Supplementary Information (SI) for Green Chemistry.
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Supporting Information

Transition Metal-Free *α,β*-C(sp³)−H Dehydrogenative Diazotization of Piperidines under Mild Conditions

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MATERIALS AND METHODS

1. General information.

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere and monitored by thin-layer chromatography (TLC). Concentration under reduced pressure was performed by rotary evaporation at 50–60 °C at an appropriate pressure. Purified compounds were further dried under vacuum (10^{-6}–10^{-3} bar). Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

Solvents

All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification and used as received.

Chromatography

Thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254) was performed using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light and I_2 stain. Column chromatography was performed on silica gel (200-300 mesh).

Spectroscopy and Instruments

NMR spectra were recorded on Bruker-600 spectrometer operating at (600 MHz, 565 MHz and 151 MHz), for ^{1}H, ^{19}F and ^{13}C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent residual peak as the internal standard. For ^{1}H-NMR: $CDCl_3$, 7.26; For ^{13}C-NMR: $CDCl_3$, 77.16; ^{19}F-NMR spectra were referenced using a unified chemical shift scale based on the ^{1}H resonance of tetramethylsilane (1% v/v solution in the respective solvent). Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration.

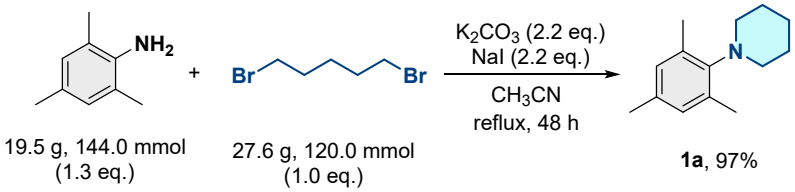
Instrument

All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

EXPERIMENTAL DATA

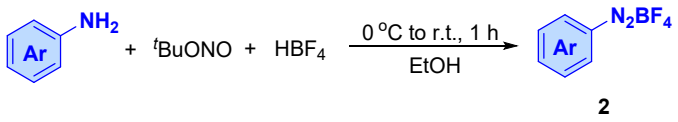
2. Substrates preparation.

2.1. Method A [1] (preparation of substrates 1)



Procedure for *N*-mesitylpiperidine (1a): A mixture of mesitylamine (19.5 g, 144 mmol), 1,5-dibromopentane (27.6 g, 120 mmol), K_2CO_3 (36.5 g, 264 mmol), and NaI (39.6 g, 264 mmol) in CH_3CN (400 mL) was stirred for 48 h under reflux. After cooling to room temperature, Et_2O was added, and the precipitate was filtered off. All the volatiles in the filtrate were removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (hexane) to give **1a** (23.7 g, 97% yield). Similarly, the other *N*-arylpiperidine derivatives were prepared from the corresponding arylamines.

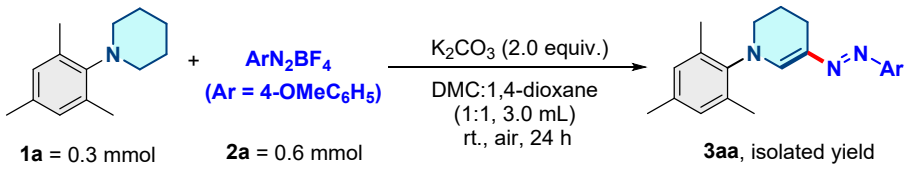
2.2. Method B [2] (preparation of substrates 2)



Appropriate arylamine (10.0 mmol) was dissolved in EtOH (3.0 mL) and hydrofluoroboric acid (48% w/w in water, 2.5 mL). The reaction mixture was cooled to 0 °C, *tert*-butyl nitrite (2.7 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1.0 hour. The resulting precipitate was collected by filtration. The crude product was dissolved into acetone (about 20.0 mL, for some low solubility product, more acetone was used), and the solution was gently heated, and then diethyl ether was added until the recrystallized product precipitated completely. The diazonium salt was collected by filtration, washed several times by cold diethyl ether and dried under vacuum.

3. Optimization of reaction conditions

Table S1. Optimization of the reaction conditions. [a]



1a = 0.3 mmol **2a** = 0.6 mmol **3aa**, isolated yield

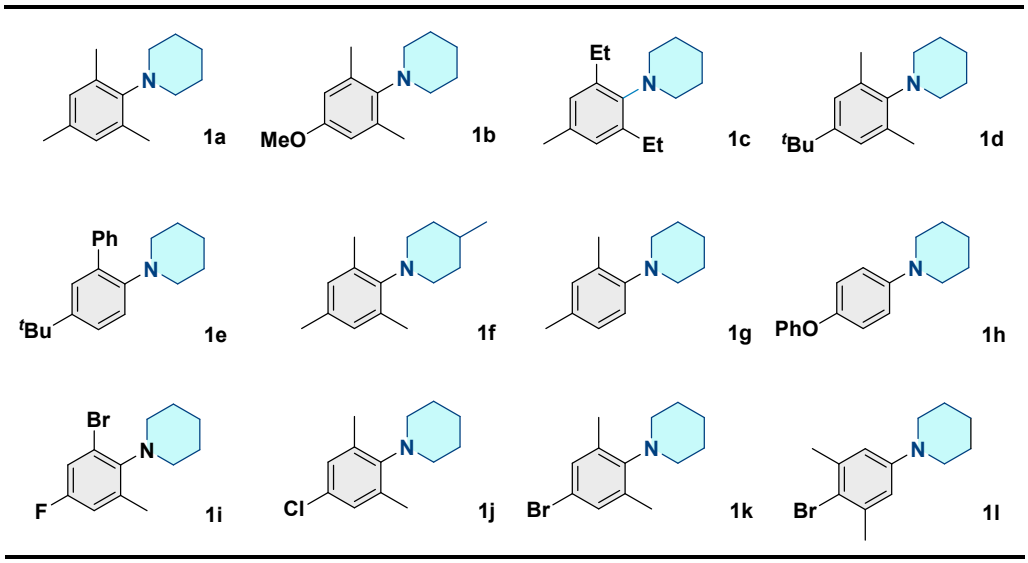
Entry	Base	Solvent	Temp.	Time	Yield (%)[b]
1.	**K_2CO_3**	**DMC:1,4-dioxane = 1:1**	**26 °C**	**24 h**	**72**
2.	Na_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	26
3.	$NaHCO_3$	DMC:1,4-dioxane = 1:1	26 °C	24 h	35
4.	Cs_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	45
5.	KOH	DMC:1,4-dioxane = 1:1	26 °C	24 h	trace
6.	K_2CO_3	H_2O	26 °C	24 h	28
7.	K_2CO_3	EtOH	26 °C	24 h	57
8.	K_2CO_3	DMC	26 °C	24 h	37
9.	K_2CO_3	MeCN	26 °C	24 h	41
10.	K_2CO_3	1,4-Dioxane	26 °C	24 h	62
11.	K_2CO_3	1,3-Dioxolane	26 °C	24 h	48
12.	K_2CO_3	Acetone	26 °C	24 h	56
13.	K_2CO_3	DMC:1,4-dioxane = 1:2	26 °C	24 h	48
14.	K_2CO_3	DMC:1,4-dioxane = 2:1	26 °C	24 h	36
15.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	18 h	59
16.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	12 h	49
17.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	48[c]
18.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	71[d]
19.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	54[e]
20.	K_2CO_3	DMC:1,4-dioxane = 1:1	26 °C	24 h	33[f]

[a]Reaction conditions, unless specified otherwise: **1a** (0.3 mmol), **2a** (0.6 mmol), Base (0.6 mmol) and solvent (DMC:1,4-dioxane = 1:1, 3.0 mL) were stirred at 26 °C under air for 24 h.

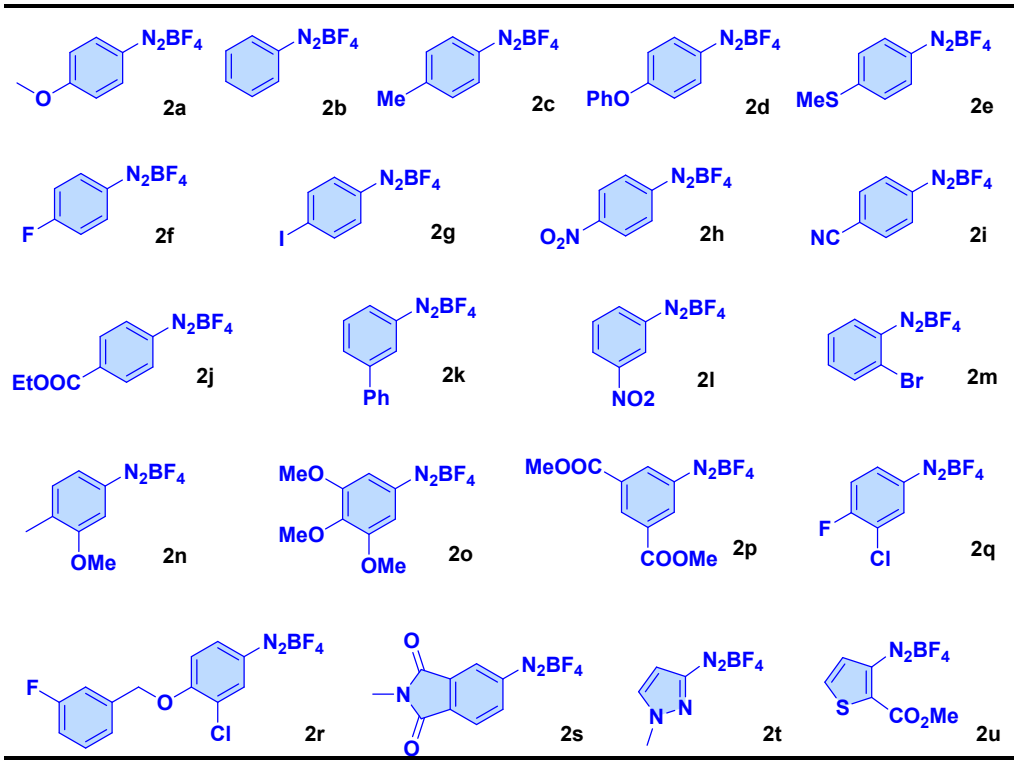
[b]Isolated yield., [c]1.0 equivalent of K_2CO_3. [d]3.0 equivalent of K_2CO_3. [e]2.0 mL of DMC:1,4-dioxane (1:1, 3.0 mL) as the solvent. [f]Ar instead of O_2.

4. Summary of substrates

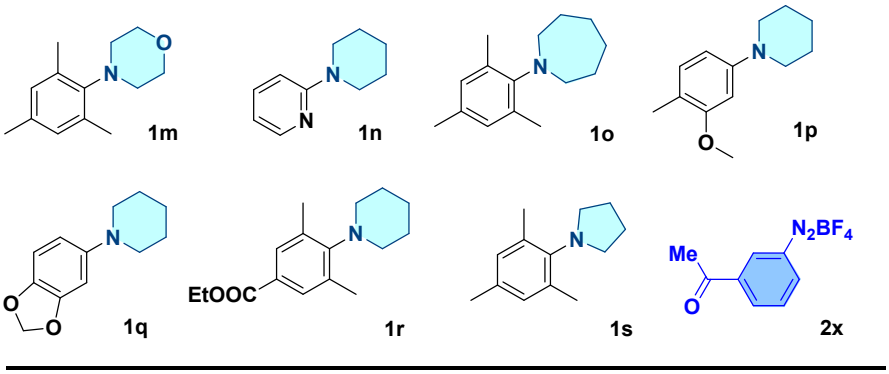
Scheme S1. Scope of piperidine compounds.



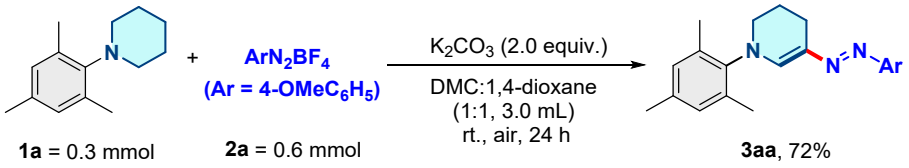
Scheme S2. Scope of diazonium salt compounds.



Scheme S3. Other unsuccessful substrates.

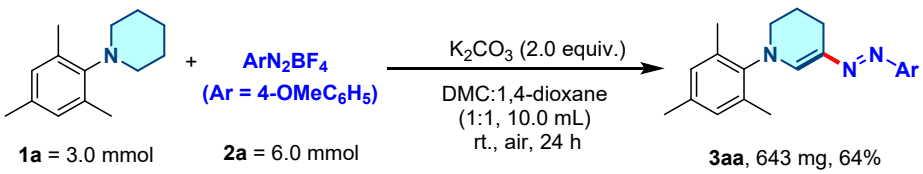


5. Typical procedure for the synthesis of 3aa. *p*-Methoxydiazonium salt **2a** (133.2 mg, 0.6 mmol), potassium carbonate (K_2CO_3, 89.2 mg, 0.6 mmol), dimethyl carbonate (DMC,1.5 ml), 1,4-dioxane (1.5 mL), and *N*-mesitylpiperidine **1a** (60.9 mg, 0.3 mmol) were sequentially added to a reaction tube. The mixture was stirred at room temperature for 24 h under an air atmosphere. Upon completion of the reaction, the solvent was removed by vacuum rotary evaporation. The residual material was purified by preparative thin-layer chromatography on silica gel using petroleum ether/ethyl acetate (5:1，v/v) as the eluent, yielding **3aa** as a pale yellow solid (72.4 mg, 72% yield).

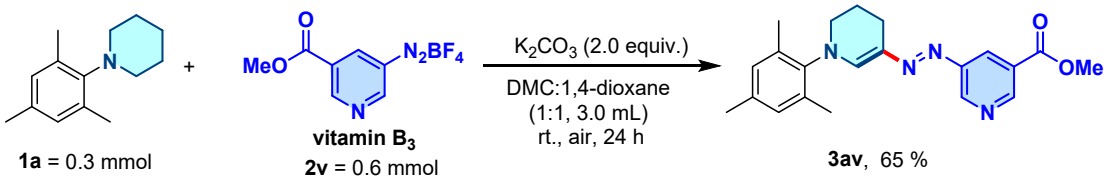


6. Synthetic application.

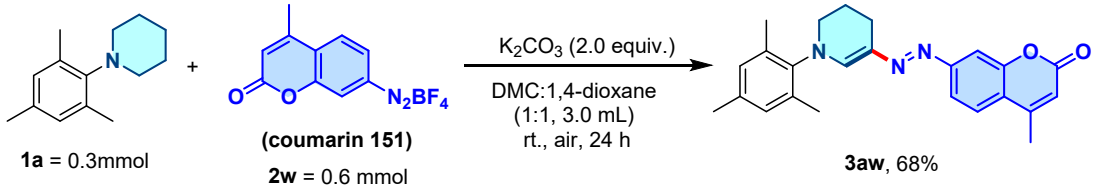
(1) *p*-Methoxydiazonium salt **2a** (1332.0 mg, 6.0 mmol), potassium carbonate (K_2CO_3, 892.0 mg, 6 mmol), dimethyl carbonate (DMC,5.0 ml), 1,4-dioxane (5.0 mL), and N-Mes piperidine **1a** (609.0 mg, 3.0 mmol) were sequentially added to a reaction tube. The mixture was stirred at room temperature for 24 h under an air atmosphere. Upon completion of the reaction, the solvent was removed by vacuum rotary evaporation. The residual material was purified by preparative thin-layer chromatography on silica gel using petroleum ether/ethyl acetate (5:1, v/v) as the eluent, yielding **3aa** as yellow solid (643.0 mg, 64% yield).



(2) Compound **2v** (150.6 mg, 0.6 mmol), potassium carbonate (K_2CO_3, 82.9 mg, 0.6 mmol), dimethyl carbonate (DMC, 1.5 ml), 1,4-dioxane (1.5 mL), and *N*-mesitylpiperidine **1a** (60.9 mg, 0.3 mmol) were sequentially added to a reaction tube. Under an air atmosphere, the mixture was stirred at room temperature for 24 h to proceed with the reaction. After the reaction was completed, a pale yellow reaction solution was obtained. Subsequently, the reaction solution was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1, v/v) as the eluent, affording the target product **3av** as a yellow solid (71.0 mg, 65% yield).

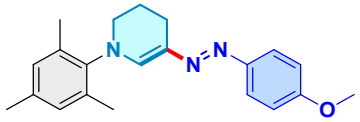


(3) Compound **2w** (164.4 mg, 0.6 mmol), potassium carbonate (K_2CO_3, 82.9 mg, 0.6 mmol), dimethyl carbonate (DMC, 1.5ml), 1,4-dioxane (1.5 mL), and *N*-mesitylpiperidine **1a** (60.9 mg, 0.3 mmol) were sequentially added to a reaction tube. Under an air atmosphere, the mixture was stirred at room temperature for 24 h to proceed with the reaction. After the reaction was completed, a pale yellow reaction solution was obtained. Subsequently, the reaction solution was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1, v/v) as the eluent, affording the target product **3aw** as a yellow solid (75.0 mg, 68% yield).



7.MNR data of the obtained compounds.

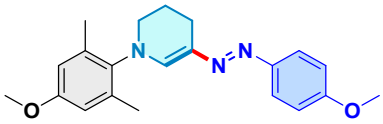
(1) (*E*)-1-mesityl-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3aa)



Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (72 mg, 72% yield); m.p.: 99.6-100.2 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.19 (s, 1H), 6.94 (s, 2H),

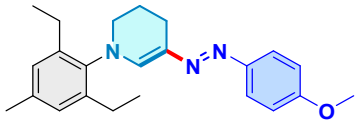
6.91 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 3.52 – 3.41 (m, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 6H), 2.14 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) ^{13}C NMR (151 MHz, Chloroform-*d*)) δ 158.4, 148.3, 147.7, 141.2, 137.2, 135.4, 132.9, 129.3, 121.9, 113.8, 55.2, 48.6, 21.0, 20.8, 19.8, 17.7. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}N_3O$: 336.2070; found: 336.2064.

(2) (*E*)-1-(4-methoxy-2,6-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ba)



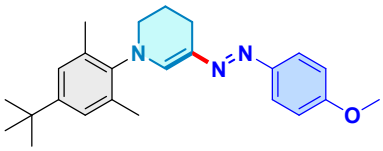
Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (68 mg, 65% yield); m.p.: 113.7-114.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.19 (s, 1H), 6.91 – 6.88 (m, 2H), 6.64 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.47 – 3.44 (m, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.26 (s, 6H), 2.14 (q, *J* = 6.1, 5.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.64, 158.54, 137.24, 137.06, 133.15, 122.00, 114.08, 113.77, 55.50, 55.42, 49.25, 21.22, 20.06, 18.31. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}N_3O_2$: 352.2019; found: 352.2012.

(3) (*E*)-1-(2,6-diethyl-4-methylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ca)



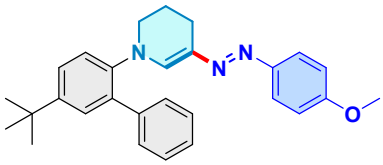
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (82 mg, 75% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 9.0 Hz, 2H), 7.23 (s, 1H), 7.00 (s, 2H), 6.95 – 6.91 (m, 2H), 3.83 (s, 3H), 3.52 – 3.49 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.68 – 2.59 (m, 4H), 2.38 (s, 3H), 2.19 – 2.14 (m, 2H), 1.27 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.5, 148.6, 148.4, 141.8, 140.4, 137.9, 132.8, 127.6, 122.1, 113.9, 55.3, 50.1, 24.2, 21.2, 21.1, 19.9, 15.41. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{29}N_3O$: 364.2383; found: 364.2375.

(4) (*E*)-1-(4-(tert-butyl)-2,6-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3da)



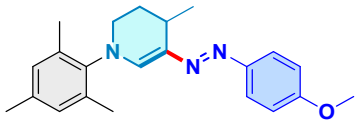
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (88 mg, 77% yield); m.p.: 173.7-174.5 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.24 – 7.21 (m, 1H), 7.14 – 7.12 (m, 2H), 6.93 – 6.90 (m, 2H), 3.82 (s, 3H), 3.50 – 3.47 (m, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.31 – 2.30 (m, 6H), 2.17 – 2.12 (m, 2H), 1.34 (d, *J* = 1.0 Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 150.6, 148.2, 141.3, 135.2, 133.1, 125.8, 122.1, 114.0, 55.4, 48.8, 34.4, 31.4, 21.2, 20.0, 18.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{31}N_3O$: 378.2539; found: 378.2531.

(5) (*E*)-1-(5-(tert-butyl)-[1,1'-biphenyl]-2-yl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ea)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (45 mg, 35% yield); m.p.: 126.8-127.5 ℃ ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.63 (s, 1H), 7.46 (dtd, *J* = 13.8, 8.2, 2.3 Hz, 5H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.28 (d, *J* = 5.4 Hz, 1H), 6.98 – 6.93 (m, 2H), 3.86 (s, 3H), 3.13 (t, *J* = 5.6 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.75 (p, *J* = 6.4 Hz, 2H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.9, 136.1, 128.8, 128.8, 128.7, 127.6, 125.3, 122.1, 114.1, 55.5, 50.1, 34.7, 31.4, 20.7, 20.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{31}N_3O$: 426.2539; found: 426.2531.

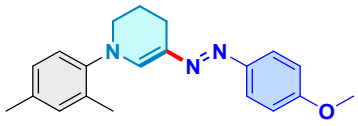
(6) (*E*)-1-mesityl-5-((4-methoxyphenyl)diazenyl)-4-methyl-1,2,3,4-tetrahydropyridine (3fa)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (79 mg, 75% yield); m.p.: 134.4-135.3 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 9.0 Hz, 2H), 7.13 (s, 1H), 6.98 – 6.94 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 3.74 (td, *J* = 13.0, 3.4 Hz, 1H), 3.54 (p, *J* = 6.8 Hz, 1H), 3.29 – 3.20 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.23 – 2.17 (m, 1H), 1.86 (ddt, *J* =

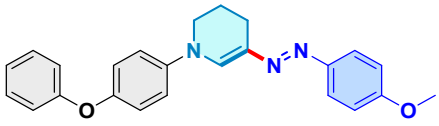
13.3, 3.8, 2.1 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.5, 148.4, 147.0, 141.3, 137.6, 137.4, 136.0, 135.4, 129.4, 129.4, 122.0, 113.9, 55.4, 44.6, 28.0, 23.3, 20.9, 19.1, 17.8, 17.7. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{27}N_3O$: 350.2226; found: 350.2221.

(7) (*E*)-1-(2,4-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ga)



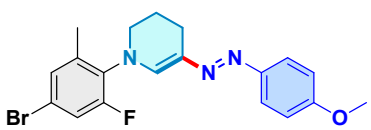
Petroleum ether and ethyl acetate (20:1) were used as eluents. Yellow liquid (44 mg, 46% yield); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.66 – 7.56 (m, 2H), 7.36 (s, 1H), 7.08 (dq, J = 2.1, 0.7 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.93 – 6.88 (m, 2H), 3.82 (s, 3H), 3.55 (d, *J* = 5.6 Hz, 2H), 2.74 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.13 – 2.08 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 150.1, 141.1, 137.8, 137.7, 135.4, 133.8, 129.5, 122.9, 91.0, 49.1, 21.0, 21.0, 19.9, 17.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}N_3O$: 322.1913; found: 322.1908.

(8) (*E*)-5-((4-methoxyphenyl)diazenyl)-1-(4-phenoxyphenyl)-1,2,3,4-tetrahydropyridine (3ha)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (15 mg, 13% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.71 – 7.54 (m, 2H), 7.41 – 7.30 (m, 2H), 7.26 (s, 1H), 7.21 – 7.07 (m, 3H), 7.09 – 6.97 (m, 4H), 6.93 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 3.77 – 3.70 (m, 2H), 2.71 (t, *J* = 6.5 Hz, 2H), 2.16 – 2.07 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 157.7, 136.5, 129.9, 123.2, 122.5, 120.3, 119.0, 118.4, 114.1, 55.6, 47.6, 21.2, 20.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{23}N_3O_2$: 386.1863; found: 386.1856.

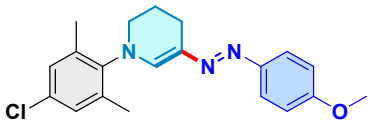
(9) (lopropylmethyl)-3,6-bis(phenylthio)quinolin-2(1*H*)-one (3ia)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (79 mg, 65% yield);

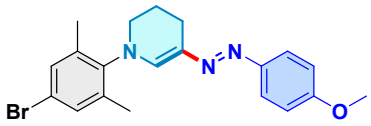
m.p.: 107.3-108.2 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.60 (m, 2H), 7.24 – 7.19 (m, 1H), 7.13 (s, 1H), 6.95 – 6.92 (m, 1H), 6.91 – 6.89 (m, 2H), 3.81 (s, 3H), 3.59 – 3.55 (m, 1H), 3.37 – 3.33 (m, 1H), 2.80 – 2.75 (m, 1H), 2.73 – 2.68 (m, 1H), 2.32 (s, 3H), 2.20 (dddt, *J* = 11.4, 5.6, 3.8, 1.9 Hz, 1H), 2.13 – 2.08 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.7, 160.0, 158.9, 147.4 (d, *J* = 137.1 Hz), 140.3 (d, *J* = 8.9 Hz), 139.8 (d, *J* = 3.4 Hz), 133.9, 124.2 (d, *J* = 10.7 Hz), 122.3, 118.2 (d, *J* = 25.3 Hz), 117.0 (d, *J* = 21.7 Hz), 113.9, 55.4, 48.6, 20.9, 19.7, 18.8. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -111.45. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{19}BrFN_3O$: 404.0768; found: 404.0762.

(10) (*E*)-1-(4-chloro-2,6-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ja)



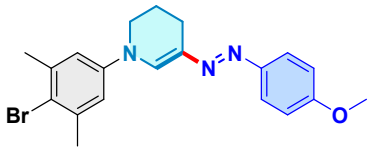
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (71 mg, 67% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.43 (m, 2H), 7.06 (s, 1H), 7.00 (t, *J* = 0.8 Hz, 2H), 6.82 – 6.77 (m, 2H), 3.71 (s, 3H), 3.36 – 3.31 (m, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 2.16 (d, *J* = 0.7 Hz, 6H), 2.04 – 1.99 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.8, 142.2, 137.7, 133.4, 133.0, 128.6, 122.0, 114.0, 55.4, 48.8, 21.0, 20.0, 17.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}ClN_3O$: 356.1524; found: 356.1517.

(11) (*E*)-1-(4-bromo-2,6-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ka)



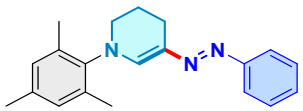
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (58 mg, 49% yield); m.p.: 152-154 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.71 (m, 2H), 7.37 (d, *J* = 1.8 Hz, 2H), 7.02 – 7.00 (m, 2H), 3.92 (s, 3H), 3.55 – 3.53 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 6H), 2.24 – 2.21 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 137.2, 136.8, 135.8, 135.6, 133.2, 131.2, 130.3, 130.1, 129.7, 129.6, 129.2, 128.3, 126.7, 121.6, 115.2, 30.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}BrN_3O$: 400.1019; found: 400.1013.

(12) (*E*)-1-(4-bromo-3,5-dimethylphenyl)-5-((4-methoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3la)



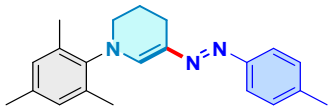
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (61 mg, 51% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 2H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.17 (s, 1H), 7.01 (dd, *J* = 2.1, 1.1 Hz, 1H), 6.91 – 6.88 (m, 2H), 3.81 (s, 3H), 3.60 (dddd, *J* = 12.2, 7.1, 3.8, 1.0 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.84 – 2.78 (m, 1H), 2.72 (ddd, *J* = 16.6, 7.4, 5.7 Hz, 1H), 2.30 (d, *J* = 5.2 Hz, 6H), 2.24 – 2.18 (m, 1H), 2.14 – 2.08 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 140.7, 139.3, 137.9, 133.6, 131.5, 131.0, 123.2, 122.1, 113.9, 55.4, 48.7, 20.9, 20.7, 19.8, 18.4. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}BrN_3O$: 400.1019; found: 400.1012.

(13) (*E*)-1-mesityl-5-(phenyldiazenyl)-1,2,3,4-tetrahydropyridine (3ab)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (55 mg, 60% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 2H), 7.44 – 7.37 (m, 2H), 7.30 (s, 1H), 7.24 – 7.18 (m, 1H), 6.97 (s, 2H), 3.54 – 3.47 (m, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 6H), 2.21 – 2.14 (m, 2H) . ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.2, 149.2, 141.1, 137.5, 135.4, 133.5, 129.4, 128.6, 126.4, 120.9, 48.9, 21.0, 20.9, 19.9, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}N_3$:306.1964; found: 306.1960.

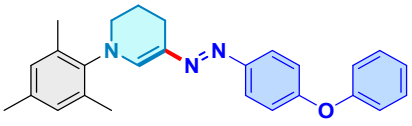
(14) (*E*)-1-mesityl-5-(p-tolyldiazenyl)-1,2,3,4-tetrahydropyridine (3ac)



Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow liquid (68 mg, 71% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.50 (m, 2H), 7.27 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 2H), 3.53 – 3.47 (m, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H), 2.30 (s, 6H), 2.19 – 2.15 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0, 148.7, 141.2, 137.5, 136.2, 135.5, 133.2, 129.4, 129.3, 120.7, 48.8, 21.1, 21.1, 20.9, 19.9, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}N_3$:

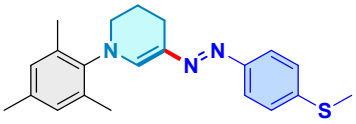
320.2121; found: 320.2116.

(15) (*E*)-1-mesityl-5-((4-phenoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ad)



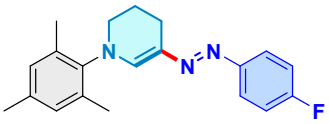
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (73 mg, 61% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (td, *J* = 7.5, 1.8 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.26 (m, 4H), 7.21 (td, *J* = 8.9, 2.0 Hz, 2H), 7.12 (td, *J* = 7.6, 1.8 Hz, 1H), 7.03 (dtd, *J* = 15.0, 7.9, 1.2 Hz, 2H), 6.91 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 250.3 Hz), 161.6, 159.4, 138.6, 137.7, 137.2, 133.9, 132.6, 132.5, 132.5, 130.6, 130.3, 130.2, 129.4, 129.2, 129.2, 128.8, 127.4 (d), 125.6 (d, *J* = 3.8 Hz), 124.8 (d, *J* = 3.7 Hz), 123.4 (d, *J* = 17.5 Hz), 121.3, 117.2, 116.9 (d, *J* = 22.3 Hz), 116.0 (d, *J* = 21.7 Hz). HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{17}F_2NOS_2$: 398.2226; found: 398.2222.

