

Visible-light-promoted selenylation/cyclization of *o*-(1-alkynyl) benzoates to access seleno-substituted isocumarins

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General information

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All the reactions were carried out under air atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or DMSO-d_6 at 400 MHz. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. Melting points were measured with a micro melting point apparatus. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI or APCI ionization source. LC-MS was obtained on Agilent Technologies (6545 Q-TOF). UV/Vis spectra were recorded using a Shimadzu UV-2600 spectrophotometer. The photoinduced reactions were conducted in a photoreactor: the quartz tube was irradiated using a 50 W white LED lamp (manufactured by Jiadeng, model: CSDT, broadband source = 400-840 nm). The distance between the lamp bulb and the reaction test tube was 3 cm.

Photographic depiction of the reaction setup

The photoinduced reactions were conducted in a photoreactor: the quartz tube was irradiated using a 50 W white LED lamp (manufactured by Jiadeng, model: CSDT, broadband source = 400-840 nm), and a photo of the reaction system (Fig. S1). The distance between the lamp bulb and the reaction test tube was 3 cm.

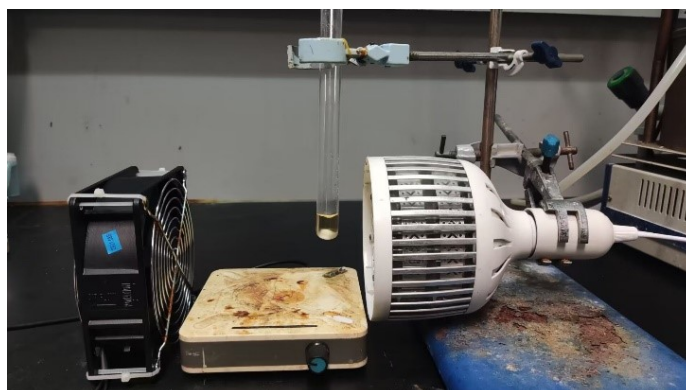
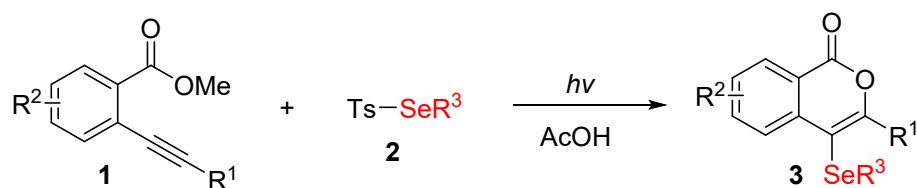


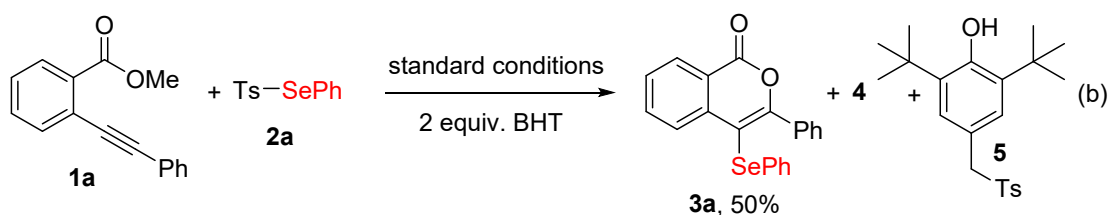
Fig. S1. The photographic of the reaction setup

General Procedure for the Synthesis of Compounds 3.



A solution of *o*-(1-alkynyl)benzoate **1** (0.30 mmol, 1.0 equiv), selenosulfonates **2** (0.33 mmol, 1.1 equiv) in HOAc (3.0 mL) was stirred under the irradiation of 50 W white LEDs (the distance between the tube and the light source was 3 cm) in air atmosphere, and the progress of the reaction was monitored by TLC. After the reaction was complete, saturated sodium bicarbonate solution was added and the resulting mixture was extracted with ethyl acetate (3×5 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2 , petroleum ether/ethyl acetate) yielding the desired products **3**.

Control experiments



A solution of **1a** (23.6 mg, 0.1 mmol), **2a** (34.3 mg, 0.11 mmol), BHT (44.0 mg, 0.2 mmol) in HOAc (1.0 mL) was stirred under the irradiation of 50 W white LEDs in air atmosphere for 3 h. Then the solution was analyzed by LC-MS, **5** was detected (Figure S2), HRMS (m/z) (ESI): calcd for $C_{22}H_{30}NaO_3S$, 397.1808, $[M+Na]^+$ found, 397.1808. The solution was quenched by saturated sodium bicarbonate solution, and extracted with ethyl acetate (3×5 mL), and the organic layer was removed under reduced pressure. The residue was purified by flash column chromatography to give **3a** (18.9 mg, 50%) and byproduct **4** (13.0 mg). 1,2-Diphenyldisilane (**4**). 1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H), 7.25 – 7.19 (m, 3H).

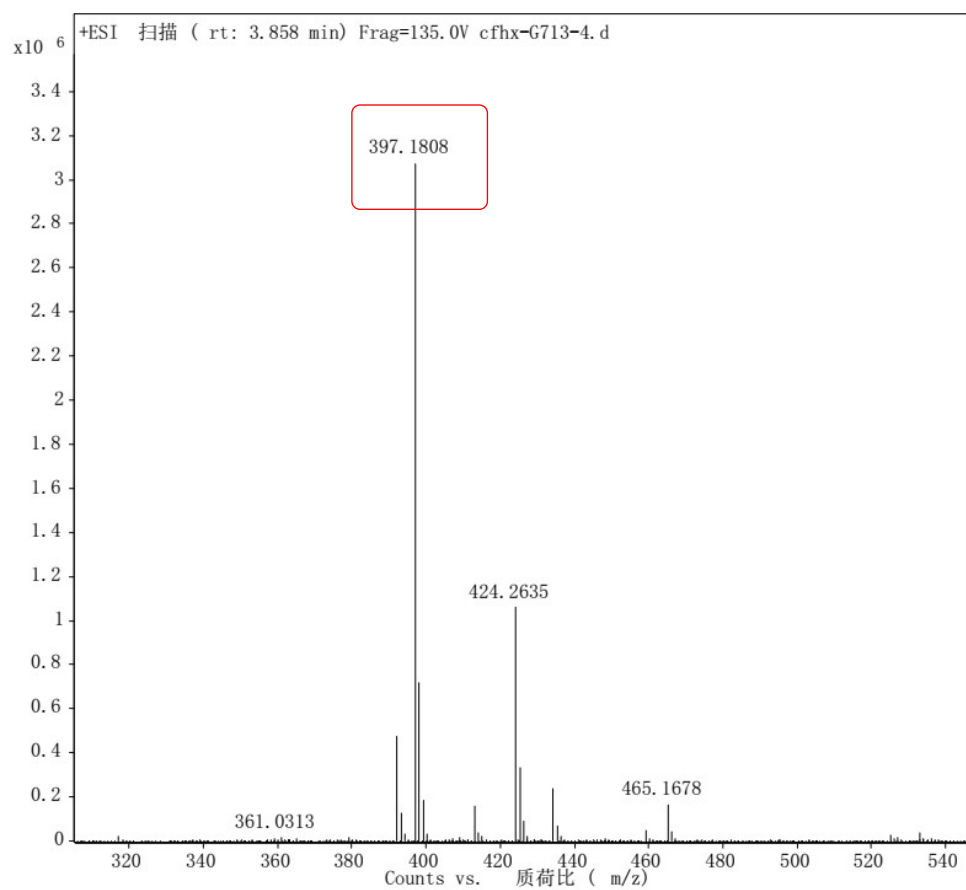


Fig. S2. The LC-MS analysis of **5**

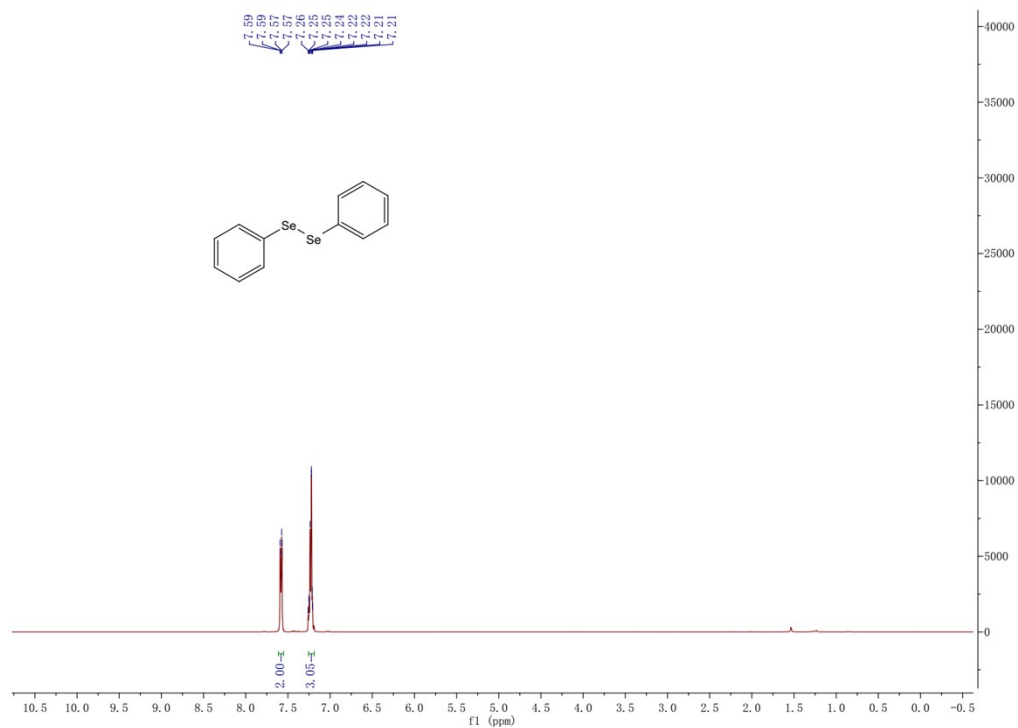
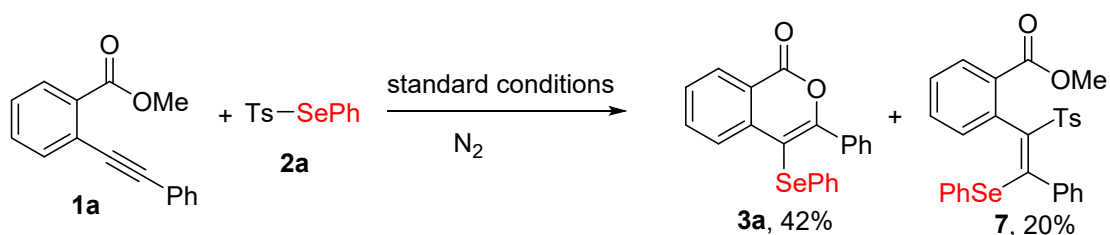


Fig. S3. ^1H NMR spectrum (400 M, CDCl_3) of **4**



A solution of **1a** (23.6 mg, 0.1 mmol), **2a** (34.3 mg, 0.11 mmol), in HOAc (1.0 mL) was stirred under the irradiation of 50 W white LEDs in N_2 atmosphere for 3 h. Then the solution was analyzed by LC-MS, **7** were detected (Figure S4). **7**, HRMS (m/z) (ESI): calcd for $C_{29}H_{24}NaO_4SSe$, 571.0453, $[M+Na]^+$ found, 571.0452. The solution was quenched by saturated sodium bicarbonate solution, and extracted with ethyl acetate (3×5 mL), and the organic layer was removed under reduced pressure. The residue was purified by flash column chromatography to give **3a** (15.9 mg, 42%).

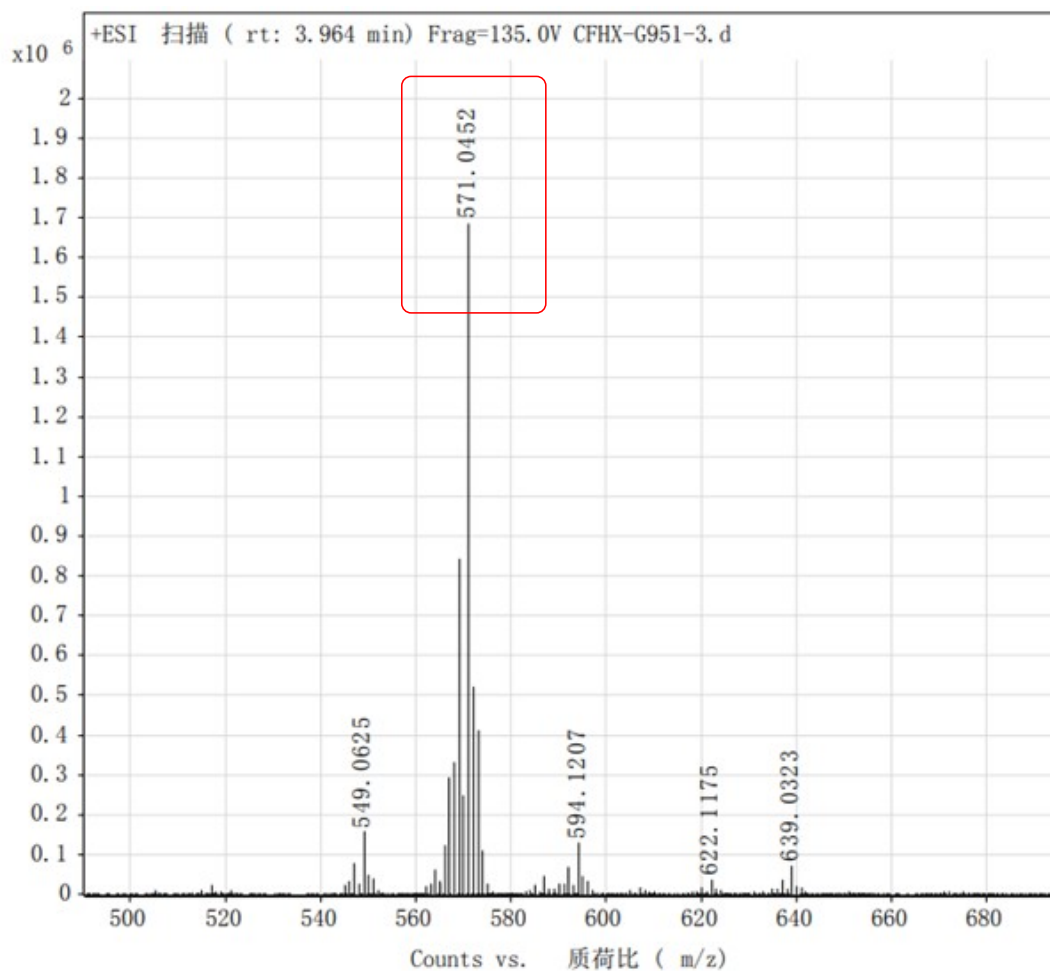
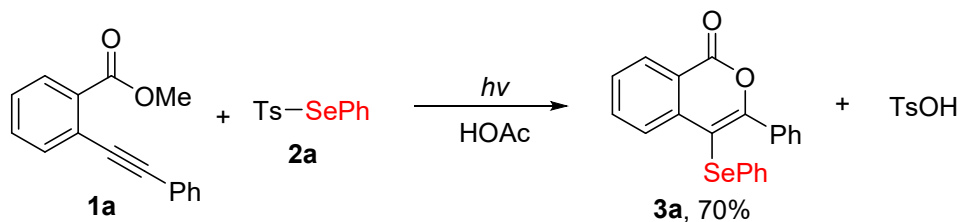


Fig. S4. The LC-MS analysis of **7**



A solution of **1a** (23.6 mg, 0.1 mmol), **2a** (34.3 mg, 0.11 mmol), in HOAc (1.0 mL) was stirred under the irradiation of 50 W white LEDs in air atmosphere for 3 h. Then the solution was analyzed by LC-MS, TsOH was detected (Figure S5), HRMS (m/z) (ESI): calcd for $C_7H_8NaO_3S$, 195.0086, $[M+Na]^+$ found, 195.0087. The solution was quenched by saturated sodium bicarbonate solution, and extracted with ethyl acetate (3×5 mL), and the organic layer was removed under reduced pressure. The residue was purified by flash column chromatography to give **3a** (26.5 mg, 70%).

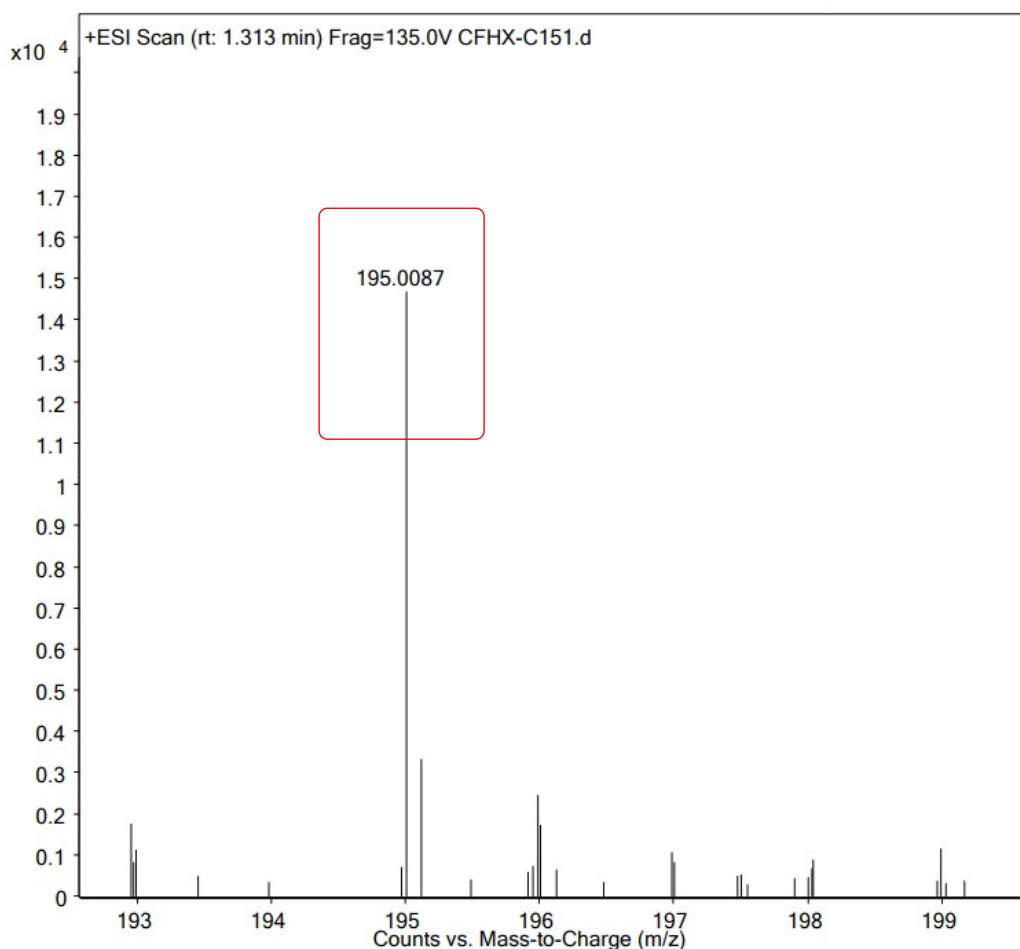


Fig. S5. The LC-MS analysis of TsOH

Effect of Visible Light Irradiation

The reaction between **1a** (0.1 mmol), **2a** (0.15 mmol) in HOAc (1.0 mL) was conducted under the standard conditions on a 0.1 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (50 W white LEDs) under an air atmosphere at room temperature with 1 h and followed by stirring in the absence of light with 1 h. At each time point, one reaction system was suspended and the yield was detected by GC.

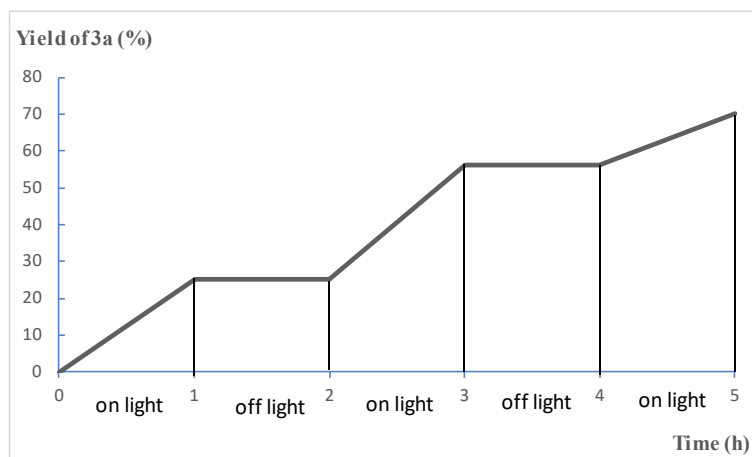


Fig. S5. On/off Experiments

UV/Vis Absorption Experiment

The UV/Vis absorption spectra of **1a**, **2a** and (PhSe)₂ were recorded in 1 cm path quartz cuvettes in a concentration of 0.025 M by using a Shimadzu UV-2600 spectrophotometer, respectively (Fig. 4). These results indicating that **2a** and/or **4** served as photoactive substrates absorbing in visible region and undergoing homolysis.

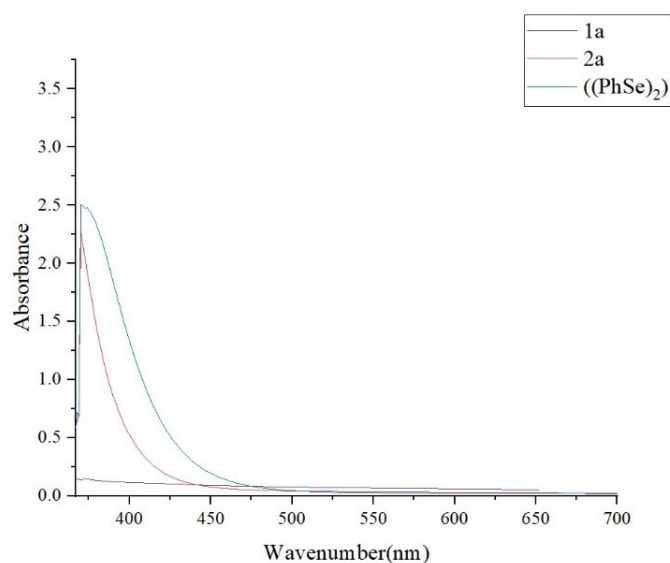
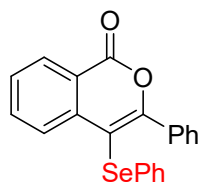


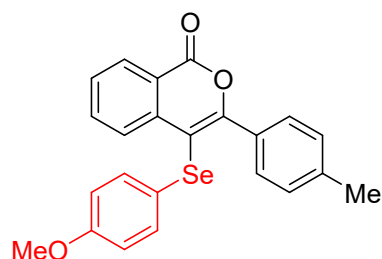
Fig. S6. UV/Vis Absorption Experiment

Characterization Data



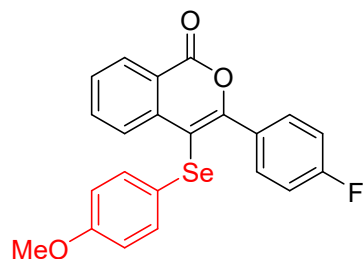
3-Phenyl-4-(phenylselanyl)-1*H*-isochromen-1-one (3a).¹

Yellow solid, (79.4 mg, 70% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 126-127 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.37 (d, $J = 7.8$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.72 – 7.67 (m, 3H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.47 – 7.38 (m, 3H), 7.23 – 7.12 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.6, 159.5, 138.3, 135.3, 133.9, 131.8, 130.1, 129.6, 129.4, 128.7, 128.6, 128.2, 127.7, 126.4, 120.7, 104.7. HRMS (m/z) (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{O}_2\text{Se}$ 379.0232 $[\text{M}+\text{H}]^+$ found 379.0229.



4-((4-Methoxyphenyl)selanyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (3b).

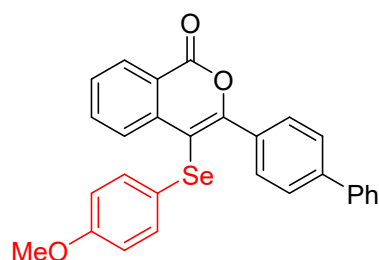
Yellow oil, (77.2 mg, 61% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.22 (d, $J = 7.2$ Hz, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.86 – 7.81 (m, 1H), 7.64 – 7.56 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.66 (s, 3H), 2.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 159.0, 158.4, 140.0, 137.8, 135.7, 131.3, 130.8, 129.6, 129.1, 128.9, 128.4, 127.8, 120.9, 120.5, 115.4, 104.7, 55.1, 21.0. HRMS (m/z) (ESI): calcd for $\text{C}_{23}\text{H}_{18}\text{NaO}_3\text{Se}$ 445.0313 $[\text{M}+\text{Na}]^+$ found 445.0312.



3-(4-Fluorophenyl)-4-((4-methoxyphenyl)selanyl)-1*H*-isochromen-1-one (3c).

