A sustainable strategic approach for N-alkylation of amines with activation of alcohols triggered via hydrogen auto-transfer reaction using Pd(II) complex: Evidences for metal-ligand cooperativity

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Preparation of 3,5-di(tert-butyl)-2-hydroxy azobenzene [LH₂]⁺

The synthesis of the ligand [**LH₂**]⁺ was performed by procedure that is used in the first step of the preparation of azo dye, the first being the synthesis of an aromatic diazonium salt of the azo-amine {(E)-2-(phenyldiazenyl)aniline}. To an aqueous solution of 2.0 mmol of amine, was added 8.0 mmol of conc. HCl until the solution was nearly clear (azo-amine does not dissolve completely in the acidic solution of HCl). The mixture was cooled below 0 °C. After that, a solution of 2.5 mmol of NaNO₂ was added dropwise. The second step is neutralization of the diazonium salt by the aqueous solution of NaOH at temperature less than 5 °C. Upon addition of the NaOH, brownish colour ppt come out as neutralization reaction going to competition. After 3-4 h, the ppt was filtered out and purify by column chromatography. This gives blood red colour solid ligand [**LH₂**]⁺ with the yield approximately 20% . The desired product is fully characterized by ¹H and ¹³C NMR spectroscopies (fig. S11-S12).

Mercury drop experiment:
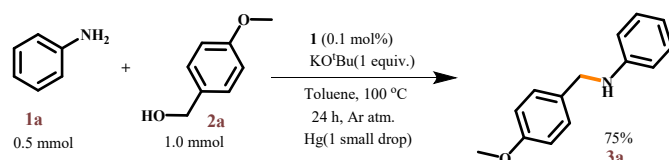
We performed a mercury drop test to figure out the homogeneity of the **1** in N-alkylation reaction. Schlenk flask was charged with 1.0 mmol alcohol, 0.5 mmol aniline, 1 equiv. of base and 0.1 mol% of catalyst **1** and linked to the condenser under argon flow. A small drop of mercury was added to this reaction mixture, and the mixture was refluxed for 24 hours at 100 °C. After a 24-hour period, the product's isolation confirmed the catalyst's homogeneous behaviour.

Optimization of the reaction conditions

The general method for N-alkylation reaction with amines and alcohols as substrates

To a 10 mL seal tube charged with a PTFE stirring magnetic bar, was added catalyst (0.1 mol%), alcohol (1.0 mmol), amine (0.5 mmol), base (1 equivalent), and solvent. The reaction mixture was stirred for 24 h at 100 °C. After cooled to rt, the crude reaction mixture was diluted with 5 mL of DCM, extracted three times through a Whatman Filter Paper Grade 42, and collected for column chromatography.

(1) Solvent screening

Table S1. Solvent screenings

Entry	Solvent	Yield. (%)
1	Benzene	82
2	DMSO	55
3	Toluene	92
4	DMF	76
5	Xylene	85
6	THF	70
7	ACN	Trace
8	EtOH	40
9	-	15

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (0.1 mol%), KOᵗBu (1 equiv.) and solvent (3 mL), seal tube, 100 °C oil bath, 24 h.

(2) Base screening

Table S2. Base screenings

Entry	Base	Yield. (%)
1	KO^{t}Bu	92
2	NaO^{t}Bu	60
3	NaOH	18
4	KOH	15
5	Cs$_2$CO$_3$	48
6	K$_3$PO$_4$	Trace
7	--	Trace

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (0.1 mol%), Base (1 equiv.) and Toluene (3 mL), seal tube, 100 °C oil bath, 24 h.

(3) Reactant ratio screening

Table S3. Reactant ratio Screenings

Entry	Molar ratio of reactants (1a : 2a)	Yield. (%)
1	0.5 : 0.5	72
2	0.5 : 1.0	92
3	0.5 : 1.5	92
4	1.0 : 0.5	90
5	1.5 : 0.5	85

Reaction conditions: **1a**, **2a**, **1** (0.1 mol%), KO^{t}Bu (1 equiv.) and Toluene (3 mL), seal tube, 100 °C oil bath, 24 h.

(4) Base amount screening

Table S4. Base Amount Screenings

Entry	Base (KO^{t}Bu) amount (equiv.)	Yield. (%)
1	0	16
2	0.5	78
3	1.0	92
4	1.1	92
5	1.5	92

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (0.1 mol%), Base (**x** equiv.) and Toluene (3 mL), seal tube, 100 °C oil bath, 24 h.

(5) Catalyst screening

Table S5. Optimization of catalysts

Entry	Catalysts	N-alkylation (%)	imine (%)
1	**1**	92	trace
2	PdCl$_2$	10	15
3	Pd(oAc)$_2$	n.d	12
4	PdCl$_2$(PPh$_3$)$_2$	13	20
5	**L**	-	35
6	-	-	18

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (0.1 mol%), KO^{t}Bu (1 equiv.) and Toluene (3 mL), seal tube, 100 ^{o}C oil bath, 24 h.

(6) Catalyst loading screening

Table S6. Catalyst Loading Screenings

Entry	Catalyst loading (mol %)	Yield. (%)
1	0.01	38
2	0.02	52
3	0.05	76
4	0.1	92
5	0.2	92
6	0.5	92
7	1.0	92

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (x mol%), KO^{t}Bu (1 equiv.) and Toluene (3 mL), seal tube, 100 ^{o}C oil bath, 24 h.

(7) Temperature screening

Table S7. Temperature screenings

Entry	Temperature (°C)	Yield. (%)
1	50	35
2	70	77
3	100	92
4	110	92
5	120	92

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (0.1 mol %), KO^{t}Bu (1 equiv.) and Toluene (3 mL), seal tube, Temp(^{o}C) oil bath, 24 h.

(8) Reaction time screening

Table S8. Reaction Time Screenings

Entry	Reaction time	Yield. (%)
1	1.0 h	trace
2	6.0 h	44
3	12.0 h	64
4	18.0 h	78
5	24.0 h	92

Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), **1** (0.1 mol %), KO^{t}Bu (1 equiv.) and Toluene (3 mL), seal tube, 100 °C oil bath, Time (h).

Figure S1. (a) Plausible mechanism of alcohol oxidation in presence of air and (b) Electronic absorption spectra change during the formation of I$_3^-$ ion in presence of H$_2$O$_2$ (detection of H$_2$O$_2$ from the reaction mixture).
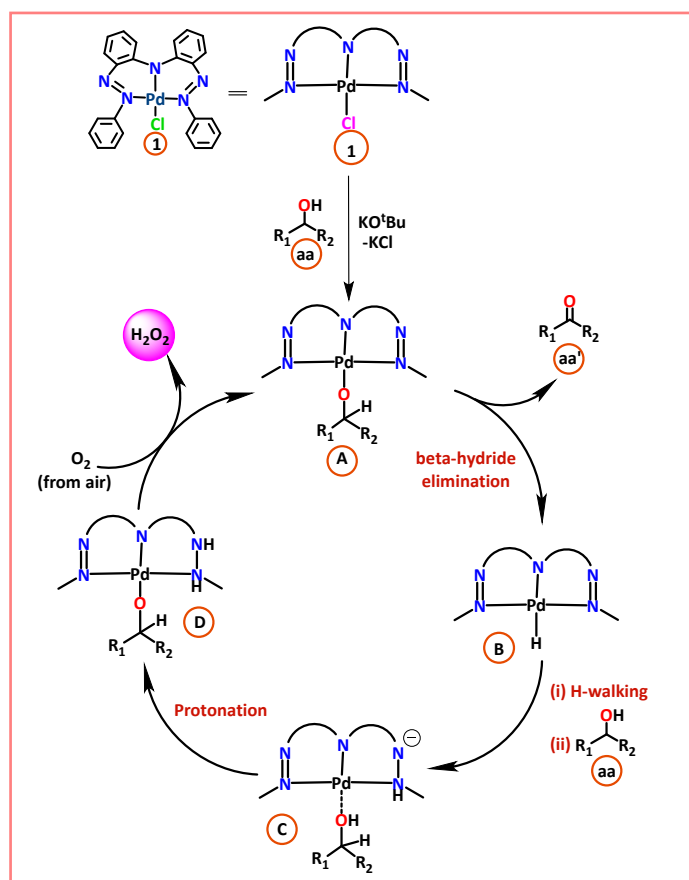
(a) Plausible mechanism of alcohol oxidation in presence of air

5
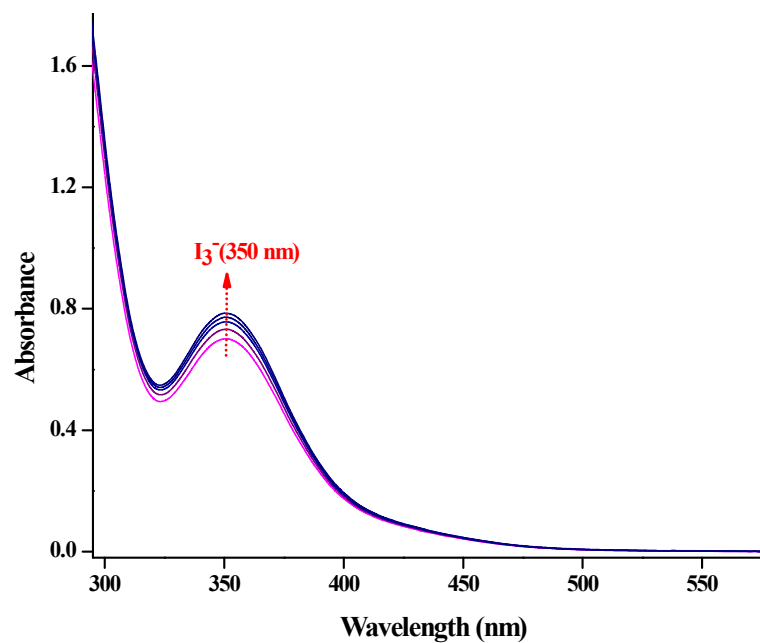
(b) Electronic absorption spectra change during the formation of I_3^- ion

Figure S2. Studies for intermediate formation and quantifying progress of reaction over time
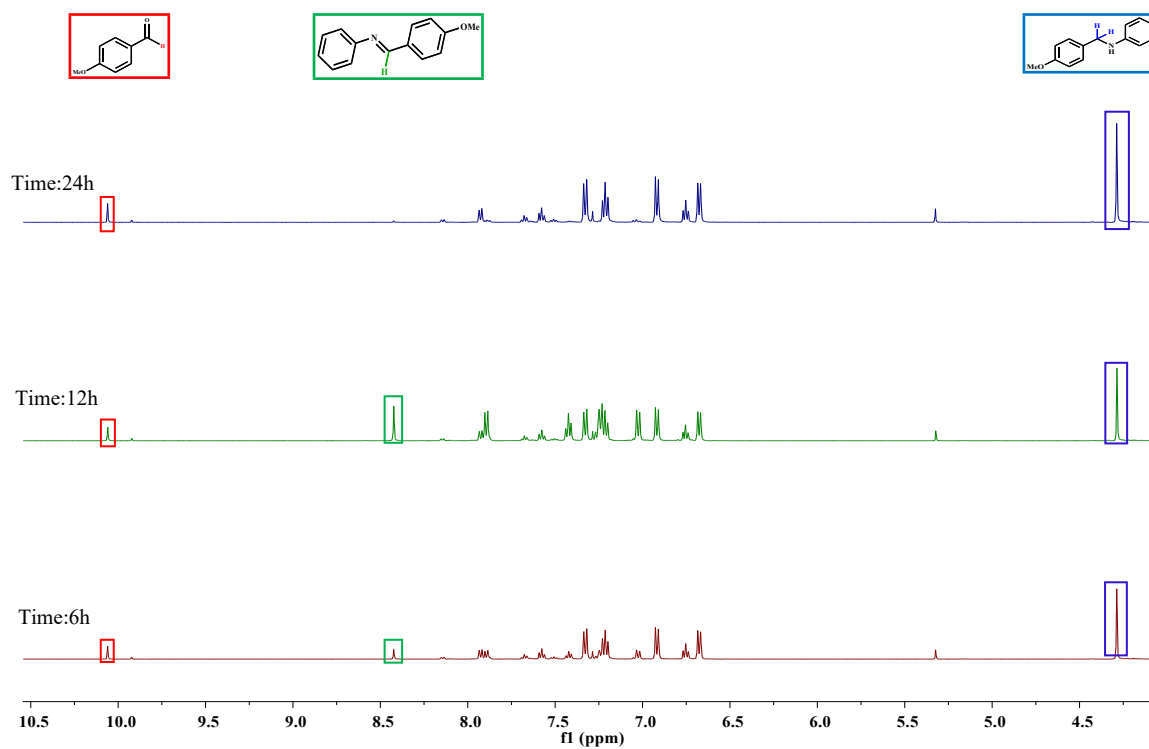
Figure S2. ^1H NMR spectra (500 MHz) of crude reaction mixture performed under optimized conditions (separating catalyst by flash column) after 6 h, 12 h, 24 h in CDCl$_3$.

Figure S3. Control Experiment for Detection of N-H/N-D Stretching using Methanol/Methanol-d4[1-2]

A pressure tube that had been dried in the oven and had a magnetic stir bar was filled with Methanol (CH$_3$OH) (1.0 mL), catalyst **1** (0.01 mol%,), and 1.0 equivalent of ^{t}BuOK. After that, a PTFE screw cap was used to tightly seal the tube. Over the course of 24 hours, the reaction mixture was stirred at 100 ºC. The reaction mixture was dried once the reaction had been completed. The IR spectrum of the resulting reaction mixture displayed the characteristic stretching frequencies of N-H bonds at $v_{(N-H)}$ = 2915 and 2950 cm^{-1}, respectively. An analogous experiment was conducted with methanol-d4 (CD$_3$OD), adhering to the experimental procedure already reported. Here, N-D bonds stretching was observed in the IR spectrum analysis of the reaction mixture that was generated, specifically in the regions $v_{(N-D)}$ = 2323 and 2358 cm^{-1}.
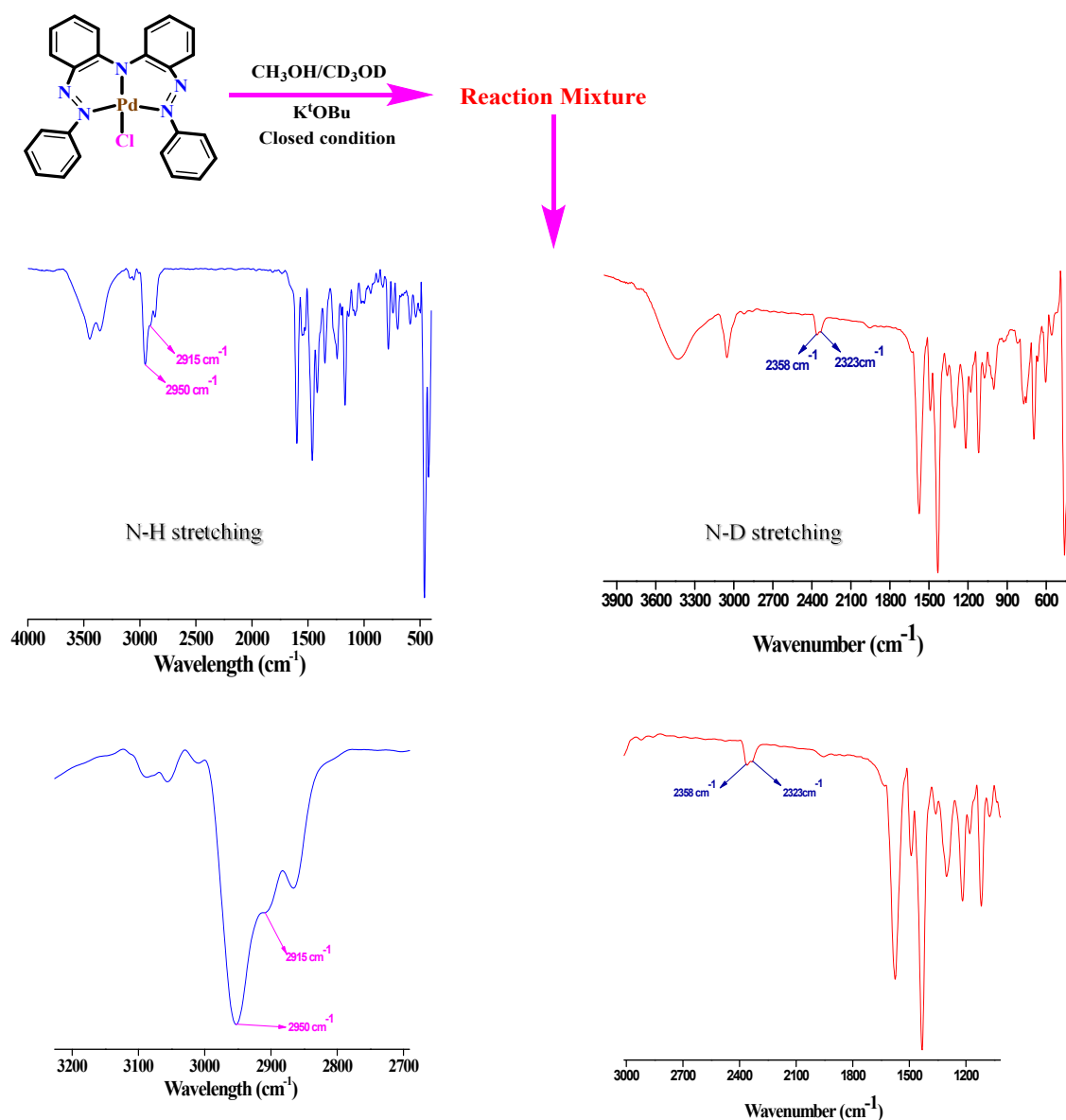
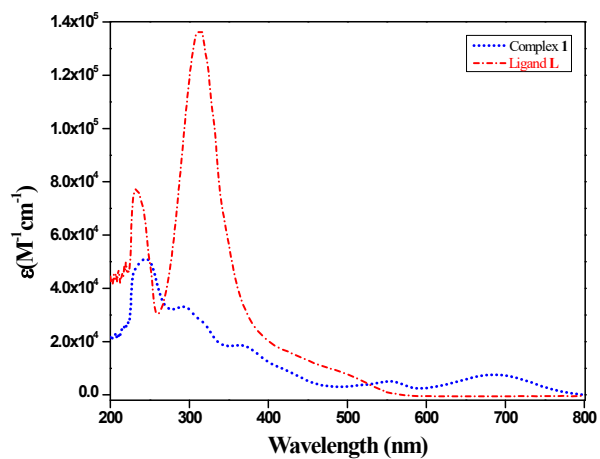**Figure S3**. IR spectra of the reaction mixture showing N-H (blue) and N-D (red) stretching.

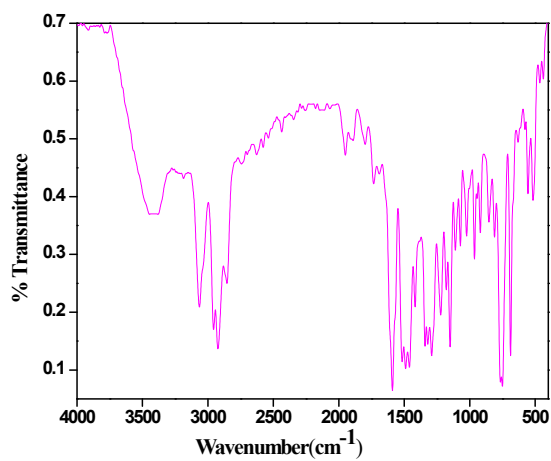**Figure S4.** Electronic absorption spectra of ligand and metal complex in CH_2Cl_2.

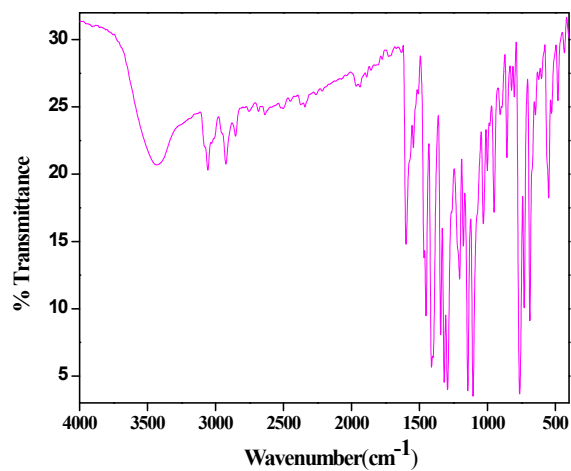**Figure S5.** IR spectra of the ligand $[LH_2]^+$

Figure S6. IR spectra of the complex [Pd(L)Cl] (**1**)

Table S9. Reaction of Alcohol and Anilines in Presence of Only KO^{t}Bu.
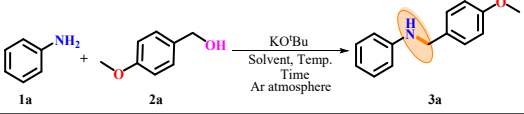
Articles	Reported Yield
[3]Elangovan, S.; Neumann, J.; Sortais, J. B.; Junge, K.; Darcel, C.; Beller, M. Efficient and Selective N-Alkylation of Amines with Alcohols Catalysed by Manganese Pince Complexes. *Nat. Commun.* **2016**, *7*, 1–8.	0% (1.0 equiv. *t*BuOK, toluene, 80 °C, 24 h)
[4] Blank, B.; Madalska, M.; Kempe, R. An Efficient Method for the Selective Iridium-Catalyzed Monoalkylation of (Hetero)Aromatic Amines with Primary Alcohols. *Adv. Synth. Catal.* **2008**, *350*, 749–758.	4% (1.0 equiv. *t*BuOK, diglyme, 110 °C, 24 h)
[5] Vellakkaran, M.; Singh, K.; Banerjee, D. An Efficient and Selective Nickel-Catalyzed Direct N-Alkylation of Anilines with Alcohols. *ACS Catal.* **2017**, *7*, 8152–8158.	0% (1.0 equiv. tBuOK, toluene, 130 °C, 48 h)
[6] Bains, A. K.; Kundu, A.; Yadav, S.; Adhikari, D. Borrowing Hydrogen-Mediated N-Alkylation Reactions by a Well-Defined Homogeneous Nickel Catalyst. *ACS Catal.* **2019**, *9*, 9051–9059.	0% (1.0 equiv. tBuOK, toluene, 130 °C, 48 h)
[7] Subaramanian, M.; Midya, S. P.; Ramar, P. M.; Balaraman, E. General Synthesis of N-Alkylation of Amines with Secondary Alcohols via Hydrogen Autotransfer. *Org. Lett.* **2019**, *21*, 8899–8903.	Trace (1.0 equiv. tBuOK, n-octane, 110 °C, 24 h)
[8] Kaloğlu, N.; Achard, M.; Bruneau, C.; Özdemir, İ. Ruthenium(II)-(Arene)-N-Heterocyclic Carbene Complexes: Efficient and Selective Catalysts for the N-Alkylation of Aromatic Amines with Alcohols. *Eur. J. Inorg. Chem.* **2019**, *2019*, 2598–2606.	0% (1.5 equiv. tBuOK, solvent free condition, 120 °C, 20 h)
[9] Huang, M.; Li, Y.; Li, Y.; Liu, J.; Shu, S.; Liu, Y.; Ke, Z. Room Temperature N-Heterocyclic Carbene Manganese Catalyzed Selective N-Alkylation of Anilines with Alcohols. *Chem. Commun.* **2019**, *55*, 6213–6216.	Trace (1.0 equiv. tBuOK, toluene, 50 °C, 24 h)
[10] Wei, D.; Yang, P.; Yu, C.; Zhao, F.; Wang, Y.; Peng, Z. N-Alkylation of Amines with Alcohols Catalyzed by Manganese(II) Chloride or Bromopentacarbonylmanganese(I). *J. Org. Chem.* **2021**, *86*, 2254–2263.	Trace (1.2 equiv. tBuOK, toluene, P(Ph)$_3$, 100 °C, 20 h)
[11] Landge, V. G.; Mondal, A.; Kumar, V.; Nandakumar, A.; Balaraman, E. Manganese Catalyzed N-Alkylation of Anilines with Alcohols: Ligand Enabled Selectivity. *Org. Biomol. Chem.* **2018**, *16*, 8175–8180.	0% (1.1 equiv. tBuOK, toluene, 140 °C, 18 h)
[12] Sankar, V.; Kathiresan, M.; Sivakumar, B.; Mannathan, S. Zinc-Catalyzed N-Alkylation of Aromatic Amines with Alcohols: A Ligand-Free Approach. 2020, pp 4409–4414.	55% (1.0 equiv. tBuOK, toluene, 140 °C, 36 h)
[13] Lan, X. B.; Ye, Z.; Yang, C.; Li, W.; Liu, J.; Huang, M.; Liu, Y.; Ke, Z. Tungsten-Catalyzed Direct N-Alkylation of Anilines with Alcohols. *ChemSusChem* **2021**, *14*, 860–865.	27% (1.0 equiv. tBuOK, toluene, 130 °C, 24 h)
Our work	Trace (1.0 equiv. tBuOK, toluene, 100 °C, 24 h)

Table S10. Crystal data and structural refinement parameters for complexes **1**.

Chemical formula	C$_{24}$ H$_{18}$ Cl N$_5$ Pd	*Formula weight*	518.28
T(K)	293.0 K	a(Å)	8.8728(9)
λ(A)(Mo-Kα)	0.71073	b(Å)	10.6090(11)
Crystal system	triclinic	c(Å)	12.3959(14)
Space group	P -1	α(°)	73.308(4)°
V(Å^3)	1066.9(2)	β(°)	73.136(4)°
Z	2	γ(°)	88.997(4)°
ρ$_{calc}$ (g/cm^3)	1.613	Crystal size/mm^3	0.28 × 0.26 × 0.21
F(000)	520.0	Theta range(°)	1.14–28.383
Data/Restraints/parameters	5361/0/280	Index ranges	−11<h < 11, −14 <k < 14, −16 <l < 16
GOF on *F*^{2}	1.089	wR_2 [all data]	0.0481
Final R indexes [I>=2σ (I)]	R_1 = 0.0187 wR_2 = 0.0466	Largest diff. peak/hole / e Å^{-3}	0.32/-0.33
Final R indexes [all data]	R_1 = 0.0207 wR_2 = 0.0481	R_{sigma}	0.0167
Reflections collected	17989	R_{int}	0.0206

GOF = [Σ[w(F$_o$^{2}–F$_c$^{2})^2] /*M*–*N*]$^{1/2}$ (*M* = number of reflections, *N* = number of parameters refined). R_1 = Σ∥F_o|− |F_c∥/Σ|F_o|. wR_2 = [Σ[w(F$_o$^{2} −F$_c$^{2})^2]/Σ [(F_o^{2})^2]]$^{1/2}$.

Table S11. Selected bond lengths (Å) and bond angles (º) of complex **1**.

