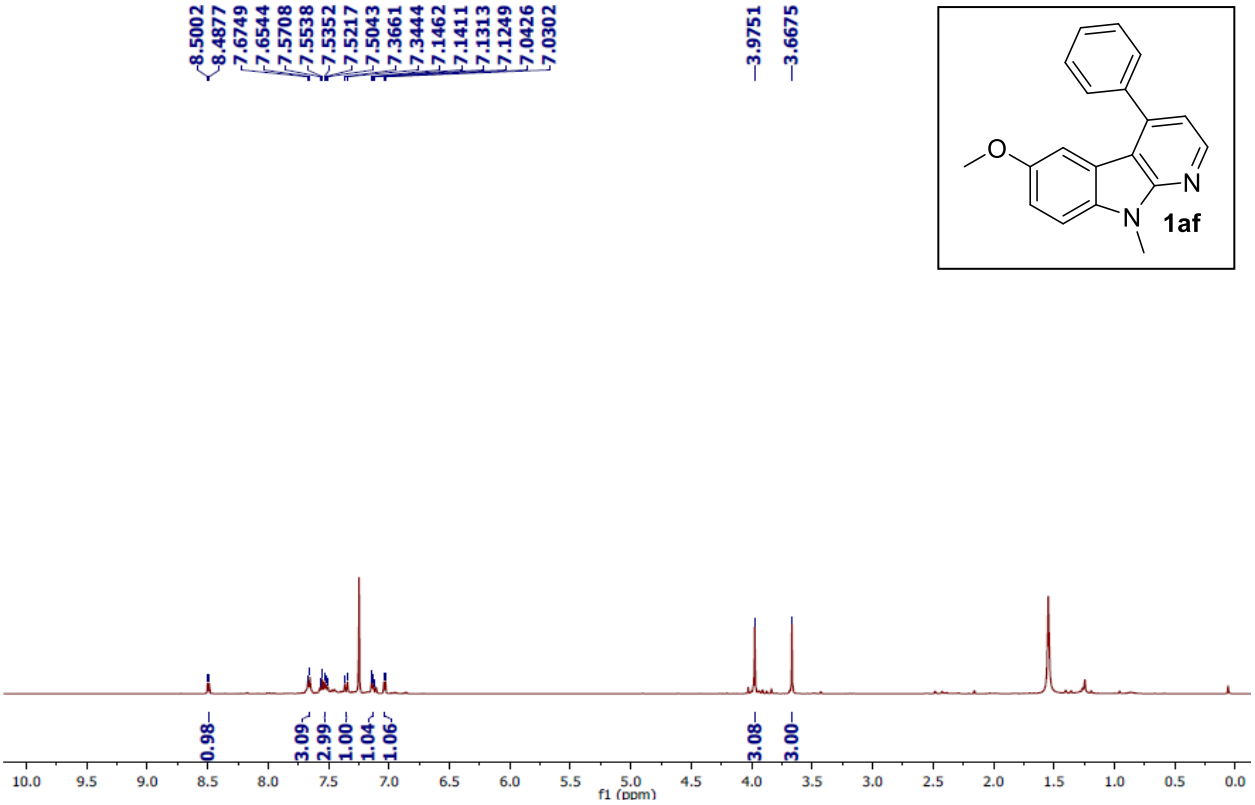
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ae**:



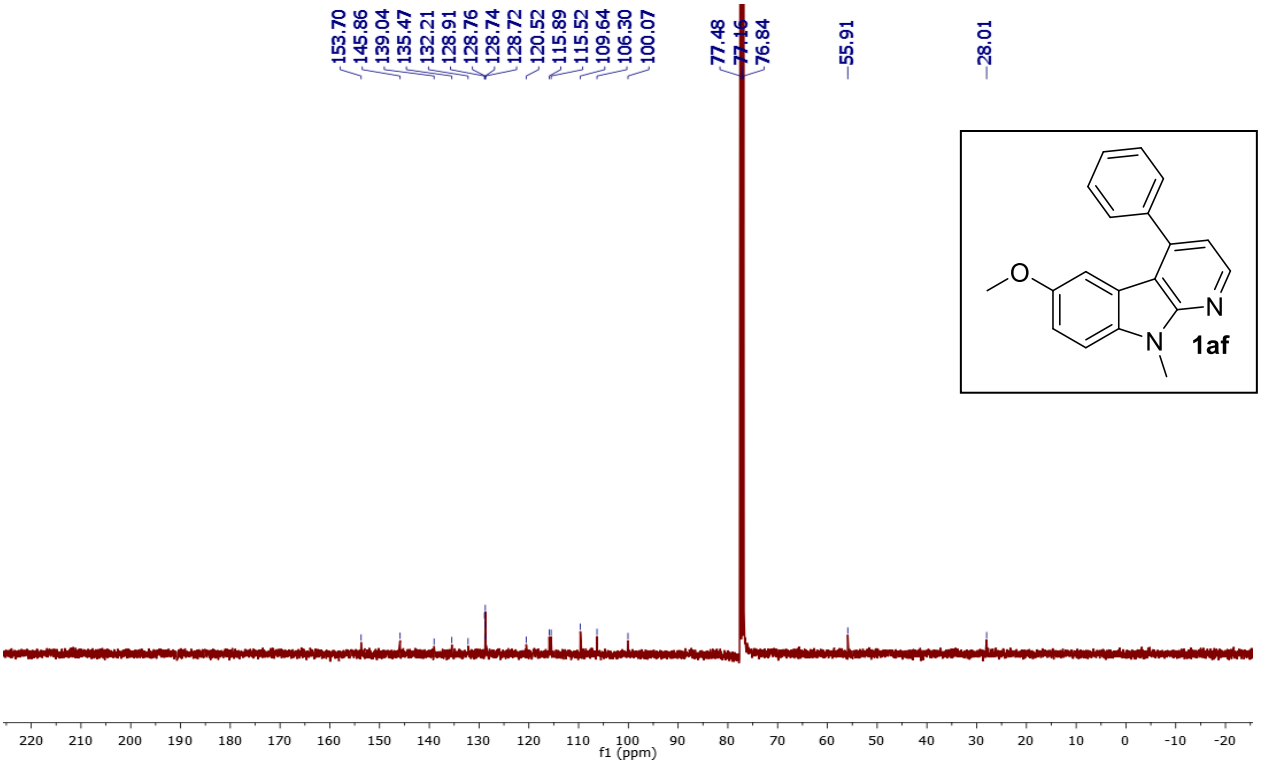
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ae:**



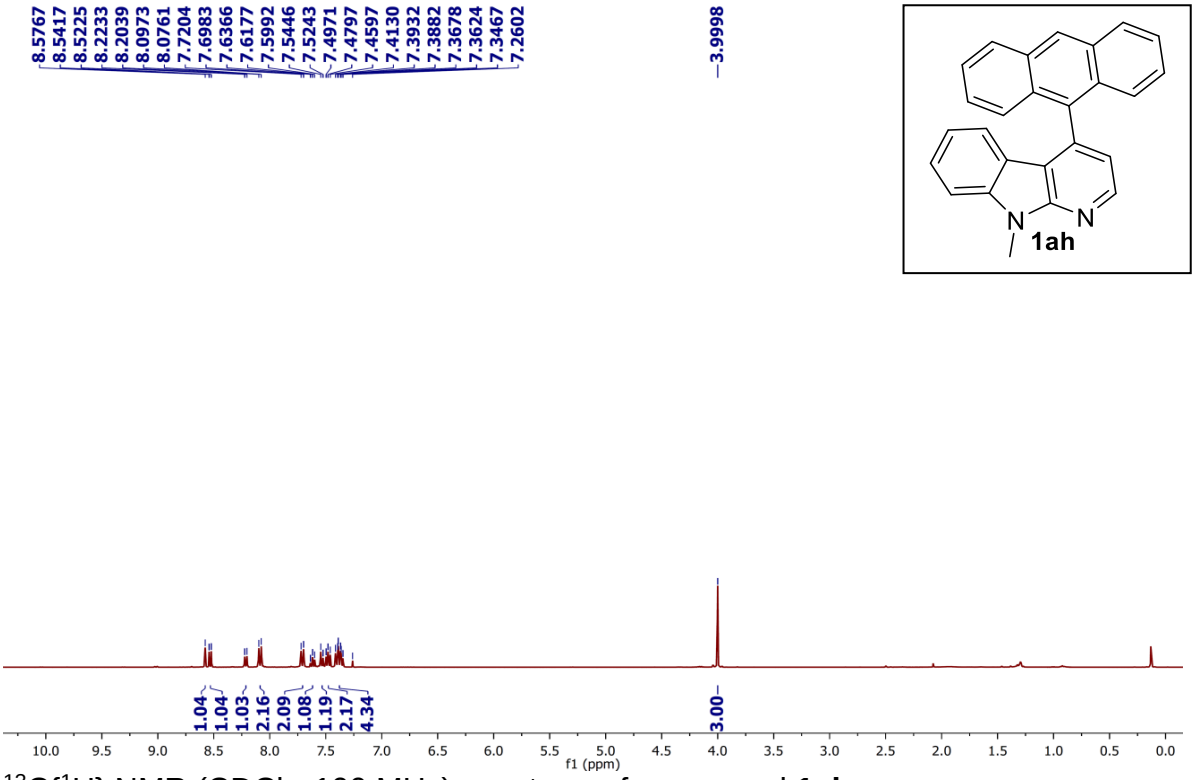
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1af**:



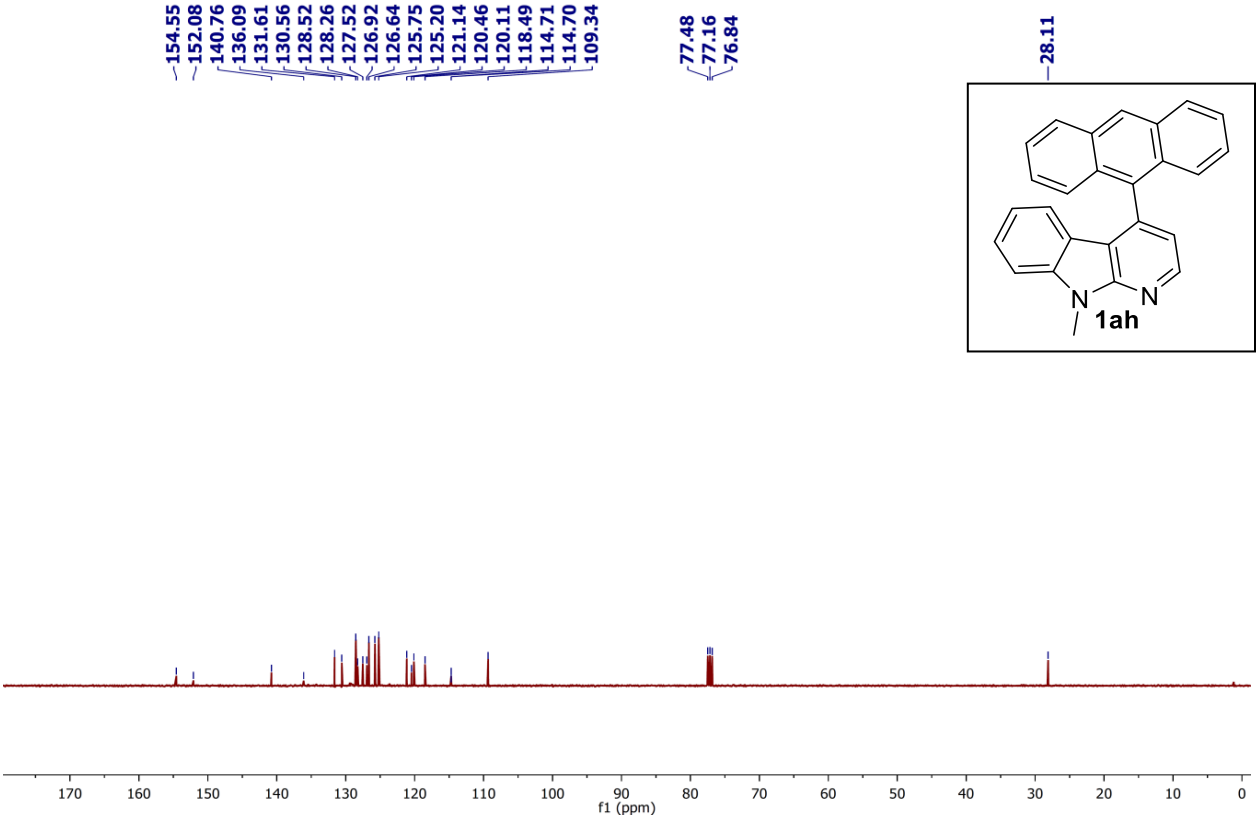
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1af:**



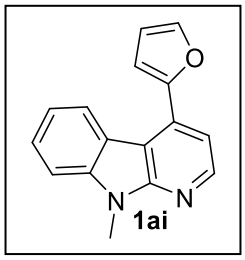
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ah**:

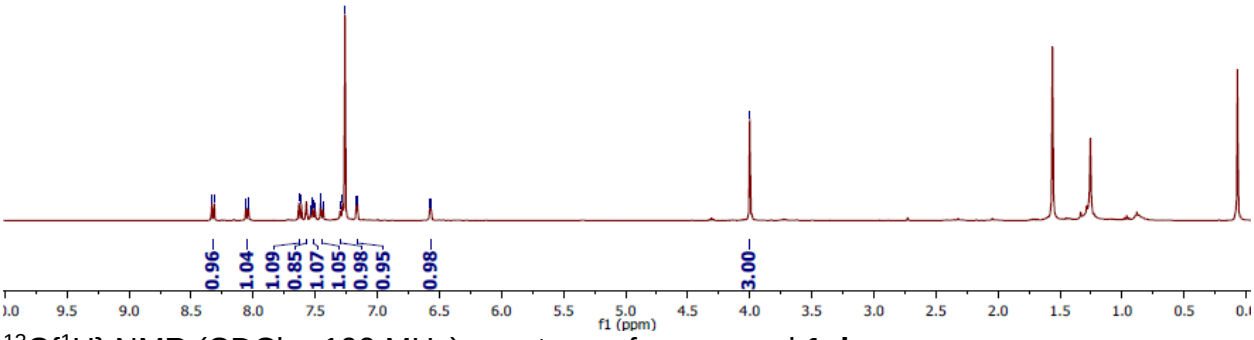


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ah**:

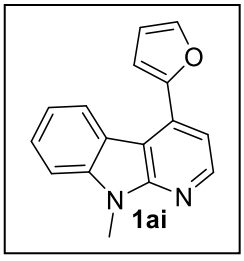


^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ai**:

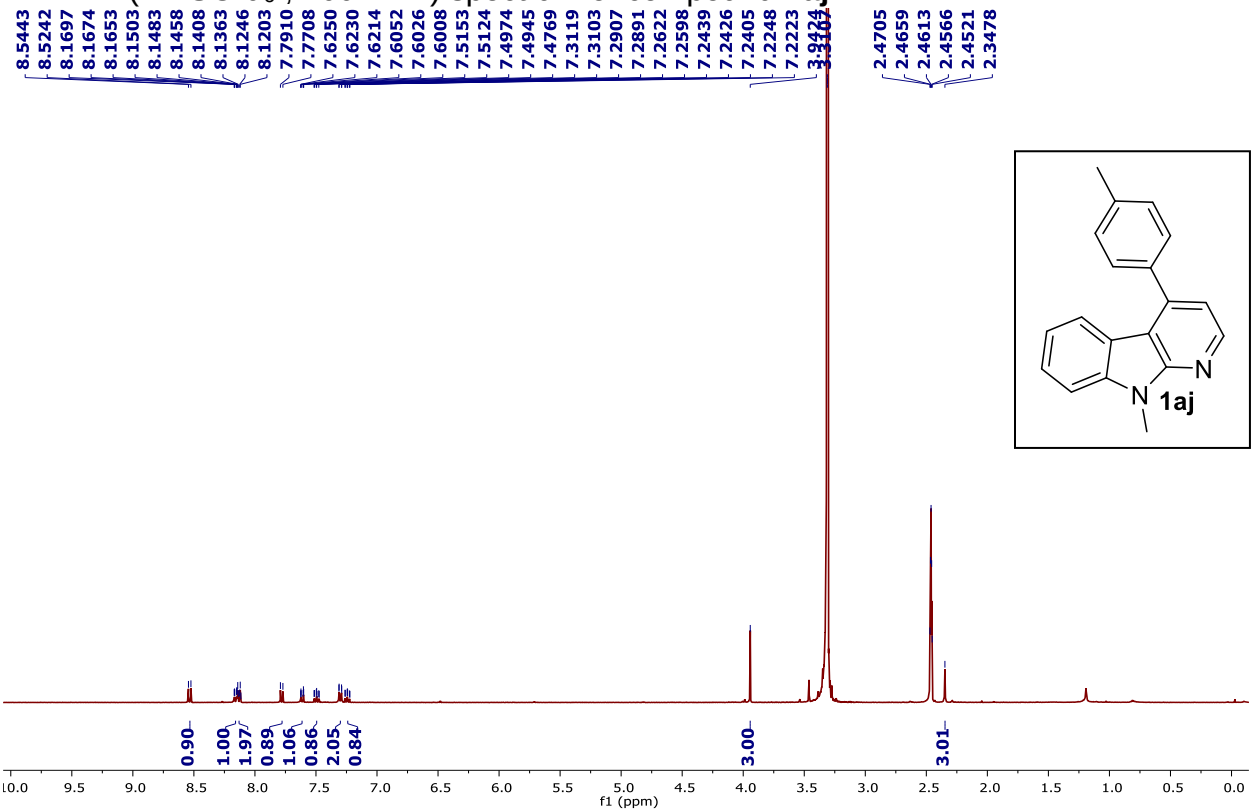




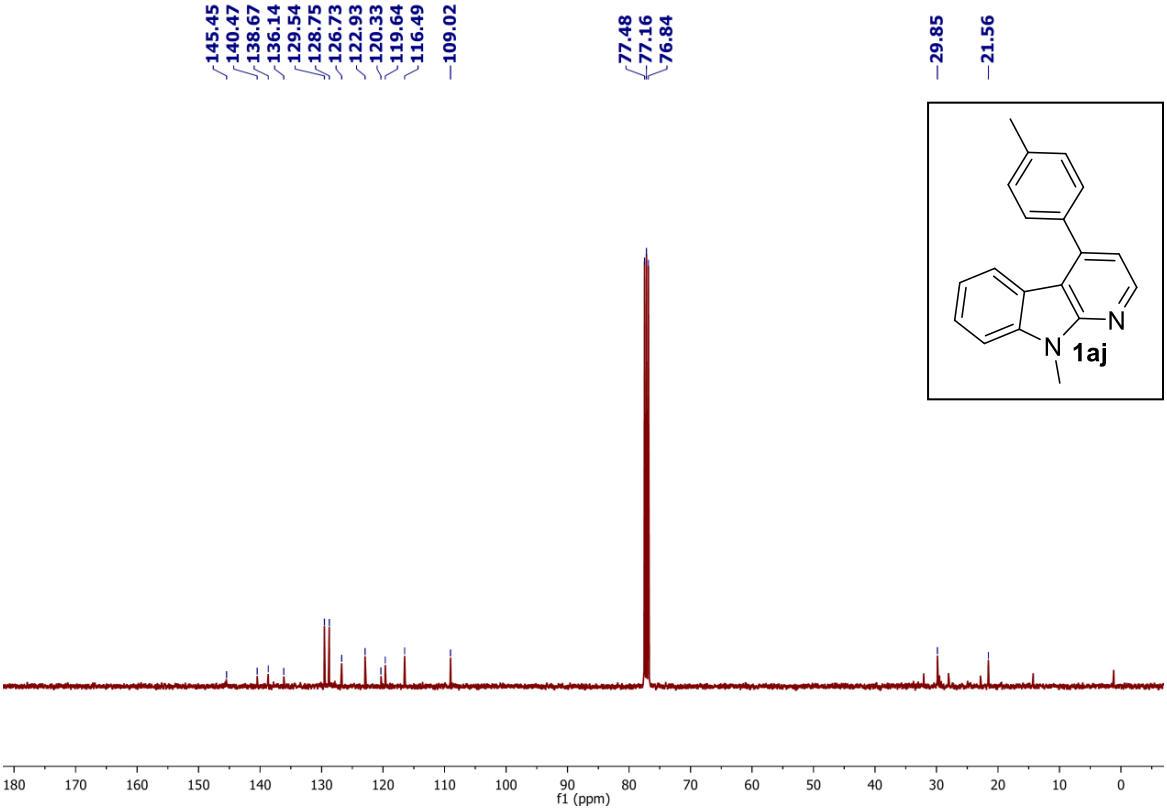
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ai**:



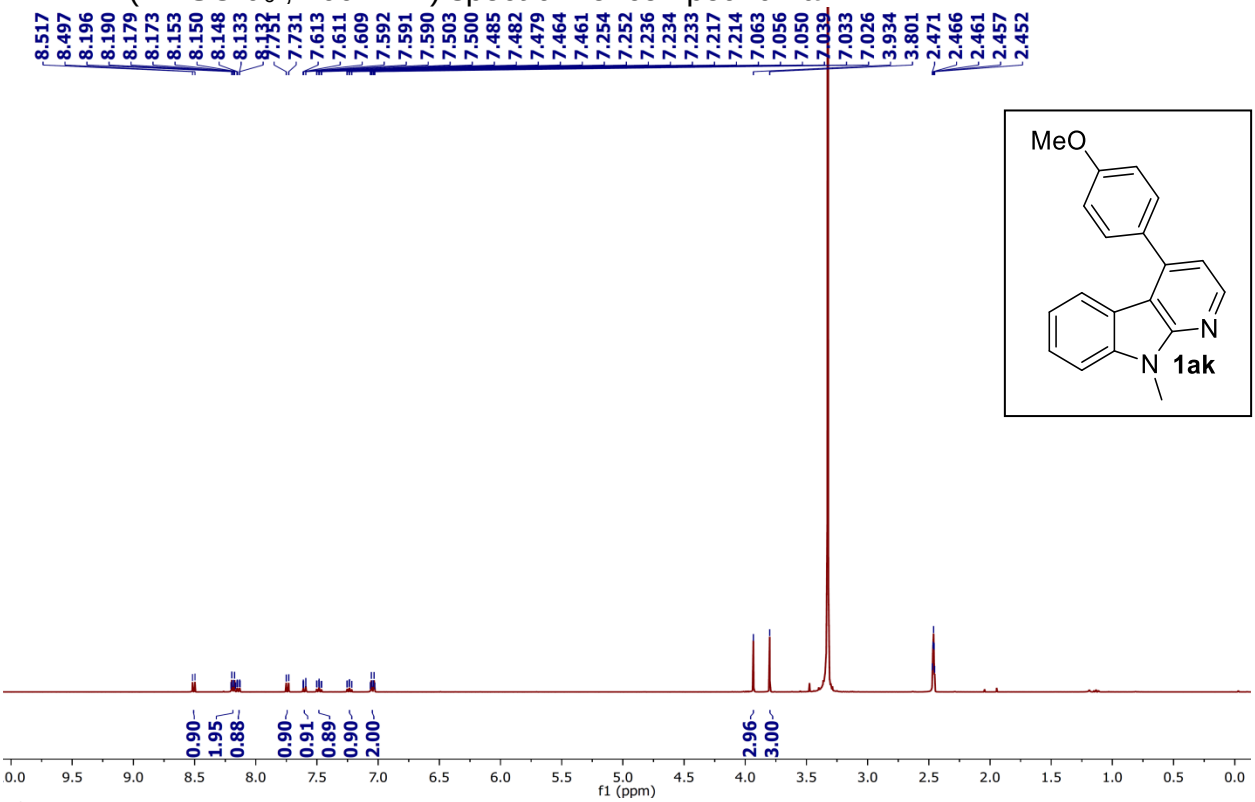
^{1}H NMR (DMSO-d_6 , 400 MHz) spectrum of compound **1aj**:



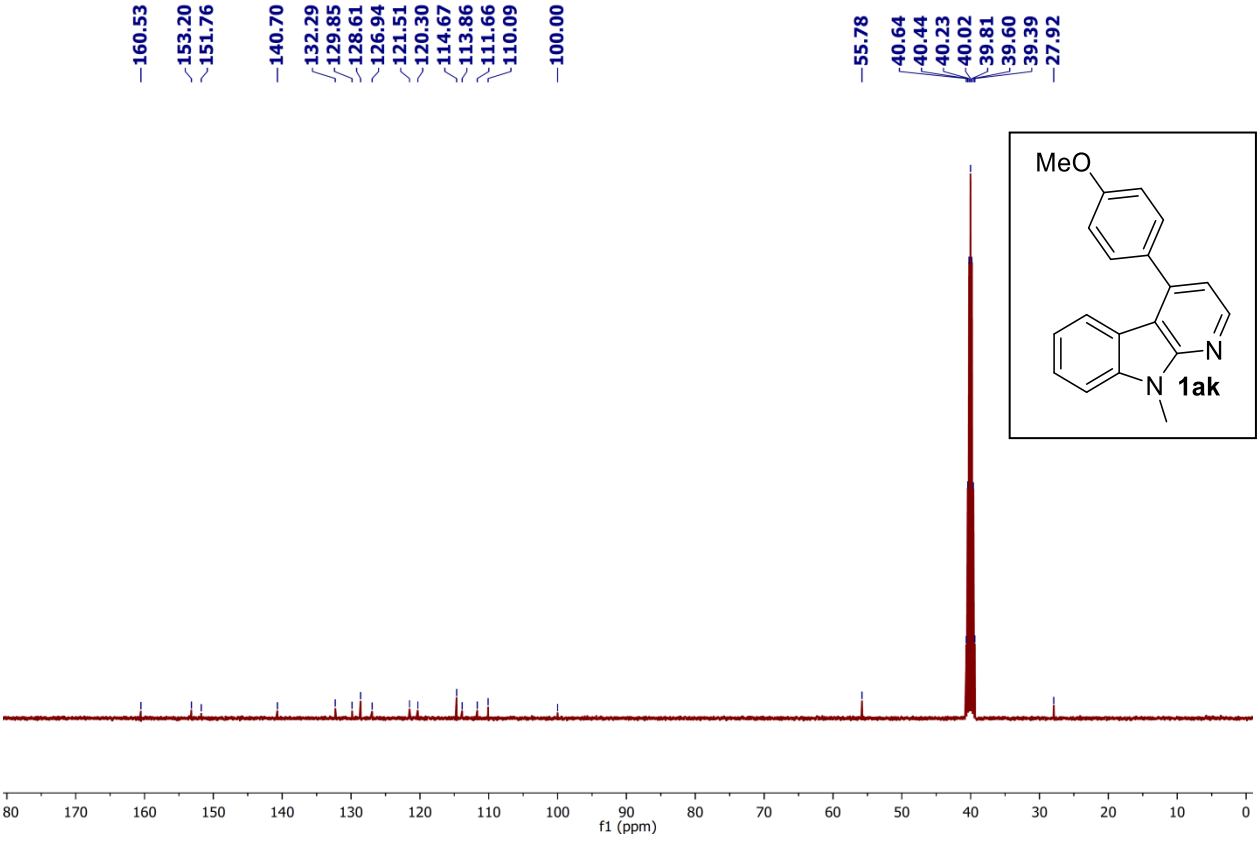
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1aj**:



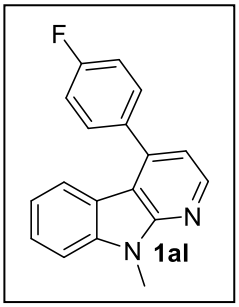
^{1}H NMR (DMSO-d$_6$, 400 MHz) spectrum of compound **1ak**:

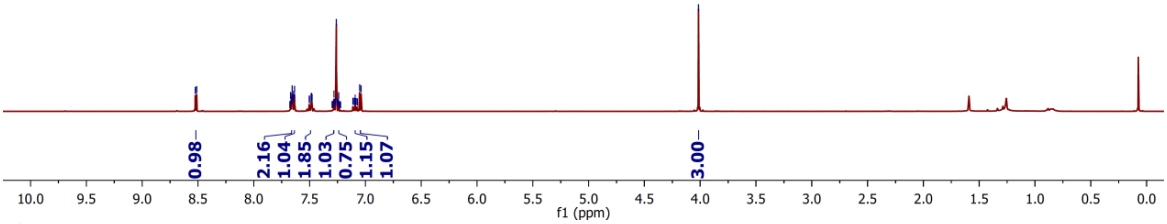


^{13}C{^{1}H} NMR (DMSO-d$_6$, 100 MHz) spectrum of compound **1ak**:

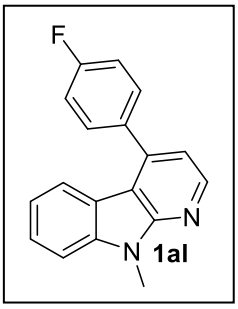


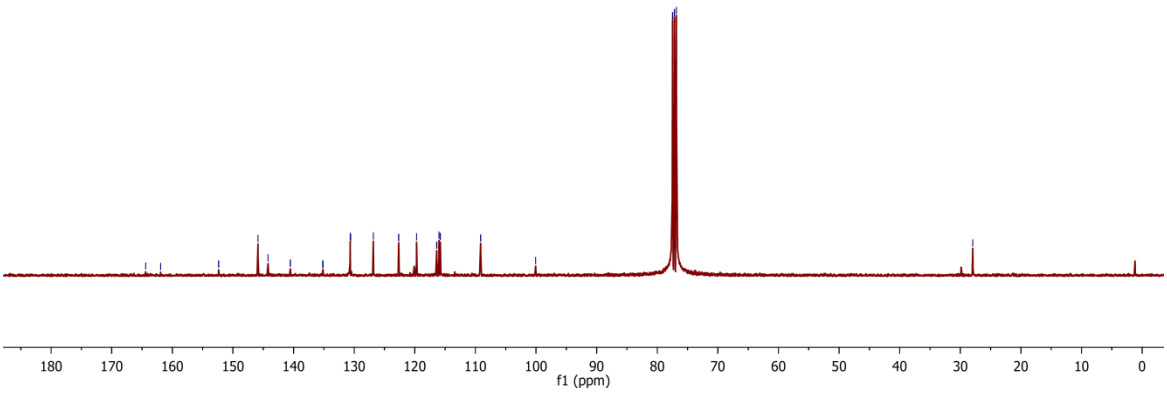
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1al**:



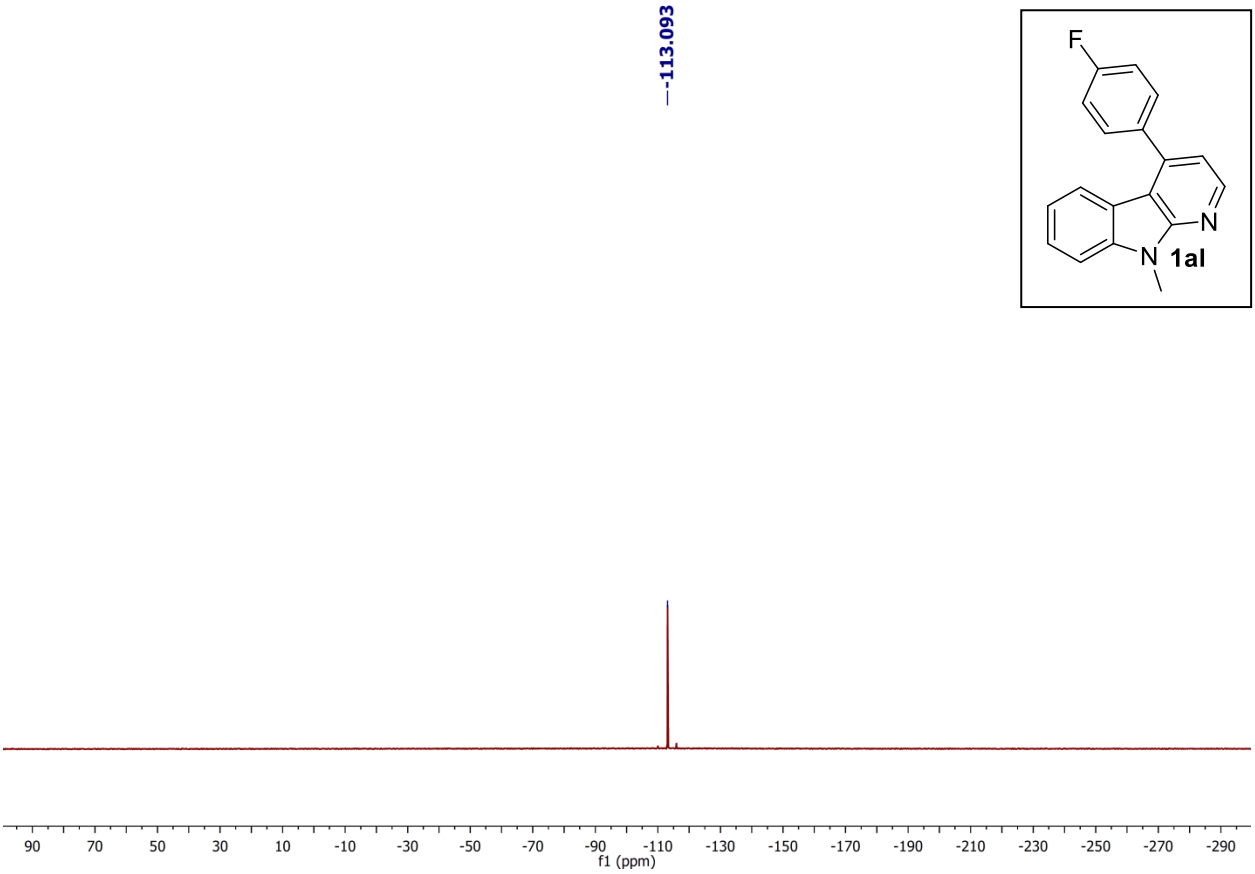


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1al**:

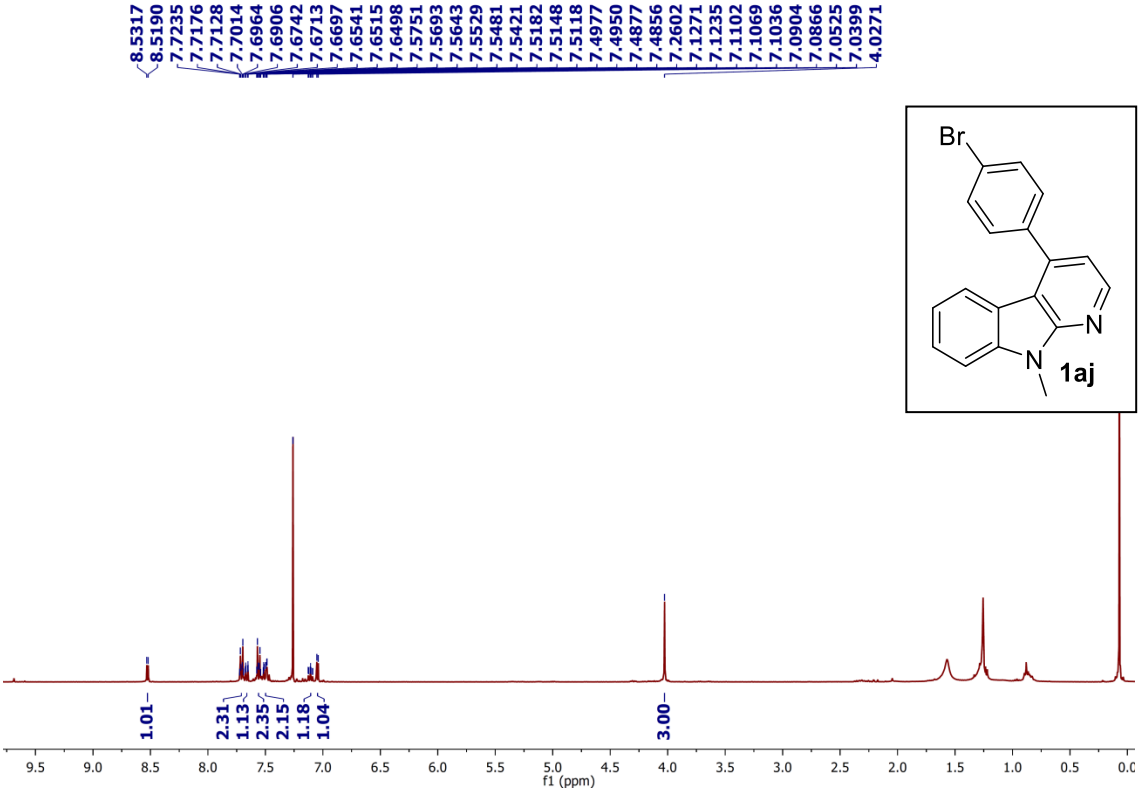




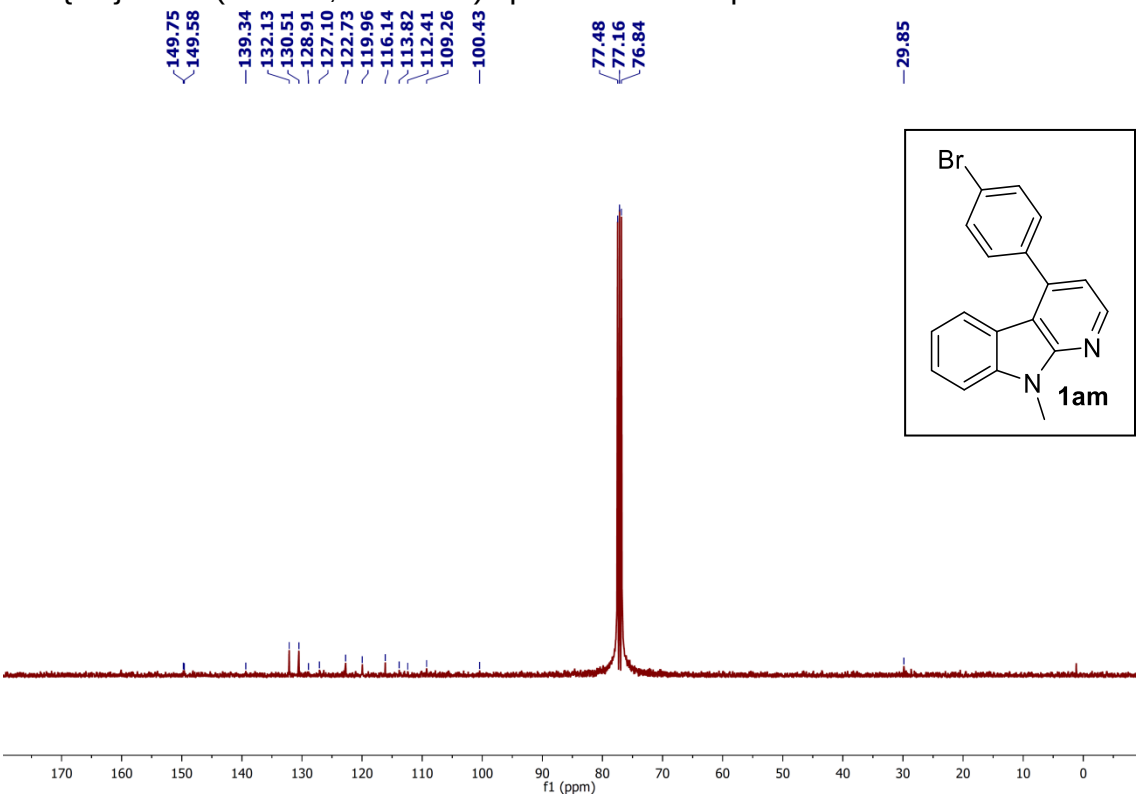
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 376 MHz) spectrum of compound **1al:**



