Supporting Information

Phosphine-catalyzed *β*-C(sp³)–H Functionalization of Cyclic Amines *via* a Halogen Based Frustrated Radical Pairs Approach

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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, p = pentet, sext = sextet, sept = septet, m = multiplet, bs = broad singlet; coupling constants in Hz; integration.

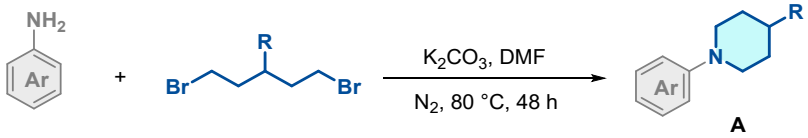
Instrument

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

EXPERIMENTAL DATA

2. Substrates preparation.

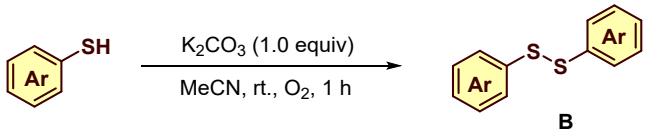
2.1. Method A [1] (preparation of substrates B1-B13)



A

To a dried round-bottom flask was charged with a magnetic stirring bar, DMF (30.0 mL) aniline (10.0 mmol), 1,5-dibromopentane (l.5 eq.), K_2CO_3 (1.5 eq.) was added successively, the flask was evacuated and backfilled with nitrogen for 3 times, and the mixture was heated to 80 °C using metal sand bath with stirring for 48 h. The reaction was monitored by TLC. After completion, the reaction was quenched with saturated $NaHCO_3$, solution, and extracted with EtOAc. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The reaction mixture was purified via column chromatography to give **A**.

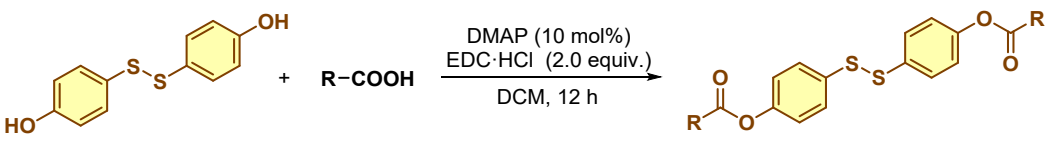
2.2. Method C [2] (preparation of substrates A2-A16)



B

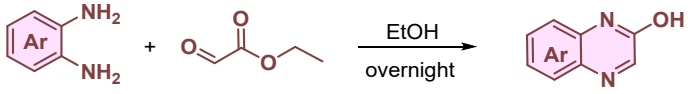
To a round bottle (50.0 mL) were added thiophenol (5.0 mmol), anhydrous potassium carbonate (0.69 g, 5.0 mmol), and MeCN (10.0 mL) sequentially, and the reaction was conducted at room temperature under oxygen atmosphere for 1 hour. And the desired **B** disulfides were obtained quantitatively, after filter and concentration.

2.3. Method C [3] (preparation of substrates A30-A35)



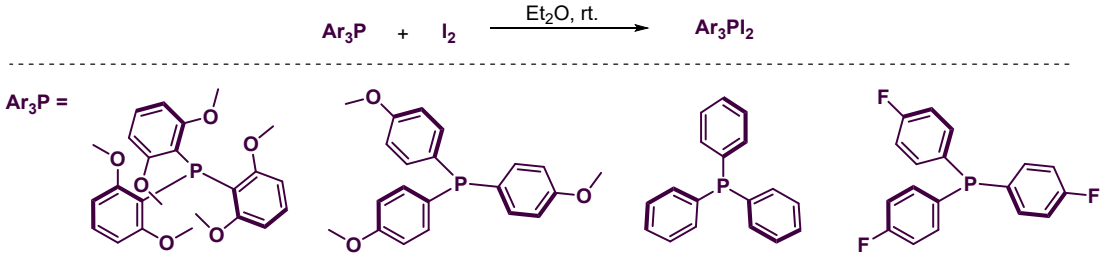
In a round-bottom flask equipped with a PTFE-coated stirring bar, the corresponding disulfide (1.0 equiv.), EDC·HCl (2.0 equiv.), the corresponding acid or corresponding alcohol (2.2 equiv.), DMAP (0.1 equiv.) were dissolved in CH_2Cl_2. The reaction was stirred at room temperature overnight, then poured in water (approx. 5.0 mL/mmol). The layers were separated, then the aqueous layer was extracted once with CH_2Cl_2 (approx. 5 mL/mmol), then the combined organic layers were washed once with distilled water (approx. 5.0 mL/mmol), dried over $MgSO_4$ and the solvent was removed in vacuo. The crude residue was purified by flash column chromatography on silica (n-hexane/EtOAc mixtures), to afford the desired ester.

2.4. Method C [4] (preparation of substrates A30-A35)



To a solution of 1,2-phenylenediamines (10.0 mmol, 1.0 equiv.) in ethanol (40.0 mL) was added ethyl glyoxalate (12.- mmol, 1.2 equiv.). The resultant reaction mixture was stirred at 25 °C overnight. Then, the mixture was filtered, washed by water and dried in vacuo.

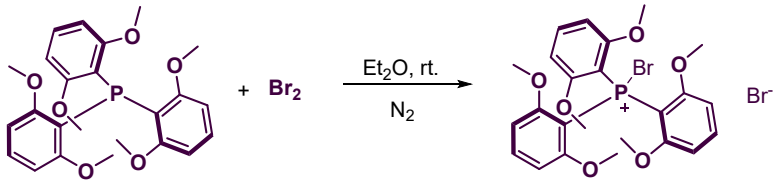
2.5. Method d [5] (preparation of substrates *Cat.* 1 – *Cat.* 4)



Ar_3P (5.0 mmol) was charged into a Schlenk flask, followed by the addition of 10.0 mL of anhydrous diethyl ether. The mixture was stirred at room temperature to suspend Ar_3P in the ether. Subsequently, I_2 (5.0 mmol) was slowly added to the aforementioned suspension. After completion of the dropwise addition, the reaction mixture was continuously stirred at room temperature until no further formation of flocculent solid was observed. Upon full completion of the reaction, the target product was obtained by filtration.

Figure S1. Color and properties of the spoke-shaped adduct

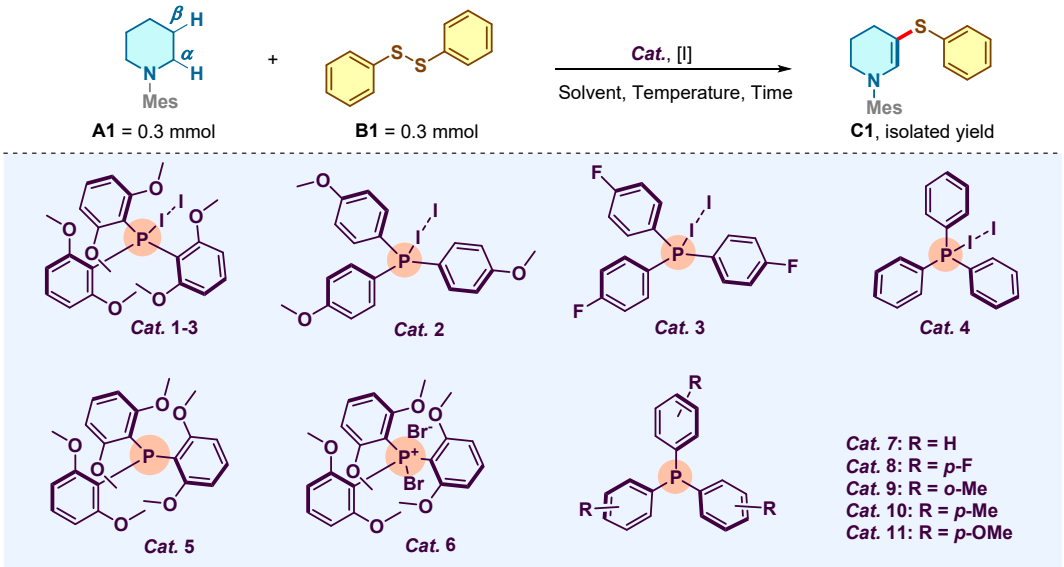
2.6. Method d [6] (preparation of substrates *Cat.* 6)



Under an N_2 atmosphere, triarylphosphine (2.21 g, 5.0 mmol) was charged into a Schlenk flask, followed by the addition of 10.0 mL of anhydrous diethyl ether. The mixture was stirred at room temperature to suspend triarylphosphine in the ether. Subsequently, Br_2 (0.79 g, 5.0 mmol) was slowly added dropwise to the aforementioned suspension. After completion of the dropwise addition, the reaction mixture was continuously stirred at room temperature until no further formation of flocculent solid was observed. Upon full completion of the reaction, the target product was obtained by filtration.

3. Optimization of reaction conditions.

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

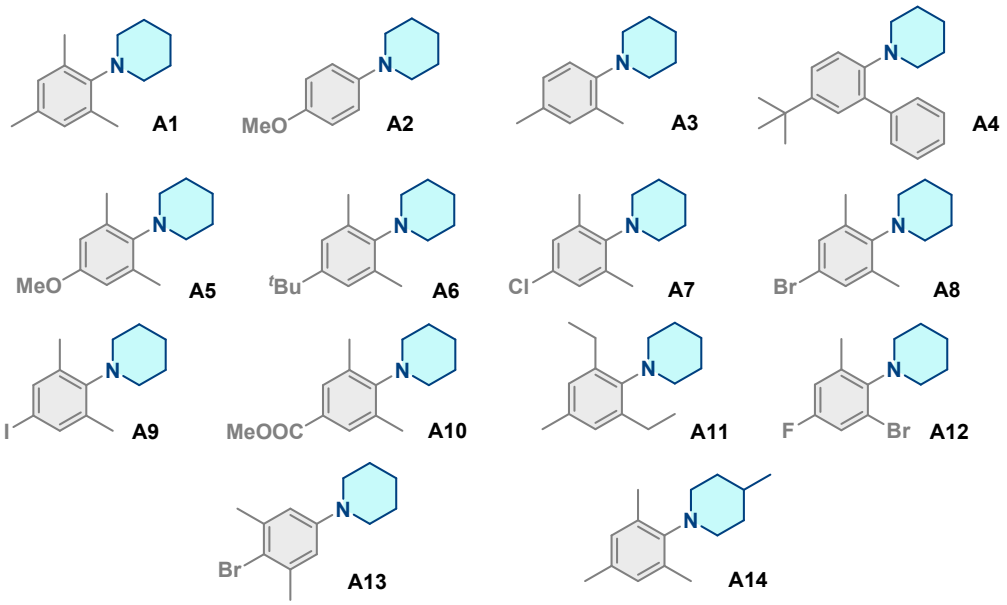


	[I]	Cat.	Sovent	Temp.	Yield (%)[b]
1.	**NaI**	***Cat.* 1-3**	1,4-Dioxane	**80** ℃	**84**
2.	NaI	***Cat.* 2**	1,4-Dioxane	80 ℃	77
3.	NaI	***Cat.* 3**	1,4-Dioxane	80 ℃	73
4.	NaI	***Cat.* 4**	1,4-Dioxane	80 ℃	21
5.	NaI	***Cat.* 5**	1,4-Dioxane	80 ℃	0
6.	NaI	***Cat.* 6**	1,4-Dioxane	80 ℃	76
7.	-	***Cat.* 6**	1,4-Dioxane	80 ℃	trace
8.	NaI	***Cat.*7-*Cat.*11**	1,4-Dioxane	80 ℃	0
9.	NaI	-	1,4-Dioxane	80 ℃	0
10.	NaI	5 mol% ***Cat.* 1-3**	1,4-Dioxane	80 ℃	67
11.	NaI	10 mol% ***Cat.* 1-3**	1,4-Dioxane	80 ℃	72
12.	NaI	15 mol% ***Cat.* 1-3**	1,4-Dioxane	80 ℃	79
13.	NaI	25 mol% ***Cat.* 1-3**	1,4-Dioxane	80 ℃	83
14.	-	***Cat.* 1-3**	1,4-Dioxane	80 ℃	62
15.	I_2	***Cat.* 1-3**	1,4-Dioxane	80 ℃	trace
16.	KI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	74
17.	NH_4I	***Cat.* 1-3**	1,4-Dioxane	80 ℃	68
18.	NaI	***Cat.* 1-3**	1,4-Dioxane	100 ℃	80
19.	NaI	***Cat.* 1-3**	1,4-Dioxane	60 ℃	58
20.	NaI	***Cat.* 1-3**	1,4-Dioxane	40 ℃	23
21.	NaI	***Cat.* 1-3**	1,3-Dioxolane	80 ℃	trace
22.	NaI	***Cat.* 1-3**	DMSO	80 ℃	72
23.	NaI	***Cat.* 1-3**	DMF	80 ℃	17
24.	NaI	***Cat.* 1-3**	Toluene	80 ℃	65
25.	NaI	***Cat.* 1-3**	DCE	80 ℃	trace
26.	NaI	***Cat.* 1-3**	CH_3CN	80 ℃	26
27.	NaI	***Cat.* 1-3**	$CHCl_3$	80 ℃	33
28.	NaI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	72 [c]
29.	NaI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	79 [d]
30.	NaI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	82 [e]
31.	NaI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	86 [f]
32.	NaI	***Cat.* 1-3**	1,4-Dioxane	80 ℃	20 [g]

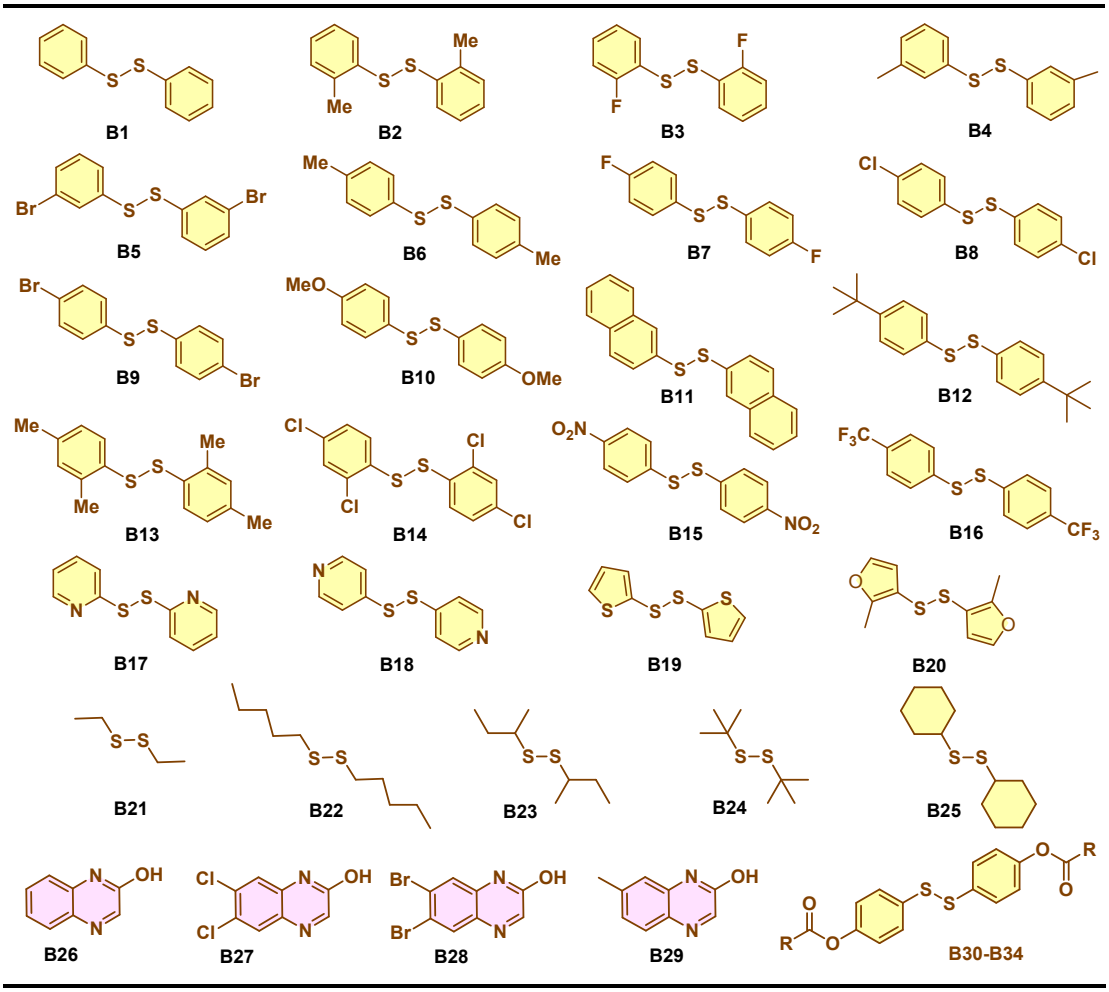
[a]Reaction conditions, unless specified otherwise: **A1** (0.3 mmol), **B1** (0.3 mmol), ***Cat.* 1-3** (0.06 mmol), NaI (0.6 mmol) and 1,4-dioxane (2.0 mL) were stirred under air atmosphere at 80 °C for 12 h. [b]Isolated yield. [c]NaI (0.3 mmol). [d]NaI (0.45 mmol). [e]NaI (0.75 mmol) DMSO = dimethyl sulfoxide. DMF = *N*,*N*-dimethylformamide dimethyl. DCE = 1,2-dichloroethane. [f]O_2 instead of air. [g]Ar instead of air.

4. Summary of substrates.

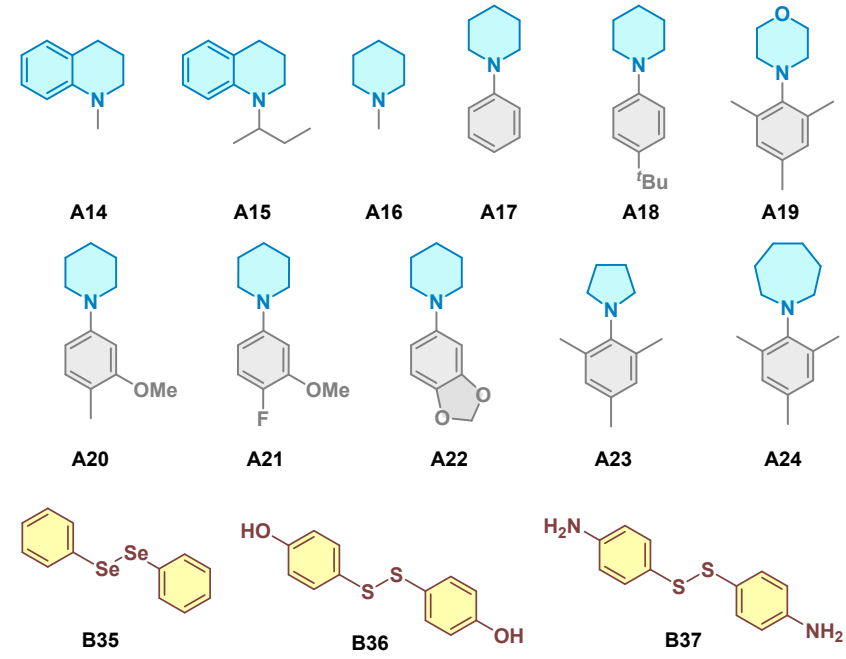
Scheme S1. Scope of *N*-substituted piperidine derivatives.



Scheme S2. Scope of sulfide compounds.

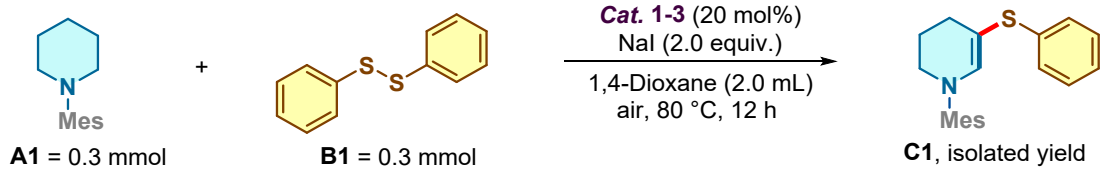


Scheme S3. Other unsuccessful substrates.



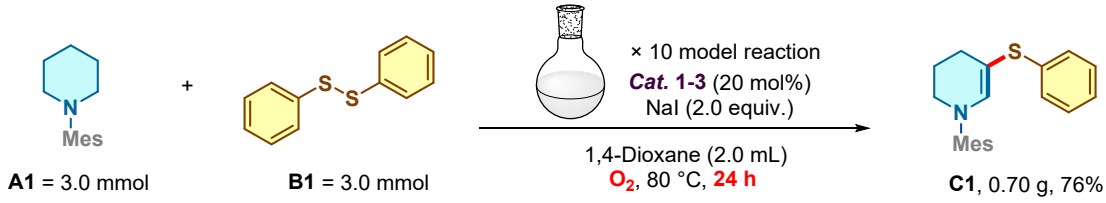
5. Typical procedure for the synthesis of C1.

Add diphenyl disulfide **B1** (65.0 mg, 0.3 mmol), ***Cat.* 1-3** (42.0 mg, 0.06 mmol), NaI (90 mg, 0.6 mmol), 1,4-dioxane (2.0 mL), and *N*-Mes piperidine **A1** (61.0 mg, 0.3 mmol) sequentially into a reaction tube. Stir the mixture at 80 °C for 12 hours under an air. Concentrate the resulting mixture by removing the solvent under vacuum, then purify the residue *via* silica gel preparative thin-layer chromatography using petroleum ether as the eluent to obtain a colorless liquid **C1** (78.0 mg, yield 84%).

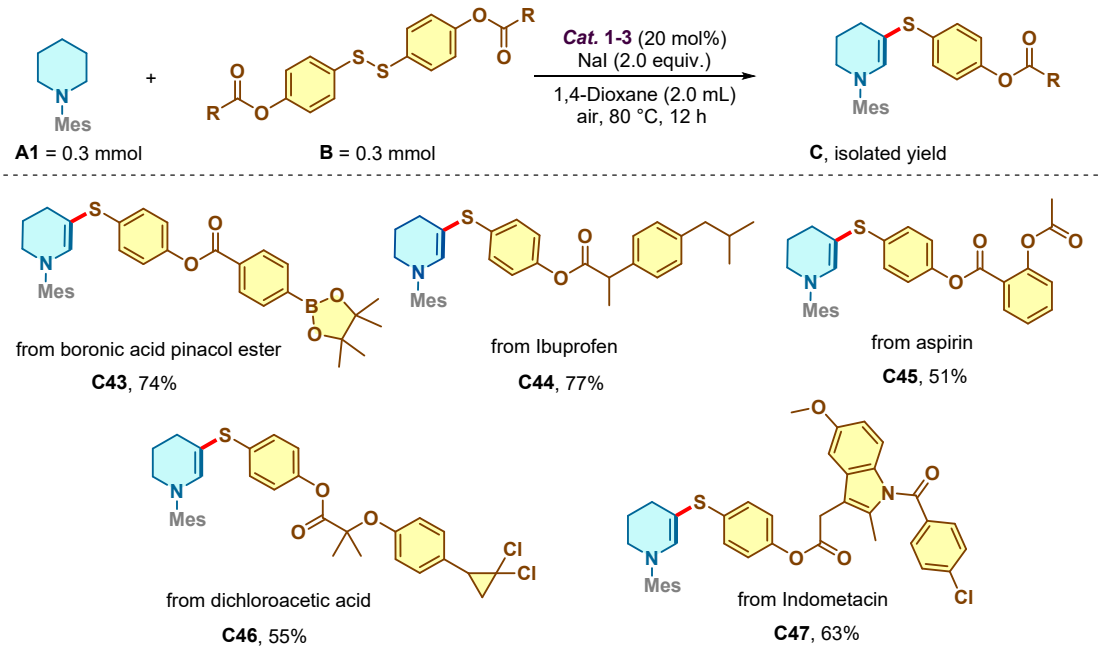


6. Synthetic application.

(1) Add diphenyl disulfide **B1** (0.65 g, 3.0 mmol), ***Cat.* 1-3** (0.42 g, 0.6 mmol), NaI (0.9 g, 6.0 mmol), 1,4-dioxane (20.0 mL), and *N*-Mes piperidine **A1** (0.61 g, 3.0 mmol) sequentially into a reaction tube. Stir the mixture at 80 °C for 24 hours under O_2 atmosphere. Concentrate the resulting mixture by removing the solvent under vacuum, then purify the residue via silica gel column chromatography using petroleum ether as the eluent to obtain a colorless liquid **C1** (0.70 g, yield 76%).



(2) Add diphenyl disulfide **B** (0.3 mmol), ***Cat.* 1-3** (42 mg, 0.06 mmol), NaI (90 mg, 0.6 mmol), 1,4-dioxane (2.0 mL), and *N*-Mes piperidine **A1** (0.3 mmol) sequentially into a reaction tube. Stir the mixture at 80 °C for 12 hours under air atmosphere. Concentrate the resulting mixture by removing the solvent under vacuum, then purify the residue via silica gel preparative thin-layer chromatography using petroleum ether as the eluent to obtain **C**.



Special Notes: No α-sulfurated product was observed in this reaction. During substrate scope exploration, we found that some substrates underwent competitive reactions between aromatic ring sulfuration and the desired β-functionalization. As presented below:

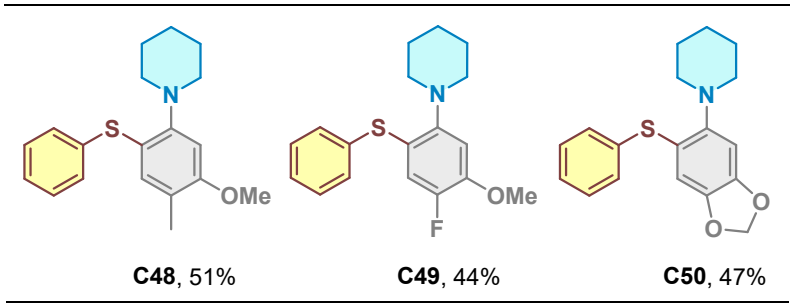
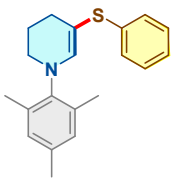


Figure S2. Aromatic ring sulfuration products

7. NMR data of the obtained compounds.

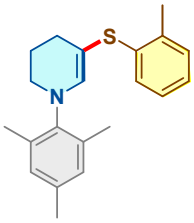
(1) 1-mesityl-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C1)



Petroleum ether were used as eluents. Colorless liquid (78 mg, 84% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 5.9 Hz, 4H), 7.12 – 7.09 (m, 1H), 6.90 (s, 2H), 6.54 (t, *J* = 1.2 Hz, 1H),

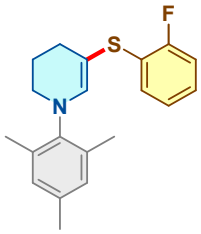
3.33 – 3.30 (m, 2H), 2.36 – 2.32 (m, 2H), 2.29 (s, 3H), 2.27 (s, 6H), 2.14 – 2.10 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.8, 142.3, 140.5, 136.5, 136.5, 129.4, 128.8, 125.7, 124.5, 90.3, 46.8, 27.2, 23.5, 21.0, 18.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}NS$: 310.1623; found: 310.1618.

(2) 1-mesityl-5-(*o*-tolylthio)-1,2,3,4-tetrahydropyridine (C2)



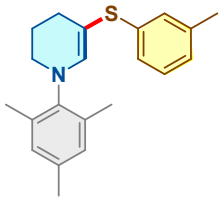
Petroleum ether were used as eluents. Colorless liquid (75mg, 78% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.57 (td, *J* = 8.1, 6.0 Hz, 1H), 7.50 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.26 – 7.18 (m, 7H), 7.12 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.06 (dt, *J* = 8.8, 2.2 Hz, 1H), 6.91 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.9, 142.3, 139.4, 136.5, 136.5, 134.8, 130.0, 129.3, 126.2, 124.5, 124.1, 89.3, 46.8, 27.2, 23.5, 20.9, 19.8, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}NS$: 324.1780; found: 324.1776.

(3) 5-((2-fluorophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C3)



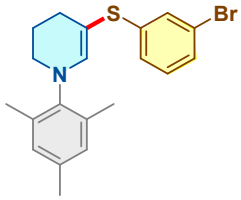
Petroleum ether were used as eluents. Colorless liquid (82 mg, 83% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 1H), 7.13 – 7.07 (m, 2H), 7.01 (ddd, *J* = 9.6, 7.6, 1.6 Hz, 1H), 6.90 (s, 2H), 6.56 (d, *J* = 1.2 Hz, 1H), 3.35 – 3.31 (m, 2H), 2.35 – 2.32 (m, 2H), 2.30 (s, 3H), 2.27 (s, 6H), 2.15 – 2.11 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4 (d, *J* = 243.1 Hz), 144.6, 142.2, 136.6, 136.4, 129.4, 127.8 (d, *J* = 16.9 Hz), 127.2 (d, *J* = 3.0 Hz), 125.8 (d, *J* = 7.2 Hz), 124.3 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 21.3 Hz), 87.6, 46.8, 27.1, 23.4, 20.9, 18.2. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.09. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}FNS$: 328.1529; found: 328.1523.

(4) 1-mesityl-5-(*m*-tolylthio)-1,2,3,4-tetrahydropyridine (C4)



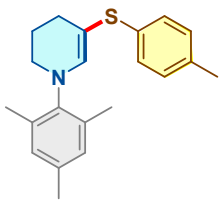
Petroleum ether were used as eluents. Colorless liquid (79 mg, 82% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 1.8 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.95 – 6.91 (m, 3H), 6.55 (s, 1H), 3.35 – 3.32 (m, 2H), 2.35 (s, 5H), 2.31 (s, 3H), 2.29 (s, 6H), 2.15 – 2.11 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.8, 142.3, 140.3, 138.4, 136.5, 129.3, 128.6, 126.4, 125.4, 122.7, 90.4, 46.8, 27.3, 23.5, 21.5, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}NS$: 324.1780; found: 324.1773.

(5) 5-((3-bromophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C5)



Petroleum ether were used as eluents. Colorless liquid (92 mg, 79% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (t, *J* = 1.8 Hz, 1H), 7.20 (ddd, *J* = 7.7, 2.0, 1.1 Hz, 1H), 7.16 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 1.2 Hz, 2H), 6.52 (t, *J* = 1.1 Hz, 1H), 3.33 – 3.31 (m, 2H), 2.33 – 2.30 (m, 2H), 2.28 (s, 3H), 2.26 (s, 6H), 2.14 – 2.10 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.7, 143.5, 142.1, 136.7, 136.5, 130.1, 129.4, 128.1, 127.4, 124.2, 123.1, 89.2, 46.8, 27.2, 23.4, 21.0, 18.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}BrNS$: 388.0729; found: 388.0721.

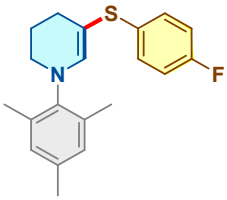
(6) 1-mesityl-5-(*p*-tolylthio)-1,2,3,4-tetrahydropyridine (C6)



Petroleum ether were used as eluents. Colorless liquid (84 mg, 87% yield); ^{1}H NMR (600 MHz,

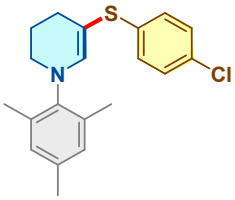
Chloroform-*d*) δ 7.20 – 7.17 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 2H), 6.53 (d, *J* = 1.2 Hz, 1H), 3.32 – 3.29 (m, 2H), 2.33 (d, *J* = 3.3 Hz, 5H), 2.29 (s, 3H), 2.27 (s, 6H), 2.10 (p, *J* = 6.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.3, 142.3, 136.6, 136.5, 136.4, 134.3, 129.6, 129.3, 126.1, 91.0, 46.8, 27.2, 23.5, 21.0, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}NS$: 324.1780; found: 324.1779.

(7) 5-((4-fluorophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C7)



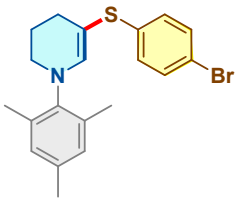
Petroleum ether were used as eluents. Colorless liquid (80 mg, 81% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 – 7.19 (m, 2H), 7.00 – 6.96 (m, 2H), 6.89 (s, 2H), 6.53 (s, 1H), 3.31 – 3.28 (m, 2H), 2.29 (d, *J* = 6.0 Hz, 5H), 2.25 (s, 6H), 2.09 (p, *J* = 6.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.93 (d, *J* = 243.3 Hz), 143.6, 142.2, 136.6, 136.4, 135.1 (d, *J* = 3.1 Hz), 129.4, 127.7 (d, *J* = 7.7 Hz), 115.8 (d, *J* = 22.0 Hz), 90.9, 46.8, 27.1, 23.5, 21.0, 18.2. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -118.98. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}FNS$: 328.1522; found: 328.1529.

(8) 5-((4-chlorophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C8)



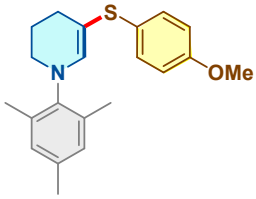
Petroleum ether were used as eluents. Colorless liquid (78 mg, 76% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.23 (m, 2H), 7.19 – 7.17 (m, 2H), 6.90 (s, 2H), 6.53 (s, 1H), 3.33 – 3.30 (m, 2H), 2.31 (t, *J* = 6.0 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 6H), 2.11 (m, *J* = 6.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.1, 142.2, 139.2, 136.6, 136.4, 130.1, 129.4, 128.8, 127.0, 89.8, 46.8, 27.1, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}ClNS$: 344.1234; found: 344.1230.

(9) 5-((4-bromophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C9)



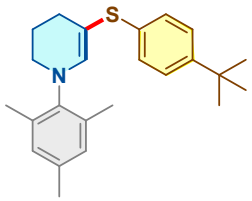
Petroleum ether were used as eluents. Colorless liquid (93 mg, 80% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.37 (m, 2H), 7.14 – 7.12 (m, 2H), 6.90 (s, 2H), 6.53 (s, 1H), 3.33 – 3.30 (m, 2H), 2.30 (d, *J* = 10.4 Hz, 5H), 2.26 (s, 6H), 2.13 – 2.09 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.1, 142.1, 139.9, 136.6, 136.4, 131.7, 129.4, 127.3, 117.9, 89.6, 46.7, 27.0, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}BrNS$: 388.0729; found: 388.0729.

(10) 1-mesityl-5-((4-methoxyphenyl)thio)-1,2,3,4-tetrahydropyridine (C10)



Petroleum ether were used as eluents. Colorless liquid (78 mg, 77% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 2H), 6.91 (s, 2H), 6.89 – 6.86 (m, 2H), 6.54 (t, *J* = 1.2 Hz, 1H), 3.81 (s, 3H), 3.31 – 3.28 (m, 2H), 2.30 (d, *J* = 6.0 Hz, 5H), 2.28 (s, 6H), 2.10 – 2.07 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7, 142.7, 142.3, 136.5, 136.4, 130.4, 129.3, 128.2, 114.5, 92.2, 55.4, 46.8, 27.1, 23.5, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}NOS$: 340.1729; found: 340.1723.

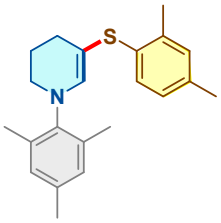
(11) 5-((4-(*tert*-butyl)phenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C11)



Petroleum ether were used as eluents. Colorless liquid (81 mg, 74% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 2H), 6.53 (s, 1H), 3.31 (t, *J* = 5.5 Hz, 2H), 2.34 (t, *J* = 6.2 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 6H), 2.13 – 2.10 (m, 2H), 1.33 (s,

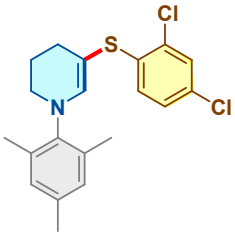
9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.6, 143.5, 142.3, 136.8, 136.5, 136.4, 129.3, 125.8, 125.5, 90.6, 46.8, 34.4, 31.5, 27.2, 23.5, 21.0, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{31}NS$: 366.2249; found: 366.2245.

(12) 5-((2,4-dimethylphenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C12)



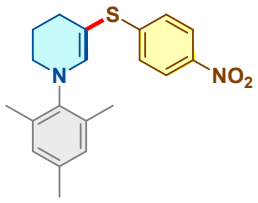
Petroleum ether were used as eluents. Colorless liquid (80 mg, 79% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.89 (s, 2H), 6.50 (d, *J* = 1.2 Hz, 1H), 3.33 – 3.30 (m, 2H), 2.31 (d, *J* = 11.6 Hz, 8H), 2.28 (s, 3H), 2.26 (s, 6H), 2.12 (q, *J* = 5.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.4, 142.4, 136.5, 136.4, 135.5, 135.0, 133.9, 131.0, 129.3, 126.9, 125.1, 90.0, 46.8, 27.2, 23.5, 20.9, 20.8, 19.8, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{27}NS$: 338.1936; found: 338.1929.

(13) 5-((2,4-dichlorophenyl)thio)-1-mesityl-1,2,3,4-tetrahydropyridine (C13)



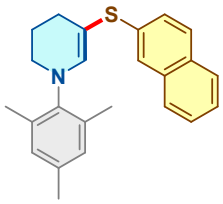
Petroleum ether were used as eluents. Colorless liquid (80 mg, 71% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 2.2 Hz, 1H), 7.20 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 2H), 6.54 (d, *J* = 1.1 Hz, 1H), 3.35 – 3.32 (m, 2H), 2.31 (t, *J* = 6.2 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 6H), 2.16 – 2.12 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.2, 142.0, 138.8, 136.7, 136.3, 130.9, 129.9, 129.4, 129.2, 127.1, 126.5, 87.6, 46.8, 26.9, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}Cl_2NS$: 378.0844; found: 378.0837.

(14) 1-mesityl-5-((4-nitrophenyl)thio)-1,2,3,4-tetrahydropyridine (C14)



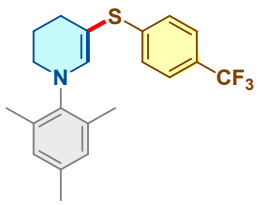
Petroleum ether were used as eluents. Yellow liquid (64 mg, 61% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 – 8.09 (m, 2H), 7.33 – 7.29 (m, 2H), 6.89 (s, 2H), 6.55 (d, *J* = 1.0 Hz, 1H), 3.37 – 3.34 (m, 2H), 2.34 (t, *J* = 6.2 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 6H), 2.15 (q, *J* = 5.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.1, 145.3, 144.7, 141.9, 136.9, 136.2, 129.4, 124.8, 124.0, 87.3, 46.7, 27.0, 23.2, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{22}N_2O_2S$: 355.1474; found: 355.1467.

(15) 1-mesityl-5-(naphthalen-2-ylthio)-1,2,3,4-tetrahydropyridine (C15)



Petroleum ether were used as eluents. Pale yellow liquid (75 mg, 70% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 – 7.79 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.44 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.41 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 6.93 (s, 2H), 6.63 (d, *J* = 1.3 Hz, 1H), 3.38 – 3.35 (m, 2H), 2.42 – 2.38 (m, 2H), 2.33 (s, 6H), 2.31 (s, 3H), 2.18 – 2.15 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.0, 142.3, 138.1, 136.5, 136.5, 134.0, 131.4, 129.4, 128.2, 127.8, 126.9, 126.3, 124.9, 124.9, 123.3, 90.3, 46.8, 27.3, 23.5, 21.0, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{25}NS$: 360.1780; found: 360.1772.

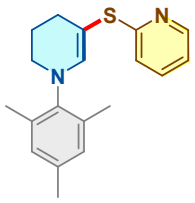
(16) 1-mesityl-5-((4-(trifluoromethyl)phenyl)thio)-1,2,3,4-tetrahydropyridine (C16)



Petroleum ether were used as eluents. Colorless liquid (64 mg, 57% yield); ^{1}H NMR (600 MHz,

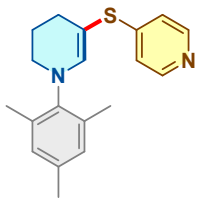
Chloroform-*d*) δ 7.52 – 7.49 (m, 2H), 7.33 – 7.30 (m, 2H), 6.89 (s, 2H), 6.54 (t, *J* = 1.2 Hz, 1H), 3.35 – 3.31 (m, 2H), 2.34 – 2.31 (m, 2H), 2.28 (s, 3H), 2.26 (s, 6H), 2.13 (q, *J* = 5.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.4, 144.8, 142.1, 136.8, 136.4, 129.4, 125.6 (q, *J* = 3.9 Hz), 126.6 – 123.6 (m), 125.1, 88.5, 46.8, 27.1, 23.4, 21.0, 18.2. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.08. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{22}F_3NS$: 378.1498; found: 378.1492.

(17) 2-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)pyridine (C17)



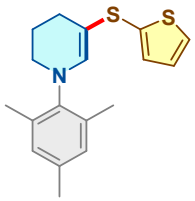
Petroleum ether and ethyl acetate (9:1) were used as eluents. Pale yellow liquid (55 mg, 60% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.40 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.4, 1.9 Hz, 1H), 7.22 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.94 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.87 (d, *J* = 1.2 Hz, 2H), 6.55 (d, *J* = 1.2 Hz, 1H), 3.34 – 3.30 (m, 2H), 2.41 – 2.38 (m, 2H), 2.26 (s, 3H), 2.24 (s, 6H), 2.15 – 2.11 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.8, 149.6, 144.6, 142.1, 136.6, 136.4, 136.4, 129.4, 119.1, 118.8, 89.0, 46.7, 27.4, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{22}N_2S$: 311.1576; found: 311.1570.

(18) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)pyridine (C18)



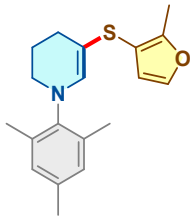
Petroleum ether and ethyl acetate (9:1) were used as eluents. Pale yellow liquid (45 mg, 49% yield); m.p. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.38 – 8.34 (m, 2H), 7.15 – 7.10 (m, 2H), 6.88 (s, 2H), 6.51 (d, *J* = 1.1 Hz, 1H), 3.35 – 3.31 (m, 2H), 2.32 (t, *J* = 6.0 Hz, 2H), 2.27 (s, 3H), 2.24 (s, 6H), 2.16 – 2.12 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 153.3, 149.1, 145.3, 141.9, 136.8, 136.3, 129.4, 119.9, 86.7, 46.7, 27.1, 23.2, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{22}N_2S$: 311.1576; found: 311.1570.

(19) 1-mesityl-5-(thiophen-2-ylthio)-1,2,3,4-tetrahydropyridine (C19)



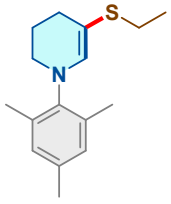
Petroleum ether were used as eluents. Pale yellow liquid (69 mg, 73% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 5.2, 1.3 Hz, 1H), 6.98 (dd, *J* = 3.4, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.91 (s, 2H), 6.58 (s, 1H), 3.27 – 3.24 (m, 2H), 2.39 (td, *J* = 6.2, 1.2 Hz, 2H), 2.30 (s, 3H), 2.26 (s, 6H), 2.08 – 2.04 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.3, 142.2, 141.4, 136.5, 136.4, 129.3, 127.5, 127.4, 126.1, 94.5, 46.7, 27.0, 23.3, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{21}NS_2$: 316.1188; found: 316.1184.

(20) 1-mesityl-5-((2-methylfuran-3-yl)thio)-1,2,3,4-tetrahydropyridine (C20)



Petroleum ether were used as eluents. Yellow liquid (67 mg, 72% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 2.0 Hz, 1H), 6.89 (s, 2H), 6.47 (d, *J* = 1.2 Hz, 1H), 6.34 (d, *J* = 1.9 Hz, 1H), 3.22 – 3.19 (m, 2H), 2.36 (s, 3H), 2.29 (s, 3H), 2.27 – 2.24 (m, 2H), 2.23 (s, 6H), 2.03 – 1.99 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.2, 142.5, 140.0, 139.8, 136.6, 136.2, 129.3, 114.2, 113.0, 94.7, 46.7, 27.1, 23.4, 20.9, 18.2, 11.9. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}NOS$: 314.1573; found: 314.1569.

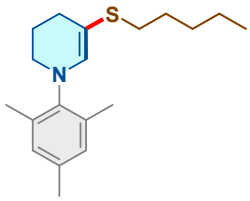
(21) 5-(ethylthio)-1-mesityl-1,2,3,4-tetrahydropyridine (C21)



Petroleum ether were used as eluents. colorless liquid (62 mg, 80% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.87 – 6.85 (m, 2H), 6.34 (d, *J* = 1.3 Hz, 1H), 3.22 – 3.20 (m, 2H), 2.49 (q, *J* = 7.3 Hz, 2H), 2.32 (td, *J* = 6.2, 1.2 Hz, 2H), 2.26 (s, 3H), 2.19 (s, 6H), 2.05 – 2.02 (m, 2H), 1.20 (t, *J* =

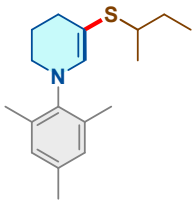
7.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.6, 141.1, 136.6, 136.2, 129.3, 92.6, 46.7, 27.7, 27.7, 23.4, 20.9, 18.2, 14.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{23}NS$: 262.1623; found: 262.1620.

(22) 1-mesityl-5-(pentylthio)-1,2,3,4-tetrahydropyridine (C22)



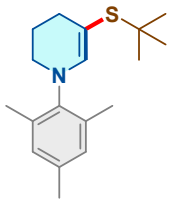
Petroleum ether were used as eluents. Colorless liquid (75 mg, 83% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 6.34 (s, 1H), 3.22 – 3.19 (m, 2H), 2.50 – 2.47 (m, 2H), 2.35 – 2.32 (m, 2H), 2.27 (s, 3H), 2.20 (s, 6H), 2.06 – 2.02 (m, 2H), 1.57 (t, *J* = 7.5 Hz, 2H), 1.38 – 1.31 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.6, 140.8, 136.6, 136.1, 129.2, 93.0, 46.7, 33.8, 30.8, 29.0, 27.6, 23.4, 22.5, 20.9, 18.2, 14.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{29}NS$: 304.2093; found: 304.2090.

(23) 5-(sec-butylthio)-1-mesityl-1,2,3,4-tetrahydropyridine (C23)



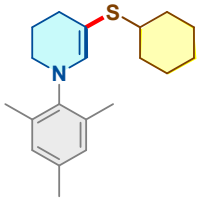
Petroleum ether were used as eluents. Colorless liquid (68 mg, 78% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.87 – 6.86 (m, 2H), 6.32 (t, *J* = 1.2 Hz, 1H), 3.22 – 3.20 (m, 2H), 2.72 (td, *J* = 7.0, 6.0 Hz, 1H), 2.35 – 2.32 (m, 2H), 2.26 (s, 3H), 2.20 (d, *J* = 2.6 Hz, 6H), 2.05 – 2.01 (m, 2H), 1.63 (ddd, *J* = 13.5, 7.4, 6.0 Hz, 1H), 1.46 – 1.42 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.5, 143.2, 140.6, 139.6, 138.1, 137.4, 137.4, 137.1, 135.5, 132.8, 132.2, 131.6, 130.4, 130.2, 130.2, 130.1, 129.1, 128.8, 128.6, 128.4, 127.9, 127.6, 125.3, 121.5, 116.8, 21.4, 21.1, 20.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{27}NS$: 290.1936; found: 290.1933.

(24) 5-(*tert*-butylthio)-1-mesityl-1,2,3,4-tetrahydropyridine (C24)



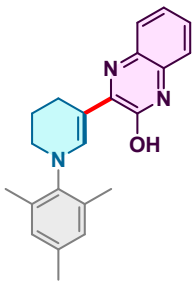
Petroleum ether were used as eluents. Colorless liquid (18 mg, 21% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.59 (m, 3H), 7.56 – 7.53 (m, 2H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.28 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.05 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.94 (s, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.6, 141.9, 136.6, 136.6, 136.1, 129.2, 92.6, 46.7, 43.0, 29.2, 29.0, 23.3, 20.9, 20.2, 18.1, 18.1, 11.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{27}NS$: 290.1936; found: 290.1932.

(25) 5-(cyclohexylthio)-1-mesityl-1,2,3,4-tetrahydropyridine (C25)



Petroleum ether were used as eluents. Colorless liquid (37 mg, 40% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.87 (s, 2H), 6.34 (d, *J* = 1.2 Hz, 1H), 3.24 – 3.21 (m, 2H), 2.44 – 2.40 (m, 2H), 2.26 (s, 3H), 2.21 (s, 6H), 2.04 – 2.00 (m, 2H), 1.27 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.1, 142.5, 136.7, 136.3, 129.2, 92.5, 46.6, 45.4, 31.3, 31.1, 24.5, 23.2, 20.9, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{29}NS$: 316.2093; found: 316.2088.

