Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2024

N-alkylation of Amines with primary/secondary alcohols using novel Cobalt(II) inverse triazolyl-pyridine complex

Bhawana Shekhawat, Puneet Singh Gahlaut, Deepak Gautam and Barun Jana[ID*]

Supporting Information

Contents **Page No.**

1. General Information

All the solvents (Toluene, xylene, and tetrahydrofuran (THF)) used in the synthesis of [ptmtbt] ligand, Co-complex and catalytic reactions were purified *via* distillation under an argon atmosphere, and were stored over 4Å molecular sieves. All other reagents and chemicals were purchased from commercially available sources and were used without further purification. Analytical TLC test was performed using a Merck 60 F254 silica gel plate of 0.25 mm thickness. Column chromatographic separation was performed using Merck 60 silica gel of 230-400 mesh. The NMR spectra were collected in JEOL ECS-400 (400 MHz) spectrometer using tetramethyl silane (TMS) as the internal reference. Q-TOF mass spectrometer (serial no. YA 263) was used for HRMS analysis. All the catalytic reactions were performed under ambient atmosphere. 2-azido pyridine was synthesized following a literature procedure[1].

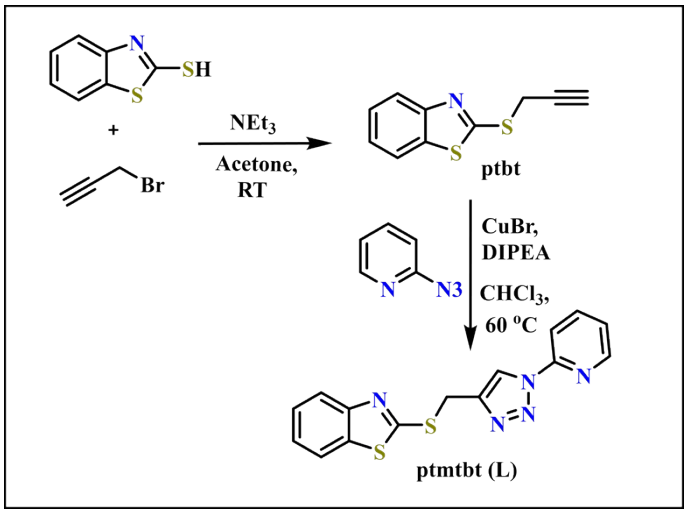
2. Characterization data of ligand and catalyst

Synthesis of 2-(prop-2-yn-1-ylthio) benzo[d]thiazole [ptbt]

The ligand precursor [ptbt] was synthesised *via* a modified process as documented in the literature[2]. At first, equimolar amount of 2-mercaptobenzothiazole (1mmol) and triethylamine (1mmol) were mixed in 2 mL of acetone in a 25 mL round bottom flask and was allowed to stir for 15 minutes at room temperature. Next, little excess amount of propargyl bromide (1.1mmol) was added into the reaction mixture dropwise and the suspension was allowed to stir for approximately one hour at room temperature. The reaction mixture was worked up with ethyl acetate and was finally purified by column chromatography employing hexane/ethyl acetate (99:1) as the solvent mixture (Yield 88 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.84 – 7.82 (m, 1H), 7.71-7.68 (m, 1H), 7.38 – 7.34 (m, 1H), 7.26 – 7.22 (m, 1H), 4.06 (d, *J* = 2.6 Hz, 2H), 2.23 (t, *J* = 2.6 Hz, 1H).

Synthesis of 2-(((1-(pyridin-2-yl)-1H-1,2,3-triazol-4-yl) methyl) thio) benzo[d]thiazole [ptmtbt]

2-azidopyridine (1.1mmol) and [ptbt] (1mmol) were mixed in a 100 mL round bottle flask and the reaction mixture was then agitated for 15 minutes in 3 mL of dry chloroform under nitrogen atmosphere. Following the addition of CuBr (0.2mmol) and DIPEA (2mmol), the reaction mixture was refluxed for 20 hours while being kept under a nitrogen environment. Then the reaction solvent was removed under low pressure. The desired product was separated from the crude reaction mixture using column chromatography (40% ethyl acetate in hexane) to produce an analytically pure brown solid. Yield 56%; M.P (glass capillary). 96 - 98 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.56 (s, 1H), 8.385 (d, *J* = 4.9 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.27 – 7.19 (m, 2H), 4.72 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 166.82 (s), 151.20 (s), 148.31 (s), 138.96 (s), 134.37 (s), 126.36 (s), 124.68 (s), 123.55 (s), 120.97 (s), 120.41 (s), 113.67 (s), 27.88 (s); HRMS (ESI^{+}) m/z calculated for $C_{15}H_{11}N_5S_2$ [M + H^{+}]$^{+}$ 326.0529; found 326.0533; Elemental analysis for $C_{15}H_{11}N_5S_2$. Calculated C, 55.37; H, 3.41; N, 21.52; Found C, 55.34; H, 3.33; N, 19.65; IR $\upsilon_{max.}$ (cm^{-1}): 3162 (w, C_{sp2}-H stretch.), 3013 (w, triazole), 1457 (s, C-H bend.), 1597 (m, C-C stretch.), 744 (s, C-S stretch.).



Scheme S1: The step-wise synthesis of ligand [ptmtbt] L

Synthesis of $[Co(L)_2(NO_3)_2]$

In a 25 mL round bottom flask, 111.8 mg (2mmol) of [ptmtbt] was mixed with 50 mg (1 mmol) of $Co(NO_3)_2.6H_2O$ and then 2 mL of dry acetonitrile was added at room temperature to get a white suspension. The clear white suspension became turbid and pinkish in about 15 minutes. The reaction mixture was left to stir at room temperature for 2 hours. After the reaction was completed, the pinkish solid was filtered and then washed with acetonitrile to get rid of any remaining ligand in the final product. Analytically pure compound was obtained in the form of a pinkish solid (Fig S1). Single crystals suitable for X-ray diffraction were from a 1:1(MeOH: $CHCl_3$) solvent combination at room temperature. Yield-80% (152 mg), based on ligand [ptmtbt]. M.P. – 210-230 °C. HRMS (ESI^+) m/z calculated for $[M\text{-}NO_3^-]^+$ = 771.0116; found 771.0115 and m/z calculated for $[M\text{-}2NO_3^-]^{2+}$= 354.5116; found 354.5170; Elemental analysis for $C_{30}H_{22}CoN_{12}O_6S_4$. Calculated C, 43.22; H, 2.66; N, 20.16; Found C, 43.07; H, 2.48; N, 19.83; IR $\upsilon_{max.}$ (cm^{-1}): 3131 (w, C_{sp2} -H stretch.), 3019 (w, triazole), 1457 (s, C-H bend.), 1603 (m, C-C stretch.), 1071 (m, N=O stretch.), 755 (s, C-S stretch.).

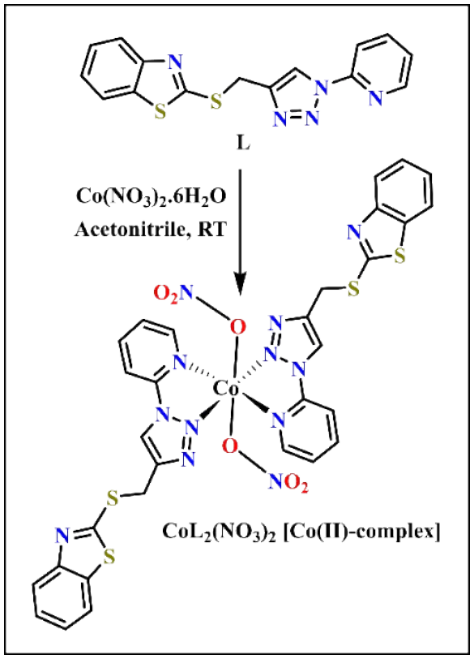


Fig S2: Synthesis of Co-complex

Characterization data of ligand and Co-complex

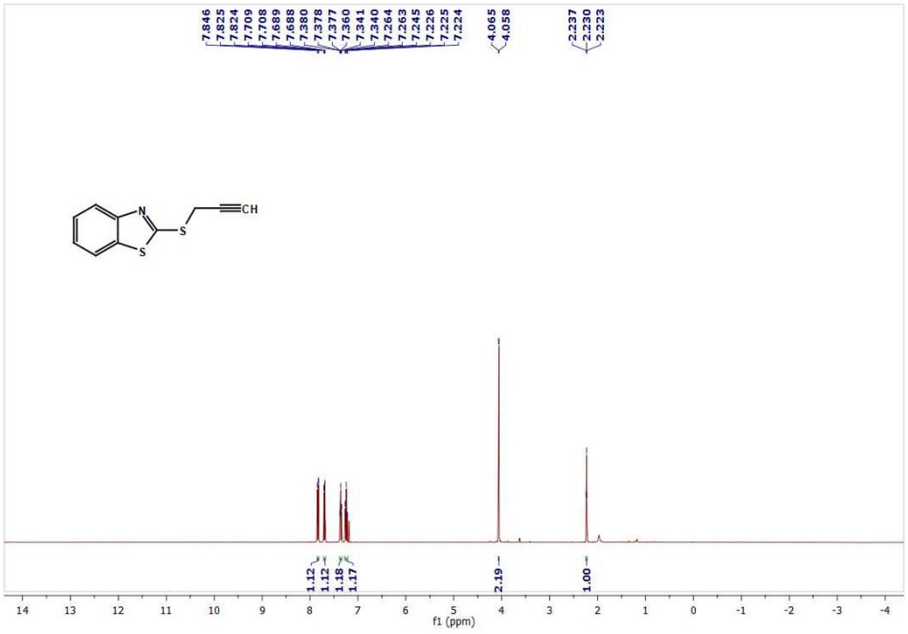


Fig. S3 ^{1}H-NMR Spectrum of **ptbt** in $CDCl_3$ (400 MHz)

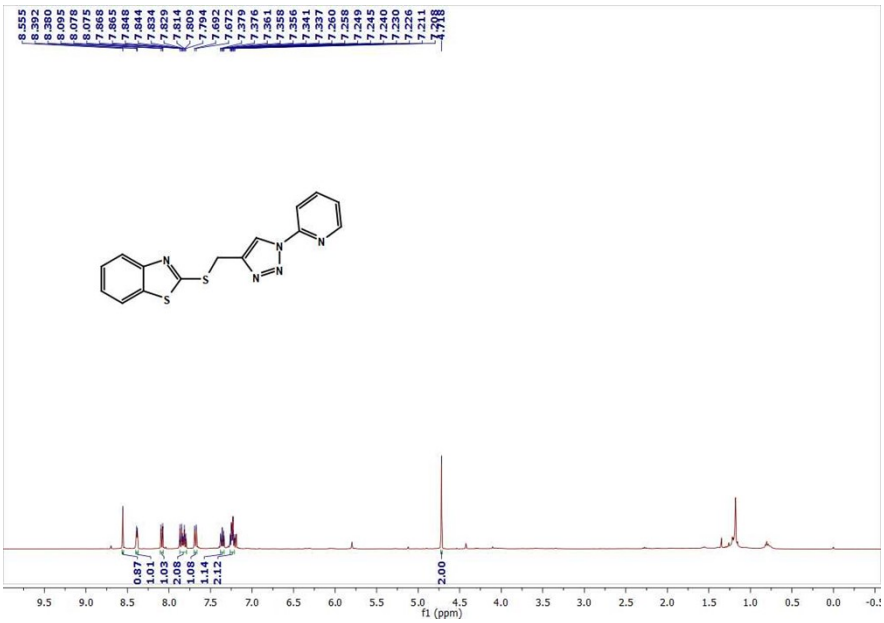


Fig. S4 ^{1}H-NMR Spectrum of **ptmtbt (L)** in $CDCl_3$ (400 MHz)

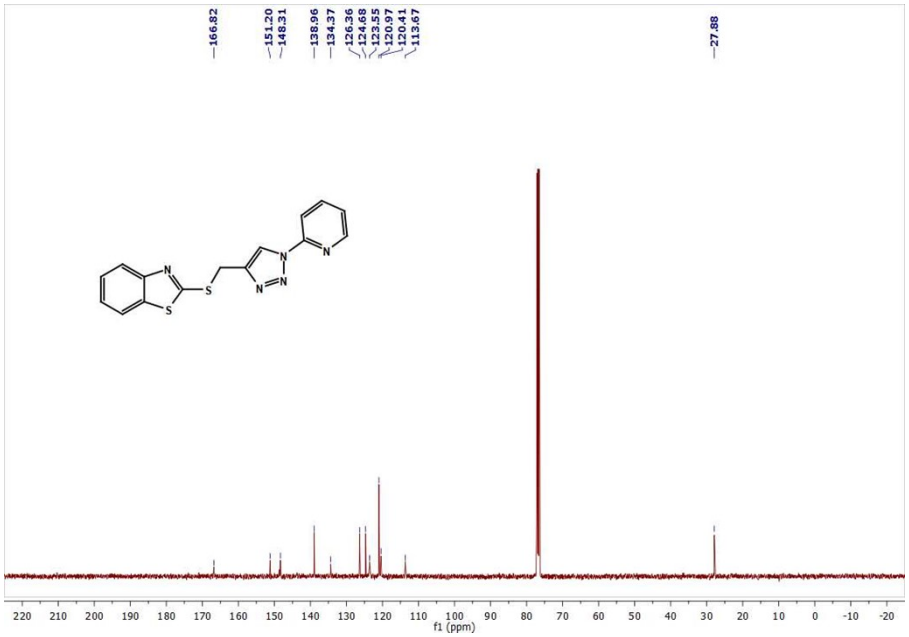


Fig.S5 ^{13}C-NMR Spectrum of **ptmtbt (L)** in $CDCl_3$ (101 MHz)