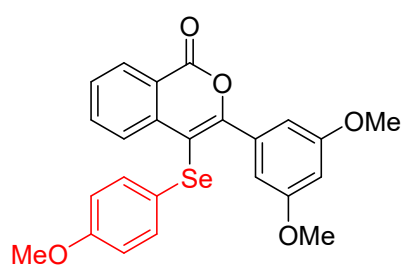
Yellow solid, (80.5 mg, 63% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 139-

140 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.23 (dd, $J = 7.8, 0.8$ Hz, 1H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.88 – 7.83 (m, 1H), 7.77 – 7.73 (m, 2H), 7.65 – 7.60 (m, 1H), 7.37 – 7.31 (m, 2H), 7.22 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.66 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 162.8 (d, $J = 248.0$ Hz), 160.8, 158.4, 157.8, 137.6, 135.7, 132.2, 132.1, 130.91, 130.6 (d, $J = 3.3$ Hz), 129.2, 129.1, 127.8, 120.6 (d, $J = 7.7$ Hz), 115.0 (d, $J = 21.9$ Hz), 105.3, 55.1. HRMS (m/z) (ESI): calcd for $\text{C}_{22}\text{H}_{15}\text{FNaO}_3\text{Se}$ 449.0063 $[\text{M}+\text{Na}]^+$ found 449.0060.



3-([1,1'-Biphenyl]-4-yl)-4-(4-methoxyphenyl)selanyl-1H-isochromen-1-one (3d).

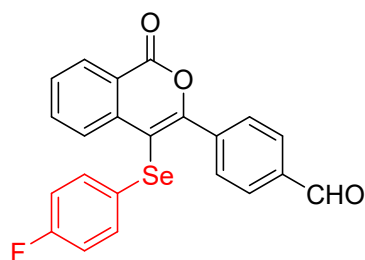
Yellow solid, (77.0 mg, 53% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 120-121 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.23 (d, $J = 7.7$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.85 – 7.77 (m, 5H), 7.73 (d, $J = 7.4$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.3$ Hz, 1H), 7.24 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.65 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 158.5, 158.4, 141.6, 139.1, 137.7, 135.6, 133.0, 130.8, 130.3, 129.1, 129.0, 128.0, 127.8, 126.8, 126.0, 120.9, 120.6, 115.4, 105.0, 55.0. HRMS (m/z) (ESI): calcd for $\text{C}_{28}\text{H}_{20}\text{NaO}_3\text{Se}$ 507.0470 $[\text{M}+\text{Na}]^+$ found 507.0471.



3-(3,5-Dimethoxyphenyl)-4-(4-methoxyphenyl)selanyl-1H-isochromen-1-one (3e).

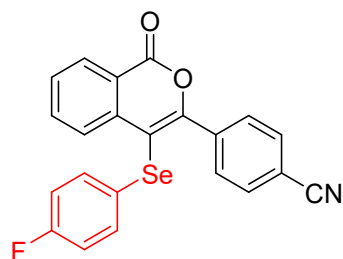
Yellow solid, (57.6 mg, 41% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 113-114 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.22 (dd, $J = 7.8, 0.8$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.87 – 7.82 (m, 1H), 7.65 – 7.60 (m, 1H), 7.27 – 7.21 (m, 2H), 6.83 – 6.79 (m, 4H), 6.64 (t, $J = 2.2$ Hz, 1H), 3.73 (s, 6H), 3.67 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.8, 159.8, 158.6, 158.3, 137.7, 135.8, 135.7, 130.8, 129.2, 129.1, 127.8, 121.1, 120.6, 115.3, 107.7, 105.1, 101.7,

55.4, 55.1. HRMS (m/z) (ESI): calcd for $C_{24}H_{20}NaO_5Se$ 491.0368 $[M+Na]^+$ found 491.0371.



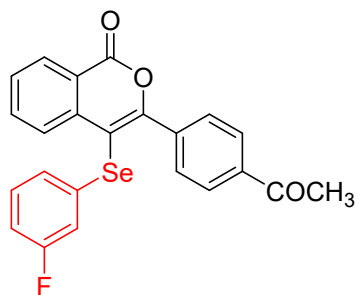
4-(4-(4-Fluorophenyl)selanyl)-1-oxo-1H-isochromen-3-ylbenzaldehyde (3f).

Yellow solid, (92.9 mg, 73% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 178-179 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 10.06 (s, 1H), 8.27 – 8.22 (m, 1H), 8.00 (d, $J = 8.3$ Hz, 2H), 7.96 – 7.84 (m, 4H), 7.68–7.64 (m, 1H), 7.37 – 7.30 (m, 2H), 7.10 – 7.02 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $DMSO-d_6$) δ 192.7, 162.4, 160.0, 159.3 (d, $J = 267.7$ Hz), 139.3, 137.2, 136.8, 135.8, 131.0 (d, $J = 7.8$ Hz), 130.4, 129.5, 129.3, 128.9, 127.7, 126.0 (d, $J = 3.0$ Hz), 120.9, 116.7 (d, $J = 21.7$ Hz), 105.4. HRMS (m/z) (ESI): calcd for $C_{22}H_{13}FNaO_3Se$ 446.9906 $[M+Na]^+$ found 446.9905.



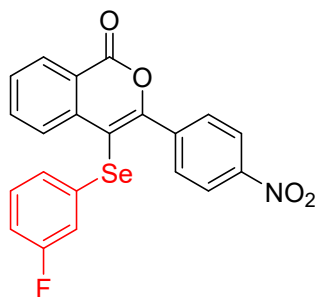
4-(4-(4-Fluorophenyl)selanyl)-1-oxo-1H-isochromen-3-ylbenzotrile (3g).

Yellow solid, (84.6 mg, 67% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 164-165 °C. 1H NMR (400 MHz, $DMSO-d_6$) δ 8.27 (dd, $J = 7.9, 0.9$ Hz, 1H), 7.12 – 7.05 (m, 6H), 8.00 – 7.88 (m, 1H), 7.39 – 7.33 (m, 2H), 7.12 – 7.05 (m, 2H). $^{13}C\{H\}$ NMR (100 MHz, $DMSO-d_6$) δ 161.2 (d, $J = 243.9$ Hz), 160.5, 157.3, 138.3, 137.1, 135.8, 131.9, 131.0 (d, $J = 7.8$ Hz), 130.5, 129.5, 129.3, 127.6, 125.9 (d, $J = 3.0$ Hz), 120.9, 118.3, 116.7 (d, $J = 21.7$ Hz), 112.5, 105.6. HRMS (m/z) (ESI): calcd for $C_{22}H_{12}FNNaO_2Se$ 443.9909 $[M+Na]^+$ found 443.9908.



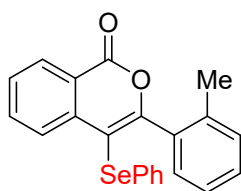
3-(4-Acetylphenyl)-4-((3-fluorophenyl)selanyl)-1*H*-isochromen-1-one (3h).

Yellow oil, (97.2 mg, 74% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.29 – 8.24 (m, 1H), 8.06 – 8.01 (m, 2H), 7.90 – 7.81 (m, 4H), 7.67 (ddd, $J = 8.1, 6.8, 1.7$ Hz, 1H), 7.28 – 7.20 (m, 2H), 7.15 (dd, $J = 6.9, 1.3$ Hz, 1H), 6.99 (ddd, $J = 8.2, 2.5, 1.8$ Hz, 1H), 2.61 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 197.5, 162.6 (d, $J = 247.3$ Hz), 160.7, 158.6, 138.1, 137.6, 137.2, 135.8, 133.7 (d, $J = 7.0$ Hz), 131.2 (d, $J = 8.3$ Hz), 129.8, 129.4, 129.3, 127.7, 127.5, 124.3 (d, $J = 2.8$ Hz), 121.0, 115.2 (d, $J = 23.5$ Hz), 113.3 (d, $J = 21.2$ Hz), 104.3, 26.9. HRMS (m/z) (ESI): calcd for $\text{C}_{23}\text{H}_{16}\text{FO}_3\text{Se}$ 439.0243 $[\text{M}+\text{H}]^+$ found 439.0246.



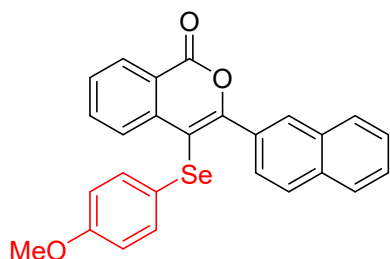
4-((3-Fluorophenyl)selanyl)-3-(4-nitrophenyl)-1*H*-isochromen-1-one (3i).

Yellow solid, (80.7 mg, 61% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 137-138 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.36 – 8.31 (m, 2H), 8.28 (d, $J = 7.6$ Hz, 1H), 8.00 – 7.94 (m, 2H), 7.91 – 7.84 (m, 2H), 7.72 – 7.66 (m, 1H), 7.28 – 7.22 (m, 2H), 7.19 – 7.15 (m, 1H), 7.02 – 6.96 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 162.6 (d, $J = 247.4$ Hz), 160.5, 157.4, 148.1, 140.1, 137.0, 135.8, 133.4 (d, $J = 7.1$ Hz), 131.2 (d, $J = 8.3$ Hz), 131.0, 129.6, 129.3, 127.5, 124.5 (d, $J = 2.8$ Hz), 123.1, 121.1, 115.4 (d, $J = 23.4$ Hz), 113.4 (d, $J = 21.2$ Hz), 105.0. HRMS (m/z) (ESI): calcd for $\text{C}_{21}\text{H}_{12}\text{FNNaO}_4\text{Se}$ 463.9808 $[\text{M}+\text{Na}]^+$ found 463.9810.



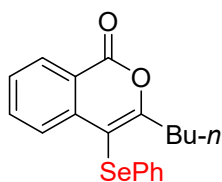
4-(Phenylselanyl)-3-(*o*-tolyl)-1*H*-isochromen-1-one (3j).²

Yellow oil, (72.9 mg, 62% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.26 (d, $J = 7.4$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.86 – 7.80 (m, 1H), 7.68 – 7.61 (m, 1H), 7.42 – 7.35 (m, 2H), 7.31 – 7.29 (m, 1H), 7.25 – 7.14 (m, 6H), 2.23 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 161.4, 159.9, 137.8, 136.8, 136.2, 134.5, 131.4, 130.5, 130.3, 130.1, 129.9, 129.8, 129.6, 129.2, 127.8, 126.8, 125.9, 121.1, 106.1, 19.6. HRMS (m/z) (ESI): calcd for $\text{C}_{22}\text{H}_{16}\text{NaO}_2\text{Se}$ 415.0208 $[\text{M}+\text{Na}]^+$ found 415.0208.



4-((4-Methoxyphenyl)selanyl)-3-(naphthalen-2-yl)-1*H*-isochromen-1-one (3l).

Yellow solid, (72.8 mg, 53% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 94-95 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.29 – 8.23 (m, 2H), 8.05 – 7.97 (m, 4H), 7.90 – 7.85 (m, 1H), 7.80 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.67 – 7.58 (m, 3H), 7.22 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 8.9$ Hz, 2H), 3.66 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 158.7, 158.4, 137.8, 135.7, 133.2, 131.8, 131.4, 131.0, 129.8, 129.2, 129.1, 128.5, 127.8, 127.6, 127.5, 127.3, 126.8, 126.6, 121.0, 120.6, 115.3, 105.5, 55.1. HRMS (m/z) (ESI): calcd for $\text{C}_{26}\text{H}_{18}\text{NaO}_3\text{Se}$ 481.0313 $[\text{M}+\text{Na}]^+$ found 446.0311.



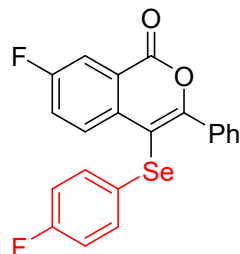
3-Butyl-4-(phenylselanyl)-1*H*-isochromen-1-one (3m).¹

Yellow oil, (60.2 mg, 56% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.14 (d, $J = 7.2$ Hz, 1H), 7.83 – 7.74 (m, 2H), 7.56 – 7.51 (m, 1H), 7.28 – 7.13 (m, 5H), 2.99 – 2.93 (m, 2H), 1.62 – 1.53 (m, 2H), 1.33 – 1.24 (m, 2H), 0.81 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 163.2, 160.9, 137.6, 135.6, 130.9, 129.6, 129.1, 128.5, 128.4, 126.8, 126.4, 120.0, 103.4, 33.7, 29.5, 21.6, 13.6. HRMS (m/z) (ESI): calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2\text{Se}$ 359.0545 $[\text{M}+\text{H}]^+$ found 359.0545.



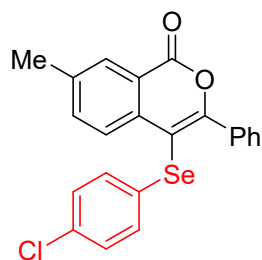
4-(Phenylselanyl)-1H-isochromen-1-one (3n).²

Yellow oil, (53.5 mg, 59% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.19 (dd, $J = 7.8, 0.6$ Hz, 1H), 8.14 (s, 1H), 7.86 – 7.81 (m, 1H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.65 – 7.60 (m, 1H), 7.42 – 7.38 (m, 2H), 7.27 – 7.18 (m, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 151.0, 136.4, 135.7, 130.3, 129.6, 129.5, 129.4, 126.9, 126.7, 121.5, 106.4. HRMS (m/z) (ESI): calcd for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Se}$ 302.9919 $[\text{M}+\text{H}]^+$ found 302.9920.



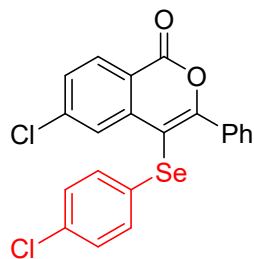
7-Fluoro-4-((4-fluorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3o).

Yellow solid, (87.0 mg, 70% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 142–143 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.98– 7.95 (m, 1H), 7.93– 7.80 (m, 1H), 7.75 – 7.69 (m, 1H), 7.65 (dd, $J = 7.6, 1.8$ Hz, 2H), 7.51 – 7.44 (m, 3H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 161.6 (d, $J = 248.7$ Hz), 160.1, 160.0, 158.9 (d, $J = 2.4$ Hz), 134.3 (d, $J = 2.3$ Hz), 133.7, 131.2, 130.6 (d, $J = 8.2$ Hz), 130.2, 129.5, 129.4, 127.9, 123.7 (d, $J = 22.8$ Hz), 122.4 (d, $J = 8.2$ Hz), 114.5 (d, $J = 23.4$ Hz), 103.1. HRMS (m/z) (ESI): calcd for $\text{C}_{21}\text{H}_{13}\text{F}_2\text{O}_2\text{Se}$ 415.0043 $[\text{M}+\text{H}]^+$ found 415.0040.



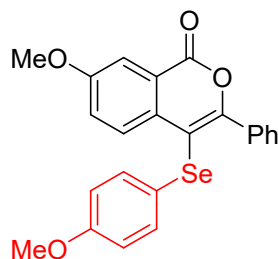
4-((4-Chlorophenyl)selanyl)-7-methyl-3-phenyl-1H-isochromen-1-one (3p).³

Yellow solid, (97.1 mg, 76% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 160-161 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.05 (s, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.67 – 7.63 (m, 3H), 7.49 – 7.44 (m, 3H), 7.30 – 7.23 (m, 4H), 2.43 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 158.7, 139.2, 136.9, 135.0, 134.0, 131.1, 130.4, 130.2, 130.1, 129.5, 128.9, 127.9, 127.5, 120.5, 103.8, 20.7. HRMS (m/z) (ESI): calcd for $\text{C}_{22}\text{H}_{16}\text{ClO}_2\text{Se}$ 426.9999 $[\text{M}+\text{H}]^+$ found 427.0000.



6-Chloro-4-((4-chlorophenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3q).

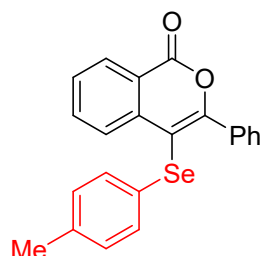
Yellow solid, (97.7 mg, 73% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 115-116 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.24 – 8.18 (m, 1H), 7.80– 7.79 (m, 1H), 7.66 – 7.63 (m, 3H), 7.51 – 7.44 (m, 3H), 7.35 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 160.1, 140.8, 139.4, 133.7, 131.5, 131.4, 130.4, 130.2, 129.9, 129.5, 129.4, 129.2, 127.9, 126.6, 119.5, 102.7. HRMS (m/z) (ESI): calcd for $\text{C}_{21}\text{H}_{12}\text{Cl}_2\text{NaO}_2\text{Se}$ 468.9272 $[\text{M}+\text{Na}]^+$ found 468.9274.



7-Methoxy-4-((4-methoxyphenyl)selanyl)-3-phenyl-1H-isochromen-1-one (3r).

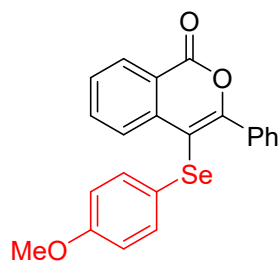
Yellow solid, (59.1 mg, 45% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 158-159 °C. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.91 (d, $J = 8.9$ Hz, 1H), 7.67 (dd, $J = 7.0, 2.3$ Hz, 2H),

7.62 (d, $J = 2.7$ Hz, 1H), 7.49 – 7.42 (m, 4H), 7.19 (d, $J = 8.7$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 3.87 (s, 3H), 3.66 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.8, 159.5, 158.4, 156.6, 134.0, 131.1, 130.8, 129.9, 129.8, 129.7, 127.9, 124.0, 121.7, 120.9, 115.4, 110.4, 104.7, 55.8, 55.1. HRMS (m/z) (ESI): calcd for $\text{C}_{23}\text{H}_{18}\text{NaO}_4\text{Se}$ 461.0263 $[\text{M}+\text{Na}]^+$ found 461.0264.



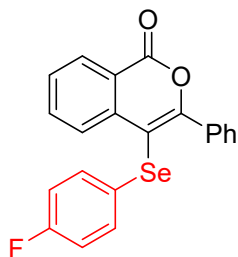
3-Phenyl-4-(*p*-tolylselanyl)-1*H*-isochromen-1-one (3s).²

Yellow solid, (81.2 mg, 69% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 164–165 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 8.1$ Hz, 1H), 7.84 (t, $J = 7.7$ Hz, 1H), 7.69 – 7.61 (m, 3H), 7.50 – 7.47 (m, 3H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 2.19 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.9, 159.1, 137.7, 135.9, 135.7, 134.1, 130.3, 130.1, 129.5, 129.2, 129.1, 128.6, 127.9, 127.7, 127.5, 120.6, 104.2, 20.5. HRMS (m/z) (ESI): calcd for $\text{C}_{22}\text{H}_{17}\text{O}_2\text{Se}$ 393.0388 $[\text{M}+\text{H}]^+$ found 393.0386.



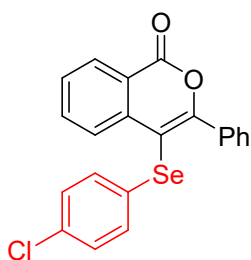
4-((4-Methoxyphenyl)selanyl)-3-phenyl-1*H*-isochromen-1-one (3t).¹

Yellow oil, (64.9 mg, 53% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). ^1H NMR (400 MHz, CDCl_3) δ 8.34 (dd, $J = 7.9, 1.0$ Hz, 1H), 8.13 (d, $J = 8.1$ Hz, 1H), 7.75 – 7.66 (m, 3H), 7.54 – 7.49 (m, 1H), 7.47 – 7.39 (m, 3H), 7.18 – 7.11 (m, 2H), 6.73 (d, $J = 8.9$ Hz, 2H), 3.72 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.7, 158.9, 158.8, 138.4, 135.2, 134.0, 131.4, 130.0, 129.8, 129.6, 128.5, 128.2, 127.7, 121.3, 120.8, 115.1, 105.9, 55.2. HRMS (m/z) (ESI): calcd for $\text{C}_{22}\text{H}_{16}\text{NaO}_3\text{Se}$ 431.0157 $[\text{M}+\text{Na}]^+$ found 431.0155.



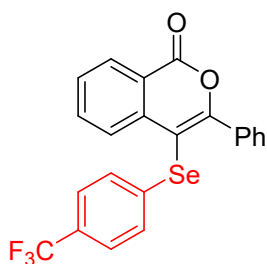
4-((4-Fluorophenyl)selanyl)-3-phenyl-1*H*-isochromen-1-one (3u).¹

Yellow solid, (85.5 mg, 72% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 133-134 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.92 (d, $J = 7.6$ Hz, 1H), 7.87 – 7.81 (m, 1H), 7.69 – 7.61 (m, 3H), 7.52 – 7.45 (m, 3H), 7.35 – 7.30 (m, 2H), 7.09 – 7.03 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.3, 160.8, 159.3, 137.5, 135.7, 134.0, 130.8 (d, $J = 7.8$ Hz), 130.1, 129.5, 129.2, 129.1, 127.9, 127.6, 126.2 (d, $J = 3.1$ Hz), 120.6, 116.6 (d, $J = 21.7$ Hz), 104.4. HRMS (m/z) (ESI): calcd for C₂₁H₁₃FN₂O₂Se 418.9957 [M+Na]⁺ found 418.9956.



4-((4-Chlorophenyl)selanyl)-3-phenyl-1*H*-isochromen-1-one (3v).¹

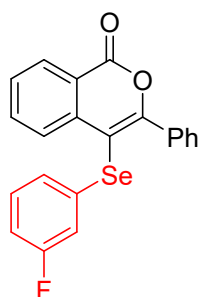
Yellow solid, (91.5 mg, 74% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 146-147 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.25 (d, $J = 7.8$ Hz, 1H), 7.90 – 7.82 (m, 2H), 7.68 – 7.62 (m, 3H), 7.51 – 7.45 (m, 3H), 7.31 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.5$ Hz, 2H). ¹³C {¹H} NMR (100 MHz, DMSO-*d*₆) δ 160.8, 159.6, 137.4, 135.8, 134.0, 131.1, 130.4, 130.1, 129.4, 129.2, 129.1, 127.9, 127.5, 120.7, 103.8. HRMS (m/z) (ESI): calcd for C₂₁H₁₃ClNaO₂Se 434.9662 [M+Na]⁺ found 434.9663.



3-Phenyl-4-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-isochromen-1-one (3w).⁴

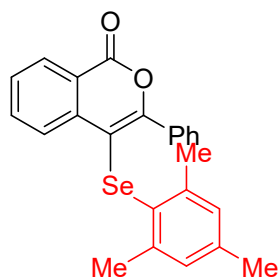
Yellow solid, (95.0 mg, 71% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1), m.p. = 165-

166 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.69 – 7.63 (m, 3H), 7.54 – 7.44 (m, 7H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.8, 160.0, 138.0, 137.3, 135.9, 133.9, 130.2, 129.3, 129.2, 128.6, 128.0, 127.3, 126.6 (q, *J* = 32.0 Hz), 126.1 (q, *J* = 3.6 Hz), 124.2 (d, *J* = 271.9 Hz), 120.7, 103.2. HRMS (*m/z*) (ESI): calcd for C₂₂H₁₄F₃O₂Se 447.0106 [M+H]⁺ found 447.0105.



4-((3-Fluorophenyl)selanyl)-3-phenyl-1*H*-isochromen-1-one (3x).

Yellow solid, (84.3 mg, 71% yield), *R*_f = 0.5 (petroleum ether: ethyl acetate= 30:1), m.p. = 125-126 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.71 – 7.65 (m, 2H), 7.65 – 7.60 (m, 1H), 7.50 – 7.43 (m, 3H), 7.27 – 7.17 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 8.5, 2.2 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.5 (d, *J* = 247.4 Hz), 160.8, 159.7, 137.4, 135.6, 134.0, 133.9 (d, *J* = 7.0 Hz), 131.2 (d, *J* = 8.2 Hz), 130.1, 129.4, 129.2, 129.1, 127.9, 127.4, 124.3 (d, *J* = 2.8 Hz), 120.7, 115.2 (d, *J* = 23.4 Hz), 113.2 (d, *J* = 21.2 Hz), 103.5. HRMS (*m/z*) (ESI): calcd for C₂₁H₁₃FNaO₂Se 418.9957 [M+Na]⁺ found 418.9958.

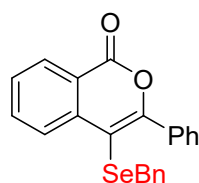


4-(Mesitylselanyl)-3-phenyl-1*H*-isochromen-1-one (3y).¹

Yellow solid, (63.0 mg, 50% yield), *R*_f = 0.5 (petroleum ether: ethyl acetate= 30:1), m.p. = 132-133 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.21 – 8.16 (m, 1H), 7.80 – 7.74 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.46 (m, 6H), 6.76 (s, 2H), 2.14 (s, 6H), 2.10 (s, 3H). ¹³C NMR (100MHz, DMSO-*d*₆) δ 160.8, 155.9, 140.7, 137.7, 137.4, 135.3,

133.8, 130.1, 129.6, 129.3, 129.0, 128.9, 127.9, 127.5, 126.9, 120.1, 106.3, 23.2, 20.3.

HRMS (m/z) (ESI): calcd for $C_{24}H_{20}NaO_2Se$ 443.0521 $[M+Na]^+$ found 443.0520.



4-(Benzylselanyl)-3-phenyl-1H-isochromen-1-one (3z).

