

## Supporting Information

### Synthesis of Selenated Tetracyclic Indoloazulenes *via* Iodine and Diorganyl

#### Diselenides

Khin Myat Noe Win,<sup>a</sup> Amol D. Sonawane<sup>a</sup> and Mamoru Koketsu<sup>\*,a</sup>.

<sup>a</sup>Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Gifu 501-1193 Japan.

#### List of the Content:

Experimental: General	2
Diselenides preparation	2
General procedure and spectral data for the synthesis of 3,3'-((2-(phenylethynyl)phenyl)methylene)bis(1 <i>H</i> -indole) <b>2a-2e</b>	3-5
General procedure and spectral data for the synthesis of 12-(1 <i>H</i> -indol-3-yl)-7-(methylselanyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2- <i>b</i> ]indole <b>3a-3o</b>	6-17

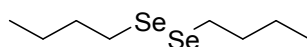
## Experimental: General

All solvents and reagents were purchased from the suppliers and used without further purification. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Reactions were monitored by thin-layer chromatography (TLC) carried on silica plates using UV-light or Iodine chamber for visualization. Column chromatography was performed on silica gel (60-120 mesh) using *n*-hexane and ethyl acetate as eluents. Evaporation and condensation were carried out *in vacuo*. NMR spectra were recorded with JEOL JNM-ECS 400 spectrometers with tetramethylsilane as an internal standard. Chemical shifts  $\delta$  and coupling constants  $J$  are given in ppm (parts per million) and Hz (hertz), respectively. The following abbreviations were used as follows: s: singlet, d: doublet, t: triplet, m: multiplet. Additionally unknown compounds are characterized by HRMS analysis. All known compounds data are in consistent with the given literature reports. Scale up reactions also performed as per the given general procedure without any deviation. Melting points were measured by a Yanaco micromelting point apparatus.

### Diselenides preparation:

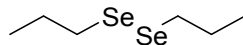
#### Preparation of 1,2-dibutyldiselenide

Selenium (200 mg, 2.53 mmol) was added to a stirred solution of sodium borohydride (191 mg, 5.07 mmol) in ethanol (20 mL) at 0°C. Stirring was continued for 30 min; at this temperature. Additionally, selenium (200 mg, 2.53 mmol) was added to reaction mixture and stirred for 30 min at 0°C. Finally the iodobutane (1.01 mL, 8.87 mmol) was added over a period of 5 min. After stirring for a further hour at room temperature, the reaction mixture was extracted with hexane and washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude product was purified over silica gel column chromatography (SiO<sub>2</sub>: *n*-hexane / toluene = 20/1) to afford the dibutyl diselenides as orange coloured liquid.



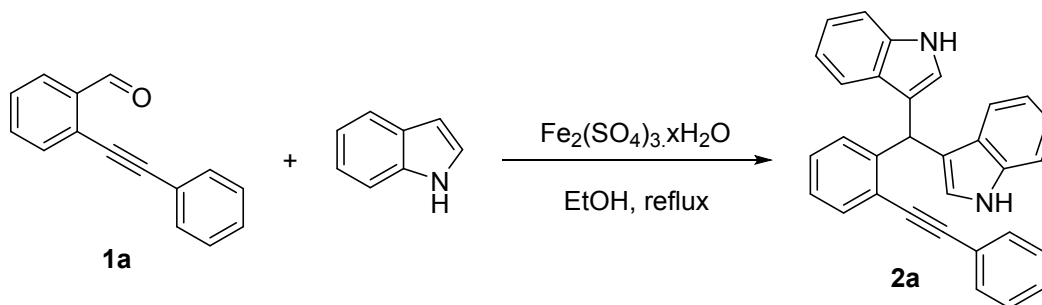
Yield: 72%; Orange coloured liquid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.92 (4H, t,  $J$  = 7.6 Hz), 1.68-1.75 (4H, m), 1.42 (4H, q,  $J$  = 7.5 Hz), 0.93 (6H, t,  $J$  = 7.3 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  33.2, 30.0, 22.7, 13.7; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  307.8.