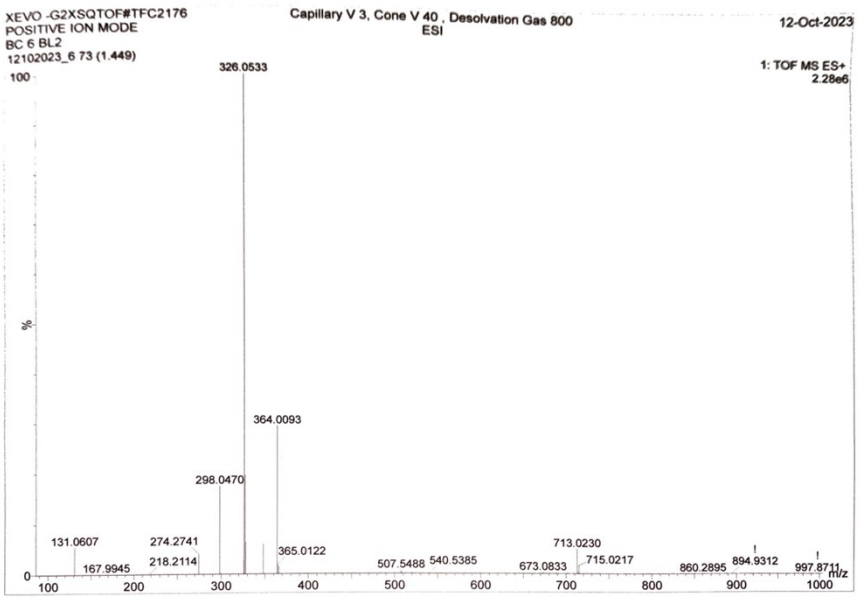


Fig.S6 ESI Mass spectrum of **L**

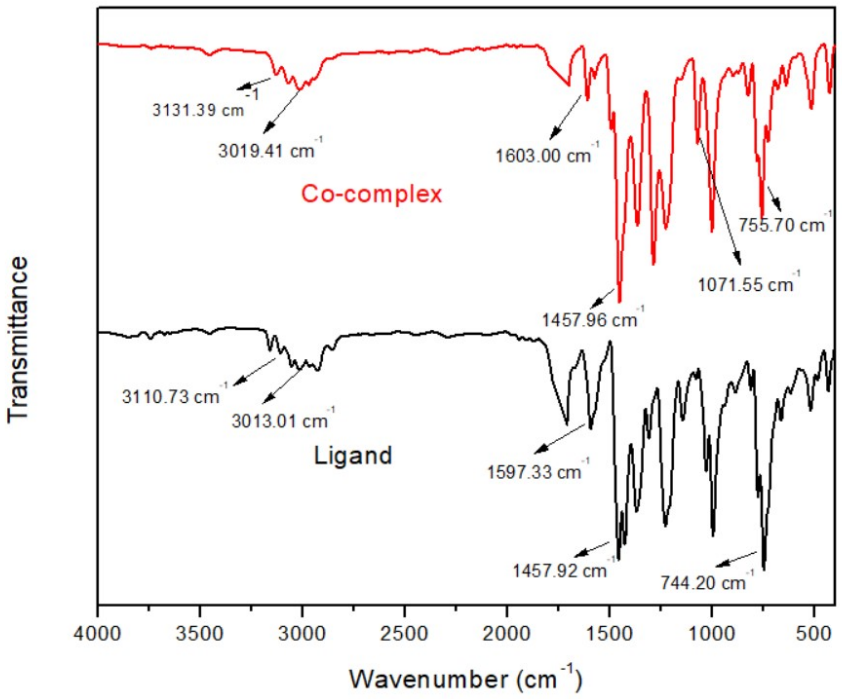


Fig.S7 FT-IR spectrum of ligand **L** and **Co-complex**

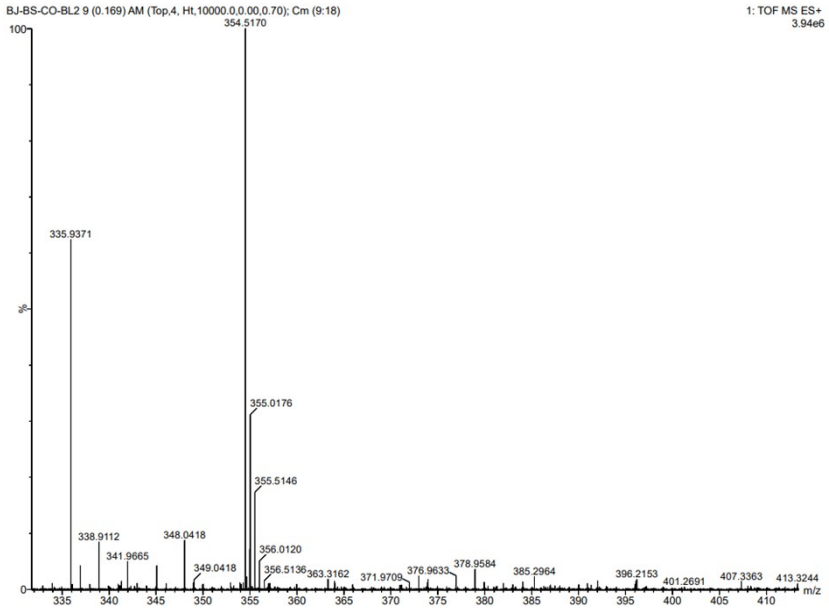


Fig.S8 ESI Mass spectrum of **Co-complex** $[Co\text{-}2NO_3^-]^{2+}$

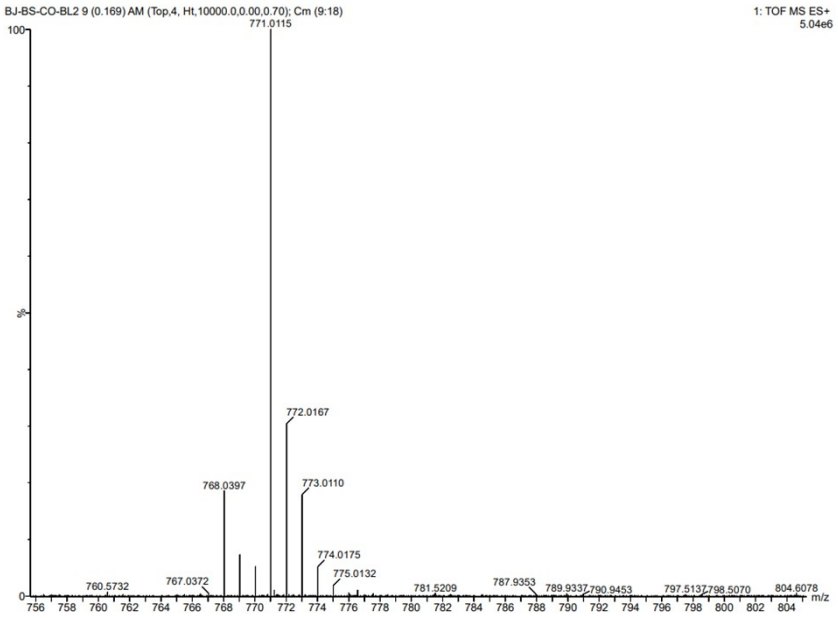


Fig.S9 ESI Mass spectrum of **Co-complex [Co-NO_3^-]$^+$**

3. Crystallographic information of catalyst

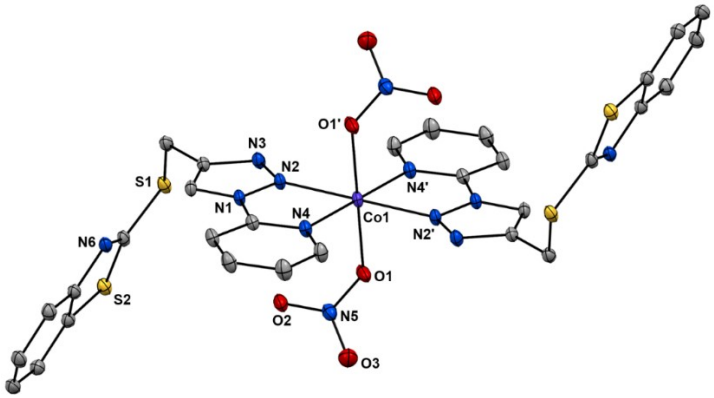


Fig S10. Solid-state molecular structure of **Co-complex**. Thermal ellipsoids were drawn with 30% probability. All the hydrogen atoms are eliminated for the clarity in the molecular structure.

Table 1. Crystal Data and structure refinement for Co-complex.

Identification code	**3**
Empirical formula	$C_{30}H_{22}CoN_{12}O_6\ S_4$

Formula weight	833.77
Temperature/K	100(2)
Crystal system	Triclinic
Space group	P - 1
a/Å	7.7485(4)
b/Å	10.1105(5)
c/Å	12.1657(6)
α/°	103.064(1)
β/°	92.240(1)
γ/°	112.226(1)
Volume/Å^3	851.18(7)
Z	1
ρ_{calc}g/cm^3	1.627
μ/mm^{-1}	0.814
F(000)	425.0
Crystal size/mm^3	0.18 × 0.12 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.25 to 28.34
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	13509
Independent reflections	4230 [R_{int} = 0.0278, R_{sigma} = 0.0297]
Data/restraints/parameters	4230/0/241
Goodness-of-fit on F^2	0.944

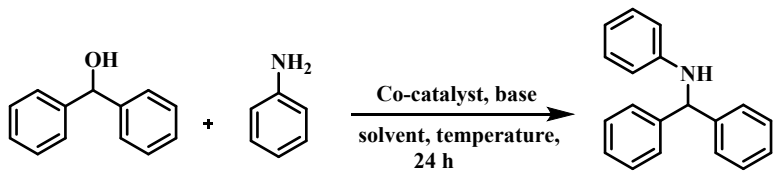
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.1150
Final R indexes [all data]	R_1 = 0.0390, wR_2 = 0.1226
Largest diff. peak/hole / e $Å^{-3}$	0.664 / -0.563
CCDC number	2337813

Table 2. Selected bond lengths (Å) and bond angles (°) in the Molecular structure of **Co-complex**.

Bond lengths (Å)		**Bond angles (°)**	
Co1-N2	2.1041 (13)	N2-Co1-N4	76.86 (5)
Co1-N4	2.1149 (14)	N2-Co1-O1	95.20 (6)
Co1-O1	2.0554 (13)	N4-Co1-O1	93.79 (6)
N1-N2	1.3481 (18)	N2-Co1-N3	137.90 (11)
N2-N3	1.3041 (19)	N1-N2-N3	113.47 (10)

4. General procedure for the N-alkylation of amines using primary and secondary alcohols

Table 3: Optimization of reaction conditions with secondary alcohols

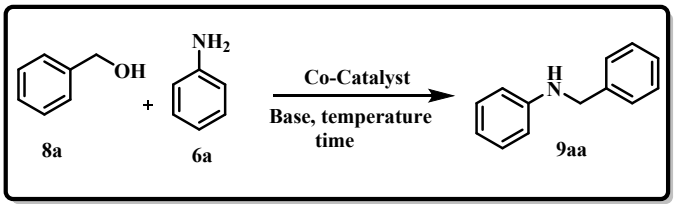


Entry	**Catalyst (mol%)**	**Solvent**	**Base**	**T (°C)**	**[c]Yield**
1.	Co-catalyst (2 mol%)	Toluene	KO^{t}Bu	110 °C	65%
2.	Co-catalyst (2 mol%)	Toluene	KO^{t}Bu	120 °C	70%

3.	Co-catalyst (2 mol%)	Toluene	KO^{t}Bu	140 ˚C	90%
4.	Co-catalyst (1 mol%)	Toluene	KO^{t}Bu	140 ˚C	92%
5.	-	Toluene	KO^{t}Bu	140 ˚C	n.r.
6.	Co-catalyst (1 mol%)	Toluene	-	140 ˚C	n.r.
7.	Co-catalyst (1 mol%)	Toluene	K_2CO_3	140 ˚C	32%
8.	Co-catalyst (1 mol%)	Toluene	KOH	140 ˚C	45%
9.	Co-catalyst (1 mol%)	Toluene	Cs_2CO_3	140 ˚C	n.r.
10.	Co-catalyst (1 mol%)	Toluene	K_3PO_4	140 ˚C	trace
11.	Co-catalyst (1 mol%)	Xylene	KO^{t}Bu	140 ˚C	79%
12.	Co-catalyst (1 mol%)	ACN	KO^{t}Bu	140 ˚C	trace
13.	Co-catalyst (1 mol%)	DMSO	KO^{t}Bu	140 ˚C	48%
14.	Co-catalyst (1 mol%)	THF	KO^{t}Bu	140 ˚C	50%
[b]15.	$Co(NO_3)_2.6H_2O$ (1mol%)	Toluene	KO^{t}Bu	140 ˚C	58%
16.	$CoCl_2$ (1 mol%)	Toluene	KO^{t}Bu	140 ˚C	trace

Reaction conditions: diphenylmethanol 6a (0.55 mmol), aniline 5a (0.5 mmol), Co-catalyst (1mol%), base (0.38 mmol), 2mL of toluene, at 140 ^{o}C for 24 h. [b]Used in 1:2 ratio of $Co(NO_3)_2.6H_2O$ and L1. [c]Yield of pure isolated product. n.r. = no reaction.

Table 4. Optimization of reaction condition with primary alcohols

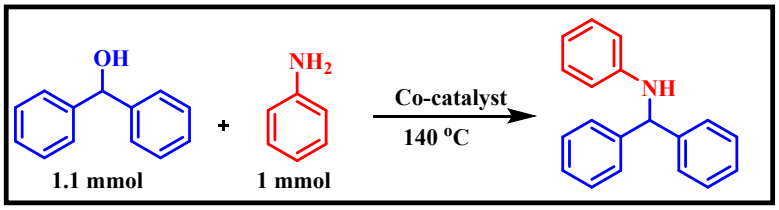


Entry	Base	T (^{o}C)	Time (hours)	[c]Yield
1.	KO^{t}Bu	140 ^{o}C	24	98%
2.	K_2CO_3	140 ^{o}C	24	60%

3.	KOH	140 °C	24	96%
4.	KOH	120 °C	24	94%
5.	KOH	110 °C	24	92%
6.	KOH	110 °C	12	91%
7.	KOH	110 °C	6	97%

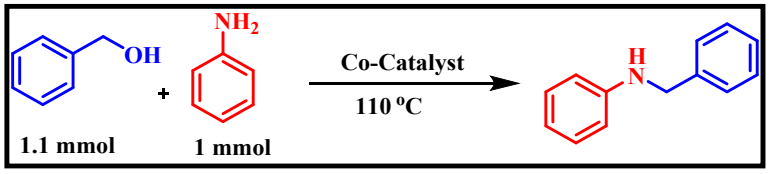
[a]Reaction conditions: benzyl alcohol 8a (0.55 mmol), aniline 6a (0.5 mmol), Co-catalyst (1mol%), base (0.25 mmol), 2mL of toluene, at 110 °C for 6 h. [b]Yield of pure isolated product.

General Procedure of N-alkylation of Amines with secondary alcohols



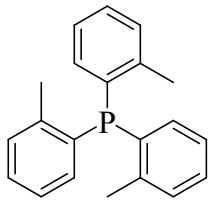
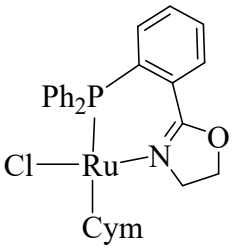
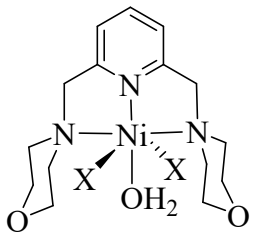
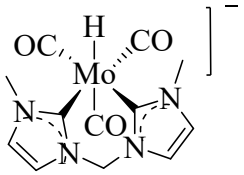
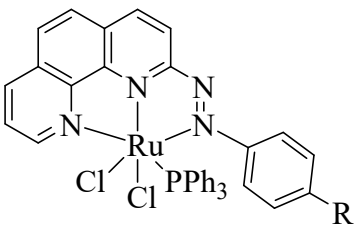
In a sealed tube containing toluene solvent, a combination of aniline (1 mmol), KO^{t}Bu (0.75 mmol) diphenylmethanol (1.1 mmol) and Co-catalyst (1 mol%) was heated for 24 hours at 140 °C. After cooling the reaction mixture to room temperature, ethyl acetate (3 x 20 mL) and 10 mL of water were added to the complete workup. Then, anhydrous Na_2SO_4 was used to dry the mixed organic layers, followed by filtering and concentrated under low pressure to get the crude residue. This was then further refined using column chromatography on silica gel (230-400 mesh) in hexane. Products were recovered as pale yellow, oily liquids when solvent was extracted at decreased pressure in a respectable yield of between 70% to 99%.

General Procedure of N-alkylation of Amines with primary alcohols



Benzyl alcohol 8a (1.1 mmol), aniline 6a (1mmol), KOH (0.5 mmol), Co-catalyst (1 mol%), and toluene (2 mL) were added to a 15 mL oven dried screw capped reaction tube. A magnetic stirring bar was then used to agitate the reaction mixture for 6 hours at 110 °C in an oil bath. Following the reaction completion, the crude mixture was worked up with 3 □ 5 mL of ethyl acetate. The residue was then refined using silica gel column chromatography (230-400 mesh particle size) with an eluent consisting of hexane and ethyl acetate to yield the N-alkylated product in between 90-99%.

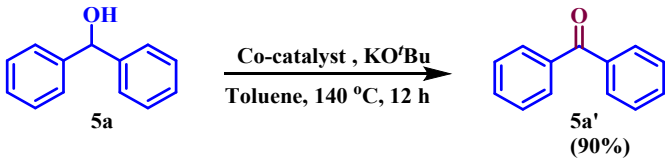
Table 5: Comparison table with respect to previous work

S. No.	Catalyst	Reaction conditions	References
1.	$Ru_3(CO)_{12}$ 	[Cat. 2 mol%, ligand 6 mol%, 110 °C, 24 h]	3
2.	Ph_2CHBr	[Cat. 20 mol%, N_2, 120 °C, 24 h]	4
3.		[Cat. 2 mol%, 0.5 equiv. *t*-BuOK, 110 °C, 24 h]	5
4.		[Cat. 1 mol%, 1 equiv. *t*-BuOK, n-octane, 140 °C, 24 h]	6
5.		[cat. 2 mol%, 1.1 equiv. *t*-BuOK, n-hexane, 130 °C, 24 h]	7
6.		[cat. 0.5 mol%, 0.5 equiv. *t*-BuOK, toluene, 120 °C,16 h]	8
7.	**Our work**	[cat. 1 mol%, 0.75 equiv., *t*-BuOK, toluene, 140 °C, 24 h]	

6. Mechanistic analysis

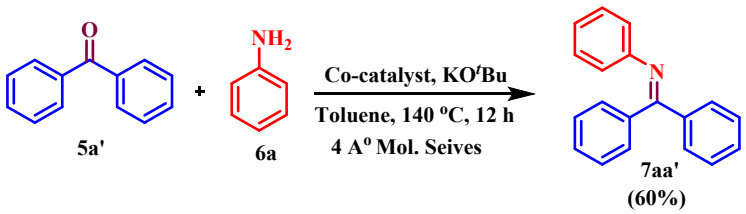
Identification of dehydrogenative product

Diphenylmethanol 5a (0.5 mmol), KO^{t}Bu (0.38 mmol), Co-catalyst (1 mol%) and toluene (1 mL) were introduced in a mild stream of nitrogen to an oven-dried screw cap reaction tube (15 mL). After that, the reaction mixture was agitated for 12 hours at 140 °C using a magnetic stirring bar. Following the reaction completion, the crude mixture was filtered through a celite filter and cleaned with ethyl acetate (3 x 5 mL). The solvent was then removed under vacuum, and the residue was then purified using silica gel column chromatography (230-400 mesh) with ethyl acetate and hexane as an eluent to yield the benzophenone product 5a' in an 90% yield.



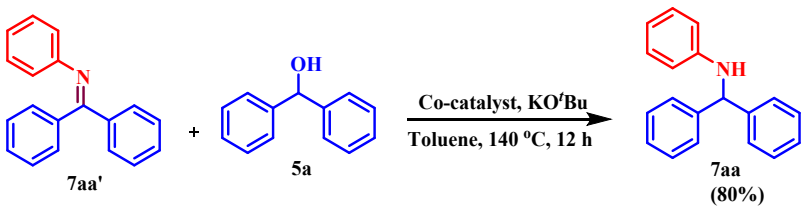
Synthesis of ketimine

The following steps were taken in an oven-dried screw cap reaction tube (15 mL): benzophenone 5a' (1.0 mmol), aniline 6a (1.0 mmol), KO^{t}Bu (0.75 mmol), Co-catalyst (1 mol%), toluene (1mL) and 4 Å molecular sieves; the reaction mixture was then refluxed for 12 hours. Following the completion of the reaction, the crude mixture was filtered through a celite filter and washed with ethyl acetate (3x5 mL). The solvent was then removed under vacuum, and the residue was then purified by silica gel column chromatography (230-400 mesh size) using hexane and ethyl acetate as an eluent. This process produced the N-(diphenylmethylene) aniline 7aa' in 60%.



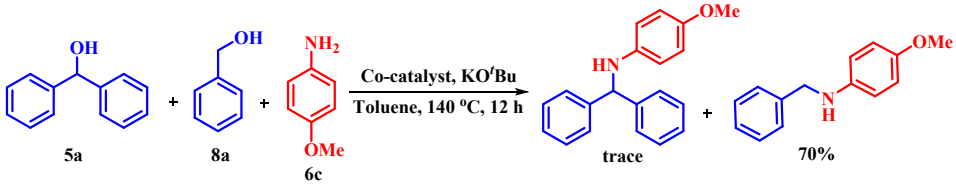
Intermediate ketimine hydrogenation with secondary alcohols

Diphenylmethanol 5a (0.55 mmol), N-(diphenylmethylene) aniline 7aa' (0.5 mmol), KO^{t}Bu (0.38 mmol), Co-catalyst (1 mol%) and toluene (1 mL) were introduced in a mild stream of nitrogen to an oven-dried screw cap reaction tube (15 mL). After that, the reaction mixture was agitated for 12 hours at 140 °C using a magnetic stirring bar. Following the reaction's conclusion, the crude mixture was filtered using the celite filter and cleaned with ethyl acetate (3x5 mL). The solvent was then removed under vacuum, and the residue was then purified using silica gel column chromatography (230-400 mesh particle size) with hexane and ethyl acetate as an eluent to yield the hydrogenated product 7aa in 80% yield.



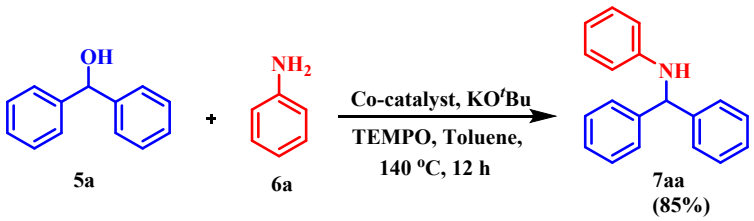
Competitive experiment

Diphenylmethanol 5a (1.1 mmol), benzyl alcohol 8a (1.1 mmol) and 4-methoxy aniline 6c (1 mmol), KO^{t}Bu (0.38 mmol), Co-catalyst (1 mol%) and toluene (1 mL) were added to 15 mL screw capped reaction tube that had been oven dried. After that, the reaction mixture was agitated at 140 °C for 12 h. Following the end of the reaction, the crude mixture was allowed to cool to room temperature before being concentrated in vacuum and residue was then purified using silica gel column chromatography (230-400 mesh) with hexane and ethyl acetate as an eluent to yield the N-alkylated product 9ca in 70% yield.