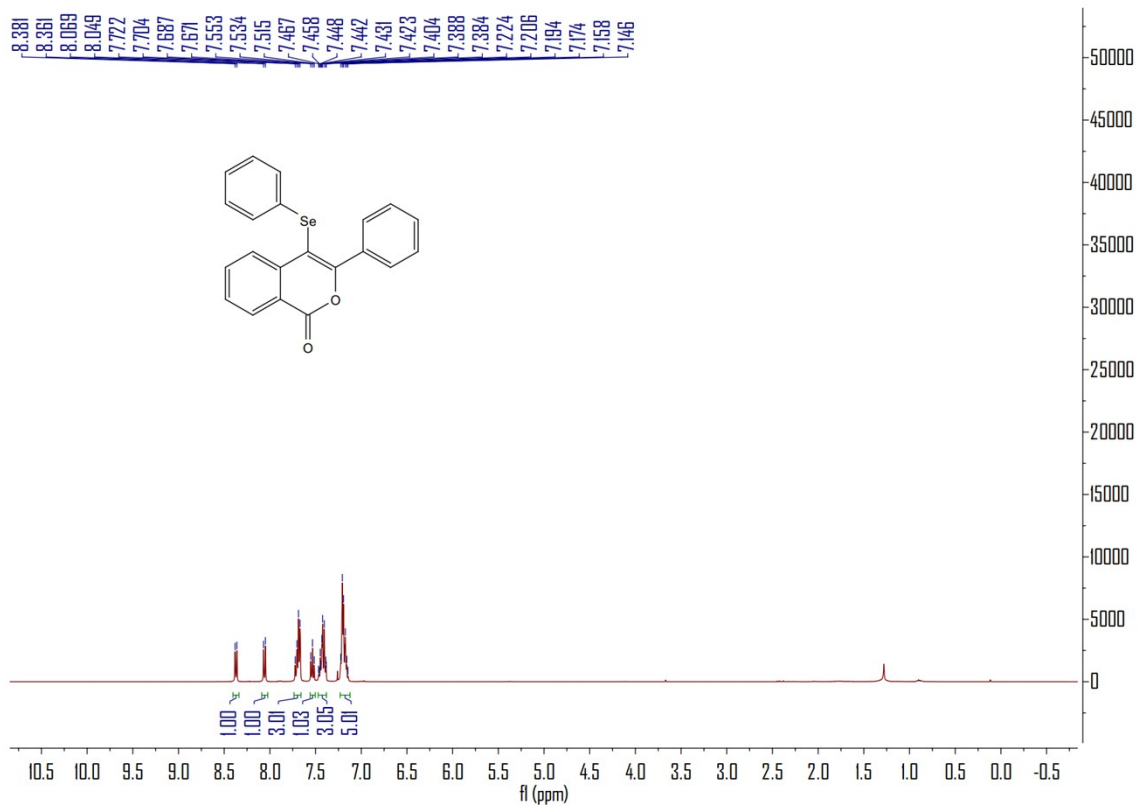
Yellow oil, (43.5 mg, 37% yield), $R_f = 0.5$ (petroleum ether: ethyl acetate= 30:1). 1H NMR (400 MHz, $DMSO-d_6$) δ 8.20 (dd, $J = 7.9, 1.0$ Hz, 1H), 8.11 (d, $J = 7.9$ Hz, 1H), 7.94 – 7.88 (m, 1H), 7.67 – 7.61 (m, 1H), 7.46 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 7.12 – 7.06 (m, 3H), 6.85 – 6.82 (m, 2H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 160.8, 158.4, 138.1, 137.8, 135.7, 134.0, 129.6, 129.1, 128.8, 128.7, 128.1, 127.9, 127.6, 126.7, 125.5, 119.9, 104.7, 31.4. HRMS (m/z) (ESI): calcd for $C_{22}H_{16}NaO_2Se$ 415.0208 $[M+Na]^+$ found 415.0206.

References

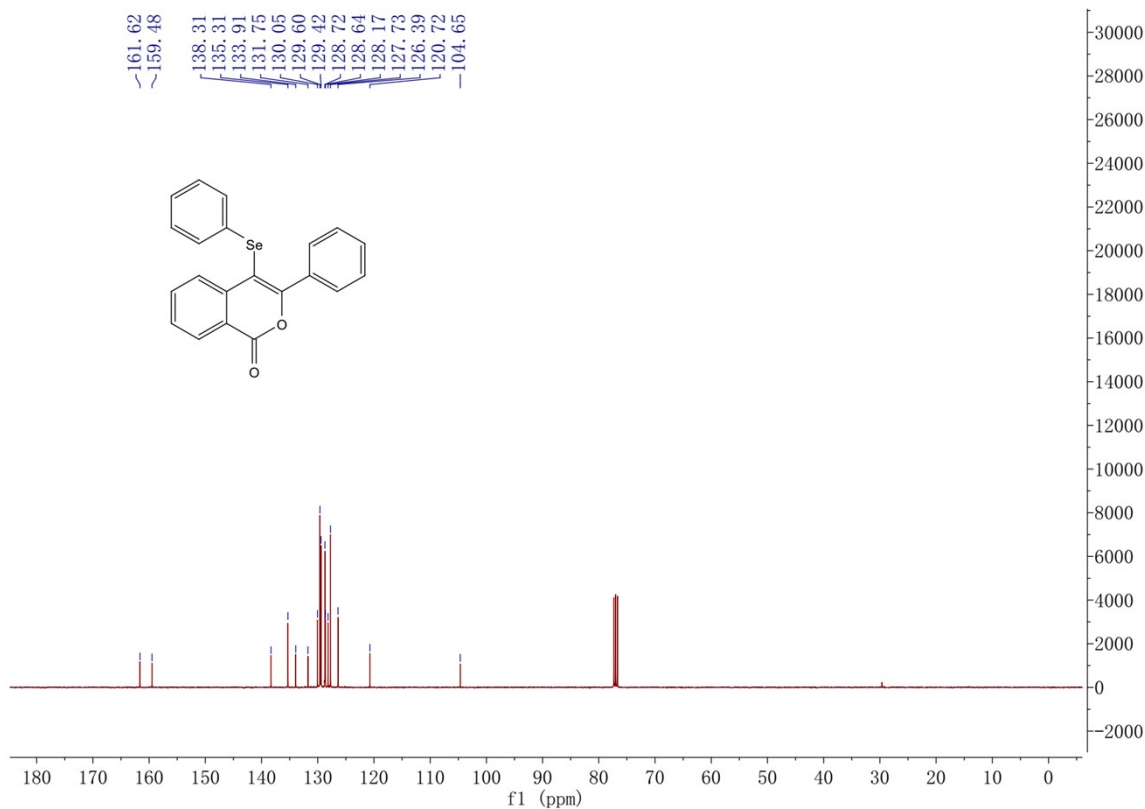
1. H. A. Goulart, J. S. S. Neto, A. M. Barcellos, K. B. Silva, M. C. de Moraes, R. G. Jacob, E. J. Lenardao, T. Barcellos, G. Perin, *J. Org. Chem.* 2021, **86**, 14016.
2. X. Lin, Z. Fang, C. Zeng, C. Zhu, X. Pang, C. Liu, W. He, J. Duan, N. Qin, K. Guo, *Chem. Eur. J.* 2020, **26**, 13738.
3. A. Speraça, B. Godoi, S. Pinton, D. F. Back, P. H. Menezes, G. Zeni, *J. Org. Chem.* 2011, **76**, 6789.
4. G. Jin, W. Gao, Y. Zhou, M. Liu, H. Wu, *RSC Adv.* 2020, **10**, 30439.

Copies of NMR spectra for all products

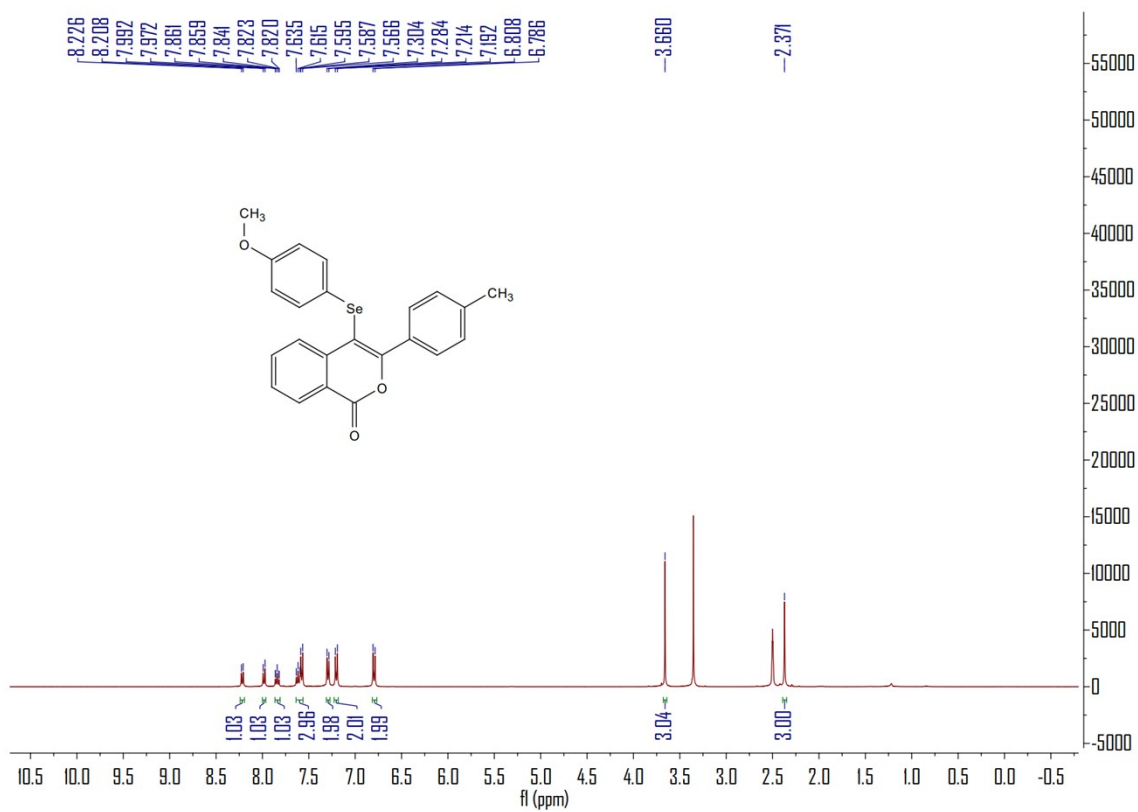
^1H NMR spectrum (400 M, CDCl_3) of **3a**



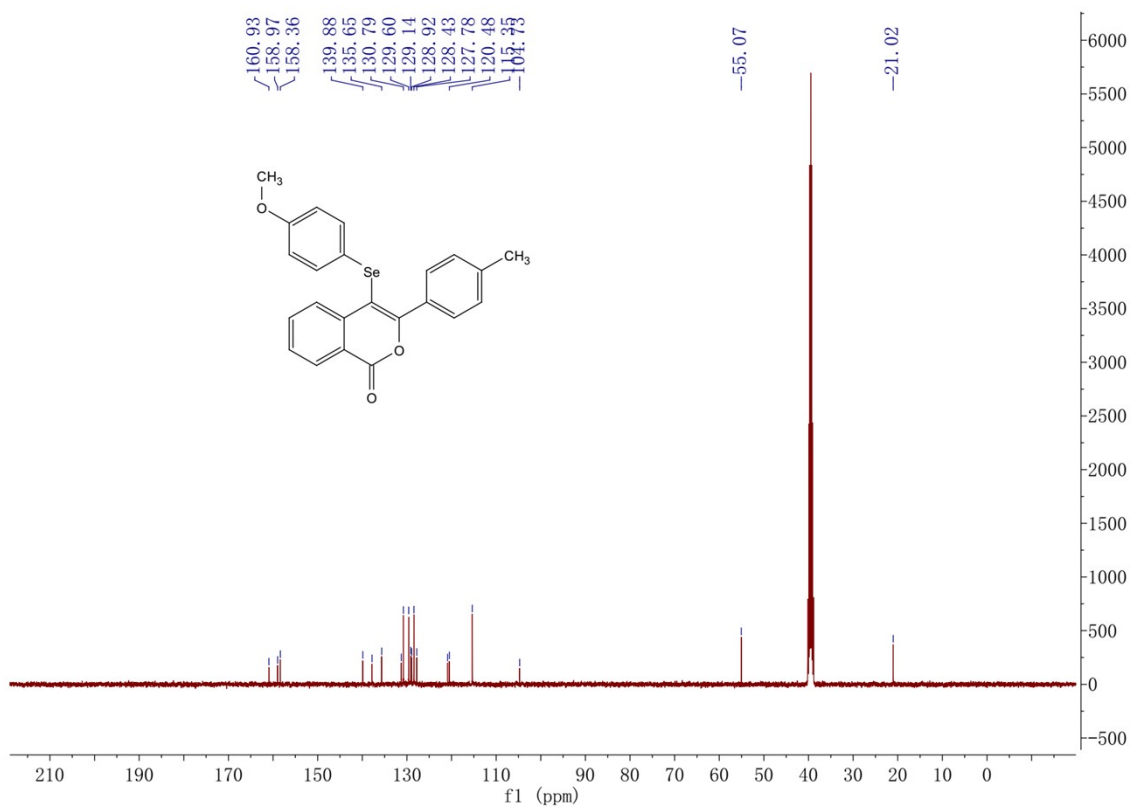
^{13}C NMR spectrum (100 M, CDCl_3) of **3a**



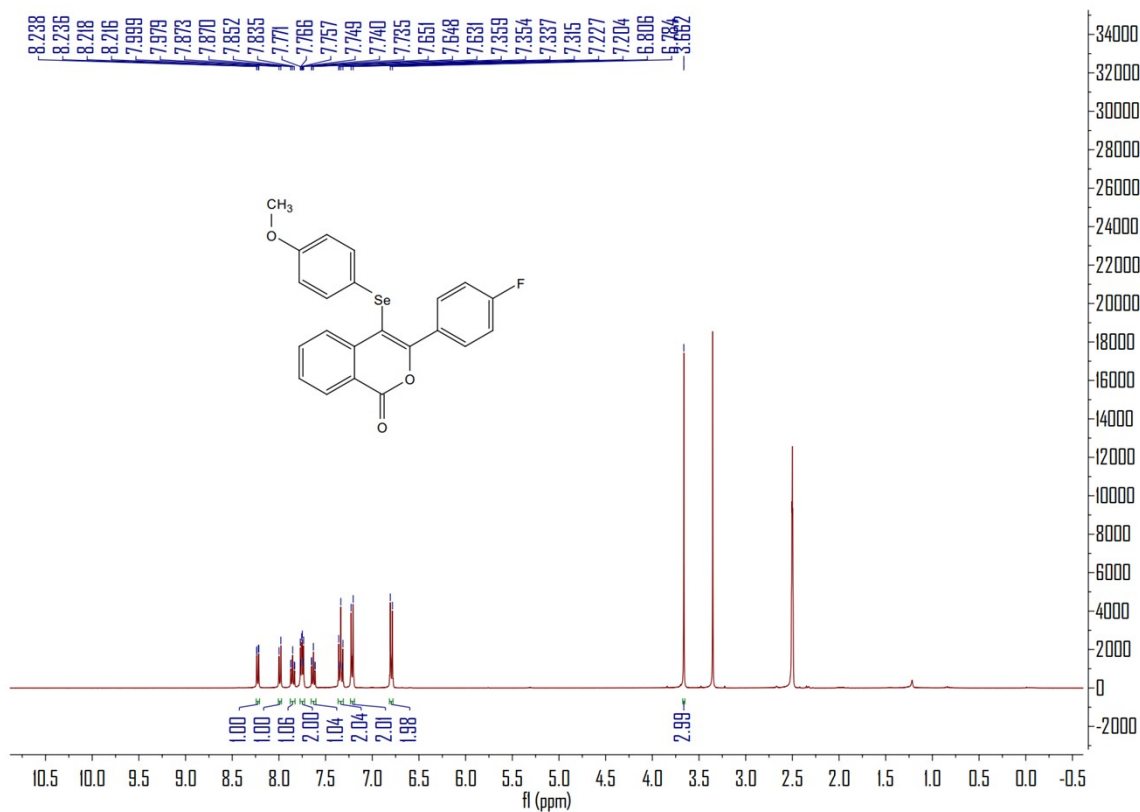
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3b**



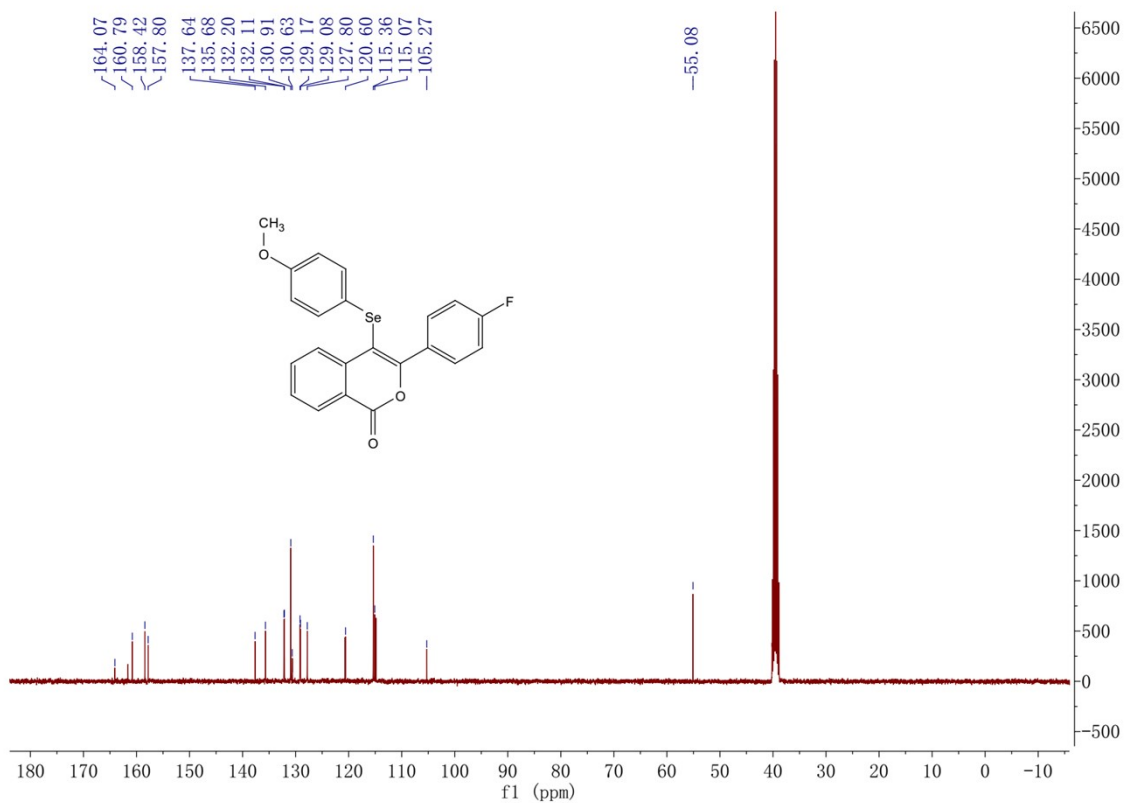
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3b**



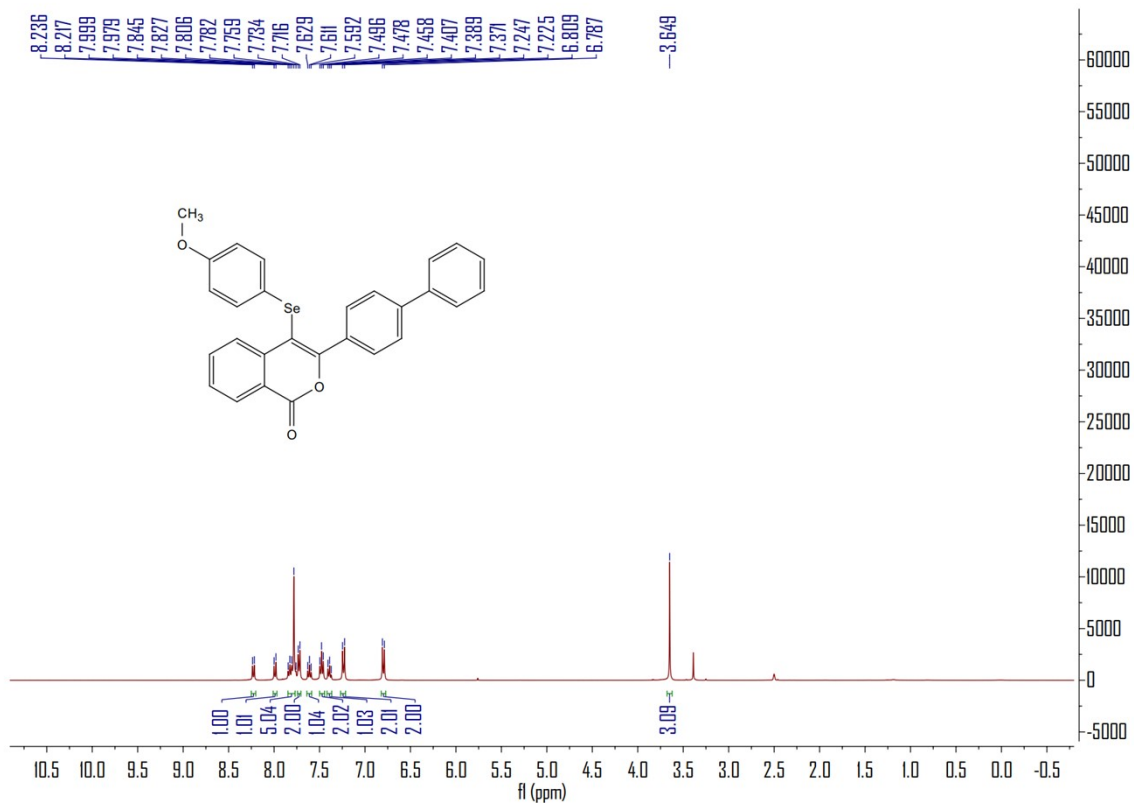
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3c**



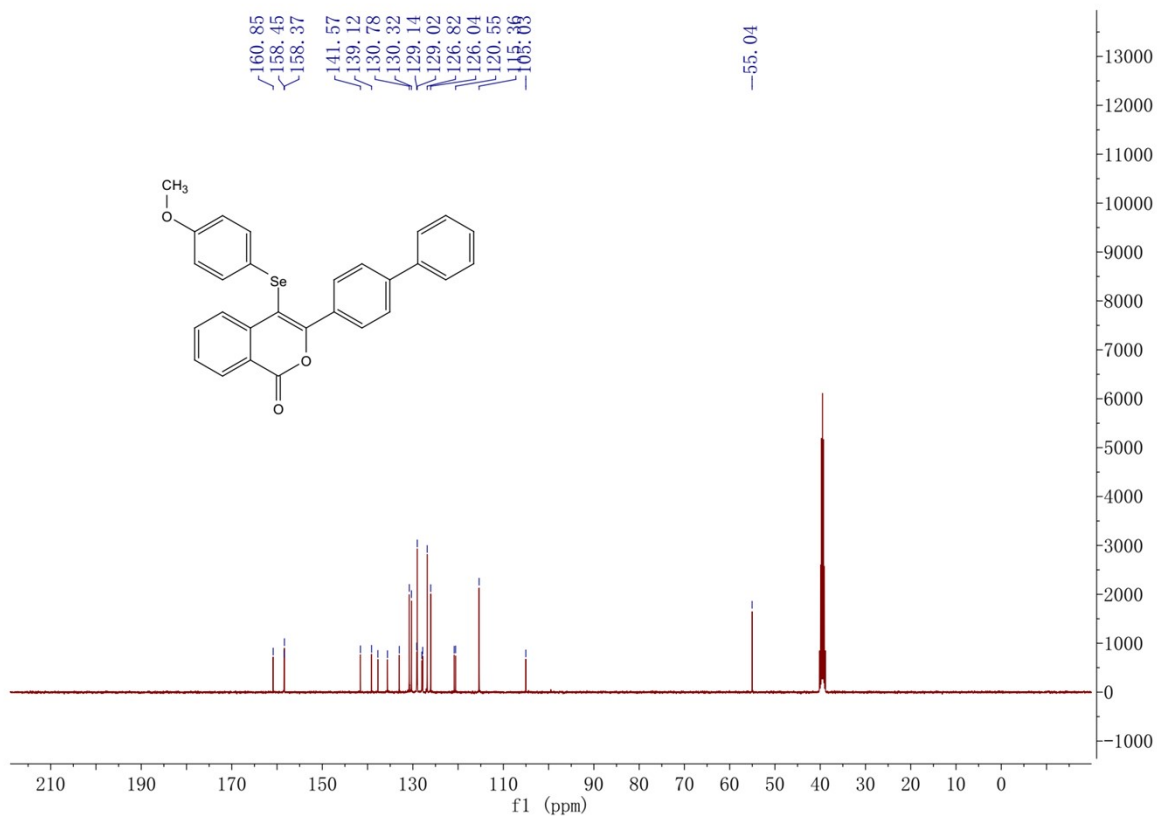
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3c**



