

Electronic Supporting Information

FeCl₃-Catalyzed Oxidative Diselenylation of Pyrrole-tethered Indoles

Jing Zhou, Xue Sheng, Man Jiang, and Hai-Lei Cui*

Laboratory of Asymmetric Synthesis, College of Chemistry and Environmental Engineering,
Chongqing University of Arts and Sciences, 319 Honghe Ave., Yongchuan, Chongqing, 402160, P.R.
China; Email: cuihailei616@163.com;

Table of Contents

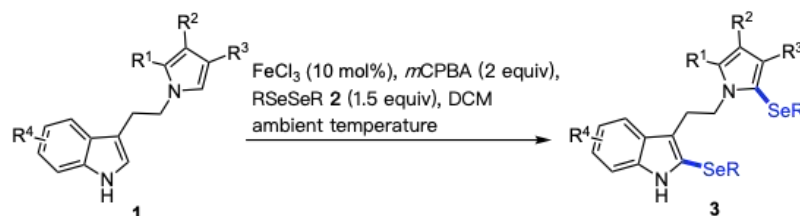
| | |
|--|-----|
| 1. General Methods | S2 |
| 2. General Procedure for the Synthesis of Compound 3 and 5 | S2 |
| 3. NMR Spectra | S12 |
| 4. Crystal Data of Compound 3g | S35 |
| 5. Crystal Data of Compound 3a' | S36 |

1. General methods

^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz NMR spectrometer. Chemical shifts are reported in ppm downfield from CDCl_3 ($\delta = 7.26$ ppm) for ^1H NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$ ppm) for ^{13}C NMR spectroscopy. Coupling constants are given in Hz. ESI-MS analysis was performed using a LTQ Orbitrap mass spectrometer. Compounds **3g** and **3a'** were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero, equipped with an AtlasS2 CCD using Cu $K\alpha$ radiation. The data was collected and processed using CrysAlisPro.

All reagents and solvents were obtained from commercial sources and used without further purification. Compounds **1** and **4a** were prepared following reported procedures.^{1,2} FeCl_3 (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd.. *m*CPBA (85%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All compounds **1** and **4** were known compounds.

2. General procedure for the synthesis of compounds **3** (compounds **5**)



A mixture of FeCl_3 (0.01 mmol, 0.1 equiv, 1.7 mg), pyrrole-tethered indole **1** (or 3-substituted indole **4**, 0.1 mmol, 1 equiv), diselenide **2** (0.15 mmol, 1.5 equiv) and *m*CPBA (0.2 mmol, 2 equiv, 34.5 mg) in DCM (1mL) was stirred at ambient temperature for the indicated times shown in Scheme 3 and Scheme 4 under air atmosphere. Upon the complete consumption of substrate **1** or **4** (monitored by TLC), the reaction mixture was diluted with DCM (2 mL), washed with *sat aq* K_2CO_3 solution (2 mL x2), and dried over Na_2SO_4 . The organic phase was concentrated and the residue was purified directly by the silica gel flash chromatography (Hexane/EtOAc) to afford compound **3** or **5**.

For the synthesis of compound **5**, 1 equiv of diselenide **2** and 1 equiv of *m*CPBA were used.

methyl

2-methyl-4-phenyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrole-3-carbo

xylate (3a). Yellow solid, 43.7 mg, 65%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.56 – 7.50 (m, 1H), 7.35 – 7.20 (m, 8H), 7.20 – 7.04 (m, 10H), 4.24 – 4.14 (m, 2H), 3.58 (s, 3H), 3.26 – 3.14 (m, 2H), 2.51 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 165.7, 139.2, 137.6, 136.2, 135.6, 134.1, 132.0, 130.3, 129.4, 129.23, 129.20, 128.0, 127.5, 127.1, 126.60, 126.56, 125.9, 123.4, 120.0, 119.6, 119.3, 119.0, 113.8, 112.5, 111.0, 50.6, 46.5, 27.6, 12.3. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₅H₃₀N₂NaO₂Se₂⁺ 693.0530; Found 693.0538.

1 mmol scale synthesis of compound 3a: A mixture of FeCl₃ (0.1 mmol, 0.1 equiv, 17 mg), pyrrole-tethered indole **1a** (1 mmol, 1 equiv, 358.0 mg), diselenide **2a** (1.5 mmol, 1.5 equiv, 468 mg) and *m*CPBA (2 mmol, 2 equiv, 345 mg) in DCM (10 mL) was stirred at ambient temperature for 15.9 h. Upon the complete consumption of substrate **1a** (monitored by TLC), the reaction mixture was diluted with DCM (10 mL), washed with *sat aq* K₂CO₃ solution (20 mL x2), and dried over Na₂SO₄. The organic phase was concentrated and the residue was purified directly by the silica gel flash chromatography (Hexane/EtOAc) to afford compound **3a** as a white solid (370.4 mg, 55% yield).

Synthesis of compound 3a': Compound **3a'** was prepared following the general procedure in the absence of FeCl₃ (ambient temperature for 34 hours).

methyl 2-methyl-4-phenyl-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrole-3-carboxylate methyl (3a'). Yellow solid, 15.4 mg, 30%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.23 (m, 5H), 7.23 – 7.04 (m, 7H), 6.87 (d, *J* = 2.3 Hz, 1H), 4.35 – 4.22 (m, 2H), 3.59 (s, 3H), 3.08 – 2.95 (m, 2H), 2.58 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 165.8, 139.1, 136.2, 136.1, 135.6, 134.0, 130.3, 129.3, 128.2, 127.2, 127.1, 126.6, 126.1, 122.2, 122.1, 119.6, 118.6, 114.0, 112.1, 111.2, 50.6, 46.9, 27.0, 12.5. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₉H₂₇N₂O₂Se₂⁺ 515.1232; Found 515.1240.

4-(4-chlorophenyl)-2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrole-3-carboxylate (3b). Yellow solid, 21.3 mg, 61% (performed at 0.05 mmol scale); Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H),

7.52 (d, $J = 7.9$ Hz, 1H), 7.33 (d, $J = 8.2$ Hz, 1H), 7.26 – 7.20 (m, 4H), 7.19 – 7.08 (m, 10H), 7.06 – 6.99 (m, 2H), 4.23 – 4.16 (m, 2H), 3.60 (s, 3H), 3.23 – 3.14 (m, 2H), 2.50 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 165.5, 139.4, 137.6, 134.7, 134.3, 133.9, 132.5, 131.9, 131.6, 129.5, 129.32, 129.25, 127.9, 127.5, 127.3, 126.7, 126.1, 123.4, 120.1, 119.5, 119.3, 119.0, 114.1, 112.4, 111.0, 50.7, 46.5, 27.6, 12.4. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{29}\text{ClN}_2\text{NaO}_2\text{Se}_2^+$ 727.0140; Found 727.0147.

1-(2-methyl-4-phenyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)ethan-1-one (3c). Yellow solid, 34.8 mg, 53%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.54 – 7.49 (m, 1H), 7.34 – 7.29 (m, 4H), 7.26 – 7.20 (m, 4H), 7.19 – 7.01 (m, 10H), 4.25 – 4.13 (m, 2H), 3.25 – 3.16 (m, 2H), 2.47 (s, 3H), 1.87 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 197.2, 138.3, 137.6, 136.7, 135.2, 133.9, 132.0, 130.4, 129.4, 129.2, 128.0, 127.9, 127.5, 127.2, 126.6, 126.0, 123.4, 123.2, 120.0, 119.6, 119.3, 119.0, 113.7, 111.0, 46.2, 31.0, 27.5, 12.4. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{30}\text{N}_2\text{NaOSe}_2^+$ 677.0581; Found 677.0590.

1-(4-(4-methoxyphenyl)-2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)ethan-1-one (3d). Yellow solid, 35.5 mg, 52%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.01 (m, 13H), 6.89 – 6.82 (m, 2H), 4.23 – 4.14 (m, 2H), 3.81 (s, 3H), 3.23 – 3.15 (m, 2H), 2.46 (s, 3H), 1.90 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 197.3, 158.8, 138.2, 137.6, 134.9, 134.0, 132.0, 131.4, 129.4, 129.2, 128.8, 127.9, 127.5, 126.6, 125.9, 123.4, 123.3, 120.0, 119.6, 119.3, 119.0, 113.8, 113.4, 111.0, 55.1, 46.2, 31.0, 27.6, 12.4. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{NaO}_2\text{Se}_2^+$ 707.0686; Found 707.0695.

1-(2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-4-(p-tolyl)-1H-pyrrol-3-yl)ethan-1-one (3e). Yellow solid, 27.9 mg, 42%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.22 (ddd, $J = 8.2, 7.0, 1.2$ Hz, 1H), 7.19 – 7.03 (m, 15H), 4.25 – 4.13 (m, 2H), 3.26 – 3.15 (m, 2H), 2.46 (s, 3H), 2.35 (s, 3H), 1.89 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*)

δ 197.2, 138.3, 137.6, 136.9, 135.3, 134.0, 133.6, 132.0, 130.2, 129.5, 129.3, 129.2, 128.7, 128.0, 127.5, 126.6, 125.9, 123.4, 123.3, 120.0, 119.6, 119.3, 119.0, 113.6, 111.0, 46.2, 31.0, 27.6, 21.3, 12.4. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{36}H_{32}N_2NaOSe_2^+$ 691.0737; Found 691.0734.

1-(2-methyl-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-4-(p-tolyl)-1H-pyrrol-3-yl)ethan-1-one (3e'). Performed with 7 mol% of $FeCl_3$, 1.1 equiv of diselenide **2a** and 1.5 equiv of *m*CPBA in DCM (0.14 M); White solid, 20.4 mg, 29%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 93/7); 1H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.00 (m, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.24 – 7.01 (m, 11H), 6.89 (d, $J = 2.1$ Hz, 1H), 4.33 – 4.24 (m, 2H), 3.06 – 2.94 (m, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 1.92 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 197.3, 138.1, 136.9, 136.1, 135.3, 133.9, 133.6, 130.3, 129.2, 128.7, 128.2, 127.2, 126.1, 123.2, 122.2, 122.1, 119.5, 118.6, 113.8, 112.1, 111.2, 46.7, 31.0, 26.9, 21.3, 12.7. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{30}H_{28}N_2NaOSe^+$ 535.1259; Found 535.1328.

1-(4-(4-chlorophenyl)-2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)ethan-1-one (3f). Yellow solid, 35.6 mg, 52%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); 1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.36 – 7.27 (m, 3H), 7.23 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 7.19 – 7.07 (m, 11H), 7.02 – 6.97 (m, 2H), 4.24 – 4.14 (m, 2H), 3.24 – 3.14 (m, 2H), 2.46 (s, 3H), 1.89 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 196.7, 138.5, 137.6, 135.1, 133.7, 133.2, 131.7, 129.5, 129.3, 129.2, 128.1, 127.9, 127.5, 126.6, 126.1, 123.4, 123.2, 120.0, 119.4, 119.3, 118.9, 114.0, 111.0, 46.3, 31.1, 27.5, 12.4. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{35}H_{29}ClN_2NaOSe_2^+$ 711.0191; Found 711.0193.

1-(4-(3-chlorophenyl)-2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)ethan-1-one (3g). Pale yellow solid, 33.2 mg, 48%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); 1H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.53 – 7.47 (m, 1H), 7.33 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.31 – 7.20 (m, 3H), 7.19 – 7.05 (m, 11H), 7.03 – 6.97 (m, 2H), 4.26 – 4.16 (m, 2H), 3.24 – 3.14 (m, 2H), 2.46 (s, 3H), 1.90 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 196.6, 138.5, 138.4, 137.6, 133.6, 133.5, 131.9, 130.5, 129.5, 129.3, 129.2, 129.1,

128.6, 128.2, 127.5, 127.3, 126.6, 126.2, 123.4, 120.0, 119.4, 119.4, 118.9, 114.3, 111.0, 46.3, 31.1, 27.5, 12.4. HRMS (ESI) m/z: [M + Na]⁺ C₃₅H₂₉ClN₂NaOSe₂⁺ 711.0191; Found 711.0197.

1-(2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-4-(thiophen-2-yl)-1H-pyrrolo-3-yl)ethan-1-one (3h). Yellow solid, 26.7 mg, 41%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.05 (m, 14H), 7.01 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.87 (dd, *J* = 3.4, 1.2 Hz, 1H), 4.25 – 4.13 (m, 2H), 3.23 – 3.13 (m, 2H), 2.45 (s, 3H), 2.02 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 196.9, 138.5, 137.5, 137.1, 133.6, 132.0, 129.5, 129.3, 129.2, 128.4, 128.3, 127.5, 126.8, 126.7, 126.6, 126.2, 126.1, 124.0, 123.4, 120.0, 119.5, 119.3, 118.9, 116.1, 111.0, 46.4, 30.3, 27.5, 12.4. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₃H₂₈N₂NaOSSe₂⁺ 683.0145; Found 683.0154.

1-(4-cyclohexyl-2-methyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrolo-3-yl)ethan-1-one (3i). Yellow solid, 11.1 mg, 17%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.05 (m, 12H), 4.11 – 3.99 (m, 2H), 3.16 – 3.06 (m, 3H), 2.45 (s, 3H), 2.26 (s, 3H), 2.09 – 1.92 (m, 2H), 1.75 – 1.72 (m, 2H), 1.67 – 1.63 (m, 3H), 1.27 – 1.26 (m, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 197.9, 138.1, 137.5, 135.9, 134.7, 132.0, 129.5, 129.3, 129.2, 127.6, 127.5, 126.6, 125.8, 123.4, 120.0, 119.13, 119.08, 111.3, 110.9, 46.0, 38.2, 32.4, 32.1, 27.7, 27.4, 26.0, 12.9. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₃₅H₃₆N₂NaOSSe₂⁺ 683.1050; Found 683.1057.

(2-butyl-4-phenyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrolo-3-yl)(phenyl)methanone (3j). Yellow solid, 34.7 mg, 46%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.02 (m, 17H), 7.01 – 6.92 (m, 3H), 4.35 – 4.25 (m, 2H), 3.38 – 3.27 (m, 2H), 2.87 – 2.76 (m, 2H), 1.56 – 1.45 (m, 2H), 1.27 – 1.22 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 194.2, 142.9, 139.4, 137.6, 135.2, 135.1, 134.2, 131.8, 131.4, 130.5, 129.6, 129.5, 129.3, 129.1, 127.8, 127.6, 127.4, 127.2, 126.6, 126.2, 125.9, 123.4, 121.5, 120.0, 119.1, 119.0, 112.3, 111.0, 46.5, 32.8, 28.3, 25.8, 22.7, 13.8. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₄₃H₃₈N₂NaOSSe₂⁺ 781.1207; Found 781.1210.

(2-butyl-4-phenyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)(3,5-dimethoxyphenyl)methanone (3k). Pale yellow solid, 41.7 mg, 51%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 6.98 (m, 16H), 6.76 (d, *J* = 2.4 Hz, 2H), 6.34 (t, *J* = 2.3 Hz, 1H), 4.33 – 4.22 (m, 2H), 3.69 (s, 6H), 3.38 – 3.28 (m, 2H), 2.83 – 2.70 (m, 2H), 1.52 – 1.46 (m, 2H), 1.26 – 1.19 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 193.6, 159.8, 143.0, 141.4, 137.7, 135.2, 135.1, 134.3, 131.9, 130.2, 129.5, 129.3, 129.1, 127.7, 127.5, 127.3, 126.6, 126.3, 125.9, 123.4, 121.5, 120.0, 119.9, 119.1, 119.0, 112.4, 111.0, 107.4, 104.7, 55.4, 46.5, 32.8, 28.3, 25.8, 22.7, 13.8. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₄₅H₄₂N₂NaO₃Se₂⁺ 841.1418; Found 841.1427.

(4-(2-bromophenyl)-2-butyl-5-(phenylselanyl)-1-(2-(2-(phenylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrol-3-yl)(phenyl)methanone (3l). Yellow solid, 37.7 mg, 45%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.55 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 – 6.96 (m, 18H), 6.81 (td, *J* = 7.7, 1.8 Hz, 1H), 4.28 – 4.26 (m, 2H), 3.33 (ddd, *J* = 8.9, 6.8, 1.8 Hz, 2H), 2.93 – 2.74 (m, 2H), 1.54 – 1.50 (m, 2H), 1.29 – 1.23 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 193.7, 143.3, 139.6, 137.6, 136.6, 133.9, 133.4, 132.1, 131.8, 131.1, 129.5, 129.4, 129.23, 129.17, 129.1, 128.3, 128.1, 127.6, 127.2, 126.6, 126.2, 126.0, 125.3, 123.4, 120.1, 120.0, 119.13, 119.08, 114.1, 111.0, 46.6, 32.7, 28.3, 25.9, 22.7, 13.8. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₄₃H₃₇BrN₂NaOSe₂⁺ 859.0312; Found 859.0312.

1-(1-(2-(5-methoxy-2-(phenylselanyl)-1H-indol-3-yl)ethyl)-2-methyl-4-phenyl-5-(phenylselanyl)-1H-pyrrol-3-yl)ethan-1-one (3m). Yellow solid, 35.3 mg, 52%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.30 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.21 – 7.05 (m, 11H), 7.02 – 6.97 (m, 2H), 6.90 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.24 – 4.15 (m, 2H), 3.83 (s, 3H), 3.24 – 3.14 (m, 2H), 2.47 (s, 3H), 1.87 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 197.1, 154.3, 138.3, 136.6, 135.1, 133.9, 132.7, 130.4, 129.4, 129.29, 129.25, 129.1, 127.88, 127.85, 127.2, 126.6, 126.0, 123.3, 119.6, 119.2, 114.0, 113.7, 111.9, 100.3, 55.8, 46.1,

31.0, 27.6, 12.4. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{36}H_{32}N_2NaO_2Se_2^+$ 707.0686; Found 707.0687.

methyl

5-(benzylselanyl)-1-(2-(2-(benzylselanyl)-1H-indol-3-yl)ethyl)-2-methyl-4-phenyl-1H-pyrrole-3-carboxylate (3n). White solid, 49.1 mg, 70%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 9/1); 1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.59 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.39 – 7.25 (m, 6H), 7.24 – 7.22 (m, 1H), 7.20 – 7.17 (m, 3H), 7.15 – 7.06 (m, 4H), 7.03 – 6.97 (m, 2H), 6.87 – 6.82 (m, 2H), 3.88 (s, 2H), 3.86 – 3.80 (m, 2H), 3.56 (s, 3H), 3.53 (s, 2H), 2.94 – 2.85 (m, 2H), 2.46 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 165.9, 139.0, 138.5, 138.1, 137.3, 136.8, 134.2, 130.5, 128.59, 128.55, 128.5, 128.3, 127.4, 127.1, 127.0, 126.7, 126.4, 123.0, 120.3, 119.7, 119.3, 118.9, 115.6, 112.0, 110.7, 50.5, 45.8, 34.1, 33.3, 27.2, 12.4. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{37}H_{34}N_2NaO_2Se_2^+$ 721.0843; Found 721.0853.

(4-(2-bromophenyl)-2-butyl-5-(methylselanyl)-1-(2-(2-(methylselanyl)-1H-indol-3-yl)ethyl)-1H-pyrrole-3-yl)(phenyl)methanone (3o). Yellow solid, 34.4 mg, 48%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); 1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.70 – 7.64 (m, 1H), 7.54 – 7.48 (m, 2H), 7.36 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.29 – 7.03 (m, 8H), 6.88 (ddd, $J = 8.1, 7.2, 2.0$ Hz, 1H), 4.47 – 4.37 (m, 2H), 3.41 – 3.32 (m, 2H), 2.88 – 2.77 (m, 2H), 2.28 (s, 3H), 1.88 (s, 3H), 1.66 – 1.58 (m, 2H), 1.36 – 1.29 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 193.7, 141.9, 139.9, 137.3, 137.3, 133.4, 132.0, 131.7, 130.9, 129.5, 129.3, 127.9, 127.8, 127.1, 126.2, 125.3, 122.9, 121.6, 121.4, 120.0, 118.7, 118.0, 116.4, 110.8, 46.5, 32.7, 28.5, 26.0, 22.9, 13.8, 10.3, 9.9. HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{33}H_{33}BrN_2NaOSe_2^+$ 734.9999; Found 734.9995.

methyl

2-methyl-5-(methylselanyl)-1-(2-(2-(methylselanyl)-1H-indol-3-yl)ethyl)-4-phenyl-1H-pyrrole-3-carboxylate (3p). White solid, 33.8 mg, 62%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 17/3); 1H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.40 – 7.26 (m, 6H), 7.23 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 1H), 7.15 (td, $J = 7.5, 7.1, 1.1$ Hz, 1H), 4.42 – 4.33 (m, 2H), 3.55

(s, 3H), 3.31 – 3.21 (m, 2H), 2.60 (s, 3H), 2.23 (s, 3H), 1.91 (s, 3H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 165.8, 137.8, 137.3, 136.9, 133.4, 130.4, 127.6, 127.1, 126.4, 123.0, 121.5, 120.0, 118.6, 117.9, 116.5, 112.2, 110.8, 50.8, 46.5, 27.9, 12.3, 11.0, 9.8. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{NaO}_2\text{Se}_2^+$ 569.0217; Found 569.0226.

