Electronic Supplementary Information

Direct Sb–S cross-coupling of halostibines with thiols and disulfides at room temperature: facile and efficient approaches to thiostibines

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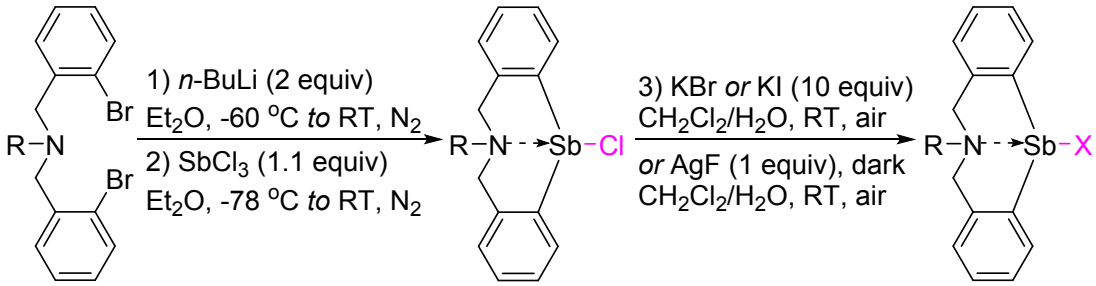
1. General remarks

The commercially available chemicals were purchased from Adamas-beta and Saan Chemical Technology (Shanghai) Co., Ltd. Unless noted otherwise, materials and solvents obtained from commercial suppliers were used without further purification. The halostibines **1a**–**1g** were prepared according to previous literatures,[1–2] as shown in Scheme S1. Reactions were performed in a Schlenk tube under standard conditions. Products were purified by flash chromatography on aluminum oxide (200–300 mesh) or silica gel (200–300 mesh), using ethyl acetate/*n*-hexane as an eluent. Melting points were determined using the XT-4 micro melting point apparatus and are uncorrected. Proton, carbon, and fluorine nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR spectroscopy) spectrometer with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Chemicals shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS). Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet). Coupling constants (J) are reported in hertz. The NMR yields were determined by ^{1}H NMR spectra with mesitylene as an internal standard. The crystallographic data of compounds **4a**, **4f**, and **4v** were collected at 150 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Mass spectra were recorded using a GC-MS TQ8040. High resolution mass spectra were measured on a Thermo Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions.



L1, R = Ph
L2, R = Cy
L3, R = ^{t}Bu

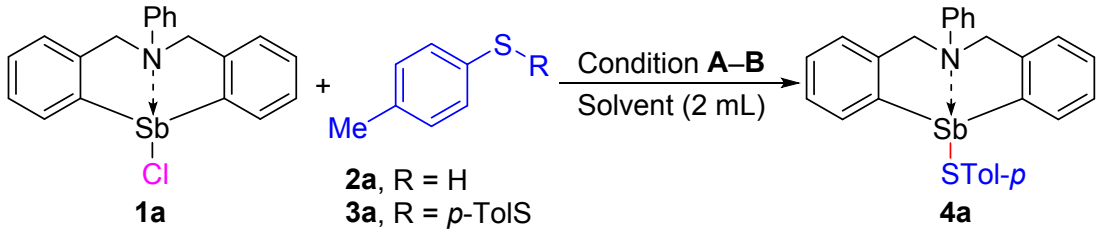
1a, R = Ph
1b, R = Cy
1c, R = ^{t}Bu

1e, R = Ph, X = Br
1f, R = Ph, X = I
1g, R = Ph, X = F

Scheme S1 Synthetic routes for the preparation of halostibines containing azastibocine frameworks.

2. Optimisation of reaction conditions

Table S1 Screening of solvent.[a]



Entry	Sulfur (equiv)	Solvent (mL)	Yield of **4a** (%)[b]
1	**2a** (0.3)	DMF (2)	90
2	**2a** (0.3)	DMAc (2)	91
3	**2a** (0.3)	1,4-dioxane (2)	84
4	**2a** (0.3)	THF (2)	80
5	**2a** (0.3)	toluene (2)	62
6	**2a** (0.3)	MeCN (2)	75
7	**2a** (0.3)	1,2-DCE (2)	81
8	**2a** (0.3)	DCM (2)	77
9	**2a** (0.3)	*i*-PrOH (2)	trace
10	**2a** (0.3)	*n*-hexane (2)	trace
11	**2a** (0.3)	cyclohexane (2)	trace
12	**2a** (0.3)	H_2O (2)	N.D.
13	**3a** (0.15)	DMF (2)	88
14	**3a** (0.15)	DMAc (2)	83
15	**3a** (0.15)	1,4-dioxane (2)	trace
16	**3a** (0.15)	THF (2)	N.D.
17	**3a** (0.15)	toluene (2)	N.D.
18	**3a** (0.15)	MeCN (2)	23
19	**3a** (0.15)	1,2-DCE (2)	N.D.
20	**3a** (0.15)	DCM (2)	N.D.
21	**3a** (0.15)	*i*-PrOH (2)	N.D.
22	**3a** (0.15)	*n*-hexane (2)	N.D.
23	**3a** (0.15)	cyclohexane (2)	N.D.
24	**3a** (0.15)	H_2O (2)	N.D.

[a] Reaction conditions **A**: chlorostibine **1a** (128.1 mg, 0.3 mmol), *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol), solvent (2 mL), air atmosphere, room temperature, 2 h. Reaction conditions **B**: chlorostibine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (36.9 mg, 0.15 mmol), Zn (0.3 mmol), solvent (2 mL), nitrogen atmosphere, room temperature, 6 h. [b] ^{1}H NMR yield using mesitylene (0.3 mmol) as internal standard. [c] Not detected.

3. General procedure for the preparation of thiostibines

General procedure 1: starting from thiols (GP1)

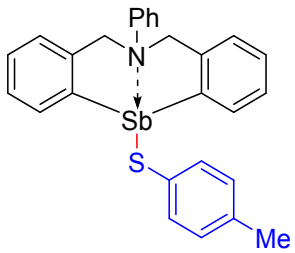
A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with halostibine **1** (0.3 mmol), thiol **2** (0.3 mmol, 1 equiv), and DMSO (2 mL). Then the mixture was vigorously stirred at room temperature under air for 2–12 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide or silica gel, eluting with ethyl acetate/*n*-hexane, to afford the desired product.

General procedure 2: starting from disulfides (GP2)

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with halostibine **1** (0.3 mmol), disulfide **3** (0.15 mmol, 0.5 equiv), Zn (0.3 mmol, 1 equiv) and DMSO (2 mL). The tube was evacuated and filled with N_2, and vigorously stirred at room temperature for 6–12 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide or silica gel, eluting with ethyl acetate/*n*-hexane, to afford the desired product.

4. Analytical data for products

6-phenyl-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4a)



For chlorostibine: According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from

50:1 to 10:1), the title compound was obtained as a white solid (140.5 mg, 91% yield).

For chlorostibine: According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in 2 mL DMSO. With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (137.5 mg, 89% yield).

For bromostibine: According to the **GP1**, reaction was conducted using 12-bromo-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1e** (141.0 mg, 0.3 mmol) and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (143.7 mg, 93% yield).

For bromostibine: According to the **GP2**, reaction was conducted using 12-bromo-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1e** (141.0 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in 2 mL DMSO. With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (129.7 mg, 84% yield).

For iodostibine: According to the **GP1**, reaction was conducted using 12-iodo-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1f** (155.4 mg, 0.3 mmol) and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (135.9 mg, 88% yield).

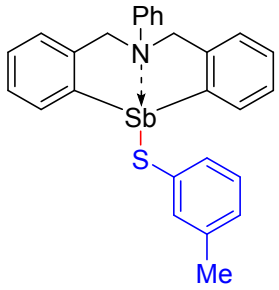
For iodostibine: According to the **GP2**, reaction was conducted using 12-iodo-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1f** (155.4 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in 2 mL DMSO. With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (123.6 mg, 80% yield).

For fluorostibine: According to the **GP1**, reaction was conducted using 12-fluoro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1g** (123.3 mg, 0.3 mmol) and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). The crude reaction mixture was analyzed by TLC, and only a trace amount of the title compound was detected.

For fluorostibine: According to the **GP2**, reaction was conducted using 12-fluoro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1g** (123.3 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). The crude reaction mixture was analyzed by TLC, and only a trace amount of the title compound was detected.

Mp: 185–187 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 7.0 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 6.9 Hz, 2H), 7.25 (t, J = 6.8 Hz, 2H), 7.19–7.12 (m, 4H), 7.07 (d, J = 7.6 Hz, 2H), 6.98–6.92 (m, 3H), 4.57 (d, J = 15.0 Hz, 2H), 4.32 (d, J = 15.0 Hz, 2H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.2, 143.3, 137.5, 135.8, 135.0, 134.2, 133.5, 129.4, 129.1, 128.8, 128.7, 126.0, 123.4, 118.5, 59.0, 20.9; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NSSb$ $[M+H]^+$: 516.0746, found: 516.0742.

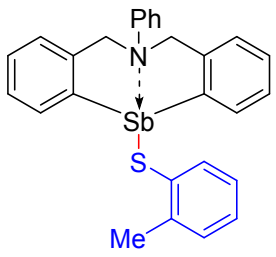
6-phenyl-12-(*m*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4b)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and *m*-toluenethiol **2b** (36 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (134.4 mg, 87% yield).

Mp: 193–195 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 7.1 Hz, 2H), 7.36–7.34 (m, 3H), 7.30–7.27 (m, 3H), 7.23–7.15 (m, 4H), 7.10 (d, J = 7.7 Hz, 2H), 7.01 (q, J = 8.2 Hz, 2H), 6.89 (d, J = 7.4 Hz, 2H), 4.62 (d, J = 15.0 Hz, 2H), 4.37 (d, J = 15.0 Hz, 2H), 2.22 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.3, 143.4, 138.2, 137.5, 137.0, 135.9, 134.9, 131.3, 129.2, 128.8, 128.8, 128.4, 126.3, 126.0, 123.5, 118.6, 59.1, 21.2; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NSSb$ $[M+H]^+$: 516.0746; found: 516.0748.

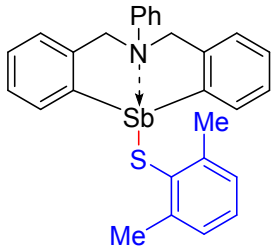
6-phenyl-12-(*o*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4c)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and *o*-toluenethiol **2c** (35 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (126.7 mg, 82% yield).

Mp: 199–200 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.46 (d, J = 7.1 Hz, 2H), 7.46 (d, J = 7.1 Hz, 1H), 7.34 (t, J = 7.0 Hz, 2H), 7.26 (t, J = 7.1 Hz, 2H), 7.18–7.12 (m, 5H), 7.06 (d, J = 7.6 Hz, 2H), 7.00–6.94 (m, 3H), 4.57 (d, J = 15.0 Hz, 2H), 4.32 (d, J = 14.2 Hz, 2H), 2.55 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.2, 143.4, 141.0, 137.5, 136.9, 136.0, 135.4, 129.8, 129.1, 128.8, 128.7, 126.0, 126.0, 125.7, 123.4, 118.5, 59.0, 22.6; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NSSb$ $[M+H]^+$: 516.0746; found: 516.0745.

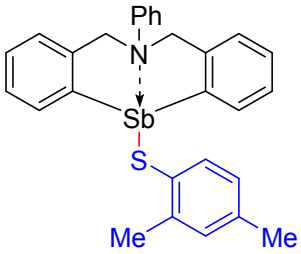
12-((2,6-dimethylphenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4d)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2,6-dimethylthiophenol **2d** (40 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (133.3 mg, 84% yield).

Mp: 212–213 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.63 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.19–7.13 (m, 4H), 7.02 (d, J = 7.3 Hz, 2H), 6.96–6.94 (m, 2H), 4.57 (d, J = 15.0 Hz, 2H), 4.31 (d, J = 15.0 Hz, 2H), 2.53 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.5, 143.3, 142.9, 137.8, 136.1, 136.1, 129.1, 128.8, 128.7, 127.6, 125.9, 125.9, 123.3, 118.3, 59.0, 24.5; **HRMS *m/z* (ESI)** calcd. for $C_{28}H_{27}NSSb$ $[M+H]^+$: 530.0902; found: 530.0907.

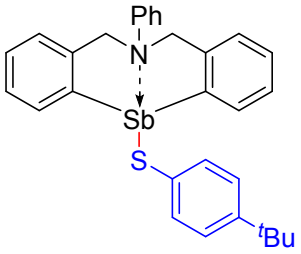
12-((2,4-dimethylphenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4e)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2,4-dimethylbenzenethiol **2e** (41 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (136.5 mg, 86% yield).

Mp: 203–205 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.75 (d, J = 6.3 Hz, 2H), 7.65–7.49 (m, 5H), 7.39–7.37 (m, 2H), 7.28 (d, J = 6.8 Hz, 2H), 7.21–7.19 (m, 2H), 7.03 (s, 1H), 4.77 (d, J = 15.0 Hz, 2H), 4.52 (d, J = 15.0 Hz, 2H), 2.78 (s, 3H), 2.43 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.1, 143.3, 140.8, 137.4, 135.9, 135.5, 135.3, 132.9, 130.8, 129.0, 128.7, 128.6, 126.9, 126.0, 123.2, 118.4, 58.8, 22.5, 20.8; **HRMS *m/z* (ESI)** calcd. for $C_{28}H_{27}NSSb$ $[M+H]^+$: 530.0902; found: 530.0903.

12-((4-(*tert*-butyl)phenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4f)

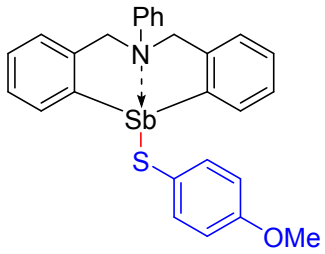


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-*tert*-butylbenzenethiol **2f** (52 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (135.4 mg, 81% yield).

Mp: 233–234 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 7.0 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 6.9 Hz, 2H), 7.31 (t, J = 7.0 Hz, 2H), 7.25–7.12 (m, 8H), 7.02 (t, J = 6.9 Hz, 1H), 4.66 (d, J = 15.0 Hz, 2H), 4.41 (d, J = 15.0 Hz, 2H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.4, 148.3, 143.4, 137.6, 136.0, 133.8, 133.6,

129.2, 128.8, 126.0, 125.7, 123.5, 118.6, 59.1, 34.3, 31.3; **HRMS *m/z* (ESI)** calcd. for $C_{30}H_{31}NSSb$ $[M+H]^+$: 558.1215; found: 558.1218.

12-((4-methoxyphenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4g)

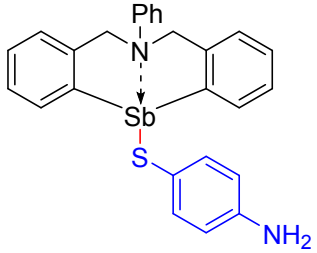


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-methoxybenzenethiol **2g** (37 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 20:1 to 2:1), the title compound was obtained as a white solid (130.6 mg, 82% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), bis(4-methoxyphenyl) disulfide **3b** (41.8 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 20:1 to 2:1), the title compound was obtained as a white solid (117.9 mg, 74% yield).

Mp: 187–189 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 7.3 Hz, 2H), 7.41 (d, J = 7.4 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.26 (t, J = 7.3 Hz, 2H), 7.20–7.13 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 7.0 Hz, 1H), 6.68 (d, J = 7.5 Hz, 2H), 4.58 (d, J = 15.0 Hz, 2H), 4.32 (d, J = 15.0 Hz, 2H), 3.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 157.9, 148.2, 143.4, 137.5, 135.8, 135.5, 129.1, 128.8, 128.7, 127.4, 126.0, 123.4, 118.5, 114.3, 59.0, 55.1; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NOSSb$ $[M+H]^+$: 532.0695; found: 532.0692.

4-((6-phenyl-6,7-dihydrodibenzo[*c,f*][*1,5*]azastibocin-12(5H)-yl)thio)aniline (4h)

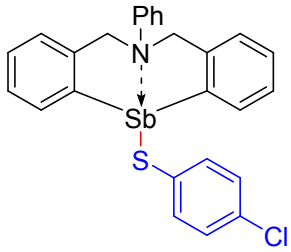


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-aminobenzenethiol **2h** (37.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 20:1 to 2:1), the title compound was obtained as a white solid (114.6 mg, 74% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), 4,4'-dithiodianiline **3c** (37.3 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 20:1 to 2:1), the title compound was obtained as a white solid (105.3 mg, 68% yield).

Mp: 168–170 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 7.1 Hz, 2H), 7.35 (t, J = 6.8 Hz, 2H), 7.29 (t, J = 7.2 Hz, 4H), 7.22–7.15 (m, 4H), 7.09 (d, J = 7.6 Hz, 2H), 6.99 (t, J = 6.6 Hz, 1H), 6.47 (d, J = 7.1 Hz, 2H), 4.61 (d, J = 15.0 Hz, 2H), 4.36 (d, J = 14.9 Hz, 2H), 3.48 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.3, 144.5, 143.4, 137.7, 135.9, 135.6, 129.1, 128.7, 126.0, 124.2, 123.3, 118.5, 115.7, 59.0; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{24}N_2SSb$ $[M+H]^+$: 517.0698; found: 517.0691.

12-((4-chlorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4i)

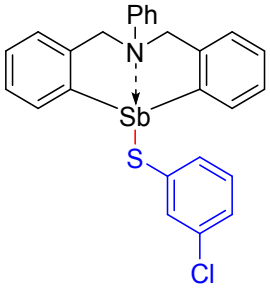


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-chlorobenzenethiol **2i** (43.4 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (149.2 mg, 93% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), bis(4-chlorophenyl) disulfide **3d** (43.1 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (139.6 mg, 87% yield).

Mp: 221–223 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.31 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 7.7 Hz, 2H), 7.34 (t, J = 7.1 Hz, 2H), 7.28 (t, J = 7.2 Hz, 2H), 7.22–7.15 (m, 4H), 7.11–7.06 (m, 4H), 7.00 (t, J = 7.0 Hz, 1H), 4.61 (d, J = 15.0 Hz, 2H), 4.36 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.0, 143.3, 137.2, 136.3, 135.8, 135.3, 131.2, 129.2, 128.9, 128.8, 128.5, 126.1, 123.7, 118.7, 59.2; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}ClNSSb$ $[M+H]^+$: 536.0200; found: 536.0193.

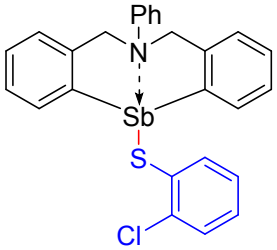
12-((3-chlorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][*1*,*5*]azastibocine (4j)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][*1*,*5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 3-chlorobenzenethiol **2j** (35 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (144.5 mg, 90% yield).

Mp: 232–234 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.31 (d, J = 7.0 Hz, 2H), 7.52 (s, 1H), 7.34–7.30 (m, 3H), 7.25 (t, J = 6.8 Hz, 2H), 7.20–7.07 (m, 6H), 6.99–6.96 (m, 3H), 4.57 (d, J = 15.0 Hz, 2H), 4.32 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.9, 143.3, 140.1, 137.1, 135.7, 133.8, 133.6, 132.3, 129.4, 129.2, 128.9, 128.8, 126.1, 125.4, 123.8, 118.7, 59.2; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}ClNSSb$ $[M+H]^+$: 536.0200; found: 536.0197.

12-((2-chlorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][*1*,*5*]azastibocine (4k)



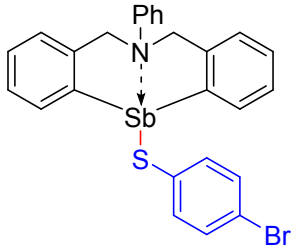
According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][*1*,*5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2-

chlorobenzenethiol **2k** (34 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (141.2 mg, 88% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), bis(2-chlorophenyl) disulfide **3e** (43.1 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (134.8 mg, 84% yield).

Mp: 207–209 °C; **^{1}H NMR (400 MHz, CDCl$_3$,)**: δ 8.48 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 3.6 Hz, 1H), 7.37–7.25 (m, 5H), 7.21–7.08 (m, 6H), 7.00–6.98 (m, 3H), 4.58 (d, J = 15.0 Hz, 2H), 4.35 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.1, 143.3, 138.1, 137.4, 137.1, 136.5, 136.2, 129.5, 129.2, 128.9, 128.8, 126.6, 126.6, 126.0, 123.7, 118.8, 59.3; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}ClNSSb$ $[M+H]^+$: 536.0200; found: 536.0193.

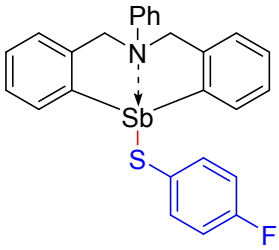
12-((4-bromophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4l)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-bromobenzenethiol **2l** (56.7 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (147.4 mg, 85% yield).

Mp: 218–220 °C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.41 (d, J = 7.2 Hz, 2H), 7.46–7.44 (m, 4H), 7.39 (d, J = 7.1 Hz, 2H), 7.33–7.26 (m, 6H), 7.21 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 7.0 Hz, 1H), 4.72 (d, J = 15.0 Hz, 2H), 4.47 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.0, 143.3, 137.2, 137.1, 135.8, 135.7, 131.4, 129.2, 128.9, 128.8, 126.1, 123.8, 119.2, 118.7, 59.2; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}BrNSSb$ $[M+H]^+$: 579.9695; found: 579.9700.

12-((4-fluorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4m)

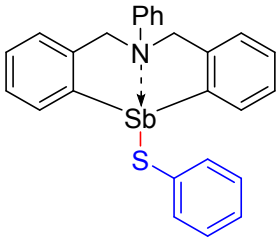


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 4-fluorobenzenethiol **2m** (38.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (135.5 mg, 87% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), bis(4-fluorophenyl) disulfide **3f** (38.1 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1),the title compound was obtained as a white solid (124.6 mg, 80% yield).

Mp: 234–236 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.34 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 4.8 Hz, 2H), 7.33 (t, J = 7.1 Hz, 2H), 7.26 (t, J = 7.2 Hz, 2H), 7.20–7.13 (m, 4H), 7.08 (d, J = 7.7 Hz, 2H), 6.98 (t, J = 7.0 Hz, 1H), 6.80 (t, J = 8.0 Hz, 2H), 4.58 (d, J = 15.0 Hz, 2H), 4.33 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$; list of signals, C–F coupling not resolved)**: δ 162.5, 160.0, 148.1, 143.4, 137.3, 135.7, 135.7, 135.6, 132.4, 132.4, 129.2, 128.9, 128.8, 126.1, 123.6, 118.6, 115.6, 115.4, 59.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.99; **HRMS *m/z* (ESI)** calcd. for $C_{21}H_{20}S_2Sb$ $[M+H]^+$: 520.0495; found: 520.0499.

6-phenyl-12-(phenylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4n)

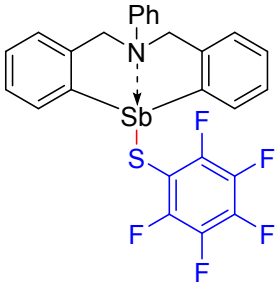


According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), diphenyl disulfide **3g** (32.8 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl

acetate from 50:1 to 10:1), the title compound was obtained as a white solid (129.3 mg, 86% yield).

Mp: 189–191 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.36 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.34 (t, J = 7.1 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 7.21–7.03 (m, 9H), 6.99 (t, J = 7.0 Hz, 1H), 4.60 (d, J = 15.0 Hz, 2H), 4.35 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.2, 143.4, 137.5, 137.4, 135.9, 134.2, 129.2, 128.8, 128.8, 128.5, 126.0, 125.3, 123.5, 118.7, 59.1; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{23}NSSb$ $[M+H]^+$: 502.0509; found: 502.0505.

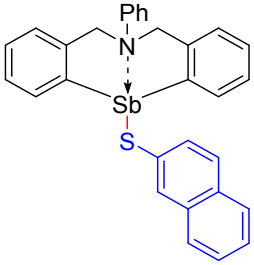
12-((perfluorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4o)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and pentafluorobenzenethiol **2n** (40 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1),, the title compound was obtained as a white solid (122.3 mg, 69% yield).

Mp: 233–235 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.47 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.28–7.20 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 4.66 (d, J = 15.0 Hz, 2H), 4.44 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$; list of signals, C–F coupling not resolved)**: δ 149.4, 149.4, 149.3, 147.8, 147.0, 147.0, 146.9, 146.9, 143.2, 137.4, 136.0, 129.4, 129.2, 129.1, 126.0, 124.5, 119.1, 59.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -131.09 (dd, J = 26.3, 7.5 Hz, 2F), -158.06 (t, J = 22.6 Hz, 1F), -162.72–-162.86 (m, 2F); **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{18}F_5NSSb$ $[M+H]^+$: 592.0118; found: 592.0110.

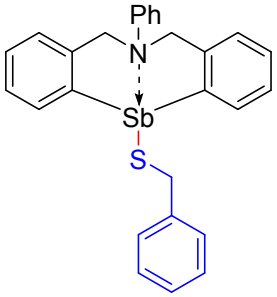
12-(naphthalen-2-ylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4p)



According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2-naphthalenethiol **2o** (48.0 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 20:1 to 5:1), the title compound was obtained as a white solid (119.0 mg, 72% yield).

Mp: 221–223 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.63 (d, J = 7.3 Hz, 2H), 8.19 (s, 1H), 7.84–7.75 (m, 4H), 7.55–7.42 (m, 6H), 7.34–7.27 (m, 4H), 7.21 (d, J = 7.8 Hz, 2H), 7.12 (t, J = 7.0 Hz, 1H), 4.68 (d, J = 15.0 Hz, 2H), 4.44 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.0, 143.3, 137.3, 135.8, 135.1, 133.7, 132.6, 132.3, 131.3, 129.1, 128.8, 128.8, 127.8, 127.5, 126.7, 126.0, 126.0, 125.0, 123.5, 118.6, 59.0; **HRMS *m/z* (ESI)** calcd. for $C_{30}H_{25}NSSb$ $[M+H]^+$: 552.0746; found: 552.0739.

