Electronic Supplementary Information

Facile synthesis and antifungal evaluation of hypervalent organoantimony(III) and -bismuth(III) thioates with tridentate *C*,*N*,*C*-coordinating ligands†

Zixiu Wang,‡[a] Yan Huang,‡[a] Dandan Deng,[a] Shan Li,*[a] Yimei Yu,[a] Yifei Ye,[a] Yi Chen,*[b] and Jian Lei*[a]

[a] Key Laboratory of Prevention and Treatment of Cardiovascular and Cerebrovascular Disease of the Ministry of Education, Key Laboratory of Biomaterials and Biofabrication in Tissue Engineering of Jiangxi Province, College of Pharmacy, Gannan Medical University, Ganzhou 341000, PR China.
E-mail: lishan9041@gmu.edu.cn, drjianlei@163.com

[b] School of Medicine, Hunan University of Chinese Medicine, Changsha 410208, PR China.
E-mail: chenyi@hnucm.edu.cn

‡ These authors contributed equally.

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1. General information

The commercially available reagents, such as antimony trichloride, bismuth trichloride, 2-bromobenzyl bromide, *n*-butyllithium, aniline, cyclohexylamine, *t*-butylamine, thiols, disulfides, and various additives, were purchased from Adamas-beta (Shanghai, China), Macklin (Shanghai, China), Energy chemical (Shanghai, China), and Sigma-Aldrich (Shanghai, China). Unless noted otherwise, the reagents and solvents obtained from commercial suppliers were used without further purification. The organoantimony (**1a**–**1f**) and -bismuth halides (**4a**–**4c**) were prepared according to previous literature.[1–3] The air- and moisture-sensitive operations were conducted with a standard Schlenk technique under N_2. All products were purified by flash chromatography on silica gel (200–300 mesh) or aluminum oxide (200–300 mesh), using EA/*n*-hexane as an eluent.

Melting points were determined using the XT-4 micro melting point apparatus and were uncorrected. The ^{1}H, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Brucker ADVANCE III spectrometer operating at 400 MHz, 101 MHz, and 376 MHz, respectively, and chemical 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), and coupling constants (J) were reported in hertz. High-resolution mass spectra were measured on a Thermo Fisher Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions. FT-IR spectra were recorded on a Nicolet 380 FT-IR instrument (KBr discs). Single crystal X-ray diffraction analysis was performed on a Bruker D8 Quest diffractometer by using graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures of **3a**, **3b**, **3s**, **3x**, **5a**, and **5d** were solved using intrinsic phasing methods (SHELXT) completed by Fourier synthesis and refined by full-matrix least-squares procedures.[4–6] The CCDC numbers are 2059928 (**3a**), 2059929 (**3b**), 2296027 (**3s**), 2059930 (**3x**), 2337084 (**5a**), 2337085 (**5d**), respectively. The drawings were created with the Diamond program version 4.6.4 for Windows (Bonn, Germany), including the polyhedra for the coordination geometries of compounds **5a** and **5d**.[7–8] GC-MS analysis was performed on a Shimadzu GCMS-TQ8040 triple quadrupole mass spectrometer. According to the methods reported in the previous literature,[9–10] the clog*P* values of selected compounds were calculated using ChemDraw Ultra version 14.0 for Windows (CambridgeSoft, MA, USA).

2. Synthesis and characterization of starting materials

Synthesis of organoantimony and -bismuth chlorides

Initially, ^{n}BuLi (45 mmol, 1.6 M, 28 mL) was added dropwise under N_2 to a cooled (-60 °C) solution of *N*-containing ligand precursors (20 mmol; **L1**, 8.56 g; **L2**, 8.18 g; **L3**, 8.70 g) in anhydrous Et_2O (100 mL) and reacted at RT for approximately 3 h. Subsequently, the obtained mixture was added directly to $SbCl_3$ (20 mmol, 4.56 g) or $BiCl_3$ (20 mmol, 6.30 g) at -78 °C, followed by continuously stirring overnight at RT. Upon completion, the mixture was subject to evaporation. The residue was extracted with CH_2Cl_2 and washed with deionized water. After being dried, concentrated, and recrystallized (hexane/CH_2Cl_2), the desired compound was delivered.

Synthesis of organoantimony bromide

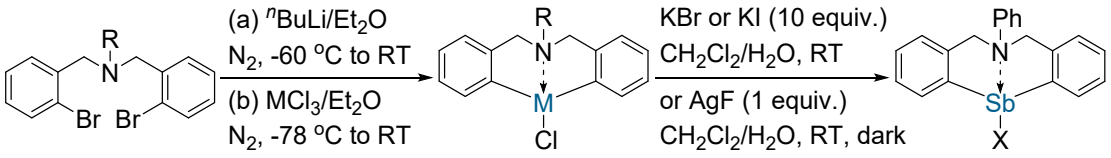
The solutions of organoantimony chloride **1a** (1 mmol, 427 mg, in CH_2Cl_2) and KBr (10 mmol, 1.19 g, in deionized water) were added to a 50 mL Schlenk tube, followed by reacting at RT overnight. Upon completion, the resulting organic layer was dried and mixed with hexane to afford compound **1d** by recrystallization.

Synthesis of organoantimony iodide

The solutions of organoantimony chloride **1a** (1 mmol, 427 mg, in CH_2Cl_2) and KI (10 mmol, 1.66 g, in deionized water) were added to a 50 mL Schlenk tube, followed by reacting at RT overnight. Upon completion, the resulting organic layer was dried and mixed with hexane to afford compound **1e** by recrystallization.

Synthesis of organoantimony fluoride

The solutions of organoantimony chloride **1a** (1 mmol, 427 mg, in CH_2Cl_2) and AgF (1 mmol, 126 mg, in deionized water) were added to a 50 mL Schlenk tube, followed by reacting overnight in the dark at RT. Upon completion, the resulting organic layer was dried and mixed with hexane to afford compound **1f** by recrystallization.



R = Ph (**L1**)
R = ^{t}Bu (**L2**)
R = Cy (**L3**)

R = Ph, M = Sb (**1a**), Bi (**4a**)
R = ^{t}Bu, M = Sb (**1b**), Bi (**4b**)
R = Cy, M = Sb (**1c**), Bi (**4c**)

X = Br (**1d**)
X = I (**1e**)
X = F (**1f**)

Fig. S1 Synthetic routes for the preparation of organoantimony (**1a**–**1f**) and -bismuth (**4a**–**4c**) halides.

3. General procedure for the synthesis of target products

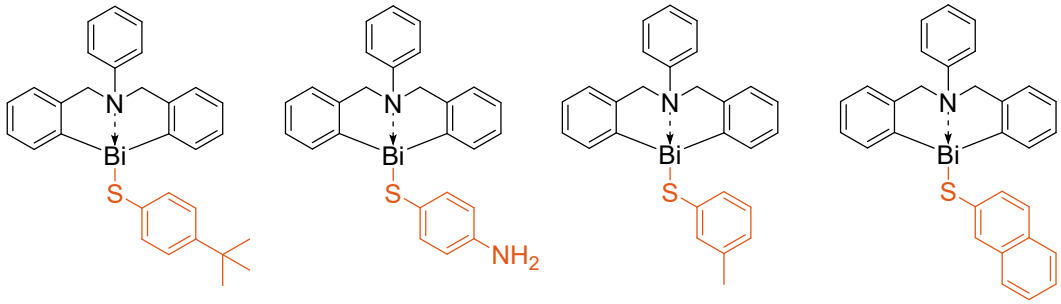
Additive-free synthesis starting from thiols

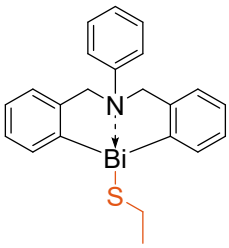
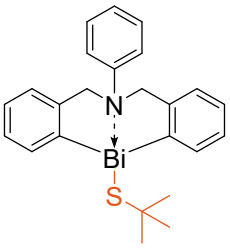
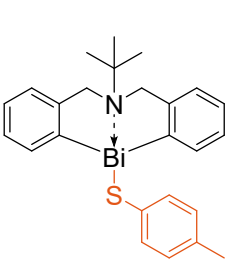
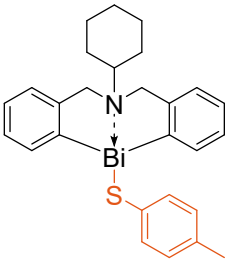
A solution of organoantimony (**1a**–**1f**) and -bismuth (**4a**–**4c**) halides (0.3 mmol) and thiol (**2**, 0.3 mmol) in DMSO (2 mL) was added to a 25 mL Schlenk tube, followed by vigorous stirring at room temperature for a specified time under open-flask conditions. Upon completion of the reaction, the mixture was diluted with deionized water and extracted with dichloromethane at least five times. Subsequently, 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 or aluminum oxide, eluting with EA/*n*-hexane, to afford the desired product.

DTT-mediated synthesis starting from disulfides

A solution of organoantimony (**1a**–**1f**) and -bismuth (**4a**–**4c**) halides (0.3 mmol), disulfide (**2'**, 0.15 mmol), and DTT (0.23 mmol) in DMSO (2 mL) was added to a 25 mL Schlenk tube, followed by vigorous stirring at room temperature for a specified time under N_2. Upon completion of the reaction, the mixture was diluted with deionized water and extracted with dichloromethane at least five times. Subsequently, 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 or aluminum oxide, eluting with EA/*n*-hexane, to afford the desired product.

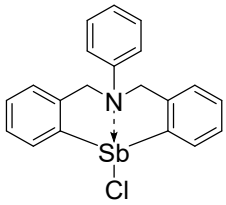
Unsatisfied examples

Only a trace amount of the desired product was obtained under both Cond. **A** and **B**

No reaction took place under both Cond. **A** and **B**

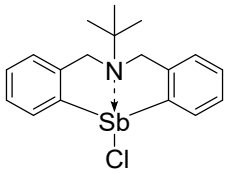
4. Analytical data

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



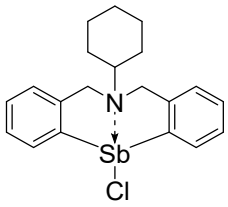
White solid; **Mp**: 225–227 °C; **Yield**: 68% (5.81 g); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.35–8.23 (m, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.33–7.29 (m,4H), 7.25–7.15 (m, 5H), 4.70 (d, J = 15.0 Hz, 2H), 4.52 (d, J = 14.9 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.9, 143.0, 140.5, 135.2, 129.5, 129.2, 129.2, 125.4, 125.3, 119.7, 61.2.

6-(*tert*-butyl)-12-chloro-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (1b)



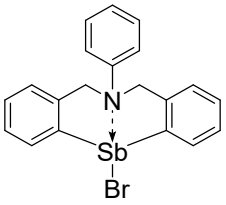
White solid; **Mp**: 209–211 °C; **Yield**: 75% (6.11 g); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37–8.24 (m, 2H), 7.31–7.27 (m, 2H), 7.25–7.20 (m, 2H), 7.08 (t, J = 7.4 Hz, 2H), 4.36 (d, J = 15.3 Hz, 2H), 3.96 (d, J = 15.4 Hz, 2H), 1.31 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.0, 139.8, 134.8, 128.9, 128.4, 124.5, 60.4, 57.2, 27.0.

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



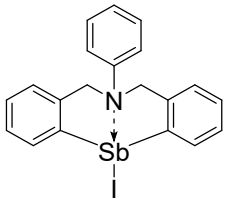
White solid; **Mp**: 261–263 °C; **Yield**: 70% (6.06 g); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37–8.25 (m, 2H), 7.37–7.33 (m, 2H), 7.28–7.24 (m, 2H), 7.10 (d, J = 7.1 Hz, 2H), 4.19 (d, J = 15.1 Hz, 2H), 4.04 (d, J = 15.1 Hz, 2H), 3.09–3.02 (m, 1H), 2.02 (d, J = 11.8 Hz, 2H), 1.83 (d, J = 13.0 Hz, 2H), 1.65 (d, J = 13.1 Hz, 1H), 1.42–1.23 (m, 4H), 1.15–1.04 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.0, 140.2, 135.0, 128.9, 128.8, 124.7, 65.4, 57.8, 29.6, 25.7, 25.5.

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



White solid; **Mp**: 235–237 °C; **Yield**: 89% (418.3 mg); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.28–8.16 (m, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.28–7.22 (m, 4H), 7.17 (d, J = 7.2 Hz, 2H), 7.14–7.07 (m, 3H), 4.62 (d, J = 14.9 Hz, 2H), 4.46 (d, J = 14.9 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.9, 143.1, 140.5, 138.1, 136.7, 135.2, 129.6, 129.2, 125.3, 119.7, 61.2.

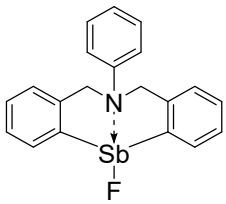
12-iodo-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (1e)



White solid; **Mp**: 201–203 °C; **Yield**: 86% (445.5 mg); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.46–8.44 (m, 2H), 7.37–7.33 (m, 4H), 7.31 (t, J = 7.2 Hz, 2H), 7.25–7.22 (m, 2H), 7.19–7.15 (m, 3H), 4.67 (d,

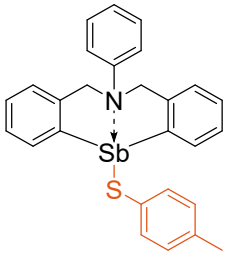
J = 14.8 Hz, 2H), 4.51 (d, *J* = 14.9 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 147.5, 142.9, 140.0, 134.0, 129.6, 129.5, 129.4, 125.5, 125.3, 119.8, 60.9.

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



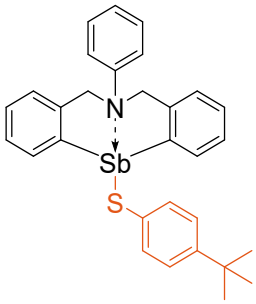
White solid; **Mp**: 222–224 °C; **Yield**: 92% (378.1 mg); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 7.93 (d, *J* = 7.4 Hz, 2H), 7.31–7.26 (m, 4H), 7.24–7.18 (m, 4H), 7.15–7.11 (m, 1H), 4.67 (d, *J* = 15.0 Hz, 2H), 4.46 (d, *J* = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 148.5, 144.6 (d, *J* = 6.7 Hz), 143.1, 133.4 (d, *J* = 6.2 Hz), 129.5, 128.9, 128.8, 125.2, 125.0, 119.4, 61.2 (d, *J* = 2 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: -198.63.

6-phenyl-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3a)



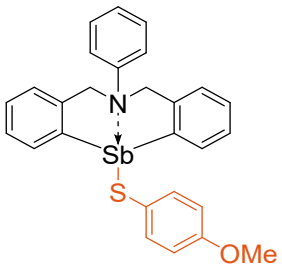
White solid; **Mp**: 185–187 °C; **Yield**: 91% (140.6 mg, *additive-free synthesis*), 87% (134.4 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 8.36 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34–7.30 (m, 2H), 7.27–7.23 (m, 2H), 7.19–7.12 (m, 4H), 7.07–7.05 (m, 2H), 6.98–6.92 (m, 3H), 4.56 (d, *J* = 15.0 Hz, 2H), 4.31 (d, *J* = 15.0 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 148.1, 143.3, 137.4, 135.8, 135.0, 134.2, 133.4, 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; **FT-IR (KBr, cm^{-1})**: *ν* 3050, 2900, 2850, 2360, 1590, 1490, 1450, 1200, 1120, 1080, 1020, 970, 839, 808, 781, 752, 690.

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



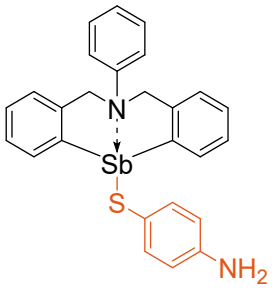
White solid; **Mp**: 233–234 °C; **Yield**: 81% (135.4 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 8.37 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.44–7.42 (m, 2H), 7.39–7.35 (m, 2H), 7.32–7.28 (m, 2H), 7.25–7.11 (m, 8H), 7.02 (t, *J* = 7.2 Hz, 1H), 4.65 (d, *J* = 15.0 Hz, 2H), 4.40 (d, *J* = 15.0 Hz, 2H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 148.4, 148.3, 143.4, 137.8, 137.5, 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; **FT-IR (KBr, cm^{-1})**: *ν* 3050, 2960, 2900, 2860, 1590, 1490, 1460, 1440, 1390, 1360, 1190, 1120, 1020, 823, 756, 690.

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



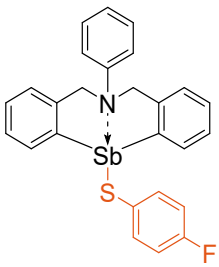
White solid; **Mp**: 187–189 °C; **Yield**: 82% (130.6 mg, *additive-free synthesis*), 77% (122.7 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (dd, J = 7.4, 1.1 Hz, 2H), 7.43–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.30–7.26 (m, 2H), 7.22–7.15 (m, 4H), 7.10–7.07 (m, 2H), 6.99 (t, J = 7.3 Hz, 1H), 6.72–6.68 (m, 2H), 4.60 (d, J = 15.0 Hz, 2H), 4.35 (d, J = 15.1 Hz, 2H), 3.68 (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, 55.2; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NOSSb$ $[M+H]^+$: 532.0695; found: 532.0692; **FT-IR (KBr, cm^{-1})**: ν 3050, 2900, 2850, 2360, 2340, 1590, 1490, 1440, 1280, 1250, 1210, 1180, 1110, 1030, 924, 825, 775, 752, 746, 688.

4-((6-phenyl-6,7-dihydrodibenzo[*c*,*f*][1,5]azastibocin-12(5H)-yl)thio)aniline (3d)



Yellow solid; **Mp**: 168–170 °C; **Yield**: 74% (114.6 mg, *additive-free synthesis*), 58% (89.8 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.36 (dd, J = 7.6 Hz, 2H), 7.33 (t, J = 6.8 Hz, 2H), 7.28–7.24 (m, 4H), 7.19–7.12 (m, 4H), 7.05 (d, J = 8.2 Hz, 2H), 6.96 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 8.4 Hz, 2H), 4.57 (d, J = 15.1 Hz, 2H), 4.31 (d, J = 15.0 Hz, 2H), 3.43 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.2, 144.5, 143.4, 137.6, 135.8, 135.5, 129.1, 128.7, 128.7, 126.0, 124.0, 123.2, 118.4, 115.7, 58.9; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{24}N_2SSb$ $[M+H]^+$: 517.0698; found: 517.0691; **FT-IR (KBr, cm^{-1})**: ν 3390, 3060, 2900, 2850, 2360, 1590, 1490, 1440, 1350, 1280, 1210, 1190, 1120, 1080, 822, 777, 752, 692.

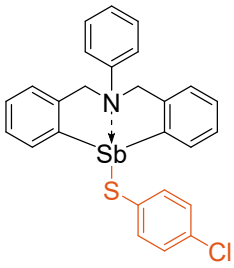
12-((4-fluorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3e)



White solid; **Mp**: 234–236 °C; **Yield**: 87% (135.5 mg, *additive-free synthesis*), 74% (115.2 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.34 (dd, J = 7.4, 1.4 Hz, 2H), 7.45–7.42 (m, 2H), 7.36–7.32 (m, 2H), 7.29–7.25 (m, 2H), 7.21–7.08 (m, 6H), 6.99 (t, J = 7.3 Hz, 1H), 6.81 (t, J = 8.7 Hz, 2H), 4.60 (d, J = 15.0 Hz, 2H), 4.34 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$; list**

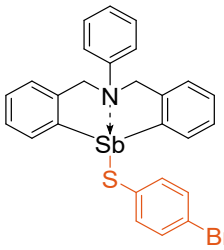
of signals, C–F coupling not resolved): δ 162.4, 160.0, 148.0, 143.3, 137.2, 135.7, 135.6, 132.4, 132.3, 129.2, 128.9, 128.8, 126.1, 123.6, 118.6, 115.6, 115.4, 59.1; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -109.24; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}FNSSb$ $[M+H]^+$: 520.0495; found: 520.0499; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2910, 2860, 1590, 1490, 1360, 1220, 1090, 829, 754, 690, 627.

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



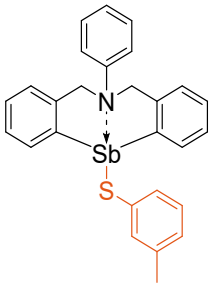
White solid; **Mp**: 221–223 °C; **Yield**: 91% (146.1 mg, *additive-free synthesis*), 83% (133.2 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.31 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.32–7.28 (m, 2H), 7.25–7.21 (m, 2H), 7.18–7.10 (m, 4H), 7.07–7.02 (m, 4H), 6.95 (t, *J* = 7.2 Hz, 1H), 4.55 (d, *J* = 15.1 Hz, 2H), 4.30 (d, *J* = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.8, 143.3, 137.1, 136.4, 135.7, 135.3, 131.0, 129.1, 128.9, 128.8, 128.5, 126.0, 123.7, 118.6, 59.1; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}ClNSSb$ $[M+H]^+$: 536.0200; found: 536.0193; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2900, 2860, 2360, 1590, 1490, 1470, 1440, 1200, 1090, 1010, 820, 756, 692.

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



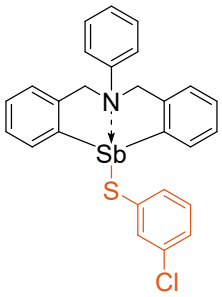
White solid; **Mp**: 218–220 °C; **Yield**: 85% (147.6 mg, *additive-free synthesis*), 78% (135.5 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.30 (d, *J* = 7.3 Hz, 2H), 7.34–7.27 (m, 4H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 3H), 7.12 (d, *J* = 5.8 Hz, 3H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 4.54 (d, *J* = 15.0 Hz, 2H), 4.29 (d, *J* = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.8, 143.2, 137.1, 137.0, 135.6, 135.6, 131.3, 129.1, 128.9, 128.8, 126.0, 123.7, 119.0, 118.6, 59.1; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}BrNSSb$ $[M+H]^+$: 579.9695; found: 579.9700; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2910, 2860, 2360, 1590, 1490, 1460, 1440, 1380, 1350, 1310, 1250, 1200, 1090, 1000, 930, 814, 754, 692, 540.

6-phenyl-12-(*m*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3h)



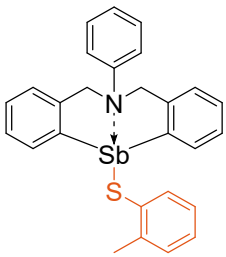
White solid; **Mp**: 193–195 °C; **Yield**: 85% (131.3 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.37 (d, J = 7.4 Hz, 2H), 7.35–7.23 (m, 6H), 7.19–7.05 (m, 6H), 7.02–6.94 (m, 2H), 6.86 (d, J = 7.6 Hz, 1H), 4.56 (d, J = 15.0 Hz, 2H), 4.31 (d, J = 15.1 Hz, 2H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.1, 143.3, 138.1, 137.4, 137.0, 135.8, 134.9, 131.3, 129.1, 128.8, 128.7, 128.4, 126.3, 126.0, 123.4, 118.6, 59.0, 21.2; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{25}NSSb$ $[M+H]^+$: 516.0746; found: 516.0748; **FT-IR (KBr, cm^{-1})**: ν 3050, 2900, 2850, 2360, 1590, 1490, 1460, 1440, 1350, 1310, 1210, 1190, 775, 748, 683.

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



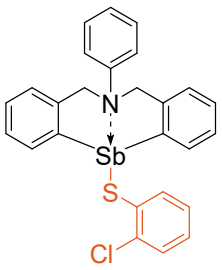
White solid; **Mp**: 232–234 °C; **Yield**: 87% (139.6 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.31 (d, J = 7.4 Hz, 2H), 7.52 (s, 1H), 7.35–7.28 (m, 3H), 7.23 (t, J = 7.3 Hz, 2H), 7.18–7.05 (m, 6H), 6.97–6.94 (m, 3H), 4.54 (d, J = 15.0 Hz, 2H), 4.29 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 147.8, 143.3, 140.1, 137.0, 135.7, 133.7, 133.5, 132.3, 129.4, 129.2, 128.9, 128.8, 126.1, 125.4, 123.7, 118.7, 59.1; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}ClNSSb$ $[M+H]^+$: 536.0200; found: 536.0197; **FT-IR (KBr, cm^{-1})**: ν 3160, 3050, 2900, 2850, 2360, 1940, 1590, 1570, 1490, 1450, 1200, 1110, 1080, 1020, 872, 820, 777, 750, 688, 621.

6-phenyl-12-(*o*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3j)



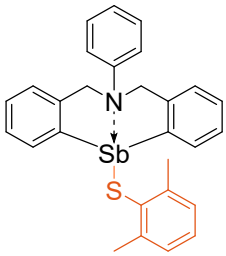
White solid; **Mp**: 199–200 °C; **Yield**: 82% (126.7 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.46 (dd, J = 7.6, 1.3 Hz, 2H), 7.46 (dd, J = 7.4, 1.7 Hz, 1H), 7.34 (t, J = 7.3 Hz, 2H), 7.27–7.23 (m, 2H), 7.18–7.10 (m, 5H), 7.05 (d, J = 8.2 Hz, 2H), 7.00–6.91 (m, 3H), 4.56 (d, J = 15.0 Hz, 2H), 4.31 (d, J = 15.0 Hz, 2H), 2.54 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 148.1, 143.4, 141.0, 137.4, 136.9, 135.9, 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; **FT-IR (KBr, cm^{-1})**: ν 3050, 2910, 2850, 1590, 1490, 1460, 1350, 1210, 1190, 1060, 754, 690.

12-((2-chlorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3k)



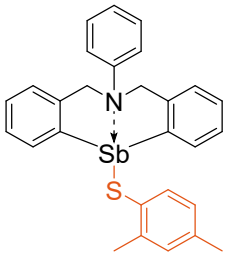
White solid; **Mp**: 207–209 °C; **Yield**: 88% (141.2 mg, *additive-free synthesis*), 75% (120.4 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.48 (dd, J = 7.4, 1.4 Hz, 2H), 7.61–7.56 (m, 1H), 7.38–7.26 (m, 5H), 7.21–7.14 (m, 4H), 7.10–7.08 (m, 2H), 7.02–6.96 (m, 3H), 4.59 (d, J = 15.0 Hz, 2H), 4.32 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.1, 143.3, 138.0, 137.4, 137.0, 136.5, 136.2, 129.5, 129.2, 128.9, 128.8, 126.7, 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; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2900, 2850, 2060, 1590, 1490, 1440, 1210, 1190, 1130, 1110, 1020, 930, 775, 742, 683.

12-((2,6-dimethylphenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3l)



White solid; **Mp**: 212–213 °C; **Yield**: 84% (133.3 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.63 (dd, J = 7.5, 1.4 Hz, 2H), 7.42–7.38 (m, 2H), 7.31–7.27 (m, 2H), 7.20–7.14 (m, 4H), 7.03 (t, J = 8.0 Hz, 4H), 6.99–6.92 (m, 2H), 4.59 (d, J = 15.0 Hz, 2H), 4.32 (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, 129.2, 128.8, 128.7, 127.6, 125.9, 125.9, 123.3, 118.3, 58.9, 24.5; **HRMS *m/z* (ESI)** calcd. for $C_{28}H_{27}NSSb$ $[M+H]^+$: 530.0902; found: 530.0907; **FT-IR (KBr, cm^{-1})**: *v* 3050, 1590, 1490, 1350, 1210, 1190, 818, 777, 752.

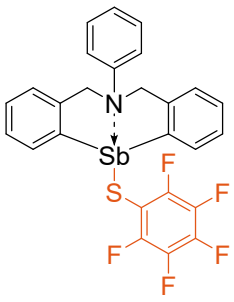
12-((2,4-dimethylphenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3m)



White solid; **Mp**: 203–205 °C; **Yield**: 86% (136.5 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.47 (dd, J = 7.5, 1.3 Hz, 2H), 7.40–7.35 (m, 3H), 7.32–7.28 (m, 2H), 7.22–7.16 (m, 4H), 7.09 (d, J = 7.8 Hz, 2H), 7.01–6.97 (m, 2H), 6.79 (dd, J = 7.9, 2.1 Hz, 1H), 4.62 (d, J = 15.0 Hz, 2H), 4.37 (d, J = 15.0 Hz, 2H), 2.51 (s, 3H), 2.21 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.3, 143.4, 141.0, 137.6, 136.0, 135.6, 135.5, 132.9, 130.8, 129.2, 128.8, 128.8, 126.9, 126.0, 123.4, 118.5, 59.0, 22.5, 20.9; **HRMS *m/z* (ESI)** calcd. for $C_{28}H_{27}NSSb$ $[M+H]^+$: 530.0902; found: 530.0903;

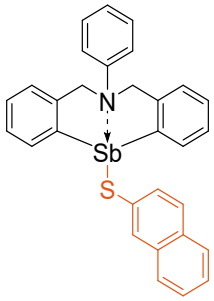
FT-IR (KBr, cm^{-1}): *v* 3060, 2910, 2850, 2360, 1590, 1490, 1430, 1350, 1190, 1100, 1050, 926, 812, 760, 690.

12-((perfluorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3n)



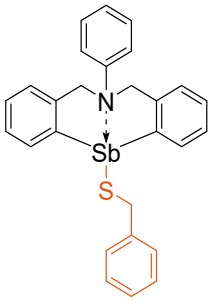
White solid; **Mp**: 233–235 °C; **Yield**: 69% (122.3 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.47 (dd, J = 7.5, 1.3 Hz, 2H), 7.43–7.39 (m, 2H), 7.36–7.32 (m, 2H), 7.28–7.20 (m, 4H), 7.15 (d, J = 7.7 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 4.67 (d, J = 15.0 Hz, 2H), 4.44 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$; list of signals, C–F coupling not resolved)**: δ 147.8, 147.0, 147.0, 146.9, 146.9, 143.2, 140.5, 140.4, 140.4, 140.4, 140.3, 139.1, 139.0, 139.0, 138.9, 138.8, 138.8, 137.9, 137.9, 137.9, 137.8, 137.8, 137.4, 136.0, 129.4, 129.2, 129.1, 126.0, 124.5, 119.1, 112.7, 59.9; **^{19}F NMR (376 MHz, CDCl$_3$)**: δ -131.01–-131.10 (m, 2F), -157.98 (t, J = 20.9 Hz, 1F), -162.64–-162.79 (m, 2F); **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{18}F_5NSSb$ $[M+H]^+$: 592.0118; found: 592.0110; **FT-IR (KBr, cm^{-1})**: *v* 3060, 2910, 2860, 1510, 1480, 1190, 1080, 976, 860, 783, 752, 696.

12-(naphthalen-2-ylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5] azastibocine (3o)



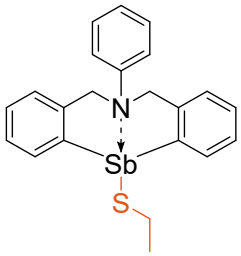
White solid; **Mp**: 221–223 °C; **Yield**: 72% (119.0 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.67 (d, J = 7.5 Hz, 2H), 8.23 (s, 1H), 7.87–7.79 (m, 4H), 7.56–7.46 (m, 6H), 7.34–7.13 (m, 7H), 4.69 (d, J = 15.2 Hz, 2H), 4.45 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 147.9, 146.5, 143.3, 137.3, 135.8, 135.1, 133.7, 132.6, 132.2, 131.3, 129.1, 128.8, 128.7, 127.8, 127.4, 126.7, 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; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2910, 2860, 2360, 2340, 1920, 1590, 1490, 1430, 1210, 1180, 1120, 1110, 1070, 1020, 966, 935, 820, 744, 688.

12-(benzylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3p)



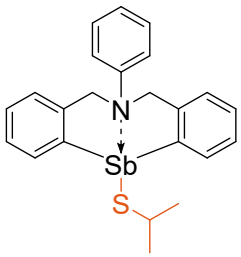
White solid; **Mp**: 232–234 °C; **Yield**: 63% (97.3 mg, *additive-free synthesis*), 54% (83.4 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16–8.14 (m, 2H), 7.36 (d, J = 7.5 Hz, 2H), 7.28–7.22 (m, 8H), 7.17–7.10 (m, 5H), 7.02 (t, J = 7.3 Hz, 1H), 4.61 (d, J = 15.0 Hz, 2H), 4.34 (d, J = 15.0 Hz, 2H), 3.96 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.4, 143.1, 142.5, 136.2, 135.9, 129.1, 128.7, 128.6, 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; **FT-IR (KBr, cm^{-1})**: ν 3060, 2930, 2860, 2360, 2330, 1590, 1510, 1480, 1360, 1190, 1080, 974, 862, 779, 754, 694.

12-(ethylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3q)



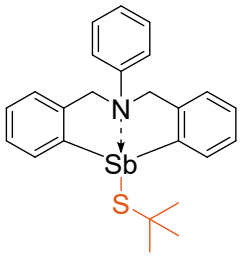
Colorless oil; **Yield**: 42% (57.1 mg, *additive-free synthesis*), 41% (55.7 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.22 (d, J = 7.2 Hz, 2H), 7.31–7.22 (m, 6H), 7.12 (t, J = 8.5 Hz, 4H), 7.00 (t, J = 7.3 Hz, 1H), 4.63 (d, J = 15.1 Hz, 2H), 4.34 (d, J = 15.0 Hz, 2H), 2.78 (q, J = 7.4 Hz, 2H), 1.36 (t, J = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.3, 143.1, 136.2, 135.8, 129.1, 128.6, 128.5, 126.0, 122.9, 118.2, 58.5, 23.6, 20.3; **HRMS *m/z* (ESI)** calcd. for $C_{22}H_{23}NSSb$ $[M+H]^+$: 454.0518; found: 454.0514; **FT-IR (KBr, cm^{-1})**: ν 3050, 2950, 2910, 2860, 2360, 1590, 1500, 1430, 1210, 1190, 1130, 756, 688.

12-(isopropylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3r)



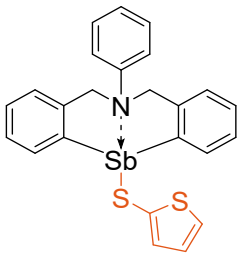
Colorless oil; **Yield**: 46% (64.5 mg, *additive-free synthesis*), 40% (56.0 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.25 (dd, J = 7.2, 1.6 Hz, 2H), 7.34–7.24 (m, 6H), 7.18–7.13 (m, 4H), 7.03 (t, J = 7.4 Hz, 1H), 4.67 (d, J = 15.0 Hz, 2H), 4.37 (d, J = 15.0 Hz, 2H), 3.23–3.17 (m, 1H), 1.43 (d, J = 6.7 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, 58.5, 34.6, 28.7; **HRMS *m/z* (ESI)** calcd. for $C_{23}H_{25}NSSb$ $[M+H]^+$: 468.0746; found: 468.0753; **FT-IR (KBr, cm^{-1})**: ν 3050, 2950, 2910, 2850, 1590, 1500, 1440, 1250, 1210, 1190, 777, 750, 688.

12-(*tert*-butylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3s)



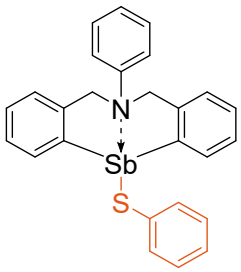
White solid; **Mp**: 211–213 °C; **Yield**: 56% (80.8 mg, *additive-free synthesis*), 49% (70.7 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.36 (d, J = 7.4 Hz, 2H), 7.37–7.29 (m, 6H), 7.18 (t, J = 6.2 Hz, 4H), 7.08–7.04 (m, 1H), 4.70 (d, J = 14.9 Hz, 2H), 4.40 (d, J = 15.0 Hz, 2H), 1.58 (d, J = 1.8 Hz, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.6, 143.3, 136.1, 135.5, 129.1, 128.5, 128.4, 126.1, 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; **FT-IR (KBr, cm^{-1})**: ν 3050, 2960, 2850, 1590, 1490, 1460, 1440, 1360, 1210, 1120, 690.

6-phenyl-12-(thiophen-2-ylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3t)



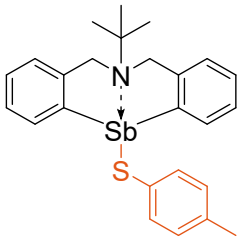
Yellow solid; **Mp**: 214–216 °C; **Yield**: 71% (108.0 mg, *additive-free synthesis*), 62% (94.3 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.33 (dd, J = 7.4, 1.4 Hz, 2H), 7.40–7.36 (m, 2H), 7.33–7.29 (m, 2H), 7.26–7.18 (m, 4H), 7.14–7.12 (m, 2H), 7.06–7.01 (m, 2H), 7.02–7.01 (m, 1H), 6.84 (dd, J = 5.4, 3.5 Hz, 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 148.1, 143.4, 137.9, 136.3, 135.8, 132.1, 129.3, 129.0, 128.9, 127.6, 126.1, 126.0, 123.9, 118.8, 59.4; **HRMS *m/z* (ESI)** calcd. for $C_{24}H_{21}NS_2Sb$ $[M+H]^+$: 508.0154; found: 508.0158; **FT-IR (KBr, cm^{-1})**: ν 3050, 2920, 2850, 2360, 1590, 1500, 1430, 1220, 1190, 835, 777, 756, 698.

6-phenyl-12-(phenylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azastibocine (3u)



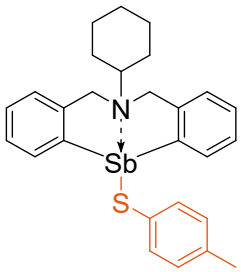
White solid; **Mp**: 189–191 °C; **Yield**: 82% (123.3 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.27 (dd, J = 7.4, 1.4 Hz, 2H), 7.42–7.40 (m, 2H), 7.27–7.23 (m, 2H), 7.20–7.16 (m, 2H), 7.12–6.93 (m, 9H), 6.89 (t, J = 7.3 Hz, 1H), 4.50 (d, J = 15.0 Hz, 2H), 4.25 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.1, 143.4, 137.5, 137.4, 135.9, 134.2, 129.2, 128.8, 128.8, 128.5, 126.0, 125.3, 123.5, 118.6, 59.1; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{23}NSSb$ $[M+H]^+$: 502.0509; found: 502.0505; **FT-IR (KBr, cm^{-1})**: ν 3050, 2900, 2850, 2360, 1940, 1590, 1490, 1430, 1350, 1300, 1250, 1200, 1110, 1080, 1020, 930, 777, 750, 690.

6-(*tert*-butyl)-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3v)



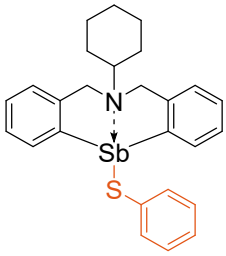
White solid; **Mp**: 206–208 °C; **Yield**: 72% (106.9 mg, *additive-free synthesis*), 69% (102.5 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.57 (d, J = 7.3 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.44–7.40 (m, 2H), 7.36–7.32 (m, 2H), 7.17 (dd, J = 10.2, 7.4 Hz, 4H), 4.32 (d, J = 15.4 Hz, 2H), 3.94 (d, J = 15.3 Hz, 2H), 2.41 (s, 3H), 1.33 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.4, 137.4, 135.4, 134.9, 134.1, 133.9, 129.1, 128.4, 127.9, 125.3, 58.8, 55.6, 26.7, 20.8; **HRMS *m/z* (ESI)** calcd. for $C_{25}H_{29}NSSb$ $[M+H]^+$: 496.1059; found: 496.1060; **FT-IR (KBr, cm^{-1})**: ν 3050, 2970, 2910, 2850, 2360, 1600, 1490, 1380, 1190, 1090, 930, 796, 754, 625.

6-cyclohexyl-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3w)



White solid; **Mp**: 207–208 °C; **Yield**: 78% (121.9 mg, *additive-free synthesis*), 72% (112.6 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.32 (dd, J = 48.6, 7.4 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 6.7 Hz, 2H), 7.24 (dd, J = 8.6, 4.7 Hz, 2H), 7.07 (d, J = 7.5 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 4.04 (d, J = 15.0 Hz, 2H), 3.91 (d, J = 15.1 Hz, 2H), 2.92 (t, J = 9.7 Hz, 1H), 2.28 (s, 3H), 1.99 (d, J = 10.9 Hz, 2H), 1.76 (d, J = 12.7 Hz, 2H), 1.62 (s, 1H), 1.35–1.03 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.4, 138.0, 135.7, 135.1, 134.4, 134.2, 129.3, 128.5, 128.3, 125.6, 64.0, 56.2, 29.2, 25.8, 25.7, 20.9; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{31}NSSb$ $[M+H]^+$: 522.1215; found: 522.1220; **FT-IR (KBr, cm^{-1})**: ν 3060, 2930, 2920, 2850, 1640, 1590, 1490, 1440, 1080, 812, 754.

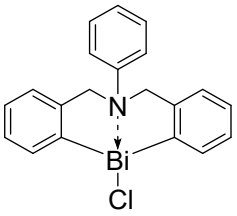
6-cyclohexyl-12-(phenylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azastibocine (3x)



White solid; **Mp**: 195–197 °C; **Yield**: 80% (121.7 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.37 (dd, J = 7.5, 1.4 Hz, 2H), 7.56–7.53 (m, 2H), 7.30–7.26 (m, 2H), 7.22–7.14 (m, 4H), 7.09–7.03 (m, 3H), 3.99 (d, J = 15.2 Hz, 2H), 3.86 (d, J = 15.1 Hz, 2H), 2.90–2.83 (m, 1H), 1.94 (d, J = 9.4 Hz, 2H), 1.71 (d, J = 12.9 Hz, 2H), 1.57–1.52 (m, 1H), 1.31–0.96 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$, TMS)**: δ 144.4, 139.2, 137.7, 135.5, 134.0, 128.5, 128.3, 128.2, 125.5, 124.6, 63.9, 56.1, 29.1, 25.7, 25.6; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{29}NSSb$ $[M+H]^+$: 508.0931;

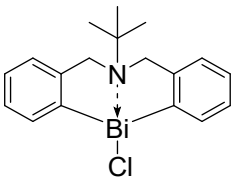
found: 508.0936; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2940, 2850, 2360, 1930, 1580, 1440, 1270, 1200, 1080, 1020, 895, 742, 692.

12-chloro-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azabismocine (4a)



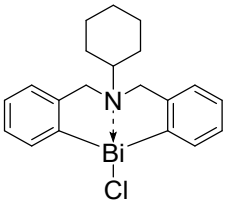
White solid; **Mp**: 251–253 °C; **Yield**: 81% (8.34 g); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.85–8.68 (m, 2H), 7.60–7.50 (m, 4H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 4.85 (d, J = 15.0 Hz, 2H), 4.62 (d, J = 15.0 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 169.6, 148.4, 147.9, 140.4, 132.0, 129.8, 128.4, 128.0, 125.1, 119.1, 63.2.

6-(*tert*-butyl)-12-chloro-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azabismocine (4b)



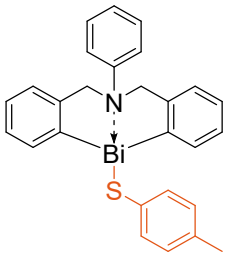
White solid; **Mp**: 258–260 °C; **Yield**: 86% (8.51 g); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.75 (s, 2H), 7.45–7.39 (m, 4H), 7.32 (t, J = 7.4 Hz, 2H), 4.49 (d, J = 15.4 Hz, 2H), 4.11 (d, J = 15.4 Hz, 2H), 1.30 (s, 9H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 167.4, 151.0, 139.9, 130.8, 128.1, 127.2, 60.1, 27.6.

12-chloro-6-cyclohexyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azabismocine (4c)



White solid; **Mp**: 261–263 °C; **Yield**: 80% (8.34 g); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.74 (t, J = 7.1 Hz, 2H), 7.45–7.38 (m, 4H), 7.31 (t, J = 7.2 Hz, 2H), 4.35 (d, J = 15.2 Hz, 2H), 4.15 (d, J = 15.2 Hz, 2H), 2.93 (t, J = 11.1 Hz, 1H), 1.98 (d, J = 11.6 Hz, 2H), 1.83 (d, J = 12.8 Hz, 2H), 1.64 (d, J = 10.0 Hz, 1H), 1.41–1.22 (m, 4H), 1.15–1.04 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 167.6, 149.7, 139.8, 130.9, 128.0, 127.5, 64.8, 60.6, 30.7, 25.6, 25.4.

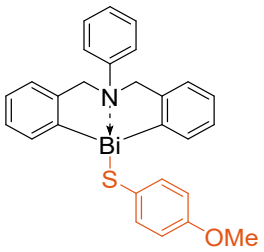
6-phenyl-12-(*p*-tolylthio)-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azabismocine (5a)



White solid; **Mp**: 163–165 °C; **Yield**: 76% (137.5 mg, *additive-free synthesis*), 68% (123.0 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 9.01 (dd, J = 7.4, 1.3 Hz, 2H), 7.60–7.58 (m, 2H), 7.55–7.52 (m, 4H), 7.49–7.45 (m, 2H), 7.34–7.30 (m, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.11–7.08 (m, 3H), 4.79 (d, J = 15.1 Hz, 2H), 4.50 (d, J = 15.2 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 162.9, 148.4, 146.7, 139.3, 134.7, 134.6, 134.3, 131.0, 129.2, 128.1, 127.9, 122.9, 117.9, 60.6, 20.8; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{24}BiNSNa$ $[M+Na]^+$: 626.1331; found:

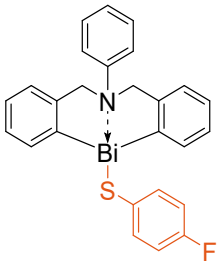
626.1334; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2850, 2360, 1590, 1490, 1460, 1210, 1190, 1090, 1020, 966, 887, 800, 775, 744, 681.

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



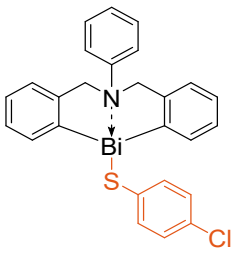
Yellow solid; **Mp**: 186–188 °C; **Yield**: 65% (120.7 mg, *additive-free synthesis*), 60% (111.4 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.84 (d, J = 7.4 Hz, 2H), 7.49–7.45 (m, 2H), 7.40 (d, J = 8.7 Hz, 4H), 7.36–7.32 (m, 2H), 7.21–7.17 (m, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.69 (d, J = 8.8 Hz, 2H), 4.68 (d, J = 15.1 Hz, 2H), 4.38 (d, J = 15.1 Hz, 2H), 3.68 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$, C–F coupling not resolved)**: δ 162.9, 157.8, 153.5, 148.6, 146.8, 139.3, 135.9, 131.1, 129.3, 128.2, 128.0, 123.0, 117.9, 114.2, 60.7, 55.2; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{24}BiNOSNa$ $[M+Na]^+$: 642.1280; found: 642.1274; **FT-IR (KBr, cm^{-1})**: *v* 3050, 3020, 2950, 2900, 2850, 2830, 1590, 1490, 1450, 1430, 1270, 1240, 1220, 1190, 1170, 1100, 930, 820, 754, 690, 634.

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



White solid; **Mp**: 146–148 °C; **Yield**: 77% (140.2 mg, *additive-free synthesis*), 68% (123.9 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.97 (d, J = 7.4 Hz, 2H), 7.61–7.53 (m, 6H), 7.49–7.45 (m, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H), 6.94 (t, J = 8.4 Hz, 2H), 4.81 (d, J = 15.1 Hz, 2H), 4.51 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$, list of signals, C–F coupling not resolved)**: δ 163.0, 162.3, 159.9, 148.4, 146.8, 139.2, 136.0, 135.9, 133.2, 133.2, 131.1, 129.3, 128.2, 128.0, 123.1, 118.0, 115.4, 115.2, 60.7; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -117.49; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{21}BiFNSNa$ $[M+Na]^+$: 630.1080; found: 630.1087; **FT-IR (KBr, cm^{-1})**: *v* 3040, 2910, 2850, 1600, 1490, 1430, 1350, 1220, 1190, 1080, 827, 773, 750, 696, 625.

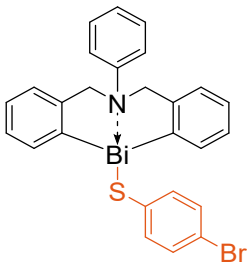
12-((4-chlorophenyl)thio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][*1*,*5*] azabismocine (5d)



White solid; **Mp**: 169–171 °C; **Yield**: 80% (149.5 mg, *additive-free synthesis*), 74% (138.3 mg, *DTT-mediated synthesis*); **^{1}H**

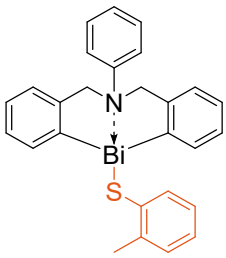
NMR (400 MHz, $CDCl_3$): δ 8.78 (d, J = 7.4 Hz, 2H), 7.47–7.32 (m, 8H), 7.20 (t, J = 7.9 Hz, 2H), 7.06 (t, J = 7.1 Hz, 4H), 6.98 (t, J = 7.4 Hz, 1H), 4.69 (d, J = 15.2 Hz, 2H), 4.39 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.2, 148.4, 146.9, 139.3, 137.2, 135.8, 131.2, 130.9, 129.4, 128.4, 128.3, 128.1, 123.3, 118.1, 60.9; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{21}BiClNSNa$ $[M+Na]^+$: 646.0785; found: 646.0781; **FT-IR (KBr, cm^{-1})**: ν 3040, 2900, 2850, 1960, 1890, 1600, 1490, 1470, 1310, 1210, 1190, 1010, 818, 775, 750, 694, 540.