Bond lengths(Length/Å)			
Pd(1)—Cl(1)	2.3092(4)	N(1)—C(1)	1.3696(19)
Pd(1)—N(1)	1.9774(12)	N(1)—C(13)	1.374(2)
Pd(1)—N(3)	2.0190(12)	N(2)—C(18)	1.381(2)
Pd(1)—N(5)	2.0191(13)	N(3)—C(19)	1.4469(19)
N2—N3	1.2666(17)	N(4)—C(6)	1.378(2)
N4—N5	1.2701(19)	N(5)—C(7)	1.443(2)
Bond angles(Angle/ º)			
N(1)—Pd(1)—Cl(1)	179.18(4)	N(1)—C(13)—C(14)	120.94(15)
N(1)—Pd(1)—N(3)	88.81(5)	N(1)—C(1)—C(2)	121.02(15)

N(1)—Pd(1)—N(5)	87.59(5)	C(19)—N(3)—Pd(1)	121.02(9)
N(3)—Pd(1)—Cl(1)	91.99(4)	C(7)—N(5)—Pd(1)	120.63(10)
N(3)—Pd(1)—N(5)	176.39(5)	N(3)—N(2)—C(18)	121.40(13)
N(5)—Pd(1)—Cl(1)	91.62(4)	N(3)—N(2)—C(19)	112.10(12)
C(1)—N(1)—Pd(1)	119.15(10)	N(5)—N(4)—C(6)	121.25(14)
C(13)—N(1)—Pd(1)	118.99(10)	N(4)—N(5)—C(7)	113.05(13)
N(2)—N(3)—Pd(1)	126.74(10)	C(1)—N(1)—C(13)	121.81(13)
N(4)—N(5)—Pd(1)	126.16(11)	C(1)—C(2)—C(3)	121.16(18)

Table S12. Conversion of benzyl alcohol to benzaldehyde in presence of air.
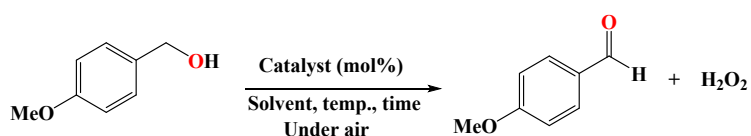
S.N.	Catalysts/mol%	Solvent	Temp.	Time(h)	Yields(%)
1.	1/0.1	Toluene	50	12	70
2	1/0.1	Toluene	50	24	86
3	1/0.1	Toluene	100	12	90
4	**1/0.1**	**Toluene**	**100**	**24**	**99**
5	1/0.01	Toluene	100	24	56
6.	1/0.05	Toluene	100	24	85
7.	1/0.2	Toluene	100	24	99
8.	1/0.5	Toluene	100	24	99
9.	1/1.0	Toluene	100	24	99
10.	1/0.1	THF	100	12	58
11.	1/0.1	Xylene	100	24	61
12.	1/0.1	Benzene	100	24	65
13.	1/0.1	DMSO	100	24	35
14.	1/0.1	Ethanol	100	24	22
15.	1/0.1	DMF	100	24	33
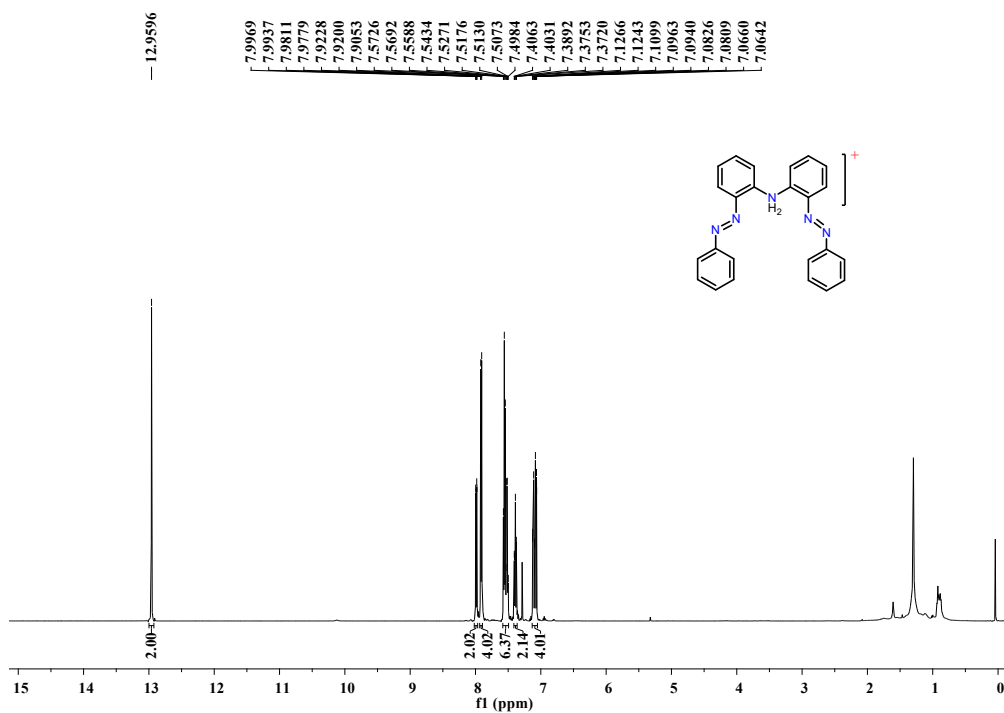
Figure S7. ^{1}H NMR spectrum of ligand **[LH$_2$]$^+$** in CDCl$_3$ (500 MHz).
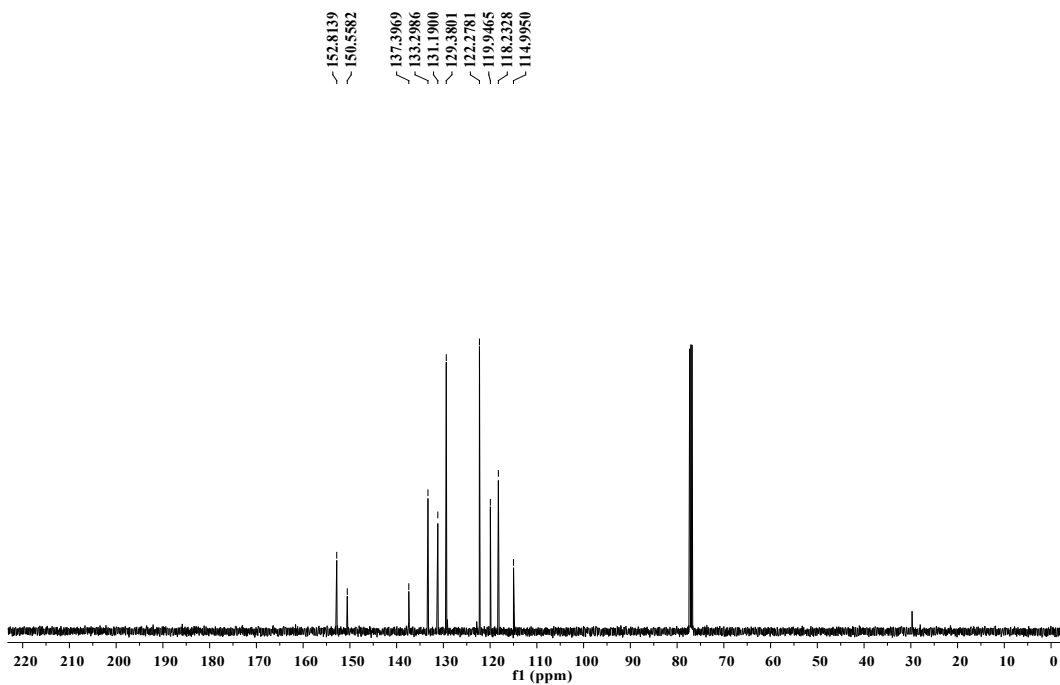
Figure S8. ^{13}C NMR spectrum of ligand **[LH$_2$]$^+$** in CDCl$_3$ (500 MHz).

12

7.9802
7.9775
7.9637
7.9610
7.8793
7.8758
7.8631
7.8606
7.4359
7.4192
7.3468
7.3429
7.3355
7.3205
7.3101
7.3057
7.3021
7.2612
7.1717
7.1572
7.1422

H$_2$O

CH$_2$Cl$_2$

C$_6$H$_{14}$

2.00
3.26
2.02
7.17
2.21
2.05

f1 (ppm)
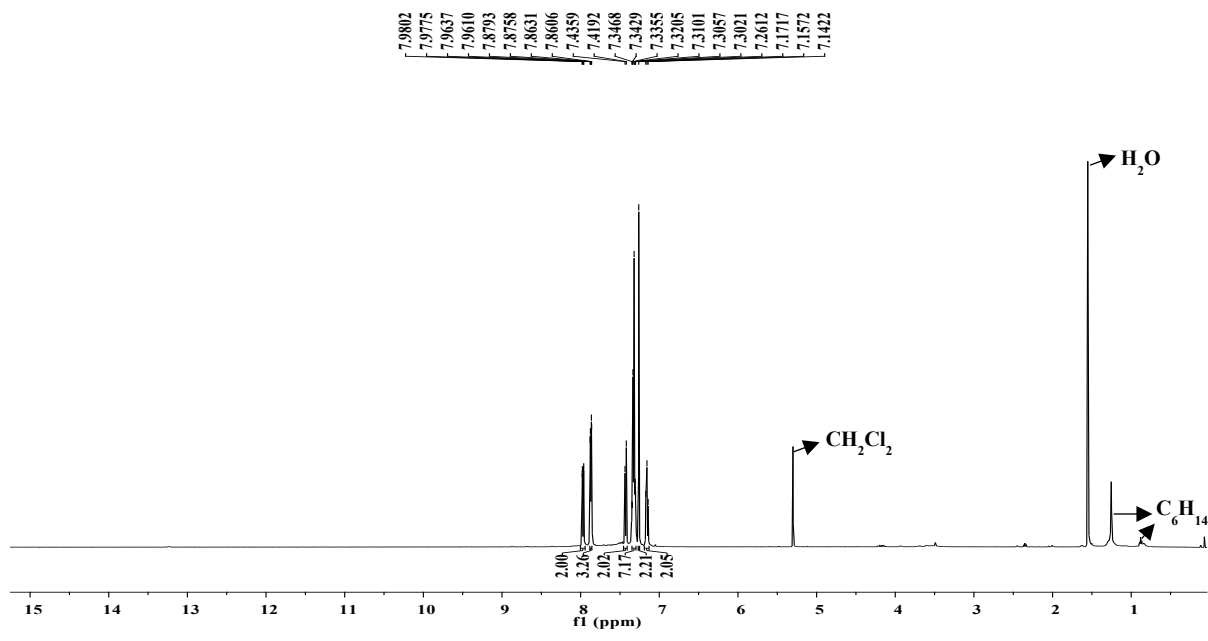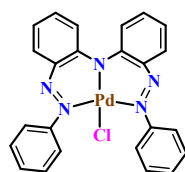
Figure S9. ^{1}H NMR spectrum of complex **[Pd(L)Cl]** in CDCl$_3$ (500 MHz).
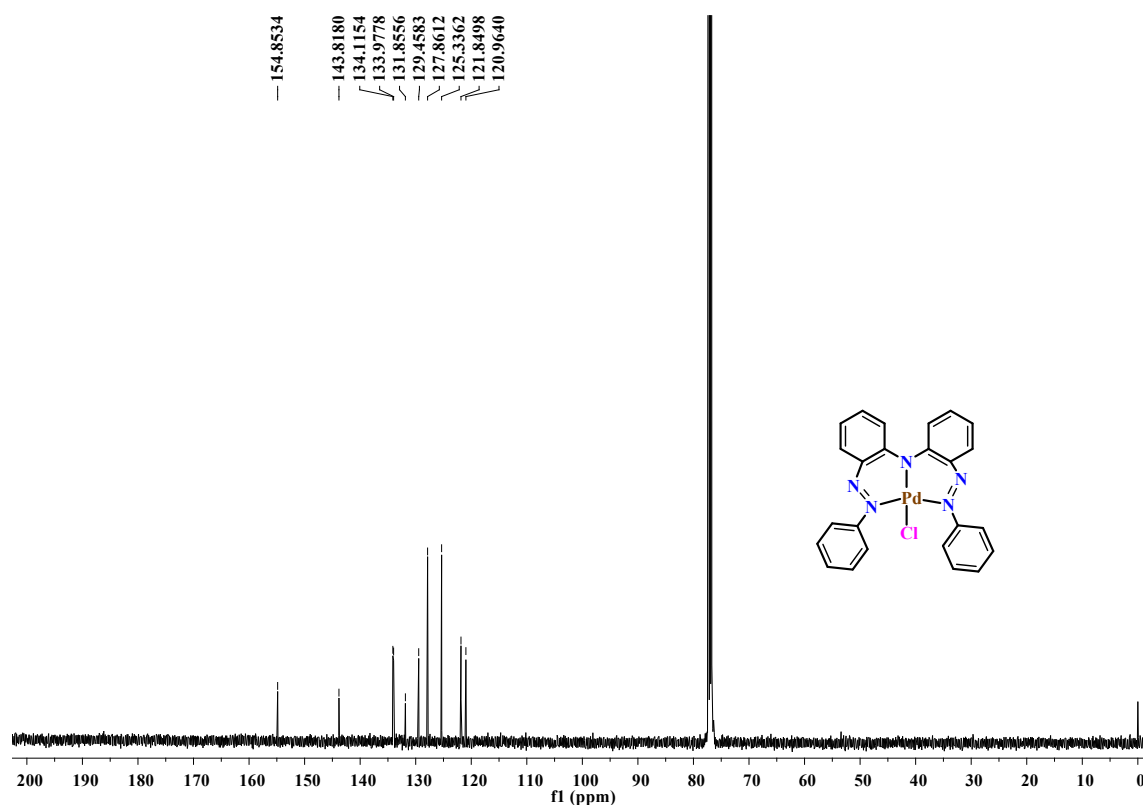
Figure S10. ^{13}C NMR spectrum of complex **[Pd(L)Cl]** in CDCl$_3$ (500 MHz).

NMR data of desired N-alkylated products-

N-(4-methoxybenzyl)aniline (3a).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H), 7.17 − 7.10 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 2H), 4.18 (s, 2H), 3.87 (s, 1H), 3.73 (s, 3H); ^{13}C

NMR (126 MHz, CDCl$_3$) δ 158.98 (s), 148.37 (s), 131.58 (s), 129.39 (s), 128.92 (s), 117.59 (s), 115.00 (s), 114.15 (s), 112.98 (s), 55.38 (s), 47.86 (s).

N-(3-nitrobenzyl)aniline (3b).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (s, 1H), 7.87 (m, 1H), 7.53 (d, J = 6.2 Hz, 2H), 7.23 (t, J = 7.9 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.7 Hz, 2H), 4.47 (s, 2H), 4.19 (br s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 152.99 (s), 147.98 (s), 140.87 (s), 130.02 (s), 129.42 (s), 129.33 (s), 122.03 (s), 121.57 (s), 117.78 (s), 112.97 (s), 48.11 (s).

4-chloro-N-(4-chlorobenzyl)aniline (3c).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 (q, J = 8.6 Hz, 4H), 7.14 (d, J = 8.9 Hz, 2H), 6.55 (d, J = 8.9 Hz, 2H), 4.31 (s, 2H), 4.13 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.36 (s), 137.52 (s), 133.06 (s), 129.14 (s), 128.86 (s), 128.65 (s), 122.40 (s), 114.02 (s), 47.67 (s).

N-(4-chlorobenzyl)-2-methoxyaniline (3d).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24 (s, 4H), 6.79 (td, J = 7.7, 1.2 Hz, 1H), 6.74 (dd, J = 7.9, 1.0 Hz, 1H), 6.65 (td, J = 7.8, 1.4 Hz, 1H), 6.48 (dd, J = 7.8, 1.2 Hz, 1H), 4.62 (s, 1H), 4.25 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.93 (s), 138.35 (s), 137.93 (s), 132.83 (s), 128.83 (s), 128.80 (s), 121.41 (s), 117.03 (s), 110.24 (s), 109.58 (s), 55.51 (s), 47.41 (s).

2-fluoro-N-(4-fluorobenzyl)aniline (3e).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (dd, J = 8.6, 5.4 Hz, 2H), 7.31 (dd, J = 7.9, 1.4 Hz, 1H), 7.16 − 7.10 (m, 1H), 7.07 (t, J = 8.7 Hz, 2H), 6.68 (td, J = 7.7, 1.4 Hz, 1H), 6.63 (dd, J = 8.1, 1.2 Hz, 1H), 4.75 (s, 1H), 4.41 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 163.13 (s), 161.18 (s), 143.69 (s), 134.44 (s), 129.17 (s), 128.78 (s), 127.81 (s), 119.22 (s), 117.63 (s), 115.66 (s), 115.49 (s), 111.52 (s), 47.21 (s).

N-(thiophen-2-ylmethyl)aniline (3f).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 − 7.24 (m, 3H), 7.15 − 7.03 (m, 2H), 6.93 − 6.83 (m, 1H), 6.78 (d, J = 7.9 Hz, 2H), 4.59 (s, 2H), 4.12 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.74 (s), 143.12 (s), 129.41 (s), 126.99 (s), 125.14 (s), 124.70 (s), 118.19 (s), 113.29 (s), 43.58 (s).

N-(furan-2-ylmethyl)aniline (3g).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (s, 1H), 7.23 − 7.12 (m, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.7 Hz, 2H), 6.32 (dd, J = 3.1, 1.9 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 4.31 (s, 2H), 4.01 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 152.77 (s), 147.65 (s), 141.93 (s), 129.25 (s), 118.05 (s), 113.18 (s), 110.34 (s), 106.99 (s), 41.47 (s).

N-(pyridin-2-ylmethyl)aniline (3h).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.62 (d, J = 4.8 Hz, 1H), 7.65 (td, J = 7.7, 1.6 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.24 − 7.09 (m, 3H), 6.77 (t, J = 7.3 Hz, 1H), 6.71 (dd, J = 8.5, 0.8 Hz, 2H), 4.80 (s, 1H), 4.49 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.63 (s), 149.21 (s), 147.97 (s), 136.69 (s), 129.30 (s), 122.14 (s), 121.63 (s), 117.61 (s), 113.09 (s), 49.32 (s).

N-(2-bromobenzyl)pyridin-2-amine (3i).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.12 (d, J = 3.9 Hz, 1H), 7.58 (d, J = 7.0 Hz, 1H), 7.46 − 7.39 (m, 2H), 7.27 (t, J = 6.9 Hz, 1H), 7.15 (td, J = 7.8, 1.5 Hz, 1H), 6.66 − 6.56 (m, 1H), 6.38 (t, J = 10.0 Hz, 1H), 5.21 (s, 1H), 4.60 (d, J = 6.3 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.45 (s), 148.25 (s), 138.13 (s), 137.55 (s), 132.80 (s), 129.22 (s), 128.74 (s), 127.56 (s), 123.41 (s), 113.34 (s), 106.84 (s), 46.42 (s).

N-(naphthalen-1-ylmethyl)pyridin-2-amine (3j).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, J = 6.0 Hz, 1H), 8.02 − 7.95 (m, 1H), 7.87 − 7.79 (m, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.47 − 7.42 (m, 3H), 7.37 − 7.30 (m, 2H), 6.53 (t, J = 5.9 Hz, 1H), 6.28 (d, J = 8.4 Hz, 1H), 4.97 (br s, 1H), 4.84 (d, J = 5.4 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.64 (s), 148.18 (s), 137.56 (s), 133.92 (s), 131.54 (s), 128.83 (s), 128.19 (s), 126.40 (s), 125.90 (s), 125.76 (s), 125.57 (s), 123.55 (s), 115.00 (s), 113.12 (s), 107.12 (s), 44.35 (s).

N-benzylpyridin-2-amine (3k).

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Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, *J* = 4.9 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.59 – 6.50 (m, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 5.16 (s, 1H), 4.47 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.74 (s), 148.20 (s), 139.24 (s), 137.53 (s), 128.66 (s), 127.43 (s), 127.25 (s), 113.11 (s), 106.77 (s), 46.33 (s).

N-(thiophen-2-ylmethyl)pyridin-2-amine (3l).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 (d, *J* = 4.8 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.23 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.63 (dd, *J* = 6.7, 5.5 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 1H), 5.02 (s, 1H), 4.70 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.14 (s), 148.08 (s), 142.63 (s), 137.54 (s), 126.85 (s), 125.21 (s), 124.66 (s), 114.99 (s), 113.51 (s), 107.33 (s), 41.32 (s).

N-(furan-2-ylmethyl)pyridin-2-amine (3m).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 3.9 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.36 (s, 1H), 6.66 – 6.56 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.32 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.24 (d, *J* = 2.6 Hz, 1H), 5.08 (s, 1H), 4.51 (d, *J* = 4.7 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.29 (s), 152.69 (s), 148.03 (s), 141.90 (s), 137.44 (s), 113.34 (s), 110.35 (s), 107.24 (s), 106.87 (s), 39.36 (s).

N-(4-ethoxybenzyl)quinolin-8-amine (3n).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.69 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.33 (dd, *J* = 10.2, 5.0 Hz, 4H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.50 (s, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 4.00 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.22 (s), 146.90 (s), 144.68 (s), 138.28 (s), 136.01 (s), 131.09 (s), 128.74 (s), 128.67 (s), 127.82 (s), 121.41 (s), 114.64 (s), 114.06 (s), 105.09 (s), 63.48 (s), 47.24 (s), 14.91 (s).

N-(2-bromobenzyl)-3-methylpyridin-2-amine (3o).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.15 (td, *J* = 7.7, 1.6 Hz, 1H), 6.57 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.80 (d, *J* = 5.9 Hz, 2H), 4.64 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.42 (s), 145.51 (s), 139.04 (s), 136.92 (s), 132.75 (s), 130.27 (s), 128.69 (s), 127.47 (s), 123.87 (s), 116.62 (s), 113.08 (s), 45.82 (s), 16.95 (s).

3-methyl-N-(4-methylbenzyl)pyridin-2-amine (3p).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.15 (d, *J* = 5.0 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.62 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.74 (d, *J* = 5.3 Hz, 2H), 4.47 (br s, 1H), 2.43 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.80 (s), 145.53 (s), 137.06 (s), 136.90 (s), 136.81 (s), 129.36 (s), 127.97 (s), 116.61 (s), 112.92 (s), 45.71 (s), 21.20 (s), 17.02 (s).

3-methyl-N-(thiophen-2-ylmethyl)pyridin-2-amine (3q).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.12 (d, *J* = 4.3 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.61 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.91 (d, *J* = 5.5 Hz, 2H), 4.51 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 156.21 (s), 145.40 (s), 143.22 (s), 137.02 (s), 126.77 (s), 125.46 (s), 124.69 (s), 116.81 (s), 113.35 (s), 40.71 (s), 16.92 (s).

N-benzylpentan-1-amine (3r).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.31 – 7.24 (m, 1H), 3.82 (s, 2H), 2.67 (t, *J* = 7.25 Hz, 2H), 1.78 (s, 1H), 1.61 – 1.51 (m, 2H), 1.41 – 1.29 (m, 4H), 0.95 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.57 (s), 128.38 (s), 128.14 (s), 126.88 (s), 54.12 (s), 49.52 (s), 29.82 (s), 29.61 (s), 22.66 (s), 14.09 (s).

N-(4-methylbenzyl)butan-1-amine (3s).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 3.79 (s, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.71 (s, 1H), 1.54 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.45 – 1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.47 (s), 136.40 (s), 129.07 (s), 128.12 (s), 53.82 (s), 49.15 (s), 32.25 (s), 21.10 (s), 20.54 (s), 14.07 (s).

N-(4-chlorobenzyl)butan-1-amine (3t).
Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 – 7.18 (m, 4H), 3.72 (s, 2H), 2.68 – 2.50 (m, 2H), 1.71 (s, 1H), 1.51 – 1.43 (m, 2H), 1.34 (dt, *J* = 14.5, 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 139.04 (s), 132.49 (s), 129.41 (s), 128.42 (s), 53.28 (s), 49.10 (s), 32.19 (s), 20.46 (s), 14.00 (s).

N-(4-fluorobenzyl)butan-1-amine (3u).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (dd, J = 8.5, 5.5 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H), 3.77 (s, 2H), 2.84 (s, 1H), 2.63 (t, J = 7.3 Hz, 2H), 1.52 (dt, J = 14.9, 7.4 Hz, 2H), 1.34 (dq, J = 14.6, 7.3 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.97 (s), 161.02 (s), 129.92 (s), 129.85 (s), 115.27 (s), 115.10 (s), 52.95 (s), 48.79 (s), 31.73 (s), 20.41 (s), 13.92 (s).

N-isopentylaniline (3v).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.21 (dd, J = 8.4, 7.4 Hz, 2H), 6.72 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 7.7 Hz, 2H), 3.60 (s, 1H), 3.19 – 3.11 (m, 2H), 1.76 (tt, J = 13.3, 6.7 Hz, 1H), 1.55 (dd, J = 14.6, 7.0 Hz, 2H), 0.99 (d, J = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 148.58 (s), 129.23 (s), 117.11 (s), 112.71 (s), 42.16 (s), 38.62 (s), 26.02 (s), 22.63 (s).

N,N'-(1,3-phenylenebis(methylene))dianiline (3w).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (s, 1H), 7.40 – 7.32 (m, 3H), 7.24 (t, J = 7.9 Hz, 4H), 6.79 (t, J = 7.3 Hz, 2H), 6.69 (d, J = 7.7 Hz, 4H), 4.37 (s, 4H), 4.08 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 148.16 (s), 139.99 (s), 129.32 (s), 128.99 (s), 126.63 (s), 126.44 (s), 117.67 (s), 112.94 (s), 48.32 (s).

N^1,N^2-bis(4-chlorobenzyl)benzene-1,2-diamine (3x).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 (s, 8H), 6.85 – 6.79 (m, 2H), 6.72 – 6.66 (m, 2H), 4.33 (s, 4H), 3.68 (s, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.88 (s), 136.89 (s), 133.00 (s), 129.06 (s), 128.77 (s), 119.74 (s), 112.33 (s), 48.14 (s).

(E)-2-(phenyldiazenyl)-N-(pyridin-2-ylmethyl)aniline (3y).

Purified by silica gel column chromatography; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.53 (t, J = 5.0 Hz, 3H), 8.64 – 8.60 (m, 3H), 7.91 – 7.89 (m, 4H), 7.88 (dd, J = 2.0, 1.3 Hz, 4H), 7.56 (d, J = 1.8 Hz, 3H), 7.46 (dd, J = 8.3, 7.0 Hz, 6H), 7.37 (d, J = 7.3 Hz, 3H), 7.26 (d, J = 7.9 Hz, 3H), 7.21 (s, 3H), 7.15 – 7.11 (m, 3H), 6.79 (s, 3H), 6.70 (dd, J = 8.4, 0.7 Hz, 3H), 4.62 (d, J = 5.4 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.02 (s), 152.94 (s), 149.41 (s), 143.09 (s), 136.83 (d, J = 1.1 Hz), 132.84 (s), 130.89 (s), 129.89 (s), 129.21 (s), 122.29 (d, J = 8.0 Hz), 121.35 (s), 116.31 (s), 112.36 (s), 48.53 (s).

2-chloro-6-(1-phenyl-2-(pyridin-2-ylmethyl)hydrazineyl)pyridine (3z)

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl3) δ 8.53 (d, J = 4.8 Hz, 1H), 7.56 (td, J = 7.6, 1.7 Hz, 1H), 7.37 – 7.26 (m, 6H), 7.18 – 7.10 (m, 2H), 6.68 (dd, J = 20.9, 7.9 Hz, 2H), 5.93 (s, 1H), 4.26 (d, J = 2.3 Hz, 2H); ^{13}C NMR (126 MHz, CDCl3) δ 157.80 (s), 157.65 (s), 149.33 (s), 149.20 (s), 143.71 (s), 139.36 (s), 136.31 (s), 129.22 (s), 125.70 (s), 125.25 (s), 123.23 (s), 122.21 (s), 113.74 (s), 107.25 (s), 55.29 (s).

