

Supporting Information

Metal- and Photocatalyst-Free Visible-Light-Promoted Regioselective Selenylation of Coumarin Derivatives via Oxidation-Induced C-H Functionalization

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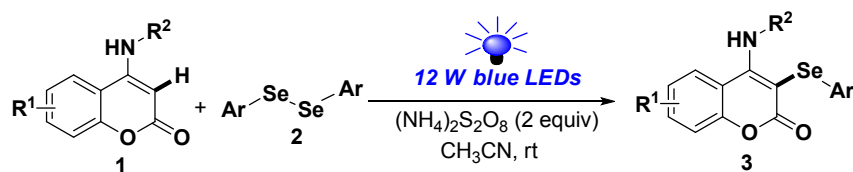
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General information

All commercially available reagent-grade chemicals were purchased from chemical suppliers and used as received without further purification unless otherwise stated. 4-amino substituted coumarins were prepared according to previous literatures.¹ ¹H and ¹³C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded using either tetramethylsilane (TMS) as the internal standard in CDCl₃ (¹H NMR: TMS at 0.00 ppm, CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.0 ppm) The chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t) and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

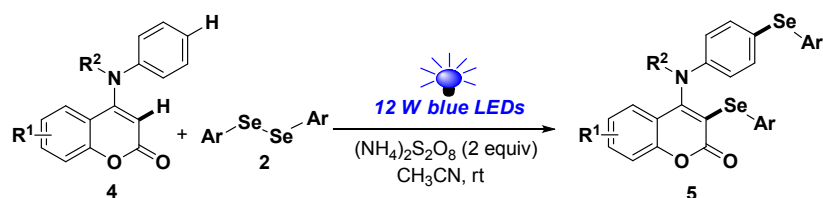
General experimental procedures for visible-light-promoted C-3 Selenylation of coumarin derivatives



A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with 4-

(phenylamino)-2*H*-pyran-2-ones (**1**) (0.2 mmol), diphenyl diselenide (**2**) (0.15 mmol), ammonium persulfate (2 equiv, 0.4 mmol), and CH₃CN (2 mL). The solution was stirred at room temperature with the irradiation of a 12 W blue LED lamp for 24 h. After completion of the reaction (TLC), the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the corresponding products (**3**).

General experimental procedures for visible-light-promoted dual selenylation of *N*-substituted 4-(phenylamino)-2*H*-chromen-2-ones

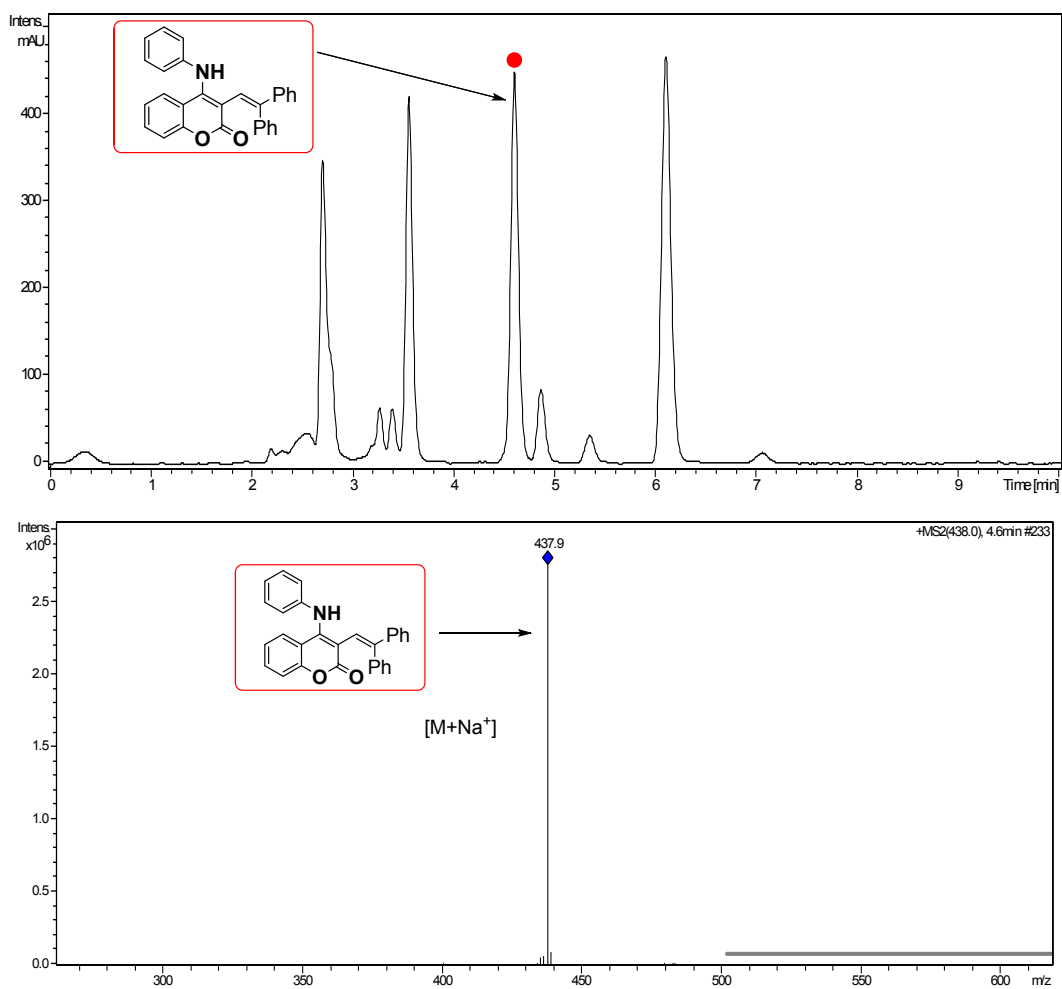


A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with *N*-substituted 4-(phenylamino)-2*H*-chromen-2-ones (**4**) (0.2 mmol), diphenyl diselenide (**2**) (0.2 mmol), ammonium persulfate (2 equiv, 0.4 mmol), and CH₃CN (2mL). The solution was stirred at room temperature with the irradiation of a 12 W blue LED lamp for 24 h. After completion of the reaction (TLC), the solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give the corresponding products (**5**).

Experiments of investigations on the mechanism

A 25 ml Schlenk tube equipped with a magnetic stirring bar was charged with 4-(phenylamino)-2*H*-pyran-2-one (0.2 mmol), 1,2-diphenyldiselenane (0.15 mmol), 1,1-

Diphenylethylene (0.3 mmol), ammonium persulfate (2 equiv, 0.4 mmol), and CH₃CN (2mL). The solution was stirred at room temperature with the irradiation of a 12 W blue LED lamp for 10 h. Afterwards, 30 uL of the mixture was quickly taken out into a small tube and analyzed by LC-MS (Figure 1).



