

## Supporting Information

# A Metal-free Four-component Sulfonylation, Giese Cyclization, Selenylation Cascade *via* Insertion of Sulfur Dioxide

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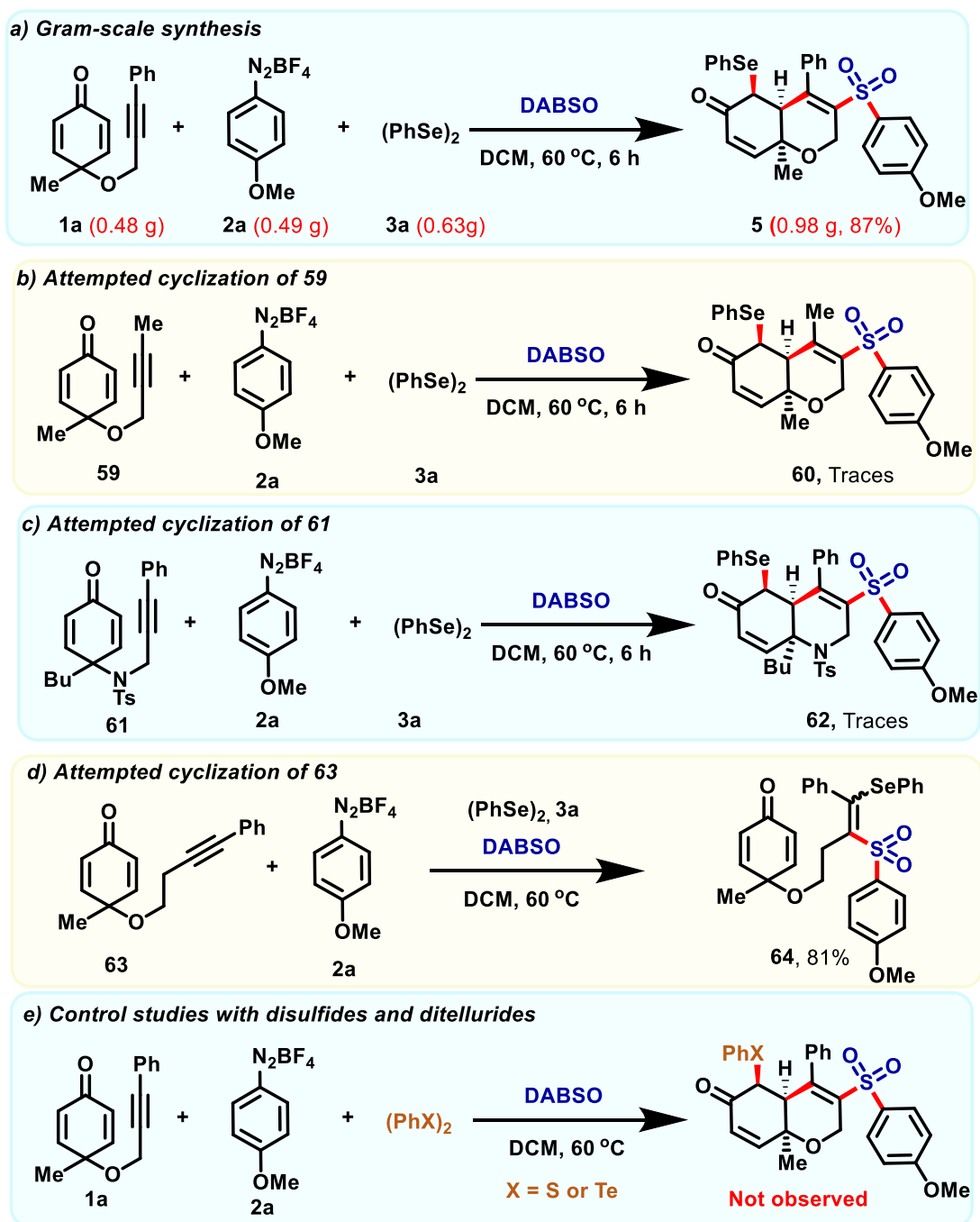
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### **1. Methods**

All reactions were carried out under air atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Reactions were monitored using thin-layer chromatography (SiO<sub>2</sub>). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F<sub>254</sub>). TLC plates were visualized with UV light (254 nm) or KMnO<sub>4</sub> stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR studies were performed on Bruker Avance DPX at 400 MHz (<sup>1</sup>H) or 500 MHz (<sup>1</sup>H) and at 100 MHz (<sup>13</sup>C) or 125 MHz (<sup>13</sup>C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl<sub>3</sub> (δH = 7.26 and δC = 77.02) ppm as internal standards, and coupling constants (*J*) are

given in Hz. HRMS were recorded on Bruker MaXis impact mass spectrometer using ESI-TOF techniques. Alkynylcyclohexadienones were synthesized as per the previous literature.<sup>1</sup>

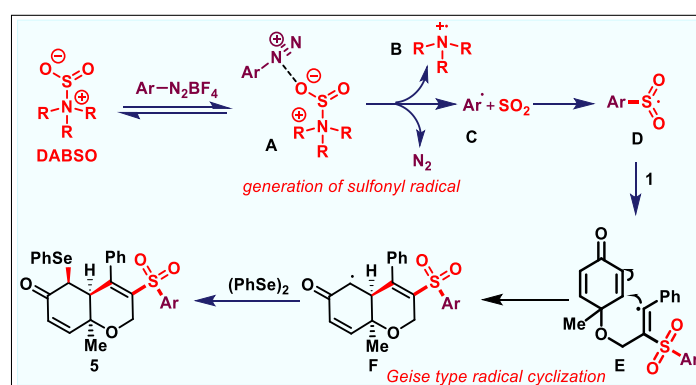


**Scheme S1:** Further studies

The reaction was scalable at 1g scale without much loss in yield wherein 0.48 g of **1a** on reaction with 0.49 g of **2a** and 0.63 g of **3a** provided 0.98 g of the dihydrochromenone **5** in 87% (Scheme S1a). Aliphatic alkynylcyclohexadienone **59** also failed to deliver the corresponding product

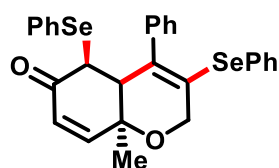
(Scheme S1b). We then found that nitrogen tethered cyclohexadienone **61** failed to deliver the corresponding product under the current conditions and a messy reaction was observed (Scheme S1c). Interestingly, homopropargyl derived cyclohexadienone **63** failed to undergo Giese cyclization and only alkyne addition product **64** was isolated in 81% (Scheme S1d). Finally, employing disulfide or ditelluride instead of diselenide did not deliver the corresponding sulfide or telluride (Scheme S1e).

## 2. Plausible mechanism



We propose the following mechanism for our reaction based on our control studies and previous literature. Initially an electrostatic interaction between DABSO and the diazonium salt would furnish the adduct **A**. This adduct on subsequent homolytic cleavage and single electron transfer would generate the aryl radical **C** and  $\text{SO}_2$  gas. Aryl radical reacts with  $\text{SO}_2$  to give the arylsulfonyl radical **D**. This radical then attacks the alkyne of cyclohexadienone forming the radical intermediate **E**. This intermediate **E** undergoes Giese type cyclization onto the enone furnishing the  $\alpha$ -carbonyl radical **F**. The regioselective attack of the diselenide onto the intermediate **F** generates the final product **5**.

### 8a-methyl-4-phenyl-3,5-bis(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (**4**)



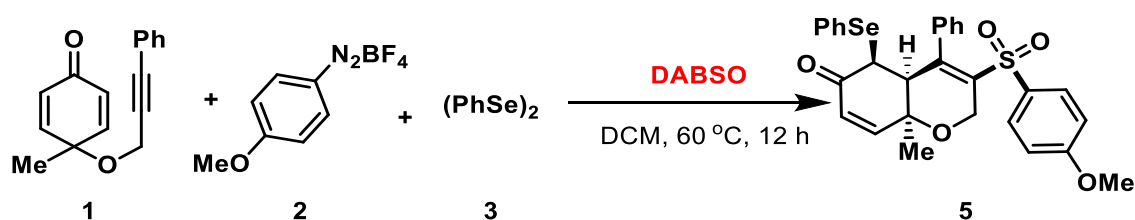
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J$  = 6.1, 2.7 Hz, 3H), 7.50 (d,  $J$  = 7.7 Hz, 2H), 7.38 (br, 4H), 7.33 – 7.21 (m, 7H), 6.56 (d,  $J$  = 10.2 Hz, 1H), 6.11 (d,  $J$  = 10.2 Hz, 1H), 4.44 (d,  $J$

= 17.1 Hz, 1H), 4.24 (dd,  $J$  = 17.1, 1.8 Hz, 1H), 3.56 (d,  $J$  = 4.1 Hz, 1H), 3.19 (s, 1H), 1.55 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.4, 147.2, 139.6, 139.1, 134.4, 133.1, 130.5, 129.4, 129.2, 129.0, 128.6, 128.4, 128.3, 128.3, 127.5, 127.4, 126.6, 68.8, 66.0, 49.0, 47.8, 22.9. Data in accordance to the previous literature.<sup>2</sup>

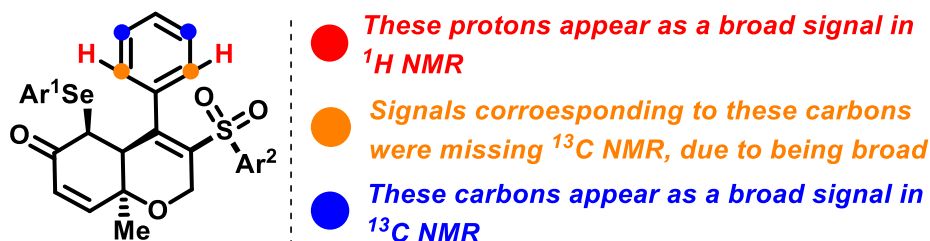
### 3. Experimental procedures

**General procedure for the cascade cyclization with diazonium salts:**

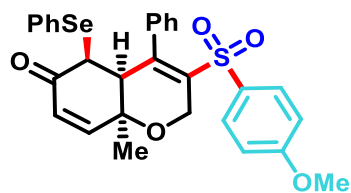


In a reaction vial equipped with magnetic stirring bar, was added alkyne **1** (24 mg, 0.1 mmol), aryldiazonium salt **2a** (27.0 mg, 0.12 mmol), DABSO (29 mg, 0.12 mmol), diphenyldiselenide (31.2 mg, 0.1 mmol) followed DCM (1.5 mL). The reaction was then kept under stirring for 12 hrs at 60 °C. The reaction mass was then diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). Organic layer was dried over  $\text{Na}_2\text{SO}_4$ , evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (8:2) to give 51.6 mg, 91% yield of the desired product **5**.

**Note:** Peaks corresponding 2xCH were found to be missing in the  $^{13}\text{C}$  NMR of the products most probably due to them being broad. Also peak broadening was observed in  $^{13}\text{C}$  and  $^1\text{H}$  NMR as shown in the figure below. This could be due to the restricted rotation around the tetra substituted alkene similar observation was also reported by Lam and co-workers.<sup>3</sup>



**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (5)**



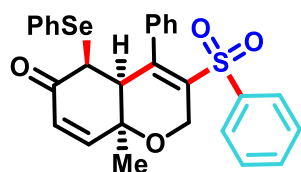
Brown sticky solid, 51.6 mg 91% yield, 0.3 Rf in 40 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.40 (t, *J* = 8.3 Hz, 4H), 7.39 – 7.16 (m, 7H), 7.03 (br, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 10.2 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.65 (dd, *J* = 17.6, 1.9 Hz, 1H), 3.84 (s, 3H), 3.40 (d, *J* = 3.9 Hz, 1H), 2.85 (s, 1H), 1.46 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.64, 163.43, 146.40, 144.93, 138.63, 135.61, 133.99, 132.55, 130.30, 129.71, 129.13, 128.76, 128.29, 128.05, 127.67, 113.99, 68.40, 61.30, 55.69, 48.40, 47.44, 22.64. A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>27</sub>O<sub>5</sub>SSe 567.0739; found 567.0731.

**8a-methyl-4-phenyl-5-(phenylselanyl)-3-(phenylsulfonyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (6)**



Brown sticky solid, 46.7 mg 87% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

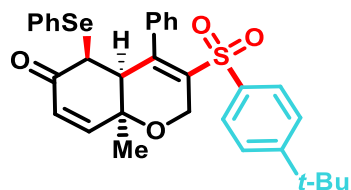
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.57 – 7.51 (m, 1H), 7.51 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.25 (m, 4H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.00 (b, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.11 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.99 (d, *J* = 17.7 Hz, 1H), 4.71 (dd, *J* = 17.7, 2.5 Hz, 1H), 3.42 (dd, *J* = 4.2, 1.1 Hz, 1H), 2.93 – 2.83 (m, 1H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.6 (C), 146.3 (CH), 145.9 (C), 141.0 (C), 138.2 (C), 135.3 (C), 134.0 (2 x CH), 133.2 (CH), 130.2 (C), 129.2 (2 x CH), 128.8 (CH), 128.8 (2 x CH), 128.3 (CH), 128.1 (2 x CH), 127.7 (CH), 127.4 (2 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 48.4

(CH), 47.4 (CH), 22.6 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>25</sub>O<sub>4</sub>SSe 537.0633; found 537.0638.