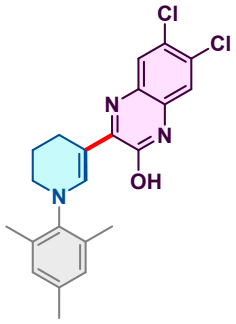
(26) 3-(1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)quinoxalin-2-ol (C26)



Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (88 mg, 85% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.58 (s, 1H), 8.95 (s, 1H), 7.69 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.23 (ddd, *J* = 8.3, 7.3, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.4, 7.3, 1.4 Hz, 1H), 6.97 (d, *J* = 6.3 Hz, 3H), 3.47 –

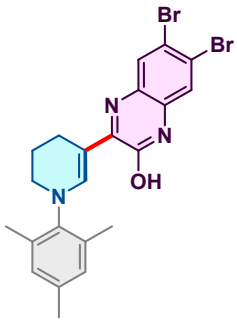
3.42 (m, 2H), 2.87 (t, J = 6.3 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 6H), 2.20 (q, J = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9, 152.3, 146.6, 142.6, 137.0, 135.7, 134.6, 129.4, 128.6, 127.0, 125.7, 123.7, 114.5, 106.0, 47.7, 22.1, 21.6, 21.0, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{23}N_3O$: 346.1913; found: 346.1909.

(27) 6,7-dichloro-3-(1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)quinoxalin-2-ol (C27)



Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (91 mg, 74% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.12 (s, 1H), 8.92 (s, 1H), 7.71 (s, 1H), 7.02 (s, 1H), 6.95 (s, 2H), 3.46 – 3.42 (m, 2H), 2.79 (t, J = 6.3 Hz, 2H), 2.30 (s, 3H), 2.28 (s, 6H), 2.19 – 2.16 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8, 152.4, 147.8, 142.3, 137.3, 135.3, 134.1, 129.6, 128.6, 127.6, 127.6, 127.2, 115.6, 106.3, 47.9, 21.9, 21.4, 21.0, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{21}Cl_2N_3O$: 414.1134; found: 414.1129.

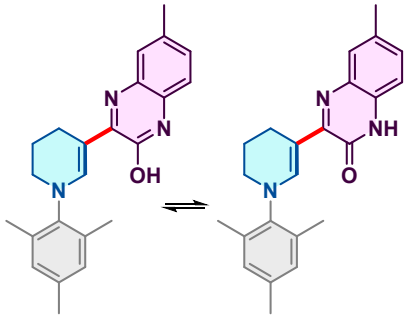
(28) 6,7-dibromo-3-(1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)quinoxalin-2-ol (C28)



Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (106 mg, 71% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.75 (s, 1H), 8.89 (s, 1H), 7.88 (s, 1H), 7.20 (s, 1H), 6.93 (s, 2H), 3.44 – 3.41 (m, 2H), 2.78 (t, J = 6.3 Hz, 2H), 2.29 (s, 3H), 2.27 (s, 6H), 2.18 – 2.14 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8, 152.6, 147.9, 142.3, 137.3, 135.3, 134.8, 130.8, 129.7, 128.3, 120.2, 118.7, 118.6, 106.5, 48.0, 21.9, 21.5, 21.1, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$

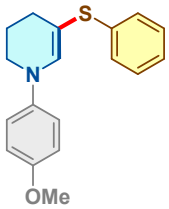
Calcd. for $C_{22}H_{21}Br_2N_3O$: 502.0124; found: 502.0116.

(29) 3-(1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)-6-methylquinoxalin-2-ol (C29)



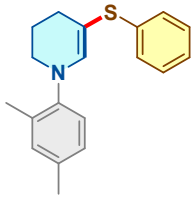
Petroleum ether and ethyl acetate (5:1) were used as eluents. Yellow solid (92 mg, 86% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.15 (s, 1H), 11.71 (s, 2H), 8.93 (s, 2H), 8.90 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 2H), 7.02 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.97 – 6.91 (m, 10H), 6.86 (d, *J* = 8.1 Hz, 3H), 6.76 (s, 1H), 3.43 (t, *J* = 5.5 Hz, 7H), 2.85 (t, *J* = 6.3 Hz, 7H), 2.41 (s, 8H), 2.33 (d, *J* = 2.5 Hz, 11H), 2.29 (d, *J* = 6.7 Hz, 25H), 2.18 (p, *J* = 6.0 Hz, 8H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.3, 156.9, 152.2, 151.5, 146.3, 145.9, 142.7, 142.6, 136.8, 136.8, 136.2, 135.8, 135.7, 134.4, 133.2, 132.6, 129.4, 128.5, 127.0, 126.8, 126.7, 126.3, 125.1, 114.7, 114.2, 106.0, 105.8, 47.7, 47.6, 22.1, 22.1, 21.6, 21.3, 21.1, 21.0, 18.2, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{25}N_3O$: 360.2070; found: 360.2066.

(30) 1-(4-methoxyphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C30)



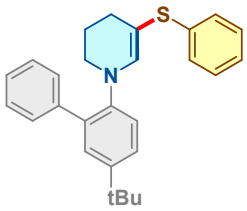
Petroleum ether were used as eluents. Pale yellow liquid (29 mg, 33% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 4H), 7.13 – 7.10 (m, 1H), 7.08 (d, *J* = 1.3 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.89 – 6.85 (m, 2H), 3.79 (s, 3H), 3.56 – 3.53 (m, 2H), 2.30 – 2.27 (m, 2H), 2.09 – 2.05 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.5, 140.4, 139.4, 139.1, 128.9, 126.3, 124.9, 117.9, 114.7, 97.9, 55.7, 45.8, 27.1, 23.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}NOS$: 298.1260; found: 298.1254.

(31) 1-(2,4-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C31)



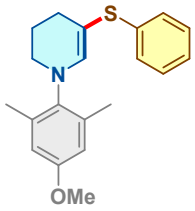
Petroleum ether were used as eluents. Colorless liquid (34 mg, 39% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 5.8 Hz, 4H), 7.12 (dq, *J* = 8.5, 2.6 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 1.3 Hz, 1H), 3.41 – 3.38 (m, 2H), 2.31 (d, *J* = 7.7 Hz, 8H), 2.08 – 2.03 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.5, 143.2, 139.6, 134.8, 132.8, 132.1, 128.8, 127.4, 126.1, 124.7, 124.6, 95.5, 48.3, 27.2, 23.5, 20.9, 18.4. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{21}NS$: 296.1467; found: 296.1460.

(32) 1-(5-(*tert*-butyl)-[1,1'-biphenyl]-2-yl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C32)



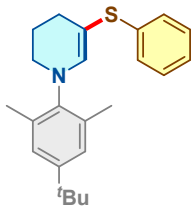
Petroleum ether were used as eluents. Pale yellow liquid (48 mg, 40% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 4H), 7.41 – 7.37 (m, 3H), 7.31 – 7.28 (m, 2H), 7.21 – 7.18 (m, 2H), 7.14 (t, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 1.2 Hz, 1H), 3.15 – 3.12 (m, 2H), 2.20 – 2.17 (m, 2H), 1.82 (q, *J* = 5.8 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.5, 143.0, 142.4, 140.8, 139.3, 135.1, 129.1, 128.7, 128.7, 128.6, 127.0, 126.3, 125.3, 124.7, 123.7, 96.6, 48.0, 34.5, 31.5, 27.2, 23.0. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{29}NS$: 400.2093; found: 400.2092.

(33) 1-(4-(*tert*-butyl)-2,6-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C33)



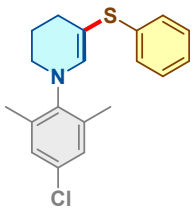
Petroleum ether were used as eluents. Pale yellow liquid (78 mg, 80% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.0 Hz, 4H), 7.08 (tt, *J* = 6.3, 2.3 Hz, 1H), 6.60 (s, 2H), 6.51 (d, *J* = 1.2 Hz, 1H), 3.76 (s, 3H), 3.28 (dd, *J* = 6.5, 4.5 Hz, 2H), 2.32 – 2.29 (m, 2H), 2.26 (s, 6H), 2.10 (q, *J* = 5.8 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.8, 144.0, 140.5, 138.1, 138.1, 128.7, 125.7, 124.4, 113.5, 90.1, 55.3, 46.9, 27.1, 23.5, 18.5. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{23}NOS$: 326.1573; found: 326.1568.

(34) 1-(4-(*tert*-butyl)-2,6-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C34)



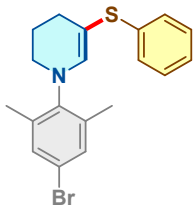
Petroleum ether were used as eluents. Pale yellow liquid (96 mg, 91% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 4H), 7.13 – 7.10 (m, 3H), 6.58 (s, 1H), 3.36 – 3.33 (m, 2H), 2.37 – 2.34 (m, 2H), 2.32 (s, 6H), 2.15 – 2.11 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.6, 143.8, 142.2, 140.5, 136.0, 128.7, 125.8, 125.6, 124.4, 90.2, 46.7, 34.4, 31.5, 27.2, 23.5, 18.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{29}NS$: 352.2903; found: 352.2087.

(35) 1-(4-chloro-2,6-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C35)



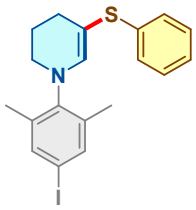
Petroleum ether were used as eluents. Red solid (69 mg, 70% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 4H), 7.10 (tt, *J* = 7.0, 1.6 Hz, 1H), 7.06 (s, 2H), 6.48 (d, *J* = 1.2 Hz, 1H), 3.30 – 3.27 (m, 2H), 2.34 – 2.31 (m, 2H), 2.27 (s, 6H), 2.13 – 2.08 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.3, 142.9, 140.0, 138.6, 131.9, 128.8, 128.5, 125.8, 124.6, 91.8, 46.7, 27.1, 23.4, 18.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}ClNS$: 330.1077; found: 330.1075.

(36) 1-(4-bromo-2,6-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C36)



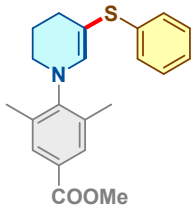
Petroleum ether were used as eluents. Light black solid (80 mg, 72% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.91 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.55 – 7.48 (m, 7H), 7.17 – 7.12 (m, 2H), 6.75 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.8, 142.7, 139.9, 138.9, 131.4, 128.7, 125.8, 124.6, 120.0, 91.9, 46.6, 27.0, 23.4, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}BrNS$: 374.0572; found: 374.0570.

(37) 1-(4-iodo-2,6-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C37)



Petroleum ether were used as eluents. Black solid (87 mg, 69% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (s, 2H), 7.27 – 7.24 (m, 4H), 7.12 – 7.08 (m, 1H), 6.47 (d, *J* = 1.4 Hz, 1H), 3.28 (t, *J* = 5.5 Hz, 2H), 2.31 (t, *J* = 6.2 Hz, 2H), 2.24 (s, 6H), 2.09 (q, *J* = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.6, 142.7, 139.9, 139.1, 137.6, 128.8, 125.9, 124.7, 92.0, 46.7, 27.1, 23.4, 18.0. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}INS$: 422.0433; found: 422.0429.

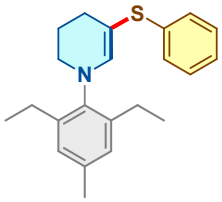
(38) methyl 3,5-dimethyl-4-(5-(phenylthio)-3,4-dihydropyridin-1(2H)-yl)benzoate (C38)



Petroleum ether were used as eluents. Pale yellow liquid (48 mg, 46% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (s, 2H), 7.25 – 7.21 (m, 4H), 7.08 (tt, *J* = 7.0, 1.6 Hz, 1H), 6.49 (d, *J* = 1.3

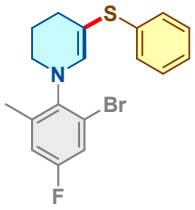
Hz, 1H), 3.88 (s, 3H), 3.30 (dd, *J* = 6.6, 4.4 Hz, 2H), 2.31 (s, 8H), 2.09 (p, *J* = 6.2 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.0, 148.9, 142.4, 139.8, 136.7, 130.1, 128.8, 128.1, 126.0, 124.7, 92.7, 52.2, 46.7, 27.2, 23.5, 18.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{23}NO_2S$: 354.1522; found: 354.1515.

(39) 1-(2,6-diethyl-4-methylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C39)



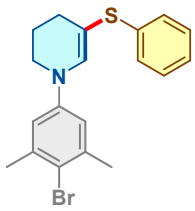
Petroleum ether were used as eluents. Pale yellow liquid (84 mg, 83% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 4.9 Hz, 4H), 7.13 (tt, *J* = 5.1, 3.6 Hz, 1H), 6.97 (s, 2H), 6.59 (s, 1H), 3.37 – 3.35 (m, 2H), 2.65 (ddd, *J* = 29.1, 14.5, 7.2 Hz, 4H), 2.37 (d, *J* = 5.8 Hz, 5H), 2.15 (q, *J* = 5.8 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.6, 142.8, 141.3, 140.5, 137.1, 128.7, 127.6, 125.7, 124.4, 89.8, 48.1, 27.1, 24.5, 23.4, 21.2, 15.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{27}NS$: 338.1936; found: 338.1930.

(40) 1-(2-bromo-4-fluoro-6-methylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C40)



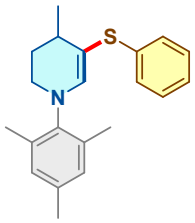
Petroleum ether were used as eluents. Pale yellow liquid (41 mg, 37% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 4H), 7.21 – 7.18 (m, 1H), 7.12 – 7.08 (m, 1H), 6.91 (ddd, *J* = 8.7, 2.9, 0.8 Hz, 1H), 6.47 (t, *J* = 1.3 Hz, 1H), 3.46 – 3.42 (m, 1H), 3.23 (ddd, *J* = 11.2, 7.4, 3.2 Hz, 1H), 2.34 (s, 3H), 2.32 – 2.30 (m, 2H), 2.18 (dddd, *J* = 13.1, 6.4, 3.6, 1.3 Hz, 1H), 2.10 – 2.05 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.5 (d, *J* = 250.3 Hz), 142.4, 140.9 (d, *J* = 8.7 Hz), 140.8 (d, *J* = 3.6 Hz), 128.8, 126.1, 125.1 (d, *J* = 10.6 Hz), 124.7, 118.2 (d, *J* = 25.1 Hz), 116.9 (d, *J* = 21.6 Hz), 93.1, 46.7, 27.0, 23.2, 19.1. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.38. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{17}BrFNS$: 378.0321; found: 378.0320.

(41) 1-(4-bromo-3,5-dimethylphenyl)-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C41)



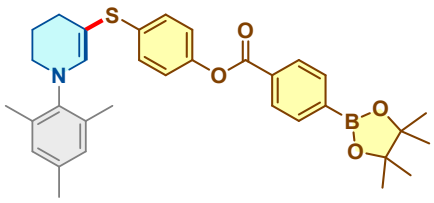
Petroleum ether were used as eluents. Pale yellow liquid (34 mg, 31% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.91 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.55 – 7.48 (m, 7H), 7.17 – 7.12 (m, 2H), 6.75 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6, 145.6, 143.5, 141.1, 138.7, 136.7, 135.7, 134.1, 134.0, 133.7, 131.4, 131.0, 130.7, 130.0, 129.6, 129.0, 128.4, 127.8, 117.9, 117.5. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{20}BrNS$: 374.0572; found: 374.0569.

(42) 1-mesityl-4-methyl-5-(phenylthio)-1,2,3,4-tetrahydropyridine (C42)



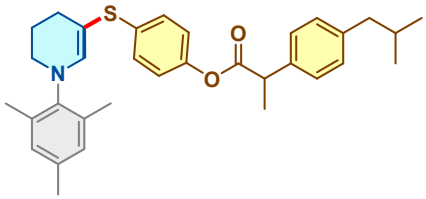
Petroleum ether were used as eluents. Pale yellow liquid (82 mg, 85% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 4H), 7.07 (tt, *J* = 6.2, 2.2 Hz, 1H), 6.90 – 6.86 (m, 2H), 6.50 (s, 1H), 3.42 (ddd, *J* = 12.4, 10.5, 3.3 Hz, 1H), 3.20 (dt, *J* = 12.4, 4.7 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.27 (d, *J* = 3.2 Hz, 6H), 2.22 (s, 3H), 2.16 (ddt, *J* = 7.9, 3.7, 2.6 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.0, 142.2, 141.5, 136.8, 136.6, 136.2, 129.4, 129.3, 128.7, 125.7, 124.4, 95.9, 43.5, 30.6, 30.5, 21.4, 21.0, 18.2, 18.1. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{21}H_{25}NS$: 324.1780; found: 324.1774.

(43) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (C43)



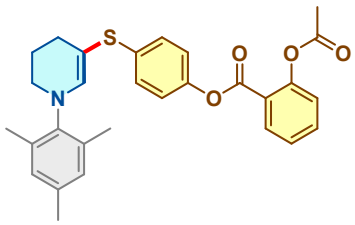
Petroleum ether were used as eluents. Pale yellow oil liquid (123 mg, 74% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 – 8.18 (m, 2H), 8.00 – 7.95 (m, 2H), 7.35 – 7.30 (m, 2H), 7.19 – 7.14 (m, 2H), 6.90 (s, 2H), 6.57 (d, *J* = 1.2 Hz, 1H), 3.38 – 3.27 (m, 2H), 2.36 (t, *J* = 6.2 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 6H), 2.12 (p, *J* = 6.0 Hz, 2H), 1.40 (s, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.3, 148.2, 143.8, 142.2, 137.8, 136.5, 136.4, 134.8, 131.8, 129.3, 129.2, 126.7, 122.0, 90.4, 84.3, 46.7, 27.1, 24.9, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{38}BNO_4S$: 556.2682; found: 556.2682.

(44) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)phenyl 2-(4-isobutylphenyl)propanoate (C44)



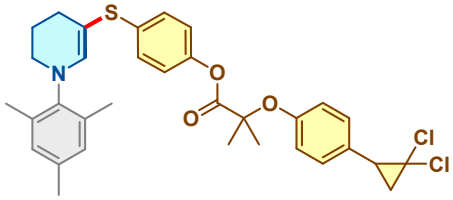
Petroleum ether were used as eluents. Pale yellow liquid (119 mg, 77% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.35 (m, 2H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.00 – 6.96 (m, 2H), 6.93 (s, 2H), 6.57 (d, *J* = 1.2 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 1H), 3.33 (dd, *J* = 6.6, 4.4 Hz, 2H), 2.54 (d, *J* = 7.2 Hz, 2H), 2.33 (d, *J* = 11.9 Hz, 5H), 2.29 (s, 6H), 2.12 (p, *J* = 6.1 Hz, 2H), 1.94 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.3, 148.2, 143.7, 142.2, 140.8, 137.5, 137.3, 136.4, 136.3, 129.5, 129.3, 127.2, 126.6, 121.7, 90.5, 46.7, 45.3, 45.1, 30.2, 27.0, 23.4, 22.4, 20.9, 18.6, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{39}NO_2S$: 514.2774; found: 514.2767.

(45) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)phenyl 2-acetoxybenzoate (C45)



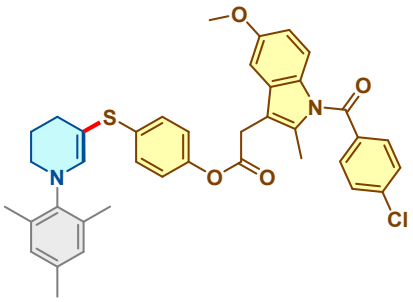
Petroleum ether were used as eluents. Pale yellow liquid (75 mg, 51% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.65 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.19 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.91 (d, *J* = 1.3 Hz, 2H), 6.56 (d, *J* = 1.2 Hz, 1H), 3.32 (dd, *J* = 6.4, 4.5 Hz, 2H), 2.35 (d, *J* = 9.7 Hz, 5H), 2.30 (s, 3H), 2.28 (s, 6H), 2.13 (dt, *J* = 12.2, 6.1 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.7, 163.1, 151.2, 147.8, 143.9, 142.1, 138.2, 136.5, 136.4, 134.6, 132.2, 129.3, 126.7, 126.2, 124.0, 122.6, 121.9, 90.1, 46.7, 27.1, 23.4, 21.1, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{29}NO_4S$: 488.1890; found: 488.1885.

(46) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)phenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (C46)



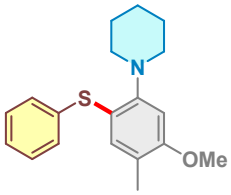
Petroleum ether were used as eluents. Pale yellow liquid (98 mg, 55% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 7.21 – 7.18 (m, 2H), 6.99 – 6.96 (m, 2H), 6.91 (s, 2H), 6.91 – 6.88 (m, 2H), 6.54 (s, 1H), 3.31 (dd, *J* = 6.5, 4.5 Hz, 2H), 2.89 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.31 (d, *J* = 11.1 Hz, 5H), 2.27 (s, 6H), 2.11 (p, *J* = 6.0 Hz, 2H), 1.98 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.85 – 1.82 (m, 1H), 1.79 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 155.1, 147.7, 143.9, 142.1, 138.1, 136.5, 136.4, 129.8, 129.3, 128.4, 126.6, 121.6, 118.5, 90.1, 79.4, 60.9, 46.7, 34.8, 27.0, 25.8, 25.6, 23.4, 20.9, 18.2. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{33}H_{35}Cl_2NO_3S$: 596.1787; found: 596.1782.

(47) 4-((1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)thio)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate (C47)



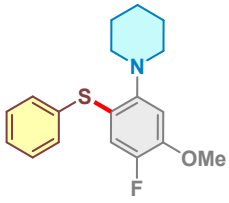
Petroleum ether were used as eluents. Pale yellow liquid (125 mg, 63% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 – 7.66 (m, 2H), 7.51 – 7.46 (m, 2H), 7.25 – 7.20 (m, 2H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.89 (s, 2H), 6.71 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.52 (d, *J* = 1.2 Hz, 1H), 3.90 (s, 2H), 3.85 (s, 3H), 3.29 (dd, *J* = 6.4, 4.6 Hz, 2H), 2.46 (s, 3H), 2.28 (d, *J* = 8.9 Hz, 5H), 2.24 (s, 6H), 2.09 (m, *J* = 5.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.5, 168.4, 156.2, 148.0, 143.9, 142.2, 139.4, 138.0, 136.5, 136.4, 136.2, 133.9, 131.3, 130.9, 130.6, 129.3, 129.2, 126.7, 121.7, 115.1, 112.1, 111.9, 101.3, 90.2, 55.8, 46.7, 30.6, 27.1, 23.4, 20.9, 18.2, 13.5. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{39}H_{37}ClN_2O_4S$: 665.2235; found: 665.2228.

(48) 1-(5-methoxy-4-methyl-2-(phenylthio)phenyl)piperidine (C48)



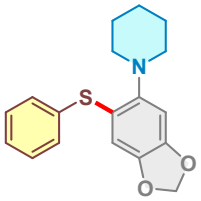
Petroleum ether were used as eluents. Colorless liquid (48 mg, 51% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 5.4 Hz, 4H), 7.17 (ddd, *J* = 8.5, 5.8, 2.9 Hz, 1H), 7.02 (d, *J* = 0.9 Hz, 1H), 6.62 (s, 1H), 3.85 (s, 3H), 2.98 (t, *J* = 5.2 Hz, 4H), 2.11 (s, 3H), 1.63 (q, *J* = 5.6 Hz, 4H), 1.52 (p, *J* = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1, 153.4, 137.7, 135.4, 129.5, 128.8, 125.8, 121.8, 119.9, 103.0, 55.5, 53.7, 26.4, 24.4, 15.6. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}NOS$: 314.1564; found: 314.1567.

(49) 1-(4-fluoro-5-methoxy-2-(phenylthio)phenyl)piperidine (C49)



Petroleum ether were used as eluents. Pale yellow liquid (42 mg, 44% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 11.9 Hz, 1H), 3.87 (s, 3H), 2.91 (t, *J* = 5.3 Hz, 4H), 1.68 (dt, *J* = 10.6, 5.2 Hz, 4H), 1.54 (p, *J* = 5.9, 5.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.8, 148.7 (d, *J* = 2.8 Hz), 148.2, 146.4 (d, *J* = 11.6 Hz), 134.7, 132.5, 129.3, 127.6, 124.7 (d, *J* = 6.0 Hz), 117.4 (d, *J* = 21.1 Hz), 106.4, 56.7, 53.8, 26.4, 24.3. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -140.44. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{20}FNOS$: 318.1312; found: 318.1317.

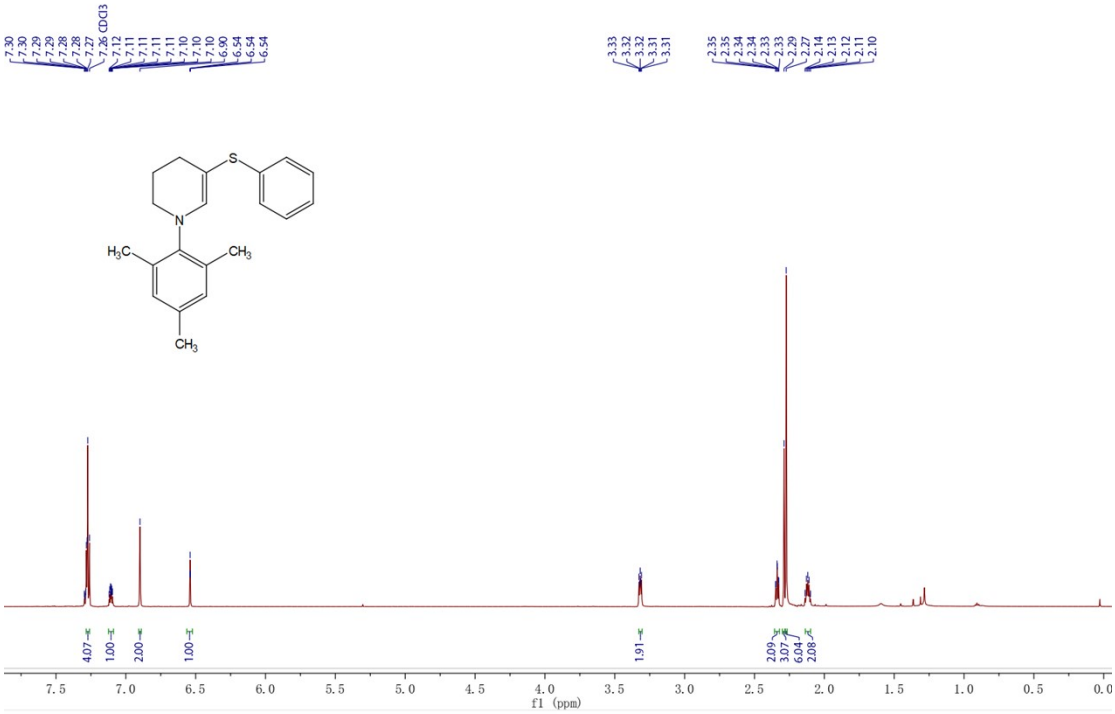
(50) 1-(6-(phenylthio)benzo[d][1,3]dioxol-5-yl)piperidine (C50)



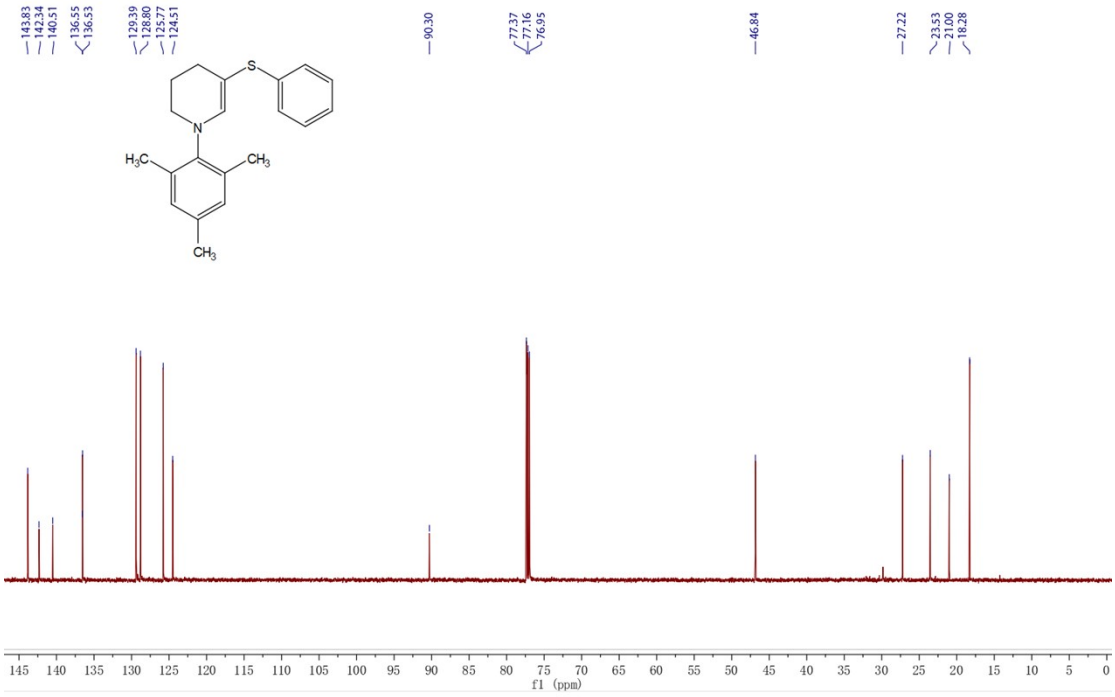
Petroleum ether were used as eluents. Colorless liquid (44 mg, 47% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.40 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 6.73 (s, 1H), 6.51 (s, 1H), 5.90 (s, 2H), 2.88 (t, *J* = 5.2 Hz, 3H), 1.70 – 1.68 (m, 3H), 1.54 (p, *J* = 9.2, 7.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.3, 147.0, 143.9, 135.7, 132.2, 129.2, 127.2, 125.0, 110.1, 102.2, 101.3, 54.1, 26.5, 24.3. HRMS (ESI-Orbitrap) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}NO_2S$: 314.1209; found: 314.1203.

8. NMR spectra of the obtained compounds.

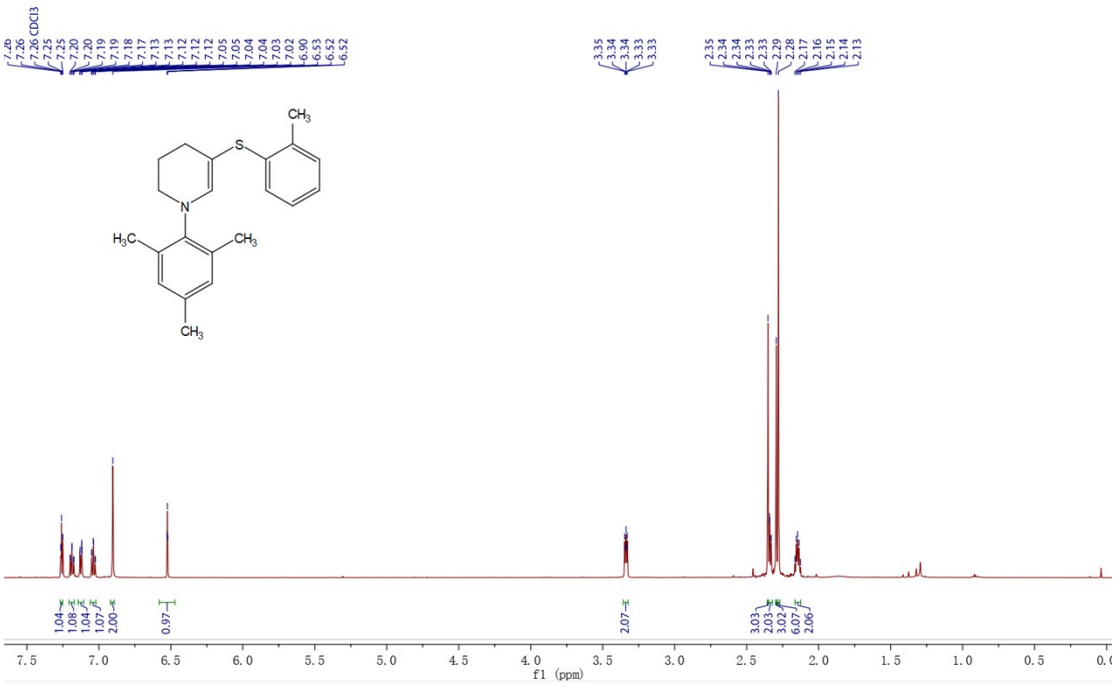
(1) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C1



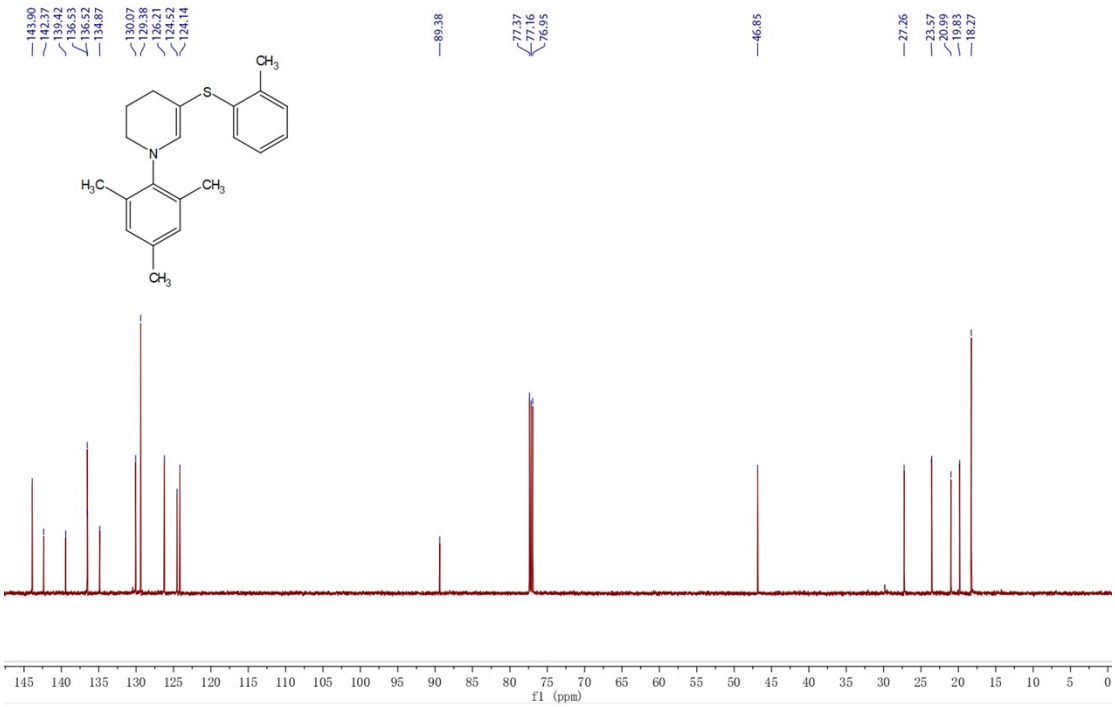
(2) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C1



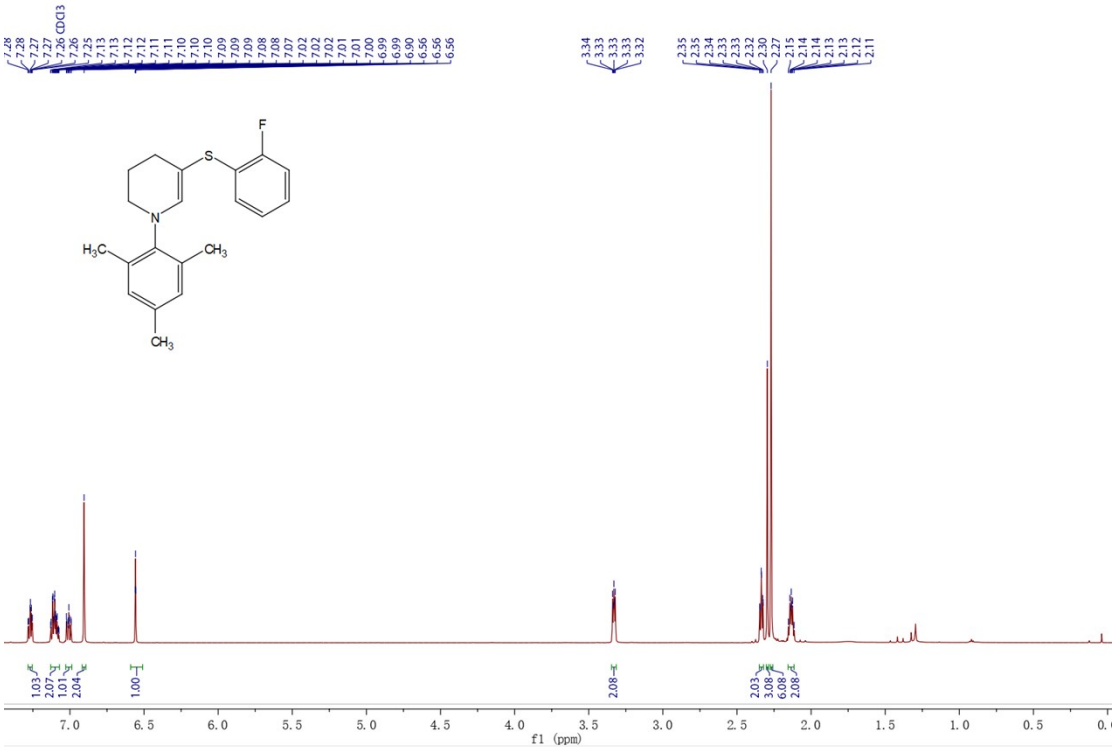
(3) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C2



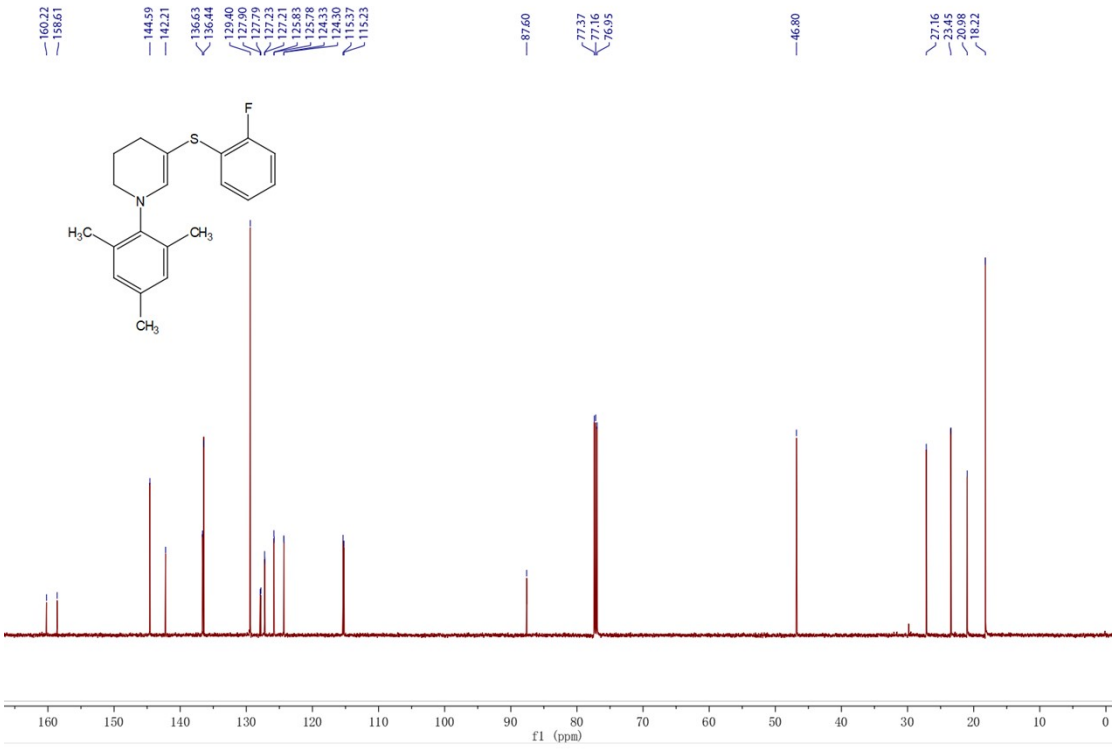
(4) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C2



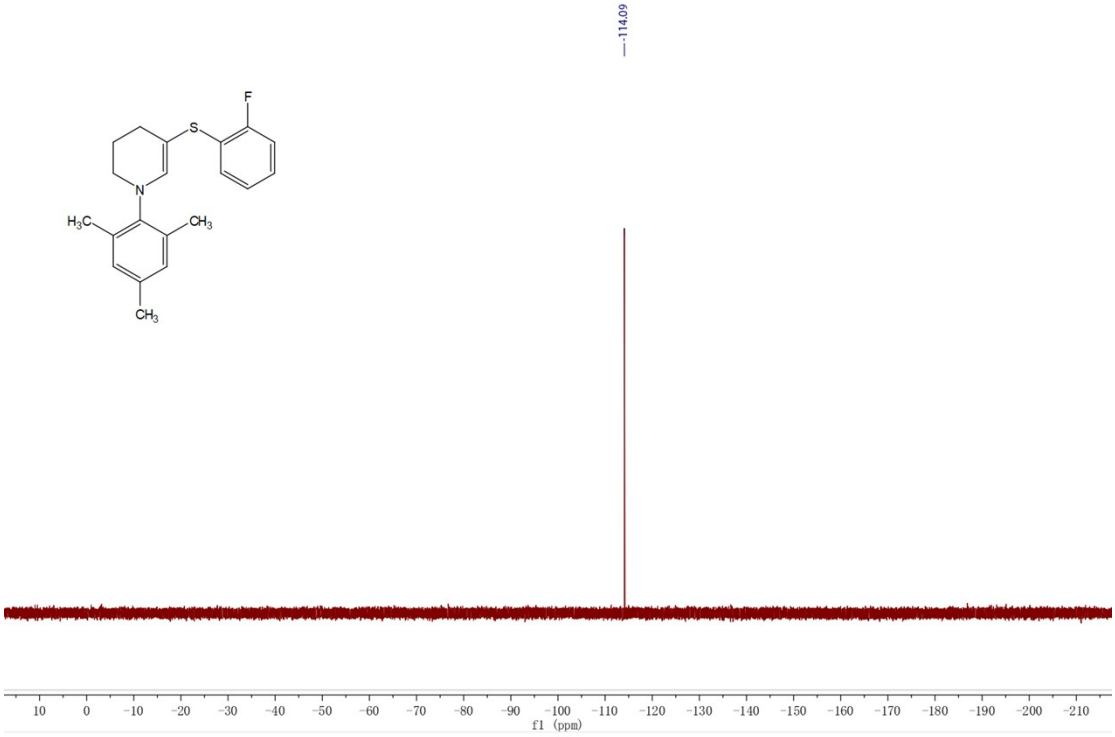
(5) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C3



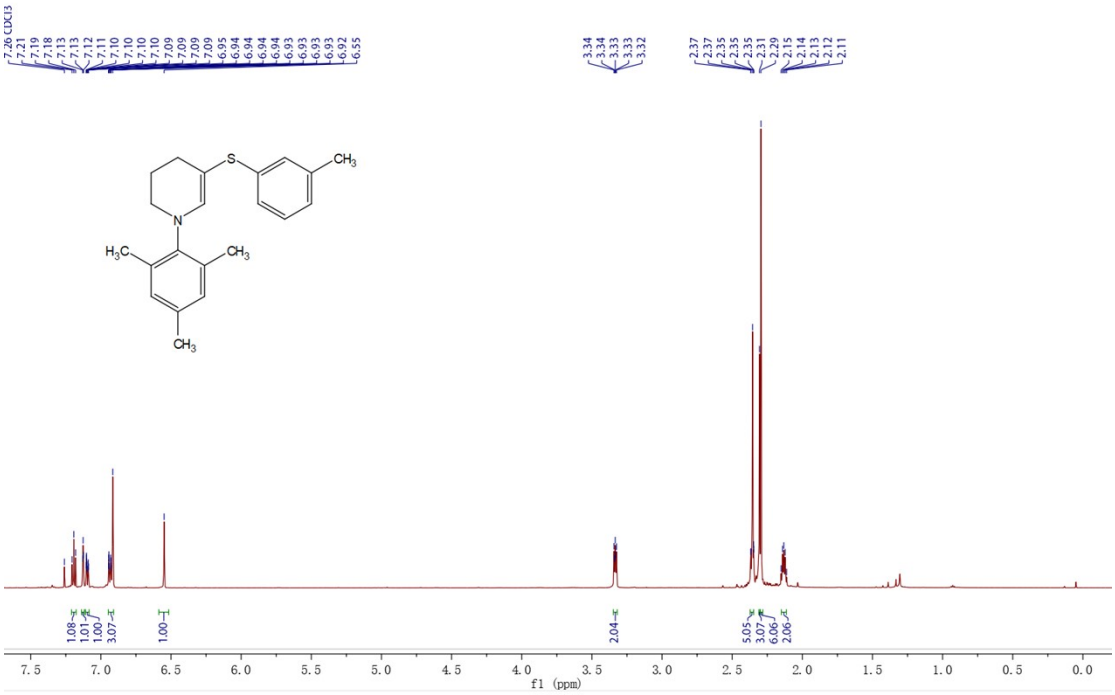
(6) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C3



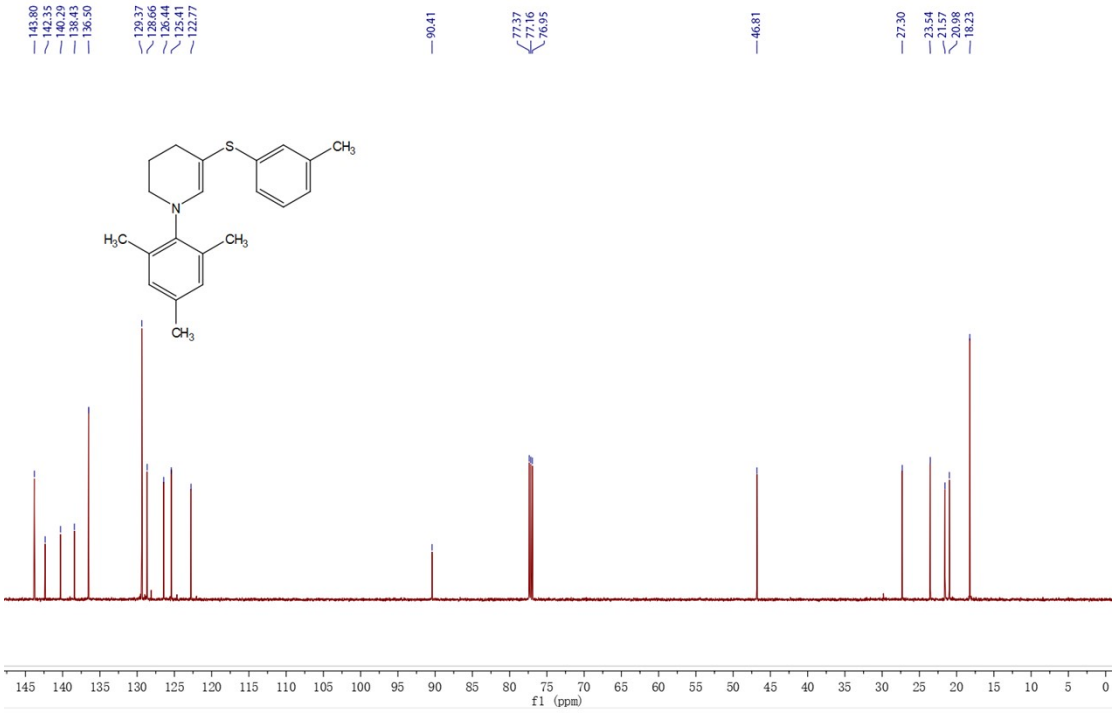
(7) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of C3



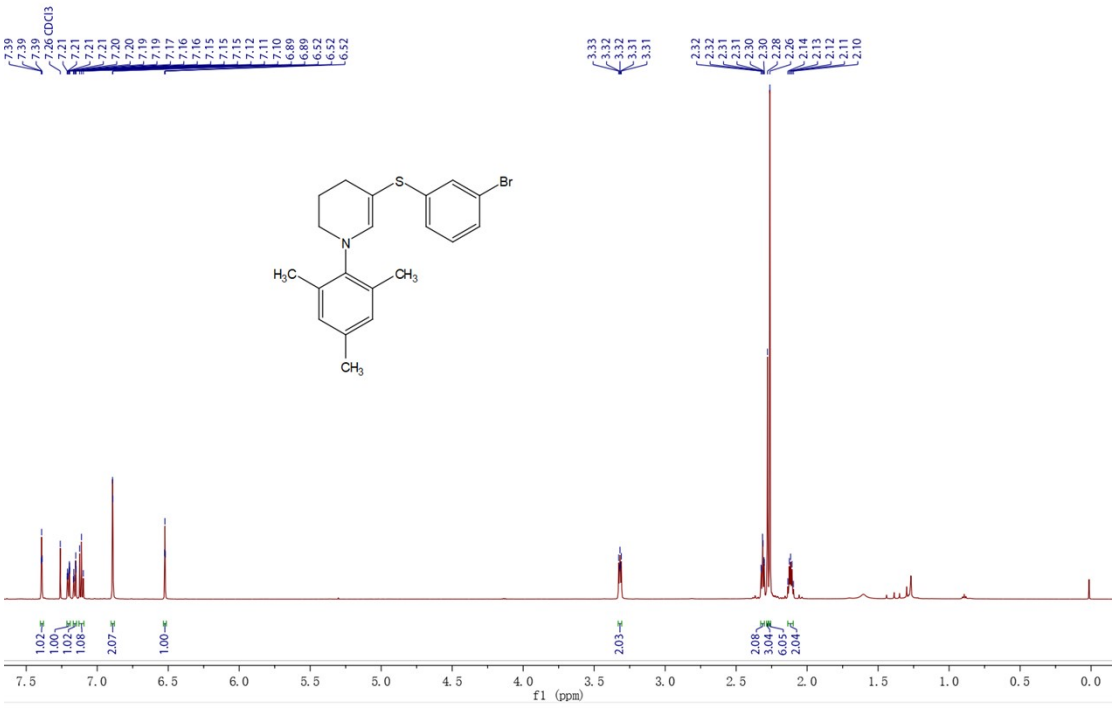
(8) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C4