1H-indole (4a).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (s), 7.65 (dd, J = 7.9, 0.9 Hz), 7.38 (dd, J = 8.1, 0.9 Hz), 7.22 – 7.17 (m), 7.15 – 7.10 (m), 6.55 (ddd, J = 3.1, 2.0, 0.9 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.85 (s), 127.92 (s), 124.24 (s), 122.08 (s), 120.83 (s), 119.91 (s), 111.12 (s), 102.71 (s).

5-methoxy-1H-indole (4b).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (s), 7.29 – 7.25 (m), 7.16 (t, J = 2.7 Hz), 7.14 (d, J = 2.5 Hz), 6.89 (dd, J = 8.8, 2.5 Hz), 6.50 (ddd, J = 3.1, 2.1, 0.9 Hz), 3.87 (s); ^{13}C NMR (126 MHz, CDCl$_3$) δ 154.26 (s), 131.07 (s), 128.37 (s), 125.05 (s), 112.44 (s), 111.87 (s), 102.44 (s), 55.97 (s).

6-chloro-1H-indole (4c).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 (s), 7.54 (d, J = 8.4 Hz), 7.40 – 7.36 (m), 7.19 (dd, J = 3.1, 2.5 Hz), 7.09 (dd, J = 8.4, 1.8 Hz), 6.53 (ddd, J = 3.0, 2.0, 0.9 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 136.20 (s), 127.94 (s), 126.51 (s), 124.93 (s), 121.64 (s), 120.67 (s), 111.05 (s), 102.87 (s).

6-bromo-1H-indole (4d).

Purified by silica gel column chromatography; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (s), 7.78 (d, J = 1.6 Hz), 7.29 – 7.23 (m), 7.21 – 7.18 (m), 6.49 (ddd, J = 3.0, 2.0, 0.8 Hz); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.47 (s), 129.71 (s), 125.49 (s), 124.93 (s), 123.30 (s), 113.11 (s), 112.55 (s), 102.38 (s).

(E)-1-(4-methoxyphenyl)-N-phenylmethanimine (2a").

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.89 (d, J = 8.6 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.25 (t, J = 8.5 Hz, 3H), 7.02 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H).
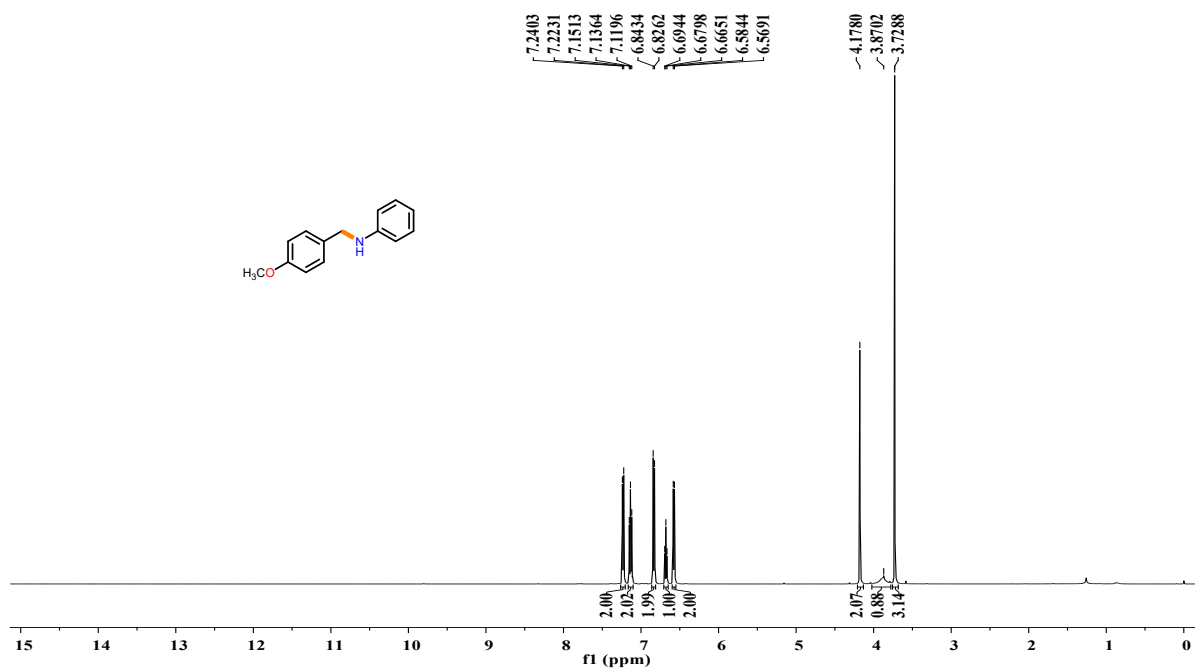
Figure S11. ^{1}H NMR spectrum of **3a** in CDCl$_3$ (500 MHz).
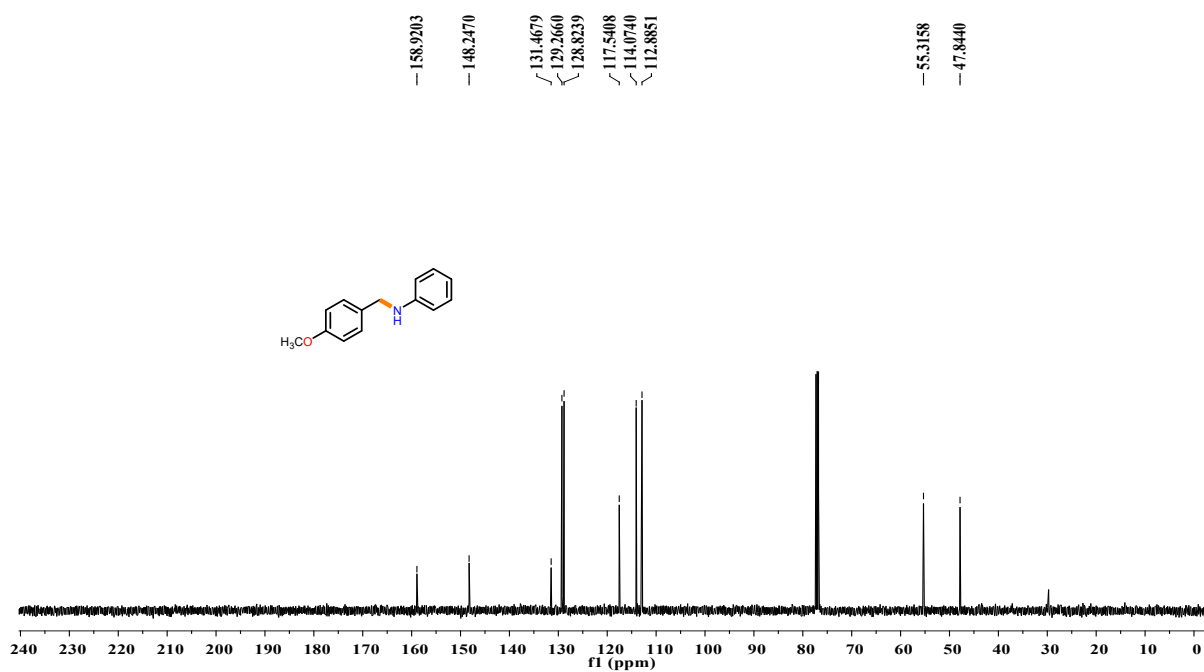
Figure S12. ^{13}C NMR spectrum of **3a** in CDCl$_3$ (500 MHz).

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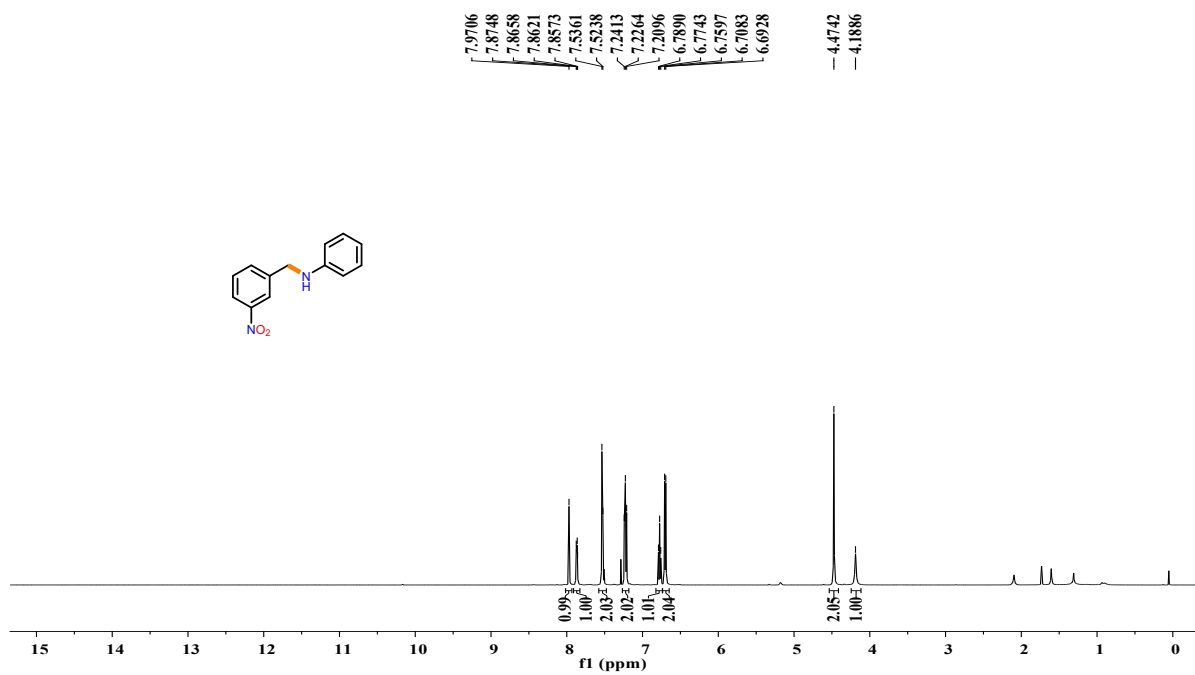
Figure S13. ^{1}H NMR spectrum of **3b** in CDCl$_3$ (500 MHz).
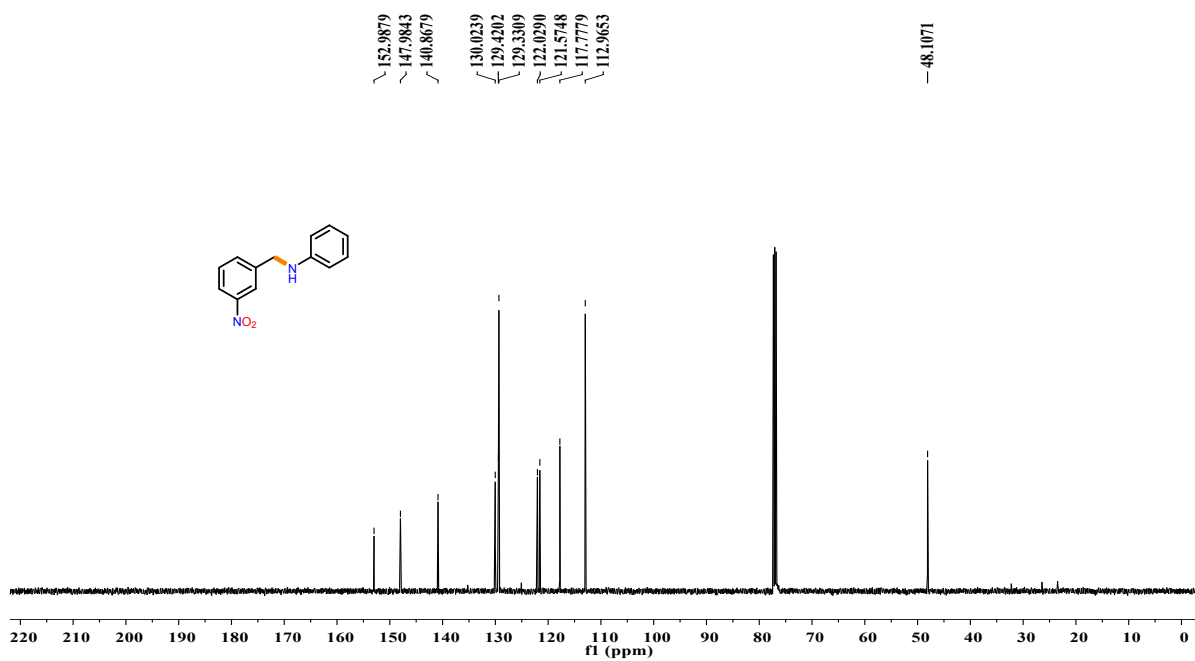
Figure S14. ^{13}C NMR spectrum of **3b** in CDCl$_3$ (500 MHz).
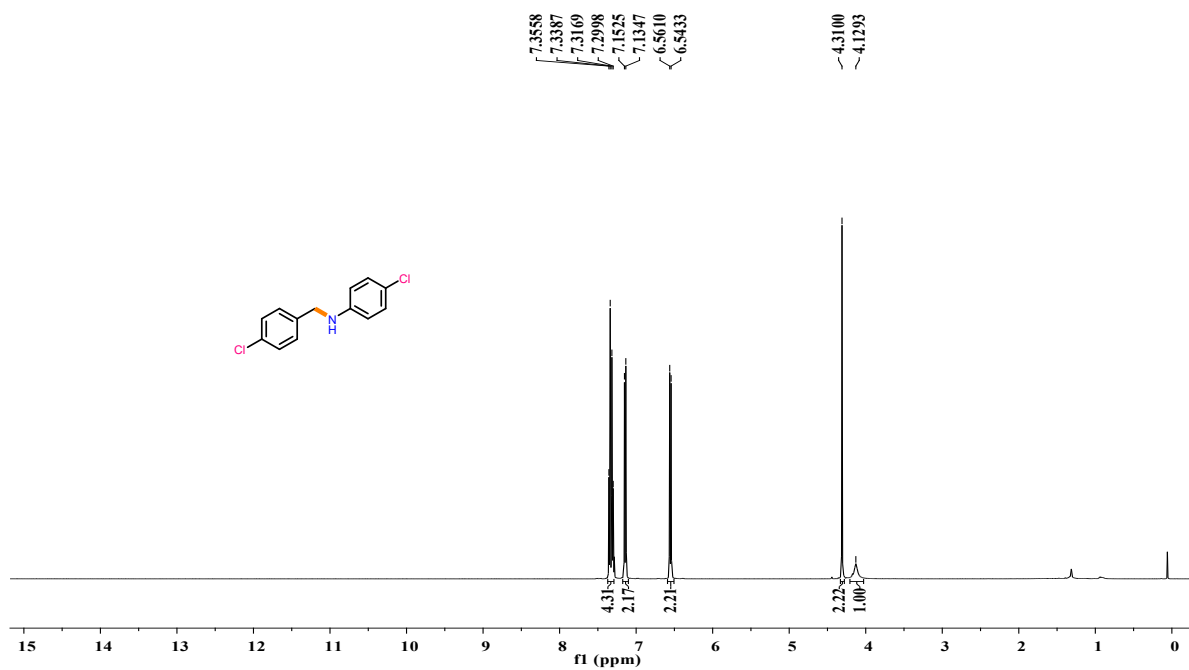
Figure S15. ^{1}H NMR spectrum of **3c** in CDCl$_3$ (500 MHz).
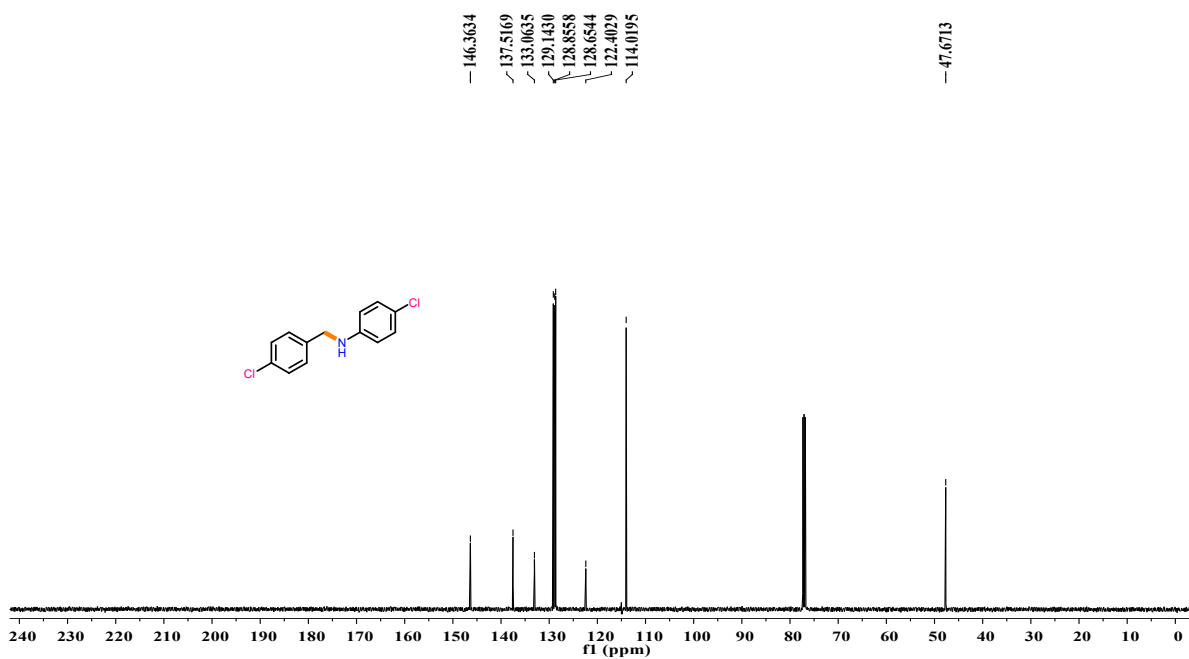
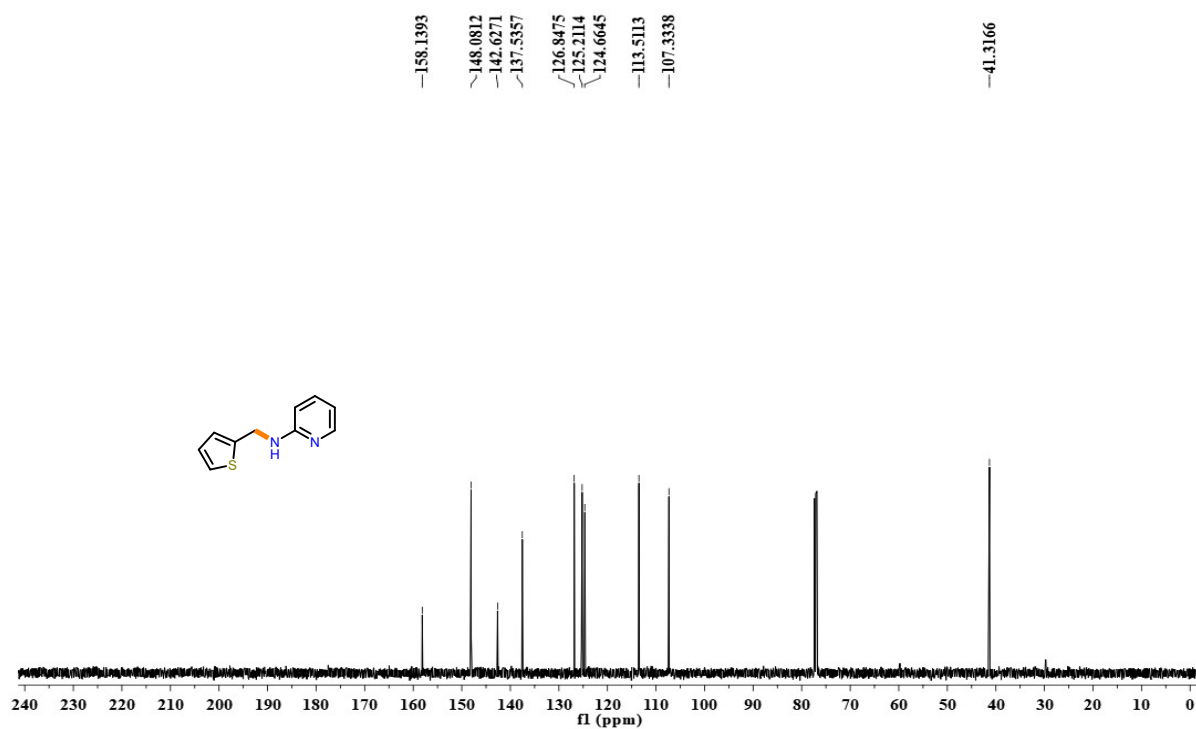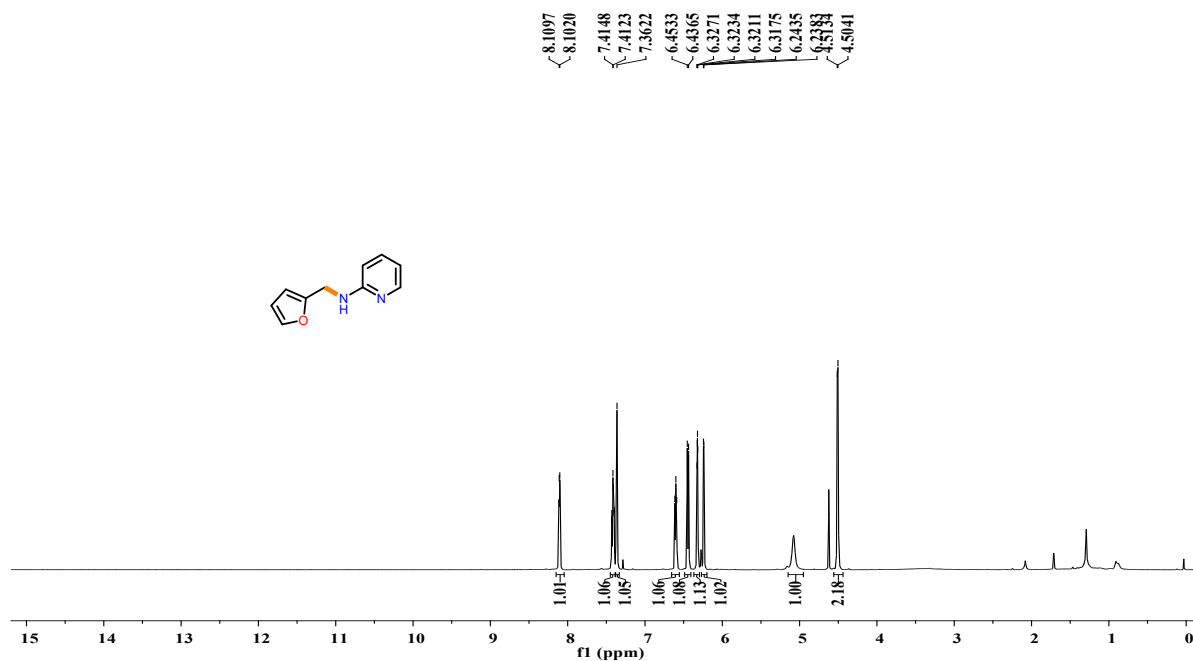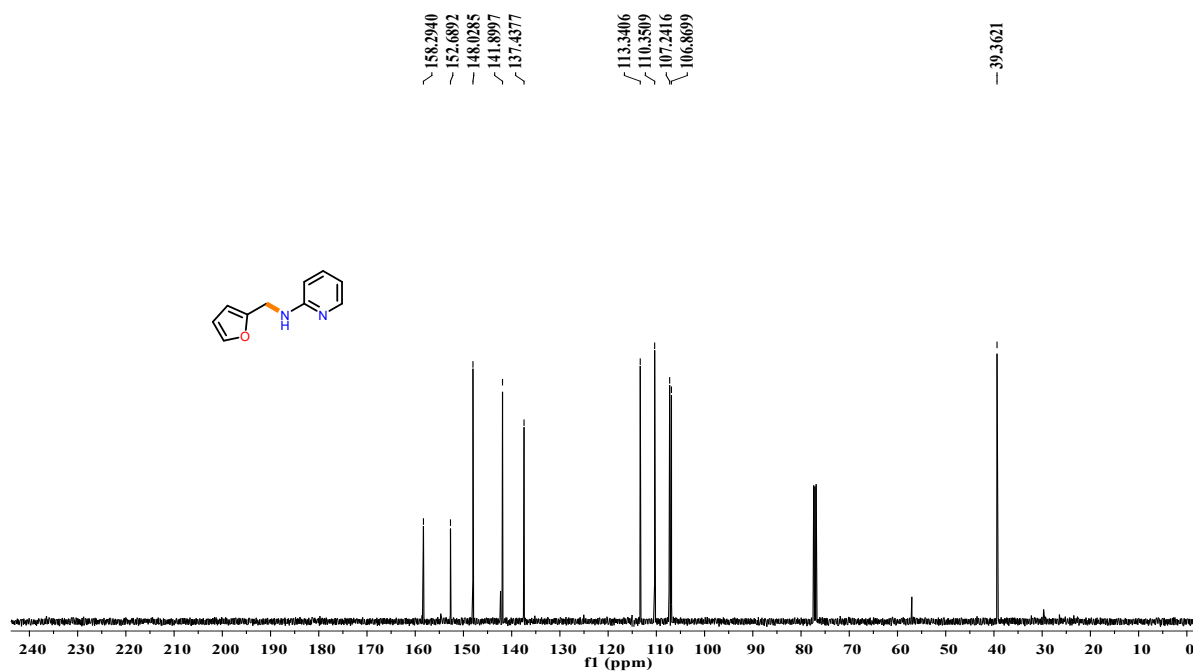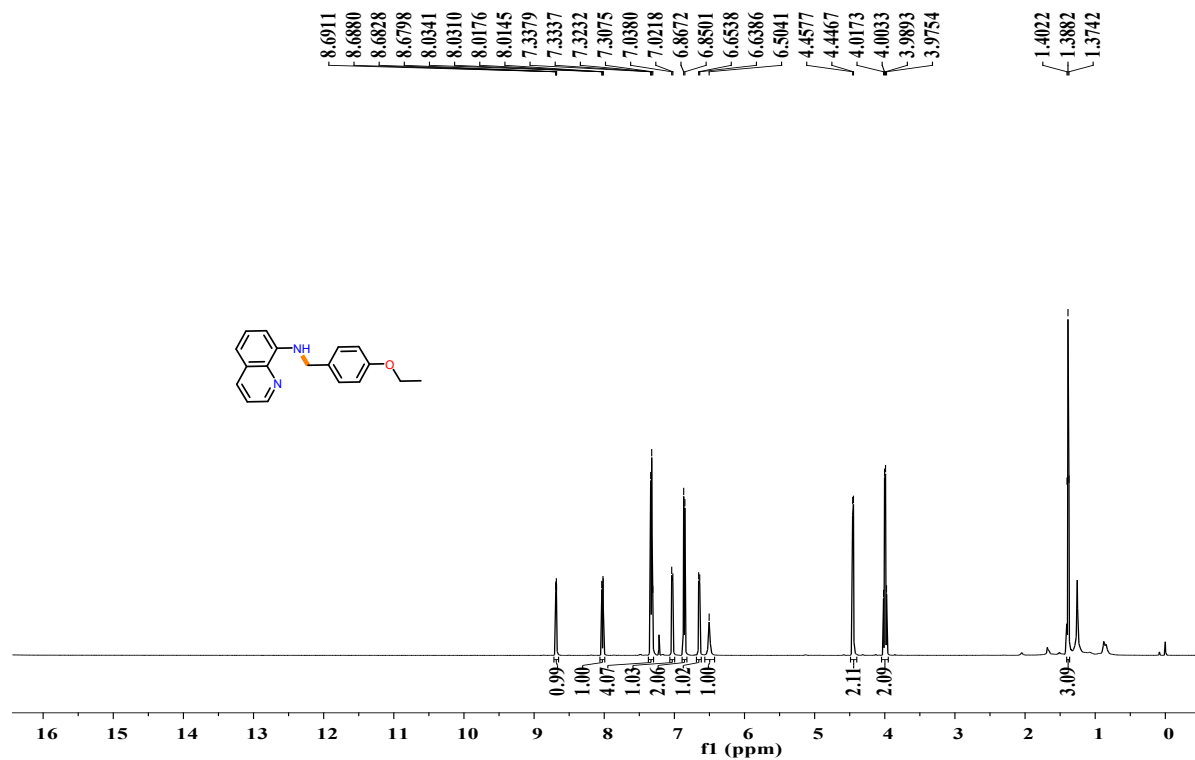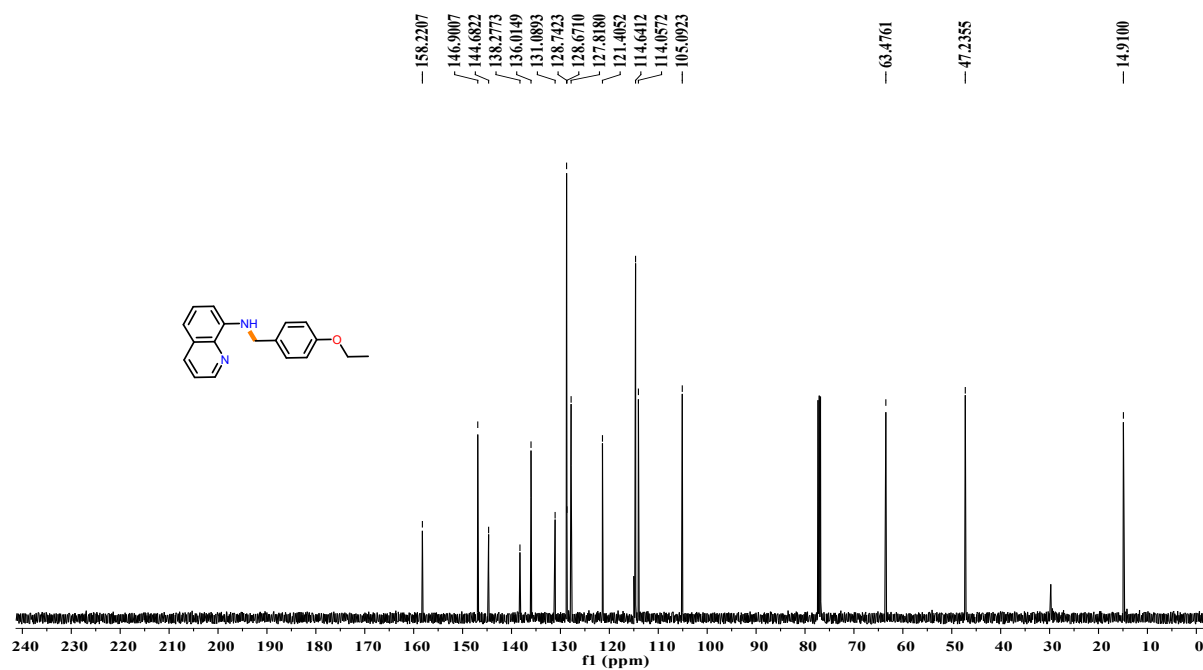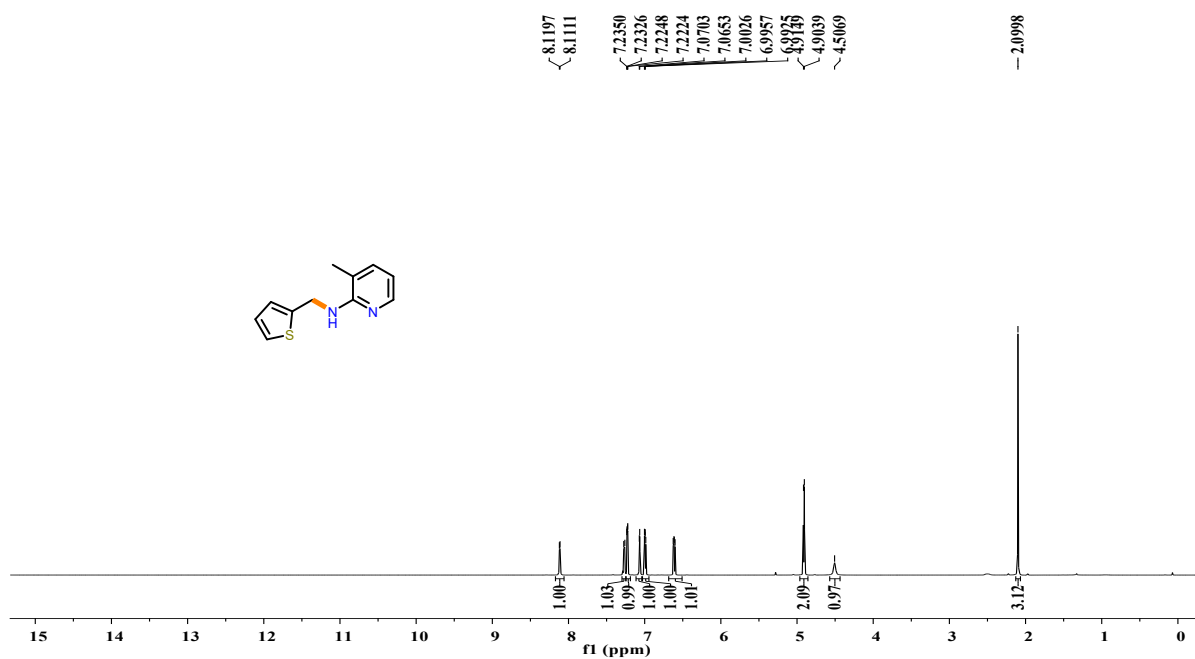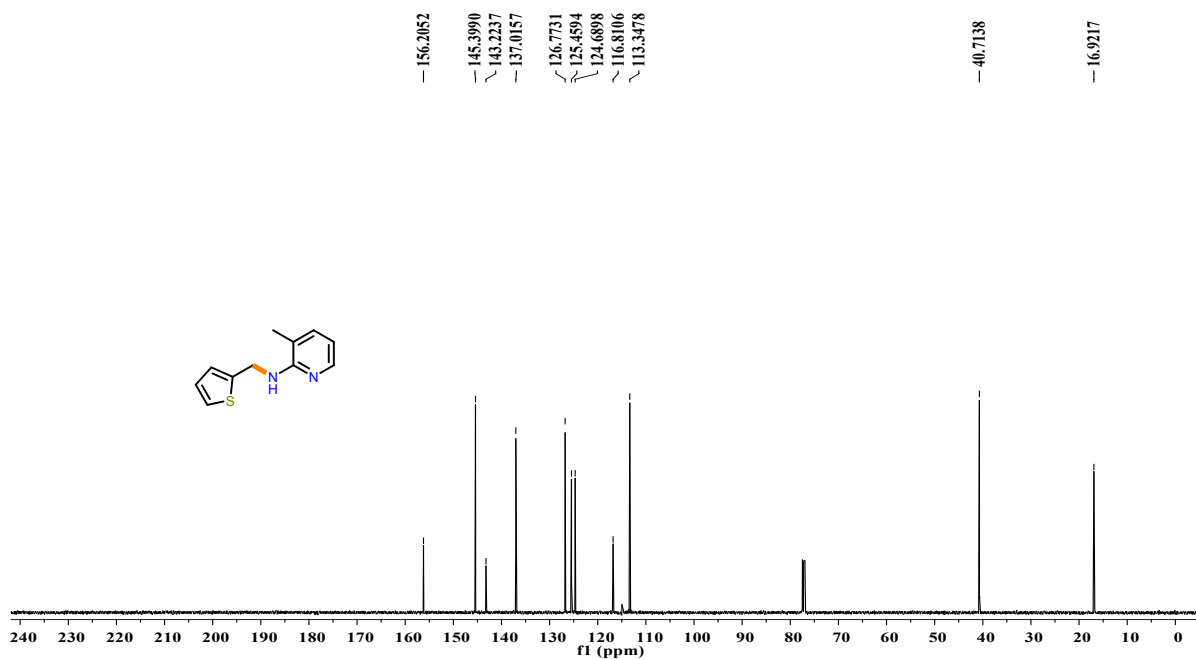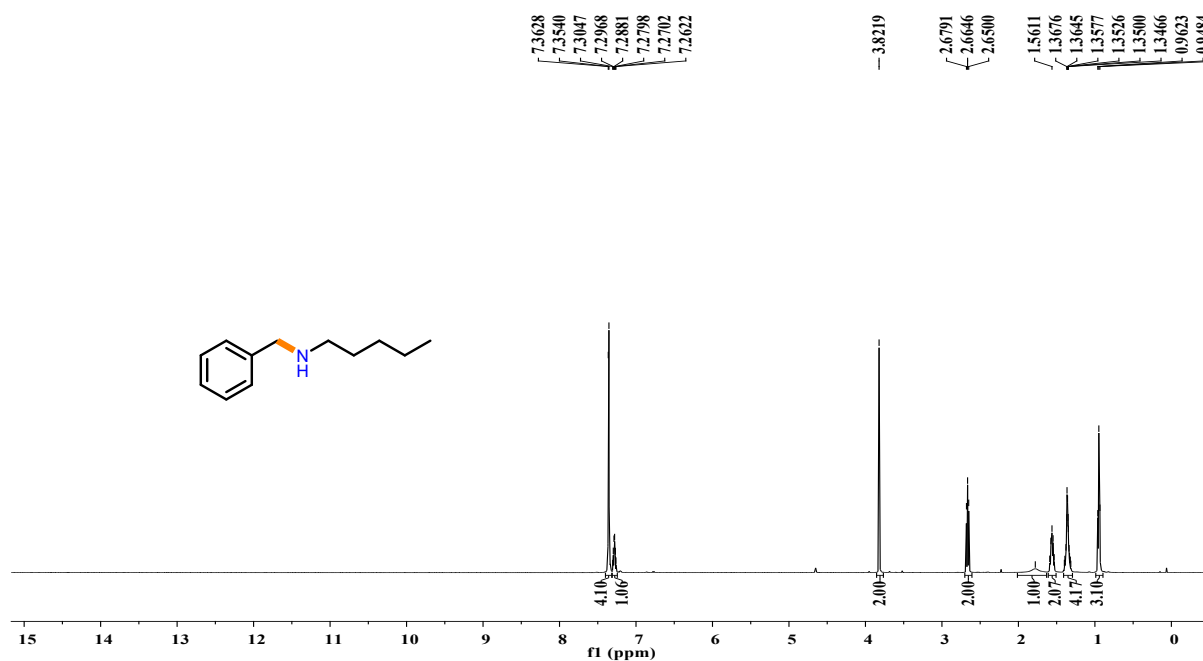**Figure S16**. ^{13}C NMR spectrum of **3c** in CDCl$_3$ (500 MHz).

