Support Information

LMCT-Homolysis-Enabled C−H Functionalization of Arylamines

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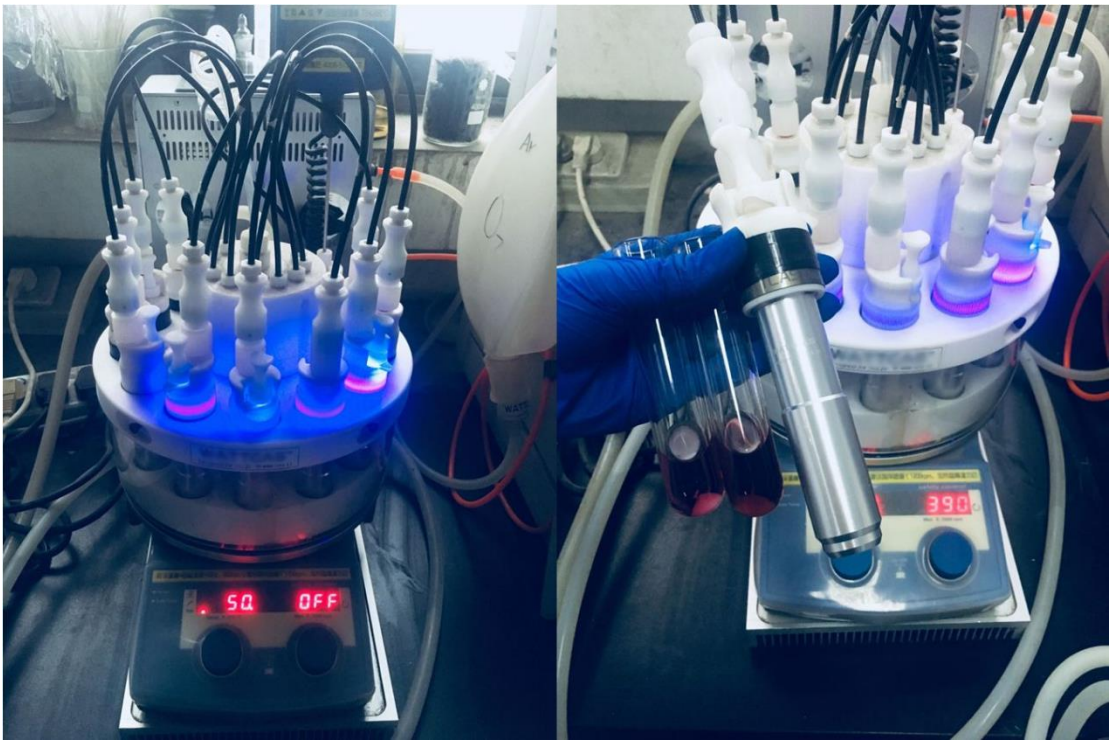


Figure S1. Details for the photochemical reaction setup.

The light Source and the Material of the Irradiation Vessel

Manufacturer: Xi'an WATTECS experimental equipment Co. Ltd

Model: WP-TEC-1020SL

Broadband source: X = 460 nm (light power: 42W).

Material of the irradiation vessel: borosilicate reaction tube (20 ml)

Distance from the light source to the irradiation vessel: 2.0 cm

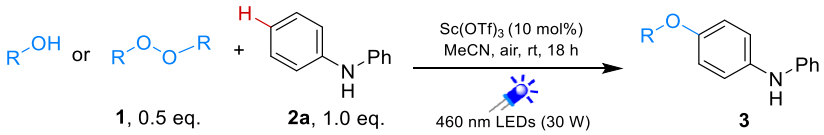
Not use any filt

1.General Considerations

All chemicals and reagents were used of commercial grade and were used without no further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-600 (1H: 600 MHz, 13C: 150 MHz) 、Bruker DRX-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or Bruker DRX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz)using Acetone-d6. DMSO and $CDCl_3$ as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and *J* values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

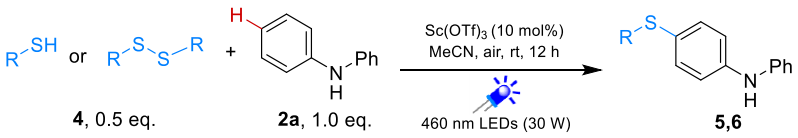
2.General Procedure for preparing compounds **3,5,6,8,9,10.**

General Procedure 1 for preparing asymmetric oxides **3**.



Under air atmosphere, eroxybenzoyl and phenol and benzyl alcohol **1** (0.05 mmol, 0.5 equiv), arylamine **2a** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (10 mol%, 0.01mmol) in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 18h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

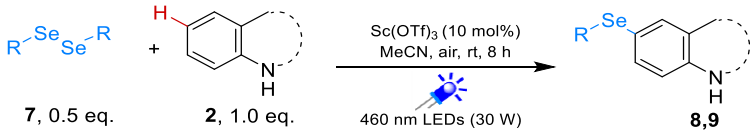
General Procedure 2 for preparing unsymmetrical sulfides **5**,**6**.



Under air atmosphere, dithioether **4** (0.05 mmol, 0.5 equiv) or thiole (0.1 mmol, 1.0 equiv), arylamine **2** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (10 mol%, 0.01mmol) in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30W) and monitored by TLC. After stirring for 12 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the

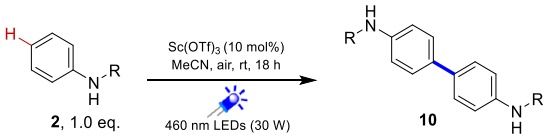
products. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

General Procedure 3 for preparing unsymmetrical selenides **8, 9**.



Under air atmosphere, diselenide **7** (0.05 mmol, 0.5 equiv), arylamine **2** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (10 mol%, 0.01mmol) in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 8h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS .

General Procedure 4 for preparing asymmetric oxides **10**.

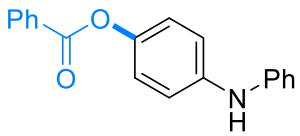


Under air atmosphere, arylamine **2** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (10 mol%, 0.01mmol) in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 18 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

3. Spectroscopic Data of **3,5,6,8,9,10.**

Spectroscopic Data of **(3a)**

4-(phenylamino)phenyl benzoate

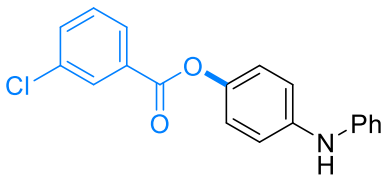


Synthesized according to General Procedure 1. the obtained product was a yellow solid(46%yield, 40mg, VPetroleum ether/VEthyl acetate = 50:1, Rf = 0.4); Mp:96-98℃; IR(KBr): 3373, 1724, 1597, 1518, 1493, 1325, 1273, 1196, 1067, 642cm-1; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.17 – 8.10 (m, 2H), 7.60 – 7.54 (m, 1H), 7.45 (dd, *J* = 8.4, 2H), 7.24 – 7.19 (m, 2H), 7.09 – 6.97 (m, 6H), 6.87 (t, *J* = 7.3, 1H), 5.65 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 164.5, 143.8, 142.2, 139.9, 132.5, 129.1, 128.6, 128.4, 127.5, 121.4, 120.0, 117.8, 116.6; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{15}NO_2$ [M+Na]+, 312.0095; found: 312.0094.

Data consistent with those previously reported.[1]

Spectroscopic Data of **(3b)**

4-(phenylamino)phenyl 3-chlorobenzoate

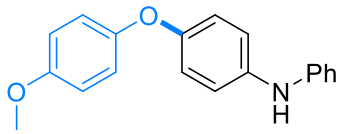


Synthesized according to General Procedure 1. the obtained product was a yellow solid(60%yield, 58mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 70:1, R_f = 0.4); Mp:99-100℃; IR(KBr): 3366, 1587, 1488, 1425, 1278, 1169, 1073, 692cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.06 – 7.93 (m, 2H), 7.56 (dd, *J* = 8.1Hz, 1H), 7.48 – 6.69 (m, 10H), 5.38 (s, 1H).; **^{13}C NMR** (100 MHz, Chloroform-d) δ 162.6, 141.5, 133.8, 132.8, 129.2,

128.9, 128.3, 127.3, 125.8, 121.8, 120.7, 120.6, 118.3, 117.6.; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{15Cl}NO_2$ [M+H]+, 324.0786; found: 324.0788.

Spectroscopic Data of **(3c)**

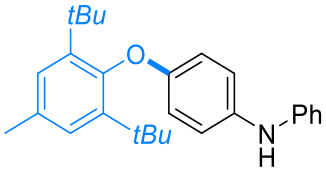
4-(4-methoxyphenoxy)-N-phenylaniline



Synthesized according to General Procedure 1. The obtained product was a colourful solid(43%yield, 38mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **MP**:83-85℃; **IR**(KBr): 3354, 1745, 1647, 1439, 1316, 1215, 1057, 687cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.17 (m, 2H), 7.07 – 6.53 (m, 11H), 5.51 (s, 1H), 3.73 (s, 3H);**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.5, 151.8, 150.1, 143.2, 136.9, 128.3, 120.8, 119.8, 119.2, 118.9, 118.1, 115.4, 113.8, 54.6; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$, 292.1332; found:292.1331.

Spectroscopic Data of **(3d)**

4-(2,6-di-tert-butyl-4-methylphenoxy)-N-phenylaniline

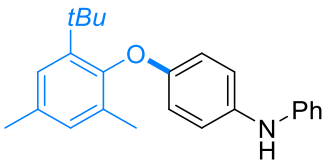


Synthesized according to General Procedure 1. The obtained product was a white oil(57%yield, 66mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **IR**(KBr): 3271, 1754, 1628, 1481, 1316, 1254, 1172, 1051, 635cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 2H), 7.07 – 7.03 (m, 2H), 7.01 – 6.97 (m, 2H), 6.95 – 6.92 (m, 2H), 6.88 – 6.83 (m, 1H), 6.49 (s, 2H), 5.63 (s, 1H), 1.34 (s, 3H), 1.16 (s, 18H); **^{13}C NMR** (100 MHz, Chloroform-d)δ 146.1, 143.3, 141.7, 141.0, 133.0, 128.3, 126.2, 120.2,

117.0, 116.6, 33.6, 28.5, 23.9; **HRMS** (TOF-ESI+): m/z calcd for $C_{27}H_{34}NO$ $[M+H]^+$, 388.2629. found: 388.2635.

Spectroscopic Data of **(3e)**

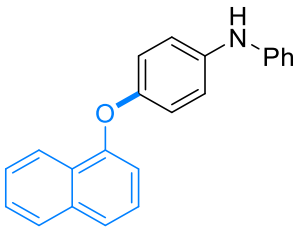
4-(2-(tert-butyl)-4,6-dimethylphenoxy)-N-phenylaniline



Synthesized according to General Procedure 1. The obtained product was a white oil(46%yield, 48mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.4); **IR**(KBr): 3264, 1732, 1625, 1473, 1324, 1256, 1172, 1041, 655cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.02 – 6.81 (m, 5H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.54 (s, 1H), 5.65 (s, 1H), 1.82 (s, 3H), 1.53 (s, 3H), 1.18 (s, 9H);**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 148.5, 148.1, 142.1, 141.7, 141.2, 132.5, 132.5, 128.3, 128.3, 126.2, 120.2, 117.0, 116.6, 33.5, 28.3, 23.6, 15.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{24}H_{28}NO$ $[M+H]^+$, 346.2165.; found:346.2166.

Spectroscopic Data of **(3f)**

4-(naphthalen-1-yloxy)-N-phenylaniline

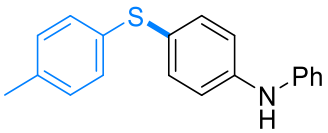


Synthesized according to General Procedure 1. The obtained product was a purple solid(41%yield, 38mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.4);**MP**:188-190°C;**IR**(KBr): 3652, 2234, 1842, 1663, 1527, 1342, 1264, 1165, 1051, 672cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 – 8.07 (m, 1H), 8.06 – 7.99 (m, 1H), 7.73 – 7.63 (m, 2H), 7.52 – 7.45 (m, 2H), 7.29 – 7.23 (m, 2H), 7.17 – 7.07 (m, 3H), 7.08 – 6.87 (m, 5H), 5.93 (s, 1H);**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.2, 144.7, 140.3,

132.7, 132.6, 131.6, 131.2, 130.1, 128.5, 125.9, 124.8, 123.6, 121.6, 118.7, 114.7; **HRMS** (TOF-ESI+): m/z calcd for $C_{22}H_{17}NO$ $[M+H]^+$, 312.1383; found:312.1385.

Spectroscopic Data of **(5a)**

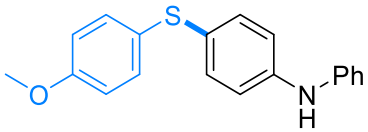
N-phenyl-4-(p-tolylthio)aniline



Synthesized according to General Procedure 2. The obtained product was a brown oil(66%yield, 57mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3435, 2997, 2655, 2414, 1670, 1021, 796, 722, 621cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.33 – 7.14 (m, 4H), 7.14 – 7.06 (m, 2H), 7.06 – 6.96 (m, 4H), 6.96 – 6.85 (m, 3H), 5.69 (s, 1H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 143.2, 142.3, 136.1, 134.4, 134.2, 129.8, 129.4, 129.4, 125.1, 121.8, 118.6, 117.7, 21.0; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{18}NS$ $[M+H]^+$, 292.1154; found, 292.1156.

Spectroscopic Data of **(5b)**

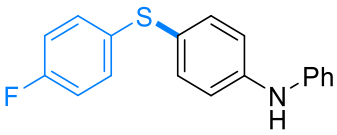
4-((4-methoxyphenyl)thio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a white solid(67%yield, 61mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 100:1, R_f = 0.3); **Mp**:54-55℃; **IR**(KBr): 3395, 3056, 2975, 1929, 1591, 1497, 1315, 1039, 804, 746, 555cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.30 – 7.10 (m, 6H), 7.04 – 6.95 (m, 2H), 6.95 – 6.82 (m, 3H), 6.82 – 6.68 (m, 2H), 5.64 (s, 1H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 159.0, 142.5, 142.5, 132.8, 132.6, 129.4, 127.4, 127.2, 121.5, 118.3, 118.0, 114.8, 55.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{18}NOS$ $[M+H]^+$, 308.1104; found, 308.1104.

Spectroscopic Data of **(5c)**

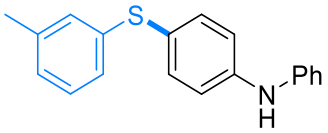
4-((4-fluorophenyl)thio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a white oil(43%yield, 39mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3516, 3188, 2962, 2423, 2258, 1927, 1669, 1026, 750, 648, 561cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.60 – 7.08 (m, 7H), 7.08 – 6.97 (m, 2H), 6.97 – 6.86 (m, 4H), 5.72 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 160.5(J_{C-F} = 254 Hz), 142.6, 141.0, 133.4, 129.9 (d, J = 9Hz), 128.4, 123.4, 120.9, 117.8, 116.6, 115.9 (J = 22 Hz); **^{19}F NMR** (376 MHz, Chloroform-d) δ -116.29 cm^{-1}; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{15}FNS$ $[M+H]^+$, 296.0904; found, 296.0905.

Spectroscopic Data of **(5d)**

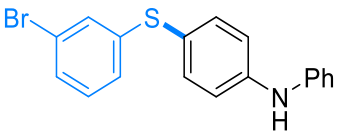
N-phenyl-4-(m-tolylthio)aniline



Synthesized according to General Procedure 2. The obtained product was a brown oil(68%yield, 60mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3388, 2999, 2543, 2222, 2052, 1927, 1635, 1136, 735, 639, 559cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.70 – 7.14 (m, 5H), 7.16 – 7.01 (m, 3H), 7.01 – 6.80 (m, 5H), 5.72 (s, 1H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 143.6, 142.1, 138.8, 138.3, 135.0, 129.4, 129.0, 128.8, 126.7, 125.5, 123.9, 121.9, 118.8, 117.6, 21.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{18}NS$ $[M+H]^+$, 292.1154; found, 292.1156.

Spectroscopic Data of **(5e)**

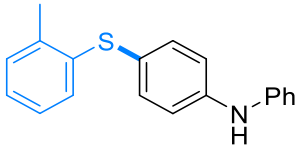
4-((3-bromophenyl)thio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a brown oil(44%yield, 45mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3348, 3192, 2751, 2512, 1927, 1504, 1017, 753, 630，560cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.49 – 7.21 (m, 4H), 7.21 – 7.12 (m, 3H), 7.10 – 7.05 (m, 2H), 7.05 – 6.90 (m, 4H), 5.79 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 143.4, 140.8, 140.6, 135.0, 129.1, 128.7, 128.4, 127.4, 124.8, 121.9, 121.3, 120.4, 118.3, 116.3 ; HRMS (TOF-ESI+): m/z calcd for $C_{18}H_{15}BrNS$ $[M+H]^+$, 356.0103; found, 356.0100.

Spectroscopic Data of **(5f)**

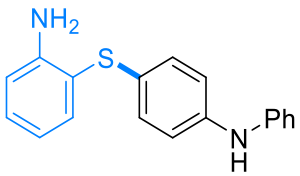
N-phenyl-4-(o-tolylthio)aniline



Synthesized according to General Procedure 2. The obtained product was a brown oil(63%yield, 55mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3465, 3056, 2535, 2049,1927, 1595, 1099, 755, 604, 553cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.54 – 7.13 (m, 5H), 7.14 – 7.06 (m, 1H), 7.06 – 6.82 (m, 7H), 5.71 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 142.3, 141.2, 136.2, 135.9, 133.4, 129.2, 128.4, 127.9, 125.4, 125.0, 122.7, 120.8, 117.7, 116.8, 19.3; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{18}NS$ $[M+H]^+$, 292.1154; found, 292.1156.

Spectroscopic Data of **(5g)**

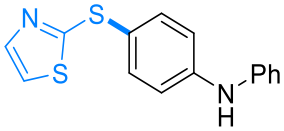
4-((2-aminophenyl)thio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a purple oil(66%yield, 58mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3500, 3143, 2648, 2254, 1607, 1159, 789, 604，501cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.34 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 – 7.06 (m, 3H), 7.06 – 6.98 (m, 2H), 6.98 – 6.91 (m, 2H), 6.92 – 6.76 (m, 3H), 6.67 (m, 2H), 5.59 (s, 1H), 4.21 (s, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 147.0, 141.8, 140.6, 135.3, 129.4, 128.5, 128.3, 125.9, 120.2, 117.7, 117.5, 116.9, 115.6, 114.3; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{17}N_2S$ $[M+H]^+$, 293.1107; found, 293.1110.

Spectroscopic Data of **(5h)**

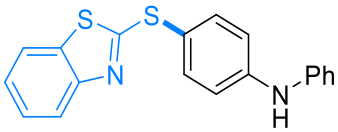
4-((4,5-dihydrothiazol-2-yl)thio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a white solid; (56%yield, 48mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ =20:1, R_f = 0.4); **Mp**:140-141℃; **IR**(KBr): 3430, 2968, 2542, 2246, 1926, 1590, 1126, 922, 798, 644, 562 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 7.69 (d, *J* = 3.4 Hz, 1H), 7.59 – 7.45 (m, 3H), 7.37 – 7.25 (m, 2H), 7.16 (td, *J* = 8.6, 1.7 Hz, 4H), 6.95 (tt, *J* = 7.3, 1.2 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 169.4, 146.7, 143.8, 142.2, 137.1, 129.8, 121.9, 121.0, 119.2, 117.7, 116.8; **HRMS** (TOF-ESI+): m/z calcd for $C_{15}H_{13}N_2S_2[M+H]^+$, 285.0515; found, 285.0516.

Spectroscopic Data of **(5i)**

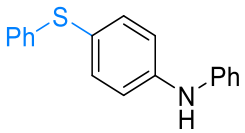
4-(benzo[d]thiazol-2-ylthio)-N-phenylaniline



Synthesized according to General Procedure 2. The obtained product was a pale yellow solid; (42%yield, 42mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ =20:1, R_f = 0.4); **Mp**:102-103℃; **IR**(KBr): 3474, 3317, 2765, 2545, 2249, 1928, 1566, 1035, 788, 633 cm^{-1}; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.63 – 7.53 (m, 2H), 7.46 – 7.27 (m, 3H), 7.26 – 7.15 (m, 3H), 7.15 – 6.94 (m, 3H), 6.01 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.2, 145.3, 140.0, 136.5, 134.4, 128.5, 125.0, 123.0, 122.0, 120.7, 119.7, 119.1, 117.3, 115.7; **HRMS** (TOF-ESI+): m/z calcd for $C_{19}H_{15}N_2S_2[M+H]^+$, 335.0671; found, 335.0672.

Spectroscopic Data of **(6a)**

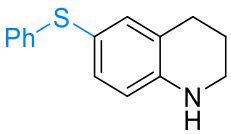
N-phenyl-4-(phenylthio)aniline



Synthesized according to General Procedure 2. The obtained product was a brown oil(47%yield, 39mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3461, 2977, 2419, 1928, 1650, 1271, 1040, 885, 740, 688 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.04 (m, 11H), 7.03 – 6.83 (m, 3H), 5.77 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 142.7, 141.0, 137.7, 134.2, 128.4, 127.9, 127.1, 124.7, 122.4, 120.9, 117.9, 116.5; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{16}NS$ $[M+H]^+$, 278.0098; found, 278.0098.

Spectroscopic Data of **(6b)**

6-(phenylthio)-1,2,3,4-tetrahydroquinoline

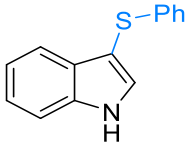


Synthesized according to General Procedure 2. The obtained product was a yellow oil(43%yield, 33mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3305, 3033,

2970, 2415, 2139, 1927, 1478, 1013, 736, 634, 551cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.19 (s, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.08 – 6.85 (m, 4H), 6.59 – 6.18 (m, 1H), 3.95 (s, 1H), 3.43 – 3.12 (m, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 1.87 (p, *J* = 6.1 Hz, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 144.4, 139.4, 135.4, 133.0, 127.7, 125.7, 123.8, 121.2, 116.4, 113.6, 40.8, 25.8, 20.6; **HRMS** (TOF-ESI+): m/z calcd for $C_{15}H_{16}NS$ $[M+H]^+$,242.0998; found, 242.0993.

Spectroscopic Data of **(6c)**

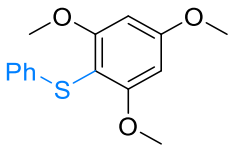
3-(phenylthio)-1H-indole



Synthesized according to General Procedure 2. The obtained product was a white solid(42%yield, 27mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.4); **Mp**:156-157℃; **IR**(KBr): 3452, 3021, 1436, 1404, 1332, 1322, 1278, 751, 698cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.36 (s, 1H), 7.58 – 7.50 (m, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.38 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.12 – 7.06 (m, 3H), 7.05 – 6.96 (m, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 138.2, 135.4, 129.6, 128.0, 127.6, 124.8, 123.7, 122.0, 119.9, 118.6, 110.5, 101.8; Data consistent with those previously reported. [2]

Spectroscopic Data of **(6d)**

phenyl(2,4,6-trimethoxyphenyl)sulfane

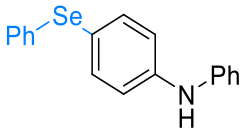


Synthesized according to General Procedure 2. The obtained product was a white solid(38%yield, 30mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.5); **Mp**:122-123℃; **IR**(KBr): 3011, 2941, 2839, 1738, 1576, 1454, 1339, 1228, 1185, 1093, 1022, 742, 653cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.09 (dd, *J* = 8.7, 6.7 Hz, 2H), 6.96 (td,

J = 7.3, 1.4 Hz, 3H), 6.15 (s, 2H), 3.81 (s, 3H), 3.74 (s, 6H); **^{13}C NMR** (100 MHz,Chloroform-d) δ 161.9, 161.5, 137.6, 127.5, 124.6, 123.3, 97.5, 90.1, 55.3, 54.4. Data consistent with those previously reported. [3]

Spectroscopic Data of **(8a)**

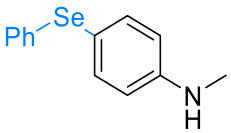
N-phenyl-4-(phenylselanyl)aniline



Synthesized according to General Procedure 3. The obtained product was a brown oil(83%yield, 81mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **IR**(KBr): 3522, 3238, 2542, 2259, 1926, 1584, 1038, 716, 640cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.08 (m, 7H), 7.06 – 6.99 (m, 2H), 6.91 (d, *J* = 8.6 Hz, 3H), 5.69 (s, 1H); 13C NMR (100MHz, Chloroform-d) δ 142.6, 141.1, 135.4, 132.3, 129.8, 128.4, 128.1, 125.4, 120.8, 118.3, 117.8, 116.7; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{16}NSe$ $[M+H]^+$, 326.0442; found, 326.0441.

Spectroscopic Data of **(8b)**

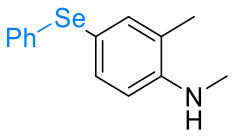
N-methyl-4-(phenylselanyl)aniline



Synthesized according to General Procedure 3. The obtained product was a brown oil (86%yield, 69mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 200:1, R_f = 0.4); **IR**(KBr): 3420, 2925, 1595, 1503, 1317, 1181, 745cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.41 – 7.34 (m, 2H), 7.24 – 7.02 (m, 5H), 6.50 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 1H), 2.78 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 148.5, 136.3, 133.5, 128.7, 128.0, 124.8, 113.5, 112.2, 29.5; Data consistent with those previously reported.[4]

Spectroscopic Data of **(8c)**

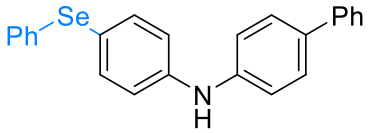
N,2-dimethyl-4-(phenylselanyl)aniline



Synthesized according to General Procedure 3. The obtained product was a yellow oil (76%yield, 63mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 200:1, R_f = 0.4); **IR**(KBr): 3420, 2925, 1595, 1503, 1317, 1181, 745cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.14 – 7.00(m, 3H), 6.48 (d, *J* = 8.3 Hz, 1H), 3.63 (s, 1H), 2.83 (s, 3H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 147.7, 137.7, 135.5, 134.8, 129.7, 129.0, 125.8, 123.0, 114.0, 109.9, 30.6, 17.2; **HRMS** (TOF-ESI+): m/z calcd for $C_{14}H_{16}NSe$ $[M+H]^+$, 278.0442; found, 278.0438.

Spectroscopic Data of **(8d)**

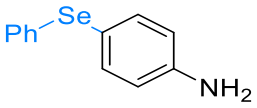
N-(4-(phenylselanyl)phenyl)-[1,1'-biphenyl]-4-amine



Synthesized according to General Procedure 3. The obtained product was a white solid(87%yield, 117mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 100:1, R_f = 0.3); **Mp**:149-150℃; **IR**(KBr): 3321, 2979, 1929, 1591, 1320, 1050, 744, 642cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.70 – 7.26 (m, 10H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.20 – 7.00 (m, 5H), 6.94 (d, *J* = 8.6 Hz, 2H), 5.75 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 142.3, 140.5, 139.6, 135.3, 133.5, 129.9, 128.1, 127.7, 127.0, 125.7, 125.6, 125.4, 118.7, 117.7, 117.0; **HRMS** (TOF-ESI+): m/z calcd for $C_{24}H_{20}NSe$ $[M+H]^+$, 402.0755; found, 402.0750.

Spectroscopic Data of **(8e)**

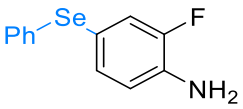
4-(phenylselanyl)aniline



Synthesized according to General Procedure 3. The obtained product was a white solid(88%yield, 66mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.4); **Mp**:89-91℃; **IR**(KBr): 3447, 3358, 1607, 1486, 1054, 650 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 7.14 – 7.01 (m, 3H), 6.69 – 6.31 (m, 2H), 3.67 (s, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 145.8, 136.1, 133.1, 129.0, 128.0, 125.0, 115.3, 115.0; Data consistent with those previously reported. [5]

Spectroscopic Data of **(8f)**

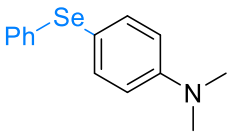
2-fluoro-4-(phenylselanyl)aniline



Synthesized according to General Procedure 3. The obtained product was a yellow oil(69%yield, 55mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.4); **IR**(KBr): 3468, 3372, 1610, 1476, 1064, 632 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 6.91 (m, 7H), 6.72 (t, *J* = 8.6 Hz, 1H), 3.83 (s, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.3(d, $J_{C\text{-}F}$ =242 Hz), 133.9(d, *J* =13 Hz), 132.0, 130.7(d, *J* =3 Hz), 129.8, 128.2, 125.5, 121.1(d, *J* =19 Hz), 116.3(d, *J* =4 Hz), 115.6(d, *J* =6 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -133.8; **HRMS** (TOF-ESI+): m/z calcd for $C_{12}H_{11}FNSe$ $[M+H]^+$: 268.0035; found:268.0035.

Spectroscopic Data of **(8g)**

N,N-dimethyl-4-(phenylselanyl)aniline

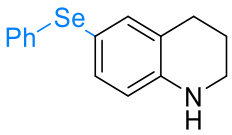


Synthesized according to General Procedure 3. The obtained product was a yellow oil(91%yield, 75mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 50:1, R_f = 0.4); **IR**(KBr): 3067, 1589,

1503, 1360, 1193, 652cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.45 – 7.37 (m, 2H), 7.24 – 7.14 (m, 2H), 7.14 – 7.00 (m, 3H), 6.64 – 6.52 (m, 2H), 2.89 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 150.6, 137.2, 134.7, 129.8, 129.0, 125.8, 113.7, 113.2, 40.4; Data consistent with those previously reported. [2]

Spectroscopic Data of **(8h)**

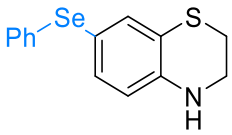
6-(phenylselanyl)-1,2,3,4-tetrahydroquinoline



Synthesized according to General Procedure 3. The obtained product was a yellow solid(89%yield, 78mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **Mp**:47-49℃; **IR**(KBr): 3414, 2927, 1595, 1501, 1475, 1437, 1299, 1021, 810, 735, 690; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.26 – 7.01 (m, 7H), 6.34 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 1H), 3.28 – 3.21 (m, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 1.91 – 1.80 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 144.2, 136.4, 133.9, 133.7, 128.7, 127.9, 124.7, 121.4, 113.8, 112.7, 40.8, 25.8, 20.7; Data consistent with those previously reported. [4]

Spectroscopic Data of **(8i)**

7-(phenylselanyl)-3,4-dihydro-2H-benzo[b][1,4]thiazine

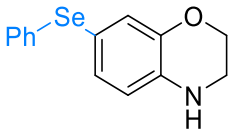


Synthesized according to General Procedure 3. The obtained product was a yellow solid(72%yield, 66mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **Mp**:108-109℃; **IR**(KBr): 3474, 2994, 2944, 1766, 1245, 1056, 746, 693; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.27 – 7.17 (m, 3H), 7.17 – 7.01 (m, 4H), 6.33 (d, *J* = 8.2 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.62 – 3.53 (m, 2H), 3.02 – 2.93 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 142.0, 135.0, 133.9, 133.2, 130.3, 129.1, 126.1, 116.9, 116.0, 115.7,

42.3, 25.6; **HRMS** (TOF-ESI+): m/z calcd for $C_{14}H_{14}NSSe$ $[M+H]^+$, 308.0007; found, 308.0005.

Spectroscopic Data of **(8j)**

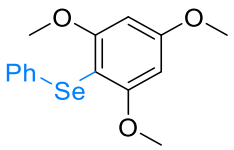
7-(phenylselanyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine



Synthesized according to General Procedure 3. The obtained product was a brown oil(85%yield, 75mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **IR**(KBr): 3298, 2976, 2261, 1929, 1588, 1041, 745, 652cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 – 6.84 (m, 6H), 6.80 – 6.48 (m, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 4.21 – 4.03 (m, 2H), 3.77 (s, 1H), 3.32 (dt, *J* = 6.3, 3.2 Hz, 2H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 143.2, 133.1, 132.7, 129.5, 128.0, 127.7, 125.1, 122.7, 115.4, 114.9, 114.6, 64.0, 39.7; **HRMS** (TOF-ESI+): m/z calcd for $C_{14}H_{14}NOSe$ $[M+H]^+$, 292.0235; found, 292.0231.

Spectroscopic Data of **(8k)**

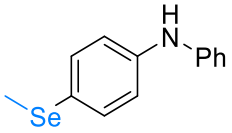
phenyl(2,4,6-trimethoxyphenyl)selane



Synthesized according to General Procedure 3. The obtained product was a white solid(65%yield, 63mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **Mp**:99-100℃; **IR**(KBr): 1578, 1467, 1452, 1409, 1336, 1228, 1204, 1162, 1123, 814, 735cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.15 – 6.98 (m, 5H), 6.13 (s, 2H), 3.78 (s, 3H), 3.71 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 163.0, 161.9, 133.6, 128.7, 128.7, 125.3, 97.0, 91.2, 56.3, 55.4; Data consistent with those previously reported. [4]

Spectroscopic Data of **(8l)**

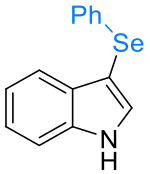
4-(methylselanyl)-N-phenylaniline



Synthesized according to General Procedure 3. The obtained product was a white solid(67%yield, 53mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.3); **Mp**:78-80℃; **IR**(KBr): 3417, 2956, 2548, 1585, 1407, 1178, 762, 647cm^{-1}; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.13 (m, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.95 – 6.83 (m, 3H), 5.62 (s, 1H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 141.69, 141.13, 132.15, 128.35, 120.64, 120.25, 117.32, 116.97, 7.58; **HRMS** (TOF-ESI+): m/z calcd for $C_{14}H_{14}NSSe$ $[M+H]^+$, 307.9998. ; **HRMS** (TOF-ESI+): m/z calcd for $C_{13}H_{14}NSe$ $[M+H]^+$, 264.0286; found, 264.0287.

Spectroscopic Data of **(9a)**

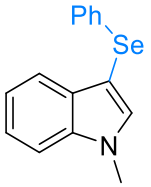
3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white solid(81%yield, 75mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **Mp**:145-146℃; **IR**(KBr): 3410, 3123, 3049, 2921, 1646, 1573, 1451, 1236, 1020, 825, 730, 684 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.33 (s, 1H), 7.56 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.50 – 7.30 (m, 2H), 7.29 – 6.94 (m, 7H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 136.4, 133.8, 131.3, 130.0, 129.0, 128.7, 125.6, 123.0, 120.9, 120.4, 111.39, 98.2; Data consistent with those previously reported. [4]

Spectroscopic Data of **(9b)**

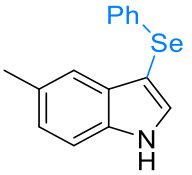
1-methyl-3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white oil(97%yield, 84mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **Mp**:67℃; **IR**(KBr): 3439, 3109, 1573, 1503, 1474, 1236, 1021, 738 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.56 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.34 – 6.97 (m, 9H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 136.5, 134.7, 133.3, 129.8, 128.0, 127.6, 124.6, 121.5, 119.5, 119.5, 108.6, 94.9, 32.17; Data consistent with those previously reported.[4]

Spectroscopic Data of **(9c)**

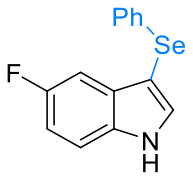
5-methyl-3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white solid(84%yield, 72mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **Mp**:107-108℃; **IR**(KBr): 3407, 1575, 1474, 1437, 1391, 1112, 1069, 1019, 797, 741, 646cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.37 – 7.95 (s, 1H), 7.24 (d, *J* = 2.6 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.08 – 7.03 (m, 2H), 7.03 – 6.89 (m, 4H), 6.74 (d, *J* = 7.0 Hz, 1H), 2.55 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 136.9, 136.2, 132.6, 132.3, 129.1, 128.1, 128.9, 127.3, 125.4, 123.0, 122.5, 109.4, 96.8, 18.9; Data consistent with those previously reported.[4]

Spectroscopic Data of **(9d)**

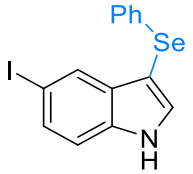
5-fluoro-3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white solid(99%yield, 87mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **Mp**:161-162℃; **IR**(KBr): 3416, 3044, 2259, 1927, 1668, 1267, 1024, 785, 646 cm^{-1}; **^{1}H NMR** (400 MHz, Acetone-d6) δ 10.95 (s, 1H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.35 – 7.08 (m, 6H), 7.01 (m, *J* = 9.1, 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, Acetone-d6) δ 158.4(d, J_{C-F} = 231 Hz), 134.5(d, *J* = 80 Hz), 134.3, 130.8(dd, *J* = 10 Hz), 129.0, 128.4, 125.7, 113.2(d, *J* = 9 Hz), 113.1(d, *J* = 9 Hz)110.7, 110.4, 104.2, 104.0, 96.4; **19F NMR** (376 MHz, Acetone) δ -124.94; Data consistent with those previously reported. [4]

Spectroscopic Data of **(9e)**

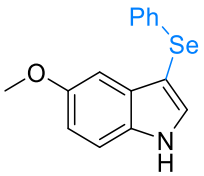
5-iodo-3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white solid(95%yield, 114mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); Mp:125-128℃; **IR**(KBr): 3451, 2984, 2139, 1927, 1274, 1088, 883, 740, 654 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.37 (s, 1H), 7.90 (d, *J* = 1.7 Hz, 1H), 7.71 – 7.30 (m, 2H), 7.30 – 6.84 (m, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 134.5, 132.3, 131.5, 131.0, 130.4, 128.2, 128.0, 127.6, 124.8, 112.3, 96.5, 83.6; Data consistent with those previously reported. [6]

Spectroscopic Data of **(9f)**

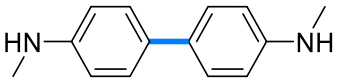
5-methoxy-3-(phenylselanyl)-1H-indole



Synthesized according to General Procedure 3. The obtained product was a white oil(87%yield, 78mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.5); **IR**(KBr): 3401, 3198, 2419, 1926, 1441, 1166, 1028, 825, 788, 727, 634, 552 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.48 – 8.01 (m, 1H), 7.34 (d, *J* = 2.6 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.11 – 6.95 (m, 4H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 155.1, 134.0, 132.0, 131.3, 130.8, 129.0, 128.5, 125.6, 113.5, 112.3, 101.5, 97.6, 55.8; Data consistent with those previously reported.[6]

Spectroscopic Data of **(10a)**

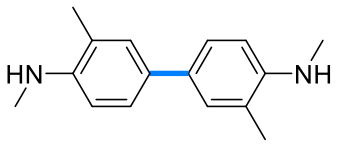
N^4,N^4'-dimethyl-[1,1'-biphenyl]-4,4'-diamine



Synthesized according to General Procedure 4. The obtained product was a yellow oil(35%yield, 22mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.4); **IR**(KBr): 3355, 2227, 1736, 1628, 1597, 1217, 1024 ,643cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 8.2 Hz, 4H), 6.48 (m, 4H), 3.71 (s, 2H), 2.74 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*)\δ 146.4, 129.9, 128.5, 111.5, 30.0; **HRMS** (TOF-ESI+): m/z calcd for $C_{14}H_{17}N_2$ $[M+H]^+$, 213.1386; found:213.1382.

Spectroscopic Data of **(10b)**

N4,N4',3,3'-tetramethyl-[1,1'-biphenyl]-4,4'-diamine

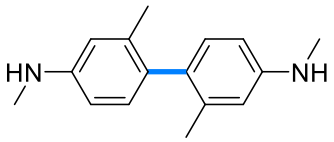


Synthesized according to General Procedure 4. The obtained product was a yellow oil(37%yield, 26mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.4); **IR**(KBr): 3432, 2145, 1836, 1528, 1226, 1075 ,756, 643cm-1; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.03 –

6.97 (m, 2H), 6.93 – 6.87 (m, 2H), 6.56 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 2H), 2.89 (s, 6H), 2.11 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 144.3, 129.5, 126.2, 121.1, 108.2, 30.0, 16.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{16}H_{21}N_2$ $[M+H]^+$, 241.1699; found:240.1696.

Spectroscopic Data of **(10c)**

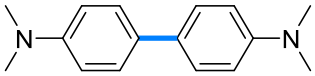
N4,N4',2,2'-tetramethyl-[1,1'-biphenyl]-4,4'-diamine



Synthesized according to General Procedure 4. The obtained product was a yellow oil(36%yield, 25mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 10:1, R_f = 0.4); **IR**(KBr): 3435, 2135, 1826, 1528, 1229, 1064 ,762, 643cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.65 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 2.6 Hz, 2H), 6.31 (d, *J* = 8.2Hz, 2H), 3.64 (s, 2H), 2.74 (s, 6H), 2.13 (s, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.6, 136.3, 128.9, 127.1, 113.4, 109.0, 30.0, 18.8; **HRMS** (TOF-ESI+): m/z calcd for $C_{16}H_{21}N_2$ $[M+H]^+$, 241.1699.; found:241.1670.

Spectroscopic Data of **(10d)**

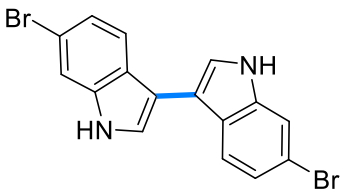
N4,N4,N4',N4'-tetramethyl-[1,1'-biphenyl]-4,4'-diamine



Synthesized according to General Procedure 4. The obtained product was a white solid (46%yield, 33mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 60:1, R_f = 0.4); **MP**:140-142℃; **IR**(KBr): 3074, 2832, 1805, 1547, 1461, 1291, 1139, 1083, 713, 633, 561 cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 – 6.85 (m, 4H), 6.73 – 6.39 (m, 4H), 2.81 (s, 12H);**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 148.0, 129.3, 128.4, 112.0, 40.0; **HRMS** (TOF-ESI+): m/z calcd for $C_{16}H_{21}N_2$ $[M+H]^+$, 241.1699.; found:241.1697.

Spectroscopic Data of **(10e)**

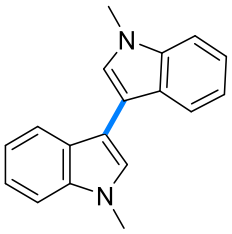
6,6'-dibromo-1H,1'H-3,3'-biindole



Synthesized according to General Procedure 4. The obtained product was a white solid (45%yield, 52mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.4); **MP**:239-240℃; **IR**(KBr): 3382, 1589, 1519, 1335, 789 cm^{-1};**^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.41 (s, 2H), 7.83 – 7.62 (m, 6H), 7.22 (dd, *J* = 8.5 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 137.7, 125.4, 123.5, 122.3, 121.7, 114.6, 114.5, 109.8; **HRMS** (TOF-ESI+): m/z calcd for $C_{16}H_{21}N_2$ $[M+H]^+$, 388.9283.; found:387.9282.

Spectroscopic Data of **(10f)**

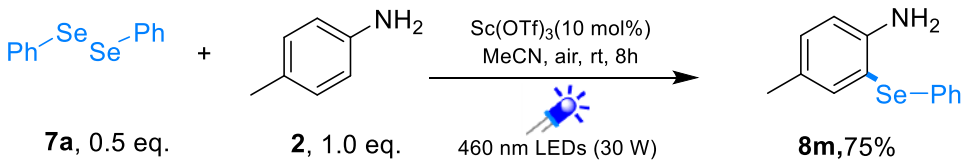
1,1'-dimethyl-1H,1'H-3,3'-biindole



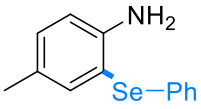
Synthesized according to General Procedure 4. The obtained product was a white solid(46%yield, 36mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1, R_f = 0.4); **Mp**:69-70℃; **IR**(KBr): 2995, 2359, 1769, 1241, 739 cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.76 (dd, *J* = 8.2Hz, 2H), 7.30 (dd, *J* = 8.2Hz, 2H), 7.27 – 7.14 (m, 4H), 7.12-7.05 (m, 2H), 3.96 – 3.56 (m, 6H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 137.1, 127.2, 126.1, 121.8, 120.3, 119.2, 109.5, 109.3, 32.9; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{16}N_2Na$ $[M+Na]^+$, 283.1210; found:283.1206.

4. Mechanistic studies

a)



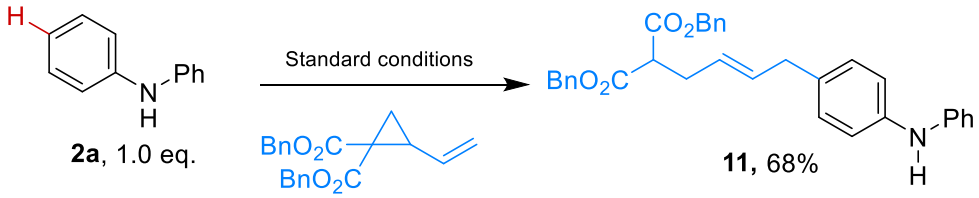
4-methyl-2-(phenylselanyl)aniline ***(8m)***.