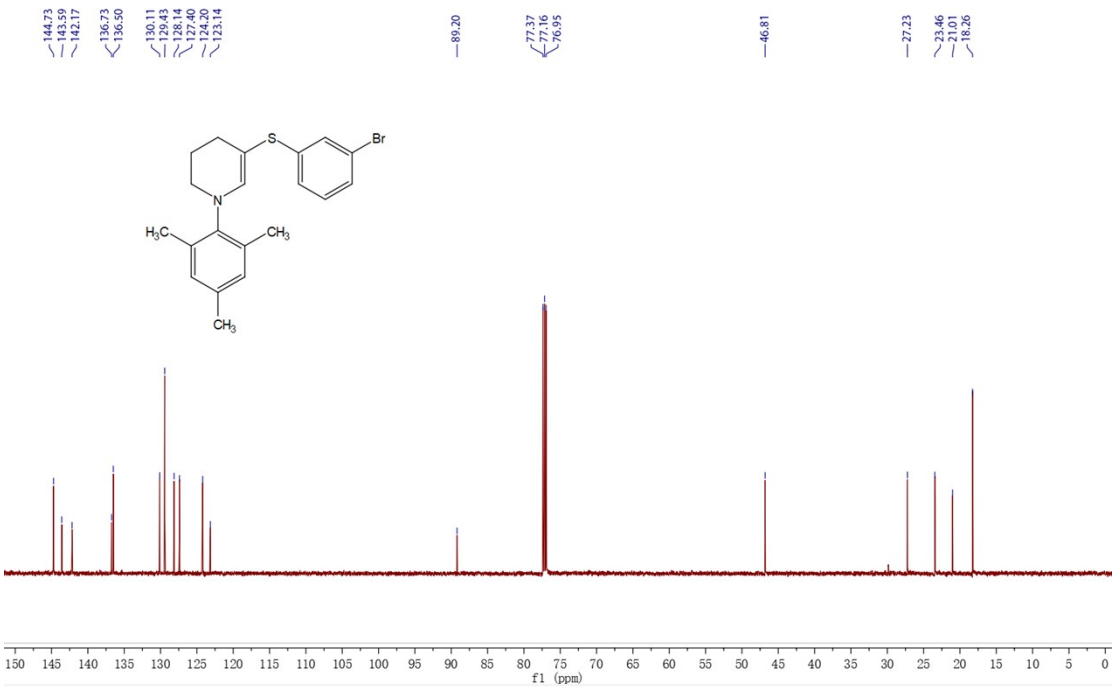
(9) ^{3}C-NMR (151 MHz, Chloroform-*d*) spectrum of C4



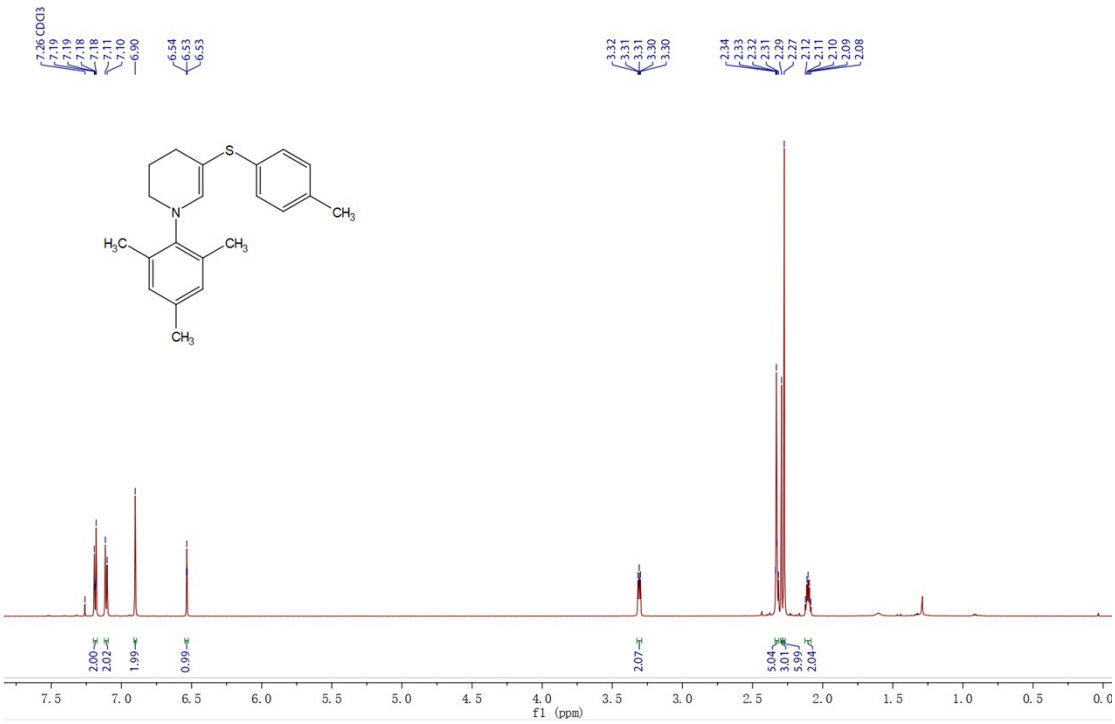
(10) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C5



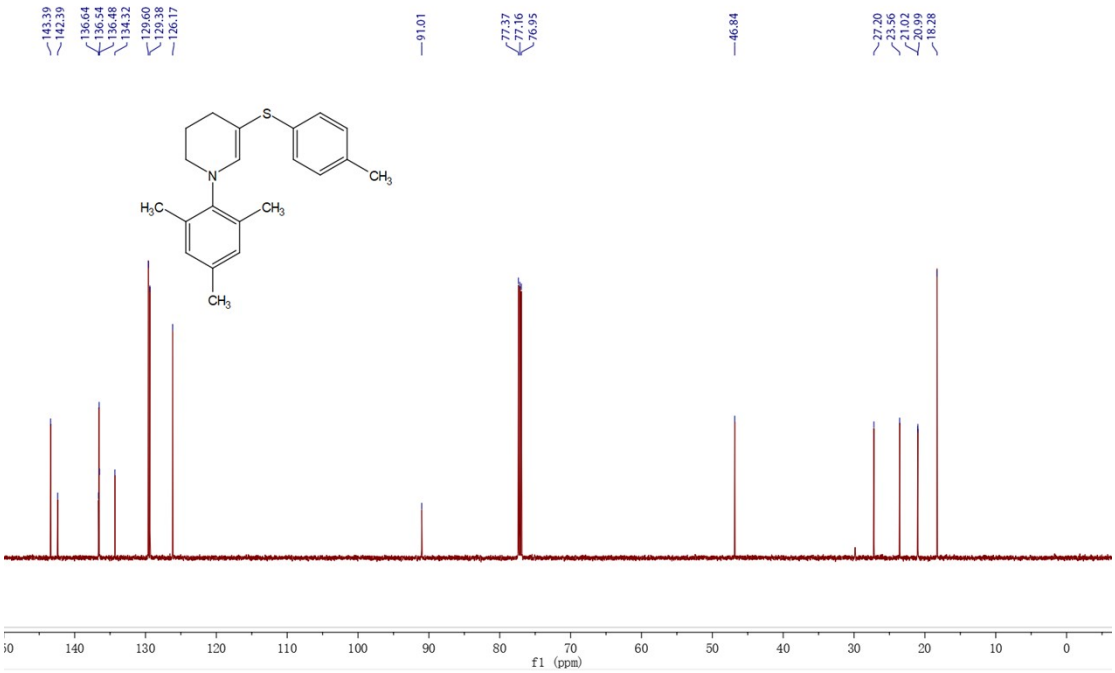
(11) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C5



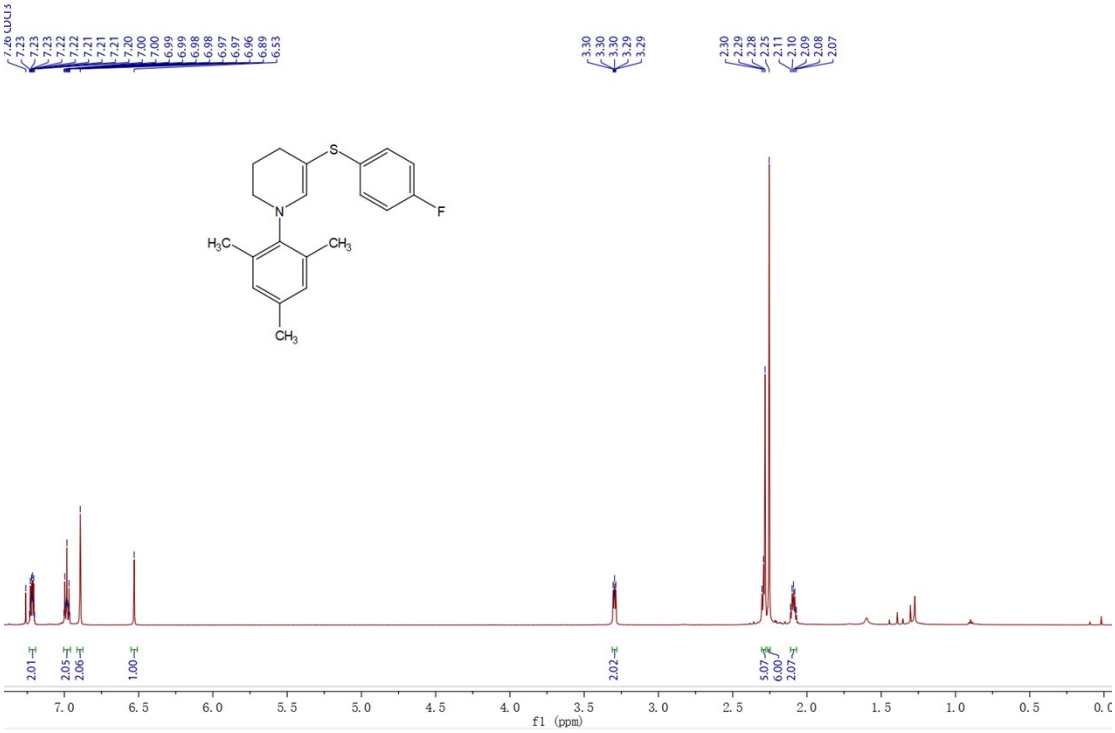
(12) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C6



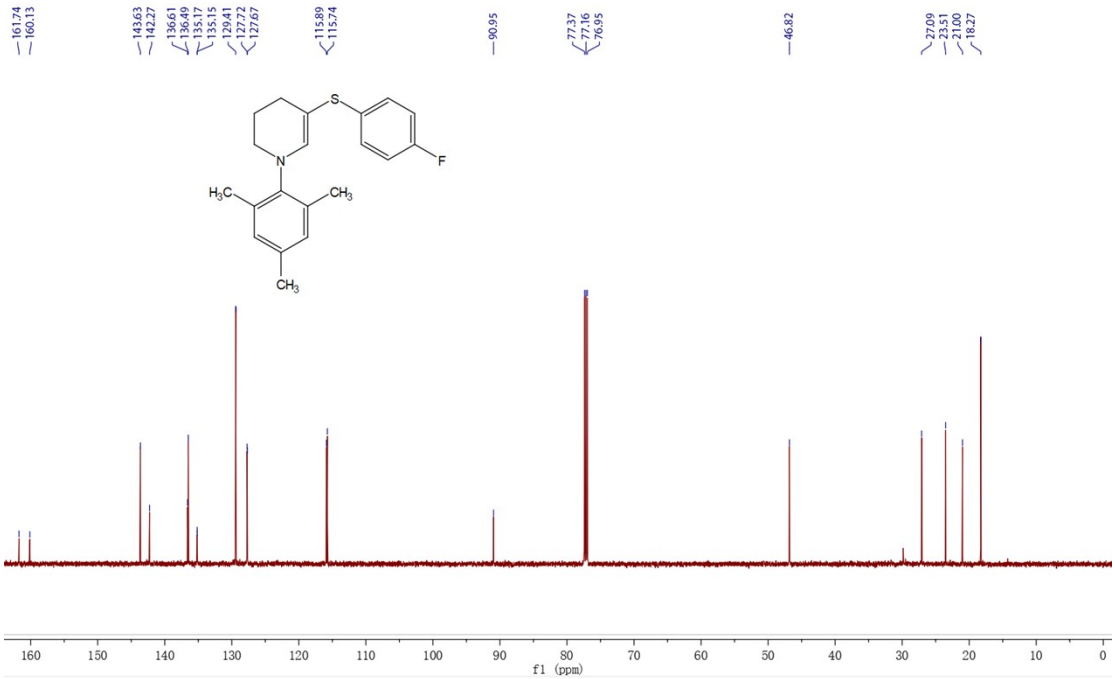
(13) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C6



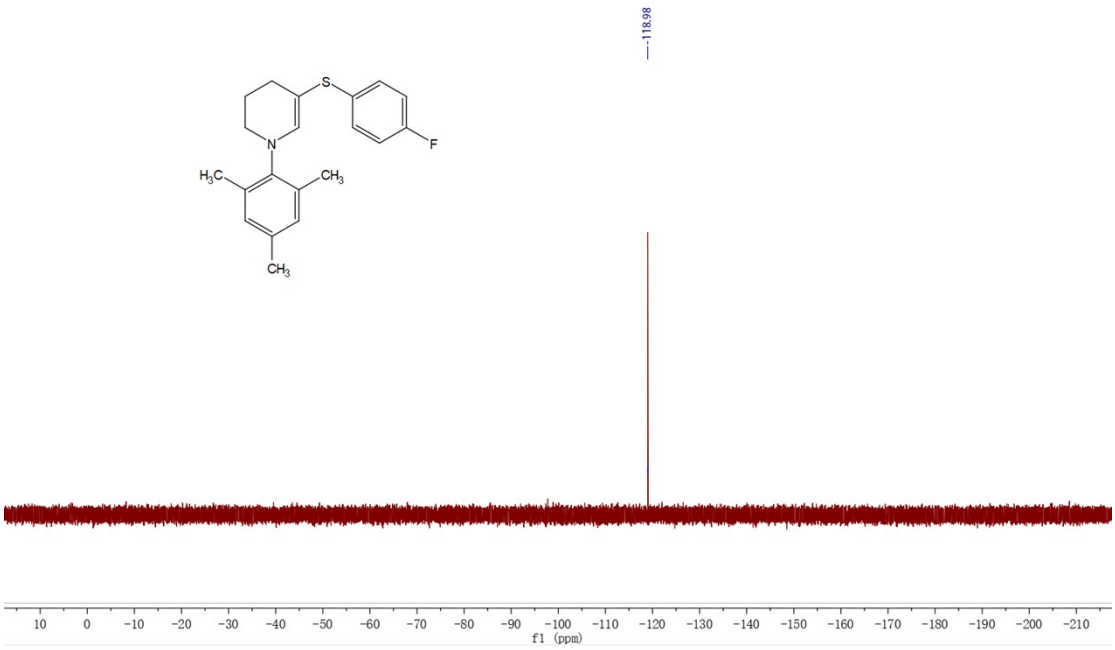
(14) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C7



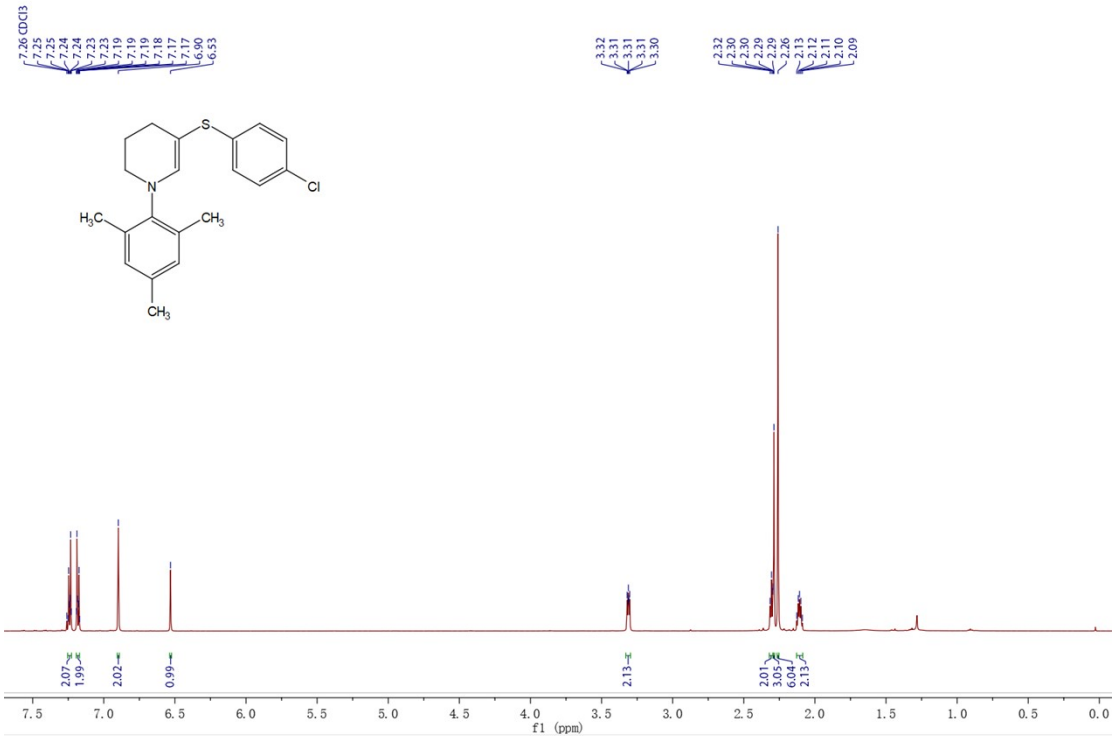
(15) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C7



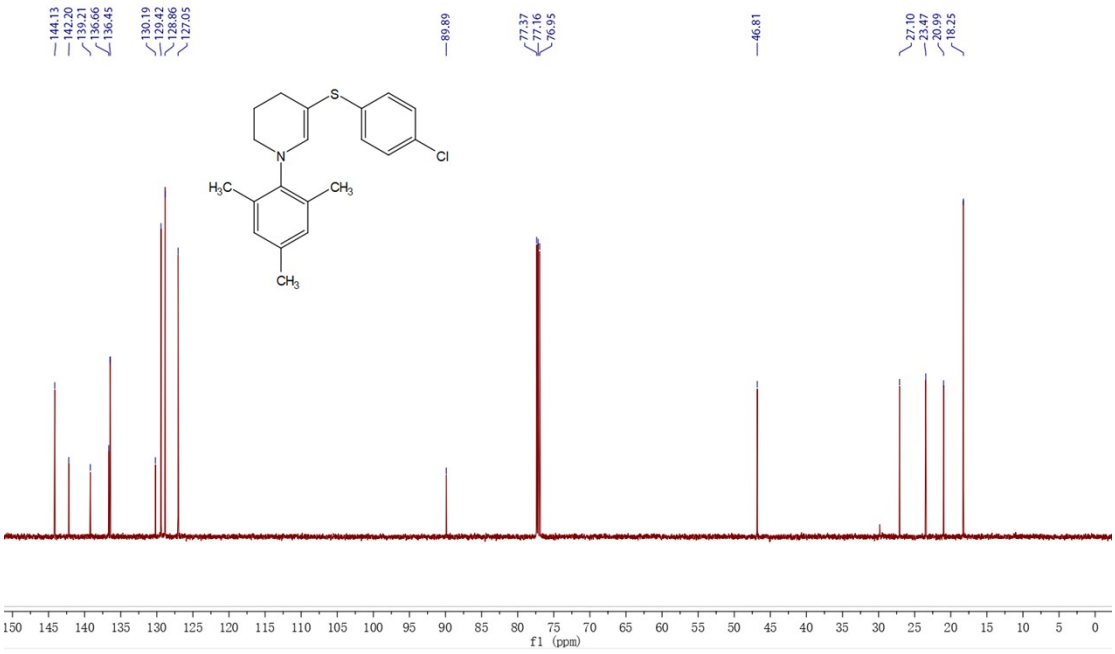
(16) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of C7



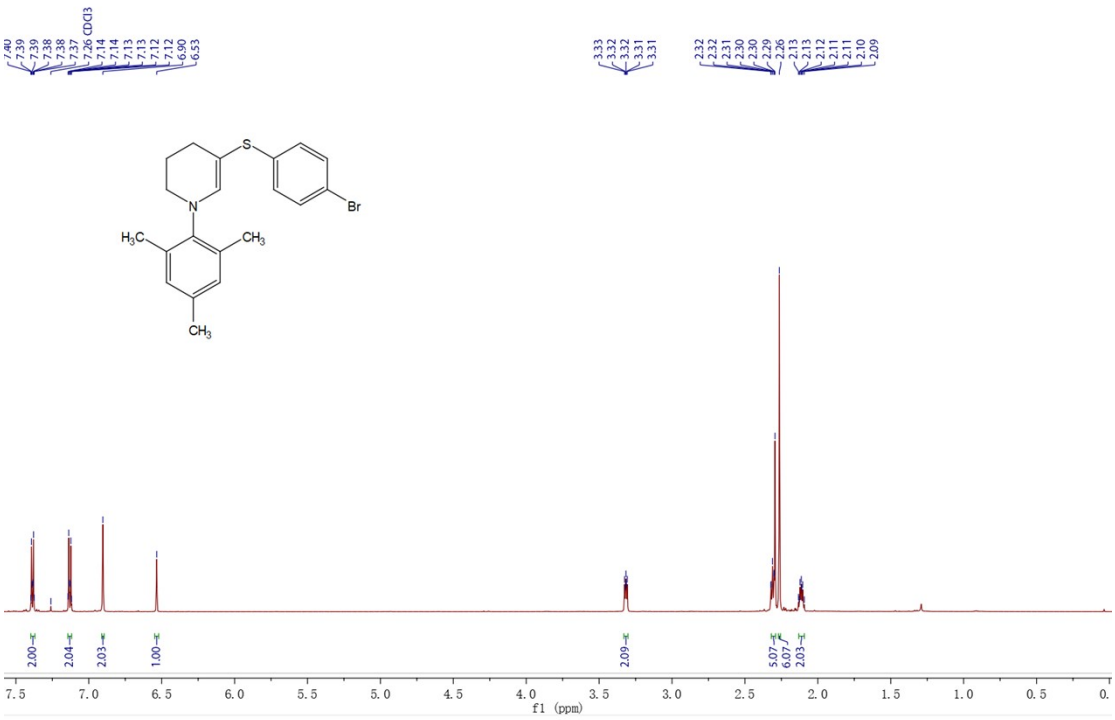
(17) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C8



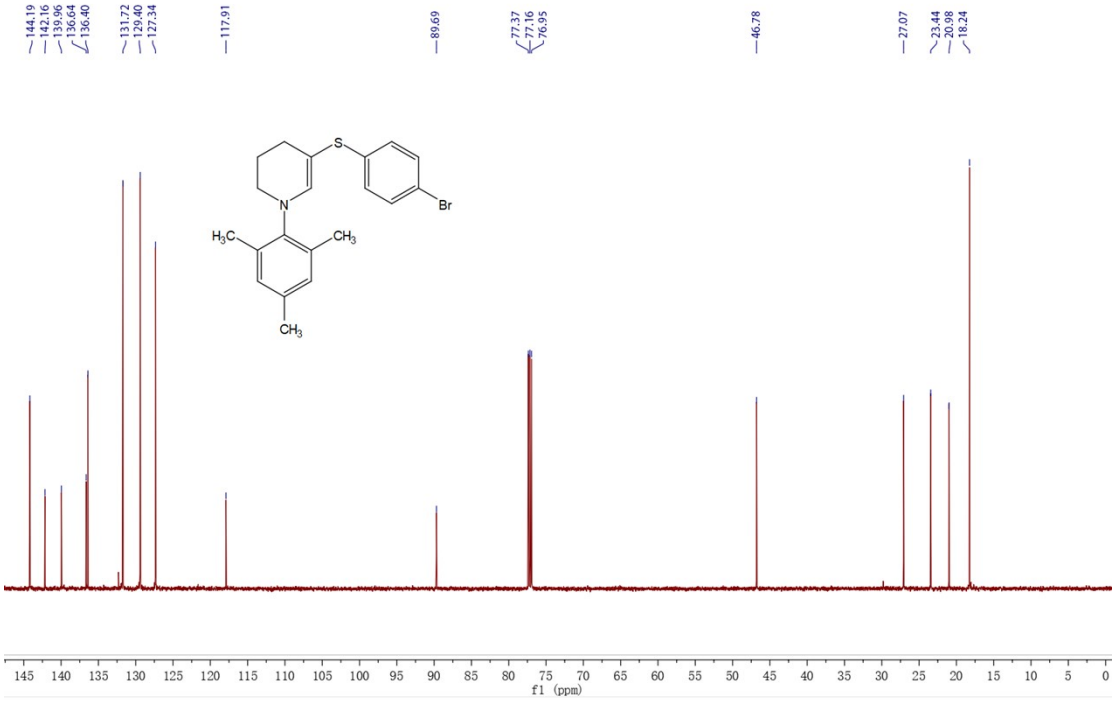
(18) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C8



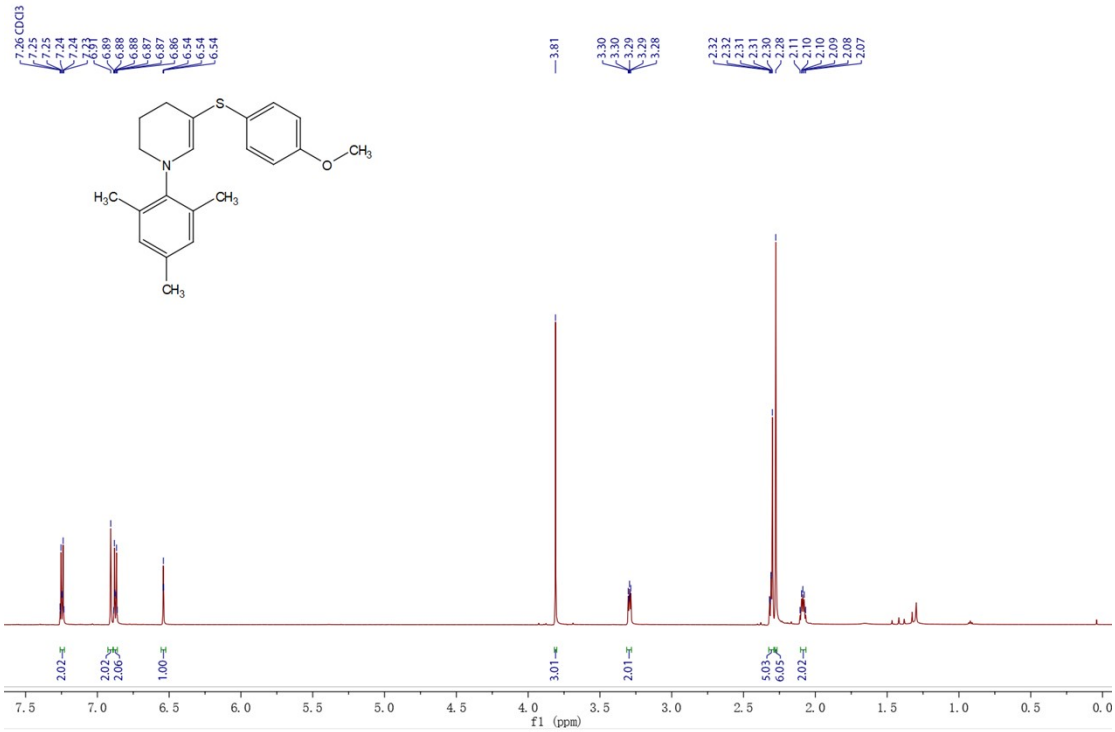
(19) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C9



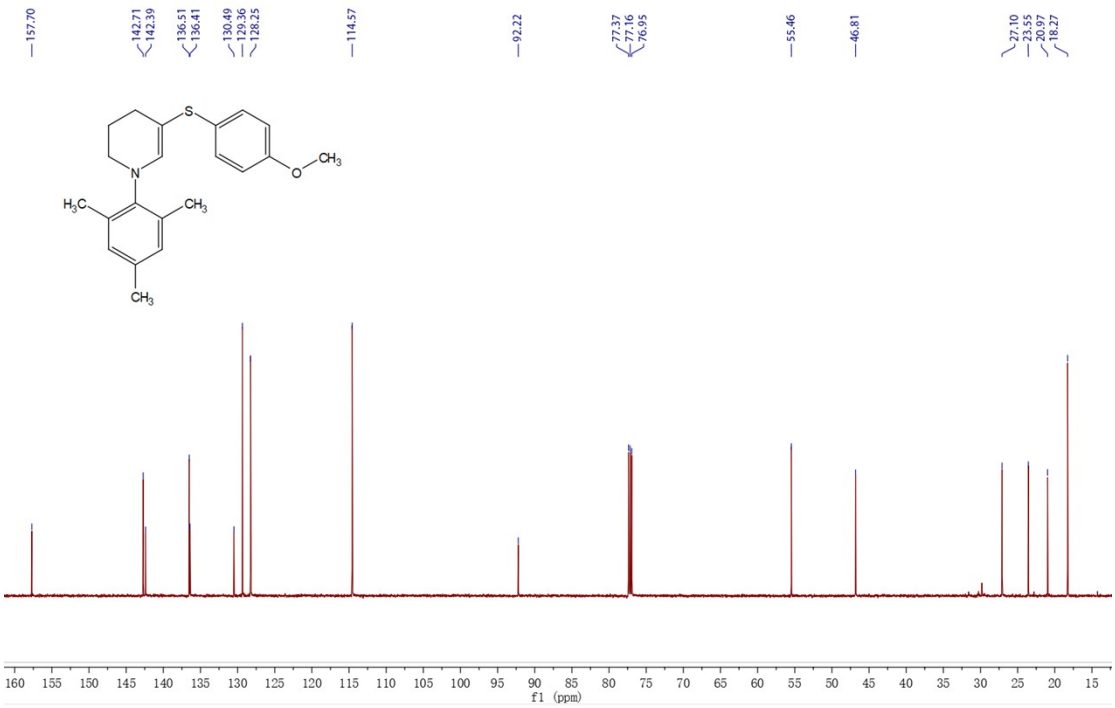
(20) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C9



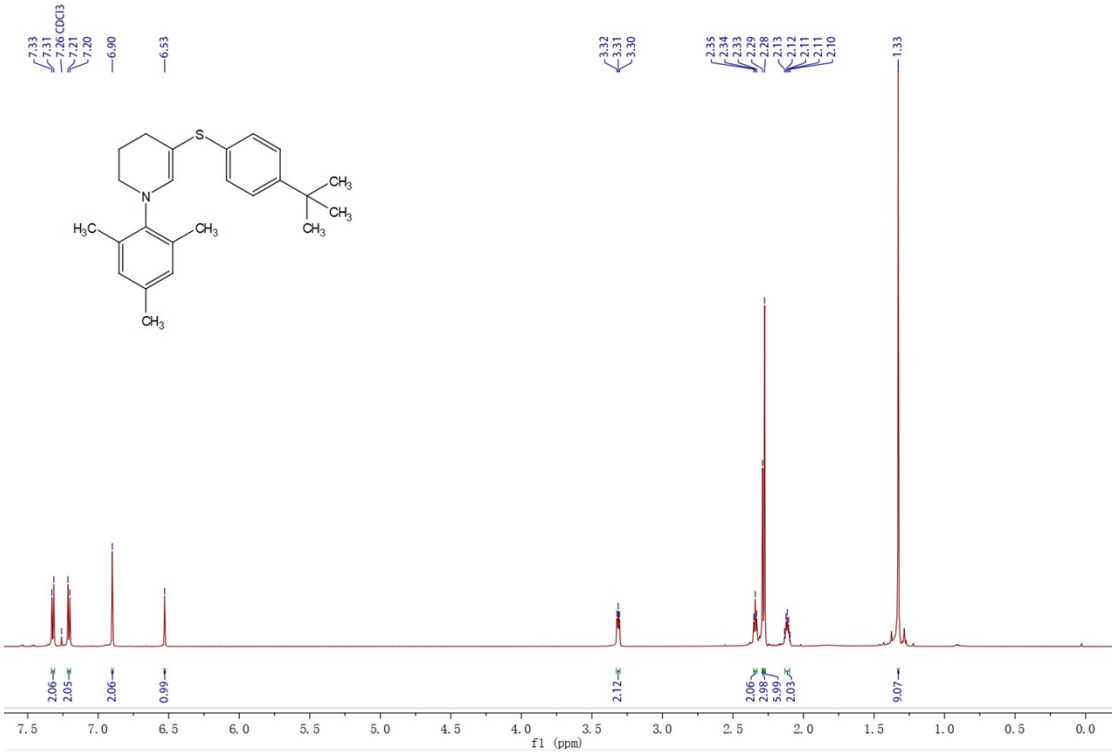
(21) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C10



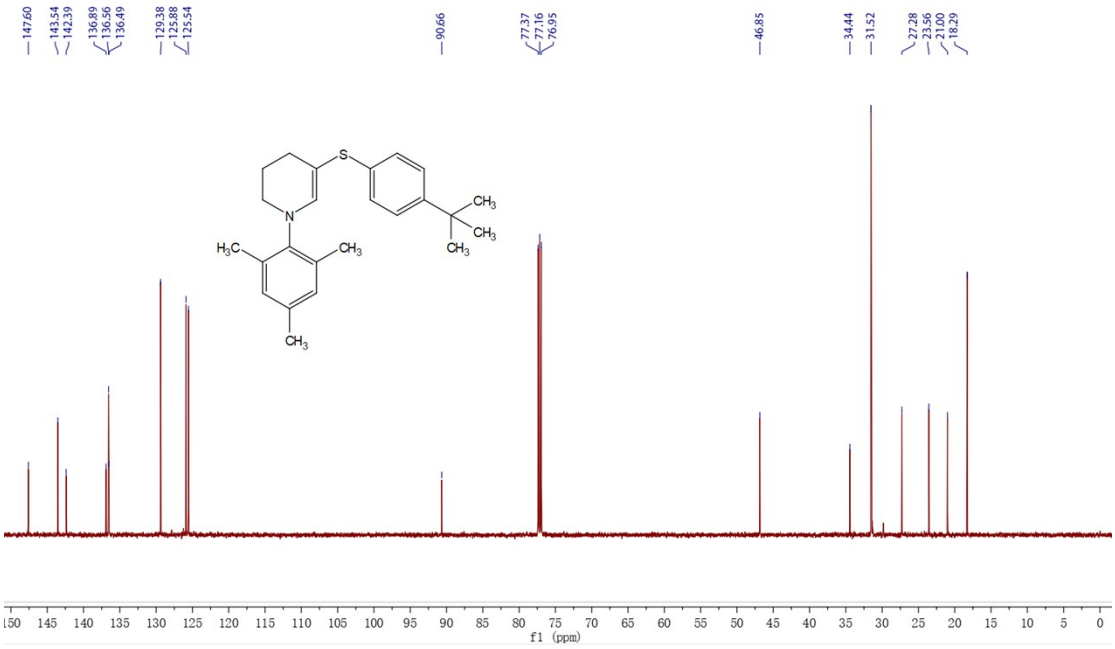
(22) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C10



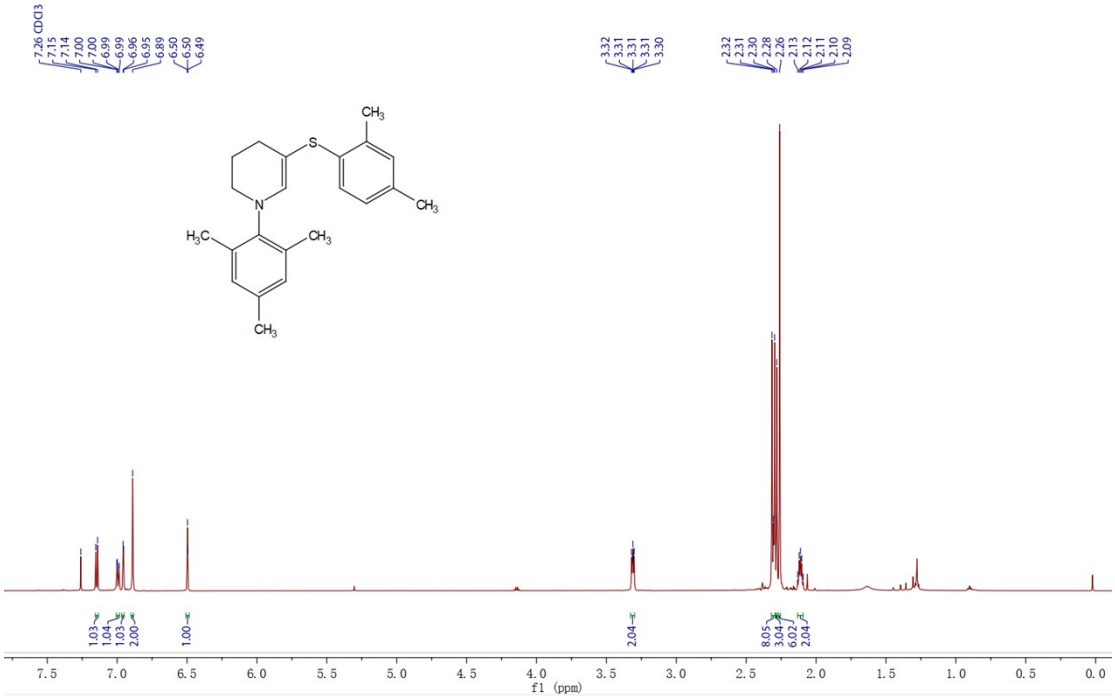
(23) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C11



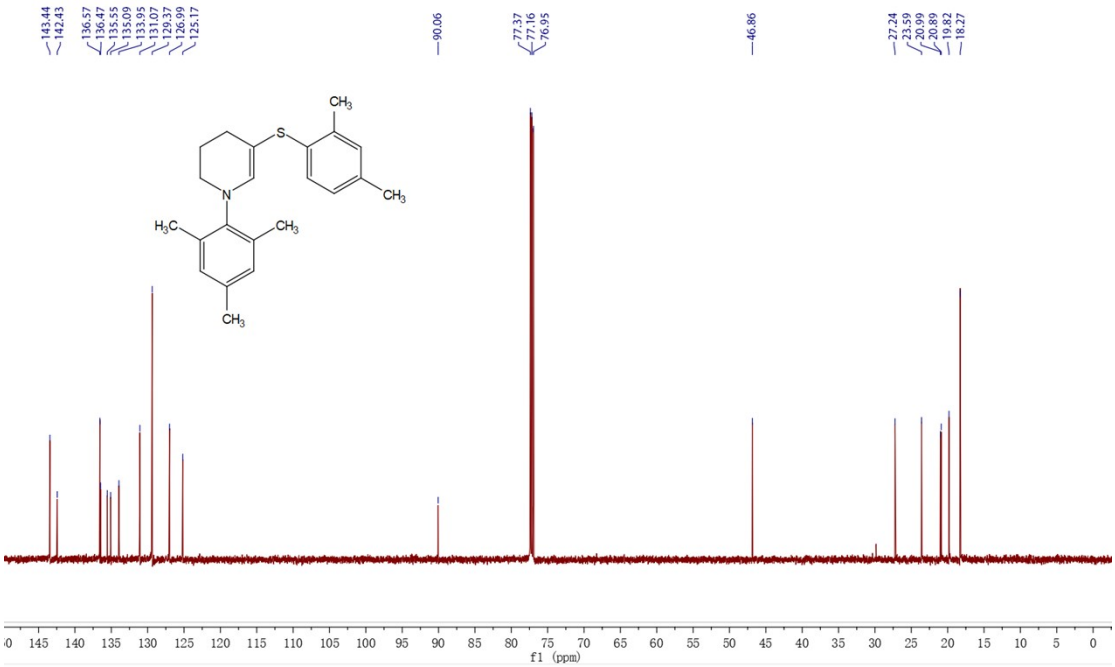
(24) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C11



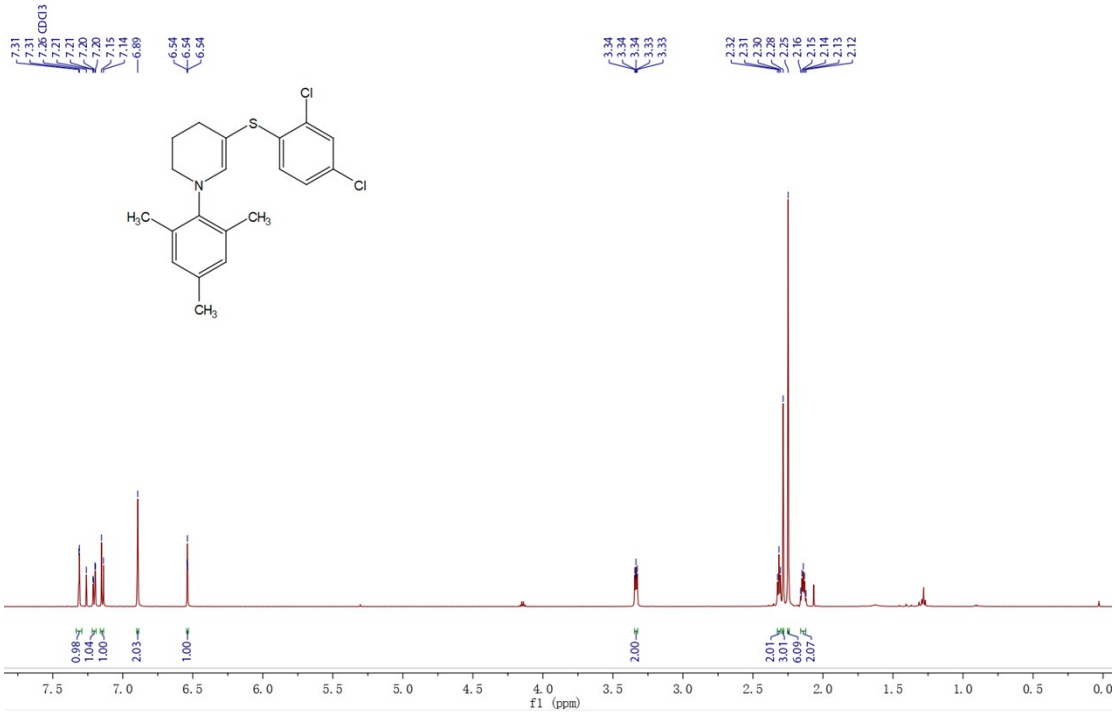
(25) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C12



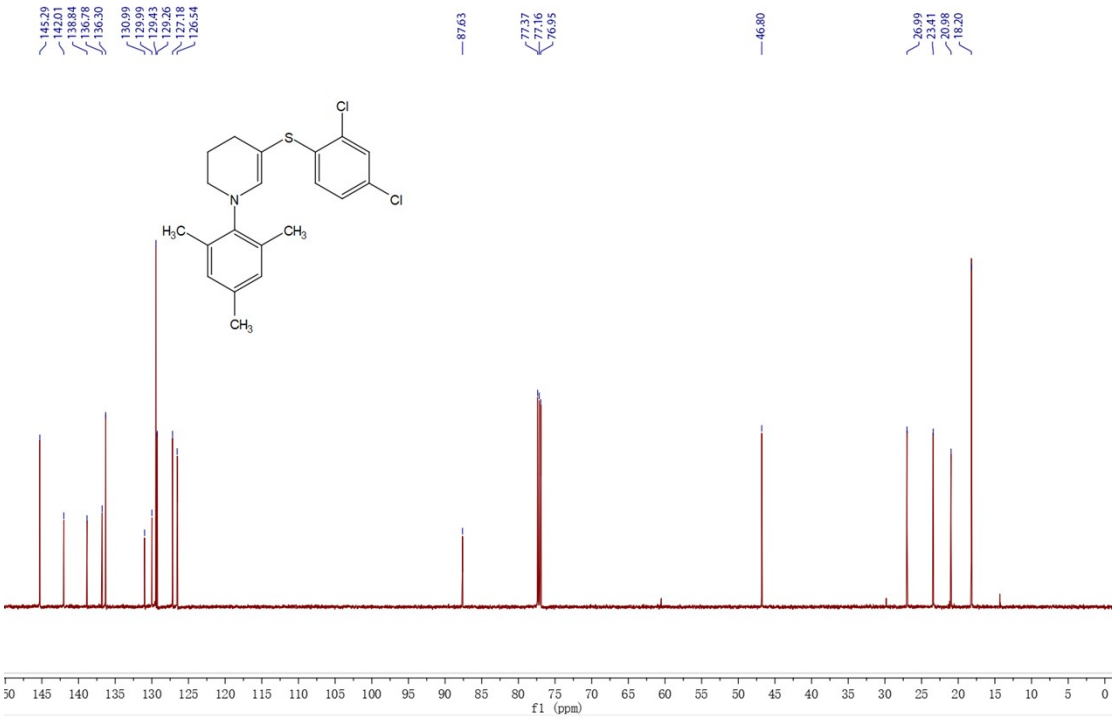
(26) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C12



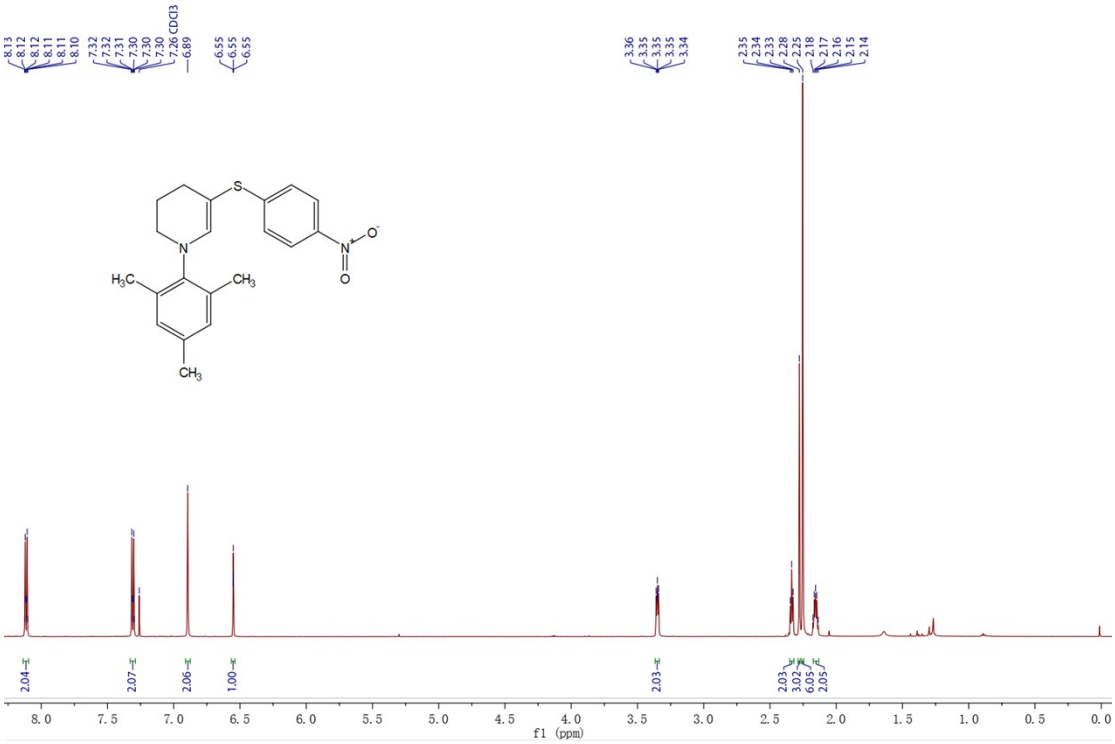
(27) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C13