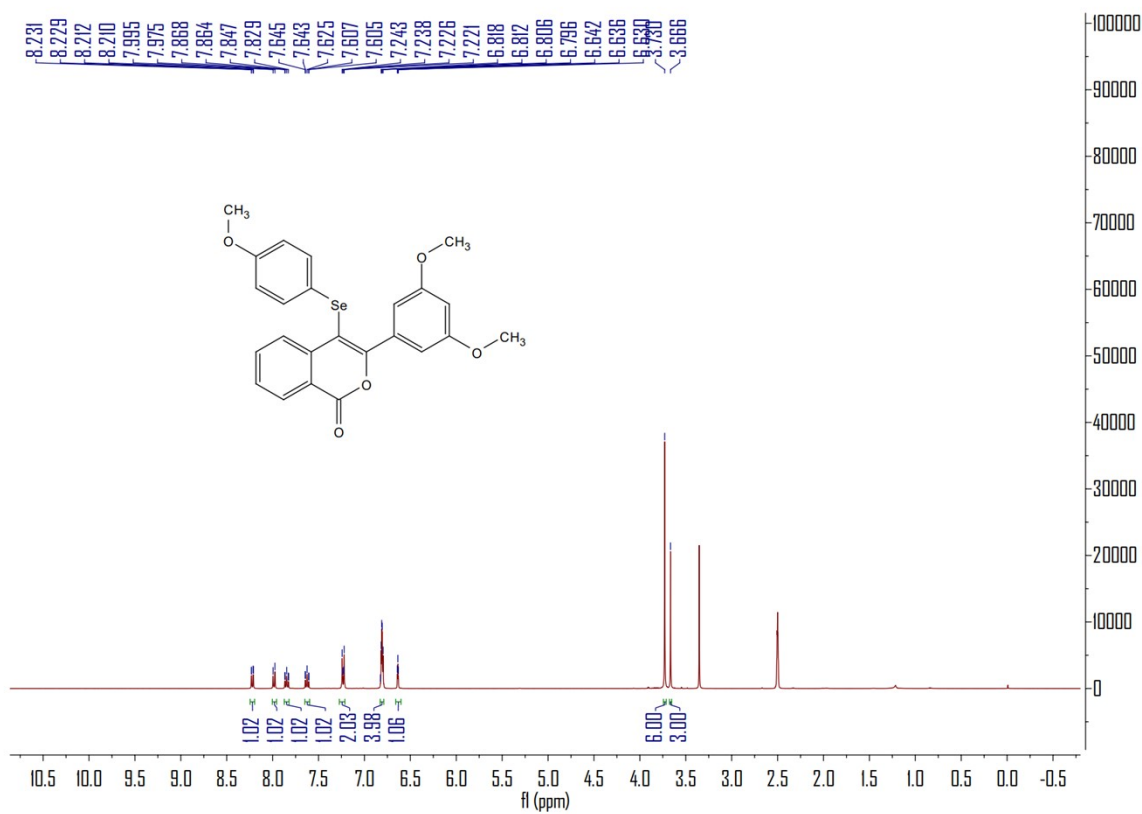
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3d**



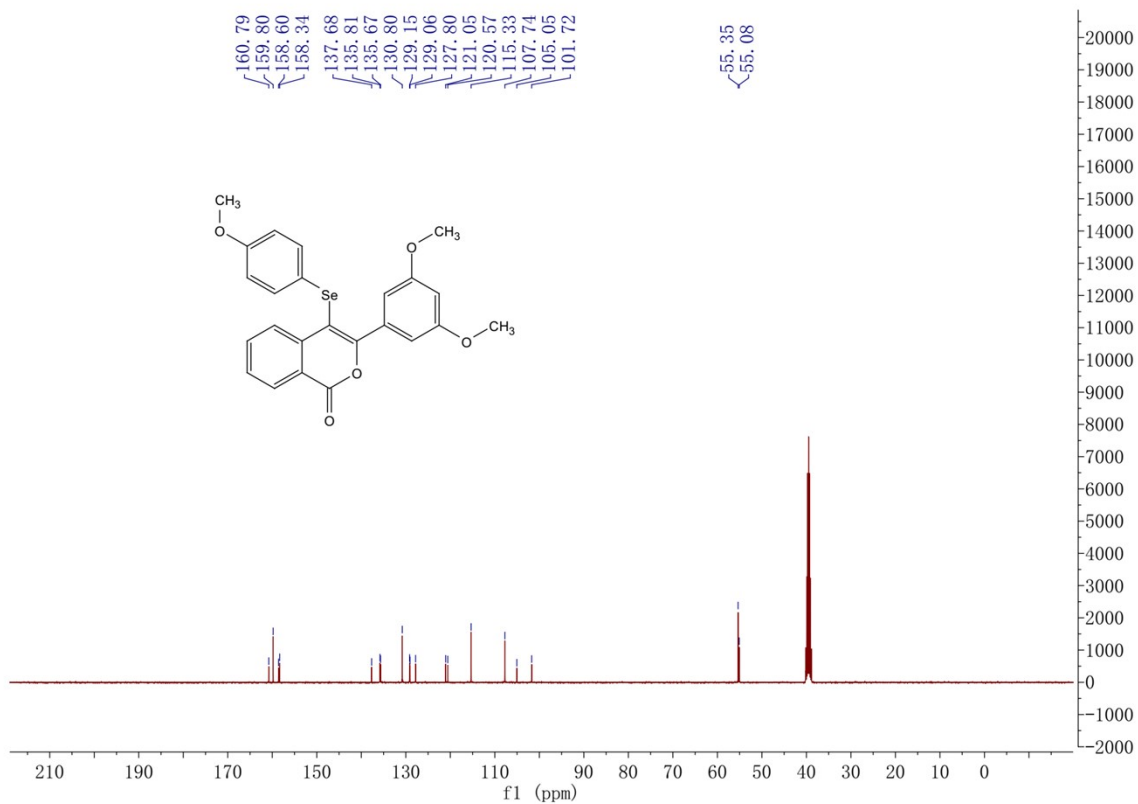
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3d**



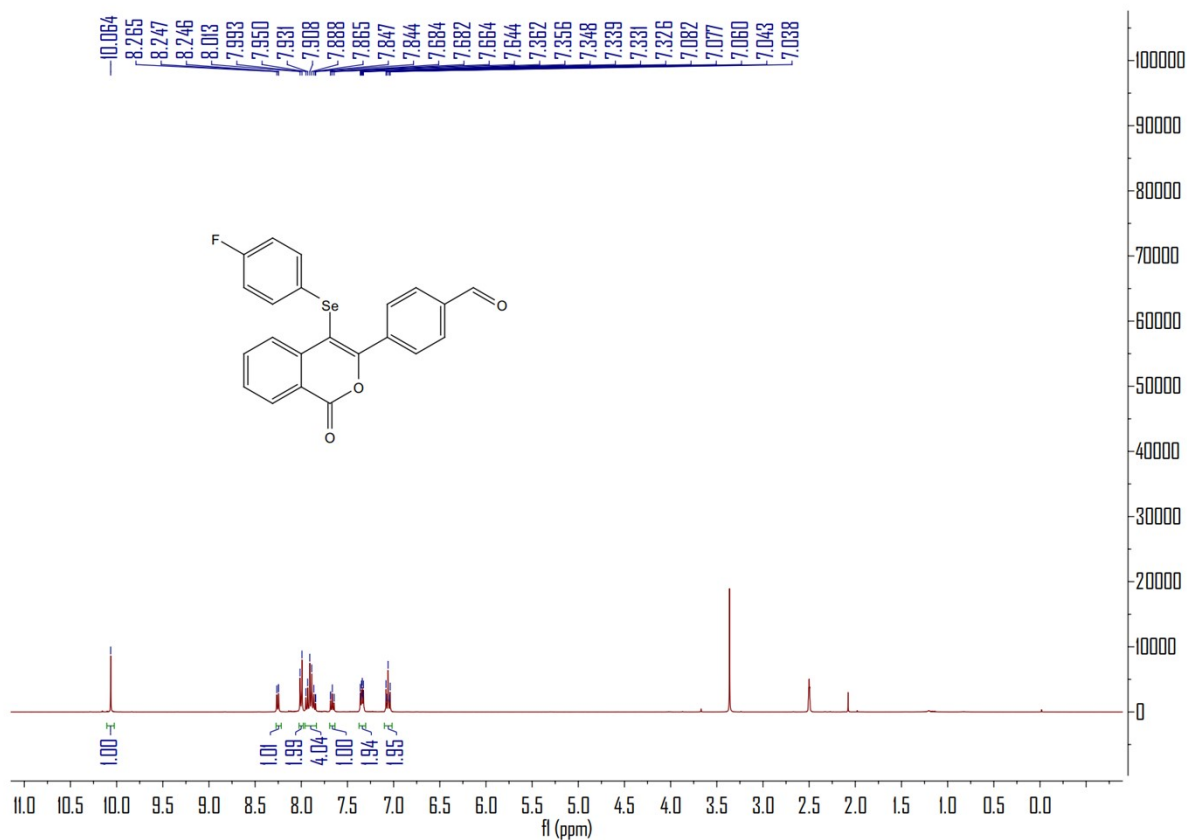
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3e**



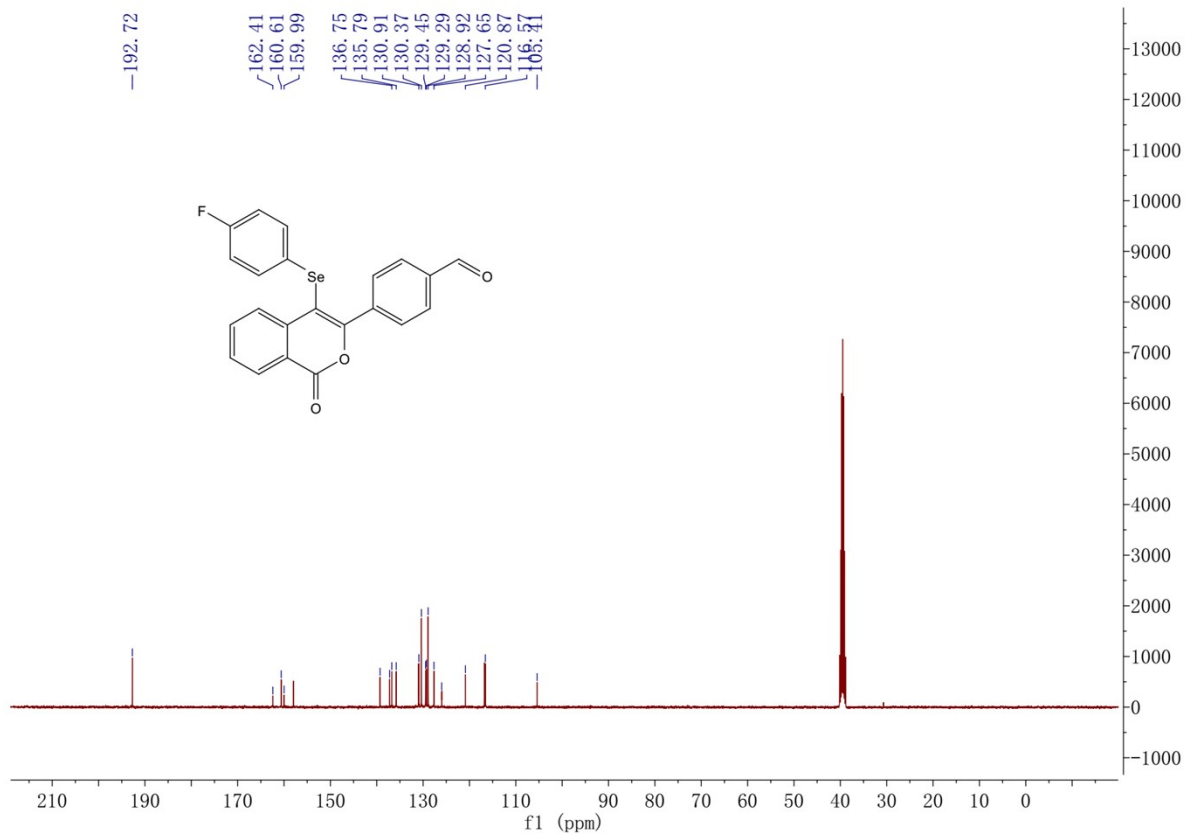
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3e**



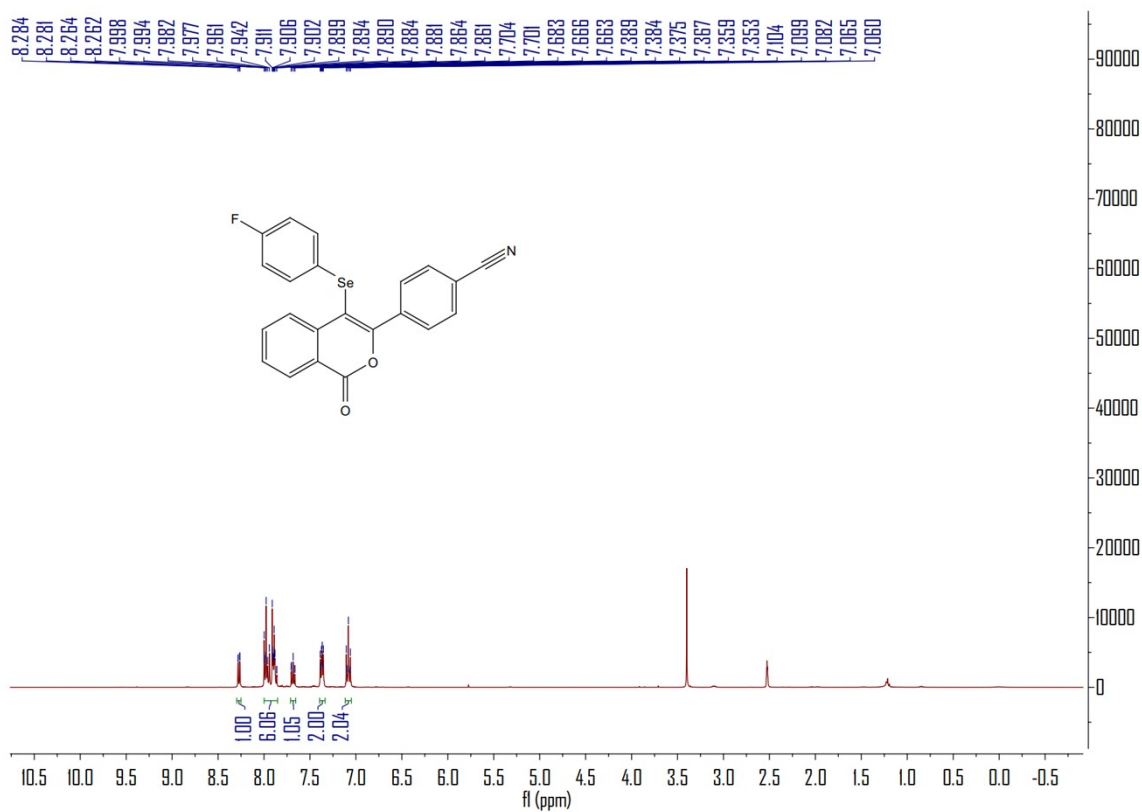
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3f**



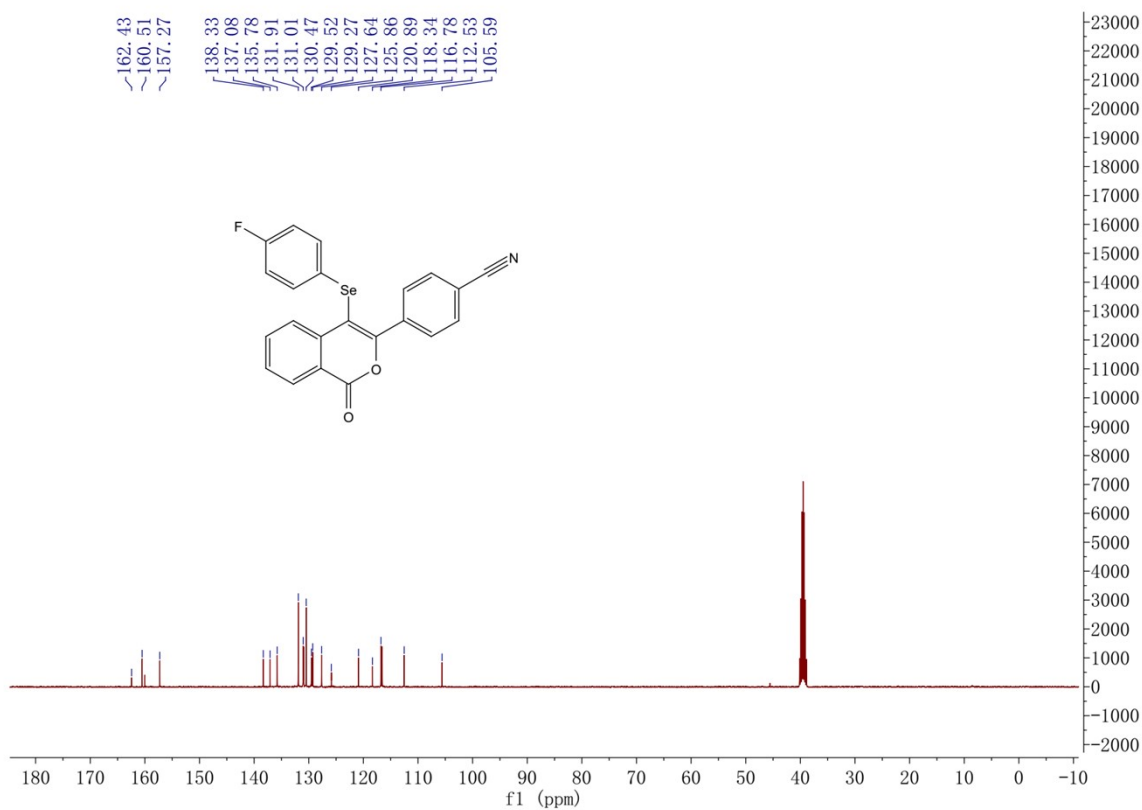
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3f**



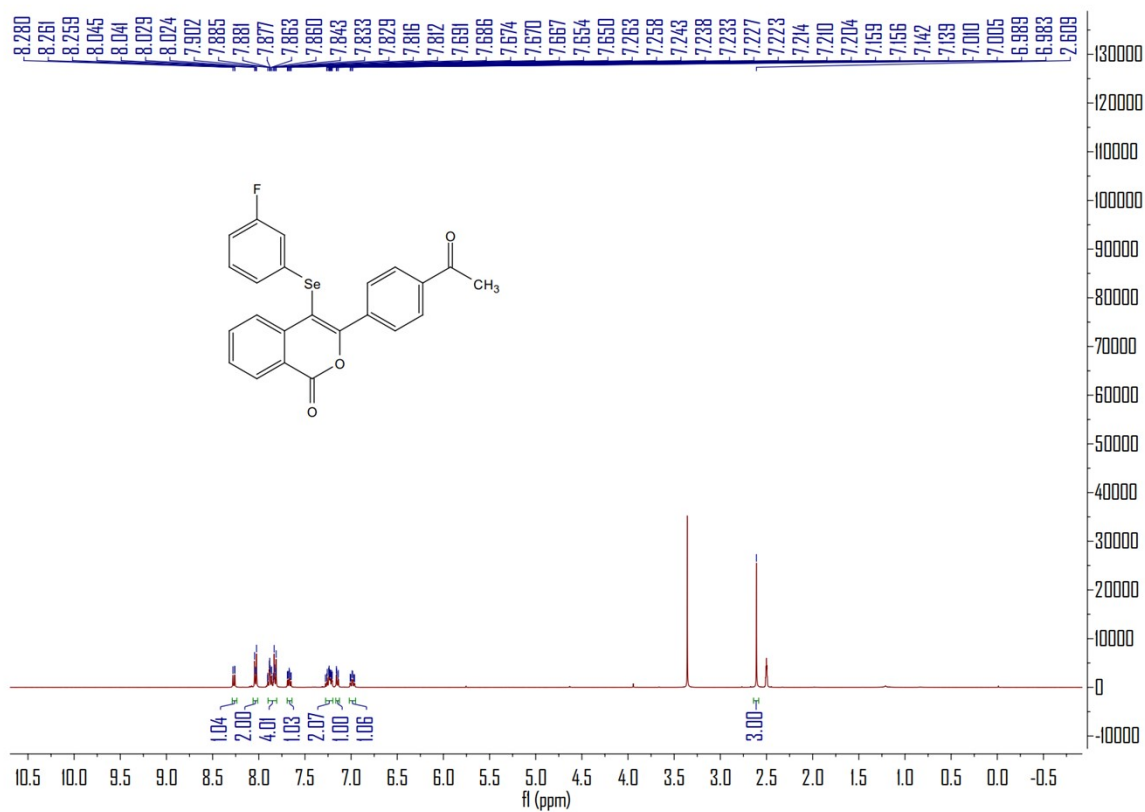
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3g**



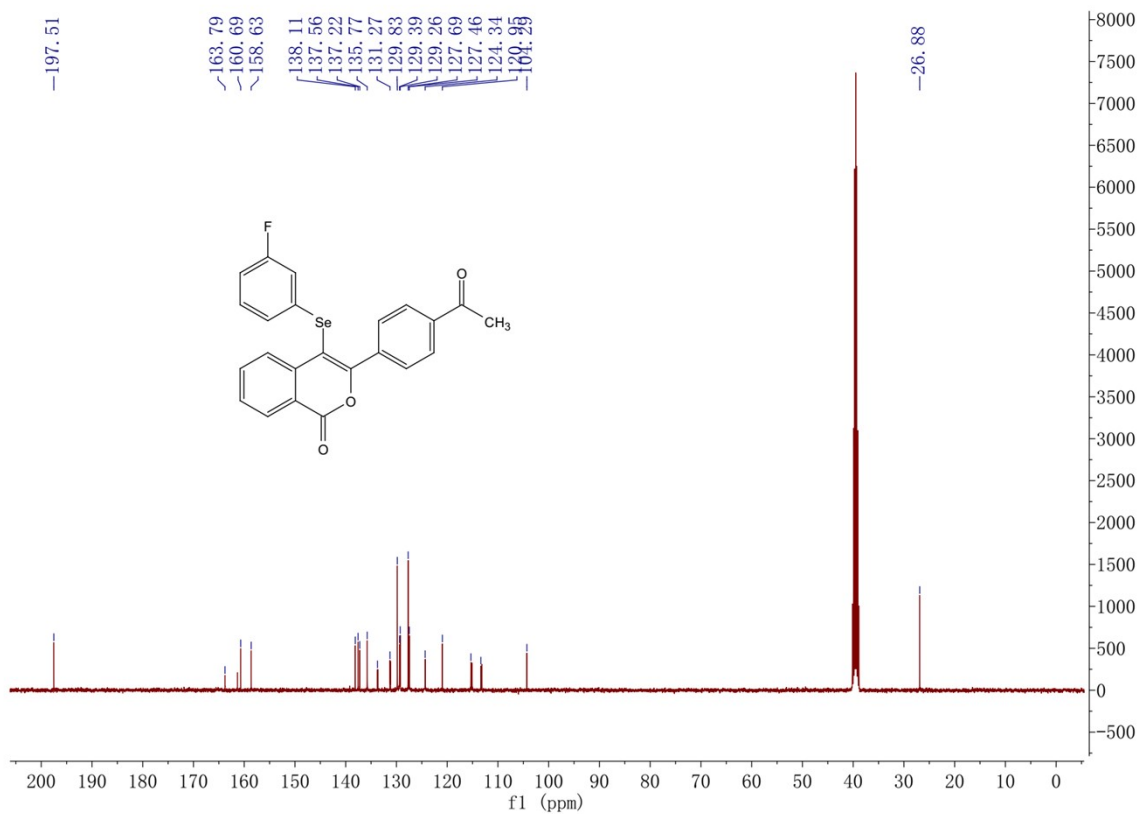
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3g**



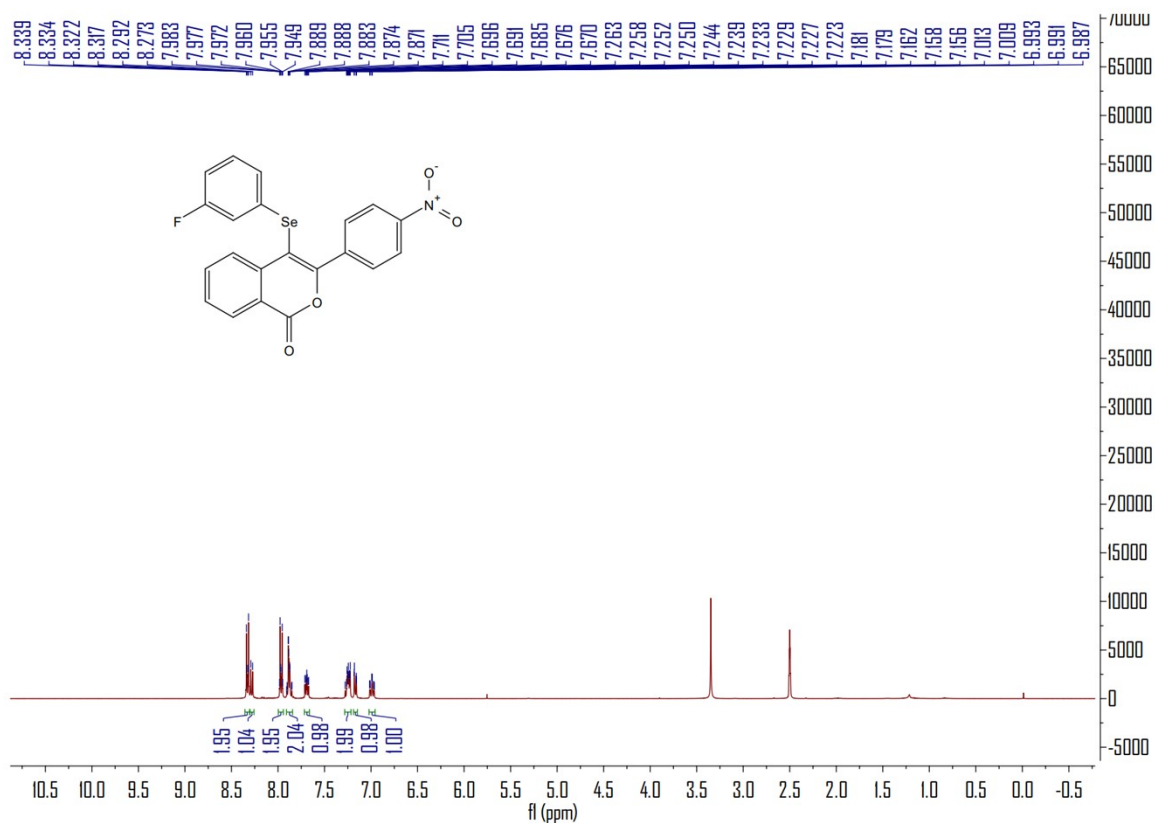
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3h**