Synthesized according to General Procedure 3. The obtained product was a yellow oil(75%yield, 58mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 30:1, R_f = 0.4); **IR**(KBr): 3458, 3365, 1611, 1490, 1066, 1079, 643cm^{-1};**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 2.0, 1H), 7.17 – 7.04 (m, 5H), 6.96 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 3.98 (s, 2H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.2, 138.7, 131.9, 131.8, 129.3, 129.2, 128.2, 126.1, 115.1, 112.7, 20.2; **HRMS** (TOF-ESI+): m/z calcd for $C_{13}H_{14}NSe$ $[M+H]^+$, 264.0286; found:264.0288.

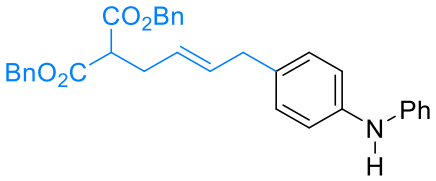
b) radical clock experients

1)



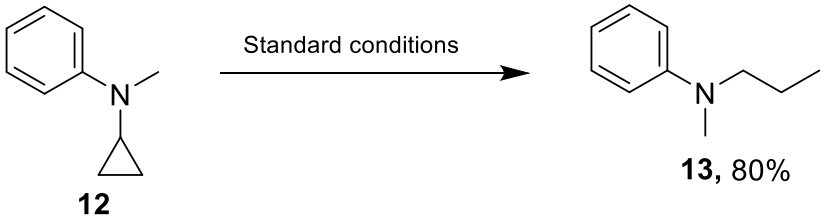
Under air atmosphere, arylamine **2a** (0.1 mmol, 1.0 equiv), dibenzyl 2-vinylcyclopropane-1,1-dicarboxylate, $Sc(OTf)_3$ (10 mol%, 0.01mmol) in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 8 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **11**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS .

dibenzyl (E)-2-(4-(4-(phenylamino)phenyl)but-2-en-1-yl)malonate***(11)***



The obtained product was a yellow oil(68%yield, 103mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 20:1, R_f = 0.4); **IR**(KBr): 3462, 3065, 1789, 1626, 1548, 1278, 1089, 864, 633cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d) δ7.24 – 7.06 (m, 15H), 6.90 – 6.77 (m, 4H), 5.57 – 5.45 (m, 2H), 5.41 – 5.21 (m, 1H), 5.08 – 4.98 (m, 4H), 3.44 (t, *J* = 7.5 Hz, 1H), 3.16 (dd, *J* = 6.1Hz, 2H), 2.63 – 2.50 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 167.56, 140.34, 134.22, 130.70, 129.48, 128.23, 127.51, 127.33, 127.24, 127.17, 126.28, 125.76, 121.31, 119.04, 119.01, 115.95, 66.14, 50.91, 34.33, 30.62; **HRMS** (TOF-ESI+): m/z calcd for $C_{33}H_{32}NO_4$ $[M+H]^+$, 506.2326; found:506.2305.

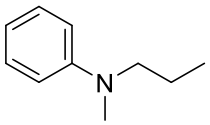
2)



12 **13,** 80%

.

N-methyl-N-propylaniline(***13***)

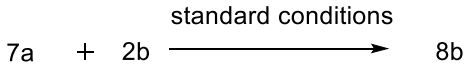


The obtained product was a yellow oil(80%yield, 36mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 150:1, R_f = 0.4); **IR**(KBr): 2958, 2129, 1596, 1505, 1372, 1120, 1082, 844, 746, 693cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-d)δ 7.38 – 6.83 (m, 2H), 6.83 – 6.33 (m, 3H), 3.43 – 3.04 (m, 2H), 2.85 (s, 3H), 1.65 – 1.26 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 148.3, 128.1, 114.7, 110.9, 53.5, 37.3, 18.8, 10.5; **HRMS** (TOF-ESI+): m/z calcd for $C_{10}H_{16}N$ $[M+H]^+$, 150.1277; found:150.1278.

For preparing product **12**

N-methylaniline **2b** (0.1 mmol, 1.0 equiv), cyclopropyl bromide (0.15 mmol, 1.5 equiv), sodium carbonate (0.2 mmol, 2.0 equiv), MeCN (1.0 mL, 0.1 M) were added to the round-bottled flask for 10 hours after reflux. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **13**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS

c)



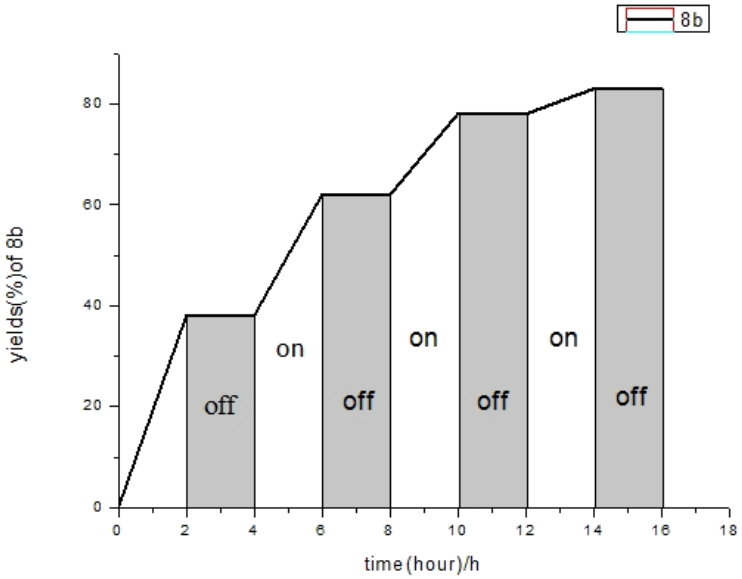


Figure S2. Switching light experient

d) UV-experiments

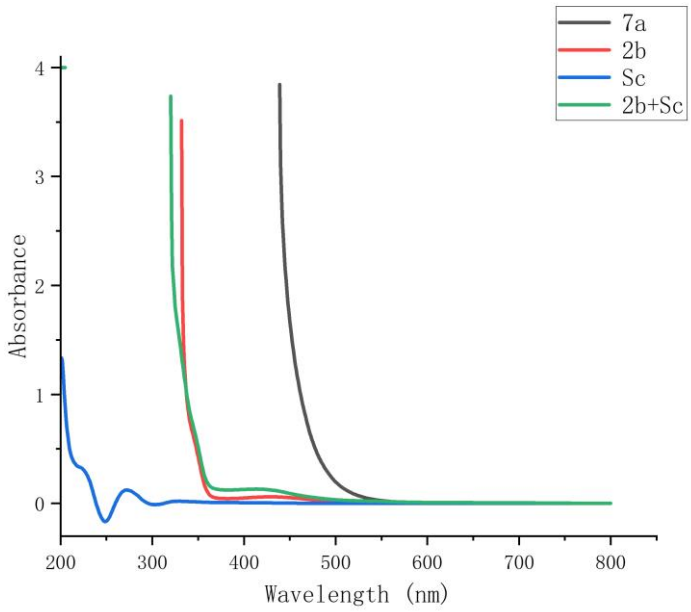


Figure S3. UV Spectra of 7a(0.4mmol), 2b(0.4mmol) and $Sc(OTf)_3$ (10mmol%) in MeCN(4mL)

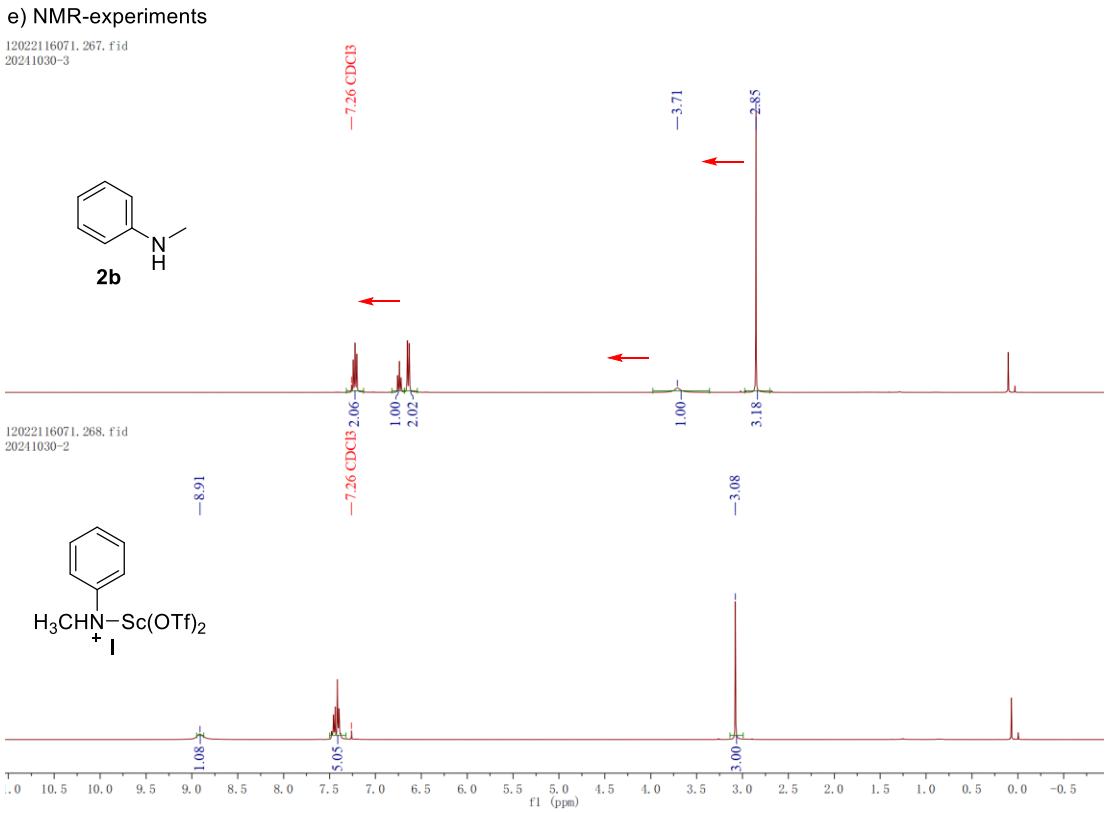
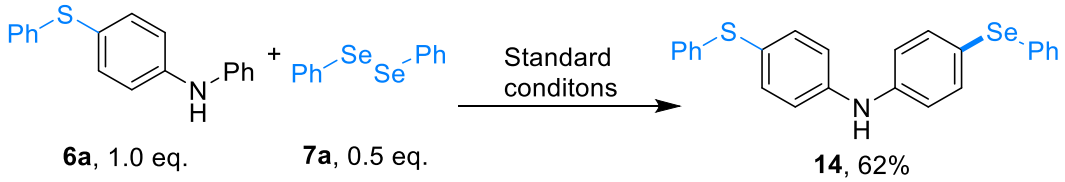


Figure S4. UV Spectra of 2b and intermediate I

Under air atmosphere, arylamine **2b** (0.1 mmol, 1.0 equiv), $Sc(OTf)_3$ (10 mol%, 0.01mmol) in $CDCl_3$ (1.0 mL, 0.1 M) were added to 20.0 mL reaction tub. After stirring for half an hour. Then, the products were further identified by NMR spectroscopy.

5. Synthetic applications

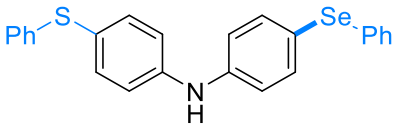
1)



6a, 1.0 eq. **7a**, 0.5 eq. **14**, 62%

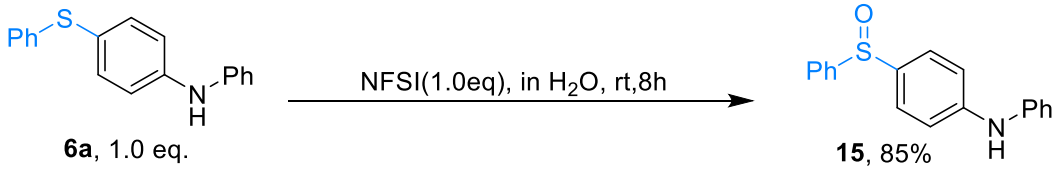
Under air atmosphere, N-phenyl-4-(phenylthio)aniline **6a** (0.1 mmol, 1.0 equiv) and selenide (0.05 mmol, 0.5 equiv) , $Sc(OTf)_3$ (10 mol%, 0.01mmol) and in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 8 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The products were further identified by HRMS .This product **14** was further identified by NMR spectroscop.

*4-(phenylselanyl)-N-(4-(phenylthio)phenyl)aniline **(14).***



The obtained product was a brown solid(62%yield, 80mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.2); **Mp**:112-114℃; **IR**(KBr): 3476, 2976, 2923, 2328, 1868, 1682, 1588, 1501, 1416, 1052, 757, 683cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.05 (m, 11H), 7.07 – 6.96 (m, 4H), 6.92 (m, 3H), 5.72 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 143.1, 140.8, 137.5, 134.6, 131.4, 130.9, 129.6, 128.4, 128.2, 127.3, 125.9, 121.4, 121.1, 118.9, 116.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{24}H_{20}NSSe$ $[M+H]^+$, 434.0476; found, 434.0475.

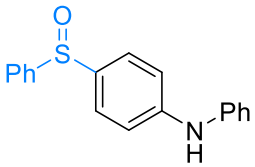
2)



6a, 1.0 eq. **15**, 85%

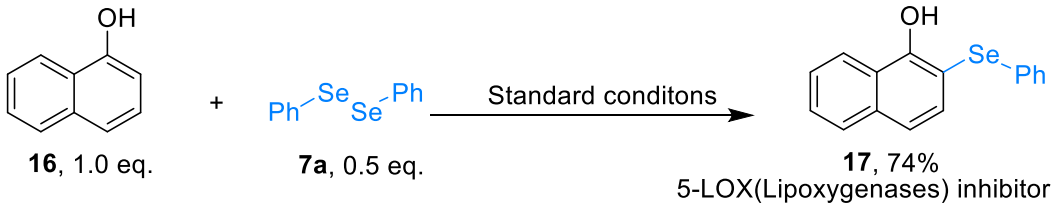
Under air atmosphere, N-phenyl-4-(phenylthio)aniline **6a** (0.1 mmol, 1.0 equiv), NFSI (0.1mmol, 1.0eq) and in H_2O (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at room temperature reflux and monitored by TLC. After stirring for 8h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The products were further identified by HRMS.This product **15** was further identified by NMR spectroscop.

*N-phenyl-4-(phenylsulfinyl)aniline**(15)**.*



The obtained product was a paleyellow oil (85%yield, 72mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 100:1, R_f = 0.4); **IR**(KBr): 3382, 2979, 2546, 2257, 2140, 1928, 1585, 1452, 1050, 790, 650cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.27 – 7.11 (m, 6H), 7.11 – 6.99 (m, 3H), 6.99 – 6.86 (m, 3H), 5.74 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.7, 141.0, 137.7, 134.2, 128.4, 127.9, 127.1, 124.7, 122.4, 120.9, 117.9, 116.5; **HRMS** (TOF-ESI+): m/z calcd for $C_{18}H_{16}NOS$ $[M+H]^+$, 294.0947; found, 294.0944.

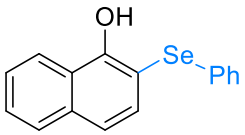
3)



16, 1.0 eq. **7a**, 0.5 eq. **17**, 74%
5-LOX(Lipoxygenases) inhibitor

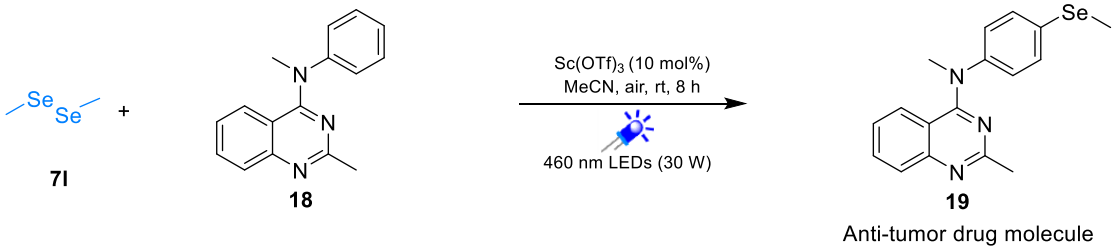
Under air atmosphere, naphthalen-1-ol **16** (0.1 mmol, 1.0 equiv) and selenide (0.05 mmol, 0.5 equiv) , $Sc(OTf)_3$ (10 mol%, 0.01mmol) and in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 8 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The products were further identified by HRMS. This product **17** was further identified by NMR spectroscop.

2-(phenylselanyl)naphthalen-1-ol ***(17)*****.**



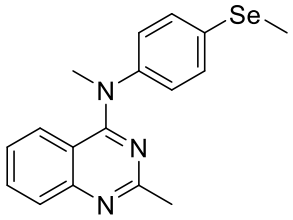
The obtained product was a pale yellow solid(74%yield, 66mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 500:1, R_f = 0.4); **Mp**:67-68℃; **IR**(KBr):3394, 3053, 1584, 1501, 1476, 1393, 1262, 1193, 1021, 878, 733, 658cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 – 8.14 (m, 1H), 7.73 (d, *J* = 7.3, 1.9 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.46 (m, 2H), 7.29 (s, 1H), 7.24 – 7.04 (m, 5H), 7.00 (s, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.8, 135.8, 133.4, 131.1, 129.5, 127.7, 127.6, 126.8, 125.8, 123.5, 123.4, 120.8, 107.6; **HRMS** (TOF-ESI+): m/z calcd for $C_{16}H_{13}OSe$ $[M+H]^+$, 301.0126, found 301.0125. Data consistent with those previously reported.[7]

4)



Under air atmosphere, compound **18** (0.1 mmol, 1.0 equiv) and selenide (0.05 mmol, 0.5 equiv) , $Sc(OTf)_3$ (10 mol%, 0.01mmol) and in MeCN (1.0 mL, 0.1 M) were added to 20.0 mL reaction tube(parallel three samples). The mixture was stirred at 460 nm light-emitting diodes (LEDs, 30 W) and monitored by TLC. After stirring for 8 h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The products were further identified by HRMS. This product **19** was further identified by NMR spectroscop.

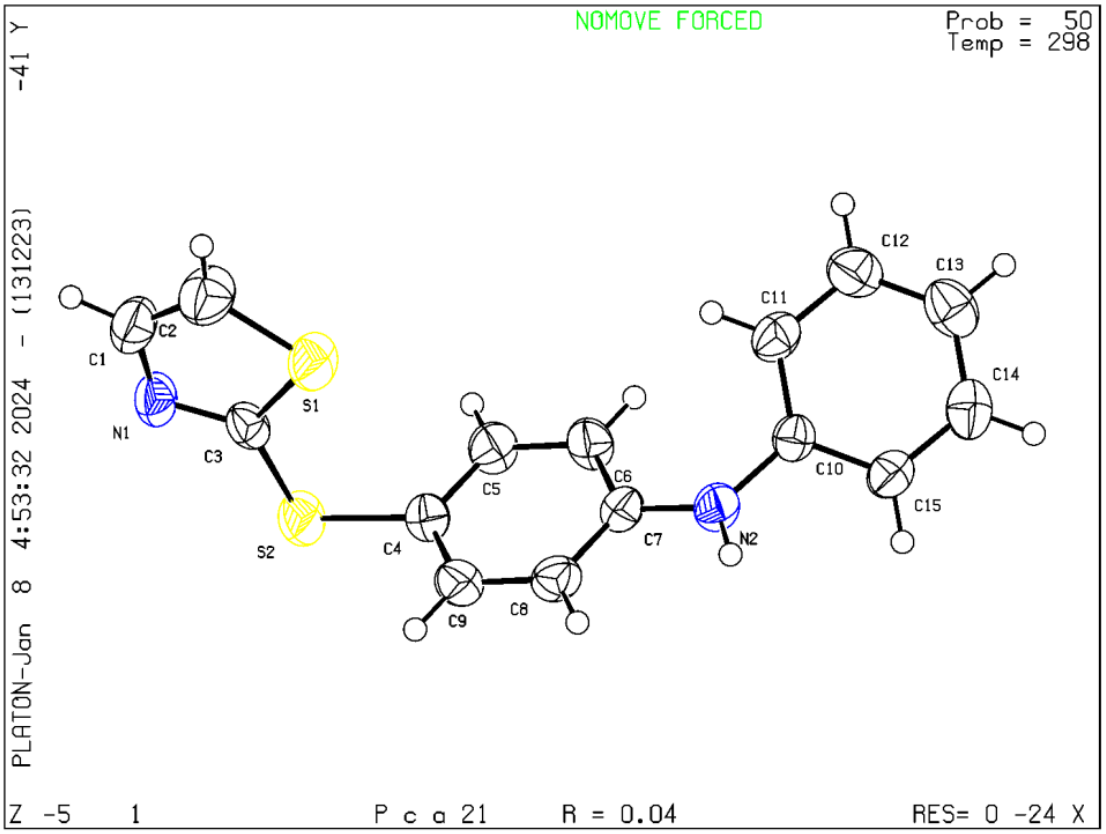
N,2-dimethyl-N-(4-(methylselanyl)phenyl)quinazolin-4-amine ***(19).***



The obtained product was a pale yellow solid (82% yield, 56mg, $V_{Petroleum\ ether}/V_{Ethyl\ acetate}$ = 5:1, R_f = 0.4); **Mp**:126-128°C; **IR**(KBr):3654, 3067, 1682, 1523, 1382, 1241, 1177, 1026, 834, 726cm^{-1}; **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.70 – 7.61 (m, 1H), 7.45 (dd, *J* = 8.4Hz, 1H), 7.32 – 7.23 (m, 2H), 7.03 – 6.82 (m, 4H), 3.51 (s, 3H), 2.65 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.4, 161.8, 152.1, 146.8, 131.9, 131.5, 129.3, 127.8, 126.2, 124.3, 114.8, 42.2, 26.5, 7.4; **HRMS** (TOF-ESI+): m/z calcd for $C_{17}H_{18}N_3Se$ $[M+H]^+$, 344.0660, found 344.0662. Data consistent with those previously reported.[8]

6. X-ray Structure and Data

X-ray Structure and Data of **5h**



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Figure S5. X-Ray crystal structure of **5h**

Table S1. Crystal data and structure refinement for **5h**

Datablock: 1

Bond precision: C-C = 0.0034 A Wavelength=0.71073

Cell: a=12.7451(8) b=6.2244(4) c=17.4968(10)
alpha=90 beta=90 gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	1388.03(15)	1388.03(15)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C15 H12 N2 S2	C15 H12 N2 S2
Sum formula	C15 H12 N2 S2	C15 H12 N2 S2
Mr	284.39	284.39
Dx,g cm-3	1.361	1.361
Z	4	4
Mu (mm-1)	0.370	0.370
F000	592.0	592.0
F000'	593.15	
h,k,lmax	17,8,23	17,8,23
Nref	3468[1791]	3339
Tmin,Tmax	0.911,0.936	0.695,0.746
Tmin'	0.908	

Correction method= # Reported T Limits: Tmin=0.695 Tmax=0.746
AbsCorr = MULTI-SCAN

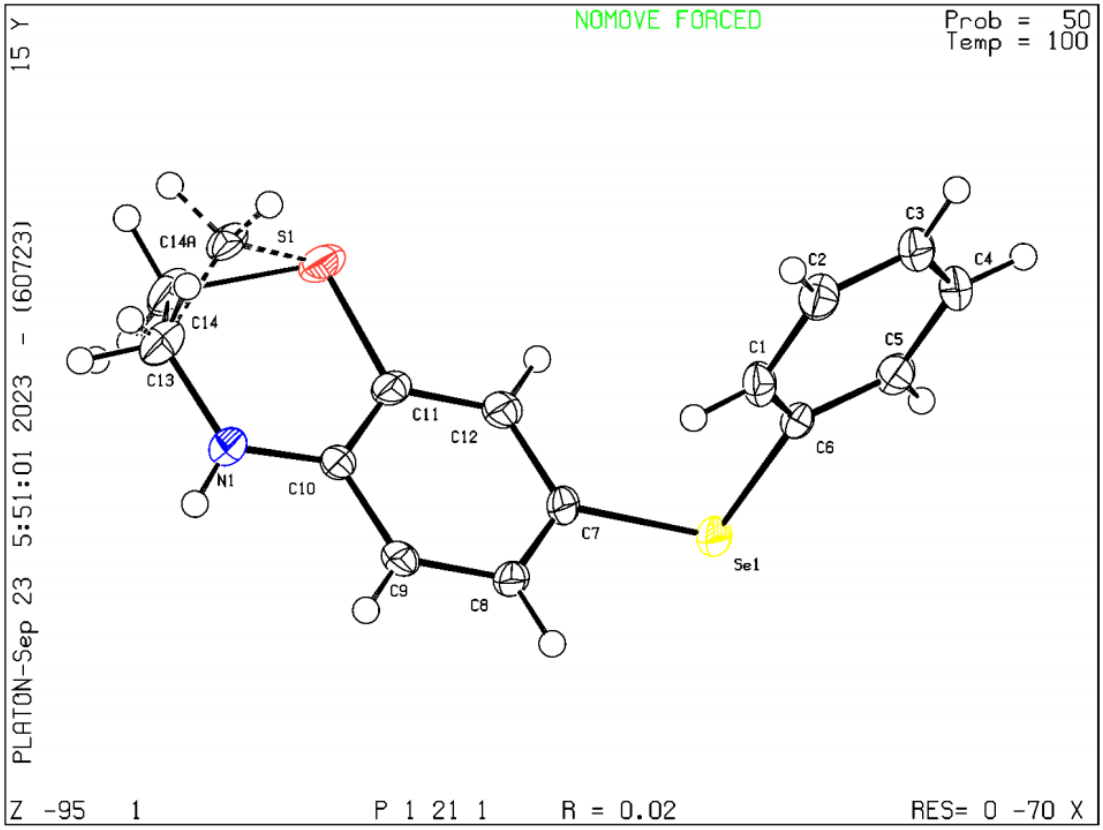
Data completeness= 1.86/0.96 Theta(max)= 28.338

R(reflections)= 0.0428(2653) wR2(reflections)= 0.0953(3339)

S = 1.086 Npar= 148

Add compound **5h** (48mg) to a 10mL sample bottle, add DCM (2mL), n-hexane (2mL) and toluene (1mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model： Bruker Apex 2. At the temperature of 298(2)K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use the φ-ω scanning method to collect all data in the range of 2.09<θ<25.01°, and use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method. Theoretically add the hydrogen atom on the C atom and use the fixed isotropic thermal parameters to modify the structure to determine its coordinates, while the hydrogen atom coordinates on the water molecule are determined by several rounds of difference Fourier synthesis.

X-ray Structure and Data of **8i**



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Figure S6. X-Ray crystal structure of **8i**

Table S22. Crystal data and structure refinement for **8i**

Datablock: 1

Bond precision: C-C = 0.0048 A Wavelength=0.71073

Cell: a=9.8644(6) b=5.9135(3) c=10.9549(6)
alpha=90 beta=103.916(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	620.28(6)	620.28(6)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C14 H13 N S Se	C14 H13 N S Se
Sum formula	C14 H13 N S Se	C14 H13 N S Se
Mr	306.27	306.27
Dx,g cm-3	1.640	1.640
Z	2	2
Mu (mm-1)	3.170	3.170
F000	308.0	308.0
F000'	308.15	
h,k,lmax	13,7,14	13,7,14
Nref	3101[1697]	2787
Tmin,Tmax	0.472,0.530	0.516,0.746
Tmin'	0.463	

Correction method= # Reported T Limits: Tmin=0.516 Tmax=0.746
AbsCorr = MULTI-SCAN

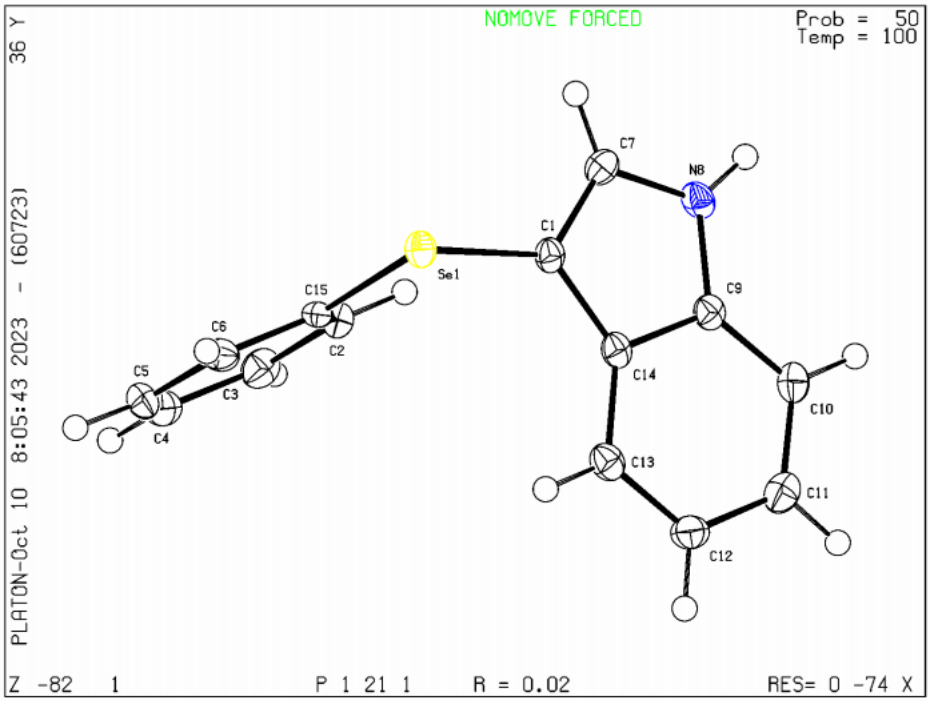
Data completeness= 1.64/0.90 Theta(max)= 28.354

R(reflections)= 0.0248(2604) wR2(reflections)= 0.0543(2787)

S = 1.031 Npar= 164

Add compound **8i** (66mg) to a 10mL sample bottle, add DCM (2mL), n-hexane (2mL) and toluene (1mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model： Bruker Apex 2. At the temperature of 298(2) K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use the φ-ω scanning method to collect all data in the range of 2.09<θ<25.01°, and use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method. Theoretically add the hydrogen atom on the C atom and use the fixed isotropic thermal parameters to modify the structure to determine its coordinates, while the hydrogen atom coordinates on the water molecule are determined by several rounds of difference Fourier synthesis.

X-ray Structure and Data of **9a**



The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Figure S7. X-Ray crystal structure of **9a**

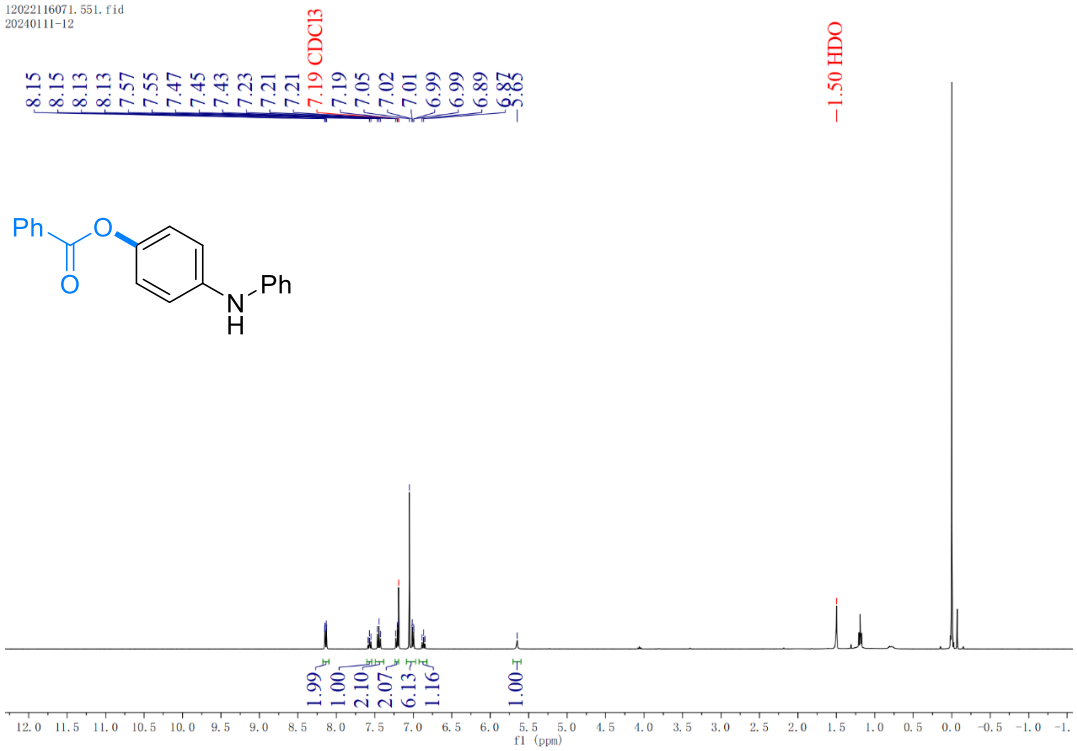
Table S3. Crystal data and structure refinement for **9a**

Datablock: 1

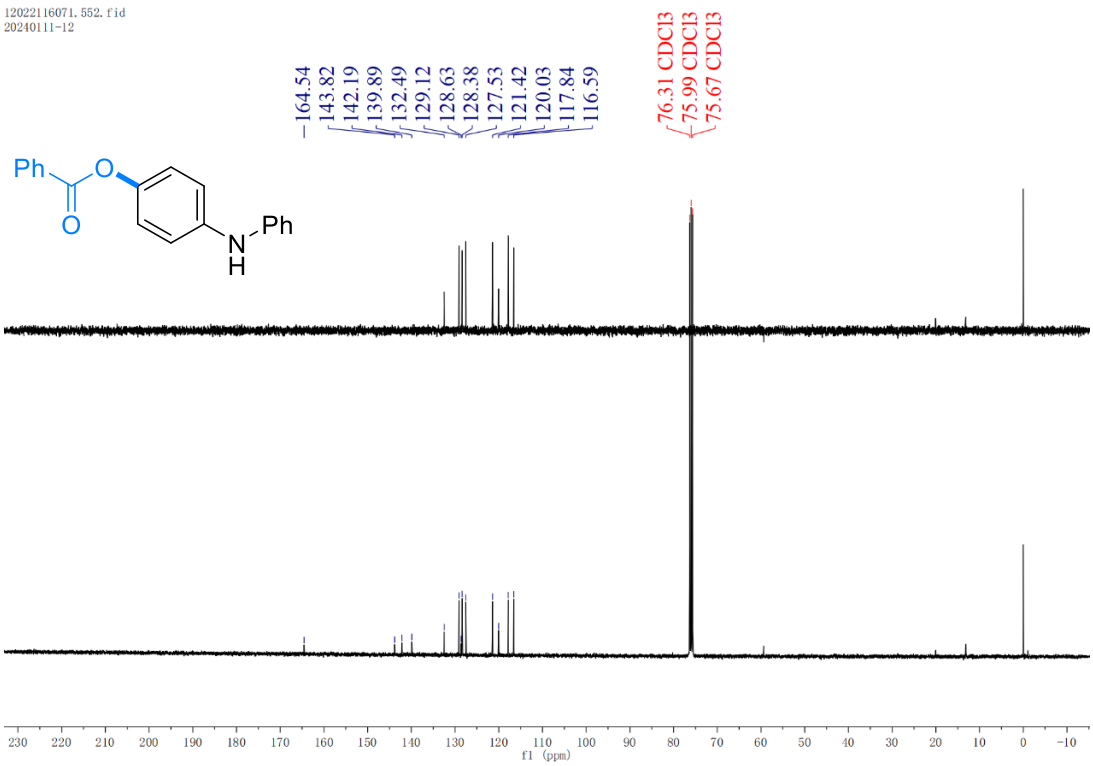
```
Bond precision:   C-C = 0.0043 A          Wavelength=0.71073

Cell:             a=9.7784(6)     b=5.9088(3)          c=9.9458(6)
                  alpha=90        beta=102.121(2)      gamma=90
Temperature:      100 K

                 Calculated                Reported
Volume           561.84(6)                 561.84(6)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C14 H11 N Se              C14 H11 N Se
Sum formula      C14 H11 N Se              C14 H11 N Se
Mr               272.20                    272.20
Dx,g cm-3        1.609                     1.609
Z                2                         2
Mu (mm-1)        3.310                     3.310
F000             272.0                     272.0
F000'            271.90
h,k,lmax         13,7,13                   13,7,13
Nref             2787[ 1526]               2782
Tmin,Tmax        0.494,0.589               0.624,0.746
Tmin'            0.447

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.82/1.00        Theta(max)= 28.285

R(reflections)= 0.0208( 2608)                    wR2(reflections)=
                                                 0.0428( 2782)
S = 1.067                  Npar= 145
```

Add compound **9a** (75mg) to a 10mL sample bottle, add DCM (2mL), n-hexane (2mL) and toluene (1mL), seal the bottle with a parafilm, poke 15 small holes on the parafilm, Place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it to the relevant test center for single crystal diffraction test to obtain relevant data. Instrument model： Bruker Apex 2. At the temperature of 298(2)K, the Mo-Kα radiation monochromated by the graphite monochromator (λ = 0.71073 Å), use the φ-ω scanning method to collect all data in the range of 2.09<θ<25.01°, and use BRUKER SAINT restores the data and performs absorption correction on the diffraction data through the SADABS program. Using SHELXTL software, the crystal structure was solved by the direct method. The coordinates of all non-hydrogen atoms and their anisotropic thermal parameters are corrected by the full matrix least square method. Theoretically add the hydrogen atom on the C atom and use the fixed isotropic thermal parameters to modify the structure to determine its coordinates, while the hydrogen atom coordinates on the water molecule are determined by several rounds of difference Fourier synthesis.

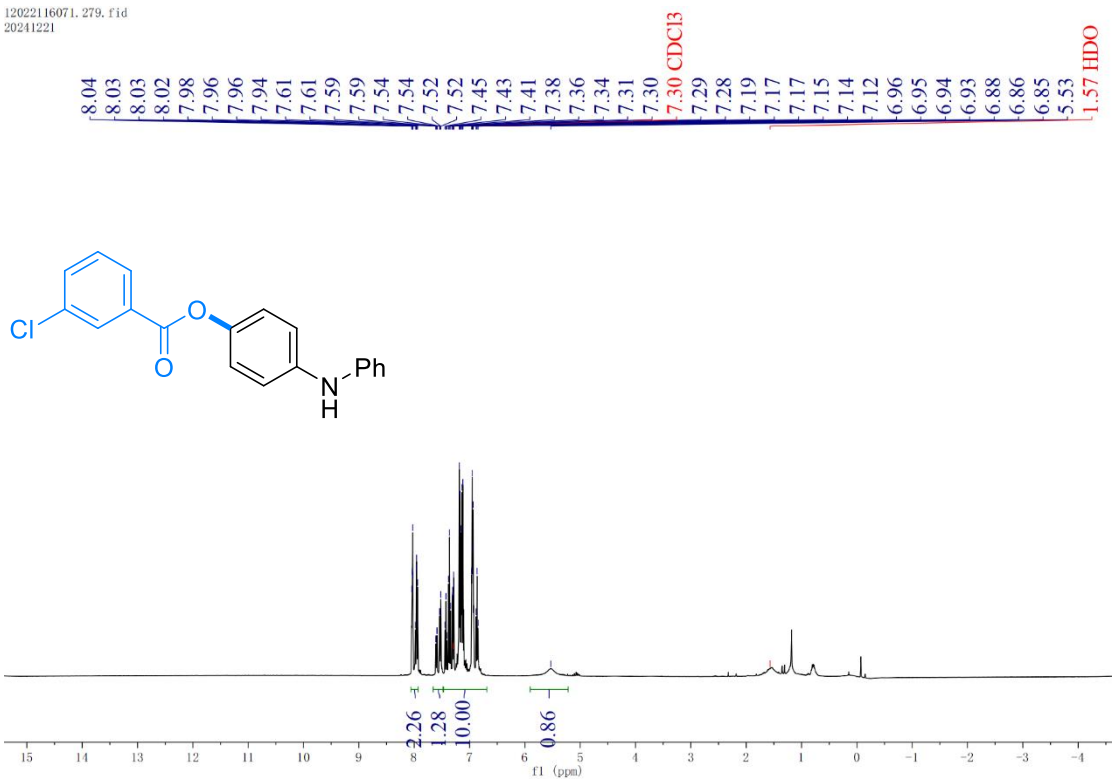
7. ^{1}H NMR and ^{13}C NMR spectra of **3,5,6,8,9,10,11,12,13,15.**



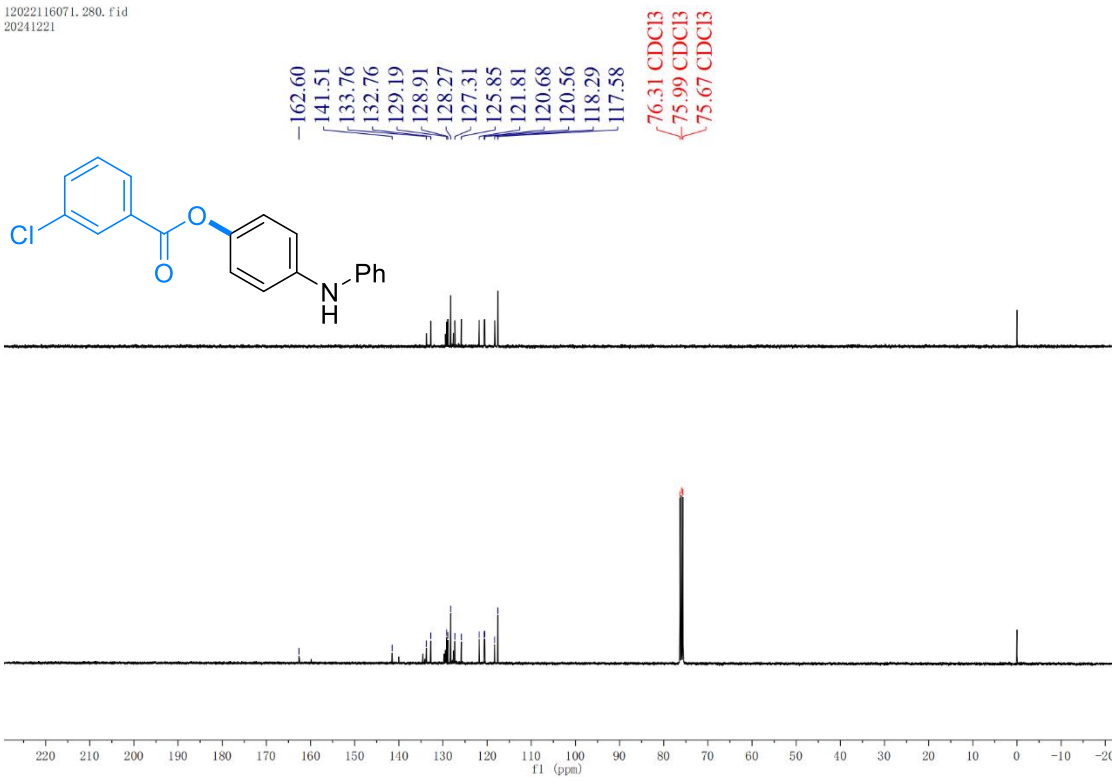
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3a**



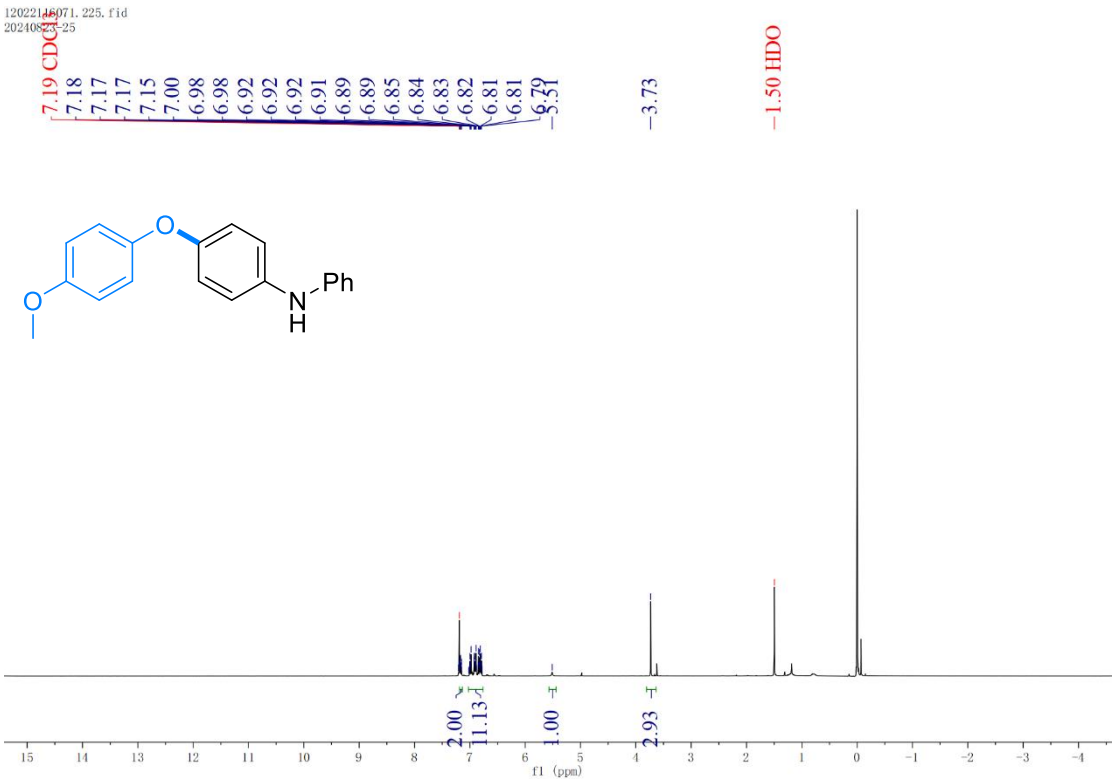
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3a**