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



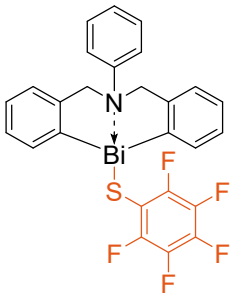
White solid; **Mp**: 176–178 °C; **Yield**: 65% (130.1 mg, *additive-free synthesis*); 57% (114.1 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.78 (d, J = 7.4 Hz, 2H), 7.49–7.42 (m, 4H), 7.37–7.32 (m, 4H), 7.24–7.20 (m, 4H), 7.09 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 4.72 (d, J = 15.2 Hz, 2H), 4.42 (d, J = 15.2 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.2, 148.4, 146.9, 139.4, 138.0, 136.2, 131.3, 131.3, 129.4, 128.3, 128.2, 123.3, 118.9, 118.1, 61.0; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{21}BiBrNSNa$ $[M+Na]^+$: 690.0280; found: 690.0281; **FT-IR (KBr, cm^{-1})**: ν 3050, 2900, 2860, 1590, 1490, 1460, 1210, 1090, 1010, 758, 692, 540.

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



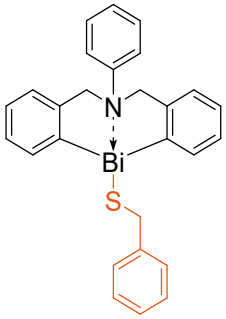
White solid; **Mp**: 186–188 °C; **Yield**: 73% (132.1 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.93 (d, J = 7.4 Hz, 2H), 7.50–7.33 (m, 7H), 7.22–7.18 (m, 2H), 7.15–7.13 (m, 1H) 7.06 (d, J = 8.2 Hz, 2H), 6.98–6.95 (m, 3H), 4.69 (d, J = 15.1 Hz, 2H), 4.40 (d, J = 15.0 Hz, 2H), 2.58 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 162.8, 148.6, 146.9, 141.3, 139.6, 137.8, 136.1, 131.2, 129.7, 129.3, 128.2, 128.0, 125.9, 125.5, 123.0, 118.0, 60.8, 22.8; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{24}BiNSNa$ $[M+Na]^+$: 626.1331; found: 626.1334; **FT-IR (KBr, cm^{-1})**: ν 3050, 2850, 2360, 1590, 1490, 1210, 1190, 744, 681.

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



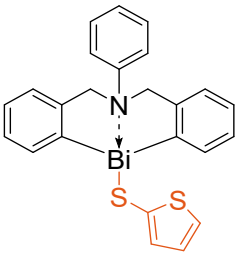
White solid; **Mp**: 228–230 °C; **Yield**: 56% (114.1 mg, *additive-free synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.93 (dd, J = 7.4, 1.2 Hz, 2H), 7.60–7.56 (m, 2H), 7.54–7.52 (m, 2H), 7.46–7.42 (m, 2H), 7.32–7.28 (m, 2H), 7.19–7.16 (m, 2H), 7.12–7.08 (m, 1H), 4.82 (d, J = 15.1 Hz, 2H), 4.55 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.4, 149.6, 148.3, 147.1, 146.9, 139.5, 137.0, 131.6, 129.6, 128.4, 124.1, 118.5, 113.8, 61.7; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -131.33–-131.43 (m, 2F), -159.33 (t, J = 18.8 Hz, 1F), -162.93–-163.08 (m, 2F); **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{17}BiF_5NSNa$ $[M+Na]^+$: 702.0703; found: 702.0707; **FT-IR (KBr, cm^{-1})**: *v* 3050, 2910, 2860, 2580, 2360, 1590, 1500, 1480, 1360, 1300, 1240, 1190, 1080, 970, 858, 777, 750, 692, 619

12-(benzylthio)-6-phenyl-5,6,7,12-tetrahydrodibenzo[*c*,*f*][1,5]azabismocine (5h)



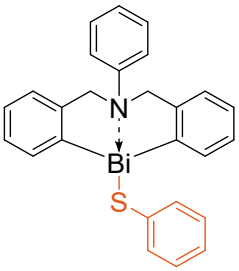
White solid; **Mp**: 120–122 °C; **Yield**: 57% (103.1 mg, *additive-free synthesis*), 50% (90.5 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.89 (d, J = 7.3 Hz, 2H), 7.61–7.43 (m, 8H), 7.48–7.40 (m, 4H), 7.35 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 4.82 (d, J = 15.1 Hz, 2H), 4.52 (d, J = 15.2 Hz, 2H), 4.47 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 158.1, 148.5, 146.2, 143.8, 139.2, 130.6, 129.0, 128.1, 128.1, 127.8, 127.7, 126.1, 122.4, 117.7, 60.0, 32.6; **HRMS *m/z* (ESI)** calcd. for $C_{27}H_{24}BiNSNa$ $[M+Na]^+$: 626.1331; found: 626.1339; **FT-IR (KBr, cm^{-1})**: *v* 3040, 3020, 2900, 2850, 2360, 1590, 1490, 1450, 1310, 1190, 1020, 966, 758, 698.

6-phenyl-12-(thiophen-2-ylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5] azabismocine (5i)



Yellow solid; **Mp**: 162–164 °C; **Yield**: 51% (91.0 mg, *additive-free synthesis*), 40% (71.4 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.80 (d, J = 7.4 Hz, 2H), 7.53–7.36 (m, 6H), 7.23 (t, J = 8.2 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 7.03–6.96 (m, 3H), 6.84–6.82 (m, 1H), 4.73 (d, J = 15.1 Hz, 2H), 4.44 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.4, 148.5, 147.1, 139.3, 137.5, 132.1, 131.4, 129.4, 128.4, 128.1, 127.6, 125.9, 123.4, 118.2, 61.2; **HRMS *m/z* (ESI)** calcd. for $C_{24}H_{20}BiNS_2Na$ $[M+Na]^+$: 618.0739; found: 618.0742; **FT-IR (KBr, cm^{-1})**: ν 3050, 2860, 2360, 1590, 1490, 1210, 1190, 976, 835, 775, 752, 692.

6-phenyl-12-(phenylthio)-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]azabismocine (5j)



White solid; **Mp**: 176–178 °C; **Yield**: 71% (125.5 mg, *DTT-mediated synthesis*); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.83 (d, J = 7.4 Hz, 2H), 7.48–7.41 (m, 4H), 7.37–7.29 (m, 4H), 7.16 (t, J = 7.7 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 7.04–6.91 (m, 4H), 4.64 (d, J = 15.1 Hz, 2H), 4.34 (d, J = 15.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 162.9, 148.4, 146.8, 139.3, 138.4, 134.6, 131.1, 129.3, 128.4, 128.2, 128.0, 125.0, 123.0, 118.0, 60.7; **HRMS *m/z* (ESI)** calcd. for $C_{26}H_{22}BiNSNa$ $[M+Na]^+$: 612.1174; found: 612.1183; **FT-IR (KBr, cm^{-1})**: ν 3040, 2850, 2360, 1590, 1580, 1490, 1310, 1240, 1190, 1080, 1020, 930, 822, 777, 752, 692.

Stability of the representative compounds

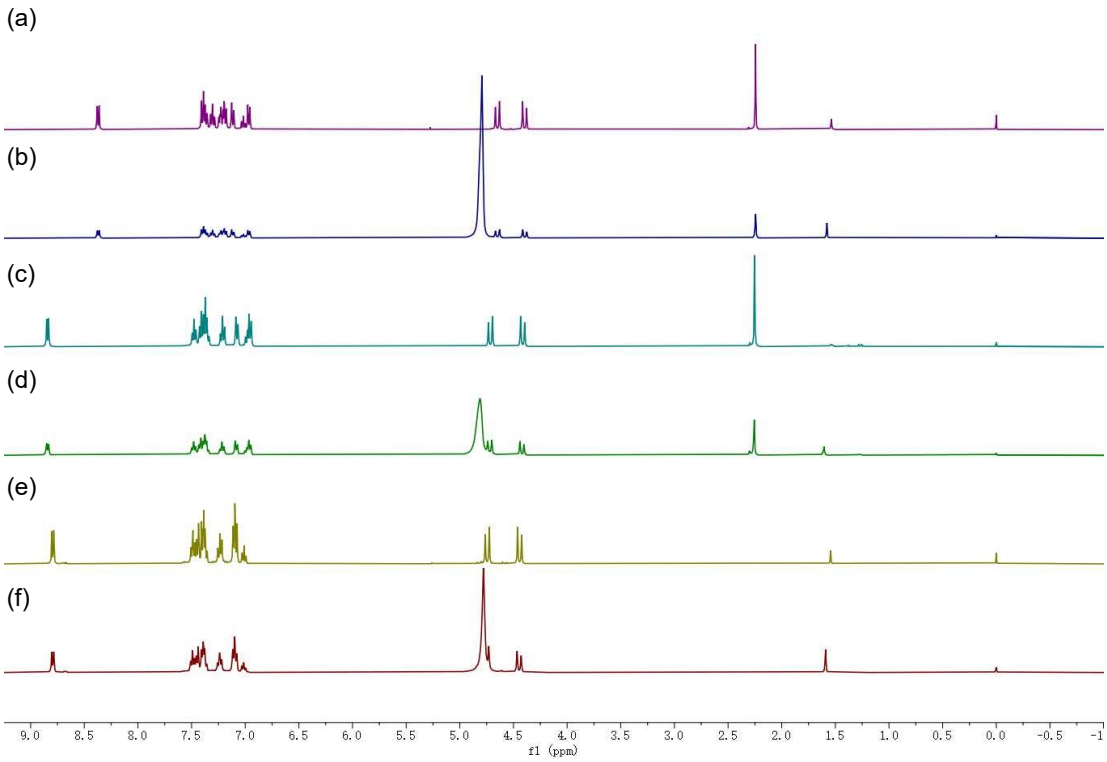


Fig. S2 ^{1}H NMR spectra for the stability experiment of **3a**, **5a**, and **5d** measured in $CDCl_3$. (a) Freshly prepared **3a**. (b) The solution of **3a** after being kept in the open air for 48 h. (c) Freshly prepared **5a**. (d) The solution of **5a** after being kept in the open air for 48 h. (e) Freshly prepared **5d**. (f) The solution of **5d** after being kept in the open air for 48 h.

5. Crystallography

Table S1 Selected bond lengths (Å) and angles (°) [a]

	3a	**3b**	**3s**	**3x**	**5a**	**5d**
M(1)–C(1)	2.171(3)	2.162(3)	2.161(5)	2.150(5)	2.244(8)	2.248(4)
M(1)–C(11)	2.158(3)	2.169(3)	2.146(7)	2.157(4)	2.254(9)	2.265(4)
M(1)–N(1)	2.592(3)	2.623(2)	2.680(6)	2.499(3)	2.728(6)	2.739(3)
M(1)–S(1)	2.4995(9)	2.5084(7)	2.478(3)	2.536(1)	2.610(2)	2.618(1)
S(1)–C(16)	1.780(3)	1.772(3)	1.875(4)	1.792(4)	1.781(10)	1.769(5)
C(1)–M(1)–C(11)	100.41(12)	101.81(9)	96.4(2)	93.9(1)	96.9(3)	93.8(1)
S(1)–M(1)–N(1)	157.36(6)	154.6(3)	159.7(1)	161.70(9)	154.5(1)	154.29(7)
C(7)–N(1)–C(9)	111.3(2)	115.1(2)	114.9(4)	109.9(3)	113.1(7)	112.5(3)

[a] M = Sb (**3a**, **3b**, **3s**, and **3x**) or Bi (**5a** and **5d**).

Table S2 Crystal data and structural refinement details for **3a**

CDCC	2059928
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
V/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
GOF 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 structural refinement details for **3b**

CDCC	2059928
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
V/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
GOF 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 structural refinement details for **3s**

CDCC	2296027
Empirical formula	$C_{24}H_{26}NSSb$
Formula weight	482.27
Temperature/K	295.26(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.6728(3)
b/Å	10.3643(3)
c/Å	11.0212(2)
α/°	104.386(3)
β/°	112.313(3)
γ/°	90.028(3)
V/Å^3	984.55(5)
Z	2
ρ_{calc}/g·cm^{-3}	1.627
μ/mm^{-1}	12.151
F(000)	488.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.858 to 133.184
Index ranges	-10 ≤ h ≤ 11, -12 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	9241
Independent reflections	3465 [R_{int} = 0.0508, R_{sigma} = 0.0511]
Data/restraints/parameters	3465/214/223
GOF on F^2	1.410
Final *R* indexes [I>2σ (I)]	R_1 = 0.1106, wR_2 = 0.3143
Final *R* indexes [all data]	R_1 = 0.1214, wR_2 = 0.3294
Largest diff. peak/hole / e Å^{-3}	1.02/-1.09

Table S5 Crystal data and structural refinement details for **3x**

CDCC	2059930
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
V/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
GOF 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

Table S6 Crystal data and structural refinement details for **5a**

CDCC	2337084
Empirical formula	C28H25BiCl3NS
Formula weight	722.88
Temperature/K	292.96(17)
Crystal system	triclinic
Space group	P-1
a/Å	10.3272(4)
b/Å	11.2900(4)
c/Å	12.5870(3)
α/°	92.032(2)
β/°	100.634(3)
γ/°	108.806(3)
V/Å^3	1358.24(8)
Z	2
ρ_{calc}/g·cm^{-3}	1.768
μ/mm^{-1}	16.300
F(000)	700.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.184 to 133.202
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	12049
Independent reflections	4750 [R_{int} = 0.0326, R_{sigma} = 0.0299]
Data/restraints/parameters	4750/60/345
GOF on F^2	1.060
Final *R* indexes [I>2σ (I)]	R_1 = 0.0492, wR_2 = 0.1225
Final *R* indexes [all data]	R_1 = 0.0518, wR_2 = 0.1241
Largest diff. peak/hole / e Å^{-3}	1.08/-1.05

Table S7 Crystal data and structural refinement details for **5d**

CDCC	2337085
Empirical formula	C26H21BiClNS
Formula weight	623.93
Temperature/K	293.00(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	7.80600(10)
b/Å	13.52470(10)
c/Å	21.4223(2)
α/°	90
β/°	96.2140(10)
γ/°	90
V/Å^3	2248.35(4)
Z	4
ρ_{calc}/g·cm^{-3}	1.843
μ/mm^{-1}	17.441
F(000)	1200.0
Crystal size/mm^3	0.13 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.744 to 148.512
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 16, -20 ≤ l ≤ 26
Reflections collected	12325
Independent reflections	4451 [R_{int} = 0.0224, R_{sigma} = 0.0192]
Data/restraints/parameters	4451/0/271
GOF on F^2	1.094
Final *R* indexes [I>2σ (I)]	R_1 = 0.0269, wR_2 = 0.0683
Final *R* indexes [all data]	R_1 = 0.0280, wR_2 = 0.0691
Largest diff. peak/hole / e Å^{-3}	0.65/-1.63

6. Mechanistic studies

Impact of reaction temperature on the transformation of thiol 2a to disulfide 2a'

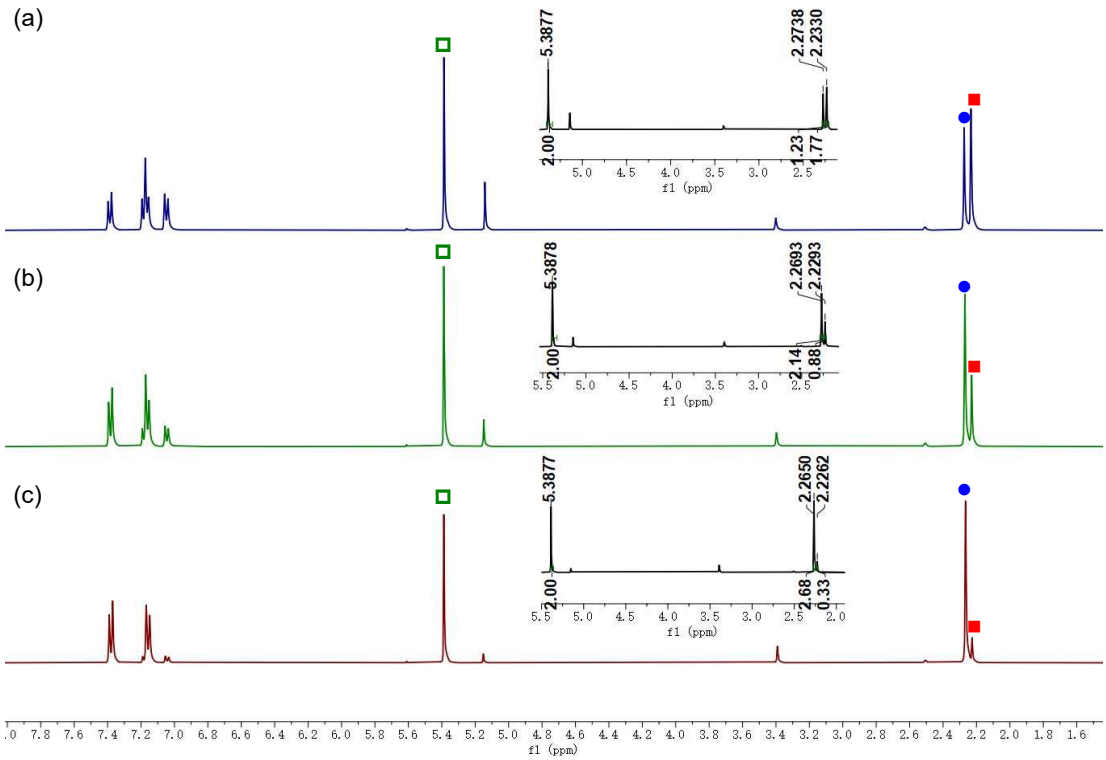


Fig. S3 ^{1}H NMR spectra for the oxidative homocoupling reaction of 4-methylbenzenethiol **2a** performed at different temperatures using dibromomethane (0.3 mmol) as an internal standard (■,**2a**; ●, **2a'**; ◘, dibromomethane). (a) Performed at RT. (b) Performed at 60 °C. (c) Performed at 80 °C.

Stability experiment of DTT under standard conditions

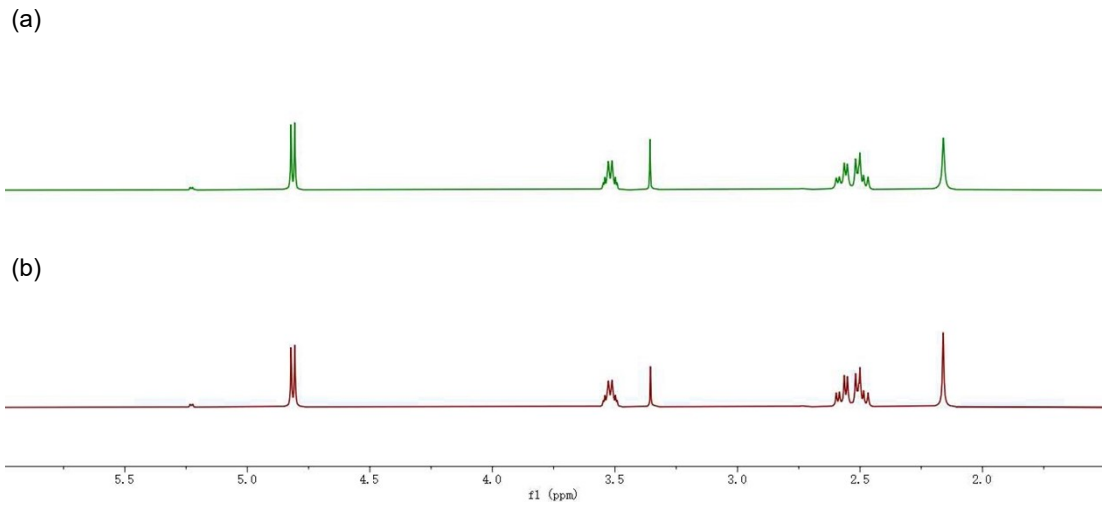


Fig. S4 ^{1}H NMR spectra for the stability experiment of DTT measured in DMSO-d_6. (a) Newly purchased. (b) After being stirred at RT under N_2 for 6 h.

Transformation of disulfide 2a' to thiol 2a in the presence of DTT

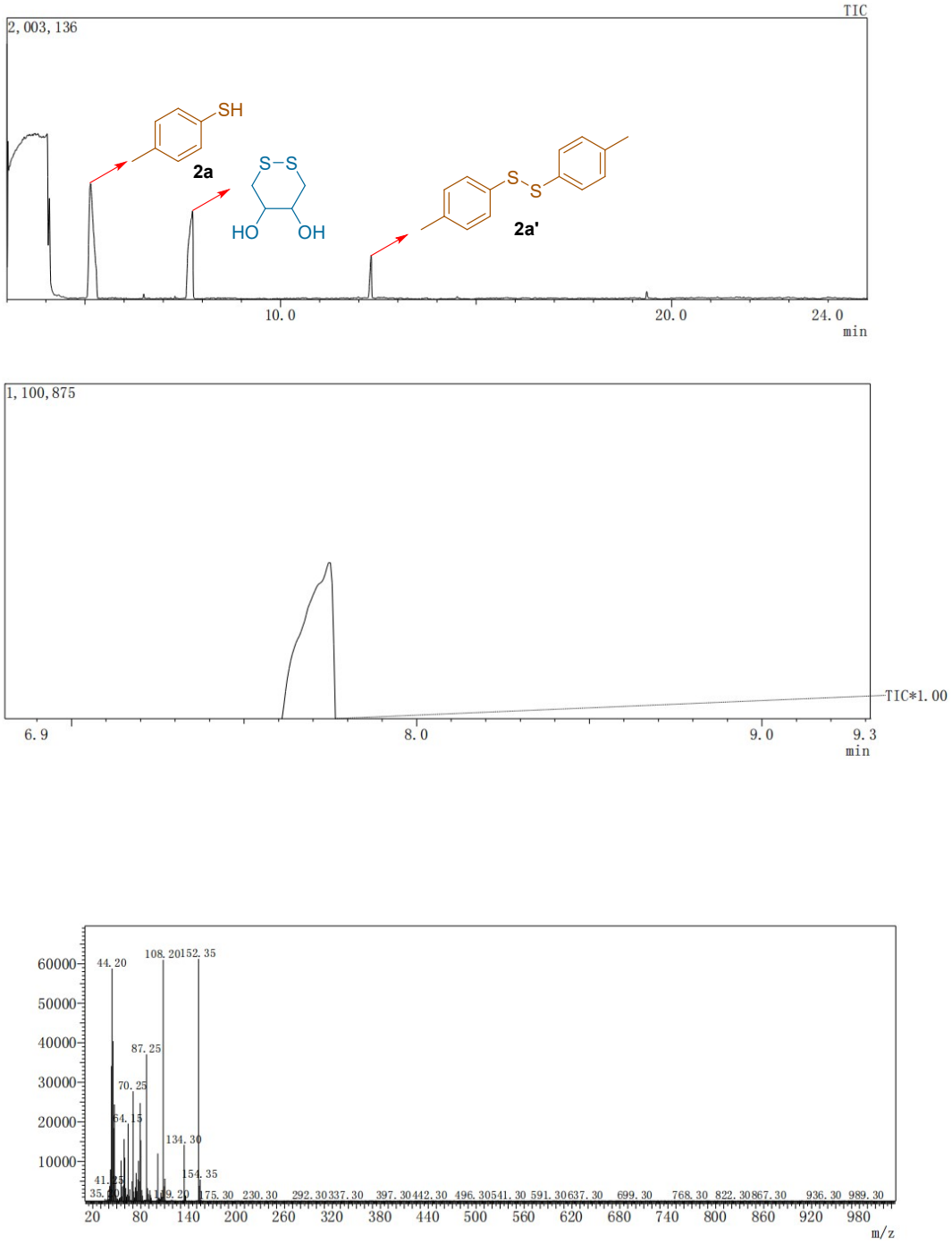


Fig. S5 GC-MS analysis for the reaction mixture of disulfide **2a'** and DTT stirred at RT under N_2 for 6 h.

Stability experiment of organoantimony(III) chloride 1a under standard conditions

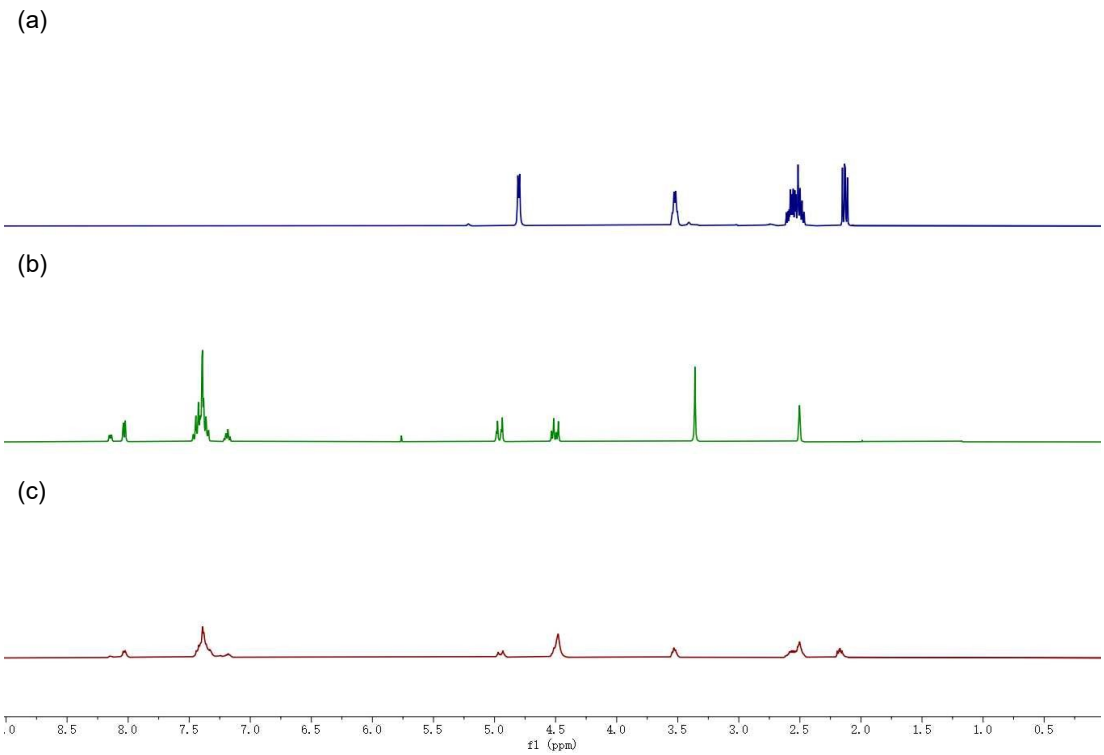


Fig. S6 ^{1}H NMR spectra for the stability experiment of **1a** measured in DMSO-d_6. (a) Newly purchased DTT. (b) Freshly prepared organoantimony(III) chloride **1a**. (c) Reaction mixture of **1a** and DTT stirred at RT under N_2 for 6 h.

7. Antifungal evaluation

Microbial strain and growth conditions

The selected *Candida albicans* strain (ATCC10231) was purchased from Luwei Technology Co., Ltd. (Shanghai, China) and cultured in the Sabouraud glucose agar (Aoboxing Bio-Tech, Beijing, China) at 37 °C. The fungal suspensions equivalent to the density of 0.5 McFarland (approximately 1.5×10^8 CFU/mL) were prepared in Muller-Hinton broth (MHB, Aoboxing Bio-Tech, Beijing, China) medium (dissolved in sterile water) by comparing the density standard and were stocked at 4 °C prior to use.

Determination of minimal inhibitory concentrations

The antifungal activity of organoantimony thioates **3a**–**3x**, organobismuth thioates **5a**–**5j**, and organobismuth chloride **4a** was evaluated by measuring the minimal inhibitory

concentrations (MICs) through a broth microdilution method referring to previous works.[9–11] Initially, each of the tested compounds was dissolved in DMSO (Phygene Biotechnology, Fuzhou, China), followed by diluting with sterile water containing 2% Tween 20 (Solarbio Science & Technology, Beijing, China) and MHB medium to a concentration of 500 μM. Subsequently, 100 μL of the original solution was transferred to the 96-well plate for gradient dilution. Also, 100 μL of diluted inoculum (approximately 5×10^5 CFU/mL) was transferred to the same 96-well plate and exposed to the designated compounds at concentrations of 250.00, 125.00, 62.50, 31.25, 15.63, 7.81, 3.91, 1.95, 0.98, 0.49, 0.24, and 0.12 μM, respectively. Upon completion, the plate was incubated at 37 °C for 24 h. All assays were repeated at least three times. MIC was defined as the lowest concentration of the compounds that inhibits the visible growth of *C. albicans*. Fluconazole (Adamas Life, Shanghai, China) was employed as the control group.

Time-kill analysis

According to the previous literature,[9–11] time-kill analysis was conducted by monitoring viable fungal cell count decrease with time through a plate counting method. The density of the initial inoculum was about 5×10^5 CFU/mL. After being independently incubated with compound **5a** at various concentrations (0.5 × MIC, 1 × MIC, 2 × MIC, and 4 × MIC) for 4, 8, 12, and 24 hrs, serial dilutions were plated onto plate count agar (PCA, Aoboxing Bio-Tech, Beijing, China). Upon completion, the microbes were cultured at 37 ℃ for an additional 24 h. The number of colonies formed by fungal survivors was quantified, and the results were expressed as the logarithm of colony-forming units per milliliter.

Determination of antibiofilm activity

The antibiofilm activity of the representative compounds was explored by means of crystal violet staining, referring to previous works.[9,11] Briefly, 100 μL of diluted inoculum (approximately 5×10^5 CFU/mL) was respectively added to a 96-well plate and exposed to the selected organobismuth thioates (**5a** and **5d**) at concentrations of 0.25 × MIC, 0.5 × MIC, and 1 × MIC, followed by culturing at 37 ℃ for 24 h. After the supernatants had been discarded, the resulting biofilm cells were washed with neutral PBS buffer, stained with 0.1% crystal violet (Solarbio Science & Technology, Beijing, China), washed with sterile water, and dried at RT, successively. Upon completion, 200 μL of 33% AcOH was added, and the absorbance at 595 nm was

determined on a Varioskan LUX microplate absorbance reader (Thermo Fisher, USA). All tests were repeated three times, and the values of the blank group (inoculum only) were regarded as 100%.

8. References

1 J. Lei, Y. Liu, Y. Ou, C. T. Au, Y. Chen and S. F. Yin, *Eur. J. Med. Chem.*, 2019, **177**, 350–361.

2 Y. P. Liu, J. Lei, L. W. Tang, Y. Peng, C. T. Au, Y. Chen and S. F. Yin, *Eur. J. Med. Chem.*, 2017, **139**, 826–835.

3 S. Shimada, O. Yamazaki, T. Tanaka, Y. Suzuki and M. Tanaka, *J. Organomet. Chem.*, 2004, **689**, 3012–3023.

4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

5 G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112–122.

6 D. Kratzert, I. Krossing and J. J. Holstein, *J. Appl. Cryst.*, 2015, **48**, 933–938.

7 B. Barszcz, J. Masternak and M. Kowalik, *Coord. Chem. Rev.*, 2021, **443**, 213935.

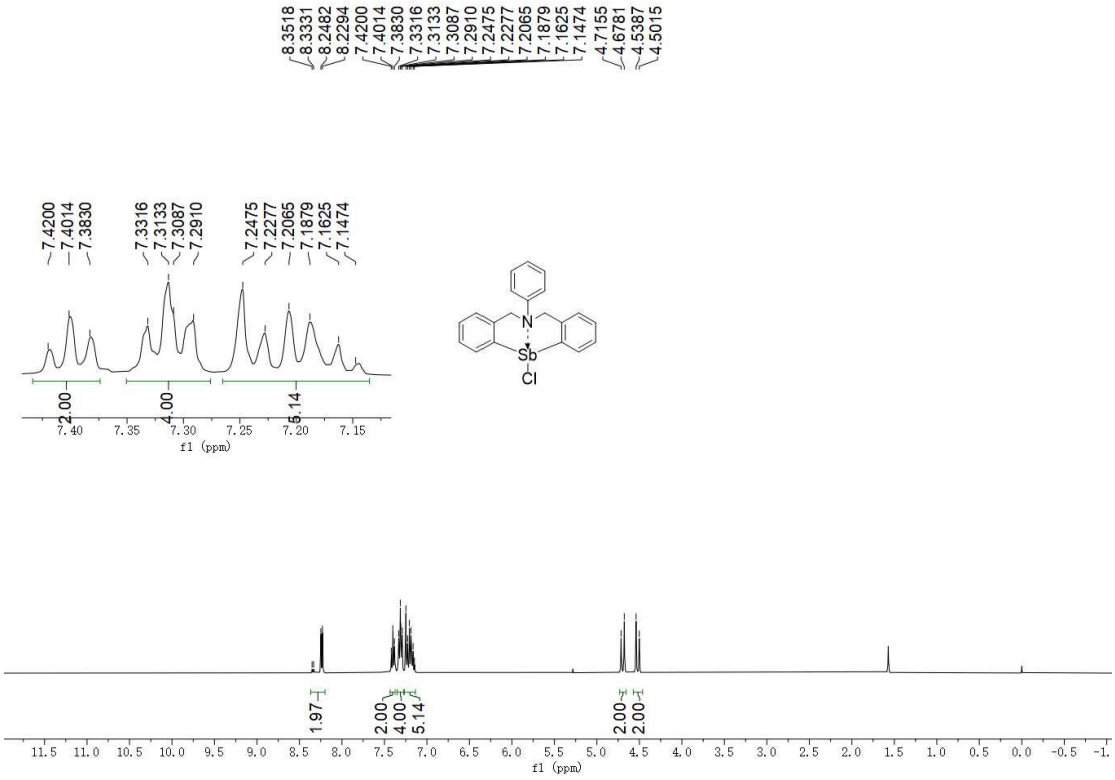
8 L. Shimoni-Livny, J. P. Glusker and C. W. Bock, *Inorg. Chem.*, 1998, **37**, 1853–1867.

9 L. J. Stephens, S. Munuganti, R. N. Duffin, M. V. Werrett and P. C. Andrews, *Inorg. Chem.*, 2020, **59**, 3494–3508.

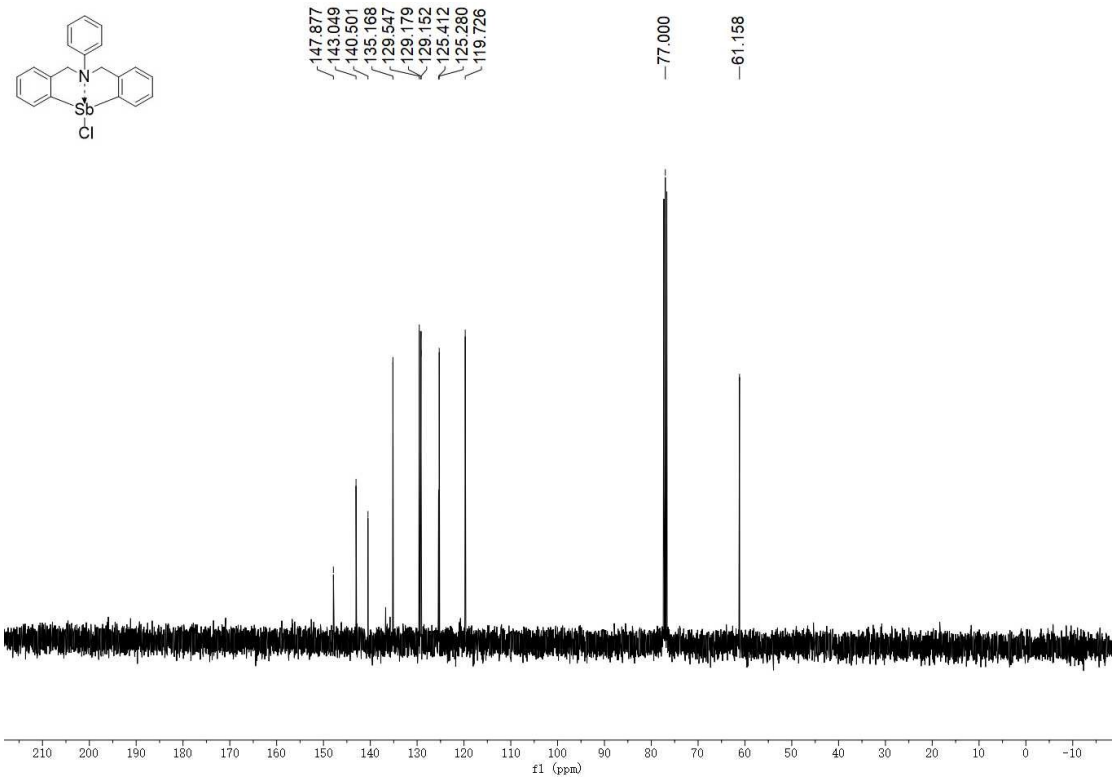
10 W. Li, Y. Huang, Y. Liu, Z. Wang, S. Li, Y. Chen, Y. Ye, S. F. Yin and J. Lei, *Appl. Organomet. Chem.*, 2023, **37**, e7141.

11 Y. Ma, M. Wei, X. Wang, L. Jiang, Y. Xiong, J. Cheng, Y. Tan, X. Liao and J. Wang, *Appl. Organomet. Chem.*, 2022, **36**, e6858.

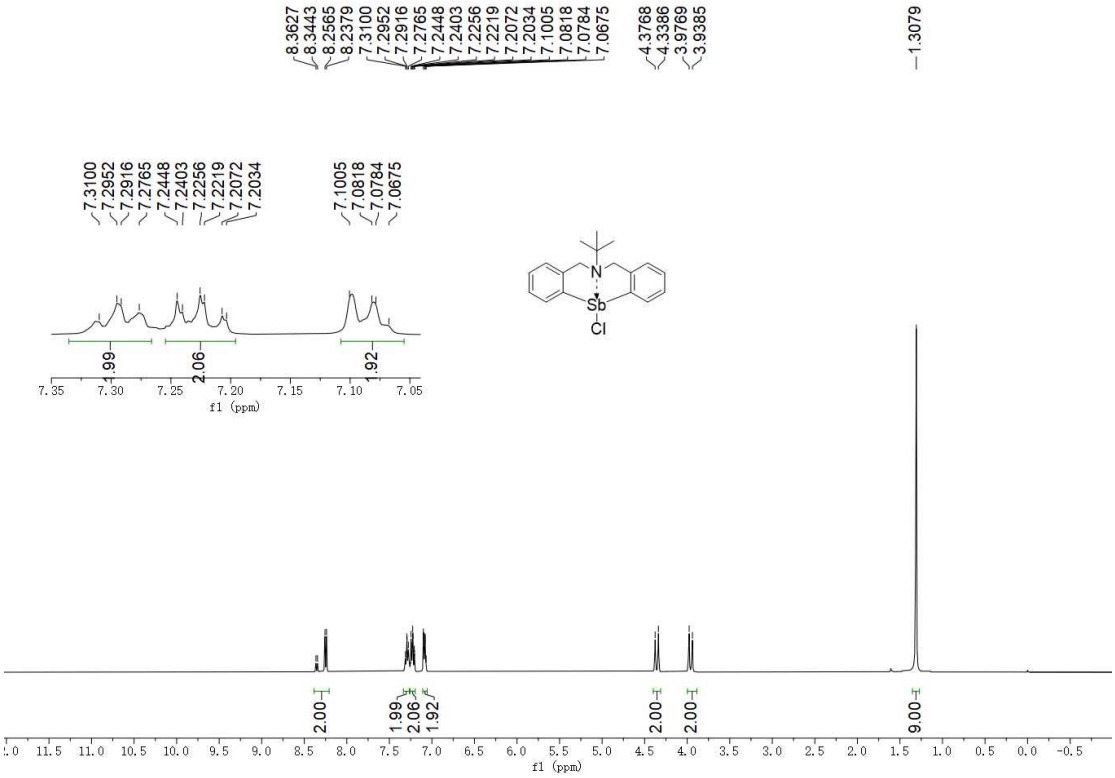
9. NMR Spectra



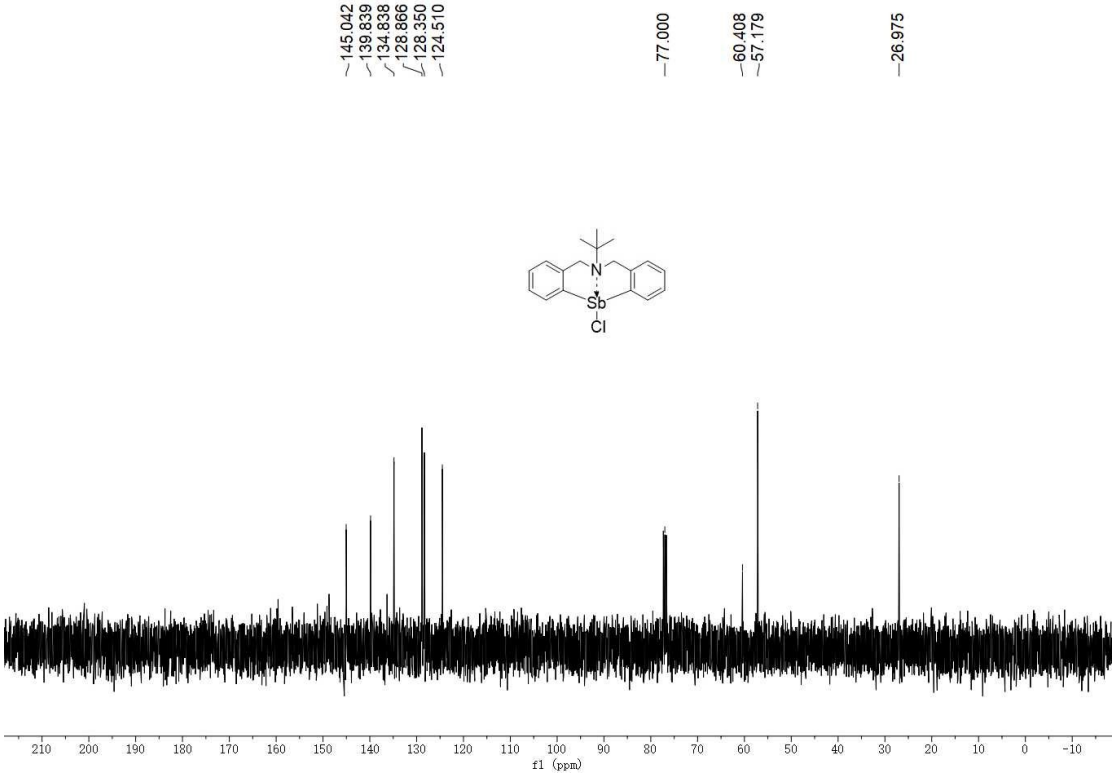
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1a**



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



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



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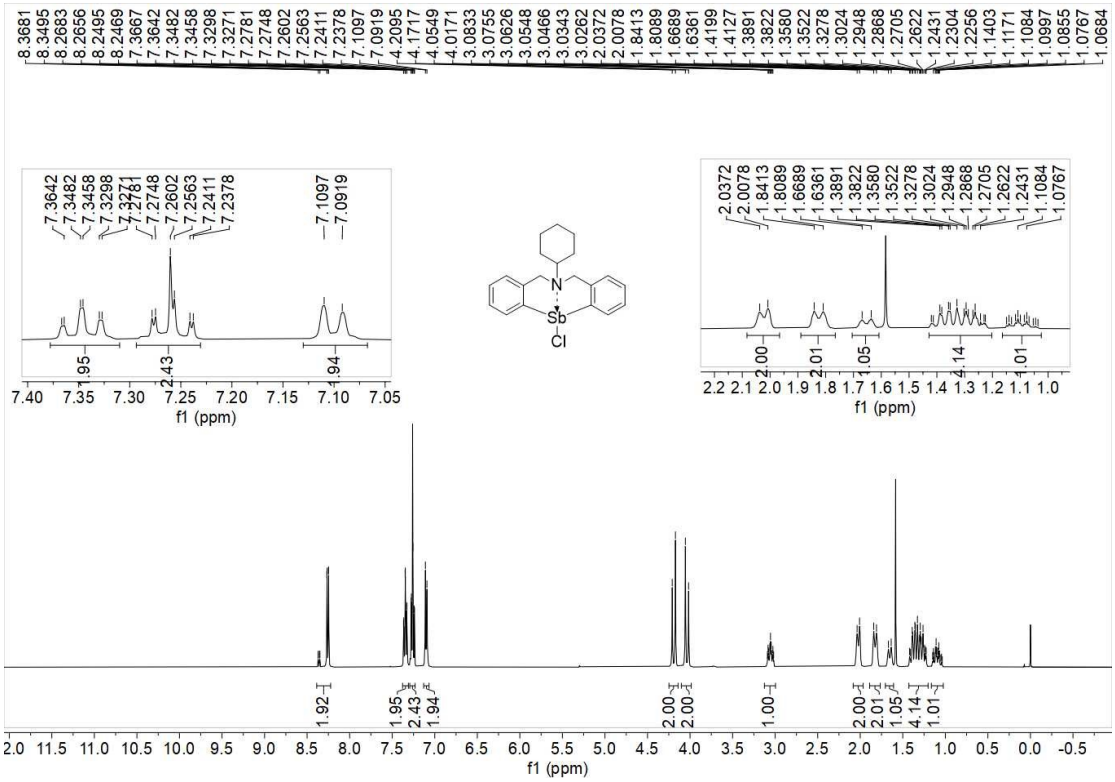
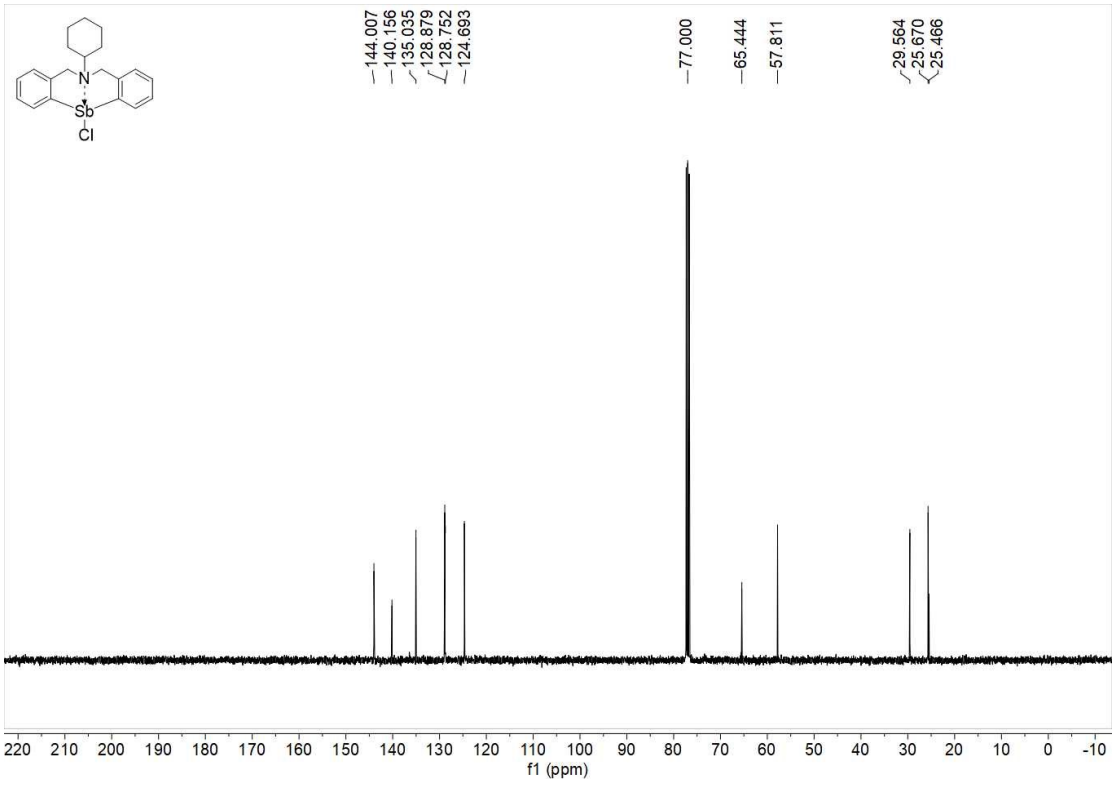