Synthesis of compound **4a**

To a stirring suspension of L-tryptophan methyl ester hydrochloride (10 mmol, 1 equiv, 2.54 g) and NaOH (20 mmol, 2 equiv, 0.8 g) in DCM (15 mL) and H₂O (4 mL) was added benzoyl chloride (10 mmol, 1 equiv, 1.16 mL) at ambient temperature. The resulting mixture was stirred at ambient temperature for 64 min. Then the organic phase was separated, dried over Na₂SO₄, and purified directly by the silica gel flash chromatography (Hexane/EtOAc = 1/1) to afford compound **4a** as a white foam solid (1.87 g, 58% yield).

methyl benzoyl-L-tryptophanate (4a). Known compound²; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.69 (dt, $J = 7.2, 1.3$ Hz, 2H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.51 – 7.45 (m, 1H), 7.42 – 7.30 (m, 3H), 7.22 – 7.15 (m, 1H), 7.12 – 7.05 (m, 1H), 7.00 (d, $J = 2.3$ Hz, 1H), 6.69 (d, $J = 7.7$ Hz, 1H), 5.16 (dt, $J = 7.7, 5.2$ Hz, 1H), 3.72 (s, 3H), 3.53 – 3.38 (m, 2H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 172.4, 166.9, 136.1, 133.9, 131.7, 128.5, 127.7, 127.1, 122.8, 122.3, 119.8, 118.7, 111.3, 110.1, 53.5, 52.4, 27.7.

methyl (S)-2-benzamido-3-(2-(phenylselanyl)-1H-indol-3-yl)propanoate (5a). White solid, 26.3 mg, 55%; $[\alpha]_D^{25} = -16.3$ (c 0.44, EtOH); Purified by a silica gel flash chromatography (Hexane/EtOAc = 4/1); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.71 – 7.60 (m, 3H), 7.49 – 7.41 (m, 1H), 7.40 – 7.28 (m, 3H), 7.24 – 7.07 (m, 7H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.12 (dt, $J = 7.6, 5.9$ Hz, 1H), 3.71 (s, 3H), 3.56 (dd, $J = 14.5, 5.6$ Hz, 1H), 3.49 (dd, $J = 14.5, 6.2$ Hz, 1H); ^{13}C {1H} NMR (100 MHz, Chloroform-*d*) δ 172.3, 167.0, 137.7, 133.6, 131.5, 131.2, 129.6, 129.5, 128.4, 127.8, 127.1, 126.8, 123.3, 120.1, 119.0, 117.4, 111.0, 53.5, 52.5, 28.3. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{NaO}_3\text{Se}^+$ 501.0688; Found 501.0695.

methyl (S)-2-benzamido-3-(2-(benzylselanyl)-1H-indol-3-yl)propanoate (5b). White solid, 41.3 mg, 84%; $[\alpha]_D^{25} = -66.1$ (c 0.38, EtOH); Purified by a silica gel flash chromatography (Hexane/EtOAc =

3/1); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.71 – 7.64 (m, 2H), 7.60 – 7.55 (m, 1H), 7.49 – 7.43 (m, 1H), 7.37 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.24 – 7.14 (m, 5H), 7.07 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.01 (dt, *J* = 7.6, 6.0 Hz, 1H), 3.91 – 3.90 (m, 2H), 3.70 (s, 3H), 3.30 (dd, *J* = 14.4, 5.8 Hz, 1H), 3.23 (dd, *J* = 14.4, 6.2 Hz, 1H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 172.4, 166.9, 138.7, 137.4, 133.8, 131.6, 128.7, 128.5, 128.4, 127.6, 127.1, 123.1, 120.8, 119.9, 118.9, 117.3, 110.7, 53.4, 52.5, 33.6, 28.0. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₆H₂₄N₂NaO₃Se₂⁺ 515.0844; Found 515.0853.

methyl (S)-2-benzamido-3-(2-(methylelanyl)-1H-indol-3-yl)propanoate (5c). White solid, 23.8 mg, 57%; [α]_D²⁵ = -26.4 (c 0.47, EtOH); Purified by a silica gel flash chromatography (Hexane/EtOAc = 3/1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.73 – 7.66 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.44 (m, 1H), 7.42 – 7.35 (m, 2H), 7.29 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.17 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.09 (dt, *J* = 7.6, 5.9 Hz, 1H), 3.72 (s, 3H), 3.56 – 3.43 (m, 2H), 2.20 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 172.4, 167.1, 137.4, 133.7, 131.6, 128.4, 127.8, 127.1, 122.9, 122.0, 120.0, 118.6, 115.5, 110.7, 53.5, 52.5, 28.2, 9.8. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₀N₂NaO₃Se⁺ 439.0531; Found 439.0540.

N-(2-(5-methoxy-2-(methylelanyl)-1H-indol-3-yl)ethyl)acetamide (5d). White solid, 18.8 mg, 58%; Purified by a silica gel flash chromatography (Hexane/EtOAc = 1/1); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.63 (s, 1H), 3.85 (s, 3H), 3.56 – 3.51 (m, 2H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.23 (s, 3H), 1.92 (s, 3H); ¹³C {1H} NMR (100 MHz, Chloroform-*d*) δ 170.1, 154.2, 132.5, 128.0, 121.6, 118.2, 113.2, 111.5, 100.1, 55.9, 40.3, 25.7, 23.4, 9.9. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₈N₂NaO₂Se⁺ 349.0426; Found 349.0423.

methyl-3-methyl-1-phenyl-6,6a,11,11a-tetrahydro-5H-indolizinof[8,7-b]indole-2-carboxylate (6).

Known compound.^{1a} Prepared with **1a** (0.1 mmol) and FeCl₃ (33.0 mg, 2 equiv, 0.2 mmol) in DCM/TFE (1 mL, 1:1) at ambient temperature. White solid, 20.3 mg, 57%; Purified by a silica gel

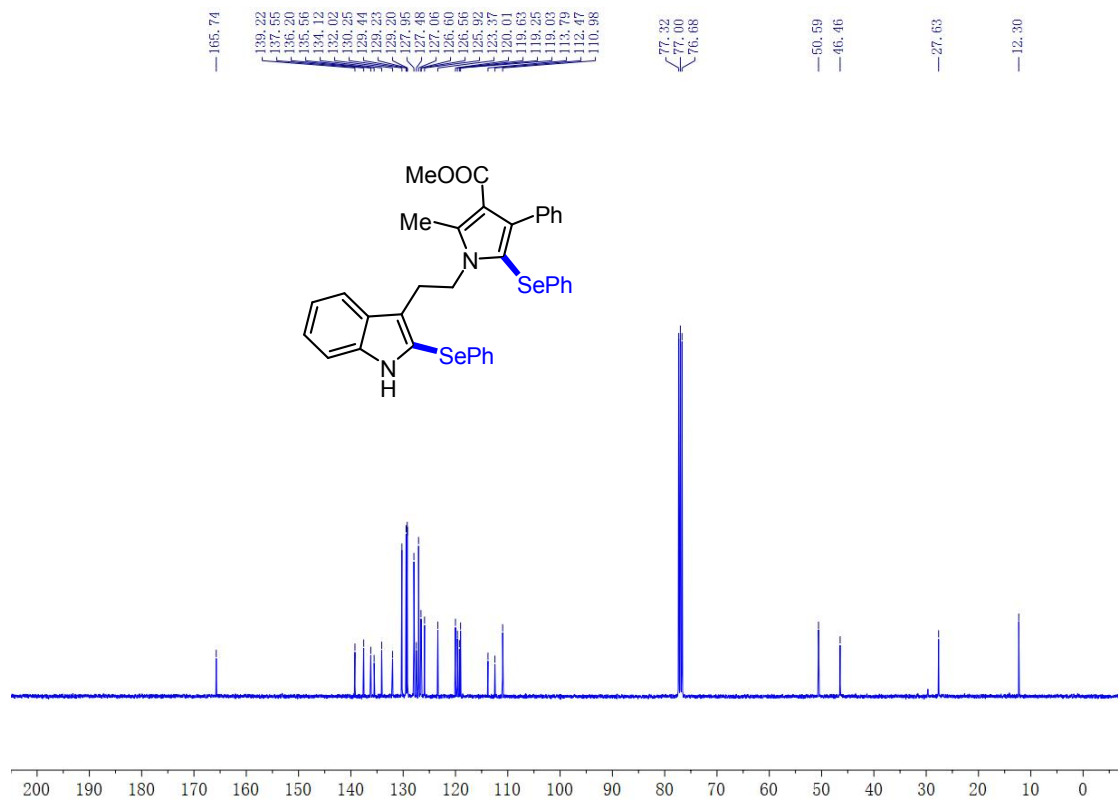
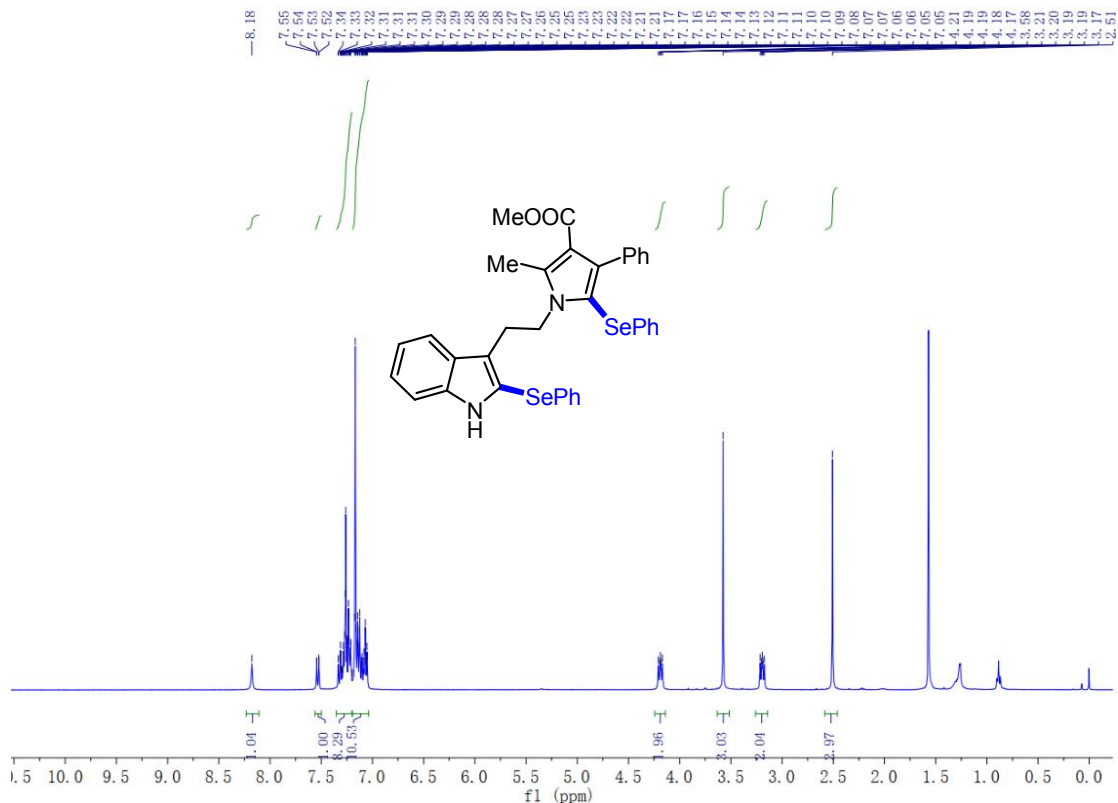
flash chromatography (Hexane/EtOAc = 19/1); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 8.5 Hz, 1H), 3.90 – 3.80 (m, 2H), 3.70 (s, 1H), 3.57 – 3.50 (m, 4H), 2.52 (s, 3H), 2.33 – 2.10 (m, 2H).

Reference:

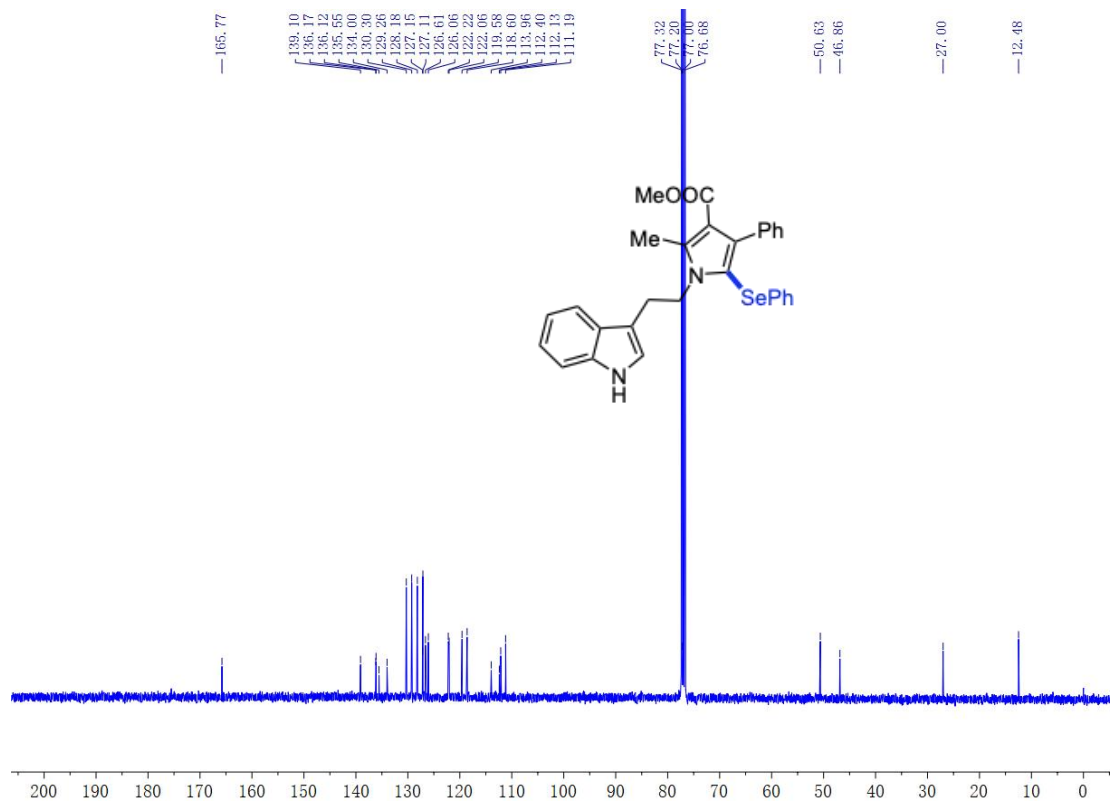
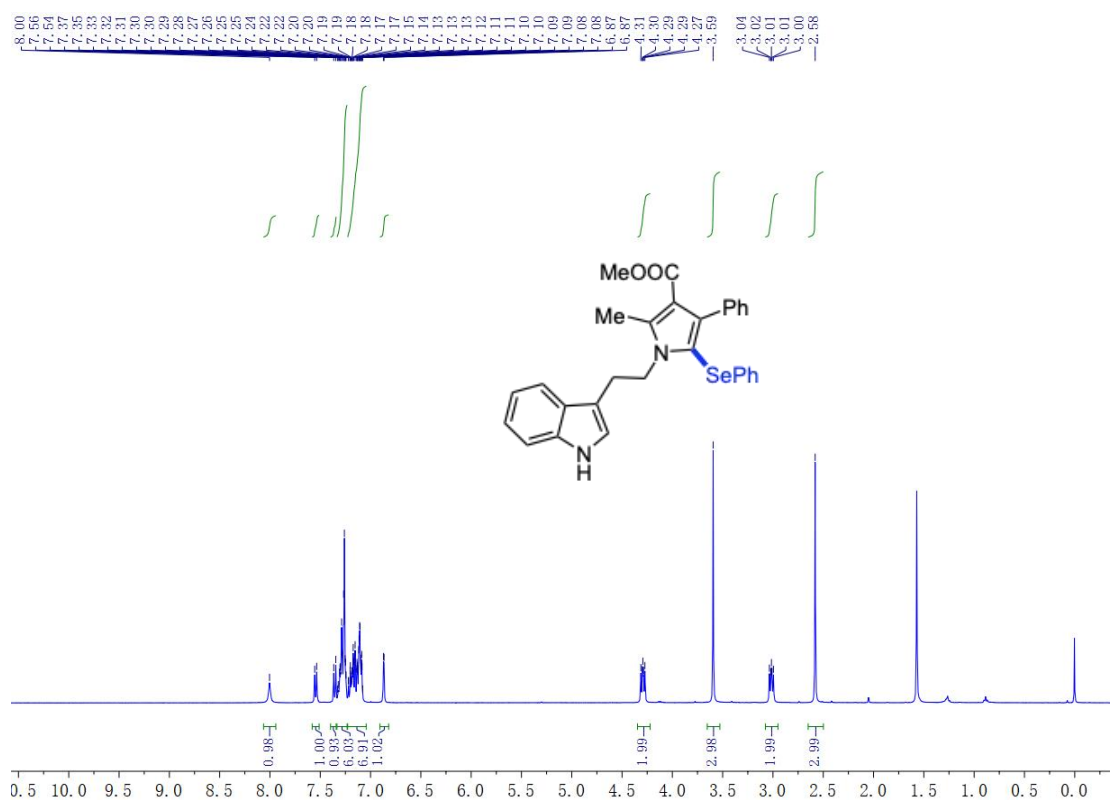
1. (a) H.-L. Cui, S.-W. Liu and X. Xiao, *J. Org. Chem.*, 2020, **85**, 15382-15395; (b) X. Xiao, X.-H. Chen, X.-X. Wang, F.-Y. Wu and H.-L. Cui, *Tetrahedron Lett* 2021, **77**, 153255; (c) X.; Xiao, X.-H. Chen, X.-X. Wang, W.-Z. Li and H.-L. Cui, *Synthesis* 2022, **54**, 2019-2030; (d) X.-H. Chen, Y.-M. Li, X. Huang and H.-L. Cui, *J. Org. Chem.* 2023, **88**, 16400–16409.
- 2 (a) X.-H. Chen and H.-L. Cui, *Asian J. Org. Chem.* 2022, **11**, e202100761; (b) H. L. S. Maia, L. S. Monteiro, J. Sebastião, *Eur. J. Org. Chem.* 2001, 1967-1970; (c) A. J. Metrano, S. J. Miller, *J. Org. Chem.* 2014, **79**, 1542–1554.