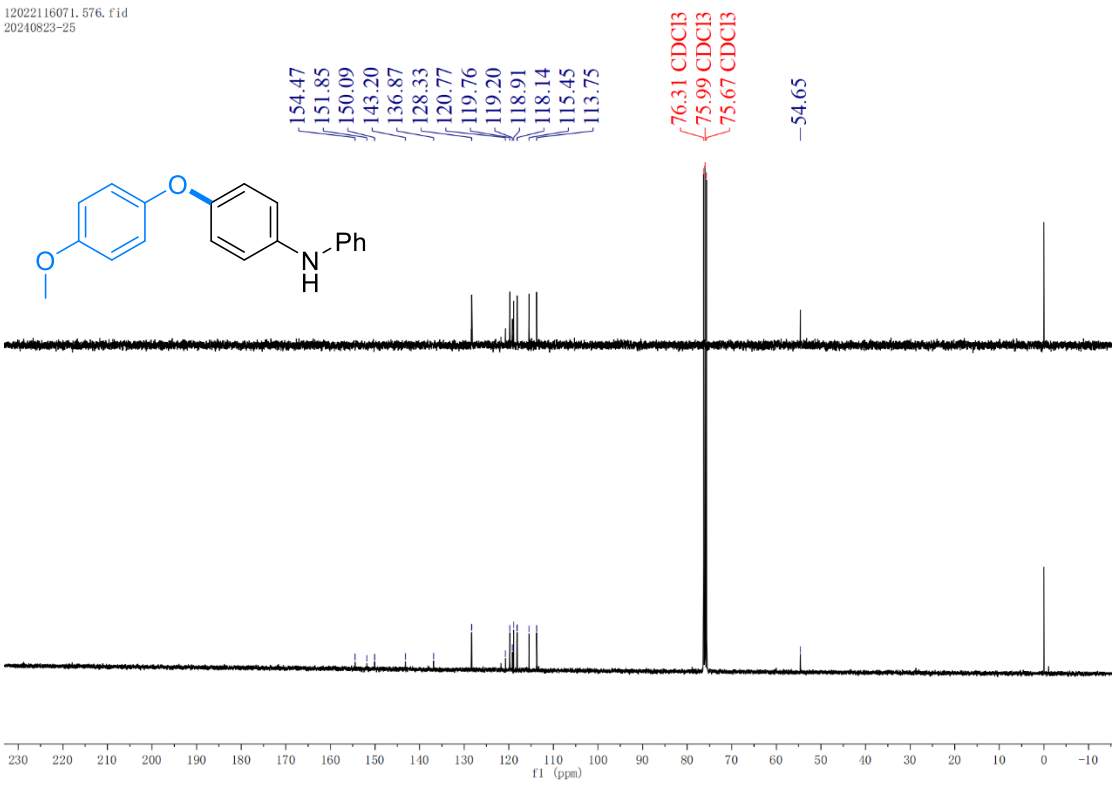
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3b**



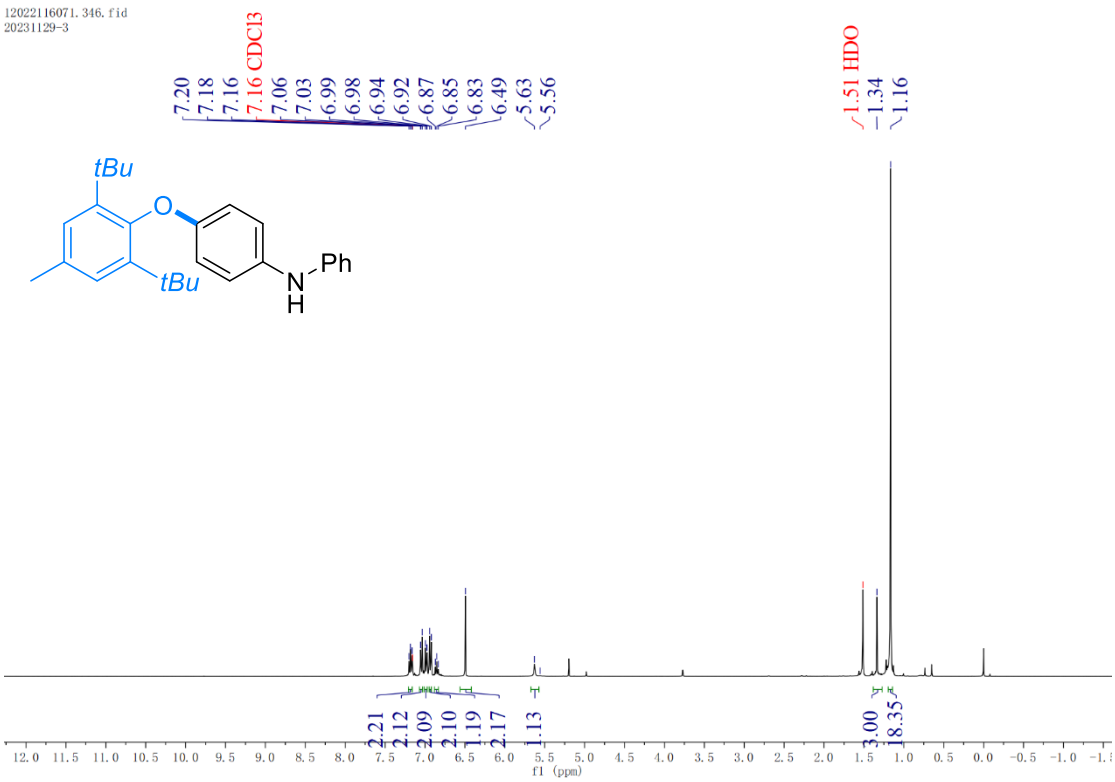
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3b**



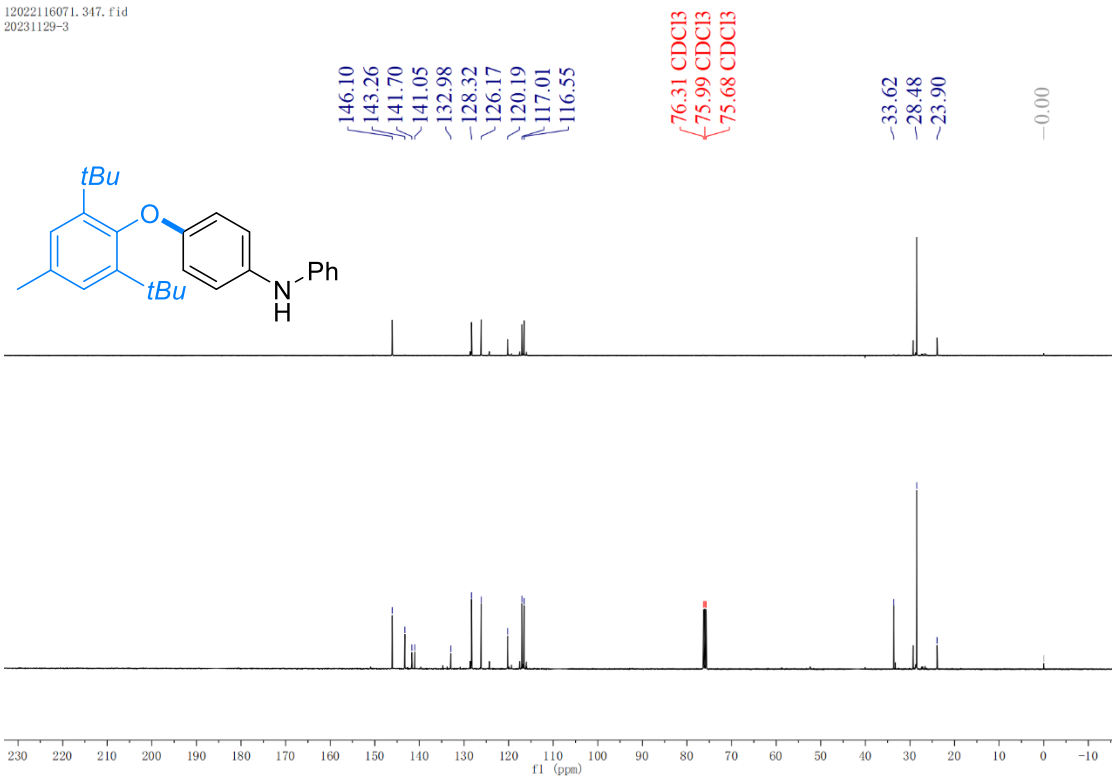
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3c**



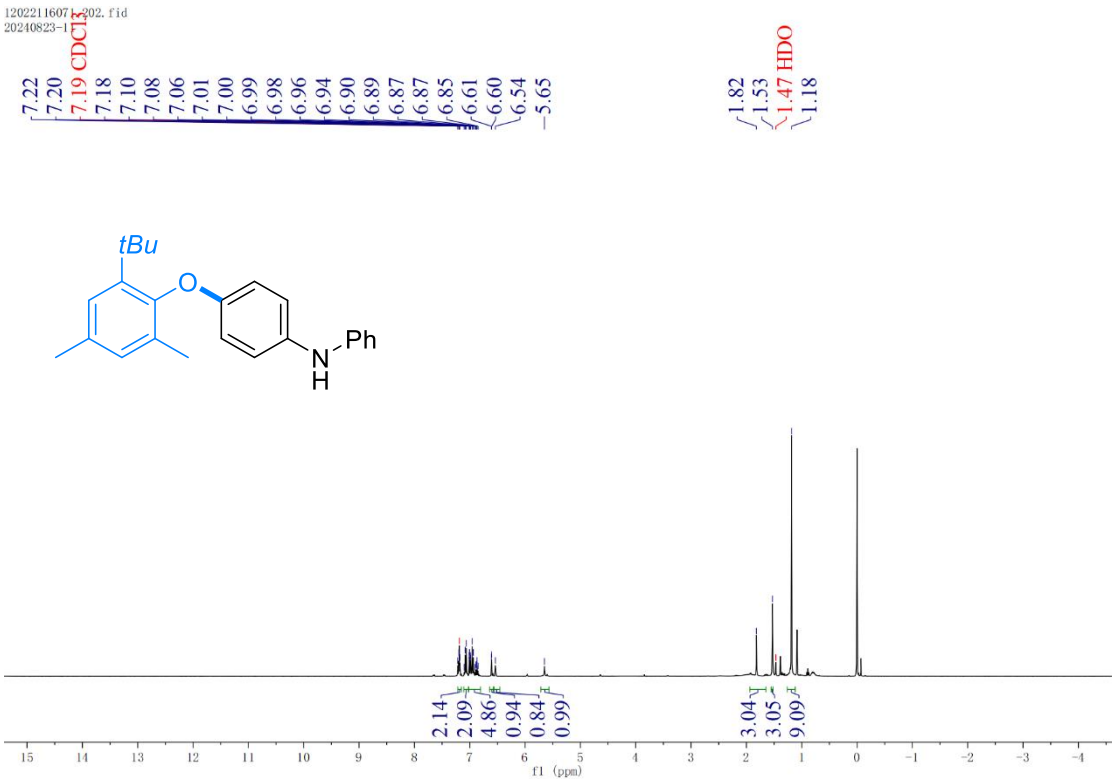
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3c**



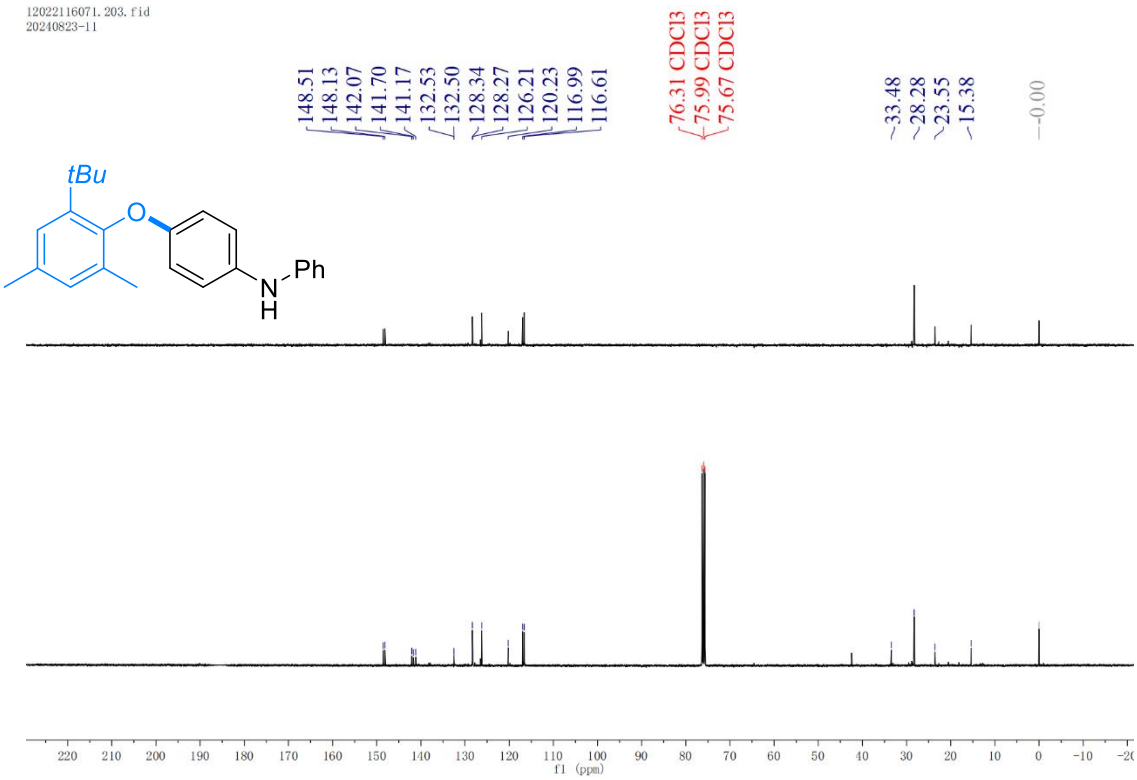
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3d**



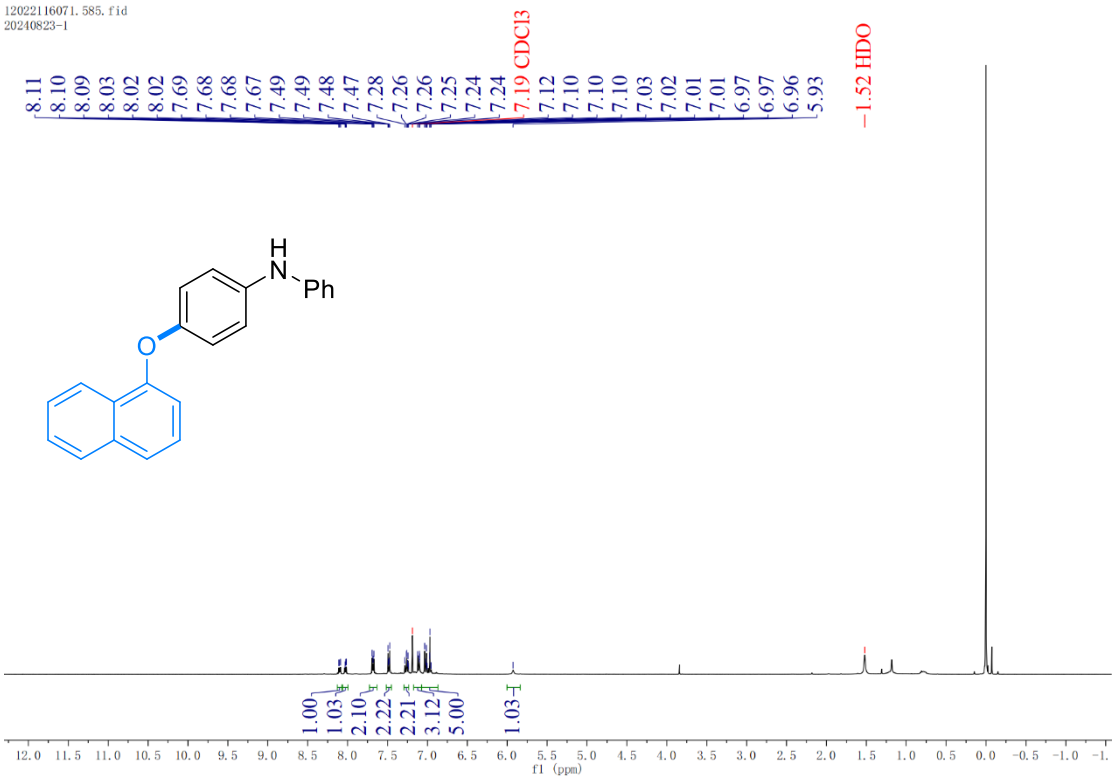
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3d**



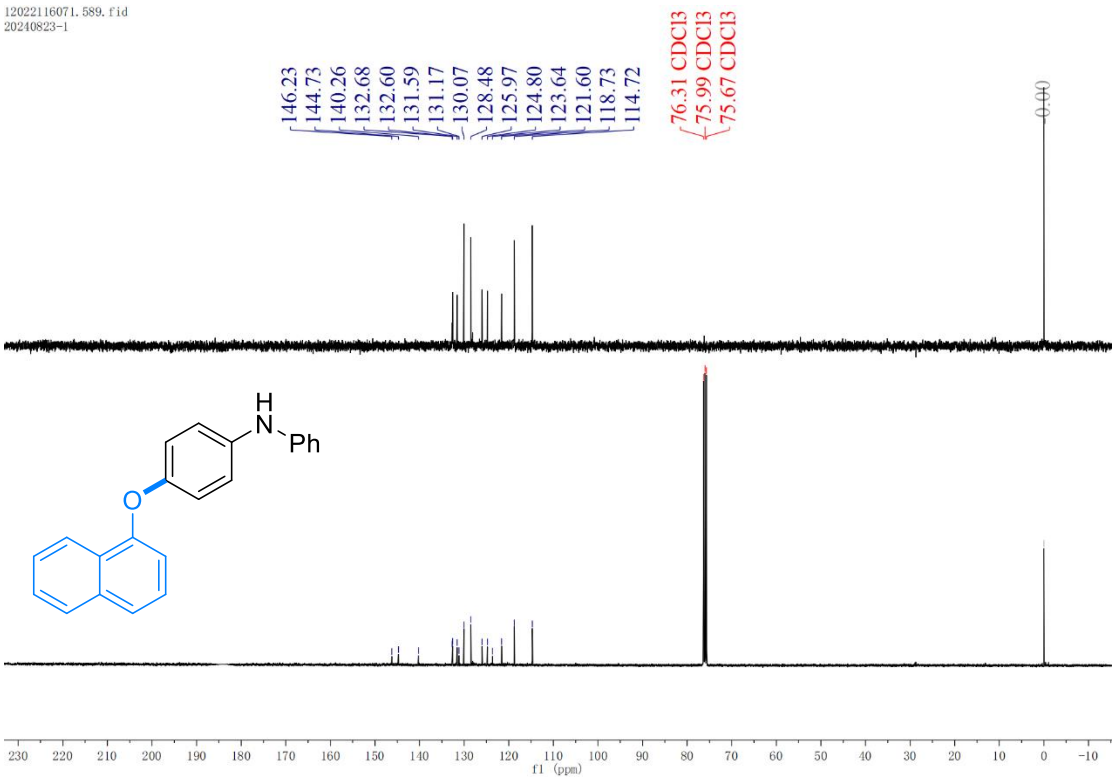
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3e**



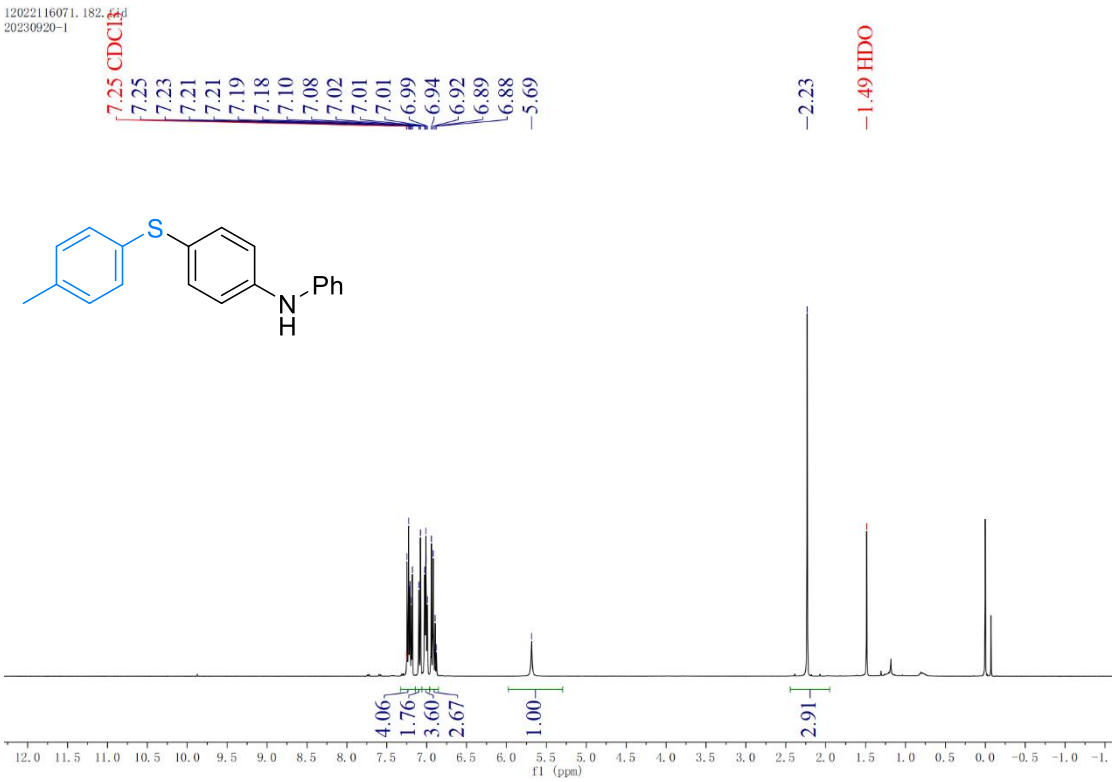
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3e**



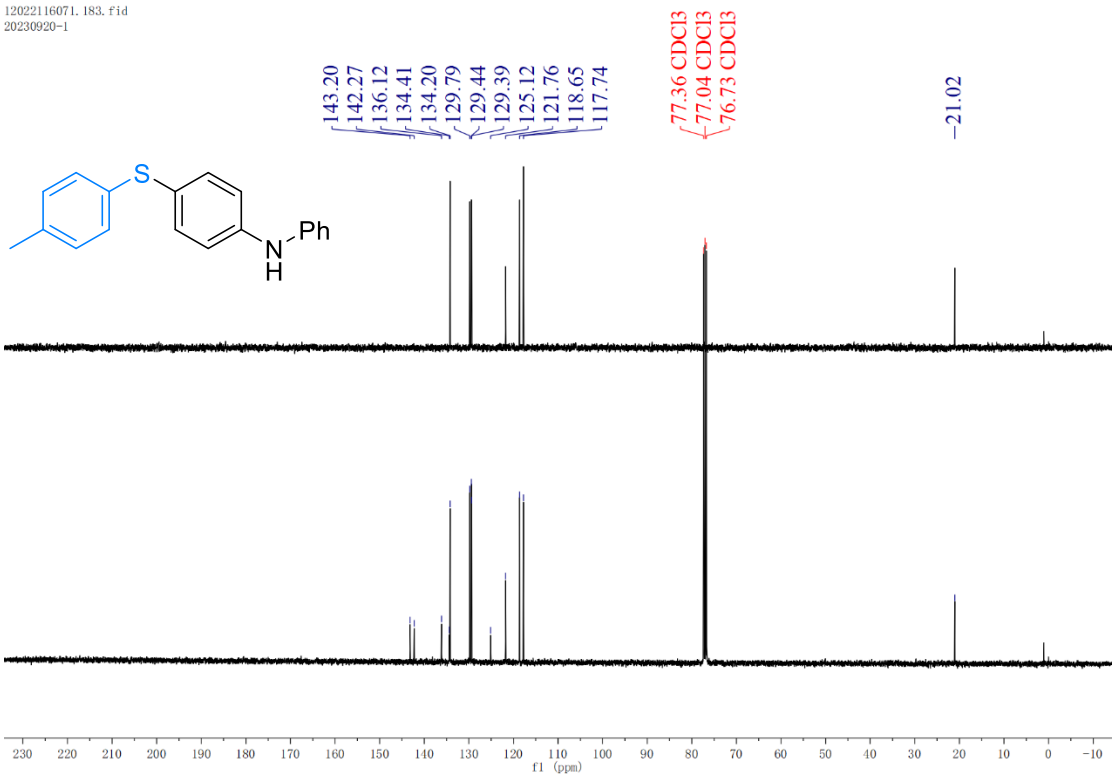
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 3f**



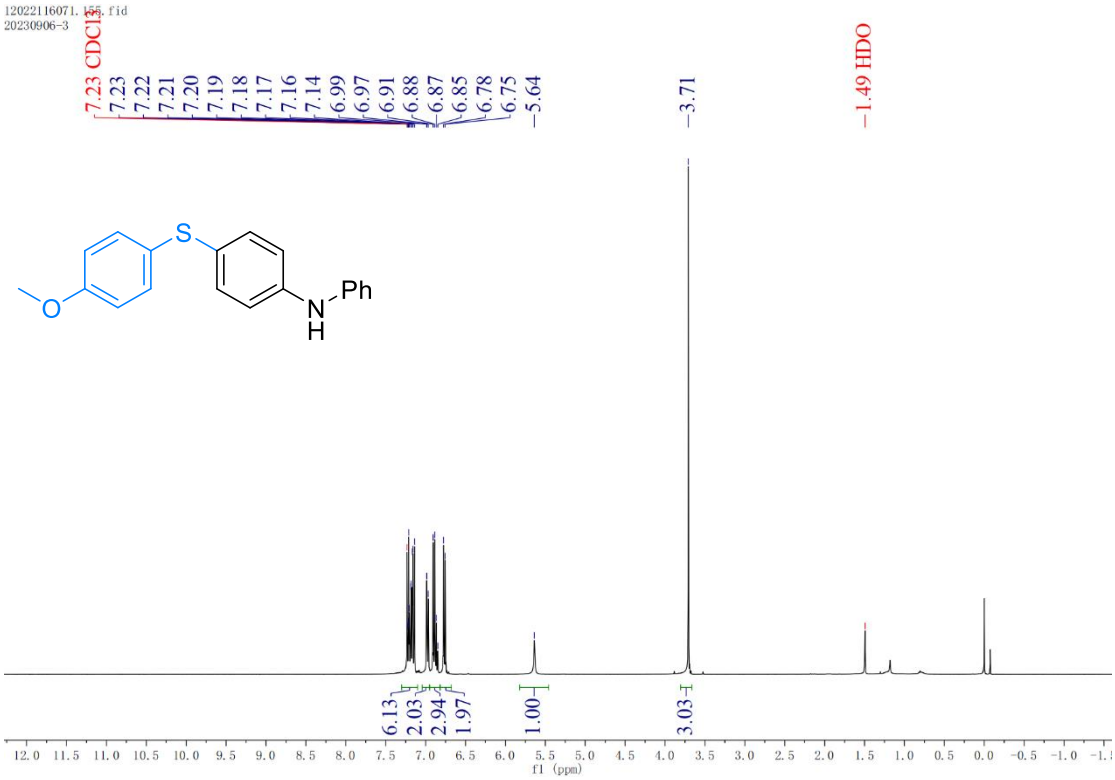
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 3f**



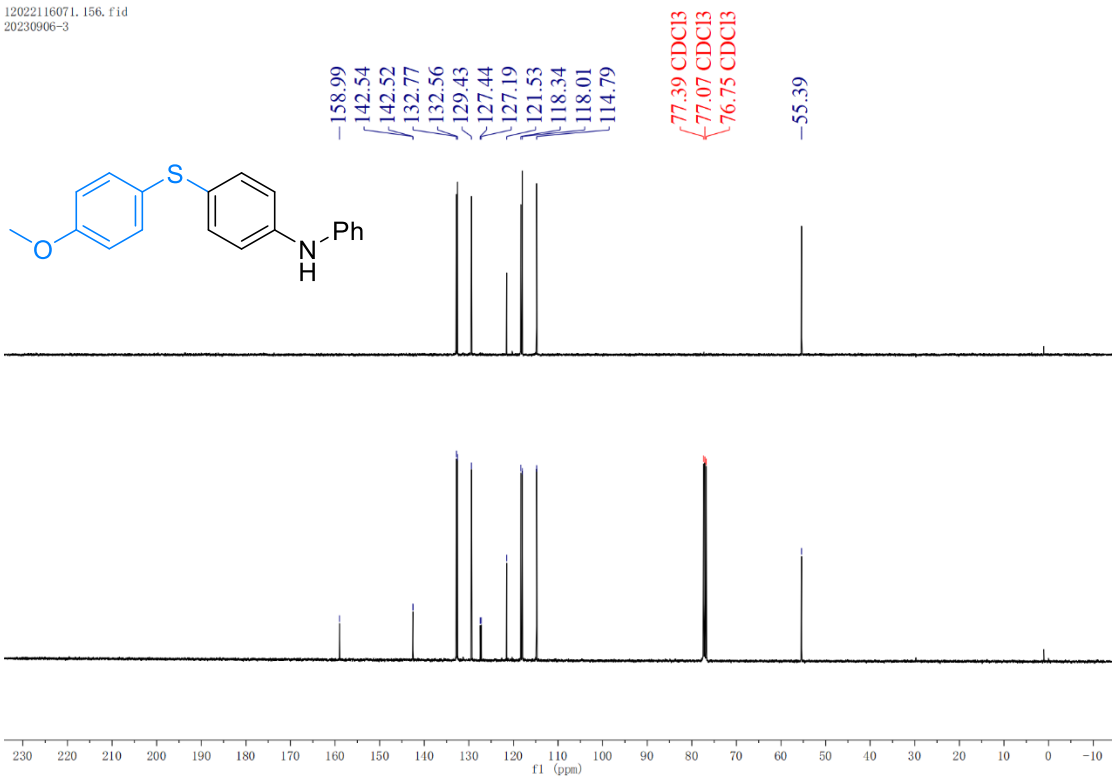
[1]H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5a**



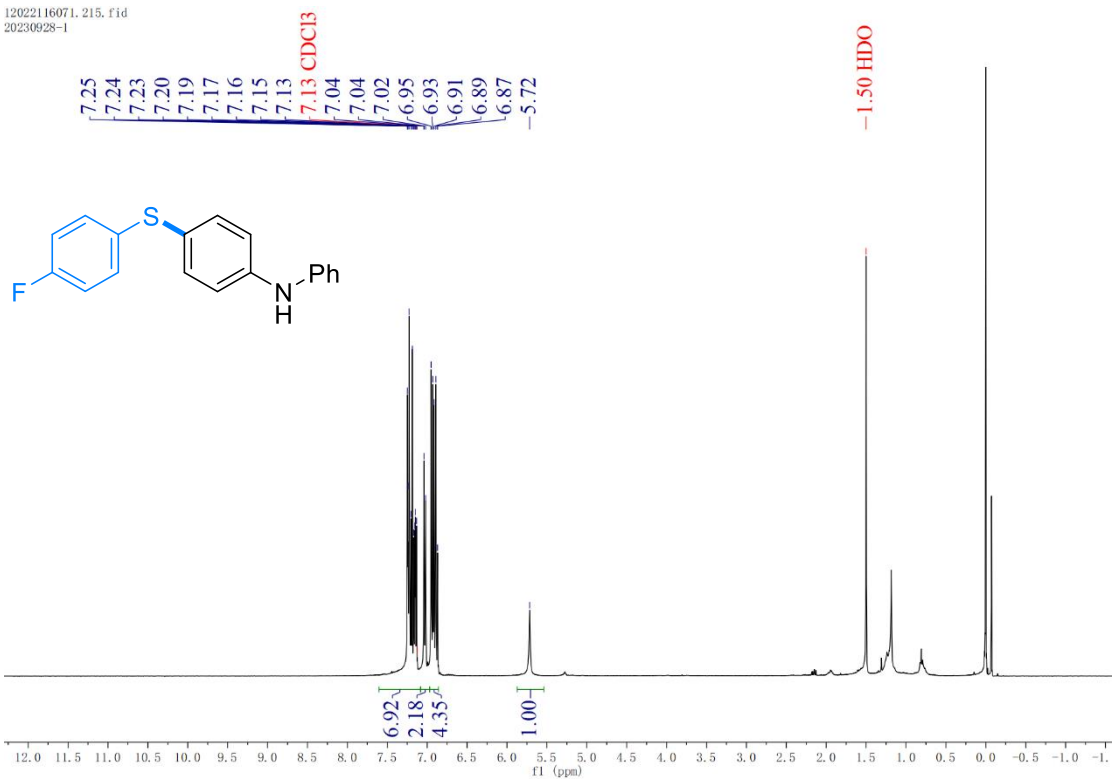
[13]C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5a**



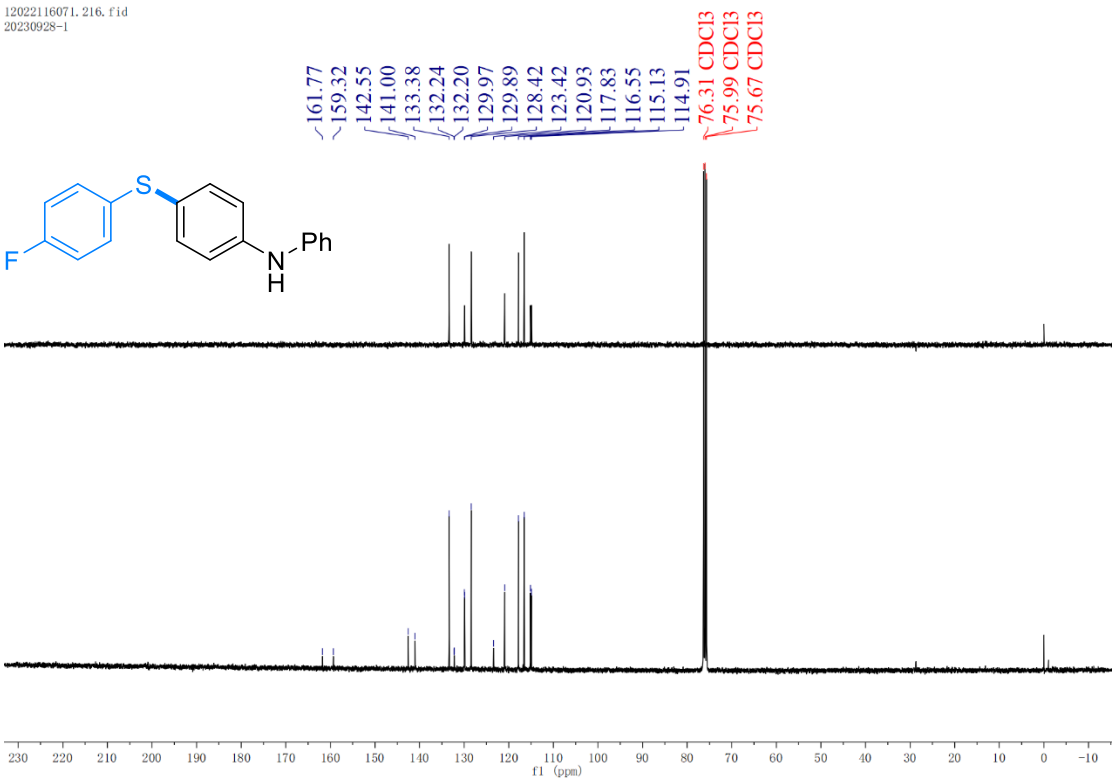
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5b**



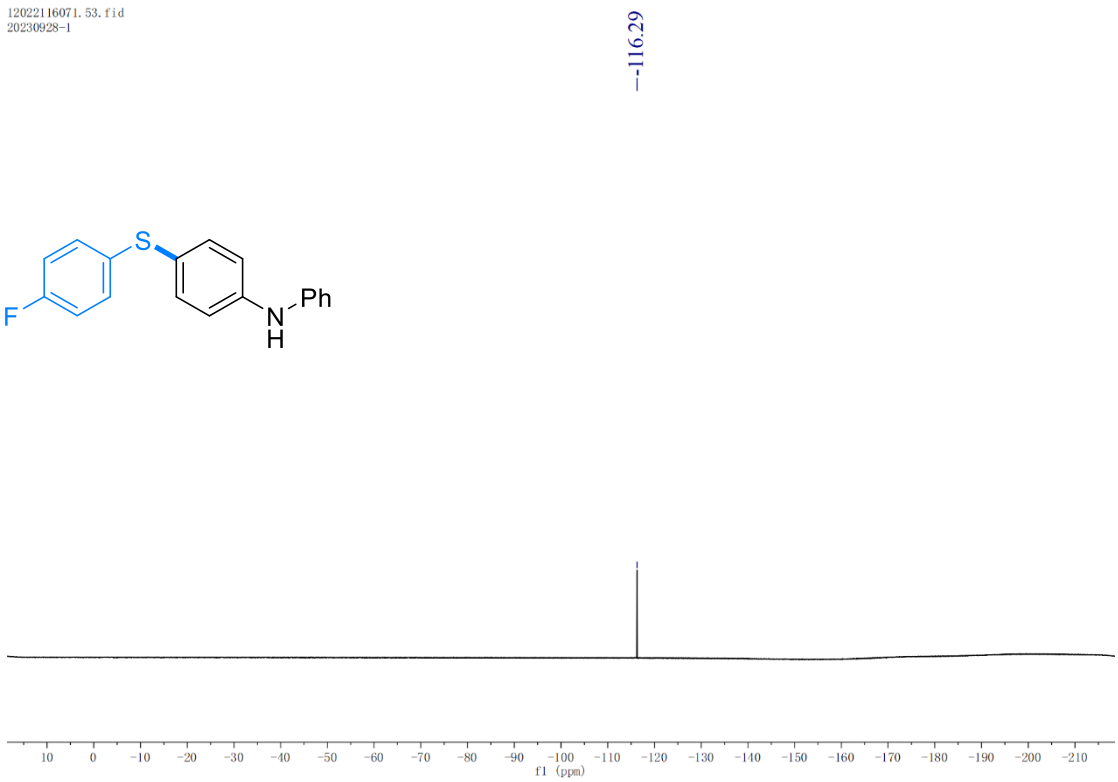
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5b**



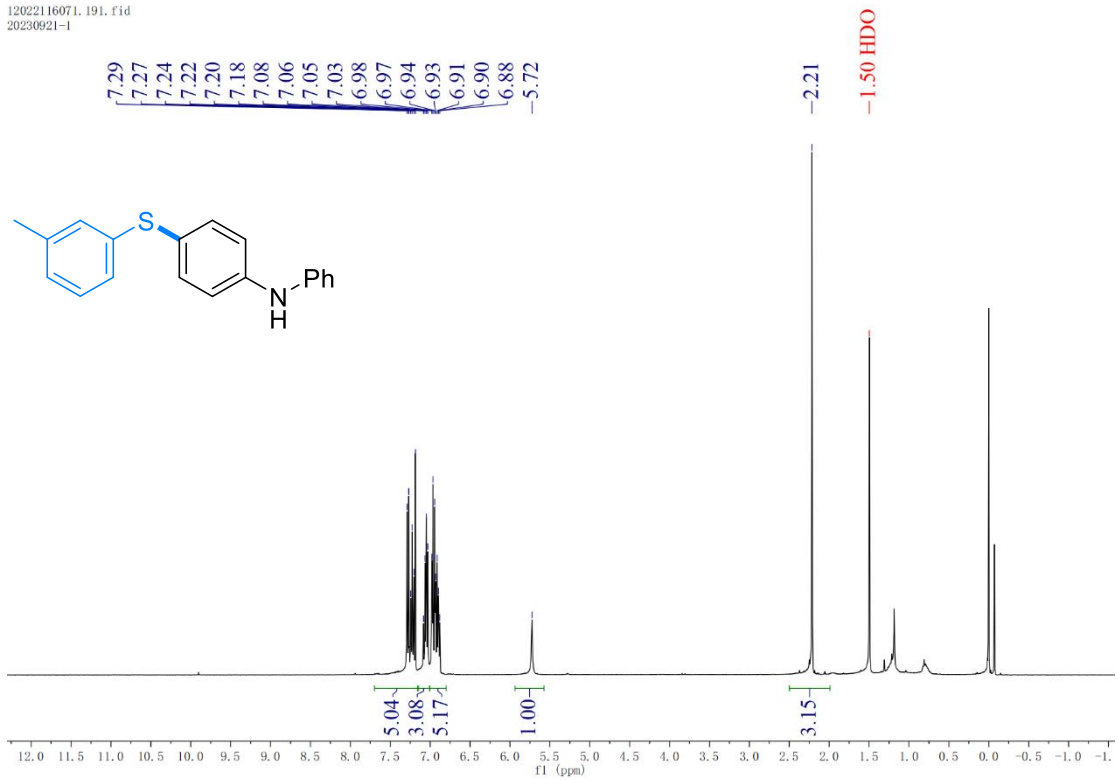
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5c**



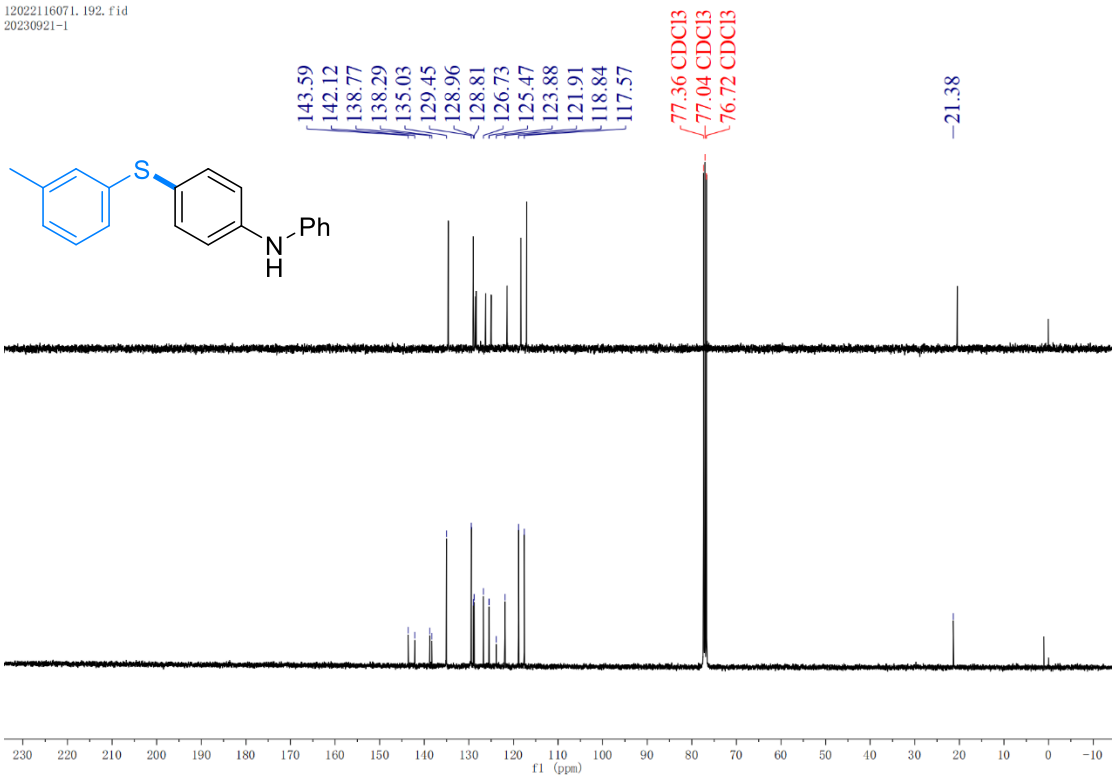
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5c**