(16) (*E*)-1-mesityl-5-((4-(methylthio)phenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ae)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (72 mg, 68% yield); m.p.: 132.0-132.8 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.80 (m, 2H), 7.59 – 7.57 (m, 2H), 7.56 (s, 1H), 7.26 (s, 2H), 3.84 – 3.74 (m, 2H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.81 (s, 3H), 2.63 (s, 3H), 2.58 (s, 6H), 2.49 – 2.44 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.0, 149.1, 141.2, 137.6, 136.0, 135.5, 133.5, 129.5, 127.2, 121.4, 49.0, 21.1, 21.0, 19.9, 17.9, 16.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}N_3S$: 352.1841; found: 352.1837.

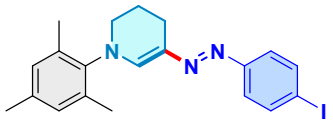
(17) (*E*)-5-((4-fluorophenyl)diazenyl)-1-mesityl-1,2,3,4-tetrahydropyridine (3af)



Petroleum ether and ethyl acetate (6:1) were used as eluents. Yellow liquid (69 mg, 71% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.26 (s, 1H), 7.08 – 7.03 (m, 2H), 6.96 (s, 2H), 3.52 – 3.48 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 6H), 2.17 (ddt, *J* = 8.4, 6.8, 2.8 Hz,

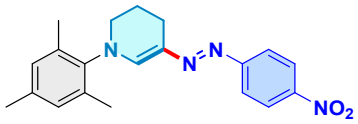
2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.6 (d, *J* = 245.3 Hz), 150.8 (d, *J* = 3.0 Hz), 149.2, 141.2, 137.7, 135.5, 133.4, 129.5, 122.30(d, *J* = 8.1 Hz), 115.4 (d, *J* = 22.3 Hz), 48.9, 21.0 (d, *J* = 20.4 Hz), 19.9, 17.91. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.61.. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}FN_3$: 324.1870; found: 324.1866.

(18) (*E*)-5-((4-iodophenyl)diazenyl)-1-mesityl-1,2,3,4-tetrahydropyridine (3ag)



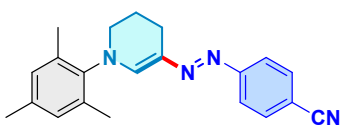
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (70 mg, 54% yield); m.p.: 133.8-134.5 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.39 – 7.36 (m, 2H), 7.27 (s, 1H), 6.95 (s, 2H), 3.58 – 3.45 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 6H), 2.17 – 2.13 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.8, 150.2, 141.1, 137.8, 137.7, 135.4, 133.8, 129.5, 122.9, 91.0, 49.1, 21.1, 21.0, 19.9, 17.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}IN_3$: 432.0931; found: 432.0926.

(19) (*E*)-1-mesityl-5-((4-nitrophenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ah)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (66 mg, 63% yield); m.p.: 199.3-200.4 ℃; ^{1}H NMR (600 MHz, Chloroform-d) δ 8.20 (d, *J* = 9.1 Hz, 2H), 7.66 (d, *J* = 9.1 Hz, 2H), 7.39 (s, 1H), 6.99 – 6.89 (m, 2H), 3.54 (d, *J* = 5.7 Hz, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 6H), 2.18 (dt, *J* = 12.1, 6.4 Hz, 2H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.8, 153.0, 145.0, 140.7, 138.4, 135.8, 134.9, 129.7, 124.8, 120.9, 49.5, 21.0, 20.9, 20.0, 17.. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}N_4O_2$: 351.1815; found: 351.1810.

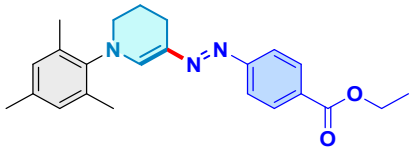
(20) (*E*)-4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)benzonitrile (3ai)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (57 mg, 58% yield); m.p.: 110.8-111.6 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7

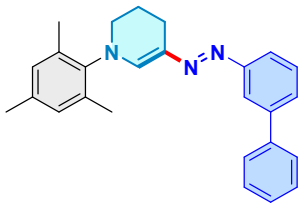
Hz, 2H), 7.34 (s, 1H), 6.95 (s, 2H), 3.54 – 3.51 (m, 2H), 2.79 (t, J = 6.4 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 6H), 2.18 – 2.14 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1, 152.3, 140.8, 138.2, 132.9, 129.65, 121.3, 119.8, 108.2, 49.4, 21.0, 20.9, 20.0, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}N_4$: 331.1917; found: 331.1912.

(21) ethyl (*E*)-4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)benzoate (3aj)



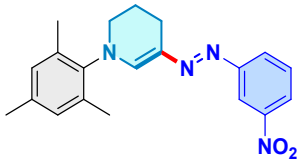
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (70 mg, 62% yield); m.p.: 158.4-159.6 ℃ ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 2H), 7.67 – 7.60 (m, 2H), 7.32 (s, 1H), 6.96 – 6.89 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.54 – 3.47 (m, 2H), 2.80 (t, J = 6.4 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 6H), 2.17 – 2.13 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 157.5, 151.2, 141.0, 138.0, 135.2, 134.6, 130.5, 129.5, 127.5, 120.6, 60.7, 49.2, 21.0, 19.9, 17.8, 14.4. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{27}N_3O_2$: 378.2176; found: 378.2171.

(22) (*E*)-5-([1,1'-biphenyl]-3-yldiazenyl)-1-mesityl-1,2,3,4-tetrahydropyridine (3ak)



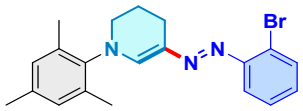
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (67 mg, 59% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (p, J = 1.0 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.68 – 7.65 (m, 1H), 7.47 (d, J = 4.2 Hz, 2H), 7.46 – 7.44 (m, 2H), 7.37 – 7.34 (m, 1H), 7.33 (s, 1H), 6.96 (s, 2H), 3.53 – 3.50 (m, 2H), 2.86 (t, J = 6.4 Hz, 2H), 2.33 (s, 3H), 2.29 (s, 6H), 2.20 – 2.17 (m, 2H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.6, 149.9, 141.7, 141.3, 141.2, 137.7, 135.5, 133.6, 129.5, 129.2, 128.6, 127.2, 127.1, 125.2, 119.8, 119.8, 77.3, 77.1, 76.9, 49.0, 21.1, 21.0, 20.0, 17.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{27}N_3$: 382.2277; found: 382.2272.

(23) (*E*)-1-mesityl-5-((3-nitrophenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3al)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (68 mg, 65% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.41 (t, *J* = 2.1 Hz, 1H), 8.01 – 7.93 (m, 1H), 7.90 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.25 (s, 1H), 6.93 (s, 2H), 3.55 – 3.49 (m, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 2.25 (s, 6H), 2.16 (dtt, *J* = 8.4, 5.9, 2.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3, 151.6, 149.0, 140.8, 138.0, 135.1, 134.2, 129.5, 129.2, 120.0, 114.7, 49.2, 20.9, 20.9, 19.9, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}N_4O_2$: 351.1815; found: 351.1809.

(24) (*E*)-5-((2-bromophenyl)diazenyl)-1-mesityl-1,2,3,4-tetrahydropyridine (3am)



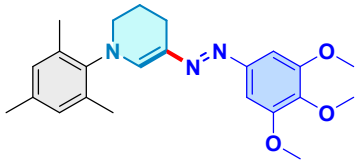
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (71 mg, 62% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.32 (s, 1H), 7.29 – 7.26 (m, 1H), 7.03 (ddd, *J* = 7.9, 7.2, 1.7 Hz, 1H), 6.96 (s, 2H), 3.53 – 3.51 (m, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 6H), 2.20 – 2.17 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.1, 150.3, 141.1, 137.8, 135.3, 135.0, 133.0, 129.5, 127.7, 127.2, 122.3, 117.6, 49.2, 21.0, 21.0, 20.1, 17.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}BrN_3$: 384.1069; found: 384.1065.

(25) (*E*)-1-mesityl-5-((3-methoxy-4-methylphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3an)

Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (70 mg, 67% yield); m.p.: 130.9-131.7 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (s, 1H), 7.22 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 2H), 3.88 (s, 3H), 3.52 – 3.44 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 6H), 2.24 (s, 3H), 2.16 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1, 153.6, 149.0, 141.3, 137.6, 135.5, 133.2, 130.5, 129.4, 125.0, 114.0 101.7, 55.2,

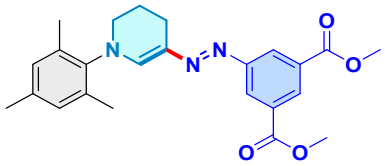
48.9, 21.1, 20.9, 20.0, 17.9, 16.1.HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{27}N_3O$: 350.2226; found: 350.2221.

(26) (*E*)-1-mesityl-5-((3,4,5-trimethoxyphenyl)diazenyl)-1,2,3,4-tetrahydropyridine (3ao)



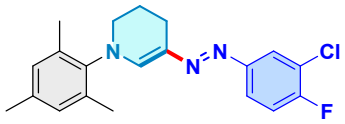
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (78 mg, 66% yield); m.p.: 129.4-130.3 ℃; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.25 (s, 1H), 6.94 (s, 2H), 6.92 (s, 2H), 3.88 (s, 6H), 3.84 (s, 3H), 3.47 (dd, *J* = 6.6, 4.7 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 2.25 (s, 6H), 2.16 – 2.12 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.3, 150.3, 149.1, 141.1, 137.6, 136.7, 135.4, 133.0, 129.3, 97.9, 60.86, 55.8, 48.8, 21.0 20.8, 19.8, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{29}N_3O_3$: 396.2281; found: 396.2277.

(27) dimethyl (*E*)-5-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)isophthalate (3ap)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid(62 mg, 49% yield); m.p.: 171.9-172.7 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.46 (t, *J* = 1.6 Hz, 1H), 8.42 (d, *J* = 1.6 Hz, 2H), 7.33 (s, 1H), 7.11 – 6.63 (m, 2H), 3.91 (s, 6H), 3.52 – 3.43 (m, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.28 (s, 3H), 2.23 (s, 6H), 2.17 – 2.12 (m, 2H). ^{113}C NMR (151 MHz, $CDCl_3$) δ 198.5, 154.4, 150.4, 141.0, 137.8, 137.8, 135.3, 133.8, 129.5, 128.9, 125.7, 125.4, 121.1, 49.0, 26.8, 21.0, 20.9, 19.9, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{15}NOS_4$: 422.2074; found: 422.2069.

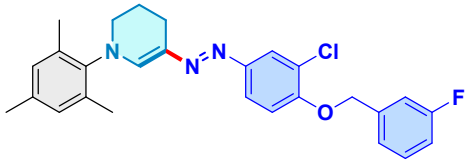
(28) (*E*)-5-((3-chloro-4-fluorophenyl)diazenyl)-1-mesityl-1,2,3,4-tetrahydropyridine (3aq)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (62 mg, 58% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.1, 2.4 Hz, 1H), 7.49 (ddd, *J* = 8.8, 4.6, 2.4 Hz, 1H), 7.27 (s, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 2H), 3.51 – 3.48 (m, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.32 (s,

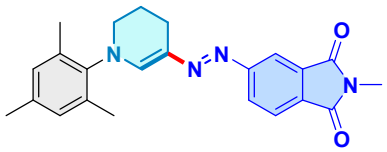
3H), 2.26 (s, 6H), 2.17 – 2.14 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 246.1 Hz), 152.3, 149.2 (d, *J* = 15.2 Hz), 141.1, 139.3 (d, *J* = 7.2 Hz), 137.6, 135.4, 133.3, 130.1 (d, *J* = 8.2 Hz), 129.4, 123.8, 122.4 (d, *J* = 2.8 Hz), 121.6, 121.3, 114.8, 114.6, 114.0 (d, *J* = 10.5 Hz), 113.9, 70.2, 48.9, 21.0, 20.9, 19.9, 17.8. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.73. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}ClFN_3$: 358.1480; found:358.1476.

(29) (*E*)-1-mesityl-5-((1-methyl-1H-pyrazol-3-yl)diazenyl)-1,2,3,4-tetrahydropyridine (3ar)



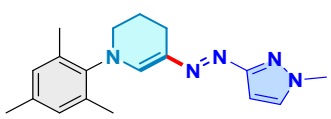
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid (71 mg, 51% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.35 (td, *J* = 8.2, 6.0 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.03 – 6.99 (m, 1H), 6.97 – 6.94 (m, 3H), 5.14 (s, 2H), 3.50 – 3.47 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.27 (s, 6H), 2.17 – 2.13 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.0, 141.2, 137.6, 135.52, 133.7, 94.9, 48.9, 39.1, 21.0, 19.7, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. For $C_{27}H_{27}ClFN_3O$: 464.1899; found: 464.1896.

(30) (*E*)-5-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)-2-methylisoindoline-1,3-dione) (3as)



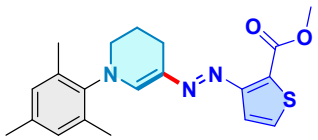
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (89 mg, 77% yield); m.p.: 194.7-195.6 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 – 7.97 (m, 1H), 7.84 (d, *J* = 1.7 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.38 (s, 1H), 6.96 (d, *J* = 1.2 Hz, 2H), 3.57 – 3.52 (m, 2H), 3.16 (s, 3H), 2.82 (s, 2H), 2.32 (s, 3H), 2.26 (s, 6H), 2.22 – 2.17 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.8, 168.7, 159.3, 152.6, 140.7, 138.2, 135.2, 134.9, 133.5, 129.6, 128.1, 126.8, 123.9, 114.6, 49.4, 23.9, 21.0, 20.9, 20.0, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{24}N_4O_2$: 389.1972; found: 389.1966.

(31) (*E*)-1-mesityl-5-((1-methyl-1H-pyrazol-3-yl)diazenyl)-1,2,3,4-tetrahydropyridine (3at)



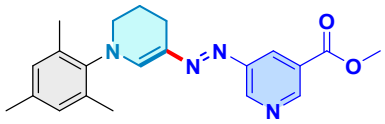
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow liquid(67 mg, 72% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.20 (s, 1H), 6.91 (d, *J* = 1.2 Hz, 2H), 6.33 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.51 – 3.37 (m, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.28 (s, 3H), 2.22 (s, 6H), 2.14 – 2.08 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.0, 141.2, 137.6, 135.52, 133.7, 94.9, 48.9, 39.1, 21.0, 19.7, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{23}N_5$: 310.2026; found: 310.2021.

(32) methyl (*E*)-3-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)thiophene-2-carboxylate (3au)



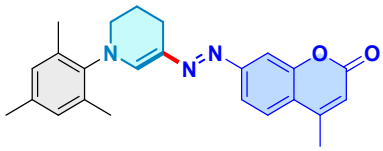
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (78 mg, 71% yield); m.p.: 128.7-129.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 5.4 Hz, 1H), 7.30 (d, *J* = 5.4 Hz, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 6.93 (d, *J* = 1.1 Hz, 2H), 3.90 (s, 3H), 3.52 – 3.48 (m, 2H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 2.23 (s, 6H), 2.17 – 2.13 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8, 160.0, 151.1, 140.97, 137.9, 135.2, 135.1, 129.5, 129.5, 120.8, 119.8, 51.8, 49.3, 20.9, 20.9, 19.9, 17.7. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}N_3O_2S$: 370.1571; found: 370.1578.

(33) methyl (*E*)-5-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)nicotinate (3av)



Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (71 mg, 65% yield); m.p.: 147.6-148.4 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.93 (dd, *J* = 17.8, 2.2 Hz, 2H), 8.37 (t, *J* = 2.2 Hz, 1H), 7.31 (s, 1H), 6.87 (s, 2H), 3.87 (s, 3H), 3.48 – 3.44 (m, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 2.24 (s, 3H), 2.19 (s, 6H), 2.13 – 2.08 (m, 2H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.9, 151.5, 149.3, 148.3, 147.2, 140.6, 137.8, 134.8, 134.6 129.3, 126.2, 126.0, 52.0, 49.0, 20.7, 20.7, 19.6, 17.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{24}N_4O_2$: 365.1972; found: 365.1958

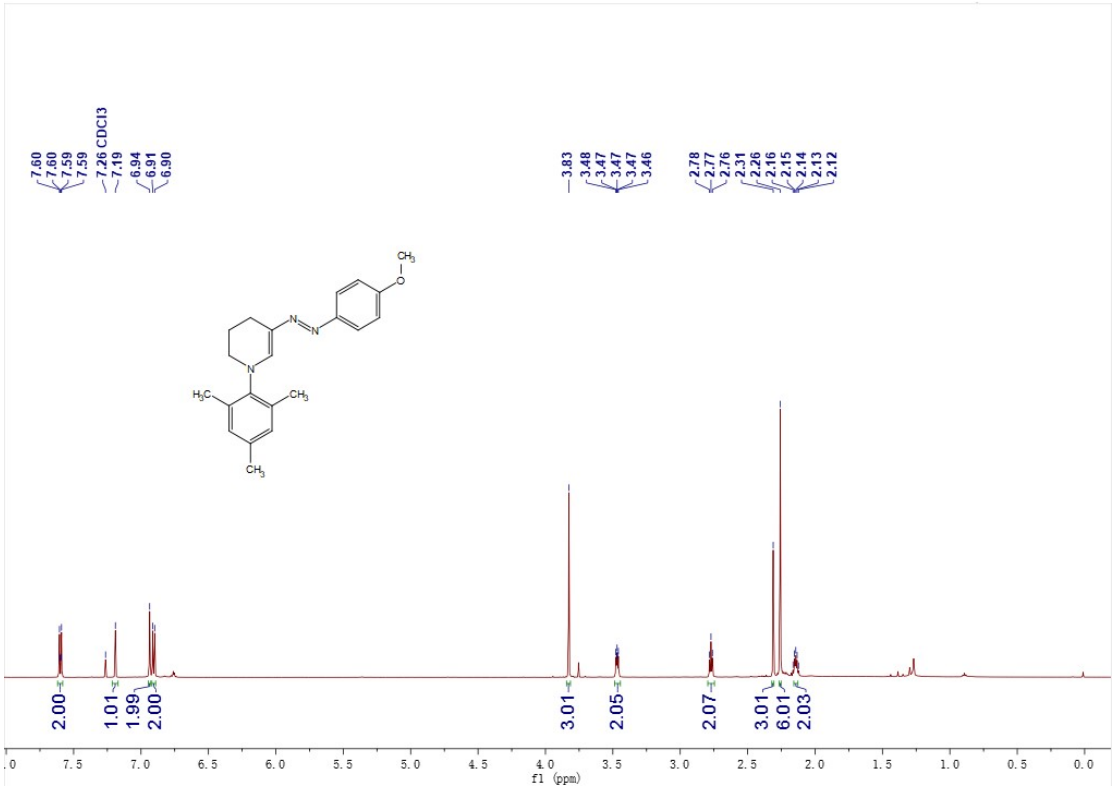
(34) (*E*)-7-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)diazenyl)-4-methyl-2*H*-chromen-2-one (3aw)



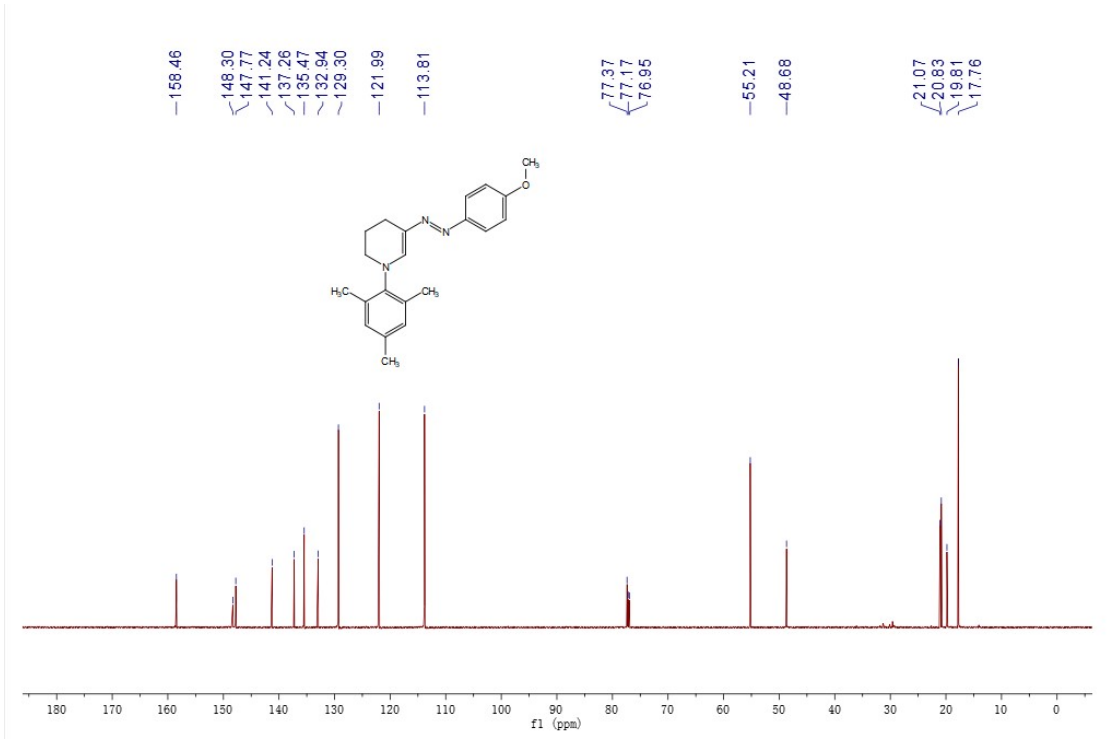
Petroleum ether and ethyl acetate (10:1) were used as eluents. Yellow solid (79 mg, 68% yield); m.p.: 189.3-190.8 ℃; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.33 (s, 1H), 6.94 (s, 2H), 6.16 (d, *J* = 1.5 Hz, 1H), 3.55 – 3.48 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.40 (d, *J* = 1.3 Hz, 3H), 2.30 (s, 3H), 2.25 (s, 6H), 2.16 (dt, *J* = 10.7, 6.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.7, 154.6, 152.5, 151.9, 140.9, 138.1, 135.1, 134.9, 129.6, 124.8, 118.1, 117.8, 113.2, 107.8, 49.4, 21.0, 20.97, 20.0, 18.7, 17.8. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. For $C_{24}H_{25}N_3O_2$: 388.2019; found: 388.2014

8. NMR spectra of the obtained compounds.

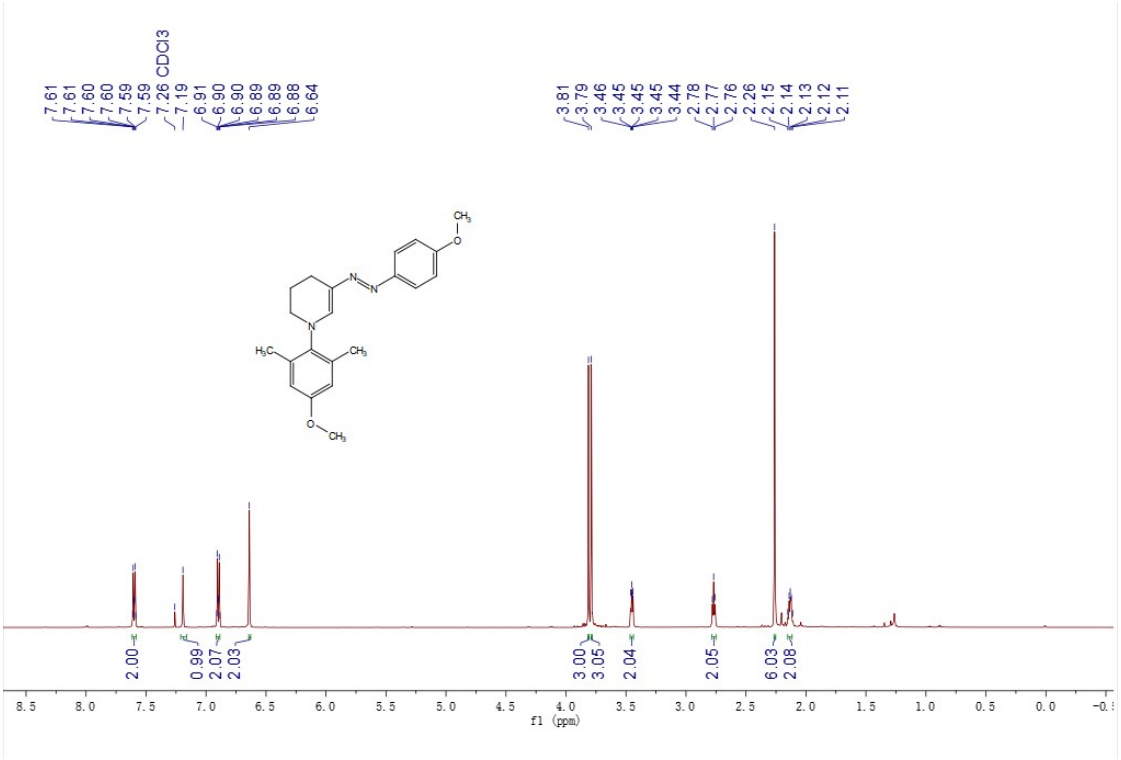
(1) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aa



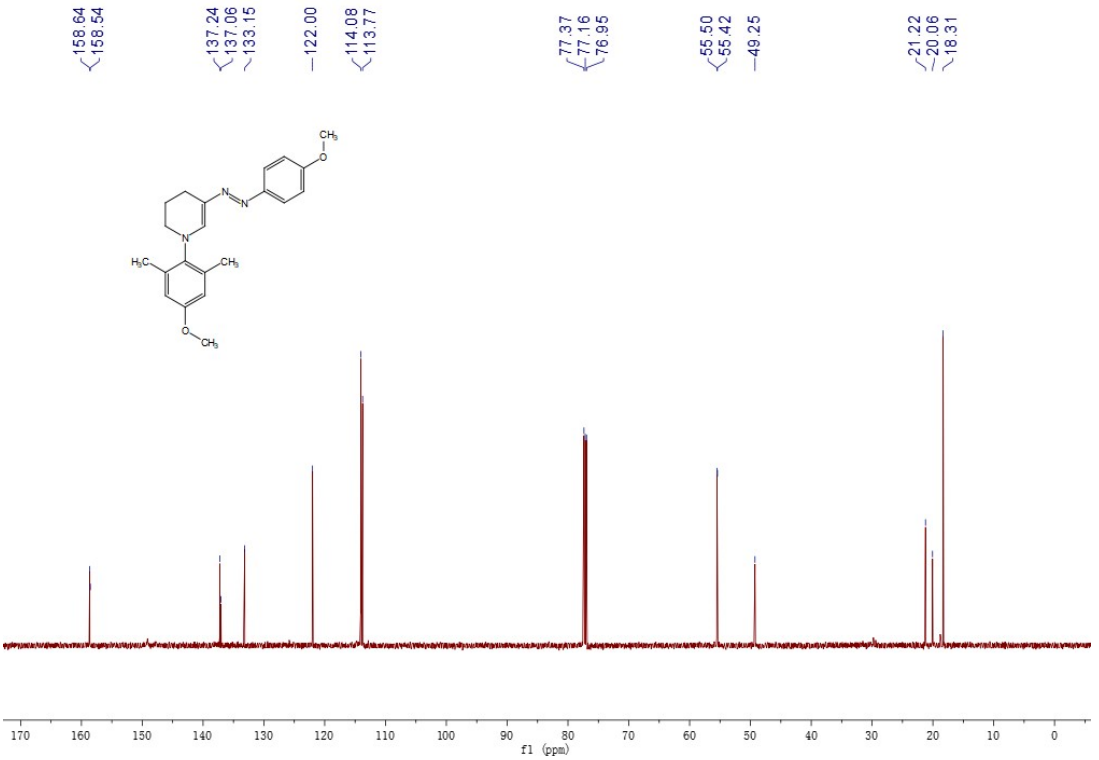
(2) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aa



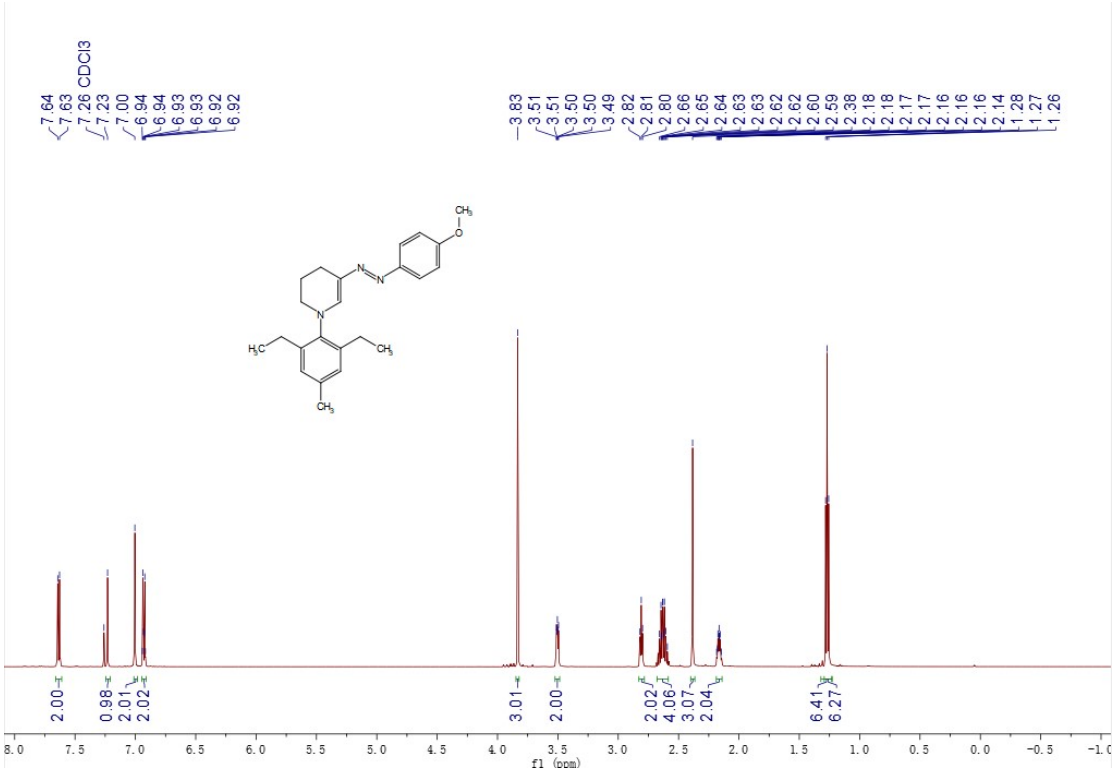
(3) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ba