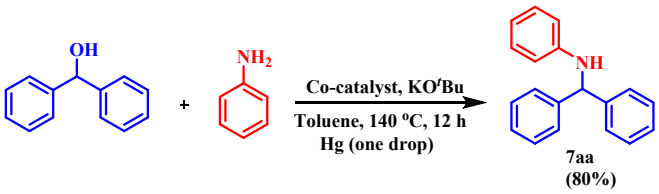
Reaction with radical scavenger

Under a moderate stream of nitrogen, the following were added to a 15 mL of screw cap reaction tube that had been dried in oven: diphenylmethanol 5a (0.55 mmol), aniline 6a (0.5 mmol), TEMPO (1 mmol), KO^{t}Bu (0.38 mmol), Co-catalyst (1 mol%), and toluene (1 mL). At 140 °C, the reaction mixture was then agitated for 12 hours. The crude reaction mixture was concentrated in a vacuum after being cooled to room temperature and filtered through a celite pad with the several washings (3x3 mL ethyl acetate). The intended product was obtained by purifying the residue using silica gel column chromatography (eluent: hexane and ethyl acetate) in 85% yield.



Mercury Poisoning Experiment

We have conducted a mercury drop experiment to determine the heterogeneity or homogeneity of catalyst 1 in the acceptorless dehydrogenative coupling process (ADC). A standard mercury drop test involved charging the reaction tube with 0.5 mmol of aniline, 0.55 mmol of diphenylmethanol, 0.38 mmol of KOtBu and 1 mol% of Co-catalyst, then adding toluene as solvent. After adding a drop of mercury to this reaction mixture, the mixture was agitated for 12 hours at 140 °C. Consequently, the mercury provided a high yield of 7aa under standard conditions without influencing the production of desired product. Therefore, it validates catalyst 1 majorly homogenous character.



Using Co-catalyst for the N-alkylation process, a potential mechanistic cycle is suggested based on the aforementioned results (See Fig. S11). The complex A is produced by the displacement reaction of the precatalyst I in the presence of alkoxide. Subsequently, the removal of β-hydride from A yielded the Co(II) hydride species B. The removal of ketone from C formed later on, and this subsequently underwent a condensation reaction with amines to generate imines. Following the synthesis of complex E and the accompanying N-alkylated secondary amine product, the imine intermediate was hydrogenated by Co(II) hydride species D. Lastly, the complex A is renewed by a reaction between the complex E and alcohol. As a result, the process work through the routes of hydrogenation, condensation, and dehydrogenation (See Scheme 6). After the reaction was performed for 6 hours, we obtained the intermediates D or E mass (cal.967.1526; found 967.1527) by taking a mass spectrum which confirms that intermediate D or E formed during the reaction (See Fig. S12).

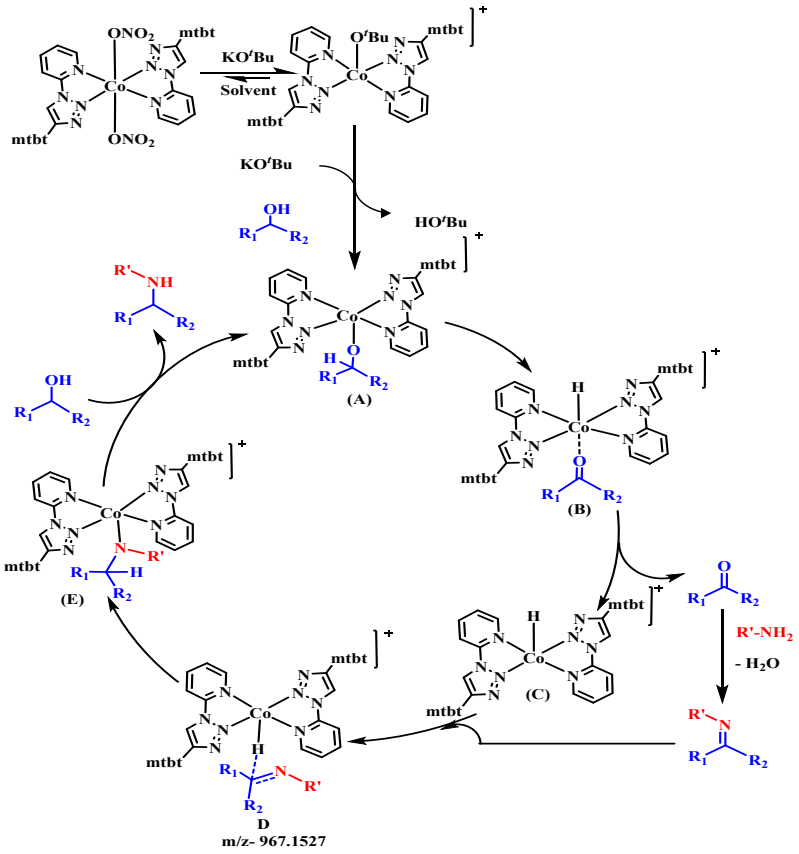


Fig. S11 Plausible mechanism

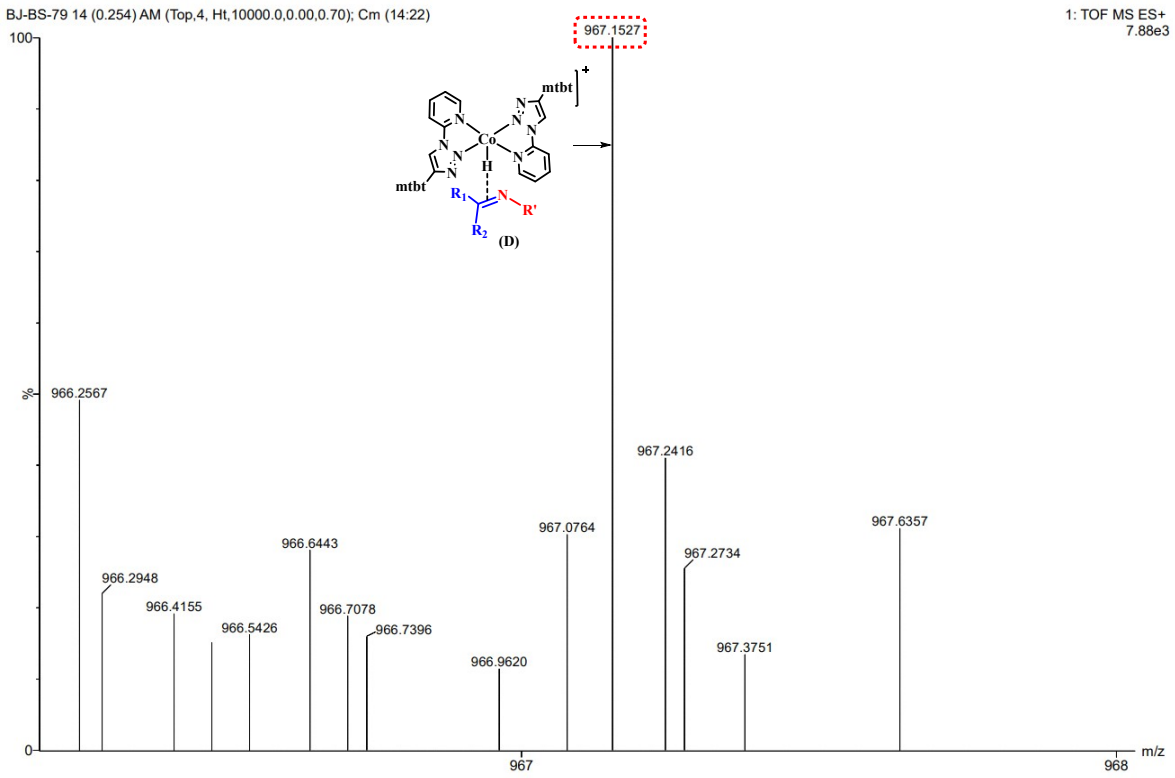
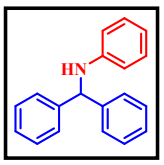


Fig.S12 - ESI Mass Spectrum of D or E

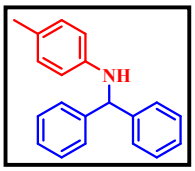
7. Characterization data of N-alkylation of Amines

N-benzhydrylaniline (7aa)



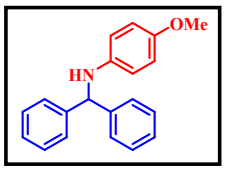
Pale yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.39 (m, 8H), 7.25-7.29 (m, 2H), 7.11-7.15 (m, 2H), 6.69-6.73 (m, 1H), 6.55-6.57 (m, 2H), 5.52 (s, 1H), 4.24 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.45 (s), 143.04 (s), 129.23 (s), 128.86 (s), 127.54 (s), 127.47 (s), 117.74 (s), 113.57 (s), 63.12 (s). Yield - 92%.

N-benzhydryl-4-methylaniline (7ab)



Brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.33 (m, 8H), 7.30-7.26 (m, 2H), 6.98 – 6.96 (m, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 4.15 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.83 (s), 142.83 (s), 129.30 (s), 128.40 (s), 127.13 (d, *J* = 16.6 Hz), 126.97 (s), 113.27 (s), 100.00 (s), 63.01 (s), 20.06 (s). Yield-85%.

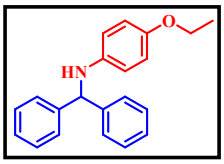
N-benzhydryl-4-methoxyaniline (7ac)



Pale yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.25 (m, 4H), 7.22 – 7.18 (m, 4H), 7.11-7.15 (m, 2H), 6.62-6.68 (m, 2H), 6.37-6.41 (m, 2H), 5.31 (s, 1H), 3.57 (s,

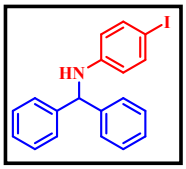
3H). The spectral measurements correlate well with values reported in the literature[6]. Yield- 89%.

N-benzhydryl-4-ethoxyaniline (7ad)



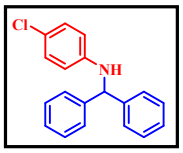
Pale yellow. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.39 (m, 4H), 7.36 – 7.32 (m, 4H), 7.29 – 7.25 (m, 2H), 6.75 – 6.73 (m, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 5.45 (s, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.55 (s), 143.37 (s), 128.84 (s), 128.42 (s), 127.55 (s) 127.41 (s), 115.67 (s), 114.75 (s), 64.11 (s), 63.96 (s) 15.15 (s). Yield- 90%.

N-benzhydryl-4-iodoaniline (7ae)



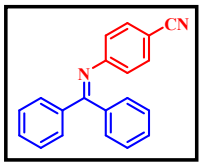
Pale yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 6H), 7.37 – 7.32 (m, 4H), 7.14-7.11 (m, 2H), 6.54-6.50 (m, 2H), 5.55 (s, 1H), 4.32 (s, 1H). The spectral measurements correlate well with values reported in the literature[6]. Yield- 75%.

N-benzhydryl-4-chloroaniline (7af)



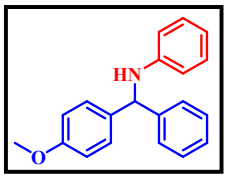
Brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 8H), 7.36 – 7.34 (m, 2H), 7.15-7.11 (m, 2H), 6.54-6.50 (m, 2H), 5.55 (s, 1H), 4.32 (s, 1H). The spectral measurements correlate well with values reported in the literature[6]. Yield- 78%.

4- ((diphenyl methylene) amino) benzonitrile (7ag)



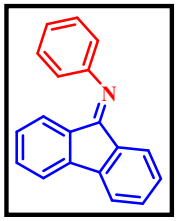
Pale yellow. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74-7.72 (m, 2H), 7.42-7.40 (m, 4H), 7.33-7.732 (m, 4H), 7.08-7.06 (m, 2H), 6.76-6.74 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.72 (s), 130.99 (s), 127.78 (s), 127.47 (s), 126.71 (s), 126.11 (s), 125.79 (s), 125.29 (s), 124.74 (s), 119.60 (s), 110.12 (s). Yield- 80%.

N- ((4- methoxyphenyl) (phenyl) methyl) aniline (7ba)



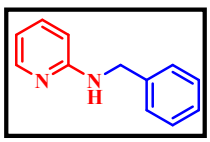
Pale yellow. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 4H), 7.32 – 7.28 (m, 3H), 7.18 – 7.14 (m, 2H), 6.91 – 6.89 (m, 2H), 6.76 – 6.71 (m, 1H), 6.60-6.57 (m, 2H), 5.51 (s, 1H), 4.25 (s, 1H), 3.81 (t, 3H). The spectral measurements correlate well with values reported in the literature[6]. Yield- 86%.

N-phenyl-9*H*-fluoren-9-imine (7ca)



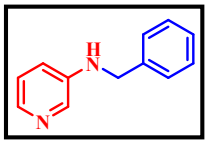
Pale yellow. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66-7.64 (m, 3H), 7.60 – 7.58 (m, 1H), 7.52 – 7.47 (m, 4H), 7.47 (d, *J* = 1.1 Hz, 1H), 7.42-7.26 (m, 1H), 7.30 – 7.26 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.06 (s), 144.52 (s), 134.79 (s), 134.23 (s), 129.40 (s), 129.17 (s), 127.76 (s), 127.16 (s), 124.42 (s), 120.40 (s), 118.33 (s). Yield- 90%.

N-benzylpyridin-2-amine (9af)



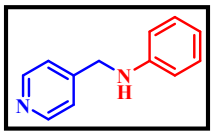
White crystalline solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.39 – 7.31 (m, 5H), 7.29-7.27 (m, 1H), 6.58 – 6.55 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 5.29 (s, 1H), 4.48 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.83 (s), 148.18 (s), 139.31 (s), 137.68 (s), 128.74 (s),127.49 (S) 127.32 (s), 113.15 (s), 106.84 (s), 46.39 (s). Yield- 98%.

N-benzylpyridin-3-amine (9ad)



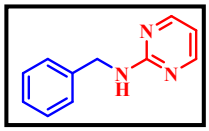
Brownish liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-7.94 (m, 1H), 7.81-7.80 (m, 1H), 7.24-7.20 (m, 4H), 7.18 – 7.13 (m, 1H), 6.94-6.91 (m, 1H), 6.77 – 6.74 (m, 1H), 4.20 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.68 (s), 138.26 (s), 135.77 (s), 128.85 (s), 128.48 (s), 127.46 (s), 127.01 (s), 123.98 (s), 118.86 (s), 47.74 (s). Yield- 98%.

N-(pyridine-4-ylmethyl) aniline (9ba)



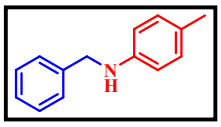
Yellowish liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74-7.72 (m, 2H), 6.54 – 6.52 (m, 3H), 6.38 – 6.34 (m, 1H), 5.96-5.91 (m, 1H), 5.7-5.75 (m, 2H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.96 (s), 147.40 (s), 129.46 (s), 122.42 (s), 118.20 (s), 112.95 (s), 47.08 (s). Yield- 96%.

N-benzlpyrimidin-2-amine (9ag)



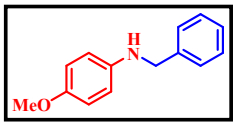
White crystalline solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09-8.07 (m, 1H), 7.36 – 7.25 (m, 6H), 6.55 (s, 1H), 6.45-6.43 (m, 1H), 4.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.40 (s), 158.09 (s), 139.21 (s), 128.68 (s), 127.74 (s), 127.30 (s), 110.63 (s), 45.56 (s). Yield- 99%.

N-benzyl-4-methylaniline (9ab)



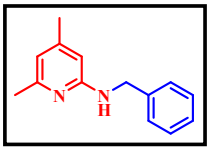
Yellowish liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.20 (m, 5H), 6.89 – 6.86 (m, 2H), 6.47-6.45 (m, 2H), 4.19 (s, 2H), 2.13 (s, 3H). The spectral measurements correlate well with values reported in the literature[9]. Yield- 99%.

N-benzyl-4-methoxyaniline (9ac)



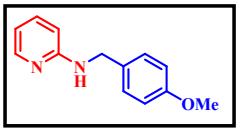
Yellowish liquid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.15 (m, 5H), 6.70-6.68 (m, 2H), 6.53-6.51 (m, 2H), 4.19 (s, 2H), 3.65 (s, 3H). The spectral measurements correlate well with the values reported in the literature[9]. Yield- 90%.

N-benzyl-4,6-dimethylpyridine-2-amine (9ae)



White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.23 (m, 5H), 6.32 – 6.32 (m, 1H), 6.00 (s, 1H), 4.92 (s, 1H), 4.44 (s, 2H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.73 (s), 156.70 (s), 149.08 (s), 139.42 (s), 128.67 (s),127.41 (s), 127.23 (s), 114.24 (s), 103.34 (s), 46.68 (s), 24.20 (s), 21.25 (s). Yield- 96%.

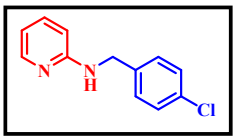
N-(4-methoxybenzyl)pyridine-2-amine (9cf)



White crystal. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08-8.07 (m, 1H), 7.40 – 7.35 (m, 1H), 7.28-7.25 (m, 2H), 6.87-6.84 (m, 2H), 6.58 – 6.55 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H),

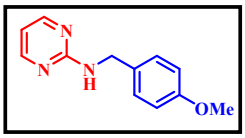
4.91 (s, 1H), 4.41 (s, 2H), 3.78 (s, 3H). The spectral measurements correlate well with values reported in the literature[10].Yield- 99%.

N-(4-chlorobenzyl)pyridine-2-amine (9df)



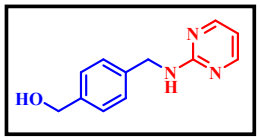
White crystal. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 1H), 7.41 – 7.36 (m, 1H), 7.28 (s, 3H), 6.60 - 6.57 (m, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.95 (s, 1H), 4.48 (s, 2H). The spectral measurements correlate well with values reported in the literature[10]. Yield- 95%.

N-(4-methoxybenzyl)pyrimidin-2-amine (9cg)



Yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 0.7 Hz, 2H), 7.28 – 7.25 (m, 2H), 6.86 – 6.84 (m, 2H), 6.50 - 6.48 (M, 1H), 5.88 (s, 1H), 4.54 (d, *J* = 5.7 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.31 (s), 158.93 (s), 158.14 (s), 131.16 (s), 128.97 (s), 114.05 (s), 110.74 (s), 55.38 (s), 45.02 (s). Yield- 94%.

(4-((pyrimidin-2-ylamino)methyl)phenyl)methanol (9eg)



White crystal. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18-8.17 (m, 2H), 7.30-7.22 (m, 4H), 6.50-6.48 (m, 1H), 5.71 (s, 1H), 4.63 (s, 2H), 4.52 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.14 (s), 158.15 (s), 140.34 (s), 138.34 (s), 127.62 (s), 127.33 (s), 110.84 (s), 64.84 (s), 45.08 (s). Yield- 80%.