**3-((4-(tert-butyl)phenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (7).**



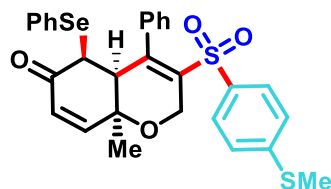
Reddish brown sticky solid, 49.8 mg 84% yield, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.46 – 7.33 (m, 6H), 7.31-7.24 (m, 4H), 7.16 (t, *J* = 7.7 Hz, 2H), 7.00 (br, 1H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.7 Hz, 1H), 4.73 (dd, *J* = 17.7, 1.9 Hz, 1H), 3.41 (d, *J* = 3.5 Hz, 1H), 2.87 (s, 1H), 1.53 (s, 3H), 1.34 (s, 9H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 157.1 (C), 146.4 (CH), 145.2 (C), 138.6 (C), 137.9 (C), 135.5 (C), 134.0 (2 x CH), 130.3 (C), 129.1 (2 x CH), 128.6 (CH), 128.3 (CH), 128.0 (2 x CH), 127.7 (CH), 127.3 (2 x CH), 125.7 (2 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 48.3 (CH), 47.5 (CH), 35.2 (CH), 31.1 (3 x CH<sub>3</sub>), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>33</sub>O<sub>4</sub>SSe 593.1259; found 593.1273.

**8a-methyl-3-((4-(methylthio)phenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (8)**



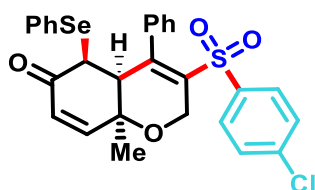
Yellow oil, 47.2 mg 81% yield, 0.3 R<sub>f</sub> in 40 % EtOAc in pet. ether

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.45 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.33 – 7.20 (m, 6H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.01 (br, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.12 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.97 (d, *J* = 17.7 Hz, 1H), 4.69 (dd, *J* = 17.7, 2.5 Hz, 1H), 3.43 (dd, *J* = 4.2, 1.1 Hz, 1H), 2.88 (dd, *J* = 3.8, 2.4 Hz, 1H), 2.52 (s, 3H), 1.50 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.6 (C), 146.9 (C), 146.4 (CH), 145.5 (C), 138.4 (C), 136.6 (C), 135.5 (C), 134.0 (2 x CH), 130.3 (C), 129.2 (2 x CH), 128.8 (CH), 128.3 (CH), 128.1 (2 x CH), 127.7 (2 x CH), 127.7 (CH), 124.9 (2 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 48.4 (CH), 47.4, (CH), 22.7 (CH<sub>3</sub>), 14.8 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>27</sub>O<sub>4</sub>S<sub>2</sub>Se 583.0510; found 583.0503.

**3-((4-chlorophenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (9).**



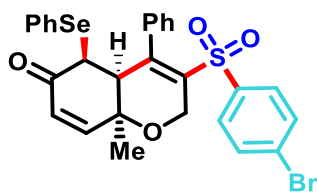
Yellow oil, 45.0 mg 79% yield, 0.2 R<sub>f</sub> in 20 % EtOAc in pet. ether

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.43 – 7.38 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.27 – 7.17 (m, 5H), 7.00 (br, 2H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.10 (d, *J* = 10.3 Hz, 1H), 4.96 (d, *J* = 17.7 Hz, 1H), 4.68 (dd, *J* = 17.7, 2.4 Hz, 1H), 3.39 (d, *J* = 4.1 Hz, 1H), 2.96 – 2.80 (m, 1H), 1.47 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 146.3 (C), 146.3 (CH), 140.0 (C), 139.4 (C), 138.2 (C), 135.2 (C), 133.9 (2 x CH), 130.2 (C), 129.2 (2 x CH), 129.0 (CH & 2 x CH), 128.9 (2 x CH), 128.4 (CH), 128.2 (2 x CH), 127.7 (CH), 68.4 (C), 61.2 (CH<sub>2</sub>), 48.4 (CH), 47.3 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>24</sub>ClO<sub>4</sub>SSe 571.0244; found 571.0247.

**3-((4-bromophenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (10).**



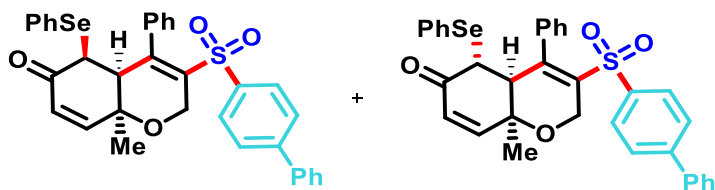
Brown oil, 47.3 mg 77% yield, 0.2 Rf in 20 % EtOAc in pet. ether

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.16 (m, 8H), 6.98 (br, 2H), 6.54 (d, *J* = 10.2 Hz, 1H), 6.10 (d, *J* = 10.2 Hz, 1H), 4.96 (d, *J* = 17.7 Hz, 1H), 4.68 (dd, *J* = 17.7, 2.4 Hz, 1H), 3.39 (d, *J* = 4.1 Hz, 1H), 2.86 (dd, *J* = 3.4, 2.4 Hz, 1H), 1.47 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 146.3 (C), 146.3 (CH), 140.0 (C), 138.2 (C), 135.2 (C), 133.9 (2 x CH), 132.0 (2 x CH), 130.2 (C), 129.2 (2 x CH), 129.0 (CH), 128.9 (2 x CH), 128.5 (C), 128.4 (CH), 128.2 (2 x CH), 127.7 (CH), 68.4 (C), 61.2 (CH<sub>2</sub>), 48.4 (CH), 47.3 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>24</sub>BrO<sub>4</sub>S<sub>2</sub>Se 614.9738; found 614.9729.

**3-([1,1'-biphenyl]-4-ylsulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (11).**



Yellow sticky solid, 50.2 mg 82% yield, 5:1 dr, 0.4 Rf in 30 % EtOAc in pet. ether

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.69 – 7.36 (m, 12.2H), 7.40 – 7.15 (m, 9.4H), 7.17 – 6.64 (m, 2.4H), 6.57 (dd, *J* = 10.2, 3.1 Hz, 1.2H), 6.12 (dd, *J* = 10.2, 1.2 Hz, 1.2H), 5.10 – 4.92 (m, 1.2H), 4.82 – 4.64 (m, 1.2H), 3.44 – 3.41 (m, 1.2 H), 2.94 – 2.79 (m, 1.2H), 1.53 (s, 3H), 1.50 (s, 0.6H).

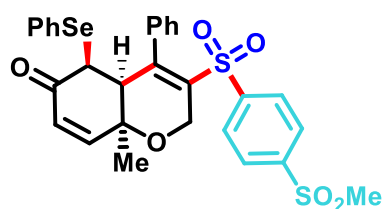
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** (*Peaks noted for the major isomer*) δ 193.6 (C), 146.4 (CH), 146.2 (C), 145.7 (C), 139.5 (C), 139.1 (C), 138.5 (C), 135.4 (C), 133.9 (2 x CH), 132.0 (CH),



130.3 (C), 129.1 (2 x CH), 129. (2 x CH), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.1 (2 x CH), 128.0 (2 x CH), 127.7 (CH), 127.7 (CH), 127.3 (4 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 48.4 (CH), 47.4 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>29</sub>O<sub>4</sub>SSe 613.0946; found 613.0954

**8a-methyl-3-((4-(methylsulfonyl)phenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (12).**



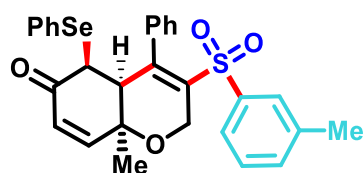
Brown sticky solid, 47.9 mg 78% yield, 0.3 R<sub>f</sub> in 50 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.23 (m, 4H), 7.18 (dd, *J* = 22.9, 15.4 Hz, 2H), 6.93 (br, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.8 Hz, 1H), 4.72 (dd, *J* = 17.8, 2.1 Hz, 1H), 3.37 (d, *J* = 4.1 Hz, 1H), 3.04 (s, 3H), 2.87 (s, 1H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.2 (C), 147.4 (C), 146.1 (CH), 146.0 (C), 144.6 (C), 137.9 (C), 134.8 (C), 133.8 (2 x CH), 130.0 (C), 129.3 (CH & 2 x CH), 128.4 (CH), 128.4 (2 x CH), 128.3 (2 x CH), 127.8 (CH & 2 x CH), 68.4 (C), 61.0 (CH<sub>2</sub>), 48.3 (CH), 47.2 (CH), 44.2 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>27</sub>O<sub>6</sub>S<sub>2</sub>Se 615.0409; found 615.0404.

**8a-methyl-4-phenyl-5-(phenylselanyl)-3-(m-tolylsulfonyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (13)**



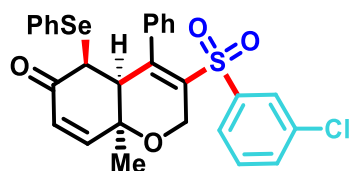
Brown sticky solid, 45.7 mg 83% yield, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.40 (d, *J* = 6.7 Hz, 2H), 7.37 – 7.09 (m, 10H), 7.00 (br, 2H), 6.54 (d, *J* = 10.2 Hz, 1H), 6.09 (d, *J* = 10.4 Hz, 1H), 4.97 (d, *J* = 17.7 Hz, 1H), 4.68 (dd, *J* = 17.7, 2.2 Hz, 1H), 3.40 (d, *J* = 3.4 Hz, 1H), 2.85 (s, 1H), 2.27 (s, 3H), 1.47 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.6, 146.4, 145.6, 140.8, 138.9, 138.4, 135.3, 134.0, 130.3, 129.1, 128.7, 128.3, 128.1, 127.9, 127.7, 124.4, 68.4, 61.3, 48.4, 47.4, 22.6, 21.1. A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>27</sub>O<sub>4</sub>SSe 551.0790; found 551.0792.

**3-((3-chlorophenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (14).**



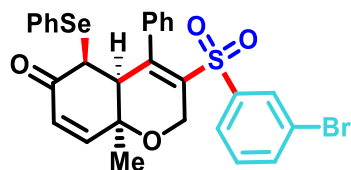
Yellow oil, 46.2 mg 81% yield, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 3H), 7.36 – 7.17 (m, 8H), 7.00 (br, 2H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.10 (d, *J* = 10.2 Hz, 1H), 4.97 (d, *J* = 17.7 Hz, 1H), 4.70 (dd, *J* = 17.7, 2.3 Hz, 1H), 3.41 (d, *J* = 4.0 Hz, 1H), 2.87 (d, *J* = 3.2 Hz, 1H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 146.6 (C), 146.2 (CH), 142.7 (C), 138.1 (C), 135.0 (C), 134.9 (C), 134.0 (2 x CH), 133.4 (CH), 130.1 (C), 130.1 (CH), 129.2 (CH & 2 x CH), 128.4 (CH), 128.2 (2 x CH), 127.9 (CH), 127.7 (CH), 125.3 (CH), 68.4 (C), 61.2 (CH<sub>2</sub>), 48.4 (CH), 47.3 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>24</sub>ClO<sub>4</sub>SSe 583.0244; found 571.0236.

**3-((3-bromophenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (15).**



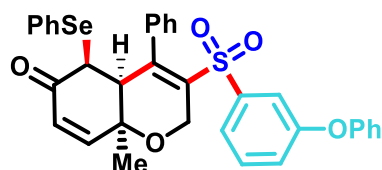
Yellow oil, 48.5 mg 79% yield, 0.4 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.19 (m, 5H), 7.05 (br, 1H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 17.8 Hz, 1H), 4.73 (d, *J* = 17.7 Hz, 1H), 3.44 (d, *J* = 2.9 Hz, 1H), 2.90 (s, 1H), 1.60 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 146.7 (C), 146.2 (CH), 142.8 (C), 138.1 (C), 136.3 (CH), 134.9 (C), 134.0 (2 x CH), 130.7 (CH), 130.3 (CH), 130.1 (C), 129.2 (CH), 129.2 (2 x CH), 128.4 (CH), 128.1 (2 x CH), 127.7 (CH), 125.8 (CH), 122.7 (C), 68.4 (C), 61.2 (CH<sub>2</sub>), 48.4 (CH), 47.3 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>24</sub>BrO<sub>4</sub>SSe 614.9738; found 614.9735.