12-(benzylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4q)

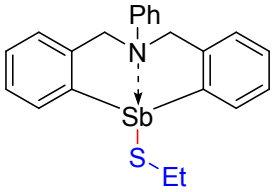


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and benzyl mercaptan **2p** (35 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 10:1 to 5:1), the title compound was obtained as a white solid (97.3 mg, 63% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), dibenzyl disulfide **3h** (37.0 mg, 0.15 mmol), and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (89.6 mg, 58% yield).

Mp: 232–234 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.15 (d, J = 5.8 Hz, 2H), 7.36 (d, J = 7.2 Hz, 2H), 7.24–7.21 (m, 8H), 7.15–7.09 (m, 5H), 7.00 (t, J = 7.1 Hz, 1H), 4.59 (d, J = 15.0 Hz, 2H), 4.31 (d, J = 15.0 Hz, 2H), 3.96 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.4, 143.1, 142.5, 136.3, 135.9, 129.1, 128.6, 128.5, 128.4, 128.3, 126.4, 126.0, 123.1, 118.4, 58.7, 33.5; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NSSb$ $[M+H]^+$: 516.0746; found: 516.0746.

12-(ethylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4r)

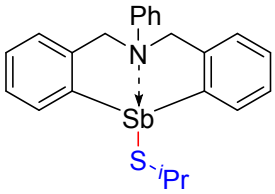


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and ethanethiol **2q** (22 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a yellow oil (57.1 mg, 42% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), diethyl disulfide **3i** (18.3 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a yellow oil (63.9 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.0 Hz, 2H), 7.34–7.25 (m, 7H), 7.18–7.13 (m, 3H), 7.03 (t, J = 7.0 Hz, 1H), 4.68 (d, J = 14.9 Hz, 2H), 4.39 (d, J = 15.0 Hz, 2H), 2.80 (q, J = 6.2 Hz, 2H), 1.37 (t, J = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.5, 143.2, 136.4, 135.9, 129.2, 128.7, 128.6, 126.0, 123.0, 118.3, 58.7, 23.7, 20.3; **HRMS *m/z* (ESI)** calcd. for $C_{22}H_{23}NSSb$ $[M+H]^+$: 454.0518; found: 454.0514.

12-(isopropylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4s)



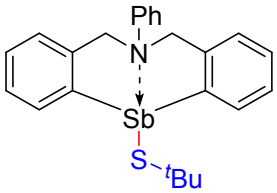
According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2-propanethiol **2r** (28 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a yellow oil (64.4 mg, 46% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), diisopropyl disulfide **3j** (24 μL, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-

hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a yellow oil (46.2 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 6.9 Hz, 2H), 7.33–7.23 (m, 6H), 7.14 (t, J = 8.4 Hz, 4H), 7.02 (t, J = 7.2 Hz, 1H), 4.66 (d, J = 15.0 Hz, 2H), 4.37 (d, J = 15.0 Hz, 2H), 3.21–3.18 (m, 1H), 1.43 (d, J = 5.7 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.6, 143.2, 136.1, 136.0, 129.2, 128.6, 128.5, 126.0, 122.8, 118.2, 58.6, 34.6, 28.7; **HRMS *m/z* (ESI)** calcd. for $C_{23}H_{25}NSSb$ $[M+H]^+$: 468.0746; found: 468.0753.

12-(*tert*-butylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4t)

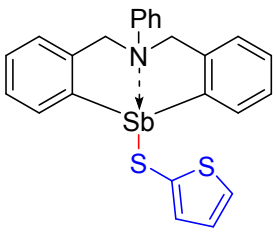


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2-methyl-2-propanethiol **2s** (34 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (80.8 mg, 56% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), di-*tert*-butyl disulfide **3k** (29 μL, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (67.8 mg, 47% yield).

Mp: 211–213 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.31 (d, J = 7.0 Hz, 2H), 7.31–7.22 (m, 6H), 7.19–7.13 (m, 4H), 7.00 (t, J = 7.0 Hz, 1H), 4.64 (d, J = 14.9 Hz, 2H), 4.34 (d, J = 15.0 Hz, 2H), 1.53 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.7, 143.3, 136.1, 135.5, 129.1, 128.5, 128.4, 126.0, 122.6, 118.1, 58.4, 43.1, 35.9; **HRMS *m/z* (ESI)** calcd. for $C_{24}H_{27}NSSb$ $[M+H]^+$: 482.0830; found: 482.0827.

6-phenyl-12-(thiophen-2-ylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4u)

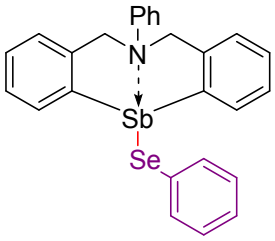


According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and 2-thiophenethiol **2t** (34.9 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (108.0 mg, 71% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), di(2-thienyl) disulfide **3l** (34.6 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (100.4 mg, 66% yield).

Mp: 214–216 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.33 (d, J = 7.0 Hz, 2H), 7.38 (t, J = 6.9 Hz, 2H), 7.31 (t, J = 6.7 Hz, 2H), 7.25–7.18 (m, 5H), 7.13 (d, J = 7.6 Hz, 2H), 7.05–7.01 (m, 2H), 6.84–6.83 (m, 1H), 4.64 (d, J = 15.0 Hz, 2H), 4.40 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.2, 143.4, 138.0, 136.4, 135.8, 132.1, 129.3, 128.9, 128.9, 127.6, 126.1, 126.0, 123.9, 118.9, 59.5; **HRMS *m/z* (ESI)** calcd. for $C_{24}H_{21}NS_2Sb$ $[M+H]^+$: 508.0154; found: 508.0158.

6-phenyl-12-(phenylselanyl)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (7)



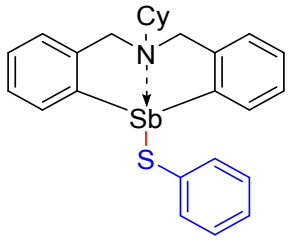
According to the **GP1**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol) and benzeneselenol **5** (32 μL, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (112.0 mg, 68% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1a** (128.1 mg, 0.3 mmol), diphenyl diselenide **6** (46.8 mg, 0.15 mmol), and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1),, the title compound was obtained as a white solid (103.8 mg, 63% yield)

Mp: 232–235 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.36 (d, J = 6.8 Hz, 2H), 7.62–7.61 (m, 2H), 7.32–7.25 (m, 4H), 7.20–7.07 (m, 9H), 6.97 (t, J = 6.9 Hz, 1H), 4.58 (d, J =

15.0 Hz, 2H), 4.33 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.1, 143.3, 137.1, 137.1, 136.0, 135.6, 129.4, 129.1, 128.8, 128.7, 126.1, 125.9, 123.4, 118.6, 59.0; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{23}NSeSb$ $[M+H]^+$: 550.0034; found: 550.0029.

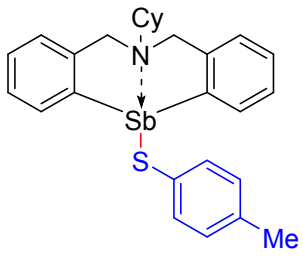
6-cyclohexyl-12-(phenylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4v)



According to the **GP2**, reaction was conducted using 12-chloro-6-cyclohexyl-5,6,7,12 -tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1b** (129.9 mg, 0.3 mmol), diphenyl disulfide **3g** (32.8 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (127.7 mg, 84% yield).

Mp: 195–197 °C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.37 (d, J = 7.1 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.23–7.14 (m, 4H), 7.09–7.03 (m, 3H), 4.01 (d, J = 15.0 Hz, 2H), 3.87 (d, J = 15.0 Hz, 2H), 2.87 (t, J = 10.4 Hz, 1H), 1.96 (d, J = 11.2 Hz, 2H), 1.72 (d, J = 12.0 Hz, 2H), 1.57 (d, J = 12.2 Hz, 1H), 1.32–0.98 (m, 5H); **^{13}C NMR (100 MHz, CDCl$_3$, TMS)**: δ 144.4, 139.2, 137.8, 135.6, 134.1, 128.5, 128.4, 128.3, 125.6, 124.6, 63.9, 56.2, 29.2, 25.7, 25.6; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{29}NSSb$ $[M+H]^+$: 508.0931; found: 508.0936.

6-cyclohexyl-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4w)

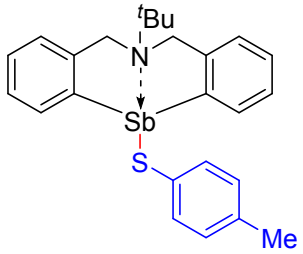


According to the **GP1**, reaction was conducted using 12-chloro-6-cyclohexyl-5,6,7,12 -tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1b** (129.9 mg, 0.3 mmol), and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (126.6 mg, 81% yield).

According to the **GP2**, reaction was conducted using 12-chloro-6-cyclohexyl-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1b** (129.9 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (117.2 mg, 75% yield).

Mp: 207–208 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.41 (d, J = 7.1 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 6.9 Hz, 2H), 7.28–7.25 (m, 2H), 7.07 (dd, J = 26.5, 7.3 Hz, 4H), 4.80 (d, J = 15.0 Hz, 2H), 3.94 (d, J = 15.0 Hz, 2H), 2.95 (t, J = 10.2 Hz, 1H), 2.31 (s, 3H), 2.03 (d, J = 11.3 Hz, 2H), 1.79 (d, J = 12.2 Hz, 2H), 1.65–1.62 (m, 1H), 1.38–1.04 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.4, 138.0, 135.7, 135.2, 134.4, 134.2, 129.3, 128.5, 128.4, 125.6, 64.0, 56.3, 29.2, 25.8, 25.7, 21.0; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{31}NSSb$ $[M+H]^+$: 522.1215; found: 522.1220.

6-(*tert*-butyl)-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine (4x)

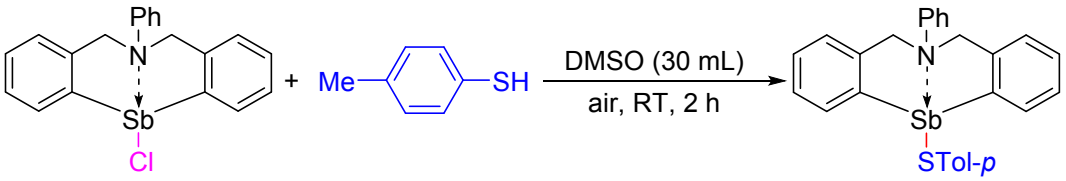


According to the **GP1**, reaction was conducted using 6-(*tert*-butyl)-12-chloro-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1c** (122.1 mg, 0.3 mmol) and *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (112.9 mg, 76% yield).

According to the **GP2**, reaction was conducted using 6-(*tert*-butyl)-12-chloro-5,6,7,12-tetrahydrodibenzo[*c,f*][*1,5*]azastibocine **1c** (122.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (37.0 mg, 0.15 mmol) and Zn (19.5 mg, 0.3 mmol) in DMSO (2 mL). With purification by flash chromatography column on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), the title compound was obtained as a white solid (108.4 mg, 73% yield).

Mp: 206–208 °C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.38 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 7.4 Hz, 2H), 7.26 (t, J = 7.0 Hz, 2H), 7.20–7.15 (m, 2H), 7.01 (dd, J = 15.7, 7.3 Hz, 4H), 4.18 (d, J = 15.4 Hz, 2H), 3.79 (d, J = 15.3 Hz, 2H), 2.25 (s, 3H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.5, 137.6, 135.6, 135.0, 134.3, 134.0, 129.2, 128.5, 128.0, 125.3, 59.0, 55.7, 26.9, 20.9; **HRMS *m/z* (ESI)** calcd. for $C_{25}H_{29}NSSb$ $[M+H]^+$: 496.1059; found: 496.1060.

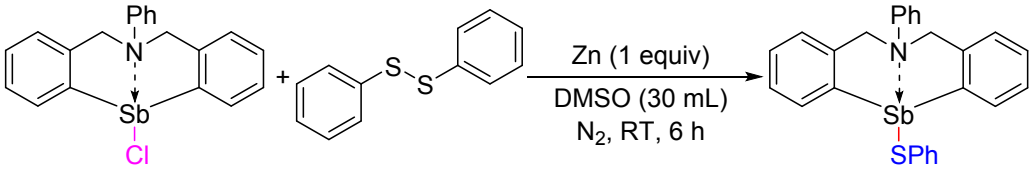
5. Gram-scale experiments



1a, 6 mmol **2a,** 6 mmol **4a**, 2.565 g

83% isolate yield

A 100 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (2.562 g, 6 mmol), *p*-toluenethiol **2a** (0.744 g, 6 mmol), and DMSO (30 mL). Then the mixture was vigorously stirred at room temperature under air for 2 h. After the reaction was accomplished, deionized water (100 mL) was added, and the mixture was extracted by dichloromethane (3×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), to afford the desired product **4a** (2.565 g, 83%).



1a, 6 mmol **3g,** 3 mmol **4n**, 2.345g

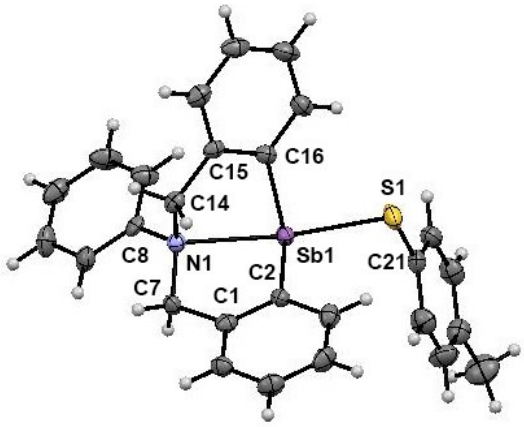
78% isolate yield

A 100 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (2.562 g, 6 mmol), diphenyl disulfide **3g** (0.656 g, 3 mmol), Zn (0.390 g, 6 mmol) and DMSO (30 mL). The tube was evacuated and filled with N_2, and vigorously stirred at room temperature for 6 h. After the reaction was accomplished, deionized water (100 mL) was added, and the mixture was extracted by dichloromethane (3×100 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (gradient *n*-hexane/ethyl acetate from 50:1 to 10:1), to afford the desired product **4n** (2.345 g, 78%).

6. X-ray crystallographic structure determination

Single crystals of compounds **4a**, **4f**, and **4v** were obtained by recrystallization in a dichloromethane/*n*-hexane mixture at room temperature. The results of the crystal structure determination and refinement for the corresponding thiostibines are given in Table S2–S4. In all cases, the crystallographic data were collected at 150 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation and were processed with CrysAlisPro. The structures were solved by direct methods using Olex2 and subsequently refined by full-matrix least squares on F^2 using SHELXL-2014.[3–5] All non-hydrogen atoms were refined anisotropically and the hydrogen atom positions were fixed geometrically at the calculated distances. The weighted R factor, wR, and goodness-of-fit S values were obtained based on F^2.

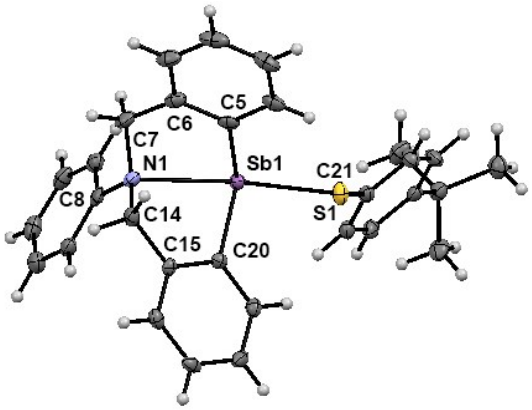
Table S2 Crystal data and structure refinement for thiostibine 4a.



Identification code	**4a**
Empirical formula	$C_{27}H_{24}NSSb$
Formula weight	516.28
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.9614(5)
b/Å	15.2361(7)
c/Å	12.3334(5)
α/°	90
β/°	92.953(4)
γ/°	90

Volume/Å^3	2244.73(17)
Z	4
ρ_{calc}g/cm^3	1.528
μ/mm^{-1}	1.336
F(000)	1040.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.252 to 49.982
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -9 ≤ l ≤ 14
Reflections collected	10124
Independent reflections	3947 [R_{int} = 0.0347, R_{sigma} = 0.0469]
Data/restraints/parameters	3947/0/272
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0608
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0665
Largest diff. peak/hole / e Å^{-3}	0.67/-0.61

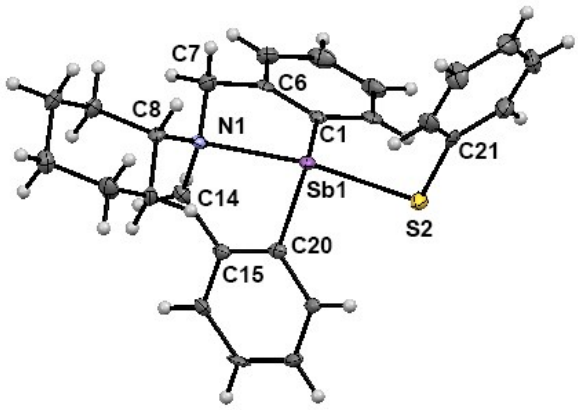
Table S3 Crystal data and structure refinement for thiostibine 4f.



Identification code	**4f**
Empirical formula	$C_{30}H_{30}NSSb$
Formula weight	558.36
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.0684(5)
b/Å	16.7181(7)

c/Å	12.4529(5)
α/°	90
β/°	99.279(4)
γ/°	90
Volume/Å^3	2479.65(19)
Z	4
ρ_{calc}g/cm^3	1.496
μ/mm^{-1}	1.216
F(000)	1136.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.114 to 49.998
Index ranges	-14 ≤ h ≤ 12, -19 ≤ k ≤ 15, -14 ≤ l ≤ 14
Reflections collected	11697
Independent reflections	4374 [R_{int} = 0.0315, R_{sigma} = 0.0415]
Data/restraints/parameters	4374/0/301
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0270, wR_2 = 0.0546
Final R indexes [all data]	R_1 = 0.0334, wR_2 = 0.0585
Largest diff. peak/hole / e Å^{-3}	0.43/-0.46

Table S4 Crystal data and structure refinement for thiostibine 4v.

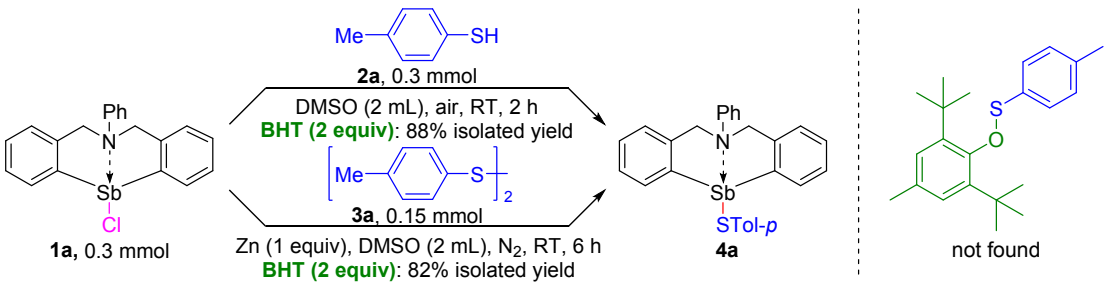


Identification code	**4v**
Empirical formula	$C_{26}H_{28}NSSb$
Formula weight	508.30
Temperature/K	150.00(10)
Crystal system	monoclinic

Space group	$P2_1/n$
a/Å	8.7657(6)
b/Å	19.2142(13)
c/Å	13.3556(9)
α/°	90
β/°	101.451(7)
γ/°	90
Volume/Å^3	2204.7(3)
Z	4
ρ_{calc}g/cm^3	1.531
μ/mm^{-1}	1.359
F(000)	1032.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.764 to 49.982
Index ranges	-10 ≤ h ≤ 10, -22 ≤ k ≤ 22, -15 ≤ l ≤ 13
Reflections collected	9478
Independent reflections	3884 [R_{int} = 0.0579, R_{sigma} = 0.0783]
Data/restraints/parameters	3884/6/262
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.0859
Final R indexes [all data]	R_1 = 0.0577, wR_2 = 0.0939
Largest diff. peak/hole / e Å^{-3}	1.10/-0.89

7. Control experiments

Radical trapping experiments

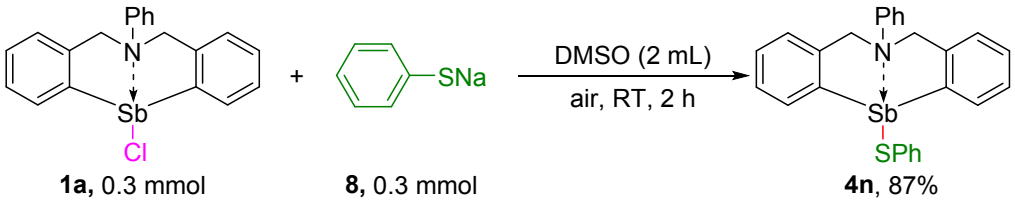


For thiol 2a: A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), *p*-toluenethiol **2a** (37.2 mg, 0.3

mmol), BHT (132.0 mg, 0.6 mmol), and DMSO (2 mL). Then the mixture was vigorously stirred at room temperature under air for 2 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, analyzed by GC-MS, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide, eluting with ethyl acetate/*n*-hexane, to afford the product **4a** in 88% (136.0 mg) isolated yields.

For disulfide 3a: A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (36.9 mg, 0.15 mmol), Zn (0.3 mmol, 1 equiv), BHT (132.0 mg, 0.6 mmol), and DMSO (2 mL). The tube was evacuated and filled with N_2, and vigorously stirred at room temperature for 6 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, analyzed by GC-MS, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide, eluting with ethyl acetate/*n*-hexane, to afford the product **4a** in 82% (126.7 mg) isolated yields.

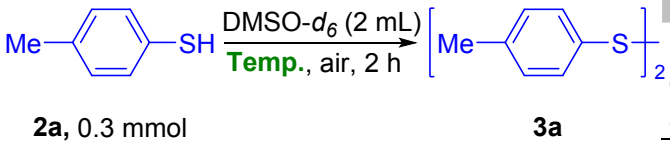
Reaction with sodium benzenethiolate



1a, 0.3 mmol **8,** 0.3 mmol **4n**, 87%

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), sodium benzenethiolate **8** (39.6 mg, 0.3 mmol) and DMSO (2 mL). Then the mixture was vigorously stirred at room temperature under air for 2 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide, eluting with ethyl acetate/*n*-hexane, to afford the product **4n** in 87% (131.3 mg) isolated yields.

The effect of reaction temperature on the oxidative homocoupling of thiol 2a



2a, 0.3 mmol

3a

Temp.	Recovery of **2a**	Yield of **3a**
RT	42%	58%
60 °C	30%	70%
80 °C	10%	90%

Three sets of reactions were carried out in a parallel manner. In each case, a 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol) and DMSO-d_6 (2 mL). Then the mixture was vigorously stirred under air for 2 h at room temperature, 60 °C, and 80 °C, respectively. After the reaction was accomplished, the reaction mixture was analyzed by ^{1}H NMR spectrum, using mesitylene (42 μL, 0.3 mmol) as an internal standard (Fig. S1).

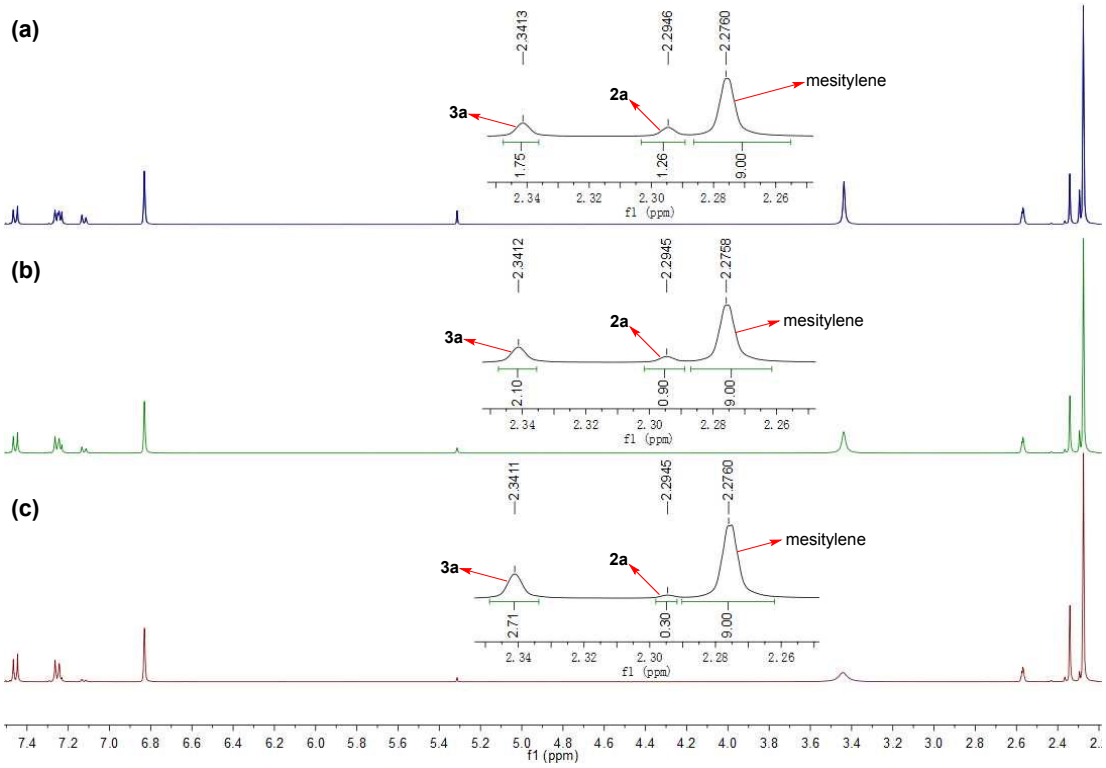
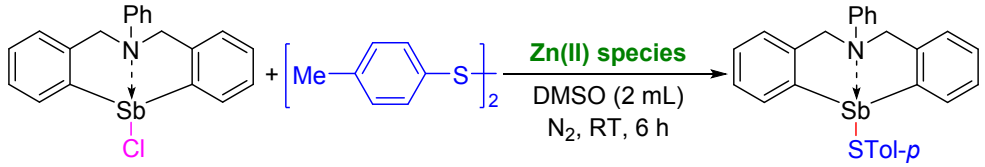


Fig. S1 ^{1}H NMR profiles for the oxidative homocoupling reaction of *p*-toluenethiol **2a** performed at different temperatures. (a) Reaction performed at room temperature. (b) Reaction performed at 60 °C. (c) Reaction performed at 80 °C.