#### Preparation of 1,2-dipropyldiselenide



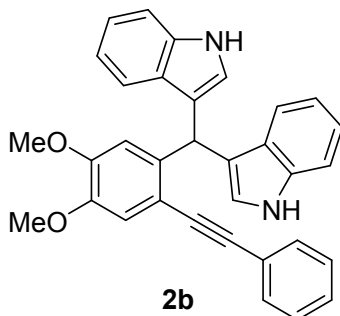
Yield: 68%; Orange coloured liquid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.86-2.94 (4H, m), 1.72-1.81 (4H, m), 1.00 (6H, t,  $J$  = 7.3 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  32.4, 24.3, 14.2; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  303.4.

**General procedure for the synthesis of 3,3'-((2-(phenylethynyl)phenyl)methylene)bis(1H-indole) 2a-2e:**



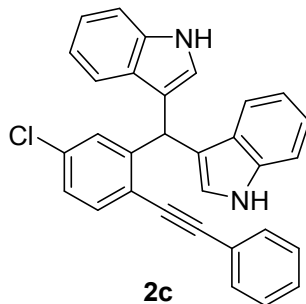
To a solution of 2-(phenylethynyl)benzaldehyde<sup>20</sup> **1a** (500 mg, 2.42 mmol, 1.0 equiv.) in dry EtOH (10 mL) was added indole (568 mg, 4.85 mmol, 2.0 equiv.) and  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  (17 mg, 15 mol%) in a round-bottom flask. The mixture was stirred at reflux condition for 1 h.<sup>19</sup> After completion of reaction, the solvent was evaporated under reduced pressure. The residue was extracted with ethyl acetate and the organic phase was washed successively with water and brine. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The resulting crude product was purified by column chromatography using *n*-hexane : ethyl acetate (70 : 30) as the eluent to afford **2a**, red solid. Yield: 84%; Melting point: 82-84°C; IR (neat): 3418, 3059, 3009, 1703, 1676, 1598, 1492, 1457, 1418, 1338, 1216, 1093, 1010, 753, 690, 667, 600  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (2H, s), 7.59 (1H, s), 7.47 (2H, s), 7.33 (2H, s), 7.24 (2H, s), 7.19 (6H, t,  $J = 3.1$  Hz), 7.01 (2H, d,  $J = 7.2$  Hz), 6.64 (2H, s), 6.52 (1H, s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 136.8, 132.3, 131.6, 128.7, 128.4, 128.5, 128.1, 127.3, 126.2, 123.8, 123.4, 122.9, 122.0, 120.0, 119.3, 119.3, 111.1, 94.0, 88.4, 38.0; HRMS (ESI):  $m/z = 423.1861$  calcd. For  $\text{C}_{31}\text{H}_{23}\text{N}_2$ , found 423.1837  $[\text{M}+\text{H}]^+$ .

### 3,3'-((4,5-Dimethoxy-2-(phenylethynyl)phenyl)methylene)bis(1H-indole) (2b)



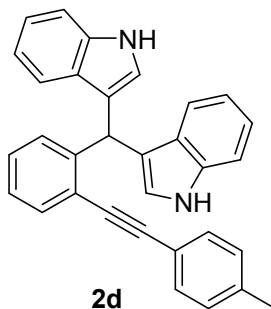
Yield: 62%; Melting point: 105-107°C; IR (neat): 3411, 3007, 1648, 1596, 1509, 1457, 1338, 1247, 1205, 1183, 1086, 1040, 855, 804, 743, 691  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (2H, s), 7.49 (2H, d,  $J = 7.6$  Hz), 7.34 (2H, d,  $J = 8.1$  Hz), 7.15-7.22 (5H, m), 7.09 (1H, s), 7.01 (2H, t,  $J = 7.2$  Hz), 6.82 (1H, s), 6.73 (2H, s), 6.48 (1H, s), 3.90 (3H, s), 3.62 (3H, s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 147.1, 139.7, 136.8, 131.4, 128.5, 127.9, 127.3, 123.6, 123.5, 122.0, 120.1, 119.5, 119.4, 114.5, 111.9, 111.0, 92.7, 88.5, 56.1, 55.9, 37.9; HRMS (ESI):  $m/z = 483.2073$  calcd. For  $\text{C}_{33}\text{H}_{27}\text{N}_2\text{O}_2$ , found 483.2056  $[\text{M}+\text{H}]^+$ .