8. ^{1}H-NMR, ^{13}C-NMR spectra of N-alkylated products

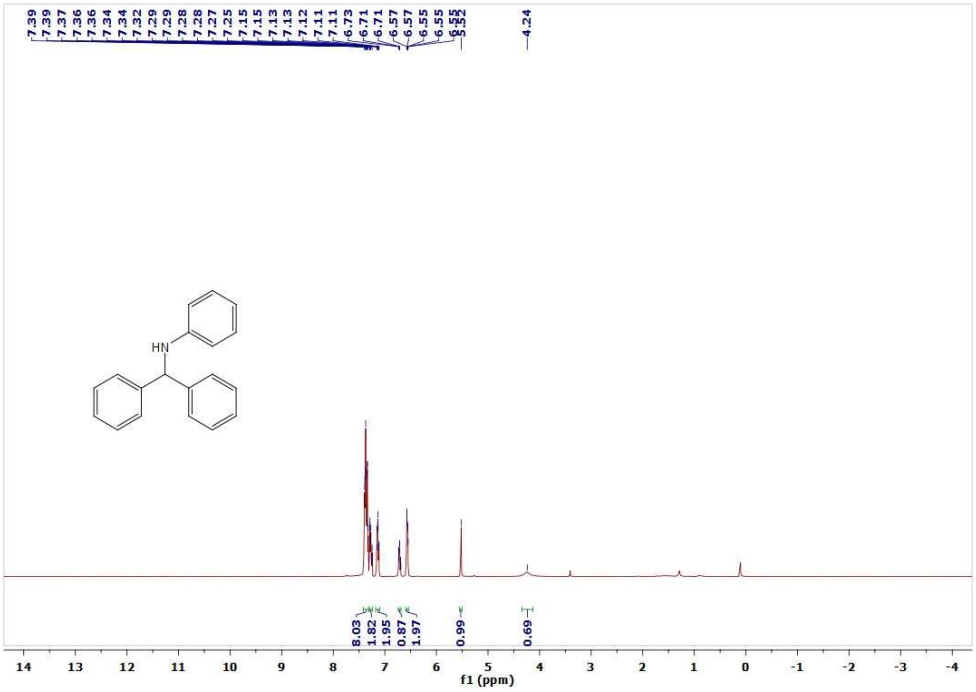


Fig. S13 ^{1}H-NMR Spectra of **7aa** in $CDCl_3$ (400 MHz)

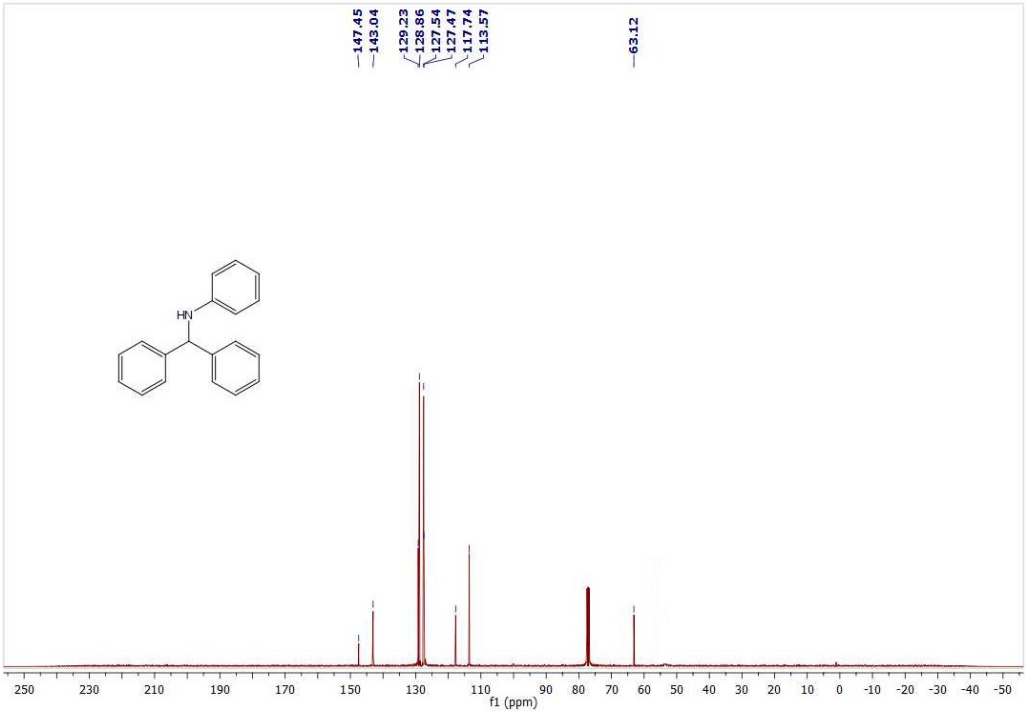


Fig.S14 $^{13}C\{^{1}H\}$-NMR Spectra of **7aa** in $CDCl_3$ (101 MHz)

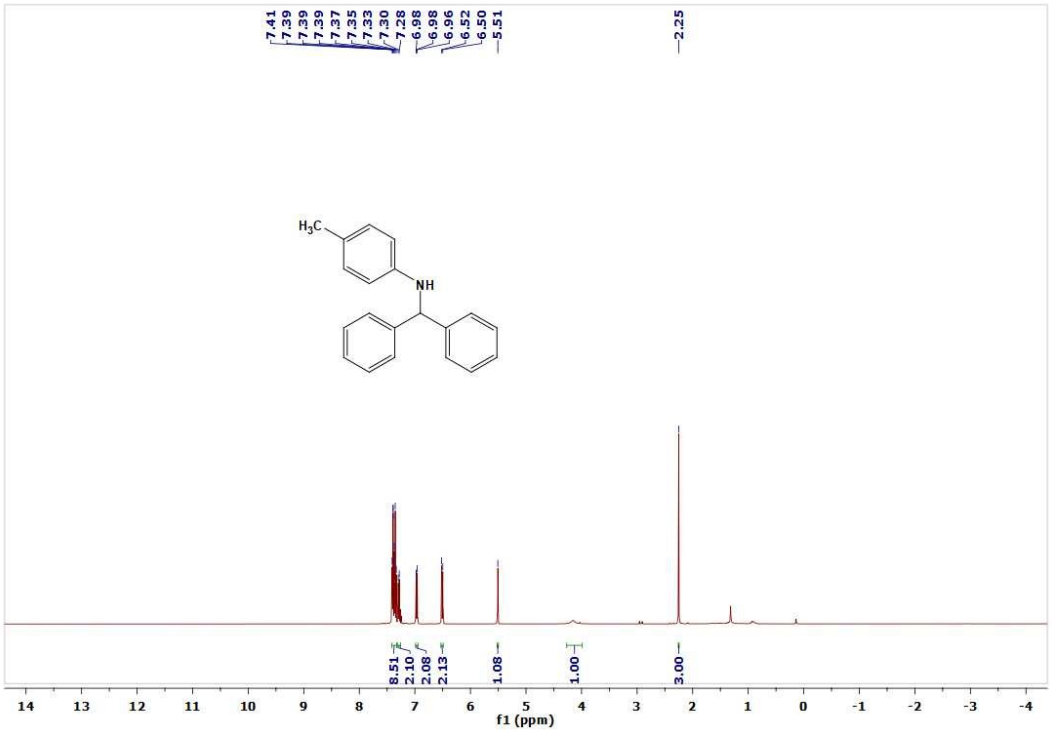


Fig.S15 ^{1}H-NMR Spectra of **7ab** in $CDCl_3$ (400 MHz)

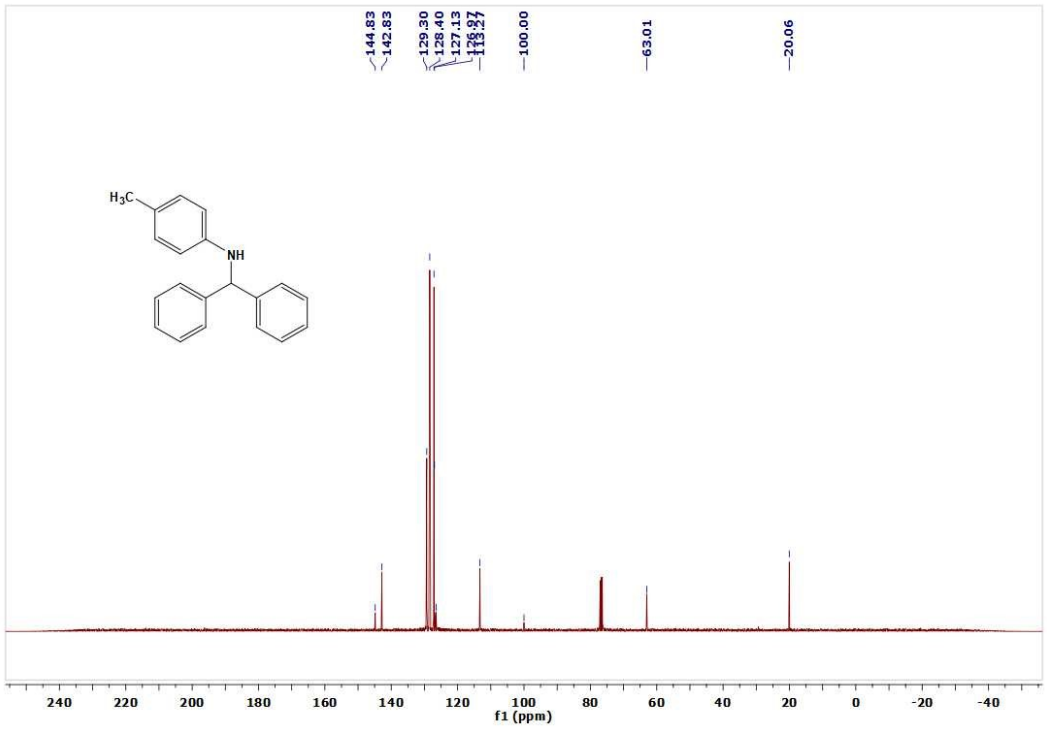


Fig.S16 $^{13}C\{^{1}H\}$-NMR Spectra of **7ab** in $CDCl_3$ (101 MHz)

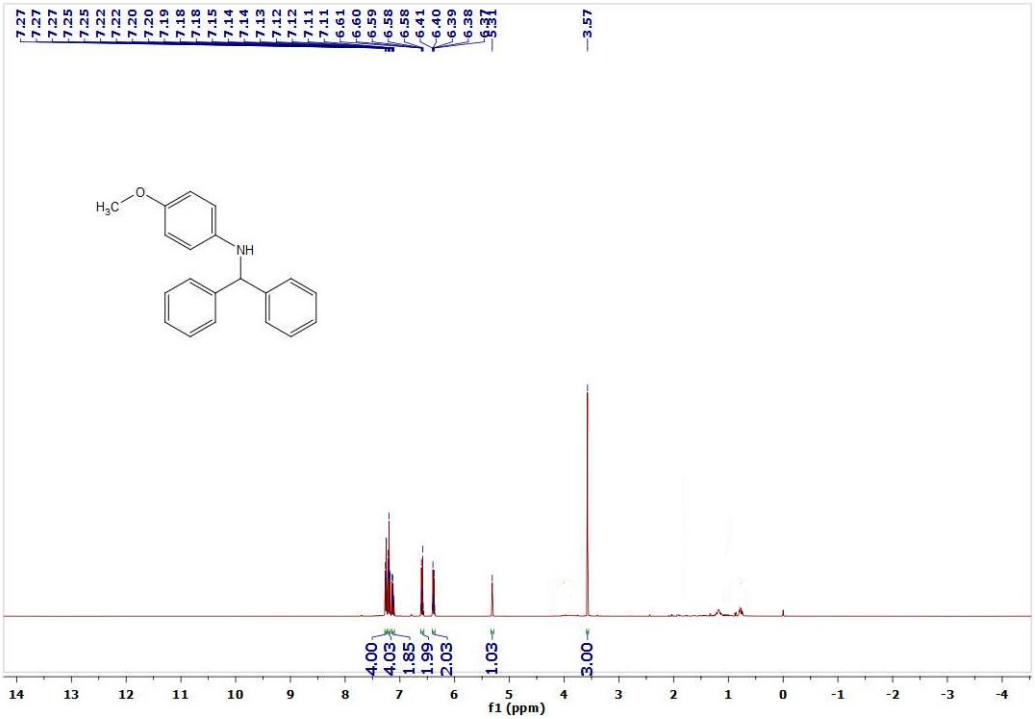


Fig.S17 ^{1}H-NMR Spectra of **7ac** in $CDCl_3$ (400 MHz)

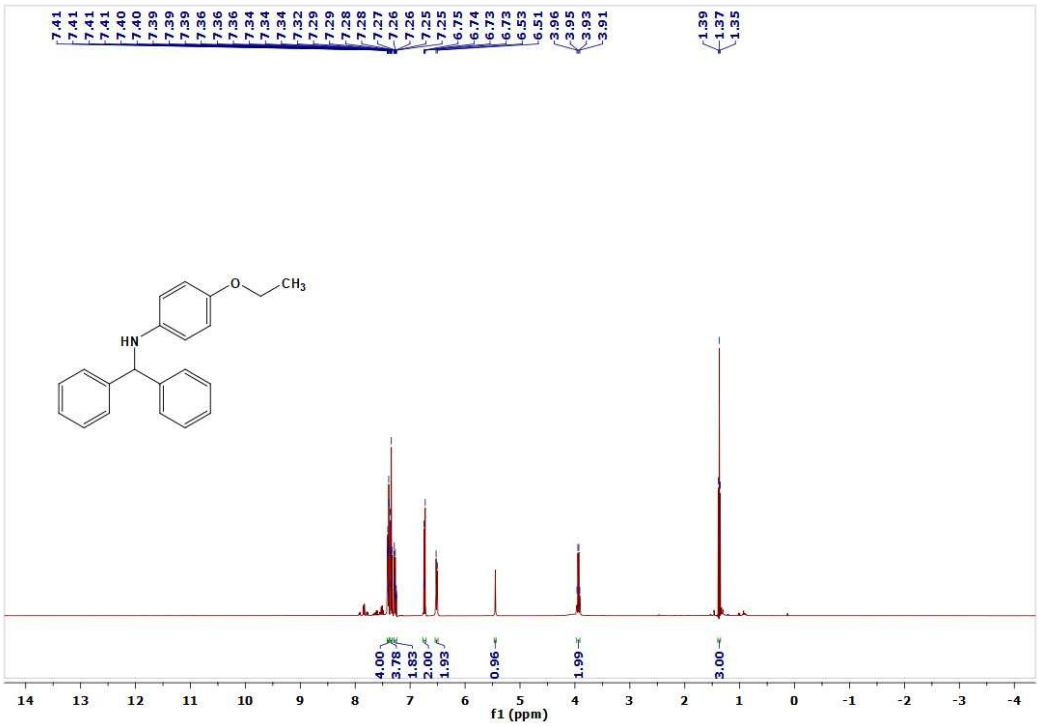


Fig.S18 ^{1}H-NMR Spectra of **7ad** in $CDCl_3$ (400 MHz)

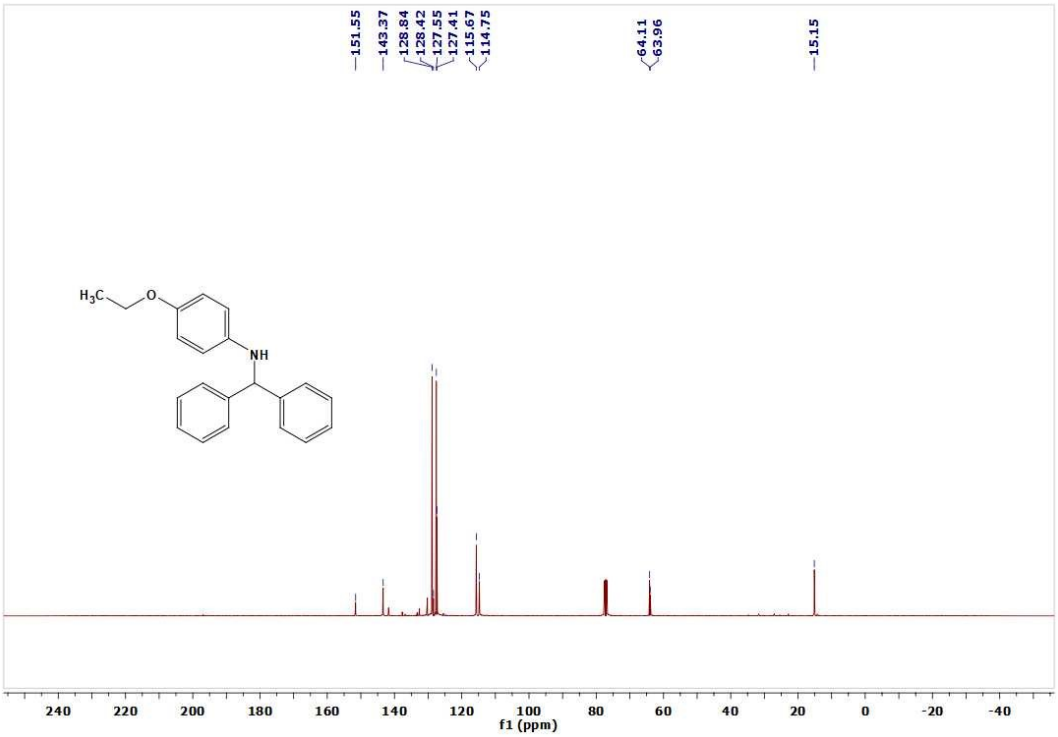


Fig.S19 $^{13}C\{^{1}H\}$-NMR Spectra of **7ad** in $CDCl_3$ (101 MHz)

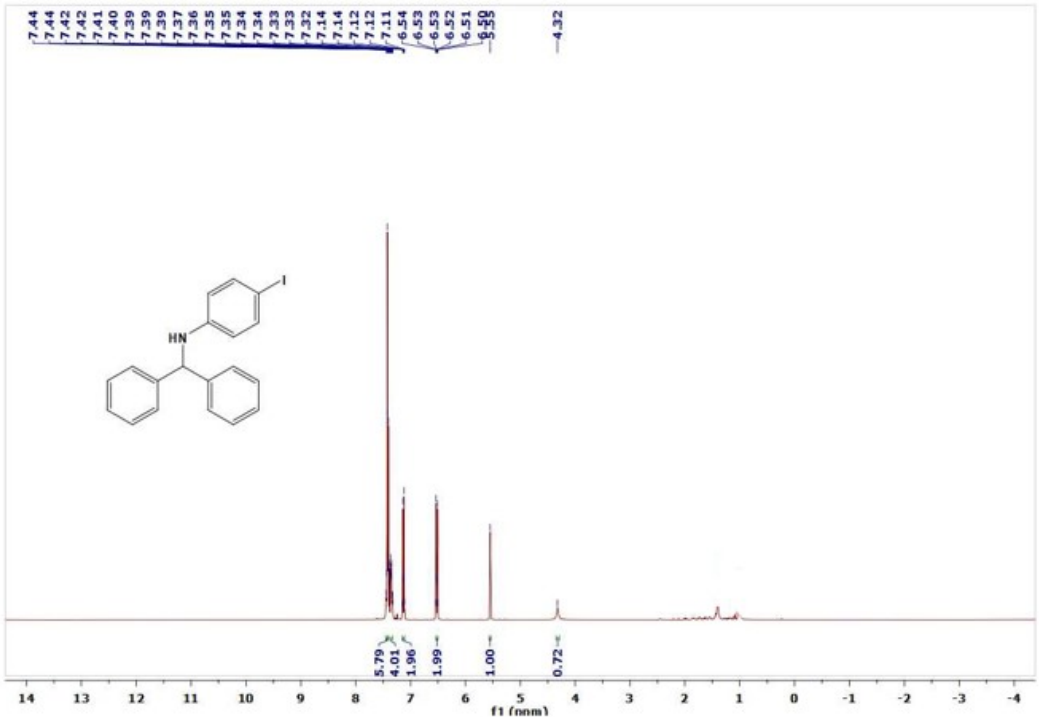


Fig.S20 ^{1}H-NMR Spectra of **7ae** in $CDCl_3$ (400 MHz)