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1c**



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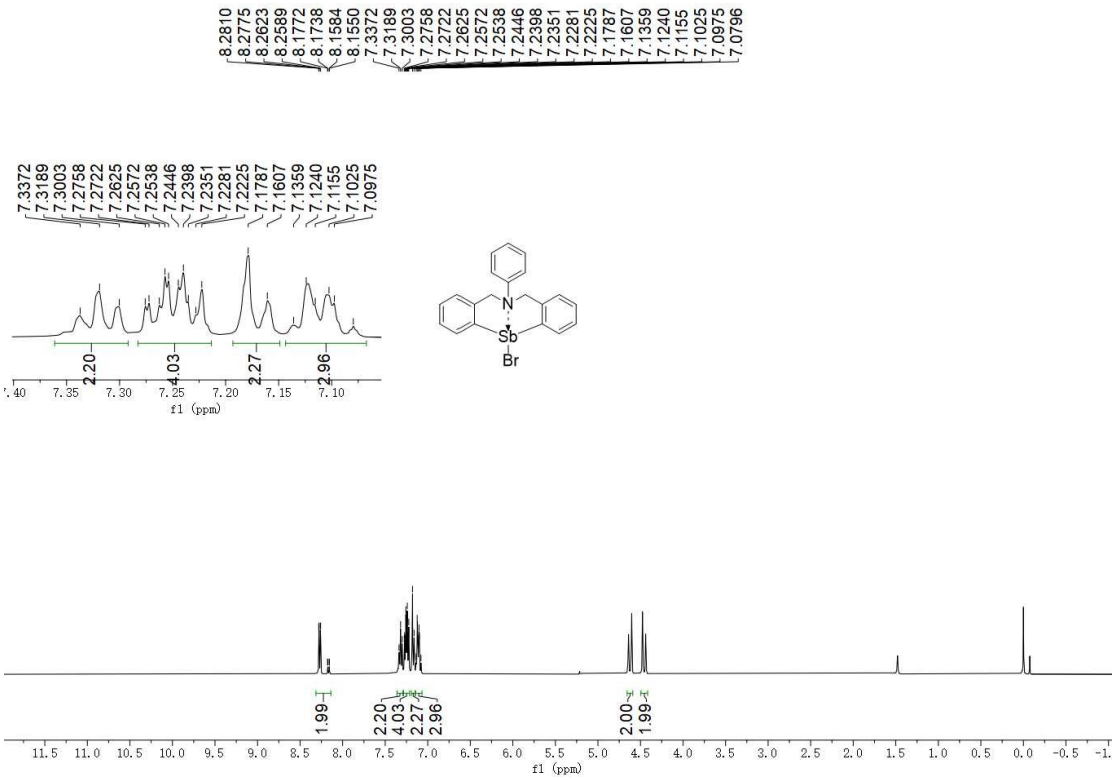
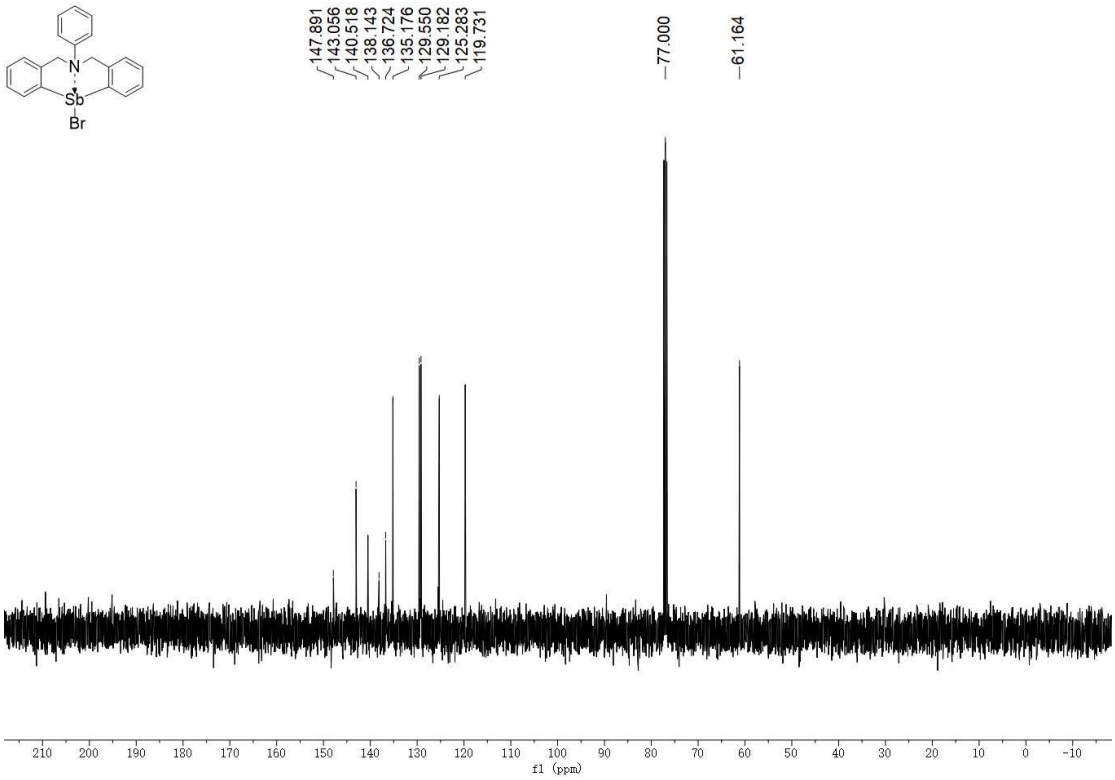
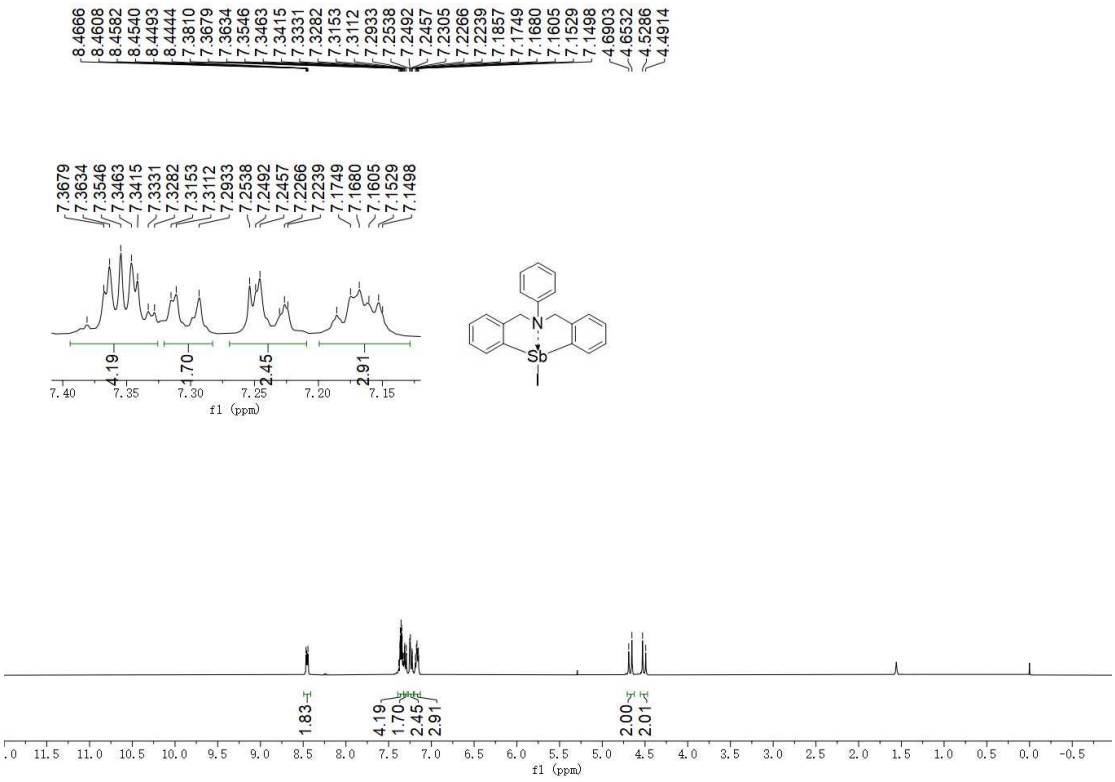


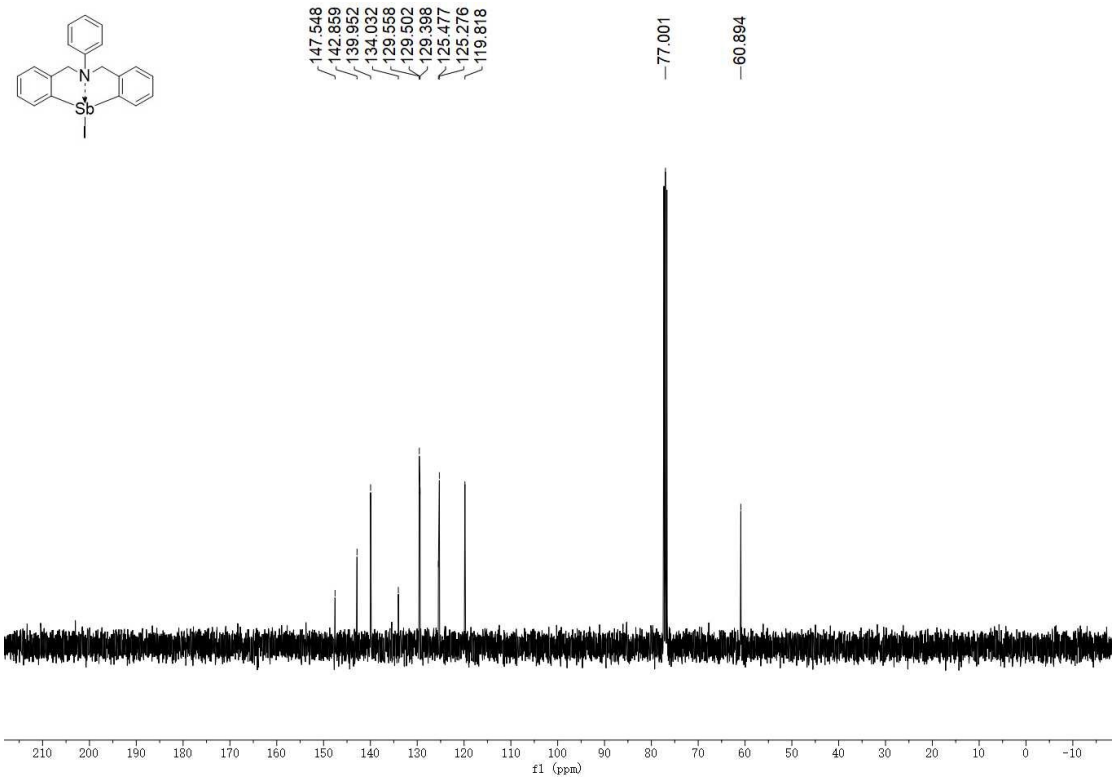
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1d**



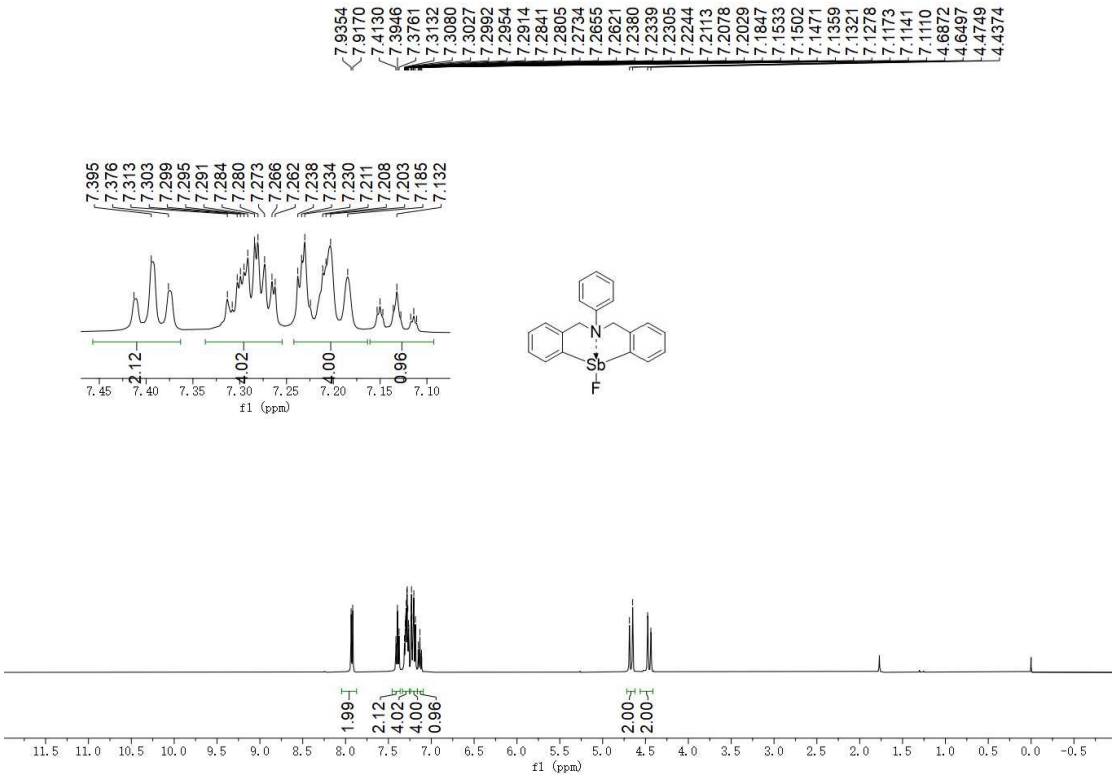
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1d**



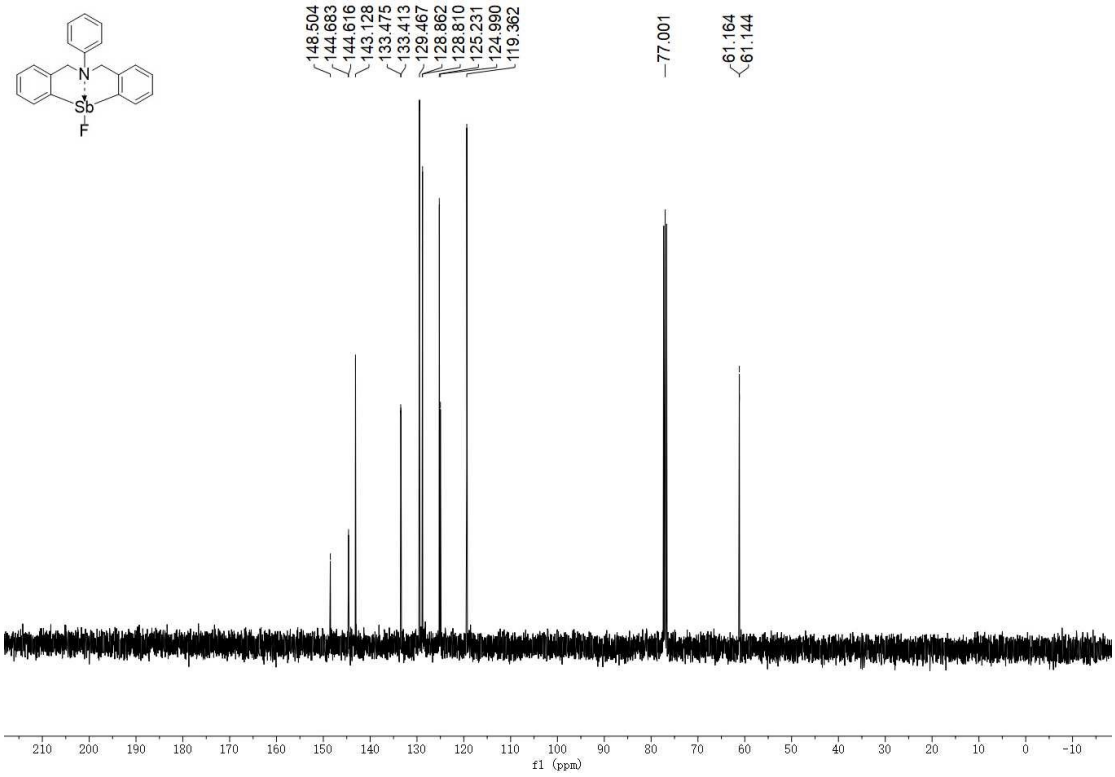
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1e**



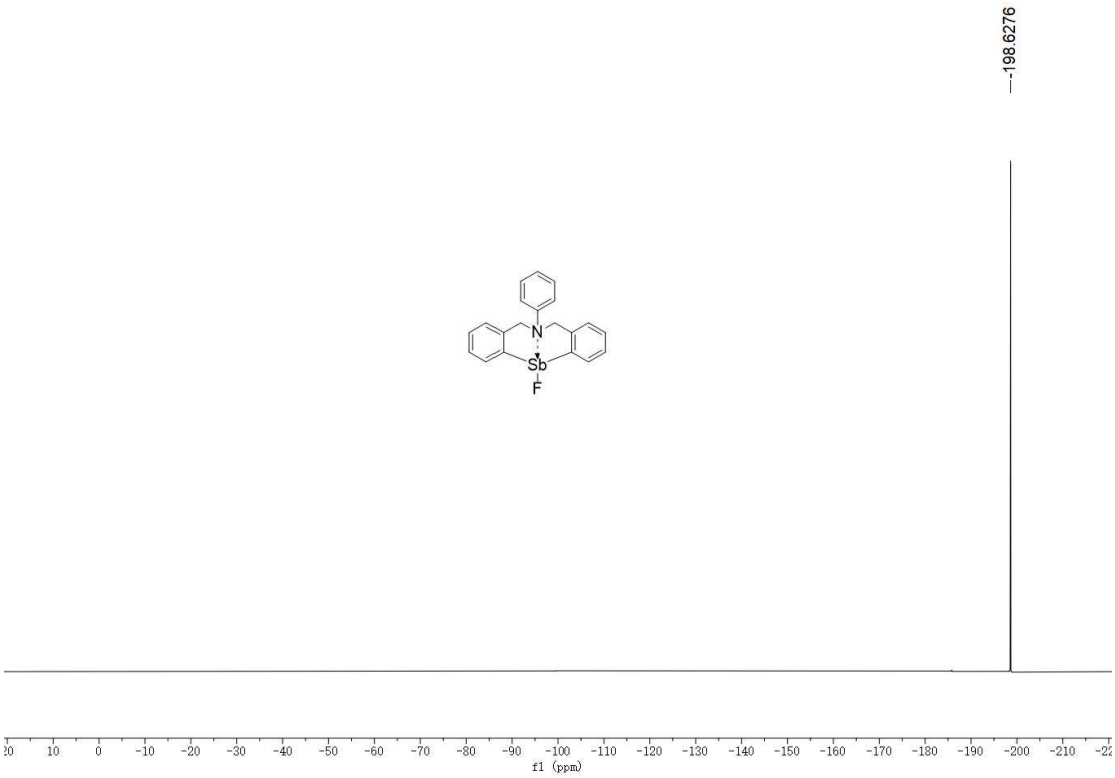
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1e**



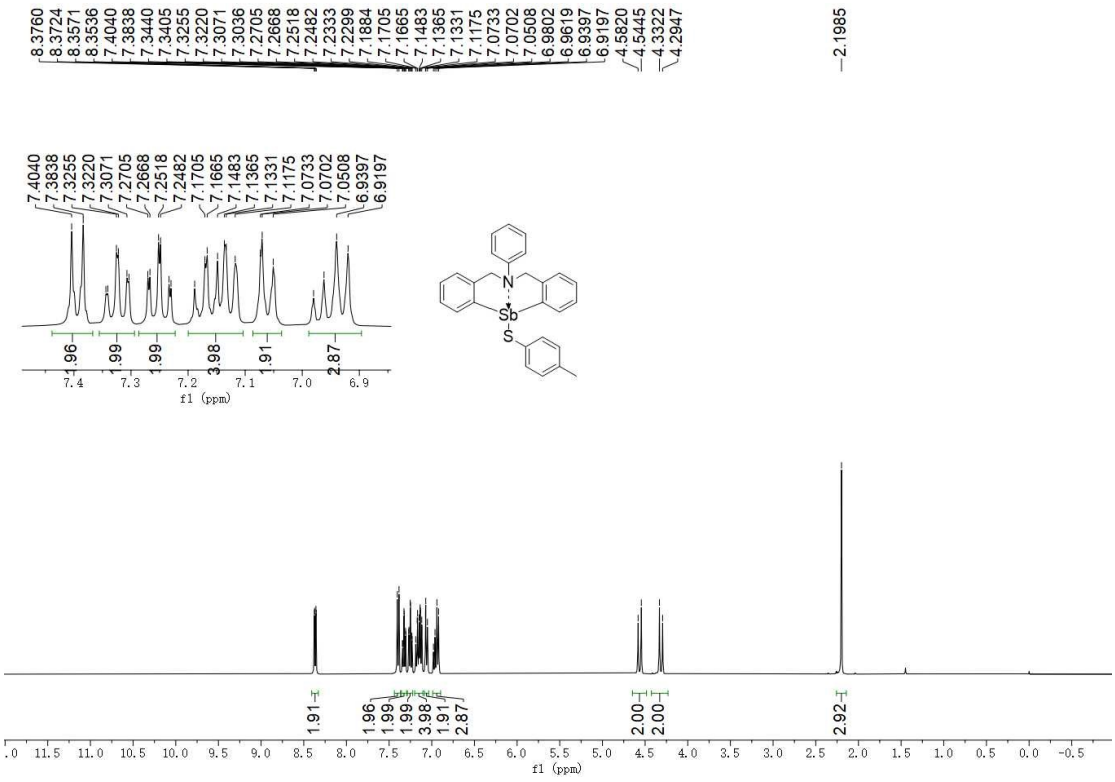
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1f**



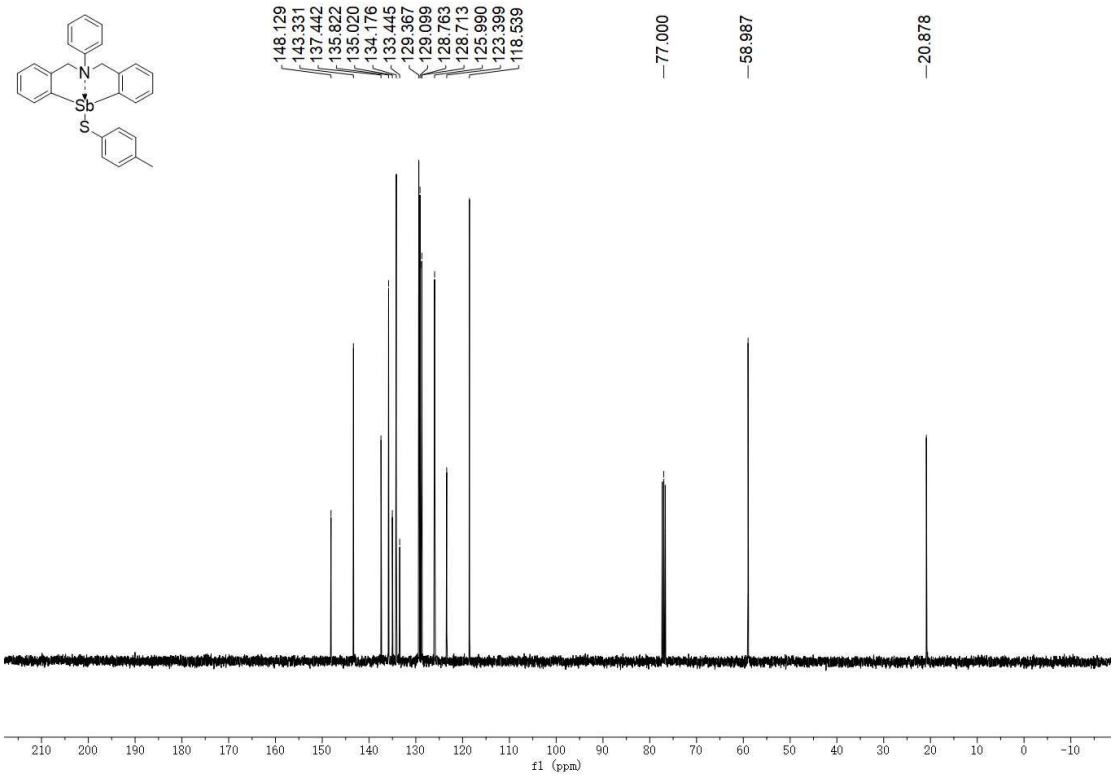
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1f**



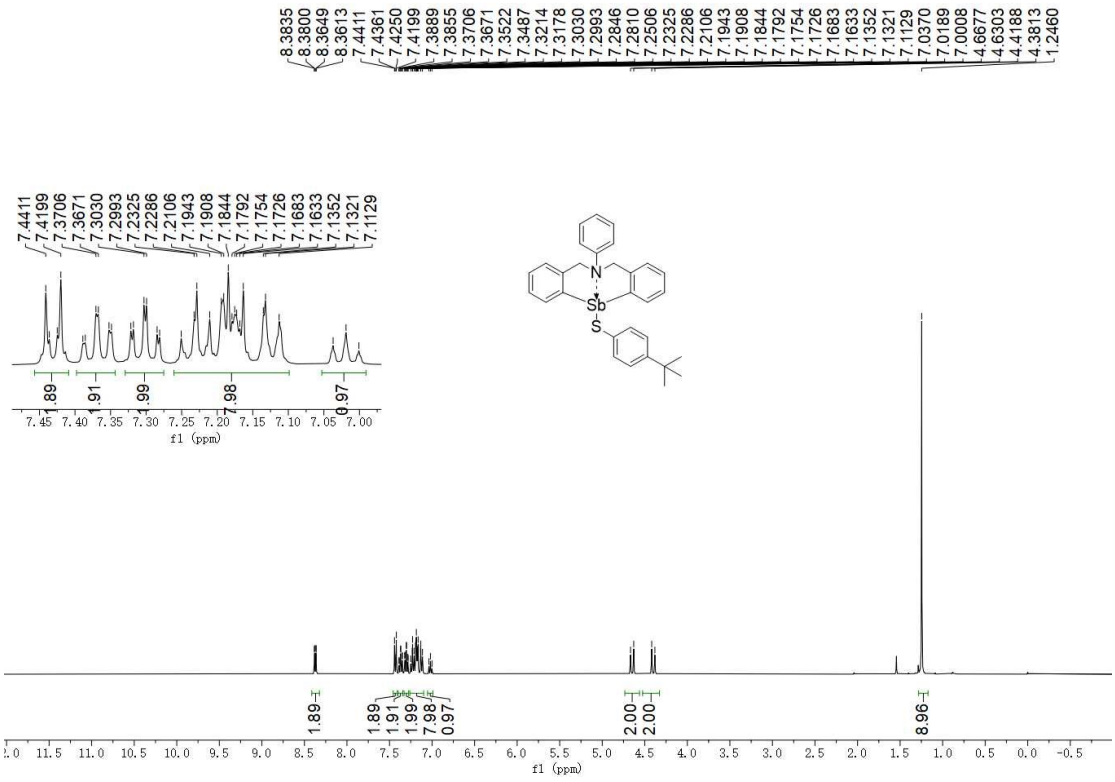
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **1f**



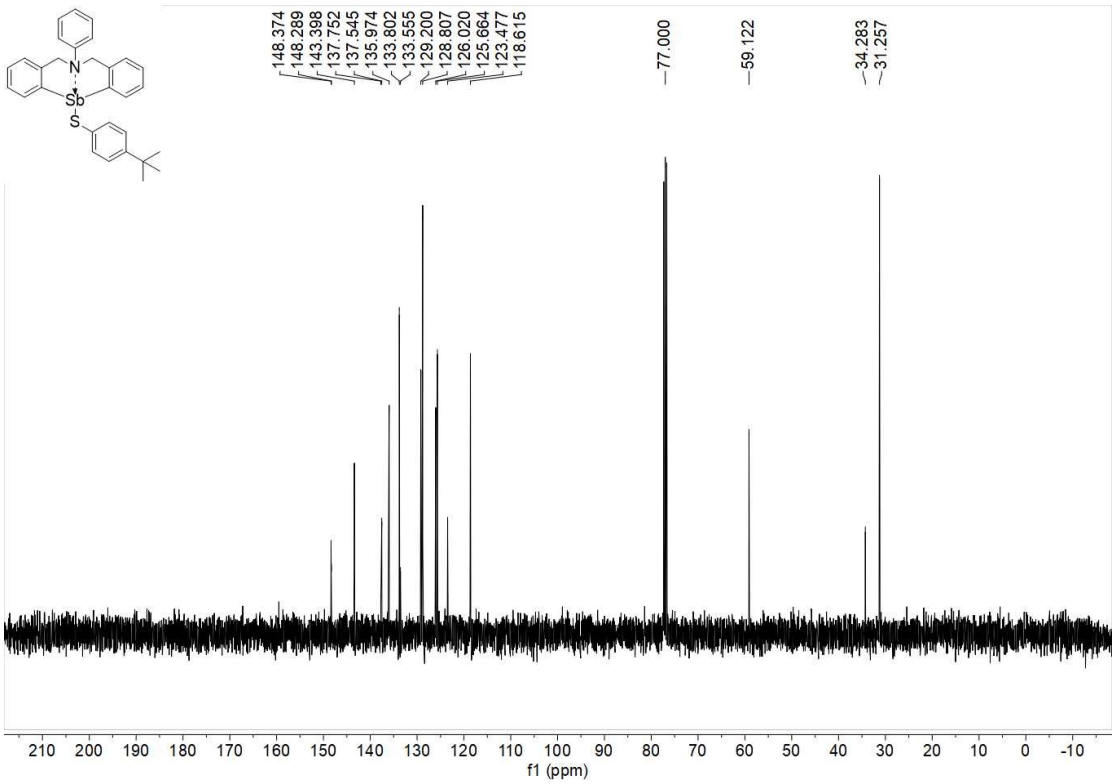
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



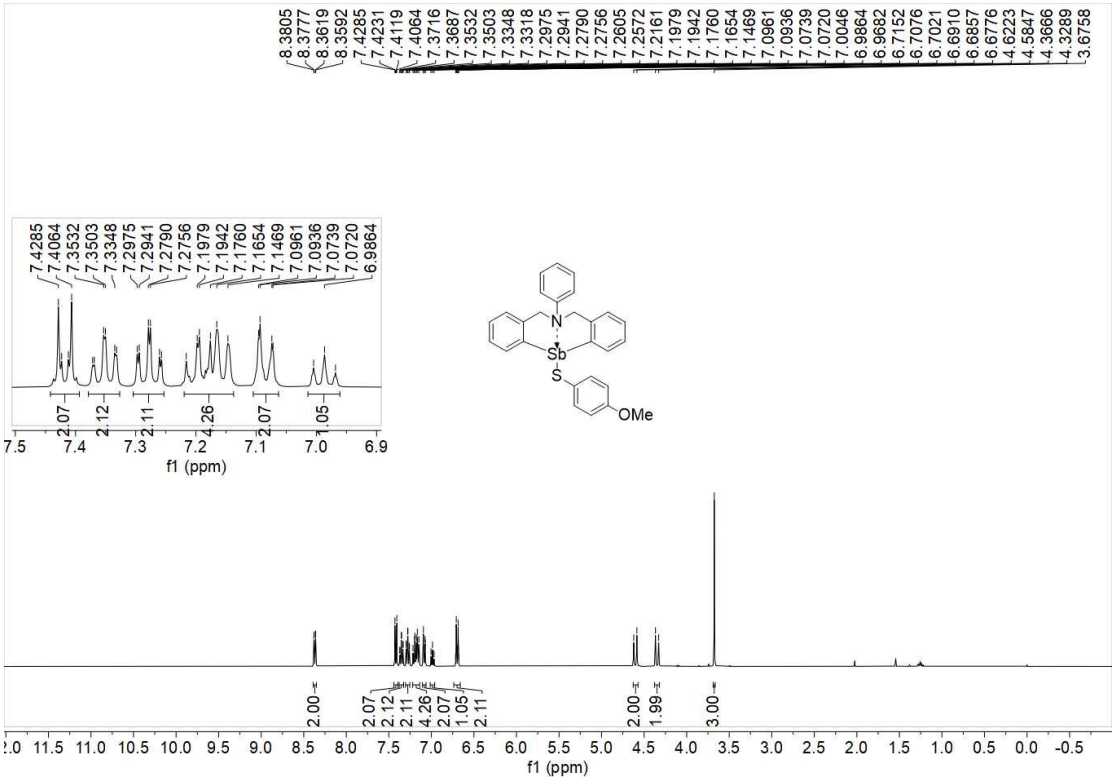
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



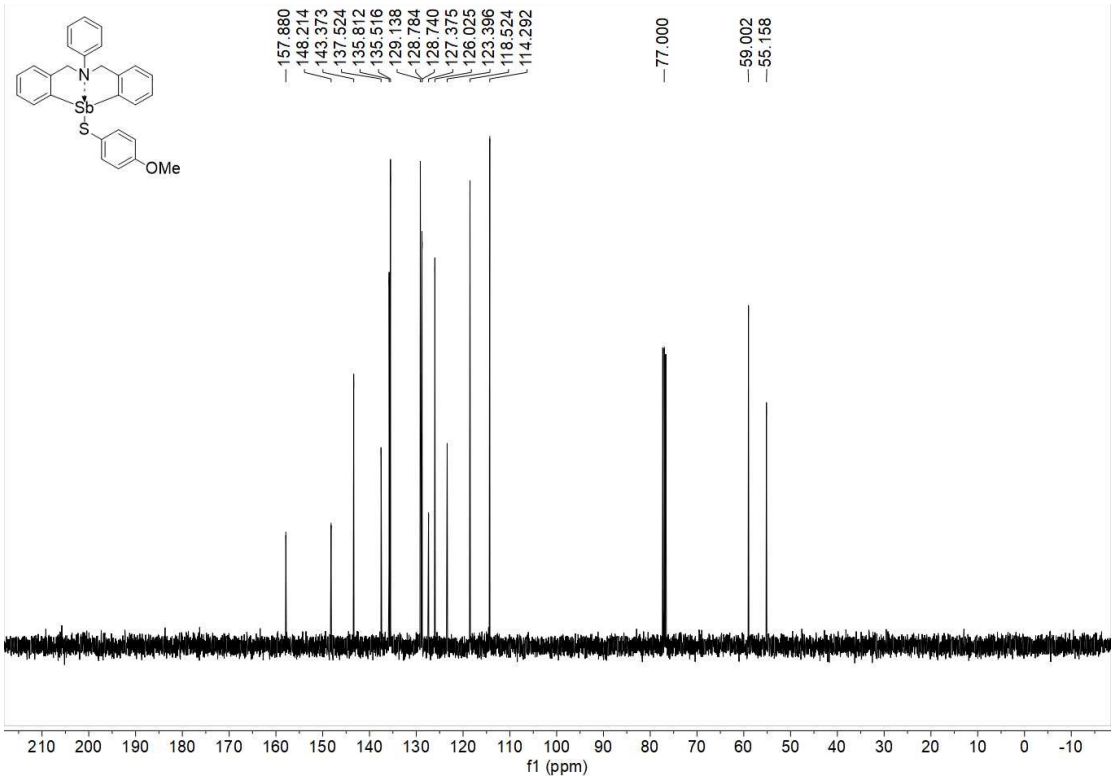
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



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



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



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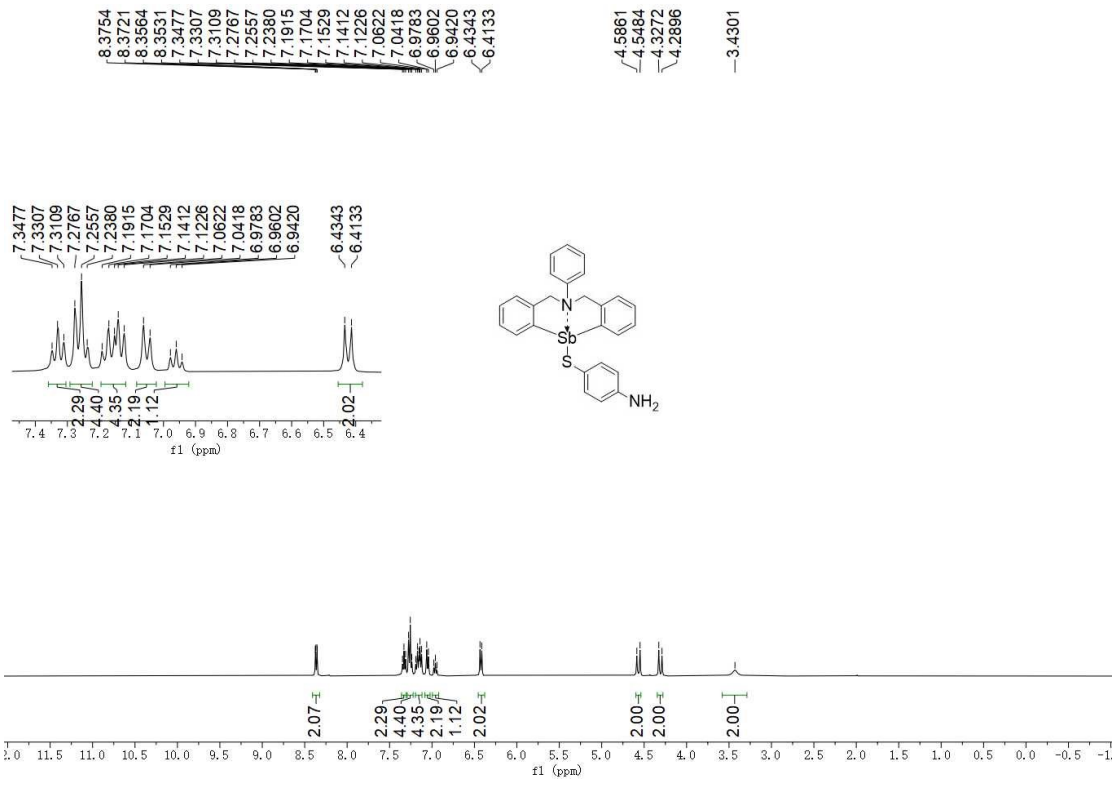
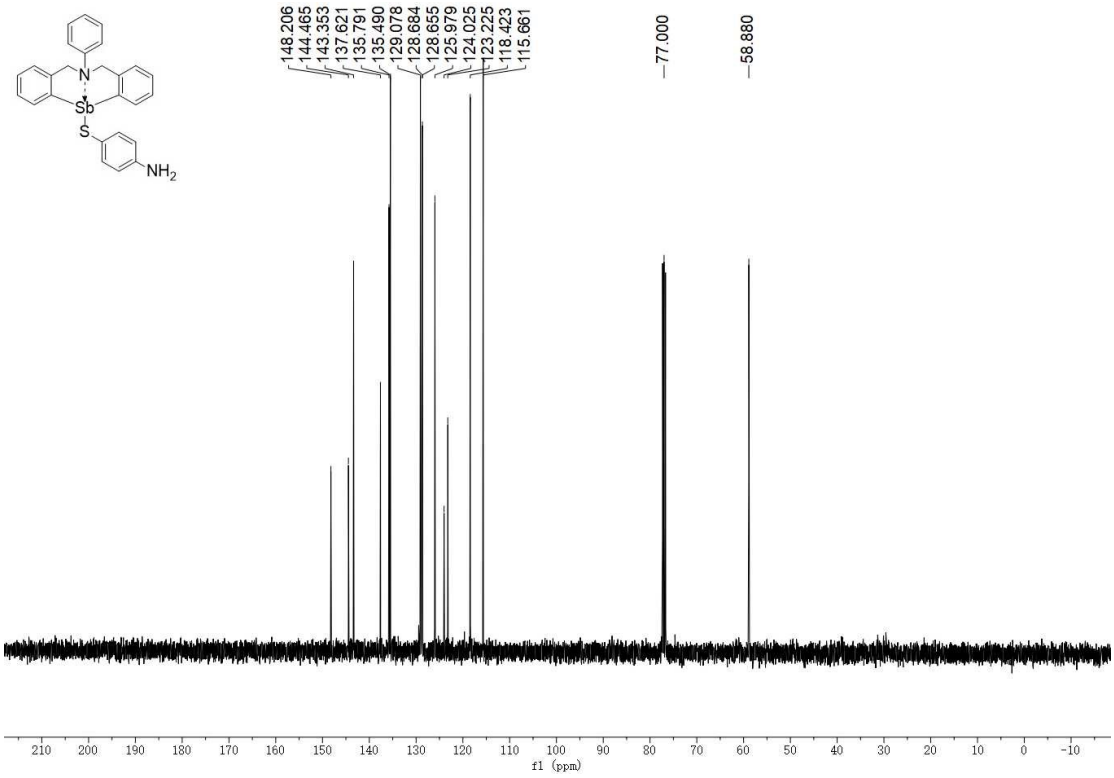
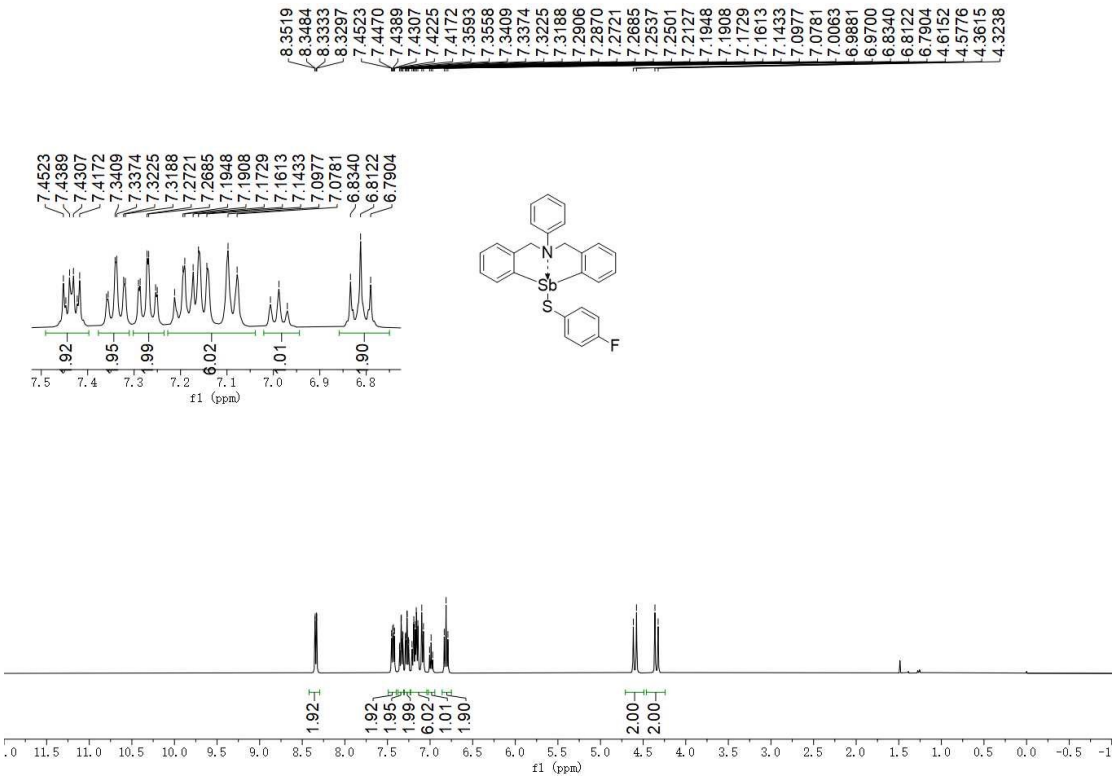


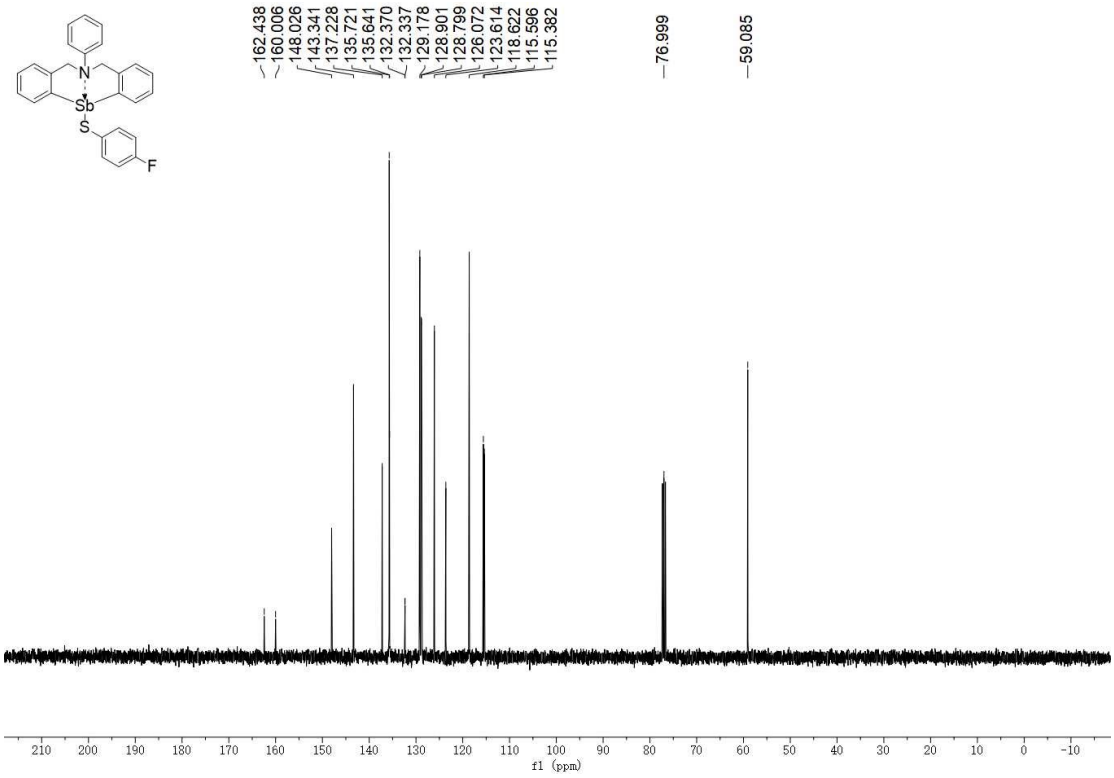
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



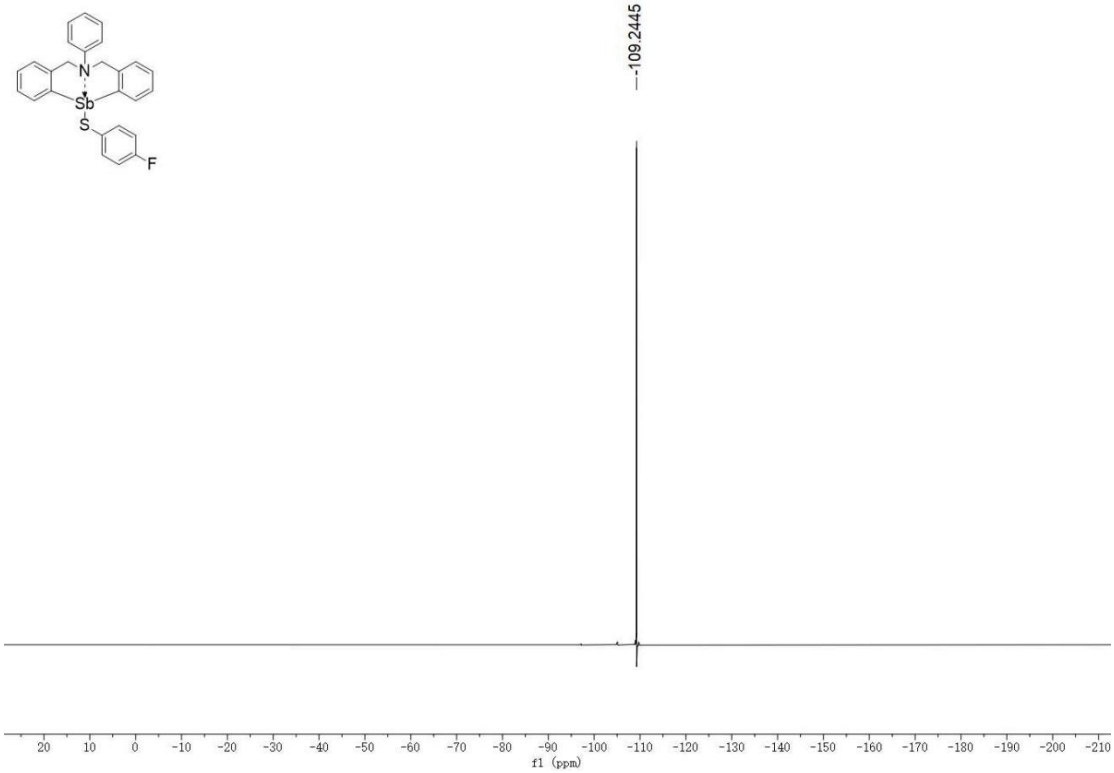
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