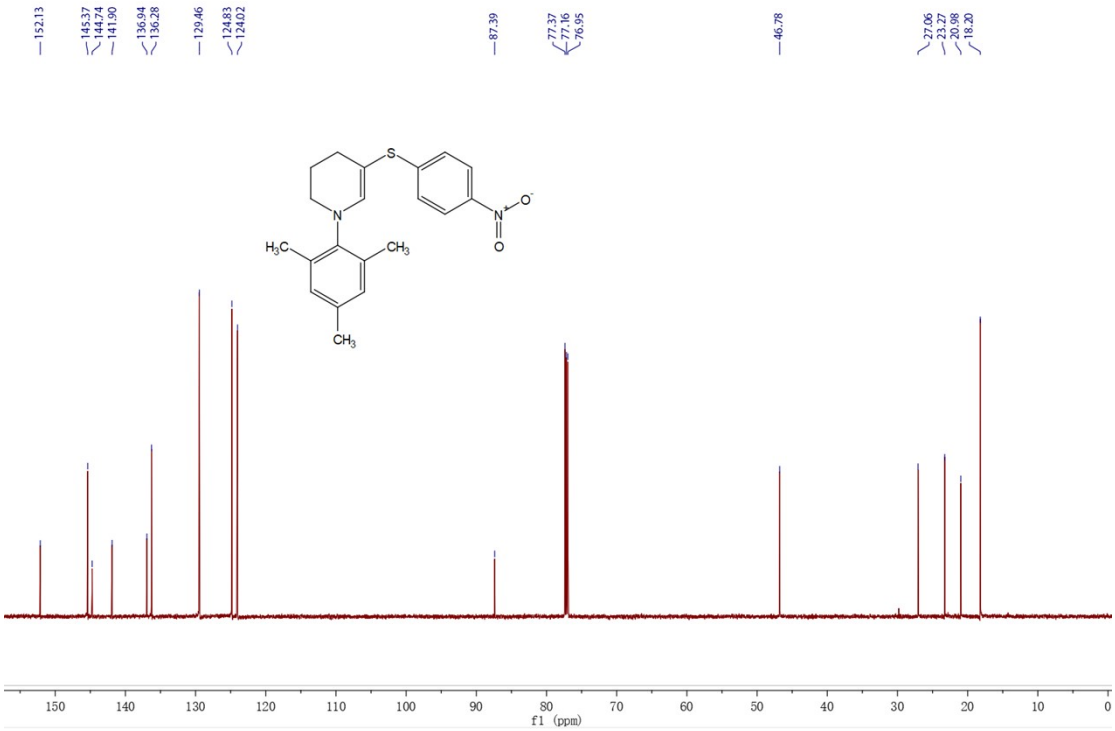
(28) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C13



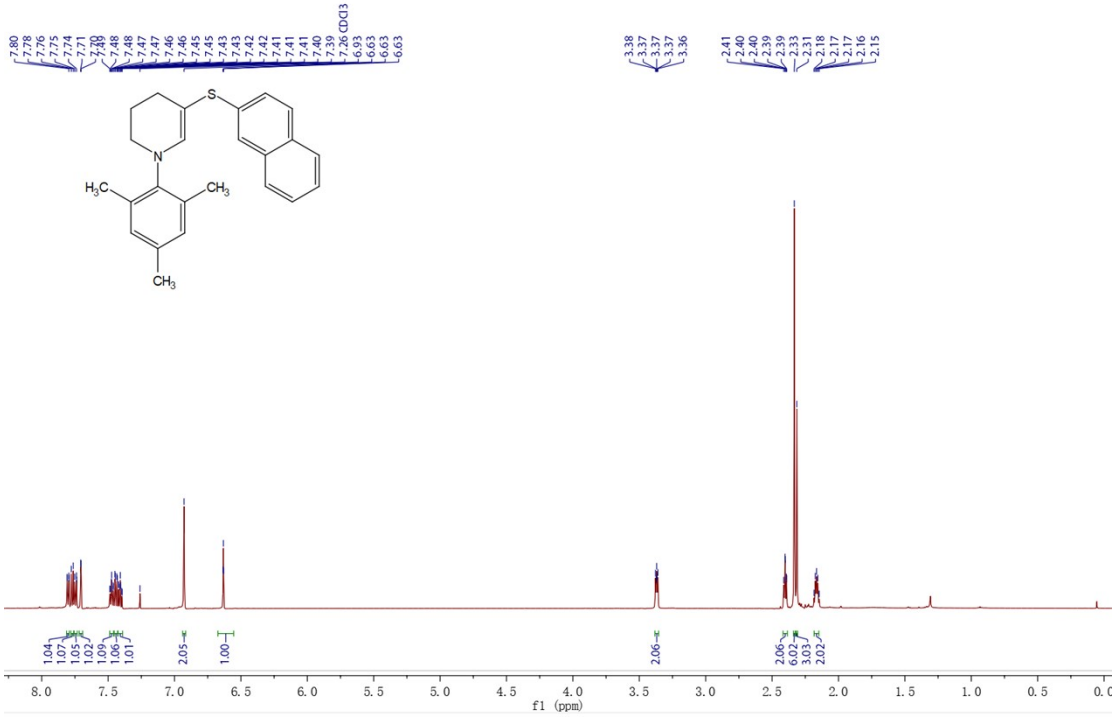
(29) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C14



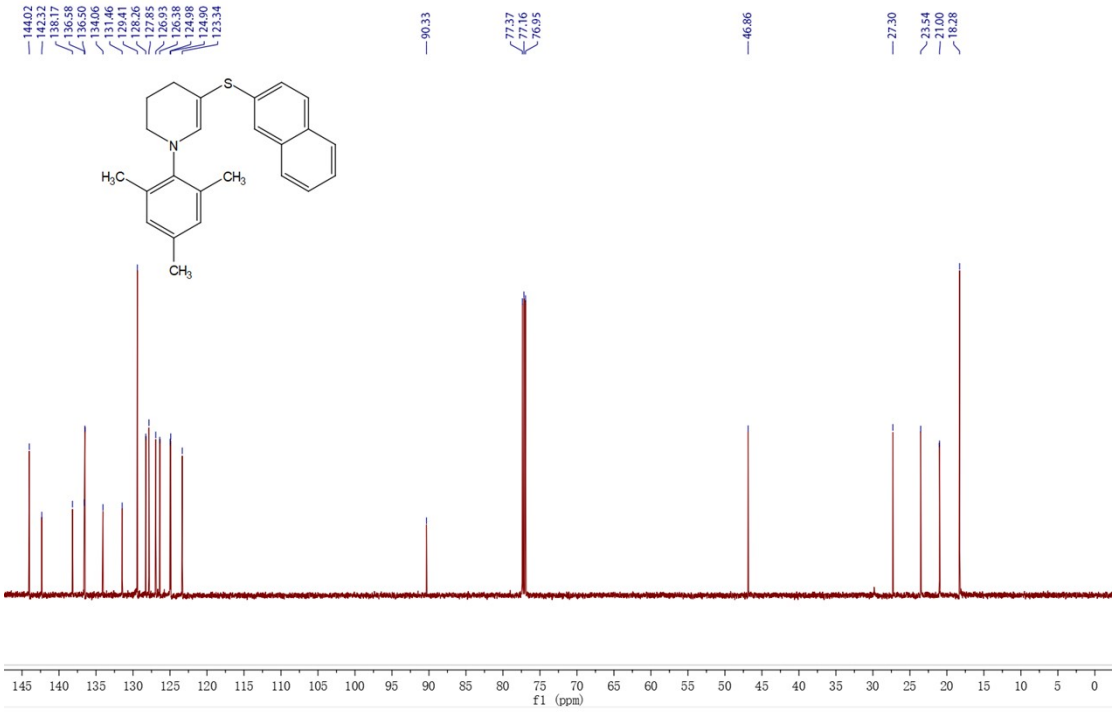
(30) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C14



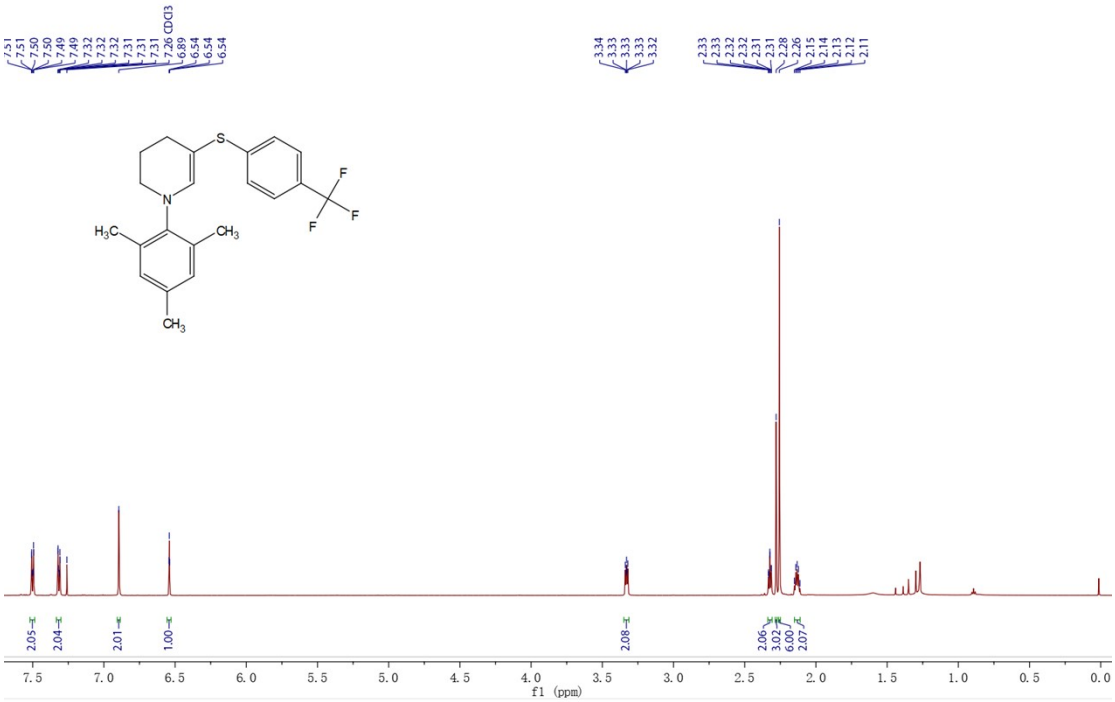
(31) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C15



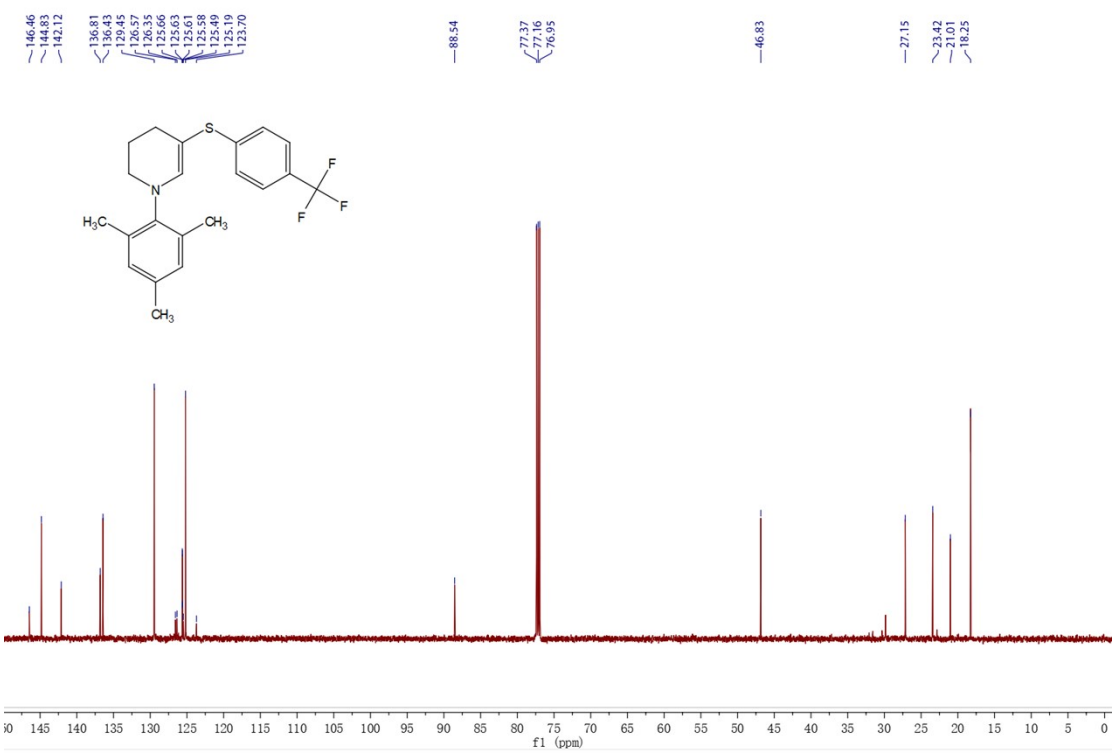
(32) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C15



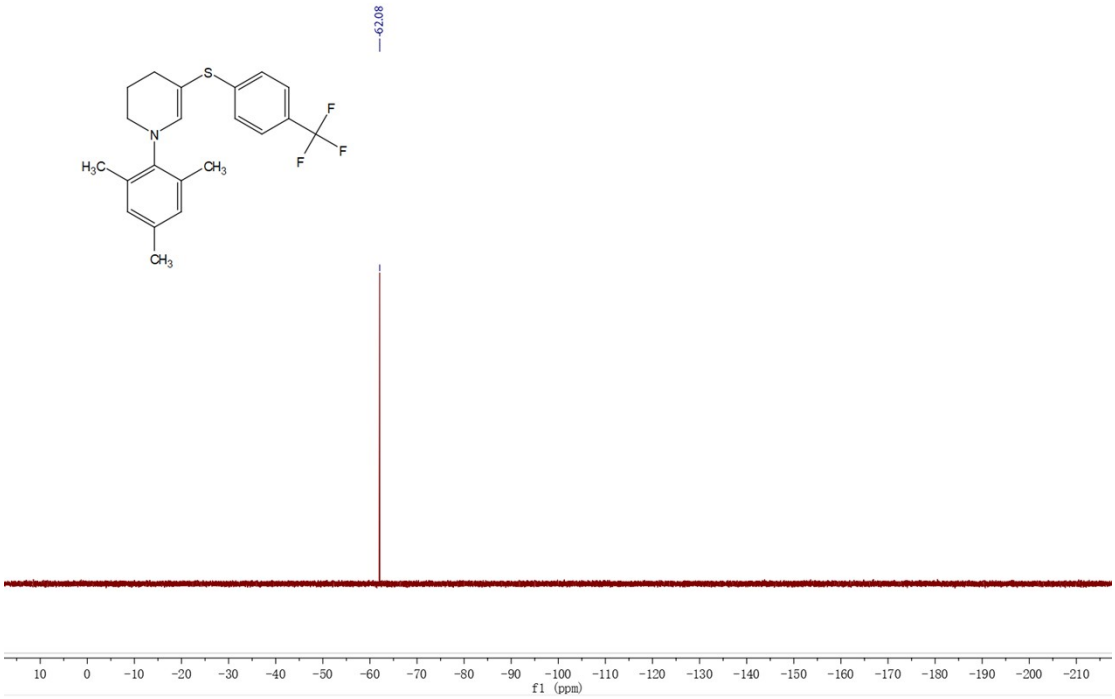
(33) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C16



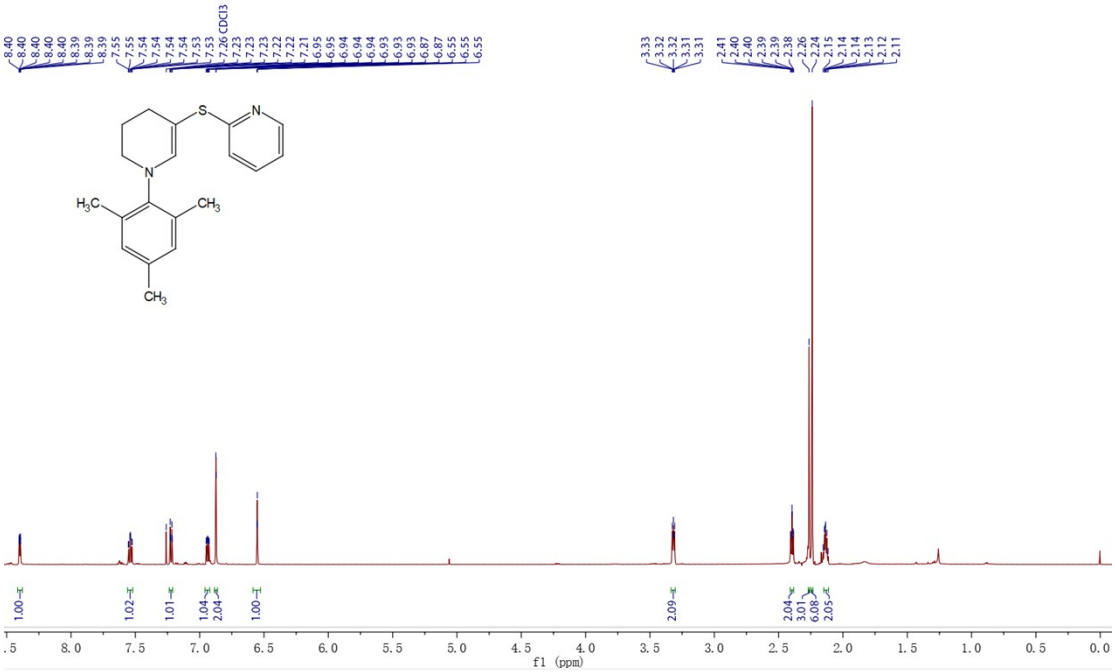
(34) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C16



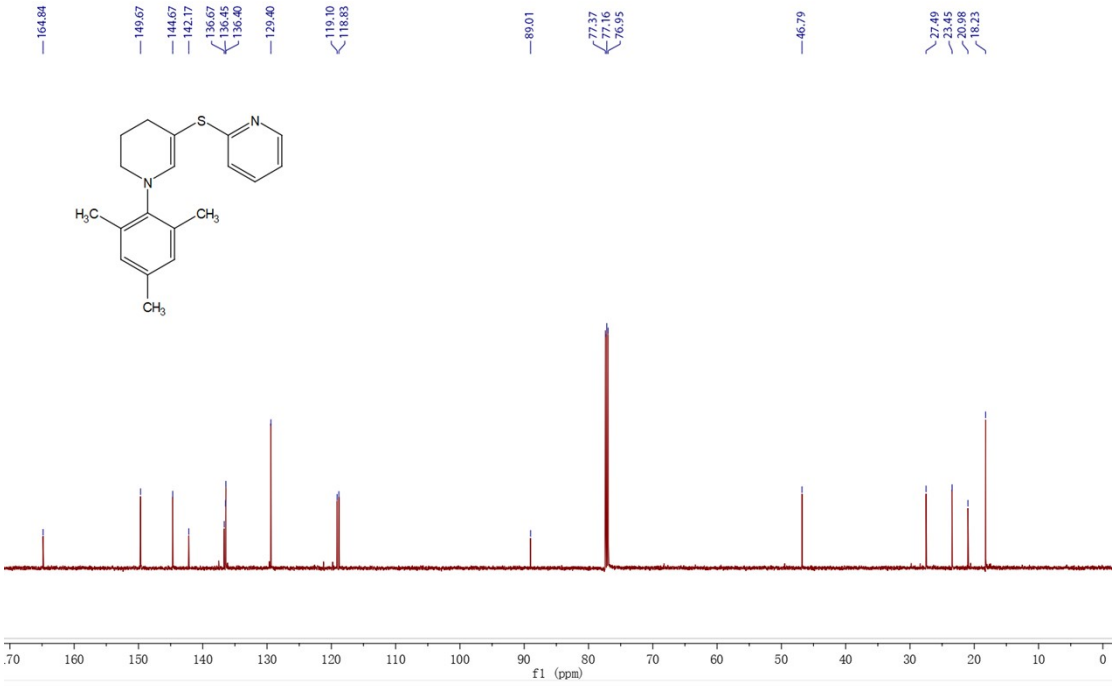
(35) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of C16



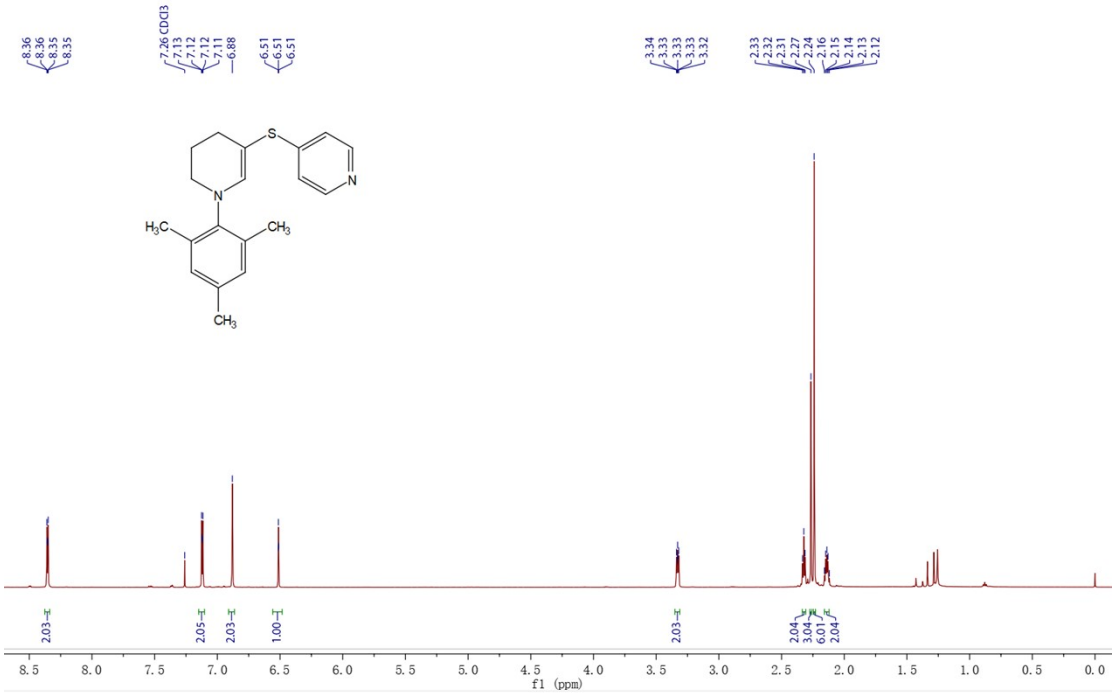
(36) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C17



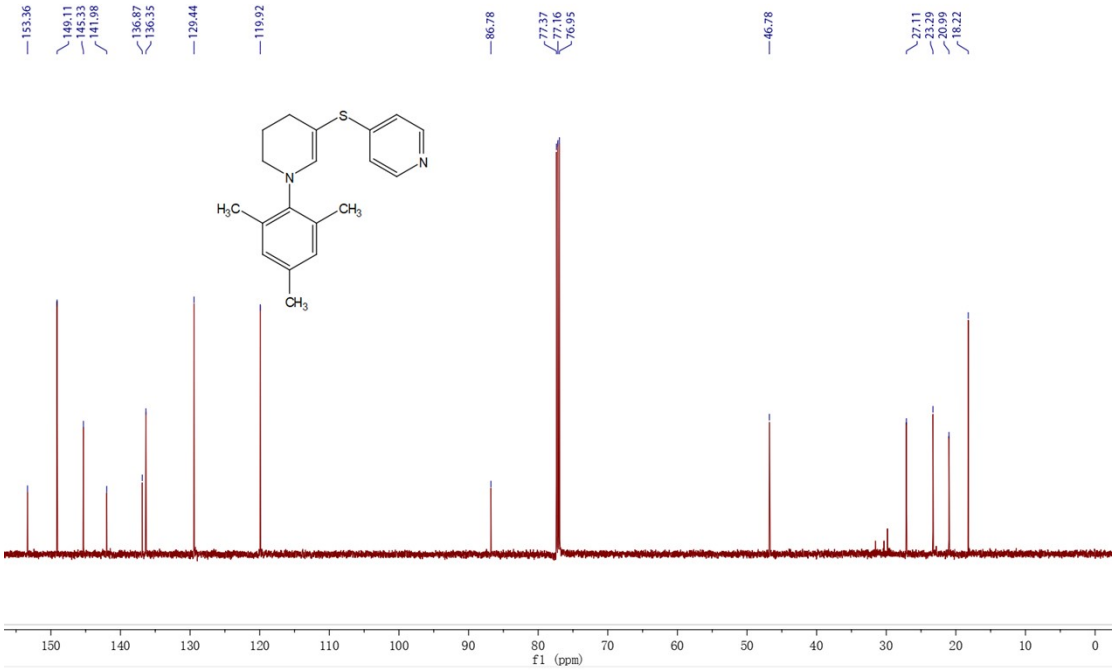
(37) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C17



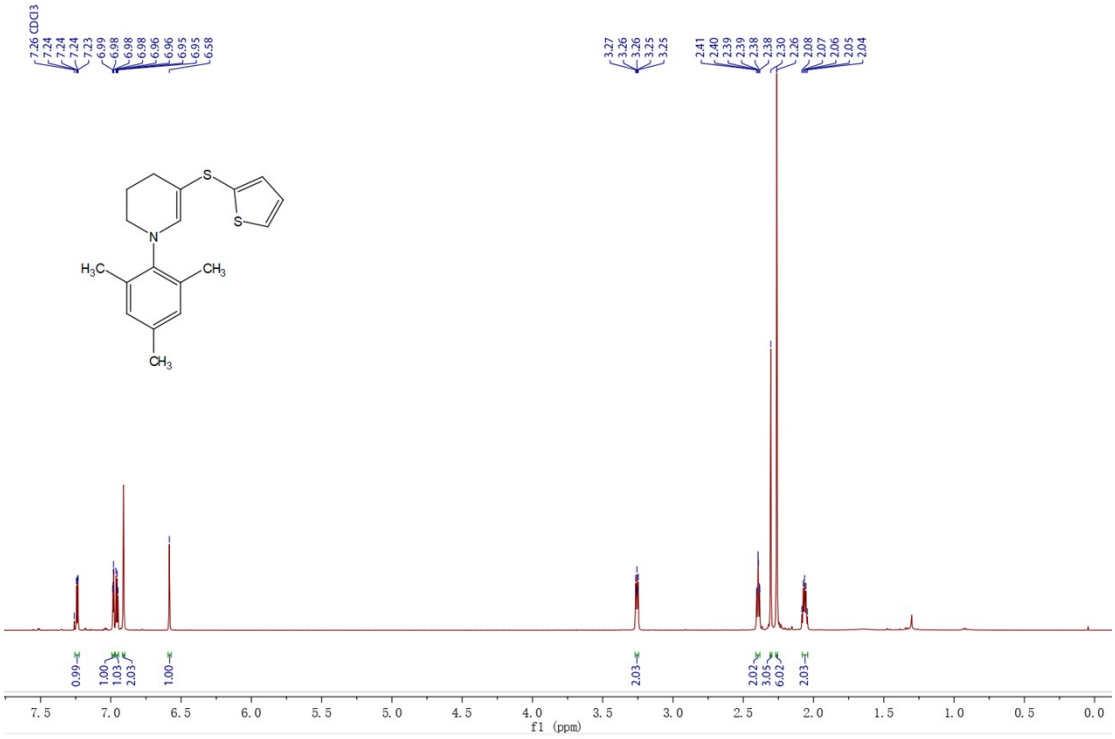
(38) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C18



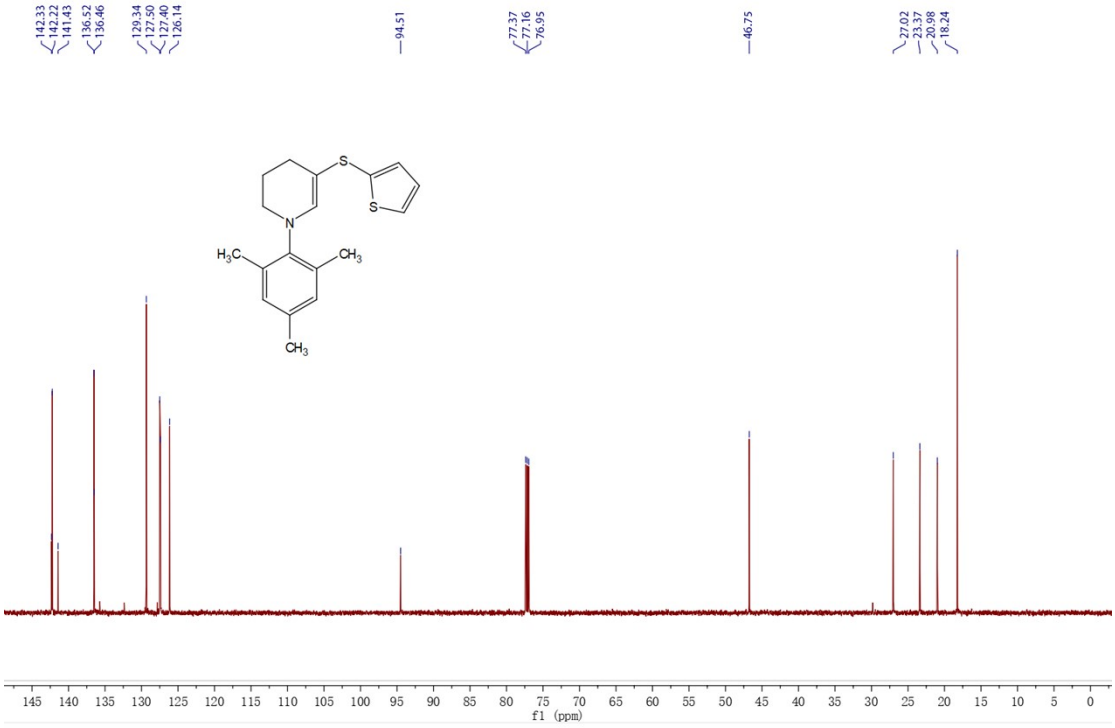
(39) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C18



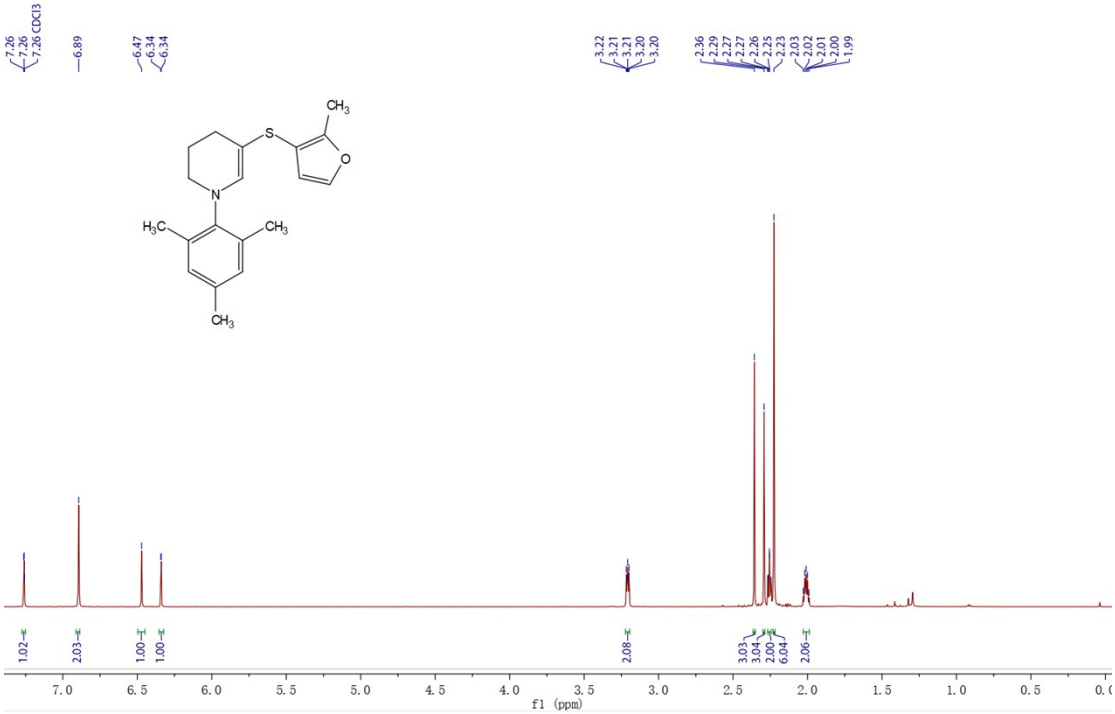
(40) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C19



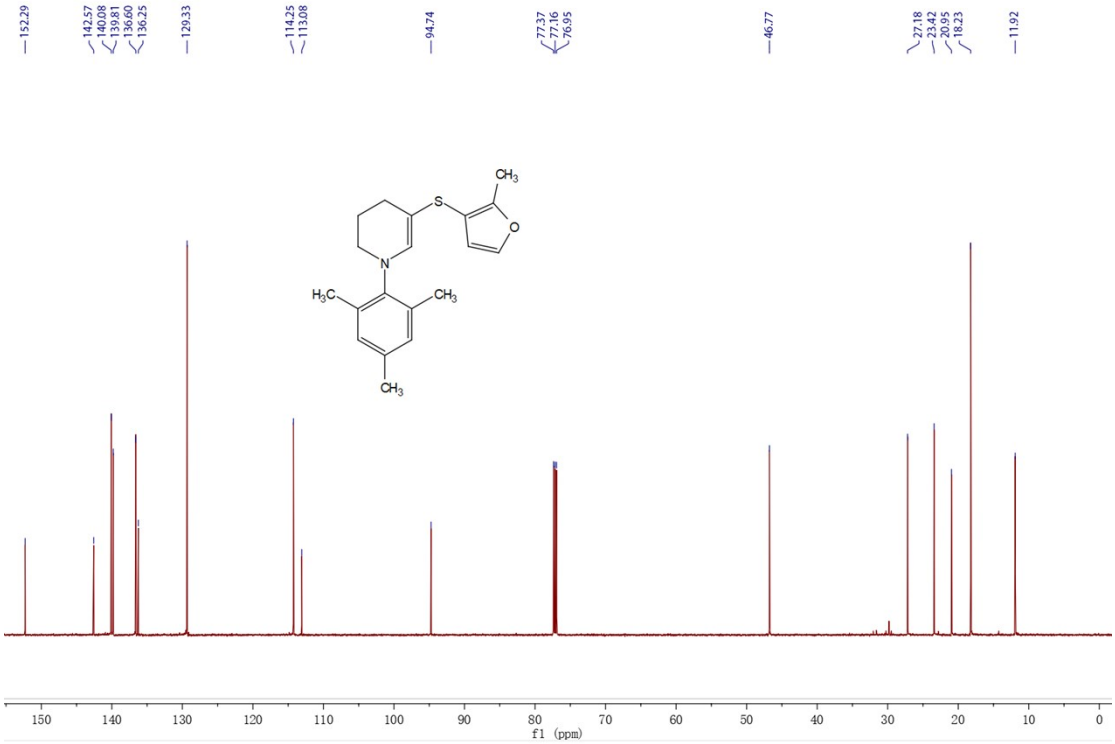
(41) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C19



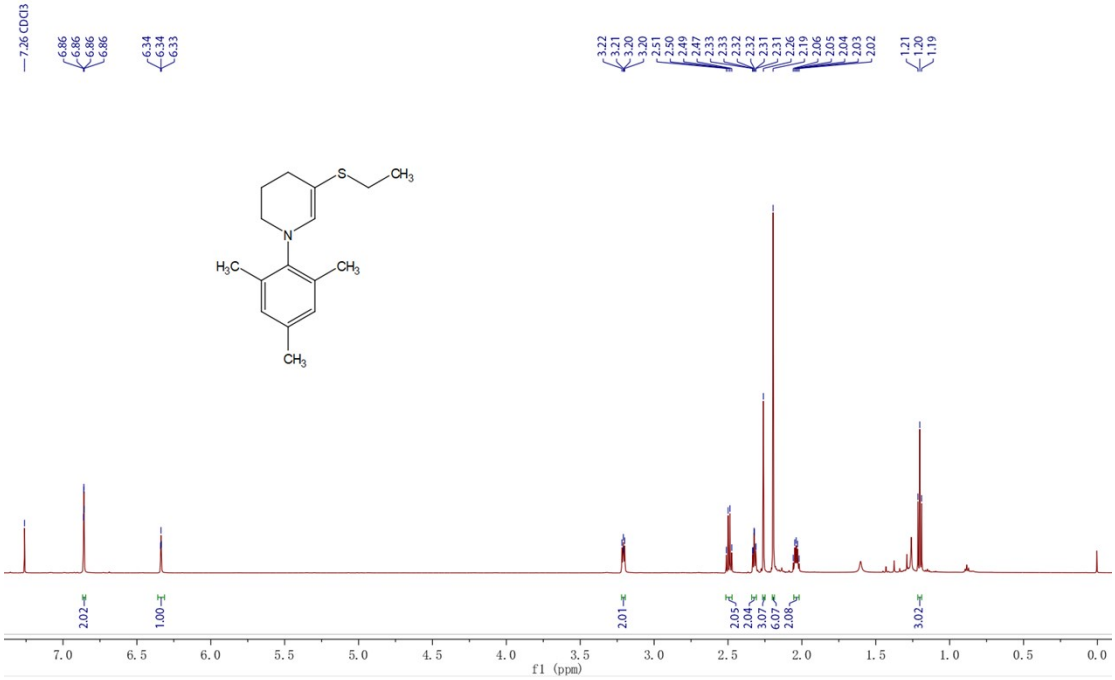
(42) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C20



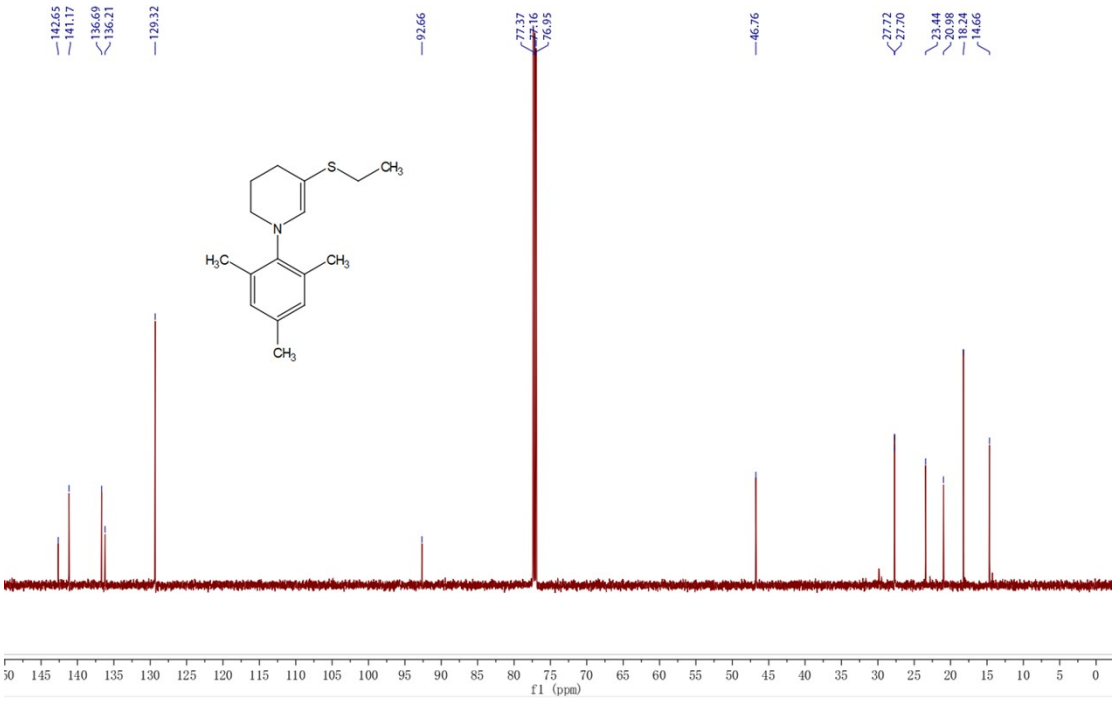
(43) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C20



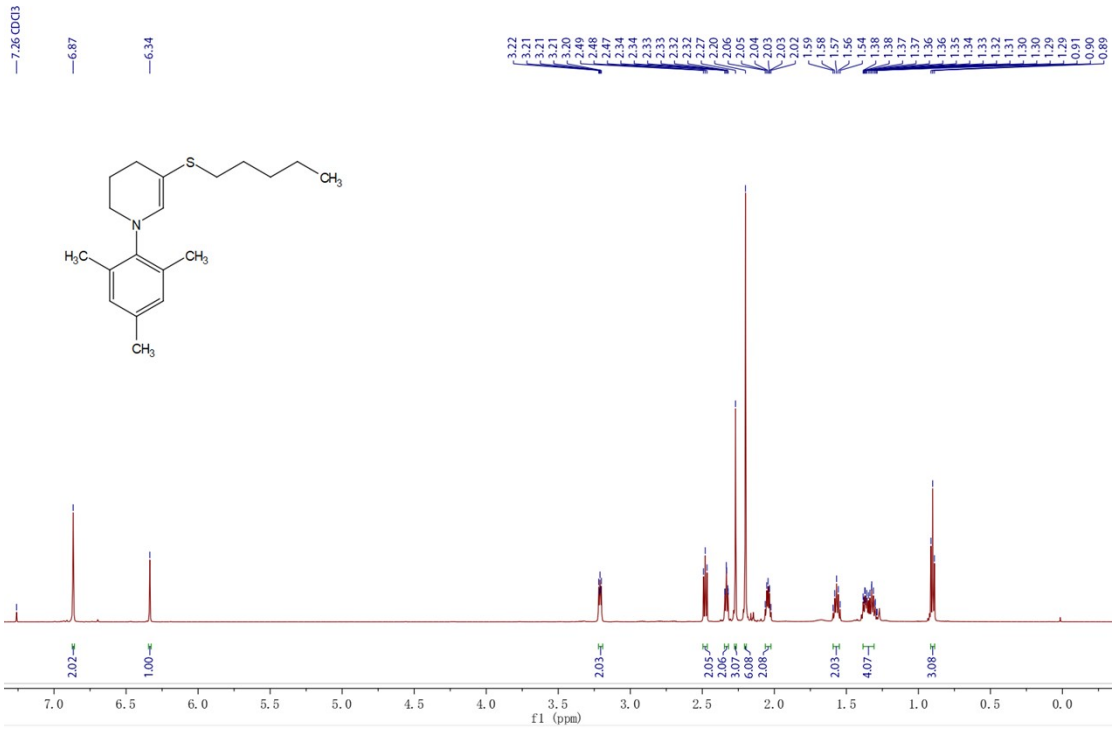
(44) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C21



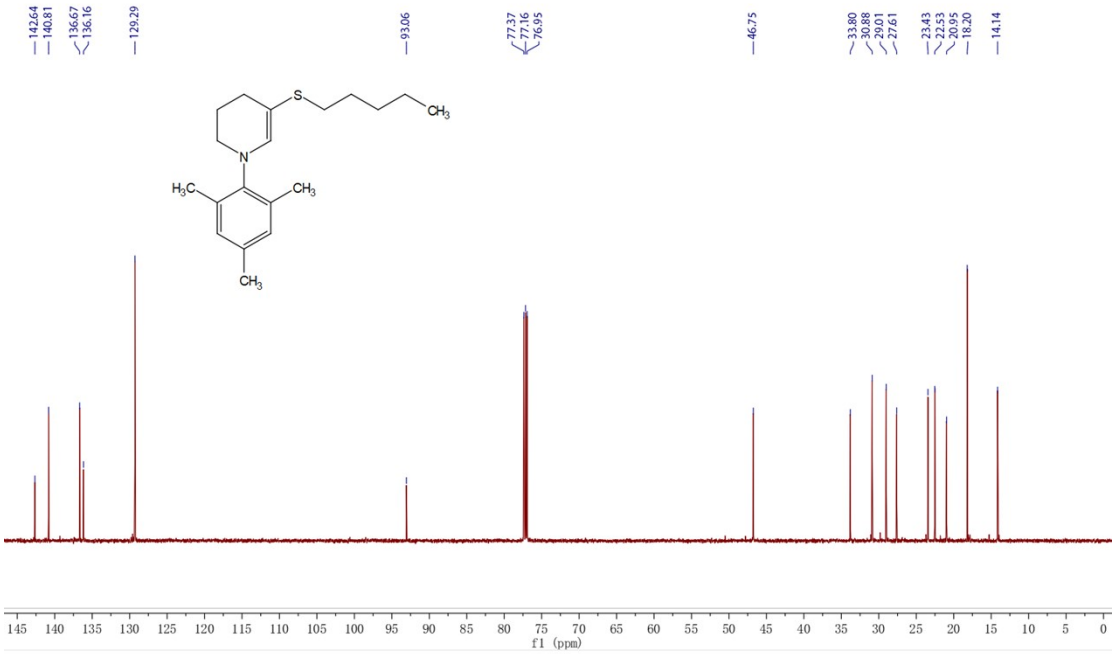
(45) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C21



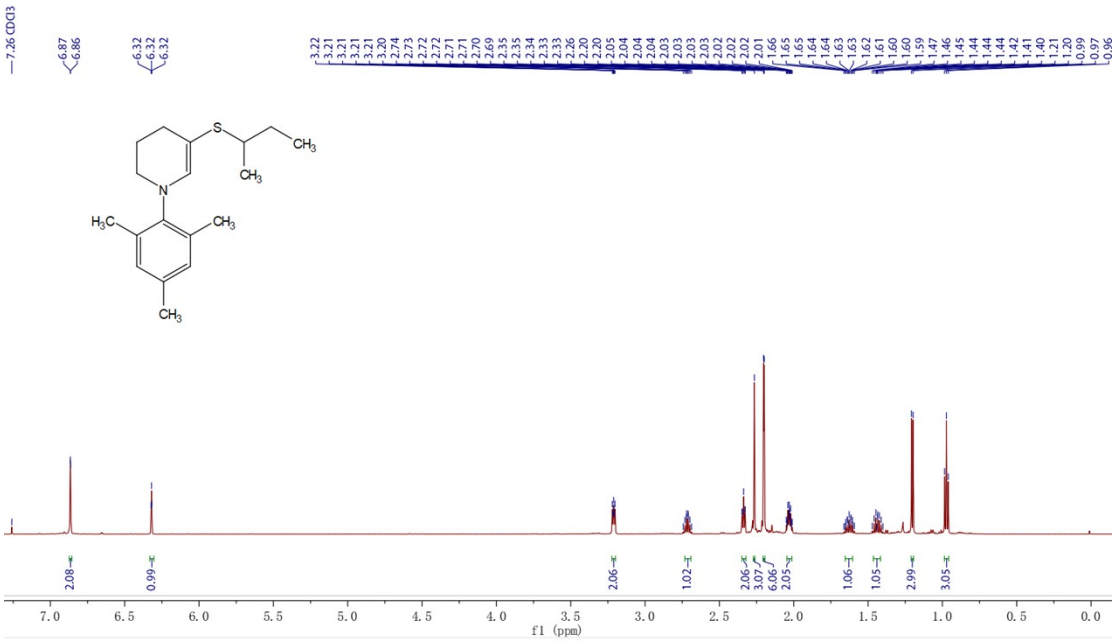
(46) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C22



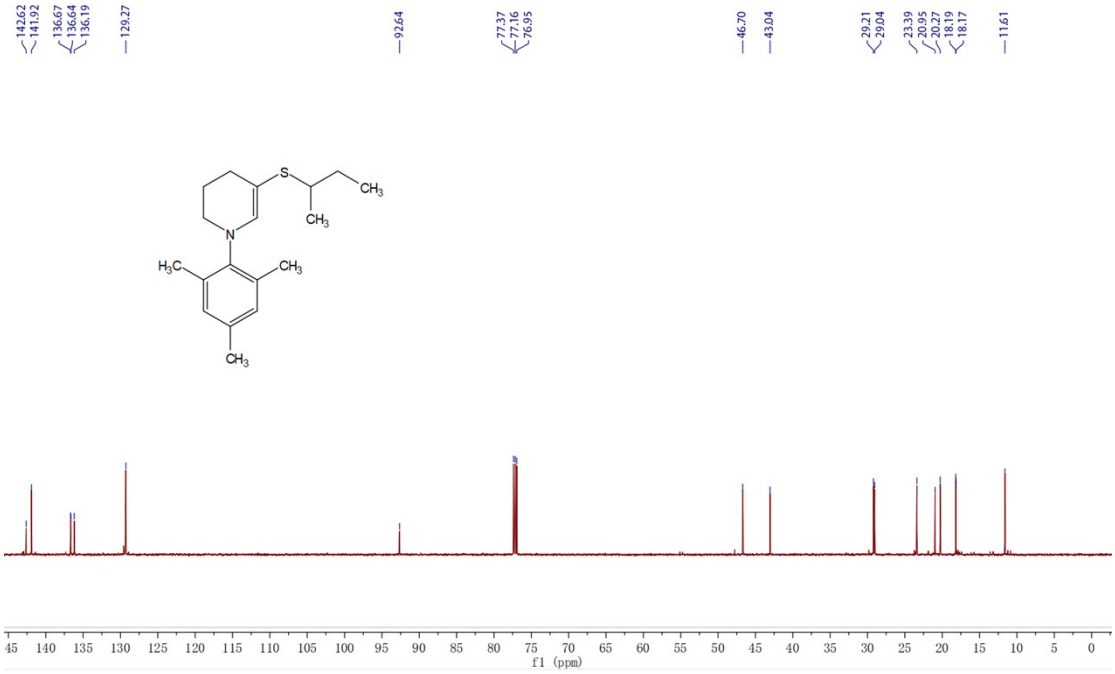
(47) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C22