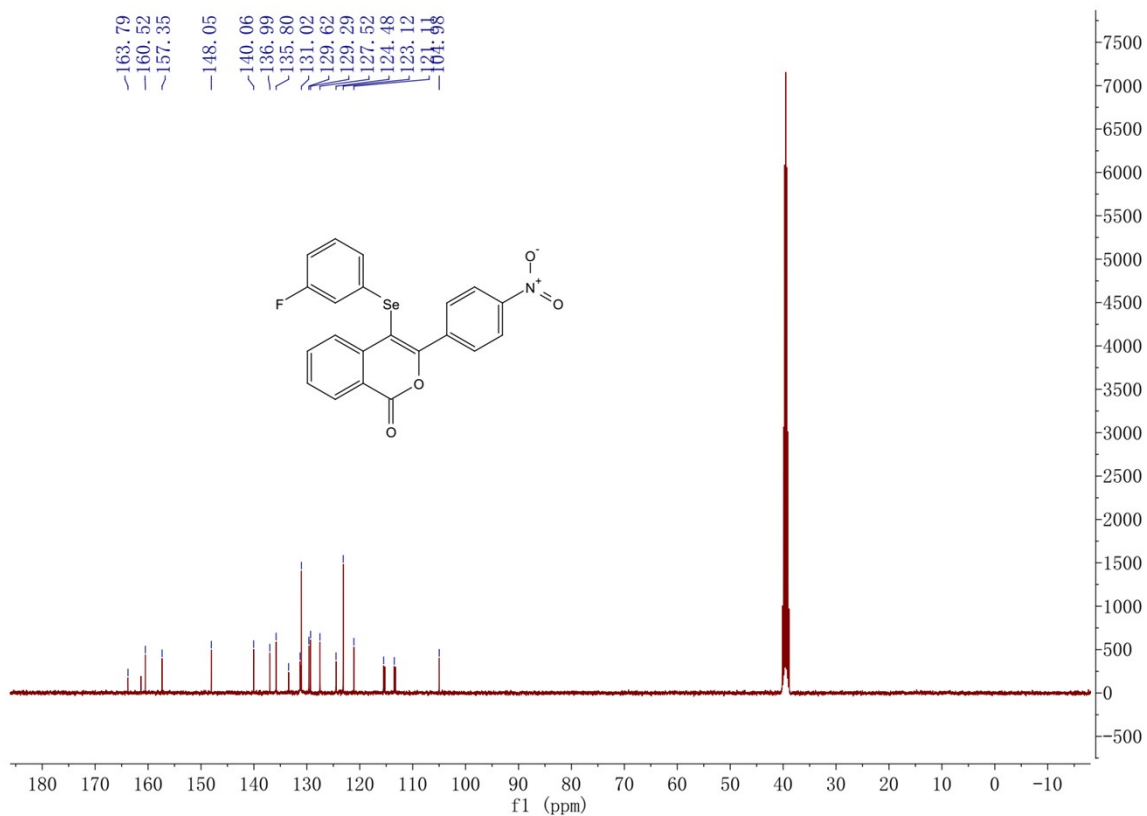
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3h**



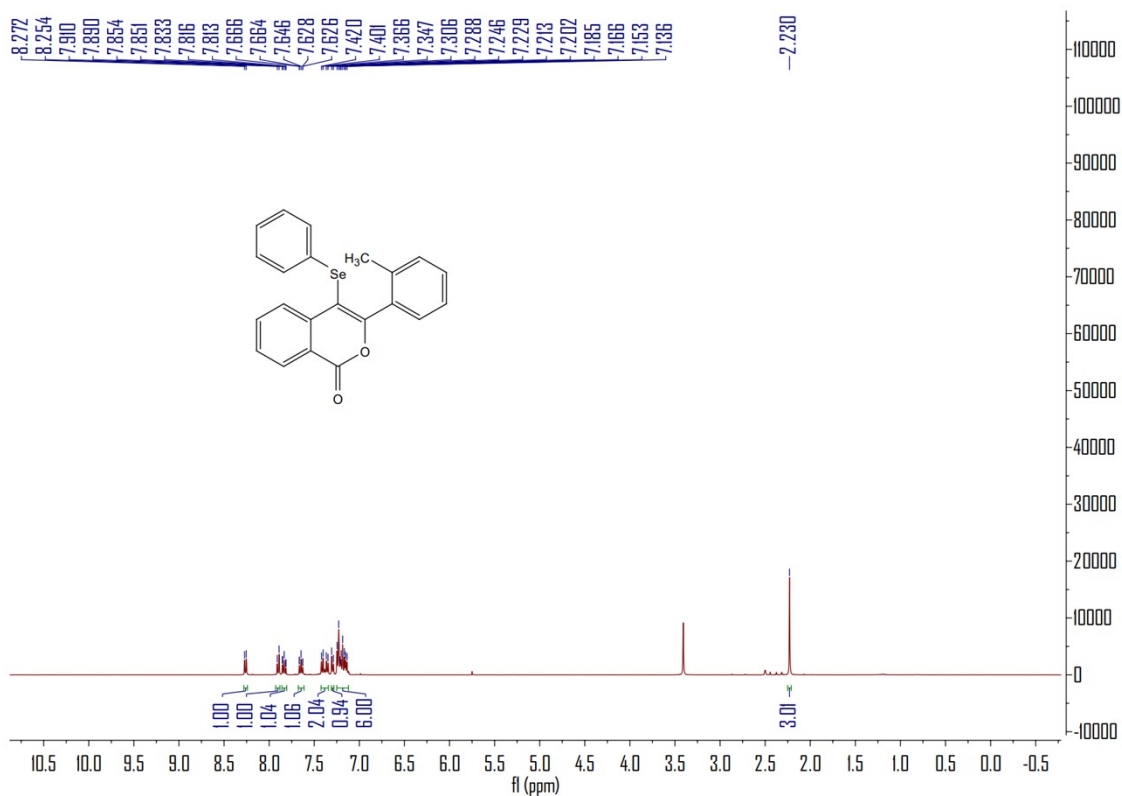
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3i**



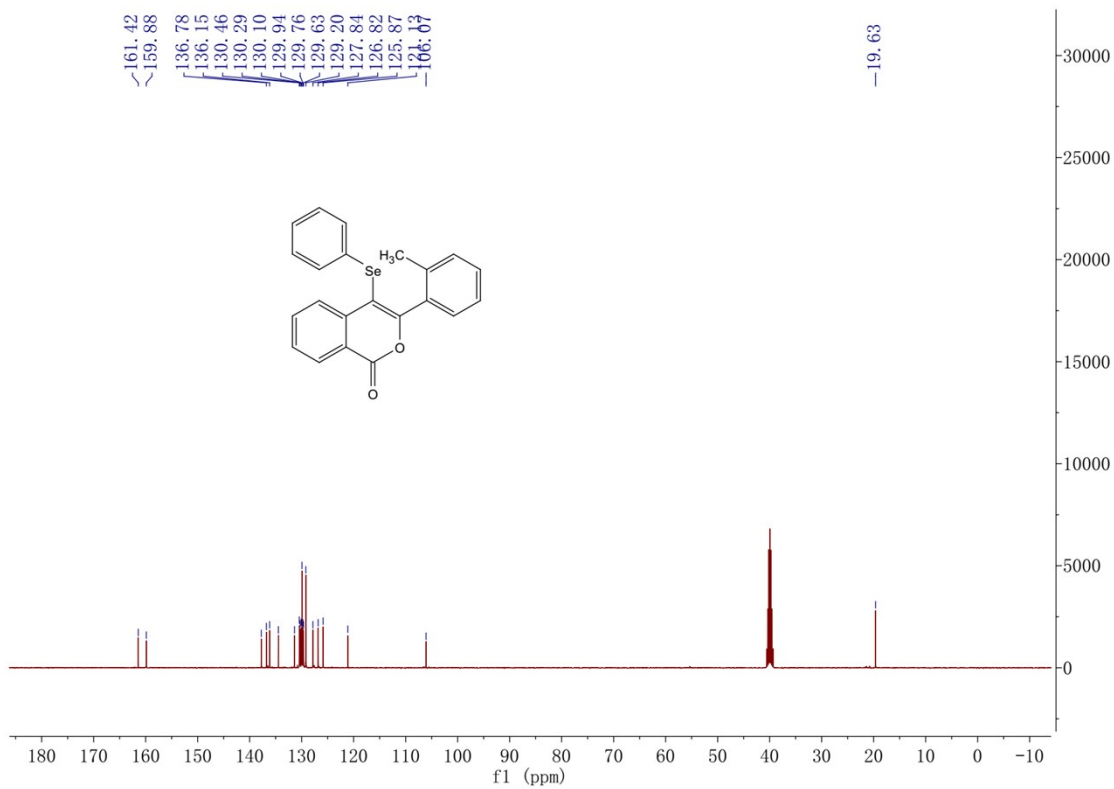
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3i**



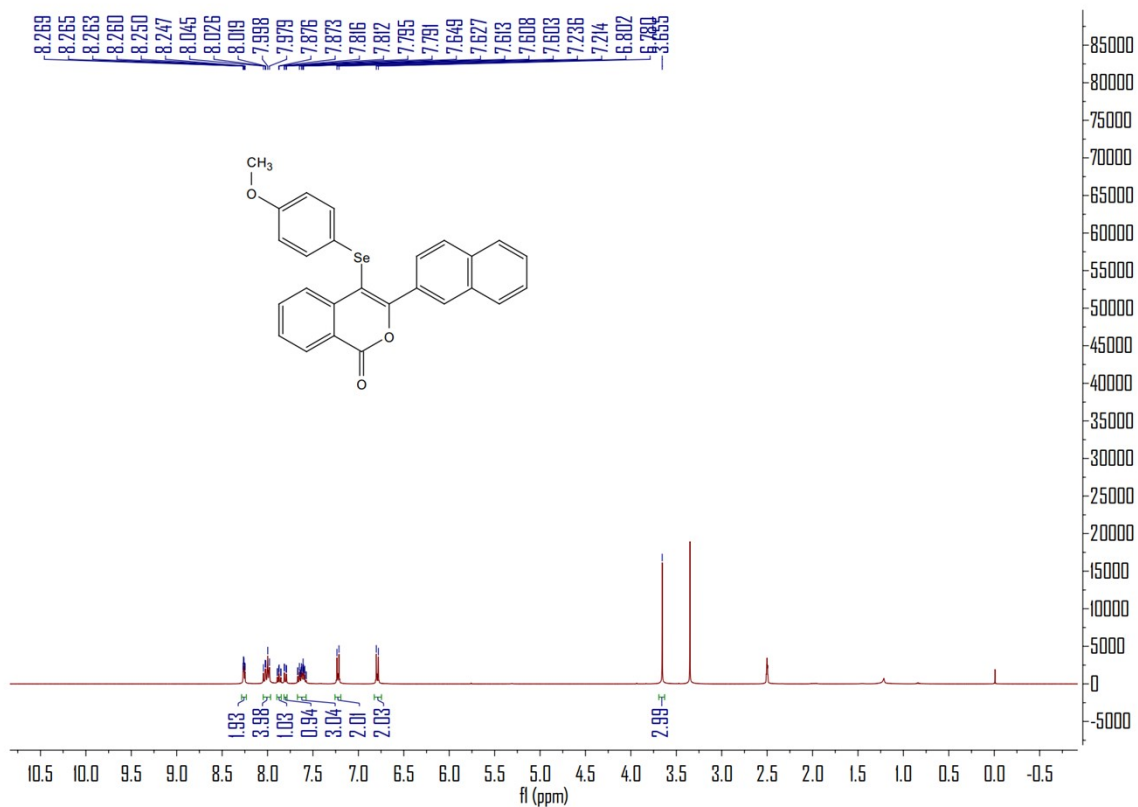
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3j**



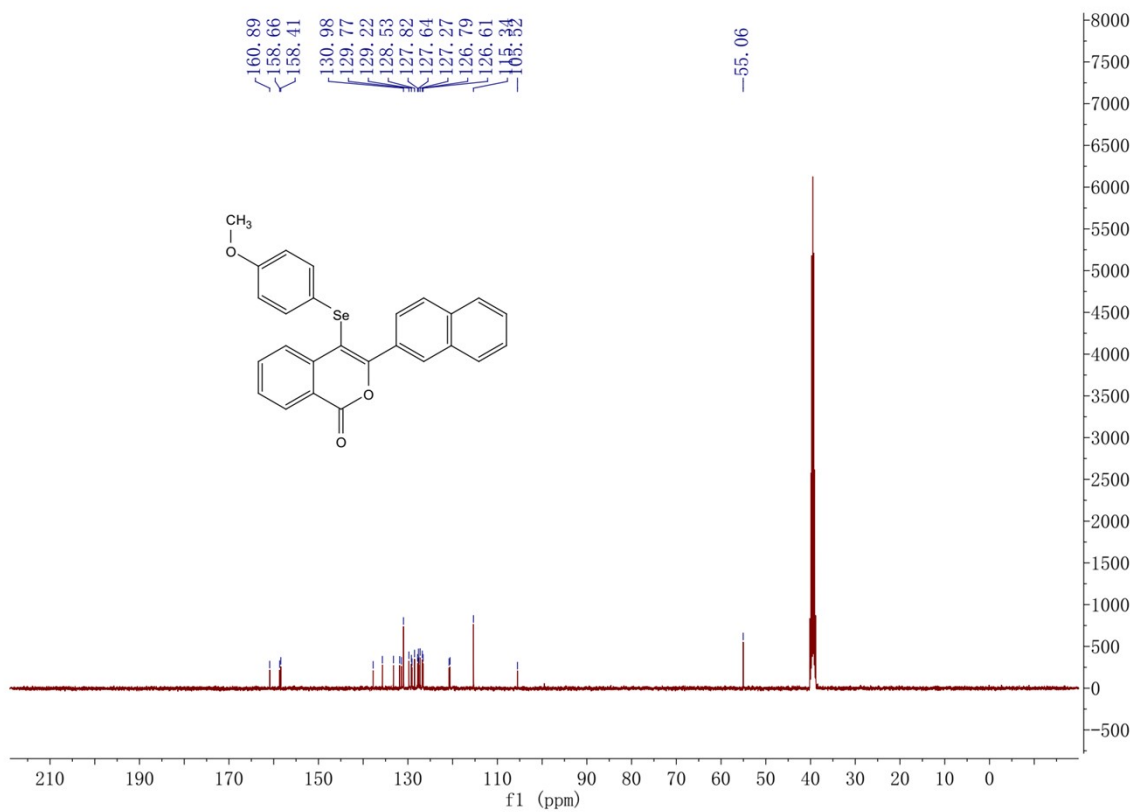
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3j**



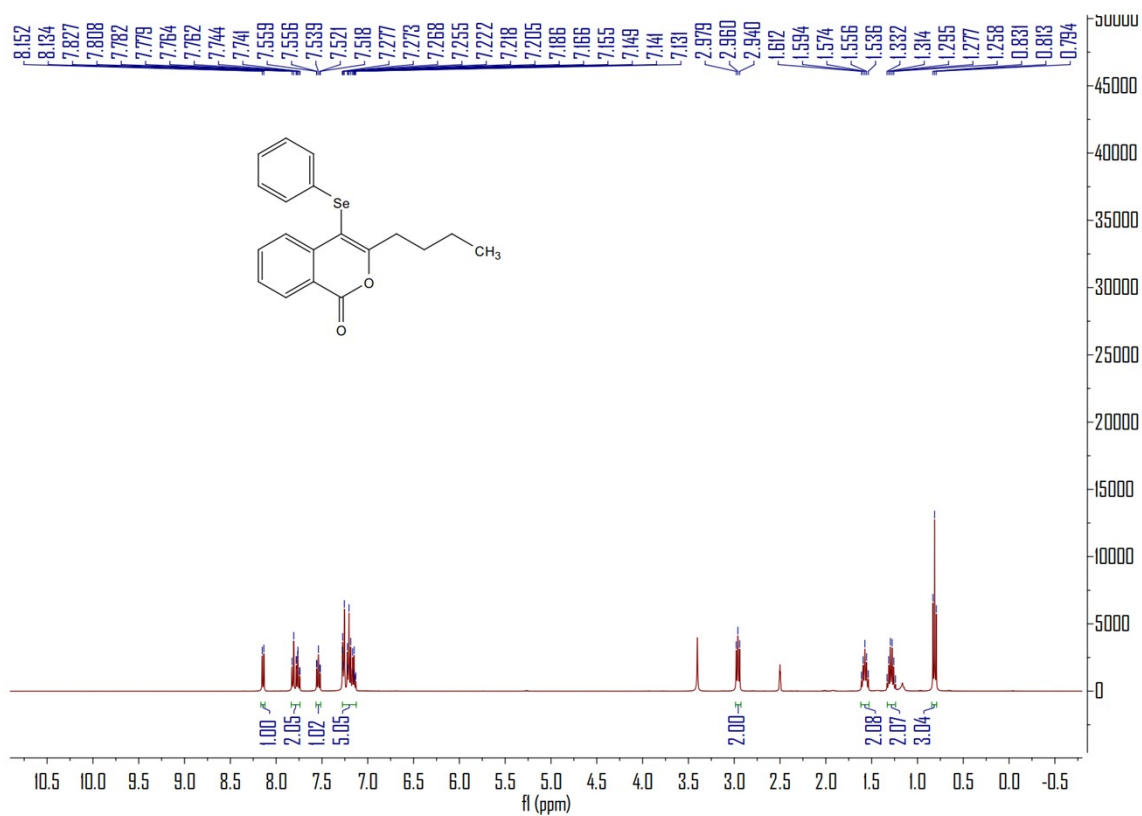
¹H NMR spectrum (400 M, DMSO-*d*₆) of **31**



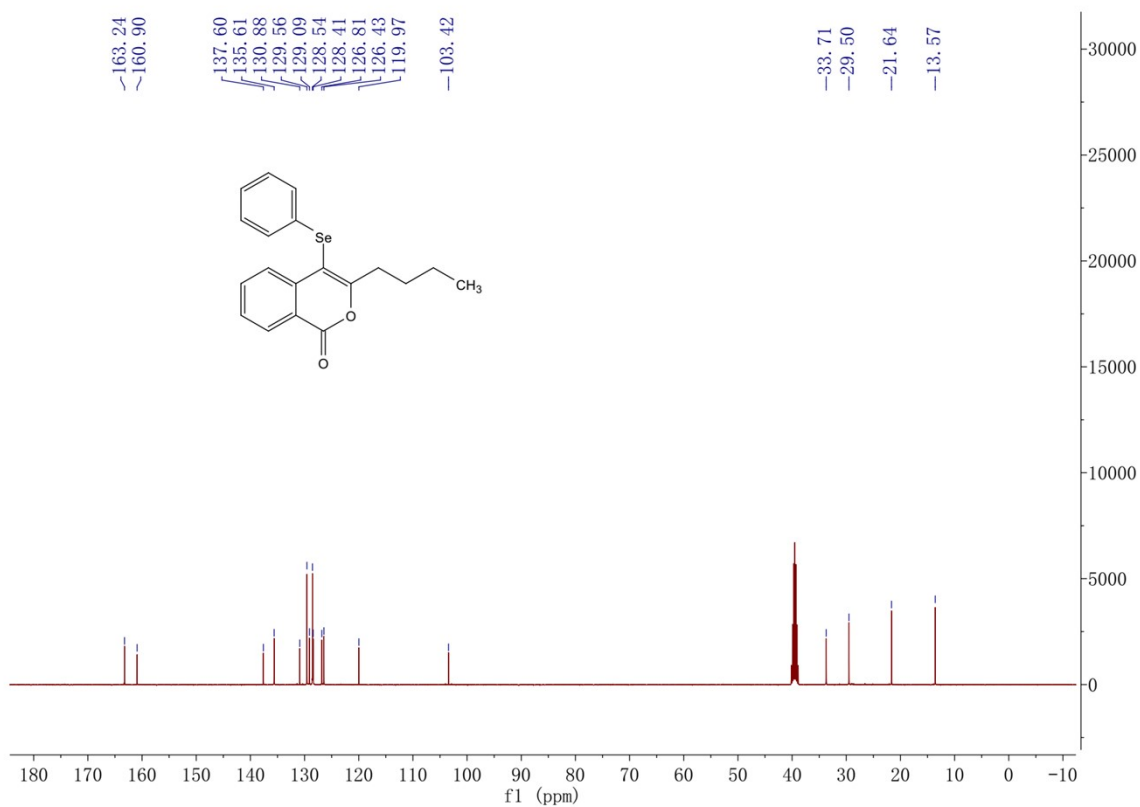
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **31**



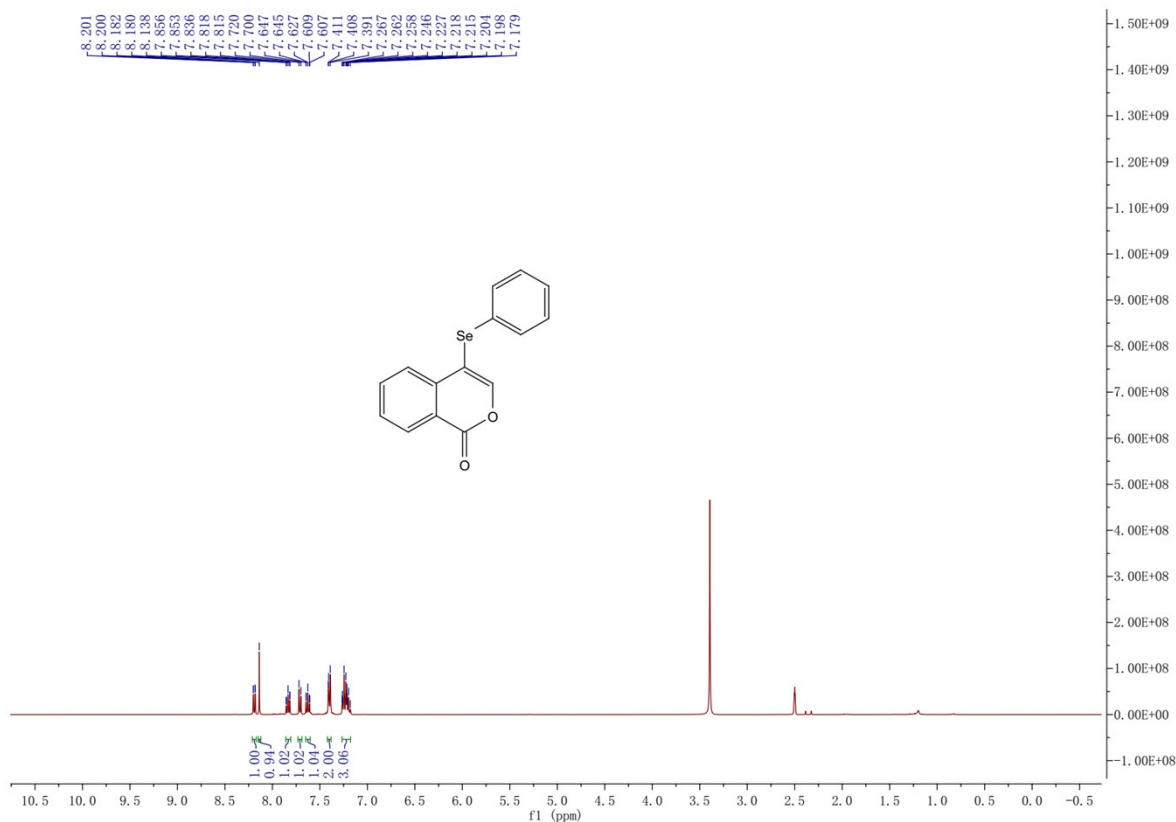
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3m**