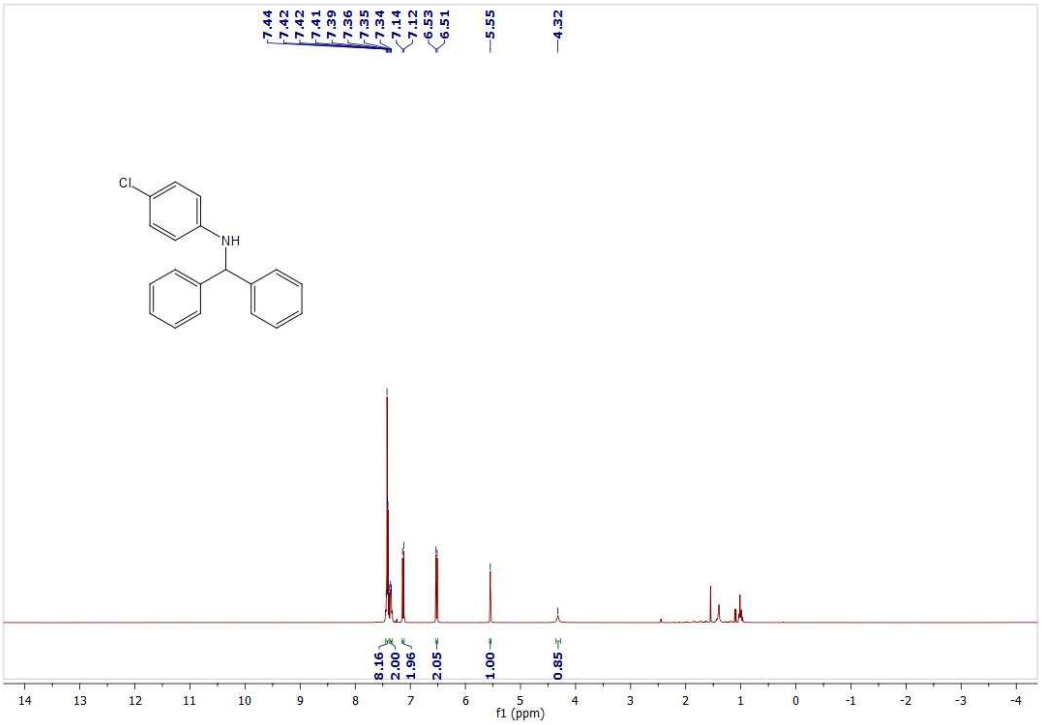


Fig.S21 ^{1}H-NMR Spectra of **7af** in $CDCl_3$ (400 MHz)

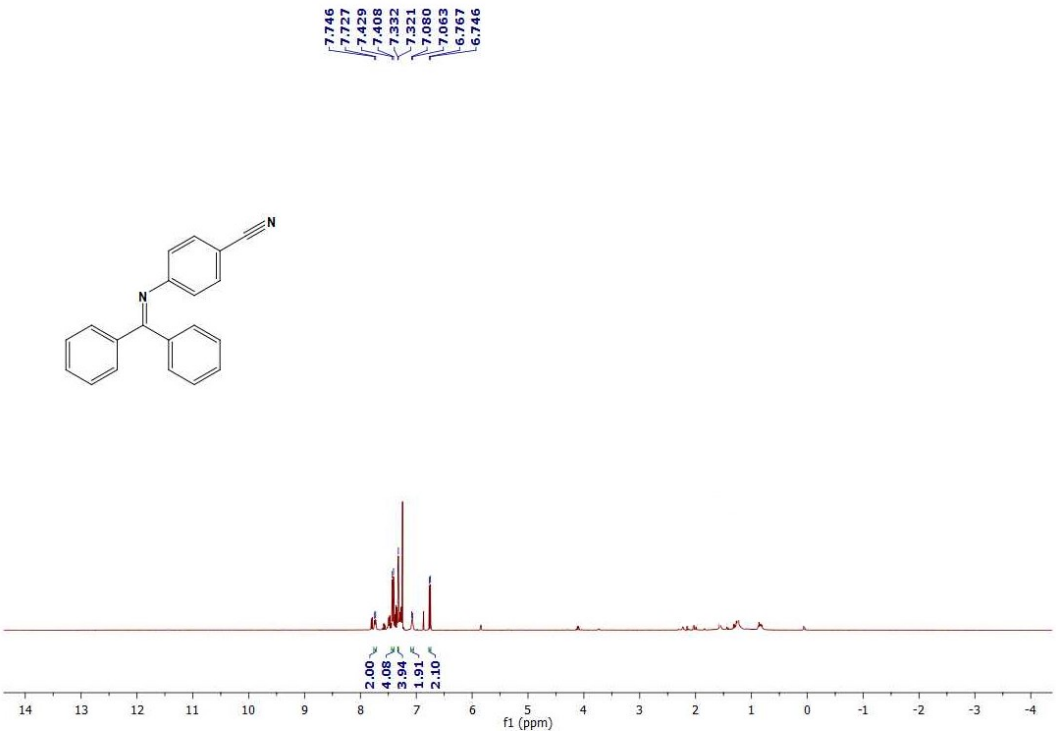


Fig.S22 ^{1}H-NMR Spectra of **7ag** in $CDCl_3$ (400 MHz)

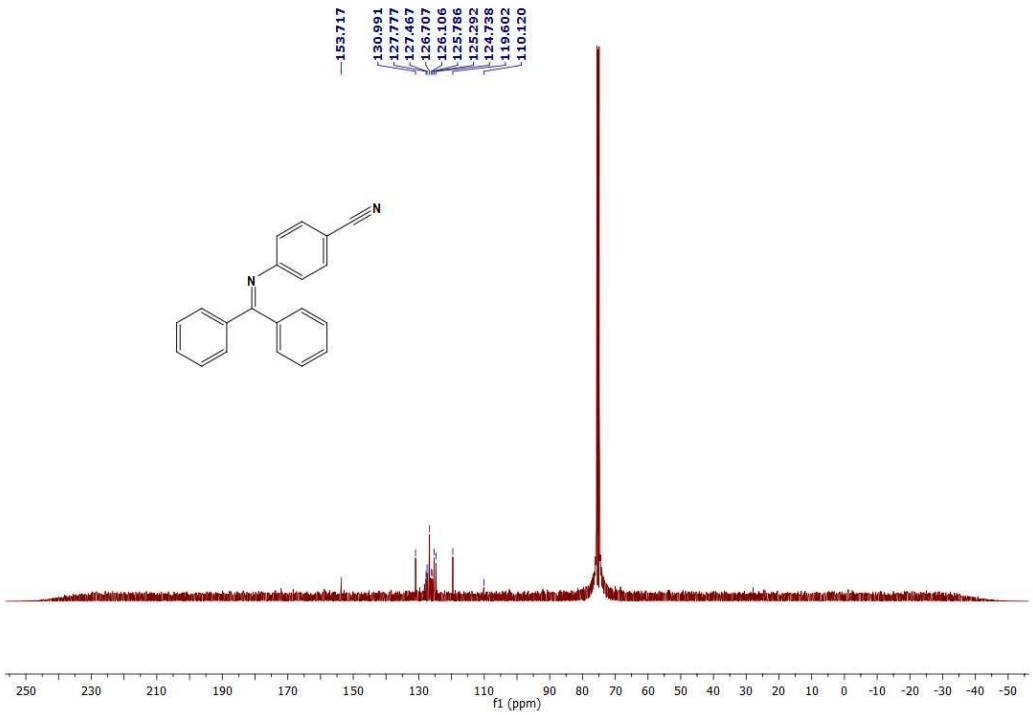


Fig.S23 $^{13}C\{^{1}H\}$-NMR Spectra of **7ag** in $CDCl_3$ (101 MHz)

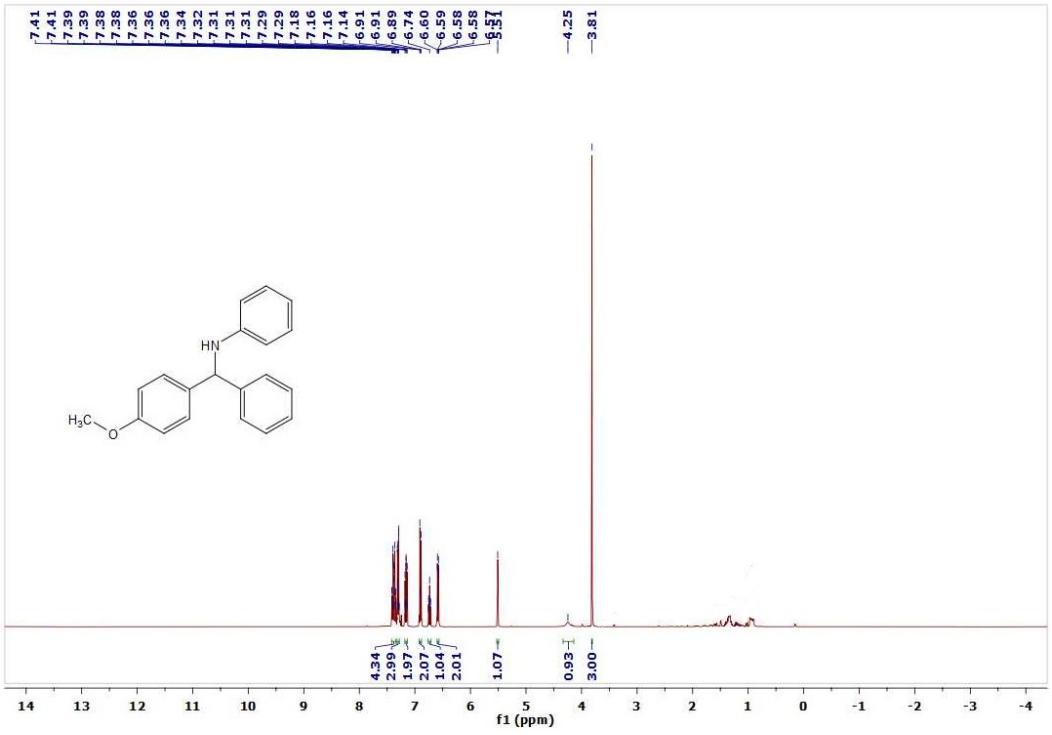


Fig.S24 ^{1}H-NMR Spectra of **7ba** in $CDCl_3$ (400 MHz)

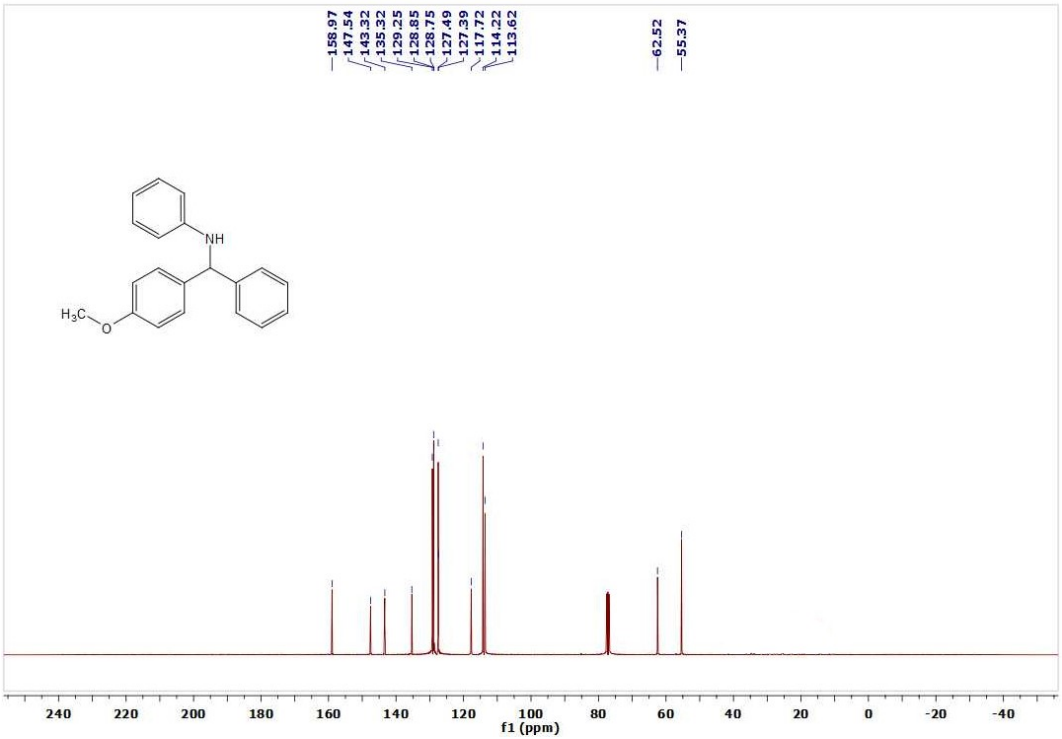


Fig.S25 $^{13}C\{^{1}H\}$-NMR Spectra of **7ba** in $CDCl_3$ (101 MHz)

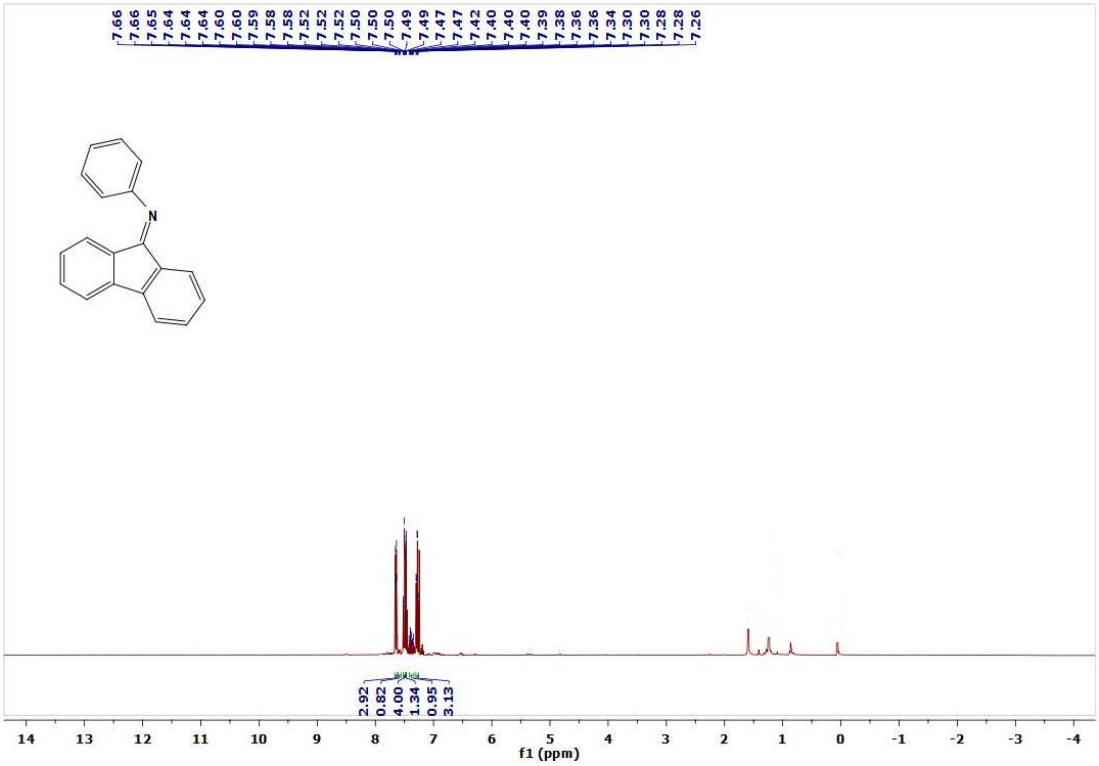


Fig.S26 ^{1}H-NMR Spectra of **7ca** in $CDCl_3$ (400 MHz)

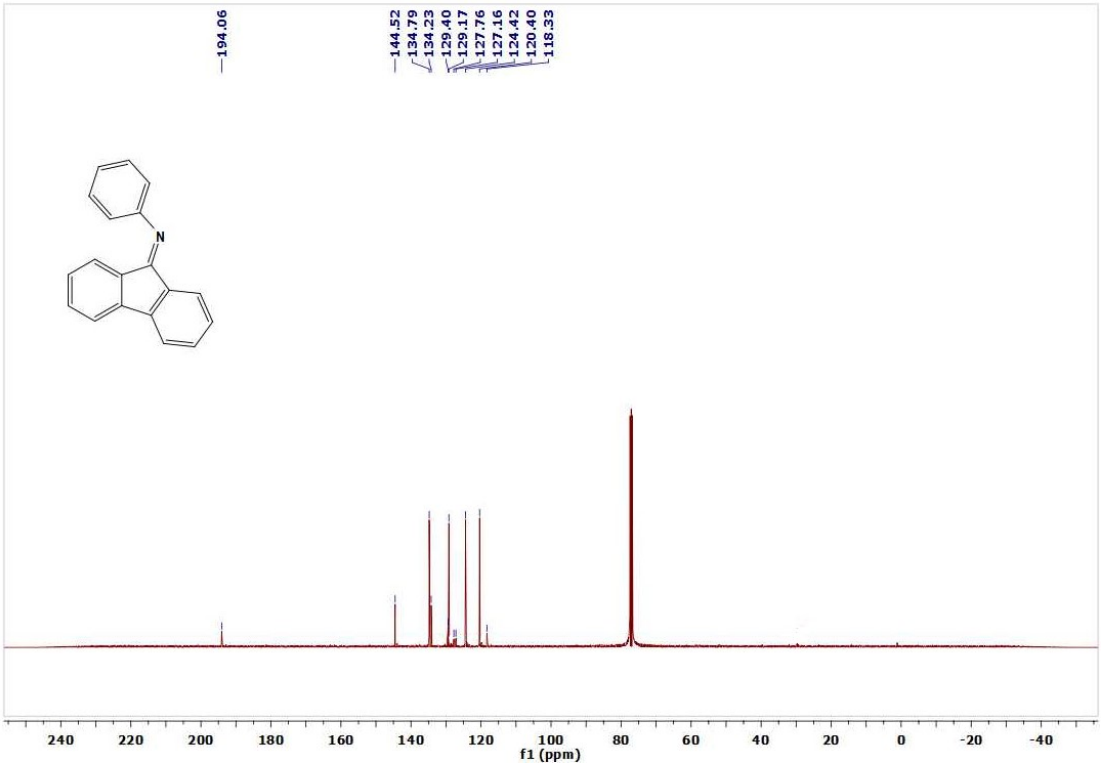


Fig.S27 $^{13}C\{^{1}H\}$-NMR Spectra of **7ca** in $CDCl_3$ (101 MHz)