**8a-methyl-3-((3-phenoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (16).**



White sticky solid, 52.0 mg 83% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

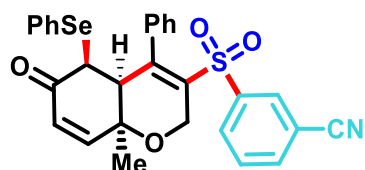
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.48 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.13 (m, 11H), 7.11 – 7.08 (m, 1H), 6.99 (dd, *J* = 8.5, 0.9 Hz, 2H), 6.92 (br, 1H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.12 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.65 (dd, *J* = 17.6, 2.5 Hz, 1H), 3.44 (dd, *J* = 4.2, 1.1 Hz, 1H), 2.90 (dd, *J* = 3.8, 2.3 Hz, 1H), 1.48 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 158.0 (C), 155.6 (C), 146.3 (CH), 146.2 (C), 142.4 (C), 137.8 (C), 135.3 (C), 134.0 (2 x CH), 130.2 (C, CH & 2 x CH), 129.2 (2 x CH),

128.9 (CH), 128.3 (CH), 128.1 (2 x CH), 127.7 (CH), 124.6 (CH), 123.1 (CH), 121.6 (CH), 119.7 (2 x CH), 116.6 (CH), 68.4 (C), 61.2 (CH<sub>2</sub>), 48.5 (CH), 47.2 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>29</sub>O<sub>5</sub>SSe 629.0895; found 629.0890.

**8a-methyl-6-oxo-4-phenyl-5-(phenylselanyl)-4a,5,6,8a-tetrahydro-2H-chromen-3-yl)sulfonyl)benzonitrile (17)**



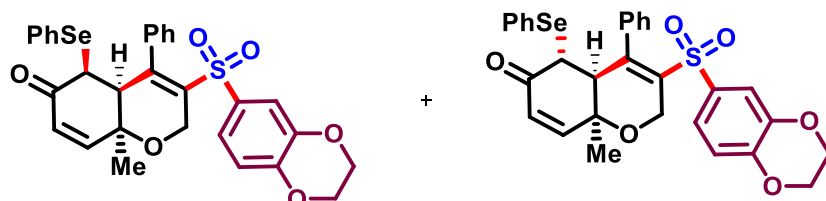
Brown oil, 45.4 mg 81% yield, 0.4 R<sub>f</sub> in 40 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.75 (dd, *J* = 19.4, 7.9 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.18 (m, 7H), 6.99 (br, 1H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.8 Hz, 1H), 4.74 (d, *J* = 17.8 Hz, 1H), 3.41 (d, *J* = 3.7 Hz, 1H), 2.89 (s, 1H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.2 (C), 147.0 (C), 146.1 (CH), 142.5 (C), 138.1 (C), 136.1 (CH), 134.7 (C), 133.9 (2 x CH), 131.4 (CH), 131.1 (CH), 130.0 (C), 129.8 (CH), 129.5 (CH), 129.3 (CH & 2 x CH), 128.5 (2 x CH), 127.7 (CH), 116.7 (C), 113.3 (C), 68.4 (C), 61.0 (CH<sub>2</sub>), 48.3 (CH), 47.1 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>24</sub>NO<sub>4</sub>SSe 562.0586; found 562.0581.

**3-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (18).**



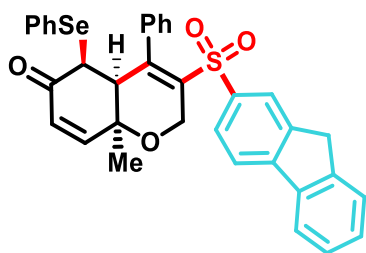
Red oil, 48.8 mg 82%, 3:1 dr., 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.50 – 7.39 (m, 3.6H), 7.37 – 7.20 (m, 8.6H), 7.16 (t, *J* = 7.5 Hz, 1.2H), 7.04 – 6.91 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.57 (dd, *J* = 10.2, 3.4 Hz, 1.3H), 6.11 (d, *J* = 10.2 Hz, 1.3H), 5.00 (d, *J* = 17.7 Hz, 0.3H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.73 (d, *J* = 17.7 Hz, 0.3H), 4.67 (d, *J* = 17.6 Hz, 0.1H), 4.45 – 4.10 (m, 5H), 3.44 (d, *J* = 4.0 Hz, 1H), 3.41 (d, *J* = 4.0 Hz, 0.3H), 2.88 (s, 1.3H), 1.52 (s, 0.9H), 1.50 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** (*Peaks noted for the major isomer*) δ 193.7 (C), 148.0 (C), 146.4 (CH), 144.9 (C), 143.2 (C), 138.5 (C), 135.6 (C), 134.0 (2 x CH), 133.2 (C), 130.4 (C), 129.1 (2 x CH), 128.7 (CH), 128.3 (CH), 127.9 (2 x CH), 127.7 (CH), 121.2 (CH), 117.5 (CH), 117.5 (CH), 68.4 (C), 64.6 (CH<sub>2</sub>), 64.1 (CH<sub>2</sub>), 61.2 (CH<sub>2</sub>), 48.4 (CH), 47.4 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>27</sub>O<sub>6</sub>SSe 595.0688; found 595.0686.

**3-((9H-fluoren-2-yl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (19)**



Yellow sticky solid, 50.0 mg 80% yield, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

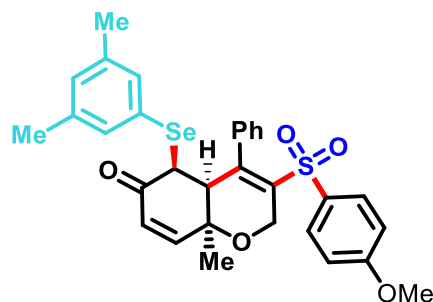
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.84 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.44 (t, *J* = 5.7 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 4H), 7.02 (br, 2H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.7 Hz, 1H), 4.74 (dd, *J* = 17.7, 1.9 Hz, 1H), 3.81 (s, 2H), 3.41 (d, *J* = 4.1 Hz, 1H), 2.85 (s, 1H), 1.48 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.6 (C), 146.7 (C), 146.4 (CH), 145.4 (C), 144.3 (C), 143.2 (C), 139.7 (C), 138.8 (C), 138.7 (C), 135.4 (C), 133.9 (2 x CH), 130.3 (C), 129.1 (2 x CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.9 (2 x CH), 127.7 (CH), 127.3 (CH), 126.5 (CH), 125.4 (CH), 124.6 (CH), 121.1 (CH), 119.9 (CH), 68.4 (C), 61.4 (CH<sub>2</sub>), 48.4 (CH),

47.4 (CH), 36.8 (CH<sub>2</sub>), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>29</sub>O<sub>4</sub>SSe 625.0946; found 625.0939.

**5-((3,5-dimethylphenyl)selanyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one (20)**



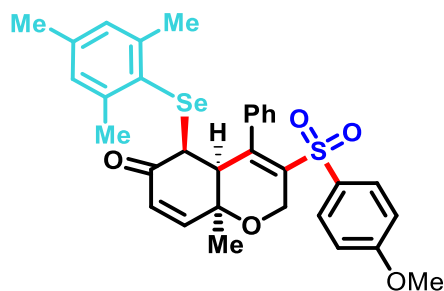
Yellow oil, 48.7 mg 82% yield, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.34 (d, *J* = 8.6 Hz, 3H), 7.30 – 7.24 (m, 2H), 7.19 (b, 2H), 7.14 – 7.06 (m, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 10.2 Hz, 1H), 6.00 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.8 Hz, 1H), 4.66 (dd, *J* = 17.8, 2.3 Hz, 1H), 3.83 (s, 3H), 3.35 (d, *J* = 4.1 Hz, 1H), 2.93 (s, 1H), 2.38 (s, 6H), 1.42 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 192.3 (C), 163.3 (C), 145.7 (CH), 144.9 (2 x C), 144.1 (C), 139.0 (C), 135.3 (C), 132.4 (C), 130.1 (C), 129.5 (2 x CH), 129.4 (CH), 129.2 (2 x CH), 129.0 (CH), 127.9 (2 x CH), 127.7 (2 x CH), 126.9 (CH), 113.9 (2 x CH), 68.6 (C), 61.4 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.4 (CH), 44.5 (CH), 24.8 (2 x CH<sub>3</sub>), 23.0 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>31</sub>O<sub>5</sub>SSe 595.1052; found 595.1060.

**5-(mesitylselanyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-phenyl-4a,8a-dihydro-2H-chromen-6(5H)-one (21)**



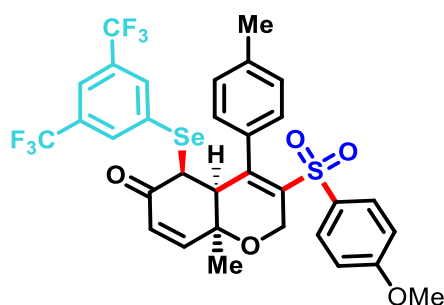
Yellow oil, 48.1 mg 79% yield, 0.5 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.31 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.10 – 7.02 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.83 (b, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 10.4 Hz, 1H), 6.19 (d, *J* = 10.4 Hz, 1H), 4.67 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.44 (dd, *J* = 17.1, 3.1 Hz, 1H), 3.81 (s, 3H), 3.42 (s, 1H), 3.15 (s, 1H), 2.03 (s, 6H), 1.79 (s, 3H), 1.26 (b, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 191.5 (C), 163.4 (C), 149.0 (2 x C), 146.9 (C), 143.2 (CH), 139.3 (C), 134.6 (C), 132.2 (C), 130.6 (C), 130.2 (C), 129.7 (2 x CH), 129.6 (CH), 128.3 (CH), 128.0 (2 x CH), 127.8 (2 x CH), 113.9 (2 x CH), 72.4 (C), 61.1 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 52.3 (CH), 43.8 (CH), 28.5 (CH<sub>3</sub>), 23.7 (2 x CH<sub>3</sub>), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>32</sub>H<sub>33</sub>O<sub>5</sub>SSe 609.1028; found 609.1035.

**5-((3,5-bis(trifluoromethyl)phenyl)selanyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-(p-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (22)**



Yellow oil, 59.4 mg 83% yield, 0.4 Rf in 30 % EtOAc in pet. ether.

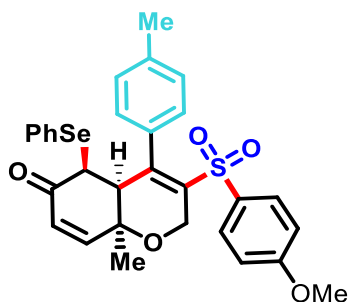
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.87 (s, 2H), 7.78 (s, 1H), 7.48 – 7.34 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.95 (b, 2H), 6.87 – 6.76 (m, 2H), 6.60 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 17.6

Hz, 1H), 4.65 (dd,  $J = 17.6, 2.5$  Hz, 1H), 3.86 (s, 3H), 3.34 (dd,  $J = 4.3, 1.2$  Hz, 1H), 2.90 (dd,  $J = 4.0, 2.1$  Hz, 1H), 2.37 (s, 3H), 1.49 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.3 (C), 163.6 (C), 147.1 (CH), 144.6 (C), 139.4 (C), 138.8 (C), 133.8 (2 x CH), 133.0 (C), 132.4 (C), 132.3 (C), 132.2 (C), 131.8 (C), 129.8 (2 x CH), 128.9 (2 x CH), 127.3 (CH), 122.8 (q,  $J = 272.2$  Hz,  $\text{CF}_3$ ), 122.1 (q,  $J = 4.2$  Hz, CH), 113.9 (2 x CH), 68.5 (C), 61.5 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 48.3 (CH), 48.1 (CH), 22.4 ( $\text{CH}_3$ ), 21.2 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{32}\text{H}_{27}\text{F}_6\text{O}_5\text{SSe}$  717.0643; found 717.0651.

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4-(p-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (23)**



Yellow sticky solid, 47.6 mg 82% yield, 0.5 Rf in 30 % EtOAc in pet. ether.