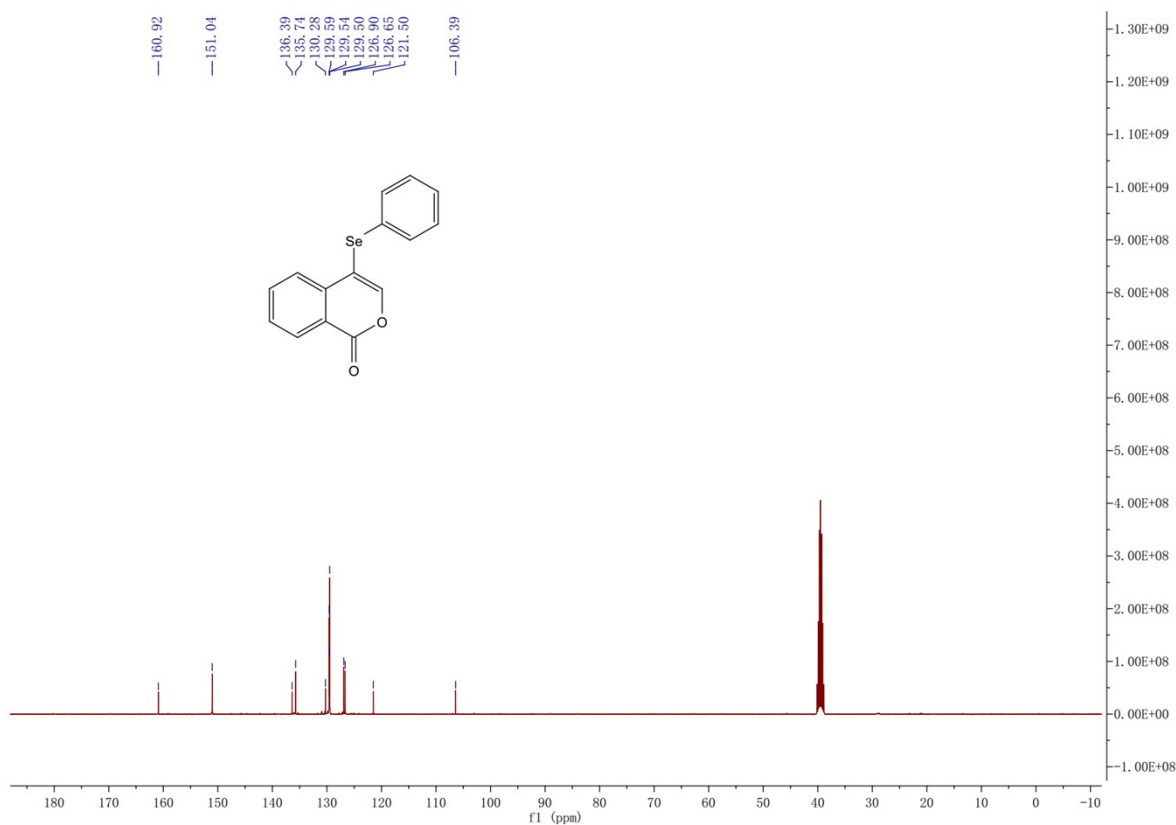
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3m**



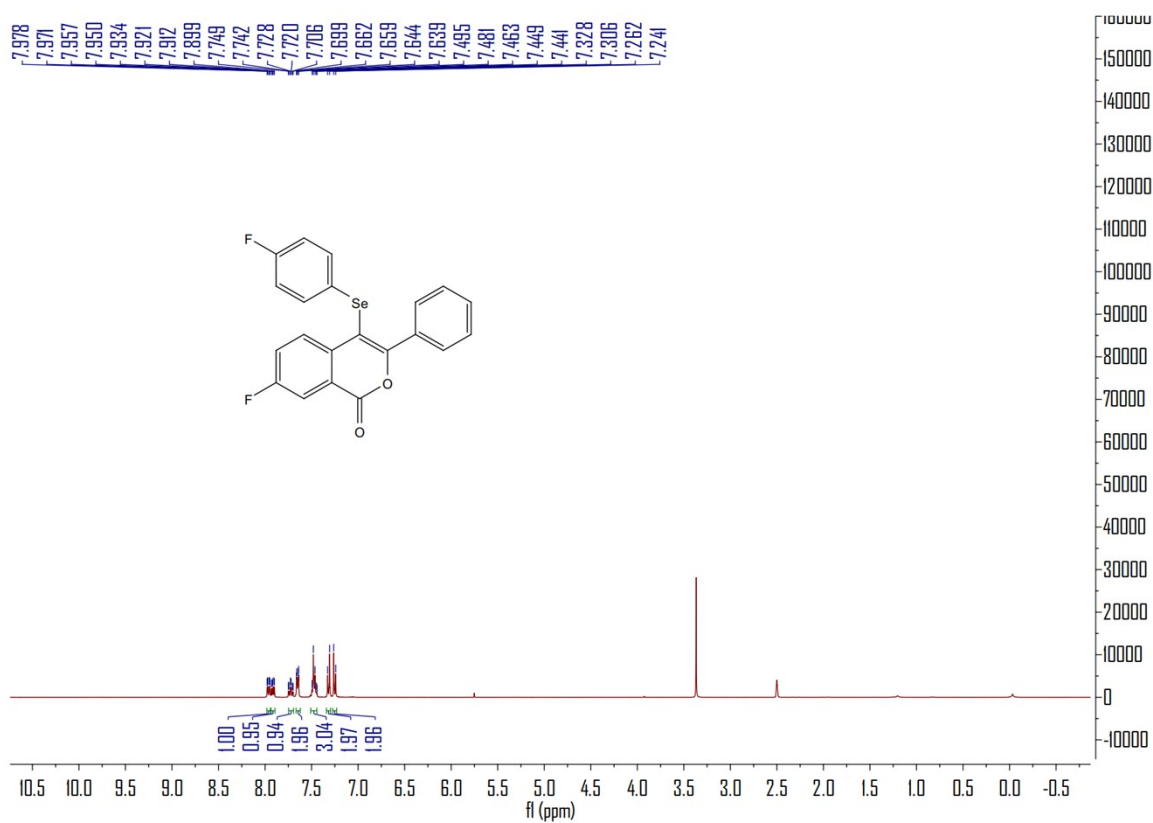
^1H NMR spectrum (400 M, $\text{DMSO-}d_6$) of **3n**



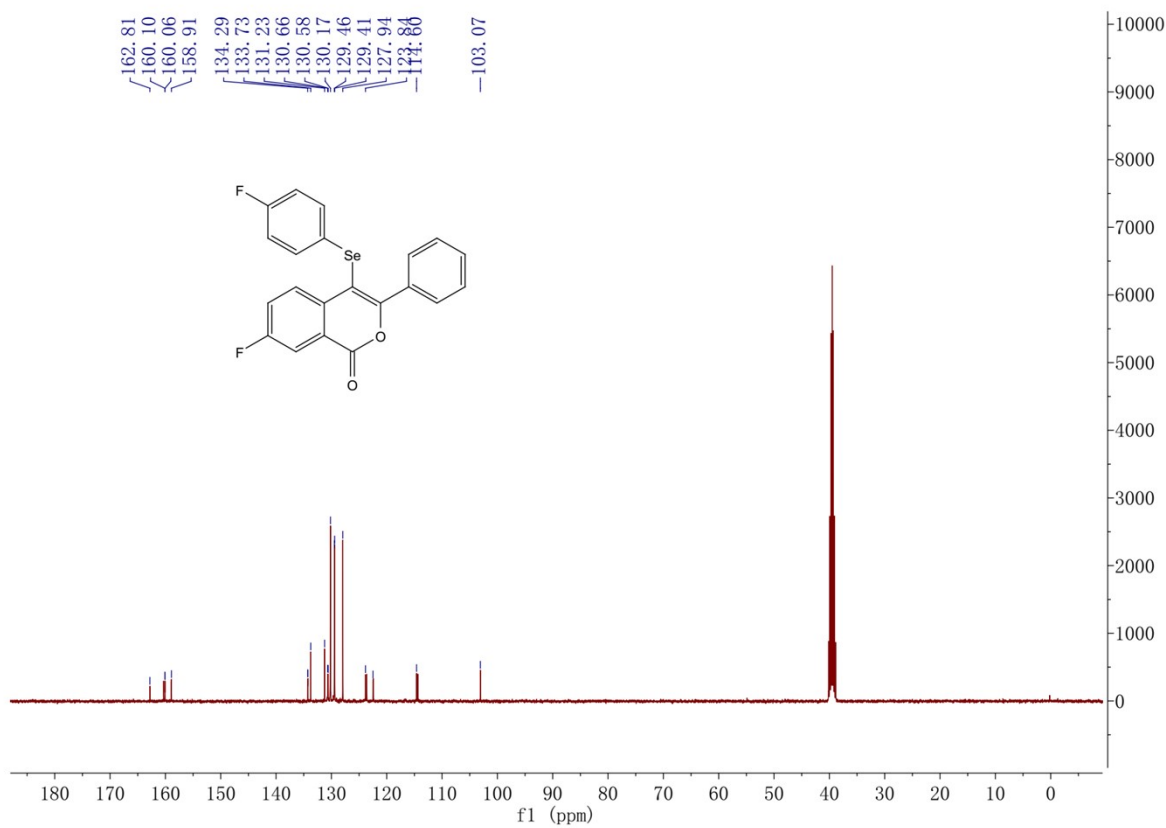
^{13}C NMR spectrum (100 M, $\text{DMSO-}d_6$) of **3n**



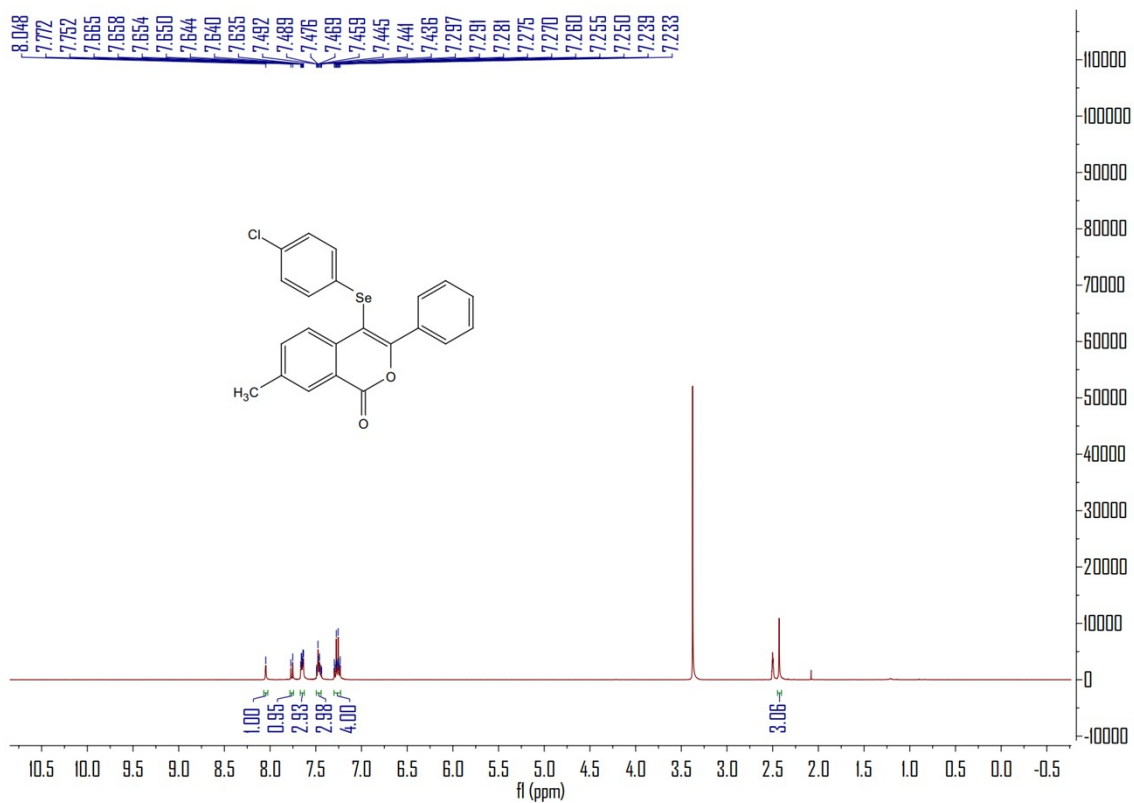
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3o**



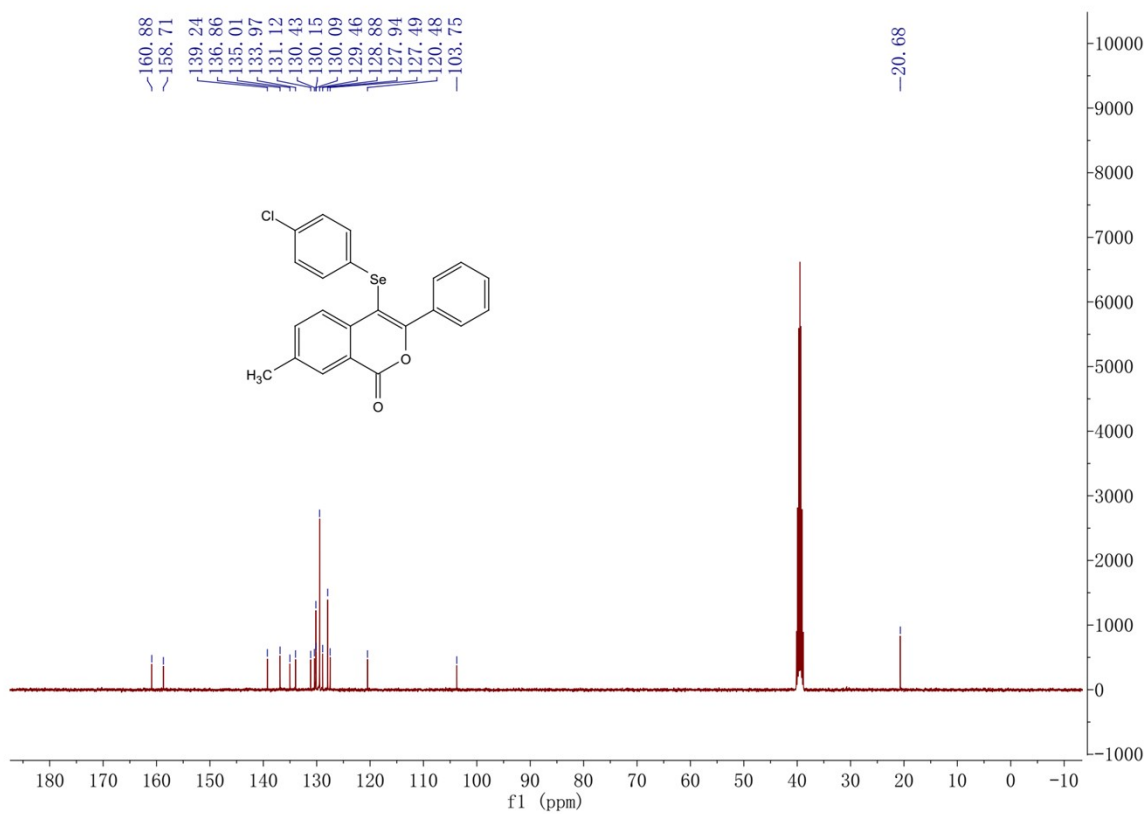
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3o**



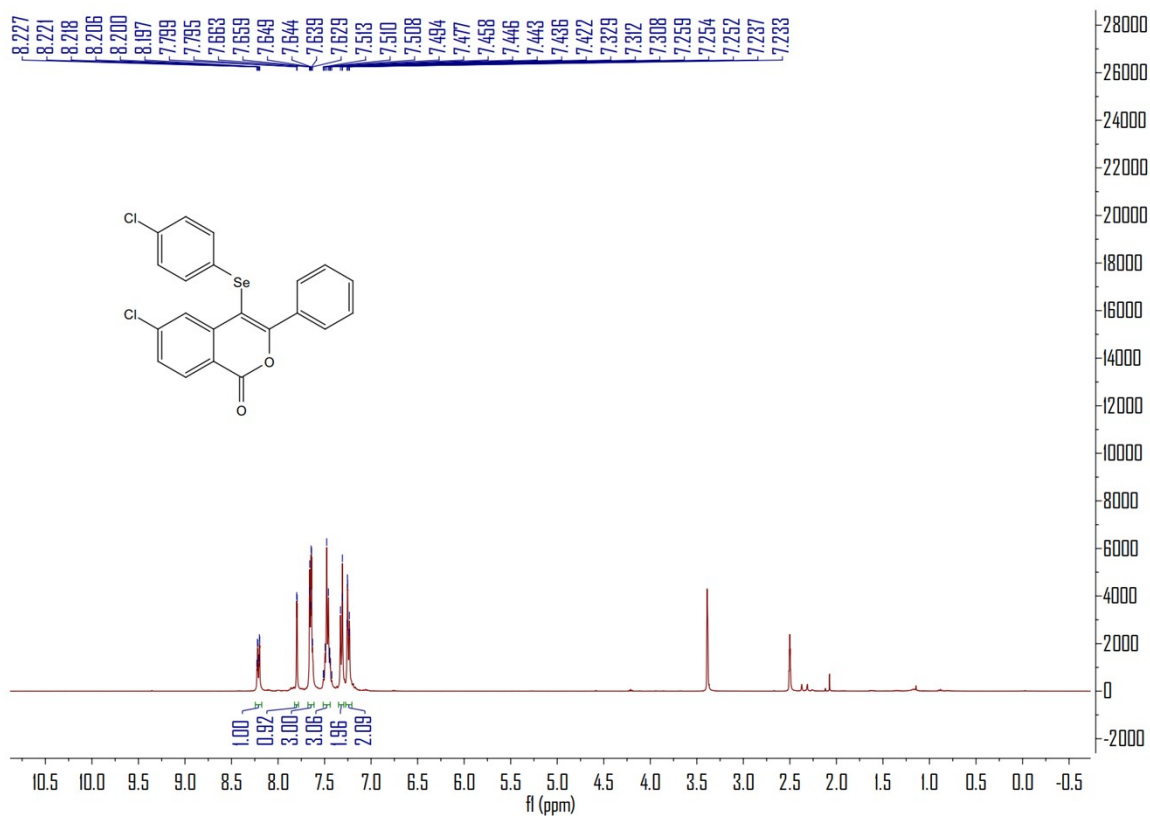
¹H NMR spectrum (400 M, DMSO-d₆) of **3p**



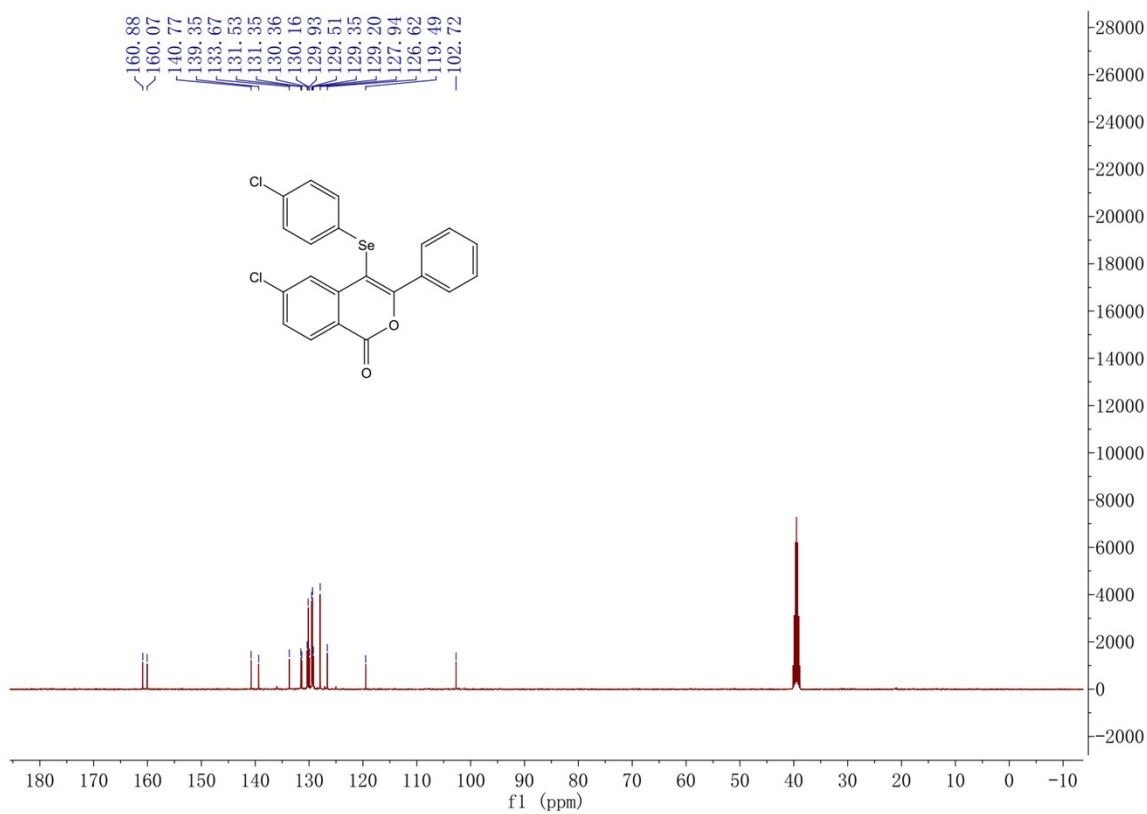
¹³C NMR spectrum (100 M, DMSO-d₆) of **3p**



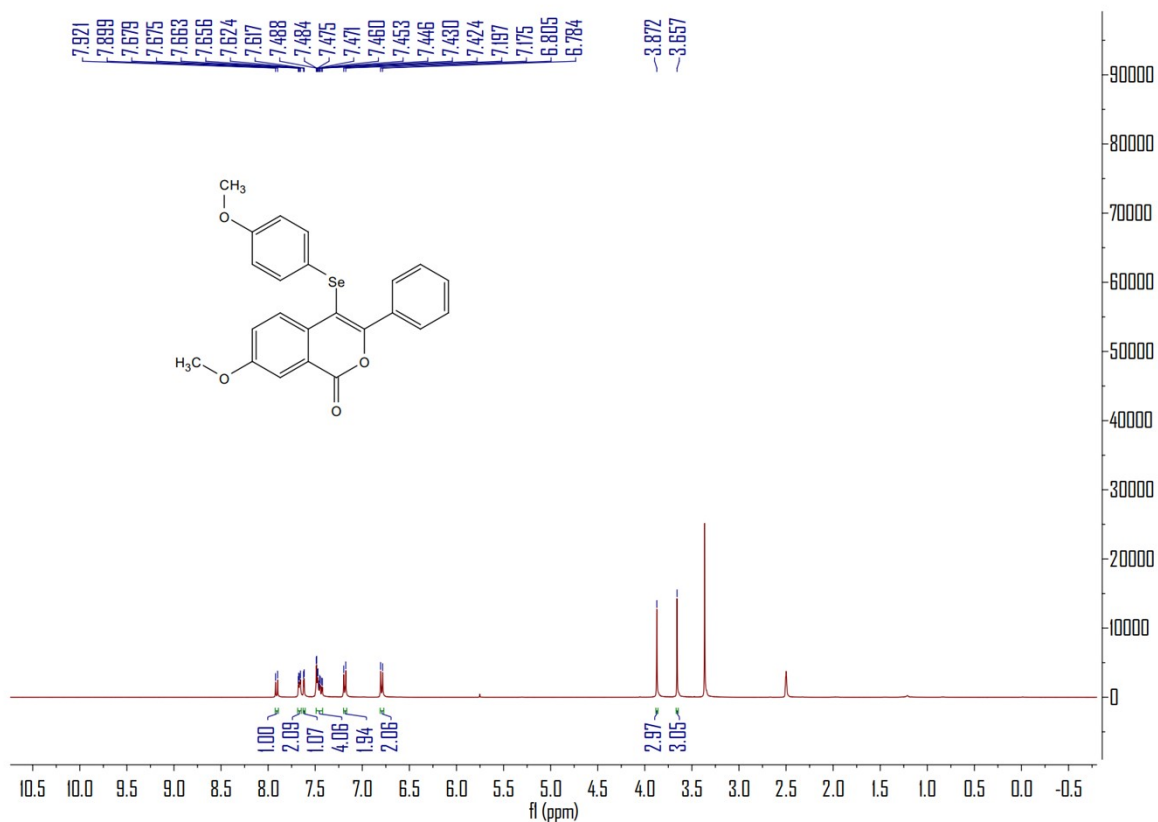
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3q**



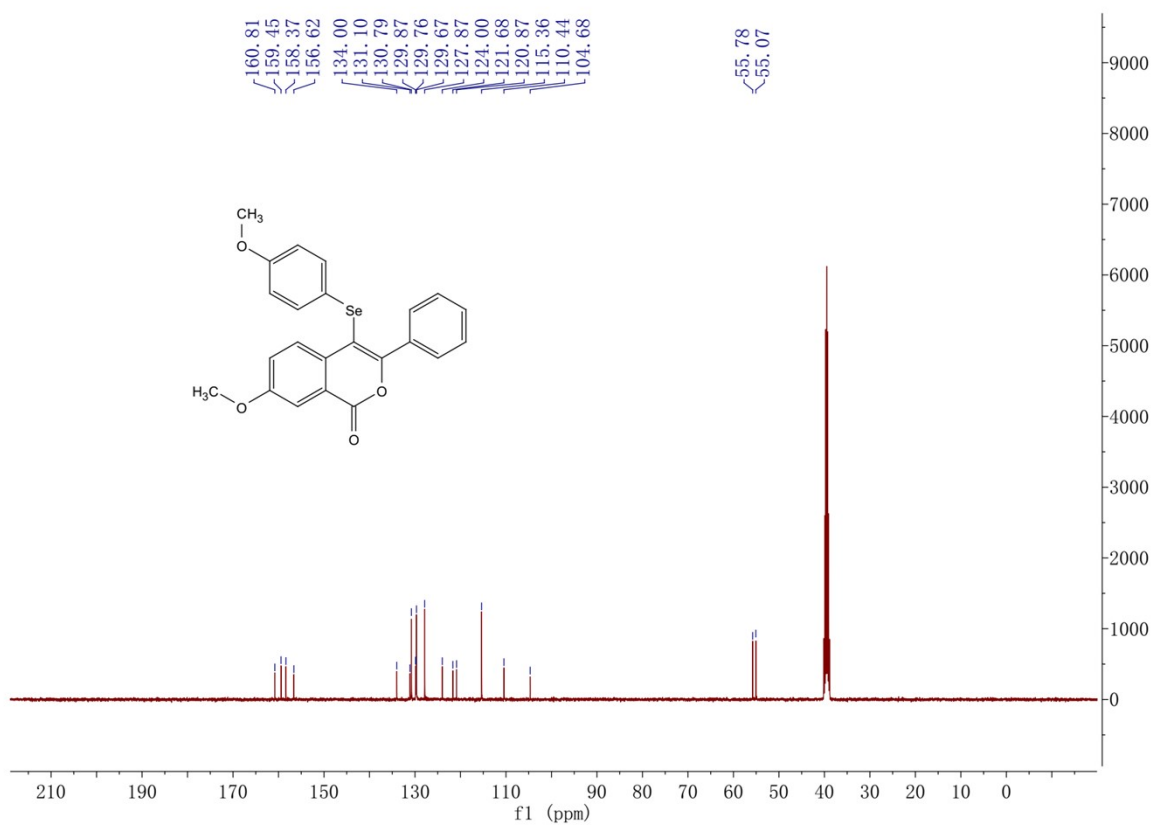
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3q**