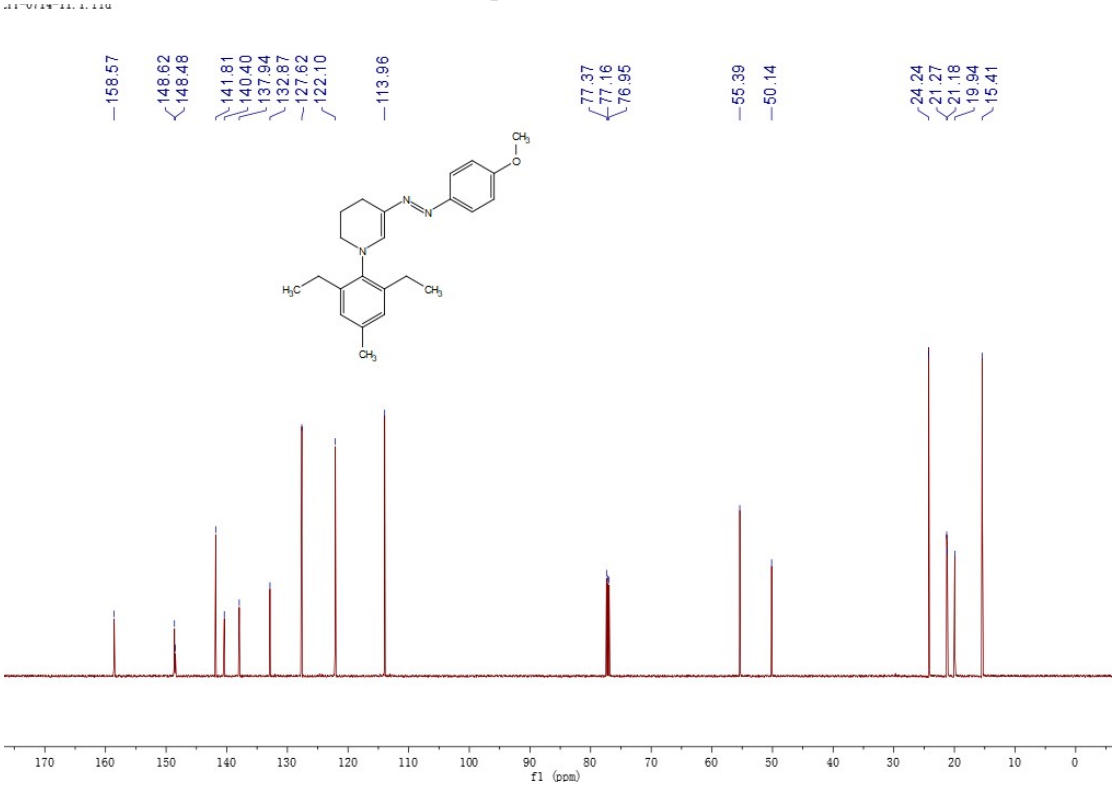
(4) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ba



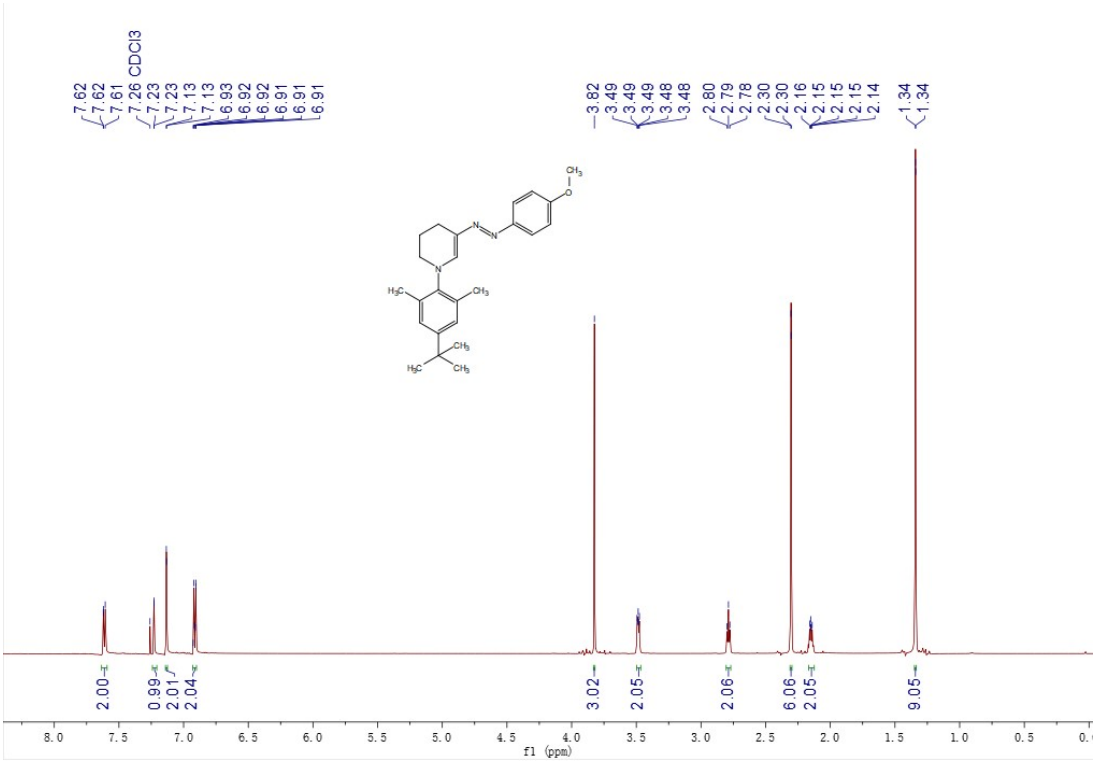
(5) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ca



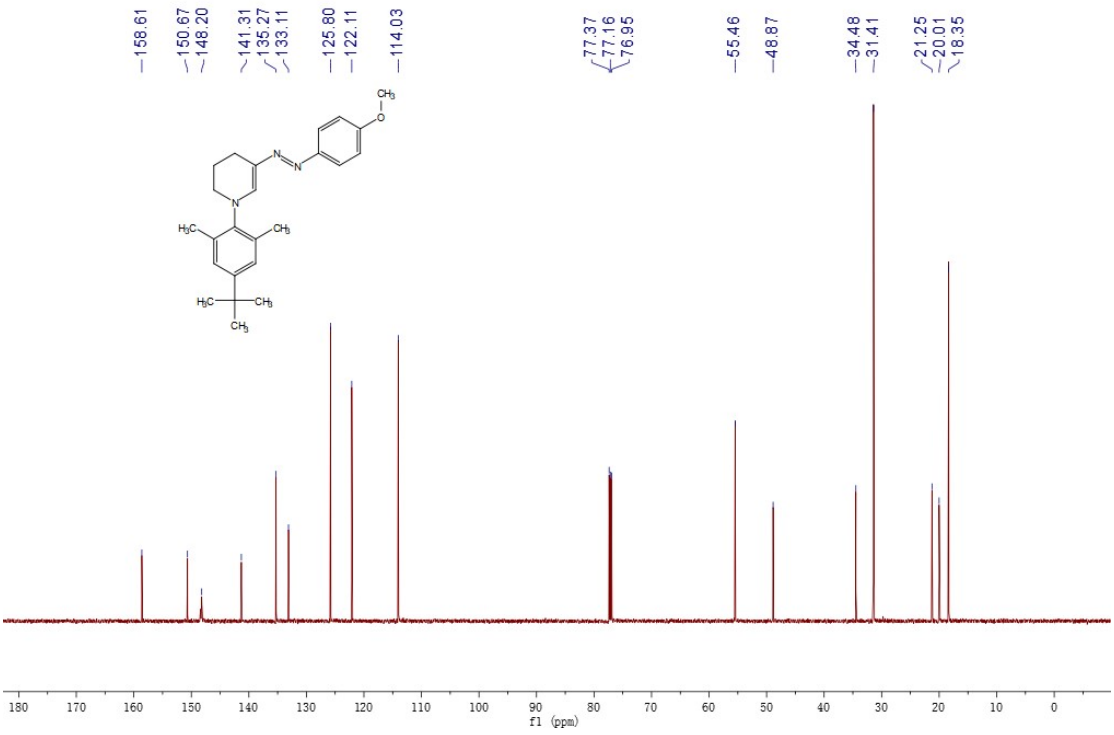
(6) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ca



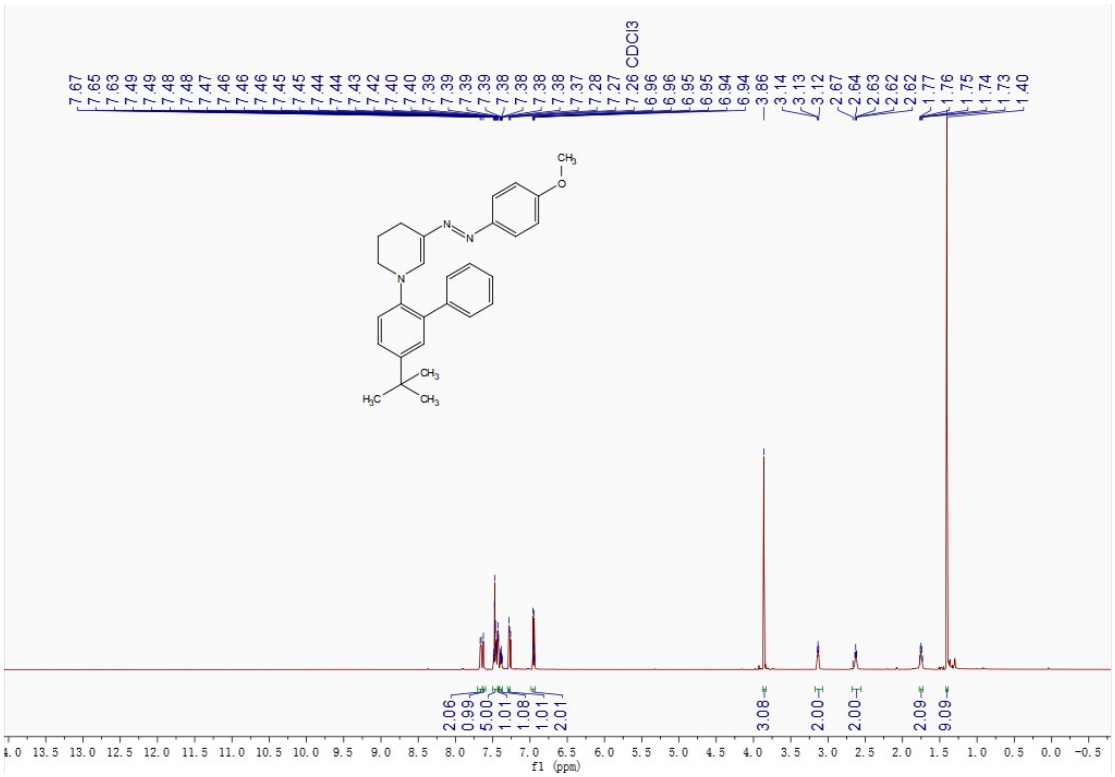
(7) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3da



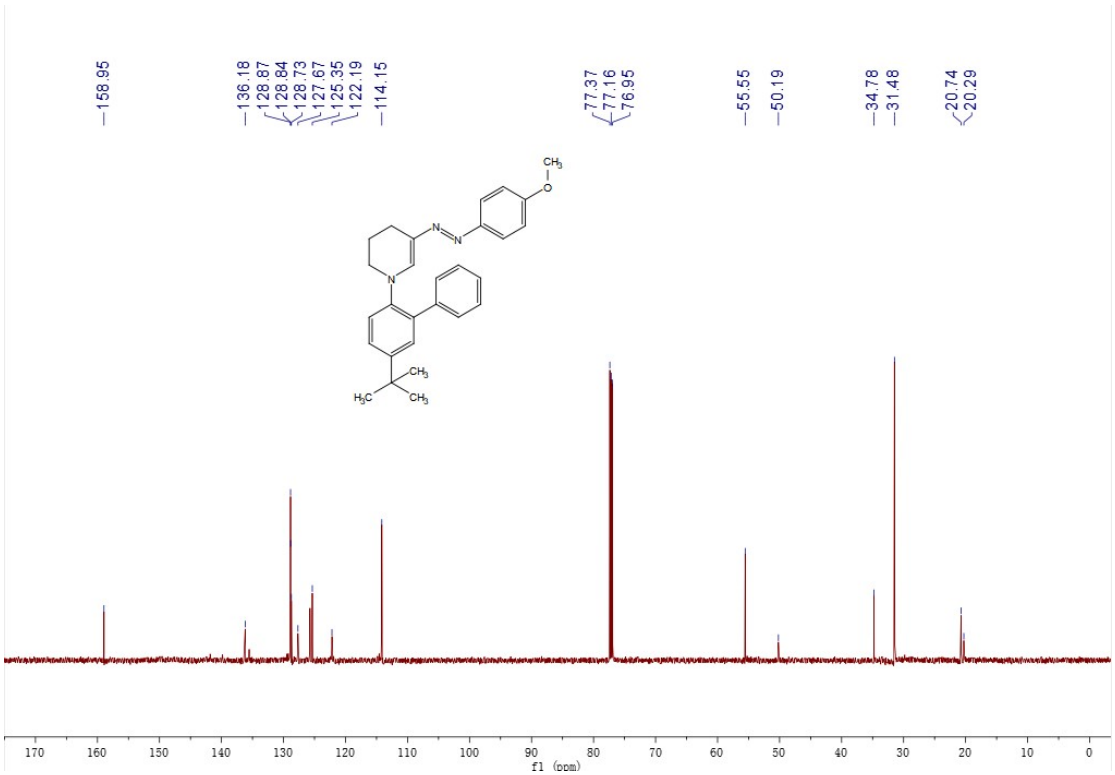
(8) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3da



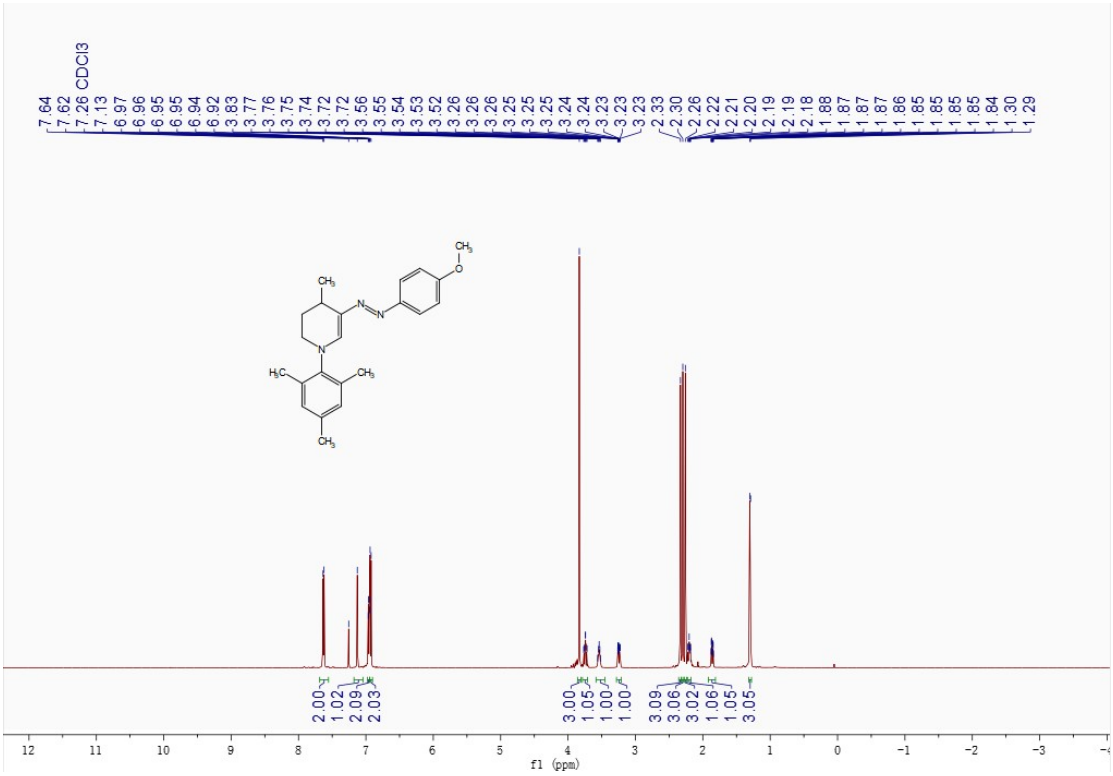
(9) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ea



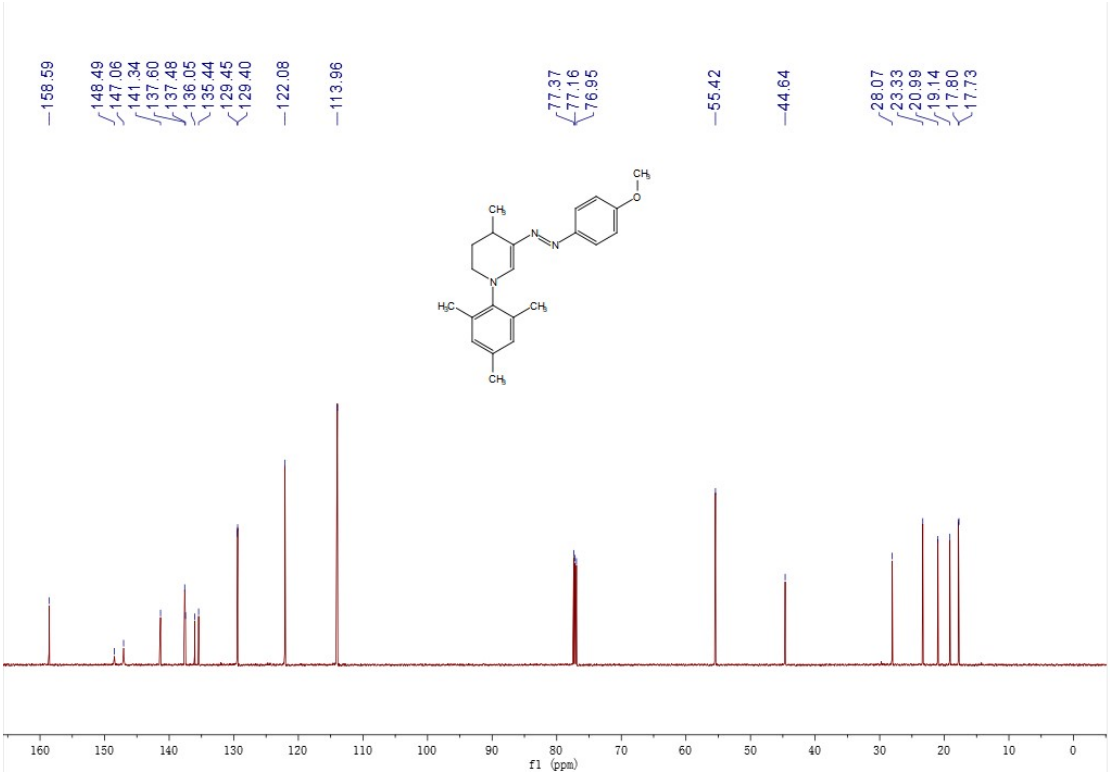
(10) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ea



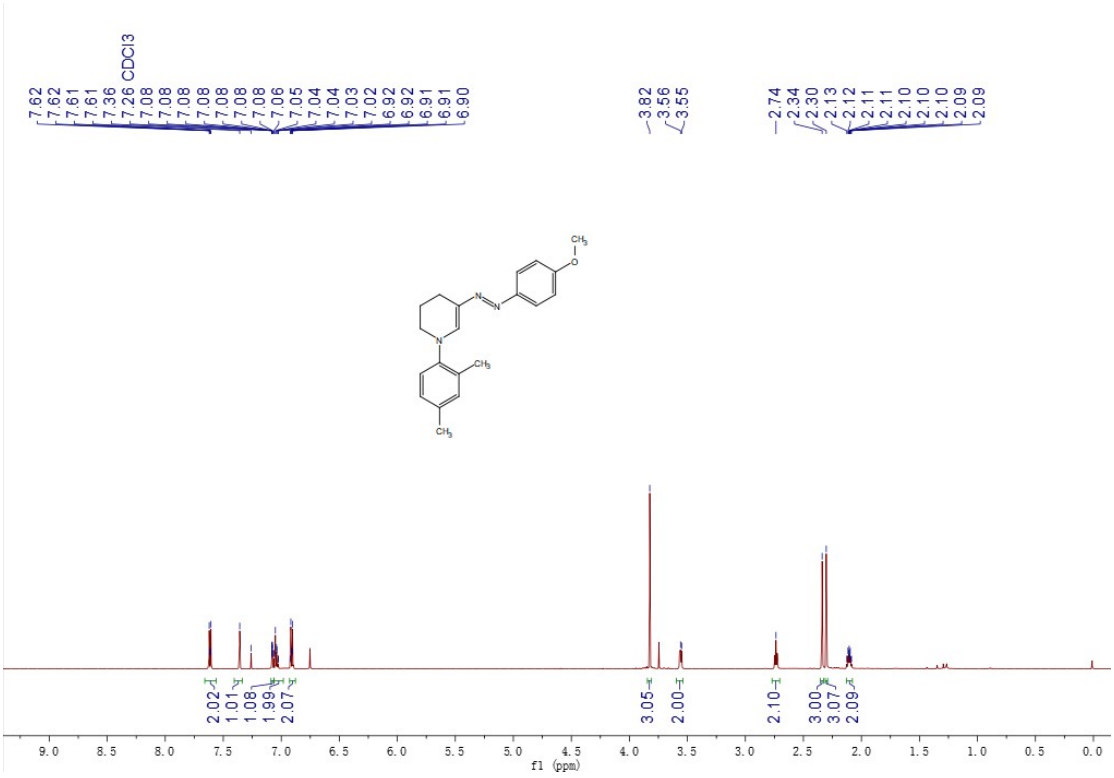
(11) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3fa



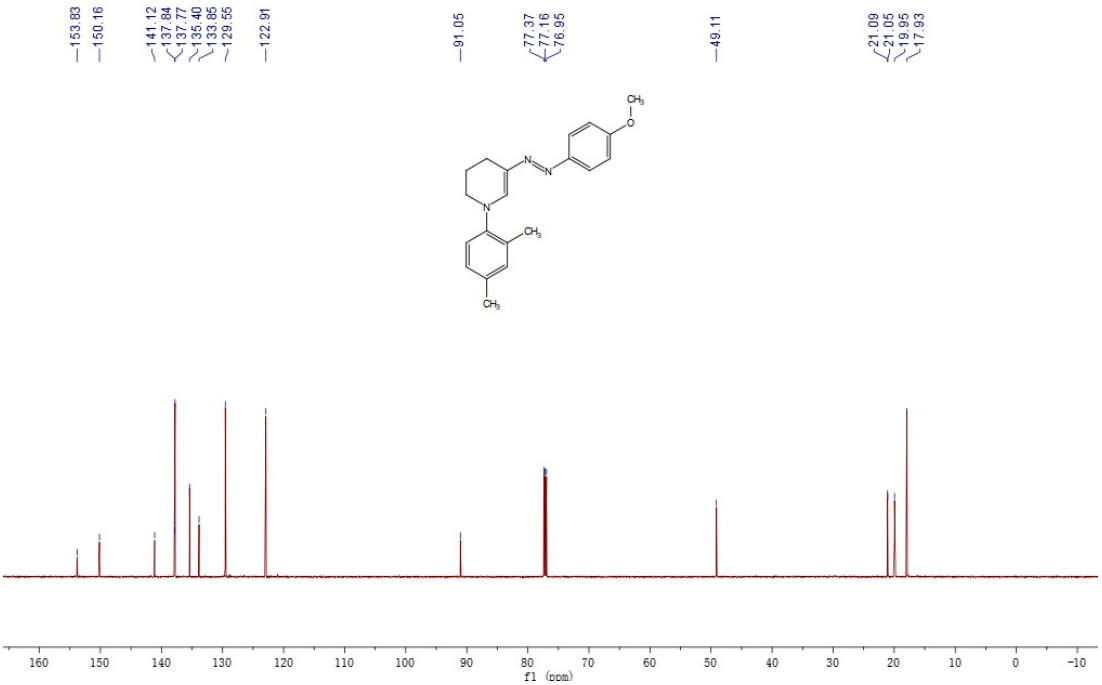
(12) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3fa



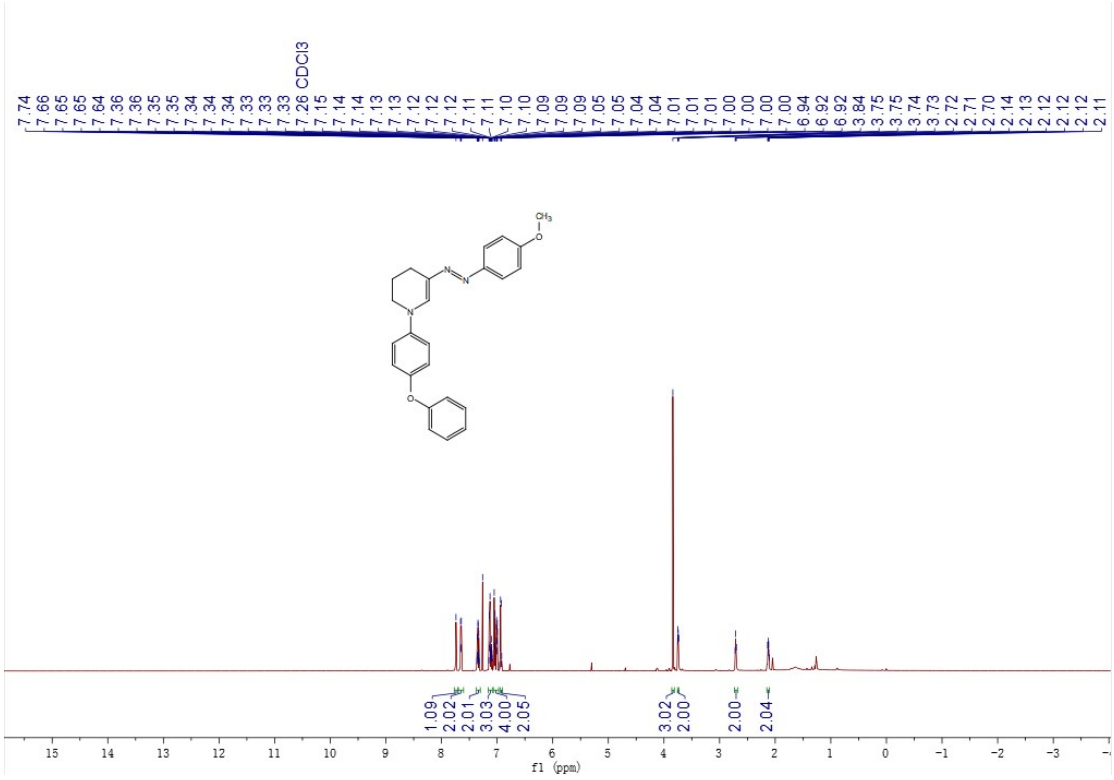
(13) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ga



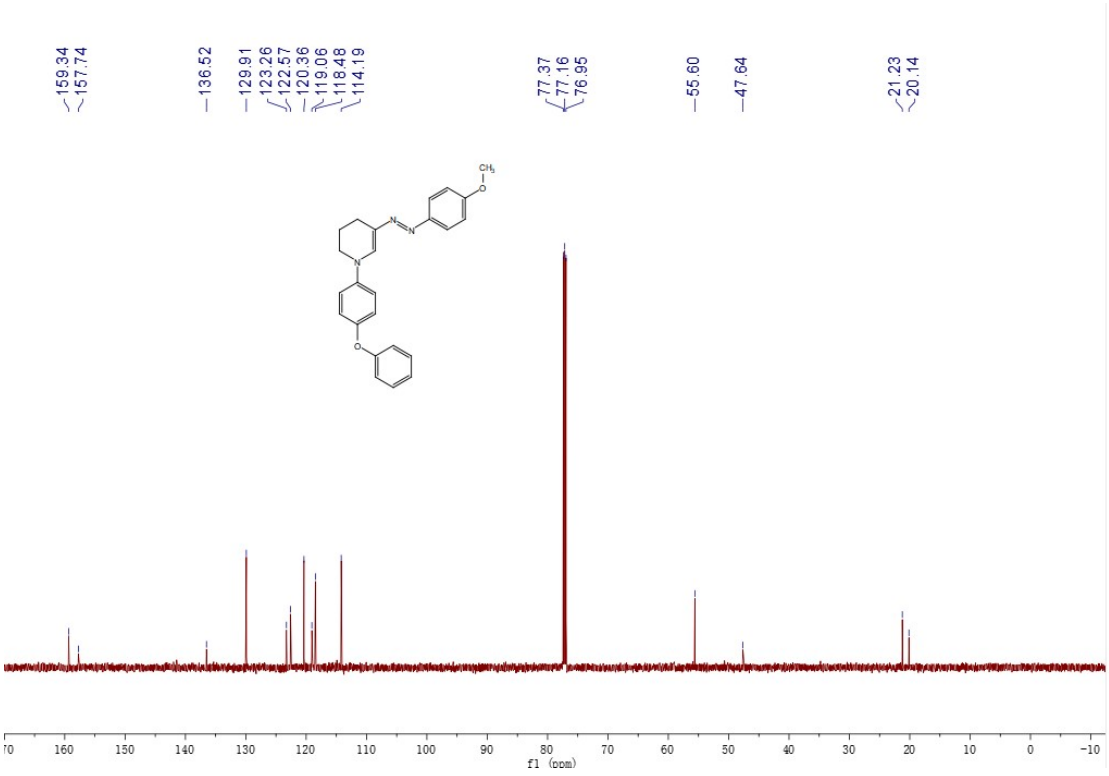
(14) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ga