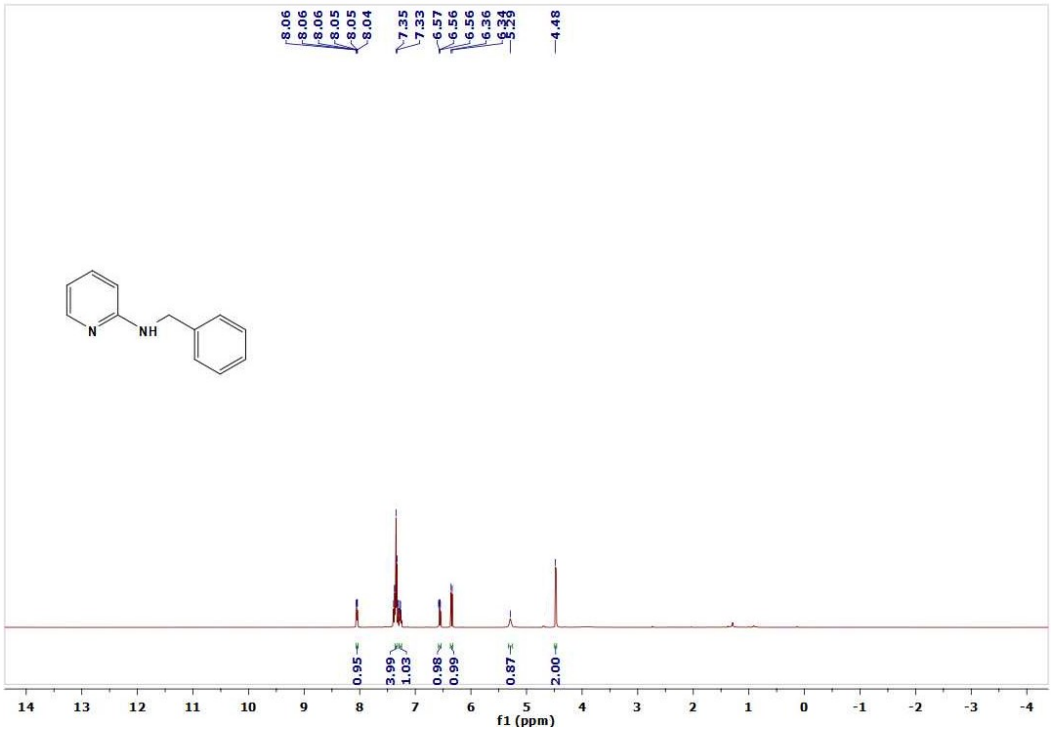


Fig.S28 ^{1}H-NMR Spectra of **9af** in $CDCl_3$ (400 MHz)

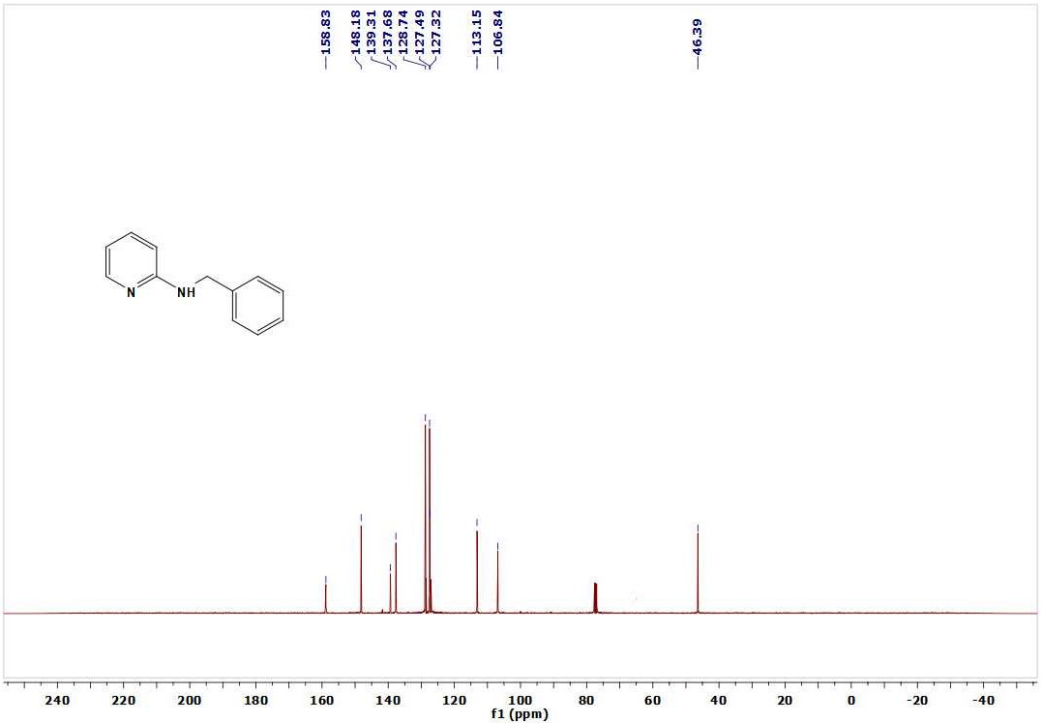


Fig.S29 $^{13}C\{^{1}H\}$-NMR Spectra of **9af** in $CDCl_3$ (101 MHz)

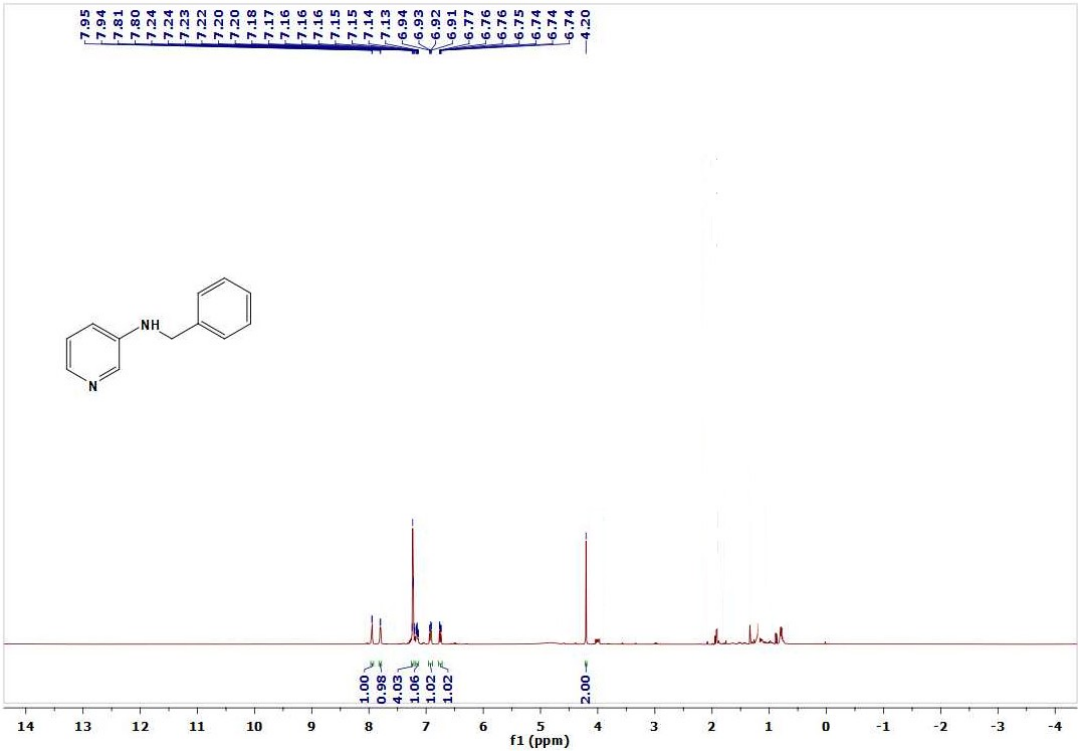


Fig.S30 ^{1}H-NMR Spectra of **9ad** in $CDCl_3$ (400 MHz)

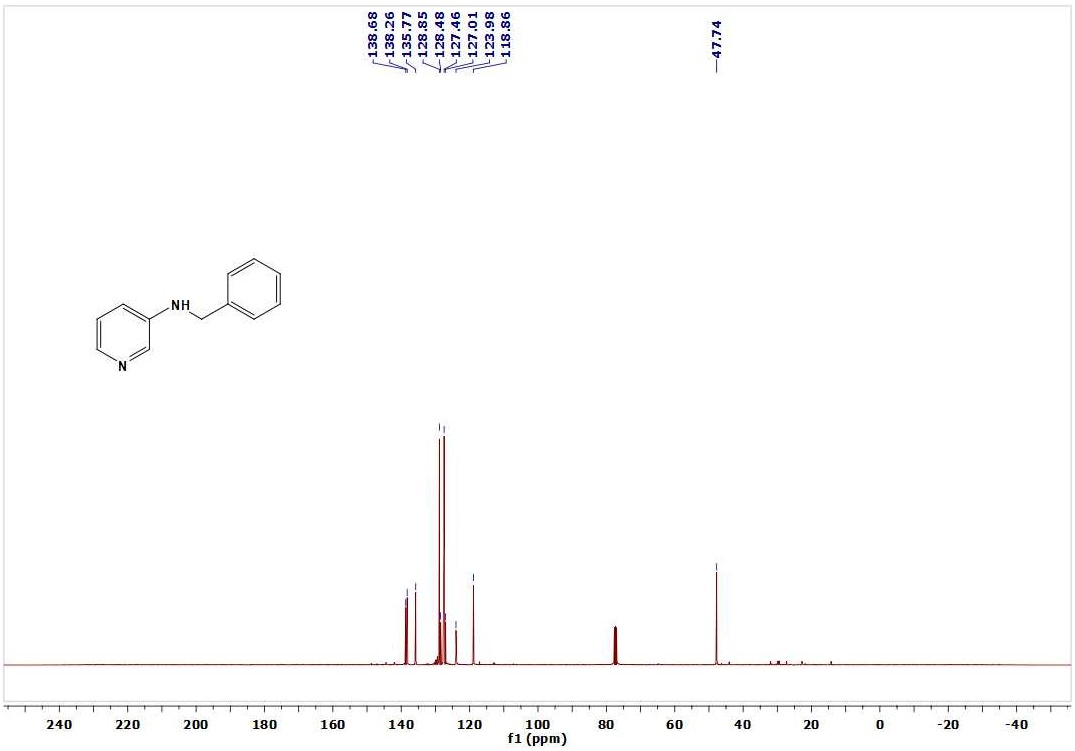


Fig.S31 $^{13}C\{^{1}H\}$-NMR Spectra of **9ad** in $CDCl_3$ (101 MHz)

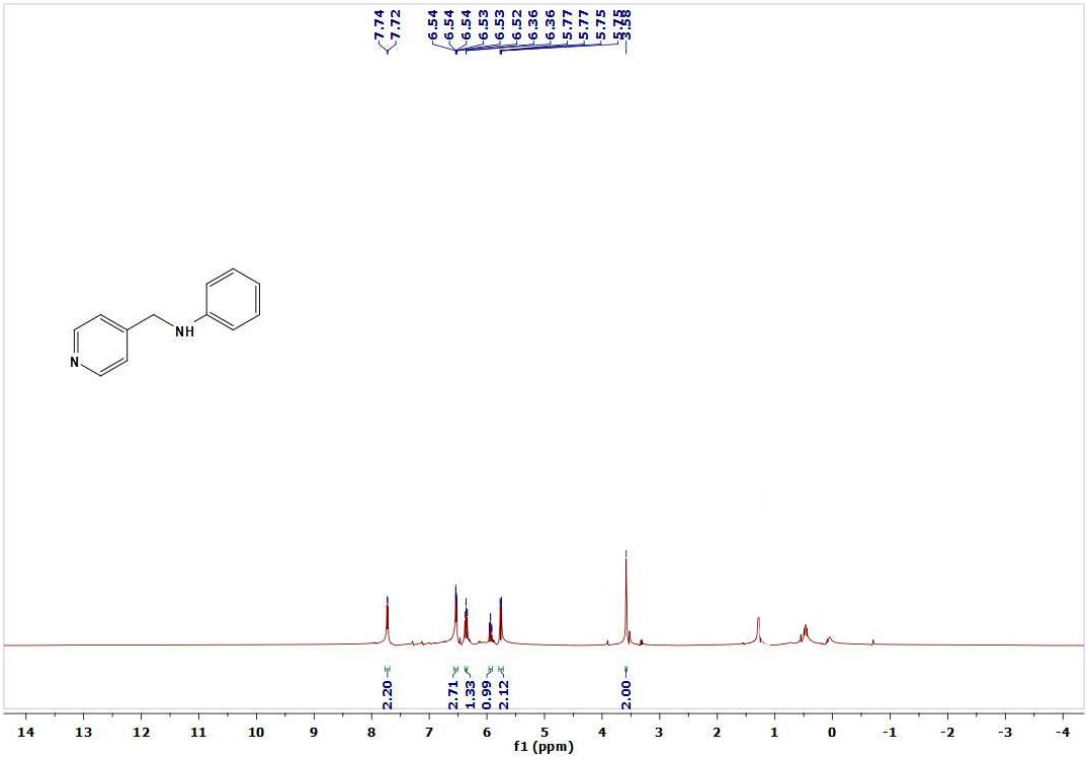


Fig.S32 ^{1}H-NMR Spectra of **9ba** in $CDCl_3$ (400 MHz)

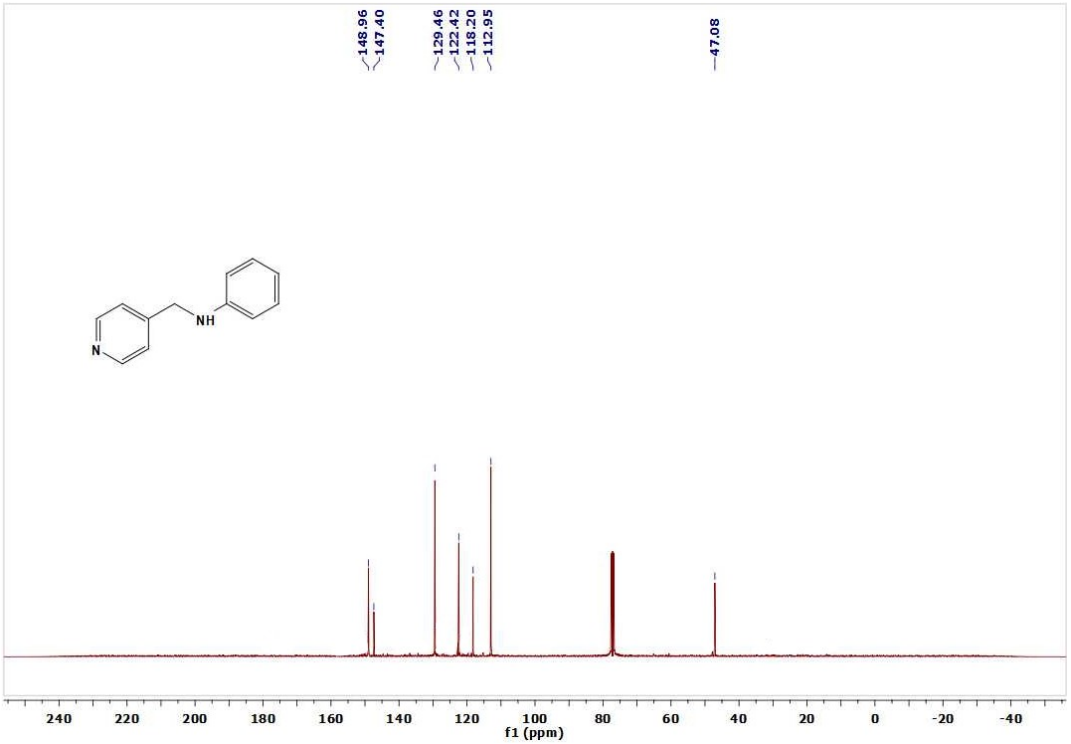


Fig.S33 $^{13}C\{^{1}H\}$-NMR Spectra of **9ba** in $CDCl_3$ (101 MHz)

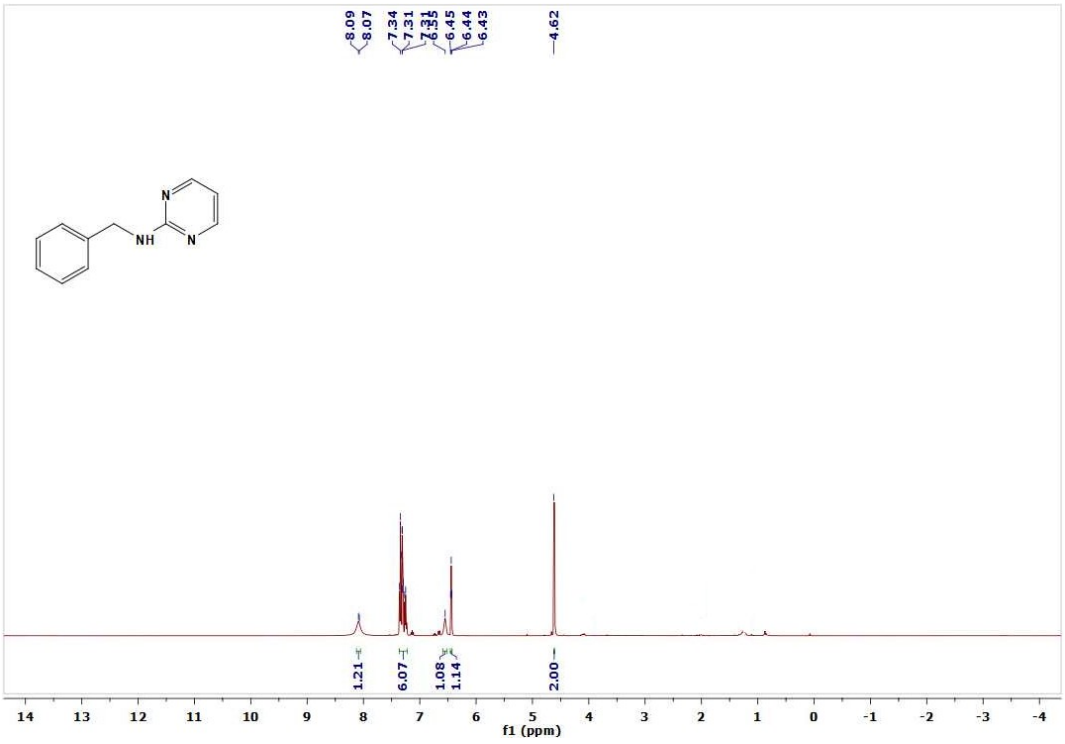


Fig.S34 ^{1}H-NMR Spectra of **9ag** in $CDCl_3$ (400 MHz)