### 3,3'-((5-Chloro-2-(phenylethynyl)phenyl)methylene)bis(1H-indole) (2c)



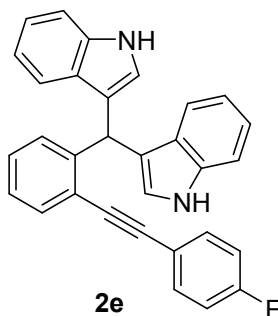
Yield: 71%; Melting point: 123-125°C; IR (neat): 3417, 3059, 3016, 2400, 1705, 1619, 1588, 1554, 1493, 1472, 1457, 1418, 1338, 1216, 1178, 1094, 1040, 1011, 906, 823, 754, 690, 667, 590  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (2H, s), 7.48 (3H, dd,  $J = 17.6, 8.0$  Hz), 7.32 (2H, d,  $J = 8.2$  Hz), 7.15-7.19 (7H, m), 7.02 (2H, t,  $J = 7.3$  Hz), 6.63 (2H, s), 6.49 (1H, s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.0, 136.8, 134.3, 133.4, 131.6, 128.8, 128.3, 127.1, 126.7, 123.8, 123.1, 122.2, 121.5, 119.8, 119.5, 118.6, 111.2, 94.9, 87.3, 37.9; HRMS (ESI):  $m/z = 479.1291$  calcd. For  $\text{C}_{33}\text{H}_{21}\text{ClN}_2$ , found 479.1288  $[\text{M}+\text{Na}]^+$ .

**3,3'-((2-(*p*-Tolylethynyl)phenyl)methylene)bis(1*H*-indole) (2d)**



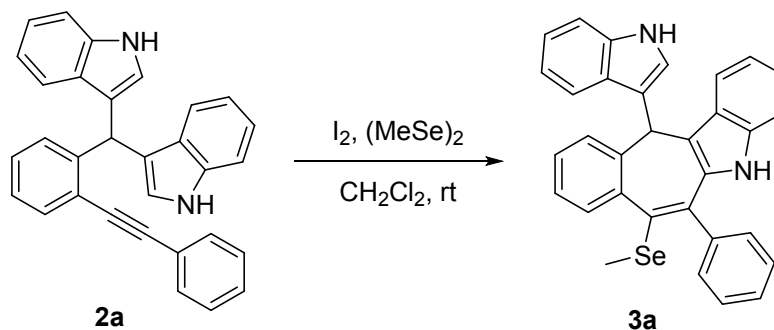
Yield: 79%; Melting point: 98-100°C; IR (neat): 3416, 3057, 1691, 1604, 1510, 1457, 1419, 1338, 1217, 1178, 1095, 818, 743 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (2H, s), 7.56-7.58 (1H, m), 7.47 (2H, d, *J* = 8.2 Hz), 7.34 (2H, d, *J* = 8.2 Hz), 7.16-7.19 (4H, m), 7.09 (2H, d, *J* = 8.2 Hz), 7.01 (3H, d, *J* = 6.9 Hz), 6.68 (2H, s), 6.52 (1H, s), 2.29 (3H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 146.0, 138.3, 136.8, 132.2, 131.5, 129.1, 128.7, 128.2, 127.3, 126.2, 123.8, 123.1, 122.0, 120.3, 120.1, 119.3, 111.1, 94.3, 87.8, 38.0, 21.56; HRMS (ESI): *m/z* = 437.2018 calcd. For C<sub>32</sub>H<sub>25</sub>N<sub>2</sub>, found 437.2006 [M+H]<sup>+</sup>.