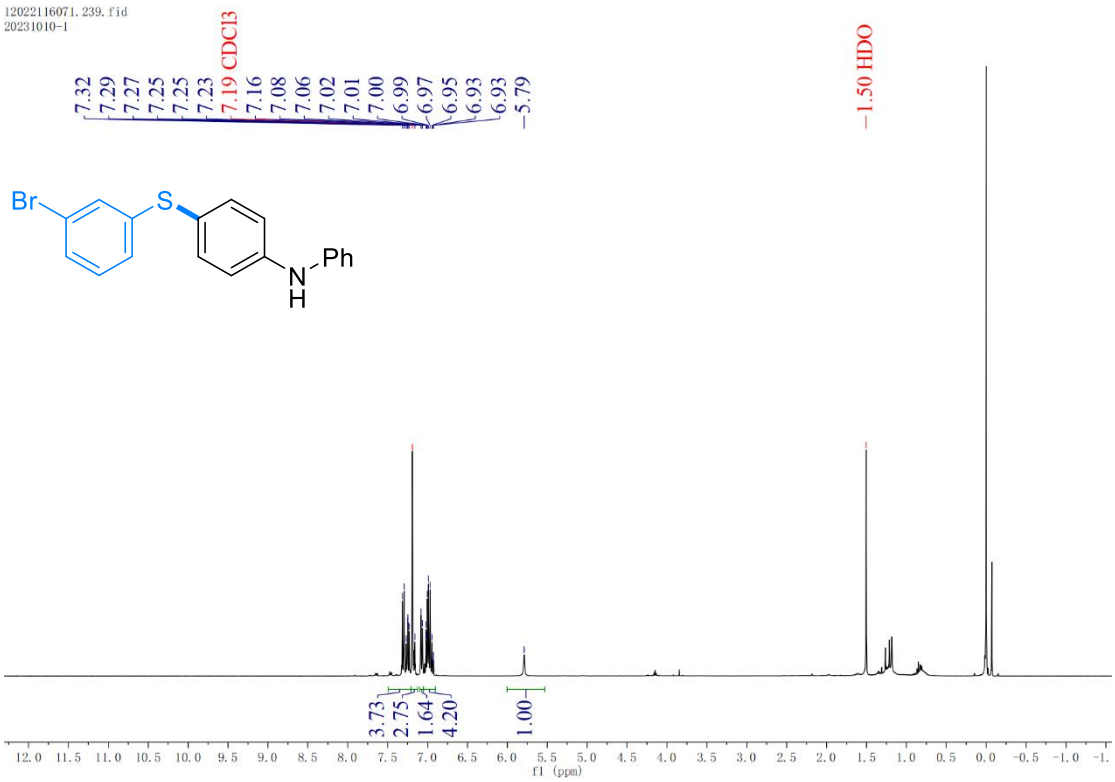
^{19}F NMR ($CDCl_3$) **Spectrum of compound 5c**



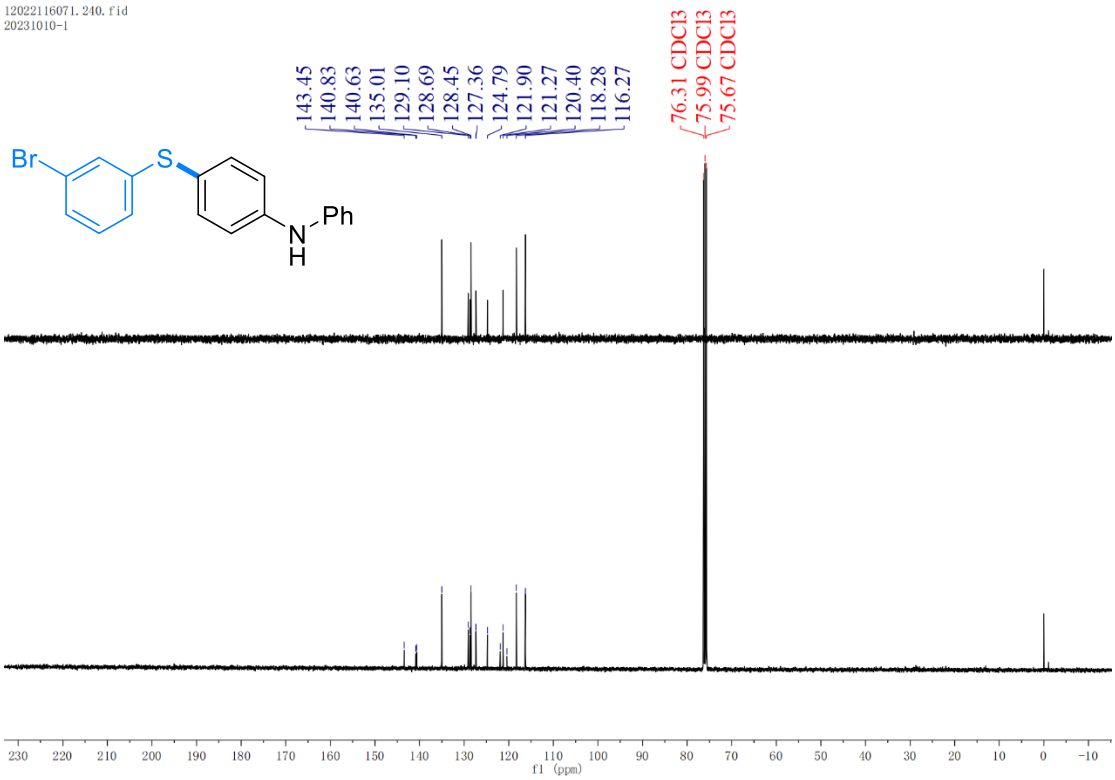
^{1}H-NMR ($CDCl_3$) **Spectra of compound 5d**



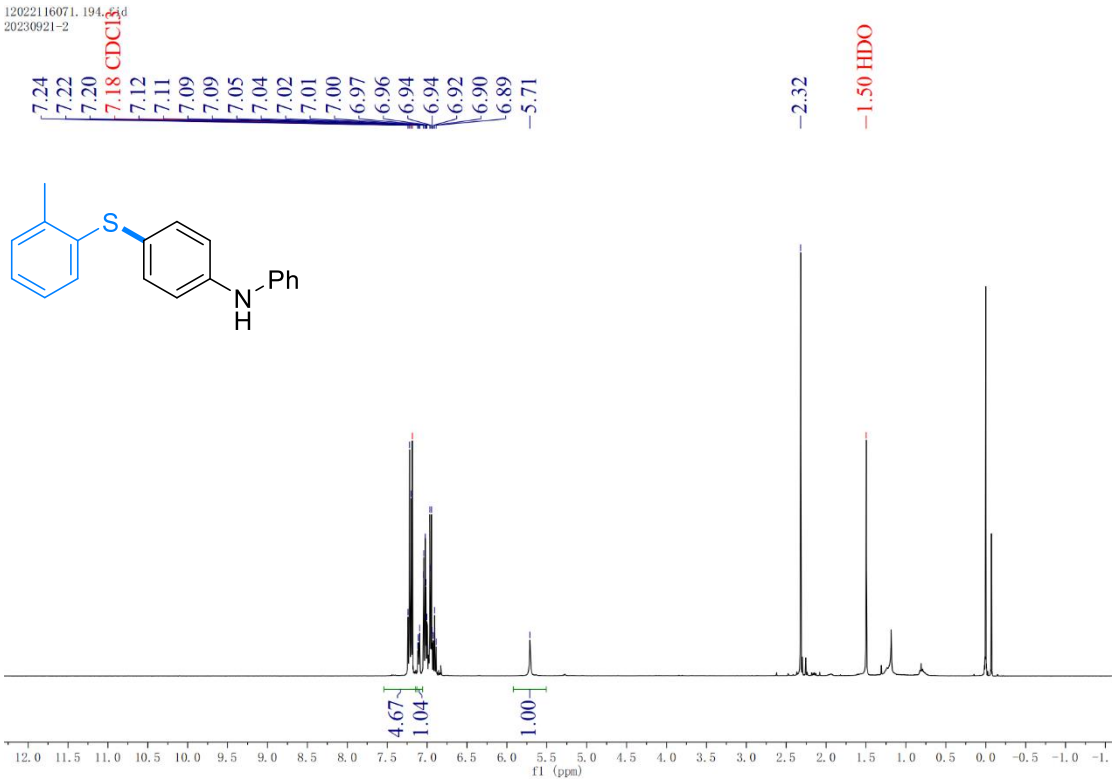
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5d**



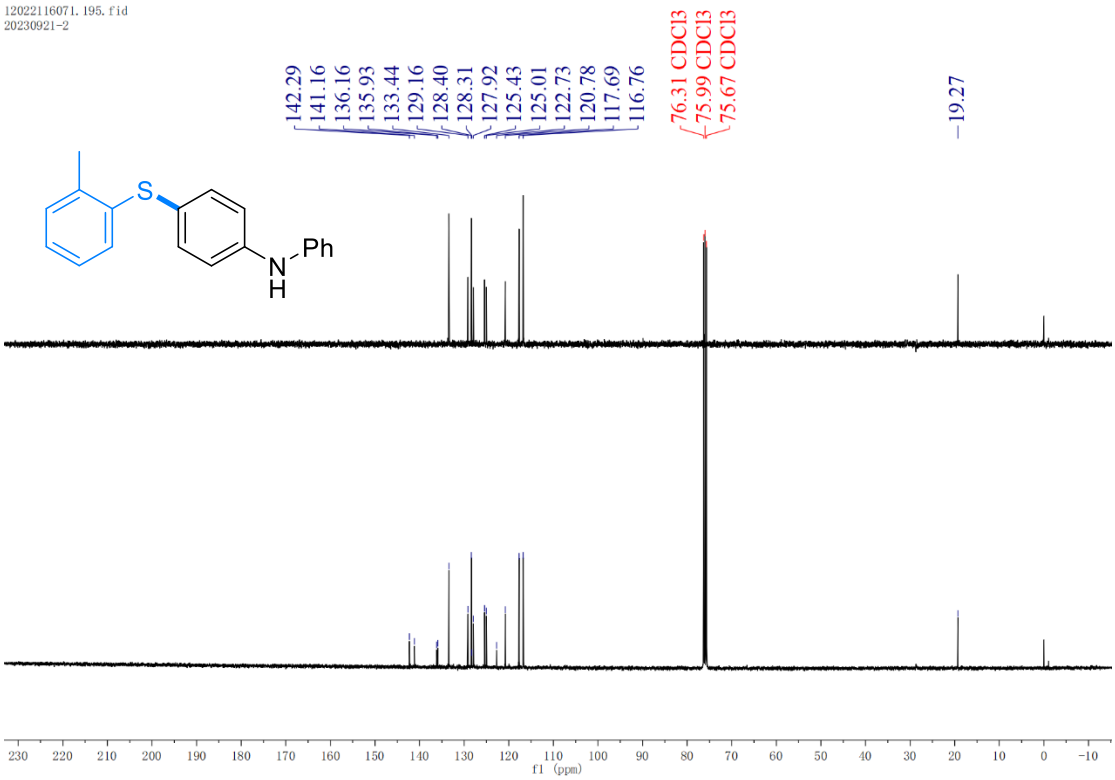
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5e**



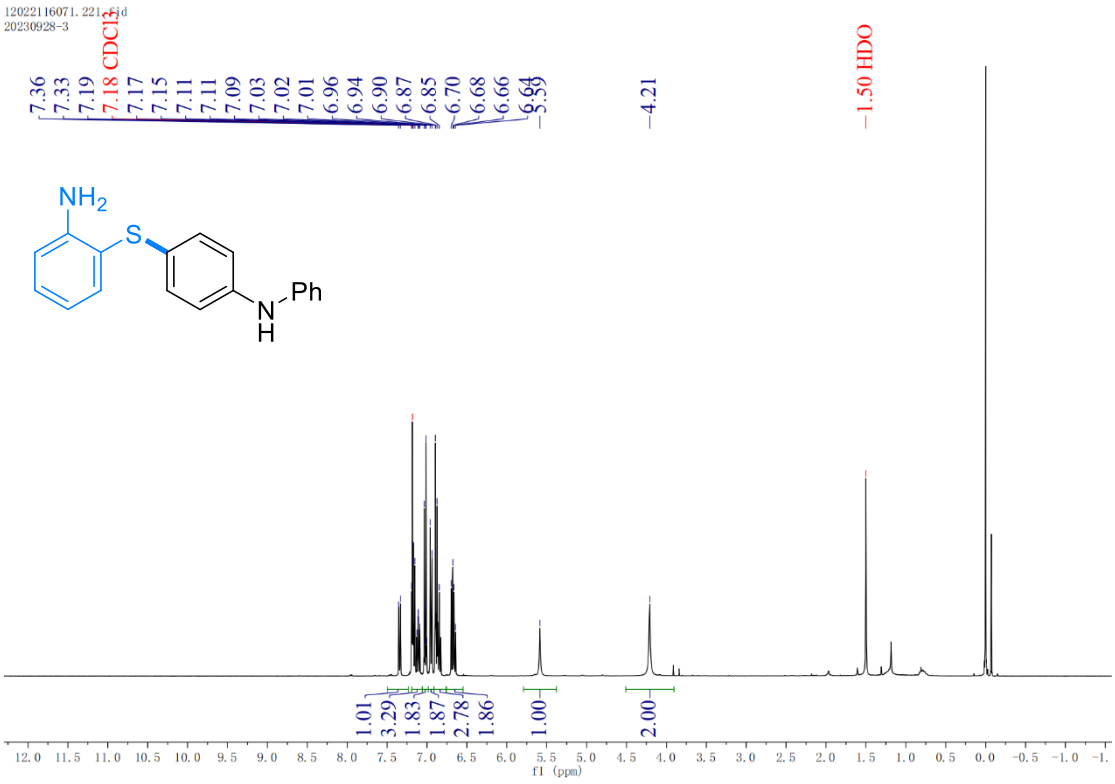
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5e**



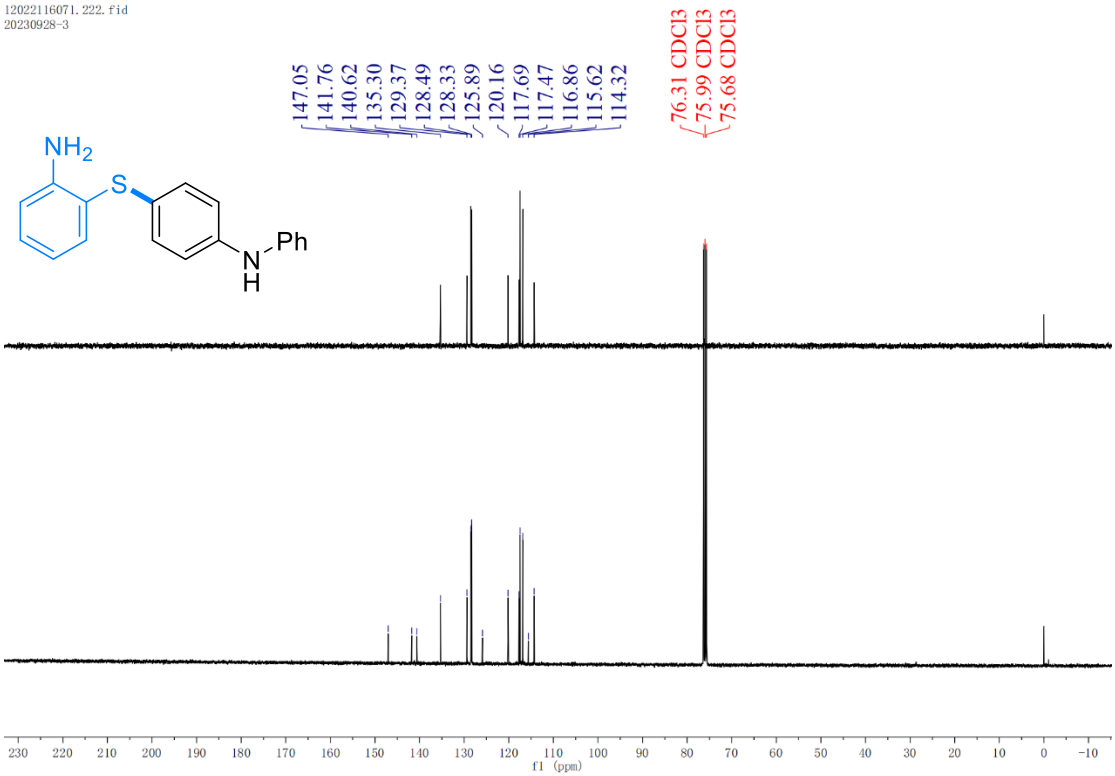
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5f**



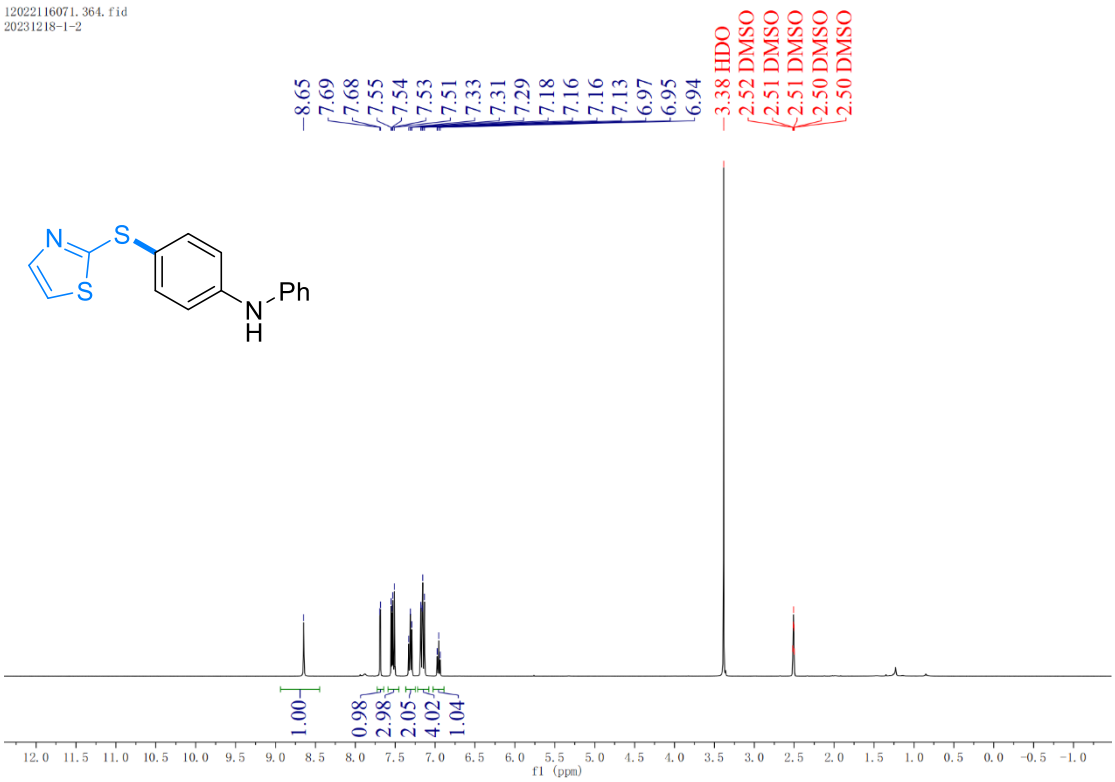
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5f**



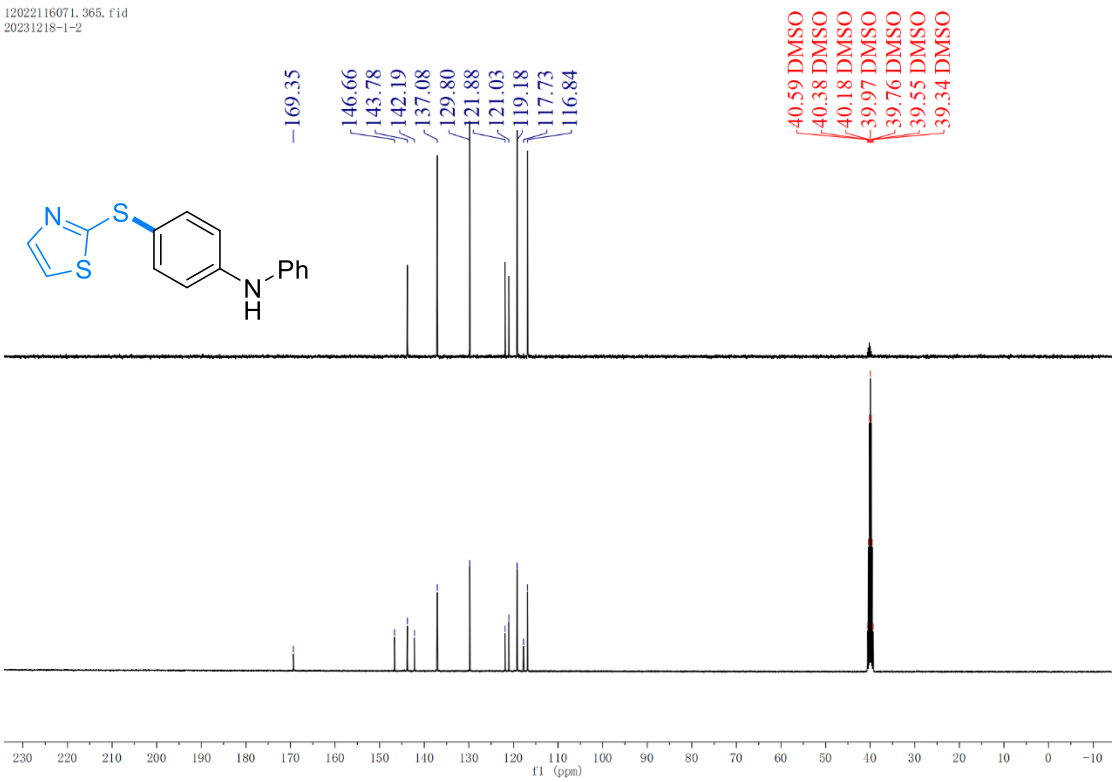
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5g**



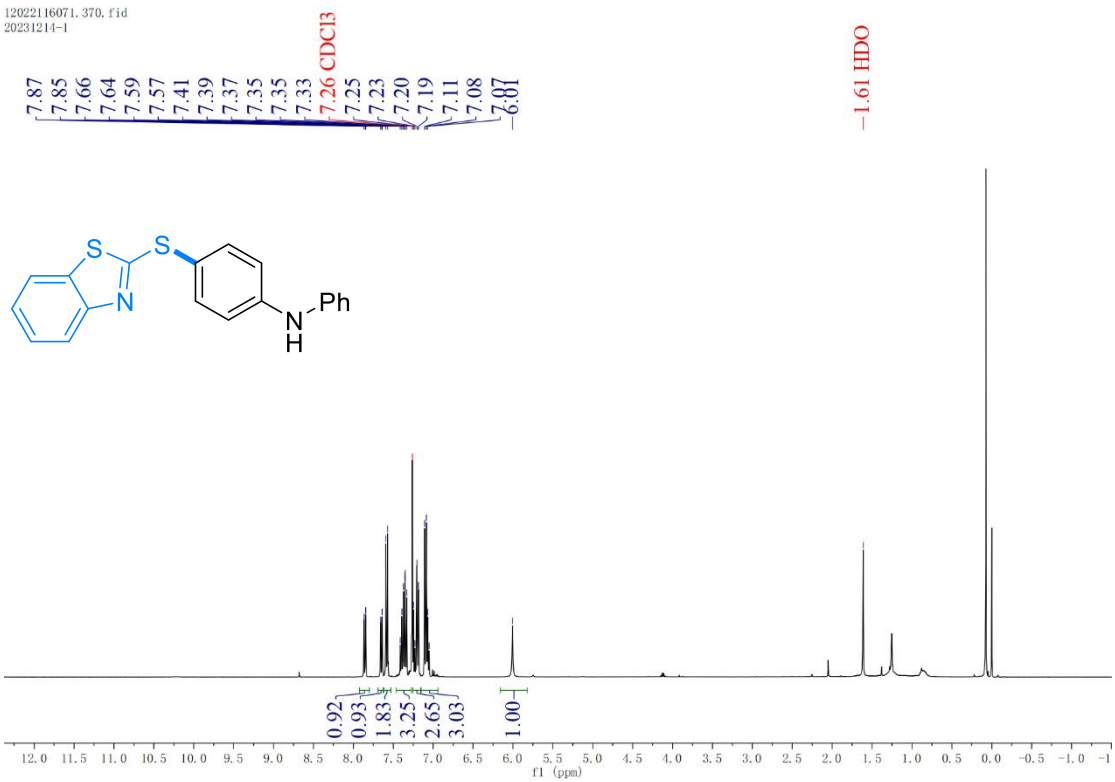
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5g**



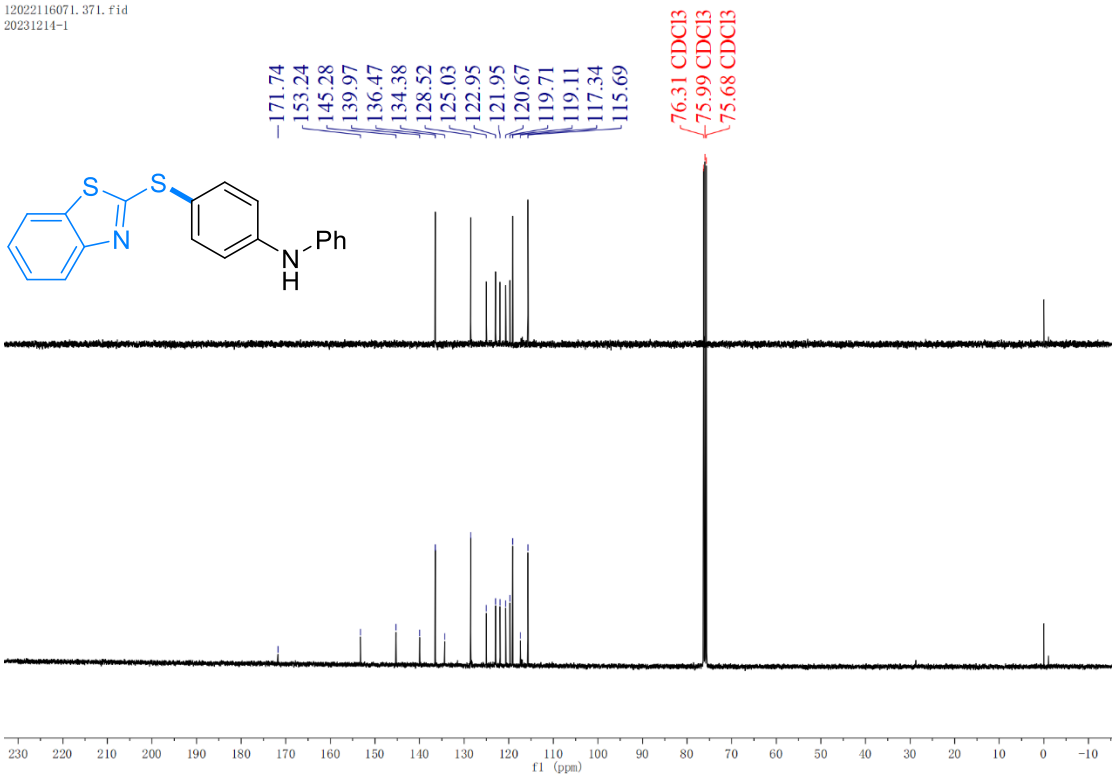
^{1}H-NMR (400 MHz, DMSO-d_6) **Spectra of compound 5h**



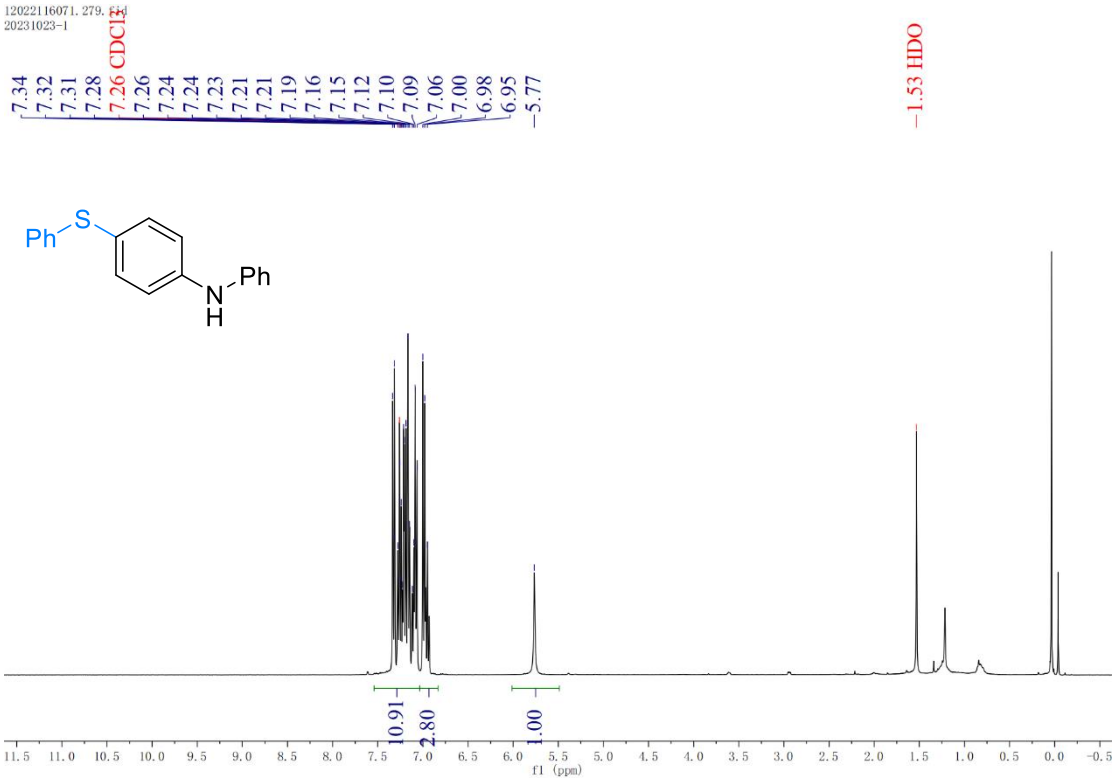
^{13}C-NMR (100 MHz, DMSO-d_6) **Spectra of compound 5h**



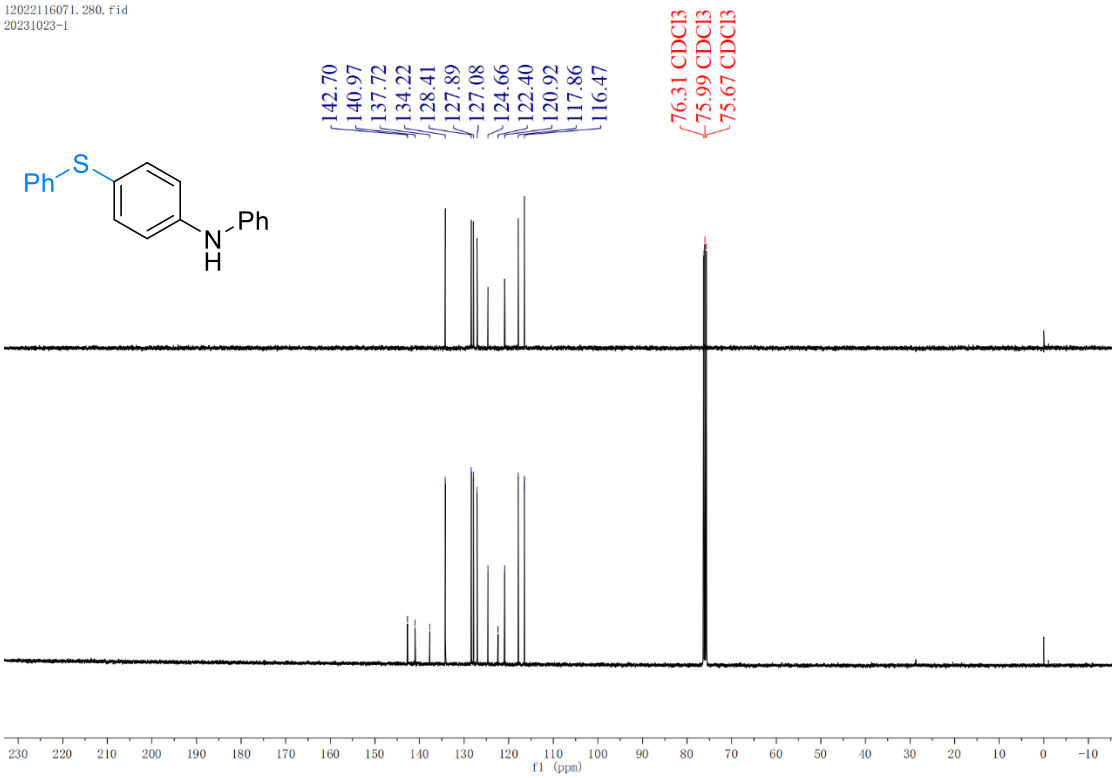
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 5i**



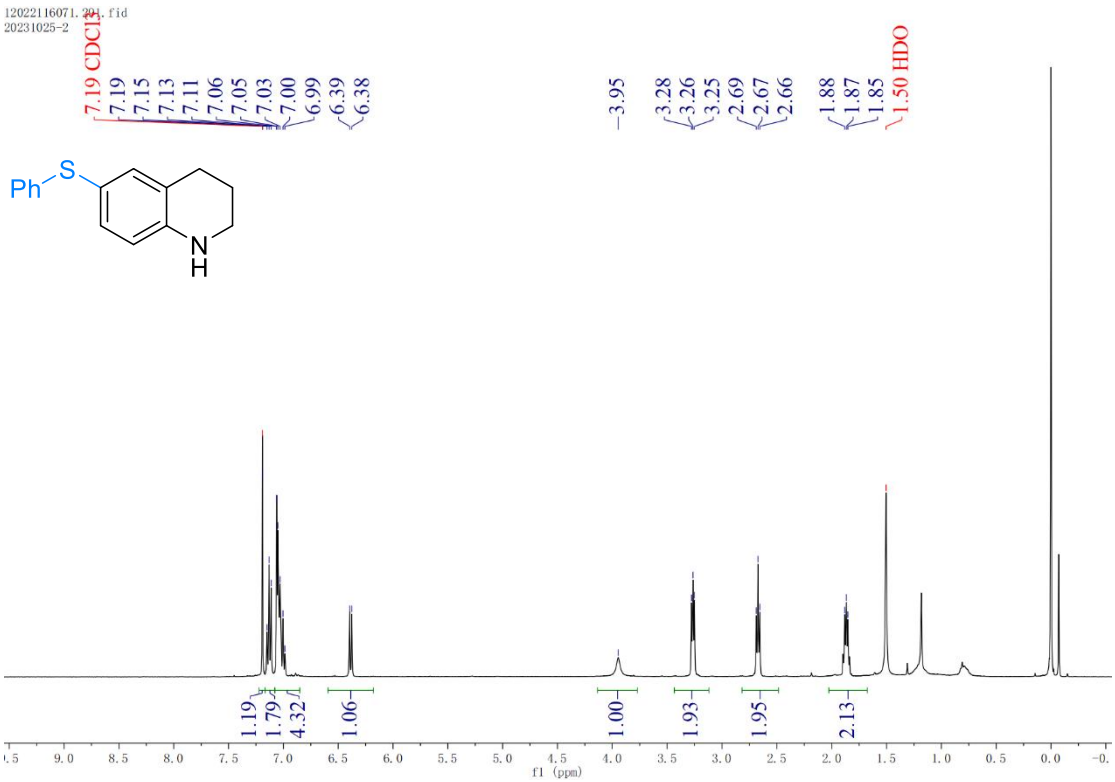
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 5i**



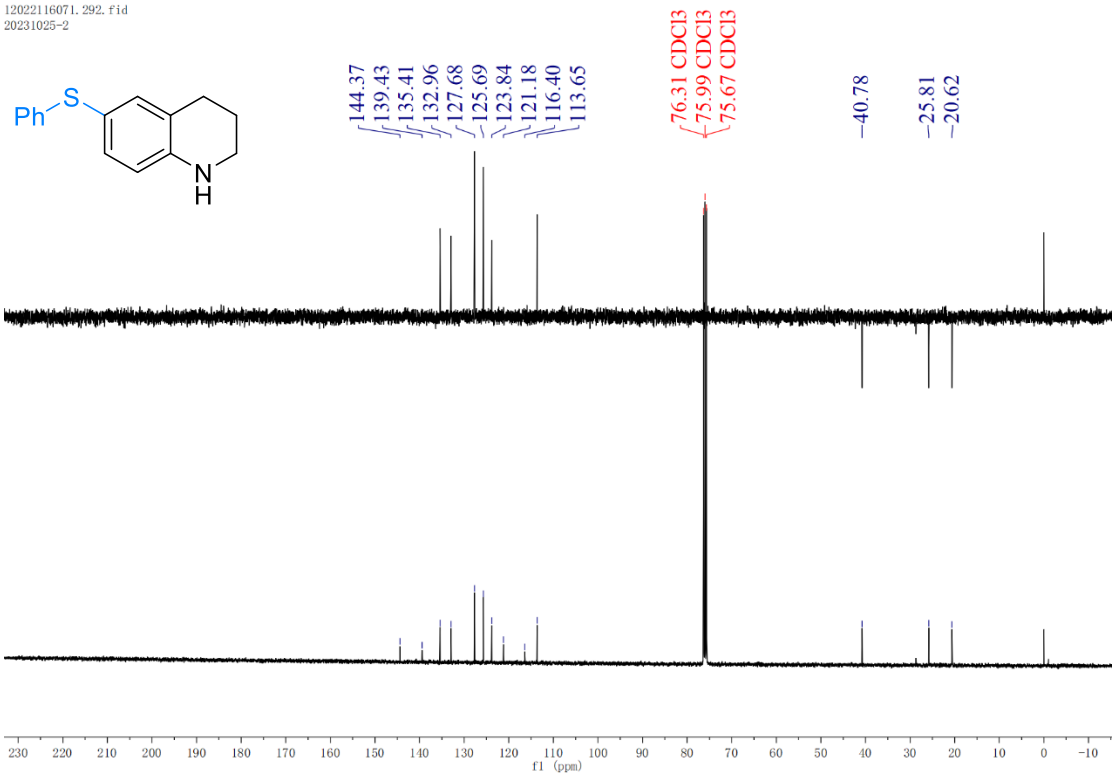
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 6a**



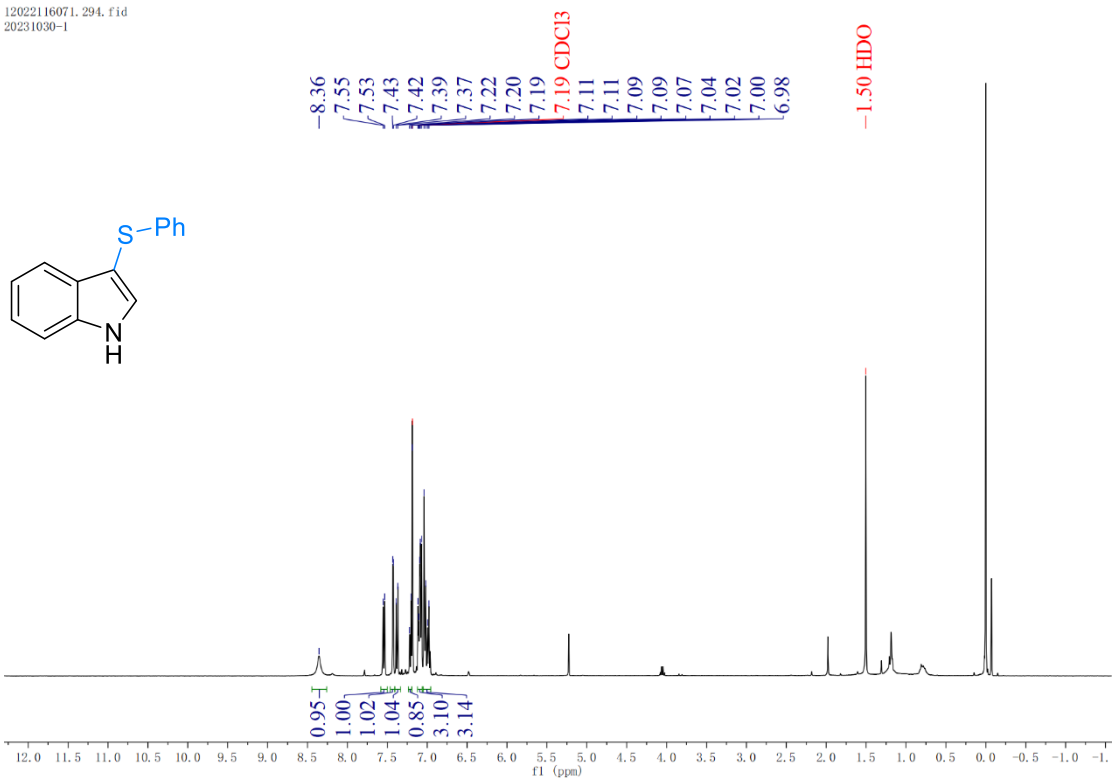
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 6a**



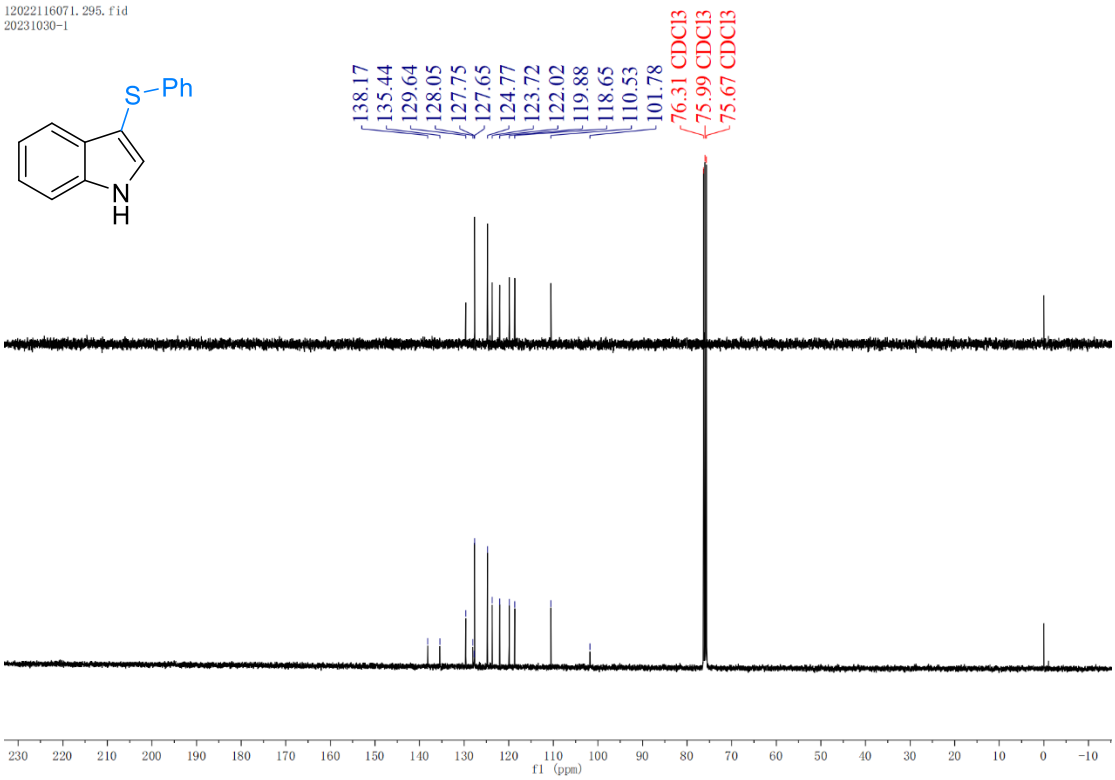
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 6b**



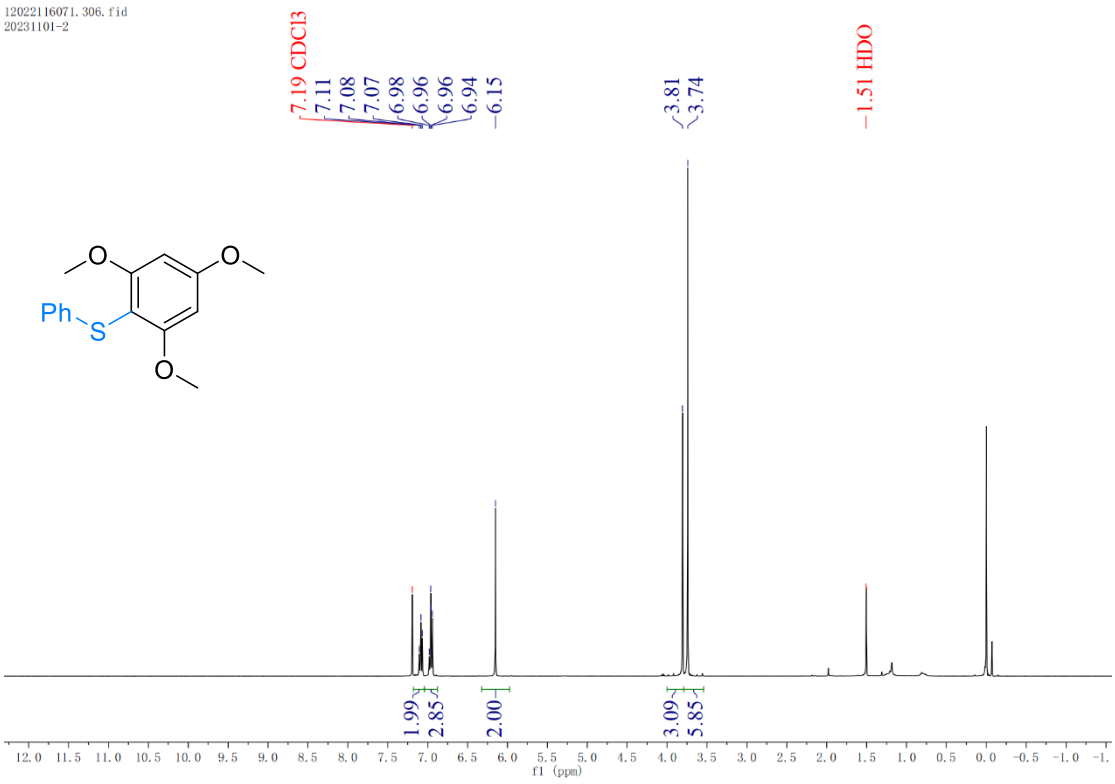
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 6b**



