Supporting Information

Chemoselective Reduction of Imines and Azobenzenes Catalyzed by Silver *N*-heterocyclic Carbene Complexes

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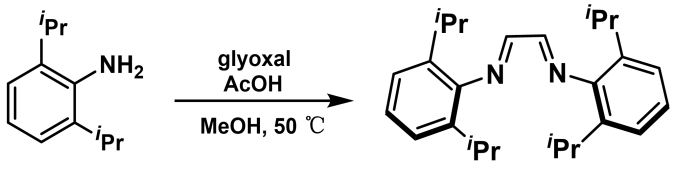
1. Materials and methods

General. All reactions dealing with air or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. ^{1}NMR spectra were measured on a JNM-ECZ400S (JEOL, Japan) spectrometer. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ or DMSO-d_6 were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Titan, Adamas-beta., and other commercial suppliers and used as received. Solvents were dried over sodium (for THF) by refluxing for overnight and freshly distilled prior to use.

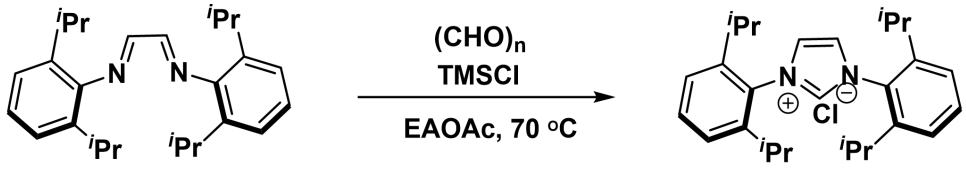
2. General procedure for the synthesis of Ag complexes

2.1 Preparation of IPrAgCl

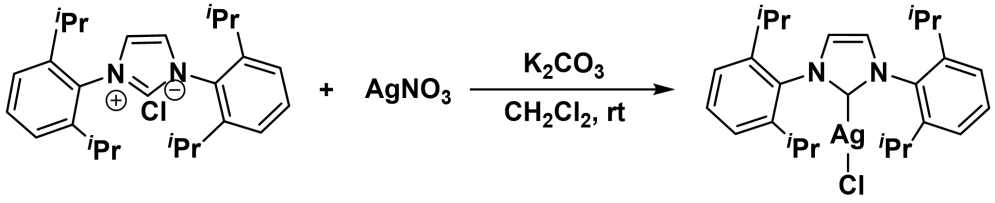


In air, to a solution of 2,6-diisopropylaniline (177 g, 1.00 mol, 2.0 equiv) and AcOH (1.00 mL, 17.5 mmol, 0.035 equiv) in MeOH (250 mL) was added a solution of glyoxal (40% in water) (29g, 0.50 mol, 1.0 equiv) in MeOH (250 mL). The mixture was stirred at 50 ºC for 15 min, then stirred at 23 ºC for 10 hours. The reaction mixture was filtered, then the filter cake was washed with MeOH (3 × 200 mL) and

dried in vacuo to afford 162 g of the title compound as a yellow solid (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.03 (s, 2H), 7.14 – 7.08 (m, 6H), 3.15 – 2.64 (m, 4H), 1.14 (d, J = 7.0 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =163.3, 148.1, 136.8, 125.9, 123.3, 28.2, 23.5. The spectroscopic data are in accordance with those described in the literature. [1]



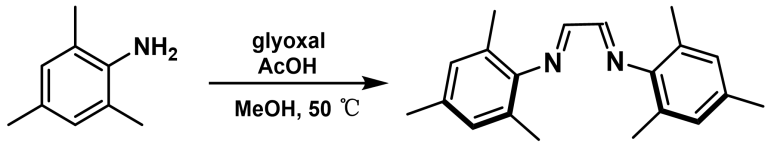
In air, to a solution of N^1,N^2-1,4-Bis(2,6-diisopropylphenyl)ethane-1,2-diimine (84.8 g, 225 mmol, 1.00 equiv) and paraformaldehyde (6.96 g, 232 mmol, 1.03 equiv) in EtOAc (2.0 L) was added a solution of TMSCl (29.4 mL, 232 mmol, 1.03 equiv) in EtOAc (30 mL) at 70 ºC dropwise over 45 min. The mixture was stirred at 70 ºC for 2 hours, then cooled to 10 ºC. The reaction mixture was filtered, then the filter cake was washed with EtOAc (3 × 150 mL) and dried in vacuo to afford 72.5 g of the title compound as a colorless solid (70% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ =10.24 (s, 1H), 8.59 (s, 2H), 7.69 (t, 2H), 7.53 (d, J = 7.8 Hz, 4H), 2.40 – 2.29 (m, 4H), 1.26 (d, J = 6.9 Hz, 12H), 1.16 (d, J = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =145.1, 139.4, 131.9, 130.1, 126.3, 124.7, 28.7, 24.2, 23.2. The spectroscopic data are in accordance with those described in the literature.[1]



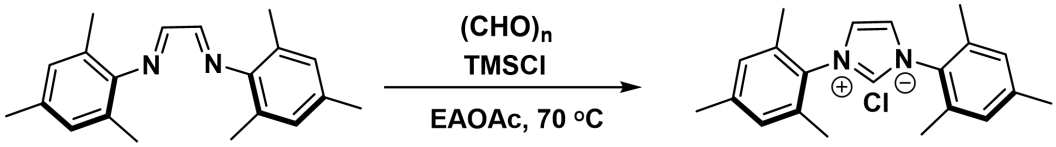
A mixture of IPr•HCl (0.3 mmol) and $AgNO_3$ (0.3 mmol) in dichloromethane (15 mL) was stirred for 2 min and then K_2CO_3 (5 mmol) was added. After 3 h, the mixture was filtered through Celite and the solvent was removed in vacuo until 2 mL (c.a.). The product was precipitated with ether (10 mL) and washed (3×5 mL) to give IPrAgCl (85%) as a white solids. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.49 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz ,4H), 7.21 (s, 2H), 2.53 (sept, J = 6.9 Hz, 4H), 1.27 (d, J = 6.8 Hz, 12H),

1.21 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.6, 134.6, 130.9, 124.5, 123.8, 28.8, 24.9, 24.1. The spectroscopic data are in accordance with those described in the literature.[2]

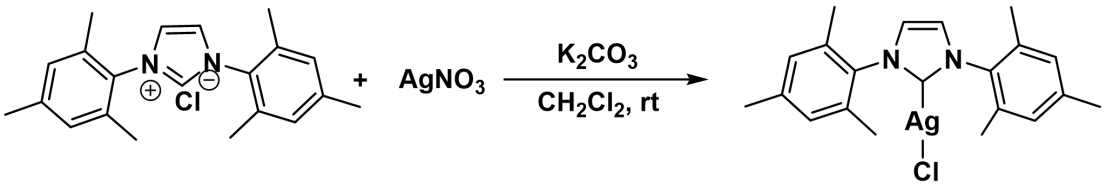
2.2 Preparation of IMesAgCl



In air, to a solution of 2,4,6-Trimethylanyline (135 g, 1.00 mol, 2.0 equiv) and AcOH (1.00 mL, 17.5 mmol, 0.035 equiv) in MeOH (250 mL) was added a solution of glyoxal (40% in water) (28g, 0.50 mol, 1.0 equiv) in MeOH (250 mL). The mixture was stirred at 50 ºC for 15 min, then stirred at 23 ºC for 10 hours. The reaction mixture was filtered, then the filter cake was washed with MeOH (3 × 200 mL) and dried in vacuo to afford 162 g of the title compound as a yellow solid (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.03 (s, 2H), 6.84 (s, 4H), 2.22 (s, 6H), 2.08 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=162.5, 146.4, 133.6, 128.0, 125.5, 19.8, 17.2. The spectroscopic data are in accordance with those described in the literature.[3]



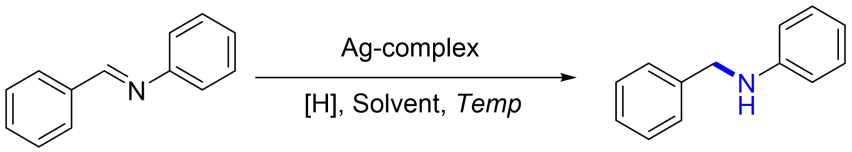
In air, to a solution of N^1,N^2-dimesitylethane-1,2-diimine (65.8 g, 225 mmol, 1.00 equiv) and paraformaldehyde (6.96 g, 232 mmol, 1.03 equiv) in EtOAc (2.0 L) was added a solution of TMSCl (29.4 mL, 232 mmol, 1.03 equiv) in EtOAc (30 mL) at 70 ºC dropwise over 45 min. The mixture was stirred at 70 ºC for 2 hours, then cooled to 10 ºC. The reaction mixture was filtered, then the filter cake was washed with EtOAc (3 × 150 mL) and dried in vacuo to afford 72.5 g of the title compound as a colorless solid (70% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ =10.45 (s, 1H), 7.61 (s, 2H), 6.95 (s, 4H), 2.27 (s, 6H), 2.09 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =140.3, 138.1, 133.1, 129.6, 128.9, 123.7, 20.2, 16.6. The spectroscopic data are in accordance with those described in the literature.[4]



A mixture of IMes•HCl (0.3 mmol) and $AgNO_3$ (0.3 mmol) in dichloromethane (15 mL) was stirred for 2 min and then K_2CO_3 (5 mmol) was added. After 3 h, the mixture was filtered through Celite and the solvent was removed in vacuo until 2 mL (c.a.). The product was precipitated with ether (10 mL) and washed (3×5 mL) to give IMesAgCl as a white solids (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.13 (s, 2H), 6.99 (s, 4H), 2.35 (s, 6H), 2.07 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =138.7, 133.6, 128.6, 121.7, 121.7, 20.1, 16.7. The spectroscopic data are in accordance with those described in the literature. [2]

3. Optimizing reaction parameters

Table S1. Investigation of the effect of solvent on hydrogenation of *N*-benzylideneaniline.[a]



1a **2a**

Entry	Catalyst	[Si-H]	Solvent	Temp./°C	Time/h	Yield/%
1	IPrAgCl	$PhSiH_3$	MeOH	rt	24	91
2	IPrAgCl	$PhSiH_3$	EtOH	rt	24	65
3	IPrAgCl	$PhSiH_3$	CH_2Cl_2	rt	24	10
4	IPrAgCl	$PhSiH_3$	EtOAc	rt	24	nd[b]
5	IPrAgCl	$PhSiH_3$	THF	rt	24	nd[b]
6	IPrAgCl	$PhSiH_3$	CF_3CH_2OH	rt	24	nd[b]
7	IPrAgCl	$PhSiH_3$	*t*-Amyl-OH	rt	24	nd[b]
8	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	24	97

[a]Reaction conditions: **1a** (0.2 mmol), IPrAgCl (0.02 mmol), $PhSiH_3$ (4 equiv), solvent (2.5 mL), at room temperature for 24 h. Isolated yield.[b]Not detected.

Table S2. Investigation of the effect of silanes on hydrogenation of *N*-benzylideneaniline.[a]

Entry	Catalyst	Reductant	Solvent	Temp./°C	Time/h	Yield/%
1	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	24	97
2	IPrAgCl	HBpin	^{i}PrOH	rt	24	41
3	IPrAgCl	Ph_2SiH_2	^{i}PrOH	rt	24	20
4	IPrAgCl	Et_3SiH	^{i}PrOH	rt	24	48
5	IPrAgCl	$(EtO)_3SiH$	^{i}PrOH	rt	24	53
6	IPrAgCl	PMHS	^{i}PrOH	rt	24	24

[a]Reaction conditions: **1a** (0.2 mmol), IPrAgCl (0.02 mmol), reductant (4 equiv), solvent (2.5 mL), at room temperature for 24 h. Isolated yield.

Table S3. Investigation of the effect of time on hydrogenation of *N*-benzylideneaniline.[a]

Entry	Catalyst	[Si-H]	Solvent	Temp./°C	Time/h	Yield/%
1	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	2	72
2	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	3	90
3	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	4	97
4	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	12	97
5	IPrAgCl	$PhSiH_3$	^{i}PrOH	rt	24	97

[a]Reaction conditions: **1a** (0.2 mmol), IPrAgCl (0.02 mmol), $PhSiH_3$ (4 equiv), solvent (2.5 mL), at room temperature. Isolated yield.

Table S4. Investigation of the effect of the amount of Ag-complex on hydrogenation of *N*-benzylideneaniline.[a]

Entry	Catalyst (X mol%)	[Si-H]	Solvent	Temp./°C	Time/h	Yield/%
1	IPrAgCl (1)	$PhSiH_3$	^{i}PrOH	rt	4	96
2	IPrAgCl (2)	$PhSiH_3$	^{i}PrOH	rt	4	96
3	IPrAgCl (5)	$PhSiH_3$	^{i}PrOH	rt	4	97
4	IPrAgCl (10)	$PhSiH_3$	^{i}PrOH	rt	4	97

[a]Reaction conditions: **1a** (0.2 mmol), IPrAgCl, $PhSiH_3$ (4 equiv), solvent (2.5 mL), at room temperature. Isolated yield.

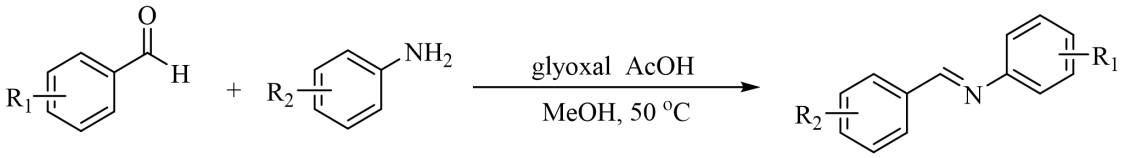
Table S5. Investigation of the effect of the amount of $PhSiH_3$ on hydrogenation of *N*-benzylideneaniline.[a]

Entry	Cataylst	$PhSiH_3$(equiv.)	Solvent	Temp. /℃	Time /h	Yield(%)
1	IPrAgCl	1.0	^{i}PrOH	25	4	50
2	IPrAgCl	2.0	^{i}PrOH	25	4	89
3	IPrAgCl	2.2	^{i}PrOH	25	4	96
4	IPrAgCl	3.0	^{i}PrOH	25	4	96
5	IPrAgCl	4.0	^{i}PrOH	25	4	97

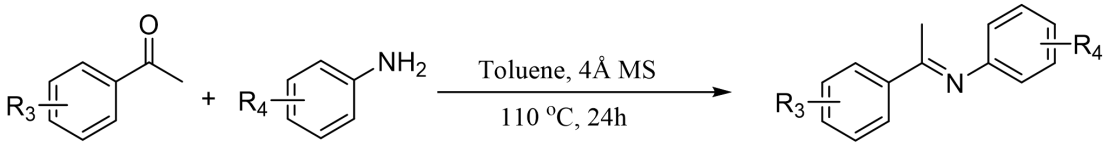
[a]Reaction conditions: **1a** (0.2 mmol), IPrAgCl (0.002 mmol), $PhSiH_3$ (4 equiv), solvent (2.5 mL), at room temperature. Isolated yield.

4. The preparation of substrates

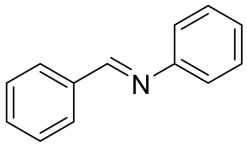
4.1 Preparation of imine compounds



In air, to a solution of aniline (9.3 g, 0.1 mol, 1.0 equiv) and AcOH (0.1 mL, 1.75 mmol, 0.035 equiv) in MeOH (25 mL) was added a solution of benzaldehyde (10.6 g, 0.1 mol, 1.0 equiv) in MeOH (25 mL). The mixture was stirred at 50 ºC for 15 min, then stirred at 23 ºC for 10 hours. The reaction mixture was filtered, then the filter cake was washed with MeOH (3 × 20 mL) and dried in vacuo to afford 16.6 g of the title compound as a Pale yellow solid.

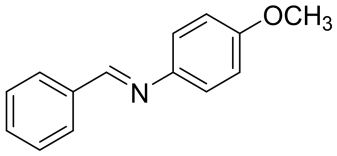


To an argon purged round bottom flask were added the carbonyl compound (50 mmol, 1.0 eq), *p*-anisidine (60 mmol, 1.2 eq) and toluene (30 mL) followed by 4Å MS (20g). The reaction was stirred at rt until TLC analysis showed complete conversion of starting material. The reaction mixture was filtered (EtOAc) to remove the molecular sieves then concentrated under reduced pressure. The crude material was purified by recrystallization or by flash column chromatography.[5]



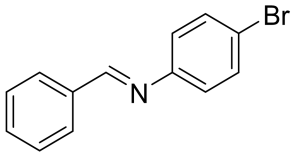
(*E*)-*N*,1-diphenylmethanimine (1a)

Pale yellow soild. Yiled: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.46 (s, 1H), 7.91 (dd, J = 6.7, 2.9 Hz, 2H), 7.48 (dd, J = 5.0, 1.9 Hz, 3H), 7.40 (t, J = 7.7 Hz, 2H), 7.25 – 7.19 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =160.6, 152.2, 136.3, 131.5, 129.3, 128.9, 128.9, 126.1, 121.0. The spectroscopic data are in accordance with those described in the literature.[6]



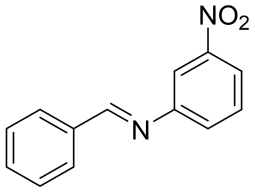
(*E*)-*N*-(4-methoxyphenyl)-1-phenylmethanimine (1b)

White soild. Yiled: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.41 (s, 1H), 7.84 – 7.79 (m, 2H), 7.41 – 7.36 (m, 3H), 7.18 – 7.15 (m, 2H), 6.89 – 6.84 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =157.4, 157.2, 143.9, 135.4, 130.0, 127.7, 127.6, 121.2, 113.3, 54.5. The spectroscopic data are in accordance with those described in the literature. [7]



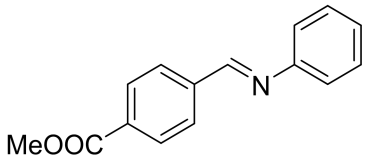
(*E*)-*N*-(4-bromophenyl)-1-phenylmethanimine (1c)

White soild. Yiled: 80 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 7.89 (d, J= 4.1 Hz, 2H), 7.50 (t, J = 8.0 Hz, 5H), 7.15 – 7.04 (d, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =159.8, 150.0 134.9, 131.2, 130.6, 127.9, 127.8, 121.6, 118.3. The spectroscopic data are in accordance with those described in the literature. [7]



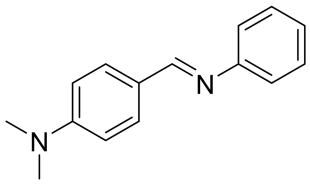
(*E*)-*N*-(3-nitrophenyl)-1-phenylmethanimine (1d)

Pale yellow soild. Yiled: 79 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.50 (s, 1H), 8.10 (dt, J = 7.5, 2.0 Hz, 1H), 8.05 (t, J = 2.0 Hz, 1H), 7.93 (dd, J = 7.9, 1.7 Hz, 2H), 7.58 – 7.51 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =161.6, 151.3, 147.9, 134.4, 131.2, 129.5, 128.2, 127.9, 125.8, 119.5, 114.4. The spectroscopic data are in accordance with those described in the literature. [8]



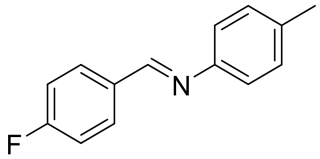
methyl (*E*)-4-((phenylimino)methyl)benzoate (1e)

White soild. Yiled: 79%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.44 (s, 1H), 8.07 (d, J = 6.7 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 7.34 (m, 2H), 7.19 (m, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =166.6, 159.2, 151.5, 140.0, 133.2, 130.0, 129.3, 128.7, 126.5, 120.9, 52.4. The spectroscopic data are in accordance with those described in the literature. [9]



(*E*)-*N,N*-dimethyl-4-((phenylimino)methyl)aniline (1f)

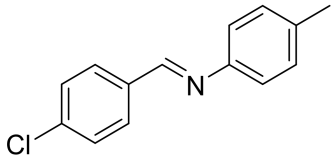
Pale yellow soild. Yiled: 40%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.35 (s, 1H), 7.70 (d, J = 9.5 Hz, 2H), 7.28 (d, J = 7.1 Hz, 2H), 7.11 (d, J = 7.2 Hz, 3H), 6.66 (d, J = 7.0 Hz, 2H), 2.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =160.5, 153.1, 152.6, 130.6, 129.2, 125.1, 124.5, 121.1, 111.7, 40.3. The spectroscopic data are in accordance with those described in the literature. [10]



(*E*)-1-(4-fluorophenyl)-*N*-(p-tolyl)methanimine (1g)

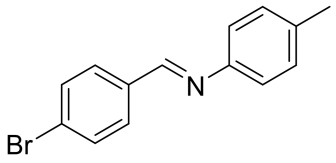
Pale yellow soild. Yiled :98%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.43 (s, 1H), 7.90 (dd, J = 8.7, 5.6 Hz, 2H), 7.24 – 7.08 (m, 6H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

=163.55(d, J_{FC}=250 Hz), 157.0, 148.152, 134.9, 131.7, 131.6, 129.7(d, J_{FC}=4.1Hz), 128.8, 119.7, 114.8(d, J_{FC}=11.6 Hz), 19.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -108.27. The spectroscopic data are in accordance with those described in the literature. [6]



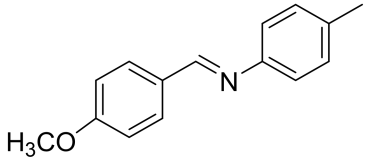
(*E*)-1-(4-chlorophenyl)-*N*-(p-tolyl)methanimine (1h)

White soild. Yiled: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.43 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 149.1, 137.2, 136.3, 134.9, 130.0, 130.0, 129.2, 120.9, 21.2. The spectroscopic data are in accordance with those described in the literature. [11]



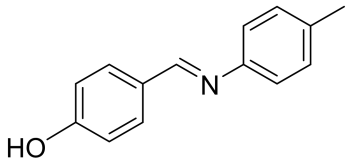
(*E*)-1-(4-bromophenyl)-*N*-(p-tolyl)methanimine (1i)

White soild. Yiled: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 1H), 7.80 – 7.73 (m, 2H), 7.63 – 7.56 (m, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.2, 149.1, 136.3, 135.4, 132.1, 130.2, 130.0, 125.8, 120.9, 21.2. The spectroscopic data are in accordance with those described in the literature. [12]



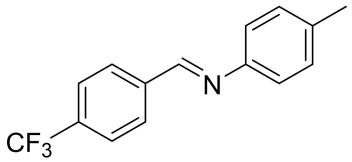
(*E*)-1-(4-methoxyphenyl)-*N*-(p-tolyl)methanimine (1j)

White soild. Yiled: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.40 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 162.2, 159.1, 149.8, 135.5, 130.5, 129.8, 129.5, 120.9 114.3, 55.5, 21.3. The spectroscopic data are in accordance with those described in the literature. [6]



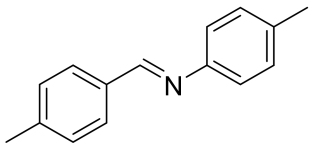
(*E*)-4-((p-tolylimino)methyl)phenol (1k)

White soild. Yiled: 98%.^{1}H NMR (400 MHz, DMSO) δ =8.26 (s, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ =160.6, 159.3, 149.4, 134.8, 130.7, 129.8, 127.7, 121.0, 115.8, 20.7. The spectroscopic data are in accordance with those described in the literature. [6]



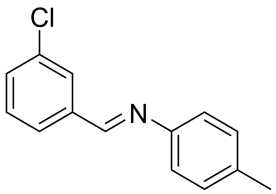
(*E*)-*N*-p-tolyl-1-(4-(trifluoromethyl)phenyl)methanimine (1l)

Whtie soild. Yiled: 98%^{1}H NMR (400 MHz, $CDCl_3$) δ =8.52 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 6.9 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 148.8, 139.5, 136.8, 132.8, 132.5, 130.0, 129.0, 125.8(d, J = 3.9 Hz), 121.02, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.61. The spectroscopic data are in accordance with those described in the literature. [6]



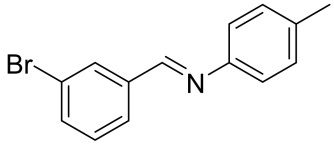
(*E*)-*N*,1-di-p-tolylmethanimine (1m)

White soild. Yiled: 90%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.44 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 2.40 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =159.8, 149.8, 1418, 135.7, 133.9 129.9 129.6, 128.8, 120.9, 21.8, 21.4. The spectroscopic data are in accordance with those described in the literature. [6]



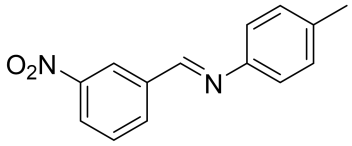
(*E*)-1-(3-chlorophenyl)-*N*-(p-tolyl)methanimine (1n)

White solid. Yiled: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.42 (s, 1H), 7.94 (s, 1H), 7.74 (d, J = 7.3 Hz, 1H), 7.48 – 7.36 (m, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 2.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.9, 149.0, 138.2, 136.5, 135.1, 131.2, 130.1, 130.0, 128.4, 127.2, 121.0, 21.2. The spectroscopic data are in accordance with those described in the literature. [11]



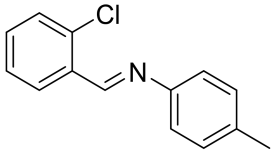
(*E*)-1-(3-bromophenyl)-*N*-(p-tolyl)methanimine (1o)

White soild. Yiled: 90%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.41 (s, 1H), 8.09 (s, 1H), 7.78 (d, J = 9.1 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =157.8, 148.9, 138.4, 136.5, 134.1, 131.3, 130.4, 130.0, 127.6, 123.2, 121.0, 21.2. The spectroscopic data are in accordance with those described in the literature. [13]



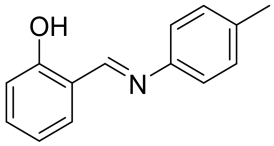
(*E*)-1-(3-nitrophenyl)-*N*-(p-tolyl)methanimine (1p)

Pale yellow soild. Yiled: 93%.^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.65 (s, 1H), 8.47 (s, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 156.4, 148.8, 148.3, 138., 137.1, 134., 130.1, 129.9, 125.5, 123.5, 121.1, 21.2. The spectroscopic data are in accordance with those described in the literature.[6]



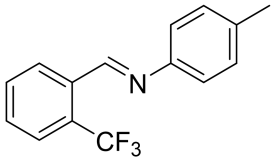
(*E*)-1-(2-chlorophenyl)-*N*-phenylmethanimine (1q)

Yellow soild. Yiled: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.85 (s, 1H), 8.16 (d, J = 4.7 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.16 – 7.08 (m, 4H), 2.31 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =156.3, 149.3, 136.5, 136.1, 133.5, 132.1, 130.1, 130.0, 128.6, 127.3, 121.2, 21.2. The spectroscopic data are in accordance with those described in the literature. [14]



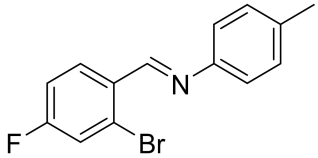
(*E*)-2-((p-tolylimino)methyl)phenol (1r)

Yellow soild. Yiled: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.63 (s, 1H), 7.42 – 7.33 (m, 2H), 7.25 – 7.17 (m, 4H), 7.02 (d, J = 8.4 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 161.9, 161.2, 146.0, 137.1, 133.1, 132.3, 130.2, 121.4, 119.4, 119.1 117.3, 21.2. The spectroscopic data are in accordance with those described in the literature. [15]



(*E*)-*N*-p-tolyl-1-(2-(trifluoromethyl)phenyl)methanimine (1s)

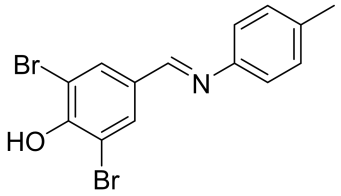
White soild. Yiled: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.84 (s, 1H), 8.45 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =155.7, 149.1, 135.61, 136.8, 134.4, 132.2, 130.6, 130.0, 128.5, 125.9, 125.8, 123.0,121.1, 21.2.^{19}F NMR (376 MHz, $CDCl_3$) δ= -56.87.



(*E*)-1-(2-bromo-3-fluorophenyl)-*N*-(p-tolyl)methanimine (1t)

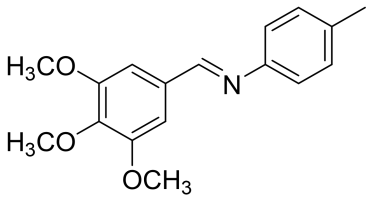
Pale yellow soild. Yiled: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.79 (s, 1H), 8.25 (dd, J = 8.8, 6.3 Hz, 1H), 7.36 (dd, J = 8.1, 2.5 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.19 –

7.10 (m, 3H), 2.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =164.0 (d, J = 256.2 Hz), 157.2, 150.0, 136.6, 131.3 (d, J = 3.3 Hz), 130.6 (d, J = 9.0 Hz), 129.99, 126.30 (d, J = 9.9 Hz), 121.2, 120.4 (d, J = 24.6 Hz), 115.5 (d, J = 21.5 Hz), 21.20. The spectroscopic data are in accordance with those described in the literature. [16]



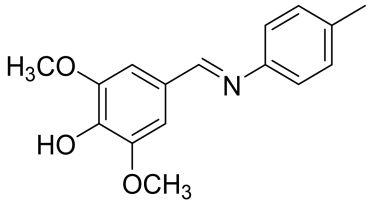
(*E*)-2,6-dibromo-4-[(p-tolylimino)methyl]phenol (1u)

Pale red soild. Yiled: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.29 (s, 1H), 8.01 (s, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 6.6 Hz, 2H), 2.38 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =155.7, 151.7, 148.7, 136.5, 132.4, 131.6, 130.0, 121.0, 110.5, 21.2.



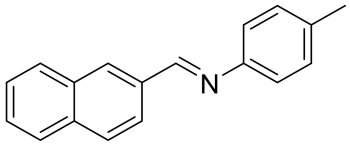
(*E*)-*N*-p-tolyl-1-(3,4,5-trimethoxyphenyl)methanimine (1v)

White soild. Yiled: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.36 (s, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.15 – 7.12 (m, 4H), 3.94 (s, 6H), 3.91 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =159.2, 153.6, 149.4, 140.8, 135.9, 132.0, 129.9, 120.9, 105.7, 61.1, 56.3, 21.1. The spectroscopic data are in accordance with those described in the literature. [17]



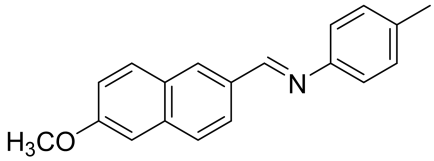
***(E)*-2,6-dimethoxy-4-((p-tolylimino)methyl)phenol (1w)**

Yellow Soild. Yiled: 55%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.34 (s, 1H), 7.22 – 7.15 (m, 4H), 7.12 (d, J = 8.3 Hz, 2H), 5.96 (s, 1H), 3.97 (s, 6H), 2.37 (s, 3H).13C NMR (100 MHz, $CDCl_3$) δ =159.5, 149.6, 147.4, 137.9, 135.6, 129.9, 128.1, 120.9, 105.6, 56.5, 21.1.



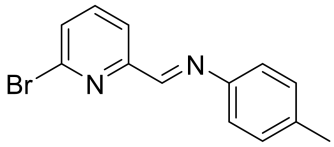
(*E*)-1-(naphthalen-2-yl)-*N*-(p-tolyl)methanimine (1x)

Pale yellow soild. Yiled: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.54 (s, 1H), 8.09 (d, J = 9.4 Hz, 2H), 7.82 (m, 3H), 7.46 (m, 2H), 7.13 (d, J = 2.7 Hz, 4H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =159.7, 149.6, 136.0, 135.1, 134.2, 133.2, 131.2, 130.0, 128.9, 128.7, 128.1, 127.6, 126.7, 124.0, 121.0, 21.2. The spectroscopic data are in accordance with those described in the literature. [18]



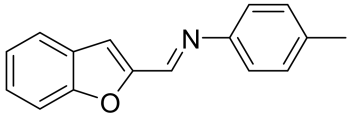
(*E*)-1-(6-methoxynaphthalen-2-yl)-*N*-(p-tolyl)methanimine (1y)

Pale yellow soild. Yiled: 75%.^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.59 (s, 1H), 8.14 – 8.11 (m, 2H), 7.82 (t, J = 8.6 Hz, 2H), 7.22 – 7.17 (m, 6H), 3.95 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 159.8, 159.1, 149.7, 136.6, 135.8, 132.2 130.1, 130.5, 129.9, 128.6, 127.6, 124.8, 121.0 119.5, 106.1, 55.2, 21.2.



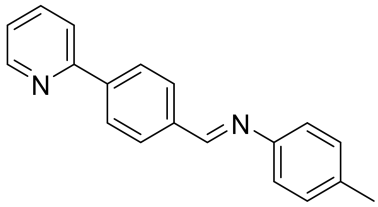
(*E)*-1-(6-bromopyridin-2-yl)-*N*-(p-tolyl)methanimine (1z)

Pale yellow soild. Yiled: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.58 (s, 1H), 8.20 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.22 (s, 4H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.1, 156.1, 147.8, 141.9, 139.1, 137.5, 130.1, 129.5, 121.4, 120.3, 21.3. The spectroscopic data are in accordance with those described in the literature. [19]



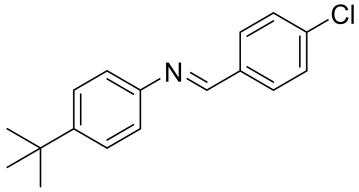
(*E*)-1-(benzofuran-2-yl)-*N*-(p-tolyl)methanimine (1aa)

Yellow soild. Yiled: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.43 (s, 1H), 7.62 (dd, J = 14.0, 8.0 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.24 – 7.18 (m, 6H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =156.0, 153.3, 148.6, 147.5, 136.9, 130.0, 127.9, 127.1, 124.3, 123.7, 122.3, 121.3, 113.1, 112.3, 21.2.



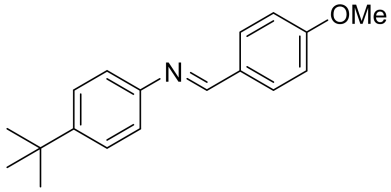
(*E*)-1-(4-(pyridin-2-yl)phenyl)-*N*-(p-tolyl)methanimine (1ab)

Pale yellow soild. Yiled: 93%.^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.66 (s, 1H), 8.45 (s, 1H), 8.04 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.76 – 7.69 (m, 2H), 7.29 – 7.04 (m, 5H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 159.2, 156.7, 150.0, 149.5, 141.94, 137.0, 136.9, 136.1, 130.0, 129.3, 127.3, 122.7, 121.0, 21.2.



(*E*)-*N*-(4-(tert-butyl)phenyl)-1-(4-chlorophenyl)methanimine (1ac)

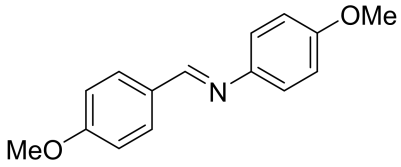
Pale yellow soild. Yiled: 88%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.44 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.45 – 7.41 (m, 4H), 7.18 (d, J = 8.5 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.3, 149.6, 149.1 137.3, 135.0, 130.0, 129.2, 126.2, 120.7, 34.7, 31.6.



(*E*)-*N*-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)methanimine (1ad)

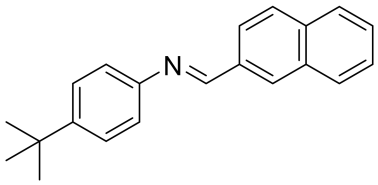
White soild. Yiled: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.41 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =162.2, 159.3, 149.8, 148.8,

130.5, 129.5, 126.1, 120.6, 114.3, 55.6, 34.6, 31.6. The spectroscopic data are in accordance with those described in the literature. [20]



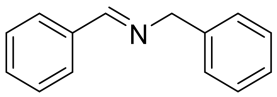
(*E*)-*N*,1-bis(4-methoxyphenyl)methanimine (1ae)

White soild. Yiled: 81%.^{1}H NMR (400 MHz, CDCl3) δ =8.40 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =162.1, 158.1, 145.4, 130.4, 129.6, 122.2, 114.5, 114.3, 55.6, 55.5. The spectroscopic data are in accordance with those described in the literature. [21]



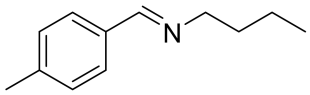
(*E*)-*N*-(4-(tert-butyl)phenyl)-1-(naphthalen-2-yl)methanimine (1af)

Pale yellow soild. Yiled: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* =8.57 (s, 1H), 8.10 (dd, *J* = 10.5, 1.9 Hz, 2H), 7.90 – 7.77 (m, 3H), 7.50 – 7.44 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* =159.9, 149.5, 149.3, 135.1, 134.2, 133.3, 131.2, 128.9, 128.8, 128.1, 127.6, 126.7, 126.2, 124.1, 120.8, 34.7, 31.6.



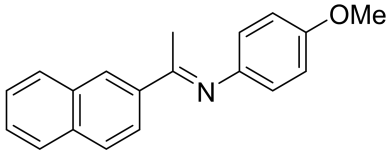
(*E*)-*N*,2-diphenylethan-1-imine (1ag)

Colorless oil. Yiled: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* =8.26 (s, 1H), 7.75 – 7.62 (m, 2H), 7.33 – 7.28 (m, 3H), 7.27 – 7.20 (m, 4H), 7.19 – 7.12 (m, 1H), 4.71 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*= 162.2, 139.5, 136.3, 131.0, 128.8, 128.7, 128.5, 128.2, 127.2, 65.2. The spectroscopic data are in accordance with those described in the literature. [7]



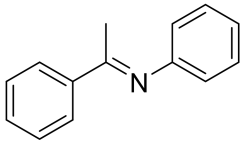
(*E*)-*N*-butyl-1-(p-tolyl)methanimine (1ah)

Colorless oil. Yiled: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (s, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 3.60 (td, J = 7.0, 1.3 Hz, 2H), 2.38 (s,3H), 1.68 (m, J = 14.5, 7.2 Hz, 2H), 1.38 (m, J = 14.7, 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 160.8, 140.8, 133.9, 129.4, 128.1, 61.6, 33.2, 21.6, 20.6, 14.0.The spectroscopic data are in accordance with those described in the literature.[40]



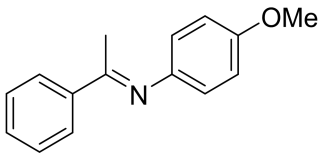
(*E*)-*N*-(4-methoxyphenyl)-1-(naphthalen-2-yl)ethan-1-imine (1ai)

Pale yellow soild. Yiled: 93%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.33 (s, 1H), 8.21 (dd, 1H), 7.97 – 7.83 (m, 3H), 7.56 – 7.48 (m, 2H), 6.94 (d, J = 7.5 Hz, 2H), 6.81 (d, J = 7.5 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =165.6, 156.0, 144.8, 137.1, 134.4, 133.0, 128.9, 128.0, 127.7, 127.6, 127.1, 126.3, 124.2, 120.8, 114.3, 55.5, 17.33. The spectroscopic data are in accordance with those described in the literature. [22]



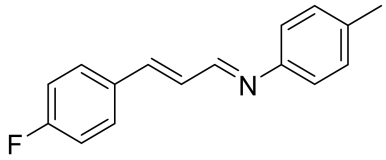
(*E*)-*N*,1-diphenylethan-1-imine (1aj)

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.95 – 7.85 (m, 2H), 7.43 – 7.34 (m, 3H), 7.30 – 7.24 (m, 2H), 7.06 – 6.94 (m, 1H), 6.78 – 6.67 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =164.5, 150.6, 138.4, 129.4, 127.9, 127.3, 126.1, 122.2, 118.3, 16.6. The spectroscopic data are in accordance with those described in the literature. [22]



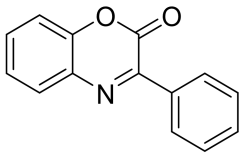
(*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (1ak)

Yellow soild. Yiled: 42%.^{1}H NMR (400 MHz, $CDCl_3$) δ =8.05 – 7.91 (m, 2H), 7.49 – 7.39 (m, 3H), 6.91 (d, J = 2.4 Hz, 2H), 6.75 (d, J = 2.4 Hz, 2H), 3.81 (s, 3H), 2.24 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =165.9, 156.1, 144.4, 139.9, 130.5, 128.5, 127.2, 120.9, 114.4, 55.6, 17.5. The spectroscopic data are in accordance with those described in the literature. [22]



(1*E*, 2*E*)-3-(4-fluorophenyl)-*N*-(p-tolyl)prop-2-en-1-imine (1ai)

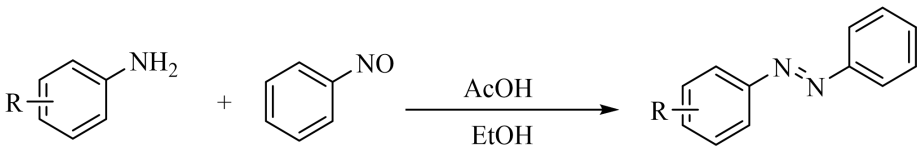
Pale yellow soild. Yiled: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.27 (d, J = 8.1 Hz, 1H), 7.51 (dd, J = 8.7, 5.4 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.12 – 7.03 (m, 6H), 2.37 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =163.5 (d, J = 250.4 Hz), 160.7, 149.1, 142.3 136.3, 132.0, 130.0, 129.3 (d, J = 8.3 Hz), 128.6 (d, J = 2.4 Hz), 121.0, 116.1 (d, J = 22 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-110.69.



3-phenyl-2H-benzo[b][1,4]oxazin-2-one (1am)

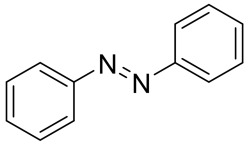
Grey soild. Yiled: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.33 (dd, J = 7.9, 1.3 Hz, 2H), 7.86 (dd, J = 7.9, 1.6 Hz, 1H), 7.55 – 7.49 (m, 4H), 7.40 (td, J = 7.7, 1.4 Hz, 1H), 7.34 (dd, J = 8.2, 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =152.5, 151.0, 146.6, 134.3, 131.8, 131.6, 131.3, 129.6, 128.6, 125.7, 116.3. The spectroscopic data are in accordance with those described in the literature. [6]

4.2 Preparation of unsymmetrical azobenzenes compounds



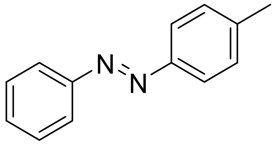
To a solution of nitrosobenzene (0.5 g, 4.7 mmol) in glacial acetic acid (12.0 mL) and EtOH (3.0 mL), the amine (1.0 equiv.) was added. The reaction mixture was stirred at

40 °C for overnight. Then, the mixture was poured into ice water and filtered to afford azobenzene crude product. The crude product was purified by silica gel column chromatography.



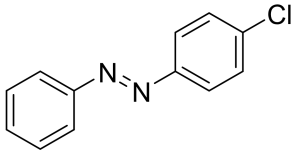
***(E)*-1,2-diphenyldiazene (3a)**

Orange solid. Yiled: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.94 (dd, 4H), 7.67 – 7.41 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ =152.8, 131.2, 129.2, 123.0. The spectroscopic data are in accordance with those described in the literature. [23]



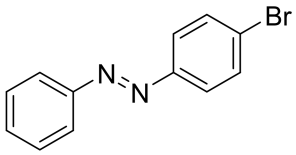
***(E)*-1-phenyl-2-(p-tolyl)diazene (3b)**

Orange soild. Yiled: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.92 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.55 – 7.46 (m, 3H), 7.33 (d, J = 7.5 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =152.8, 150.9, 141.7, 130.9, 129.9, 129.2, 123.0, 122.9, 21.7. The spectroscopic data are in accordance with those described in the literature. [23]



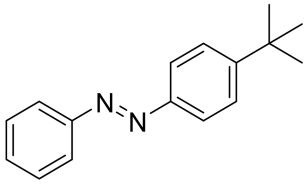
(*E*)-1-(4-chlorophenyl)-2-phenyldiazene (3c)

Orange soild. Yiled: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.92 (dd, J = 8.2, 1.6 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H), 7.54 – 7.46 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ =152.6, 151.1, 137.0, 131.4, 129.5, 129.3, 124.3, 123.1. The spectroscopic data are in accordance with those described in the literature. [23]



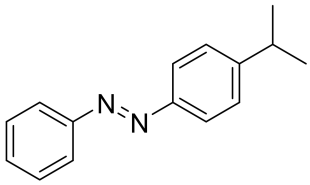
***(E)*-1-(4-bromophenyl)-2-phenyldiazene (3d)**

Orange soild. Yiled: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.91 (d, J = 10.0 Hz, 2H), 7.80 (d, J = 6.7 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.56 – 7.46 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =152.6, 151.4, 132.5, 131.5, 129.3, 125.5, 124.5, 123.1. The spectroscopic data are in accordance with those described in the literature. [23]



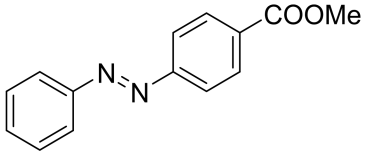
(*E*)-1-(4-(tert-butyl)phenyl)-2-phenyldiazene (3e)

Red Soild. Yiled: 85%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 4H), 7.63 – 7.43 (m, 5H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =154.7, 152.9, 150.7, 130.8, 129.2, 126.2, 122.9, 122.7, 35.2, 31.4. The spectroscopic data are in accordance with those described in the literature. [23]



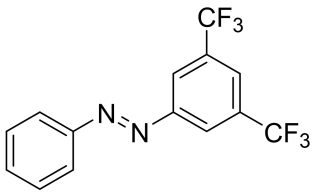
(*E*)-1-(4-isopropylphenyl)-2-phenyldiazene (3f)

Orange soild. Yiled: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.94 – 7.83 (m, 4H), 7.57 – 7.45 (m, 3H), 7.38 (d, J = 6.6 Hz, 2H), 3.00 (hept, J = 7.0 Hz, 1H), 1.31 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =152.9, 152.5, 151.2, 130.8, 129.2, 127.3, 123.1, 122.9, 102.4, 34.3, 24.0. The spectroscopic data are in accordance with those described in the literature.[24]



methyl (*E*)-4-(phenyldiazenyl)benzoate (3g)

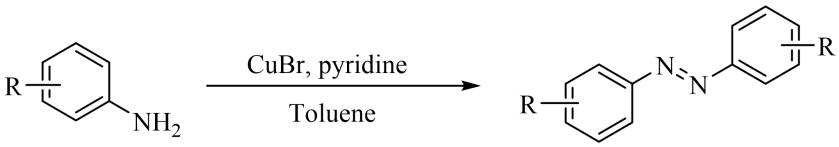
Orange soild. Yiled: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.5 Hz, 4H), 7.63 – 7.42 (m, 3H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 155.2, 152.7, 131.9, 130.8, 129.3, 123.3, 122.8, 52.5. The spectroscopic data are in accordance with those described in the literature. [25]



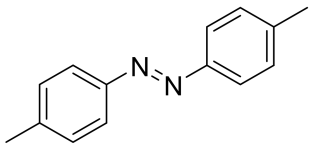
(*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-2-phenyldiazene (3h)

Orange soild. Yiled: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.36 (s, 2H), 8.03 – 7.93 (m, 3H), 7.60 – 7.51 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =152.9, 152.1, 132.8 (q, J = 35.2 Hz), 132.6, 129.5, 123.9(q, J = 3.9 Hz), 123.6, 123.3 (q, J = 272.5 Hz), 123.1 (d, J = 4.2 Hz).

4.3 Preparation of symmetrical azobenzenes Compounds

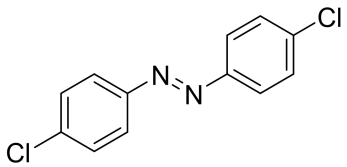


Symmetrical azoarenes: A 100 mL flask equipped with a magnetic stir bar was charged with corresponding aniline (40 mmol, 1.0 equiv.), CuBr (172 mg, 1.2 mmol, 0.03 equiv.), pyridine (284 mg, 3.6 mmol, 0.09 equiv.) and toluene (50 mL). The mixture was reacting under air at 60 ºC using an oil bath for 20 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by chromatography on silica gel to give the symmetrical azoarenes products.



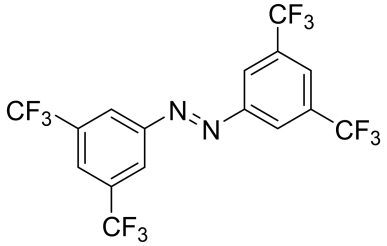
(*E*)-1,2-di-p-tolyldiazene (3i)

Orange soild. Yiled: 78%.^{1}H NMR (400 MHz, $CDCl_3$) δ =7.82 (d, J = 8.3 Hz, 4H), 7.31 (d, J = 7.7 Hz, 4H), 2.44 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ =150.9, 141.4, 129.9, 122.9, 21.6. The spectroscopic data are in accordance with those described in the literature. [23]



***(E)*-1,2-bis(4-chlorophenyl)diazene (3j)**

Orange soild. Yiled: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.87 (d, J = 8.7 Hz, 4H), 7.49 (d, J = 8.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =150.9, 137.4, 129.6, 124.3. The spectroscopic data are in accordance with those described in the literature. [26]

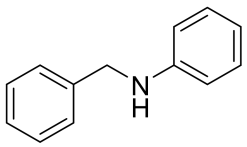


(*E*)-1,2-bis(3,5-bis(trifluoromethyl)phenyl)diazene(3k)

Orange soild. Yiled: 75%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 4H), 8.07 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.25, 133.3(q, J = 34.3 Hz), 125.37, 123.59,123.53(q, J = 272.9 Hz). The spectroscopic data are in accordance with those described in the literature. [27]

5. General procedure for IPrAgCl-catalyzed hydrogenation of imines.

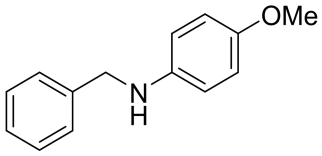
A mixture of Imine derivatives (0.2 mmol) and IPrAgCl (1 mol%) were added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$ (2.2 equiv) and *i*-PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25℃ for 4h. After quenching with saturated NH_4Cl/H_2O (10 mL), the crude product was extracted with EtOAc (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound.



***N*-benzylaniline (2a)**

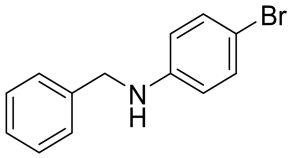
The general procedure was applied to *N*-benzylaniline (36.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow oily liquid (35.2 mg, 96% yield);^{1}H NMR (400 MHz,

$CDCl_3$) δ =7.44 – 7.30 (m, 5H), 7.22 (t, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.5 Hz, 2H), 4.36 (s, 2H), 4.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =148.2, 139.5, 129.4, 128.8, 127.6, 127.3, 117.7, 112.9, 48.4. The spectroscopic data are in accordance with those described in the literature.[28]



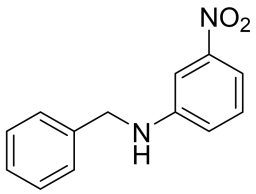
***N*-benzyl-4-methoxyaniline (2b)**

The general procedure was applied to *N*-benzyl-4-methoxyaniline (42.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (36.7 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.31 – 7.21 (m, 4H), 7.20 – 7.15 (m, 1H), 6.68 (dd, J = 8.9, 2.0 Hz, 2H), 6.51 (dd, J = 8.9, 2.0 Hz, 2H), 4.18 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =152.3, 142.6, 139.8, 128.7, 127.7, 127.3, 115.0, 114.2, 55.9, 49.3. The spectroscopic data are in accordance with those described in the literature.[29]



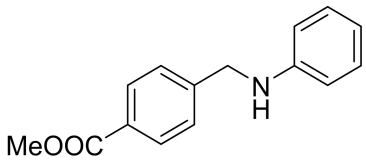
***N*-benzyl-4-bromoaniline (2c)**

The general procedure was applied to *N*-benzyl-4-bromoaniline (52.0 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (50 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.35 (dd, J = 4.5, 1.8 Hz, 4H), 7.31 – 7.27 (m, 1H), 7.24 (dd, J = 8.7, 1.9 Hz, 2H), 6.53 – 6.46 (m, 2H), 4.30 (s, 2H), 4.08 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =147.2 139.0, 132.1, 128.8, 127.5, 114.5, 109.2, 48.3. The spectroscopic data are in accordance with those described in the literature.[29]



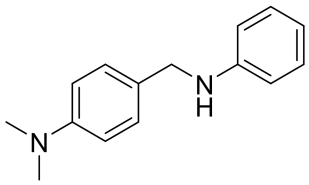
***N*-benzyl-3-nitroaniline (2d)**

The general procedure was applied to *N*-benzyl-3-nitroaniline (45.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as yellow soild (37.9 mg, 83% yield); Melting point: 106.0-107.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.42 (dd, J = 8.1, 1.3 Hz, 1H), 7.33 (t, J = 2.3 Hz, 1H), 7.27 (d, J = 4.7 Hz, 4H), 7.25 – 7.19 (m, 1H), 7.16 (t, J = 8.1 Hz, 1H), 6.78 (dd, J = 8.2, 1.5Hz, 1H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =149.5, 148.9, 138.2, 129.9, 129.0, 127.8, 127.6, 118.8, 112.2, 106.6, 48.1. The spectroscopic data are in accordance with those described in the literature.[29]



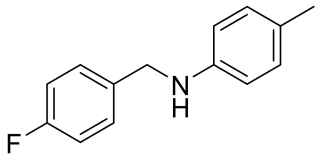
methyl 4-((phenylamino)methyl)benzoate (2e)

The general procedure was applied to methyl 4-((phenylamino)methyl)benzoate (47.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (41.5 mg, 86% yield); Melting point: 43.1-44.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.02 (d, J = 7.1 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.22 – 7.14 (t, 2H), 6.74 (td, J = 7.3, 1.2 Hz, 1H), 6.62 (d, J = 8.7 Hz, 2H), 4.41 (s, 2H), 4.18 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =167.1, 147.8, 145.1, 130.0, 129.4, 129.1, 127.2, 117.9, 113.0, 52.2, 48.0. The spectroscopic data are in accordance with those described in the literature.[30]



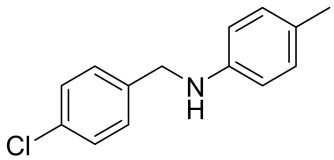
***N,N*-dimethyl-4-((phenylamino)methyl)aniline (2f)**

The general procedure was applied to *N,N*-dimethyl-4-((phenylamino)methyl)aniline (44.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h, IPrAgCl (10 mol%). The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow soild (36.2 mg, 80% yield); Melting point: 72.3-74.6℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.16 (d, J = 8.7 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.67 – 6.61 (m, 3H), 6.56 (d, J = 8.6 Hz, 2H), 4.12 (s, 2H), 3.79 (brs, 1H), 2.86 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ =150.2, 148.5, 129.3, 128.9, 127.5, 117.4, 112.9, 48.0, 40.9. The spectroscopic data are in accordance with those described in the literature.[31]



***N*-(4-fluorobenzyl)-4-methylaniline (2g)**

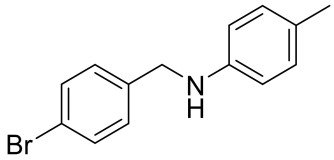
The general procedure was applied to *N,N*-dimethyl-4-((phenylamino)methyl)aniline (42.7 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow oily liquid (32.3 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.25 (dd, J = 8.4, 5.5 Hz, 2H), 6.93 (dd, J = 16.4, 7.7 Hz, 4H), 6.47 (d, J = 8.4 Hz, 2H), 4.19 (s, 2H), 3.82 (brs, 1H), 2.16 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =161.0 (d, J = 244.9 Hz), 144.6, 134.3, 128.7, 127.9 (d, J = 7.9 Hz), 125.9, 114.4 (d, J = 21.3 Hz), 112.0, 46.9, 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-115.65. The spectroscopic data are in accordance with those described in the literature.[6]



***N*-(4-chlorobenzyl)-4-methylaniline (2h)**

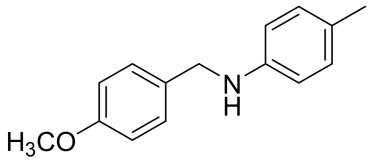
The general procedure was applied to *N*-(4-chlorobenzyl)-4-methylaniline (45.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the

title compound as pale yellow soild (42.2 mg, 91% yield); Melting point: 49.6-50.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.27 – 7.09 (m, 4H), 6.89 (d, J = 6.1 Hz, 2H), 6.43 (d, J = 5.2 Hz, 2H), 4.17 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.7, 138.3, 132.8, 129.9, 128.8, 127.1, 113.1, 48.0, 20.5. The spectroscopic data are in accordance with those described in the literature.[28]



***N*-(4-bromobenzyl)-4-methylaniline (2i)**

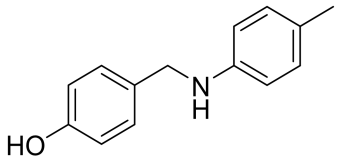
The general procedure was applied to *N*-(4-bromobenzyl)-4-methylaniline (54.8 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as brown soild (52.5 mg, 95% yield); Melting point: 60.5-61.4℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.35 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 8.5 Hz, 2H), 4.16 (s, 2H), 3.83 (brs, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.6, 138.9, 131.2, 129.9, 129.1, 127.1, 120.9, 113.1 48.0, 20.5. The spectroscopic data are in accordance with those described in the literature.[28]



***N*-(4-methoxybenzyl)-4-methylaniline (2j)**

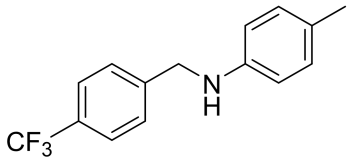
The general procedure was applied to *N*-(4-methoxybenzyl)-4-methylaniline (45 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow soild (39.1 mg, 86% yield); Melting point: 78.5-80.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.72 (d, J = 8.6 Hz, 2H),7.04 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 4.26 (s, 2H), 3.83 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.8, 146.1, 131.2, 129.8, 128.9, 126.8, 114.1,

113.1 55.4, 48.2, 20.5. The spectroscopic data are in accordance with those described in the literature.[28]



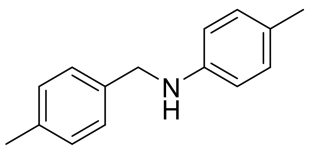
4-[(p-tolylamino)methyl]phenol (2k)

The general procedure was applied to 4-[(p-tolylamino)methyl]phenol (42.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (37.1 mg, 87% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.23 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 4.22 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =155.0, 145.9, 131.5, 129.9, 129.1, 127.2, 115.6, 113.5, 48.4, 20.5. The spectroscopic data are in accordance with those described in the literature.[6]



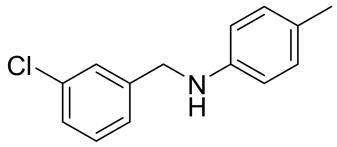
4-methyl-*N*-[4-(trifluoromethyl)benzyl]aniline (2l)

The general procedure was applied to 4-methyl-*N*-[4-(trifluoromethyl)benzyl]anilin*e* (52.7 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow soild (48.3 mg, 91% yield); Melting point: 75.4-76.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.60 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H),7.01 (d, J = 7.0 Hz, 2H), 6.55 (d, J = 6.8 Hz, 2H), 4.40 (s, 2H), 4.05 (brs, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.3, 144.1, 130.0, 127.6, 127.3, 125.7, 125.6, 113.2, 48.2, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.26. The spectroscopic data are in accordance with those described in the literature.[6]



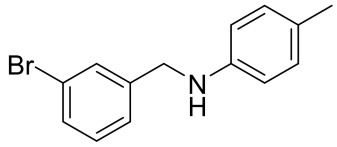
4-methyl-*N*-(4-methylbenzyl)aniline (2m)

The general procedure was applied to 4-methyl-*N*-(4-methylbenzyl)aniline (41.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h, The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as brown soild (41.8 mg, 99% yield); Melting point: 53.8-54.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.17 (d, J = 7.2 Hz, 2H), 7.06 (d, J = 7.7 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 7.1 Hz, 2H), 4.17 (s, 2H), 3.77 (brs, 1H), 2.26 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =146.1, 133.9, 136.7, 129.9, 129.4, 127.6, 126.8, 113.1, 48.5, 21.2, 20.5. The spectroscopic data are in accordance with those described in the literature.[28]



***N*-(3-chlorobenzyl)-4-methylaniline (2n)**

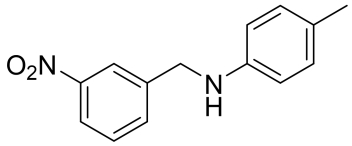
The general procedure was applied to *N*-(3-chlorobenzyl)-4-methylaniline (45.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h.The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown liquid (36.1 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.27 (s, 1H), 7.14 (s, 3H), 6.88 (d, J = 6.2 Hz, 2H), 6.43 (d, J = 6.0 Hz, 2H), 4.20 (s, 2H), 3.88 (brs, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.6, 142.1, 134.6, 130.0, 129.9, 127.5, 127.4, 127.1, 125.5, 113.1, 48.1, 20.5. The spectroscopic data are in accordance with those described in the literature.[32]



***N*-(3-bromobenzyl)-4-methylaniline (2o)**

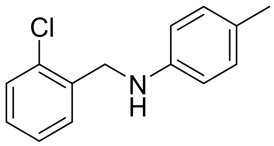
The general procedure was applied to *N*-(3-bromobenzyl)-4-methylaniline (54.8 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h.The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow liquid (47.0 mg, 85% yield);^{1}H NMR (400 MHz,

$CDCl_3$) δ =7.44 (s, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 7.1 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 8.4 Hz, 2H), 4.20 (s, 2H), 3.87 (brs, 1H), 2.15 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =145.6, 142.4, 130.5, 130.3, 130.3, 129.9, 127.2, 126.0, 122.9, 113.10, 48.2, 20.5. The spectroscopic data are in accordance with those described in the literature.[33]



4-methyl-*N*-(3-nitrobenzyl)aniline (2p)

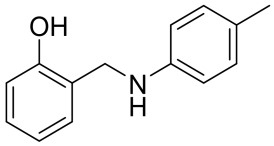
The general procedure was applied to 4-methyl-*N*-(3-nitrobenzyl)aniline (48 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=2:1) to afford the title compound as yellow soild (47.5 mg, 98% yield); Melting point: 90.2-91.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.25 (s, 1H), 8.12 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 6.4 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.00 (d, J = 6.8 Hz, 2H), 6.54 (d, J = 7.3 Hz, 2H), 4.45 (s, 2H), 4.45 (brs, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =148.6, 145.2, 142.4, 133.4, 130.0, 129.6, 127.5, 122.3, 122.2, 113.2, 47.9, 20.5 The spectroscopic data are in accordance with those described in the literature.[6]



***N*-(2-chlorobenzyl)-4-methylaniline (2q)**

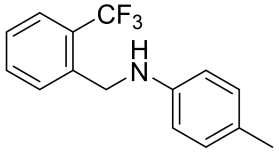
The general procedure was applied to *N*-(2-chlorobenzyl)-4-methylaniline (45.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as yellow soild (20.9 mg, 45% yield); Melting point: 118.2-120.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.59 (s, 1H), 7.27 – 7.21 (m, 1H), 7.16 – 7.08 (m, 2H), 6.95 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 4.43 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =138.2, 134.5, 133.6, 132.3, 131.2, 130.1, 129.7, 129.7, 127.3,

118.8, 49.3, 20.9. The spectroscopic data are in accordance with those described in the literature.[34]



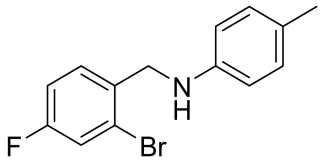
2-[(p-tolylamino)methyl]phenol (2r)

The general procedure was applied to 2-[(p-tolylamino)methyl]phenol (42.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white soild (27.2 mg, 85% yield); Melting point: 119.6-121.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.17 – 7.10 (m, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.97 (d, J = 8.1 Hz, 2H), 6.82 – 6.75 (m, 2H), 6.68 (d, J = 8.2 Hz, 2H), 4.30 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =157.1, 144.7, 130.5, 130.0, 129.3, 128.7, 123.0, 120.0, 116.8, 116.3, 49.4, 20.7. The spectroscopic data are in accordance with those described in the literature.[35]



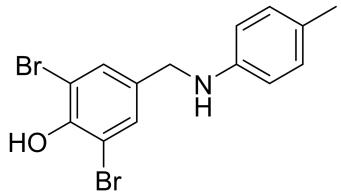
4-methyl-*N*-(2-(trifluoromethyl)benzyl)aniline (2s)

The general procedure was applied to 4-methyl-*N*-(2-(trifluoromethyl)benzyl)aniline (52.7 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow oiiy liquid (37.7 mg, 71% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.64 (dd, J = 15.4, 7.8 Hz, 2H), 7.47 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.3 Hz, 2H), 6.51 (d, J = 8.5 Hz, 2H), 4.53 (s, 2H), 4.04 (brs, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.5, 138.5, 132.3, 130.0, 128.8, 127.2, 127.1, 126.1, 126.1, 113.1, 44.9, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-60.23. HRMS (ESI): calcd for $C_{15}H_{15}F_3N$ $[M+H]^+$ 266.1157, found 266.1158.



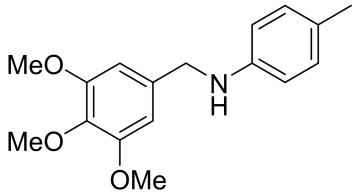
***N*-(2-bromo-4-fluorobenzyl)-4-methylaniline (2t)**

The general procedure was applied to *N*-(2-bromo-4-fluorobenzyl)-4-methylaniline (58.4 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (57.1 mg, 97% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.38 (dd, J = 8.6, 6.1 Hz, 1H), 7.33 (dd, J = 8.2, 2.6 Hz, 1H), 7.01 – 6.98 (m, 3H), 6.53 (d, J = 8.4 Hz, 2H), 4.39 (s, 2H), 4.07 (brs, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =161.6 (d, J = 249.5 Hz), 145.3, 134.4, 134.3,130.1 (d, J = 8.3 Hz), 129.9, 127.3, 123.1 (d, J = 9.5 Hz),, 120.1 (d, J = 24.5 Hz), 114.7 (d, J = 20.9 Hz), 112.0, 47.0, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -106.84. HRMS (ESI): calcd for $C_{14}H_{14}BrFN$ $[M+H]^+$ 294.0294, found 294.0293.



2,6-dibromo-4-((p-tolylamino)methyl)phenol (2u)

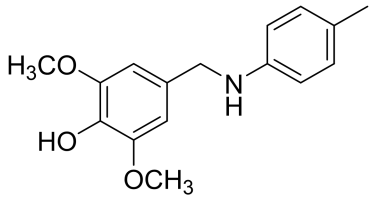
The general procedure was applied to 2,6-dibromo-4-((p-tolylamino)methyl)phenol (73.8 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h, The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown liquid (53.43 mg, 72% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.46 (s, 2H), 6.99 (d, J = 9.3 Hz, 2H), 6.52 (d, J = 8.4 Hz, 2H), 4.21 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =148.5, 145.4, 134.7, 130.9, 130.0, 127.4, 113.2, 110.1, 47.3, 20.5. HRMS (ESI): calcd for $C_{14}H_{14}Br_2NO$ $[M+H]^+$ 369.9442, found 369.9440.



4-methyl-*N*-(3,4,5-trimethoxybenzyl)aniline (2v)

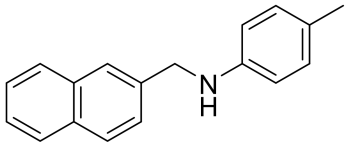
The general procedure was applied to 4-methyl-*N*-(3,4,5-trimethoxybenzyl)aniline (57 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to

afford the title compound as orange oily liquid (50.0 mg, 87 % yield);[1]H NMR (400 MHz, $CDCl_3$) δ =6.91 (d, J = 8.7 Hz, 2H), 6.52 (s, 2H), 6.49 (d, J = 8.5 Hz, 2H), 4.14 (s, 2H), 3.75 (s, 9H), 2.16 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ =153.4, 146.0, 137.0, 135.6, 129.8, 127.0, 113.1, 104.3, 60.9, 56.1, 49.2, 20.5. The spectroscopic data are in accordance with those described in the literature.[36]



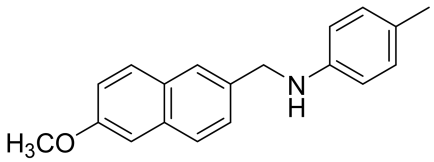
2,6-dimethoxy-4-((p-tolylamino)methyl)phenol (2w)

The general procedure was applied to 2,6-dimethoxy-4-((p-tolylamino)methyl)phenol (54.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown liquid (52.5 mg, 96% yield);[1]H NMR (400 MHz, $CDCl_3$) δ =6.92 (d, J = 8.5 Hz, 2H), 6.54 (s, 2H), 6.50 (d, J = 8.4 Hz, 2H), 4.13 (s, 2H), 3.79 (s, 6H), 2.17 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ =147.2, 146.1, 133.8, 130.8, 129.9, 127.0, 113.2, 104.3, 56.4, 49.3, 20.5. HRMS (ESI): calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$ 274.1443, found 274.1444.



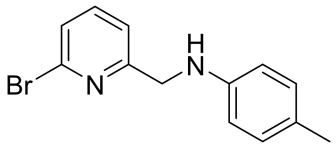
4-methyl-*N*-(naphthalen-2-ylmethyl)aniline (2x)

The general procedure was applied to 4-methyl-*N*-(naphthalen-2-ylmethyl)aniline (49.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as orange yellow soild (48.5 mg, 98% yield); Melting point: 56.5-57.3℃; [1]H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 4H), 7.63 – 7.46 (m, 3H), 7.05 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 4.50 (s, 2H), 4.04 (brs, 1H), 2.31 (s, 3H).[13]C NMR (100 MHz, $CDCl_3$) δ =146.0, 137.3, 133.6, 132.8, 129.9, 128.4, 127.9, 127.8, 126.9, 126.2, 126.0, 125.9, 125.8, 113.2, 48.9, 20.5. The spectroscopic data are in accordance with those described in the literature.[37]



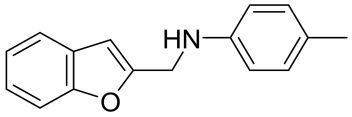
***N*-[(6-methoxynaphthalen-2-yl)methyl]-4-methylaniline (2y)**

The general procedure was applied to *N*-[(6-methoxynaphthalen-2-yl)methyl]-4-methylaniline (55.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white soild (45.5 mg, 82% yield); Melting point: 103.9-104.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.76 – 7.72 (m, 3H), 7.49 (d, J = 7.9 Hz, 1H), 7.18 (d, J = 9.4 Hz, 2H), 7.03 (d, J = 6.2 Hz, 2H), 6.54 (d, J = 5.3 Hz, 2H), 4.44 (s, 2H), 3.94 (s, 3H), 2.29 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =157.6, 146.1, 134.9, 133.9, 129.8, 129.3, 129.0, 127.3, 126.8, 126.5, 126.0, 119.0, 113.1, 105.8, 55.4, 48.8, 20.5. HRMS (ESI): calcd for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1545, found 278.1545.



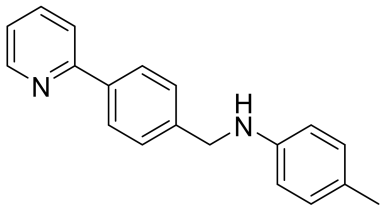
***N*-[(6-bromopyridin-2-yl)methyl]-4-methylaniline (2z)**

The general procedure was applied to *N*-[(6-bromopyridin-2-yl)methyl]-4-methylaniline (55.0 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h.The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid(52.7 mg, 95% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.47 (td, J = 7.6, 1.7 Hz, 1H), 7.33 (dd, J = 18.6, 7.0 Hz, 2H), 6.99 (d, J = 6.5 Hz, 2H), 6.55 (d, J = 6.5 Hz, 2H), 4.44 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =161.2, 145.2, 141.7, 139.1, 129.9, 127.2, 126.4, 120.3, 113.2, 49.4, 20.5. HRMS (ESI): calcd for $C_{13}H_{14}BrN_2$ $[M+H]^+$ 277.0340, found 277.0343.



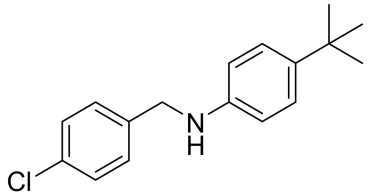
(*E*)-1-(benzofuran-2-yl)-*N*-(4-methylcyclohexa-2,4-dien-1-yl)methanimine (2aa)

The general procedure was applied to (E)-1-(benzofuran-2-yl)-*N*-(4-methylcyclohexa-2,4-dien-1-yl)methanimine (47.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as yellow soild (38.9 mg, 82% yield); Melting point: 87.4-89.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.39 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 7.7 Hz, 1H), 7.18 – 7.05 (m, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 6.49 (s, 1H), 4.35 (s, 2H), 3.94 (brs, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =156.0, 155.0, 145.2, 130.0, 128.5, 127.6, 124.0, 122.8, 120.9, 113.5, 111.2, 103.8, 42.3, 20.5. HRMS (ESI): calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1232, found 238.1234.



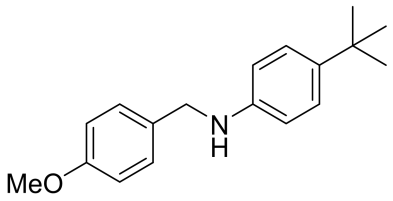
4-methyl-*N*-[4-(pyridin-2-yl)benzyl]aniline (2ab)

The general procedure was applied to 4-methyl-*N*-[4-(pyridin-2-yl)benzyl]aniline (54.5 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown soild (53.2 mg, 97% yield); Melting point: 93.8-96.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =8.58 (d, J = 5.4 Hz, 1H), 7.86 (d, J = 4.9 Hz, 2H), 7.64 – 7.54 (m, 2H), 7.36 (d, J = 6.6 Hz, 2H), 7.15 – 7.06 (m, 1H), 6.89 (d, J = 6.2 Hz, 2H), 6.47 (d, J = 4.9 Hz, 2H), 4.25 (s, 2H), 3.95 (brs, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =157.2, 149.7, 145.9, 140.7, 138.3, 136.8, 129.8, 127.8, 127.2, 126.8, 122.1, 120.2, 113.1, 48.4, 20.5. HRMS (ESI): calcd for $C_{19}H_{19}N_2$ $[M+H]^+$ 275.1548, found 275.1547.



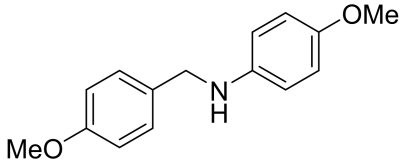
4-(tert-butyl)-*N*-(4-chlorobenzyl)aniline (2ac)

The general procedure was applied to 4-(tert-butyl)-*N*-(4-chlorobenzyl)aniline (54.4 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h.The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as brown soild (50.4 mg, 92% yield); Melting point: 97.7-98.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (s, 4H), 7.11 (d, J = 7.9 Hz, 2H), 6.47 (d, J = 8.8 Hz, 2H), 4.19 (s, 2H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.7, 140.7, 138.4, 132.9, 128.9, 128.8, 126.2, 112.7, 48.0, 34.0, 31.5. The spectroscopic data are in accordance with those described in the literature.[38]



4-(tert-butyl)-*N*-(4-methoxybenzyl)aniline (2ad)

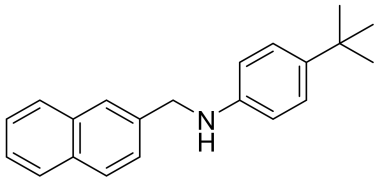
The general procedure was applied to 4-(tert-butyl)-*N*-(4-methoxybenzyl)aniline (53.5 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown soild (46.3 mg, 86% yield); Melting point: 94.1-95.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.21 (d, J = 6.9 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.51 (d, J = 6.8 Hz, 2H), 4.14 (s, 2H), 3.71 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.9, 146.0, 140.4, 131.8, 129.0, 126.1, 114.1, 112.7, 55.4, 48.2, 34.0, 31.7. The spectroscopic data are in accordance with those described in the literature.[38]



4-methoxy-*N*-(4-methoxybenzyl)aniline (2ai)

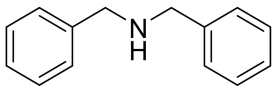
The general procedure was applied to 4-methoxy-*N*-(4-methoxybenzyl)aniline (48.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white soild (42.8 mg, 88% yield); Melting point:

123.1-124.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.31 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 4.22 (s, 2H), 3.82 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.9, 152.2, 142.6, 131.7, 128.9, 114.9, 114.2, 114.0, 55.9, 55.4, 48.8. The spectroscopic data are in accordance with those described in the literature.[39]



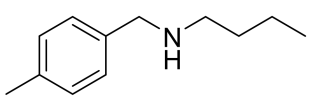
4-(tert-butyl)-*N*-(naphthalen-2-ylmethyl)aniline (2af)

The general procedure was applied to **4**-(tert-butyl)-*N*-(naphthalen-2-ylmethyl)aniline (57.5 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow soild (49.8 mg, 96% yield); Melting point: 74.8-76.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.76 – 7.65 (m, 4H), 7.41 – 7.32 (m, 3H), 7.11 (d, J = 8.6 Hz,2H), 6.52 (d, J = 8.7 Hz, 2H), 4.34 (s, 2H), 3.93 (brs, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =146.0, 140.5, 137.4, 133.6, 132.8, 128.4, 127.9, 127.8, 126.2, 126.2, 126.0, 125.9, 125.8, 112.8, 48.9, 34.0, 31.7. The spectroscopic data are in accordance with those described in the literature.[38]



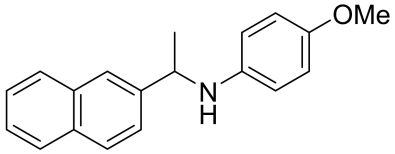
Dibenzylamine (2ag)

The general procedure was applied to Dibenzylamine (39.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as colorless oily liquid (31.6 mg, 80% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.28 – 7.22 (m, 8H), 7.20 – 7.13 (m, 2H), 3.72 (s, 4H), 1.61 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 140.4, 128.5, 128.3, 127.1, 53.2. The spectroscopic data are in accordance with those described in the literature.[36]



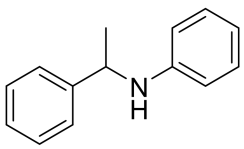
***N*-(4-methylbenzyl)butan-1-amine (2ah)**

The general procedure was applied to *N*-(4-methylbenzyl)butan-1-amine (35.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow soild (28.7 mg, 81% yield); Melting point: >300 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ =7.08 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 3.61 (s, 2H), 2.48 (t, J = 7.3 Hz, 2H), 2.22 (s, 3H), 1.37 (m, 2H), 1.26 – 1.12 (m, 2H), 0.79 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =137.2, 136.5, 129.1, 128.2, 53.7, 49.0, 32.1, 21.1, 20.5, 14.0. The spectroscopic data are in accordance with those described in the literature.[40]



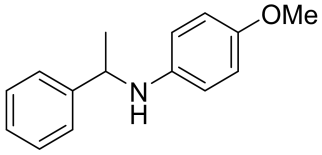
4-methoxy-*N*-(1-(naphthalen-2-yl)ethyl)aniline (2ai)

The general procedure was applied to 4-methoxy-*N*-(1-(naphthalen-2-yl)ethyl)aniline (55.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as yellow oily liquid (47.2 mg, 85% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.82 (m, 4H), 7.55 (dd, J = 8.5, 1.8 Hz, 1H), 7.51 – 7.46 (m, 2H), 6.73 (d, J = 7.5 Hz, 2H), 6.56 (d, J = 6.8 Hz, 2H), 4.61 (q, J = 7.6, 6.7 Hz, 1H), 3.71 (s, 3H), 1.61 (d, J = 6.8 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =152.0, 143.1, 141.7, 133.7, 132.8, 128.5, 127.9, 127.8, 126.1, 125.6, 124.6, 124.4, 114.8, 114.7, 55.8, 54.6, 25.3. The spectroscopic data are in accordance with those described in the literature.[22]



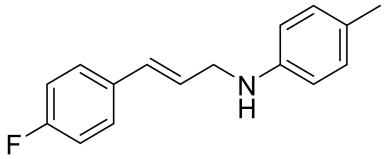
4-methyl-*N*-(1-phenylethyl)aniline (2aj)

The general procedure was applied to 4-methyl-*N*-(1-phenylethyl)aniline (39.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as pale yellow oily liquid (37.2 mg, 88% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.28 (d, J = 6.9 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.18 – 7.10 (m, 1H), 7.00 (dd, J = 8.6, 7.3 Hz, 2H), 6.56 (t, J = 7.3 Hz, 1H), 6.42 (dd, J = 8.7, 1.1 Hz, 2H), 4.40 (q, J = 6.7 Hz, 1H), 3.94 (s, 1H), 1.42 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =147.4, 145.3, 129.2, 128.8, 127.0, 126.0, 117.3, 113.4, 53.5, 25.2. The spectroscopic data are in accordance with those described in the literature.[22]



4-methoxy-*N*-(1-phenylethyl)aniline (2ak)

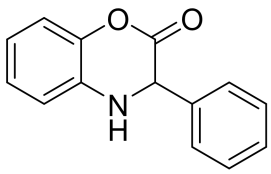
The general procedure was applied to 4-methoxy-*N*-(1-phenylethyl)aniline (45.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title co8mpound as yellow oily liquid (37.3 mg, 82% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.38 – 7.28 (m, 4H), 7.25 – 7.18 (m, 1H), 6.68 (d, J = 9.0 Hz, 2H), 6.46 (d, J = 8.9 Hz, 2H), 4.40 (q, J = 6.7 Hz, 1H), 3.68 (s, 3H), 1.48 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.0, 145.6, 141.7, 128.7, 126.9, 126.0, 114.8, 114.6, 55.8, 54.3, 25.3. The spectroscopic data are in accordance with those described in the literature.[22]



(*E*)-*N*-(3-(4-fluorophenyl)allyl)-4-methylaniline (2ai)

The general procedure was applied to (E)-*N*-(3-(4-fluorophenyl)allyl)-4-methylaniline (47.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 6 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to

afford the title compound as pale yellow soild (40.5 mg, 84% yield); Melting point: 162.4-164.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.53 – 7.31 (m, 2H), 7.02 – 6.98 (m, 4H), 6.61 – 6.56 (m, 3H), 6.24 (m, 1H), 3.91 (d, J = 5.8 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =162.4 (d, J = 245.9 Hz), 145.9, 133.2, 130.3, 129.9, 127.9 (d, J = 8.0 Hz), 127.2, 127.1, 115.6 (d, J = 21.6 Hz), 113.4, 46.6 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.58. HRMS (ESI): calcd for $C_{16}H_{17}FN$ $[M+H]^+$ 242.1345, found 242.1346.



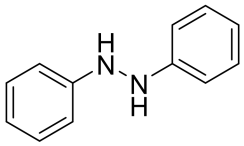
3-phenyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-2-one (2am)

The general procedure was applied to 3-phenyl-3,4-dihydro-2H-benzo[b] [1,4]oxazin-2-one (38.3 mg, 0.2 mmol) under an atmosphere of N_2 at 45 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as brown soild (38.3 mg, 85 % yield); Melting point: 75.1-76.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.41 – 7.35 (m, 5H), 7.07 – 7.00 (m, 2H), 6.87 (td, J = 7.8, 1.5 Hz, 1H), 6.81 (dd, J = 8.0, 1.5 Hz, 1H), 5.05 (d, J = 1.9 Hz, 1H), 4.30 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =165.4, 141.0, 136.4, 132.5, 129.1, 129.1, 127.6, 125.3, 120.5, 117.1, 115.0, 59.3. The spectroscopic data are in accordance with those described in the literature.[41]

6. General procedure for IPrAgCl-catalyzed reduction of azobenzenes.

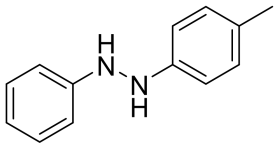
A mixture of ketone derivatives (0.2 mmol) and Ag-complex (5 mol%) were added to an oven dried high pressure tube under atmosphere of N_2. $PhSiH_3$ (2.2 equiv) and ^{i}PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25^{o}C for 24 h. After quenching with saturated NH_4Cl/H_2O (10 mL), the crude product was extracted with EtOAc (3×20 mL). The combined organic phases were dried over

anhydrous Na_2SO_4 and concentrated under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound.



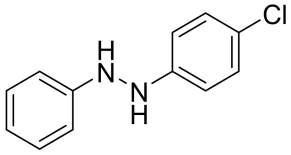
1,2-diphenylhydrazine(4a)

The general procedure was applied to 1,2-diphenylhydrazine (36.4 mg, 0.2 mmol) under an atmosphere of N_2 at 25 ºC for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow soild (33.9 mg, 92% yield); Melting point: 123.1-126.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 – 7.10 (m, 4H), 6.77 – 6.73 (m, 6H), 5.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =149.0, 129.5, 120.0, 112.4. The spectroscopic data are in accordance with those described in the literature.[42]



1-phenyl-2-(p-tolyl)hydrazine (4b)

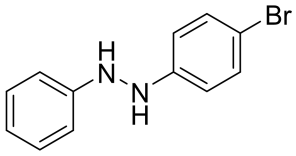
The general procedure was applied to 1-phenyl-2-(p-tolyl)hydrazine (39.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 ºC for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow soild (35.3 mg, 89% yield); Melting point: 83.1-84.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.28-7.16 (m, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.89 – 6.81 (m, 3H), 6.78 (d, J = 8.5 Hz, 2H), 5.59 (s, 1H), 5.53 (s,1H), 2.27 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ =149.2, 146.7, 130.0, 129.5, 129.3, 119.9, 112.6, 112.4, 20.6. The spectroscopic data are in accordance with those described in the literature.[42]



1-(4-chlorophenyl)-2-phenylhydrazine (4c)

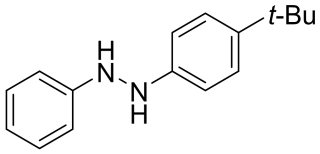
The general procedure was applied to 1-(4-chlorophenyl)-2-phenylhydrazine (43.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 ºC for 24 h. he crude product was purified

by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow soild (40.7 mg, 93% yield); Melting point: 67.2-68.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.12 (t, J = 7.3 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 682 – 6.64 (m, 5H), 5.46 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =148.5, 147.5, 129.5, 129.3, 124.4, 120.2, 113.6, 112.4. The spectroscopic data are in accordance with those described in the literature.[42]



1-(4-bromophenyl)-2-phenylhydrazine (4d)

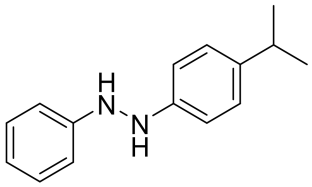
The general procedure was applied to 1-(4-bromophenyl)-2-phenylhydrazine (52.3 mg, 0.2 mmol) under an atmosphere of N_2 at 25 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow soild (47.4mg, 90% yield); Melting point: 69.8-70.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.9 Hz, 2H), 7.13 (t, J = 8.0 Hz, 2H), 6.82 – 6.67 (m, 3H), 6.64 (d, J = 8.8 Hz, 2H), 5.49 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =148.5, 148.0, 132.2, 129.5, 120.3, 114.0, 112.4, 111.6. The spectroscopic data are in accordance with those described in the literature.[42]



1-(4-(tert-butyl)phenyl)-2-phenylhydrazine(4e)

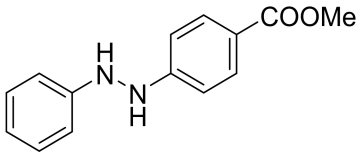
The general procedure was applied to 1-(4-(tert-butyl)phenyl)-2-phenylhydrazine (47.7 mg, 0.2 mmol) under an atmosphere of N_2 at 25 ^{o}C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow soild (38.4mg, 80% yield); Melting point: 38.9-39.6 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ =7.35 – 7.18 (m, 4H), 6.92 – 6.84 (m, 2H), 6.82 (d, J = 8.8 Hz, 2H), 5.58 (s, 1H), 5.56 (d, J=10.4 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =149.2, 146.6, 142.8, 129.4, 126.2, 119.9, 112.4, 112.2,

31.6. The spectroscopic data are in accordance with those described in the literature.[42]



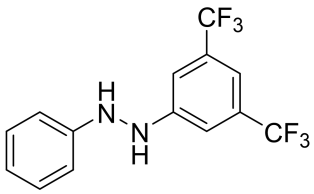
1-(4-isopropylphenyl)-2-phenylhydrazine (4f)

The general procedure was applied to 1-(4-isopropylphenyl)-2-phenylhydrazine (44.9 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow liquid (32.1 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.30 – 7.18 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.95 – 6.64 (m, 5H), 5.57 (s, 1H), 5.53 (s, 1H), 2.86 (hept, J = 7.0 Hz, 1H), 1.24 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =149.2, 147.0, 140.6, 129.5, 127.4, 119.9, 112.6, 112.5, 33.4, 24.3. The spectroscopic data are in accordance with those described in the literature.[24]



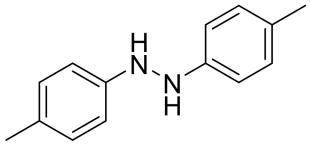
methyl 4-(2-phenylhydrazineyl)benzoate (4g)

The general procedure was applied to methyl 4-(2-phenylhydrazineyl)benzoate (48.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as yellow soild (33.9 mg, 70% yield); Melting point: 83.3-85.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.81 (d, J = 8.8 Hz, 2H), 7.26 – 7.06 (m, 2H), 6.85 – 6.56 (m, 5H), 5.89 (s, 1H), 5.64 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =167.2, 152.9, 148.1, 131.7, 129.5, 121.1, 120.5, 112.4, 111.2, 51.8. The spectroscopic data are in accordance with those described in the literature.[42]



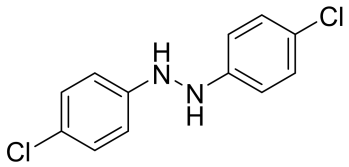
1-(3,5-bis(trifluoromethyl)phenyl)-2-phenylhydrazine (4h)

The general procedure was applied to 1-(3,5-bis(trifluoromethyl)phenyl)-2-phenylhydrazine (63.6 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h, IPrAgCl (10 mol%)The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale oily liquid (62.12 mg, 97% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ =7.41 – 7.17 (m, 5H), 6.94 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 5.89 (s, 1H), 5.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =150.2, 147.7, 134.5 (q, J = 17.8, 9.2 Hz), 133.8 (q, J = 33.3 Hz), 129.7, 127.9 (m), 124.9, 122.2, 121.1, 113.0, 112.7, 111.7. The spectroscopic data are in accordance with those described in the literature.[42]



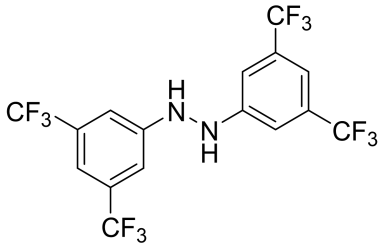
1,2-di-p-tolylhydrazine(4i)

The general procedure was applied to 1,2-di-p-tolylhydrazine (42.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as pale yellow soild (28.9 mg, 68% yield); Melting point: 146.6-147.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.03 (d, J = 8.4 Hz, 4H), 6.77 (d, J = 8.4 Hz, 4H), 5.50 (s, 2H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =146.8, 129.9, 129.2, 112.6, 20.6. The spectroscopic data are in accordance with those described in the literature.[42]



1,2-bis(4-chlorophenyl)hydrazine (4j)

The general procedure was applied to 1,2-bis(4-chlorophenyl)hydrazine (50.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as white soild (46.6 mg, 92% yield); Melting point: 126.3-127.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.17 (d, J = 8.9 Hz, 4H), 6.76 (d, J = 8.9 Hz, 4H), 5.62 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ =147.1, 129.4, 124.7, 113.6. The spectroscopic data are in accordance with those described in the literature.[42]



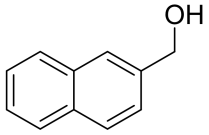
1,2-bis(3,5-bis(trifluoromethyl)phenyl)hydrazine (4k)

The general procedure was appliedto1,2-bis(3,5-bis(trifluoromethyl)phenyl)hydrazine (90.8 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as white soild (86.6 mg, 95% yield); Melting point: 295 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.39 (s, 2H), 7.29 (s, 4H), 6.12 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ =149.0, 133.2 (q, J = 33.2 Hz), 123.4 (q, J = 272.8 Hz), 114.3, 114.3, 114.2, 112.1, 112.1, 112.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ =-63.08. The spectroscopic data are in accordance with those described in the literature.[42]

7. General procedure for IPrAgCl-catalyzed hydrogenation of aldehyde and ketone.

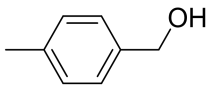
A mixture of aldehyde or ketone derivatives (0.2 mmol) and IPrAgCl (1 mol%) were added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$ (2.2 equiv) and ^{i}PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25°C for 24 h. After quenching with saturated NH_4Cl/H_2O (10 mL), the crude product was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum, the crude product was purified by

column chromatography to afford the desired hydrogenation compound.



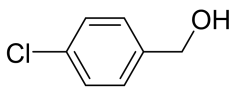
2-Naphthalenemethanol (6a)

The general procedure was applied to 2-naphthaldehyde (31.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white solid (31.0 mg, 98% yield); Melting point: 80.3-81.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.84-7.79 (m, 3H), 7.76 (s, 1H), 7.44-7.38 (m, 3H), 5.29 (t, J = 5.7 Hz, 1H), 4.62 (q, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-D_6): δ = 140.2, 132.9, 132.2, 127.6, 127.6, 127.6, 126.1, 125.5, 125.3, 124.3, 63.0. The spectroscopic data are in accordance with those described in the literature.[43]



***p*-Tolylmethanol (6b)**

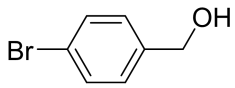
The general procedure was applied to 4-methylbenzaldehyde (24.0 mg, 0.2 mmol) under an atmosphere of N_2 at 25°C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white solid (17.1mg, 70% yield); Melting point: 61.5-62.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 4.54 (s, 2H), 2.27 (s, 3H), 1.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 137.8, 137.3, 129.2, 127.1, 65.1, 21.1 The spectroscopic data are in accordance with those described in the literature.[44]



(4-Chlorophenyl)methanol (6c)

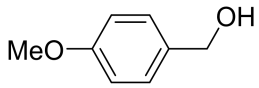
The general procedure was applied to 4-chlorobenzaldehyde (28.1 mg, 0.2 mmol)

under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=2:1) to afford the title compound as white solid (26.2 mg, 92% yield); Melting point: 74.2-76.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.26-7.17 (m, 4H), 4.56 (s, 2H), 2.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 139.2, 133.3, 128.6, 128.2, 64.4. The spectroscopic data are in accordance with those described in the literature.[45]



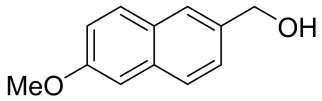
(4-bromophenyl)methanol (6d)

The general procedure was applied to (4-bromophenyl)methanol (37.0 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white solid (28.4 mg, 76% yield); Melting point: 76.5-77.0 °C;[1] H NMR (400 MHz, $CDCl_3$): δ =7.50-7.43 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.63 (s, 2H), 2.00 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =139.8, 131.7, 128.7, 121.6, 64.7. The spectroscopic data are in accordance with those described in the literature.[46]



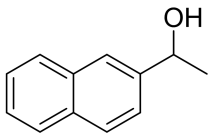
(4-Methoxyphenyl)methanol (6e)

The general procedure was applied to 4-methoxybenzaldehyde (27.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=2:1) to afford the title compound as yellow oily liquid (19.4 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.20 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 4.52 (s, 2H), 3.73 (s, 3H), 1.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.1, 133.1, 128.6, 113.9, 64.9, 55.2. The spectroscopic data are in accordance with those described in the literature.[44]



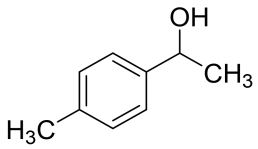
(6-Methoxynaphthalen-2-yl)methanol (6f)

The general procedure was applied to 6-methoxy-2-naphthaldehyde (37.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=2:1) to afford the title compound as white solid (30.5 mg, 81% yield); Melting point: 113.5-114.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.70 (t, J = 8.0 Hz, 2H), 7.66 (s, 1H), 7.35 (dd, J = 8.4, 1.7 Hz, 1H), 7.21 (d, J = 2.6 Hz, 1H), 7.06 (dd, J = 9.0, 2.6 Hz, 1H), 5.22 (t, J = 5.7 Hz, 1H), 4.55 (d, J = 5.7 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 157.0, 137.8, 133.5, 129.2, 128.4, 126.6, 125.9, 124.5, 118.6, 105.9, 63.1, 55.2. The spectroscopic data are in accordance with those described in the literature.[45]



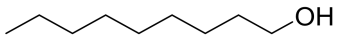
1-(Naphthalen-2-yl)ethanol (6g)

The general procedure was applied to 1-(naphthalen-2-yl)ethanone (34.1 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as white soild (33.4 mg, 97% yield). Melting point: 71.5-72.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.73 (m, 4H), 7.56-7.43 (m, 3H), 5.08 (dd, J = 6.5, 1.6 Hz, 1H), 1.98 (s, 1H), 1.59 (dd, J = 6.4, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =143.1, 133.3, 132.9, 128.3, 127.9, 127.7, 126.2, 125.8, 123.8, 70.5, 25.1. The spectroscopic data are in accordance with those described in the literature.[45]



1-(p-tolyl)ethanol (6h)

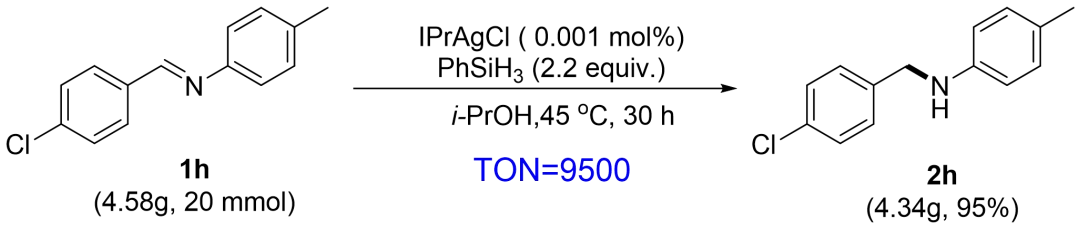
The general procedure was applied to 1-(*p*-tolyl)ethanone (26.8 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=5:1) to afford the title compound as oily liquid (19.3 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.19 (d, J = 6.3 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H), 4.79 (q, J = 6.5 Hz, 1H), 2.27 (s, 3H), 1.74 (s, 1H), 1.41 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =142.8, 137.2, 129.2, 125.3, 70.2, 25.1, 21.1. The spectroscopic data are in accordance with those described in the literature.[45]



1-Nonanol

The general procedure was applied to 1-Nonanal (37.2 mg, 0.2 mmol) under an atmosphere of N_2 at 25 °C for 24 h. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the title compound as colorless liquid (11.5 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ =3.63 (t, J = 6.7 Hz, 2H), 1.56 (p, J = 6.7 Hz, 2H), 1.44 (s, 1H), 1.41 – 1.06 (m, 12H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 62.1, 31.8, 30.9, 28.6, 28.4, 28.3, 24.7, 21.7, 13.1. The spectroscopic data are in accordance with those described in the literature.[47]

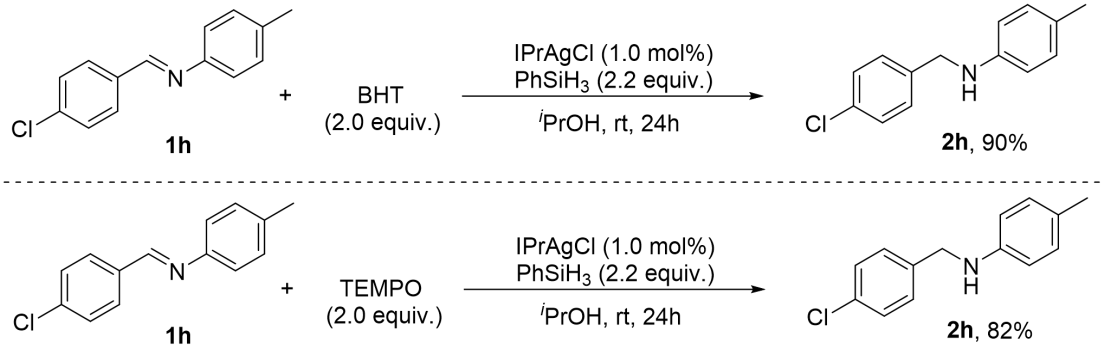
8. Gram-scale hydrogenation of 1h



A mix of substrate **1h** (18 mmol) and IPrAgCl (0.0011 g) were added to an oven dried high pressure tube under atmosphere of nitrogen, $PhSiH_3$ (2.2 equiv) and *i*-PrOH (225 mL) were added by syringe. The reaction mixture was stirred at 45 °C for 30 h. After quenched with NH_4Cl/H_2O (30 mL) and extracted with EtOAc (3×40 mL). The

combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the compound **2h.**

9. Control experiments and Deuteration experiments



A mix of substrate **1h** (0.2 mmol) and IPrAgCl (0.0011 g) were added to an oven dried high pressure tube under atmosphere of nitrogen, $PhSiH_3$ (2.2 equiv) and *i*-PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25 °C for 24 h. After quenched with NH_4Cl/H_2O (4 mL) and extracted with EtOAc (3×5 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc=10:1) to afford the compound **2h.**

10. Preparation of Silver hydride Complexes

In a nitrogen-filled glovebox a vial was charged with IPrAgCl (26.5 mg,0.05 mmol), THF-d_8 (2 mL) or C_6D_6 was added followed by $PhSiH_3$ (6.8μL, 1.1 equiv). The reaction was stirred at rt in the glovebox for 10 min, 10 h and 20 h, respectively. The reaction mixture was transferred to a NMR tube, which was sealed, before removed from the glovebox. The sample was analyzed by ^1H NMR.

