Supporting information

Cobalt-catalyzed regioselective hydrohydrazination of epoxides

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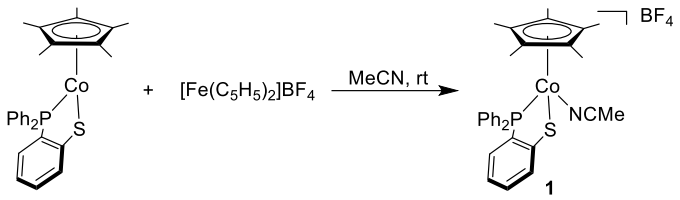
1. General procedure.

All reagents were purchased from commercial suppliers, unless specified otherwise, or prepared as described in the literature. The epoxides were purchased from commercial suppliers or prepared according to reported methods.[1] Acetonitrile, hexane, 1,2-dichloroethane and tetrahydrofuran were dried and degassed by Solvent Purification Systems. All solid heteroarenes were dried under vacuum and liquid heteroarenes were distilled prior to use. The [Cp*Co(1,2-$Ph_2PC_6H_4S$)] were prepared according to published procedures.[2] NMR spectra were recorded on Bruker 500 (500 MHz for ^1H, 126 MHz for ^{13}C, 471 MHz for ^{19}F) spectrometers. Chemical shifts for ^1H and ^{13}C spectra were referenced to residual solvent resonances and are reported relative to tetramethylsilane. High resolution mass spectra (MS) were obtained using a LC/MSD TOF spectrometer system with electrospray ionization (ESI).

2. Experimental section.

2.1 Synthesis of [Cp*Co(1,2-$Ph_2PC_6H_4S$)(NCMe)]BF_4, 1.



Scheme S1. Synthesis of [Cp*Co(1,2-$Ph_2PC_6H_4S$)(NCMe)]BF_4, **1**.

[Cp*Co(1,2-$Ph_2PC_6H_4S$)(NCMe)]BF_4, **1**. In a glovebox under nitrogen atmosphere, [Cp*Co($Ph_2PC_6H_4S$)] (487 mg, 1.0 mmol) was added to the solution of $[Cp_2Fe]BF_4$ (273 mg, 1.0 mmol) in 30 mL of MeCN, the solution color turned from red to black immediately. After stirring for 3 h at room temperature, the solution was concentrated to 5 mL. Then the solution was diluted with 50 mL of ether. The product was precipitated and isolated as black solid by filtration (556 mg, 92% yield). **[Cp*Co(1,2-$Ph_2PC_6H_4S$)(NCMe)]BF_4**, **1**, ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.89 – 7.42 (m, 11H), 7.10 (t, *J* = 6.8 Hz, 1H), 6.92 – 6.65 (m, 2H), 1.96 (s, 3H), 1.34 (s, 15H). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 66.58 (s). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 155.05, 154.86, 134.27, 134.19, 133.77, 132.65, 131.58 (d, *J* = 2.6 Hz), 131.25 (d, *J* = 2.3 Hz), 129.83, 129.75, 129.08, 129.00, 128.55, 123.74, 123.68, 98.15, 9.09, 3.30. MS (ESI) Calcd for $C_{28}H_{29}PSCo$ [M^+–MeCN]: 487.1060; Found: 487.1036.

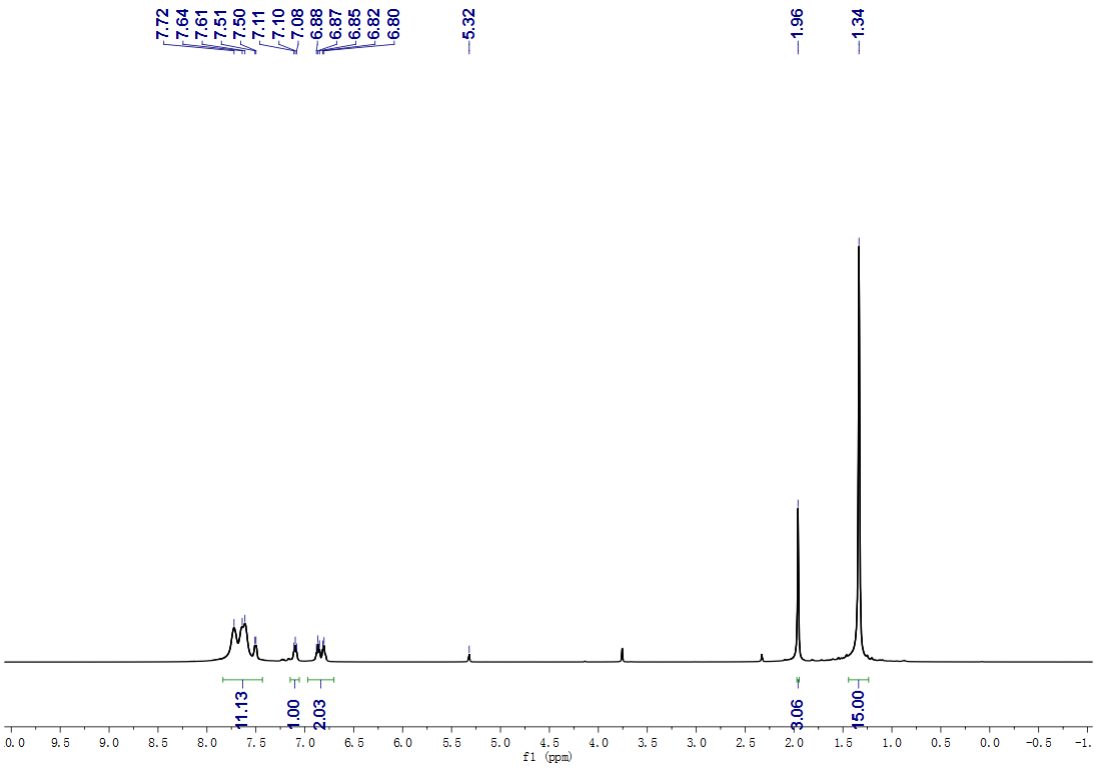


Figure S1. The ^{1}H-NMR spectral copy of compound **1**.

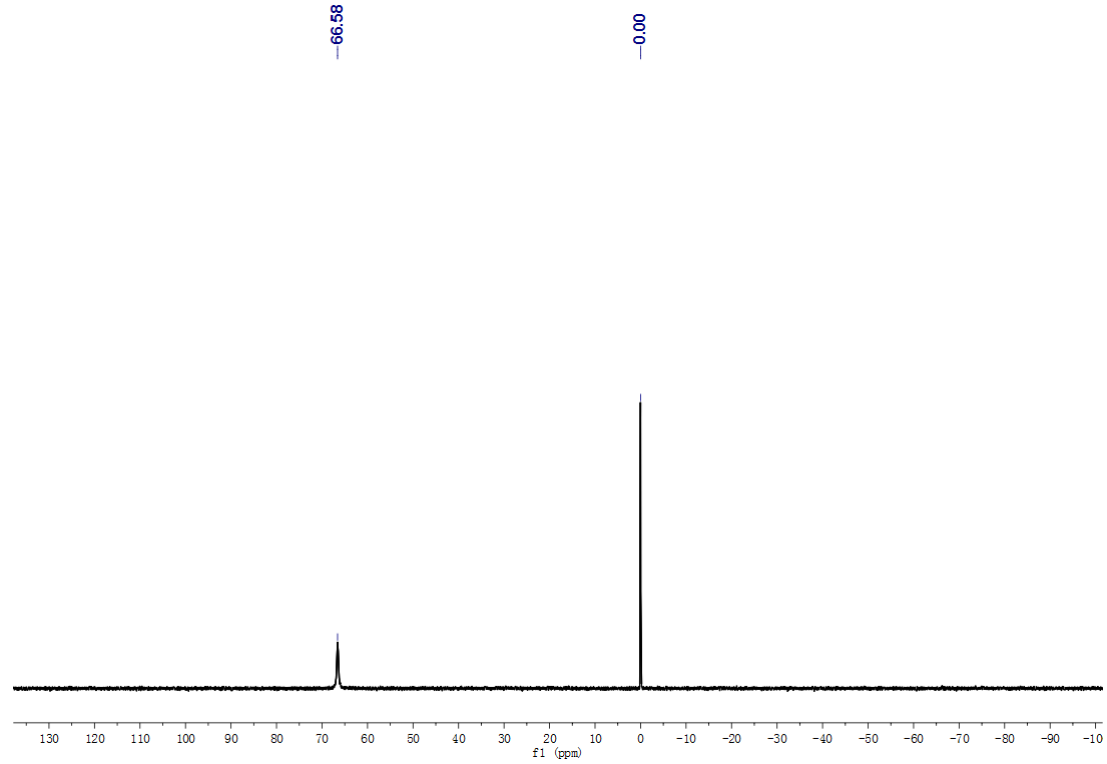


Figure S2. The ^{31}P-NMR spectral copy of compound **1**.

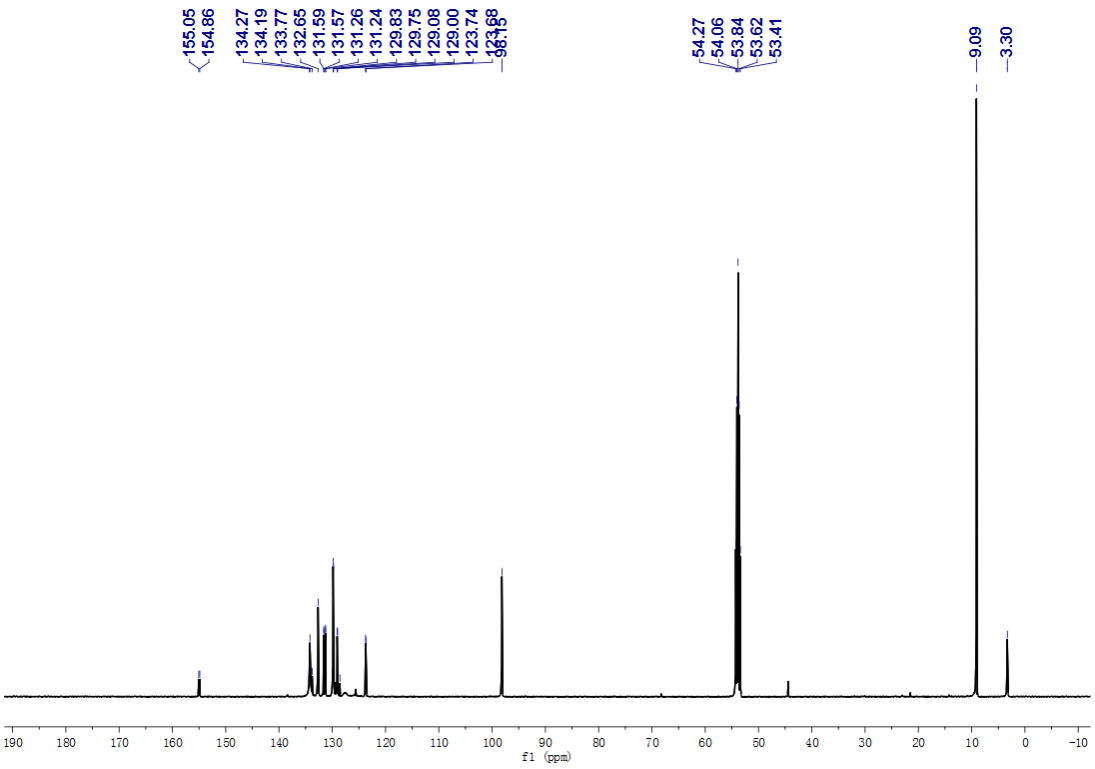
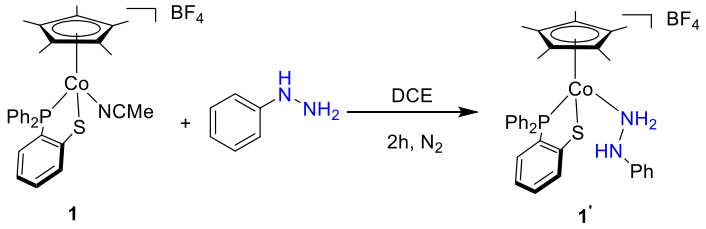


Figure S3. The ^{13}C-NMR spectral copy of compound **1**.

2.2 Reaction of 1 with phenylhydrazine.



Scheme S2. Reaction of **1** with phenylhydrazine.

In a glovebox under nitrogen atmosphere, a scintillation vial (with a magnetic stir bar) was charged with phenylhydrazine (108 mg, 1.0 mmol) and a stoichiometric amount of **1** (615 mg, 1.0 mmol) in 20 mL of DCM solution. The color turned from black to brown immediately. After stirring for 2 h at room temperature, the volatile was removed under vacuum. The product was washed with hexane (50 mL) and collected by filtration to give brown solid (686 mg, 0.095 mmol, 95% yield). **[Cp*Co(1,2-Ph$_2$PC$_6$H$_4$S)(NH$_2$NHPh)]BF$_4$**, **1'**, ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.95 – 7.31(m, 12H), 7.28 – 6.53 (m, 10H), 1.41 (s, 15H). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 65.00 (s). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 152.43, 149.13, 137.16 (d, *J* = 9.8 Hz), 135.79, 133.90, 133.42, 132.92, 132.24 (d, *J* = 7.4 Hz), 129.86, 129.79, 129.51, 124.56 (d, *J* = 6.5 Hz), 123.00, 115.55, 115.24, 99.31, 97.15, 94.42, 92.90, 9.50. MS (ESI) Calcd for $C_{34}H_{37}CoN_2PS$ [M^+]: 595.1747; Found: 595.1674.

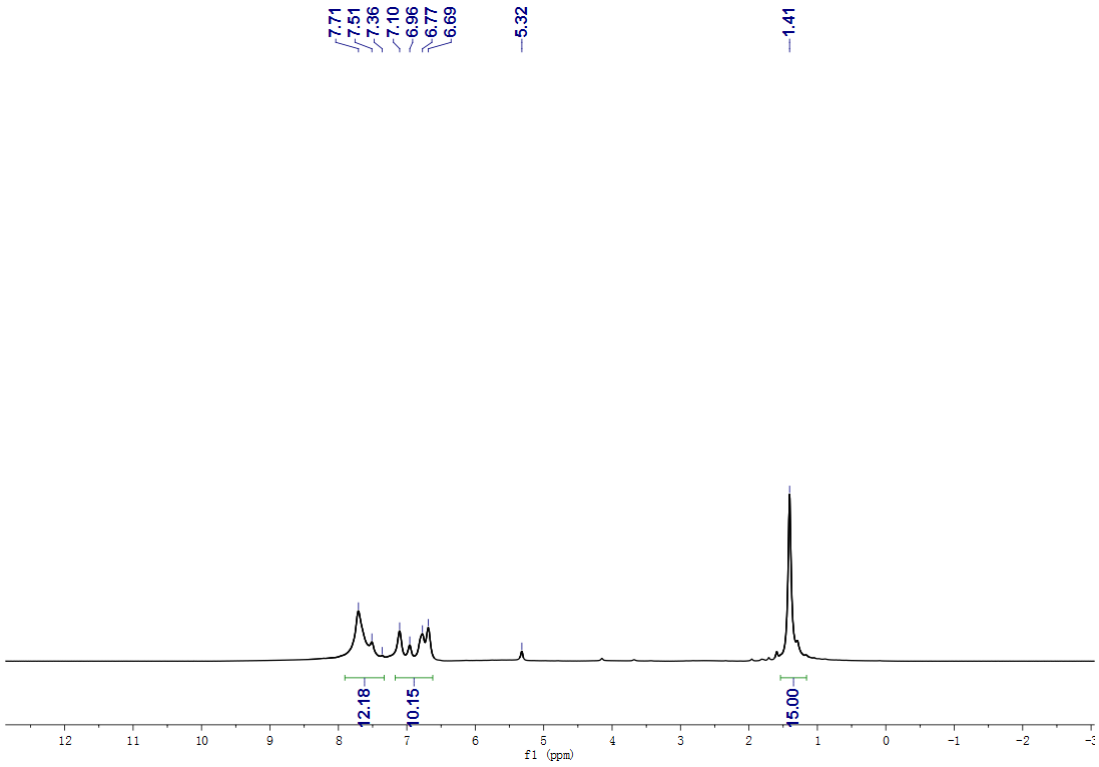


Figure S4. The ^{1}H-NMR spectral copy of compound **1**'.

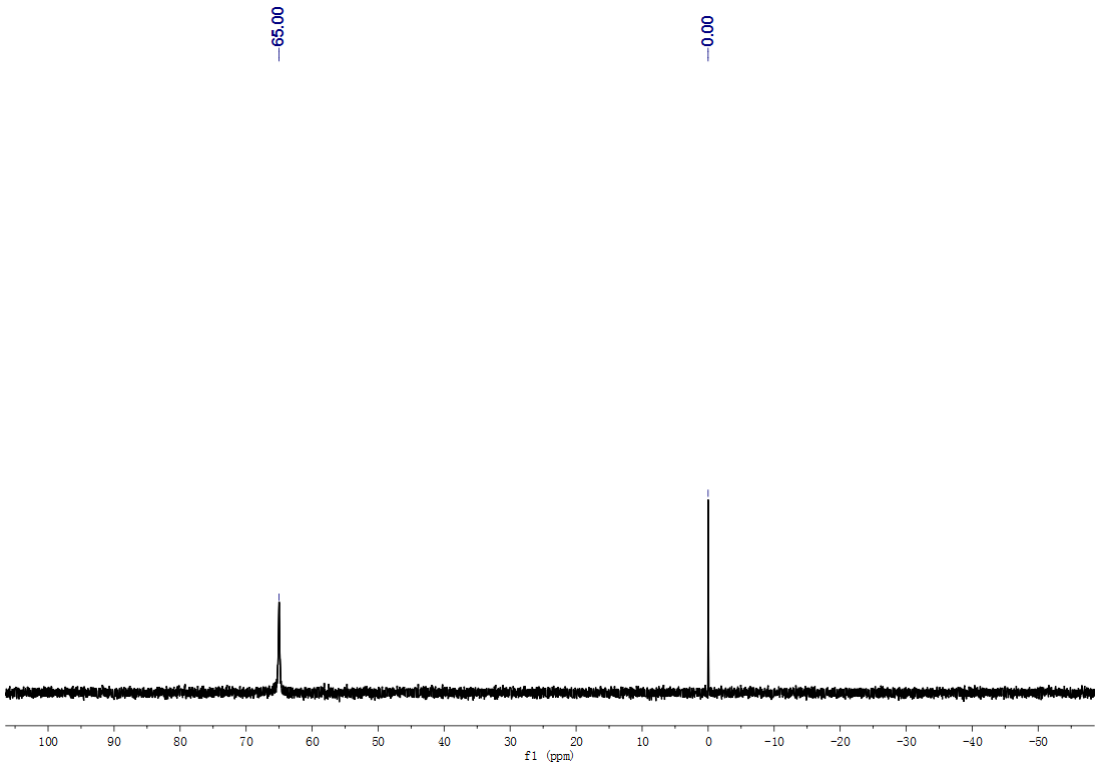


Figure S5. The ^{31}P-NMR spectral copy of compound **1'**.

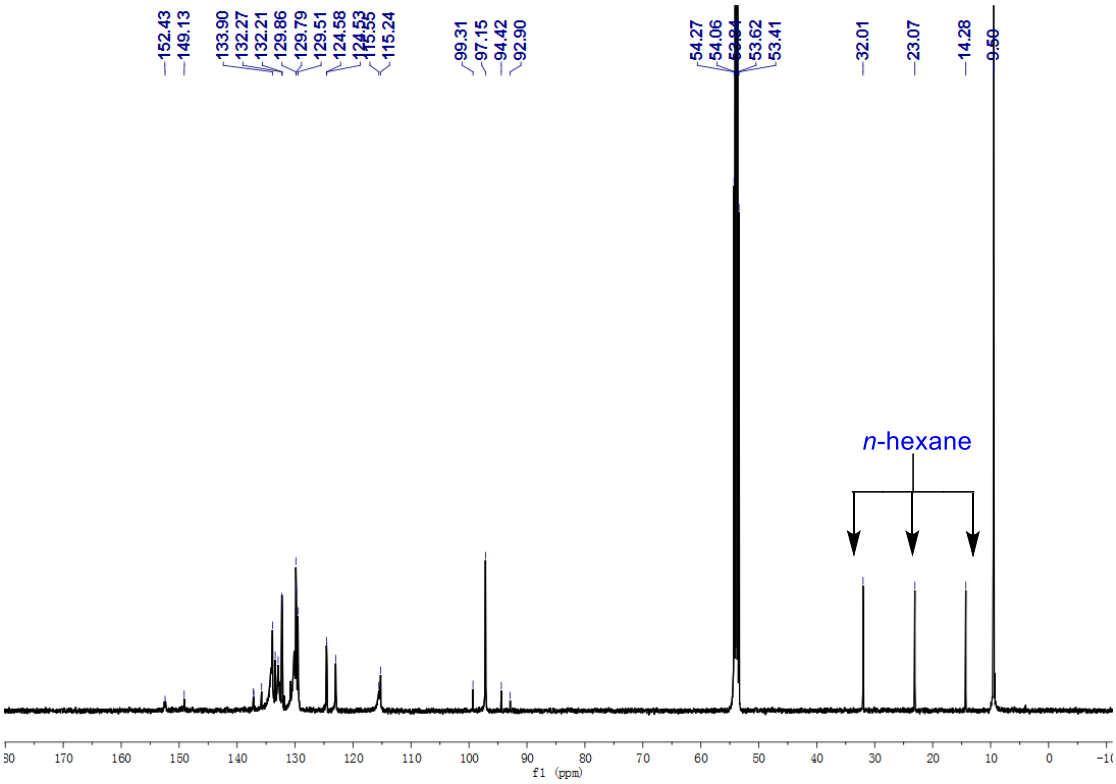
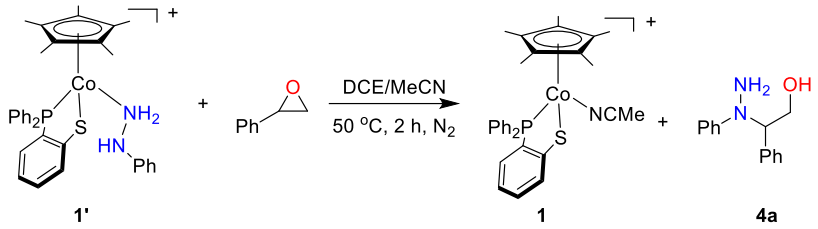


Figure S6. The ^{13}C-NMR spectral copy of compound **1**'.

2.3 Reaction of 1' with styrene oxide.



Scheme S3. Reaction of **1'** with styrene oxide.

In a glovebox under nitrogen atmosphere, a scintillation vial (with a magnetic stir bar) was charged with **1'** (68 mg, 0.1 mmol) and a stoichiometric amount of styrene oxide (12 mg, 0.1 mmol) in 5 mL of mixed solvent DCE/MeCN (v/v = 1:1). After stirring for 2 h at 50 ℃, the volatile was removed under vacuum. The residue was extracted extracted with MeCN (5 mL) in vacuo to give product **1** and **4a**.

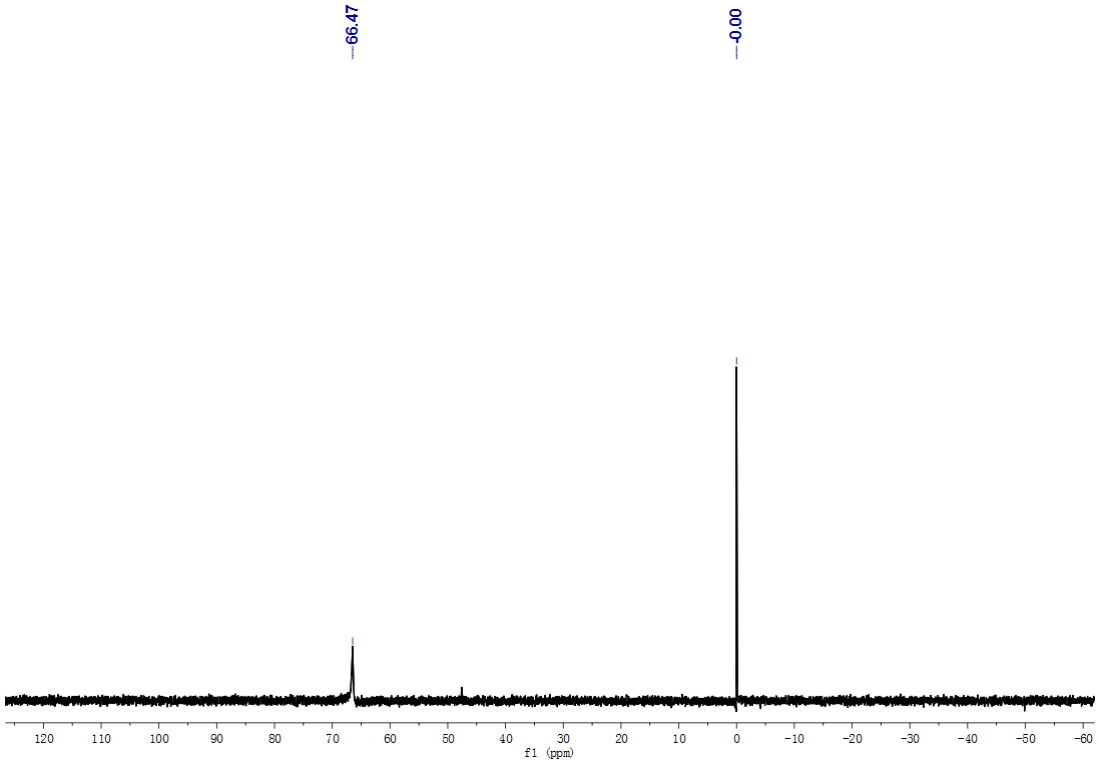


Figure S7. The ^{31}P NMR spectrum for the reaction of **1'** with styrene oxide.

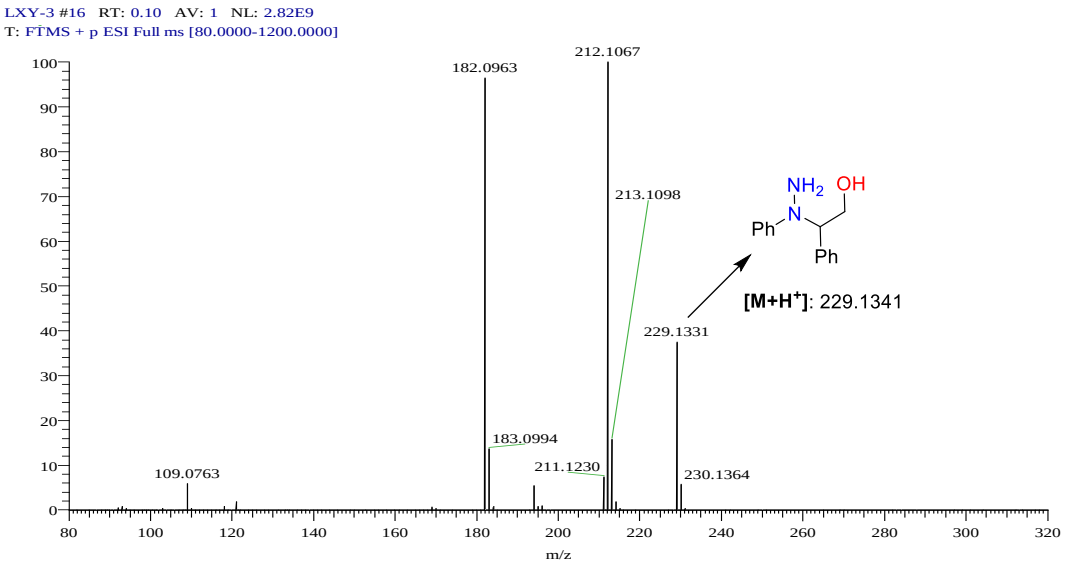
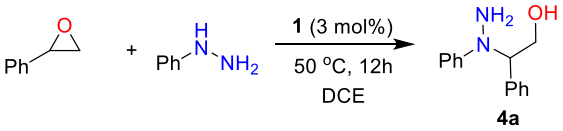


Figure S8. The MS (ESI) analysis for **4a** in the reaction of **1'** with styrene oxide.

2.4 Survey of reaction conditions.

Table S1. Optimization of reaction conditions.[a]

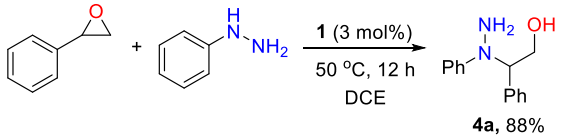


4a

Entry	Cat	Temperature	Solvent	Yield/%[b]
1	NO	25 °C	MeCN	0%
2	NO	50 °C	MeCN	0%
3	1	50 °C	MeCN	61%
4	1	50 °C	THF	43%
5	1	50 °C	$CHCl_3$	67%
6	1	50 °C	Tol	35%
7	1	50 °C	DCE	81%
8[c]	1	50 °C	DCE	92%
9	$Co(acac)_3$	50 °C	DCE	0%
10	$[Cp_2Co]PF_6$	50 °C	DCE	0%
11	$[Co(NH_3)_6]Cl_3$	50 °C	DCE	0%
12	1'	50 °C	DCE	90%

[a]Reaction conditions: styrene oxide (0.2 mmol), phenylhydrazine (0.2 mmol), cat (3 mol%), DCE (2 mL), 50 °C for 12 h under N_2. [b]Isolated yield. [c]phenylhydrazine (0.24 mmol).

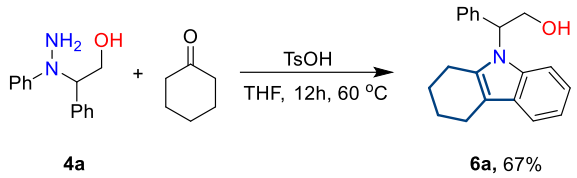
2.5 The gram scale reaction.



Scheme S4. The gram scale reaction for the synthesis of **4a**.

According to optimized conditions, **2a** styrene oxide (720 mg, 6.0 mmol, 1 equiv), phenylhydrazine (780 mg, 7.2 mmol, 1.2 equiv), **1** (110 mg, 0.18 mmol, 3 mol%), were added into 20 mL DCE. After stirring for 12 h at 50 ℃ under N_2, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product **4a** (1.204 g, 88%) as yellow solid. The product should be protected from light to avoid decomposition.

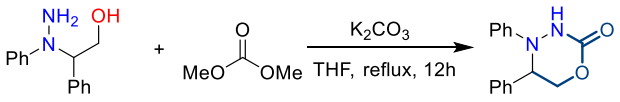
2.6 Synthetic applications of hydrazinoalcohol product.



4a **6a**, 67%

Scheme S5. Procedure for the synthesis of **6a**.

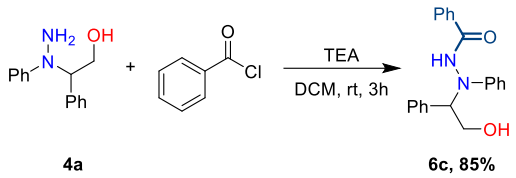
In an oven-dried Schlenk tube, **4a** (69 mg, 0.3 mmol) and a stoichiometric amount of cyclohexanone (30 mg, 0.3 mmol) was dissolved in THF (4 mL). Then *p*-toluenesulphonic acid (103 mg, 0.6 mmol) was added and the reaction mixture was stirred at 60 ℃ under nitrogen atmosphere for 12 h. Then, the solvent was concentrated by vacuo and the crude product was purified by flash column chromatography to give the title compound as yellow oil (60 mg, 67% yield).[3]



4a **6b**, 88%

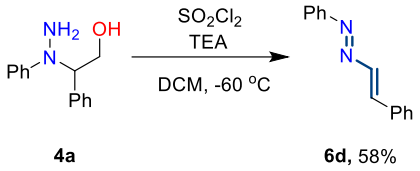
Scheme S6. Procedure for the synthesis of **6b**.

Dimethyl carbonate (135 mg, 1.5 mmol) and **4a** (69 mg, 0.3 mmol) were added to an oven-dried Schlenk tube containing THF (5 mL) and K_2CO_3 (83 mg, 0.6 mmol). The reaction mixture was refluxed for 12 h and then the mixture was concentrated. The crude product was purified by flash column chromatography, affording the title compound as white solid (67 mg, 88% yield).[4]



Scheme S7. Procedure for the synthesis of **6c**.

To an oven-dried Schlenk tube containing DCM (5 mL), trimethylamine (122 mg, 1.2 mmol) and **4a** (69 mg, 0.3 mmol) and were added under air. Subsequently, benzoyl chloride (42 mg, 0.3 mmol) in DCM (2 mL) was added dropwise. The reaction mixture was stirred for 3 h at room temperature and then the mixture was concentrated. Purification of the resulting residue by flash column chromatography on silica gel afforded product as yellow solid (85 mg, 85% yield).

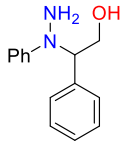


Scheme S8. Procedure for the synthesis of **6d**.

To a round bottom flask, **4a** (69 mg, 0.3 mmol) and trimethylamine (122 mg, 1.2 mmol) were added under nitrogen atmosphere. Then sulfonychloride (50 mg, 0.36 mmol) in DCM (5 mL) was added subsequently. After stirring the mixture at -60 °C temperature for 5 h, the mixture was diluted with DCM (5 mL) and washed with water (3 × 10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. Then the crude product was purified by flash column chromatography to give the desired compound as red solid (36 mg, 58% yield).

3. Experimental details and characterization data of the products.

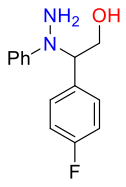
2-phenyl-2-(1-phenylhydrazinyl)ethan-1-ol (4a).



4a

Yellow solid, 42 mg, 92% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.26 (m, 4H), 7.25 – 7.22 (m, 1H), 7.19 – 7.14 (m, 2H), 6.98 – 6.89 (m, 2H), 6.73 – 6.61 (m, 1H), 4.89 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.18 (dd, *J* = 11.3, 8.2 Hz, 1H), 3.98 – 3.77 (m, 3H), 3.50 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.86, 140.44, 129.83, 129.26, 128.66, 118.42, 128.15, 113.57, 66.16, 64.58. HRMS (ESI) Calcd for $C_{14}H_{17}N_2O$ [M+H$^+$]: 229.1341; Found: 229.1334.