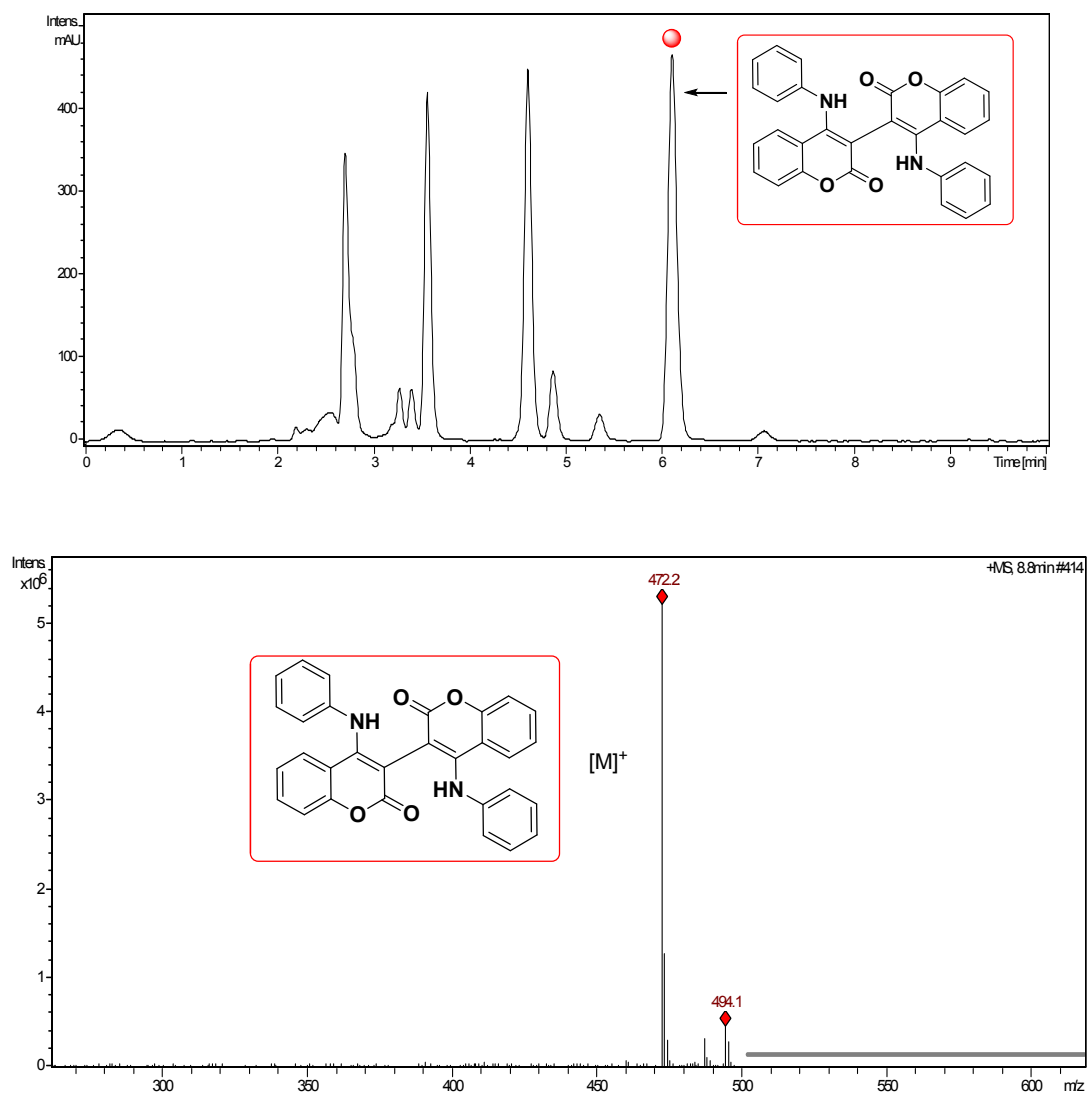
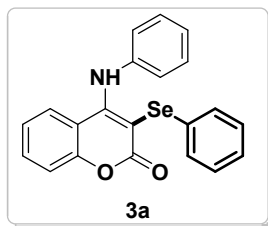


Figure 1. LC-MS spectrum of the reaction mixture

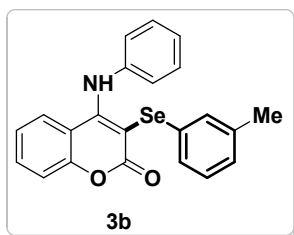
References

- [1] C. Cheng, W.-W. Chen, B. Xu, and M.-H. Xu, *J. Org. Chem.*, **2016**, *81*, 11501.

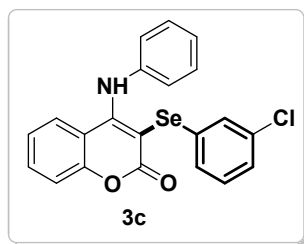
Characterization data of products 3a-3u, and 5a-5l



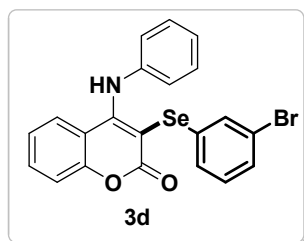
4-(phenylamino)-3-(phenylselanyl)-2H-chromen-2-one (3a). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 198.7–200.3 °C, 62.9 mg, 80% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.88 (s, br, 1H), 7.47–7.44 (m, 3H), 7.35 (d, 1H, $J = 8.3$ Hz), 7.31 (dd, 2H, $J = 7.6$ Hz, 8.0 Hz), 7.24–7.18 (m, 5H), 7.00 (d, 2H, $J = 8.0$ Hz), 6.93 (t, 1H, $J = 7.3$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 161.2, 155.9, 154.3, 141.1, 132.4, 130.6, 130.0, 129.6, 129.5, 127.3, 126.7, 125.9, 123.8, 122.9, 117.7, 113.6, 98.0. HRMS calc. for $\text{C}_{21}\text{H}_{15}\text{NO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 416.0160, found 416.0170.



4-(phenylamino)-3-(*m*-tolylselanyl)-2H-chromen-2-one (3b). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 141.5–142.4 °C, 61.1 mg, 75% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.85 (s, br, 1H), 7.45 (t, 1H, $J = 8.2$ Hz), 7.35–7.24 (m, 5H), 7.21–7.18 (m, 2H), 7.10 (t, 1H, $J = 7.6$ Hz), 7.00–6.98 (m, 3H), 6.93 (t, 1H, $J = 8.3$ Hz), 2.24 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 171.2, 161.2, 155.8, 154.3, 141.3, 139.4, 132.4, 131.4, 129.6, 129.3, 128.2, 127.7, 126.7, 125.8, 123.6, 122.9, 117.7, 113.7, 98.5, 21.3. HRMS calc. for $\text{C}_{22}\text{H}_{17}\text{NO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 430.0317, found 430.0321.