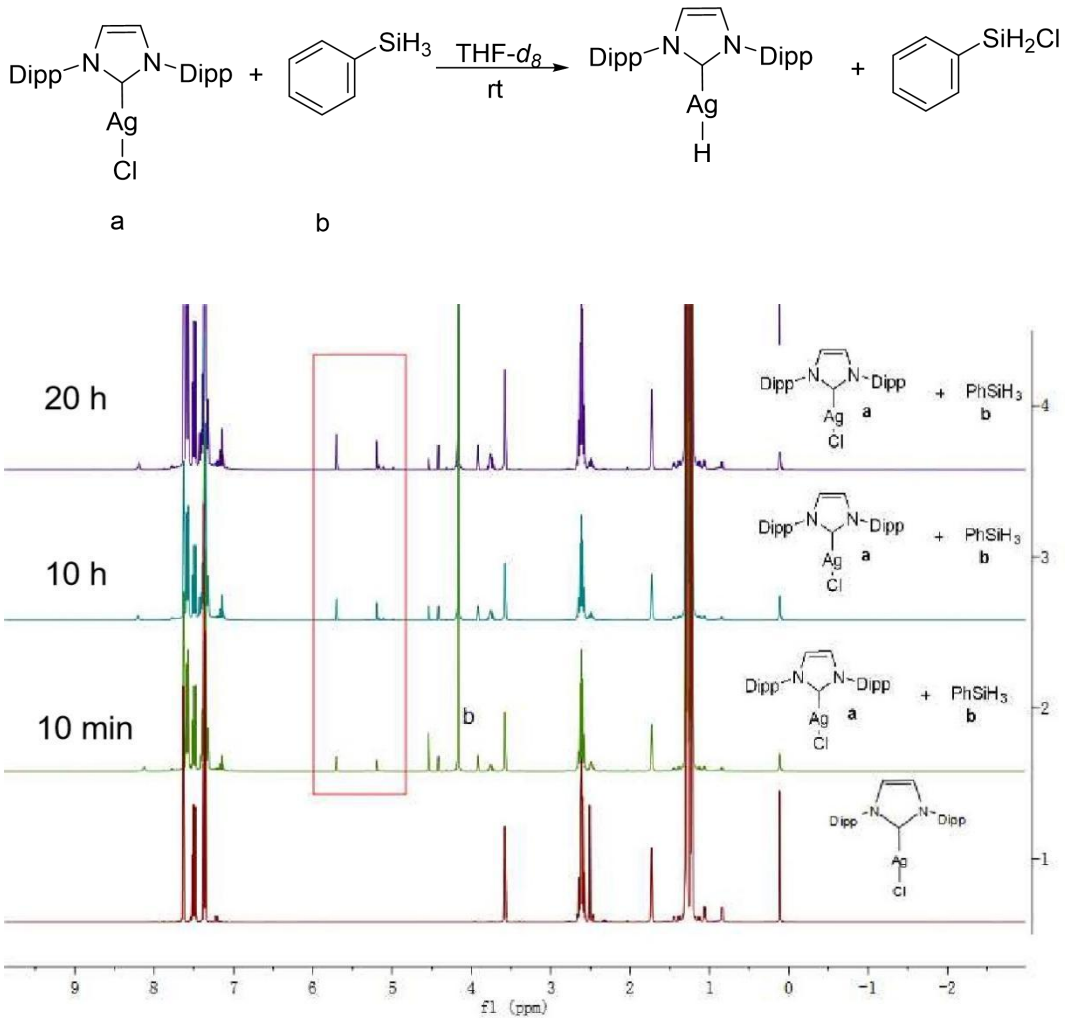


Figure S1. ^{1}H NMR spectra of the silver hydride inTHF-d_8

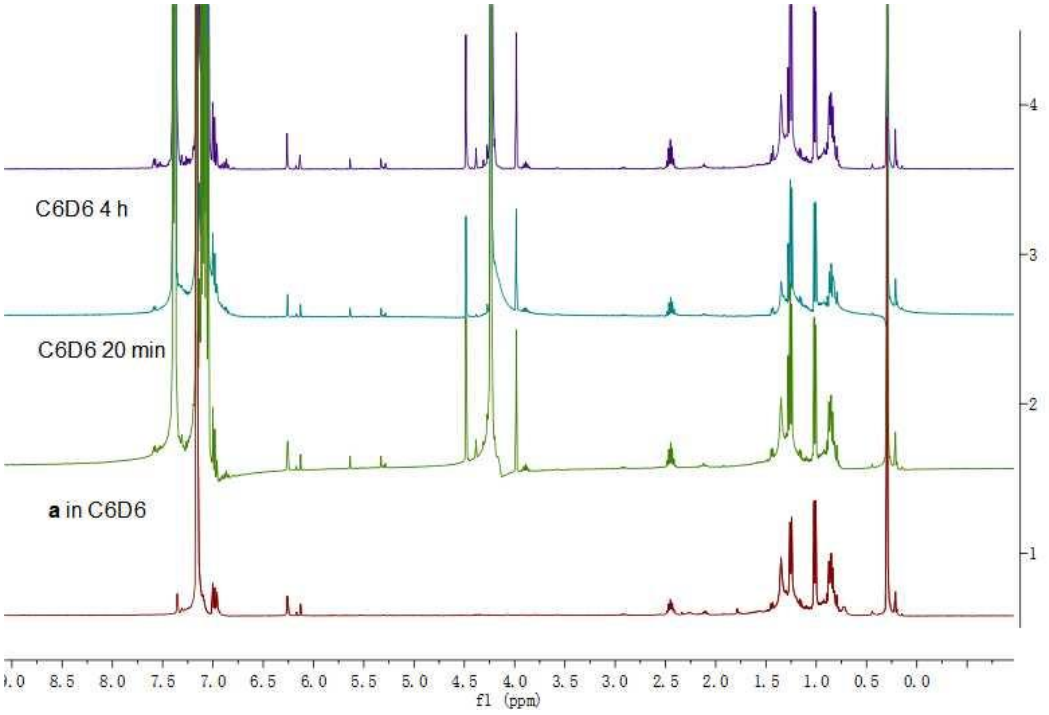


Figure S2. ^{1}H NMR spectra of the silver hydride in C_6D_6

11. Studying the reaction profile of hydrogenation of 1h

Kinetic studies were performed by treating **1h** (0.2 mmol) with IPrAgCl (1mol %), $PhSiH_3$ (2.2 equiv) and *i*-PrOH (2.5 mL) at 25 °C. The yield of **2h** and the recovery of **1h** were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The data points for reaction profiles were collected by performing multiple batches of the reaction with different reaction times.

Table S7. Studying the reaction profile of hydrogenation of 1h.

Time (h)	Yield of **2h** (%)	Recovery of **1h** (%)
0	0	1
0.083	0.20	0.75
0.167	0.26	0.65
0.25	0.33	0.61
0.333	0.40	0.54
0.417	0.46	0.50

0.5	0.69	0.25
1	0.91	0.08
1.5	0.91	0.08
2	0.92	0.07
4	0.92	0.05
8	0.92	0
12	0.92	0

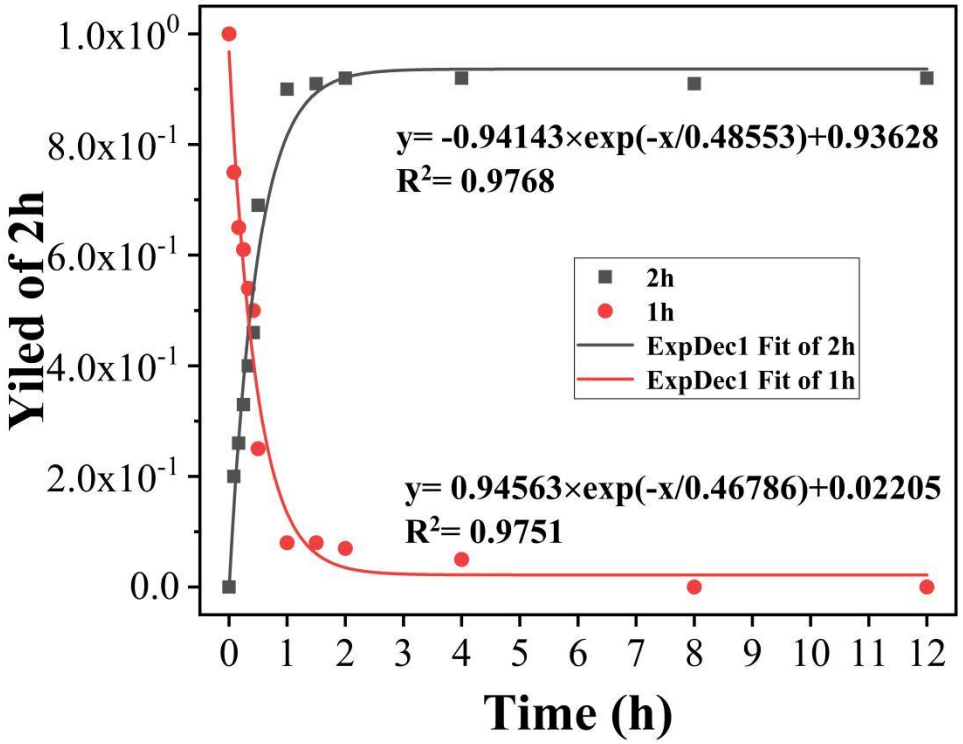


Figure S3. Reaction profile (exponential fit) for Ag-catalyzed hydrogenation of **1h**

12. Kinetic experiments by initial rate measurements for hydrogenation of 1h.

Procedure for determining the order in Substrate 1h

Substrate **1h** (0.1~0.6 mmol), and IPrAgCl (1 mol%) were added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$ (1.5 equiv) and *i*PrOH (2 mL) were added by syringe. The reaction mixture was stirred at 25 °C for 4 min. The

reaction was quenched and 1,3,5-trimethoxy benzene (0.0336 g, 0.20 mmol) was added as an internal standard for NMR analysis. Plots of the initial rate data for **2h** are shown below.

Table S8. Initial rate data obtained by varying the concentration of 1h

Entry	**1h**	$PhSiH_3$	MeOH	**1h** [M]	Initial rate [M/min]
1	0.1 mmol	0.054 mL	2.5 mL	0.03915	0.00223
2	0.2 mmol	0.054 mL	2.5 mL	0.07831	0.00271
3	0.3 mmol	0.054 mL	2.5 mL	0.1175	0.003
4	0.4 mmol	0.054 mL	2.5 mL	0.1566	0.00333
5	0.5 mmol	0.054 mL	2.5 mL	0.1958	0.00367
6	0.6 mmol	0.054 mL	2.5 mL	0.23492	0.00399

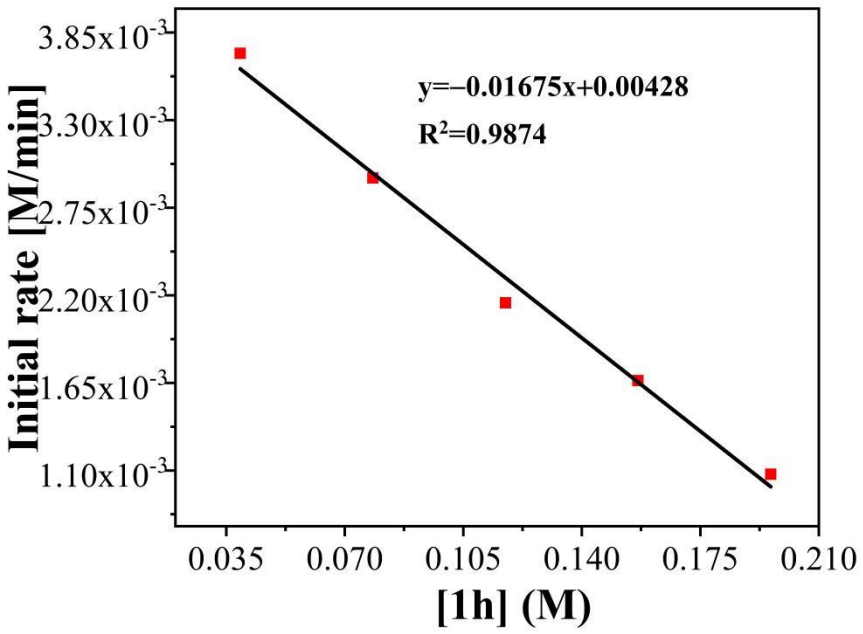


Figure S4. Plot of initial rate vs concentration of **1h**

Procedure for determining the order in IPrAgCl

Substrate **1h** (0.2mmol), and IPrAgCl (1mol%~6mol%) were added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$(2.2 equiv) and *i*PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25 °C for 4 min. The reaction was quenched and 1,3,5-trimethoxy benzene (0.0336, 0.20 mmol) was added

as an internal standard for NMR analysis. Plots of the initial rate data for **2h** are shown below.

Table S9. Initial rate data obtained by varying the concentration of IPrAgCl.

Entry	IPrAgCl (Xmol%)	$PhSiH_3$	MeOH	IPrAgCl [M]	Initial rate [M/min]
1	0.5	54	2.5 ml	0.000039154	0.003915
2	1	54	2.5 ml	0.0007831	0.005286
3	1.5	54	2.5 ml	0.0011746	0.006264
4	2	54	2.5 ml	0.001566	0.006852
5	2.5	54	2.5 ml	0.001958	0.007818
6	3	54	2.5 ml	0.0023492	0.0086139

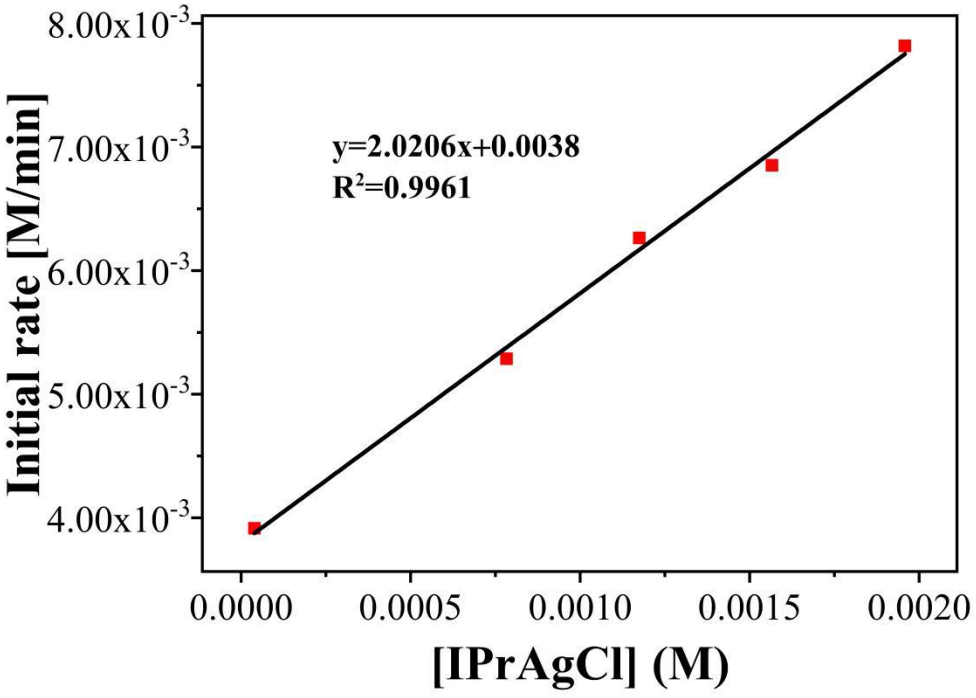


Figure S5. Plot of initial rate vs concentration of IPrAgCl

Procedure for determining the order in $PhSiH_3$

Substrate **1h** (0.2mmol), and IPrAgCl (1 mol%) were added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$ (1eq~3.4 eq) and *i*-PrOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 25 °C for 4 min. The

reaction was quenched and 1,3,5-trimethoxy benzene (0.0336, 0.20 mmol) was added as an internal standard for NMR analysis. Plots of the initial rate data for **2h** are shown below.

Table S10. Initial rate data obtained by varying the concentration of $PhSiH_3$

Entry	$PhSiH_3$ (equiv.)	MeOH	V	Si-H [M]	Initial rate [M/min]
1	1	2.5 ml	2.525	0.079207	0.003862
2	1.6	2.5 ml	2.540	0.12598	0.003937
3	2.2	2.5 ml	2.554	0.17227	0.003915
4	2.8	2.5 ml	2.569	0.217983	0.003892
5	3.4	2.5 ml	2.584	0.263157	0.004063

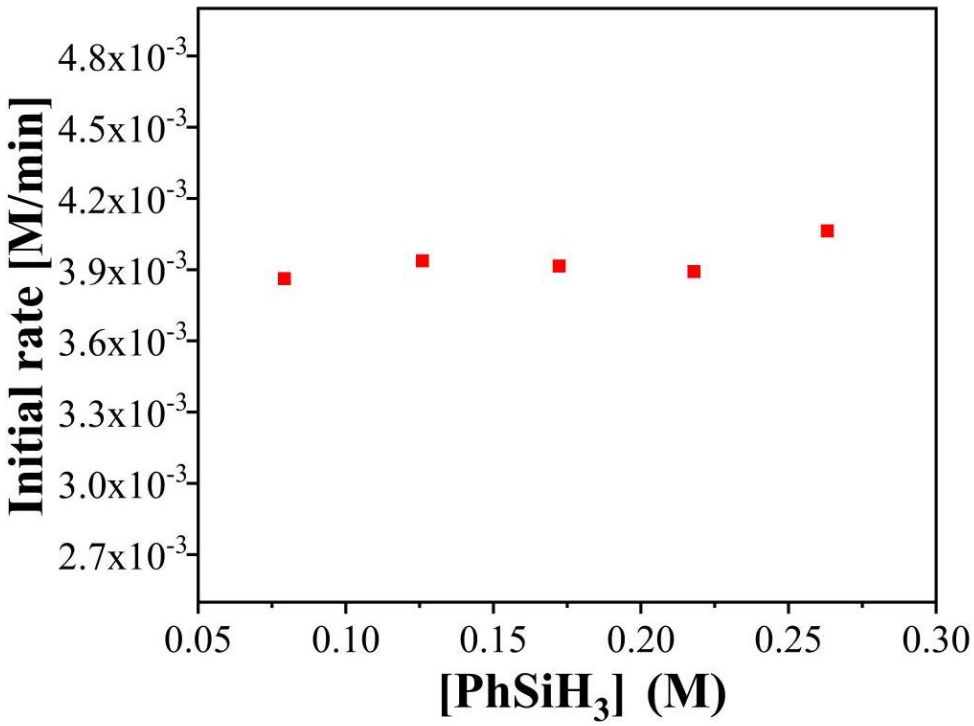


Figure S6. Plot of initial rate vs concentration of $PhSiH_3$

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13. ^{1}H, ^{13}C and ^{19}F NMR Spectra

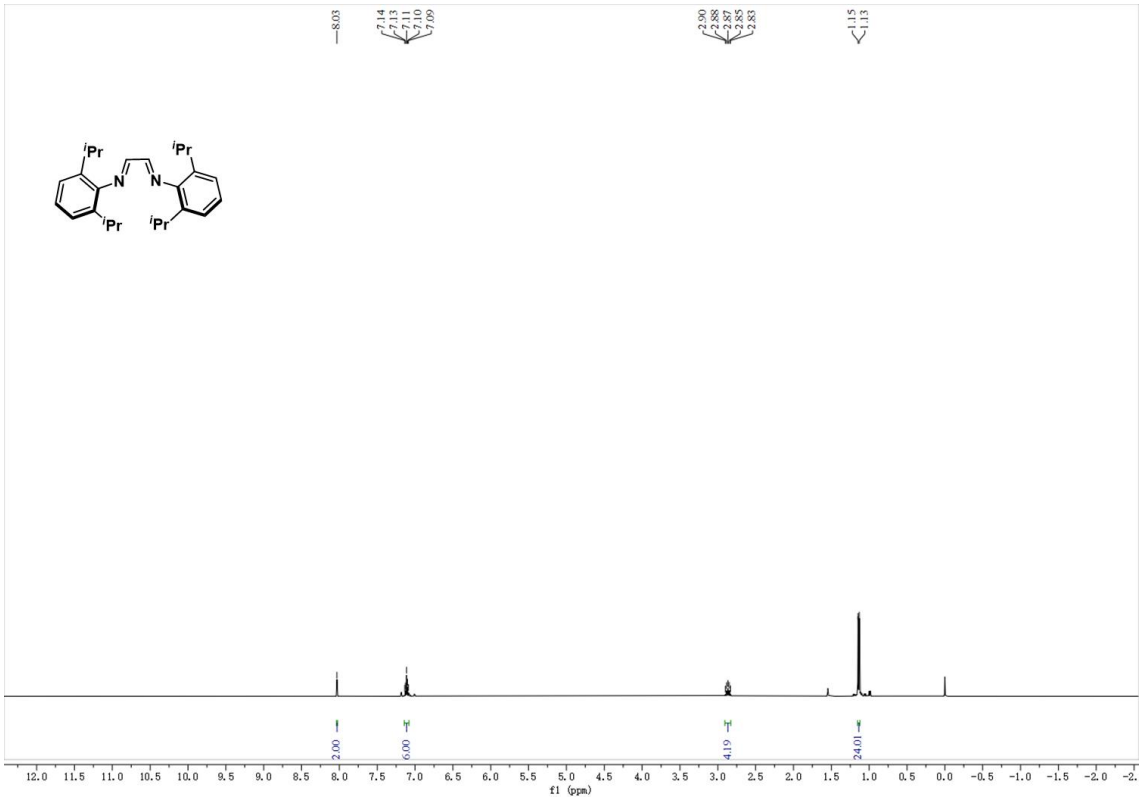

Figure S7. ^{1}H NMR spectrum of compound N^{1},N^{2}-1,4-Bis(2,6-diisopropylphenyl)ethane-1,2-diimine

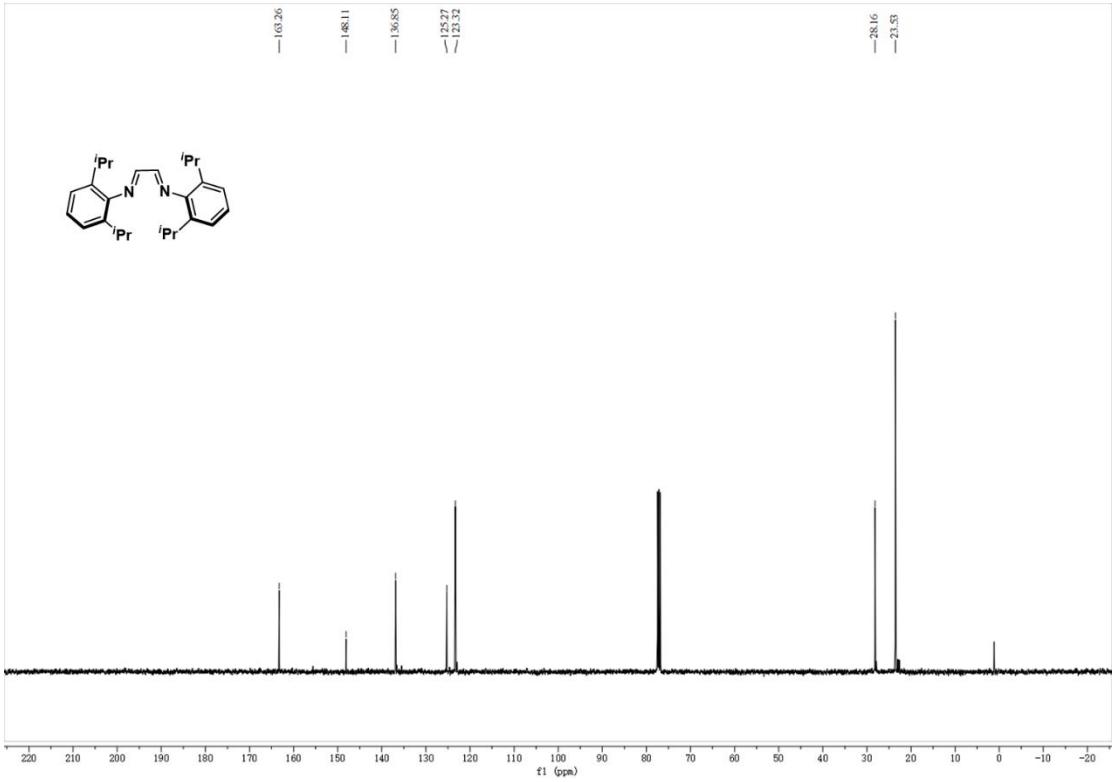

Figure S8. ^{13}C NMR spectrum of compound N^{1},N^{2}-1,4-Bis(2,6-diisopropylphenyl)ethane-1,2-diimine

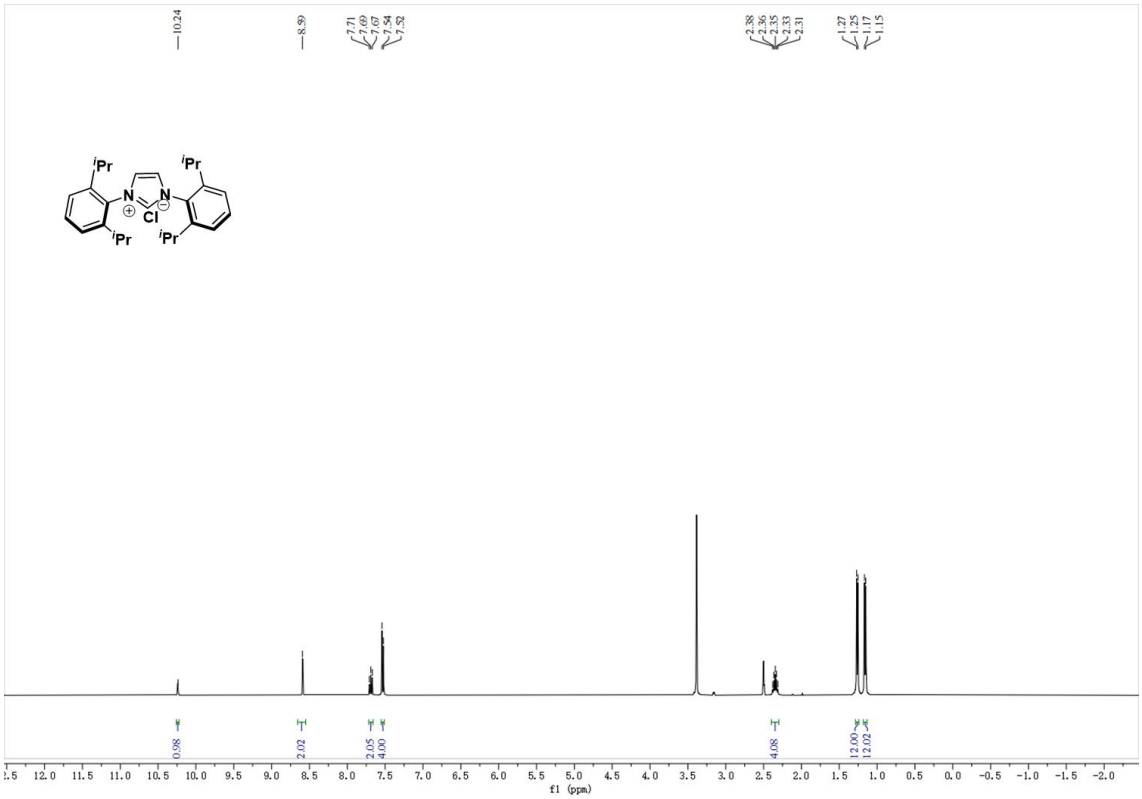

Figure S9. ^{1}H NMR spectrum of compound *N,N*'-1,4-Bis(2,6-diisopropylphenyl)imidazolium chloride

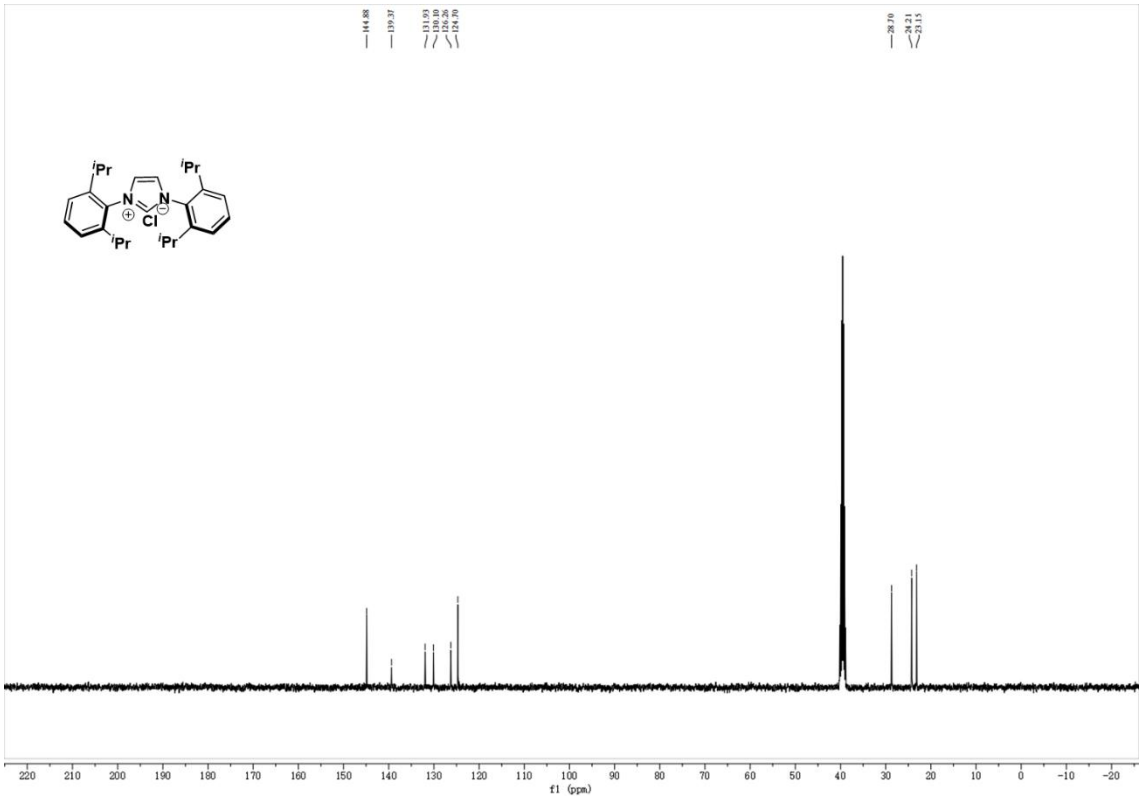

Figure S10. ^{13}C NMR spectrum of compound *N,N*'-1,4-Bis(2,6-diisopropylphenyl)imidazolium chloride

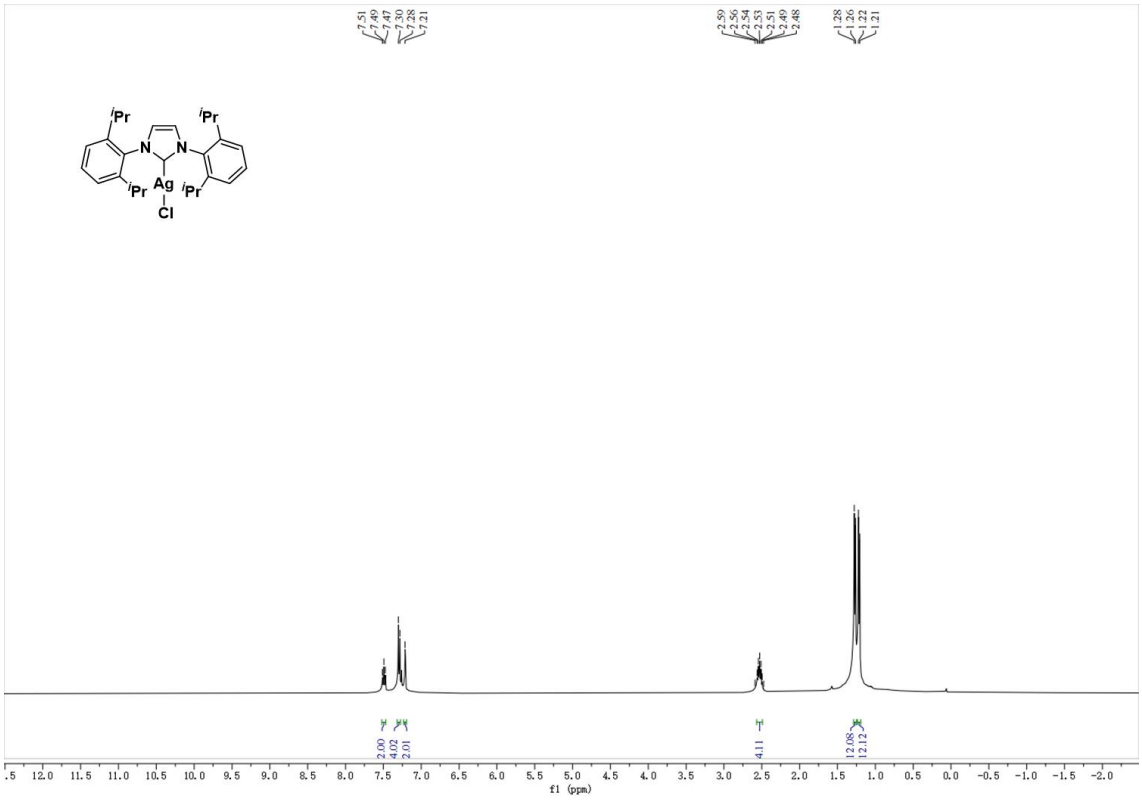

Figure 11. ^{1}H NMR spectrum of compound IPrAgCl complex

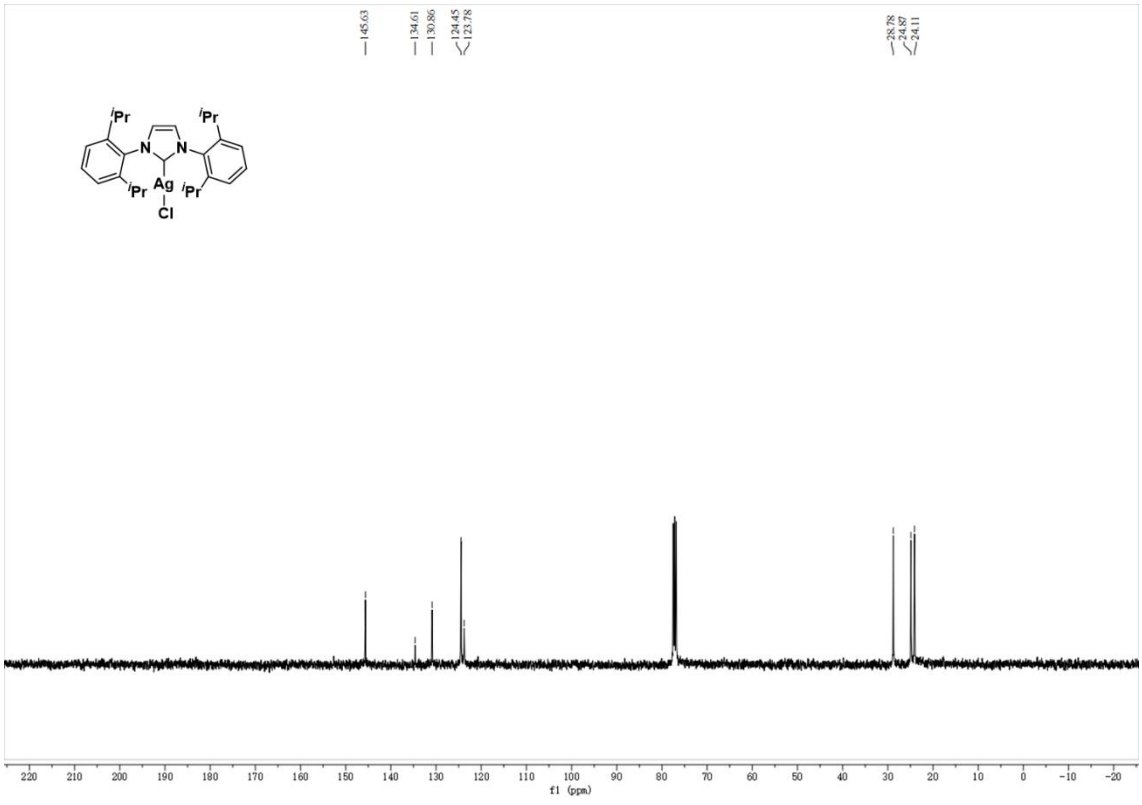

Figure S12. ^{13}C NMR spectrum of compound IPrAgCl complex

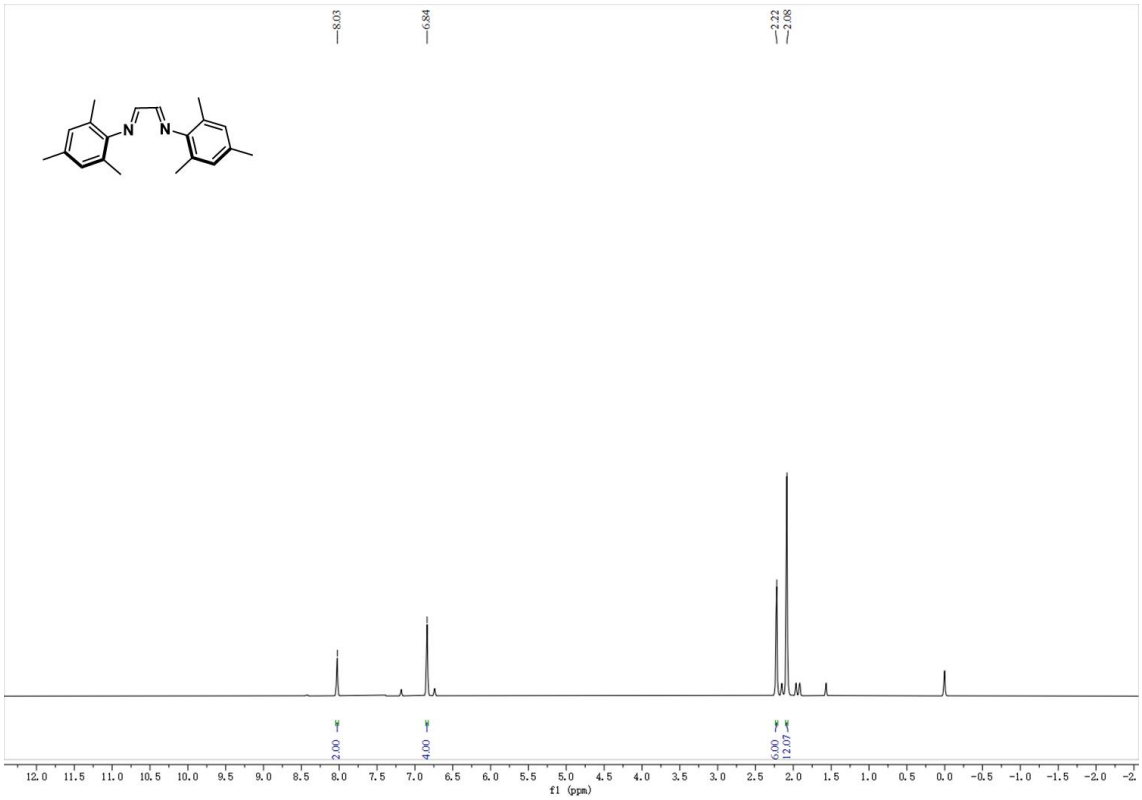

Figure S13. ^{1}H NMR spectrum of compound N^{1},N^{2}-dimesitylethane-1,2-diimine

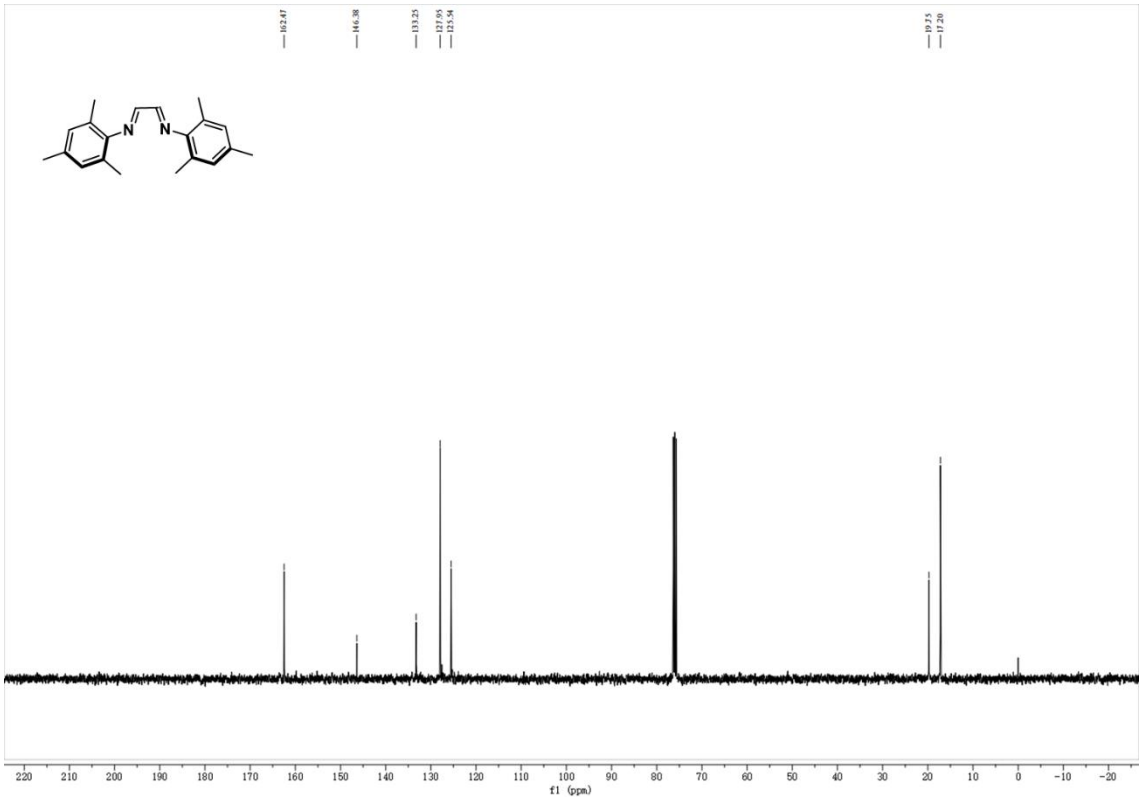

Figure S14. ^{13}C NMR spectrum of compound N^{1},N^{2}-dimesitylethane-1,2-diimine

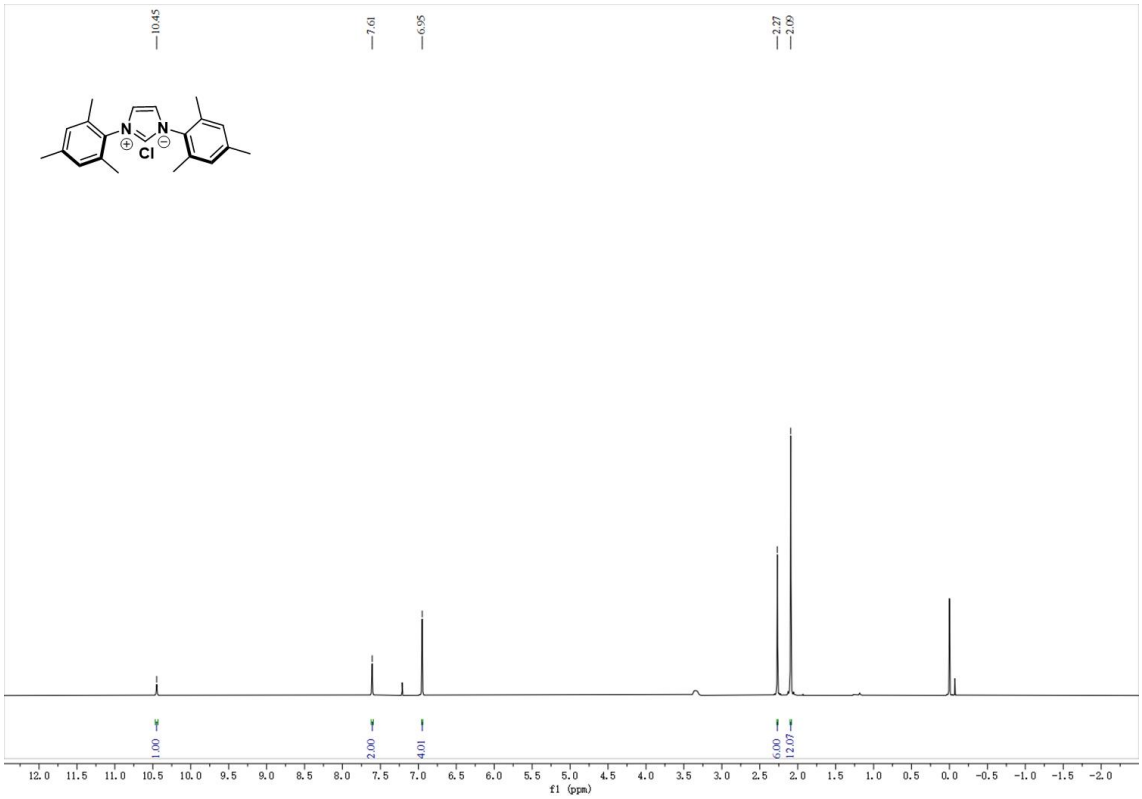

Figure S15. ^{1}H NMR spectrum of compound N^{1},N^{2}-dimesitylethane imidazolium chloride

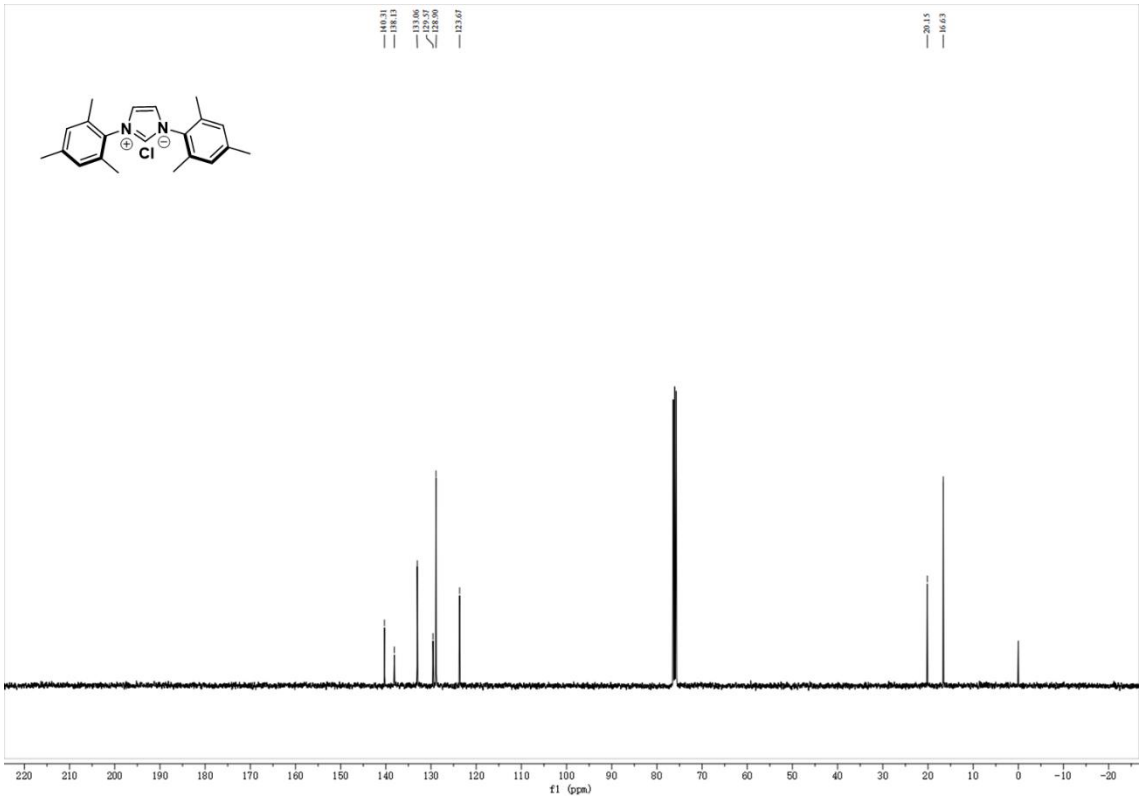

Figure S16. ^{13}C NMR spectrum of compound N^{1},N^{2}-dimesitylethane imidazolium chloride