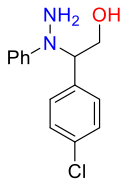
2-(4-fluorophenyl)-2-(1-phenylhydrazinyl)ethan-1-ol (4b)



4b

Yellow oil, 47 mg, 95% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.40 – 7.26 (m, 2H), 7.22 – 7.15 (m, 2H), 7.08 – 6.99 (m, 2H), 6.97 – 6.91 (m, 2H), 6.74 – 6.66 (m, 1H), 4.89 (dd, *J* = 8.0, 4.5 Hz, 1H), 4.16 (dd, *J* = 11.3, 8.0 Hz, 1H), 3.91 – 3.87 (dd, 11.3Hz, 4.5Hz, 1H), 3.84 (s, 2H). ^{19}F {1H} NMR (471 MHz, CD_3CN) δ -116.83 (s). ^{13}C NMR (126 MHz, CD_3CN) δ 162.85 (d, *J* = 243.1 Hz), 152.74, 136.41 (d, *J* = 3.1 Hz), 130.55 (d, *J* = 8.0 Hz), 129.86, 118.60, 115.80 (d, *J* = 21.3 Hz), 113.63, 65.44, 64.45. HRMS (ESI) Calcd for $C_{14}H_{16}FN_2O$ [M+H$^+$]: 247.1247; Found: 247.1251.

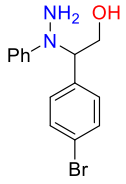
2-(4-chlorophenyl)-2-(1-phenylhydrazinyl)ethan-1-ol (4c)



4c

Yellow oil, 49 mg, 94% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.26 (m, 4H), 7.22 – 7.11 (m, 2H), 6.98 – 6.86 (m, 2H), 6.75 – 6.62 (m, 1H), 4.88 (dd, *J* = 7.8, 4.4 Hz, 1H), 4.15 (dd, *J* = 11.3, 7.8 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.82 (s, 2H).. ^{13}C NMR (126 MHz, CD_3CN) δ 152.59, 139.36, 133.25, 130.37, 129.86, 129.15, 118.59, 113.51, 65.43, 64.38. HRMS (ESI) Calcd for $C_{14}H_{16}ClN_2O$ [M+H$^+$]: 263.0951; Found: 263.0949.

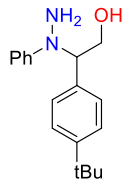
2-(4-bromophenyl)-2-(1-phenylhydrazinyl)ethan-1-ol (4d)



4d

Yellow solid, 56 mg, 92% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.46 – 7.43 (m, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 6.97 – 6.88 (m, 2H), 6.75 – 6.66 (m, 1H), 4.86 (dd, *J* = 7.8, 4.4 Hz, 1H), 4.15 (dd, *J* = 11.4, 7.8 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.58, 139.84, 132.16, 130.74, 129.88, 121.40, 118.64, 113.55, 65.51, 64.36. HRMS (ESI) Calcd for $C_{14}H_{16}BrN_2O$ [M+H$^+$]: 307.0446; Found: 307.0448.

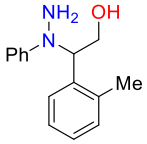
2-(4-(tert-butyl)phenyl)-2-(1-phenylhydrazinyl)ethan-1-ol (4e)



4e

White solid, 51 mg, 90% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.38 – 7.32 (m, 2H), 7.27 – 7.13 (m, 4H), 6.99 – 6.93 (m, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 4.90 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.19 (dd, *J* = 11.0, 8.4 Hz, 1H), 4.05 – 3.82 (m, 3H), 3.47 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.93, 151.02, 137.27, 129.85, 128.44, 126.19, 118.37, 113.53, 65.67, 64.58, 35.06, 31.58. HRMS (ESI) Calcd for $C_{18}H_{25}N_2O$ [M+H$^+$]: 285.1967; Found: 285.1961.

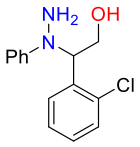
2-(1-phenylhydrazinyl)-2-(o-tolyl)ethan-1-ol (4f)



4f

White solid, 43 mg, 88% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.27 (m, 1H), 7.23 – 7.07 (m, 5H), 6.89 – 6.78 (m, 2H), 6.69 – 6.62 (m, 1H), 4.96 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.11 (dd, *J* = 11.6, 7.9 Hz, 1H), 3.97 (s, 2H), 3.84 (dd, *J* = 11.6, 4.1 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.42, 139.21, 136.91, 131.49, 129.80, 128.07, 128.04, 126.79, 118.13, 113.06, 63.61, 63.28, 19.58. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O$ [M+H$^+$]: 243.1497; Found: 243.1490.

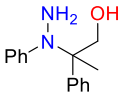
2-(2-chlorophenyl)-2-(1-phenylhydrazinyl)ethan-1-ol (4g)



4g

White solid, 49 mg, 93% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.48 – 7.44 (m, 1H), 7.43 – 7.39 (m, 1H), 7.25 – 7.19 (m, 2H), 7.19 – 7.09 (m, 2H), 6.86 – 6.76 (m, 2H), 6.73 – 6.63 (m, 1H), 5.16 (dd, *J* = 7.5, 3.9 Hz, 1H), 4.25 – 4.00 (m, 3H), 3.91 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.76 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.02, 138.86, 133.83, 130.44, 130.15, 129.91, 129.73, 128.03, 118.40, 112.77, 63.52, 63.23. HRMS (ESI) Calcd for $C_{14}H_{16}ClN_2O$ [M+H$^+$]: 263.0951; Found: 263.0997.

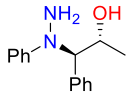
2-phenyl-2-(1-phenylhydrazinyl)propan-1-ol (4h)



4h

White solid, 39 mg, 81% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.53 – 7.39 (m, 2H), 7.38 – 7.27 (m, 2H), 7.26 – 7.16 (m, 1H), 7.05 – 6.91 (m, 2H), 6.75 – 6.46 (m, 3H), 4.38 (s, 2H), 3.83 (d, *J* = 11.7 Hz, 1H), 3.43 (d, *J* = 11.6 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 151.23, 146.24, 129.37, 128.94, 127.60, 127.04, 119.32, 117.49, 74.02, 67.64, 16.74. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O$ [M+H$^+$]: 243.1497; Found: 243.1500.

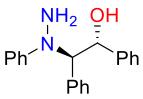
1-phenyl-1-(1-phenylhydrazinyl)propan-2-ol (4i)



4i

White solid, 35 mg, 73% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.46 – 7.36 (m, 2H), 7.33 – 7.21 (m, 3H), 7.20 – 7.07 (m, 2H), 6.94 – 6.83 (m, 2H), 6.70 – 6.64 (t, *J* = 7.3 Hz, 1H), 4.60 – 4.52 (m, 2H), 4.24 (s, 1H), 3.95 (s, 2H), 1.19 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.29, 139.68, 130.33, 129.81, 128.72, 128.03, 118.58, 113.54, 69.59, 69.44, 21.22. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O$ [M+H$^+$]: 243.1497; Found: 243.1498.

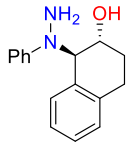
1,2-diphenyl-2-(1-phenylhydrazinyl)ethan-1-ol (4j)



4j

White solid, 41 mg, 67% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.22 (m 4H), 7.15 – 7.07 (m, 2H), 6.86 – 6.81 (m, 2H), 6.68 – 6.61 (m, 1H), 5.56 (d, *J* = 6.3 Hz, 1H), 4.97 (d, *J* = 6.3 Hz, 1H), 4.68 (s, 1H), 3.89 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.02, 144.24, 138.95, 130.25, 129.78, 128.82, 128.60, 128.13, 128.10, 127.88, 118.71, 113.49, 75.81, 69.97. HRMS (ESI) Calcd for $C_{20}H_{21}N_2O$ [M+H$^+$]: 305.1654; Found: 305.1645.

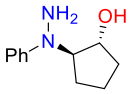
Trans-1-(1-phenylhydrazinyl)-1,2,3,4-tetrahydronaphthalen-2-ol (4k)



4k

White solid, 41 mg, 80% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.26 – 7.18 (m, 2H), 7.16 – 7.07 (m, 4H), 7.05 – 7.01 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.66 (m, 1H), 4.93 (d, *J* = 8.7 Hz, 1H), 4.18 (ddd, *J* = 12.2, 8.7, 3.7 Hz, 1H), 3.52 (s, 2H), 3.23 (s, 1H), 3.02 – 2.76 (m, 2H), 2.14 (m, 1H), 1.99 – 1.78 (m, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 154.56, 139.00, 136.53, 130.01, 129.88, 127.71, 127.34, 126.91, 117.89, 113.16, 68.61, 68.36, 31.36, 28.99. HRMS (ESI) Calcd for $C_{16}H_{19}N_2O$ [M+H$^+$]: 255.1497; Found: 255.1500.

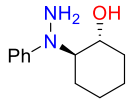
Trans-2-(1-phenylhydrazinyl)cyclopentan-1-ol (4l)



4l

White solid, 32 mg, 82% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.31 – 7.11 (m, 2H), 7.10 – 6.96 (m, 2H), 6.72 – 6.64 (m, 1H), 4.32 (ddd, *J* = 12.8, 6.7, 2.5 Hz, 1H), 3.91 (ddd, *J* = 11.3, 8.2, 3.1 Hz, 1H), 3.50 (s, 2H), 3.01 (s, 1H), 1.93 – 1.78 (m, 2H), 1.77 – 1.62 (m, 2H), 1.62 – 1.47 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 154.00, 129.82, 118.70, 114.79, 75.05, 69.49, 33.53, 25.04, 21.46. HRMS (ESI) Calcd for $C_{11}H_{17}N_2O$ [M+H$^+$]: 193.1341; Found: 193.1346.

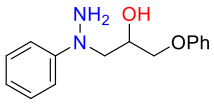
Trans-2-(1-phenylhydrazinyl)cyclohexan-1-ol (4m)



4m

White solid, 35 mg, 84% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.27 – 7.11 (m, 2H), 7.07 – 6.96 (m, 2H), 6.73 – 6.63 (m, 1H), 3.84 (ddd, *J* = 10.6, 9.4, 4.4 Hz, 1H), 3.53 (s, 2H), 3.39 (ddd, *J* = 11.7, 9.2, 3.9 Hz, 1H), 2.99 (s, 1H), 2.04 – 1.97 (m, 1H), 1.73 – 1.65 (m, 2H), 1.56 (dd, *J* = 8.7, 5.9 Hz, 1H), 1.51 – 1.40 (m, 1H), 1.38 – 1.23 (m, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 153.58, 129.81, 118.31, 114.11, 70.53, 66.71, 34.67, 25.83, 25.64, 25.32. HRMS (ESI) Calcd for $C_{12}H_{19}N_2O$ [M+H$^+$]: 207.1497; Found: 207.1498.

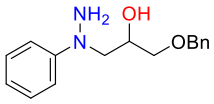
3-phenoxy-2-(1-phenylhydrazinyl)propan-1-ol (4n)



4n

Yellow solid, 45 mg, 86% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.13 (m, 2H), 7.10 – 6.85 (m, 5H), 6.78 – 6.69 (m, 1H), 4.33 – 4.27 (m, 1H), 4.15 – 3.90 (m, 4H), 3.58 (dd, *J* = 14.1, 4.2 Hz, 1H), 3.48 (dd, *J* = 14.1, 6.9 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.91, 153.61, 130.50, 129.80, 121.73, 118.94, 115.49, 114.03, 70.88, 69.63, 58.41. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O_2$ [M+H$^+$]: 259.1447; Found: 259.1446.

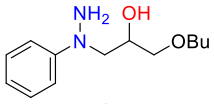
3-(benzyloxy)-2-(1-phenylhydrazinyl)propan-1-ol (4o)



4o

Yellow solid, 47 mg, 84% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.40 – 7.35(m, 4H), 7.31 (m, 1H), 7.25 – 7.17 (m, 2H), 7.06 – 6.94 (m, 2H), 6.80 – 6.60 (m, 1H), 4.55 (s, 2H), 4.15 – 4.10 (m, 1H), 3.95 (s, 2H), 3.58 – 3.48 (m, 3H), 3.37 (dd, *J* = 14.2, 7.2 Hz, 1H).^{13}C NMR (126 MHz, CD_3CN) δ 153.63, 139.79, 129.78, 129.32, 128.70, 128.50, 118.71, 113.99, 73.88, 73.49, 70.02, 58.93. HRMS (ESI) Calcd for $C_{16}H_{20}N_2O_2$ [M+H$^+$]: 273.1603; Found: 273.1593 .

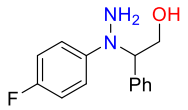
3-butoxy-2-(1-phenylhydrazinyl)propan-1-ol(4p)



4p

Yellow oil, 38 mg, 79% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.28 – 7.14 (m, 2H), 7.06 – 6.91 (m, 2H), 6.77 – 6.64 (m, 1H), 4.09 – 4.02 (m, 1H), 3.90 (s, 2H), 3.51 – 3.37 (m, 5H), 3.33 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.58 – 1.52 (m, 2H), 1.42 – 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, CD_3CN) δ 153.64, 129.76, 118.65, 113.94, 73.72, 71.79, 70.00, 58.96, 32.62, 20.10, 14.25. HRMS (ESI) Calcd for $C_{13}H_{23}N_2O_2$ [M+H$^+$]: 239.1760; Found: 239.1755.

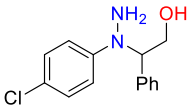
2-(1-(4-fluorophenyl)hydrazinyl)-2-phenylethan-1-ol (5a)



5a

Yellow oil, 46 mg, 92% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.37 –7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 7.09 – 6.80 (m, 4H), 4.84 (dd, *J* = 8.2, 4.4 Hz, 1H), 4.20 (dd, *J* = 11.3, 8.3 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.76 (s, 2H). ^{19}F {1H} NMR (471 MHz, CD_3CN) δ -129.36. ^{13}C NMR (126 MHz, CD_3CN) δ 156.82 (d, *J* = 234.2 Hz), 149.73, 139.81, 129.31, 128.76, 128.31, 115.97 (d, *J* = 22.2 Hz), 115.43 (d, *J* = 7.4 Hz), 67.15, 64.39. HRMS (ESI) Calcd for $C_{14}H_{16}FN_2O$ [M+H$^+$]: 247.1247; Found: 247.1248.

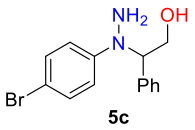
2-(1-(4-chlorophenyl)hydrazinyl)-2-phenylethan-1-ol (5b)



5b

Yellow oil, 47 mg, 90% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.37 – 7.28 (m, 4H), 7.28 – 7.22 (m, 1H), 7.17 – 7.11 (m, 2H), 7.04 – 6.84 (m, 2H), 4.87 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.18 (dd, *J* = 11.4, 8.3 Hz, 1H), 4.15 – 3.75 (m, 3H), 3.56 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 151.72, 139.84, 129.43, 129.36, 128.55, 128.30, 122.37, 114.92, 66.31, 64.21. Calcd for $C_{14}H_{16}ClN_2O$ [M+H$^+$]: 263.0951; Found: 263.0944.

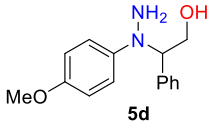
2-(1-(4-bromophenyl)hydrazinyl)-2-phenylethan-1-ol (5c)



5c

Yellow solid, 54 mg, 87% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.41 – 7.12 (m, 7H), 6.95 – 6.78 (m, 2H), 4.87 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.17 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.75 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.11, 139.85, 132.34, 129.37, 128.53, 128.31, 115.38, 109.46, 66.22, 64.20. HRMS (ESI) Calcd for $C_{14}H_{16}BrN_2O$ [M+H$^+$]: 307.0446; Found: 307.0448.

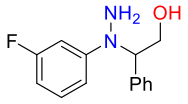
2-(1-(4-methoxyphenyl)hydrazinyl)-2-phenylethan-1-ol (5d)



5d

Yellow oil, 42 mg, 81% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.35 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 6.98 – 6.87 (m, 2H), 6.83 – 6.73 (m, 2H), 4.75 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.17 (dd, *J* = 11.2, 8.2 Hz, 1H), 3.85 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.72 (s, 2H), 3.69 (s, 5H). ^{13}C NMR (126 MHz, CD_3CN) δ 153.86, 147.42, 140.00, 129.17, 128.99, 128.21, 116.68, 115.19, 67.75, 64.84, 56.10. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O_2$ [M+H$^+$]: 259.1447; Found: 259.1448.

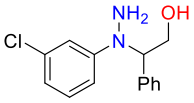
2-(1-(3-fluorophenyl)hydrazinyl)-2-phenylethan-1-ol (5e)



5e

Yellow oil, 43 mg, 84% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.35 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 7.17 – 7.11 (m, 1H), 6.78 – 6.64 (m, 2H), 6.48 – 6.27 (m, 1H), 4.91 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.20 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.93 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.80 (s, 2H). ^{19}F {1H} NMR (471 MHz, CD_3CN) δ -114.19 (s). ^{13}C NMR (126 MHz, CD_3CN) δ 164.79 (d, *J* = 239.6 Hz), 154.79 (d, *J* = 10.3 Hz), 139.90, 131.06 (d, *J* = 10.3 Hz), 129.33, 128.41, 128.25, 108.97 (d, *J* = 2.0 Hz), 104.04 (d, *J* = 21.8 Hz), 100.00 (d, *J* = 27.0 Hz), 66.00, 64.16. HRMS (ESI) Calcd for $C_{14}H_1FN_2O$ [M+H$^+$]: 247.1247; Found: 247.1253.

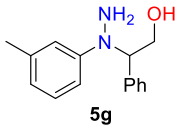
2-(1-(3-chlorophenyl)hydrazinyl)-2-phenylethan-1-ol (5f)



5f

Yellow oil, 42 mg, 80% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.29 (m, 4H), 7.29 – 7.20 (m, 1H), 7.12 (t, *J* = 8.2 Hz, 1H), 7.00 (t, *J* = 2.2 Hz, 1H), 6.73 – 6.55 (m, 1H), 6.66 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.90 (dd, *J* = 8.3, 4.4 Hz, 1H), 4.17 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.91 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.78 (s, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 154.18, 139.91, 135.35, 131.08, 129.42, 128.48, 128.34, 117.59, 112.97, 111.72, 66.07, 64.18. HRMS (ESI) Calcd for $C_{14}H_{16}ClN_2O$ [M+H$^+$]: 263.0951; Found: 263.0944.

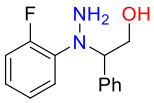
2-phenyl-2-(1-(m-tolyl)hydrazinyl)ethan-1-ol (5g)



5g

White solid, 38 mg, 78% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.34 – 7.27 (m, 4H), 7.26 – 7.19 (m, 1H), 7.07 – 7.04 (m, 1H), 6.82 (s, 1H), 6.74 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.53 (d, *J* = 7.4 Hz, 1H), 4.90 (dd, *J* = 8.1, 4.4 Hz, 1H), 4.19 (dd, *J* = 11.3, 8.1 Hz, 1H), 3.90 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.74 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 153.03, 140.49, 139.53, 129.74, 129.25, 128.71, 128.14, 119.42, 114.37, 110.93, 66.19, 64.57, 21.92. HRMS (ESI) Calcd for $C_{15}H_{19}N_2O$ [M+H$^+$]: 243.1497; Found: 243.1494.

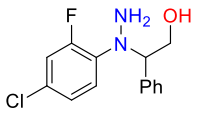
2-(1-(2-fluorophenyl)hydrazinyl)-2-phenylethan-1-ol (5h)



5h

Yellow oil, 47 mg, 83% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.33 – 7.19 (m, 5H), 7.10 – 7.02 (m, 2H), 7.00 – 6.96 (m, 1H), 6.95 – 6.89 (m, 1H), 4.65 (dd, *J* = 8.1, 4.8 Hz, 1H), 4.20 (ddd, *J* = 11.0, 8.2, 1.2 Hz, 1H), 3.83 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.72 (s, 3H). ^{19}F{^{1}H} NMR (471 MHz, CD_3CN) δ -123.02 (s). ^{13}C NMR (126 MHz, CD_3CN) δ 155.36 (d, *J* = 243.0 Hz), 141.99 (d, *J* = 8.2 Hz), 138.69, 129.31, 129.14, 128.55, 125.16 (d, *J* = 3.4 Hz), 123.85 (d, *J* = 7.9 Hz), 121.97 (d, *J* = 2.6 Hz), 116.88 (d, *J* = 21.1 Hz), 69.65 (d, *J* = 5.0 Hz), 64.37. HRMS (ESI) Calcd for $C_{14}H_{16}FN_2O$ [M+H$^+$]: 247.1247; Found: 247.1255.

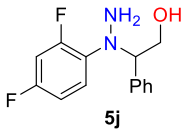
2-(1-(4-chloro-2-fluorophenyl)hydrazinyl)-2-phenylethan-1-ol (5i)



5i

White solid, 48 mg, 86% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.20 (m, 5H), 7.14 (dd, *J* = 12.5, 2.1 Hz, 1H), 7.08 – 6.95 (m, 2H), 4.64 (dd, *J* = 8.1, 5.0 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.85 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.77 (s, 2H), 3.44 (s, 1H). ^{19}F{^{1}H} NMR (471 MHz, CD_3CN) δ -120.02 (s). ^{13}C NMR (126 MHz, CD_3CN) δ 154.56 (d, *J* = 246.9 Hz), 141.28 (d, *J* = 8.2 Hz), 138.22, 129.24 (d, *J* = 5.7 Hz), 128.67, 126.87 (d, *J* = 10.0 Hz), 125.11 (d, *J* = 3.4 Hz), 122.73 (d, *J* = 3.5 Hz), 117.47, 117.27, 69.61 (d, *J* = 5.4 Hz), 63.70. HRMS (ESI) Calcd for $C_{14}H_{14}ClFN_2O$ [M+H$^+$]: 281.0857; Found: 281.0852.

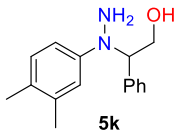
2-(1-(2,4-difluorophenyl)hydrazinyl)-2-phenylethan-1-ol (5j)



5j

Yellow solid, 48 mg, 90% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.31 – 7.17 (m, 5H), 7.08 – 7.01 (m, 1H), 6.94 – 6.88 (m, 1H), 6.83 – 6.72 (m, 1H), 4.52 (dd, *J* = 8.1, 4.8 Hz, 1H), 4.16 (ddd, *J* = 11.3, 8.1, 1.2 Hz, 1H), 3.79 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.72 (s, 2H). ^{19}F{^{1}H} NMR (471 MHz, CD_3CN) δ -118.78 (d, *J* = 5.0 Hz), -120.10 (d, *J* = 5.1 Hz). ^{13}C NMR (126 MHz, CD_3CN) δ 159.07 (dd, *J* = 241.4, 11.7 Hz), 155.62 (dd, *J* = 247.1, 12.1 Hz), 138.68 (dd, *J* = 8.9, 3.5 Hz), 138.38, 129.40, 129.18, 128.65, 123.71 (dd, *J* = 9.4, 3.9 Hz), 111.36 (dd, *J* = 21.7, 3.6 Hz), 105.14 (dd, *J* = 26.5, 25.3 Hz), 70.23 (d, *J* = 4.1 Hz), 64.50. HRMS (ESI) Calcd for $C_{14}H_{15}F_2N_2O$ [M+H$^+$]: 265.1152; Found: 265.1153.

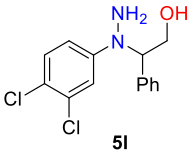
2-(1-(3,4-dimethylphenyl)hydrazinyl)-2-phenylethan-1-ol (5k)



5k

White solid, 30 mg, 58% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.15 (m, 5H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.66 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.84 (dd, *J* = 8.0, 4.3 Hz, 1H), 4.17 (dd, *J* = 11.2, 8.2 Hz, 1H), 3.87 (dd, *J* = 11.2, 4.2 Hz, 1H), 3.79 (s, 2H), 3.54 (s, 1H), 2.17 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 151.32, 140.46, 137.78, 130.85, 129.17, 128.82, 128.10, 126.78, 115.75, 111.75, 66.50, 64.69, 20.35, 18.65. HRMS (ESI) Calcd for $C_{16}H_{21}N_2O$ [M+H$^+$]: 257.1654; Found: 257.1649.

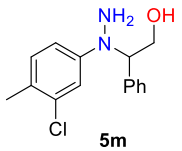
2-(1-(3,4-dichlorophenyl)hydrazinyl)-2-phenylethan-1-ol (5l)



5l

White solid, 55 mg, 92% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.34 – 7.21 (m, 6H), 7.14 (d, *J* = 2.9 Hz, 1H), 6.85 (dd, *J* = 9.1, 2.9 Hz, 1H), 4.88 (dd, *J* = 8.5, 4.4 Hz, 1H), 4.16 (dd, *J* = 11.5, 8.5 Hz, 1H), 3.97 (s, 2H), 3.91 (dd, *J* = 11.5, 4.4 Hz, 1H), 3.42 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.73, 139.41, 132.87, 131.14, 129.47, 128.45, 128.40, 119.56, 114.61, 113.27, 66.07, 63.87. HRMS (ESI) Calcd for $C_{14}H_{15}Cl_2N_2O$ [M+H$^+$]: 297.0561; Found: 297.0560.

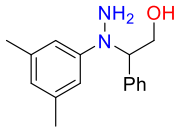
2-(1-(3-chloro-4-methylphenyl)hydrazinyl)-2-phenylethan-1-ol (5m)



5m

White solid, 48 mg, 87% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.87 (dd, *J* = 11.4, 2.6 Hz, 1H), 4.20 (dd, *J* = 11.4, 8.3 Hz, 1H), 4.05 – 3.75 (m, 3H), 3.58 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.32, 139.88, 135.18, 132.07, 129.34, 128.57, 128.28, 124.87, 113.92, 112.55, 66.31, 64.26, 18.88. HRMS (ESI) Calcd for $C_{15}H_{18}ClN_2O$ [M+H$^+$]: 277.1108; Found: 277.1097.

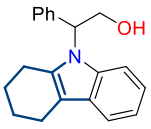
2-(1-(3,5-dimethylphenyl)hydrazinyl)-2-phenylethan-1-ol (5n)



5n

White solid, 32 mg, 62% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 – 7.26 (m, 4H), 7.26 – 7.20 (m, 1H), 6.60 (s, 2H), 6.37 (s, 1H), 4.89 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.18 (dd, *J* = 11.2, 8.2 Hz, 1H), 3.88 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.78 (s, 2H), 3.46 (s, 1H), 2.20 (s, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 153.16, 140.54, 139.35, 129.21, 128.72, 128.11, 120.47, 111.67, 66.12, 64.54, 21.80. HRMS (ESI) Calcd for $C_{16}H_{21}NO$ [M+H$^+$]: 257.1654; Found: 257.1646.

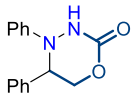
2-phenyl-2-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)ethan-1-ol (6a)



6a

Yellow oil, 60 mg, 67% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.41 – 7.36 (m, 1H), 7.29 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.96 – 6.87 (m, 2H), 5.59 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.41 (dd, *J* = 11.0, 5.9 Hz, 1H), 4.35 – 4.26 (m, 1H), 3.10 (s, 1H), 2.78 – 2.61 (m, 4H), 1.90 – 1.76 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 140.13, 137.58, 136.75, 129.41, 129.29, 128.27, 127.85, 121.11, 119.42, 118.51, 111.76, 110.48, 62.89, 60.07, 24.28, 24.00, 23.87, 21.86. HRMS (ESI) Calcd for $C_{20}H_{12}NO$ [M+H$^+$]: 292.1701; Found: 292.1697.

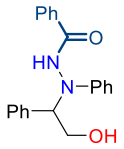
4,5-diphenyl-1,3,4-oxadiazinan-2-one (6b)



6b

White solid, 67 mg, 88% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 (m, 3H), 7.43 – 7.32 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 5.04 (d, *J* = 2.5 Hz, 1H), 4.75 (dd, *J* = 11.8, 1.2 Hz, 1H), 4.47 (dd, *J* = 11.8, 3.5 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 152.18, 151.20, 137.60, 130.44, 129.76, 129.00, 128.20, 123.90, 118.65, 66.67, 60.62. HRMS (ESI) Calcd for $C_{15}H_{15}N_2O_2$ [M+H$^+$]: 255.1134; Found: 255.1130.

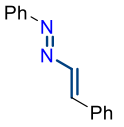
N'-(2-hydroxy-1-phenylethyl)-N'-phenylbenzohydrazide (6c)



6c

Yellow solid, 85 mg, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.15 (m, 8H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 5.29 (s, 1H), 4.73 (s, 1H), 4.09 – 3.96 (m, 1H), 3.95 – 3.85 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70, 148.41, 135.66, 132.68, 131.64, 129.44, 128.98, 128.97, 128.37, 127.54, 127.23, 120.53, 114.06, 65.35, 61.10. HRMS (ESI) Calcd for $C_{21}H_{21}N_2O_2$ [M+H$^+$]: 333.1603; Found: 316.1601.

(E)-1-phenyl-2-((E)-styryl)diazene (6d)



6d

Red solid, 36 mg, 58% yield. ^{1}H NMR (500 MHz, CD_3CN) δ 8.03 (d, *J* = 13.8 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.76 (d, *J* = 13.8 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.56 – 7.32 (m, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 153.89, 147.41, 143.57, 135.88, 131.97, 130.95, 130.32, 130.04, 129.12, 123.40. HRMS (ESI) Calcd for $C_{14}H_{13}N_2$ [M+H$^+$]: 209.1079; Found: 209.1082.

4. ^{1}H-NMR, ^{19}F-NMR and ^{13}C NMR spectra.

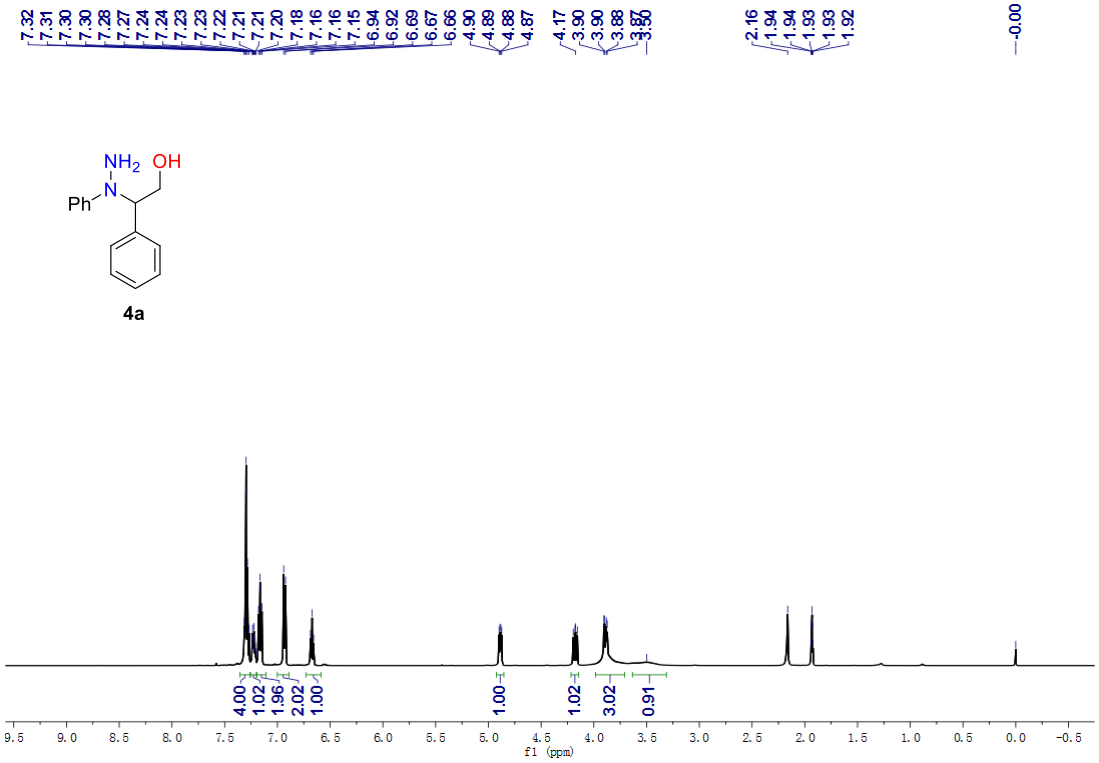


Figure S9. The ^{1}H-NMR spectral copy of compound **4a**.

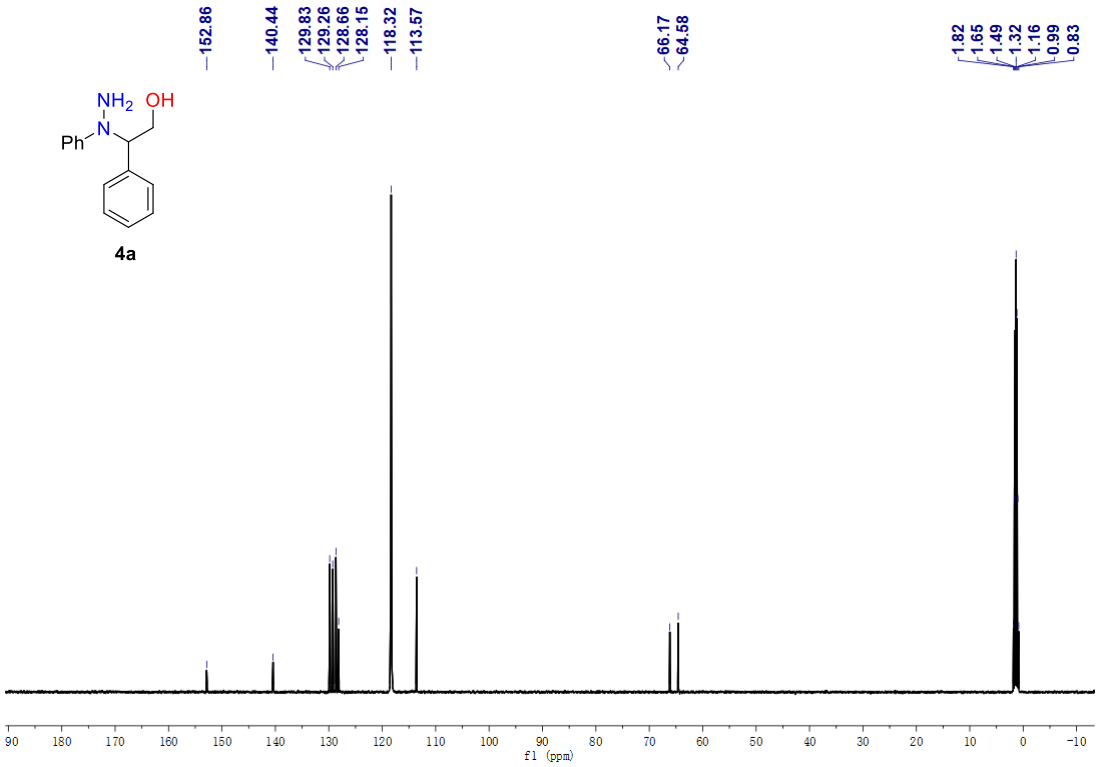


Figure S10. The ^{13}C-NMR spectral copy of compound **4a**.