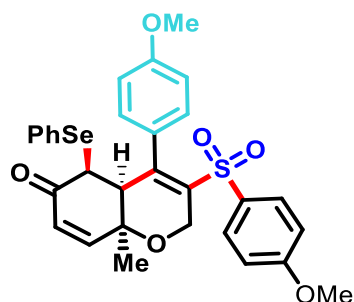
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.43 (d,  $J = 8.5$  Hz, 4H), 7.33 – 7.21 (m, 3H), 7.04 (d,  $J = 7.4$  Hz, 2H), 6.95 (br, 2H), 6.83 (d,  $J = 8.6$  Hz, 2H), 6.55 (d,  $J = 10.2$  Hz, 1H), 6.09 (d,  $J = 10.2$  Hz, 1H), 4.94 (d,  $J = 17.5$  Hz, 1H), 4.65 (d,  $J = 17.5$  Hz, 1H), 3.85 (s, 3H), 3.43 (d,  $J = 3.0$  Hz, 1H), 2.85 (s, 1H), 2.36 (s, 3H), 1.46 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.7 (C), 163.4 (C), 146.4 (CH), 145.2 (C), 138.7 (C), 138.3 (C), 134.0 (2 x CH), 132.7 (C), 132.6 (C), 130.4 (C), 129.7 (2 x CH), 129.1 (2 x CH), 128.7 (2 x CH), 128.2 (CH), 127.6 (CH), 113.9 (2 x CH), 68.4 (C), 61.3 ( $\text{CH}_2$ ), 55.7 ( $\text{CH}_3$ ), 48.5 (CH), 47.6 (CH), 22.6 ( $\text{CH}_3$ ), 21.3 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{30}\text{H}_{29}\text{O}_5\text{SSe}$  581.0895; found 581.0897.



**4-(4-methoxyphenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (24).**



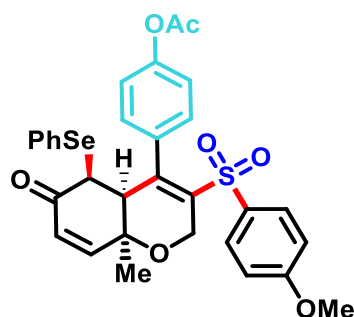
Yellow sticky solid, 50.7 mg 85% yield, 0.2 Rf in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.45 – 7.33 (m, 4H), 7.32 – 7.15 (m, 3H), 6.95 (br, 2H), 6.85 – 6.77 (m, 2H), 6.73 (dd, *J* = 7.5, 1.4 Hz, 2H), 6.52 (d, *J* = 10.2 Hz, 1H), 6.07 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.62 (dd, *J* = 17.6, 2.5 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.36 (dd, *J* = 4.2, 1.2 Hz, 1H), 2.82 (dd, *J* = 3.9, 2.2 Hz, 1H), 1.43 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.4 (C), 160.0 (C), 146.4 (CH), 145.0 (C), 138.5 (C), 134.0 (2 x CH), 132.6 (C), 130.3 (C), 129.6 (2 x CH), 129.1 (2 x CH), 128.3 (CH), 127.6 (CH), 127.5 (C), 113.9 (2 x CH), 113.5 (2 x CH), 68.5 (C), 61.4 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 55.4 (CH<sub>3</sub>), 48.4 (CH), 47.7 (CH), 22.6 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>29</sub>O<sub>6</sub>SSe 597.0845; found 597.0837.

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-6-oxo-5-(phenylselanyl)-4a,5,6,8a-tetrahydro-2H-chromen-4-yl)phenyl acetate (25)**



Brown oil, 49.4 mg 79% yield, 0.2 Rf in 30 % EtOAc in pet. ether.

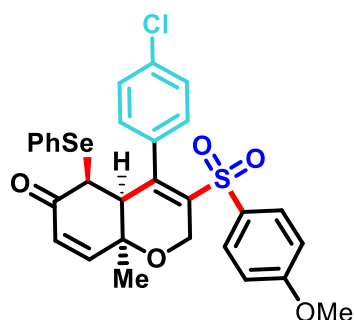
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.47 – 7.41 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 2H), 7.10 (s, 1H), 6.97 – 6.91 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 10.2 Hz, 1H),

6.12 (dd,  $J = 10.2, 1.3$  Hz, 1H), 5.01 (d,  $J = 17.8$  Hz, 1H), 4.71 (dd,  $J = 17.8, 2.5$  Hz, 1H), 3.86 (s, 3H), 3.42 (dd,  $J = 4.3, 1.3$  Hz, 1H), 2.84 (dd,  $J = 4.3, 2.4$  Hz, 1H), 2.33 (s, 3H), 1.49 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.6 (C), 168.9 (C), 163.4 (C), 151.0 (C), 146.4 (CH), 143.9 (C), 139.9 (C), 133.9 (2 x CH), 132.8 (C), 132.2 (C), 130.2 (C), 129.7 (2 x CH), 129.2 (2 x CH), 128.3 (CH), 127.7 (CH), 121.4 (2 x CH), 114.2 (2 x CH), 68.4 (C), 61.3 ( $\text{CH}_2$ ), 55.7 ( $\text{CH}_3$ ), 48.2 (CH), 47.4 (CH), 22.7 ( $\text{CH}_3$ ), 21.2 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{30}\text{H}_{29}\text{O}_7\text{SSe}$  625.0794; found 625.0802.

**(4a*S*,5*S*,8a*S*)-4-(4-chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (26)**



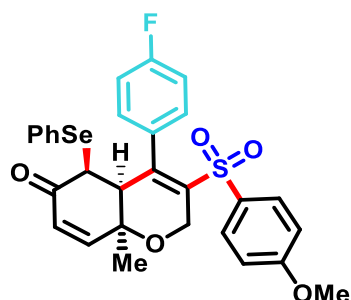
Brown oil, 48.0 mg 80% yield, 0.3  $R_f$  in 30 % EtOAc in pet. ether.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.44 – 7.36 (m, 4H), 7.29 – 7.20 (m, 3H), 7.17 (d,  $J = 8.8$  Hz, 2H), 6.98 (br, 2H), 6.84 (d,  $J = 8.9$  Hz, 2H), 6.53 (d,  $J = 10.2$  Hz, 1H), 6.09 (dd,  $J = 10.2, 1.1$  Hz, 1H), 4.91 (d,  $J = 17.7$  Hz, 1H), 4.63 (dd,  $J = 17.7, 2.4$  Hz, 1H), 3.85 (s, 3H), 3.35 (dd,  $J = 4.2, 1.0$  Hz, 1H), 2.80 (dd,  $J = 3.7, 2.3$  Hz, 1H), 1.44 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.5 (C), 163.6 (C), 146.4 (CH), 143.5 (C), 139.5 (C), 134.9 (C), 134.0 (C), 133.8 (2 x CH), 132.2 (C), 130.2 (C), 129.7 (2 x CH), 129.2 (2 x CH), 128.4 (CH), 128.3 (2 x CH), 127.7 (CH), 114.1 (2 x CH), 68.3 (C), 61.2 ( $\text{CH}_2$ ), 55.7 ( $\text{CH}_3$ ), 48.2 (CH), 47.3 (CH), 22.6 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{26}\text{ClO}_5\text{SSe}$  601.0349; found 601.0343.

**4-(4-fluorophenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (27)**



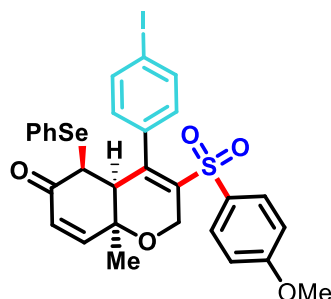
Greenish yellow oil, 51.4 mg 88% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.46 – 7.32 (m, 4H), 7.32 – 7.19 (m, 3H), 6.98 (br, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 10.2 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 4.93 (d, *J* = 17.7 Hz, 1H), 4.63 (dd, *J* = 17.7, 2.3 Hz, 1H), 3.85 (s, 3H), 3.35 (d, *J* = 4.0 Hz, 1H), 2.81 (s, 1H), 1.45 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.6 (C), 163.6 (C), 162.9 (d, *J* = 249.3 Hz, C), 146.4 (CH), 143.9 (C), 139.4 (C), 133.8 (2 x CH), 132.4 (C), 131.4 (d, *J* = 3.4 Hz, C), 130.3 (C), 129.6 (2 x CH), 129.2 (2 x CH), 128.3 (CH), 127.7 (CH), 115.1 (d, *J* = 20.3 Hz, 2 x CH), 114.1 (2 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.4 (CH), 47.4 (CH), 22.6 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+Na]<sup>+</sup> calculated for C<sub>29</sub>H<sub>25</sub>FO<sub>5</sub>NaSSe 607.0464; found 607.0495.

**4-(4-iodophenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (28)**



Brown oil, 56.0 mg 81% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

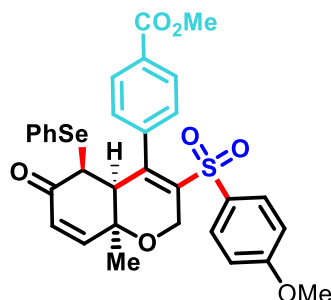
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.36 (m, 4H), 7.36 – 7.21 (m, 3H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.78 (b, 2H), 6.55 (d, *J* = 10.3 Hz, 1H), 6.11 (dd, *J* = 10.3, 1.1

Hz, 1H), 4.93 (d,  $J = 17.8$  Hz, 1H), 4.65 (dd,  $J = 17.8, 2.2$  Hz, 1H), 3.89 (s, 3H), 3.39 (d,  $J = 3.3$  Hz, 1H), 2.81 (b, 1H), 1.47 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.5 (C), 163.6 (C), 146.3 (CH), 143.4 (C), 139.5 (C), 137.1 (2 x CH), 135.2 (C), 133.8 (2 x CH), 132.2 (C), 130.2 (C), 129.7 (2 x CH), 129.2 (2 x CH), 128.4 (CH), 127.7 (CH), 114.1 (2 x CH), 94.8 (C), 68.4 (C), 61.2 ( $\text{CH}_2$ ), 55.8 ( $\text{CH}_3$ ), 48.1 (CH), 47.3 (CH), 22.7 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{26}\text{IO}_5\text{SSe}$  692.9705; found 692.9708.

**Methyl-4-(3-((4-methoxyphenyl)sulfonyl)-8a-methyl-6-oxo-5-(phenylselanyl)-4a,5,6,8a-tetrahydro-2H-chromen-4-yl)benzoate (29)**



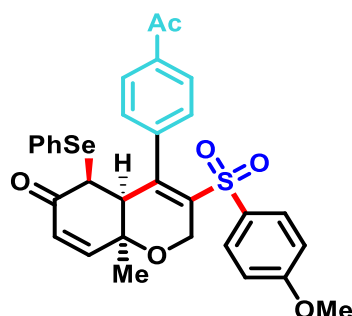
Red sticky solid, 55.0 mg 88% yield, 0.2 R<sub>f</sub> in 40 % EtOAc in pet. ether.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.86 (d,  $J = 8.2$  Hz, 2H), 7.39 (dd,  $J = 11.2, 8.1$  Hz, 4H), 7.33 – 7.19 (m, 3H), 7.10 (br, 2H), 6.82 (d,  $J = 8.8$  Hz, 2H), 6.52 (d,  $J = 10.2$  Hz, 1H), 6.07 (d,  $J = 10.2$  Hz, 1H), 4.89 (d,  $J = 17.7$  Hz, 1H), 4.62 (dd,  $J = 17.7, 1.9$  Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 3.34 (d,  $J = 3.9$  Hz, 1H), 2.84 (s, 1H), 1.45 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.4 (C), 166.4 (C), 163.7 (C), 146.4 (CH), 143.7 (C), 140.5 (C), 139.2 (C), 133.8 (2 x CH), 132.1 (C), 130.3 (C), 130.2 (C), 129.7 (2 x CH), 129.2 (4 x CH), 128.4 (CH), 127.6 (CH), 114.2 (2 x CH), 68.3 (C), 61.2 ( $\text{CH}_2$ ), 55.7 ( $\text{CH}_3$ ), 52.3 ( $\text{CH}_3$ ), 48.1 (CH), 47.2 (CH), 22.6 ( $\text{CH}_2$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{29}\text{O}_7\text{SSe}$  625.0794; found 625.0800.

**4-(4-acetylphenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (30)**



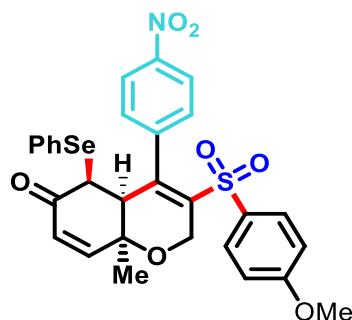
Brown oil, 53.5 mg 88% yield, 0.5 Rf in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 7.36 – 7.24 (m, 3H), 7.16 (b, 2H), 6.92 – 6.83 (m, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.11 (dd, *J* = 10.3, 1.3 Hz, 1H), 4.91 (dd, *J* = 17.7, 0.8 Hz, 1H), 4.64 (dd, *J* = 17.7, 2.5 Hz, 1H), 3.88 (s, 3H), 3.39 (dd, *J* = 4.3, 1.4 Hz, 1H), 2.87 (dd, *J* = 4.3, 2.3 Hz, 1H), 2.62 (s, 3H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.3 (C), 193.5 (C), 163.8 (C), 146.3 (CH), 143.7 (C), 140.8 (C), 139.2 (C), 137.0 (C), 133.8 (2 x CH), 132.1 (C), 130.2 (C), 129.8 (2 x CH), 129.2 (2 x CH), 128.4 (CH), 127.9 (2 x CH), 127.7 (CH), 114.2 (2 x CH), 68.3 (C), 61.2 (CH<sub>2</sub>), 55.8 (CH<sub>3</sub>), 48.2 (CH), 47.2 (CH), 26.7 (CH<sub>3</sub>), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>29</sub>O<sub>6</sub>SSe 609.0844; found 609.0844.