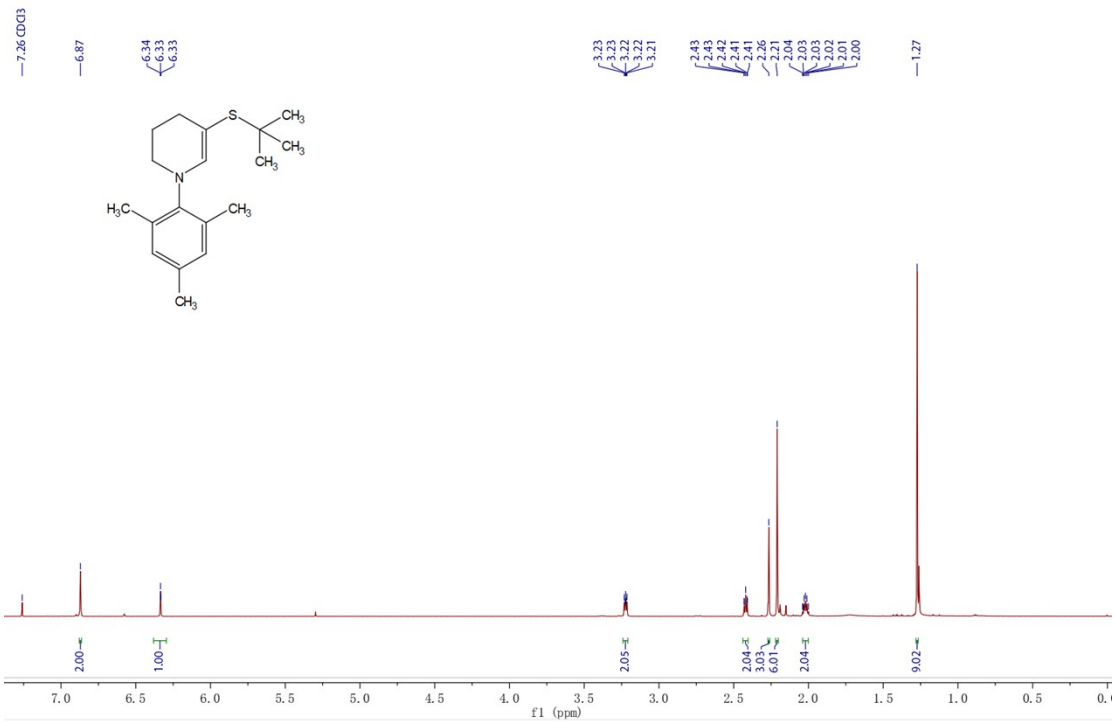
(48) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C23



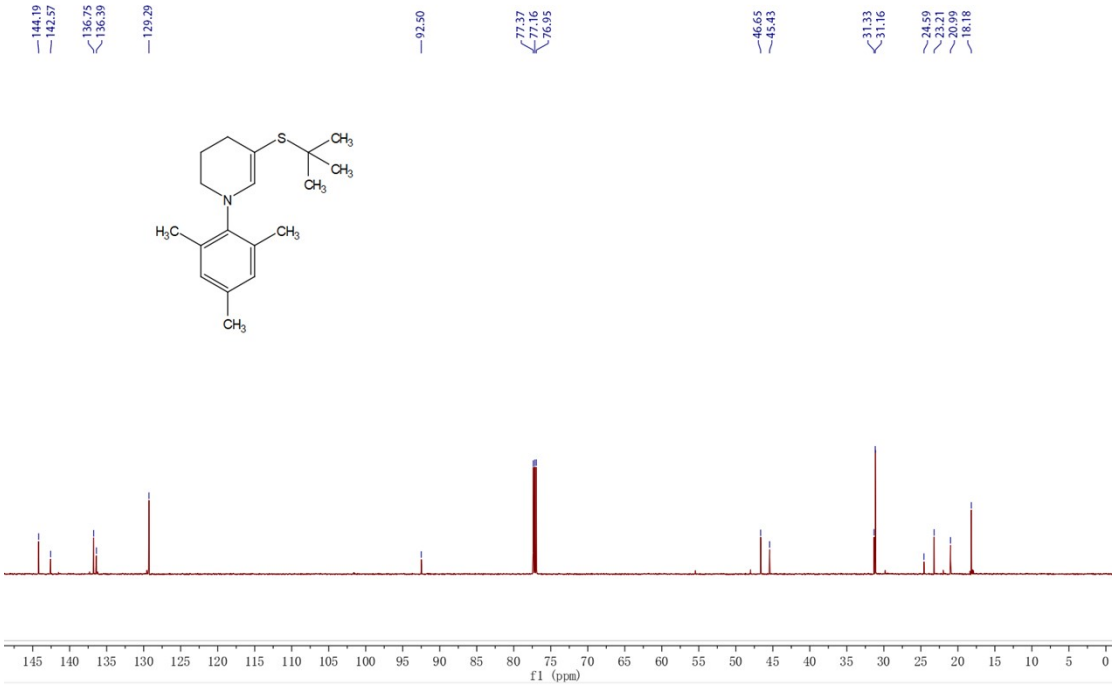
(49) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C23



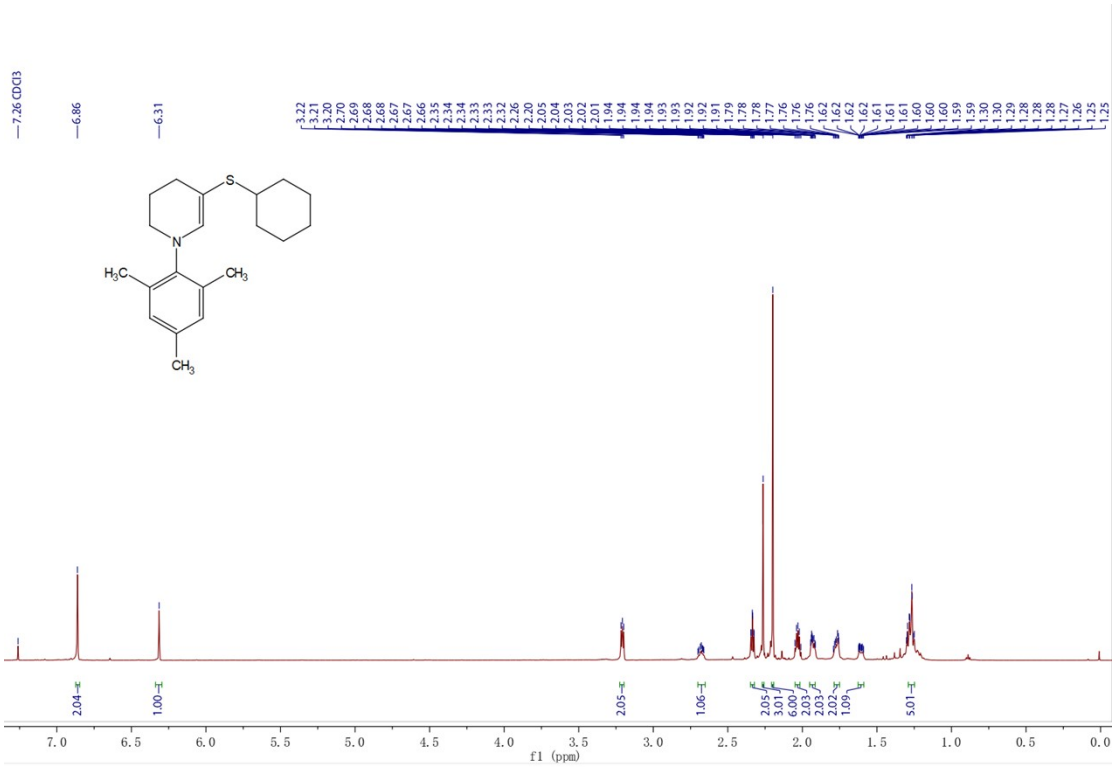
(50) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C24



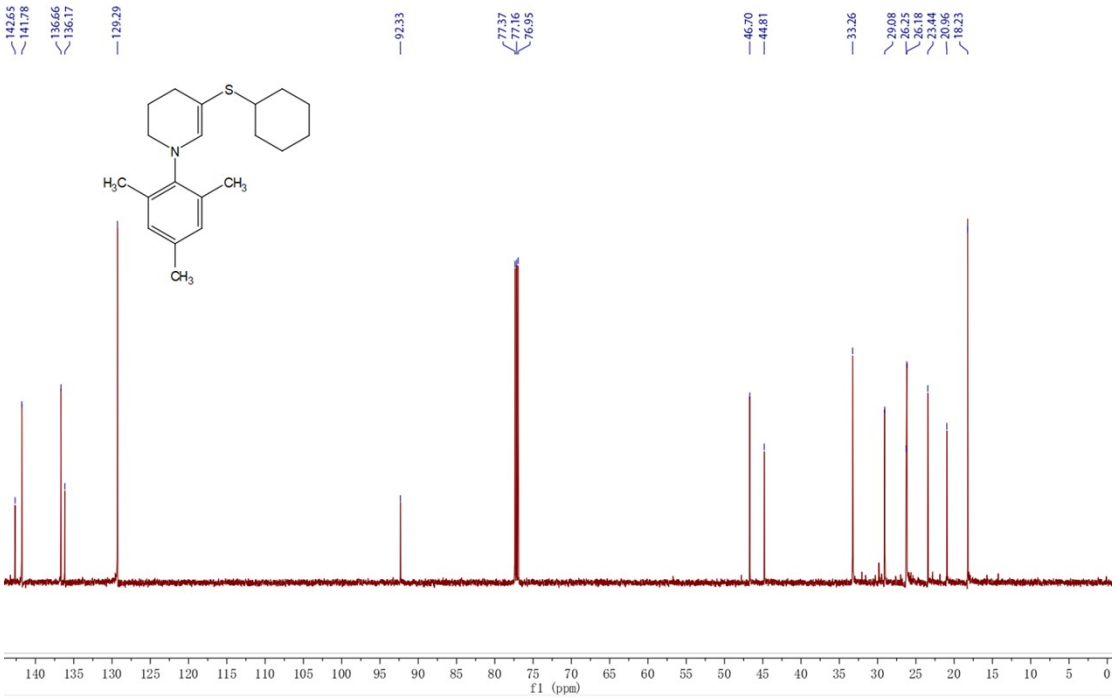
(51) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C24



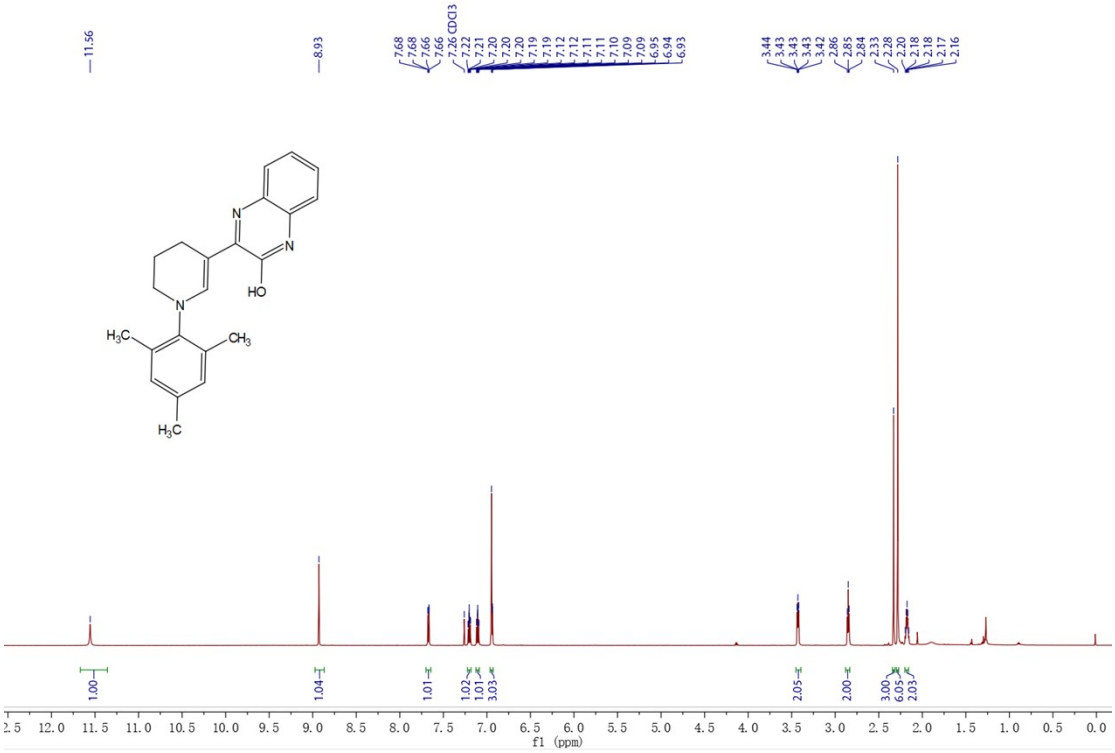
(52) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C25



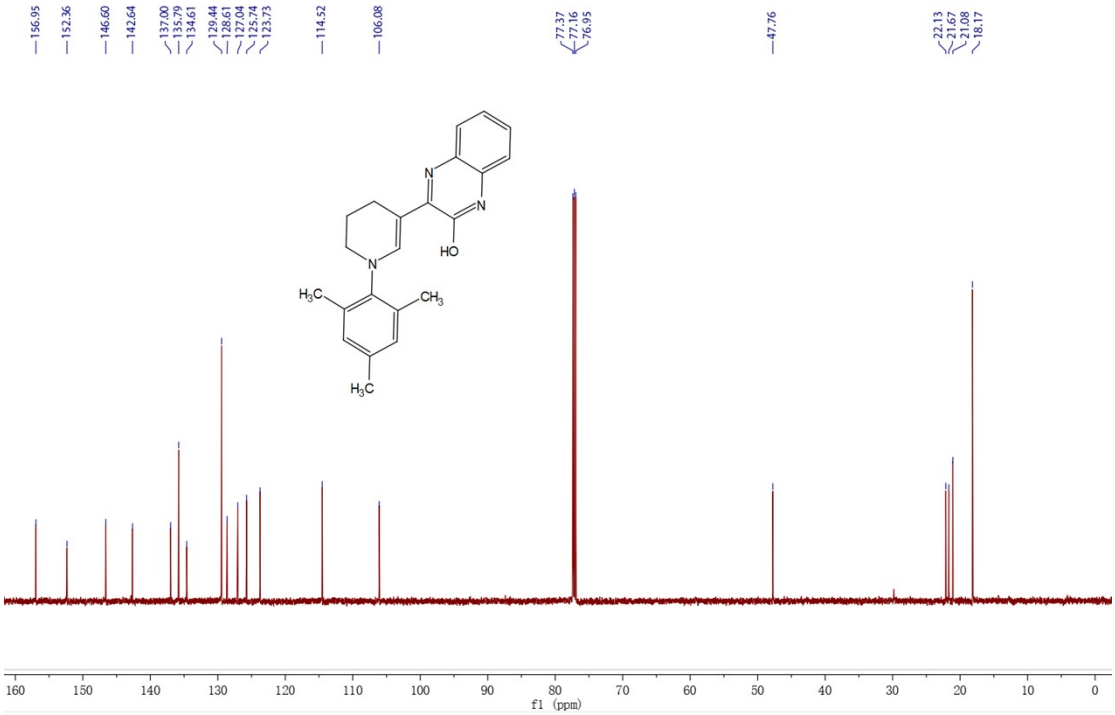
(53) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C25



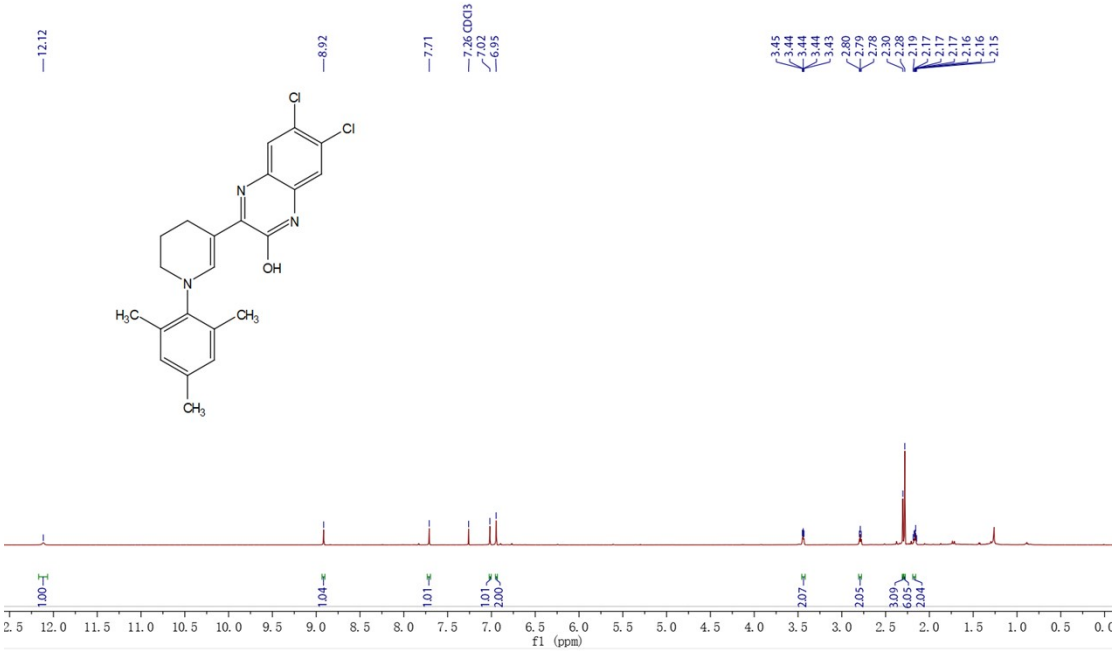
(54) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C26



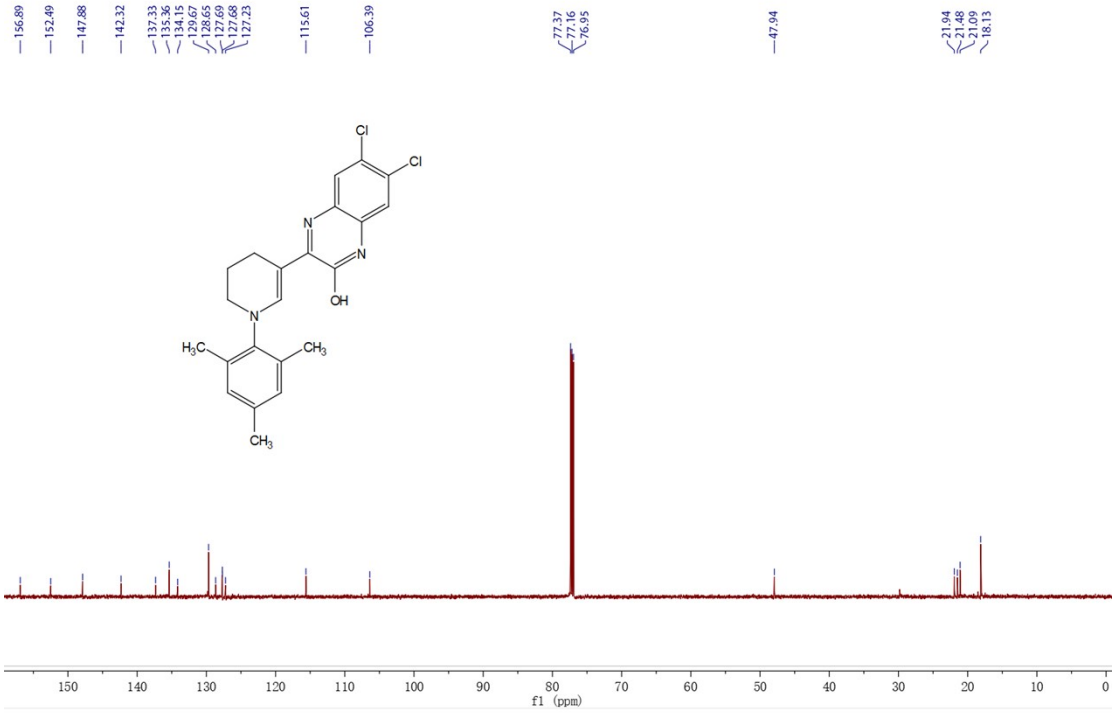
(55) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C26



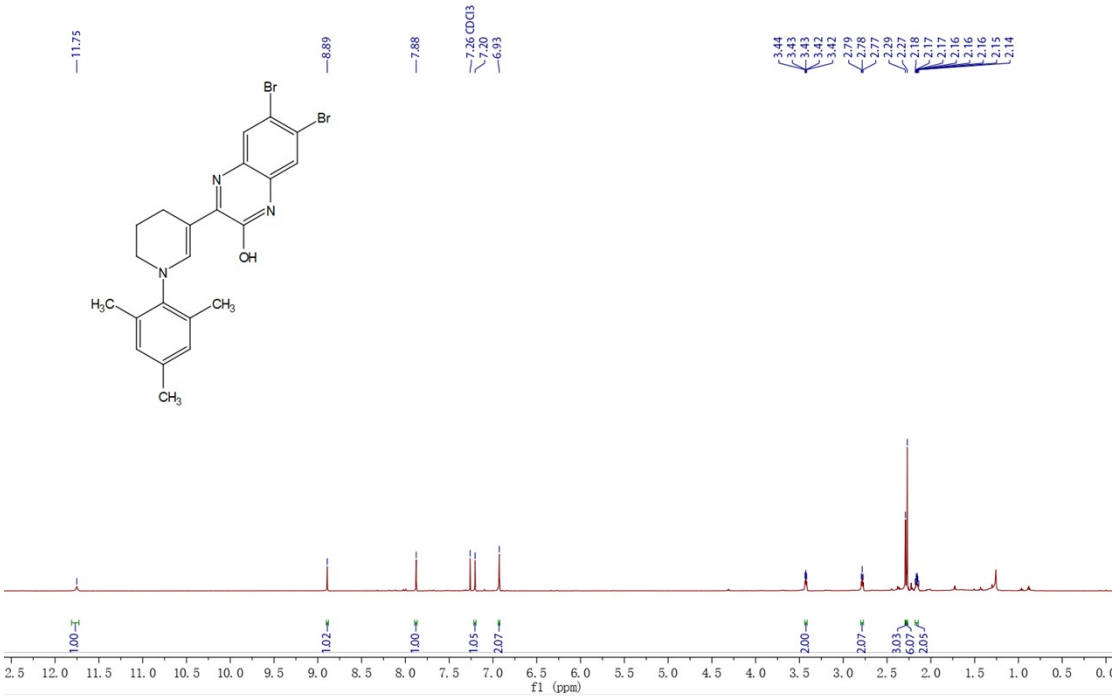
(56) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C27



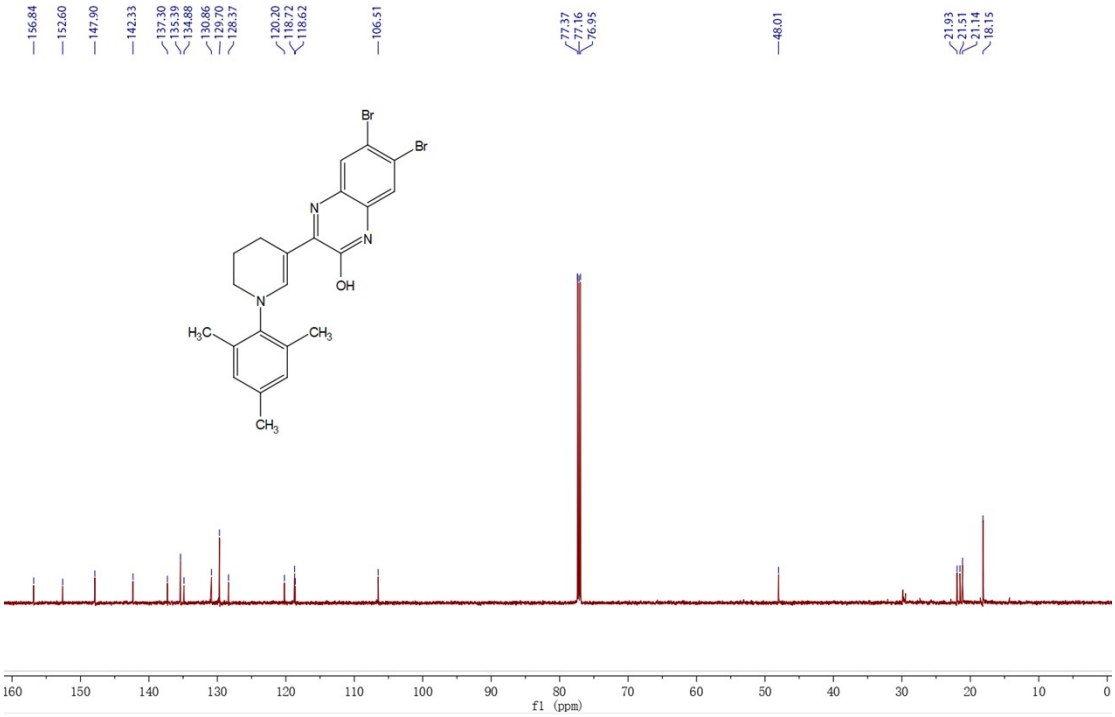
(57) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C27



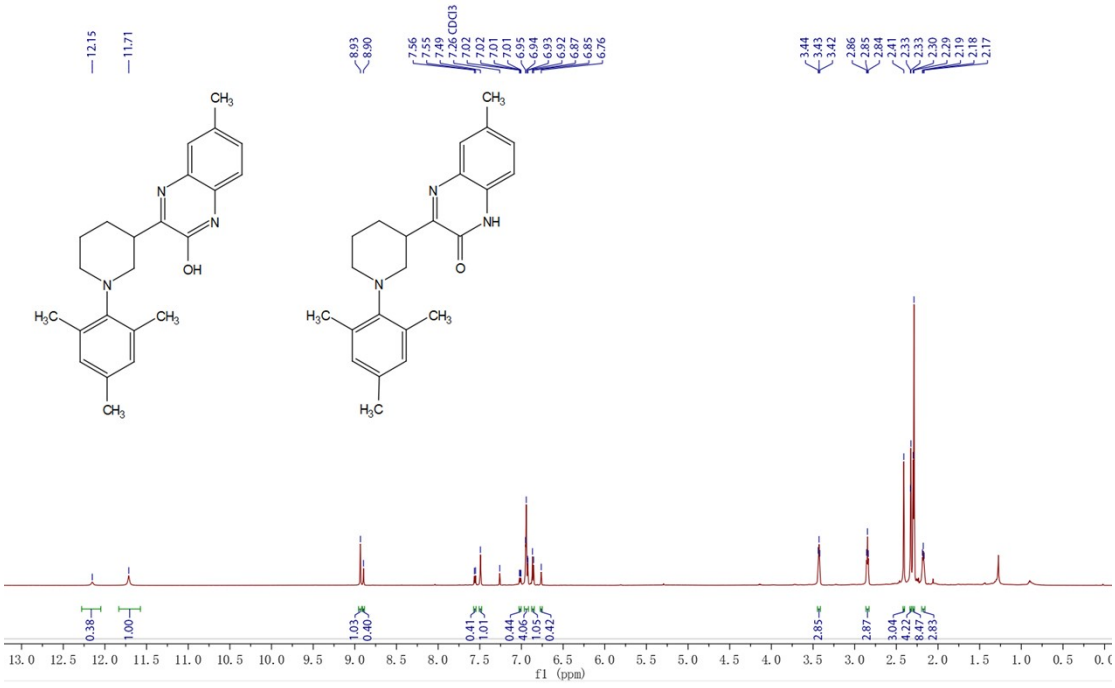
(58) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C28



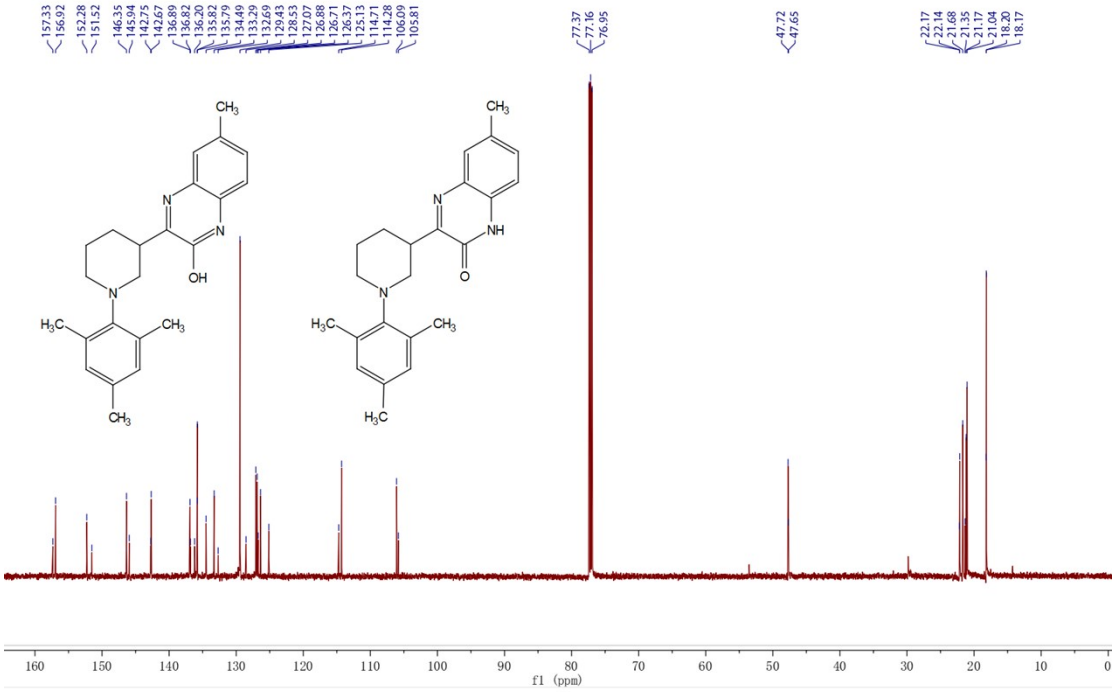
(59) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C28



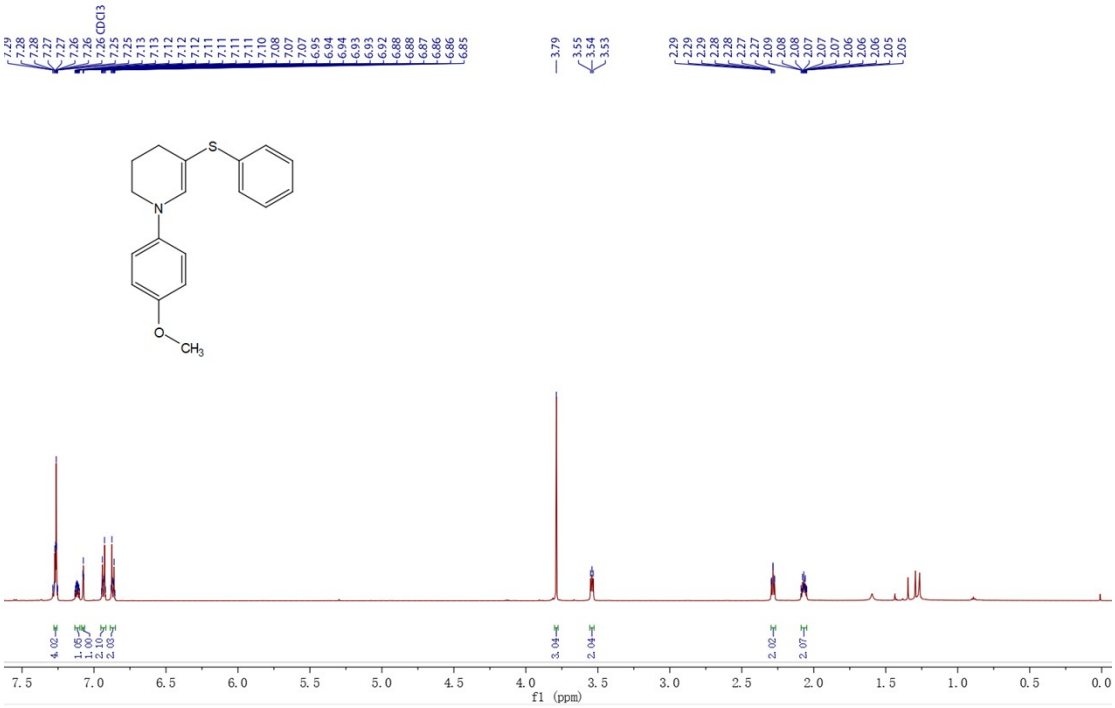
(60) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C29



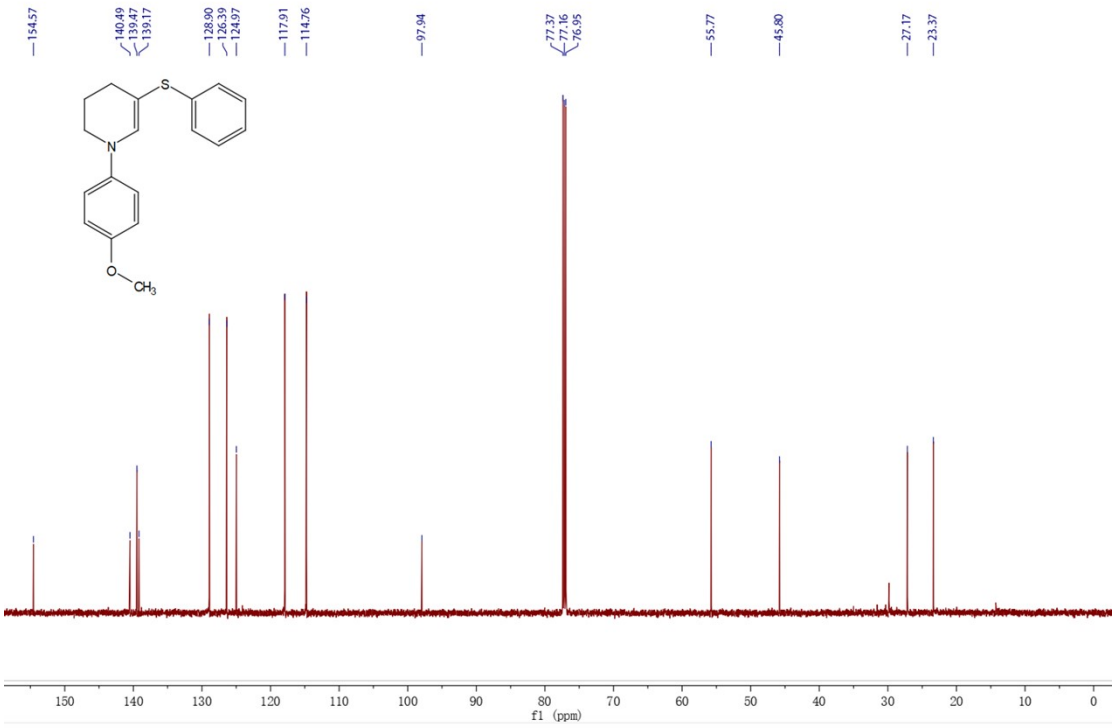
(61) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C29



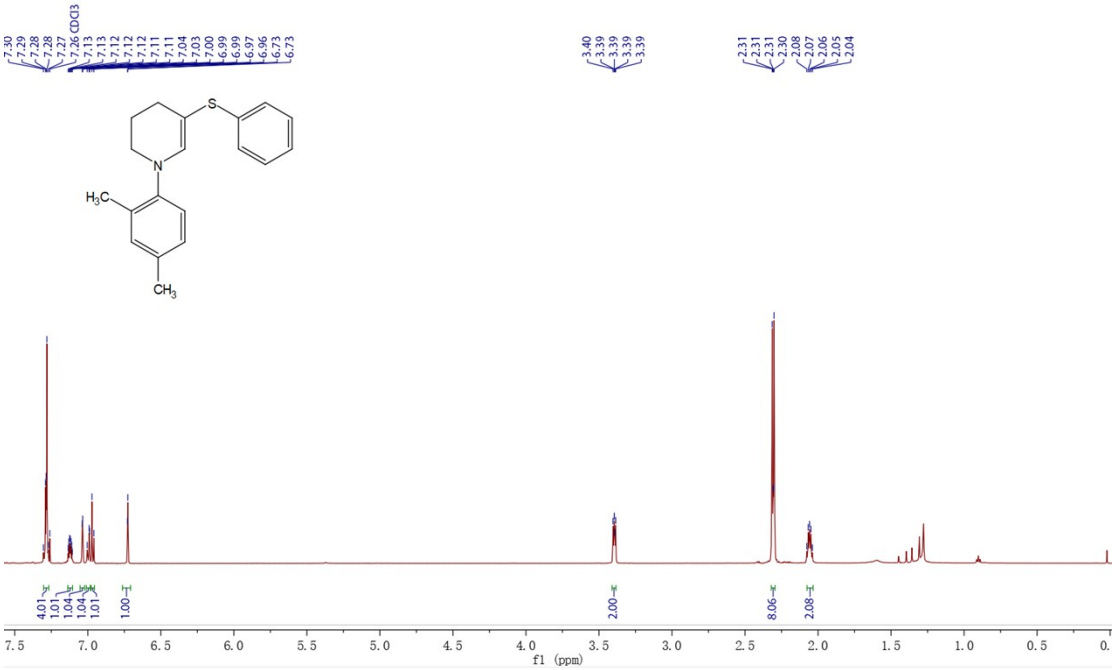
(62) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C30



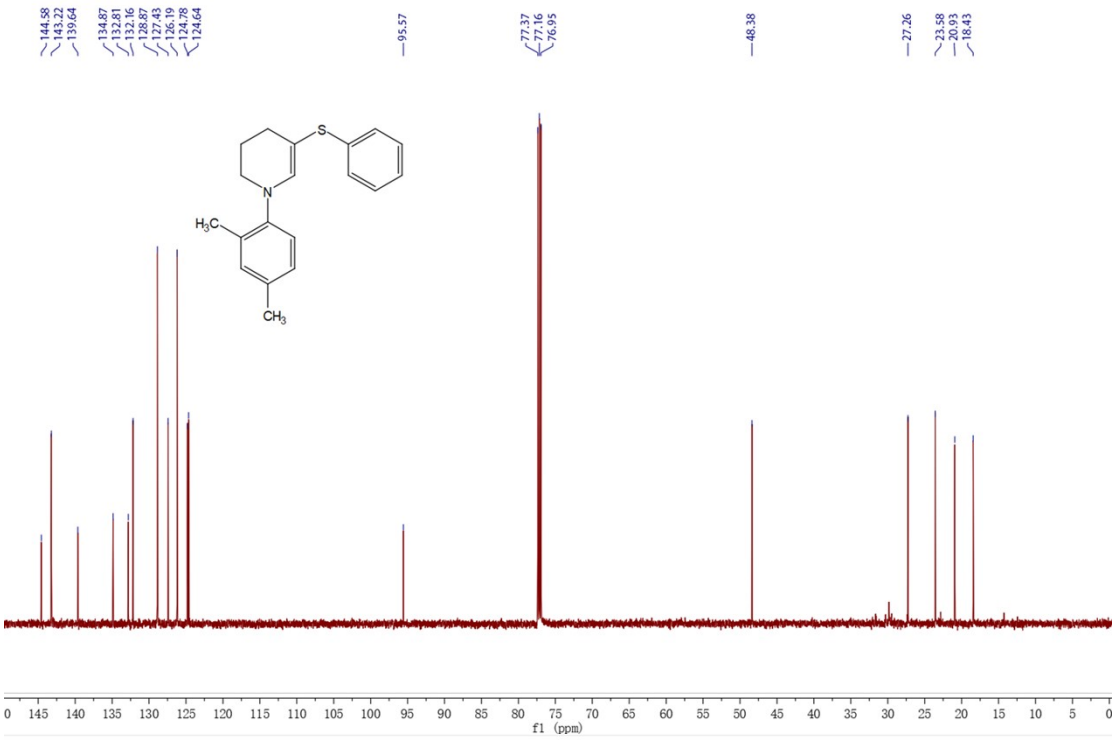
(63) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C30



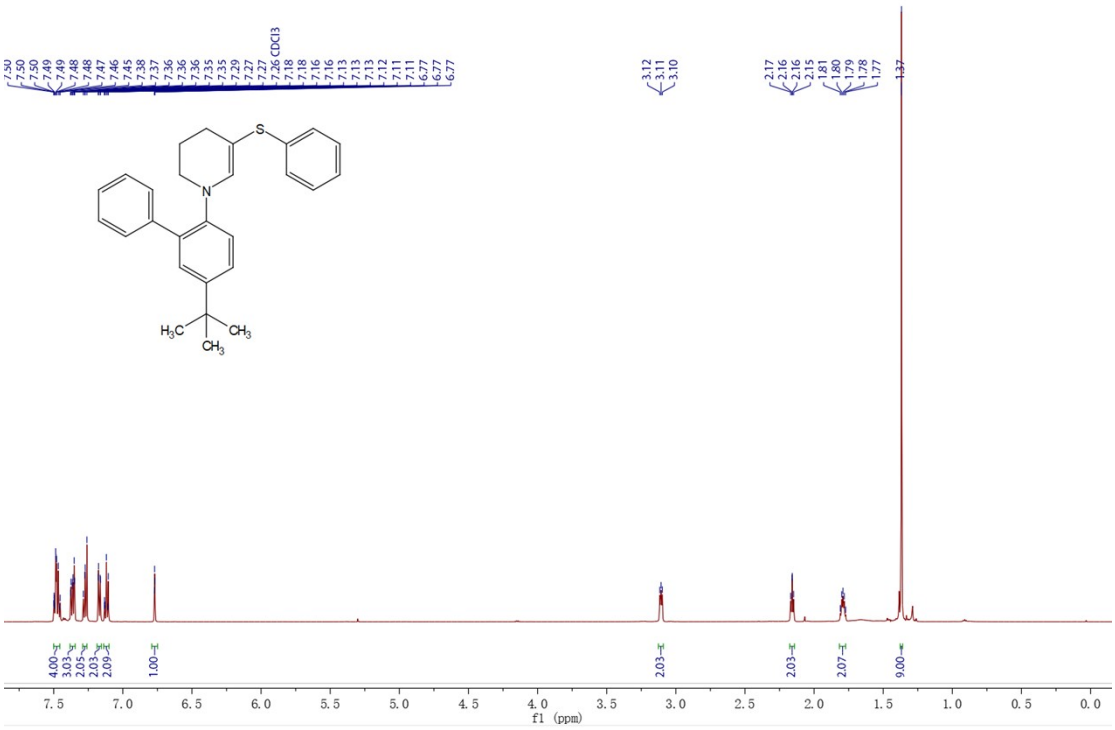
(64) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C31



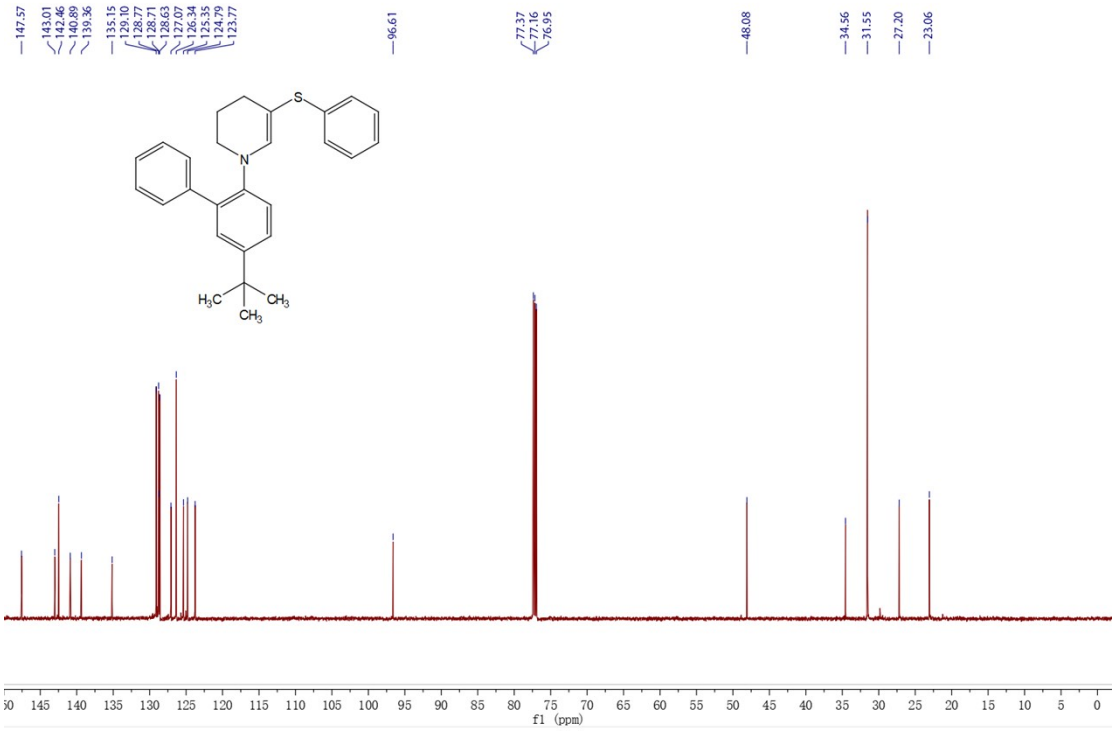
(65) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C31



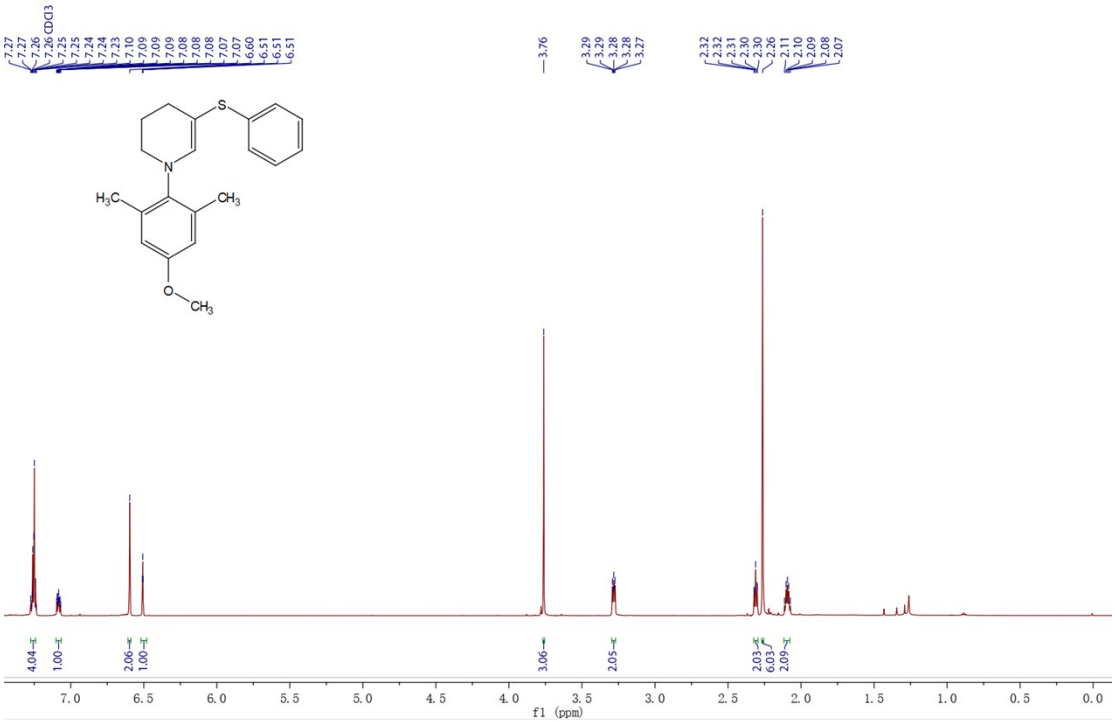
(66) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C32



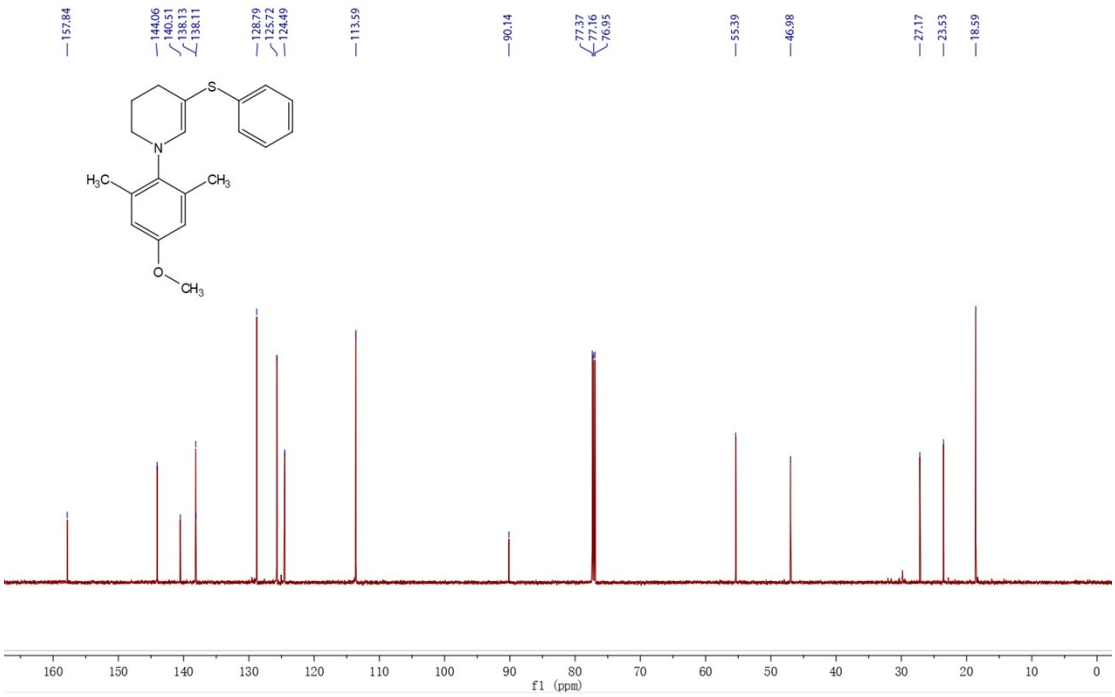
(67) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C32