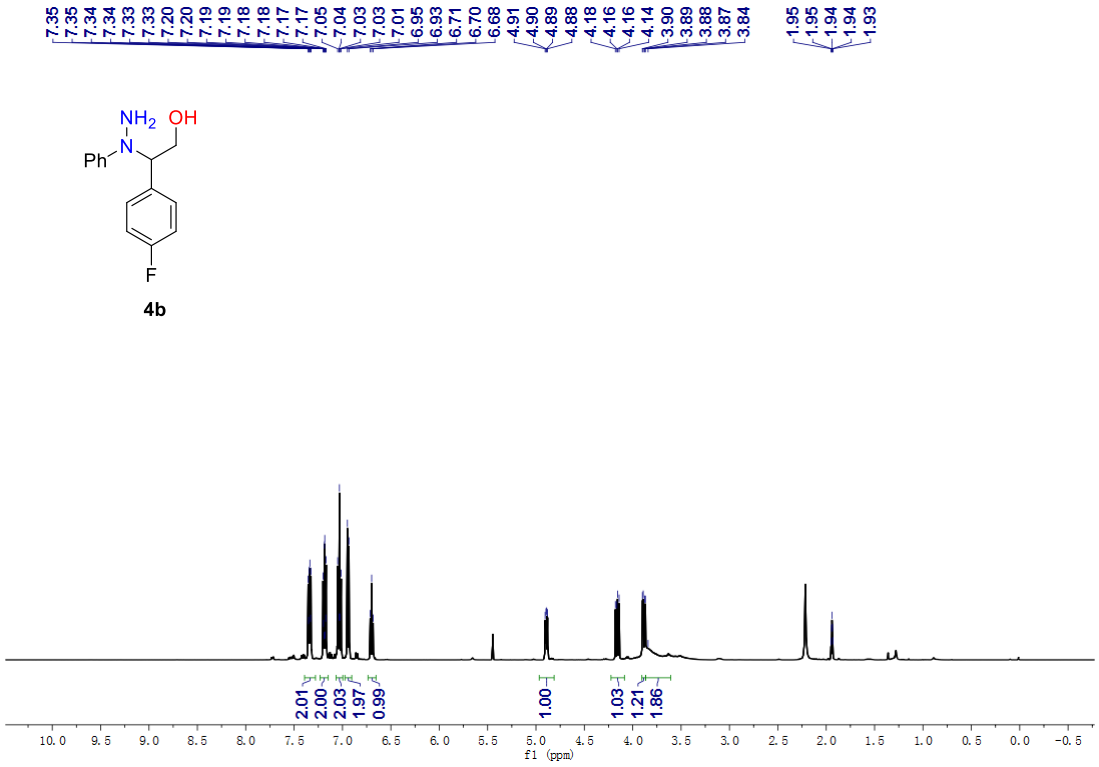


Figure S11. The ^{1}H-NMR spectral copy of compound **4b**.

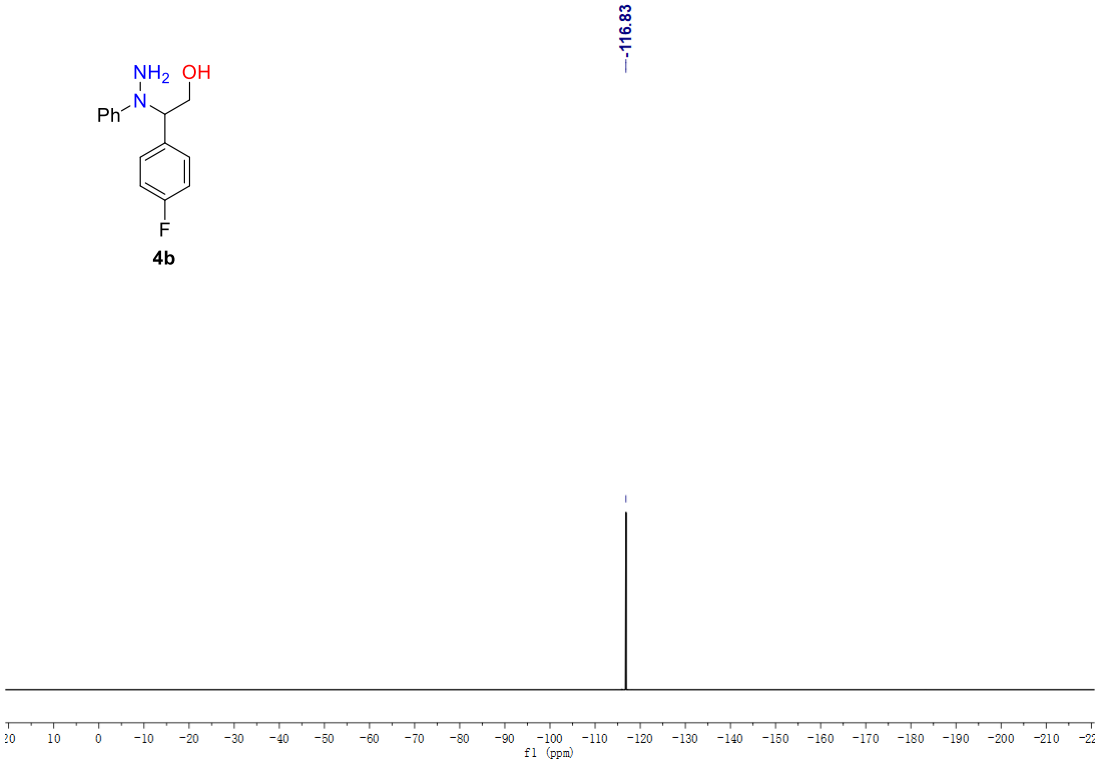


Figure S12. The ^{19}F-NMR spectral copy of compound **4b**.

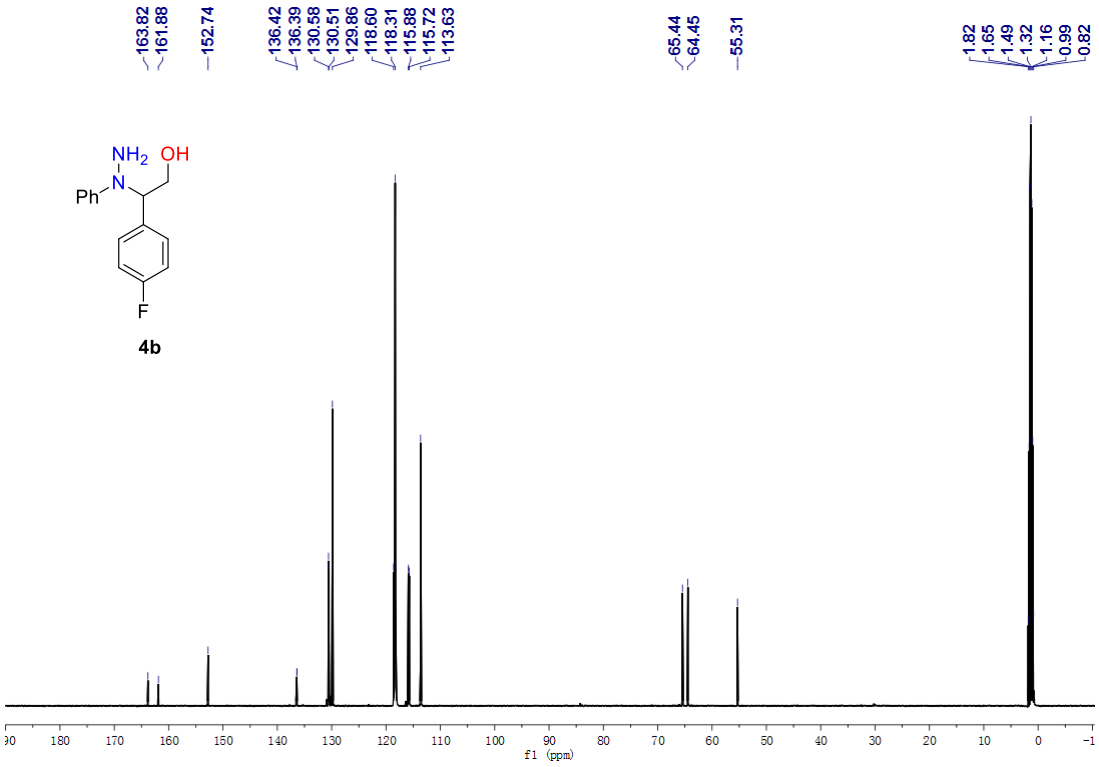


Figure S13. The ^{13}C-NMR spectral copy of compound **4b**.

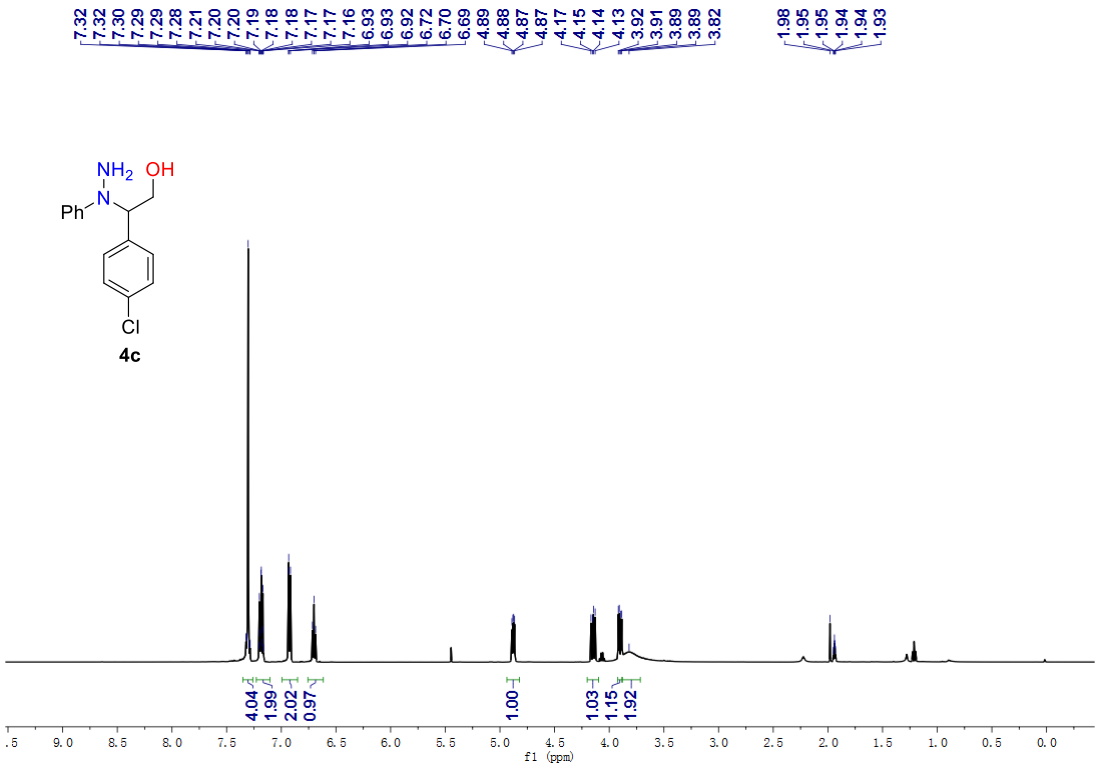


Figure S14. The ^{1}H-NMR spectral copy of compound **4c**.

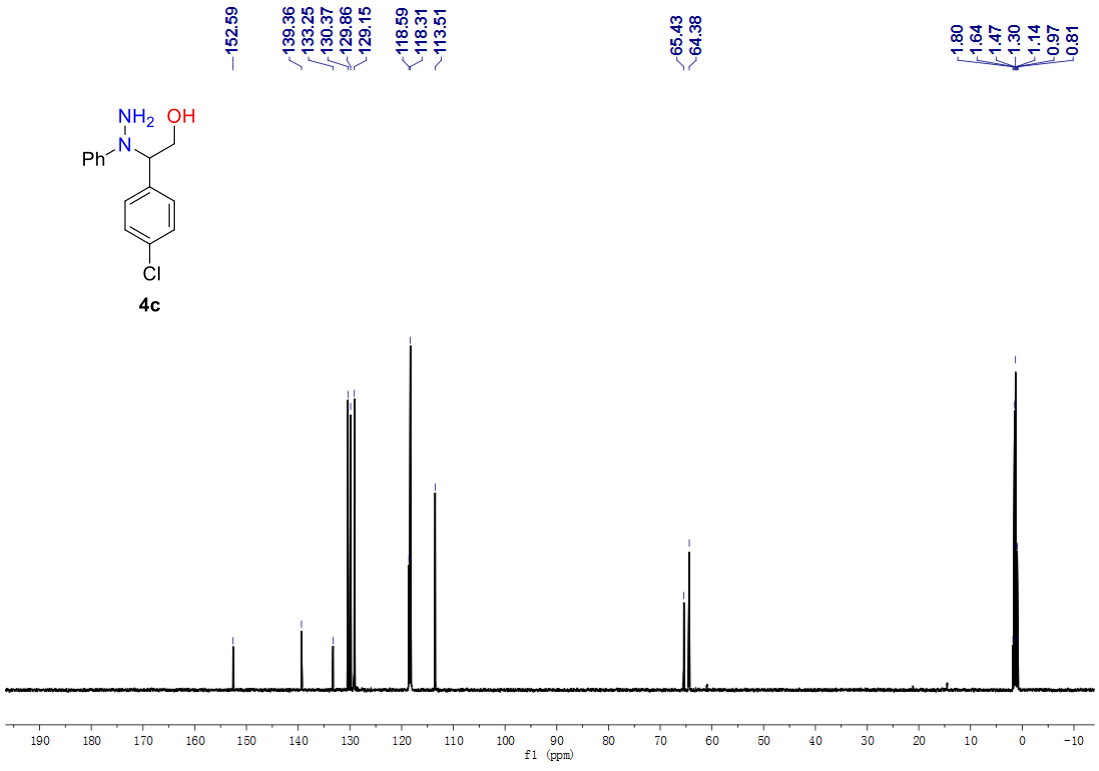


Figure S15. The ^{13}C-NMR spectral copy of compound **4c**.

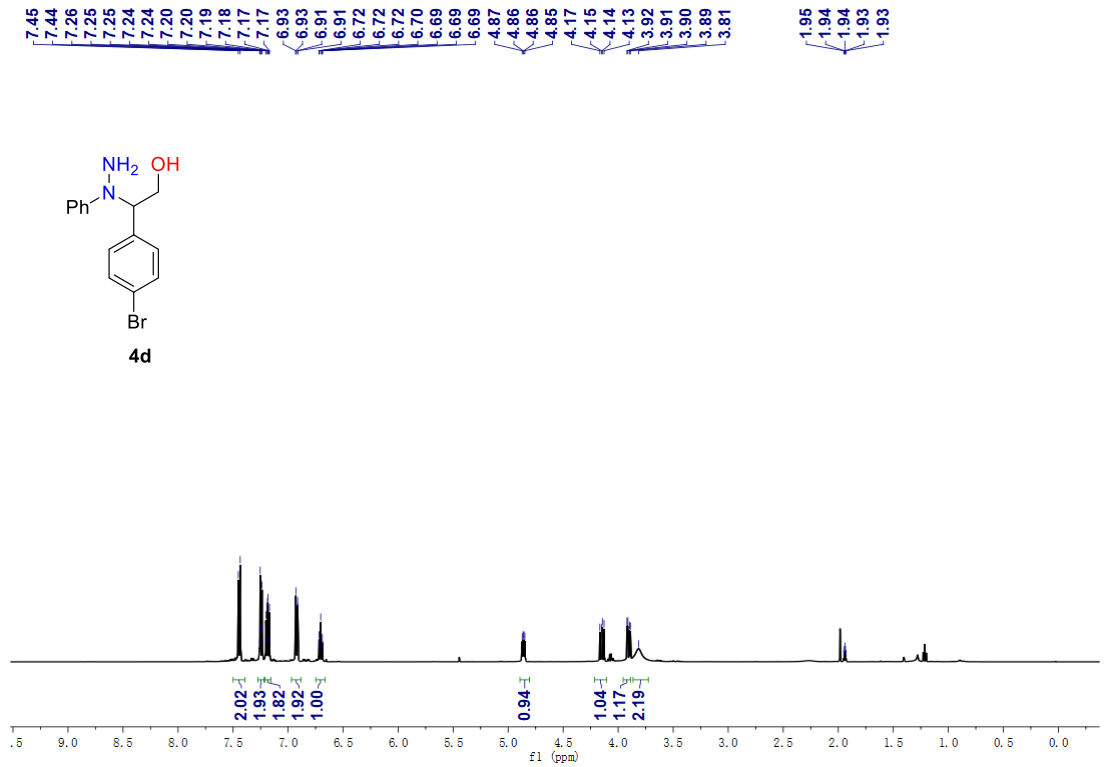


Figure S16. The ^{1}H-NMR spectral copy of compound **4d**.

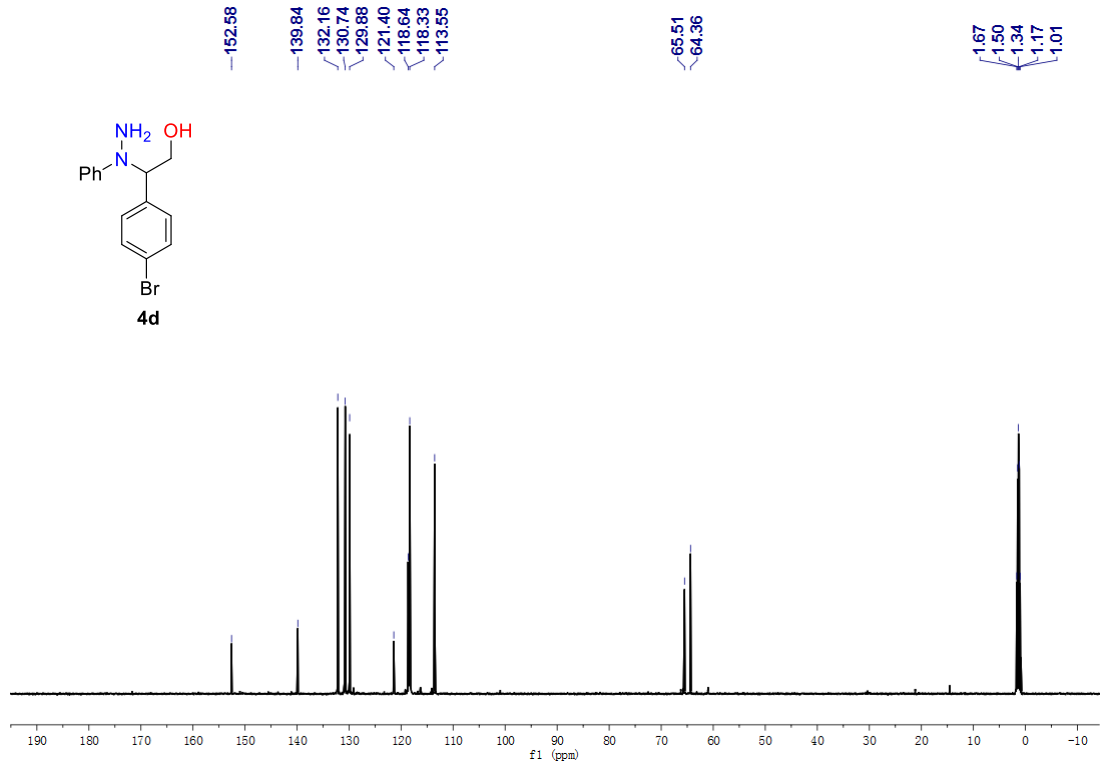


Figure S17. The ^{13}C-NMR spectral copy of compound **4d**.

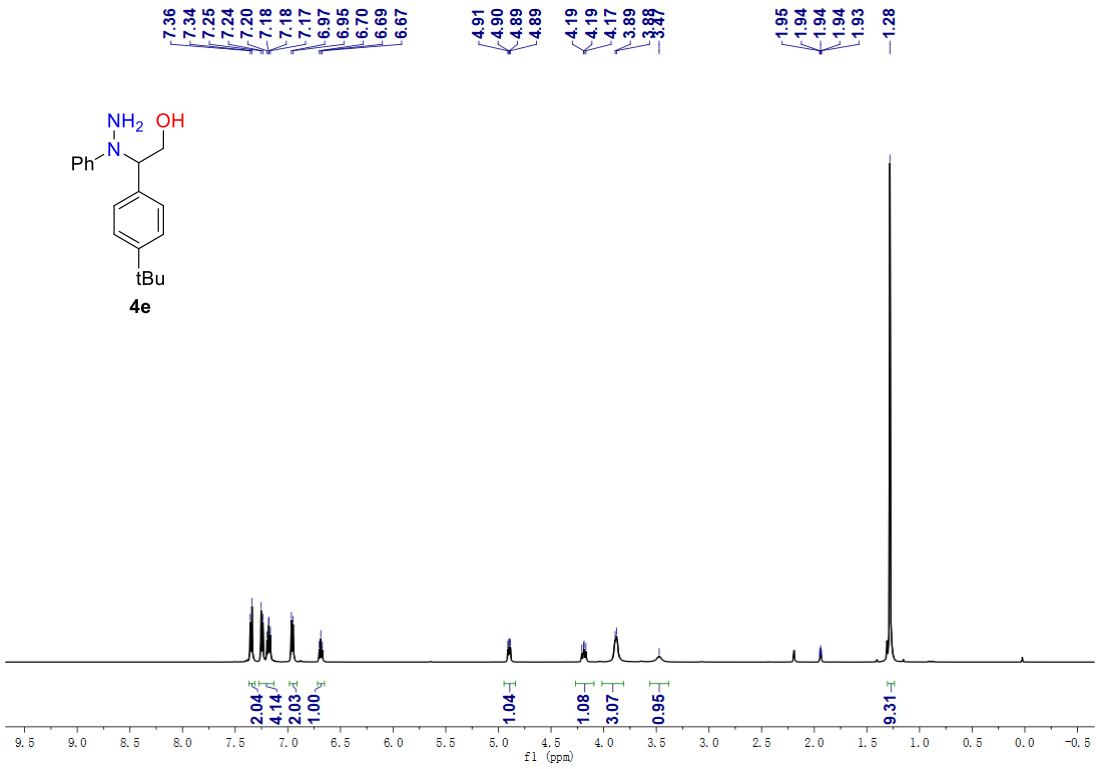


Figure S18. The ^{1}H-NMR spectral copy of compound **4e**.

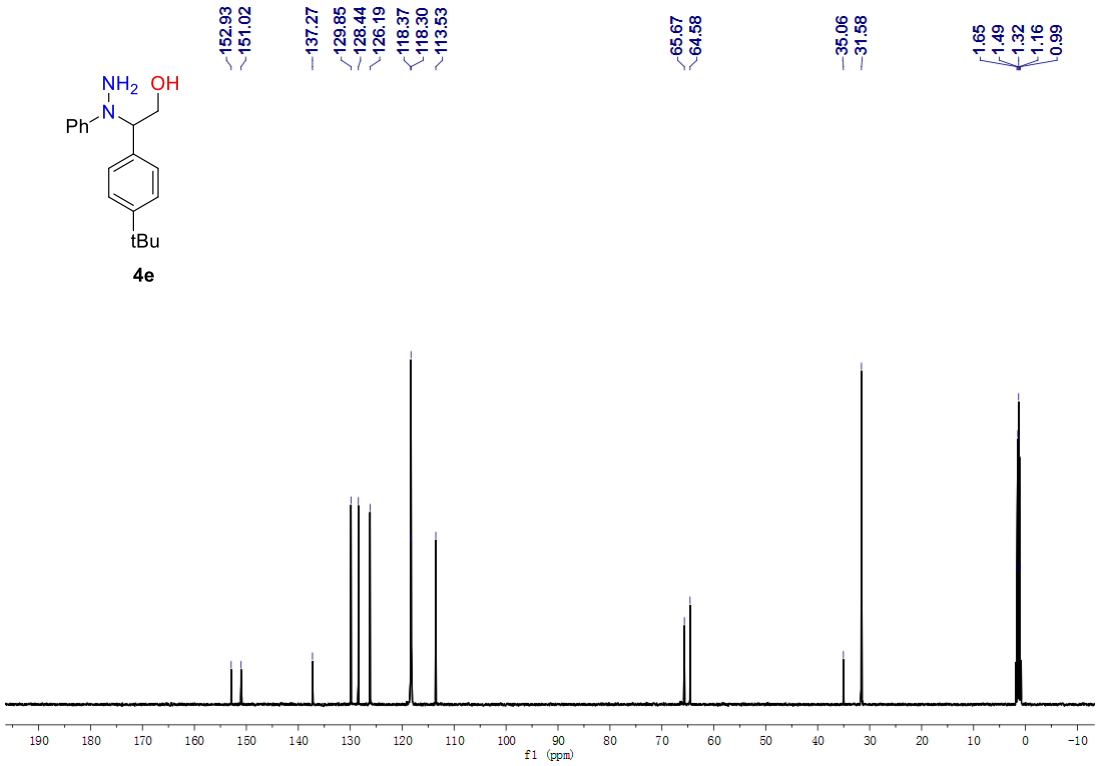


Figure S19. The ^{13}C-NMR spectral copy of compound **4e**.

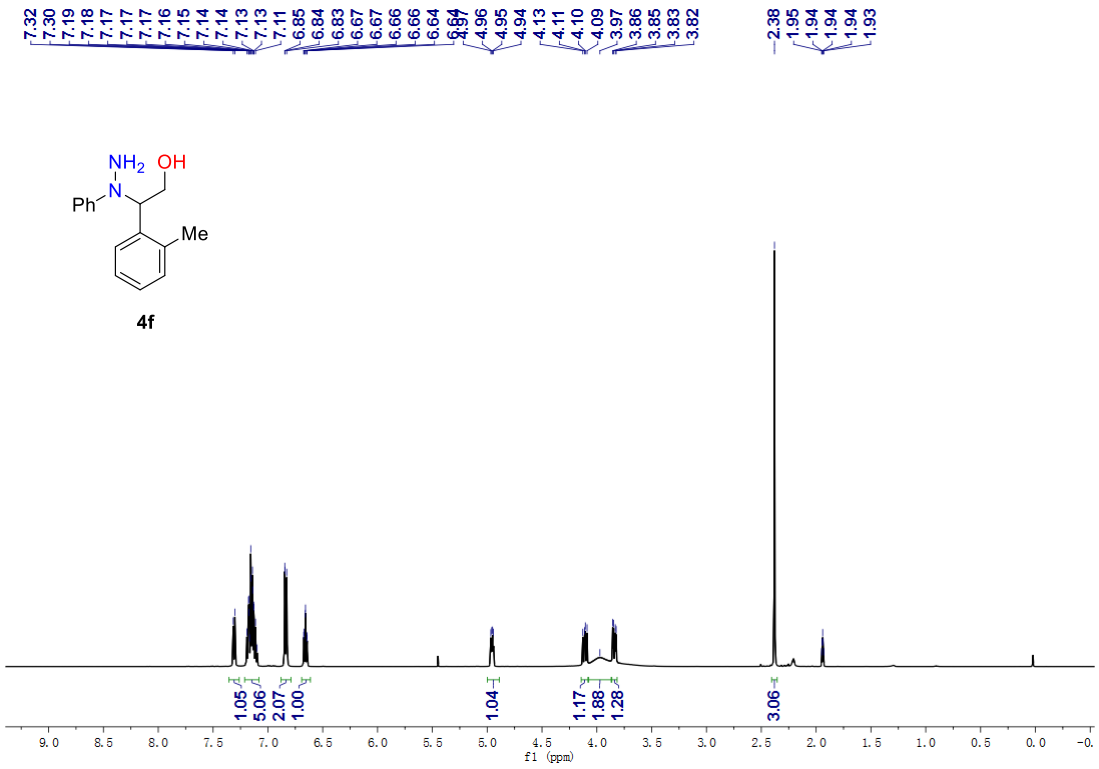


Figure S20. The ^{1}H-NMR spectral copy of compound **4f**.

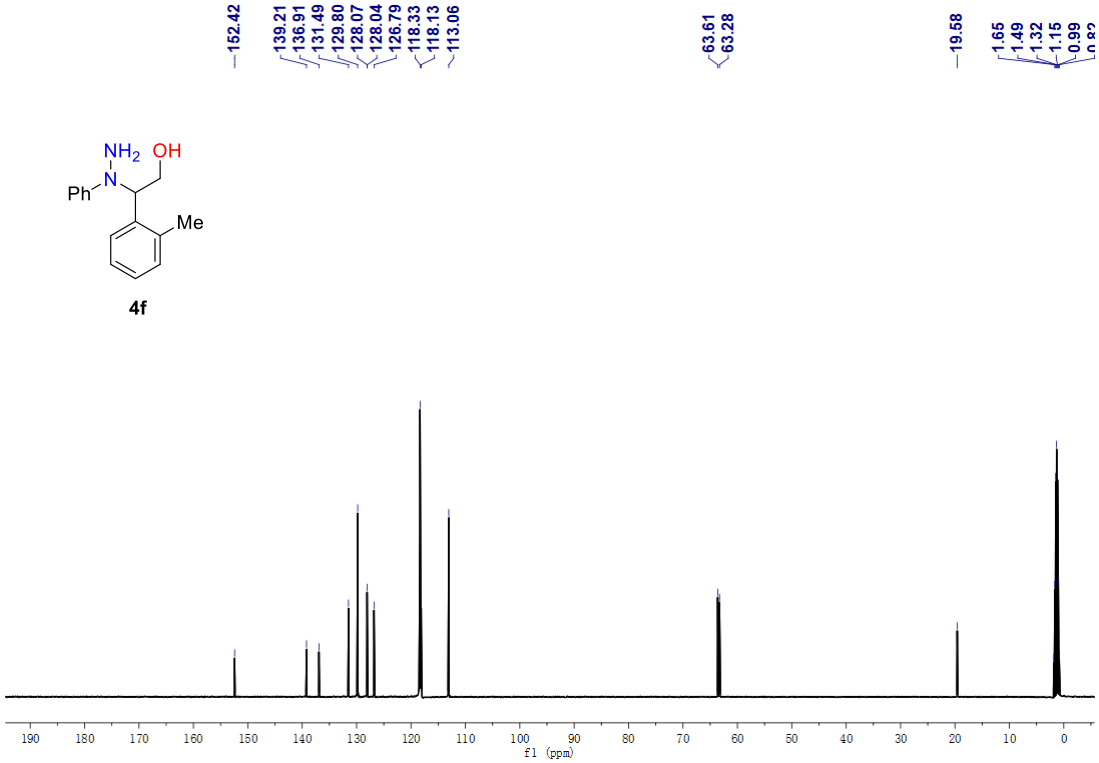


Figure S21. The ^{13}C-NMR spectral copy of compound **4f**.

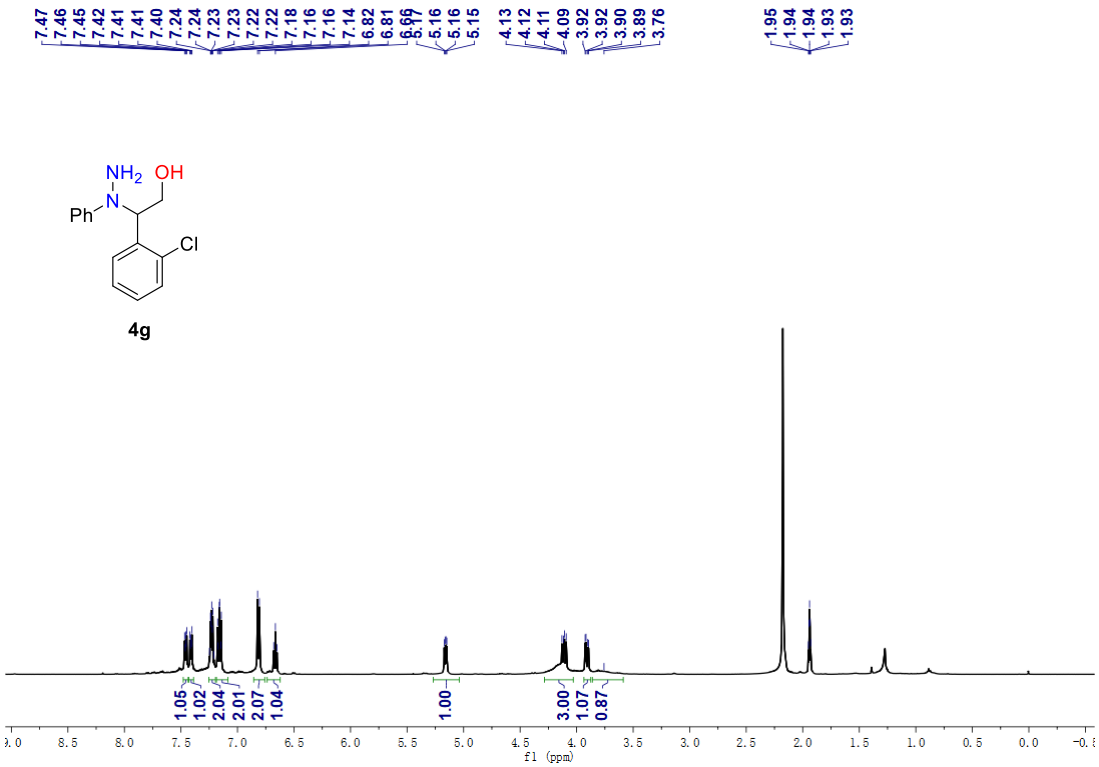


Figure S22. The ^{1}H-NMR spectral copy of compound **4g**.