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-(4-nitrophenyl)-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (31)**



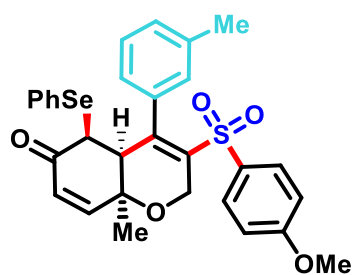
Brown oil, 51.3 mg 84% yield, 0.2 Rf in 40 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.09 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.41 (dt, *J* = 6.6, 1.5 Hz, 2H), 7.38 – 7.16 (m, 5H), 6.97 – 6.89 (m, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.14 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.90 (d, *J* = 17.8 Hz, 1H), 4.64 (dd, *J* = 17.8, 2.5 Hz, 1H), 3.90 (s, 3H), 3.36 (dd, *J* = 4.2, 1.1 Hz, 1H), 2.87 (dd, *J* = 3.9, 2.2 Hz, 1H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.3 (C), 164.0 (C), 147.9 (C), 146.3 (CH), 142.7 (C), 142.3 (C), 140.1 (C), 133.5 (2 x CH), 131.8 (C), 130.2 (C), 129.8 (2 x CH), 129.4 (2 x CH), 128.5 (CH), 127.7 (CH), 123.2 (2 x CH), 114.4 (2 x CH), 68.3 (C), 61.2 (CH<sub>2</sub>), 55.8 (CH<sub>3</sub>), 48.1 (CH), 47.1 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>26</sub>NO<sub>7</sub>SSe 612.0590; found 612.0596.

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4-(m-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (32)**



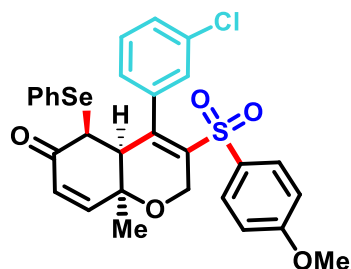
Brown sticky solid, 50.5 mg 87% yield, 0.2 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.45 – 7.34 (m, 4H), 7.31 – 7.18 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.92 (b, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 6.68 (b, 1H), 6.54 (d, *J* = 10.2 Hz, 1H), 6.09 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 3.41 (d, *J* = 3.2 Hz, 1H), 2.86 – 2.78 (m, 1H), 1.48 (s, 3).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 194.0 (C), 163.4 (C), 146.6 (CH), 145.2 (C), 138.5 (C), 135.3 (C), 133.7 (2 x CH), 132.7 (C), 130.6 (C), 129.8 (2 x CH), 129.3 (CH), 129.1 (2 x CH), 128.2 (2 x CH), 127.7 (CH), 113.8 (2 x CH), 68.4 (C), 61.3 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.3 (CH), 47.6 (CH), 22.6 (CH<sub>3</sub>), 21.1 (CH<sub>3</sub>). Signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>28</sub>O<sub>5</sub>SSe 581.0895; found 581.0894.

**4-(3-chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (33)**



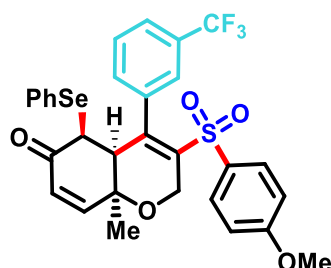
Brown sticky solid, 50.4 mg 84% yield, 0.2 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.43 (bd, *J* = 6.9 Hz, 4H), 7.36 – 7.17 (m, 6H), 7.06 (b, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.13 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.96 (d, *J* = 17.8 Hz, 1H), 4.71 (d, *J* = 17.7 Hz, 1H), 3.90 (s, 3H), 3.38 (dd, *J* = 4.2, 1.0 Hz, 1H), 2.91 – 2.75 (m, 1H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.5 (C), 163.7 (C), 146.4 (CH), 143.2 (C), 139.8 (C), 137.2 (CH), 134.1 (2 x CH), 132.3 (C), 130.1 (C), 129.8 (2 x CH), 129.3 (2 x CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 114.2 (2 x CH), 68.4 (C), 61.2 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.1 (CH), 47.4 (CH), 22.6 (CH<sub>3</sub>). Signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>26</sub>ClO<sub>5</sub>SSe 601.0349; found 601.0339.

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4-(3-(trifluoromethyl)phenyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (34)**



Brown sticky solid, 55.8 mg 88% yield, 0.3 Rf in 20 % EtOAc in pet. ether.

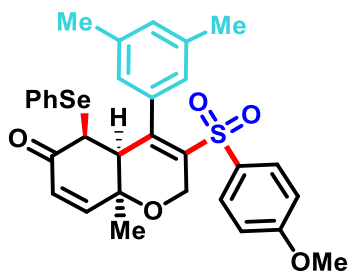
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.44-7.38 (m, 5H), 7.32 – 7.20 (m, 4H), 7.0 (br, 1H), 6.83 (d, *J* = 6.1 Hz, 1H), 6.55 (d, *J* = 10.2 Hz, 2H), 6.10 (dd, *J* = 10.2, 1.0

Hz, 1H), 4.96 (d,  $J = 17.9$  Hz, 1H), 4.71 (d,  $J = 17.5$  Hz, 1H), 3.84 (s, 3H), 3.33 (d,  $J = 3.5$  Hz, 1H), 2.89 – 2.77 (m, 1H), 1.50 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.5 (C), 163.8 (C), 146.3 (CH), 143.1 (C), 140.2 (C), 136.5 (C), 134.0 (2 x CH), 132.2 (C), 129.9 (C), 129.5 (2 x CH), 129.3 (2 x CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 125.6 (m, CH), 123.0 ((q,  $J = 272.8$  Hz,  $\text{CF}_3$ ), 114.2 (2 x CH), 68.4 (C), 61.3 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 48.2 (CH), 47.3 (CH), 22.7 ( $\text{CH}_3$ ). Signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{30}\text{H}_{26}\text{F}_3\text{O}_5\text{SSe}$  635.0613; found 635.0609.

**4-(3,5-dimethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (35)**



Brown sticky solid, 51.7 mg 87% yield, 0.5 Rf in 20 % EtOAc in pet. ether.

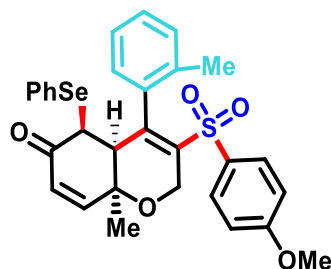
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.48 – 7.38 (m, 4H), 7.32 – 7.20 (m, 3H), 6.89 (b, 1H), 6.83 (d,  $J = 8.9$  Hz, 1H), 6.67 (b, 1H), 6.57 (d,  $J = 10.2$  Hz, 1H), 6.35 (b, 1H), 6.12 (d,  $J = 8.9$  Hz, 1H), 4.72 (dd,  $J = 17.5, 2.5$  Hz, 1H), 3.87 (s, 3H), 3.43 (d,  $J = 1.4$  Hz, 1H), 2.82 (d,  $J = 2.0$  Hz, 1H), 2.13 (b, 6H) 1.51 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  194.2 (C), 163.3 (C), 146.7 (CH), 145.4 (C), 138.2 (C), 135.4 (C), 133.6 (2 x CH), 132.9 (C), 130.9 (C), 130.1 (CH), 129.9 (2 x CH), 129.1 (2 x CH), 128.1 (CH), 127.8 (CH), 113.7 (2 x CH), 68.4 (C), 61.3 ( $\text{CH}_2$ ), 55.7 ( $\text{CH}_3$ ), 48.2 (CH), 47.8 (CH), 22.7 (2 x  $\text{CH}_3$ ), 21.0 ( $\text{CH}_3$ ). Two signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{31}\text{O}_5\text{SSe}$  595.1052; found 595.1062.



**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4-(o-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (36)**



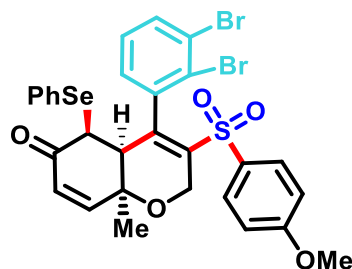
Brown sticky solid, 51.0 mg 88% yield, 0.4 Rf in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.43 – 7.36 (m, 4H), 7.29 – 7.21 (m, 3H), 7.18 (td, *J* = 7.5, 1.4 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.95 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.53 (d, *J* = 10.2 Hz, 1H), 6.09 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.77 (dd, *J* = 17.7, 2.3 Hz, 1H), 3.86 (s, 3H), 3.51 (dd, *J* = 4.1, 1.3 Hz, 1H), 2.78 (dd, *J* = 3.8, 2.1 Hz, 1H), 1.97 (s, 3H), 1.55 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 194.0 (C), 163.6 (C), 146.7 (CH), 145.0 (C), 138.5 (C), 135.0 (C), 134.0 (C), 133.4 (2 x CH), 132.4 (C), 130.6 (C, & CH), 130.1 (2 x CH), 129.3 (CH), 129.1 (2 x CH), 128.9 (CH), 128.1 (CH), 127.8 (CH), 124.9 (CH), 114.0 (2 x CH), 68.6 (C), 61.4 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 47.6 (CH), 45.8 (CH), 22.6 (CH<sub>3</sub>), 19.5 (CH<sub>3</sub>).

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>29</sub>O<sub>5</sub>SSe 581.0895; found 581.0891.

**4-(2,3-dibromophenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (37)**



Brown sticky solid, 58.4 mg 81% yield, 0.3 Rf in 10 % EtOAc in pet. ether.

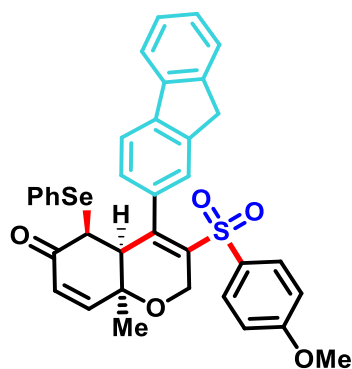
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.58 – 7.36 (m, 5H), 7.34 – 7.16 (m, 3H), 7.06 (b, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.54 (d, *J* = 10.2 Hz, 1H), 6.11 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.93 (d, *J* =

17.9 Hz, 1H), 4.68 (dd,  $J = 17.8, 2.5$  Hz, 1H), 3.89 (s, 3H), 3.34 (dd,  $J = 4.3, 1.3$  Hz, 1H), 2.77 (d,  $J = 2.0$  Hz, 1H), 1.48 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.4 (C), 163.9 (C), 146.3 (CH), 141.8 (C), 140.5 (C), 136.2 (C), 134.0 (2 x CH), 130.0 (C), 129.8 (2 x CH), 129.4 (C & 2 x CH), 128.6 (CH), 127.7 (CH), 125.4 (C), 114.2 (C & 2 x CH), 68.3 (C), 61.1 ( $\text{CH}_2$ ), 55.8 ( $\text{CH}_3$ ), 47.9 (CH), 47.2 (CH), 22.7 ( $\text{CH}_3$ ). Two signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{25}\text{Br}_2\text{O}_5\text{SSe}$  722.8949; found 722.8934.

**4-(9H-fluoren-2-yl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (38)**



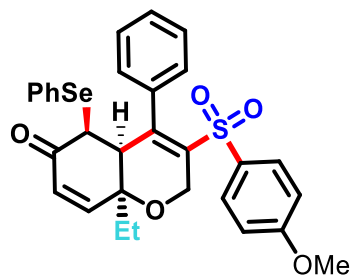
Brown sticky solid, 55.6 mg 85% yield, 0.3 R<sub>f</sub> in 20 % EtOAc in pet. ether.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.81 (d,  $J = 7.3$  Hz, 1H), 7.64 (d,  $J = 7.7$  Hz, 1H), 7.57 (d,  $J = 7.3$  Hz, 1H), 7.48 (d,  $J = 7.6$  Hz, 2H), 7.43 (t,  $J = 7.4$  Hz, 1H), 7.37 (t,  $J = 7.7$  Hz, 3H), 7.32-7.25 (m, 3H), 7.00 (br, 2H), 6.69 (d,  $J = 7.5$  Hz, 2H), 6.59 (d,  $J = 10.2$  Hz, 1H), 6.13 (d,  $J = 10.2$  Hz, 1H), 5.03 (d,  $J = 17.7$  Hz, 1H), 4.75 (d,  $J = 17.7$  Hz, 1H), 3.80 – 3.54 (bm, 5H), 3.47 (d,  $J = 2.9$  Hz, 1H), 2.93 (s, 1H), 1.54 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.9 (C), 163.3 (C), 146.6 (CH), 145.1 (C), 143.3 (C), 142.2 (C), 140.8 (C), 139.0 (C), 133.7 (C & 2 x CH), 132.6 (C), 130.7 (C), 129.8 (2 x CH), 129.1 (2 x CH), 128.2 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 125.1 (CH), 120.2 (CH), 119.5 (CH), 113.7 (2 x CH), 68.5 (C), 61.3 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 48.4 (CH), 47.7 (CH), 36.6 ( $\text{CH}_2$ ), 22.7 ( $\text{CH}_3$ ). Two signals corresponding to 2 x CH and 1x Q, could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{36}\text{H}_{30}\text{O}_5\text{SSe}$  655.1052; found 655.1049.