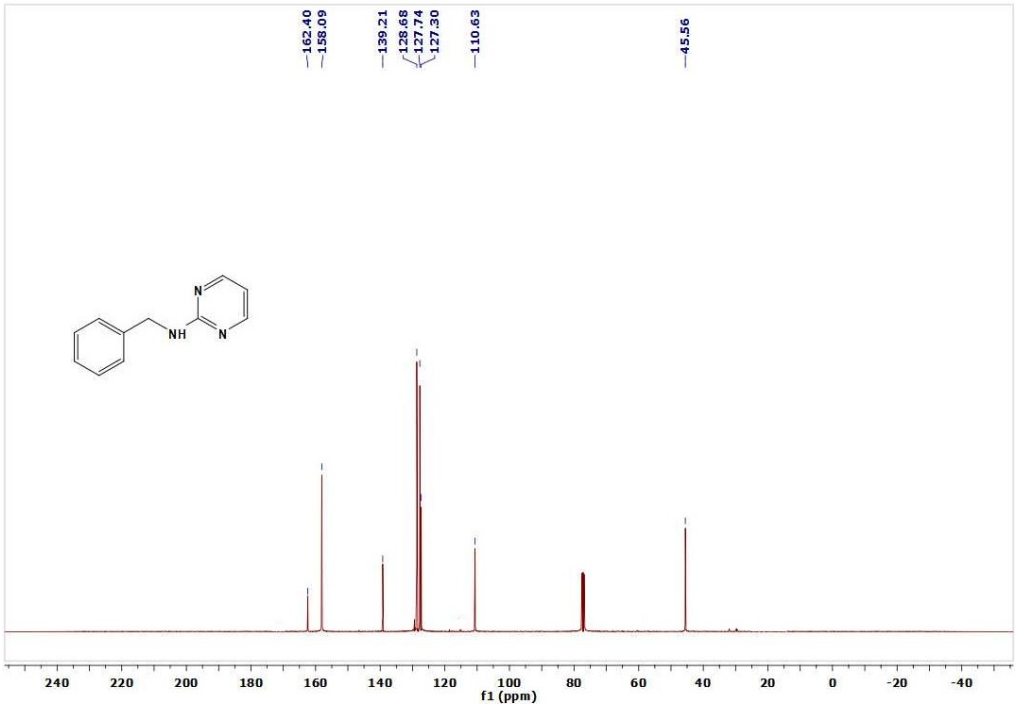


Fig.S35 $^{13}C\{^{1}H\}$-NMR Spectra of **9ag** in $CDCl_3$ (101 MHz)

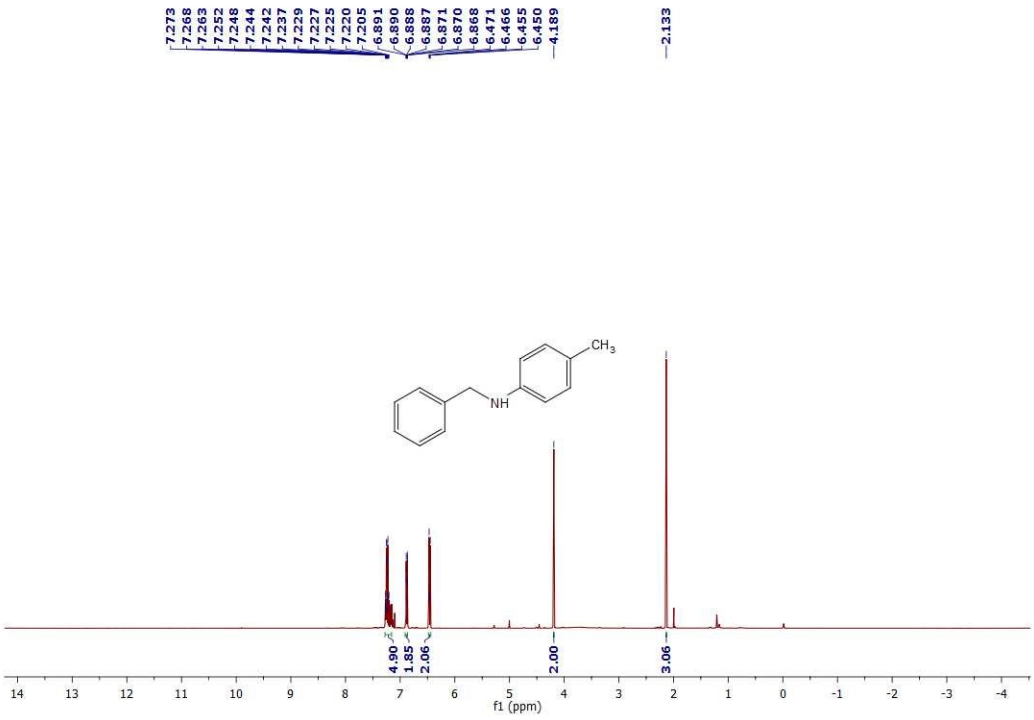


Fig.S36 ^{1}H-NMR Spectra of **9ab** in $CDCl_3$ (400 MHz)

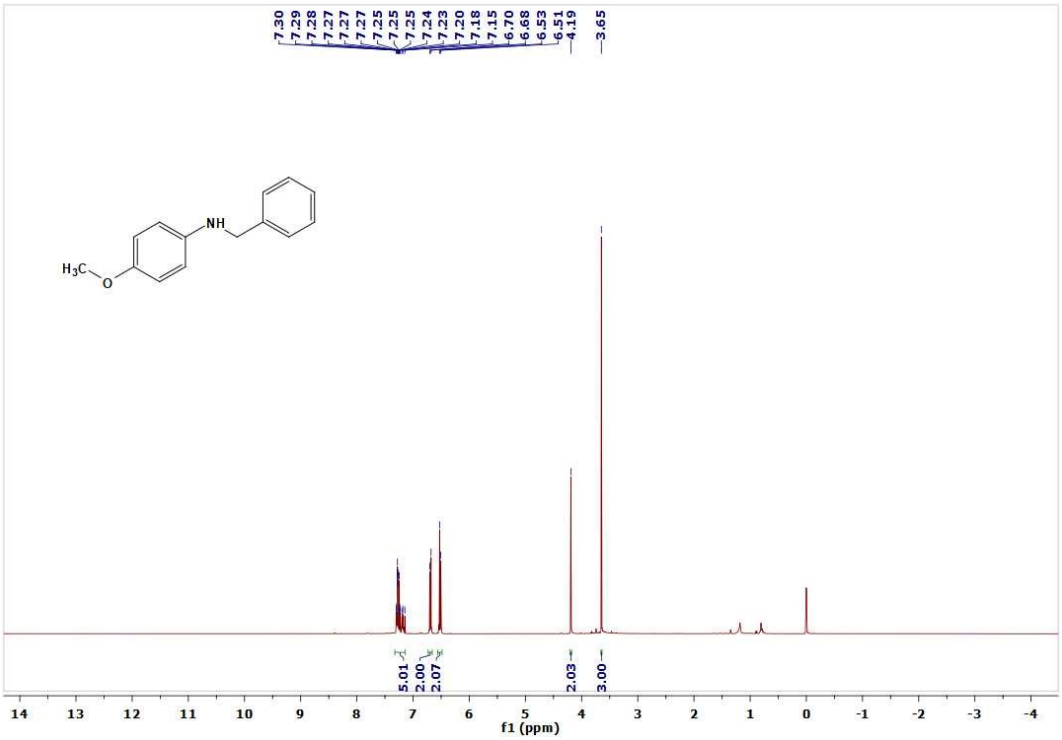


Fig.S37 ^{1}H-NMR Spectra of **9ac** in $CDCl_3$ (400 MHz)

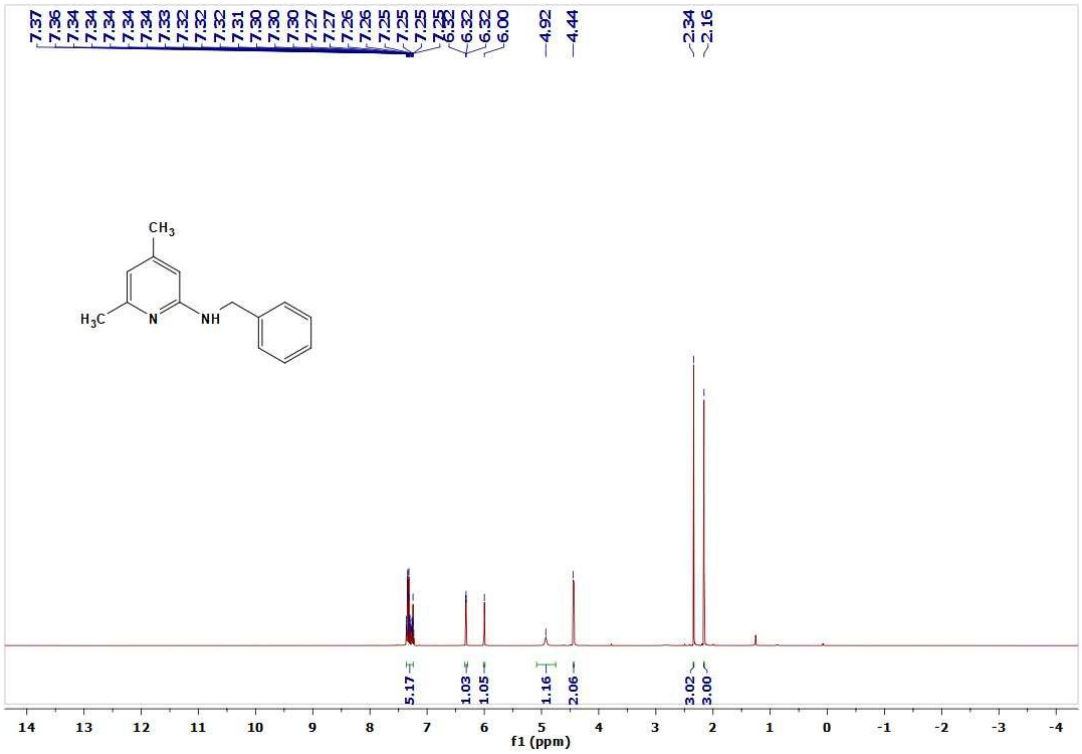


Fig.S38 ^{1}H-NMR Spectra of **9ae** in $CDCl_3$ (400 MHz)

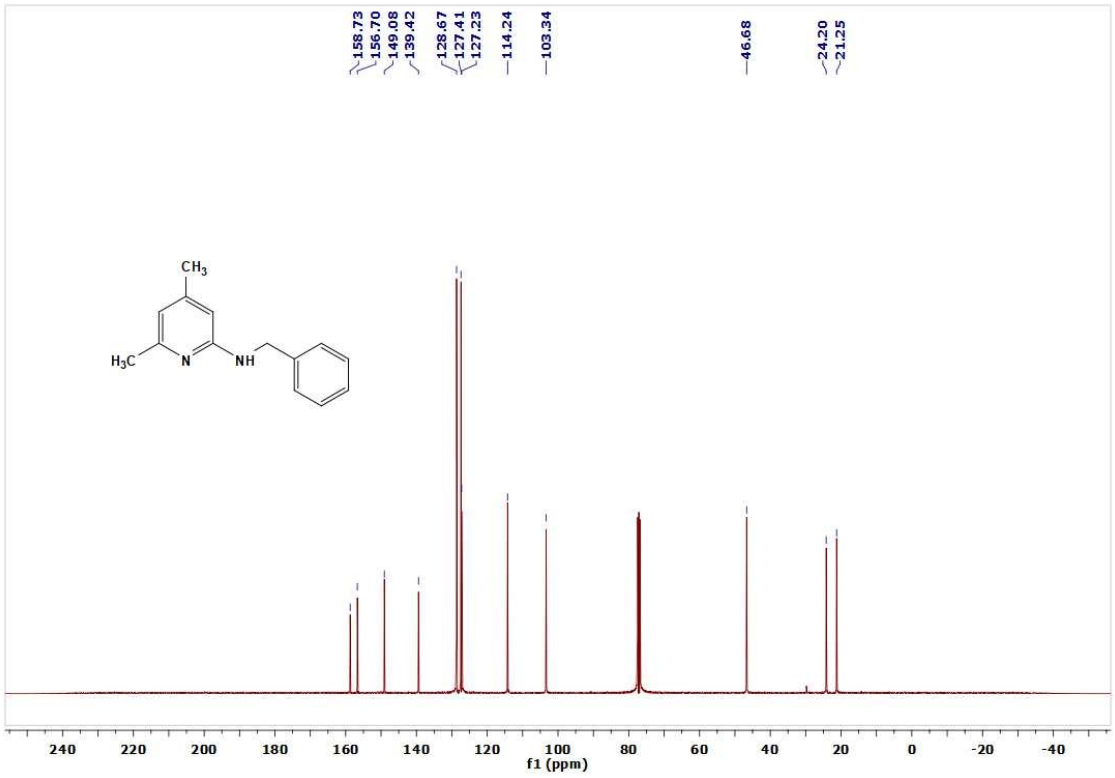


Fig.S39 $^{13}C\{^{1}H\}$-NMR Spectra of **9ae** in $CDCl_3$ (101 MHz)

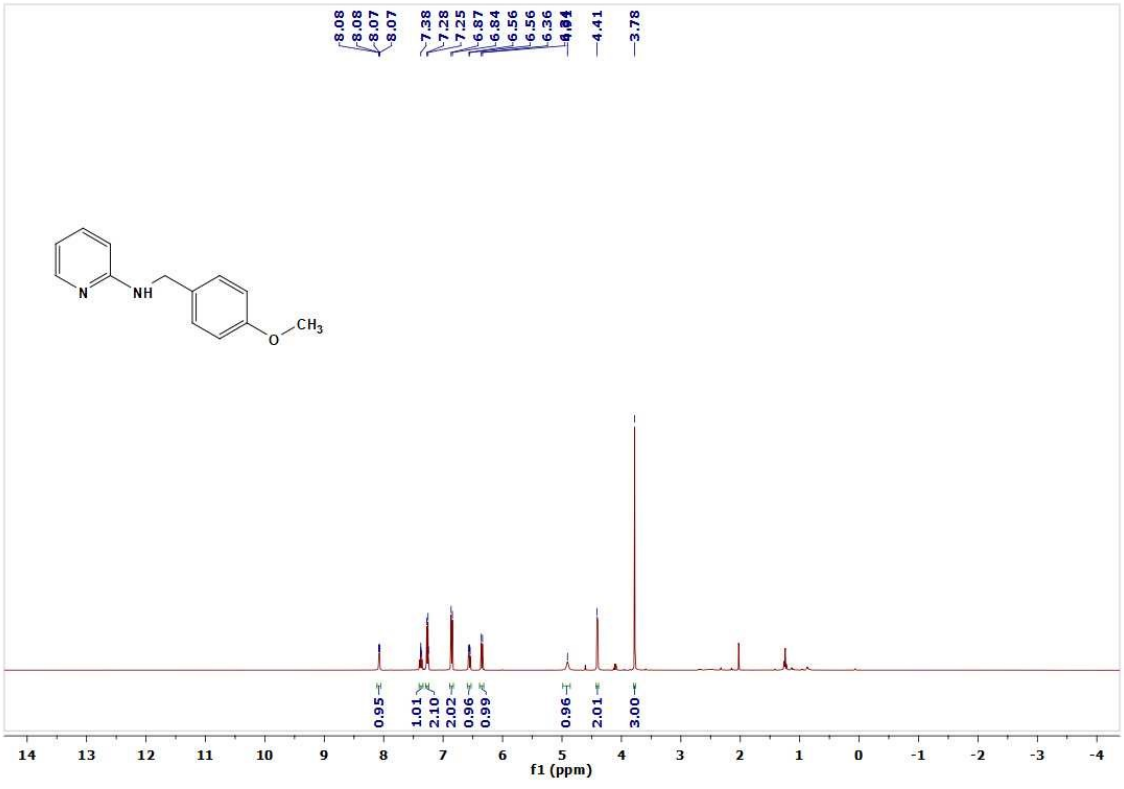


Fig.S40 ^{1}H-NMR Spectra of **9cf** in $CDCl_3$ (400 MHz)

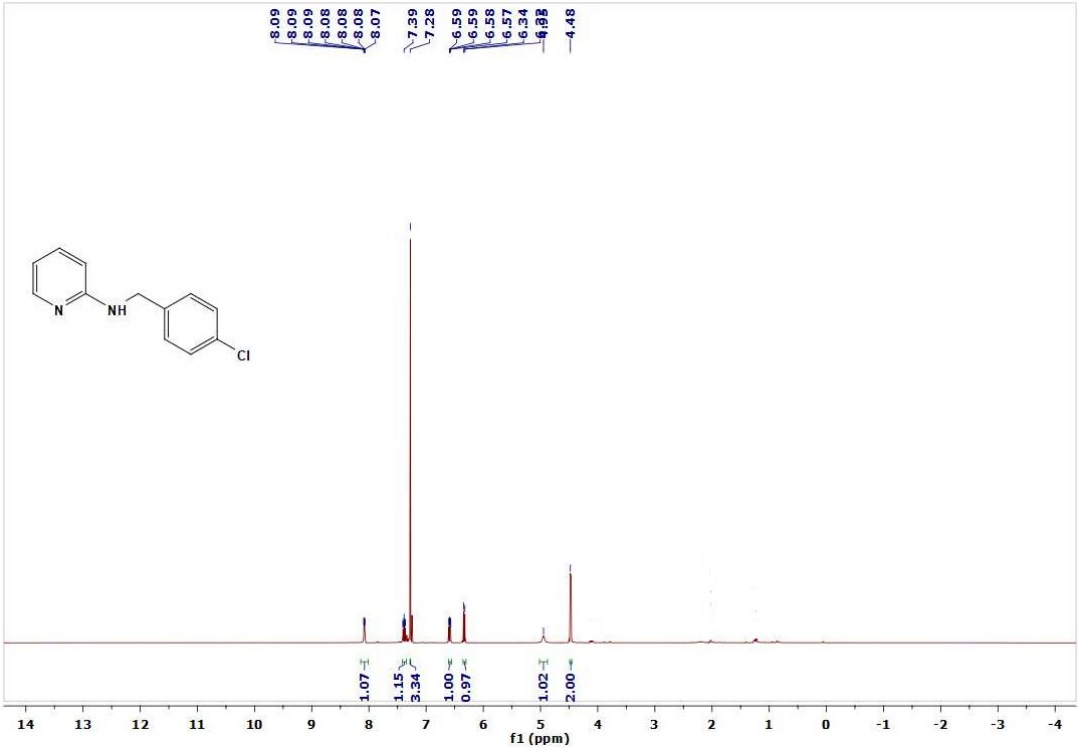


Fig.S41 ^{1}H-NMR Spectra of **9df** in $CDCl_3$ (400 MHz)