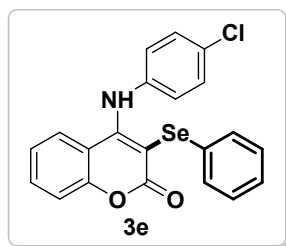


3-(3-chlorophenylselanyl)-4-(phenylamino)-2H-chromen-2-one (3c). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 133.5-135.4 °C, 64.9 mg, 76% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.85 (s, br, 1H), 7.48 (t, 1H, $J = 7.0$ Hz), 7.39-7.31 (m, 5H), 7.23 (d, 1H, $J = 7.5$ Hz), 7.20 (d, 1H, $J = 8.4$ Hz), 7.17-7.12 (m, 2H), 7.03 (d, 2H, $J = 8.1$ Hz), 6.95 (t, 1H, $J = 8.3$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 161.0, 156.3, 154.4, 140.9, 132.7, 132.6, 132.0, 130.8, 130.3, 129.7, 128.8, 126.8, 126.2, 123.9, 123.4, 123.0, 117.8, 113.5, 97.0. HRMS calc. for $\text{C}_{21}\text{H}_{14}\text{ClNO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 449.9770, found 449.9783.

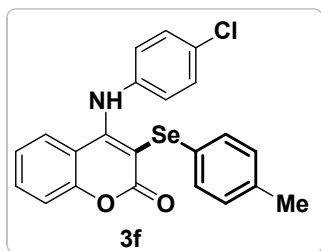


3-(3-bromophenylselanyl)-4-(phenylamino)-2H-chromen-2-one (3d). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 158.8-160.9 °C, 73.5 mg, 78% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.84 (s, br, 1H), 7.54 (s, 1H), 7.48 (t, 1H, $J = 8.5$ Hz), 7.38-7.30 (m, 5H), 7.25-7.19 (m, 2H), 7.08 (t, 1H, $J = 7.9$ Hz), 7.04 (d, 2H, $J = 7.8$ Hz), 6.95 (t, 1H, $J = 8.3$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 156.2, 151.5, 149.6, 136.2, 130.5, 128.0, 126.9, 125.7, 125.0, 124.9, 123.6, 122.6, 122.0, 121.4, 119.1, 118.3, 113.0, 108.7, 92.2. HRMS calc. for $\text{C}_{21}\text{H}_{14}\text{BrNO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$

493.9265, found 493.9274.

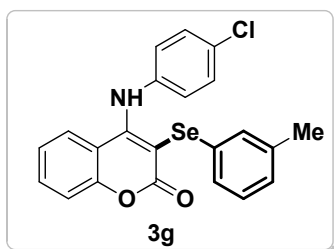


4-(4-chlorophenylamino)-3-(phenylselanyl)-2H-chromen-2-one (3e). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 141.2-142.3 °C, 72.6 mg, 85% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.73 (s, br, 1H), 7.49-7.44 (m, 3H), 7.35 (d, 1H, $J = 8.3$ Hz), 7.26-7.17 (m, 6H), 6.98 (t, 1H, $J = 7.5$ Hz), 6.91 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 159.9, 154.4, 153.2, 138.8, 131.5, 131.0, 129.8, 128.7, 128.6, 128.5, 126.4, 125.4, 123.5, 122.1, 116.7, 112.5, 98.4. HRMS calc. for $\text{C}_{21}\text{H}_{14}\text{ClNO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 449.9770, found 449.9773.

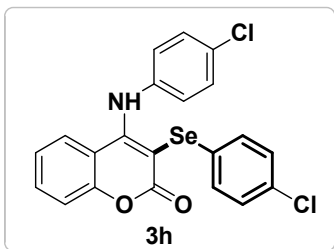


4-(4-chlorophenylamino)-3-(p-tolylselanyl)-2H-chromen-2-one (3f). Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 165.4-167.9 °C, 63.5 mg, 72% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.71 (s, br, 1H), 7.46 (t, 1H, $J = 7.2$ Hz), 7.37-7.32 (m, 3H), 7.24 (d, 2H, $J = 8.7$ Hz), 7.19 (d, 1H, $J = 8.3$ Hz), 7.01 (d, 2H, $J = 7.9$ Hz), 6.97 (t, 1H, $J = 7.2$ Hz), 6.88 (d, 2H, $J = 8.5$ Hz), 2.25 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 160.9, 155.0, 154.1, 139.9, 137.7, 132.4, 131.5, 130.8, 130.3, 129.5, 126.4, 125.8, 124.3, 123.0, 117.6, 113.6, 100.4, 20.1. HRMS calc. for

C₂₂H₁₆ClNO₂Se [M + Na]⁺ 463.9927, found 463.9914.

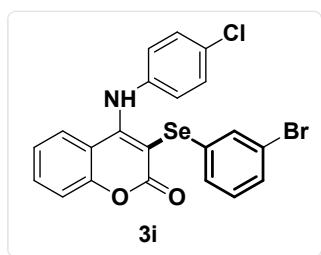


4-(4-chlorophenylamino)-3-(*m*-tolylselanyl)-2*H*-chromen-2-one (3g). Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 126.7-130.3 °C, 61.7 mg, 70% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.70 (s, br, 1H), 7.47 (t, 1H, *J* = 7.8 Hz), 7.36 (d, 1H, *J* = 8.4 Hz), 7.25-7.22 (m, 4H), 7.19 (d, 1H, *J* = 8.2 Hz), 7.08 (t, 1H, *J* = 7.6 Hz), 7.00-6.97 (m, 2H), 6.89 (d, 2H, *J* = 8.6 Hz), 2.23 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 161.0, 155.3, 154.2, 139.9, 139.5, 132.5, 131.6, 130.9, 129.6, 129.4, 129.3, 128.4, 127.9, 126.5, 124.4, 123.1, 117.7, 113.6, 99.9, 21.3. HRMS calc. for C₂₂H₁₆ClNO₂Se [M + Na]⁺ 463.9927, found 463.9938.



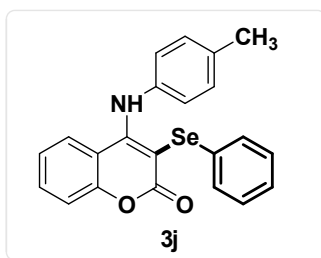
4-(4-chlorophenylamino)-3-(4-chlorophenylselanyl)-2*H*-chromen-2-one (3h). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 181.9-182.1 °C, 71.9 mg, 78% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.72 (s, br, 1H), 7.49 (t, 1H, *J* = 7.8 Hz), 7.40-7.36 (m, 3H), 7.28 (d, 2H, *J* = 8.7 Hz), 7.20-7.18 (m, 3H), 6.99 (t, 1H, *J* = 8.2 Hz), 6.93 (d, 2H, *J* = 8.2 Hz). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 155.6, 154.3, 139.6, 133.7, 132.8, 132.2, 131.4, 129.8, 129.7, 127.9, 126.5, 124.7, 123.2, 117.8,

113.4, 99.0. HRMS calc. for $C_{21}H_{13}ClNO_2Se$ $[M + Na]^+$ 483.9381, found 483.8569.