3. NMR Spectra

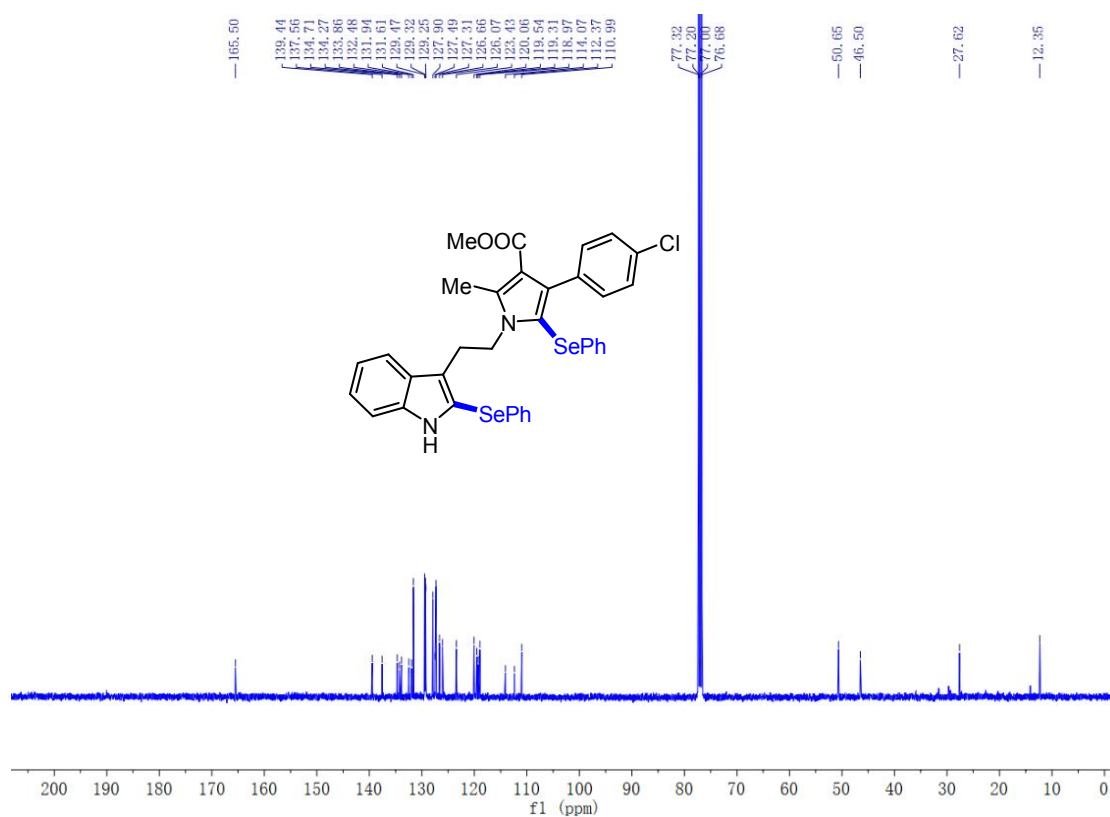
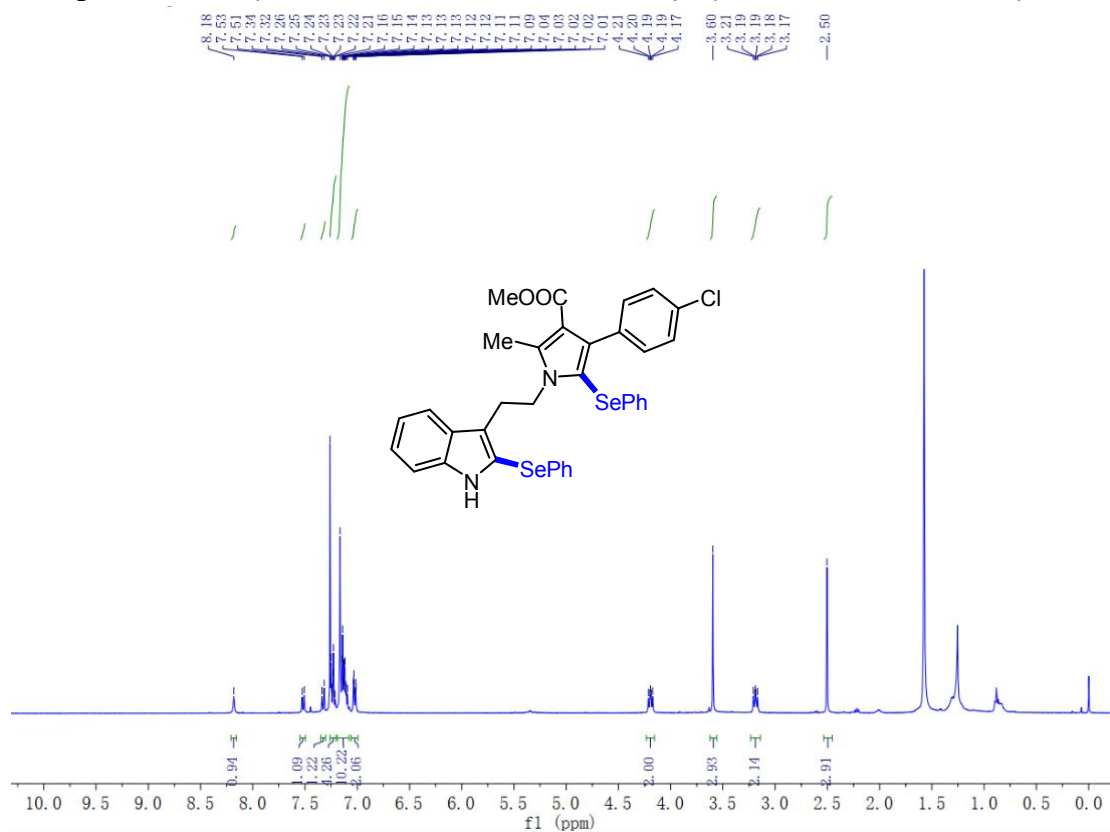
Compound of 3a (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



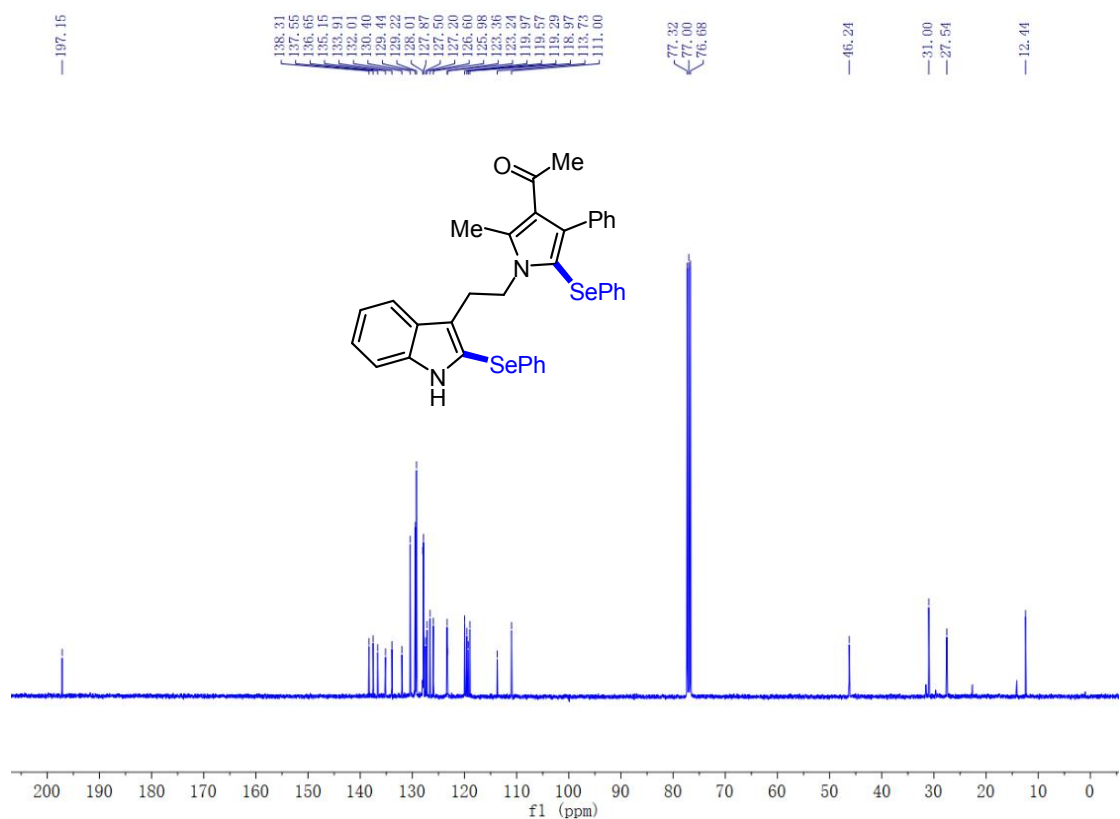
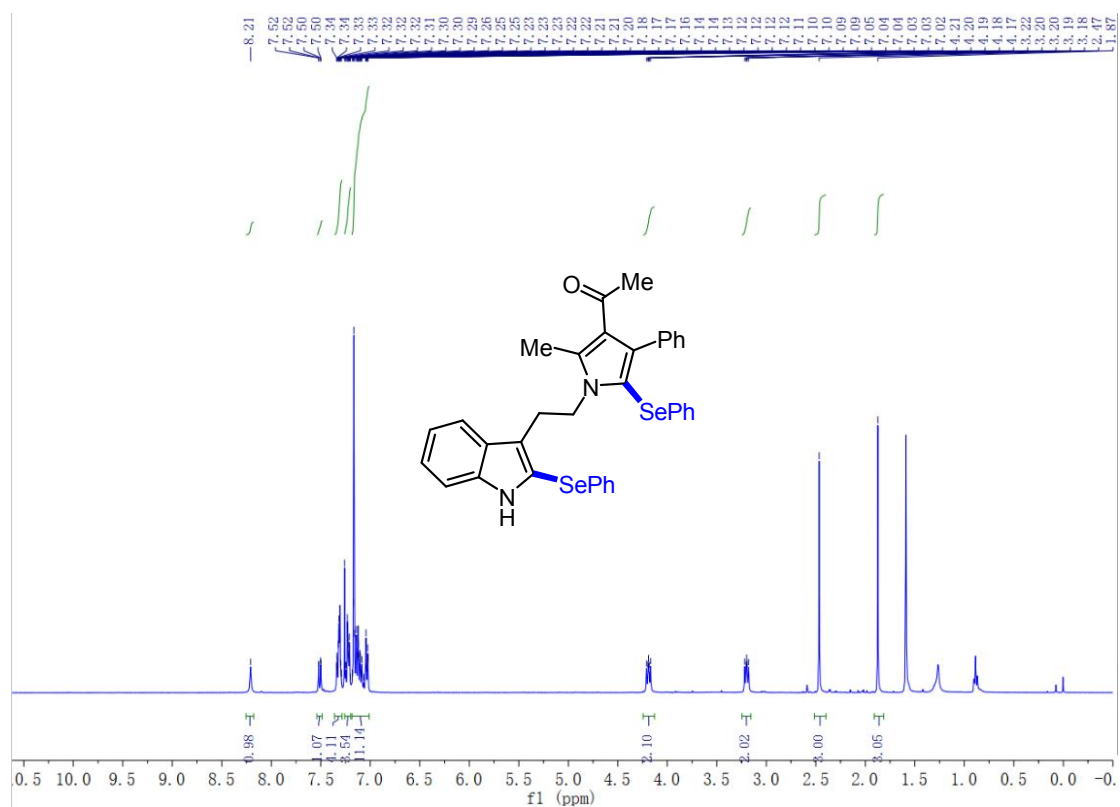
Compound of 3a' (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



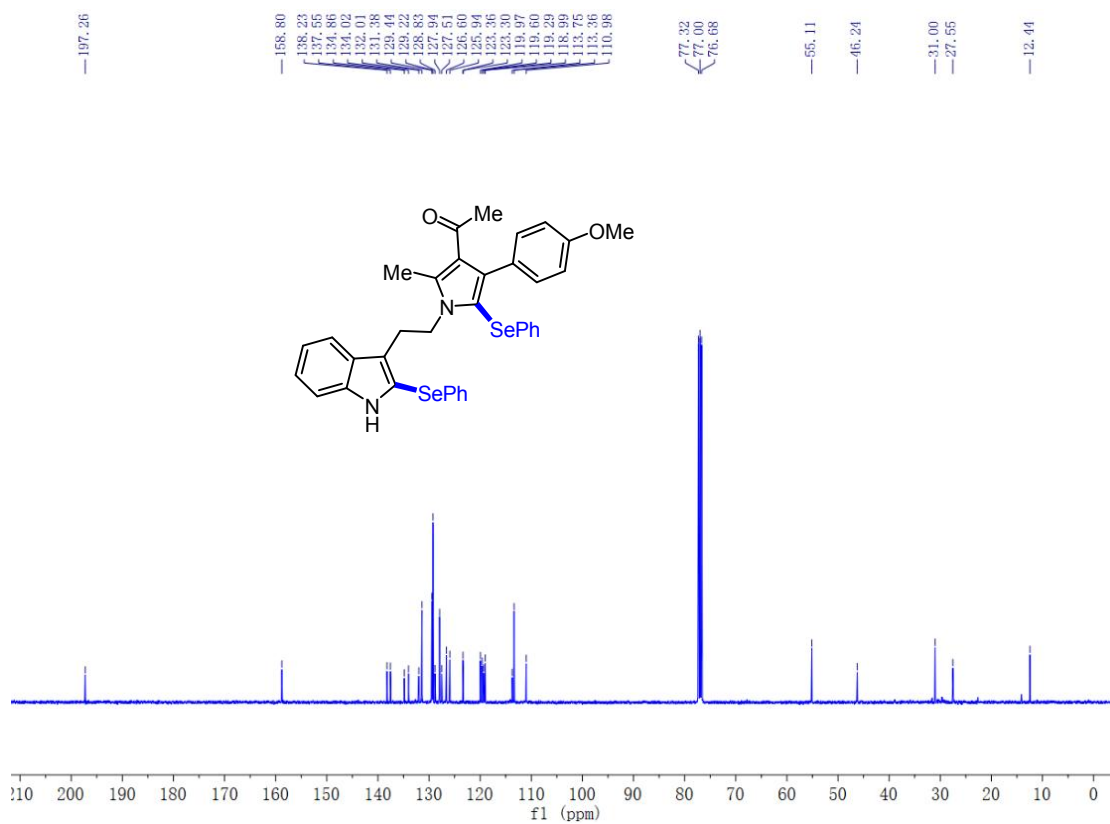
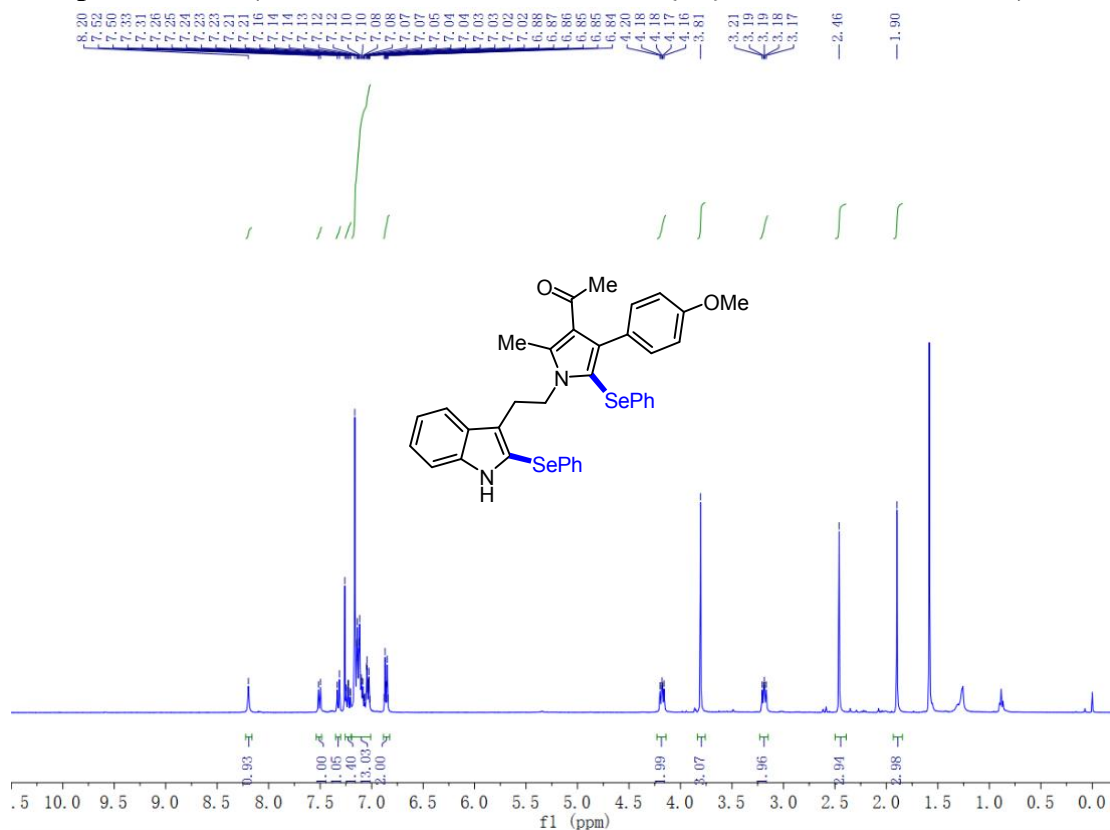
Compound of 3b (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



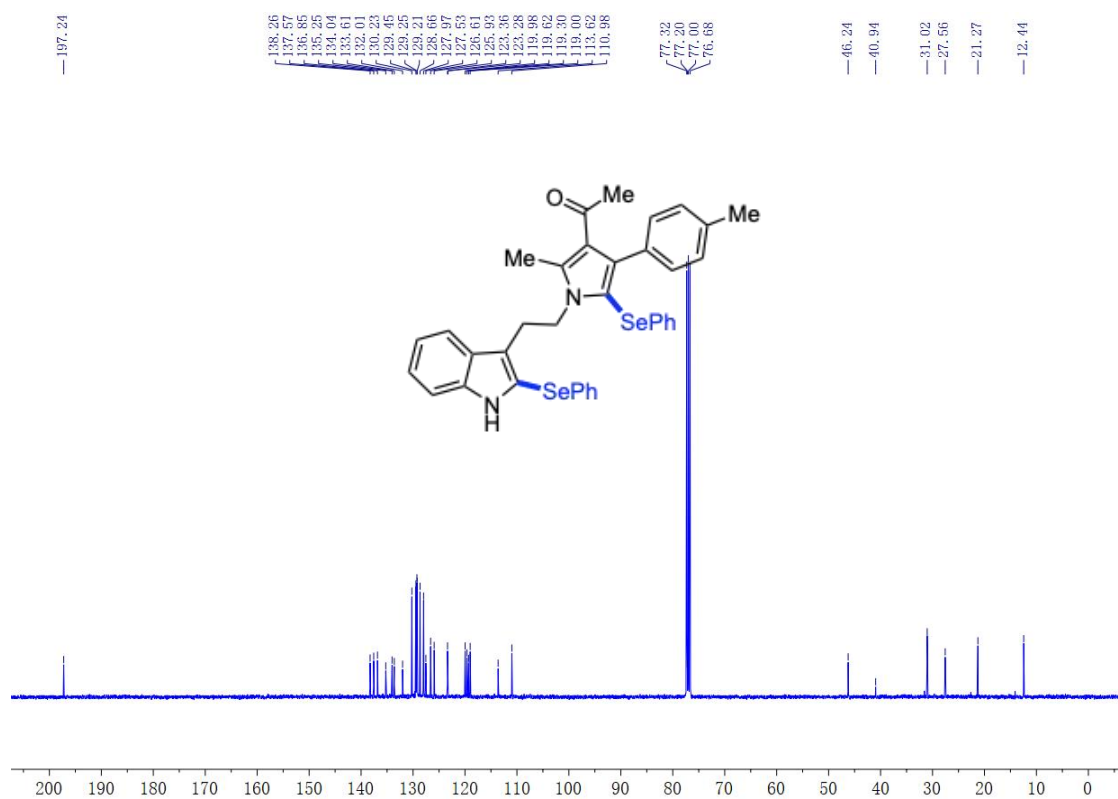
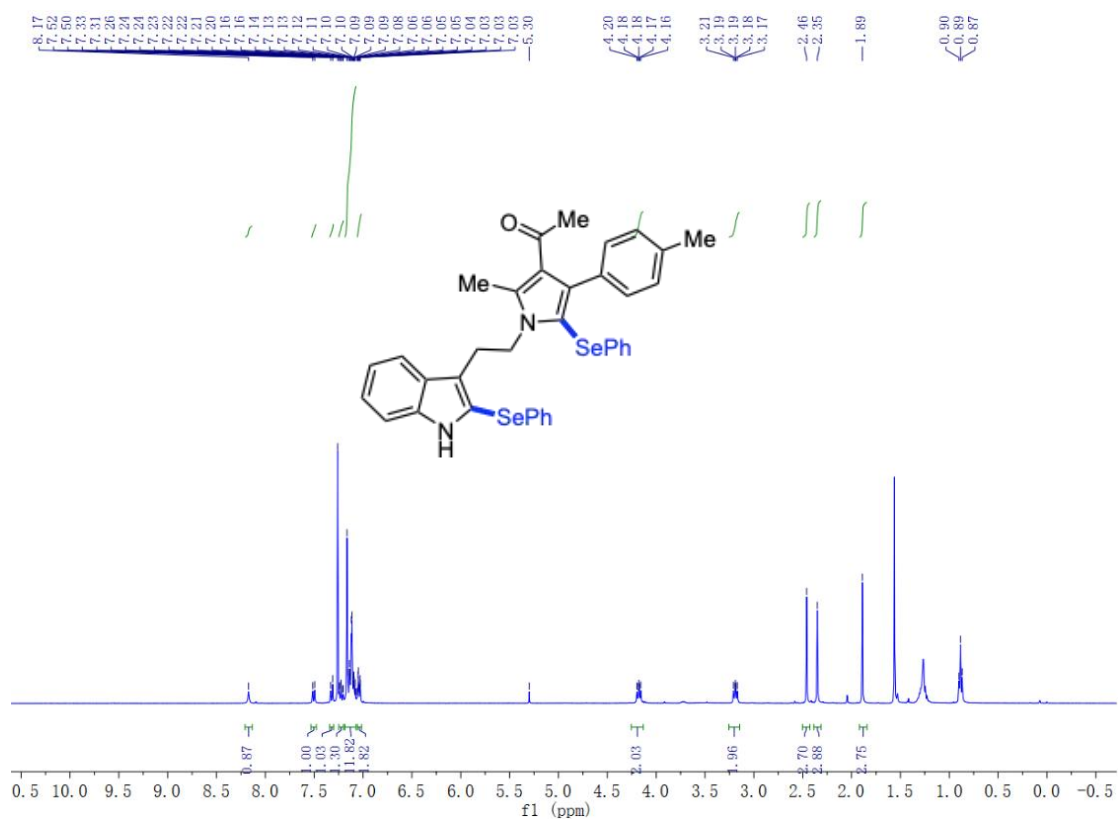
Compound of 3c (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