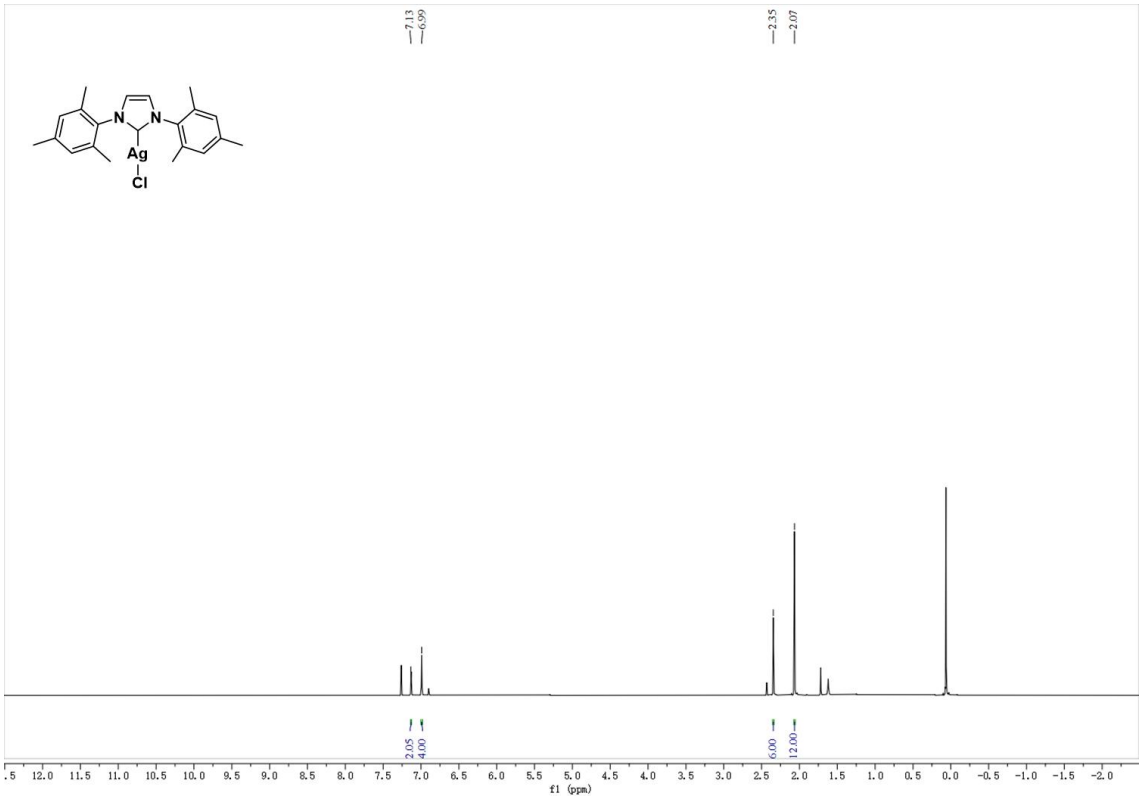

Figure S17. ^{1}H NMR spectrum of compound IMesAgCl complex

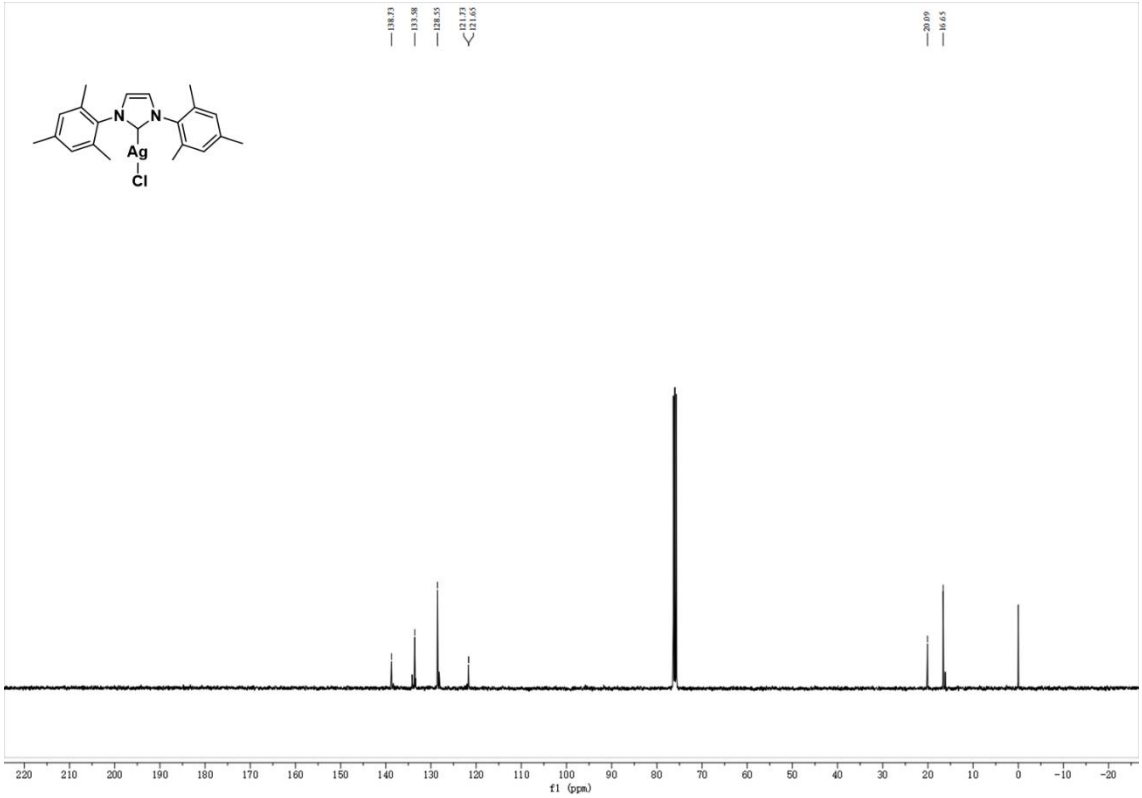

Figure S18. ^{13}C NMR spectrum of compound IMesAgCl complex

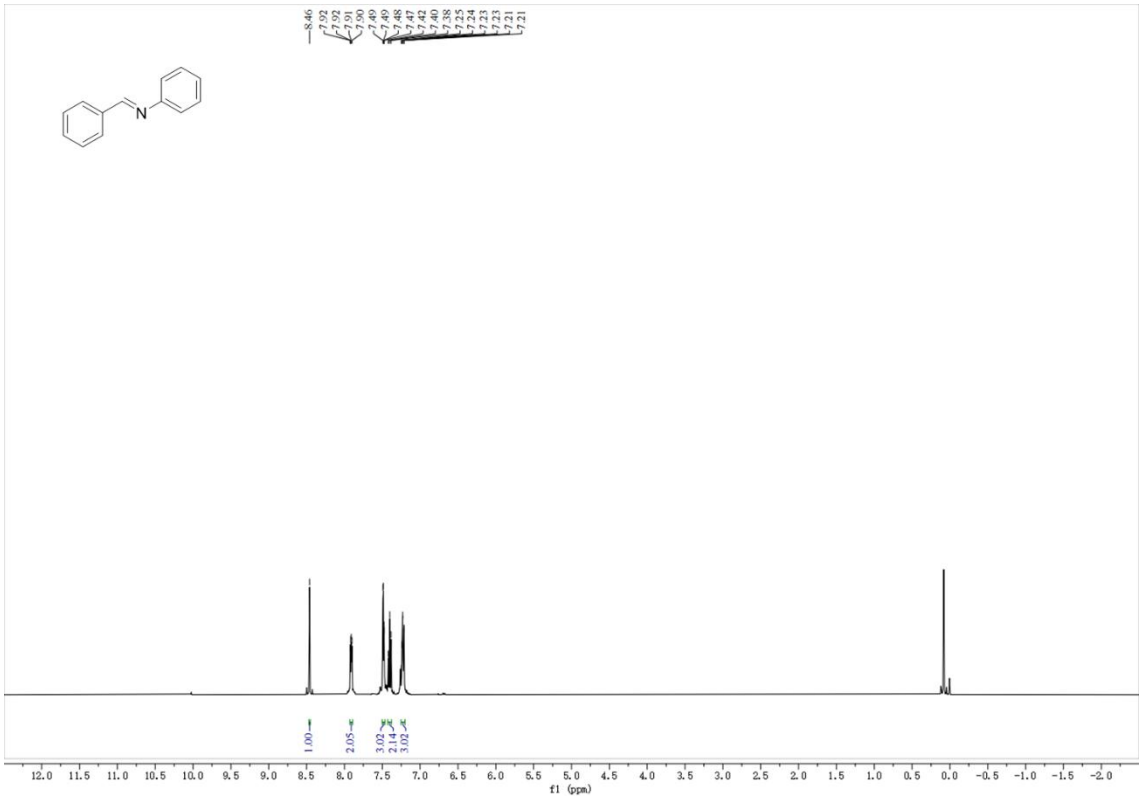

Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a**

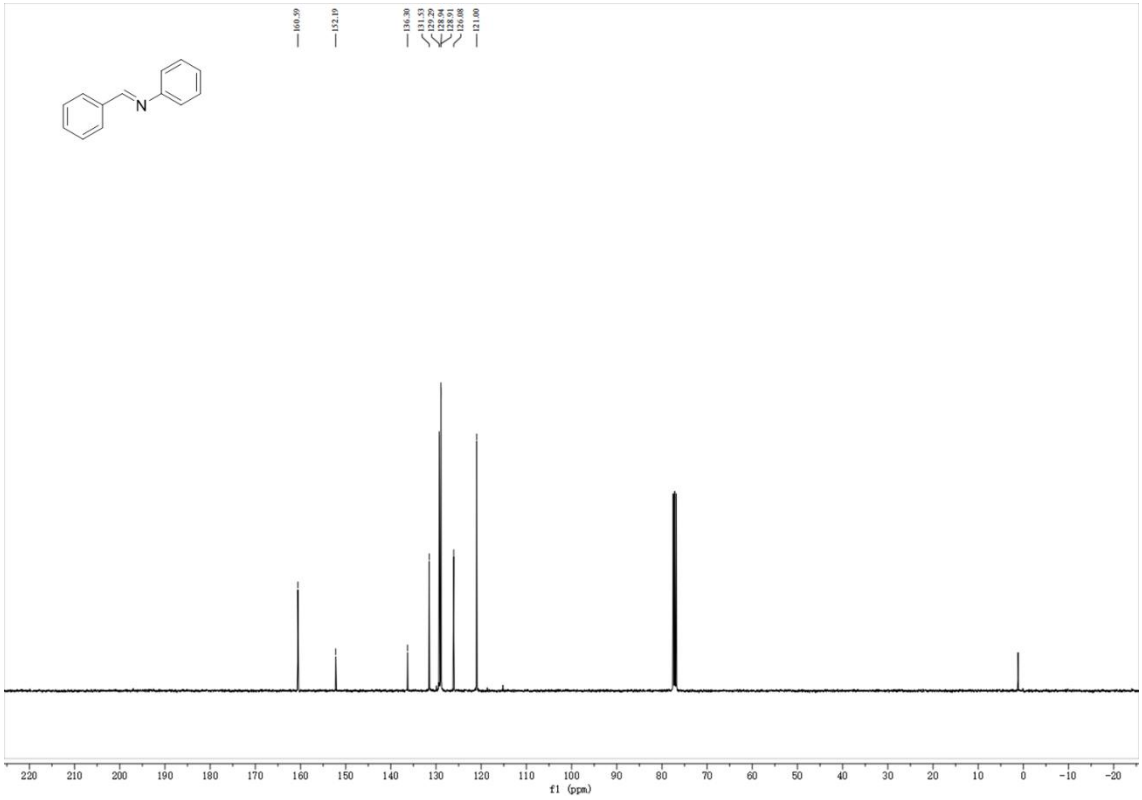

Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1a**

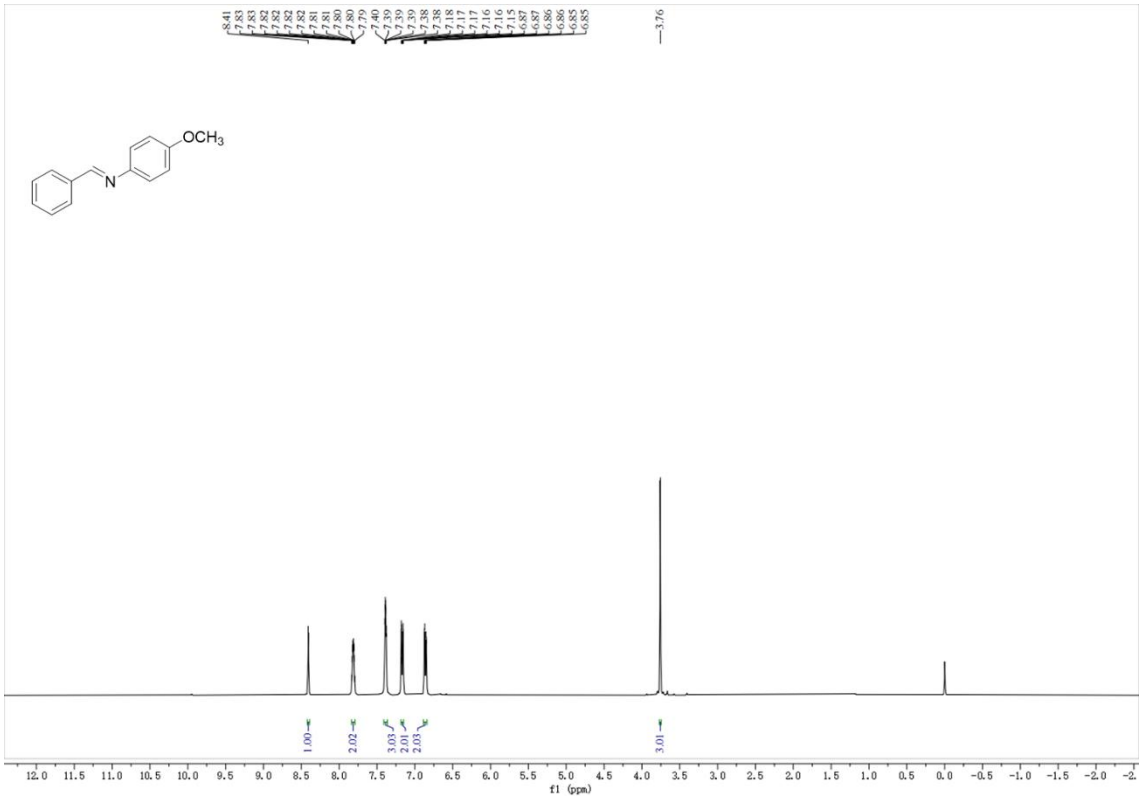

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**

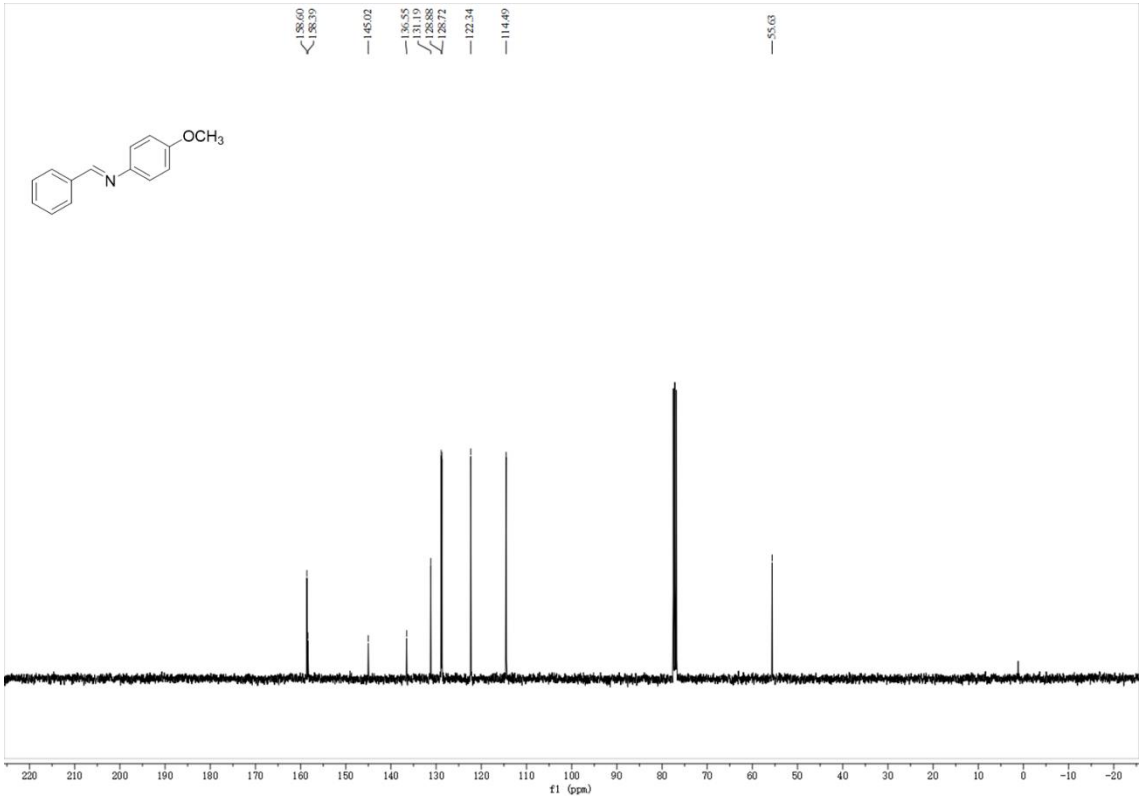

Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1b**

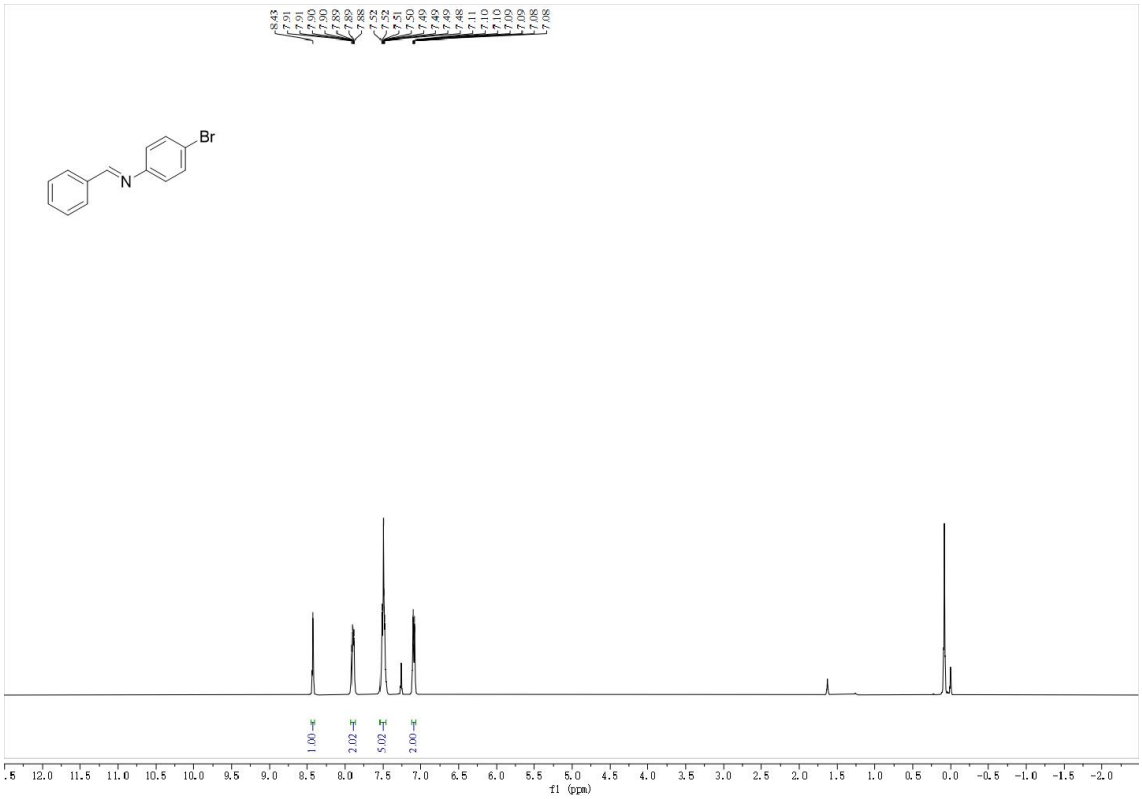

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**

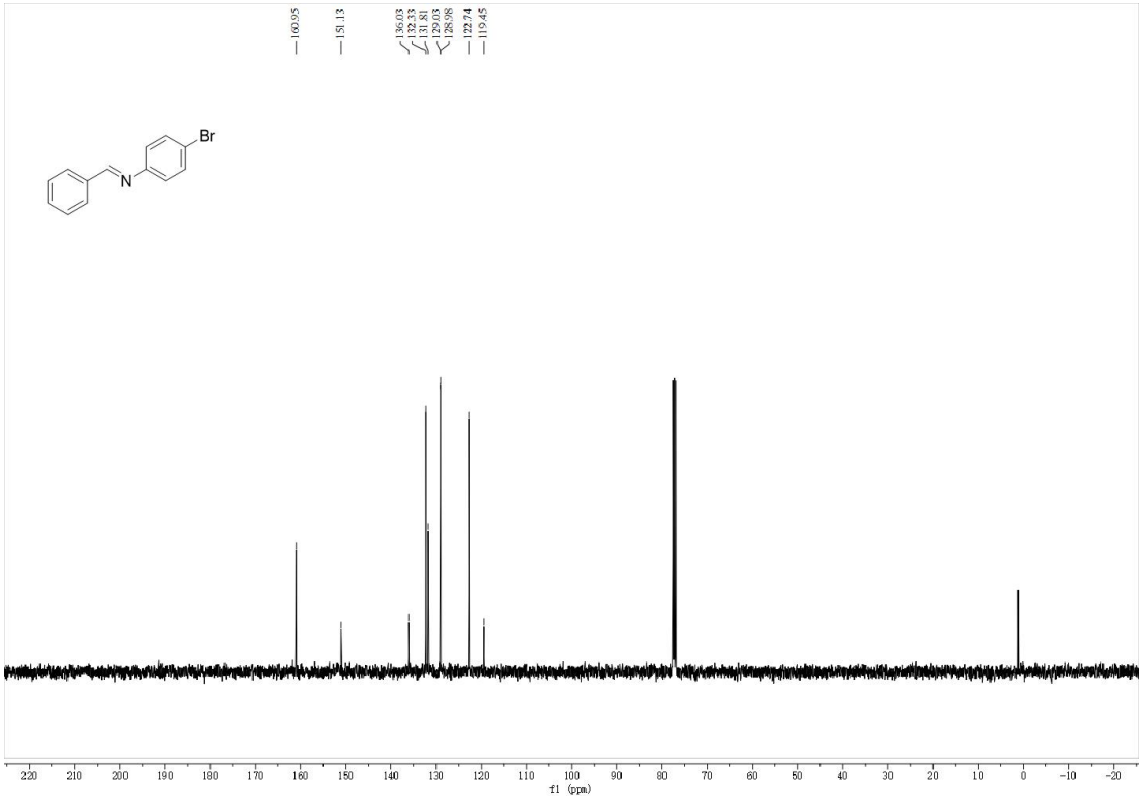

Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1c**

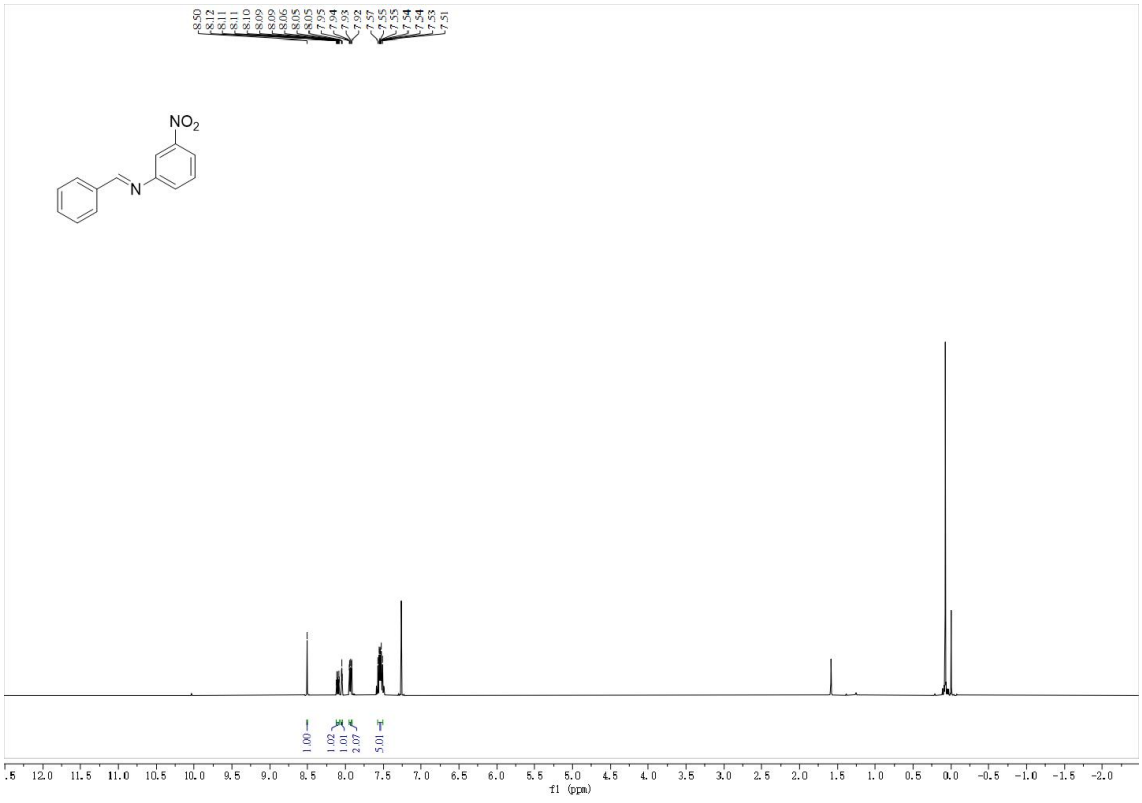

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**

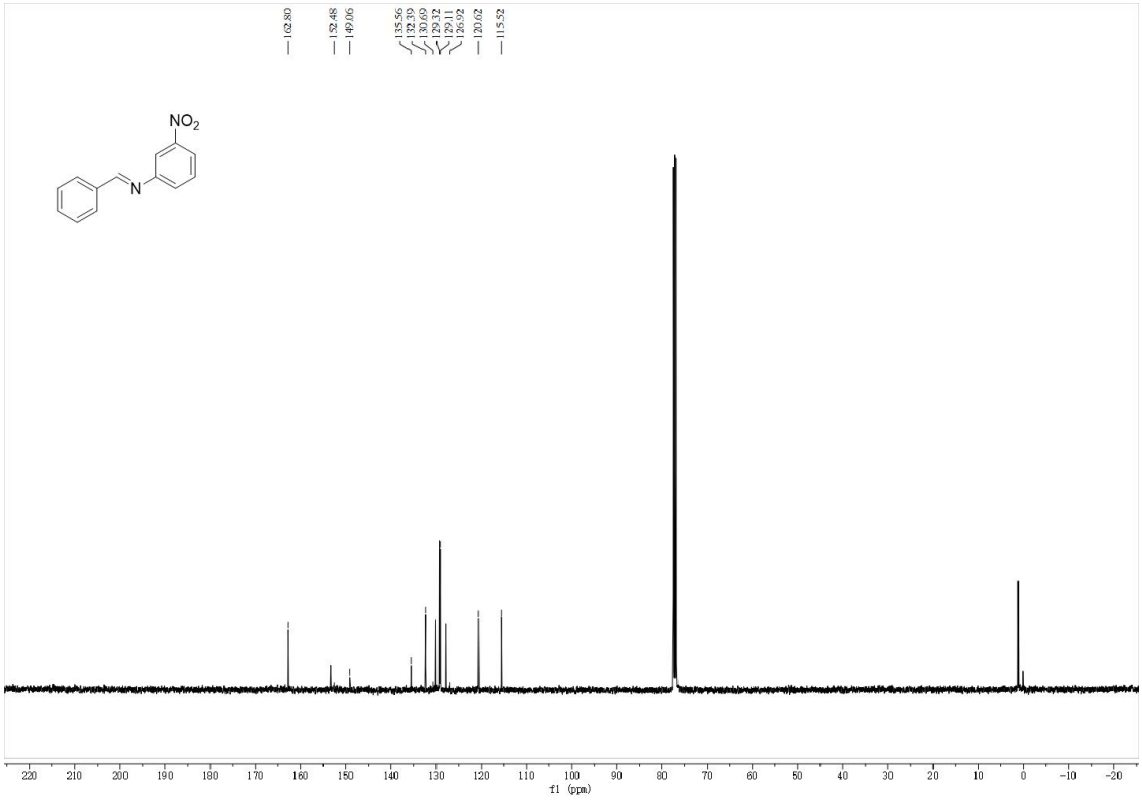

Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1d**

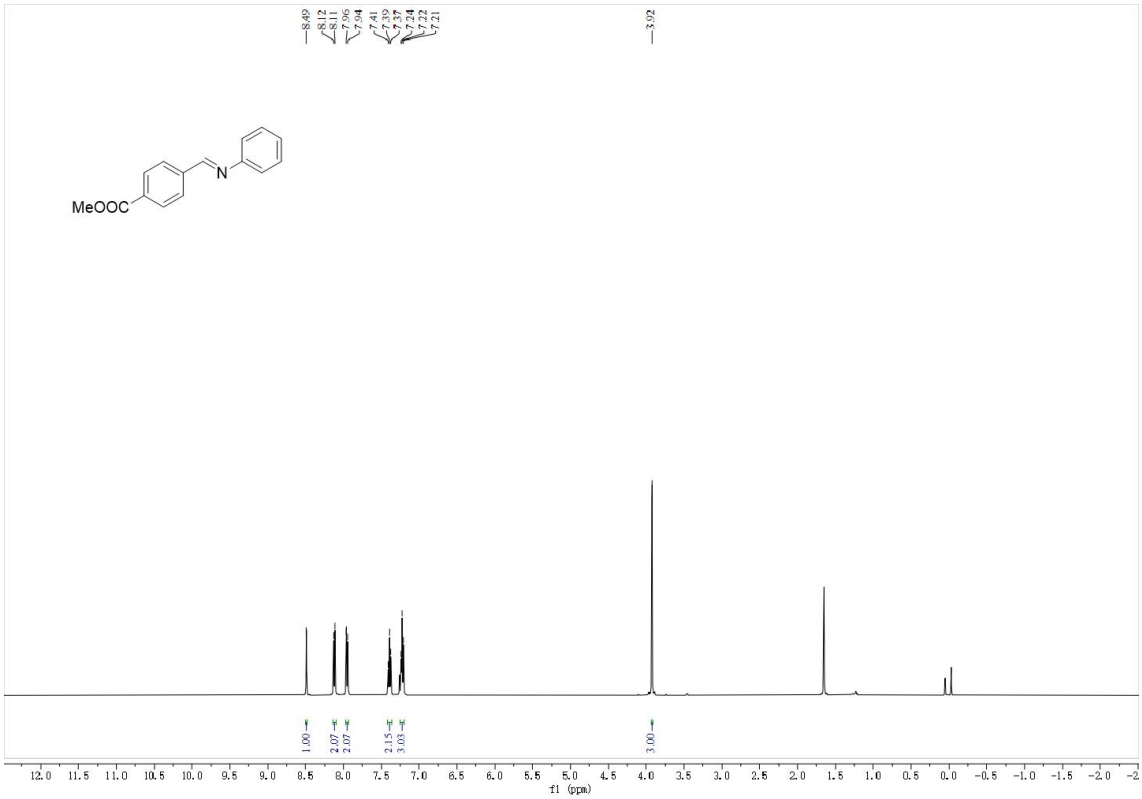

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**

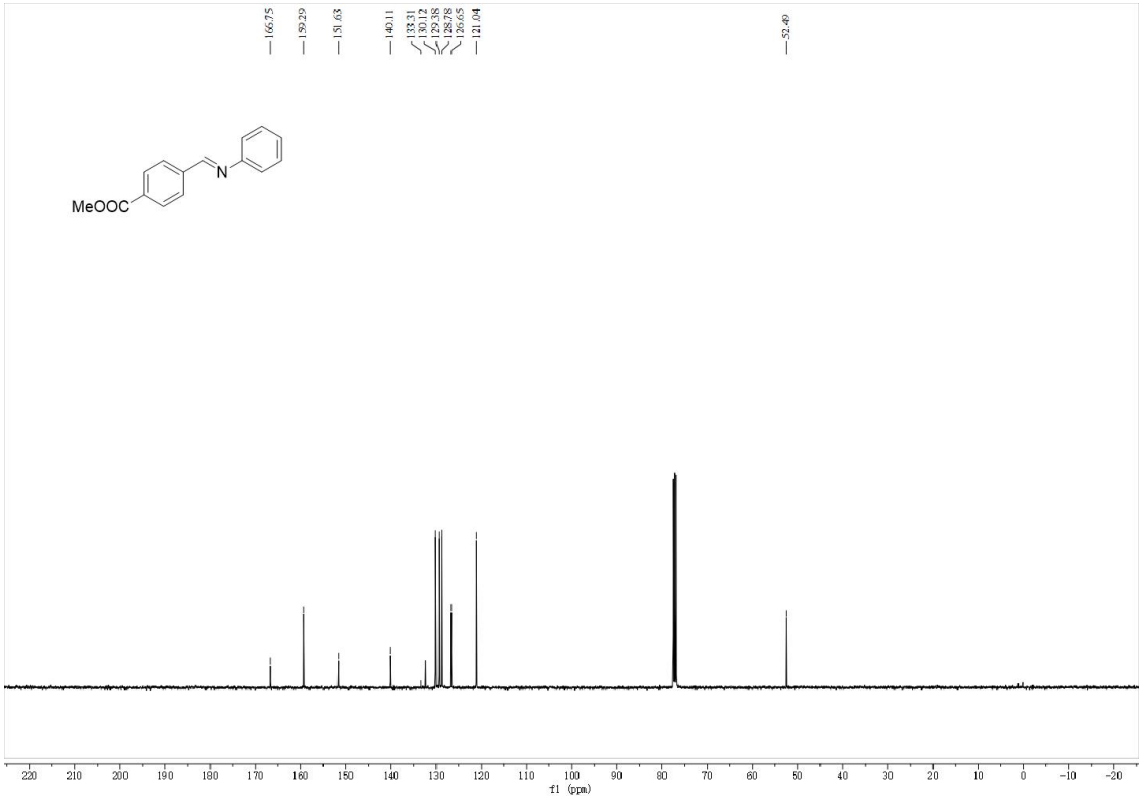

Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1e**

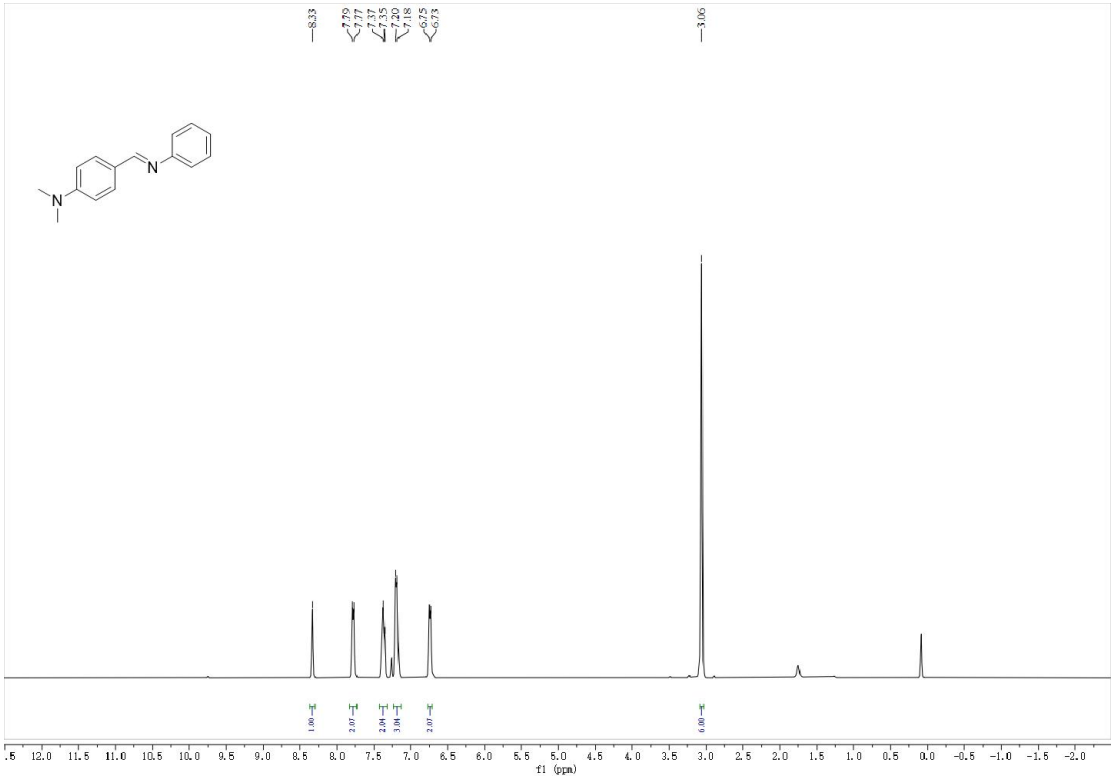

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**

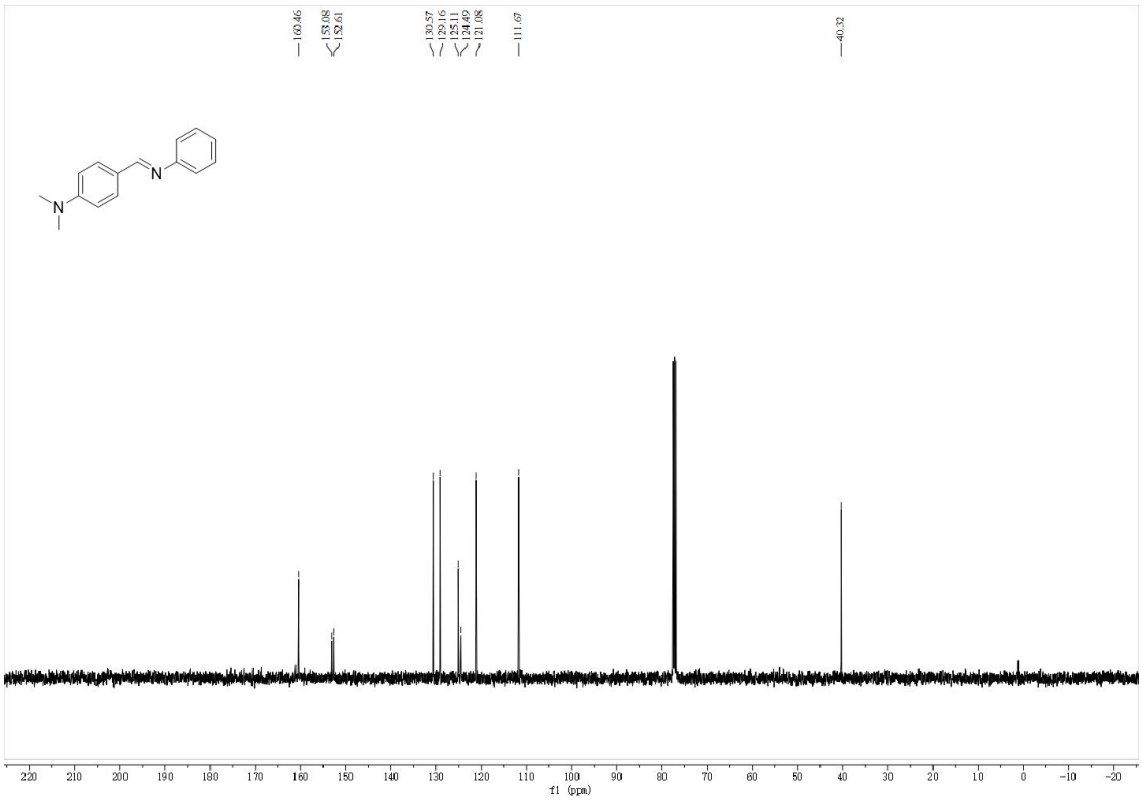

Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1f**

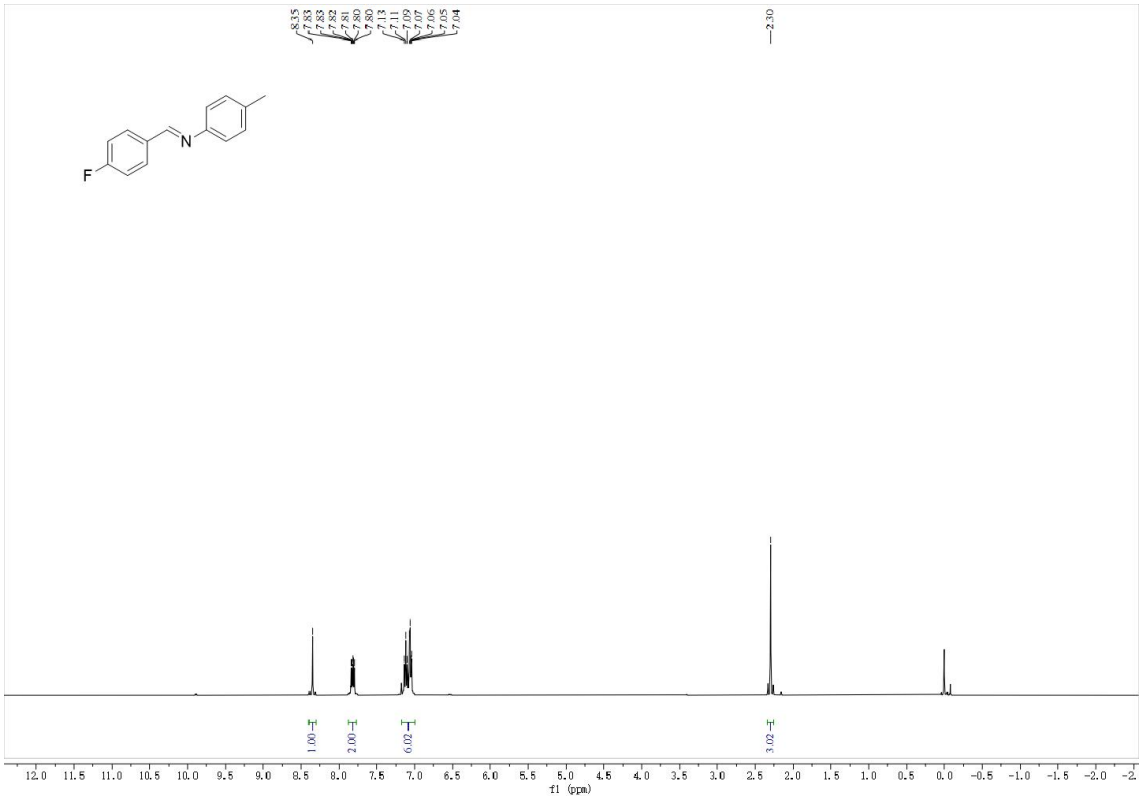

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g**

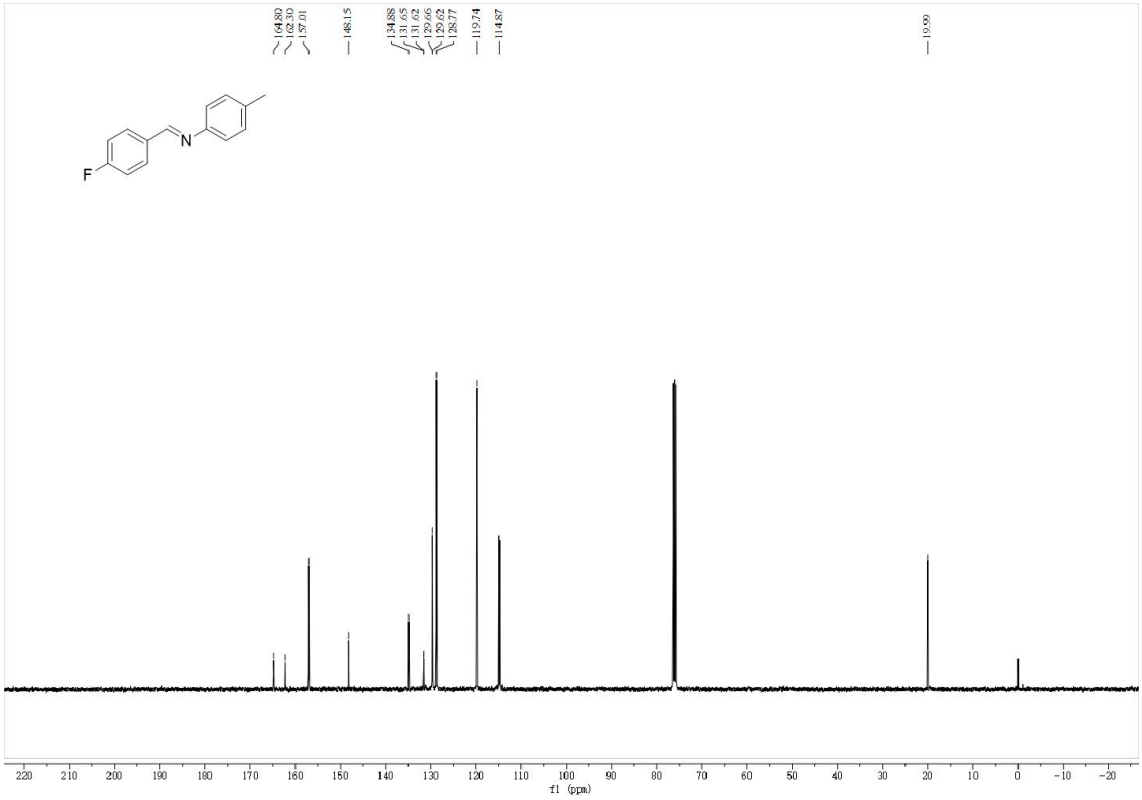

Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1g**

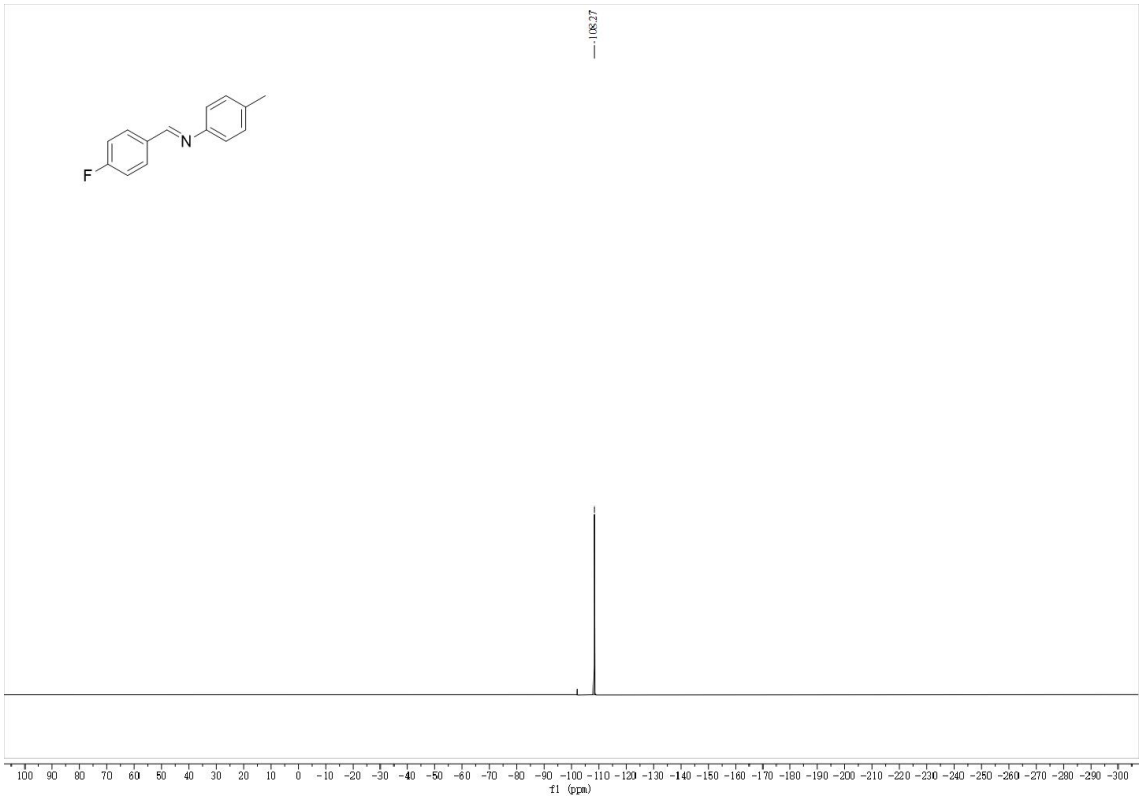

Figure S33. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1g**

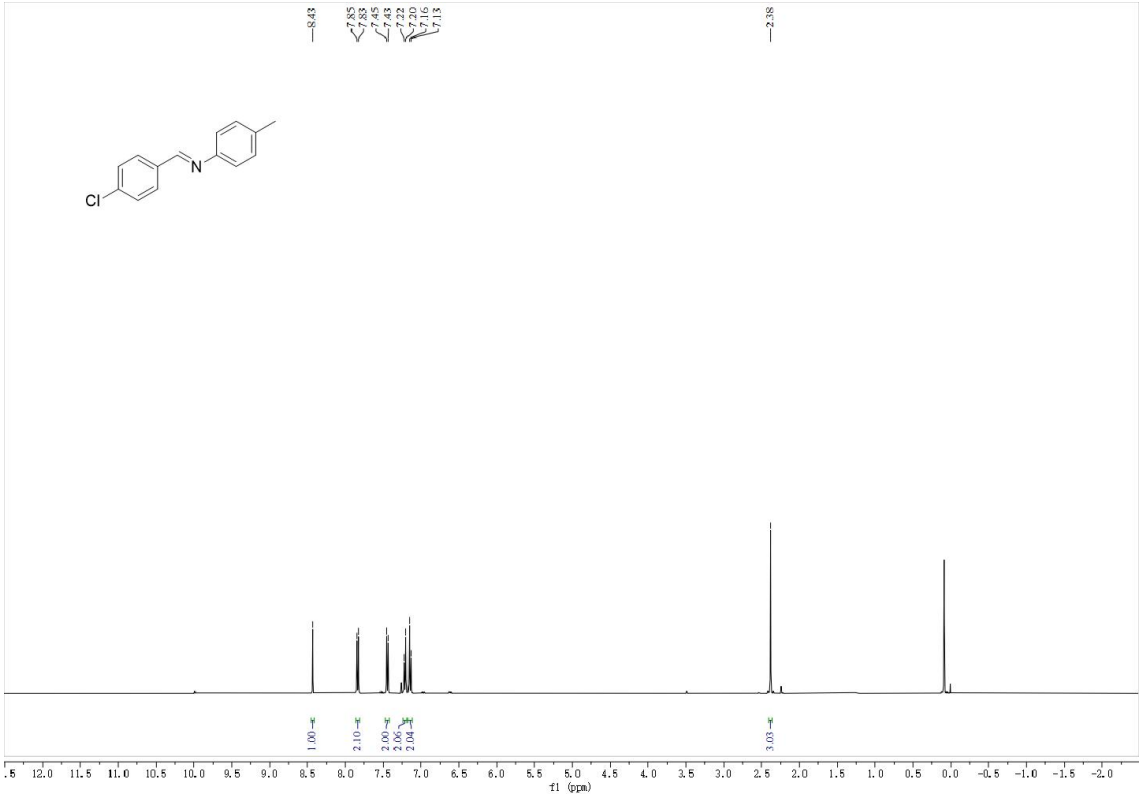

Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h**

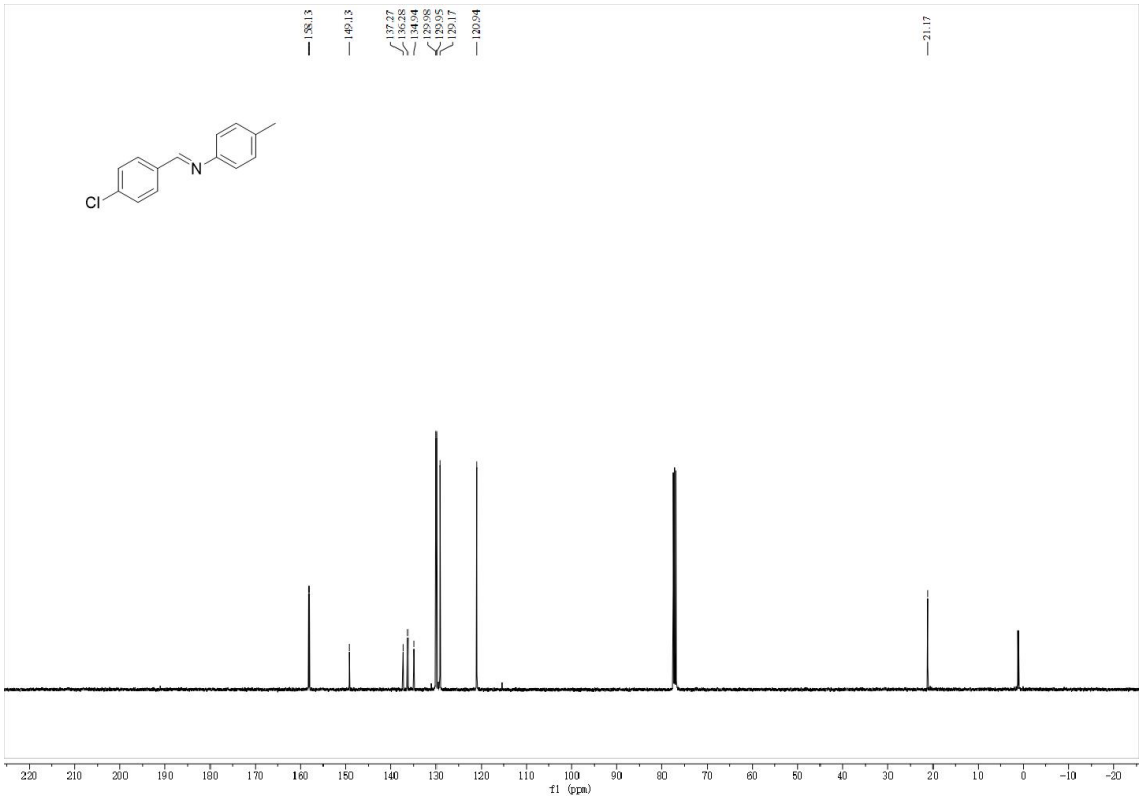

Figure S35. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1h**

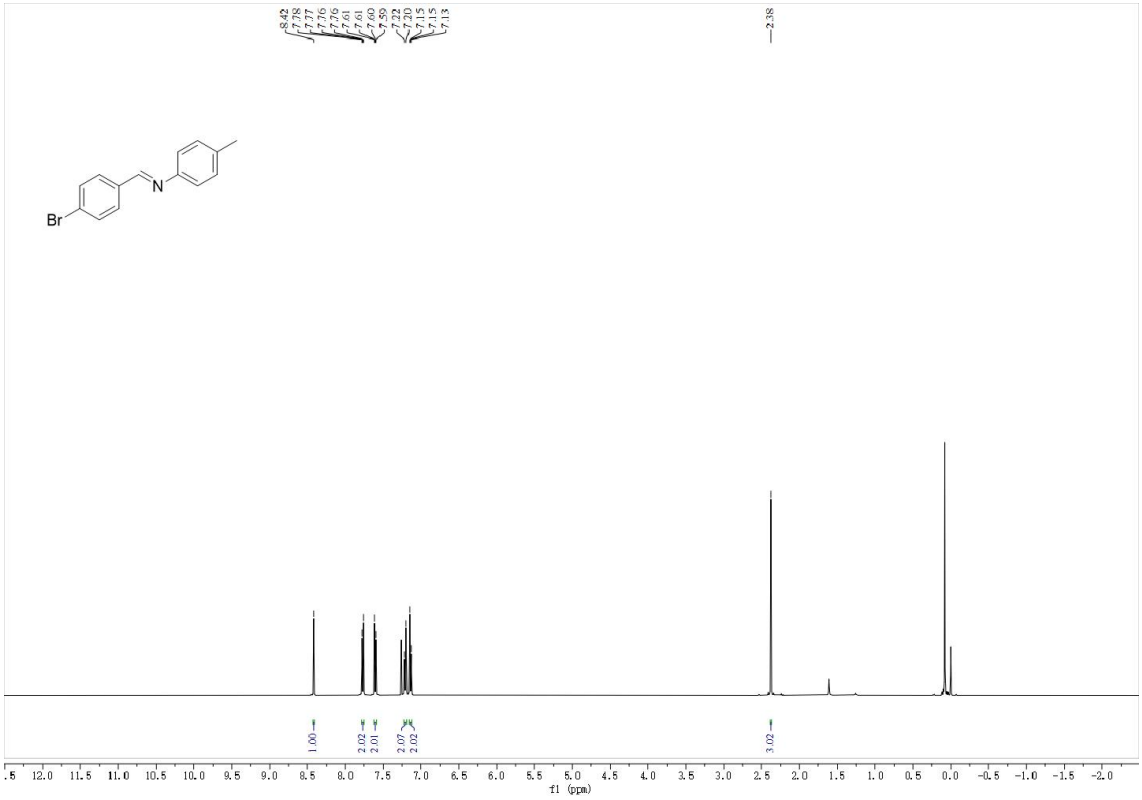

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**

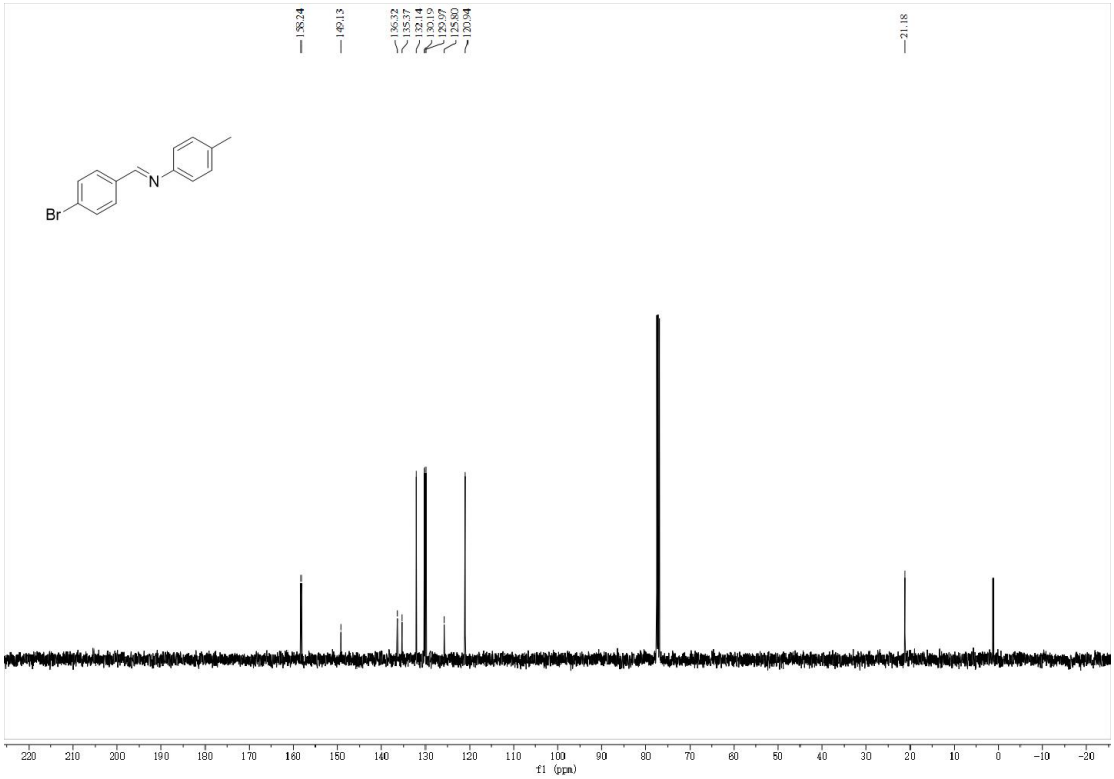

Figure S37. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1i**

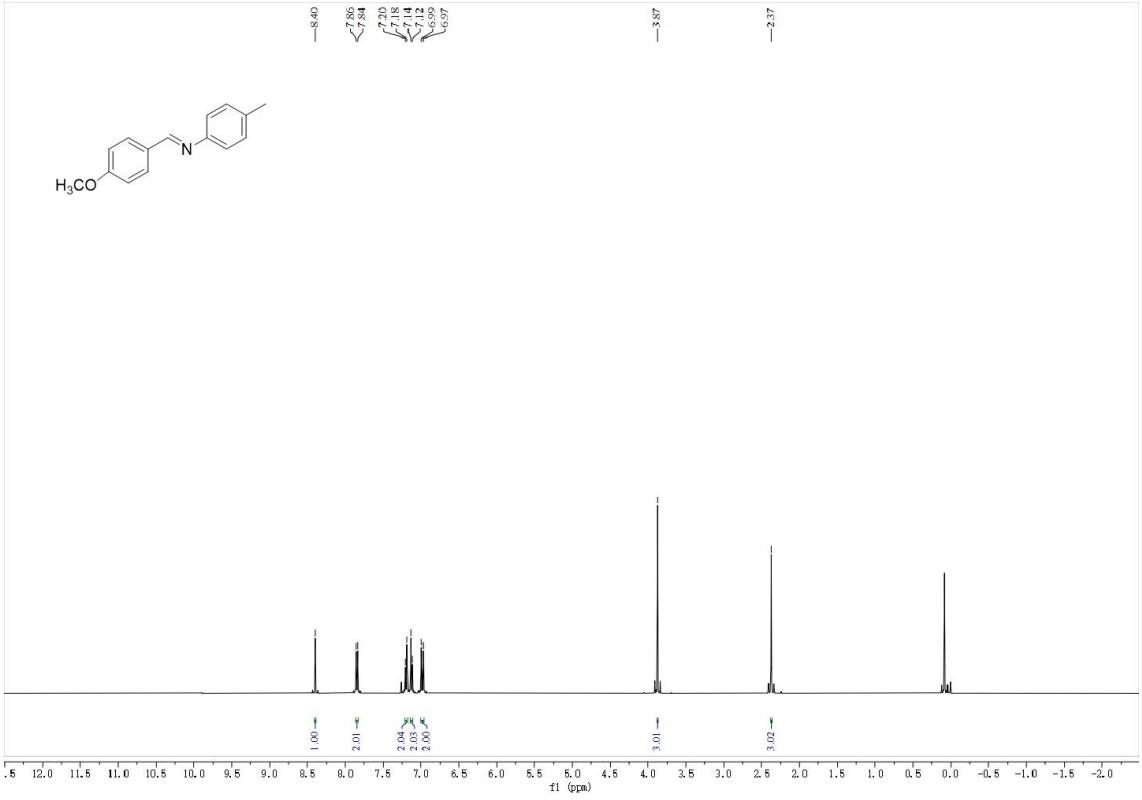

Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1*J***

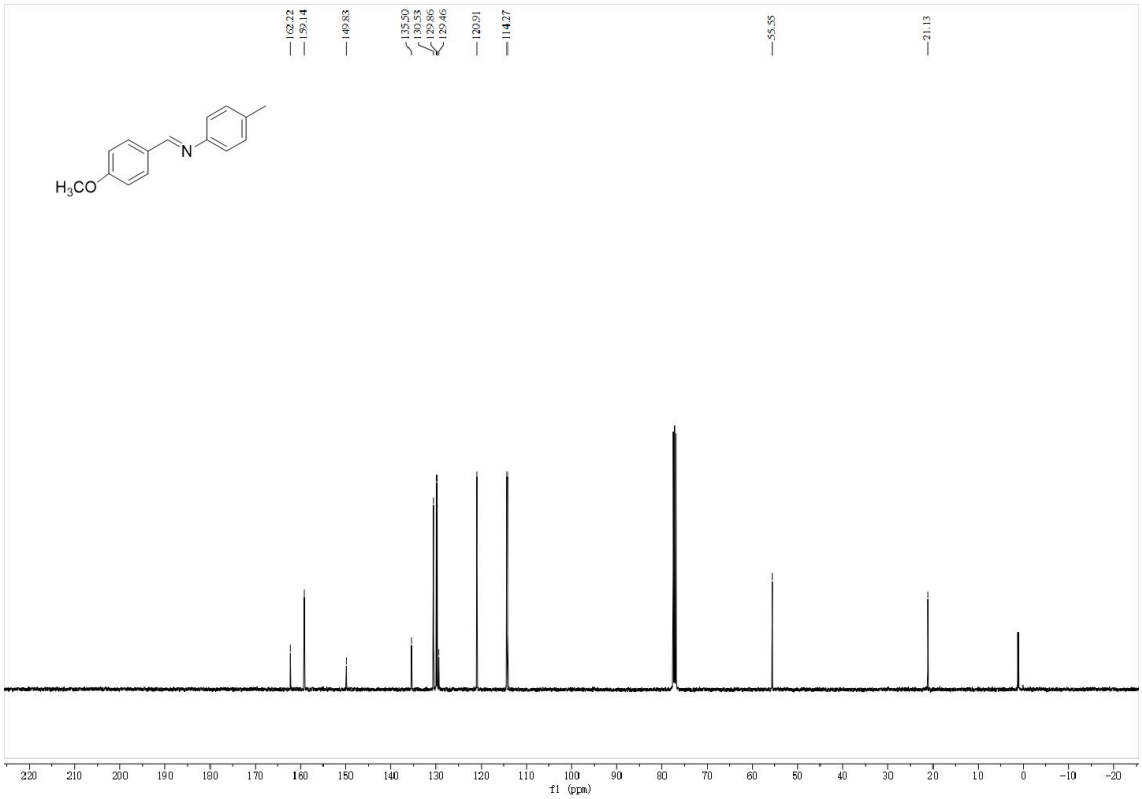

Figure S39. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1*J***

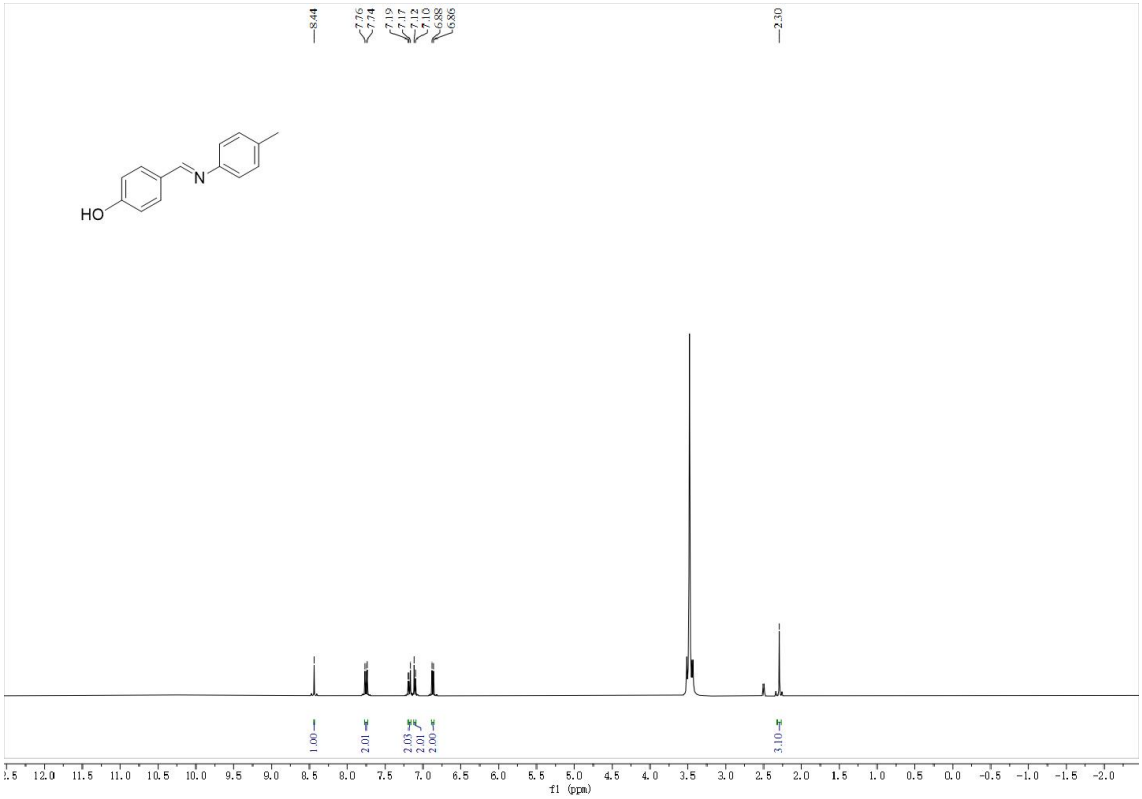

Figure S40. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **1k**

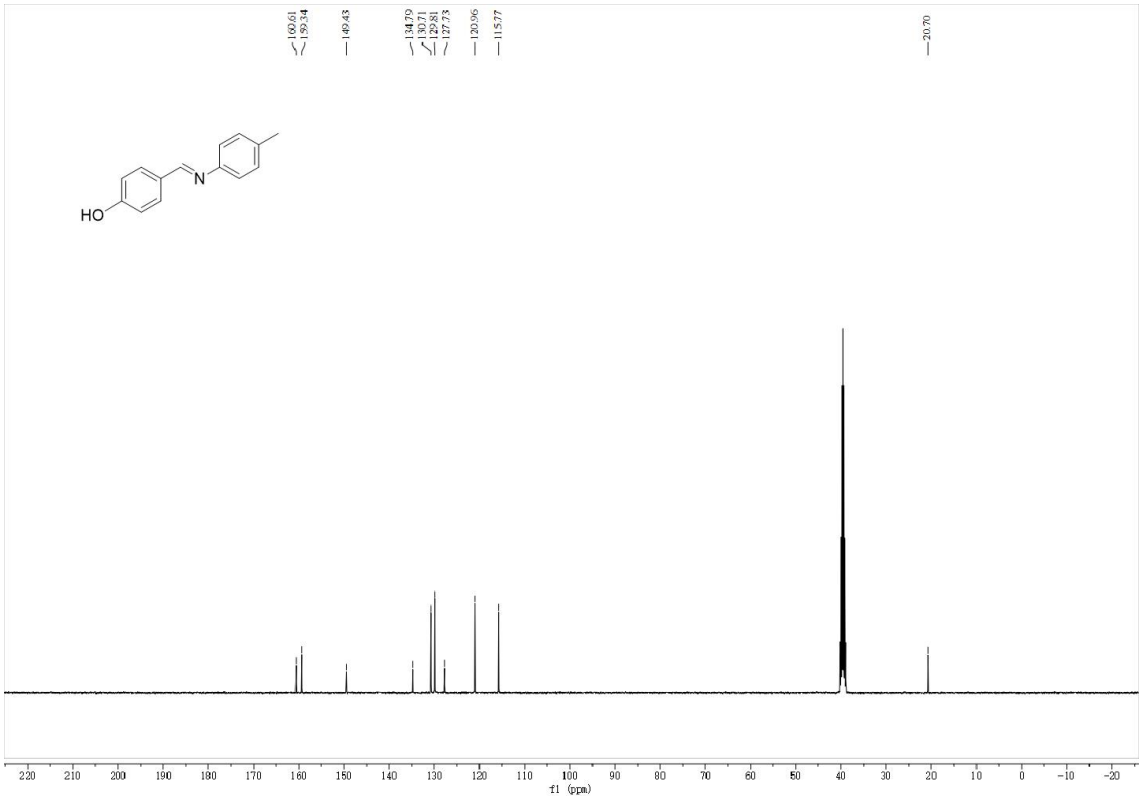

Figure S41. ^{13}C NMR (100 MHz, DMSO-D_6) spectrum of **1k**

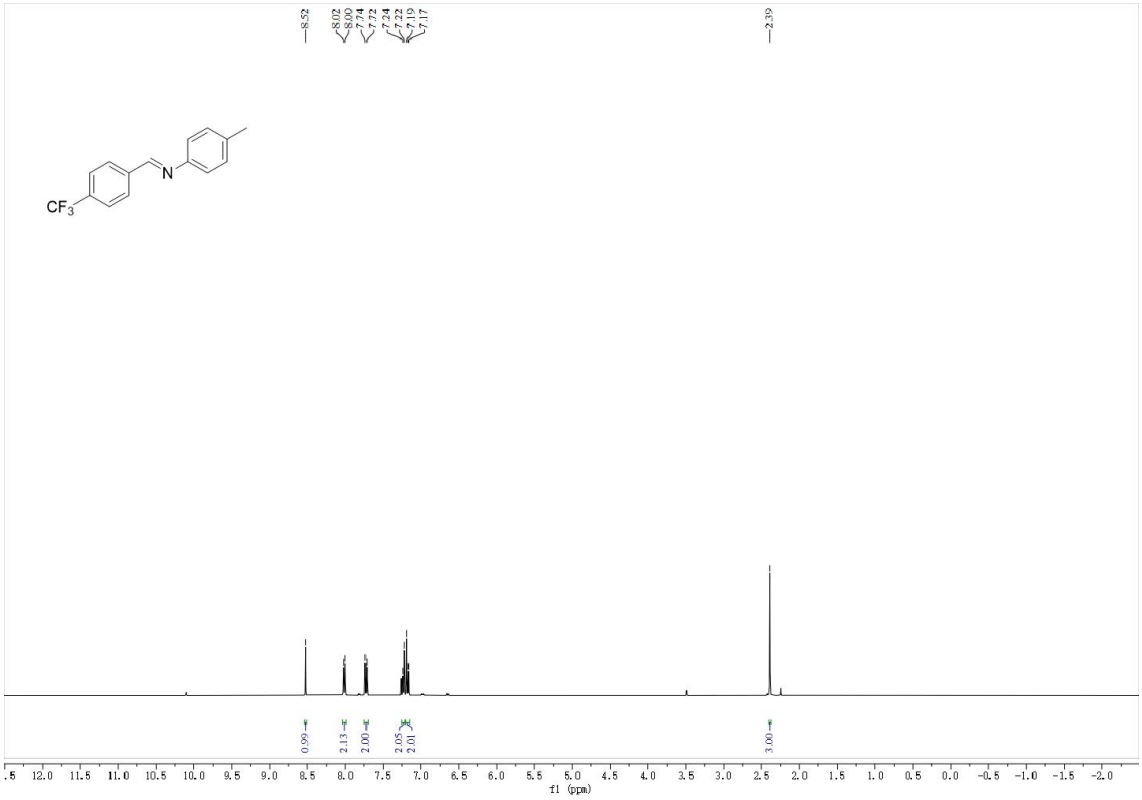

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l**

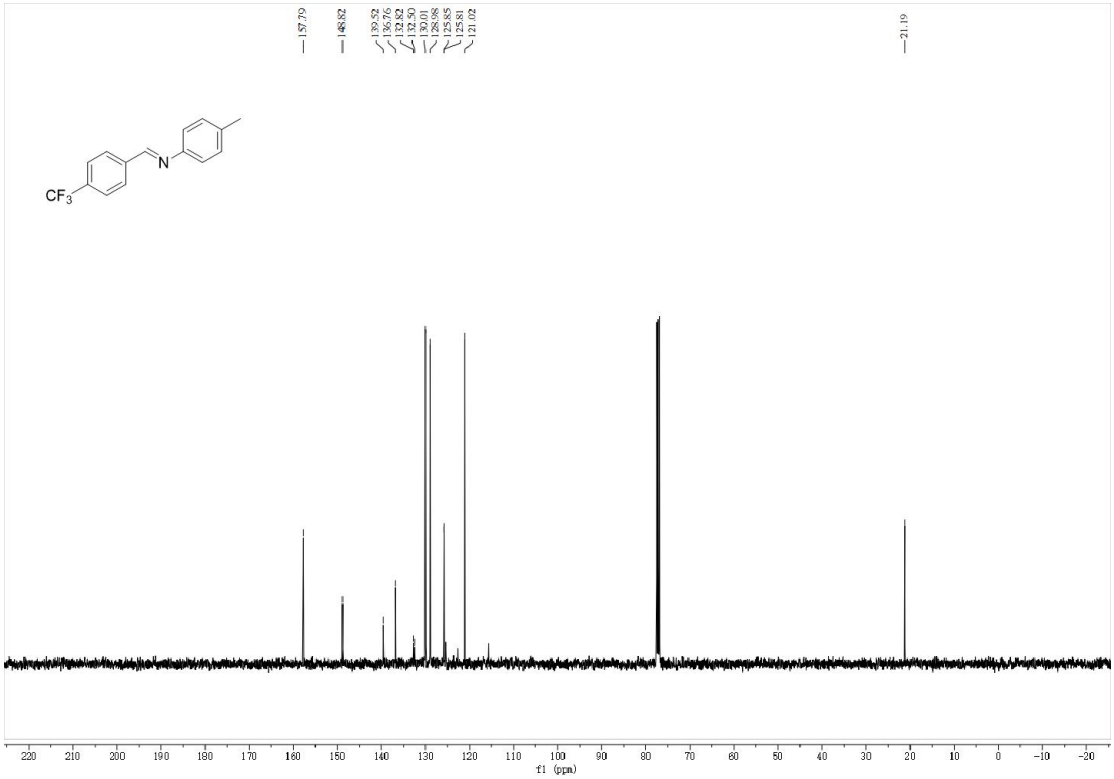

Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1l**

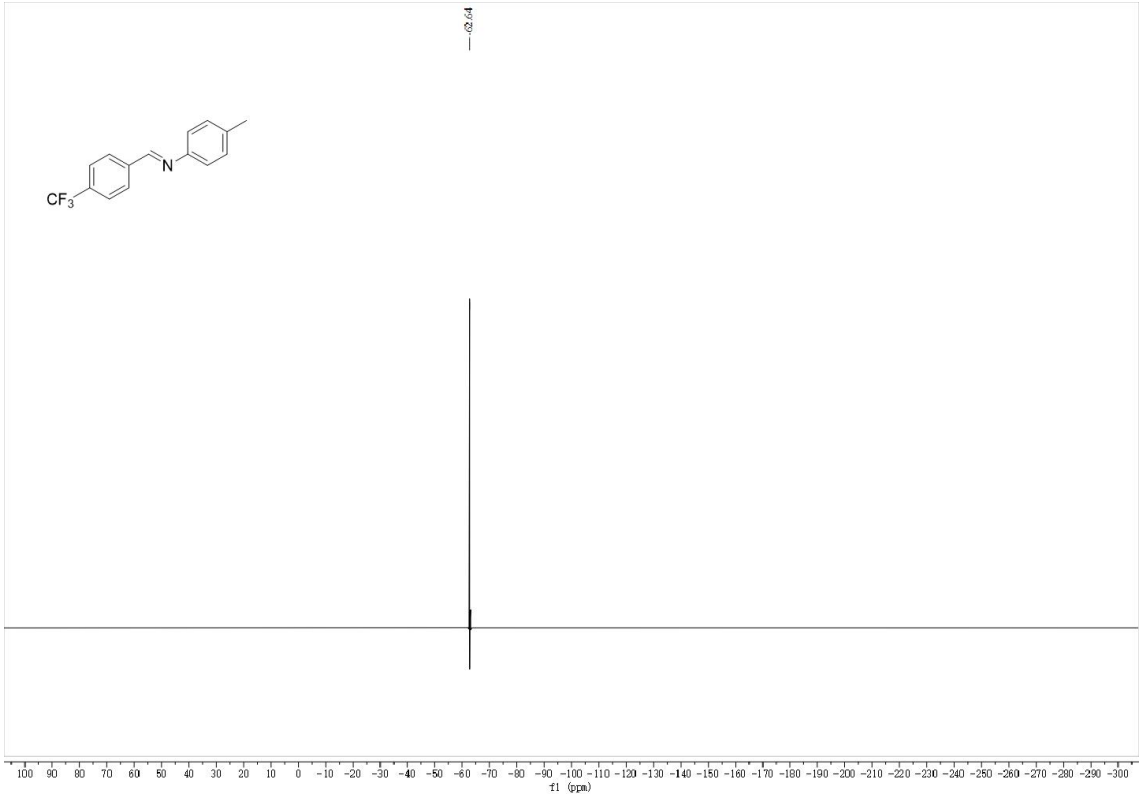

Figure S44. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1l**

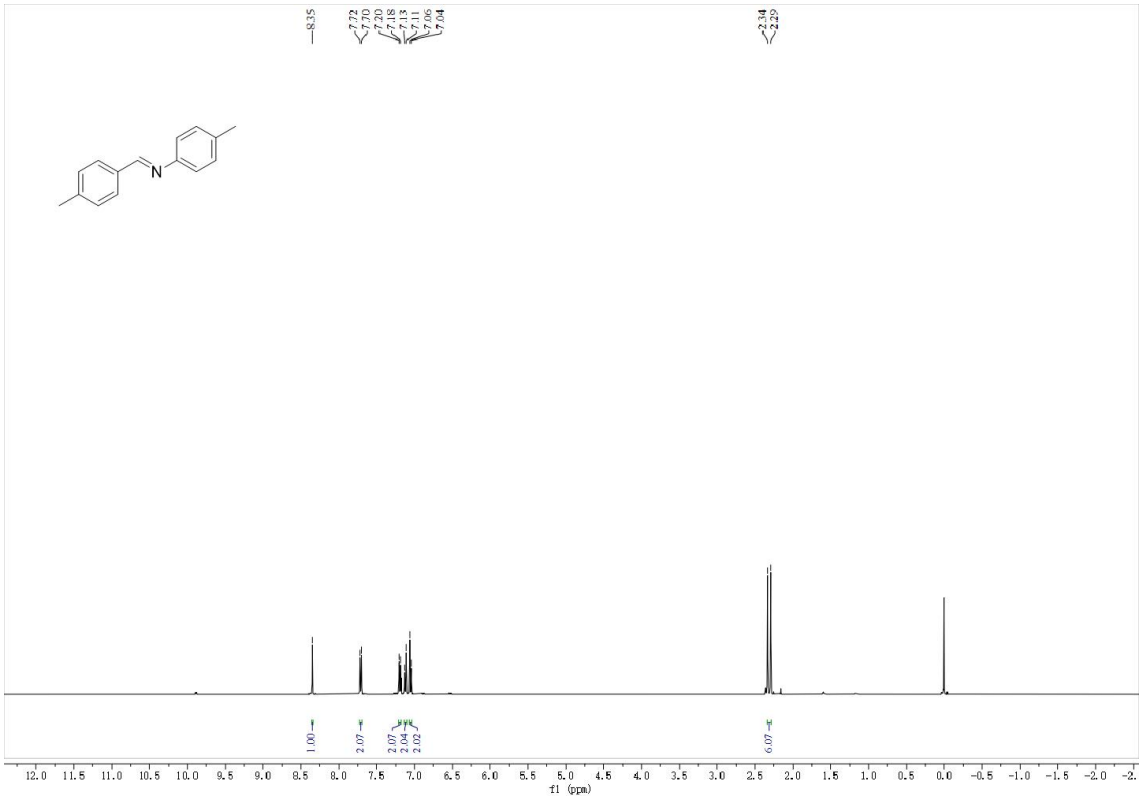

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**

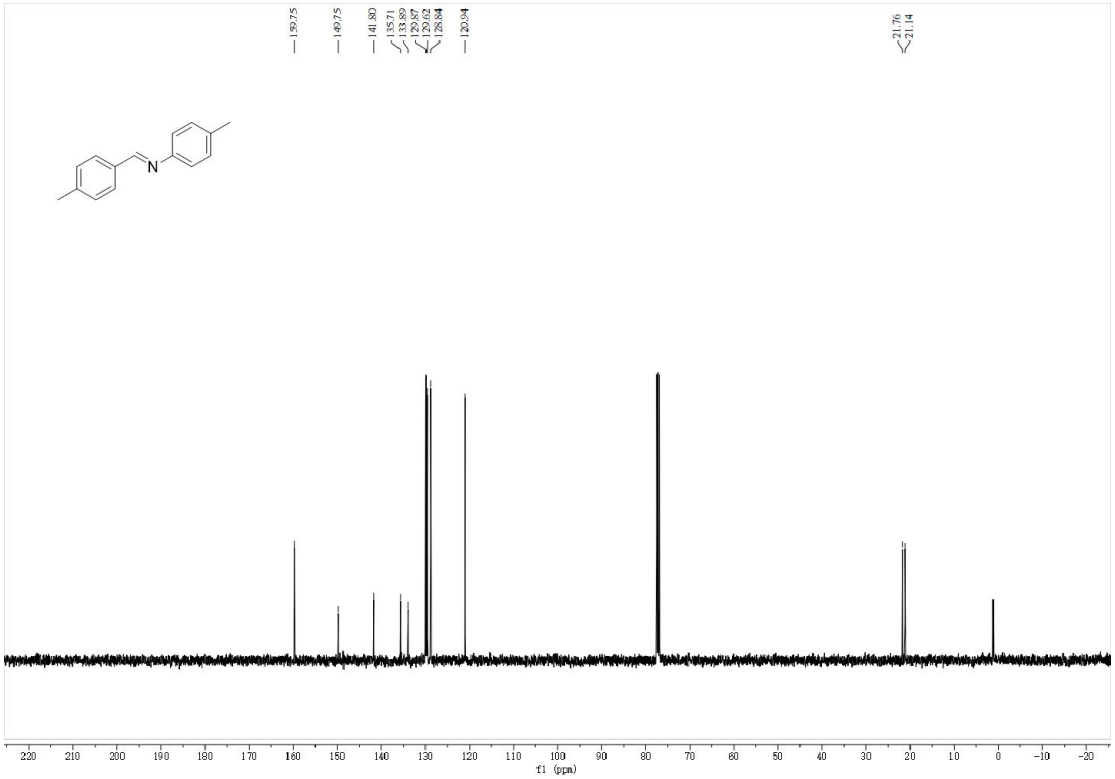

Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1m**

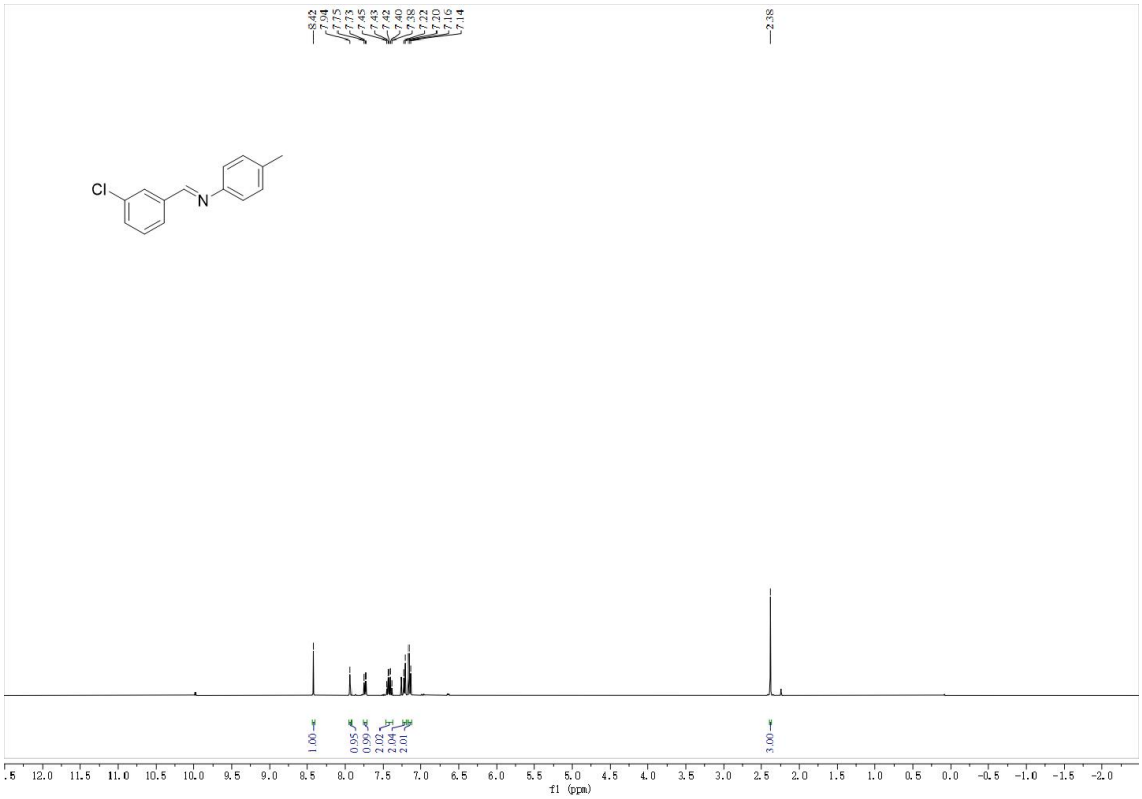

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1n**

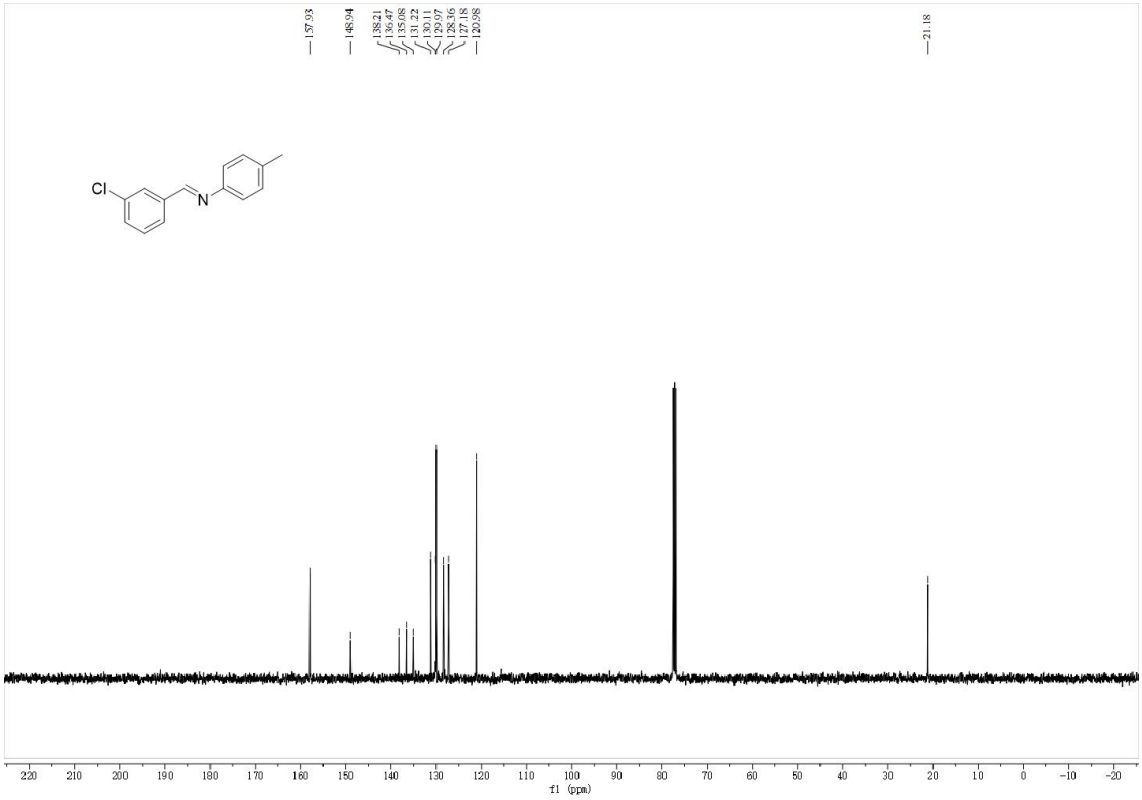

Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1n**

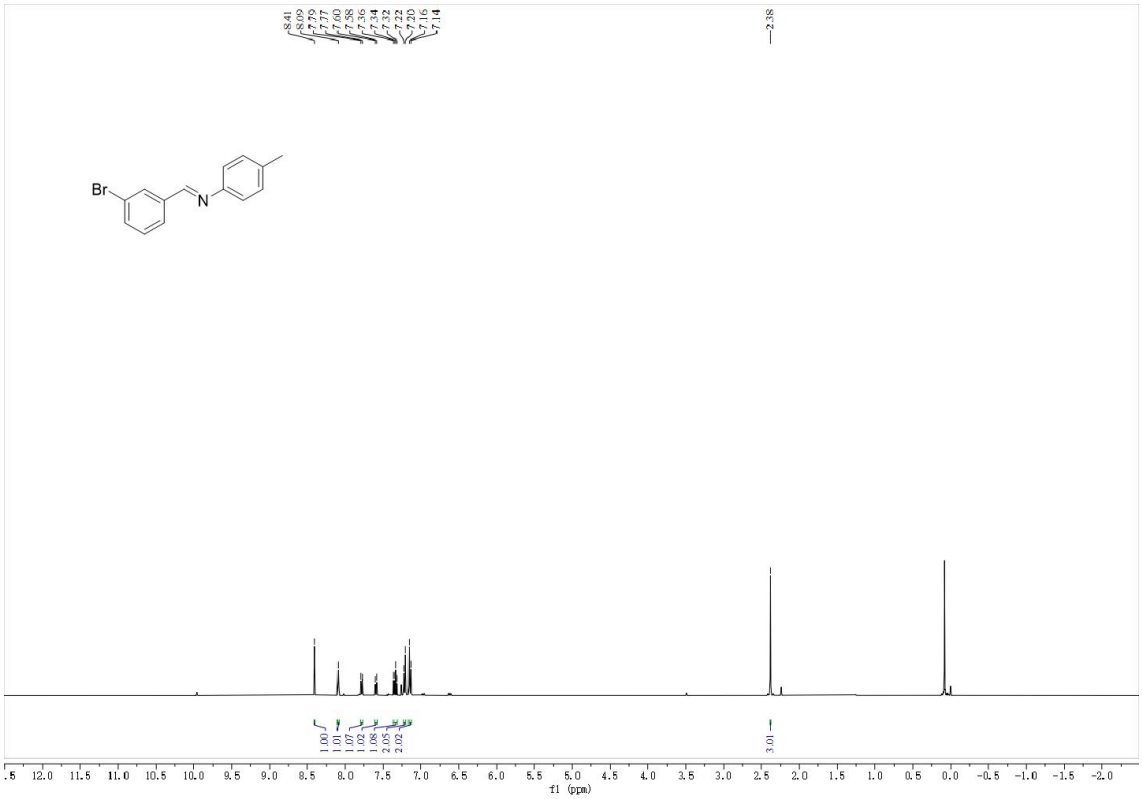

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1o**

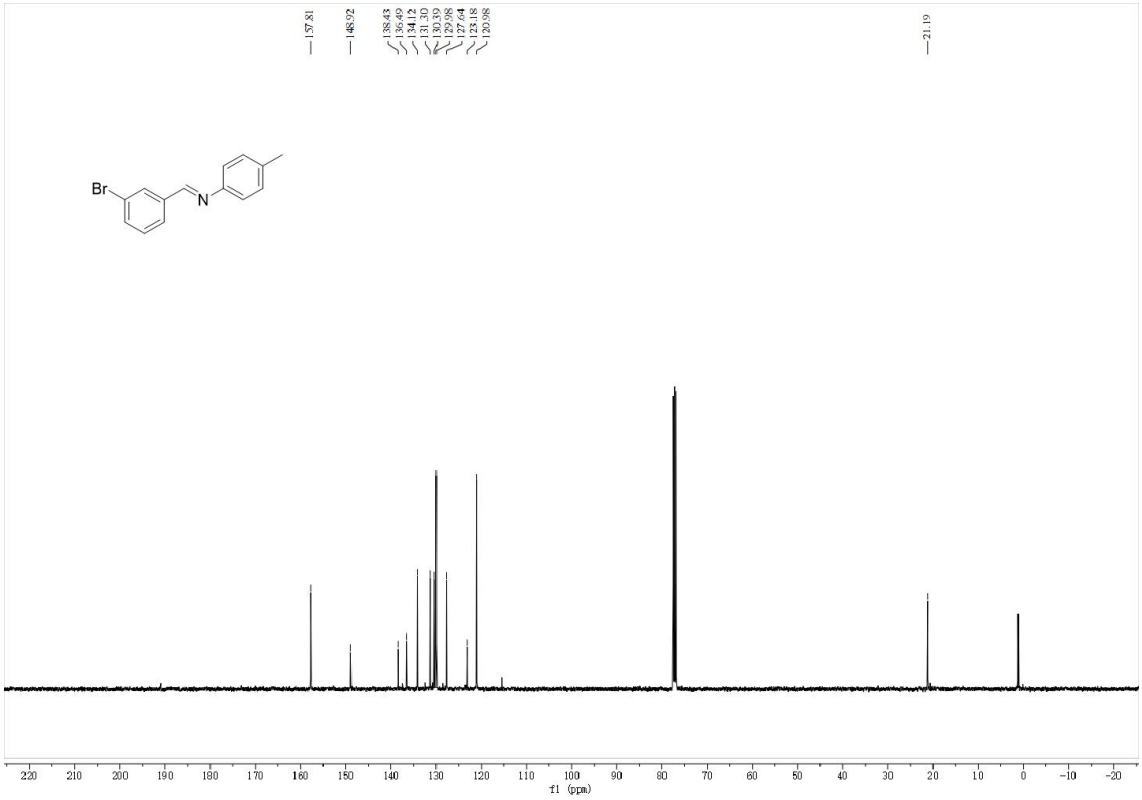

Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1o**

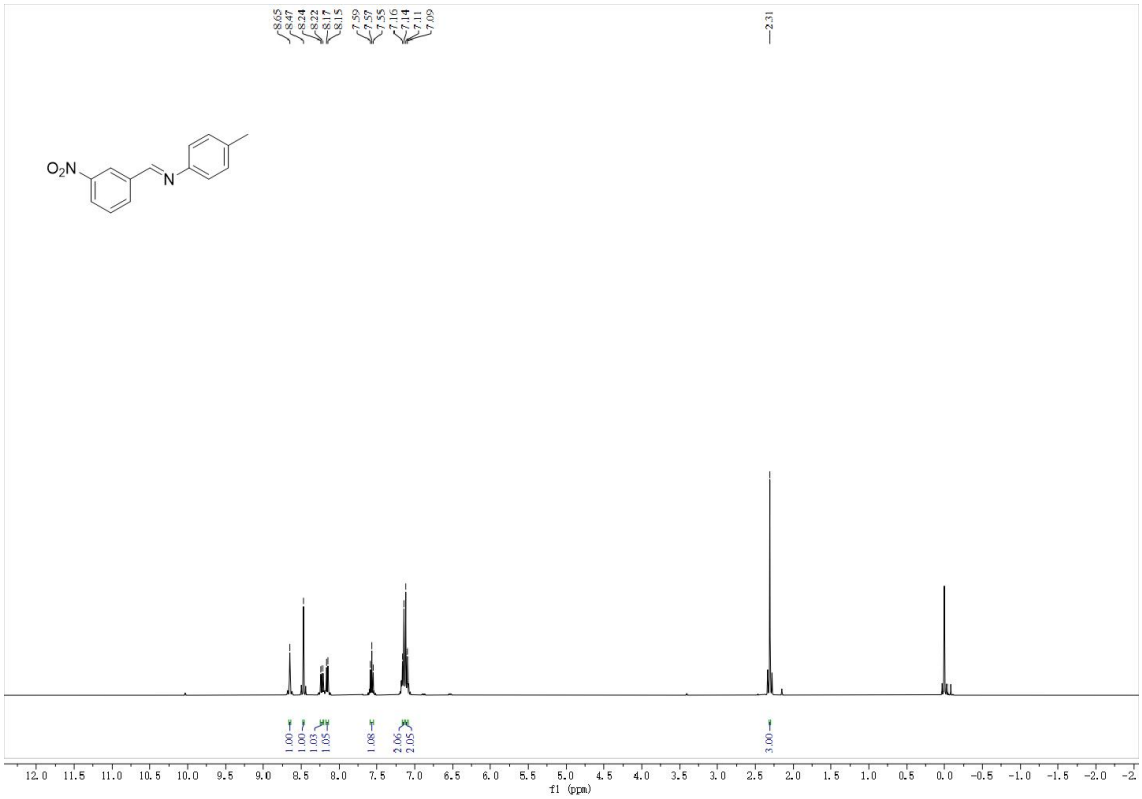

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1p**

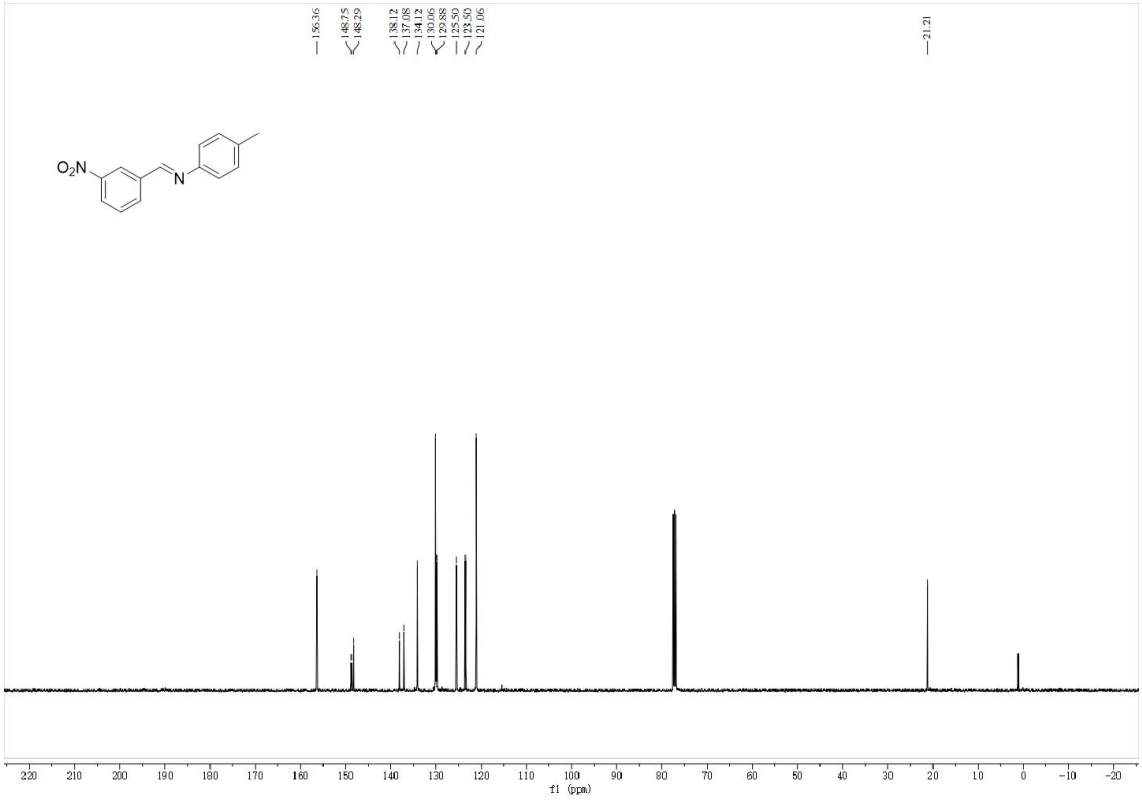

Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1p**

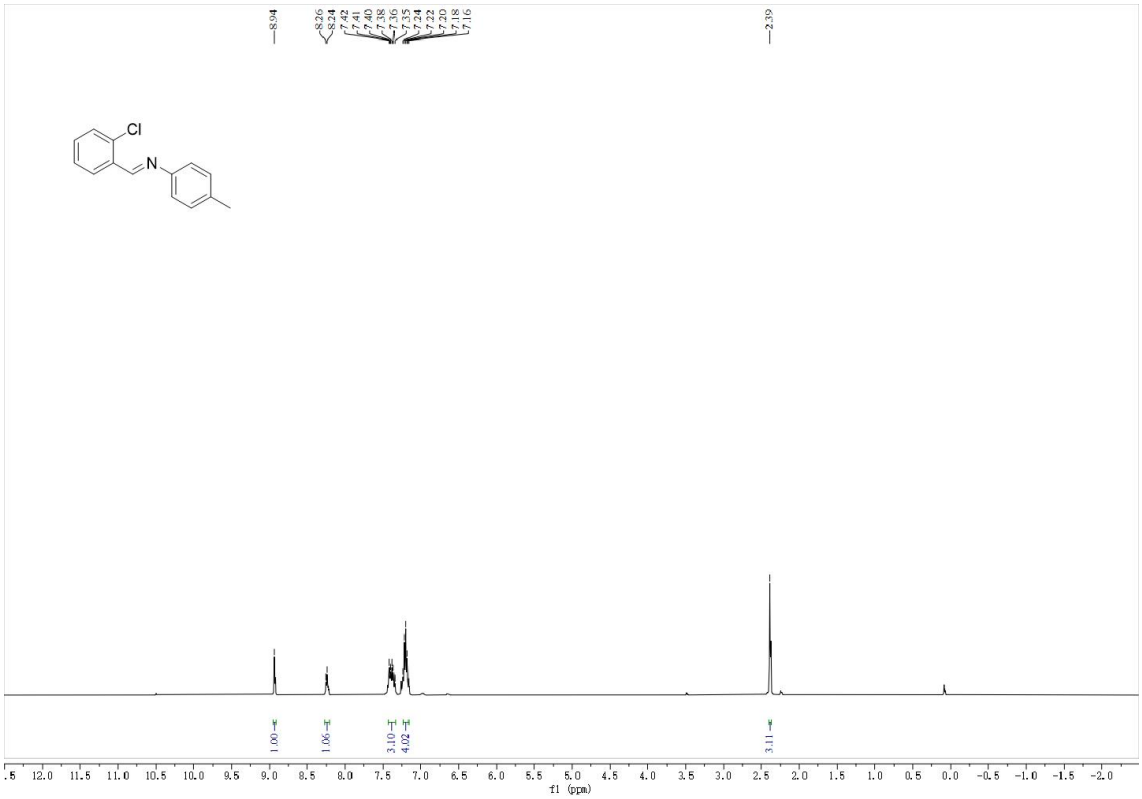

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1q**

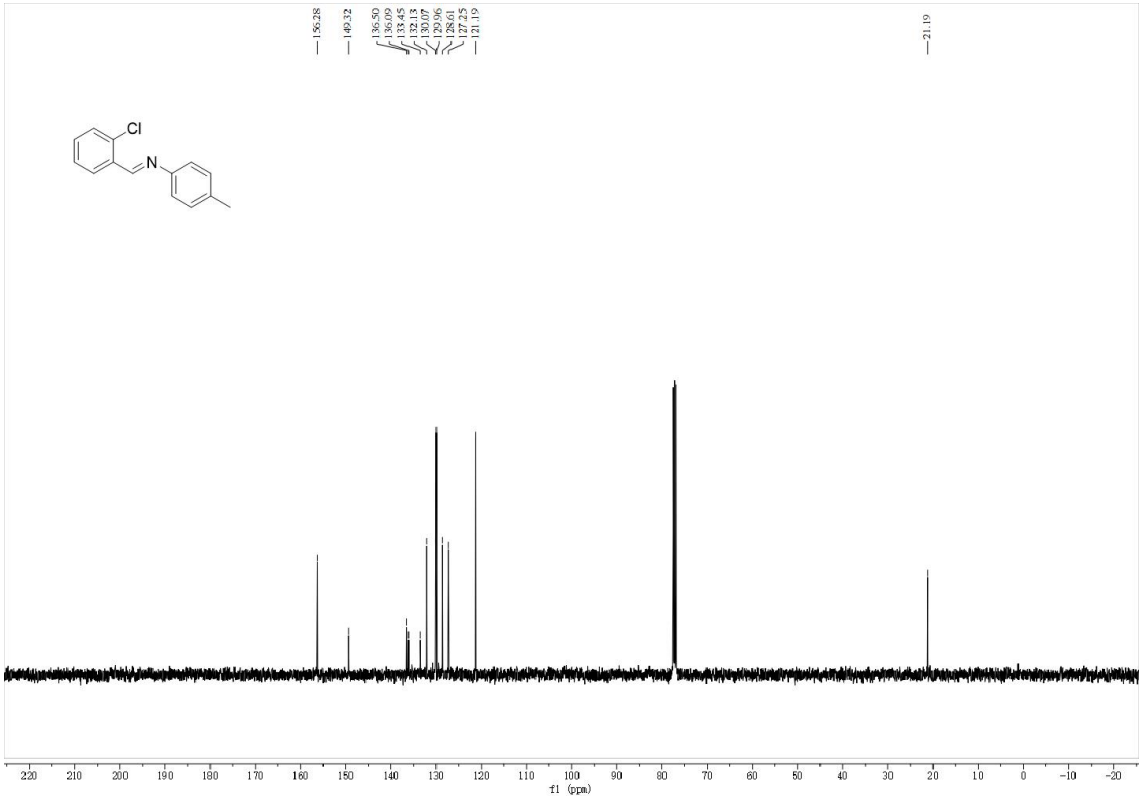

Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1q**

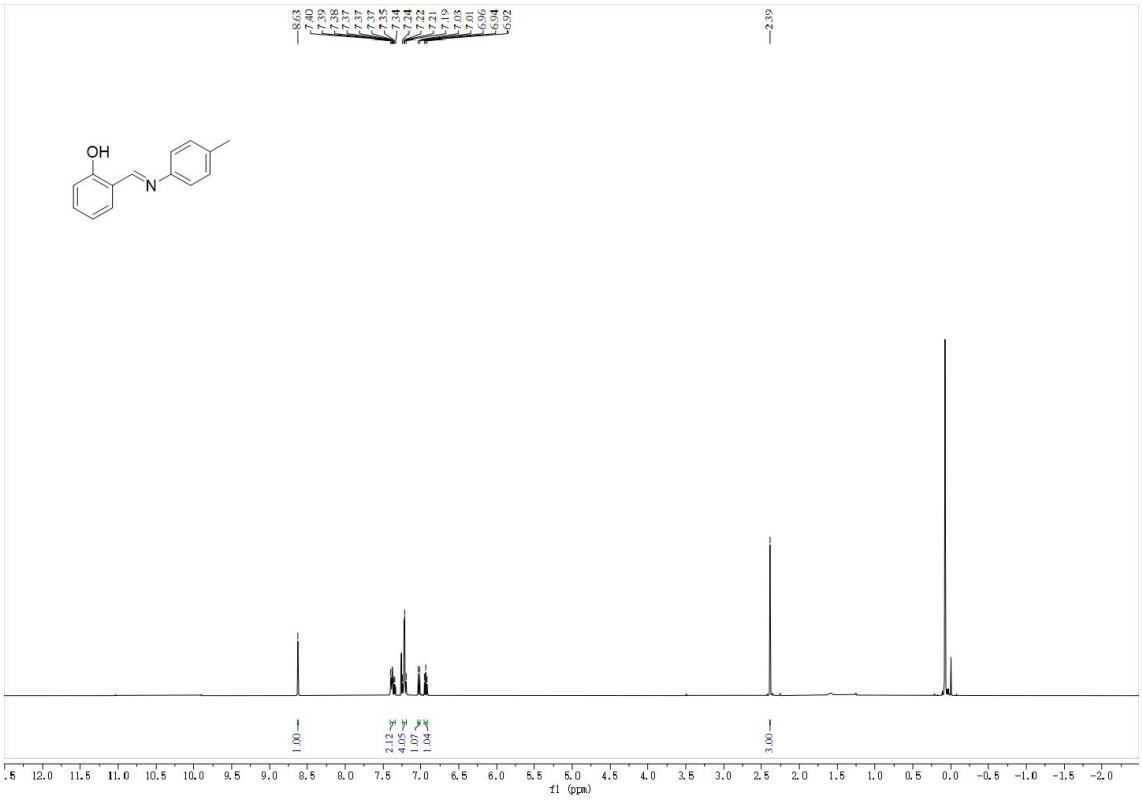

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1r**

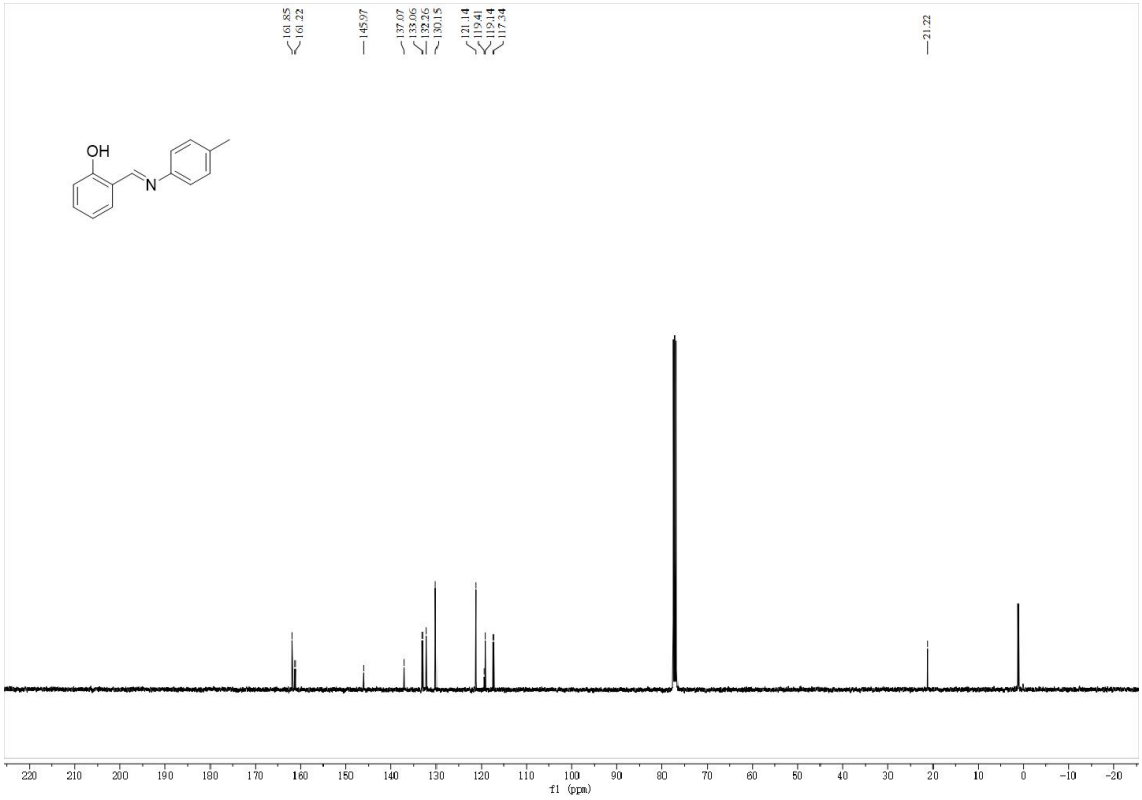

Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1r**

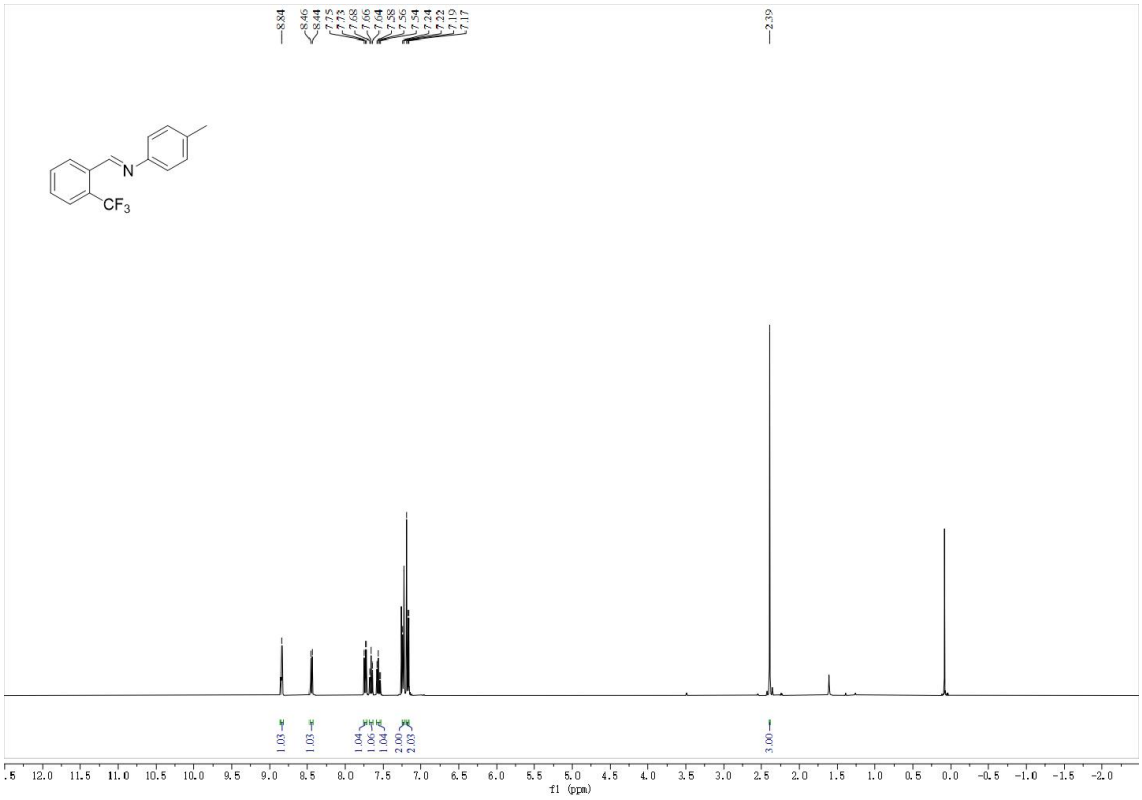

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1s**