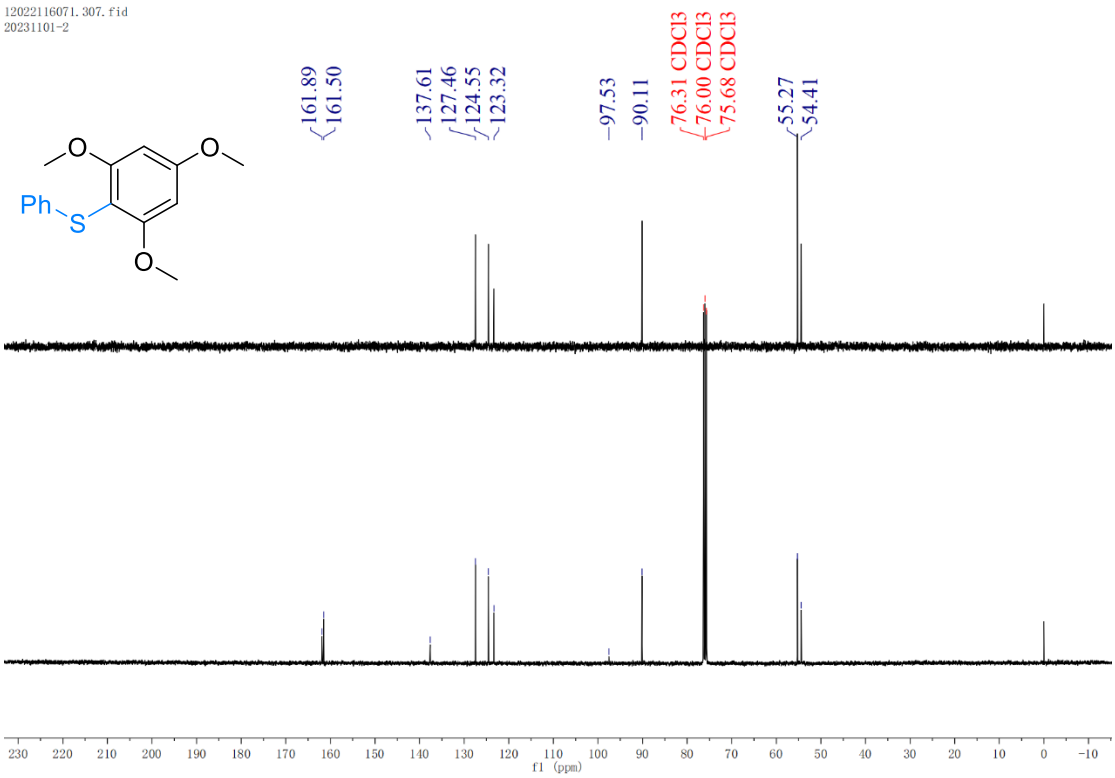
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 6c**



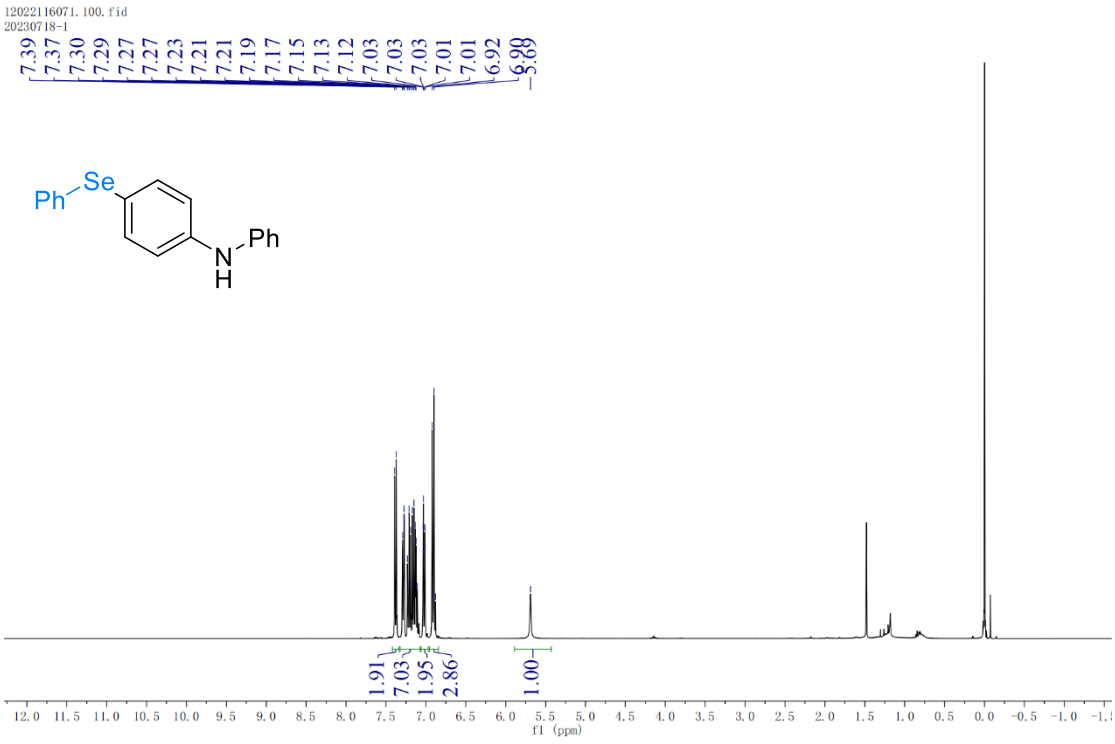
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 6c**



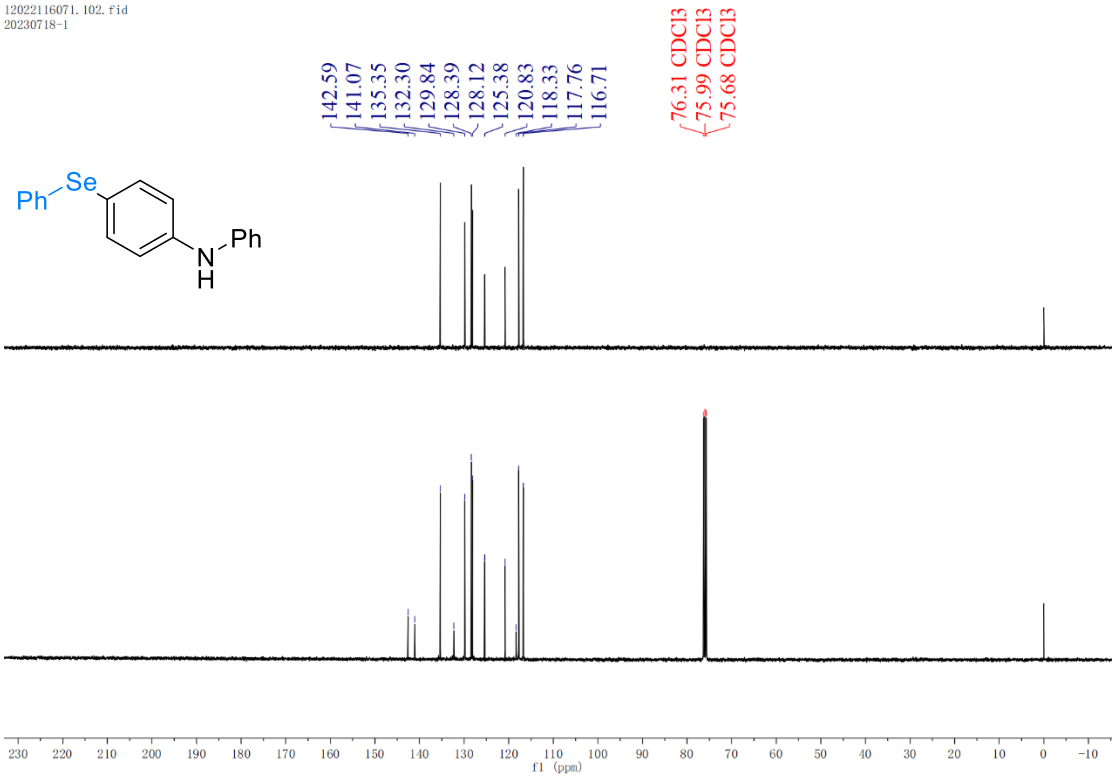
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 6d**



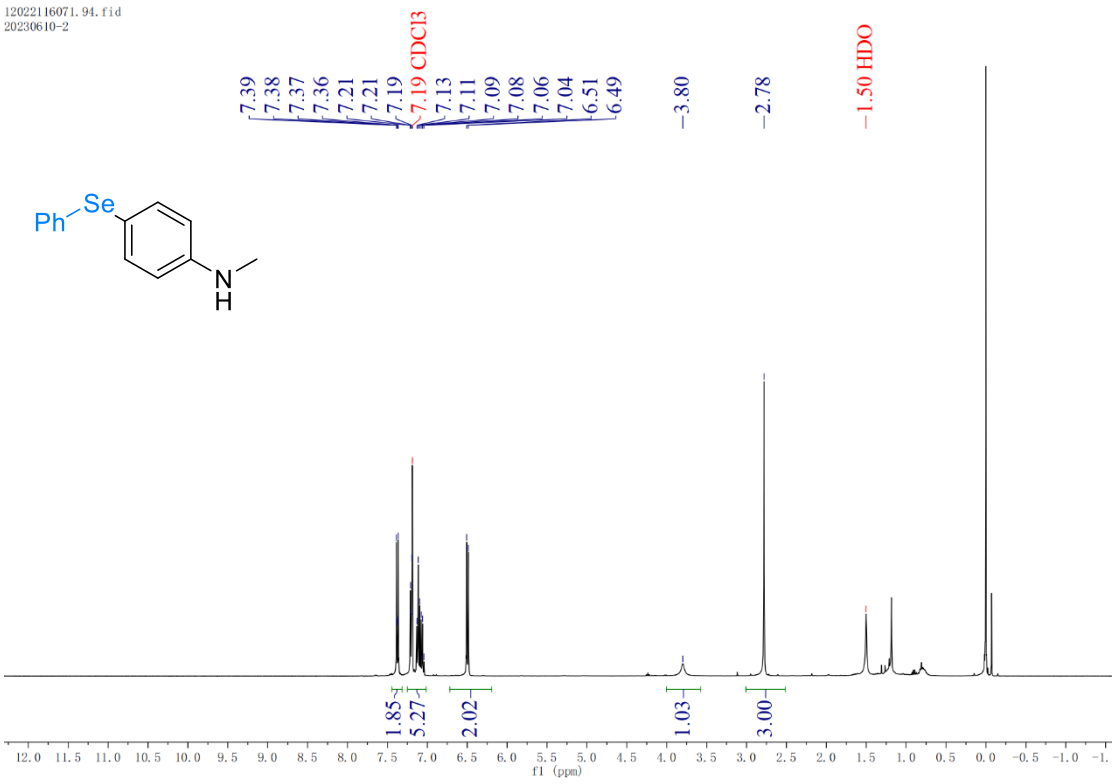
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 6d**



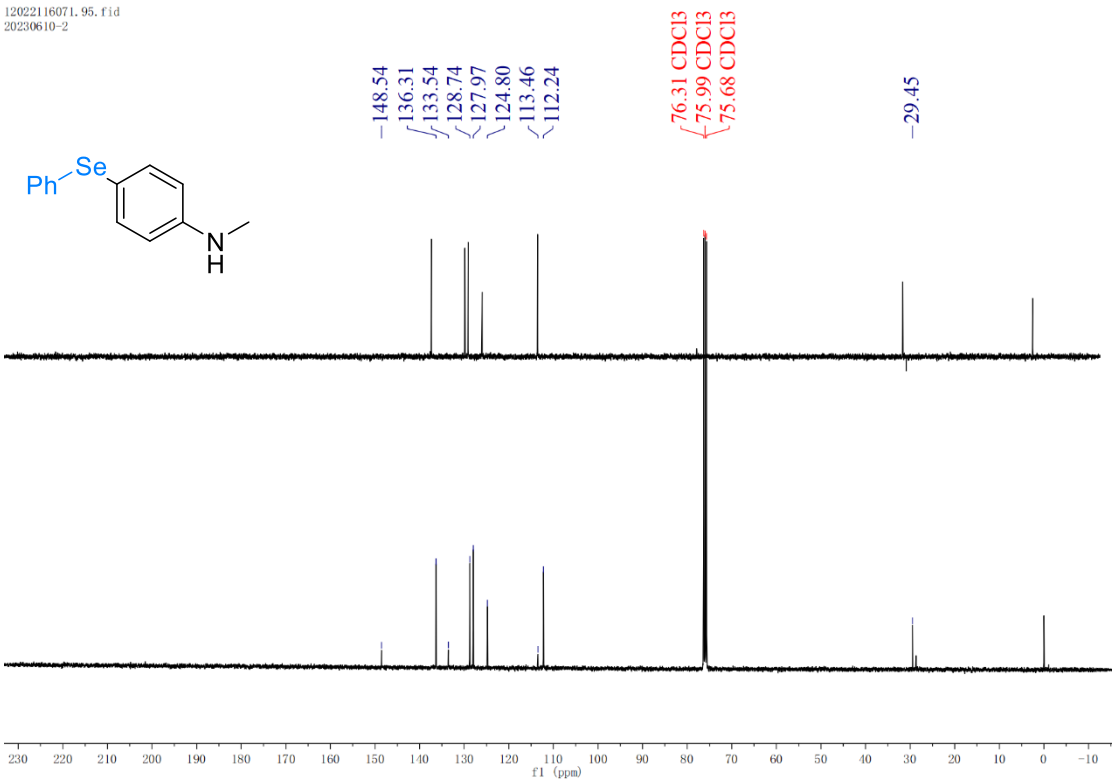
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8a**



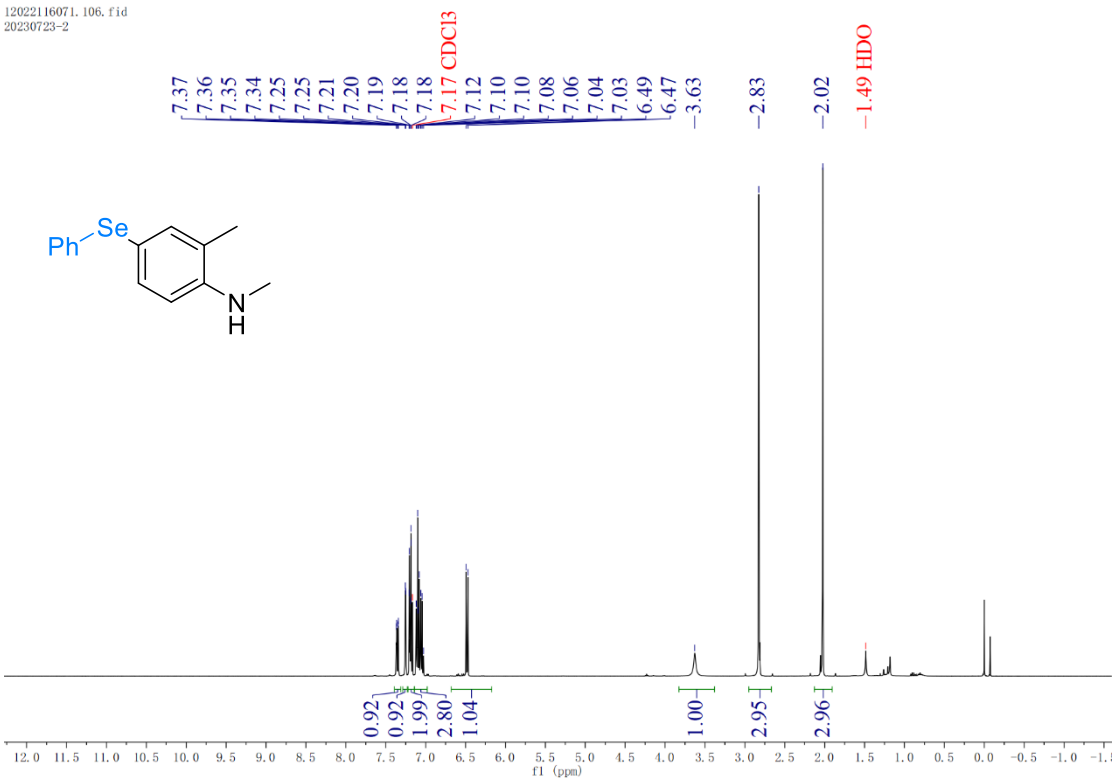
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8a**



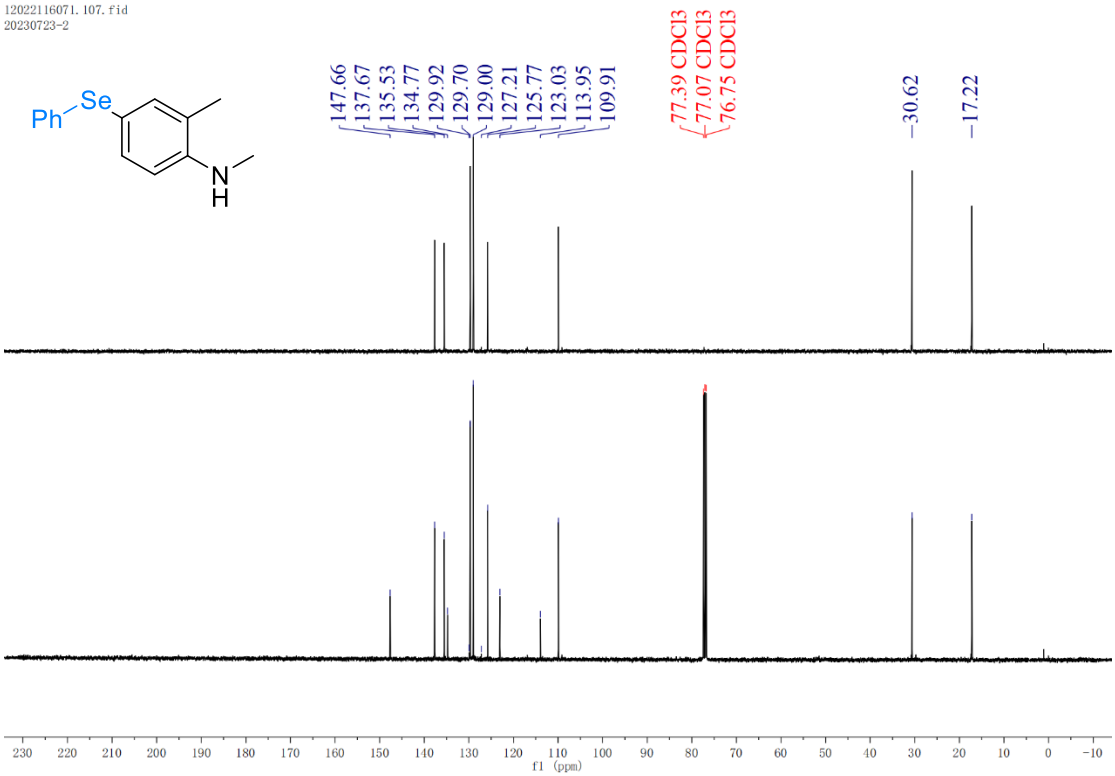
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8b**



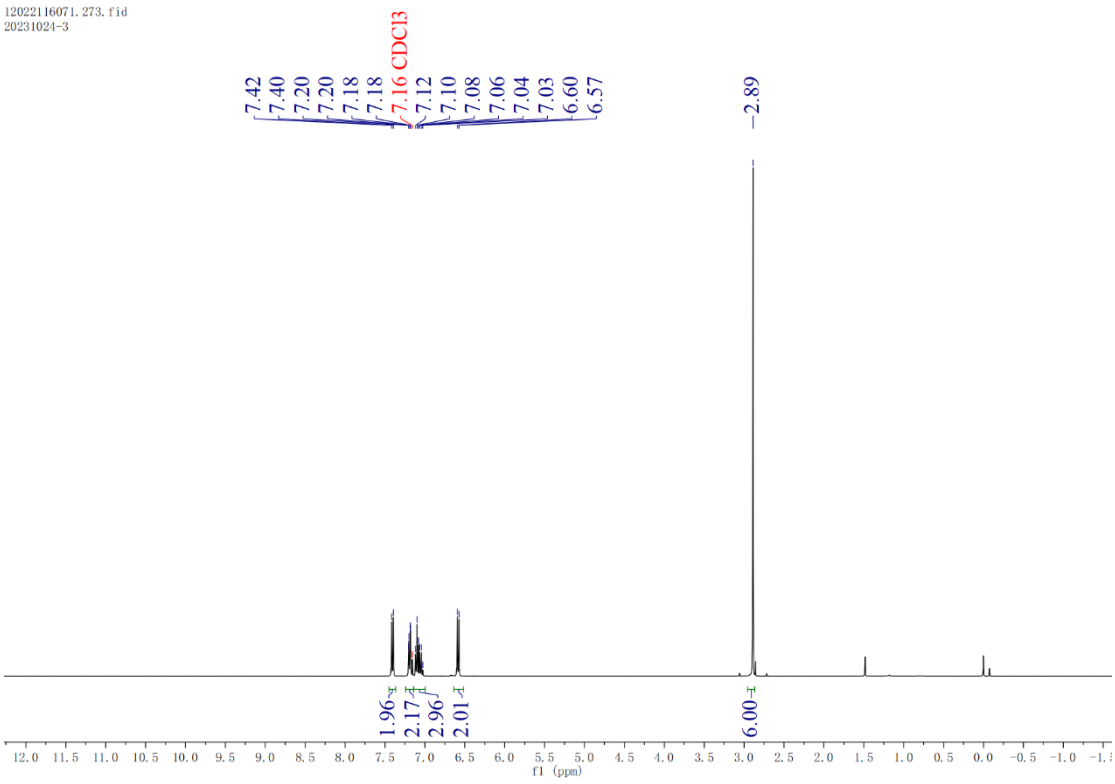
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8b**



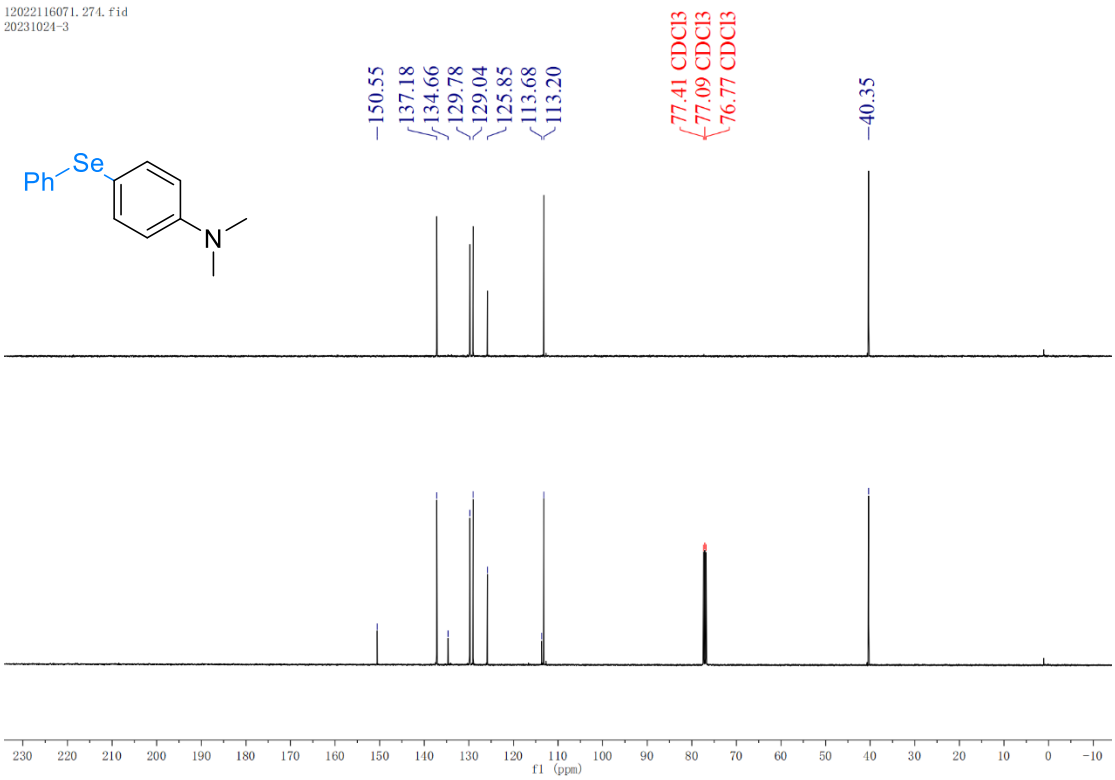
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8c**



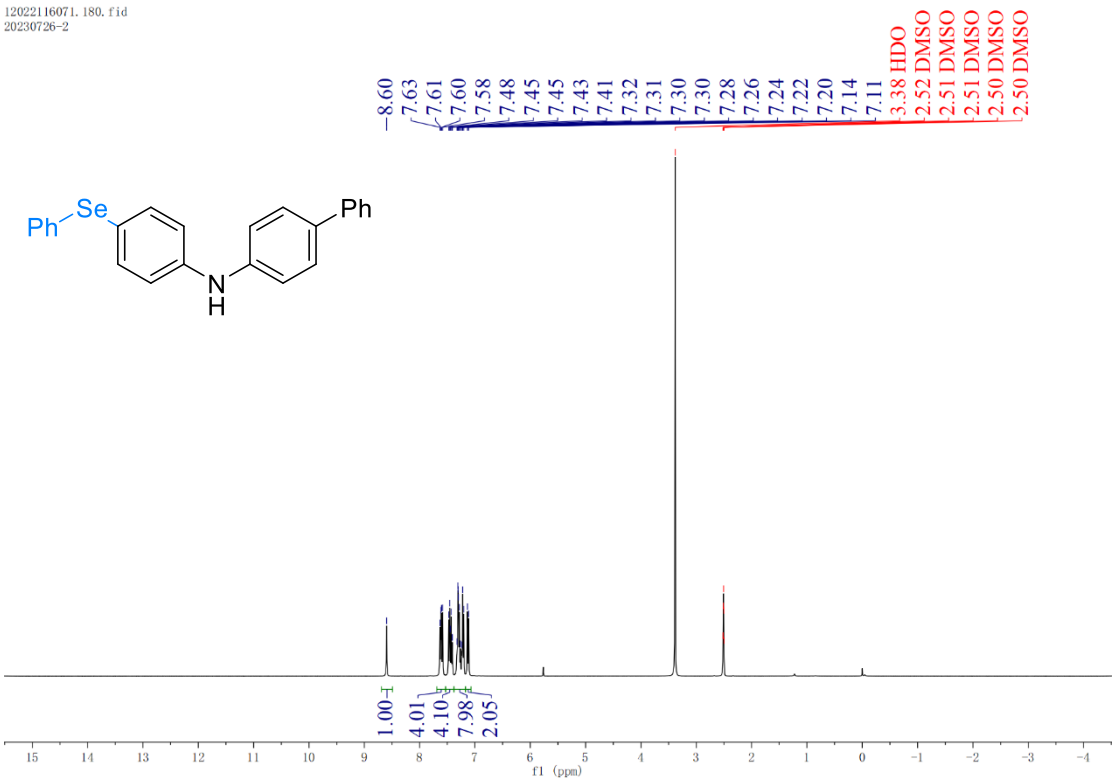
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8c**



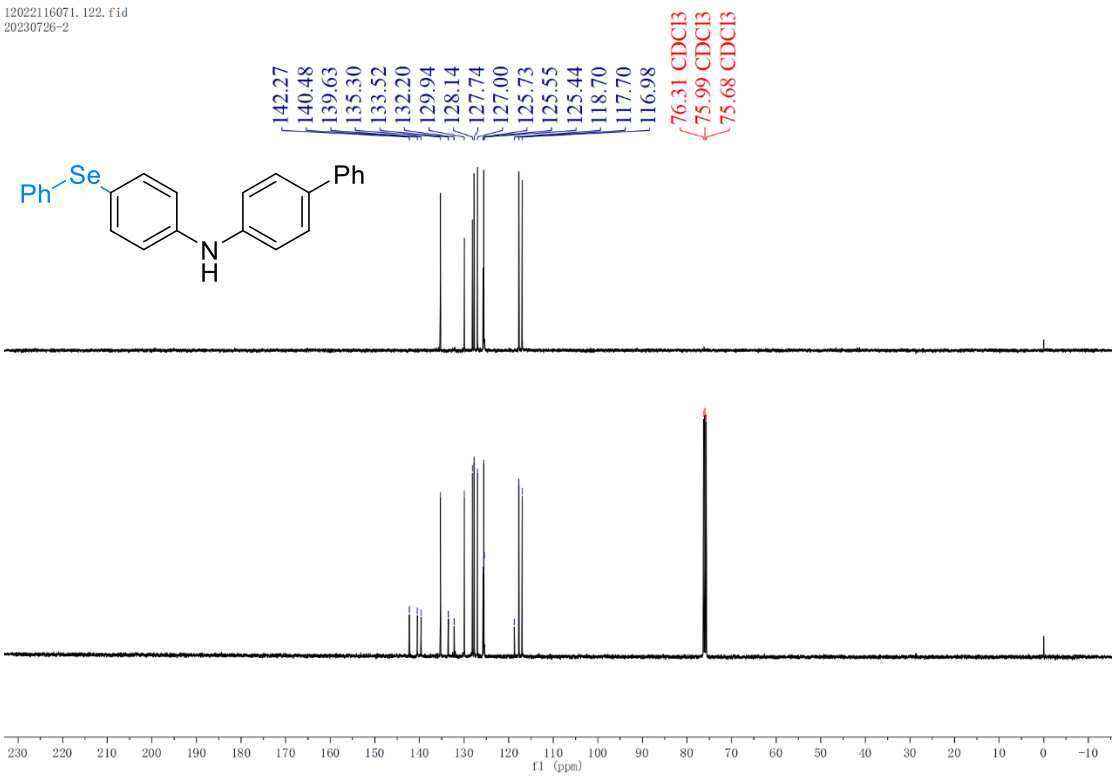
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8d**



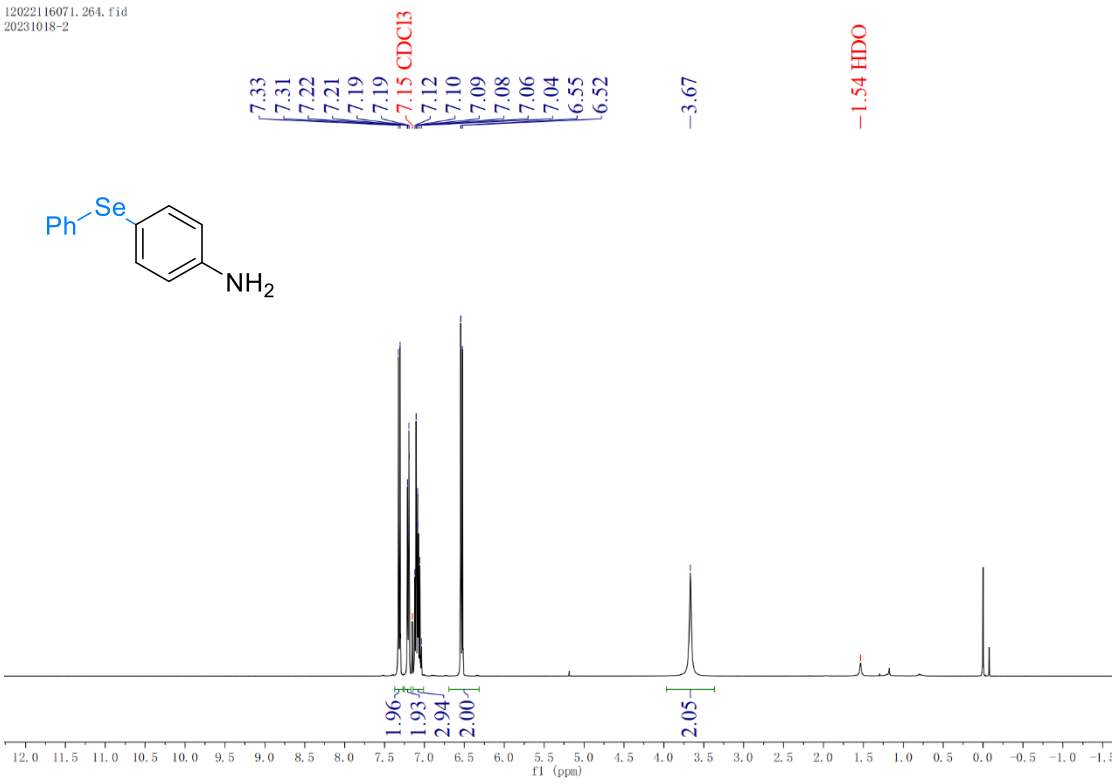
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8d**



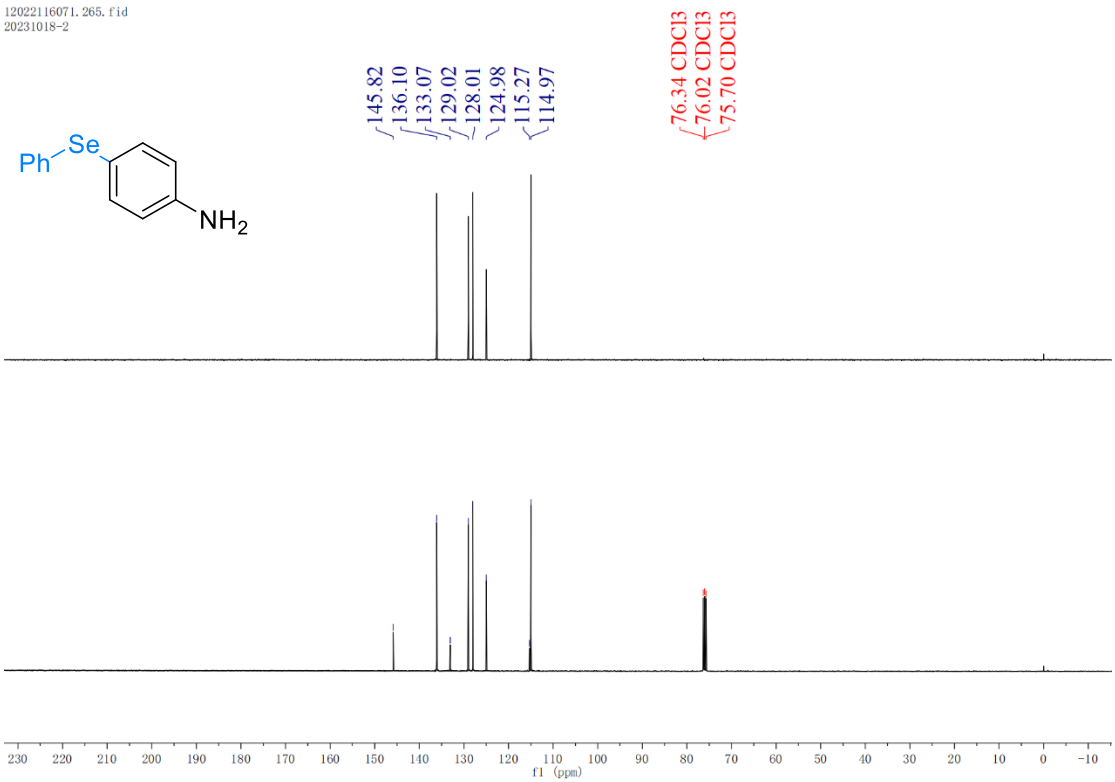
^{1}H-NMR (400 MHz, DMSO) **Spectra of compound 8e**



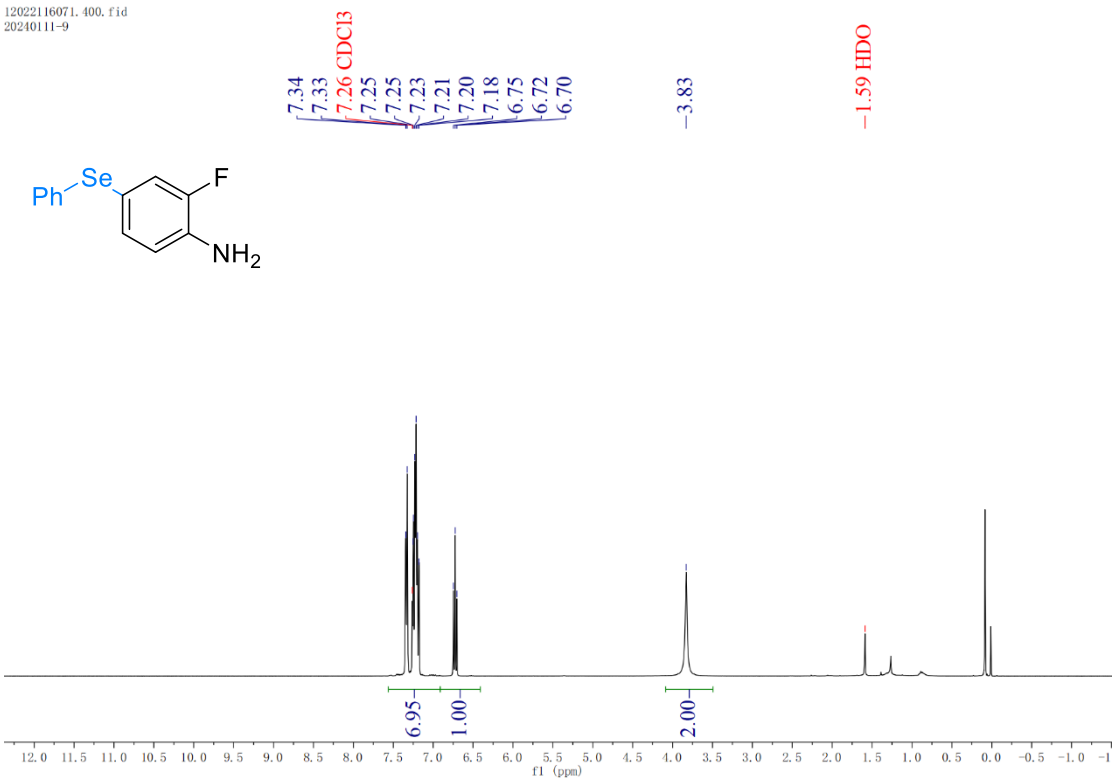
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8e**



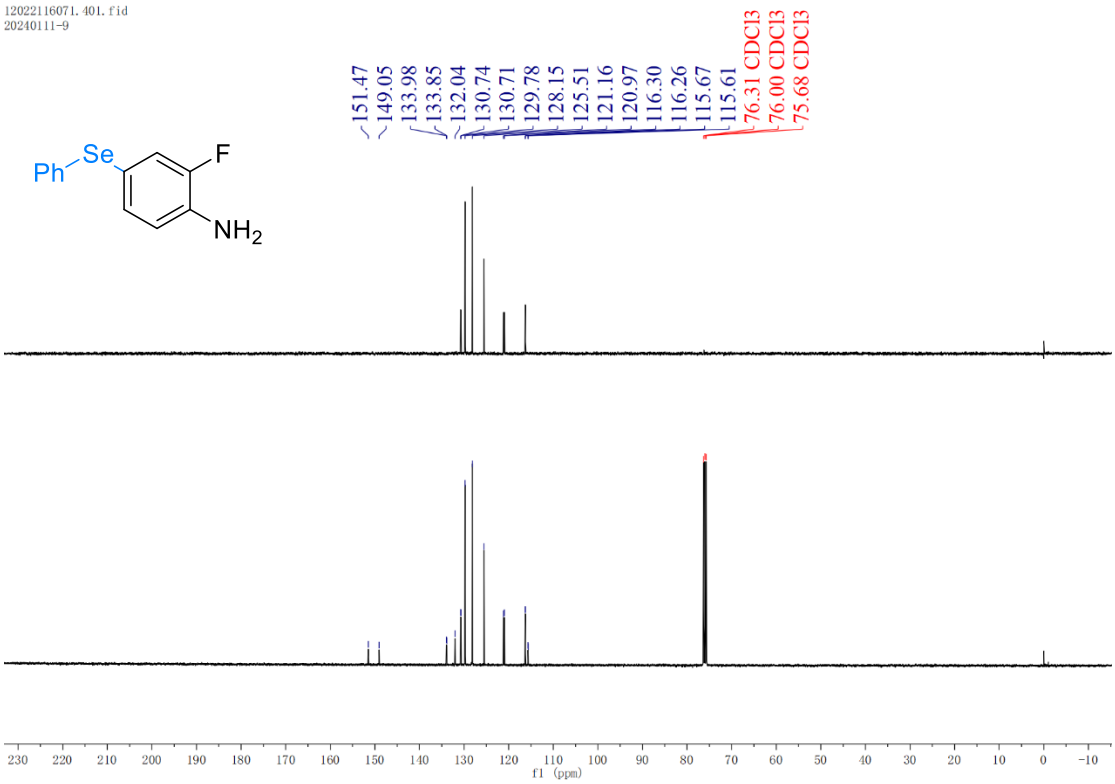
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8f**



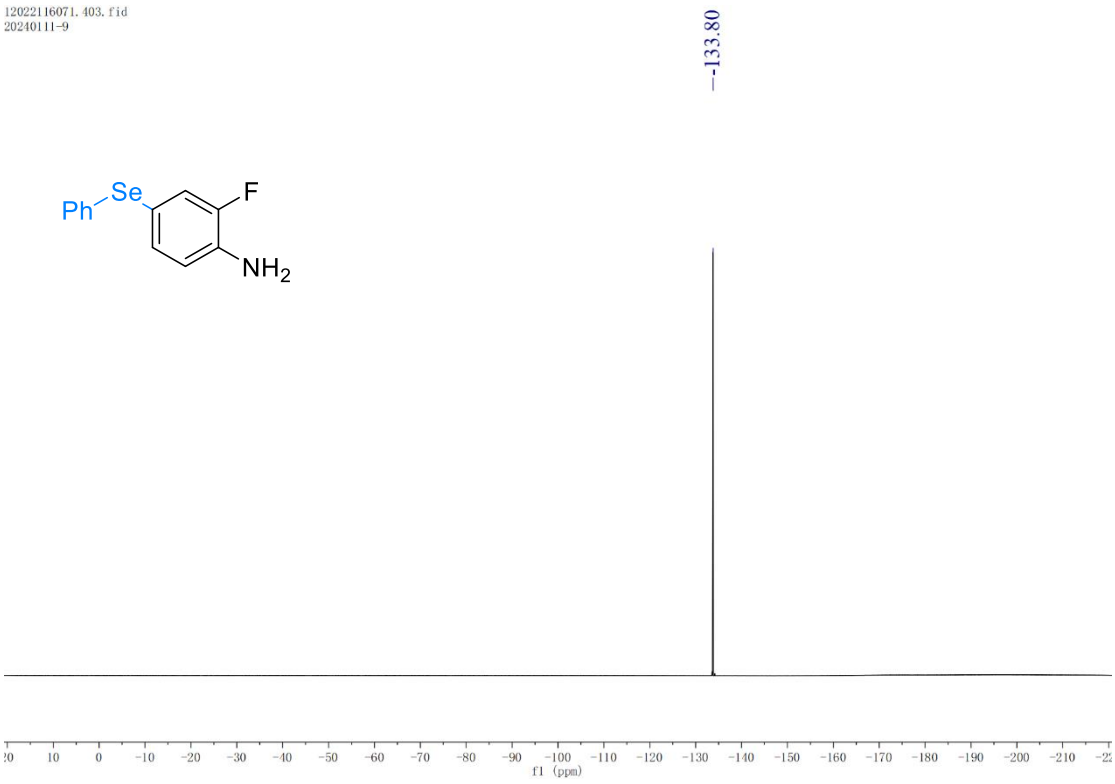
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8f**