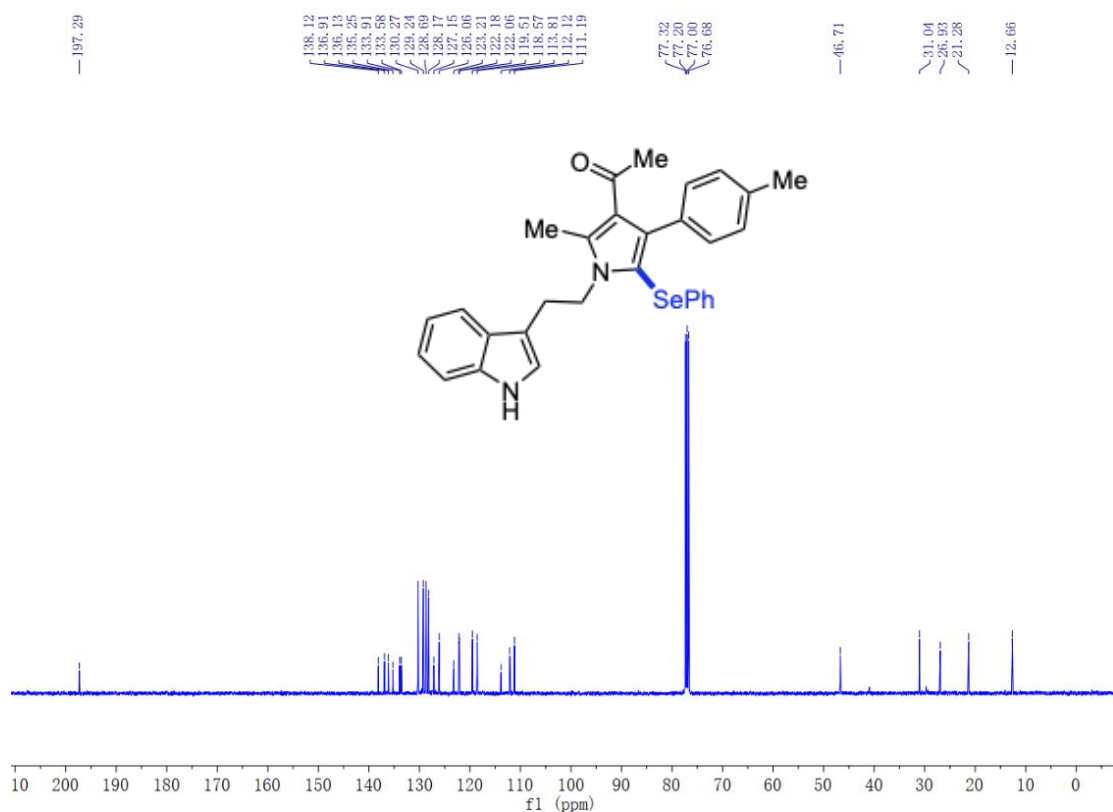
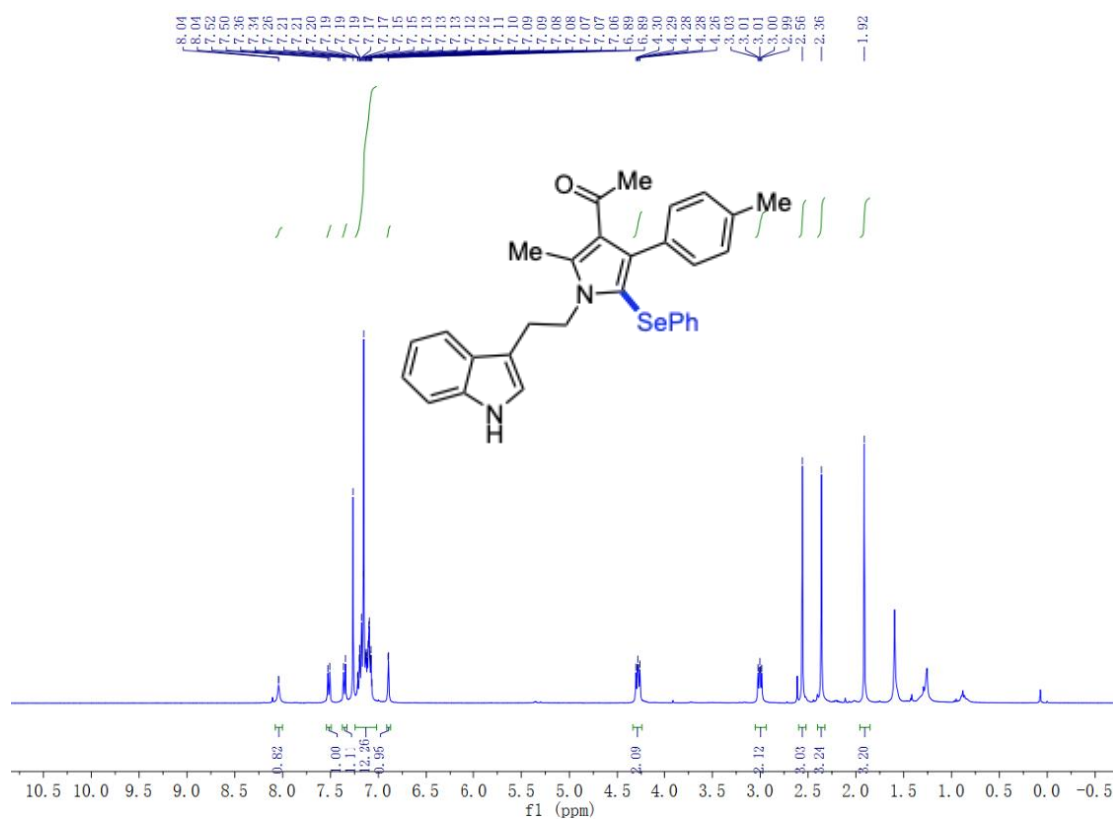
Compound of 3d (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



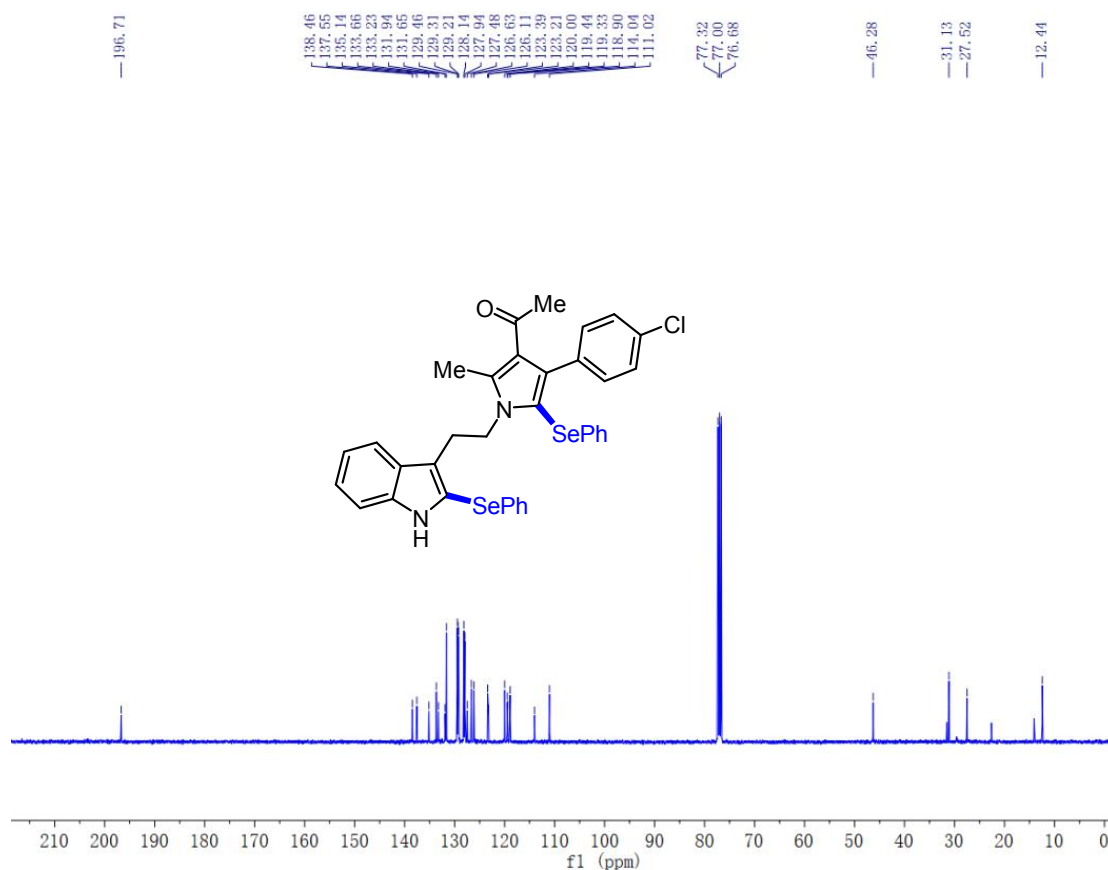
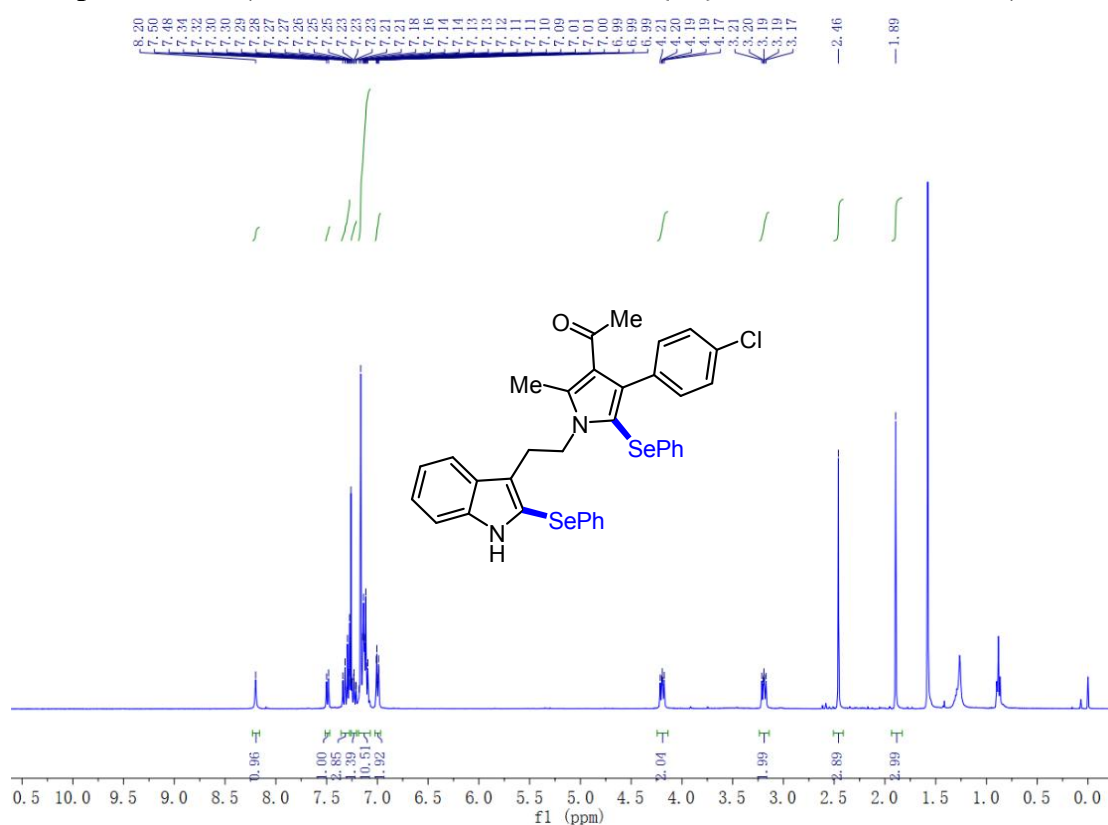
Compound of 3e (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



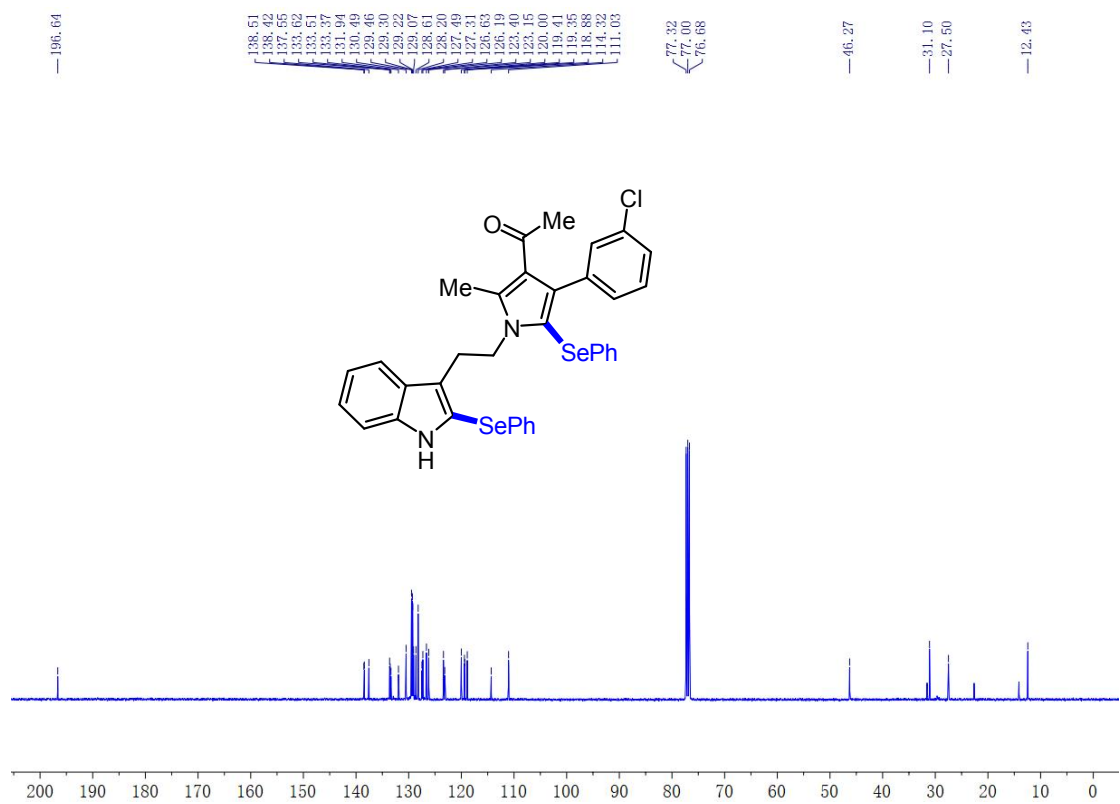
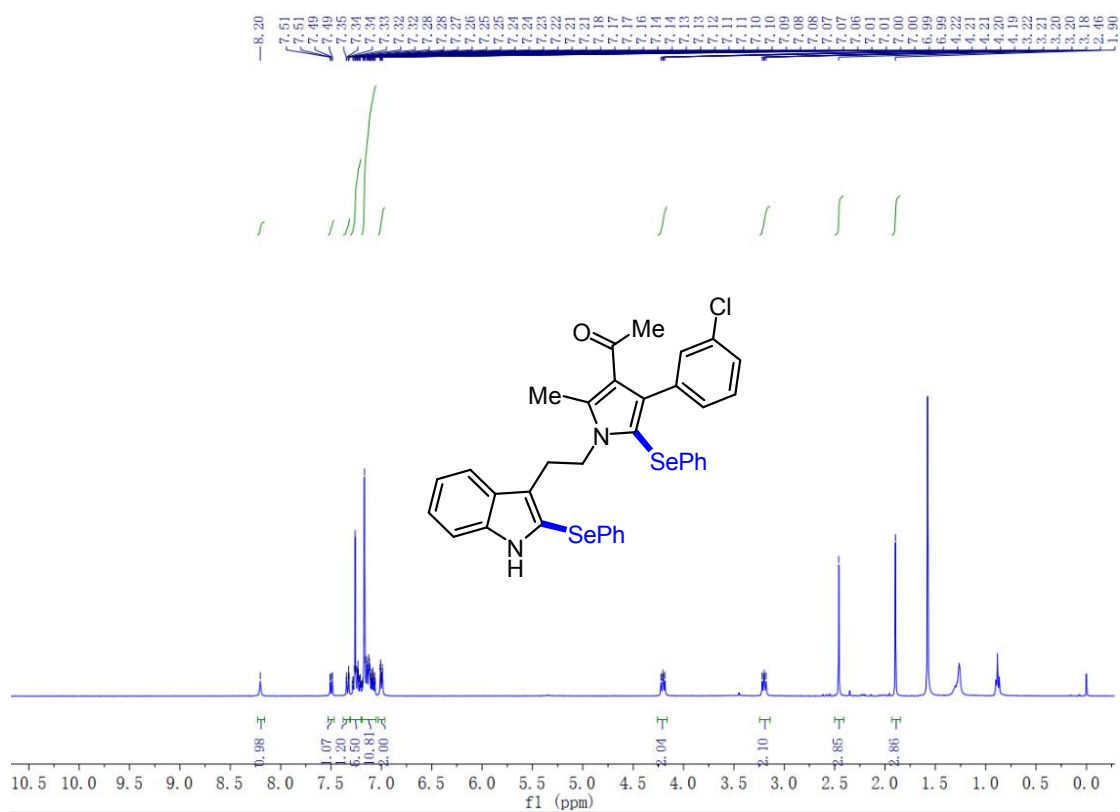
Compound of 3e' (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