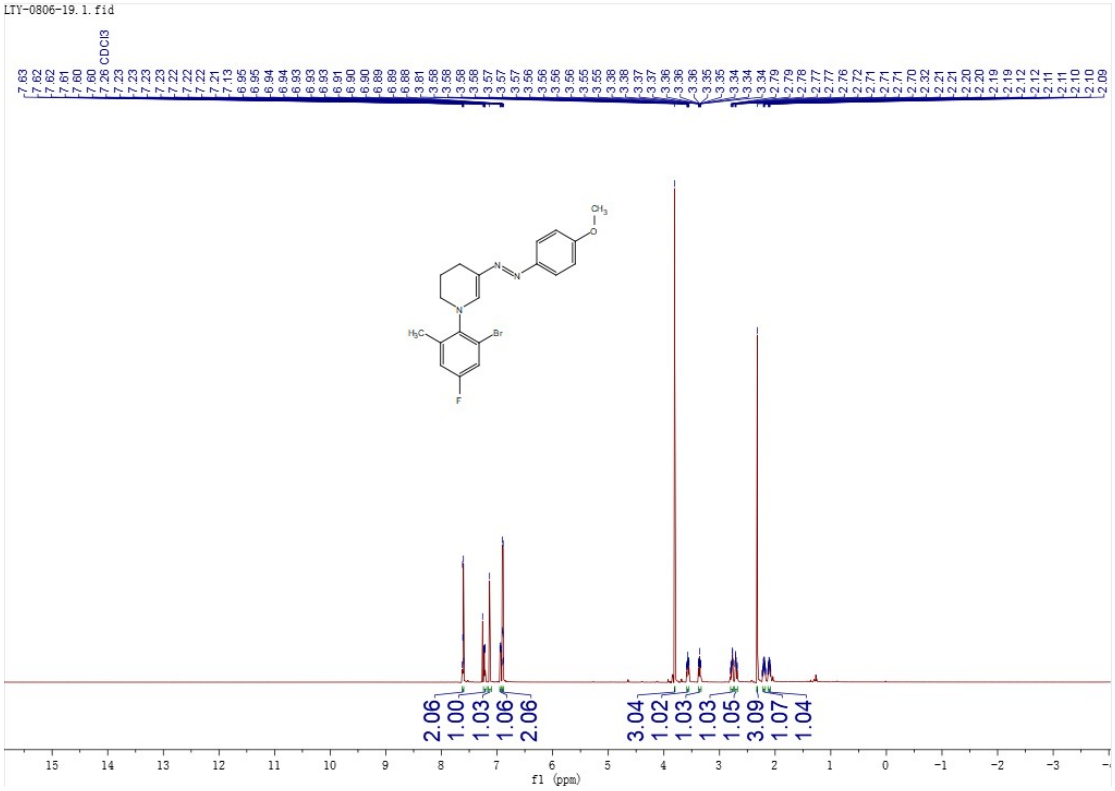
(15) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ha



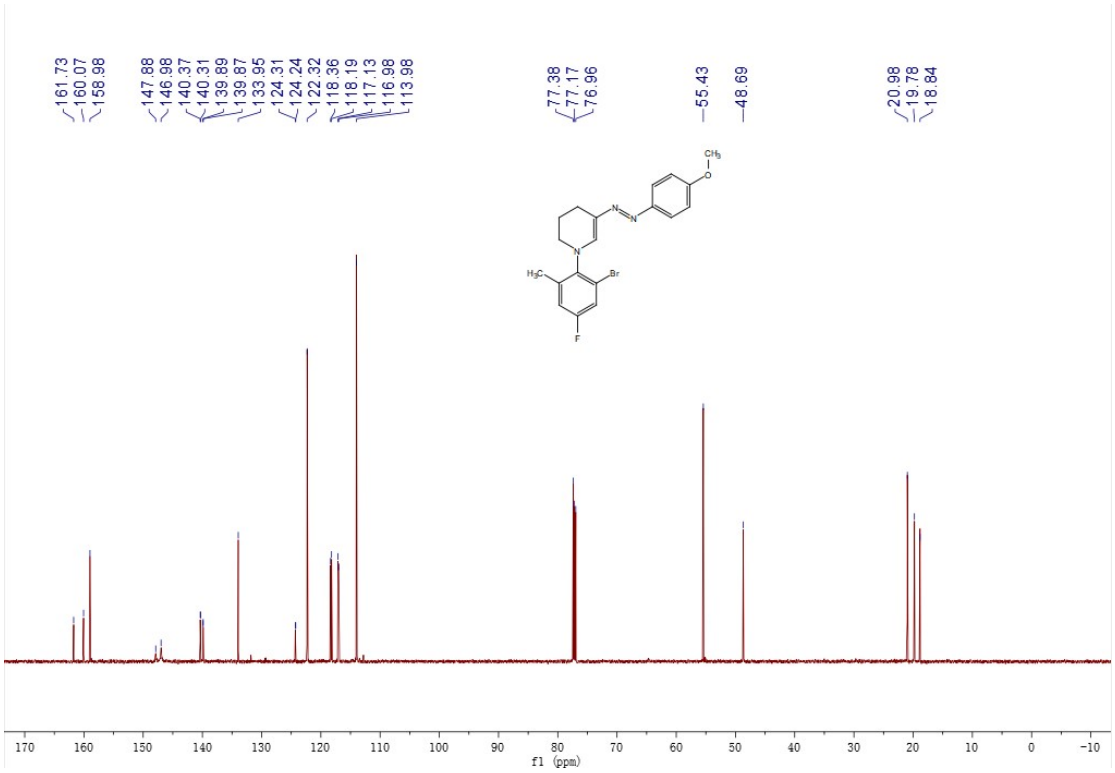
(16) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ha



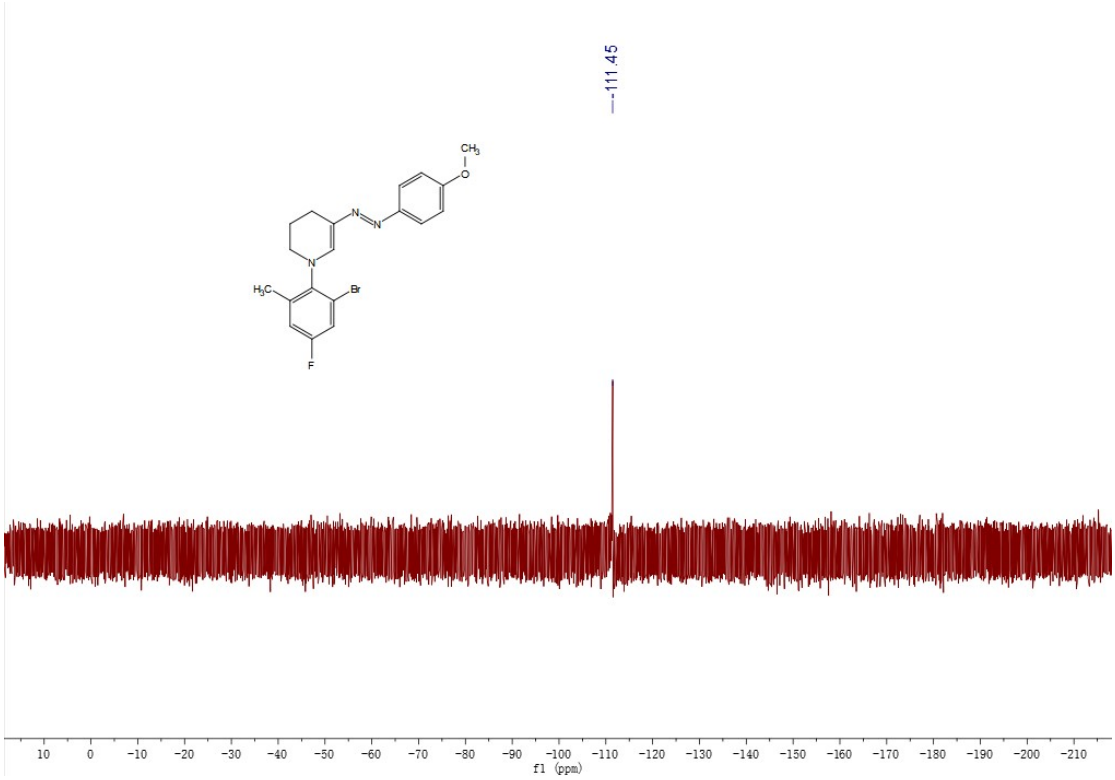
(17) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ia



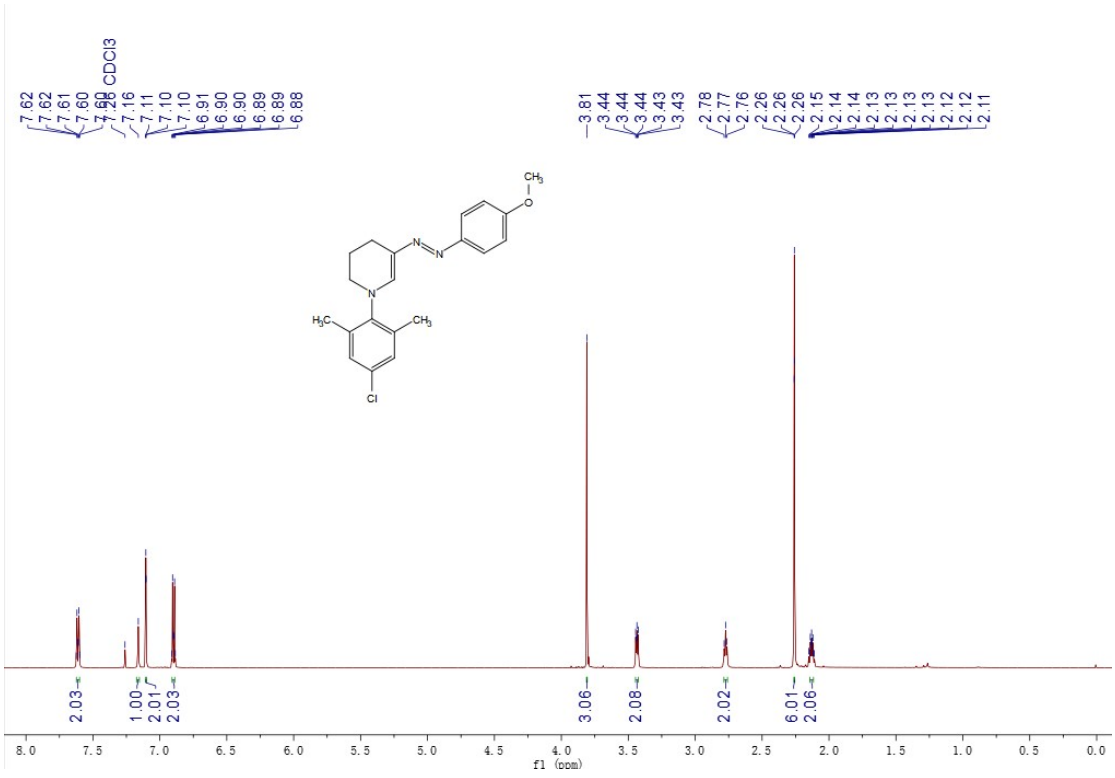
(18) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ia



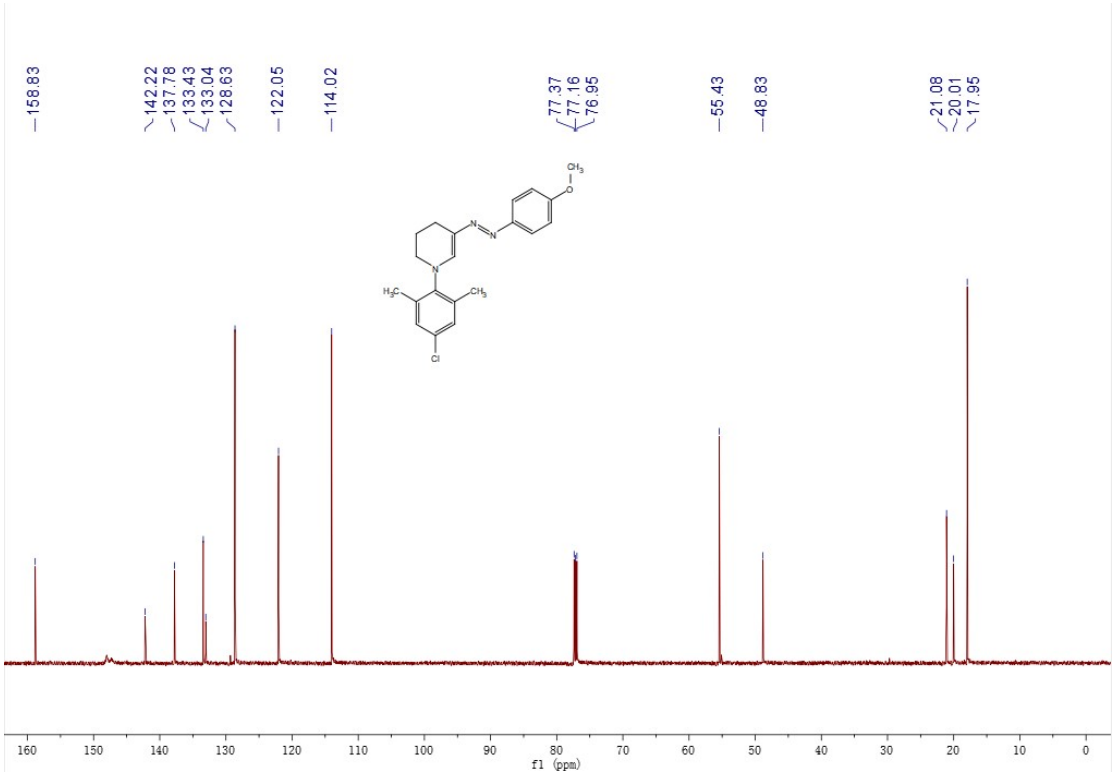
(19) ^{19}F NMR (565 MHz, Chloroform-d) spectrum of 3ia



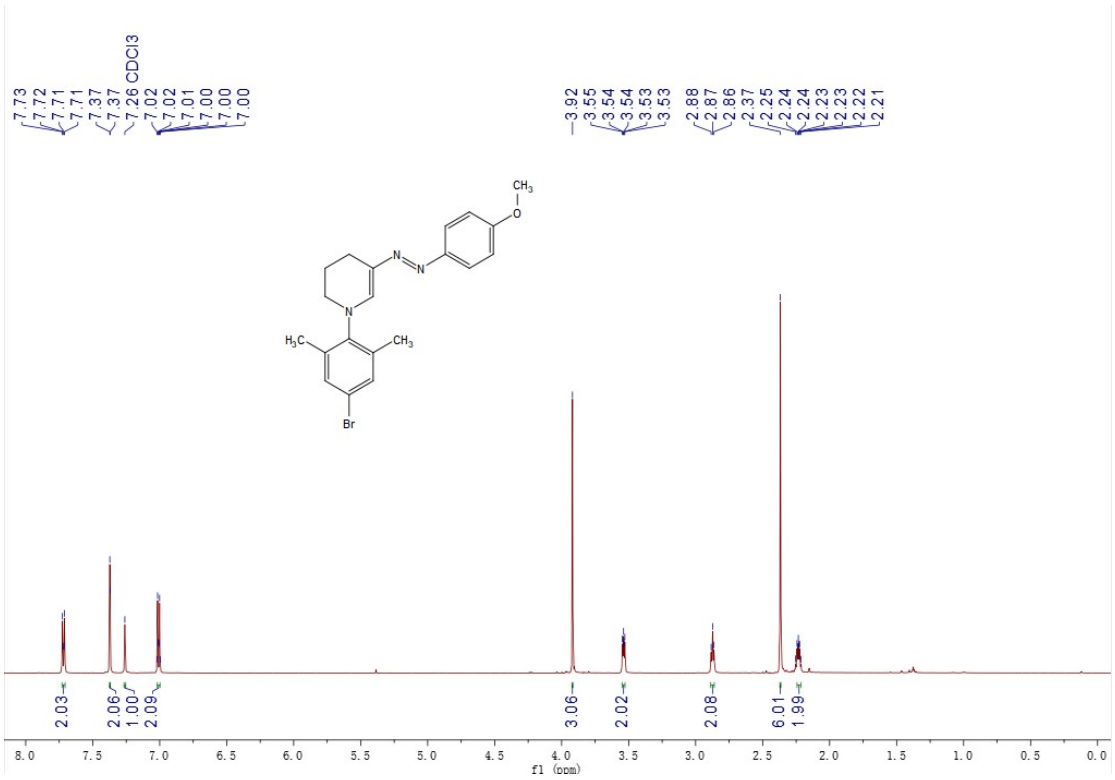
(20) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ja



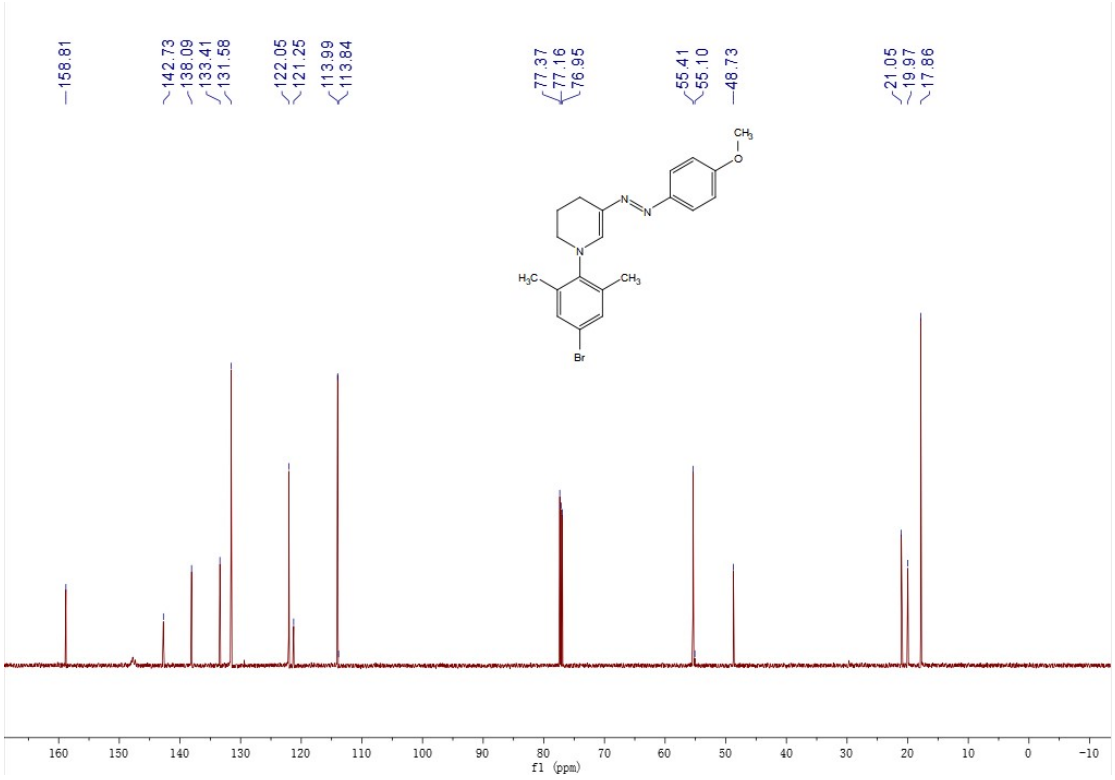
(21) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ja



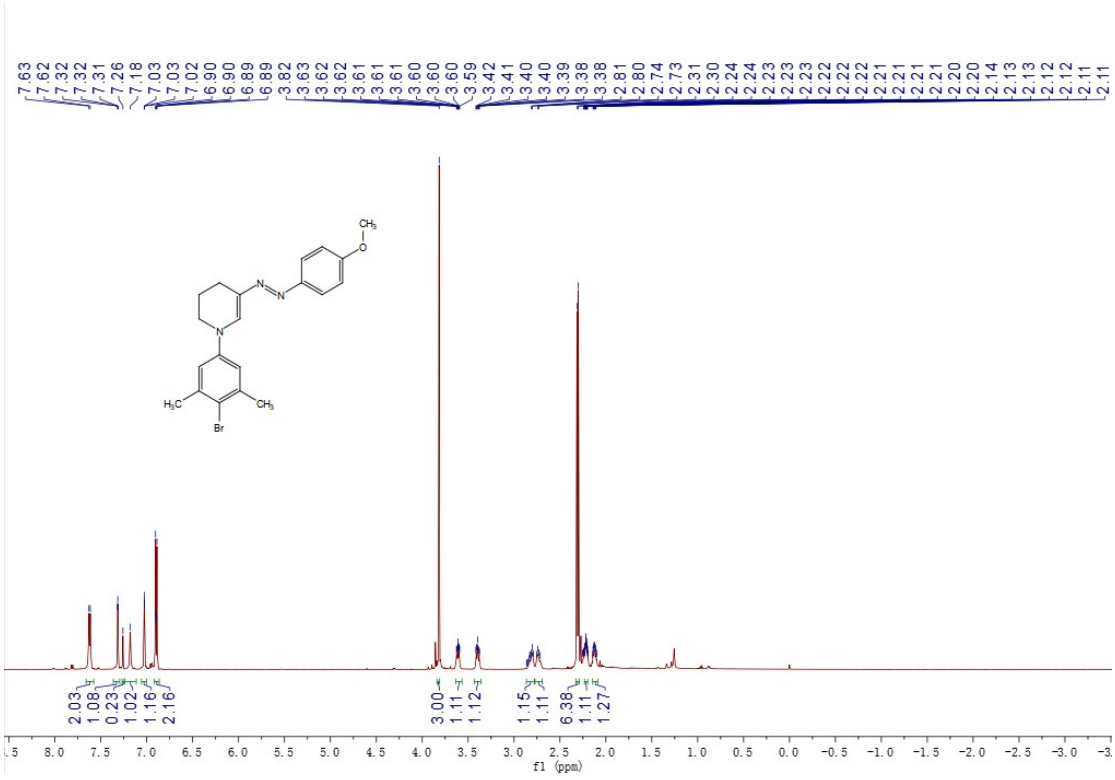
(22) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ka



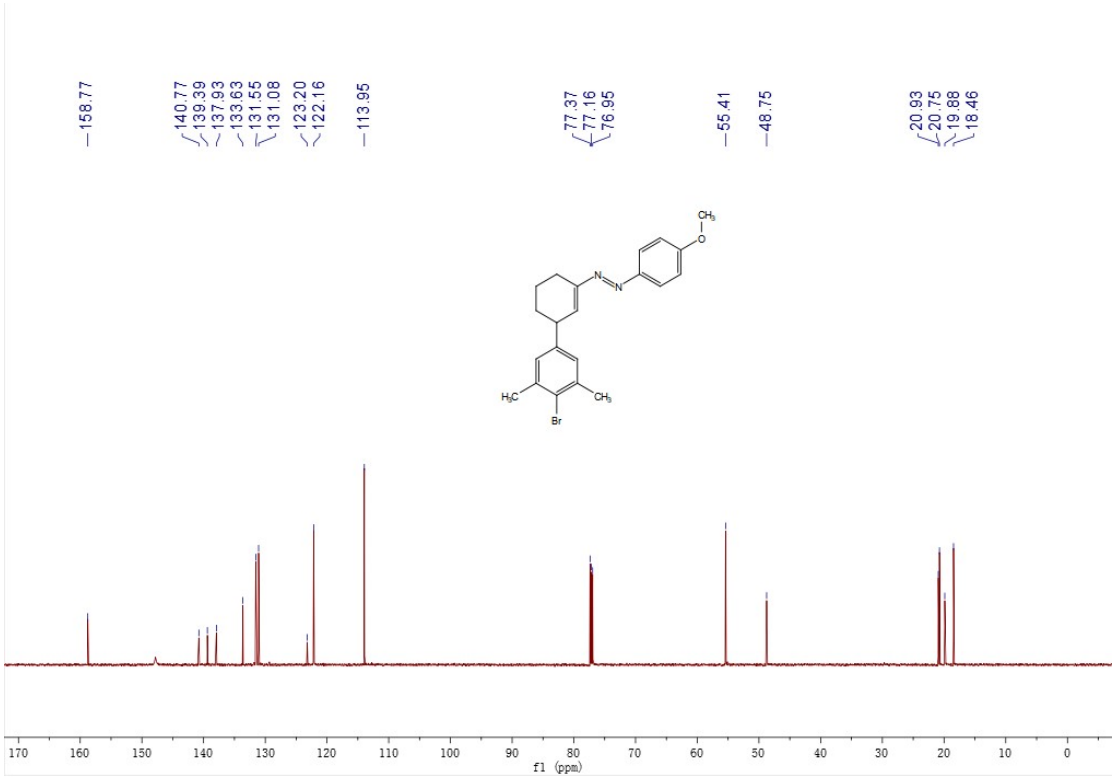
(23) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ka



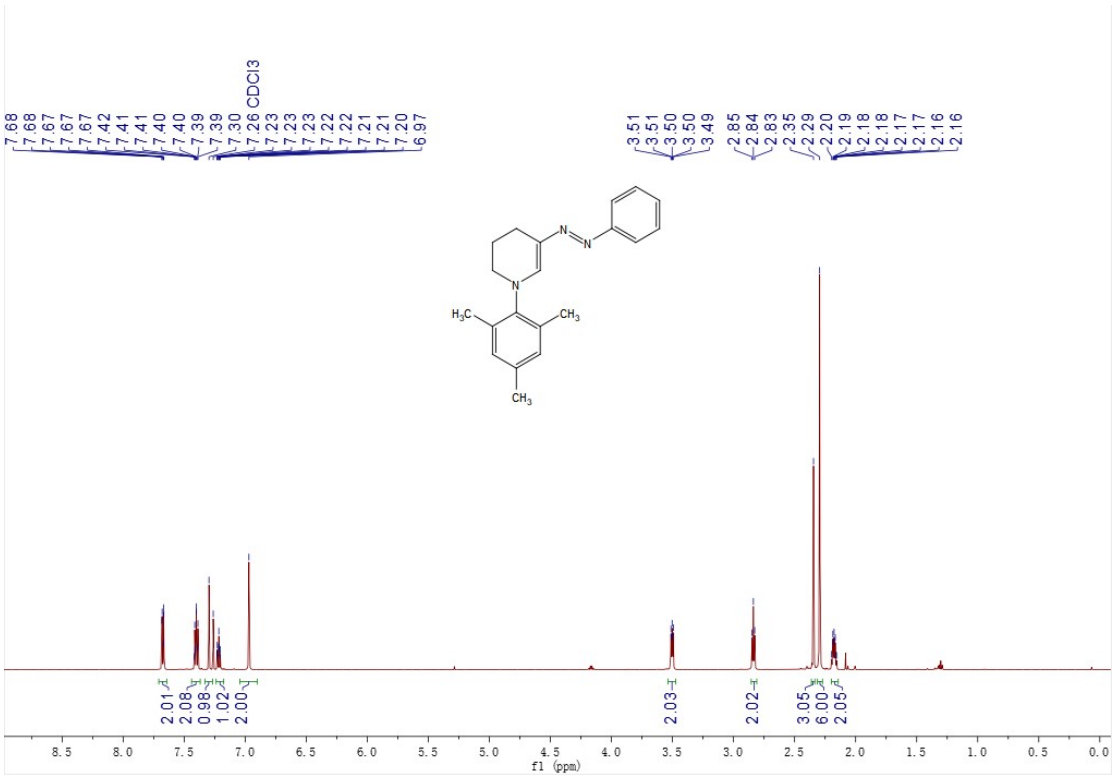
(24) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3la



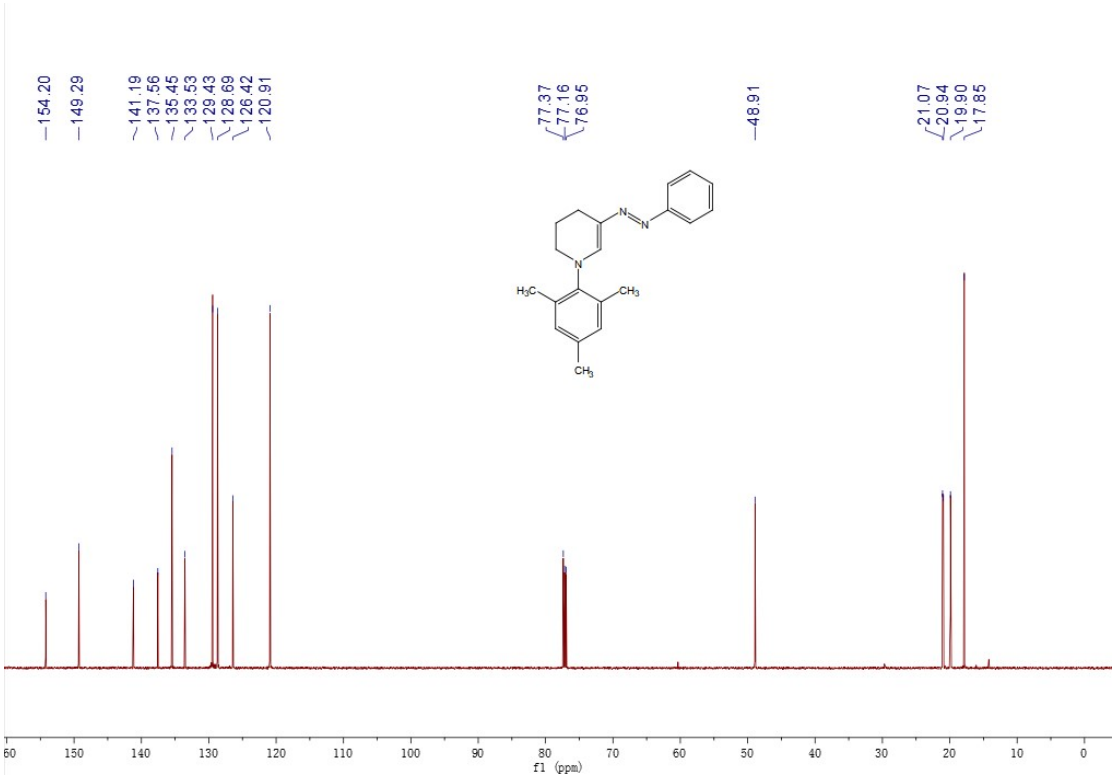
(25) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3la