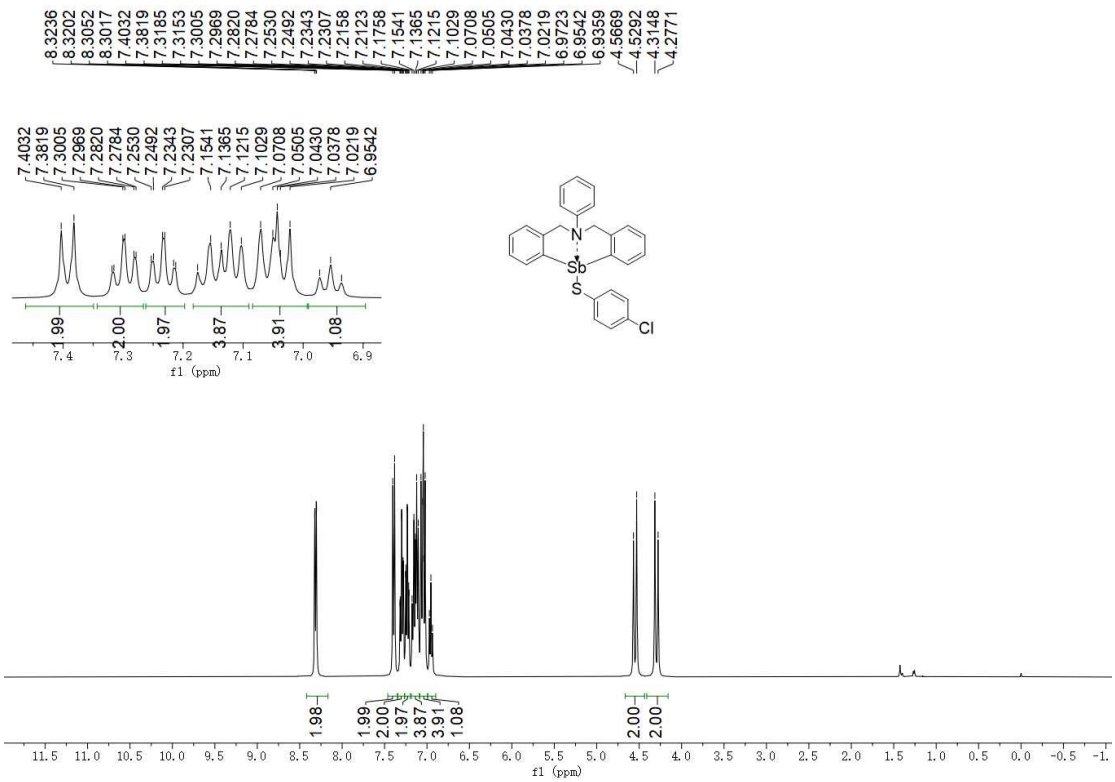
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



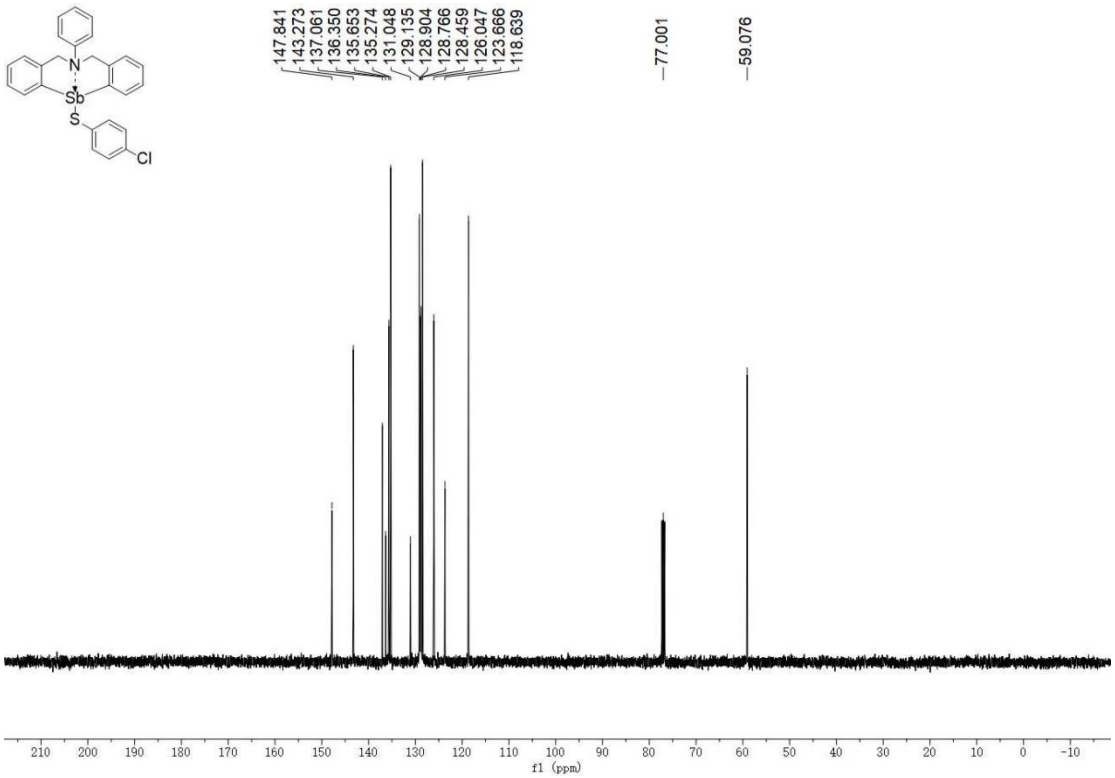
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**



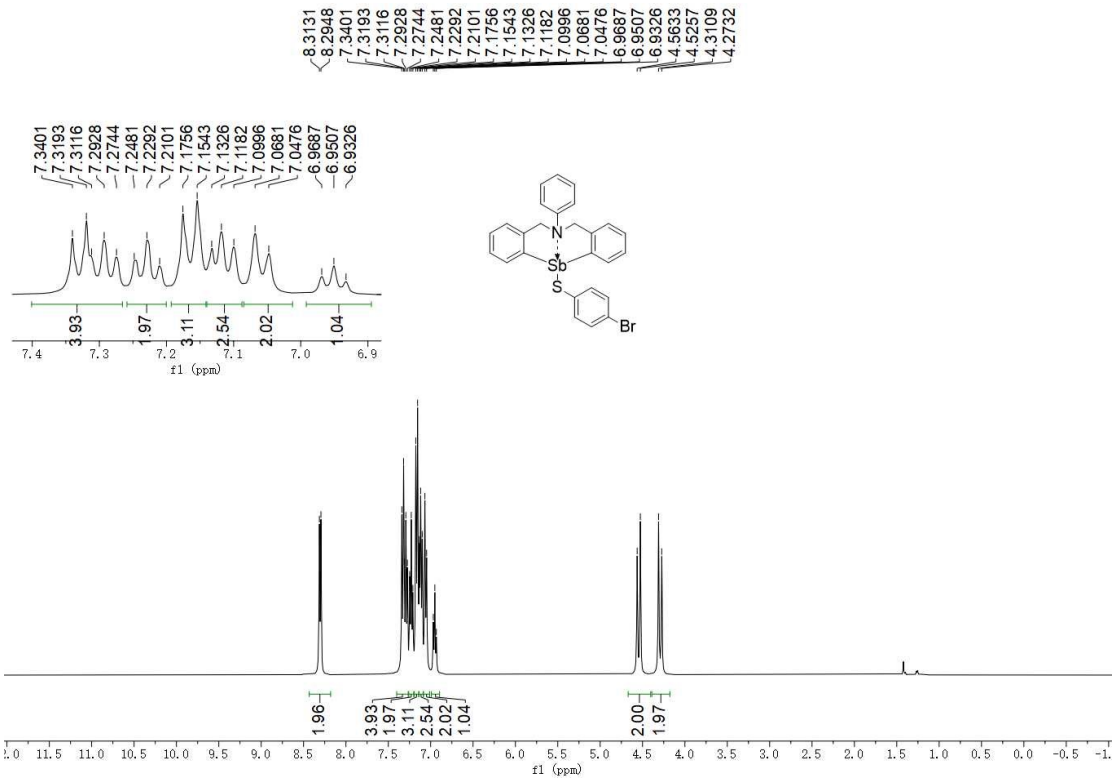
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3e**



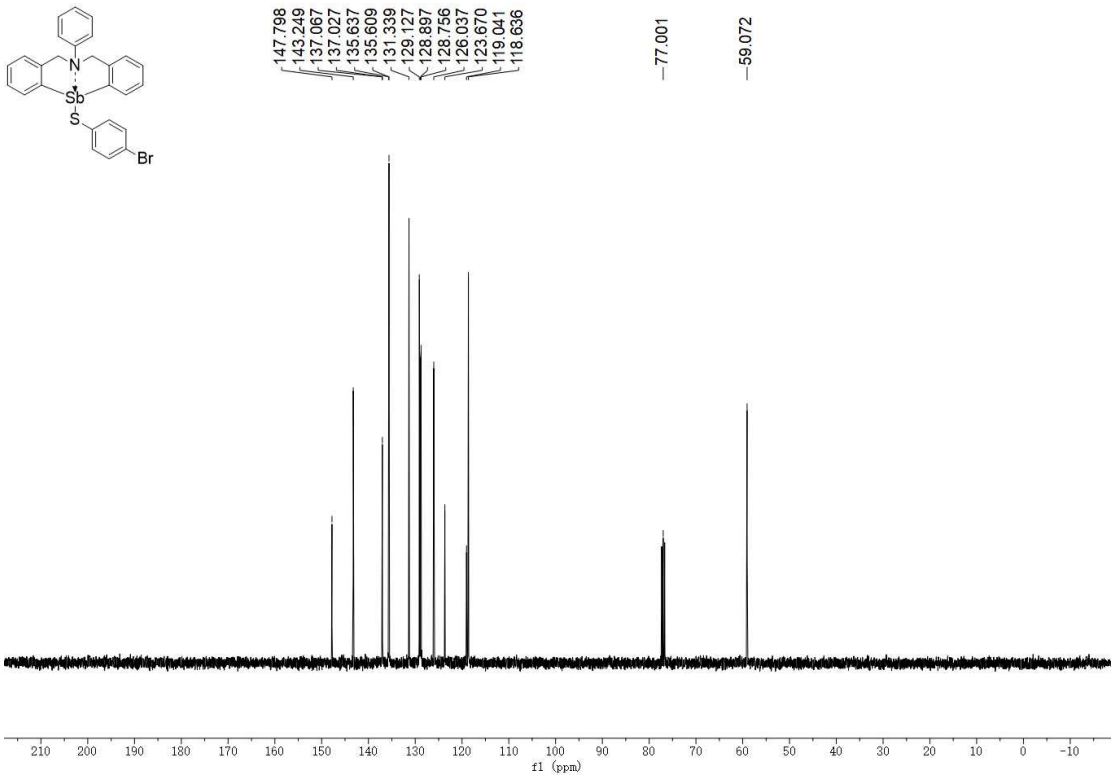
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**



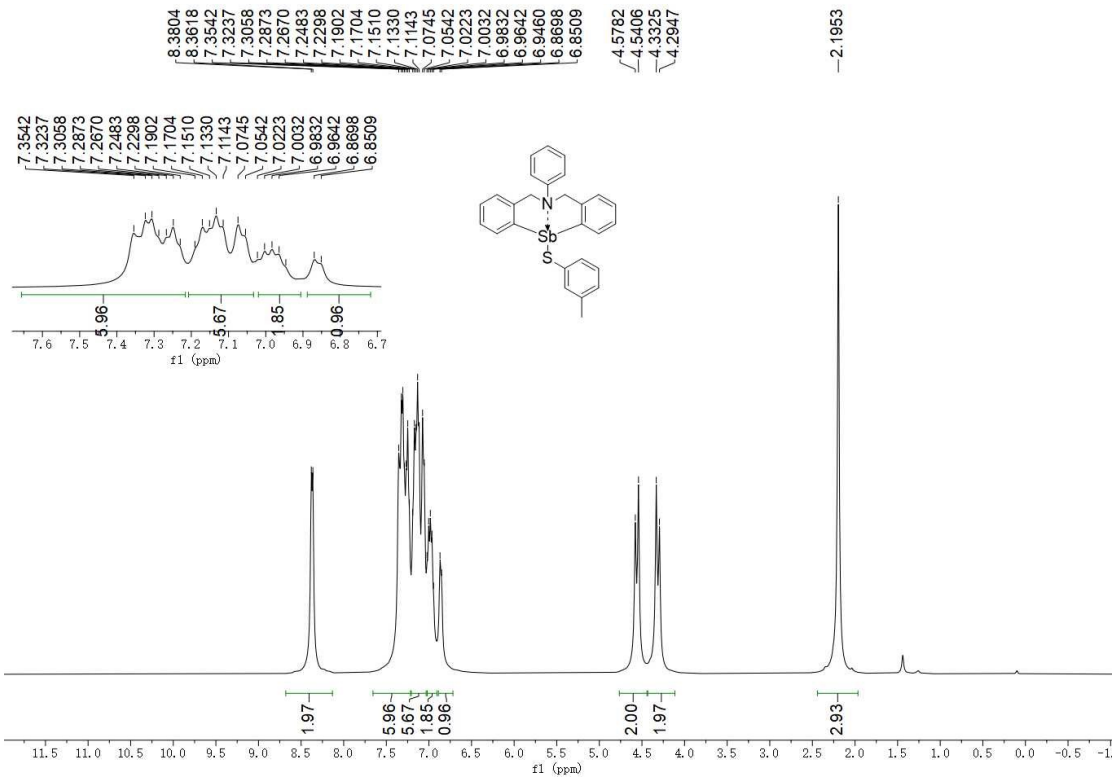
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**



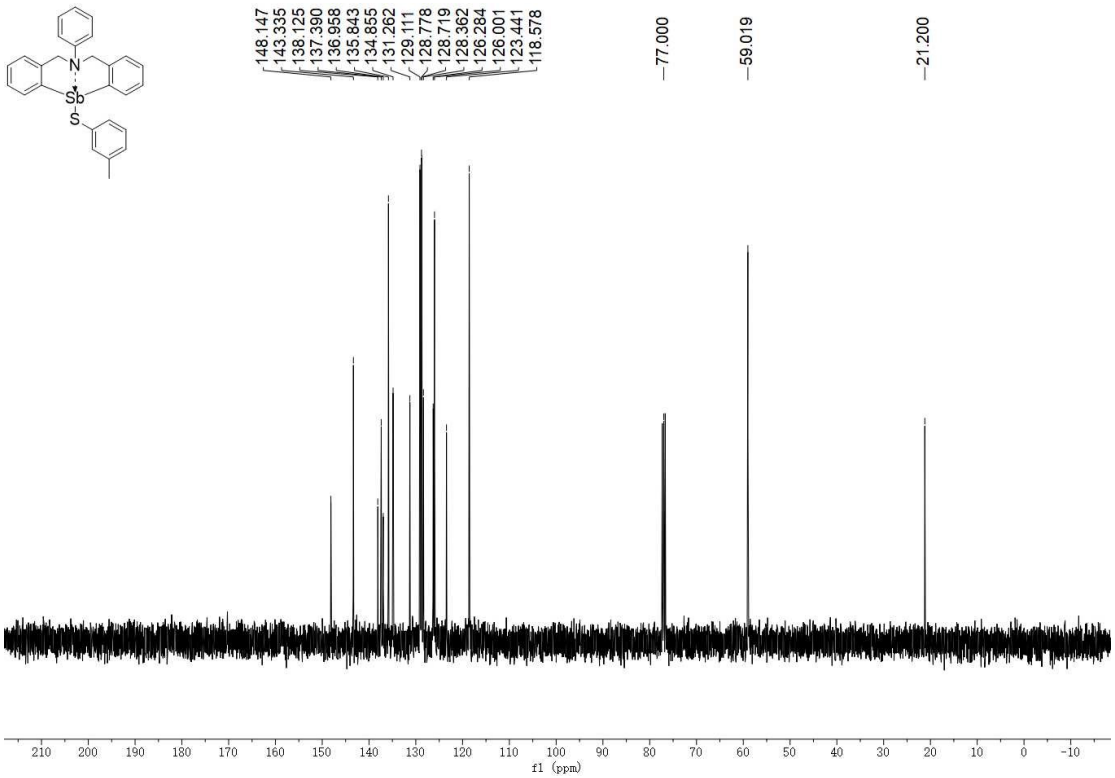
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



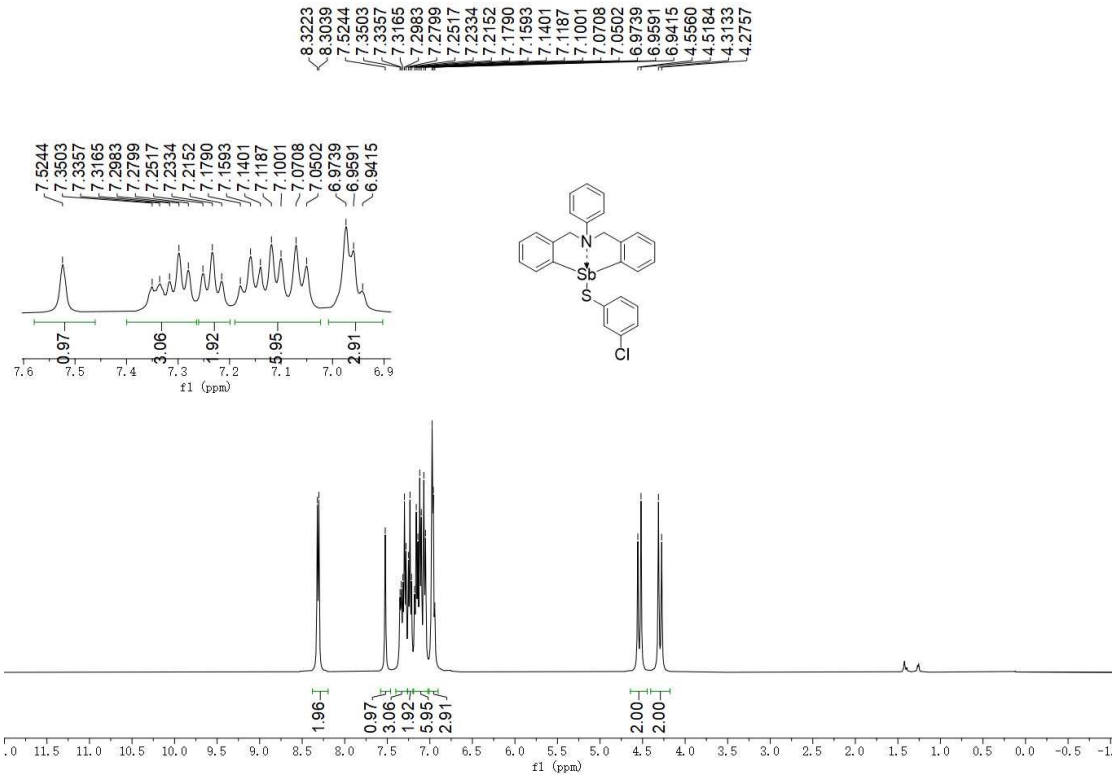
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**



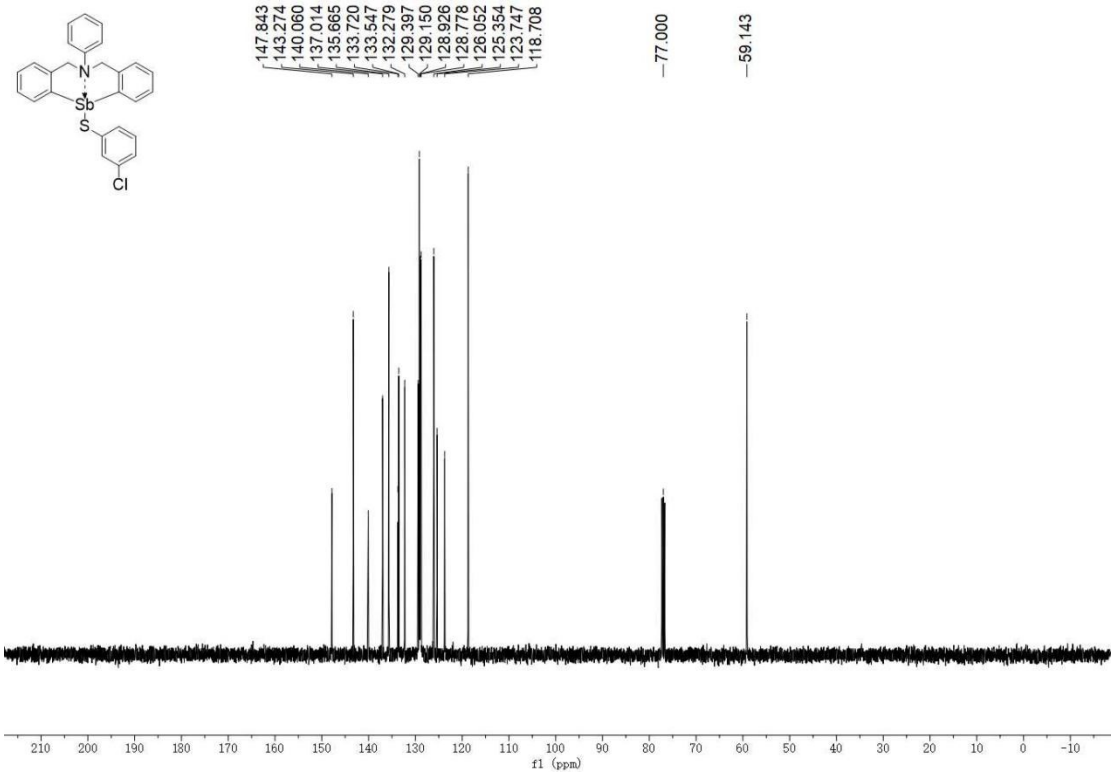
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



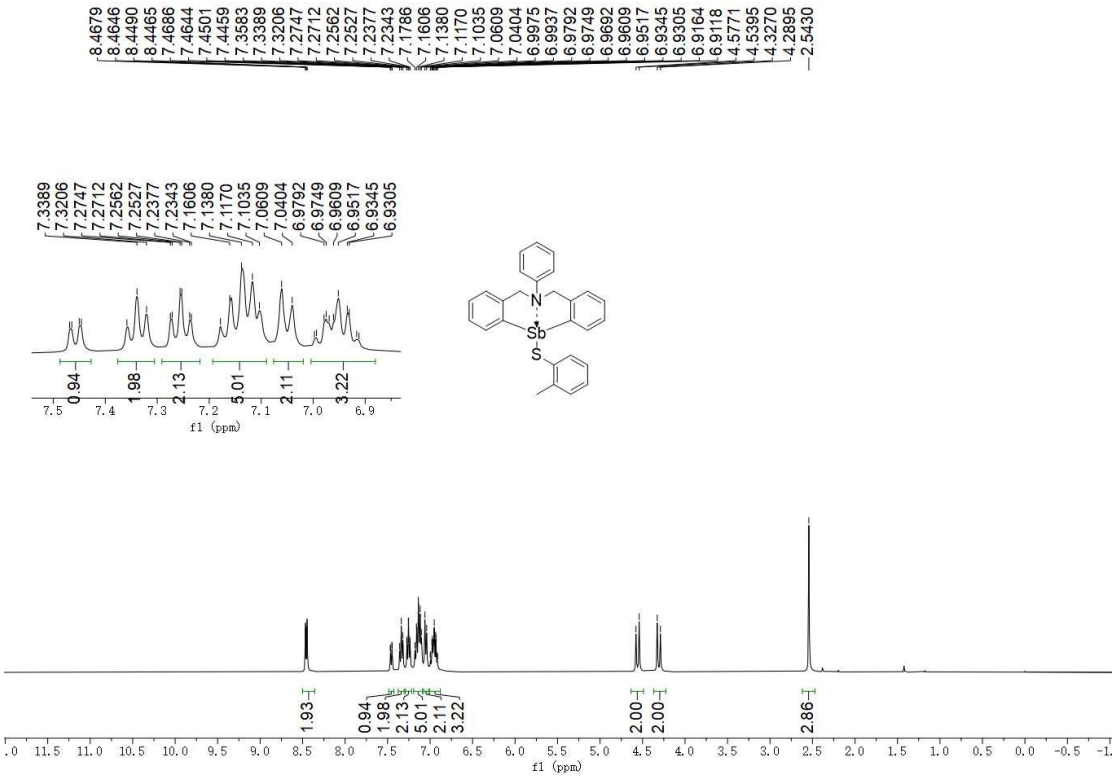
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**



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



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



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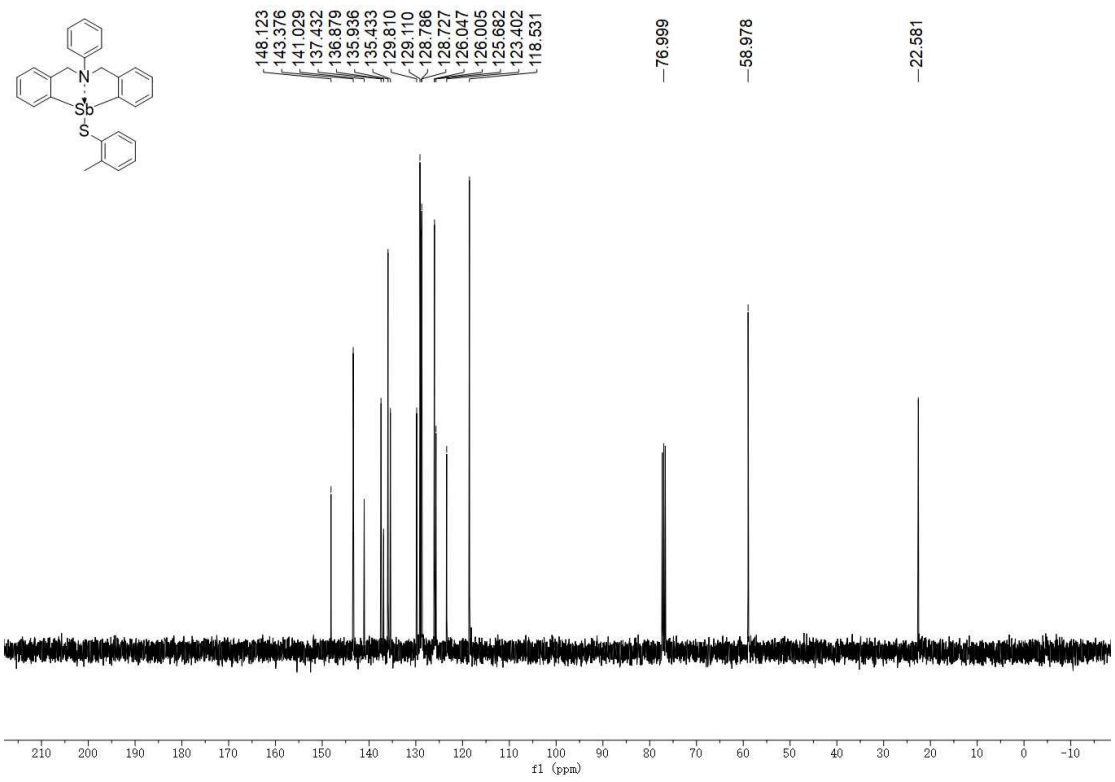

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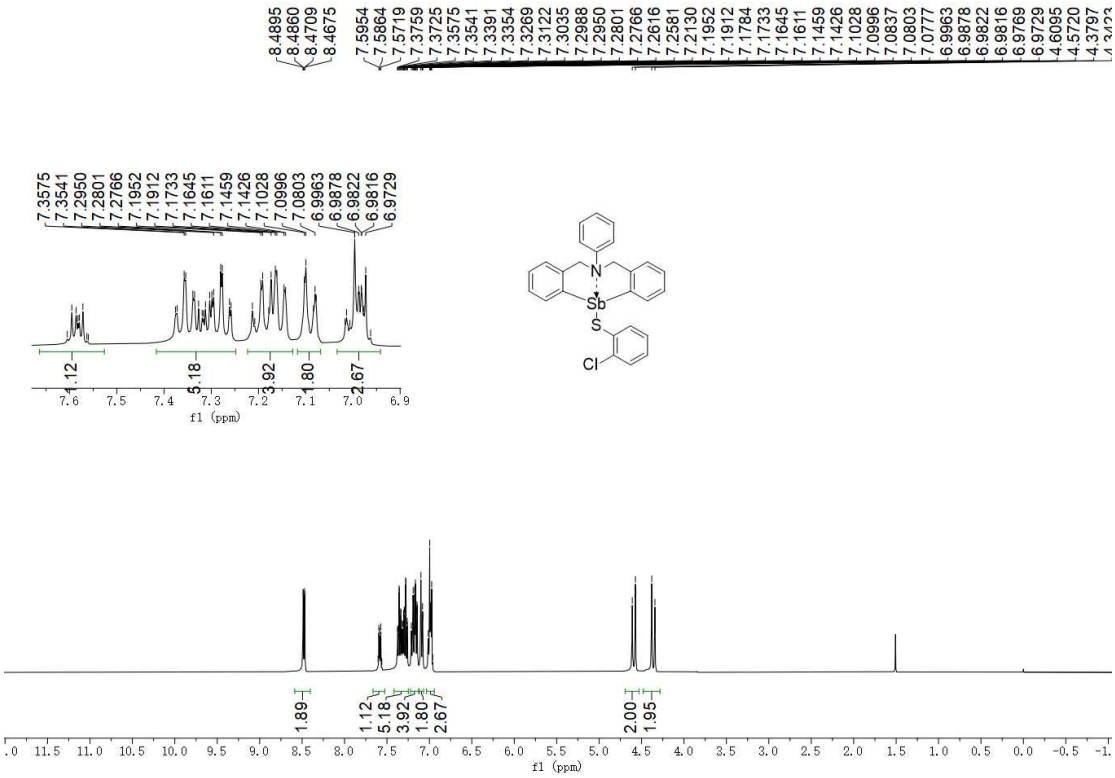
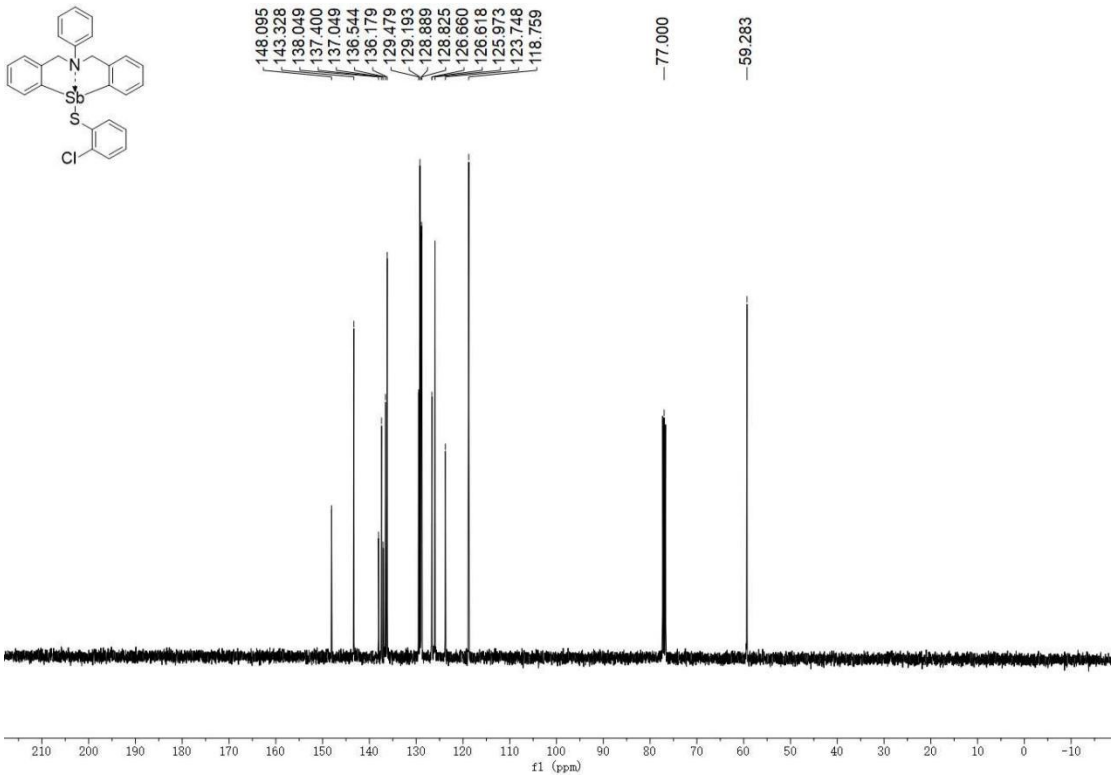
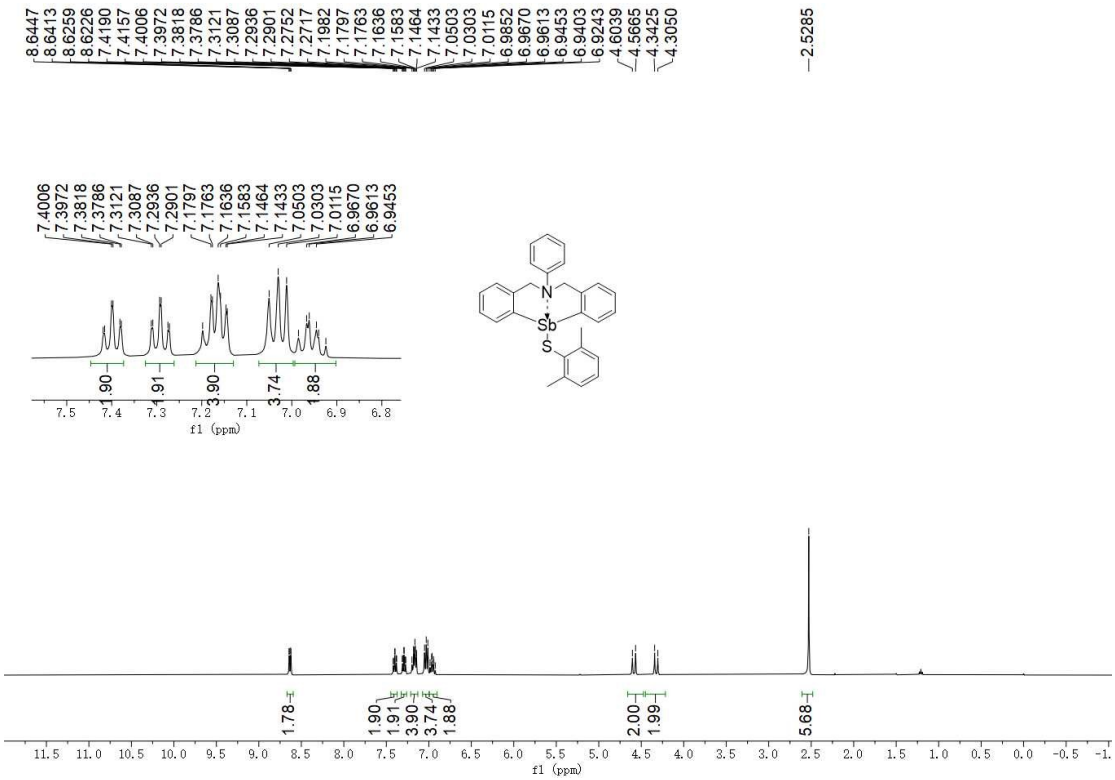


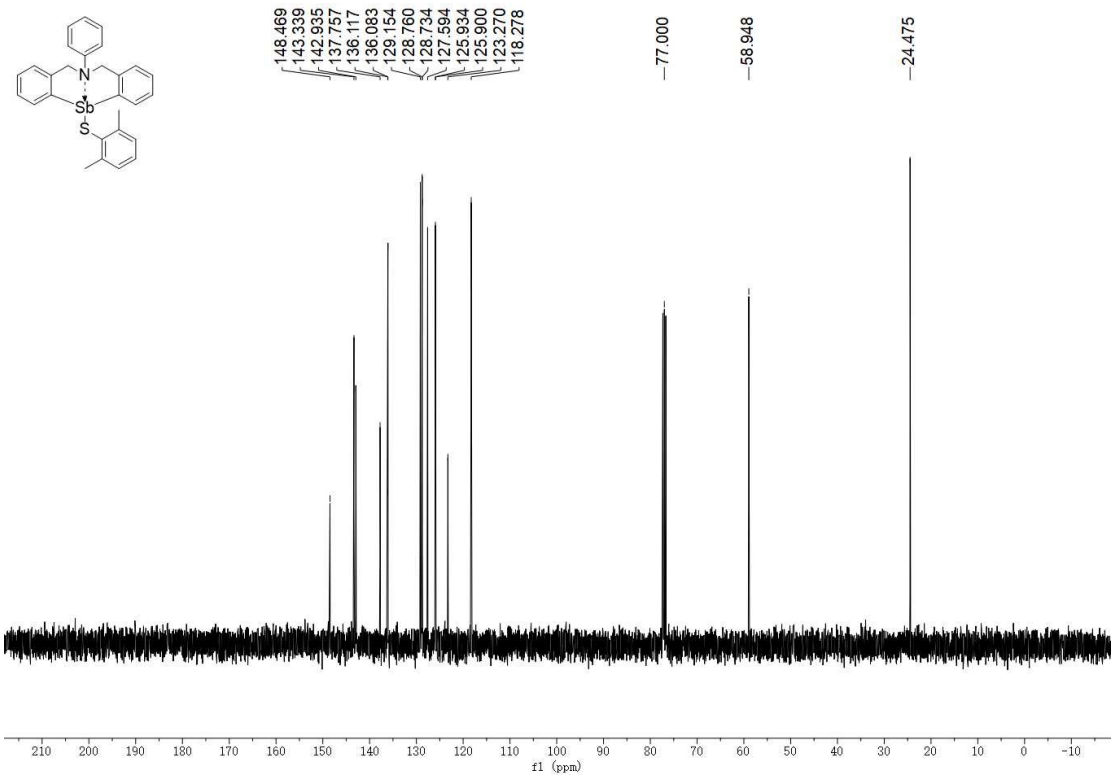
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



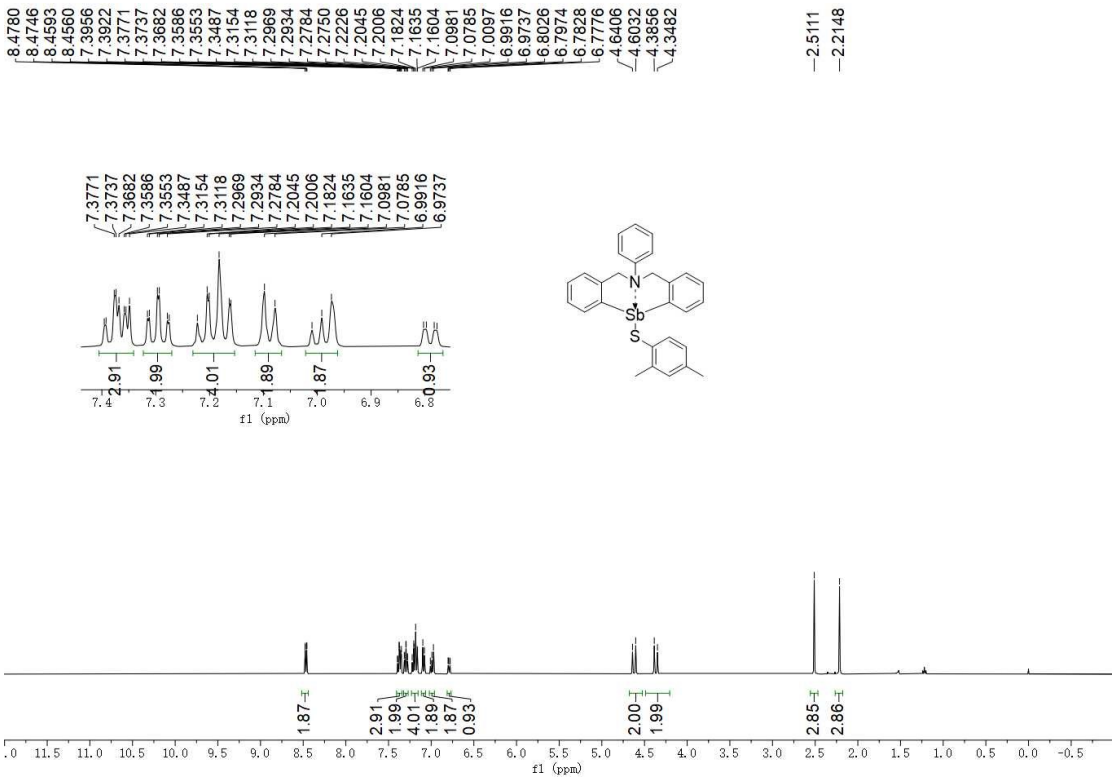
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**



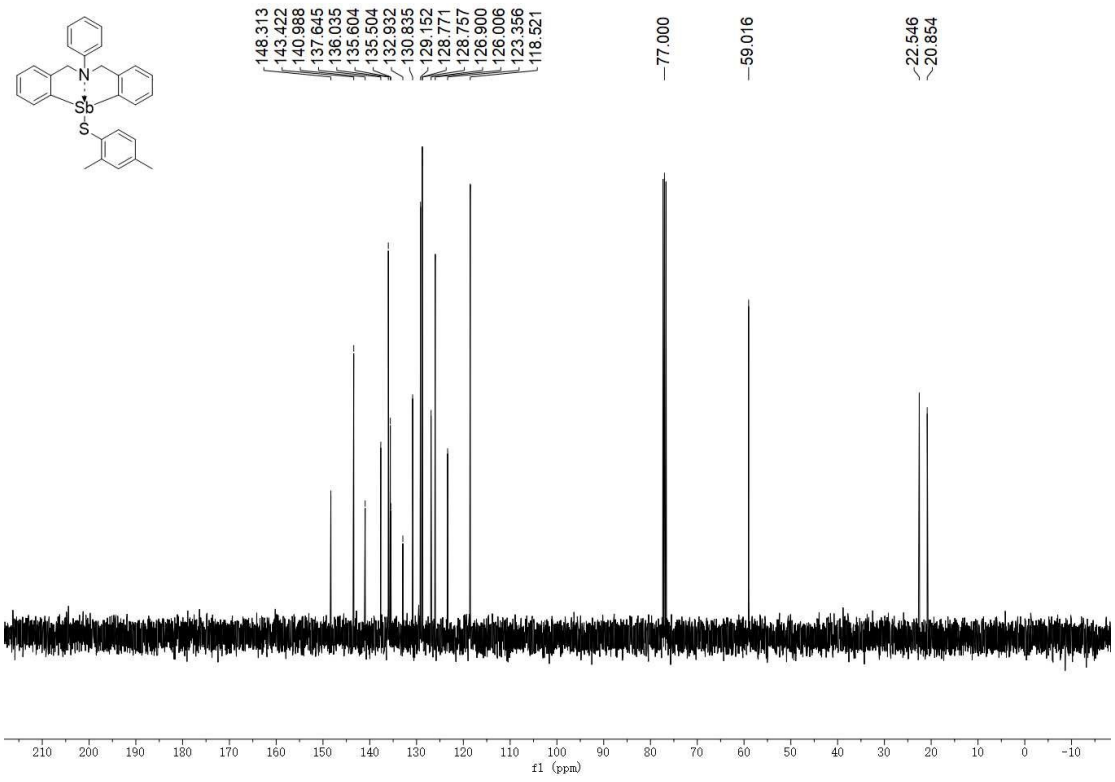
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



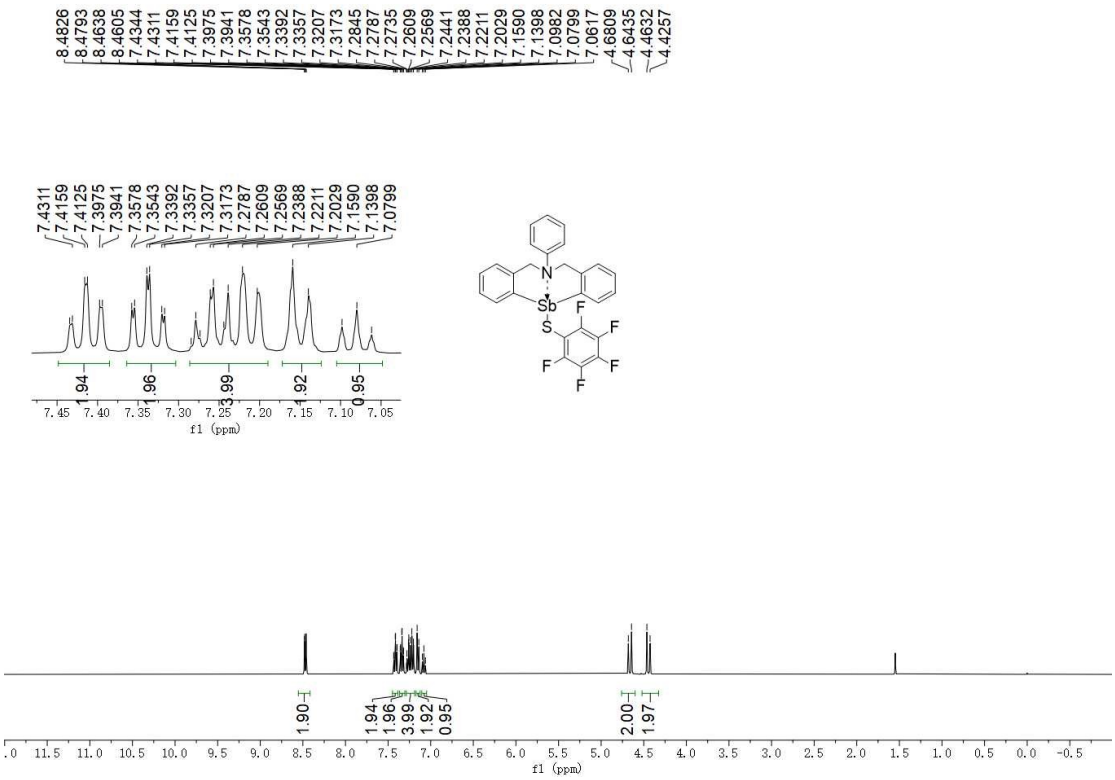
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**



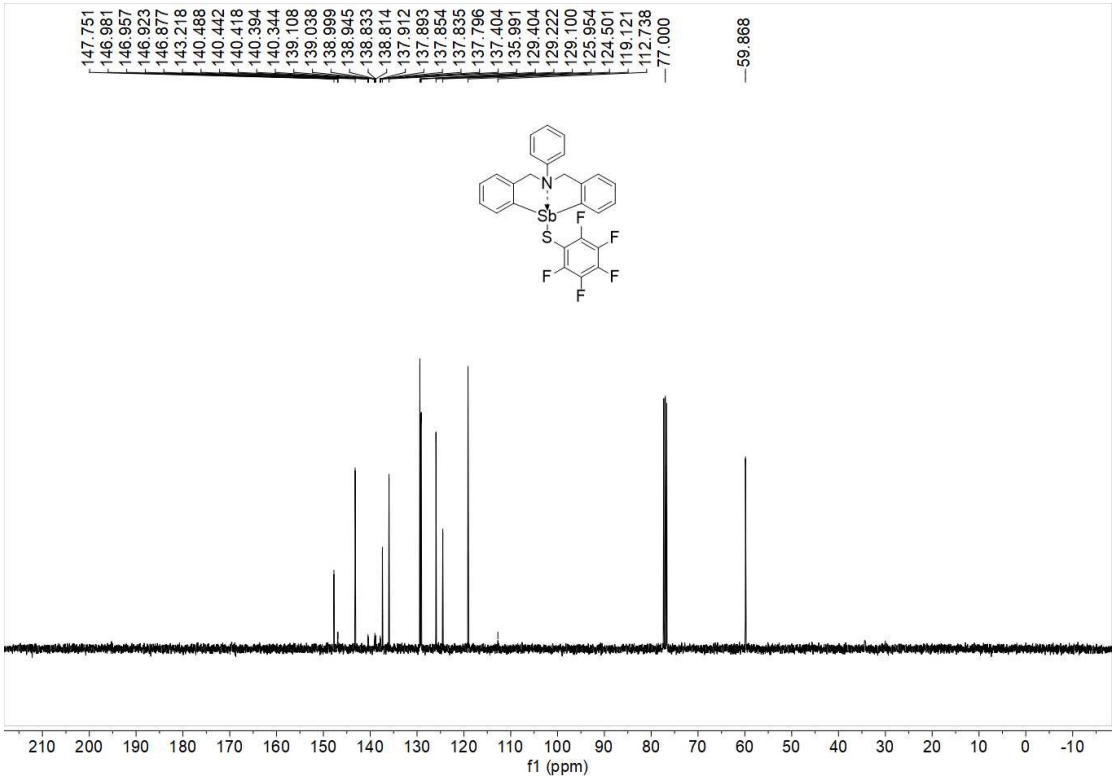
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