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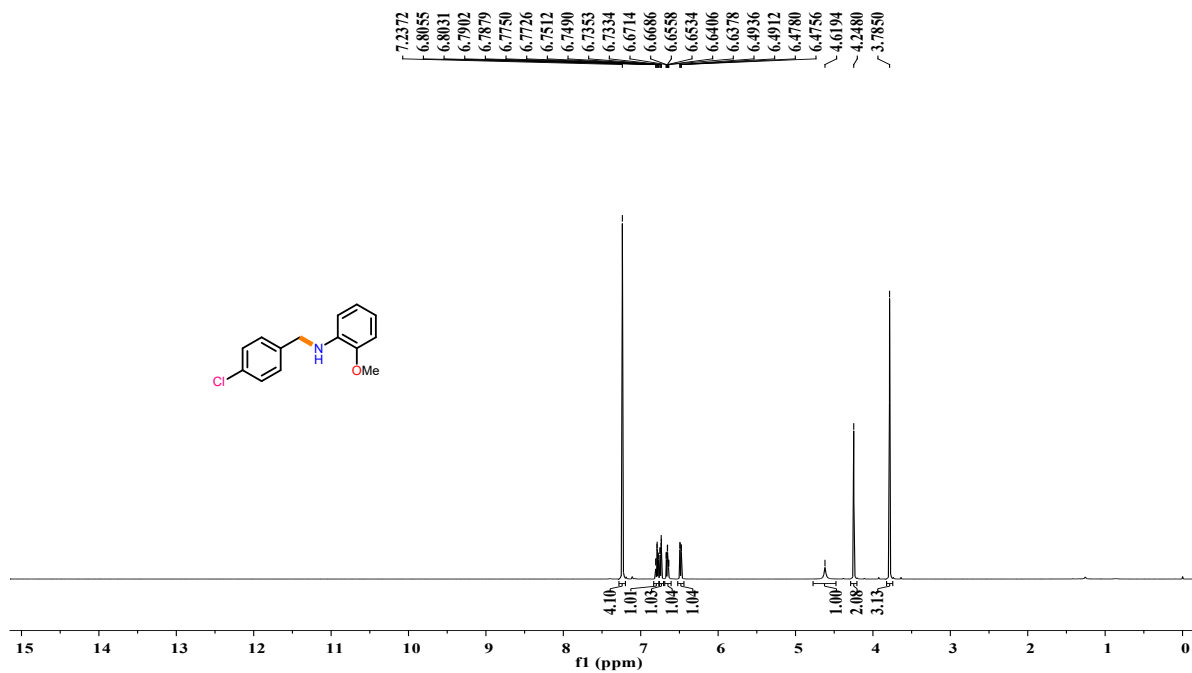
Figure S17. ^{1}H NMR spectrum of **3d** in CDCl$_3$ (500 MHz).
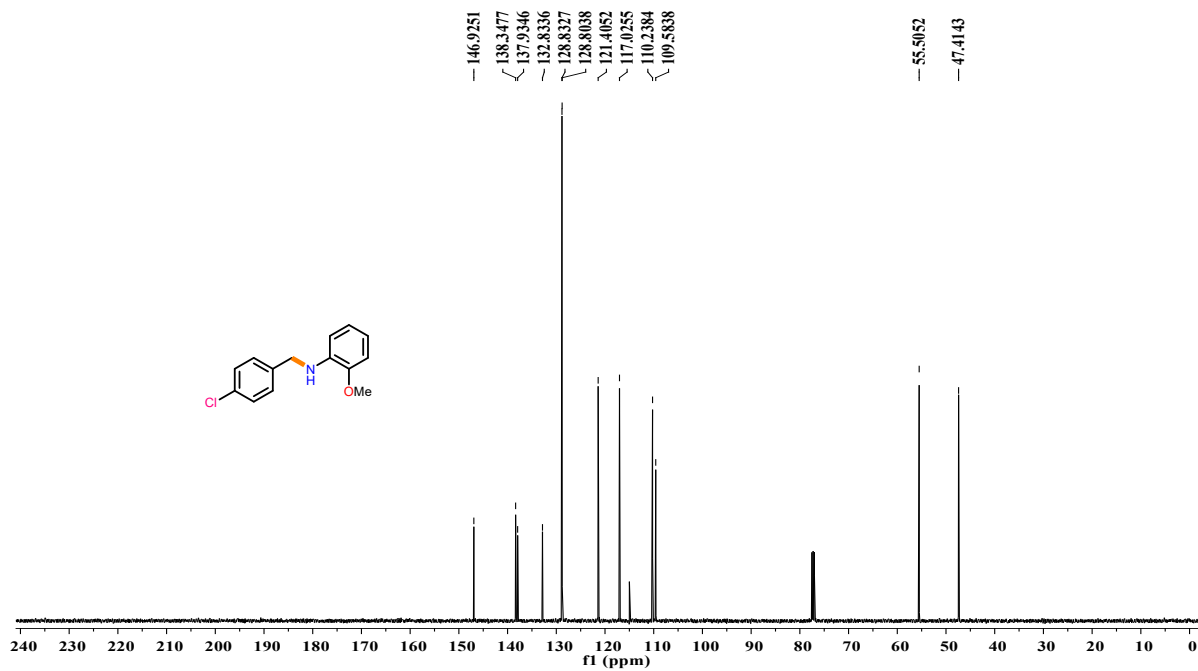
Figure S18. ^{13}C NMR spectrum of **3d** in CDCl$_3$ (500 MHz).
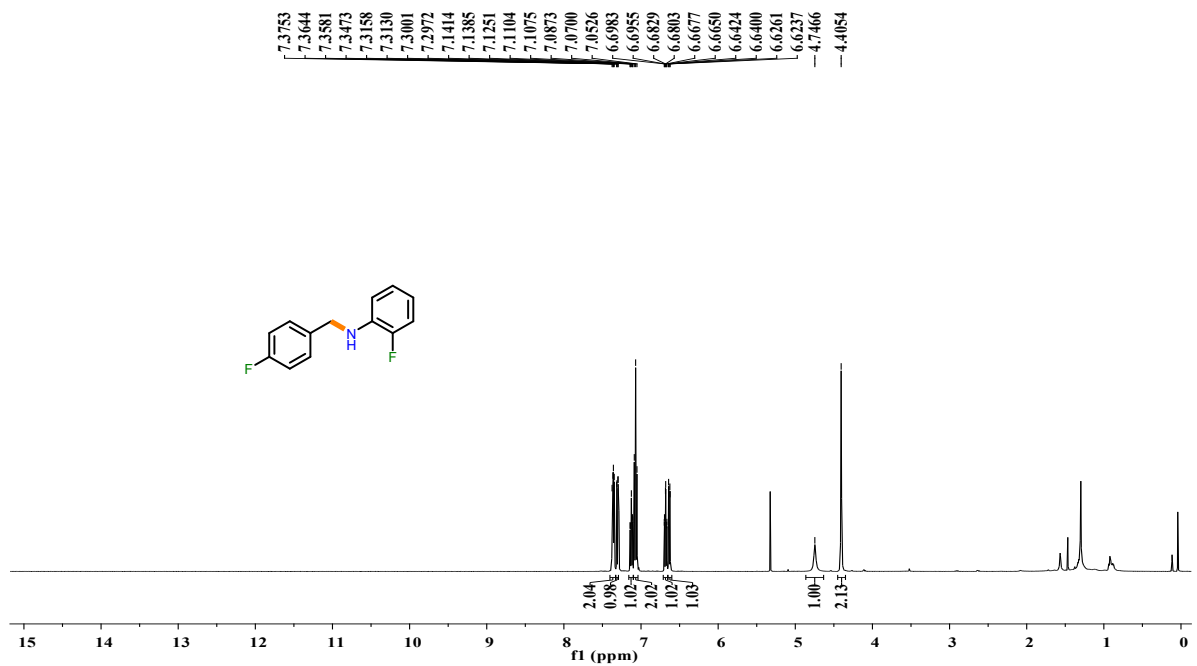
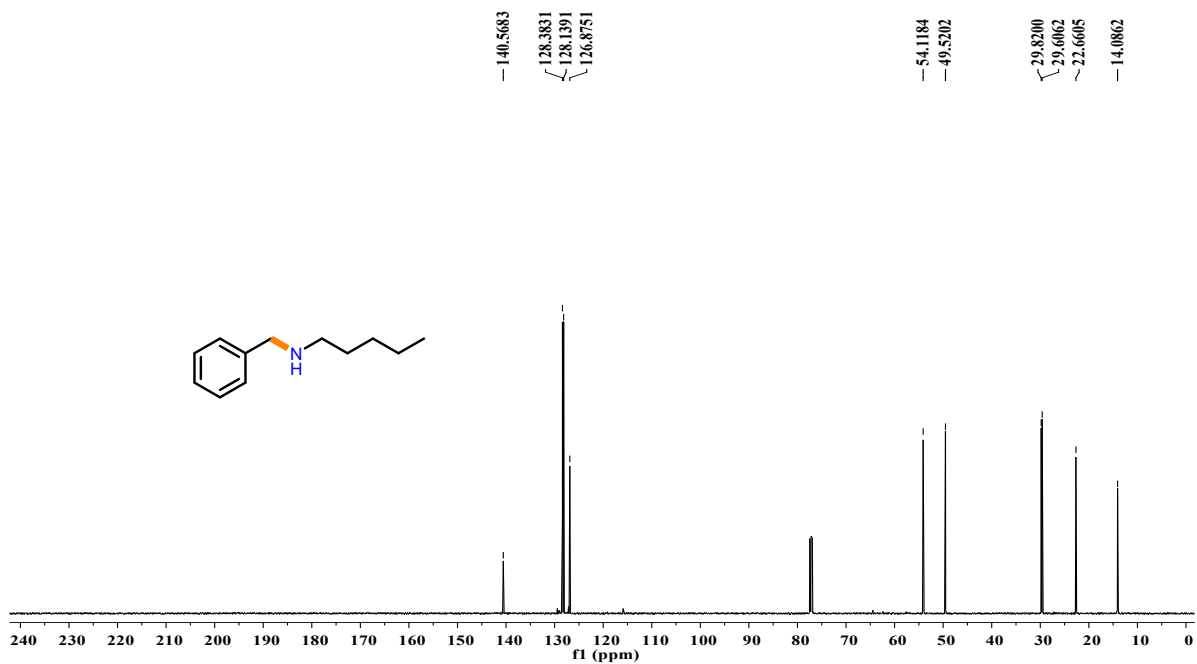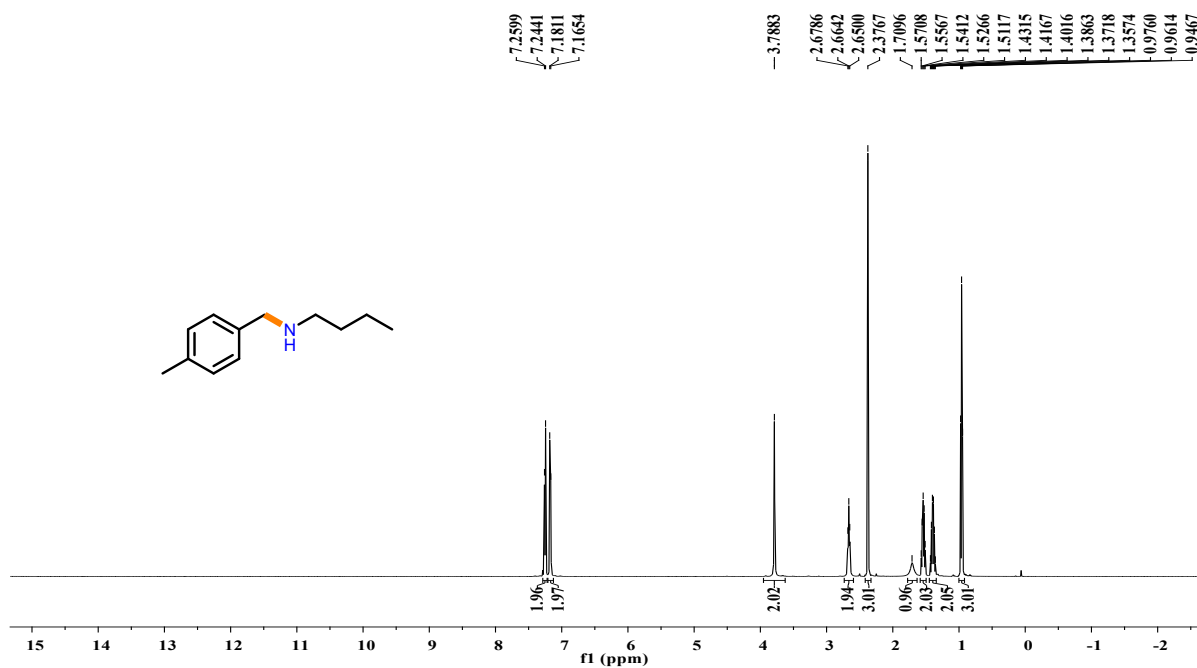**Figure S19**. ^1H NMR spectrum of **3e** in CDCl$_3$ (500 MHz).
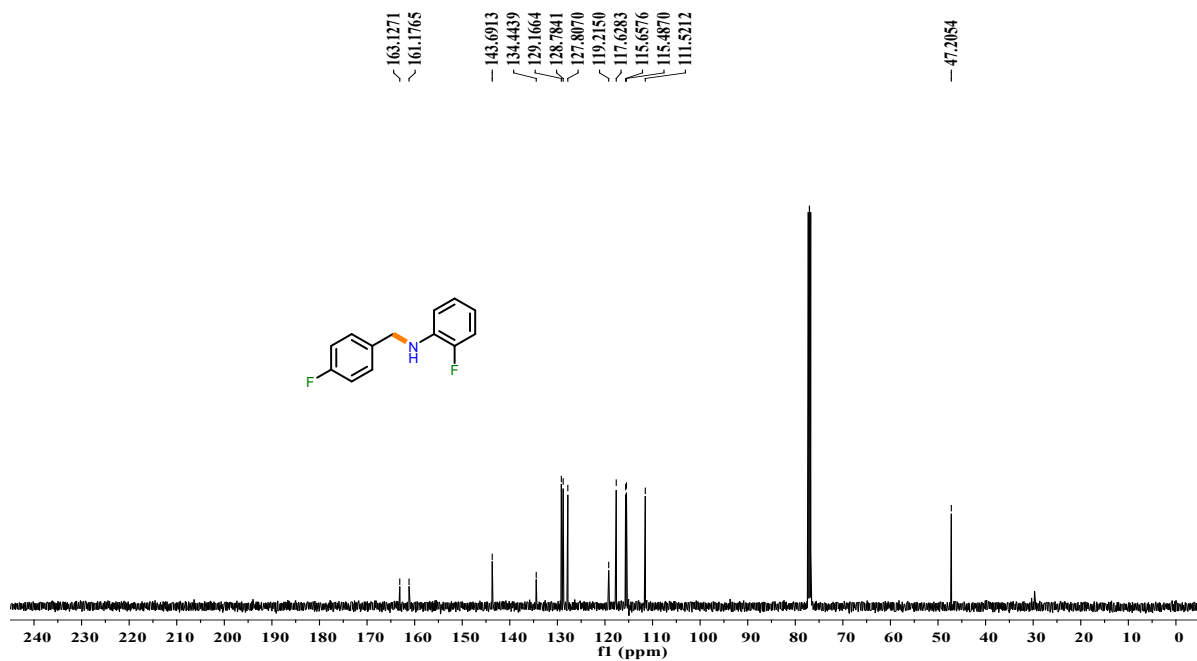
Figure S20. ^{13}C NMR spectrum of **3e** in CDCl$_3$ (500 MHz).
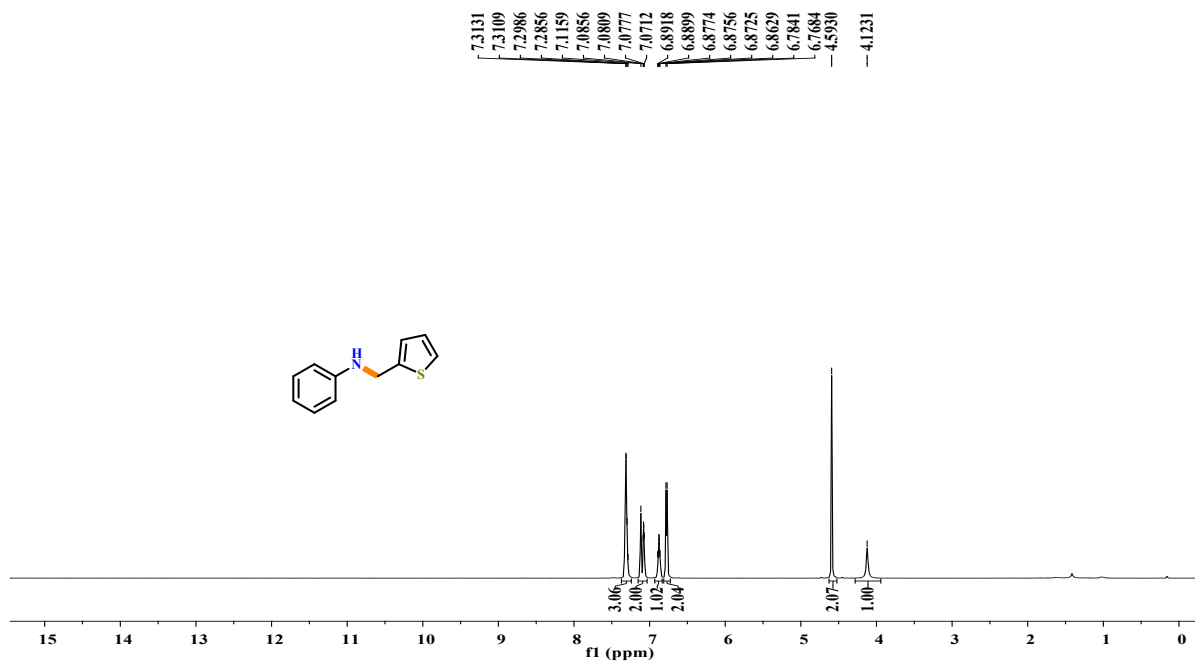
Figure S21. [^1]H NMR spectrum of **3f** in CDCl$_3$ (500 MHz).
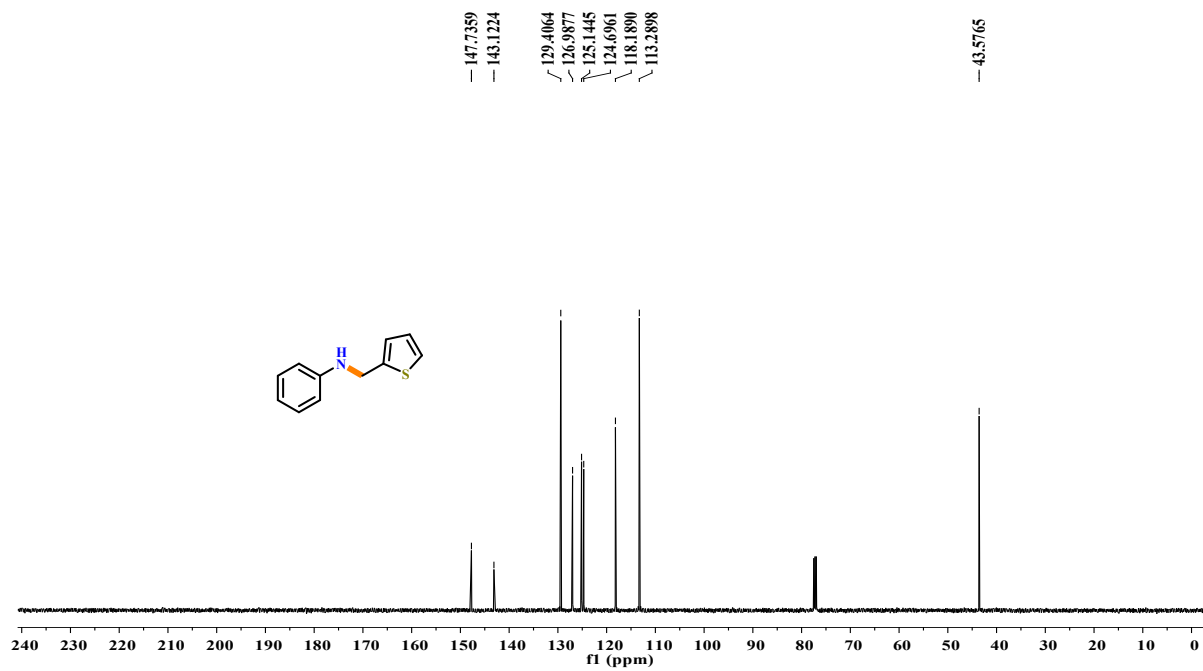
Figure S22. [^13]C NMR spectrum of **3f** in CDCl$_3$ (500 MHz).