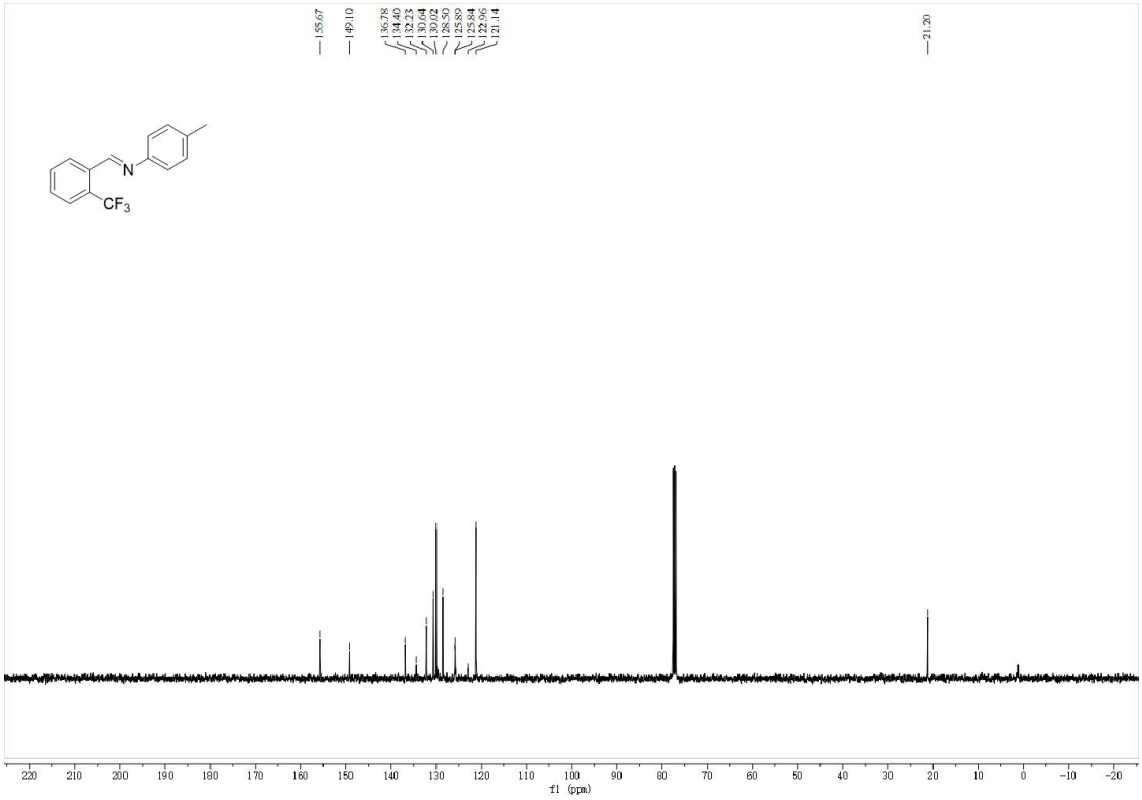

Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1s**

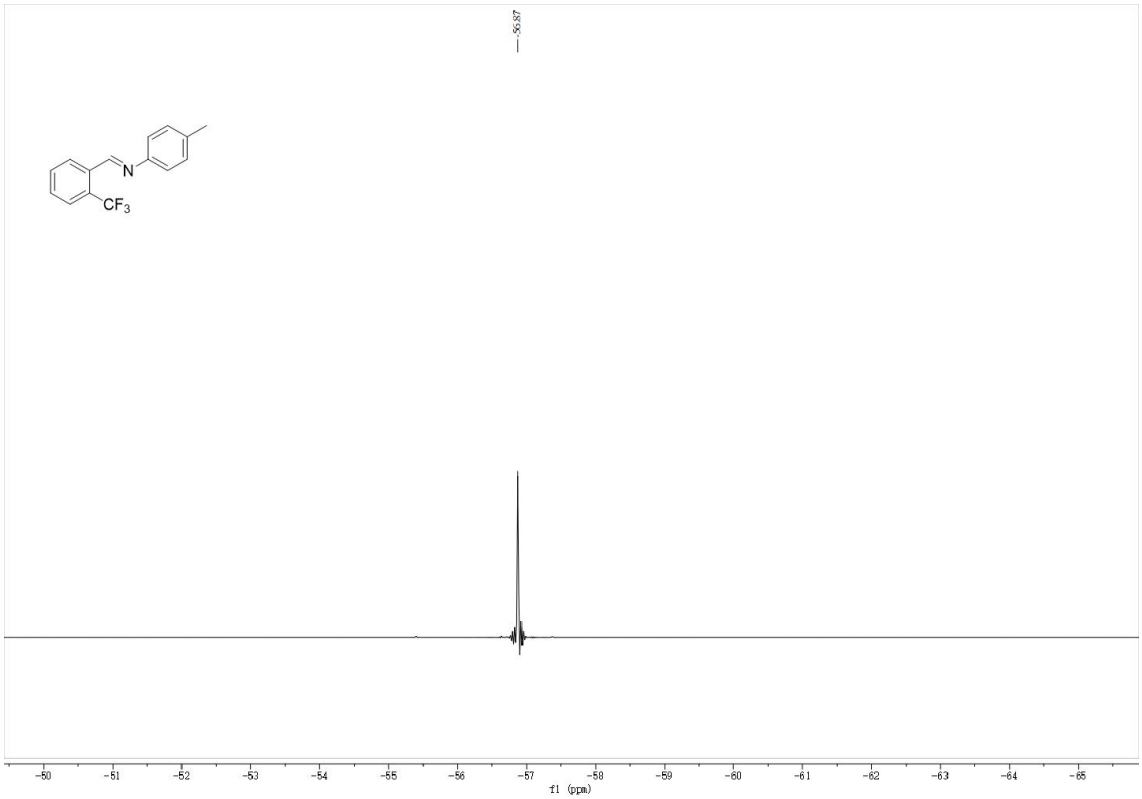

Figure S59. ^{19}F NMR spectrum of **1s**

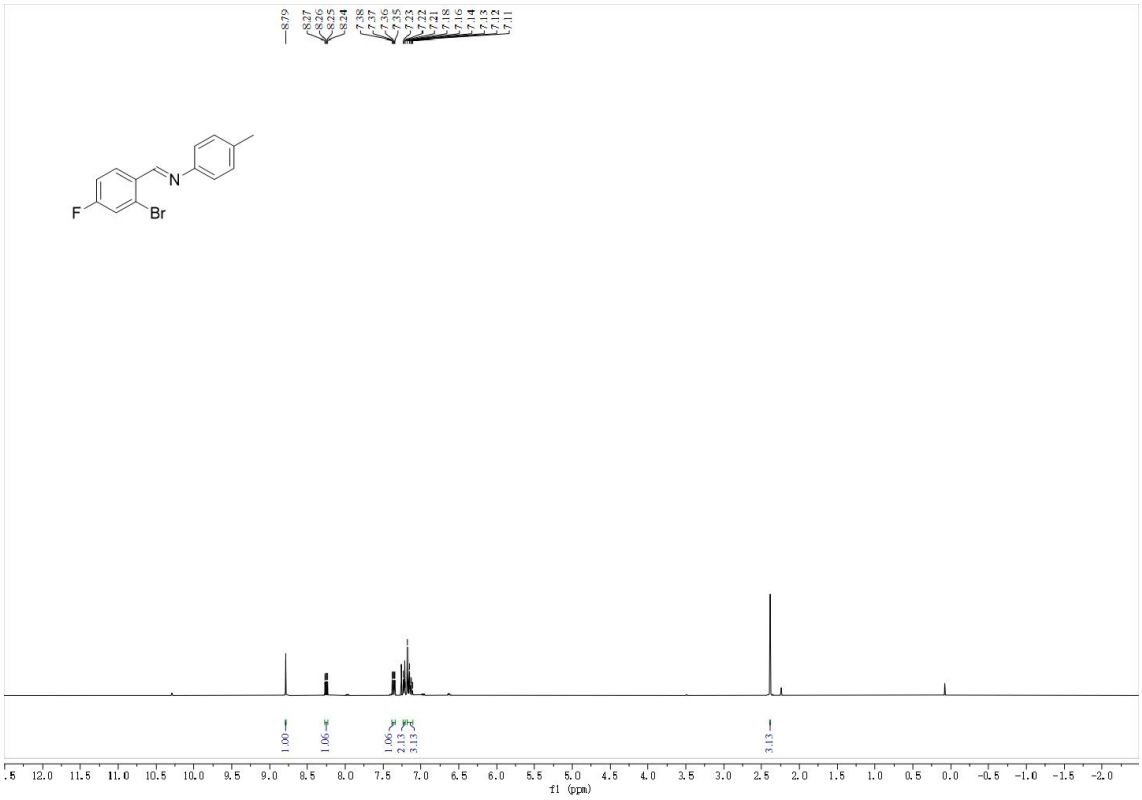

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$)spectrum of **1t**

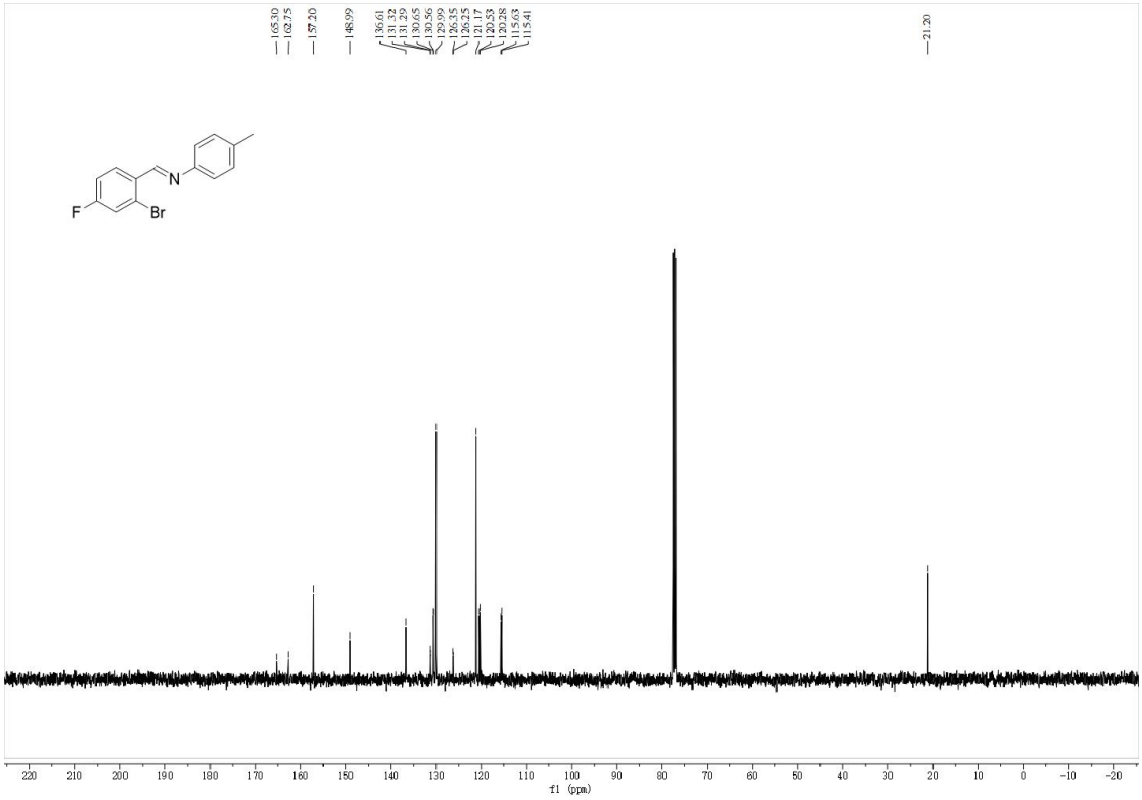

Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1t**

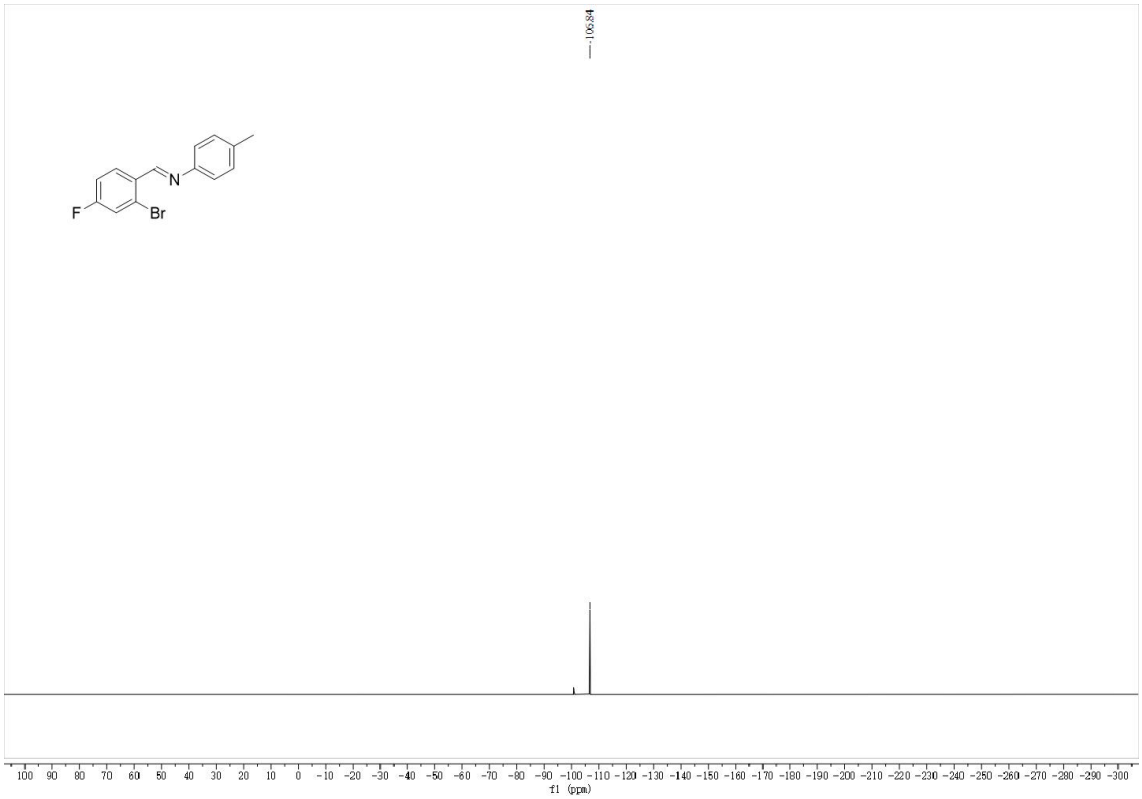

Figure S62. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1t**

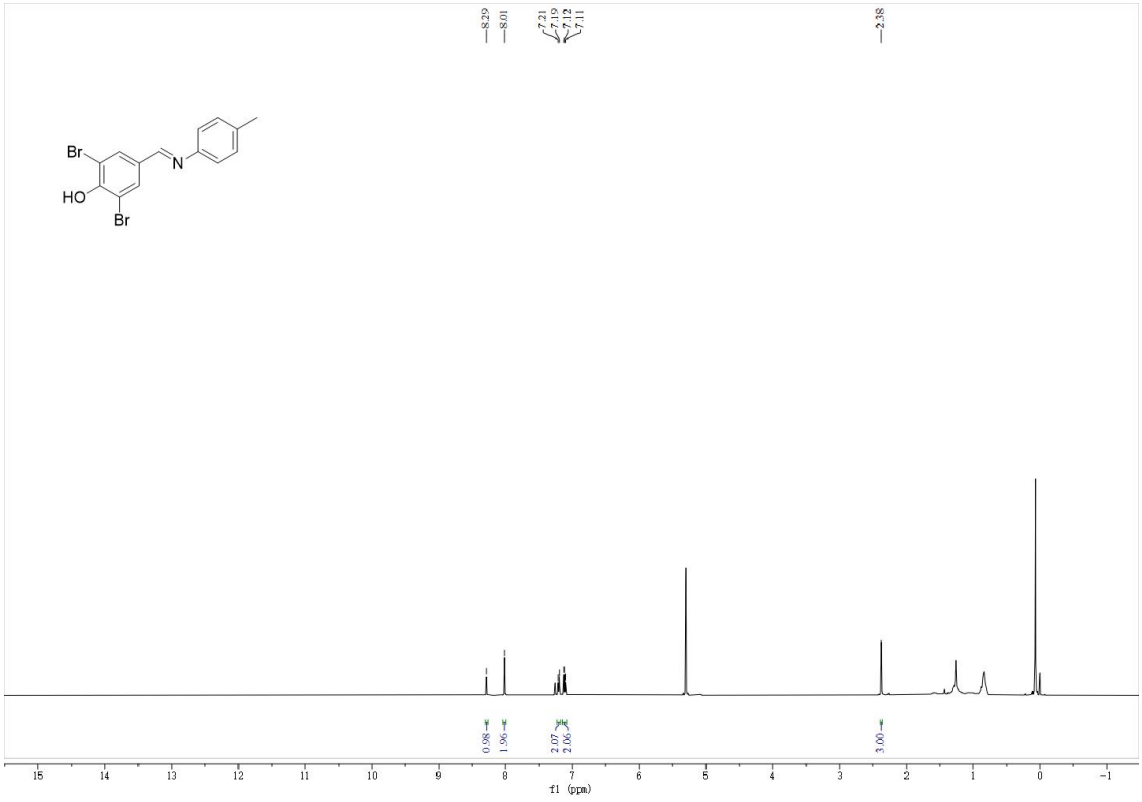

Figure S63.[1]H NMR (400 MHz, $CDCl_3$) spectrum of **1u**

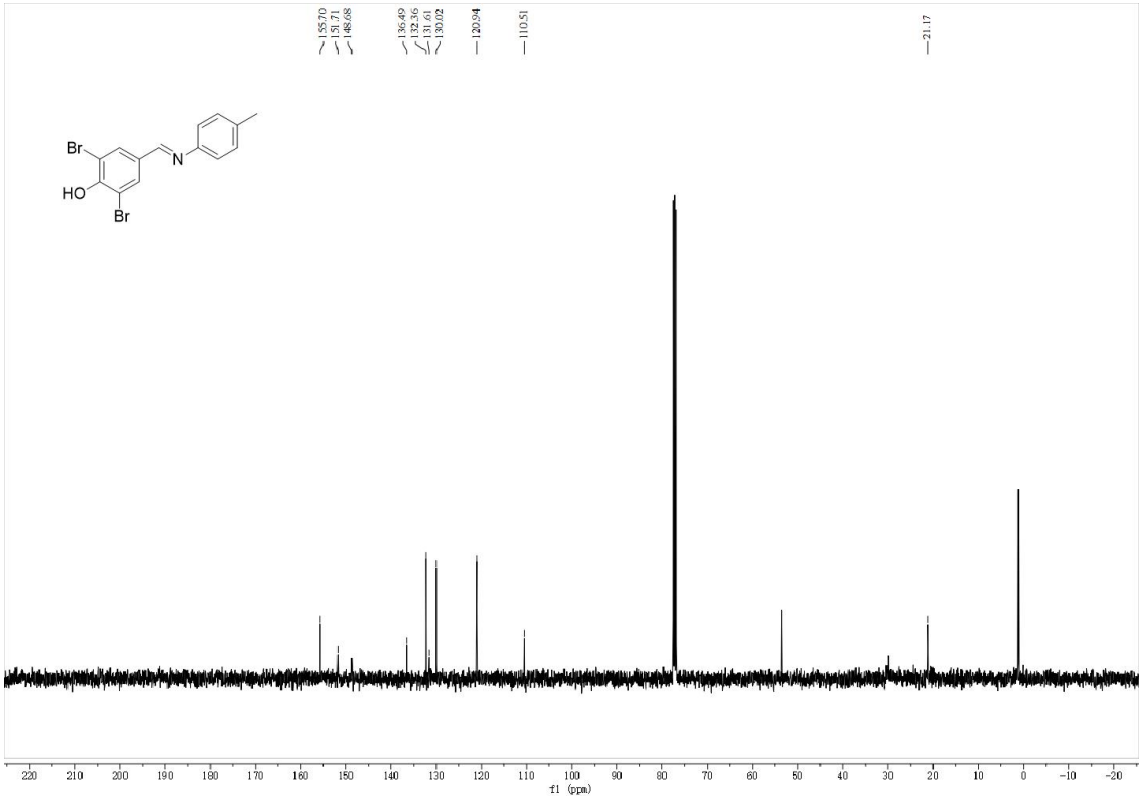

Figure S64.[13]C NMR (100 MHz, $CDCl_3$) spectrum of **1u**

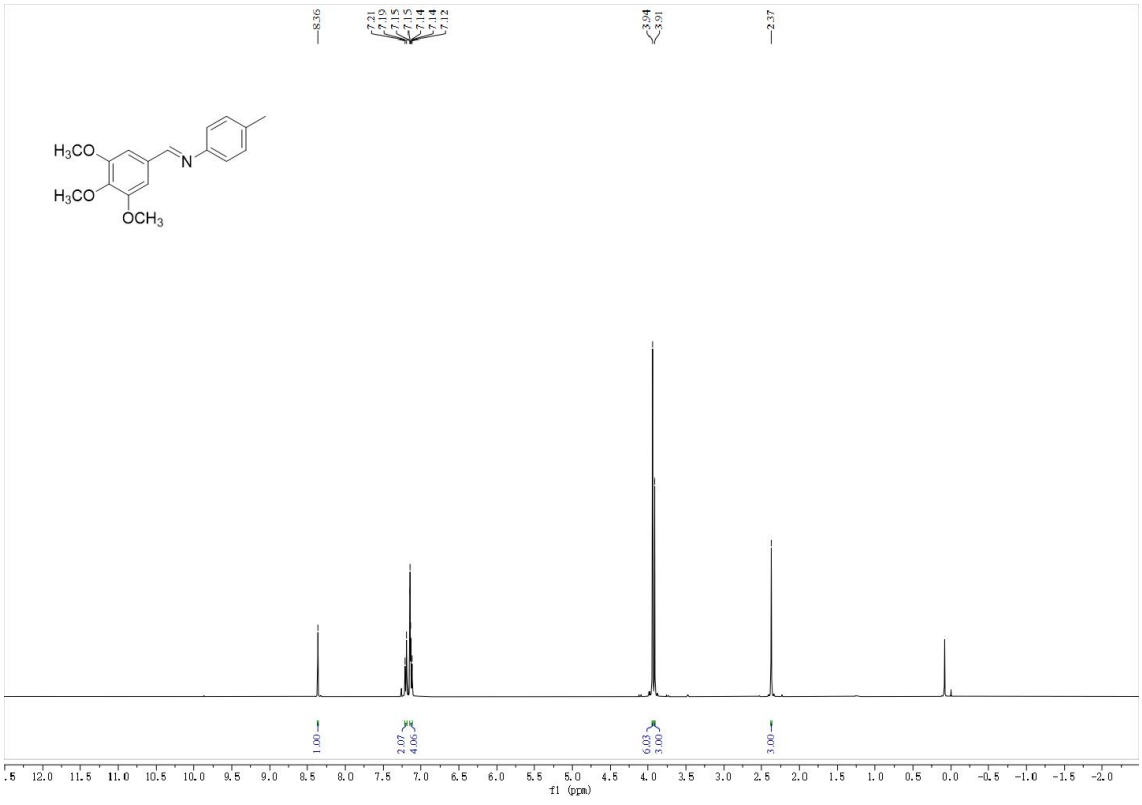

Figure S65. [1]H NMR (400 MHz, $CDCl_3$) spectrum of **1v**

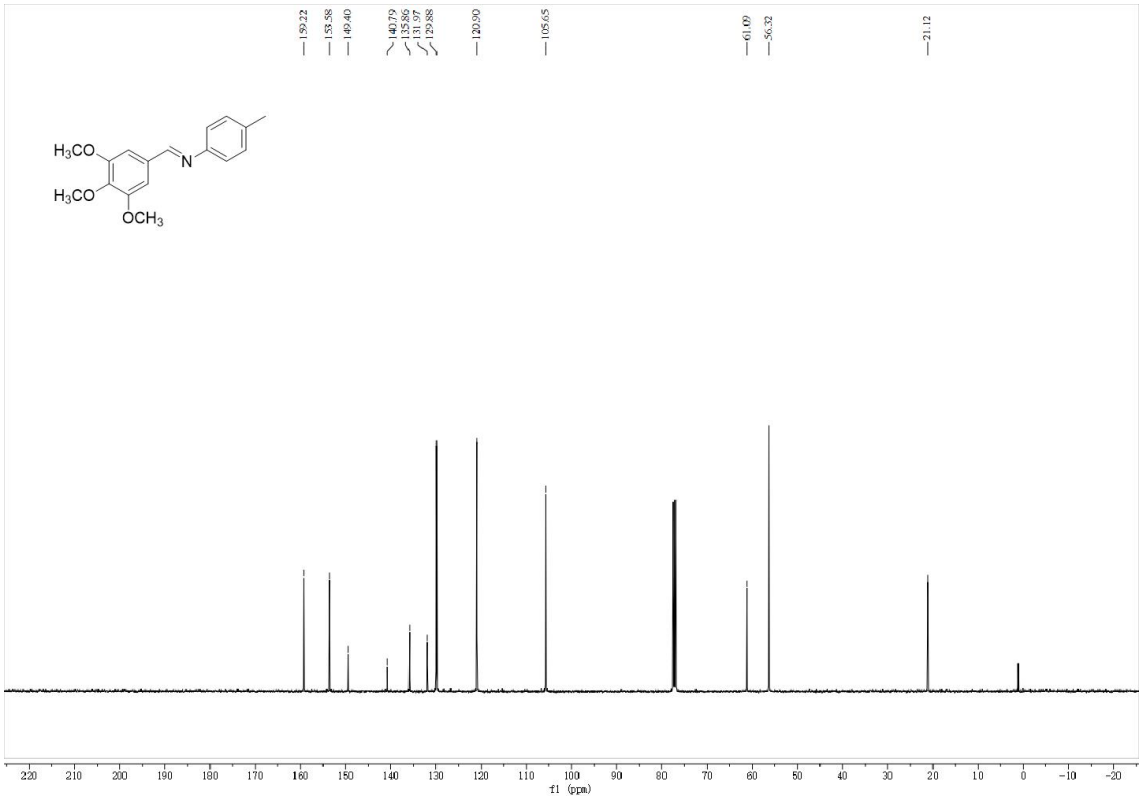

Figure S66. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1v**

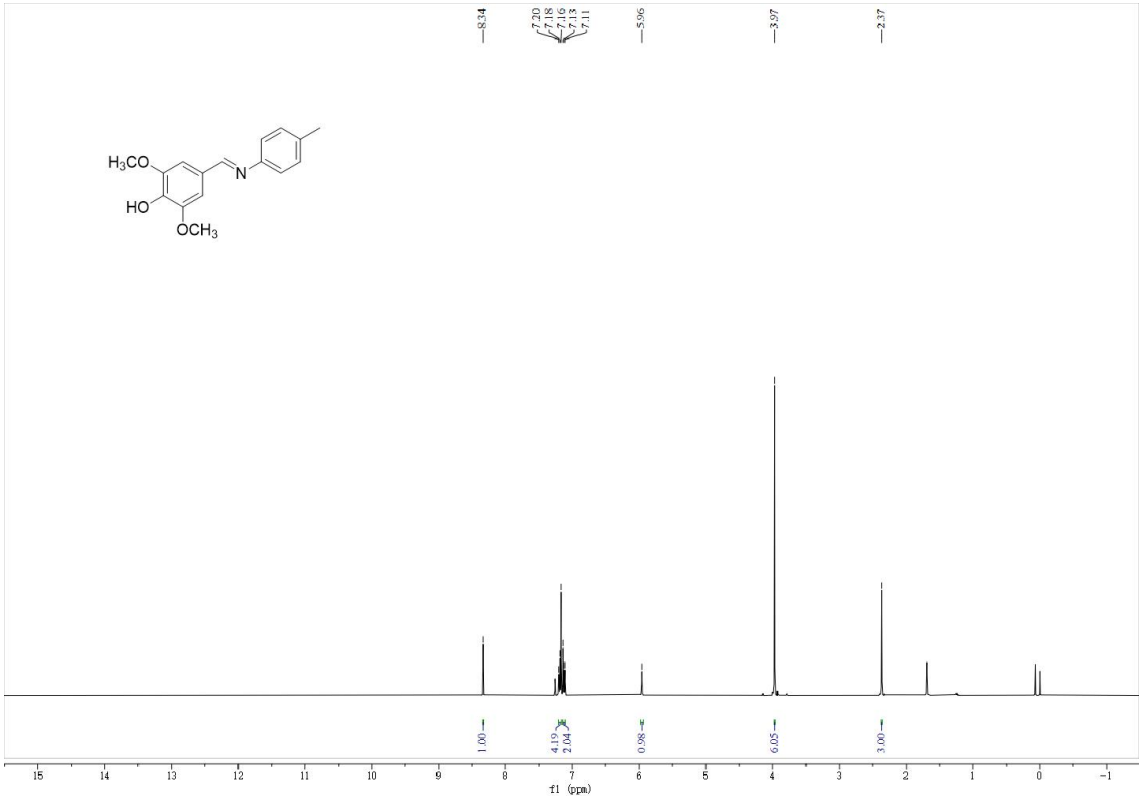

Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1w**

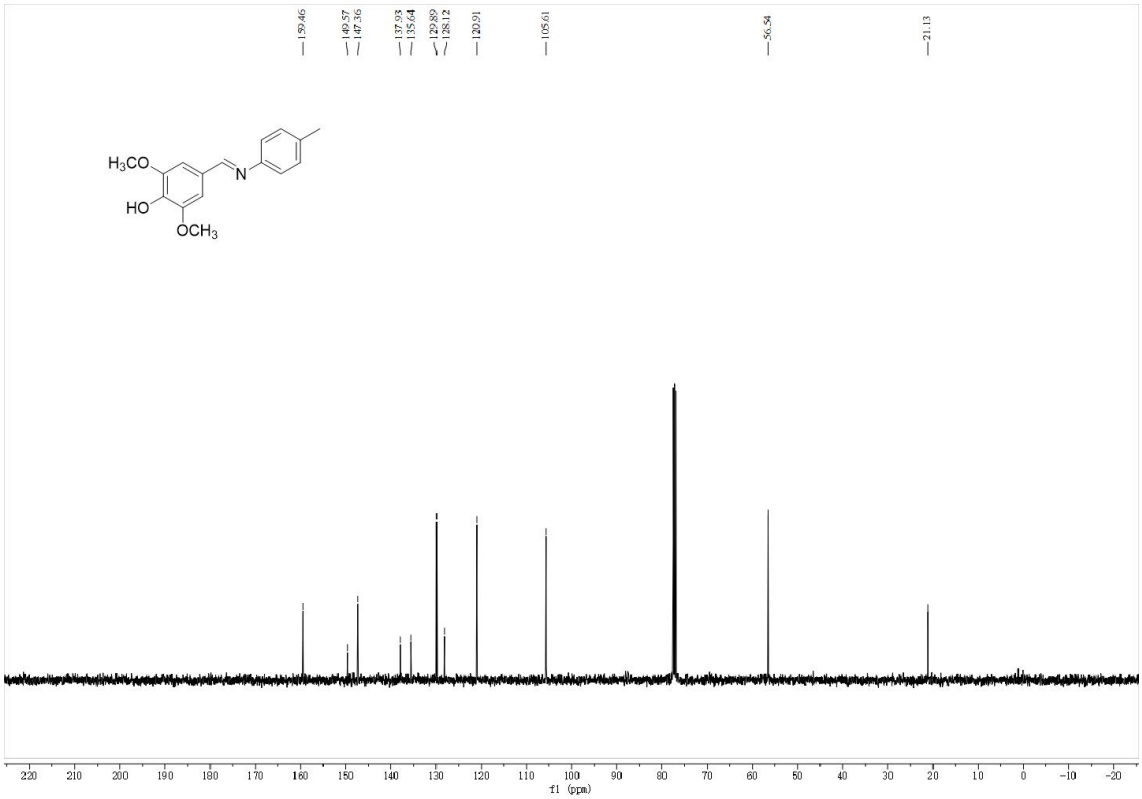

Figure S68. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1w**

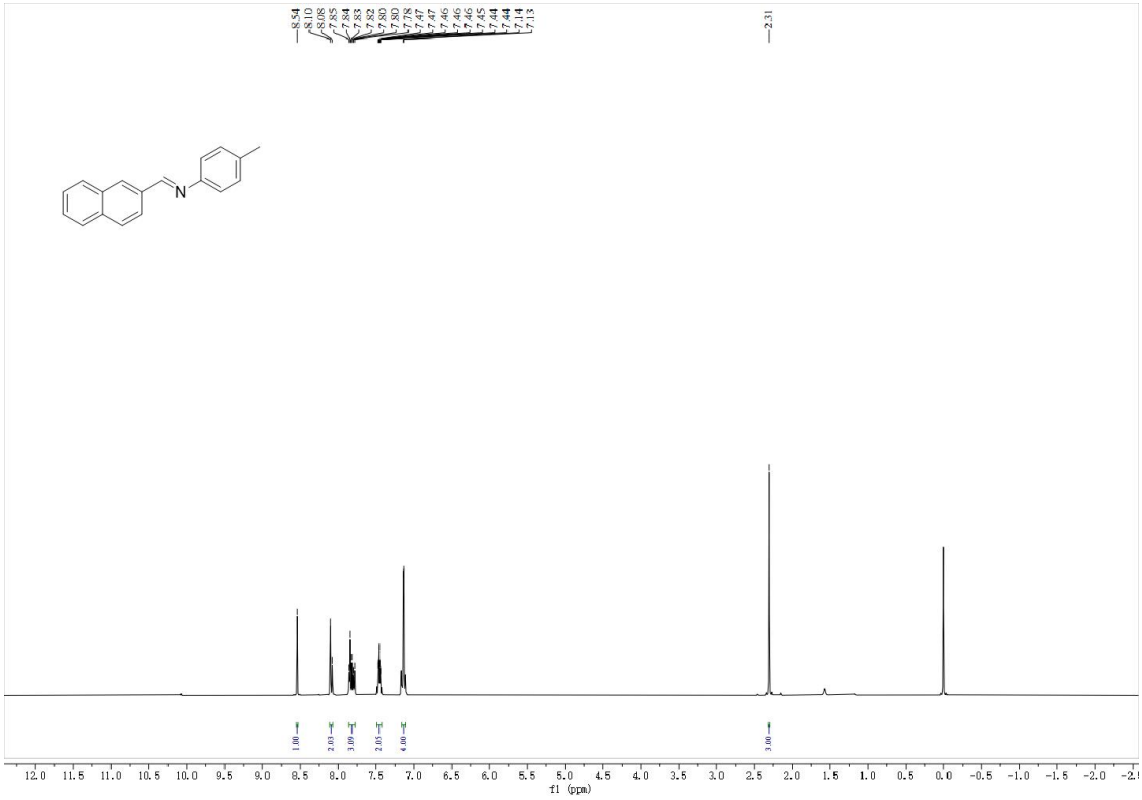

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1x**

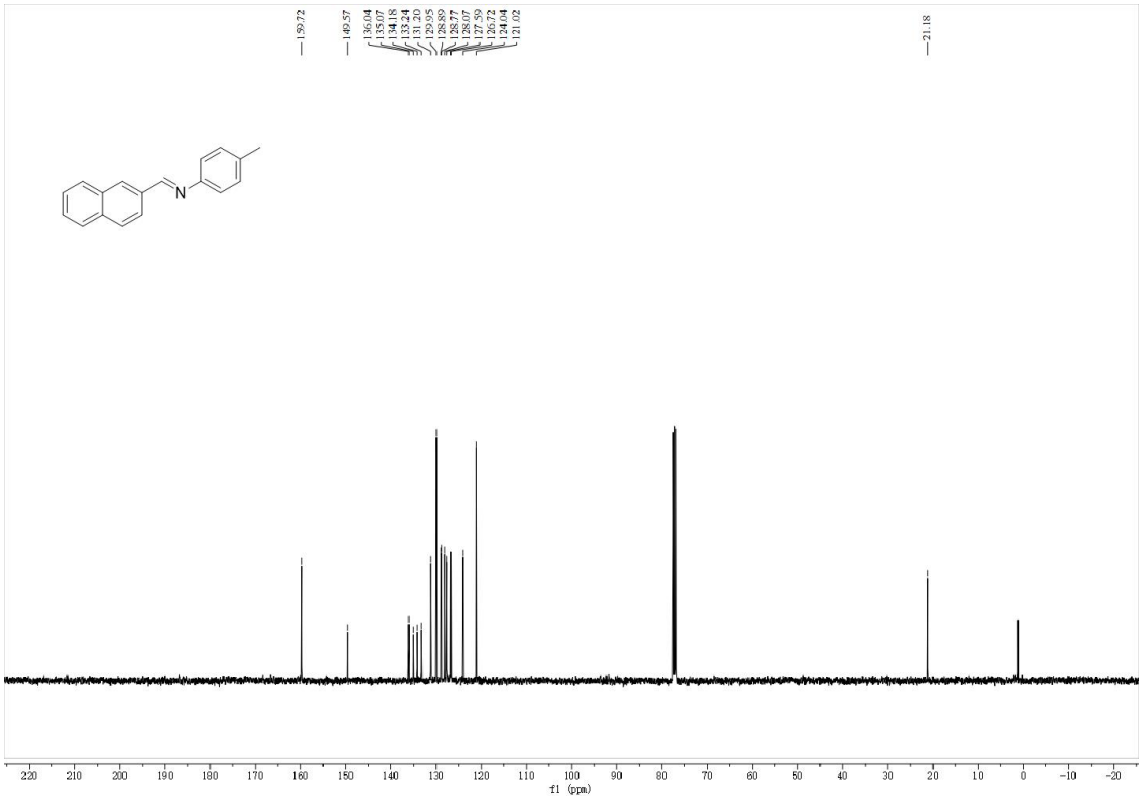

Figure 70. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1x**

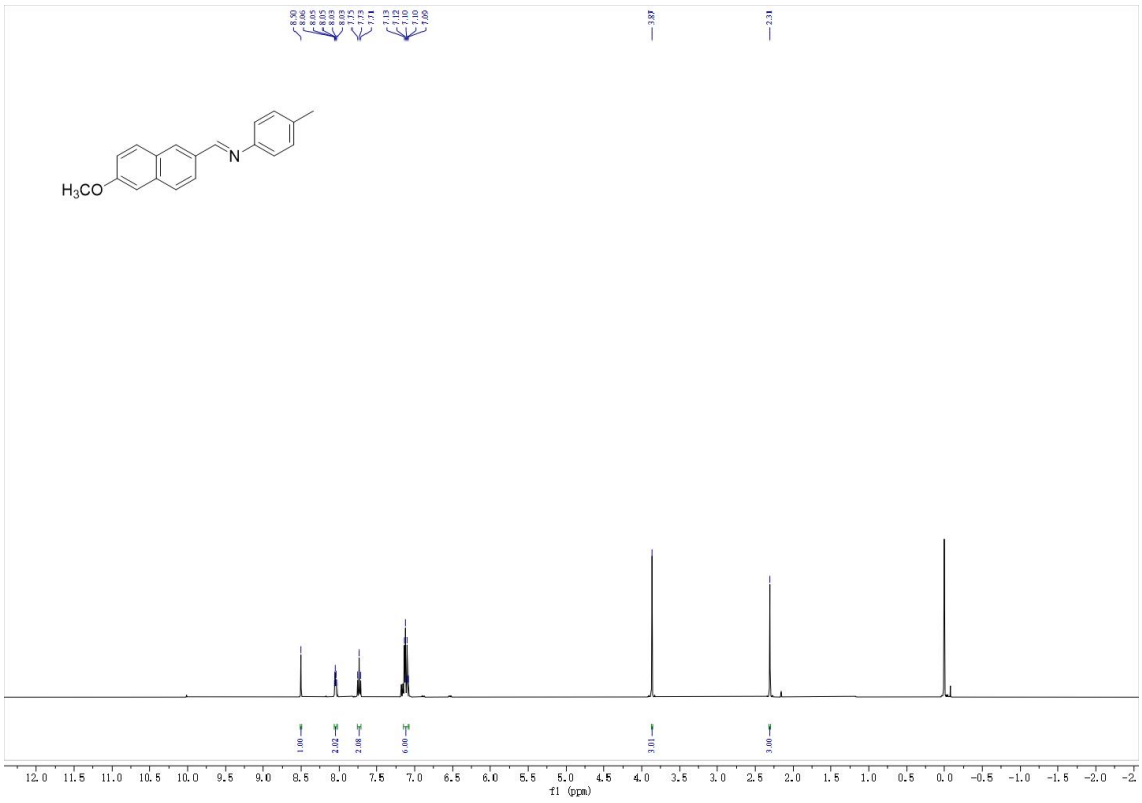

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1y**

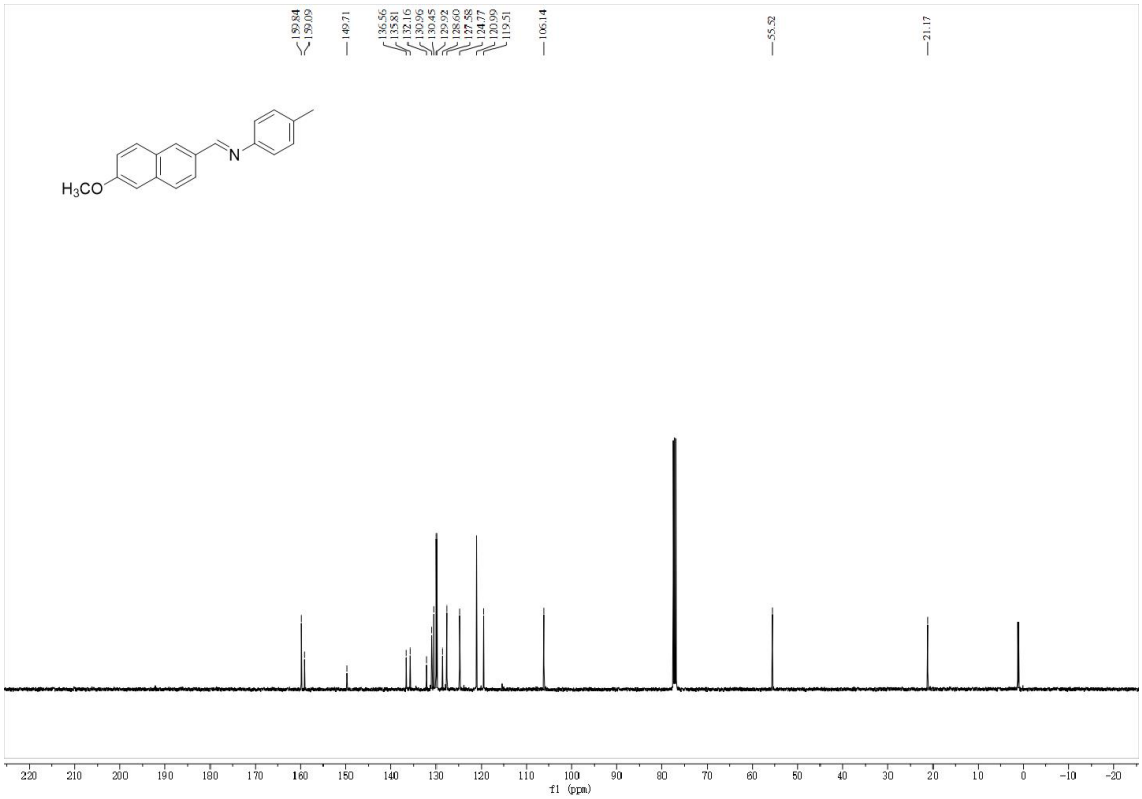

Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1y**

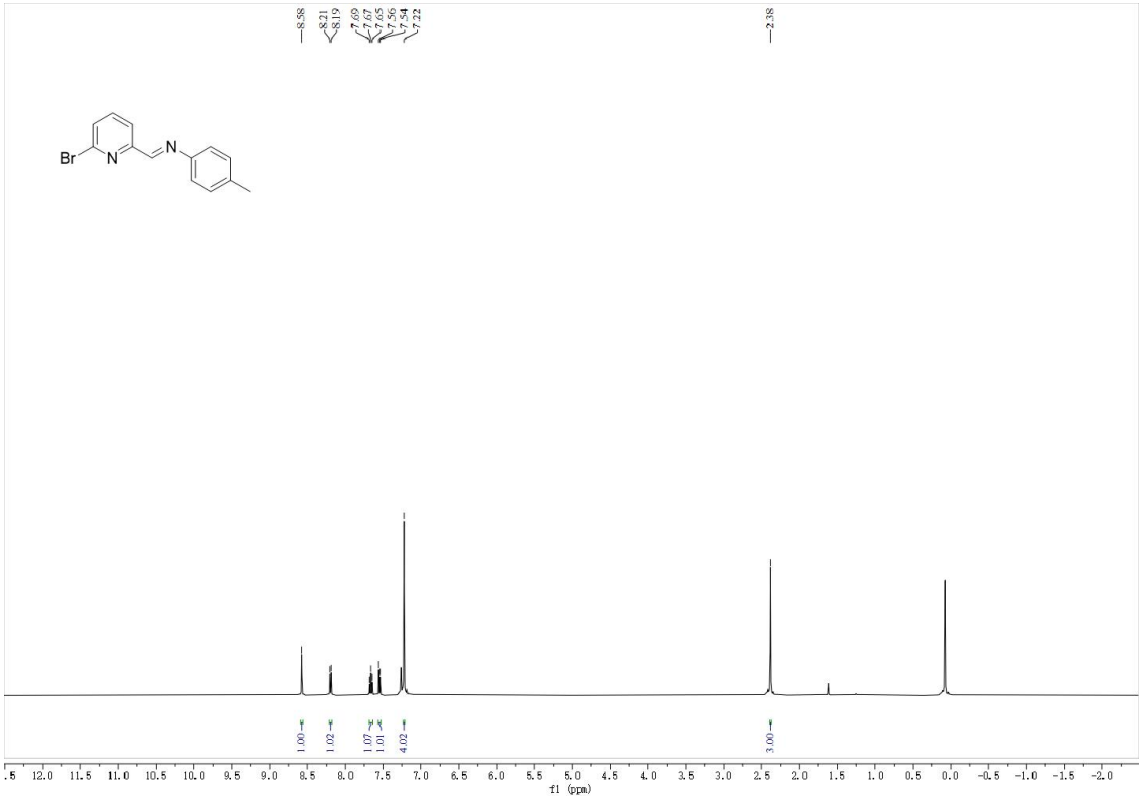

Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1z**

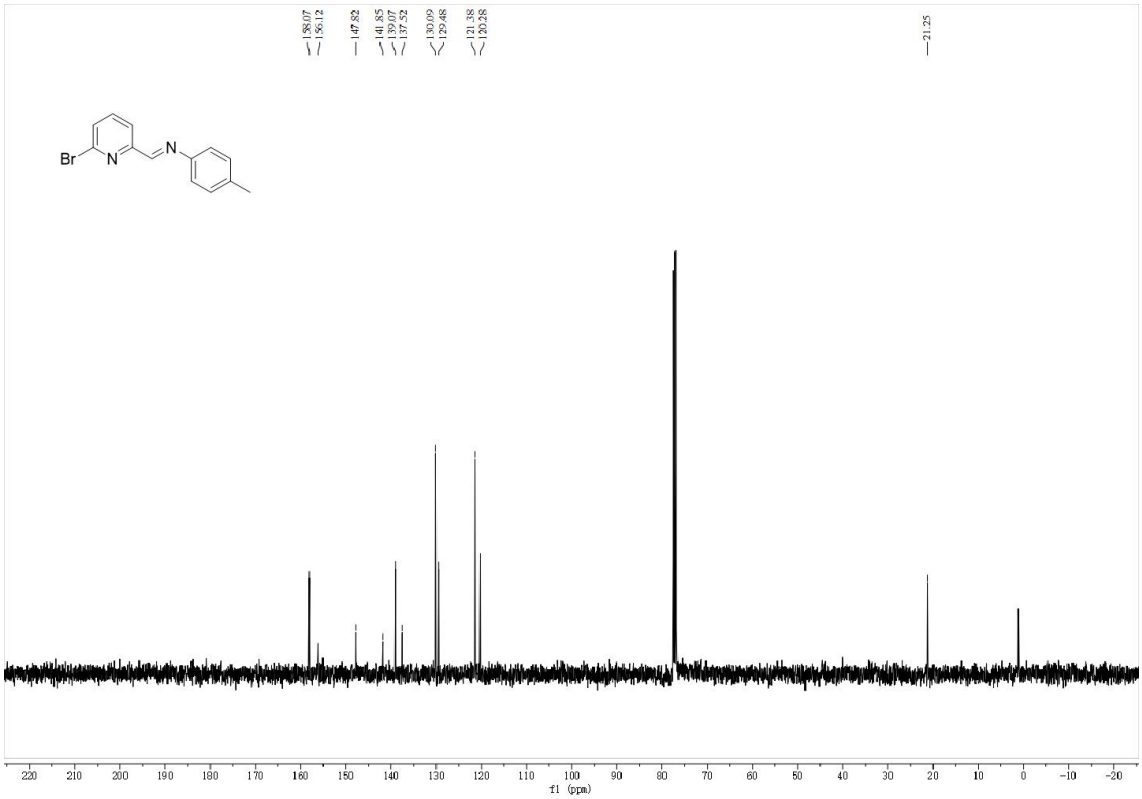

Figure S74. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1z**

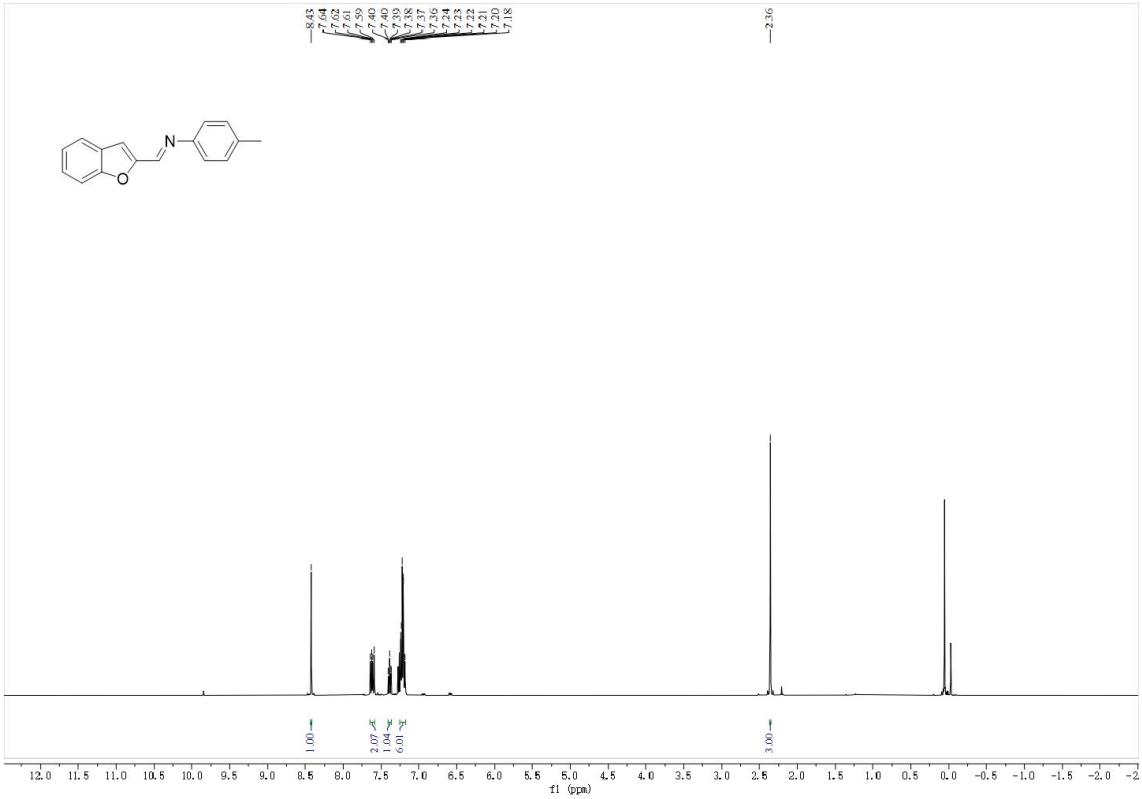

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1aa**

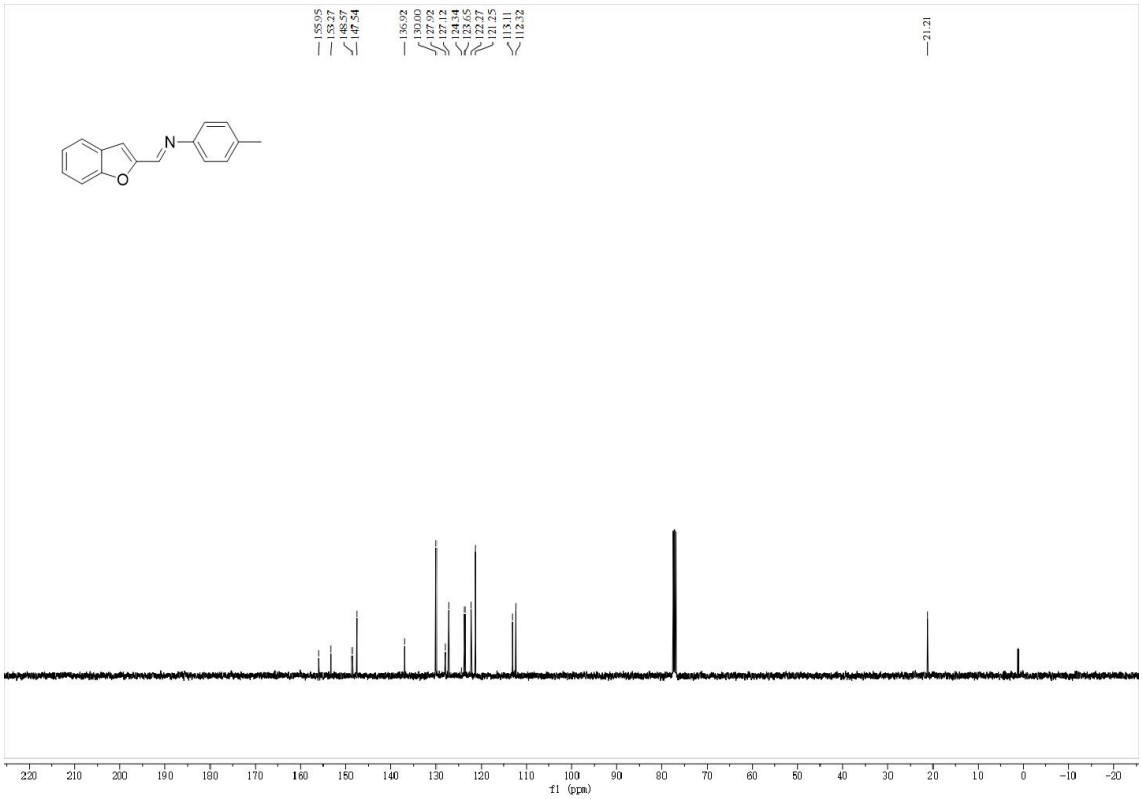

Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1aa**

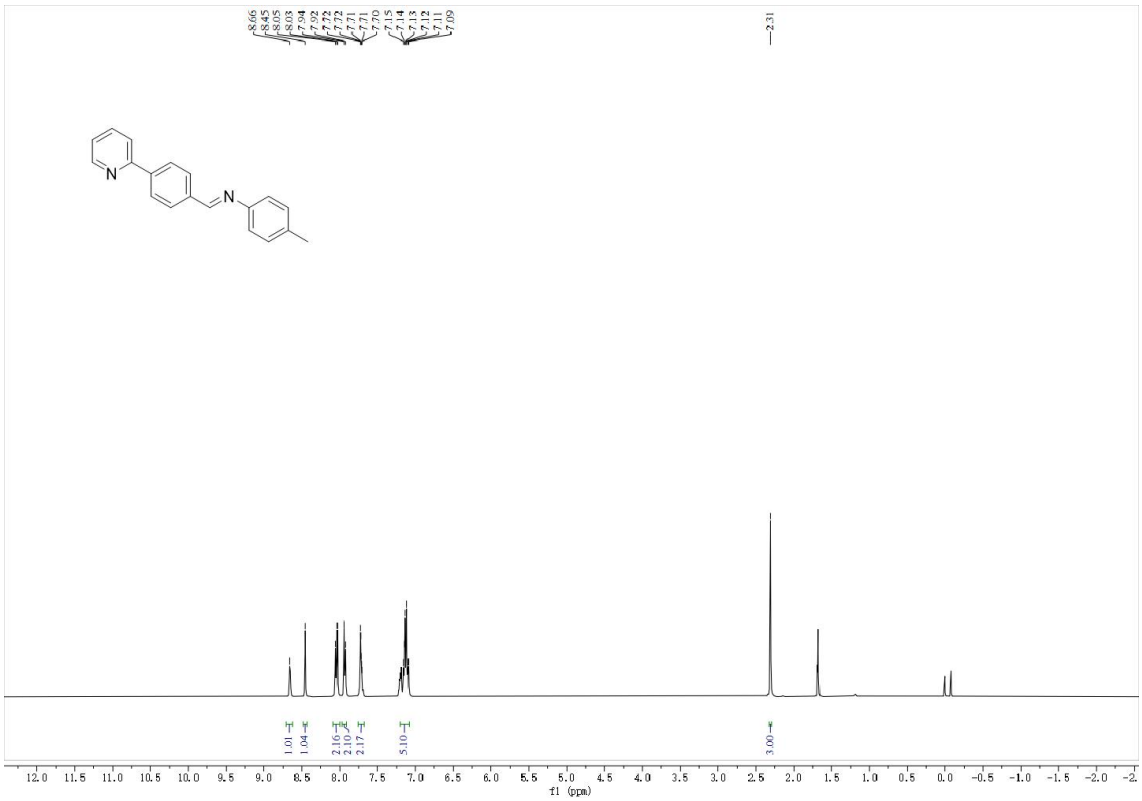

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ab**

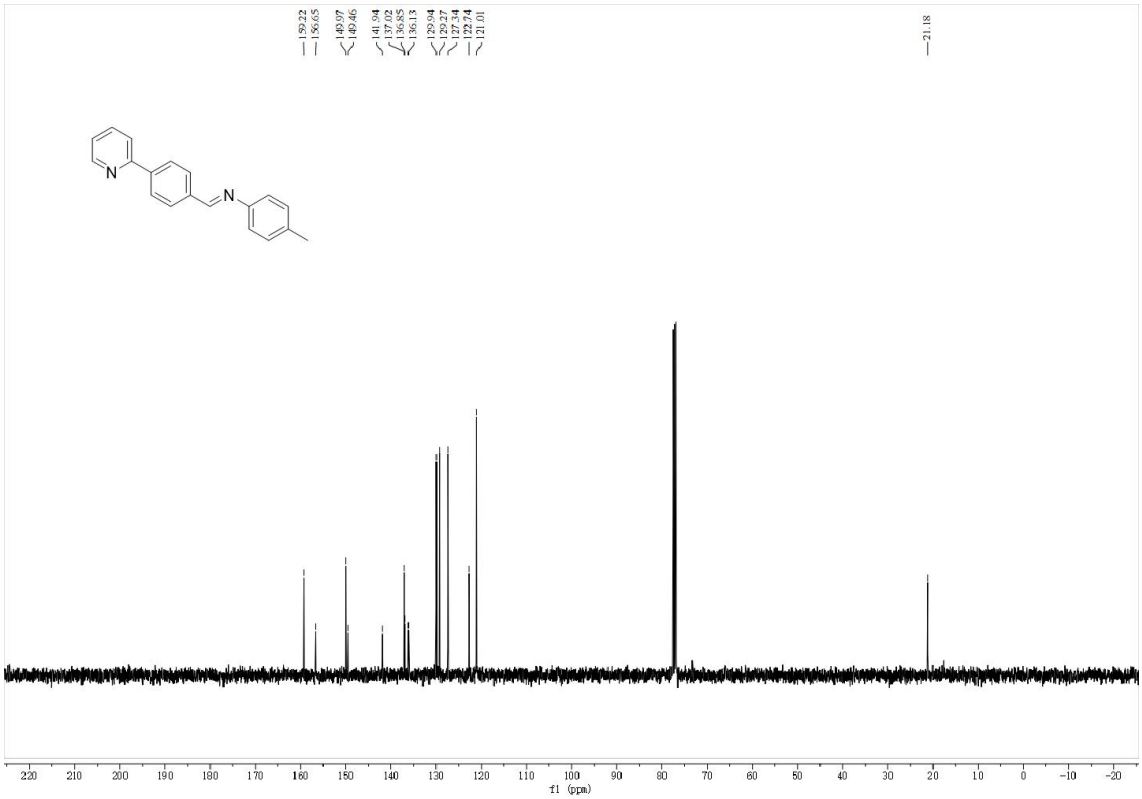

Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ab**

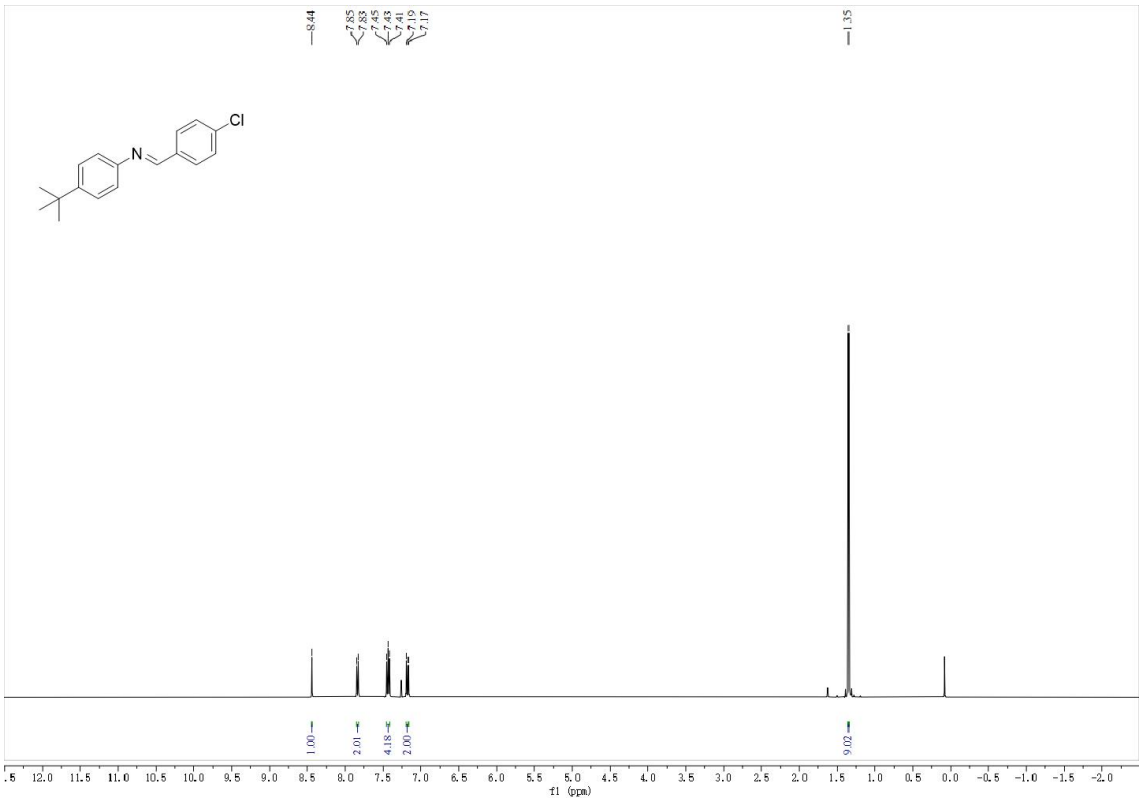

Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ac**

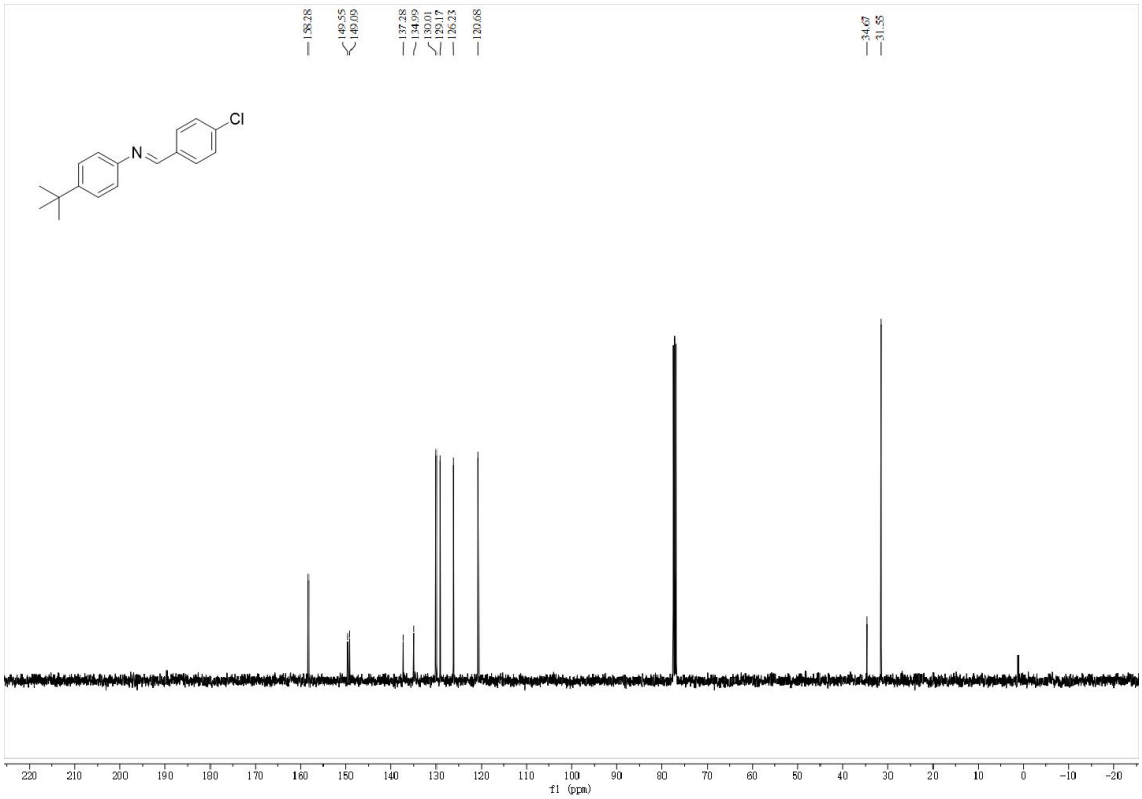

Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ac**

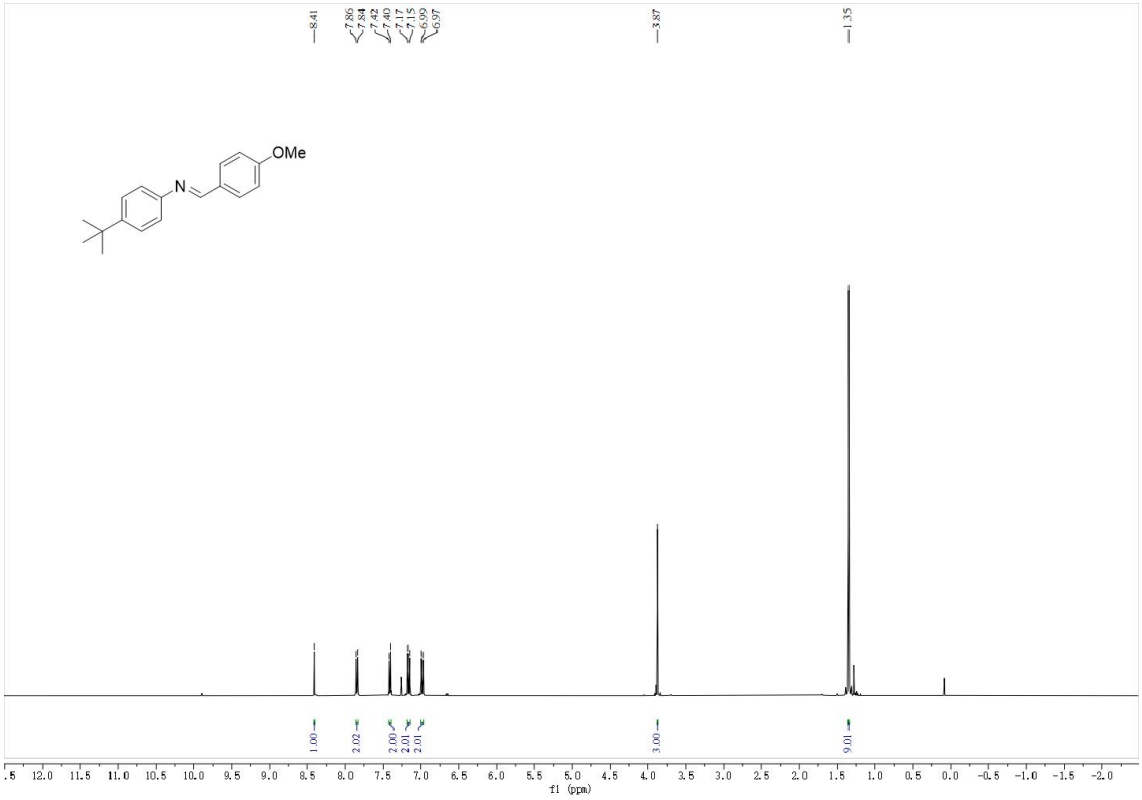

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ad**

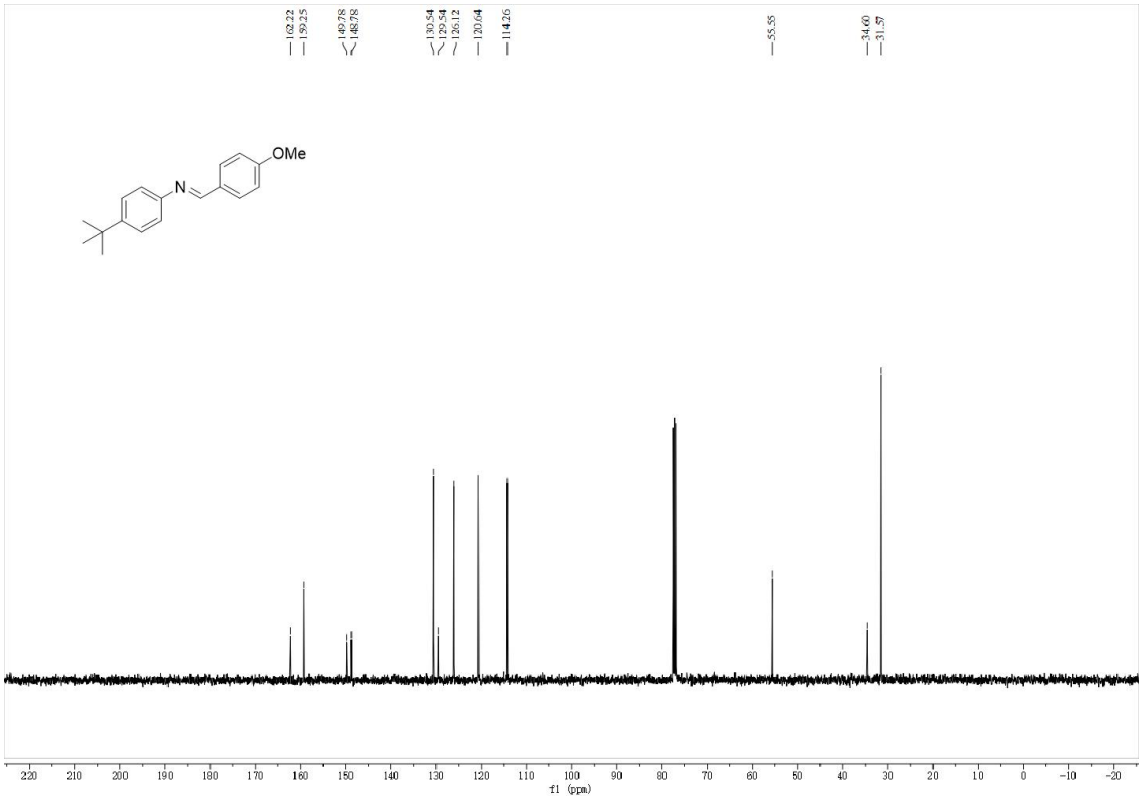

Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ad**

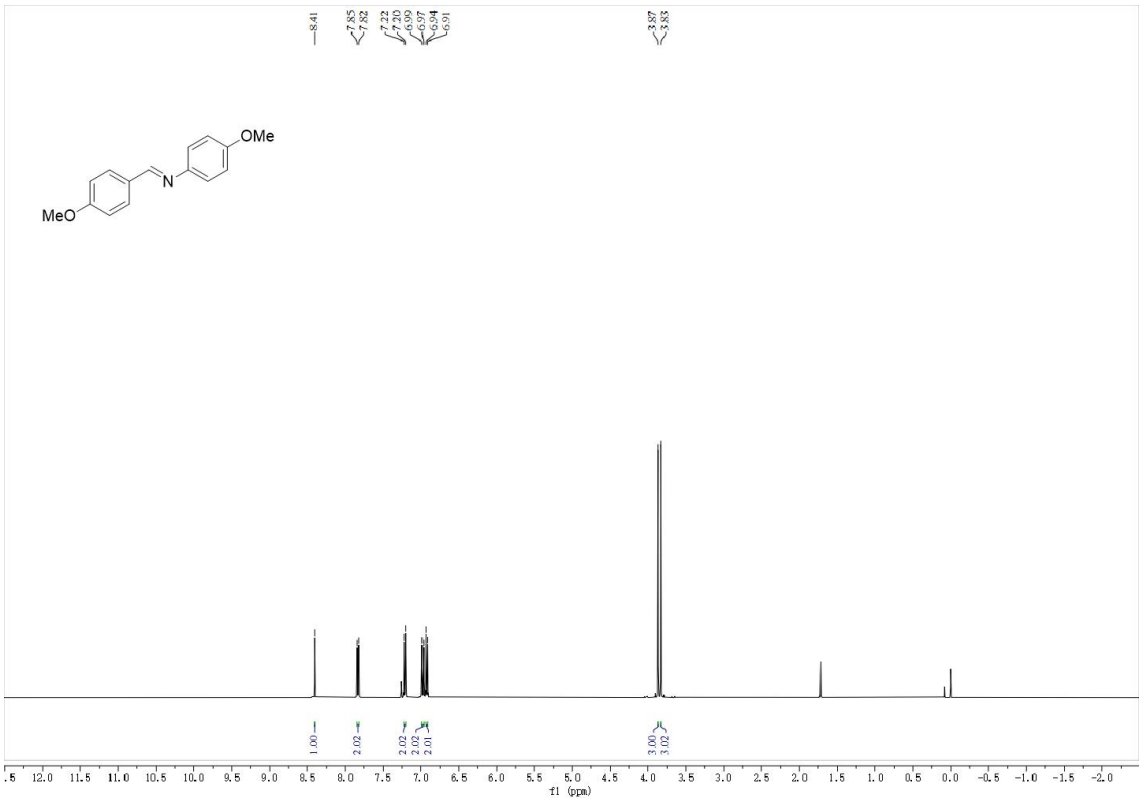

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ae**

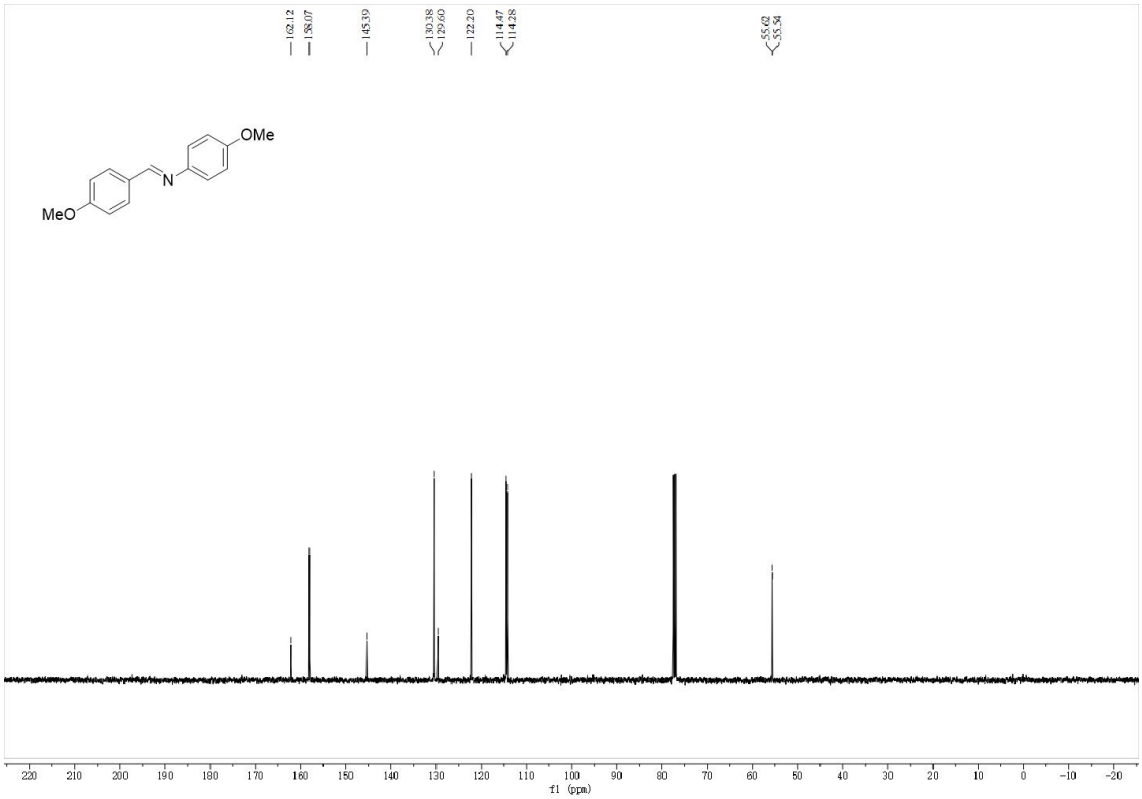

Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ae**

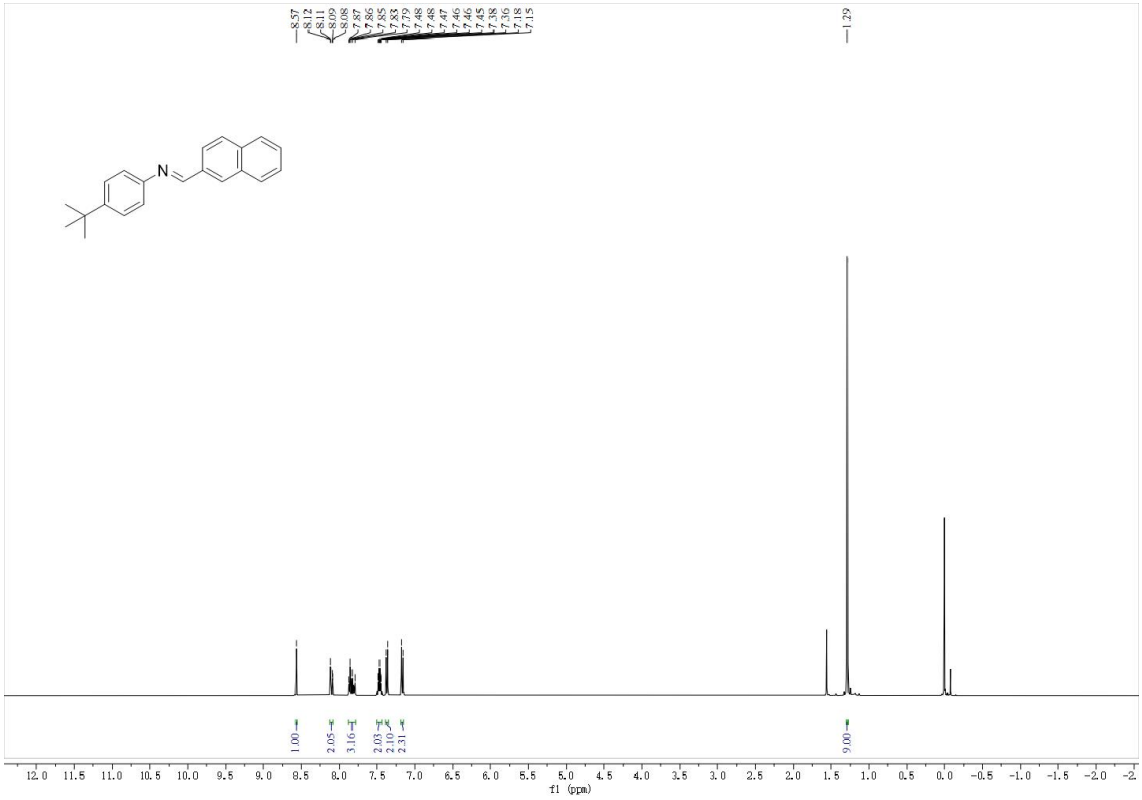

Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1af**

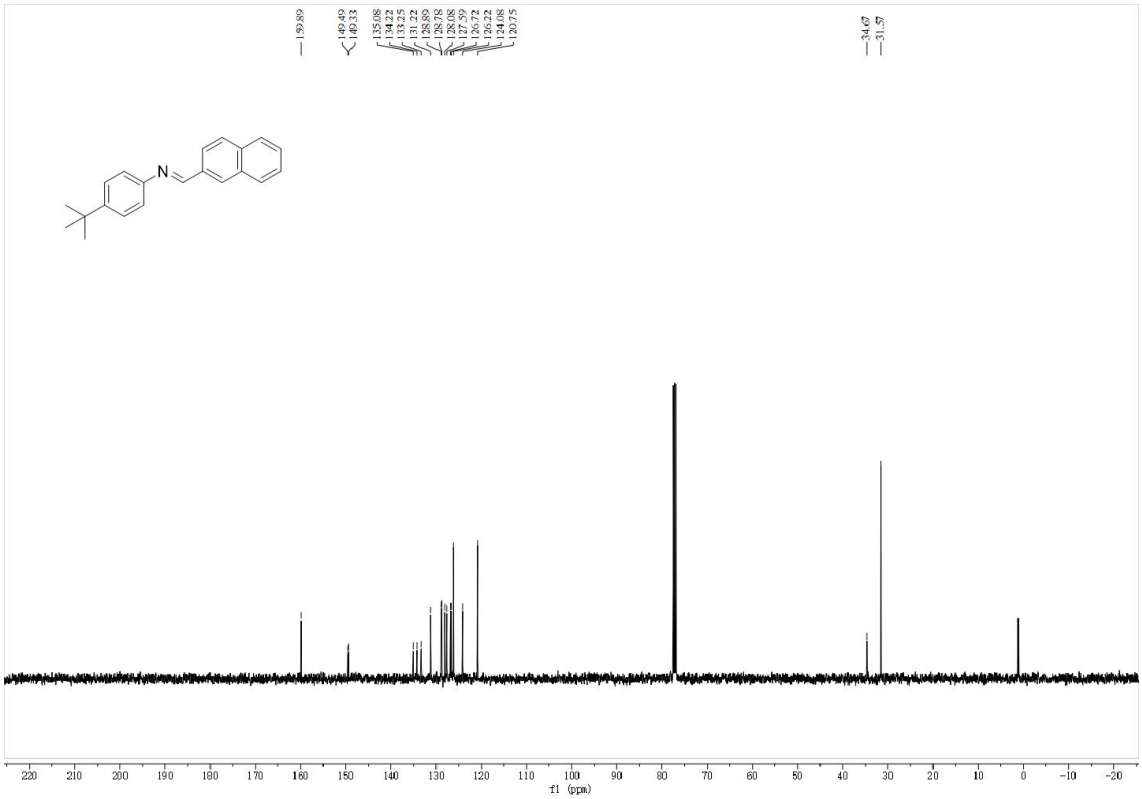

Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1af**

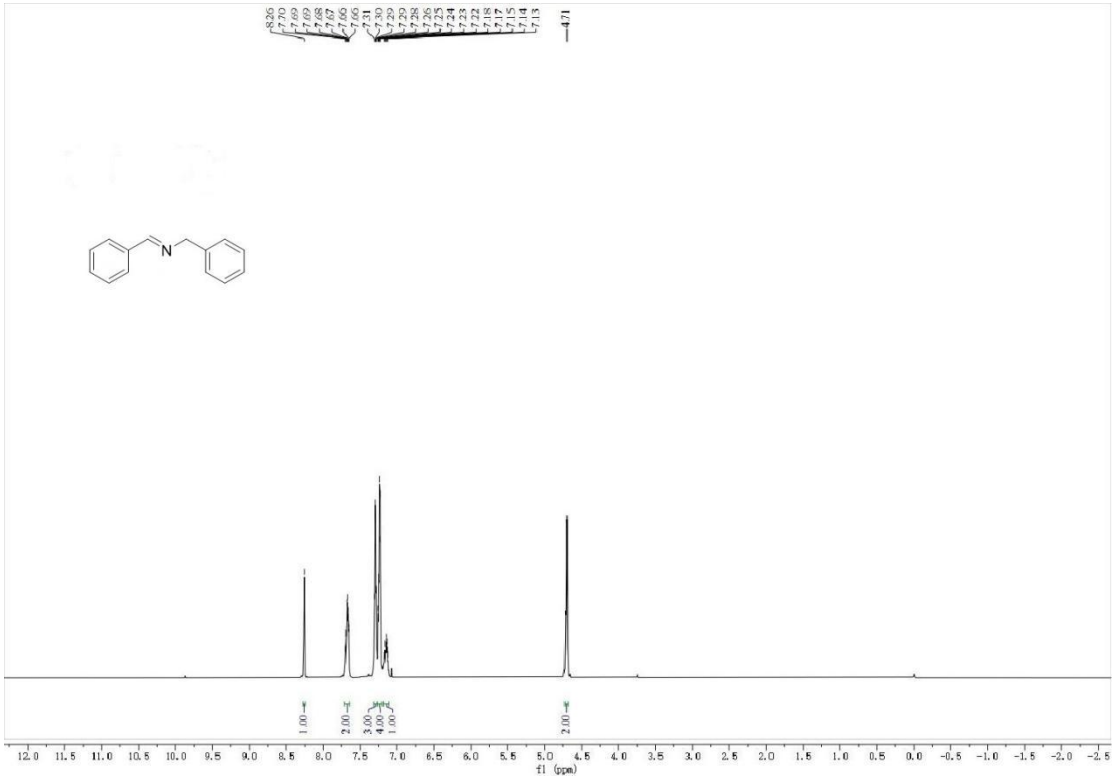

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ag**

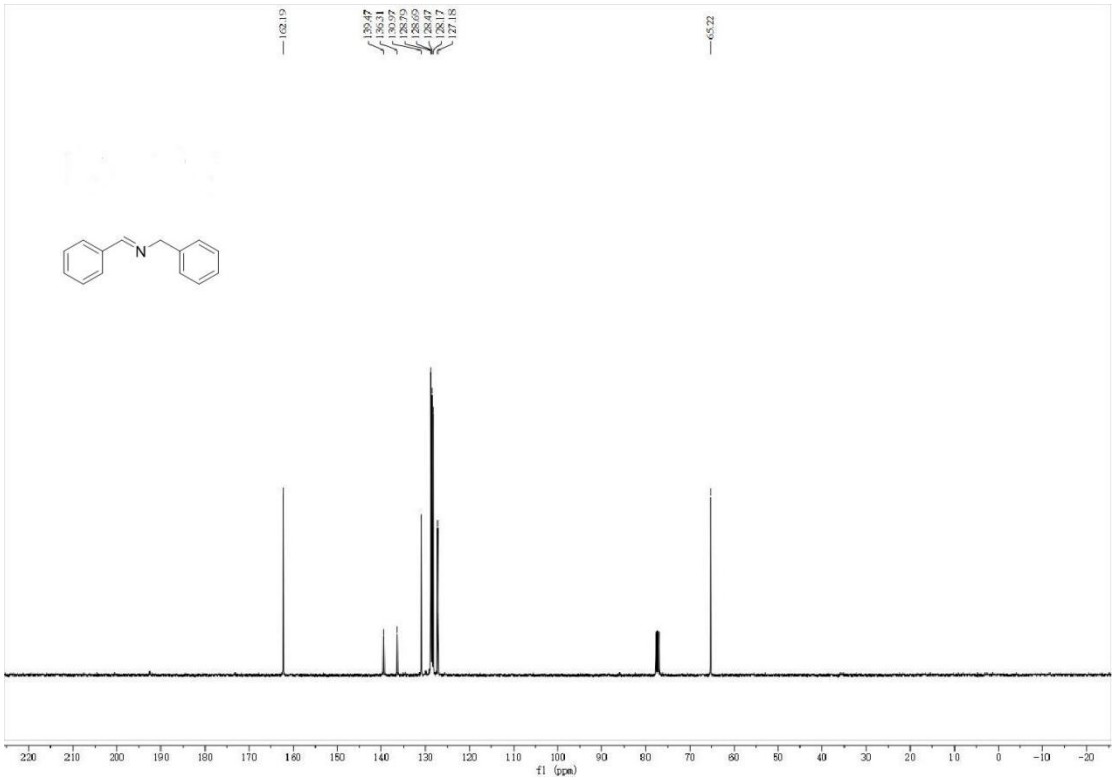

Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ag**

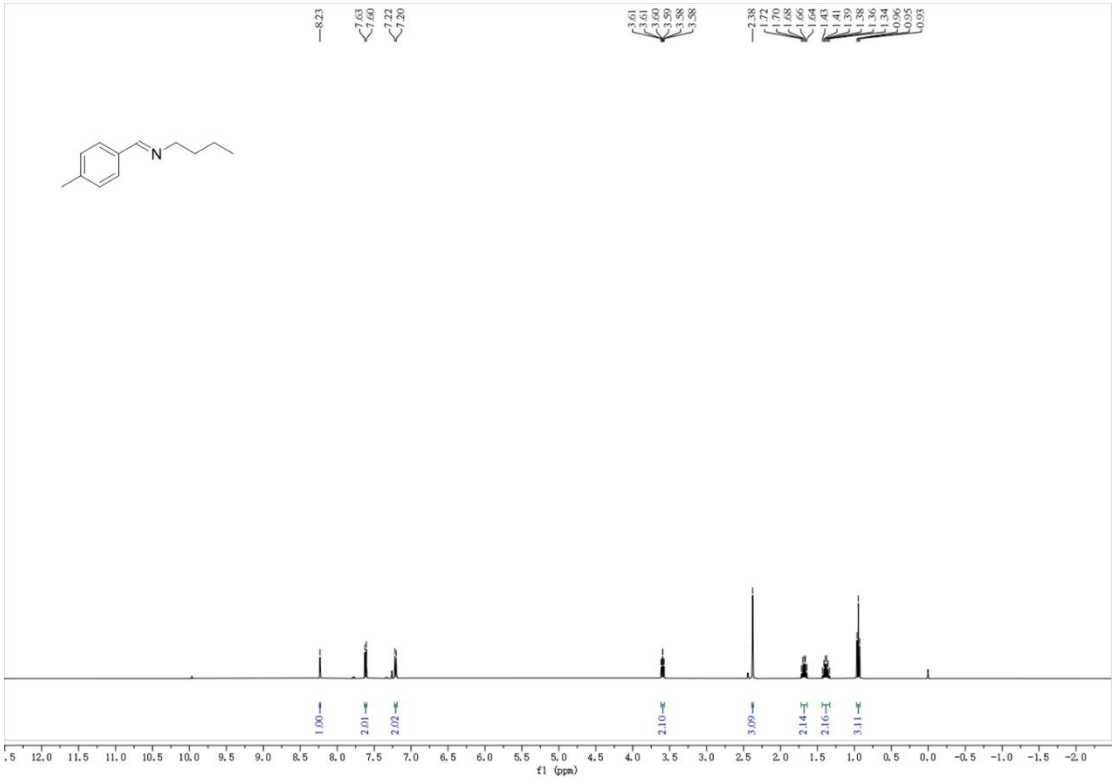

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ag**

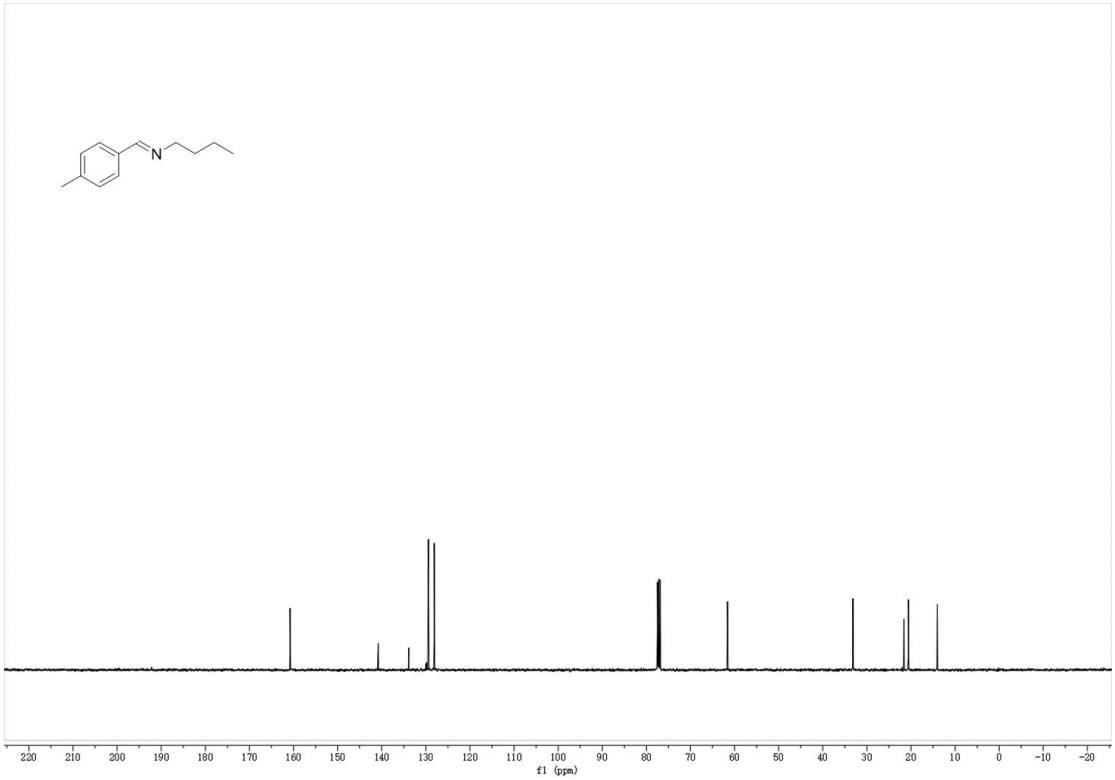

Figure S90. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ag**

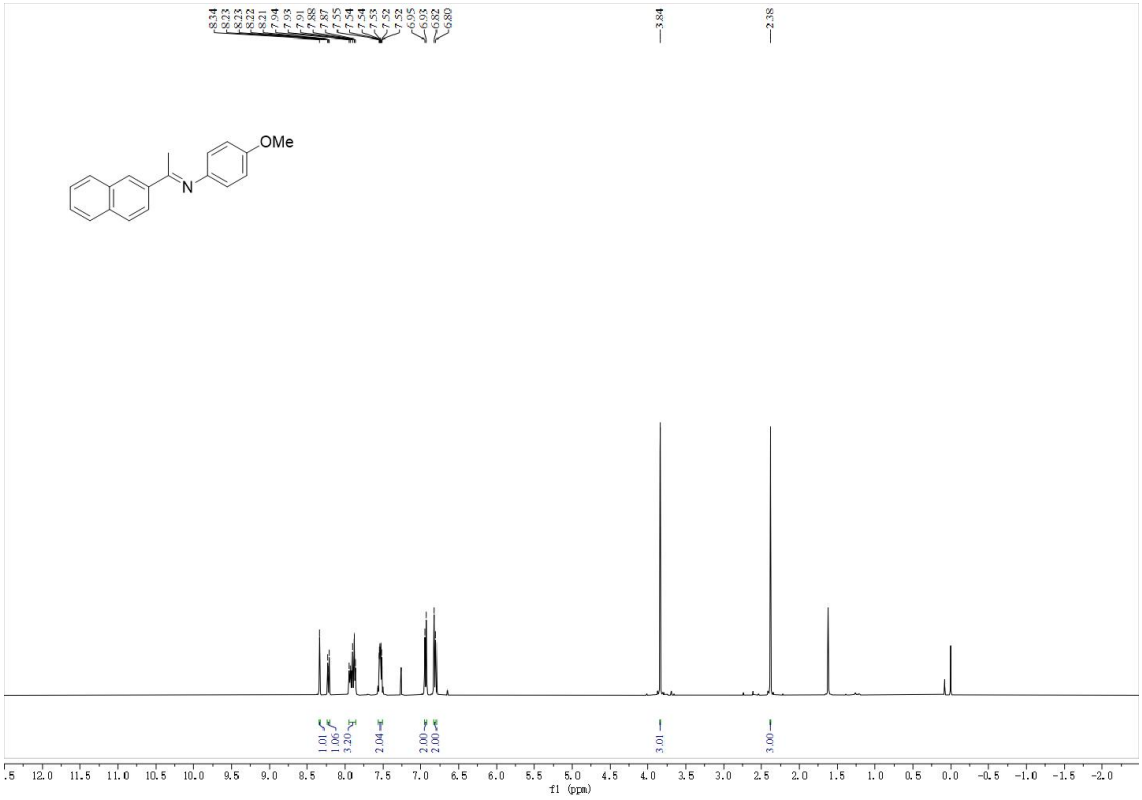

Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ai**

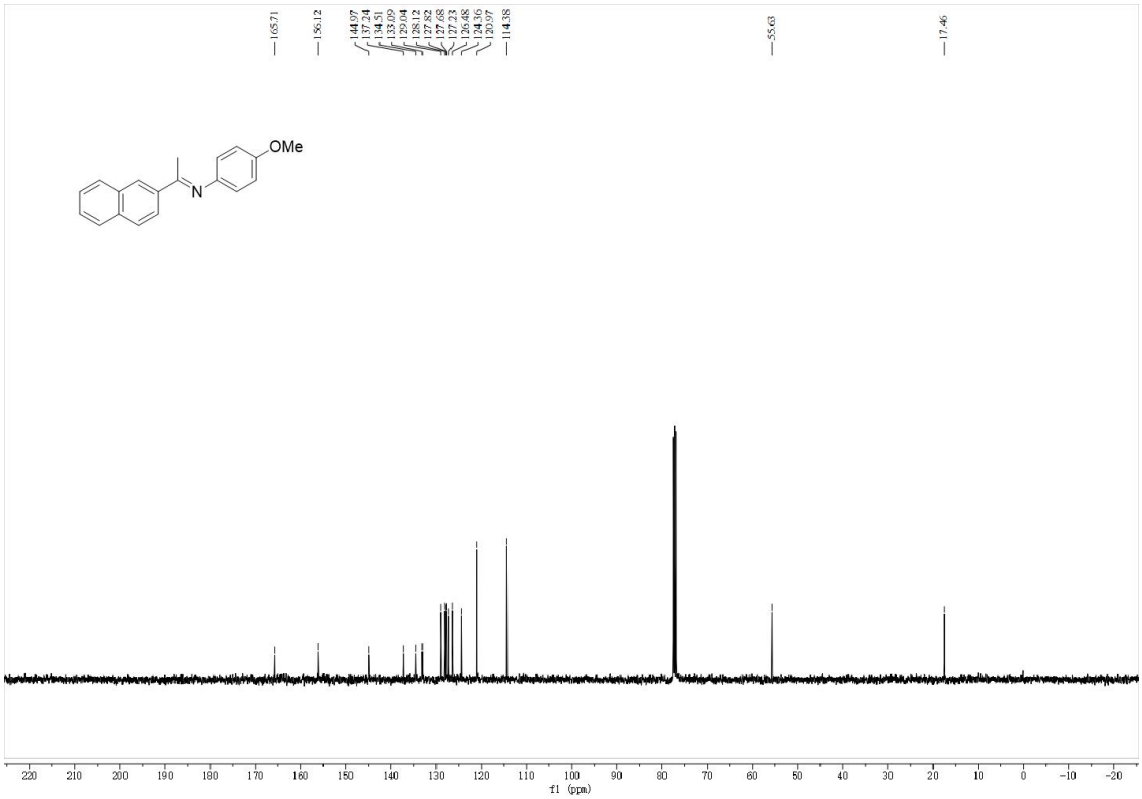

Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ai**

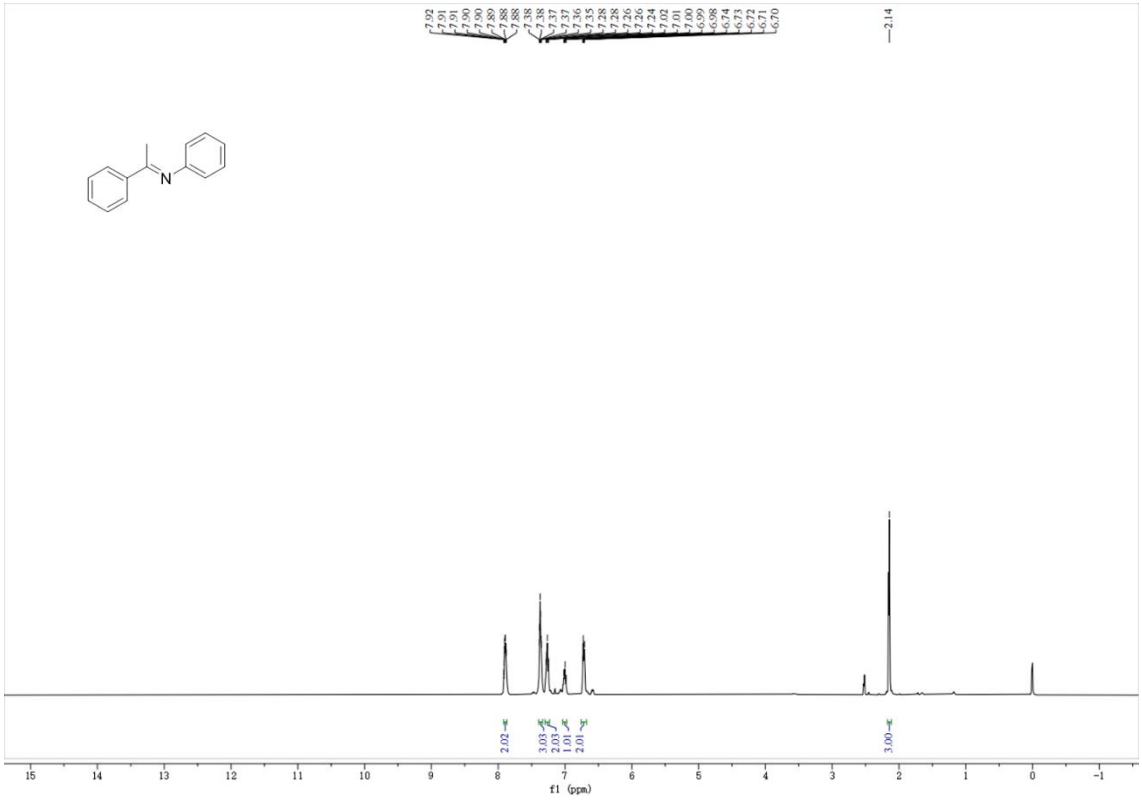

Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1aj**

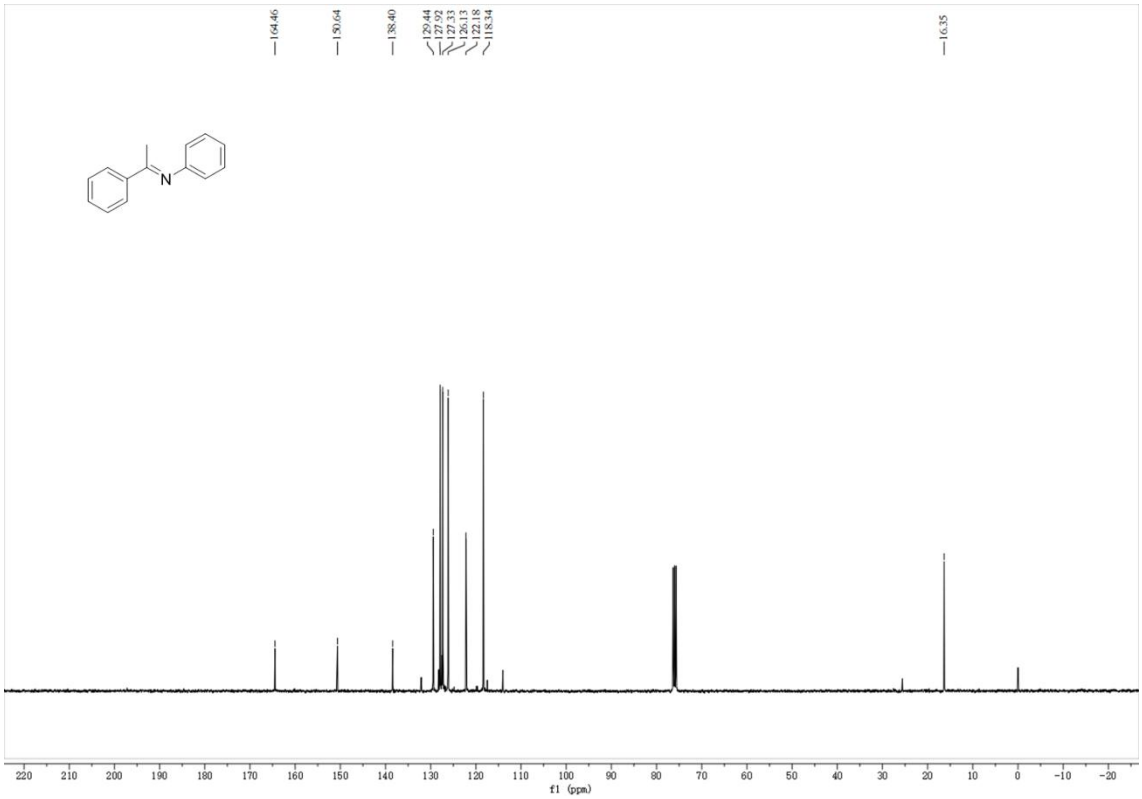

Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1aj**

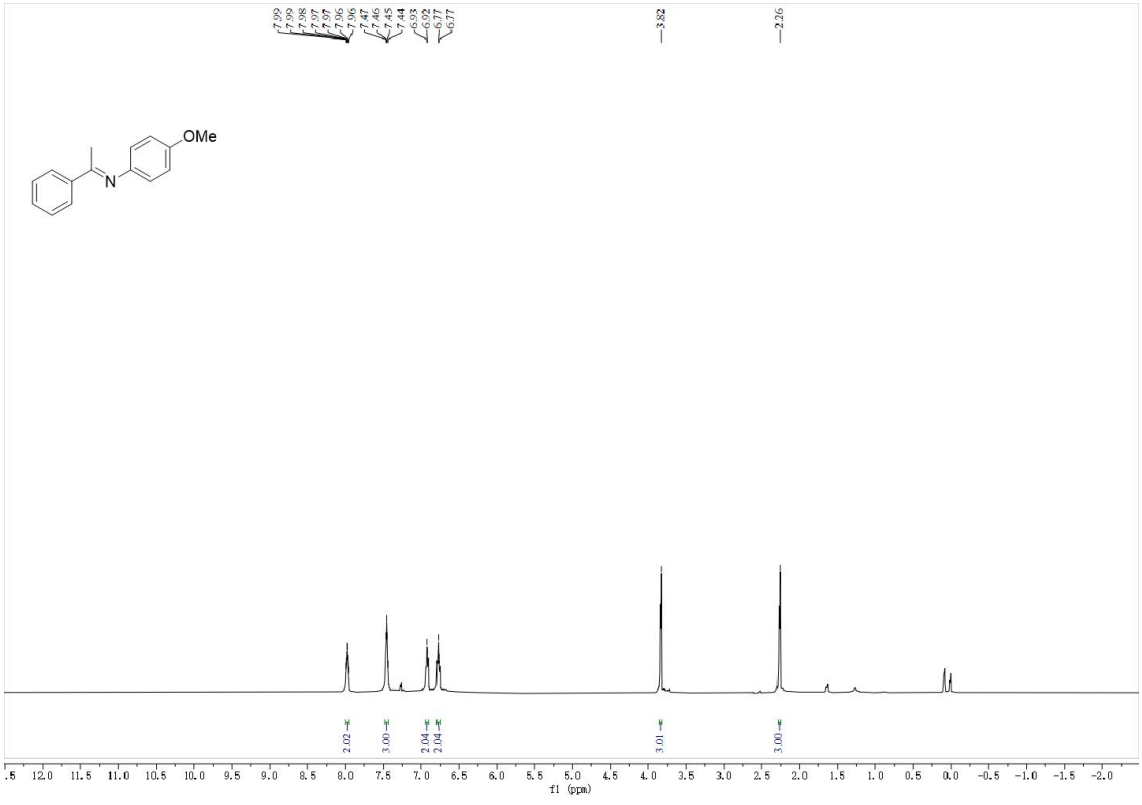

Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ak**

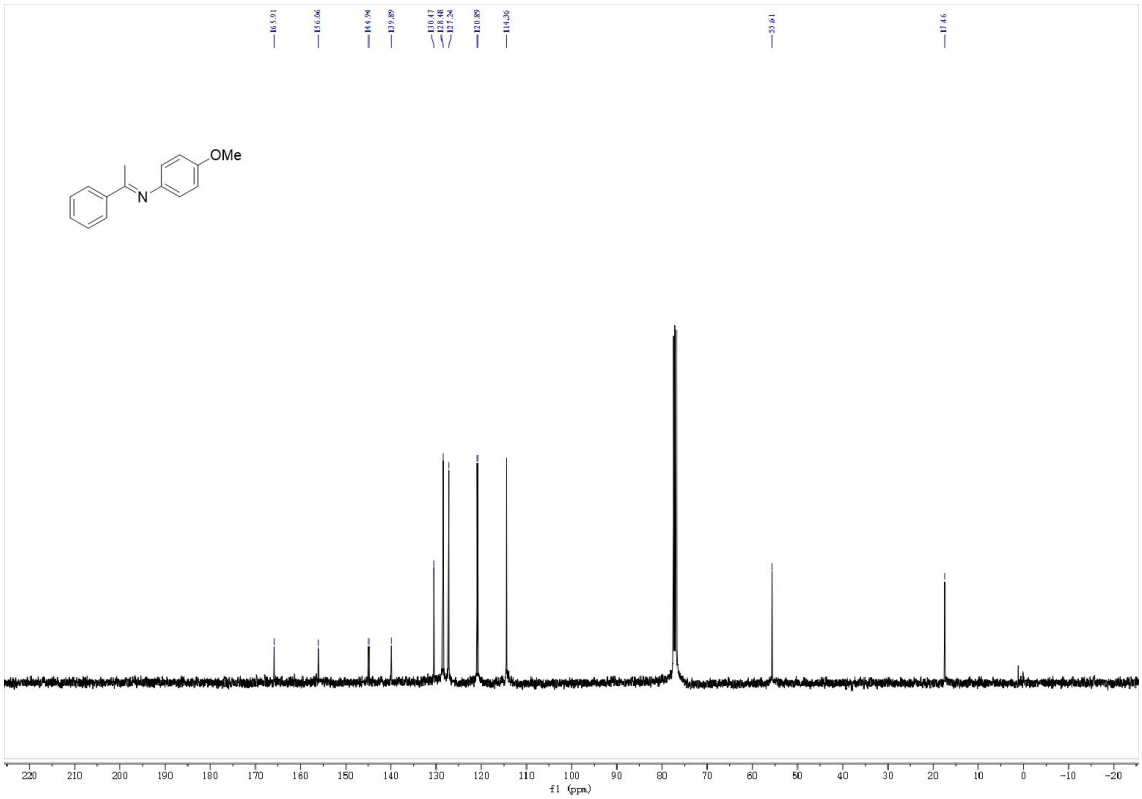

Figure S96. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ak**

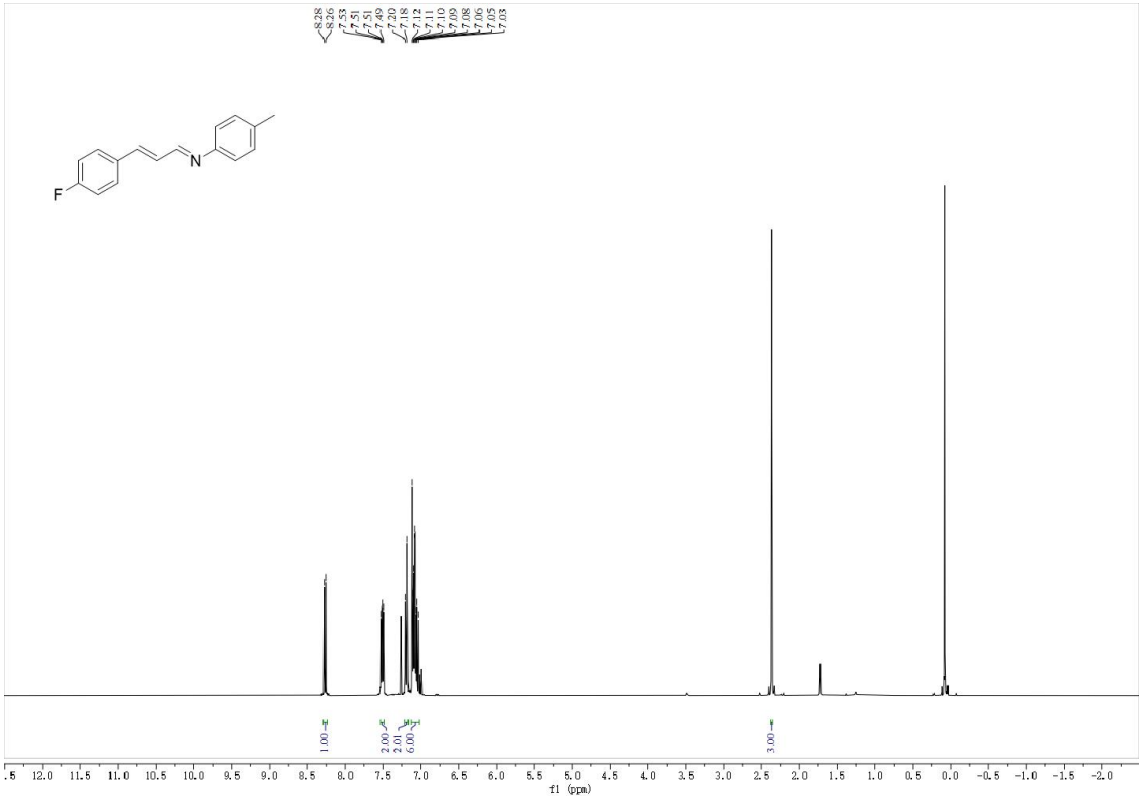

Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1al**

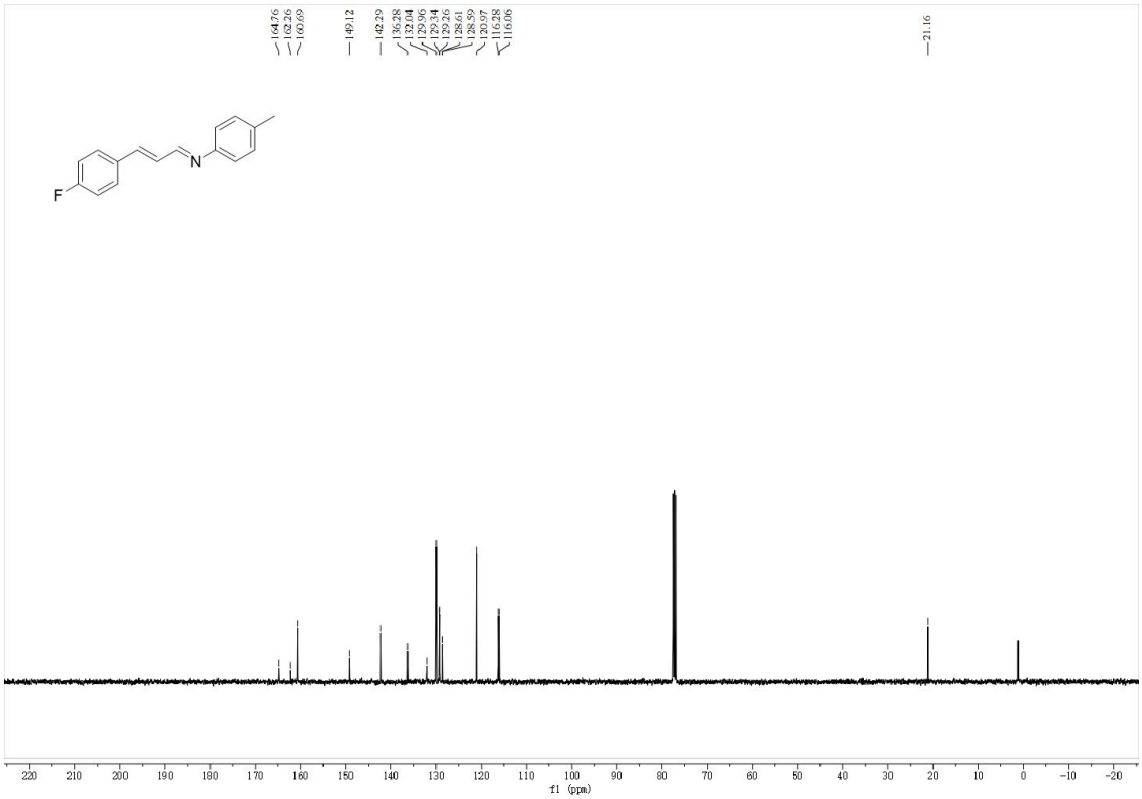

Figure S98. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1al**