Reactions in the presence of Zn(II) species

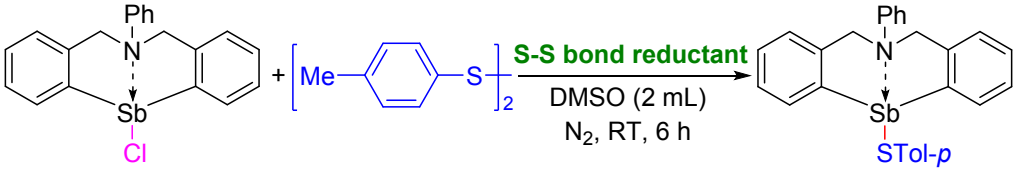


1a, 0.3 mmol **3a,** 0.15 mmol **4a**

$ZnCl_2$ (1 equiv)	N.D.
ZnO (1 equiv)	N.D.
ZnS (1 equiv)	N.D.

Three sets of reactions were carried out in a parallel manner. In each case, a 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (36.9 mg, 0.15 mmol), and DMSO (2 mL) in the presence of $ZnCl_2$ (40.8 mg, 0.3 mmol), ZnO (24.3 mg, 0.3 mmol), or ZnS (29.1 mg, 0.3 mmol), respectively. The reaction was vigorously stirred at room temperature under nitrogen atmosphere. After 6 h, the reaction mixture was analyzed by TLC, but the desired product **4a** could not be detected at all.

Reactions in the presence of representative disulfide bond reducing agents

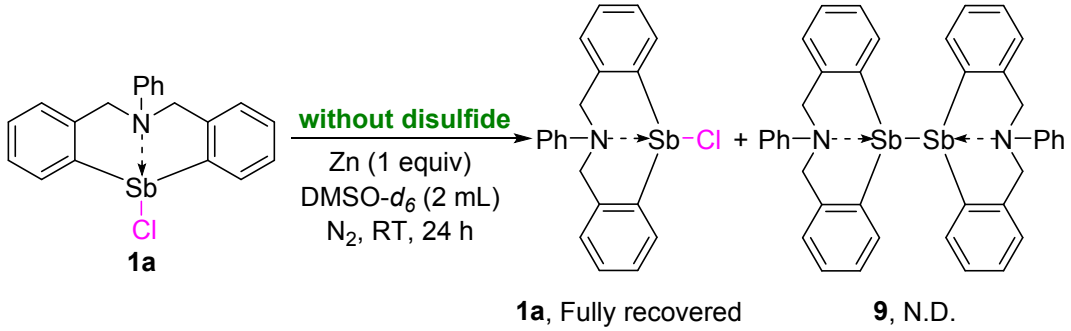


1a, 0.3 mmol **3a,** 0.15 mmol **4a**

GSH (1 equiv)	84%
DTT (1 equiv)	89%
THPP (1 equiv)	91%

Three sets of reactions were carried out in a parallel manner. In each case, a 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (36.9 mg, 0.15 mmol), and DMSO (2 mL) in the presence of glutathione (GSH), dithiothreitol (DTT), and tris(hydroxypropyl)phosphine (THPP), respectively. The reaction was vigorously stirred at room temperature under N_2 for 6 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide, eluting with ethyl acetate/*n*-hexane, to afford the product **4a** in 84% (129.8 mg), 89% (137.5 mg), and 91% (140.6 mg) isolated yields, respectively.

Reaction of chlorostibine 1a with Zn in the absence of disulfide



A 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with **1a** (42.7 mg, 0.1 mmol), Zn (6.5 mg, 0.1 mmol) and DMSO-d_6 (1 mL). Then the mixture was vigorously stirred at room temperature under nitrogen atmosphere. After 24 h, the reaction mixture was analyzed by ^{1}H NMR spectrum, together with freshly prepared **1a** as control. As shown in Fig. S2, **1a** could maintain the freshly prepared skeleton structure after being stirred with Zn in the absence of disulfide, and the homocoupling product **9** from **1a** was not observed.

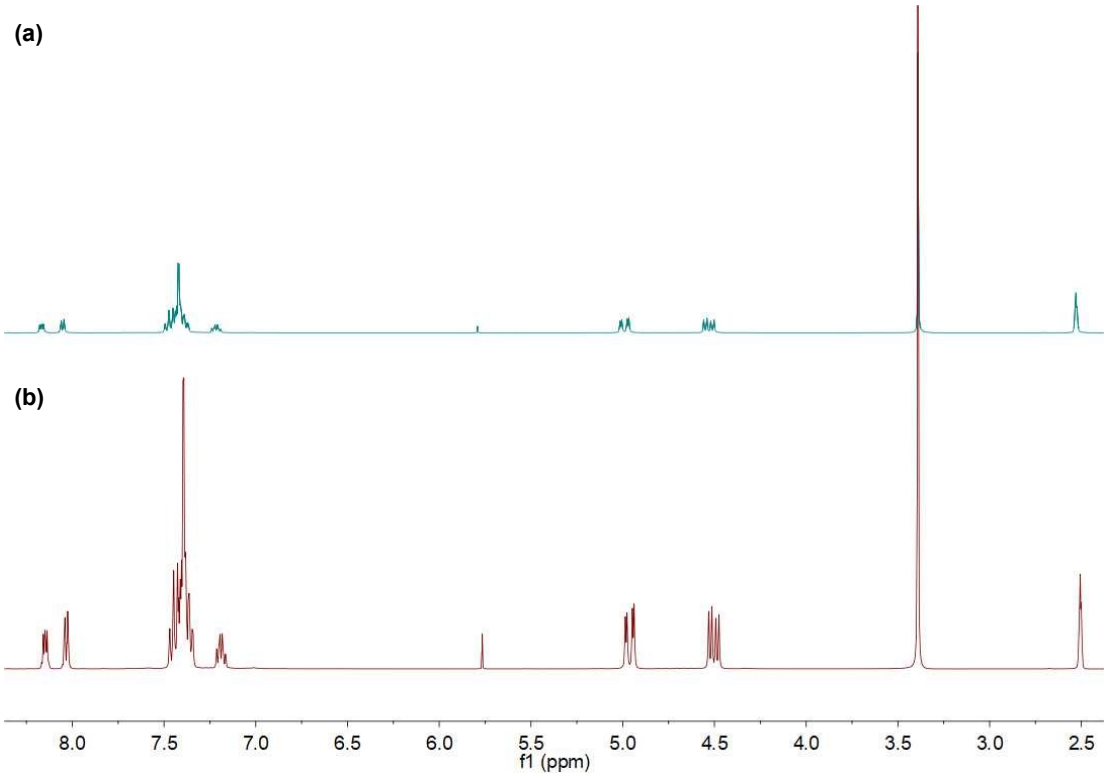
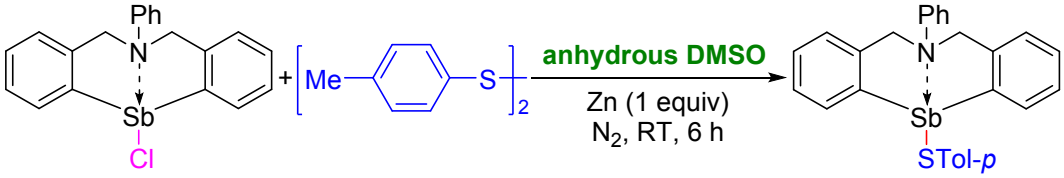


Fig. S2 ^{1}H NMR spectra of **1a** measured in DMSO-d_6. (a) Freshly prepared. (b) After being stirred with Zn at room temperature under N_2 for 24 h.

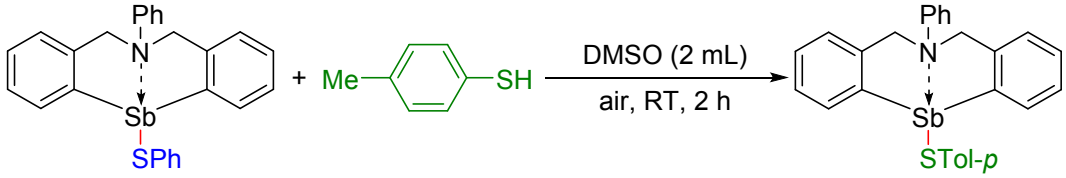
The effect of residual water on the Sb–S cross-coupling of chlorostibine 1a with disulfide 3a



1a, 0.3 mmol **3a,** 0.15 mmol **4a**, 88%

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **1a** (128.1 mg, 0.3 mmol), di-*p*-tolyl disulfide **3a** (36.9 mg, 0.15 mmol), Zn (19.5 mg, 0.3 mmol) and anhydrous DMSO (2 mL). The tube was evacuated and filled with N_2, and vigorously stirred at room temperature for 6 h. After the reaction was accomplished, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on aluminum oxide, eluting with ethyl acetate/*n*-hexane, to afford the product **4a** in 88% (135.9 mg) isolated yields.

Stability experiment of the Sb–S bond in 4n



4n, 0.3 mmol **2a,** 0.3 mmol **4a**, N.D.

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with chlorostibine **4n** (150.3 mg, 0.3 mmol), *p*-toluenethiol **2a** (37.2 mg, 0.3 mmol), and DMSO (2 mL). Then the mixture was vigorously stirred at room temperature under air for 2 h. After the reaction was accomplished, the reaction mixture was analyzed by TLC, but the desired product **4a** could not be detected. Furthermore, deionized water (10 mL) was added, and the mixture was extracted by dichloromethane (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/n-hexane, and the starting thiostibine **4n** was fully recovered (Fig. S3).

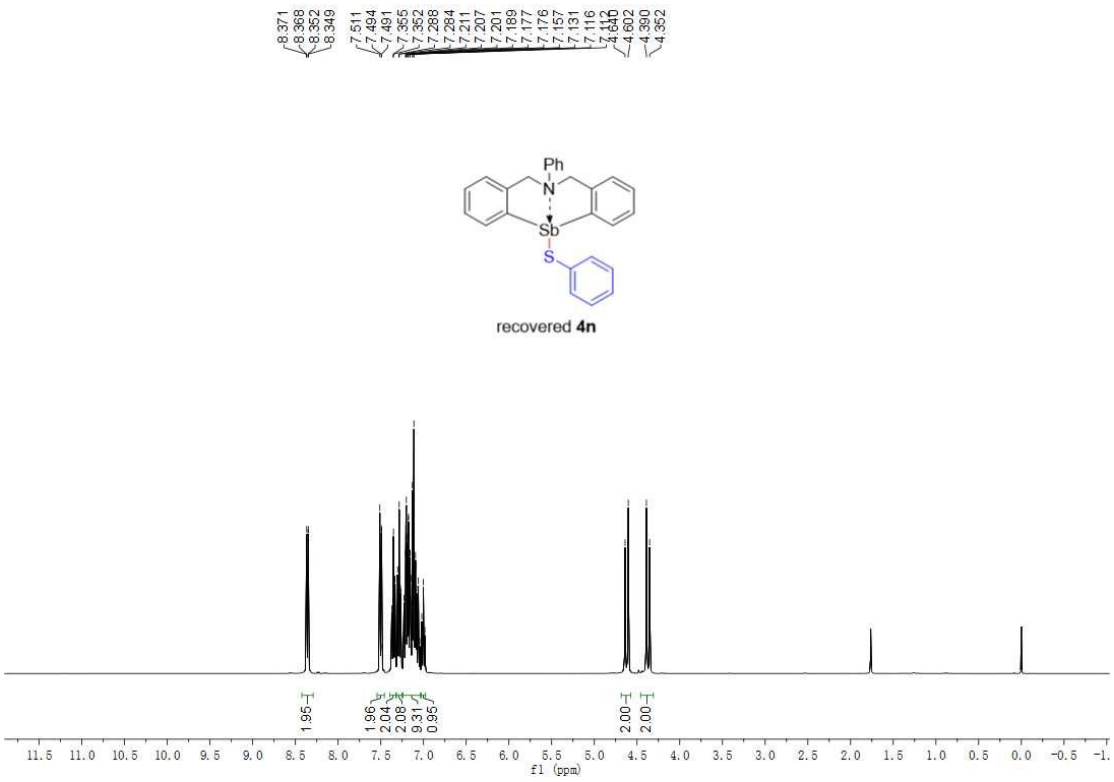


Fig. S3 ^{1}H NMR spectrum of the recovered thiostibine **4n** measured in $CDCl_3$.

8. References

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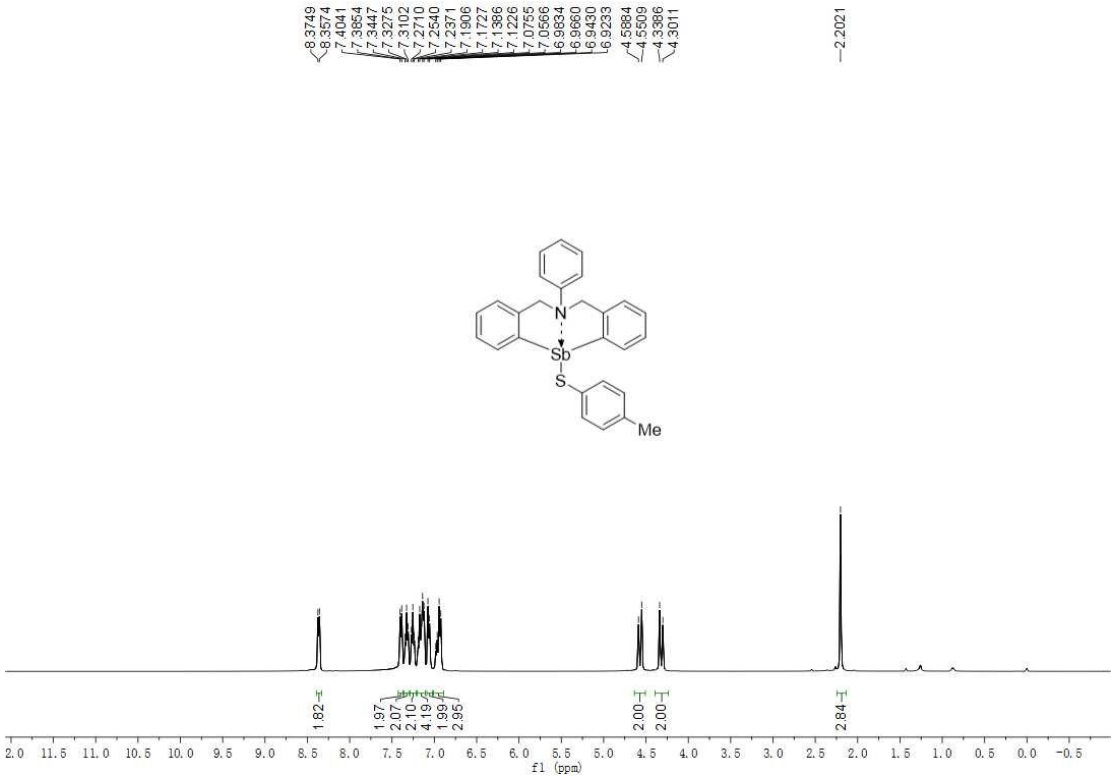
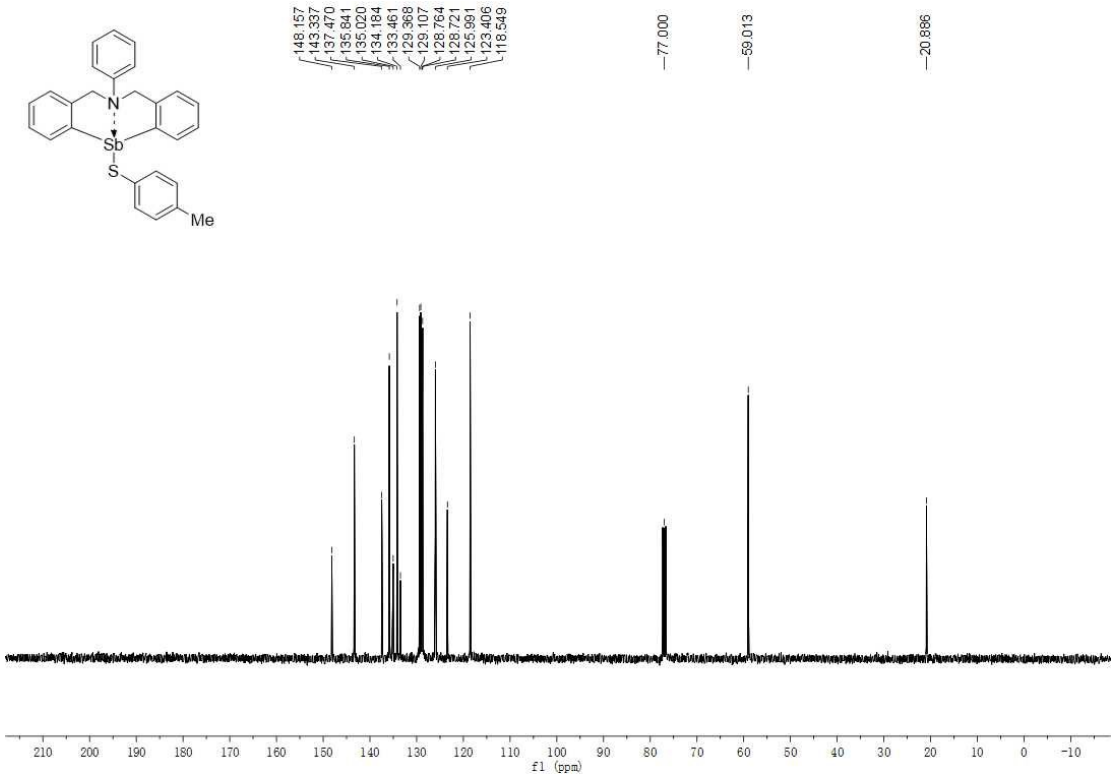
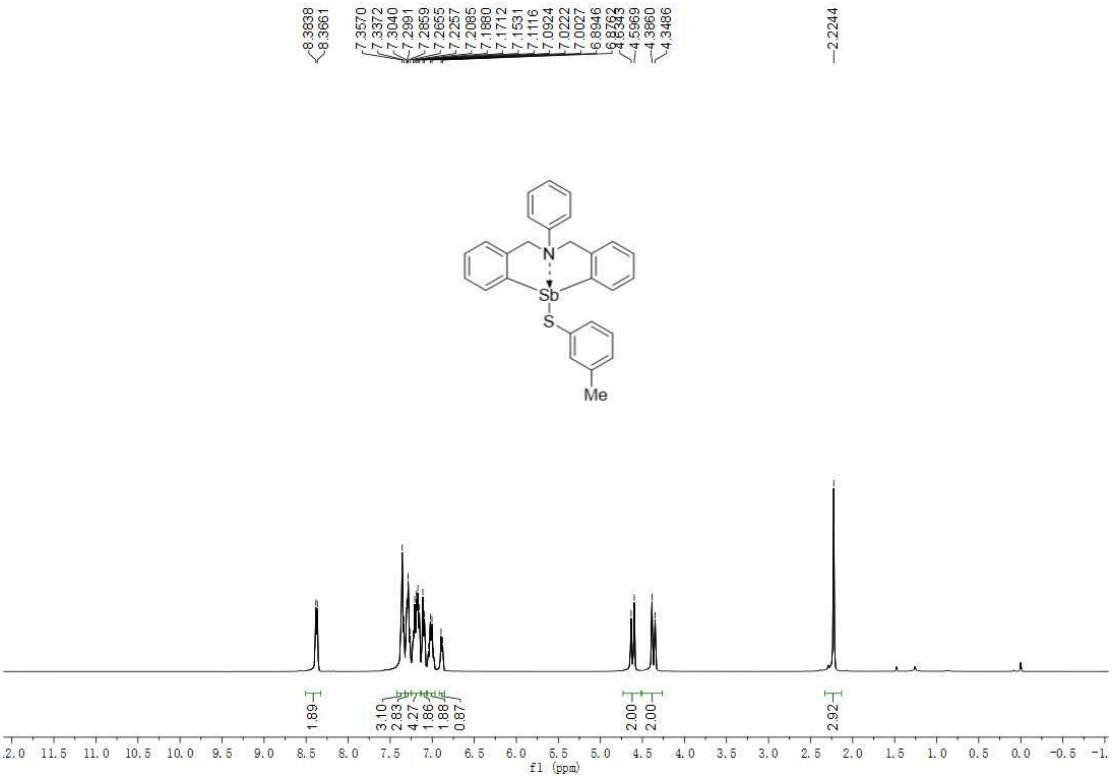
9. NMR Spectra



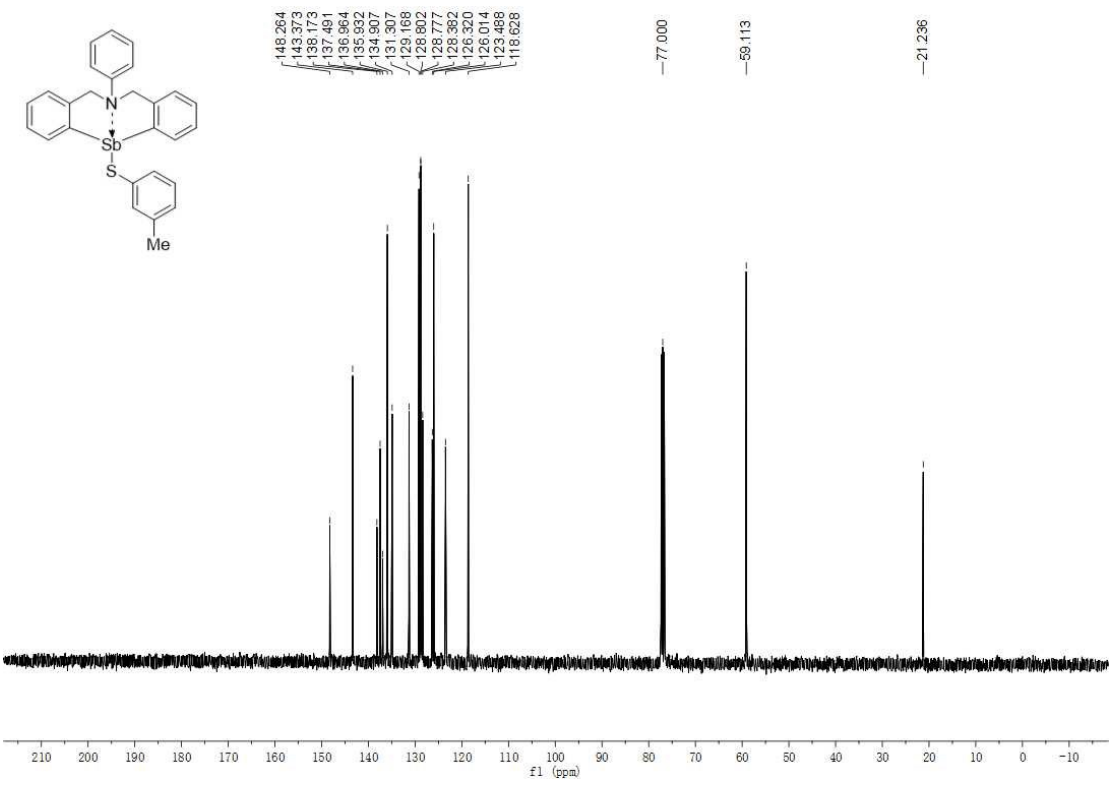
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**



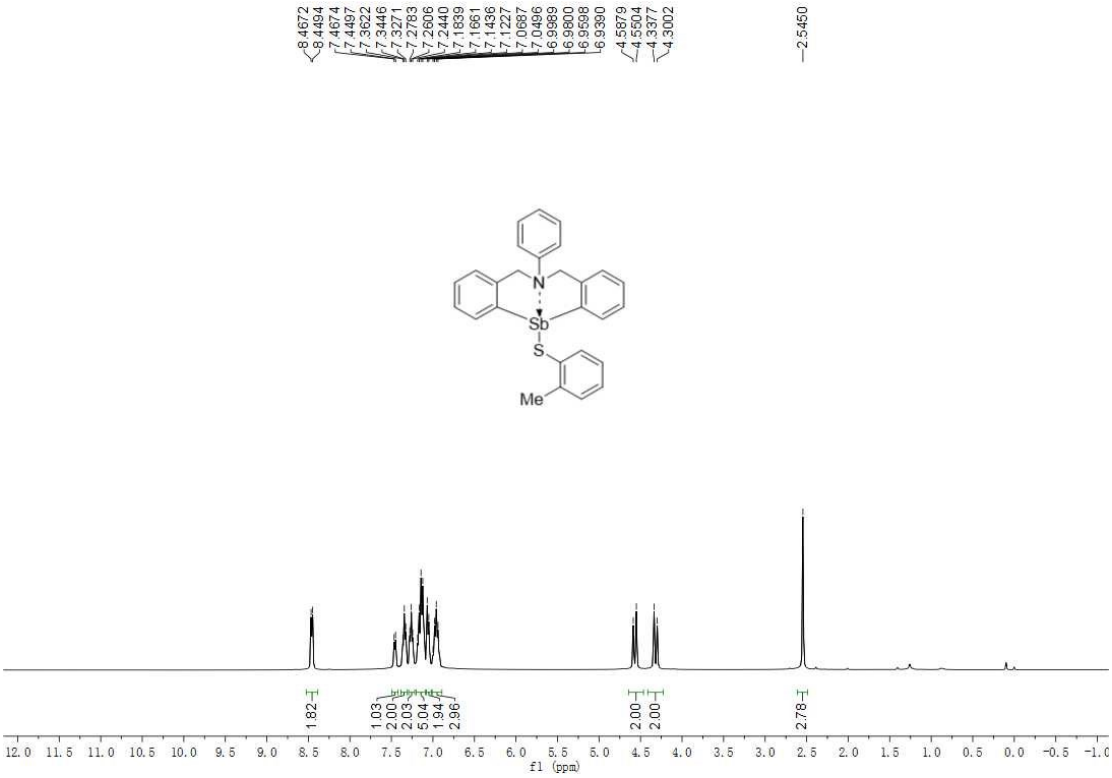
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**