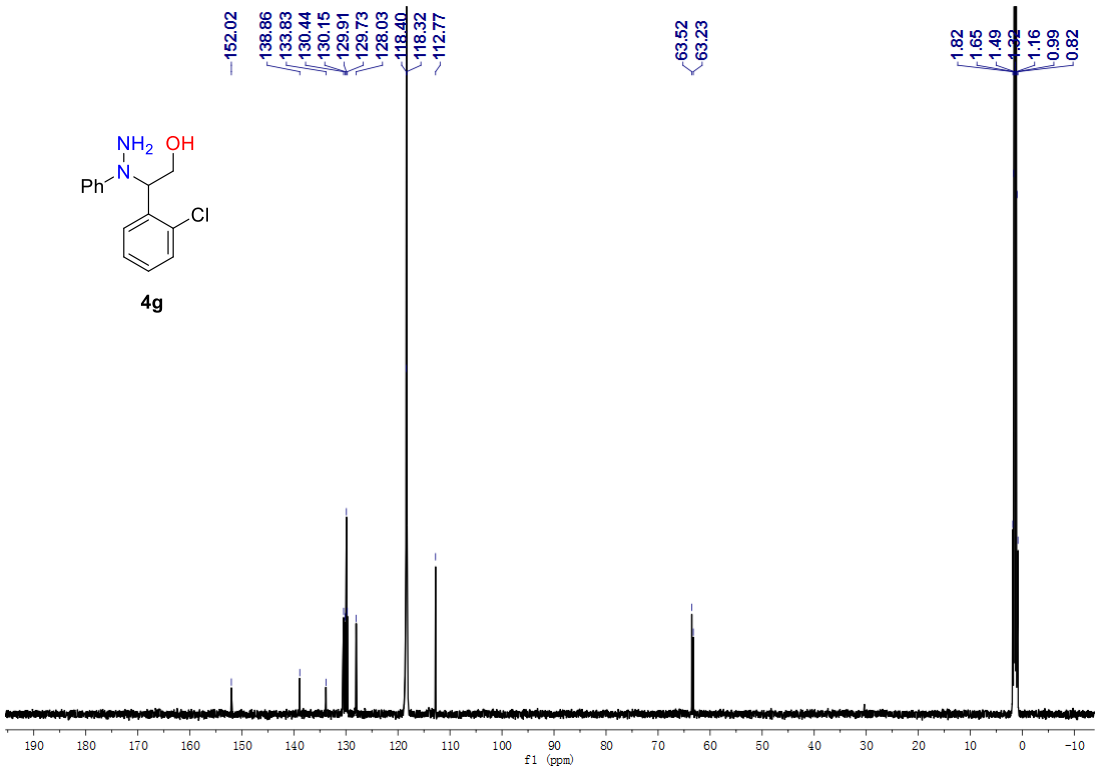


Figure S23. The ^{13}C-NMR spectral copy of compound **4g**.

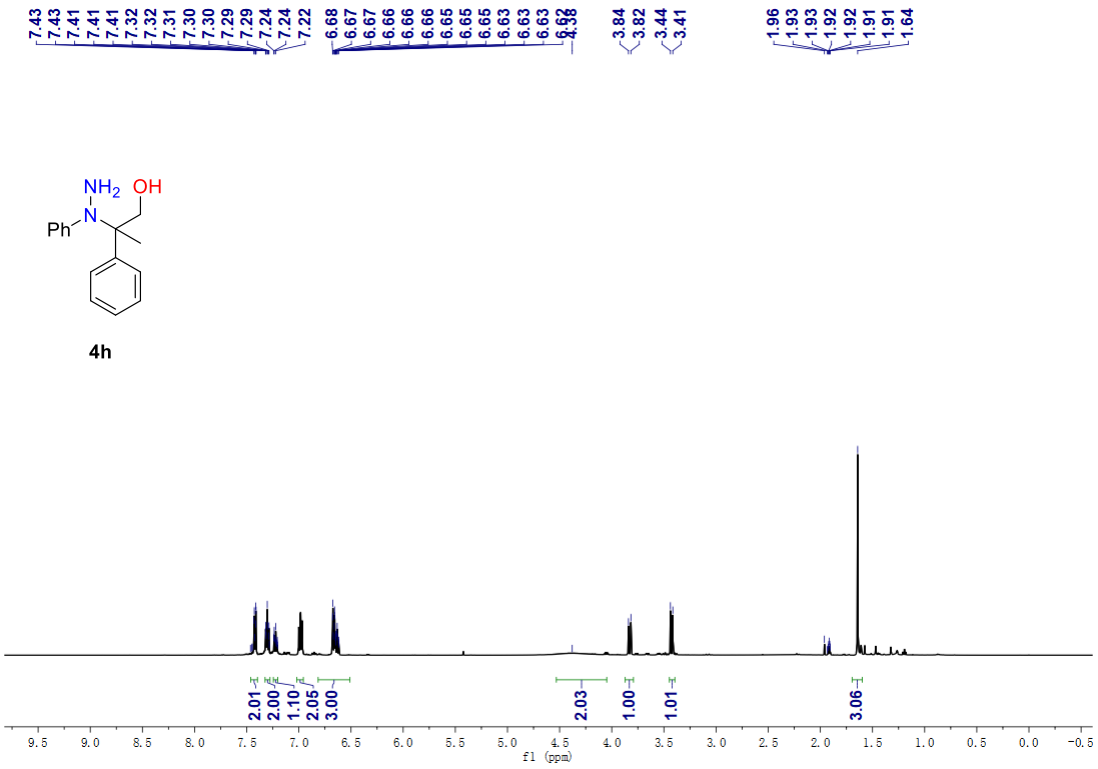


Figure S24. The ^{1}H-NMR spectral copy of compound **4h**.

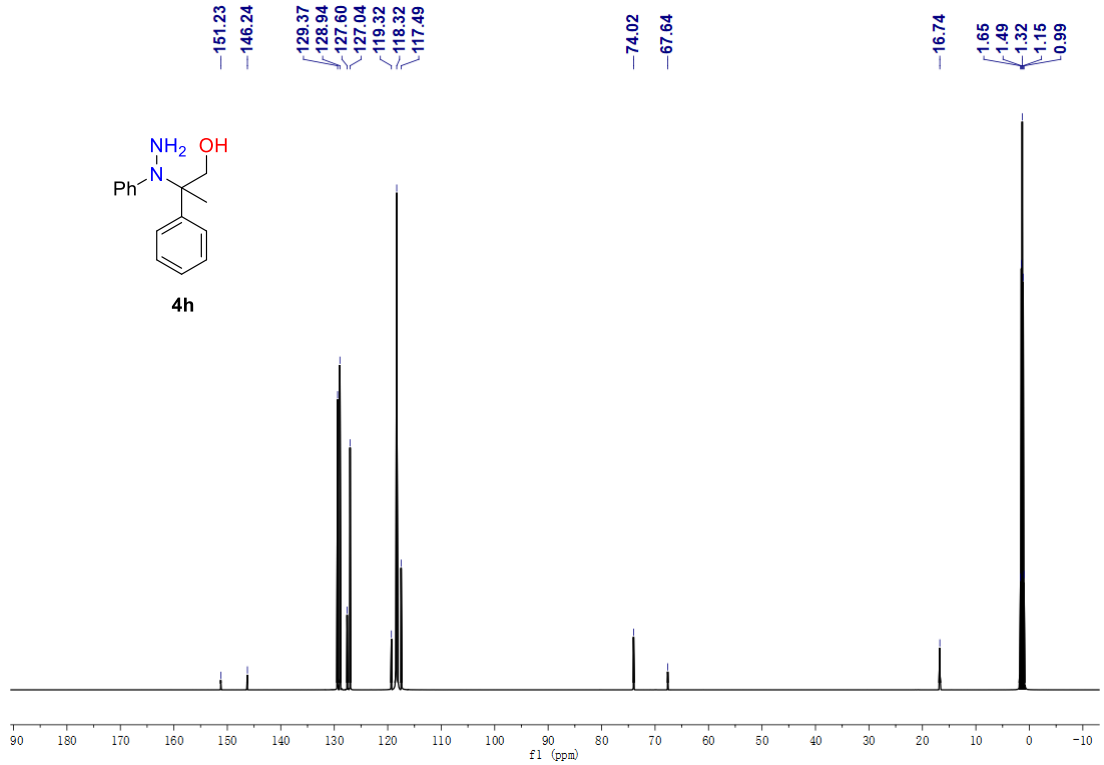


Figure S25. The ^{13}C-NMR spectral copy of compound **4h**.

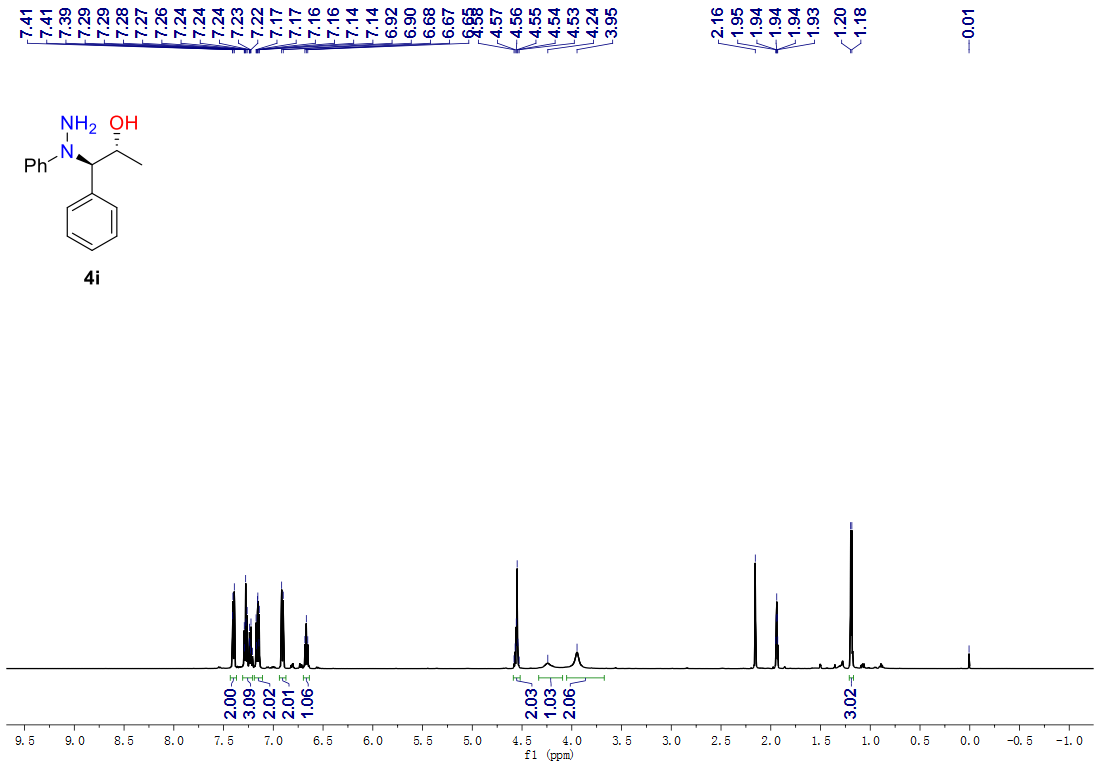


Figure S26. The ^{1}H-NMR spectral copy of compound **4i**.

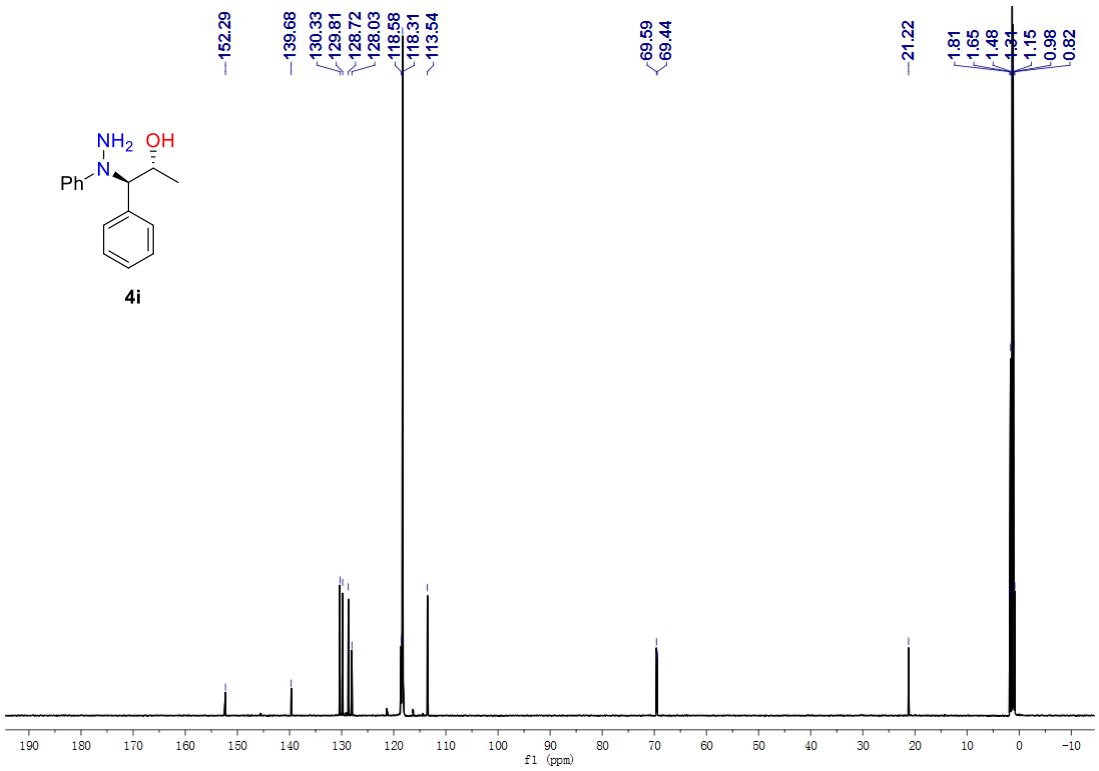


Figure S27. The ^{13}C-NMR spectral copy of compound **4i**.

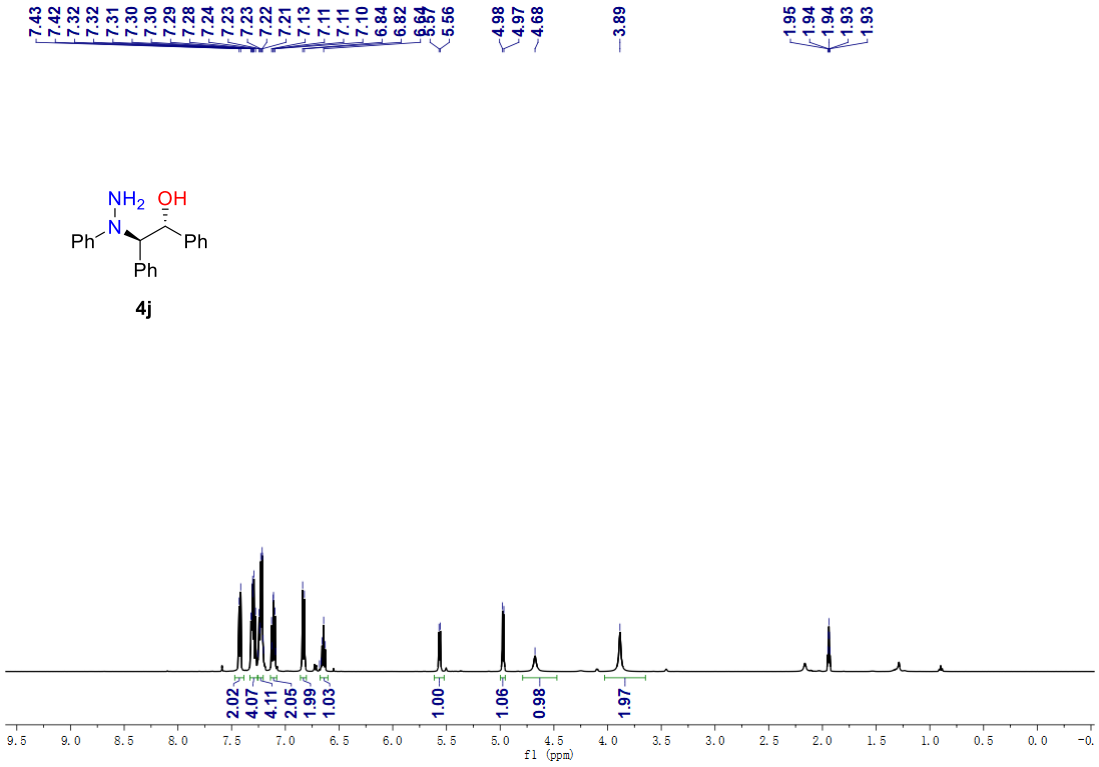


Figure S28. The ^{1}H-NMR spectral copy of compound **4j**.

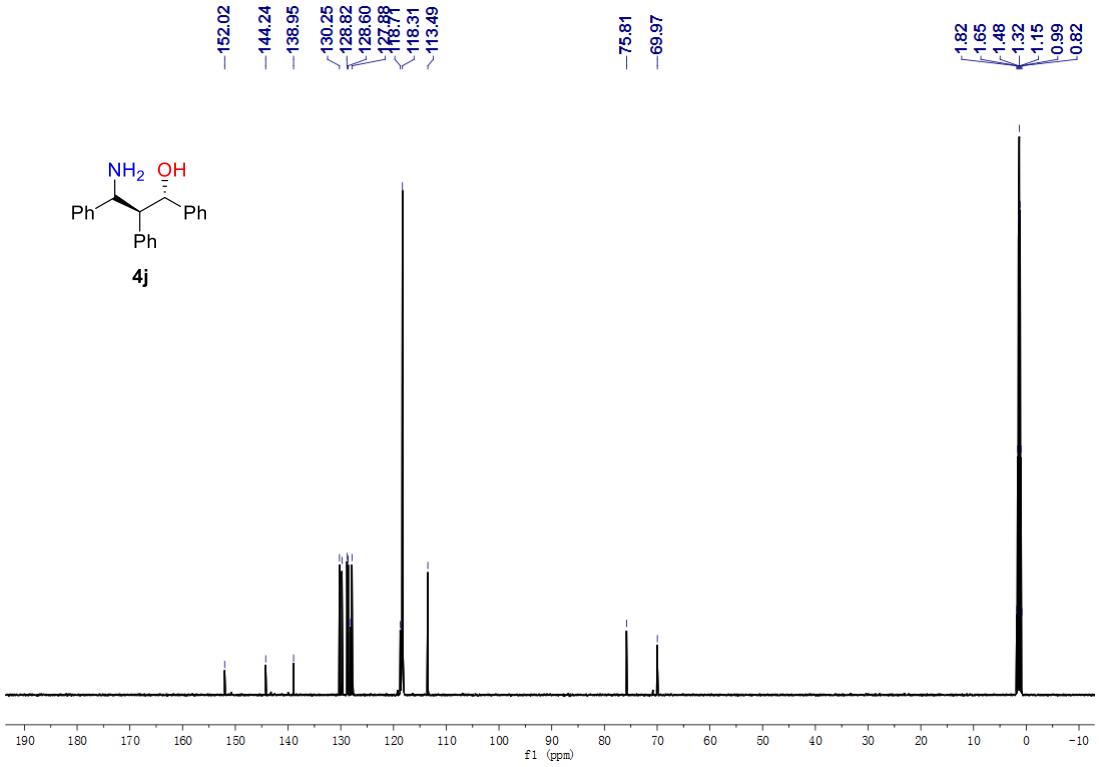


Figure S29. The ^{13}C-NMR spectral copy of compound **4j**.

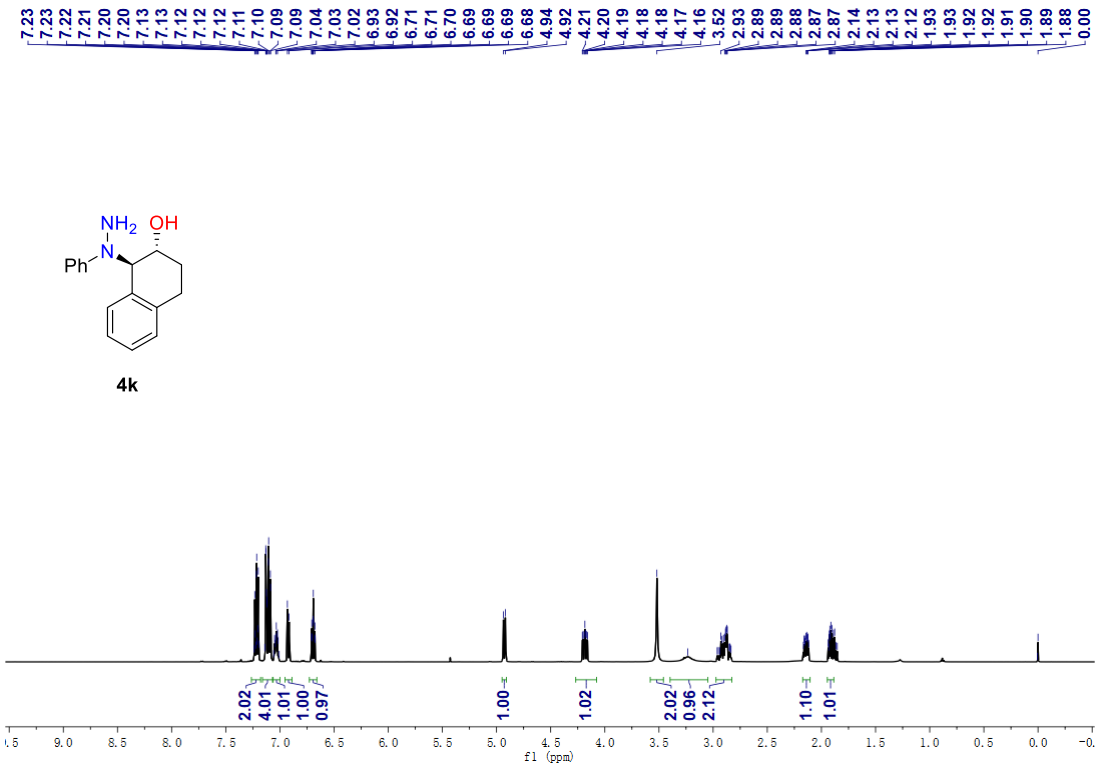


Figure S30. The ^{1}H-NMR spectral copy of compound **4k**.

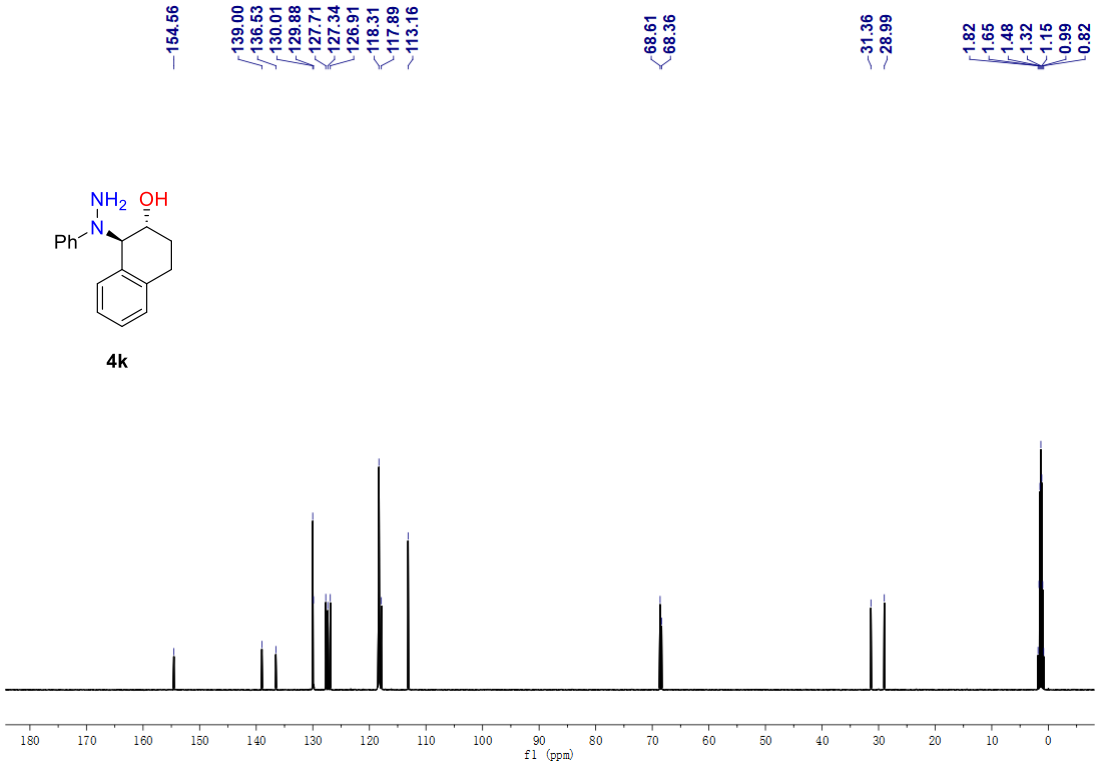


Figure S31. The ^{13}C-NMR spectral copy of compound **4k**.

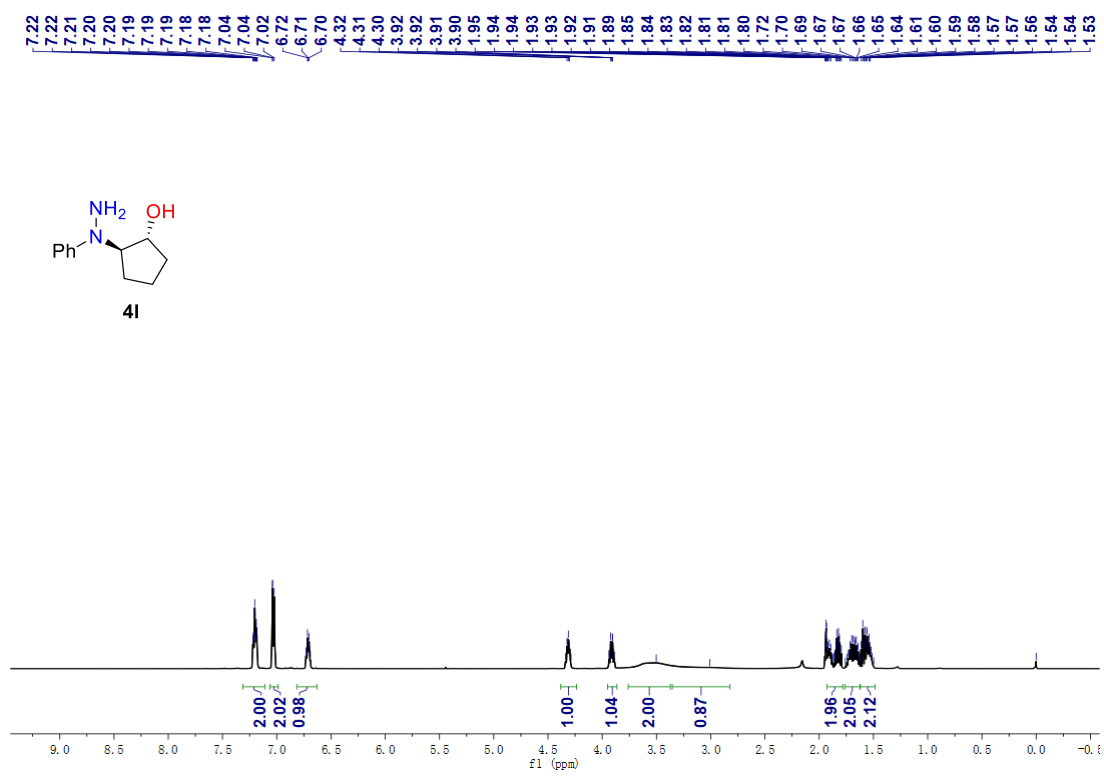


Figure S32. The ^{1}H-NMR spectral copy of compound **4l**.

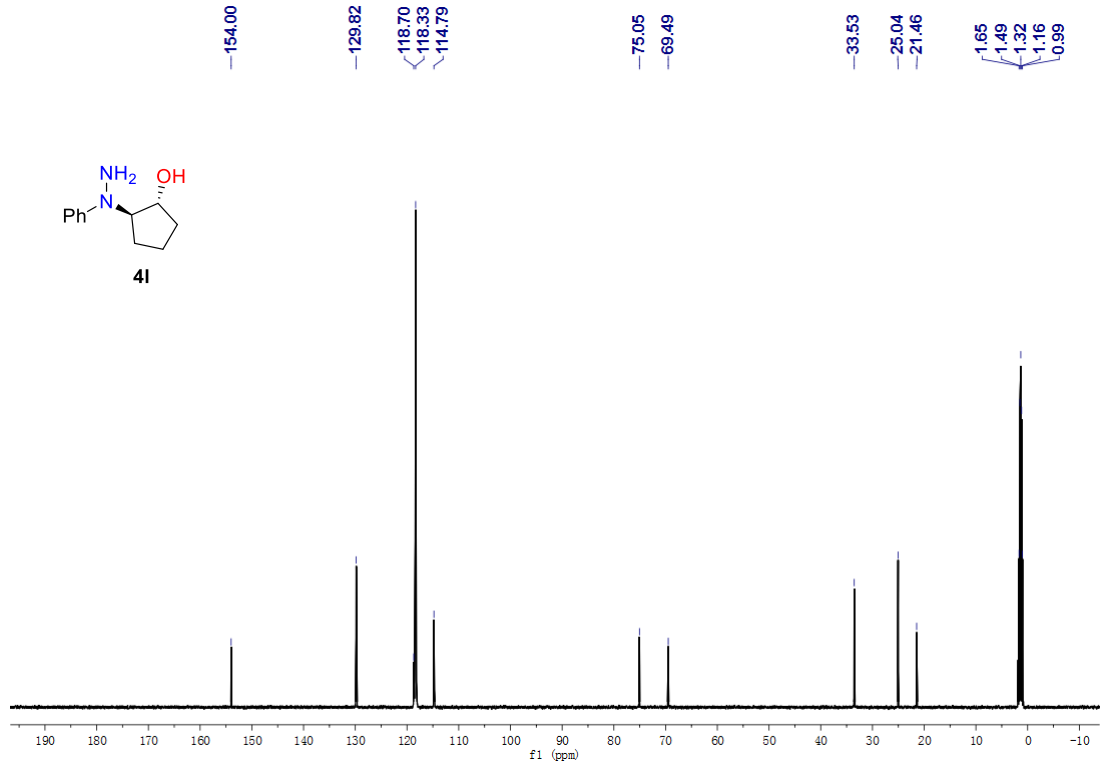


Figure S33. The ^{13}C-NMR spectral copy of compound **4l**.

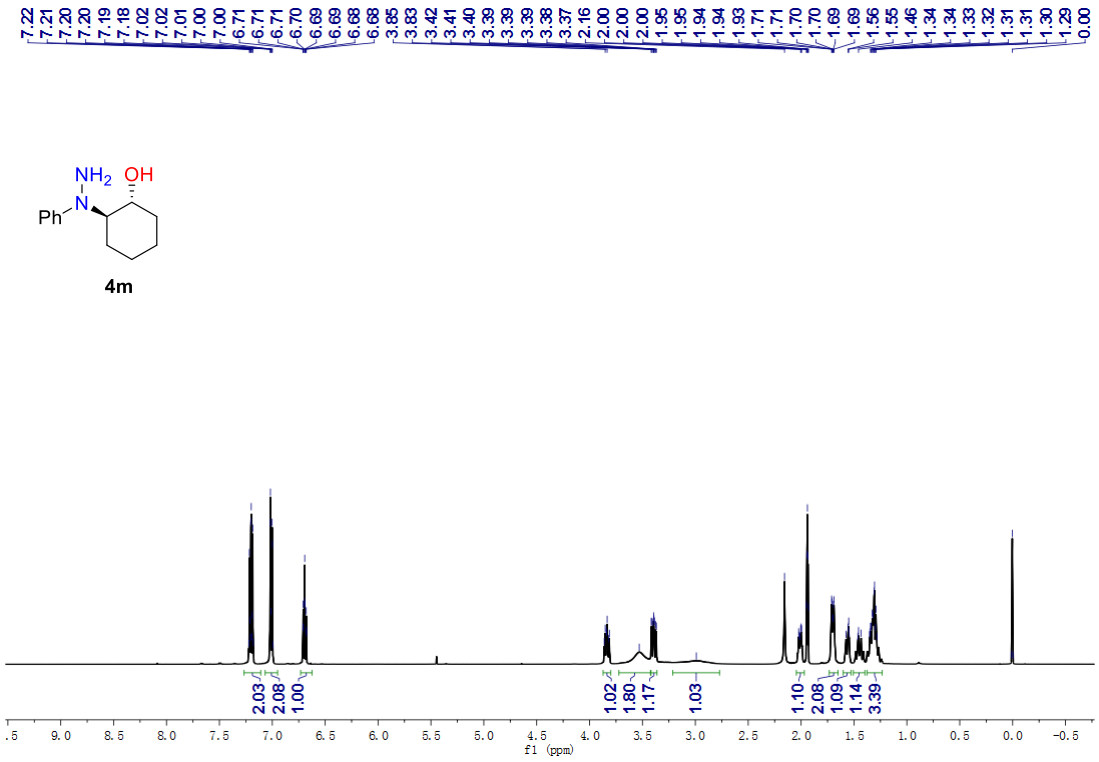


Figure S34. The ^{1}H-NMR spectral copy of compound **4m**.