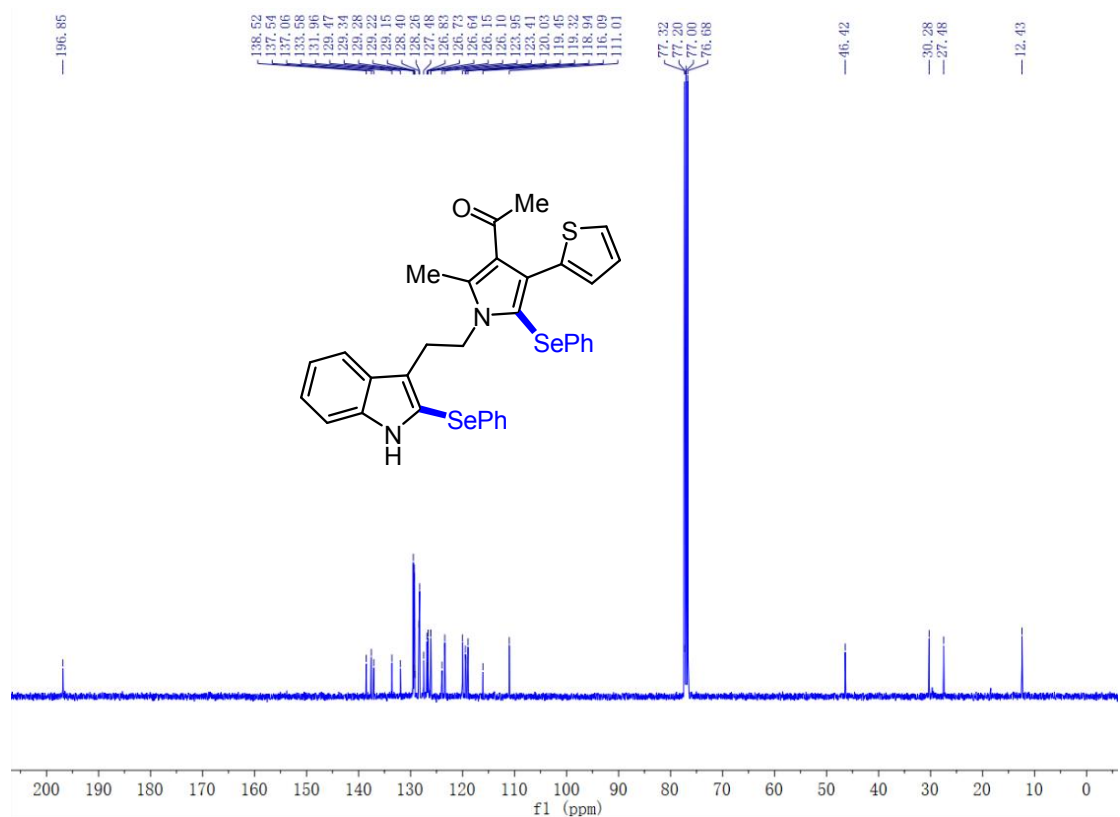
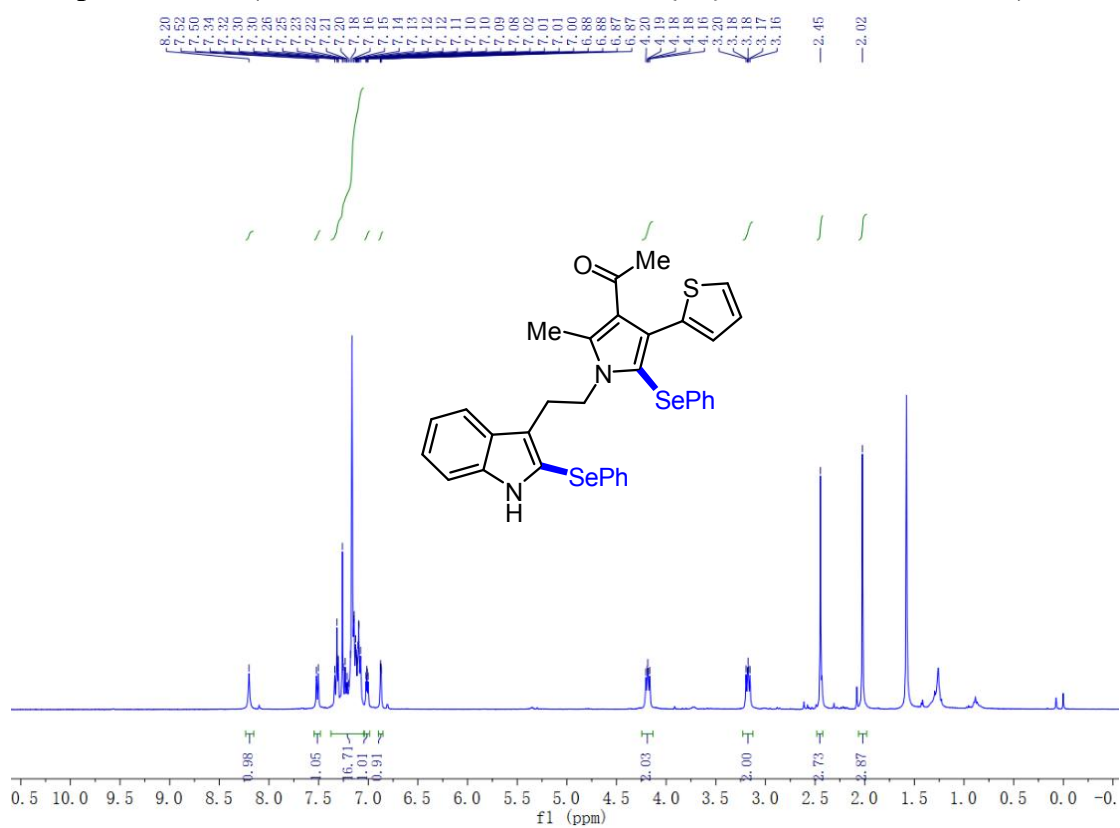
Compound of 3f (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C { ^1H } NMR, 100Hz, CDCl_3)



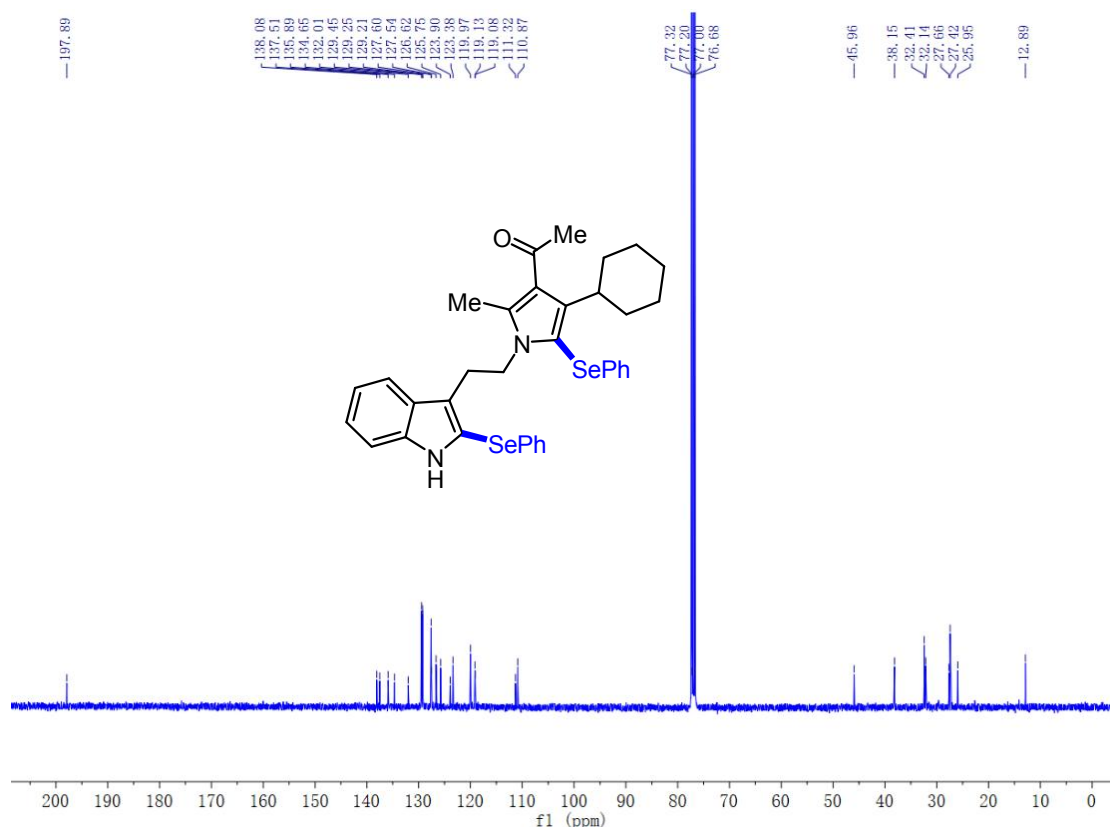
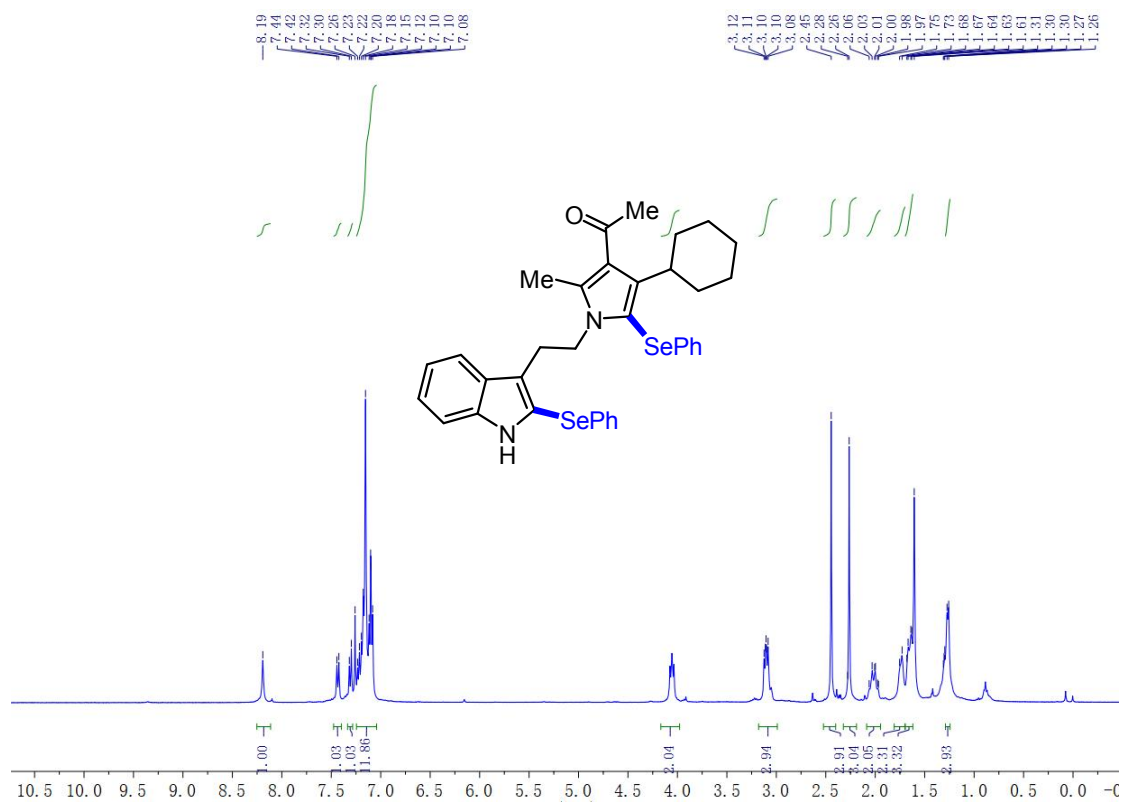
Compound of 3g (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



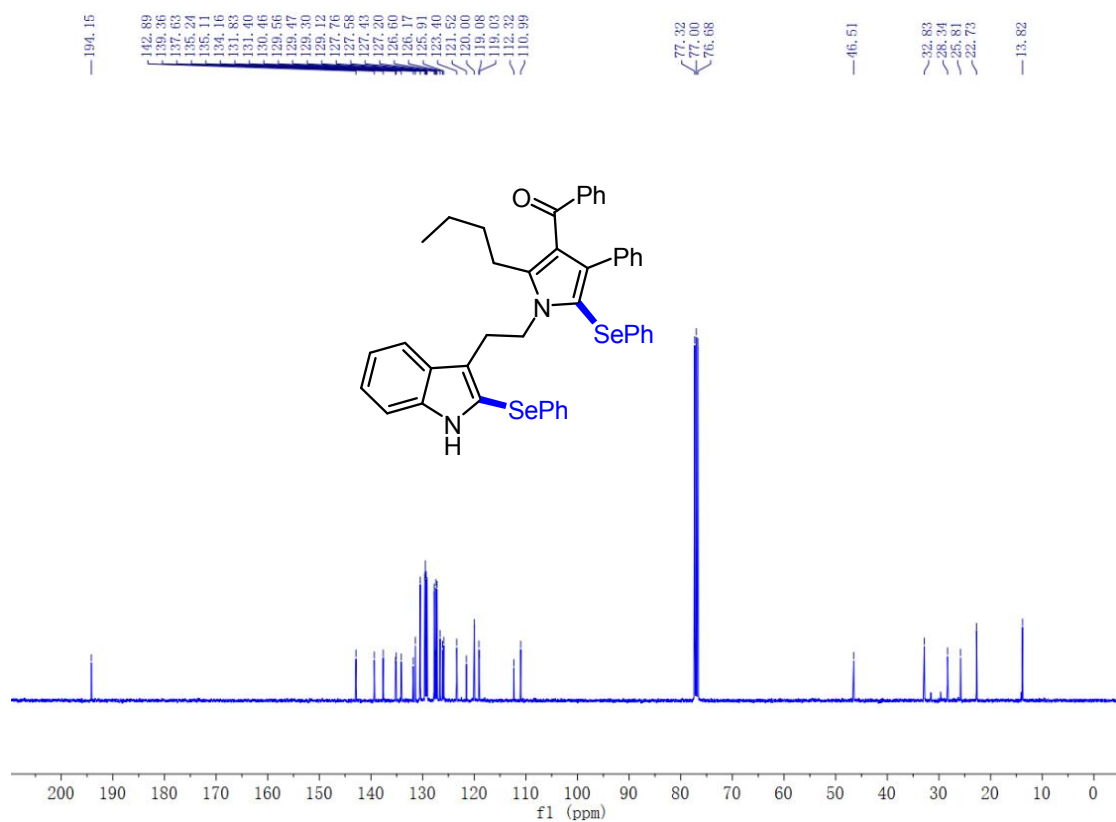
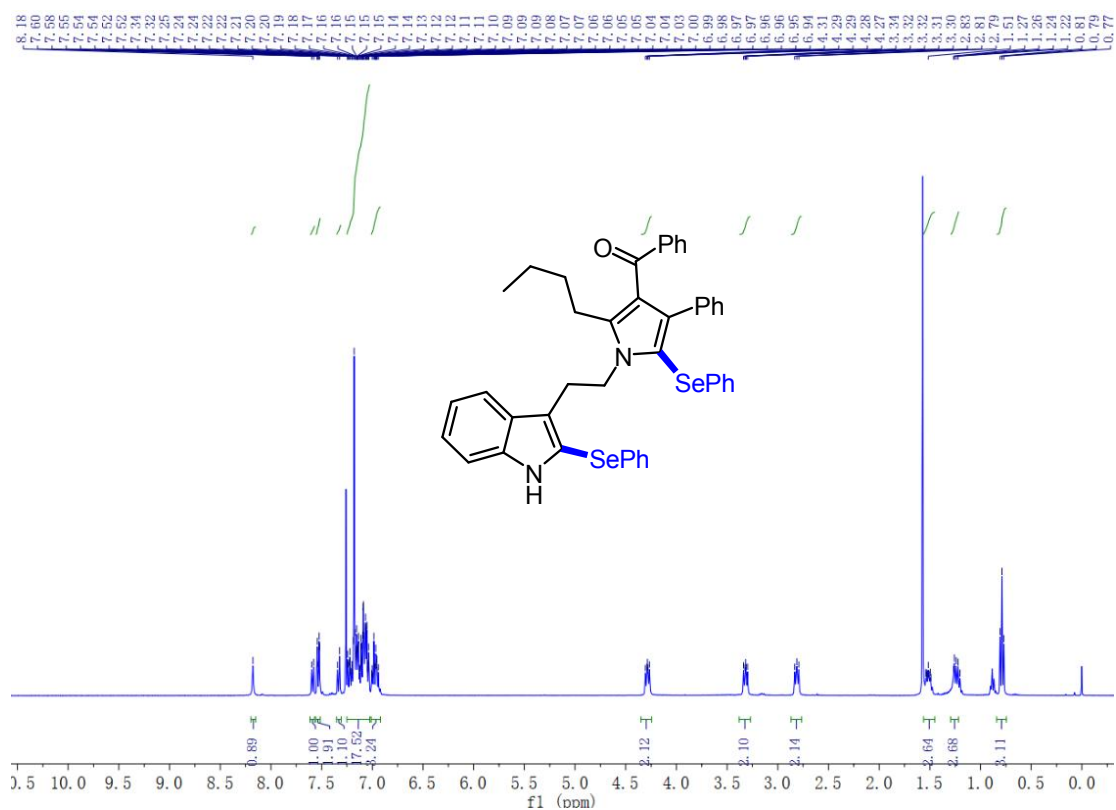
Compound of 3h (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



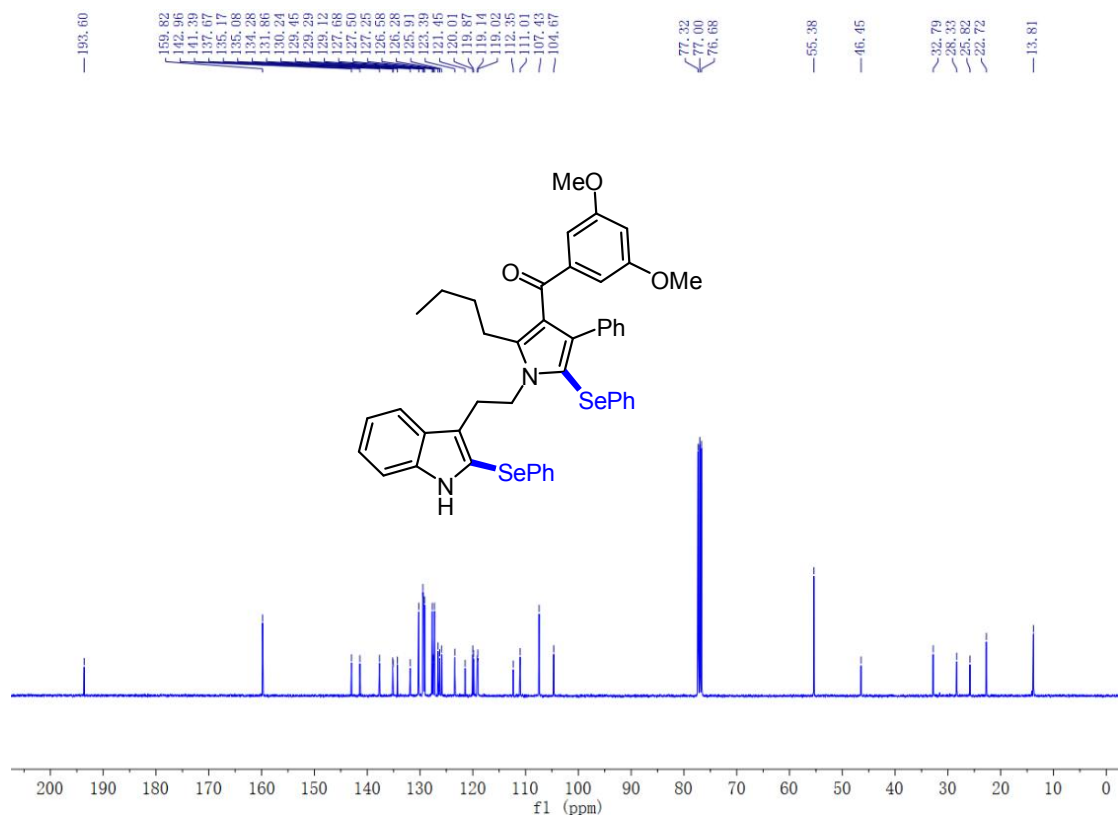
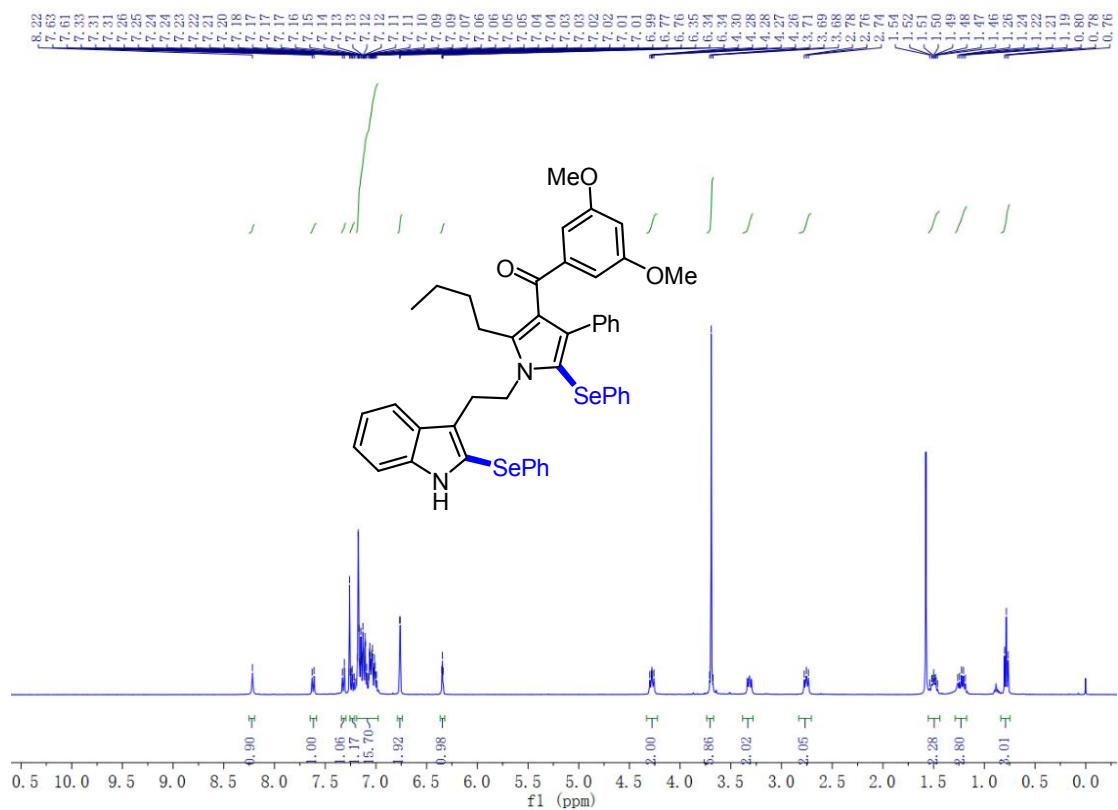
Compound of 3i (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