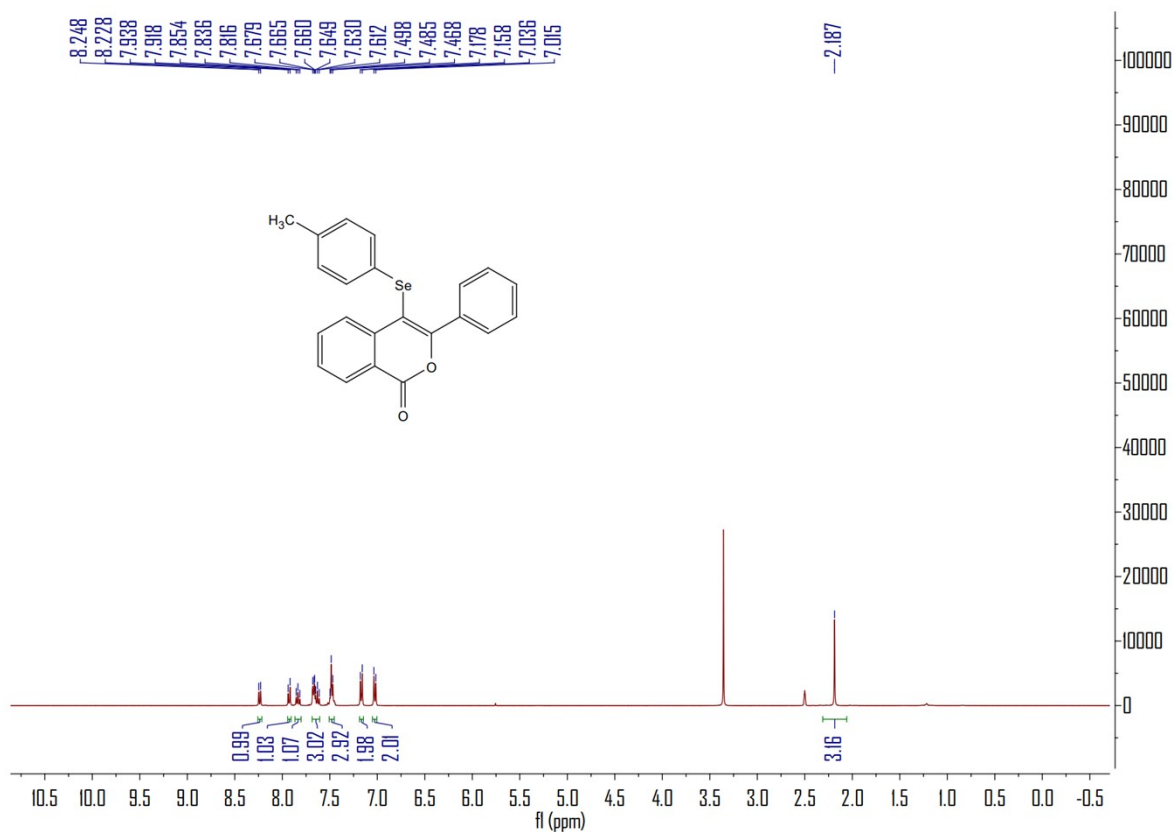
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3r**



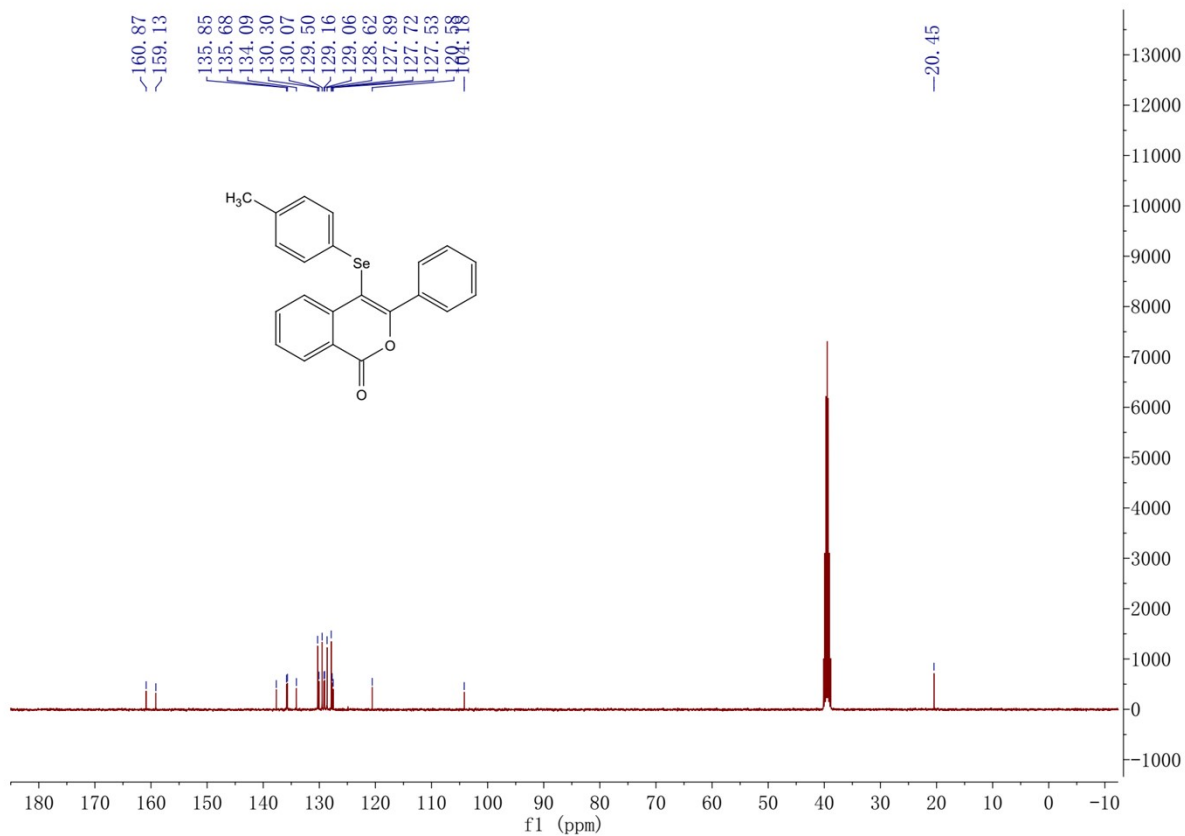
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3r**



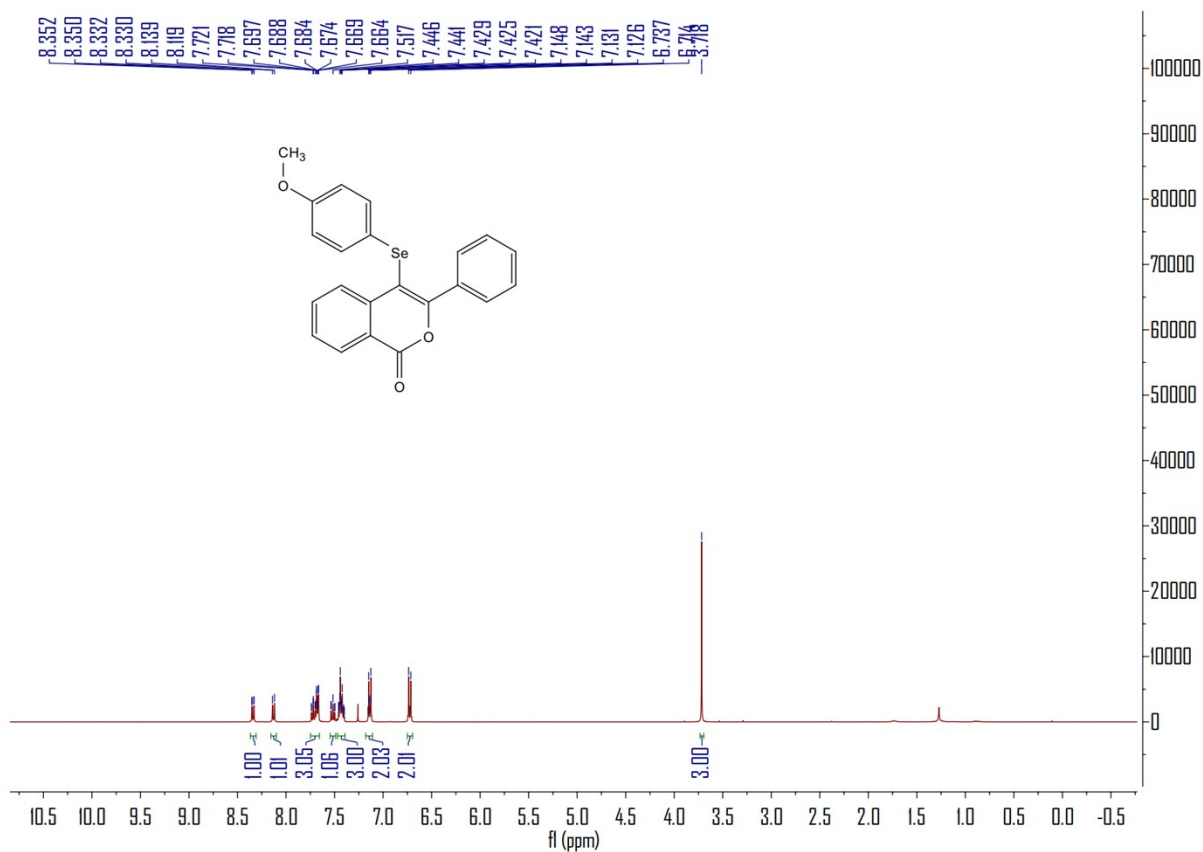
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3s**



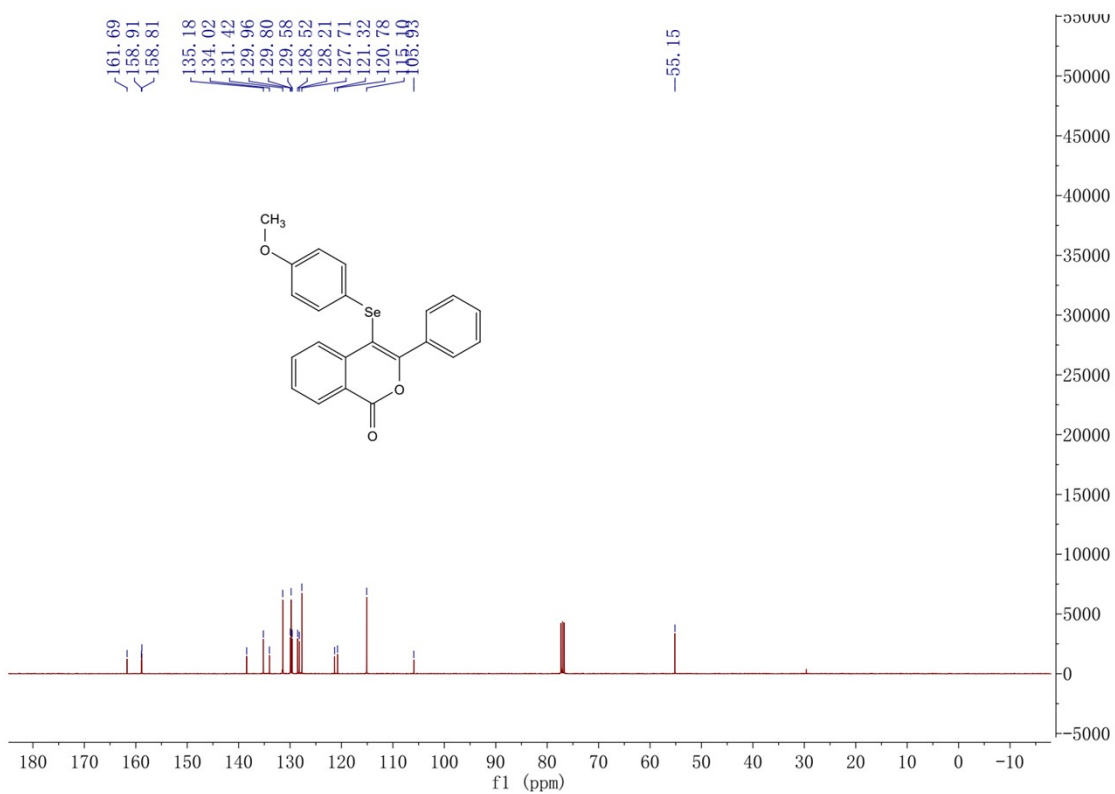
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3s**



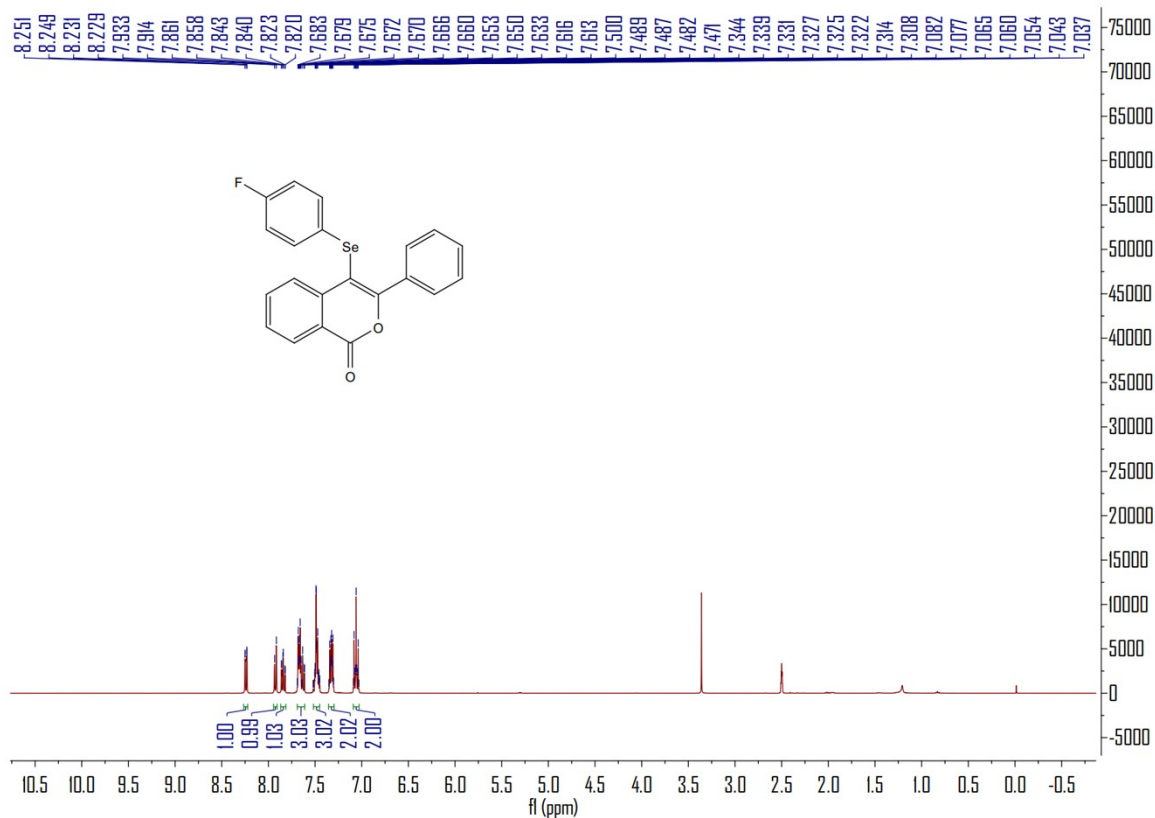
¹H NMR spectrum (400 M, CDCl₃) of **3t**



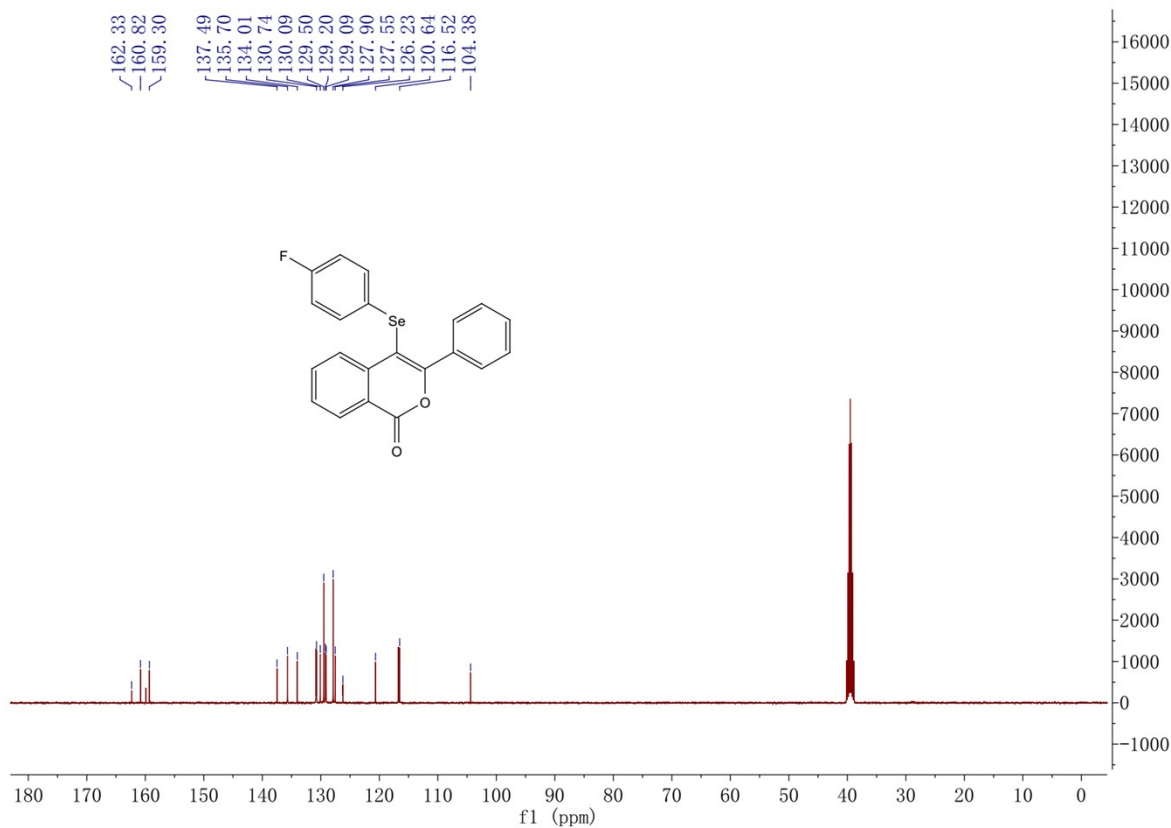
¹³C NMR spectrum (100 M, CDCl₃) of **3t**



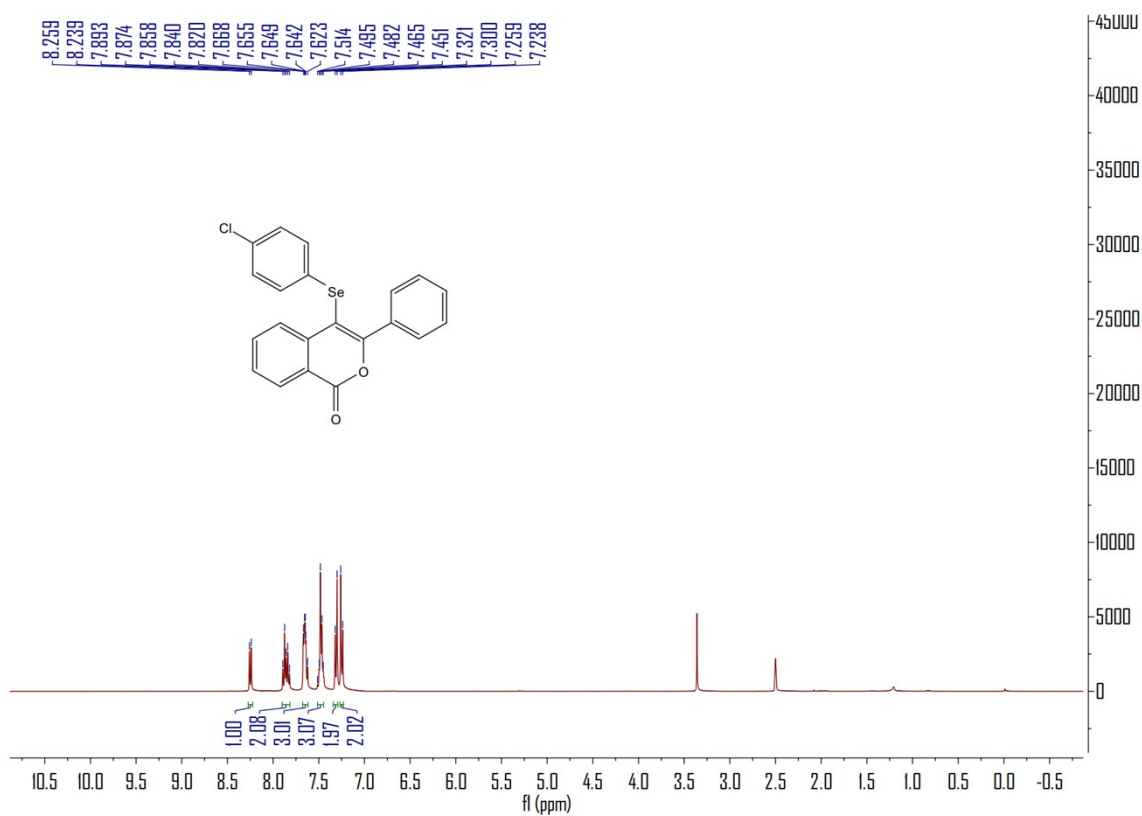
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3u**



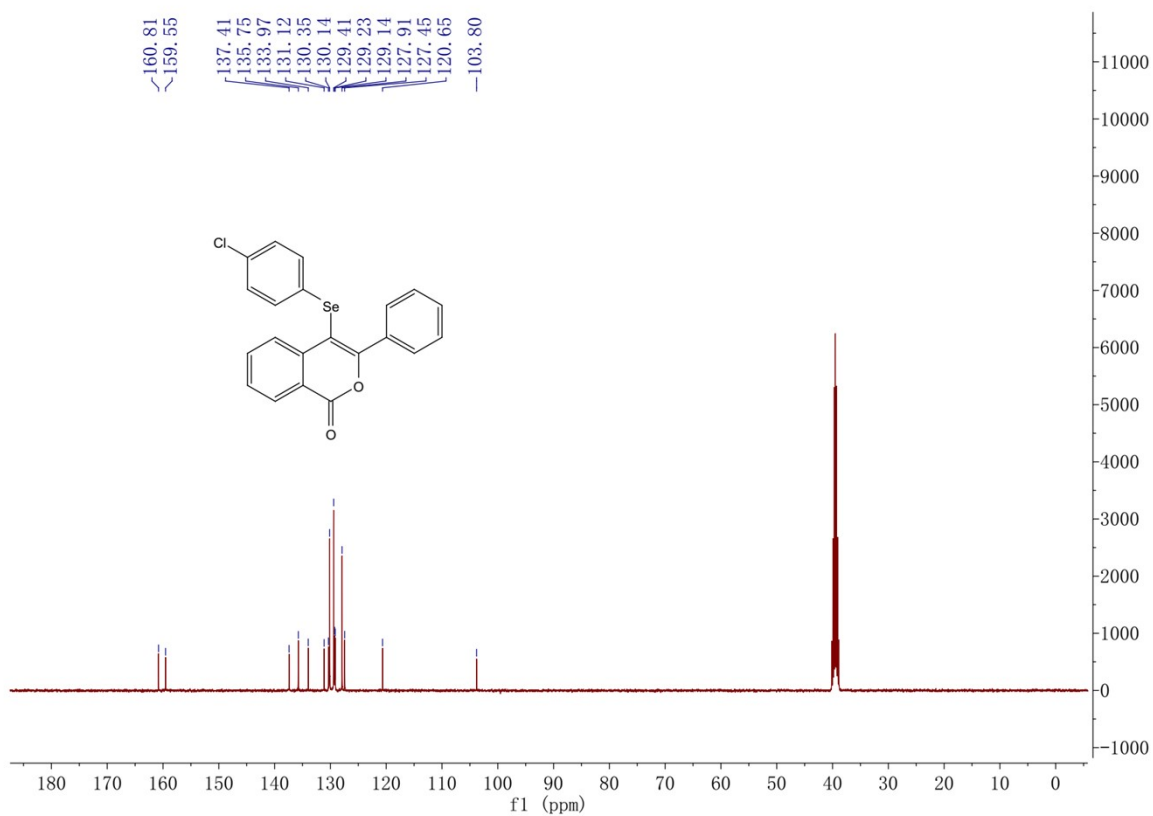
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3u**