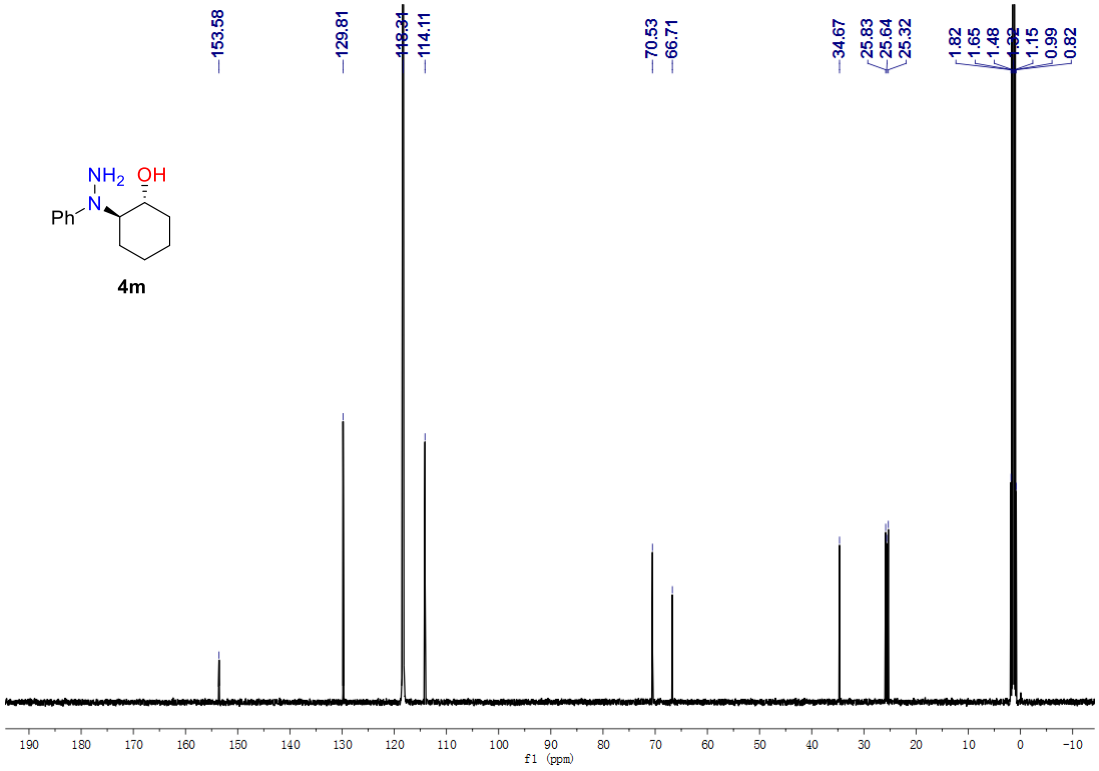


Figure S35. The ^{19}C-NMR spectral copy of compound **4m**.

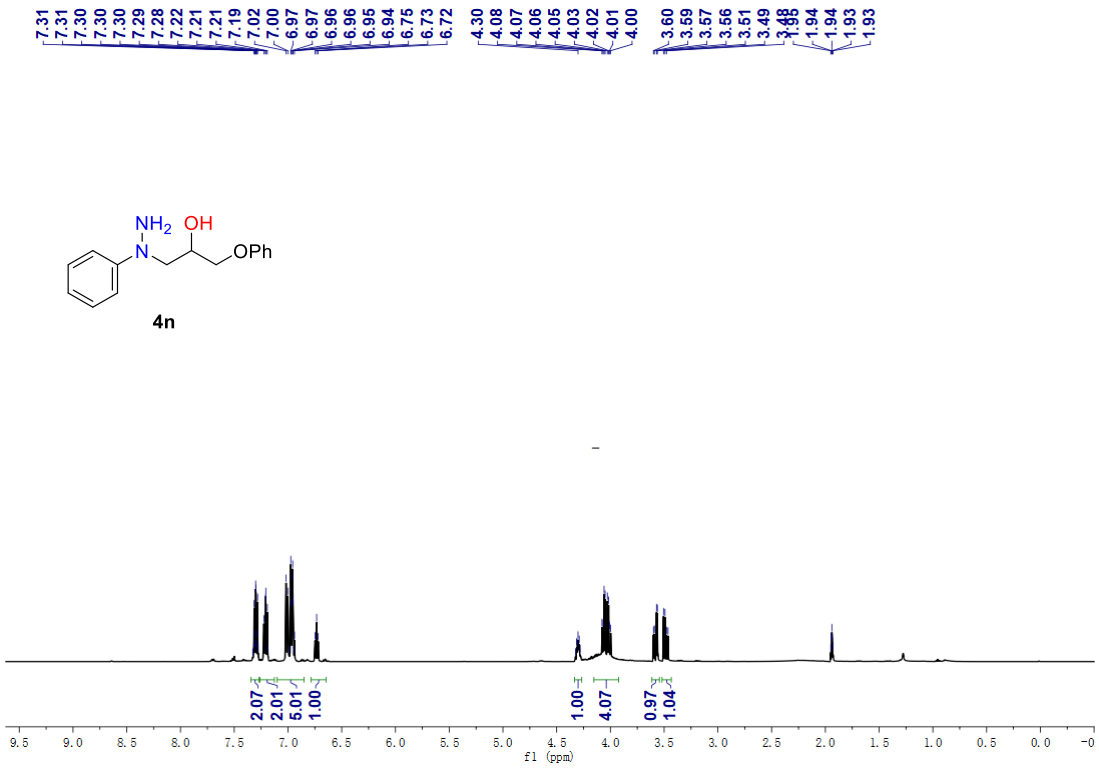


Figure S36. The ^{1}H-NMR spectral copy of compound **4n**.

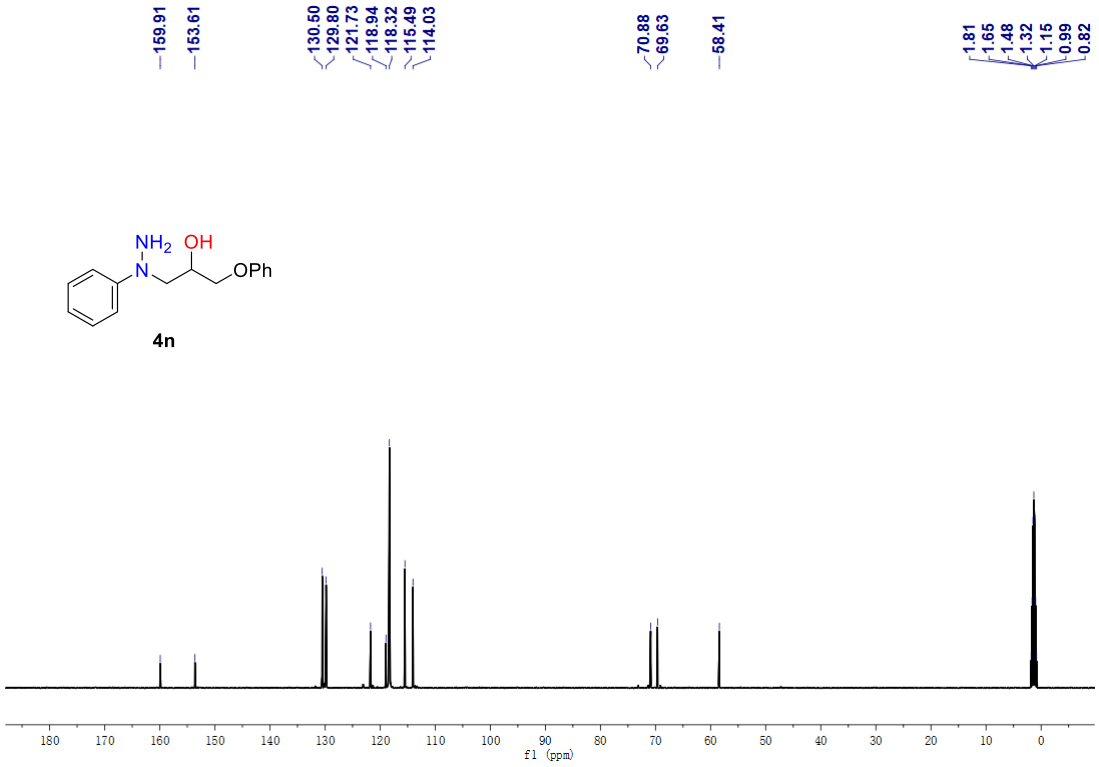


Figure S37. The ^{13}C-NMR spectral copy of compound **4n**.

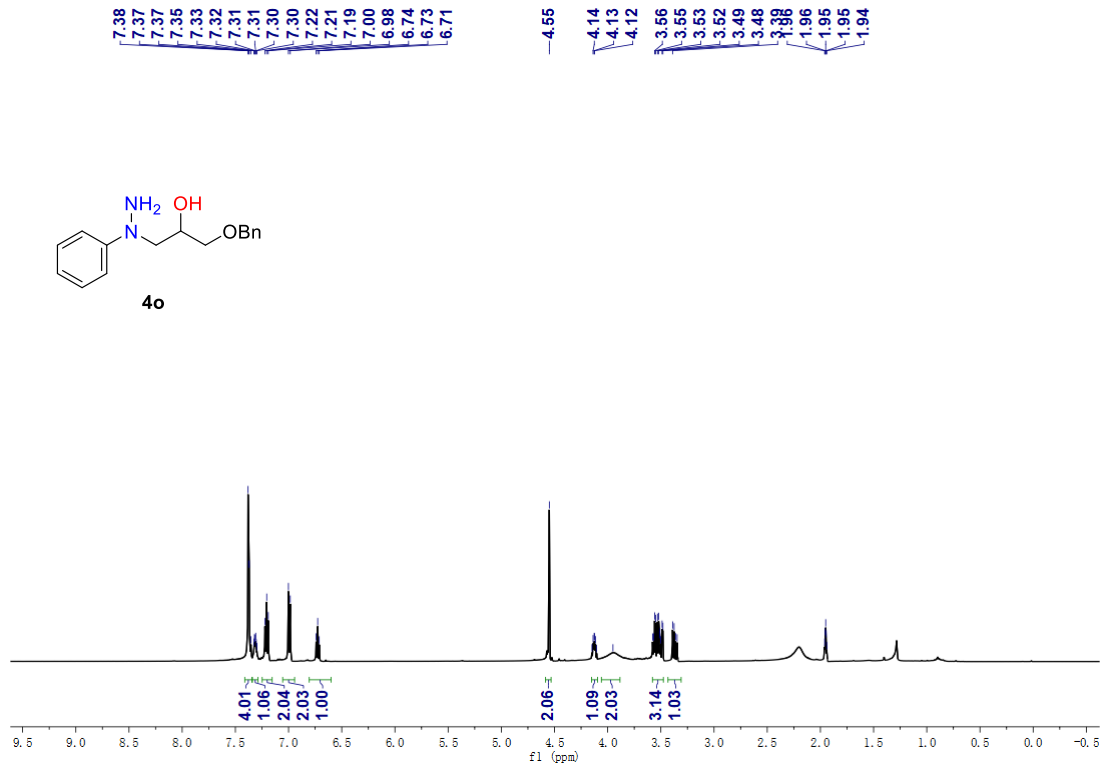


Figure S38. The ^{1}H-NMR spectral copy of compound **4o**.

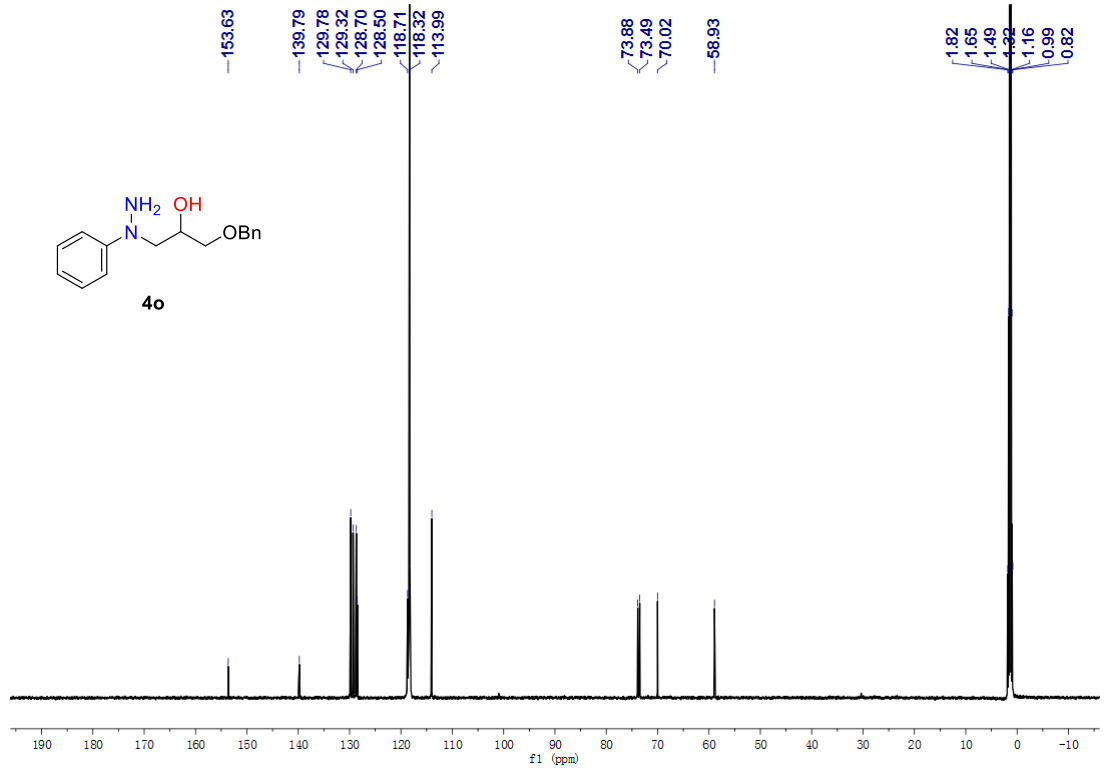


Figure S39. The ^{13}C-NMR spectral copy of compound **4o**.

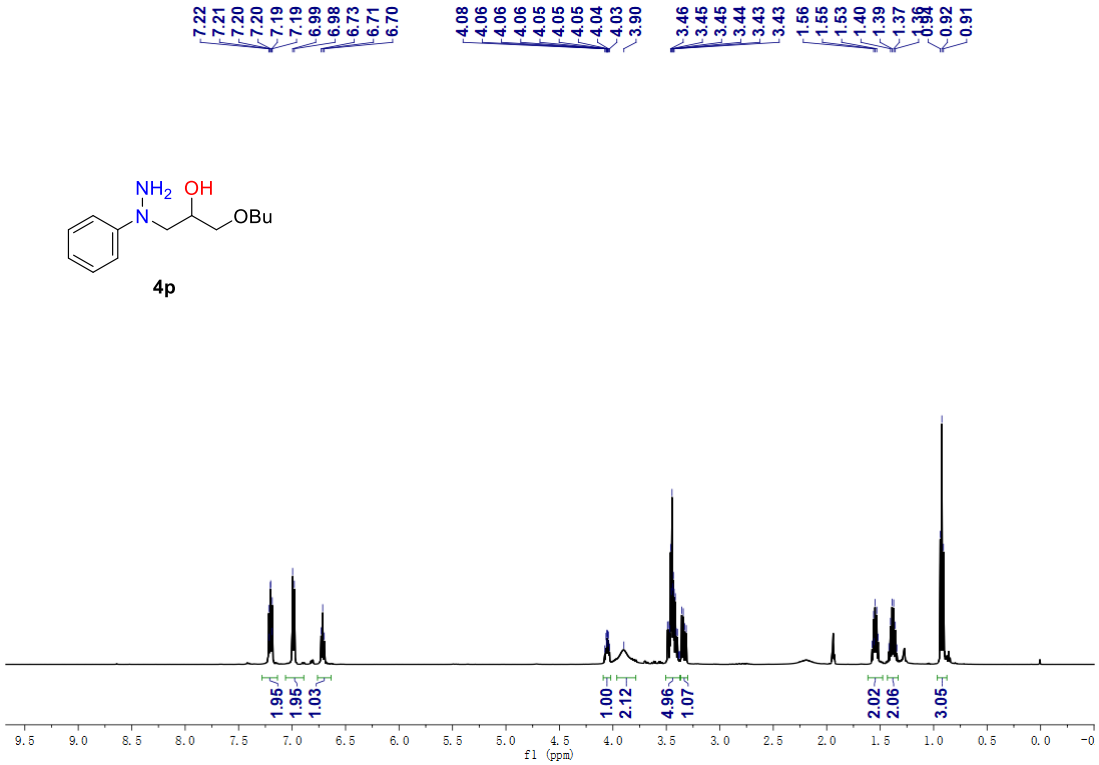


Figure S40. The ^{1}H-NMR spectral copy of compound **4p**.

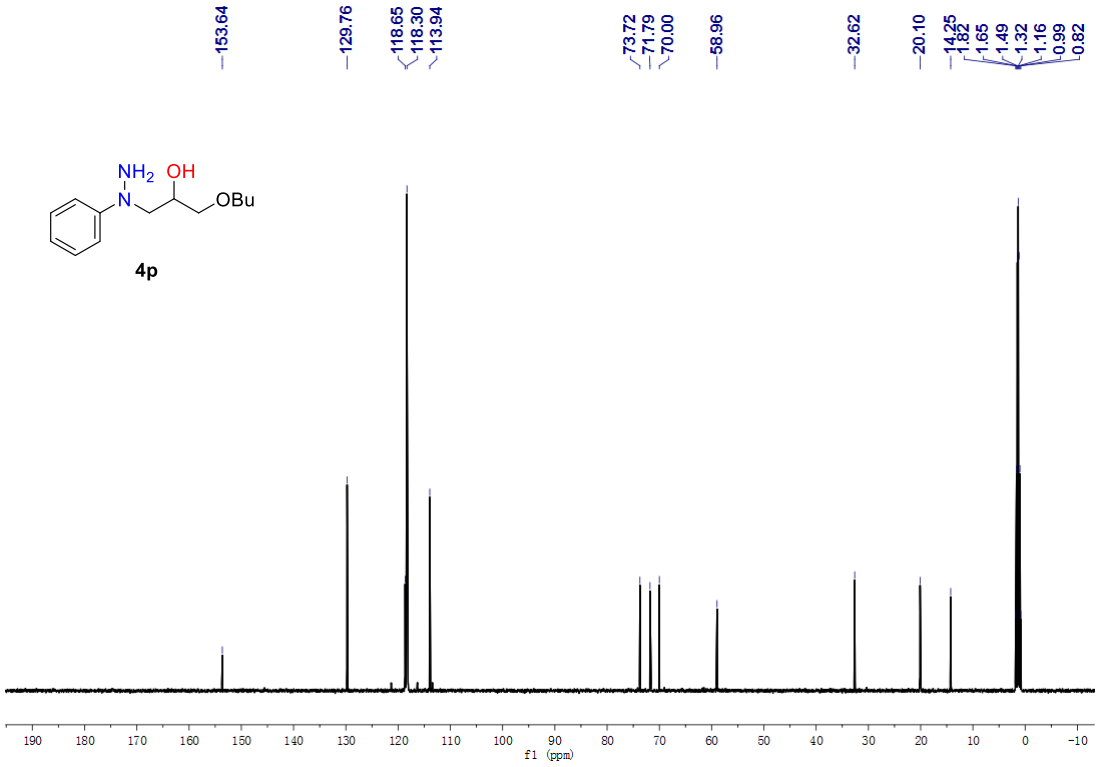


Figure S41. The ^{13}C-NMR spectral copy of compound **4p**.

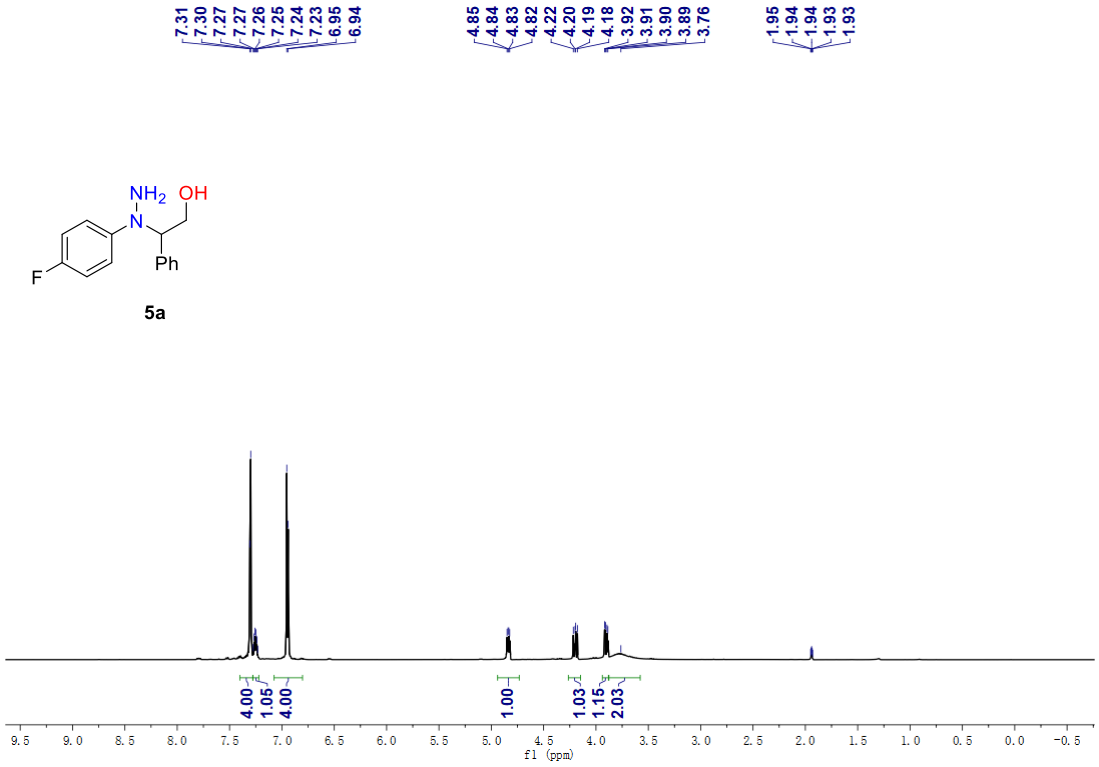


Figure S42. The ^{1}H-NMR spectral copy of compound **5a**.

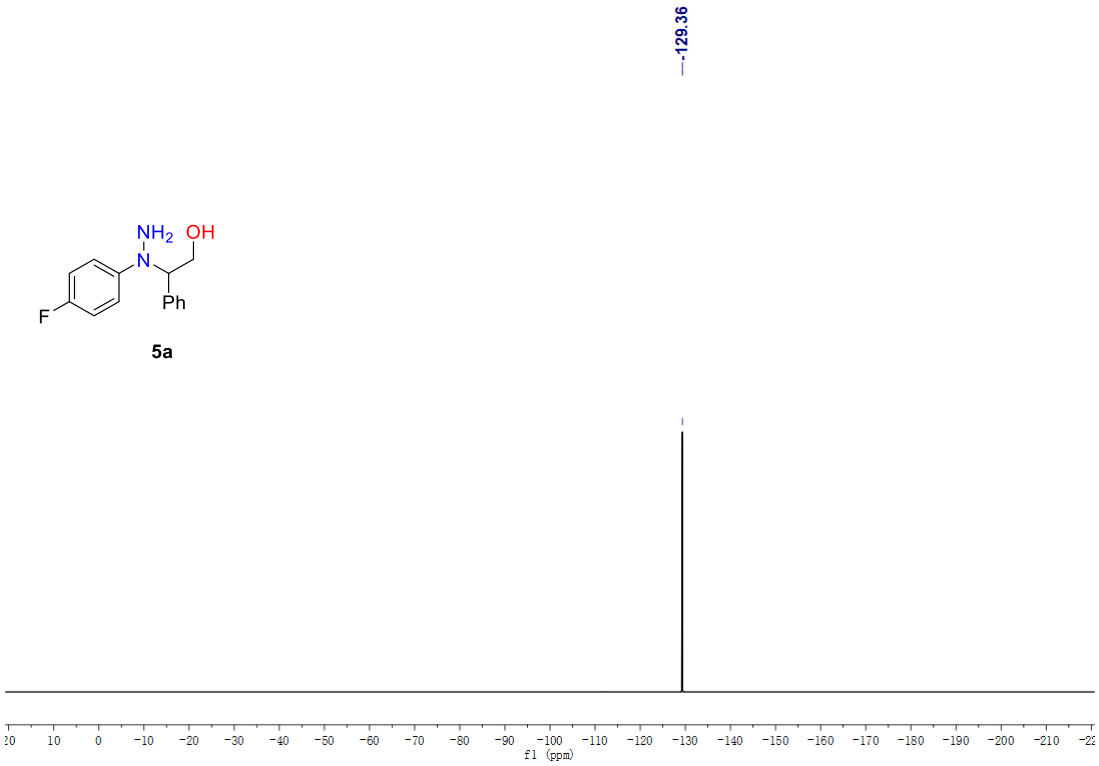


Figure S43. The ^{19}F-NMR spectral copy of compound **5a**.

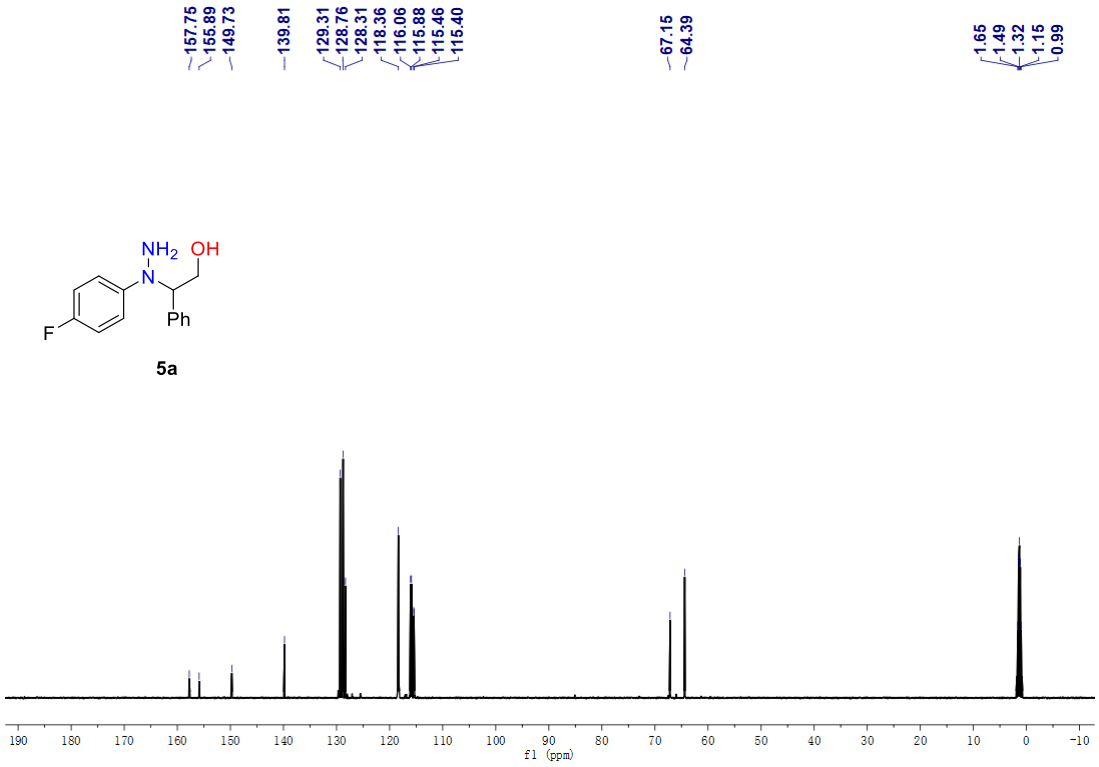


Figure S44. The ^{13}C-NMR spectral copy of compound **5a**.

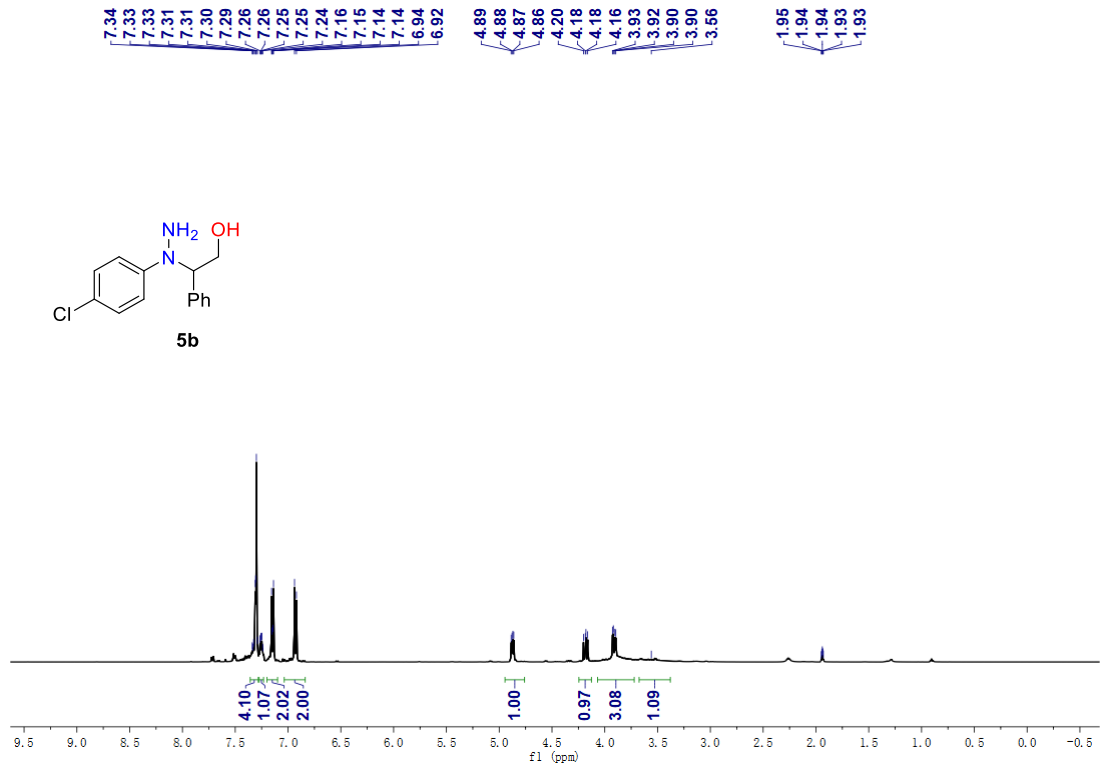


Figure S45. The ^{1}H-NMR spectral copy of compound **5b**.

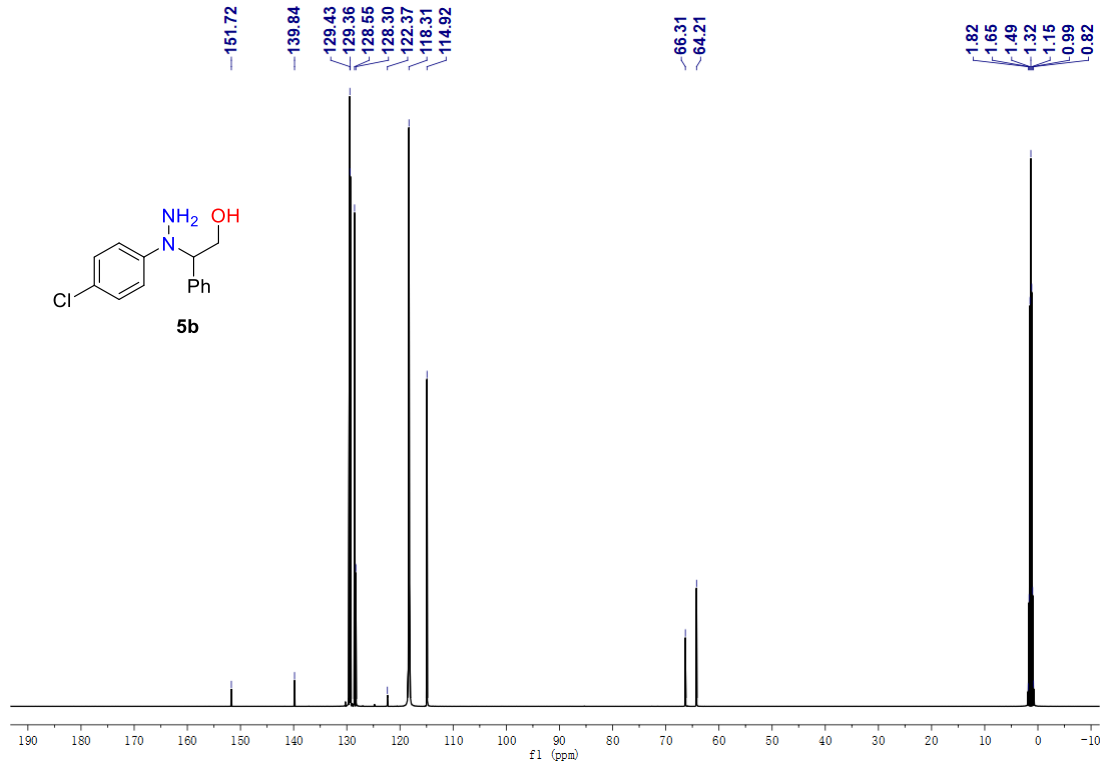


Figure S46. The ^{13}C-NMR spectral copy of compound **5b**.

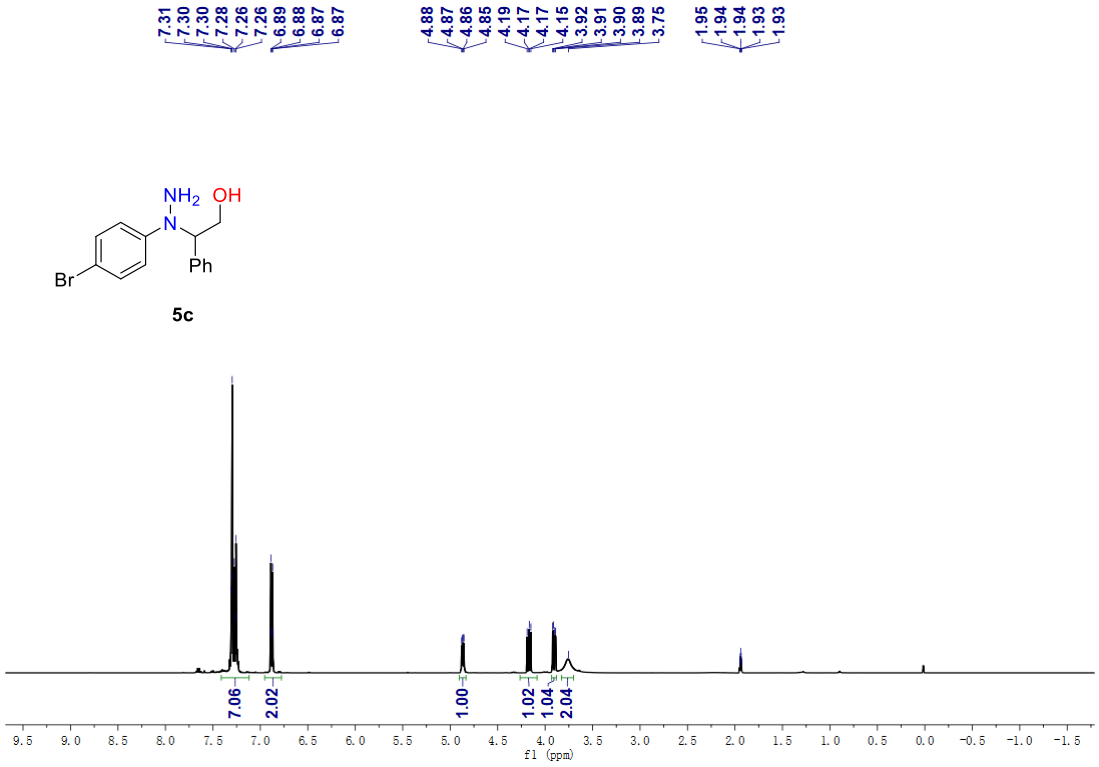


Figure S47. The ^{1}H-NMR spectral copy of compound **5c**.