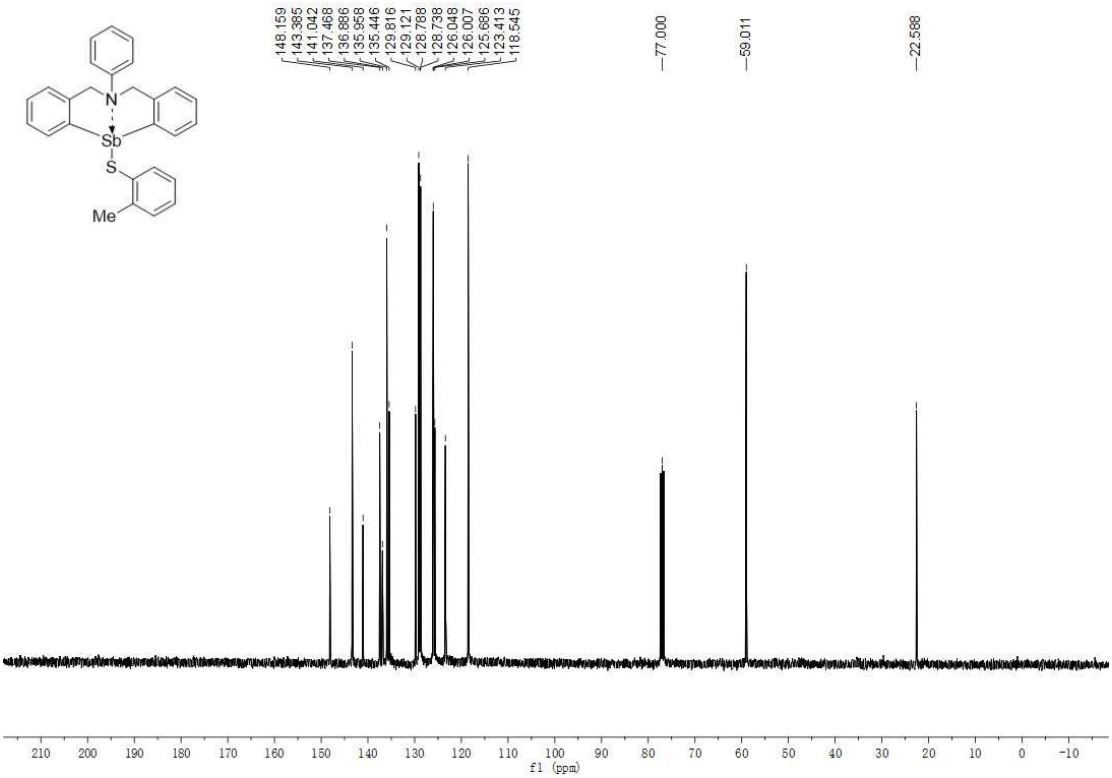
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**



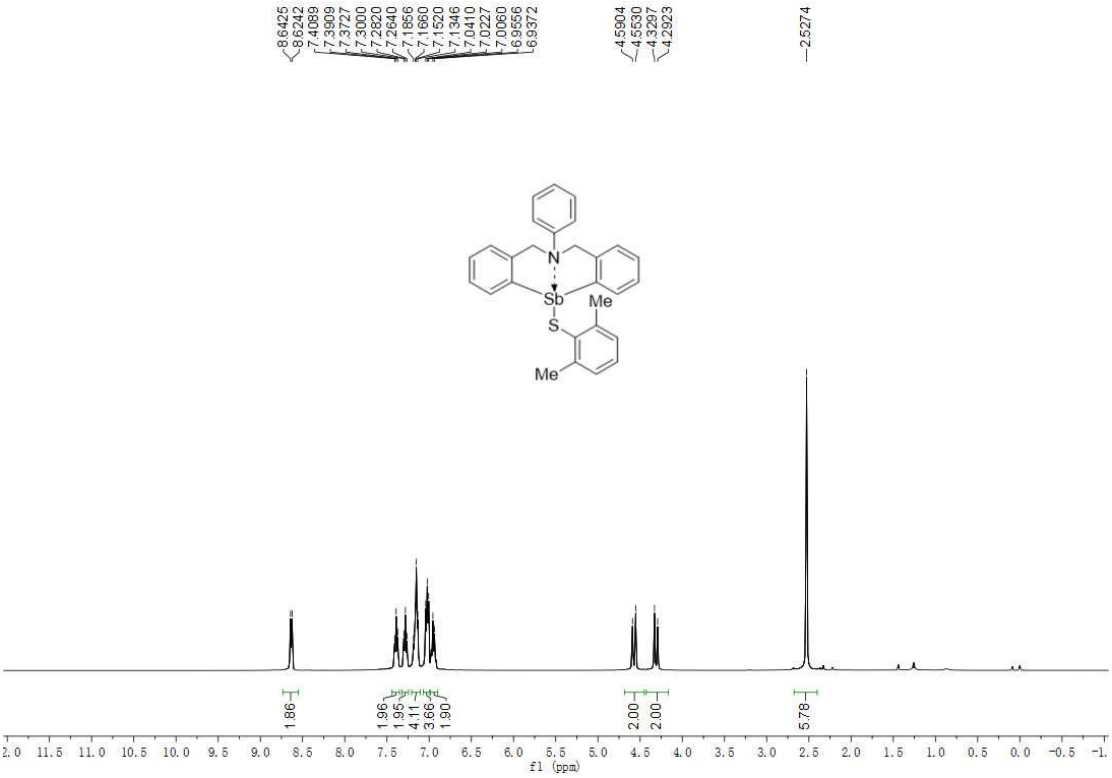
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**



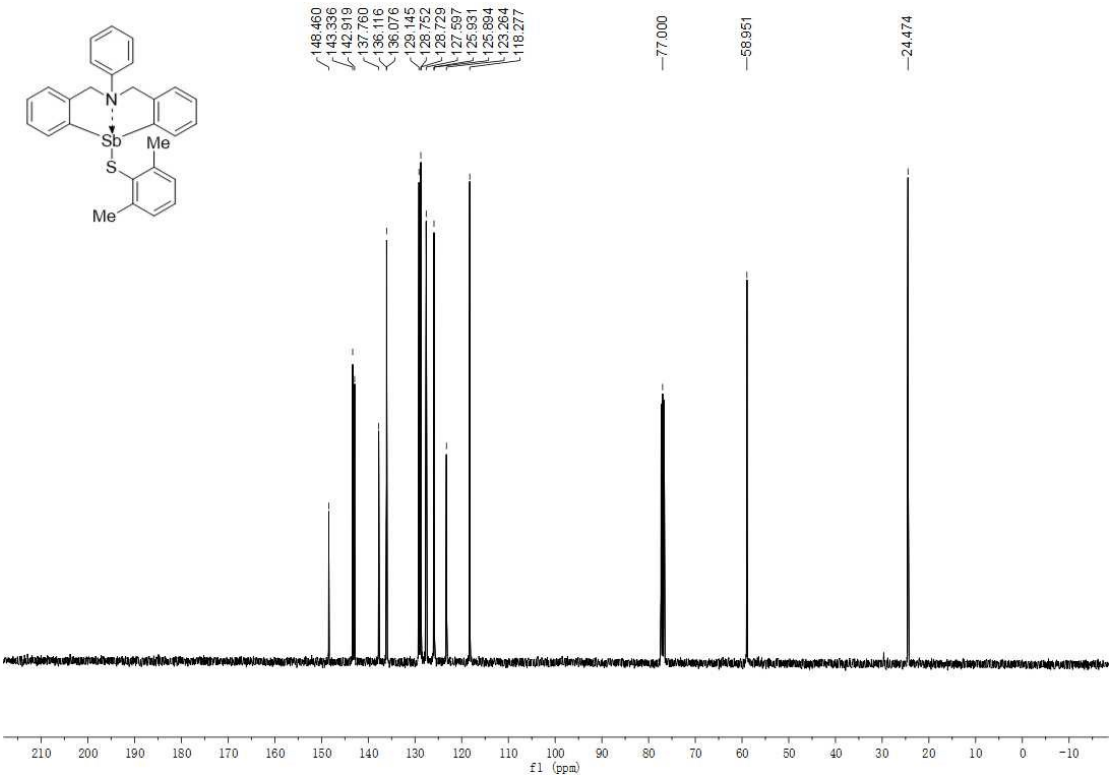
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**



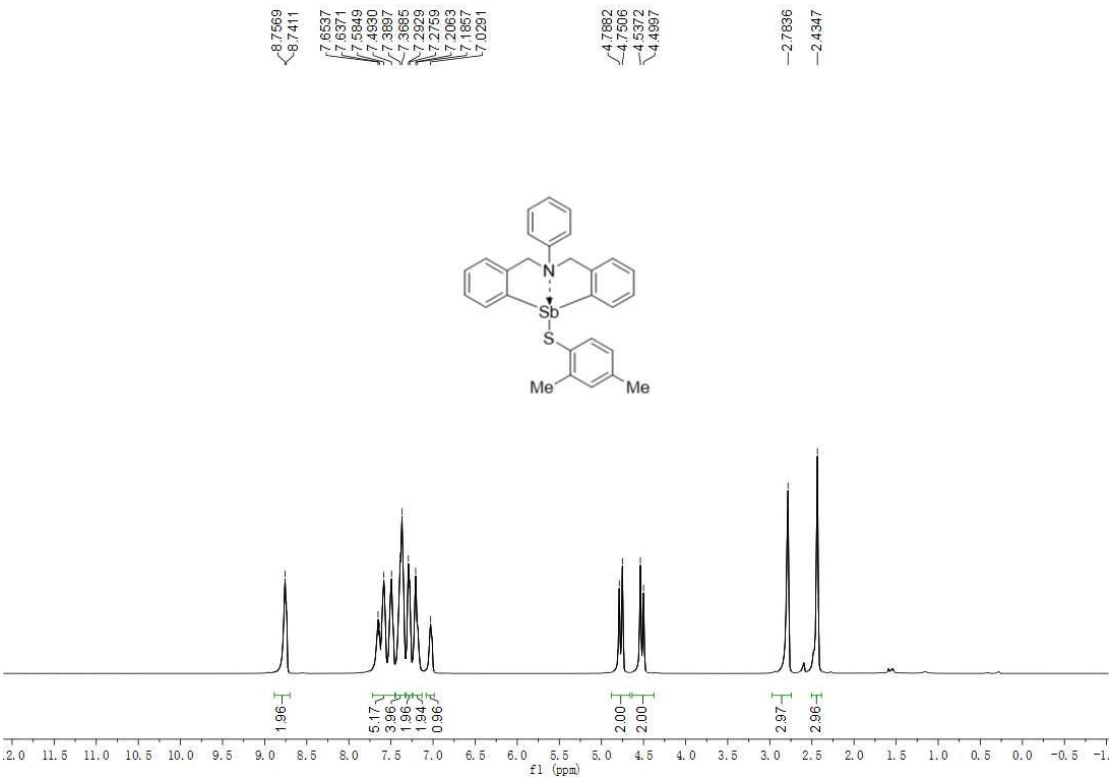
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4c**



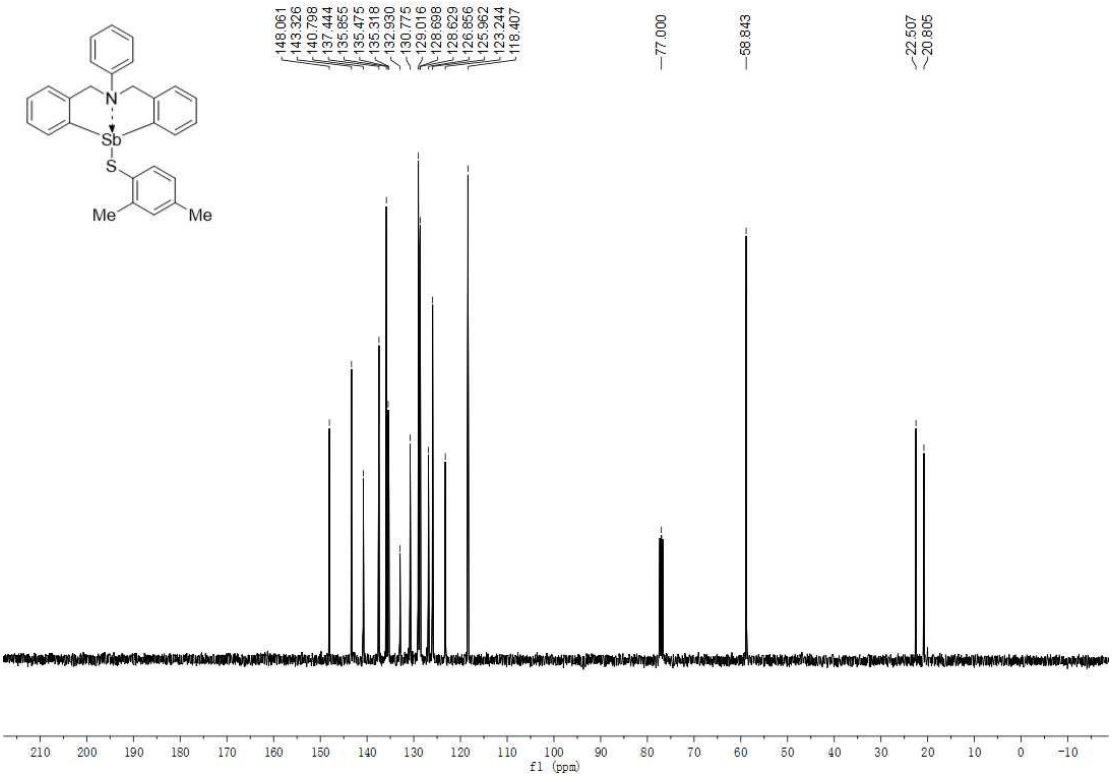
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4d**



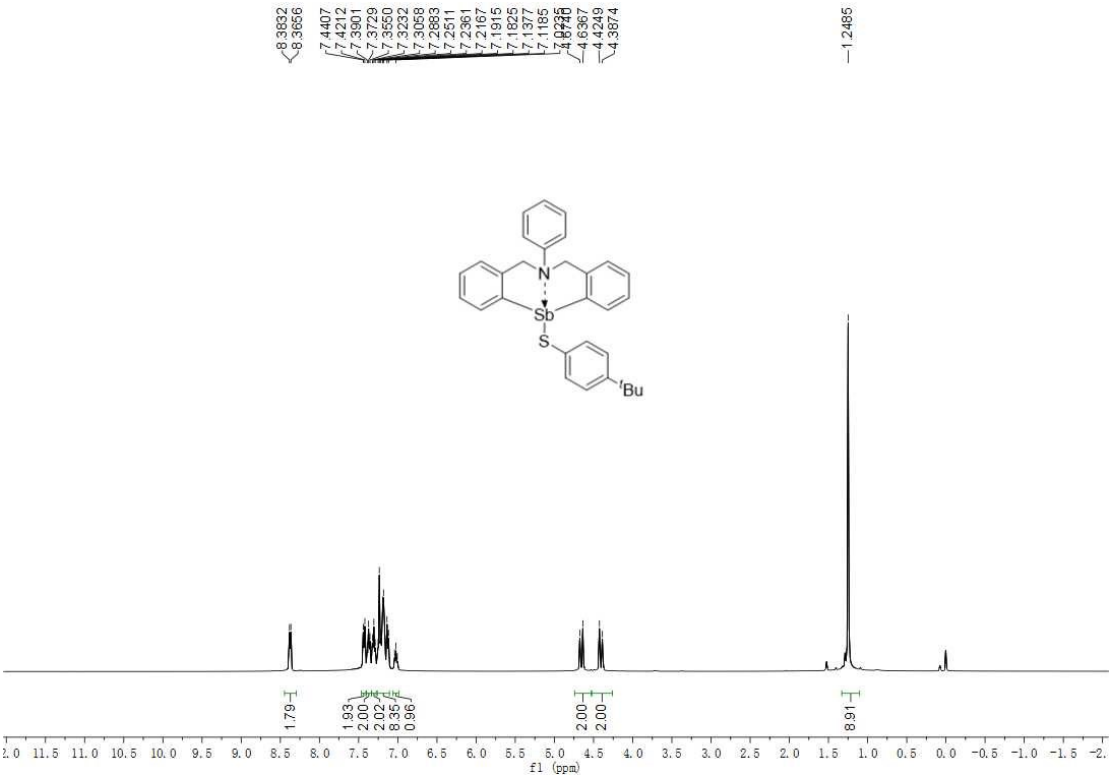
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4d**



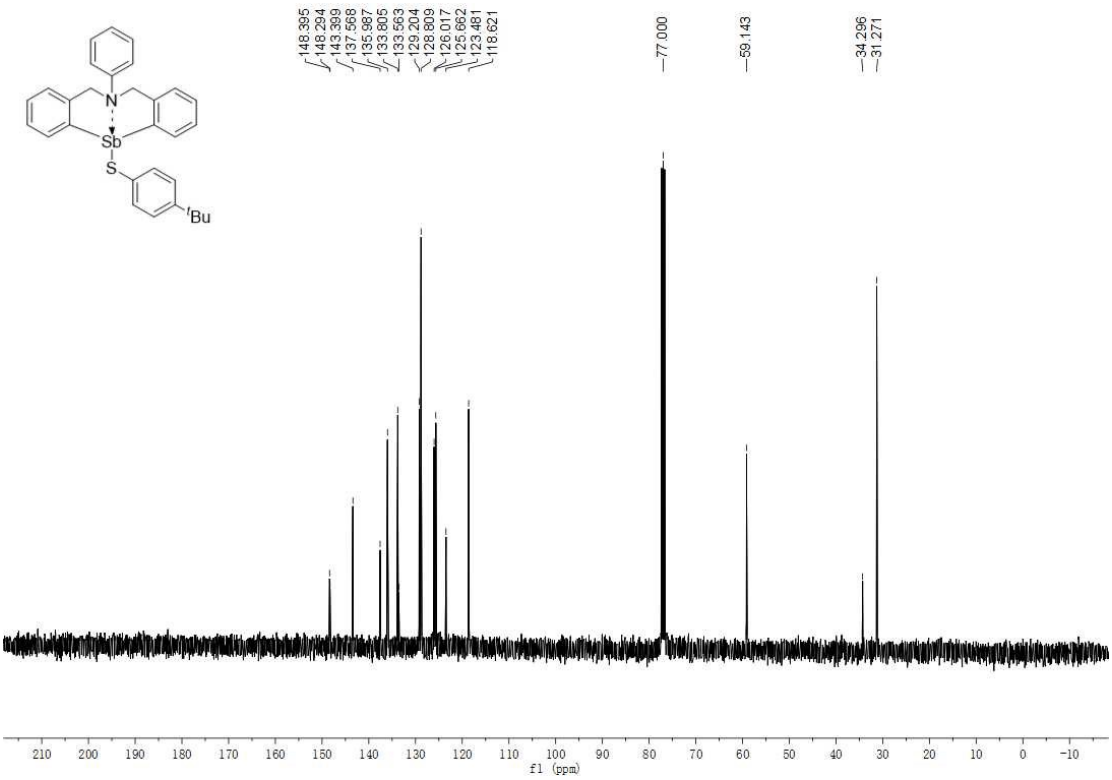
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4e**



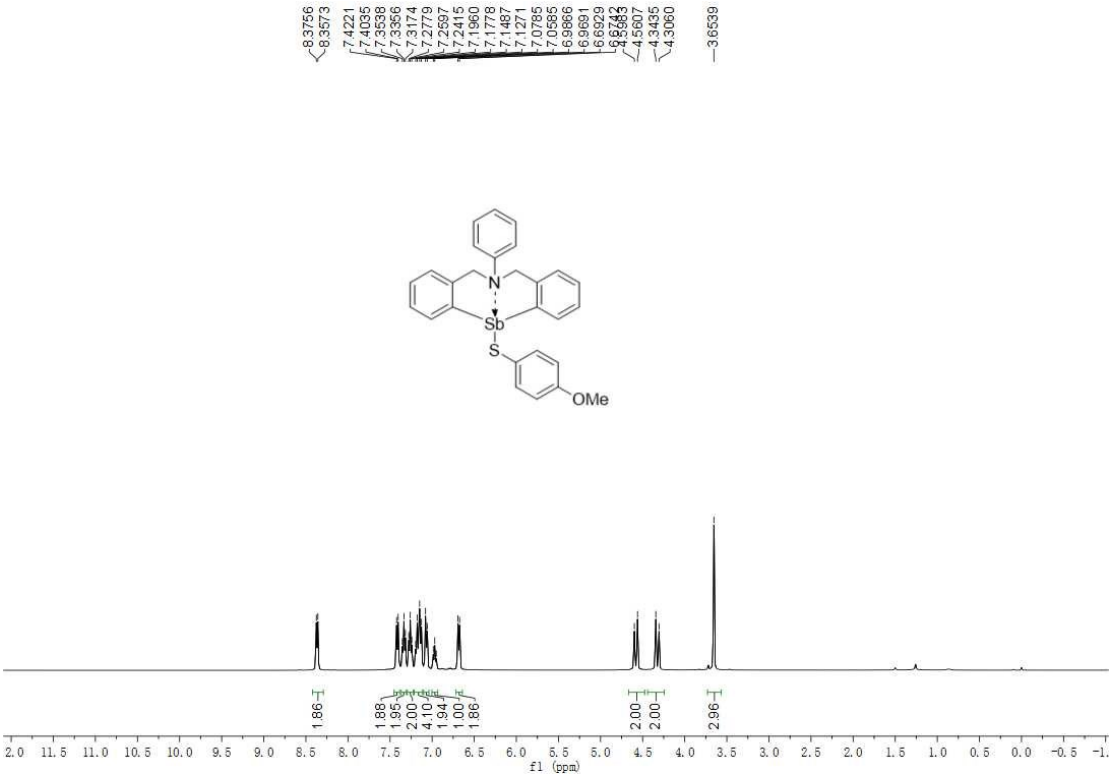
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4e**



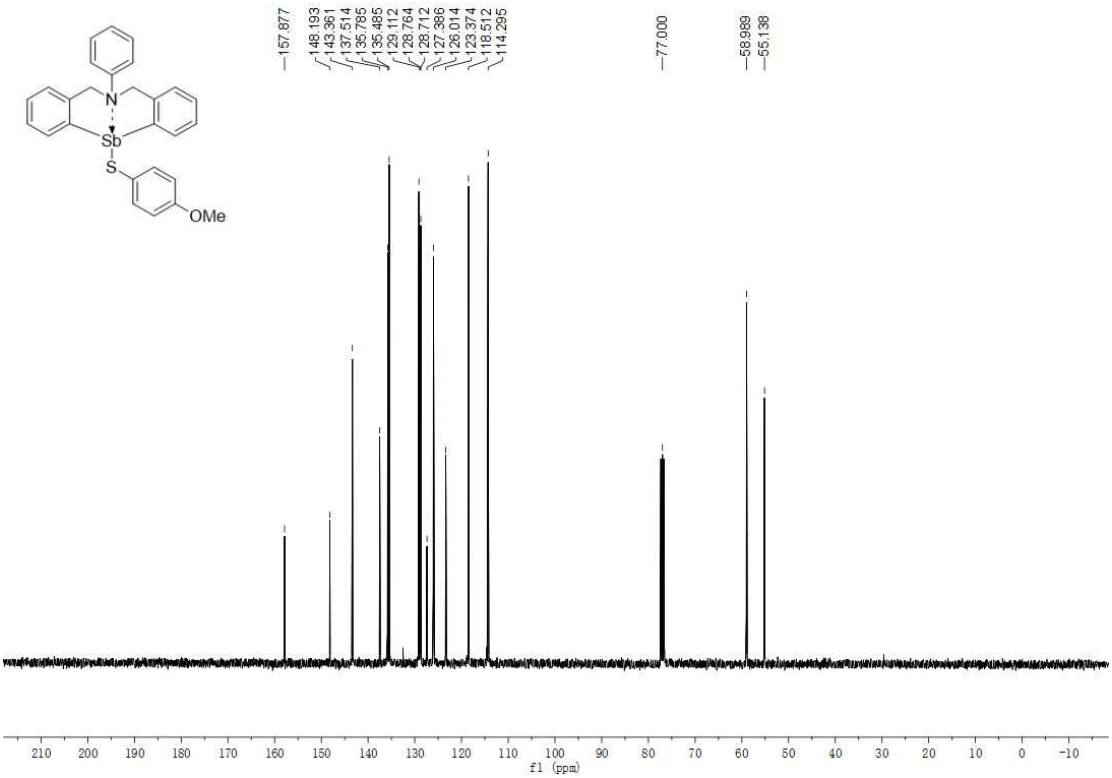
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4f**