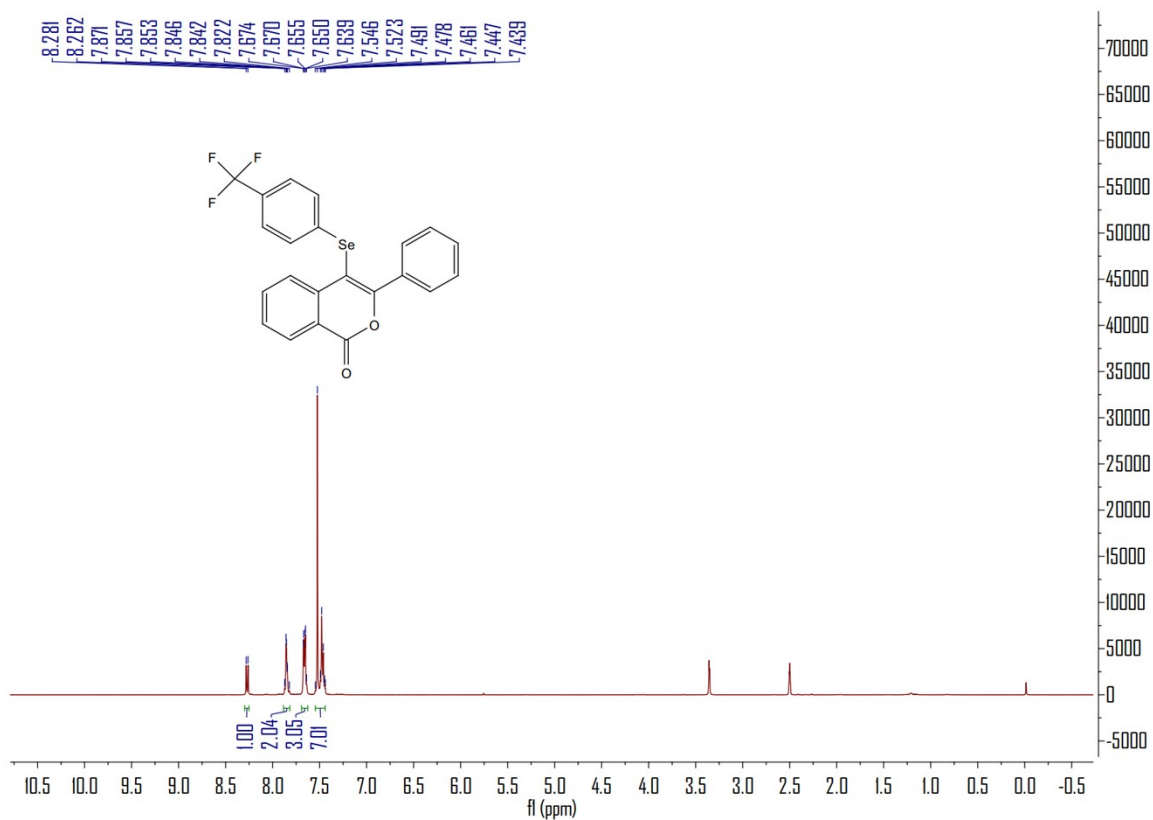
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3v**



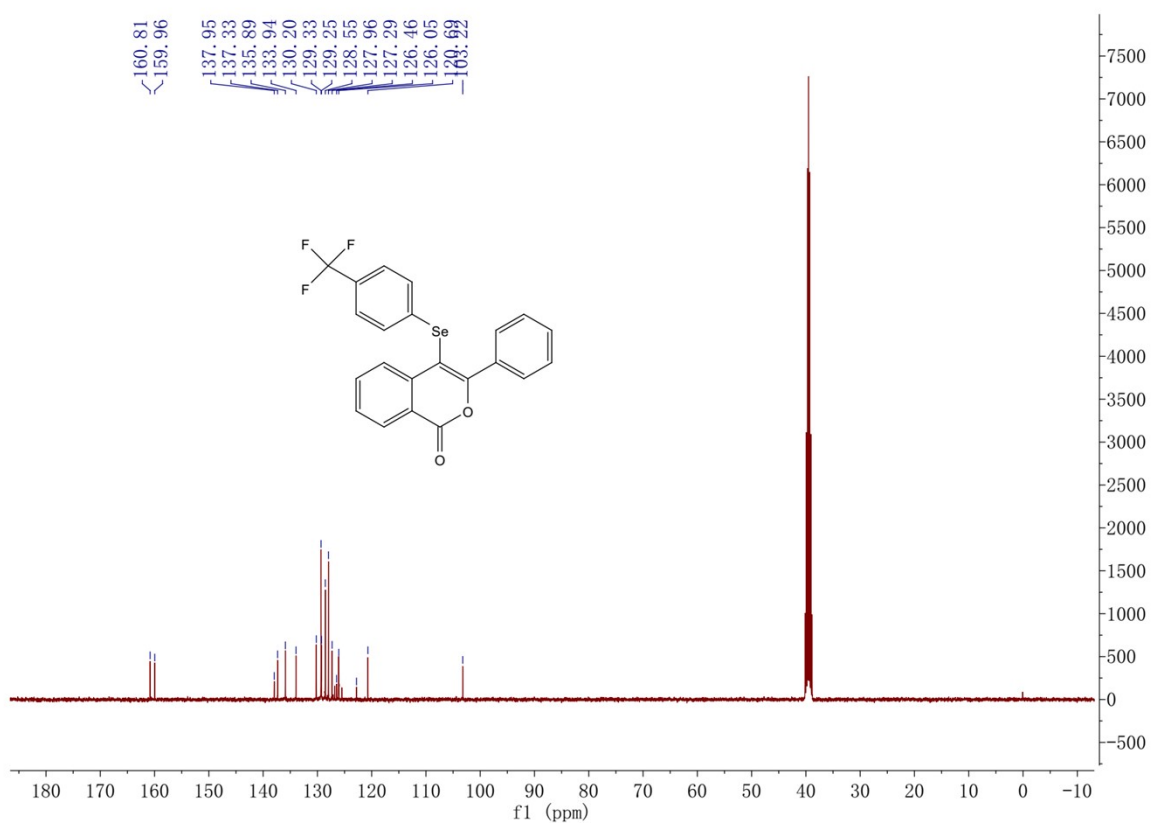
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3v**



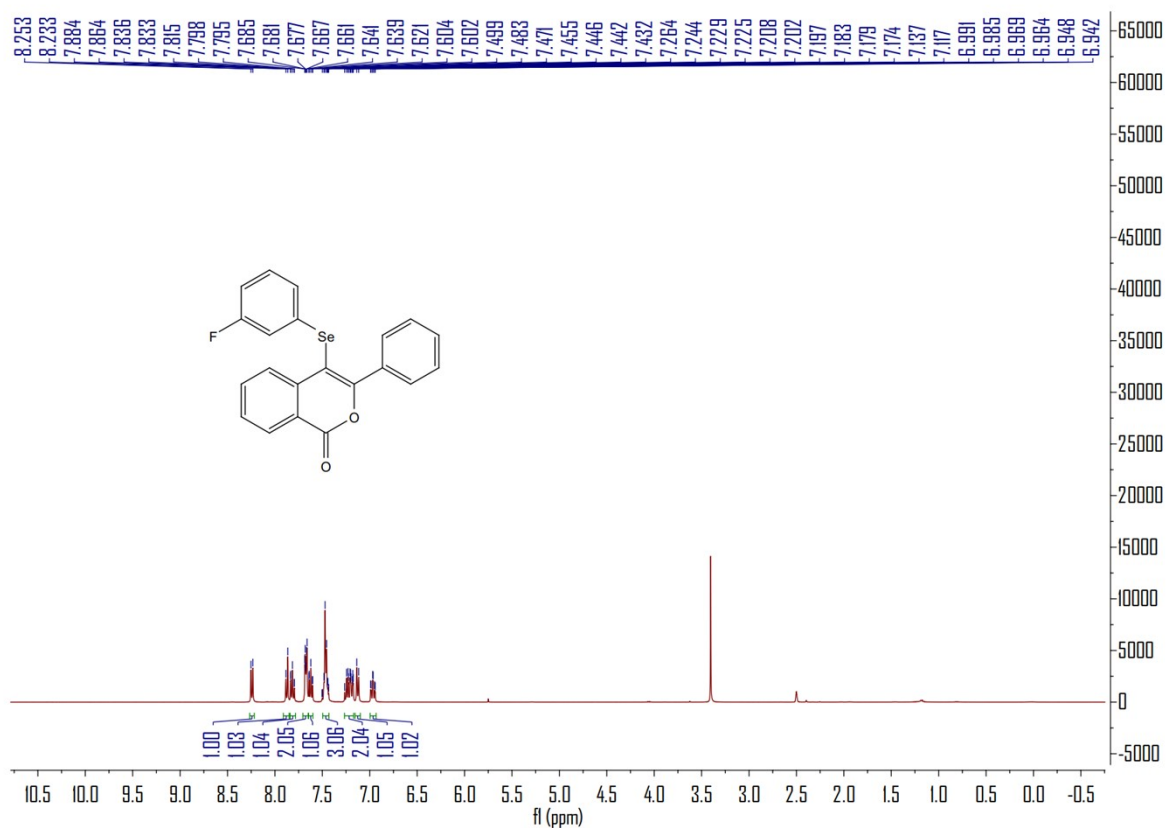
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3w**



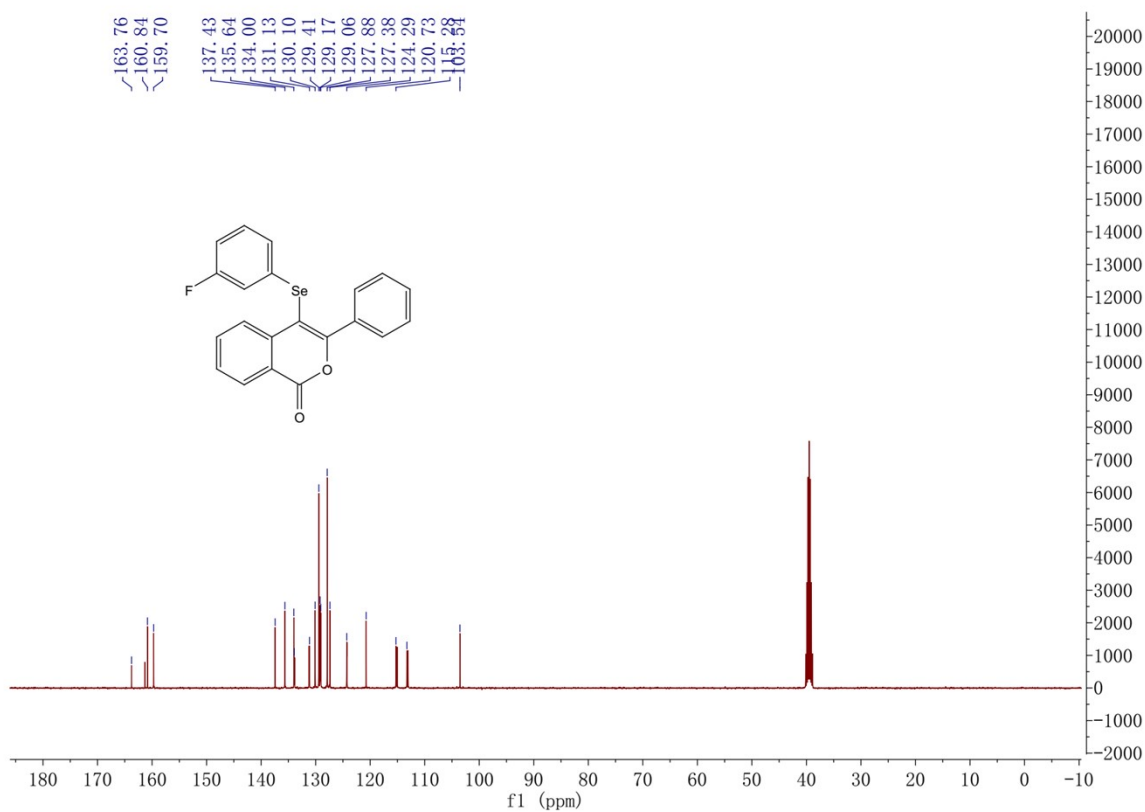
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3w**



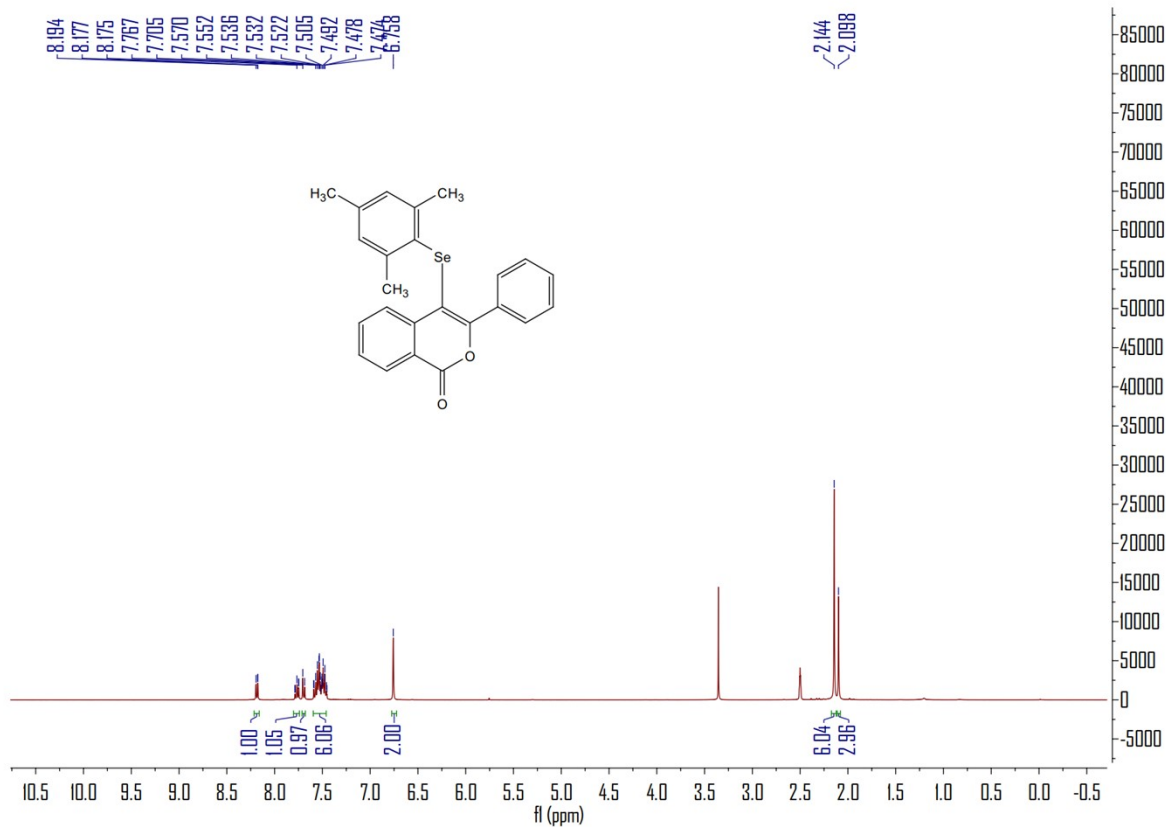
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3x**



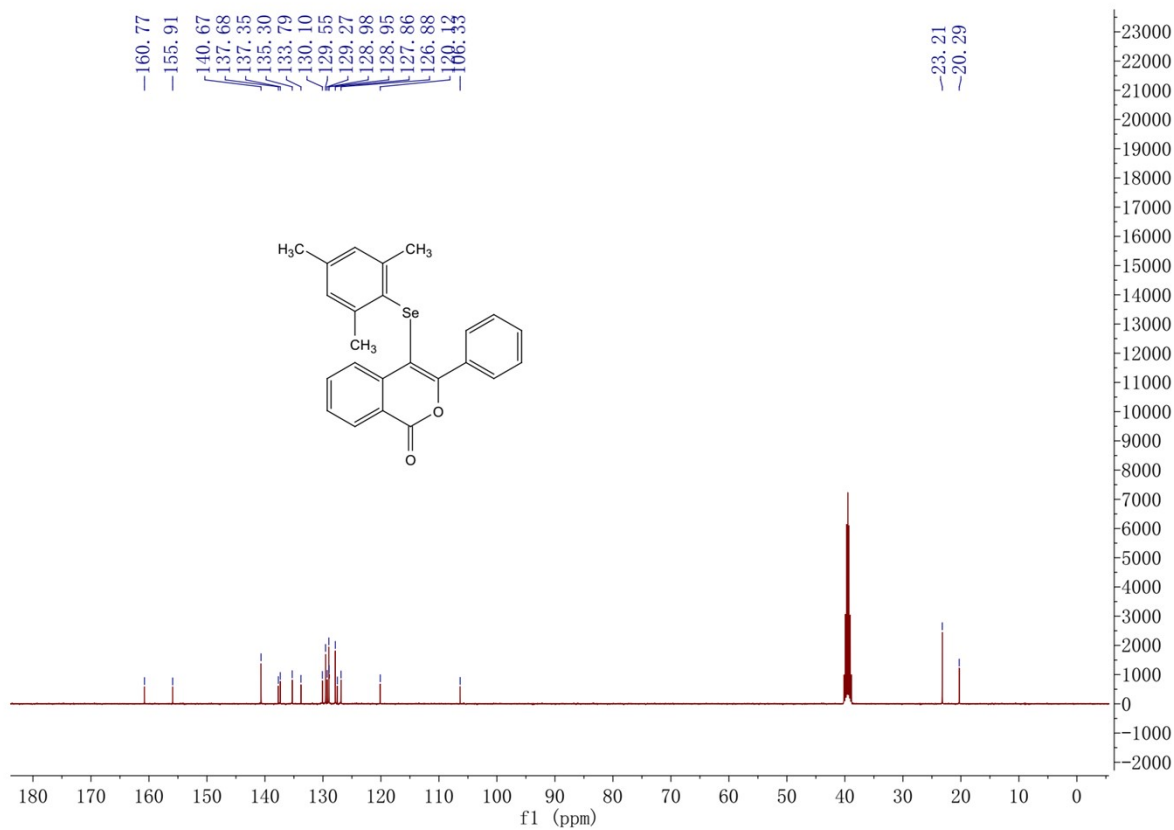
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3x**



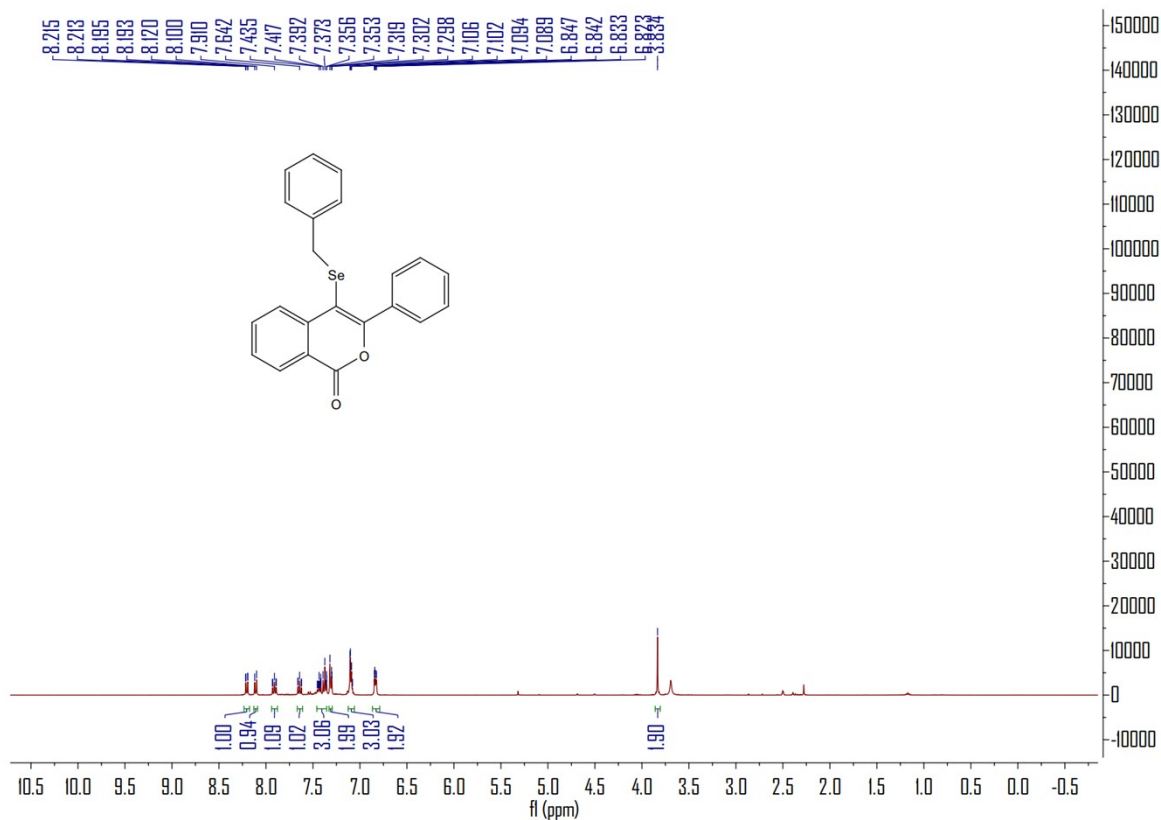
¹H NMR spectrum (400 M, DMSO-*d*₆) of **3y**



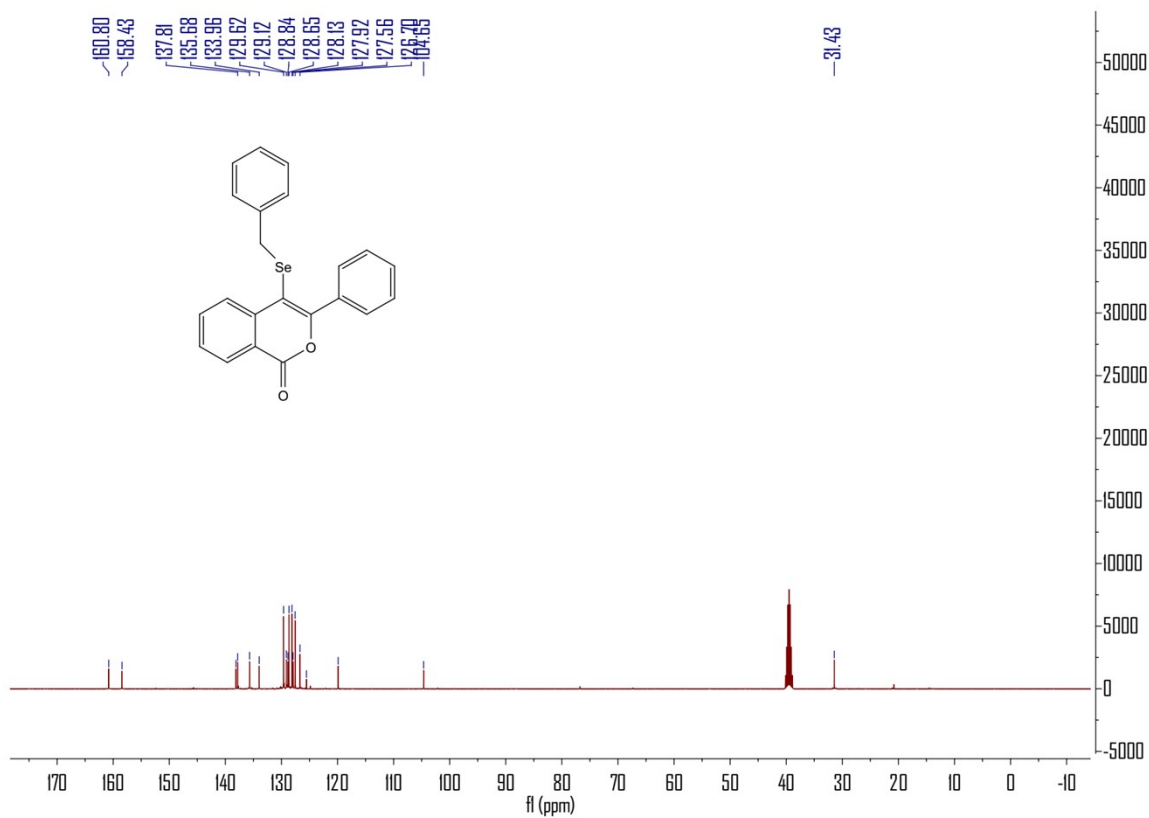
¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3y**



¹H NMR spectrum (400 M, DMSO-*d*₆) of **3z**



¹³C NMR spectrum (100 M, DMSO-*d*₆) of **3z**



HRMS Spectra for 3k

HRMS (m/z) (ESI): calcd for $C_{19}H_{12}NaO_2S$ Se, 406.9615, $[M+Na]^+$ found, 406.9615.