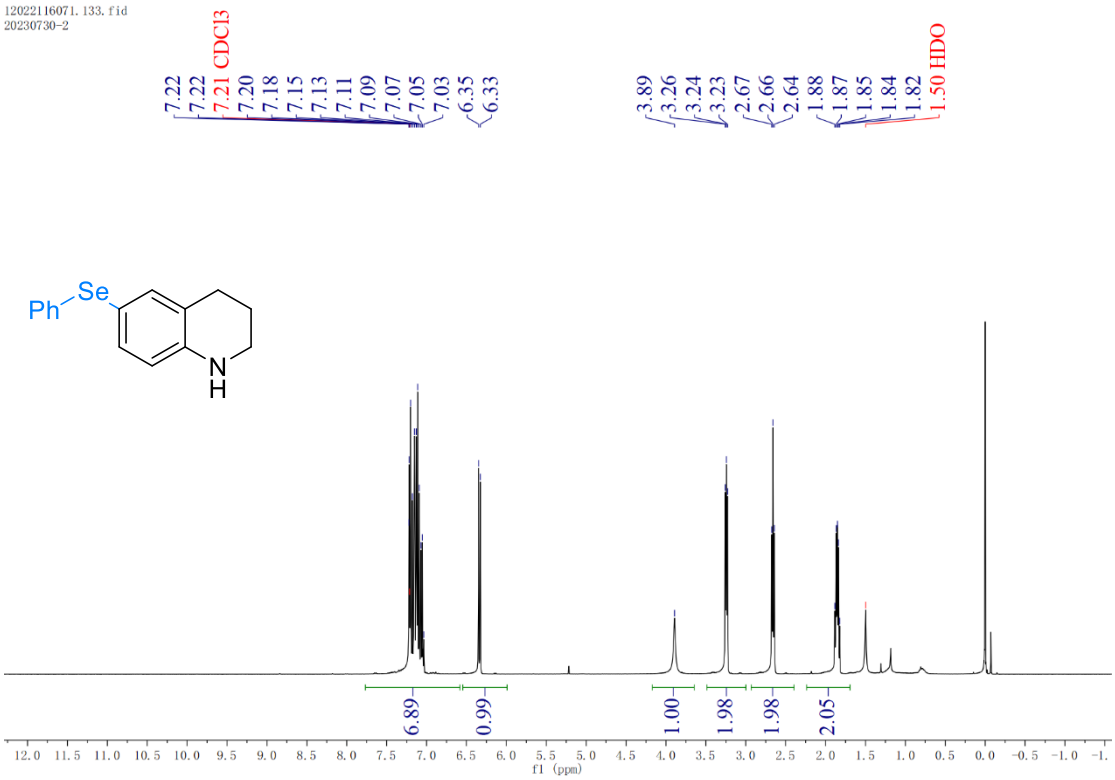
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8g**



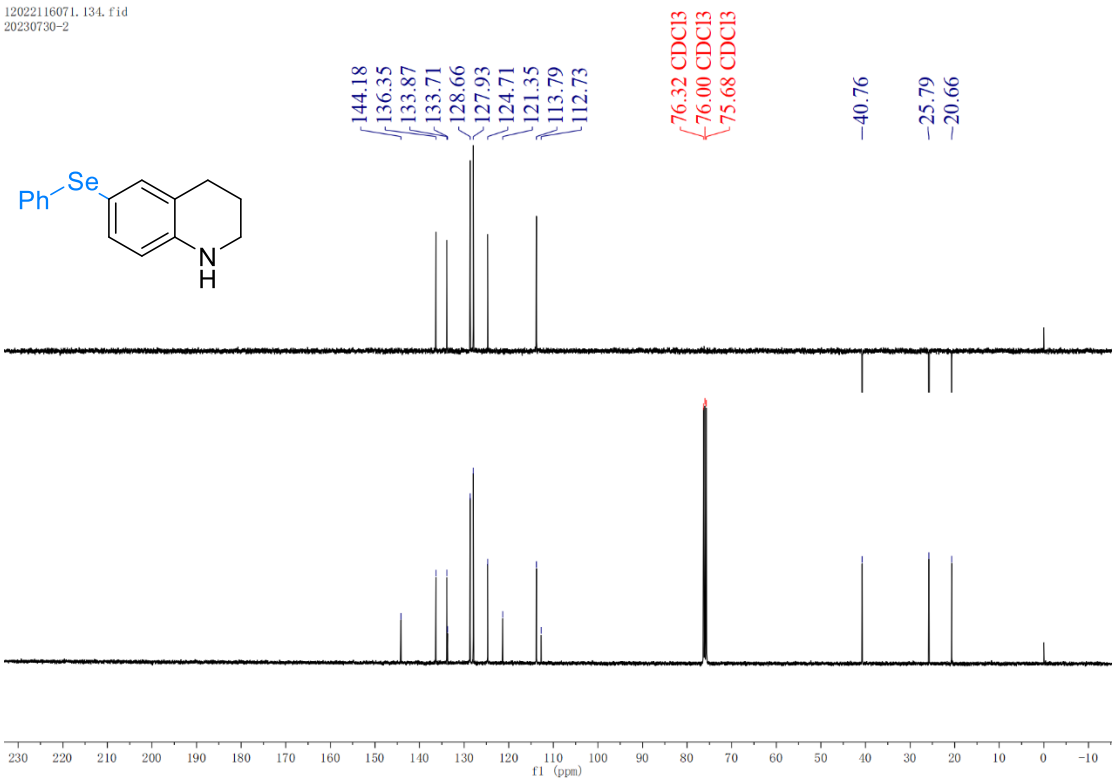
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8g**



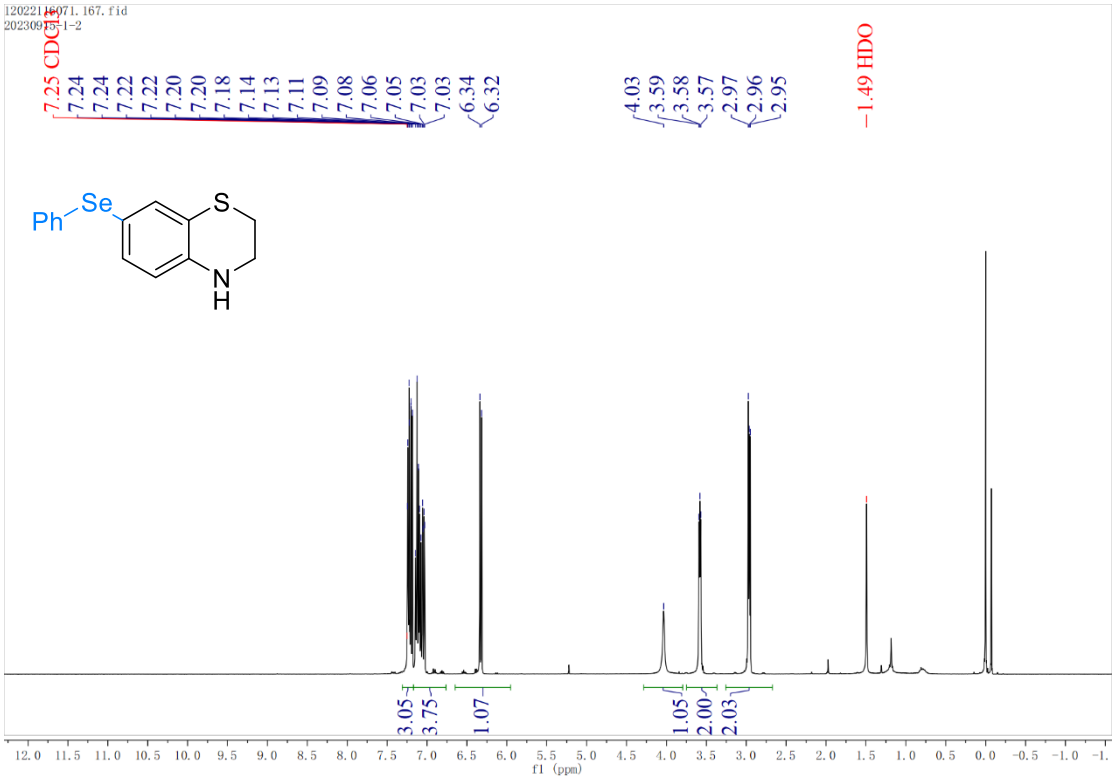
^{19}F NMR (376 MHz, $CDCl_3$) **Spectrum of compound 8g**



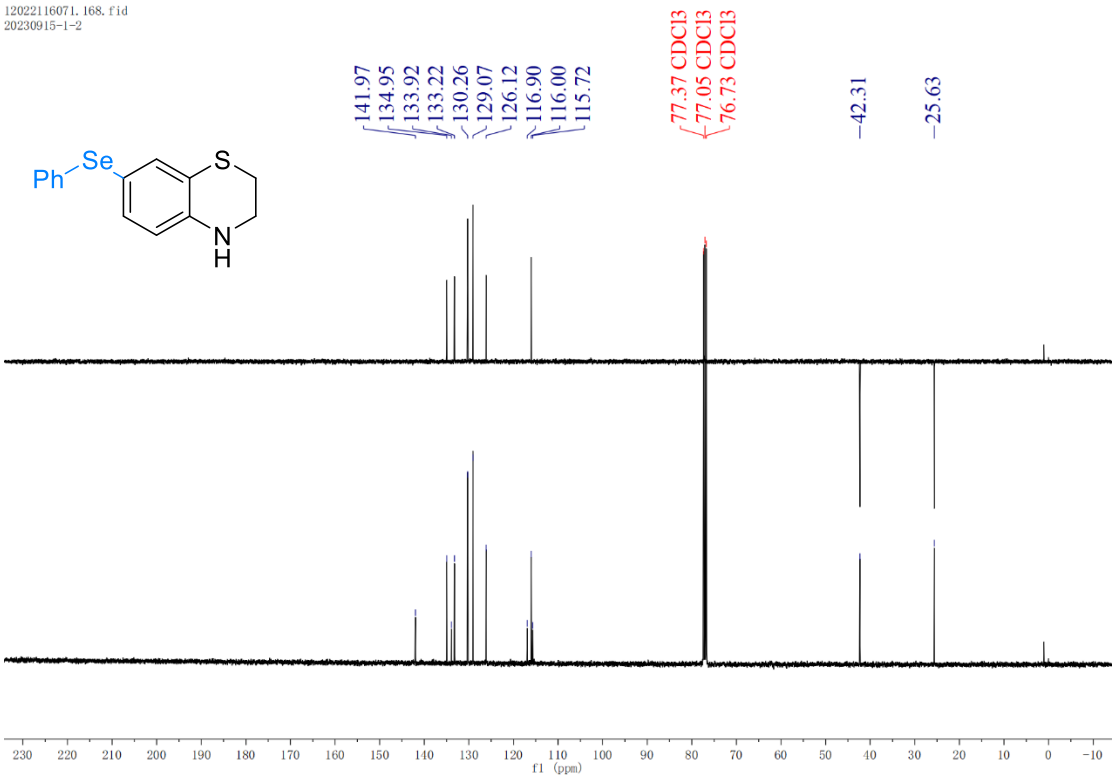
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8h**



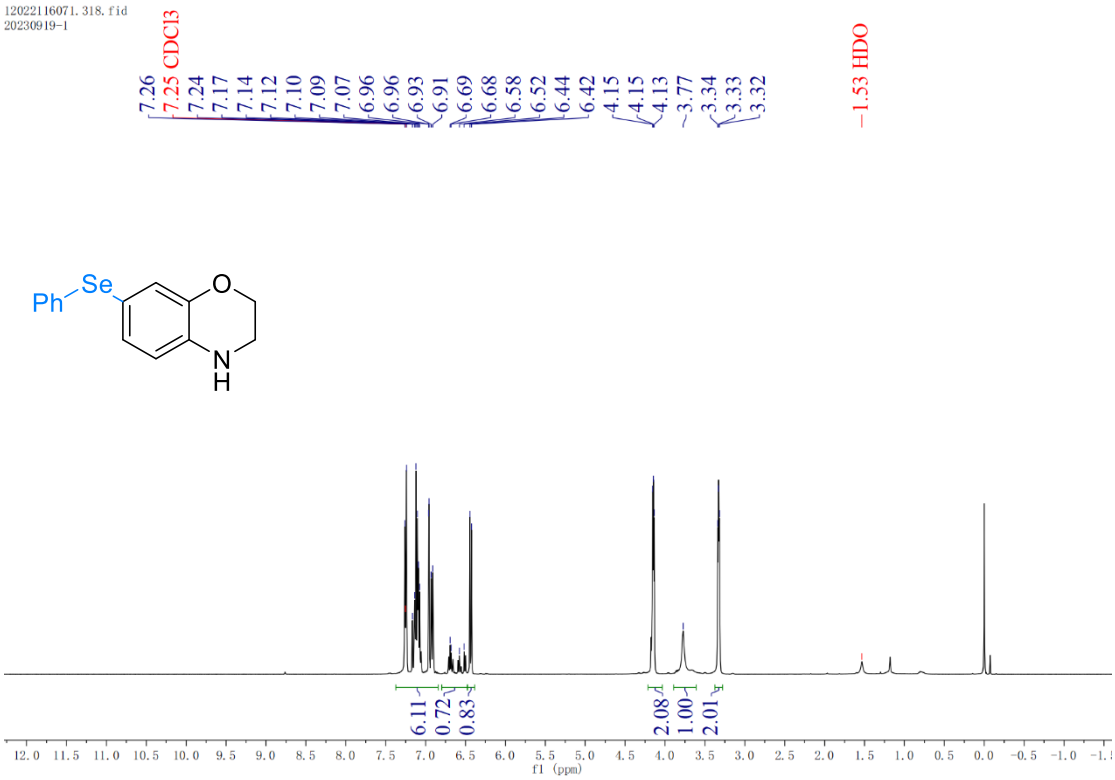
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8h**



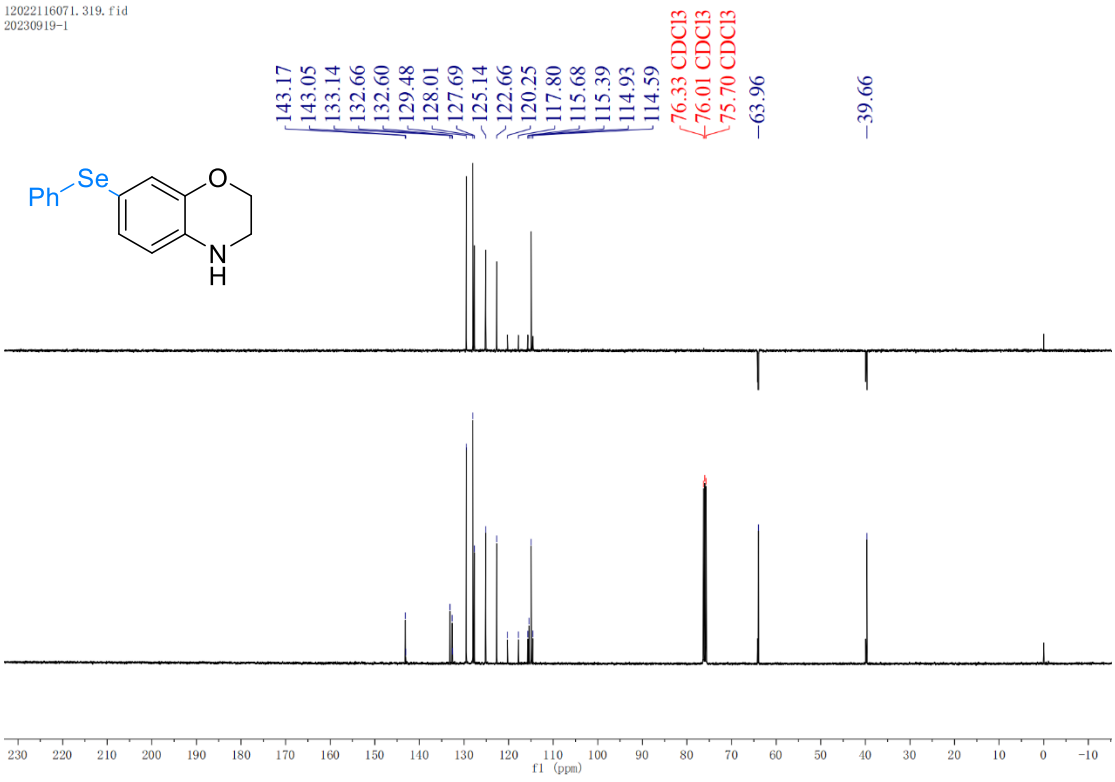
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8i**



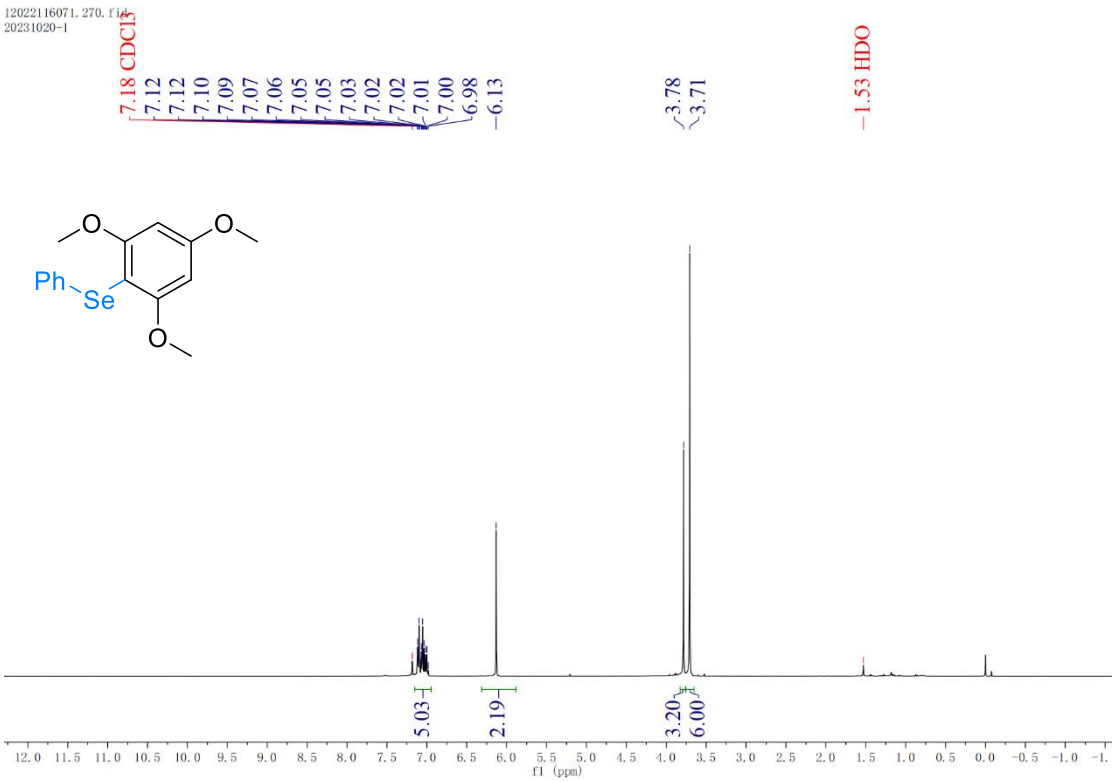
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8i**



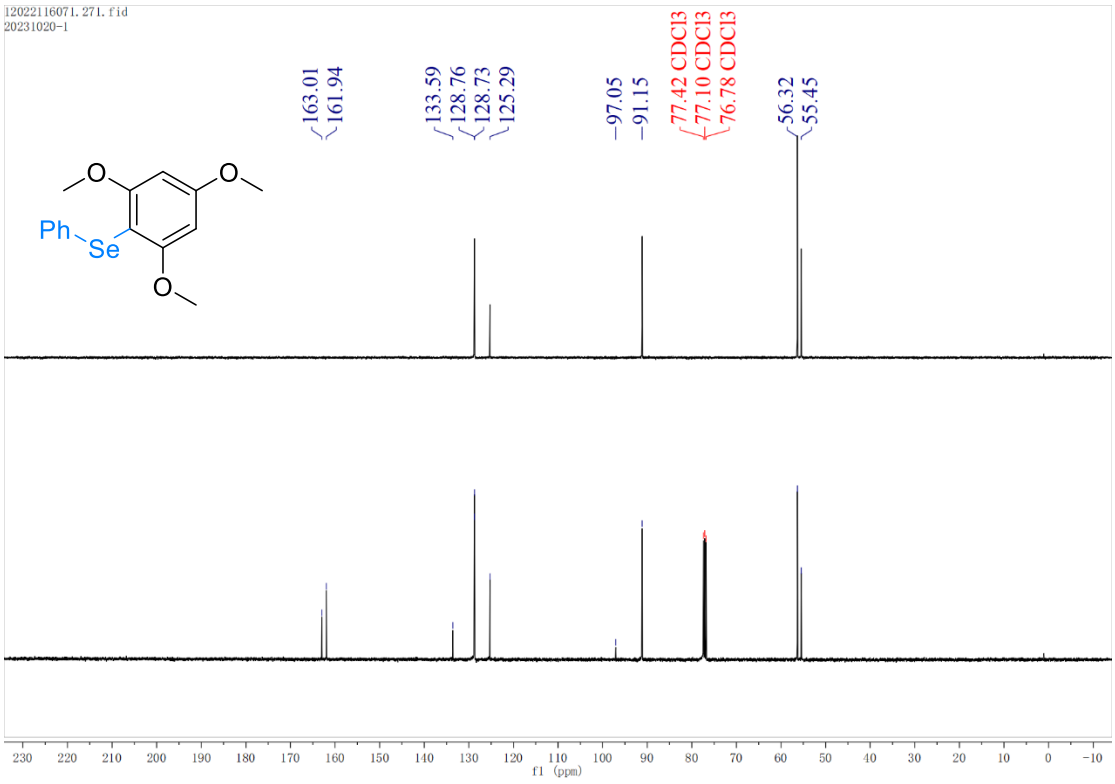
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8j**



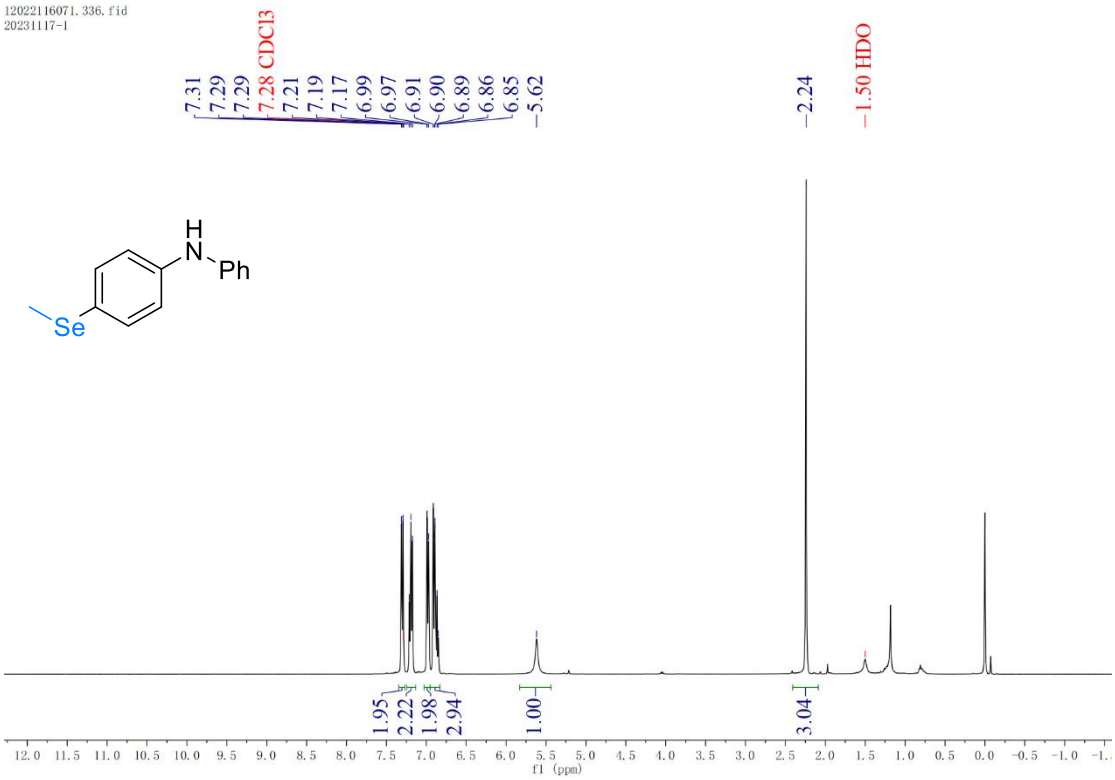
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8j**



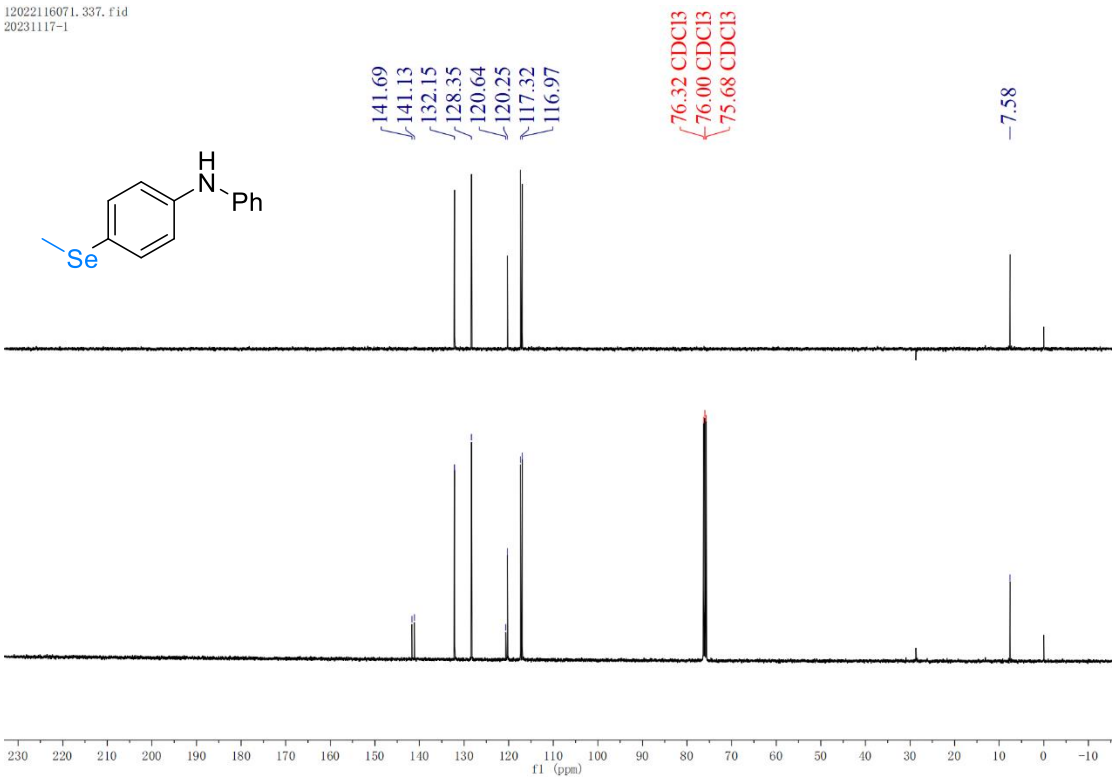
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8k**



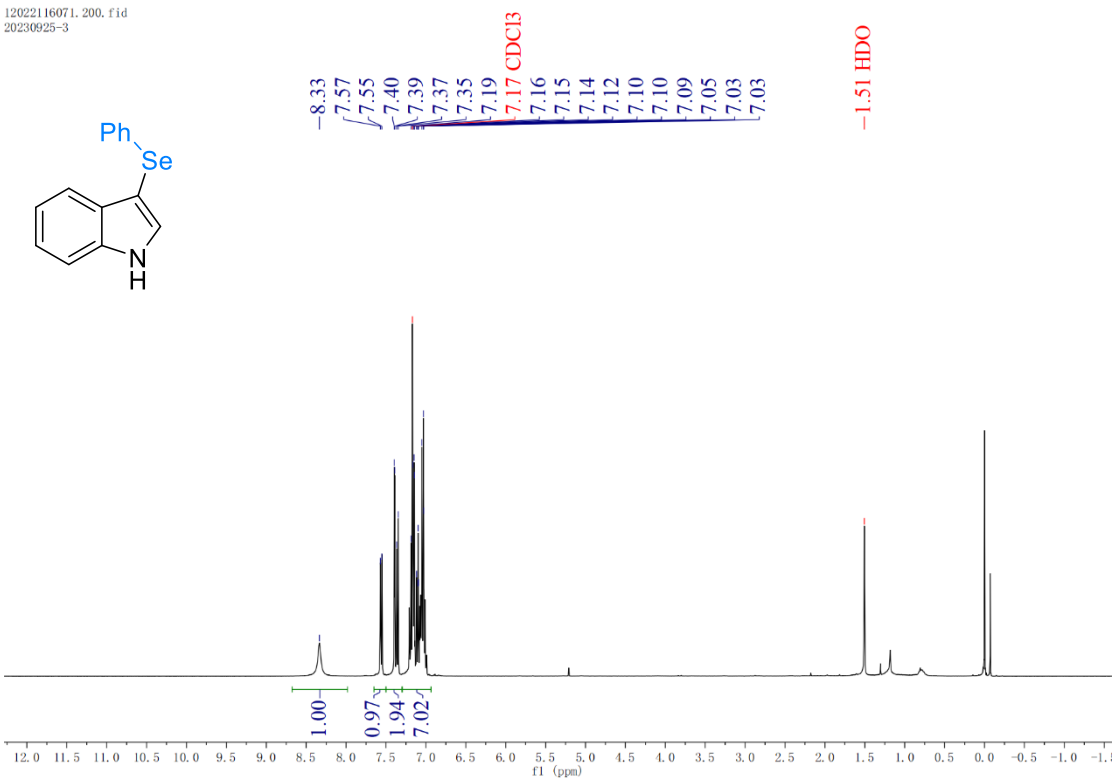
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8k**



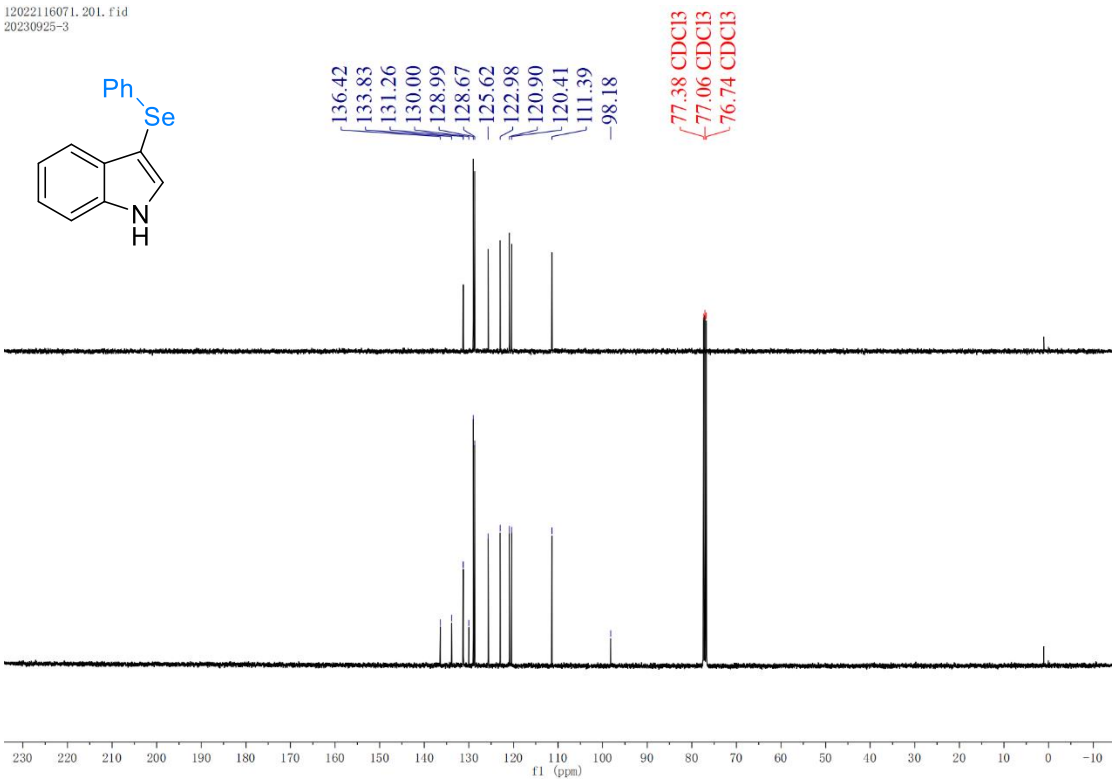
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8l**



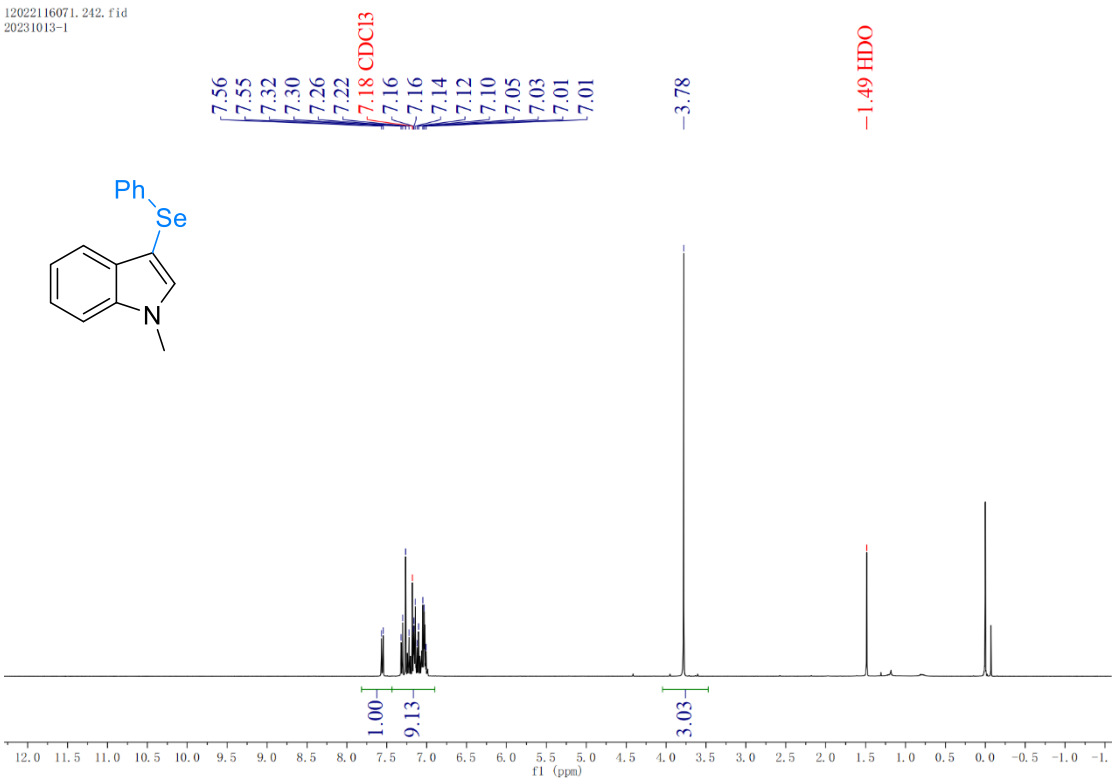
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8l**



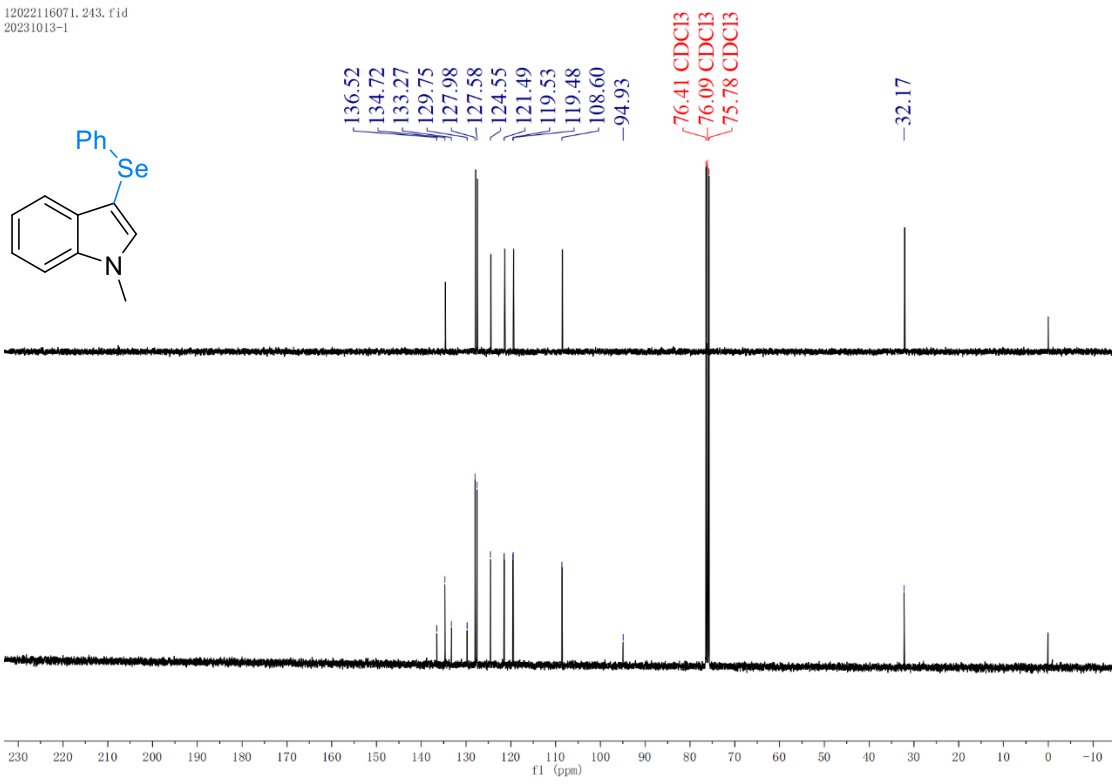
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 9a**



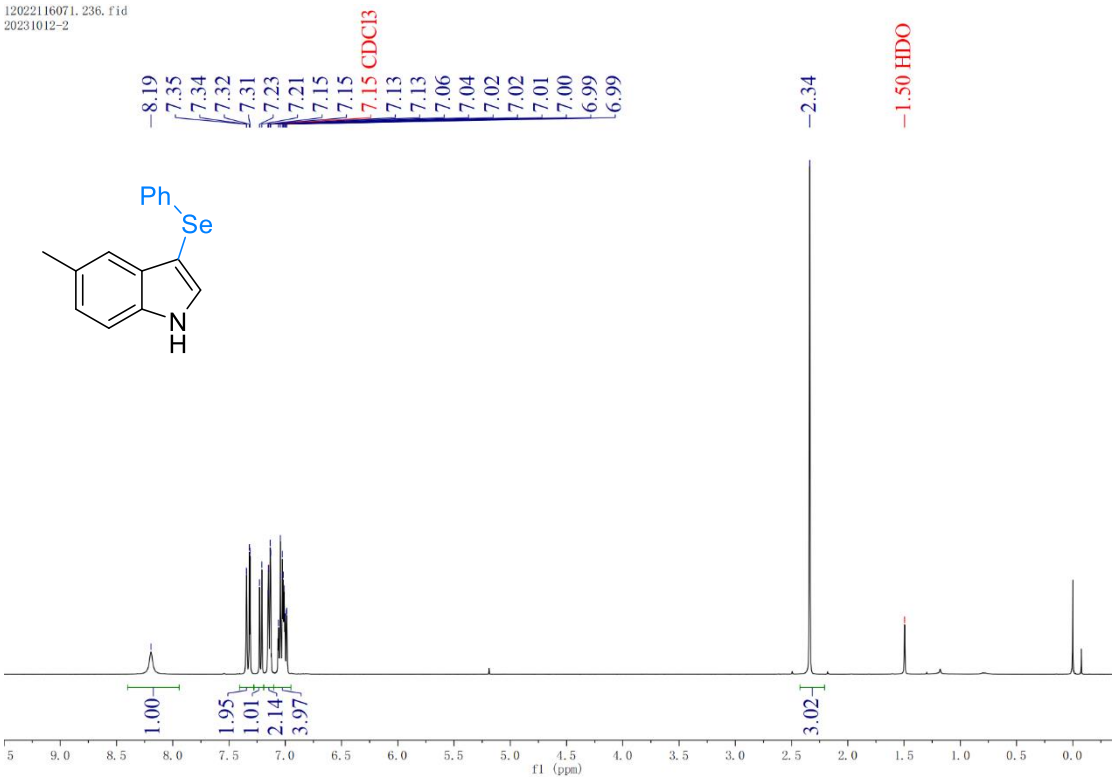
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9a**



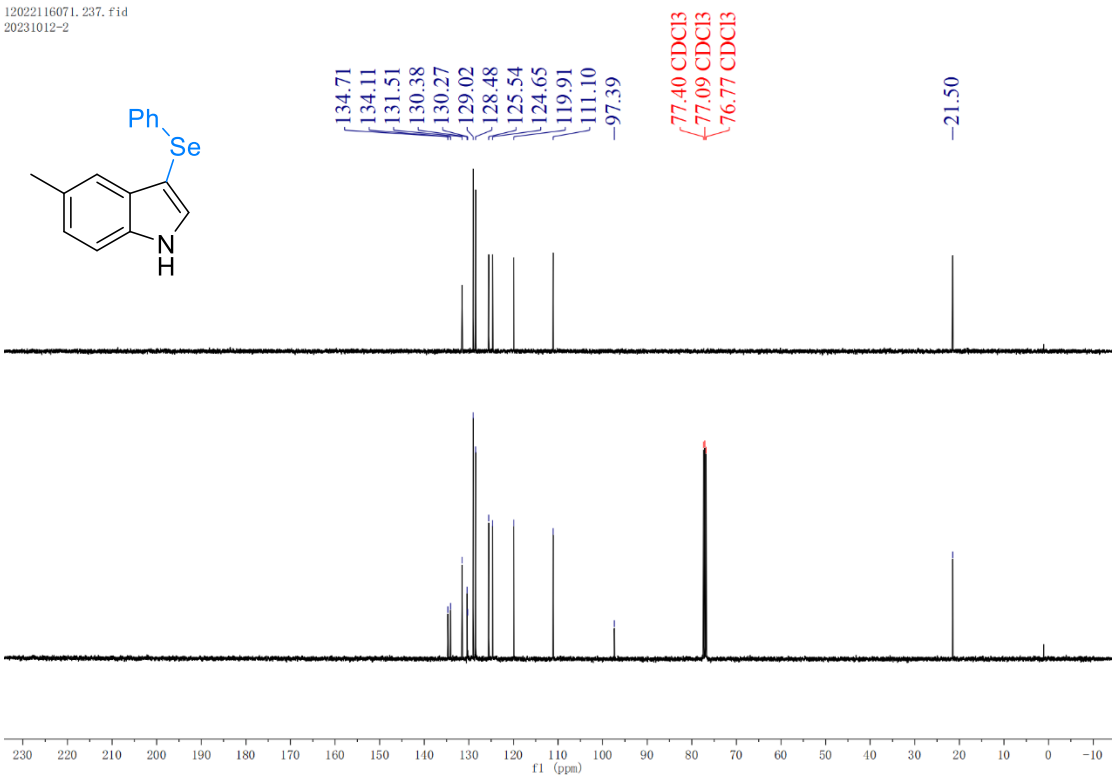
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 9b**



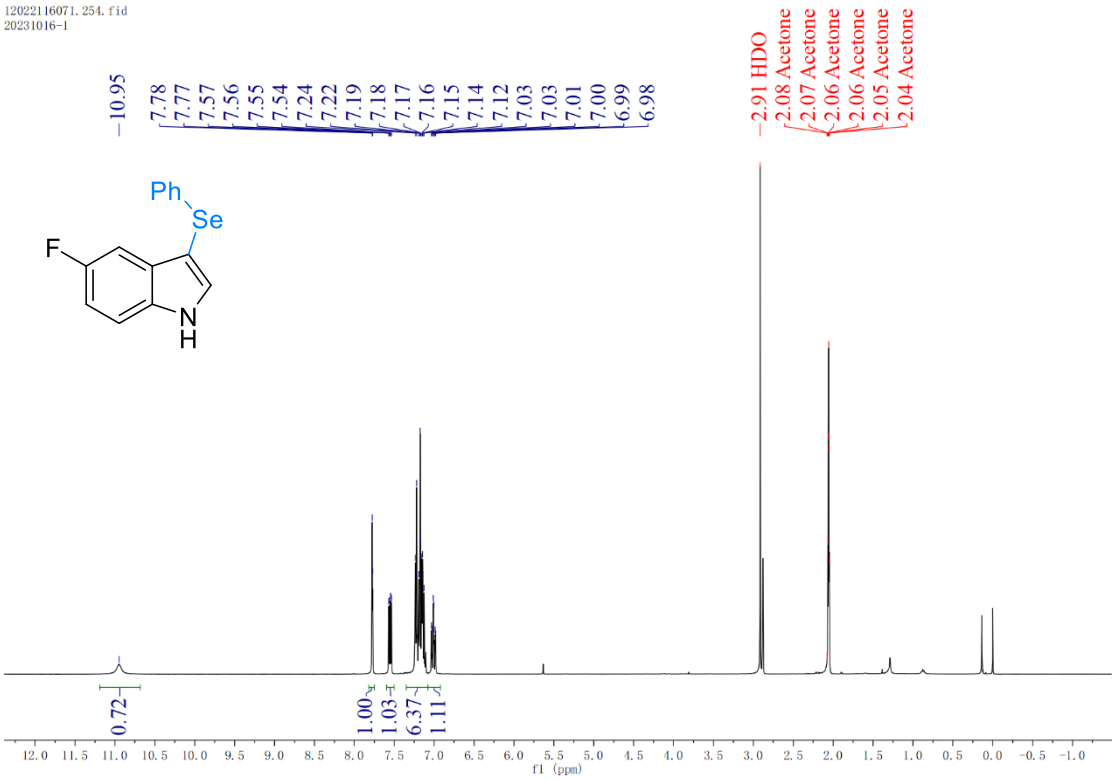
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9b**