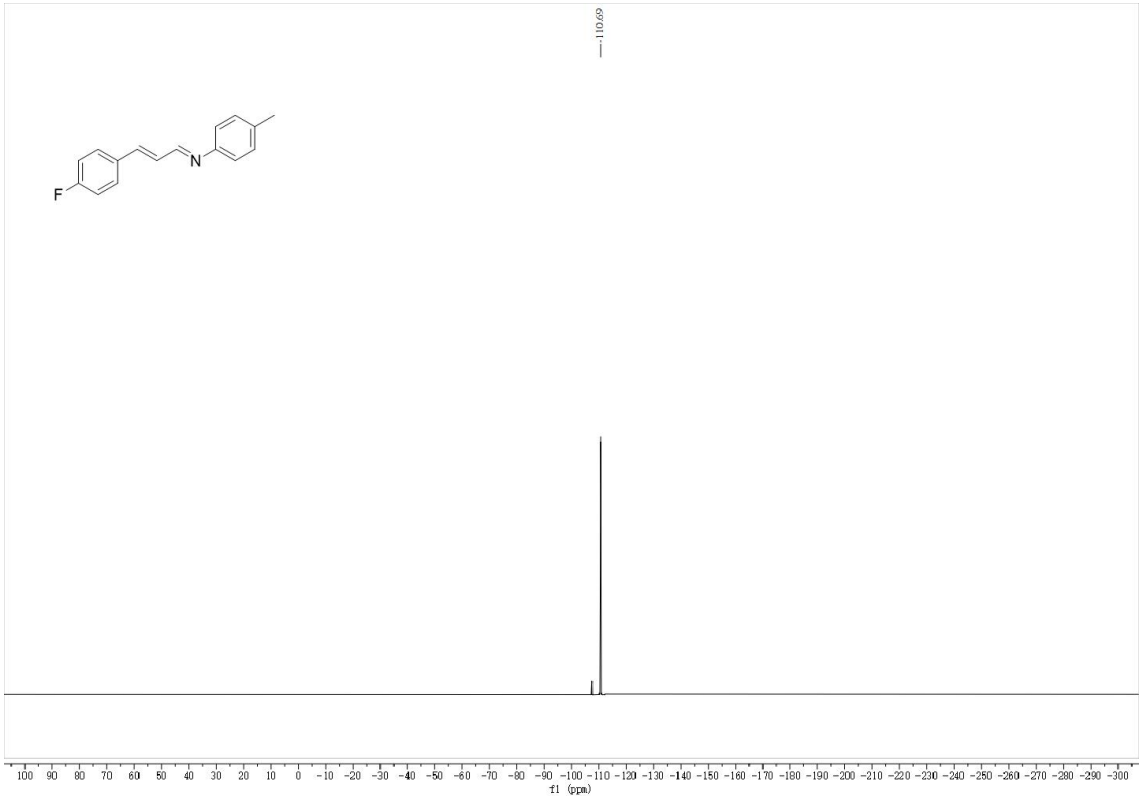

Figure S99. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1al**

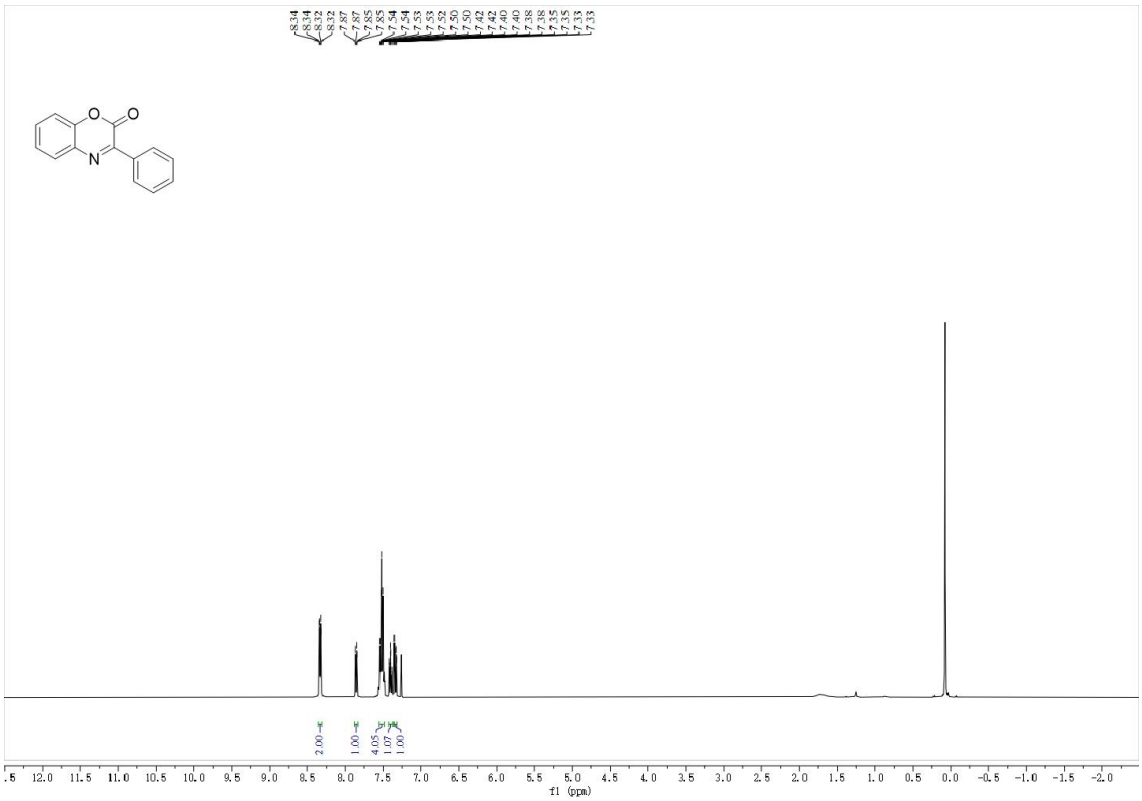

Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1am**

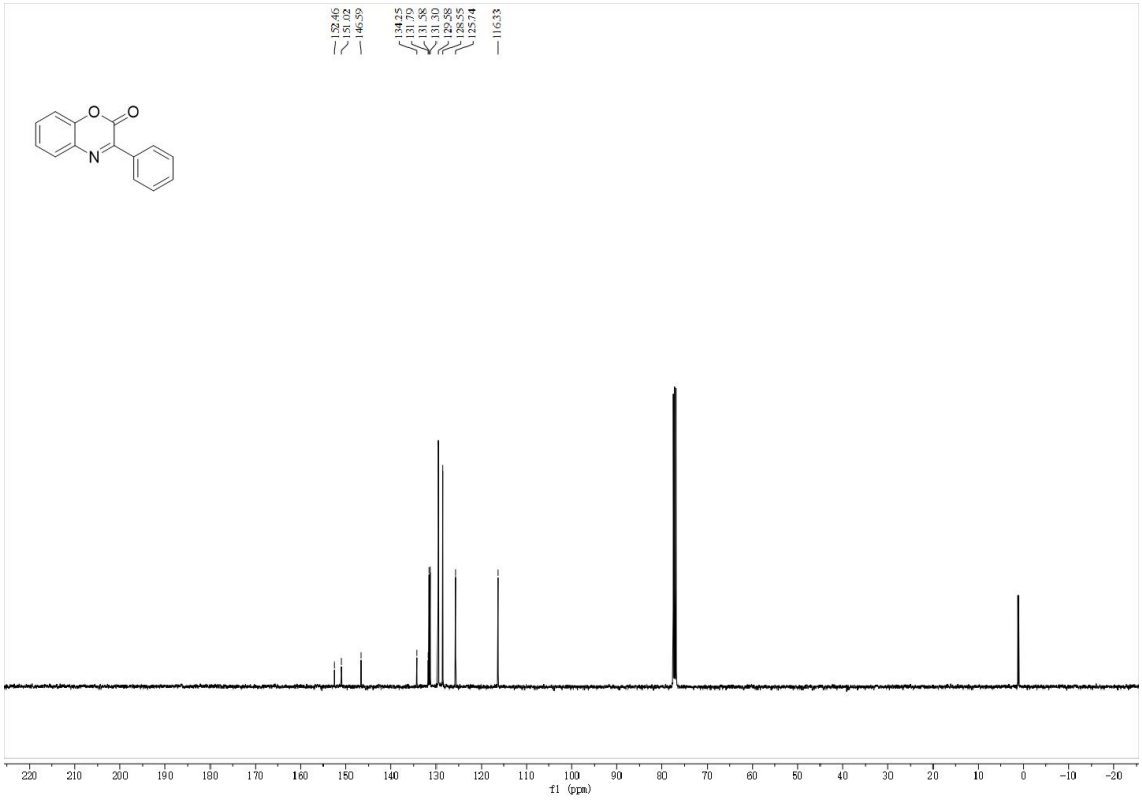

Figure S101. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1am**

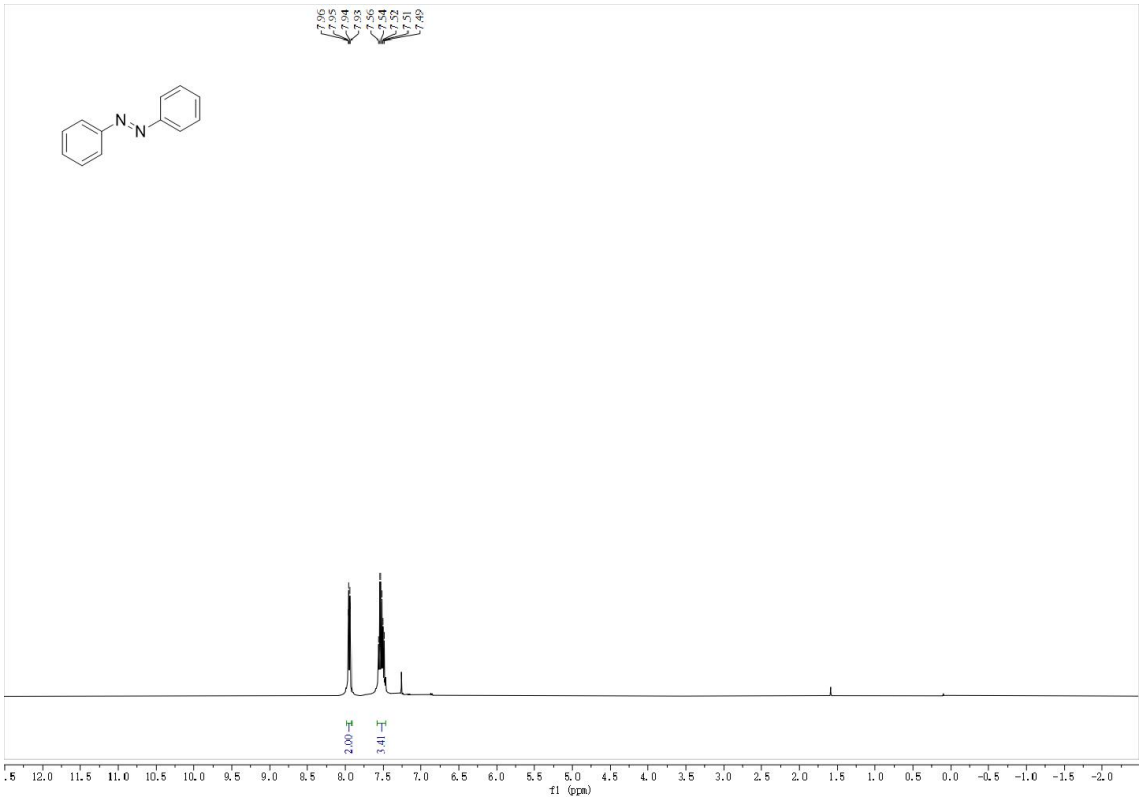

Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

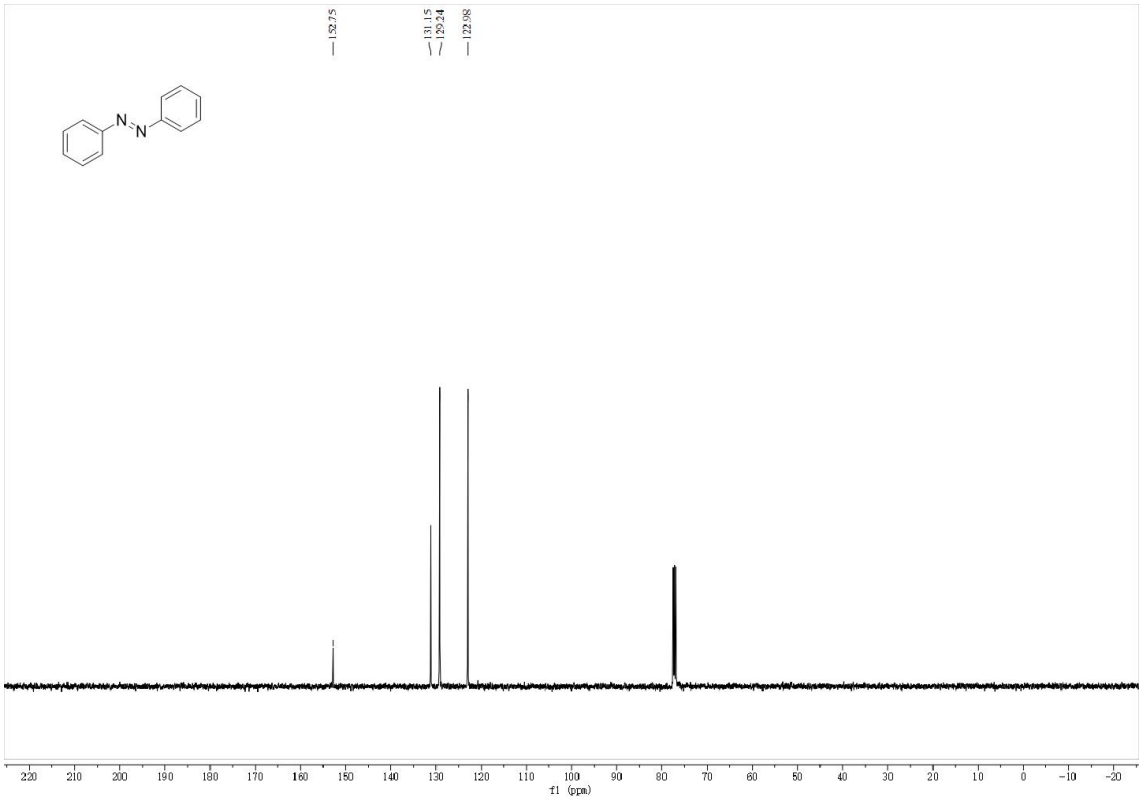

Figure S103. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3a**

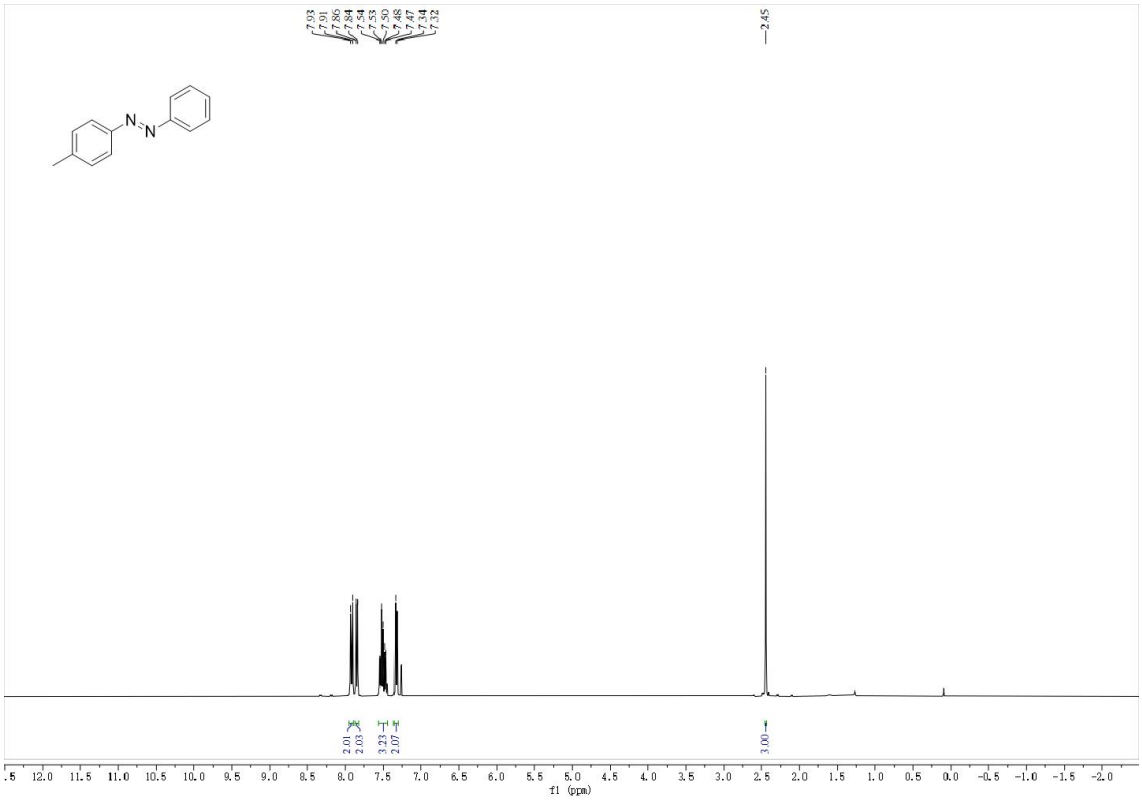

Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**

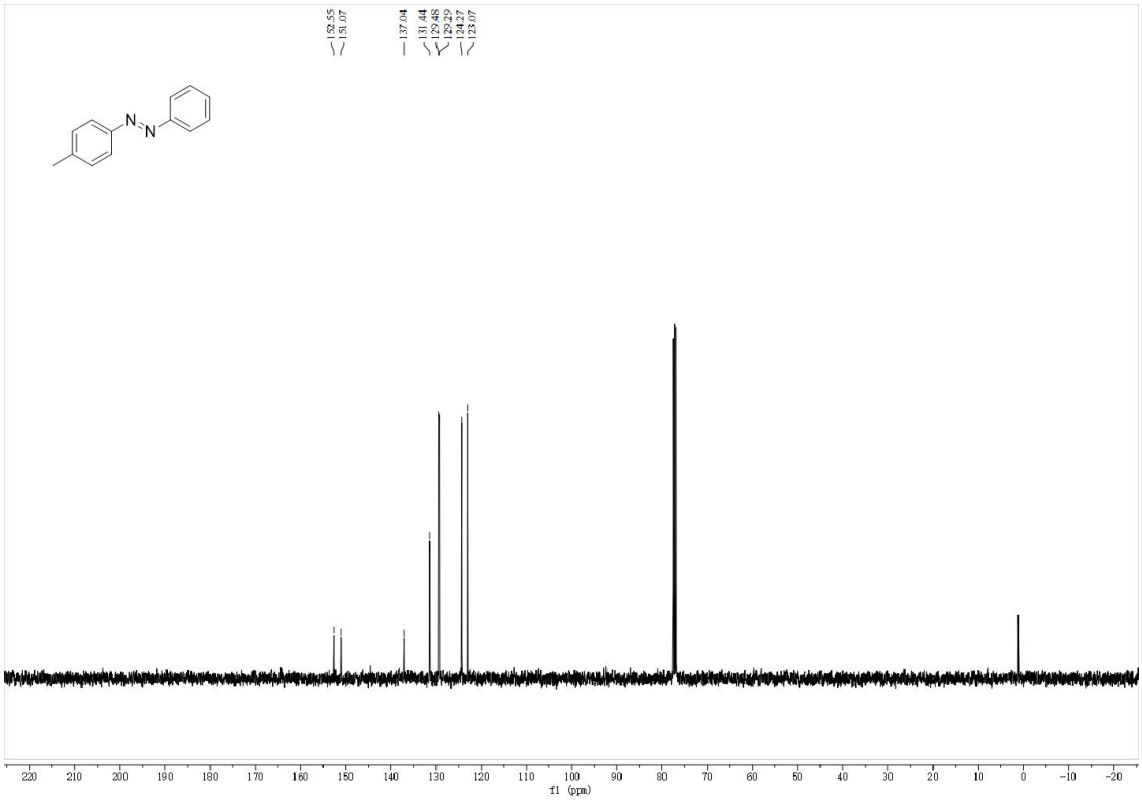

Figure S105. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b**

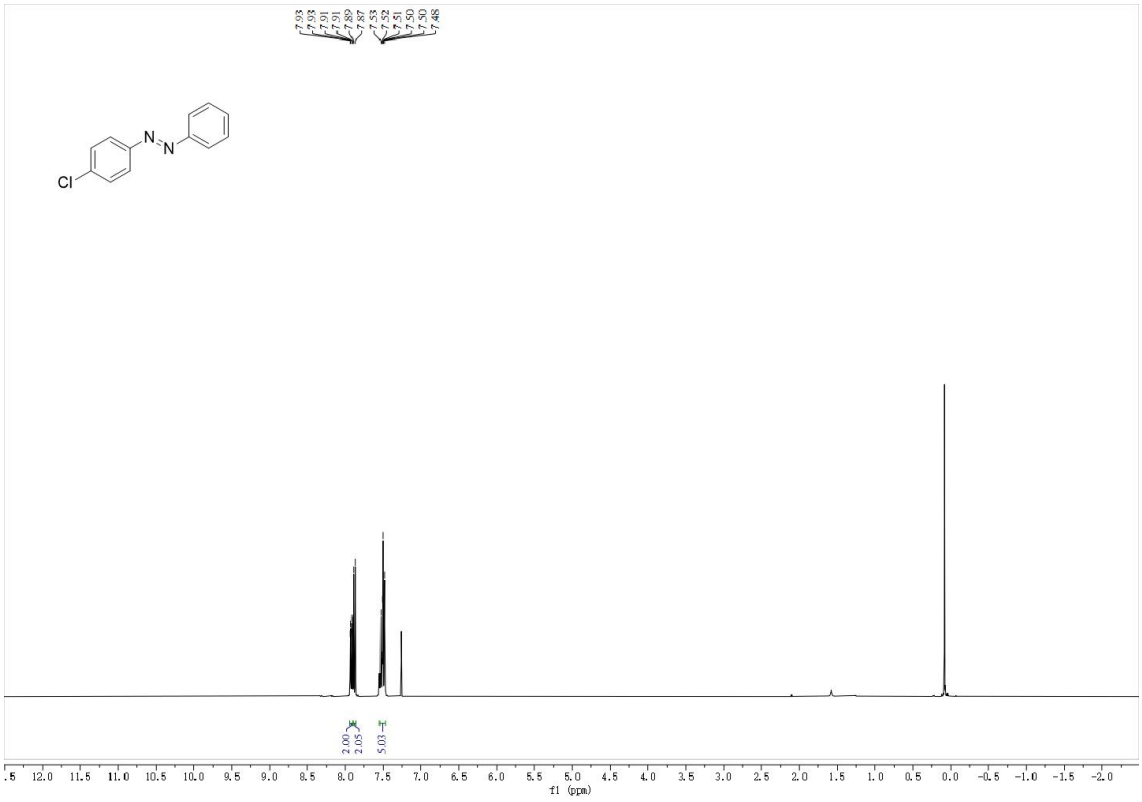

Figure S106. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**

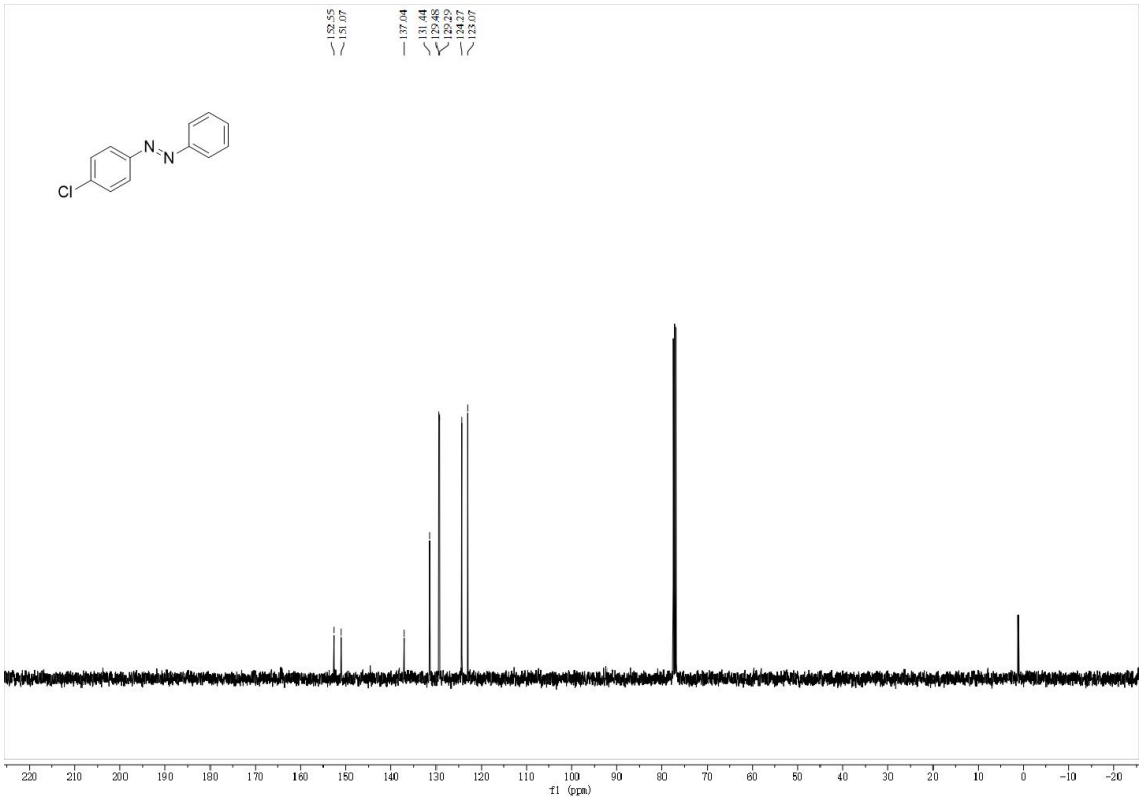

Figure S107. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c**

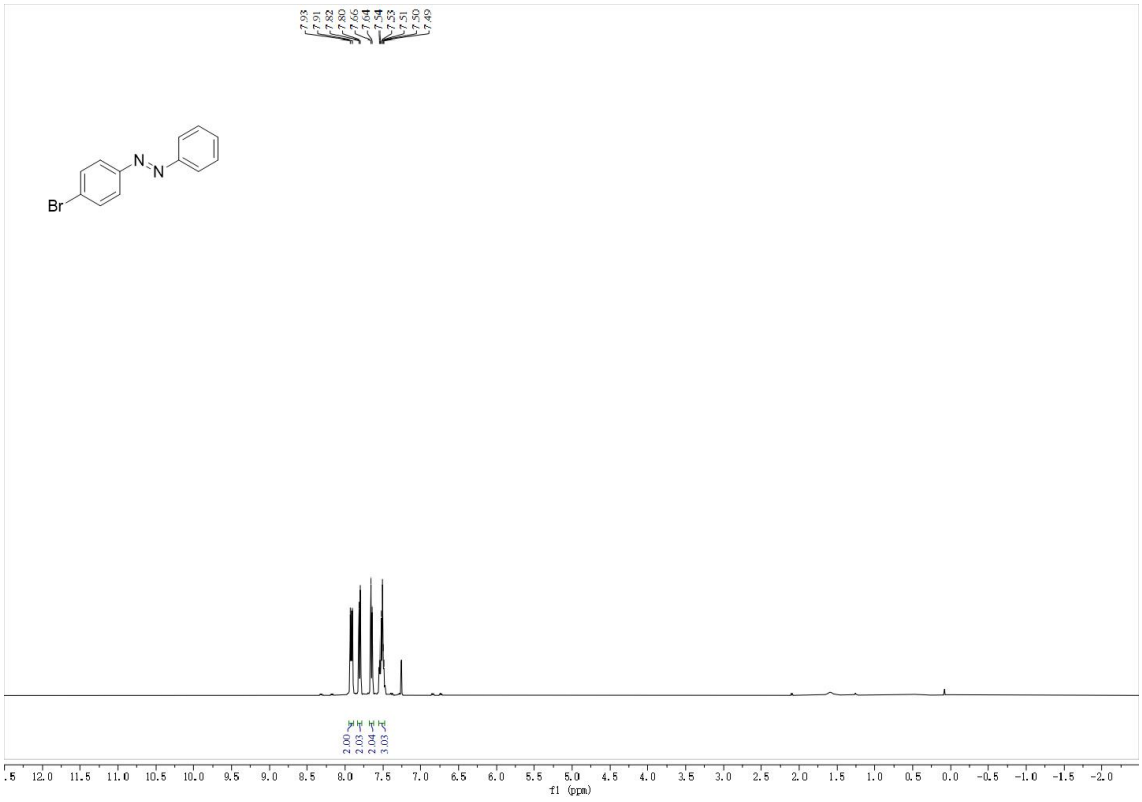

Figure S108. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**

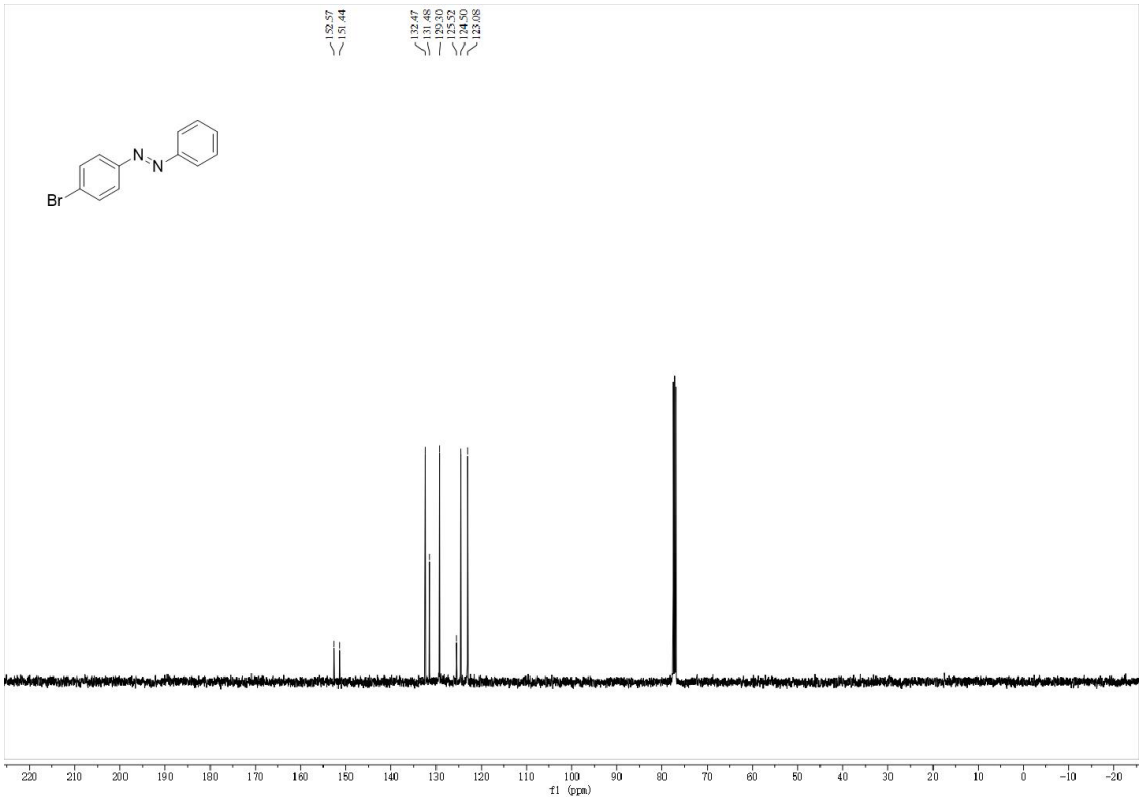

Figure S109. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3d**

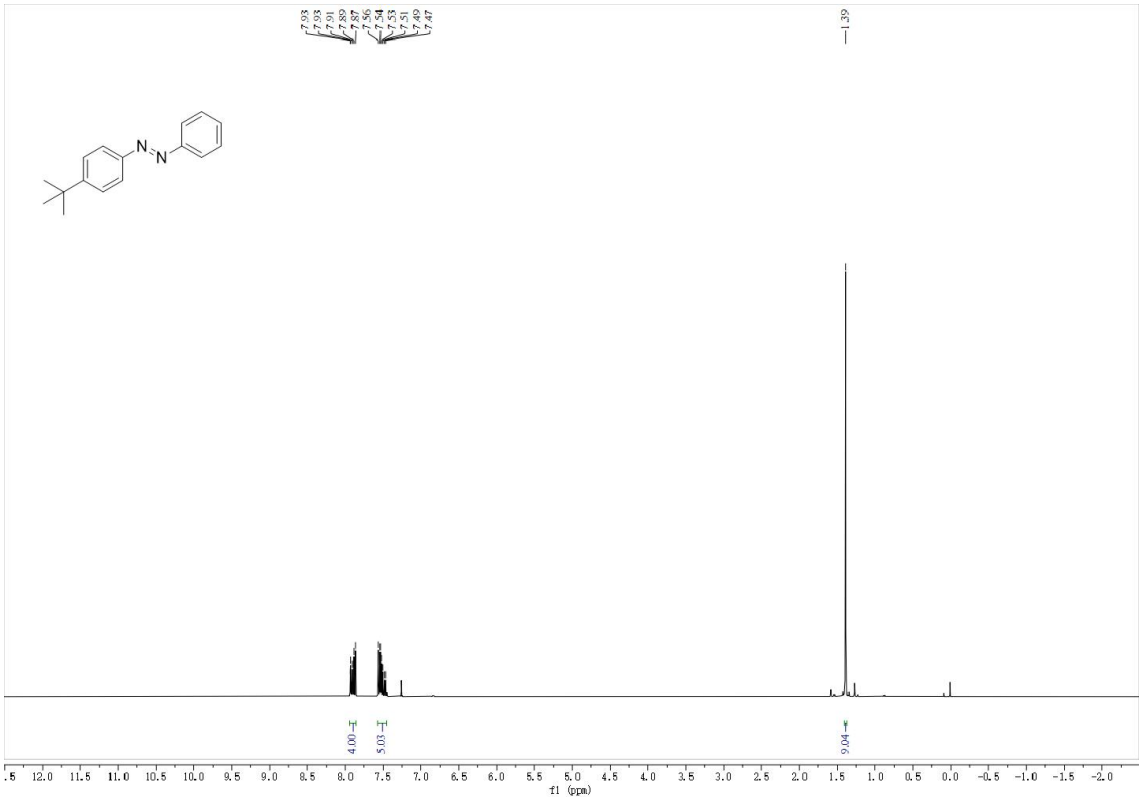

Figure S110. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**

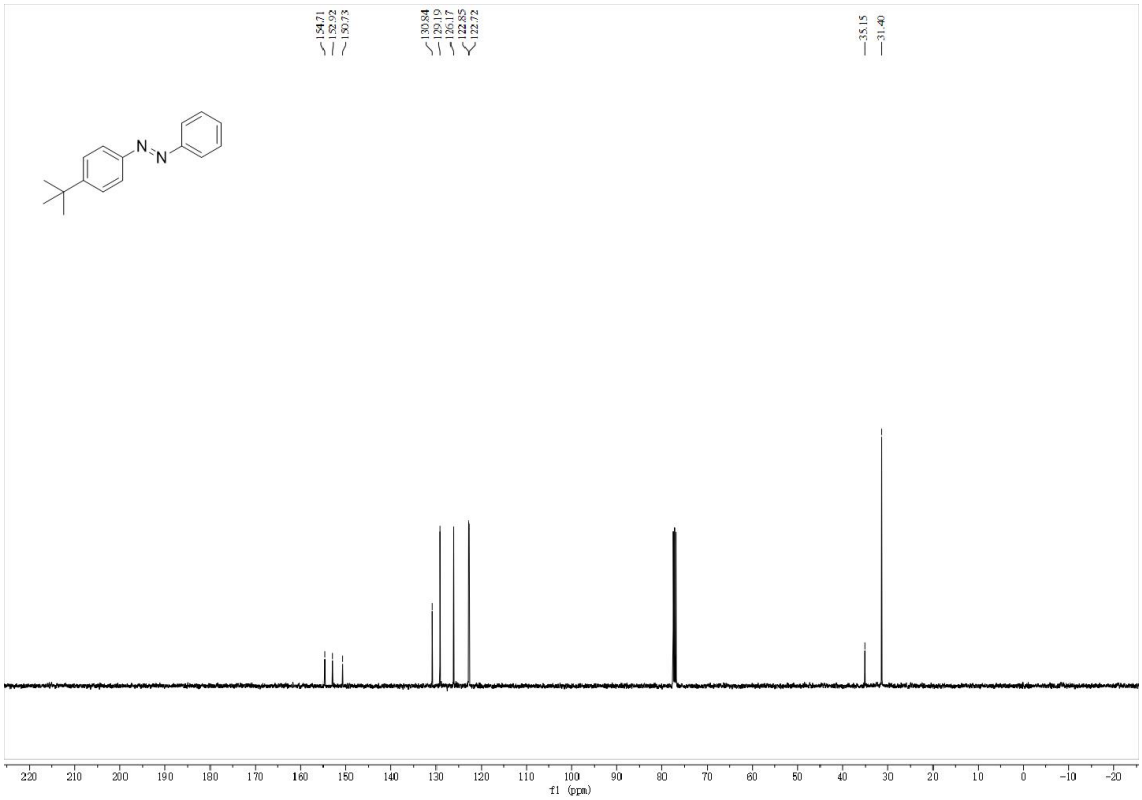

Figure S111. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3e**

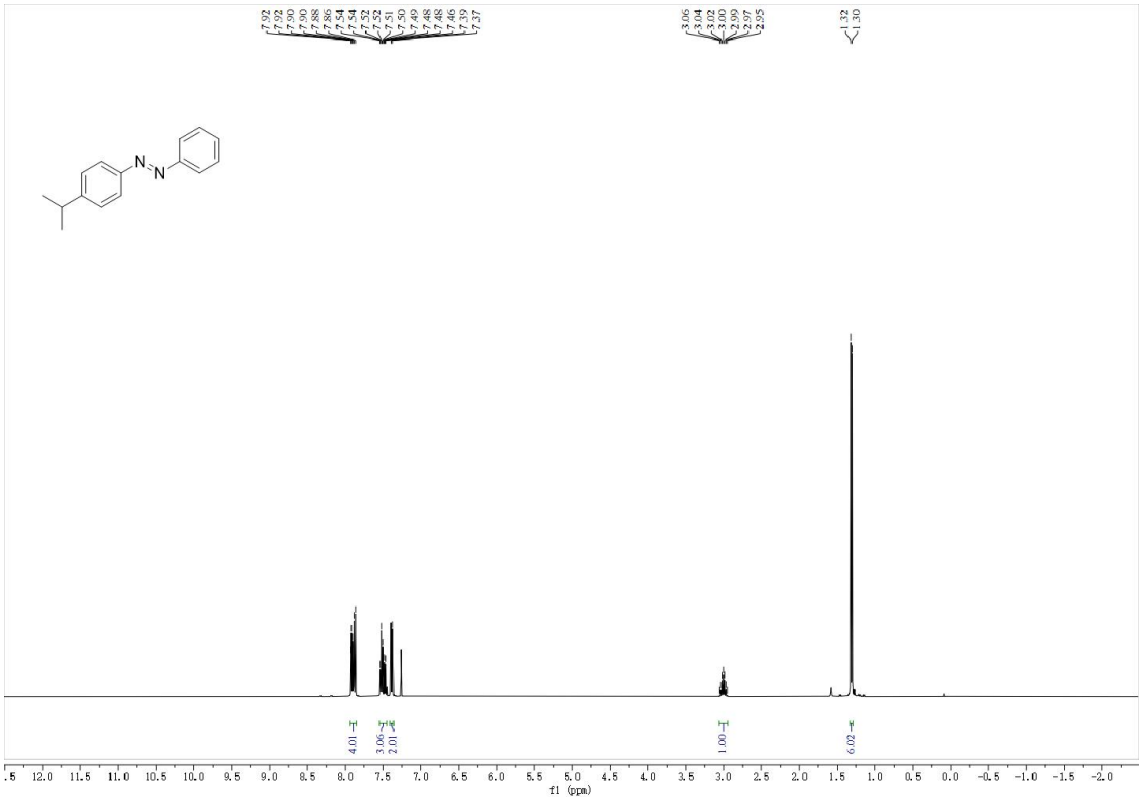

Figure S112. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**

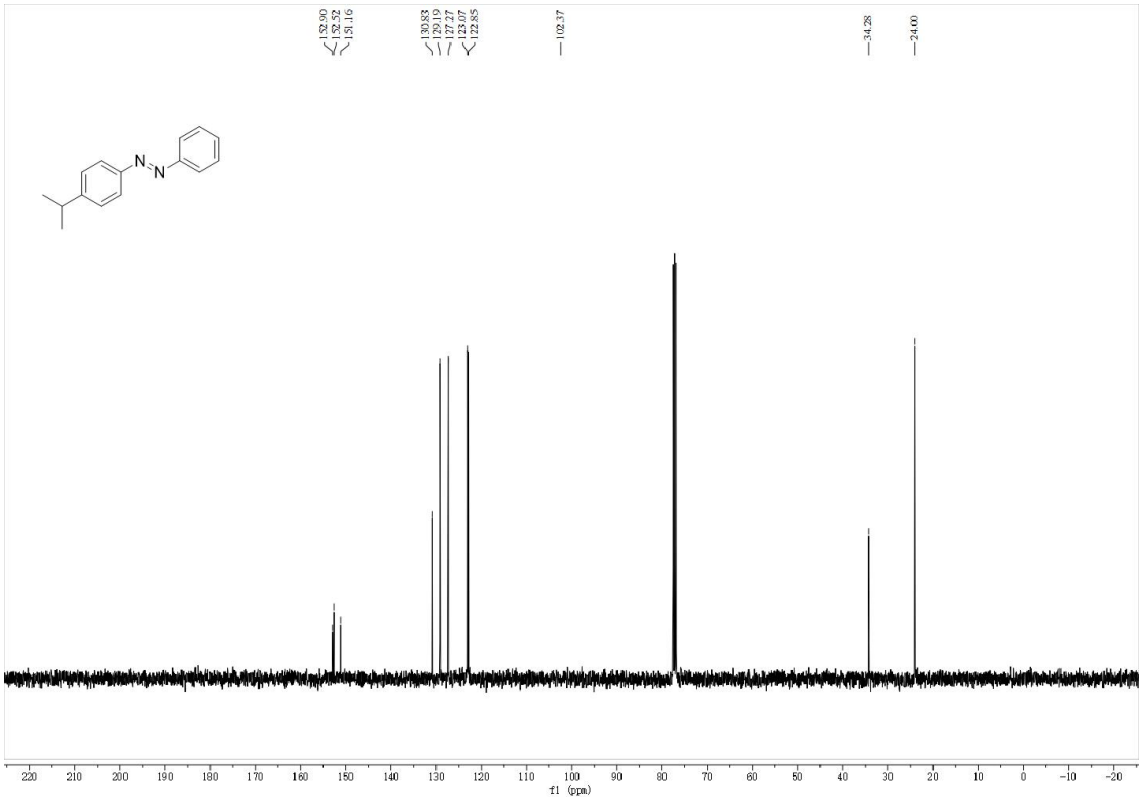

Figure S113. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3f**

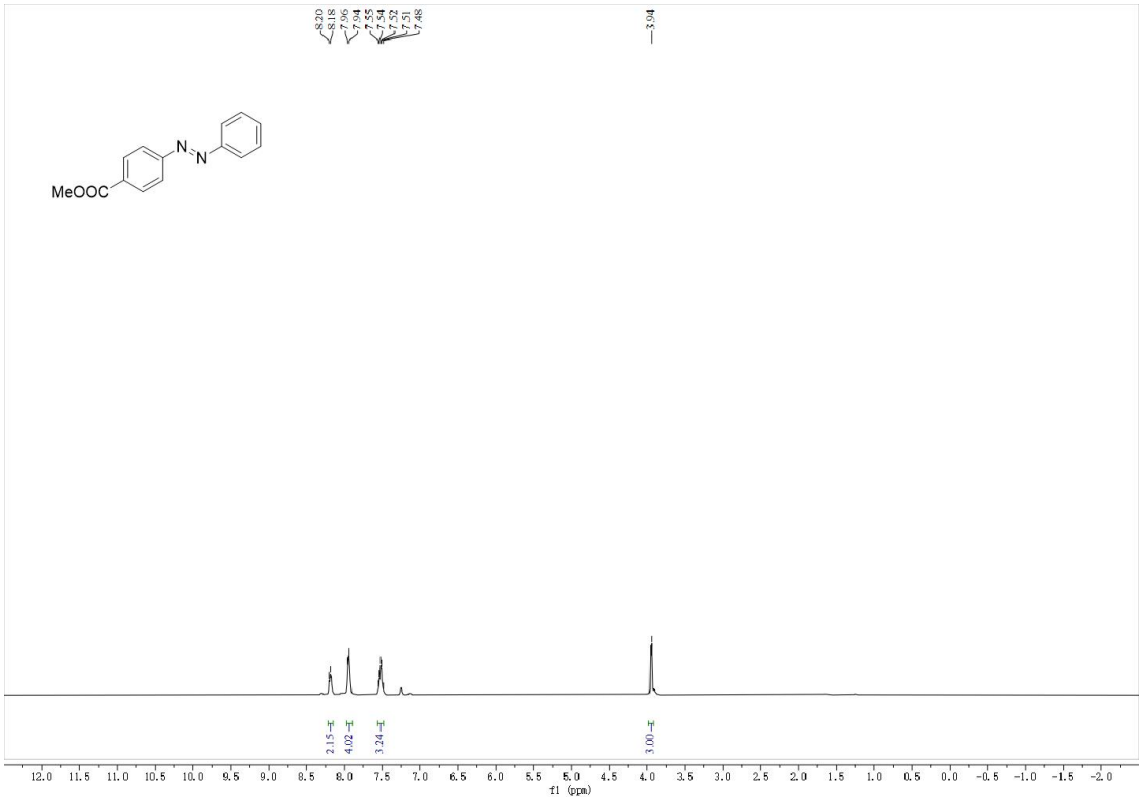

Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**

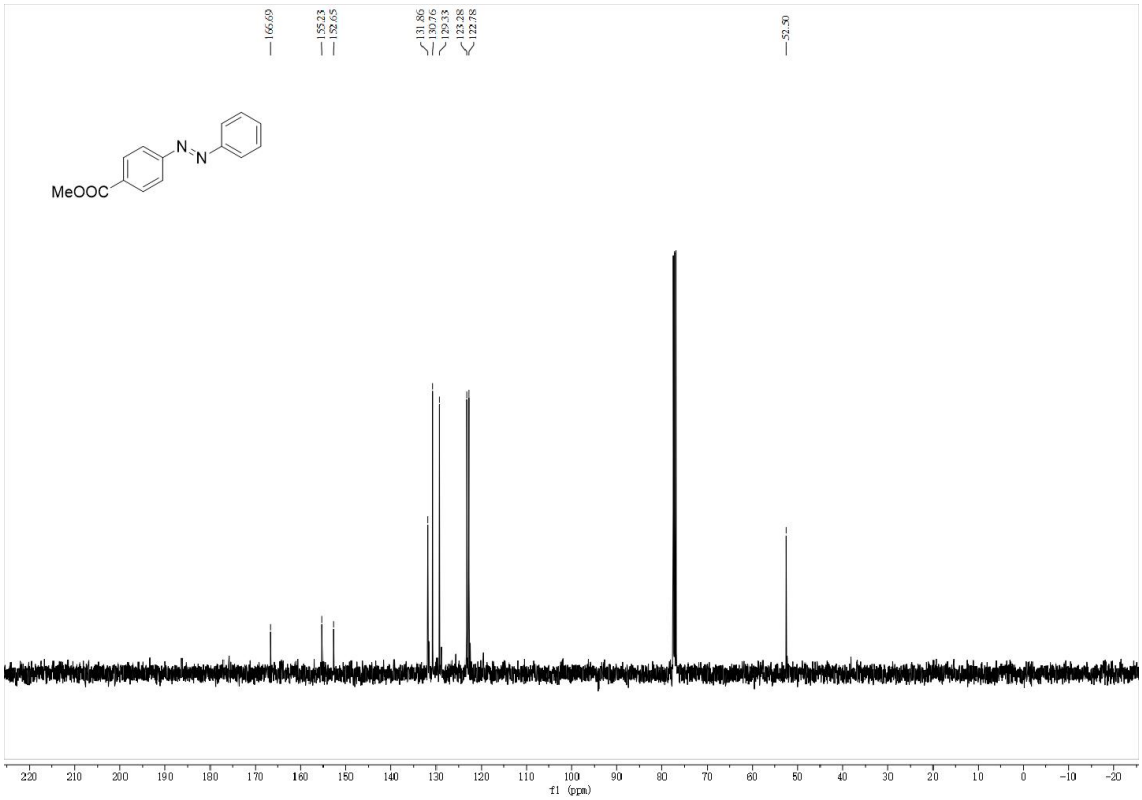

Figure S115. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3g**

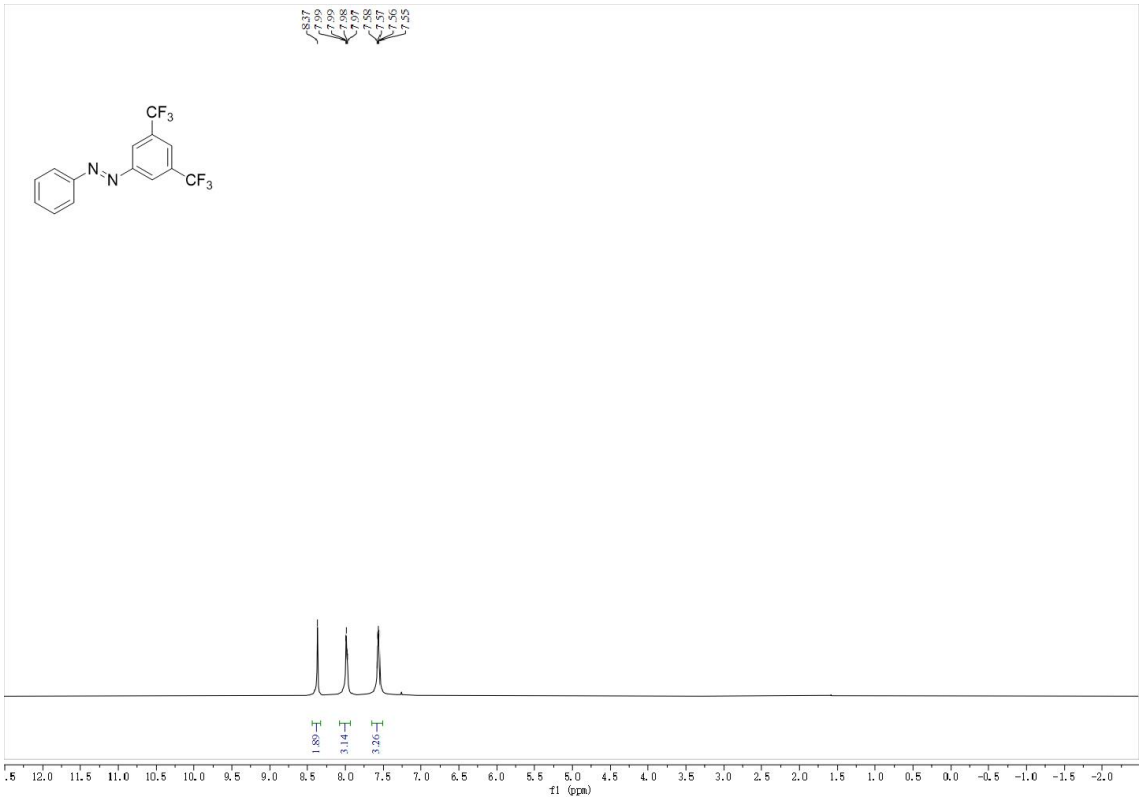

Figure S116. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**

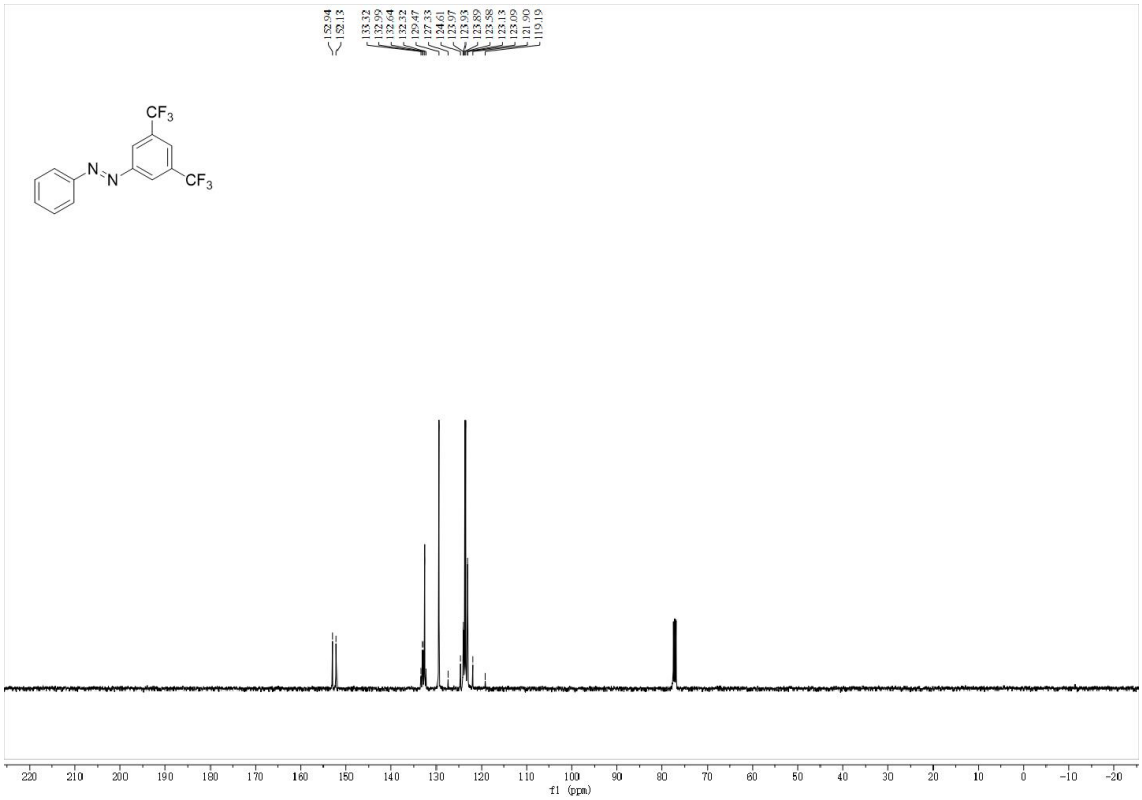

Figure S117. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3h**

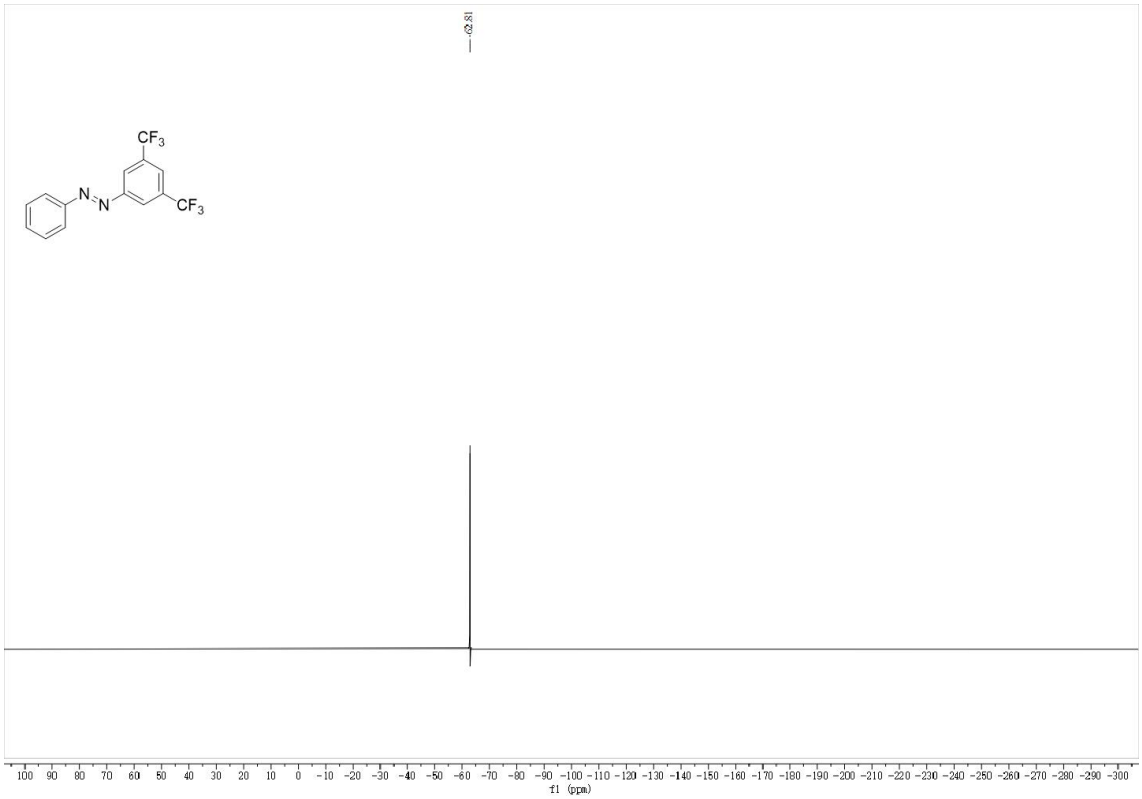

Figure S118. ^{19}F NMR (376MHz, $CDCl_3$) spectrum of **3h**

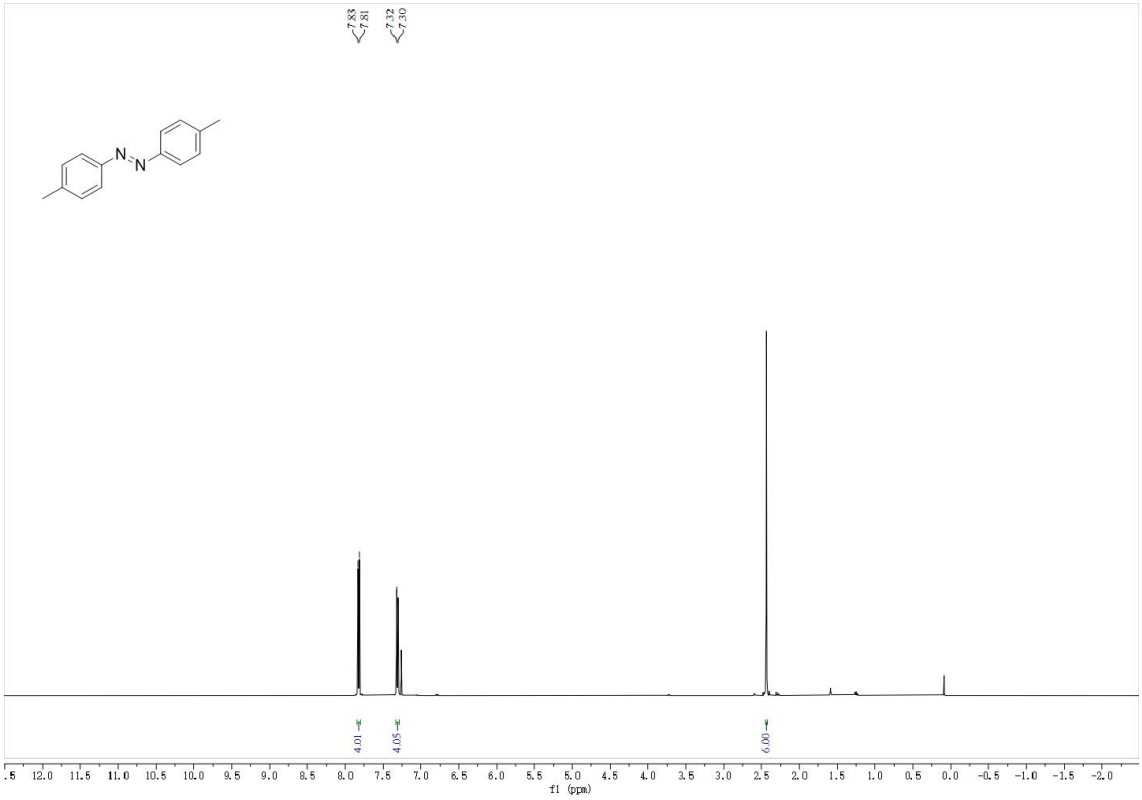

Figure S119. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**

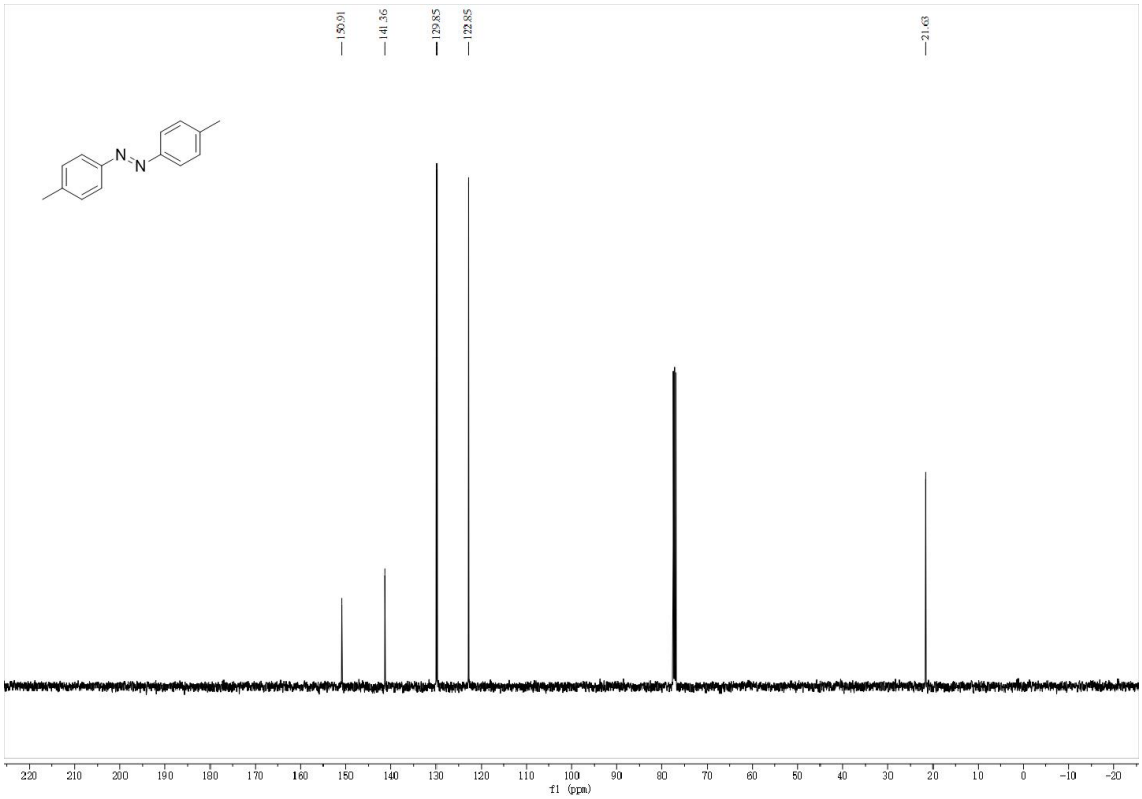

Figure S120. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3i**

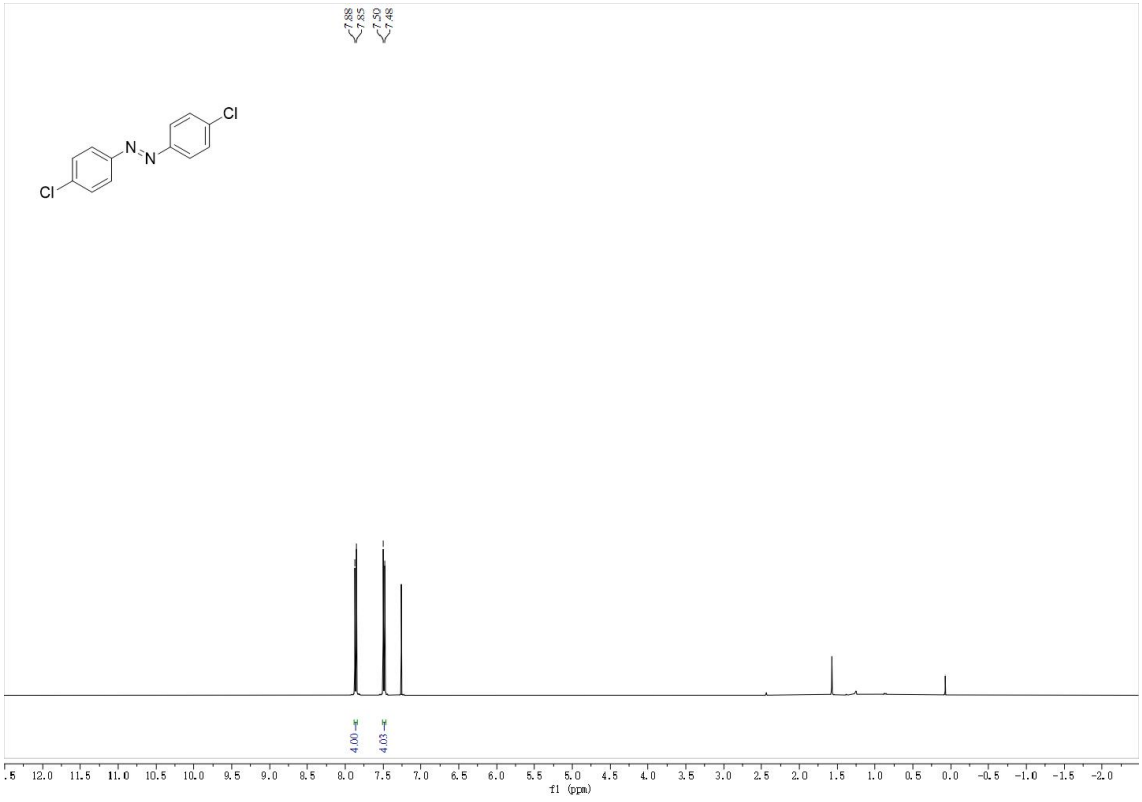

Figure S121. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***3J***

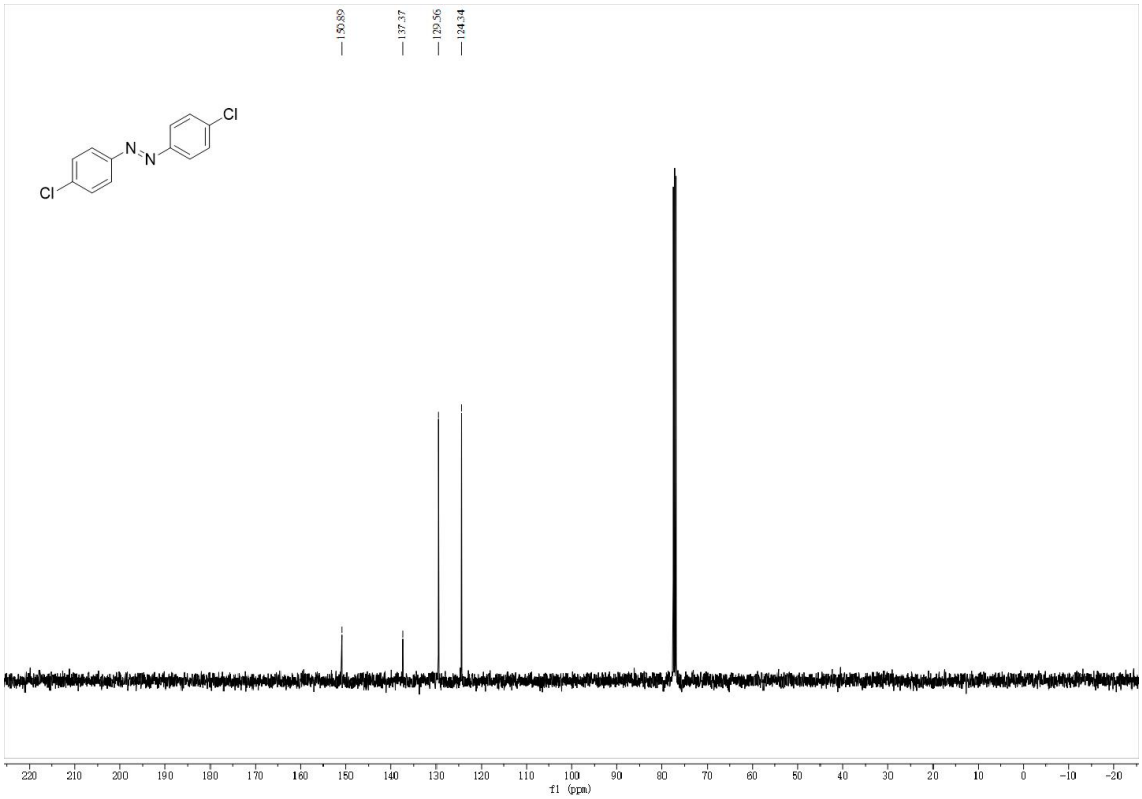

Figure S122. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3*J***

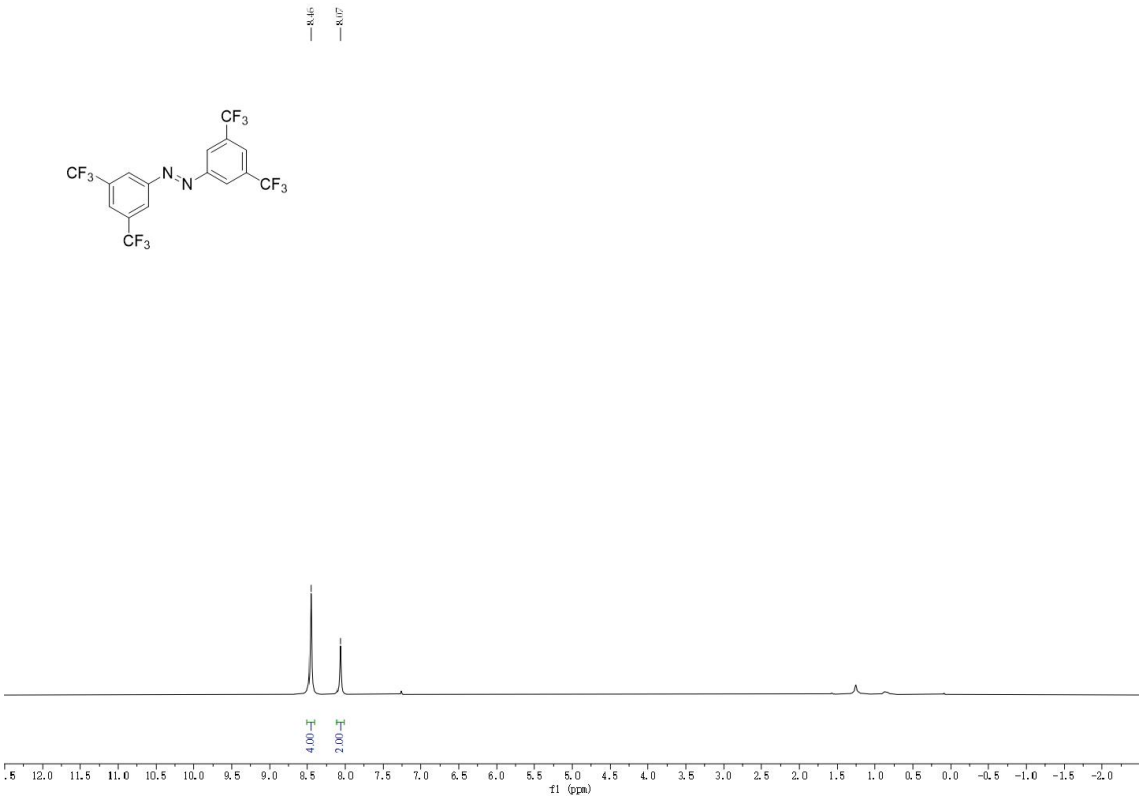

Figure S123. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**

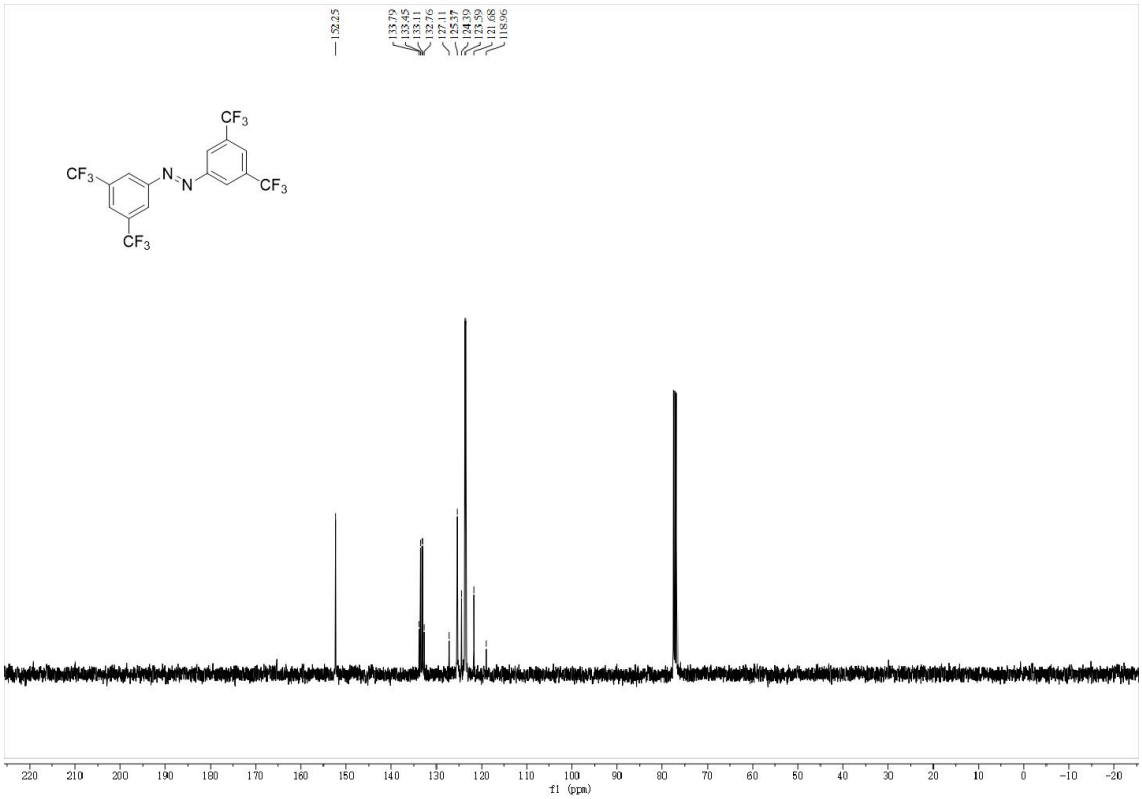

Figure S124. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3k**

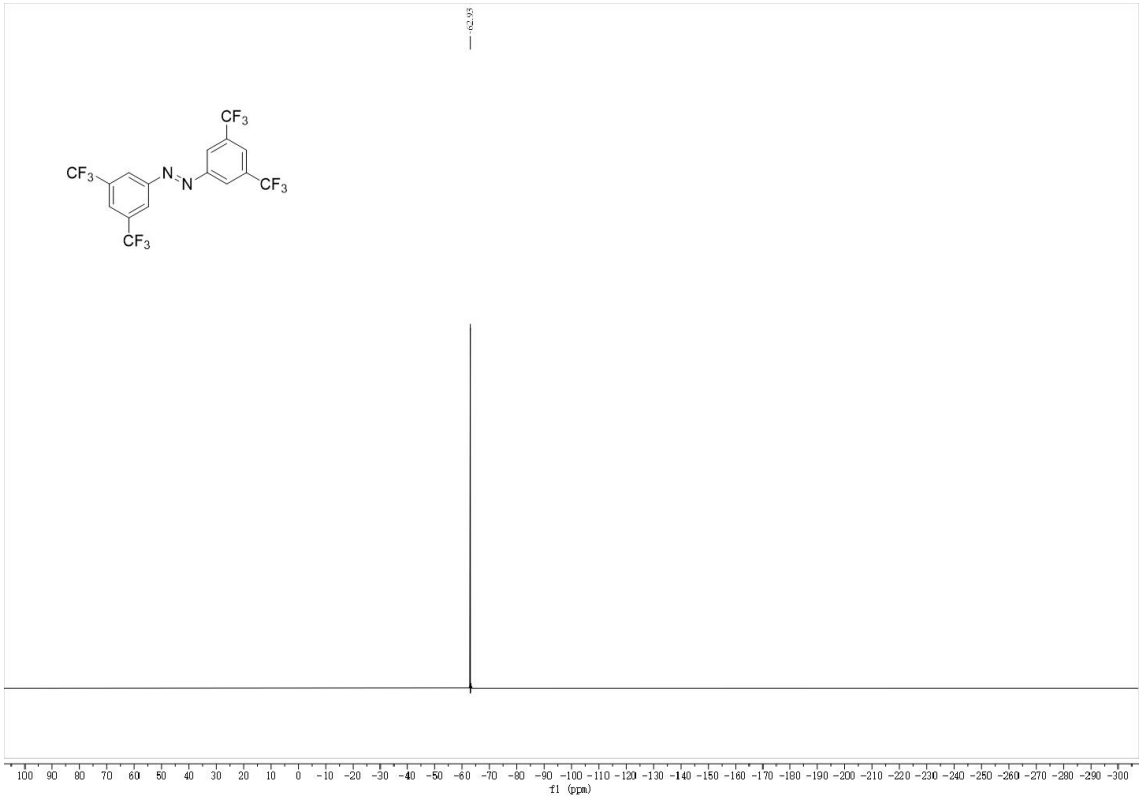

Figure S125. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3k**

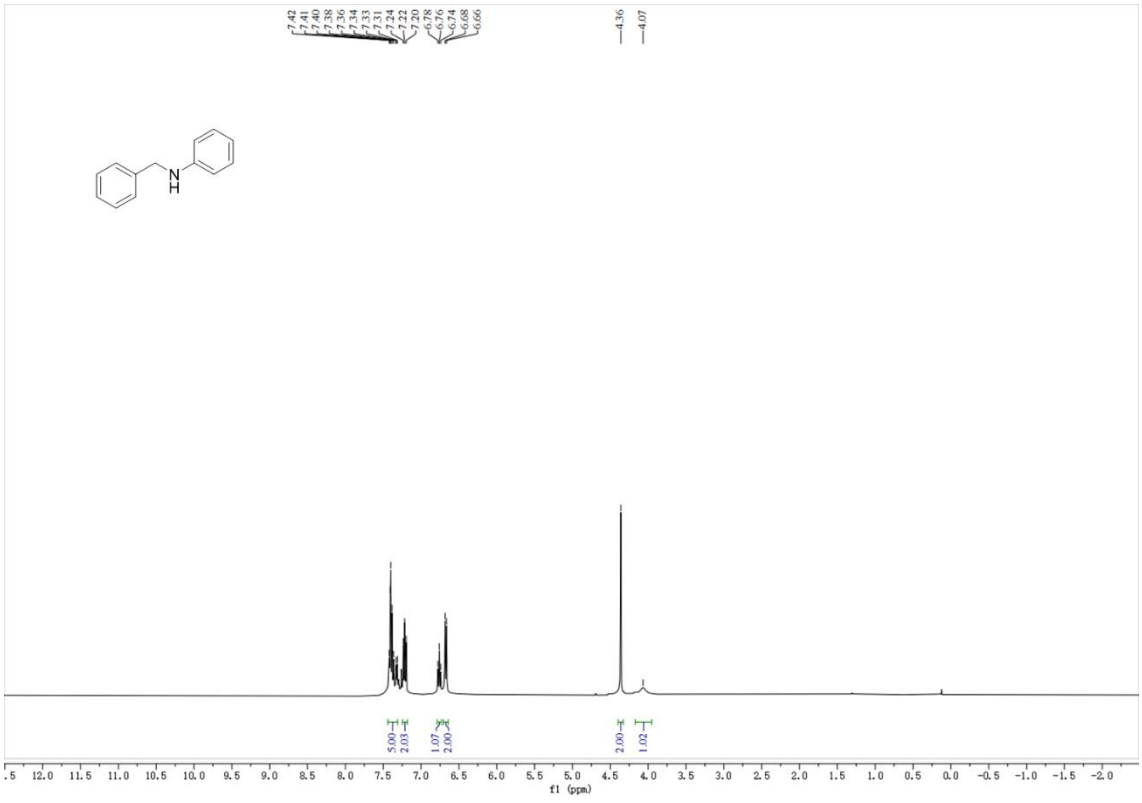

Figure S126. ^{1}H NMR spectrum of (400 MHz, $CDCl_3$) **2a**

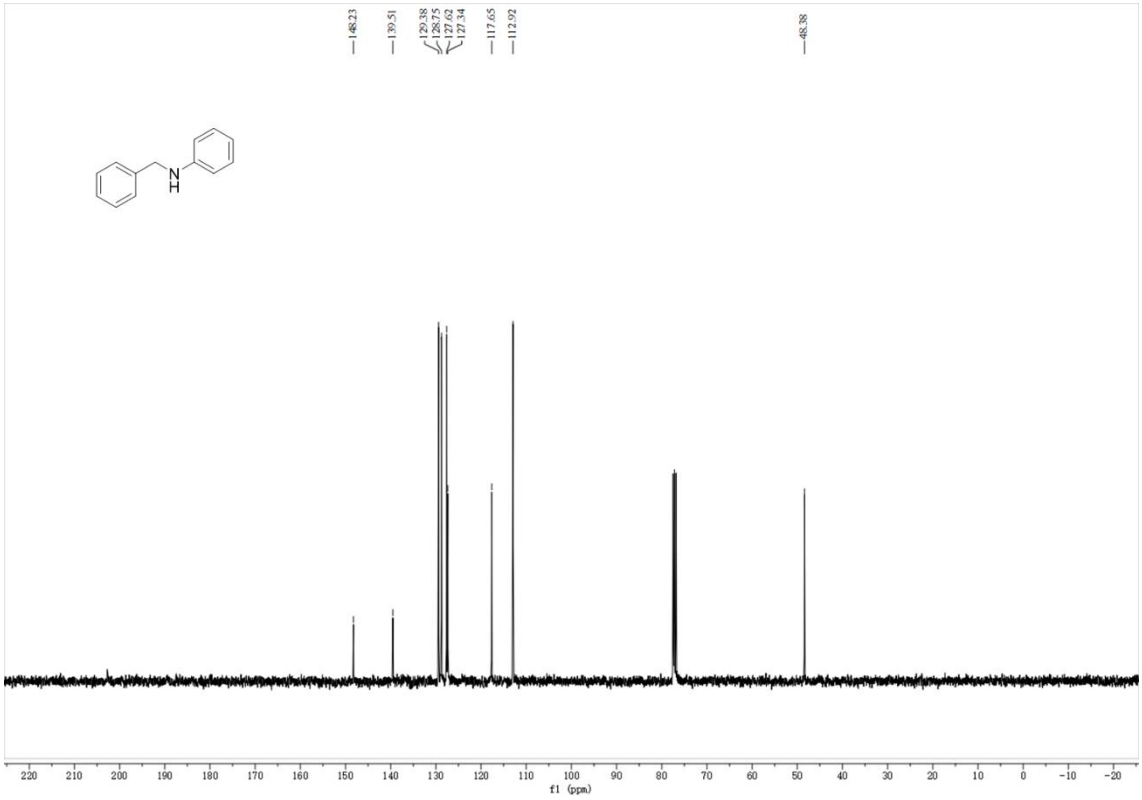

Figure S127. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2a**

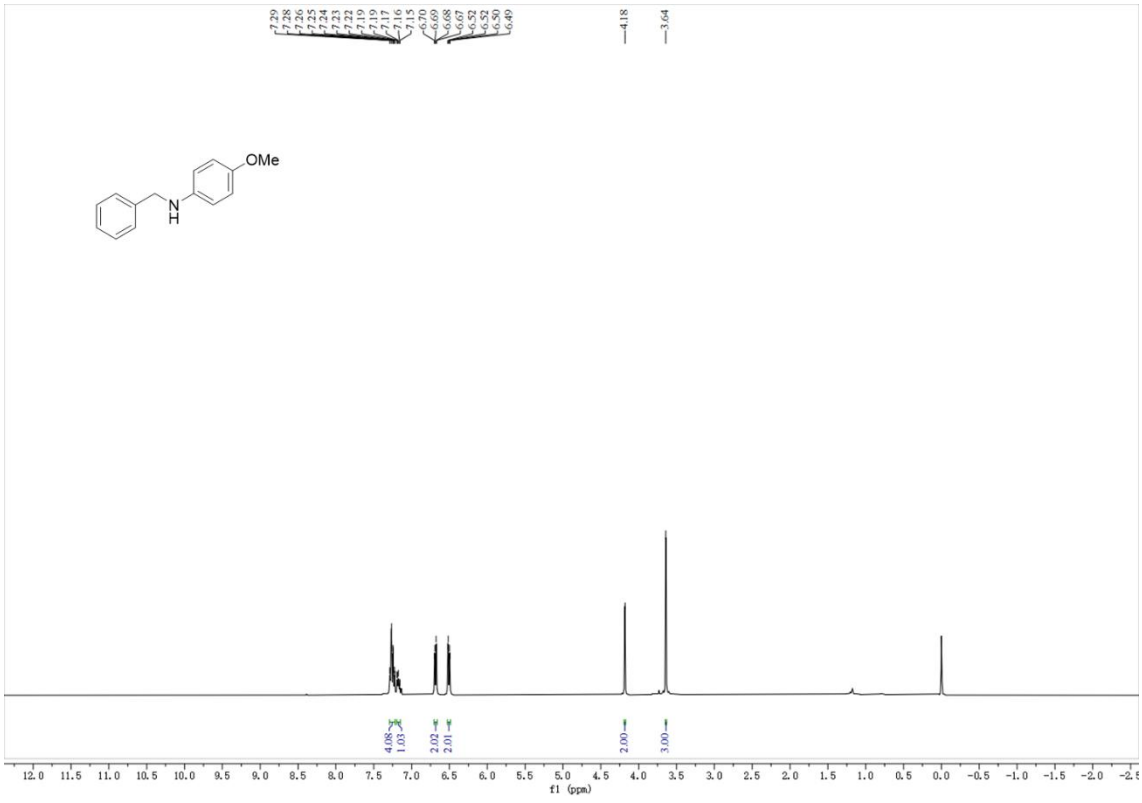

Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**

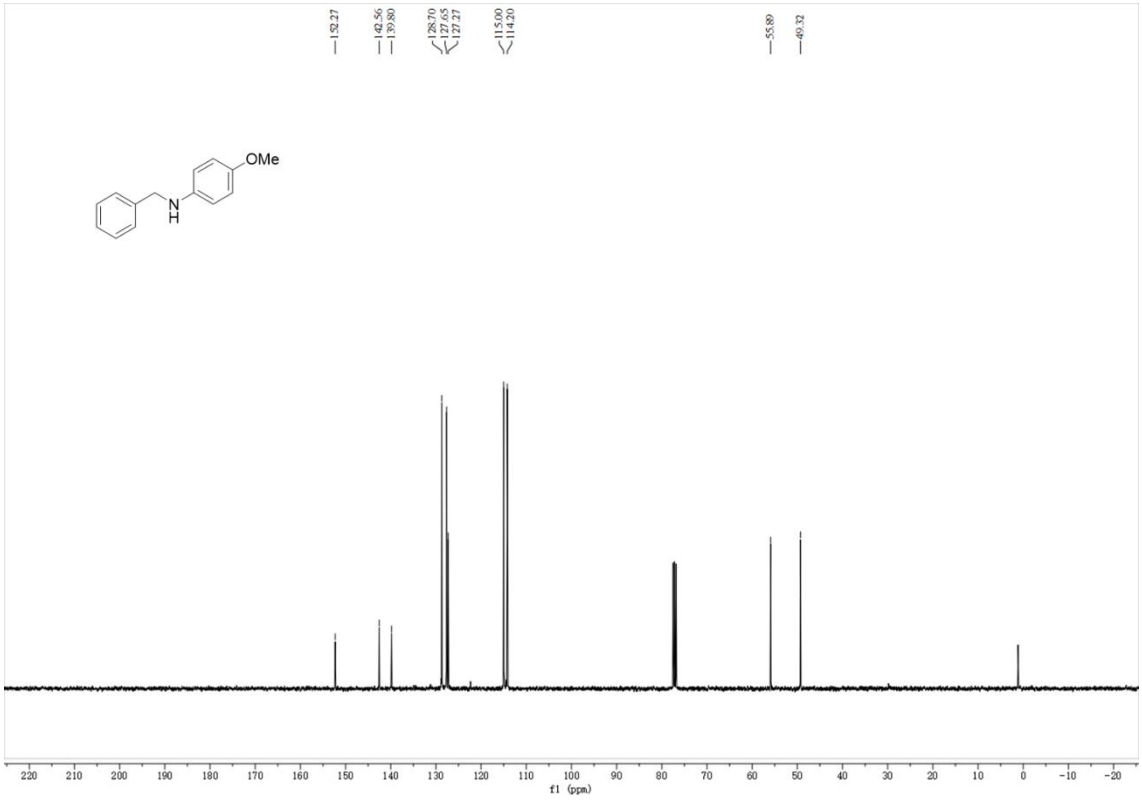

Figure S129. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2b**

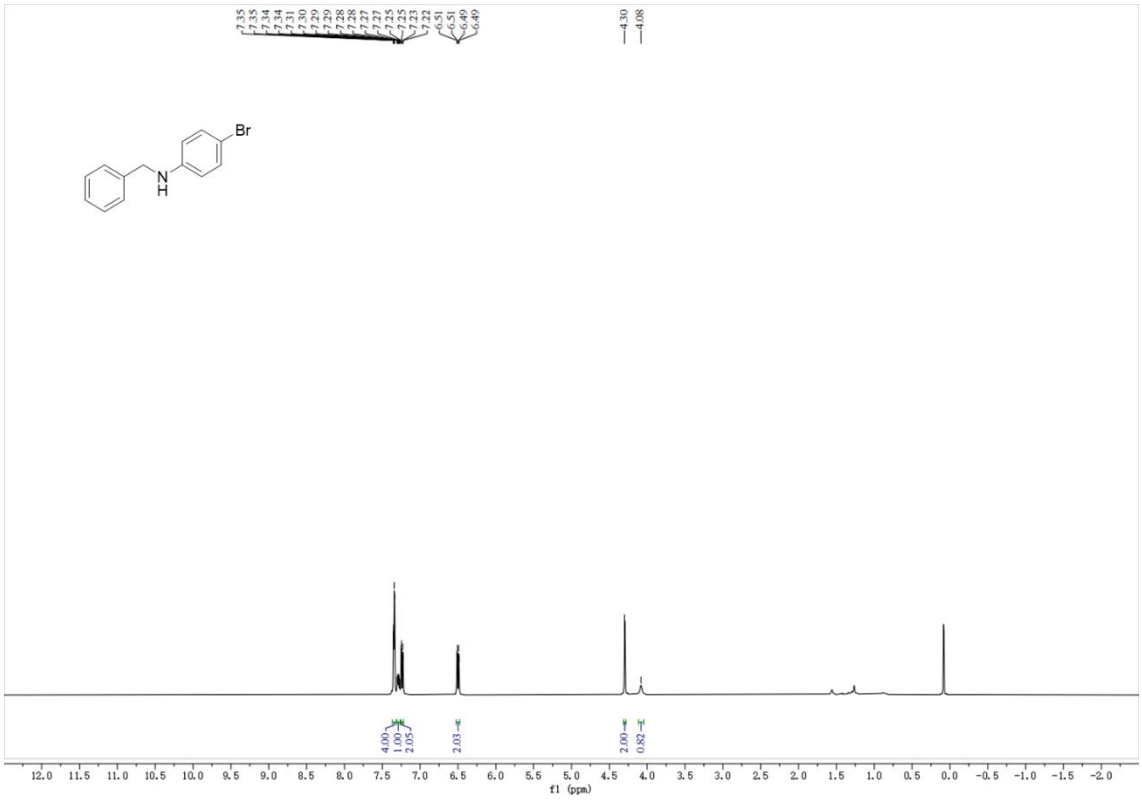

Figure S130. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**

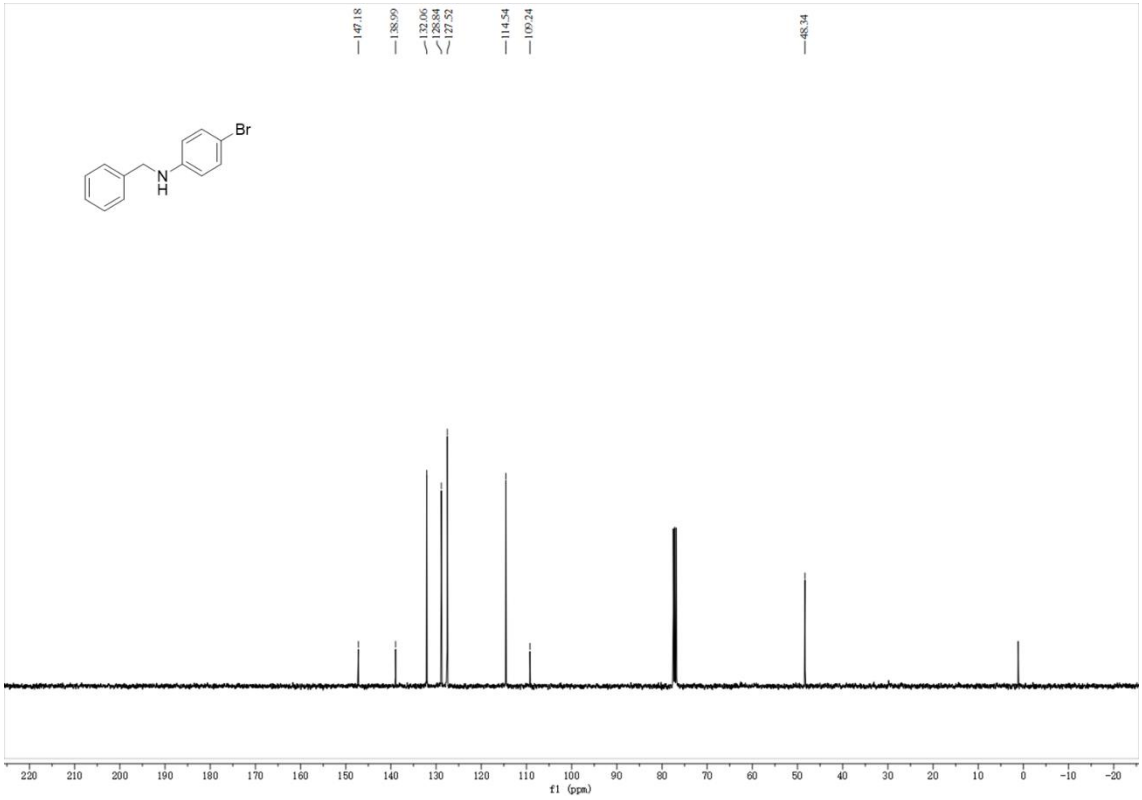

Figure S131. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2c**

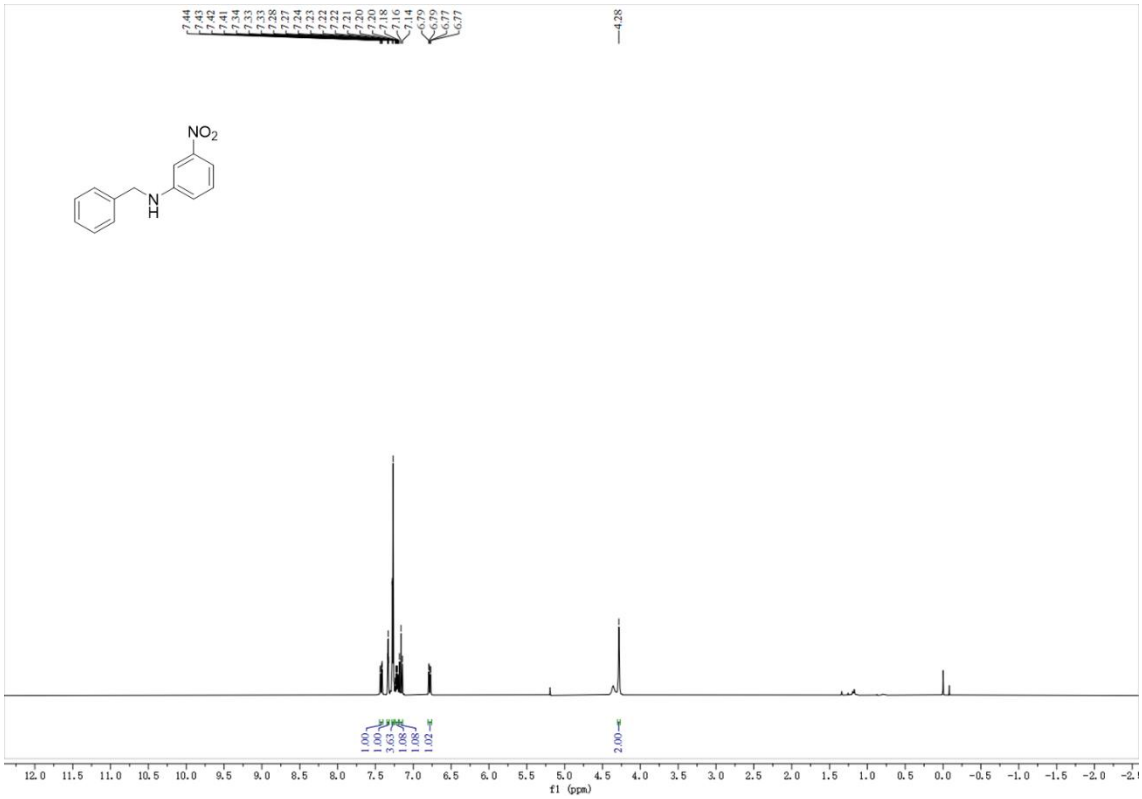

Figure S132. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**

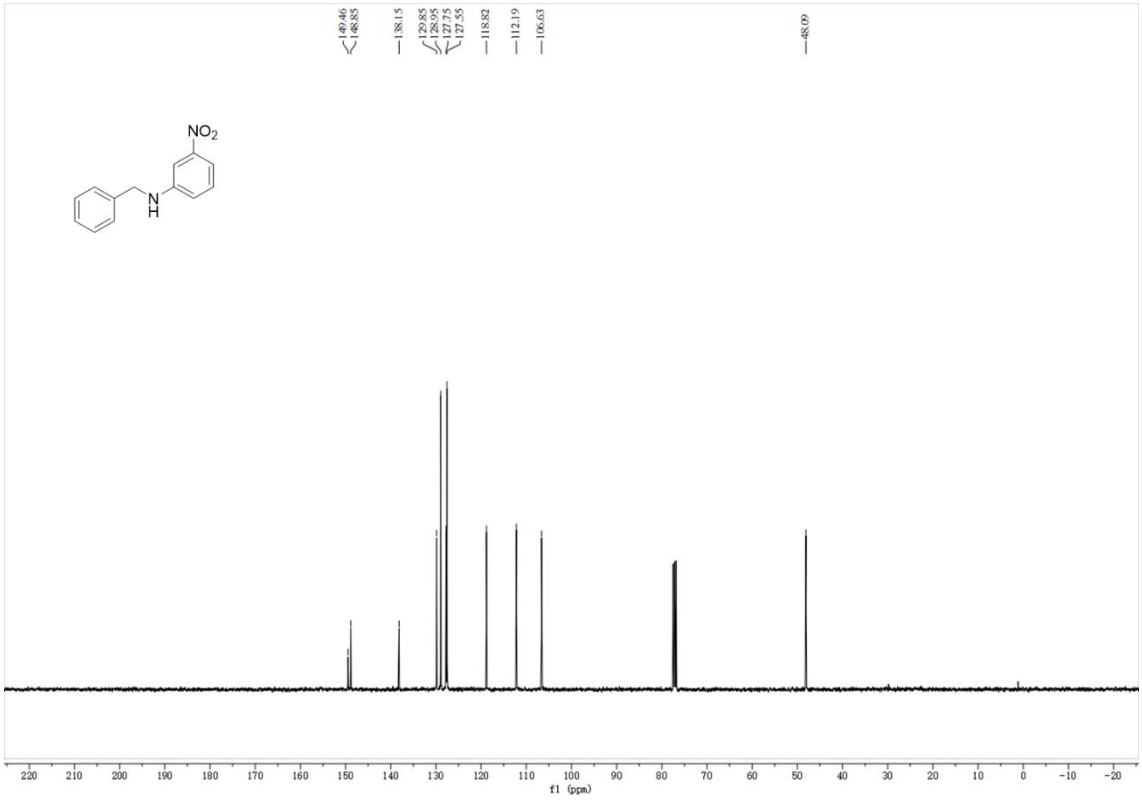

Figure S133. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2d**

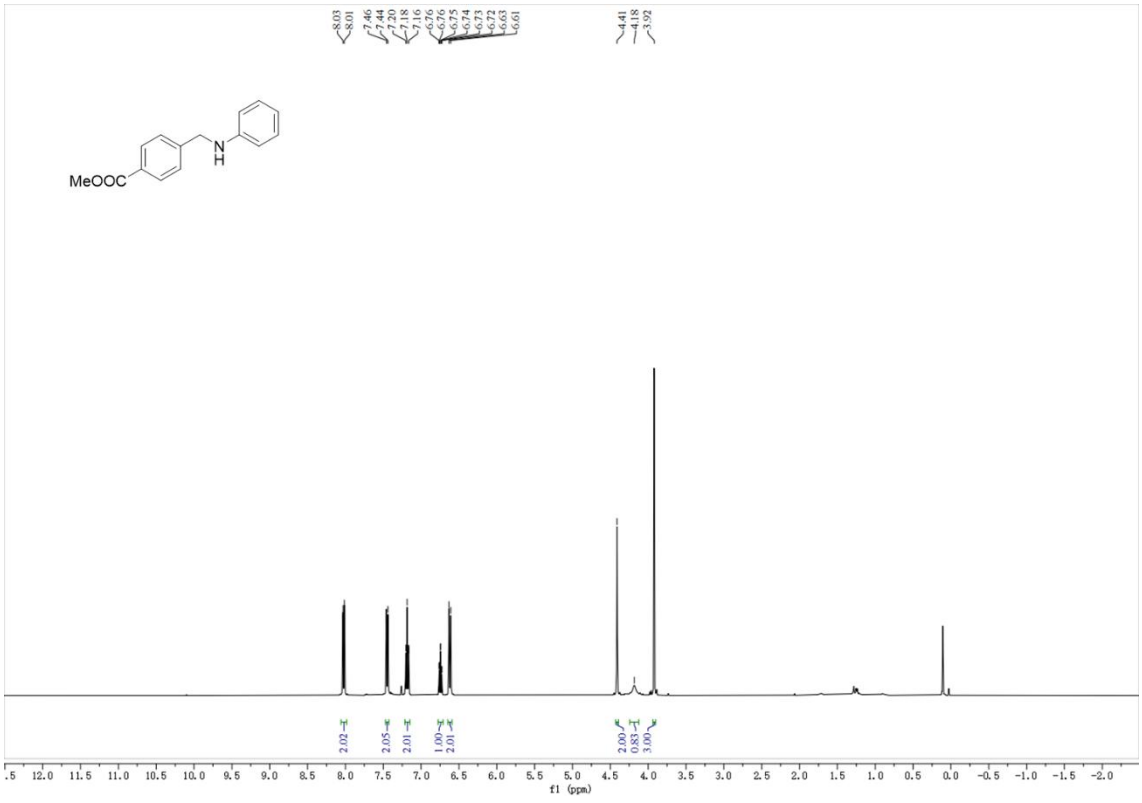

Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2e**

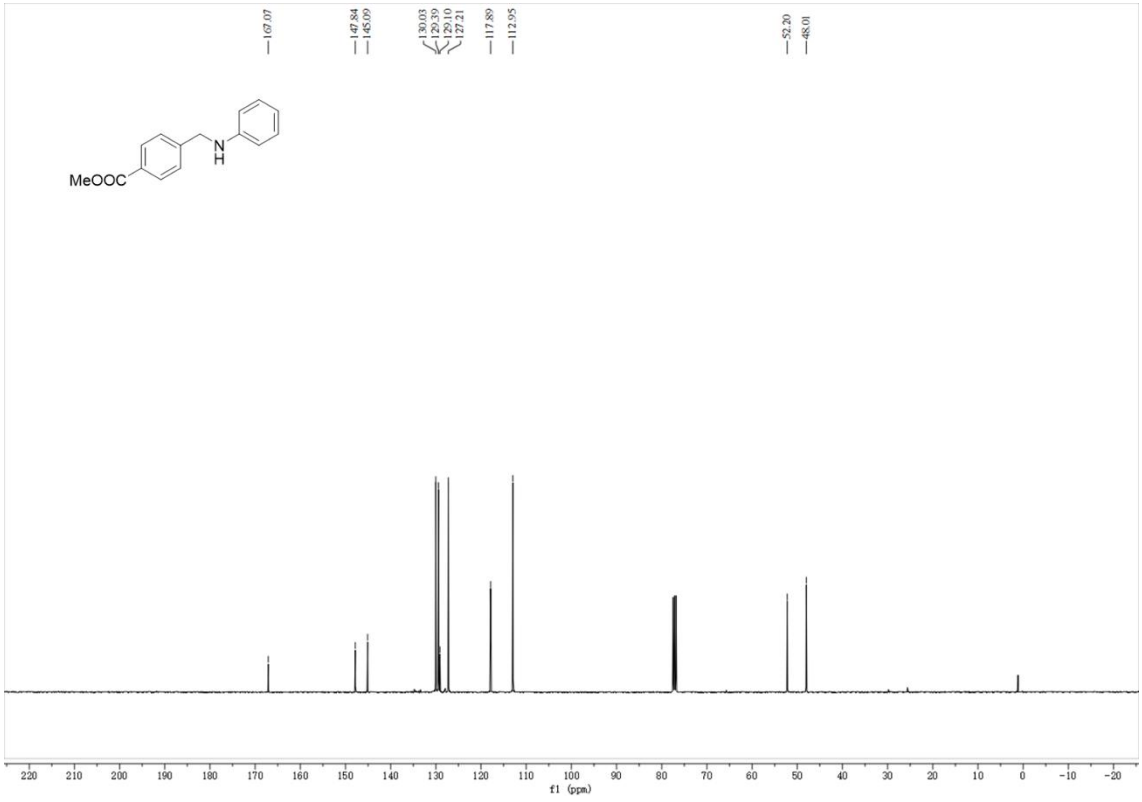

Figure S135. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2e**

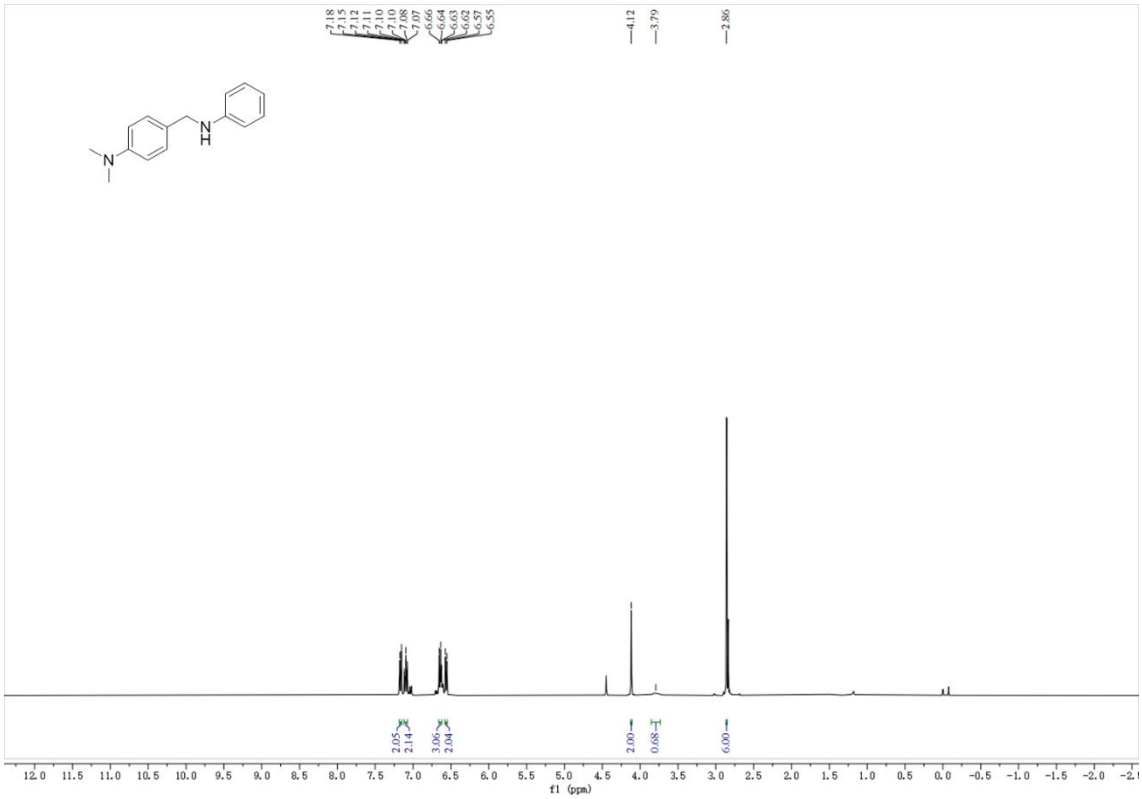

Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2f**

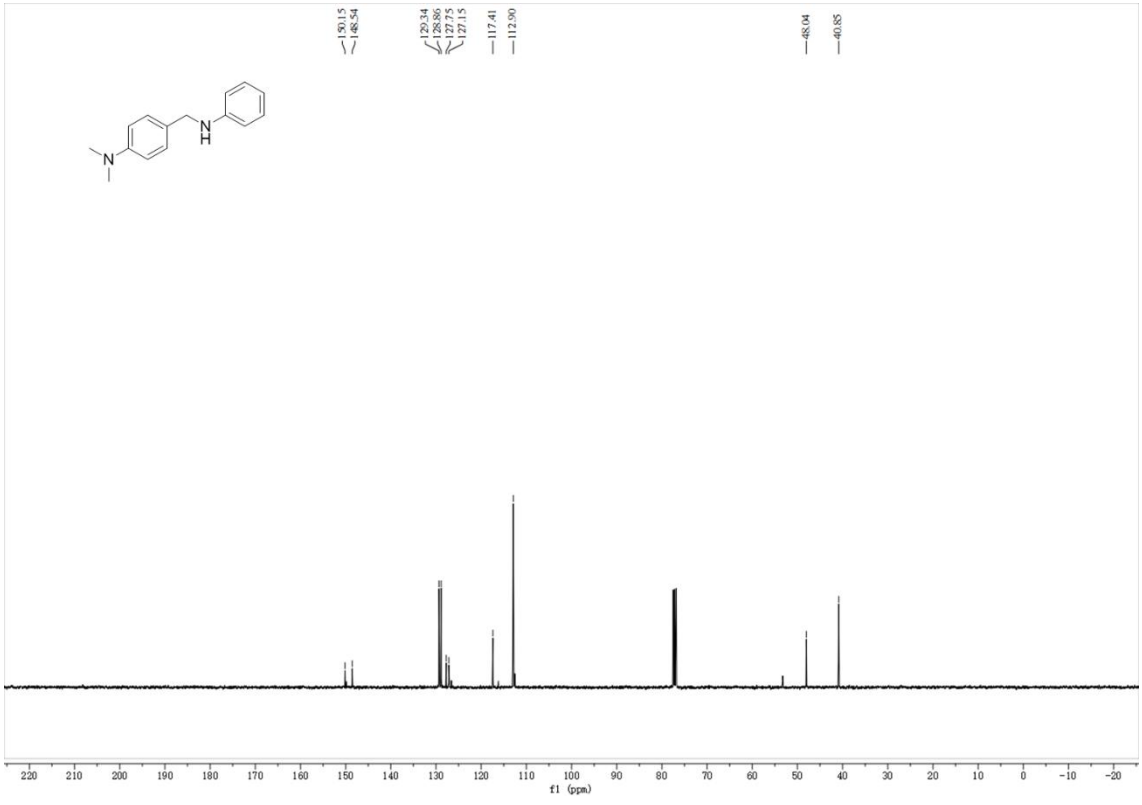