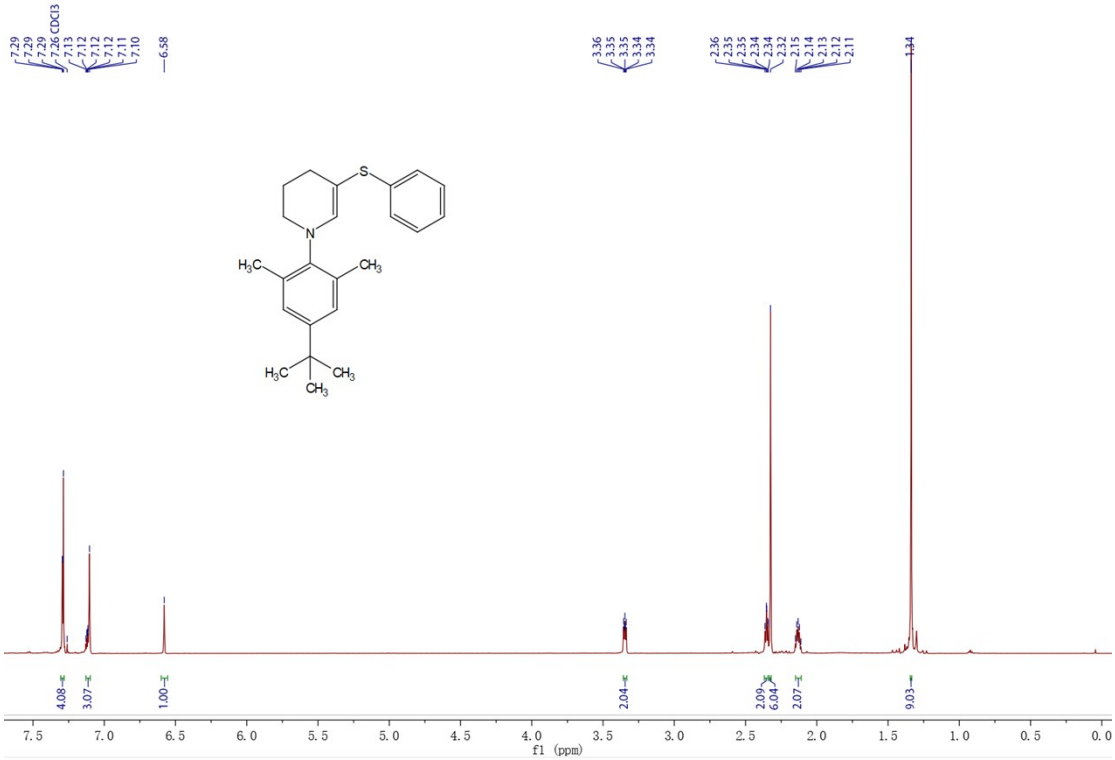
(68) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C33



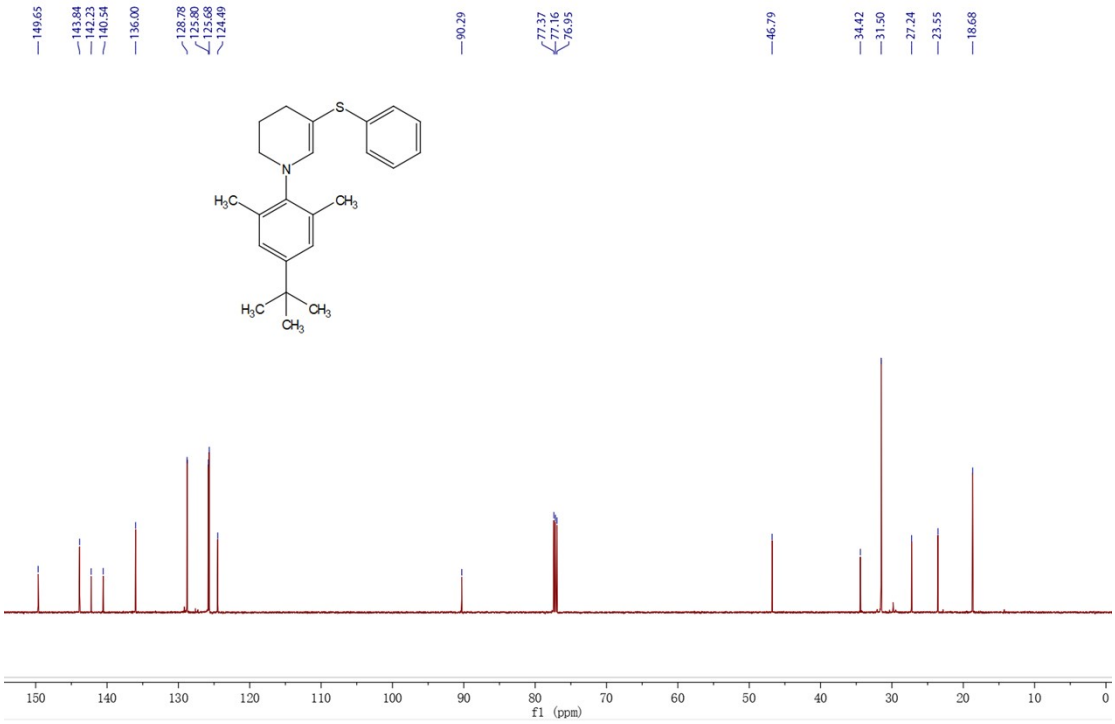
(69) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C33



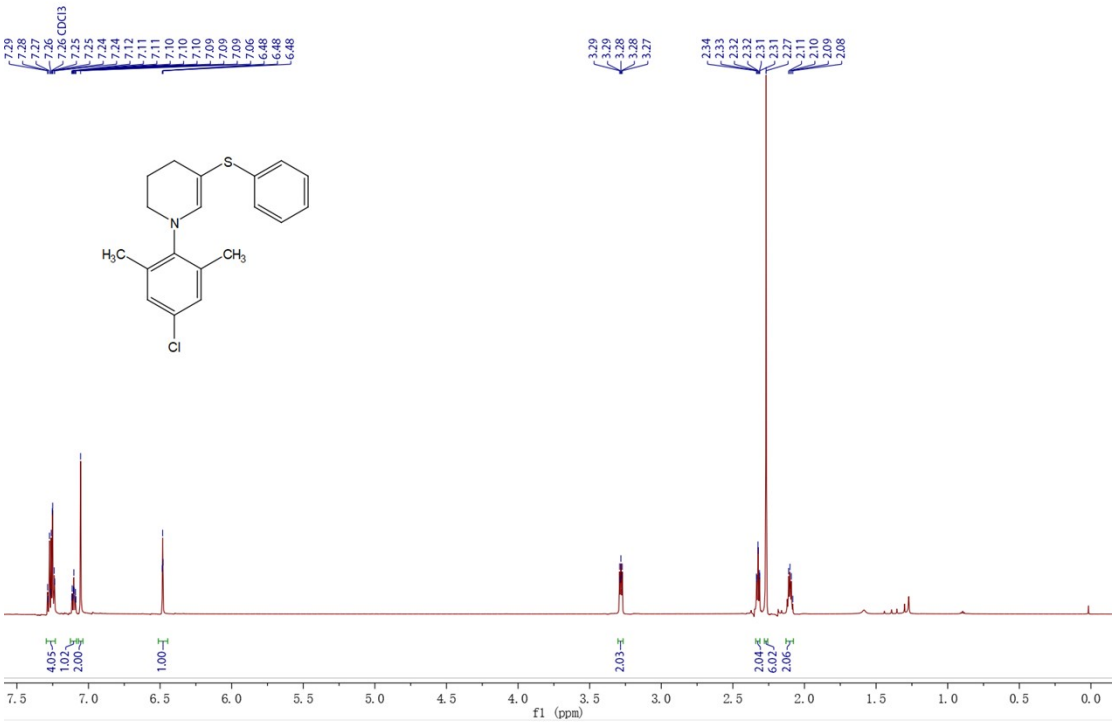
(70) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C34



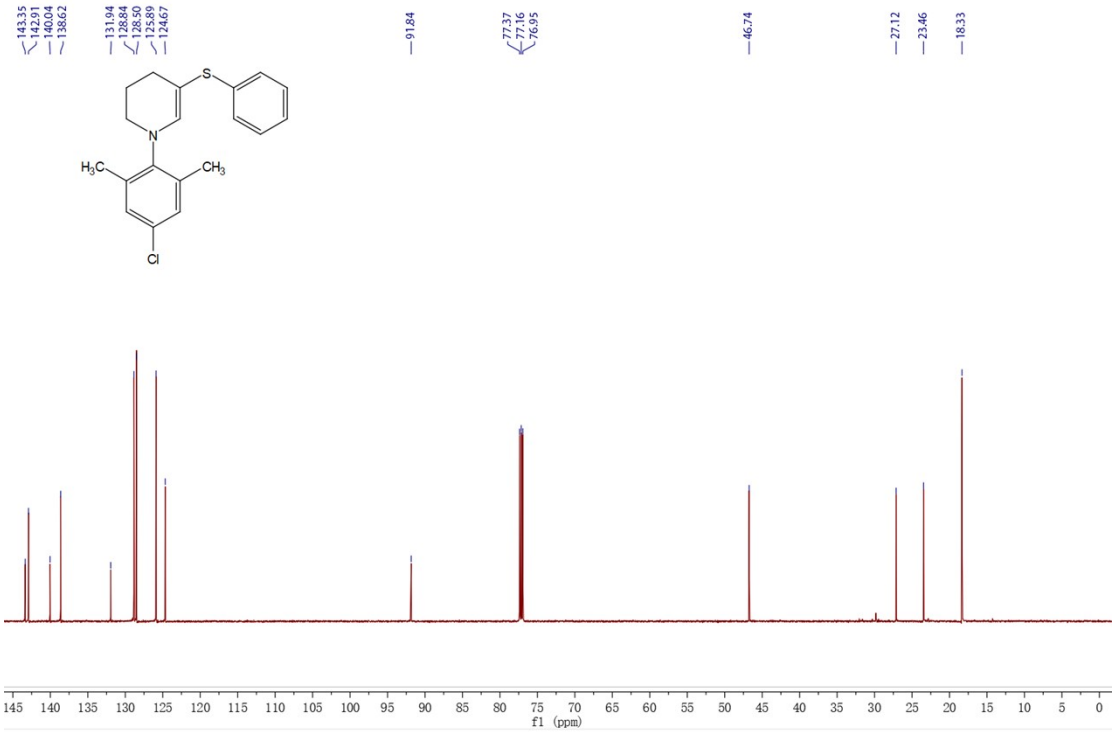
(71) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C34



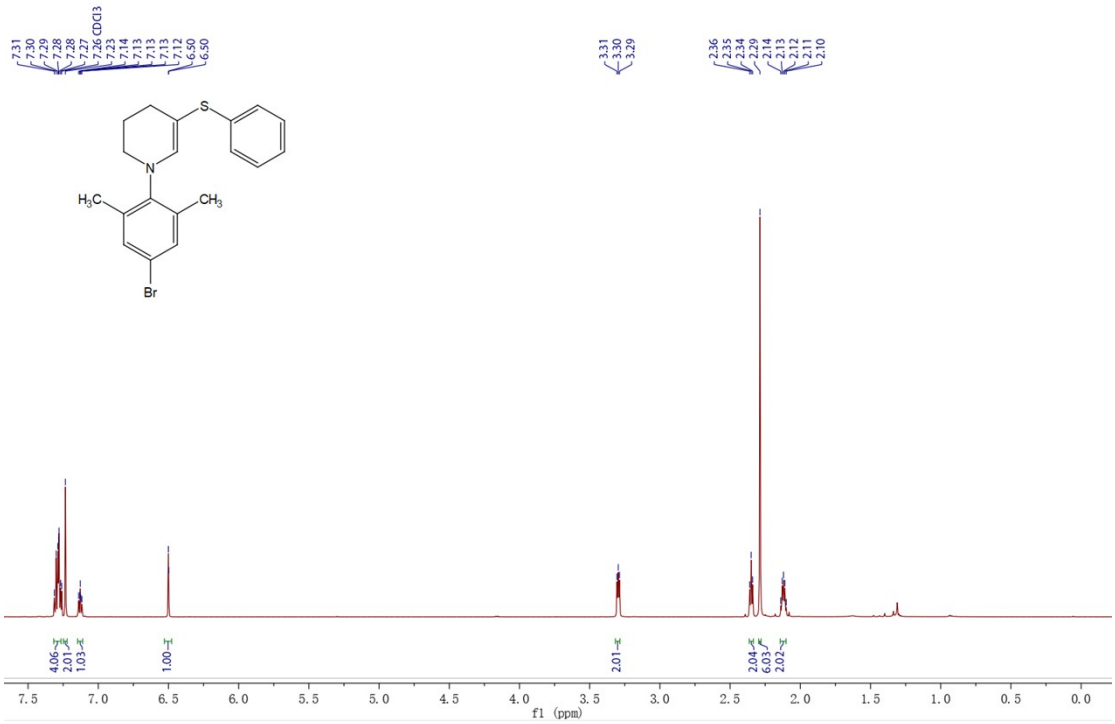
(72) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C35



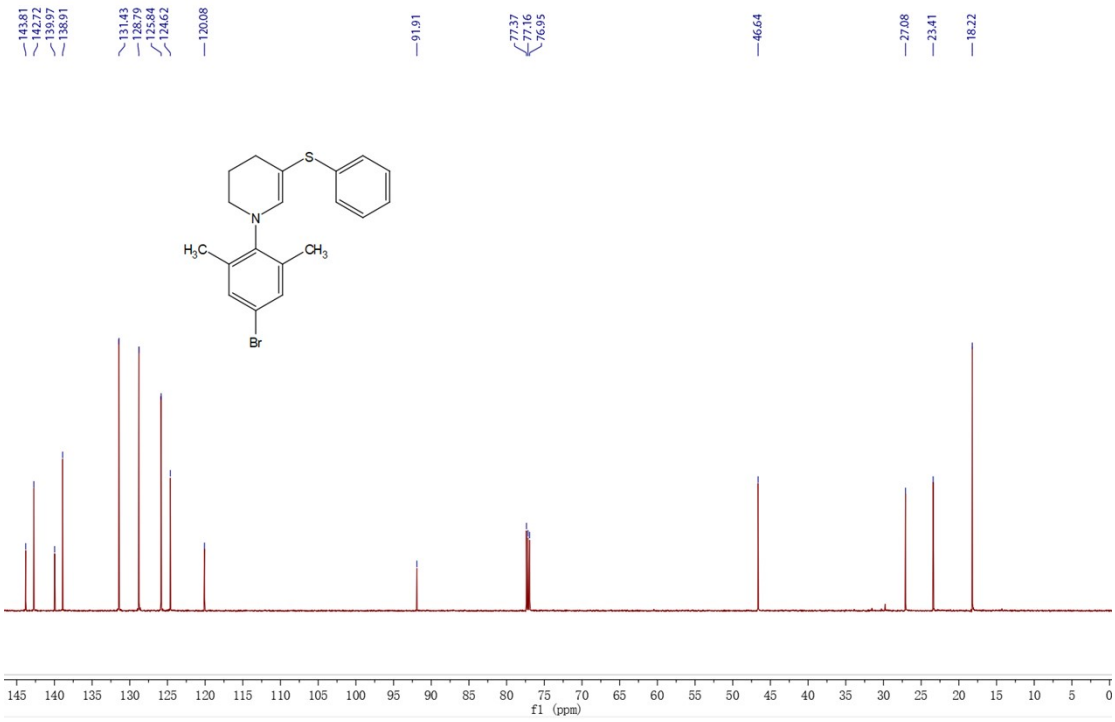
(73) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C35



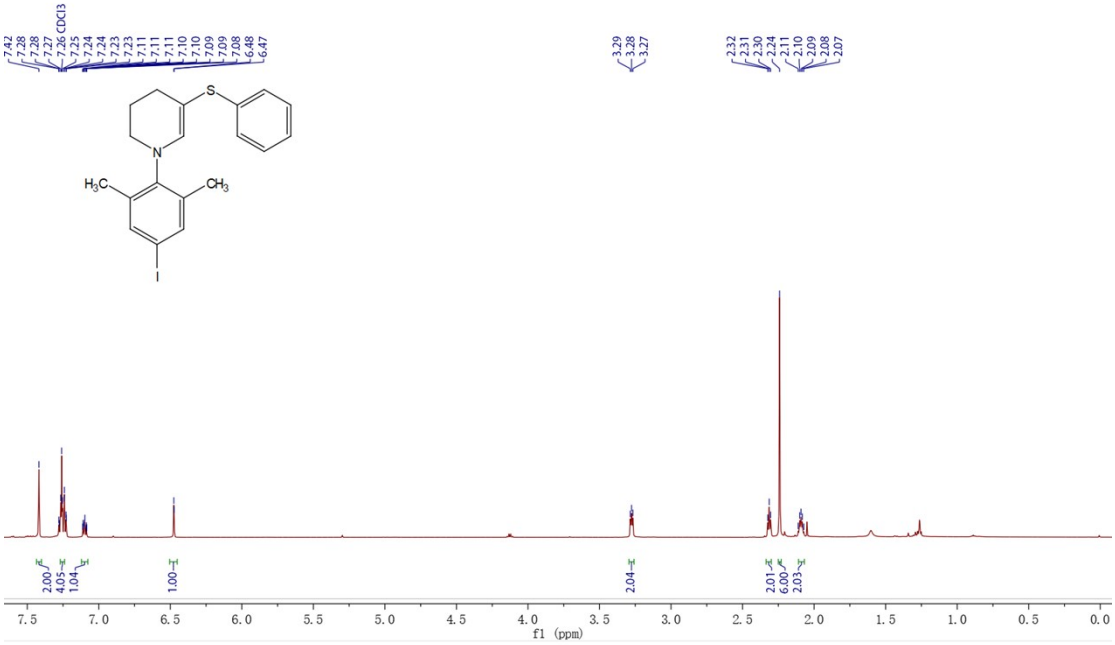
(74) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C36



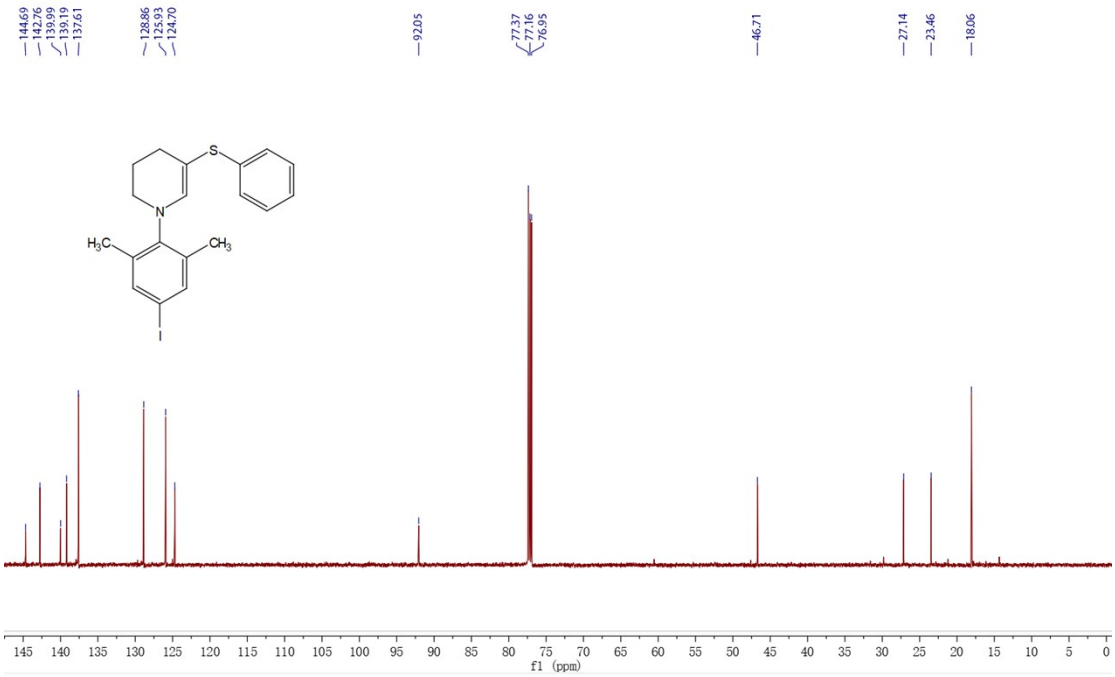
(75) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C36



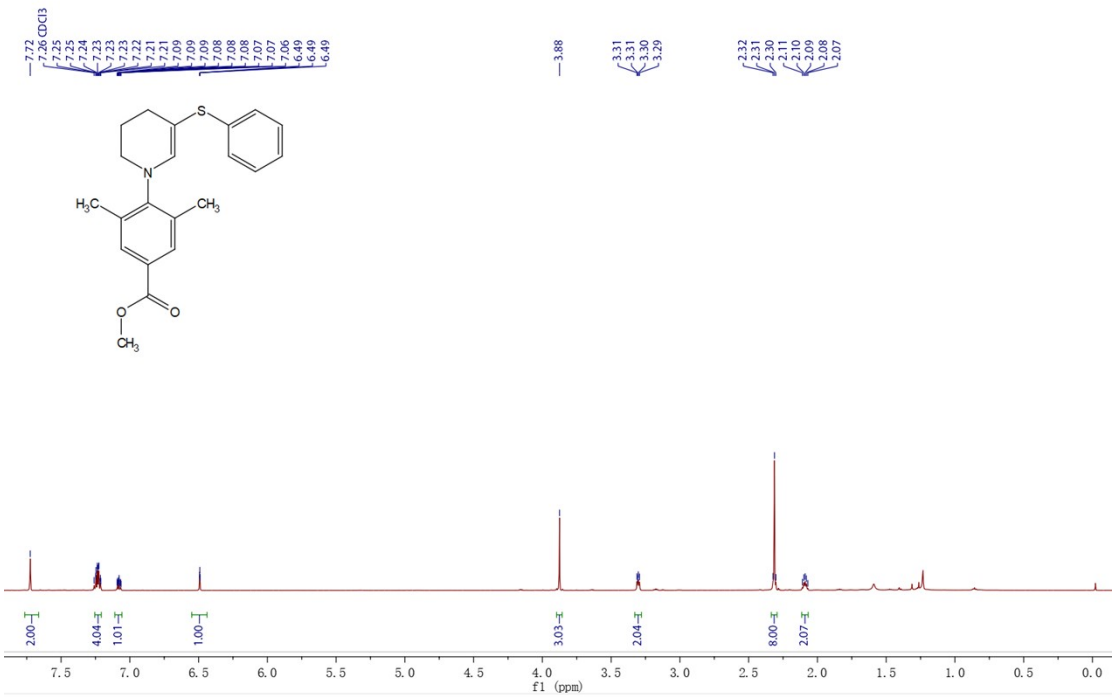
(76) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C37



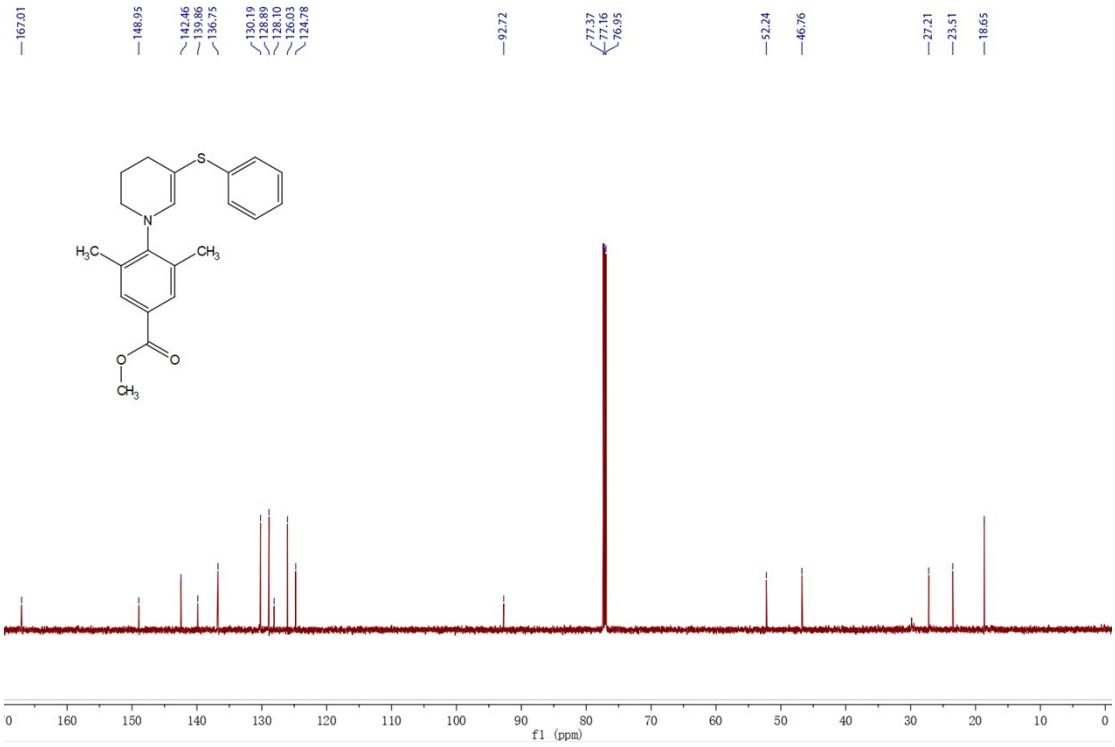
(77) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C37



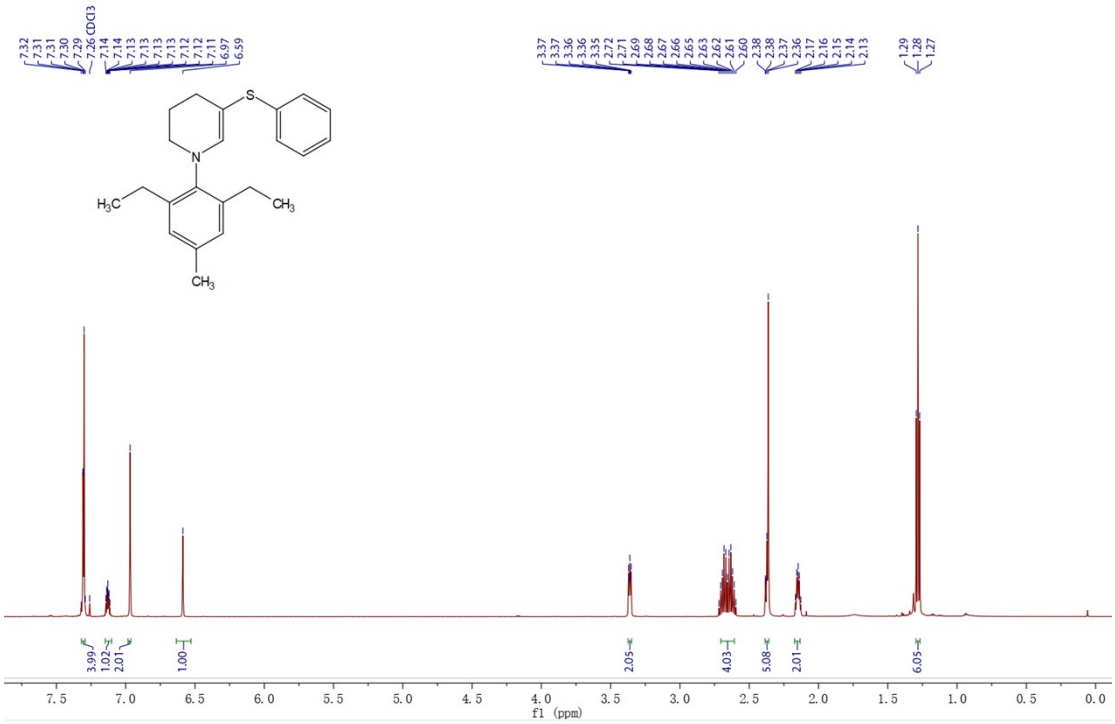
(78) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C38



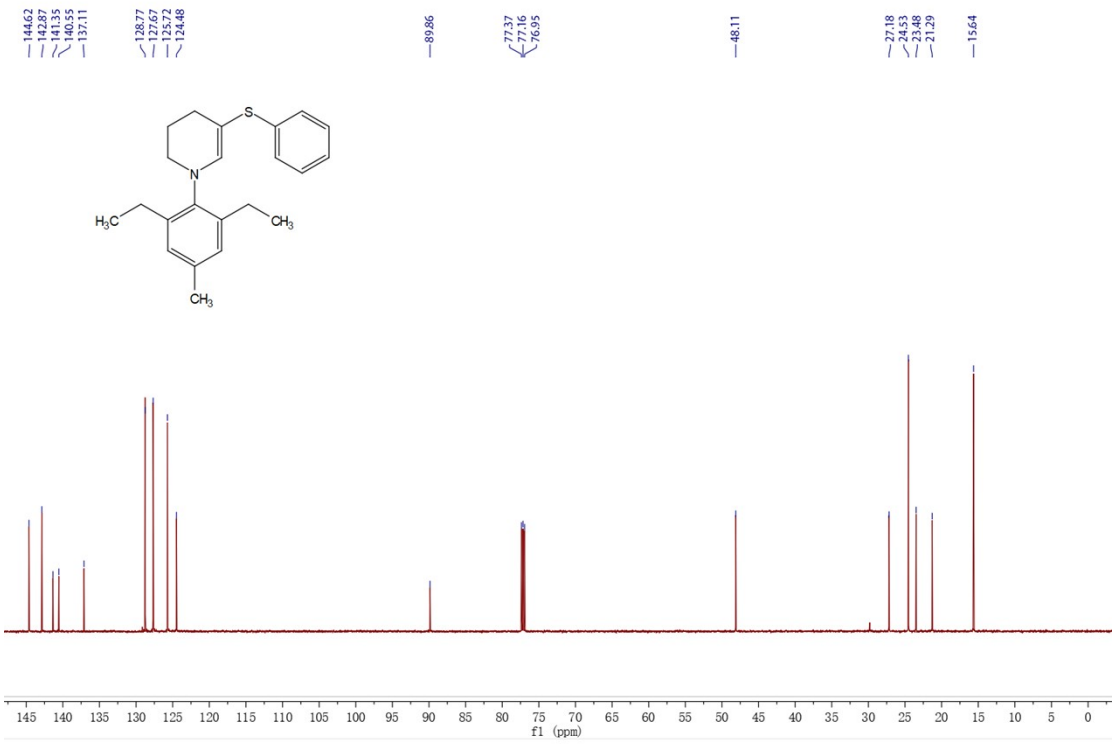
(79 ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C38



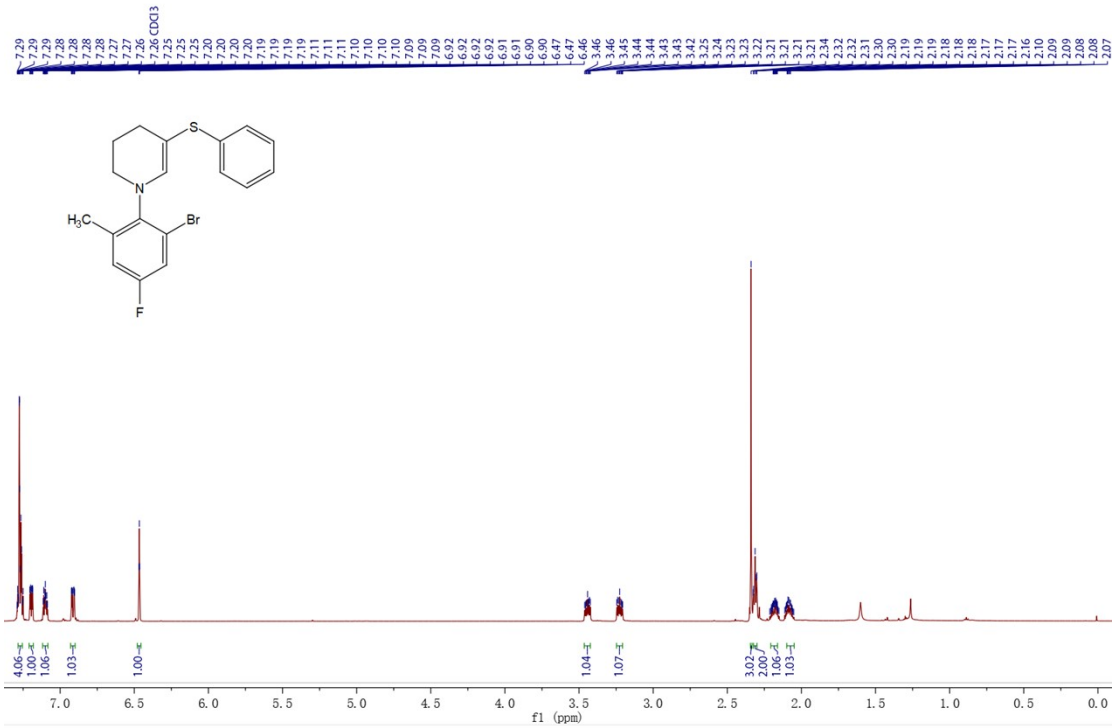
(80 ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C39



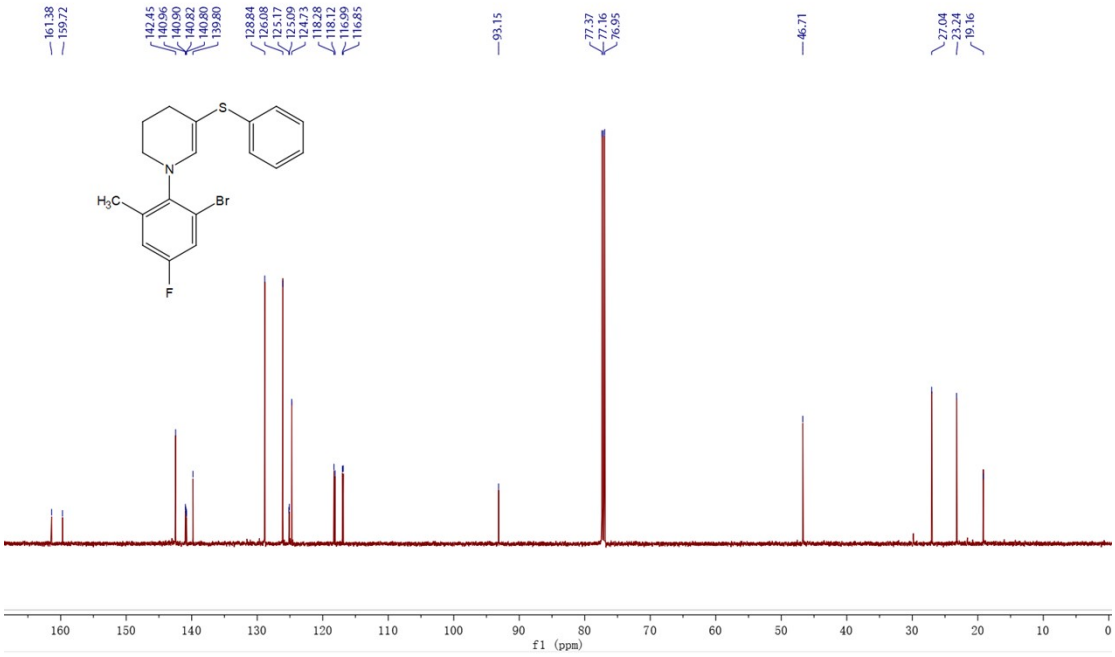
(79) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C39



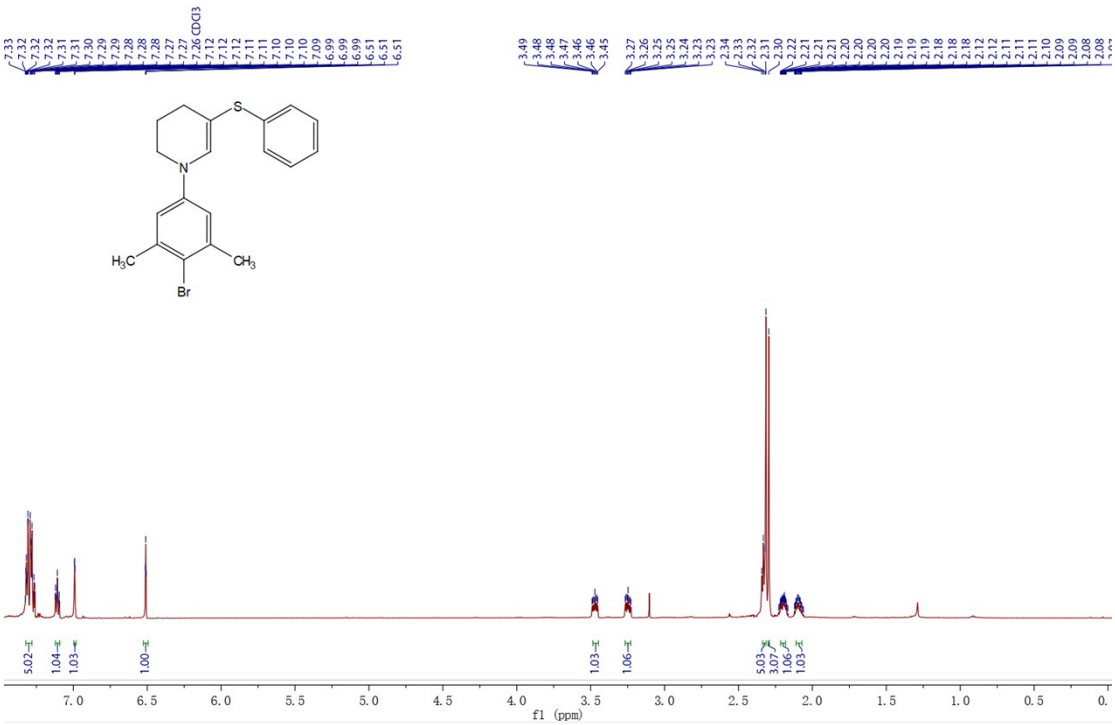
(80) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C40



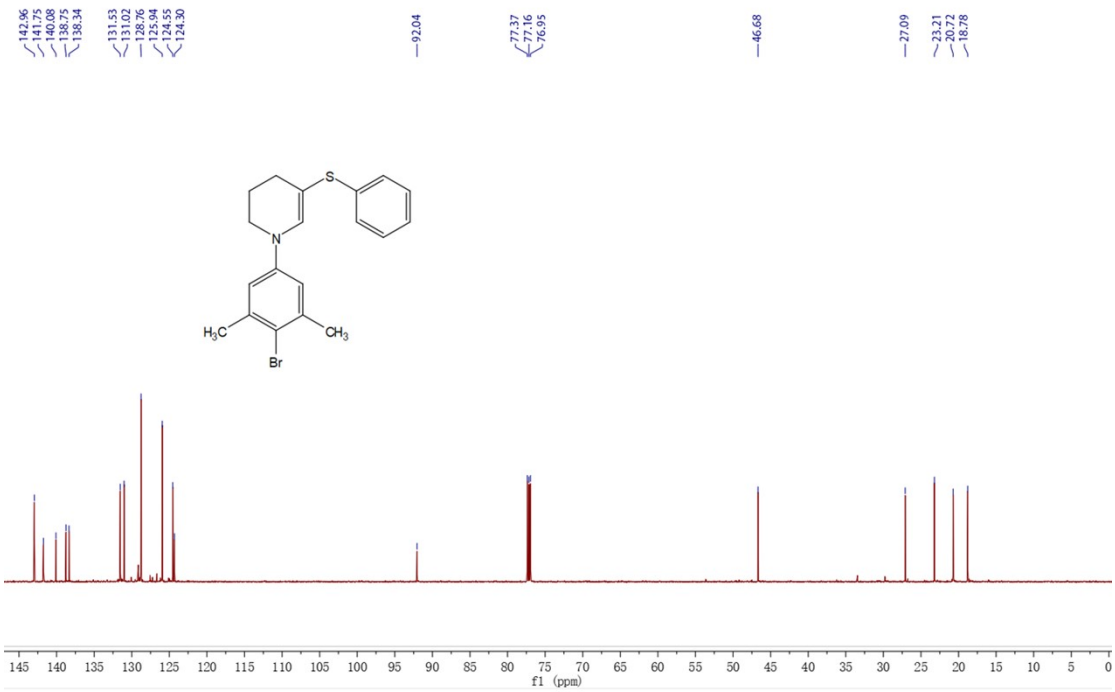
(81) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C40



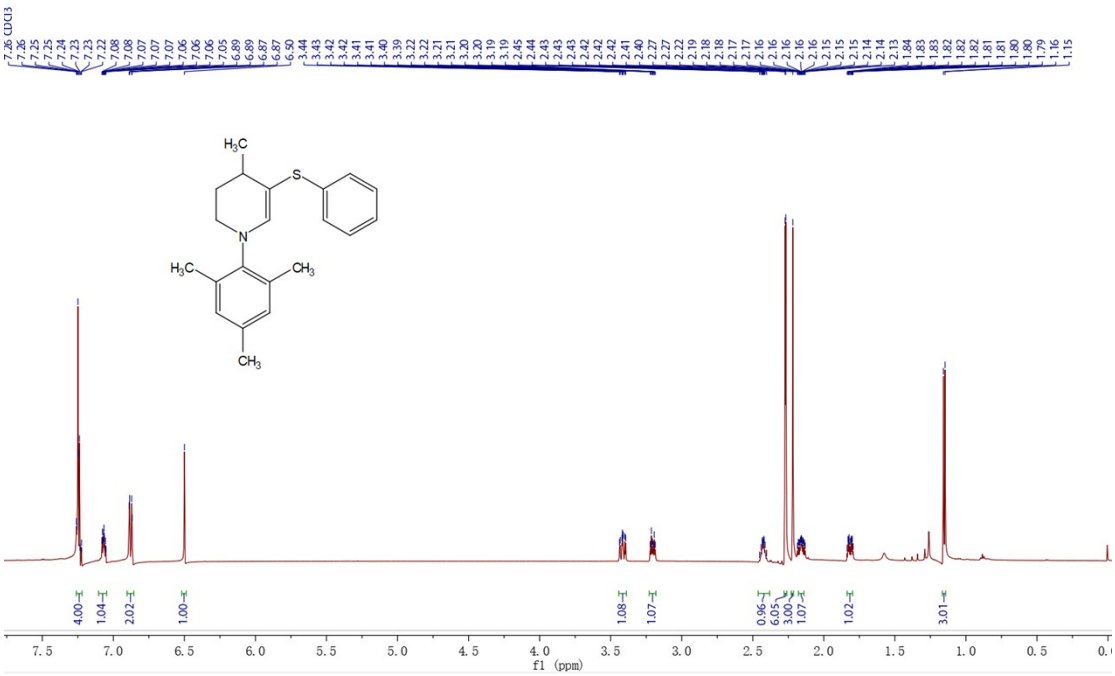
(82) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C41



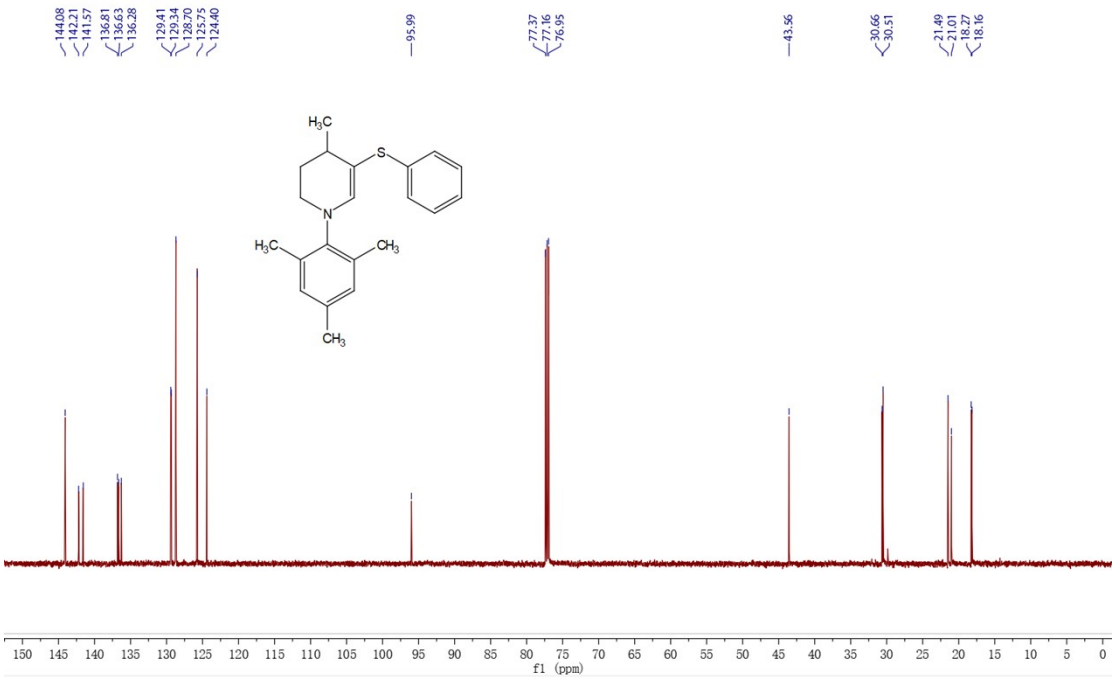
(83) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C41



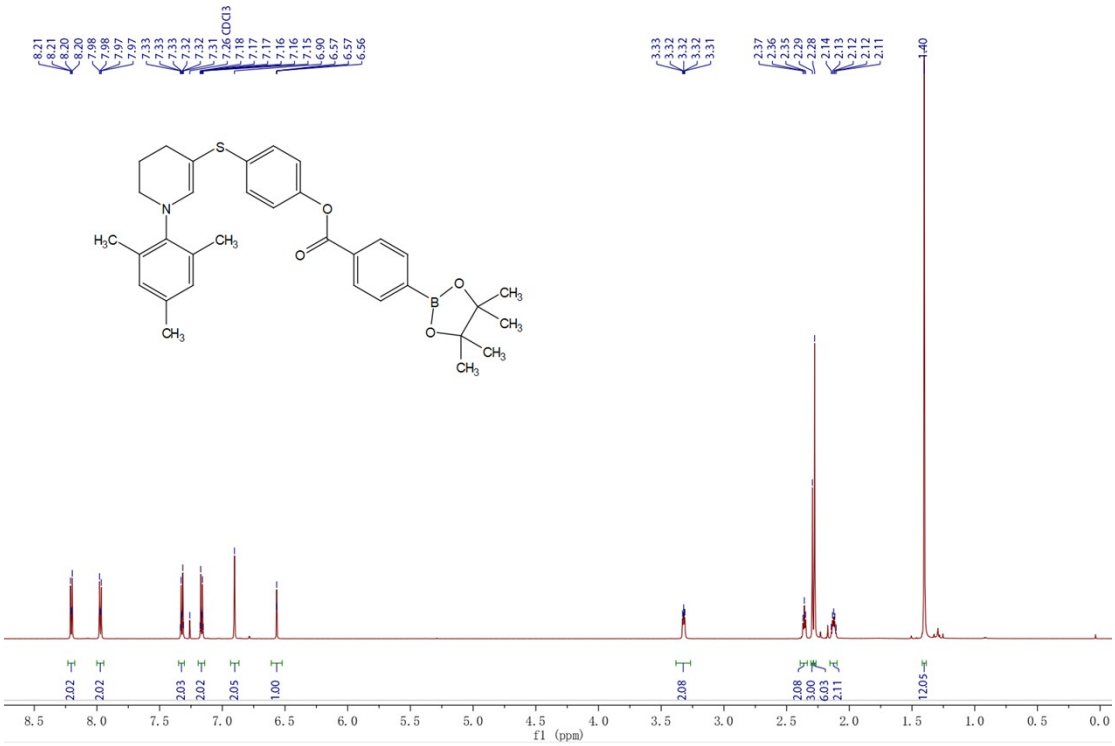
(84) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C42