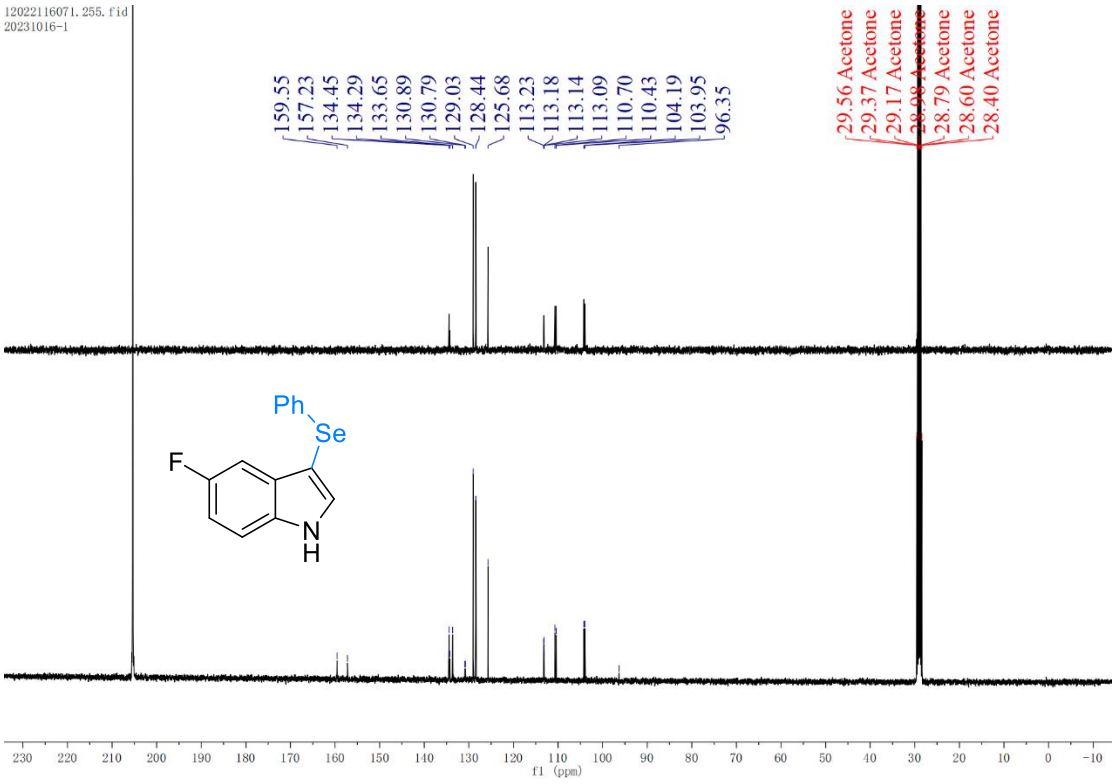
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 9c**



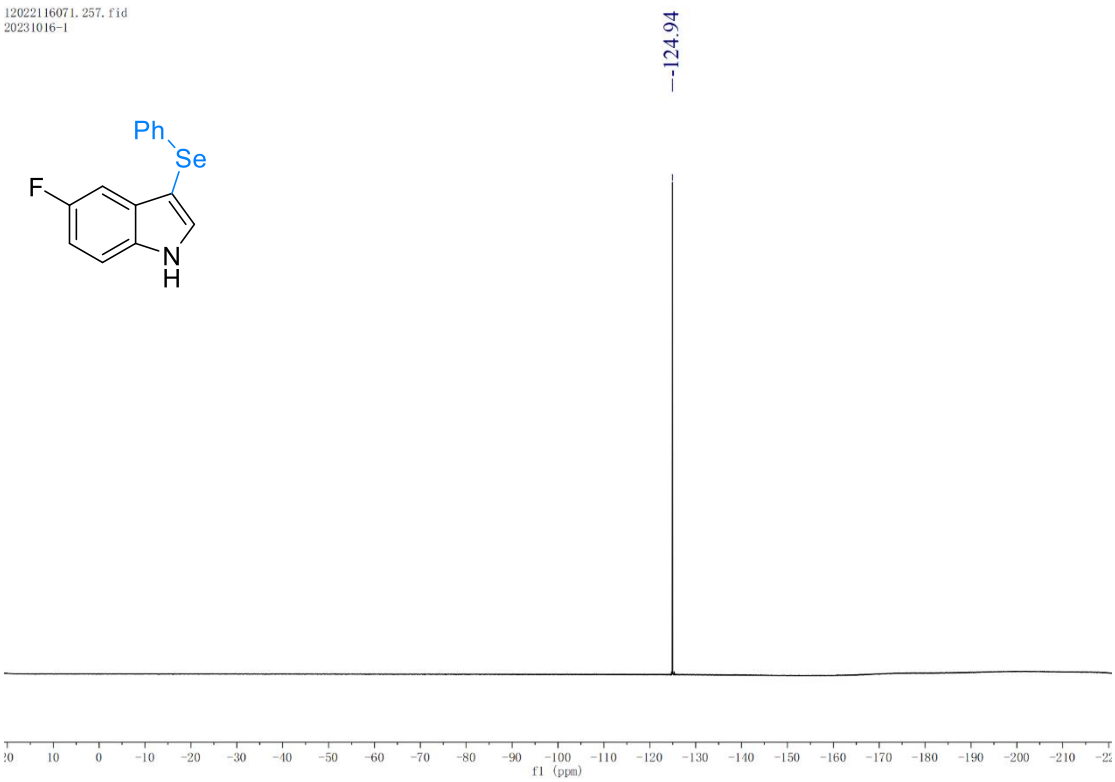
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9c**



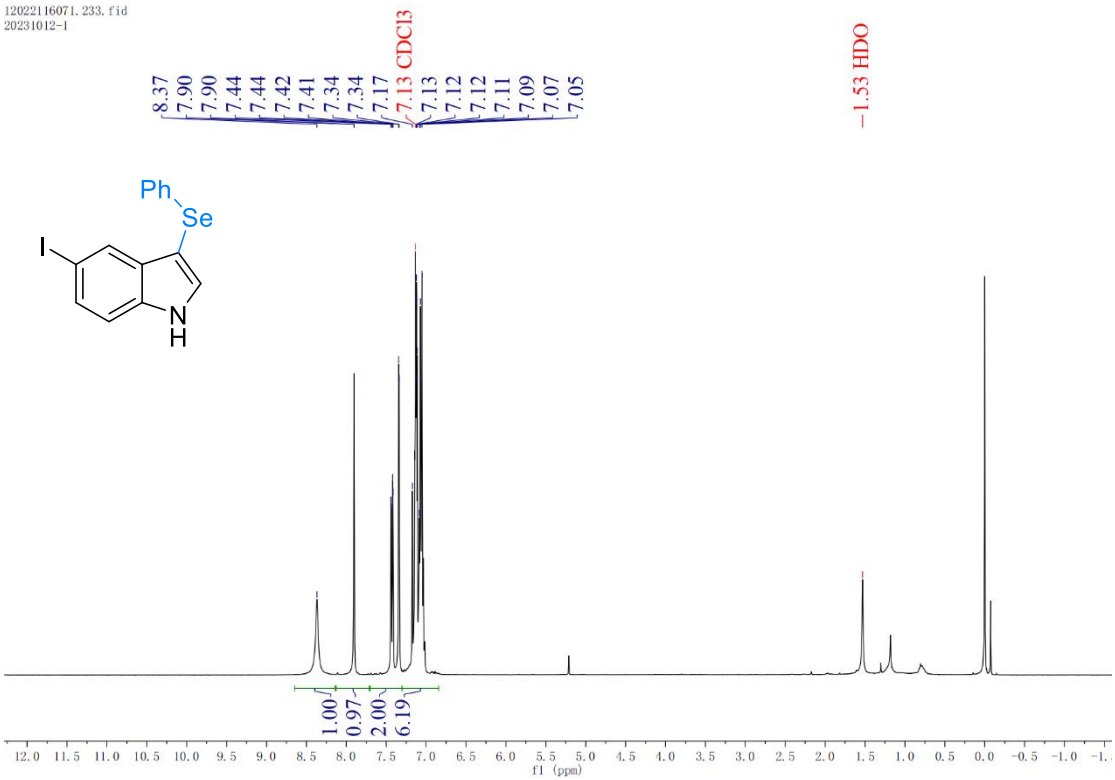
^{1}H-NMR (400 MHz, Acetone-d6) **Spectra of compound 9d**



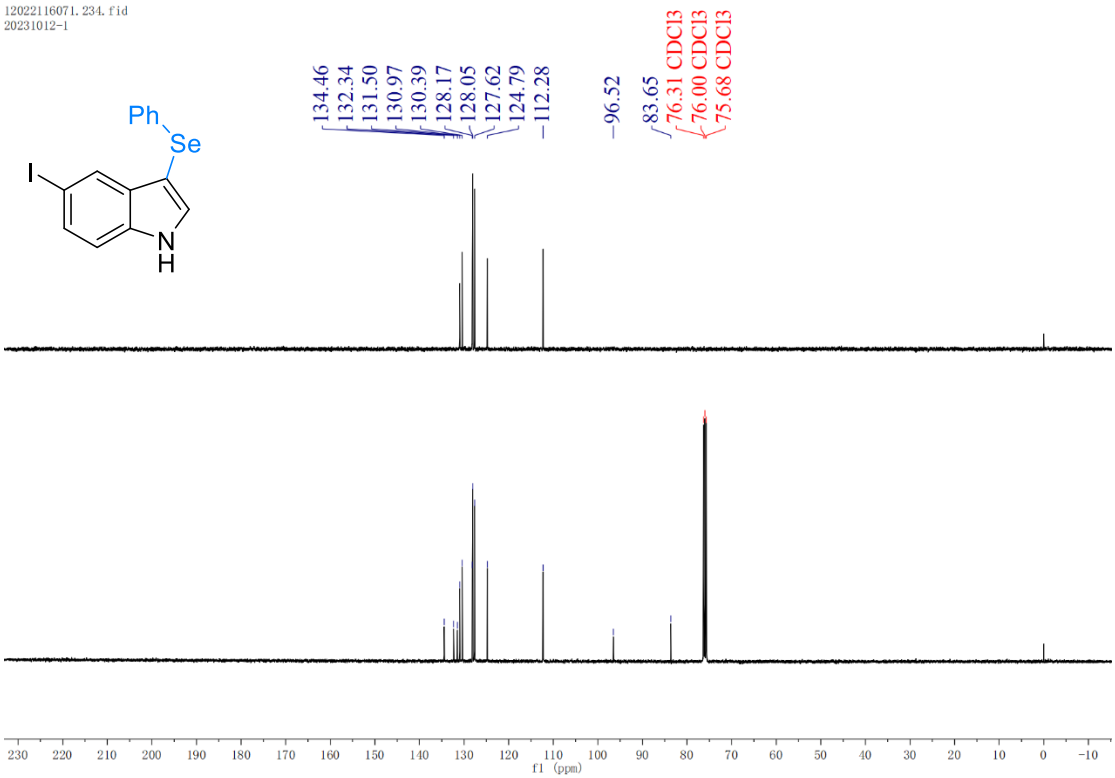
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9d**



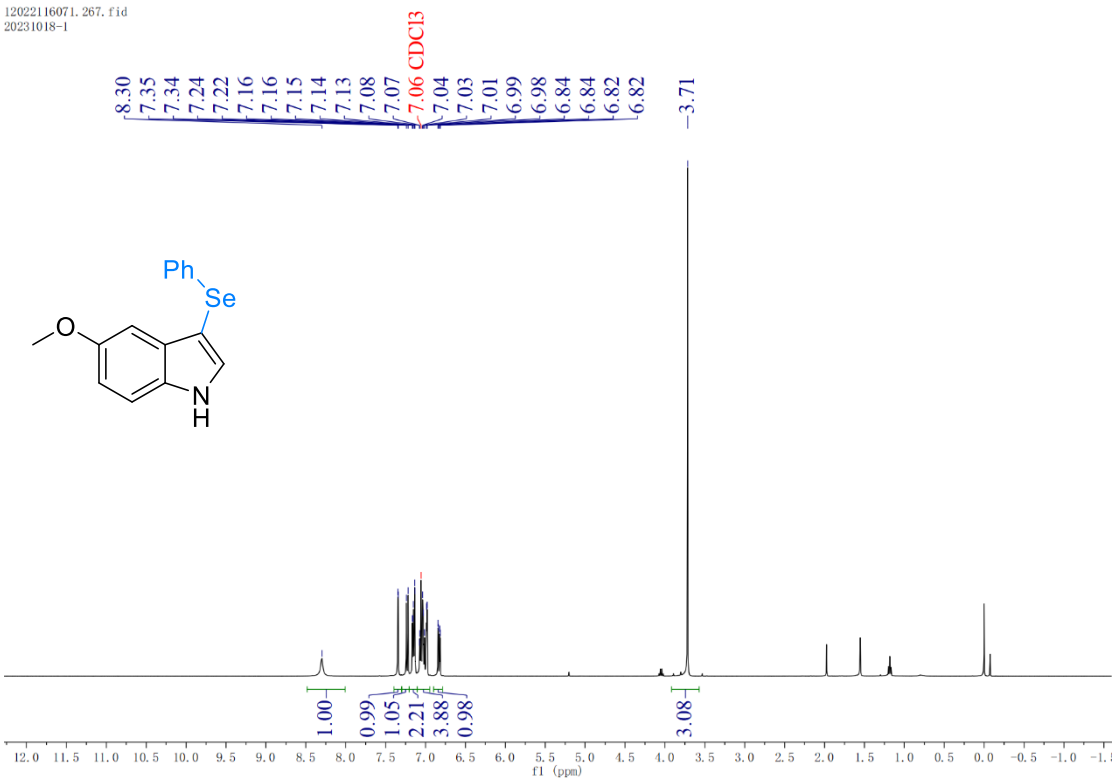
^{19}F NMR (376 MHz, $CDCl_3$) **Spectrum of compound 9d**



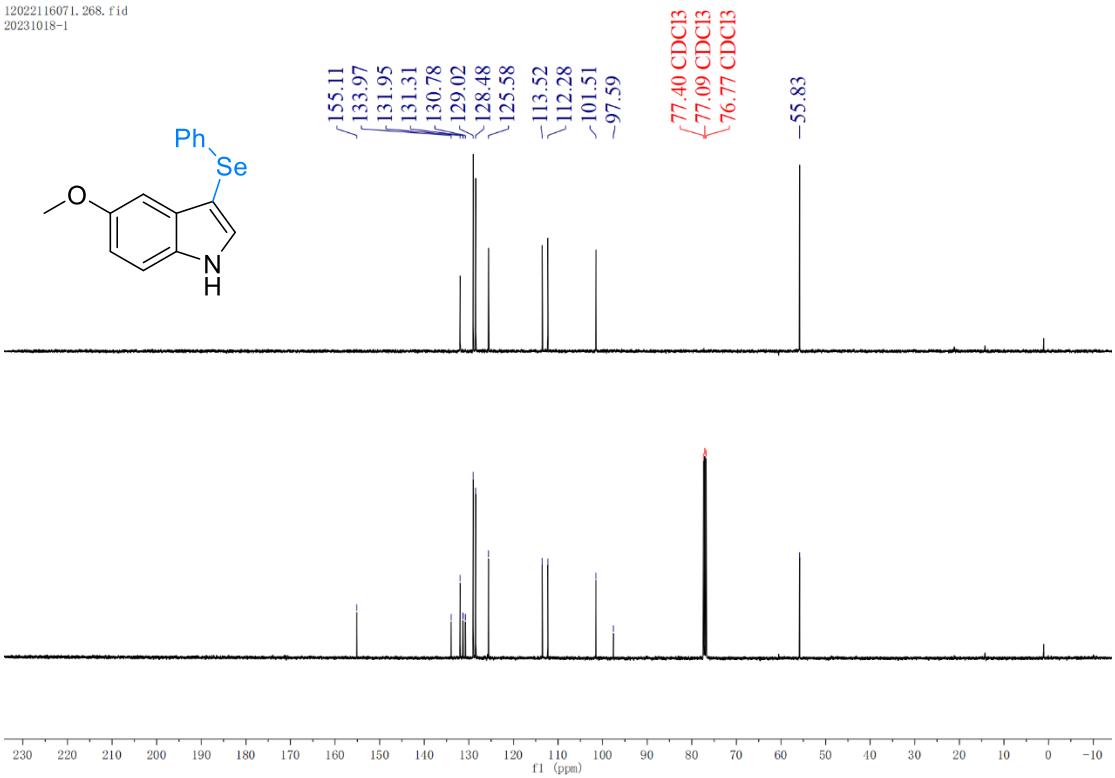
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 9e**



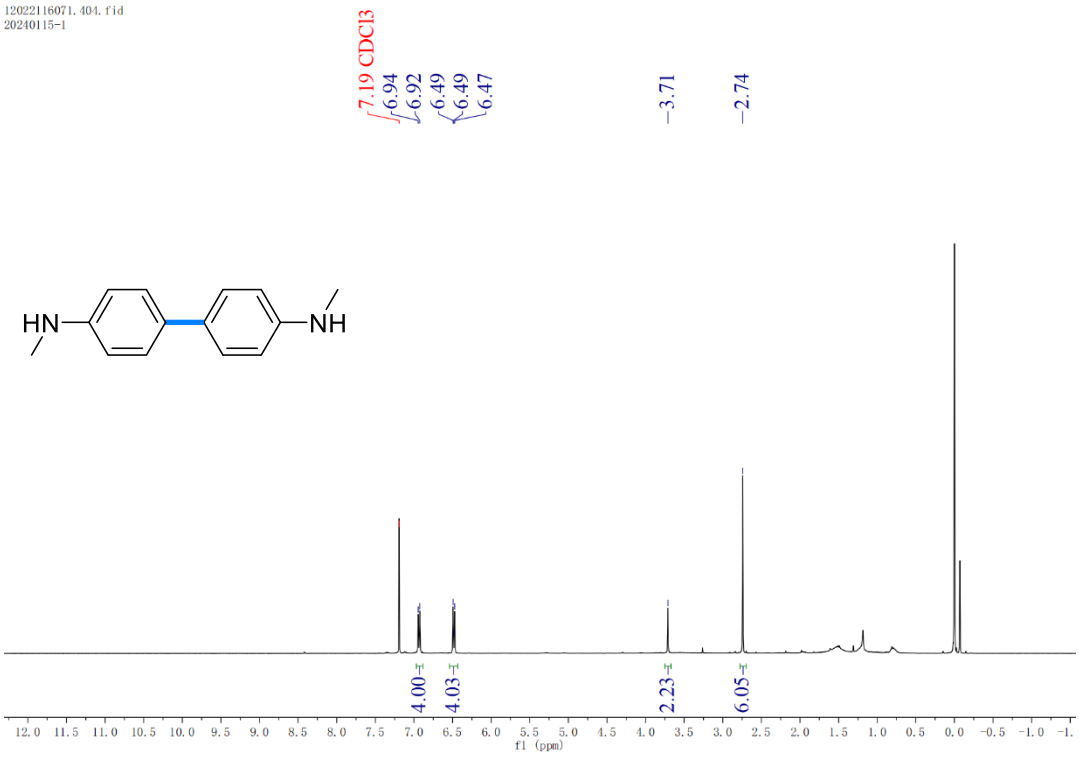
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9e**



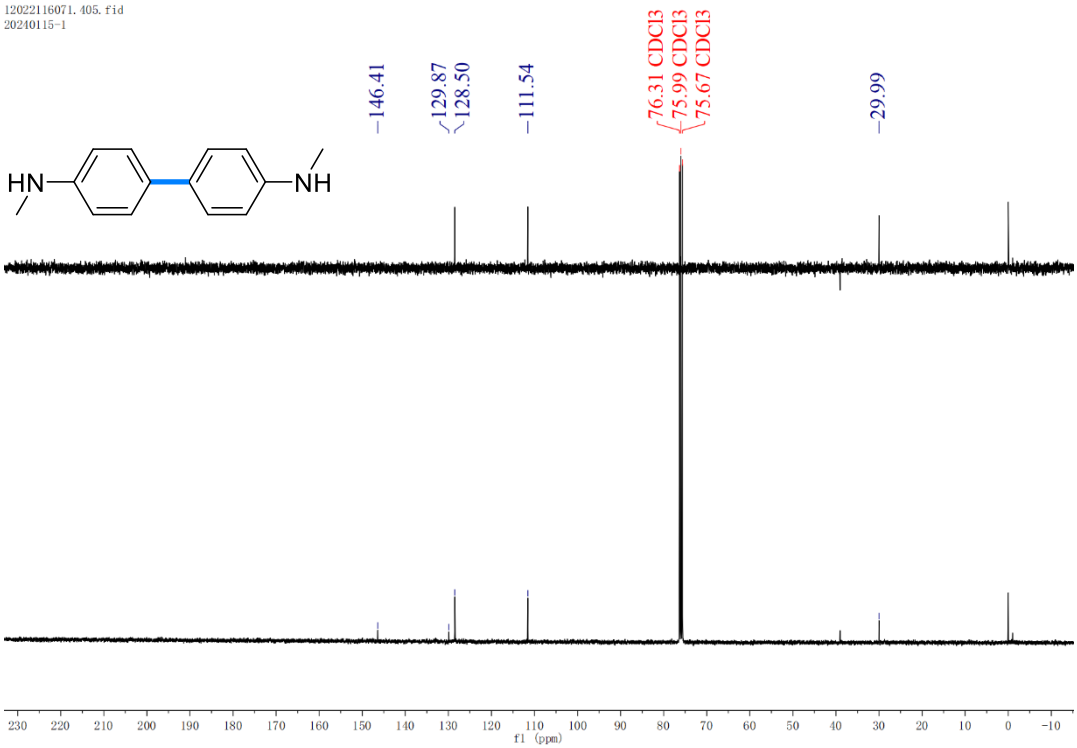
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 9f**



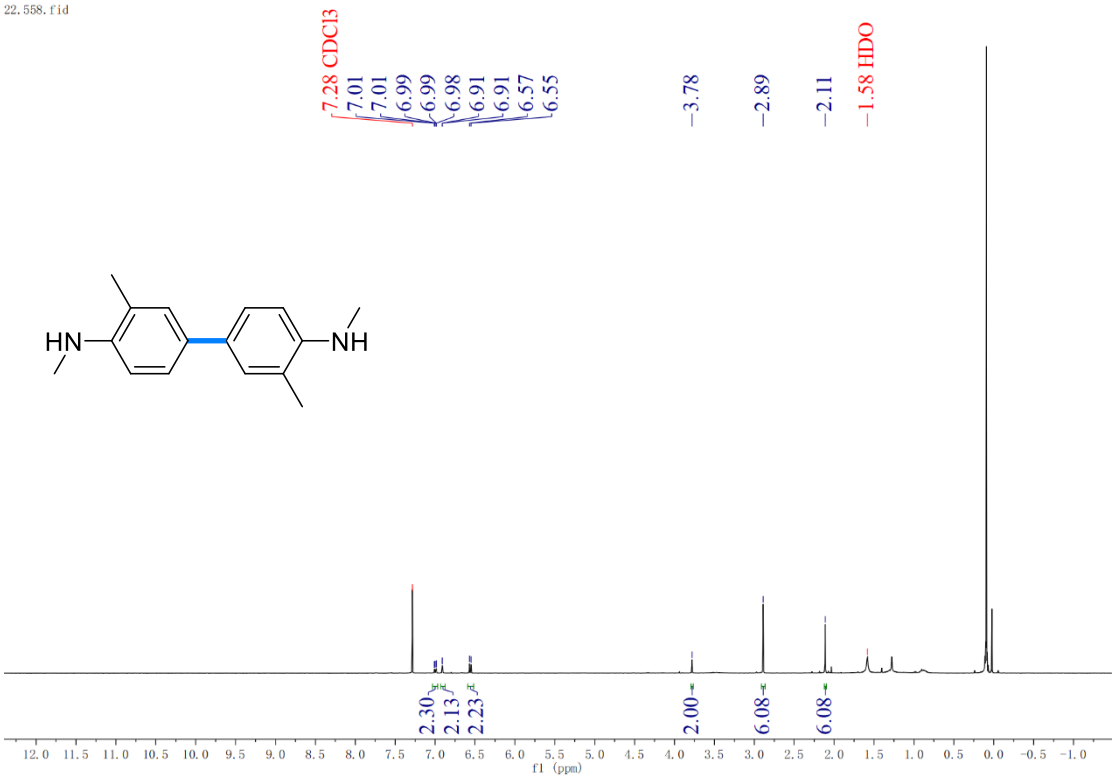
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 9f**



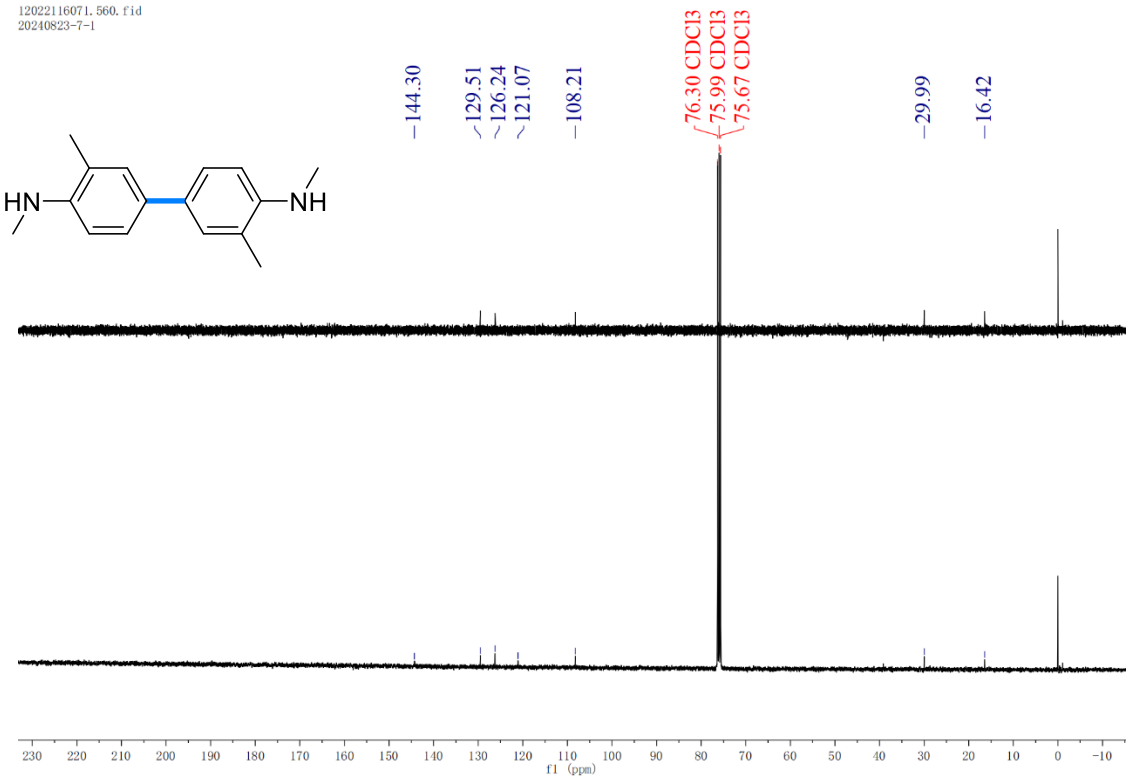
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 10a**



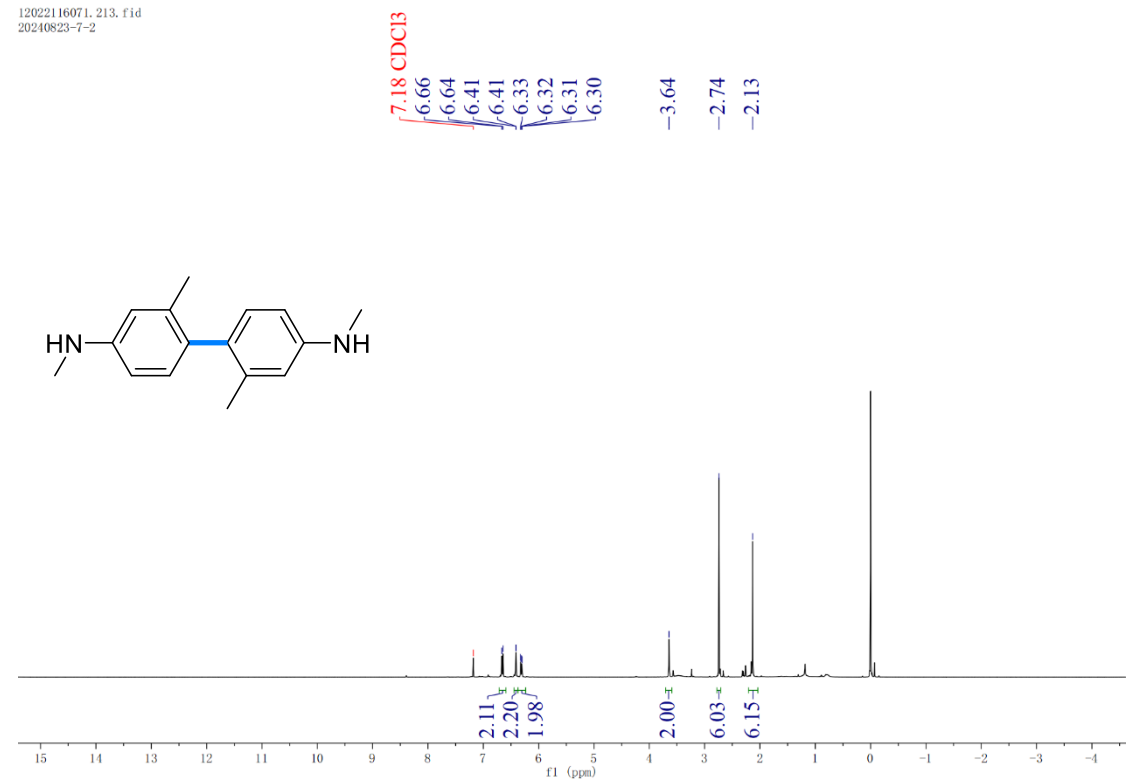
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 10a**



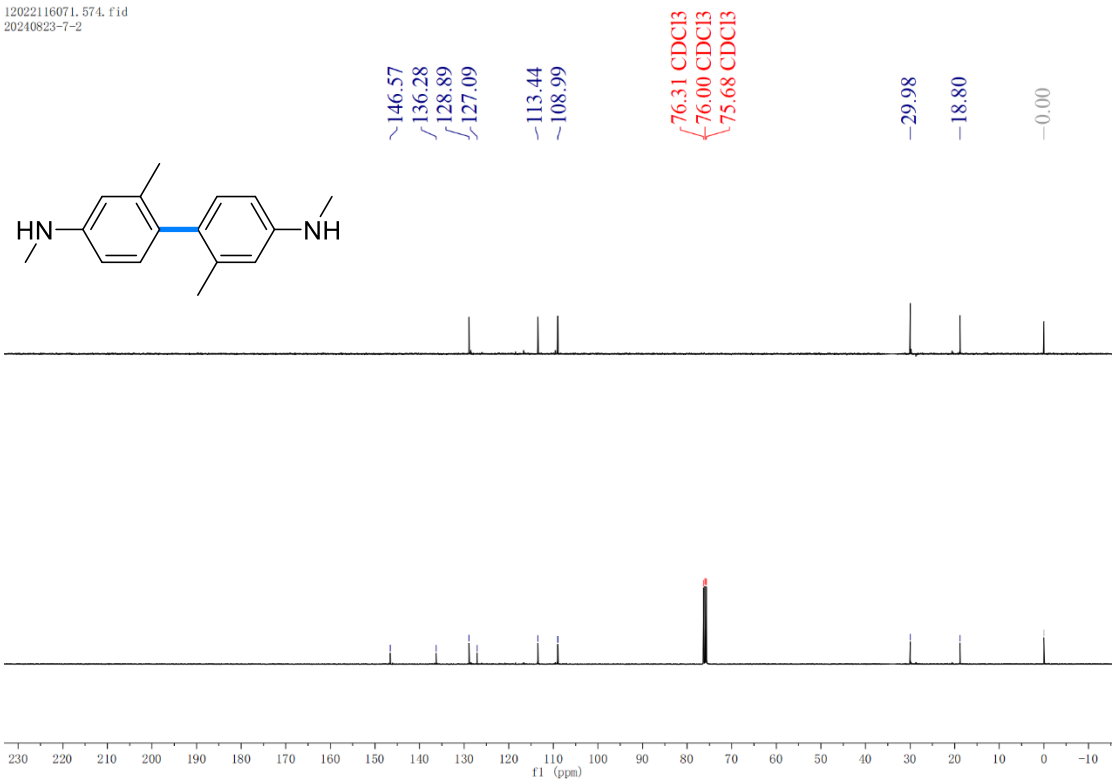
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 10b**



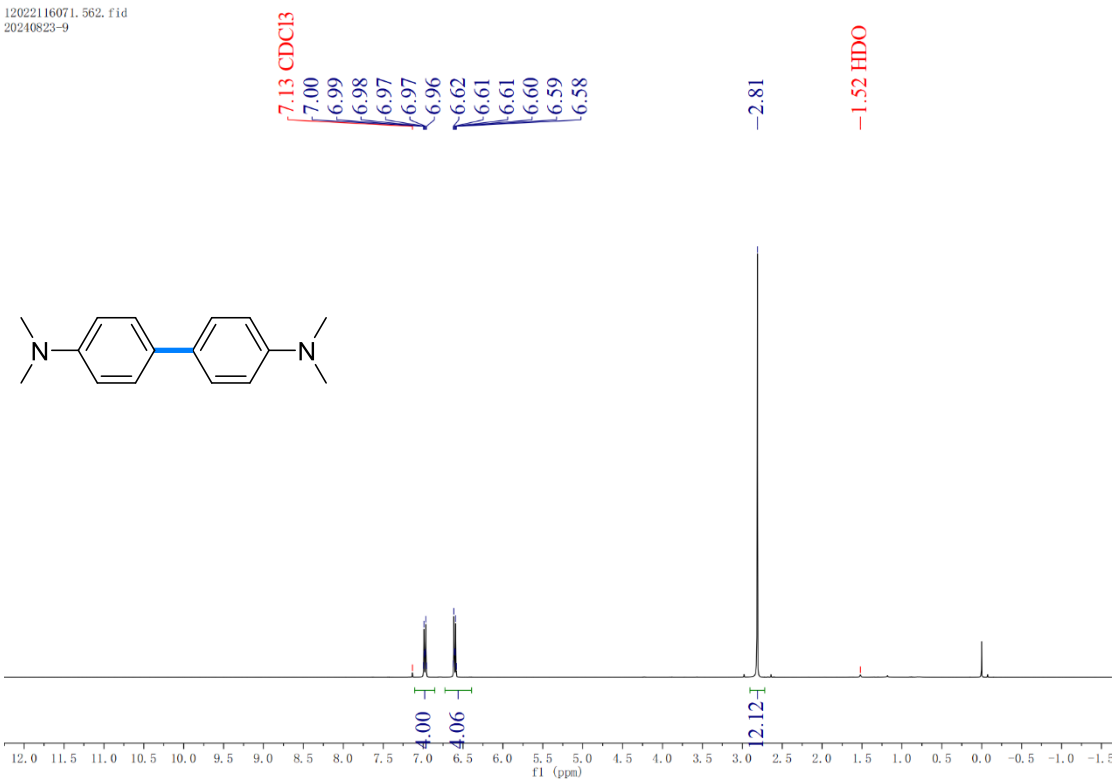
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 10b**



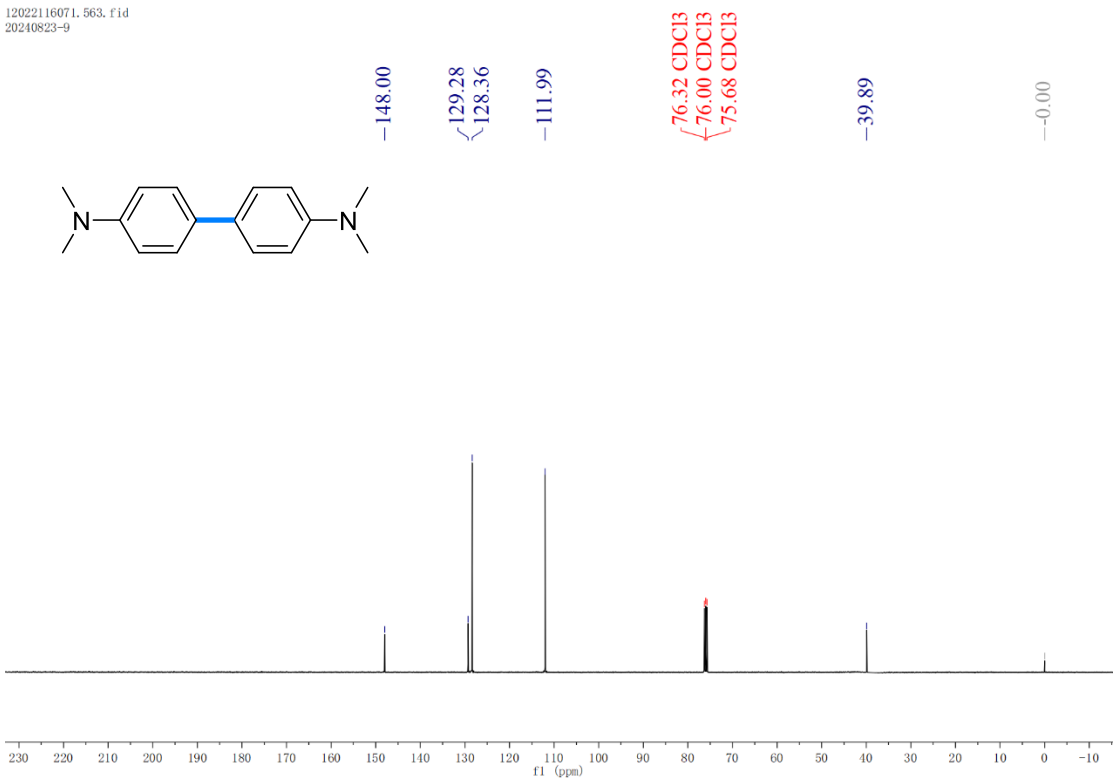
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 10c**



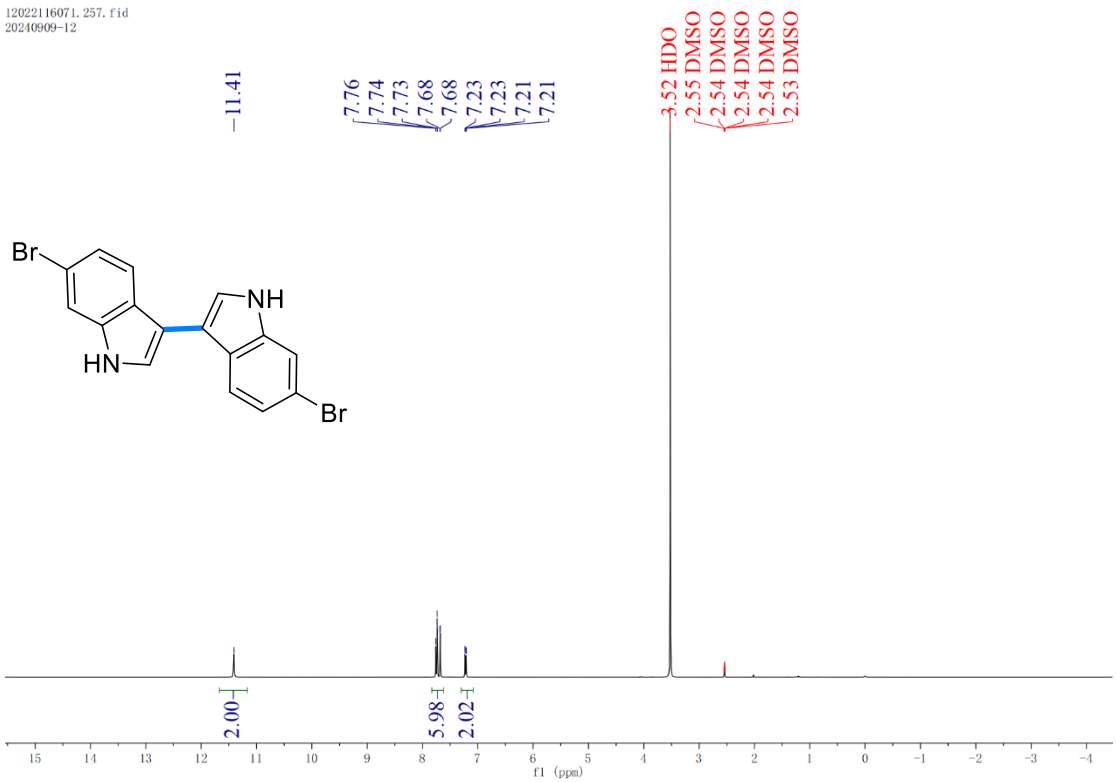
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 10c**



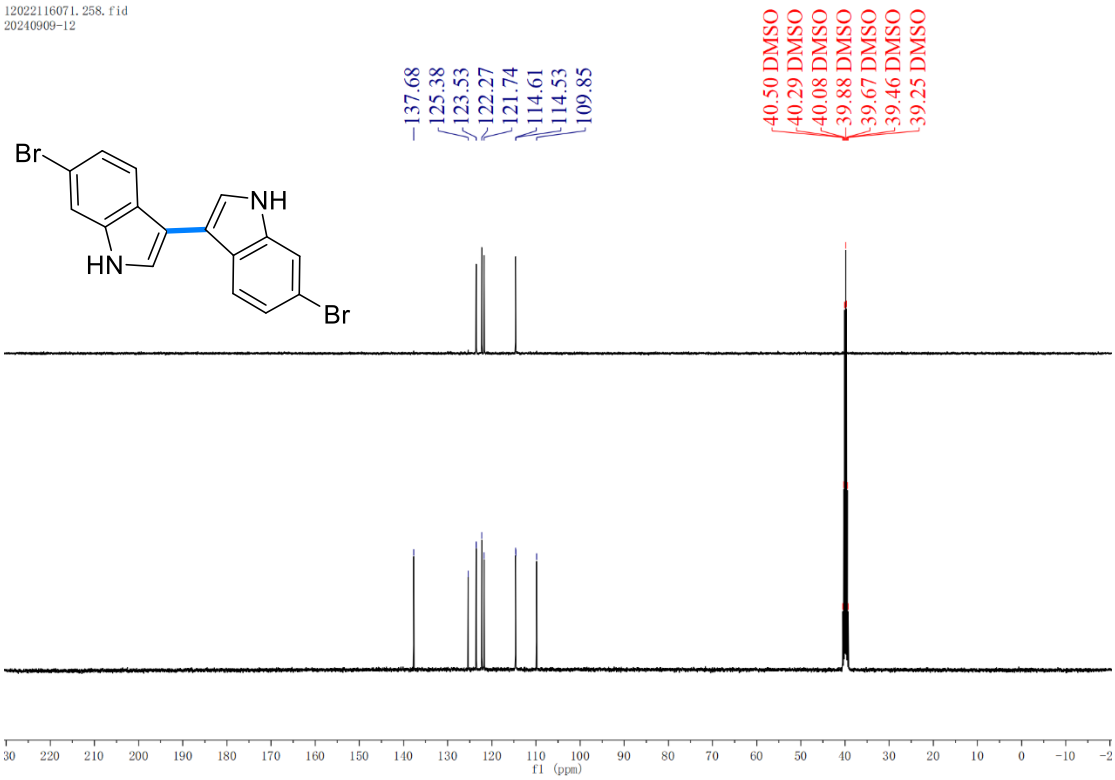
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 10d**