3-(3-bromophenylselanyl)-4-(4-chlorophenylamino)-2H-chromen-2-one (3i).

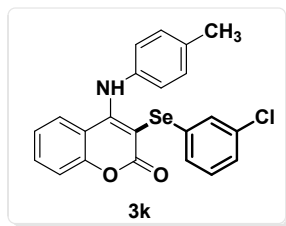
Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 190.8-193.2 °C, 83.8 mg, 83% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.68 (s, br, 1H), 7.54-7.49 (m, 2H), 7.38-7.36 (m, 2H), 7.32 (d, 1H, $J = 8.0$ Hz), 7.28 (d, 2H, $J = 8.7$ Hz), 7.20 (d, 1H, $J = 8.3$ Hz), 7.08 (t, 1H, $J = 7.9$ Hz), 7.00 (t, 1H, $J = 8.5$ Hz), 6.95 (d, 2H, $J = 8.7$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 160.8, 155.8, 154.3, 139.6, 132.9, 132.8, 131.7, 131.4, 130.8, 130.5, 129.8, 129.0, 126.5, 124.7, 123.4, 123.3, 117.9, 113.4, 98.5. HRMS calc. for $C_{21}H_{13}BrClNO_2Se$ $[M + Na]^+$ 527.8876, found 527.8862.



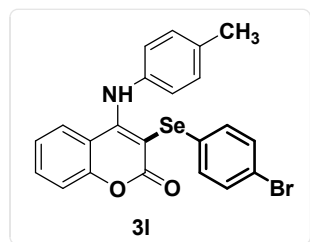
3-(3-bromophenylselanyl)-4-(4-methylphenylamino)-2H-chromen-2-one (3j).

Eluent petroleum ether/ethyl acetate (10:). Yellow solid, m.p. 106.6-107.2 °C, 57.0 mg, 70% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.90 (s, br, 1H), 7.46-7.42 (m, 3H), 7.33 (d, 1H, $J = 7.9$ Hz), 7.26-7.19 (m, 4H), 7.11 (d, 2H, $J = 8.1$ Hz), 6.94-6.90 (m, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.3, 156.1, 154.4, 138.4, 136.1, 132.4, 130.4, 130.2, 130.0, 129.5, 127.2, 126.8, 124.1, 122.8, 117.7, 113.6,

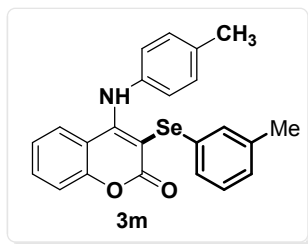
96.7, 21.0. HRMS calc. for $C_{22}H_{17}NO_2Se$ $[M + Na]^+$ 430.0317, found 430.0301.



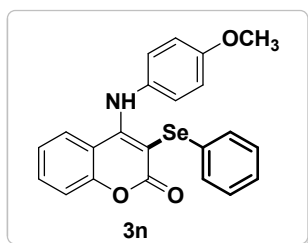
3-(3-chlorophenylselanyl)-4-(*p*-tolylamino)-2*H*-chromen-2-one (3k). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 146.7-148.5 °C, 54.7 mg, 62% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.86 (s, br, 1H), 7.47 (t, 1H, $J = 8.7$ Hz), 7.38-7.30 (m, 3H), 7.20 (d, 1H, $J = 8.2$ Hz), 7.17-7.12 (m, 4H), 6.96-6.93 (m, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.6, 156.5, 154.4, 138.2, 136.4, 135.2, 132.7, 131.8, 130.4, 130.3, 129.6, 128.1, 127.3, 126.8, 124.2, 123.0, 117.8, 113.4, 95.6, 21.0. HRMS calc. for $C_{22}H_{16}NO_2Se$ $[M + Na]^+$ 463.9927, found 463.9932.



3-(4-bromophenylselanyl)-4-(*p*-tolylamino)-2*H*-chromen-2-one (3l). Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 157.3-160.2 °C, 53.3 mg, 55% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.87 (s, br, 1H), 7.45(t, 1H, $J = 7.5$ Hz), 7.34-7.30 (m, 5H), 7.20 (d, 1H, $J = 8.3$ Hz), 7.13 (d, 2H, $J = 8.0$ Hz), 6.95-6.92 (m, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.1, 156.2, 154.4, 138.2, 136.3, 132.6, 132.5, 132.1, 130.3, 129.0, 126.8, 124.1, 122.9, 121.4, 117.7, 113.5, 96.3, 21.0. HRMS calc. for $C_{22}H_{16}BrNO_2Se$ $[M + Na]^+$ 507.9422, found 507.9436.

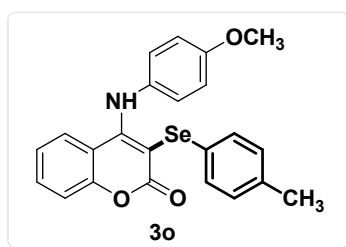


4-(*p*-tolylamino)-3-(*m*-tolylselanyl)-2*H*-chromen-2-one (3m). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 119.2-121.7 °C, 54.7 mg, 65% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.88 (s, br, 1H), 7.44 (t, 1H, J = 8.4 Hz), 7.33 (d, 1H, J = 8.3 Hz), 7.27-7.19 (m, 3H), 7.11-7.08 (m, 3H), 6.99 (d, 1H, J = 7.5 Hz), 6.94-6.90 (m, 3H), 2.35 (s, 3H), 2.25 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 161.3, 156.1, 154.3, 139.4, 138.5, 136.0, 132.3, 131.1, 130.2, 129.7, 129.3, 128.1, 127.5, 126.8, 123.9, 122.8, 117.6, 113.7, 97.1, 21.3, 21.0. HRMS calc. for C₂₃H₁₉NO₂Se [M + Na]⁺ 444.0473, found 444.0476.

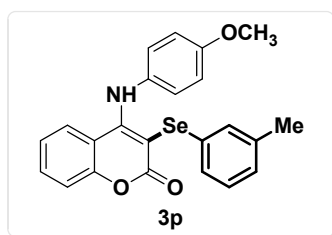


4-(4-methoxyphenylamino)-3-(phenylselanyl)-2*H*-chromen-2-one (3n). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 110.3-110.7 °C, 77.0 mg, 91.0% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.93 (s, br, 1H), 7.46-7.42 (m, 3H), 7.33 (d, 1H, J = 8.4 Hz), 7.24-7.18 (m, 3H), 7.17 (d, 1H, J = 8.3 Hz), 6.97 (d, 2H, J = 8.8 Hz), 6.91 (t, 1H, J = 8.2 Hz), 6.84 (d, 2H, J = 8.8 Hz), 3.81 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 161.3, 158.1, 156.2, 154.4, 133.7, 132.4, 130.3, 130.1, 129.5, 127.1, 126.6, 126.1, 122.9, 117.7, 114.8, 113.5, 95.5, 55.6. HRMS calc. for

$C_{22}H_{17}NO_3Se$ $[M + Na]^+$ 446.0266, found 446.0262.