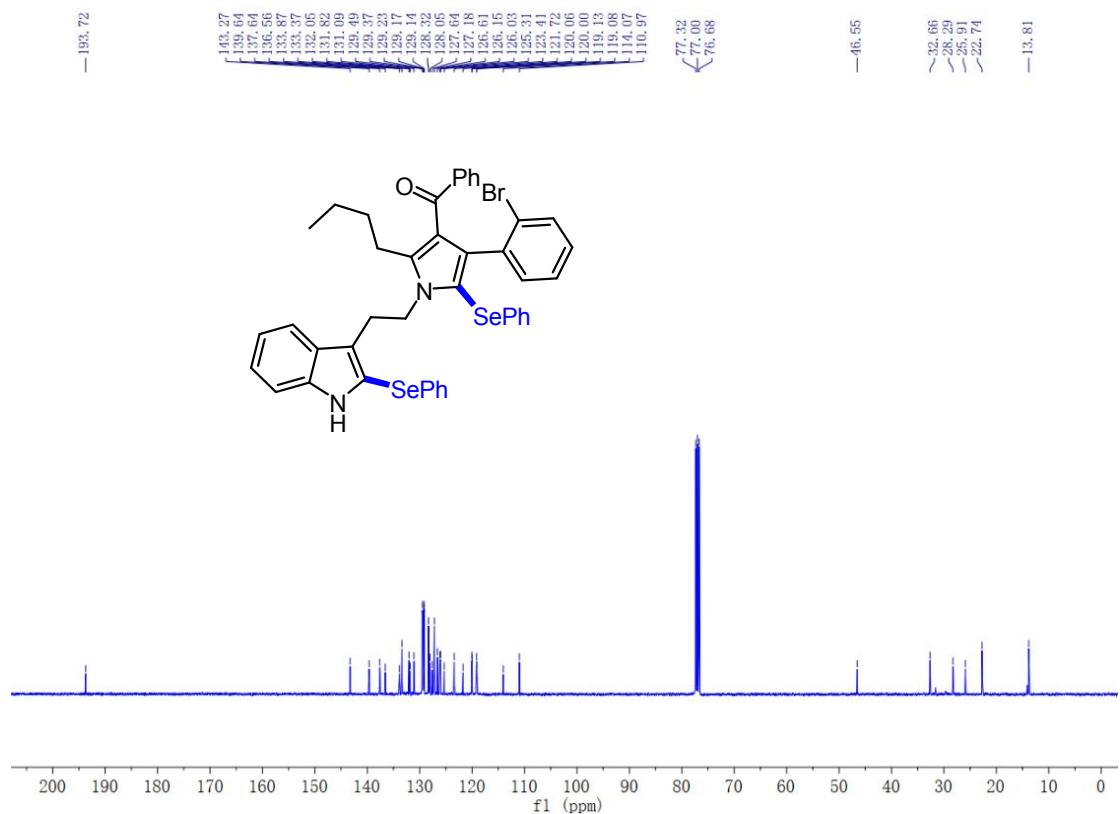
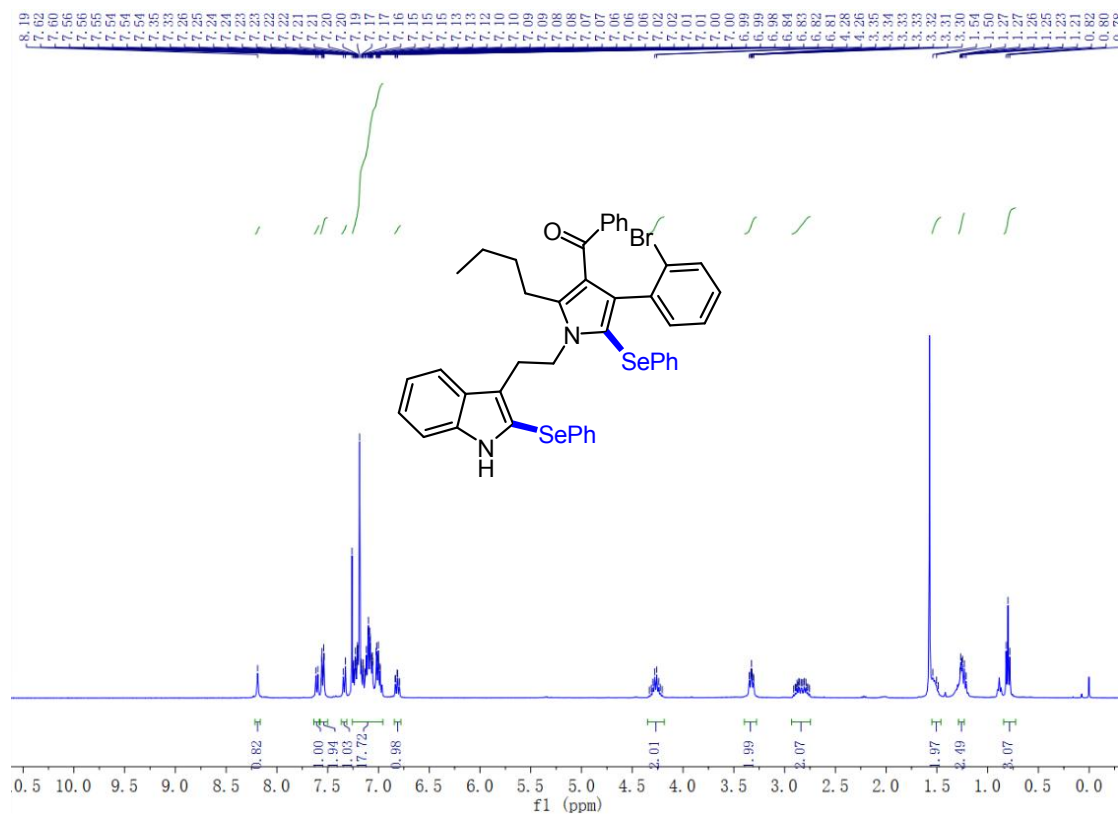
Compound of 3j (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



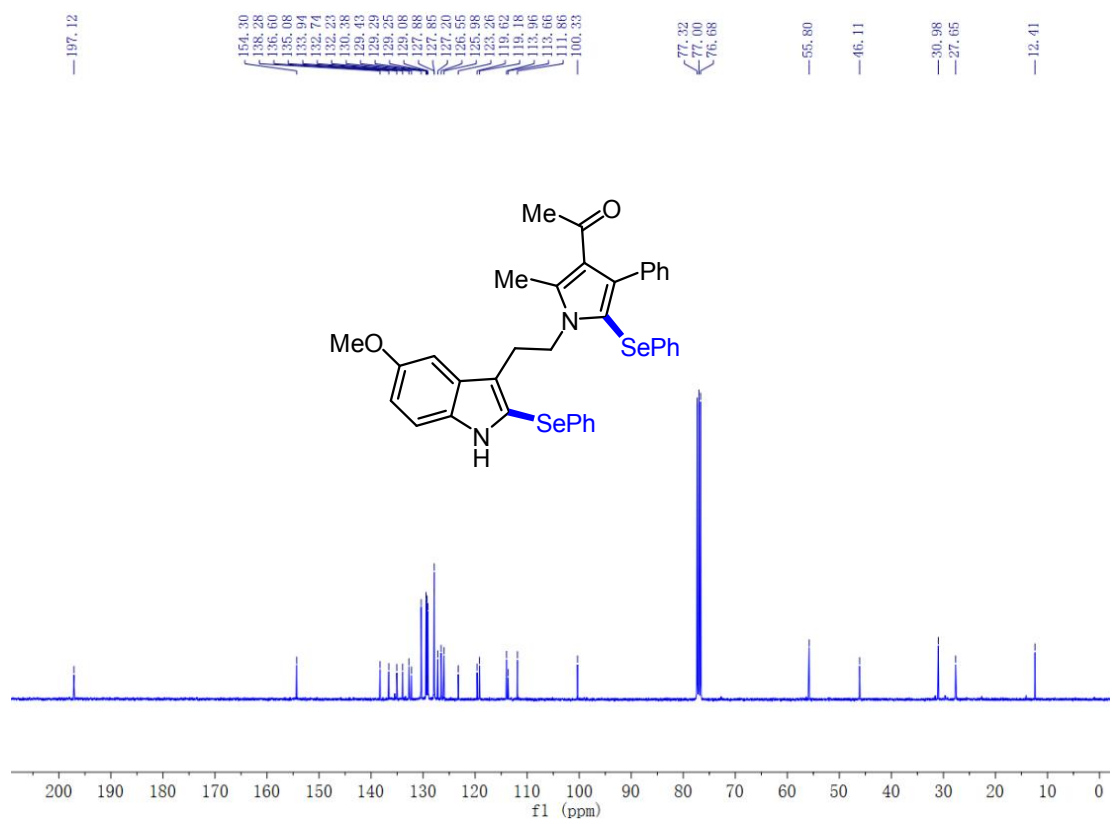
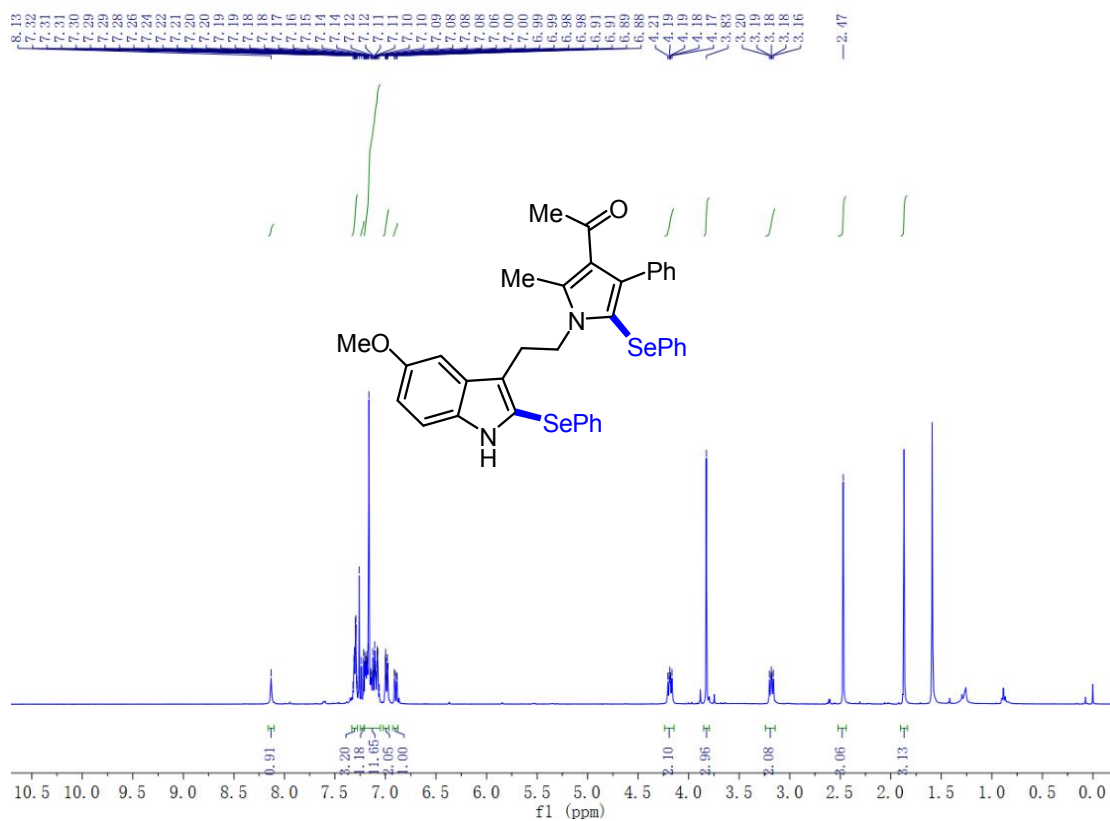
Compound of 3k (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



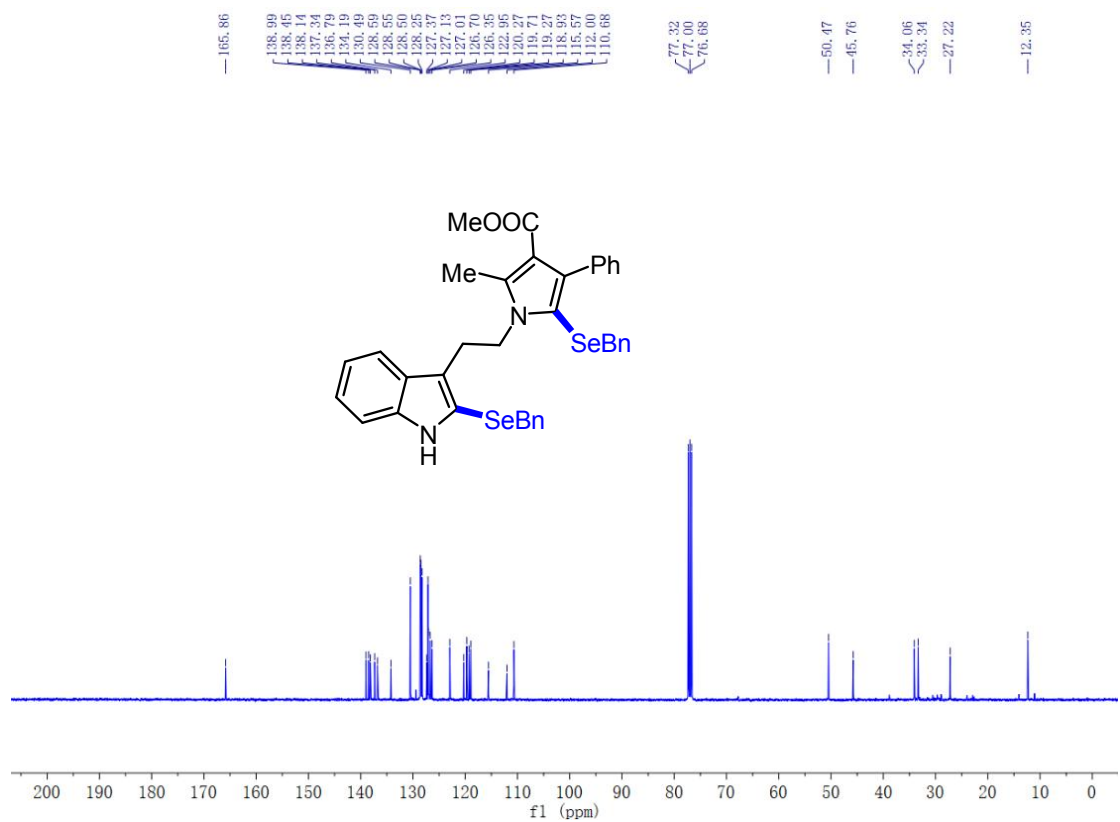
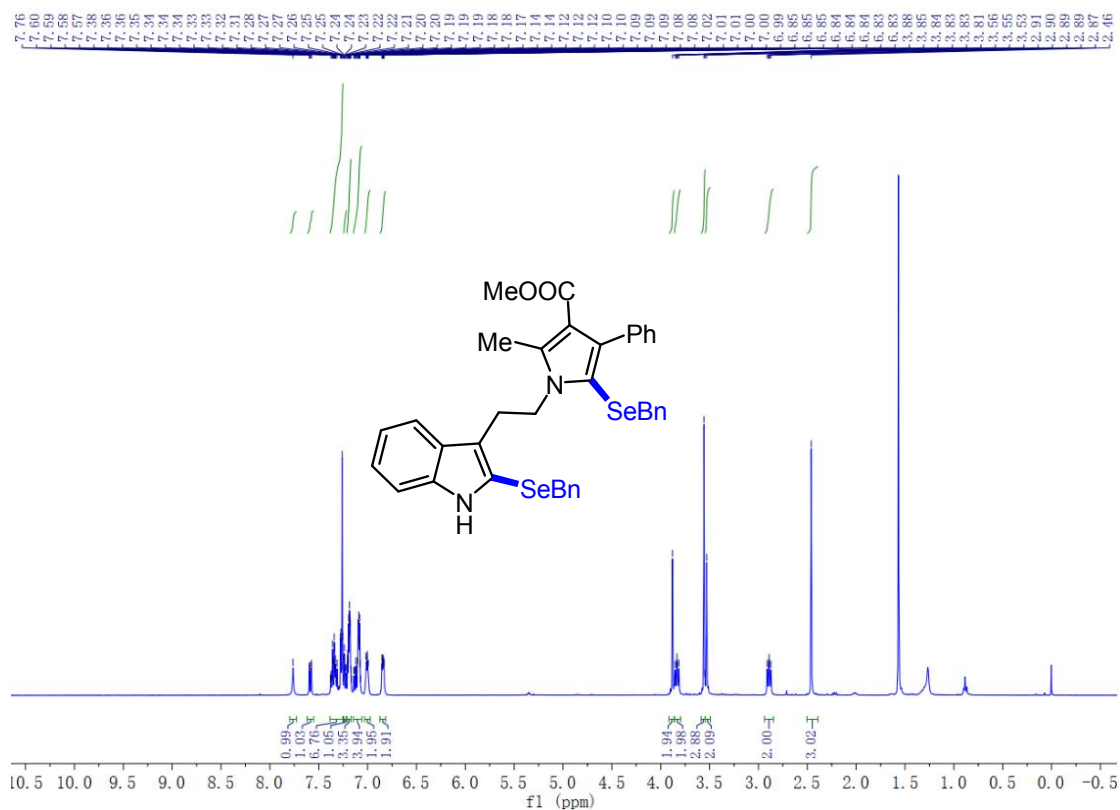
Compound of 3l (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