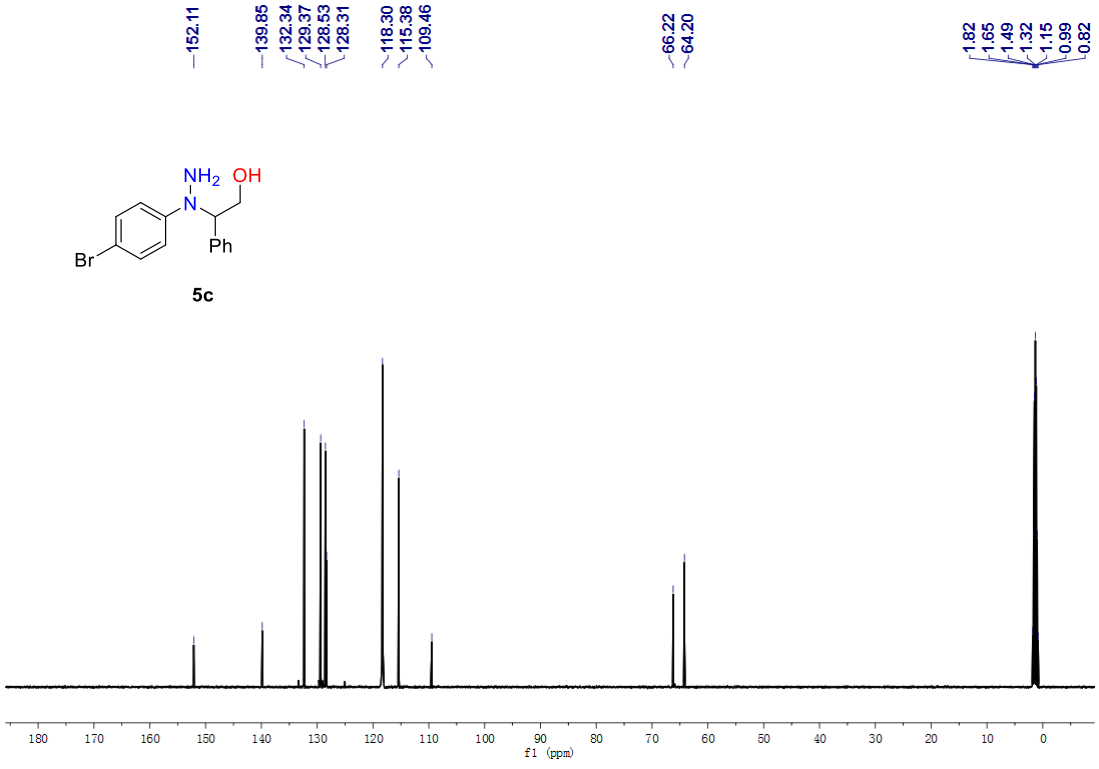


Figure S48. The ^{13}C-NMR spectral copy of compound **5c**.

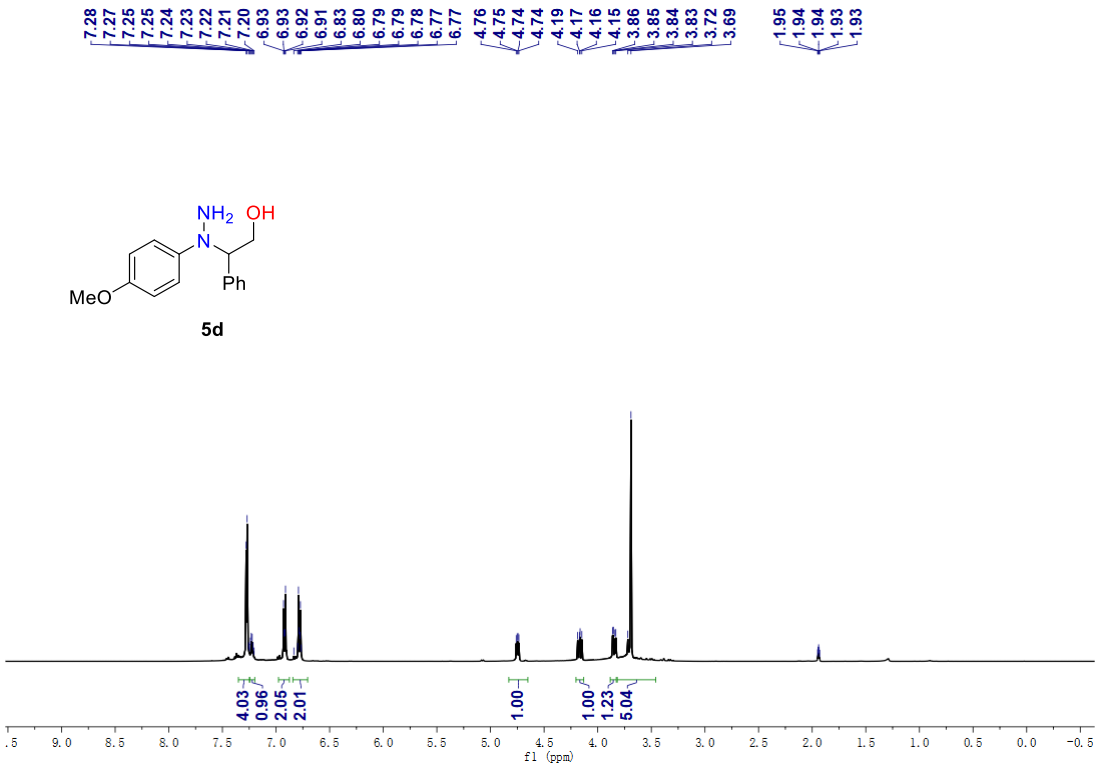


Figure S49. The ^{1}H-NMR spectral copy of compound **5d**.

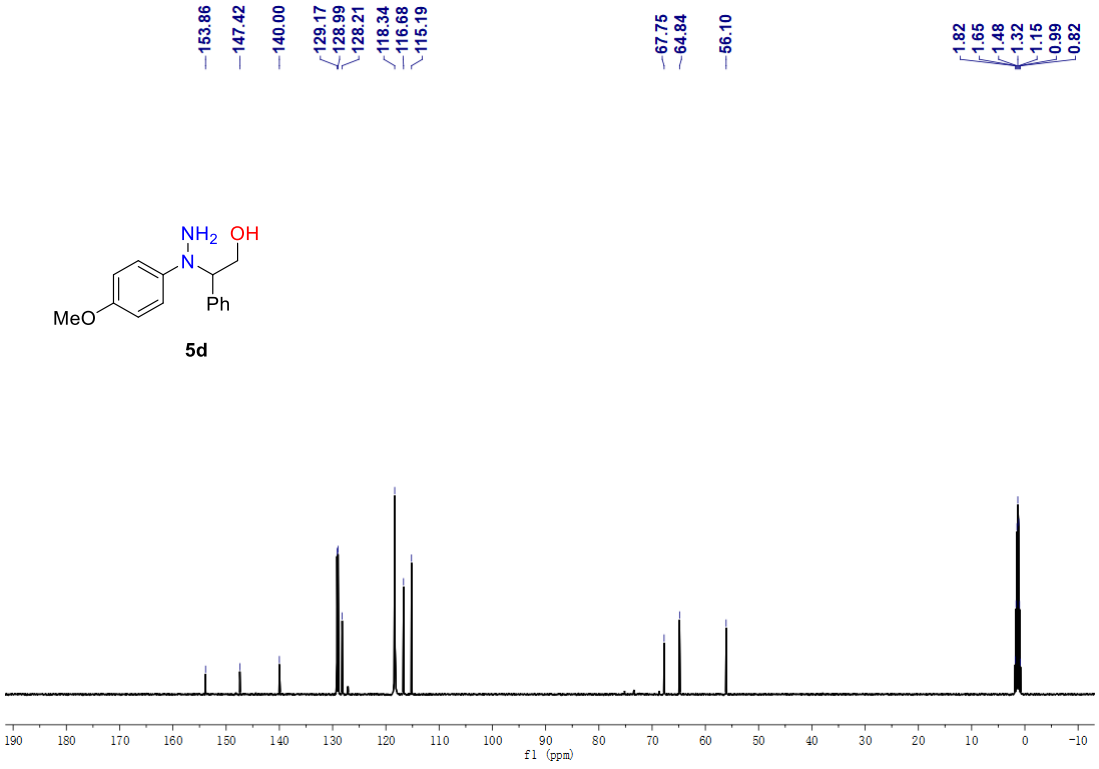


Figure S50. The ^{13}C-NMR spectral copy of compound **5d**.

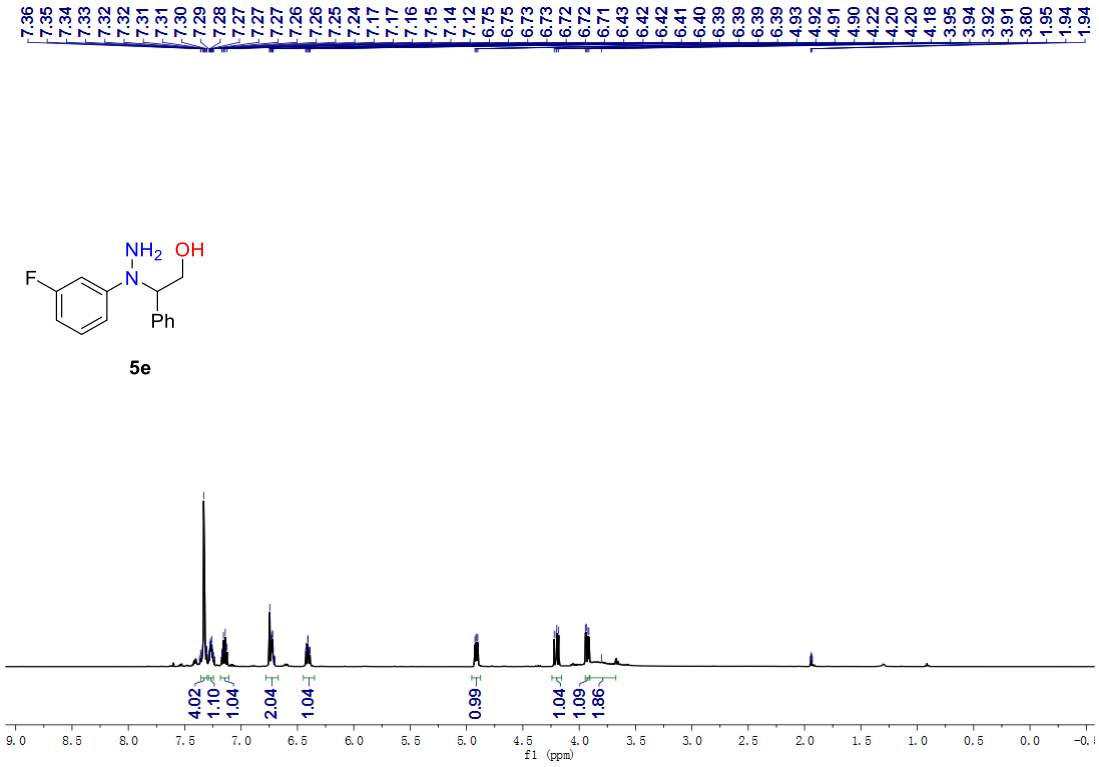


Figure S51. The ^{1}H-NMR spectral copy of compound **5e**.

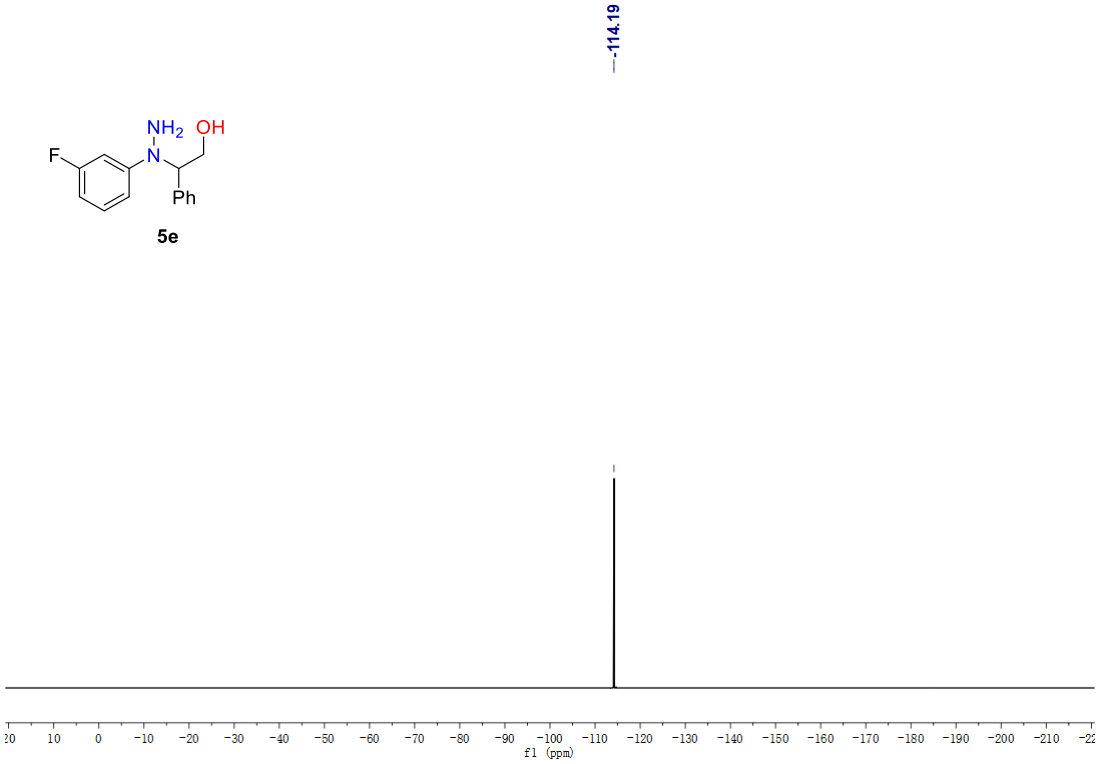


Figure S52. The ^{19}F-NMR spectral copy of compound **5e**.

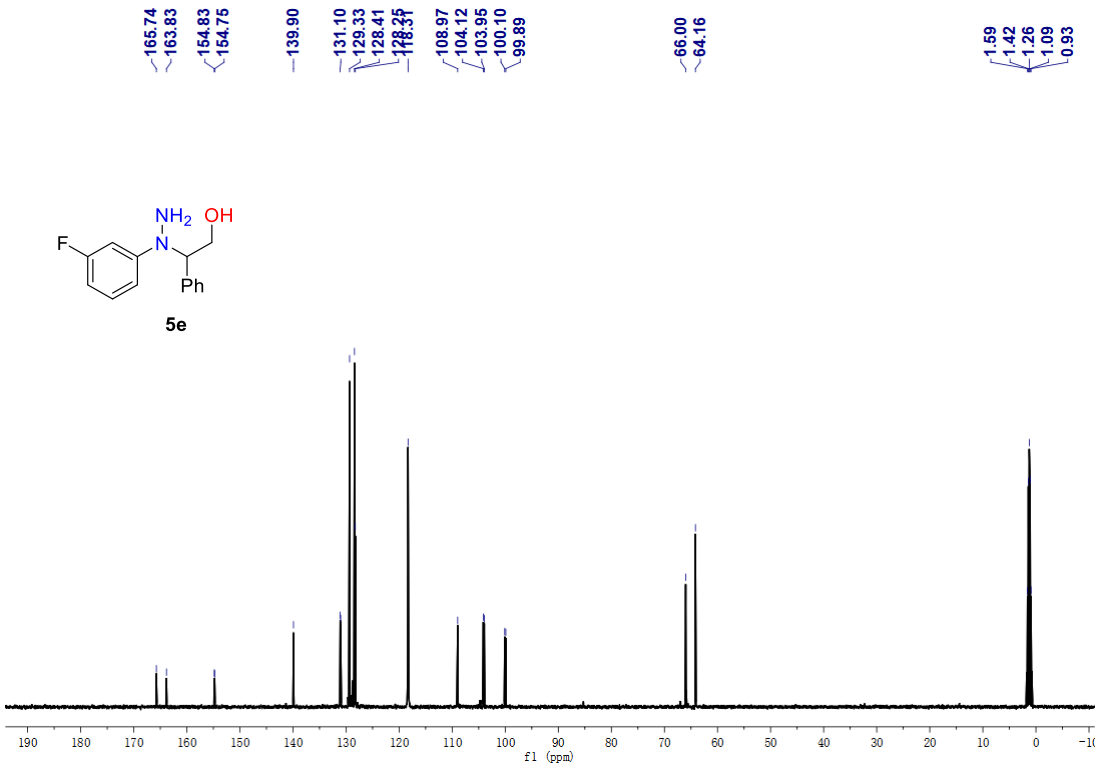


Figure S53. The ^{13}C-NMR spectral copy of compound **5e**.

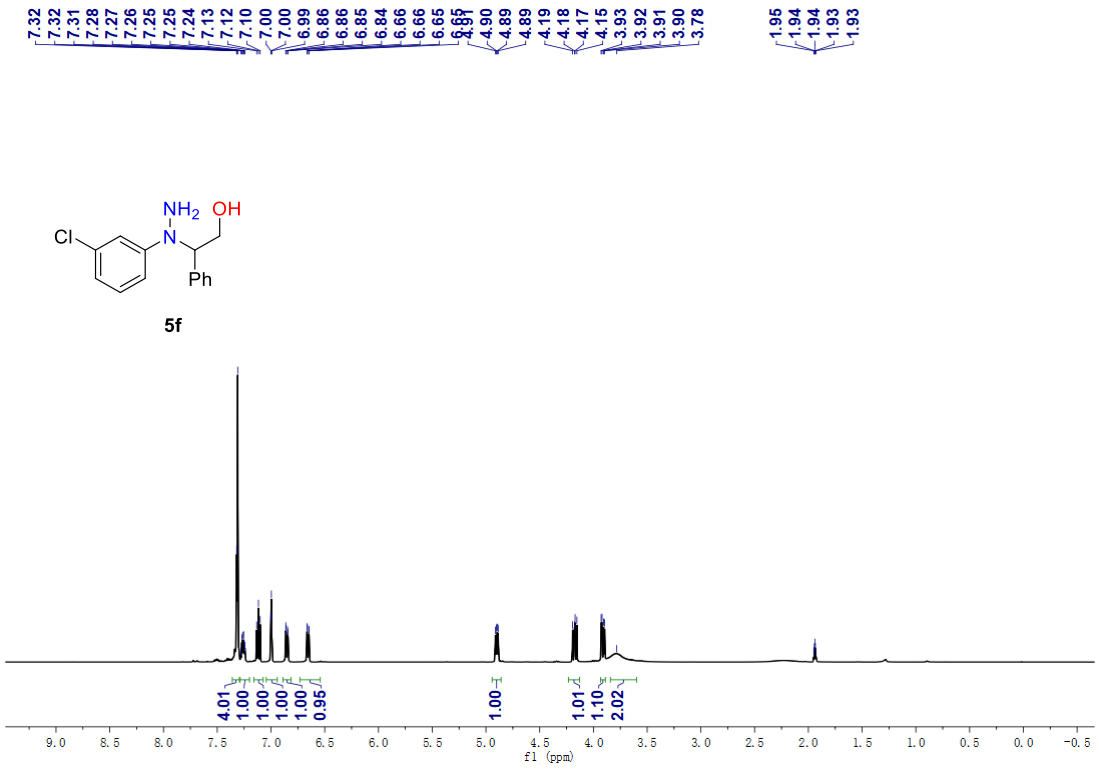


Figure S54. The ^{1}H-NMR spectral copy of compound **5f.**

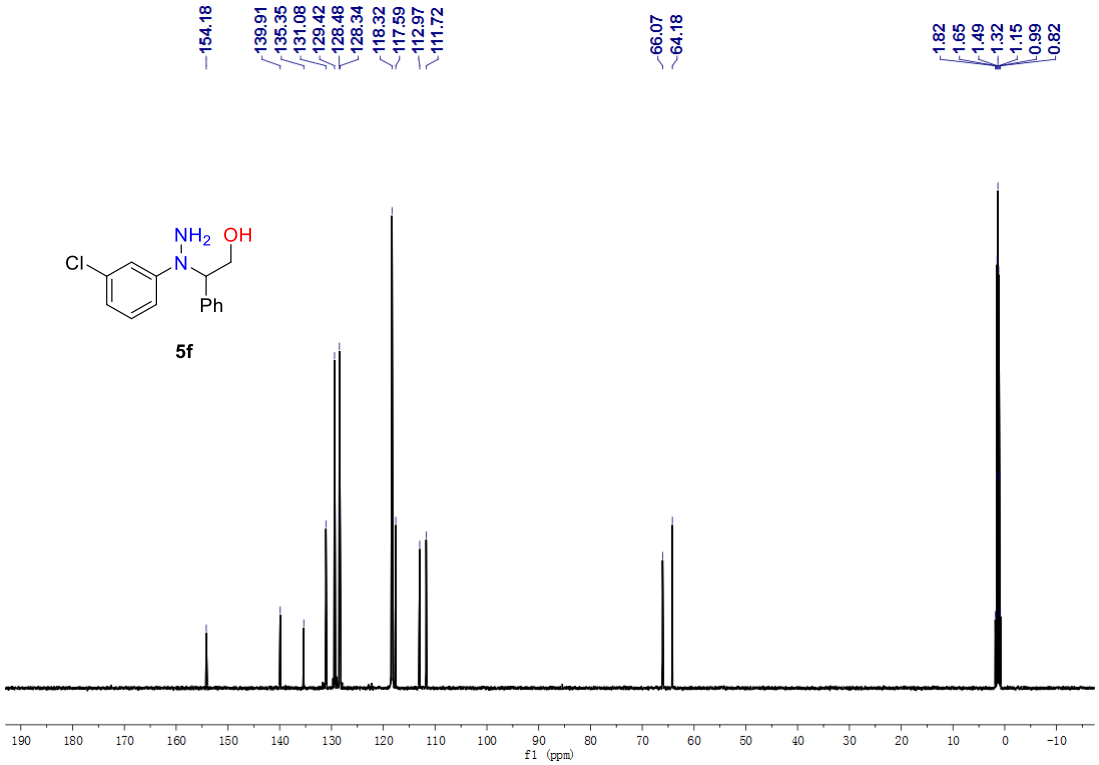


Figure S55. The ^{13}C-NMR spectral copy of compound **5f**.

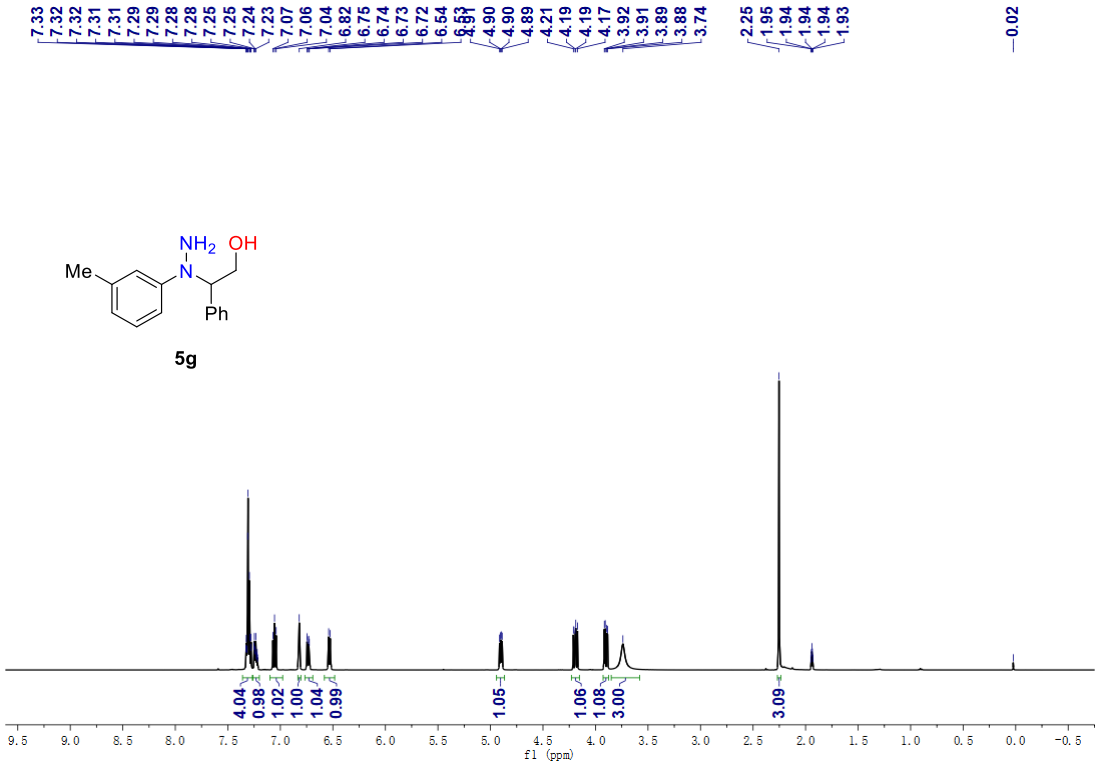


Figure S56. The ^{1}H-NMR spectral copy of compound **5g**.

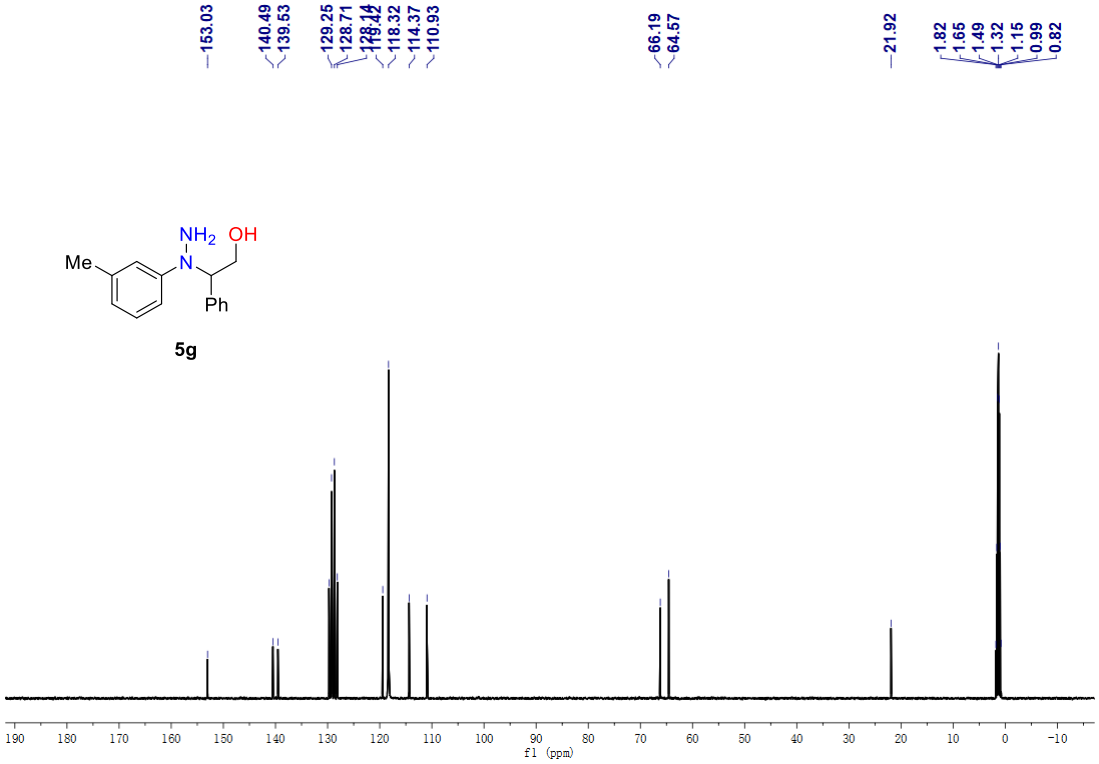


Figure S57. The ^{13}C-NMR spectral copy of compound **5g**.

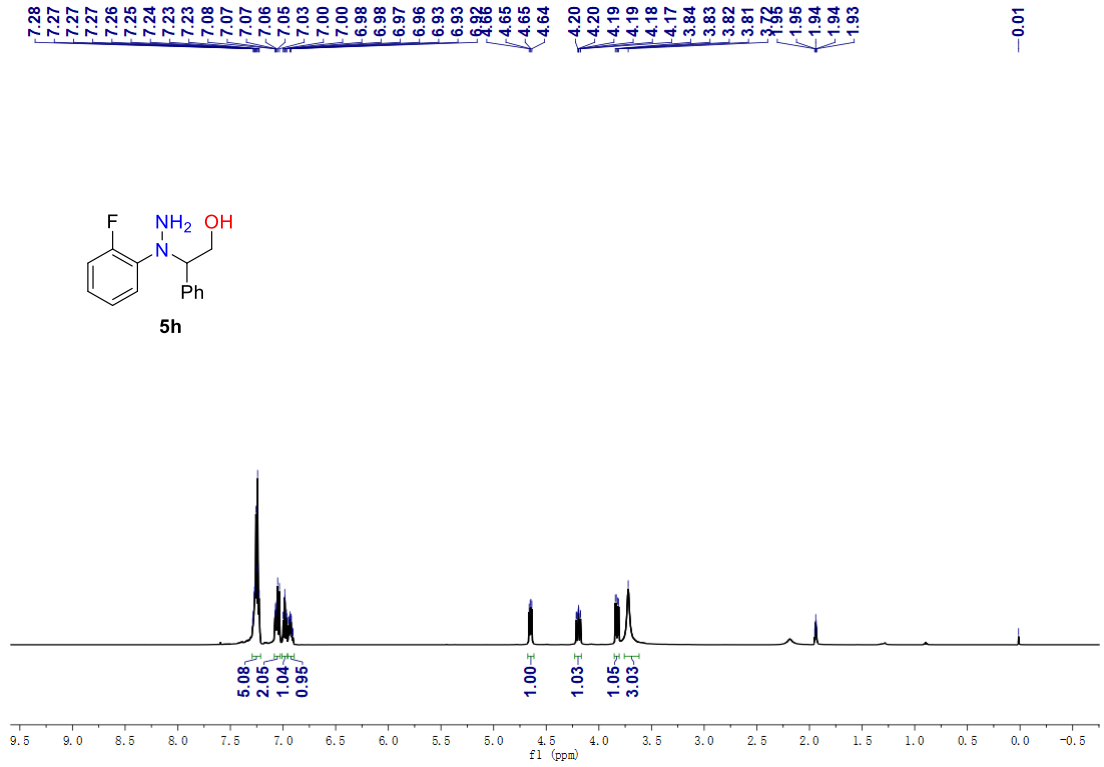


Figure S58. The ^{1}H-NMR spectral copy of compound **5h**.

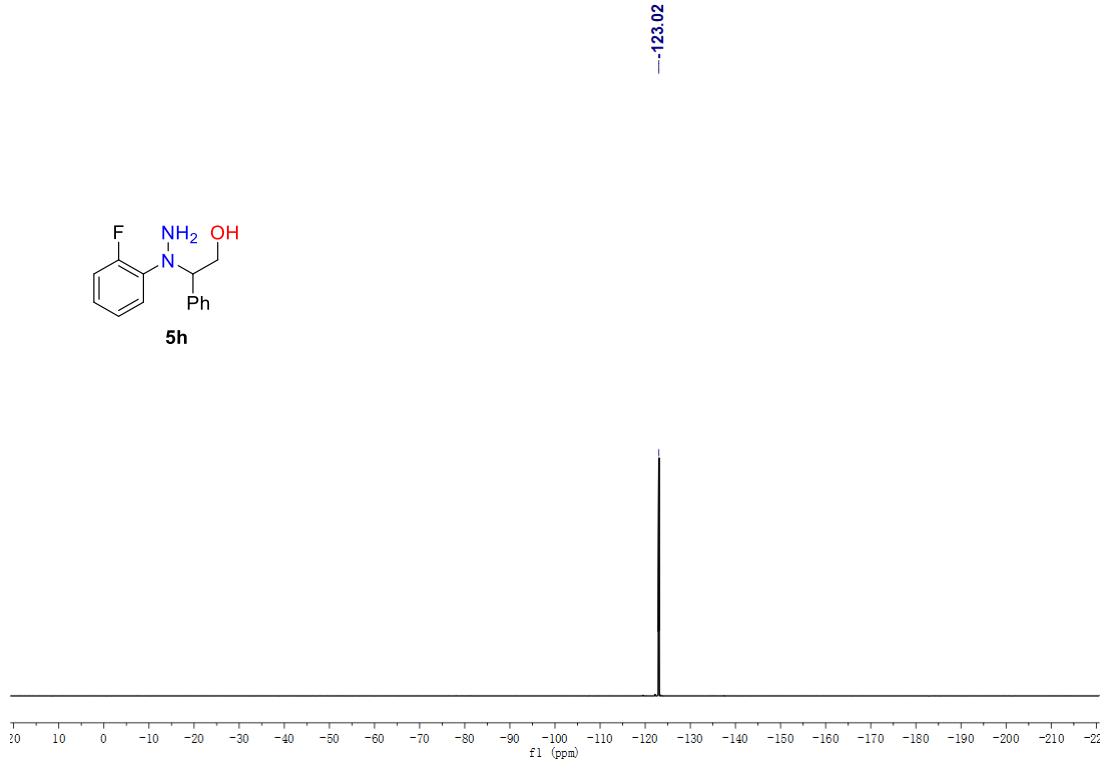


Figure S59. The ^{19}F-NMR spectral copy of compound **5h**.