(26) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ab

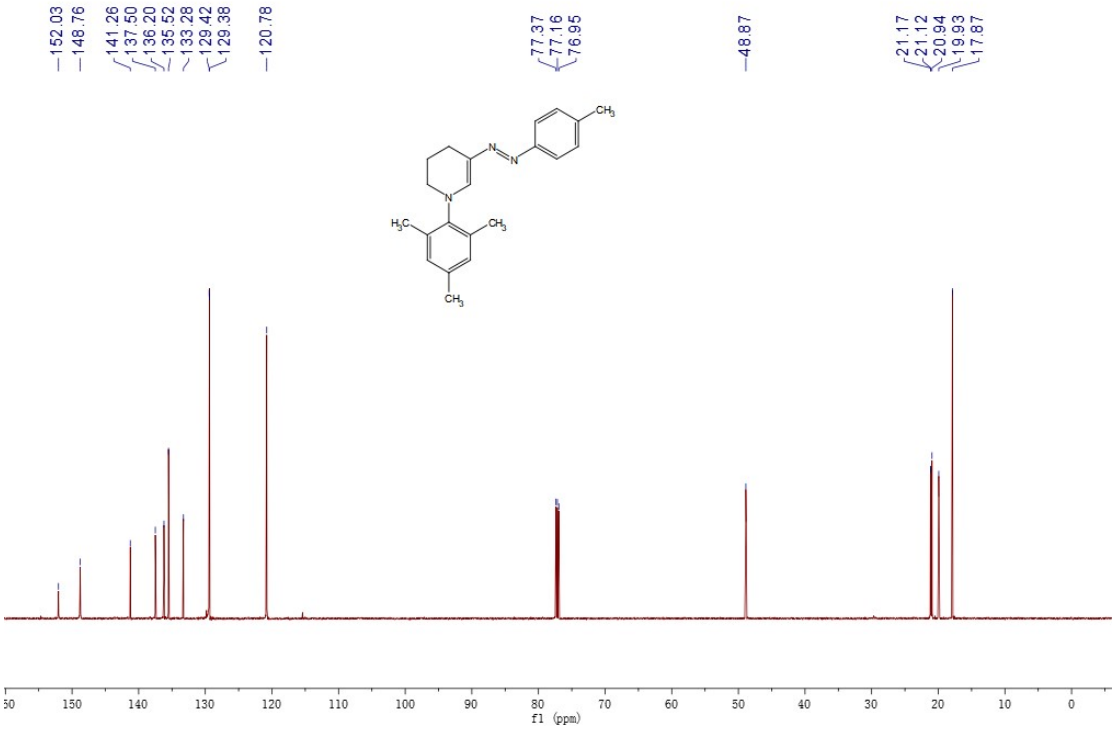


(27) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ab

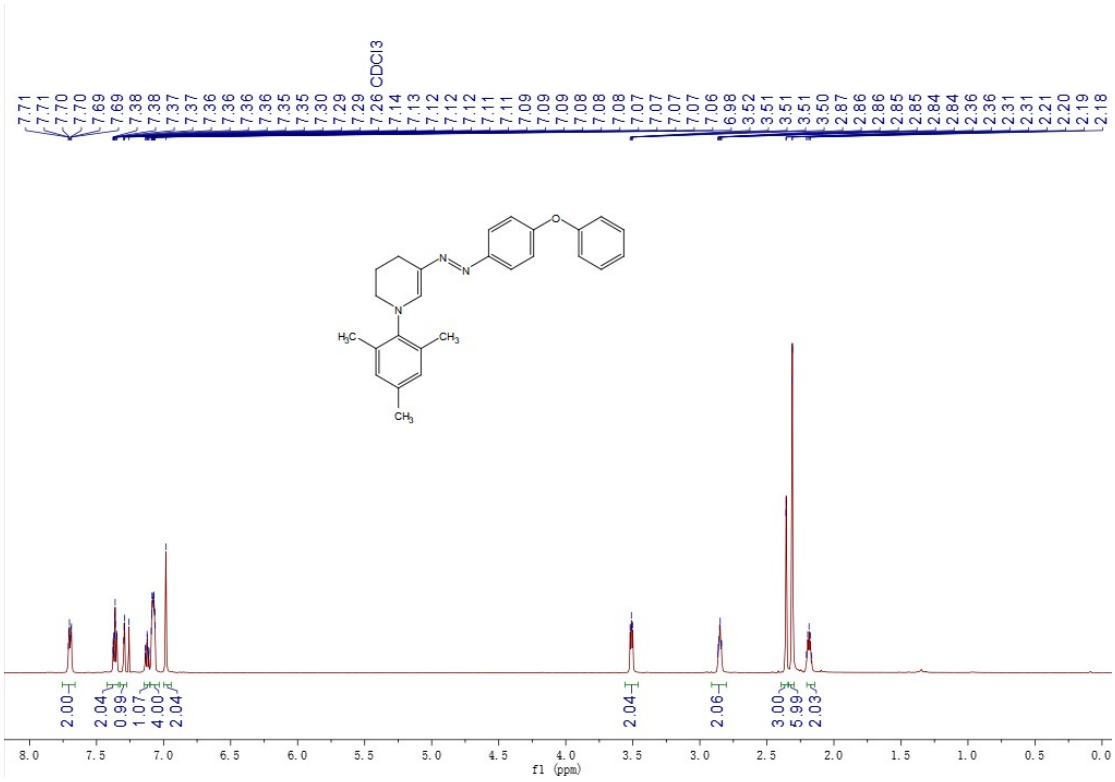


(28) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ac

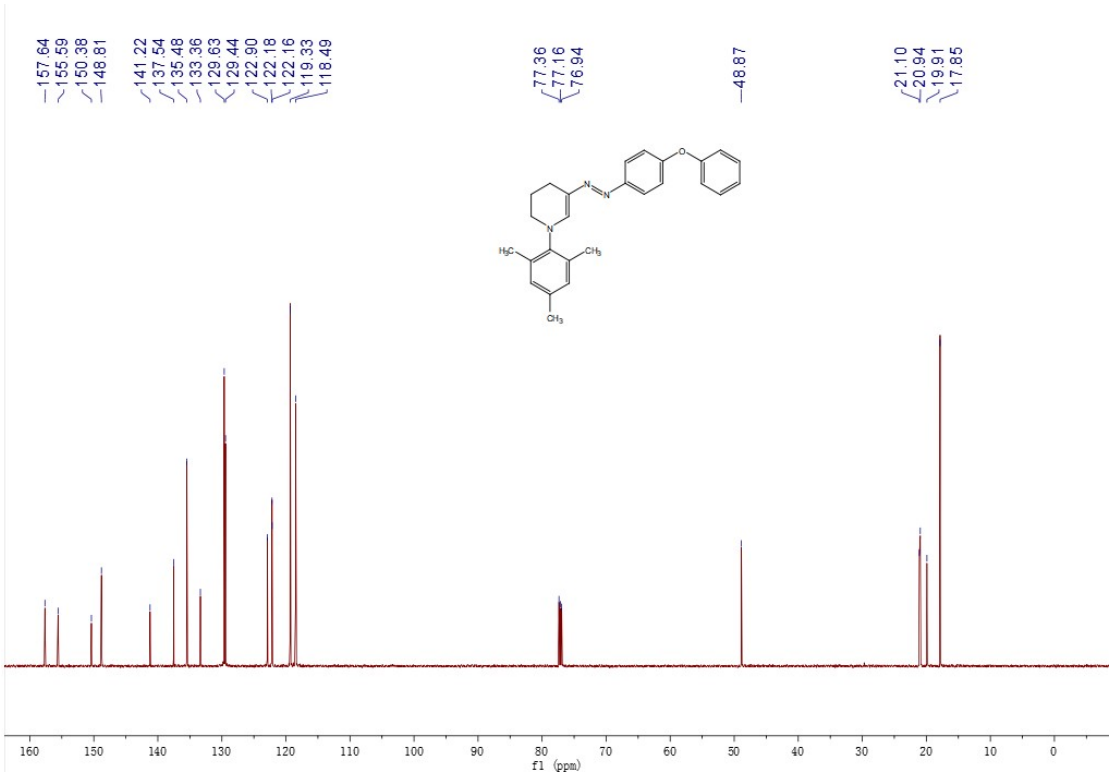
(29) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ac



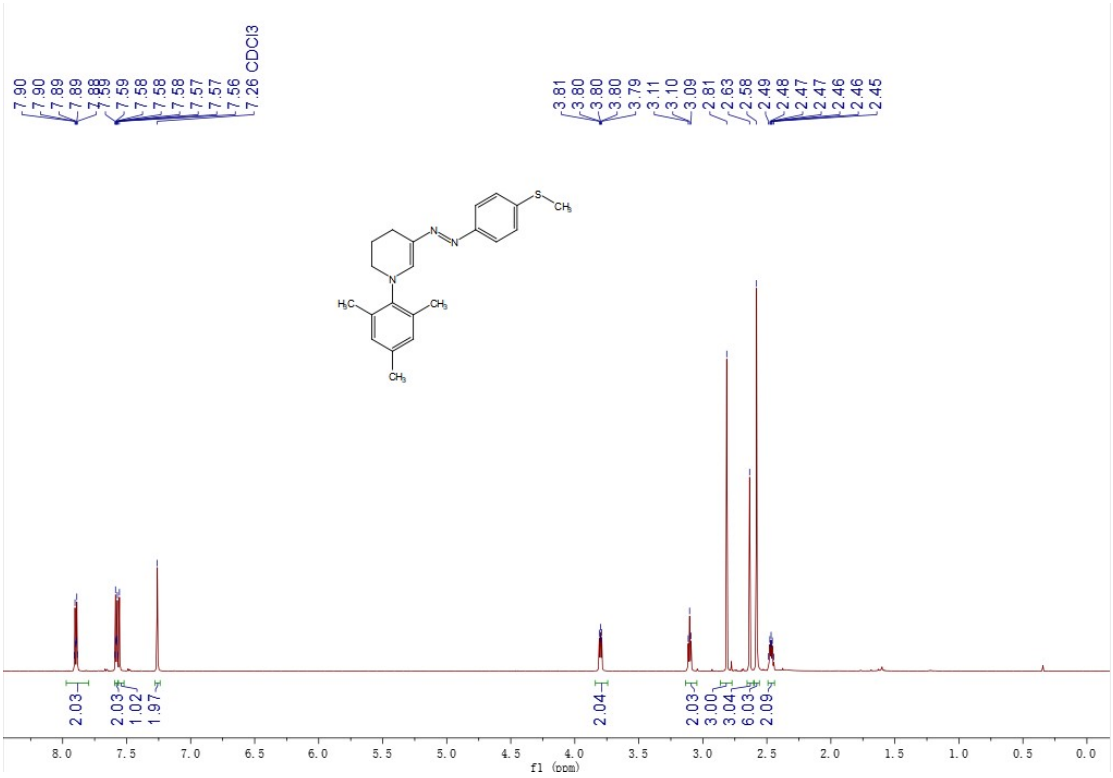
(30) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ad



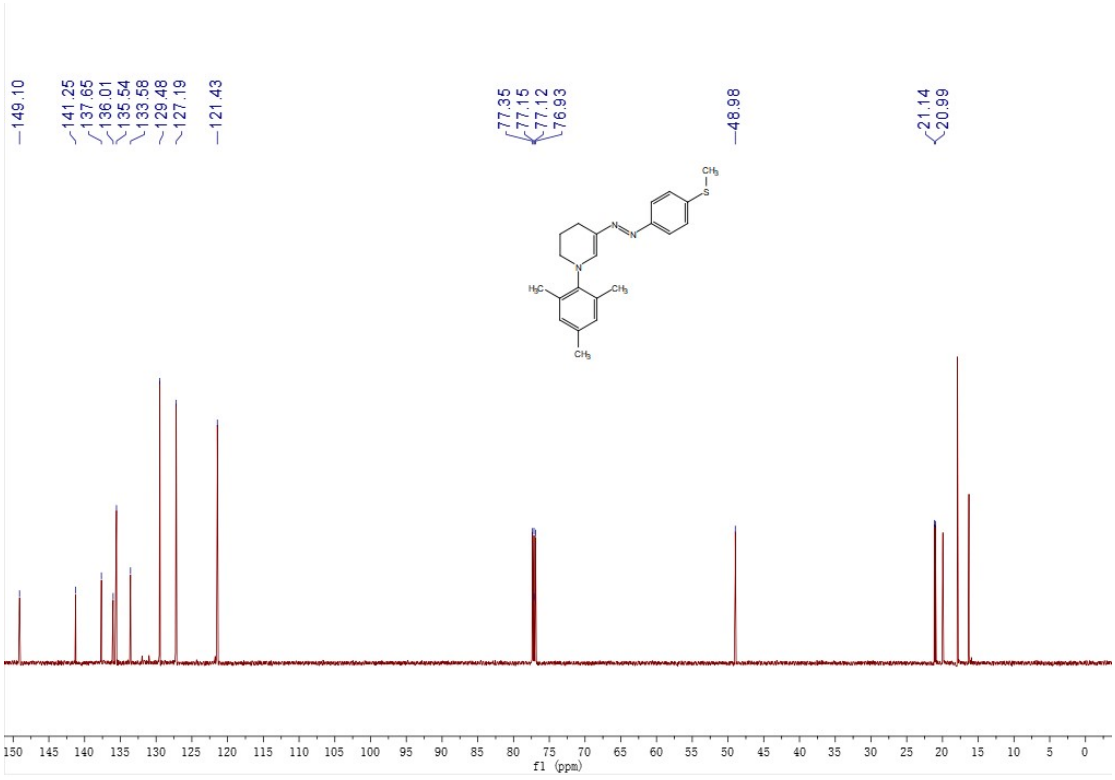
(31) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ad



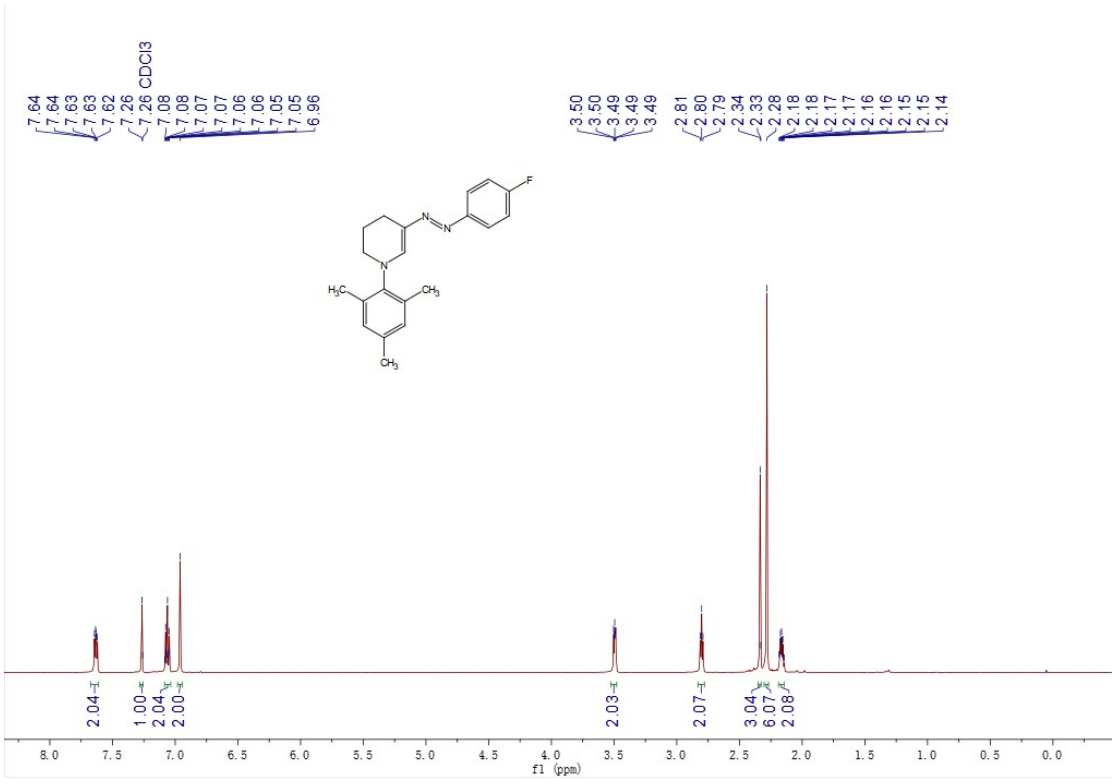
(32) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ae



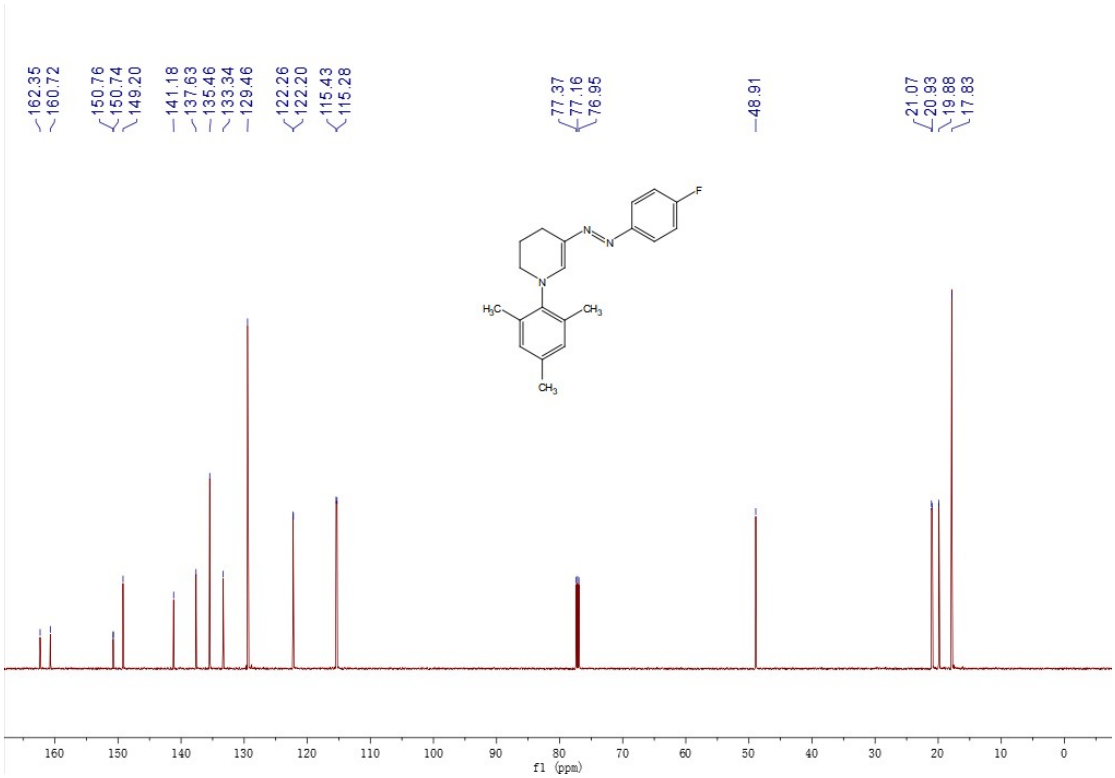
(33) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ae



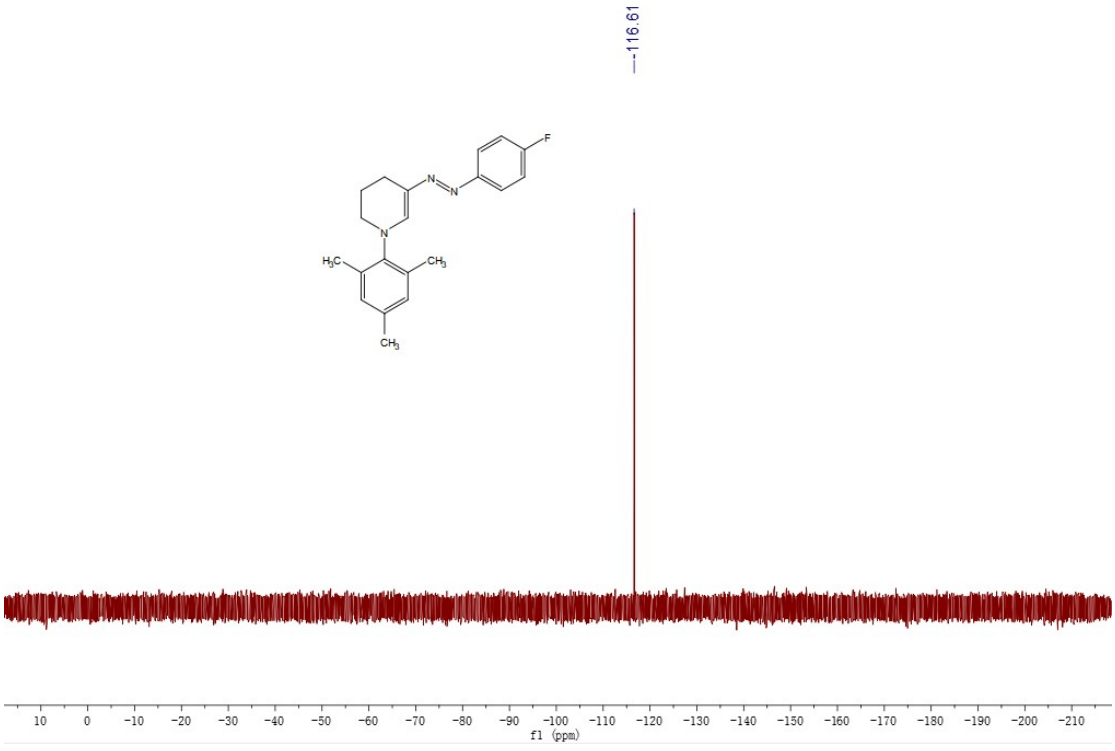
(34) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3af



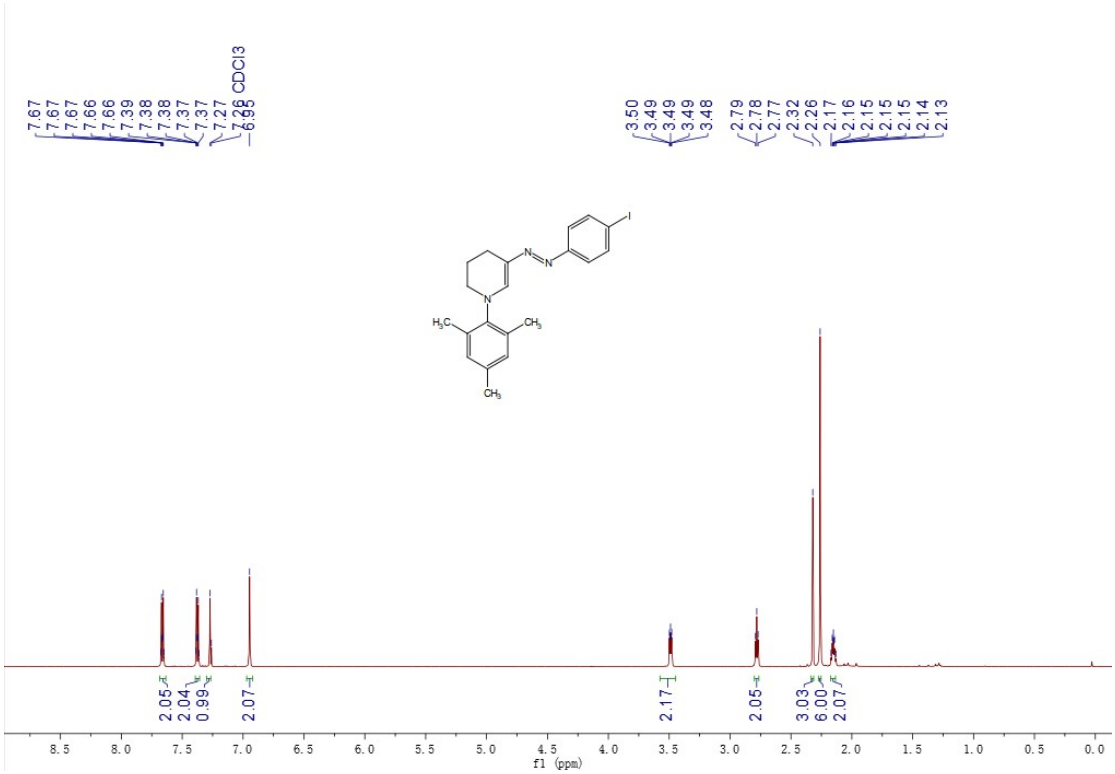
(35) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3af



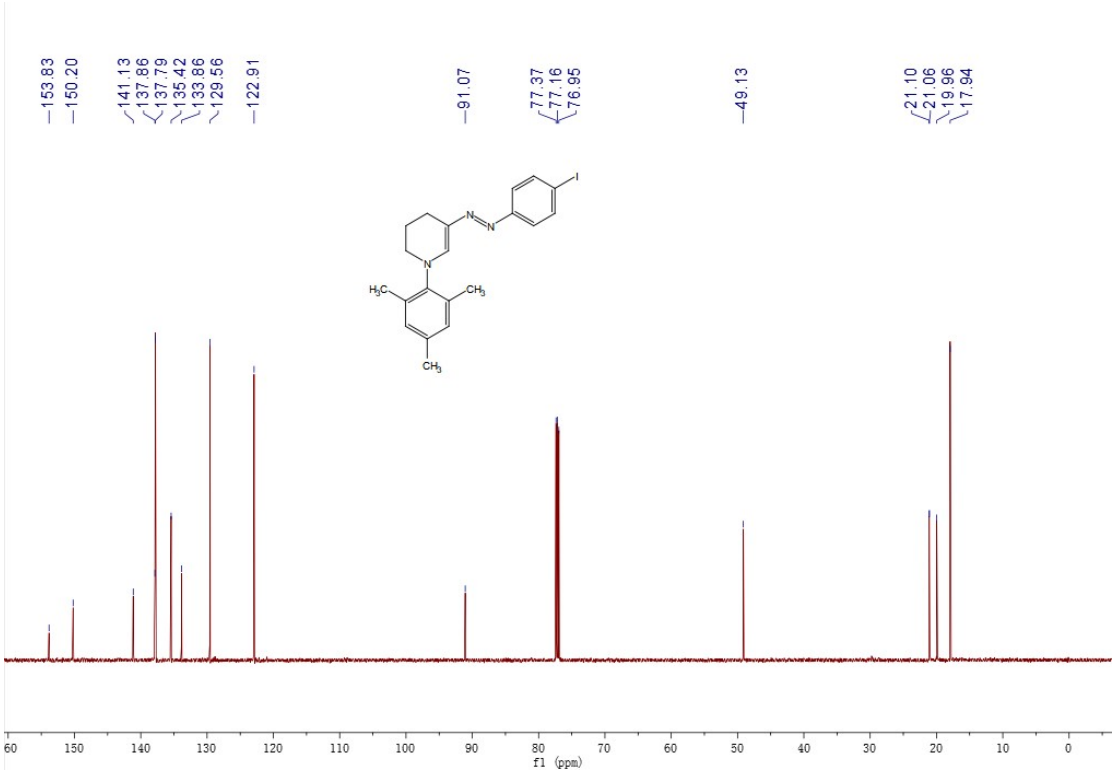
(36) ^{19}F NMR (565 MHz, Chloroform-d) spectrum of 3af



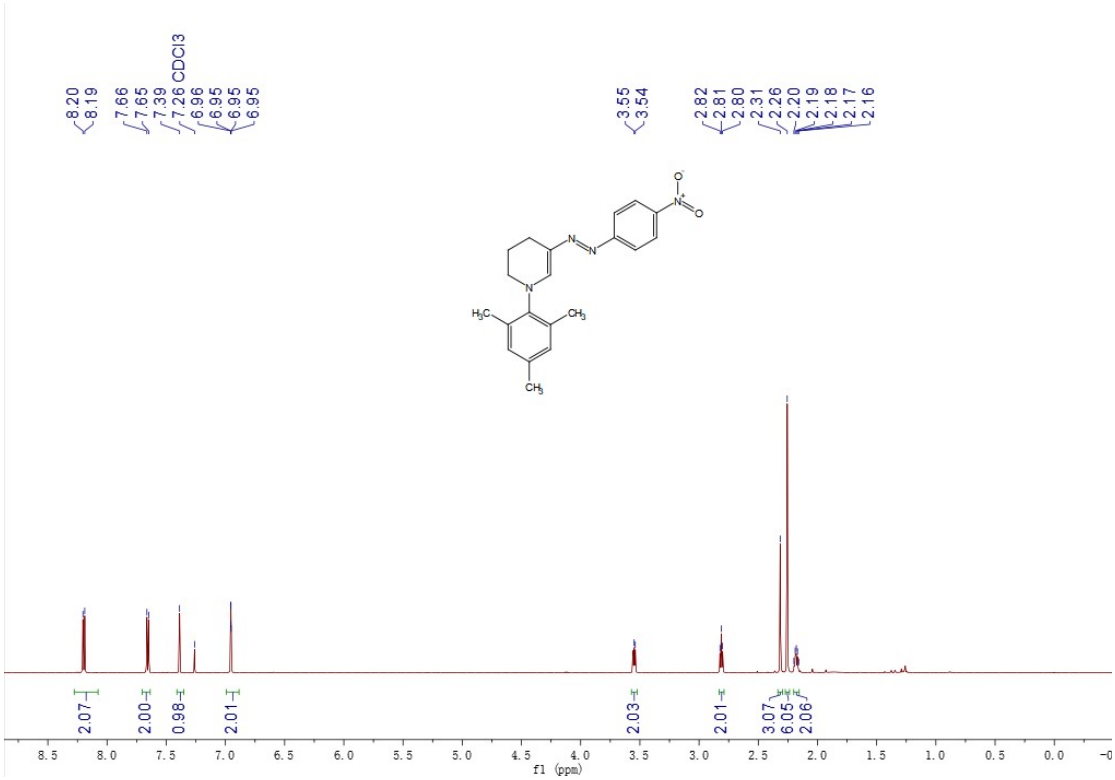
(37) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ag



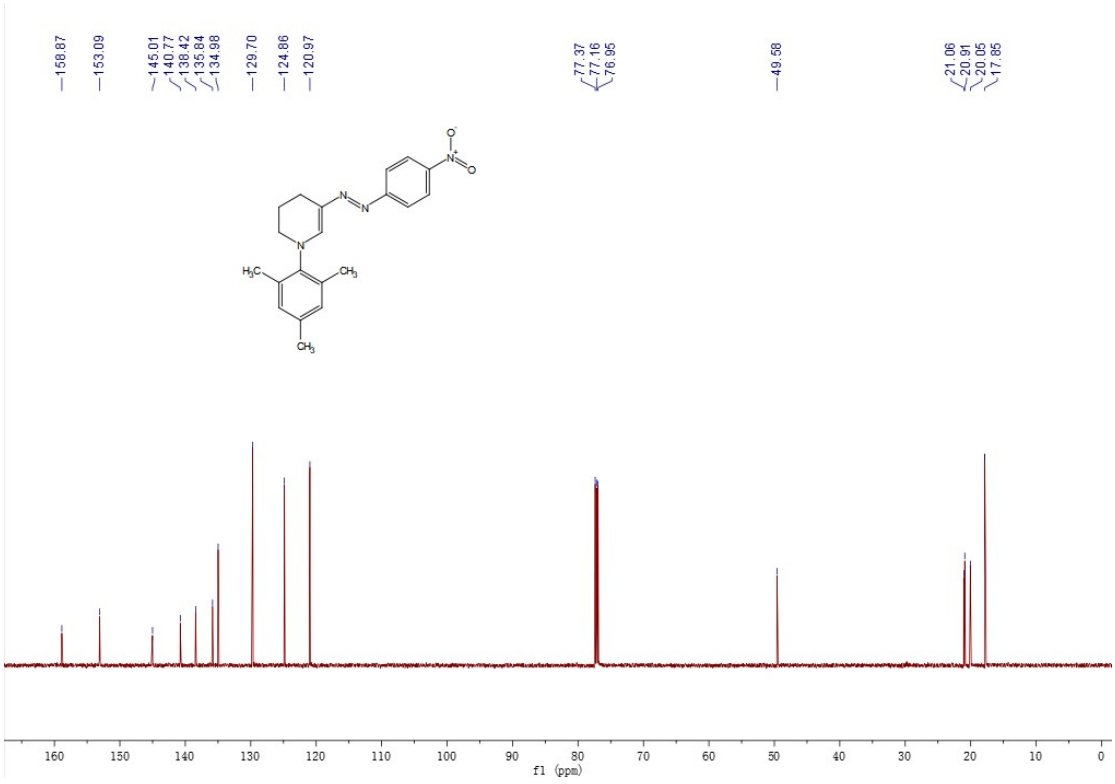
(38) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ag