Figure S137. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2f**

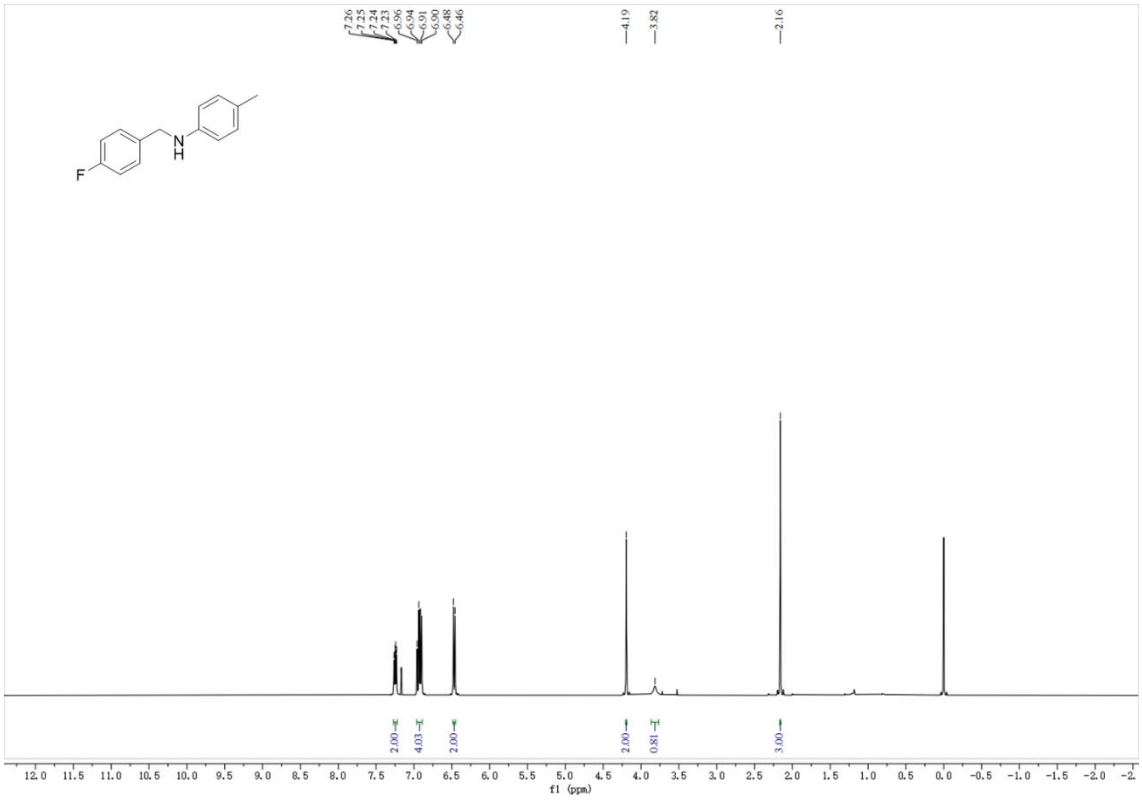

Figure S138. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2g**

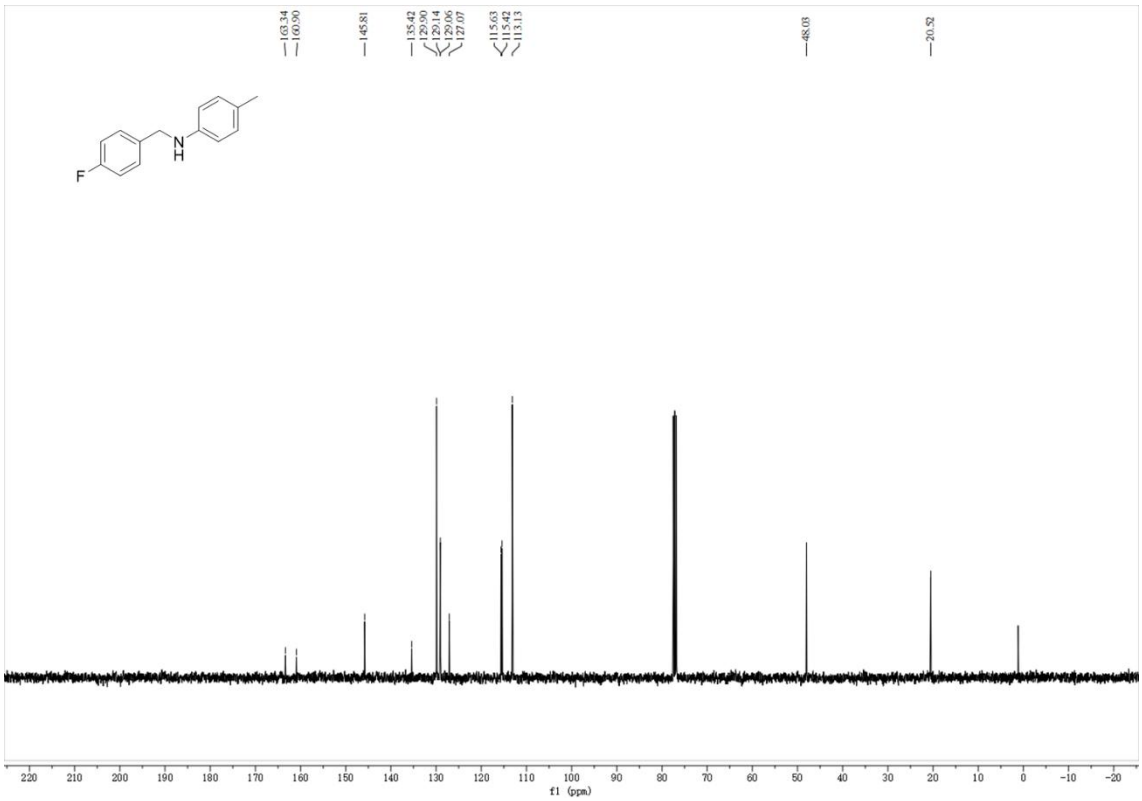

Figure S139. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2g**

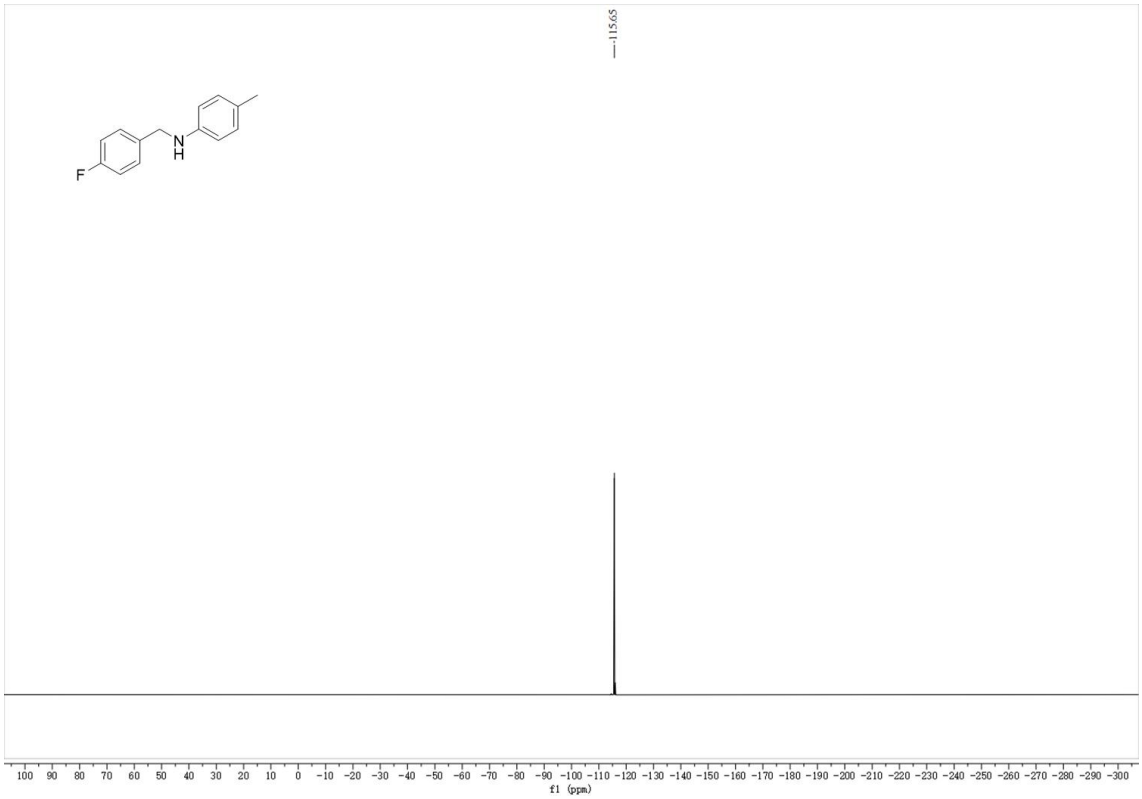

Figure S140. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2g**

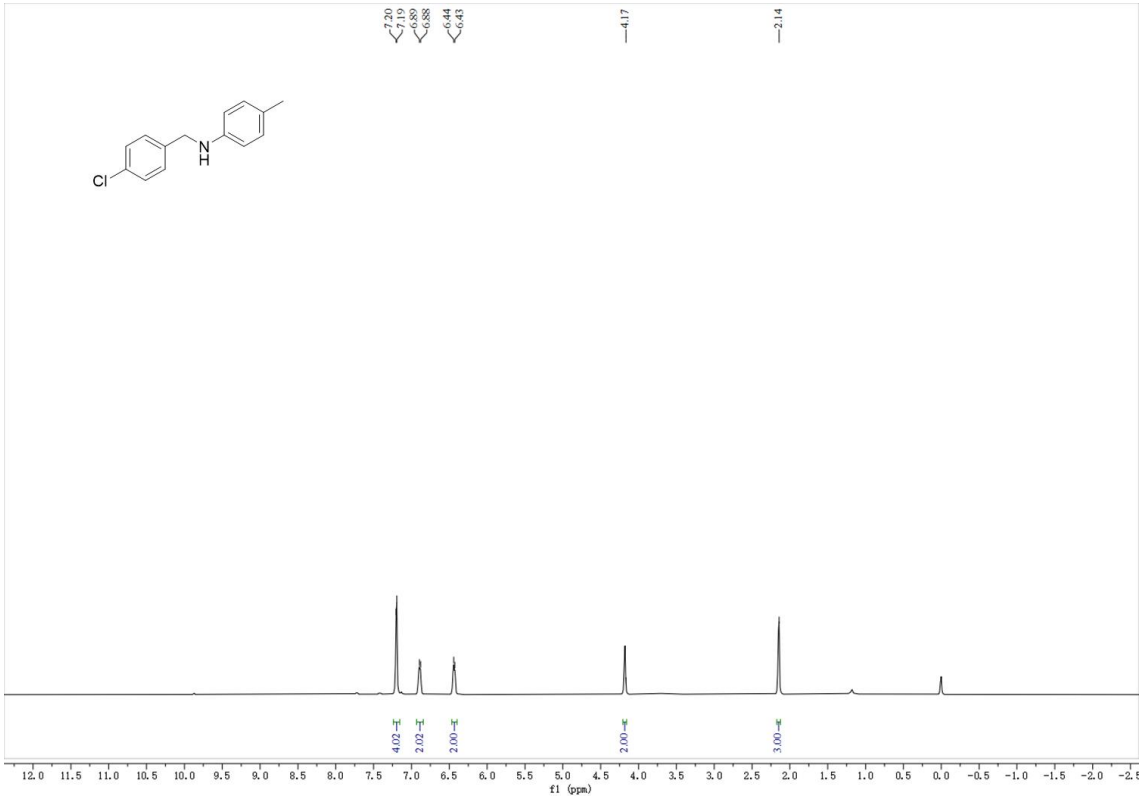

Figure S141. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**

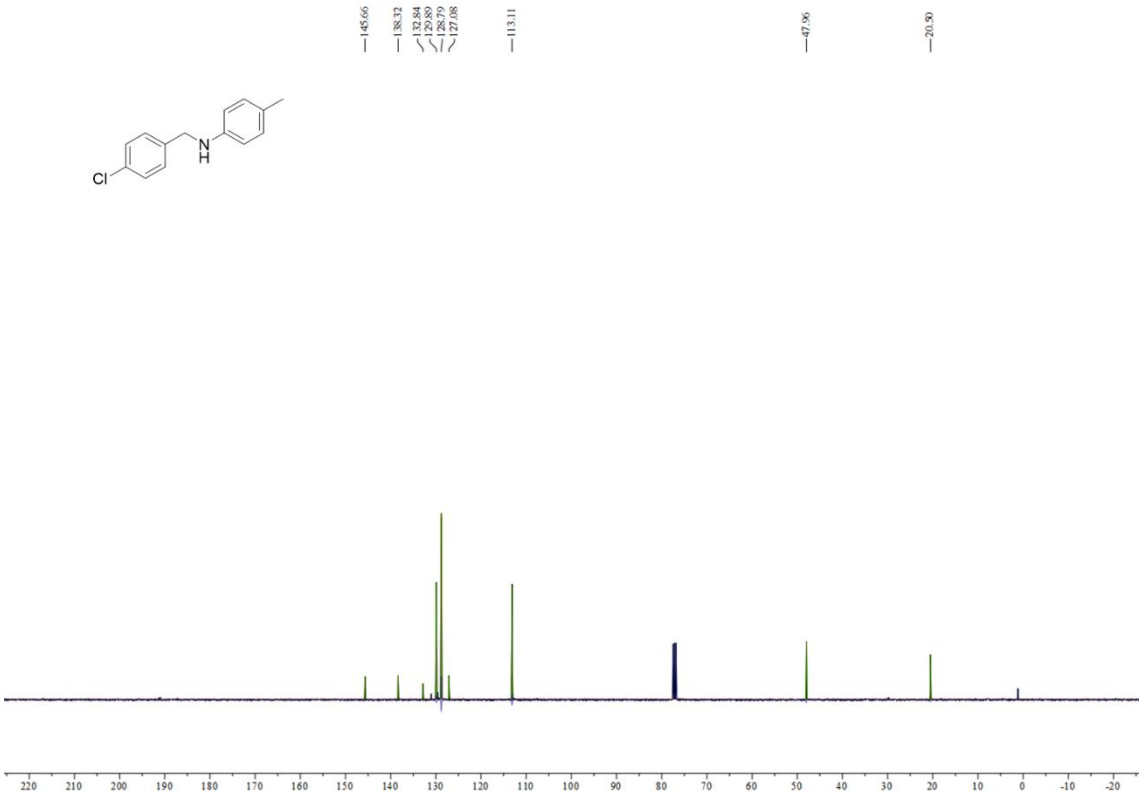

Figure S142. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2h**

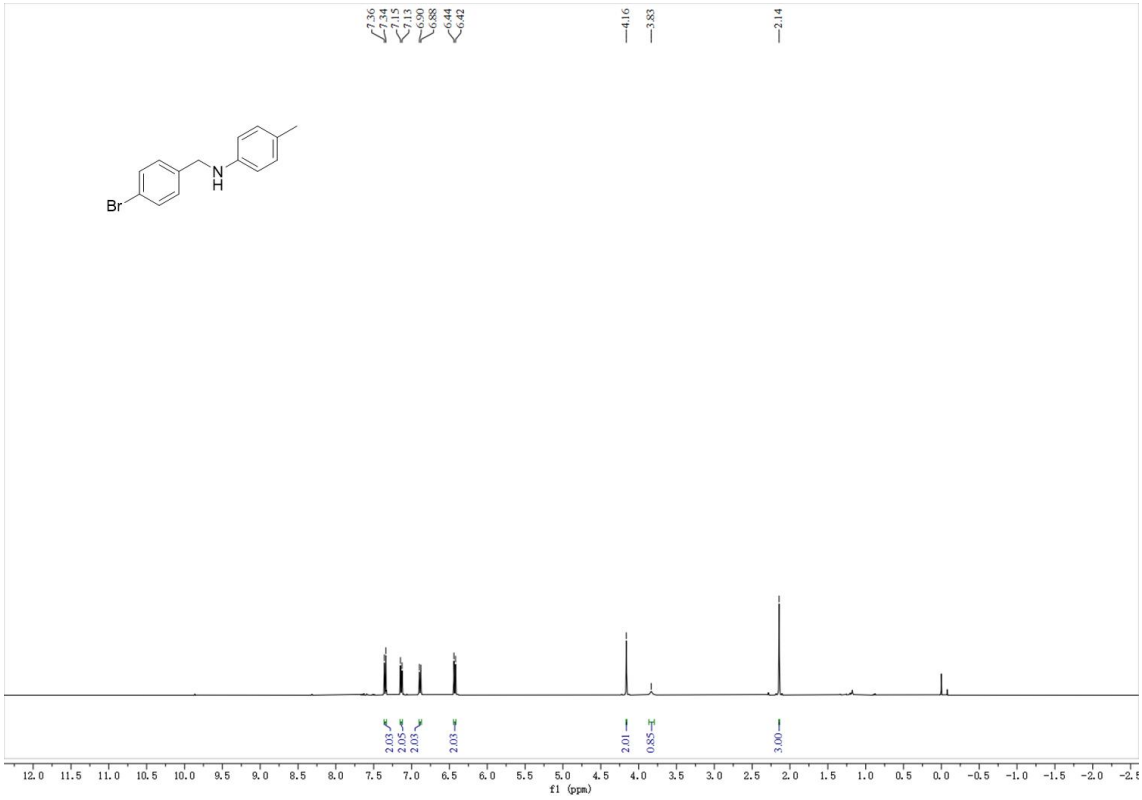

Figure S143. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**

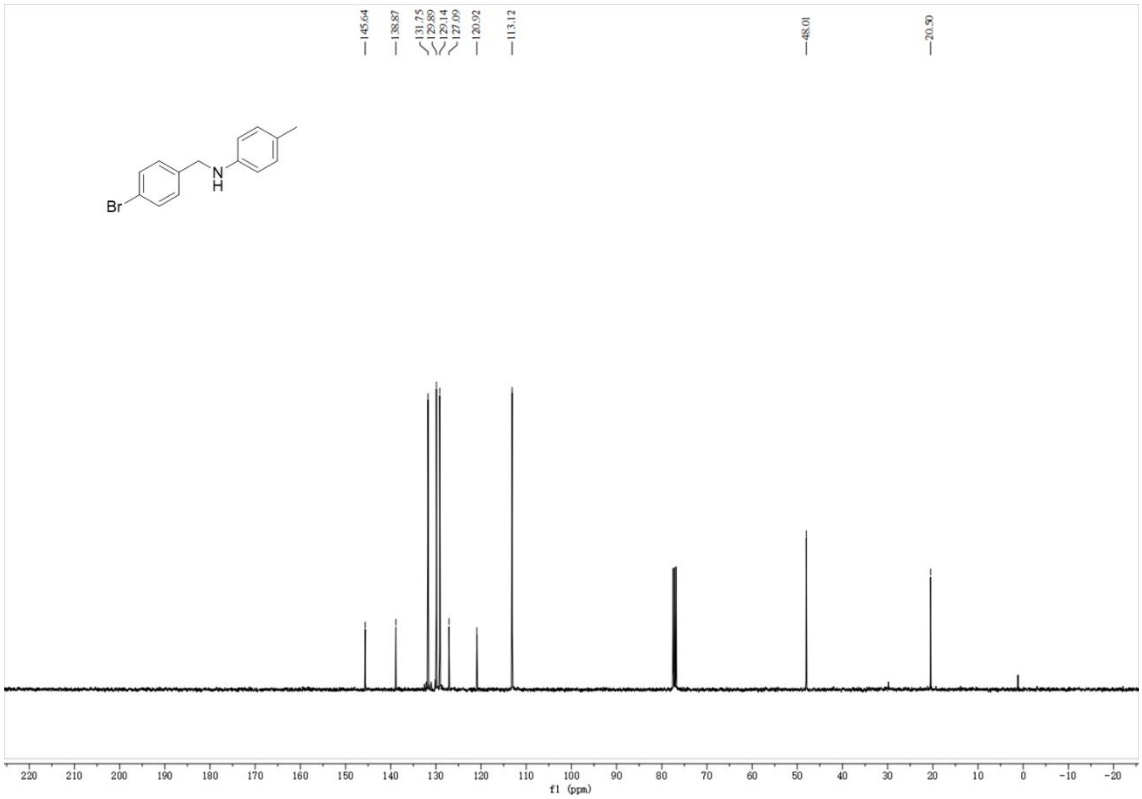

Figure S144. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2i**

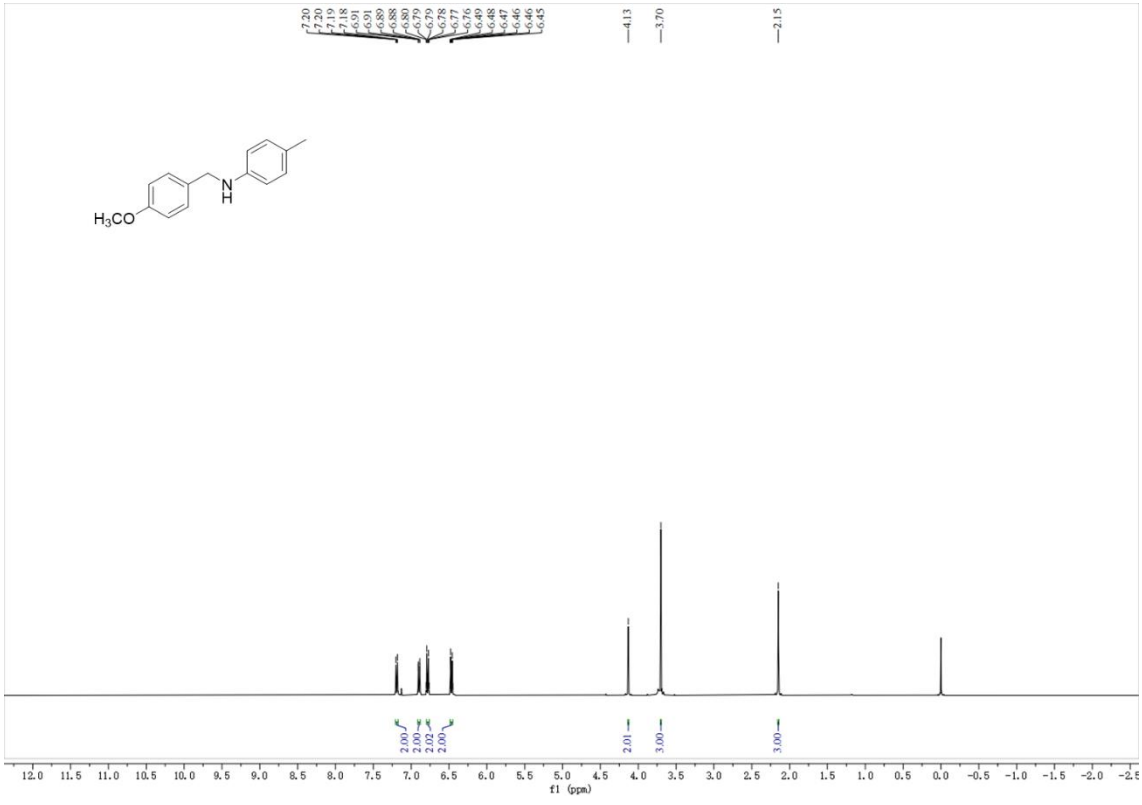

Figure S145. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2*J***

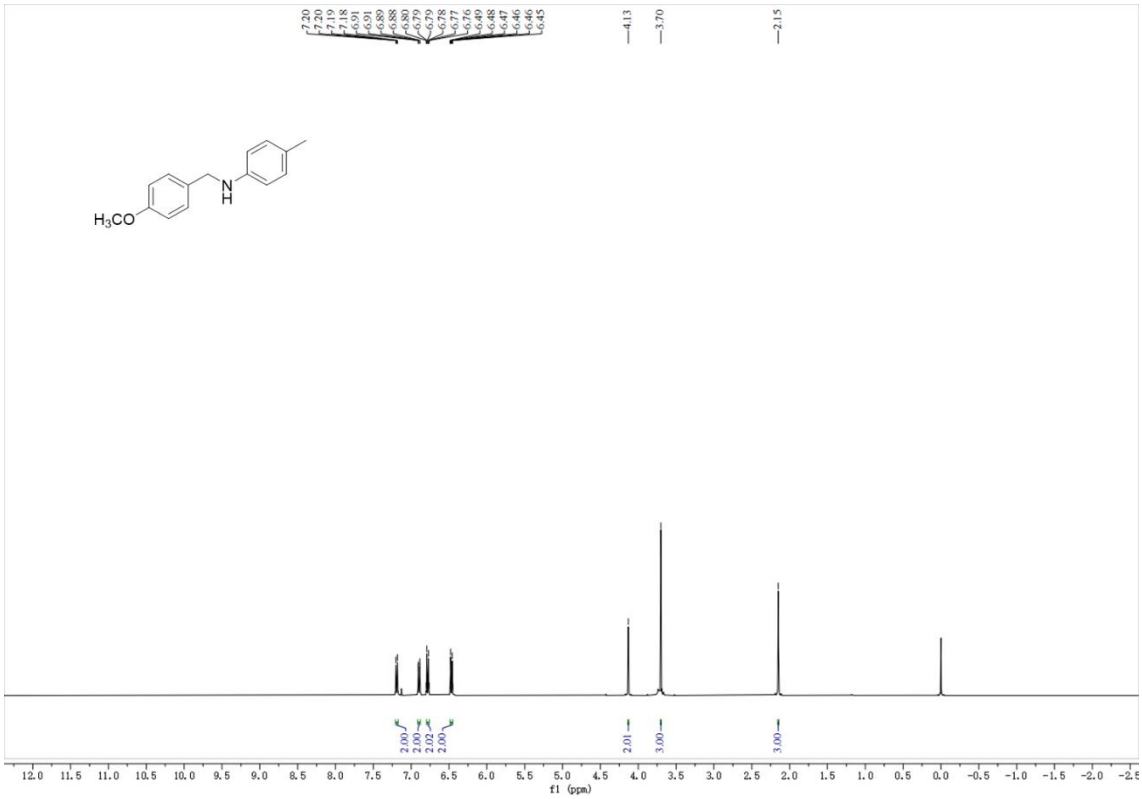

Figure S146. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2J**

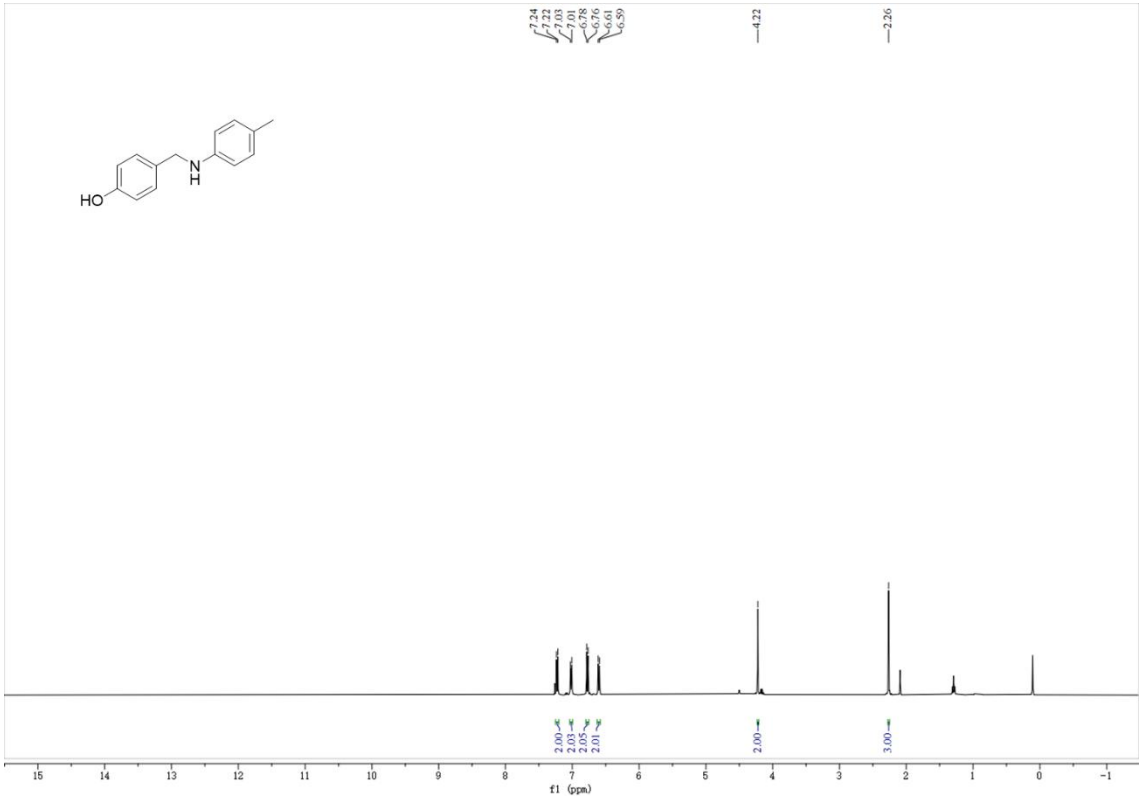

Figure S147. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**

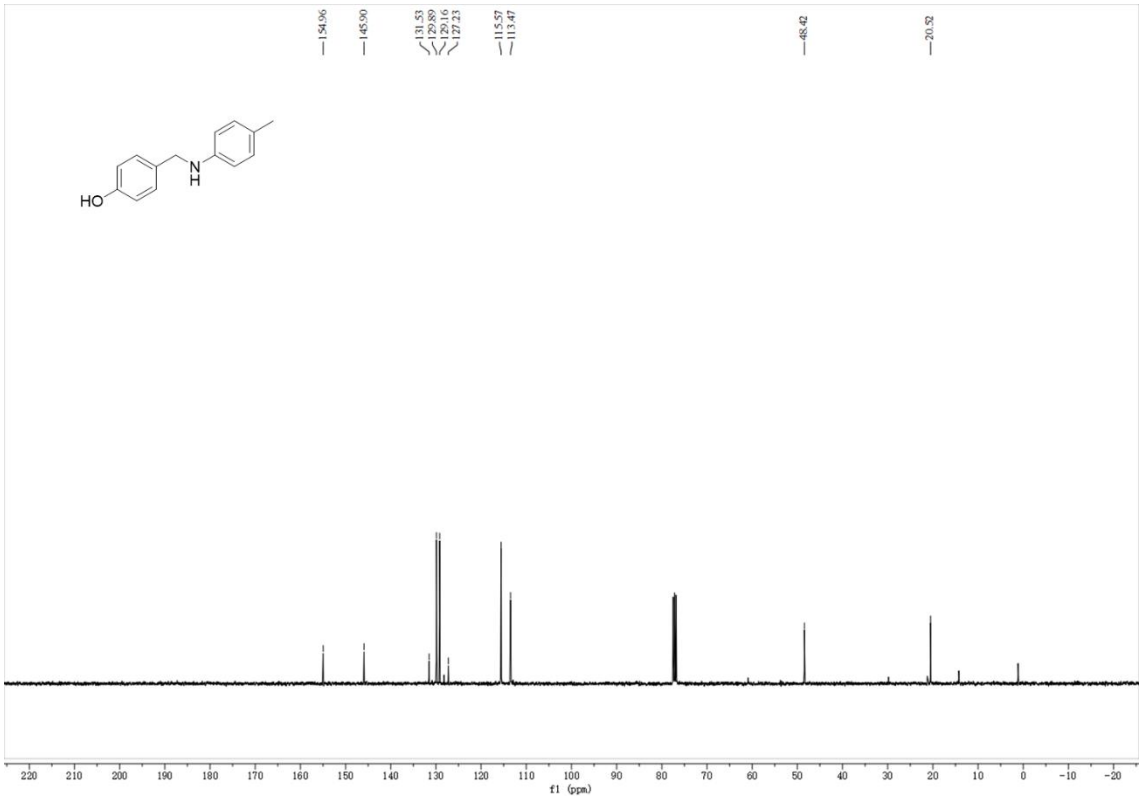

Figure S148. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2k**

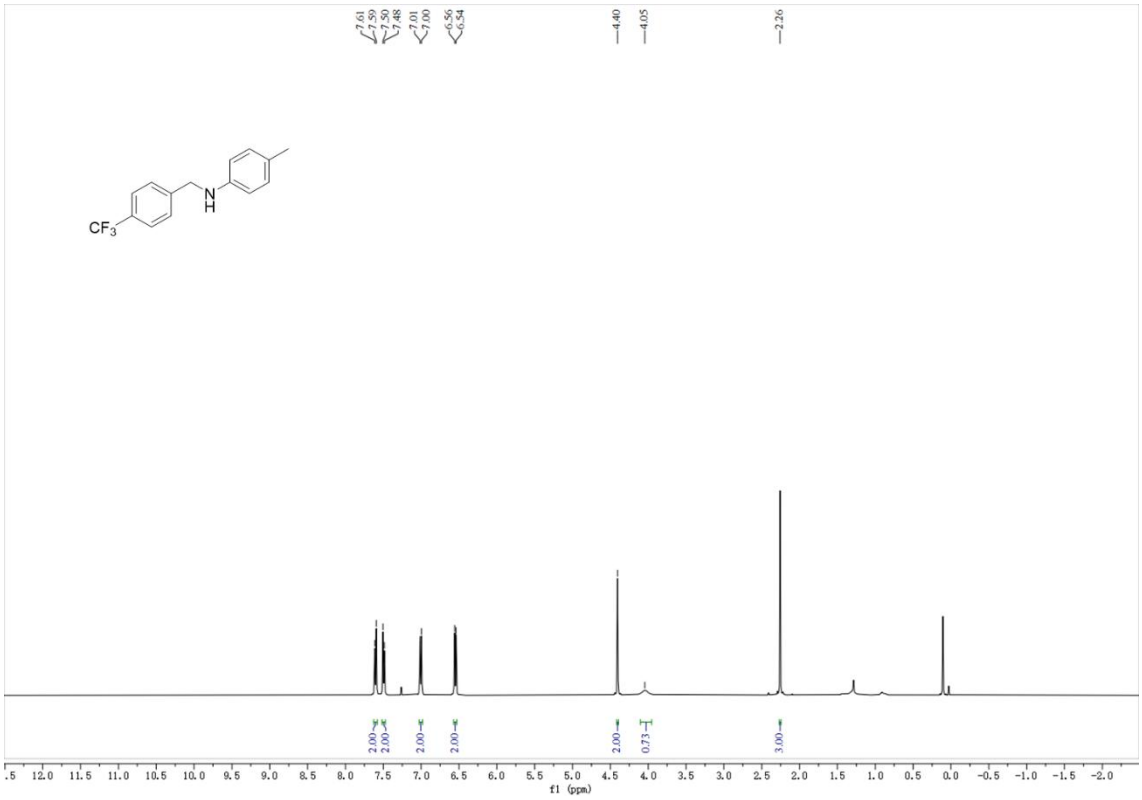

Figure S149. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**

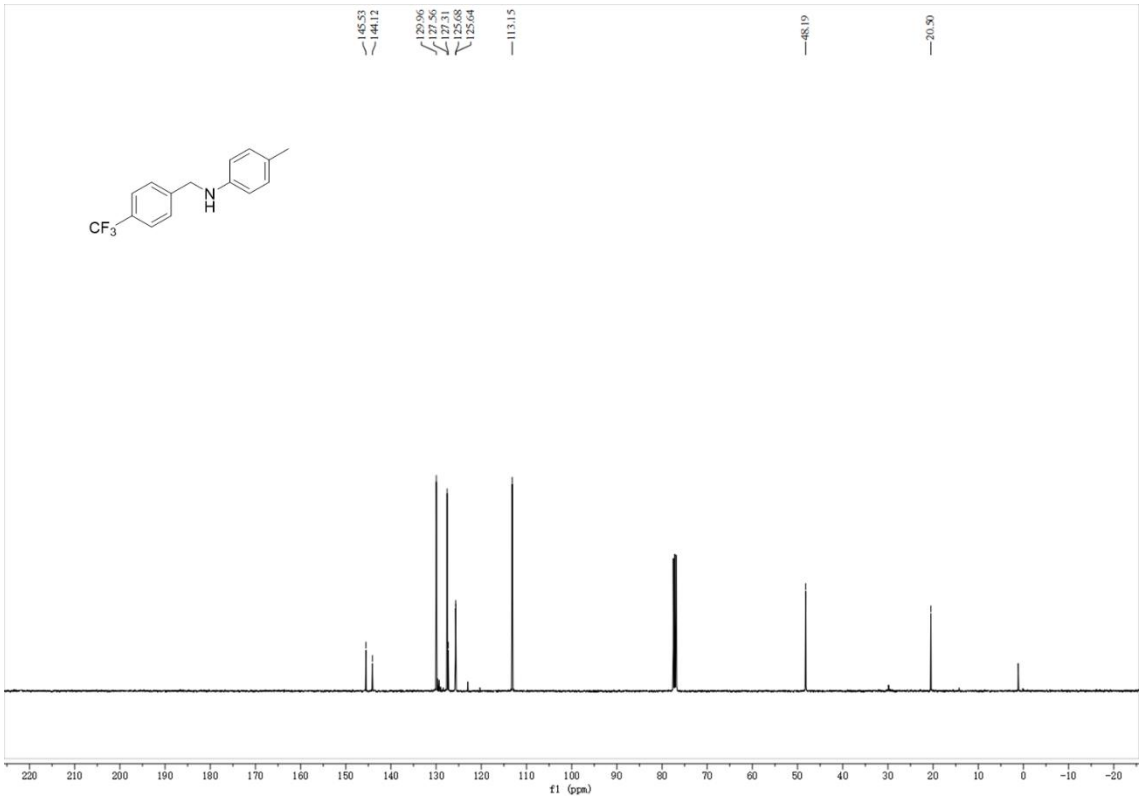

Figure S150. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **2l**

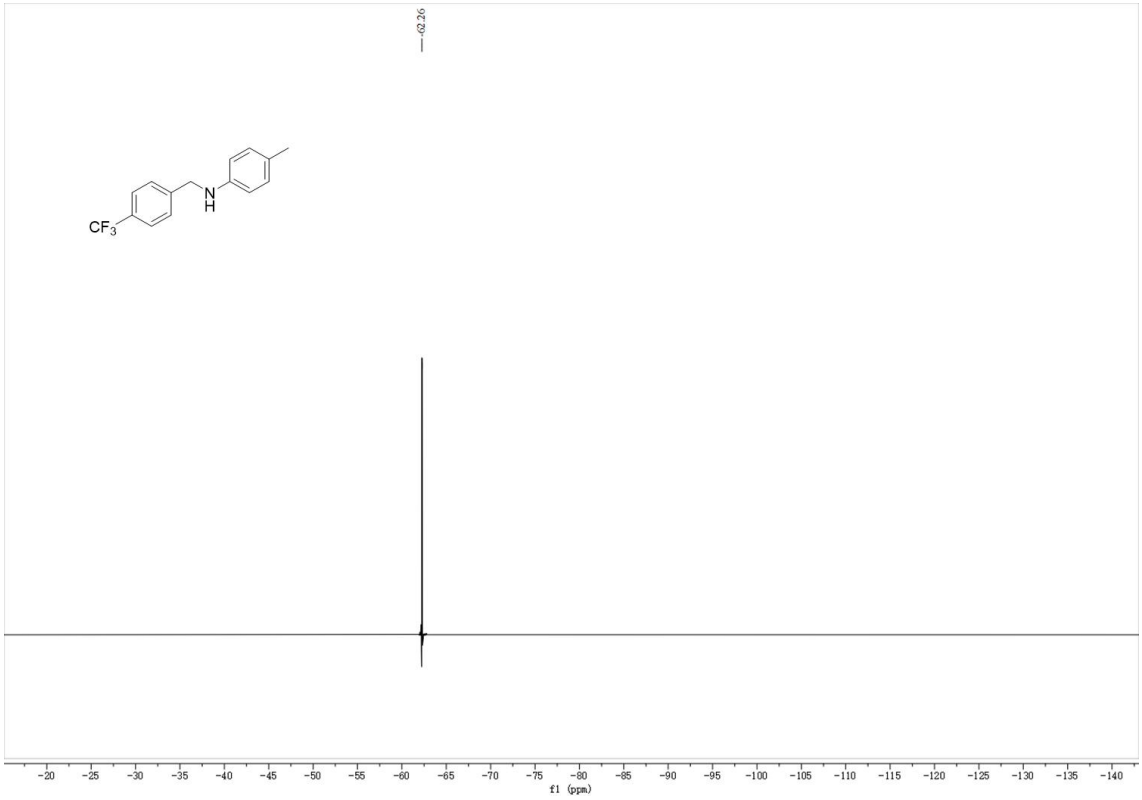

Figure S151. ^{19}F NMR (376MHz, $CDCl_3$) spectrum of **2l**

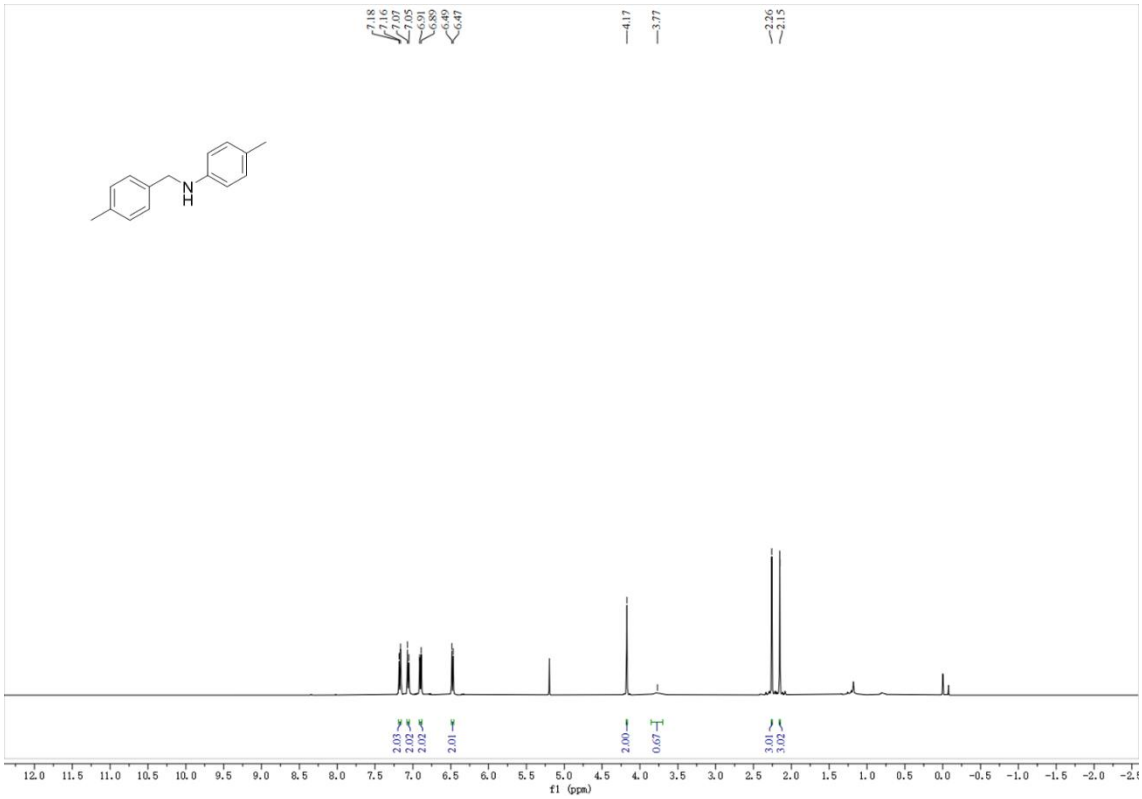

Figure S152. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**

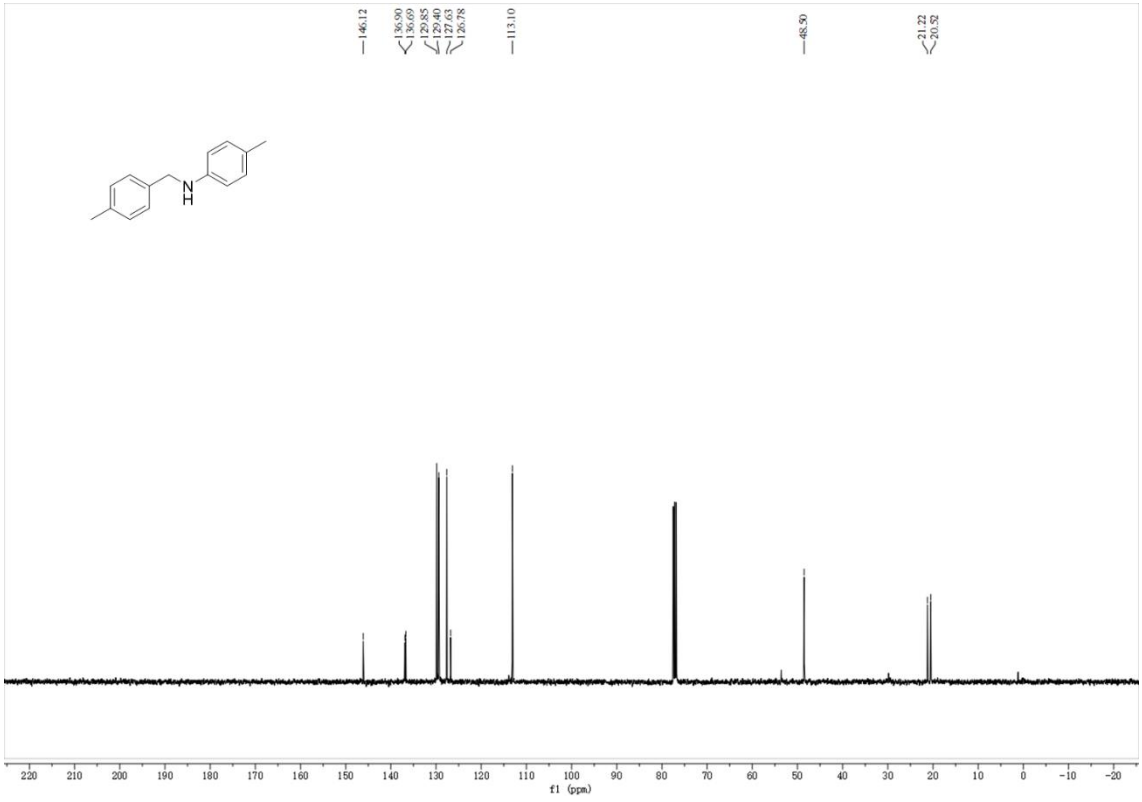

Figure S153. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2m**

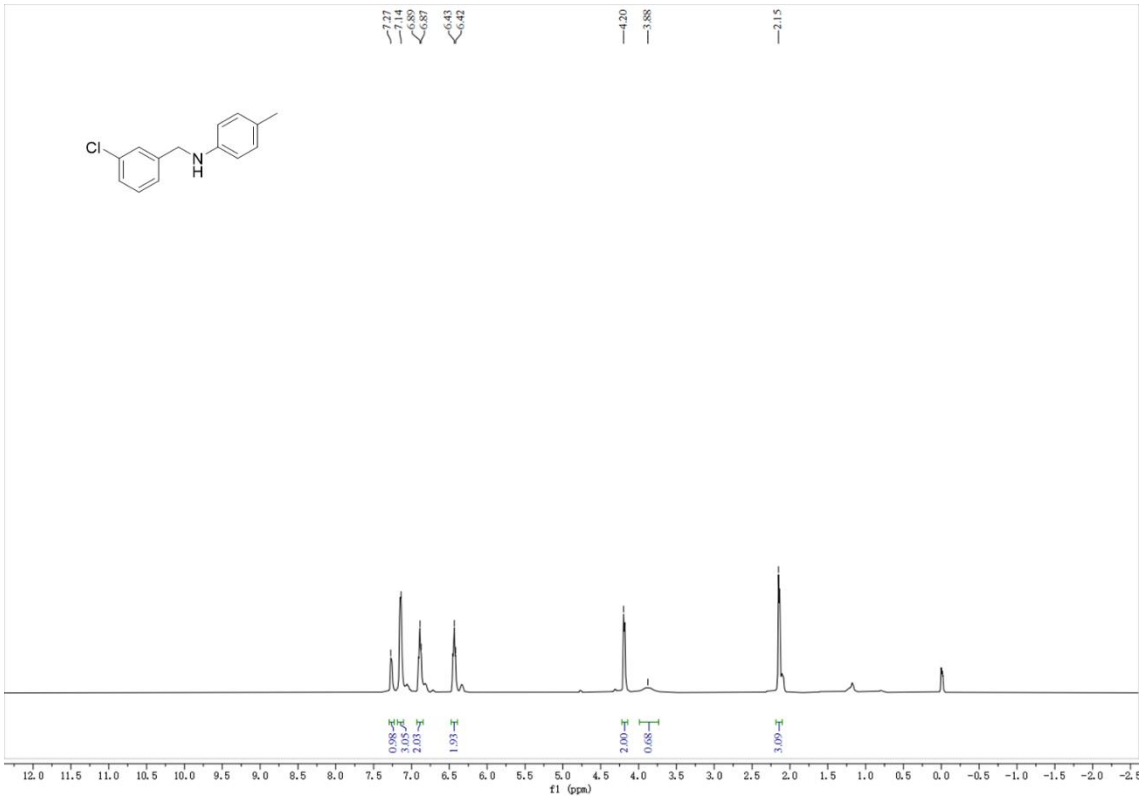

Figure S154. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2n**

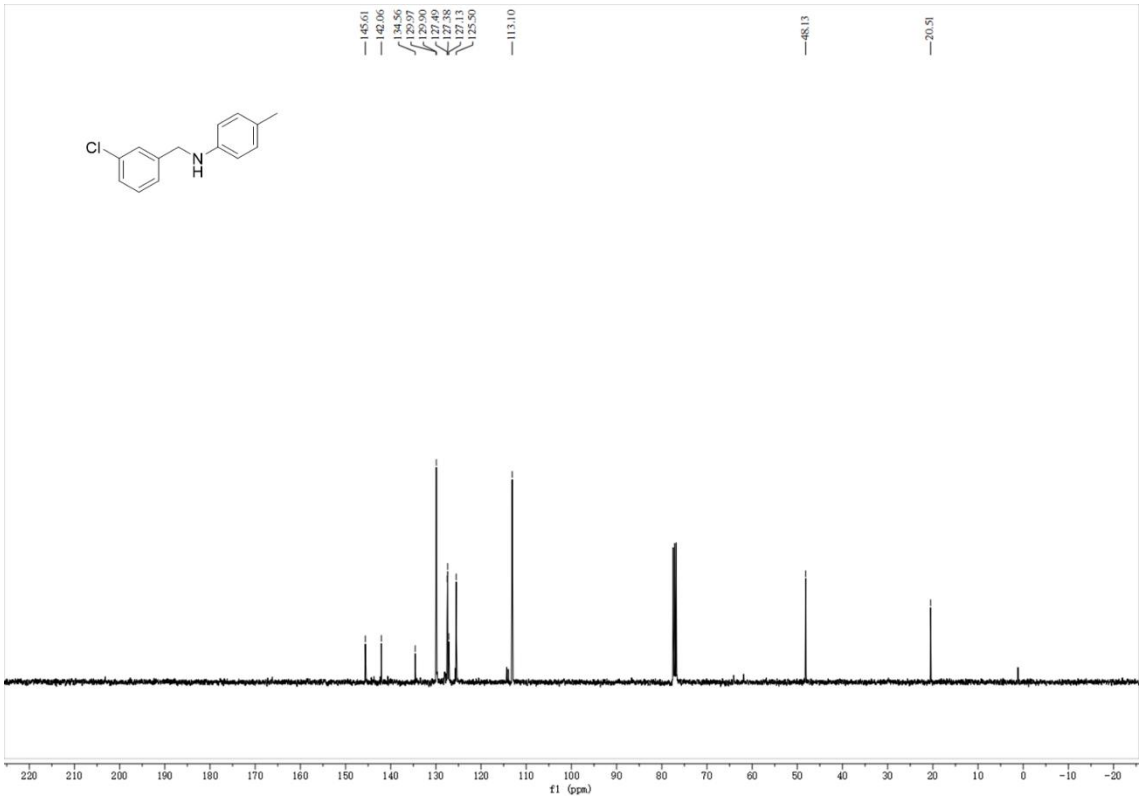

Figure S155. ^{13}C NMR(100 MHz, $CDCl_3$) spectrum of **2n**

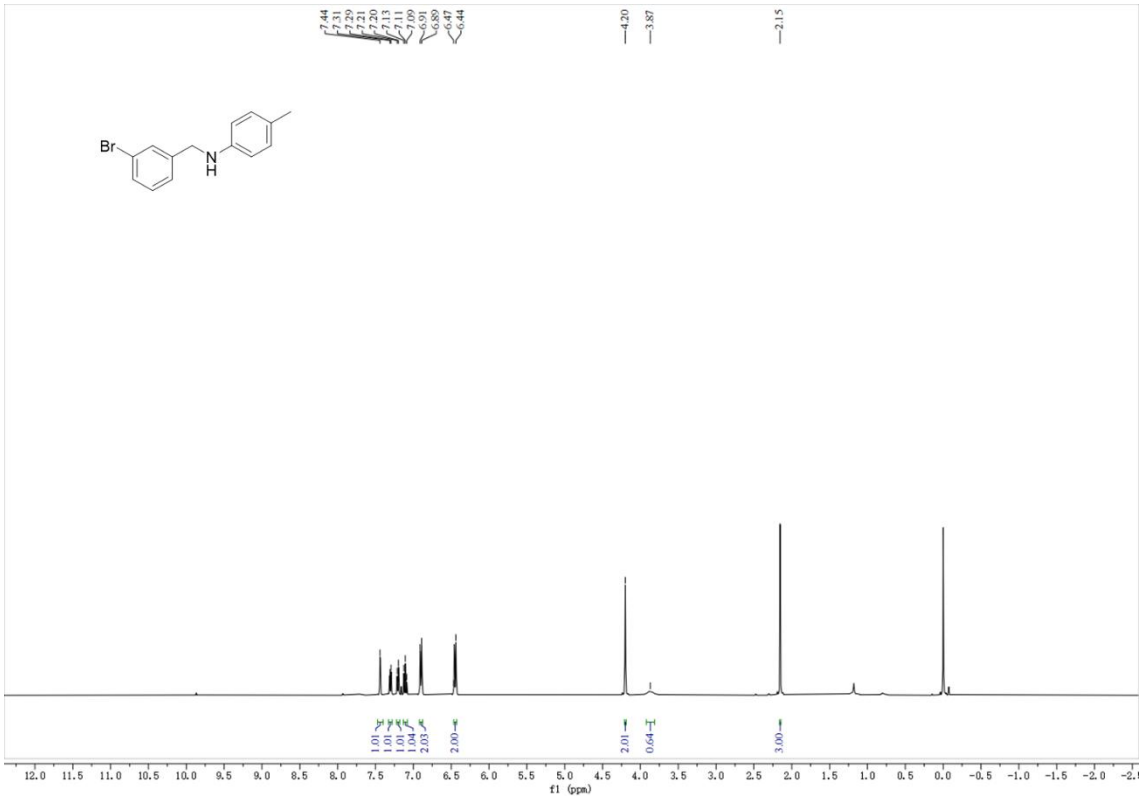

Figure S156. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**

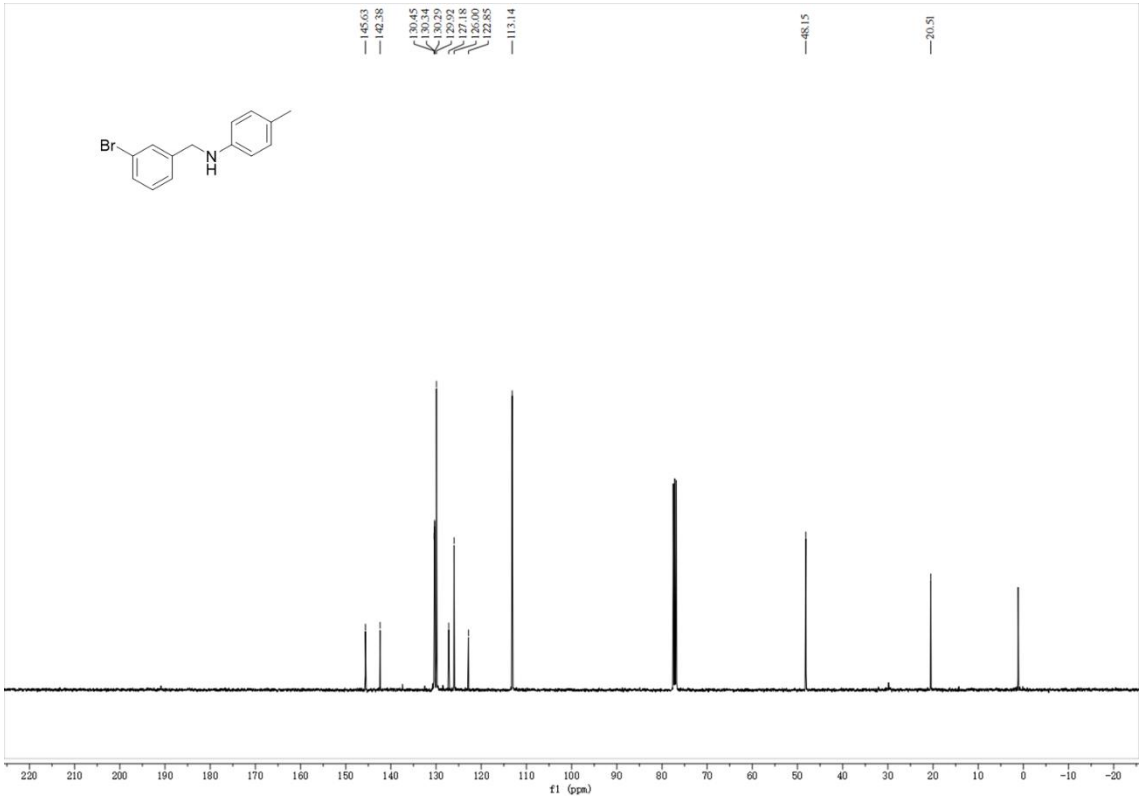

Figure S157. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2o**

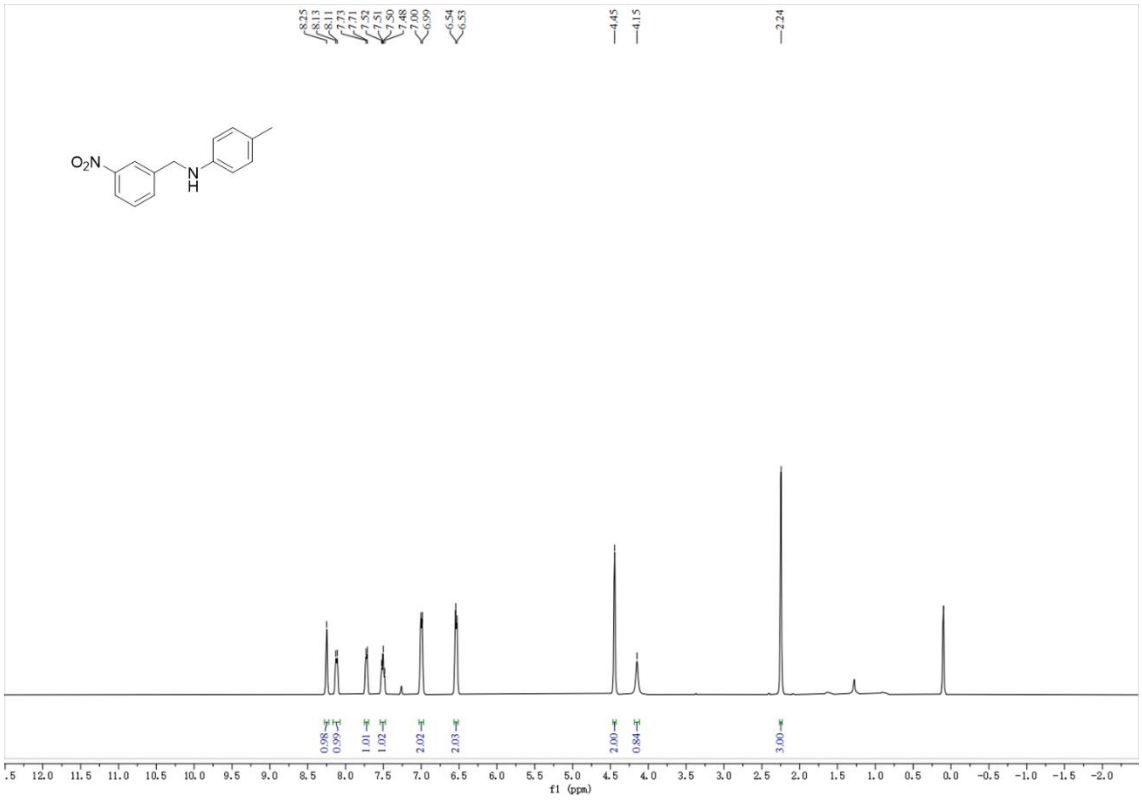

Figure S158. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**

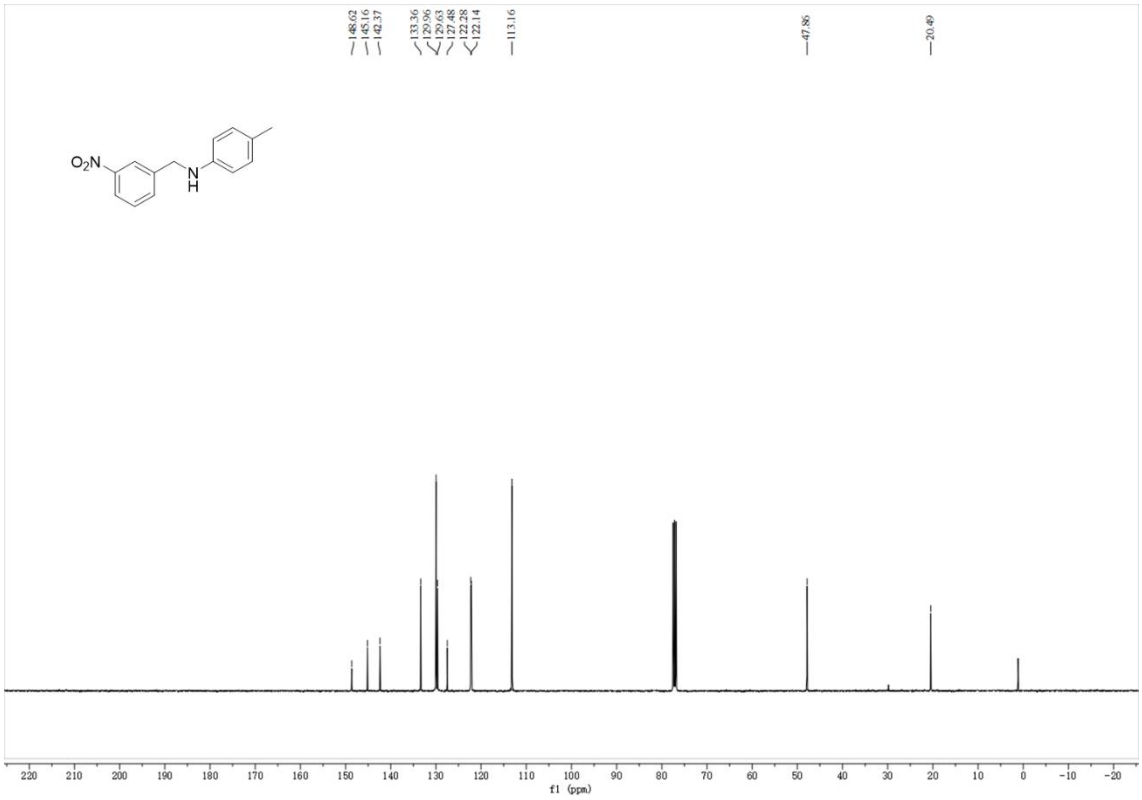

Figure S159. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2p**

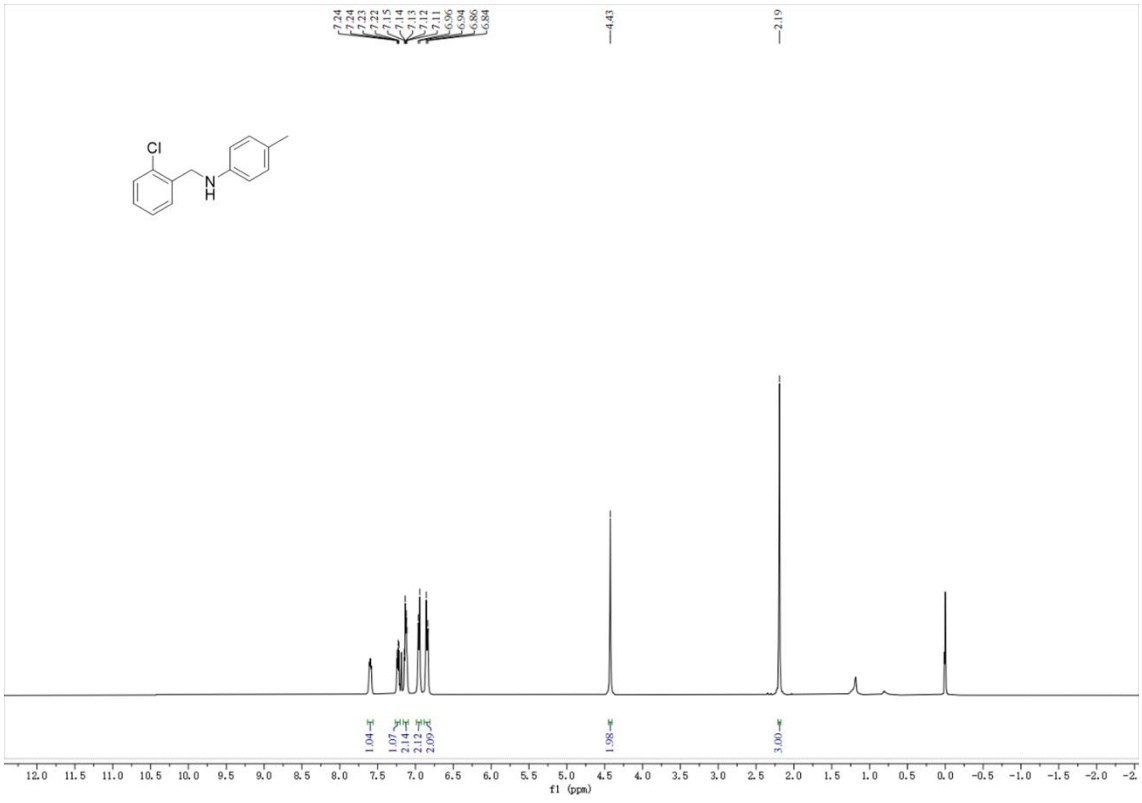

Figure S160 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2q**

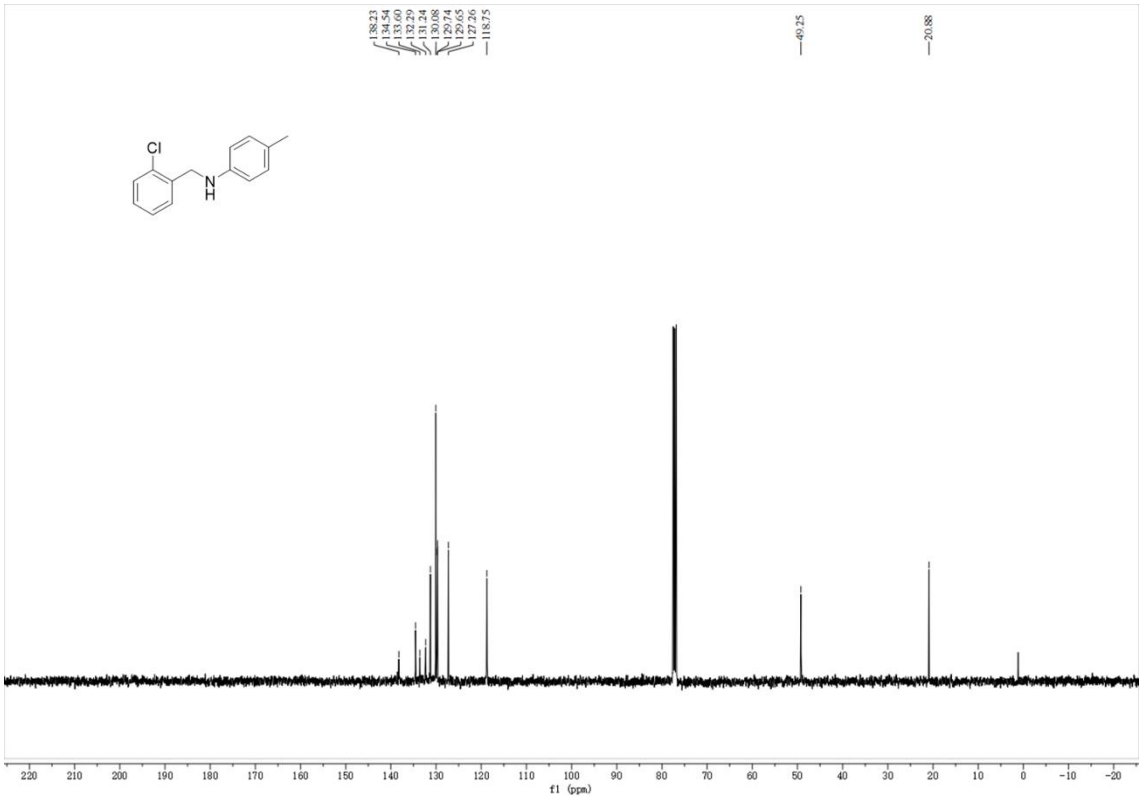

Figure S161. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2q**

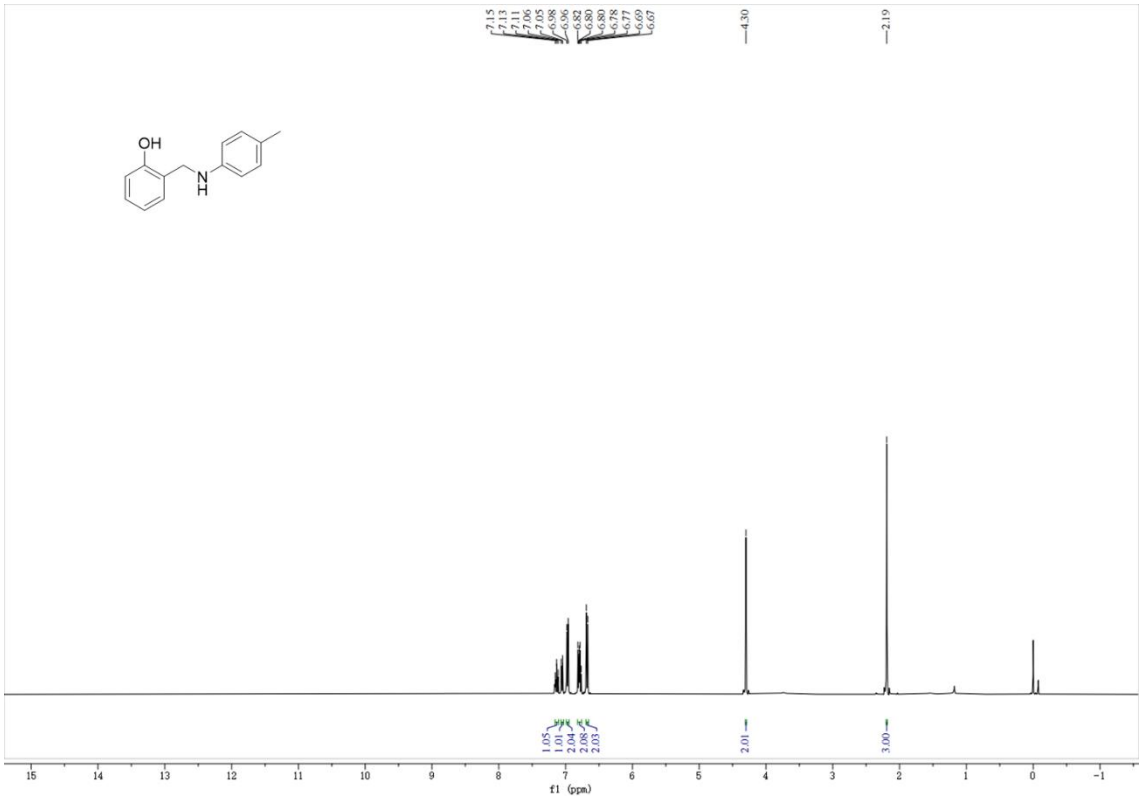

Figure S162. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2r**

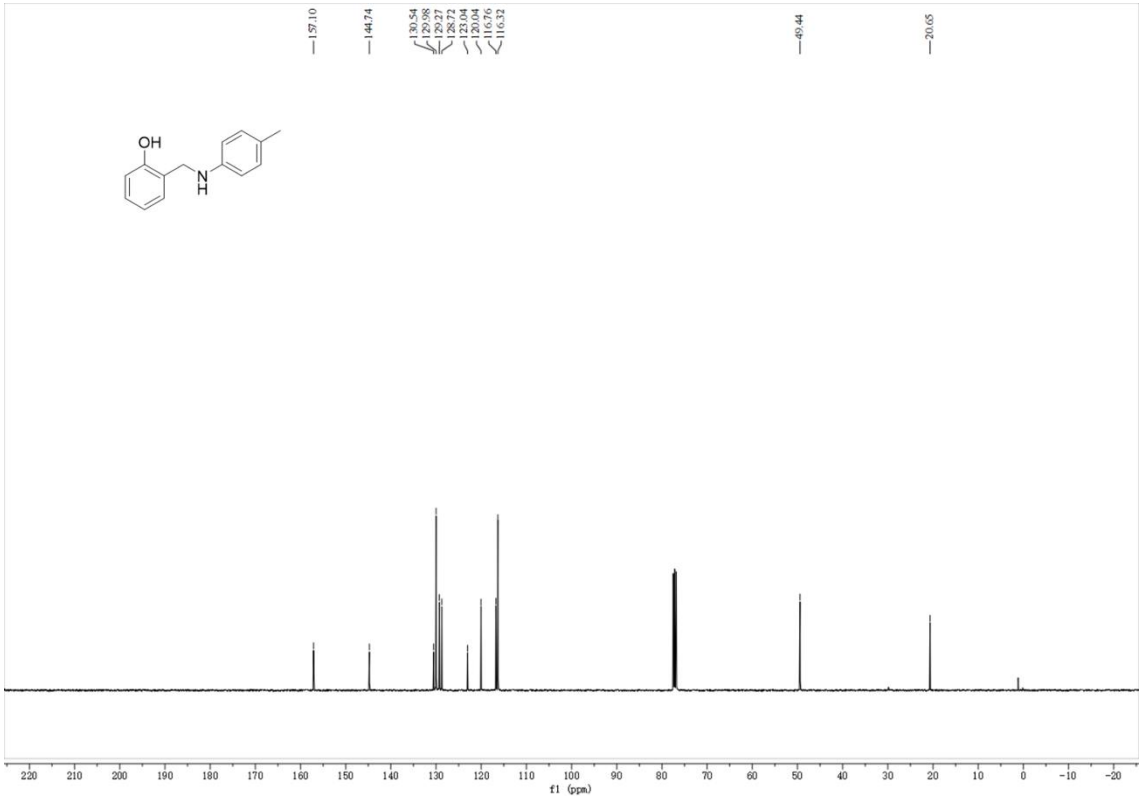

Figure S163. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2r**

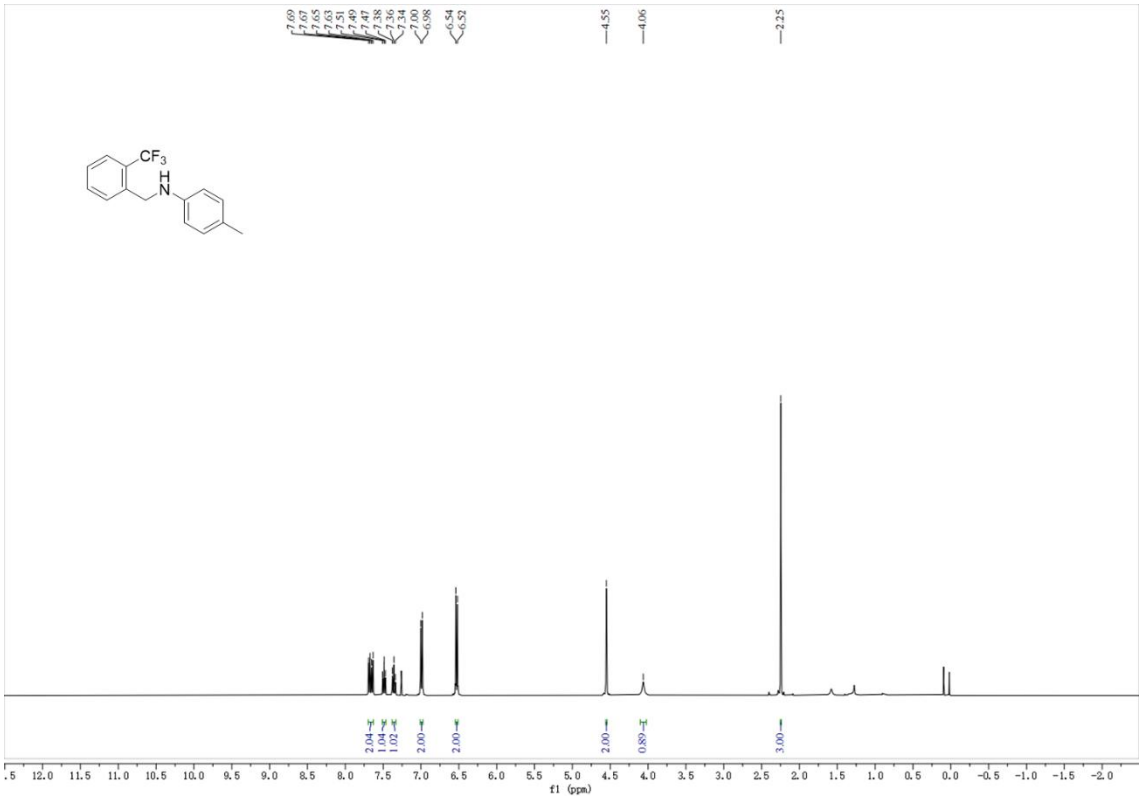

Figure S164. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2s**

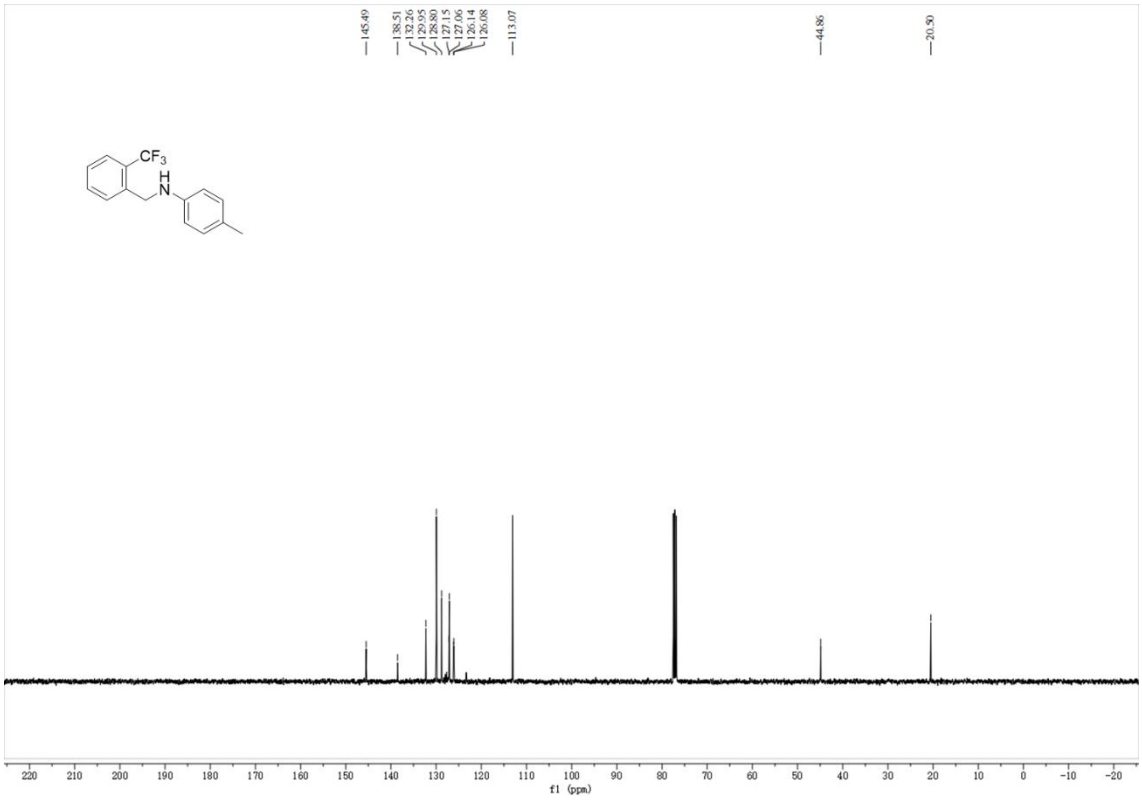

Figure S165. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2s**

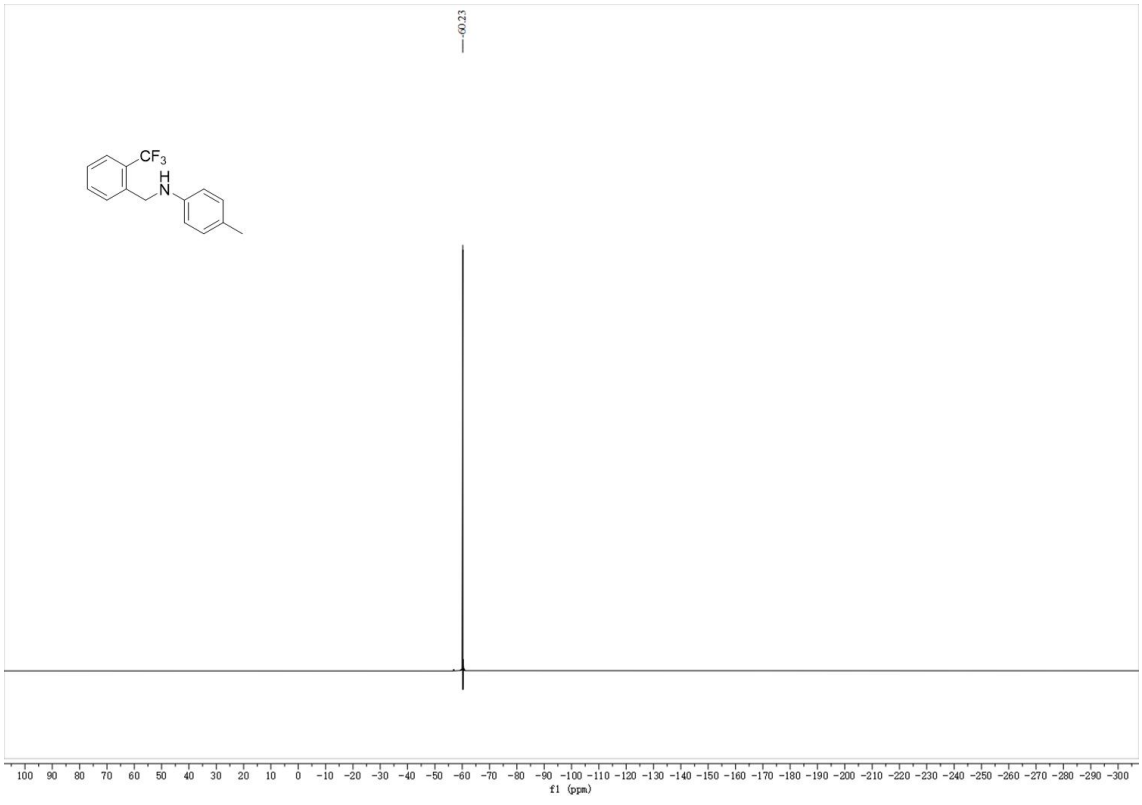

Figure S166. ^{19}F NMR (100 MHz, $CDCl_3$) spectrum of **2s**

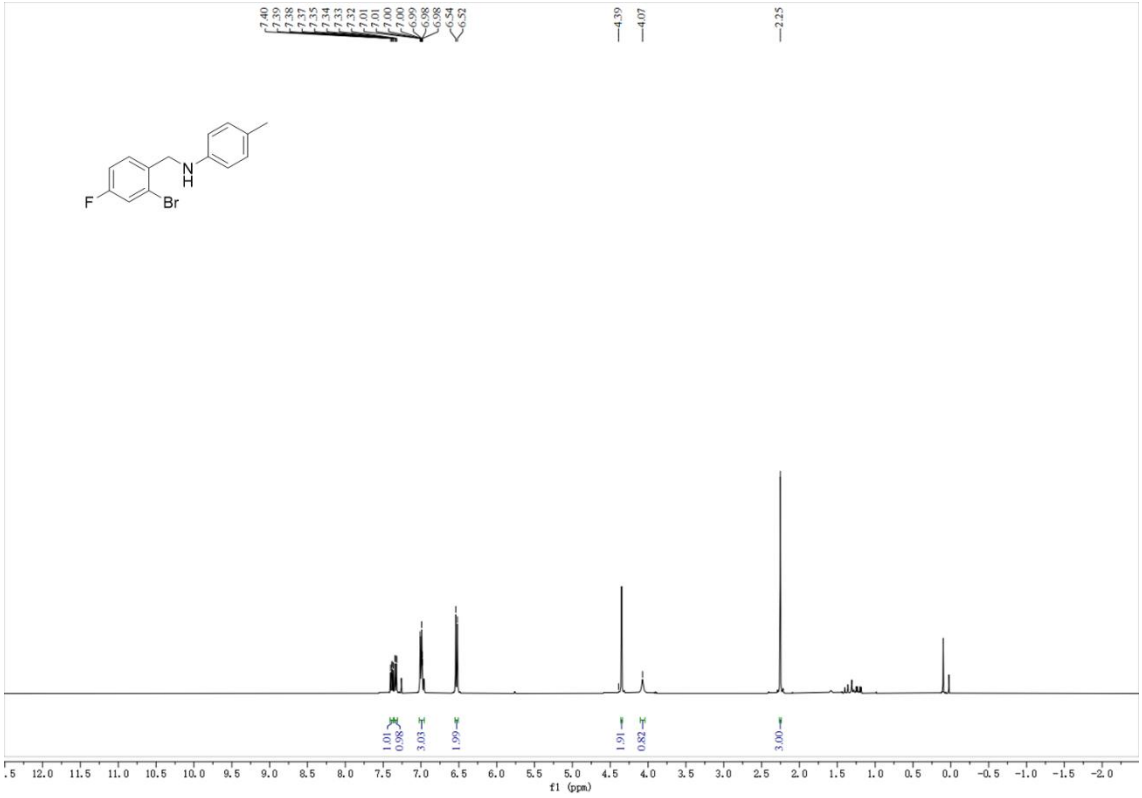

Figure S167. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2t**

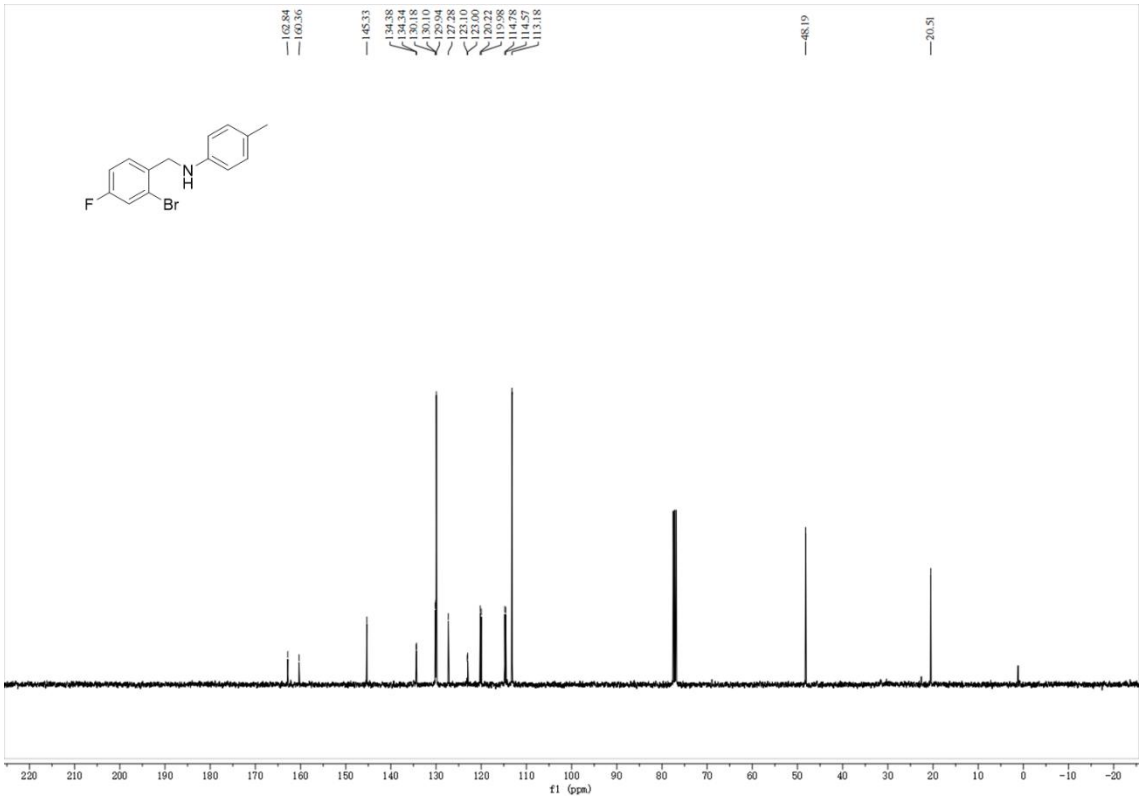

Figure S168. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2t**

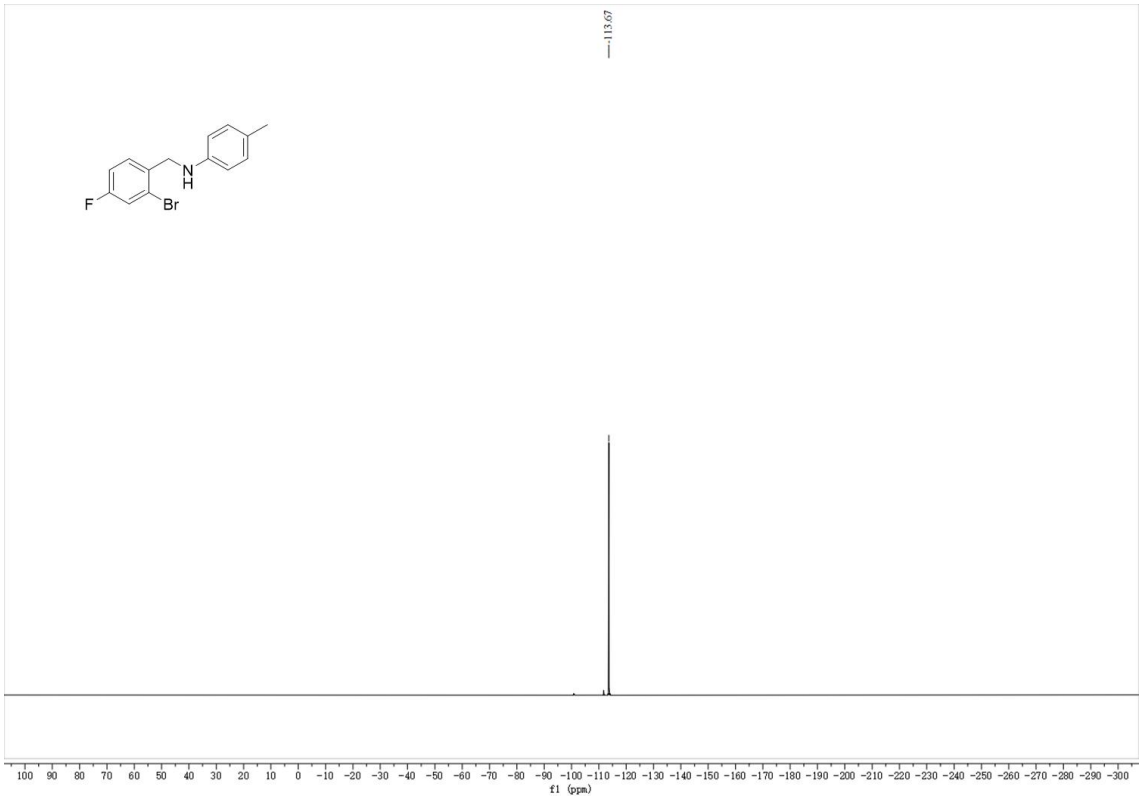

Figure S169. ^{19}F NMR(376 MHz, $CDCl_3$) spectrum of **2t**

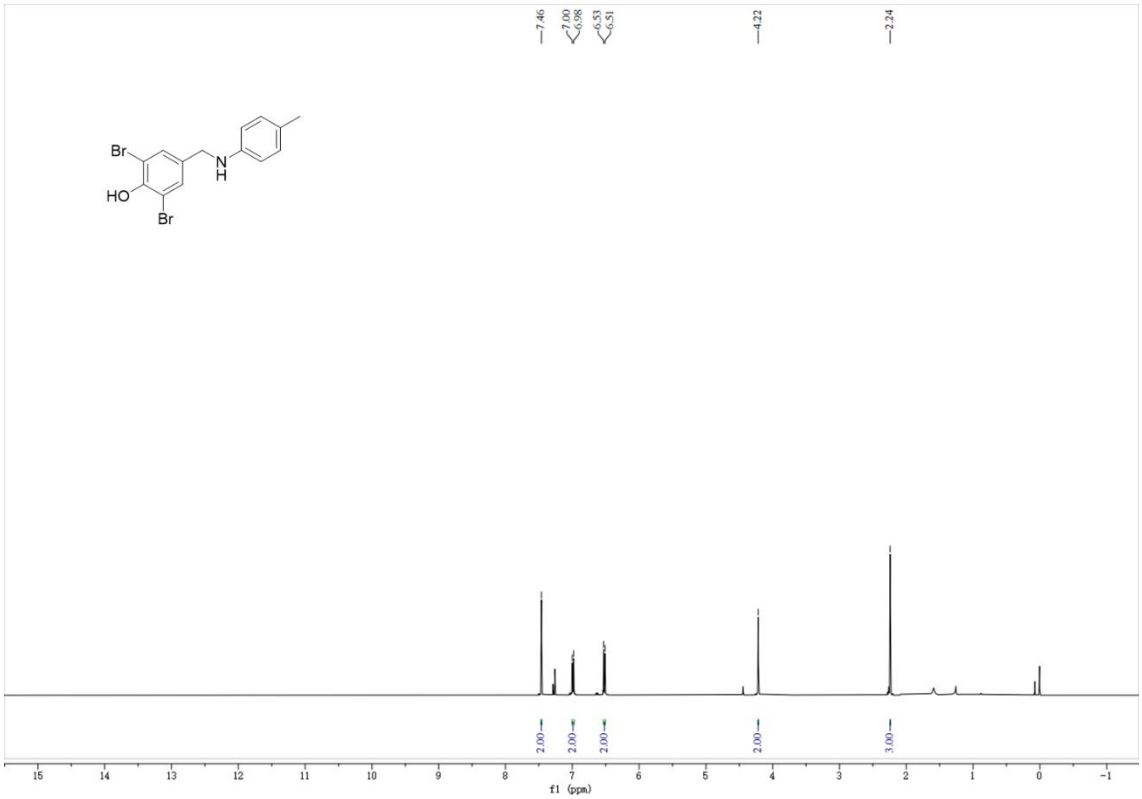

Figure S170. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2u**

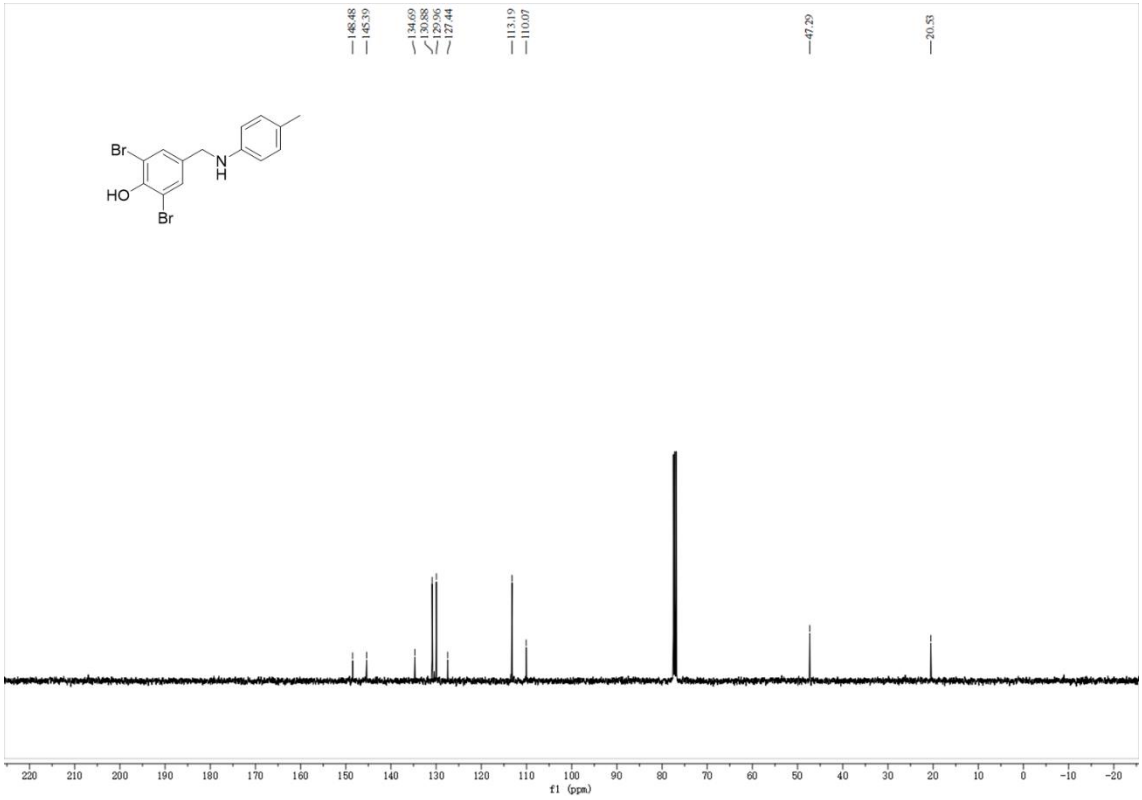

Figure S171. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2u**

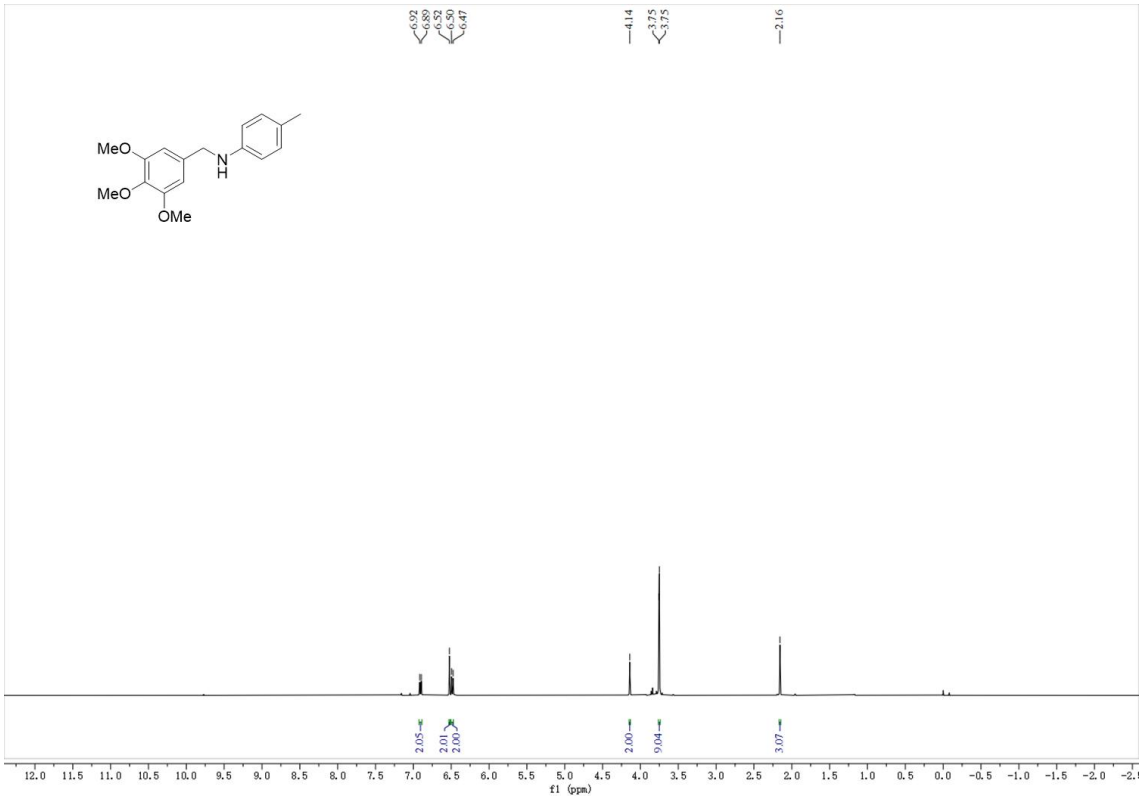

Figure S172. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2v**

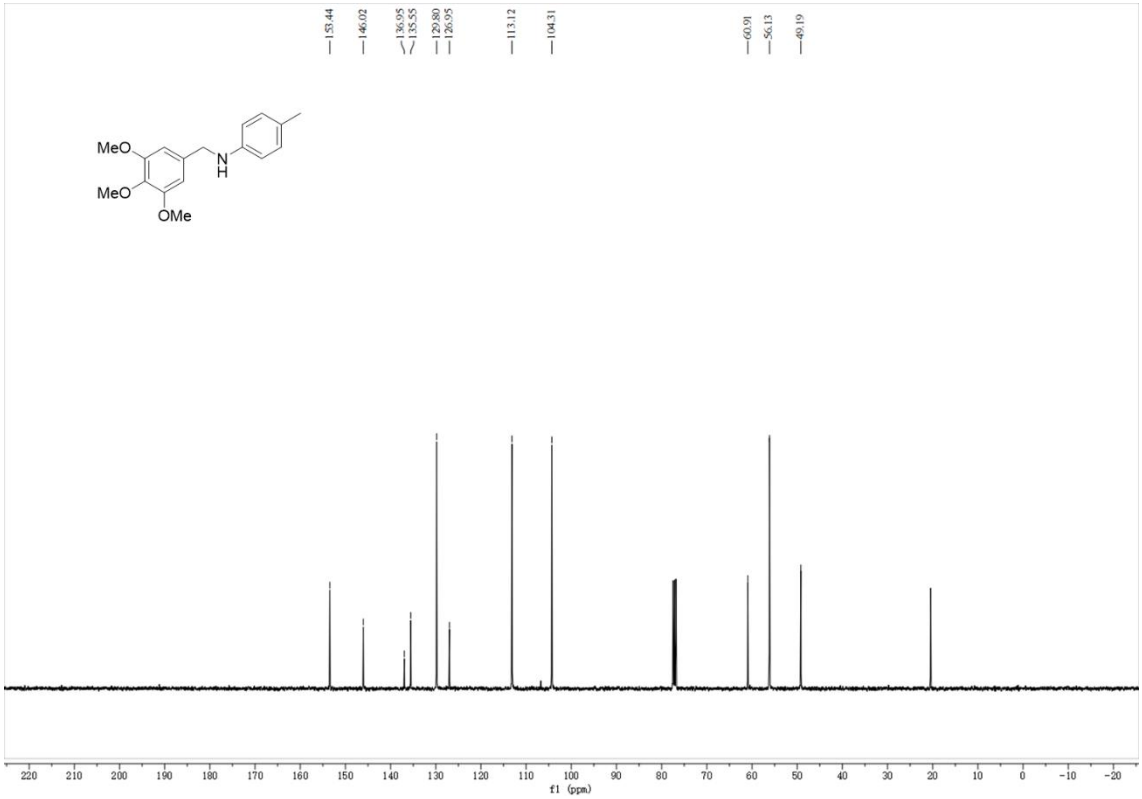

Figure S173. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2v**

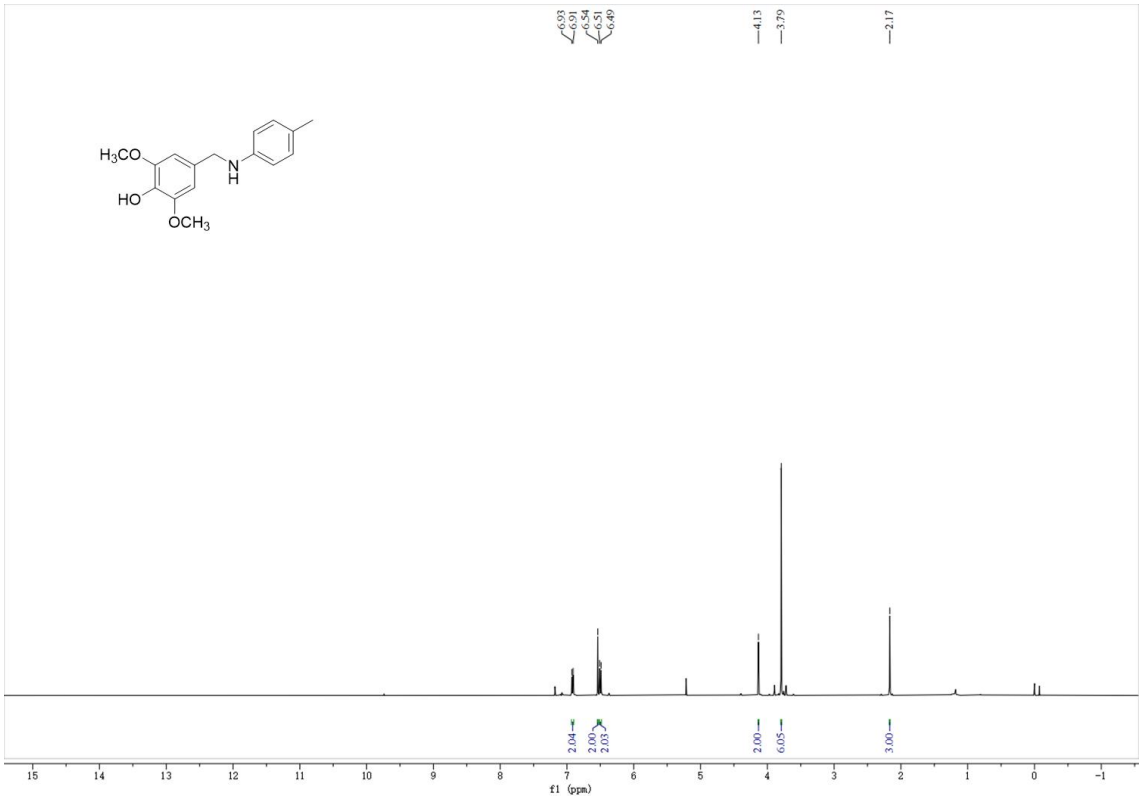

Figure S174. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2w**