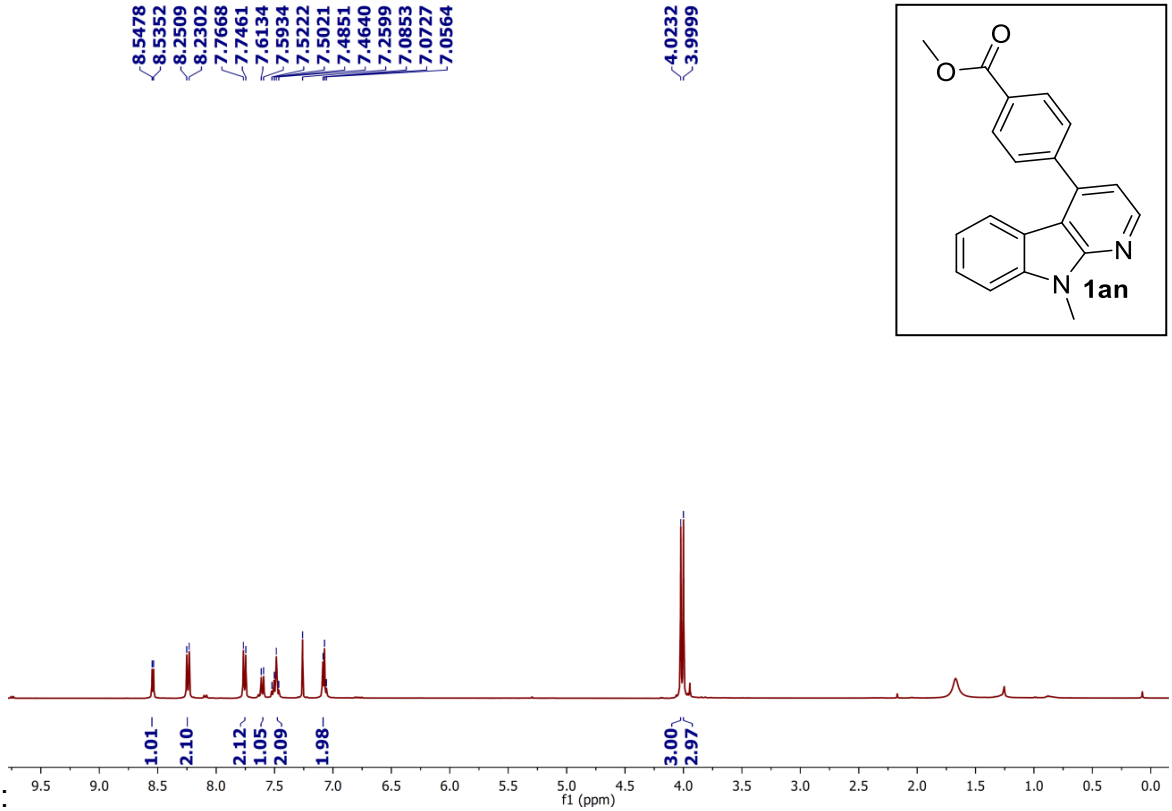
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1am**:



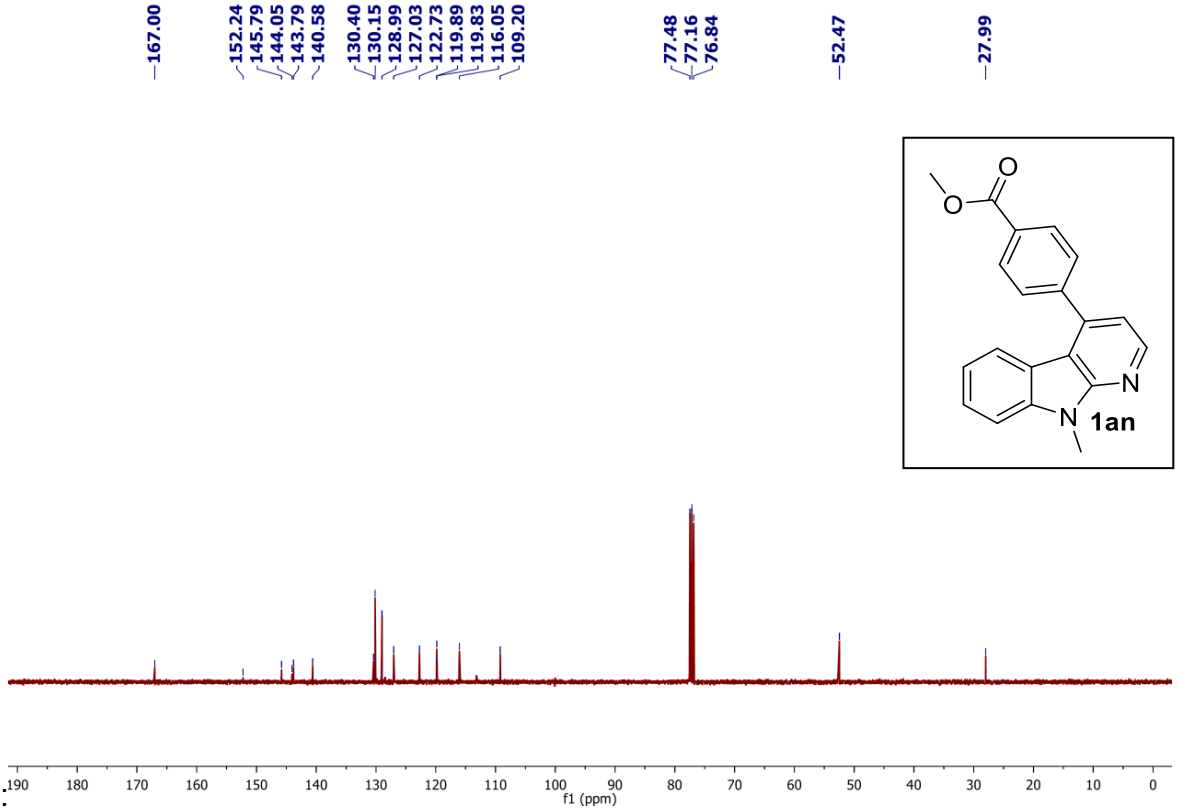
13C{1H} NMR (CDCl3 , 100 MHz) spectrum of compound **1am**:



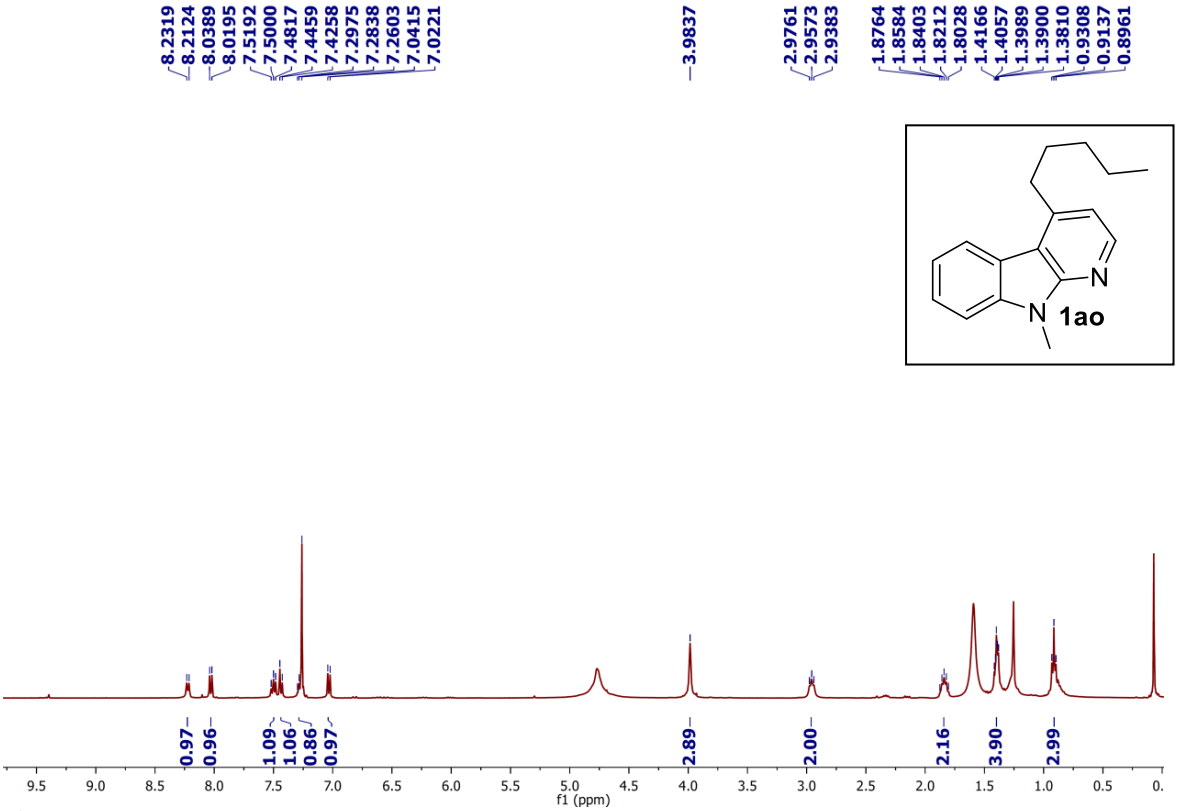
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1an**



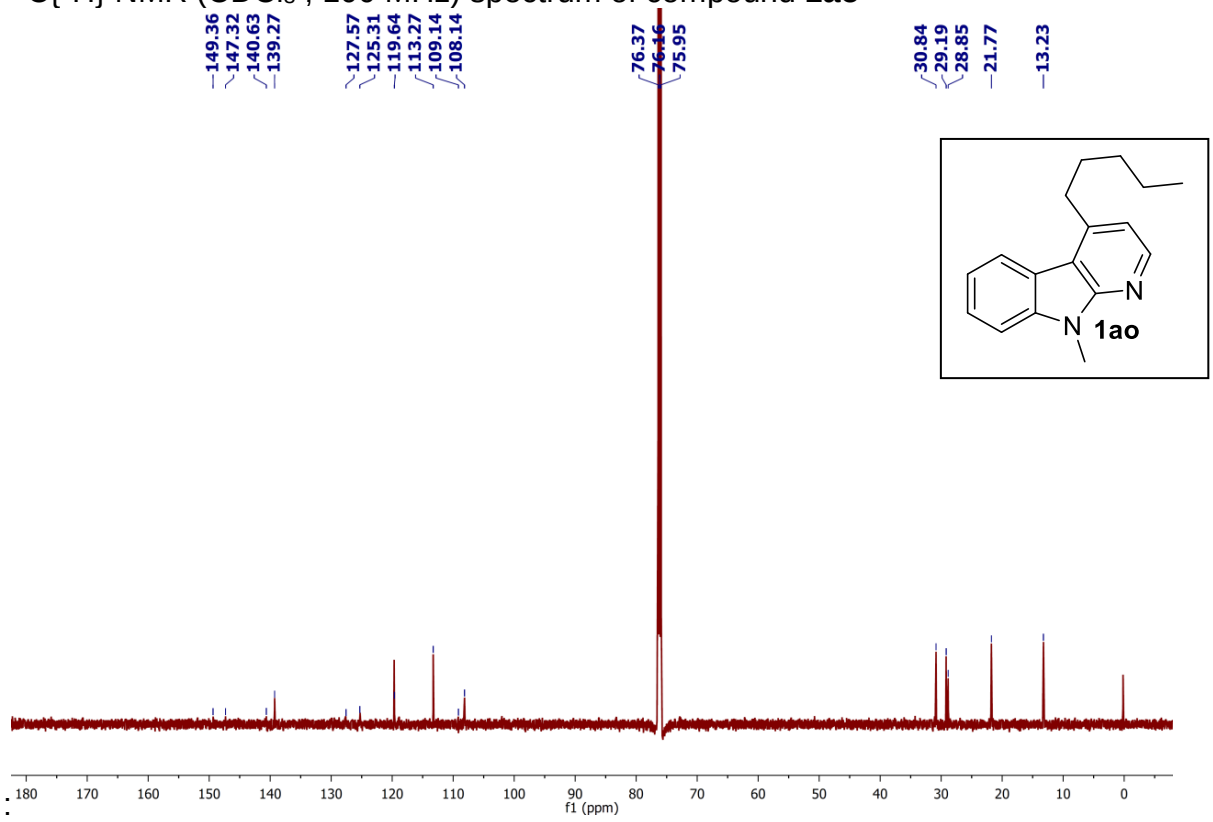
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1an**



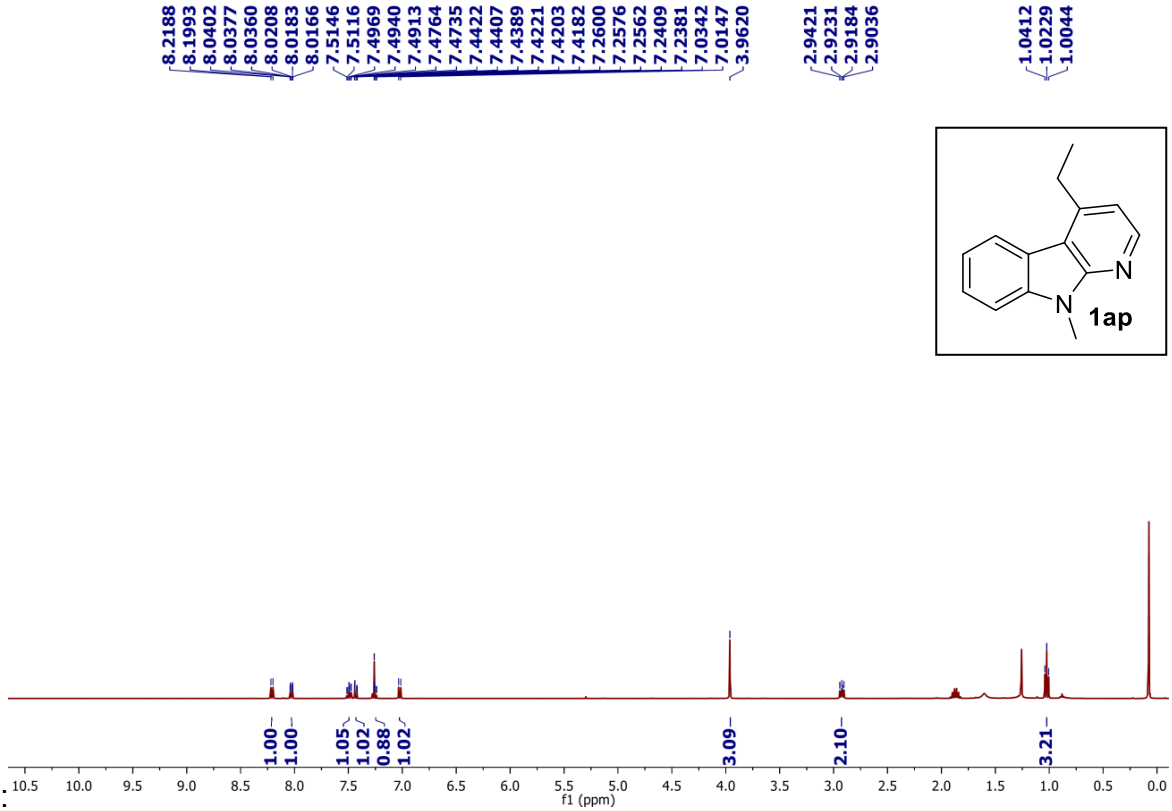
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ao**:



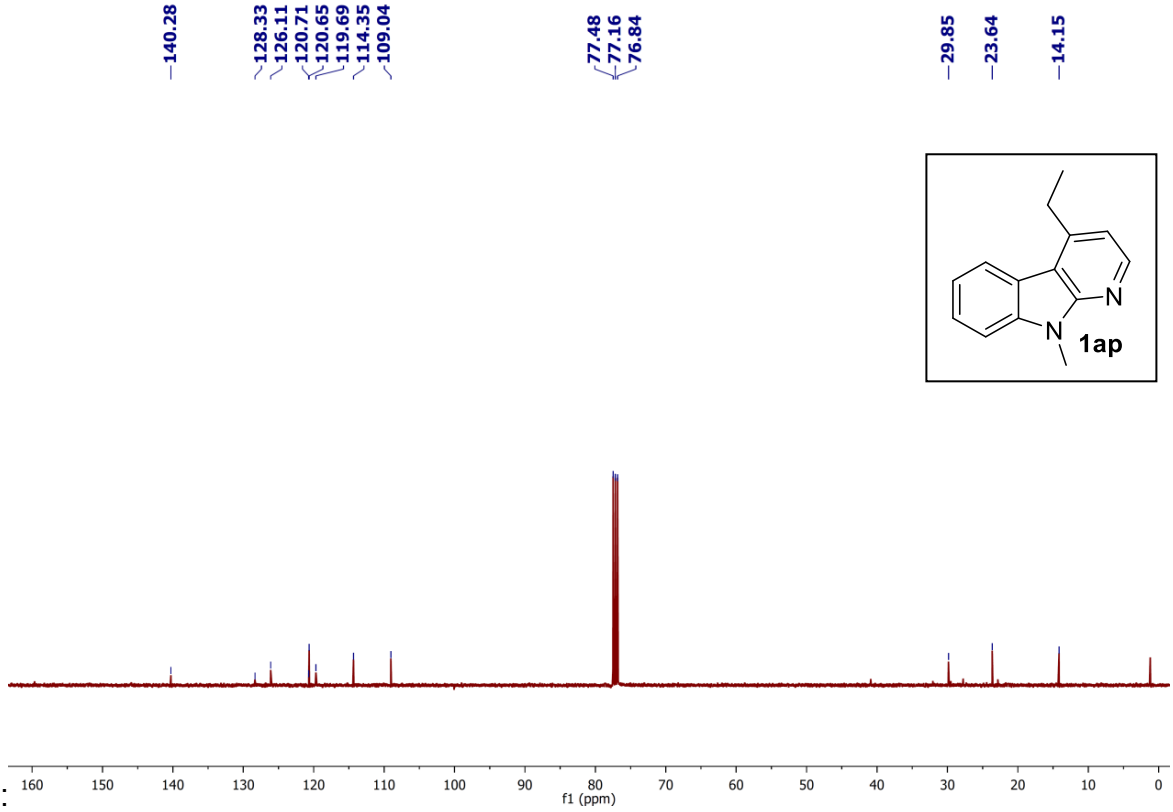
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ao**



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ap**

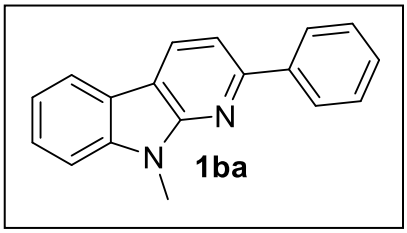


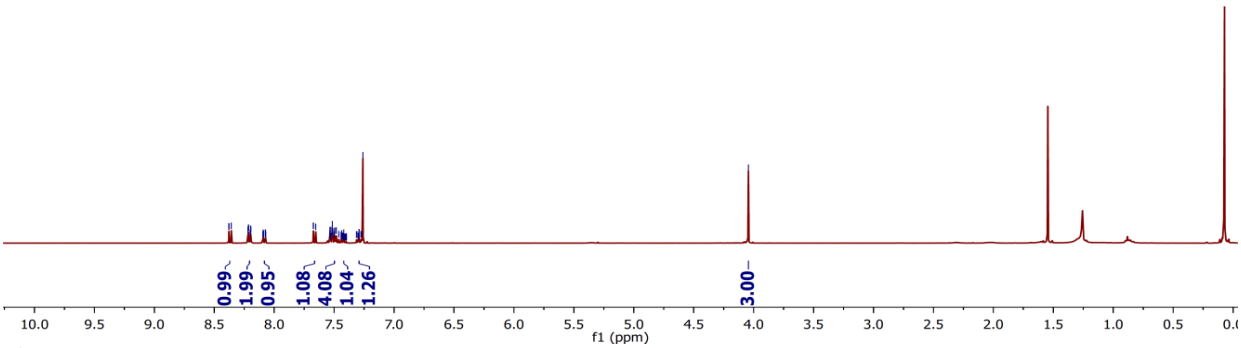
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ap**



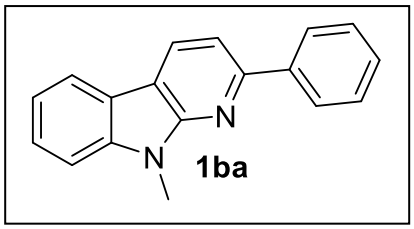
31. NMR spectra of productss1ba-1bw:

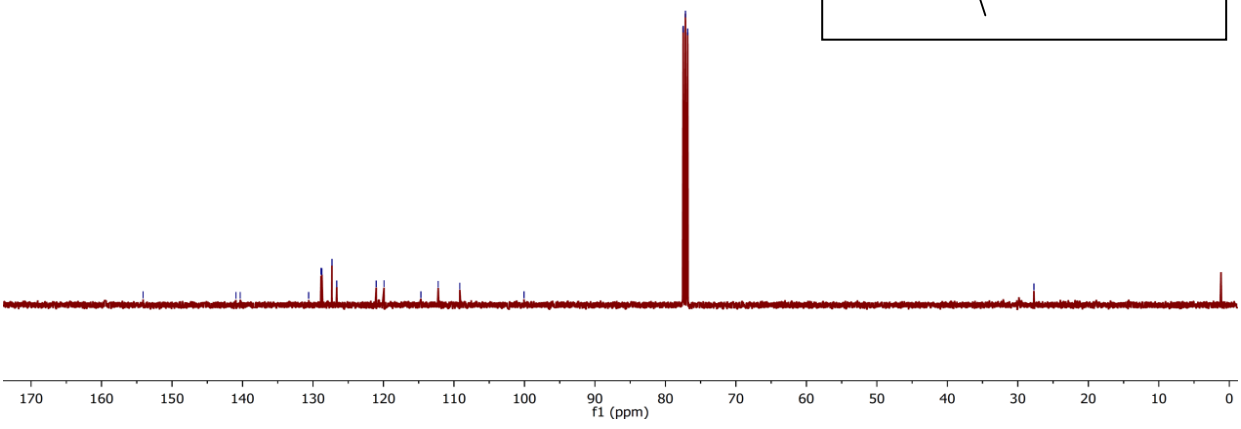
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1ba**:



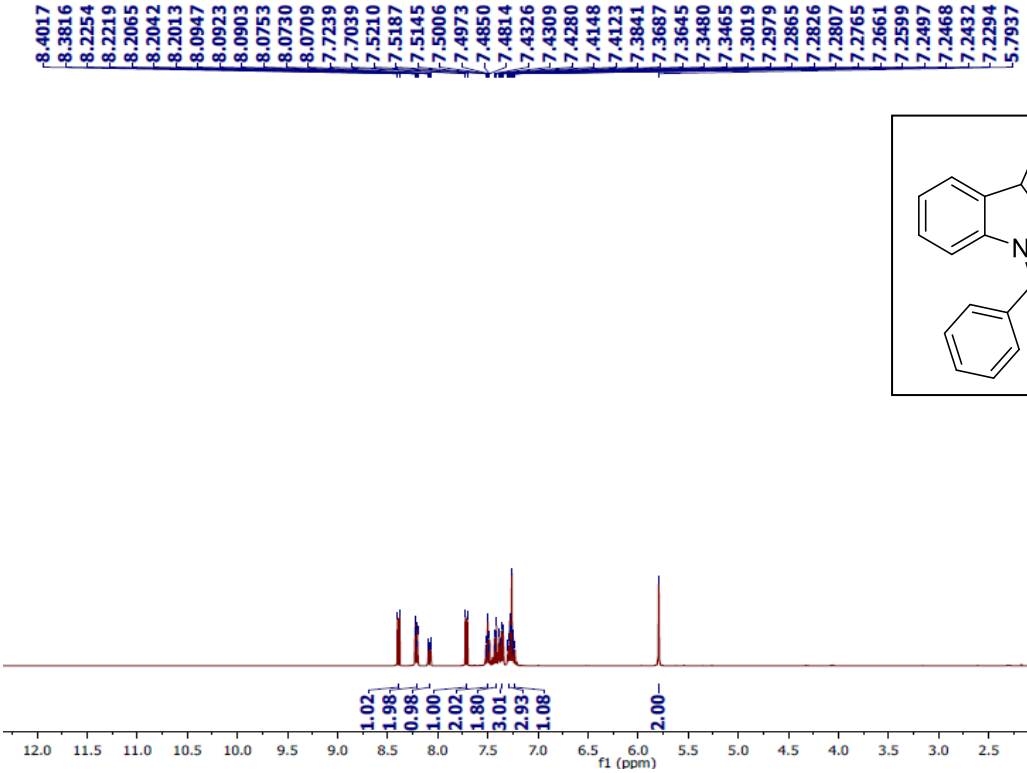


^{13}C{1H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1ba**:

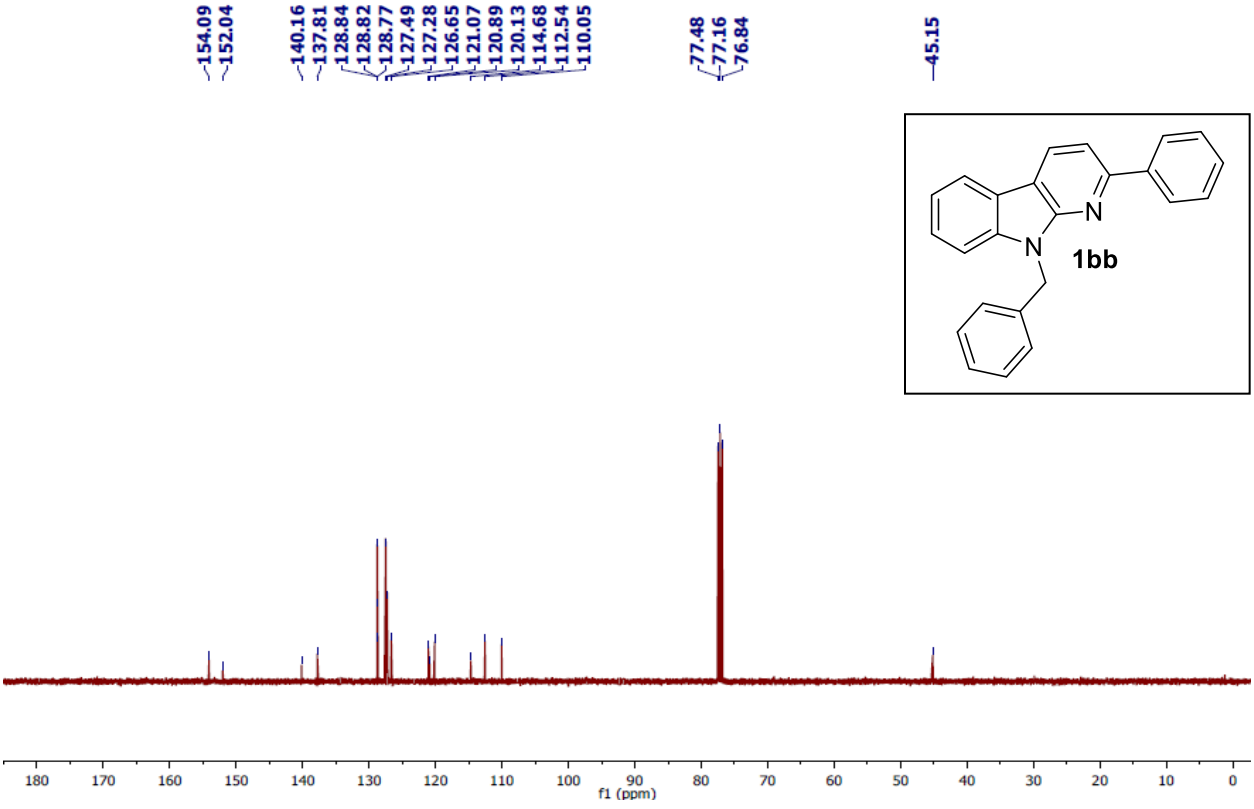




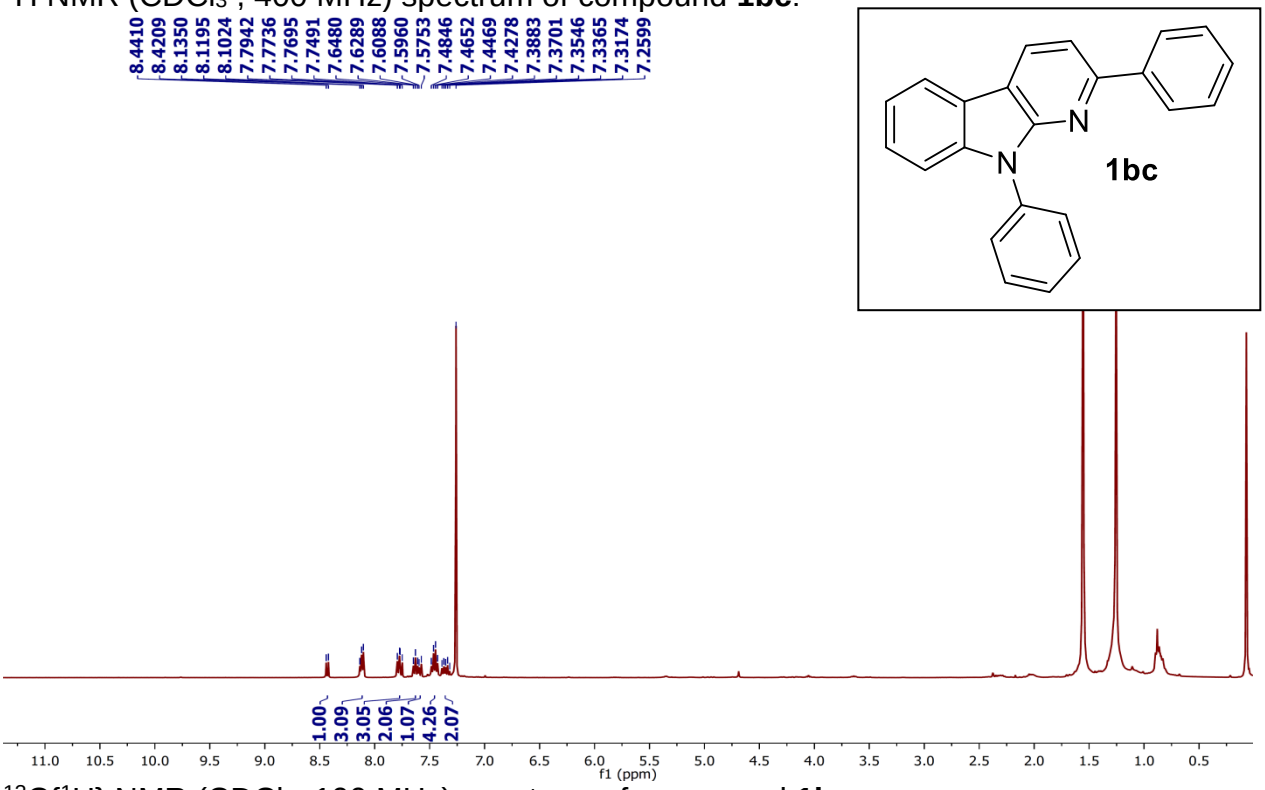
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bb**:



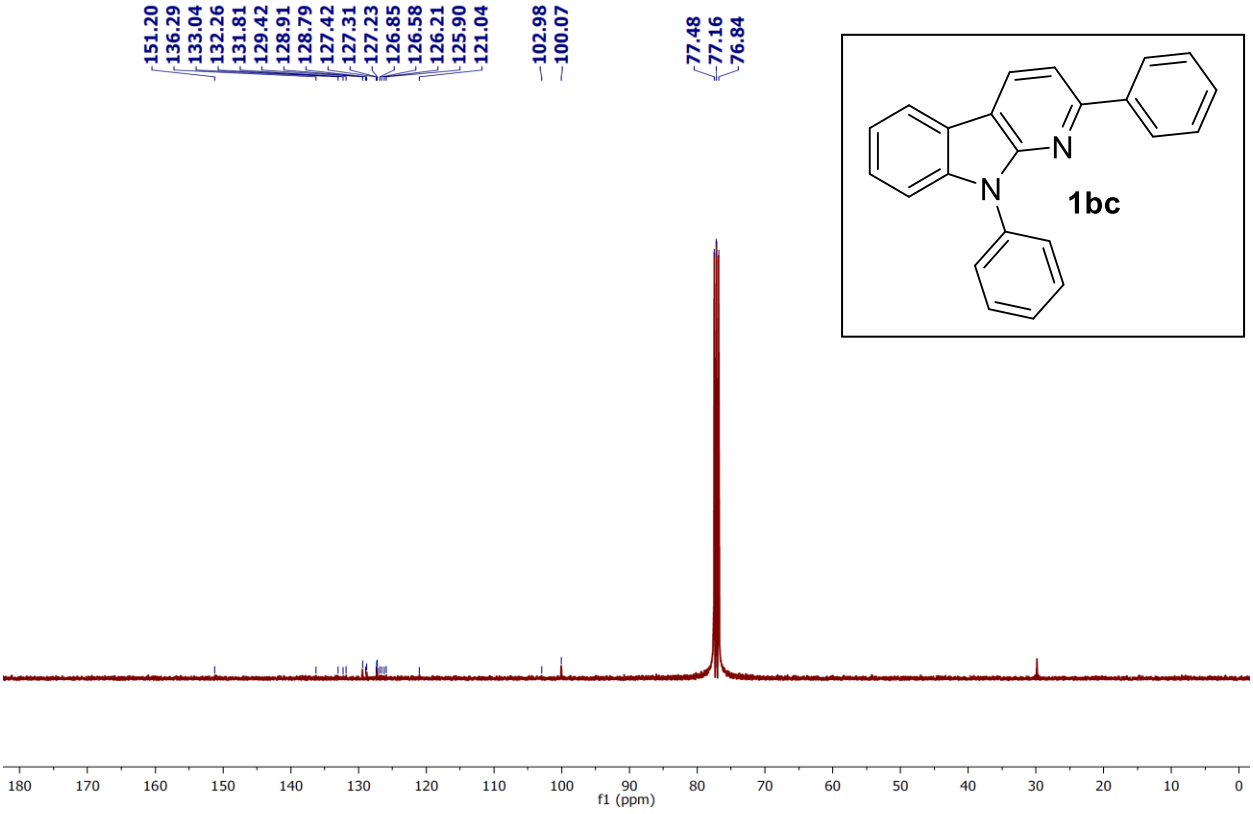
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bb**:



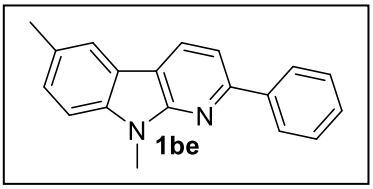
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bc**:

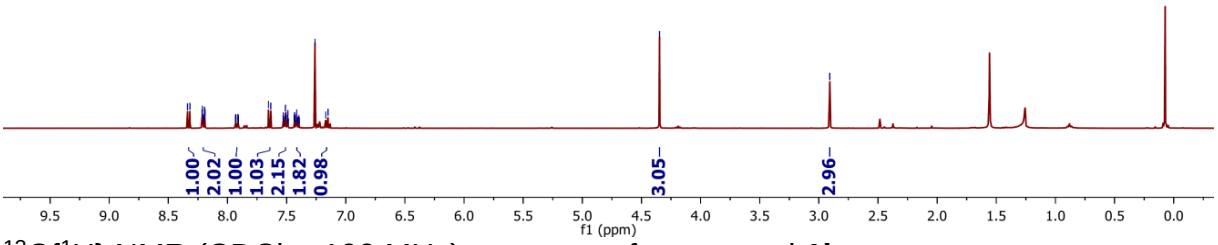


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bc**:

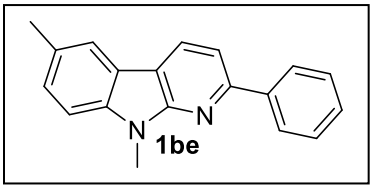


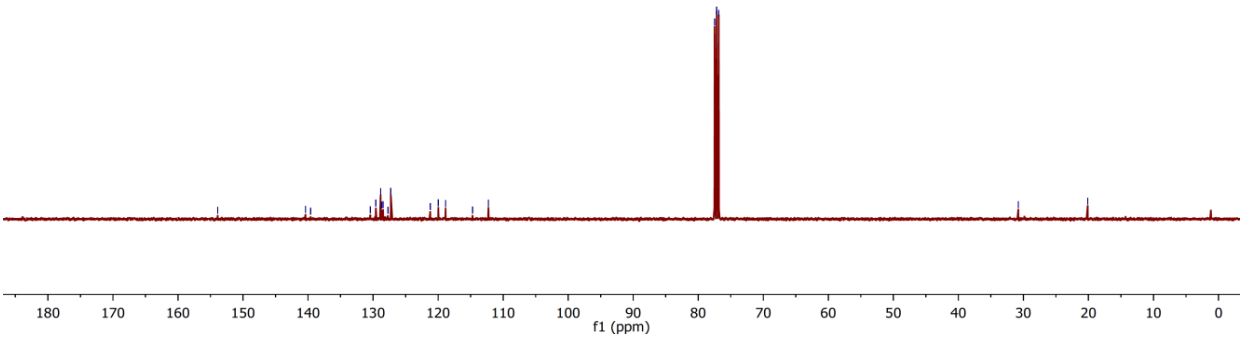
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1be**:



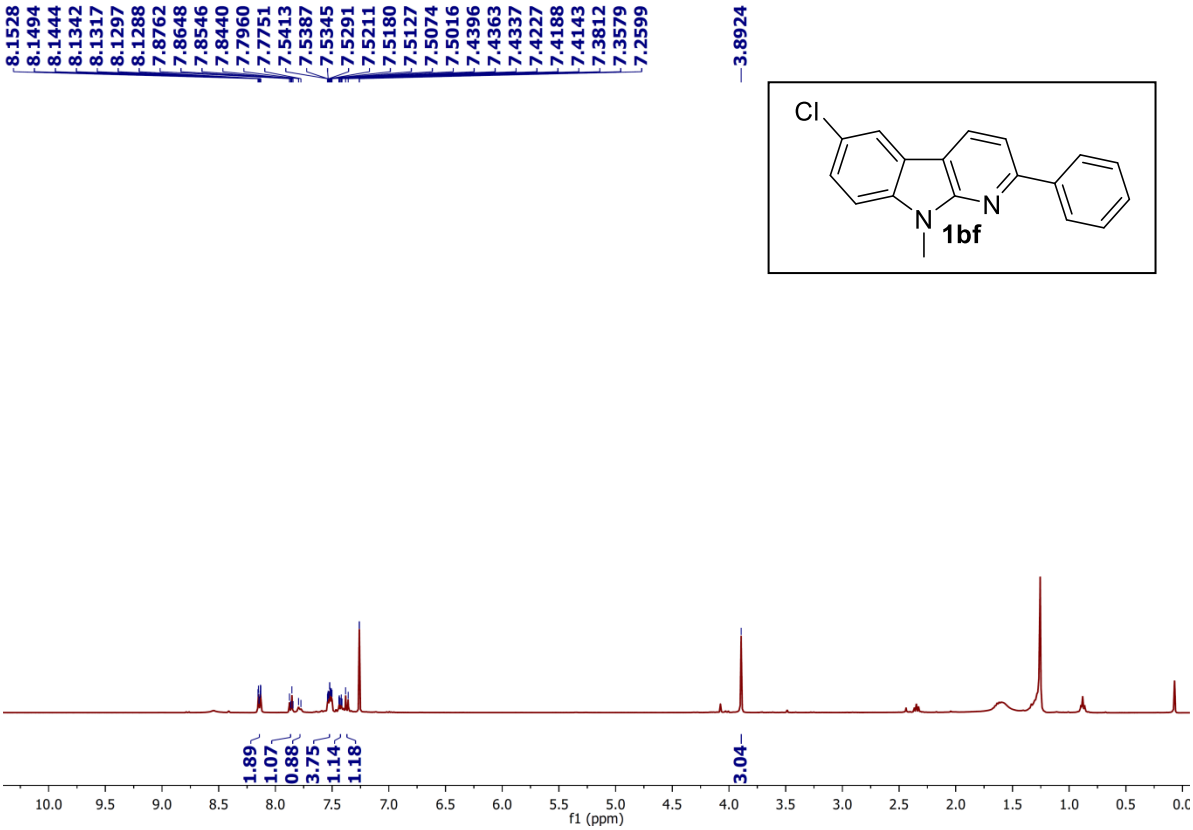


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1be:**

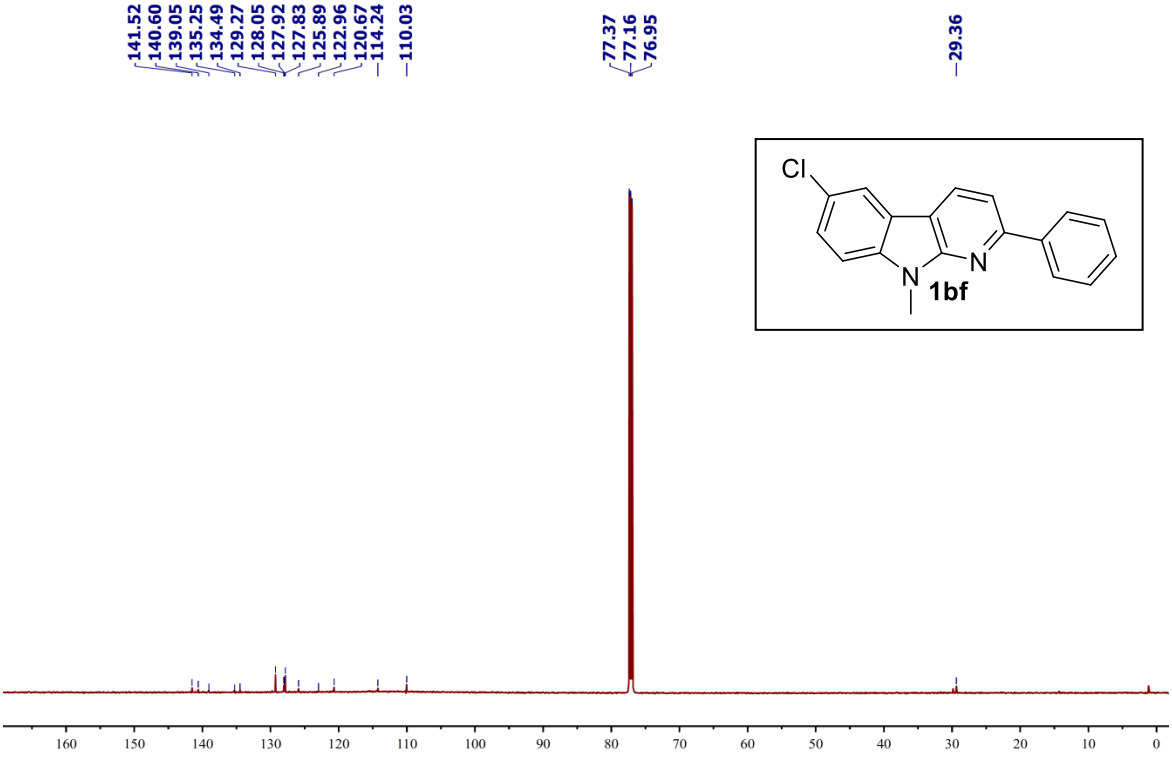




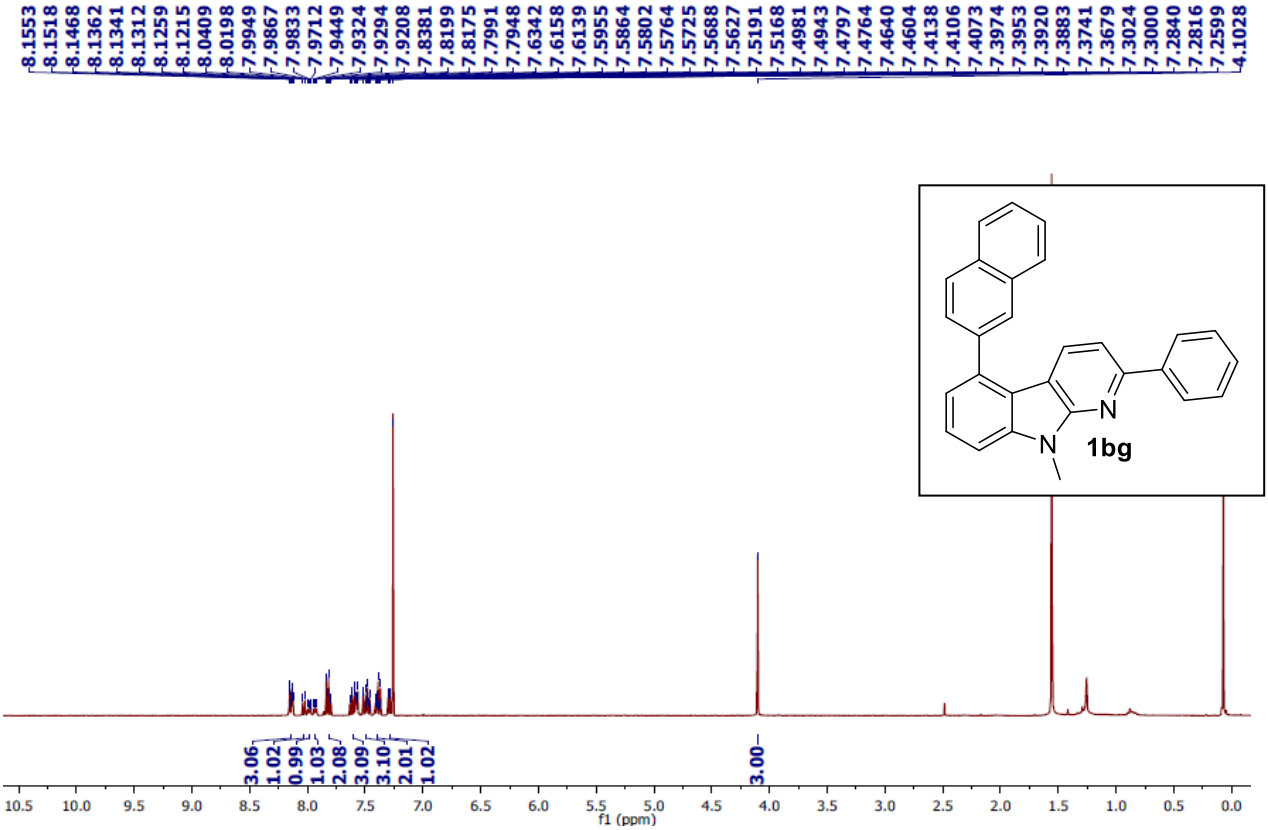
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bf**:



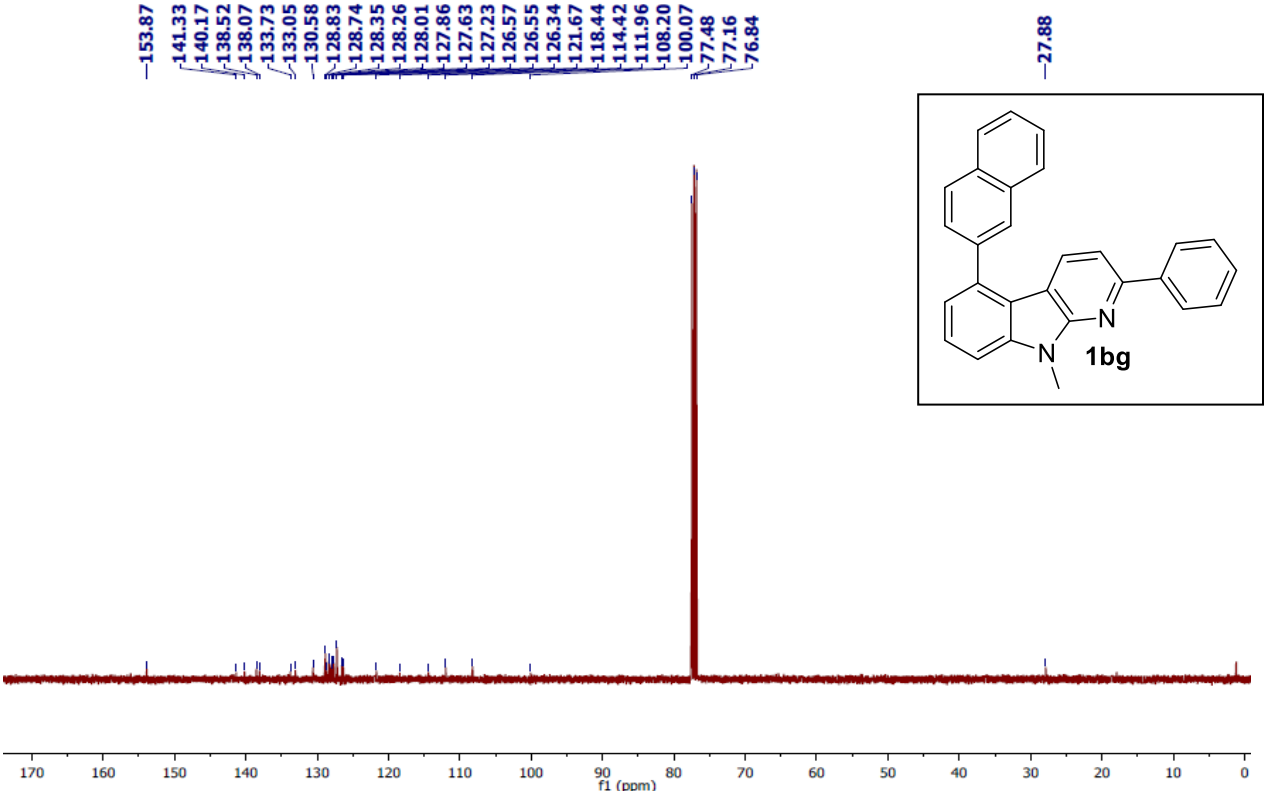
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bf:**



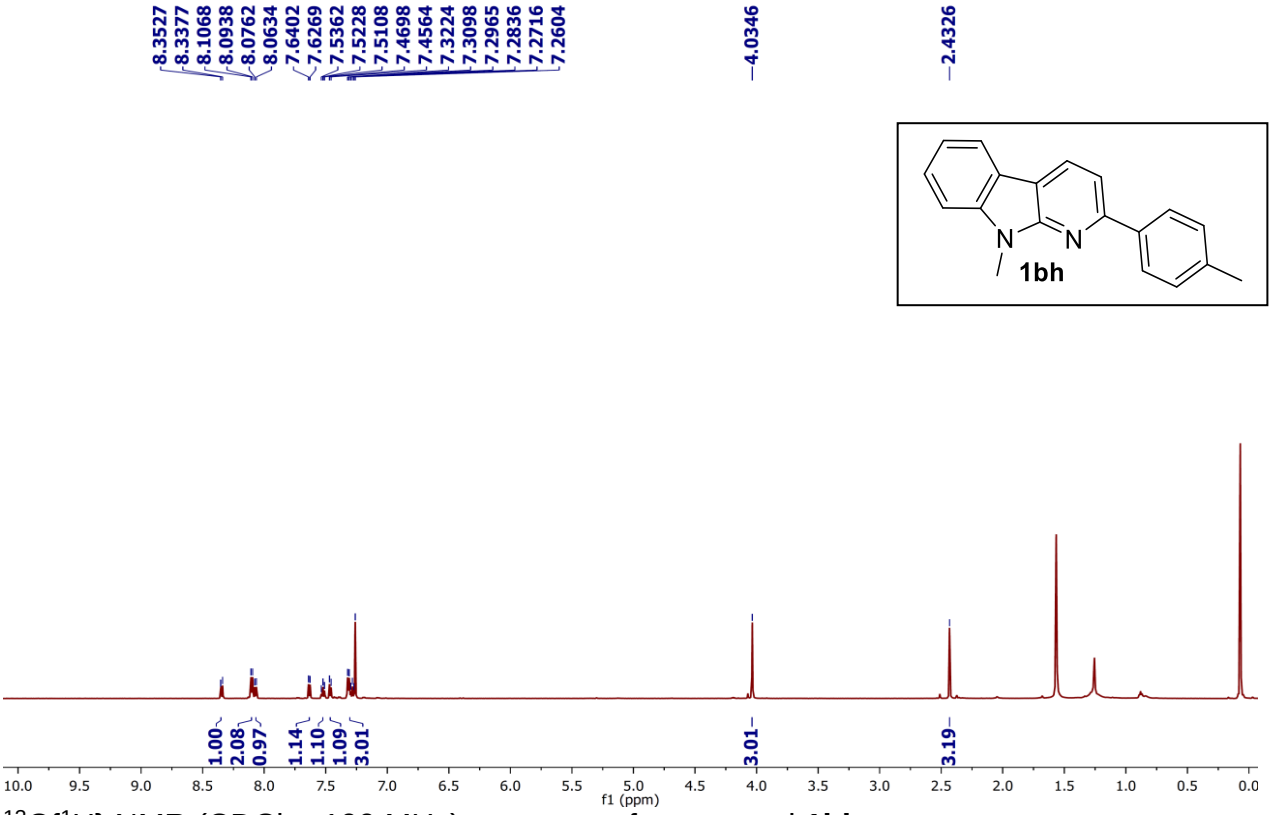
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bg**:



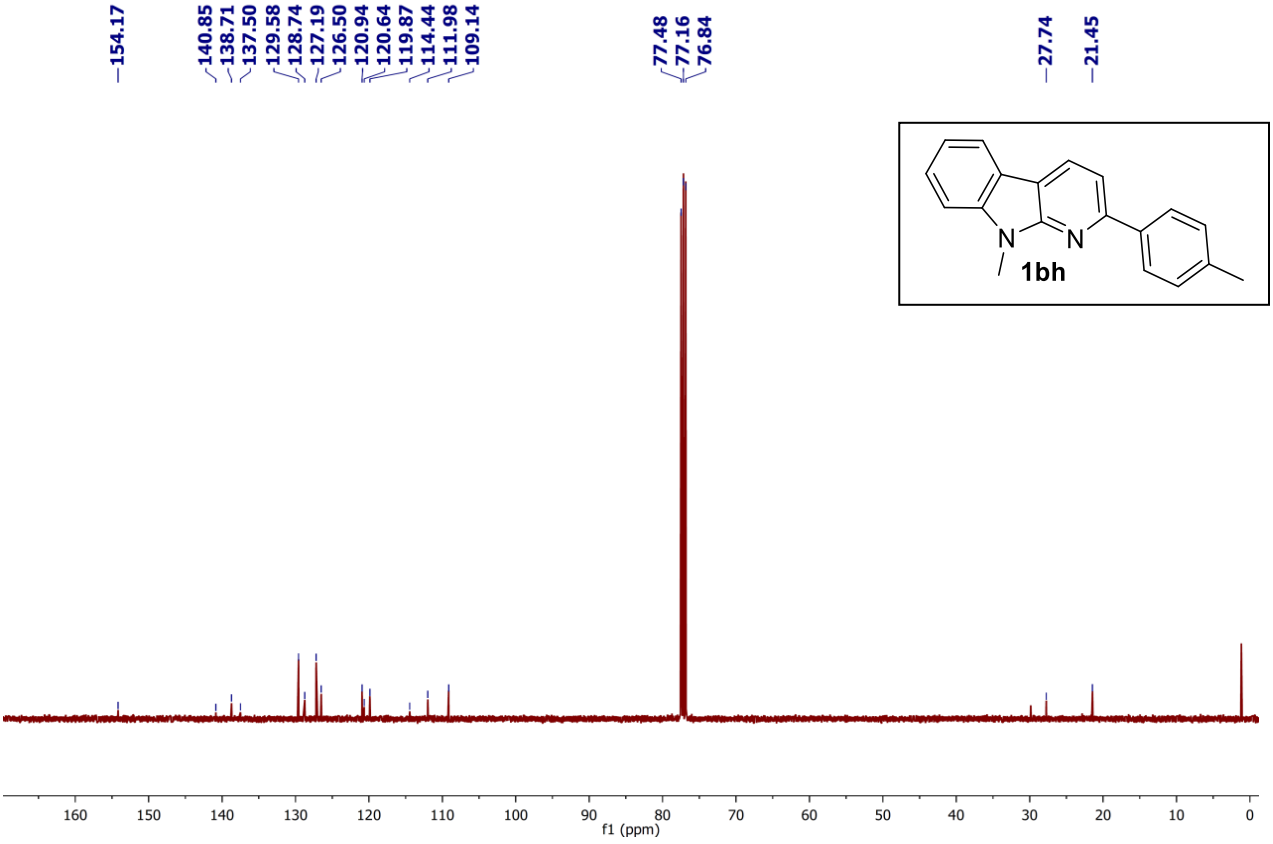
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bg:**



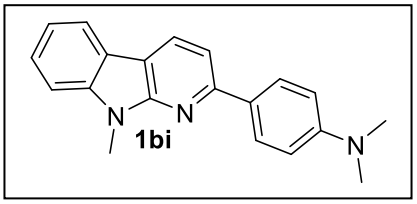
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bh:**

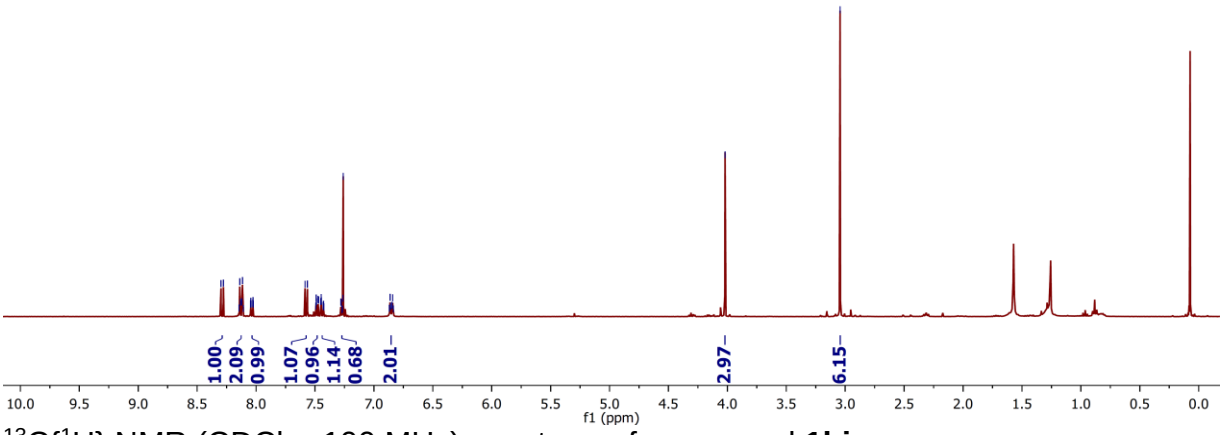


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bh**:

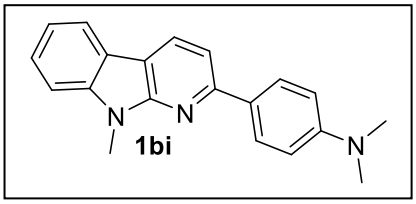


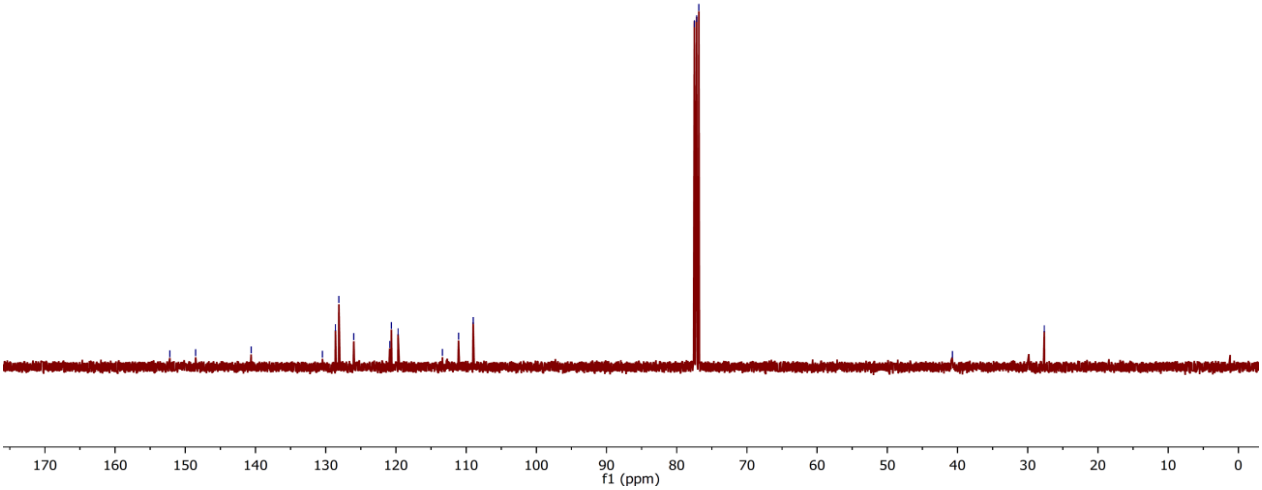
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bi**:



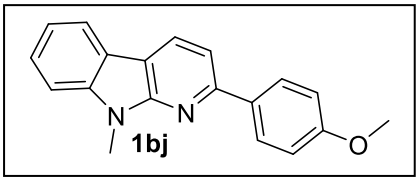


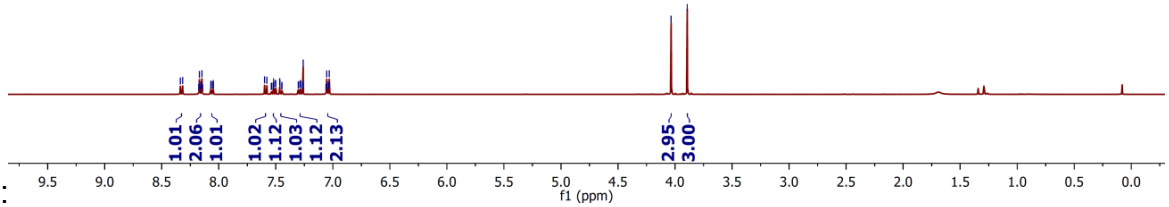
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bi**:





^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bj**





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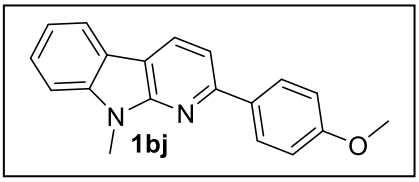
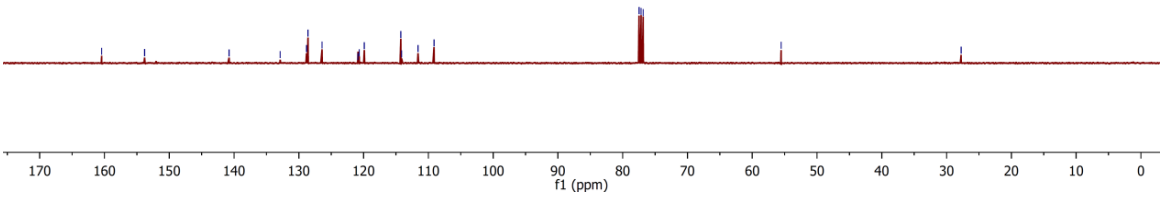
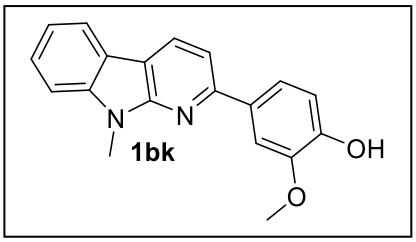
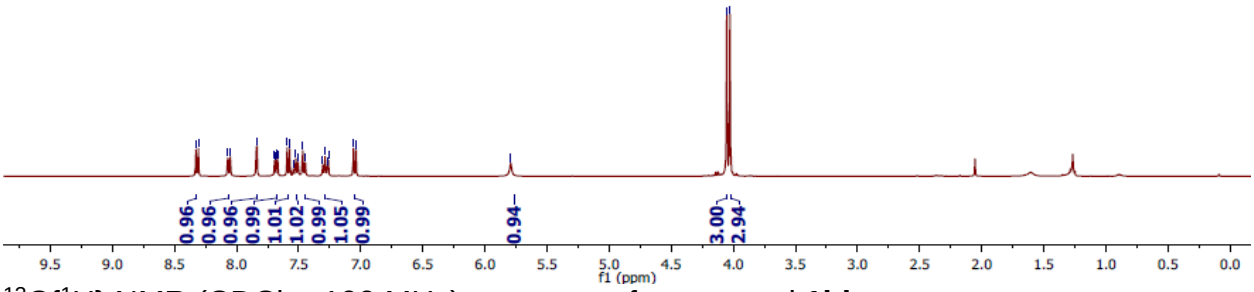
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bj**



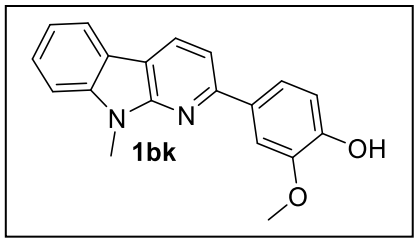


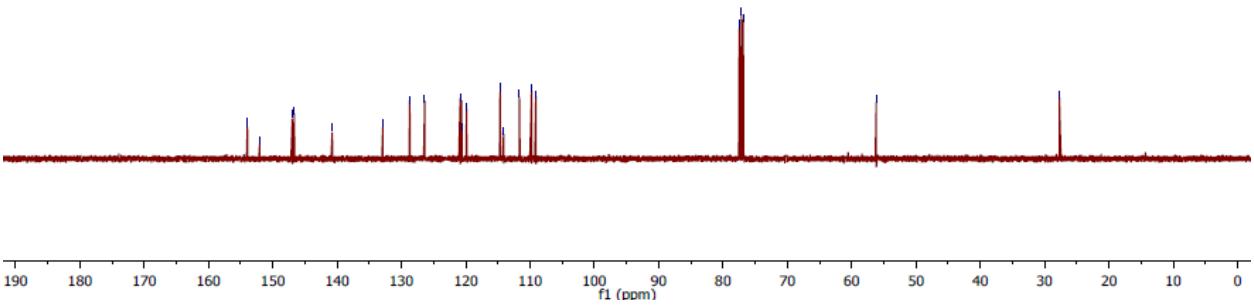
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bk**:



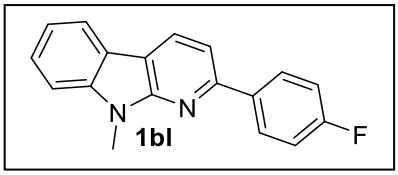


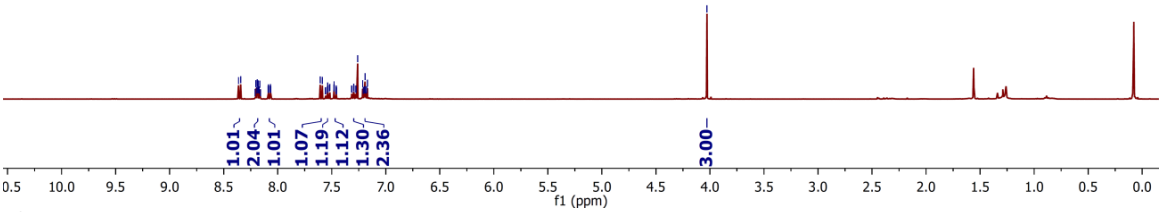
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bk**:



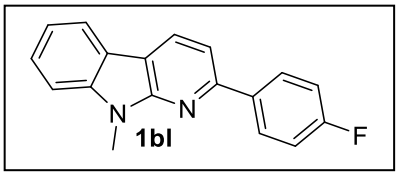


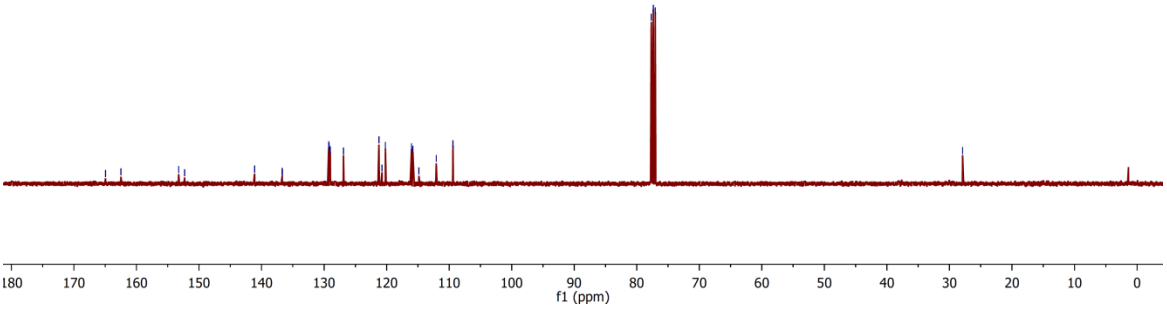
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bl**:



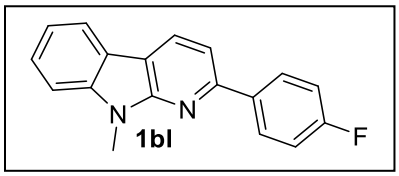


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bl**

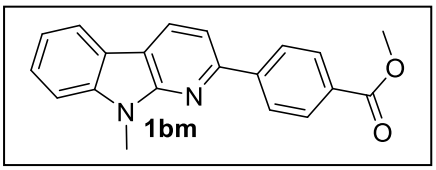


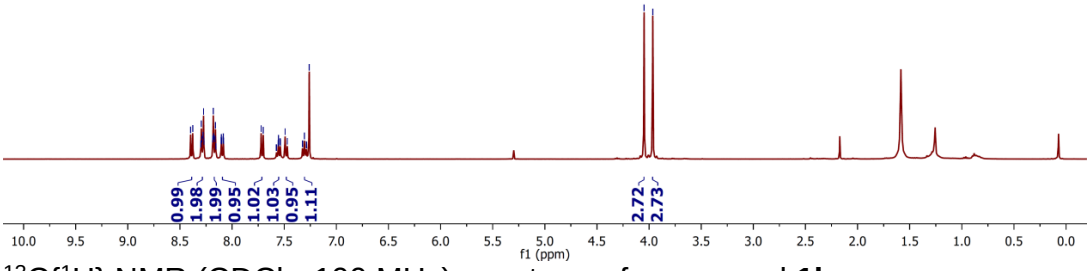


$^{19}F\{^{1}H\}$ NMR (CDCl3, 376 MHz) spectrum of compound **1bl:**

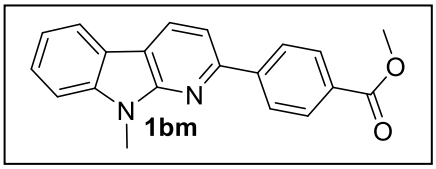


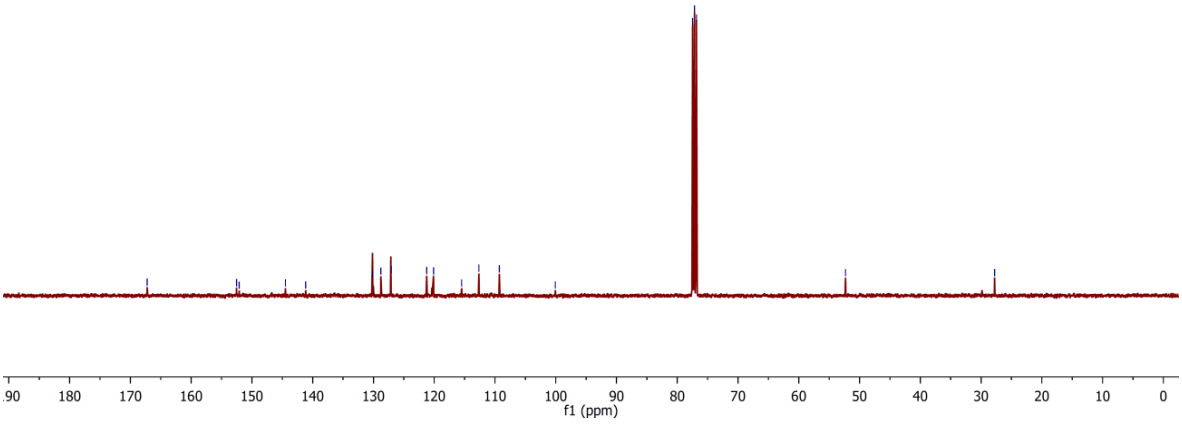
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bm**:



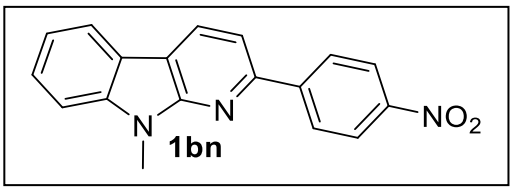


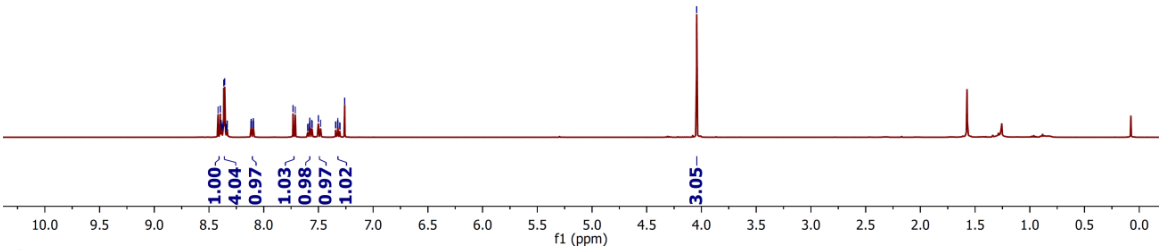
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bm**



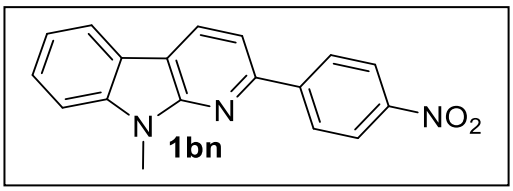


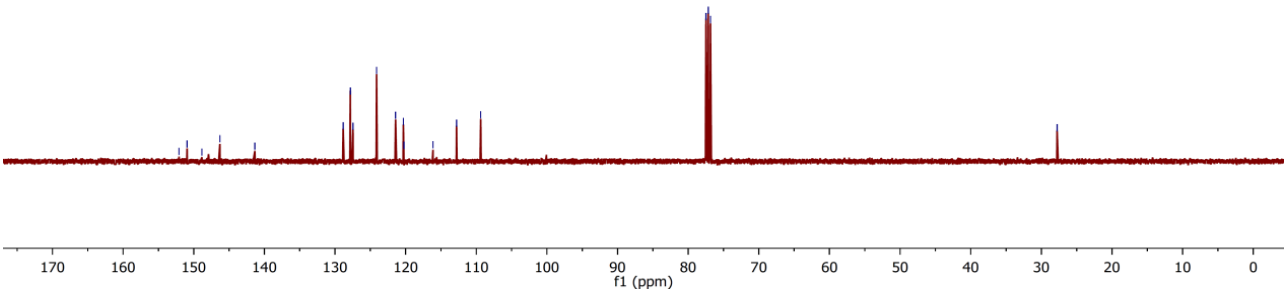
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bn**:



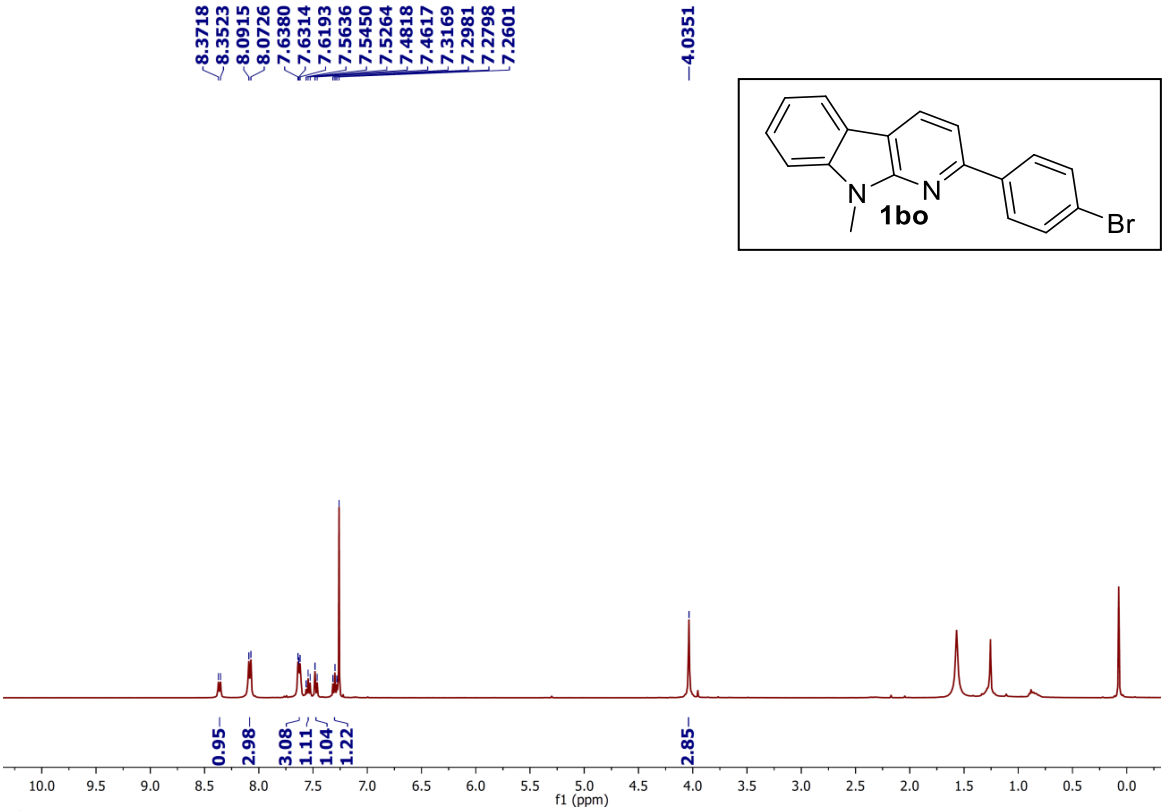


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bn**:

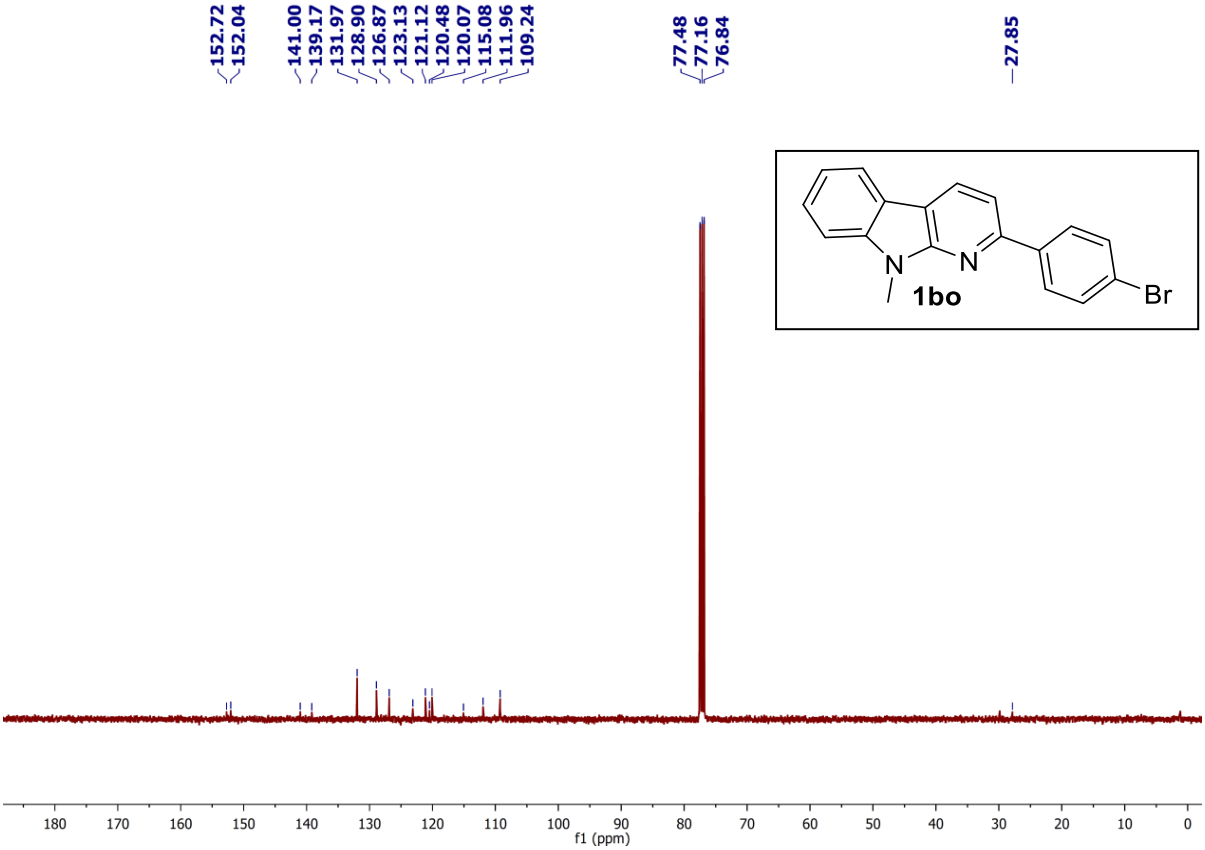




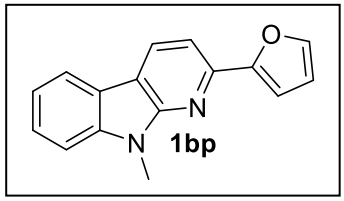
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bo**:

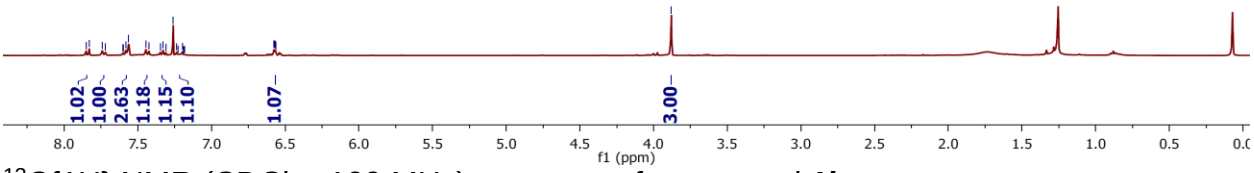


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bo**:

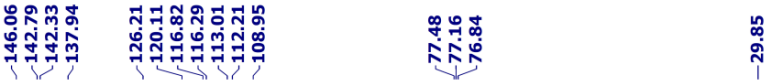


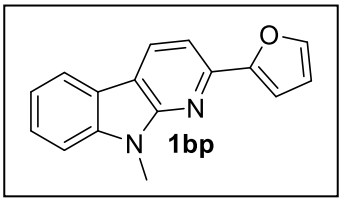
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bp**:

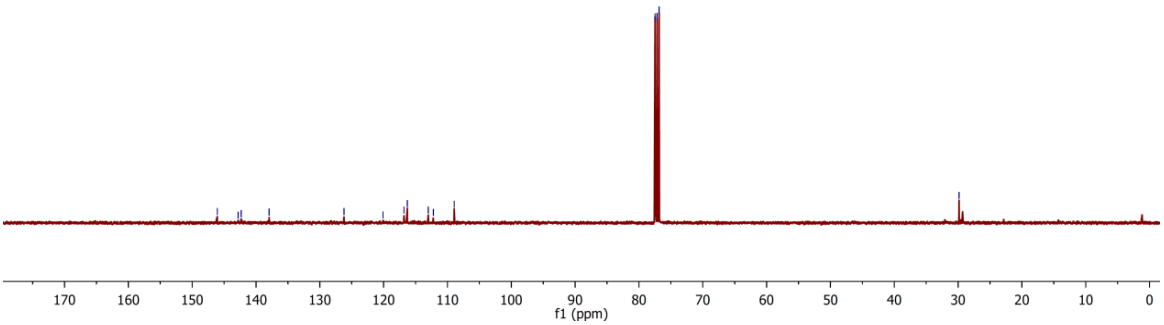




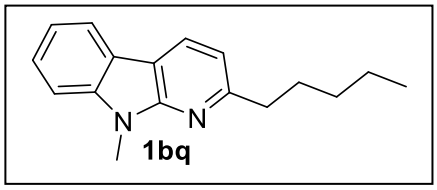
^{13}C{1H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bp**:

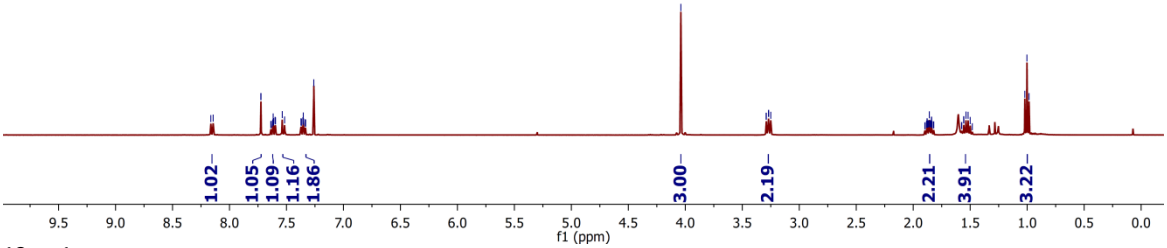




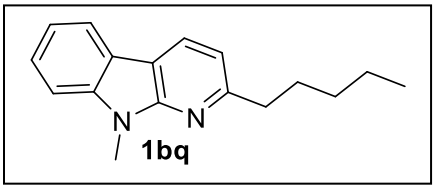


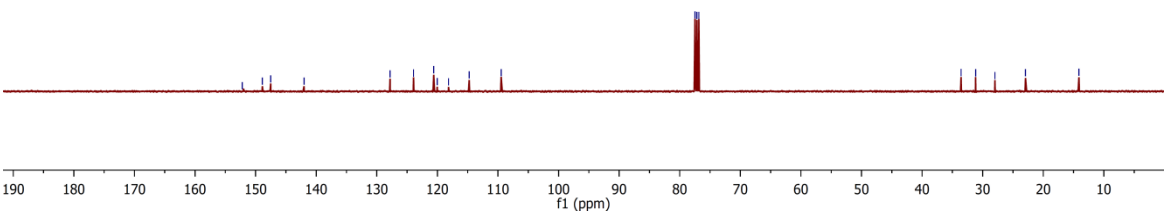
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bq**:



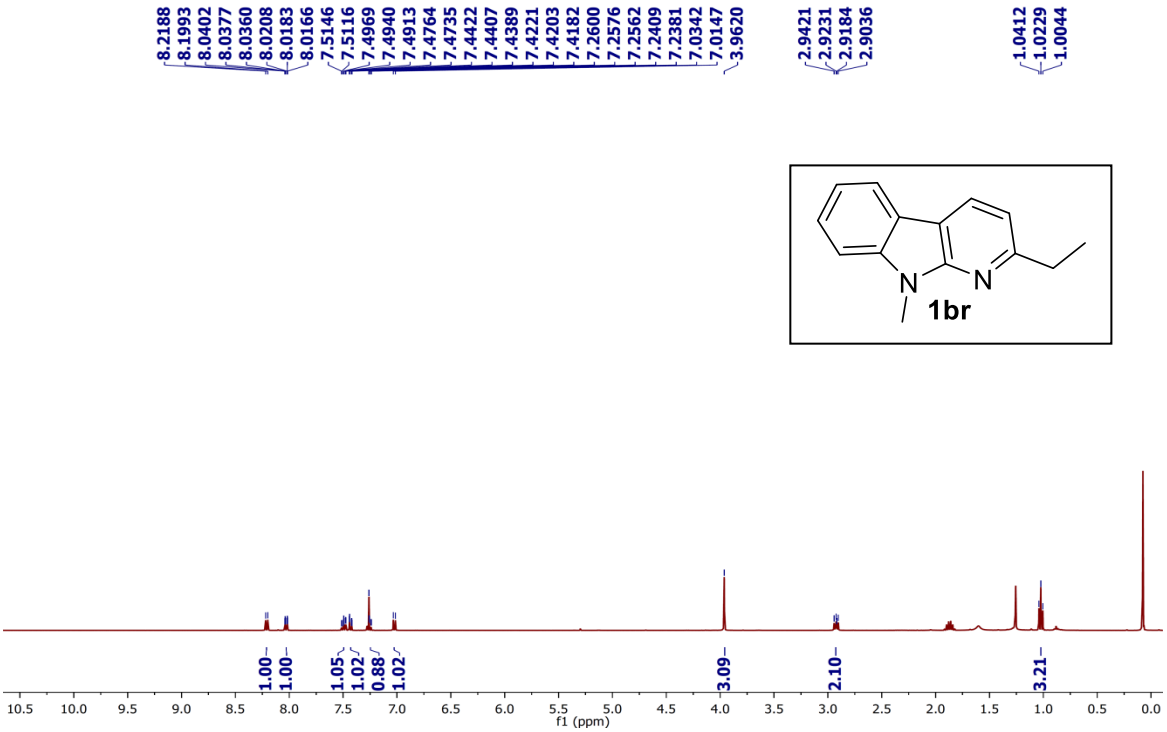


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bq**:

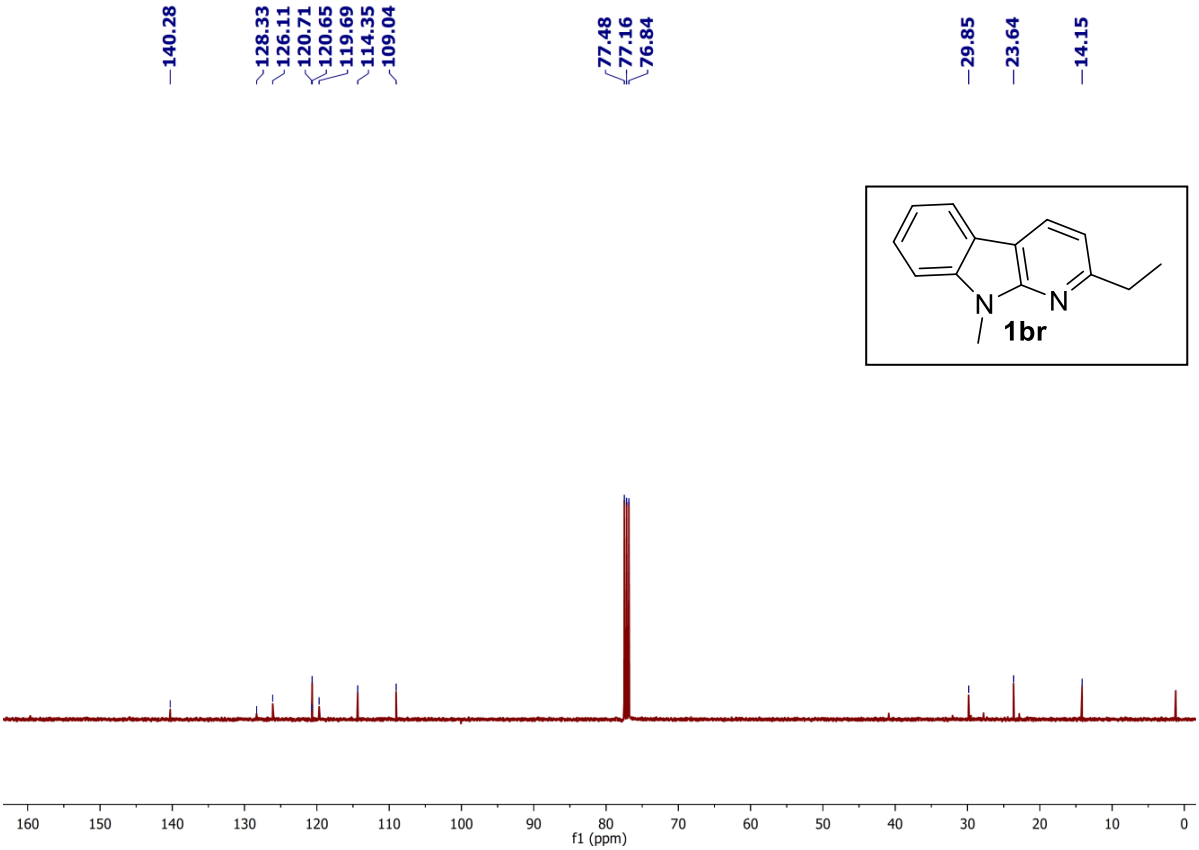




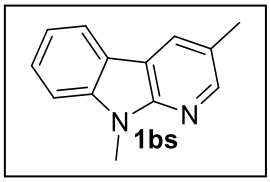
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1br:**

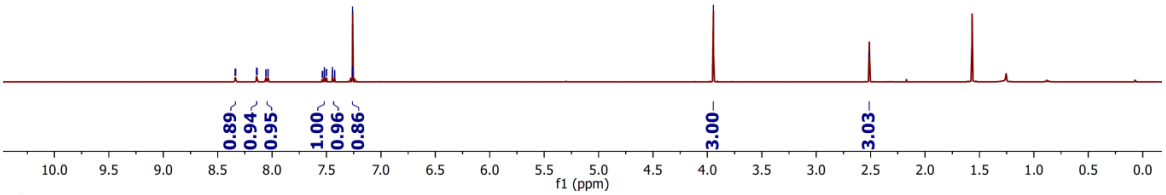


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1br:**

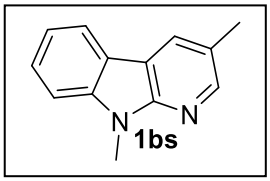


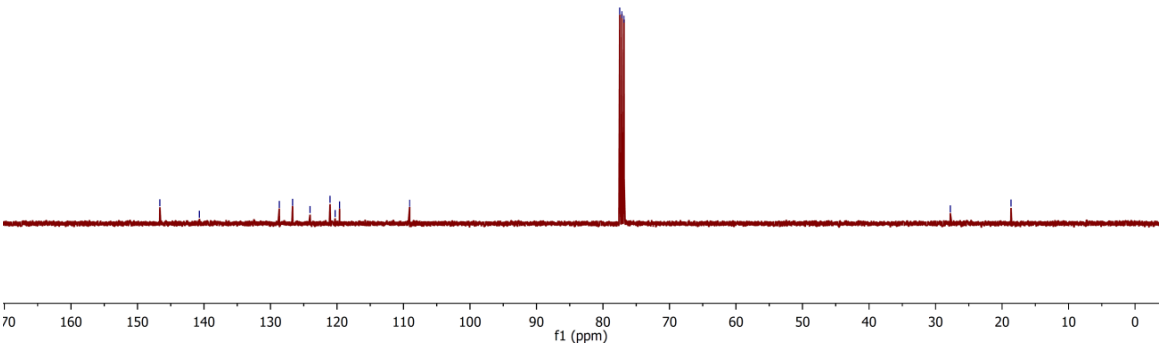
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bs**:



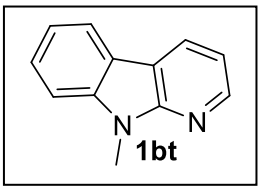


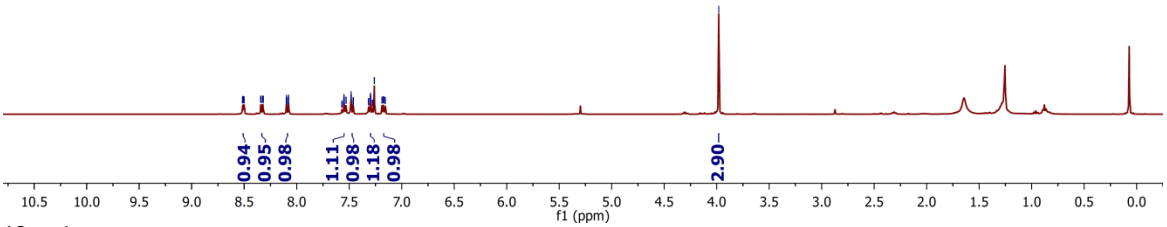
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bs**:



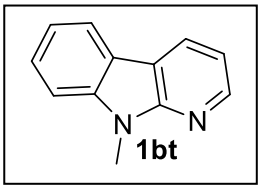


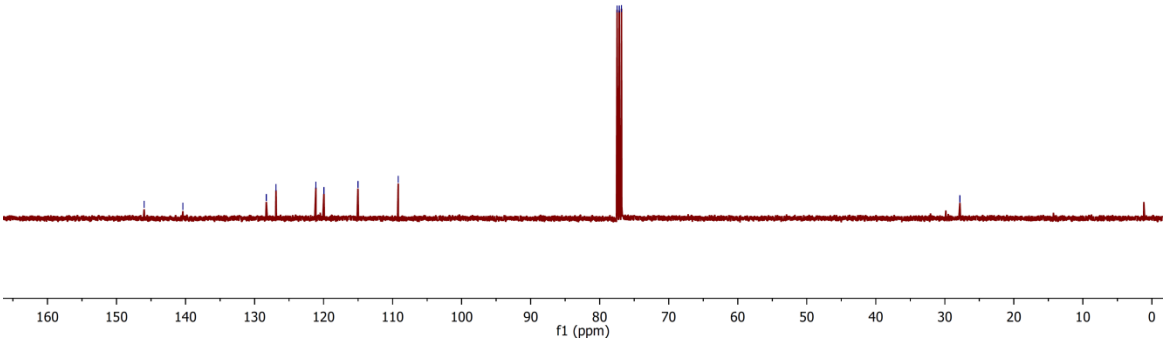
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bt**:



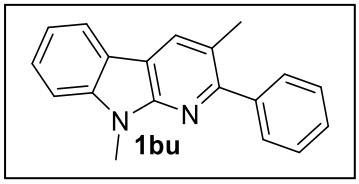


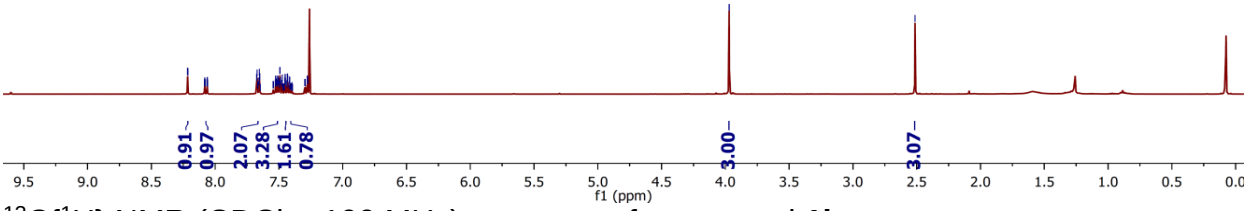
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bt**:



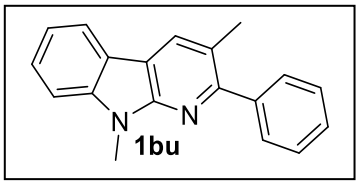


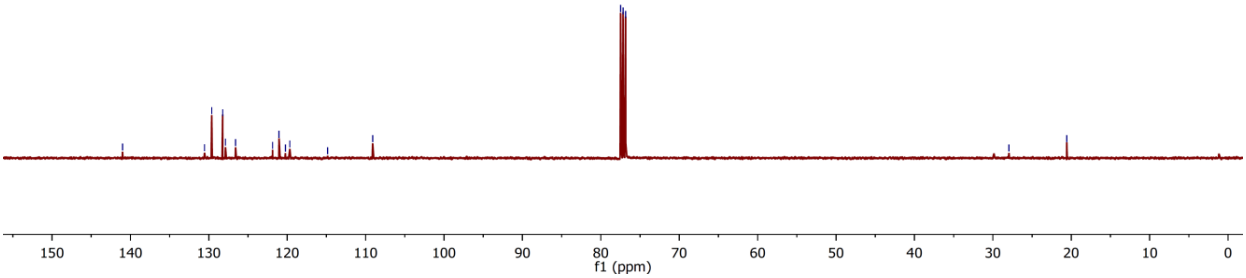
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bu**:



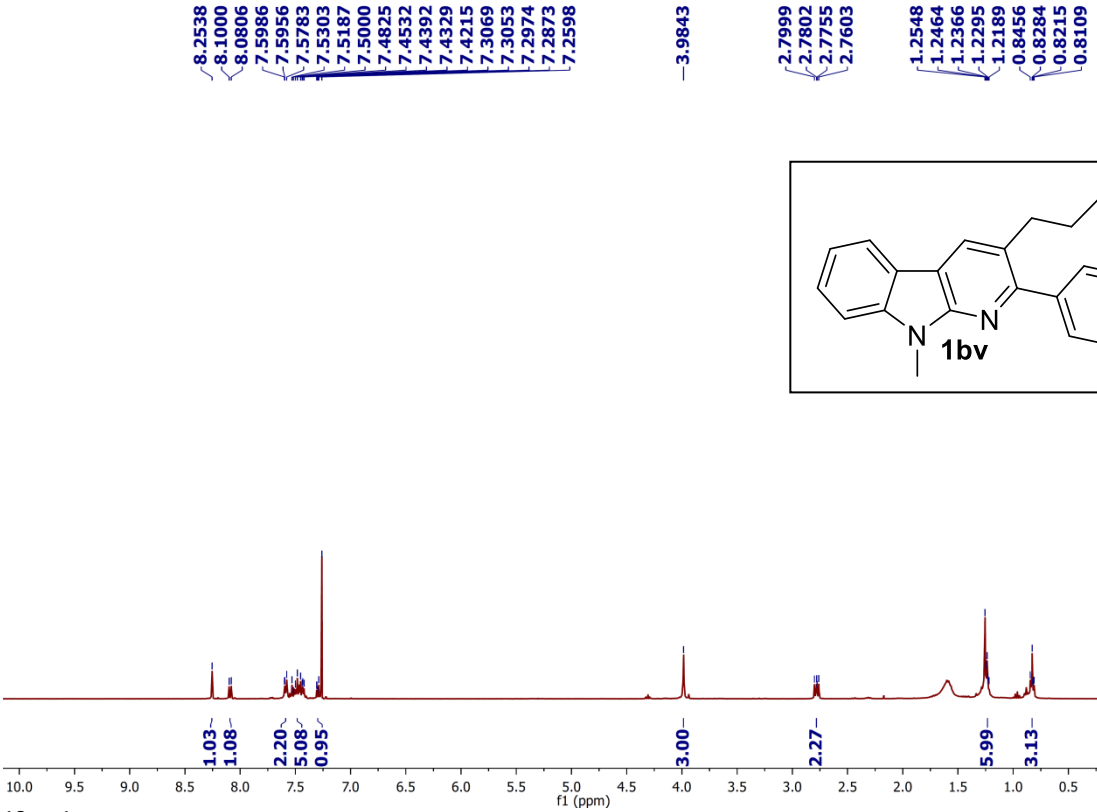


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bu**:

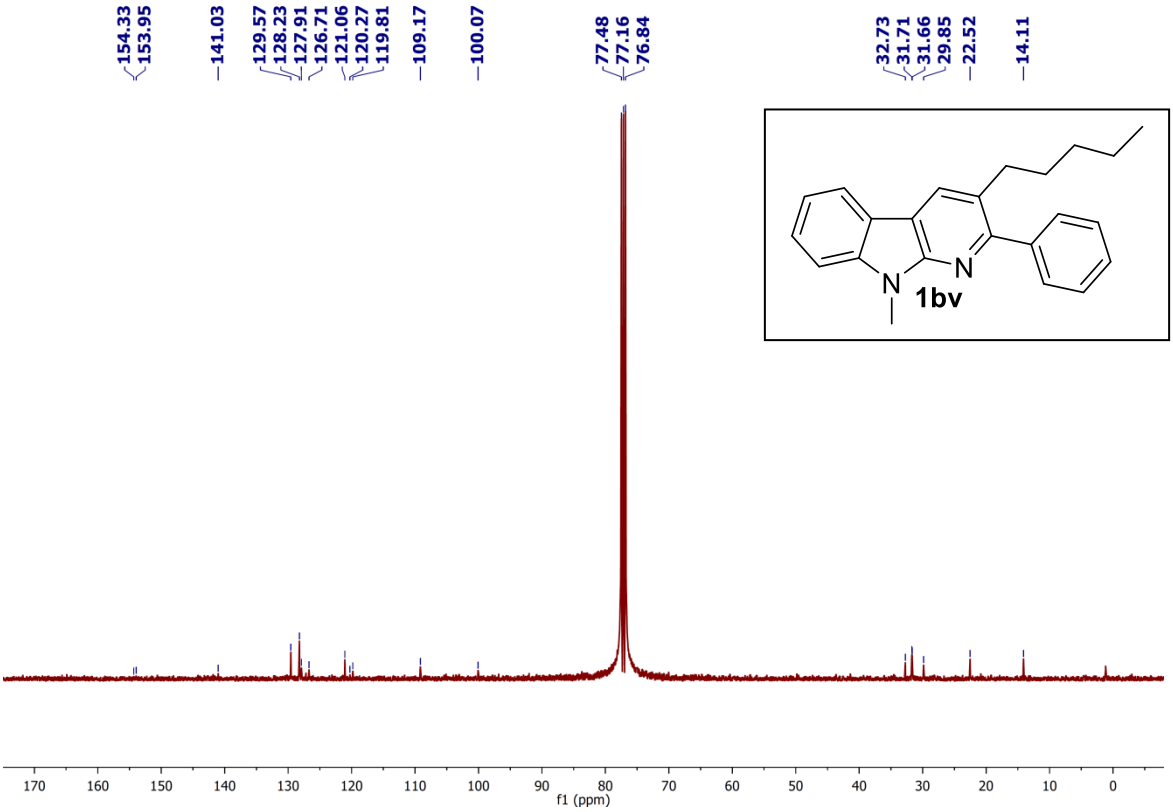




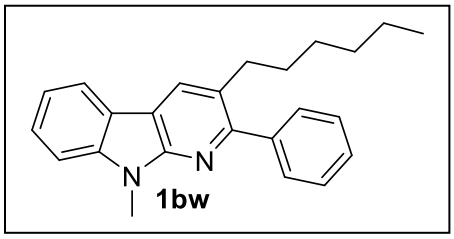
^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bv**:

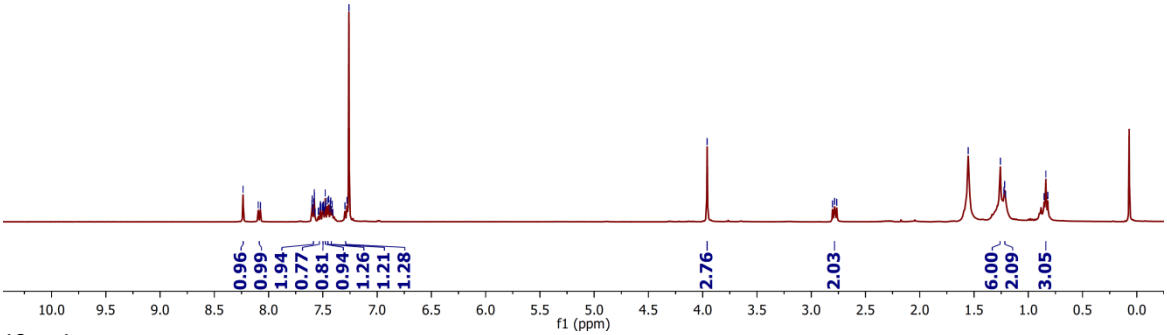


^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bv**:

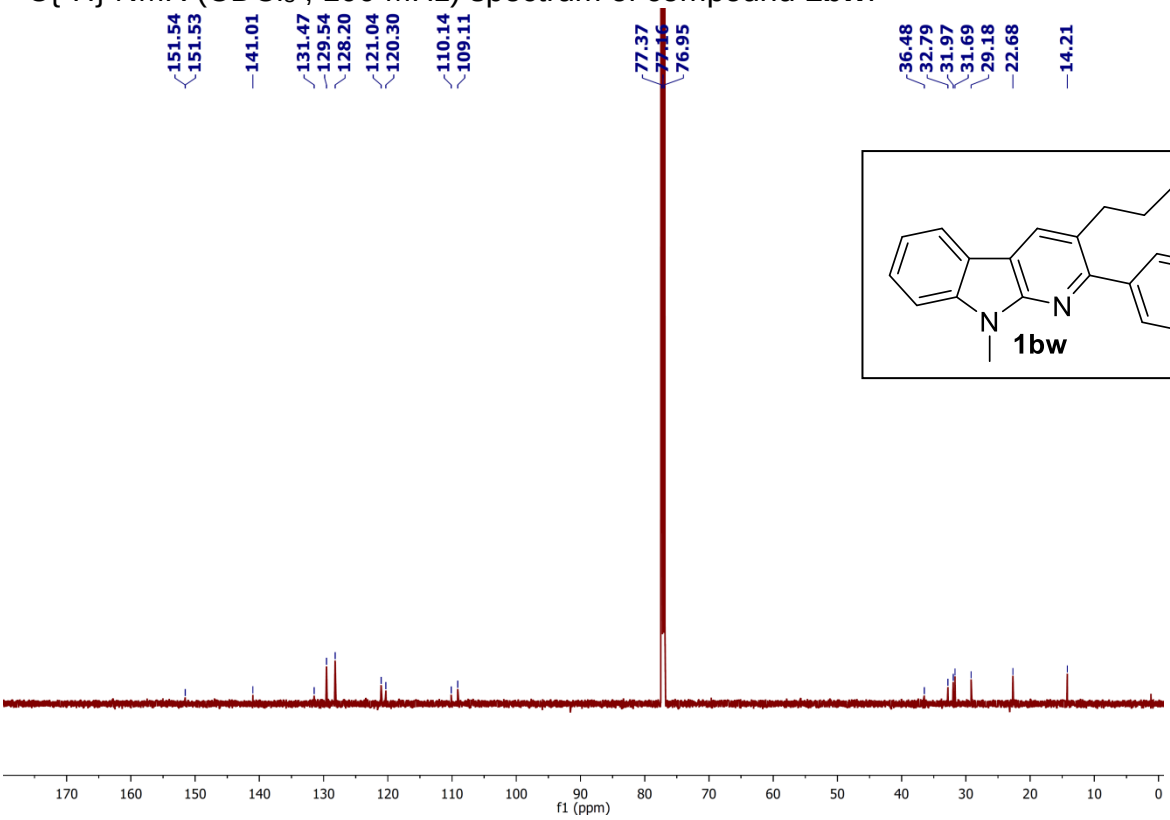


^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **1bw**:



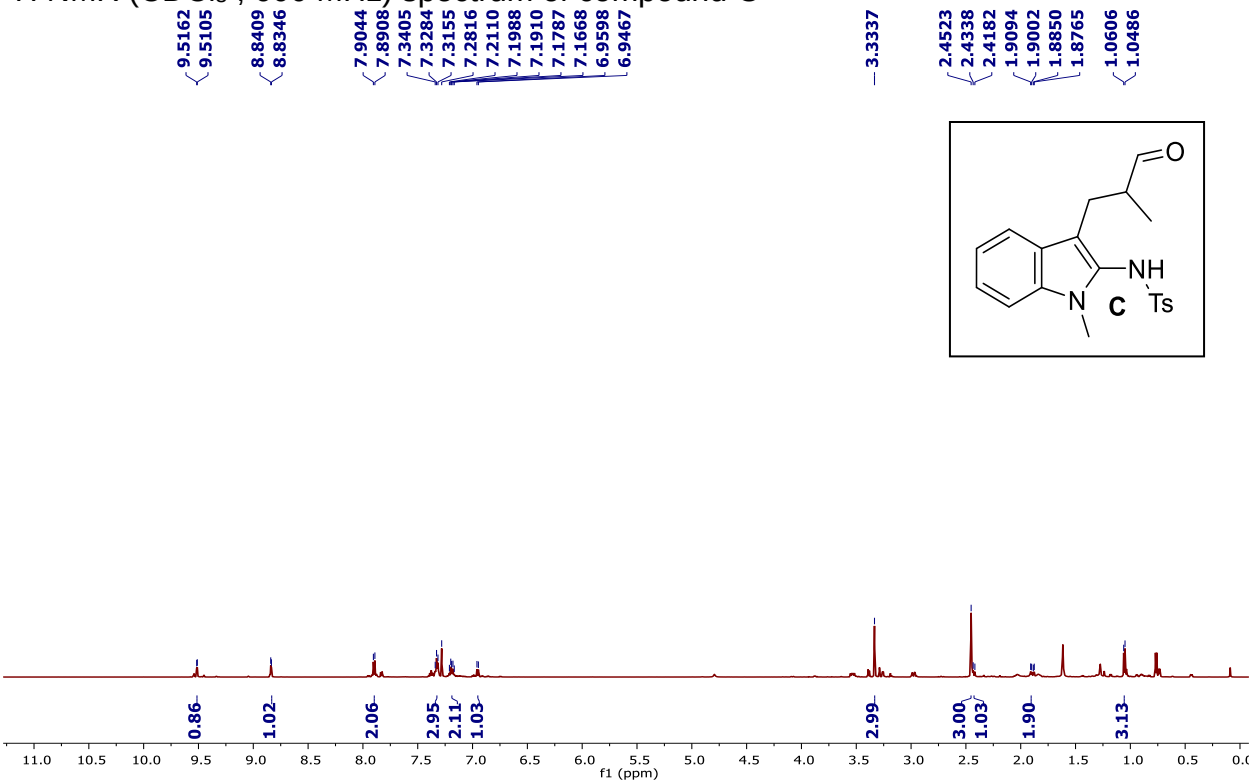


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectrum of compound **1bw**:

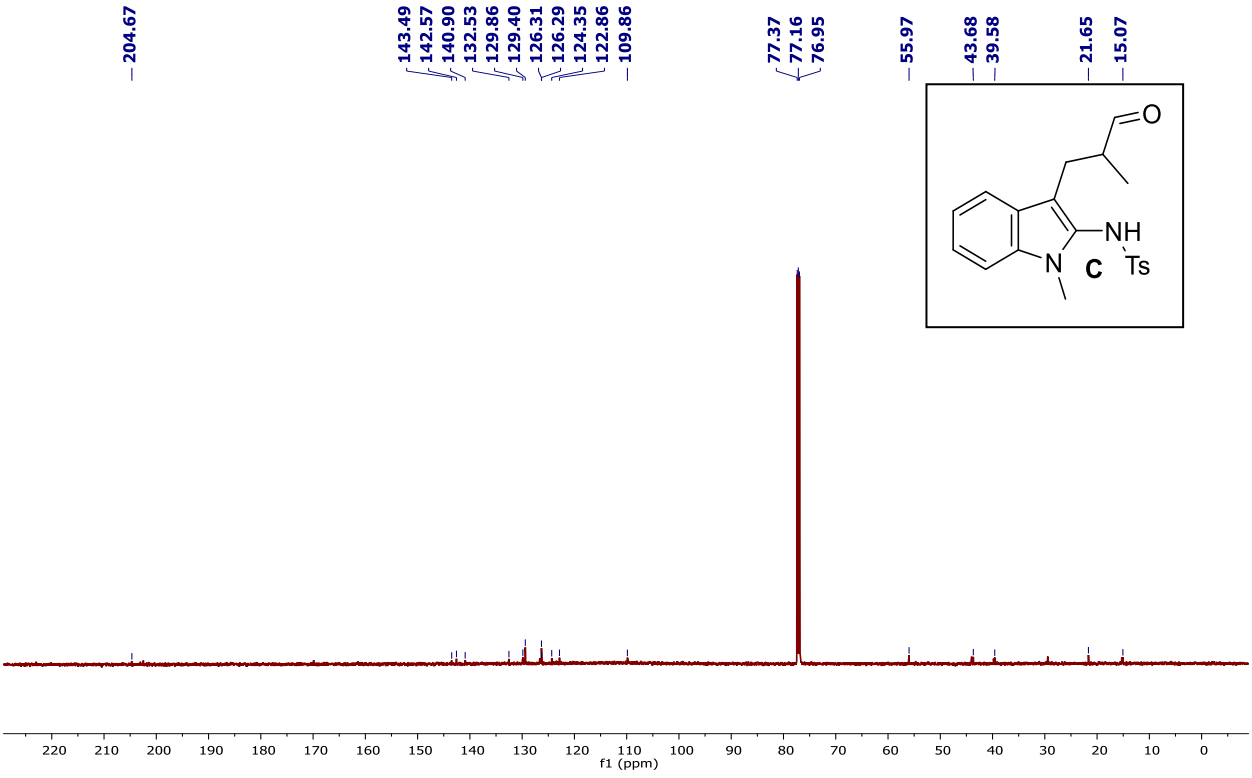


32. NMR spectra of intermediate C and C'

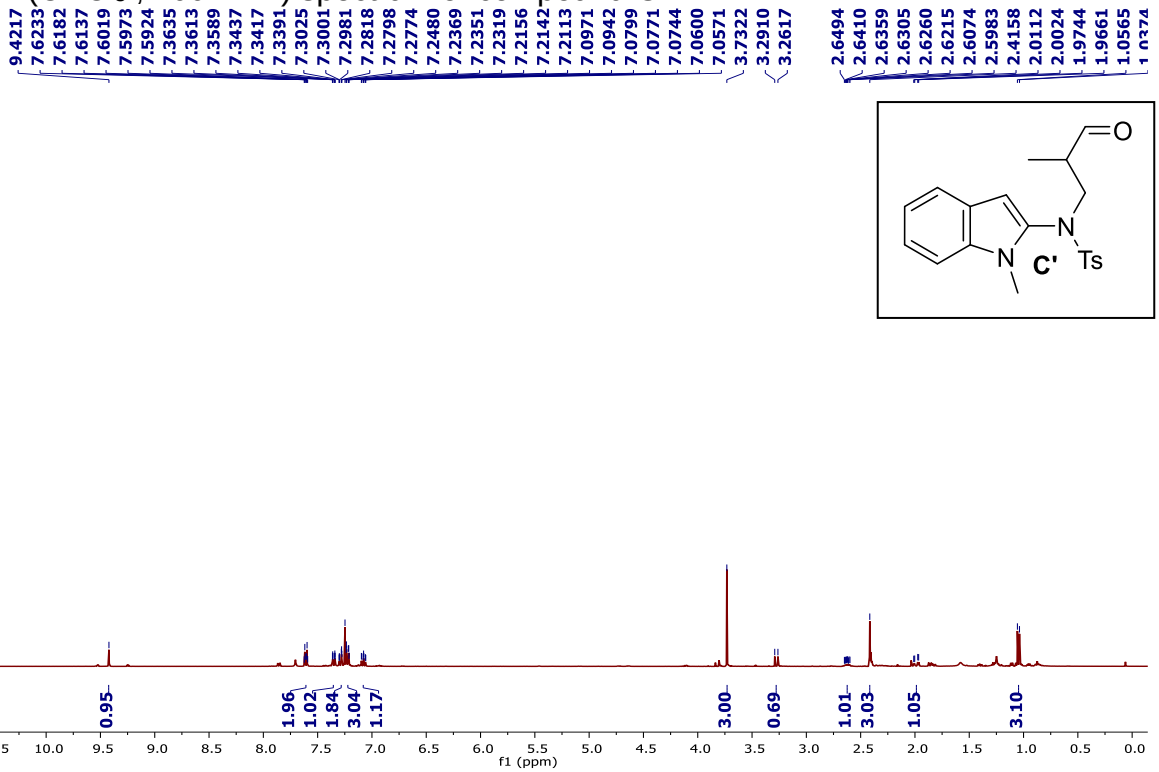
^{1}H NMR ($CDCl_3$, 600 MHz) spectrum of compound **C**



^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) spectrum of compound **C**



^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **C'**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectrum of compound **C'**