**3,3'-((2-((4-Fluorophenyl)ethynyl)phenyl)methylene)bis(1*H*-indole) (2e)**



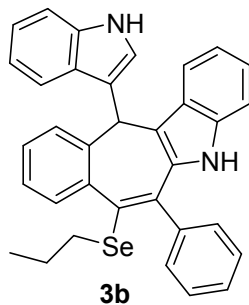
Yield: 64%; Melting point: 89-91°C; IR (neat): 3415, 3060, 1694, 1598, 1508, 1457, 1418, 1338, 1221, 1156, 1093, 1011, 836, 793, 743 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (2H, s), 7.55-7.58 (1H, m), 7.45 (2H, d, *J* = 7.8 Hz), 7.33 (2H, d, *J* = 7.8 Hz), 7.14-7.19 (3H, m), 7.09 (2H, dd, *J* = 8.9, 5.3 Hz), 7.01 (2H, d, *J* = 7.3 Hz), 6.86 (2H, t, *J* = 8.7 Hz), 6.64 (2H, s), 6.48 (1H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 146.1, 136.8, 133.5, 133.4, 132.2, 128.7, 128.5, 127.3, 126.2, 123.8, 122.8, 122.0, 120.0, 119.4, 119.3, 116.0, 115.4, 111.1, 93.0, 88.0, 38.0; HRMS (ESI): *m/z* = 441.1767 calcd. For C<sub>31</sub>H<sub>22</sub>N<sub>2</sub>F, found 441.1764 [M+H]<sup>+</sup>.

**General procedure for the synthesis of 12-(1*H*-indol-3-yl)-7-(methylselanyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole 3a-3o:**



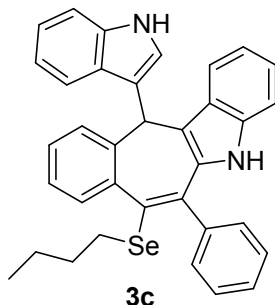
To a stirred solution of  $\text{I}_2$  (30 mg, 0.12 mmol, 1.0 equiv.) and dimethyl diselenide (45 mg, 0.24 mmol, 2.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added the corresponding 3,3'-((2-(phenylethynyl)phenyl)methylene)bis(1*H*-indole)<sup>20</sup> **2a** (50 mg, 0.12 mmol, 1.0 equiv.) at the rt. The reaction was monitored by TLC, after completion, the reaction mixture was quenched with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and water. The resulting solution was extracted using dichloromethane. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The crude product was purified by column chromatography using *n*-hexane : ethyl acetate (70 : 30) as the eluent to afford **3a**, yellow solid. Yield: 70%; Melting point: 142-144°C; IR (neat): 3420, 3056, 1487, 1456, 1443, 1316, 1271, 1218, 1151, 1137, 1011, 908, 743, 703, 667  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (1H, d,  $J = 7.8$  Hz), 7.87 (1H, d,  $J = 8.7$  Hz), 7.78 (1H, s), 7.69 (1H, d,  $J = 6.4$  Hz), 7.52 (1H, s), 7.42 (4H, t,  $J = 6.9$  Hz), 7.30 (1H, d,  $J = 6.4$  Hz), 7.18 (4H, dt,  $J = 9.2, 3.8$  Hz), 7.08 (1H, d,  $J = 8.2$  Hz), 7.02 (1H, d,  $J = 8.2$  Hz), 6.84 (1H, t,  $J = 7.6$  Hz), 6.65 (1H, s), 6.01 (1H, s), 0.99 (3H, t,  $J = 6.4$  Hz);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 140.9, 136.7, 136.6, 136.0, 135.6, 134.2, 133.2, 132.4, 129.0, 128.7, 128.5, 127.3, 126.6, 126.0, 123.0, 122.5, 121.6, 120.3, 120.1, 119.9, 119.2, 118.3, 115.3, 111.1, 111.0, 40.5, 8.9;  $^{77}\text{Se-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  245.6; HRMS (ESI):  $m/z = 517.1183$  calcd. For  $\text{C}_{32}\text{H}_{25}\text{N}_2\text{Se}$ , found 517.1176  $[\text{M}+\text{H}]^+$ .