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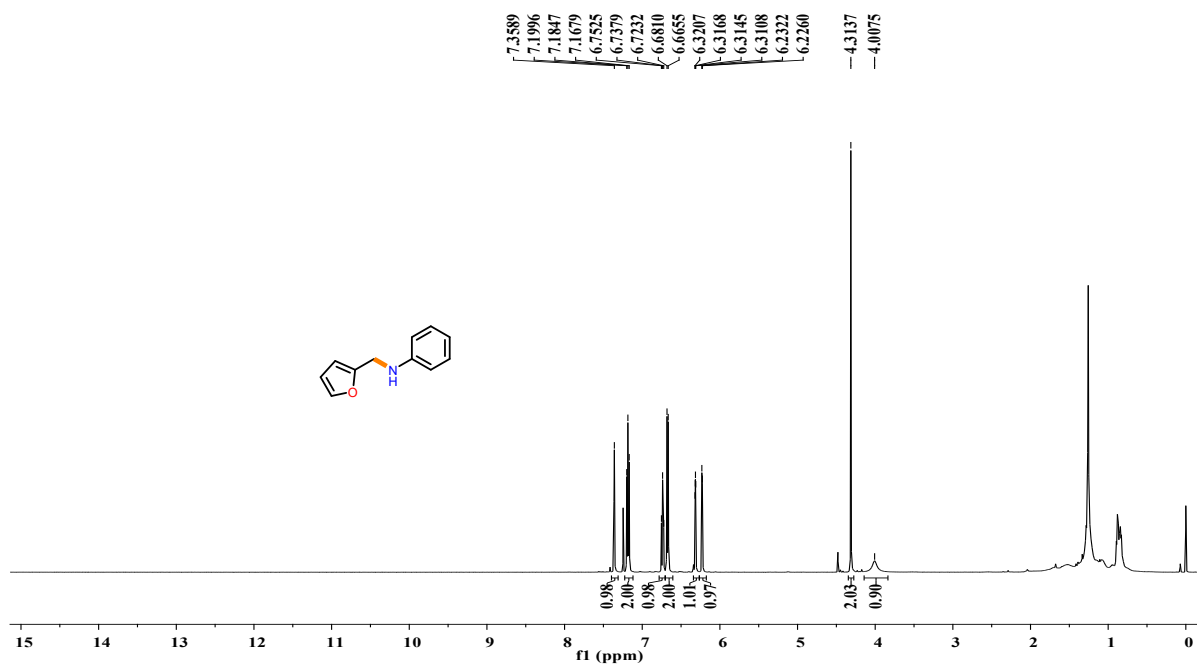
Figure S23. ^{1}H NMR spectrum of **3g** in CDCl$_3$ (500 MHz).
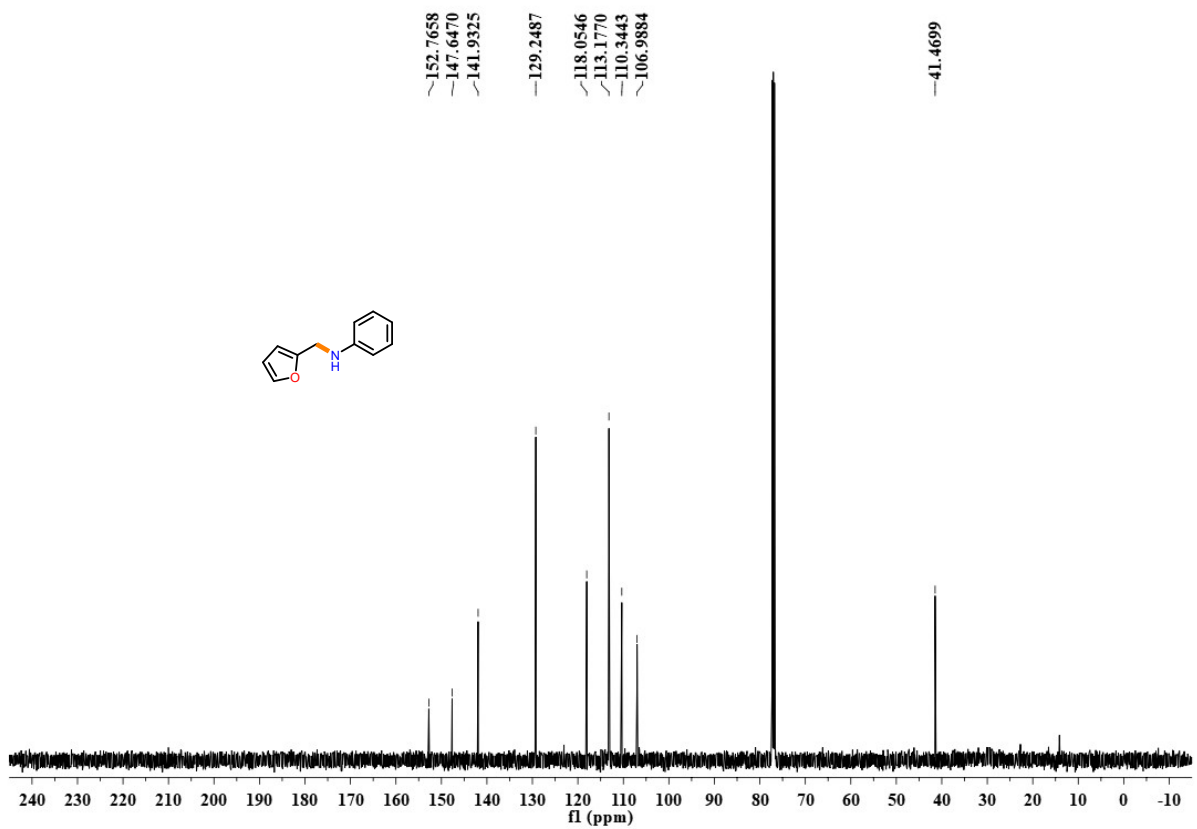
Figure S24. ^{13}C NMR spectrum of **3g** in CDCl$_3$ (500 MHz).
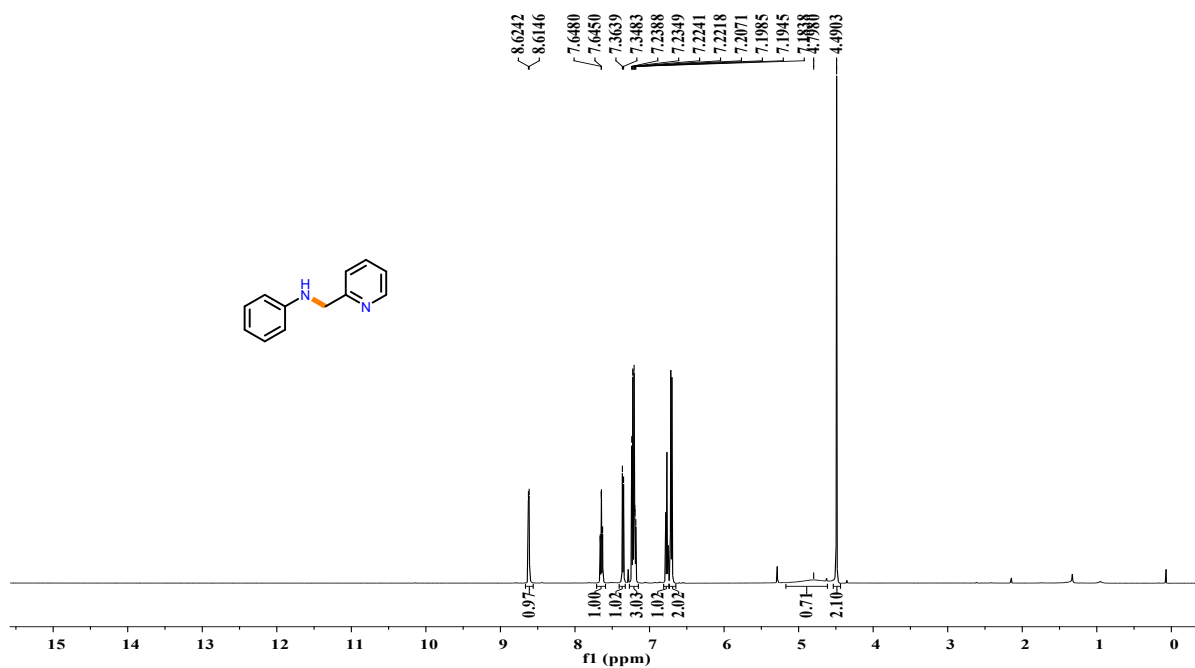
Figure S25. ^{1}H NMR spectrum of **3h** in CDCl$_3$ (500 MHz).
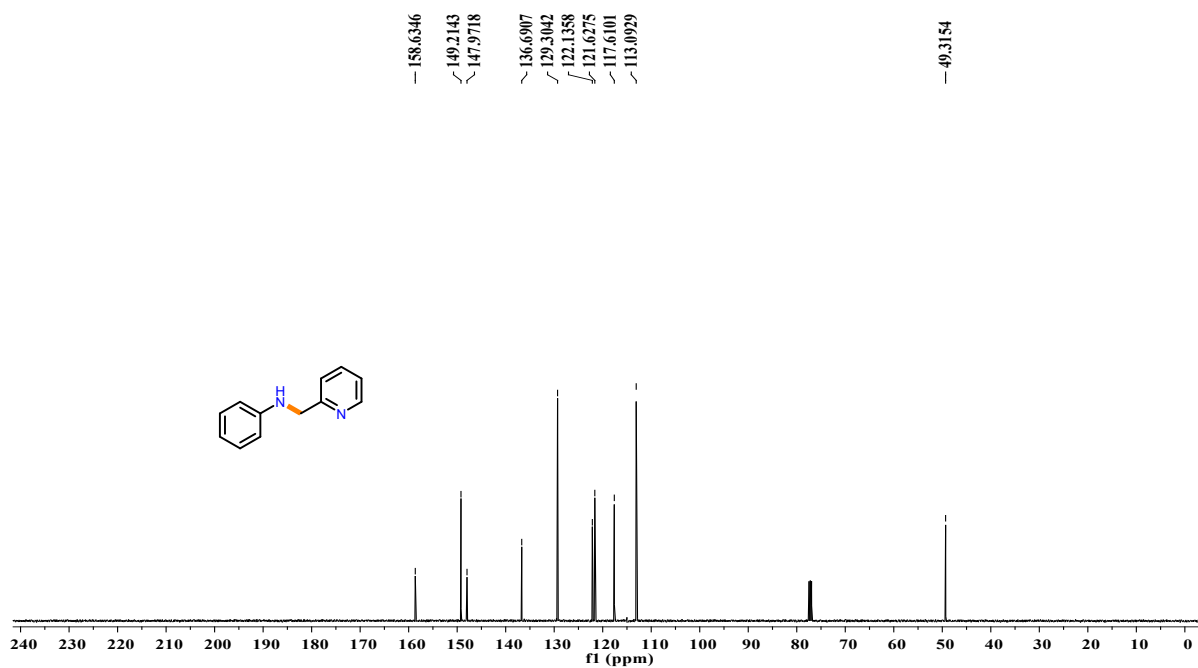
Figure S26. ^{13}C NMR spectrum of **3h** in CDCl$_3$ (500 MHz).
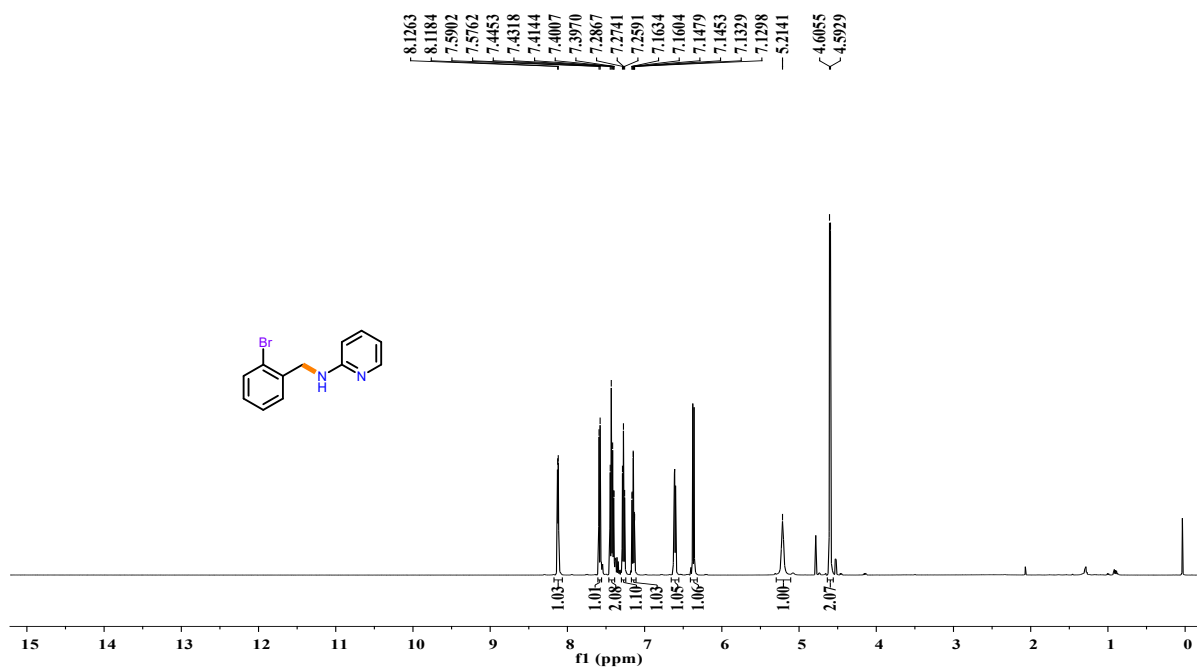
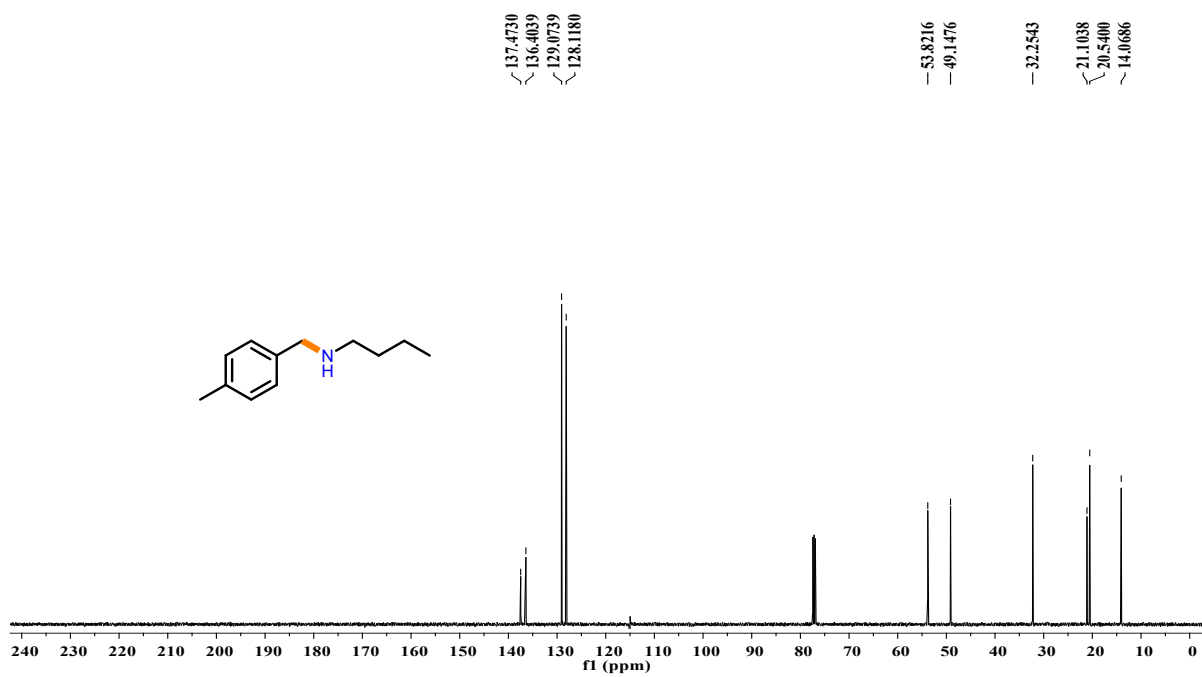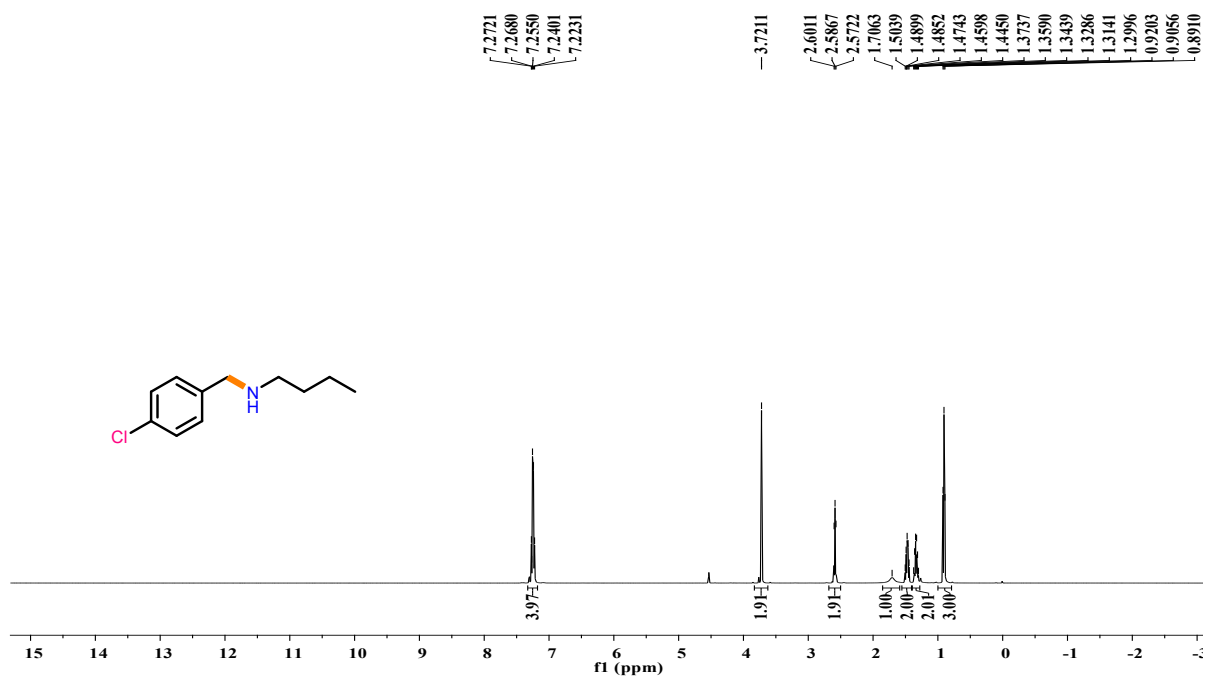**Figure S27**. ^{1}H NMR spectrum of **3i** in CDCl$_3$ (500 MHz).
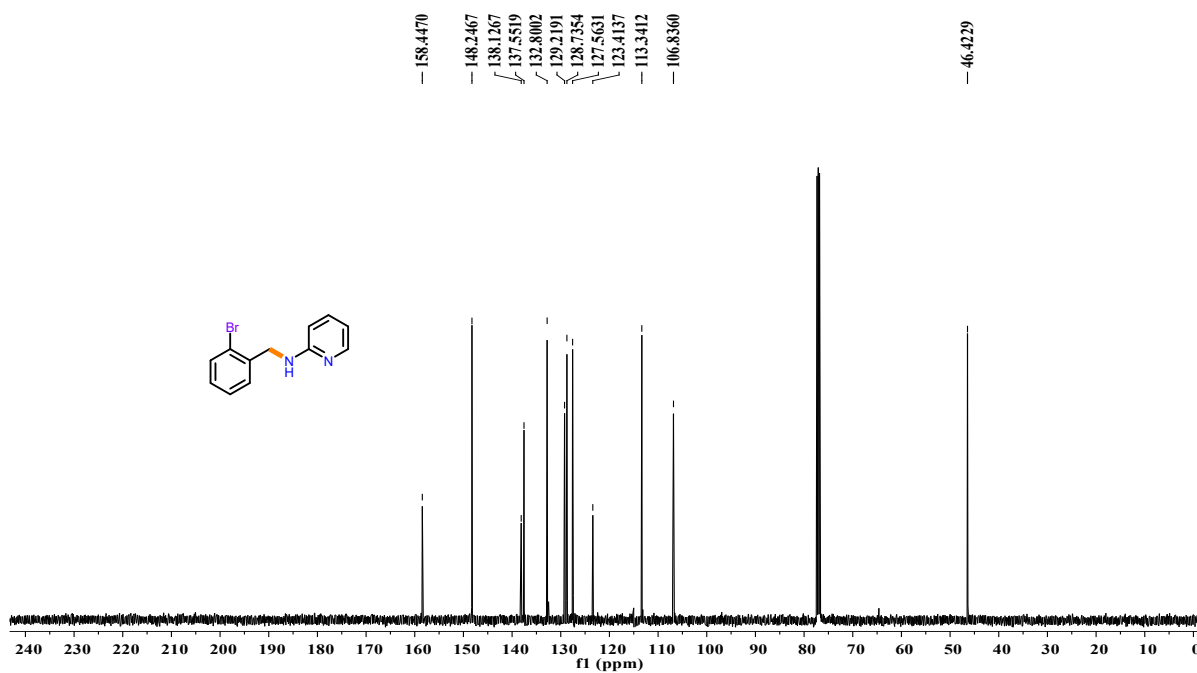
Figure S28. ^{13}C NMR spectrum of **3i** in CDCl$_3$ (500 MHz).
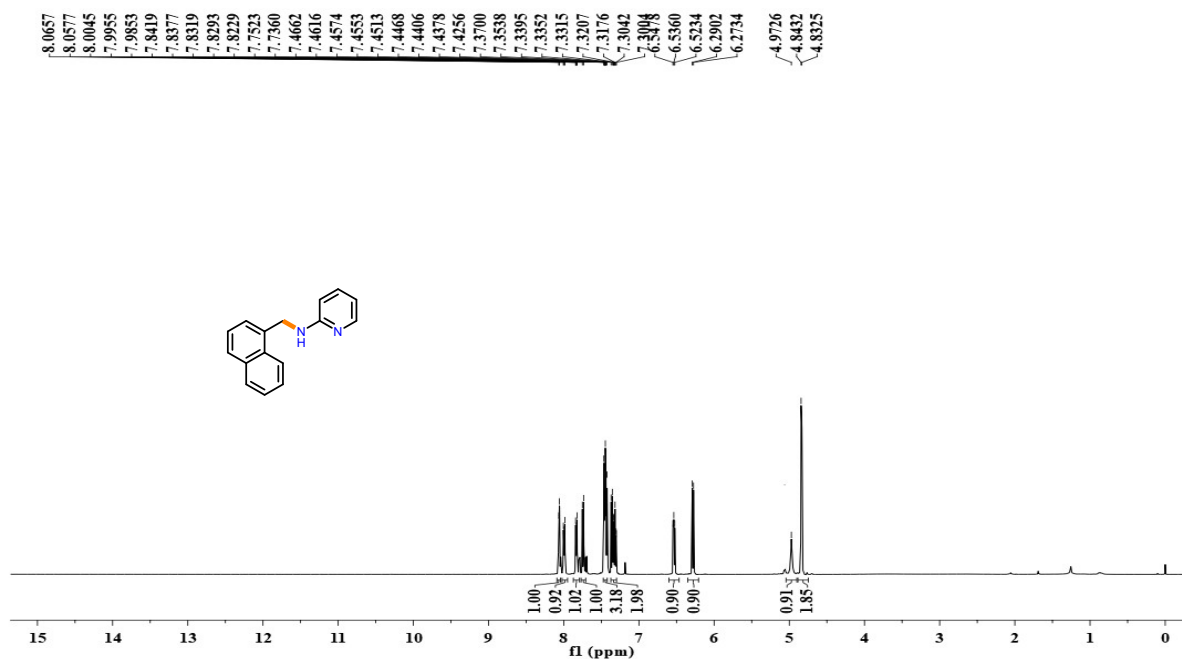
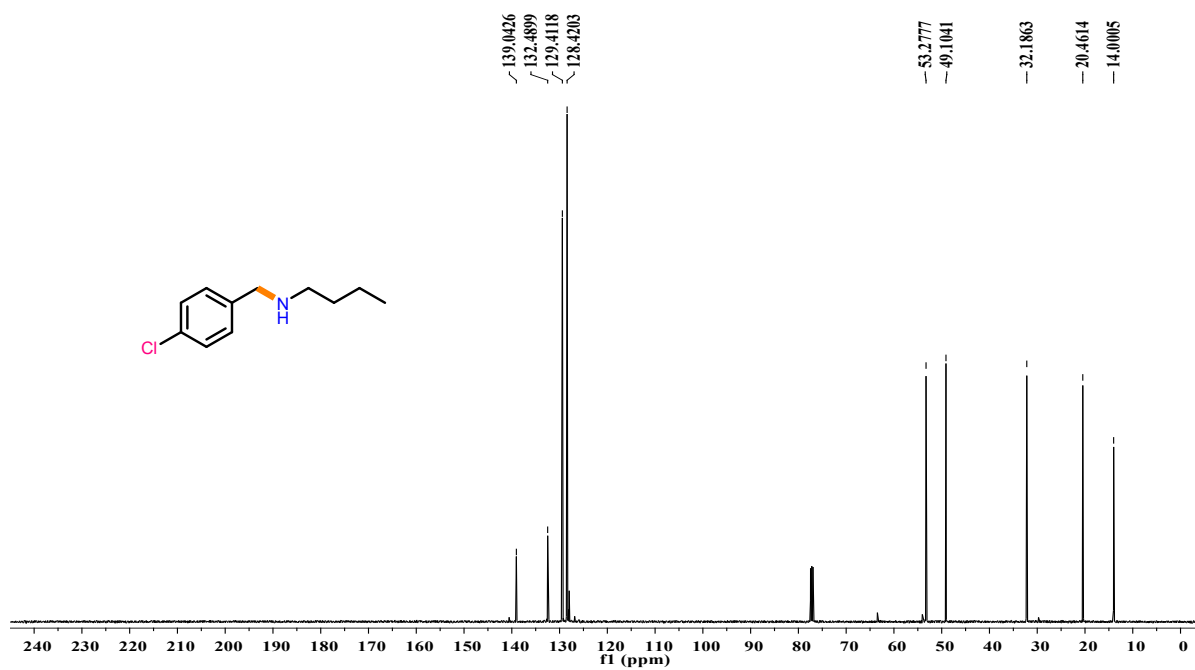**Figure S29**. ^{1}H NMR spectrum of **3j** in CDCl$_3$ (500 MHz).
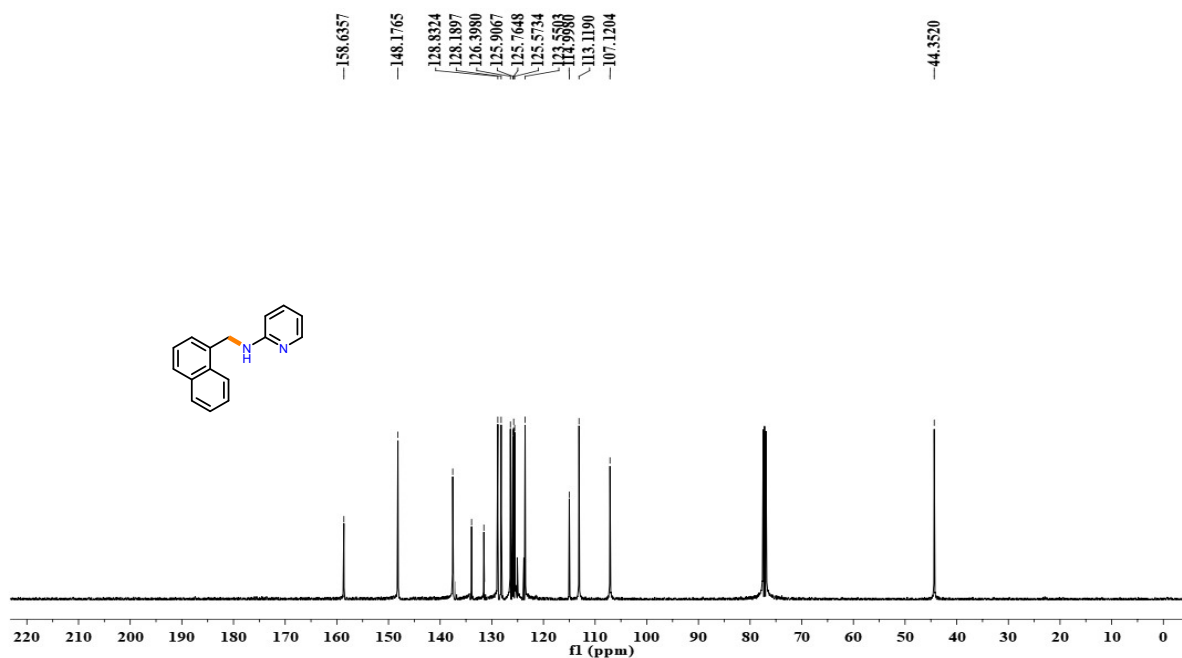
Figure S30. ^{13}C NMR spectrum of **3j** in CDCl$_3$ (500 MHz).
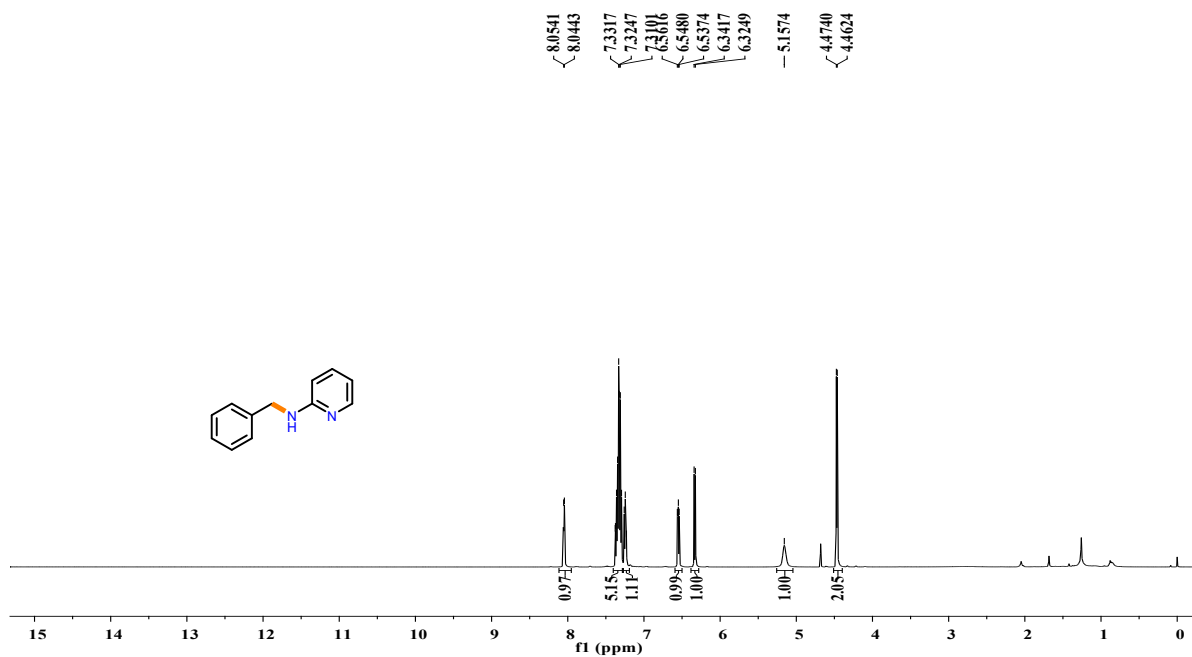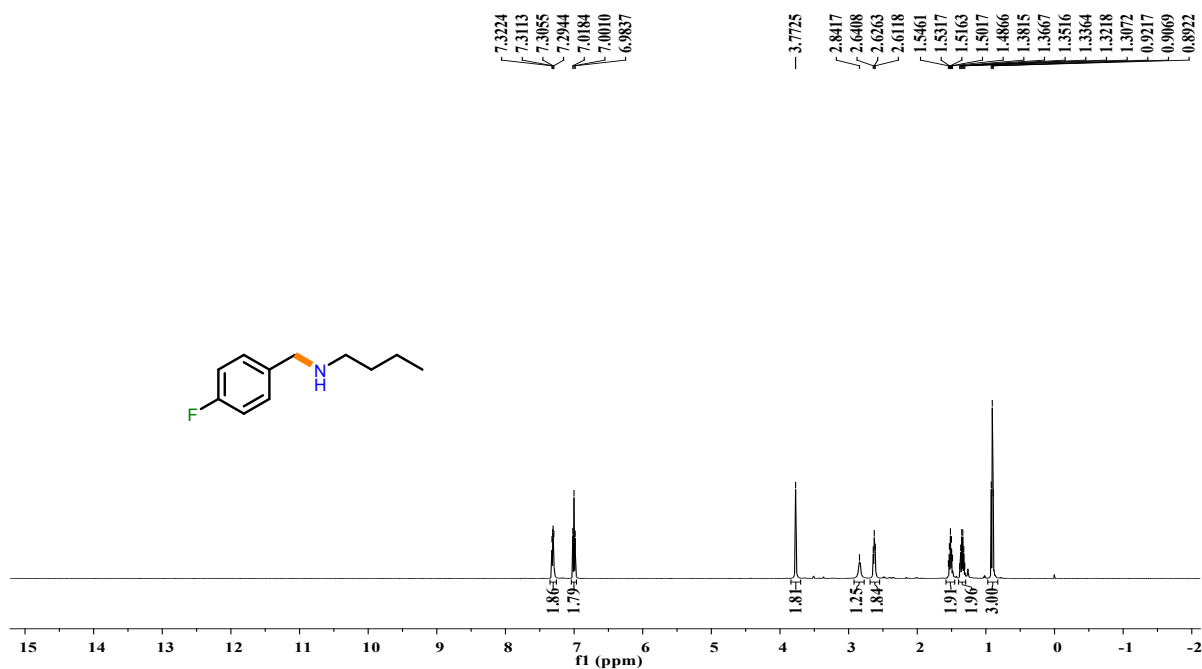
Figure S31. ^{1}H NMR spectrum of **3k** in CDCl$_3$ (500 MHz).
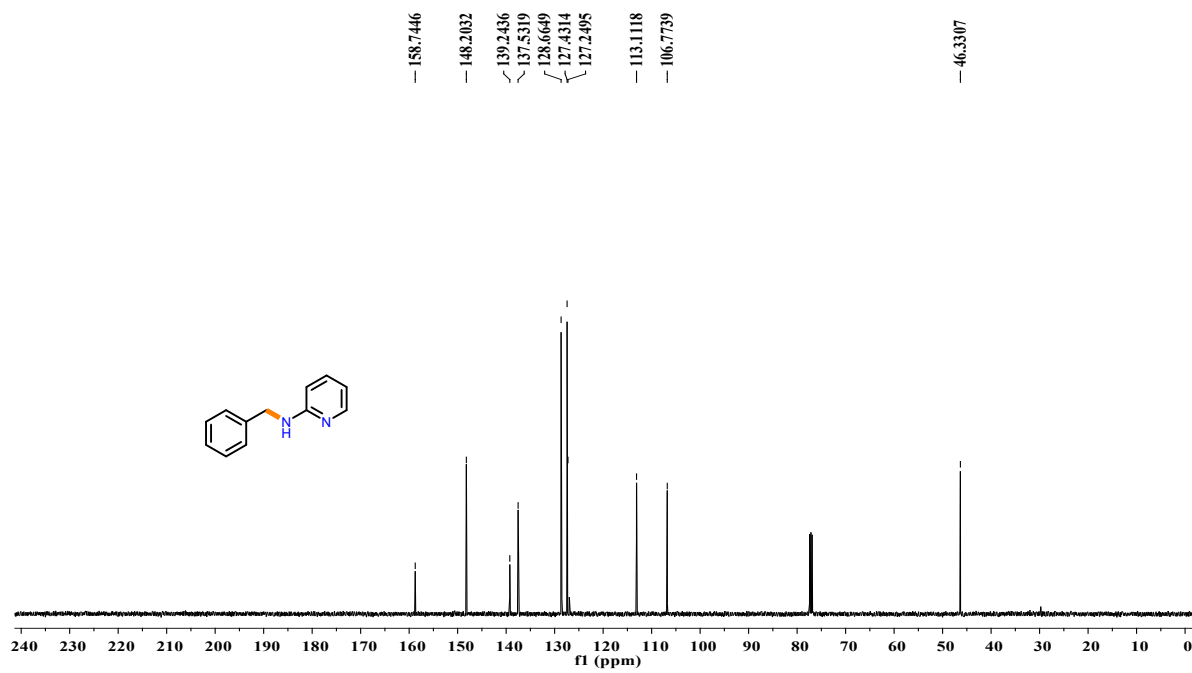
Figure S32. ^{13}C NMR spectrum of **3k** in CDCl$_3$ (500 MHz).
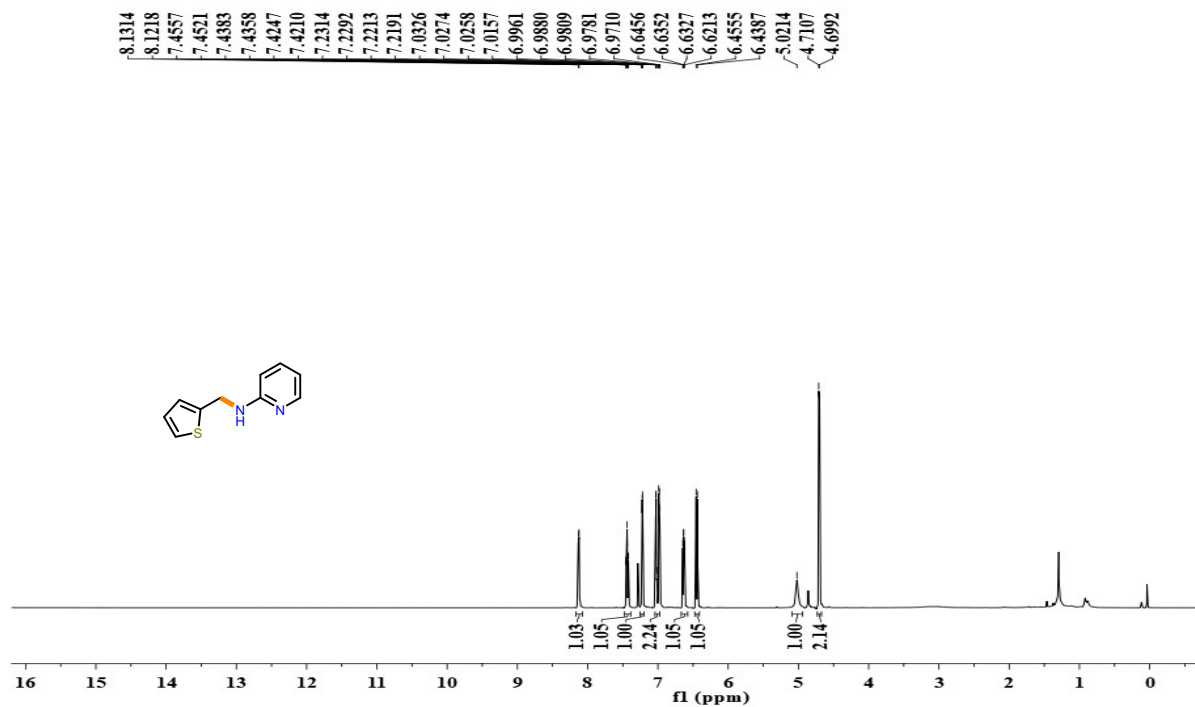
Figure S33. ^{1}H NMR spectrum of **3l** in CDCl$_3$ (500 MHz).