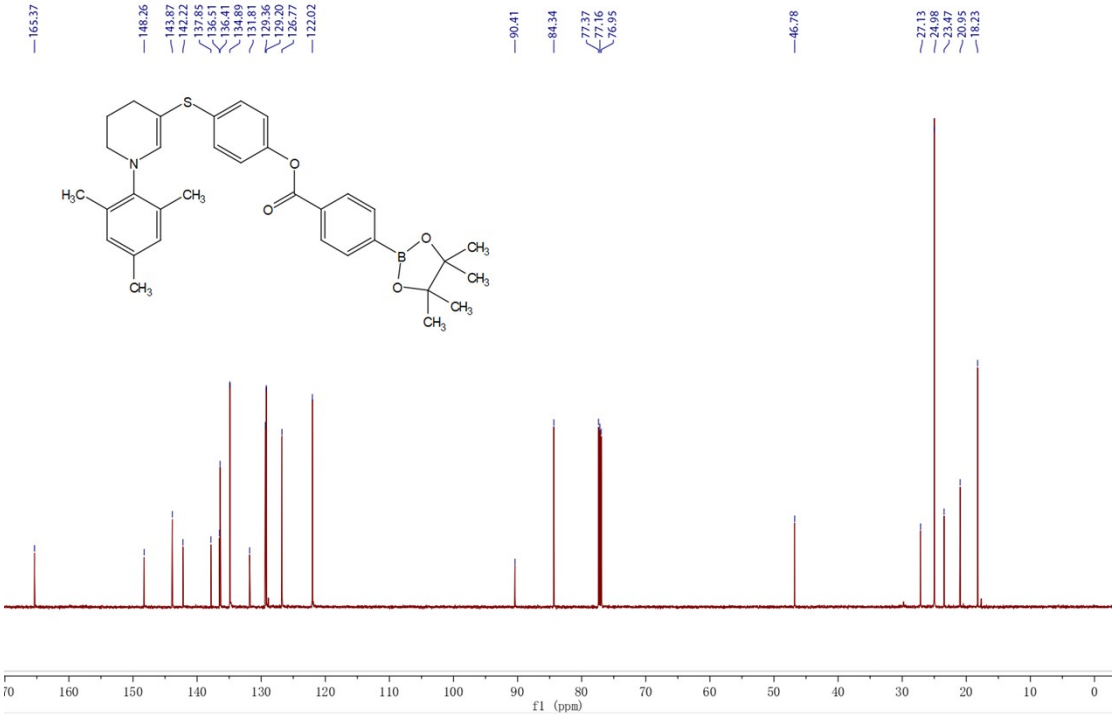
(85) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C42



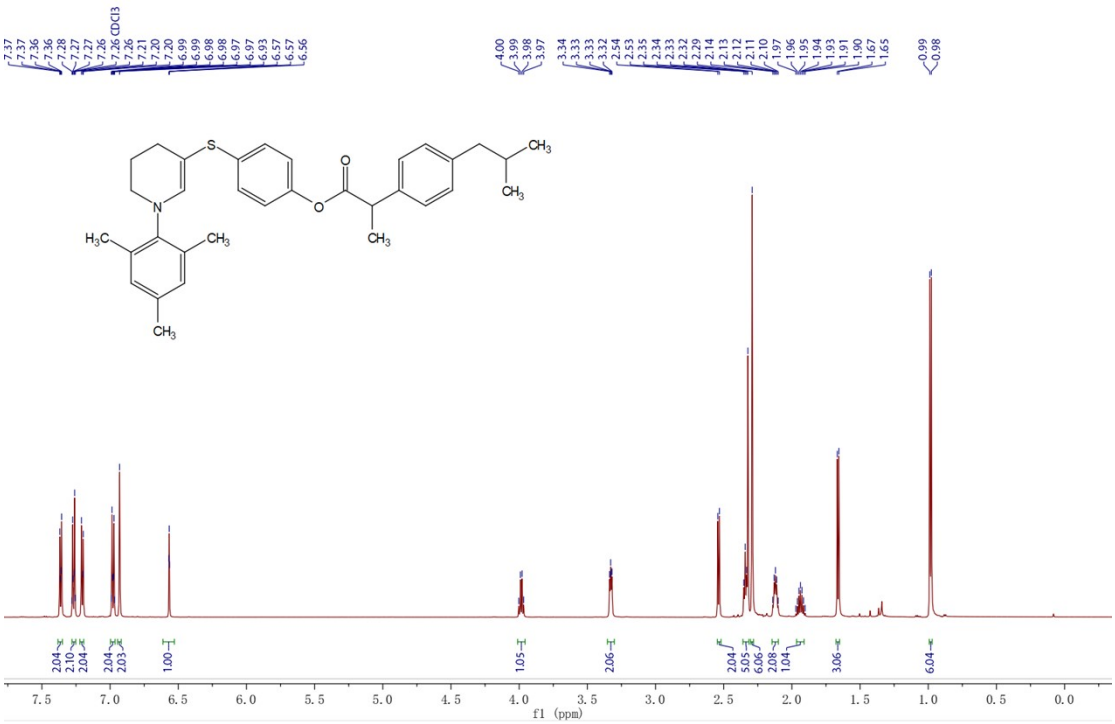
(86) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C43



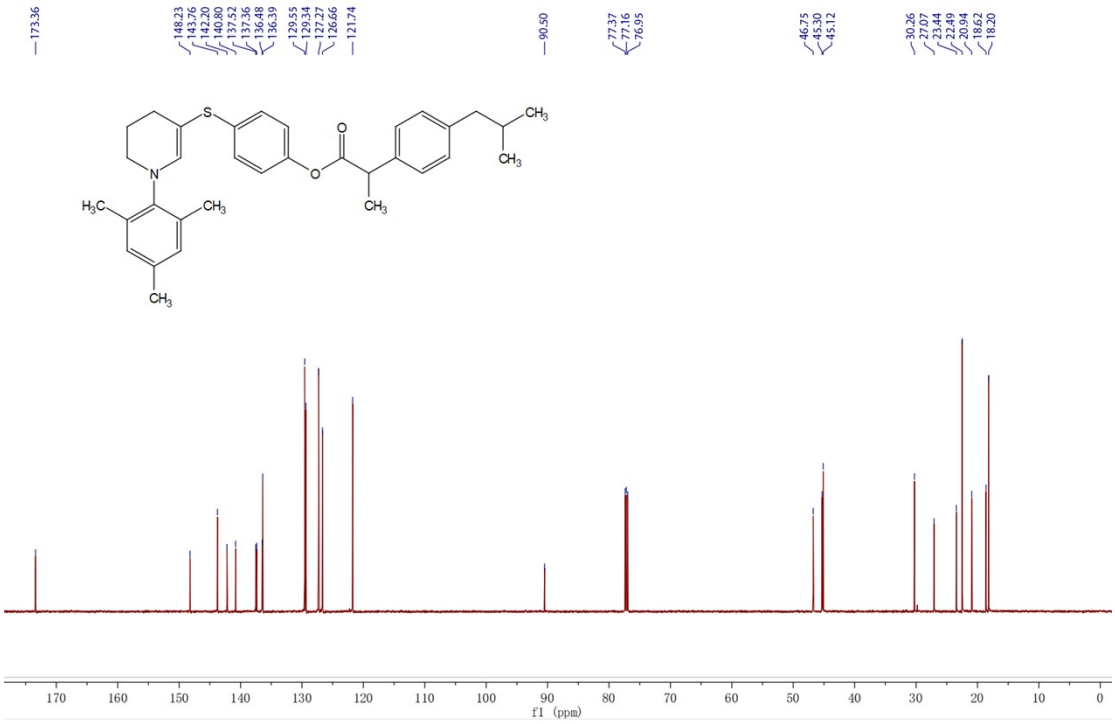
(87) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C43



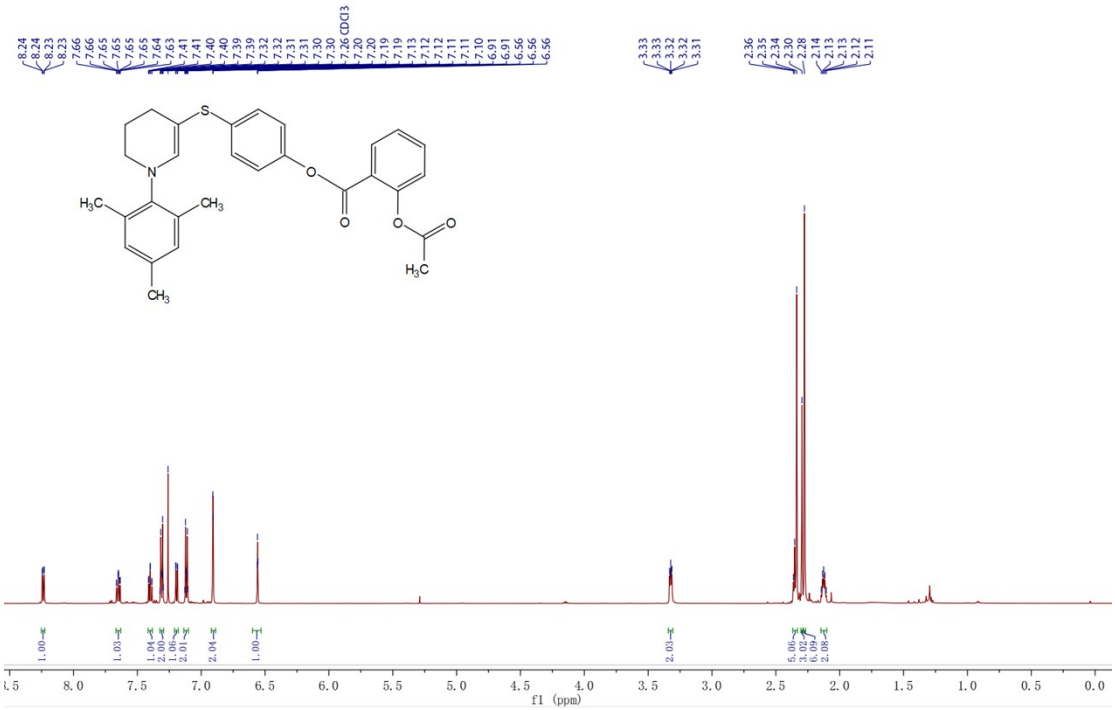
(88) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C44



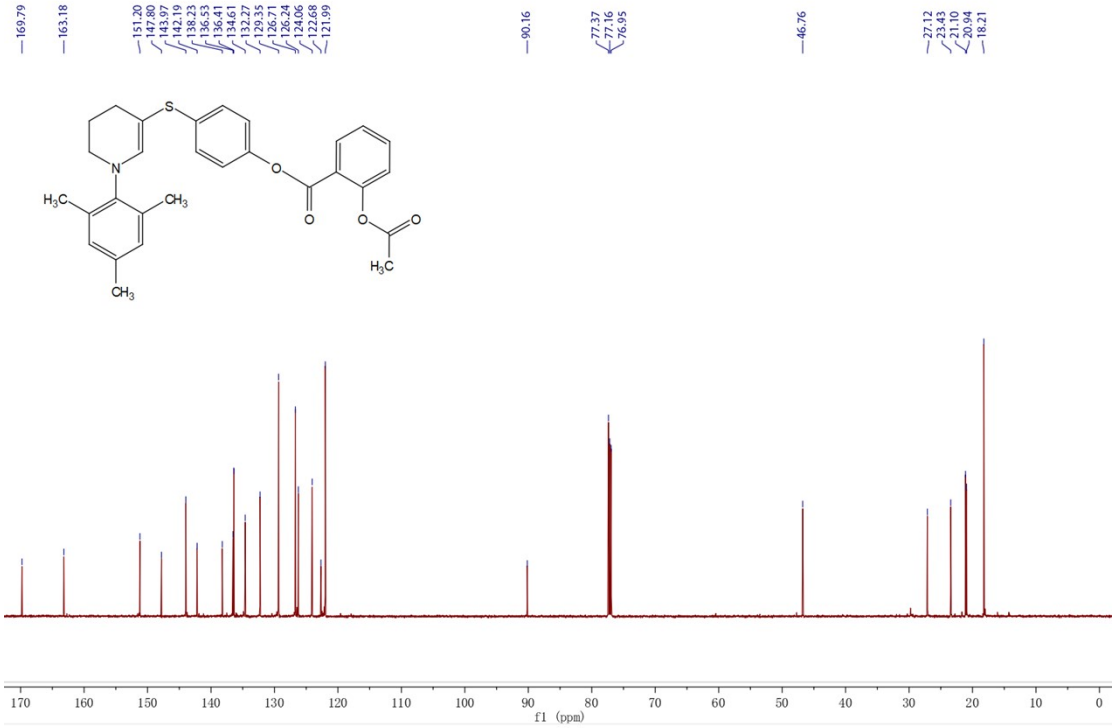
(89) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C44



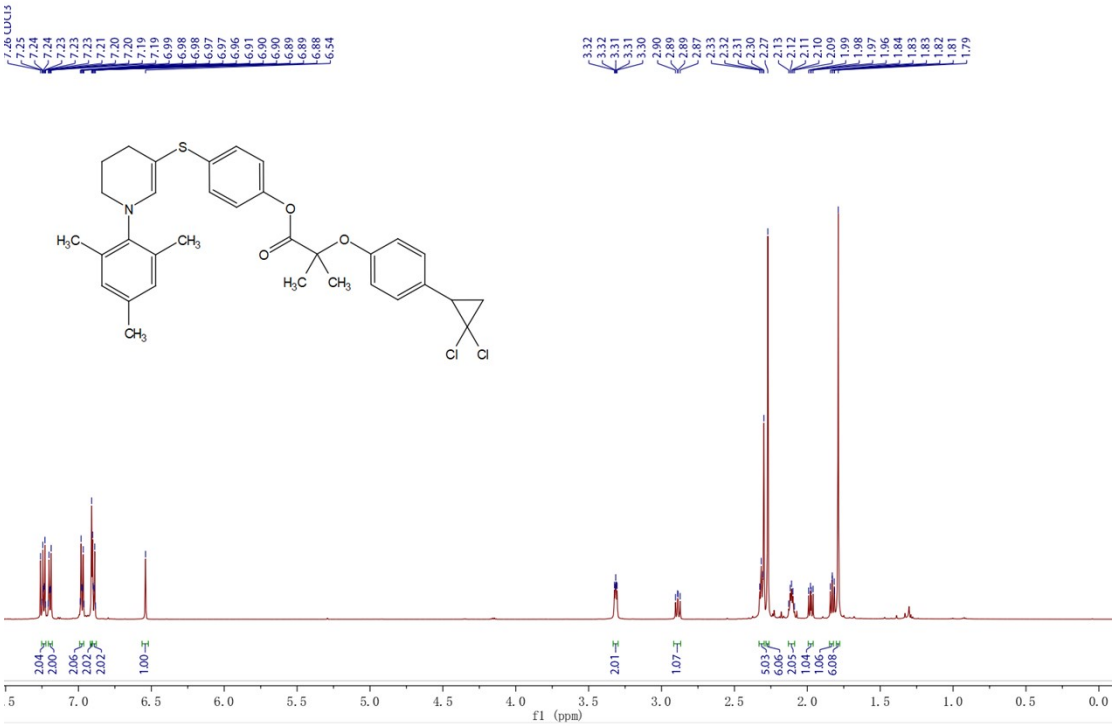
(90) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C45



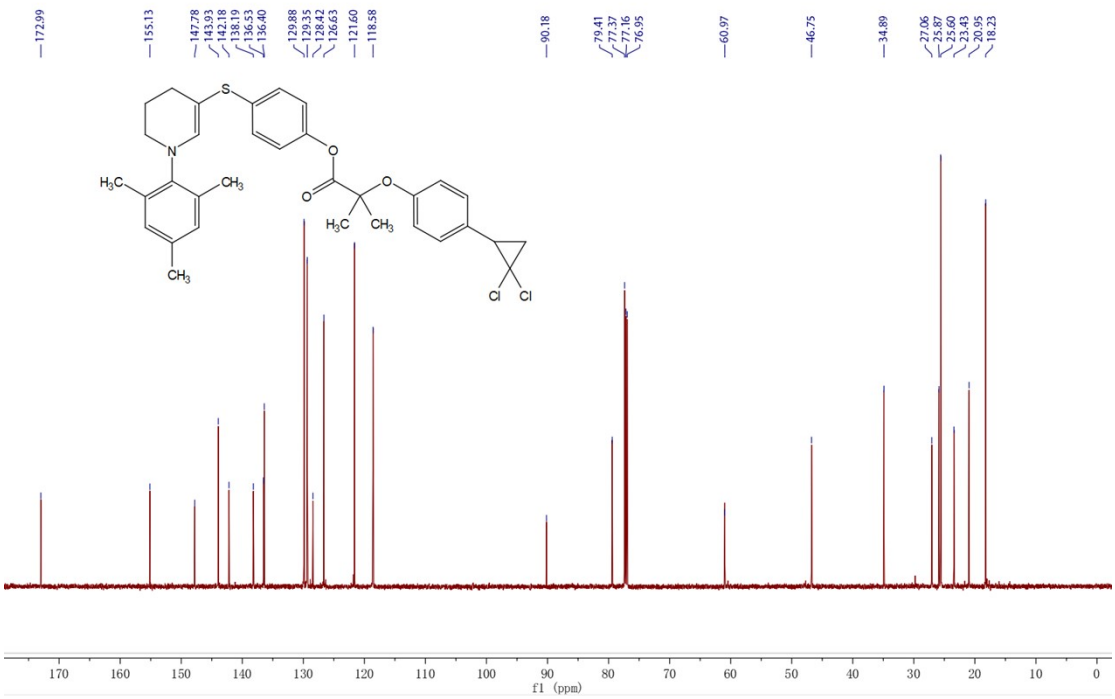
(91) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C45



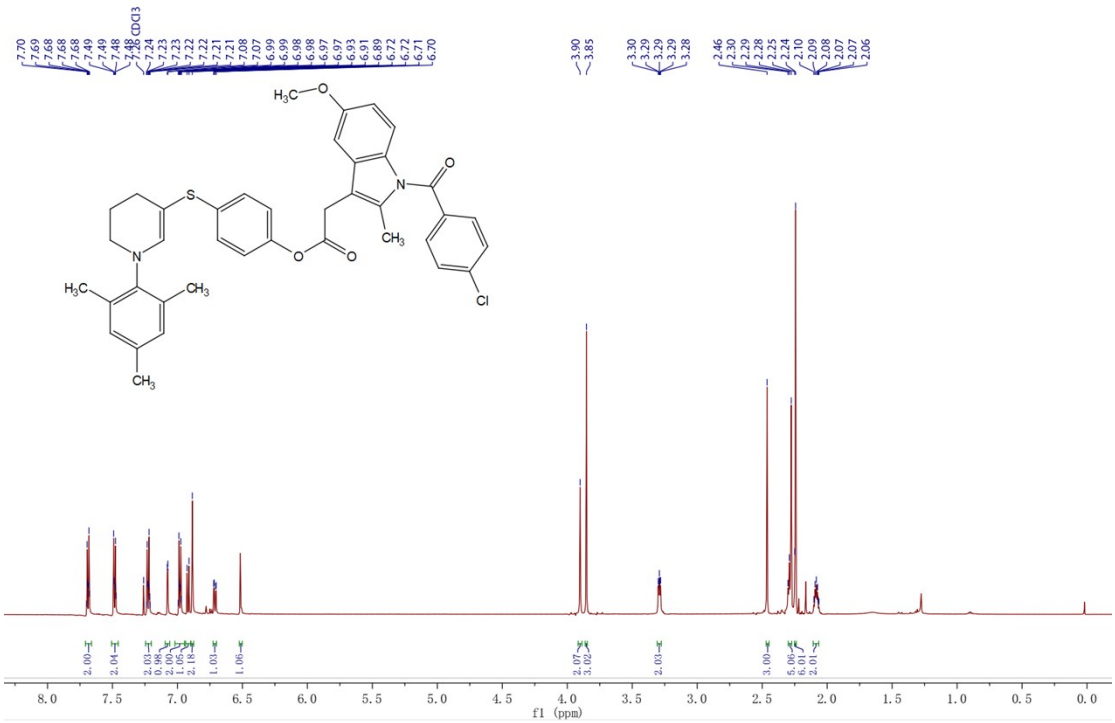
(92) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C46



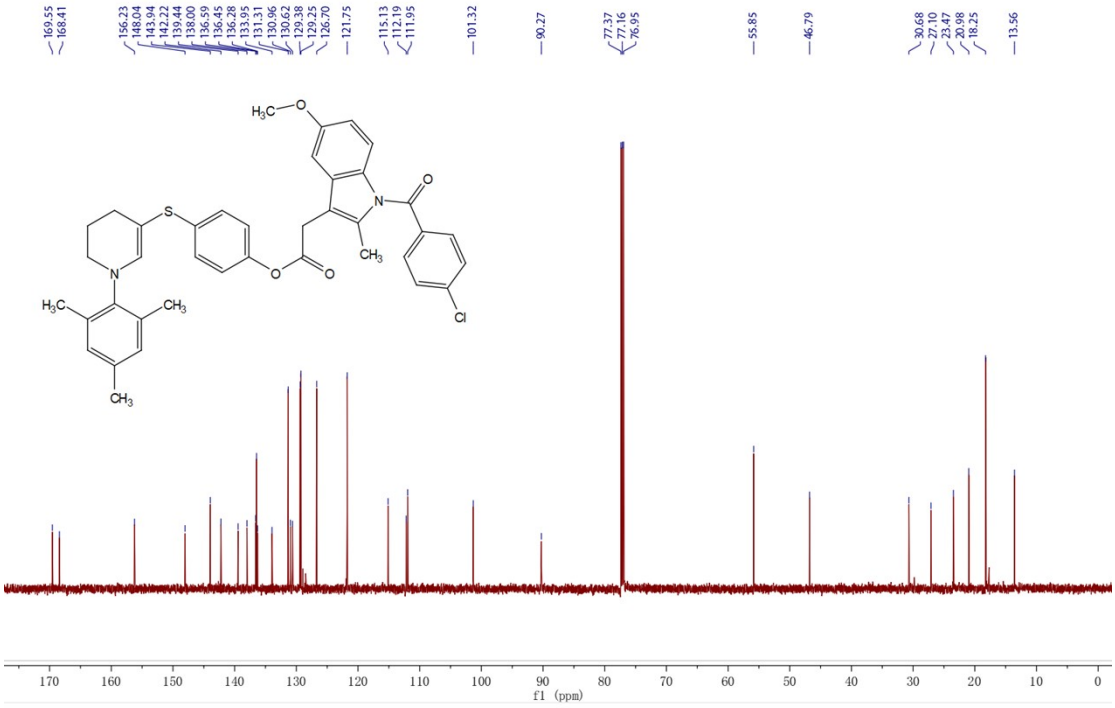
(93) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C46



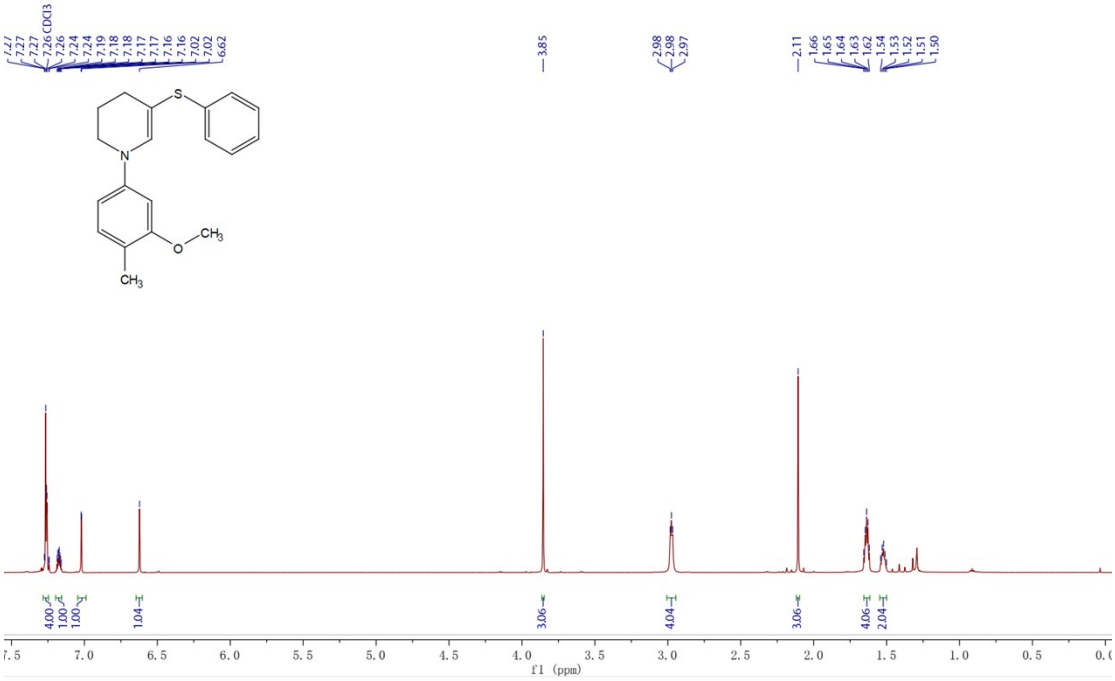
(94) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C47



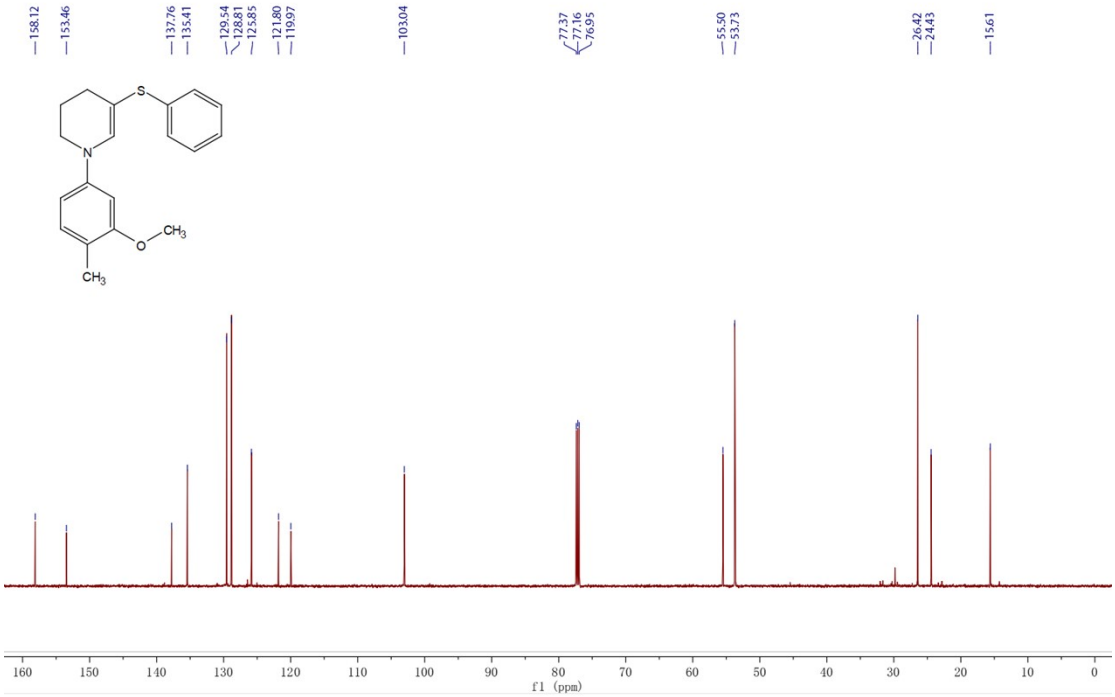
(95) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C47



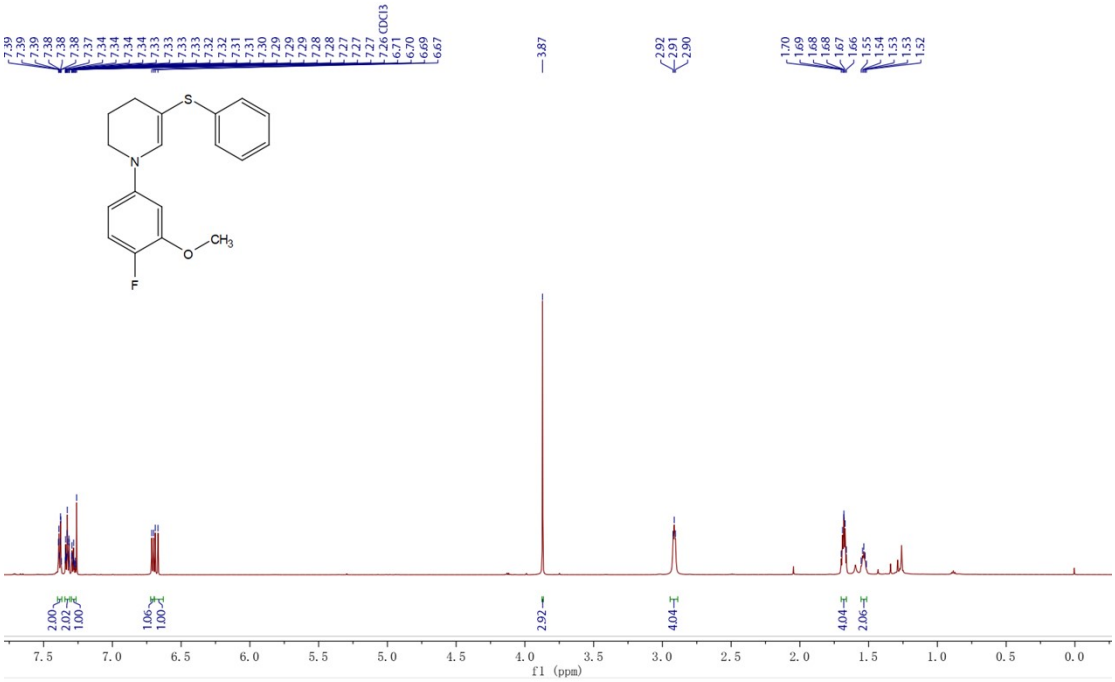
(96) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C48



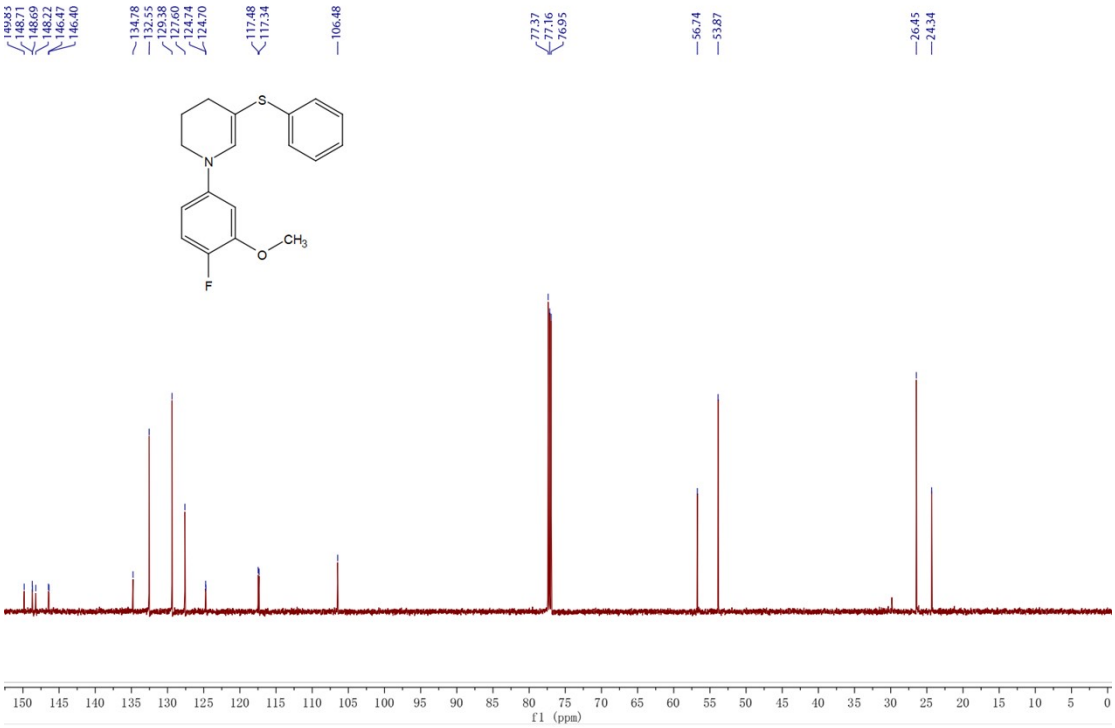
(97) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C48



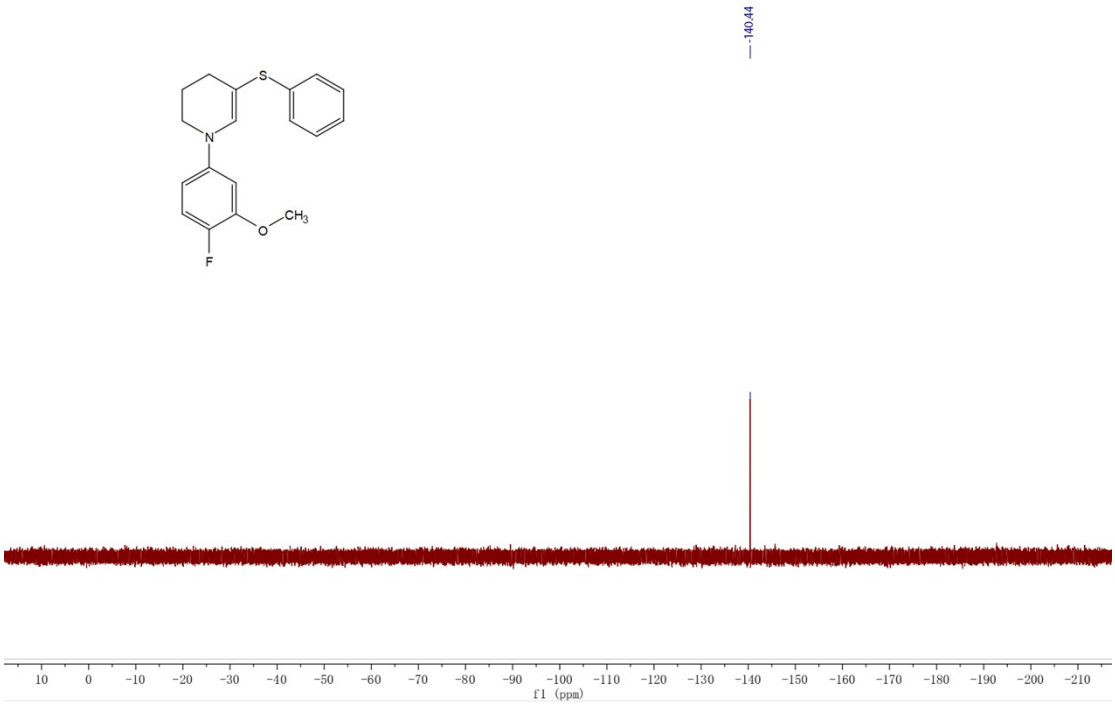
(98) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C49



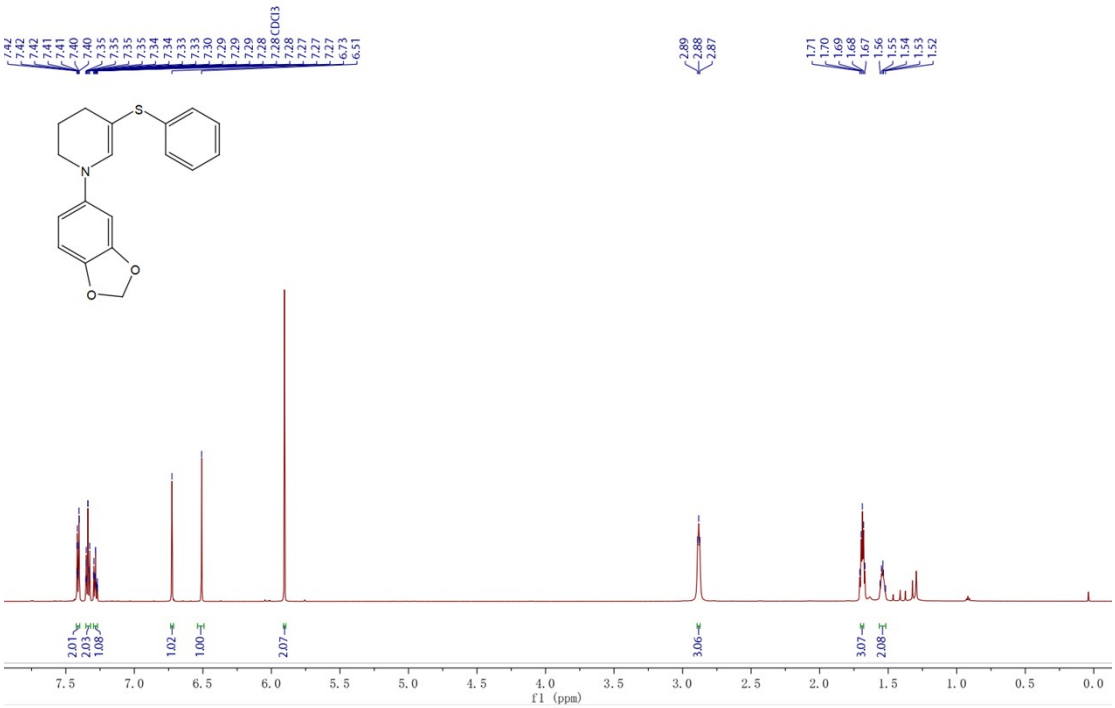
(99) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C48



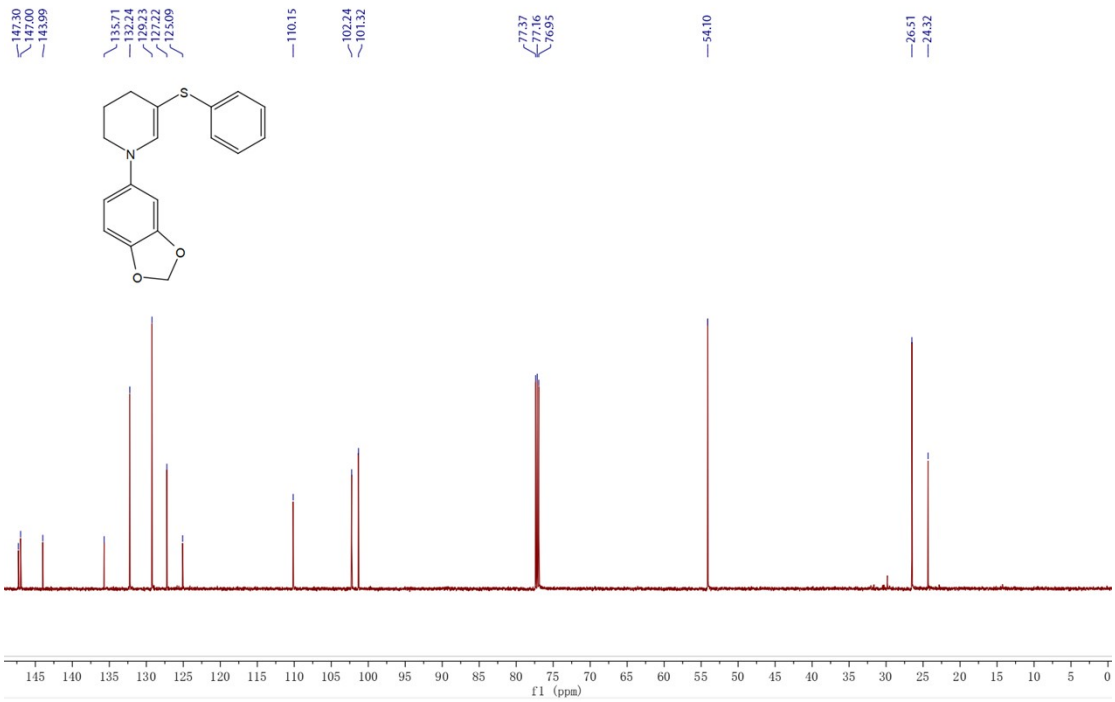
(100) ^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of C7



(101) ^{1}H-NMR (600 MHz, Chloroform-*d*) spectrum of C50



(102) ^{13}C-NMR (151 MHz, Chloroform-*d*) spectrum of C50



12. LC-MS analysis

The model reaction was carried out under standard reaction conditions for 6 hours. Subsequently, the reaction mixture was analyzed by liquid chromatography-mass spectrometry (LC-MS), and ***Cat.* 1-P** could be observed.

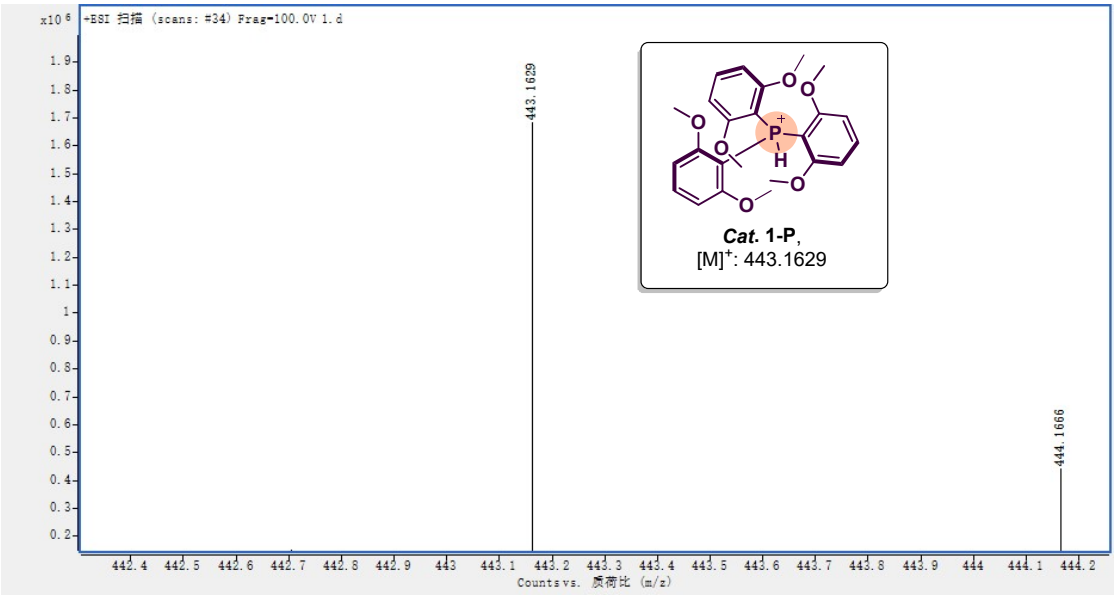


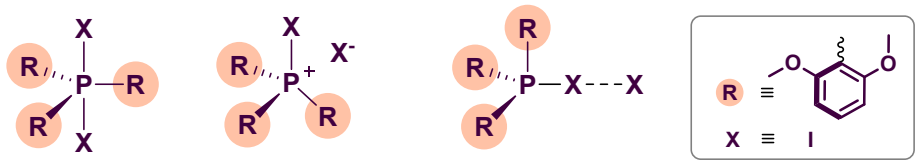
Figure S3. LC-MS analysis experiment report of the reaction mixture.

9. DFT Calculation

Computational details. All the calculations were performed using the Gaussian 16 software package.[7] Geometry optimization of the compounds was conducted at the (U)M06-2X[8](D3)[9] density functional theory level using the basis set def2-SVP[10] for all atoms. In addition, Hessian calculations for obtaining the vibrational frequencies were performed at the same level of theory as that for the geometry optimization to check whether the optimized geometrical structure is an energy minimum (with no imaginary frequency). The single-point energies calculations were performed by the (U)M06-2X(D3) density functional with the def2-TZVPP for all atoms, and the CPCM solvent model[11] was used to simulate the solvent effect of 1,4-Dioxane. Renderings of spin density plots were performed using the program *VMD*[12].

The calculation results in Table S2 indicate that the most stable conformation of the catalyst is ***Cat.* 1-3**, and all conformations of the catalyst are singlet ground state species.

Table S2. Comparison of relative electronic energies (kcal/mol) for these catalyst isomers computed at (U)M06-2X(D3)/def2-TZVPP~CPCM(1,4-Dioxane) // (U)M06-2X(D3)/def2-SVP level.

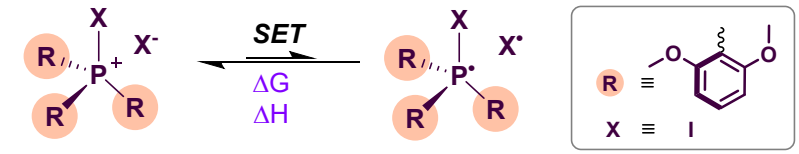


Cat. 1-1 **Cat. 1-2** **Cat. 1-3**

Entry	Cat. 1-1	Cat. 1-2	Cat. 1-3
Singlet	+12.5	+6.3	0.0
Triplet	+30.5	+25.2	+23.8

However, as shown in Table S3, calculations on the formation of transient radical pair $[R_3PX]^{\cdot}$ $[X]^{\cdot}$ by single-electron transfer in $[R_3PX]^{+}[X]^{-}/R_3PX_2$ reveal a large free energy gap (from +12.3 to +23.4 kcal/mol), which is not a thermodynamically favorable process. Meanwhile, inspired by Lin's work (*Nature* **2023**, *619*, 514-520), the process of the catalyst dissociating into two isolated radical fragments after the SET process was calculated (Table S4). However, the calculation results indicate that this is also a thermodynamically unfavorable process, with ΔG_{dis} ranging from +12.8 to +29.2 kcal/mol.

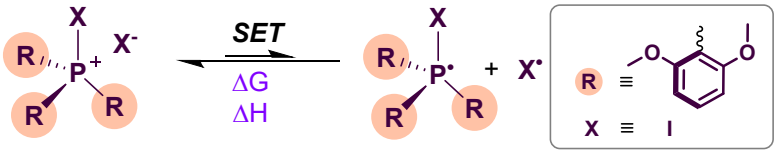
Table S3. Comparison of ΔG and ΔH (kcal/mol) for the single-electron-transfer process computed at (U)M06-2X(D3)/def2-TZVPP~CPCM(1,4-Dioxane) // (U)M06-2X(D3)/def2-SVP level.



Cat. 1-1/1-2/1-3 **FRPs 1-1/1-2/1-3**

Entry	*Cat.* 1-1	*Cat.* 1-2	*Cat.* 1-3
ΔG	+12.3	+15.2	+23.4
ΔH	+18.2	+18.5	+23.6

Table S4. Comparison of ΔG_{dis} and ΔH_{dis} (kcal/mol) for the single-electron-transfer process computed at M06-2X(D3)/def2-TZVPP~CPCM(1,4-Dioxane) // (U)M06-2X(D3)/def2-SVP level.



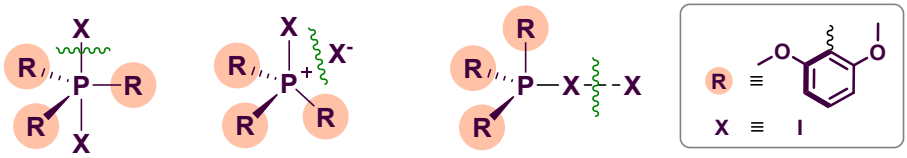
Cat. 1-1/1-2/1-3 **Frag.A1-1/1-2/1-3** **Frag.B**

Entry	*Cat.* 1-1	*Cat.* 1-2	*Cat.* 1-3
ΔG_{dis}	+12.8	+19.5	+29.2

ΔH_{dis}	+25.1	+30.7	+37.1

The bond dissociation energy (BDE) represents the electronic energy change in a homolytic cleavage process of a specific bond. For example, BDE(A-B) = E(A•) + E(B•) - E(A-B), where the structures of radicals A• and B• are directly taken from A-B with an optimization.

Table S5. Dissociation energies (kcal/mol) of these catalyst isomers computed at (U)M06-2X(D3)/def2-TZVPP~CPCM(1,4-Dioxane) // (U)M06-2X(D3)/def2-SVP level.



Trigonal bipyramidal **Cat. 1-1** | Ionic halo-phosphoniun **Cat. 1-2** | Charge-transfer molecular "spoke" adduct **Cat. 1-3**

Entry	*Cat.* 1-1	*Cat.* 1-2	*Cat.* 1-3
BDE(ΔG)	+12.8	+20.0	+29.2
BDE(ΔH)	+25.2	+31.6	+37.1

Meanwhile, the adiabatic ionization potentials (AIPs) and adiabatic electron affinities (AEAs) of the catalyst isomers were also calculated in detail, and the corresponding results are displayed in Table 6. The moderate AIP values (+119.0 ~ +130.2 kcal/mol), large positive AEAs (+83.6 ~ +69.9 kcal/mol), as well as the small fundamental gaps (E_gap, 1.54 ~ 2.61 eV) all lend favorable support to the ability of these catalysts to form frustrated radical pairs (FRPs).

Table S6. Adiabatic Ionization Potential (AIP, kcal/mol), Adiabatic Electron Affinity (AEA, kcal/mol) and Energy gaps (E_gap = AIP – AEA, eV) of these catalyst isomers computed at (U)M06-2X(D3)/def2-TZVPP~CPCM(1,4-Dioxane) // (U)M06-2X(D3)/def2-SVP level.

Entry	*Cat.* 1-1	*Cat.* 1-2	*Cat.* 1-3
AIP[a]	+119.0	+123.6	+130.2
AEA[b]	+83.6	+75.8	+69.9
E_gap	1.54	2.07	2.61

[a] AIP = ΔE_{therm}(cation) - ΔE_{therm}(neutral); [b] AEA = ΔE_{therm}(neutral) - ΔE_{therm}(anion)

As shown in Figure S4, the spin population analysis results indicate that the spin electrons are mainly contributed by the phosphorus center and the iodine center.