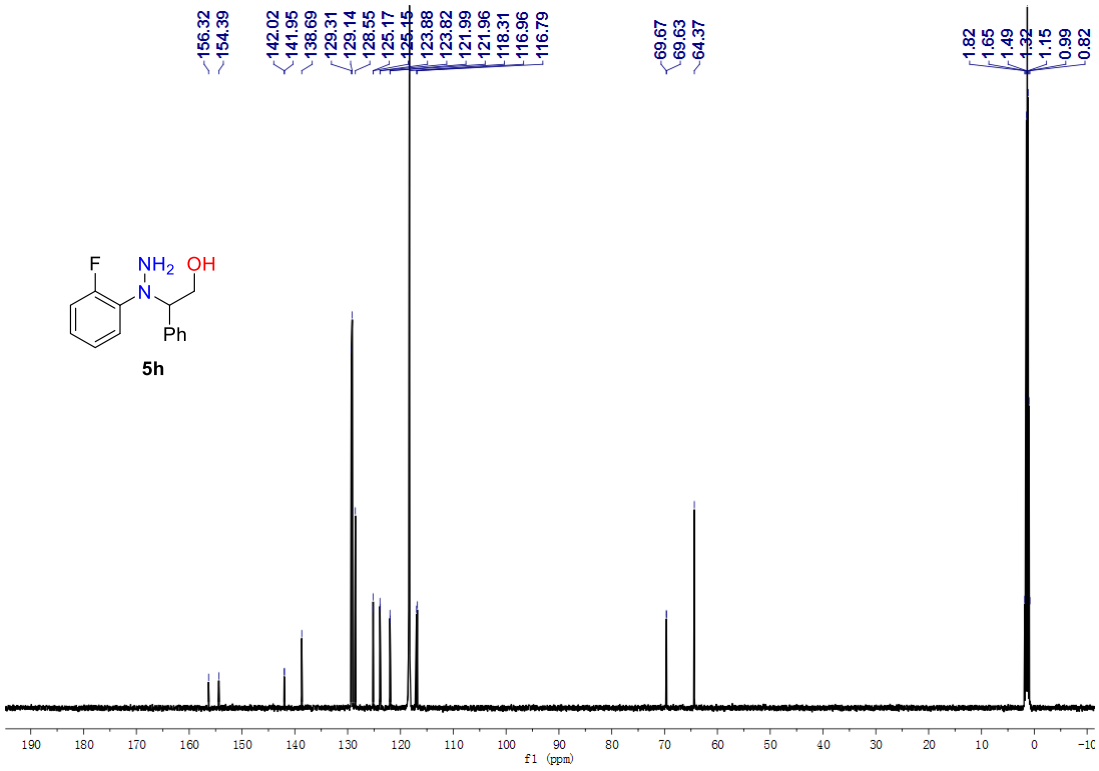


Figure S60. The ^{13}C-NMR spectral copy of compound **5h**.

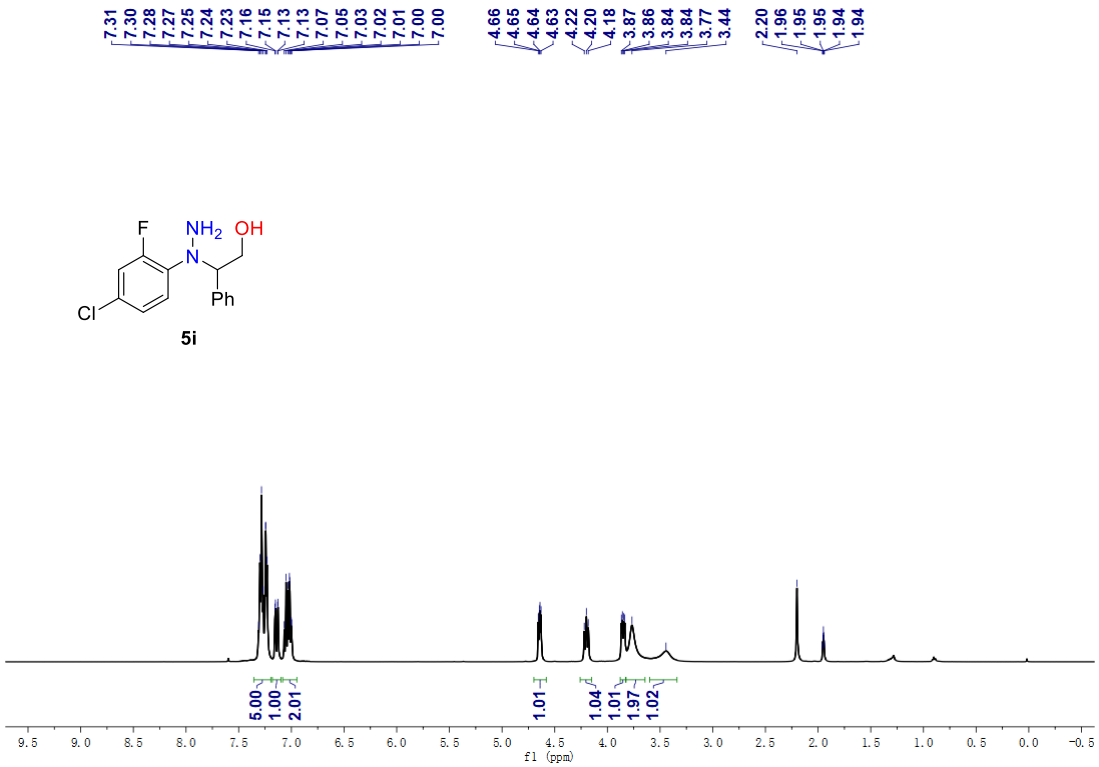


Figure S61. The ^{1}H-NMR spectral copy of compound **5i**.

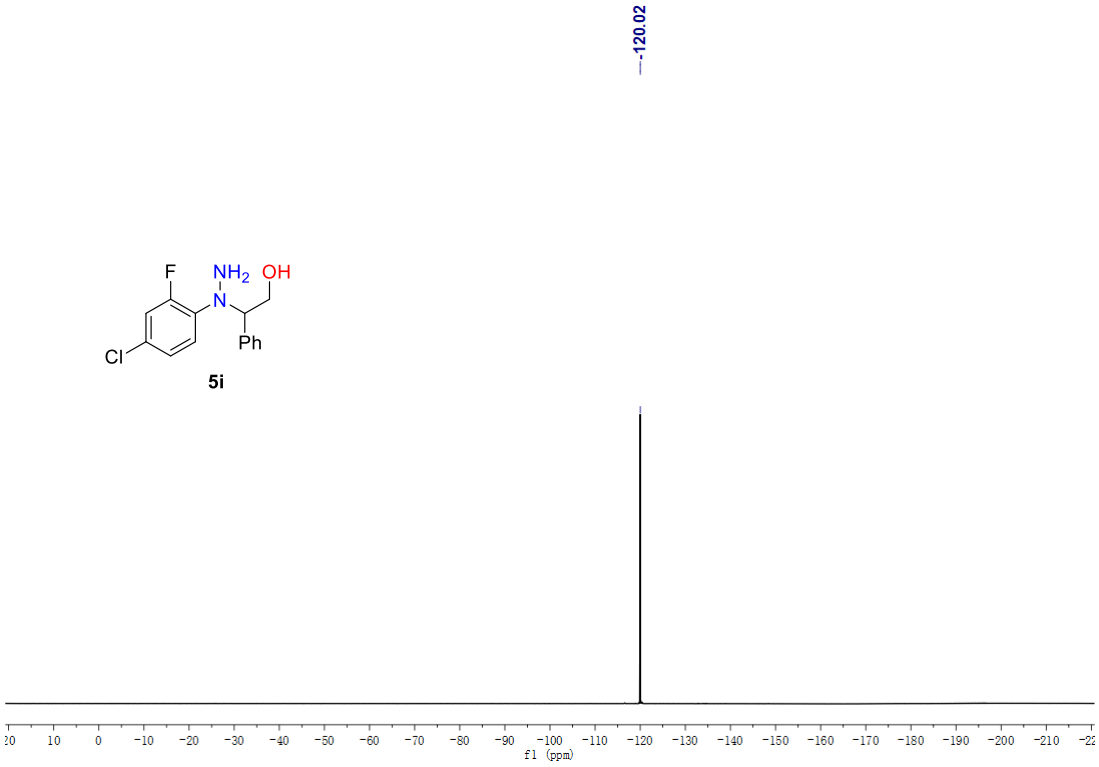


Figure S62. The ^{19}F-NMR spectral copy of compound **5i**.

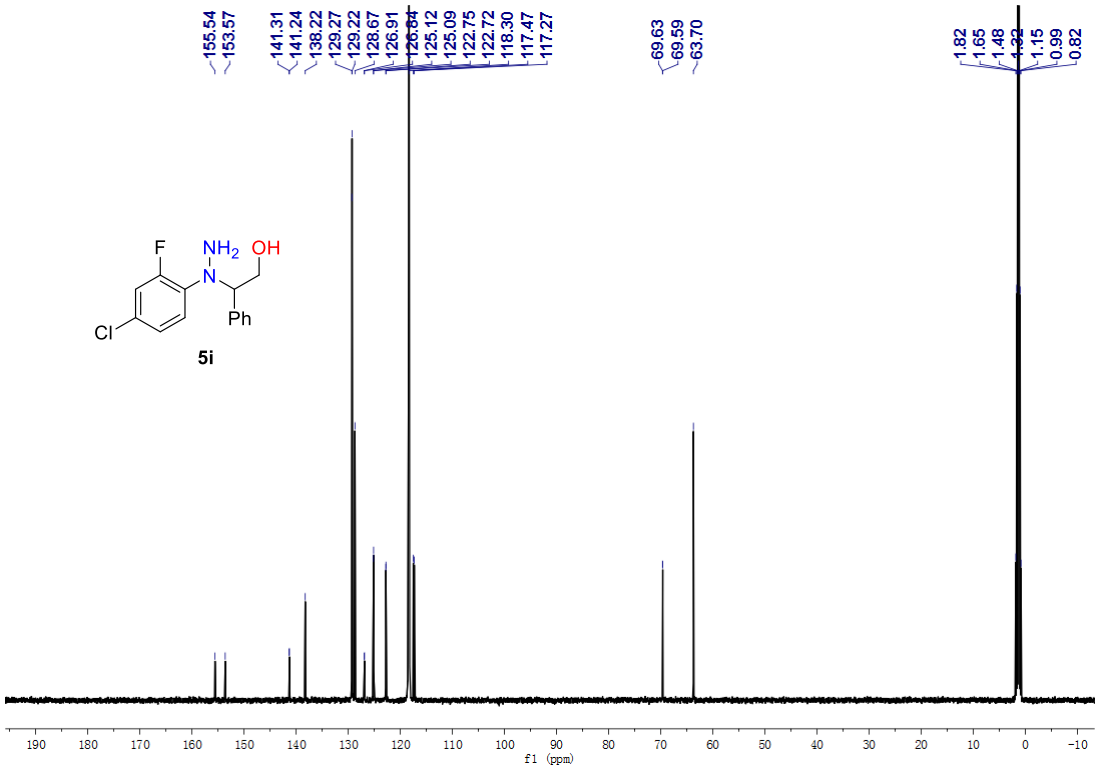


Figure S63. The ^{13}C-NMR spectral copy of compound **5i**.

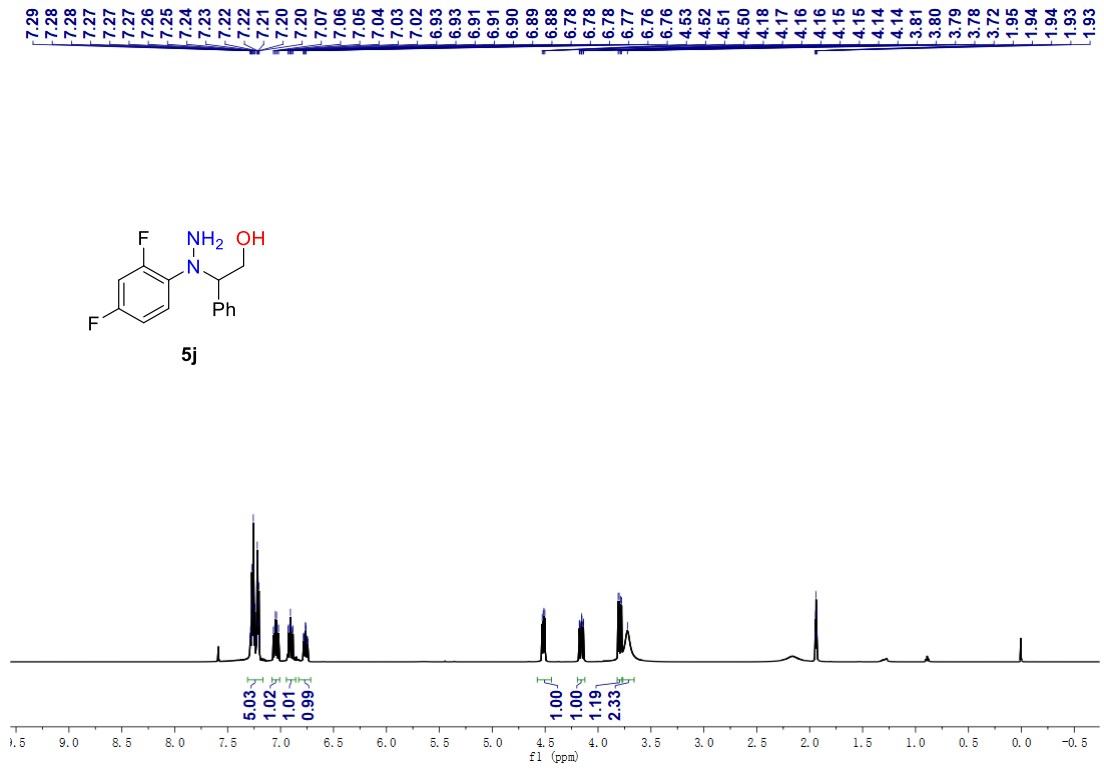


Figure S64. The ^{1}H-NMR spectral copy of compound **5j**.

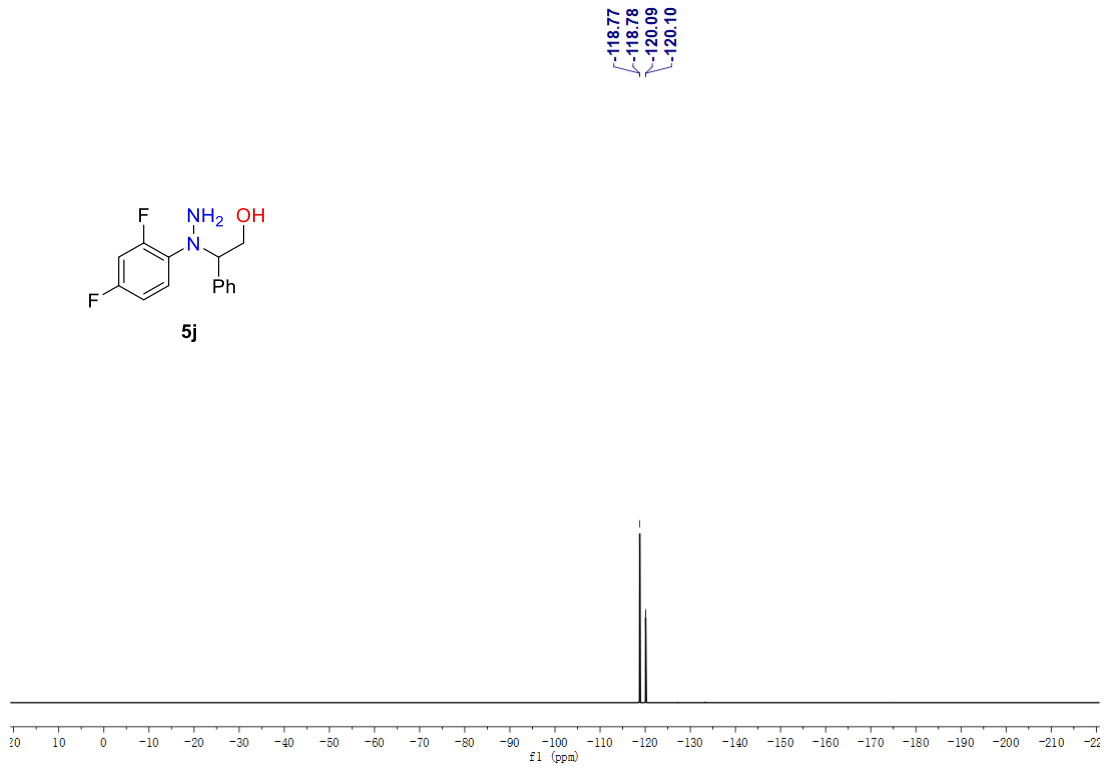


Figure S65. The ^{19}F-NMR spectral copy of compound **5j**.

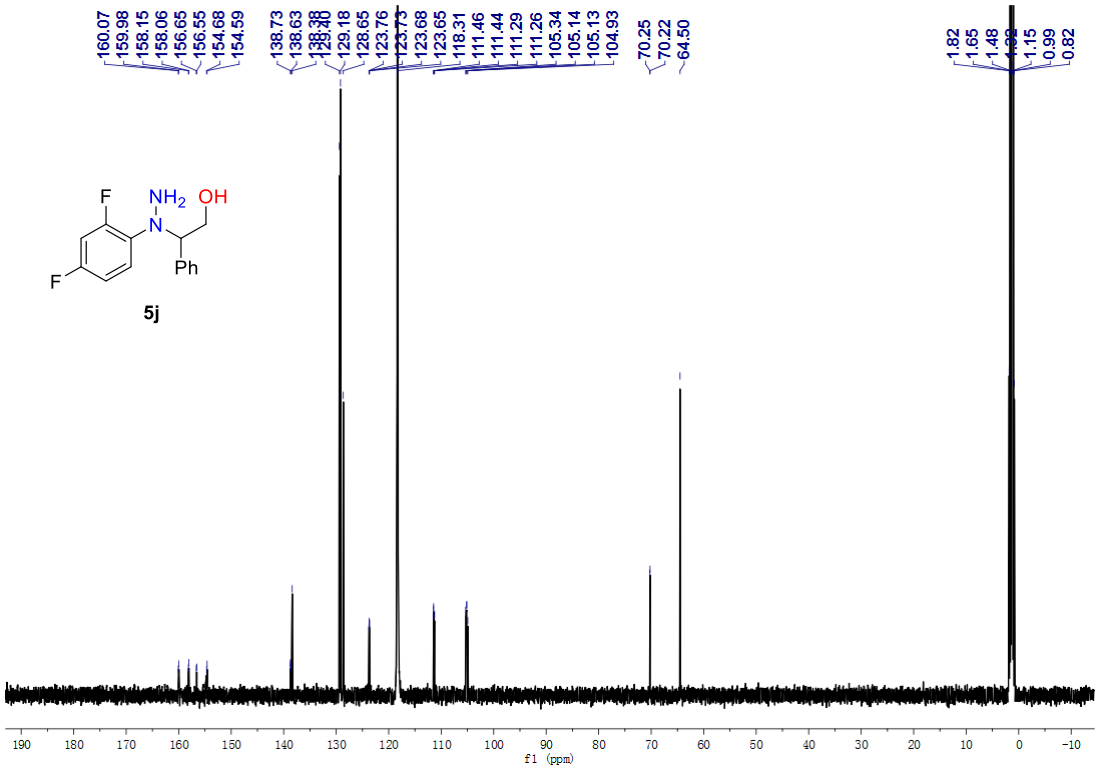


Figure S66. The ^{13}C-NMR spectral copy of compound **5j**.

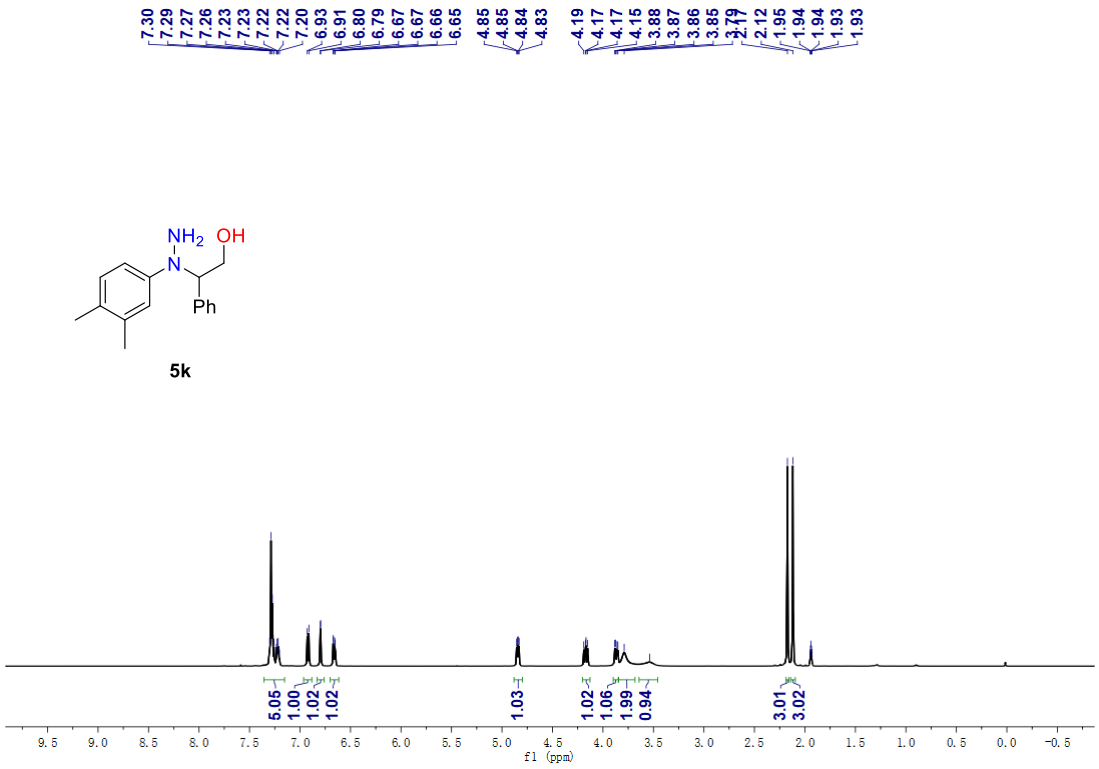


Figure S67. The ^{1}H-NMR spectral copy of compound **5k**.

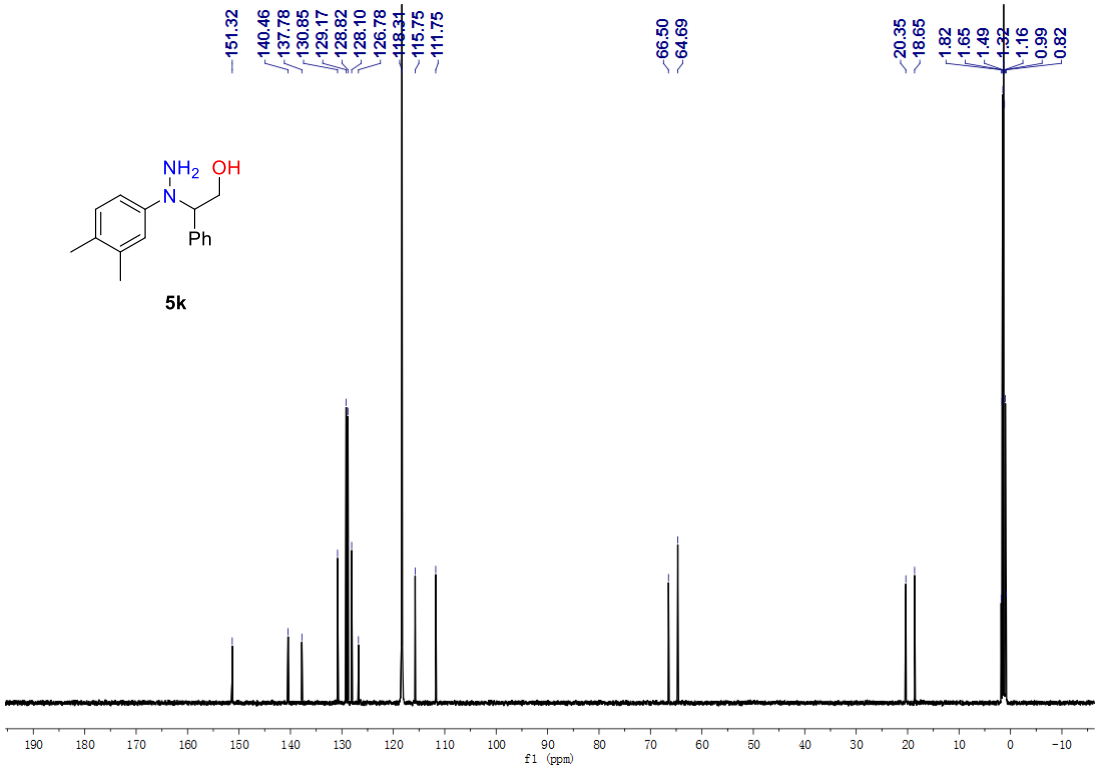


Figure S68. The ^{13}C-NMR spectral copy of compound **5k**.

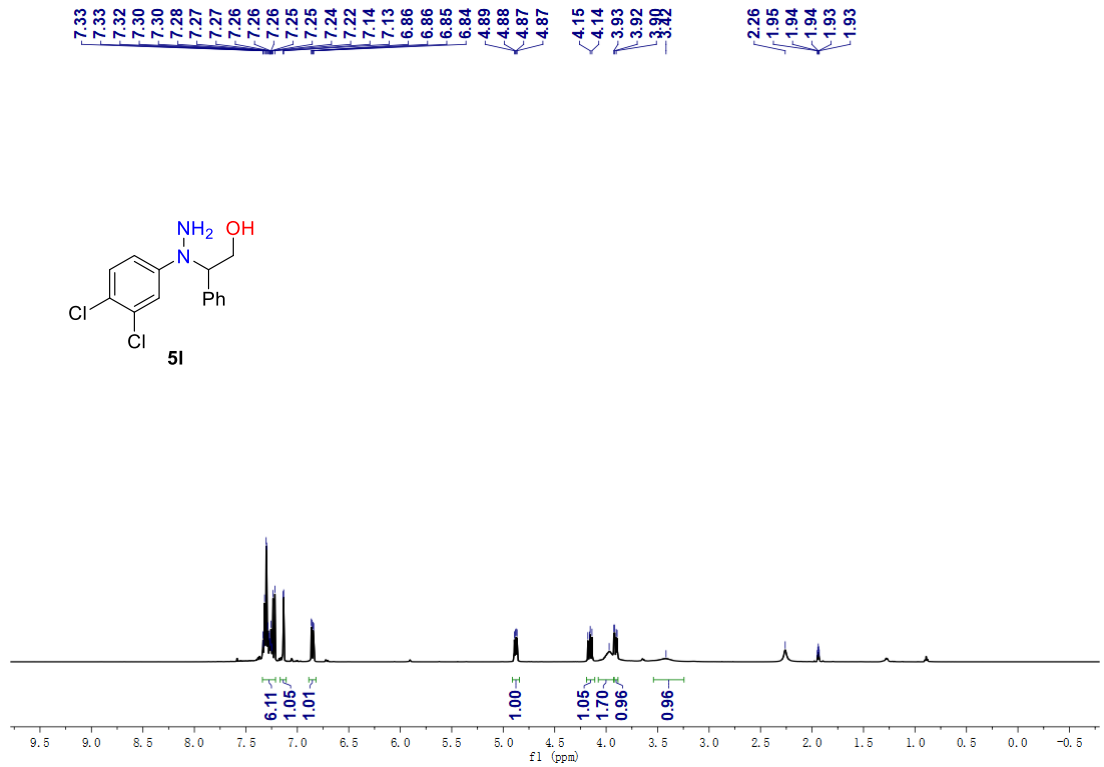


Figure S69. The ^{1}H-NMR spectral copy of compound **5l**.

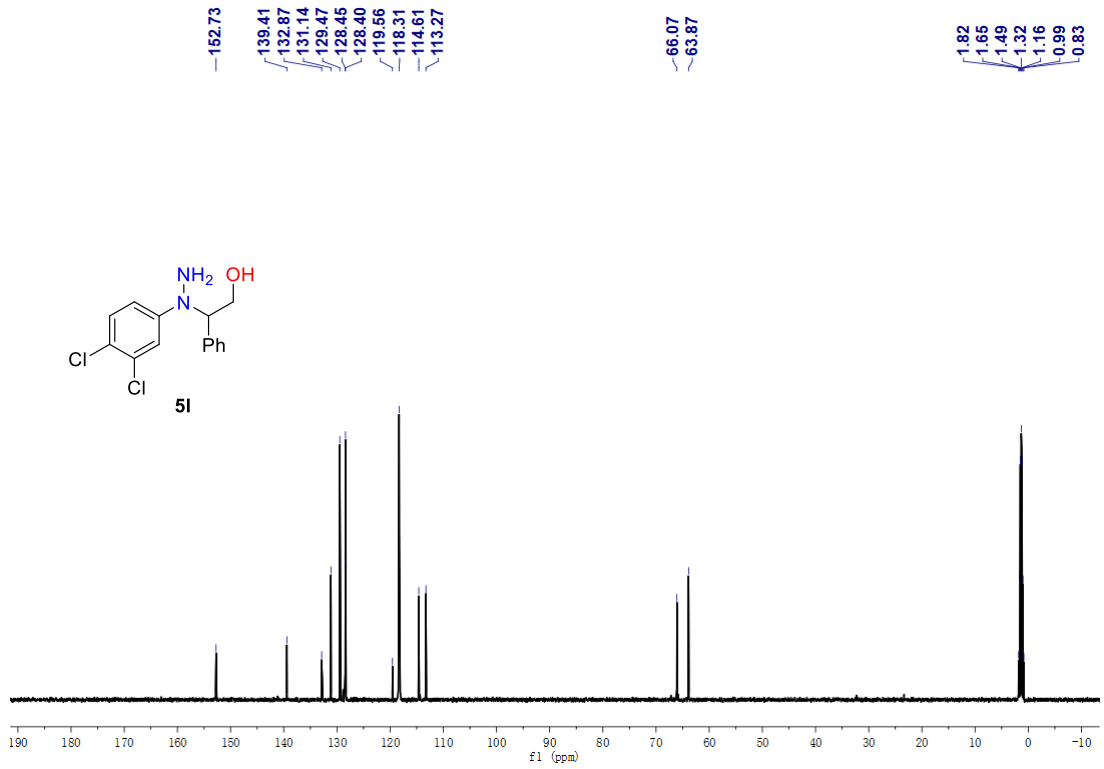


Figure S70. The ^{13}C-NMR spectral copy of compound **5l**.

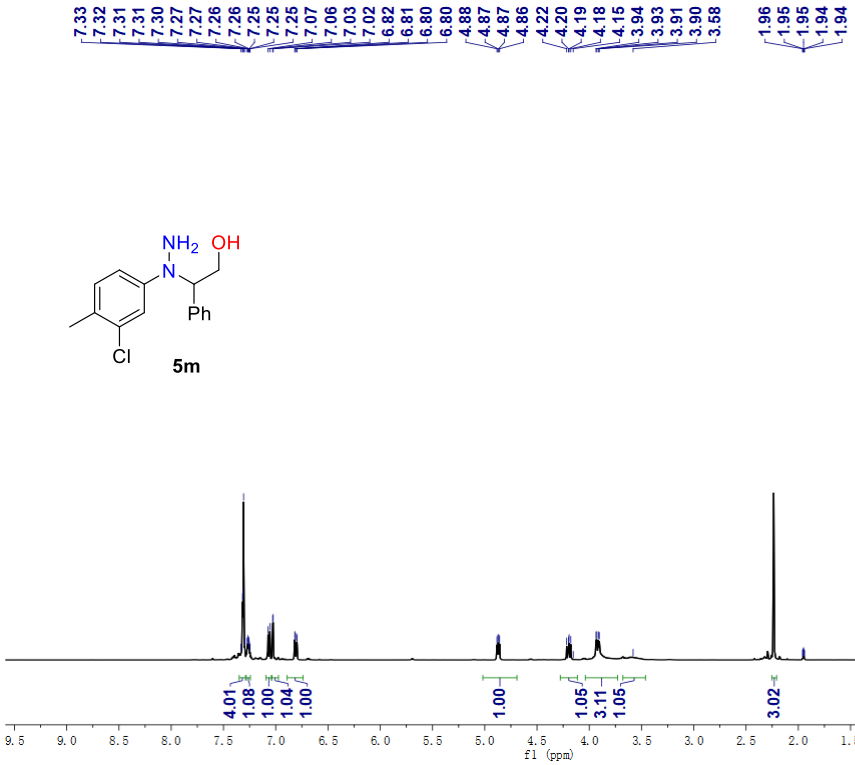


Figure S71. The ^{1}H-NMR spectral copy of compound **5m**.