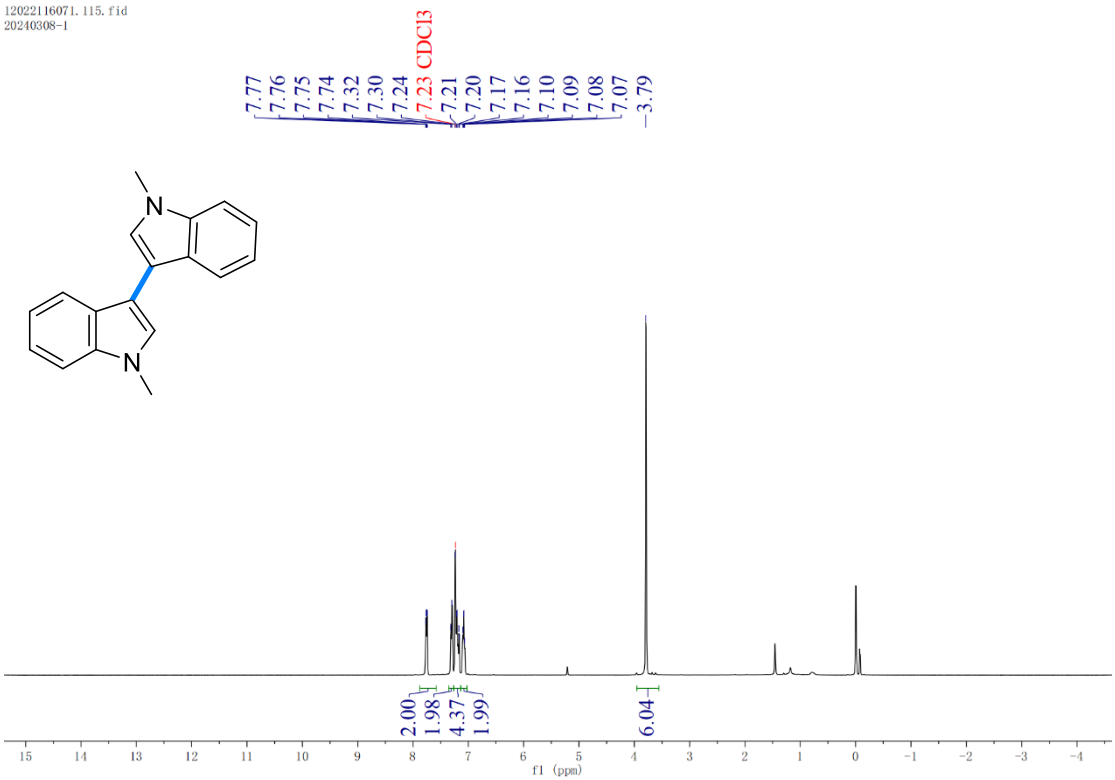
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 10d**



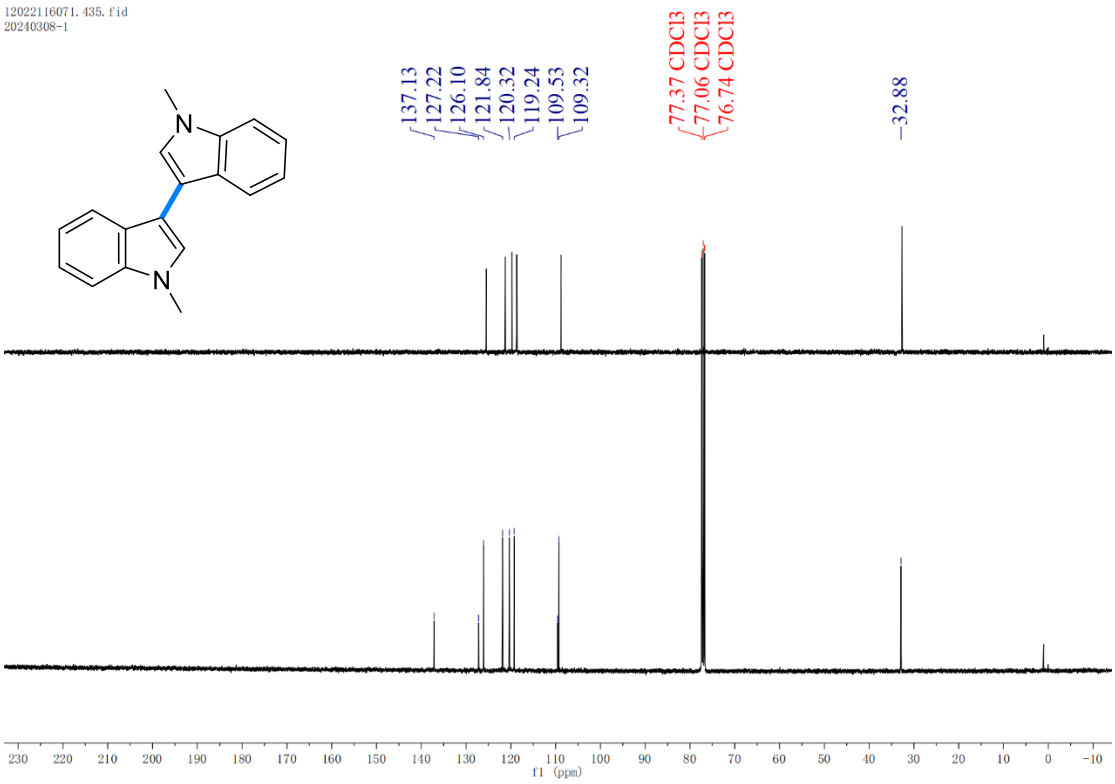
^{1}H-NMR (400 MHz, DMSO-d_6)) **Spectra of compound 10e**



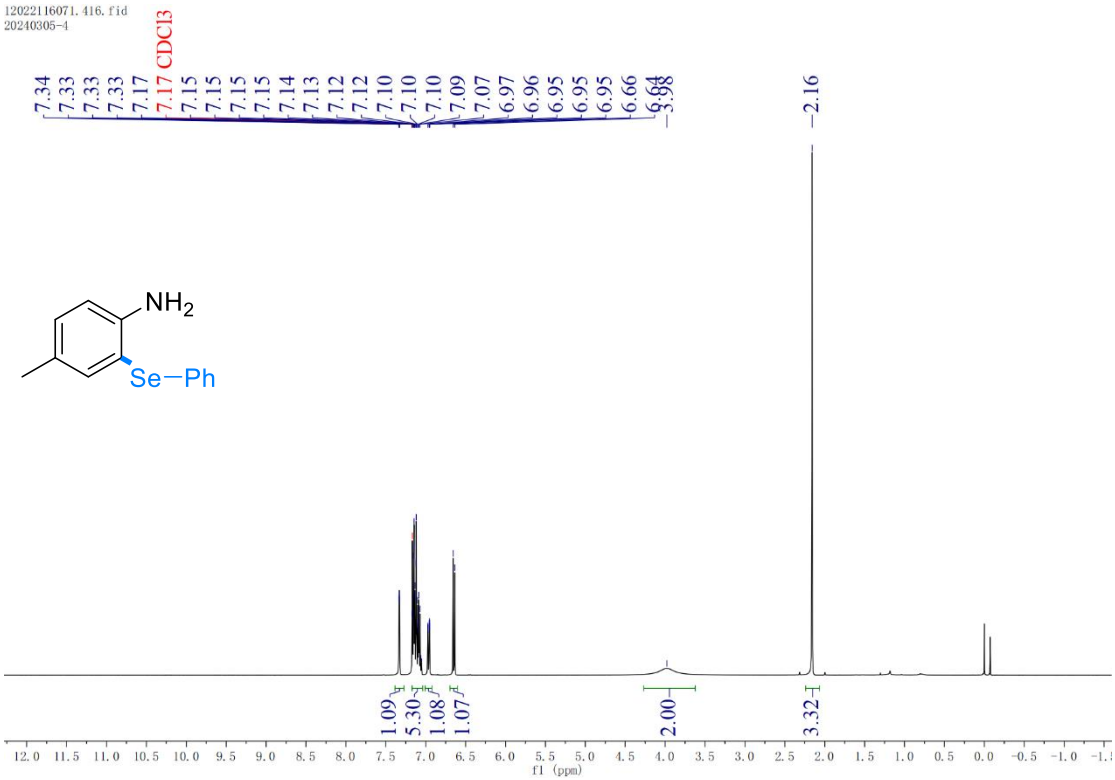
^{13}C-NMR (100 MHz, DMSO-d_6)) **Spectra of compound 10e**



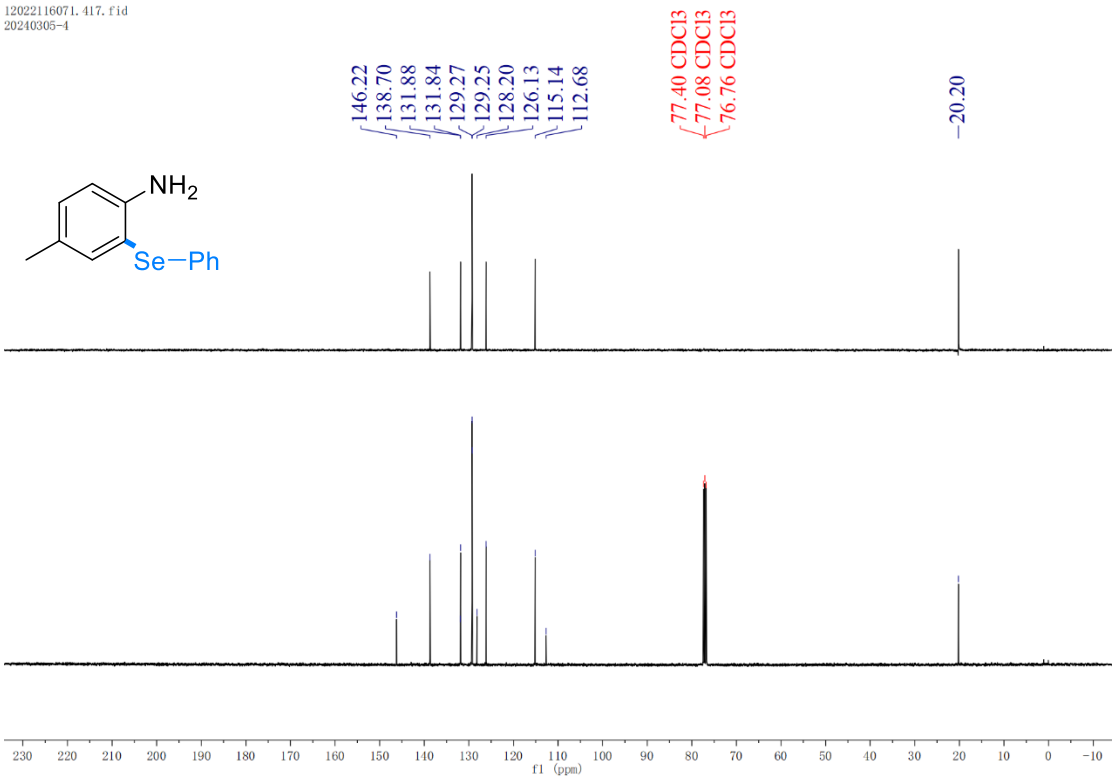
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 10f**



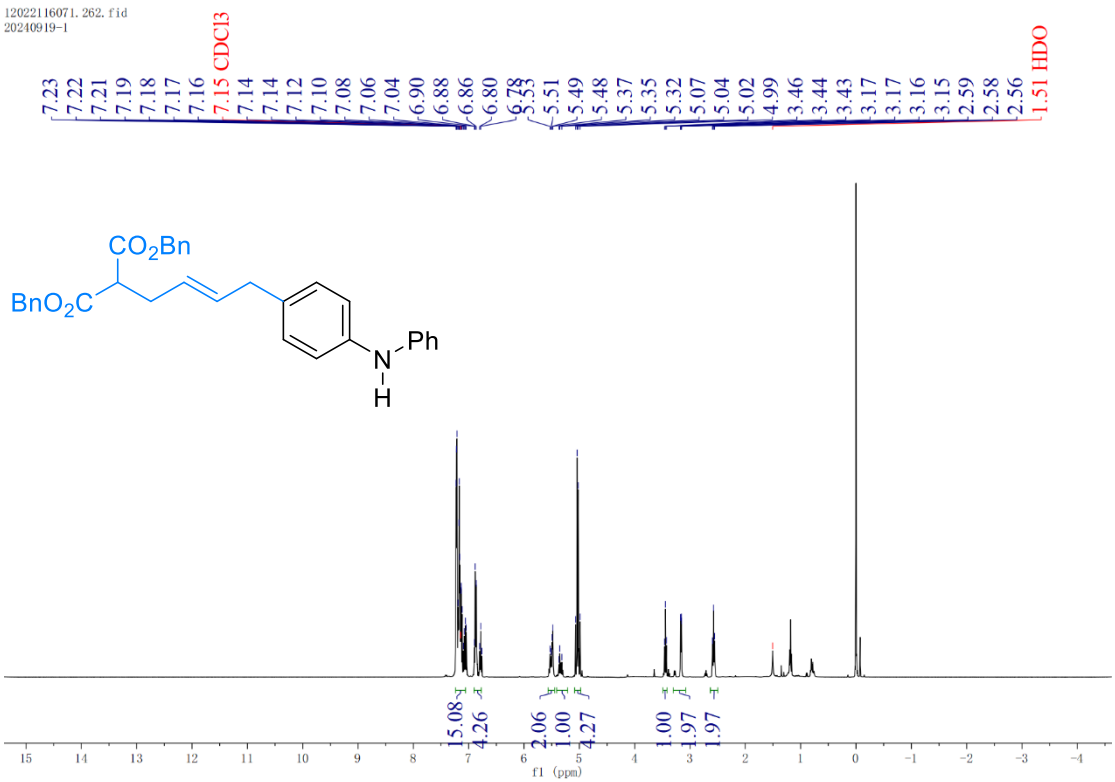
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 10f**



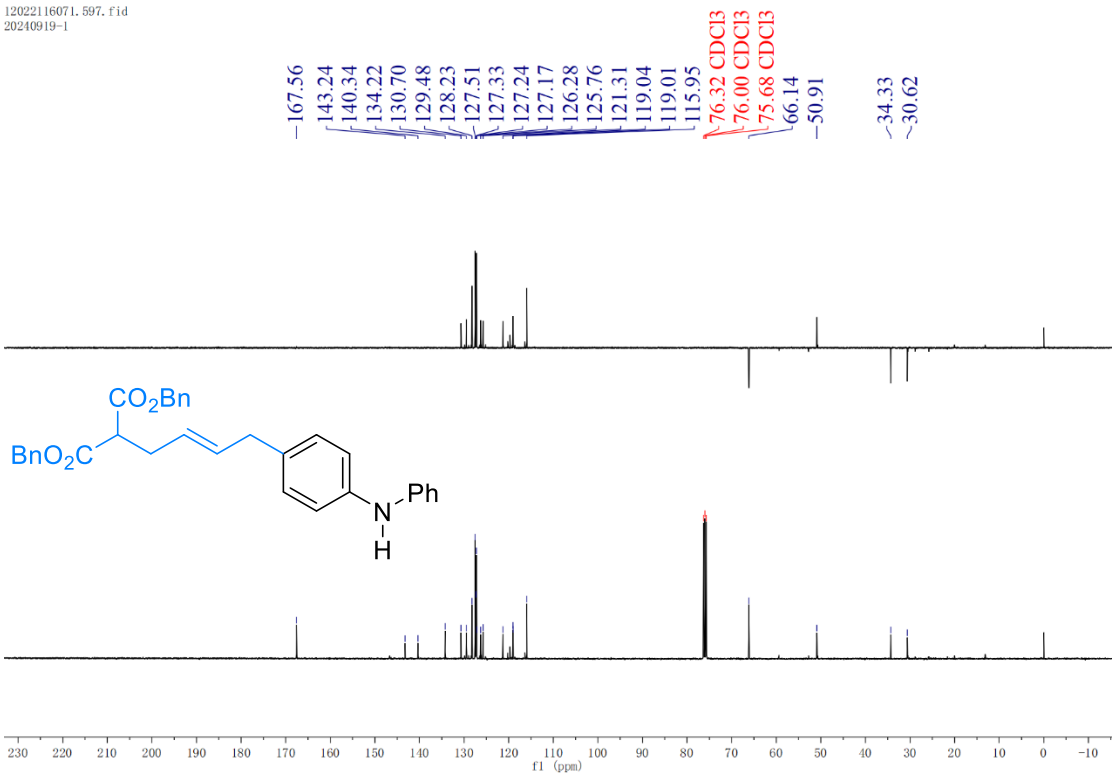
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 8m**



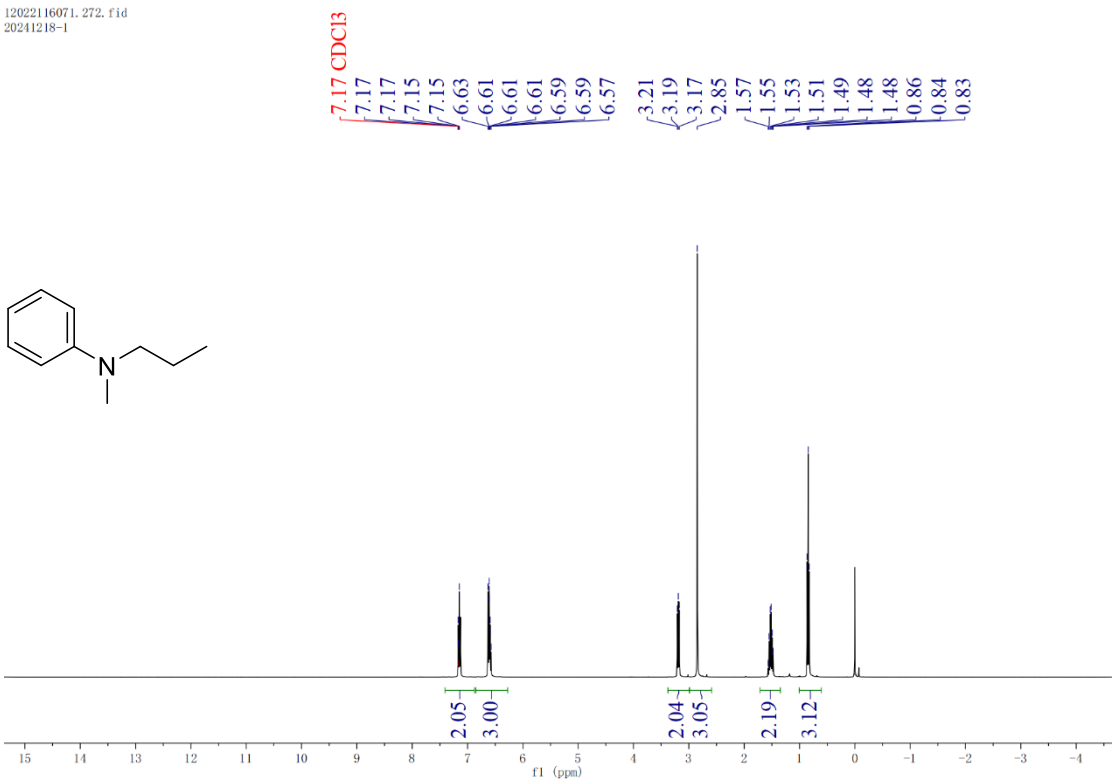
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 8m**



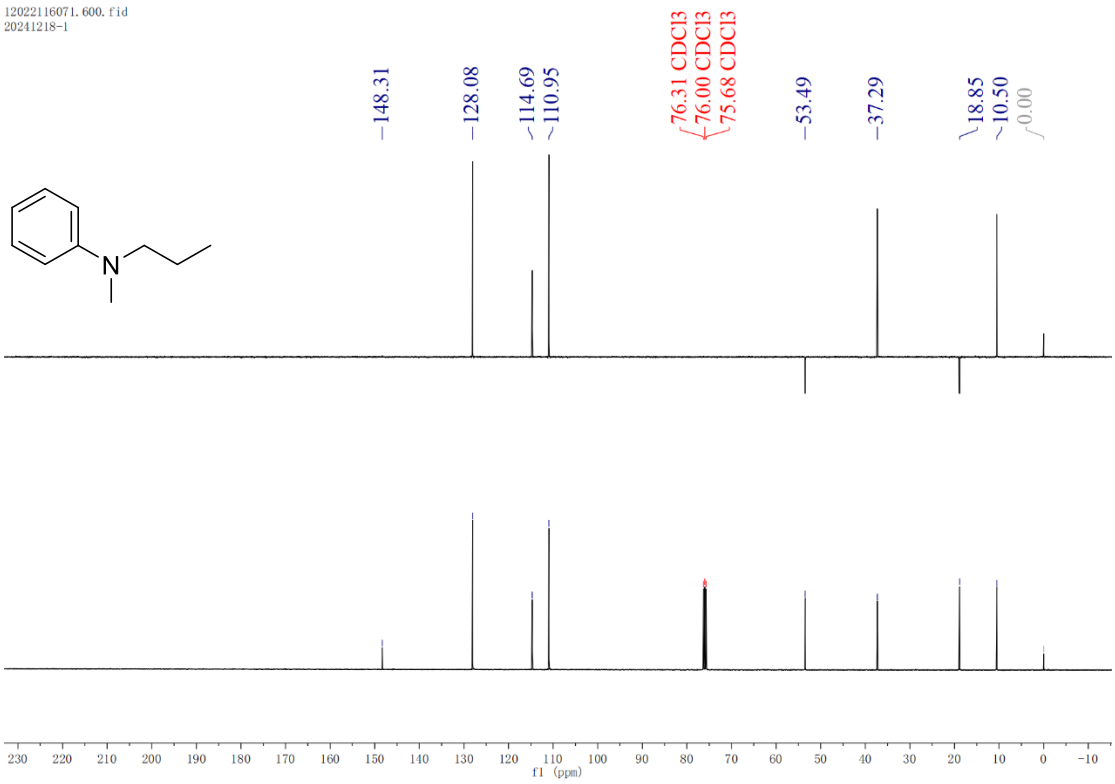
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 11**



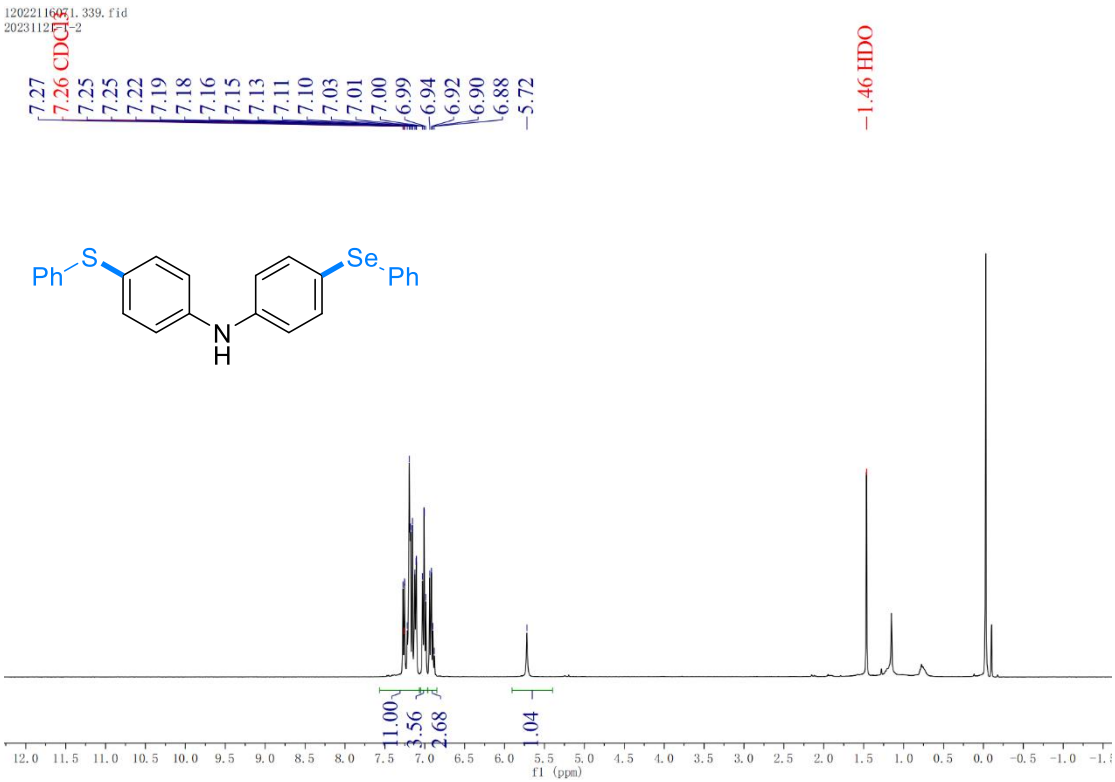
^{13}C-NMR ($CDCl_3$, 100 MHz) **Spectra of compound 11**



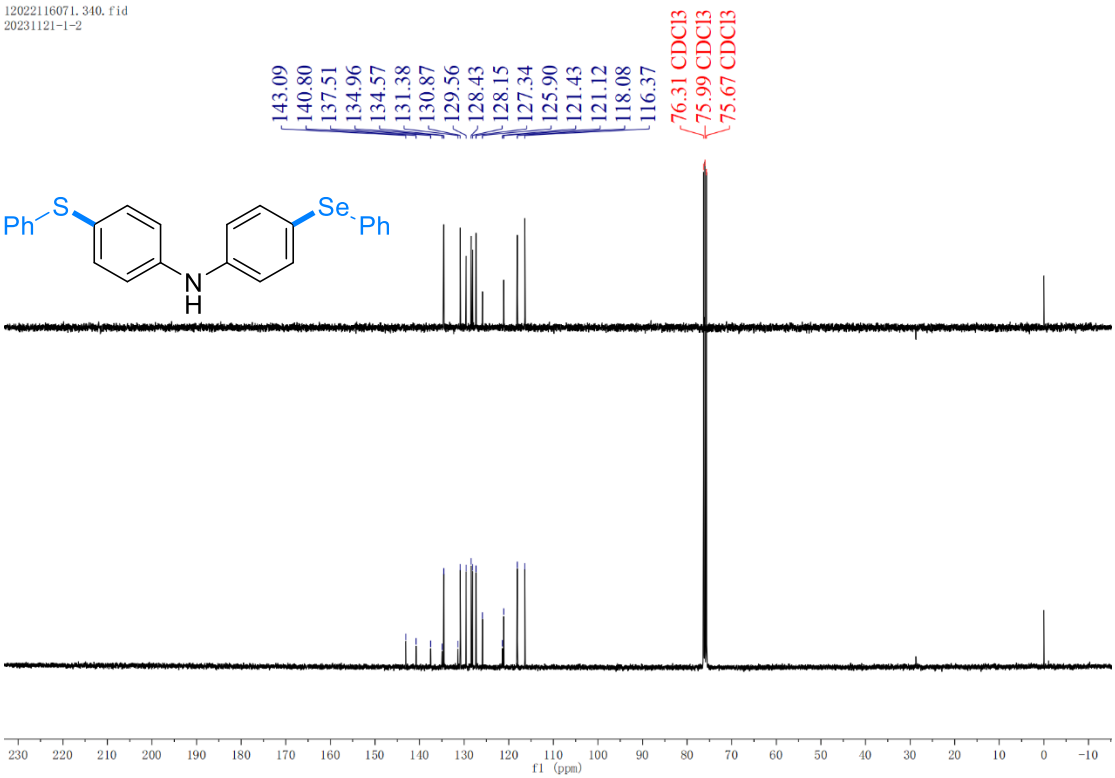
^{1}H-NMR ($CDCl_3$, 400 MHz) **Spectra of compound 13**



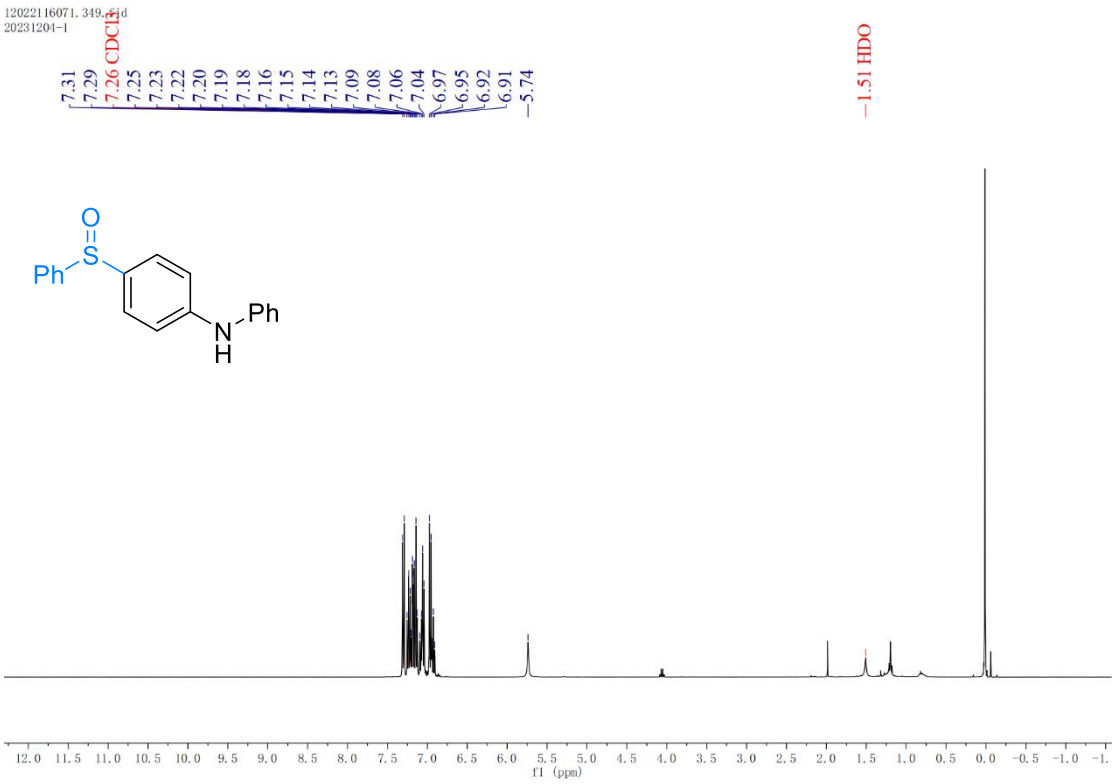
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 13**



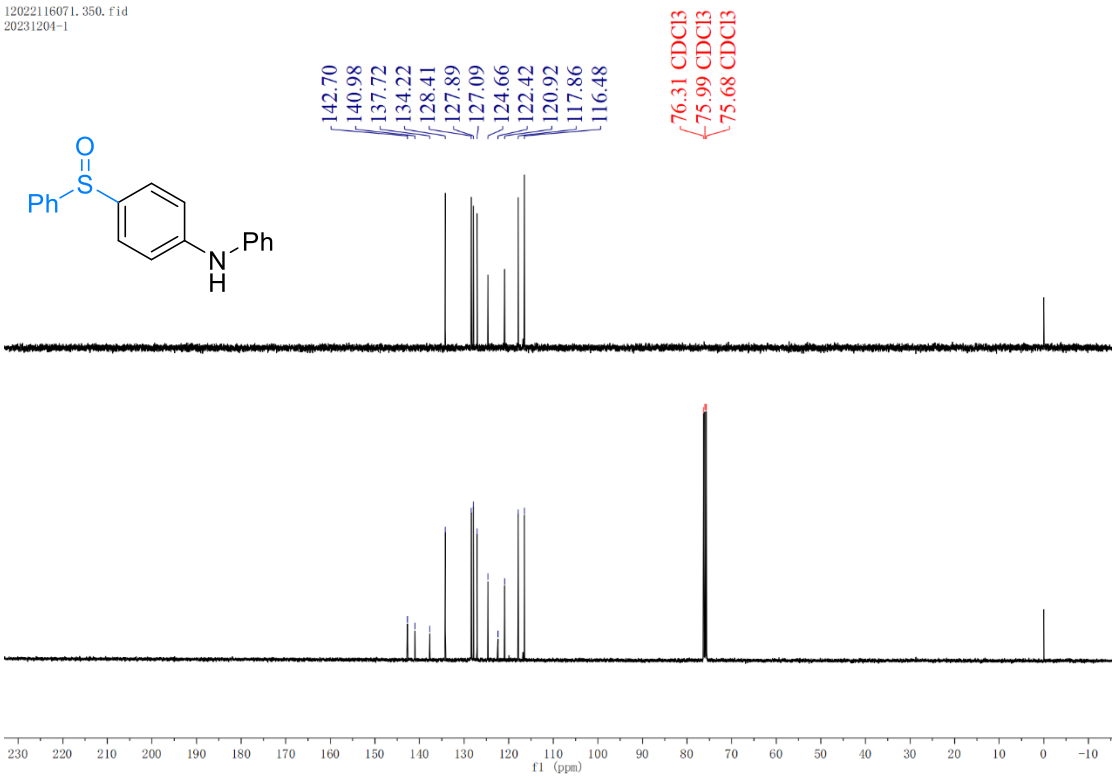
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 14**



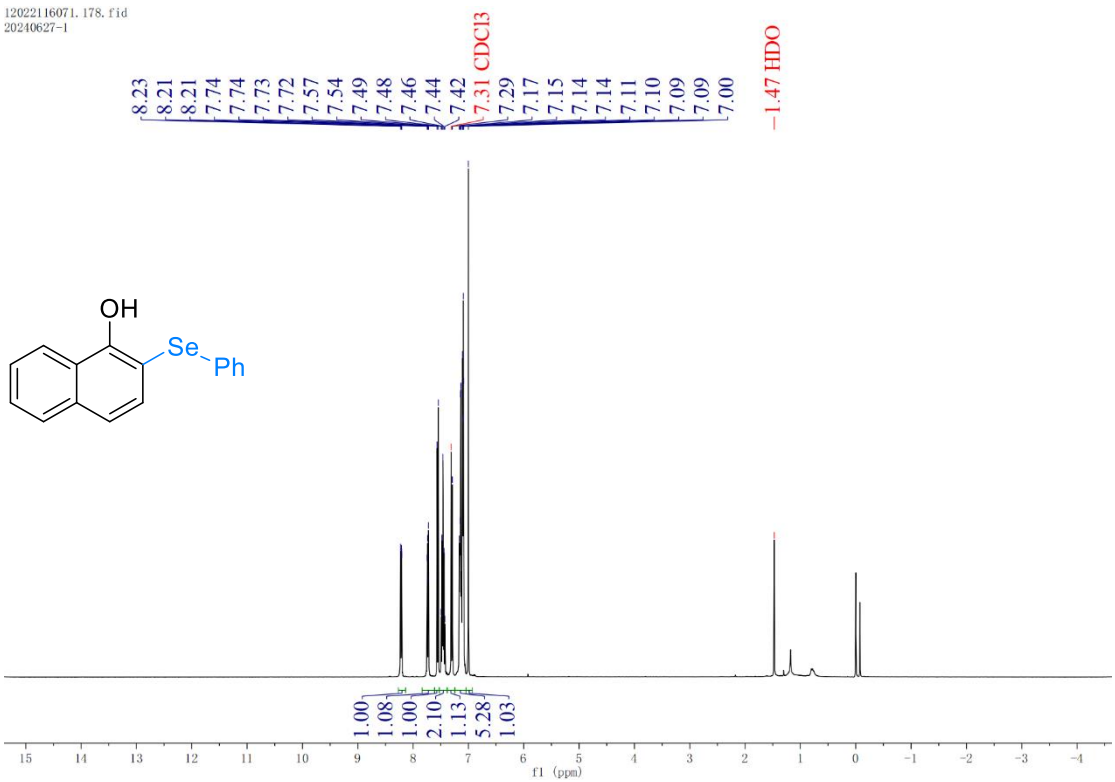
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 14**



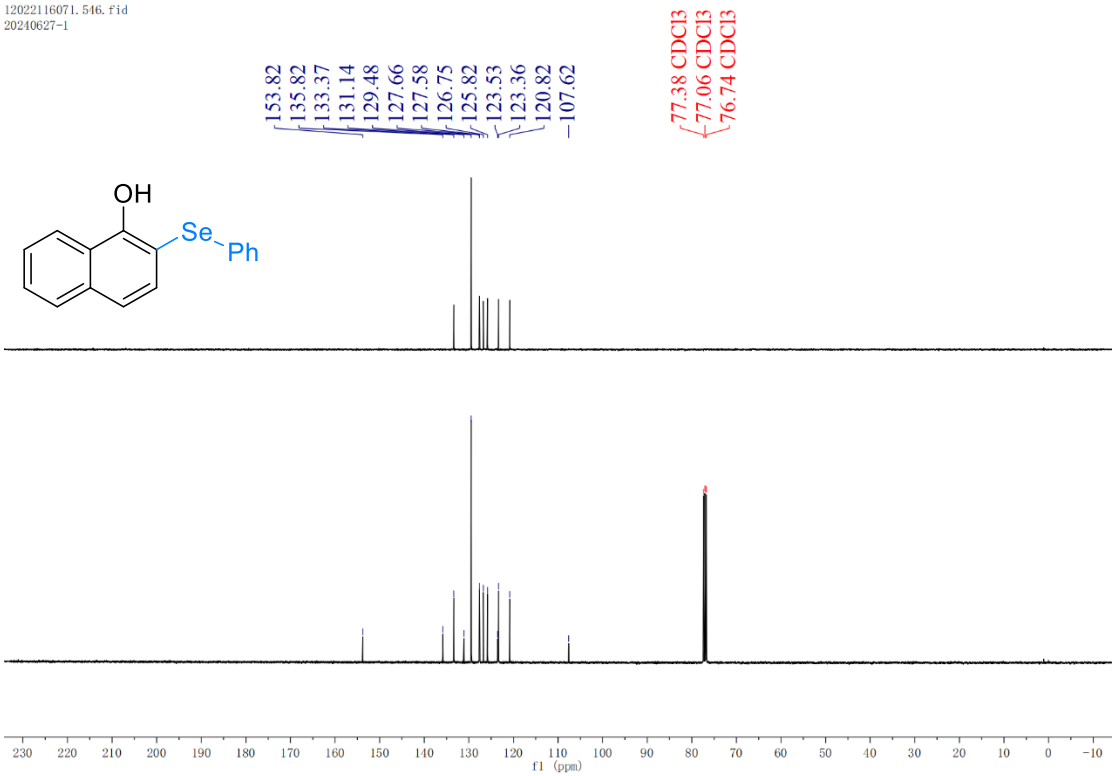
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 15**



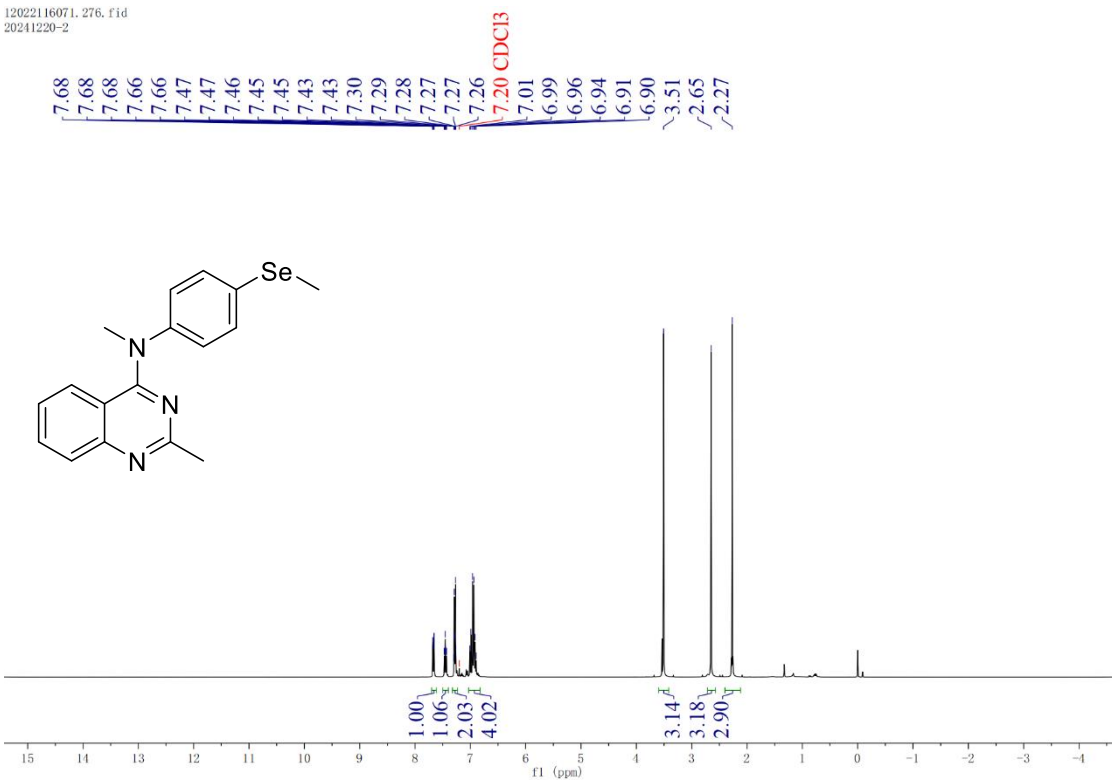
^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 15**



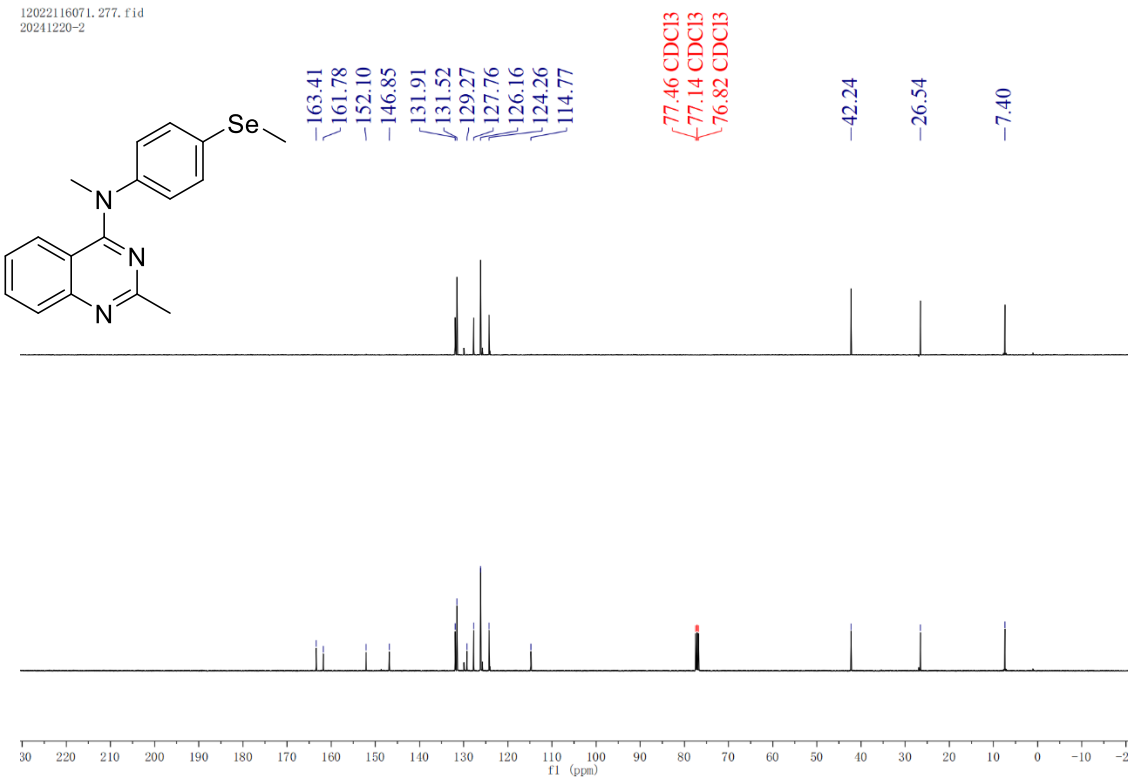
^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 17**



^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 17**



^{1}H-NMR (400 MHz, $CDCl_3$) **Spectra of compound 19**



^{13}C-NMR (100 MHz, $CDCl_3$) **Spectra of compound 19**

8. References

1) Wang S , Yao L , Ying J ,et al. Palladium-catalyzed carbonylation of iminoquinones and aryl iodides to access aryl p-amino benzoates[J]. *Org. Biomol. Chem*., **2021**, 19, 8246–8249.

2) Kumar P P, Reddy Y D, Reddy C V R, et al. Indium chloride: a versatile Lewis acid catalyst for the synthesis of 3-sulfenylindoles. *Sulfur Reports*. **2014**, *35*, 356-361.

3) José A. Fernández-Salas, Alexander P. Pulis, David J. Procter. Metal-free C–H thioarylation of arenes using sulfoxides: A direct, general diaryl sulfide synthesis. *Chem Commun*. **2016**, *52*, 12364—12367.

4) Zhang Q, Ban Y, Yuan P, et al. Visible-light-mediated aerobic selenation of (hetero)arenes with diselenides. *Green Chem.* **2017**, *19*, 5559–5563.

5) Zhou Z, He X, et al. A simple method for the preparation of arylselanyl anilines, Synthetic Communications. *Synthetic Communications*. **2018**, *19*, 2553-2558,

6) Rafique J, Saba S, Franco M S, et al. Direct, Metal-free C(sp2)−H Chalcogenation of Indoles and Imidazopyridines with Dichalcogenides Catalysed by KIO3 . *Chemistry A European Journal*, **2018**, *24*, 4173 – 4180.

7) Zhengfen L, Yonggang J, Chunxiang L, et al. Metal-Free Synthesis of Phenol-Aryl Selenides via Dehydrogenative C−Se Coupling of Aryl Selenoxides with Phenols. J. Org. Chem. **2020**, 85, 7386−7398

8) An Baijiao, Wang Bo, Hu Jinhui, et al. Synthesis and Biological Evaluation of Selenium-Containing 4-Anilinoquinazoline Derivatives as Novel Antimitotic Agents. *J. Med. Chem*, **2018**, 61, 2571−2588.