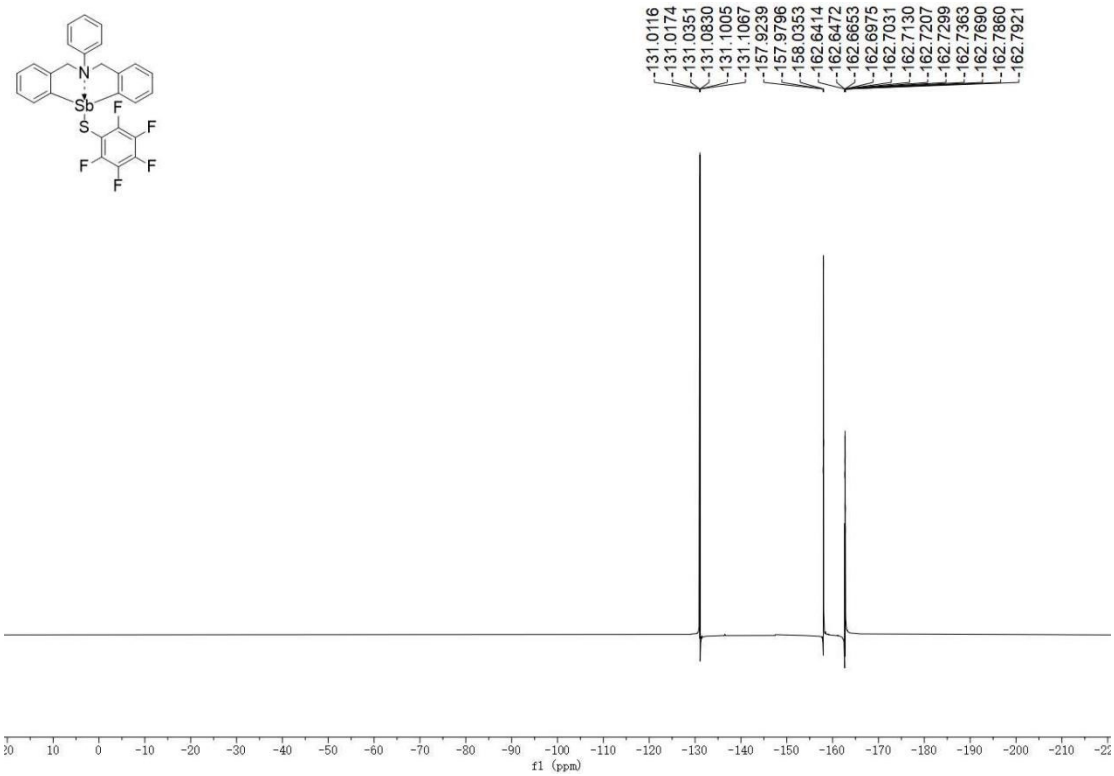
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**



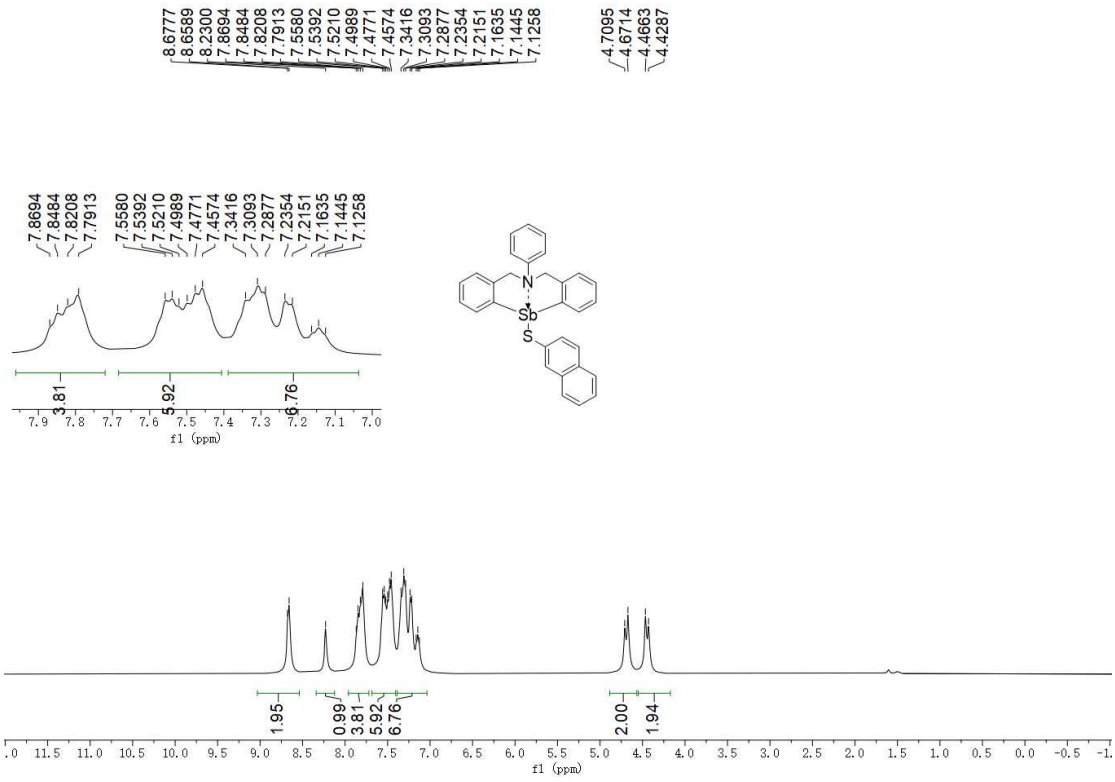
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



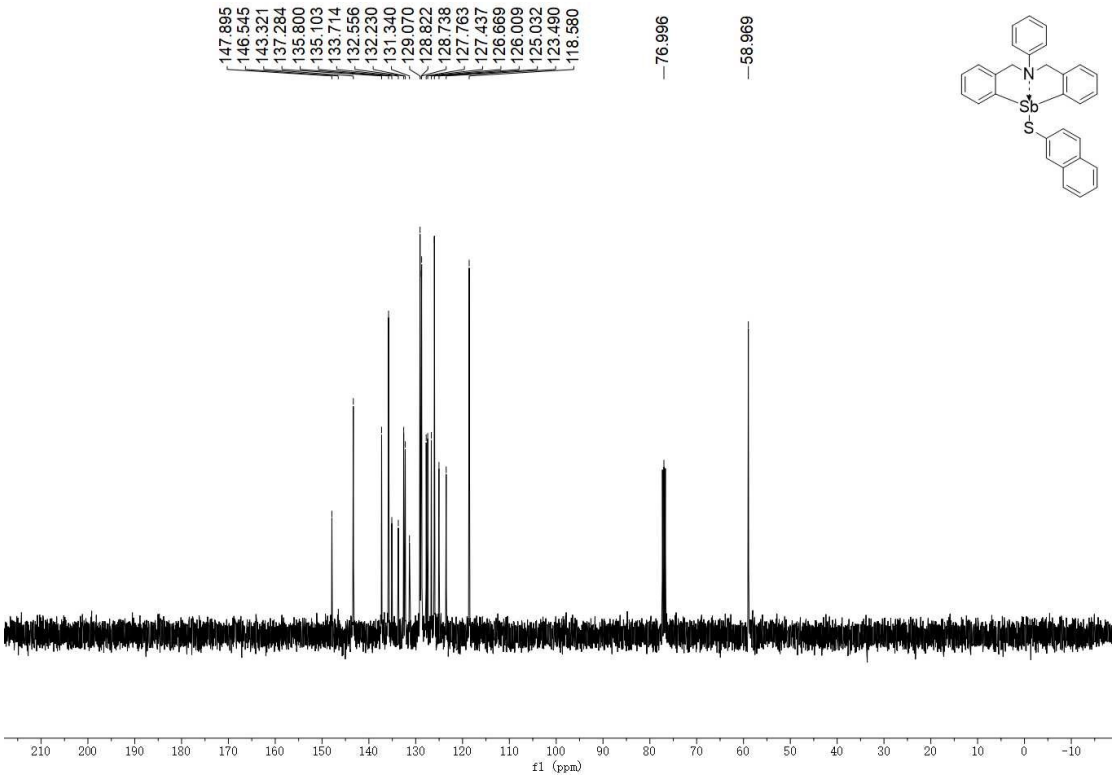
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**



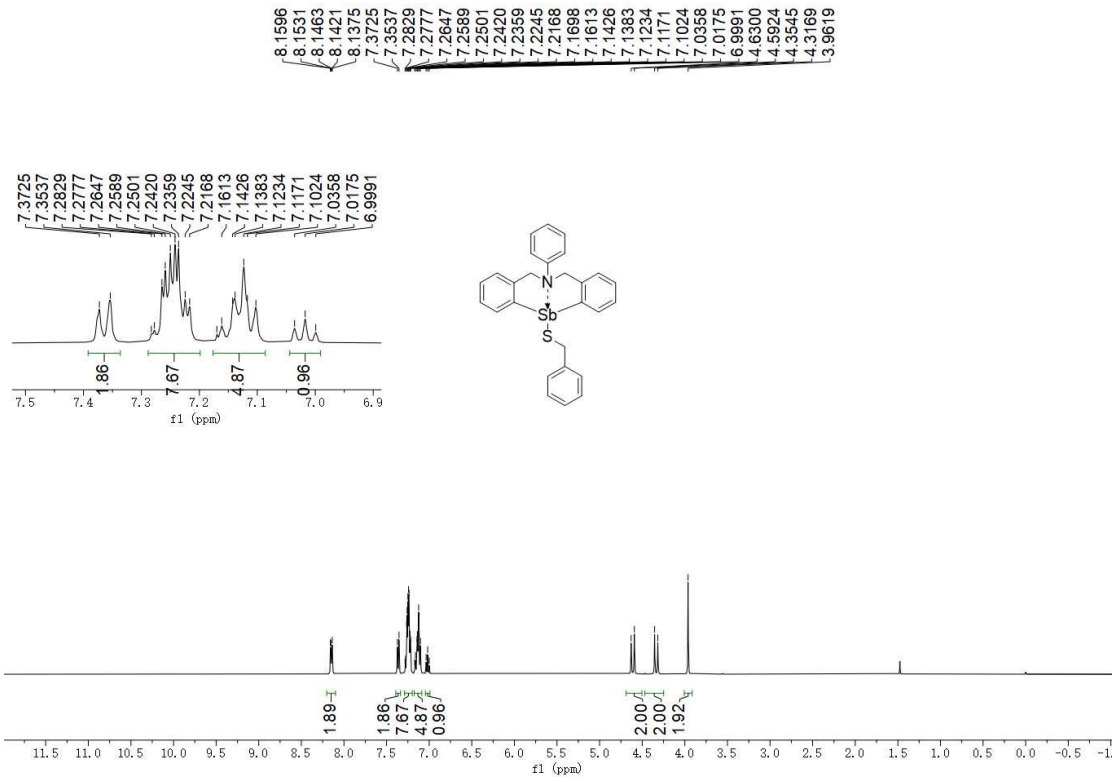
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **3n**



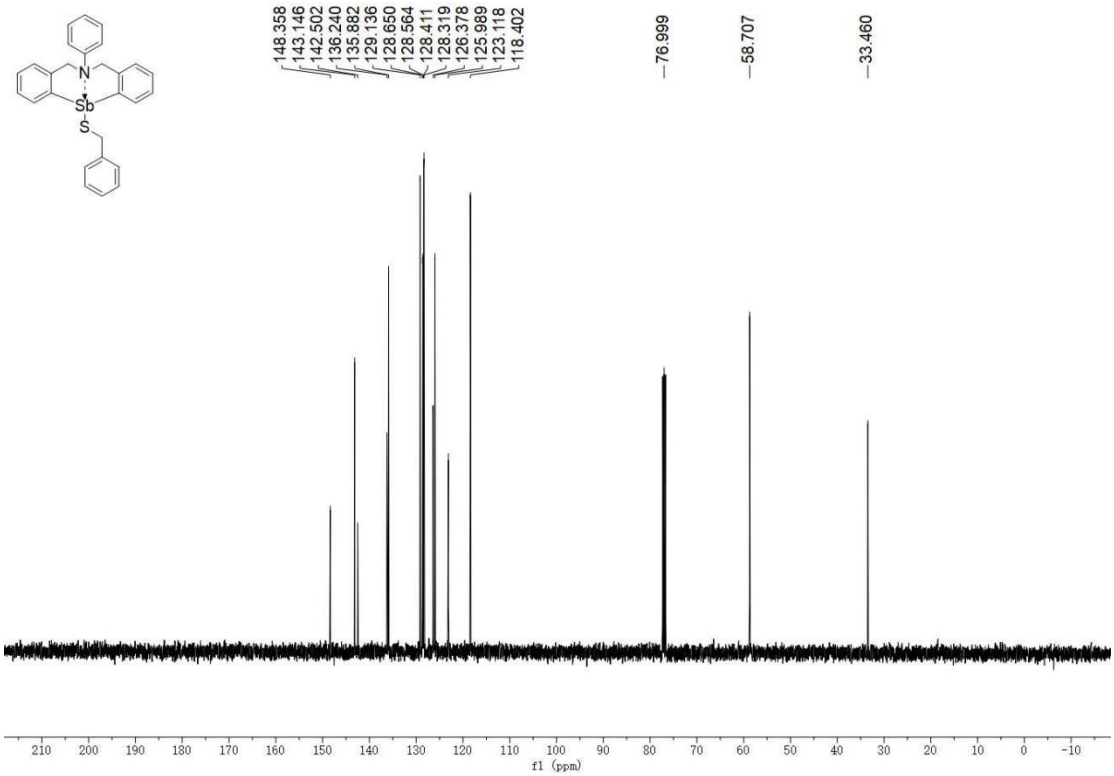
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



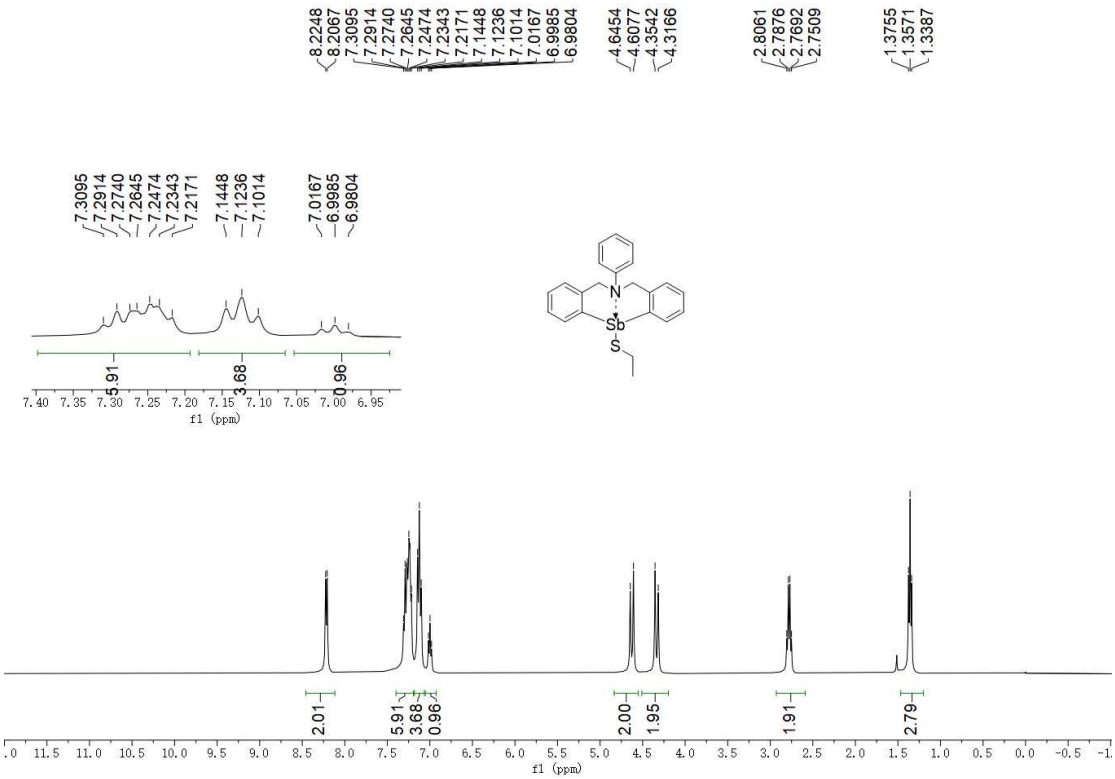
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**



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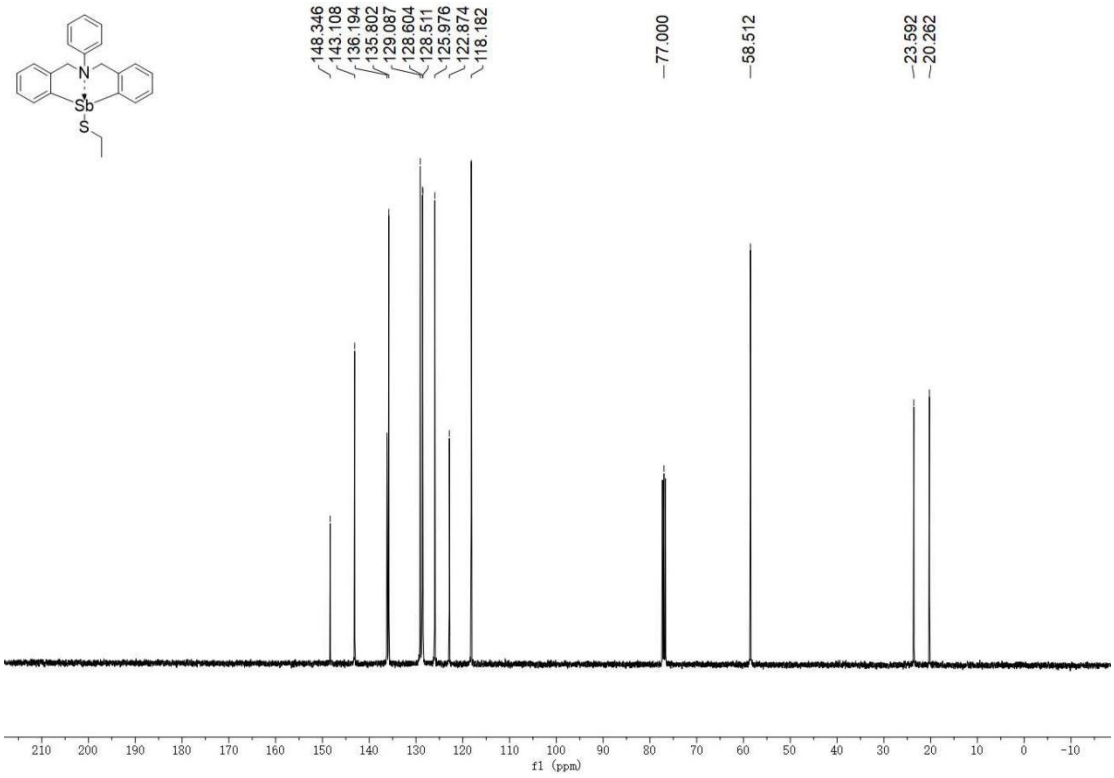
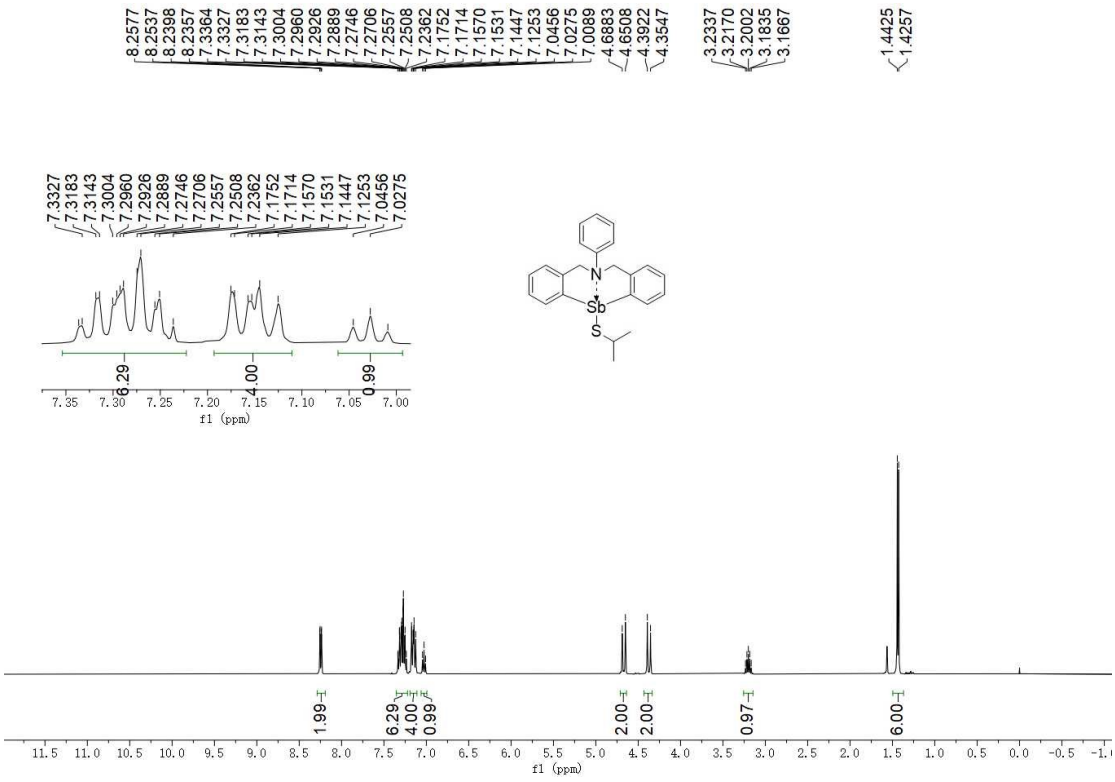
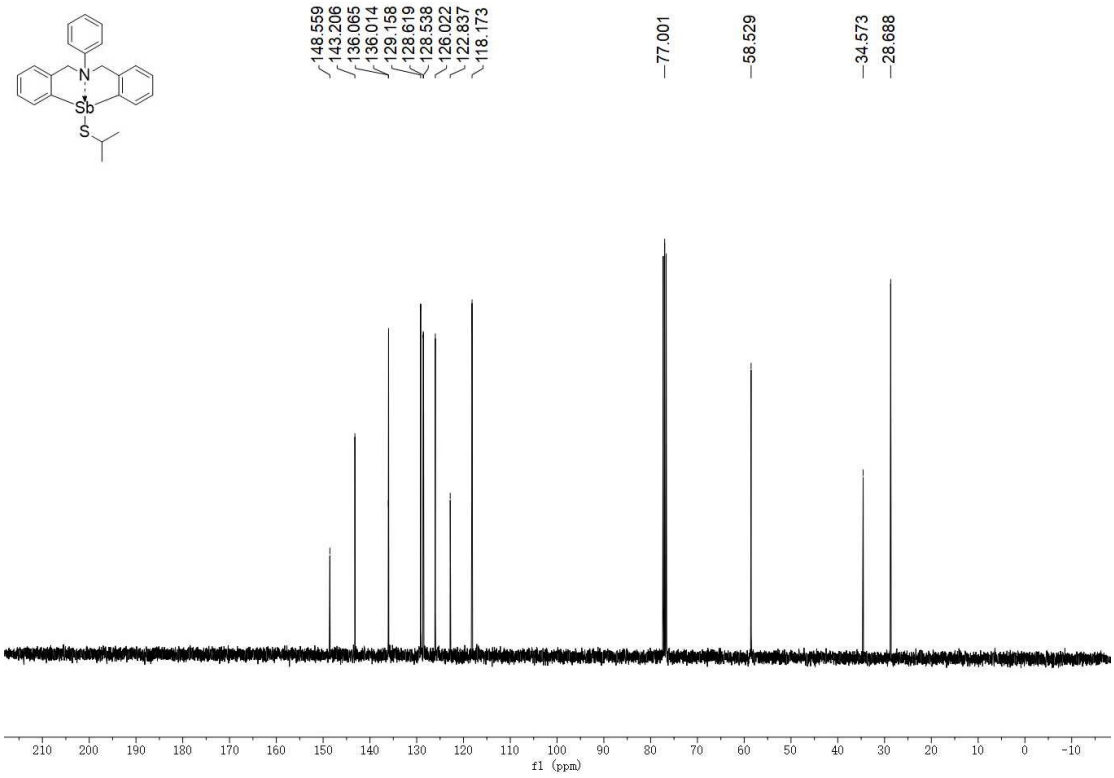


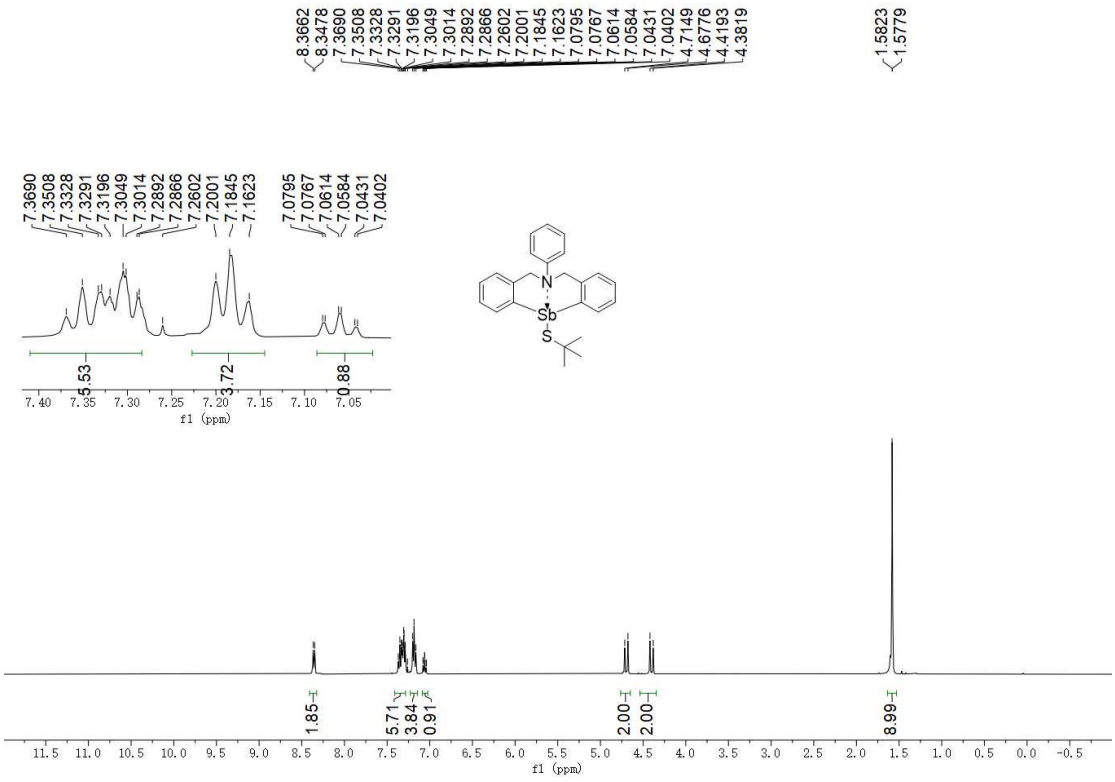
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**



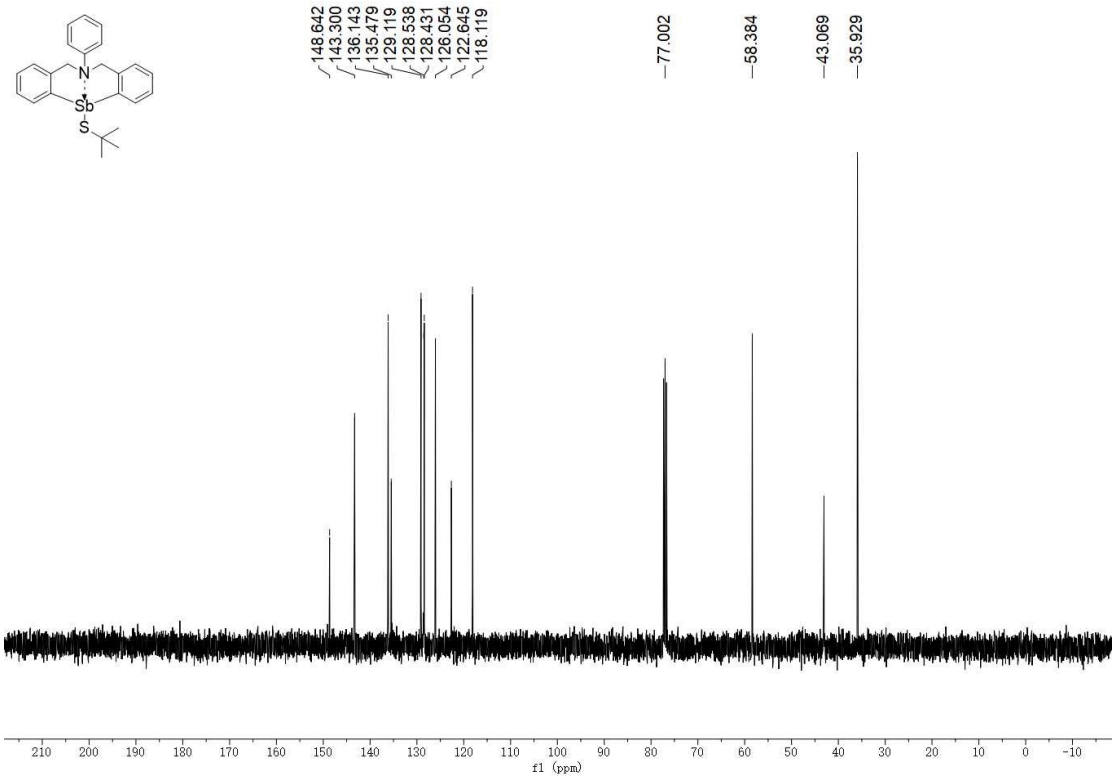
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



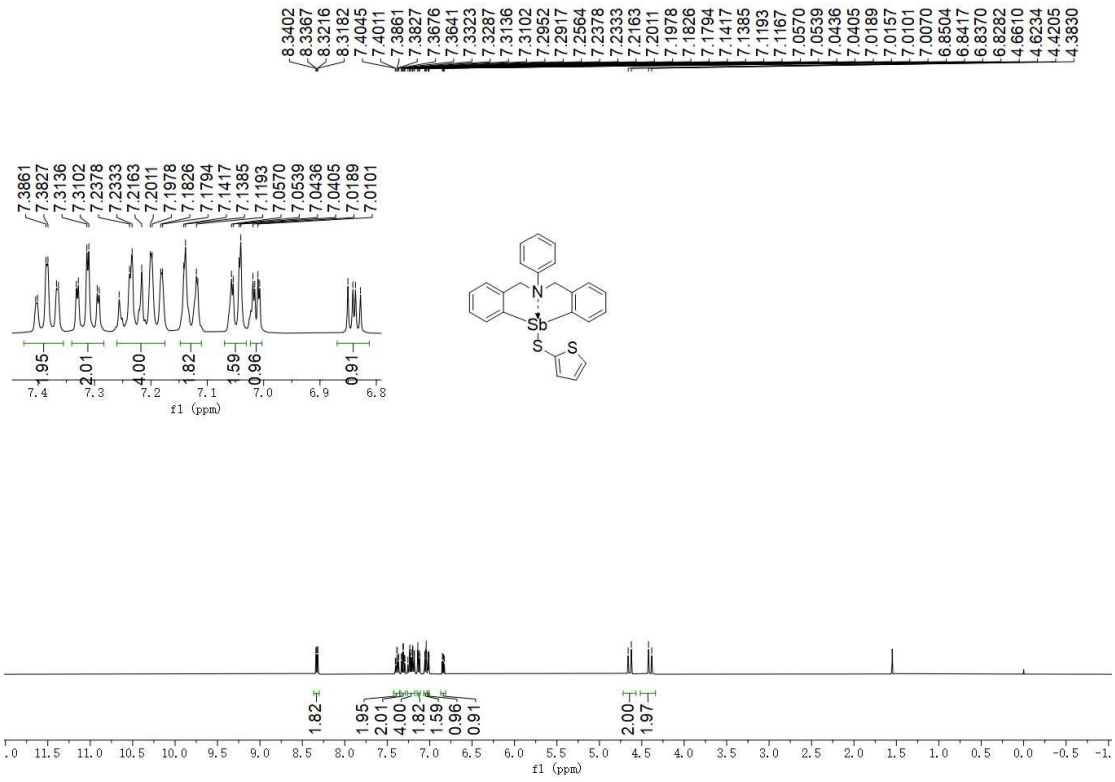
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**



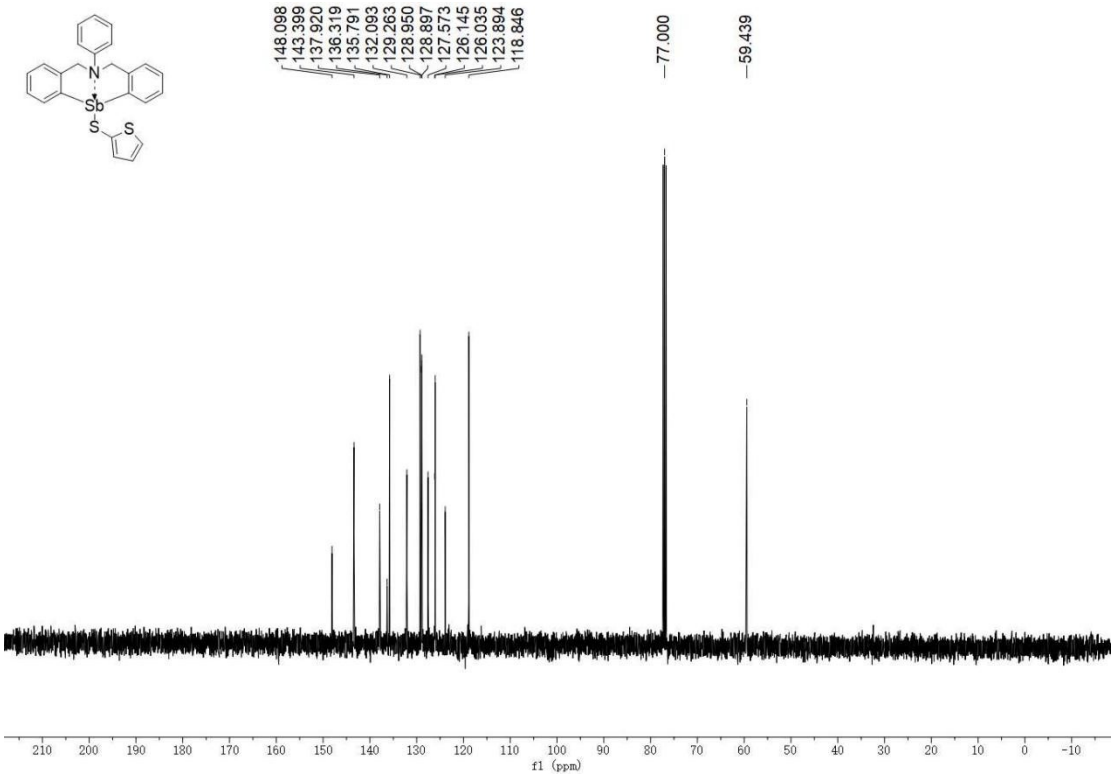
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3s**



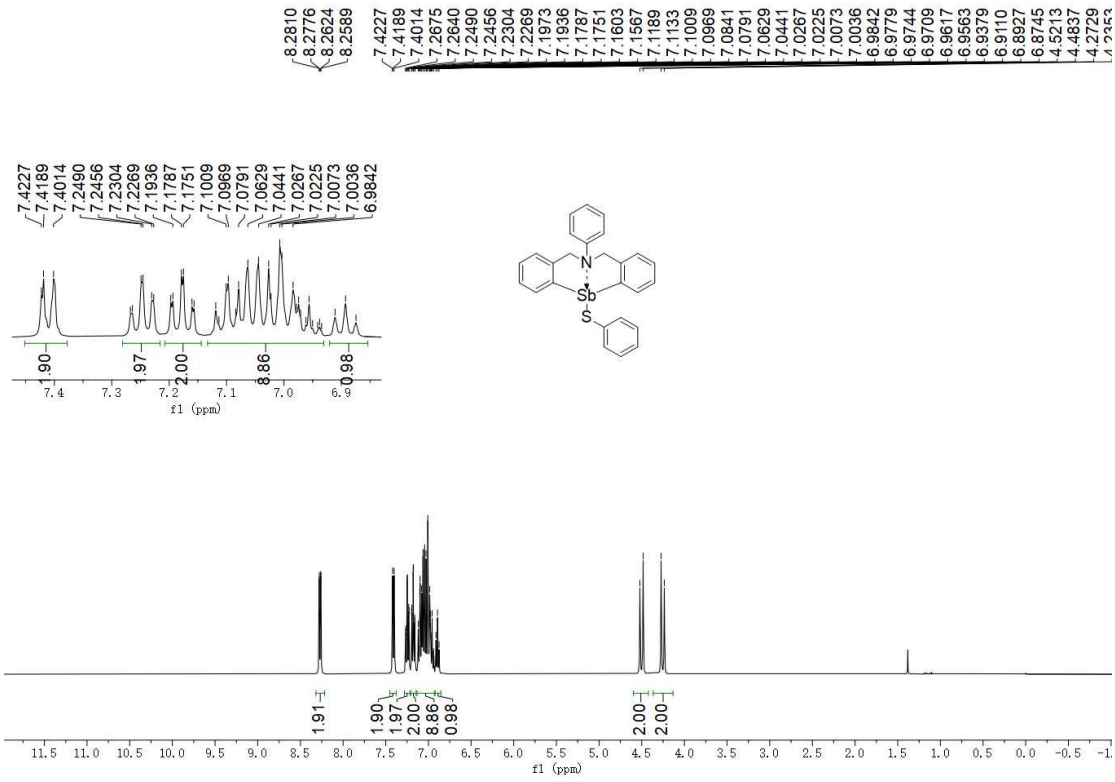
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3s**



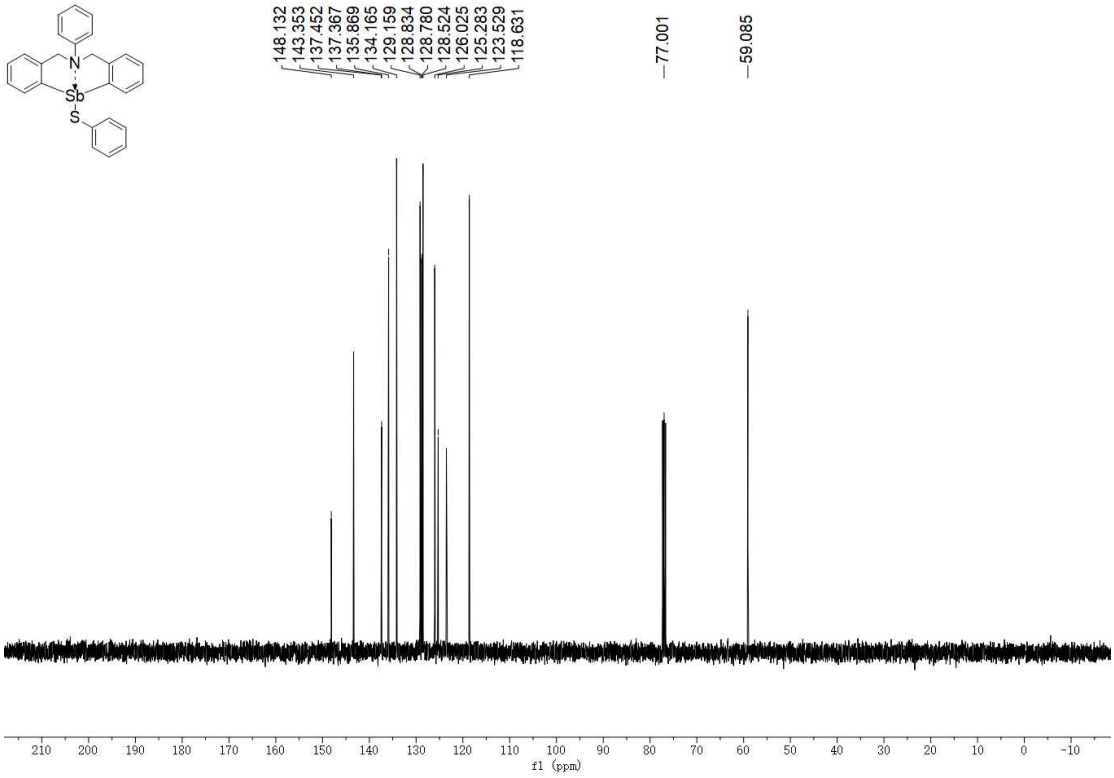
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3t**



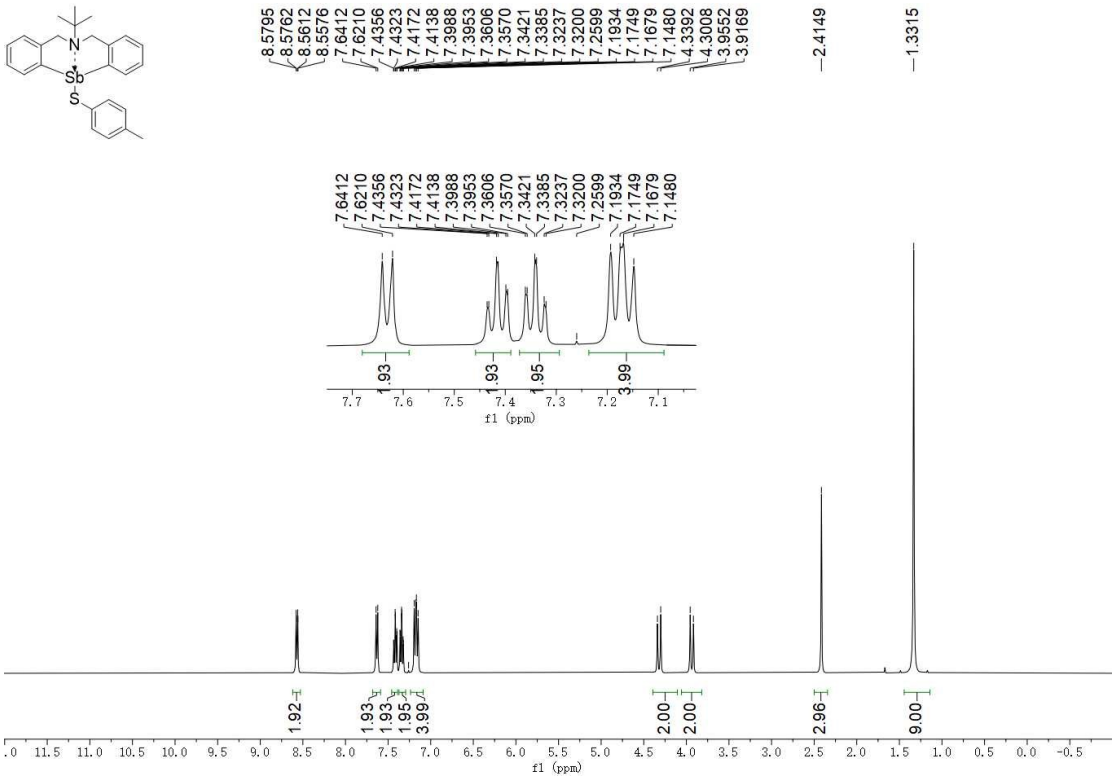
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3t**



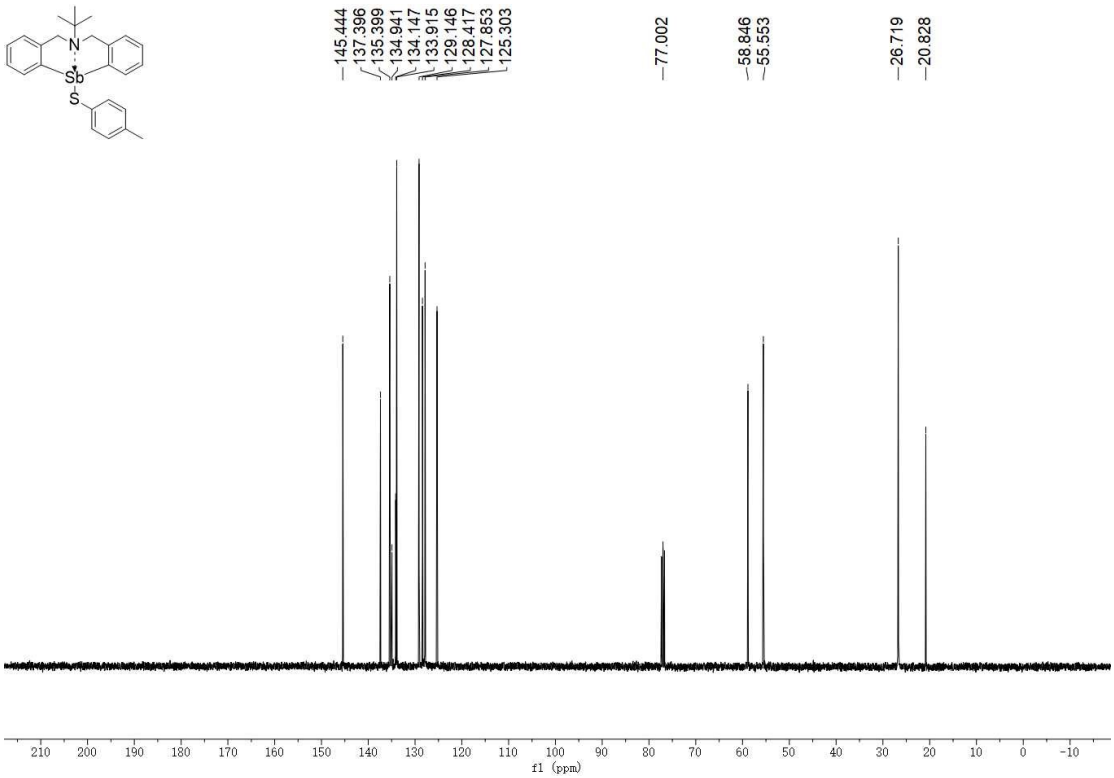
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3u**



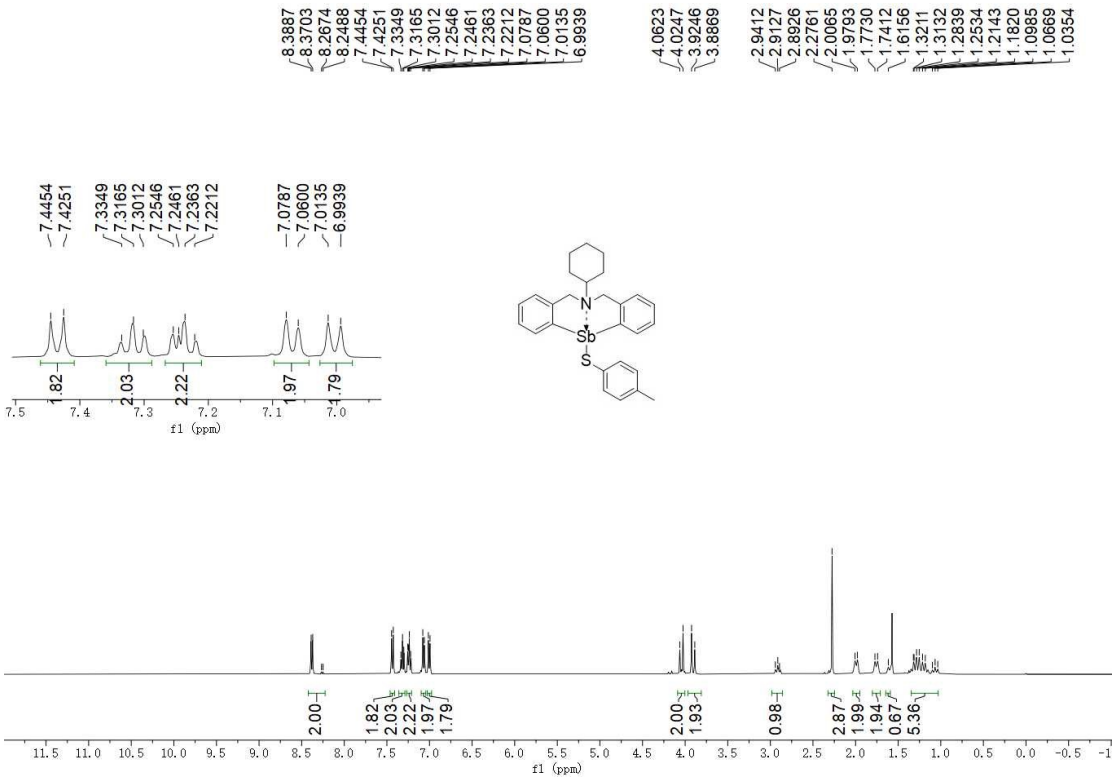
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3u**