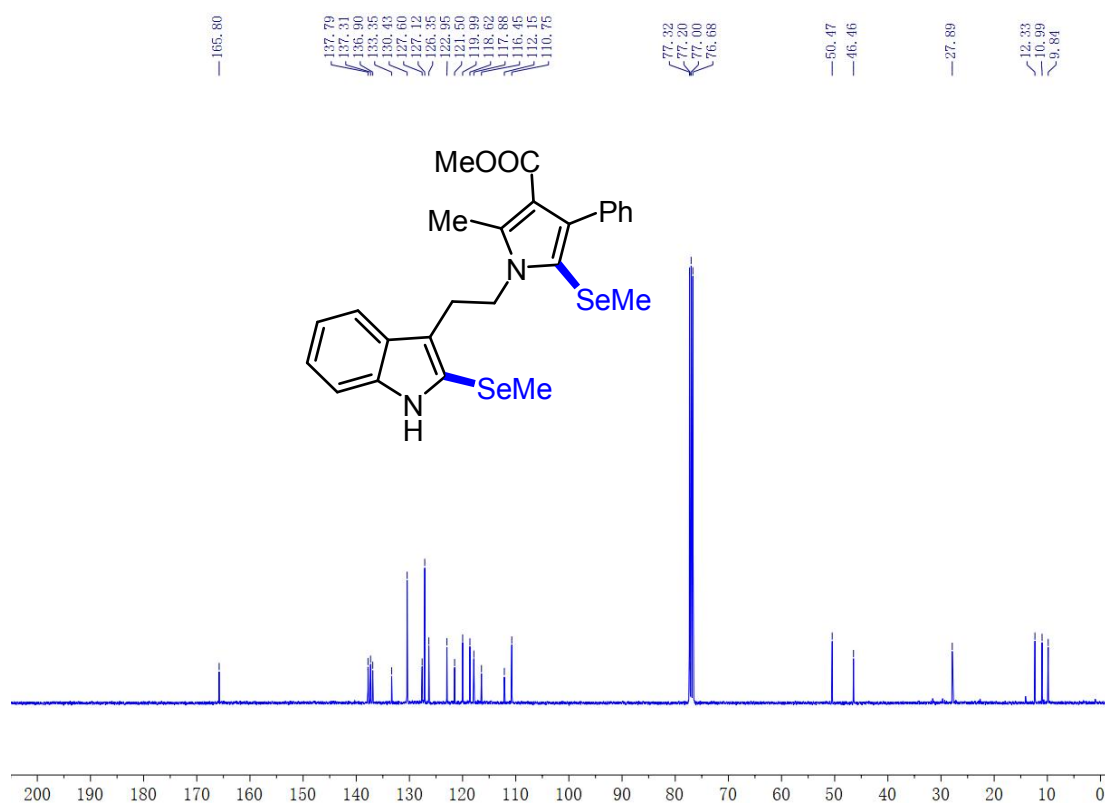
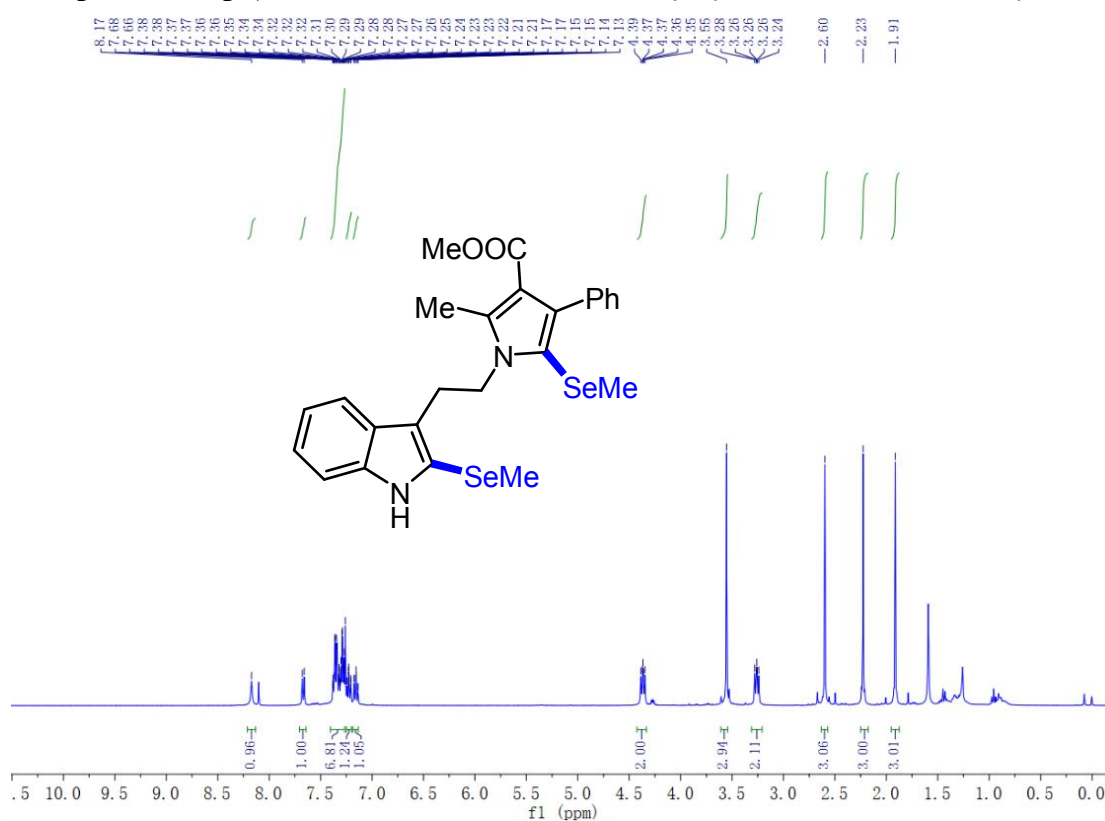
Compound of 3m (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



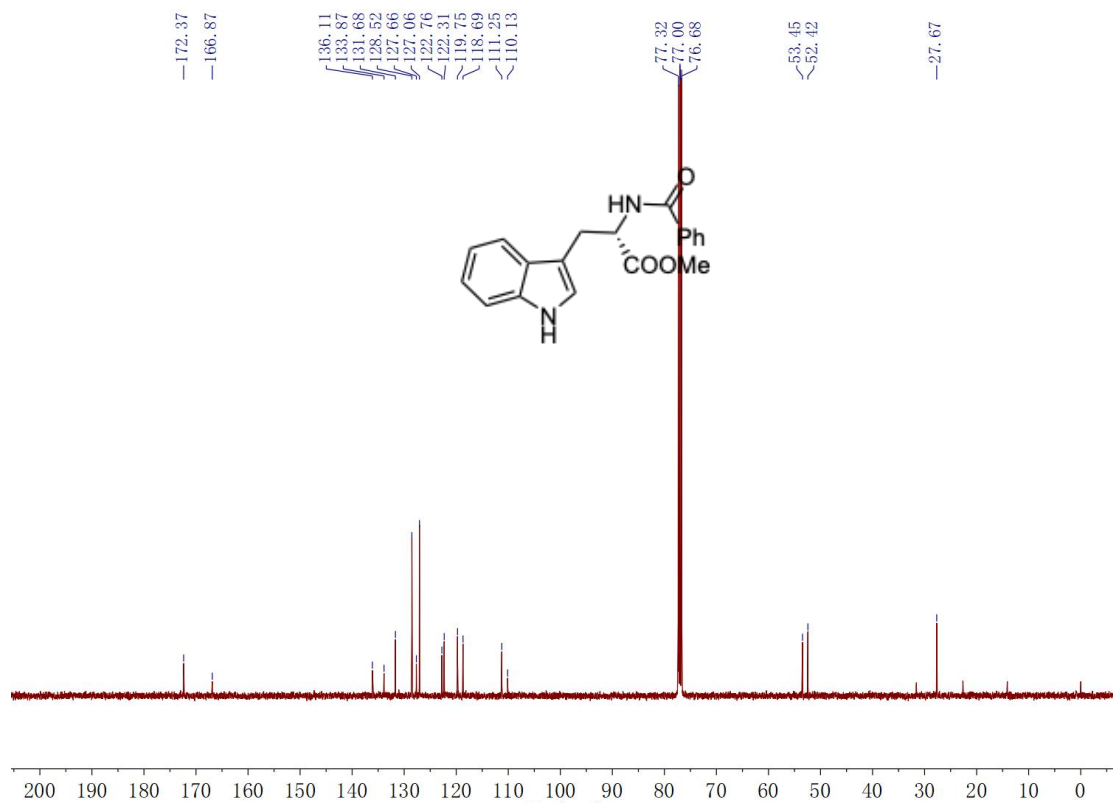
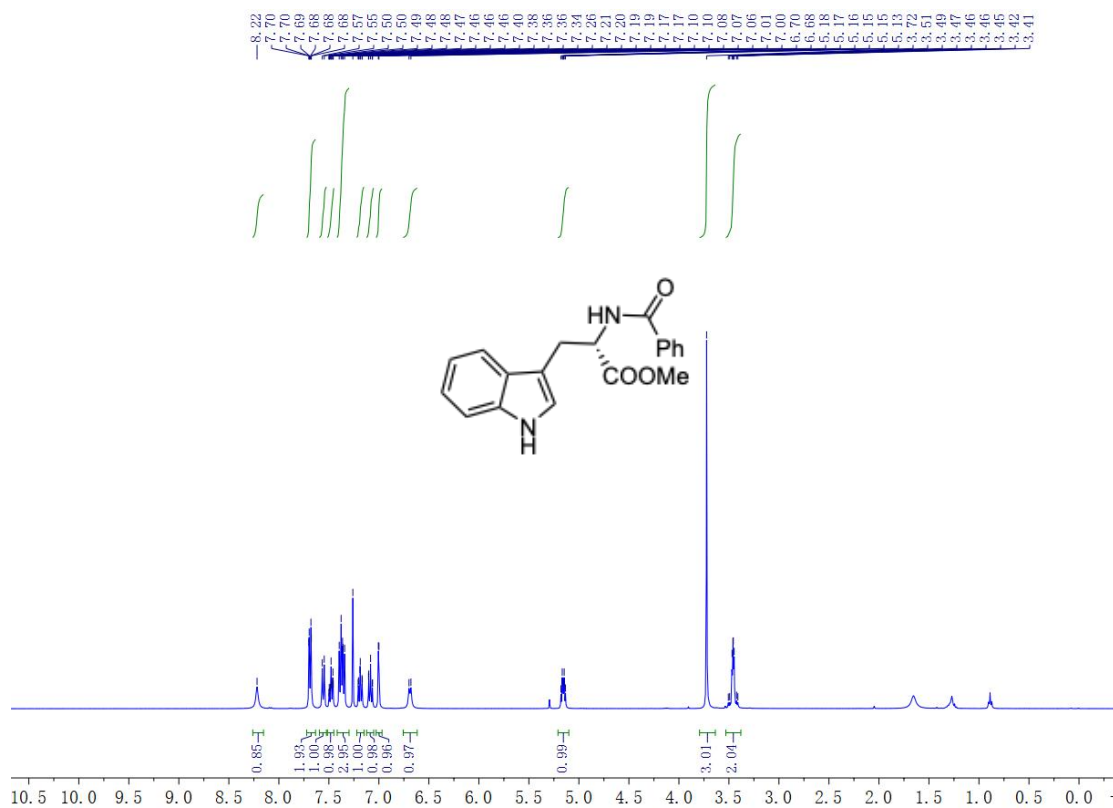
Compound of 3n (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



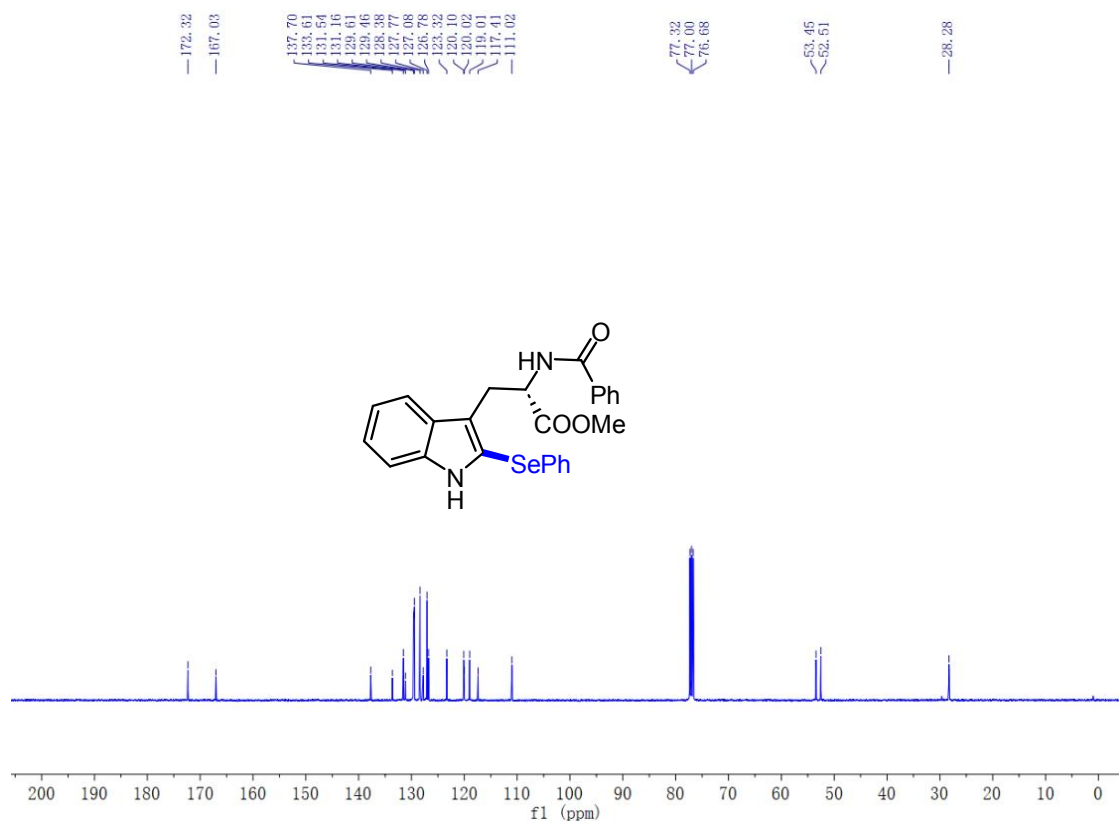
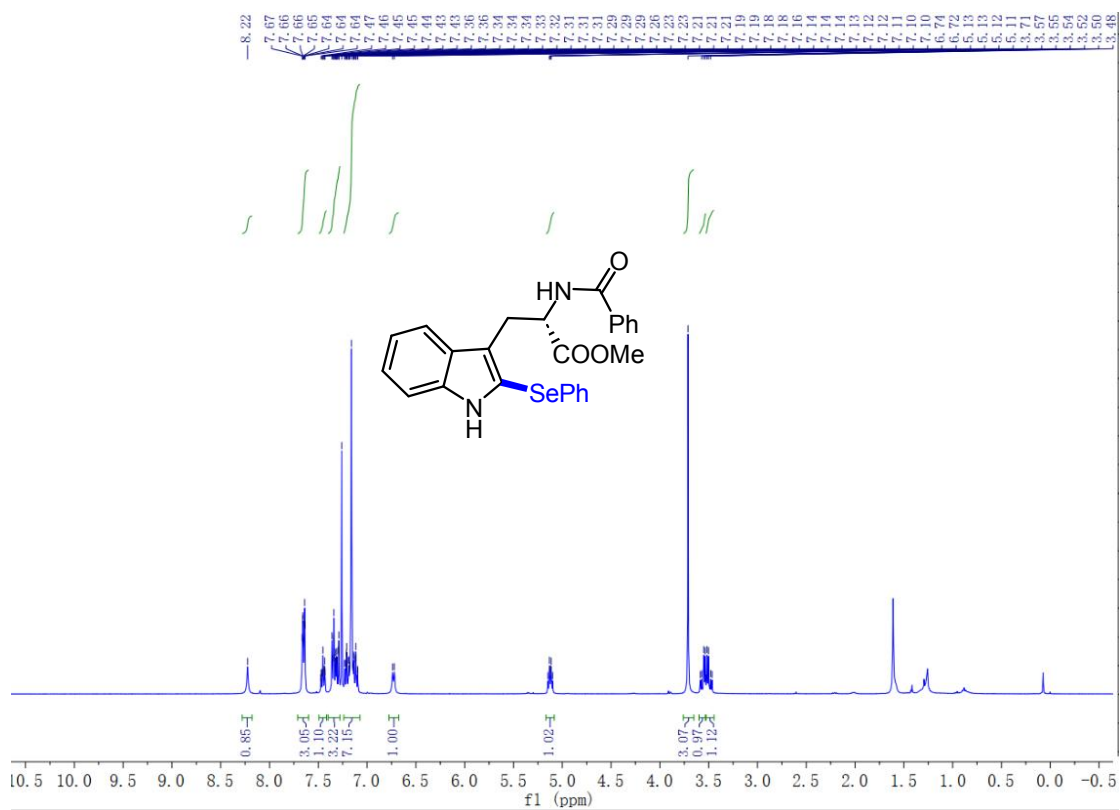
Compound of 3p (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



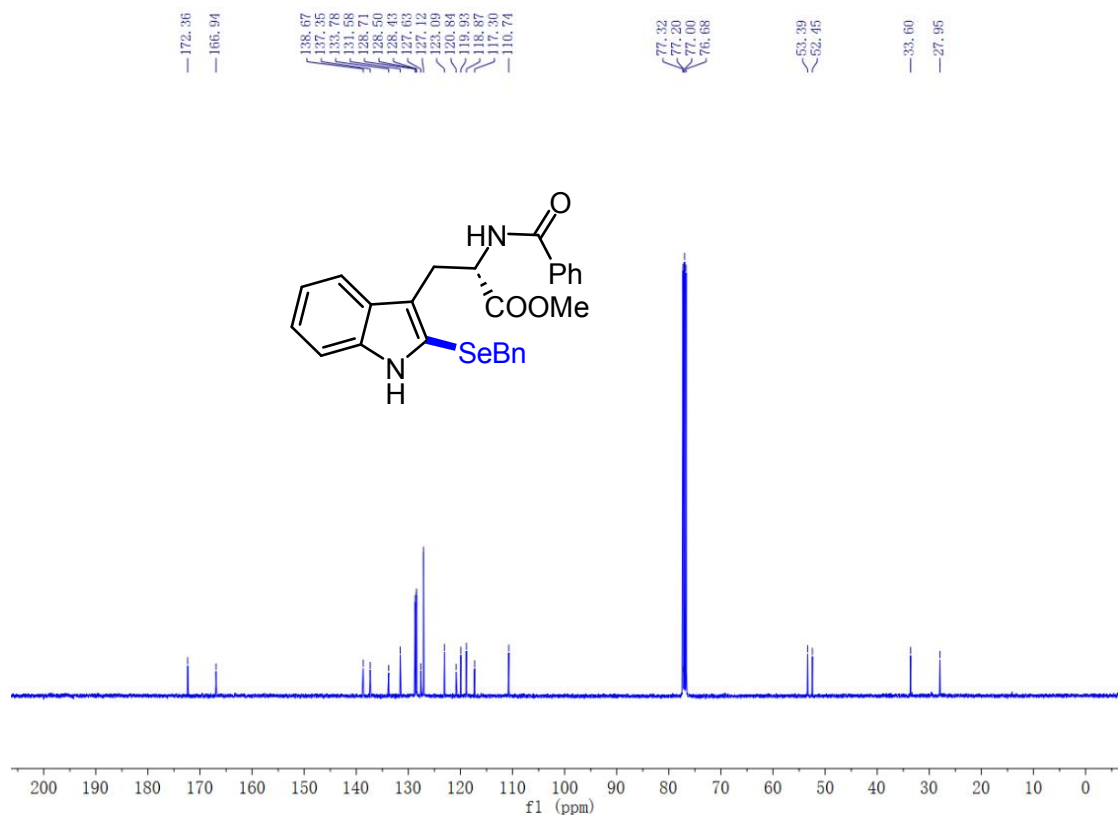
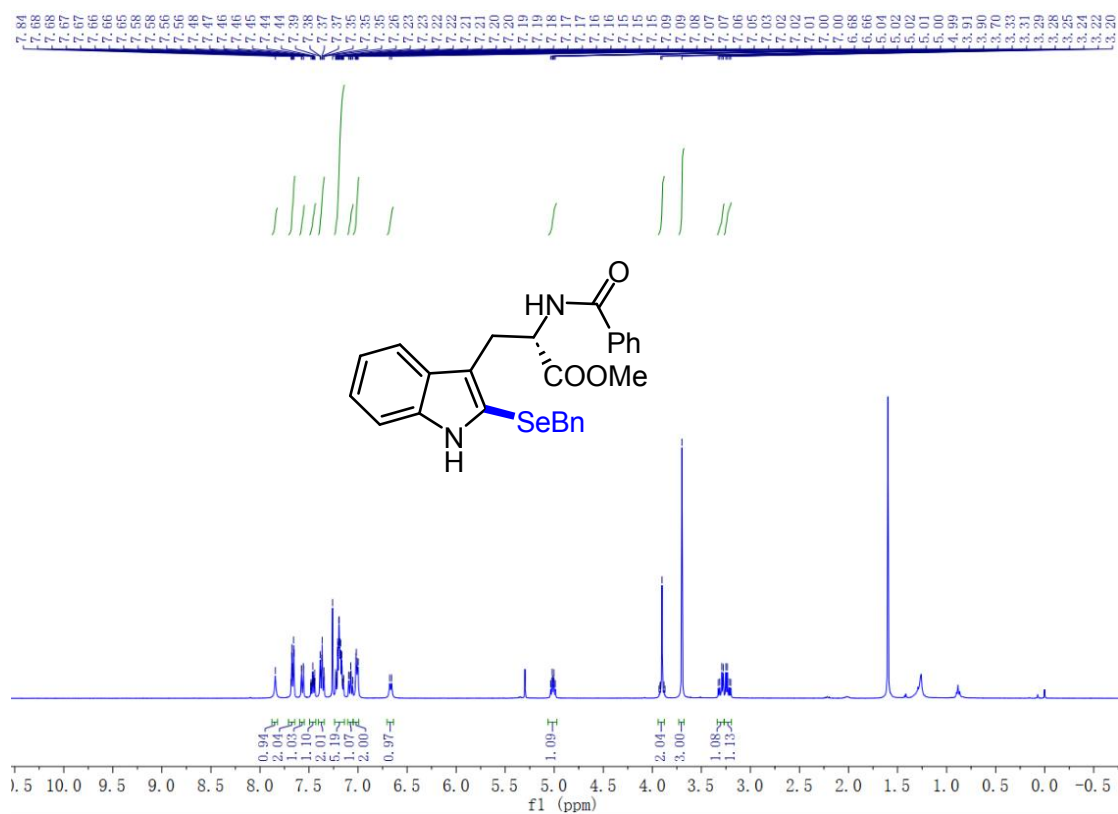
Compound of 4a (¹H NMR, 400 Hz, CDCl₃)