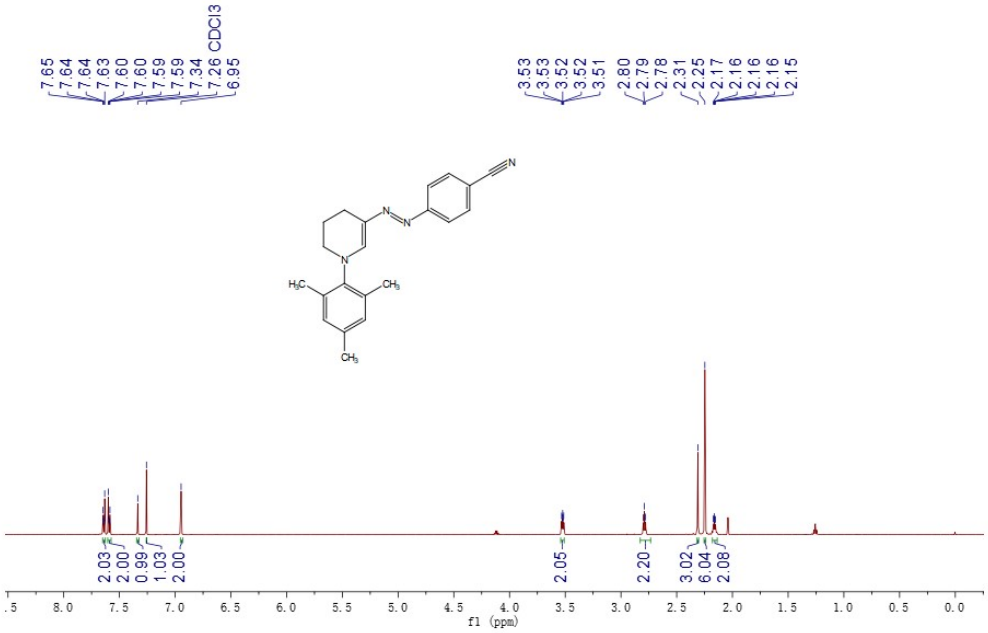
(39) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ah



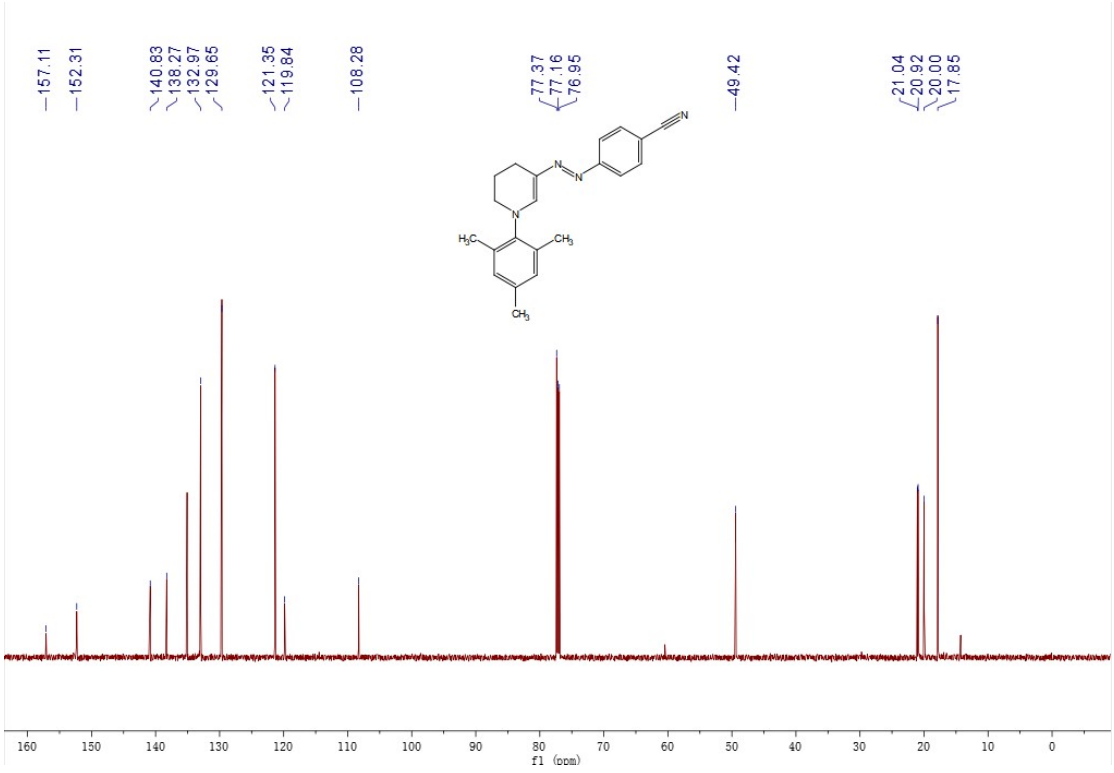
(40) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ah



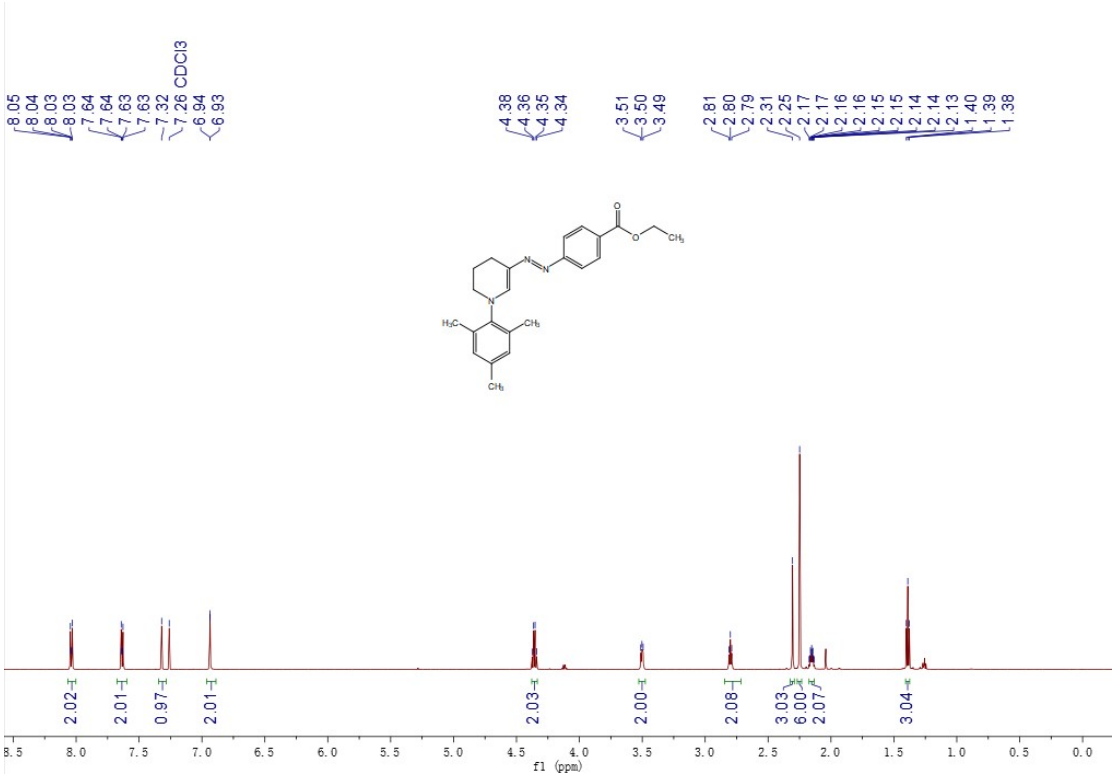
(41) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ai



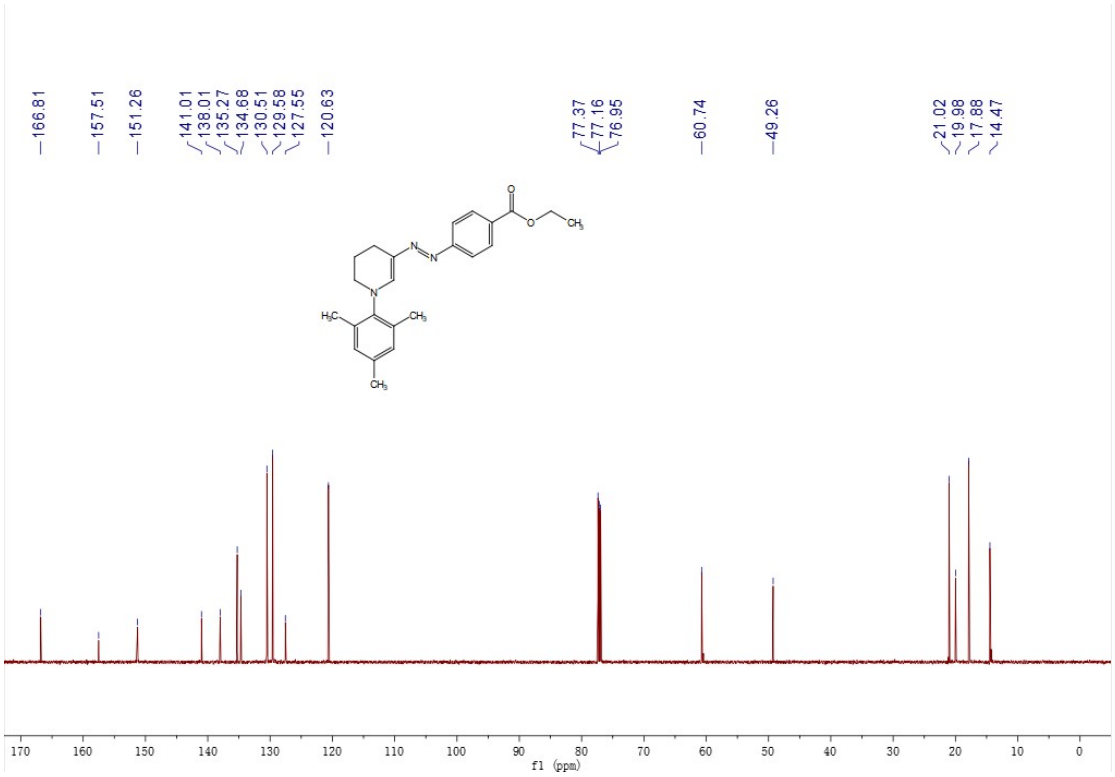
(42) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ai



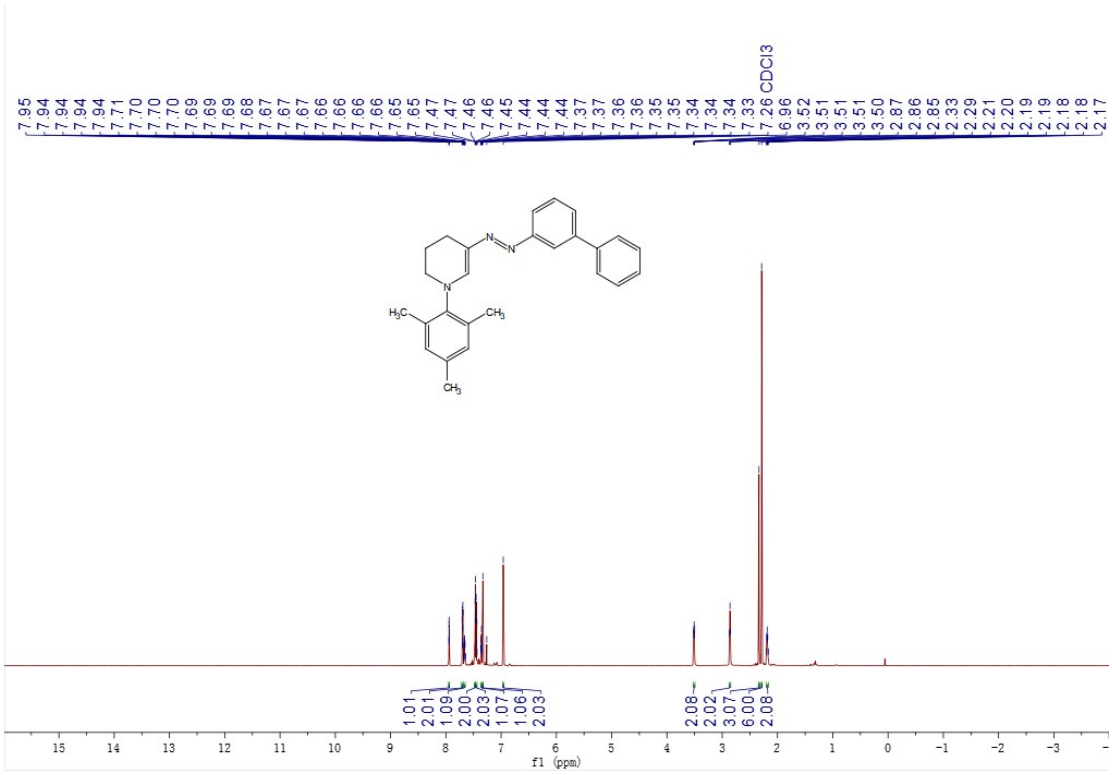
(43) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aj



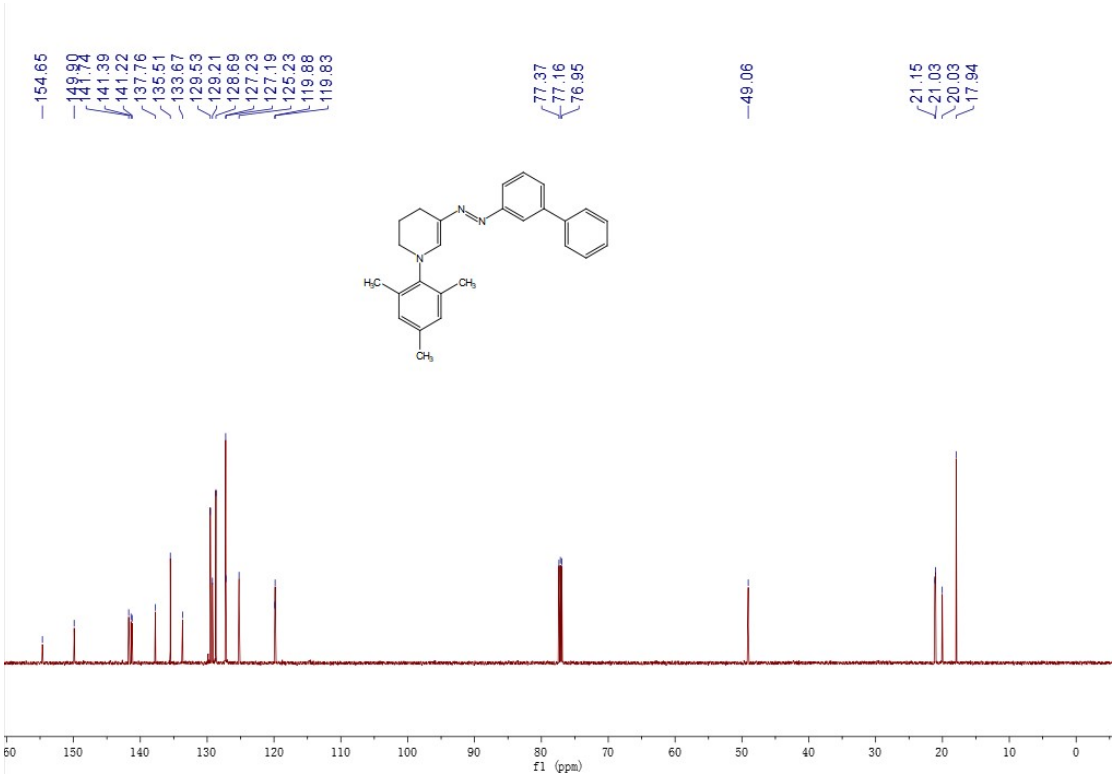
(44) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aj



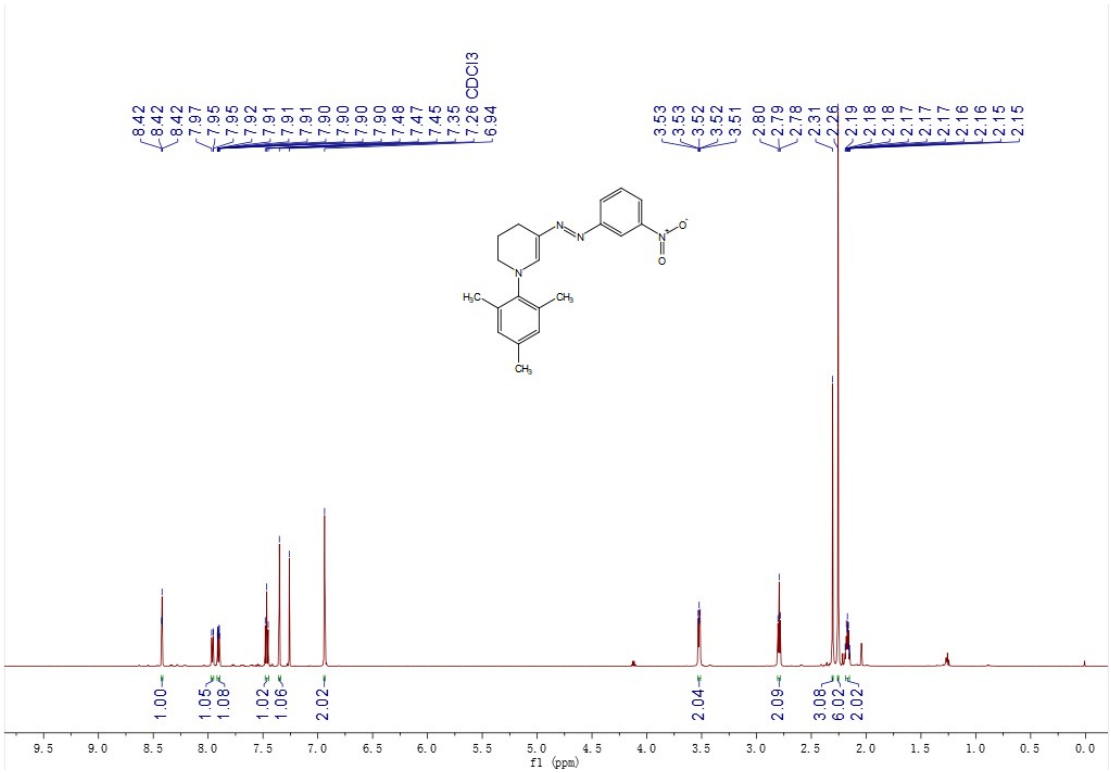
(43) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ak



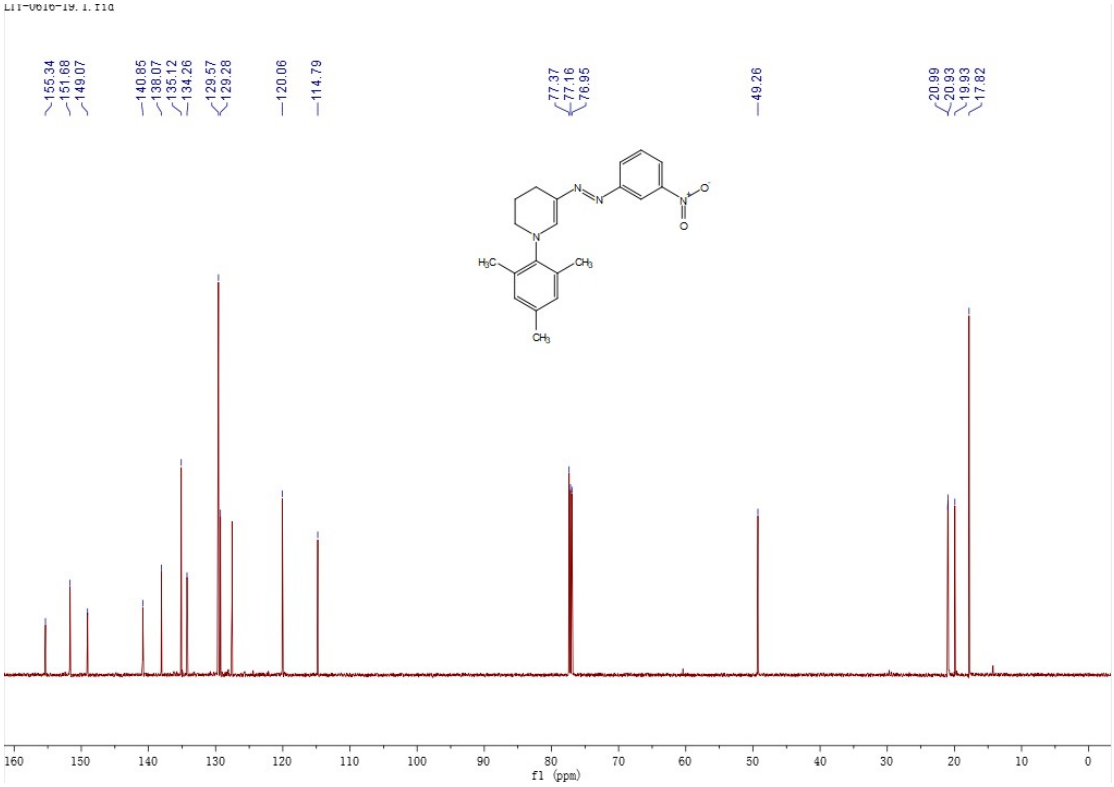
(44) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ak



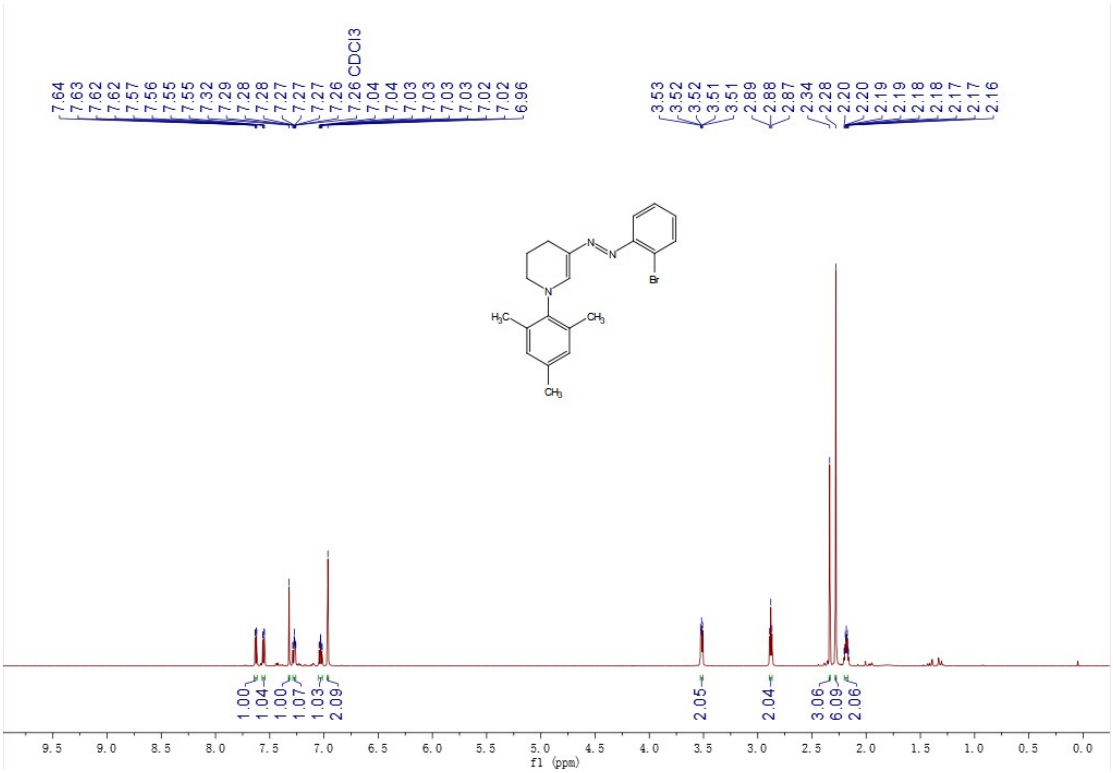
(45) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3al



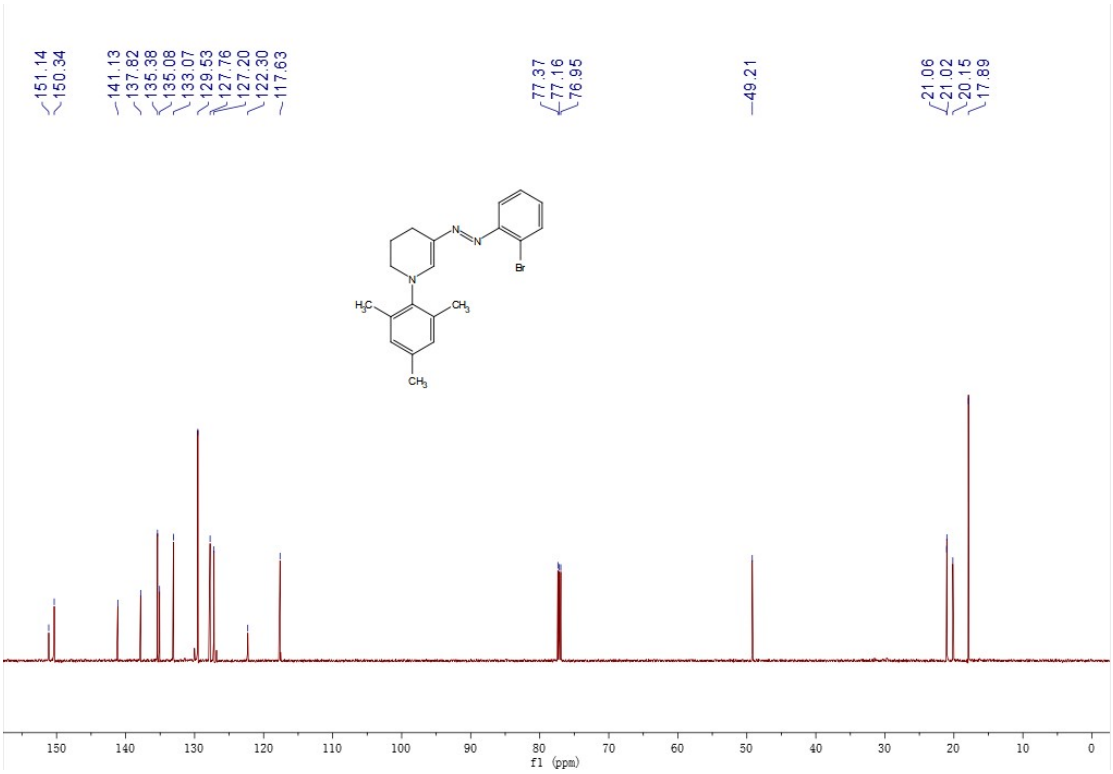
(46) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3al



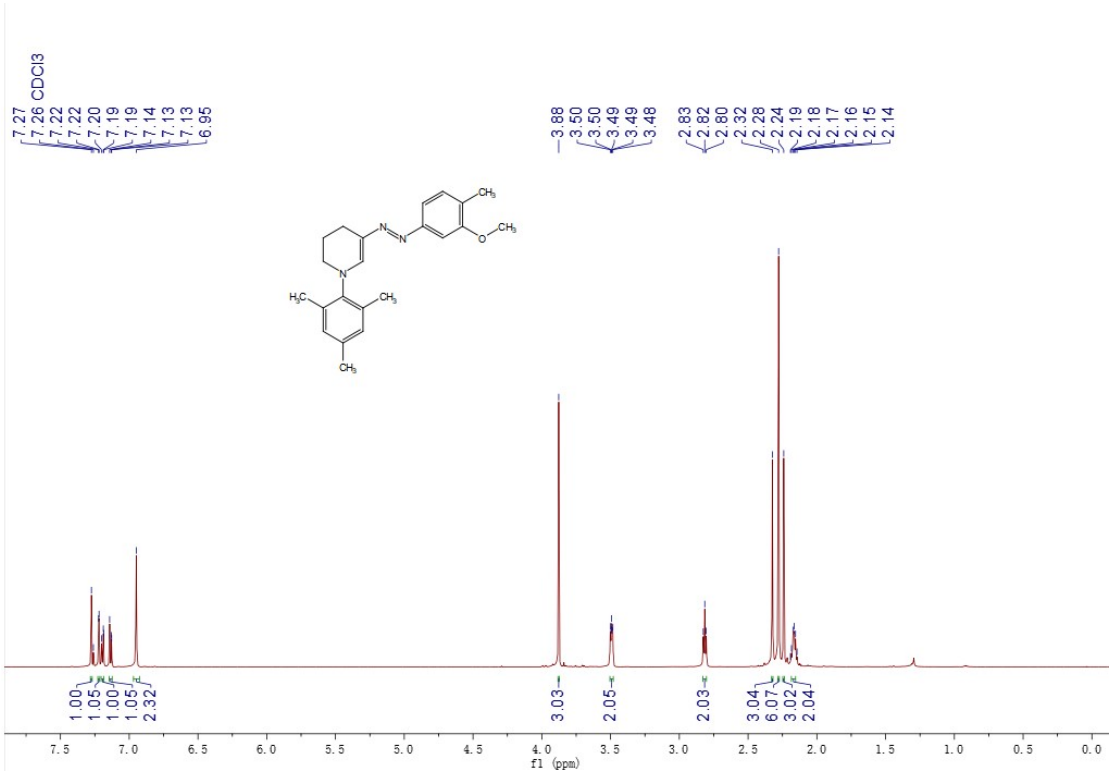
(47) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3am



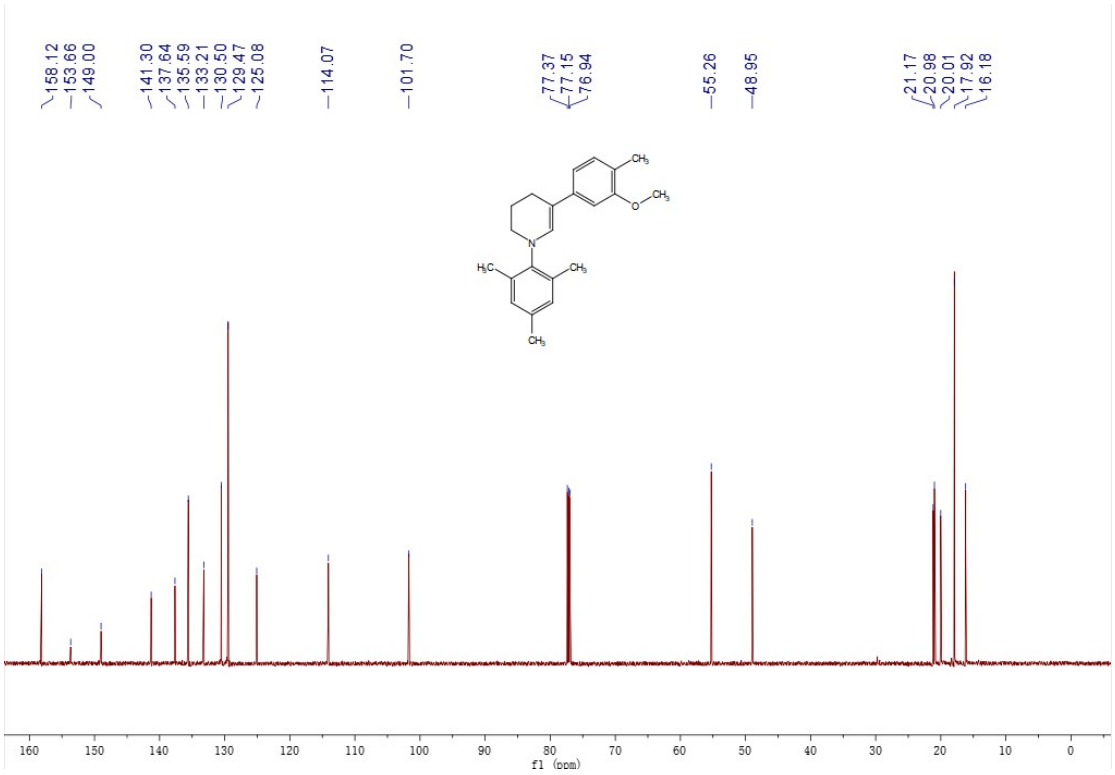
(48) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3am