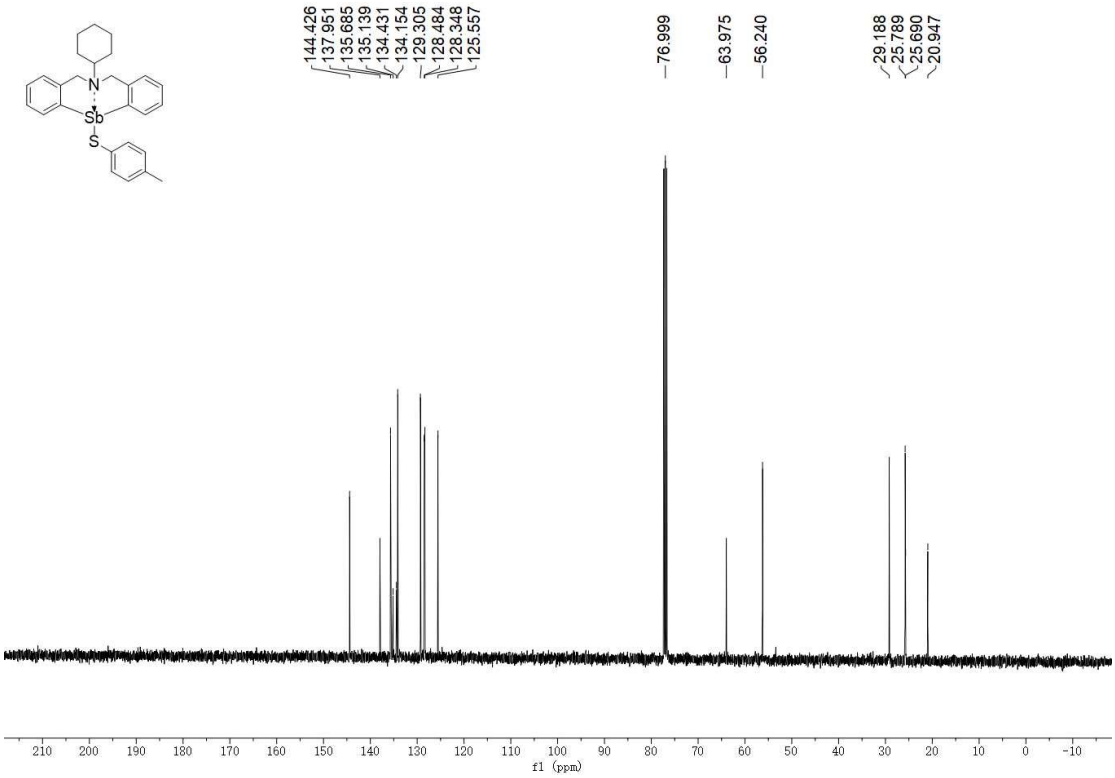
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3v**



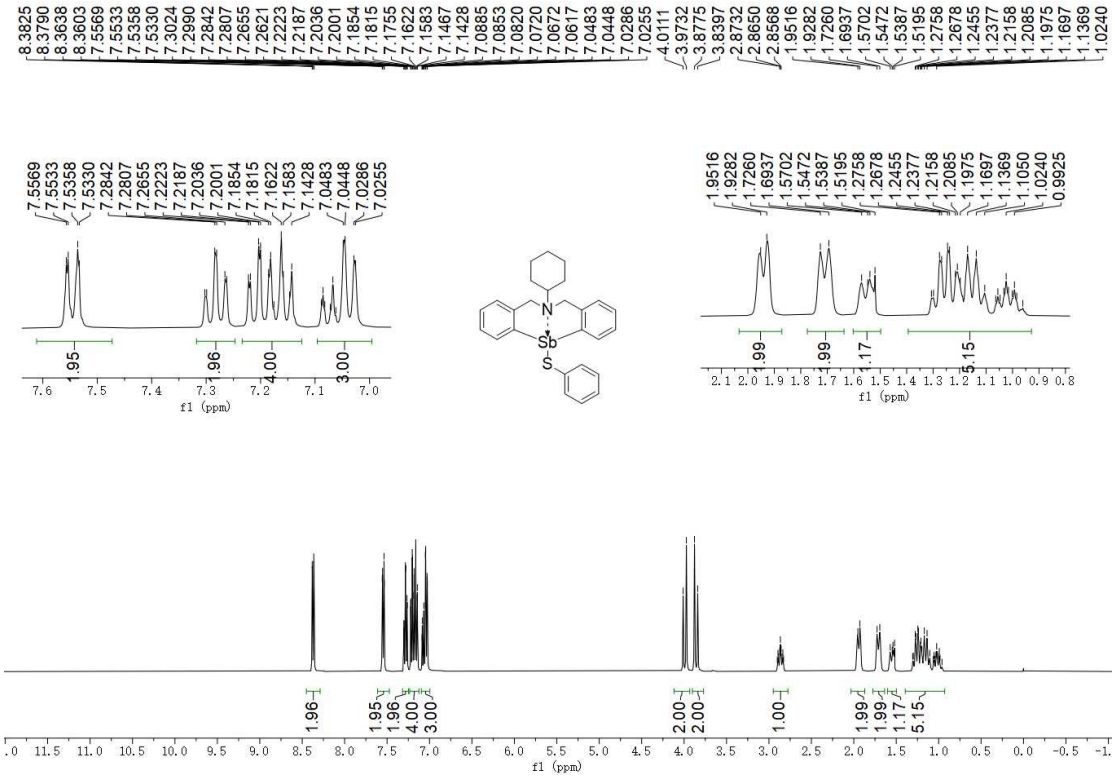
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3v**



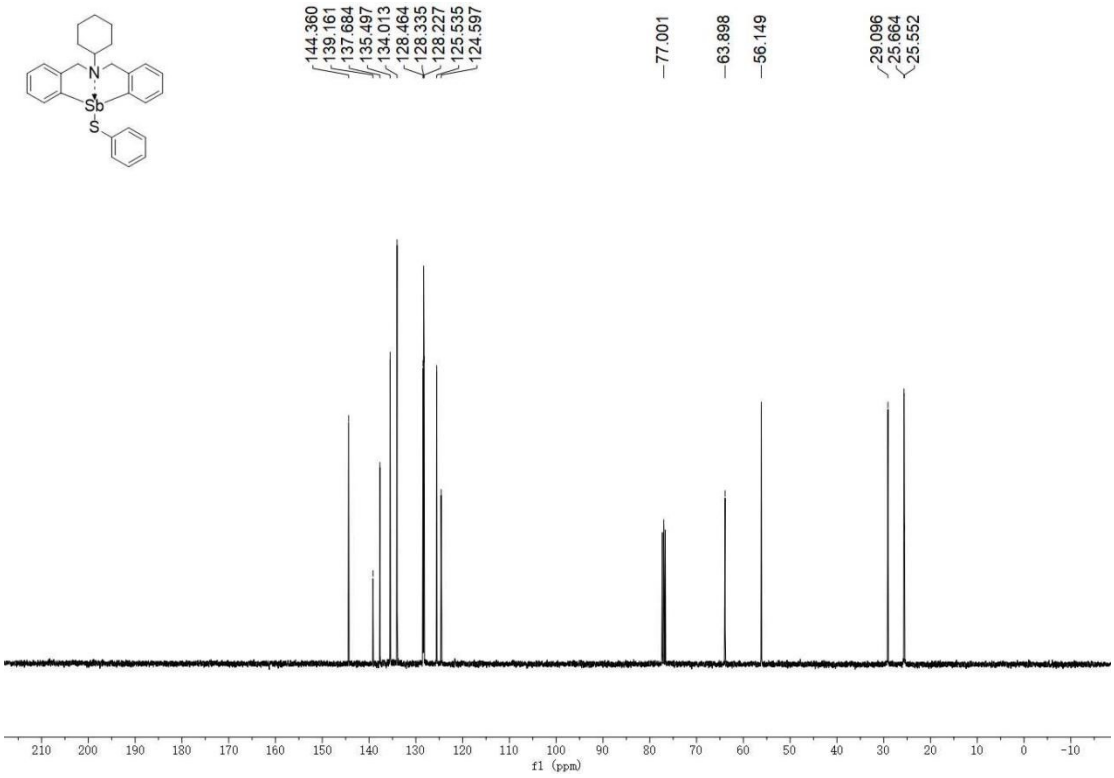
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3w**



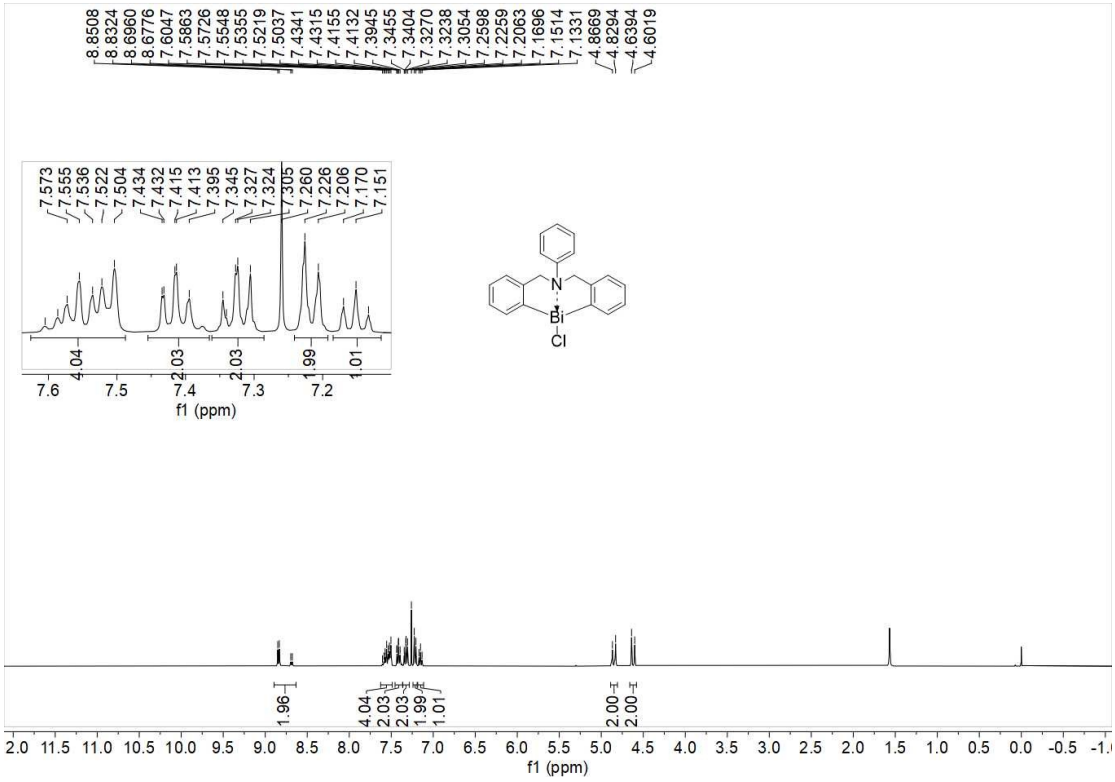
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3w**



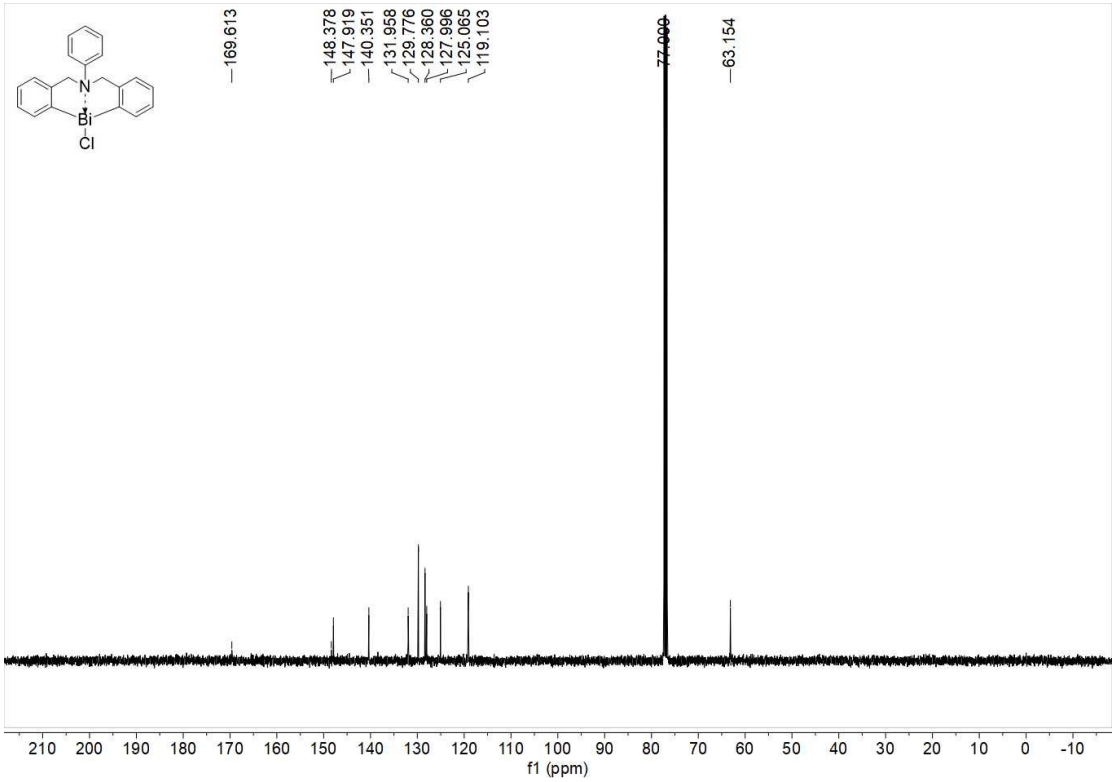
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3x**



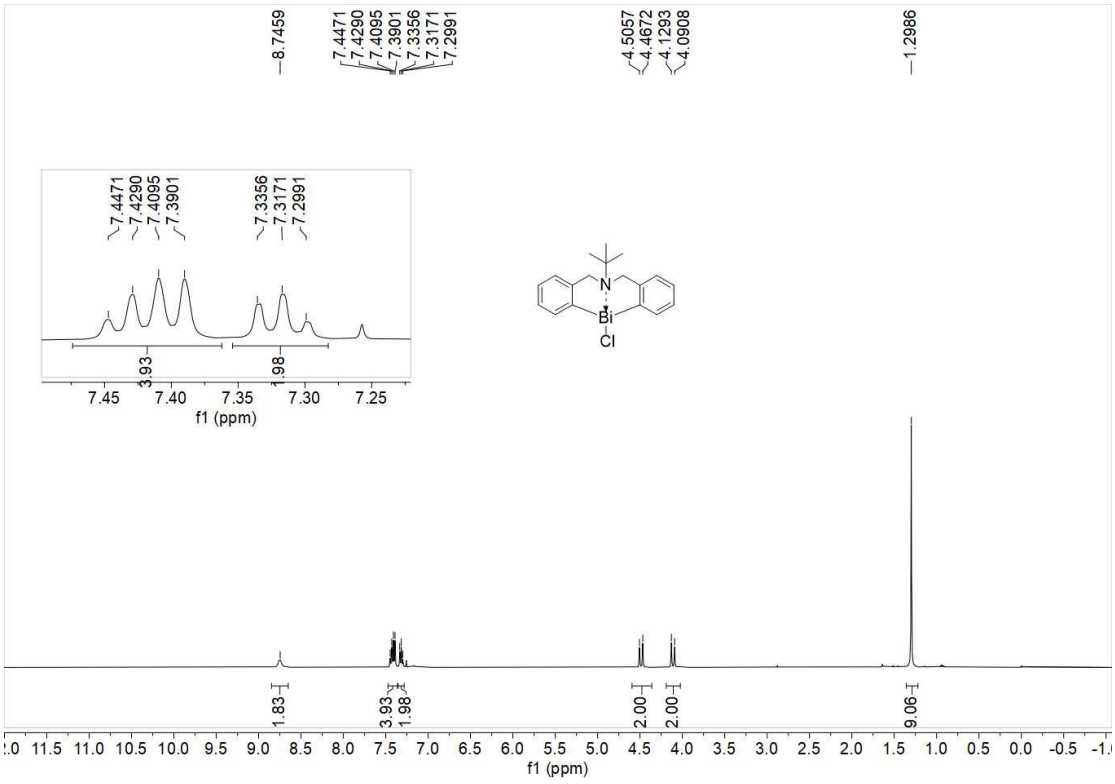
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3x**



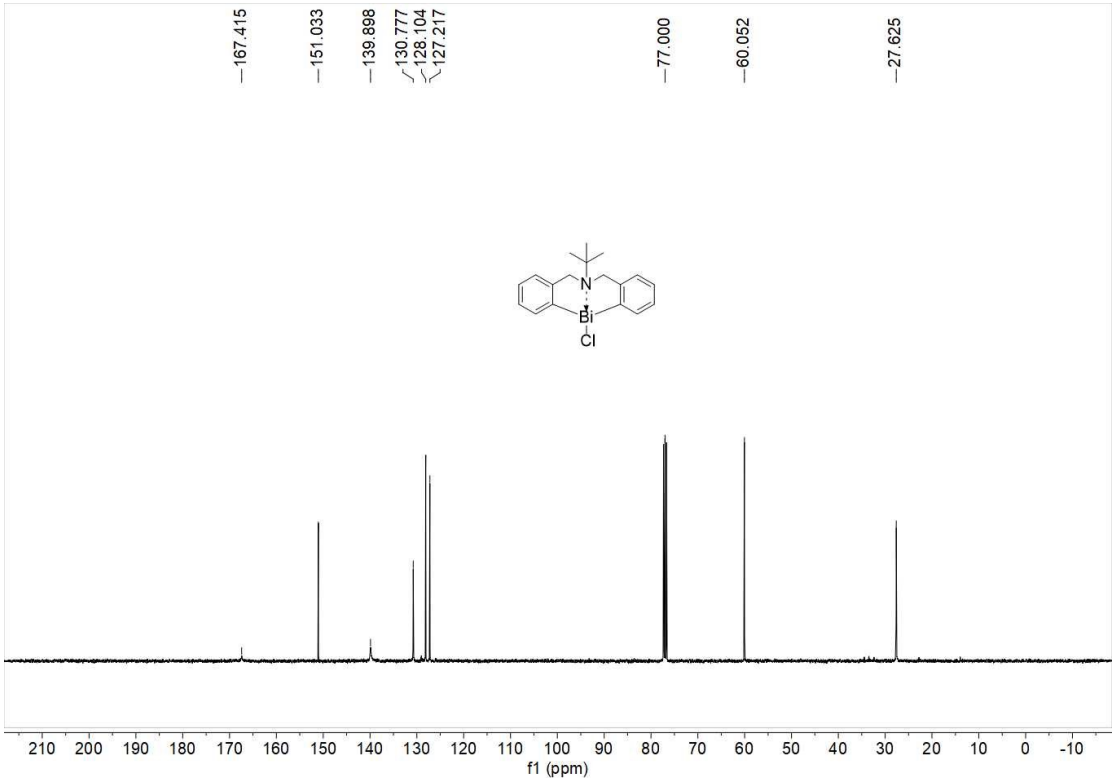
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**



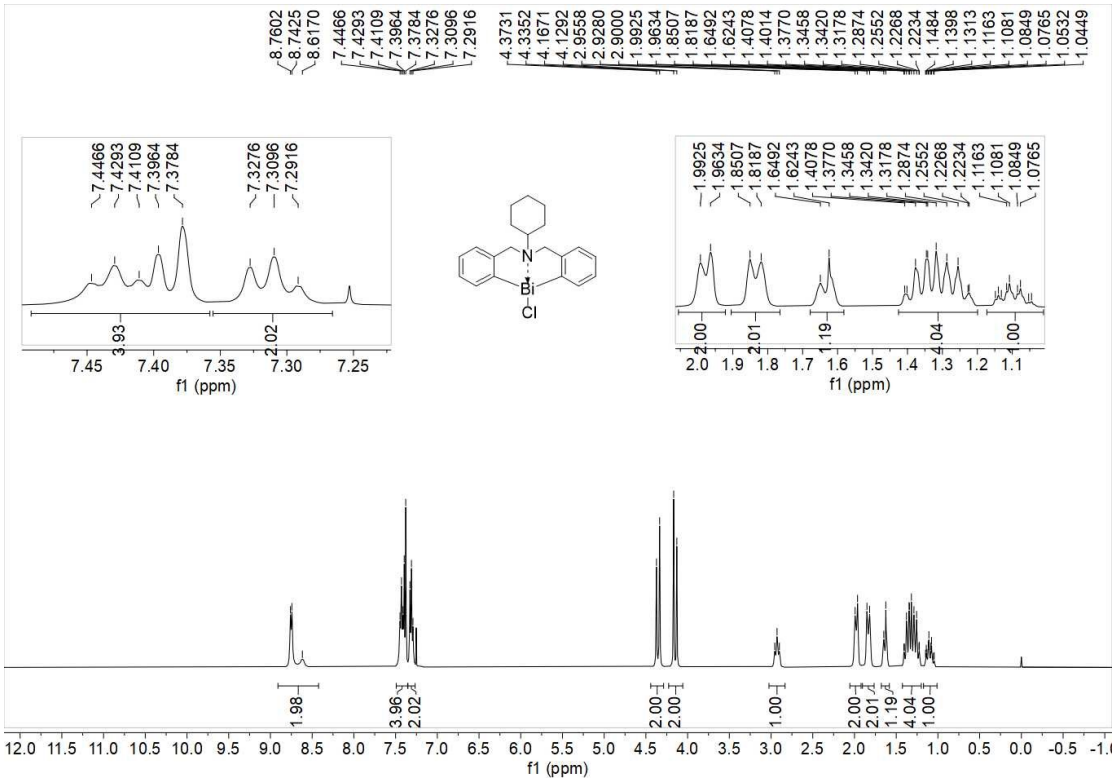
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**



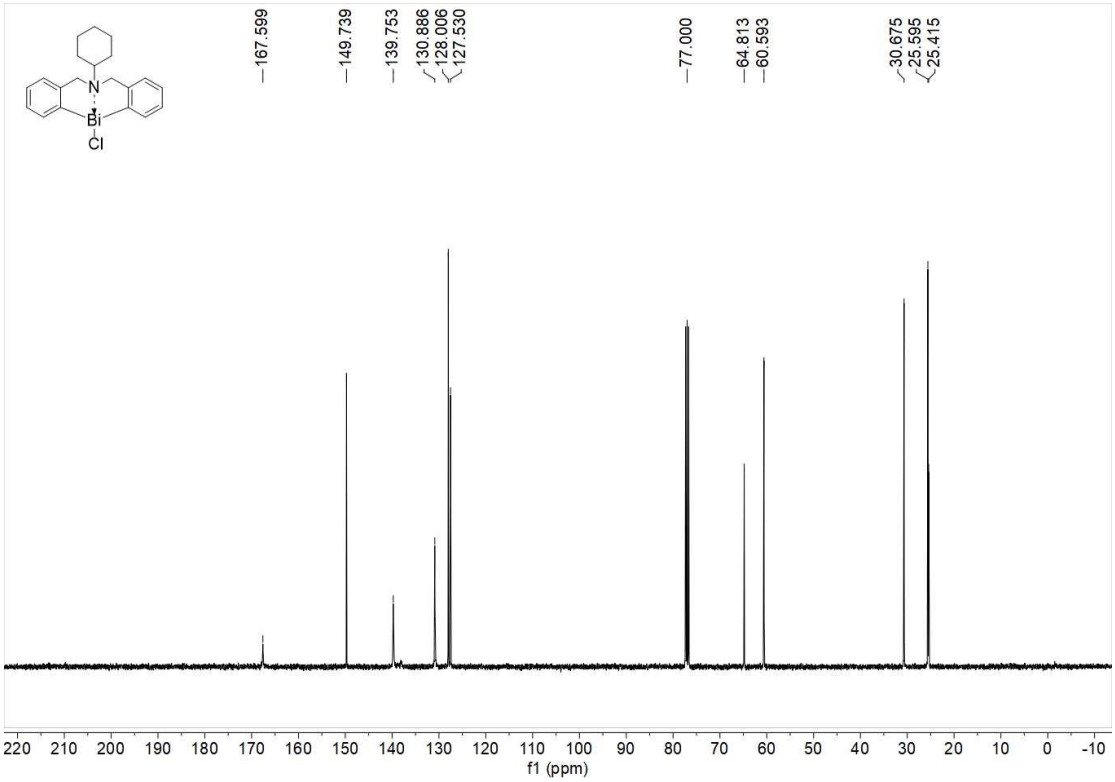
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**



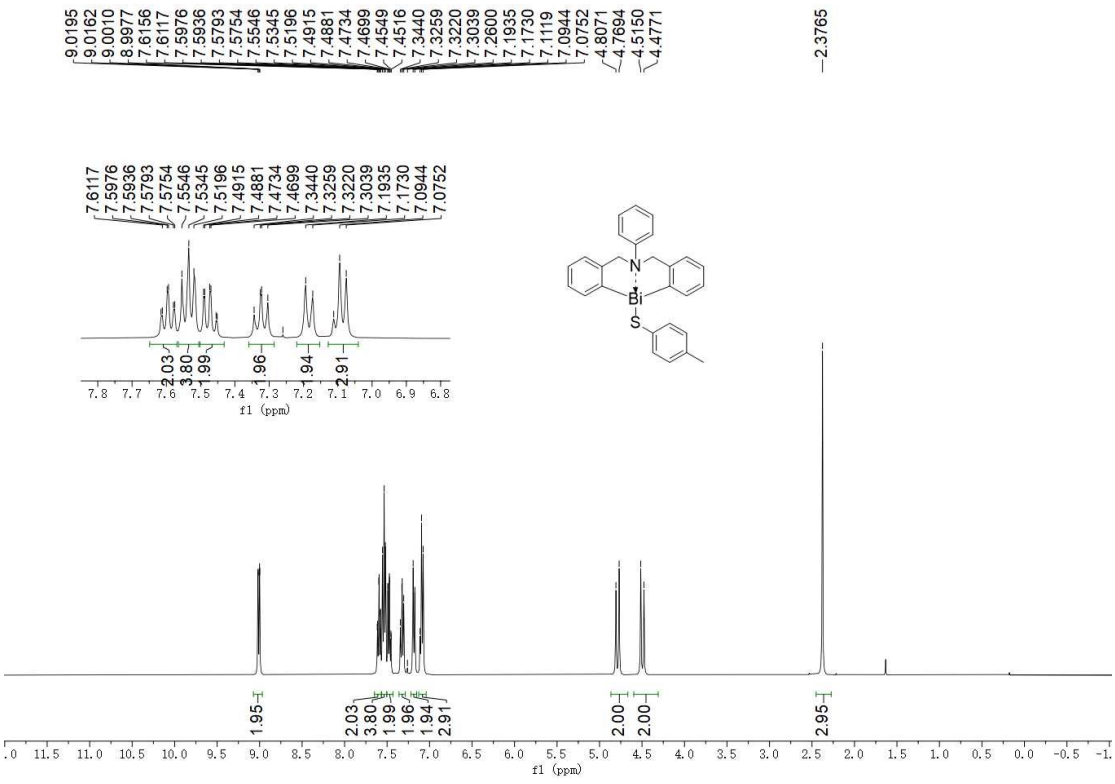
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**



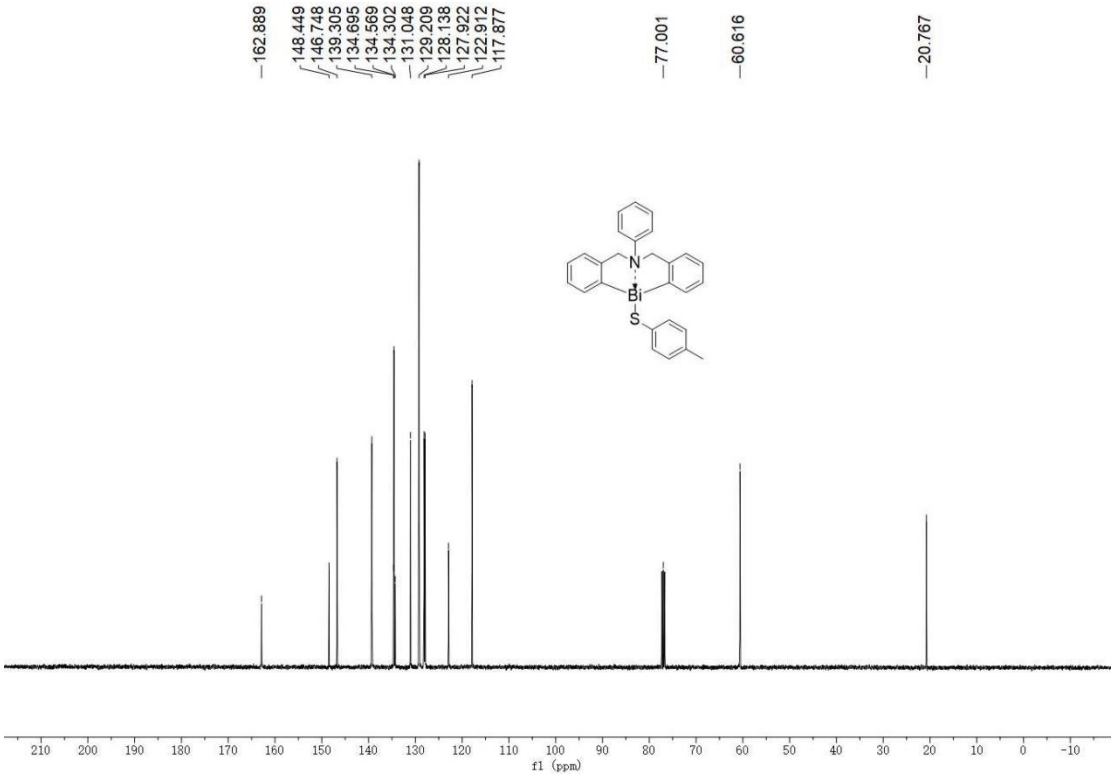
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**



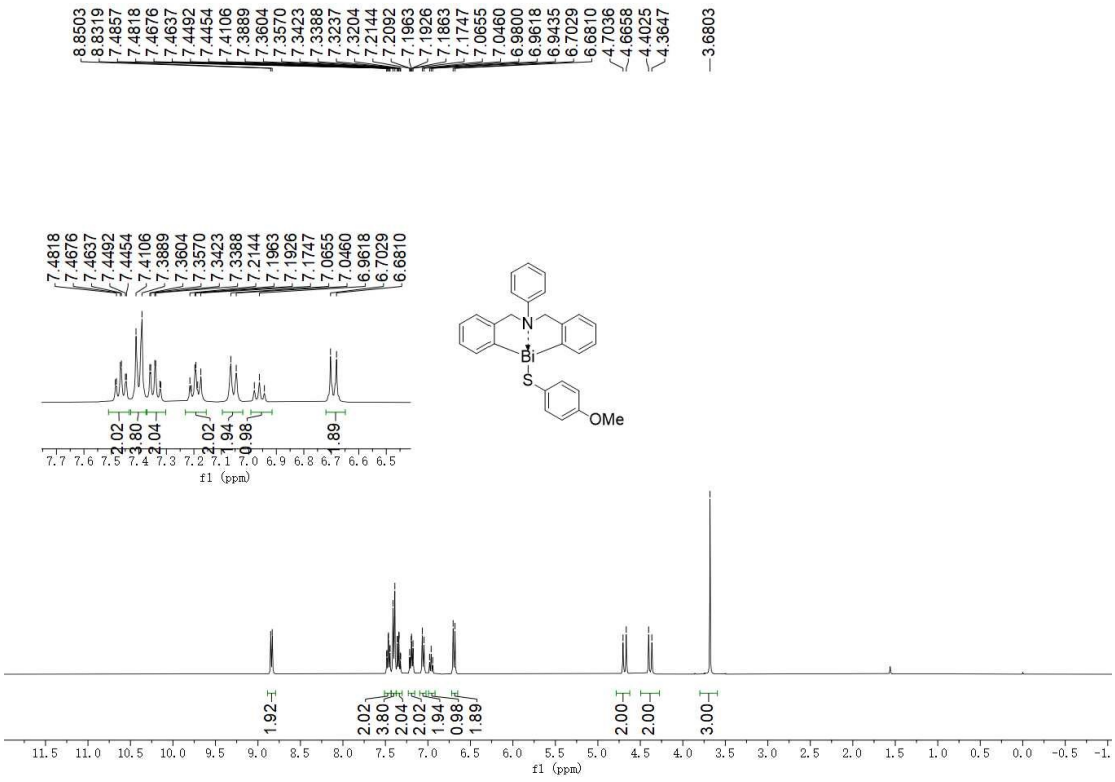
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**



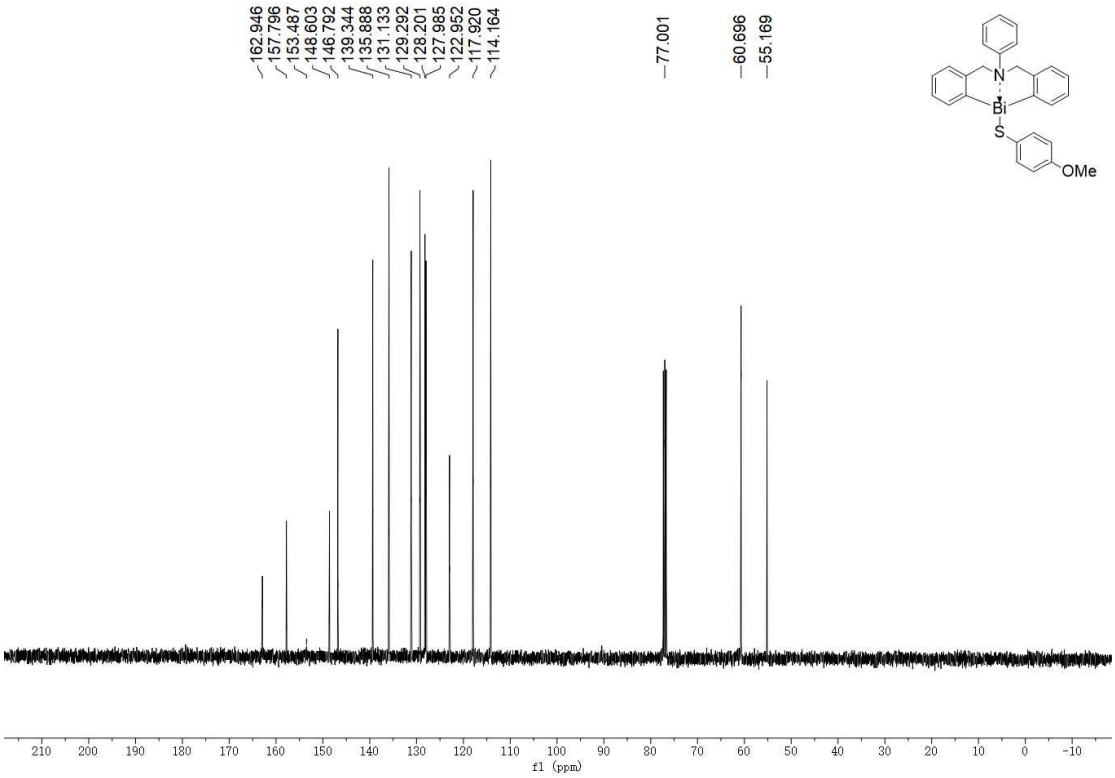
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**



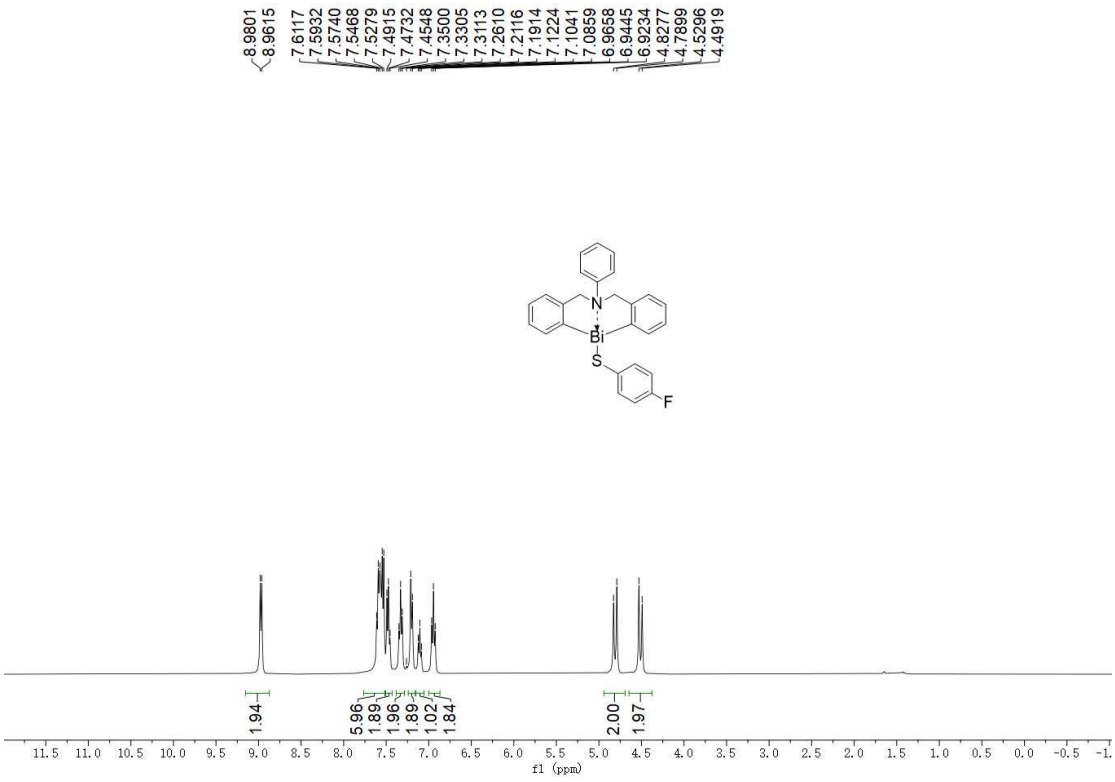
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5a**



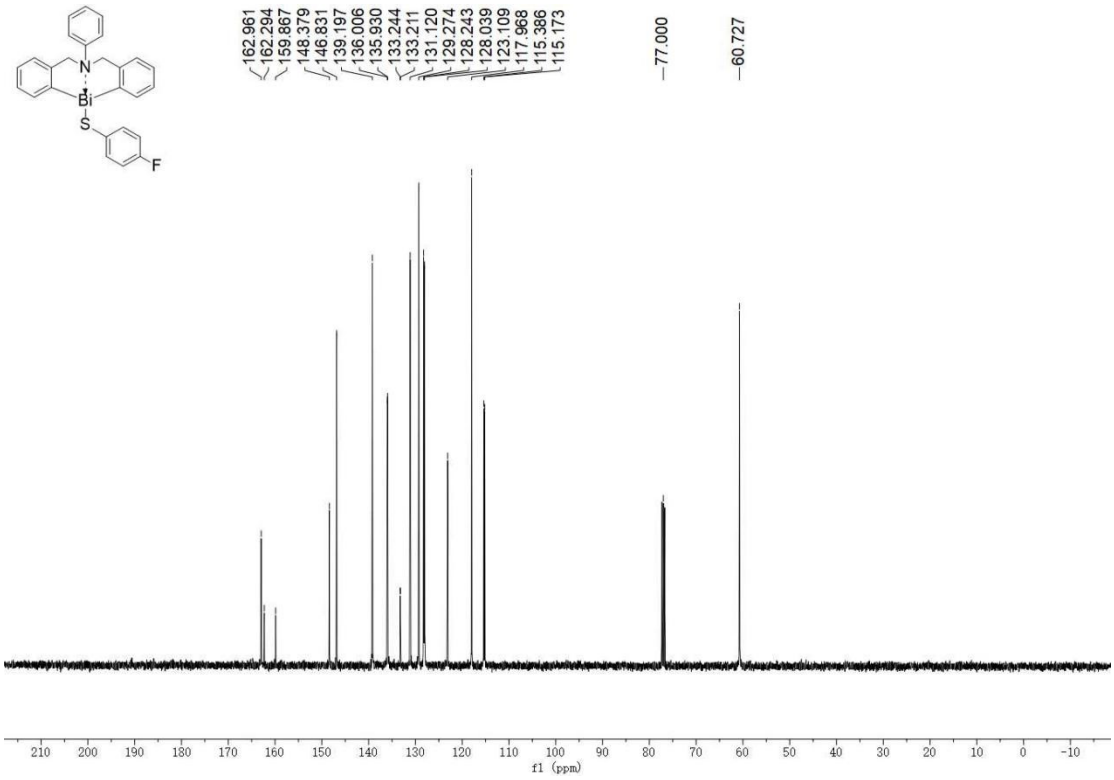
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**



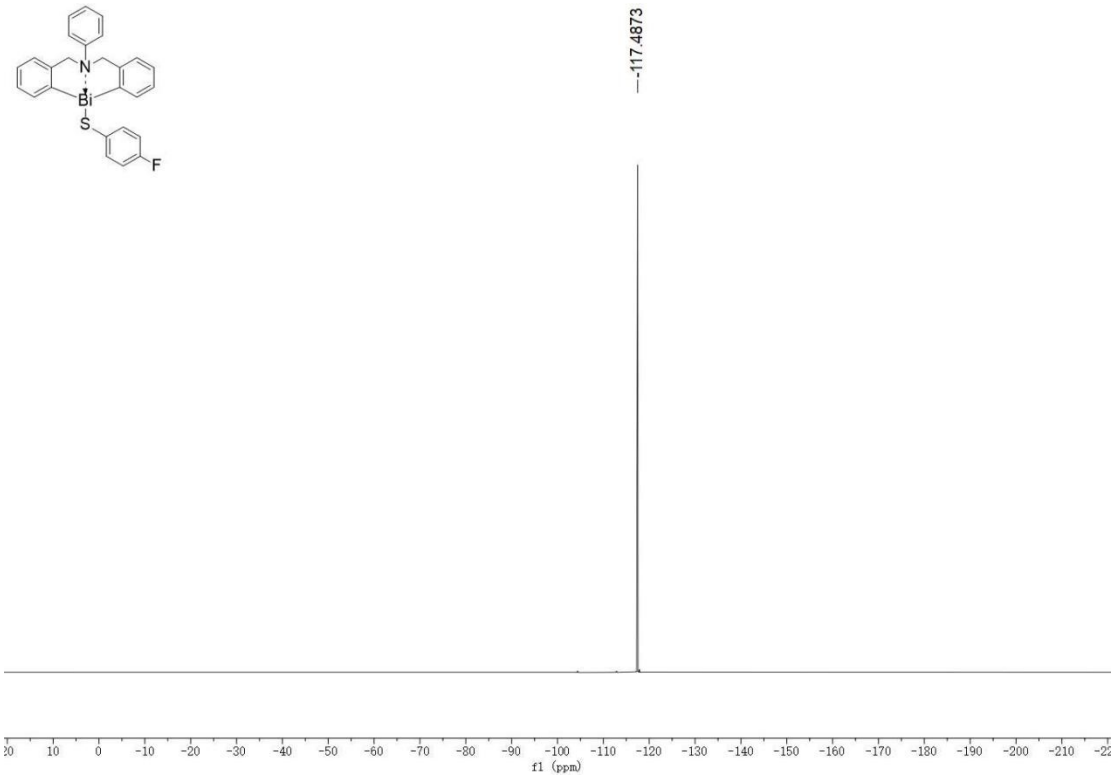
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5b**



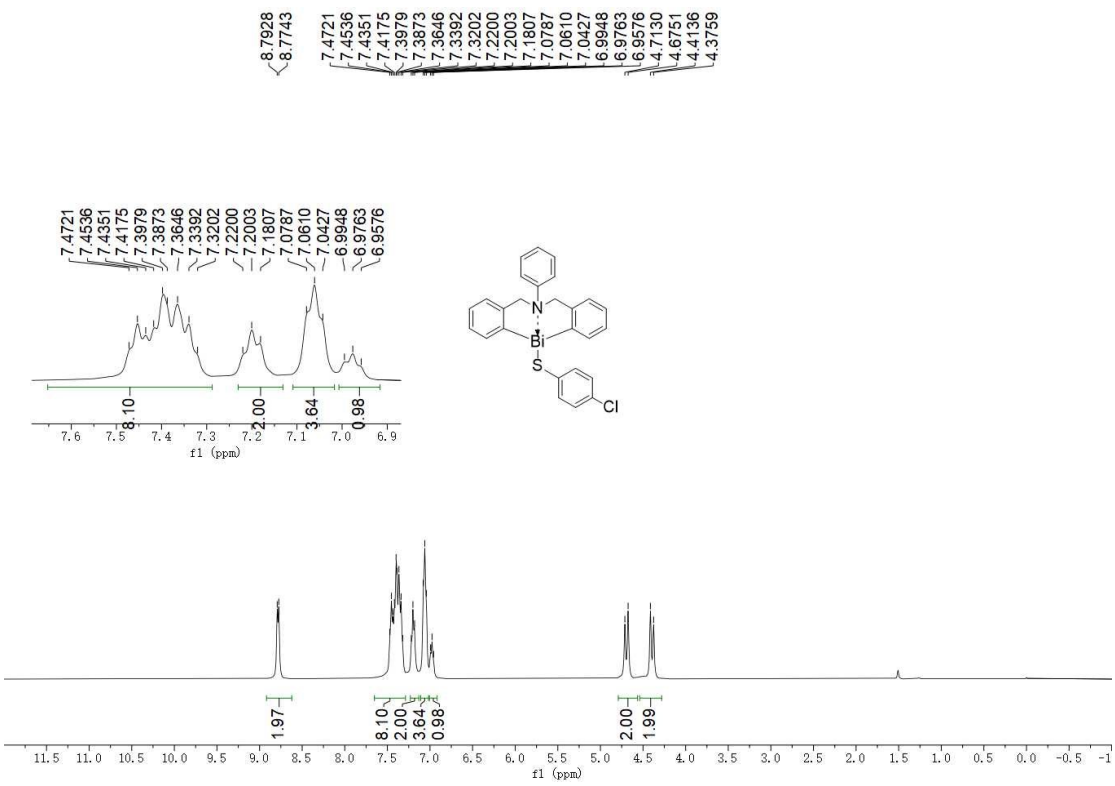
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**



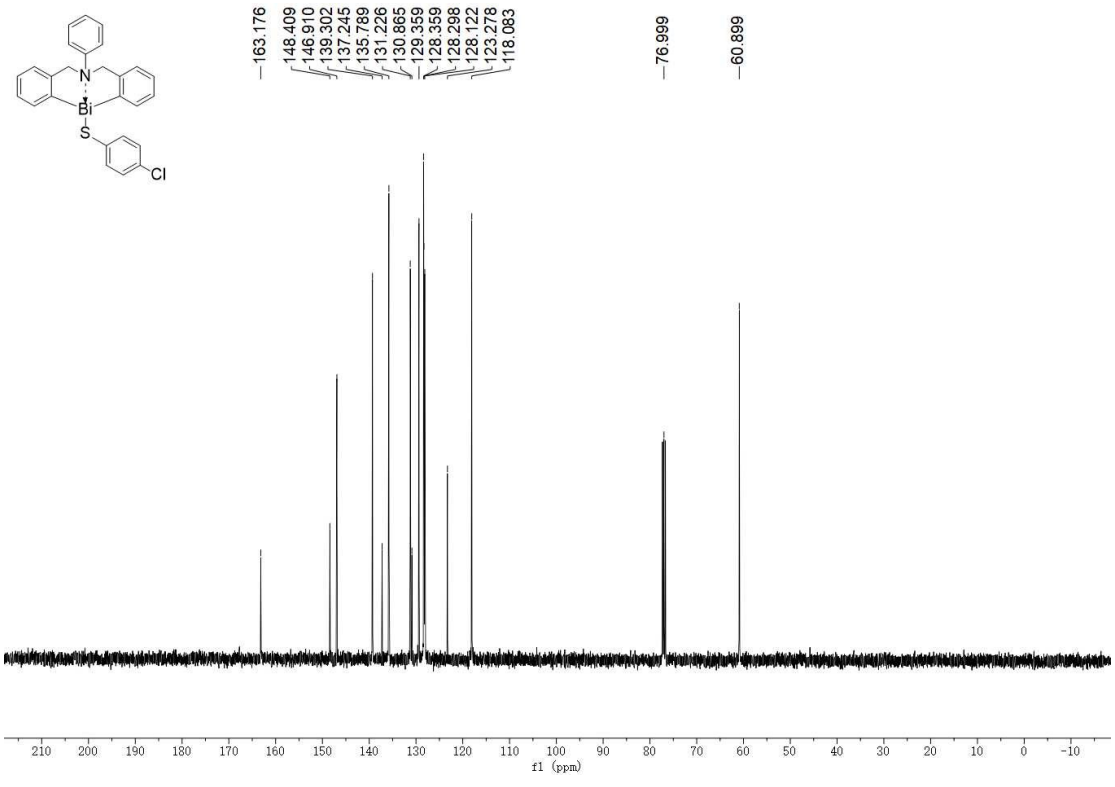
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5c**