Figure S34. ^{13}C NMR spectrum of **3l** in CDCl$_3$ (500 MHz).

Figure S35. ^{1}H NMR spectrum of **3m** in CDCl$_3$ (500 MHz).
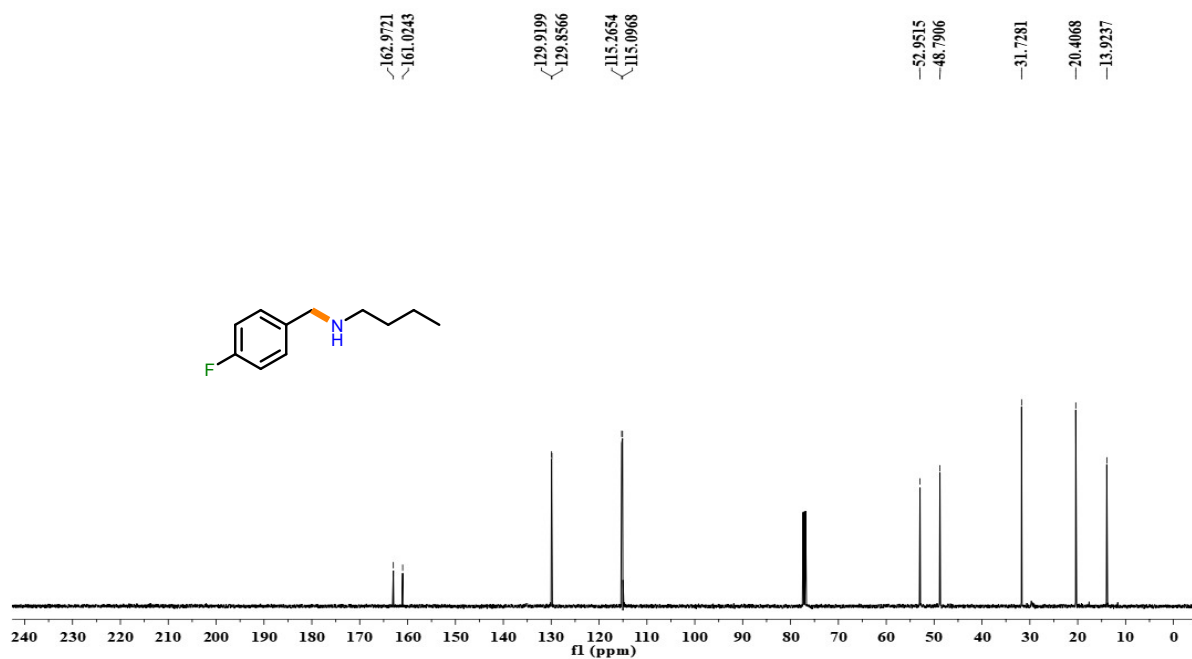
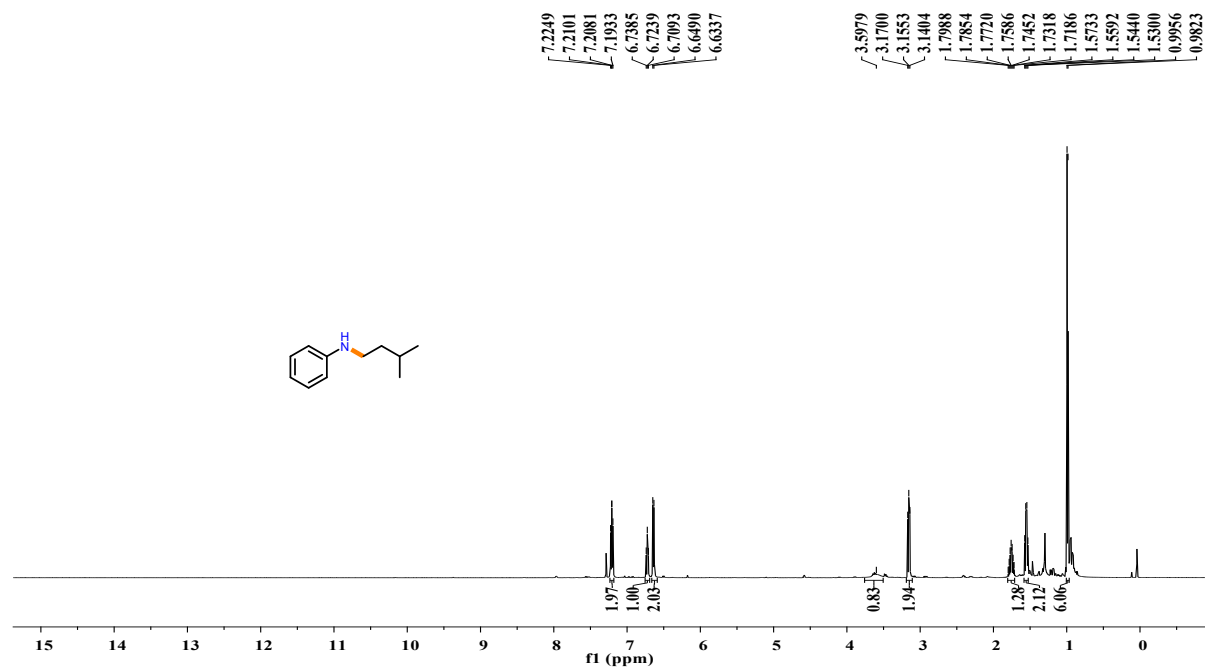**Figure S36**. ^{13}C NMR spectrum of **3m** in CDCl$_3$ (500 MHz).