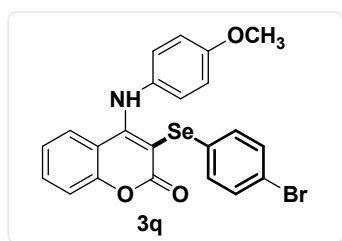


4-(4-methoxyphenylamino)-3-(*p*-tolylselanyl)-2*H*-chromen-2-one (3o). Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 118.2-120.7 °C, 58.6 mg, 67% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.93 (s, br, 1H), 7.40 (t, 1H, $J = 8.0$ Hz), 7.36 (d, 2H, $J = 7.4$ Hz), 7.30 (d, 1H, $J = 8.4$ Hz), 7.15 (d, 1H, $J = 8.3$ Hz), 7.03 (d, 2H, $J = 7.4$ Hz), 6.96 (d, 2H, $J = 8.4$ Hz), 6.90 (t, 1H, $J = 8.0$ Hz), 6.84 (d, 2H, $J = 8.4$ Hz), 3.81 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.3, 158.0, 155.9, 154.4, 137.3, 133.8, 132.2, 131.0, 130.3, 126.6, 126.3, 126.0, 122.8, 117.6, 114.8, 113.6, 96.4, 55.5, 21.1. HRMS calc. For $C_{23}H_{19}NO_3Se$ $[M + Na]^+$ 460.0422, found 460.0431.



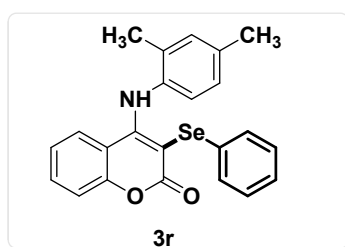
4-(4-methoxyphenylamino)-3-(*m*-tolylselanyl)-2*H*-chromen-2-one (3p). Eluent petroleum ether/ethyl acetate (12:1). Yellow solid, m.p. 120.3-121.2 °C, 69.9 mg, 80% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.91 (s, br, 1H), 7.43 (t, 1H, $J = 8.5$ Hz), 7.33 (d, 1H, $J = 8.4$ Hz), 7.27-7.23 (m, 2H), 7.16 (d, 1H, $J = 8.3$ Hz), 7.11 (t, 1H, $J = 7.7$ Hz), 7.01-6.97 (m, 3H), 6.91 (t, 1H, $J = 7.3$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.2, 158.0, 156.1, 154.4,

139.3, 133.8, 132.2, 131.0, 129.7, 129.2, 128.0, 127.3, 126.6, 125.9, 122.8, 117.6, 114.8, 113.5, 95.9, 55.5, 21.3. HRMS calc. for $C_{23}H_{19}NO_3Se$ $[M + Na]^+$ 460.0422, found 460.0434.



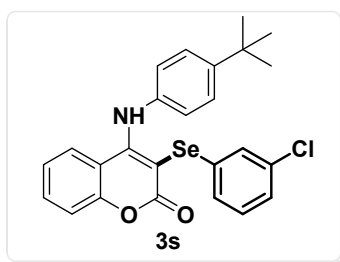
3-(4-bromophenylselanyl)-4-(4-methoxyphenylamino)-2H-chromen-2-one (3q).

Eluent petroleum ether/ethyl acetate (15:1). Yellow solid, m.p. 170.8-171.6 °C, 77.1 mg, 77% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.90 (s, br, 1H), 7.45 (t, 1H, J = 8.5 Hz), 7.34-7.30 (m, 5H), 7.16 (d, 1H, J = 8.5 Hz), 7.00 (d, 2H, J = 8.5 Hz), 6.92 (t, 1H, J = 8.1 Hz), 6.86 (d, 2H, J = 8.5 Hz), 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 161.1, 158.3, 156.4, 154.4, 133.5, 132.5, 132.4, 131.9, 129.1, 126.6, 126.1, 122.9, 121.3, 117.8, 114.9, 113.4, 95.1, 55.6. HRMS calc. for $C_{22}H_{16}NO_3Se$ $[M+ Na]^+$ 523.9371, found 523.9377.



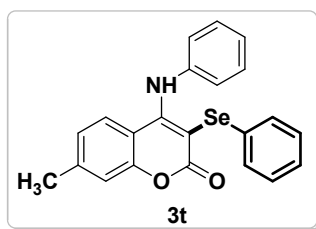
4-(2,4-dimethylphenylamino)-3-(phenylselanyl)-2H-chromen-2-one (3r). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 180.4-181.2 °C, 54.7 mg, 65% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.75 (s, br, 1H), 7.47-7.42 (m, 3H), 7.32 (d, 1H, J = 8.1 Hz), 7.24-7.19 (m, 3H), 7.07 (s, 1H), 7.01 (d, 1H, J = 8.3 Hz), 6.93-6.87

(m, 2H), 6.78 (d, 1H, $J = 8.0$ Hz), 2.33 (s, 3H), 2.09 . ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 161.5, 156.1, 154.3, 137.1, 136.5, 133.2, 132.4, 132.0, 130.4, 129.9, 129.5, 127.7, 127.2, 125.8, 125.7, 123.0, 117.7, 113.6, 94.4, 60.4. HRMS calc. for $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 444.0473, found 4440.459.



4-(4-*tert*-butylphenylamino)-3-(3-chlorophenylselanyl)-2H-chromen-2-one (3s).

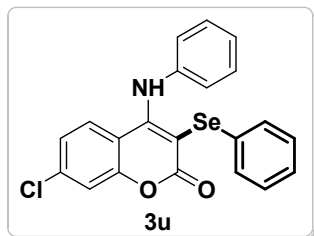
Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 109.2-110.5 °C, 82.1 mg, 85% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.87 (s, br, 1H), 7.47 (t, 1H, $J = 7.2$ Hz), 7.37-7.30 (m, 5H), 7.23 (d, 1H, $J = 8.3$ Hz), 7.14-7.11 (m, 2H), 6.99-6.93 (m, 3H), 1.32 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 156.3, 151.7, 149.6, 144.8, 133.4, 130.4, 127.9, 127.1, 125.7, 124.9, 123.4, 122.5, 122.1, 121.8, 118.9, 118.3, 113.0, 108.8, 91.1, 26.6. HRMS calc. for $\text{C}_{25}\text{H}_{22}\text{NO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 506.0396, found 506.0402.