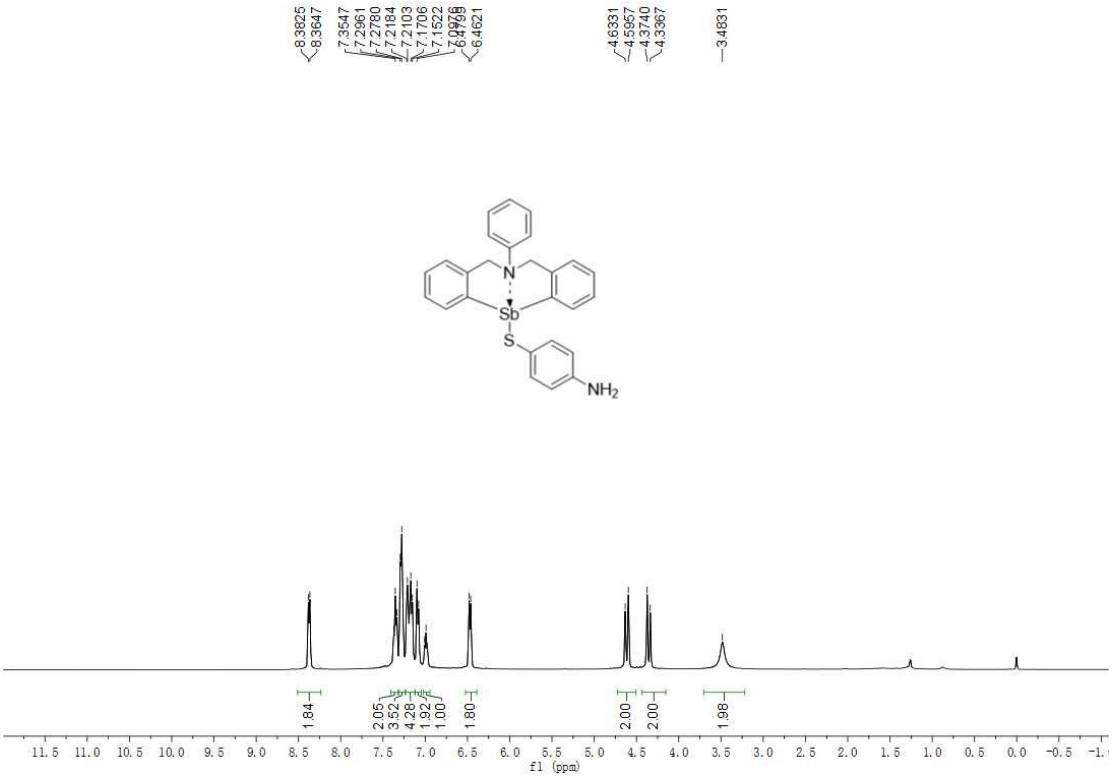
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4f**



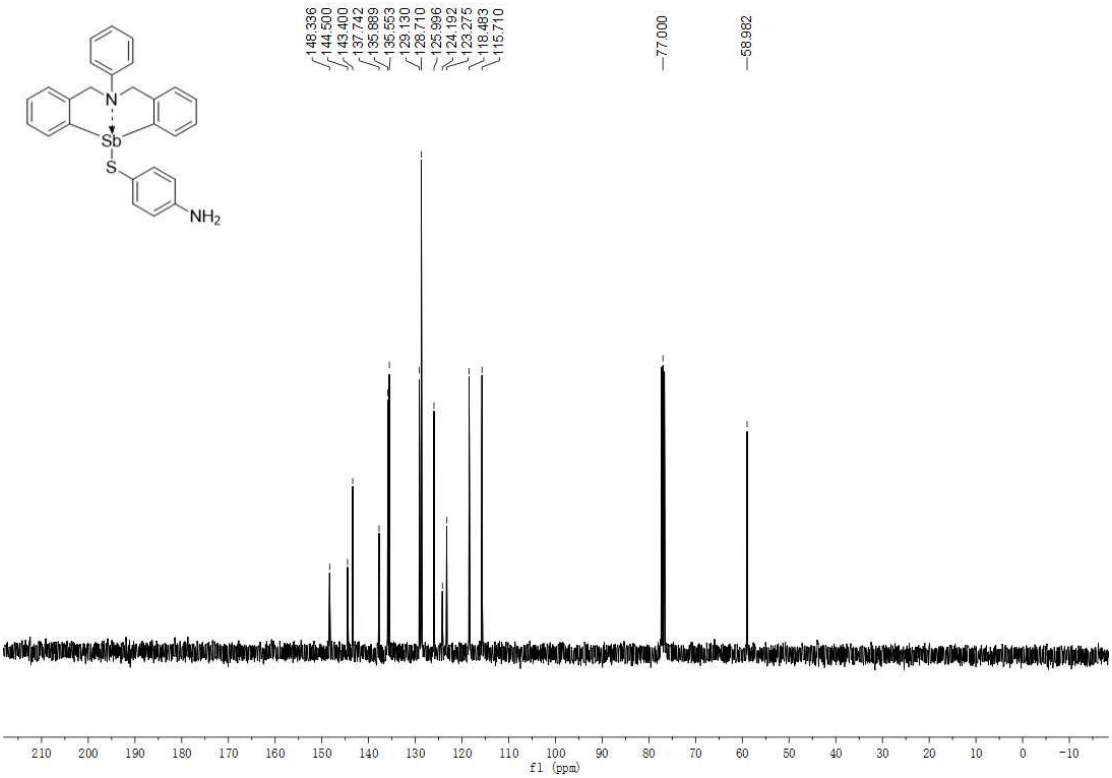
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4g**



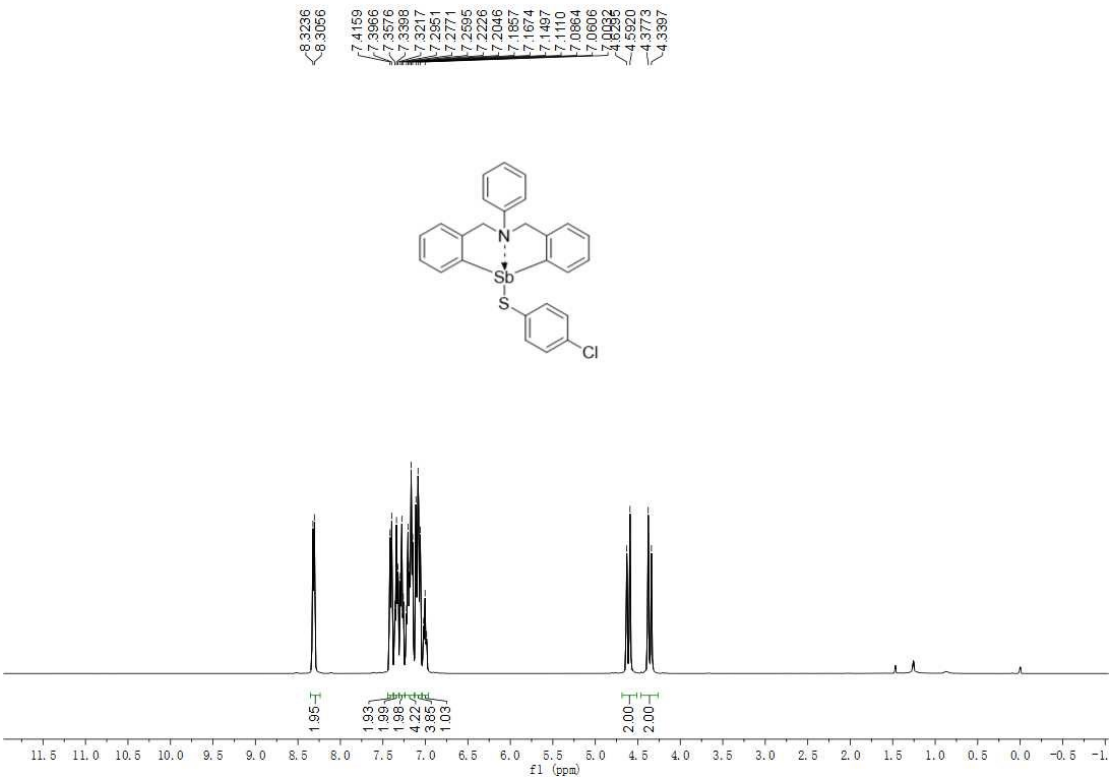
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4g**



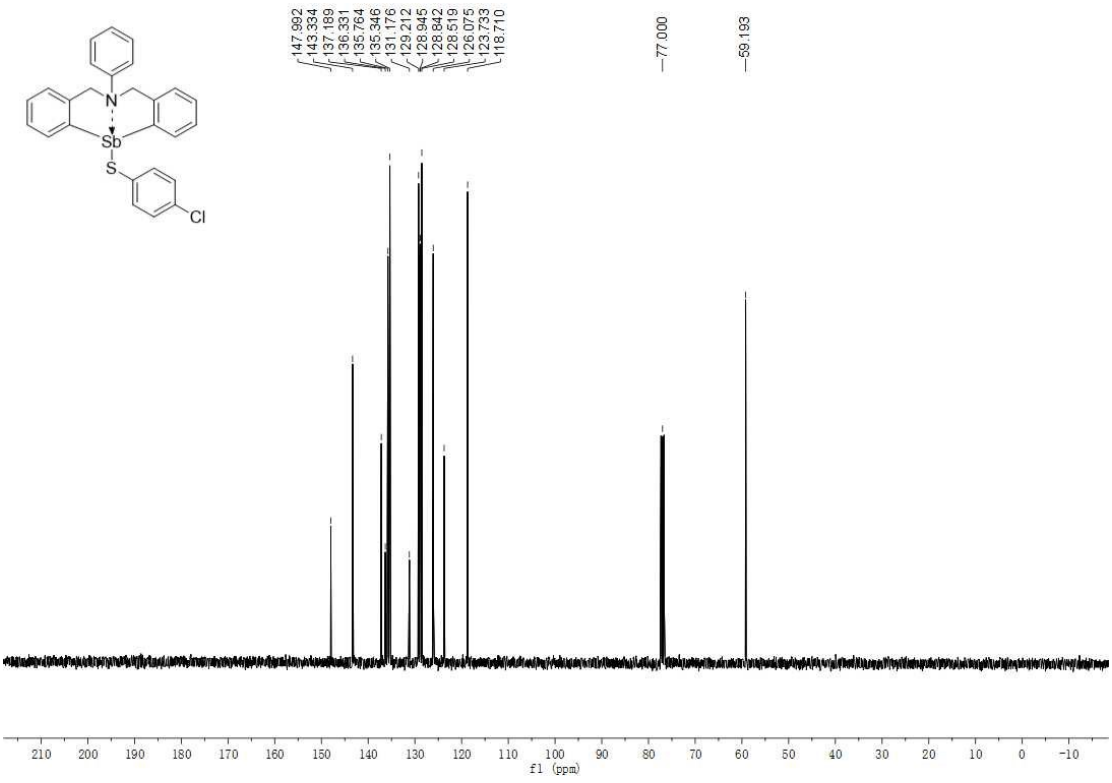
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4h**



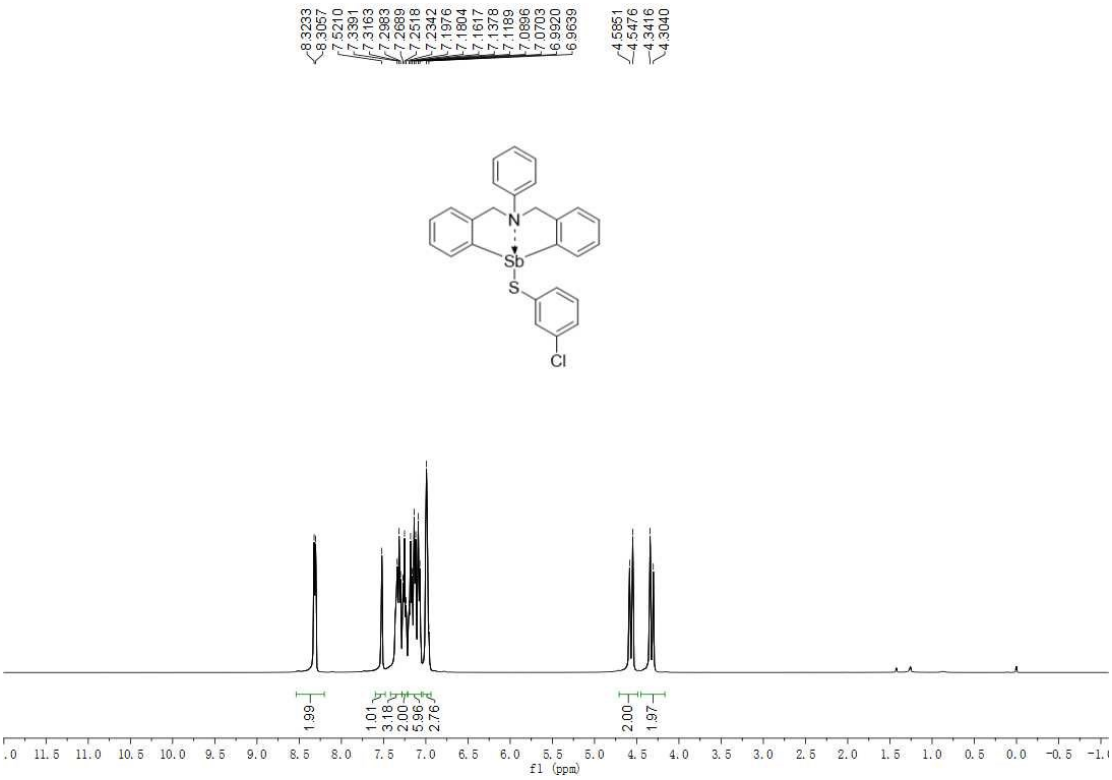
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4h**



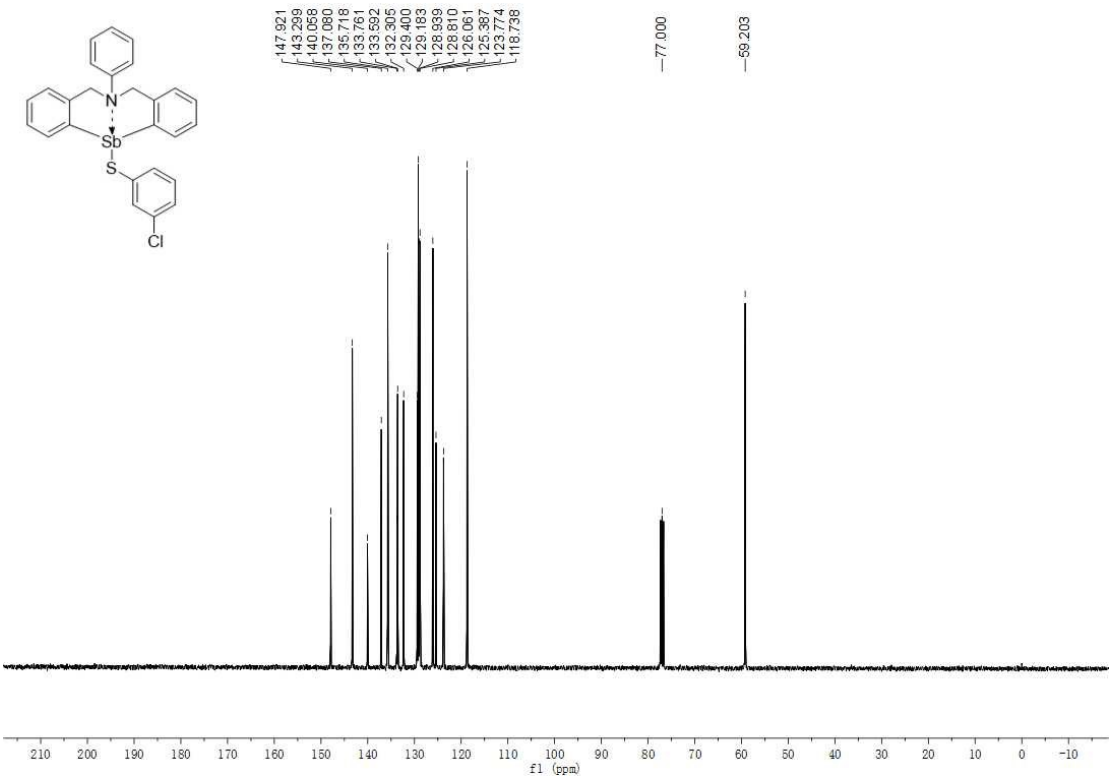
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4i**



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



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



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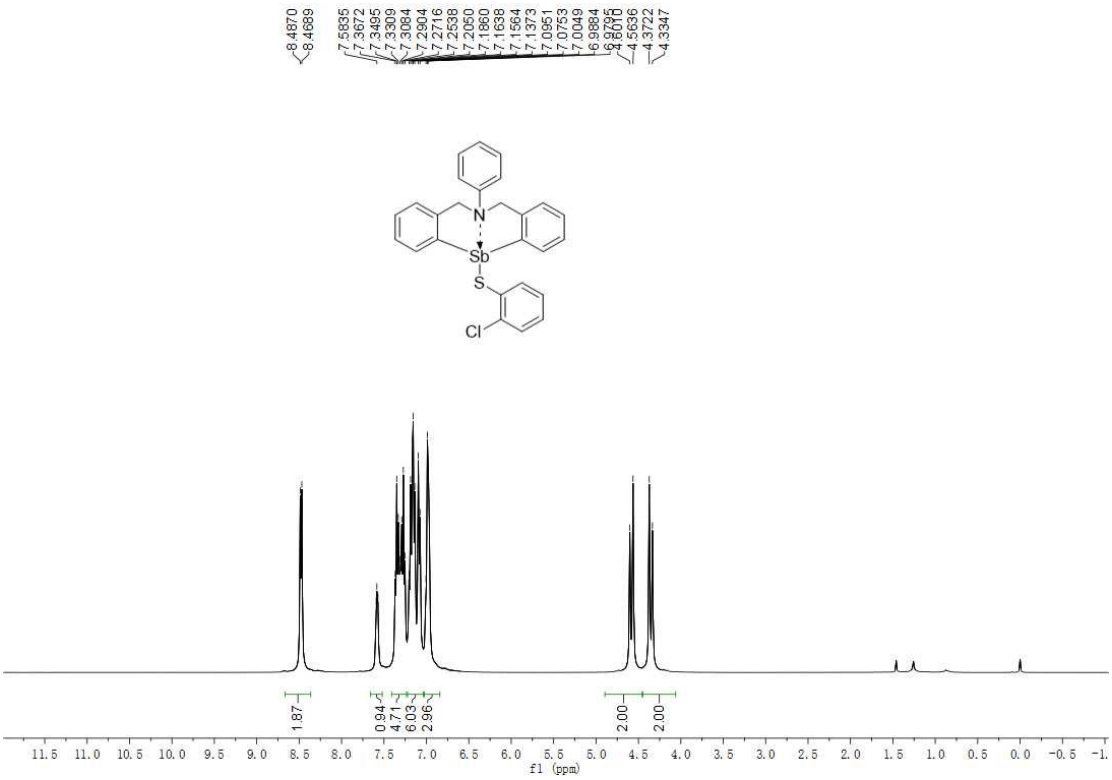

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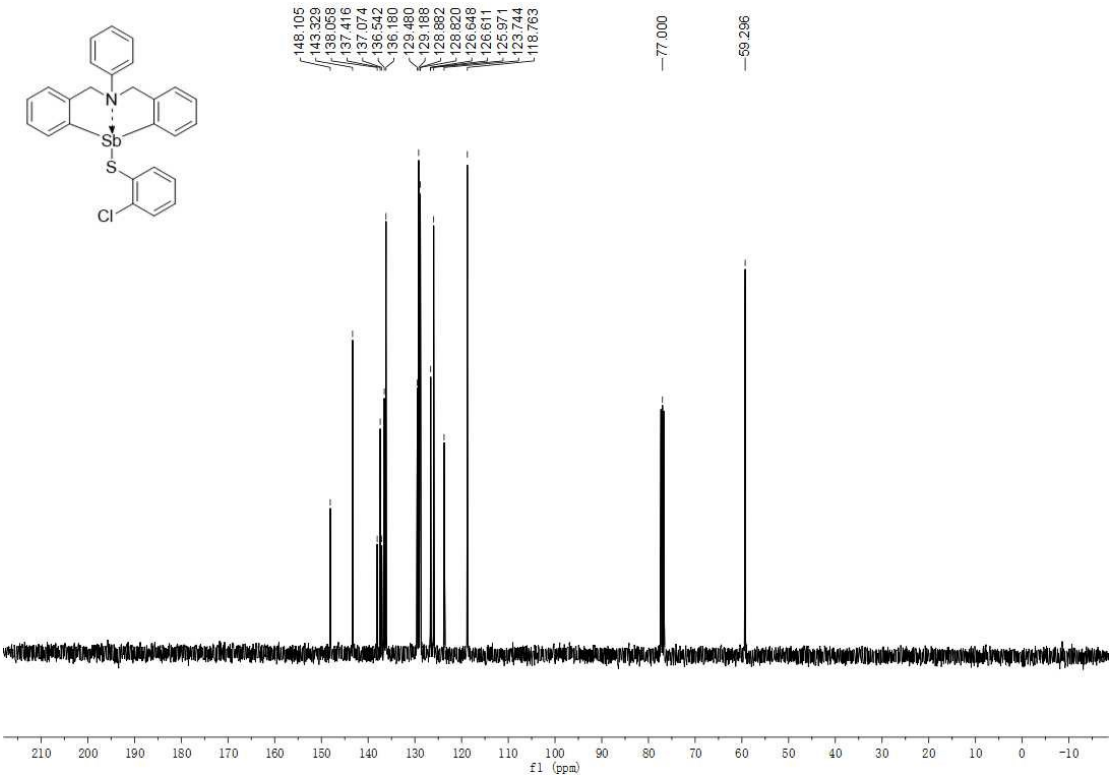

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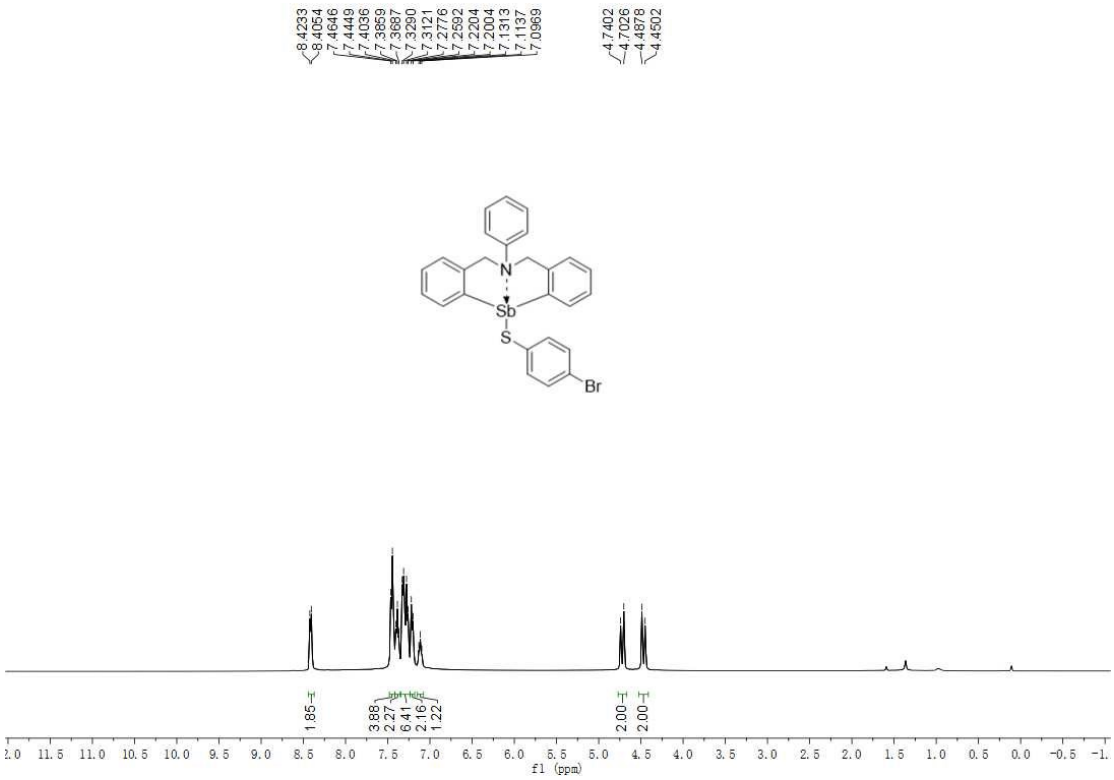
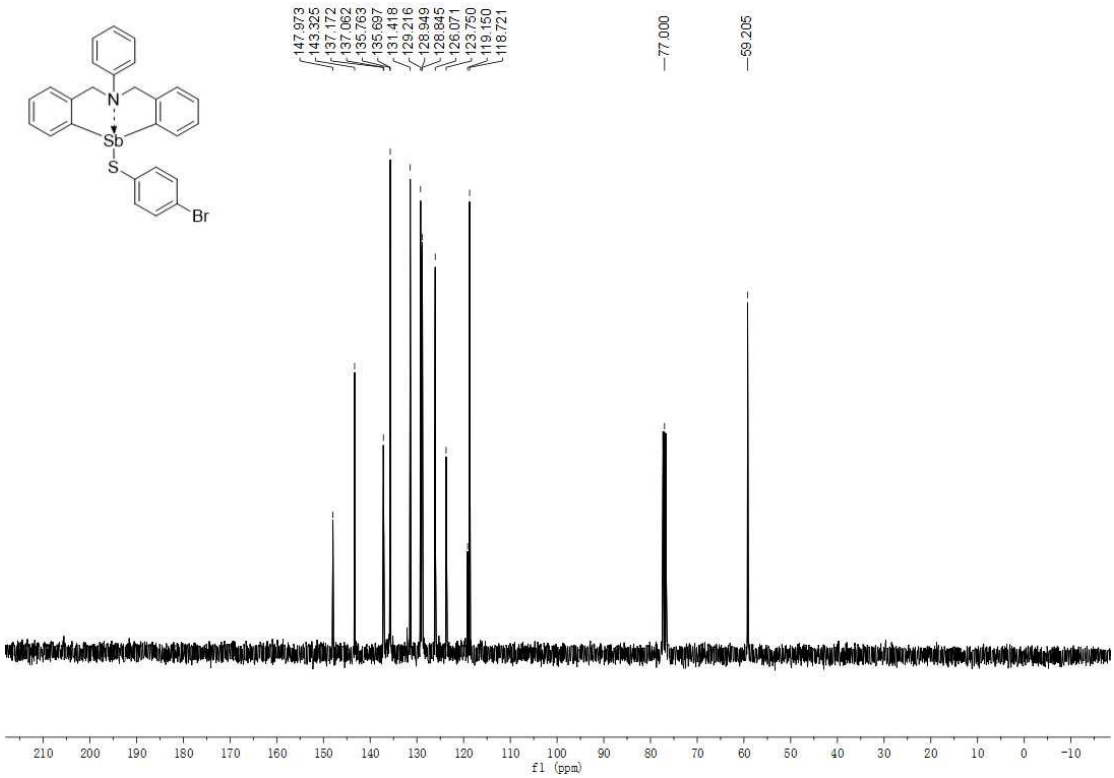
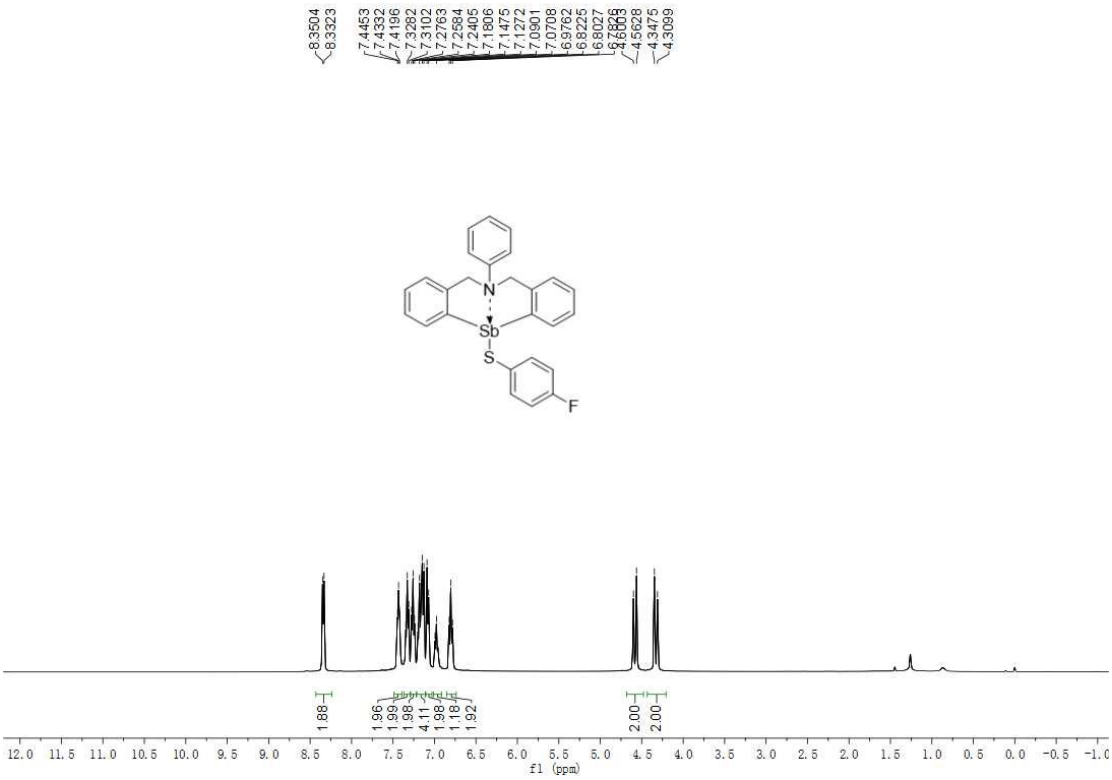