**12-(1*H*-Indol-3-yl)-6-phenyl-7-(propylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3b)**



Yield: 52%; Melting point: 165-167°C; IR (neat): 3423, 3057, 2961, 2870, 1721, 1598, 1490, 1456, 1443, 1354, 1313, 1217, 1151, 1137, 927, 743, 703, 666  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (1H, d,  $J = 7.8$  Hz), 7.83 (2H, t,  $J = 8.9$  Hz), 7.72 (1H, d,  $J = 7.3$  Hz), 7.51 (1H, s), 7.43 (3H, s), 7.28 (1H, d,  $J = 7.3$  Hz), 7.15-7.23 (6H, m), 7.03 (1H, t,  $J = 7.3$  Hz), 6.87 (1H, t,  $J = 7.6$  Hz), 6.69 (1H, s), 6.03 (1H, s), 1.67-1.73 (1H, m), 1.38 (1H, d,  $J = 6.0$  Hz), 0.74 (1H, t,  $J = 7.1$  Hz), 0.59 (1H, s), 0.23 (3H, t,  $J = 7.3$  Hz);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 141.2, 136.8, 136.8, 136.7, 135.6, 134.4, 133.5, 132.6, 129.1, 128.8, 128.6, 127.5, 126.6, 125.9, 123.0, 122.5, 121.7, 120.1, 119.9, 119.8, 119.3, 118.3, 115.0, 111.1, 111.0, 40.7, 31.1, 22.5, 14.1;  $^{77}\text{Se-NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  323.4; HRMS (ESI):  $m/z = 545.1496$  calcd. For  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{Se}$ , found 545.1505  $[\text{M}+\text{H}]^+$ .

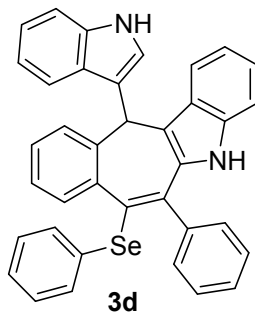
**7-(Butylselanyl)-12-(1*H*-indol-3-yl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3c)**



Yield: 63%; Melting point: 131-133°C; IR (neat): 3420, 3057, 2956, 1456, 1443, 1354, 1314, 1218, 1091, 1057, 905, 742, 702, 667 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (1H, d, *J* = 7.8 Hz), 7.84 (1H, d, *J* = 6.9 Hz), 7.79 (1H, s), 7.71 (1H, d, *J* = 7.8 Hz), 7.50 (1H, s), 7.42 (4H, d, *J* = 7.8 Hz), 7.28 (1H, d, *J* = 8.2 Hz), 7.16-7.22 (5H, m), 7.04 (1H, d, *J* = 7.8 Hz), 6.87 (1H, t, *J* = 7.6 Hz), 6.69 (1H, s), 6.02 (1H, s), 1.71-1.76 (1H, m), 1.32 (1H, t, *J* = 5.7 Hz), 0.77 (1H, d, *J* = 8.7 Hz), 0.67 (3H, t, *J* = 6.6 Hz), 0.46 (3H, t, *J* = 6.9 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 141.1, 136.8, 136.7, 136.7, 135.7, 134.3, 133.4, 132.6, 129.0, 128.6, 128.5, 127.4, 126.6, 125.8, 122.9, 122.5, 121.6, 120.0, 119.9, 119.8, 119.3, 118.3, 115.1, 111.1, 111.0, 40.6, 31.0, 28.7, 22.6, 13.3; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 323.9; HRMS (ESI): *m/z* = 559.1652 calcd. For C<sub>35</sub>H<sub>31</sub>N<sub>2</sub>Se, found 559.1651 [M+H]<sup>+</sup>.