**8a-ethyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (39)**



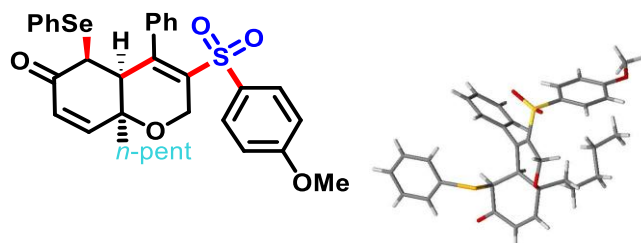
Yellow oil, 47.6 mg 82% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.43 (dd, *J* = 7.8, 6.3 Hz, 4H), 7.27 (tt, *J* = 20.1, 7.5 Hz, 6H), 7.02 (br, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 10.4 Hz, 1H), 6.19 (dd, *J* = 10.4, 0.9 Hz, 1H), 4.92 (d, *J* = 17.7 Hz, 1H), 4.67 (dd, *J* = 17.7, 2.3 Hz, 1H), 3.88 (s, 3H), 3.46 (d, *J* = 3.3 Hz, 1H), 2.98 – 2.91 (m, 1H), 2.01 – 1.86 (m, 1H), 1.81 – 1.74 (m, 1H), 1.02 (t, *J* = 7.5 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.4 (C), 144.8 (C), 144.6 (CH), 138.6 (C), 135.8 (C), 134.0 (2 x CH), 132.6 (C), 130.4 (C), 129.7 (2 x CH), 129.1 (2 x CH), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.1 (2 x CH), 114.0 (2 x CH), 71.0 (C), 61.3 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 47.8 (CH), 46.2 (CH), 27.3 (CH<sub>2</sub>), 7.9 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>29</sub>O<sub>5</sub>SSe 581.0895; found 581.0893.

**3-((4-methoxyphenyl)sulfonyl)-8a-pentyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (40)**



CCDC no. 2162704

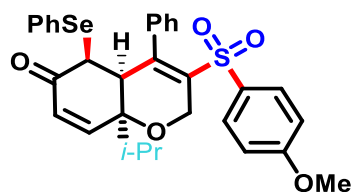
Yellow oil, 52.9 mg 85% yield, 0.3 Rf in 15 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.43 (td, *J* = 5.4, 2.7 Hz, 3H), 7.37 – 7.28 (m, 1H), 7.31 – 7.17 (m, 5H), 7.06 (b, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 10.3 Hz, 1H), 6.17 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.92 (d, *J* = 17.7 Hz, 1H), 4.63 (dd, *J* = 17.7, 2.5 Hz, 1H), 3.87 (s, 3H), 3.44 (dd, *J* = 4.3, 1.3 Hz, 1H), 2.95 (dd, *J* = 4.4, 2.2 Hz, 1H), 1.83 – 1.68 (m, 2H), 1.39 – 1.22 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.5 (C), 145.0 (C), 145.0 (CH), 138.5 (C), 135.8 (C), 134.0 (2 x CH), 132.6 (C), 130.4 (C), 129.7 (2 x CH), 129.1 (2 x CH), 128.8 (CH), 128.8 (CH), 128.3 (CH), 128.1 (2 x CH), 114.0 (2 x CH), 70.7 (C), 61.4 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 47.8 (CH), 46.7 (CH), 34.6 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 23.2 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>33</sub>H<sub>35</sub>O<sub>5</sub>SSe 623.1365; found 623.1363.

**8a-isopropyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (41)**



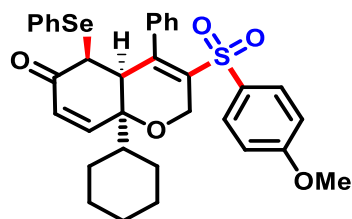
Yellow oil, 49.9 mg 84% yield, 0.3 R<sub>f</sub> in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.43 (d, *J* = 8.2 Hz, 4H), 7.35 – 7.15 (m, 8H), 6.97 (b, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 10.5 Hz, 1H), 6.26 (d, *J* = 10.5 Hz, 1H), 4.90 (d, *J* = 17.7 Hz, 1H), 4.67 (dd, *J* = 17.7, 1.9 Hz, 1H), 3.88 (s, 3H), 3.51 (d, *J* = 3.3 Hz, 1H), 3.16 (s, 1H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.5 (C), 144.5 (C), 141.8 (CH), 138.6 (C), 136.0 (C), 133.9 (2 x CH), 132.7 (C), 130.4 (CH), 129.8 (2 x CH), 129.1 (2 x CH), 129.0 (C), 128.6 (CH), 128.3 (CH), 128.1 (2 x CH), 114.0 (2 x CH), 73.2 (C), 61.3 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.4 (CH), 45.1 (CH), 29.3 (CH), 18.5 (CH<sub>3</sub>), 15.8 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>31</sub>H<sub>31</sub>O<sub>5</sub>SSe 595.1052; found 595.1057.

**8a-cyclohexyl-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (42)**



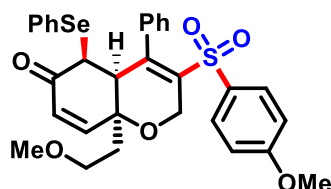
Yellow oil, 51.4 mg 81% yield, 0.5 Rf in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.49 – 7.41 (m, 4H), 7.33 – 7.24 (m, 6H), 7.00 (b, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 10.5 Hz, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 4.91 (d, *J* = 17.7 Hz, 1H), 4.66 – 4.53 (m, 1H), 3.88 (s, 3H), 3.49 (d, *J* = 3.5 Hz, 1H), 3.19 (b, 1H), 2.06 – 1.90 (m, 2H), 1.89 – 1.72 (m, 3H), 1.44 (d, *J* = 12.6 Hz, 1H), 1.23–1.15 (m, 1H), 1.24 – 1.10 (m, 3H), 0.99 – 0.86 (m, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.5 (C), 144.9 (C), 142.6 (CH), 138.4 (C), 136.0 (C), 134.1 (2 x CH), 132.8 (C), 130.5 (C), 129.9 (CH), 129.7 (2 x CH), 129.1 (2 x CH), 128.7 (CH), 128.3 (CH), 128.1 (2 x CH), 114.0 (2 x CH), 72.7 (C), 61.5 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.6 (CH), 44.9 (CH), 40.6 (CH), 29.3 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>35</sub>H<sub>35</sub>O<sub>5</sub>SSe 635.1365; found 635.1370.

**8a-(2-methoxyethyl)-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (43)**



Yellow oil, 50.7 mg 83% yield, 0.4 Rf in 40 % EtOAc in pet. ether.

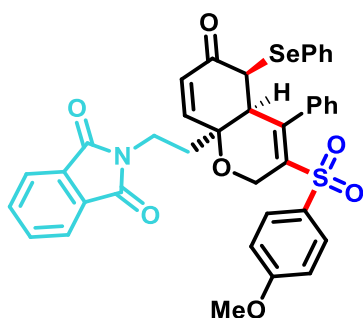
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.47 – 7.34 (m, 4H), 7.35 – 7.18 (m, 6H), 7.00 (b, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 10.3 Hz, 1H), 6.20 (d, *J* = 10.3 Hz, 1H), 4.94 (d, *J* = 17.6 Hz,

1H), 4.69 (dd,  $J = 17.6, 2.1$  Hz, 1H), 3.87 (s, 3H), 3.55-3.51 (m, 1H), 3.49 – 3.39 (m, 2H), 3.33 (b, 1H), 3.28(s, 3H), 2.26 – 2.21 (m, 1H), 2.01 – 1.90 (m, 1H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.7 (C), 163.4 (C), 145.4 (C), 145.0 (CH), 138.0 (C), 135.8 (C), 133.9 (2 x CH), 132.6 (C), 130.4 (C), 129.7 (2 x CH), 129.2 (CH), 129.1 (2 x CH), 128.7 (CH), 128.2 (CH), 128.0 (2 x CH), 114.0 (2 x CH), 70.5 (C), 67.8 ( $\text{CH}_2$ ), 61.4 ( $\text{CH}_2$ ), 58.9 ( $\text{CH}_3$ ), 55.7 ( $\text{CH}_3$ ), 48.0 (CH), 46.7 (CH), 34.7 ( $\text{CH}_2$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{31}\text{O}_6\text{SSe}$  611.1001; found 611.1006.

**2-(2-(3-((4-methoxyphenyl)sulfonyl)-6-oxo-4-phenyl-5-(phenylselanyl)-2,4a,5,6-tetrahydro-8aH-chromen-8a-yl)ethyl)isoindoline-1,3-dione (44)**



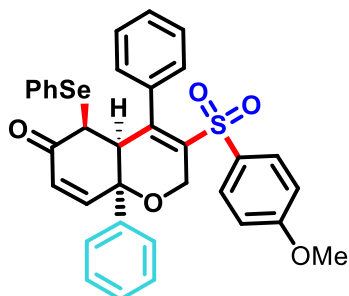
Brown sticky solid, 57.3 mg 79% yield, 0.5  $R_f$  in 50 % EtOAc in pet. ether.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.92 (dd,  $J = 5.5, 3.1$  Hz, 2H), 7.80 (dd,  $J = 5.4, 3.0$  Hz, 2H), 7.50 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.21 (m, 6H), 7.01 (b, 1H), 6.79 – 6.71 (m, 3H), 6.24 (dd,  $J = 10.3, 1.2$  Hz, 1H), 5.02 (d,  $J = 17.9$  Hz, 1H), 4.82 (dd,  $J = 17.8, 2.3$  Hz, 1H), 3.94 – 3.66 (m, 4H), 3.46 (dd,  $J = 4.2, 1.2$  Hz, 1H), 3.05 (s, 1H), 2.31 – 2.15 (m, 1H), 2.06 – 1.91 (m, 1H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.0 (C), 167.8 (2 x C), 163.32 (C), 144.5 (C), 143.0 (CH), 138.6 (C), 135.4 (C), 134.3 (2 x CH), 134.1 (2 x CH), 132.4 (C), 132.0 (2 x C), 130.2 (C), 129.8 (2 x CH), 129.6 (CH), 129.2 (2 x CH), 128.8 (CH), 128.4 (CH), 123.5 (2 x CH), 113.9 (2 x CH), 69.6 (C), 61.6 ( $\text{CH}_2$ ), 47.7 (CH), 46.6 (CH), 55.6 ( $\text{CH}_3$ ), 33.5 ( $\text{CH}_2$ ), 32.8 ( $\text{CH}_2$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{38}\text{H}_{32}\text{NO}_7\text{SSe}$  726.1059; found 726.1051.

**3-((4-methoxyphenyl)sulfonyl)-4,8a-diphenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (45)**



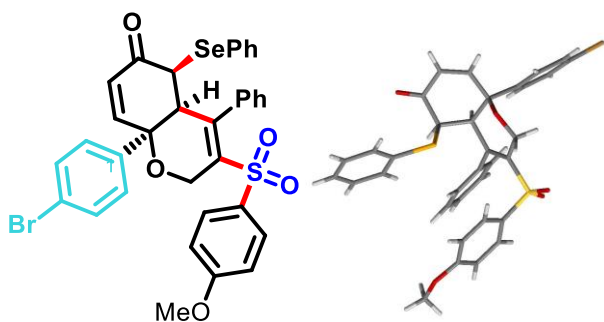
Brown oil, 52.3 mg 83% yield, 0.2 R<sub>f</sub> in 20 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.59 – 7.43 (m, 7H), 7.38 – 7.24 (m, 6H), 7.13 (b, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 10.3 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 10.2 Hz, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.38 (dd, *J* = 17.6, 2.0 Hz, 1H), 3.84 (b, 1H), 3.83 (s, 3H), 3.65 (d, *J* = 3.3 Hz, 1H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.1 (C), 147.2 (CH), 145.4 (C), 139.3 (C), 138.7 (C), 135.4 (C), 134.3 (2 x CH), 132.3 (C), 130.4 (C), 129.4 (2 x CH), 129.3 (2 x CH), 129.2 (2 x CH), 129.0 (CH), 128.9 (CH), 128.4 (CH), 128.1 (2 x CH), 127.0 (CH), 126.3 (2 x CH), 113.6 (2 x CH), 72.9 (C), 62.1 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 48.4 (CH), 45.0 (CH). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>29</sub>O<sub>5</sub>SSe 629.0895; found 629.0901.