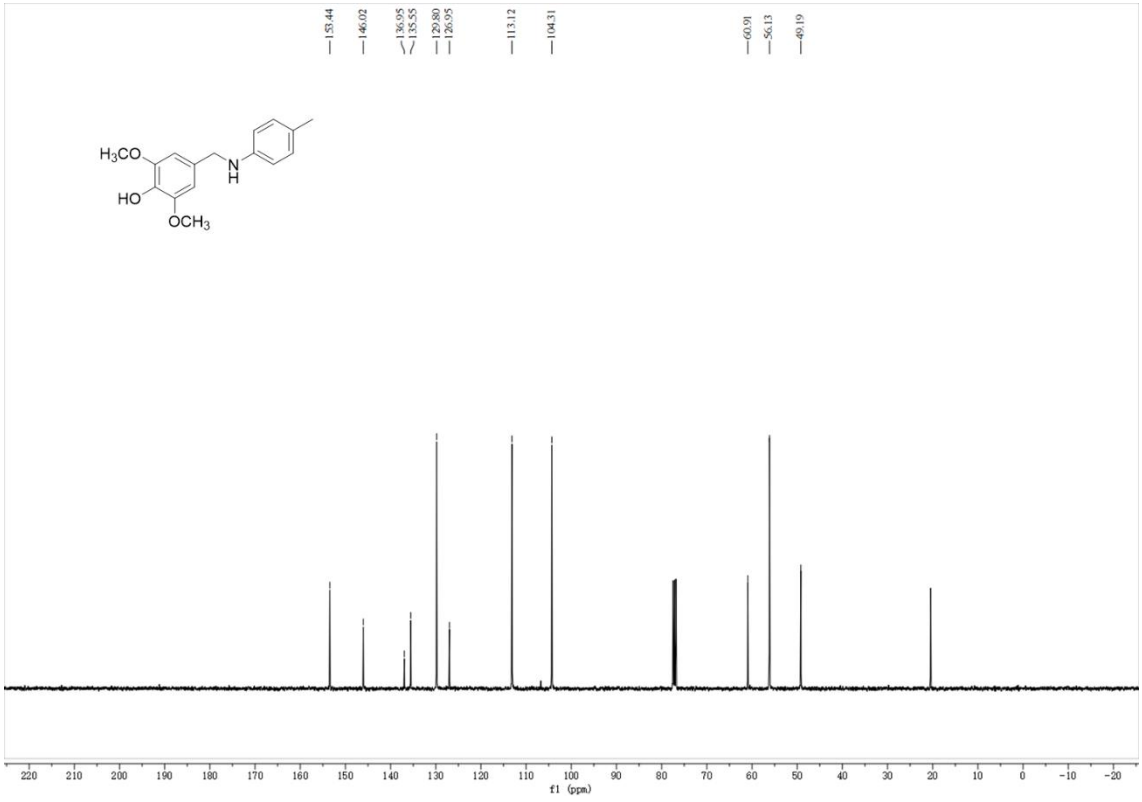

Figure S175. ^{13}C NMR spectrum of **2w**

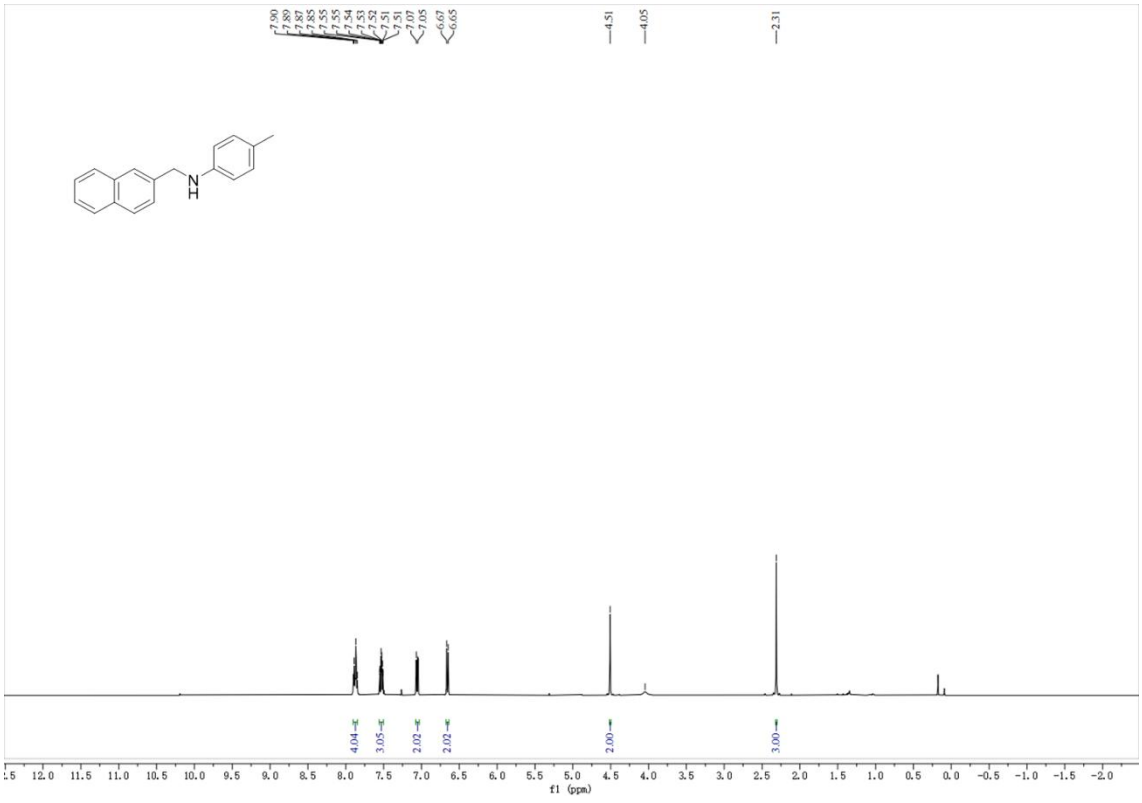

Figure S176. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2x**

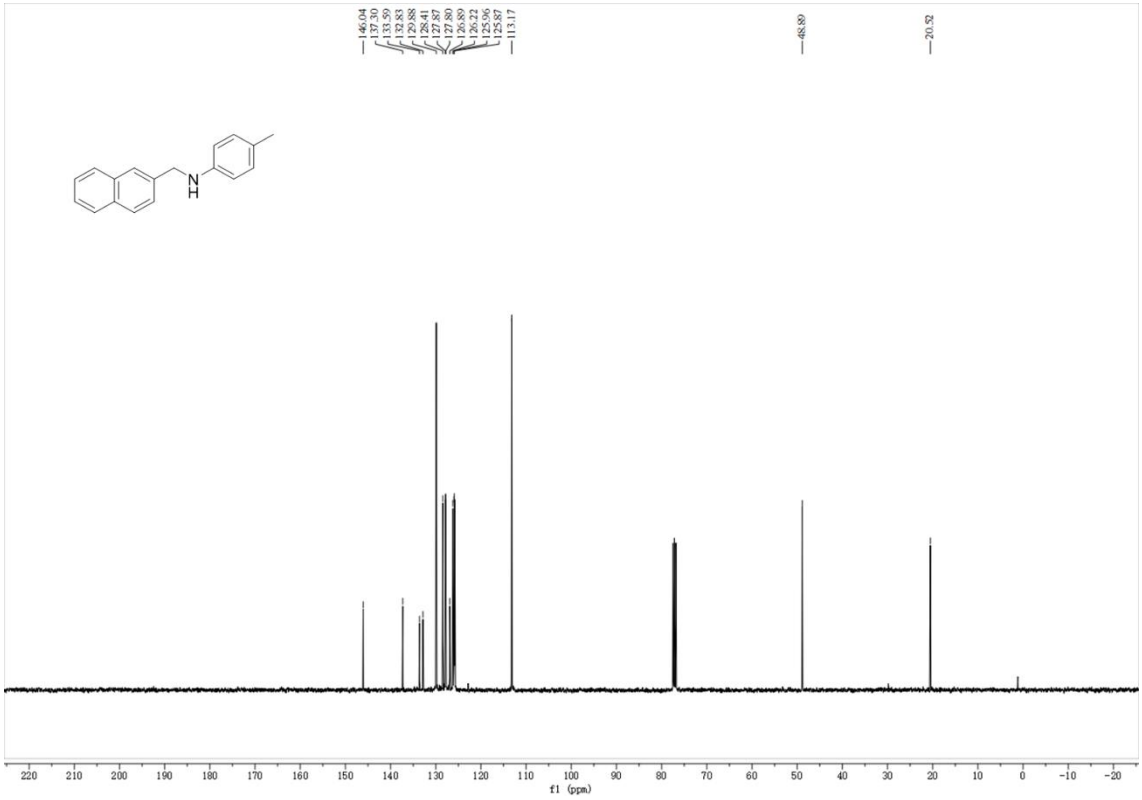

Figure S177. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2x**

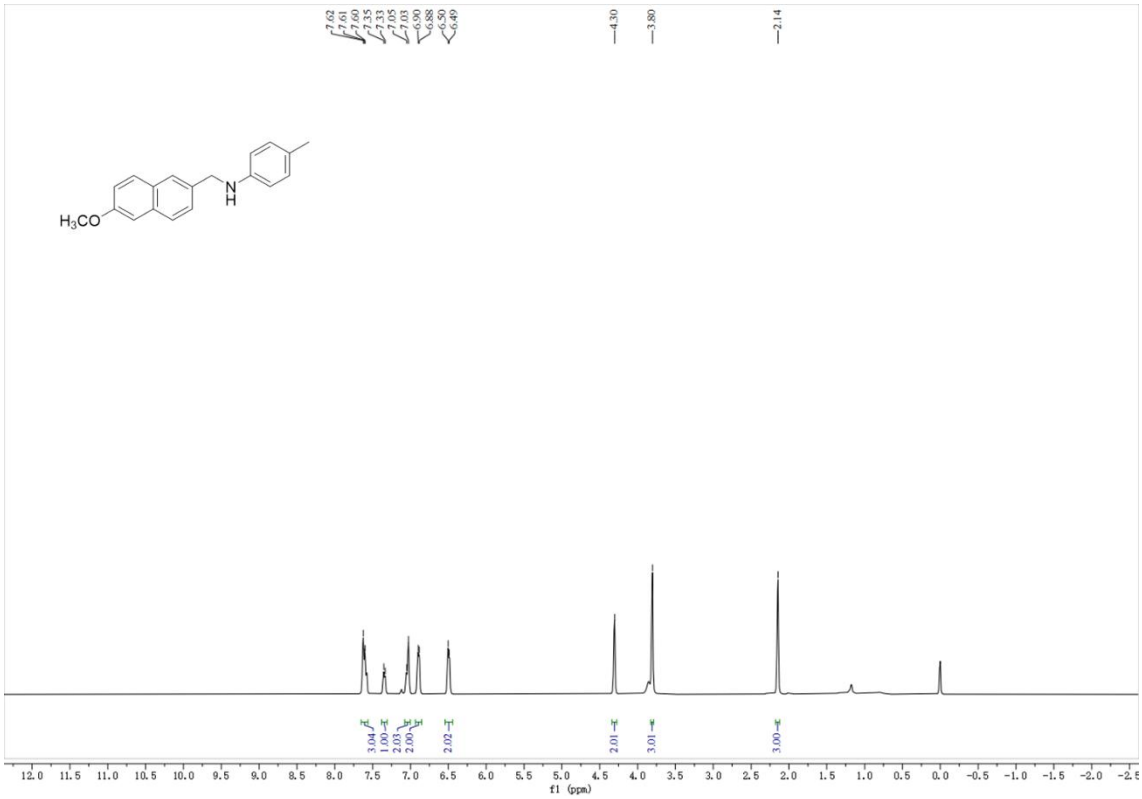

Figure S178. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2y**

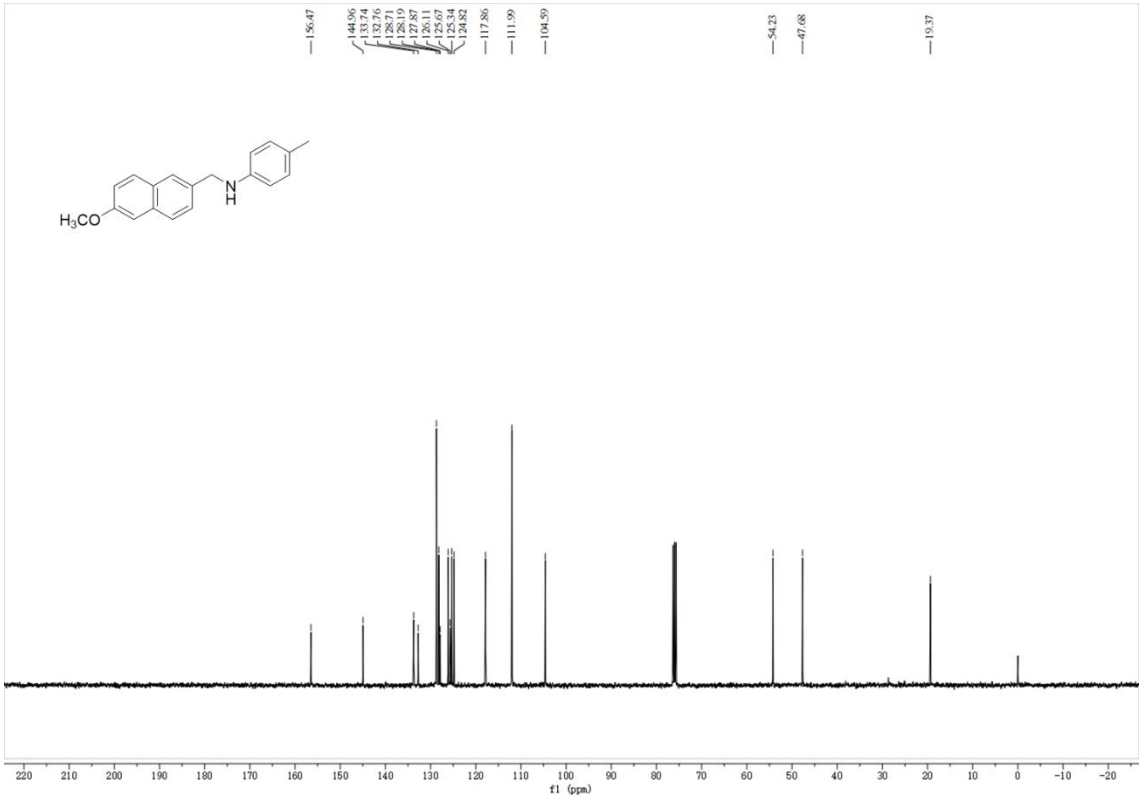

Figure S179. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2y**

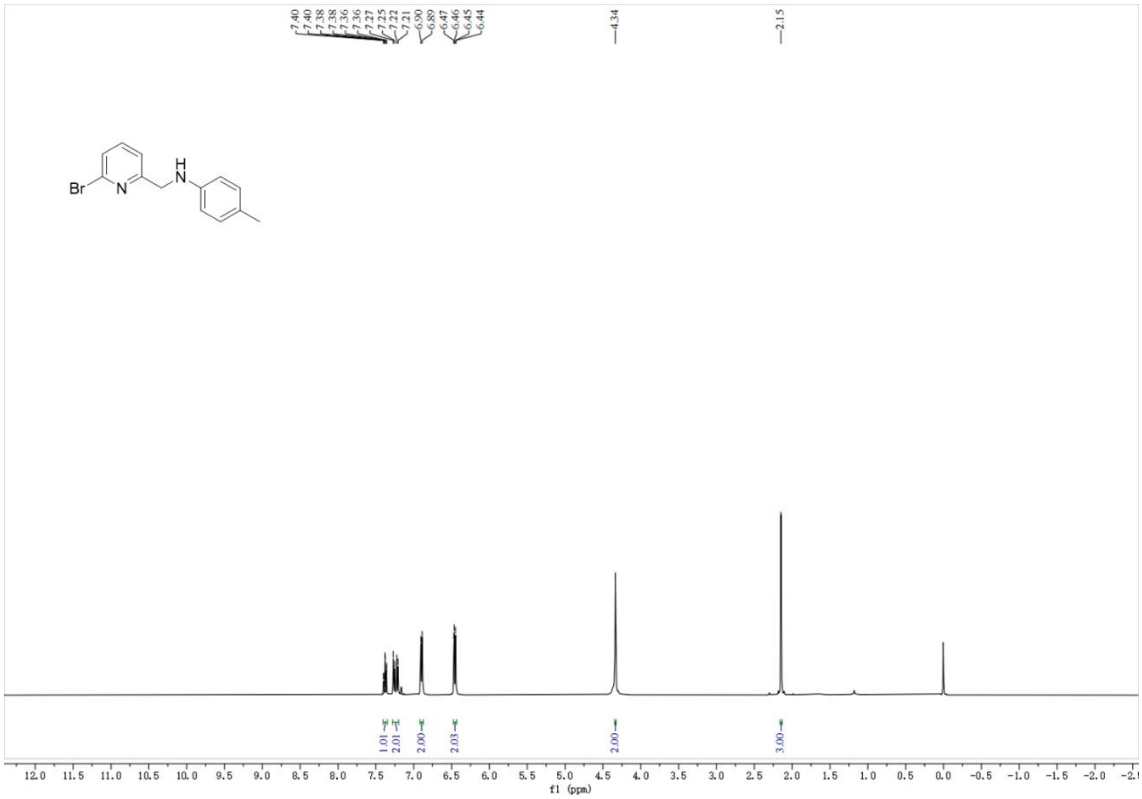

Figure S180. ^{1}H NMR (100 MHz, $CDCl_3$) spectrum of **2z**

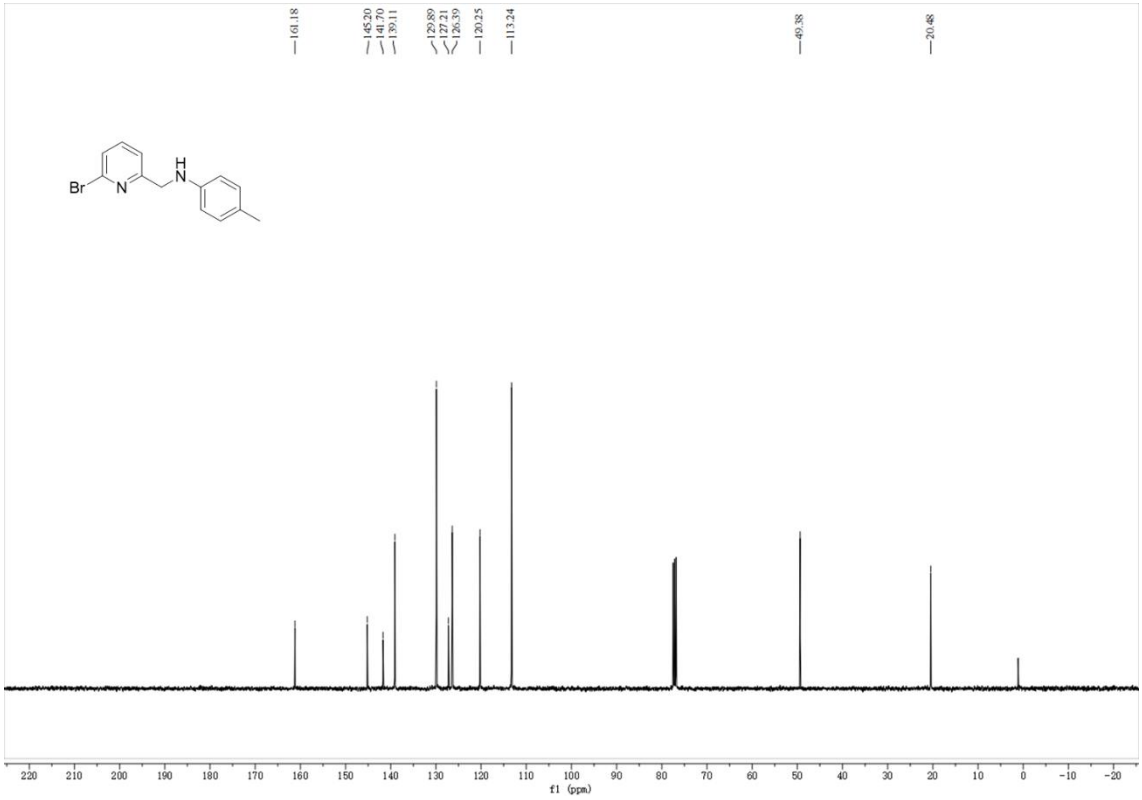

Figure S181. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2z**

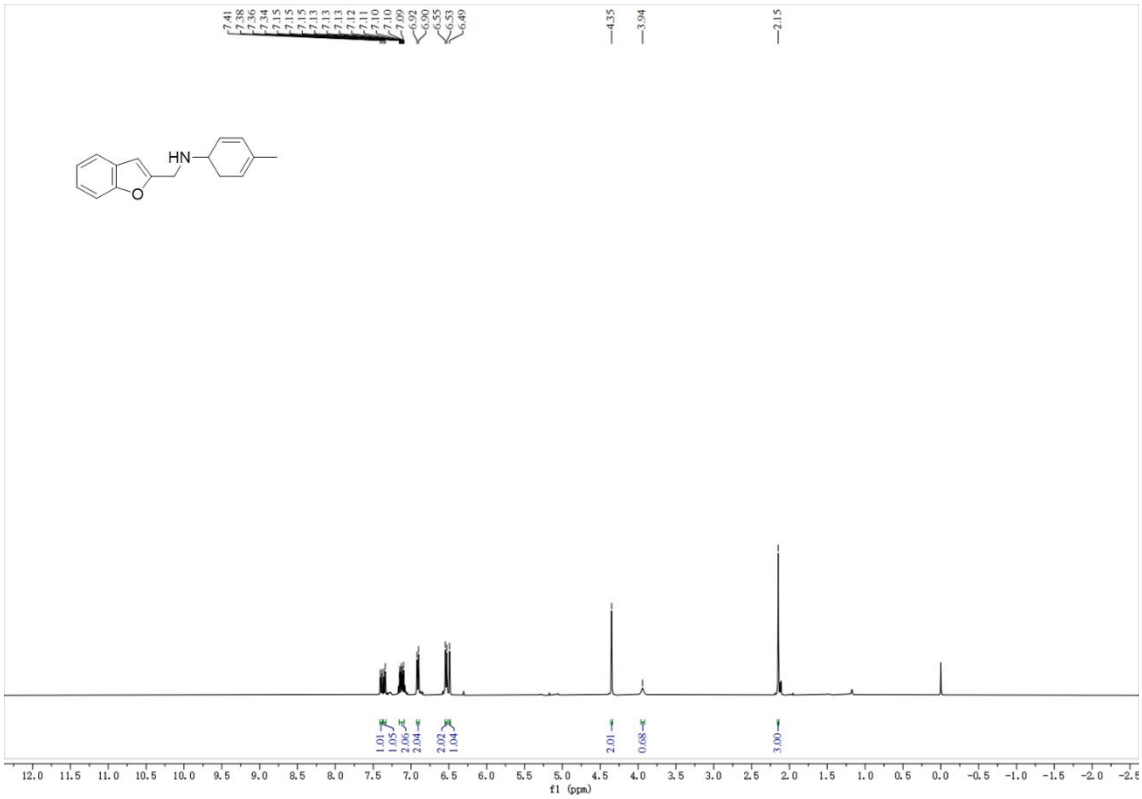

Figure S182. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2aa**

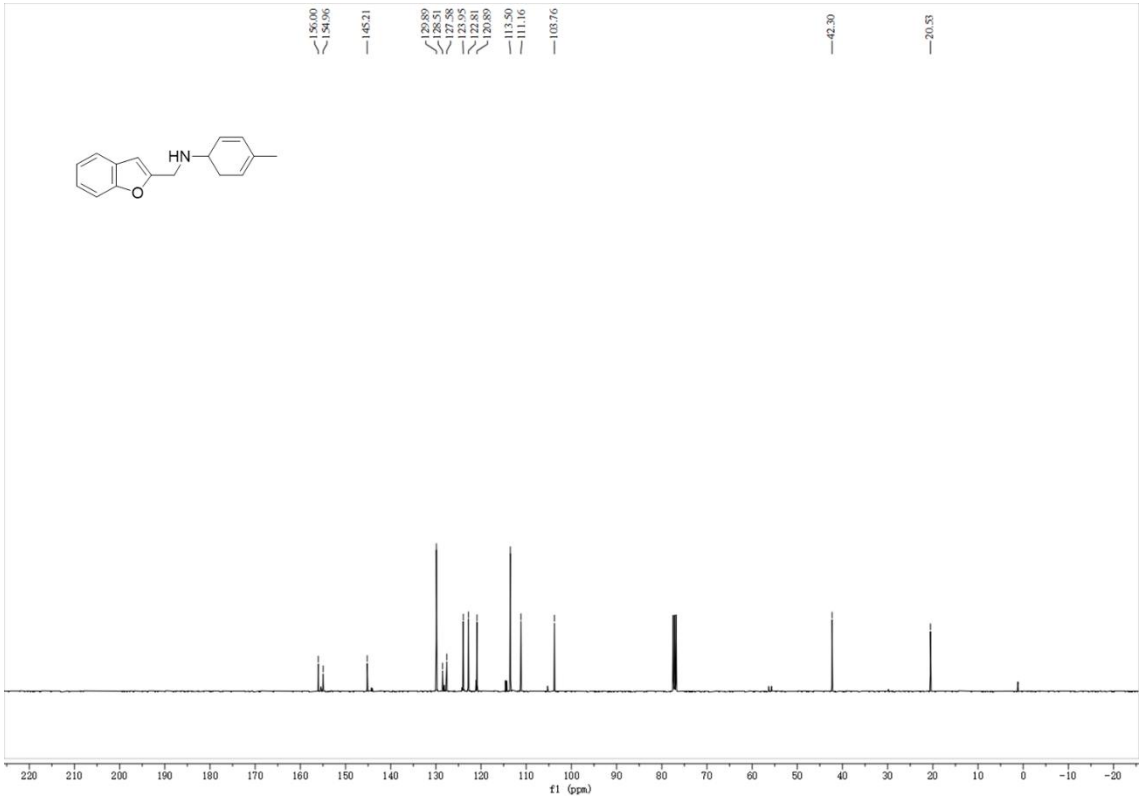

Figure S183. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2aa**

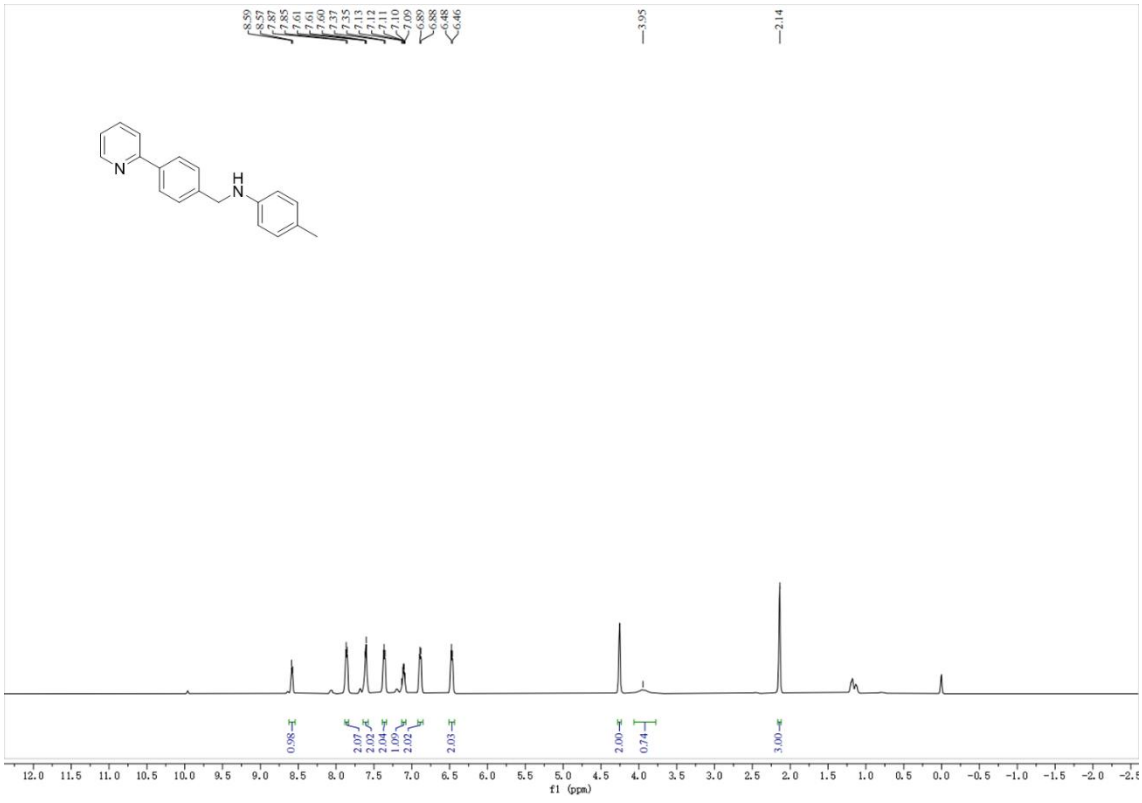

Figure S184. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ab**

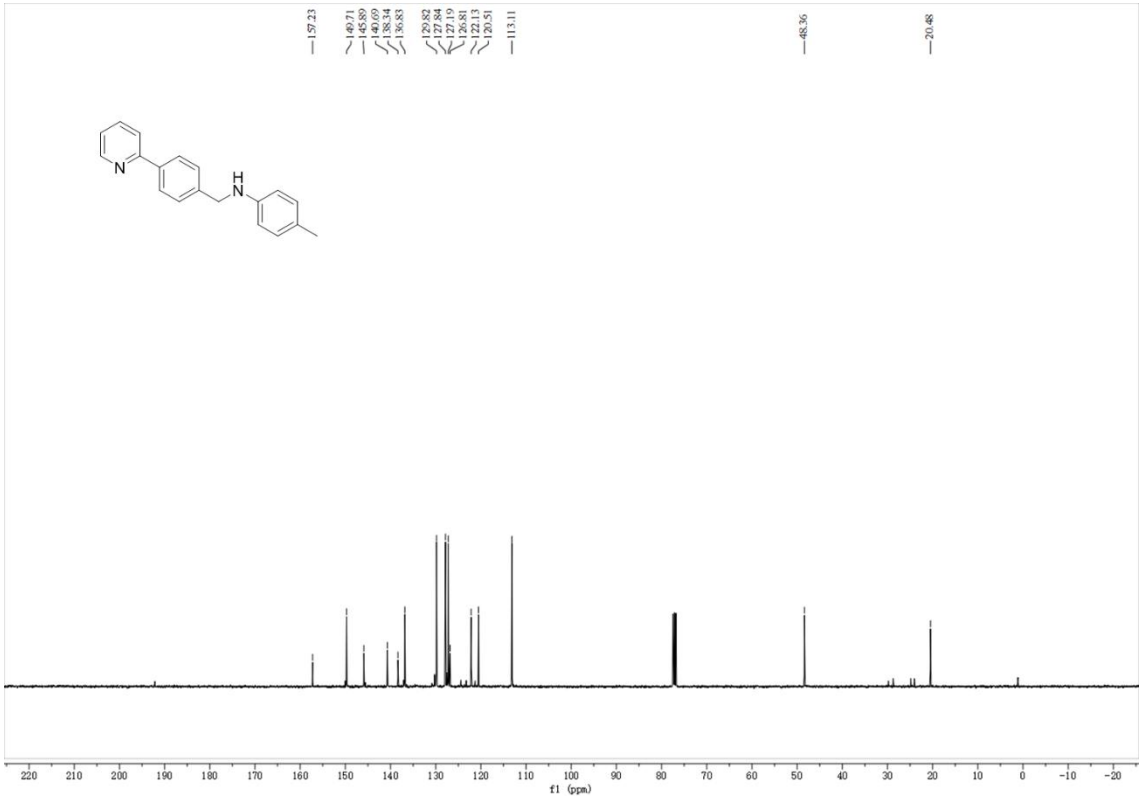

Figure S185. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ab**

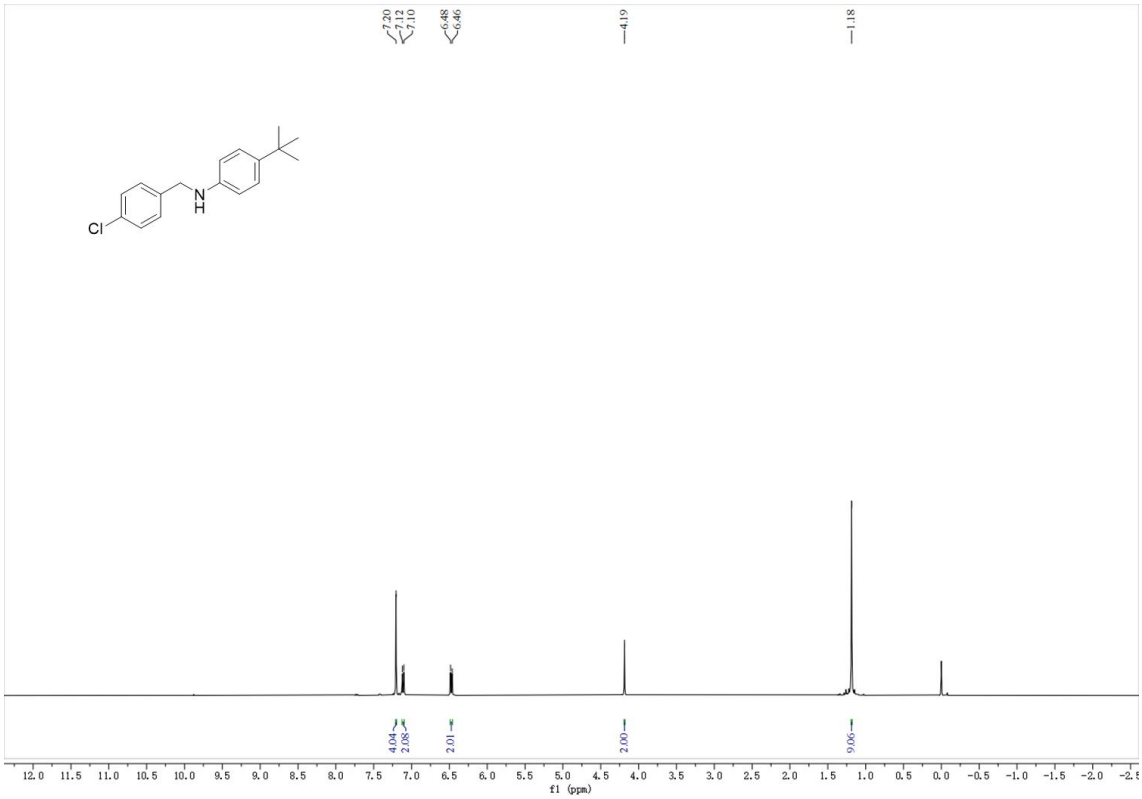

Figure S186. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ac**

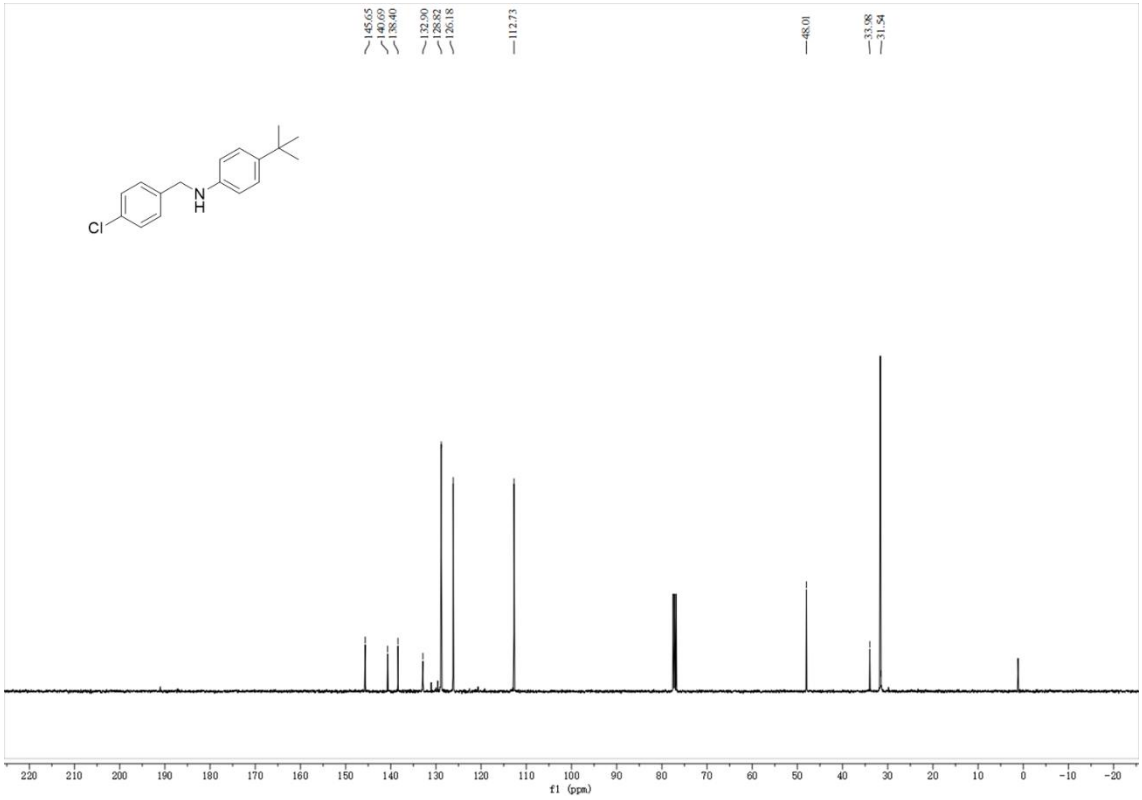

Figure S187. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ac**

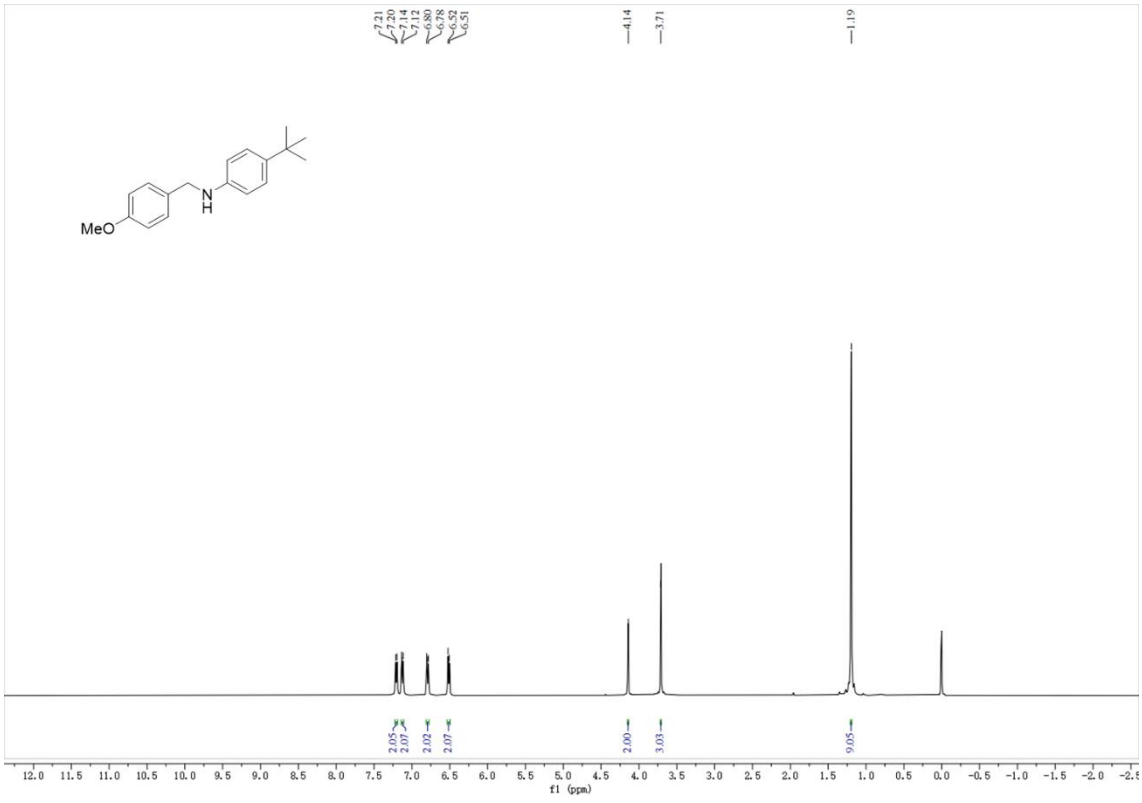

Figure S188. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ad**

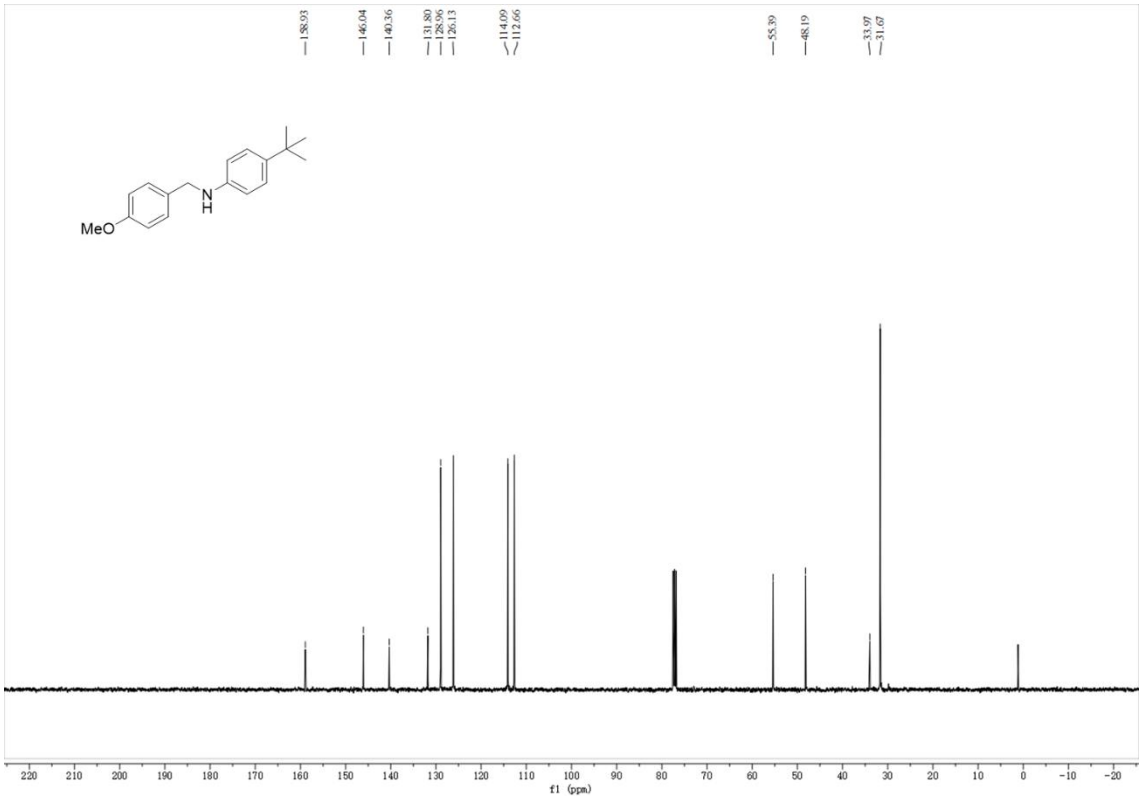

Figure S189. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ad**

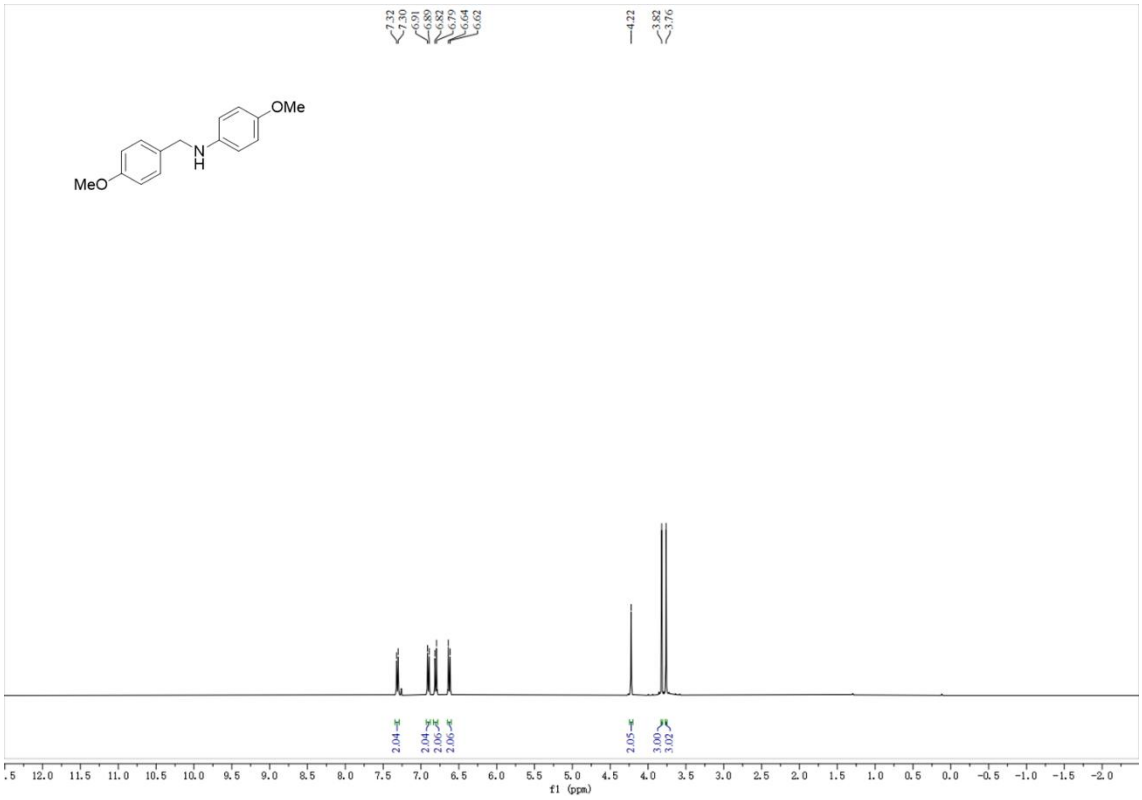

Figure S190. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ae**

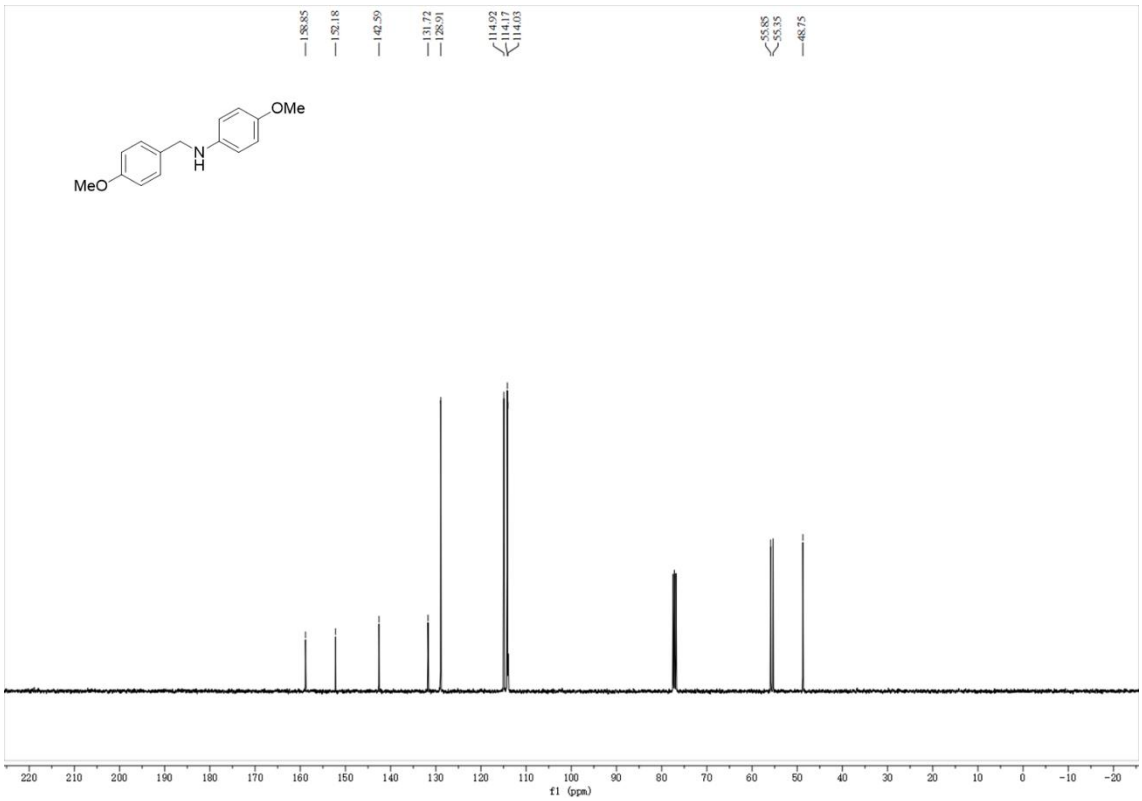

Figure S191. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ae**

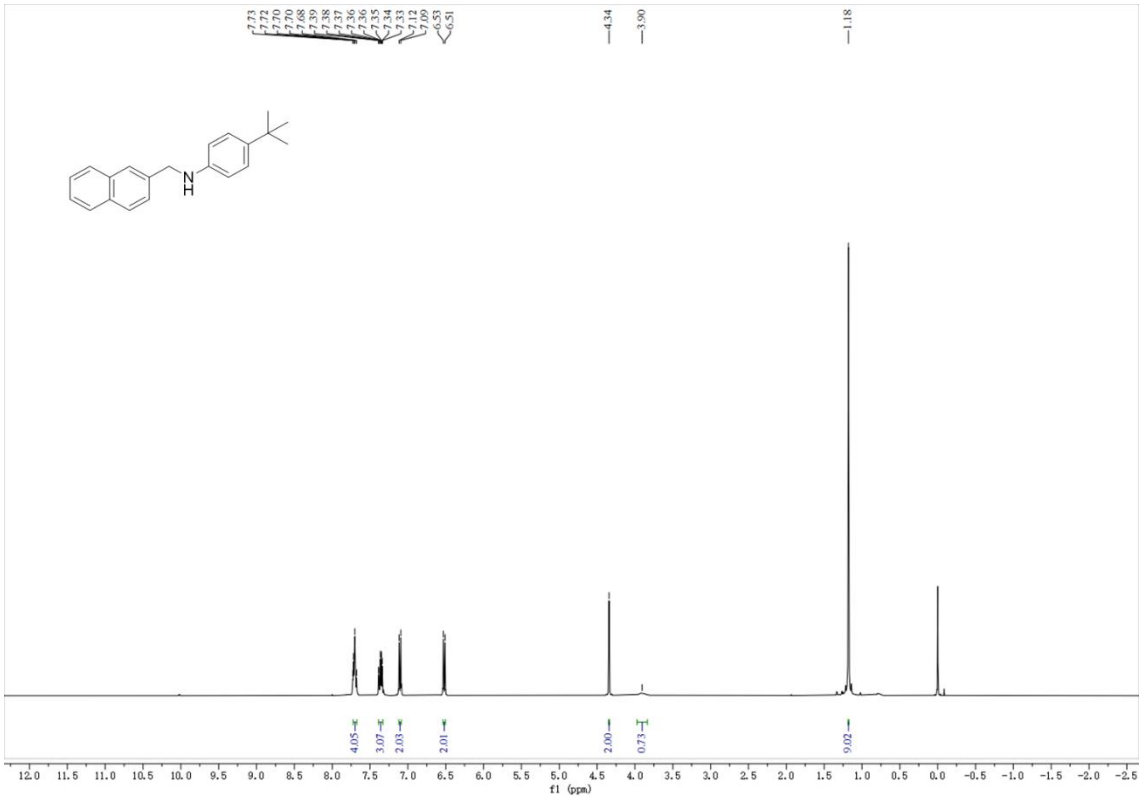

Figure S192. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2af**

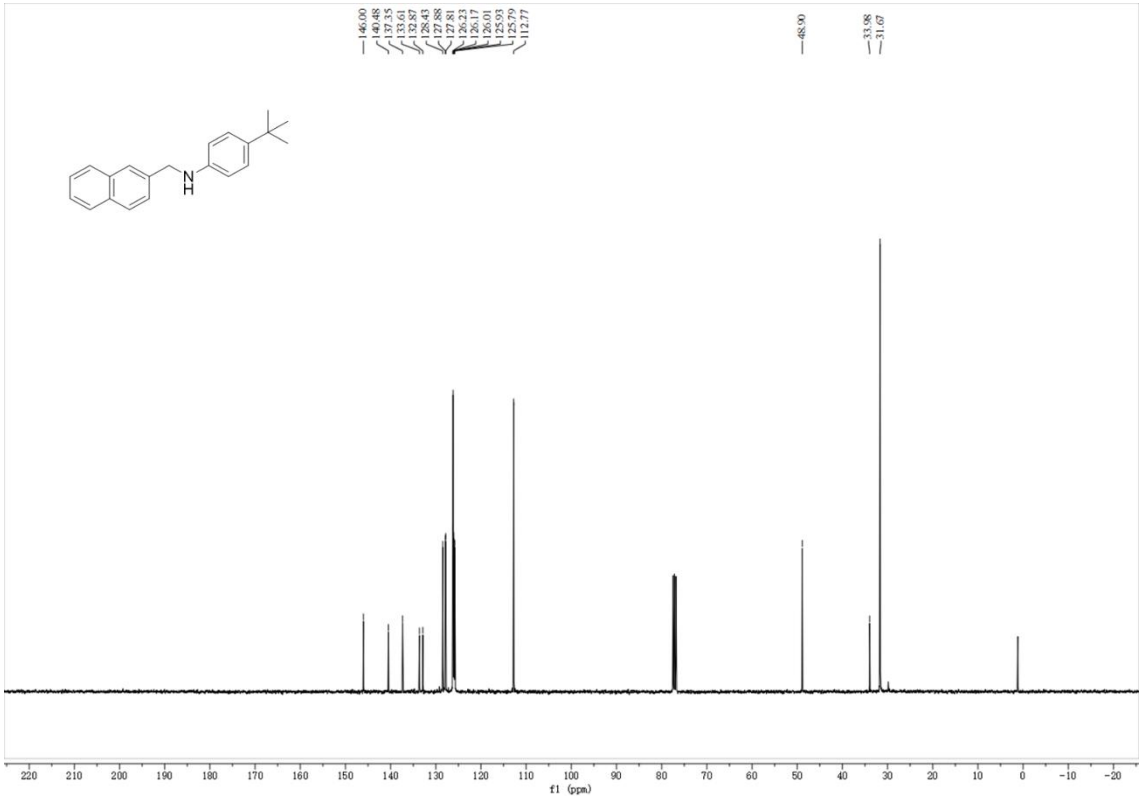

Figure S193. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2af**

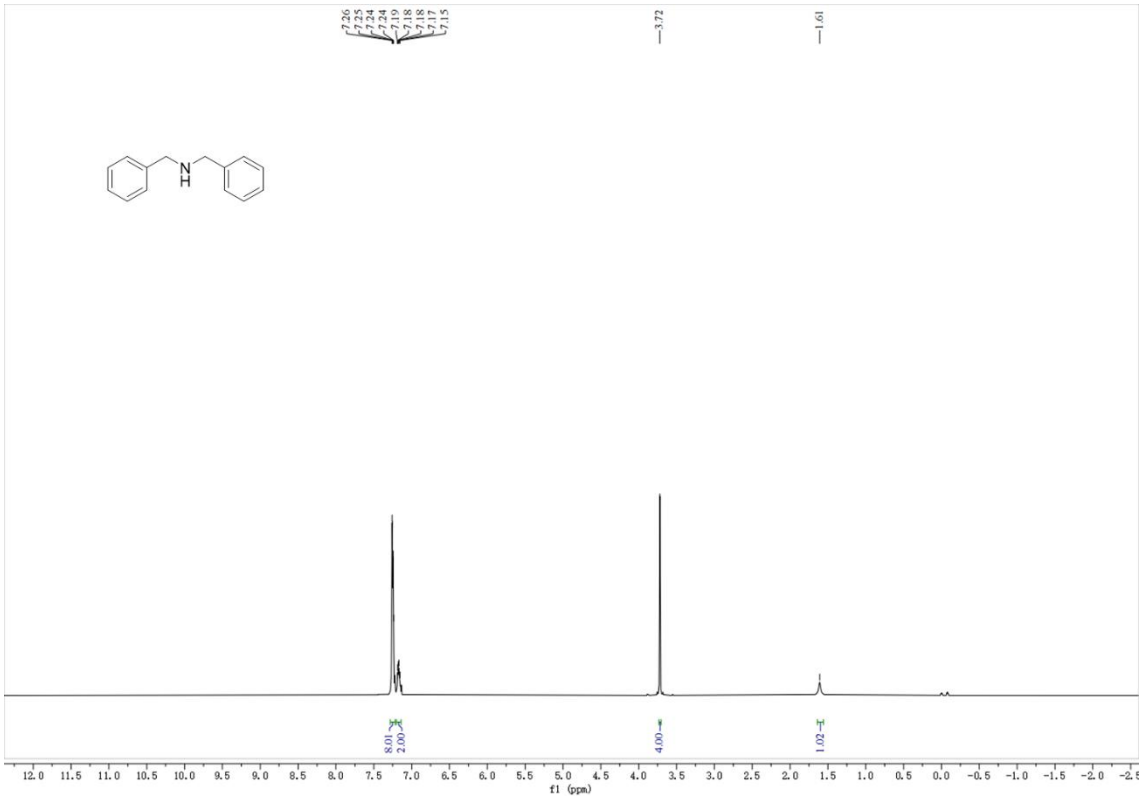

Figure S194. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ag**

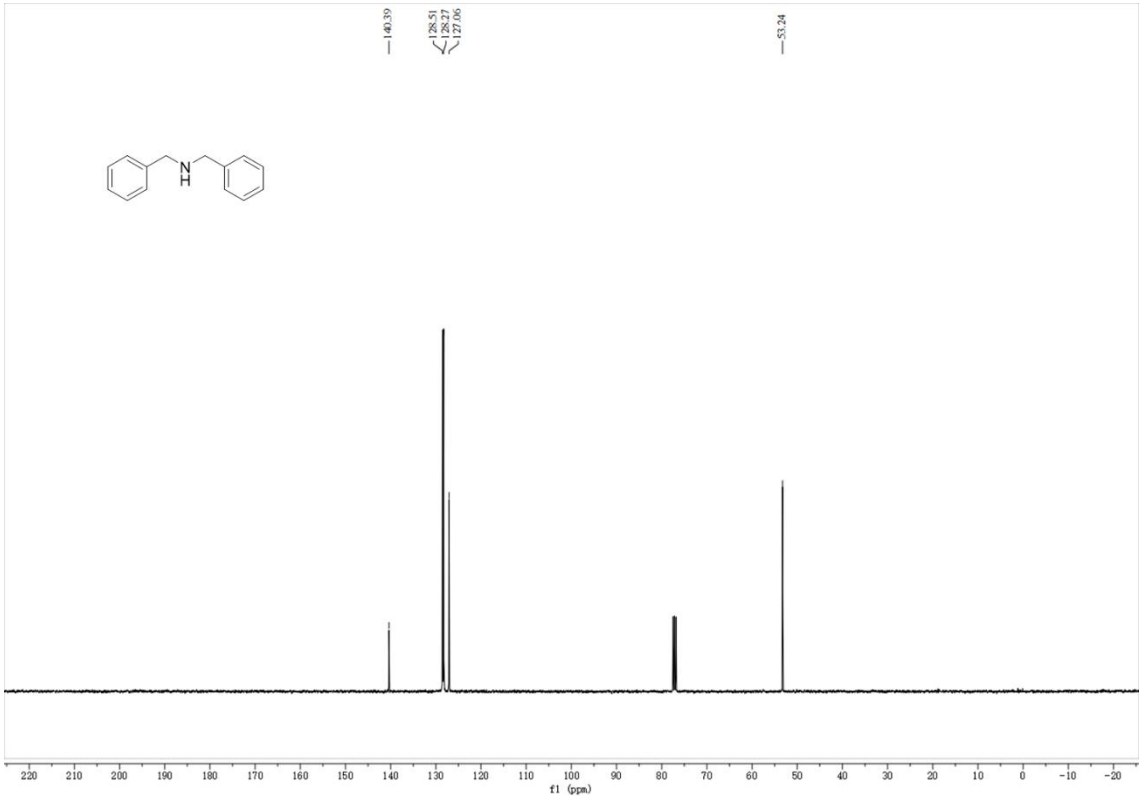

Figure S195. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ag**

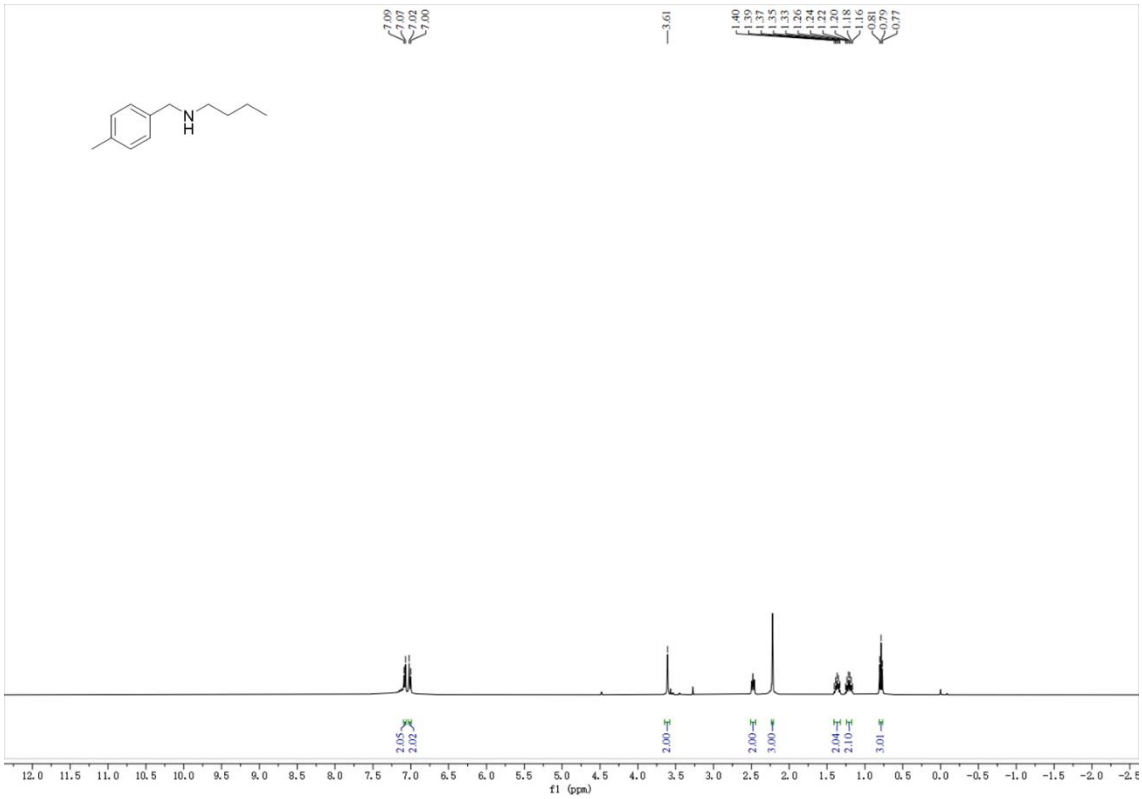

Figure S196. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ah**

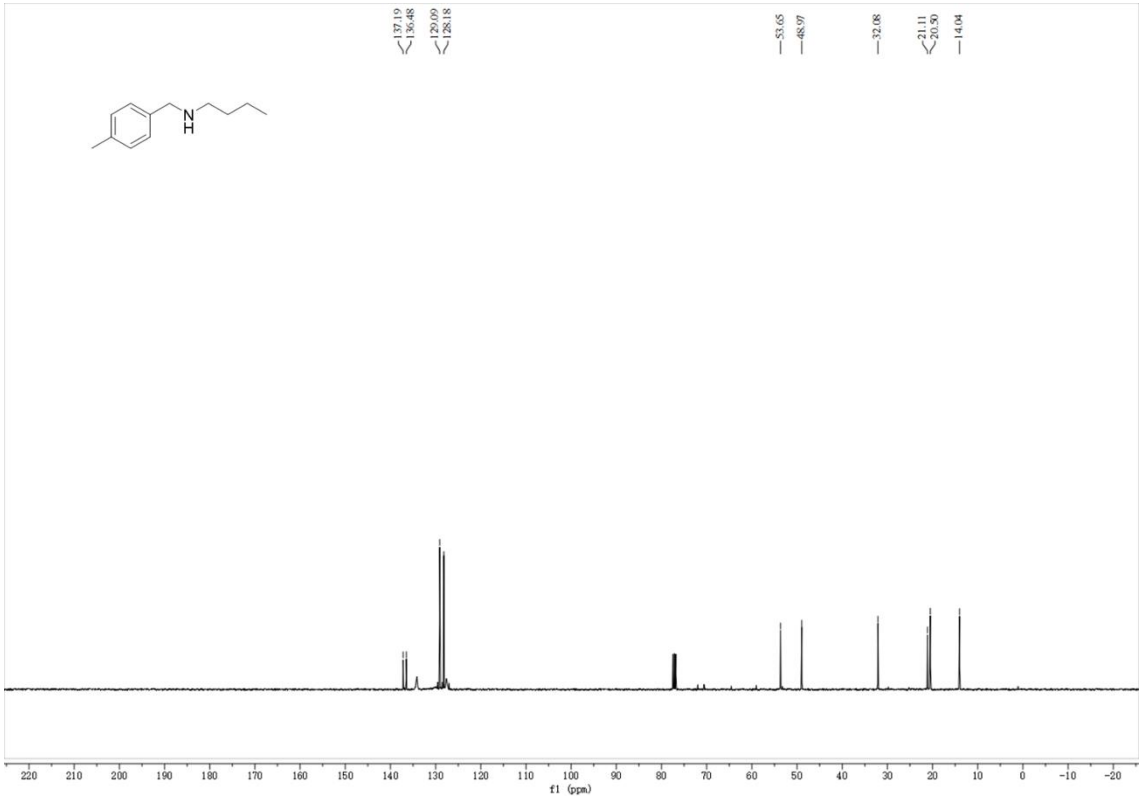

Figure S197. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ah**

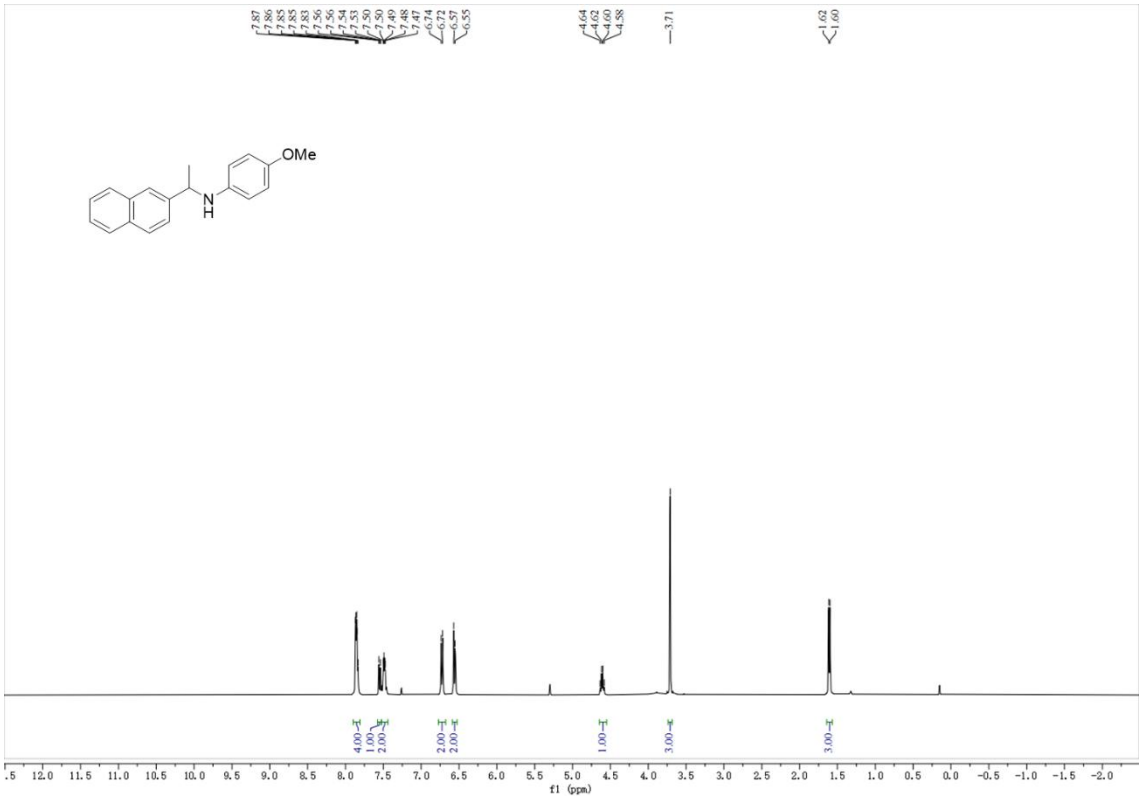

Figure S198. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ai**

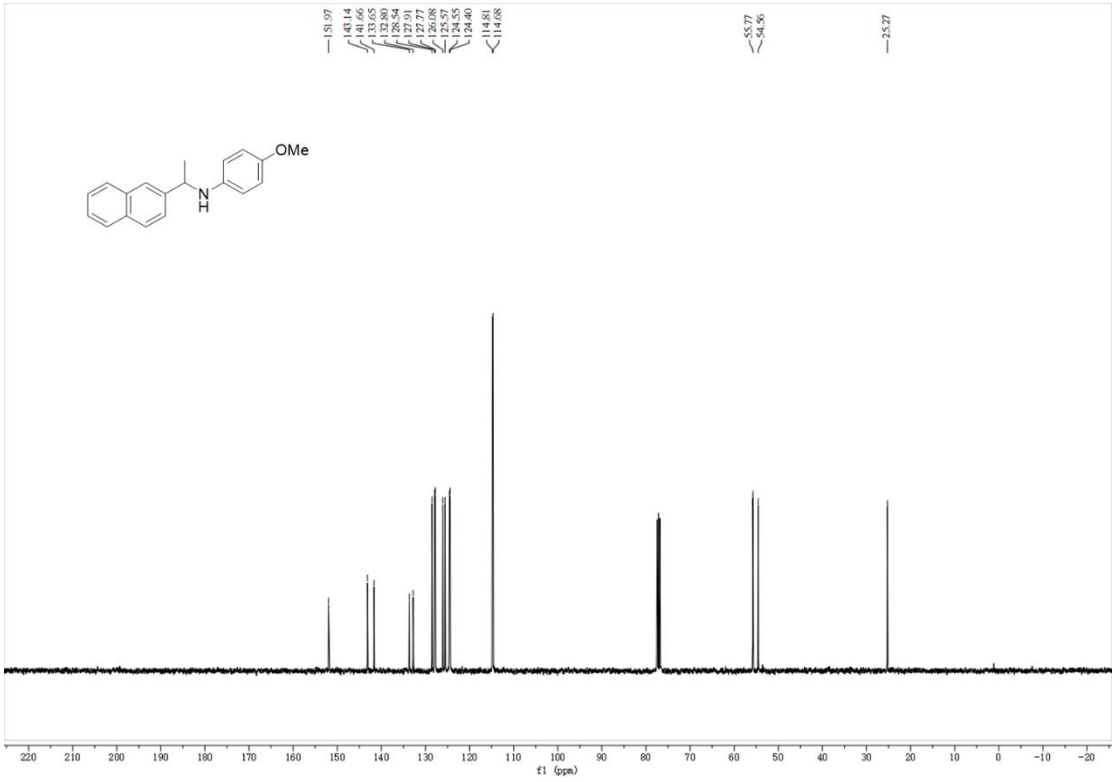

Figure S199. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ai**

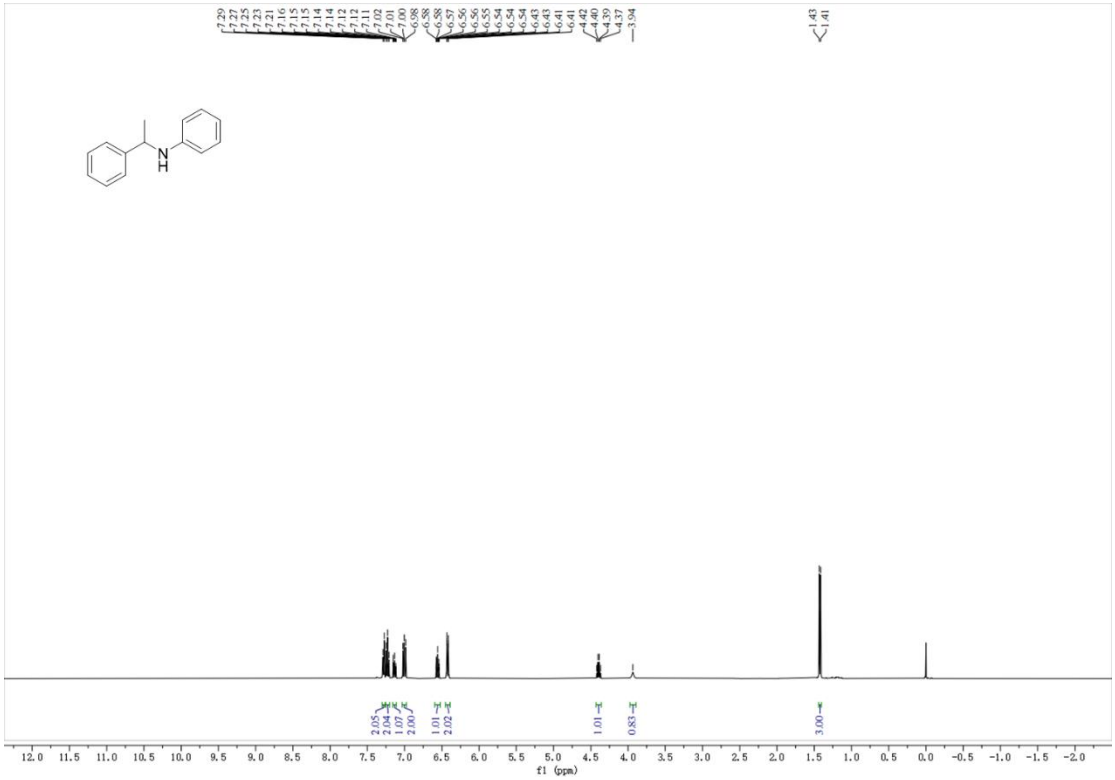

Figure S200. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2aj**

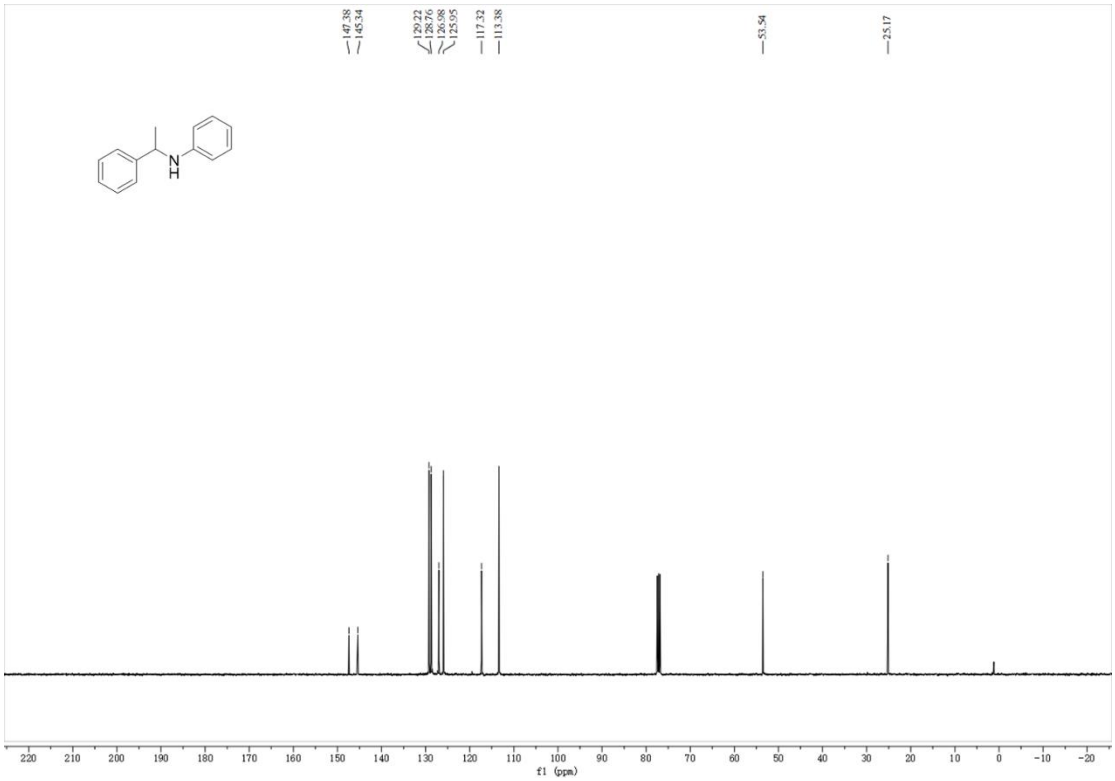

Figure S201. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2aj**

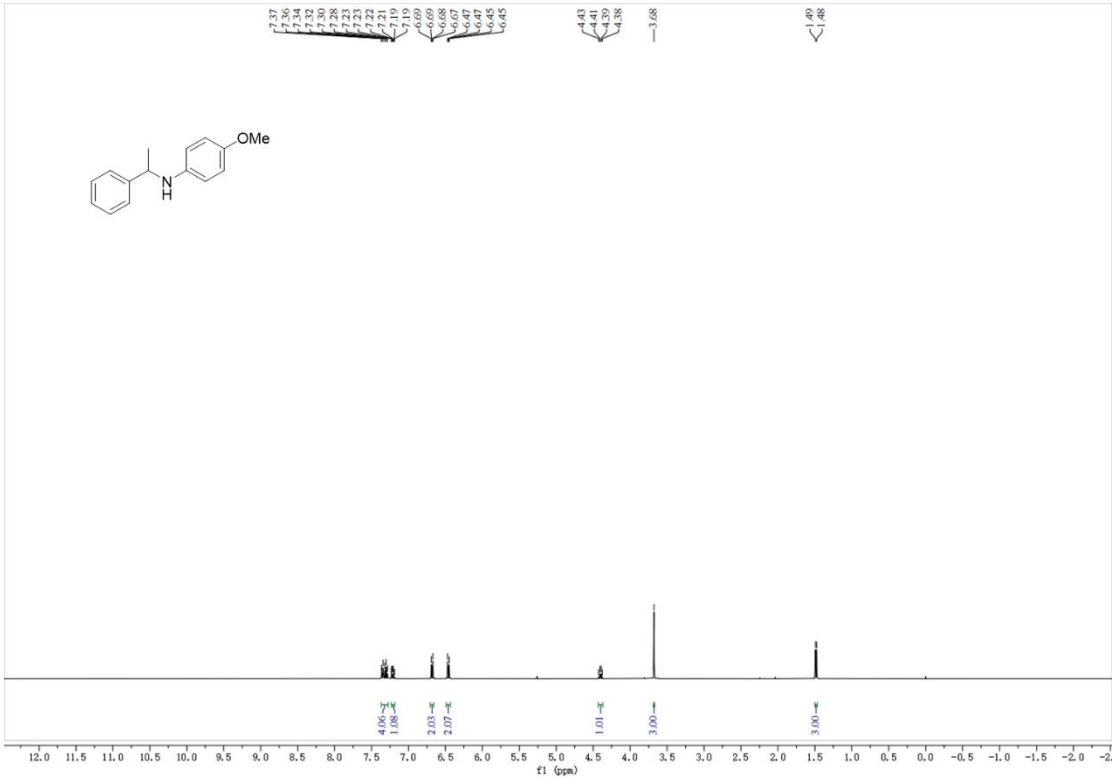

Figure S202. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ak**

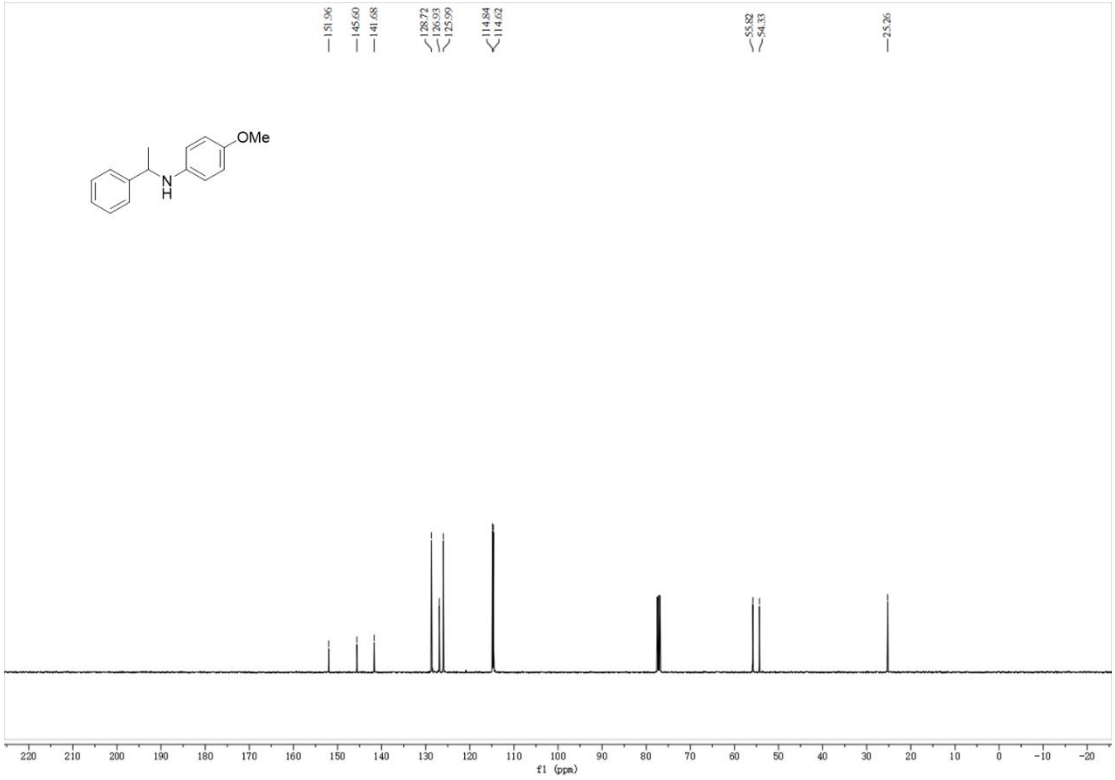

Figure S203. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ak**

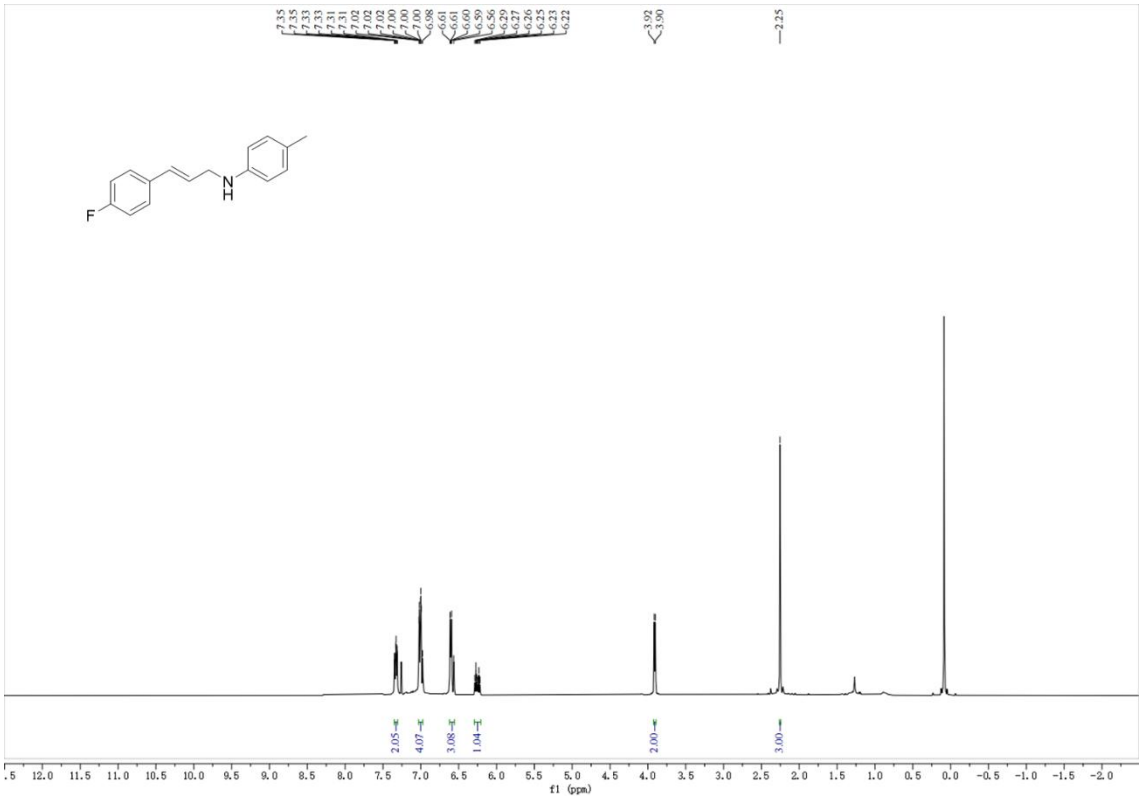

Figure S204. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2ai**

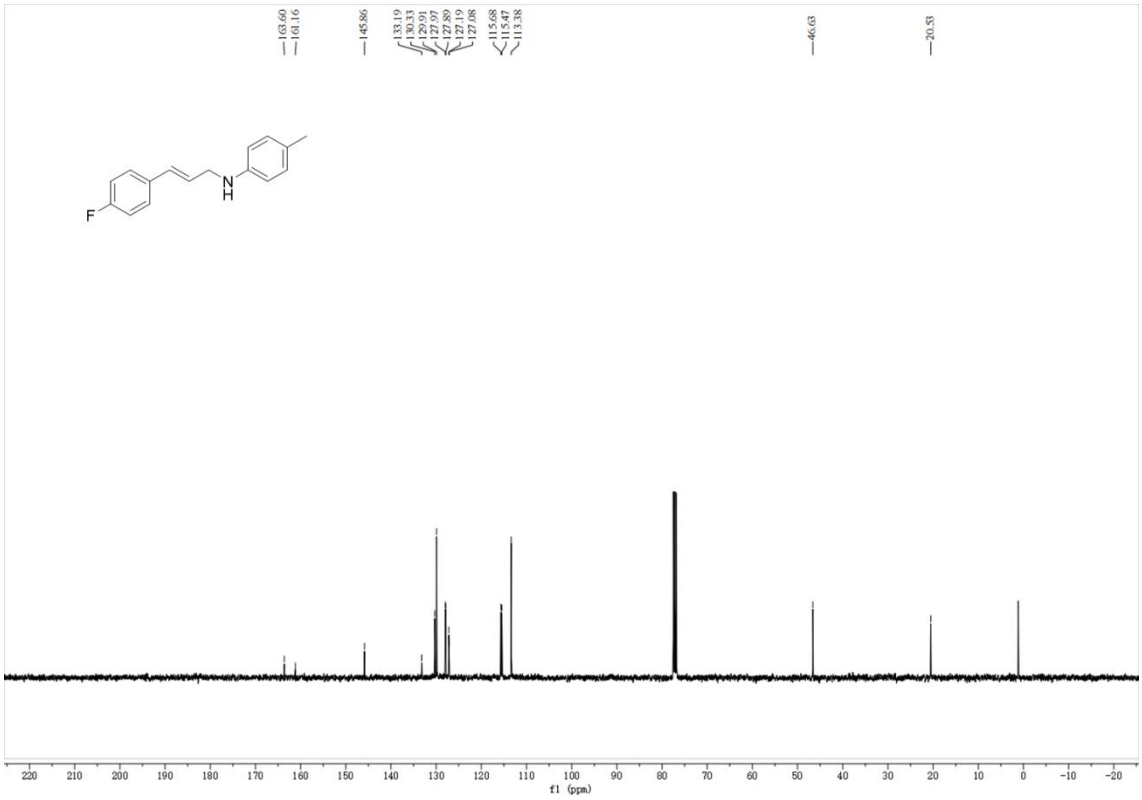

Figure S205. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2ai**

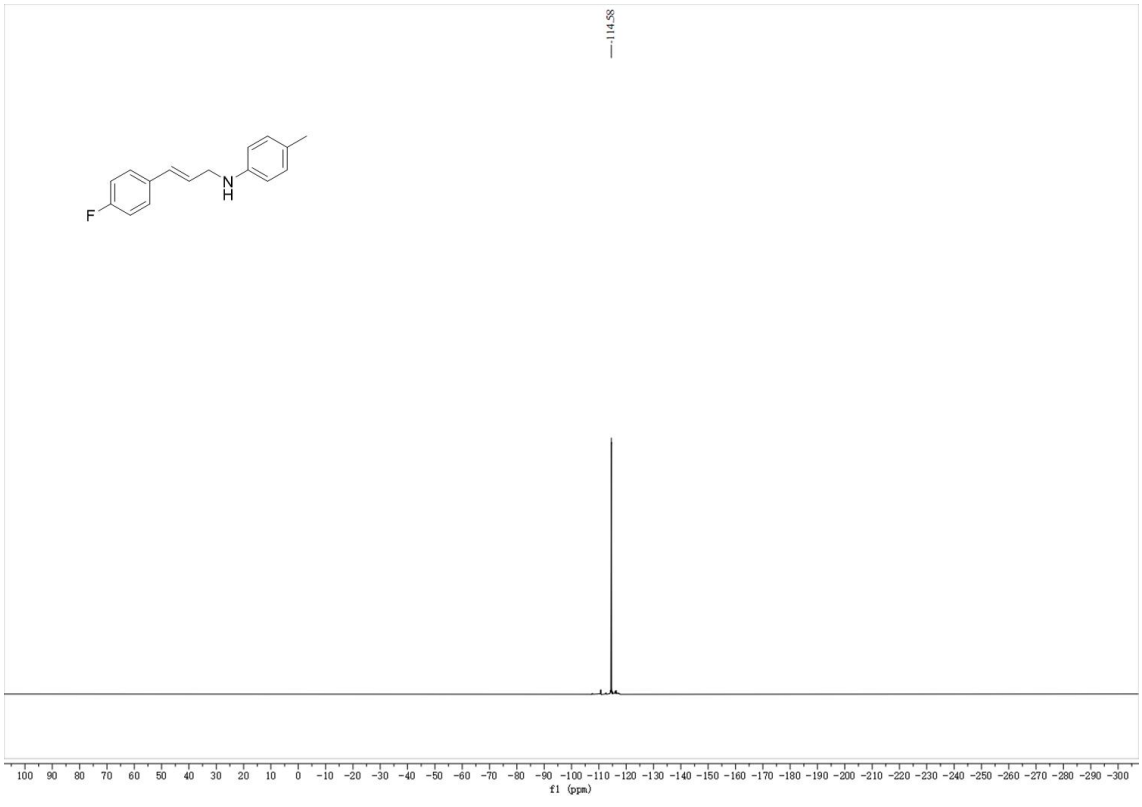

Figure S206. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2ai**

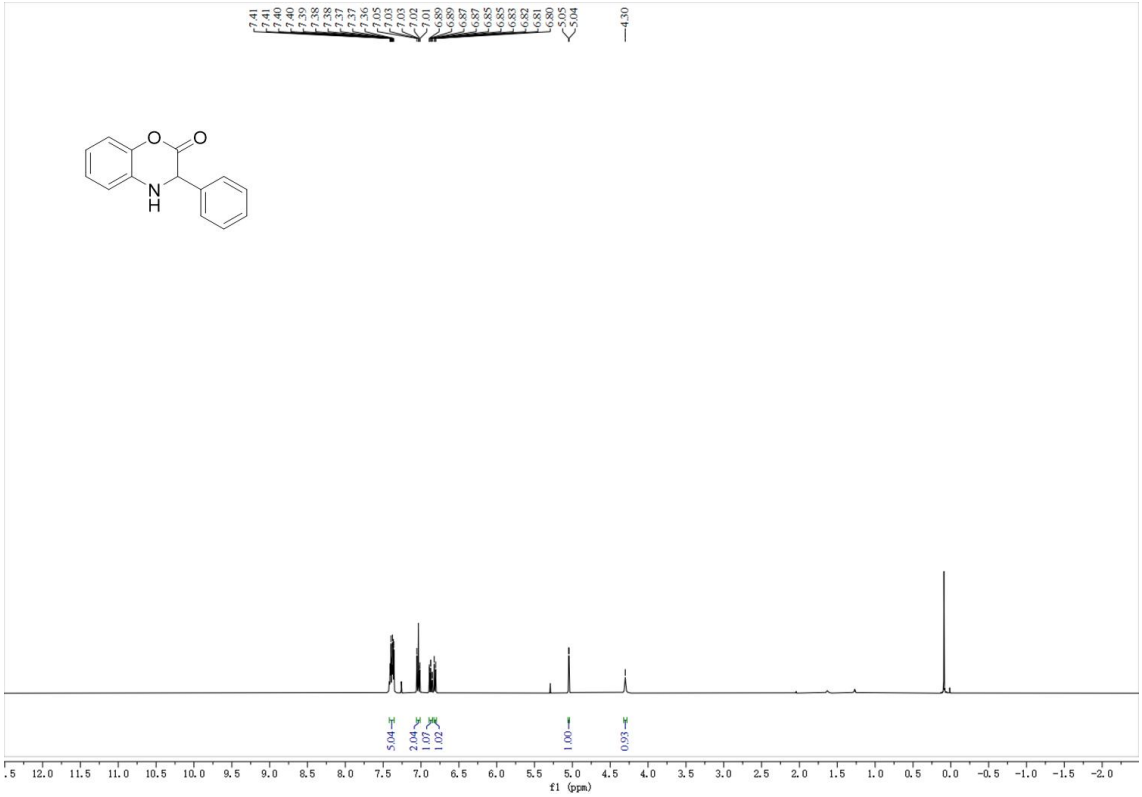

Figure S207. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2am**

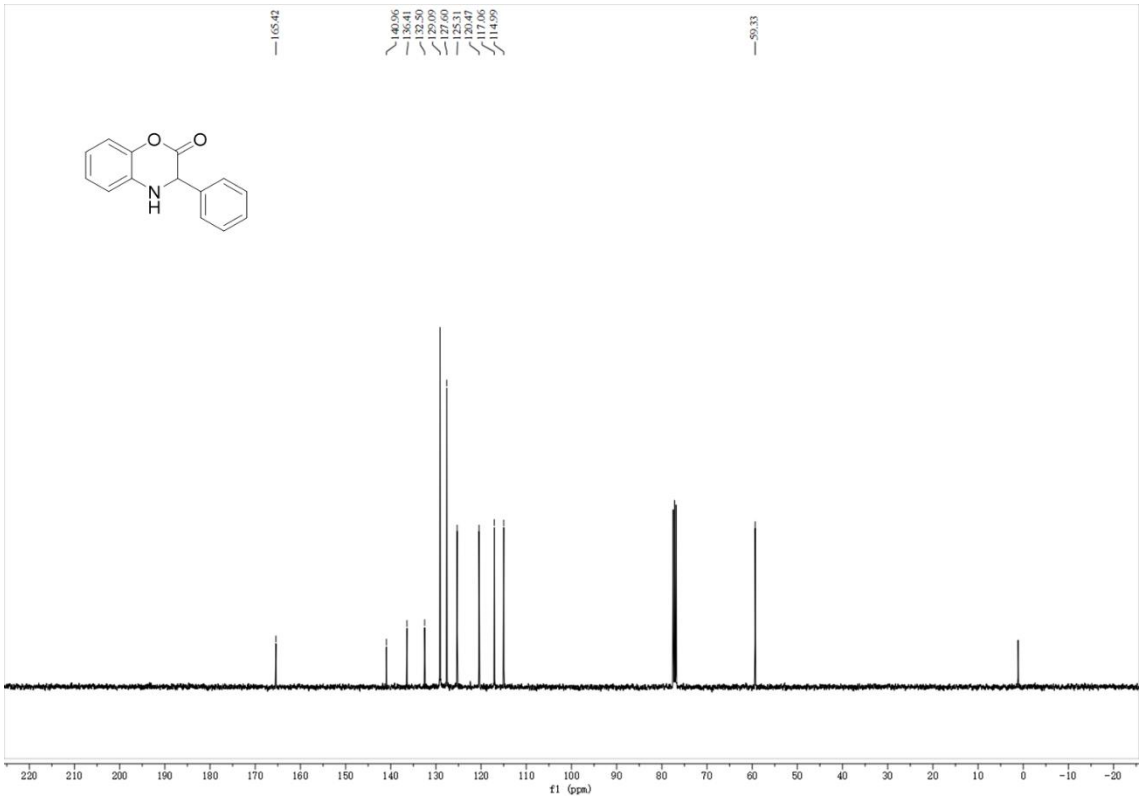

Figure S208. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2am**

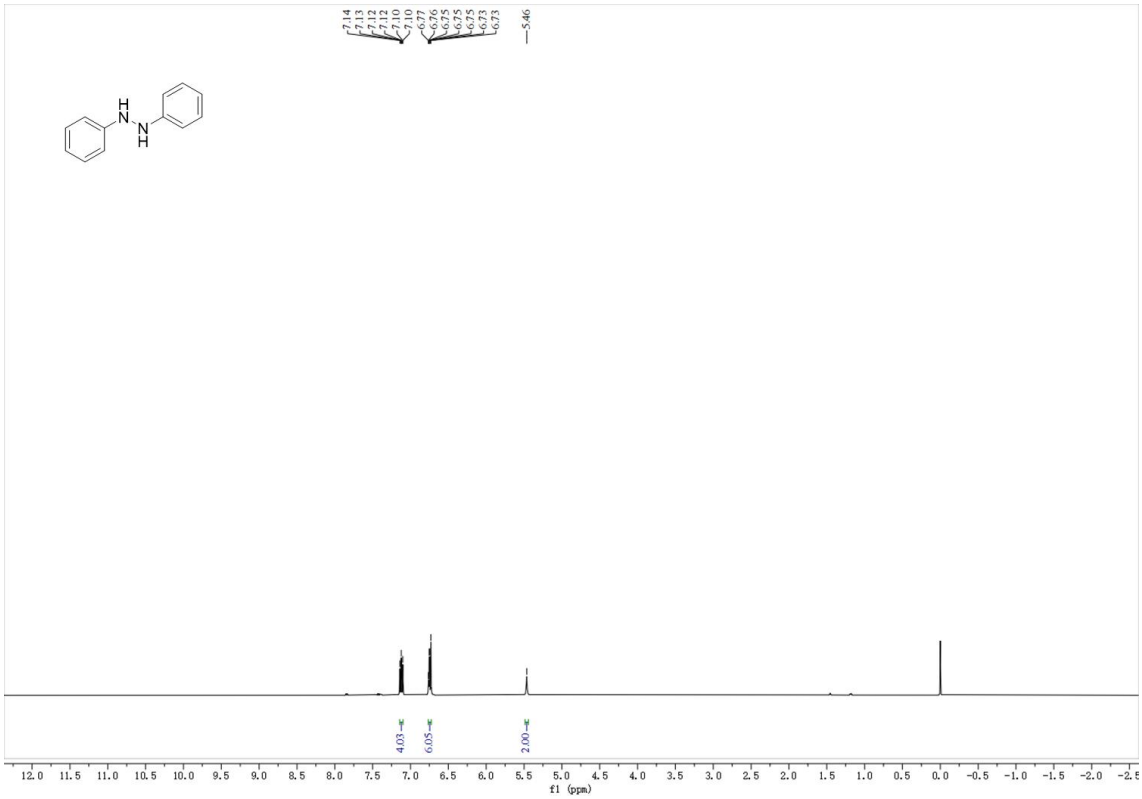

Figure S209. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**

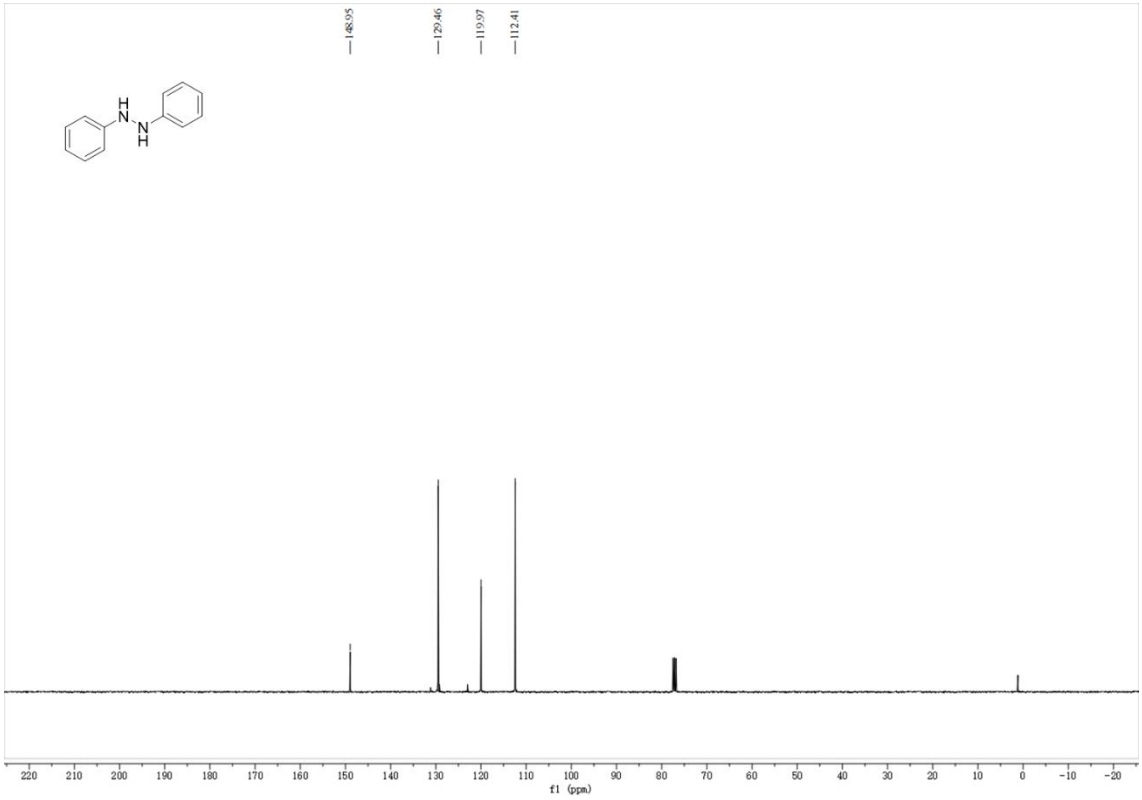

Figure S210. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**

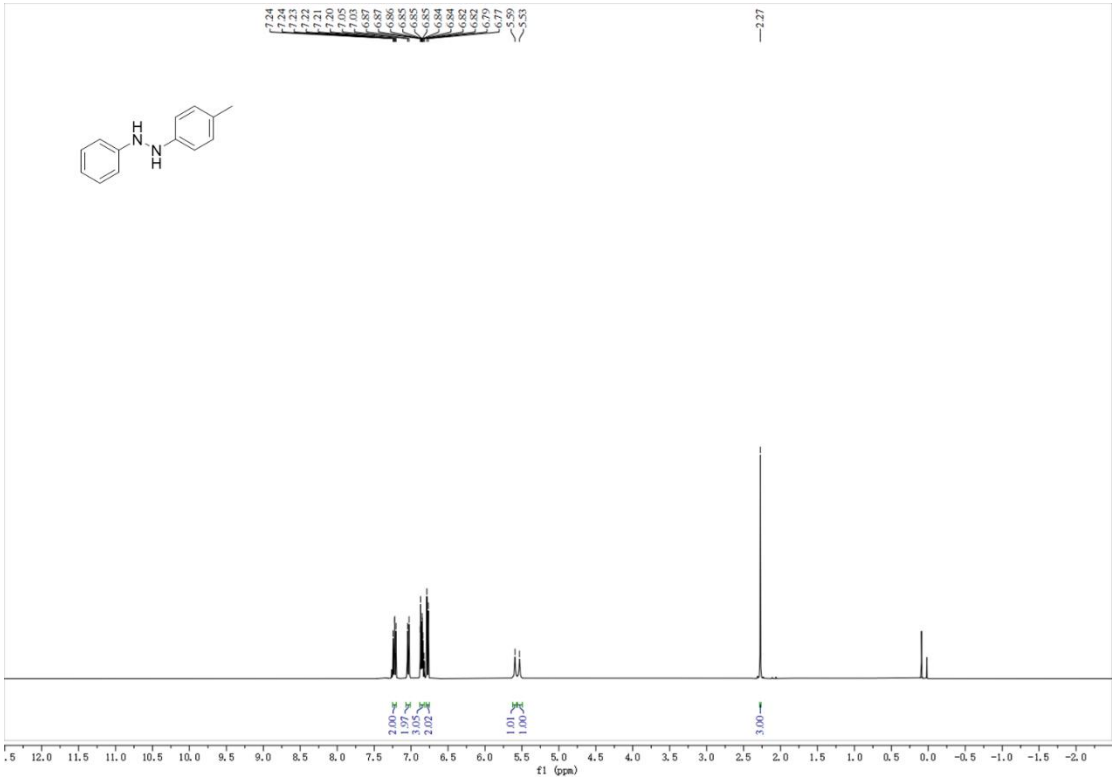

Figure S211. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**

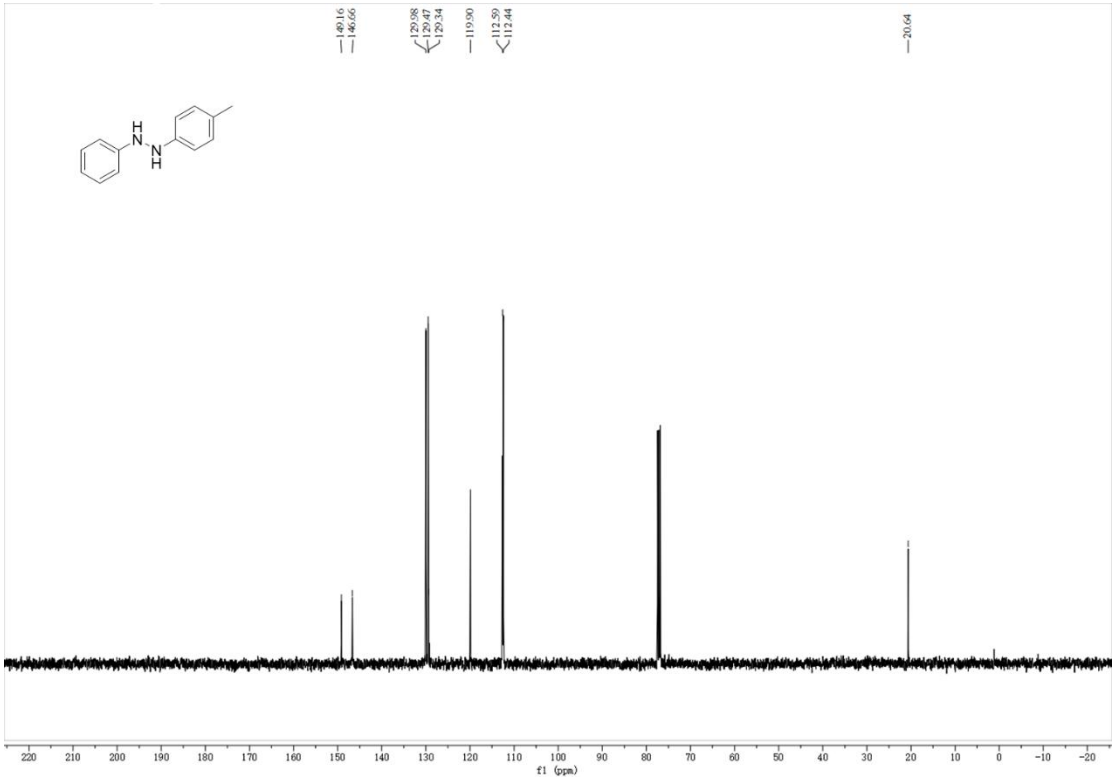