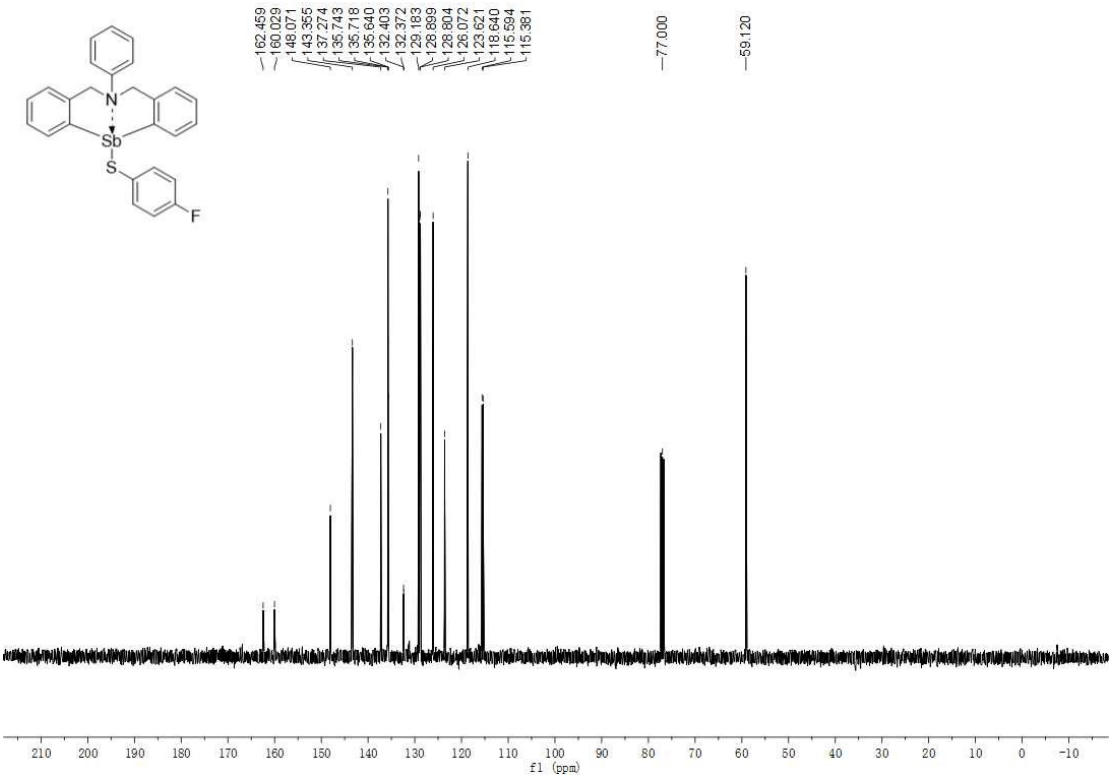
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4l**



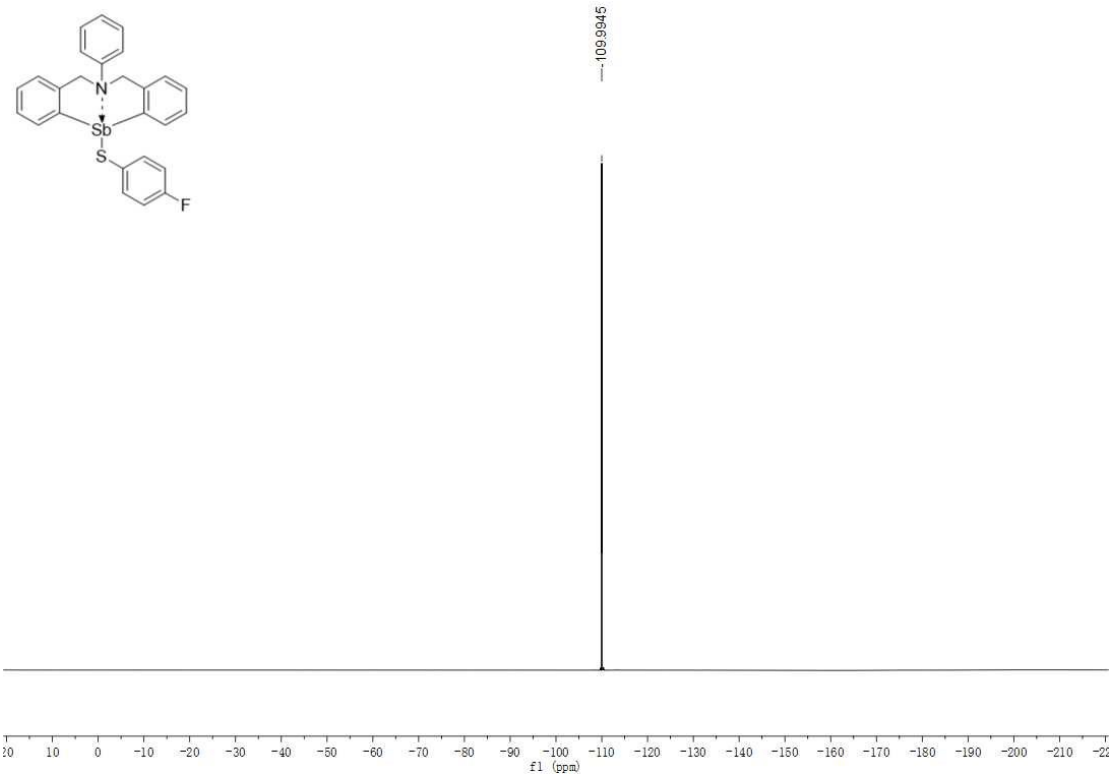
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4l**



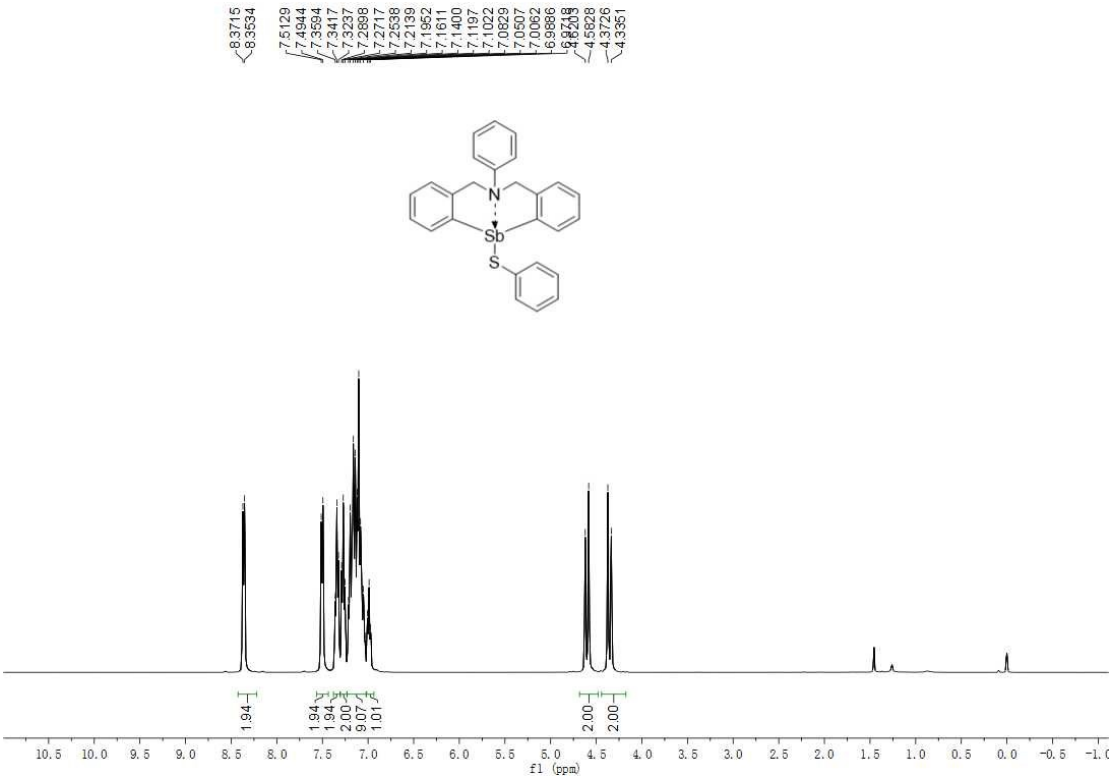
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4m**



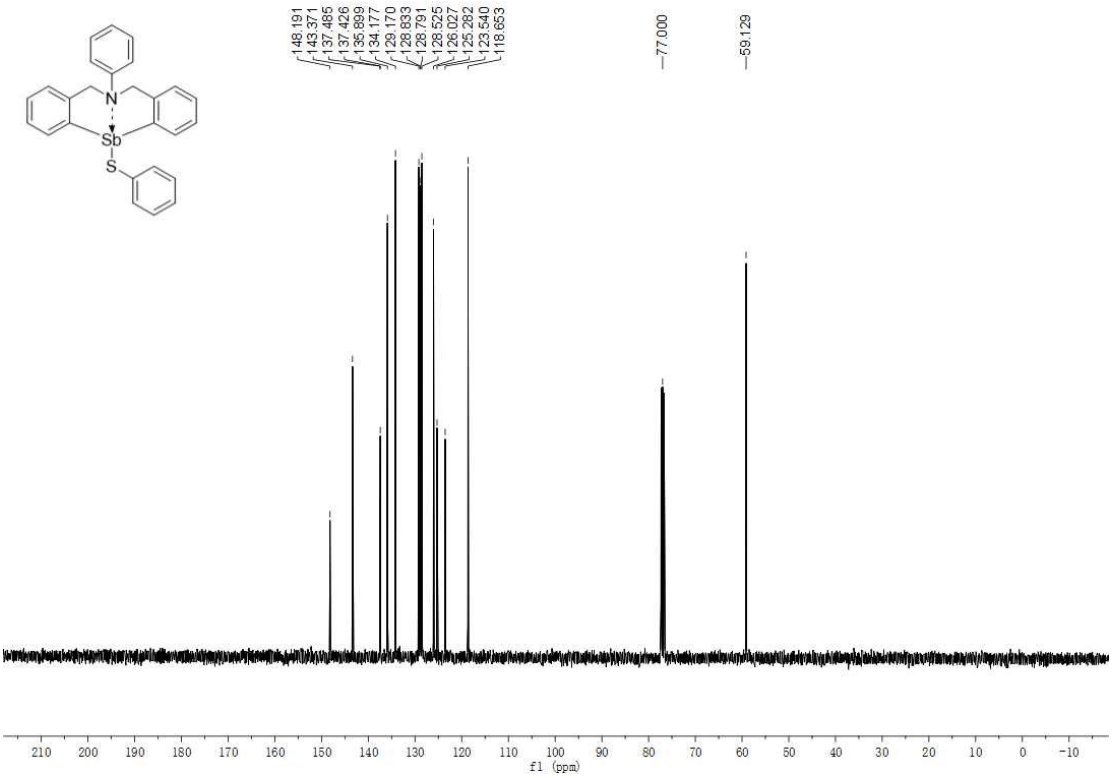
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4m**



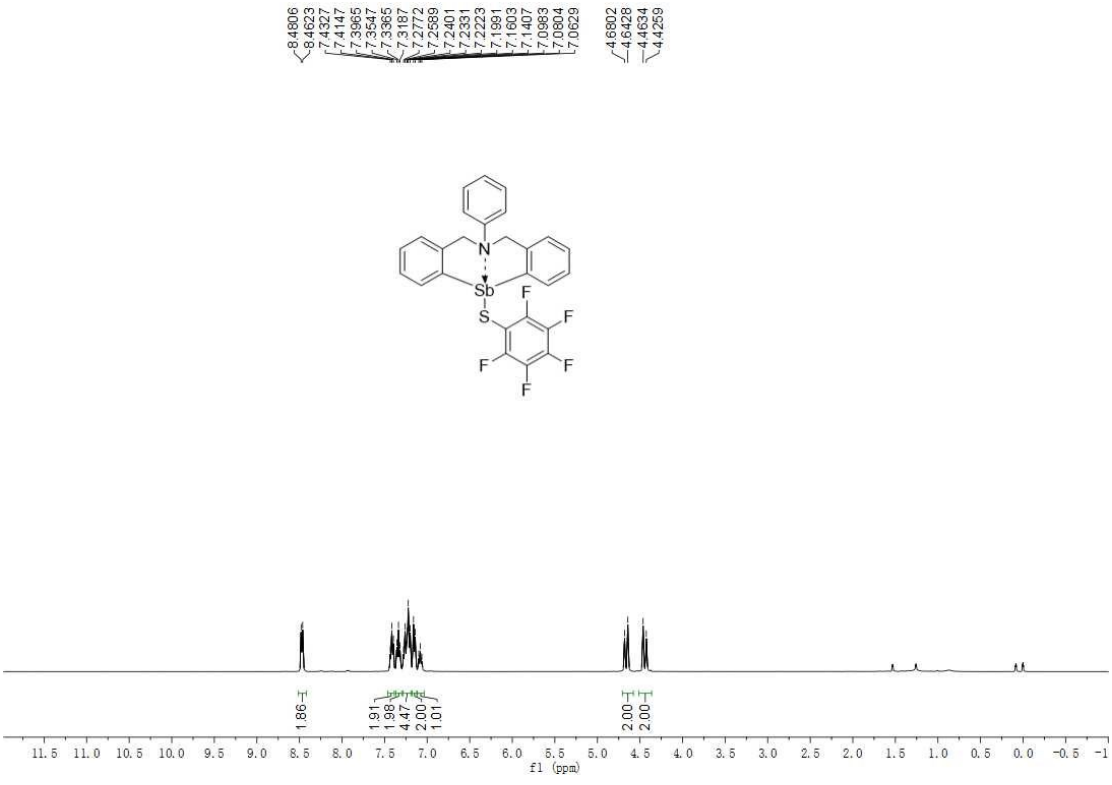
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4m**



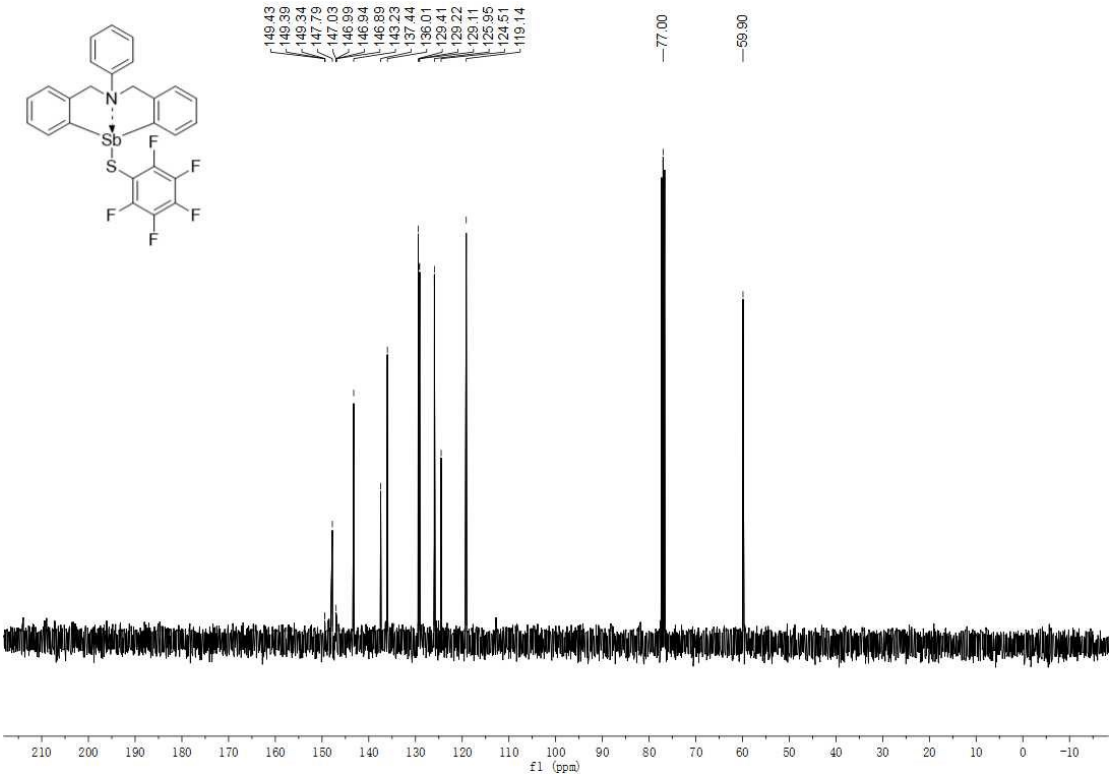
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4n**



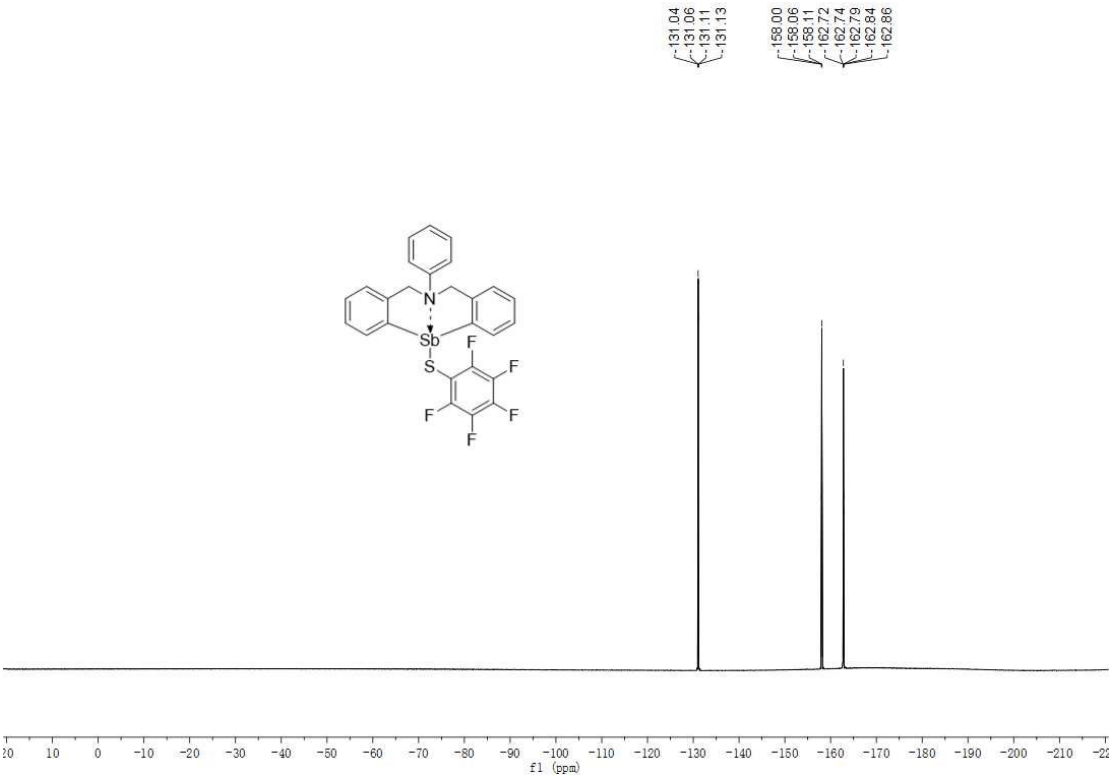
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4n**



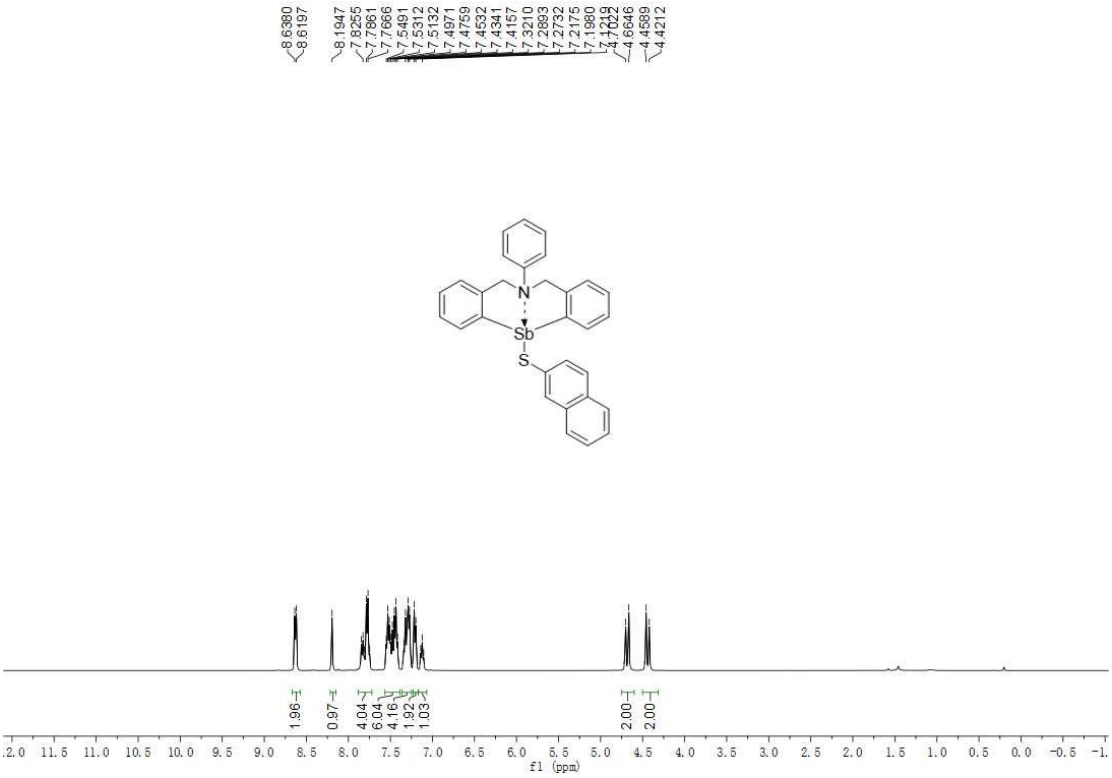
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4o**