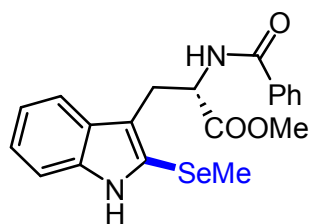
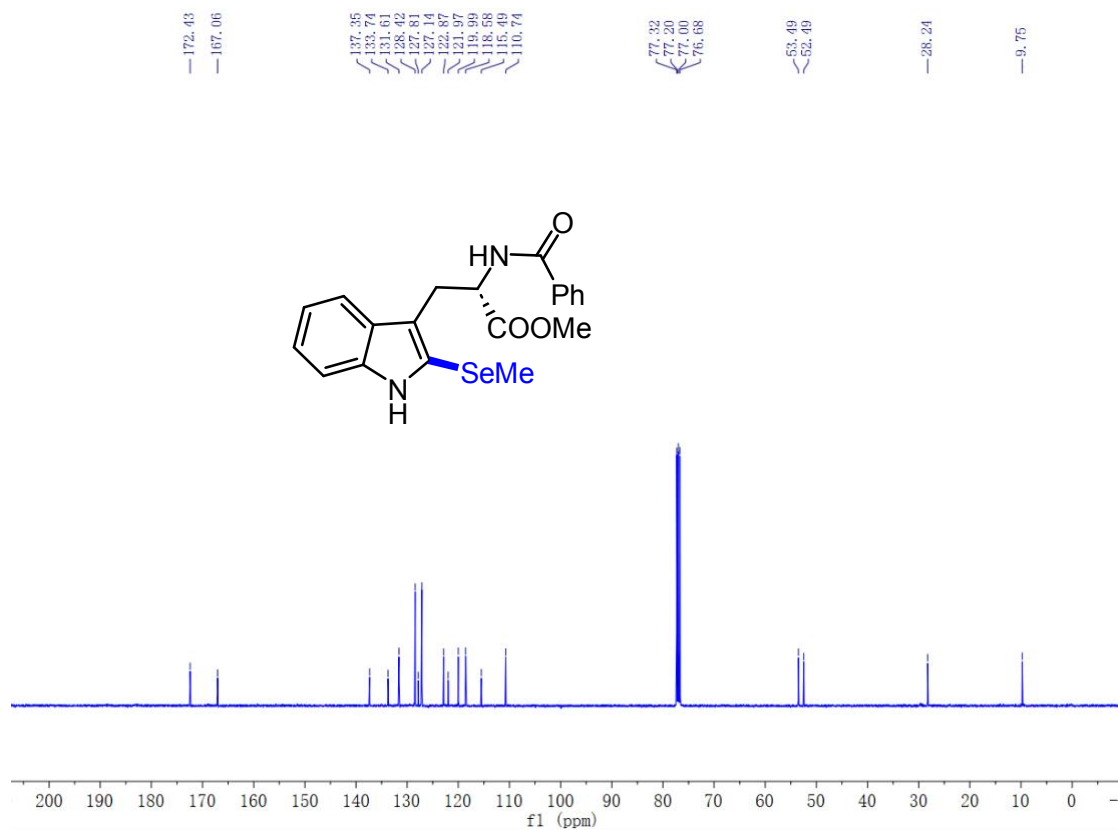
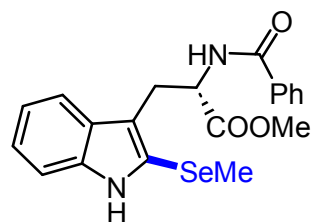
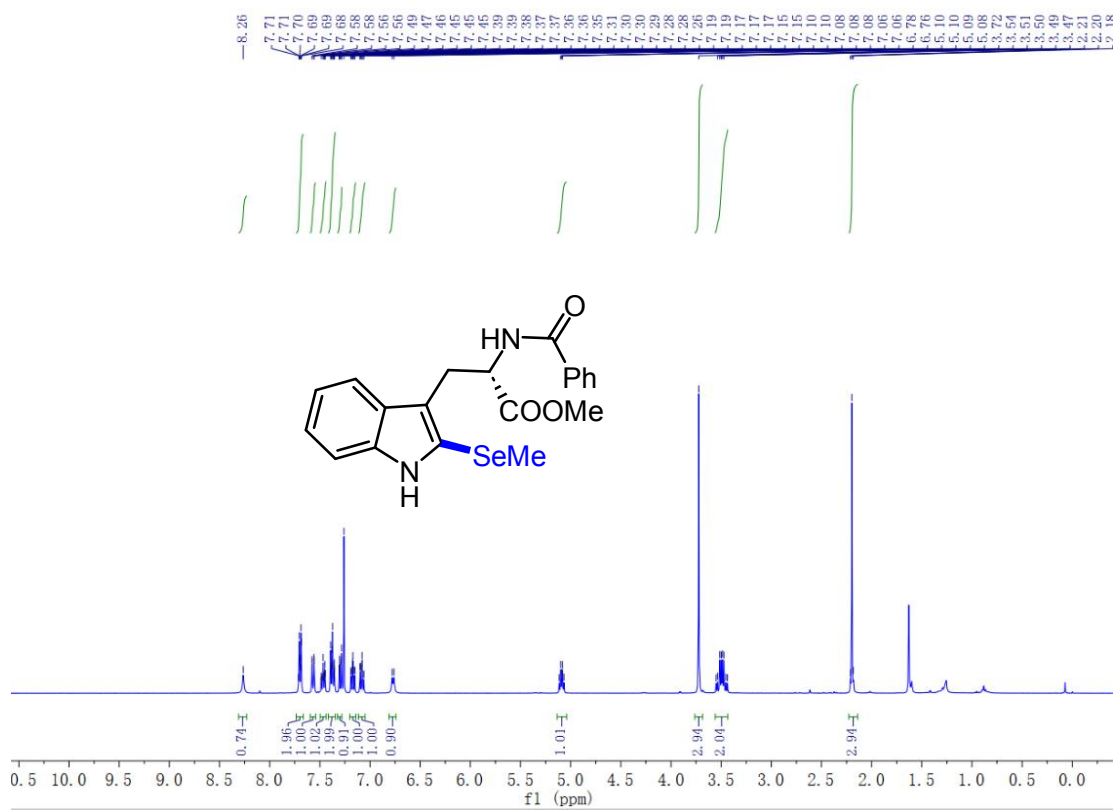
Compound of 5a (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



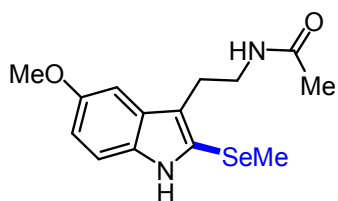
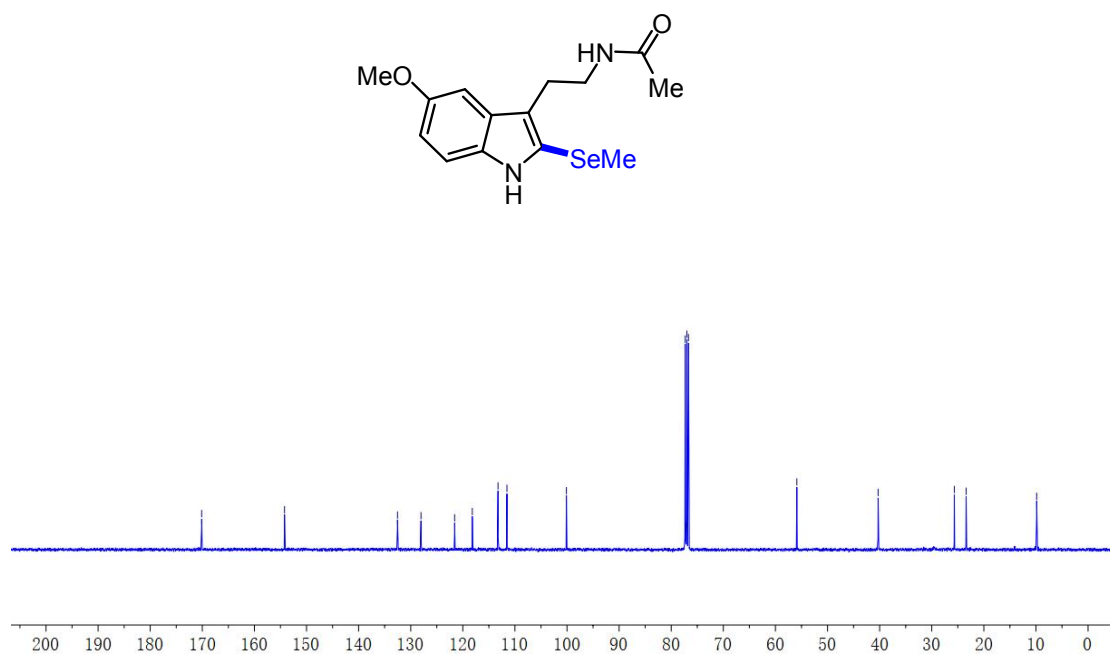
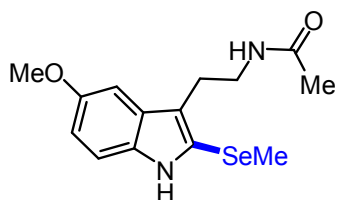
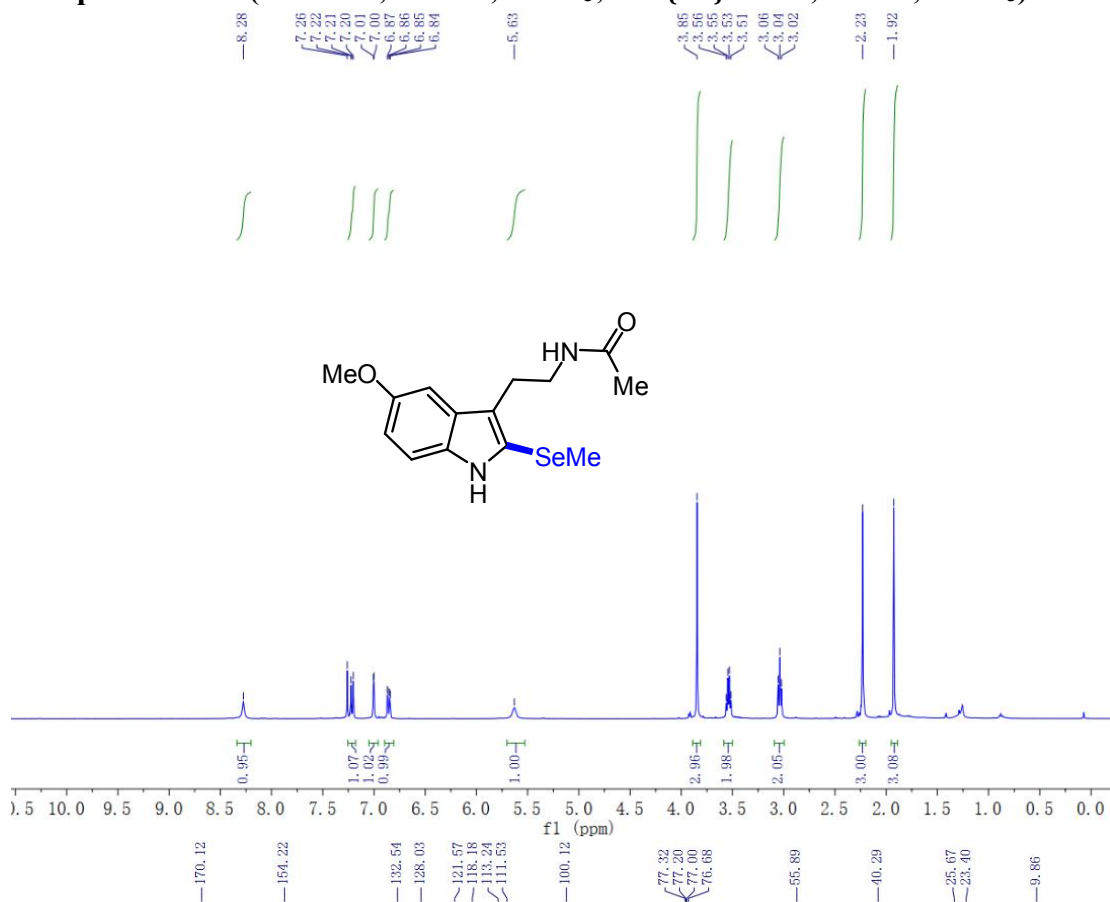
Compound of 5b (¹H NMR, 400 Hz, CDCl₃; ¹³C {¹H} NMR, 100Hz, CDCl₃)



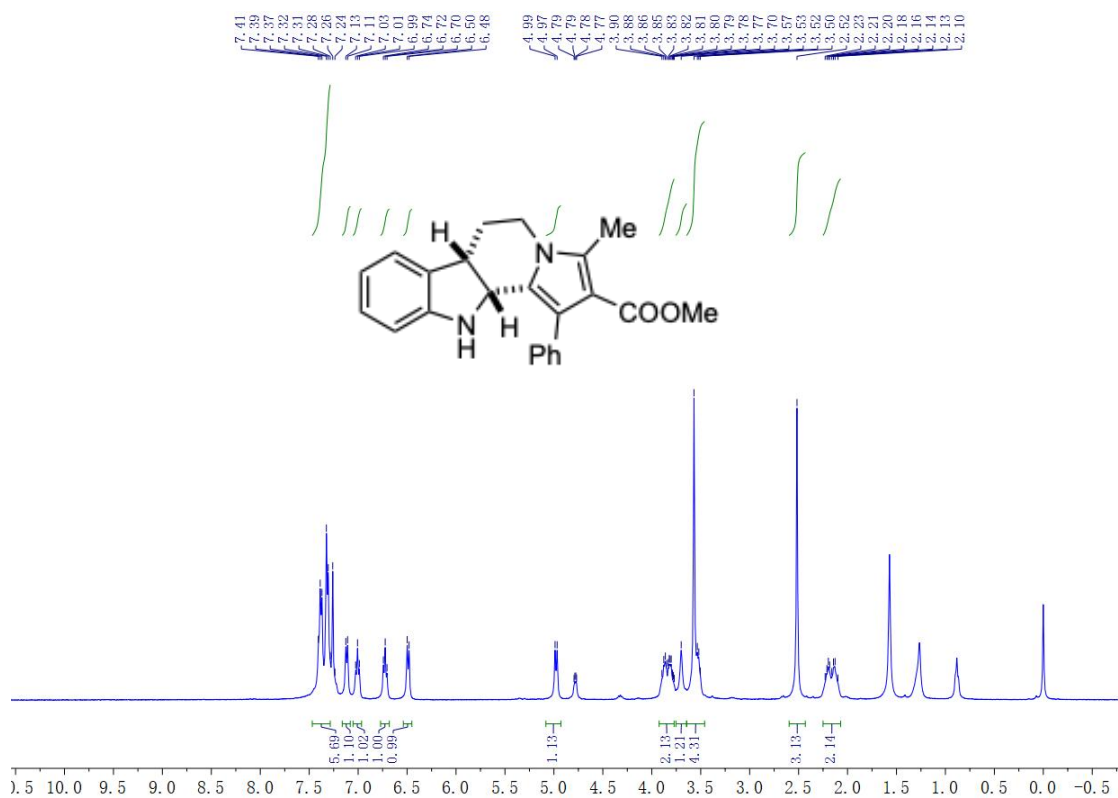
Compound of 5c (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



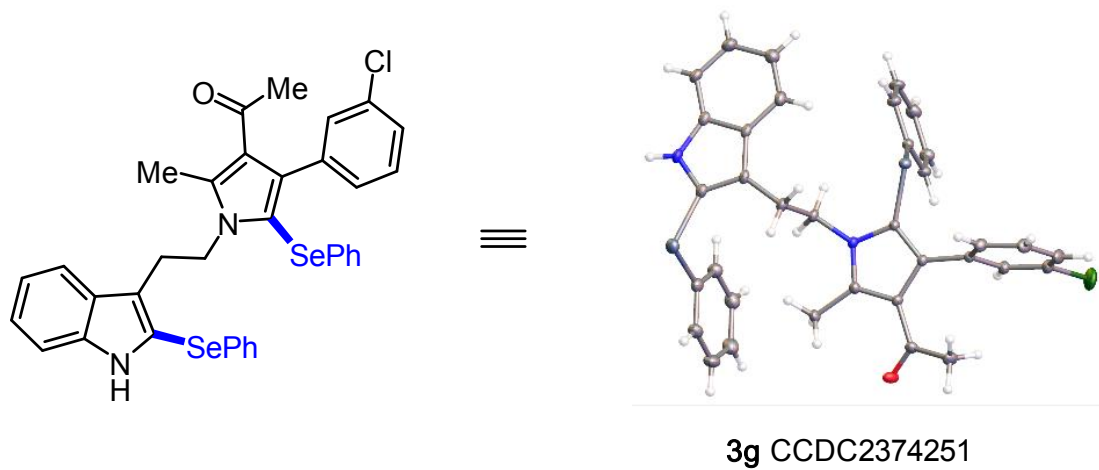
Compound of 5d (^1H NMR, 400 Hz, CDCl_3 ; ^{13}C $\{^1\text{H}\}$ NMR, 100Hz, CDCl_3)



Compound of 6 (¹H NMR, 400 Hz, CDCl₃)



4. Crystal data of compound 3g (CCDC 2374251):



| | | | |
|---|------------------------------------|----------------------------|---------------------------|
| Bond precision: | C-C = 0.0054 Å | Wavelength=1.54184 | |
| Cell: | a=10.36591 (11) alpha=90 | b=16.76936 (19) beta=90 | c=21.6439 (2) gamma=90 |
| Temperature: | 200 K | | |
| | Calculated | Reported | |
| Volume | 3762.35 (7) | 3762.36 (7) | |
| Space group | P 21 21 21 | P 21 21 21 | |
| Hall group | P 2ac 2ab | P 2ac 2ab | |
| Moiety formula | C35 H29 Cl N2 O Se2 [+ solvent] | C35 H29 Cl N2 O Se2 | |
| Sum formula | C35 H29 Cl N2 O Se2 [+ solvent] | C35 H29 Cl N2 O Se2 | |
| Mr | 686.97 | 686.97 | |
| Dx, g cm ⁻³ | 1.213 | 1.213 | |
| Z | 4 | 4 | |
| Mu (mm ⁻¹) | 3.302 | 3.302 | |
| F000 | 1384.0 | 1384.0 | |
| F000' | 1381.89 | | |
| h, k, lmax | 12, 20, 26 | 12, 20, 26 | |
| Nref | 7570 [4229] | 7343 | |
| Tmin, Tmax | 0.653, 0.695 | 0.783, 1.000 | |
| Tmin' | 0.580 | | |
| Correction method= # Reported T Limits: Tmin=0.783 Tmax=1.000 | | | |
| AbsCorr = MULTI-SCAN | | | |
| Data completeness= | 1.74/0.97 | Theta(max)= 73.382 | |
| R(reflections)= | 0.0286 (6744) | wR2(reflections)= | |
| S = 0.958 | Npar= 372 | 0.0691 (7343) | |

Probability level 50%

Crystal sample preparation: Slowly volatilizing a solution of compound **3g** in a mixture of CDCl₃/Hex gave the crystal samples.

5. Crystal data of compound **3a'** (CCDC 2411984):