Figure S37. ^{1}H NMR spectrum of **3n** in CDCl$_3$ (500 MHz).
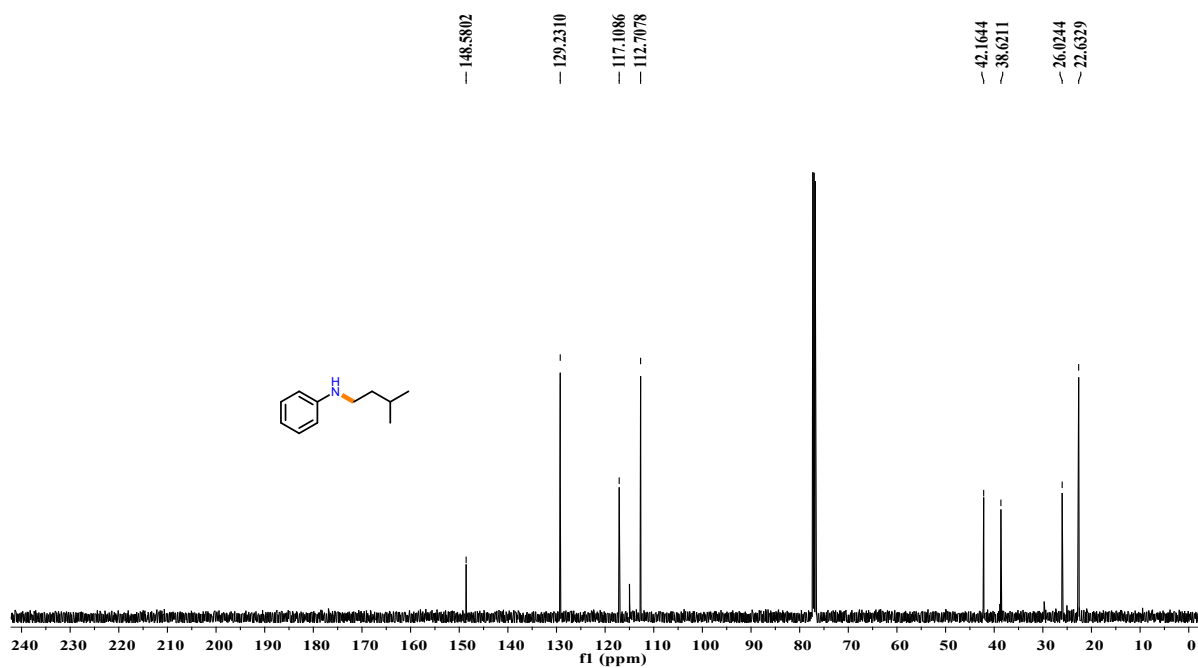
Figure S38. ^{13}C NMR spectrum of **3n** in CDCl$_3$ (500 MHz).
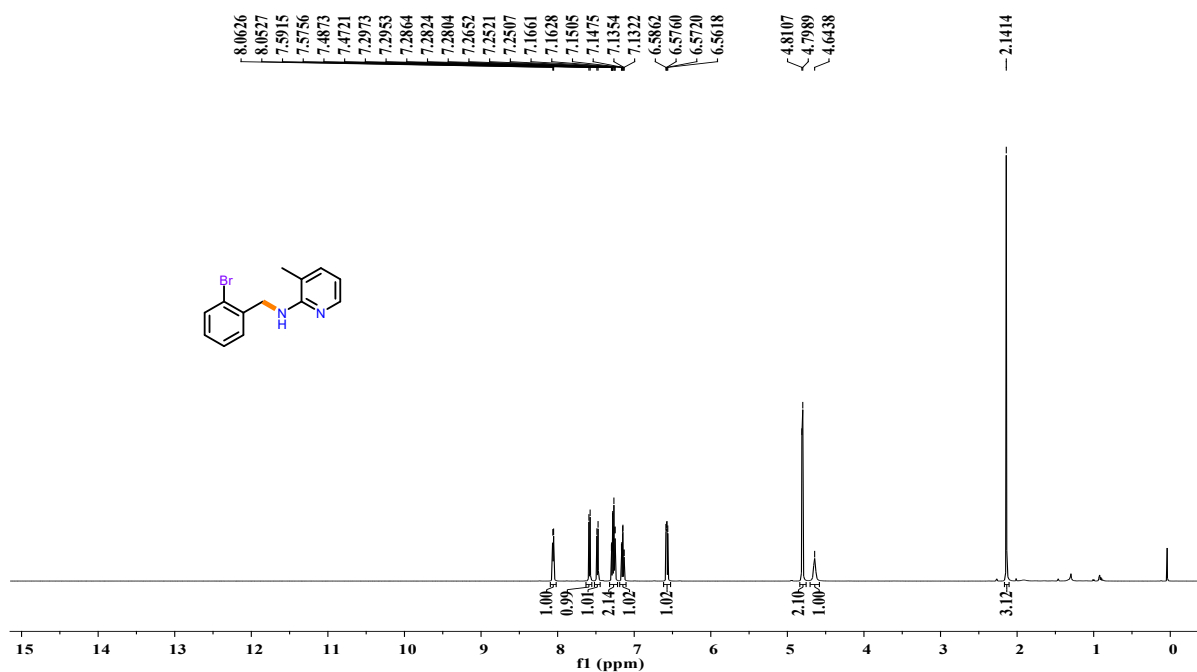
Figure S39. ^1H NMR spectrum of **3o** in CDCl$_3$ (500 MHz).
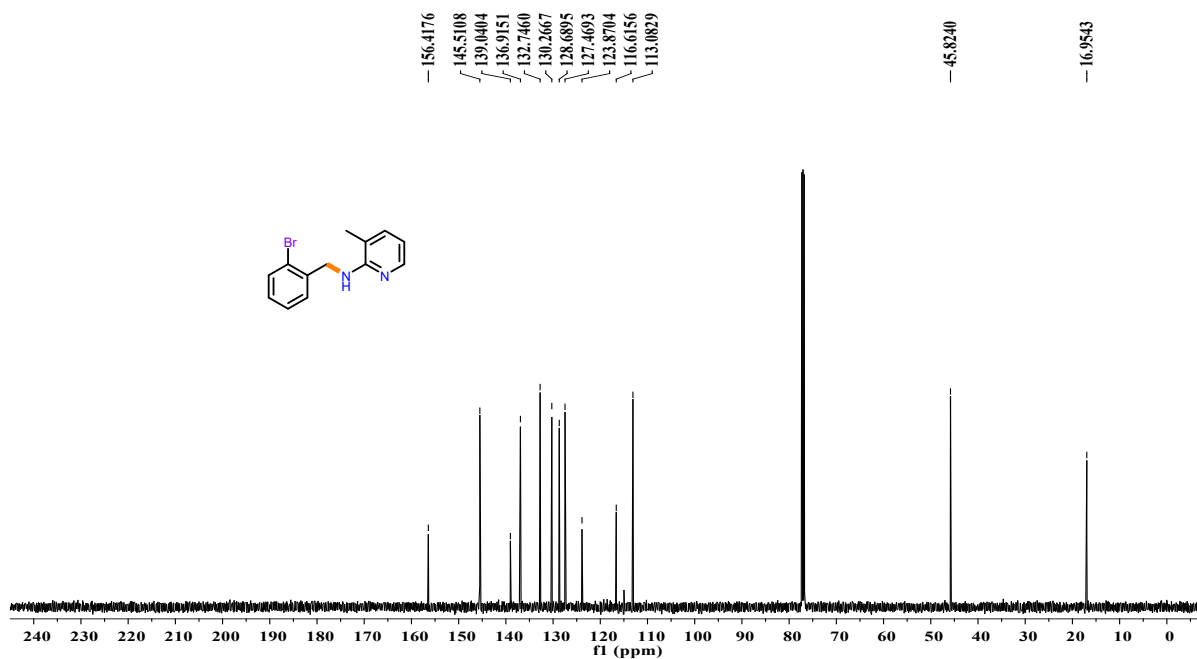
Figure S40. ^{13}C NMR spectrum of **3o** in CDCl$_3$ (500 MHz).
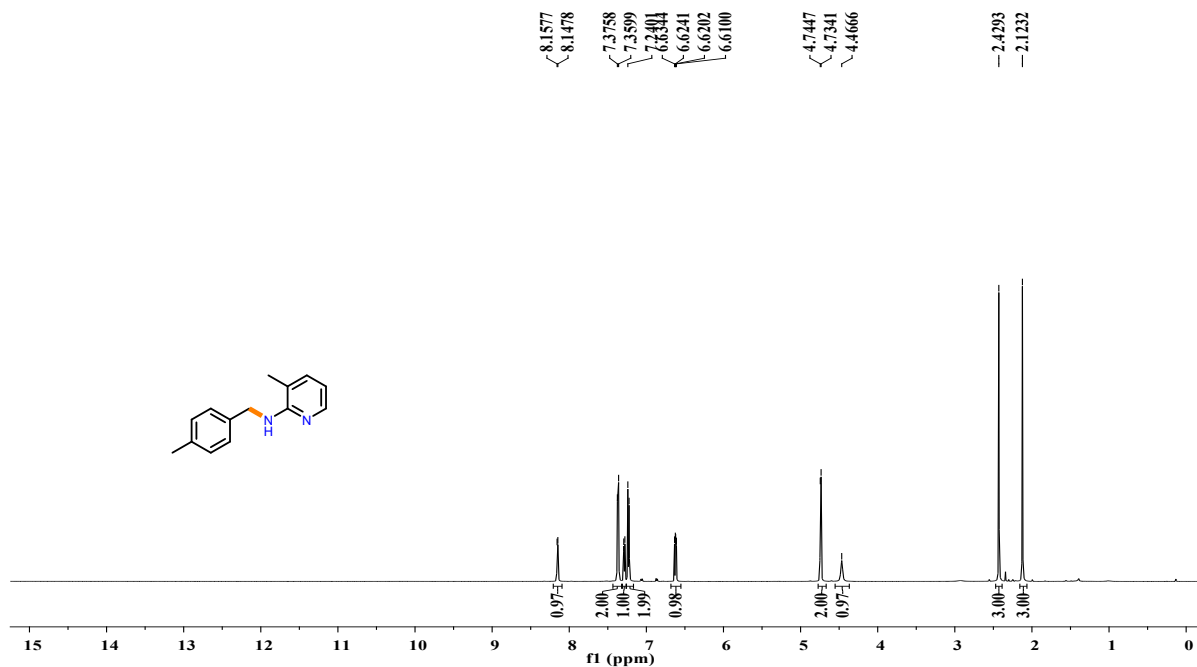
Figure S41. ^{1}H NMR spectrum of **3p** in CDCl$_3$ (500 MHz).

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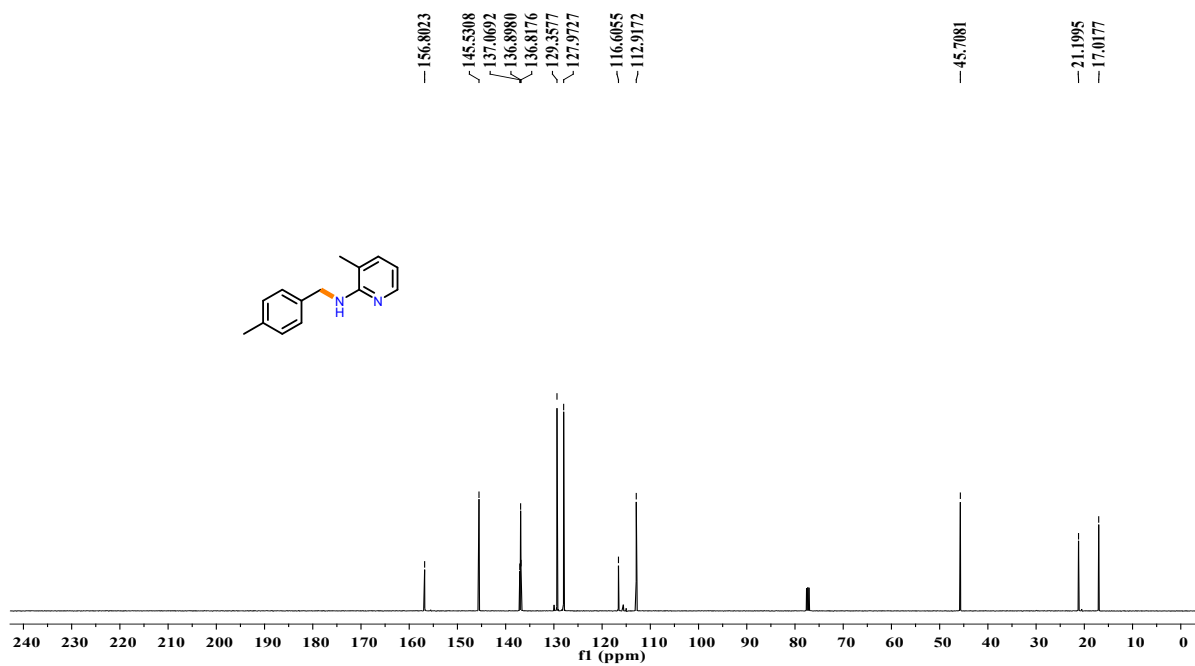
Figure S42. ^{13}C NMR spectrum of **3p** in CDCl$_3$ (500 MHz).

Figure S43. ^1H NMR spectrum of **3q** in CDCl$_3$ (500 MHz).

Figure S44. ^{13}C NMR spectrum of **3q** in CDCl$_3$ (500 MHz).

Figure S45. ^{1}H NMR spectrum of **3r** in CDCl$_3$ (500 MHz).

Figure S46. ^{13}C NMR spectrum of **3r** in CDCl$_3$ (500 MHz).

Figure S47. ^1H NMR spectrum of **3s** in CDCl$_3$ (500 MHz).

Figure S48. ^{13}C NMR spectrum of **3s** in CDCl$_3$ (500 MHz).

Figure S49. ^1H NMR spectrum of **3t** in CDCl$_3$ (500 MHz).

Figure S50. ^{13}C NMR spectrum of **3t** in CDCl$_3$ (500 MHz).

Figure S51. ^1H NMR spectrum of **3u** in CDCl$_3$ (500 MHz).

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Figure S52. ^{13}C NMR spectrum of **3u** in CDCl$_3$ (500 MHz).

Figure S53. ^{1}H NMR spectrum of **3v** in CDCl$_3$ (500 MHz).

Figure S54. ^{13}C NMR spectrum of **3v** in CDCl$_3$ (500 MHz).
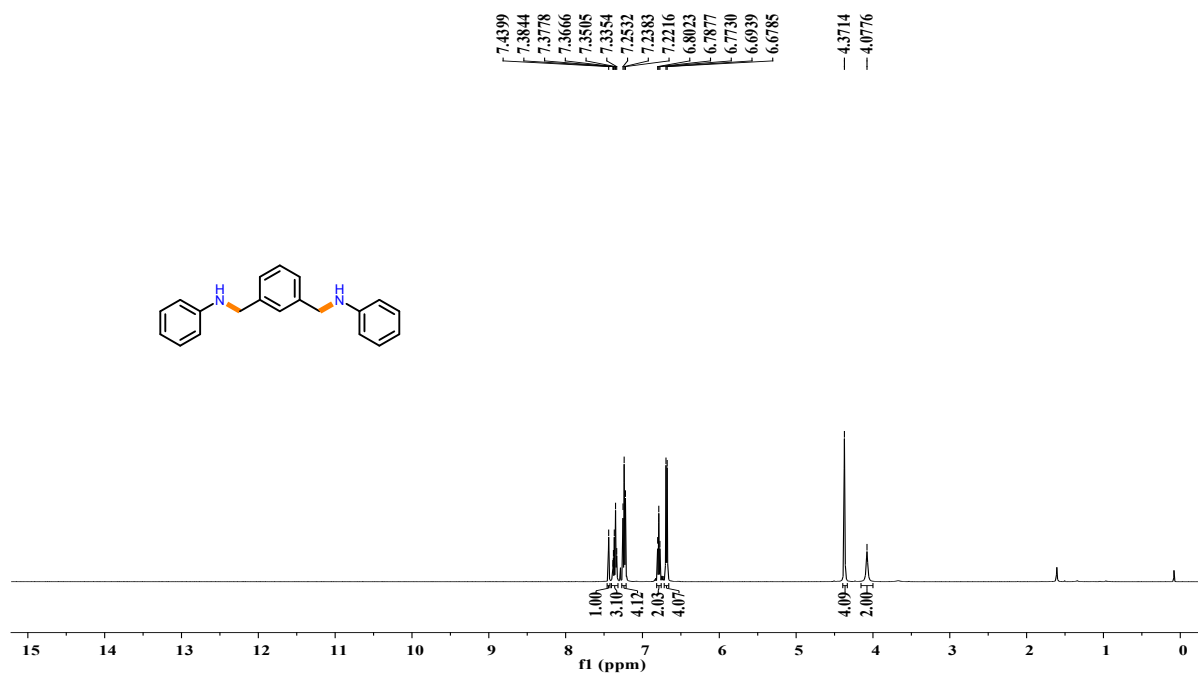
Figure S55. ^{1}H NMR spectrum of **3w** in CDCl$_3$ (500 MHz).

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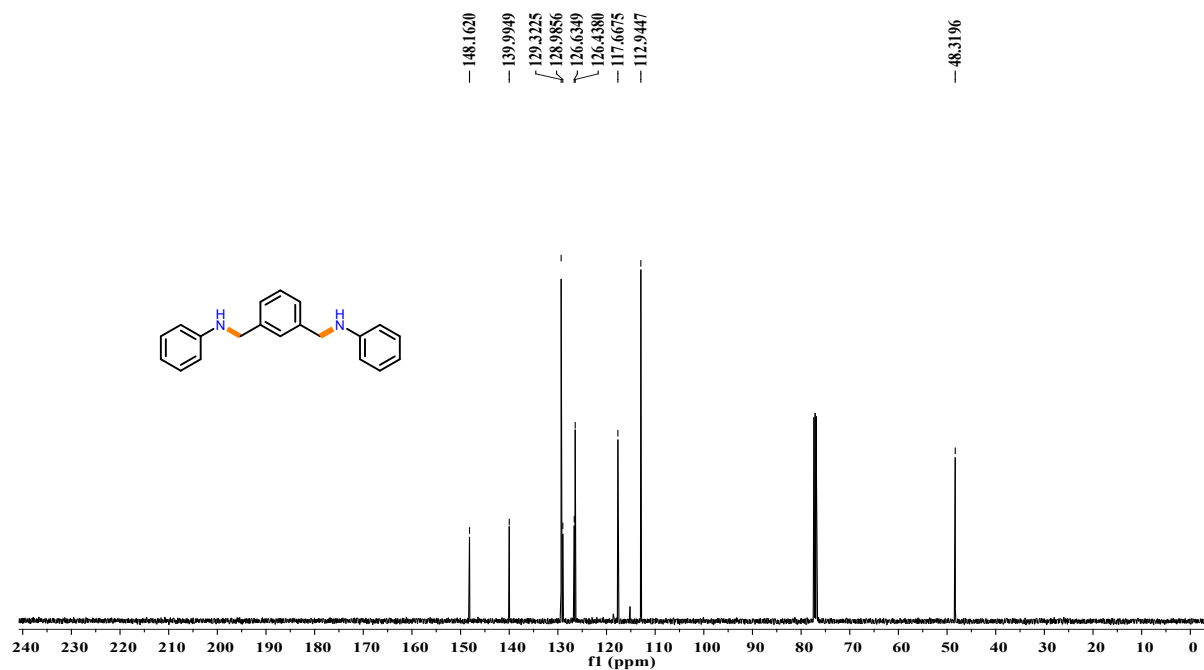
Figure S56. ^{13}C NMR spectrum of **3w** in CDCl$_3$ (500 MHz).
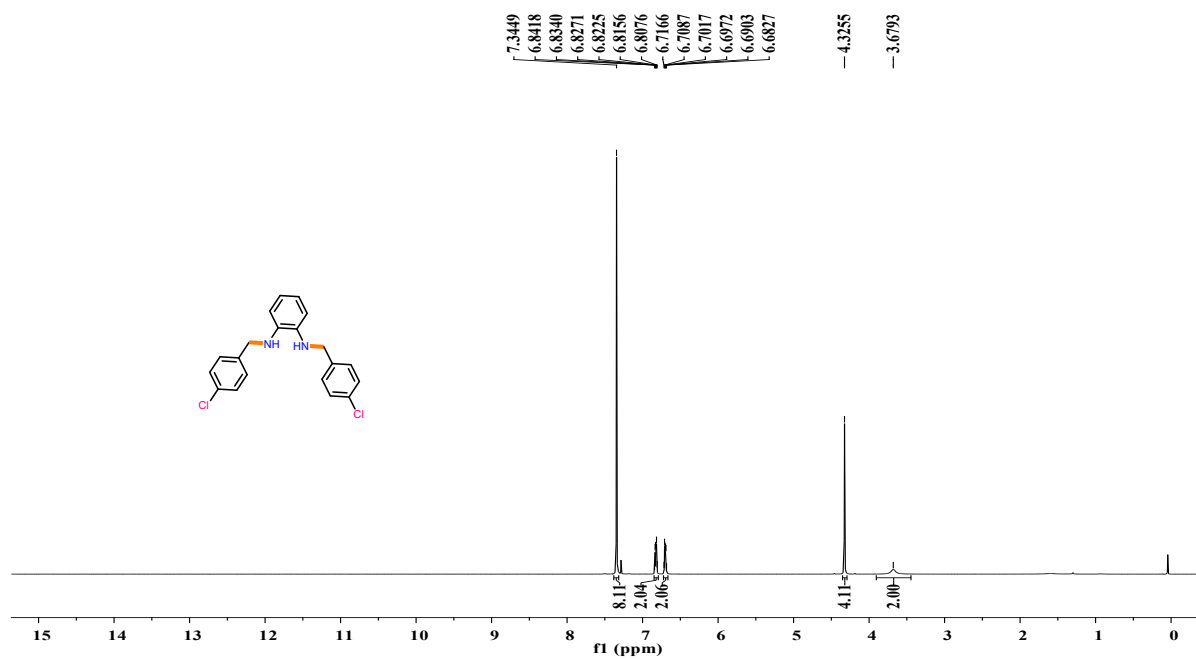
Figure S57. ^{1}H NMR spectrum of **3x** in CDCl$_3$ (500 MHz).
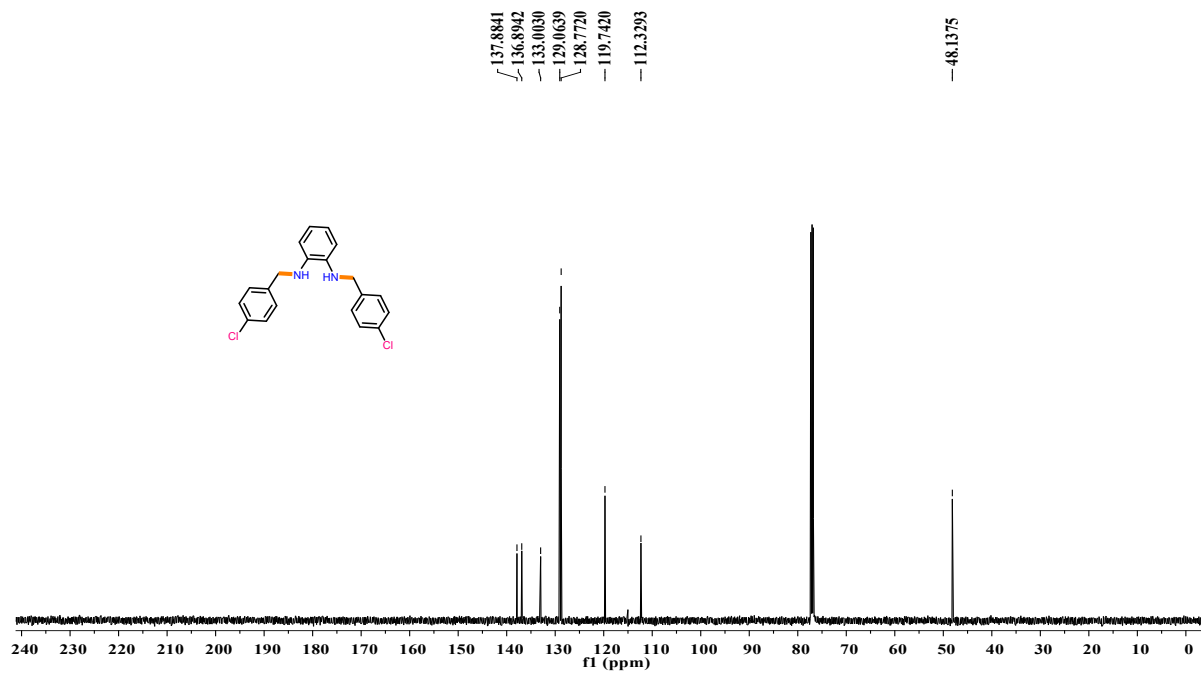
Figure S58. ^{13}C NMR spectrum of **3x** in CDCl$_3$ (500 MHz).
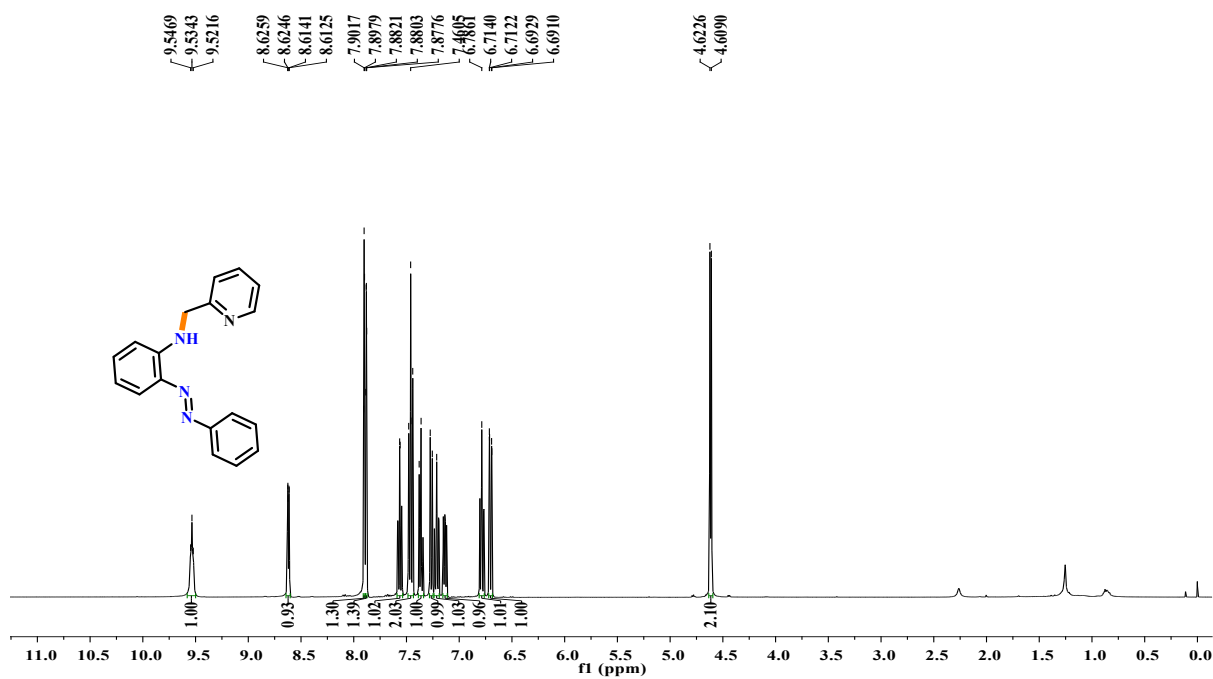
Figure S59. ^1H NMR spectrum of **3y** in CDCl$_3$ (500 MHz).
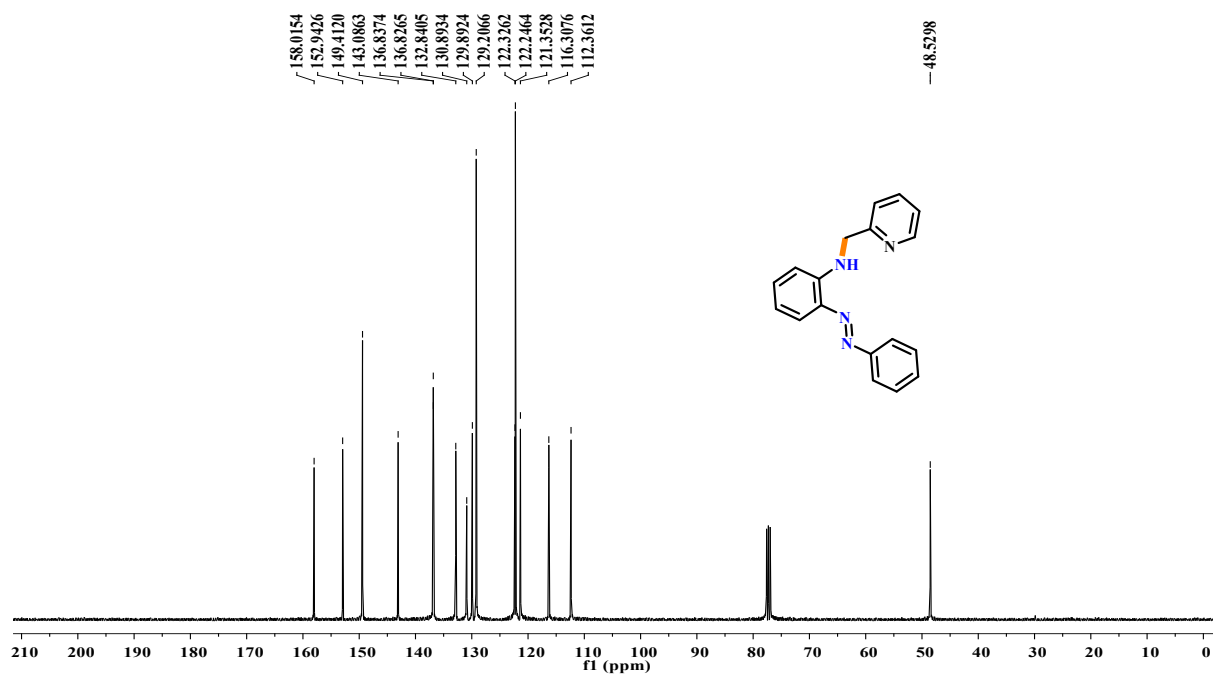
Figure S60. ^{13}C NMR spectrum of **3y** in CDCl$_3$ (500 MHz).
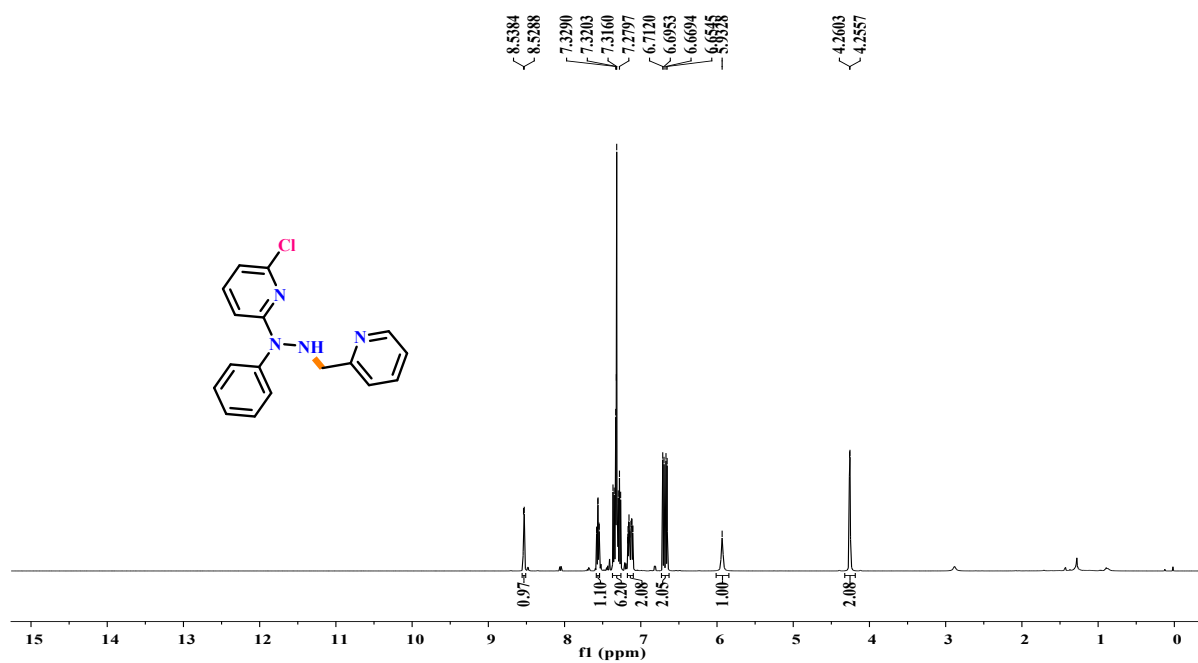
Figure S61. ^{1}H NMR spectrum of **3z** in CDCl$_3$ (500 MHz).