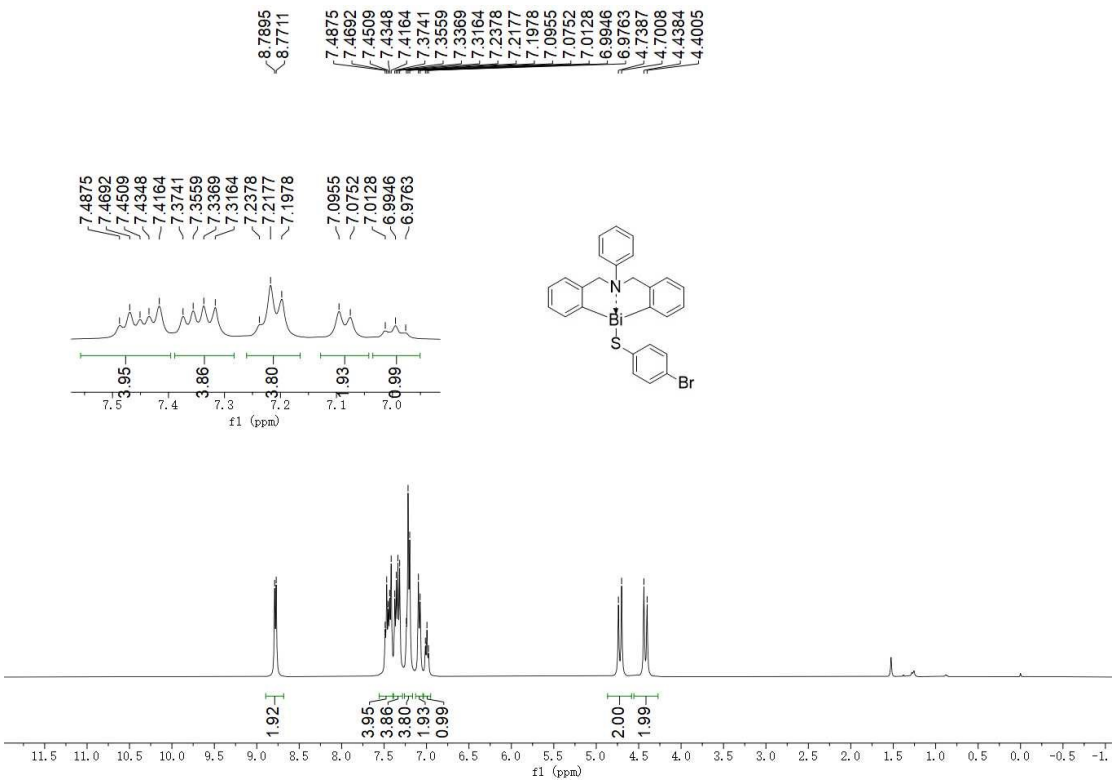
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5c**



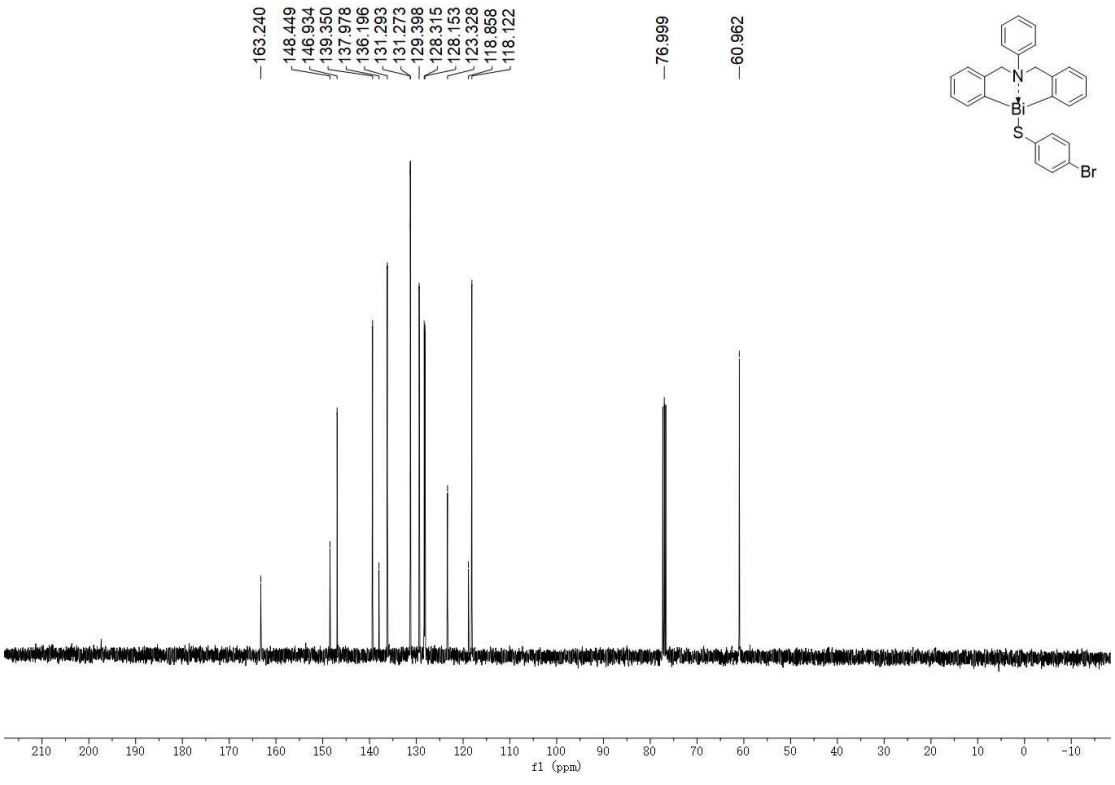
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**



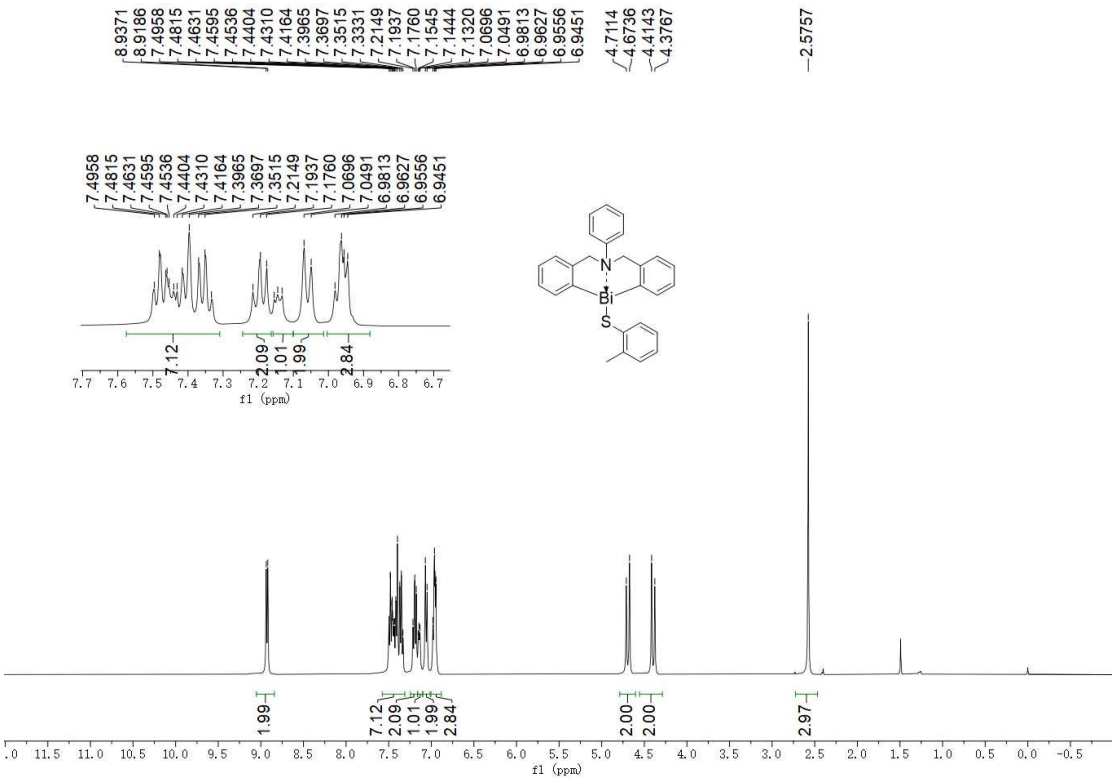
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5d**



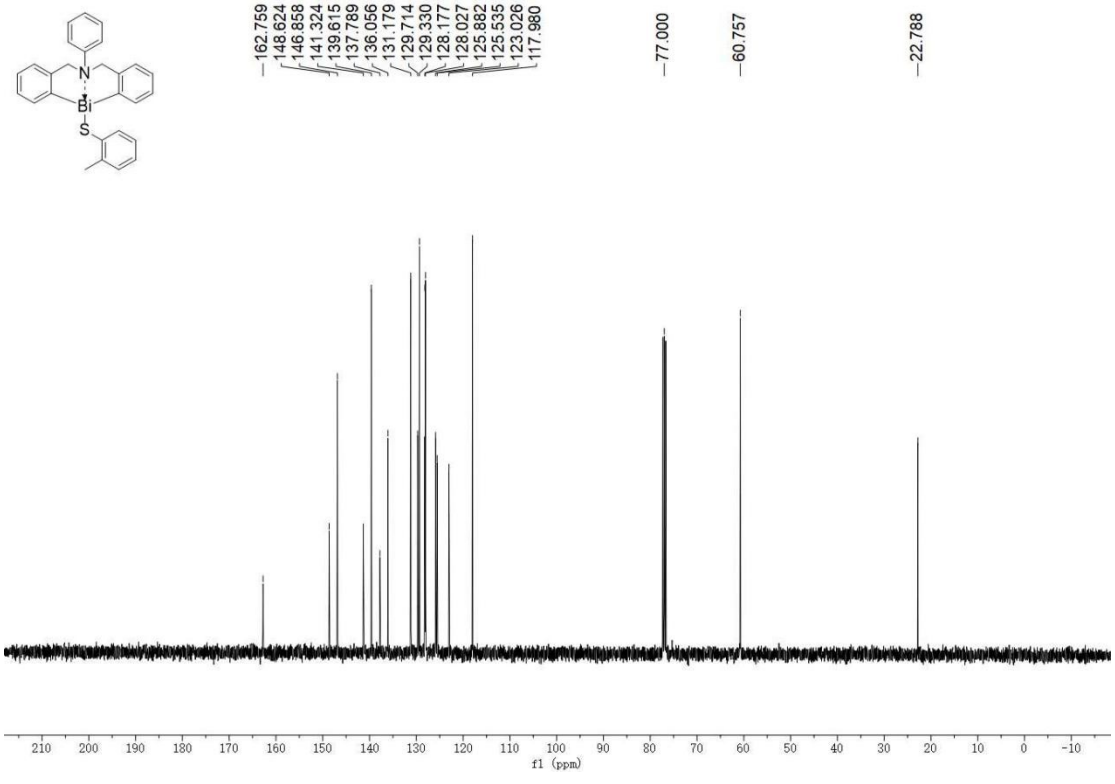
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**



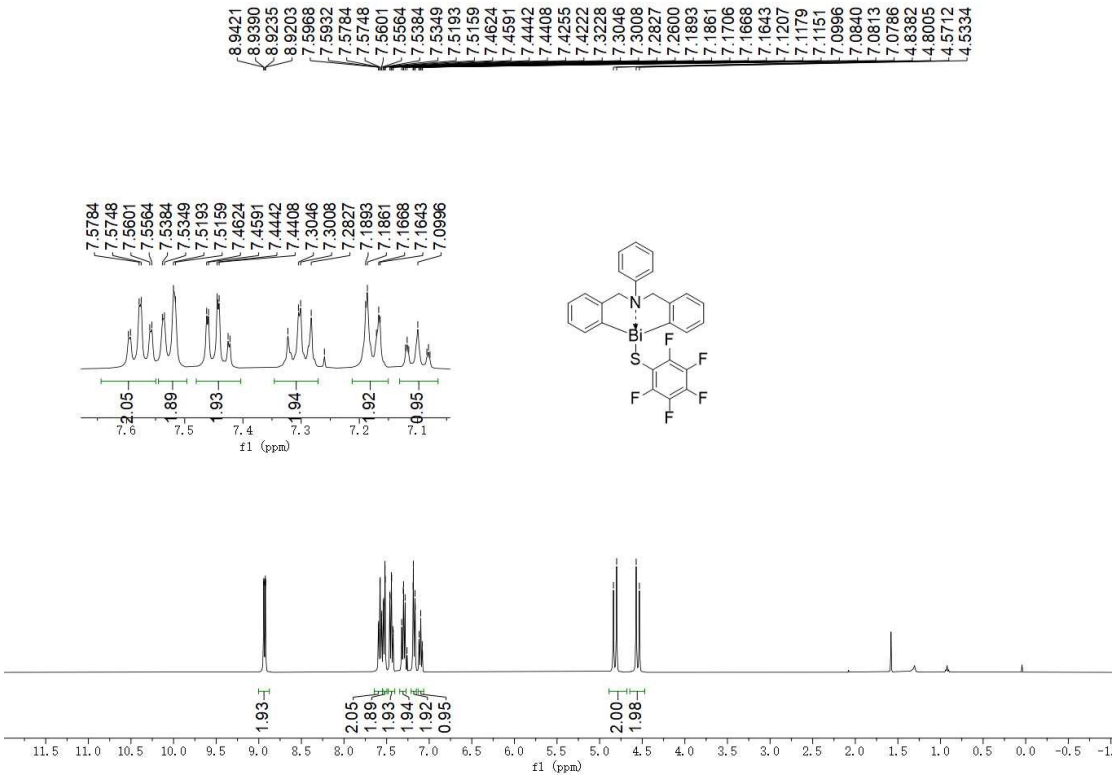
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5e**



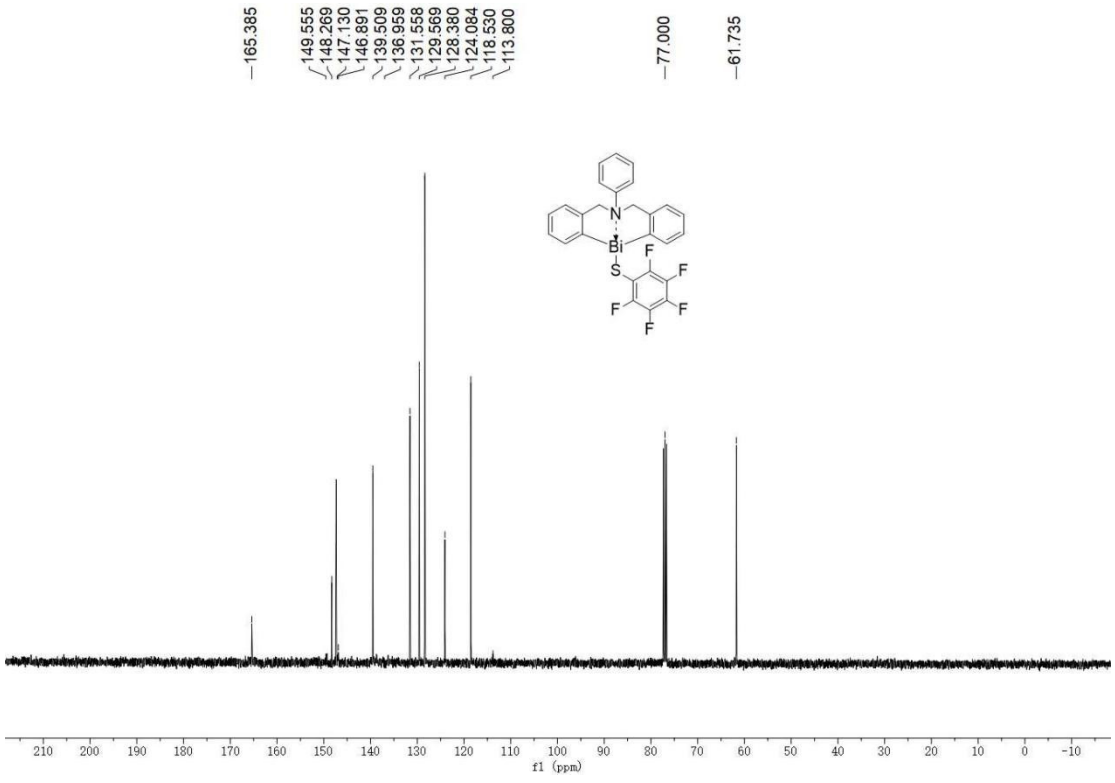
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**



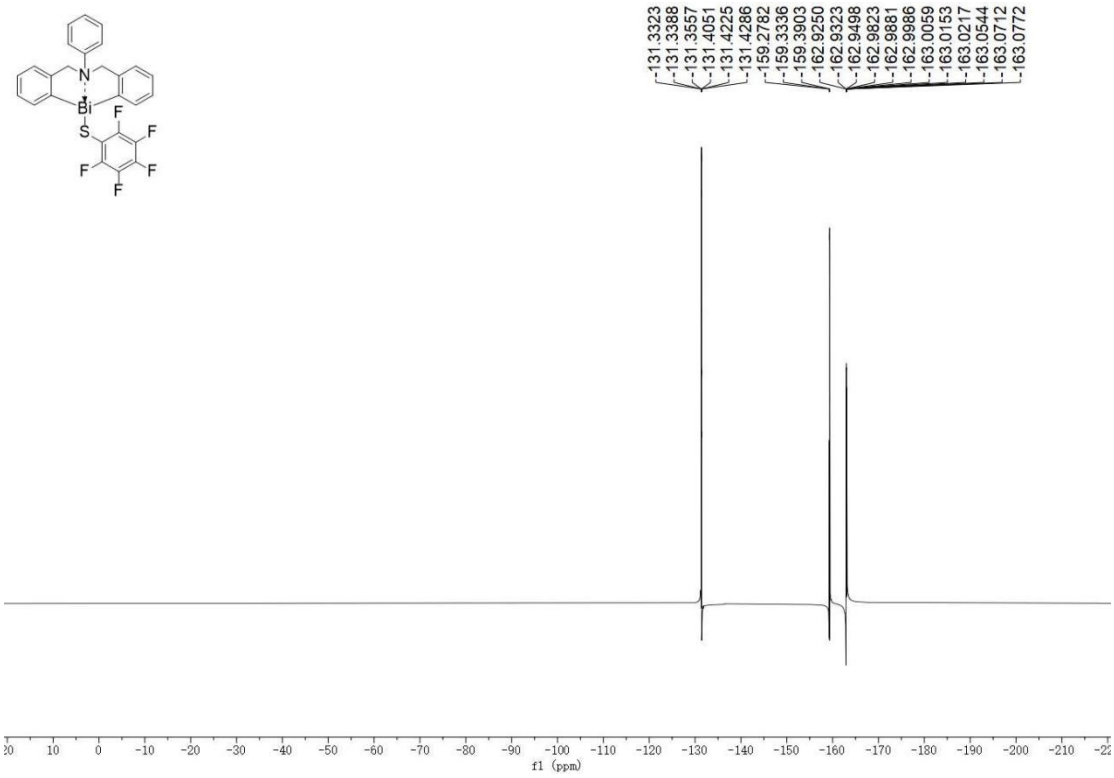
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5f**



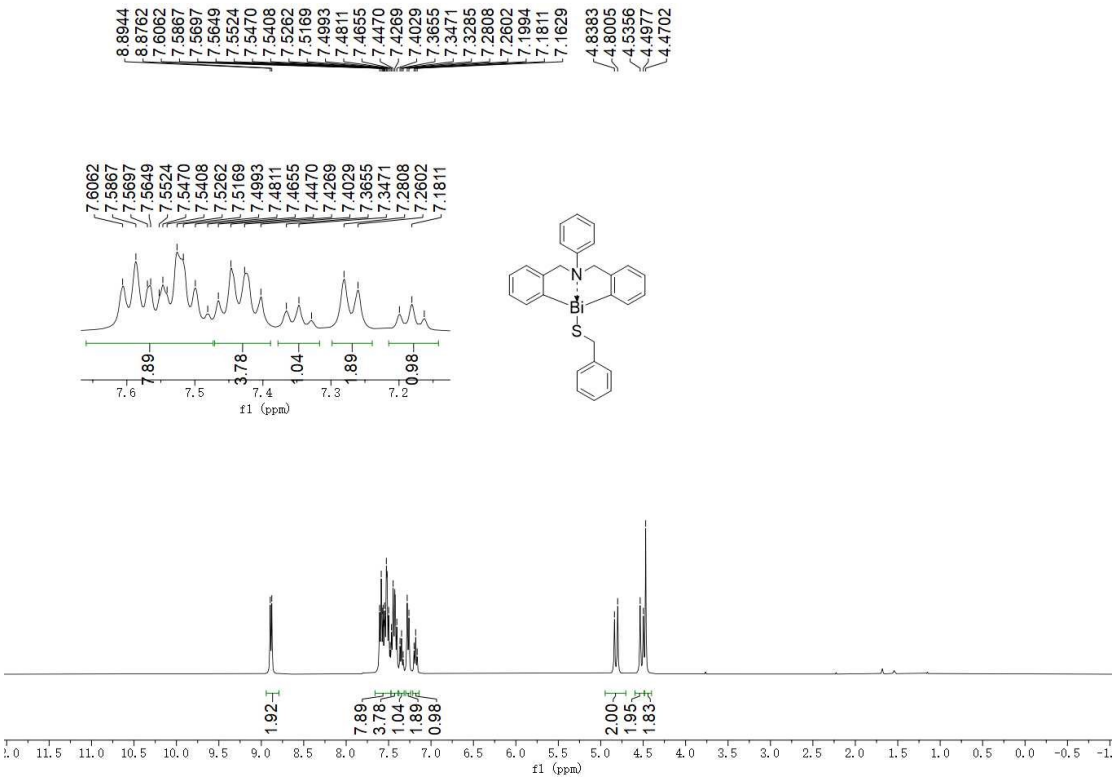
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5g**



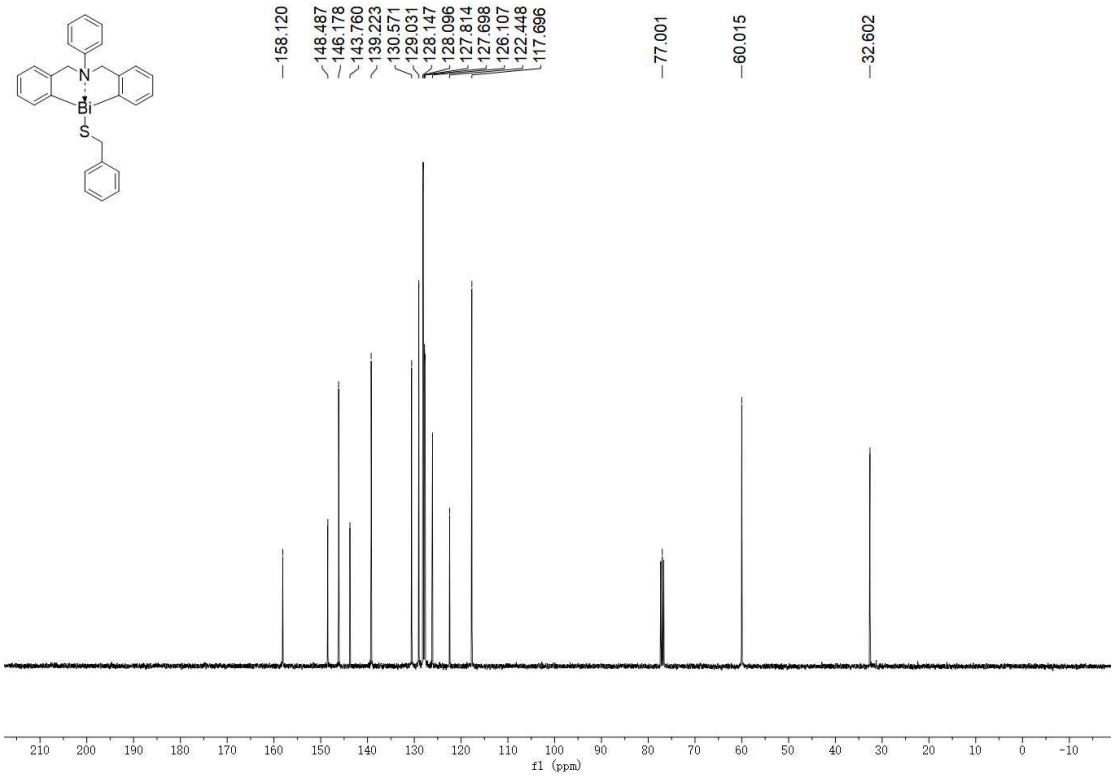
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5g**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5g**

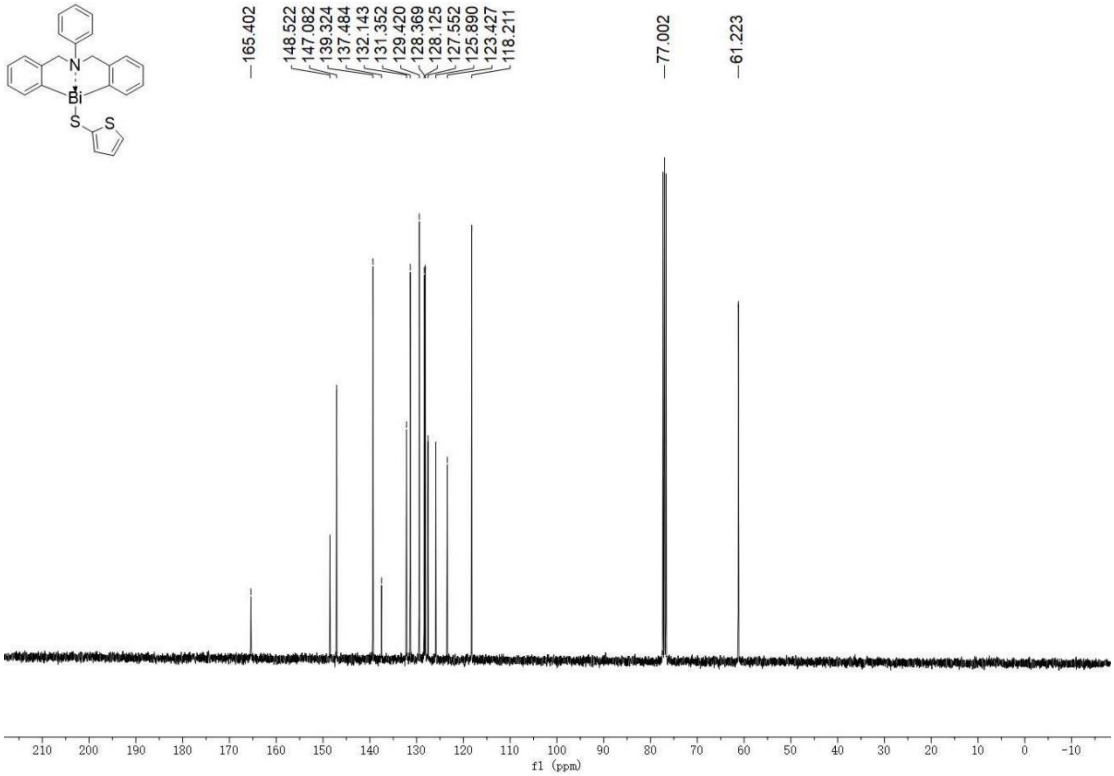


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**

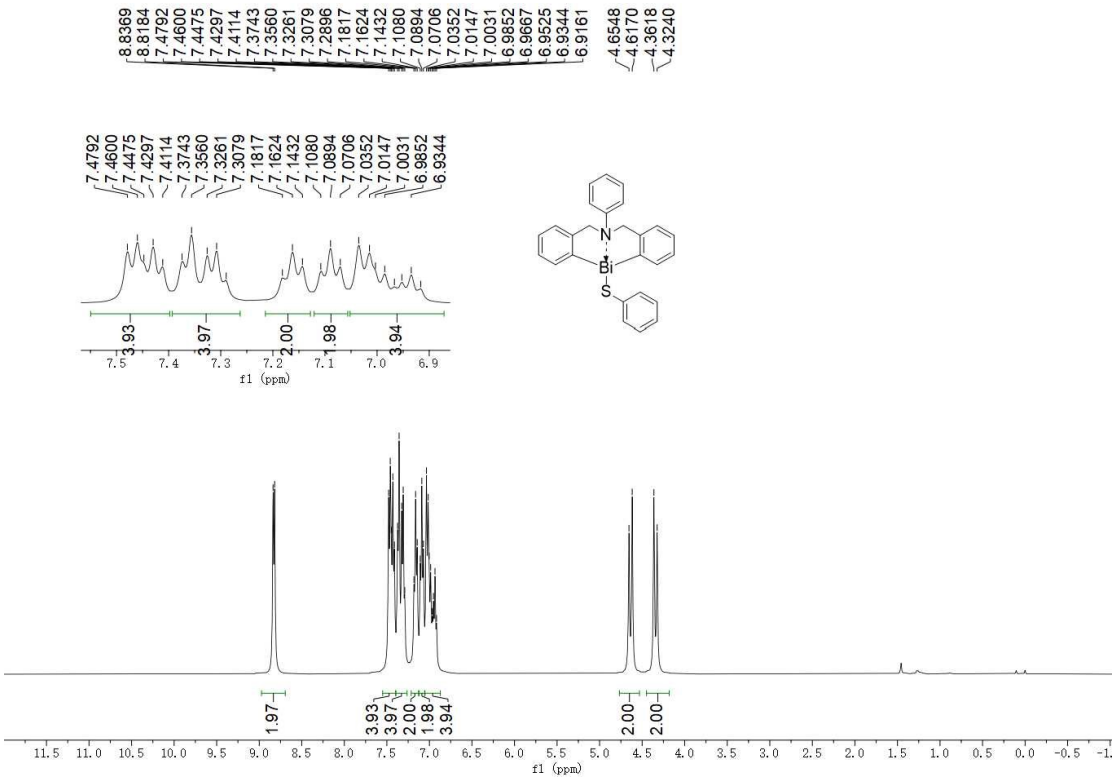


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5h**

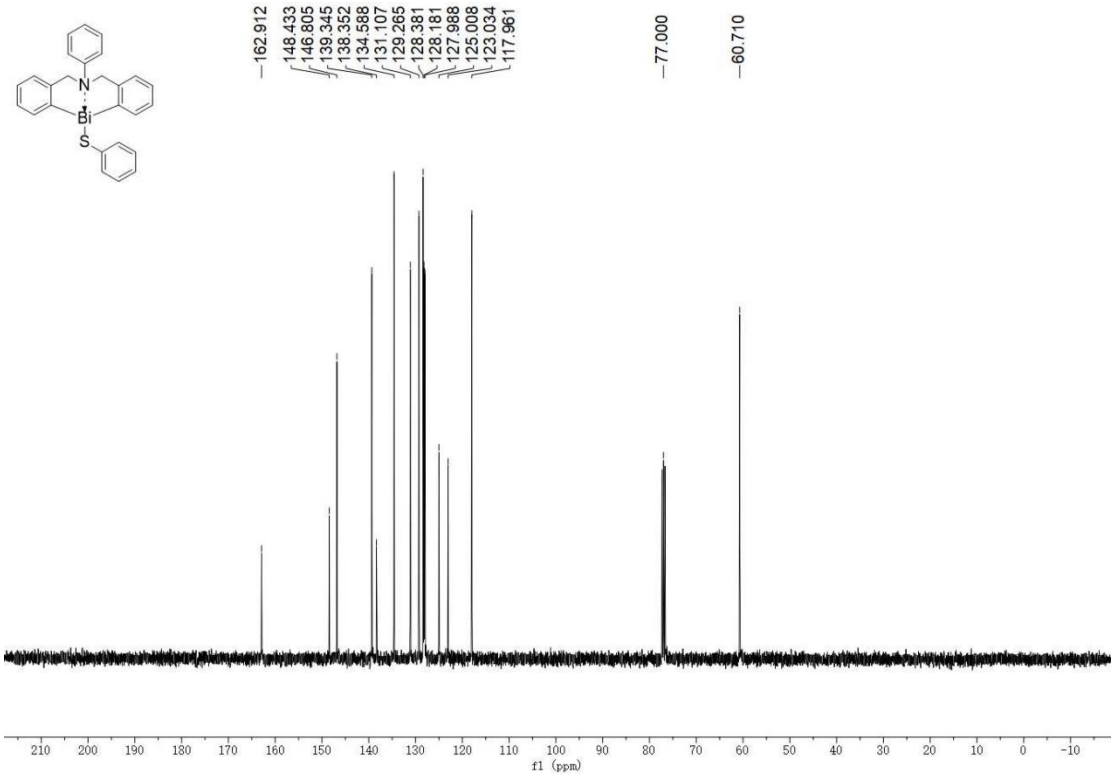
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5i**