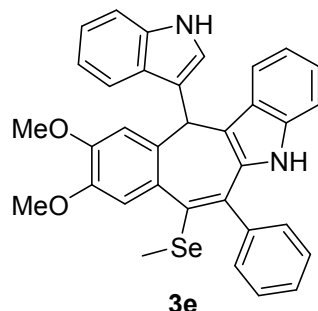


**12-(1*H*-Indol-3-yl)-6-phenyl-7-(phenylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3d)**



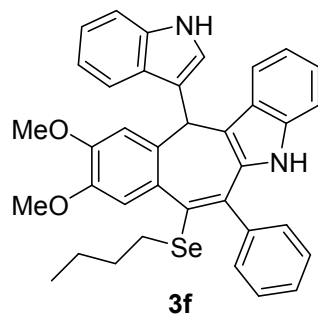
Yield: 75%; Melting point: 119-121°C; IR (neat): 3429, 3055, 1931, 1867, 1792, 1576, 1532, 1476, 1456, 1441, 1273, 1317, 1246, 1189, 1117, 1046, 982, 912, 848, 760, 738, 703 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (1H, d, *J* = 6.9 Hz), 7.89 (1H, s), 7.81 (1H, d, *J* = 7.8 Hz), 7.68 (1H, d, *J* = 6.9 Hz), 7.50-7.53 (5H, m), 7.28-7.34 (2H, m), 7.13-7.22 (4H, m), 7.00 (2H, dt, *J* = 18.2, 7.6 Hz), 6.81 (1H, s), 6.64 (1H, t, *J* = 7.3 Hz), 6.18 (2H, d, *J* = 6.9 Hz), 6.09 (3H, t, *J* = 7.6 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 143.2, 140.9, 137.0, 136.9, 135.9, 135.5, 134.7, 133.8, 132.6, 132.3, 131.8, 129.2, 129.0, 129.0, 128.2, 127.5, 126.6, 126.2, 125.5, 123.2, 122.7, 122.0, 120.2, 120.0, 119.7, 118.9, 118.5, 114.3, 111.3, 110.9, 40.9; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 448.3; HRMS (ESI): *m/z* = 579.1339 calcd. For C<sub>37</sub>H<sub>27</sub>N<sub>2</sub>Se, found 579.1332 [M+H]<sup>+</sup>.

**12-(1*H*-Indol-3-yl)-9,10-dimethoxy-7-(methylselanyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3e)**



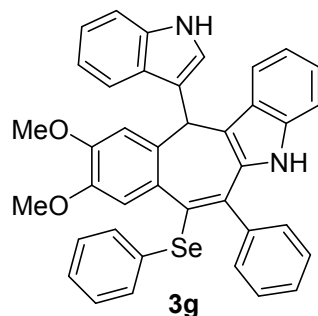
Yield: 51%; Melting point: 153-155°C; IR (neat): 3411, 3056, 3005, 2930, 2843, 1572, 1509, 1461, 1441, 1390, 1342, 1215, 1209, 1246, 1215, 1117, 1101, 1031, 1007, 858, 808, 747, 704, 665 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (1H, s), 7.80 (1H, d, *J* = 7.8 Hz), 7.52 (6H, dd, *J* = 13.5, 5.3 Hz), 7.33 (1H, d, *J* = 7.8 Hz), 7.12-7.23 (5H, m), 7.04 (1H, t, *J* = 7.1 Hz), 6.78 (1H, s), 6.66 (1H, t, *J* = 7.3 Hz), 6.18 (2H, d, *J* = 6.9 Hz), 6.10 (2H, t, *J* = 7.6 Hz), 5.99 (1H, s), 3.99 (3H, s), 3.62 (3H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 149.6, 146.1, 141.1, 137.0, 136.4, 135.1, 133.8, 132.7, 132.2, 131.9, 128.9, 128.4, 128.2, 127.3, 126.5, 126.4, 123.1, 122.6, 122.0, 120.2, 119.8, 119.6, 118.7, 118.4, 116.9, 114.6, 111.6, 111.4, 111.0, 56.1, 55.7, 40.5; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 445.8; HRMS (ESI): *m/z* = 599.1214 calcd. For C<sub>34</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>NaSe, found 599.1204 [M+Na]<sup>+</sup>.