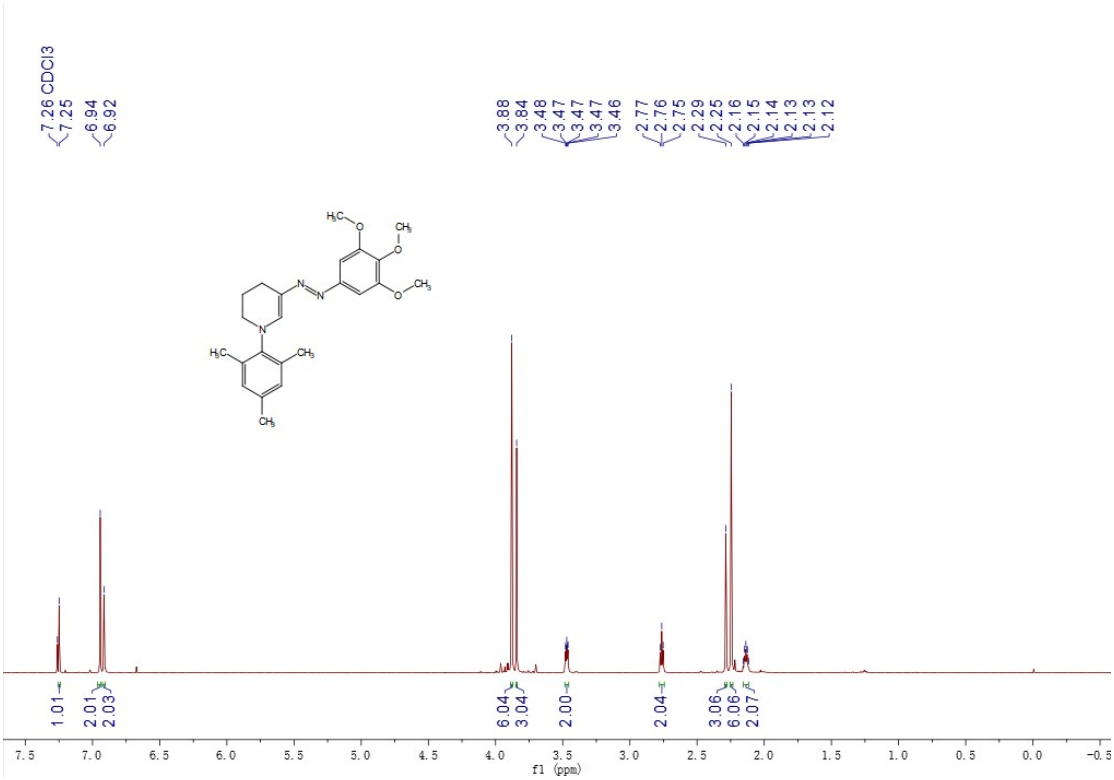
(49) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3an



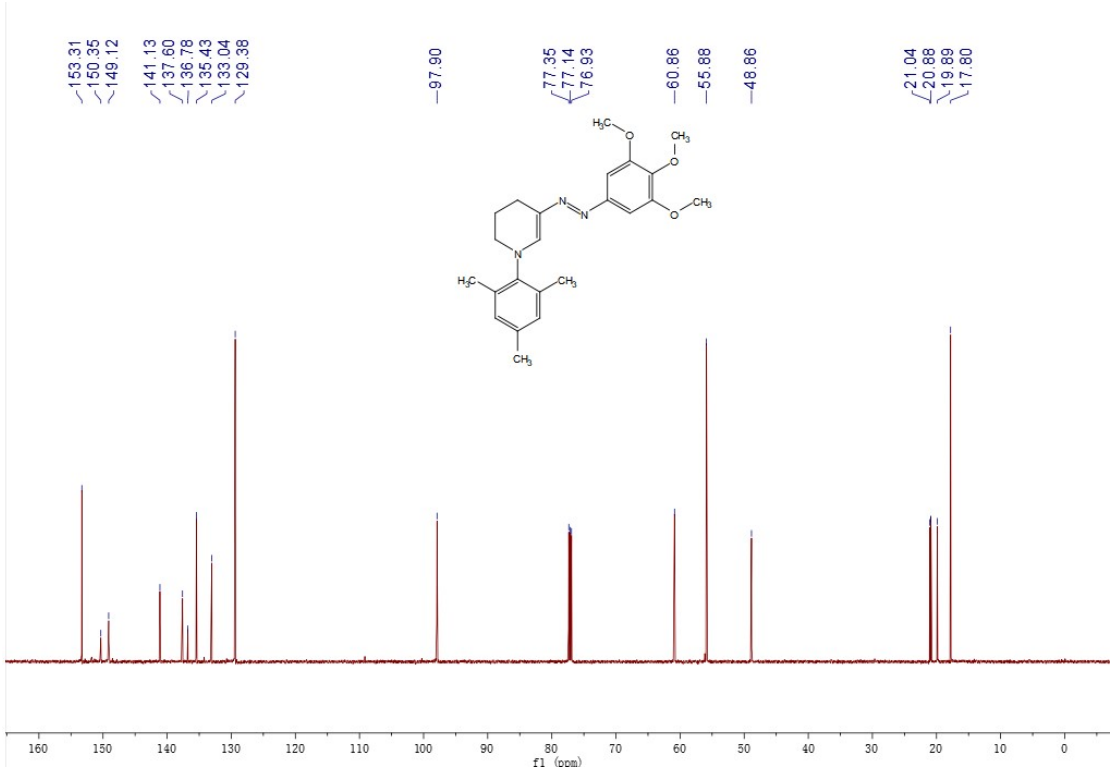
(50) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3an



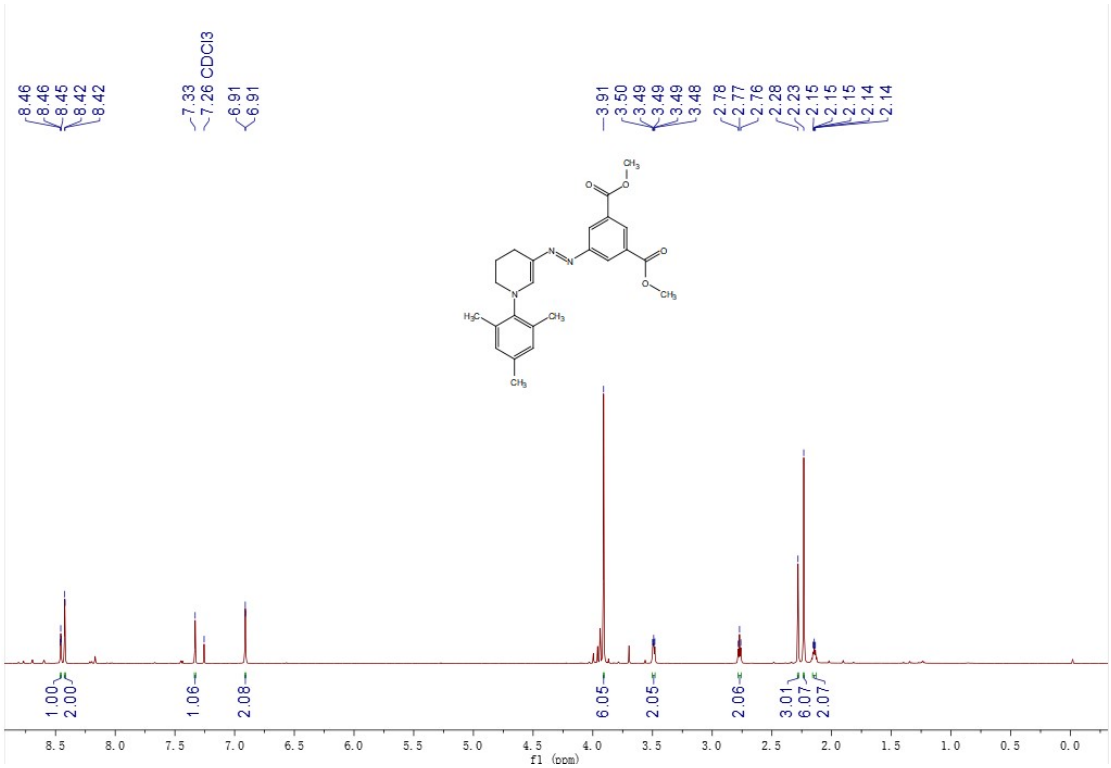
(51) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ao



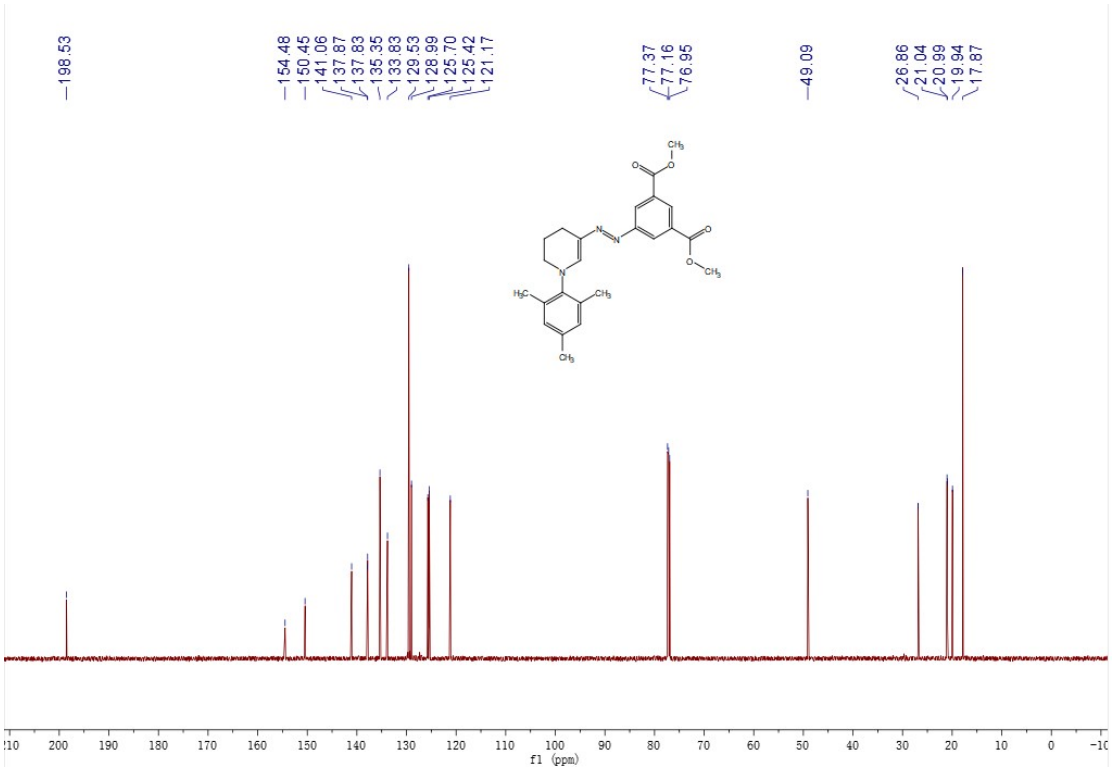
(52) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ao



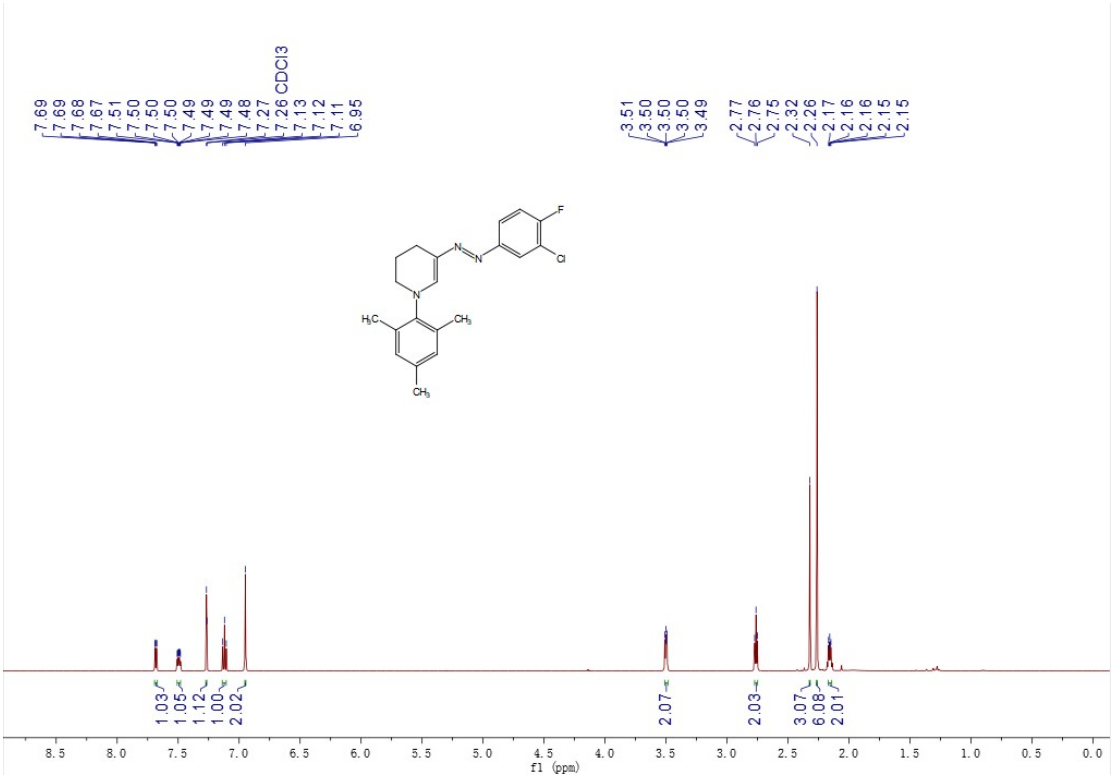
(53) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ap



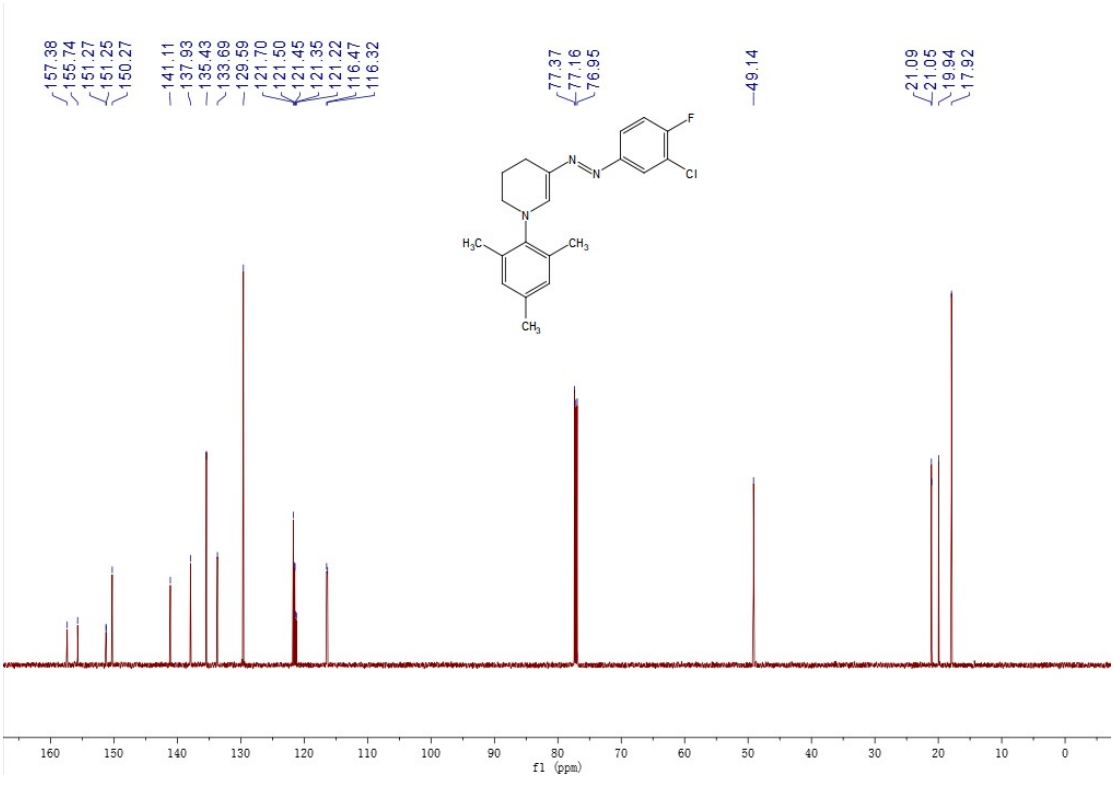
(54) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3ap



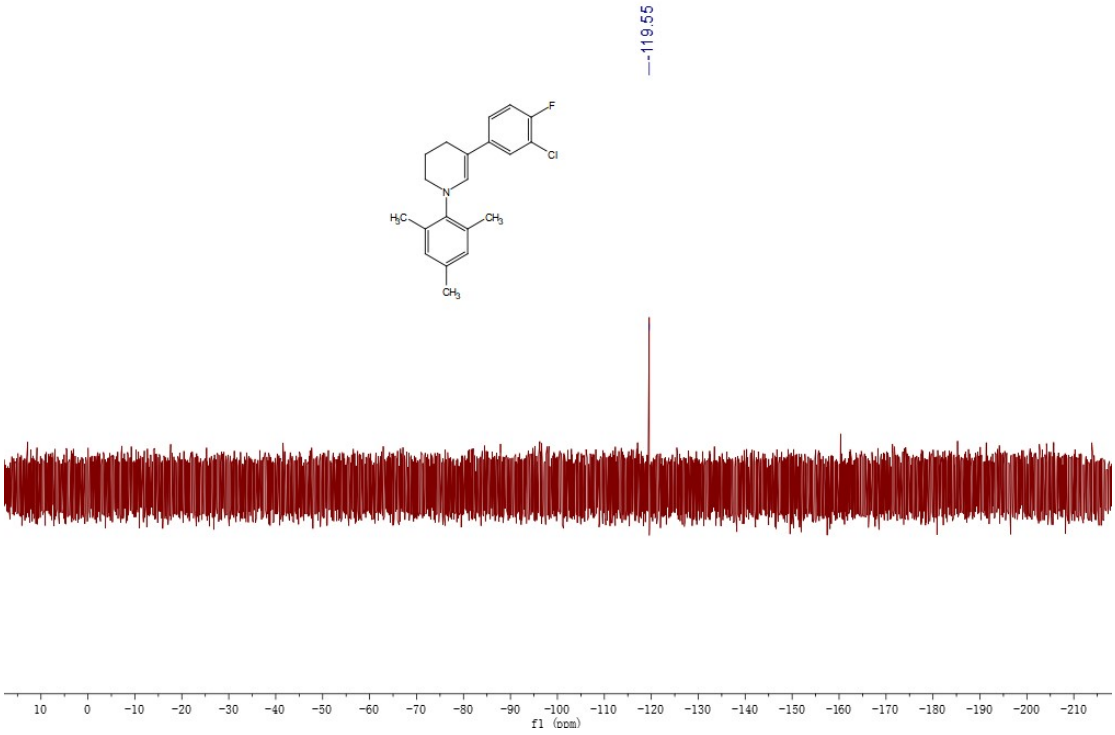
(55) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3aq



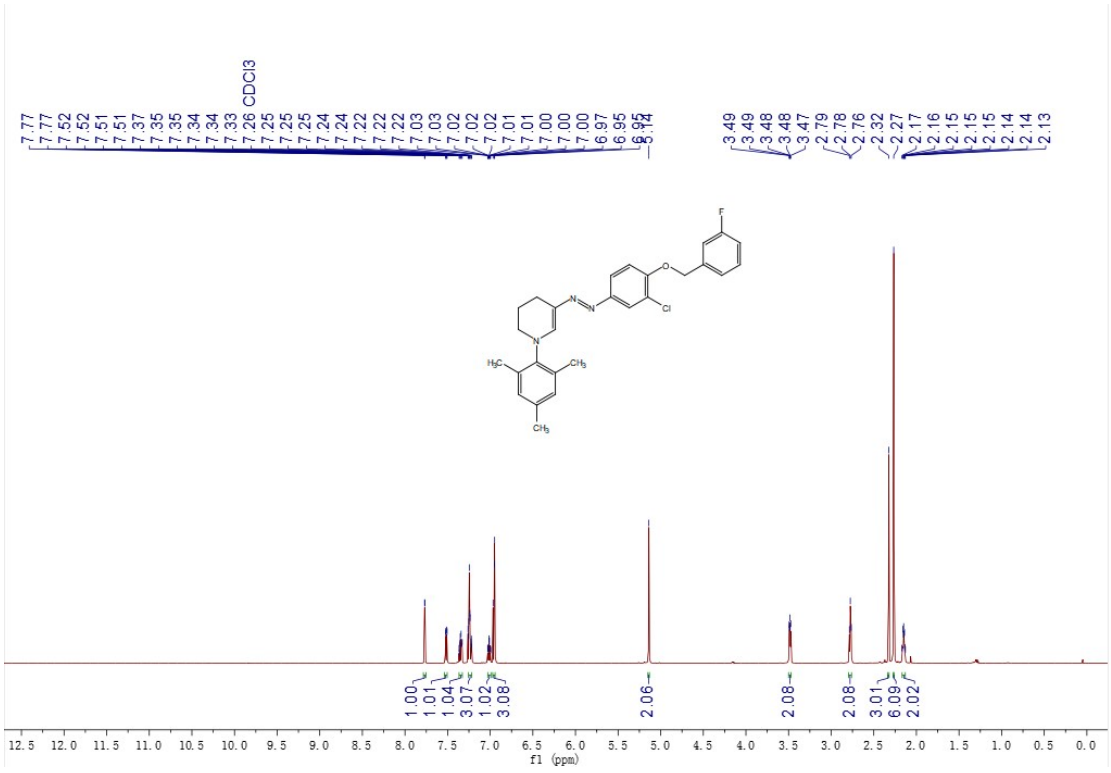
(56) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of 3aq



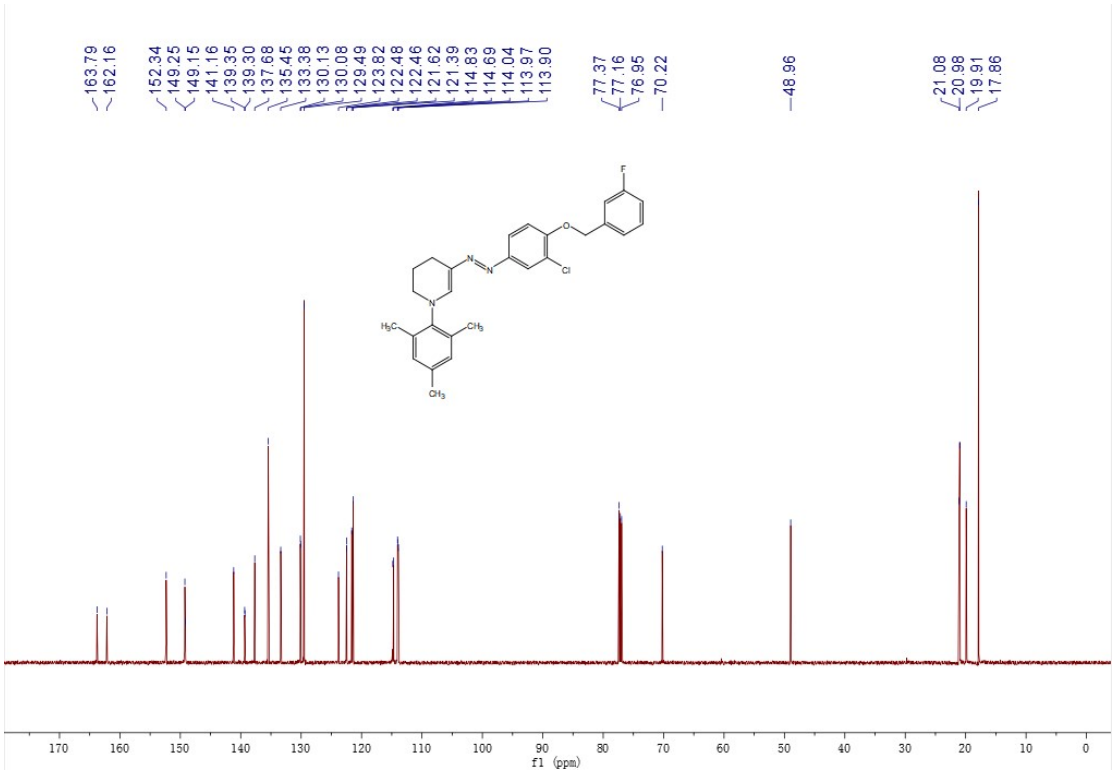
(57) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3aq



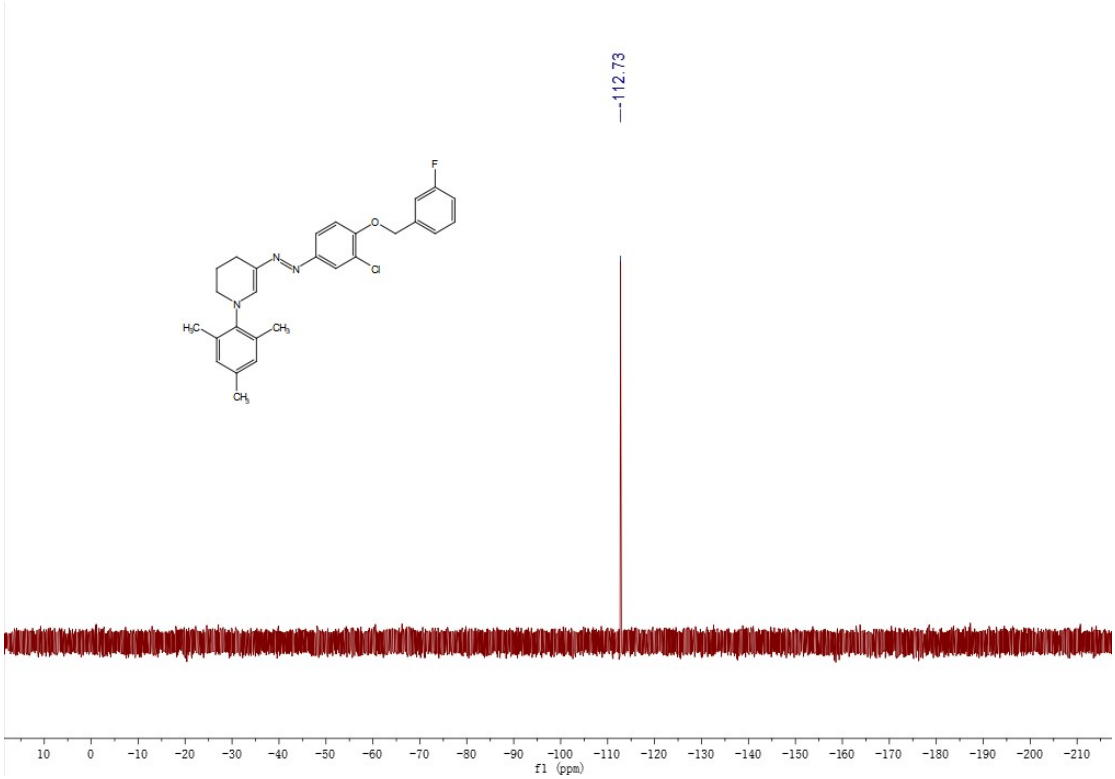
(58) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of 3ar



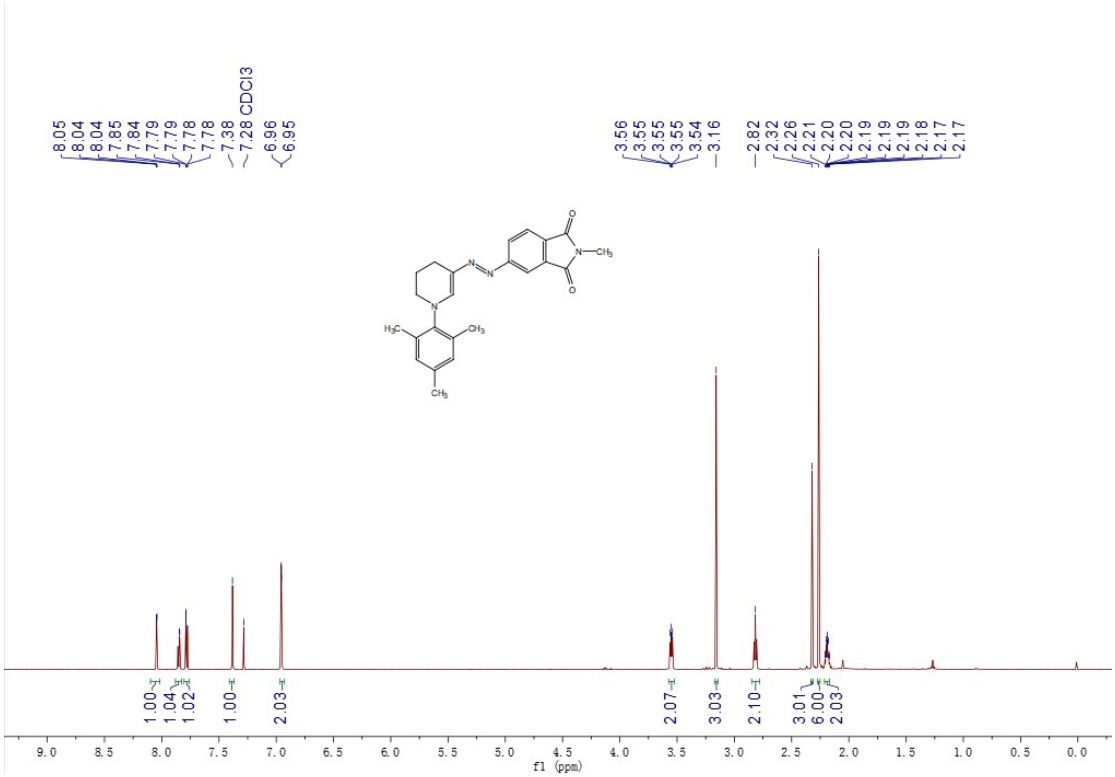
(59) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3ar