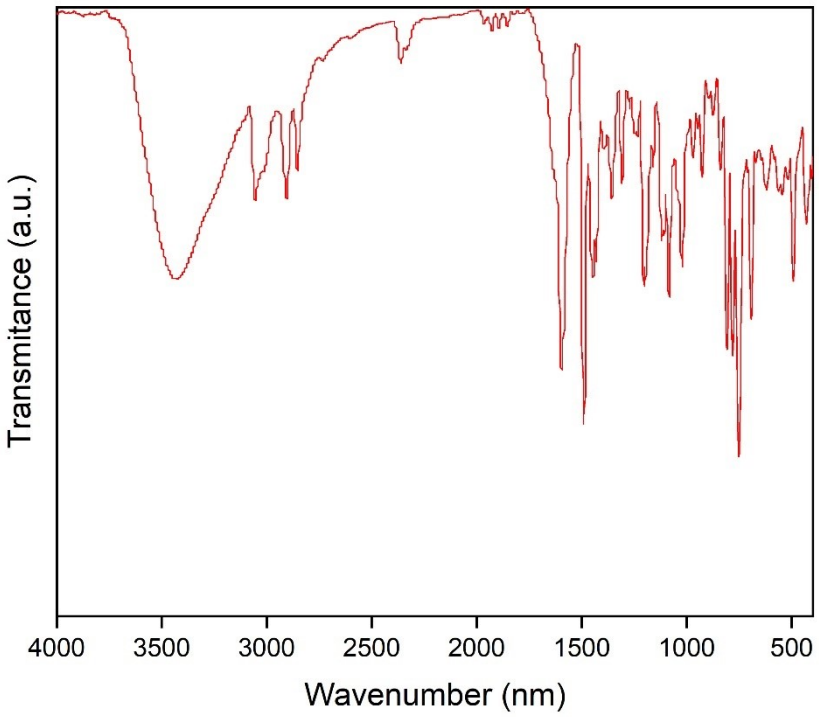


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5j**

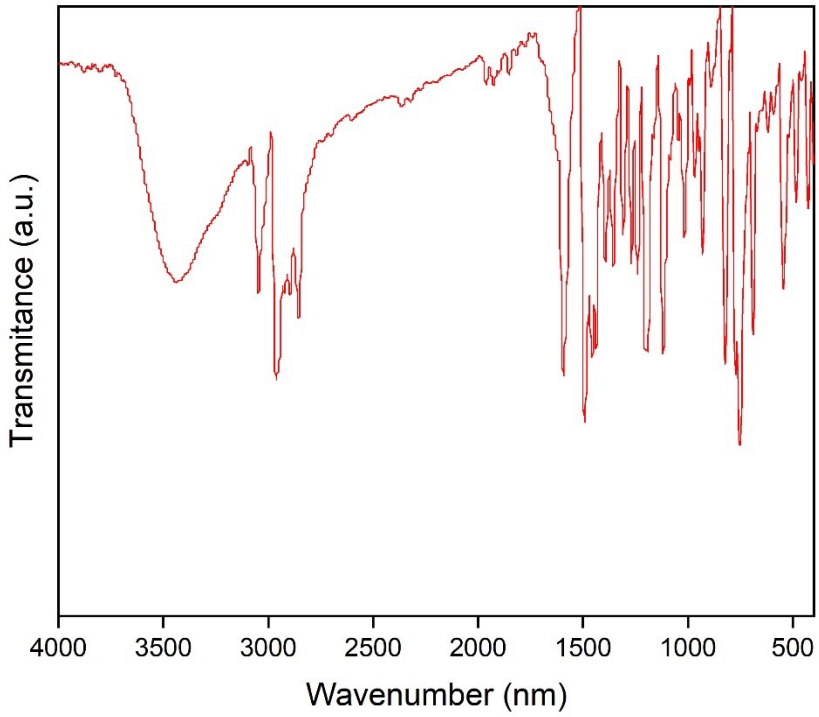


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5j**

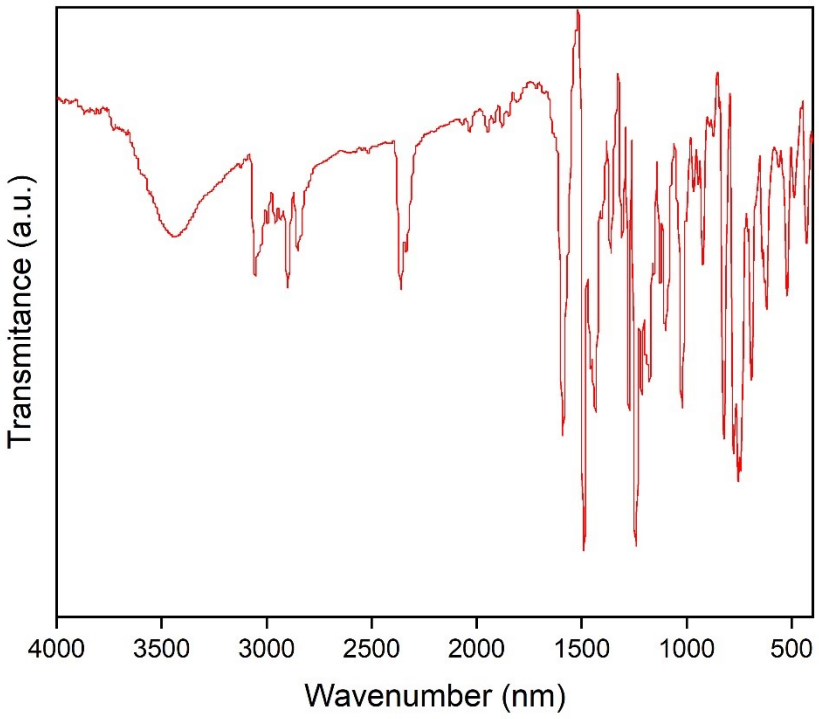
10. FT-IR spectra



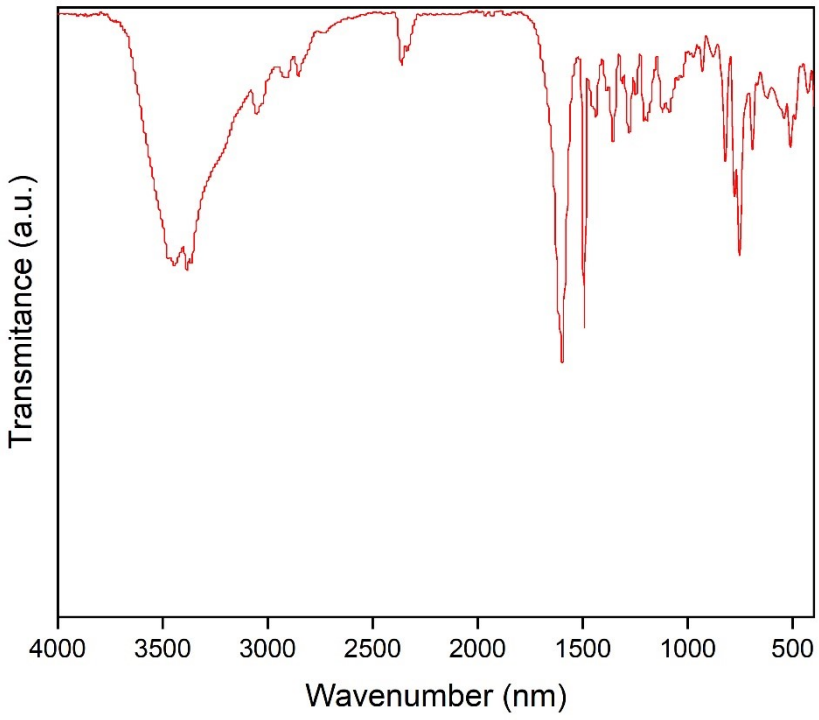
FTIR spectrum of compound **3a**



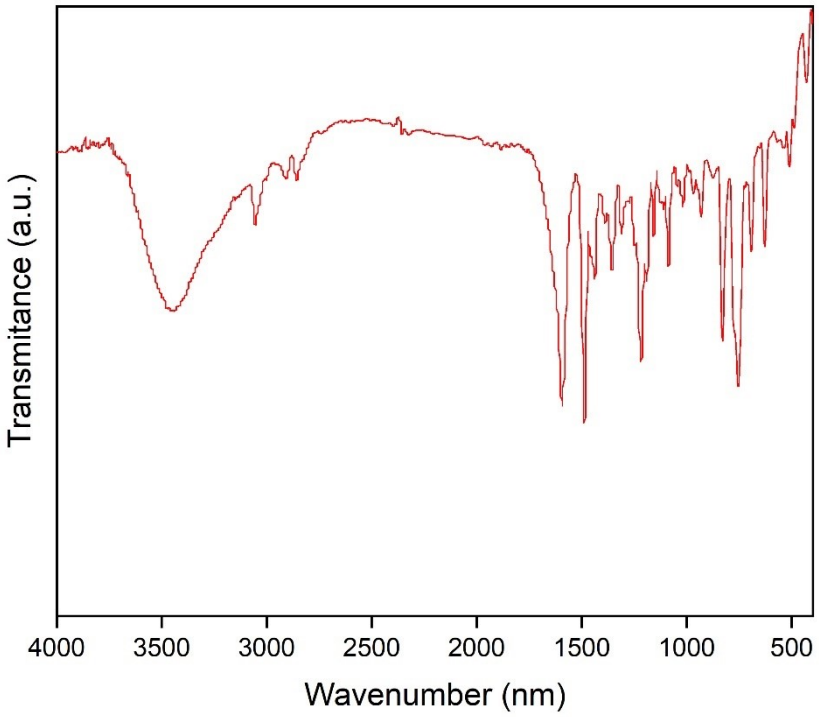
FTIR spectrum of compound **3b**



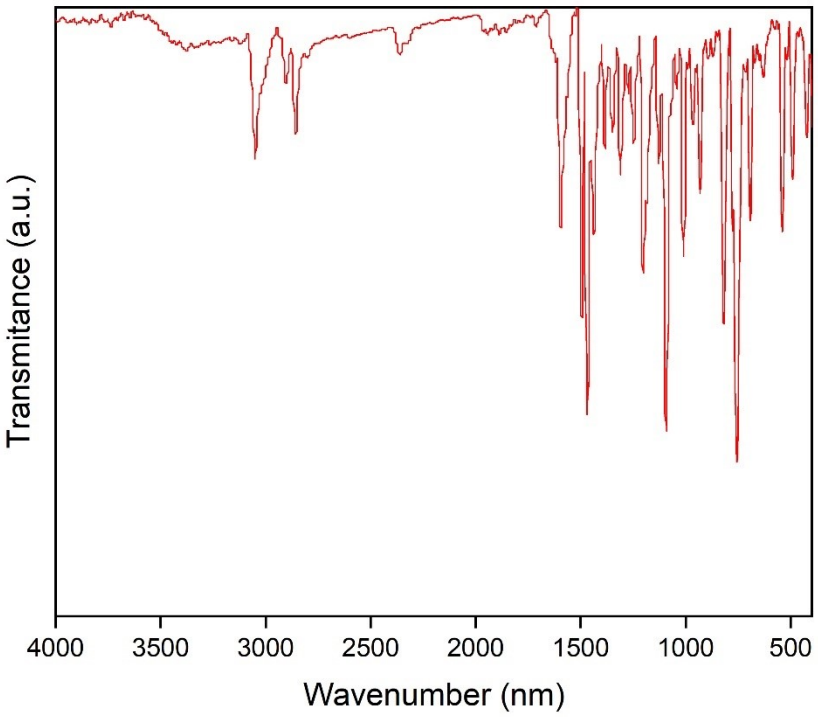
FTIR spectrum of compound **3c**



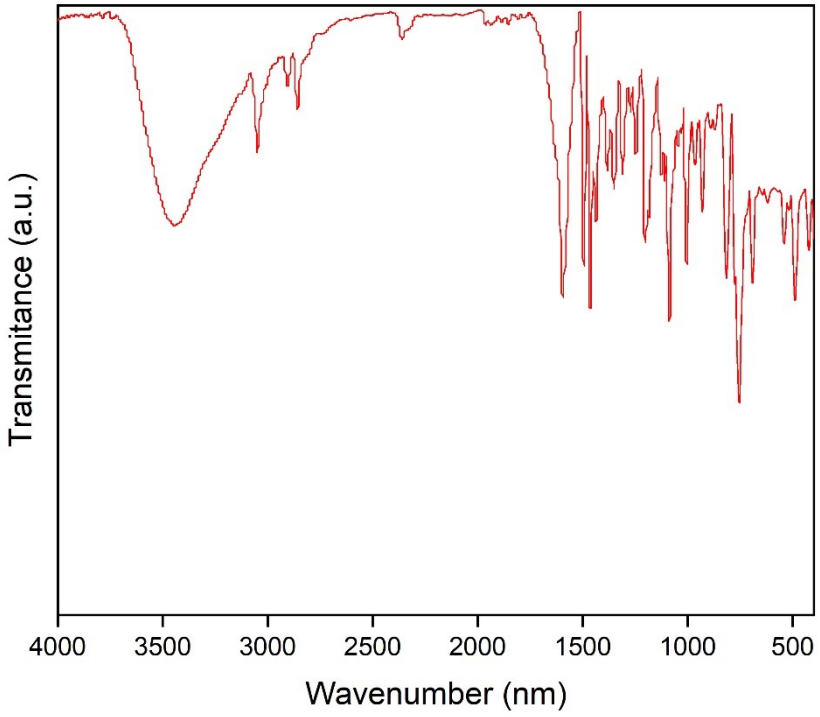
FTIR spectrum of compound **3d**



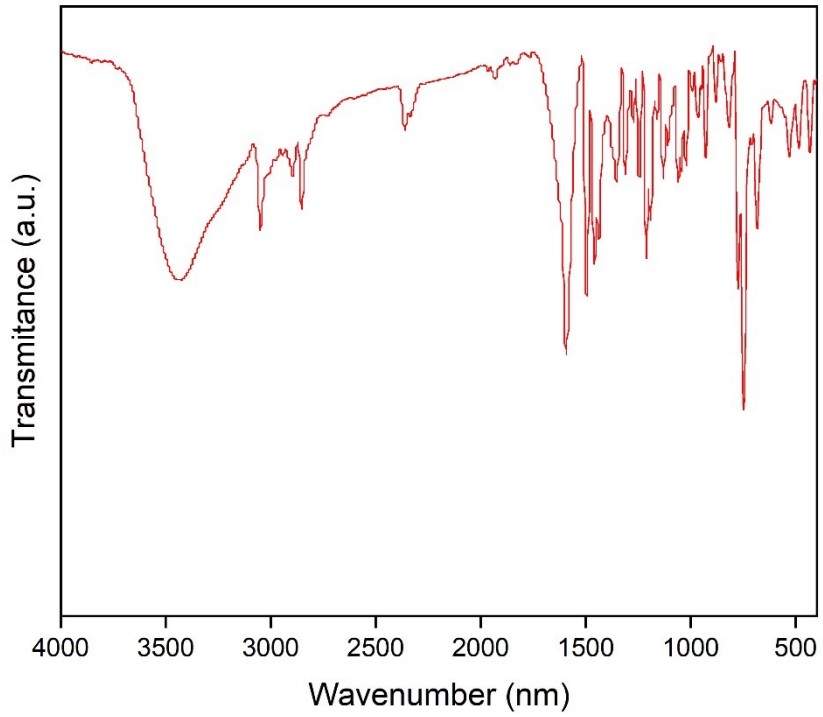
FTIR spectrum of compound **3e**



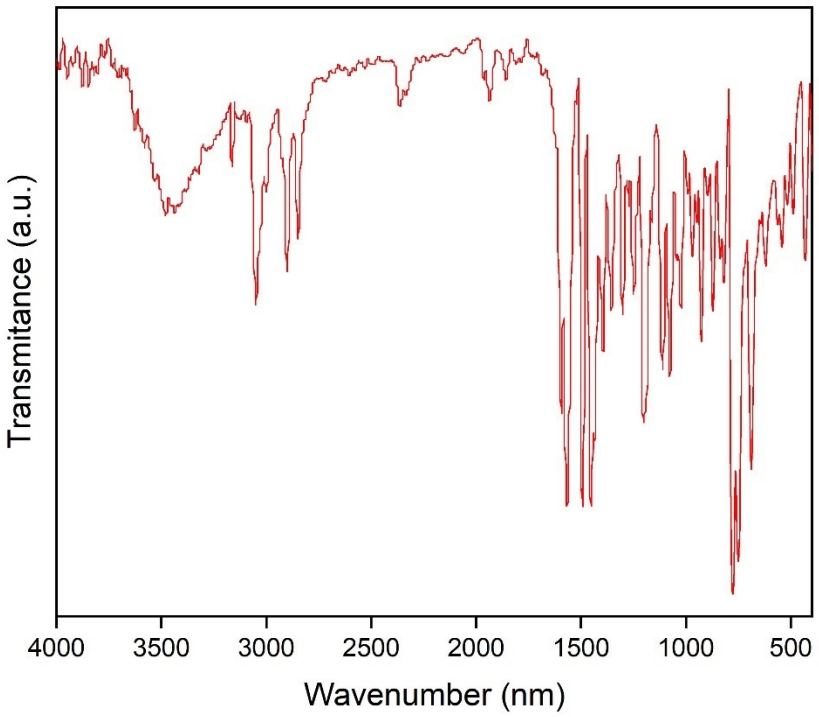
FTIR spectrum of compound **3f**



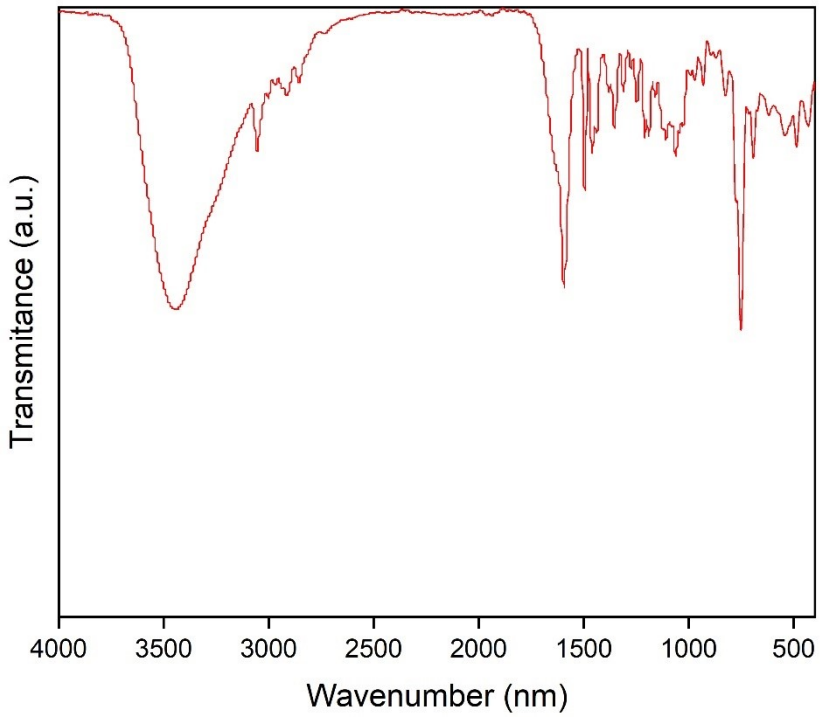
FTIR spectrum of compound **3g**



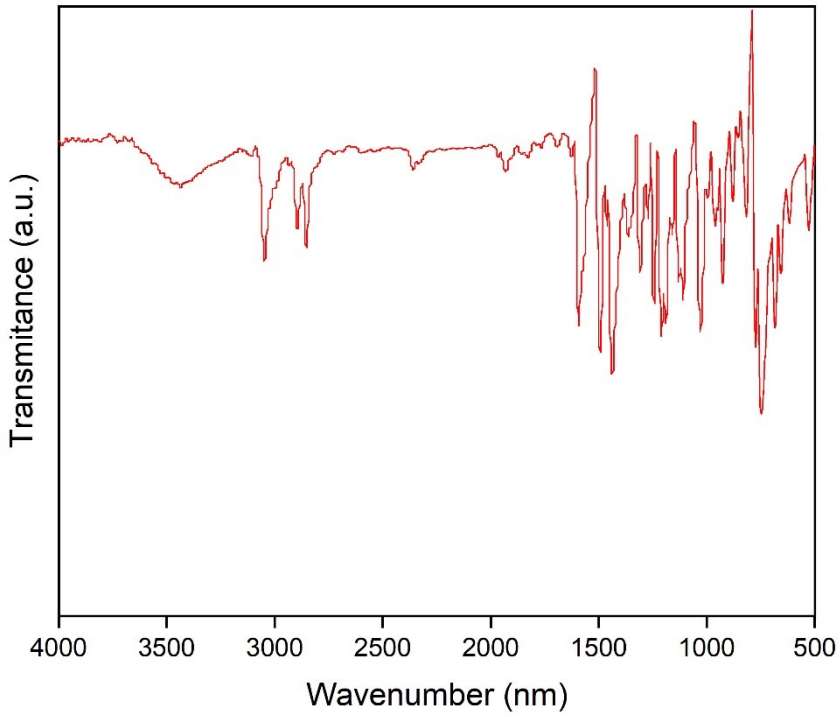
FTIR spectrum of compound **3h**



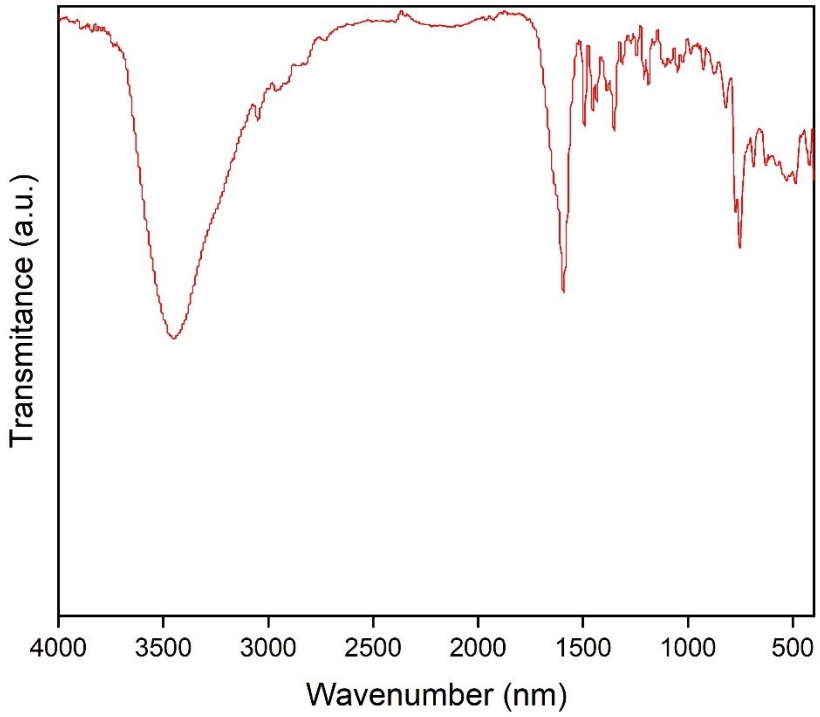
FTIR spectrum of compound **3i**



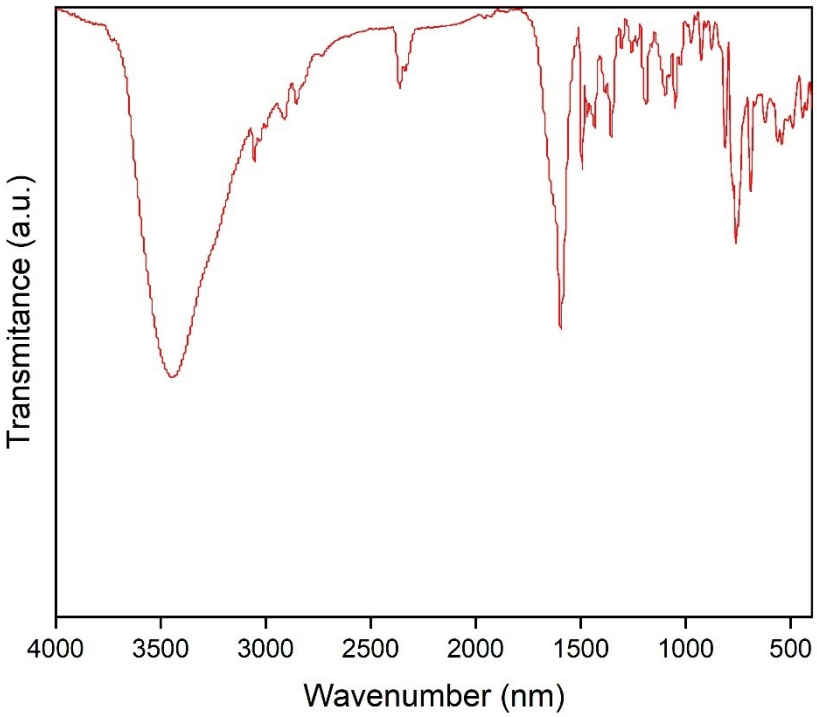
FTIR spectrum of compound **3j**



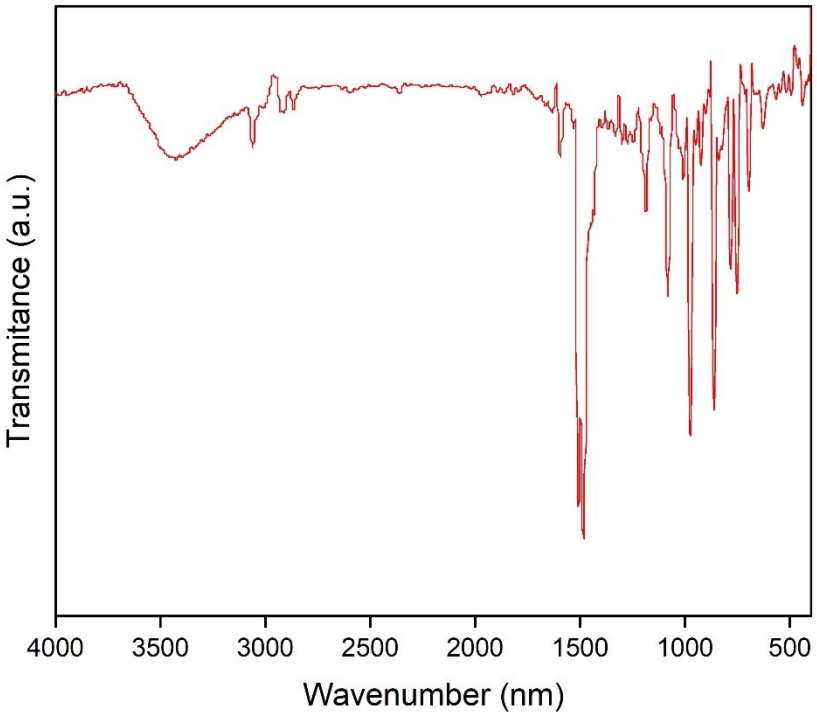
FTIR spectrum of compound **3k**



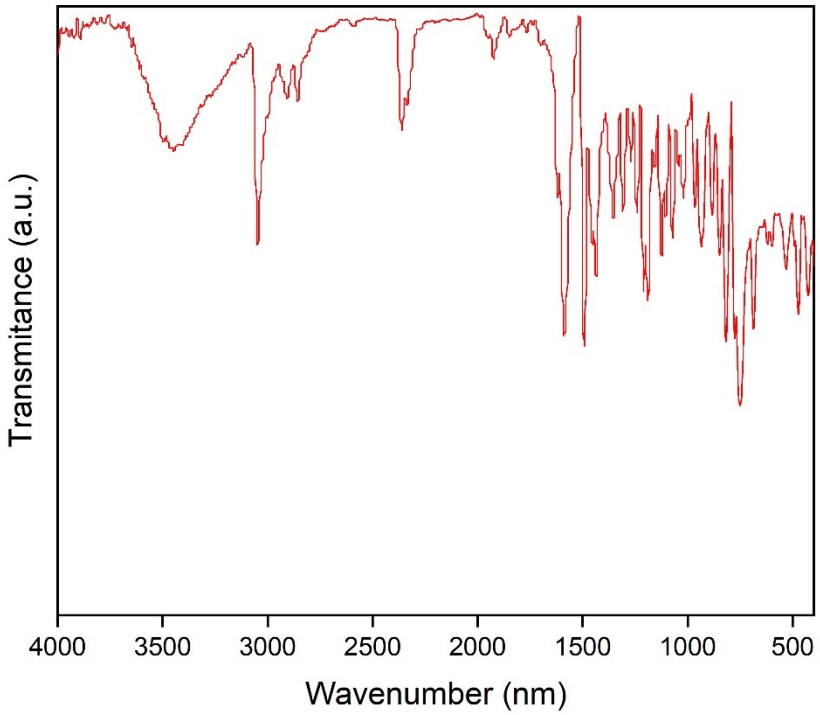
FTIR spectrum of compound **3l**



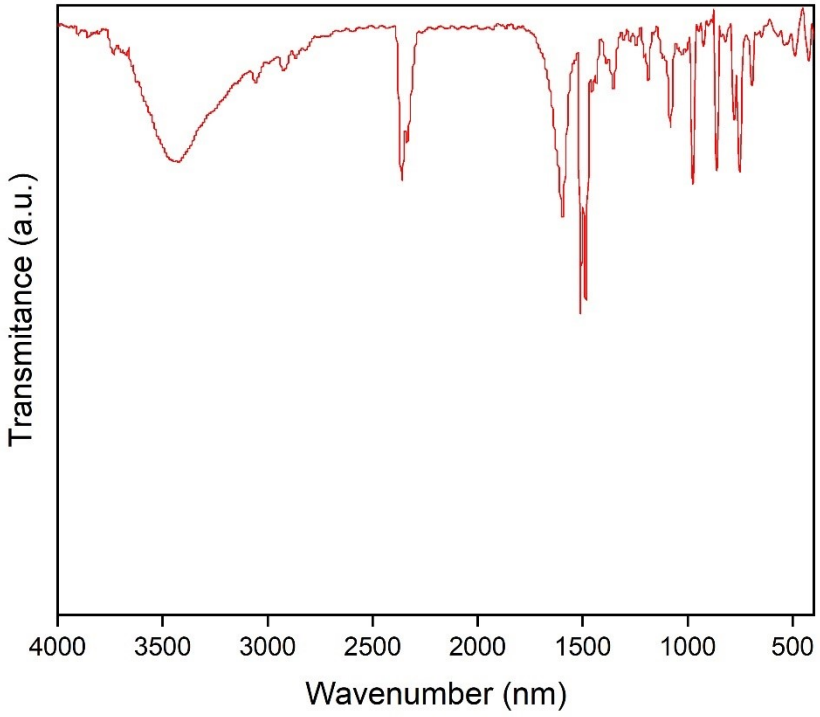
FTIR spectrum of compound **3m**



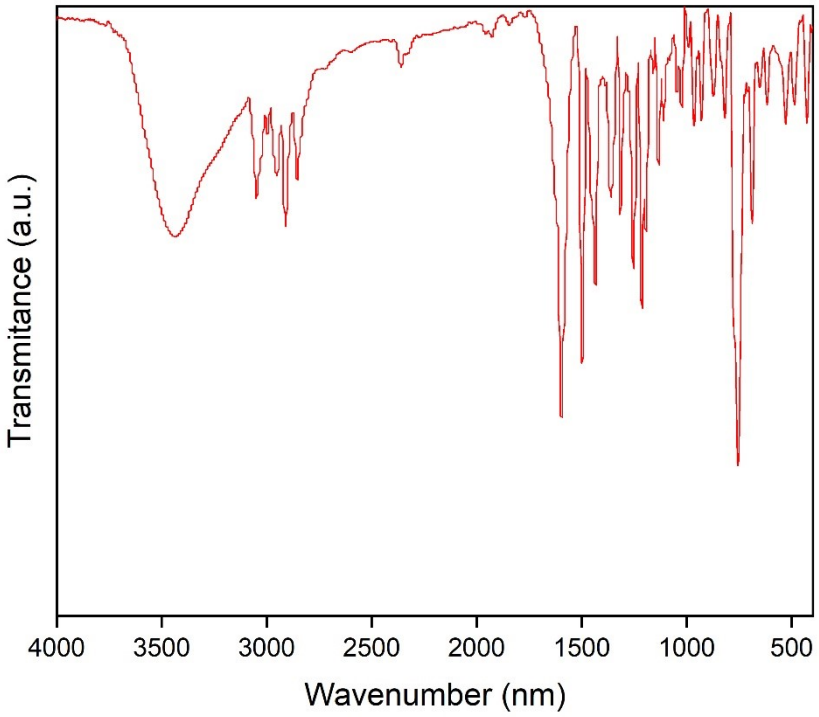
FTIR spectrum of compound **3n**



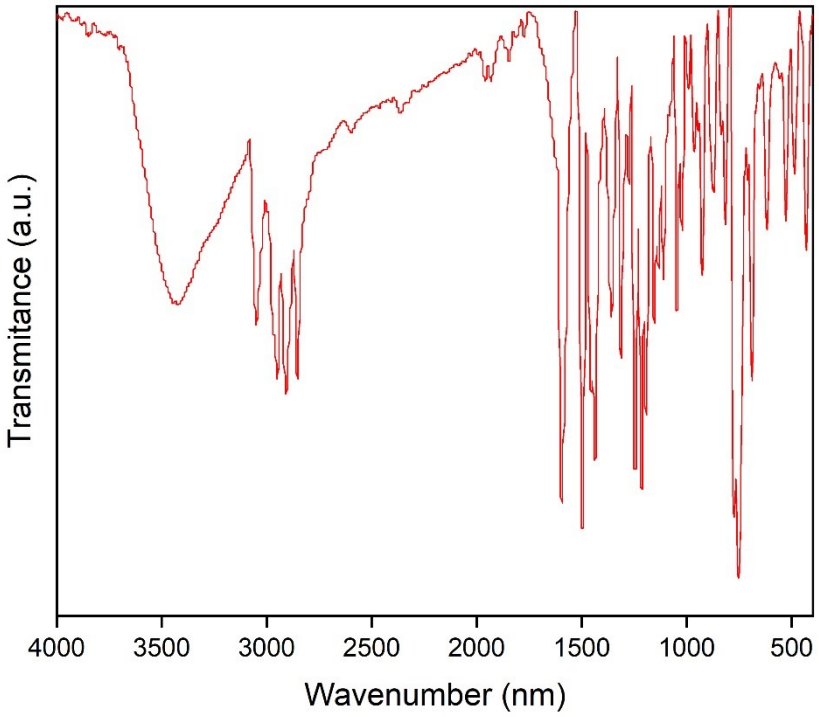
FTIR spectrum of compound **3o**



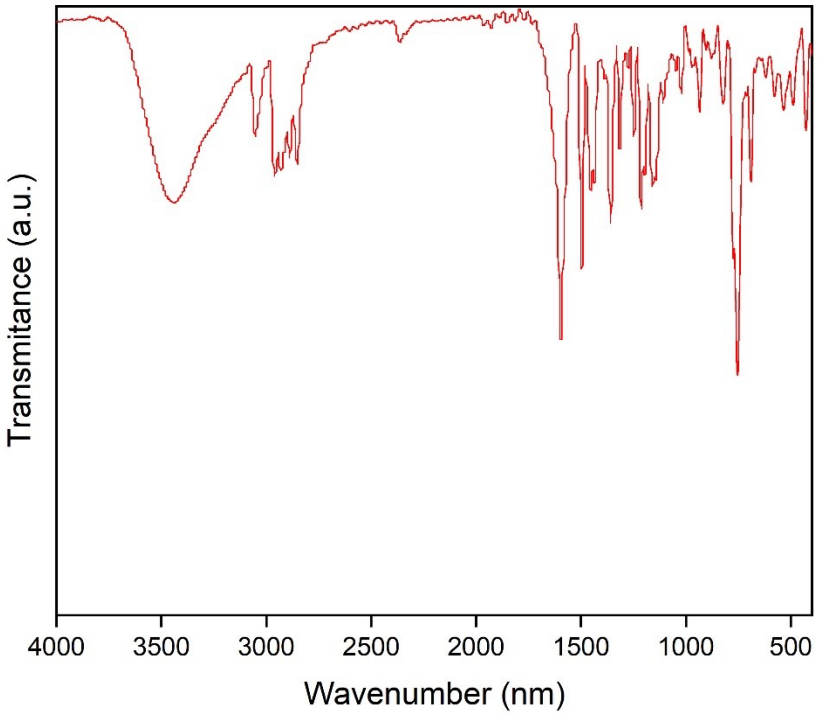
FTIR spectrum of compound **3p**



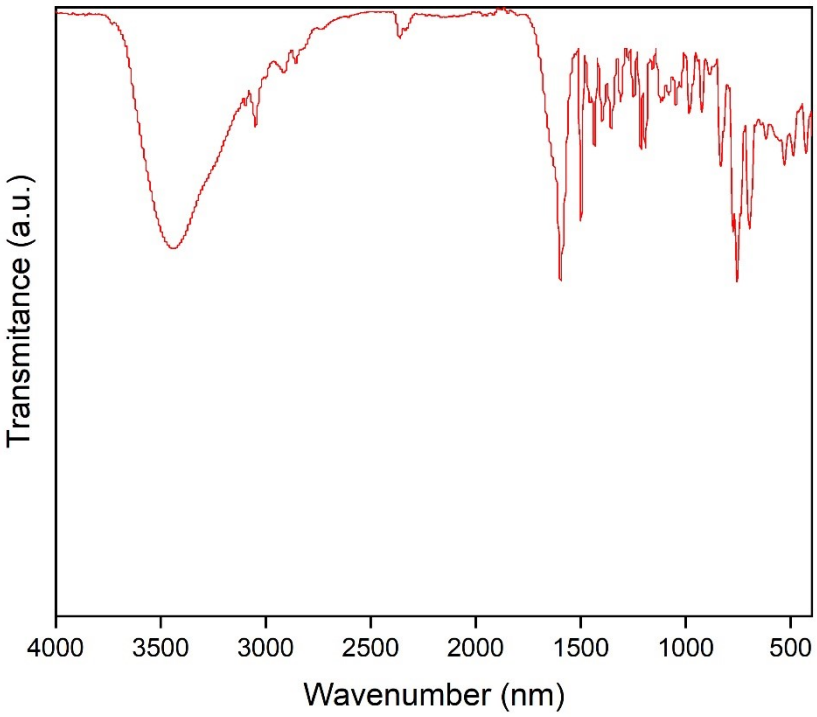
FTIR spectrum of compound **3q**



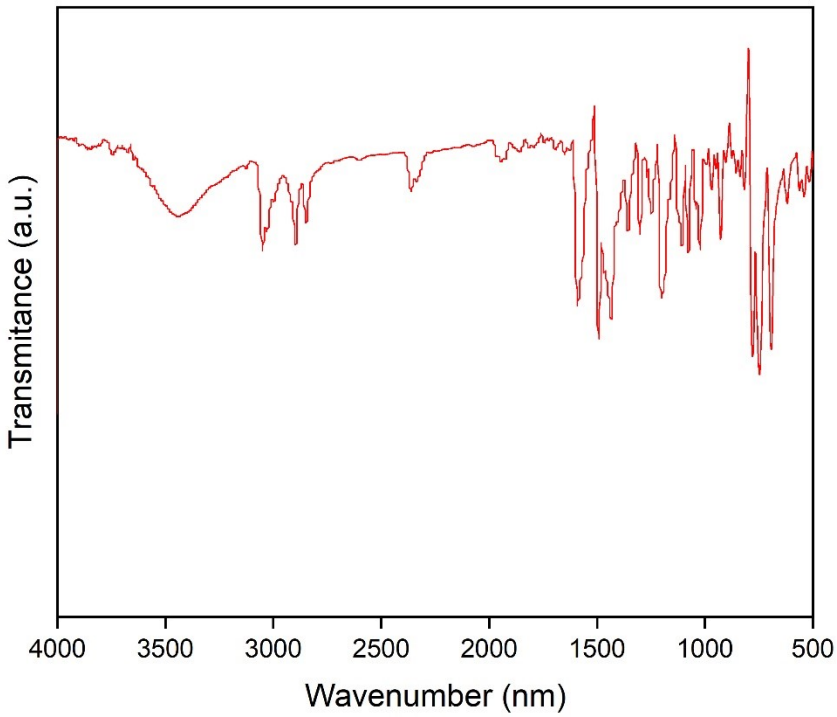
FTIR spectrum of compound **3r**



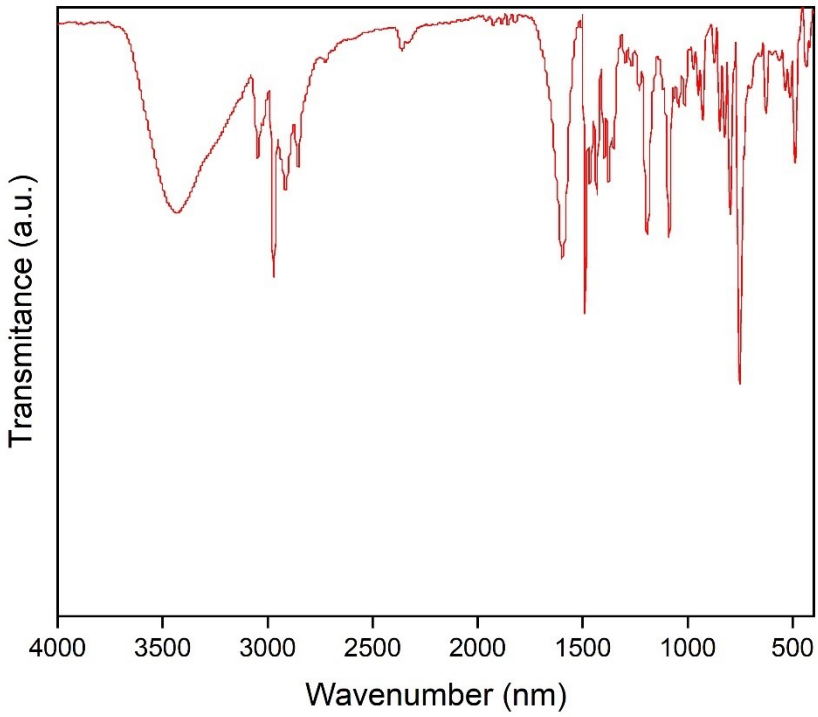
FTIR spectrum of compound **3s**



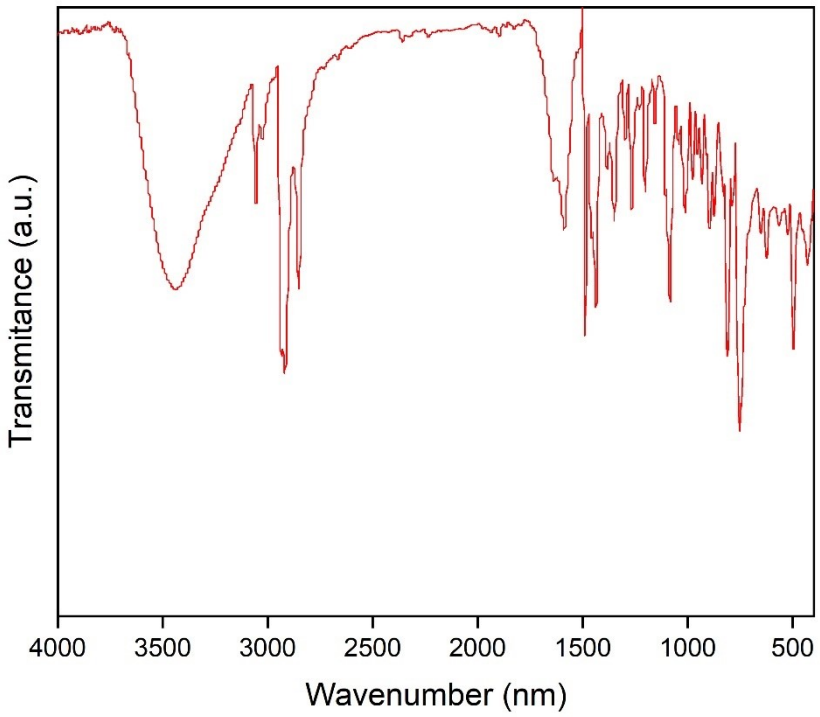
FTIR spectrum of compound **3t**



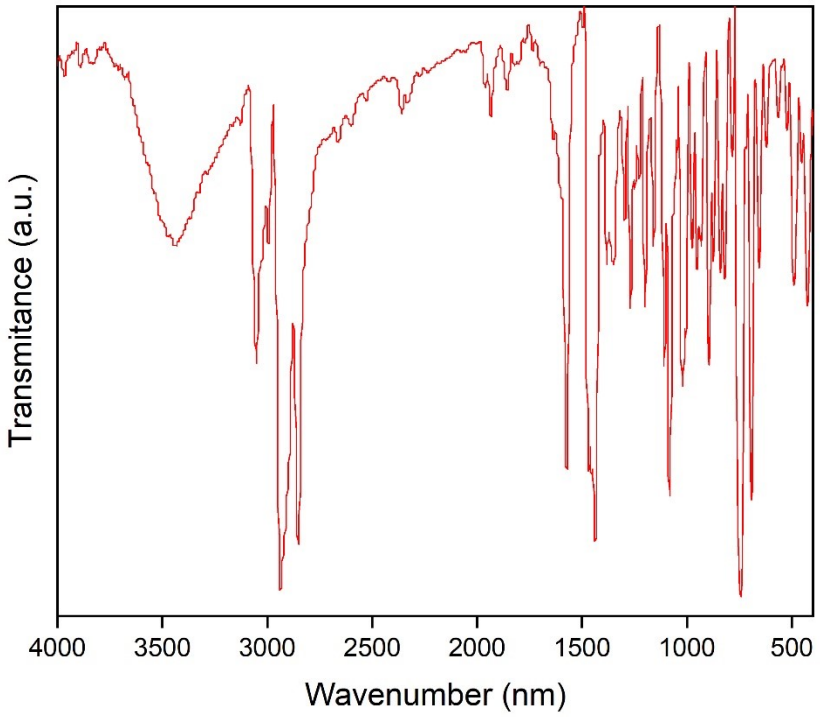
FTIR spectrum of compound **3u**



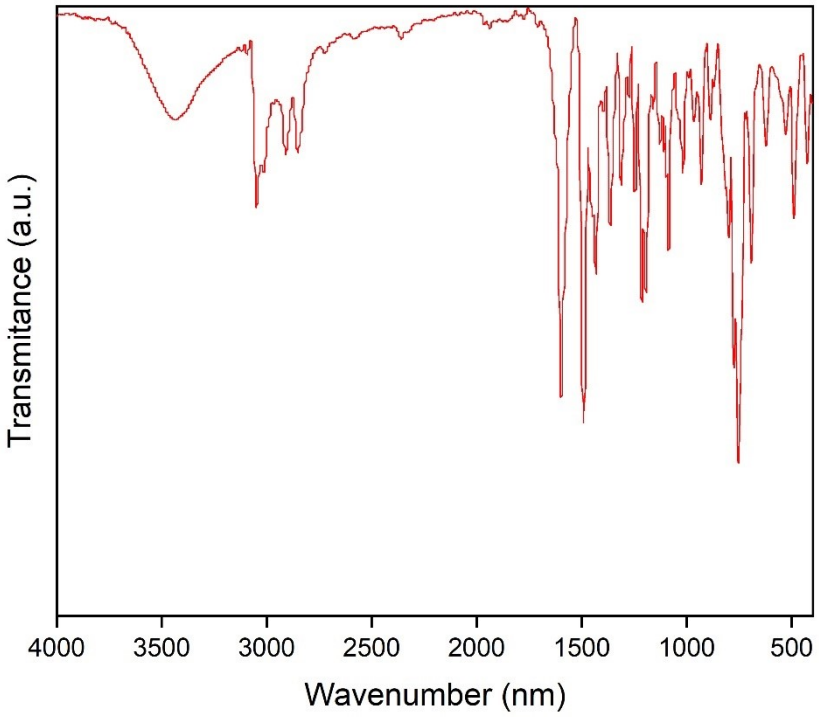
FTIR spectrum of compound **3v**



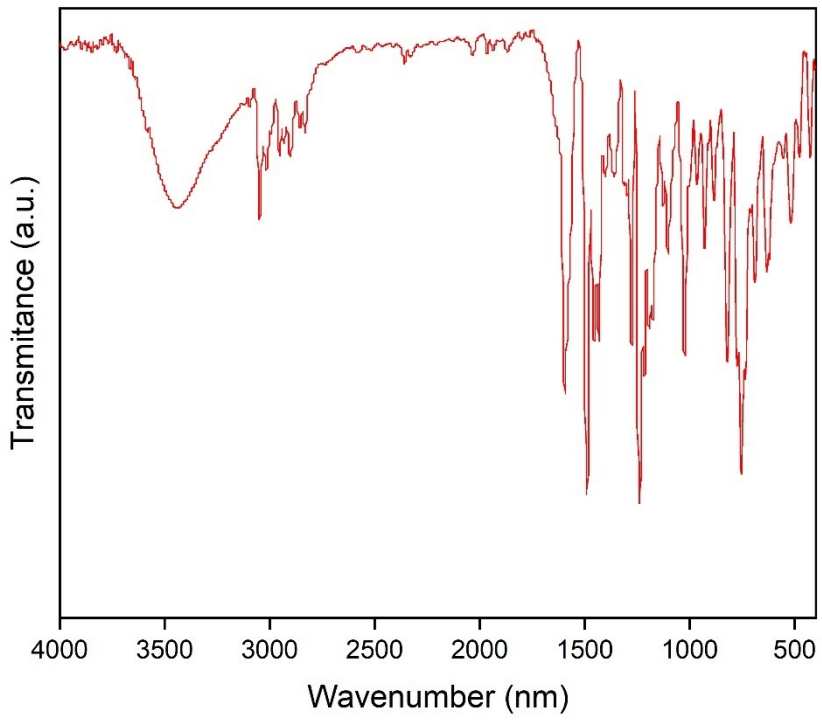
FTIR spectrum of compound **3w**



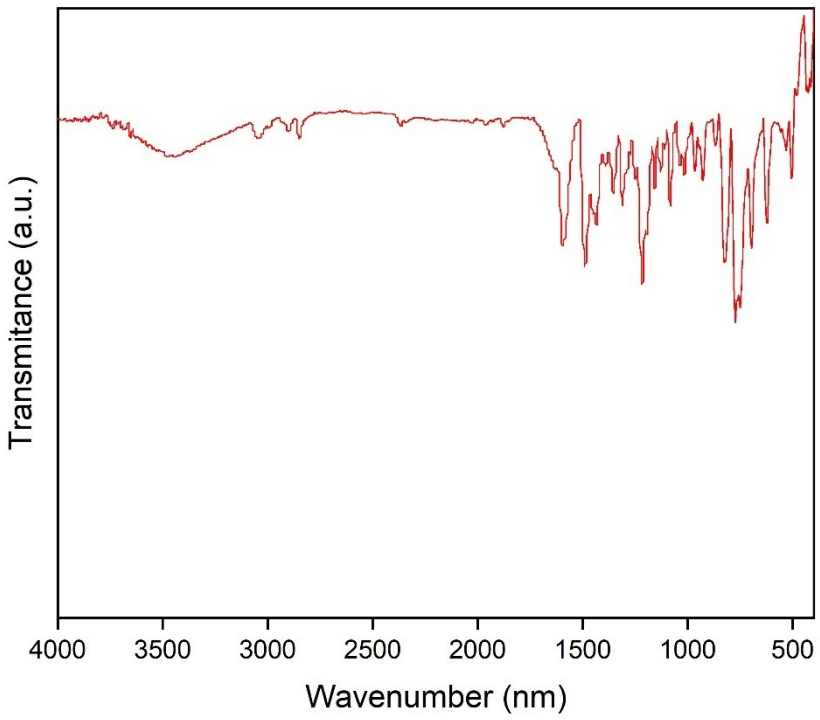
FTIR spectrum of compound **3x**



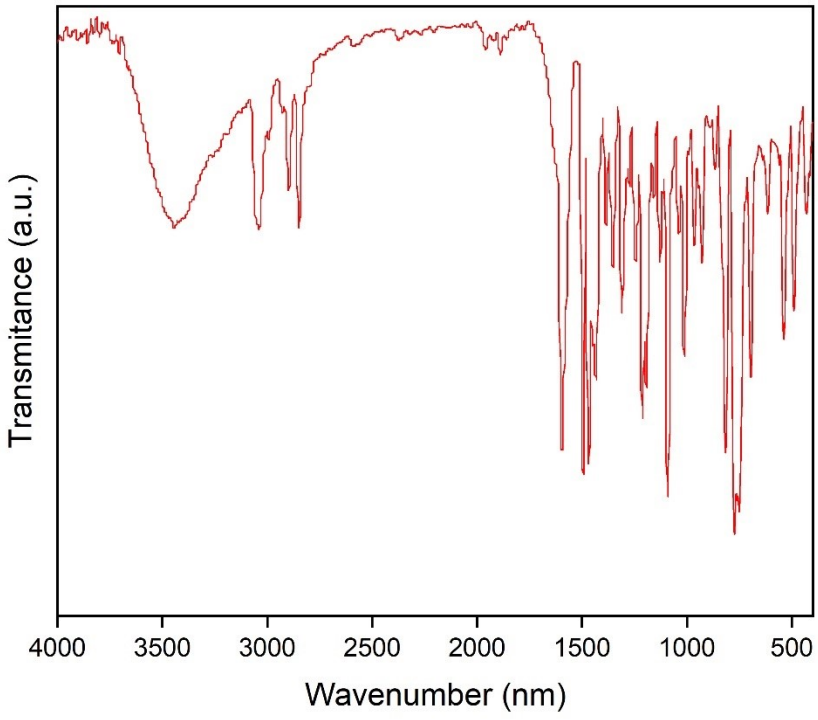
FTIR spectrum of compound **5a**



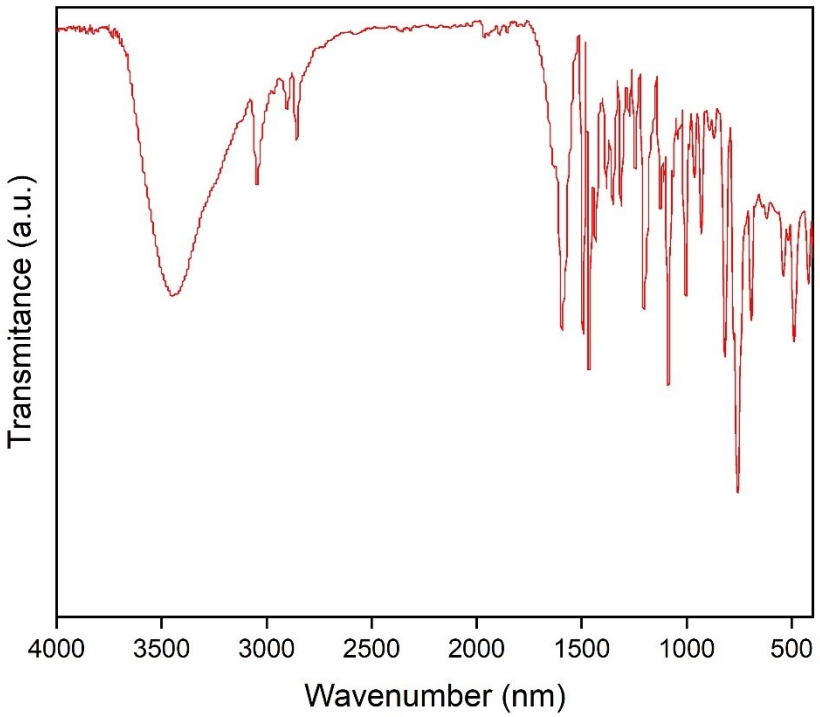
FTIR spectrum of compound **5b**



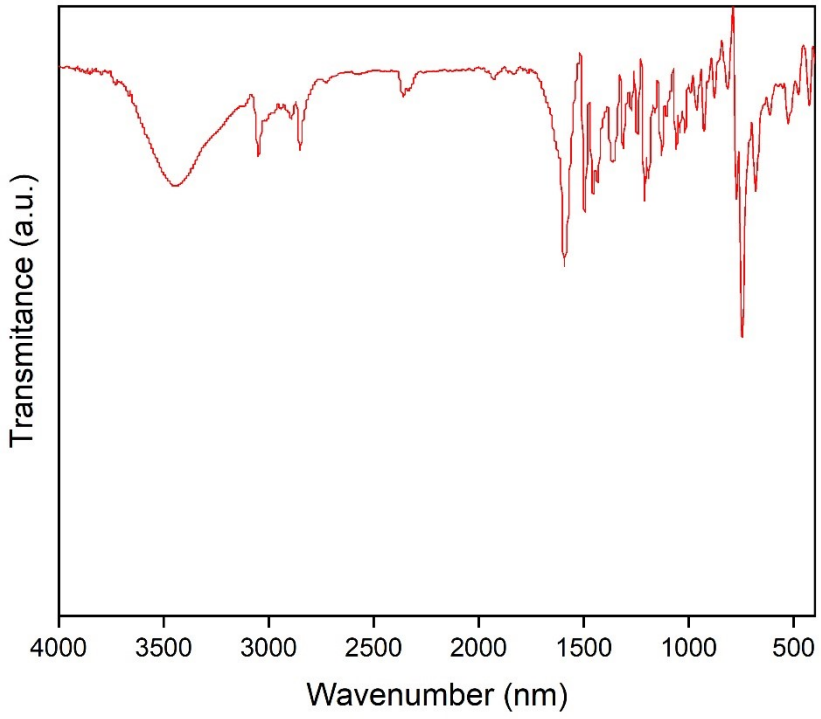
FTIR spectrum of compound **5c**



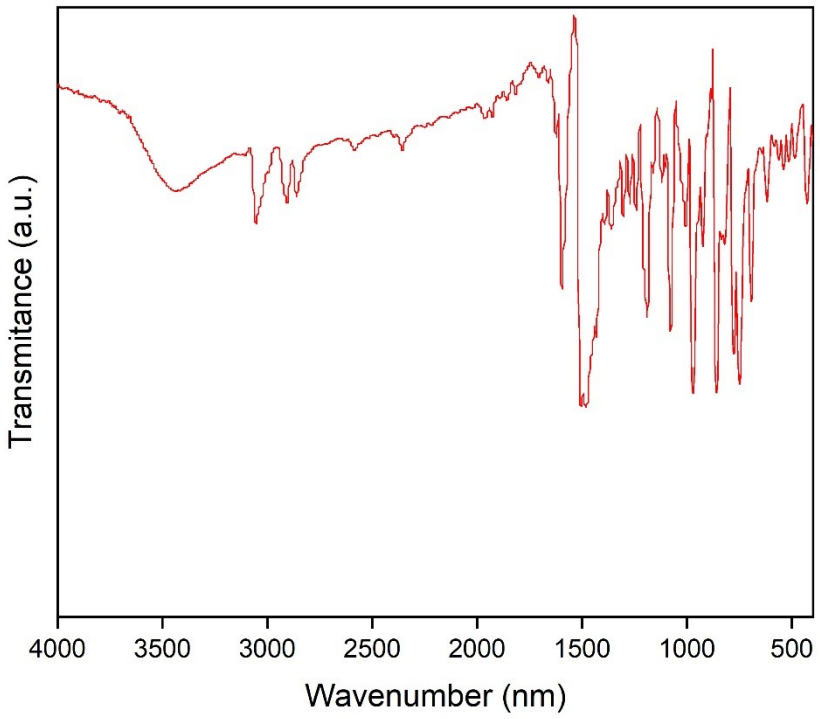
FTIR spectrum of compound **5d**



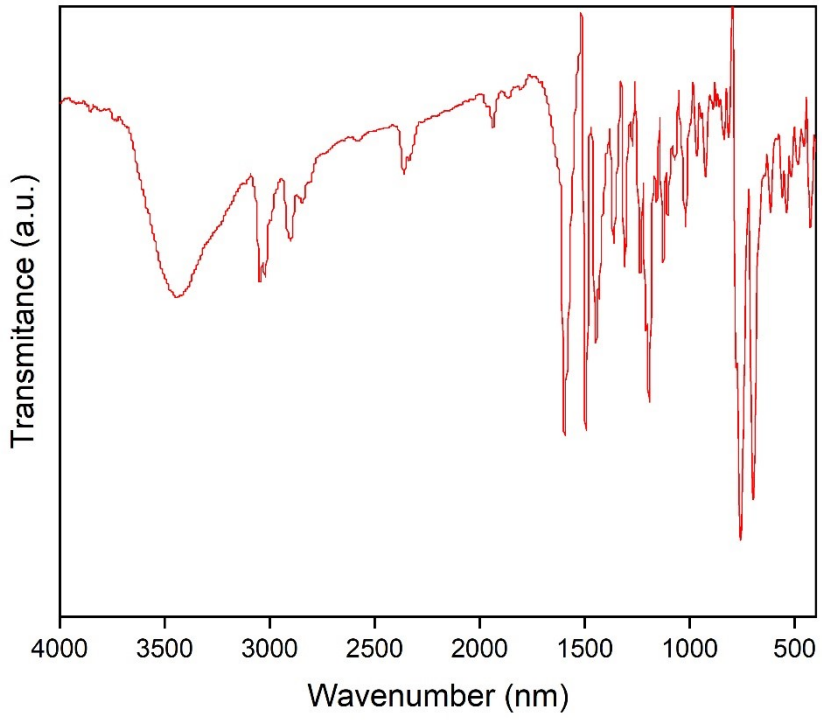
FTIR spectrum of compound **5e**



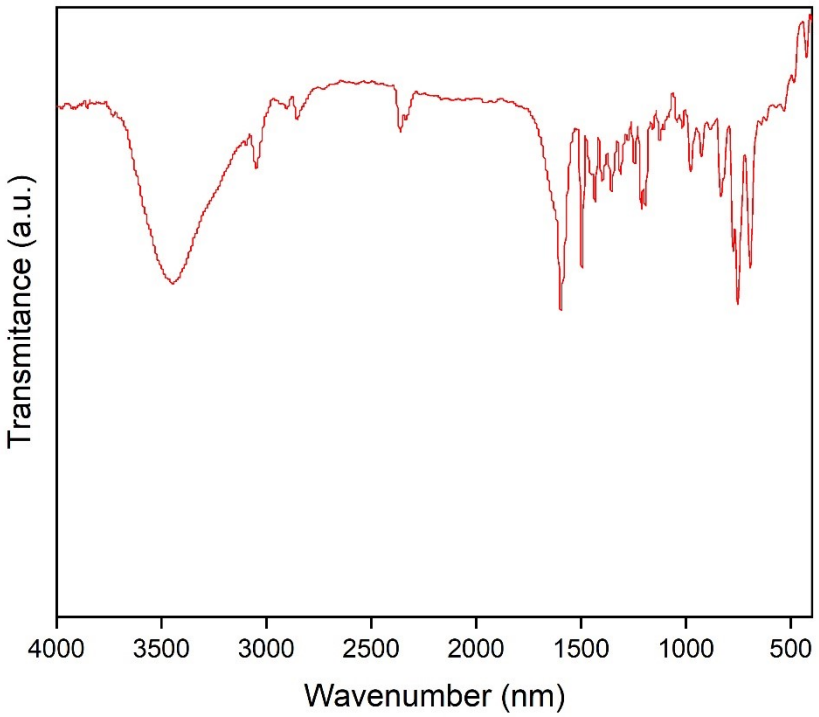
FTIR spectrum of compound **5f**



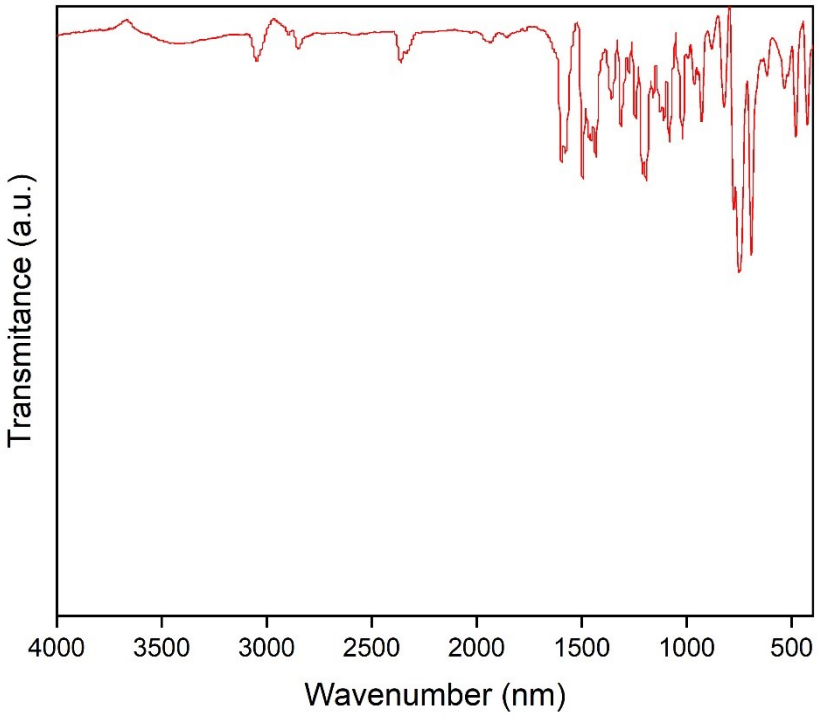
FTIR spectrum of compound **5g**



FTIR spectrum of compound **5h**



FTIR spectrum of compound **5i**



FTIR spectrum of compound **5j**