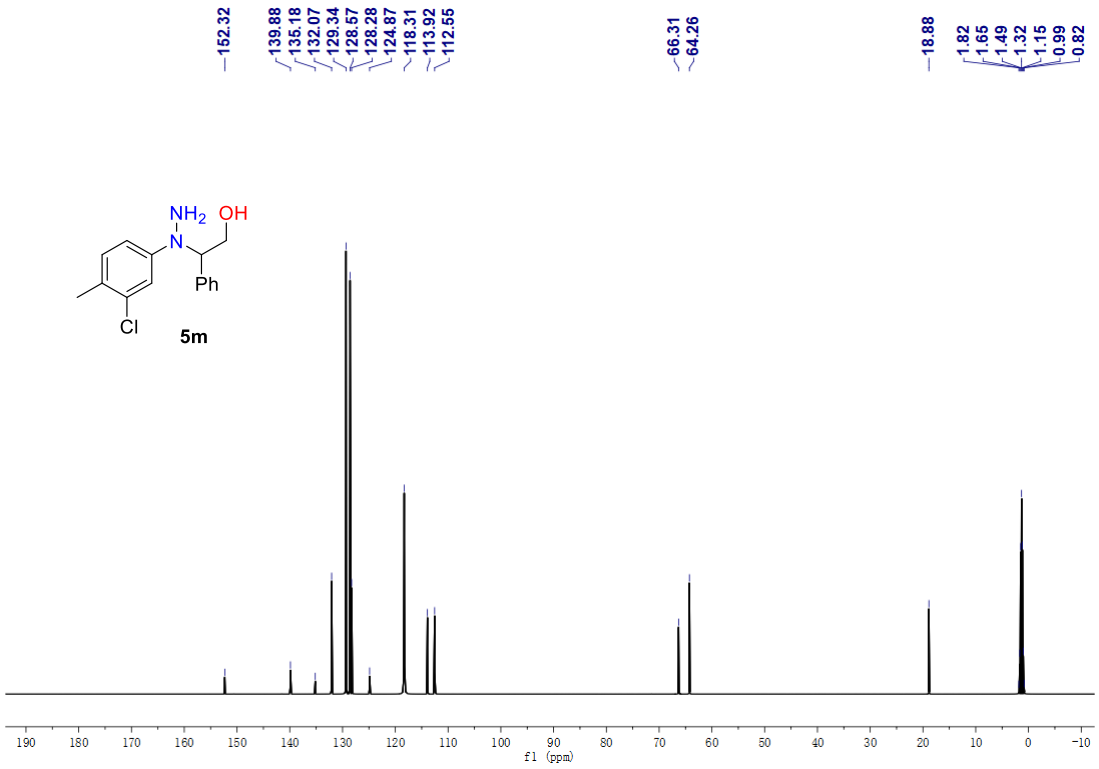


Figure S72. The ^{13}C-NMR spectral copy of compound **6m**.

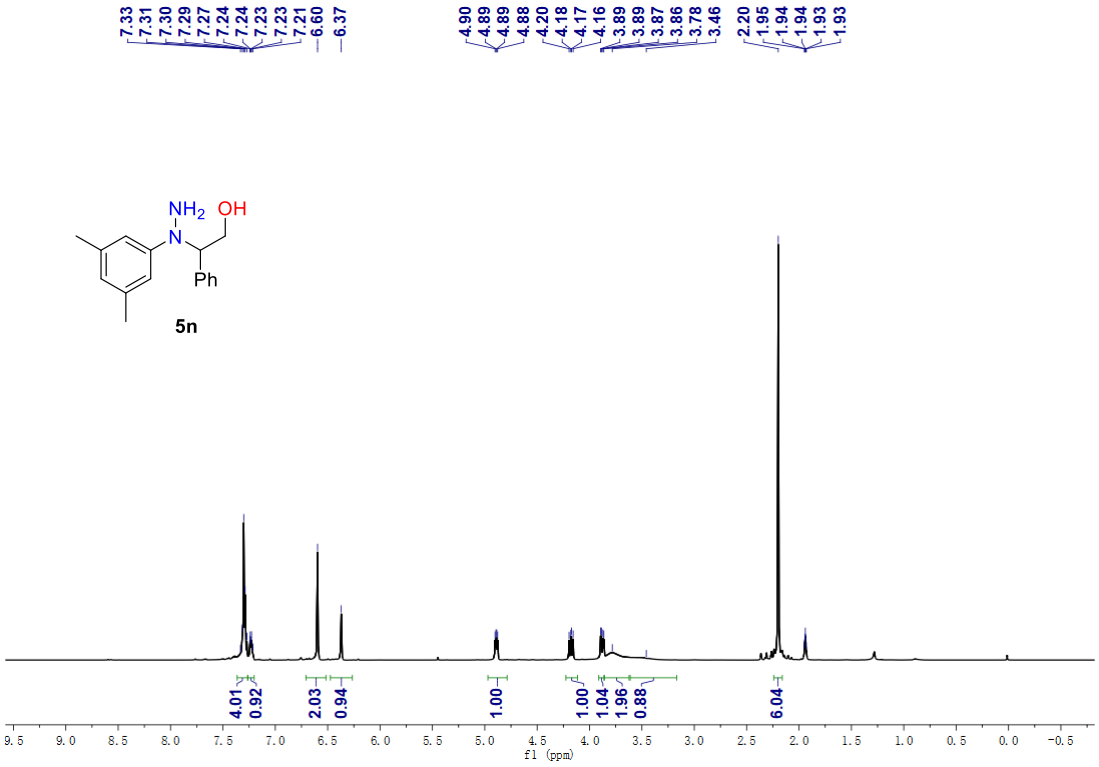


Figure S73. The ^{1}H-NMR spectral copy of compound **5n**.

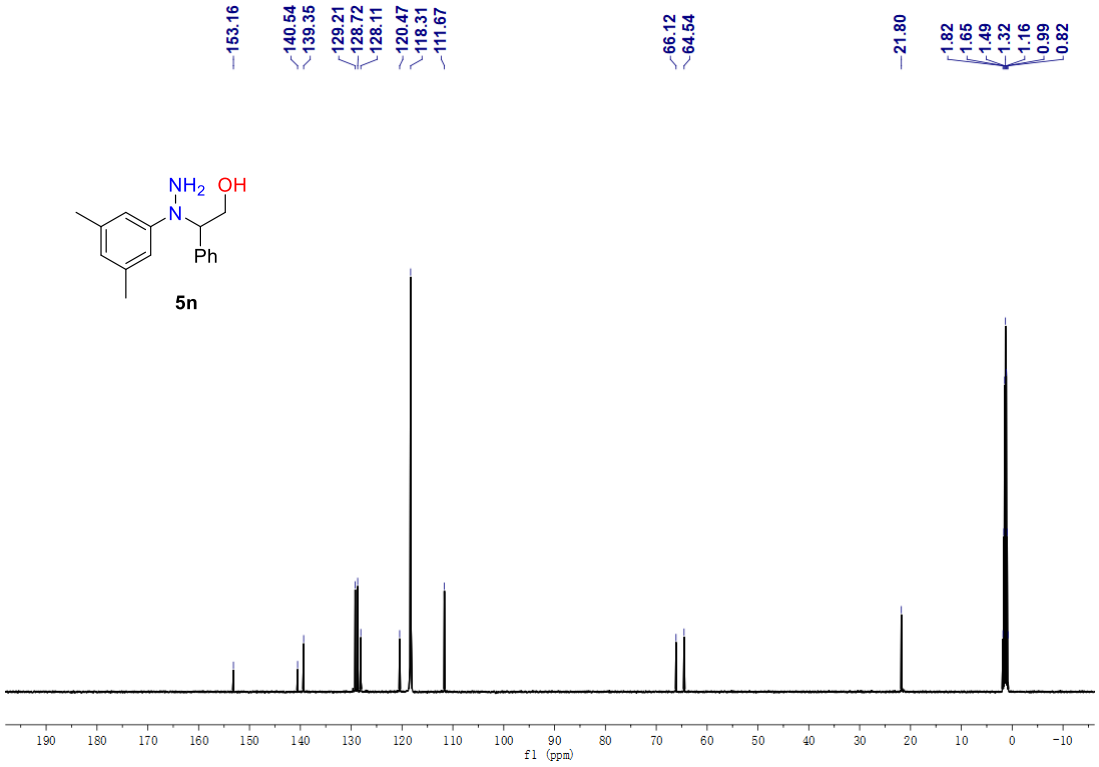


Figure S74. The ^{13}C-NMR spectral copy of compound **5n**.

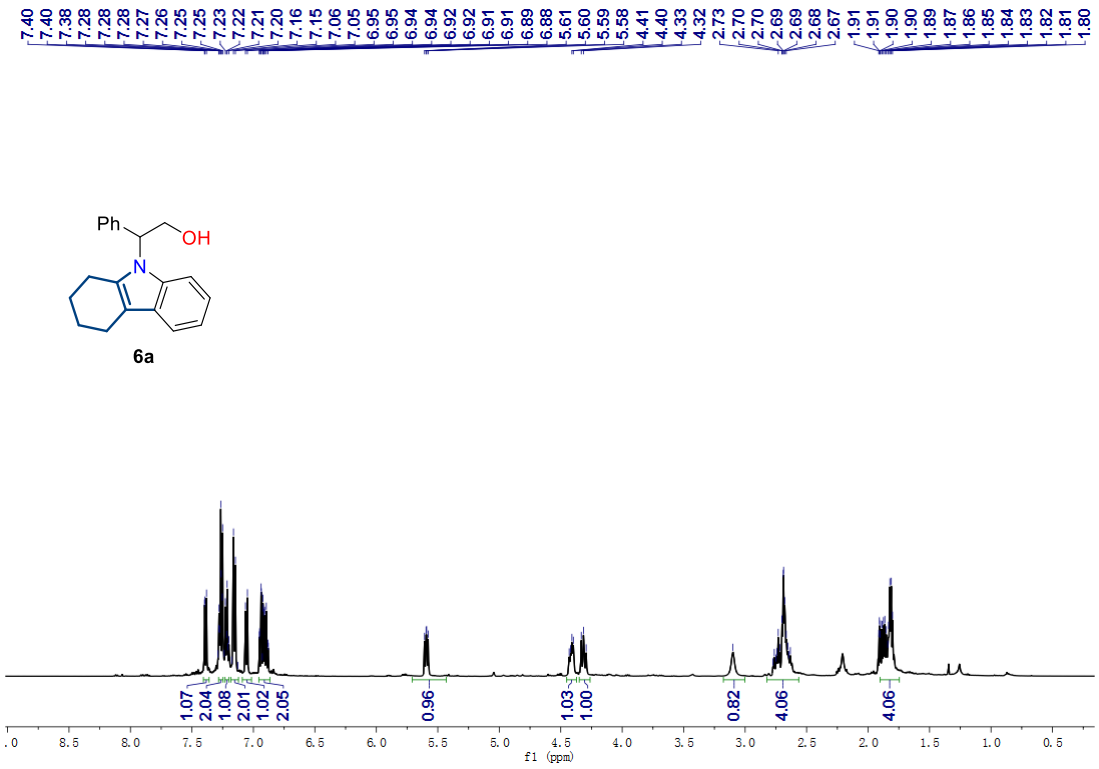


Figure S75. The ^{1}H-NMR spectral copy of compound **6a**.

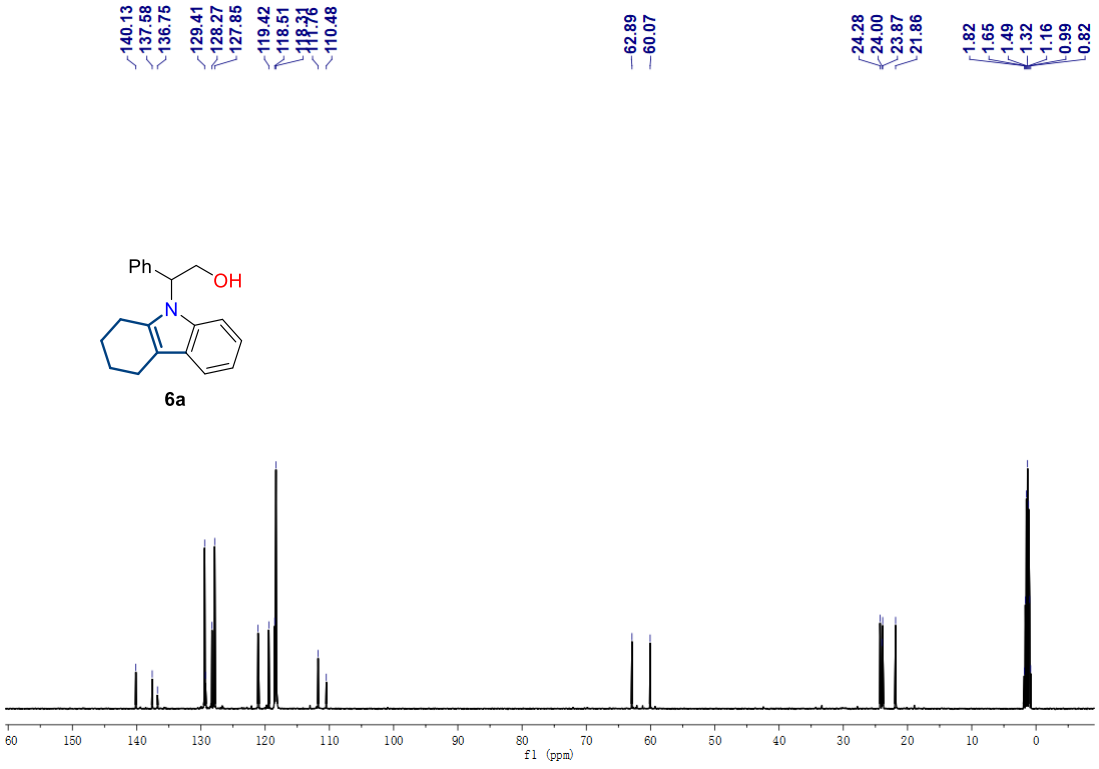


Figure S76. The ^{13}C-NMR spectral copy of compound **6a**.

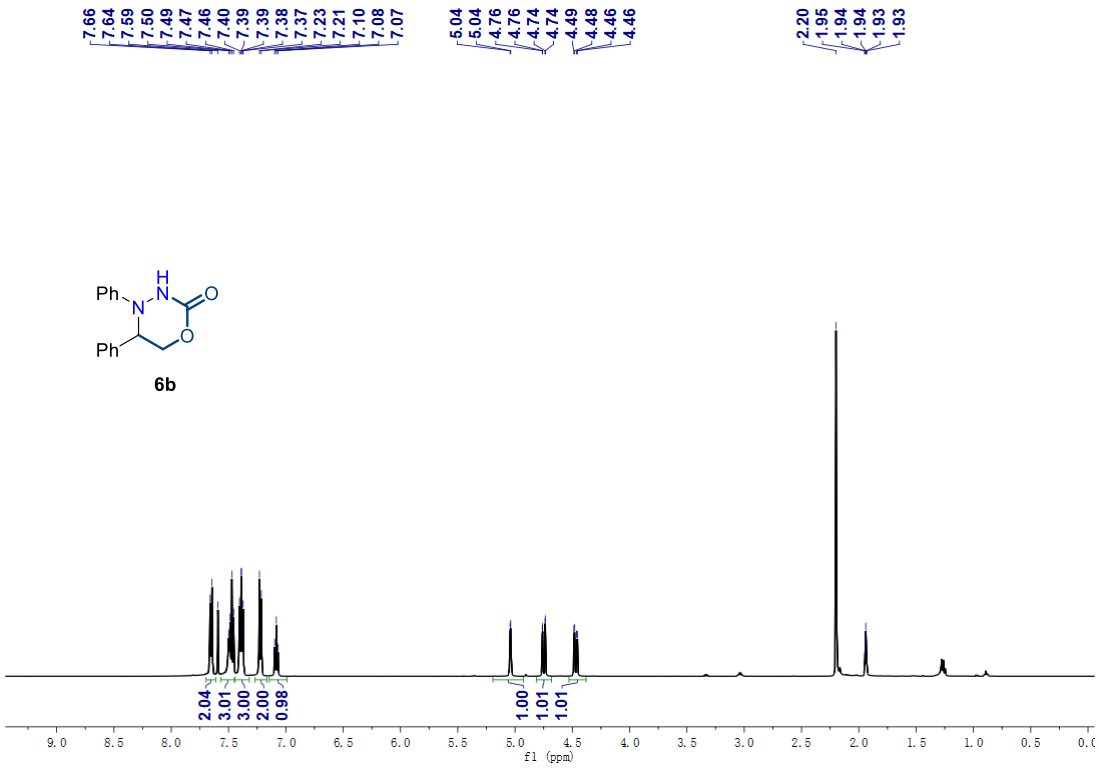


Figure S77. The ^{1}H-NMR spectral copy of compound **6b**.

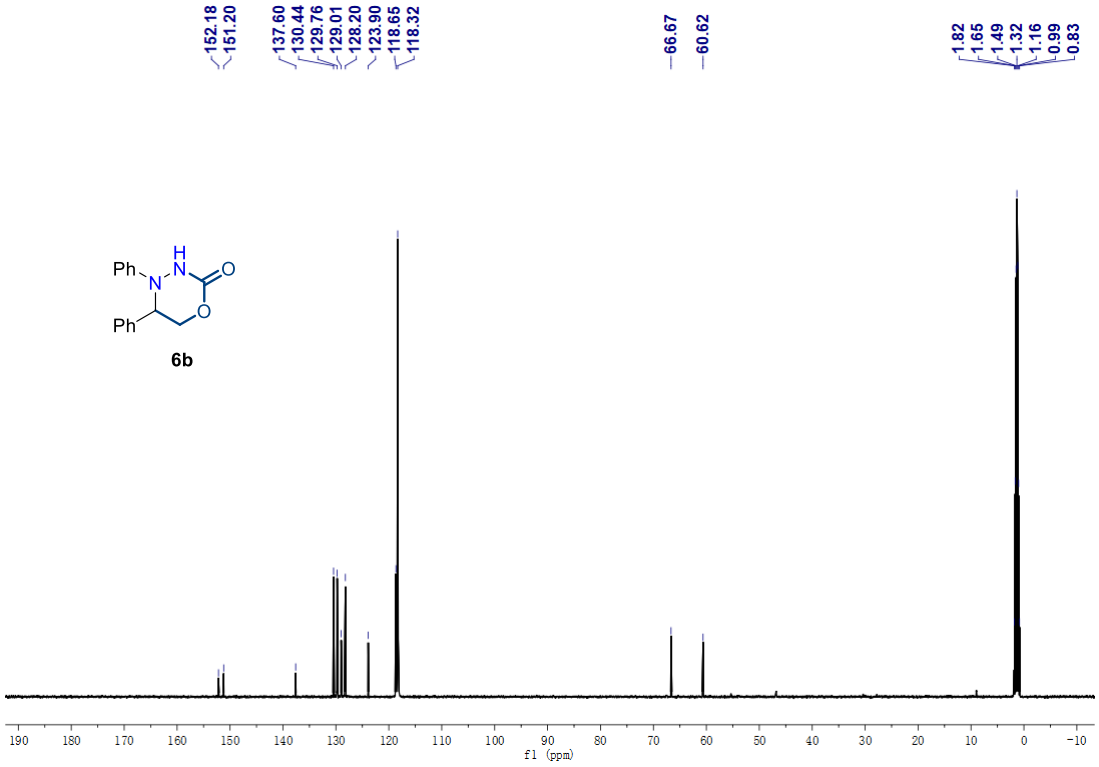


Figure S78. The ^{13}C-NMR spectral copy of compound **6b**.

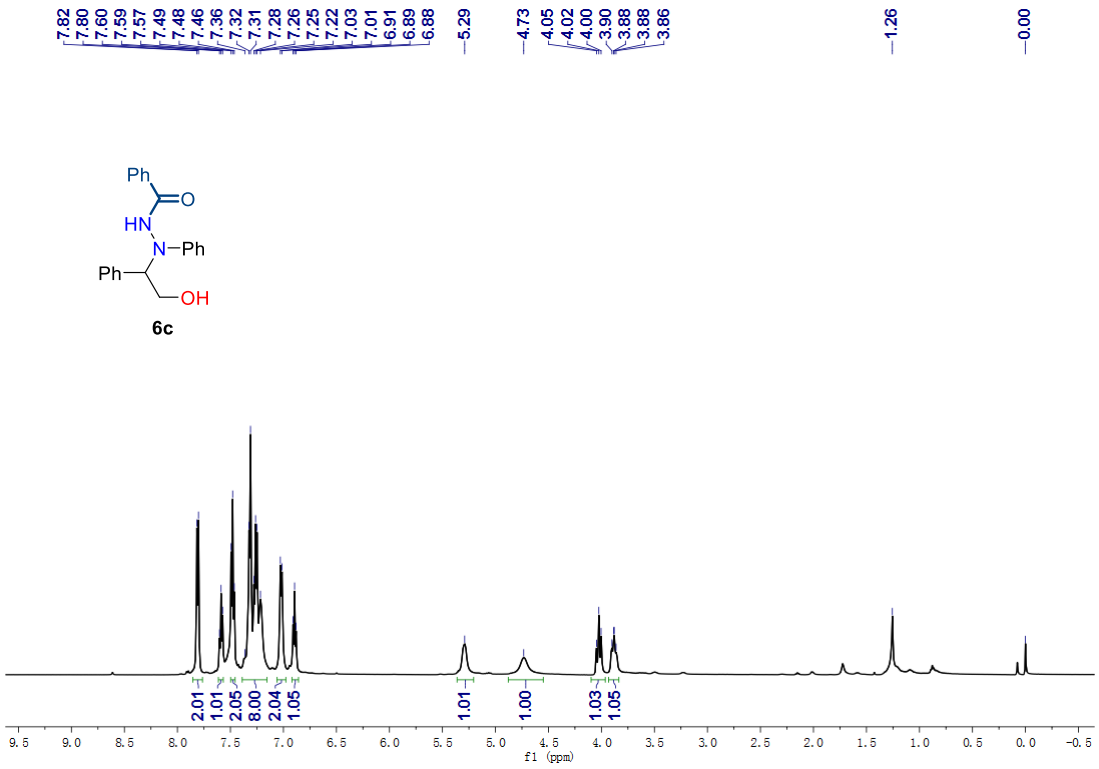


Figure S79. The ^{1}H-NMR spectral copy of compound **6c**.

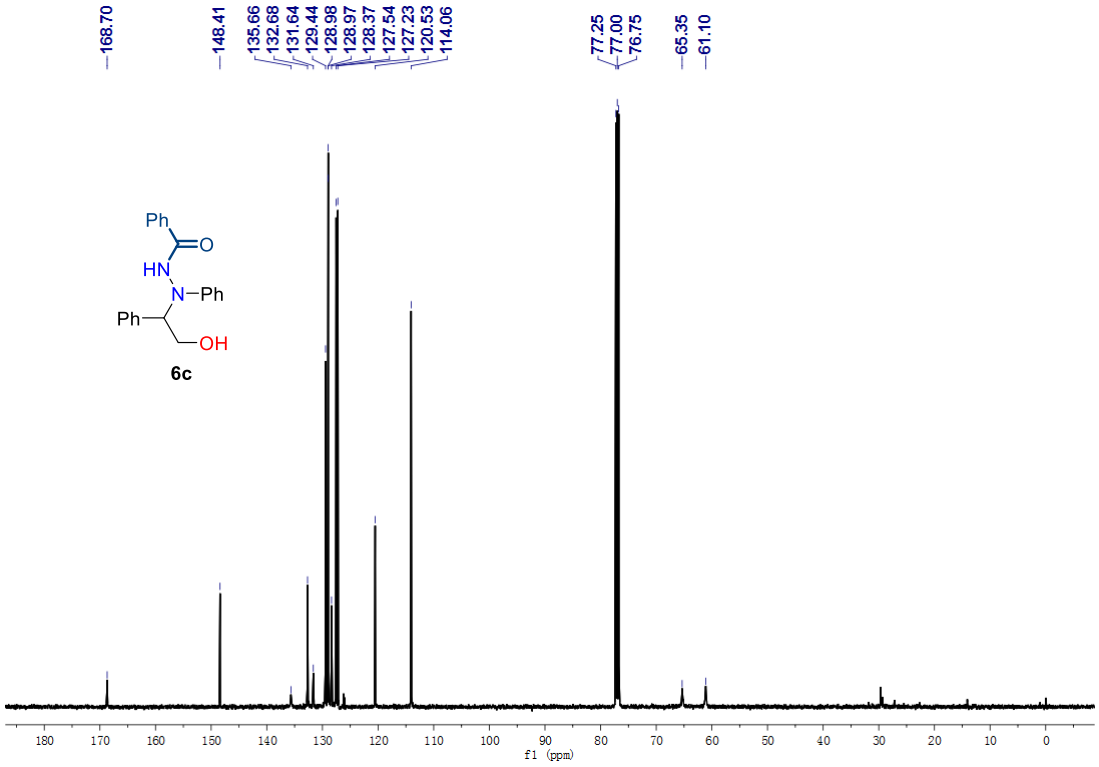


Figure S80. The ^{13}C-NMR spectral copy of compound **6c**.

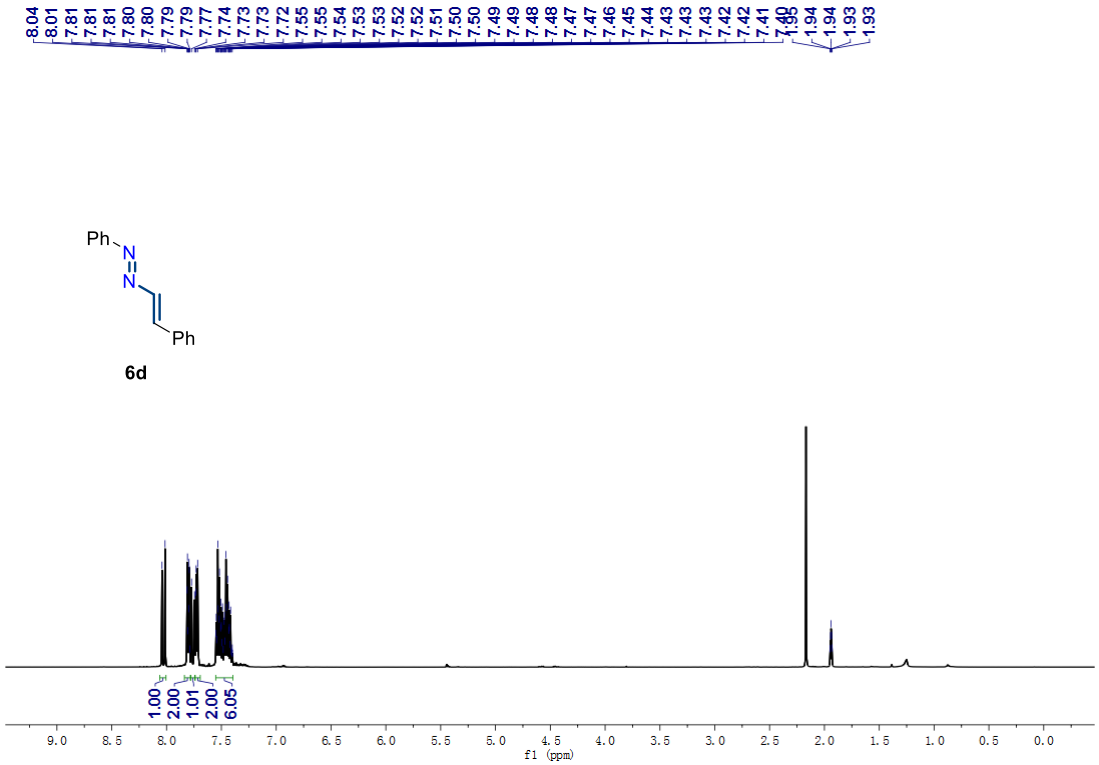


Figure S81. The ^{1}H-NMR spectral copy of compound **6d**.

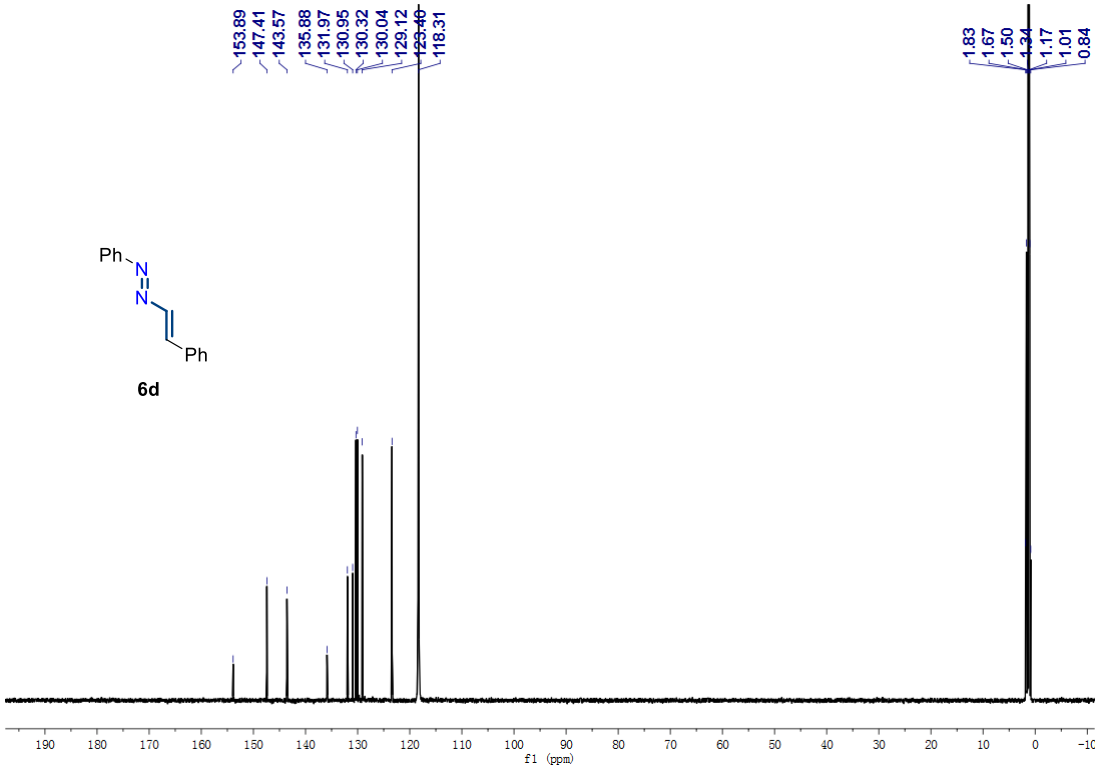
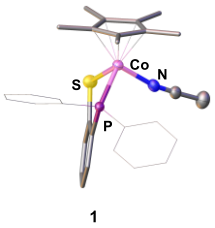


Figure S82. The ^{13}C-NMR spectral copy of compound **6d**.

5. Crystal data and structure refinement parameters.

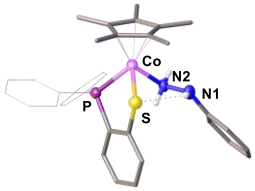


1

Figure S83. X-ray structure of **1** showing 50% probability ellipsoids. For clarity, hydrogen atoms and counteranions are omitted, and the two phenyl groups at the phosphorus site are drawn as lines.

Table S2. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	$C_{30}H_{32}BCoF_4NPS$
Formula weight	615.13
Temperature/K	173.00(10)
Crystal system	orthorhombic
Space group	Pna21
a/Å	18.0169(4)
b/Å	19.1954(5)
c/Å	9.2687(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3205.49(14)
Z	4
ρ calcg/cm^3	1.451
μ /mm-^{1}	7.206
F(000)	1440.0
Crystal size/mm^3	0.35 x 0.24 x 0.36
Radiation	Cu$K\alpha$ (λ = 1.54184)
2Θ range for data collection/°	6.728 to 134.11
Index ranges	-19 ⩽ h ⩽ 21, -22 ⩽ k ⩽ 22, -11 ⩽ l ⩽ 8
Reflections collected	9625
Independent reflections	4363 [R_{int} = 0.0496, R_{sigma} = 0.0613]
Data/restraints/parameters	4363/1/385
Goodness-of-fit on F^2	1.107
Final R indexes [I>=2σ (I)]	R_1 = 0.0520, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0608, wR_2 = 0.1241
Largest diff. peak/hole / e Å^{-3}	0.47/-0.42
Flack parameter	-0.013(6)



1'

Figure S84. X-ray structure of **1'** showing 50% probability ellipsoids. For clarity, hydrogen atoms and counteranions are omitted, and the two phenyl groups at the phosphorus site are drawn as lines.

Table S3. Crystal data and structure refinement for **1'**

Identification code	**1'**
Empirical formula	$C_{34}H_{37}BCoF_4N_2PS$
Formula weight	682.17
Temperature/K	172.99(10)
Crystal system	orthorhombic
Space group	*P*ca21
a/Å	17.7390(4)
b/Å	10.70121(19)
c/Å	33.5410(7)
α/ °	90
β/ °	90
γ/ °	90
Volume/Å^3	6367.0(2)
Z	4
ρcalcg/cm^3	1.424
μ/mm-^{1}	5.743
F(000)	2832.0
Crystal size/mm^3	0.4 x 0.31 x 0.3
Radiation	Cu*K*α (λ = 1.54184)
2Θ range for data collection/°	5.27 to 134.16
Index ranges	$-20 \leq h \leq 21$, $-12 \leq k \leq 12$, $-26 \leq l \leq 40$
Reflections collected	19264
Independent reflections	8080 [R_{int} = 0.0609, R_{sigma} = 0.0669]
Data/restraints/parameters	8080/61/803
Goodness-of-fit on F^2	1.145
Final R indexes [I>=2σ (I)]	R_1 = 0.0608, wR_2 = 0.1470
Final R indexes [all data]	R_1 = 0.0742, wR_2 = 0.1681
Largest diff. peak/hole / e Å^{-3}	1.23/-0.49
Flack parameter	-0.007(5)

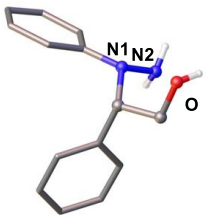


Figure S85. X-ray structure of **4a** showing 50% probability ellipsoids. For clarity, hydrogen atoms are omitted.

Table S4. Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{14}H_{16}N_2O$
Formula weight	228.12
Temperature/K	173.00(10)
Crystal system	trigonal
Space group	R3
a/Å	23.4012(7)
b/Å	23.4012(7)
c/Å	5.73617(17)
α/ °	90
β/ °	90
γ/ °	120
Volume/Å^3	2720.38(18)
Z	9
ρcalcg/cm^3	1.182
μ/mm-^{1}	0.632
F(000)	981.0
Crystal size/mm^3	0.4 x 0.21 x 0.3mm^3
Radiation	Cu$K\alpha$ (λ = 1.54184)
2Θ range for data collection/°	7.556 to 133.524
Index ranges	-21 ≤ h ≤ 27, -27 ≤ k ≤ 26, -5 ≤ l ≤ 6
Reflections collected	2191
Independent reflections	1392 [R_{int} = 0.0537, R_{sigma} = 0.0476]
Data/restraints/parameters	1392/1/156
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0682, wR_2 = 0.1882
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.2135
Largest diff. peak/hole / e Å^{-3}	0.41/-0.32
Flack parameter	-0.2(8)

6. References

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