Figure S212. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**

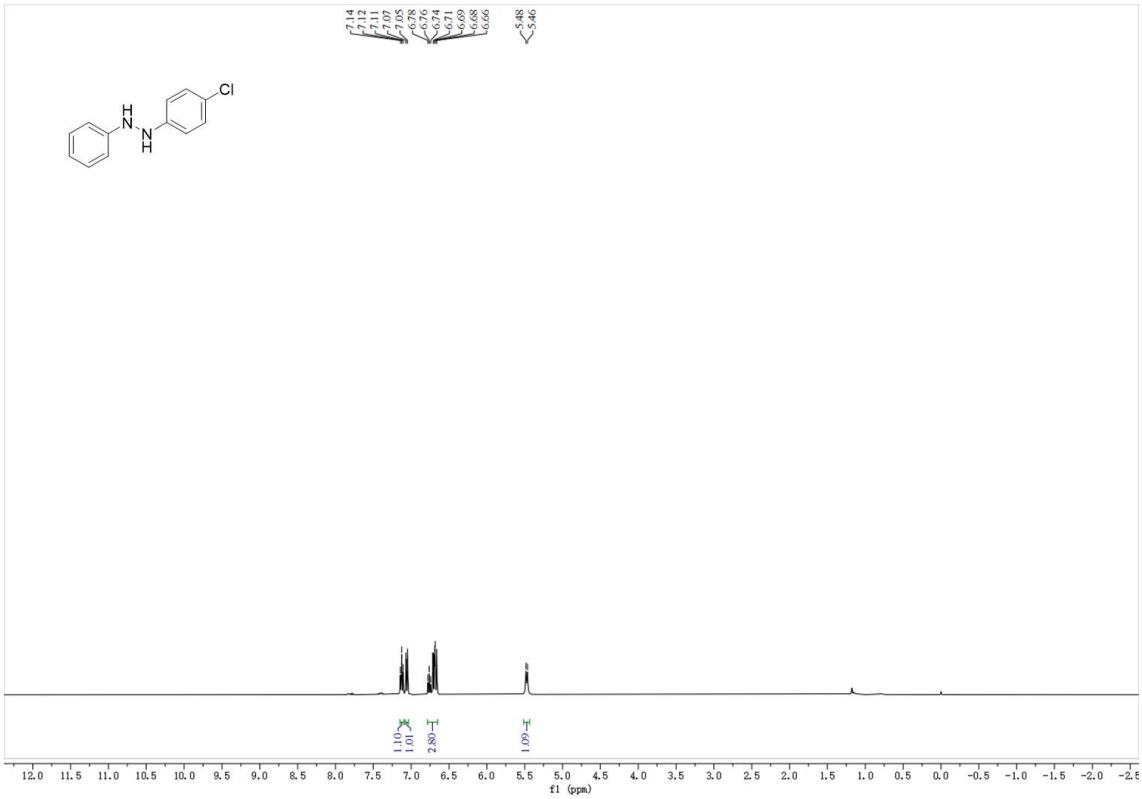

Figure S213. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

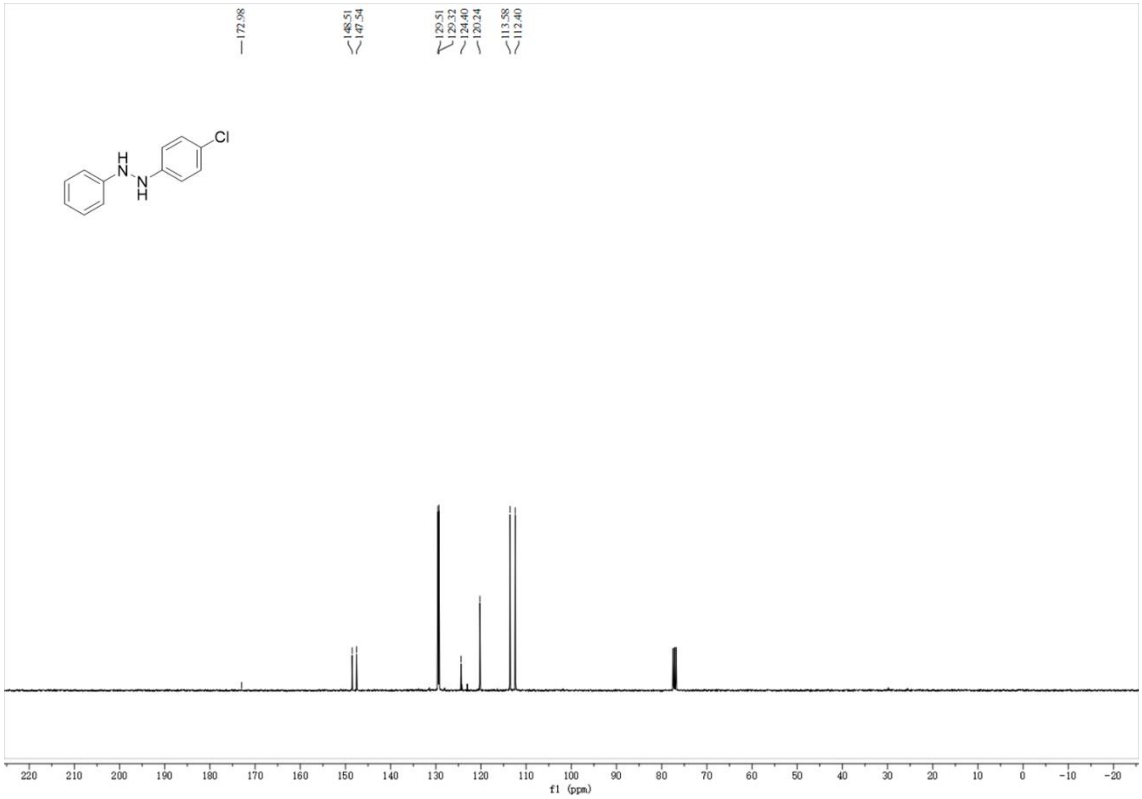

Figure S214. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4c**

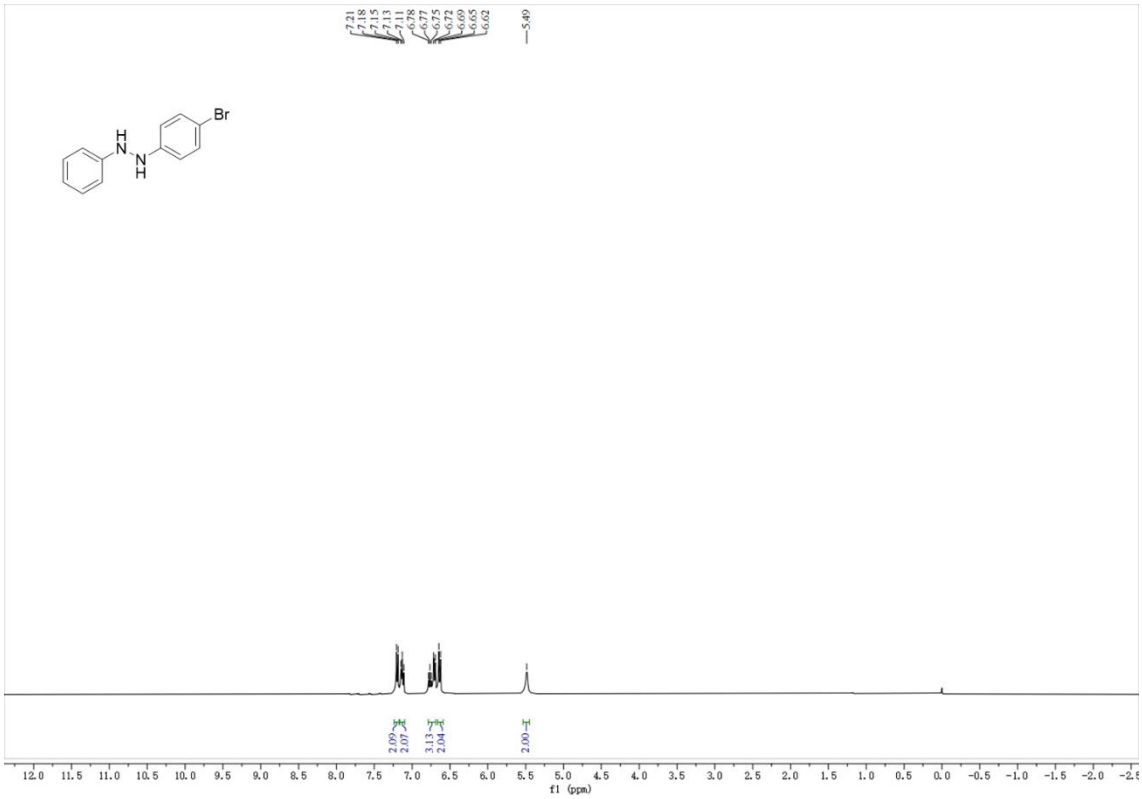

Figure S215. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**

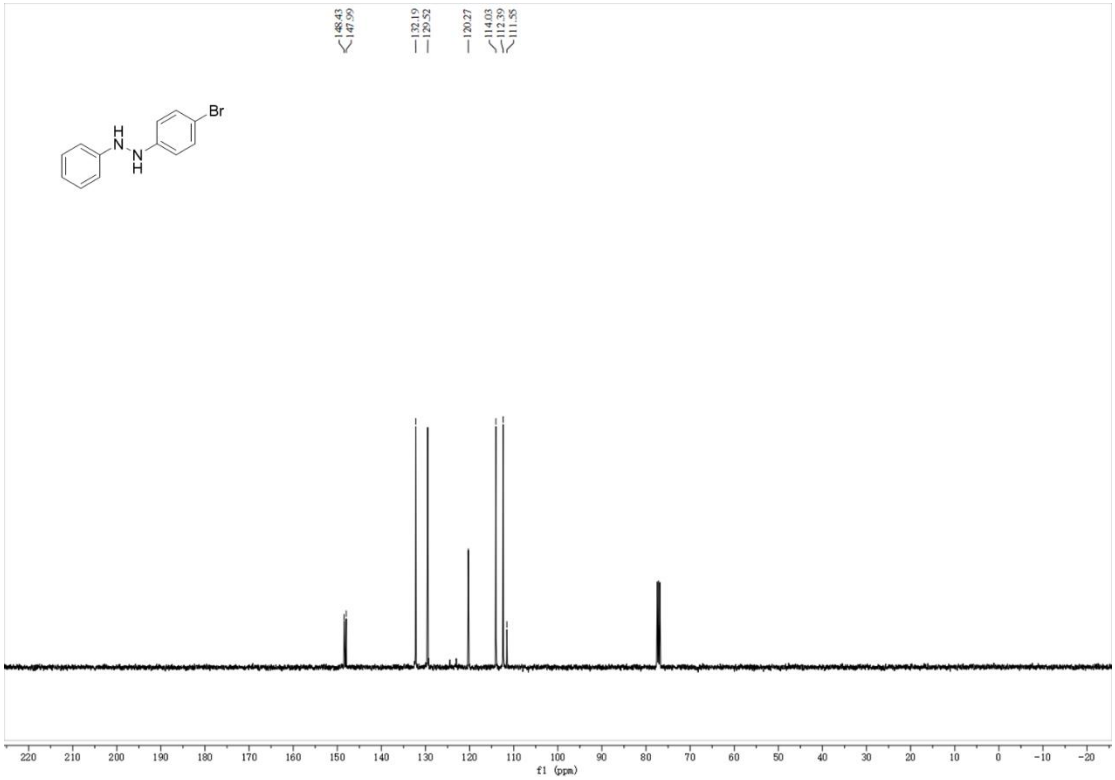

Figure S216. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4d**

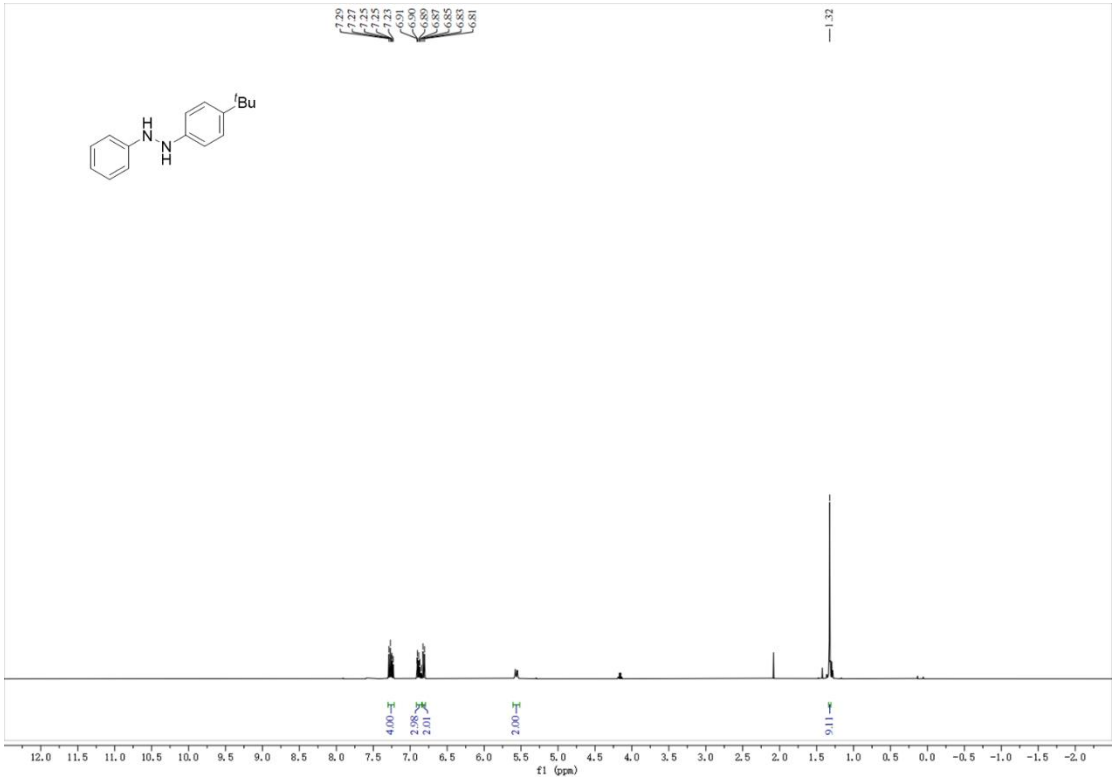

Figure S217. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**

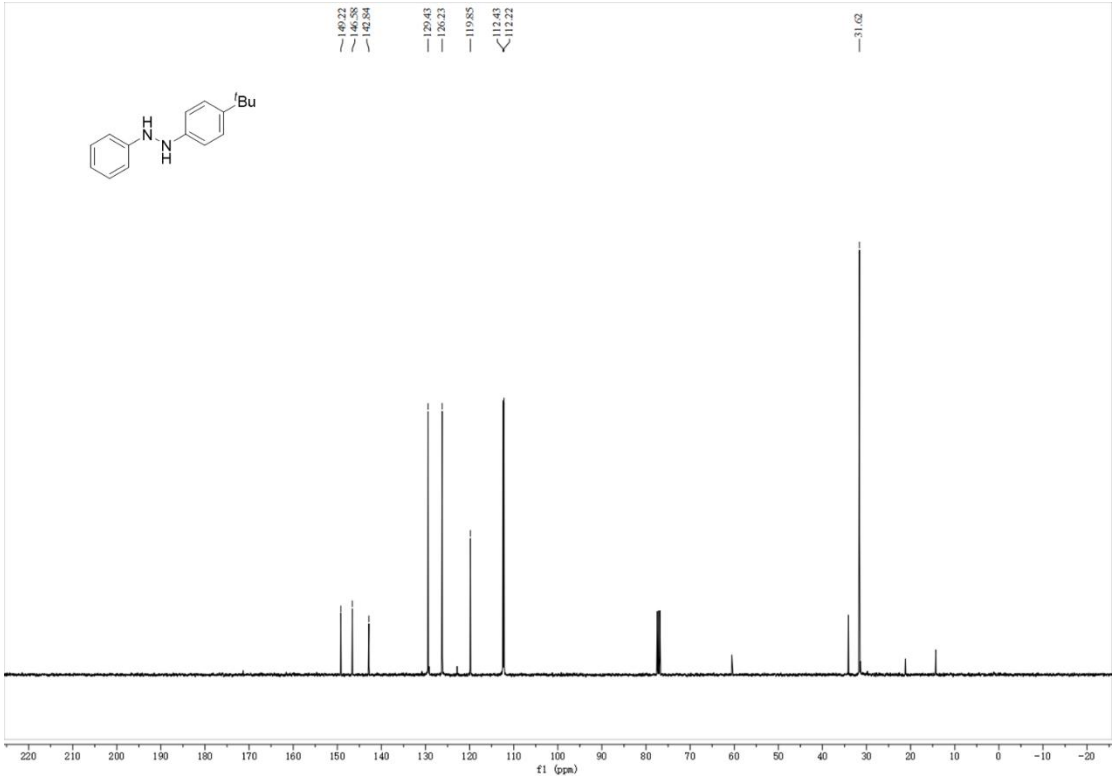

Figure S218. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4e**

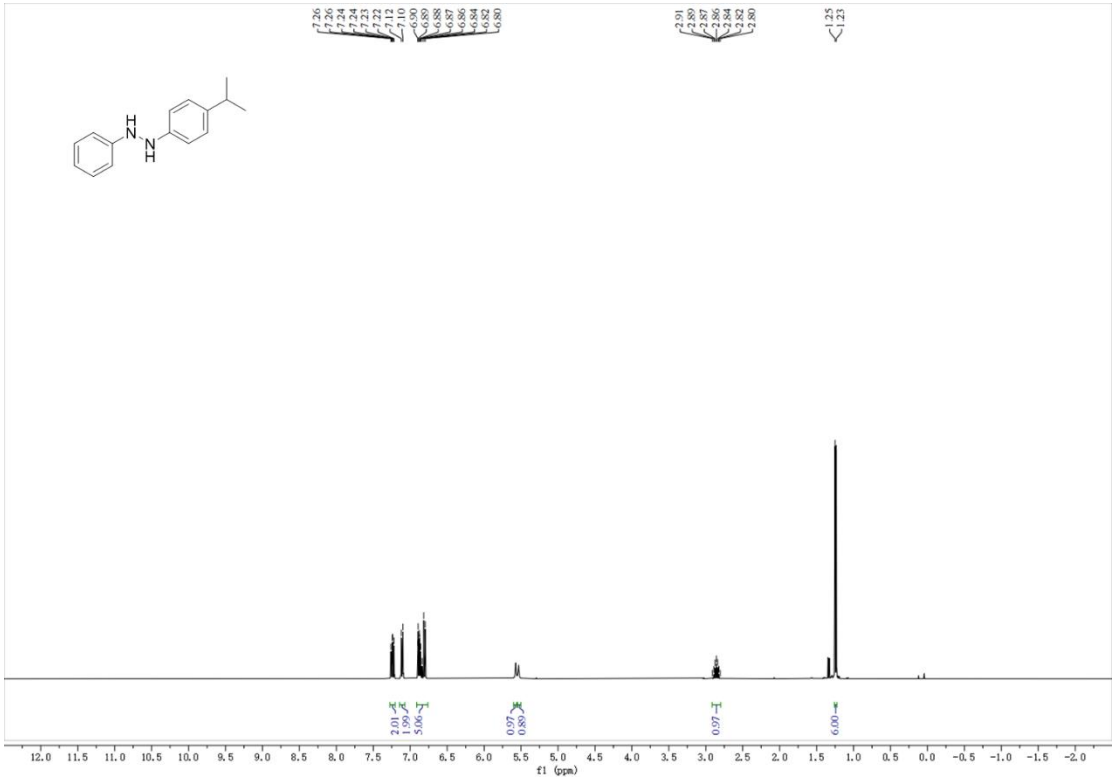

Figure S219. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**

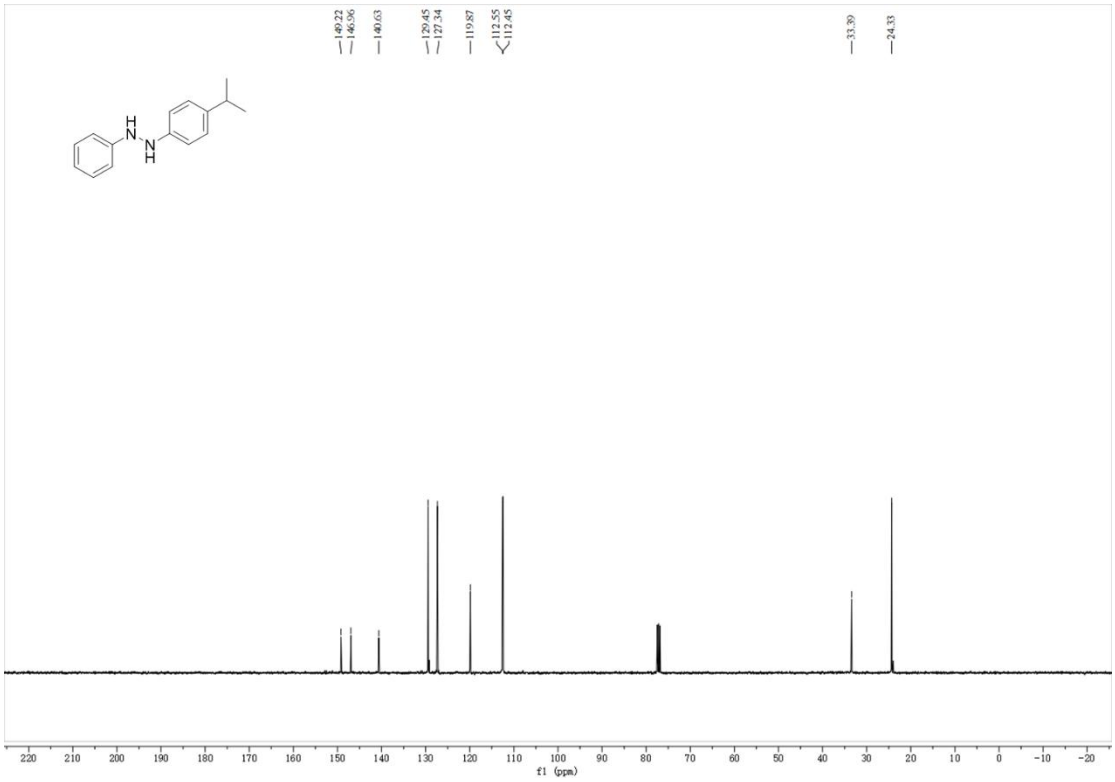

Figure S220. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4f**

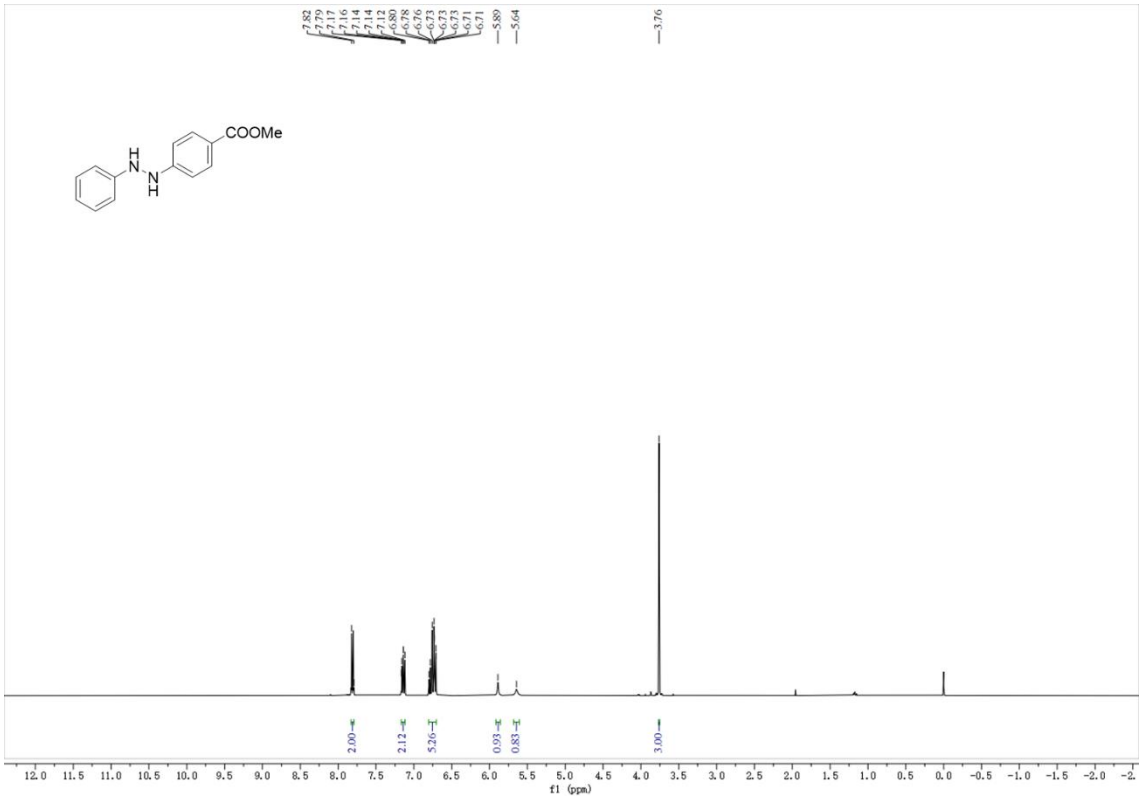

Figure S221. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**

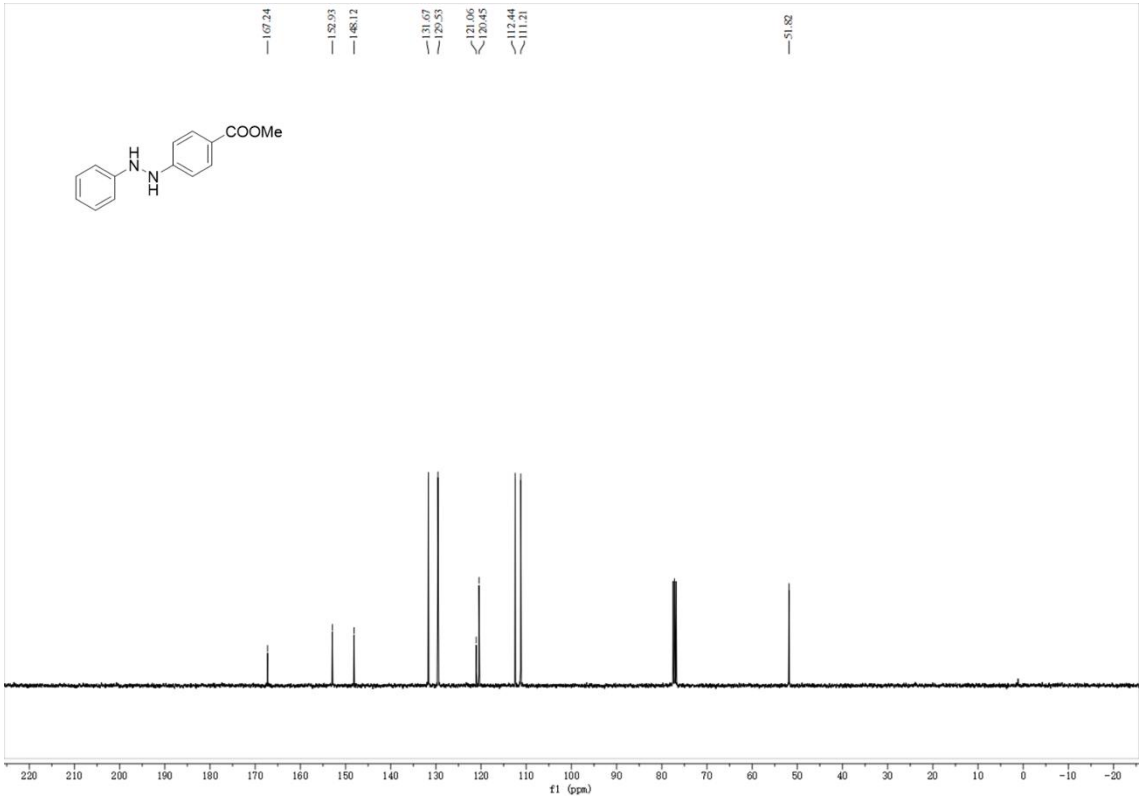

Figure S222. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4g**

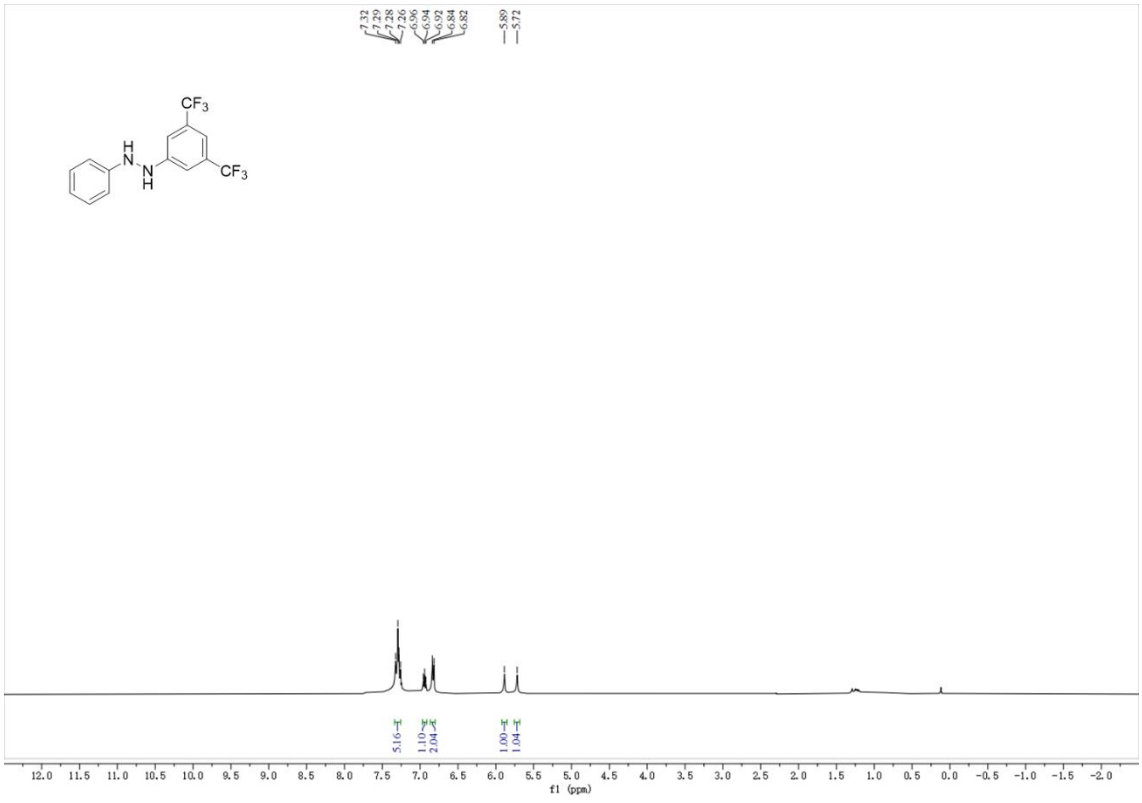

Figure S223. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**

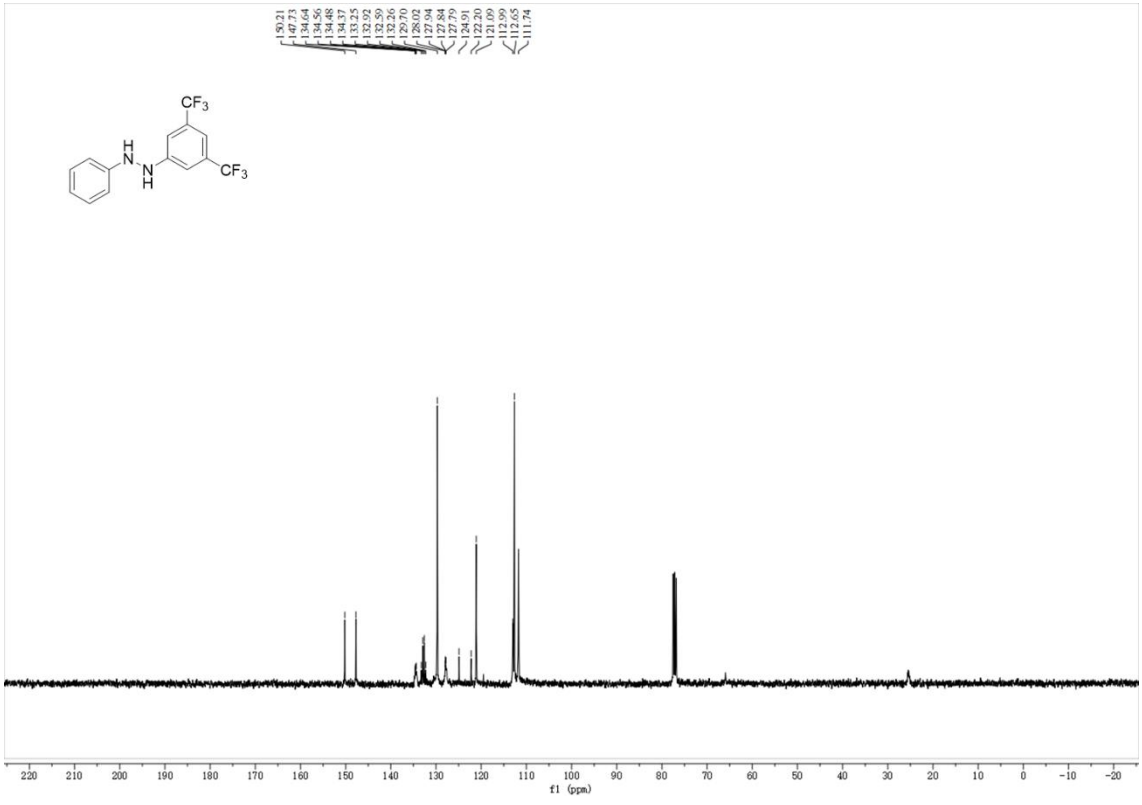

Figure S224. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4h**

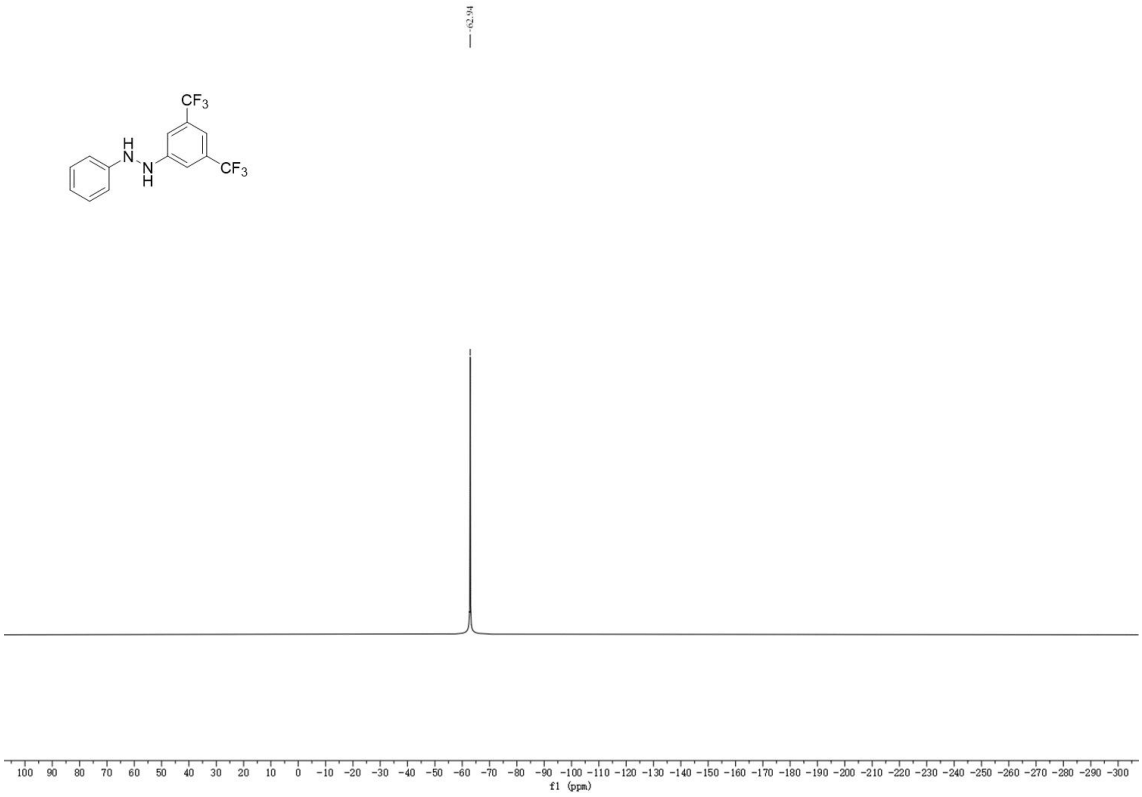

Figure S225. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4h**

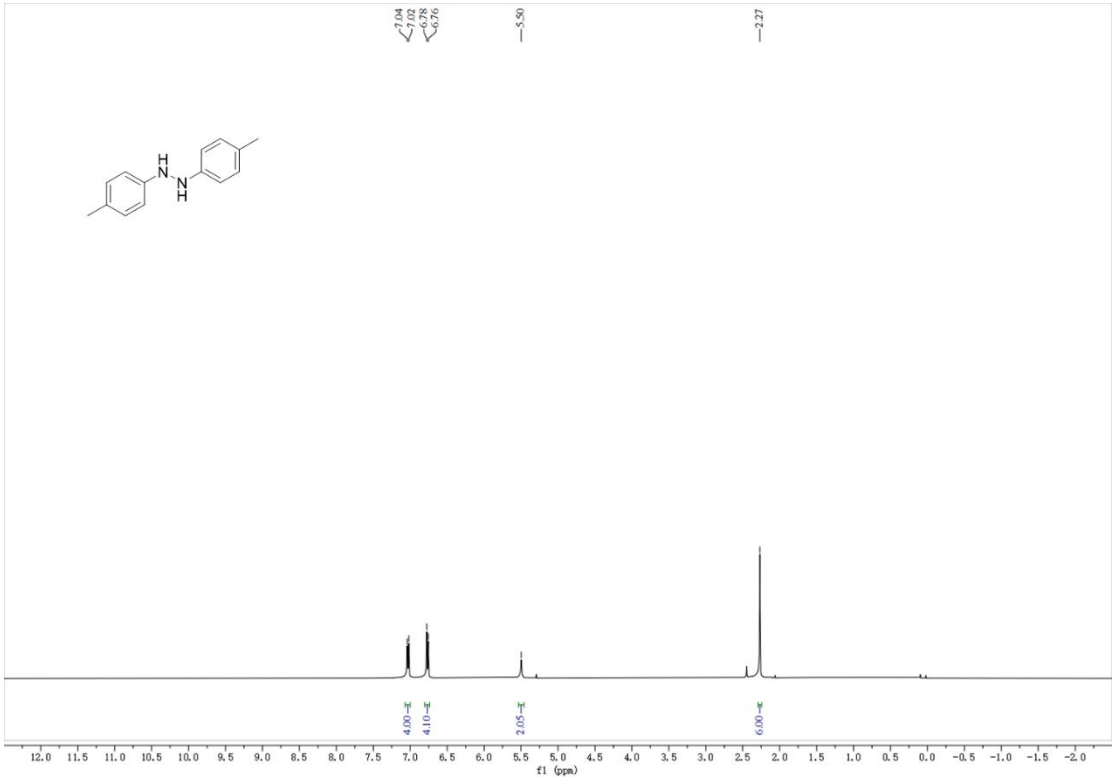

Figure S226. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**

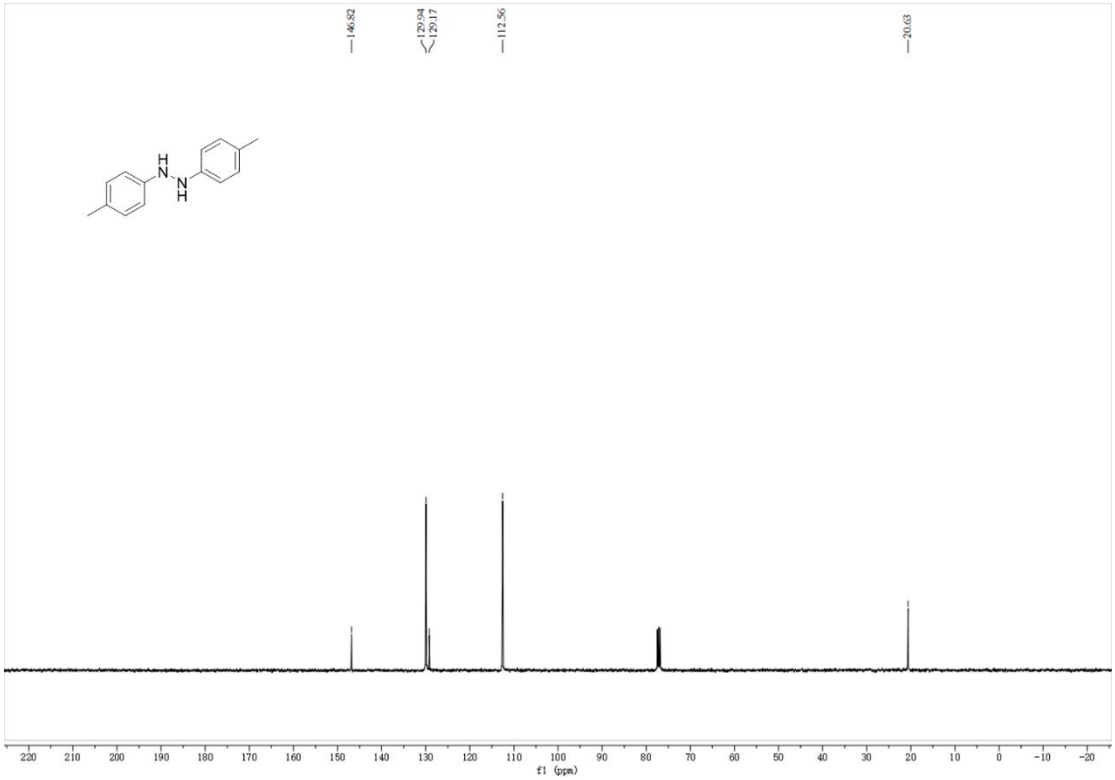

Figure S227. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4i**

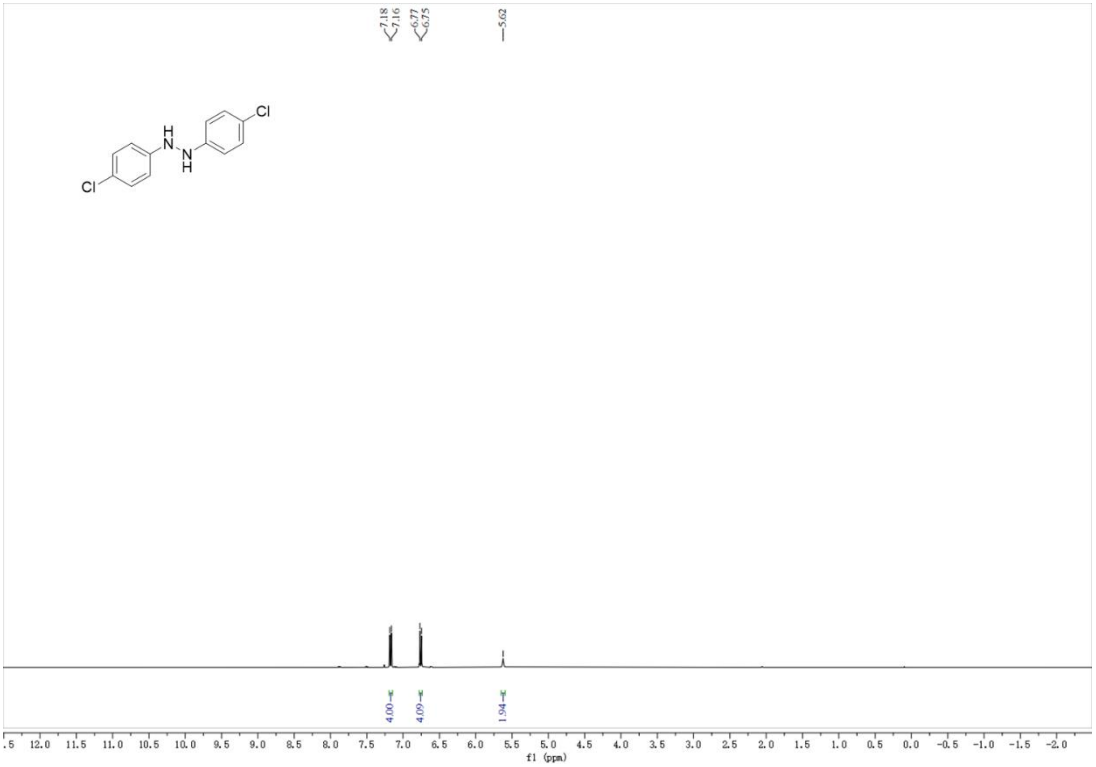

Figure S228. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**

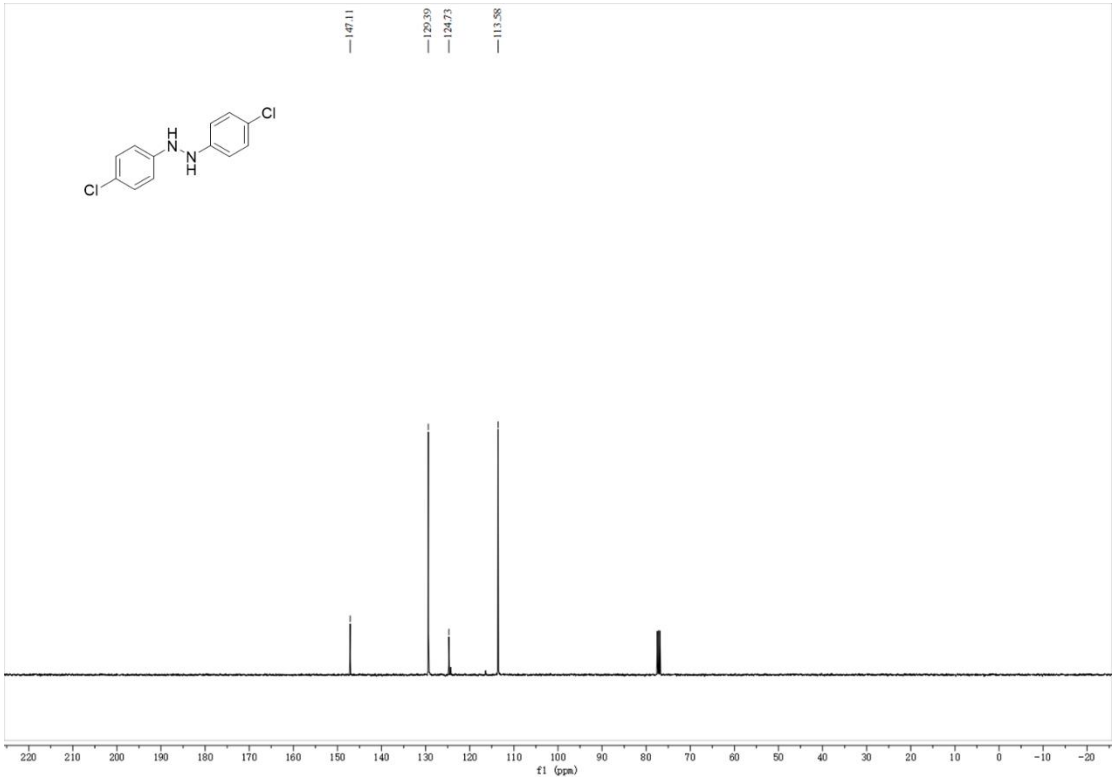

Figure S229. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4j**

Figure S230. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**

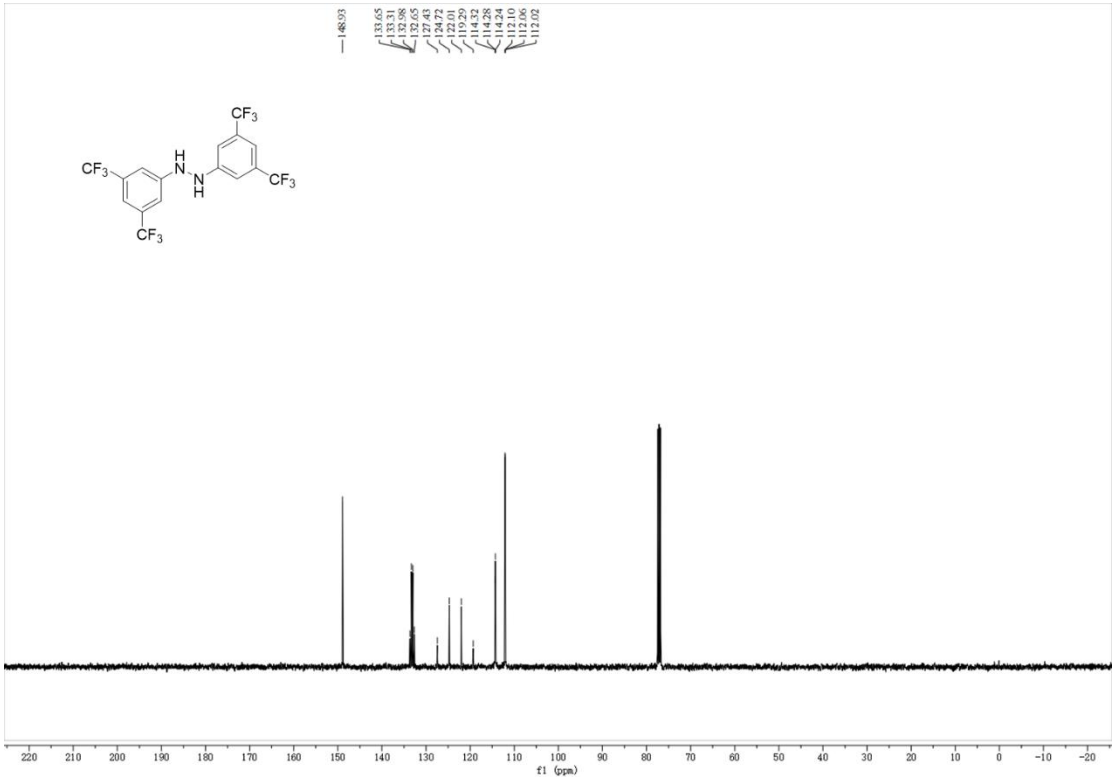

Figure S231. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4k**

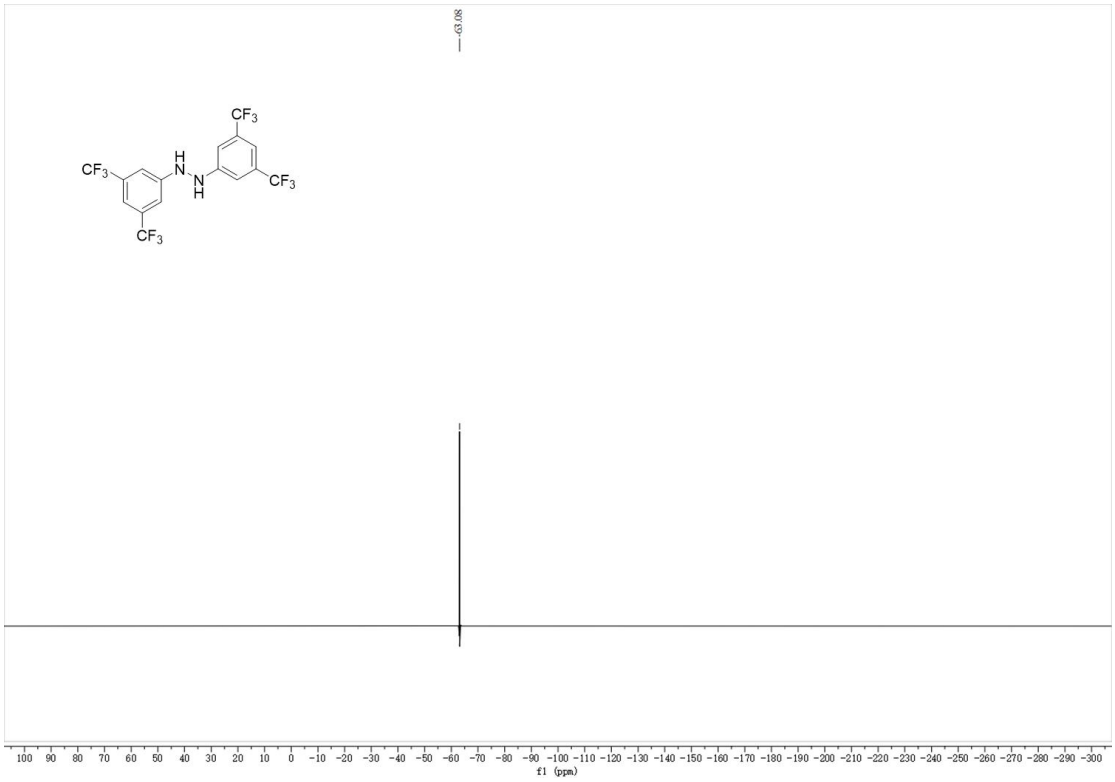

Figure S232. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4k**

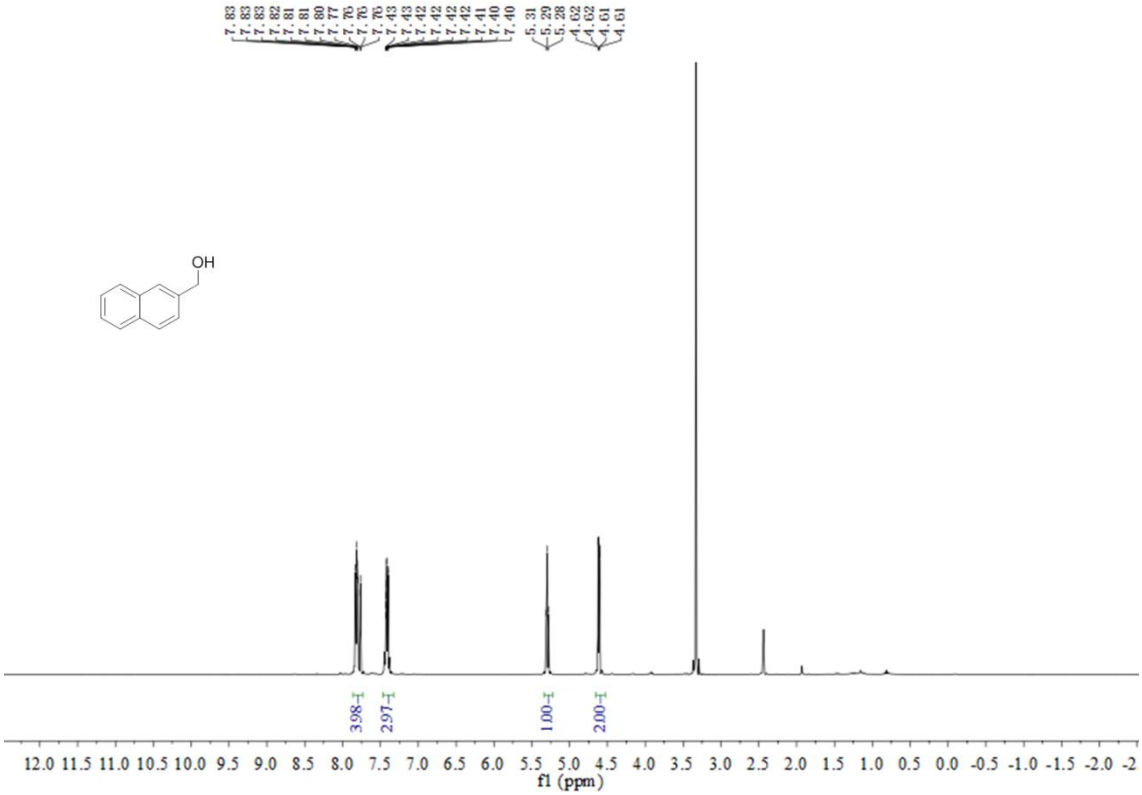

Figure S233. [1]H NMR (400 MHz, DMSO-d_6) spectrum of **6a**

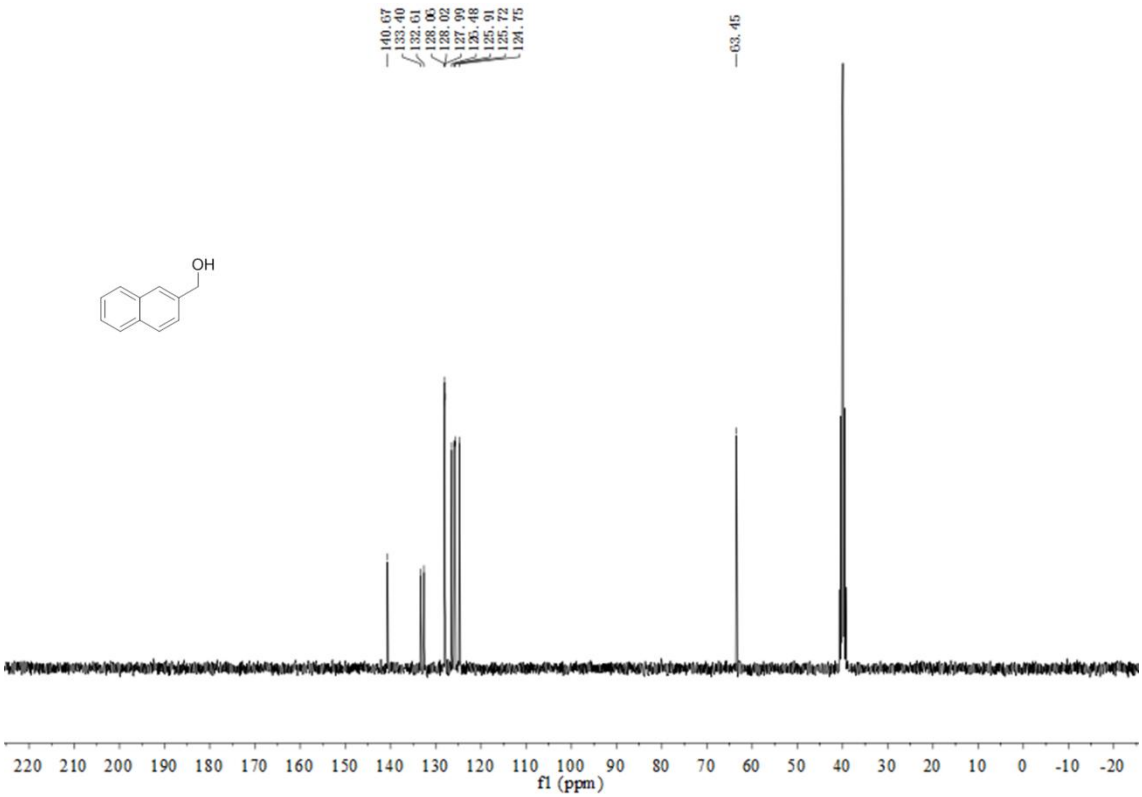

Figure S234. [13]C NMR (100 MHz, DMSO-D_6) spectrum of **6a**

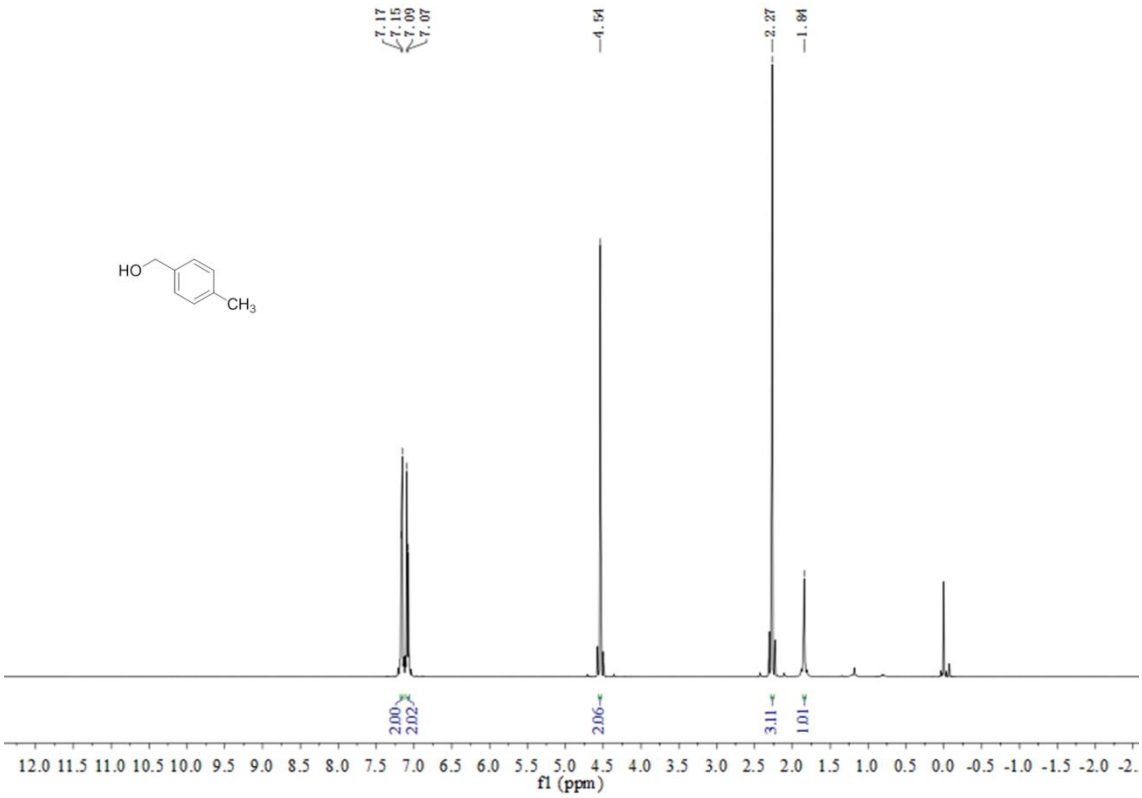

Figure S235. ^{1}H NMR (100 MHz, $CDCl_3$) spectrum of **6b**

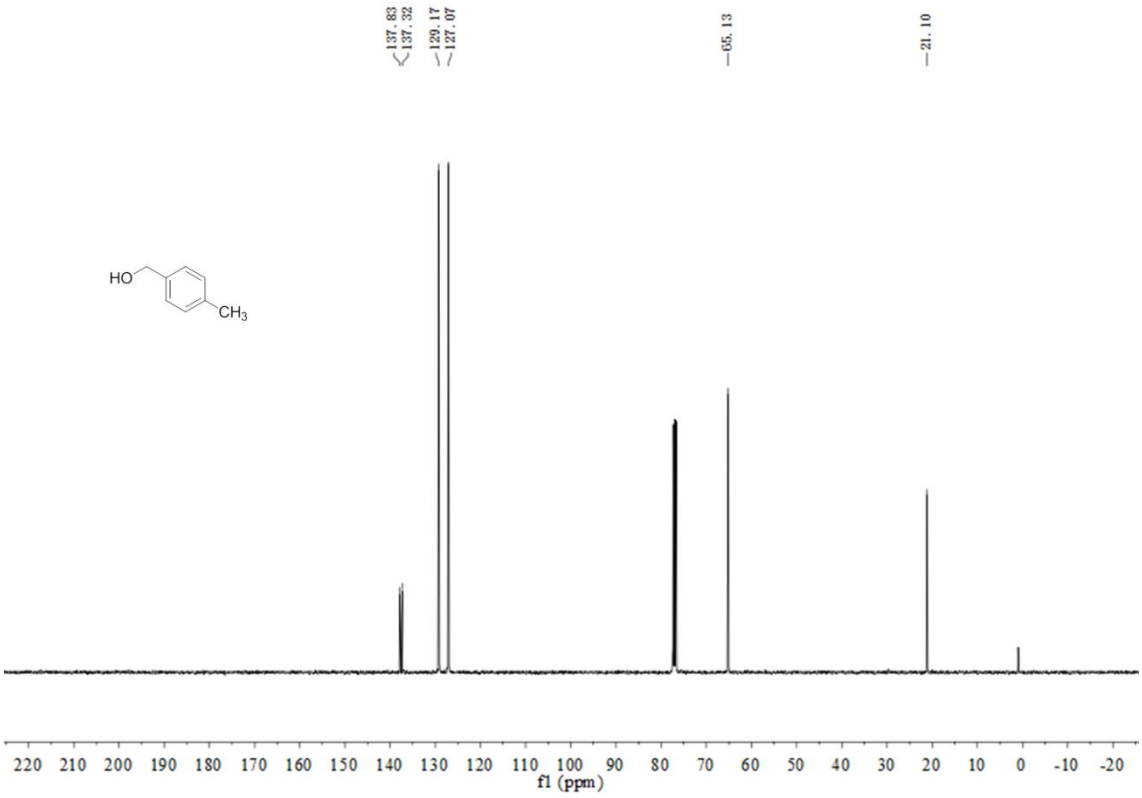

Figure S236. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6b**

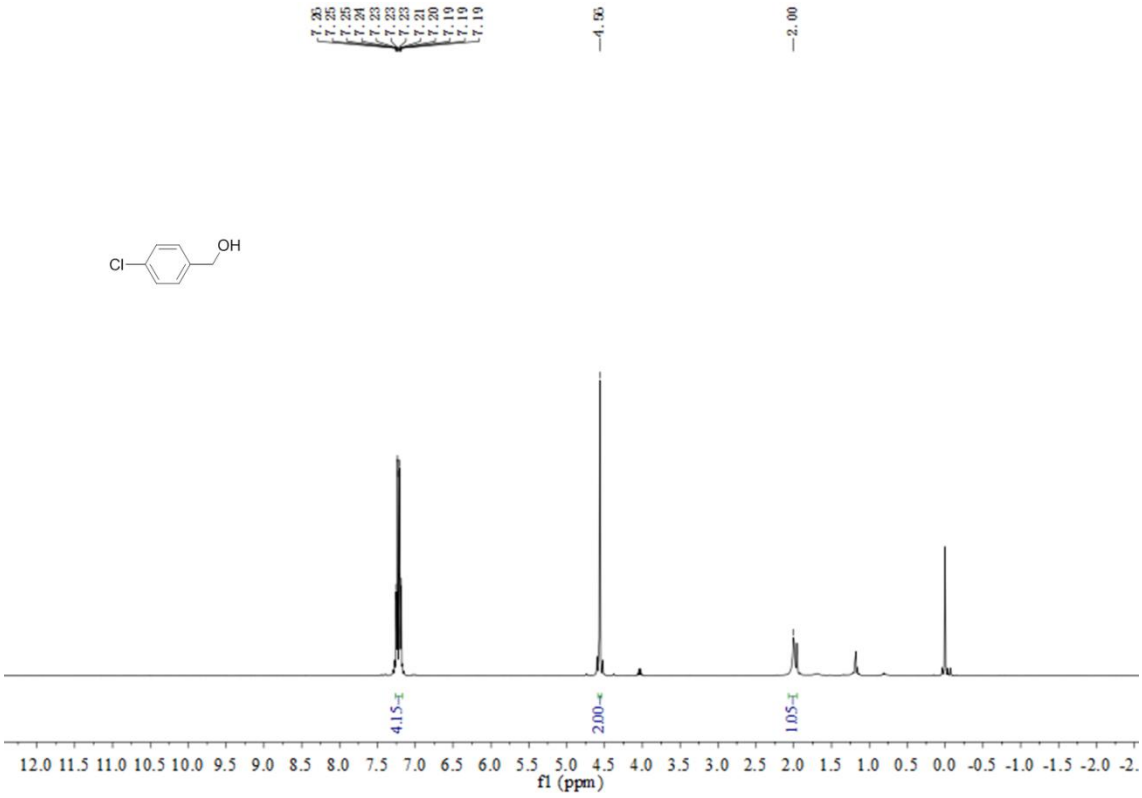

Figure S237. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6c**

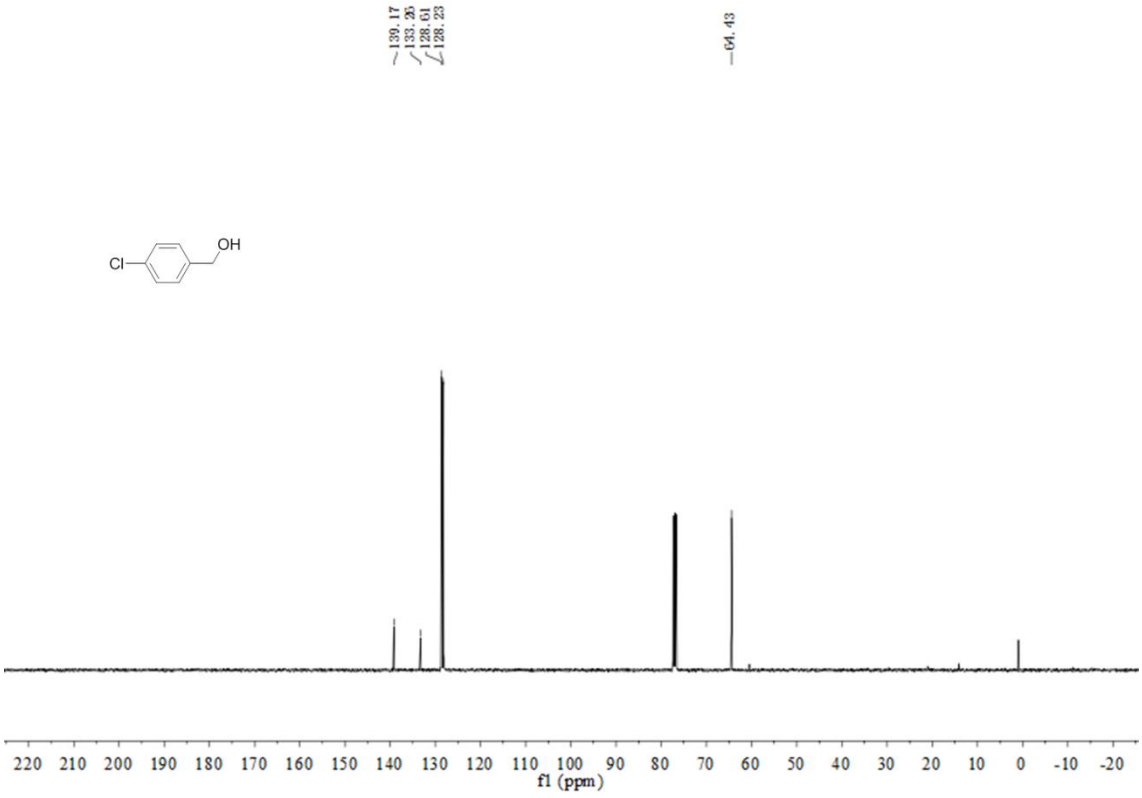

Figure S238. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6c**

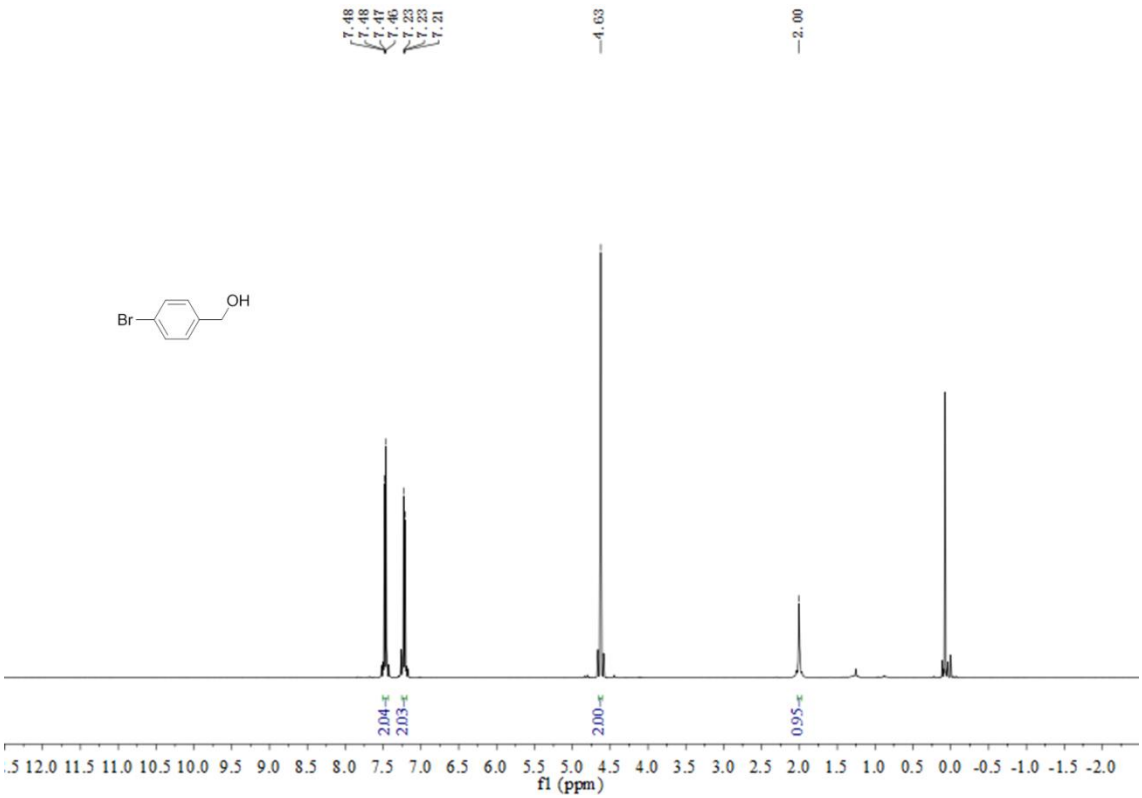

Figure S239. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6d**

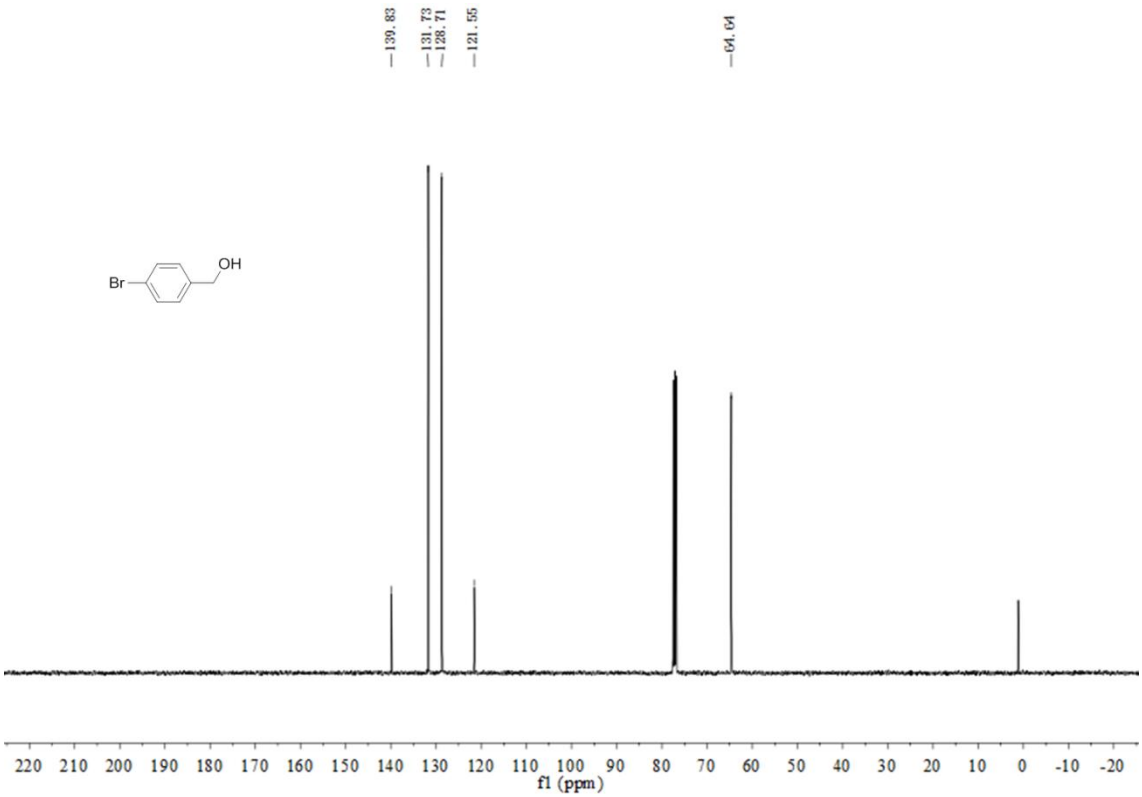

Figure S240. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6d**

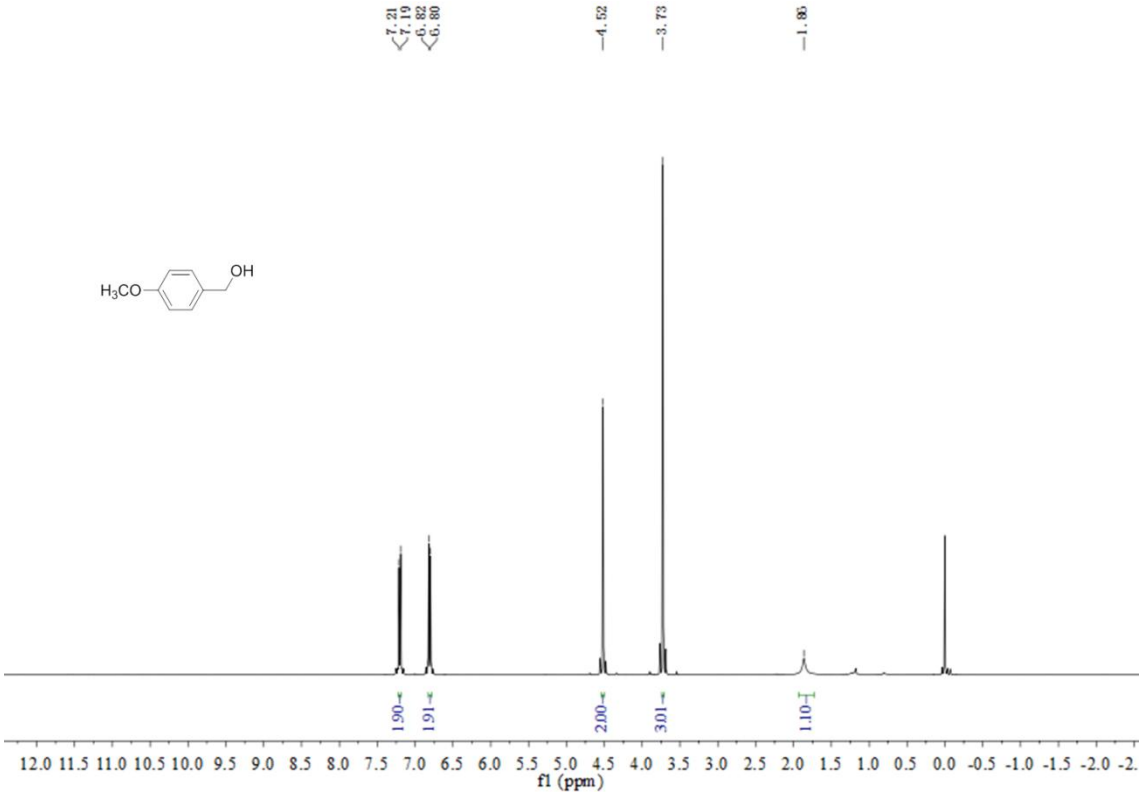

Figure S241. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6e**

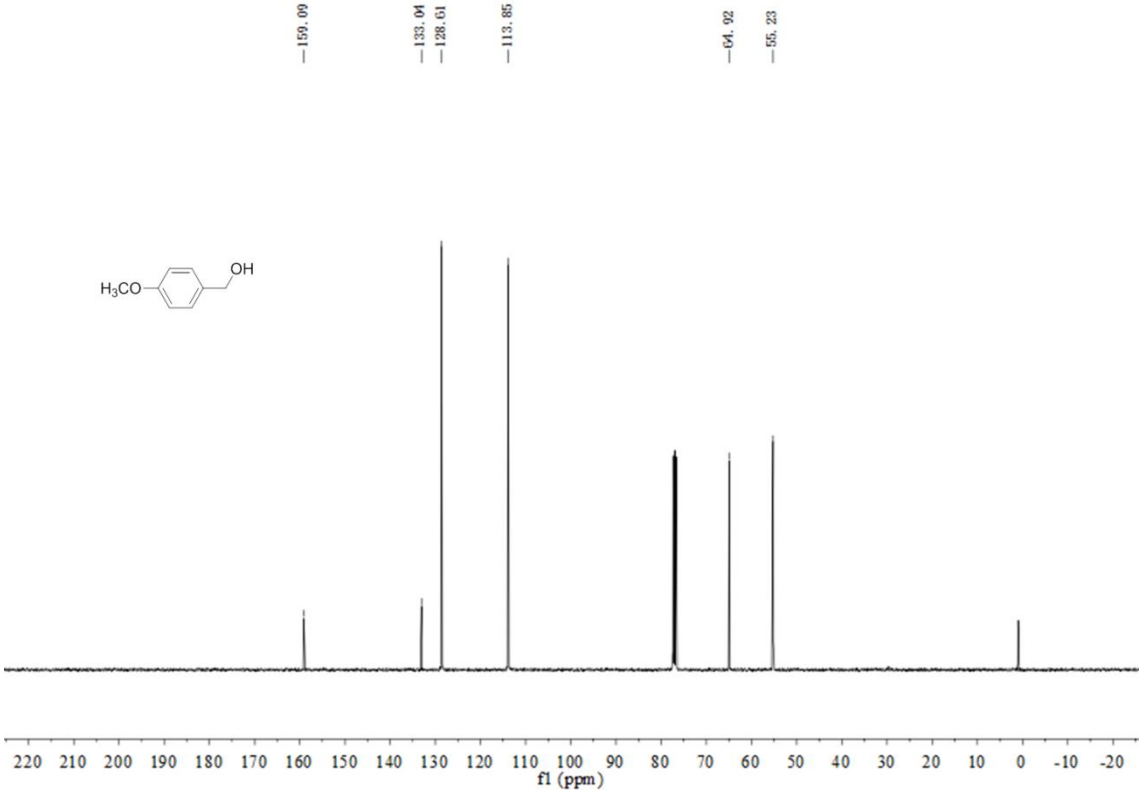

Figure S242. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6e**

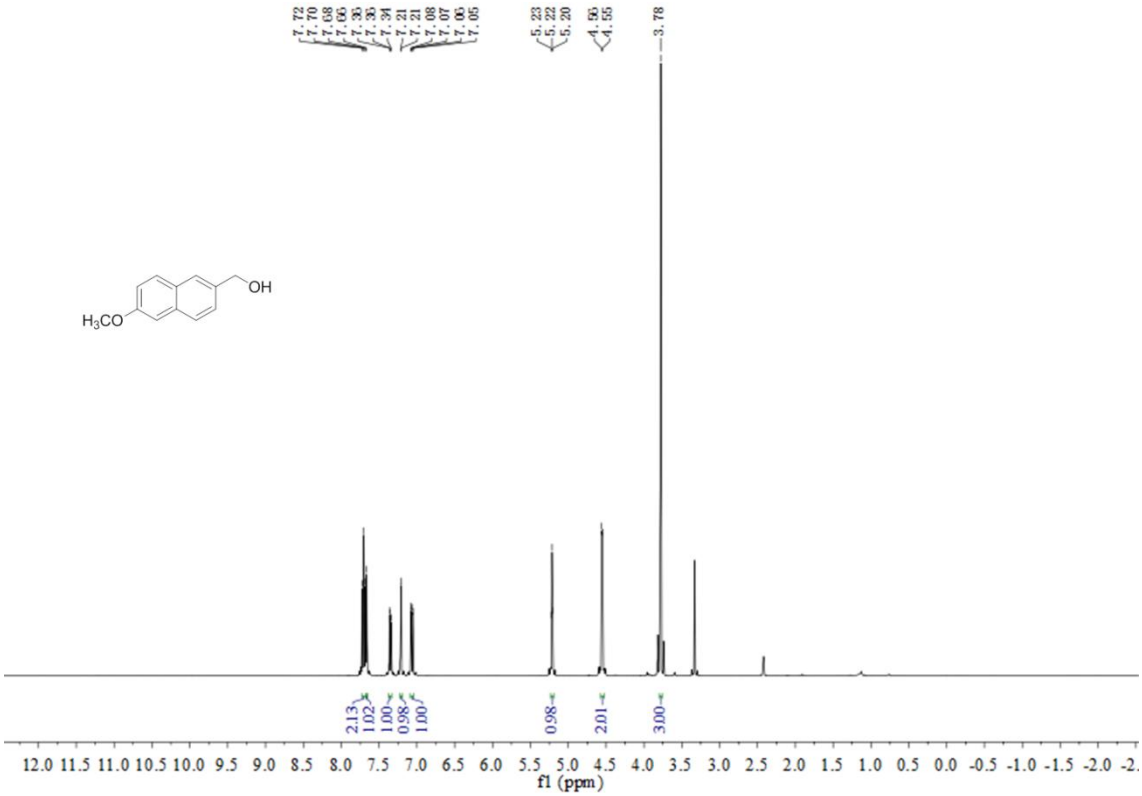

Figure S243. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6f**

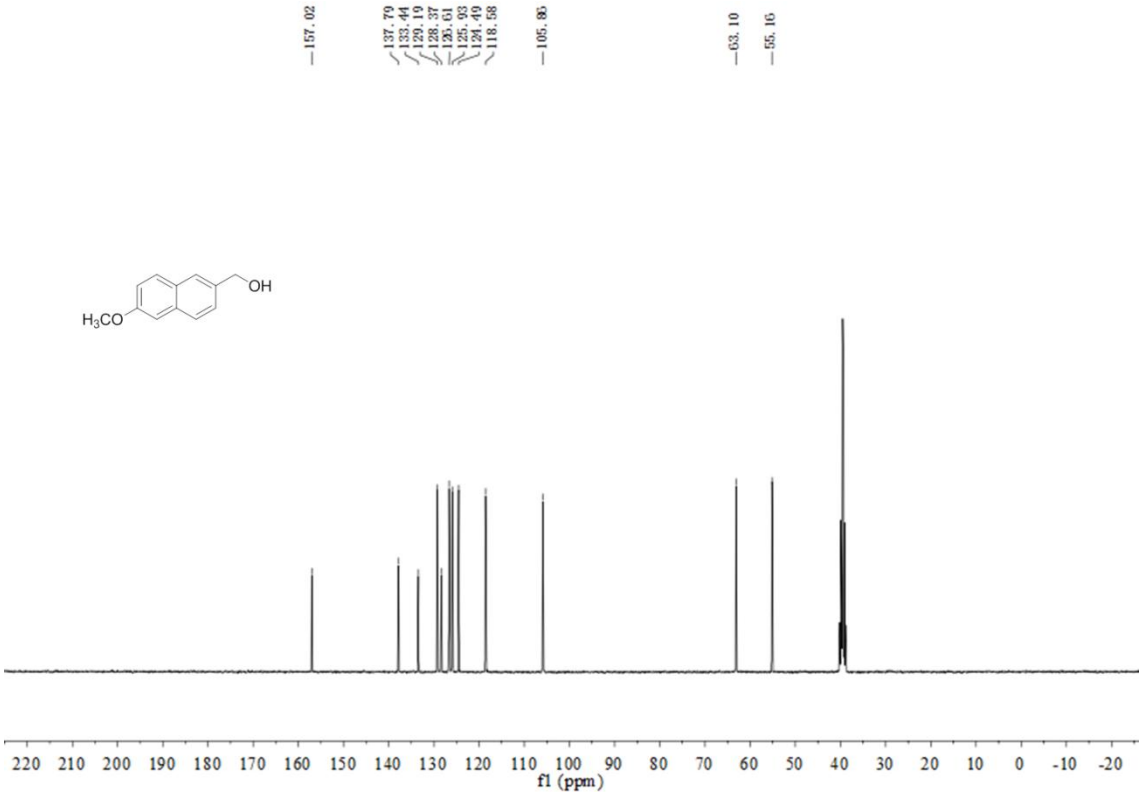

Figure S244. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **6f**

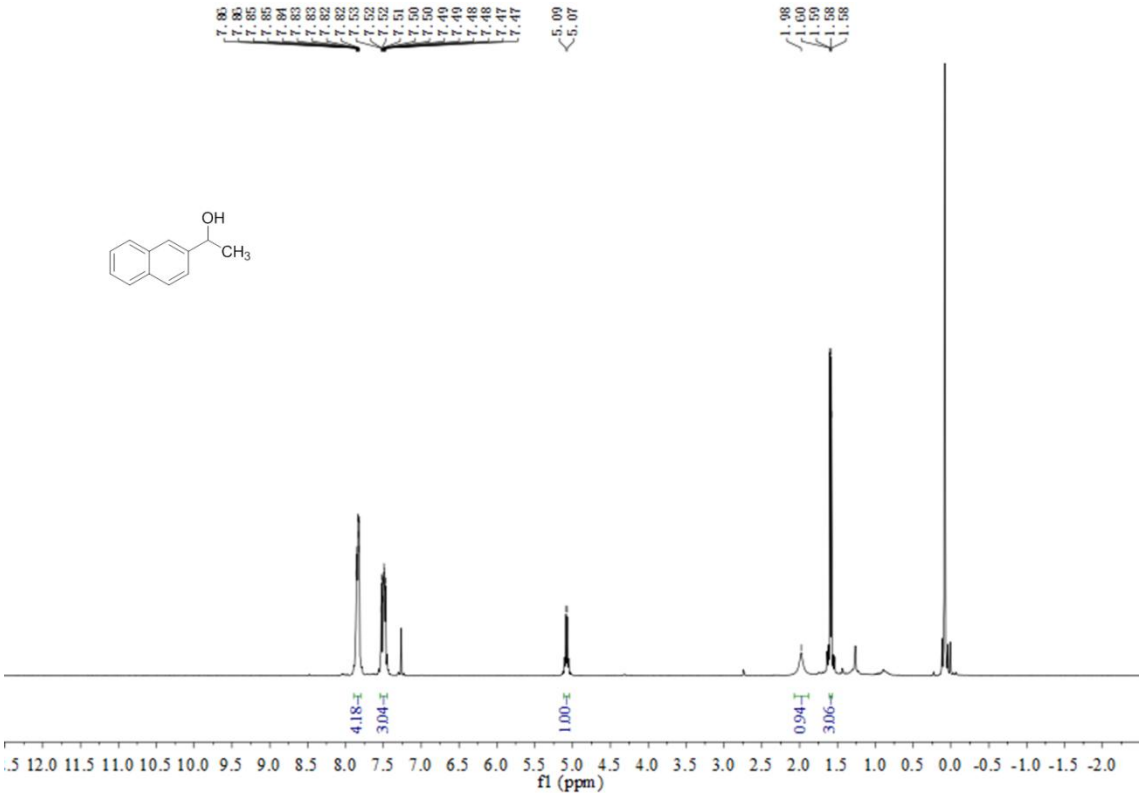

Figure S245. ^{1}H NMR (400 MHz, DMSO-D_6 spectrum of **6g**

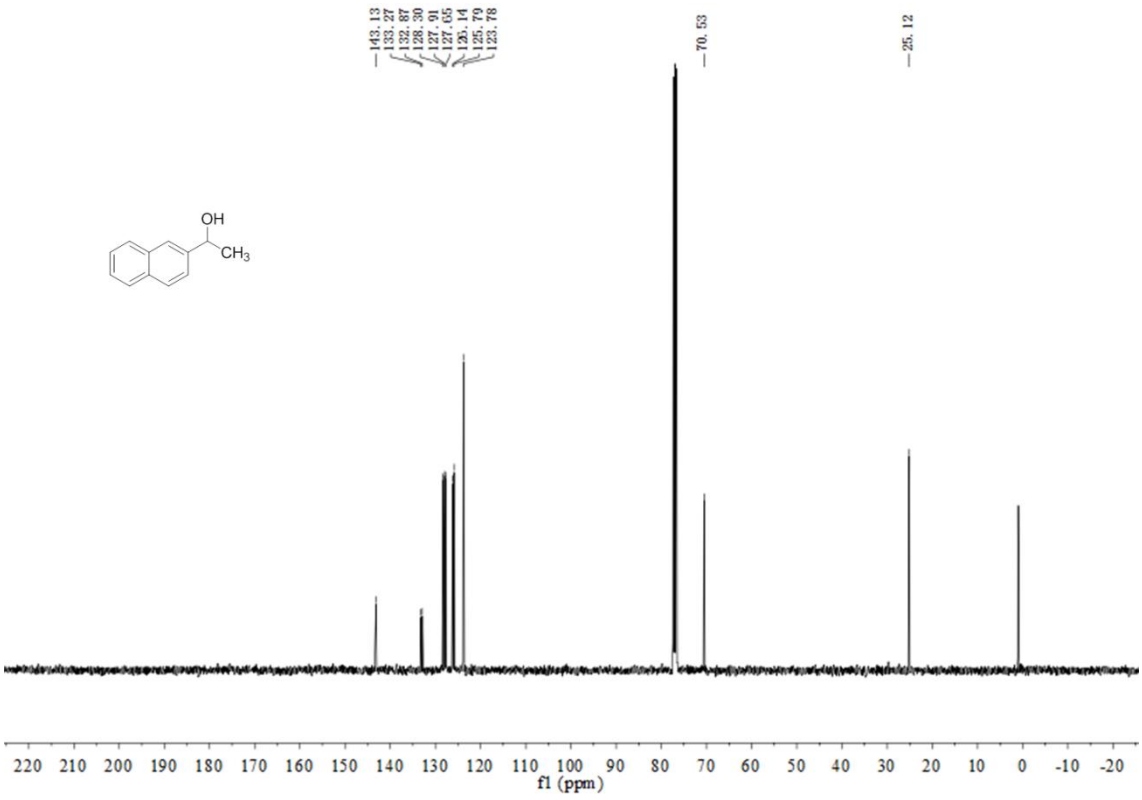

Figure S246. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6g**

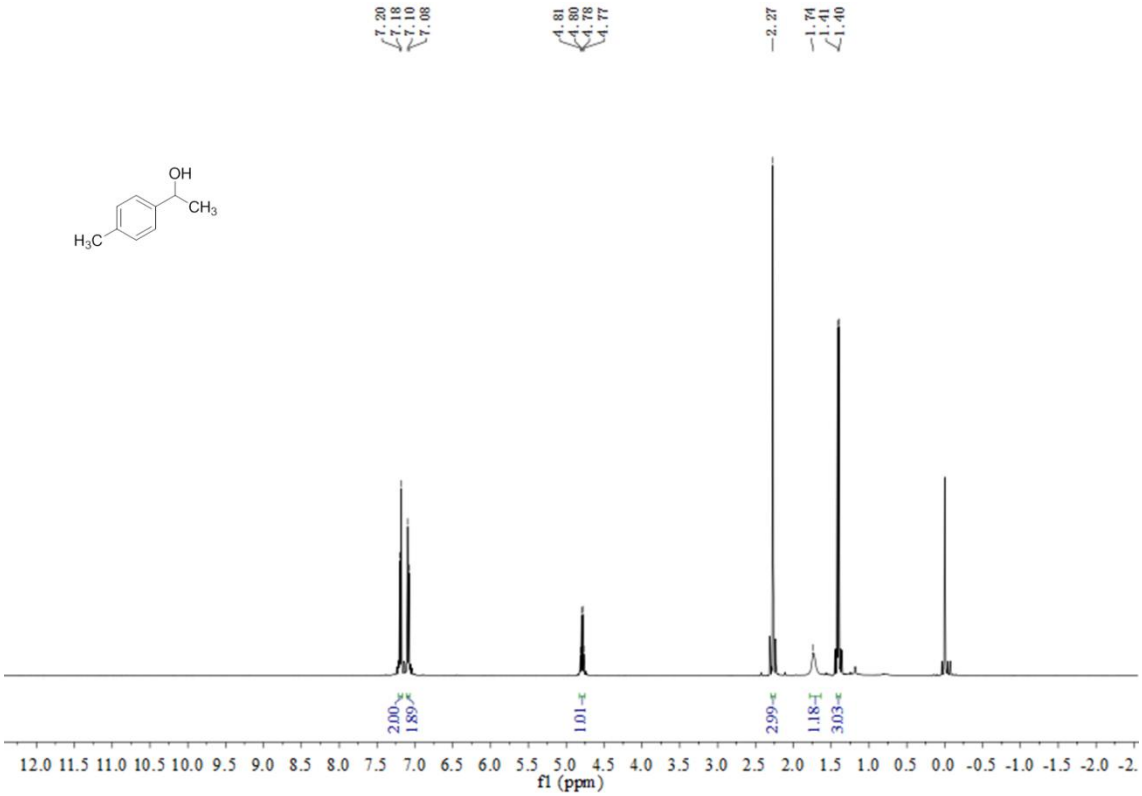

Figure S247.[1]H NMR (400 MHz, $CDCl_3$) spectrum of **6h**

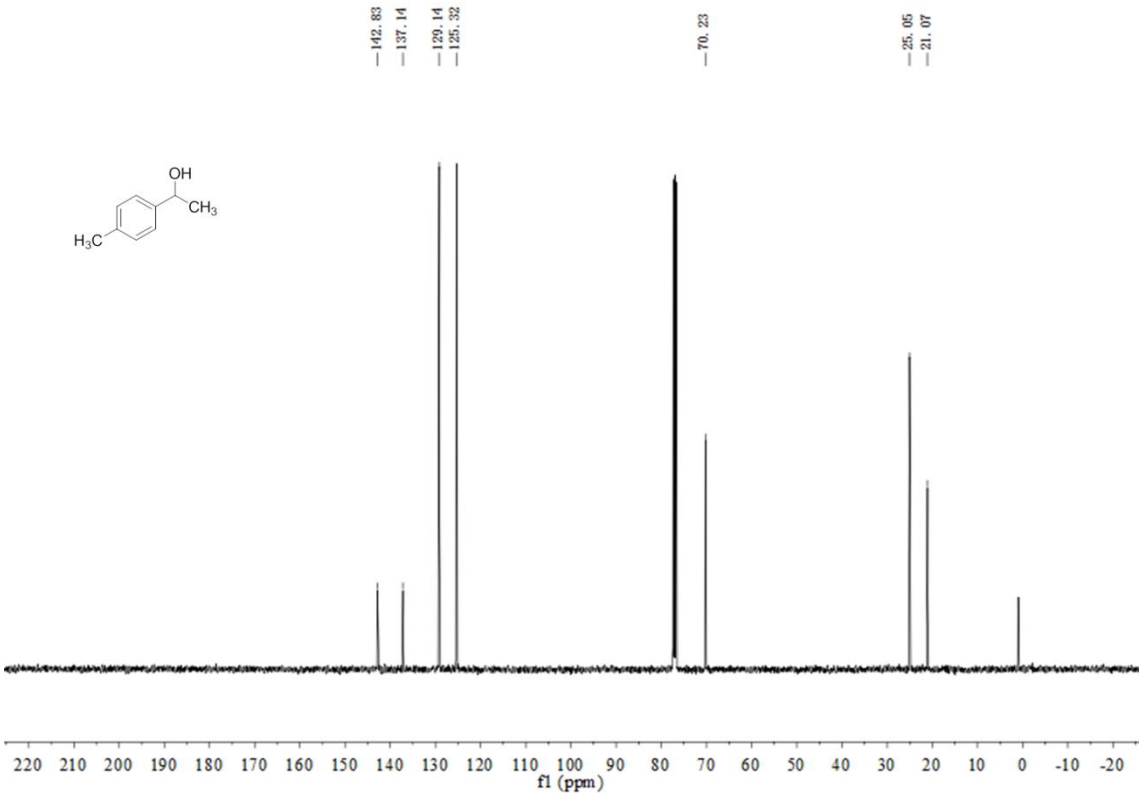

Figure S248. [13]C NMR (100 MHz, $CDCl_3$) spectrum of **6h**

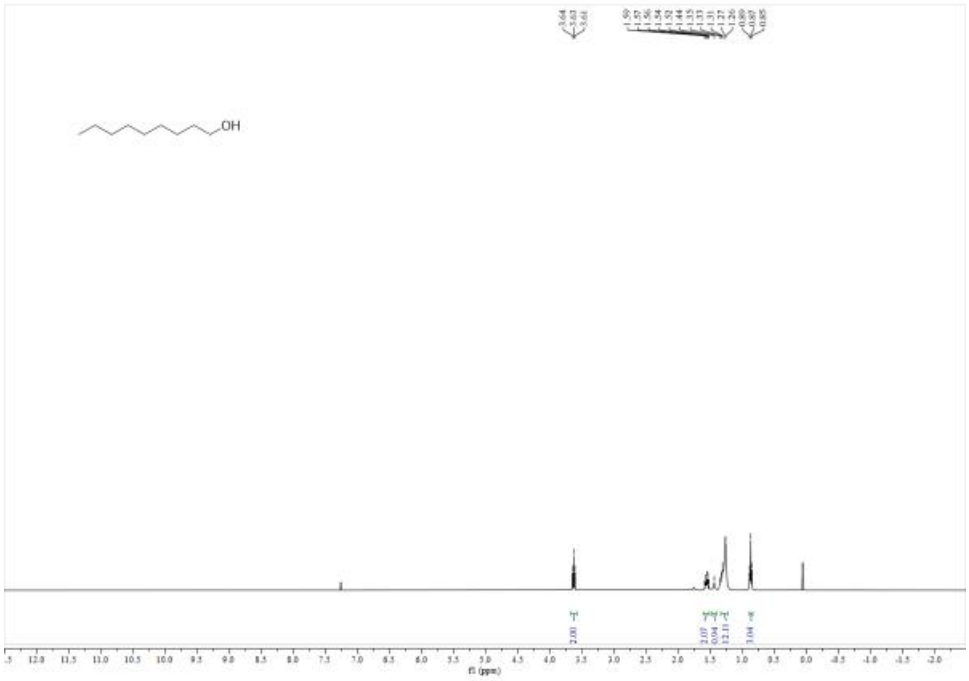

Figure S249. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6i**

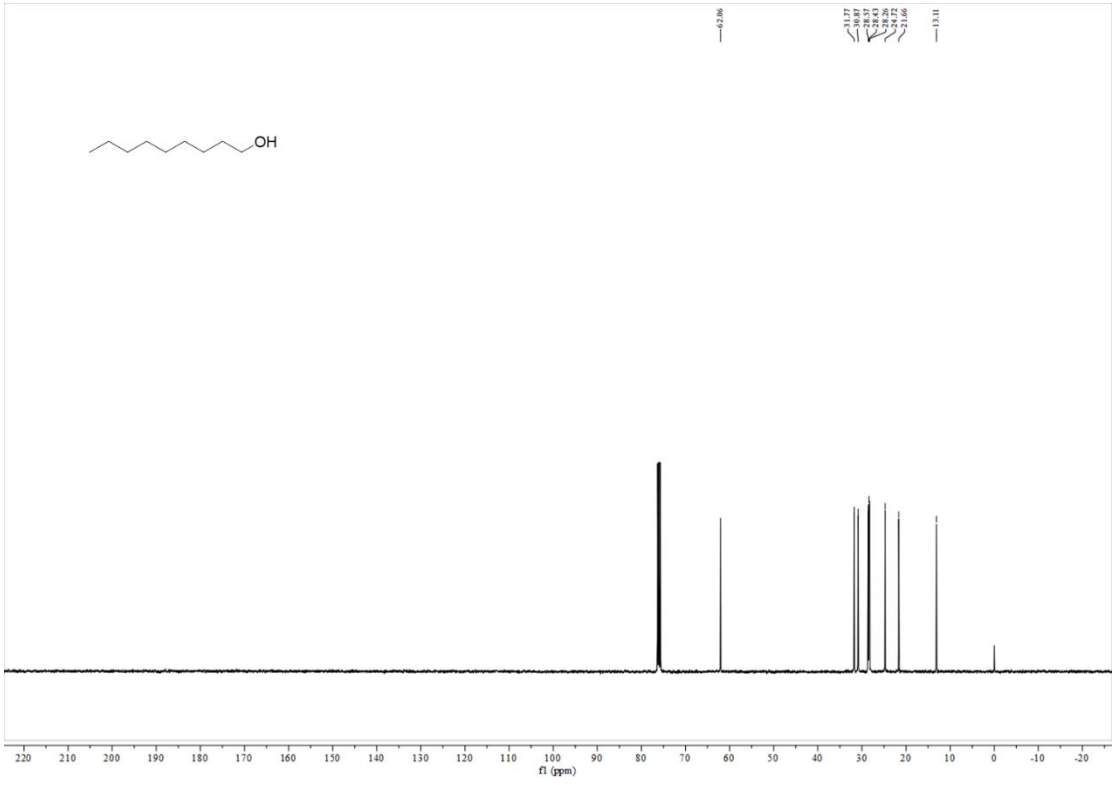

Figure S250. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6i**