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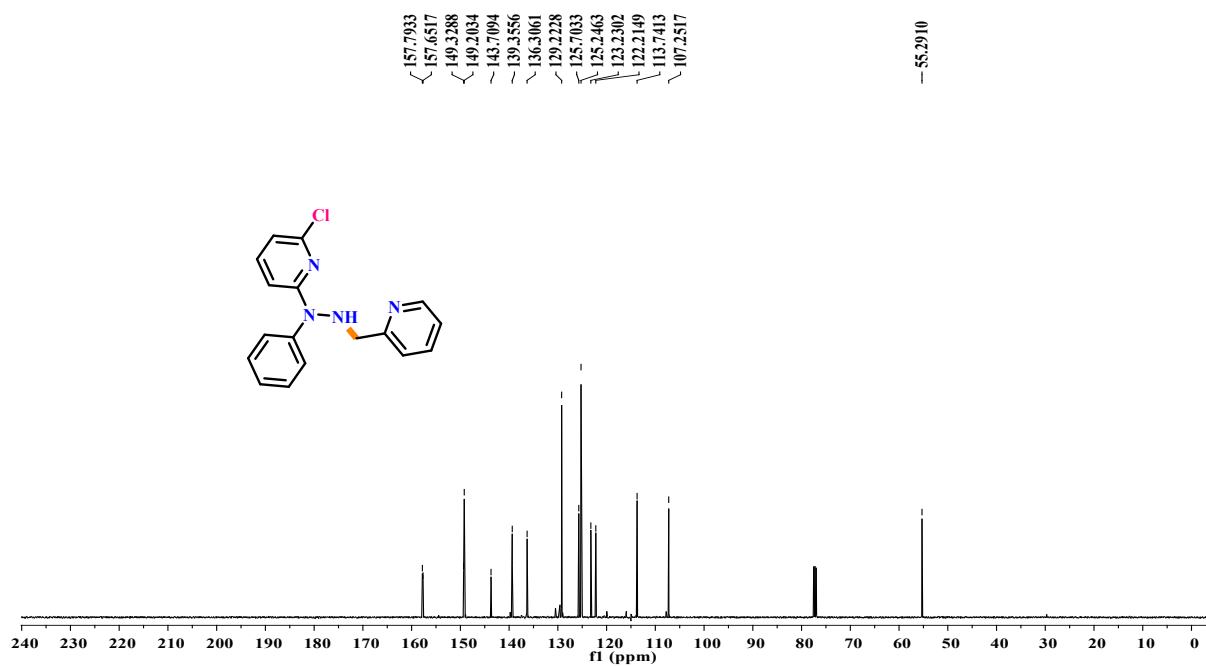
Figure S62. ^{13}C NMR spectrum of **3z** in CDCl$_3$ (500 MHz).
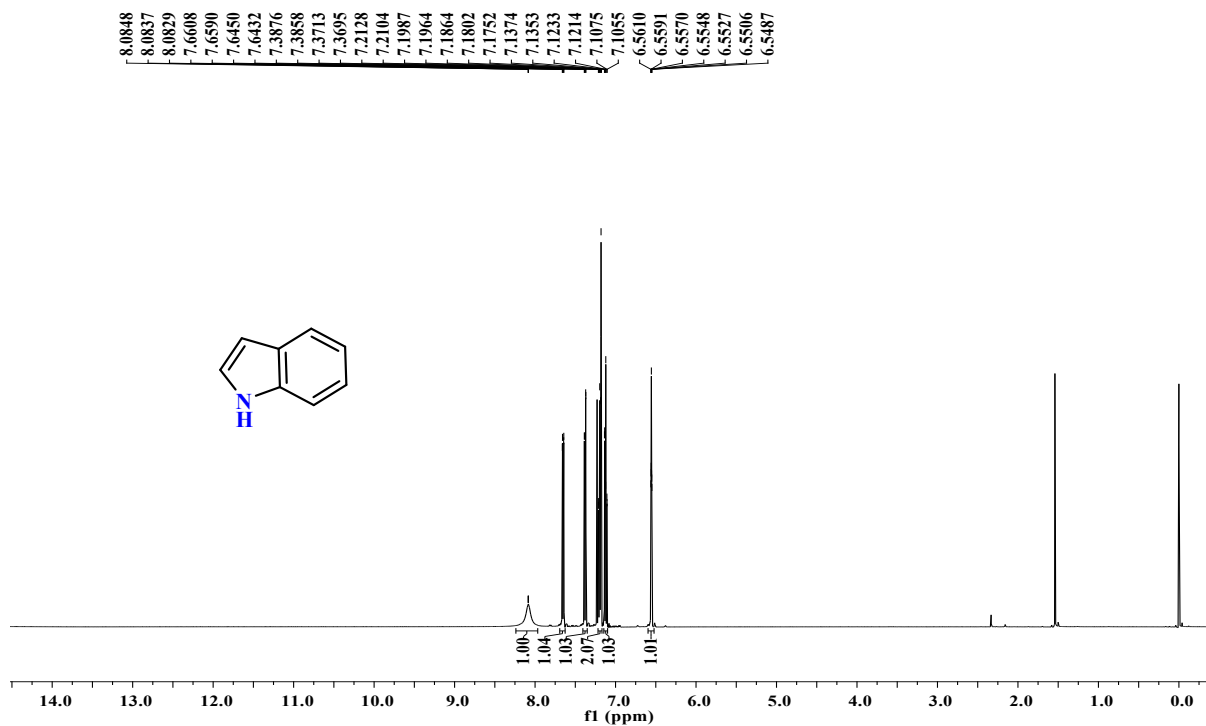

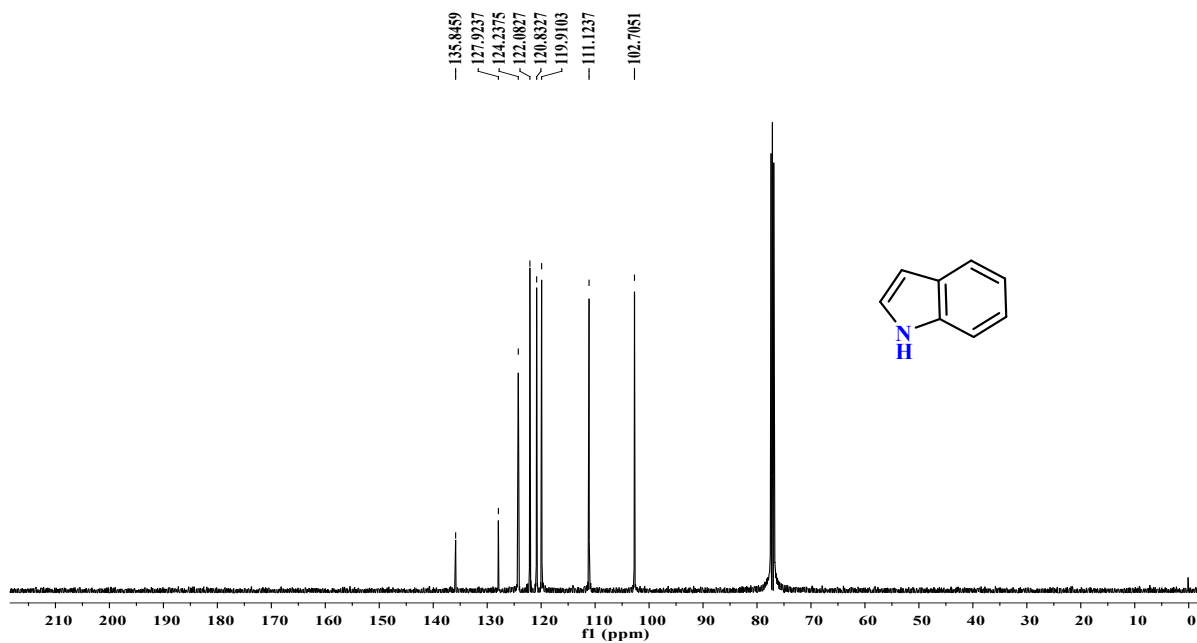**Figure S63**. ^{1}H NMR spectrum of **4a** in CDCl$_3$ (500 MHz).

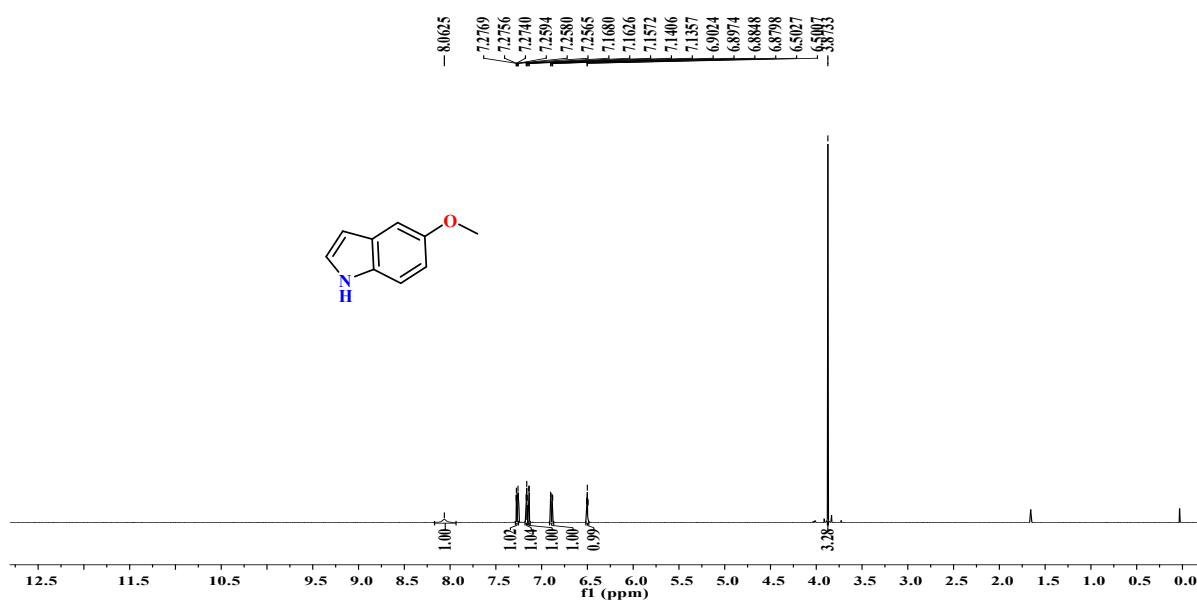**Figure S64**. ^{13}C NMR spectrum of **4a** in CDCl$_3$ (500 MHz).

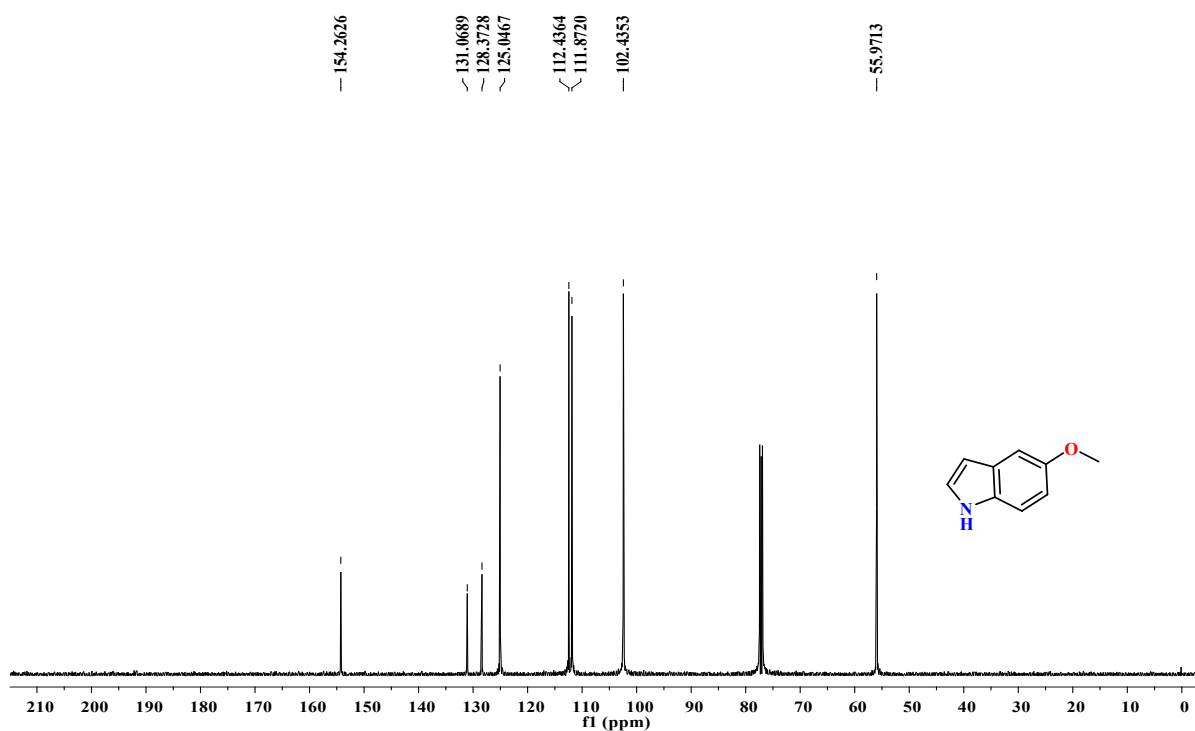**Figure S65**. ^{1}H NMR spectrum of **4b** in CDCl$_3$ (500 MHz).

Figure S66. ^{13}C NMR spectrum of **4b** in CDCl$_3$ (500 MHz).
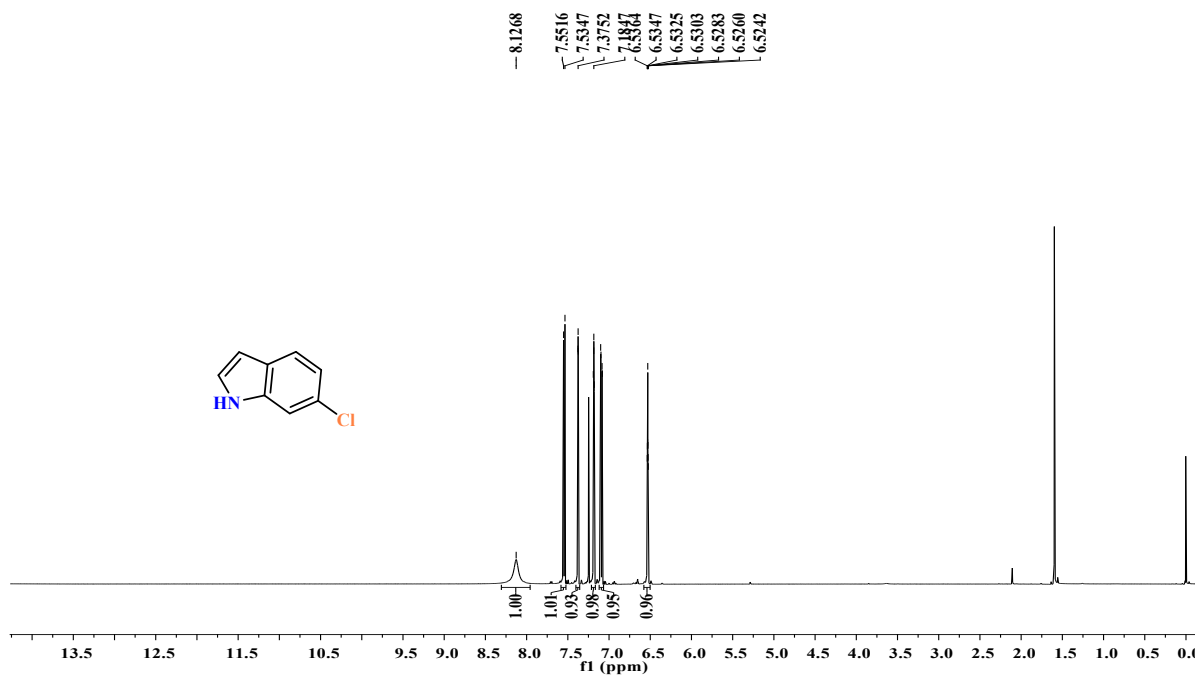

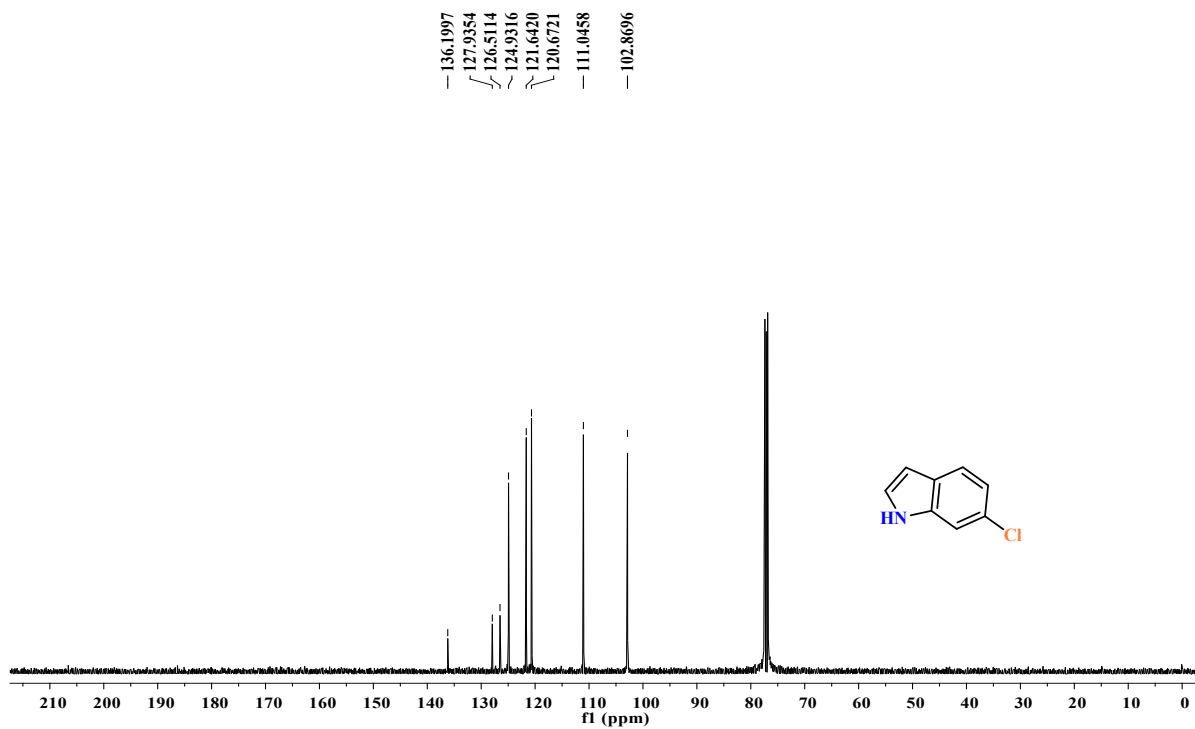**Figure S67**. ^{1}H NMR spectrum of **4c** in CDCl$_3$ (500 MHz).

Figure S68. ^{13}C NMR spectrum of **4c** in CDCl$_3$ (500 MHz).
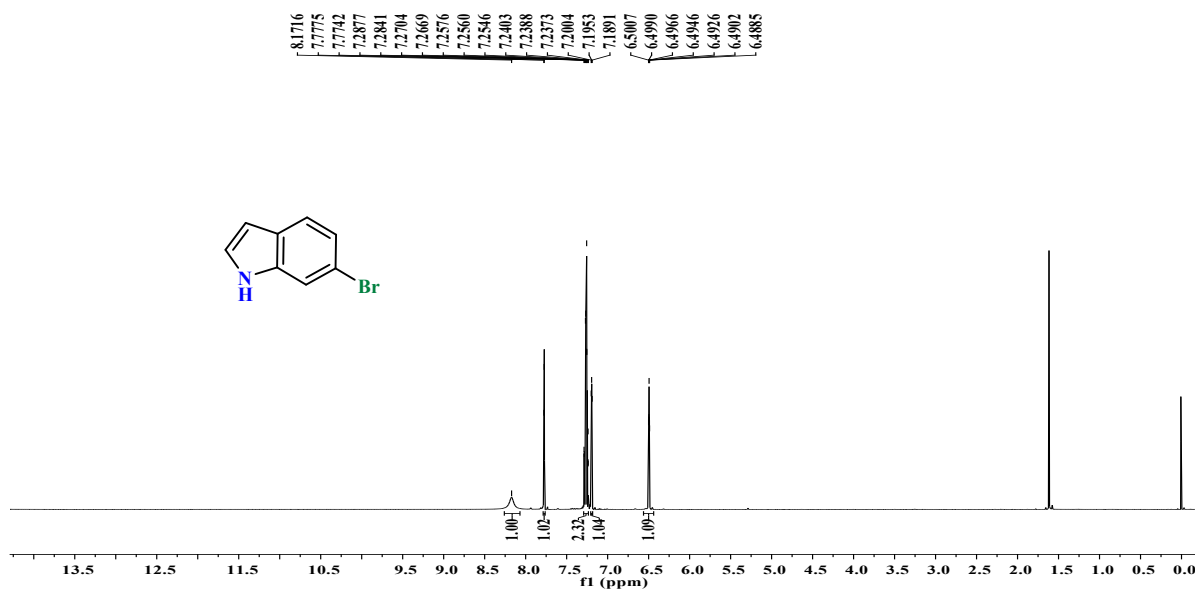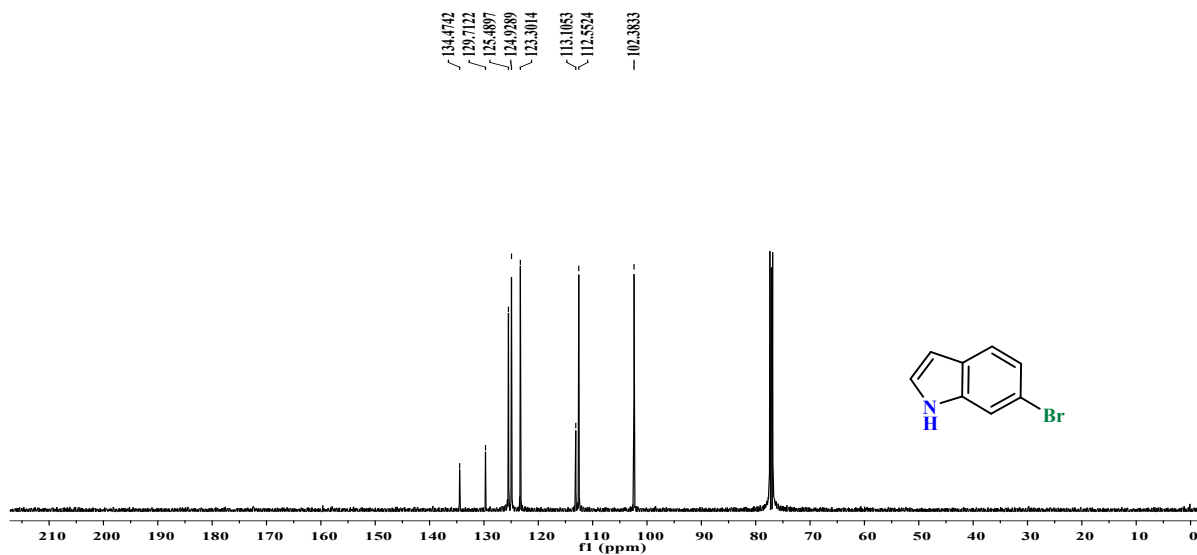

Figure S69. ^{1}H NMR spectrum of **4d** in CDCl$_3$ (500 MHz).

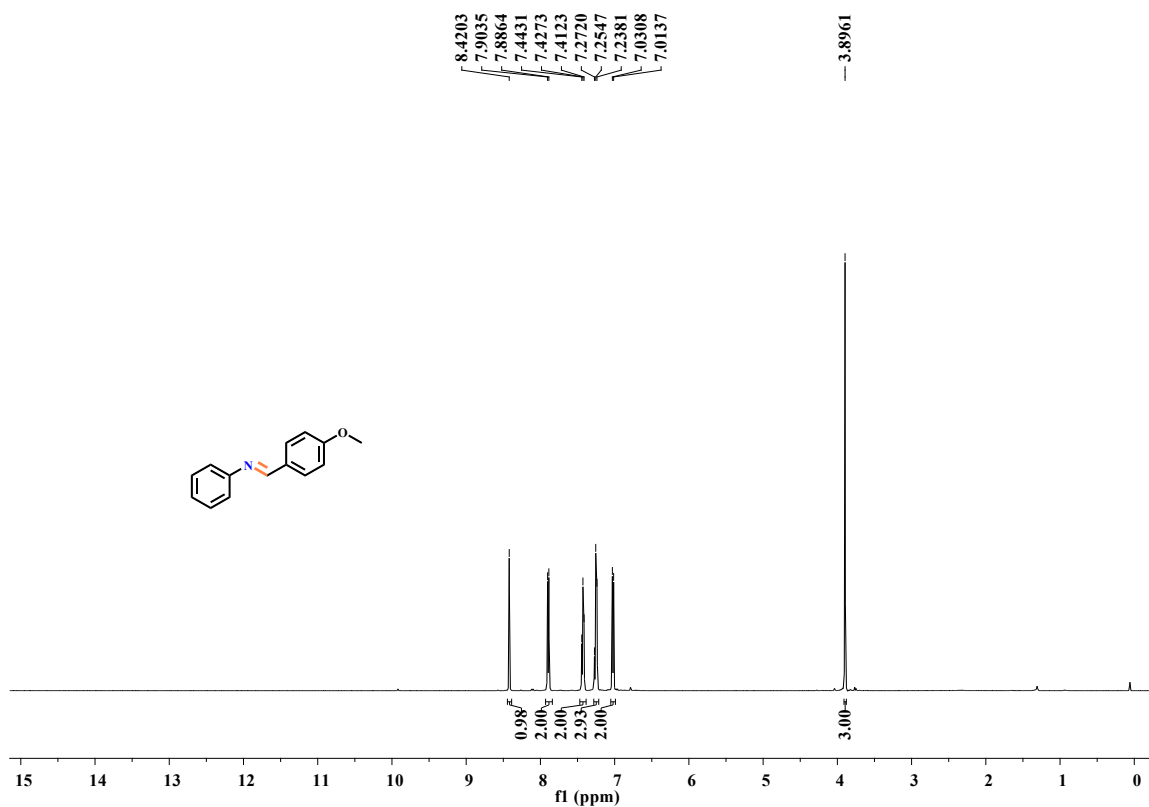**Figure S70**. ^{13}C NMR spectrum of **4d** in CDCl$_3$ (500 MHz).

Figure S71. ^1H NMR spectrum of **2a"** in CDCl$_3$ (500 MHz).

Notes and references

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