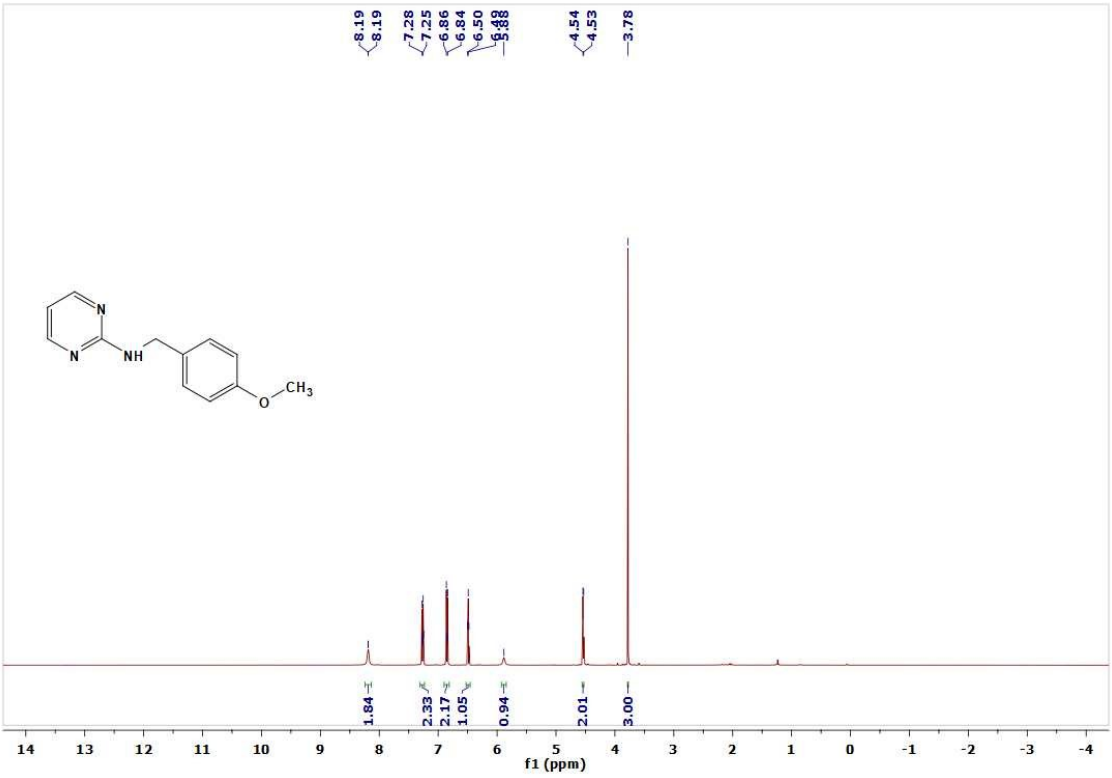


Fig.S42 ^{1}H-NMR Spectra of **9cg** in $CDCl_3$ (400 MHz)

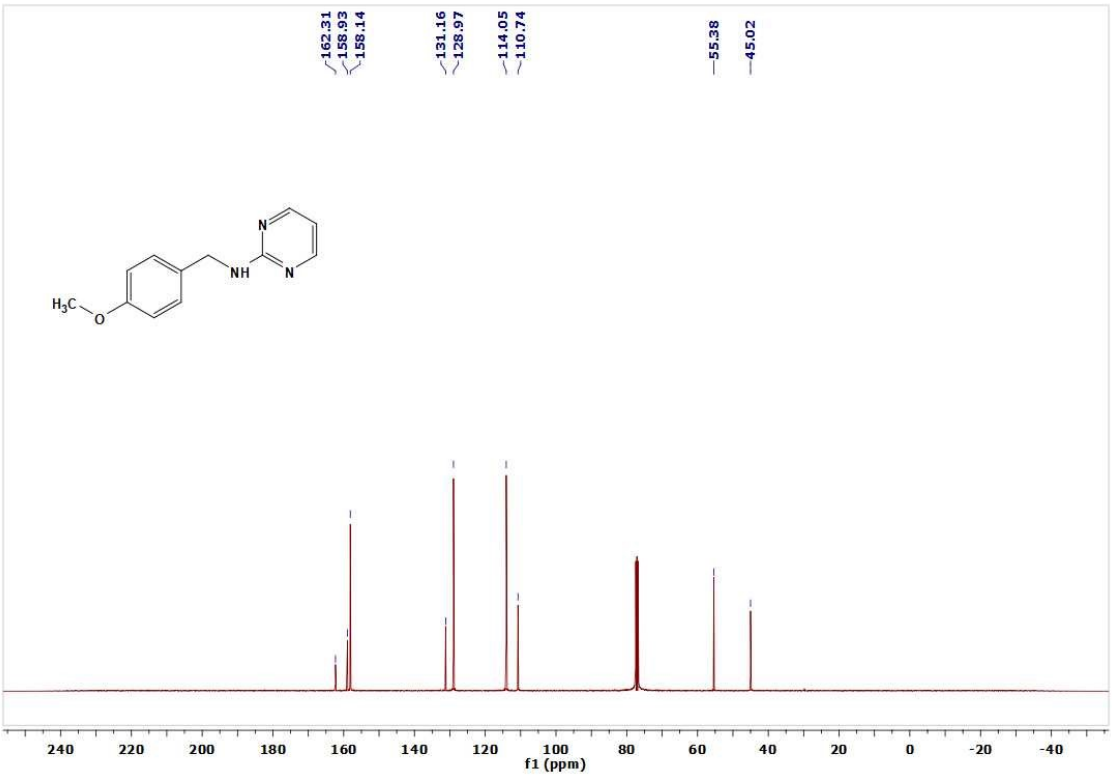


Fig.S43 $^{13}C\{^{1}H\}$-NMR Spectra of **9cg** in $CDCl_3$ (101 MHz)

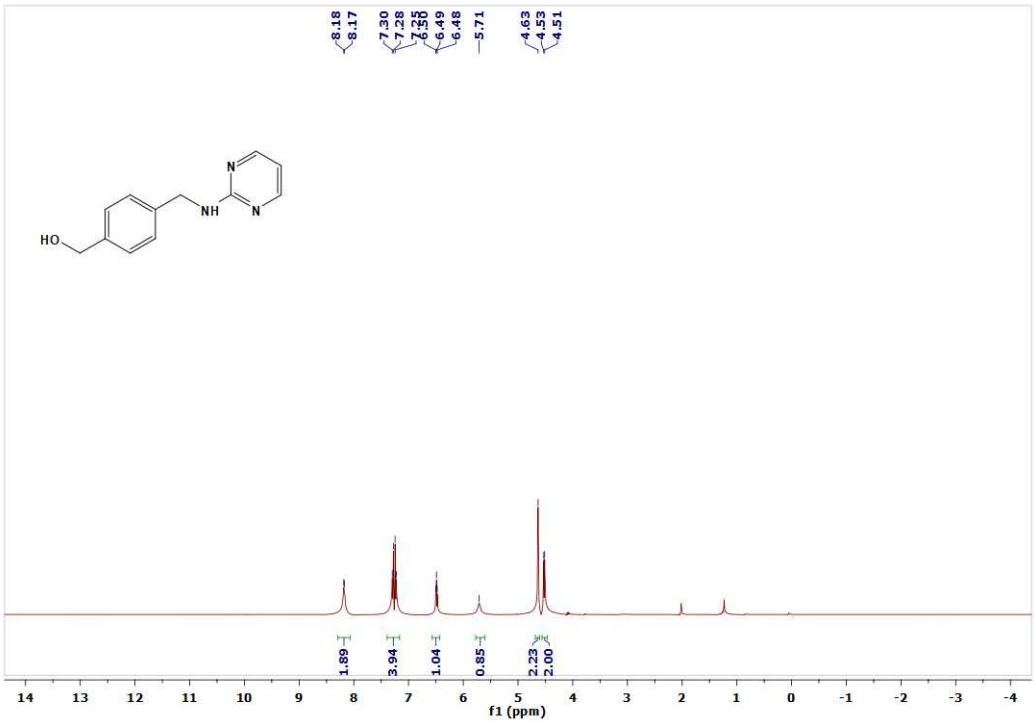


Fig.S44 ^{1}H-NMR Spectra of **9eg** in $CDCl_3$ (400 MHz)

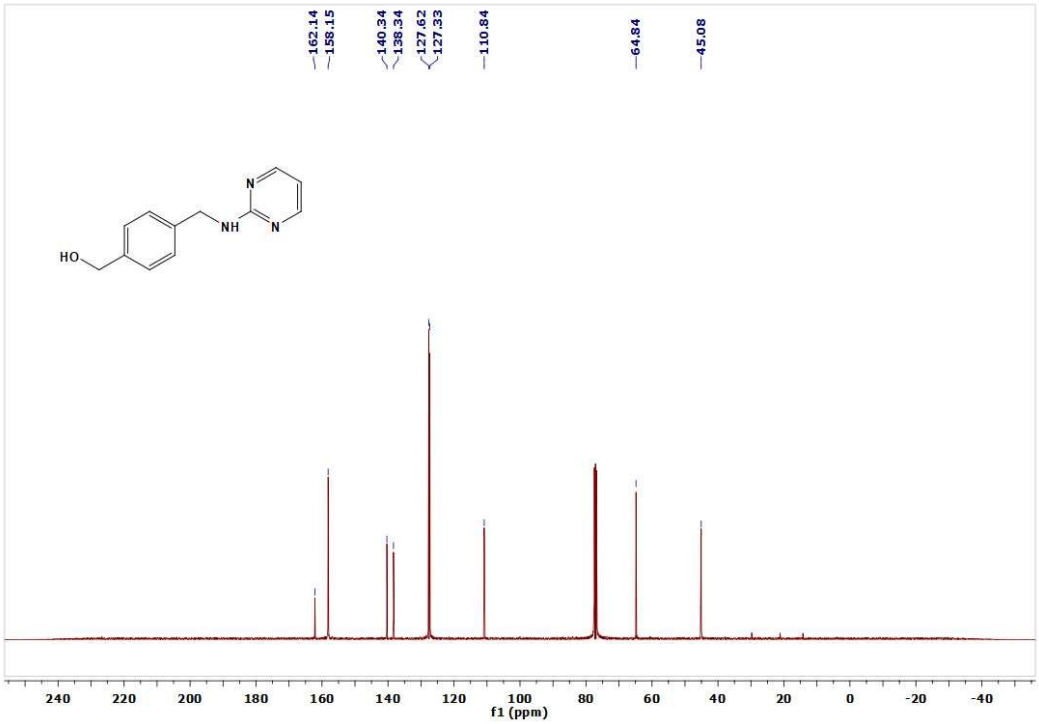


Fig.S45 $^{13}C\{^{1}H\}$-NMR Spectra of **9eg** in $CDCl_3$ (101 MHz)

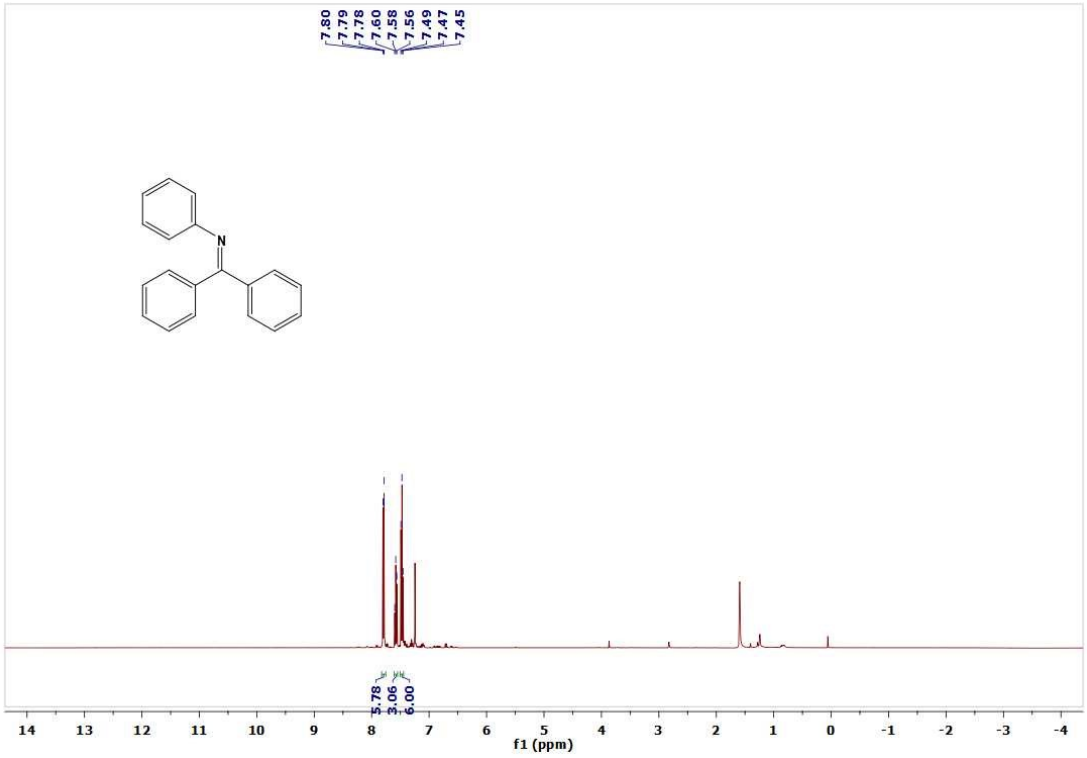


Fig.S46 ^{1}H-NMR Spectra of **7aa'** in $CDCl_3$ (400 MHz)

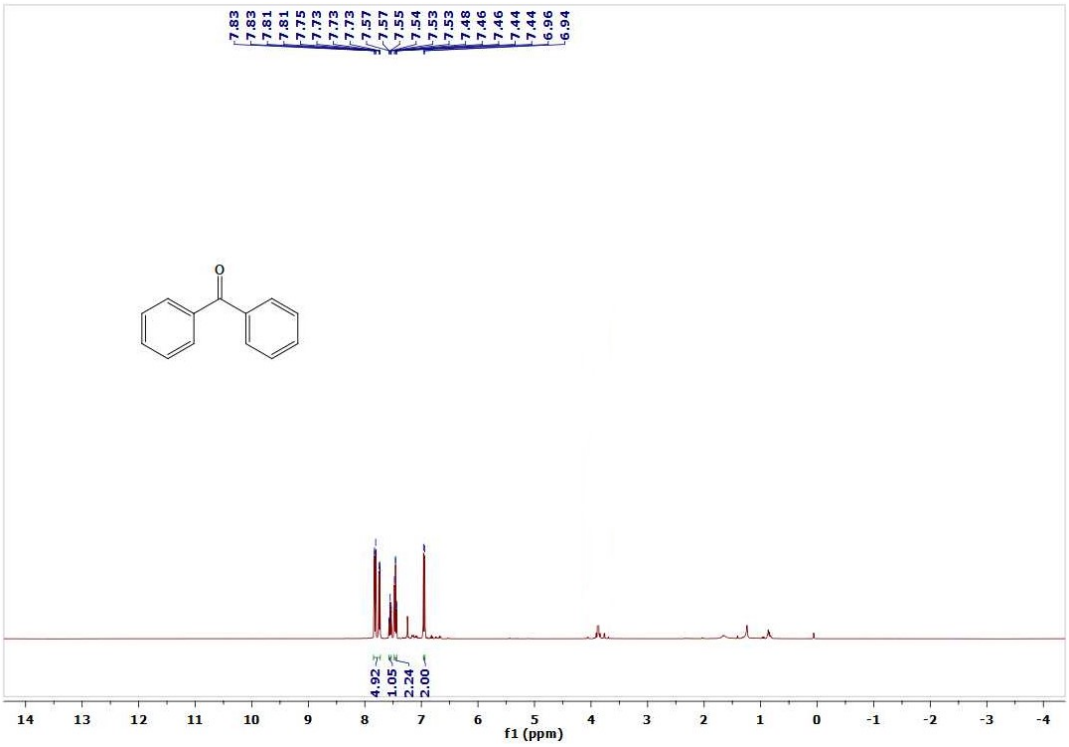


Fig.S47 ^{1}H-NMR Spectra of **5a'** in $CDCl_3$ (400 MHz)

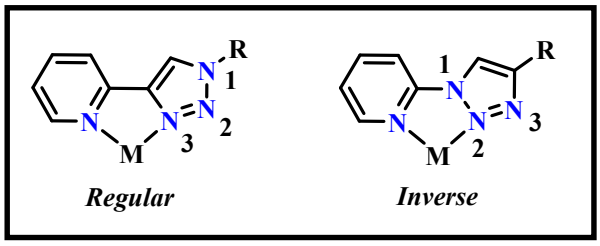


Fig.S48 Difference in between *Regular* and *Inverse* Triazolyl-Pyridine Ligand

9. References:

(1.) (a) P. S. Gahlaut, D. Gautam, B. Shekhawat, S. Kushwaha and B. Jana, *New Journal of Chemistry*, 2023, **47**, 19953-19962. (b) P. S. Gahlaut, D. Gautam, P. Lama and B. Jana, *New Journal of Chemistry*, 2023, **47**, 6871-6879.

(2) (a) A. Al Sheikh Ali, D. Khan, A. Naqvi, F. F. Al-Blewi, N. Rezki, M. R. Aouad and M. Hagar, *ACS omega*, 2020, **6**, 301-316. (b) C. Kaushik and M. Chahal, *Journal of Chemical Sciences*, 2020, **132**, 1-10.

(3) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell and M. Beller, *Chemistry–An Asian Journal*, 2007, **2**, 403-410.

(4) Q. Xu, H. Xie, E.-L. Zhang, X. Ma, J. Chen, X.-C. Yu and H. Li, *Green chemistry*, 2016, **18**, 3940-3944.

(5) K. O. Marichev and J. M. Takacs, *ACS catalysis*, 2016, **6**, 2205-2210.

(6) M. Subaramanian, S. P. Midya, P. M. Ramar and E. Balaraman, *Organic letters*, 2019, **21**, 8899-8903.

(7) W. Li, M. Huang, J. Liu, Y.-L. Huang, X.-B. Lan, Z. Ye, C. Zhao, Y. Liu and Z. Ke, *ACS Catalysis*, 2021, **11**, 10377 10382.

(8) A. K. Guin, S. Pal, S. Chakraborty, S. Chakraborty and N. D. Paul, *The Journal of Organic Chemistry*, 2023, **88**, 5944-5961.

(9) R. Sharma, A. R. TA, J. Sen, I. V. Mashevskaya and S. Chaudhary, *Organic Chemistry Frontiers*, 2023, **10**, 730-744.

(10) M. Vellakkaran, K. Singh and D. Banerjee, *ACS Catalysis*, 2017, **7**, 8152-8158.