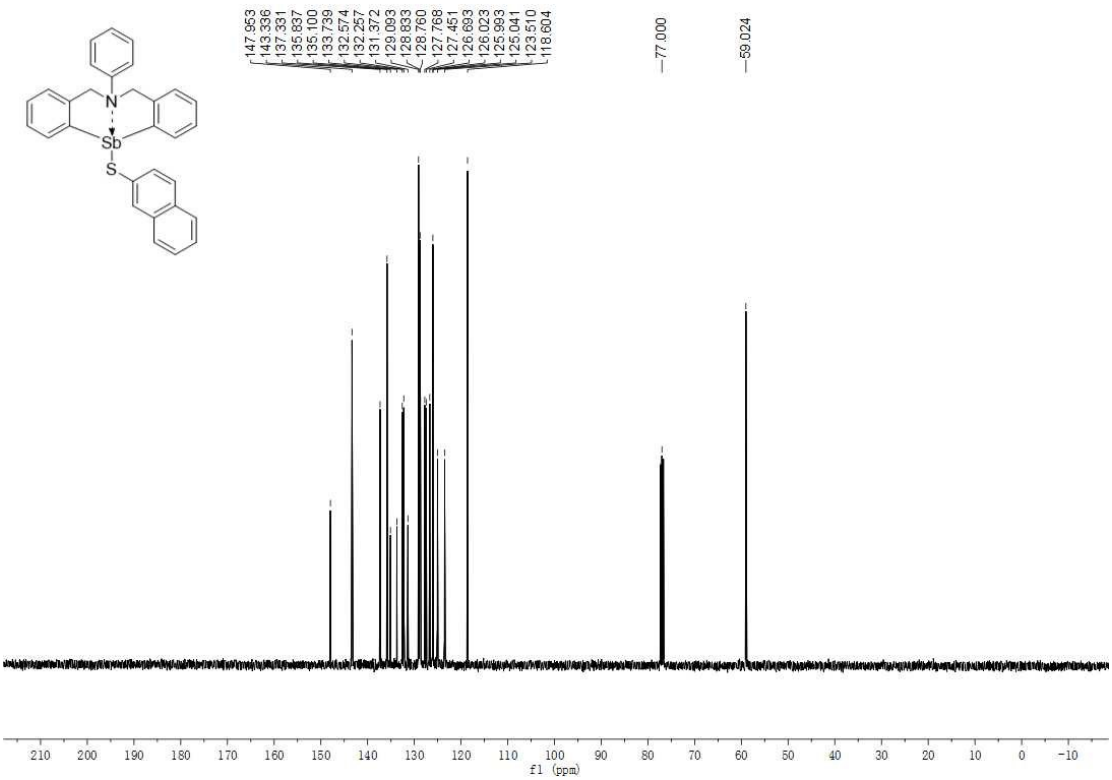
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4o**



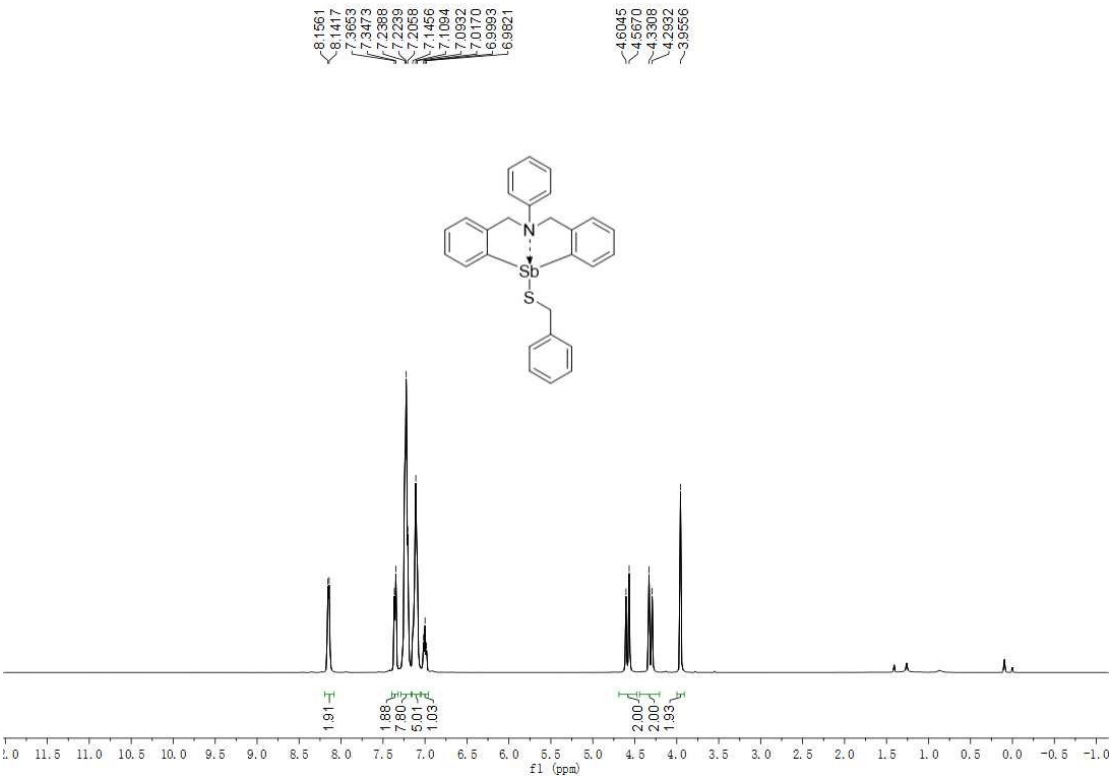
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4o**



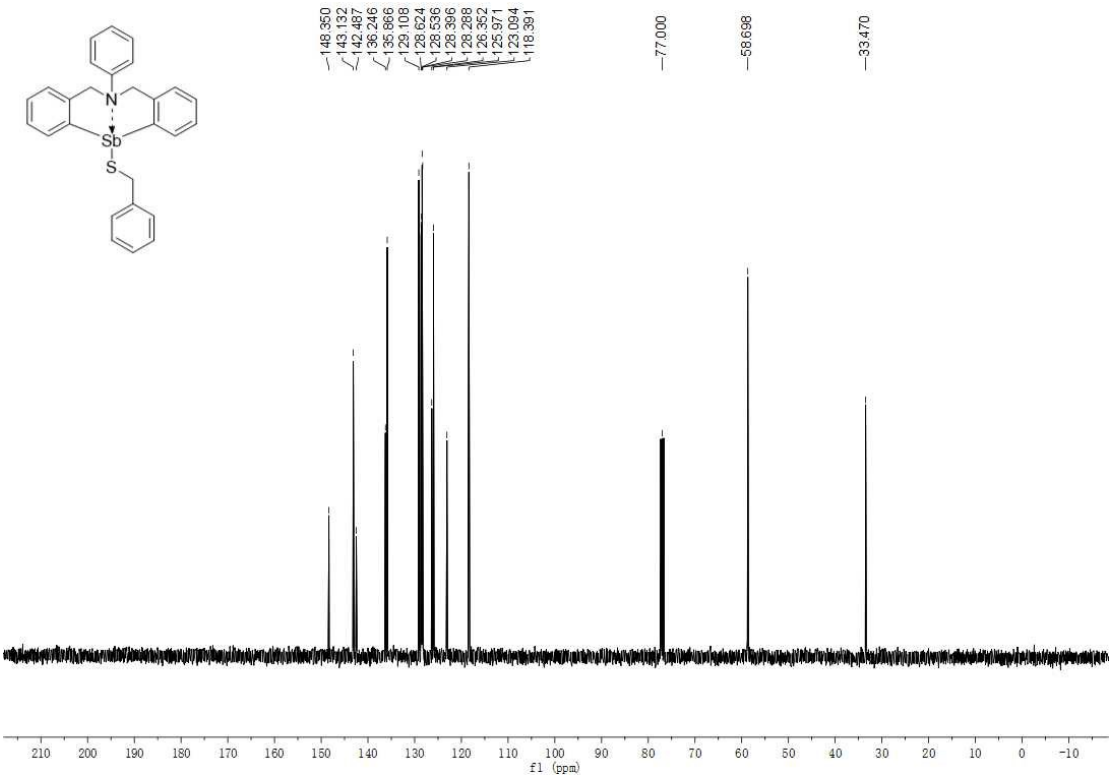
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p**



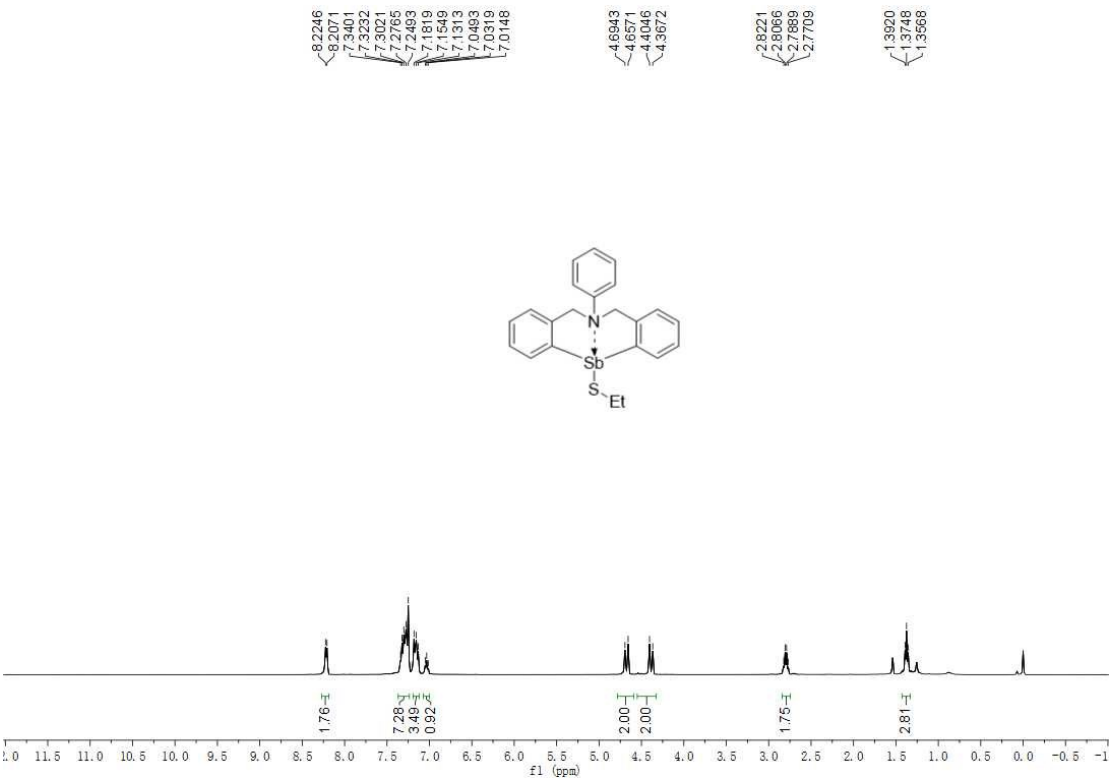
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4p**



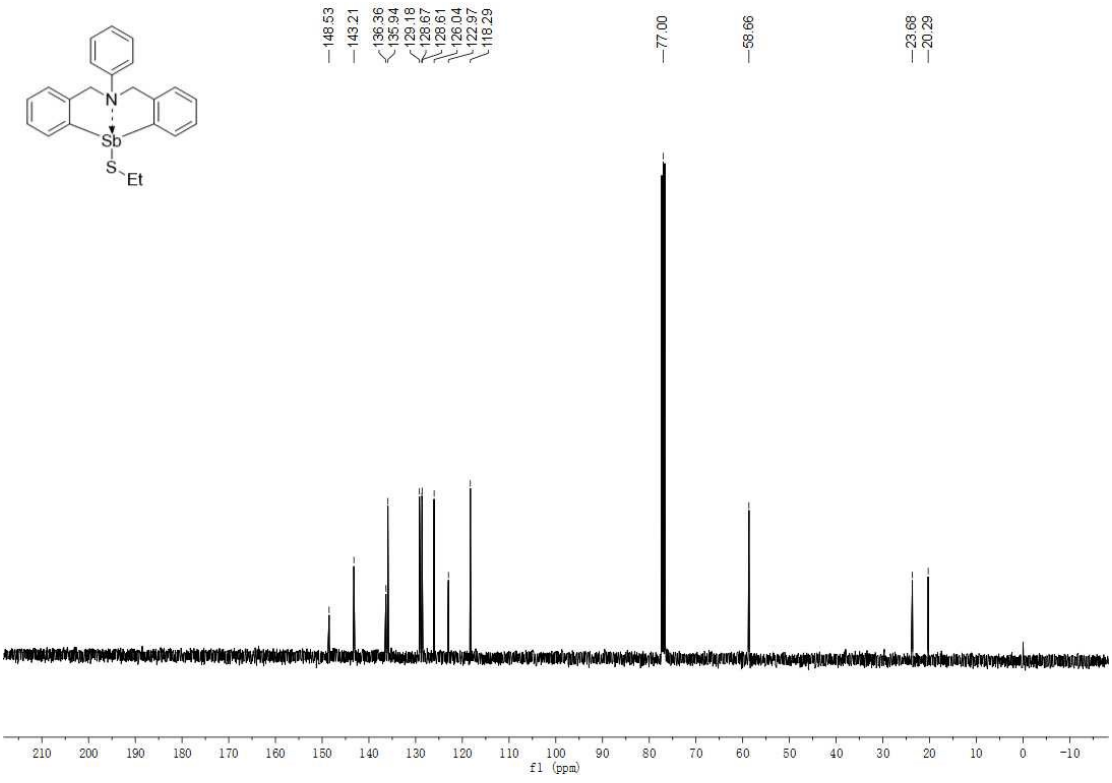
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4q**



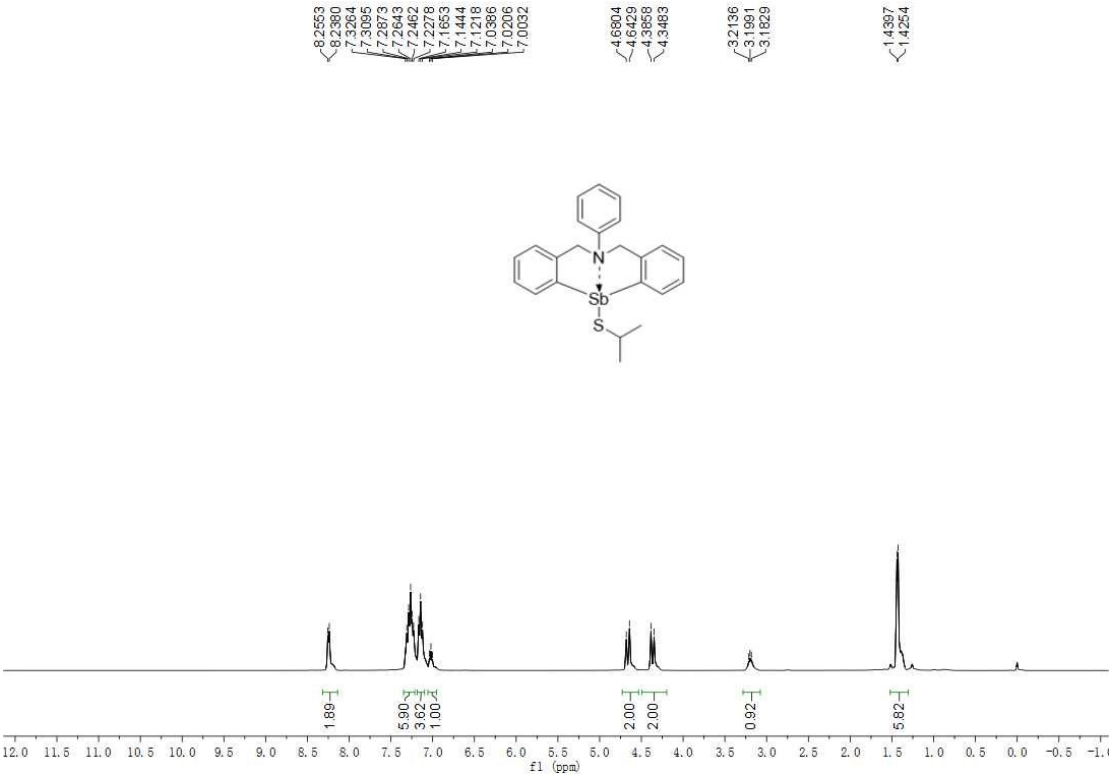
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4q**



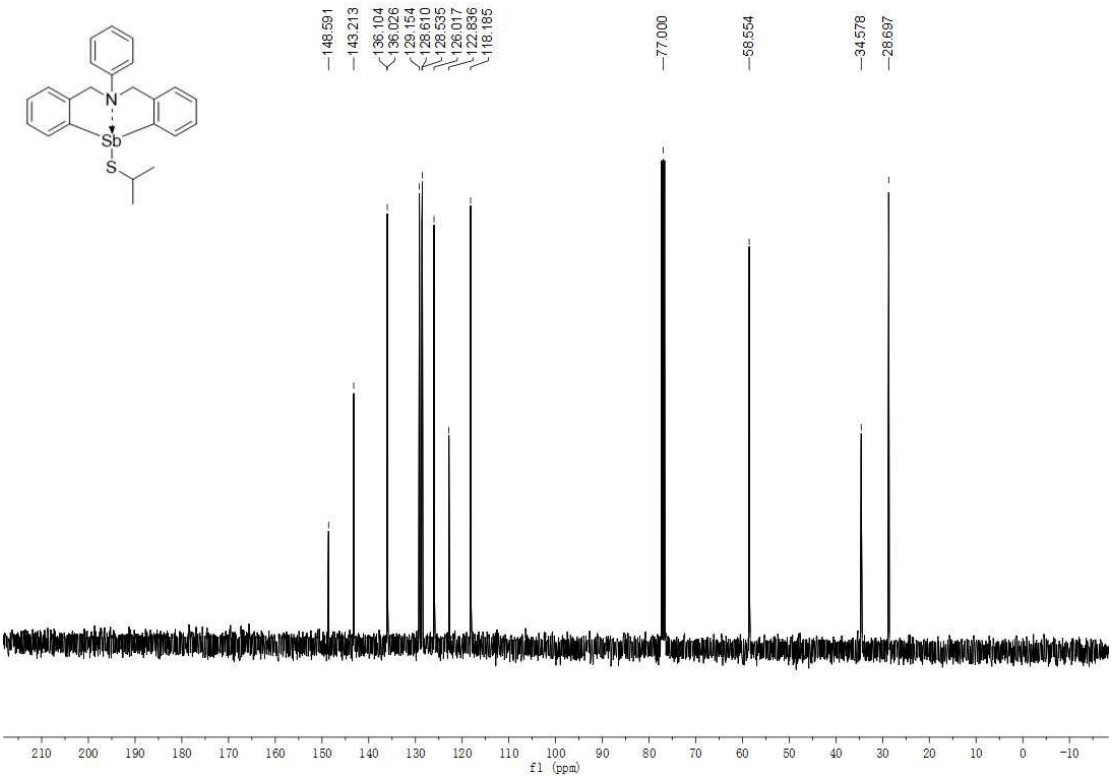
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4r**



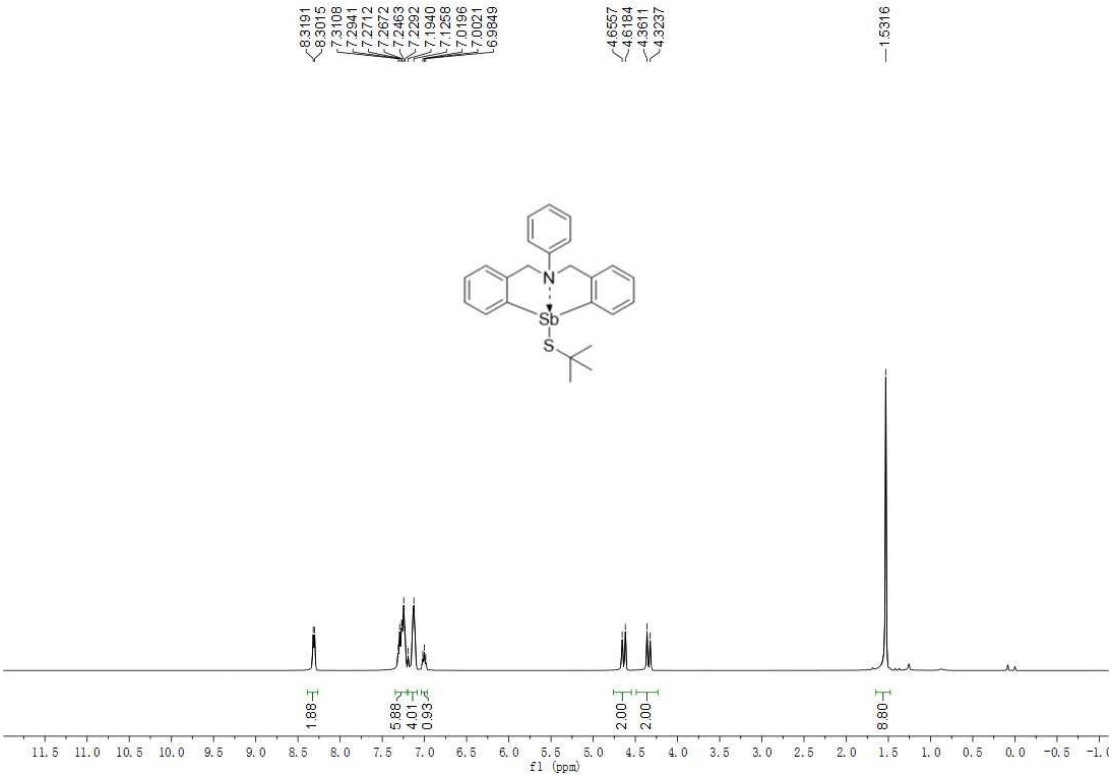
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4r**



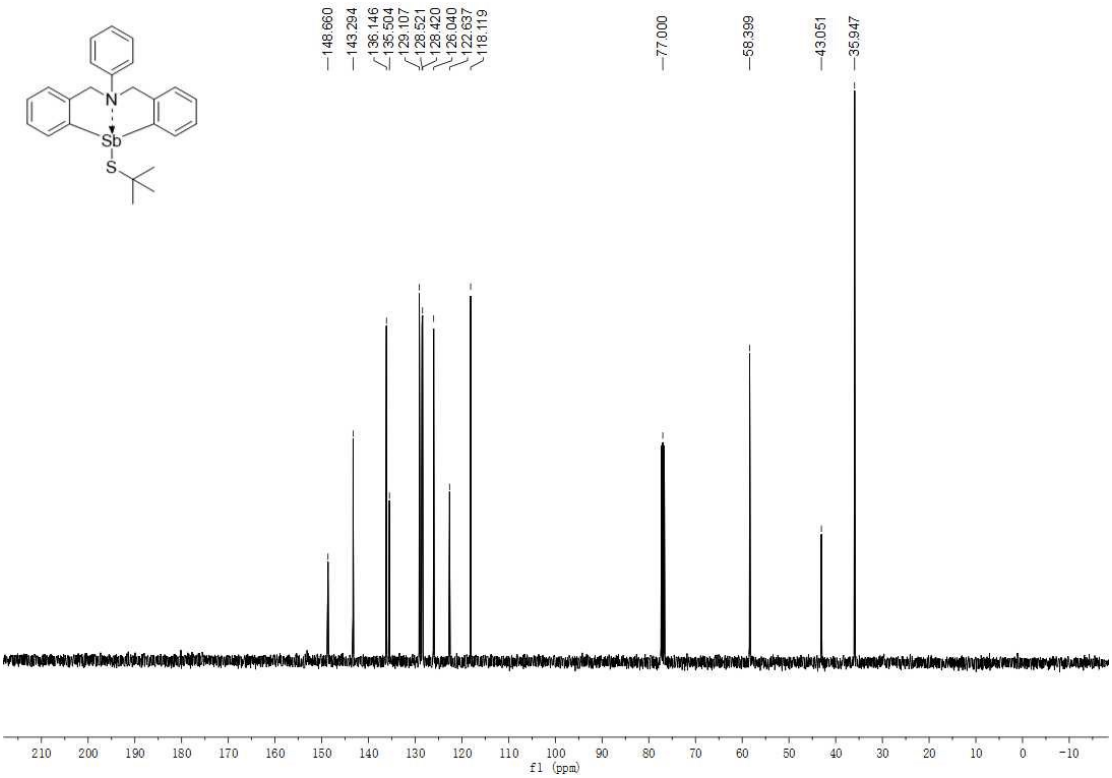
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4s**



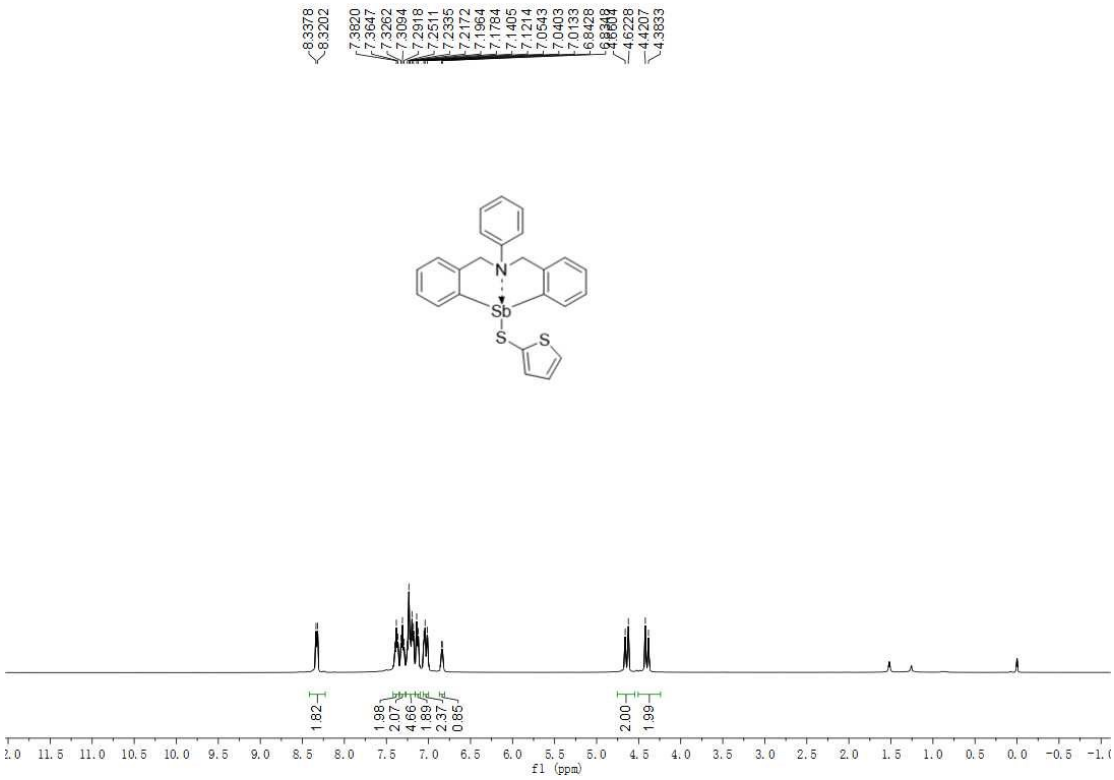
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4s**