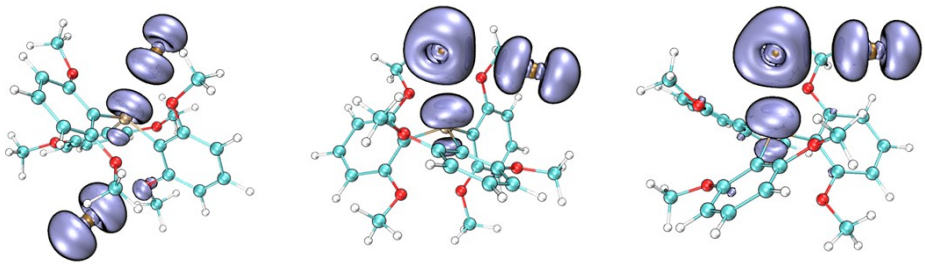


Figure S4. Spin population of catalyst isomers ***Cat.* 1-1**, ***Cat.* 1-2**, and ***Cat.* 1-3** (triplet) (isovalue = 0.005 a.u.).

Cartesian Coordinates

***Cat.* 1-1** (Singlet) M06-2X(D3)/def2-SVP E = -2317.007286 a.u.

P	0.00071100	0.00007900	0.01033400
C	-1.08437000	-1.44623800	0.01581900
C	-0.68669300	-2.63981400	-0.62219700
C	-2.33937900	-1.39112600	0.65755900
C	-1.53837300	-3.75071000	-0.62833900
O	0.51895700	-2.64751900	-1.19628900
C	-3.17334100	-2.51522700	0.66868700
O	-2.67655100	-0.23188100	1.22831400
H	-1.23430200	-4.66866600	-1.12685400
C	-2.76500600	-3.67560800	0.02122000
C	0.82271200	-3.60627200	-2.17666000
H	-4.13861200	-2.47406500	1.16883500
C	-3.69218600	-0.19589300	2.19731400
H	-3.42202000	-4.54678300	0.02279700
H	0.95437900	-4.60670000	-1.73308200
H	1.76344500	-3.28349700	-2.63628200
H	0.03726300	-3.63801700	-2.94788800
H	-4.68583200	-0.34226000	1.74321600
H	-3.64177800	0.79892000	2.65359400
H	-3.51917000	-0.95793300	2.97330500
C	-0.71057500	1.66224000	-0.00560200
C	-1.94324800	1.90475600	-0.64724300
C	-0.03734200	2.73060900	0.62315400
C	-2.48152900	3.19674100	-0.66988600
O	-2.55134400	0.85640700	-1.20798600
C	-0.59585700	4.01412900	0.61753100
O	1.13466800	2.45209200	1.19951800
H	-3.42875700	3.38456000	-1.17099000
C	-1.80497100	4.23068900	-0.03324200
C	-3.53667400	1.05862900	-2.18813200
H	-0.07915600	4.83656800	1.10763400
C	1.66867500	3.32528900	2.16090300
H	-2.23250400	5.23453900	-0.04446100
H	-4.46850200	1.44815000	-1.74662400
H	-3.72658700	0.07649500	-2.63508300
H	-3.17546500	1.74618100	-2.96885000
H	2.03821400	4.25494200	1.69817100
H	2.50464400	2.79100500	2.62573600
H	0.91912200	3.56290700	2.93196900
C	1.79584300	-0.21622900	0.00105700
C	2.38152300	-1.32683800	0.64415400
C	2.62470500	0.72125800	-0.64996700
C	3.77208200	-1.48634500	0.64444100

O	1.55152700	-2.19546900	1.22724900
C	4.01261300	0.53958700	-0.66687200
O	2.02340500	1.76586900	-1.22480600
H	4.22364700	-2.33970500	1.14592600
C	4.56689900	-0.55607100	-0.01535900
C	2.03640400	-3.08576600	2.19897600
H	4.65092100	1.25930000	-1.17502000
C	2.69243000	2.50168200	-2.21649700
H	5.64991800	-0.68891700	-0.02185400
H	2.65676700	-3.87611800	1.74573100
H	1.15352700	-3.53668000	2.66547300
H	2.61542300	-2.54896200	2.96668700
H	3.49772700	3.11817600	-1.78477000
H	1.93818200	3.15244100	-2.67260100
H	3.10453500	1.83217600	-2.98762600
I	0.00906400	0.01905300	2.88225100
I	-0.00674400	-0.01803600	-2.87744000

***Cat.* 1-1** (Triplet) (U)M06-2X(D3)/def2-SVP E = -2316.978920 a.u.

P	-0.67527100	0.05089800	0.01543300
C	-0.25718700	1.71765700	-0.56113900
C	0.52358800	2.02846300	-1.68765500
C	-0.86901600	2.76427300	0.15137700
C	0.65548400	3.36112200	-2.10578400
O	1.12241400	1.00322100	-2.31739700
C	-0.75274000	4.09329600	-0.26608200
O	-1.52799300	2.38351000	1.25971200
H	1.25605700	3.61068400	-2.97787500
C	0.01154200	4.37036000	-1.39629200
C	1.94656500	1.24972700	-3.42285900
H	-1.23697000	4.89642800	0.28633300
C	-2.45661800	3.25577200	1.85089300
H	0.11432000	5.40377400	-1.73152100
H	1.38512500	1.71796000	-4.24811800
H	2.32280700	0.27257600	-3.74758400
H	2.79992500	1.89278000	-3.15039300
H	-1.95269000	4.10319200	2.34439000
H	-2.99964700	2.66640900	2.59763200
H	-3.17064700	3.63562800	1.10335300
C	0.10781600	-0.28316700	1.62138900
C	0.92908300	0.60340000	2.34434900
C	-0.27896000	-1.48983300	2.23453500
C	1.32393500	0.29024800	3.65378500
O	1.30989500	1.73125700	1.72334200

C	0.09565100	-1.79917700	3.54464100
O	-0.99248100	-2.32507400	1.45411500
H	1.96110600	0.97037800	4.21472100
C	0.89673700	-0.89712600	4.23878100
C	2.17410400	2.62488300	2.36775700
H	-0.22119200	-2.73209600	4.00765600
C	-1.82121400	-3.29150700	2.05284300
H	1.20237600	-1.12736500	5.26062200
H	1.72520000	3.02755500	3.29094200
H	2.34612400	3.44575200	1.66172100
H	3.13711200	2.14456000	2.60952200
H	-1.23029100	-4.11904400	2.47930700
H	-2.46921100	-3.67598800	1.25757700
H	-2.44626200	-2.83731700	2.83707500
C	-0.15199600	-1.17657500	-1.21623400
C	-0.89794700	-1.17497800	-2.41014900
C	0.78218300	-2.20171100	-1.01629900
C	-0.77698200	-2.20967300	-3.34181700
O	-1.70417500	-0.11224500	-2.57454400
C	0.91293600	-3.24410000	-1.94154100
O	1.55984300	-2.11612300	0.08981200
H	-1.37196000	-2.20788600	-4.25337000
C	0.12455000	-3.24033900	-3.08808100
C	-2.78222300	-0.19490800	-3.47343300
H	1.63461600	-4.04175900	-1.77444500
C	2.14483500	-3.28211400	0.61621600
H	0.22553500	-4.05325700	-3.80872600
H	-2.43359500	-0.18096400	-4.51907600
H	-3.40842800	0.68371200	-3.28472700
H	-3.37512900	-1.10436300	-3.28895300
H	1.39240300	-4.08182400	0.70646500
H	2.51964500	-3.01333700	1.61190800
H	2.98657700	-3.63085900	-0.00384900
I	-3.63297900	-0.28113800	0.34057800
I	3.66677800	-0.06205300	-0.13845800

***Cat.* 1-2** (Singlet) M06-2X(D3)/def2-SVP E = -2317.000885 a.u.

P	-0.55513800	-0.13754100	0.02570900
C	0.33692900	-1.07086200	1.28328800
C	0.03795500	-0.66190400	2.59559300
C	1.29439000	-2.07558000	1.06166800
C	0.74354700	-1.17028100	3.68282100
O	-0.94356800	0.25715700	2.68885800
C	2.01916000	-2.57387700	2.15682700

O	1.43792200	-2.53920500	-0.17549900
H	0.52573700	-0.83896900	4.69627500
C	1.74245700	-2.11372500	3.43611800
C	-1.03113900	1.05839600	3.83958600
H	2.79594100	-3.31826800	1.99724300
C	2.63899300	-3.19288500	-0.53897400
H	2.31429500	-2.51218000	4.27587100
H	-1.38073500	0.47733300	4.70765800
H	-1.76275100	1.84064400	3.60813200
H	-0.05555300	1.51679600	4.06427800
H	3.50468200	-2.58760200	-0.23331600
H	2.62752400	-3.25507700	-1.63295300
H	2.67569300	-4.20760000	-0.10908900
C	-2.30522600	-0.56803400	0.25083600
C	-3.30889200	0.33983300	0.63249100
C	-2.64512800	-1.91768600	0.03172300
C	-4.64603900	-0.07623900	0.66874600
O	-2.92648500	1.57877400	0.97380700
C	-3.97819100	-2.33793200	0.07936400
O	-1.61029800	-2.73038800	-0.22079300
H	-5.43150700	0.62519400	0.94336800
C	-4.96099900	-1.40145400	0.38440100
C	-3.85352600	2.63171200	0.89153900
H	-4.24197800	-3.37648700	-0.10957300
C	-1.82686400	-4.04901000	-0.65685400
H	-6.00430600	-1.71870300	0.42182500
H	-4.38352700	2.61358800	-0.07427800
H	-3.27315700	3.55889200	0.97148800
H	-4.58778600	2.59336300	1.71235100
H	-2.30674600	-4.65377300	0.12850200
H	-0.83465500	-4.45607700	-0.87853700
H	-2.44626000	-4.06604300	-1.56748300
C	-0.23594800	1.64010200	0.05049200
C	-0.91102200	2.41001200	-0.92127000
C	0.76772500	2.25346600	0.83412100
C	-0.55744800	3.73329100	-1.16831100
O	-1.90564800	1.77952000	-1.58119600
C	1.12612500	3.58632400	0.57328300
O	1.30522300	1.55552900	1.82929200
H	-1.07029100	4.31356500	-1.93254300
C	0.47516300	4.29866000	-0.41945700
C	-2.30590500	2.26339700	-2.84114500
H	1.93039500	4.04749800	1.14123300
C	2.52026100	1.97614800	2.41917500

H	0.77432100	5.32894500	-0.61763900
H	-2.87669900	3.20125300	-2.74775300
H	-2.94931500	1.49104300	-3.27762000
H	-1.43322300	2.42644700	-3.49248200
H	3.27633900	2.14968600	1.63973800
H	2.84721800	1.13869500	3.04650900
H	2.35826000	2.87140200	3.04318300
I	-0.05309000	-0.78441700	-2.27940000
I	3.41270700	0.40247800	-0.70516900

Cat. **1-2** (Triplet) (U)M06-2X(D3)/def2-SVP E = -2316.987776 a.u.

P	-0.56414500	-0.16551600	0.12529400
C	-0.13710900	-0.27573000	1.88620500
C	-0.79838800	0.55252900	2.80756800
C	0.86304900	-1.15293000	2.32992500
C	-0.42870100	0.55607500	4.15532000
O	-1.76372200	1.32966500	2.28777700
C	1.24082300	-1.15329200	3.68315100
O	1.40599000	-1.96167000	1.41129400
H	-0.92484700	1.20672100	4.87299600
C	0.59411900	-0.29822500	4.56762600
C	-2.27383000	2.39208400	3.04497000
H	2.02544600	-1.81799600	4.03868400
C	2.59999200	-2.64294800	1.70190900
H	0.88918100	-0.30196700	5.61850500
H	-2.83809900	2.03408100	3.92157100
H	-2.94997600	2.94256900	2.38141600
H	-1.46320300	3.05957900	3.38107400
H	3.37462300	-1.94671400	2.05984100
H	2.93230200	-3.08723900	0.75601600
H	2.43658400	-3.43869900	2.44800100
C	-2.29366200	-0.72244400	0.05962900
C	-3.42484300	0.06912000	-0.19920100
C	-2.45499700	-2.11152600	0.21948100
C	-4.68049700	-0.53426800	-0.35706600
O	-3.24497900	1.39961200	-0.27596100
C	-3.70682200	-2.71865600	0.07558600
O	-1.32279400	-2.77614800	0.51062100
H	-5.56027200	0.07105300	-0.56741000
C	-4.80332600	-1.91398700	-0.22075900
C	-4.20242700	2.18092500	-0.93812400
H	-3.82428900	-3.79442300	0.19035400
C	-1.30915700	-4.17860700	0.51420400
H	-5.78556000	-2.37415100	-0.33992600

H	-4.44573800	1.75697700	-1.92648000
H	-3.75390400	3.17322000	-1.06944700
H	-5.13018000	2.28017400	-0.35043800
H	-1.94495600	-4.58410800	1.31792200
H	-0.26787000	-4.47017200	0.68882400
H	-1.64291700	-4.58122100	-0.45558300
C	-0.40095800	1.52957100	-0.50010600
C	-0.81991900	1.72809400	-1.83113100
C	0.32737600	2.55680300	0.12981200
C	-0.54181000	2.91314000	-2.51561300
O	-1.49253100	0.69938400	-2.38647700
C	0.60252500	3.75107100	-0.55043600
O	0.74700400	2.33662400	1.38783600
H	-0.86443400	3.04868600	-3.54607000
C	0.16808700	3.91499500	-1.85981600
C	-1.56403600	0.60285300	-3.78735400
H	1.16650300	4.54236600	-0.06113300
C	1.77081600	3.12988600	1.92893600
H	0.39575300	4.84307400	-2.38627700
H	-2.23291300	1.37013700	-4.21086800
H	-1.97001600	-0.39071500	-4.00765900
H	-0.56279600	0.69396400	-4.23692800
H	2.63787600	3.16873100	1.25041800
H	2.06411300	2.64689800	2.86892300
H	1.42201200	4.15412900	2.14306200
I	1.11573100	-1.58994700	-1.93459000
I	3.31238500	0.36373600	-0.44668900

***Cat.* 1-3** (Singlet) M06-2X(D3)/def2-SVP E = -2317.020031 a.u.

C	1.44836800	-1.03906200	-1.38478500
C	2.25738300	-0.60422200	-2.44750100
C	2.39957100	-1.39982000	-3.59342100
H	3.01263000	-1.05999000	-4.42589700
C	1.76534300	-2.63607700	-3.65503300
C	0.99908700	-3.11354900	-2.59468800
H	0.52354800	-4.09109800	-2.64967000
C	0.85877400	-2.31443100	-1.45747900
C	1.44893800	1.71888200	-0.20693500
C	2.25810200	2.42137400	0.70120100
C	2.40031000	3.81167000	0.58572200
H	3.01336100	4.36240000	1.29649600
C	1.76591400	4.48360100	-0.45369600
C	0.99945200	3.80452000	-1.39751000
H	0.52369600	4.34132100	-2.21621800

C	0.85910900	2.42003900	-1.27469100
C	1.44815600	-0.68001100	1.59250500
C	0.85822000	-0.10559800	2.73339500
C	0.99706900	-0.69217500	3.99361000
H	0.52114700	-0.25137300	4.86766400
C	1.76219700	-1.85000500	4.10987400
C	2.39698200	-2.41428700	3.00849300
H	3.00918800	-3.30581000	3.12996800
C	2.25639700	-1.81834800	1.74698800
I	-1.79263500	0.00055300	-0.00018700
P	0.90729800	0.00007000	0.00026100
I	-4.72729400	0.00050600	-0.00099600
O	0.17882700	1.65954300	-2.15282200
C	-0.81272600	2.25384700	-2.95953400
H	-1.49832300	2.86270500	-2.35026700
H	-1.37349300	1.43068500	-3.41543800
H	-0.36371200	2.87515500	-3.75109700
O	2.87653900	1.70499400	1.65492900
C	3.35387700	2.35299900	2.80423700
H	4.24624800	2.96277700	2.58831100
H	3.62414100	1.56145300	3.51351900
H	2.57424200	2.99280900	3.24929700
O	2.87600200	0.57986400	-2.30426900
C	3.35488600	1.24997400	-3.44014600
H	4.24750600	0.75730100	-3.85881300
H	3.62517800	2.26017700	-3.10989800
H	2.57621500	1.31512300	-4.21776500
O	0.17896900	-2.69429300	-0.35929300
C	-0.81435700	-3.68840400	-0.47003600
H	-1.50057300	-3.46341300	-1.30097200
H	-1.37393700	-3.67124900	0.47150400
H	-0.36719900	-4.68525700	-0.61332300
O	0.17937000	1.03609800	2.51377600
C	-0.81301300	1.43765300	3.43094200
H	-1.49972500	0.60603100	3.65182400
H	-1.37232100	2.24510900	2.94607900
H	-0.36488400	1.81123800	4.36571800
O	2.87545500	-2.28594000	0.64993900
C	3.34870200	-3.60674100	0.63480000
H	4.24063700	-3.72835000	1.27075700
H	3.61835100	-3.82463200	-0.40562700
H	2.56674100	-4.31000400	0.96528100
H	1.87563000	-2.31936600	5.08829100
H	1.88060700	5.56544300	-0.53694200

H	1.88014900	-3.24951500	-4.55000100

***Cat.* 1-3** (Triplet) (U)M06-2X(D3)/def2-SVP E = -2316.988373 a.u.

C	1.44734200	1.64549300	-0.44091900
C	2.82596000	1.91648000	-0.49129800
C	3.28982900	3.23504900	-0.38805900
H	4.35642300	3.44852200	-0.41814900
C	2.37437200	4.27530300	-0.26707800
C	1.00198300	4.04054000	-0.25345200
H	0.30168100	4.86881800	-0.16868400
C	0.54297800	2.72289100	-0.34919100
C	1.99123200	-1.26038900	0.03989400
C	2.18500600	-2.40651400	-0.75113300
C	3.01301900	-3.44373600	-0.29899400
H	3.15430900	-4.33744400	-0.90372300
C	3.67107000	-3.31601200	0.91946700
C	3.53551100	-2.17157900	1.70174900
H	4.07068500	-2.08104300	2.64501200
C	2.70201200	-1.14517300	1.25026300
C	-0.38174700	-0.44266300	-1.60654200
C	-1.16231300	-1.59872500	-1.40628000
C	-2.18282100	-1.94309400	-2.29596200
H	-2.79447500	-2.82659700	-2.12549600
C	-2.42997700	-1.11123000	-3.38332000
C	-1.67137300	0.03247500	-3.61349000
H	-1.87543900	0.65636700	-4.48138900
C	-0.63190400	0.35976900	-2.73414200
I	-0.86934600	0.09340800	2.30969800
P	0.73133200	-0.00070600	-0.26201500
I	-3.71415000	0.01526600	0.74408300
O	2.52525800	0.01476800	1.91087000
C	2.87511600	0.09623800	3.27086900
H	2.41730800	-0.72592200	3.84325400
H	2.48052200	1.05175900	3.63347400
H	3.96896000	0.07704700	3.40547400
O	1.55923900	-2.44362800	-1.93876100
C	1.38155700	-3.67464300	-2.58730200
H	2.32811200	-4.05816100	-3.00212500
H	0.67789900	-3.49115600	-3.40809600
H	0.95562100	-4.42515300	-1.90103500
O	3.65079000	0.86688100	-0.65130500
C	5.01385300	1.00966000	-0.35562500
H	5.53041100	1.63641400	-1.10086900
H	5.44124100	0.00004500	-0.37887200

H	5.15819900	1.44532200	0.64695500
O	-0.75523900	2.38453000	-0.37088000
C	-1.72448300	3.33351300	0.01158100
H	-1.49336500	3.74575300	1.00629600
H	-2.67774400	2.79558100	0.05285200
H	-1.78765100	4.15275700	-0.72337100
O	-0.83888300	-2.32467900	-0.32290100
C	-1.71893900	-3.32674700	0.13083900
H	-2.73260100	-2.92000700	0.26816800
H	-1.32747900	-3.66119000	1.09768200
H	-1.74483300	-4.17832900	-0.56935600
O	0.17474100	1.41875000	-2.92441700
C	-0.24370900	2.45679600	-3.76950100
H	-0.21035800	2.15883500	-4.83030200
H	0.45616500	3.28591400	-3.60894000
H	-1.26551900	2.78462500	-3.51707200
H	-3.23754900	-1.36127900	-4.07305400
H	4.31537700	-4.12593800	1.26496500
H	2.74074300	5.30015400	-0.18886400

Cat. **1-1_FragA** (radical) (U)M06-2X(D3)/def2-SVP E = -2019.360607 a.u.

P	0.00031700	-0.00011700	-0.11461300
C	-1.71204000	0.24196600	-0.65054200
C	-2.38720200	1.32009000	-0.04840800
C	-2.44859900	-0.65937100	-1.43749600
C	-3.77207900	1.46554000	-0.16285700
O	-1.60144400	2.18711500	0.61929700
C	-3.83932000	-0.52356000	-1.55194300
O	-1.76097100	-1.62943700	-2.06618800
H	-4.28524100	2.29499200	0.32070900
C	-4.48294800	0.53002500	-0.91082900
C	-2.16195100	2.98001900	1.63773300
H	-4.41251500	-1.22902100	-2.15075200
C	-2.43333900	-2.78542400	-2.48659900
H	-5.56542200	0.63033700	-1.00462700
H	-2.78566500	3.78774400	1.22021800
H	-1.32020300	3.41495900	2.18766500
H	-2.76002800	2.36361700	2.32649700
H	-3.04979600	-3.20123900	-1.67247500
H	-1.65773300	-3.51048300	-2.76202500
H	-3.07207100	-2.59238500	-3.36429900
C	0.64807000	-1.60244000	-0.65419700
C	0.05072600	-2.72817600	-0.05674400
C	1.80012400	-1.78705500	-1.43729200

C	0.61862000	-3.99945200	-0.17214700
O	-1.09531400	-2.48383000	0.60811300
C	2.37919500	-3.05866000	-1.55252400
O	2.29871600	-0.70495500	-2.06154700
H	0.15579700	-4.86006100	0.30776100
C	1.78706400	-4.14477500	-0.91619100
C	-1.50209100	-3.36647500	1.62572900
H	3.27901000	-3.20016000	-2.14845300
C	3.63915300	-0.70608100	-2.47196600
H	2.24246700	-5.13182700	-1.01066900
H	-1.88518400	-4.31204400	1.20755200
H	-2.30328200	-2.85734200	2.17258400
H	-0.67073200	-3.57265700	2.31739100
H	4.30180700	-1.03394600	-1.65396600
H	3.87987000	0.32949800	-2.74182100
H	3.79886100	-1.35246700	-3.35076000
C	1.06470100	1.36349900	-0.64959300
C	0.65067900	2.45326500	-1.43412800
C	2.33654800	1.40901700	-0.04875700
C	1.46315500	3.59015400	-1.54806900
O	-0.53449300	2.34409600	-2.06074000
C	3.15434500	2.53603000	-0.16270400
O	2.69557300	0.29444200	0.61747100
H	1.13761300	4.44012300	-2.14502100
C	2.69829500	3.62022100	-0.90869100
C	-1.19995900	3.50527300	-2.47783800
H	4.12980500	2.56537700	0.31977300
C	3.66164900	0.38339300	1.63676400
H	3.32599300	4.50783200	-1.00219700
H	-1.24960700	4.24587300	-1.66249100
H	-2.21647000	3.19680700	-2.75114700
H	-0.71541600	3.96309300	-3.35602500
H	4.67313100	0.52154300	1.22014400
H	3.61828400	-0.56367000	2.18571300
H	3.42512200	1.20848400	2.32621400
I	-0.00219800	-0.00627900	2.87109800

***Cat.*1-2_FragA** (radical) (U)M06-2X(D3)/def2-SVP E = -2019.360118 a.u.

P	0.10602200	0.09658200	-0.13645800
C	-0.01527500	1.89390100	0.16382900
C	-1.06760300	2.42340700	0.92750100
C	0.98244500	2.75009400	-0.32165000
C	-1.13550900	3.79451600	1.19975500
O	-1.97970700	1.52994800	1.34500500

C	0.92581600	4.12744900	-0.05118900
O	1.95905600	2.17584100	-1.04105500
H	-1.95020400	4.21211300	1.78831200
C	-0.13181500	4.62443000	0.70220300
C	-3.06454000	1.95406400	2.12117000
H	1.69518300	4.80108600	-0.42285300
C	3.00628500	2.95582400	-1.54747800
H	-0.17607800	5.69458800	0.91237000
H	-2.73020300	2.42538600	3.05991600
H	-3.64178100	1.05230800	2.35326200
H	-3.70114300	2.66548300	1.56854900
H	2.63798300	3.71953000	-2.25242200
H	3.67037300	2.26320400	-2.07685800
H	3.56537300	3.45482400	-0.73823400
C	0.18094400	-0.55527400	1.56959100
C	-0.81153500	-1.27416900	2.25597100
C	1.43849300	-0.39224100	2.17919000
C	-0.51782500	-1.88527300	3.48259900
O	-2.03597200	-1.34361300	1.69545200
C	1.73778800	-0.99470000	3.40559300
O	2.30842300	0.37726600	1.49602900
H	-1.28174000	-2.45581400	4.00835500
C	0.75101000	-1.74463800	4.03743800
C	-2.86043100	-2.43453700	2.00486600
H	2.72015500	-0.87539800	3.85915600
C	3.68613100	0.24326800	1.73436800
H	0.97108800	-2.22176200	4.99380700
H	-2.30181700	-3.38301700	1.93924500
H	-3.66623800	-2.43565700	1.25981500
H	-3.30324200	-2.34621500	3.01123300
H	3.97239500	0.68520500	2.70288100
H	4.19081600	0.78034000	0.92327600
H	3.98787000	-0.81552500	1.70281700
C	-1.41111000	-0.49913000	-0.95498900
C	-1.53876600	-1.89724200	-1.05971300
C	-2.33277600	0.30432500	-1.65220100
C	-2.55827600	-2.48814900	-1.81195500
O	-0.62724300	-2.61349600	-0.37215700
C	-3.37059500	-0.28052000	-2.39261000
O	-2.15532800	1.63803900	-1.58969400
H	-2.63804700	-3.57152500	-1.88291800
C	-3.47011800	-1.66591500	-2.46560500
C	-0.35139700	-3.93619400	-0.76035700
H	-4.08859600	0.34077500	-2.92344600

C	-3.03552000	2.49152700	-2.26617600
H	-4.27292300	-2.11335100	-3.05363900
H	-1.16984800	-4.61885900	-0.47652000
H	0.56465000	-4.22586000	-0.23351900
H	-0.17667000	-3.99717800	-1.84580900
H	-3.01579900	2.31482000	-3.35411400
H	-2.69173600	3.51172300	-2.05884400
H	-4.07067700	2.37673900	-1.90331000
I	2.36493900	-1.28089600	-1.58647500

***Cat.* 1-3_FragA** (radical) (U)M06-2X(D3)/def2-SVP E = -2019.360613 a.u.

C	-0.10936000	-1.72519200	-0.65211500
C	-1.14276100	-2.26382100	-1.43729900
C	-1.29141400	-3.65312700	-1.55217100
H	-2.09957300	-4.07128300	-2.14953700
C	-0.38851400	-4.49695300	-0.91345500
C	0.67296500	-3.99045600	-0.16734700
H	1.38251500	-4.66113400	0.31417900
C	0.81095600	-2.60485900	-0.05213900
C	-1.43825600	0.95891700	-0.65328700
C	-1.38638900	2.12337900	-1.43798700
C	-2.51445400	2.94779100	-1.55365300
H	-2.47111500	3.85697000	-2.15062500
C	-3.69760900	2.58845800	-0.91622500
C	-3.79135400	1.41565900	-0.17076800
H	-4.72761100	1.13697300	0.30981400
C	-2.66116300	0.60237700	-0.05490100
C	1.55075800	0.76747300	-0.64929000
C	1.85183100	2.00387800	-0.04810700
C	3.12131700	2.57658000	-0.15999000
H	3.34676800	3.52593900	0.32277900
C	4.09206600	1.91028800	-0.90400800
C	3.81357800	0.70677900	-1.54380400
H	4.58104300	0.21586300	-2.13945300
C	2.53544300	0.14149200	-1.43224700
I	-0.00550500	-0.00241400	2.87016900
P	0.00031500	0.00034500	-0.11534100
O	-2.65362200	-0.56896500	0.61055400
C	-3.60031000	-0.78834800	1.62830100
H	-3.63788000	0.06977900	2.31697600
H	-3.26100400	-1.67264600	2.17879900
H	-4.60285000	-0.97703300	1.20985600
O	-0.22584500	2.39177400	-2.06274800
C	0.04388900	3.70399800	-2.47555400

H	-0.55713400	3.98943000	-3.35470900
H	1.10665600	3.72993900	-2.74579400
H	-0.14302700	4.42072100	-1.65880100
O	-1.95559200	-1.39426300	-2.06377500
C	-3.22626000	-1.81830500	-2.47701000
H	-3.17180600	-2.48301300	-3.35495100
H	-3.78045700	-0.91175200	-2.74938500
H	-3.75380400	-2.33740600	-1.65972800
O	1.82027500	-2.01113900	0.61407900
C	2.48295800	-2.71964500	1.63343900
H	1.75809700	-3.18080900	2.32189400
H	3.07812900	-1.98257900	2.18357100
H	3.14866800	-3.49359100	1.21679900
O	0.83215500	2.58157600	0.61635600
C	1.11345500	3.51009000	1.63562000
H	1.87357300	3.11249500	2.32569500
H	0.17674700	3.65852500	2.18393900
H	1.45276400	4.47293700	1.21900900
O	2.18909600	-0.99668300	-2.05966900
C	3.19189400	-1.88283600	-2.47695400
H	3.74001100	-1.49905300	-3.35323200
H	2.68429900	-2.81506100	-2.75337000
H	3.90558900	-2.08349600	-1.66078200
H	5.08860700	2.34516000	-0.99568700
H	-4.57213700	3.23408500	-1.01098200
H	-0.50934100	-5.57728000	-1.00781000

FragB (I radical) (U)M06-2X(D3)/def2-SVP E = -297.602874 a.u.

I	0.00000000	0.00000000	0.00000000

***Cat.* 1-1** (radical cation) (U)M06-2X(D3)/def2-SVP E = -2316.798721 a.u.

P	0.93082500	-0.09885000	-0.21273400
C	-0.61178700	-0.30605400	-1.12294300
C	-1.40433500	0.77825700	-1.55415500
C	-0.96685400	-1.61999200	-1.50314000
C	-2.56638900	0.52985600	-2.30801900
O	-1.00325200	2.00566900	-1.22945300
C	-2.12065100	-1.86126100	-2.25566600
O	-0.12952200	-2.58063400	-1.10386100
H	-3.17679900	1.35553900	-2.66780600
C	-2.90251000	-0.78134000	-2.64561500
C	-1.79064500	3.12737500	-1.57508600
H	-2.39940900	-2.87222100	-2.54353800
C	-0.36288100	-3.92268500	-1.47693000

H	-3.80143000	-0.95893500	-3.23788000
H	-1.86601500	3.23578400	-2.66737600
H	-1.27355200	3.99705000	-1.15637200
H	-2.79723500	3.04975200	-1.13549400
H	-1.31868800	-4.28398600	-1.06738100
H	0.46152700	-4.50482000	-1.05323100
H	-0.36524400	-4.03076700	-2.57175800
C	1.09818200	-1.17011600	1.23113600
C	0.04237400	-1.89564700	1.82634800
C	2.37925300	-1.19349100	1.82367200
C	0.30454500	-2.69412000	2.94617600
O	-1.17978600	-1.76008200	1.29920800
C	2.63352400	-1.99011700	2.94329200
O	3.29442900	-0.40655300	1.24009900
H	-0.49258700	-3.26815800	3.41297500
C	1.58973200	-2.73590700	3.47947500
C	-2.22323900	-2.60463700	1.73364800
H	3.62269500	-2.02161600	3.39453800
C	4.63111500	-0.41879800	1.69382000
H	1.77855500	-3.36001600	4.35405300
H	-1.93819000	-3.66478200	1.64390700
H	-3.07898100	-2.38999400	1.08339600
H	-2.50151700	-2.39162700	2.77807100
H	4.69836700	-0.05219900	2.72905400
H	5.18164400	0.25481200	1.02896700
H	5.05955100	-1.43006100	1.62762100
C	1.19753200	1.58009000	0.40562900
C	2.25901600	2.44896900	0.09120700
C	0.23718100	1.97209700	1.36185400
C	2.34016400	3.69414300	0.73223200
O	3.15640500	2.03252200	-0.80519400
C	0.32823100	3.20493400	2.00743900
O	-0.74478500	1.08223300	1.57284800
H	3.15265200	4.37895300	0.50117000
C	1.38306600	4.05092800	1.67481400
C	4.21889800	2.87860300	-1.18536900
H	-0.41230100	3.50463900	2.74594200
C	-1.57826500	1.22023100	2.70490900
H	1.46265600	5.02071900	2.16807300
H	3.84316500	3.81338100	-1.62824900
H	4.79273100	2.32601700	-1.93688300
H	4.86789700	3.11305700	-0.32748500
H	-0.97482000	1.32272200	3.61989000
H	-2.17720600	0.30467800	2.74921200

H	-2.25028300	2.08505200	2.59750500
I	2.56713500	-0.82862700	-1.87641700
I	-4.41428600	0.49309200	0.26865400

***Cat.* 1-2** (radical anion) (U)M06-2X(D3)/def2-SVP E = -2317.096232 a.u.

P	-1.14688600	0.06375300	0.20754200
C	0.23452100	-0.69251700	1.11476500
C	1.29578600	-0.02505500	1.75217300
C	0.21712200	-2.10100100	1.13988500
C	2.33363400	-0.75920100	2.34550600
O	1.26888100	1.31816500	1.76988400
C	1.22027800	-2.83589800	1.76947700
O	-0.79932900	-2.66741400	0.45478600
H	3.20636900	-0.25133800	2.74903600
C	2.28376900	-2.14478200	2.34797700
C	2.44779700	2.01771100	2.10118700
H	1.20129400	-3.92420300	1.76682800
C	-1.06574200	-4.03041700	0.61187100
H	3.11040700	-2.70058400	2.79276000
H	2.66115400	1.94598000	3.18147600
H	2.25459900	3.06831500	1.84650900
H	3.31417000	1.63944600	1.53069400
H	-0.27636500	-4.65183500	0.15516400
H	-2.01979400	-4.21803300	0.10569000
H	-1.16487300	-4.29588100	1.67732800
C	-1.04030100	-0.49461300	-1.53423400
C	0.04174700	-1.17191200	-2.13789200
C	-2.18629900	-0.23438900	-2.30083900
C	-0.07613700	-1.63544100	-3.45882400
O	1.14462800	-1.34022500	-1.40761700
C	-2.31291900	-0.70296500	-3.61441200
O	-3.12837600	0.51875000	-1.69190100
H	0.74913800	-2.17119600	-3.92361400
C	-1.24973000	-1.40613300	-4.17125700
C	2.30877900	-1.89882100	-1.96535400
H	-3.21428700	-0.50459300	-4.19198600
C	-4.45782200	0.43844800	-2.12483800
H	-1.33049100	-1.77559300	-5.19551100
H	2.16001500	-2.96483900	-2.21055700
H	3.10064700	-1.78036400	-1.21262600
H	2.60914600	-1.35620600	-2.87701100
H	-4.60484800	0.96175500	-3.08536400
H	-5.06427600	0.91980800	-1.34837600
H	-4.77822600	-0.61138600	-2.22230700

C	-0.90001500	1.86661700	0.02804900
C	-1.89359300	2.74941800	0.47172100
C	0.24056300	2.37981600	-0.61786400
C	-1.75416500	4.13413000	0.28704700
O	-2.95659800	2.18897800	1.07534400
C	0.39211000	3.76319600	-0.79718400
O	1.13391200	1.47792000	-1.02553700
H	-2.52113600	4.82392100	0.63369200
C	-0.60946800	4.61535900	-0.34087000
C	-4.02430300	2.98442300	1.49412800
H	1.27717700	4.16371100	-1.28733900
C	2.38061500	1.89435600	-1.53413600
H	-0.49448900	5.69213200	-0.48155900
H	-3.71714400	3.70371100	2.27276400
H	-4.76889100	2.29435500	1.90891300
H	-4.46962600	3.54180700	0.65173000
H	2.25919100	2.39645300	-2.50922300
H	3.00299600	0.99696800	-1.62726000
H	2.89074900	2.56963200	-0.82927300
I	-3.75037500	-1.13838400	1.28129900
I	5.36487300	-0.00689200	0.03983500

***Cat.* 1-2** (radical cation) (U)M06-2X(D3)/def2-SVP E = -2316.799638 a.u.

P	-0.56341500	-0.14941700	-0.00682300
C	0.26110400	-1.03807400	1.33210700
C	-0.25037500	-0.69261300	2.60042000
C	1.28789800	-1.99526500	1.23295600
C	0.28817000	-1.23446700	3.76505900
O	-1.25880100	0.19252900	2.56815500
C	1.83149300	-2.53763600	2.40721900
O	1.69504000	-2.34883000	0.01172300
H	-0.09989400	-0.95995100	4.74373700
C	1.33259100	-2.14949300	3.64466800
C	-1.67420500	0.82889700	3.75504200
H	2.63550200	-3.26776800	2.35287200
C	2.83271600	-3.17215900	-0.13857000
H	1.76401900	-2.58443500	4.54740500
H	-2.13801900	0.11214800	4.44915600
H	-2.41478800	1.57703500	3.45368400
H	-0.82264300	1.32514500	4.24618100
H	3.70904800	-2.72496600	0.35483400
H	3.01943500	-3.23741600	-1.21624000
H	2.64840500	-4.17992300	0.26445200
C	-2.25352500	-0.76688100	-0.06455200

C	-3.39690400	-0.00217600	0.25358000
C	-2.39433900	-2.13529500	-0.38032300
C	-4.66275000	-0.59200200	0.16047500
O	-3.20457100	1.25777300	0.65846800
C	-3.65987400	-2.72068800	-0.46494400
O	-1.24421800	-2.79230800	-0.58250200
H	-5.55767800	-0.01801900	0.38987300
C	-4.77473900	-1.93141300	-0.20267500
C	-4.31060400	2.12201500	0.79136300
H	-3.77482300	-3.77131800	-0.72215500
C	-1.26002700	-4.15048900	-0.96702500
H	-5.76746100	-2.37919500	-0.26655200
H	-4.89495100	2.16445000	-0.14114100
H	-3.89869100	3.11341300	1.01082500
H	-4.96706400	1.80862000	1.61792000
H	-1.71889400	-4.77441500	-0.18554600
H	-0.21154200	-4.43681500	-1.09863700
H	-1.80056500	-4.28391600	-1.91610600
C	-0.41013400	1.64483400	0.08394900
C	-1.10082400	2.38783700	-0.90198000
C	0.44238800	2.32033500	0.98588500
C	-0.95692700	3.77263600	-0.98394800
O	-1.86892000	1.67014800	-1.73269900
C	0.58446500	3.71153700	0.89435600
O	1.08428900	1.58861300	1.90102000
H	-1.48462200	4.34521800	-1.74329400
C	-0.11265500	4.41320700	-0.08038000
C	-2.47056800	2.29287700	-2.84775700
H	1.23995000	4.24228800	1.58064400
C	2.09585200	2.17405500	2.69157300
H	0.00881500	5.49549300	-0.14282500
H	-3.20713200	3.04658100	-2.52963300
H	-2.97865100	1.49882900	-3.40438400
H	-1.71171600	2.76585700	-3.48918000
H	2.87271300	2.62919300	2.05808000
H	2.53174000	1.35621700	3.27622800
H	1.68051600	2.93248600	3.37333600
I	0.44635400	-0.58535900	-2.21116900
I	3.48870900	0.59678500	-0.59550000

***Cat.* 1-2** (radical anion) (U)M06-2X(D3)/def2-SVP E = -2317.093232 a.u.

P	-1.06790300	0.03201300	-0.09555300
C	0.26910100	1.21614700	-0.34777800
C	0.18403600	2.39098200	-1.11269100

C	1.45408600	0.95615700	0.37285900
C	1.24266800	3.30502000	-1.11936400
O	-0.93853700	2.57220500	-1.84630100
C	2.52942800	1.84987900	0.34636100
O	1.47149700	-0.20859400	1.03527800
H	1.18172700	4.21444300	-1.71483900
C	2.40151200	3.01542600	-0.39985400
C	-1.26328500	3.86001600	-2.27858300
H	3.47699400	1.60482900	0.82830700
C	2.51321300	-0.46108700	1.96137400
H	3.24661000	3.70445800	-0.44223100
H	-1.21133900	4.58488600	-1.44828200
H	-2.29367000	3.81157600	-2.65437700
H	-0.60205100	4.20263000	-3.09281700
H	3.49518200	-0.51287500	1.46178600
H	2.26939200	-1.42204900	2.42763100
H	2.53121200	0.32406200	2.73400400
C	-2.62028500	0.59378000	-0.84894200
C	-3.35491800	-0.11986400	-1.80859900
C	-3.21735800	1.71867100	-0.24853700
C	-4.68277700	0.23083500	-2.09352800
O	-2.72862200	-1.13121100	-2.44050800
C	-4.53725200	2.08041900	-0.53247400
O	-2.42702000	2.40504300	0.59740100
H	-5.25168200	-0.33709200	-2.82821000
C	-5.25974300	1.31998400	-1.44966800
C	-3.48601400	-2.19828700	-2.93768700
H	-4.99164300	2.94183900	-0.04560600
C	-3.01301600	3.18861900	1.60451700
H	-6.29299700	1.59007800	-1.67507500
H	-4.21678500	-2.54364500	-2.18751700
H	-2.77682500	-3.00834700	-3.15064700
H	-4.01520100	-1.93130400	-3.86851100
H	-3.45231000	4.11261300	1.19103400
H	-2.20758300	3.44663600	2.30104200
H	-3.78255900	2.61615900	2.14594700
C	-0.60826100	-1.62322800	-0.67667400
C	-1.46832600	-2.66867900	-0.29449200
C	0.63441300	-1.94884700	-1.25802000
C	-1.08585300	-4.00685000	-0.40412500
O	-2.68159200	-2.28400200	0.16473800
C	1.03202200	-3.29340500	-1.34926900
O	1.38953300	-0.94825100	-1.71465500
H	-1.75792300	-4.80357600	-0.08891500

C	0.17639500	-4.29973800	-0.92015800
C	-3.36317300	-3.11841300	1.06601300
H	2.00801700	-3.53741300	-1.76504000
C	2.79774800	-1.10265600	-1.77312400
H	0.49565000	-5.34071500	-0.99705100
H	-3.80448900	-3.99075700	0.55326900
H	-4.16107800	-2.51023900	1.50758200
H	-2.69061300	-3.45745500	1.86909800
H	3.19109500	-1.55299000	-0.84935700
H	3.23015800	-0.09943900	-1.86055400
H	3.09789900	-1.70996600	-2.64252500
I	-1.74536000	-0.19884500	2.82337900
I	5.99017400	0.02097000	-0.02390400

Cat. **1-3** (radical cation) (U)M06-2X(D3)/def2-SVP E = -2316.801499 a.u.

C	0.56003200	0.43547600	-1.33308200
C	0.85599900	-0.35977600	-2.46429700
C	1.87636400	0.03682900	-3.33732100
H	2.12604200	-0.57011000	-4.20426700
C	2.55711300	1.22711900	-3.10617100
C	2.25470300	2.05127600	-2.02694000
H	2.80023000	2.97927000	-1.87168800
C	1.25263500	1.65296100	-1.14222600
C	-1.31953800	-1.67352900	-0.29146900
C	-2.68217400	-1.95119100	-0.54190800
C	-3.11931600	-3.28093500	-0.58959000
H	-4.16660900	-3.51123600	-0.76989900
C	-2.20112300	-4.31139400	-0.42426100
C	-0.84477100	-4.06594700	-0.22901700
H	-0.14683700	-4.89347200	-0.12673800
C	-0.40169900	-2.74276100	-0.18092100
C	-1.96352000	1.23428900	0.09394900
C	-2.83067100	1.08695000	1.19959600
C	-3.79236700	2.05575700	1.48702300
H	-4.44813300	1.95500700	2.34891200
C	-3.90901700	3.15243900	0.63671900
C	-3.11197900	3.29436900	-0.49310600
H	-3.25266000	4.14803100	-1.15189400
C	-2.14407300	2.32418800	-0.78578800
I	0.51453600	-0.00798500	2.07665900
P	-0.67883100	-0.00621400	-0.11399200
I	3.86367400	0.00719100	0.82000600
O	0.88216800	-2.39189400	-0.04879200
C	1.85719500	-3.39219800	0.17652300

H	1.62247700	-3.96808700	1.08411900
H	2.80858100	-2.86710400	0.30815600
H	1.92492600	-4.07116200	-0.68711200
O	-3.49564200	-0.91151900	-0.74659500
C	-4.88346600	-1.11858600	-0.89046400
H	-5.10691900	-1.69719100	-1.79952500
H	-5.33104800	-0.12242100	-0.97444700
H	-5.29949300	-1.63680800	-0.01257900
O	0.11776100	-1.45500100	-2.66094800
C	0.44284400	-2.34688000	-3.70427200
H	0.31376100	-1.87162000	-4.68845000
H	-0.25443800	-3.18672500	-3.61238400
H	1.47669500	-2.71219800	-3.60436700
O	0.86863500	2.36914600	-0.07957600
C	1.61884700	3.50140700	0.31372800
H	2.67163900	3.22872000	0.48370200
H	1.17292100	3.85211900	1.24996800
H	1.55544500	4.29694400	-0.44428100
O	-2.66592300	-0.03512500	1.91155300
C	-3.35969500	-0.20379700	3.13079400
H	-3.14170000	0.62353400	3.82274600
H	-3.00084400	-1.14522400	3.55888400
H	-4.44487300	-0.26842300	2.95966500
O	-1.38410900	2.36403300	-1.88306900
C	-1.41699700	3.49632700	-2.72369900
H	-2.40177100	3.60856900	-3.20195600
H	-0.65680100	3.32413900	-3.49327700
H	-1.17330900	4.41198200	-2.16263600
H	-4.65906400	3.91438200	0.85373900
H	-2.55231300	-5.34356800	-0.46382100
H	3.34637900	1.52649700	-3.79732800

***Cat.* 1-3** (radical anion) (U)M06-2X(D3)/def2-SVP E = -2317.098874 a.u.

C	-3.61990500	-1.13742900	-0.73547700
C	-3.63251200	-2.39456600	-0.10444300
C	-4.82597000	-3.10998700	0.05772600
H	-4.81564900	-4.06797600	0.57708900
C	-6.01561700	-2.60954200	-0.46594900
C	-6.01853800	-1.40198800	-1.15671100
H	-6.92912600	-0.98171100	-1.58652500
C	-4.82595000	-0.68872100	-1.28830900
C	-0.84358000	-0.62086900	0.19644400
C	-1.11605600	-0.63842500	1.57314800
C	-0.09997800	-0.81190300	2.51614400

H	-0.32149600	-0.81070800	3.58282400
C	1.20831400	-0.98740200	2.06304200
C	1.51332200	-1.00458000	0.70886100
H	2.55016800	-1.12866400	0.39515500
C	0.48192500	-0.82341300	-0.22893200
C	-2.47641200	1.52997500	-0.23421800
C	-1.41397500	2.44354500	-0.39376300
C	-1.44979500	3.72754700	0.16116400
H	-0.60275800	4.40032900	0.03533900
C	-2.58520800	4.12673700	0.85683200
C	-3.65608400	3.25577800	1.02862400
H	-4.53002700	3.57236600	1.59641300
C	-3.58972800	1.95301000	0.51009900
I	4.61759500	1.57821400	0.11258200
P	-2.11270400	-0.11002300	-1.04092800
I	5.49930900	-1.53250700	-0.23916400
O	0.70829000	-0.80144600	-1.55484700
C	2.02806400	-1.01135100	-2.01171000
H	2.72376800	-0.24486700	-1.63150800
H	1.98412900	-0.95965300	-3.10552800
H	2.40977400	-1.99736100	-1.70247300
O	-2.41999500	-0.49245200	1.92010700
C	-2.73140000	0.00114500	3.19087400
H	-2.57222600	-0.75477700	3.98018000
H	-3.79405000	0.27294300	3.15951800
H	-2.13236000	0.89650600	3.42778900
O	-2.44671400	-2.88483000	0.31339500
C	-2.40563200	-3.71728600	1.43748200
H	-3.03512000	-3.31282400	2.24806100
H	-1.35953000	-3.73799700	1.76957400
H	-2.72889500	-4.74670000	1.20429700
O	-4.85856700	0.52759900	-1.92457400
C	-4.61164300	0.46294000	-3.31326800
H	-3.62794800	0.01119000	-3.51970300
H	-4.61733700	1.49312400	-3.68995900
H	-5.39588600	-0.11904200	-3.82779400
O	-0.36315900	1.99382100	-1.10839500
C	0.93697000	2.43169100	-0.77613300
H	1.12206200	3.46398800	-1.11596400
H	1.63793400	1.76044200	-1.28402100
H	1.11241600	2.35950700	0.30925000
O	-4.57087000	1.05503500	0.76467400
C	-5.87273000	1.51869600	0.97674300
H	-6.00104600	1.95424600	1.98368200

H	-6.53138800	0.64494400	0.88346500
H	-6.15609400	2.26833000	0.21963800
H	-2.63370000	5.13062700	1.28267900
H	2.02114900	-1.10737000	2.78133100
H	-6.94128200	-3.17446100	-0.34255300

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