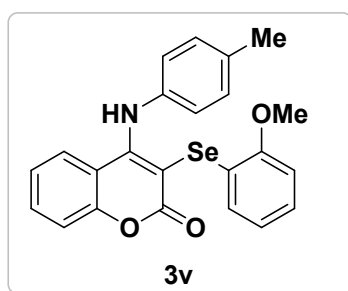
7-methyl-4-(phenylamino)-3-(phenylselanyl)-2H-chromen-2-one (3t).

Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 173.4-175.7 °C, 52.9 mg, 65% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.88 (s, br, 1H), 7.43 (d, 2H, $J = 7.9$ Hz), 7.30 (t, 2H, $J = 7.5$ Hz), 7.24-7.18 (m, 6H), 7.00 (d, 2H, $J = 7.9$ Hz), 6.93 (s, 1H),

2.07 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 161.3, 155.7, 152.3, 140.9, 133.4, 132.3, 131.0, 130.4, 129.9, 129.4, 127.1, 126.4, 125.8, 123.7, 117.2, 113.1, 97.6, 20.8. HRMS calc. for $\text{C}_{22}\text{H}_{17}\text{NO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 430.0317, found 430.0328.

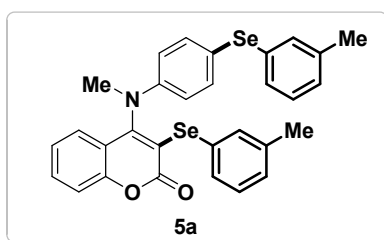


7-chloro-4-(phenylamino)-3-(phenylselanyl)-2H-chromen-2-one (3u). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 165.3-168.4 °C, 59.8 mg, 70% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.91 (s, br, 1H), 7.46-7.44 (m, 2H), 7.33-7.30 (m, 3H), 7.23-7.20 (m, 4H), 7.09 (d, 1H, $J = 8.9$ Hz), 7.00 (d, 2H, $J = 7.6$ Hz), 6.88 (d, 1H, $J = 8.9$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 160.6, 155.2, 154.7, 140.7, 138.3, 130.8, 129.8, 129.7, 129.6, 127.7, 127.4, 126.2, 123.9, 123.5, 117.7, 112.2, 97.8. HRMS calc. for $\text{C}_{21}\text{H}_{14}\text{ClNO}_2\text{Se}$ $[\text{M} + \text{Na}]^+$ 449.9770, found 449.9764.



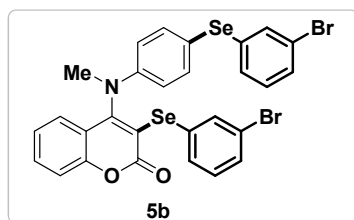
3-((2-methoxyphenyl)selanyl)-4-(p-tolylamino)-2H-chromen-2-one (3v). Eluent petroleum ether/ethyl acetate (10:1). Yellow solid, m.p. 139.7-142.2 °C, 32.3 mg, 37% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.02 (s, br, 1H), 7.44 (t, 1H, $J = 5.0$ Hz), 7.33 (d, 1H, $J = 7.8$ Hz), 7.25 (d, 1H, $J = 5.7$ Hz), 7.20-7.16 (m, 2H), 7.09 (d, 2H, $J = 8.1$ Hz), 6.93-6.88 (m, 3H), 6.84-6.79 (m, 2H), 3.82 (s, 3H), 2.84 (s, 3H). ^{13}C NMR

(CDCl₃, 125 MHz, ppm) δ 161.3, 157.3, 156.7, 154.4, 138.5, 136.8, 132.2, 130.3, 130.1, 128.2, 126.7, 124.0, 122.7, 121.8, 118.6, 117.6, 113.6, 110.5, 94.8, 55.8, 20.9. HRMS calc. for C₂₃H₁₉NNaO₃Se [M+ Na]⁺ 460.0422, found 460.0419.



4-(methyl(4-(*m*-tolylselanyl)phenyl)amino)-3-(*m*-tolylselanyl)-2*H*-chromen-2-one

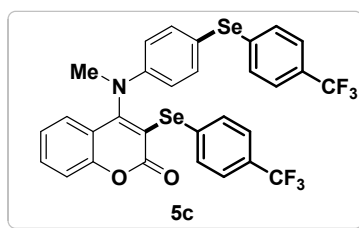
(5a). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 83.9 mg, 71% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.49 (t, 1H, *J* = 7.8 Hz), 7.37 (m, 3H), 7.27-7.23 (m, 2H), 7.19 (d, 2H, *J* = 4.8 Hz), 7.15-7.09 (m, 3H), 7.01 (m, 2H), 6.91 (d, 1H, *J* = 7.6 Hz), 6.44 (d, 2H, *J* = 8.5 Hz), 3.19 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 160.8, 157.1, 153.6, 146.1, 138.9, 136.0, 134.5, 132.9, 131.9, 131.6, 130.7, 129.0, 128.9, 128.8, 128.2, 128.1, 127.4, 125.2, 124.4, 121.1, 118.6, 118.3, 117.3, 114.6, 38.2, 21.4, 21.2. HRMS calc. for C₃₀H₂₅NOS₂ [M + H]⁺ 592.0288, found 592.0286.



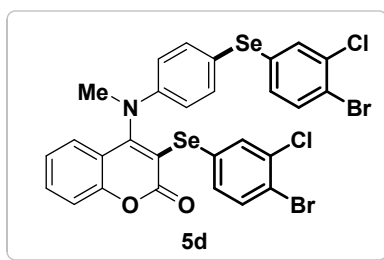
3-(3-bromophenylselanyl)-4-((4-(3-bromophenylselanyl)phenyl)(methyl)amino)-

2*H*-chromen-2-one (5b). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 112.1 mg, 78% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.53-7.51 (m, 2H), 7.40-

7.37 (m, 5H), 7.29-7.23 (m, 4H), 7.17 (dd, 1H, $J = 7.5$ Hz, $J = 7.6$ Hz), 7.06 (t, 1H, $J = 8.9$ Hz), 6.98 (t, 1H, $J = 7.6$ Hz), 6.47 (d, 2H, $J = 8.2$ Hz), 3.24 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 159.5, 156.5, 152.6, 145.4, 135.8, 135.1, 134.9, 131.6, 131.3, 131.1, 130.2, 129.3, 129.2, 129.1, 128.2, 127.8, 124.2, 123.5, 122.1, 121.7, 119.5, 117.3, 116.3, 116.2, 113.7, 37.1. HRMS calc. for $\text{C}_{28}\text{H}_{19}\text{Br}_2\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 719.8186, found 719.8188.