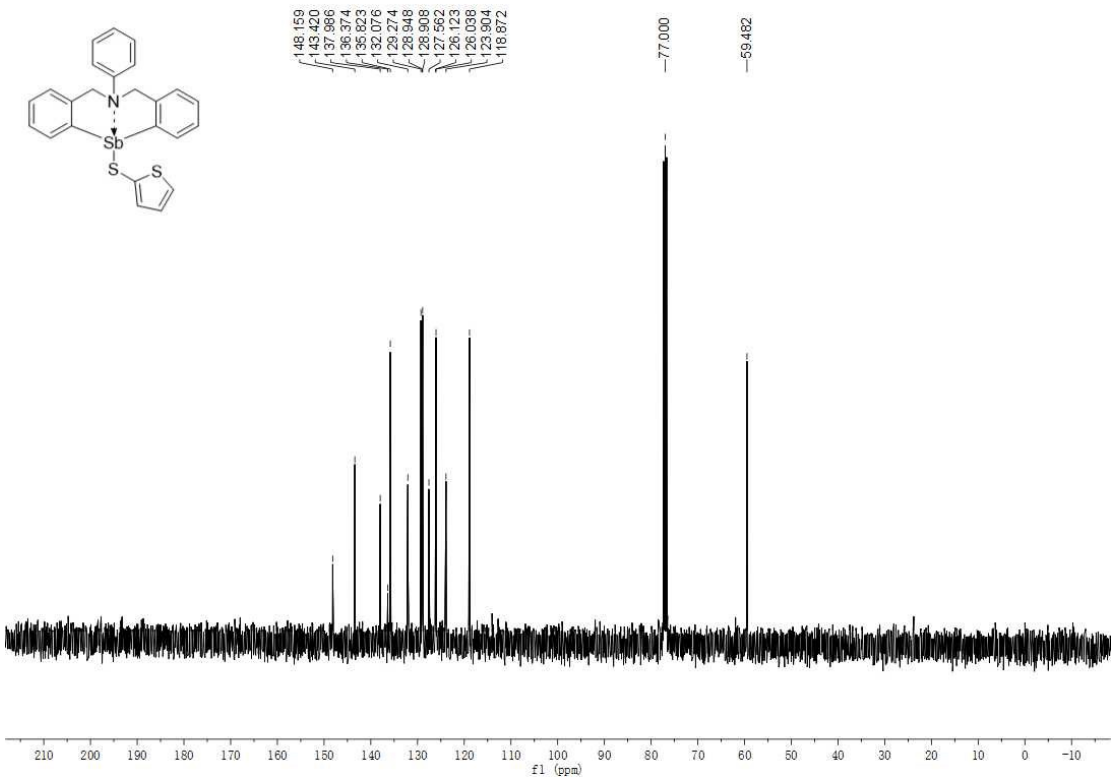
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4t**



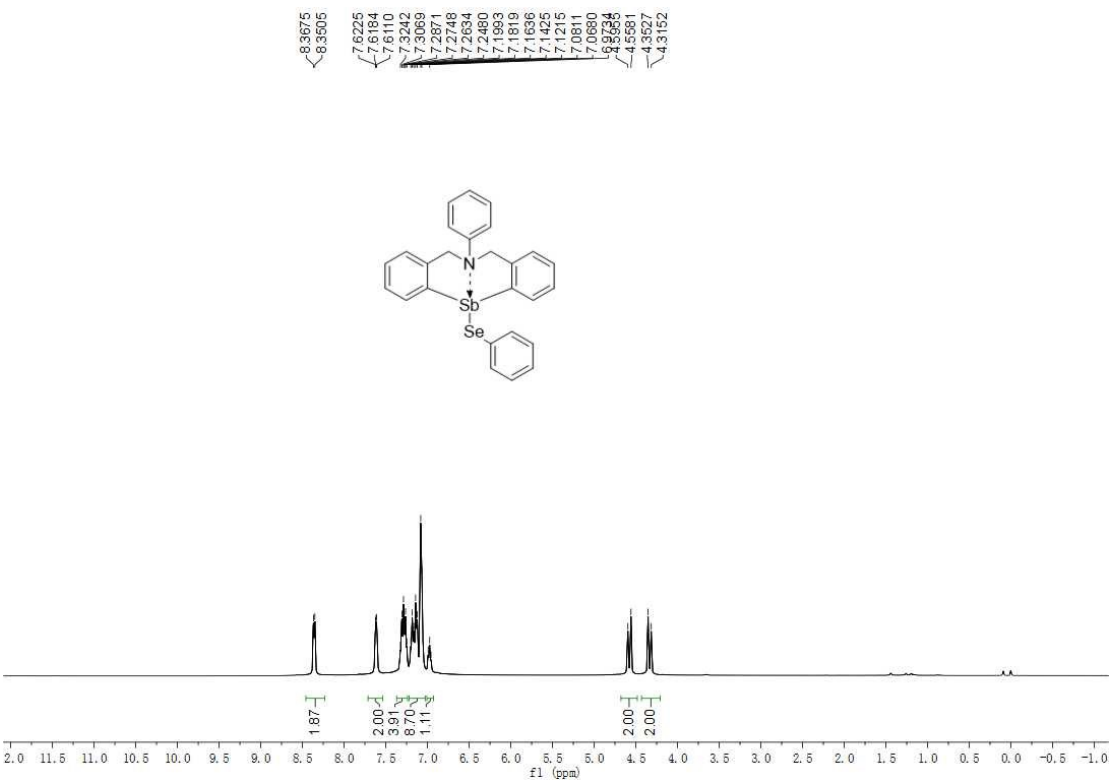
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4t**



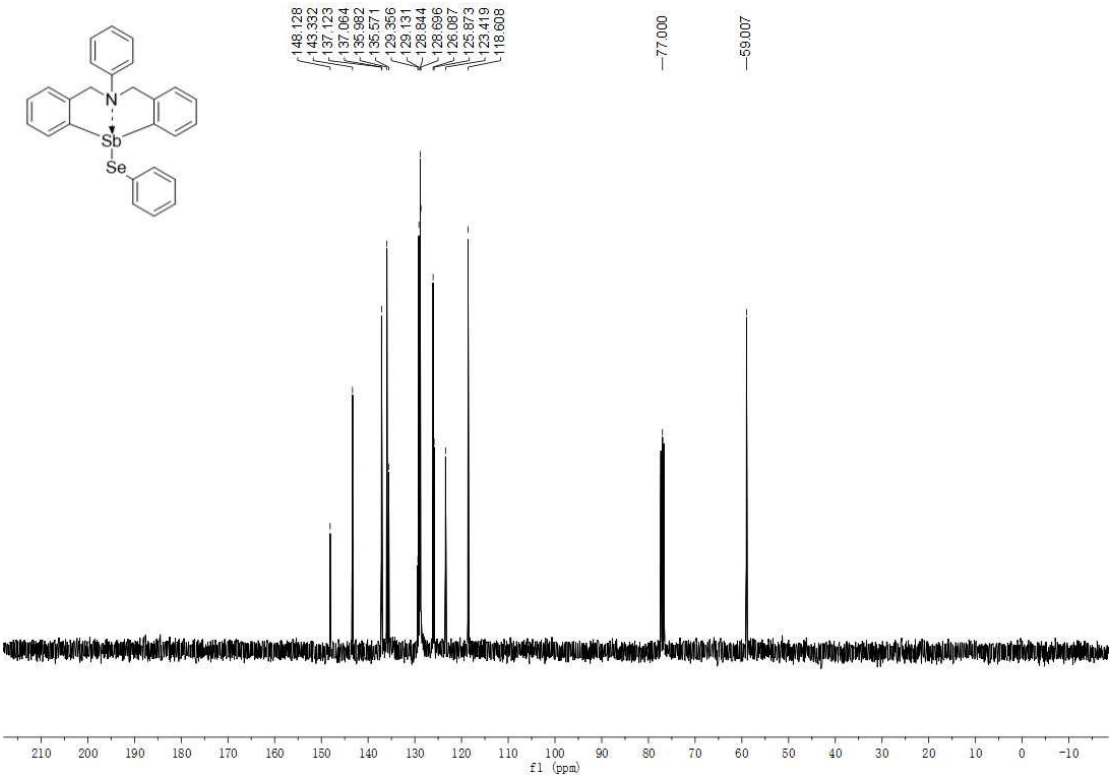
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4u**



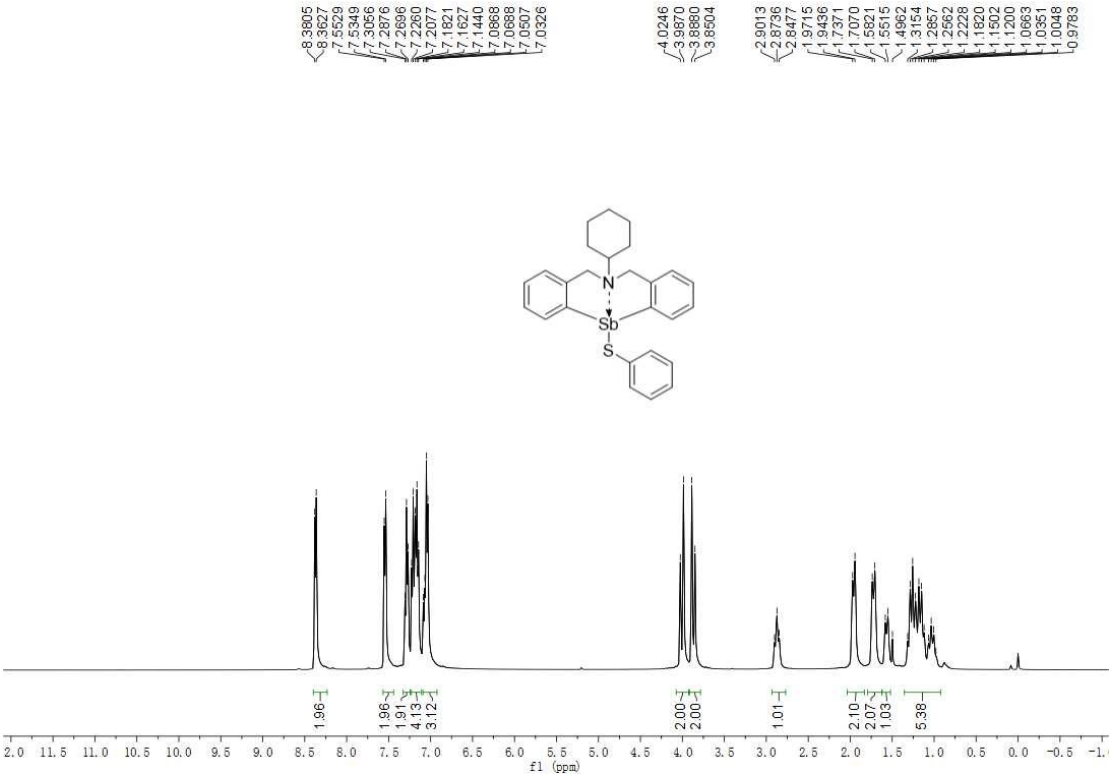
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4u**



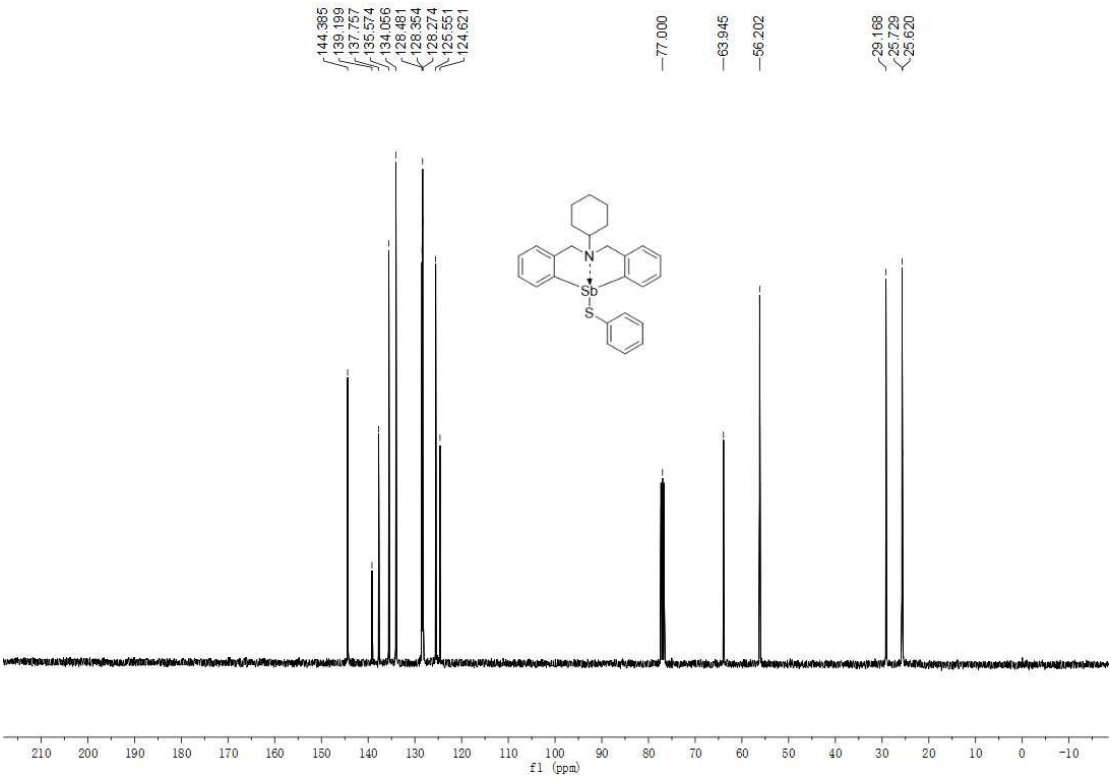
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



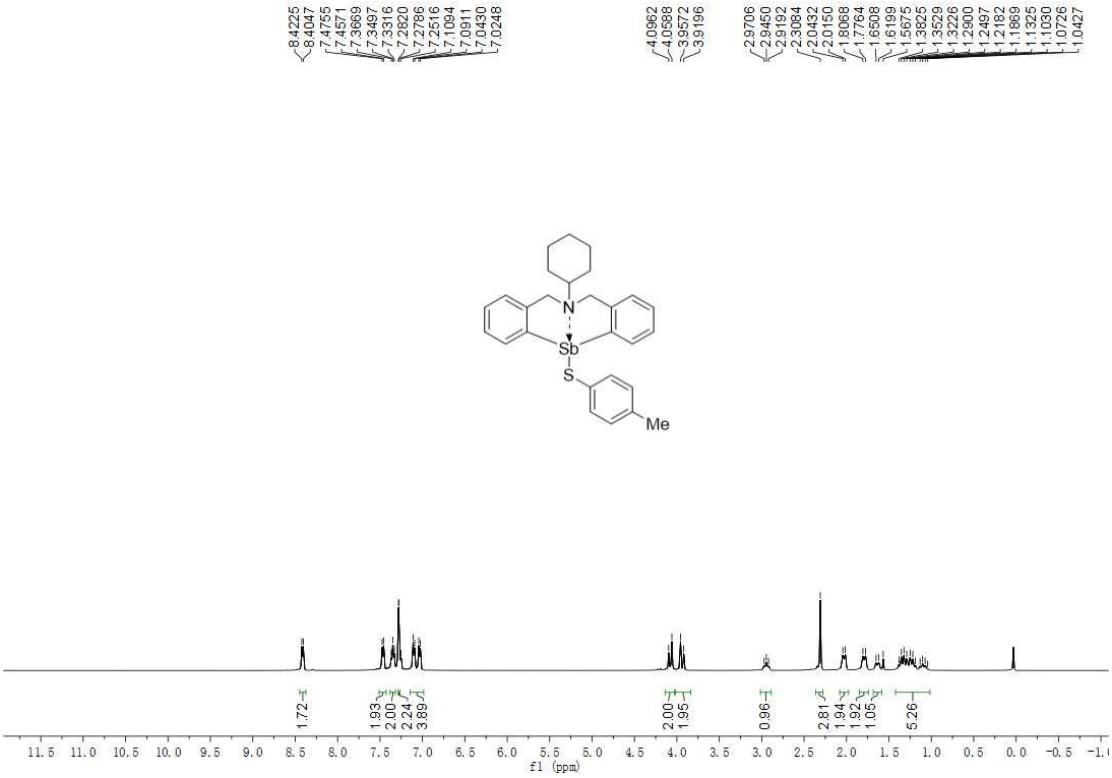
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**



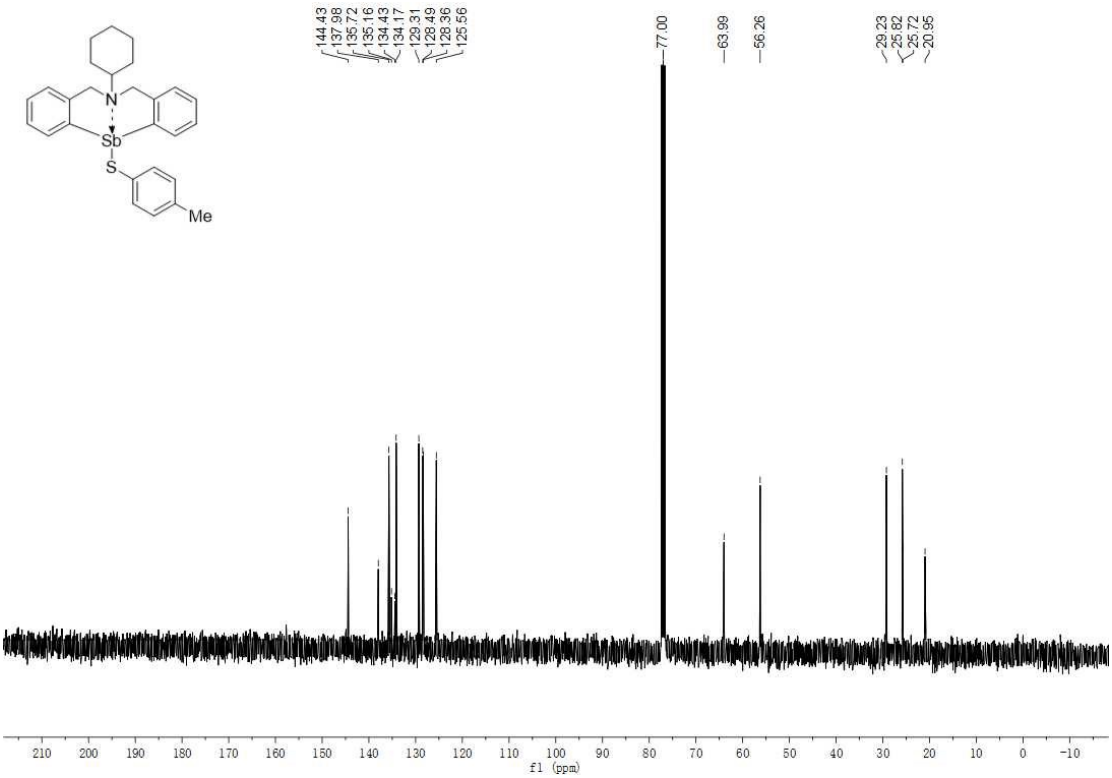
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4v**



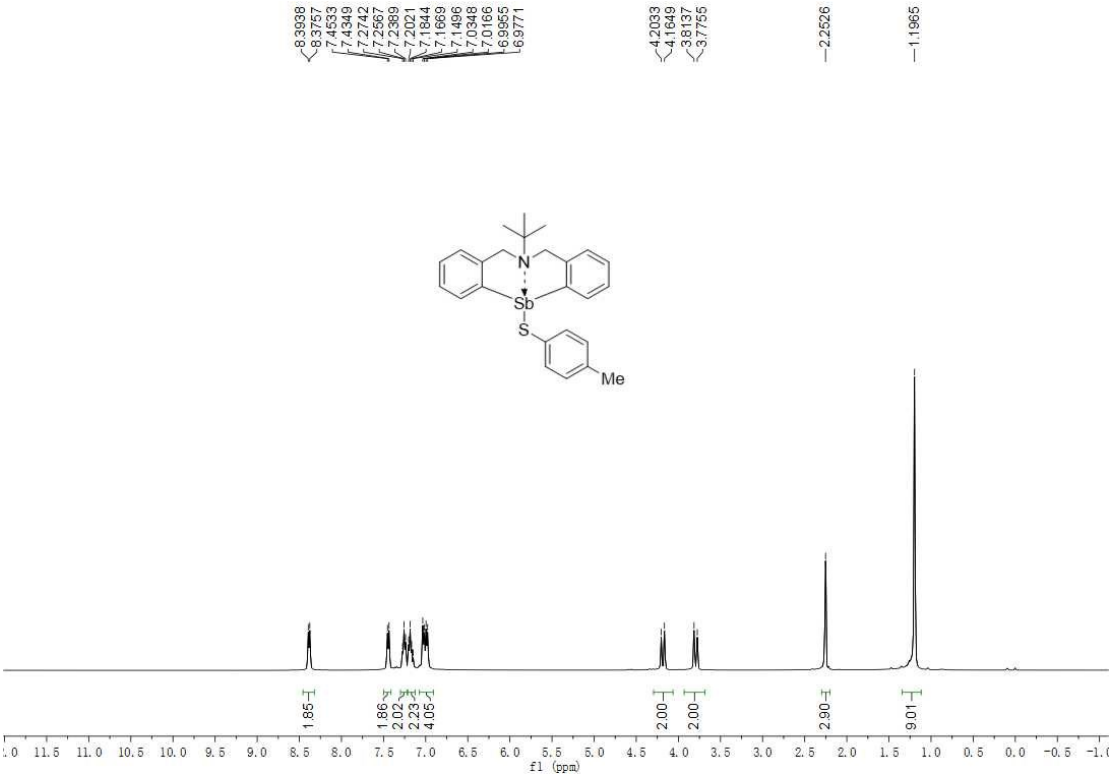
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4v**



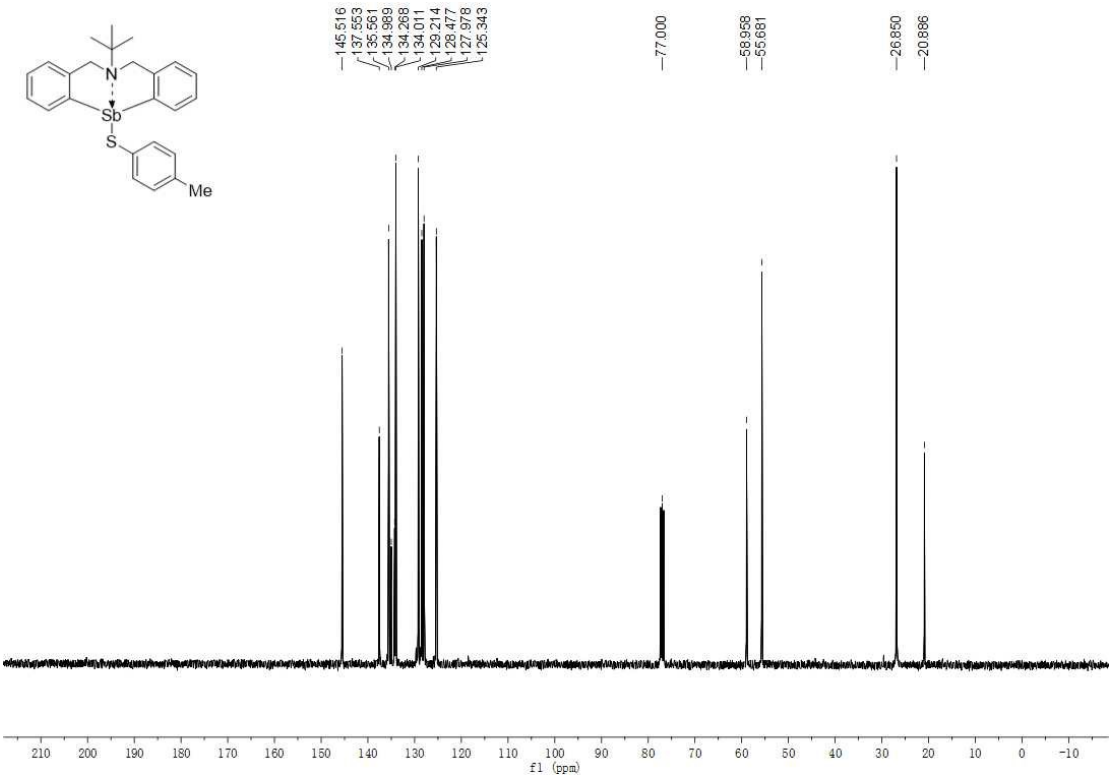
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4w**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4w**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4x**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4x**