**7-(Butylselanyl)-12-(1*H*-indol-3-yl)-9,10-dimethoxy-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3f)**



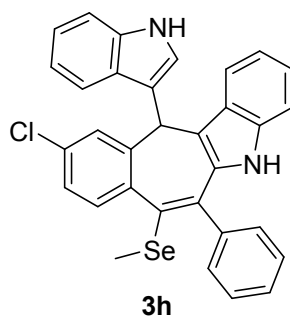
Yield: 42%; Melting point: 149-151°C; IR (neat): 3374, 3055, 2956, 2932, 1602, 1509, 1456, 1440, 1340, 1316, 1246, 1208, 1147, 1116, 1101, 1043, 923, 857, 742, 703 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (1H, d, *J* = 8.7 Hz), 7.80 (1H, s), 7.70 (1H, s), 7.51 (1H, s), 7.42 (3H, s), 7.14-7.22 (6H, m), 7.03 (1H, t, *J* = 7.8 Hz), 6.87 (1H, t, *J* = 7.6 Hz), 6.65 (1H, s), 5.91 (1H, s), 4.06 (3H, s), 3.89 (3H, s), 1.77 (1H, d, *J* = 11.0 Hz), 1.38 (1H, t, *J* = 5.7 Hz), 0.65-0.71 (4H, m), 0.49 (3H, t, *J* = 7.1 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 149.7, 146.6, 141.4, 137.1, 136.7, 135.1, 133.9, 132.6, 129.3, 128.4, 127.3, 126.5, 122.9, 122.4, 121.6, 120.0, 119.8, 119.7, 119.3, 118.2, 116.2, 115.6, 111.3, 111.1, 111.0, 56.3, 56.1, 40.3, 31.2, 28.9, 22.6, 13.4; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 320.2; HRMS (ESI): *m/z* = 641.1683 calcd. For C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>NaSe, found 641.1693 [M+Na]<sup>+</sup>.

**12-(1*H*-Indol-3-yl)-9,10-dimethoxy-6-phenyl-7-(phenylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3g)**



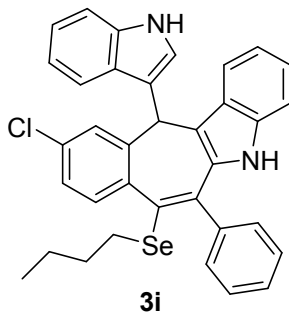
Yield: 66%; Melting point: 144-146°C; IR (neat): 3413, 3367, 3055, 3006, 2935, 2842, 1605, 1575, 1509, 1462, 1439, 1343, 1317, 1247, 1209, 1117, 1101, 1021, 1008, 809, 783, 740, 703, 691, 667 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (1H, s), 7.80 (1H, d, *J* = 7.8 Hz), 7.52 (6H, dd, *J* = 13.5, 5.3 Hz), 7.33 (1H, d, *J* = 7.8 Hz), 7.12-7.23 (5H, m), 7.04 (1H, t, *J* = 7.1 Hz), 6.78 (1H, s), 6.66 (1H, t, *J* = 7.3 Hz), 6.18 (2H, d, *J* = 6.9 Hz), 6.10 (2H, t, *J* = 7.6 Hz), 5.99 (1H, s), 3.99 (3H, s), 3.62 (3H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 149.6, 146.1, 141.1, 137.0, 136.4, 135.1, 133.9, 132.7, 132.2, 131.9, 128.9, 128.4, 128.2, 127.3, 126.5, 126.4, 123.1, 122.6, 122.0, 120.2, 119.8, 119.6, 118.7, 118.4, 116.9, 114.6, 111.6, 111.4, 111.0, 56.1, 55.7, 40.5; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 445.8; HRMS (ESI): *m/z* = 661.1370 calcd. For C<sub>39</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>NaSe, found 661.1388 [M+Na]<sup>+</sup>.

**10-Chloro-12-(1*H*-indol-3-yl)-7-(methylselanyl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3h)**



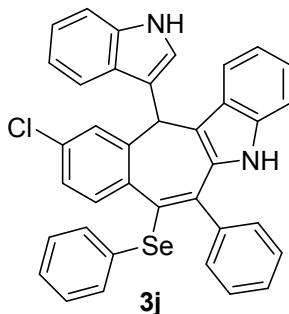
Yield: 59%; Melting point: 164-166°C; IR (neat): 3458, 3381, 3020, 2400, 2082, 1710, 1453, 1352, 1306, 1215, 1148, 1125, 1038, 927, 908, 892, 755, 668, 502, 490 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (1H, d, *J* = 8.7 Hz), 7.84-7.88 (2H, m), 7.69 (1H, d, *J* = 2.3 Hz), 7.55 (1H, s), 7.43 (3H, s), 7.19-7.23 (5H, m), 7.06 (2H, dd, *J* = 17.4, 7.8 Hz), 6.89 (1H, t, *J* = 7.6 Hz), 6.68 (1H, s), 5.97 (1H, s), 0.99 (3H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 140.5, 136.5, 134.7, 134.6, 134.4, 132.4, 128.8, 128.0, 126.4, 126.0, 123.2, 122.7, 121.8, 120.1, 120.0, 119.4, 118.3, 114.5, 111.2, 111.1, 40.3, 8.8; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 247.7; HRMS (ESI): *m/z* = 573.0613 calcd. For C<sub>32</sub>H<sub>23</sub>ClN<sub>2</sub>NaSe, found 573.0602 [M+Na]<sup>+</sup>.