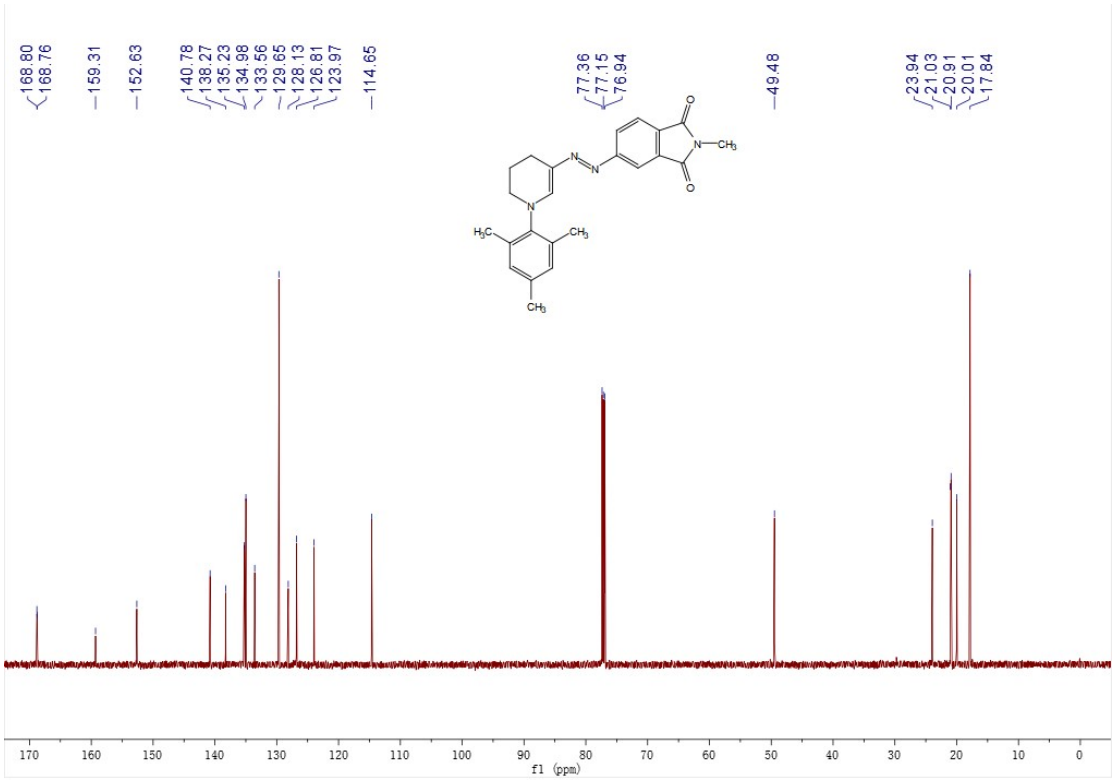
(61) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of 3ar



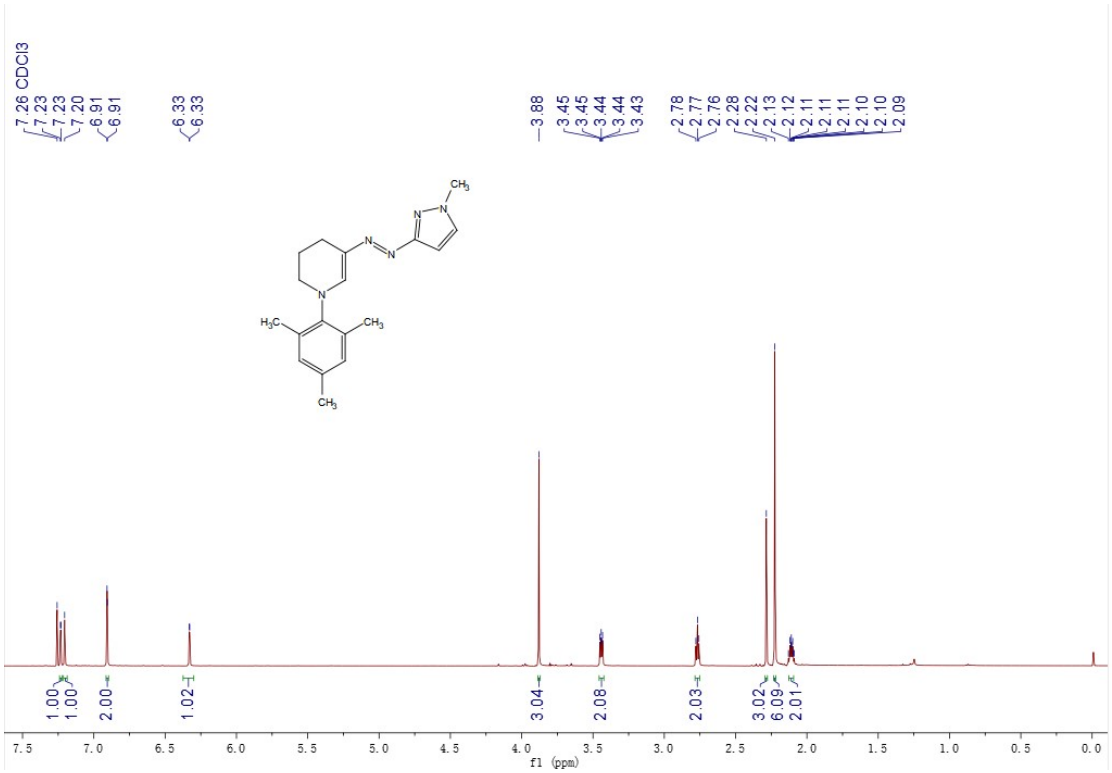
(62) ^{1}H-NMR (600 MHz, Chloroform-d) spectrum of biphenyl 3as



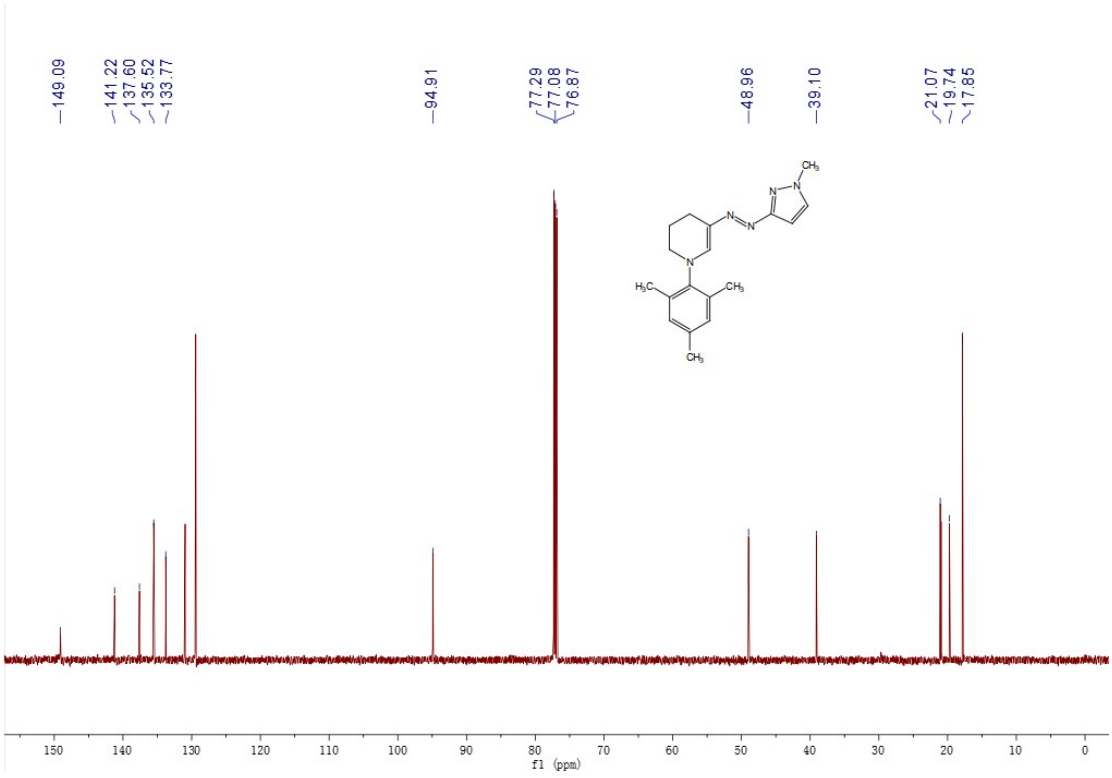
(63) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3as



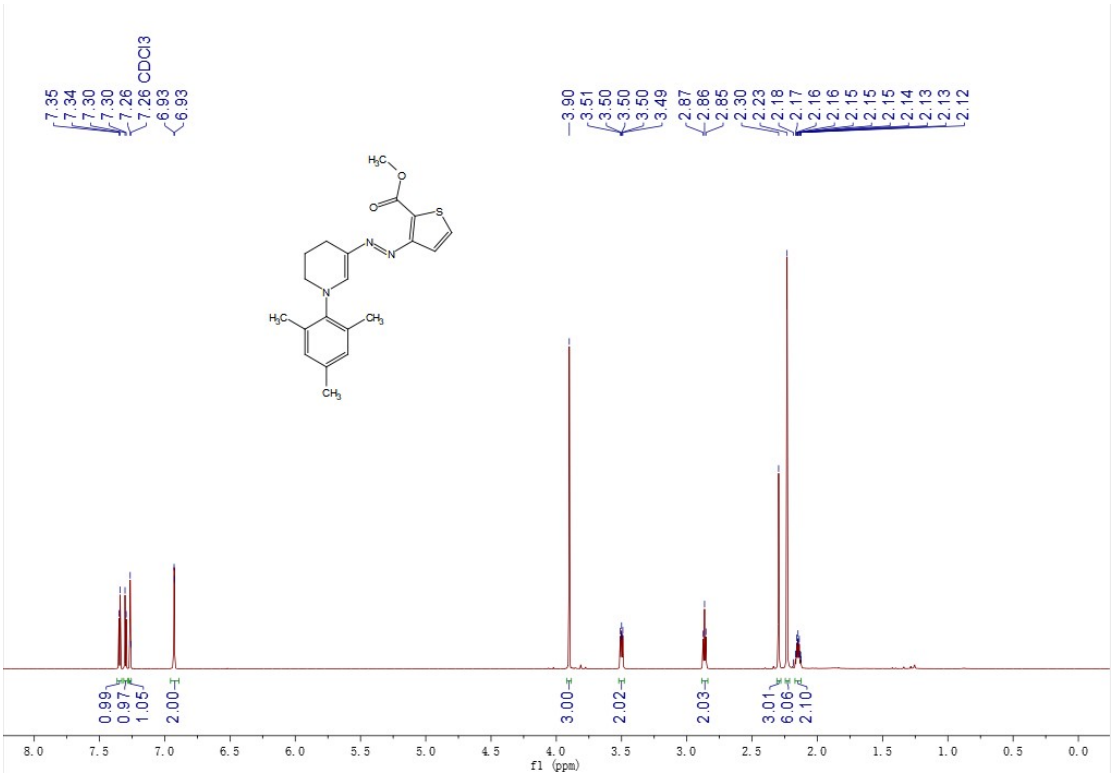
(63) ^{1}H-NMR (600 MHz, Chloroform-d) spectrum of biphenyl 3at



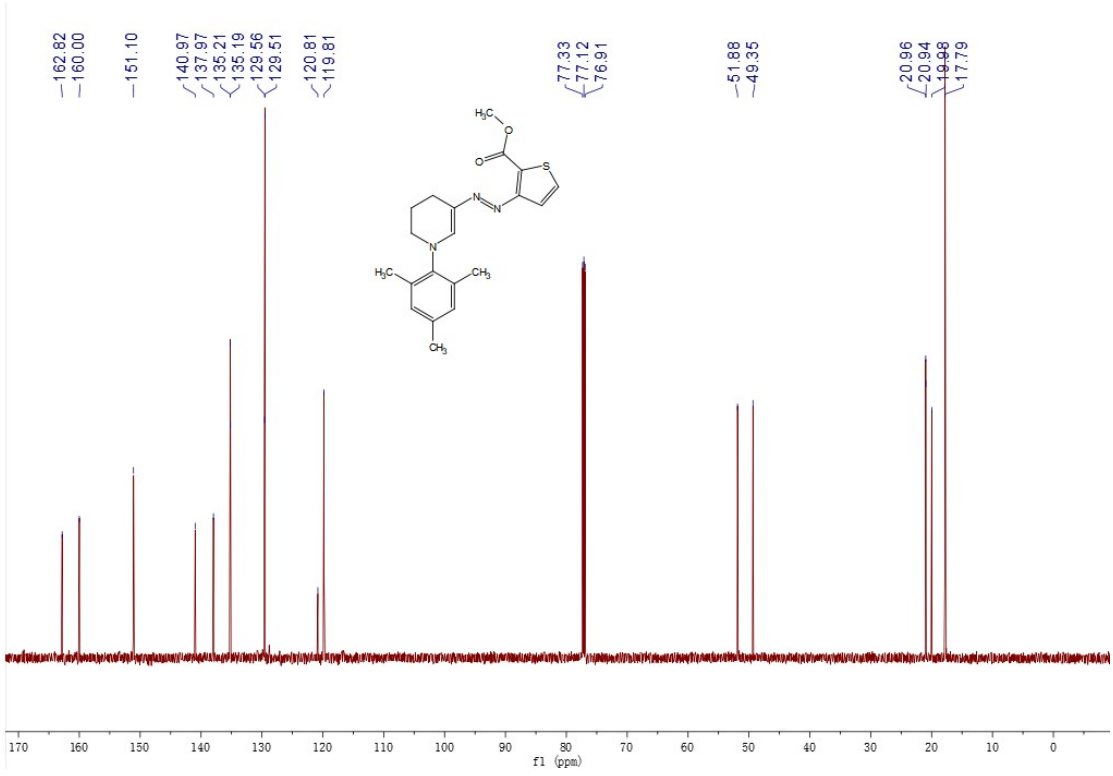
(64) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3at



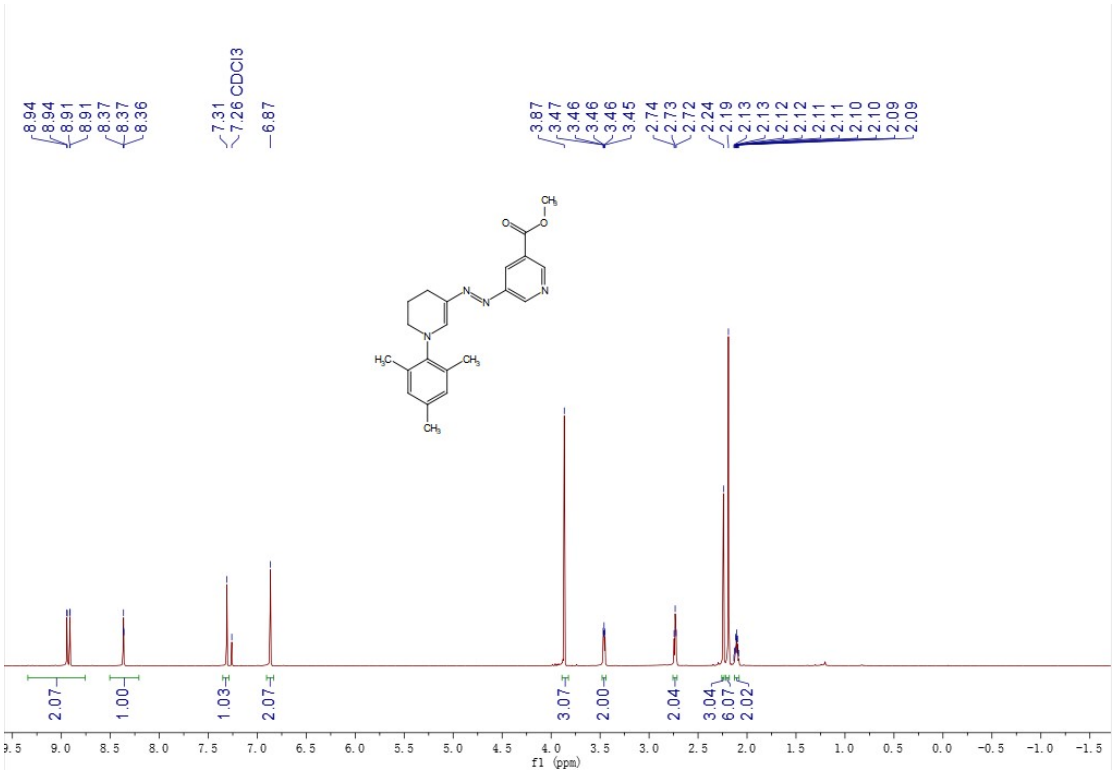
(65)^{1}H-NMR (600 MHz, Chloroform-d) spectrum of biphenyl 3au



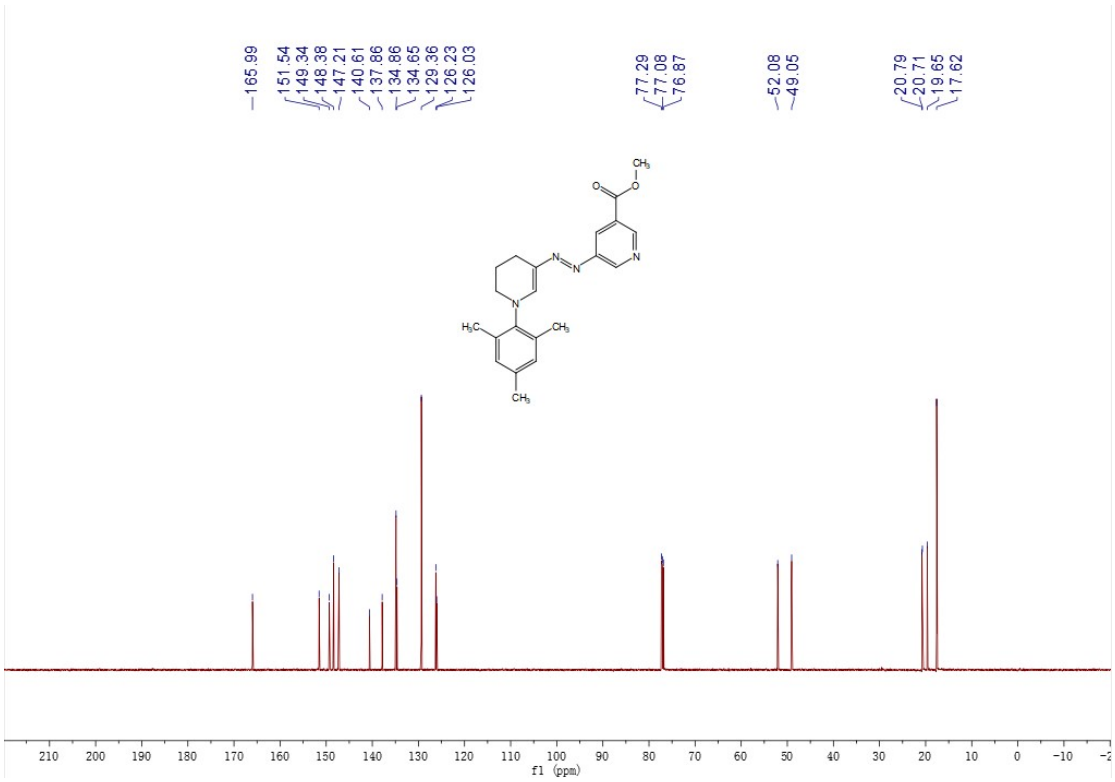
(66) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3au



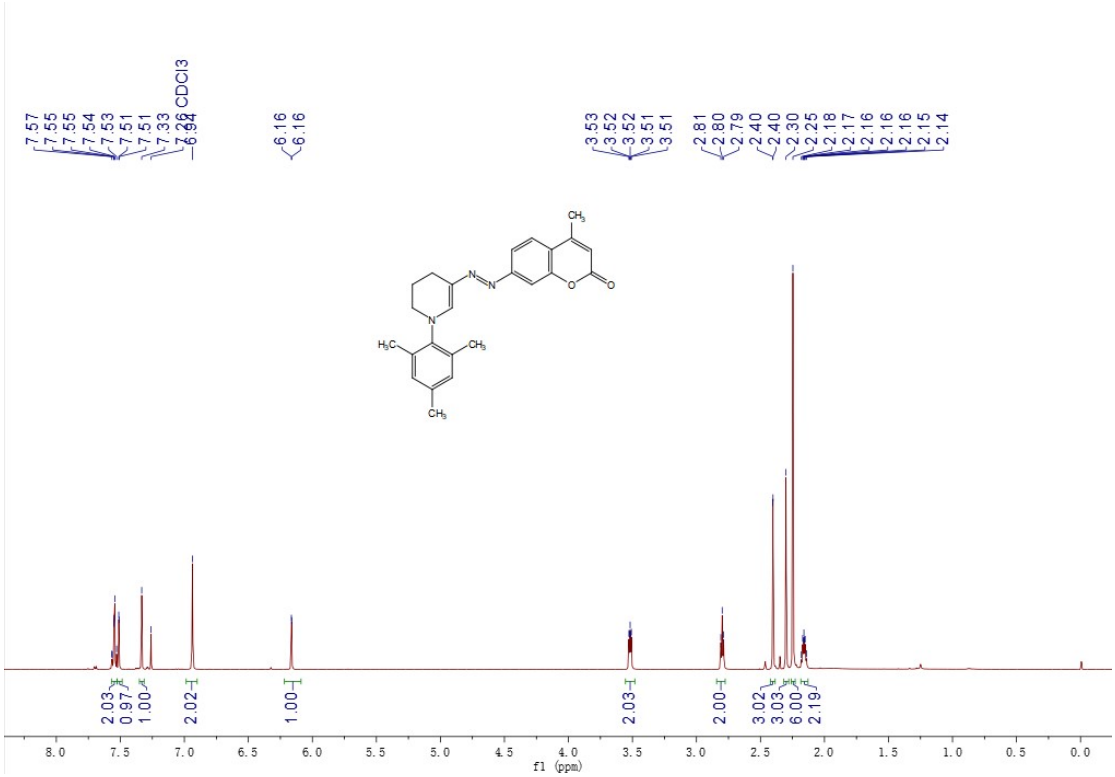
(67) ^{1}H-NMR (600 MHz, Chloroform-d) spectrum of biphenyl 3av



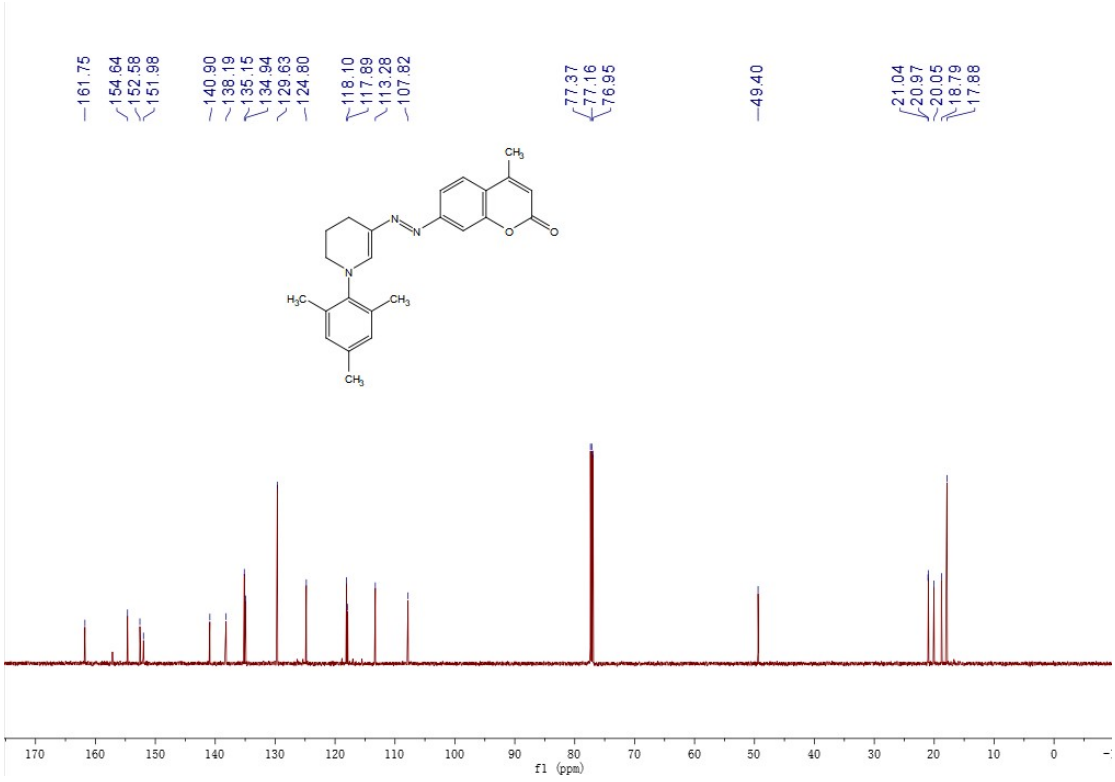
(68)^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3av



(69) ^{1}H-NMR (600 MHz, Chloroform-d) spectrum of biphenyl 3aw



(70)^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of biphenyl 3aw



9. LC-MS analyses

(1) The model reaction was carried out under standard reaction conditions for 6.0 hours. Subsequently, the reaction mixture was analyzed by liquid chromatography-mass spectrometry (LC-MS), and **I**, **II** & **3aa** could be observed.

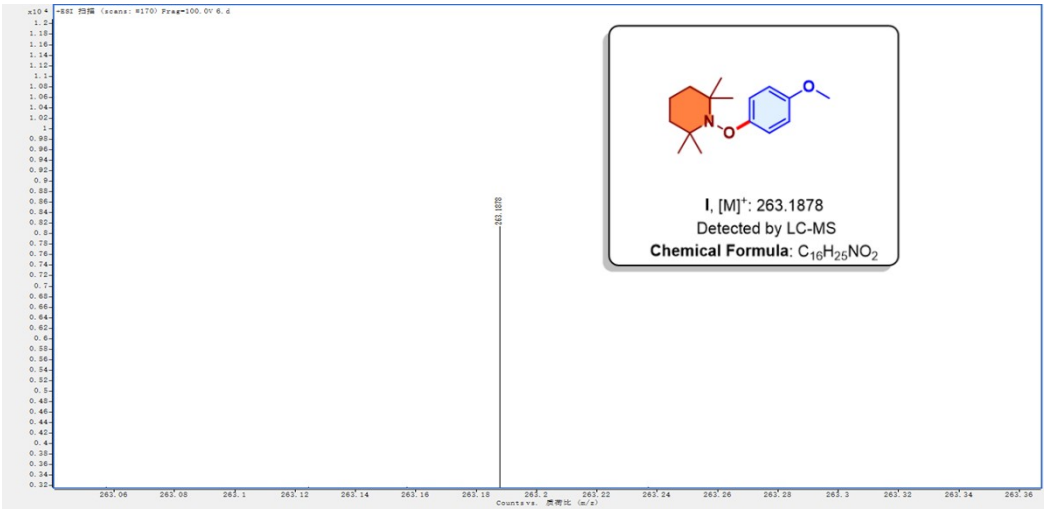


Figure S1. LC-MS analysis experiment report 1 of the reaction mixture.

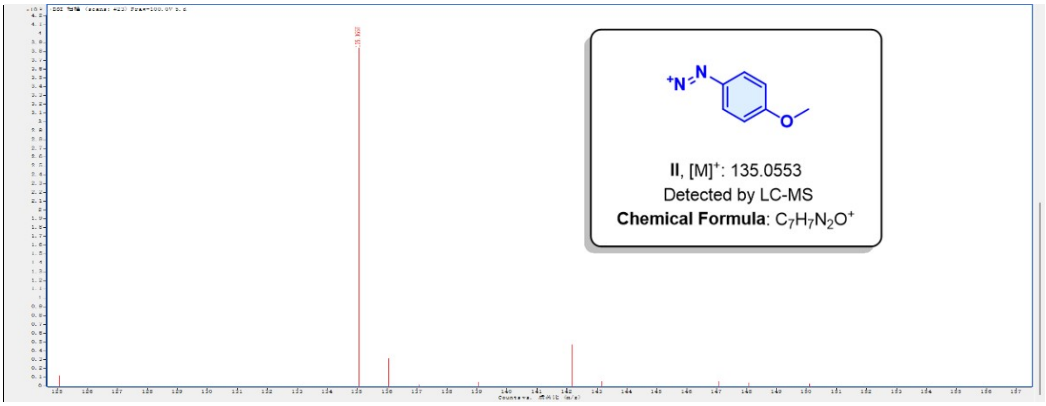


Figure S2. LC-MS analysis experiment report 2 of the reaction mixture.

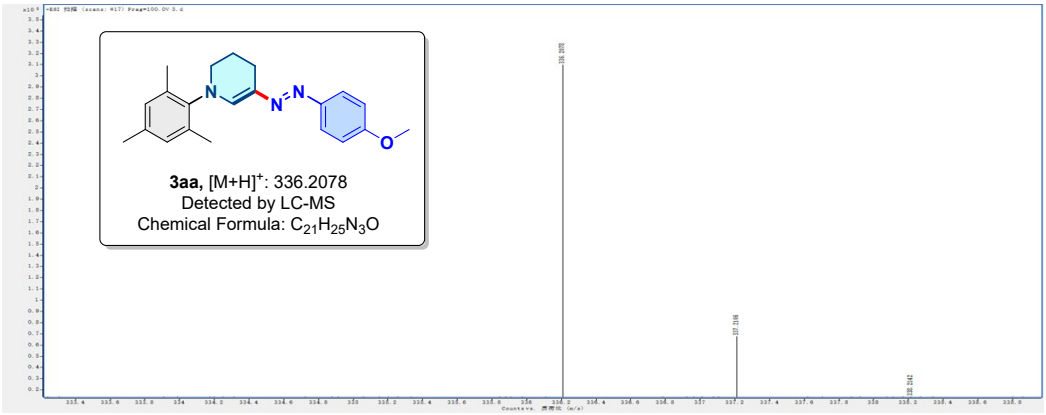


Figure S3 LC-MS analysis experiment report 3 of the reaction mixture.

10. References

[1] N. Takasu, K. Oisaki, M. Kanai, Iron-Catalyzed Oxidative C(sp3)–H Functionalization of Amines, *Org. Lett*., 2013, **15**, 1918–1921.

[2] P. Wang, Z. Yang, Z. Wang, C. Xu, L. Huang, S. Wang, H. Zhang and A. Lei, *Angew. Chem. Int. Ed.*, 2019, **131**, 15894–15898.