**8a-(4-bromophenyl)-3-((4-methoxyphenyl)sulfonyl)-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (46)**



CCDC no. 2162705

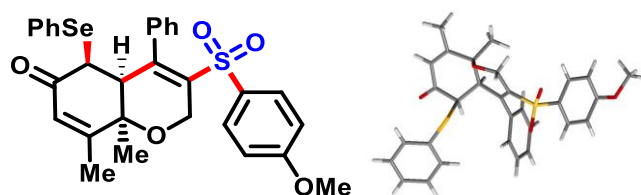
Brown oil, 57.3 mg 81% yield, 0.3 R<sub>f</sub> in 10 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 6.5 Hz, 2H), 7.42 – 7.22 (m, 8H), 7.10 (b, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 10.2 Hz, 2H), 6.06 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 17.6 Hz, 1H), 4.28 (dd, *J* = 17.6, 1.9 Hz, 1H), 3.84 (s, 3H), 3.75 (b, 1H), 3.62 (d, *J* = 3.1 Hz, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.3 (C), 163.3 (C), 146.3 (CH), 145.3 (C), 139.1 (C), 137.9 (C), 135.2 (C), 134.3 (2 x CH), 132.5 (2 x CH), 132.2 (C), 130.2 (C), 129.3 (2 x CH), 129.2 (2 x CH), 129.2 (CH), 128.5 (CH), 128.2 (2 x CH), 128.0 (2 x CH), 127.4 (CH), 123.0 (C), 113.7 (2 x CH), 72.7 (C), 62.2 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.2 (CH), 45.3 (CH). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>27</sub>BrO<sub>5</sub>SSe 707.0001; found 706.9992.

**3-((4-methoxyphenyl)sulfonyl)-8,8a-dimethyl-4-phenyl-5-(phenylselanyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (48)**



CCDC no. 2162706

Yellow sticky solid, 52.0 mg 89% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

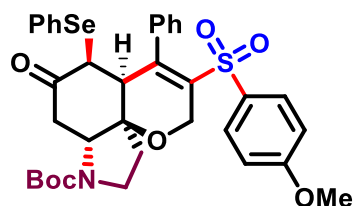
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47 – 7.36 (m, 4H), 7.35 – 7.17 (m, 6H), 7.05 (b, 2H) 6.87 – 6.77 (m, 2H), 5.98 – 5.92 (m, 1H), 4.94 (d, *J* = 17.6 Hz, 1H), 4.65 (dd, *J* = 17.6, 2.5 Hz, 1H), 3.86 (s, 3H), 3.40 (dd, *J* = 4.2, 1.1 Hz, 1H), 2.84 (dd, *J* = 3.9, 2.1 Hz, 1H), 2.09 (d, *J* = 1.3 Hz, 3H), 1.50 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.7 (C), 163.4 (C), 156.5 (C), 145.2 (C), 138.5 (C), 135.8 (C), 133.8 (2 x CH), 132.6 (C), 130.4 (C), 129.7 (2 x CH), 129.1 (2 x CH), 128.7 (CH), 128.1 (CH), 128.0 (2 x CH), 125.8 (CH), 114.0 (2 x CH), 70.7 (C), 61.4 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 49.1 (CH), 47.2 (CH), 20.9 (CH<sub>3</sub>), 18.6 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>30</sub>H<sub>29</sub>O<sub>5</sub>SSe 581.0895; found 581.0893.



***tert*-butyl-3-((4-methoxyphenyl)sulfonyl)-6-oxo-4-phenyl-5-(phenylselanyl)-2,4a,5,6,7,7a,9,10-octahydro-8H-pyrano[2,3-d]indole-8-carboxylate (**50**)**



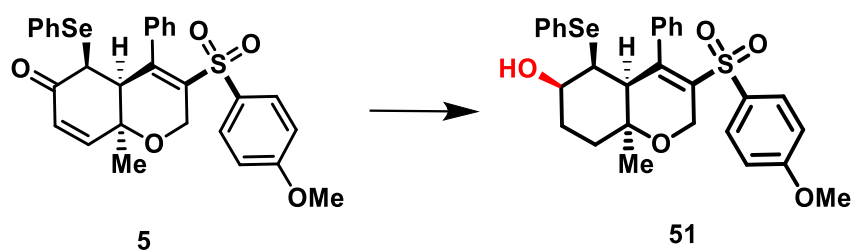
Brown sticky solid, 61.6 mg 86% yield, 0.4 R<sub>f</sub> in 40 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.46 – 7.37 (m, 4H), 7.34 – 7.20 (m, 6H), 7.02 (br, 2H), 6.81 (dd, *J* = 15.7, 8.7 Hz, 2H), 4.88 (d, *J* = 17.8 Hz, 1H), 4.62 (d, *J* = 17.8 Hz, 1H), 4.41 (br, 1H), 3.87 (s, 3H), 3.71 – 3.42 (m, 2H), 3.30 (br, 2H), 2.72 (s, 1H), 2.53 – 2.43 (m, 1H), 2.26 – 1.92 (m, 1H), 1.73 – 1.65 (m, 1H), 1.51 (s, 9H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 201.8 (C), 163.5 (C), 154.5 (C), 144.2 (C), 138.8 (C), 135.4 (C), 134.8 (2 x CH), 132.3 (C), 129.7(2 x CH), 129.2 (2 x CH), 128.9 (CH), 128.6 (CH), 128.6 (CH), 128.2 (2 x CH), 114.1(2 x CH), 80.4 (C), 61.9 (CH<sub>2</sub>), 59.7 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 47.1 (CH<sub>2</sub>), 46.9 (CH<sub>2</sub>), 44.8 (C), 41.0 (CH), 30.0 (CH), 29.7 (CH), 28.4 (3 x CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

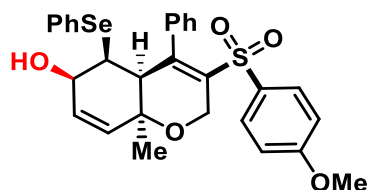
**HRMS (ESI) m/z:** [M+Na]<sup>+</sup> calculated for C<sub>35</sub>H<sub>37</sub>NNaO<sub>7</sub>SSe 718.1348; found 718.1349.

**b) Luche reduction of **5****



To a solution of **5** (56.6 mg, 0.1 mmol) in 1ml MeOH was added 0.1 eq. of CeCl<sub>3</sub>·7H<sub>2</sub>O followed by 1.5 eq of NaBH<sub>4</sub> slowly. The reaction was stirred at rt for 30 min then quenched with water then the organic layer was collected and purified by column chromatography to give 50.0 mg, 88% of the title compound **57** as a colorless oil

**3-((4-methoxyphenyl)sulfonyl)-8a-methyl-4-phenyl-5-(phenylselanyl)-4a,5,6,8a-tetrahydro-2H-chromen-6-ol (51)**



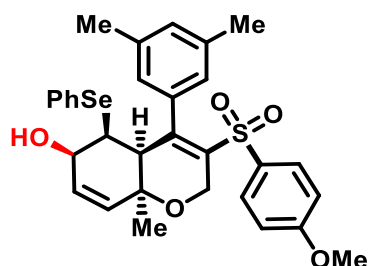
Colorless oil, 50 mg 88% yield, 0.4 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.44 – 7.39 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.27 – 7.14 (m, 4H), 7.05 (b, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 7.0 Hz, 2), 5.76 – 5.67 (m, 2H), 4.88 (d, *J* = 17.6 Hz, 1H), 4.62 (dd, *J* = 17.6, 2.4 Hz, 1H), 4.22 (d, *J* = 4.1 Hz, 1H), 3.86 (s, 3H), 3.50 (d, *J* = 3.1 Hz, 1H), 2.50 (b, 1H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 163.3 (C), 146.2 (C), 137.9 (C), 136.4 (C), 133.2 (CH), 132.9 (C), 132.1 (C), 132.0 (2 x CH), 131.9 (CH), 129.7 (2 x CH), 129.1 (2 x CH), 128.2 (CH), 127.7 (2 x CH), 126.8 (CH), 113.9 (2 x CH), 69.0 (CH), 68.7 (C), 61.1 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 53.0 (CH), 49.8 (CH), 22.9 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>29</sub>O<sub>5</sub>SSe 569.0895; found 569.0887.

**4-(3,5-dimethylphenyl)-3-((4-methoxyphenyl)sulfonyl)-8a-methyl-5-(phenylselanyl)-4a,5,6,8a-tetrahydro-2H-chromen-6-ol (52)**

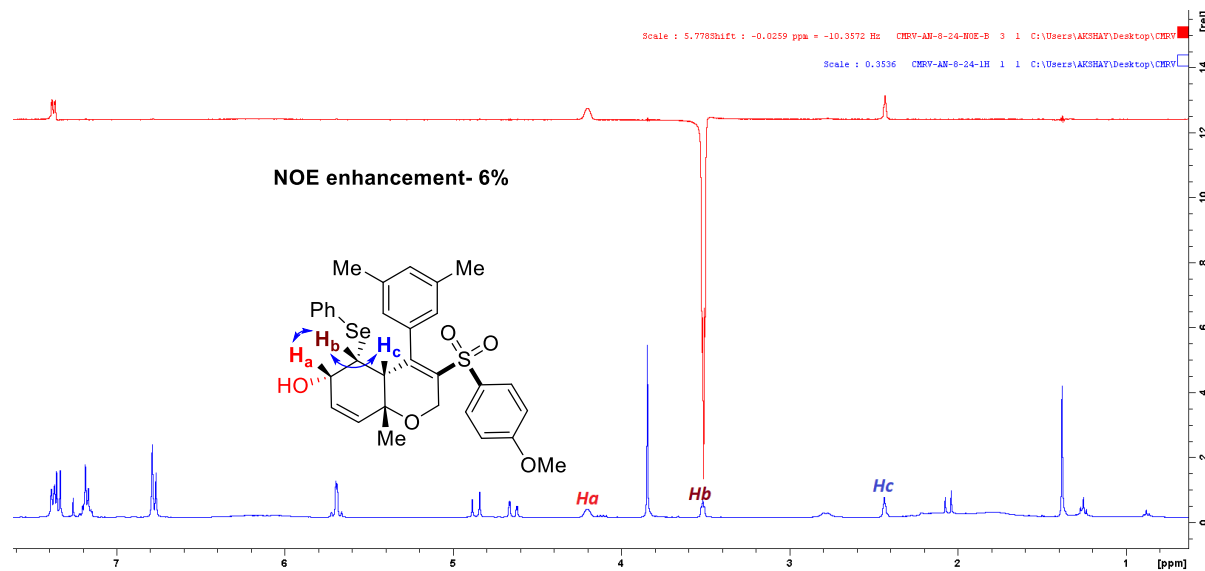
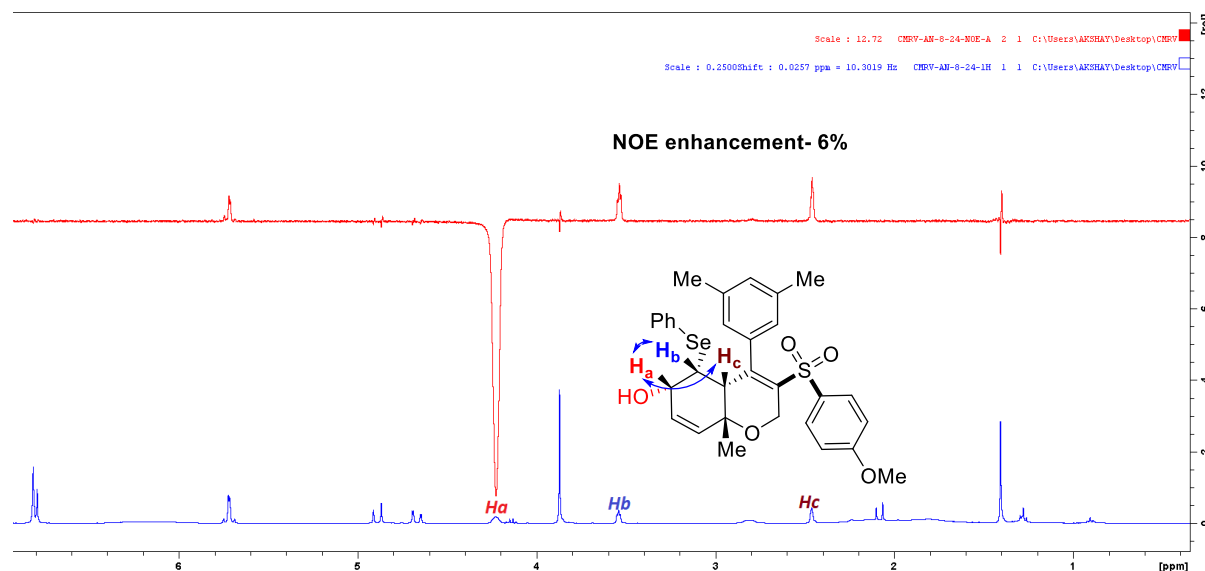