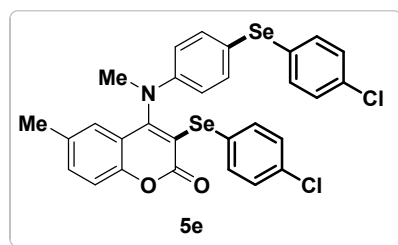


4-(methyl(4-(4-(trifluoromethyl)phenylselanyl)phenyl)amino)-3-(4-(trifluoromethyl)phenylselanyl)-2H-chromen-2-one (5c). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 111.8 mg, 80% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.57 (t, 1H, $J = 7.7$ Hz), 7.52 (d, 2H, $J = 8.2$ Hz), 7.45-7.36 (m, 8H), 7.33 (d, 2H, $J = 8.2$ Hz), 7.22 (t, 1H, $J = 7.4$ Hz), 3.31 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 160.3, 158.7, 154.0, 147.0, 139.3, 138.9, 137.4, 133.7, 132.9, 132.7, 130.2 (q, $J = 87.9$ Hz), 129.6, 125.8 (dq, $J = 7.9$ Hz), 125.3, 125.1 (q, $J = 270.7$ Hz), 124.7, 119.8, 118.3, 117.5, 116.7, 114.8, 38.3. HRMS calc. for $\text{C}_{30}\text{H}_{19}\text{F}_6\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 699.9723, found 699.9725.

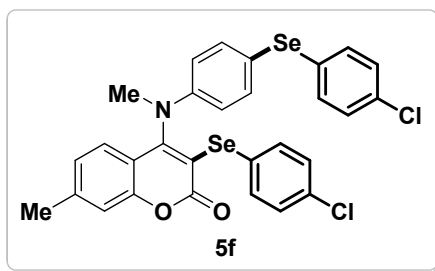


3-(4-bromo-3-chlorophenylselanyl)-4-((4-(4-bromo-3-

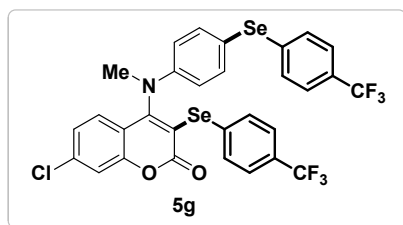
chlorophenylselanyl)phenyl)(methylamino)-2H-chromen-2-one (5d). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 116.4 mg, 74% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.55 (t, 1H, $J = 7.1$ Hz), 7.45 (s, 1H), 7.42-7.39 (m, 4H), 7.35 (d, 1H, $J = 8.3$ Hz), 7.33-7.31 (m, 2H), 7.21-7.18 (m, 2H), 7.05 (d, 1H, $J = 8.3$ Hz), 6.49 (d, 2H, $J = 8.2$ Hz), 3.29 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 160.4, 157.9, 153.8, 146.6, 136.9, 135.1, 134.9, 134.4, 134.0, 133.9, 133.1, 132.6, 131.6, 129.8, 128.4, 125.2, 124.7, 122.7, 120.3, 120.1, 118.3, 117.5, 117.2, 114.7, 38.2. HRMS calc. for $\text{C}_{28}\text{H}_{17}\text{Br}_2\text{Cl}_2\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 787.7406, found 787.7410.



3-(4-chlorophenylselanyl)-4-((4-(4-chlorophenylselanyl)phenyl)(methylamino))-6-methyl-2H-chromen-2-one (5e). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 98.0 mg, 76% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.39 (d, 2H, $J = 8.5$ Hz), 7.34 (d, 3H, $J = 8.5$ Hz), 7.28-7.25 (m, 3H), 7.17 (d, 2H, $J = 8.5$ Hz), 7.08 (d, 2H, $J = 8.4$ Hz), 6.50 (d, 2H, $J = 8.2$ Hz), 3.25 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 160.6, 157.8, 152.0, 146.6, 136.4, 135.1, 134.4, 134.3, 133.4, 132.5, 132.1, 131.6, 129.2, 129.1, 126.6, 124.7, 120.5, 118.1, 118.1, 117.8, 117.1, 114.5, 38.1, 21.0. HRMS calc. for $\text{C}_{29}\text{H}_{21}\text{Cl}_2\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 645.9353, found 645.9356.

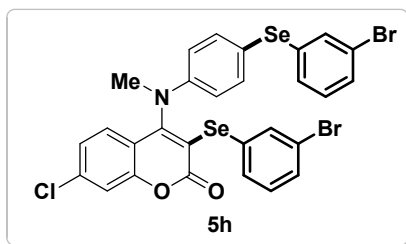


3-(4-chlorophenylselanyl)-4-((4-(4-chlorophenylselanyl)phenyl)(methyl)amino)-7-methyl-2H-chromen-2-one (5f). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 89.0 mg, 69% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.37-7.33 (m, 4H), 7.26-7.24 (m, 2H), 7.19-7.16 (m, 4H), 7.06 (d, 2H, $J = 6.7$ Hz), 6.97 (d, 2H, $J = 8.2$ Hz), 6.48 (d, 1H, $J = 8.5$ Hz), 3.25 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 159.8, 157.1, 152.9, 145.5, 142.9, 135.3, 134.0, 133.4, 131.5, 131.2, 130.5, 128.2, 128.1, 125.7, 124.7, 123.9, 118.0, 116.9, 116.4, 114.9, 113.6, 37.3, 20.7. HRMS calc. for $\text{C}_{29}\text{H}_{21}\text{Cl}_2\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 645.9353, found 643.9355.

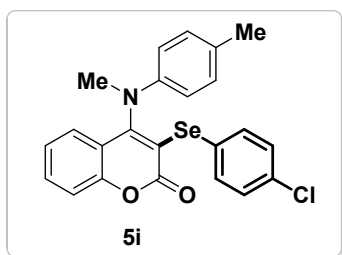


7-chloro-4-(methyl(4-(4-(trifluoromethyl)phenylselanyl)phenyl)amino)-3-(4-(trifluoromethyl)phenylselanyl)-2H-chromen-2-one (5g). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 105.5 mg, 72% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.51 (d, 2H, $J = 7.7$ Hz), 7.45-7.38 (m, 7H), 7.33 (d, 2H, $J = 8.3$ Hz), . 7.28 (d, 1H, $J = 8.6$ Hz), 7.17 (d, 1H, $J = 8.6$ Hz), 6.56 (d, 2H, $J = 8.5$ Hz), 3.30 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 159.6, 157.8, 154.0, 146.7, 139.1, 138.4, 137.3, 133.4, 133.0, 130.0 (q, $J = 32.5$ Hz), 129.6, 128.2 (q, $J = 32.3$ Hz), 126.2, 125.8 (dq, $J = 3.7$ Hz), 125.2, 123.1 (q, $J = 270.2$ Hz), 119.6, 117.6, 117.1, 116.9,

114.8, 38.2. HRMS calc. for $C_{30}H_{18}ClF_6NO_2Se_2$ $[M + H]^+$ 733.9333, found 733.9336.

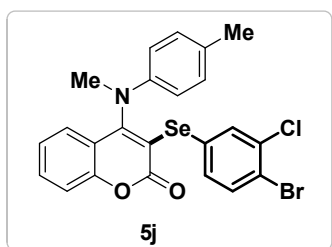


3-(3-bromophenylselanyl)-4-((4-(3-bromophenylselanyl)phenyl)(methyl)amino)-7-chloro-2H-chromen-2-one (5h). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 109.9 mg, 73% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.51 (s, 1H), 7.40-7.37 (m, 5H), 7.29-7.23 (m, 4H), 7.19 (d, 1H, $J = 8.6$ Hz), 7.12 (d, 1H, $J = 8.6$ Hz), 7.07 (t, 1H, $J = 7.9$ Hz), 6.98 (t, 1H, $J = 7.9$ Hz), 6.45 (d, 2H, $J = 8.5$ Hz), 3.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 159.0, 155.7, 152.7, 145.1, 137.0, 135.8, 135.2, 134.7, 131.7, 131.2, 130.3, 129.4, 128.8, 128.3, 127.9, 125.1, 124.1, 122.1, 121.7, 119.4, 116.7, 116.5, 115.9, 113.8, 37.1. HRMS calc. for $C_{28}H_{18}Br_2ClNO_2Se_2$ $[M + H]^+$ 753.7796, found 753.7800.



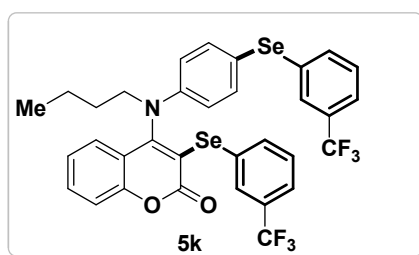
3-(4-chlorophenylselanyl)-4-(methyl(p-tolyl)amino)-2H-chromen-2-one (5i). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 73.7 mg, 81% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.51-7.49 (m, 2H), 7.38-7.34 (m, 3H), 7.27 (d, 1H, $J = 8.0$ Hz), 7.13 (t, 1H, $J = 7.3$ Hz), 7.02-6.99 (m, 3H), 6.49 (d, 2H, $J = 8.4$ Hz), 3.27 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 160.8, 159.2, 153.9, 144.0, 135.6,

132.1, 131.7, 131.1, 130.9, 130.3, 129.9, 129.1, 125.7, 124.3, 122.7, 118.9, 118.7, 117.3, 114.2, 38.8, 20.5. HRMS calc. for $C_{23}H_{18}ClNO_2Se$ $[M + H]^+$ 456.0264, found 456.0268.



3-(4-bromo-3-chlorophenylselanyl)-4-(methyl(*p*-tolyl)amino)-2*H*-chromen-2-one

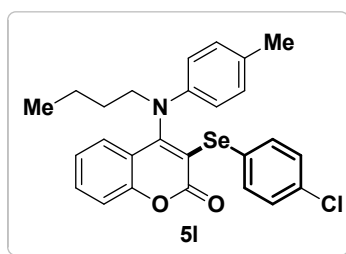
(5i). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 76.7 mg, 72% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.51 (t, 1H, $J = 7.2$ Hz), 7.43 (s, 1H), 7.39-7.31 (m, 3H), 7.19 (d, 1H, $J = 8.6$ Hz), 7.13 (t, 1H, $J = 7.4$ Hz), 6.98 (d, 2H, $J = 8.3$ Hz), 6.45 (d, 2H, $J = 8.3$ Hz), 3.30 (s, 3H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 160.8, 159.2, 153.7, 143.8, 134.7, 133.8, 132.7, 132.2, 129.8, 129.2, 129.1, 125.7, 124.3, 122.2, 118.7, 118.6, 117.2, 114.0, 38.7, 20.4. HRMS calc. for $C_{23}H_{17}BrClNO_2Se$ $[M + H]^+$ 533.9369, found 533.9371.



4-(butyl(4-(3-(trifluoromethyl)phenylselanyl)phenyl)amino)-3-(3-

(trifluoromethyl)phenylselanyl)-2*H*-chromen-2-one (5i). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 103.7mg, 70% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.99 (s, 1H), 7.51 (d, 2H, $J = 8.3$ Hz), 7.48-7.40 (m, 8H), 7.33 (d, 1H, J

= 8.2 Hz), 7.12-7.08 (m, 2H), 6.73 (s, 1H), 6.55 (d, 1H, $J = 8.5$ Hz), 2.43 (m, 2H), 2.43 (m, 2H), 1.39 (m, 2H), 1.18 (dt, 2H, $J = 7.5$ Hz), 0.81(t, 3H, $J = 7.5$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 162.3, 152.6, 145.5, 145.4, 144.9, 138.5, 138.1, 135.5, 131.3, 130.4, 129.9, 129.7, 129.3 (q, $J = 90$ Hz), 126.3 (q, $J = 3.6$ Hz), 125.9 (q, $J = 3.6$ Hz), 124.4, 123.9, 123.6 (q, $J = 273.3$ Hz), 121.5, 119.6, 117.2, 117.1, 116.8, 116.4, 30.4, 26.7, 22.6, 13.9. HRMS calc. for $\text{C}_{33}\text{H}_{25}\text{F}_6\text{NO}_2\text{Se}_2$ $[\text{M} + \text{H}]^+$ 742.0193, found 742.0200.



4-(butyl(*p*-tolyl)amino)-3-(4-chlorophenylselanyl)-2*H*-chromen-2-one (5I). Eluent petroleum ether/ethyl acetate (25:1). Yellow oil, 70.6 mg, 71% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.50-7.46 (m, 1H), 7.41 (t, 1H, $J = 8.4$ Hz), 7.33-7.29 (m, 3H), 7.25 (t, 2H, $J = 7.0$ Hz), 7.07 (d, 1H, $J = 8.0$ Hz), 7.03 (d, 1H, $J = 7.9$ Hz), 7.00 (d, 1H, $J = 8.2$ Hz), 6.52-6.40 (m, 2H), 2.53-2.41 (m, 2H), 2.30 (s, 3H), 1.42-1.33 (m, 2H), 1.22 (dt, 2H, $J = 7.5$), 0.85 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 162.6, 152.6, 146.6, 141.6, 137.4, 133.4, 132.3, 132.1, 131.1, 130.8, 129.7, 128.6, 124.7, 123.3, 118.1, 117.9, 117.1, 117.0, 116.8, 30.4, 26.2, 22.6, 20.4, 13.9. HRMS calc. for $\text{C}_{26}\text{H}_{24}\text{ClNO}_2\text{Se}$ $[\text{M} + \text{H}]^+$ 498.0734, found 498.0735.