Colorless oil, 53.6 mg 90% yield, 0.5 Rf in 30 % EtOAc in pet. ether, configuration of the stereocenter bearing the hydroxyl group was confirmed using NOE.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 – 7.29 (m, 4H), 7.24 – 7.01 (m, 3H), 6.78 (d, *J* = 8.9 Hz, 3H), 6.09 (br, 2H), 5.77 – 5.57 (m, 2H), 4.86 (d, *J* = 17.5 Hz, 2H), 4.64 (dd, *J* = 17.5, 2.4 Hz, 2H), 4.20 (br, 1H), 3.85 (s, 3H), 3.52 (t, *J* = 3.3 Hz, 1H), 2.79 (br, 1H (OH)), 2.44 (s, 1H), 1.89 (br, 6H), 1.38 (s, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  163.2 (C), 146.6 (C), 137.6 (C), 136.2 (C), 133.2 (C), 133.1 (CH), 132.5 (C), 132.0 (CH), 131.9 (2 x  $\text{CH}_3$ ), 129.8 (2 x  $\text{CH}_3$ ), 129.6 (CH), 129.0 (2 x  $\text{CH}_3$ ), 126.8 (CH), 113.7 (2 x  $\text{CH}_3$ ), 68.8 (C), 68.6 (CH), 61.1 (CH), 55.6 ( $\text{CH}_3$ ), 53.2 (CH), 49.5 (CH), 22.9 (2 x  $\text{CH}_3$ ). Two signals corresponding to 2 x CH and 2 x C could not be identified, most likely due to it being broad.

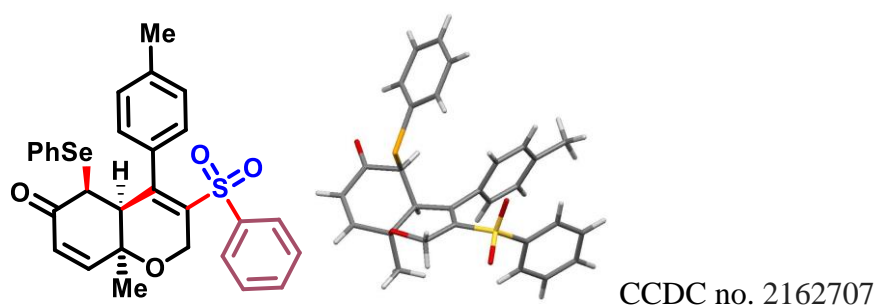
**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{31}\text{H}_{32}\text{O}_5\text{NaSSe}$  619.1028; found 619.1021.





In a reaction vial equipped with magnetic stirring bar, was added **1** (24.0 mg, 0.2 mmol), diaryliodonium salt **54** (59 mg, 0.12 mmol), diphenyldiselenide **3** (24 mg, 0.1 mmol), DABSO (29.0 mg, 0.12 mmol) followed dry DCM (0.5 mL). The reaction was stirred for 12 hrs under irradiation by White LEDs. under argon atmosphere The reaction mass was then diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). Organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (8:2) to give 34.7 mg, 63% yield of the desired product **6**.

**8a-methyl-5-(phenylselanyl)-3-(phenylsulfonyl)-4-(p-tolyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (55)**



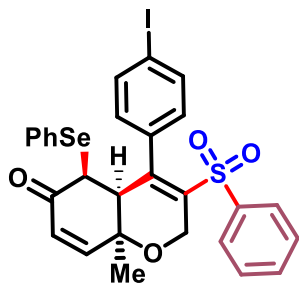
Brown sticky solid, 34.7 mg 63%, 0.4 R<sub>f</sub> in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.55-7.48 (m, 3H), 7.43 – 7.31 (m, 4H), 7.31 – 7.17 (m, 3H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.88 (b, 2H), 6.53 (d, *J* = 10.2 Hz, 1H), 6.09 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.95 (d, *J* = 17.6 Hz, 1H), 4.66 (dd, *J* = 17.6, 2.5 Hz, 1H), 3.39 (dd, *J* = 4.2, 1.2 Hz, 1H), 2.84 (dd, *J* = 3.8, 2.3 Hz, 1H), 2.33 (s, 3H), 1.45 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.6 (C), 146.3 (CH), 146.2 (C), 141.1 (C), 138.8 (C), 137.9 (C), 134.1 (2 x CH), 133.2 (CH), 132.4 (C), 130.2 (C), 129.1 (2 x CH), 128.7 (4 x CH), 128.3 (CH), 127.7 (CH), 127.4 (2 x CH), 68.5 (C), 61.4 (CH<sub>2</sub>), 48.5 (CH), 47.5 (CH), 22.6 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>29</sub>H<sub>27</sub>O<sub>4</sub>SSe 551.0790; found 551.0787.

**4-(4-iodophenyl)-8a-methyl-5-(phenylselanyl)-3-(phenylsulfonyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (56)**



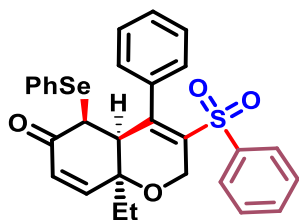
Brown sticky solid, 35.0 mg 53% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.66 – 7.54 (m, 1H), 7.53 (d, *J* = 7.4 Hz, 3H), 7.48 – 7.37 (m, 4H), 7.35 – 7.19 (m, 4H), 6.75 (b, 2H), 6.56 (d, *J* = 10.2 Hz, 1H), 6.12 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.96 (d, *J* = 17.8 Hz, 1H), 4.68 (dd, *J* = 17.8, 2.5 Hz, 1H), 3.39 (dd, *J* = 4.3, 1.3 Hz, 1H), 2.82 (b, 1H), 1.48 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 193.4 (C), 146.3 (CH), 144.6 (C), 139.0 (C), 137.2 (2 x CH), 134.9 (C), 133.8 (2 x CH), 133.5 (CH), 131.5 (C), 130.1 (C), 129.3 (2 x CH), 128.9 (2 x CH), 128.4 (CH), 127.7 (CH), 127.4 (2 x CH), 94.9 (C), 68.4 (C), 61.3 (CH<sub>2</sub>), 48.2 (CH), 47.2 (CH), 22.7 (CH<sub>3</sub>). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calculated for C<sub>28</sub>H<sub>24</sub>IO<sub>4</sub>SSe 662.9600; found 662.9602.

**8a-ethyl-4-phenyl-5-(phenylselanyl)-3-(phenylsulfonyl)-4a,8a-dihydro-2H-chromen-6(5H)-one (57)**



Brown sticky solid, 33.6 mg 61% yield, 0.4 Rf in 20 % EtOAc in pet. ether.

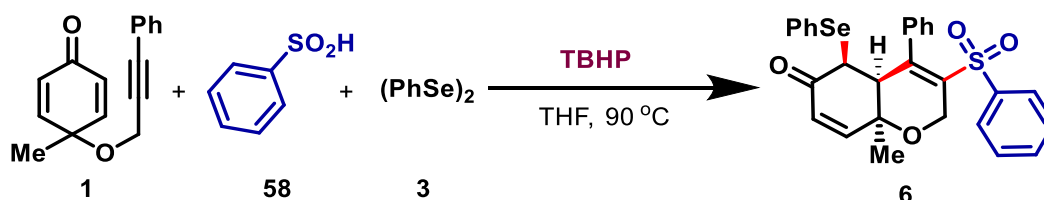
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.59 – 7.53 (m, 1H), 7.50 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.42 (dt, *J* = 6.6, 1.5 Hz, 2H), 7.38 (td, *J* = 7.4, 1.7 Hz, 2H), 7.31 (dd, *J* = 8.0, 1.9 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 2H), 6.96 (b, 2H), 6.64 (d, *J* = 10.4 Hz, 2H), 6.19 (dd, *J* = 10.4, 1.3 Hz, 2H), 4.95 (d, *J* = 17.6 Hz, 2H), 3.45 (dd, *J* = 4.2, 1.2 Hz, 1H), 2.95 (dd, *J* = 4.1, 2.1

Hz, 1H), 1.93 (dt,  $J = 14.9, 7.5$  Hz, 1H), 1.77 (dt,  $J = 14.9, 7.5$  Hz, 1H), 1.02 (t,  $J = 7.5$  Hz, 3H).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  193.6 (C), 145.8 (C), 144.5 (CH), 141.1 (C), 138.2 (C), 135.5 (C), 134.0 (2 x CH), 133.2 (CH), 130.3 (C), 129.2 (2 x CH), 129.0 (CH), 128.8 (2 x CH), 128.7 (CH), 128.3 (CH), 128.1 (2 x CH), 127.4 (2 x CH), 71.0 (C), 61.3 ( $\text{CH}_2$ ), 47.8 (CH), 46.3 (CH), 27.4 ( $\text{CH}_2$ ), 7.9 ( $\text{CH}_3$ ). A signal corresponding to 2 x CH could not be identified, most likely due to it being broad.

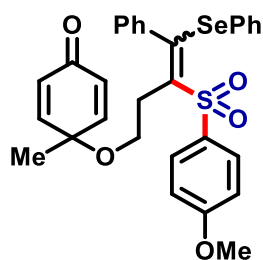
**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calculated for  $\text{C}_{29}\text{H}_{27}\text{O}_4\text{SSe}$  551.0790; found 551.0792.

**e) Three component cascade cyclization using sulfinic acids.**



In a reaction vial equipped with magnetic stirring bar, was added alkyne **1** (24 mg, 0.1 mmol), phenylsulfinic acid **58** (17.0 mg, 0.12 mmol), TBHP in decane (0.15 mmol), diphenyldiselenide **3** (23.3 mg, 0.1 mmol) followed THF (0.5 mL). The reaction was then then stirred for 12 hrs at 90 °C. The reaction mass was then diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). Organic layer was dried over  $\text{Na}_2\text{SO}_4$ , evaporated under reduced pressure and chromatographed with EtOAc in Petroleum ether (8:2) to give 36.0 mg, 67% yield of the desired product **6**.

**4-((3-((4-methoxyphenyl)sulfonyl)-4-phenyl-4-(phenylselenanyl)but-3-en-1-yl)oxy)-4-methylcyclohexa-2,5-dien-1-one (64)**



Yellow oil, 47 mg 81% yield, 0.3 Rf in 30 % EtOAc in pet. ether.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22 (d, *J* = 8.8 Hz, 3H), 7.08 (dd, *J* = 14.5, 7.5 Hz, 3H), 7.00 – 6.80 (m, 7H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 7.5 Hz, 2H), 6.36 (d, *J* = 10.0 Hz, 2H), 3.80 (s, 3H), 3.70 (t, *J* = 6.9 Hz, 2H), 3.24 (t, *J* = 6.9 Hz, 2H), 1.54 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 185.3 (C), 162.9 (C), 153.6 (C), 152.0 (2 x CH), 137.0 (2 x CH), 136.1 (C), 136.0 (C), 133.0 (C), 130.2 (2 x CH), 129.7 (2 x CH), 129.2 (2 x CH), 128.7 (CH), 128.5 (2 x CH), 127.4 (CH), 127.3 (C), 126.8 (2 x CH), 113.7 (2 x CH), 72.8 (C), 63.9 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 34.5 (CH<sub>2</sub>), 26.6 (CH<sub>3</sub>).

**HRMS (ESI) m/z:** [M+Na]<sup>+</sup> calculated for C<sub>30</sub>H<sub>28</sub>NaO<sub>5</sub>SSe 603.0715; found 603.0712.

#### 4. References

- 1) (a) Tello-Aburto, R.; Harned, A. M. *Org. Lett.* **2009**, *11*, 3998; (b) Gollapelli, K. K.; Donikela, S.; Manjula, N.; Chegondi, R. *ACS Catal.* **2018**, *8*, 1440; (c) Liu, P.; Fukui, Y.; Tian, P.; He, Z.-T.; Sun, C.-Y.; Wu, N.-Y.; Lin, G.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 11700.
- 2) Ma, X.-L.; Wang, Q.; Feng, X.-Y.; Mo, Z.-Y.; Pan, Y.-M.; Chen, Y.-Y.; Xin, M.; Xu, Y.-L. *Green Chem.* **2019**, *21*, 3547
- 3) Zhu, S.; Pathigoolla, A.; Lowe, G.; Walsh, D. A.; Cooper, M.; Lewis, W.; Lam, H. W. *Chem. Eur. J.* **2017**, *23*, 17598;



## 5. $^1\text{H}$ and $^{13}\text{C}$ Spectras