**7-(Butylselanyl)-10-chloro-12-(1*H*-indol-3-yl)-6-phenyl-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3i)**



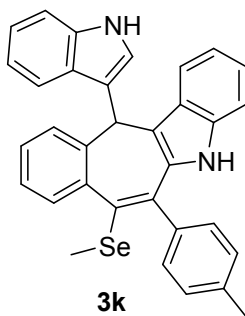
Yield: 53%; Melting point: 189-191°C; IR (neat): 3412, 3363, 2454, 1932, 1875, 1737, 1456, 1440, 1417, 1355, 1308, 1262, 1218, 1152, 1087, 1014, 881, 820, 747, 699, 619, 582, 498 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (1H, d, *J* = 8.5 Hz), 7.84 (2H, d, *J* = 8.5 Hz), 7.71 (1H, d, *J* = 2.2 Hz), 7.53 (1H, s), 7.44 (2H, s), 7.16-7.25 (7H, m), 7.05 (1H, t, *J* = 7.6 Hz), 6.91 (1H, t, *J* = 7.4 Hz), 6.70 (1H, s), 5.97 (1H, s), 1.73 (1H, dd, *J* = 11.0, 8.8 Hz), 1.26-1.31 (1H, m), 0.67-0.79 (4H, m), 0.48 (3H, t, *J* = 7.0 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 145.1, 140.8, 136.7, 135.5, 134.8, 134.5, 134.5, 132.5, 128.7, 128.1, 127.2, 126.4, 125.8, 123.2, 122.6, 121.8, 120.0, 119.9, 119.5, 119.3, 118.3, 114.3, 111.1, 111.0, 40.4, 31.0, 28.8, 22.6, 13.4; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 325.1; HRMS (ESI): *m/z* = 615.1082 calcd. For C<sub>35</sub>H<sub>29</sub>ClN<sub>2</sub>NaSe, found 615.1060 [M+Na]<sup>+</sup>.

**10-Chloro-12-(1*H*-indol-3-yl)-6-phenyl-7-(phenylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3j)**



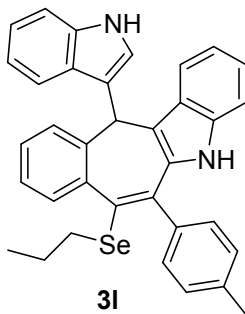
Yield: 68%; Melting point: 128-130°C; IR (neat): 3417, 3330, 2928, 2854, 2457, 2213, 2130, 1925, 1838, 1749, 1621, 1524, 1456, 1439, 1090, 1071, 995, 920, 817, 740, 662, 589 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89-7.94 (2H, m), 7.80 (1H, d, *J* = 7.8 Hz), 7.68 (1H, d, *J* = 2.3 Hz), 7.47-7.56 (5H, m), 7.36 (1H, d, *J* = 8.2 Hz), 7.16-7.23 (4H, m), 7.08 (1H, t, *J* = 7.1 Hz), 6.95 (1H, dd, *J* = 8.7, 2.3 Hz), 6.82 (1H, s), 6.67 (1H, d, *J* = 7.3 Hz), 6.10-6.18 (4H, m), 6.04 (1H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 144.2, 140.6, 137.0, 135.1, 134.6, 134.6, 134.4, 132.6, 132.3, 131.4, 129.0, 128.4, 128.4, 127.3, 126.5, 126.3, 125.6, 123.5, 122.8, 122.2, 120.1, 120.0, 119.9, 118.5, 118.3, 113.5, 111.4, 111.0, 40.6; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 446.1; HRMS (ESI): *m/z* = 635.0769 calcd. For C<sub>37</sub>H<sub>25</sub>ClN<sub>2</sub>NaSe, found 635.0758 [M+Na]<sup>+</sup>.

**12-(1*H*-Indol-3-yl)-7-(methylselanyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3k)**



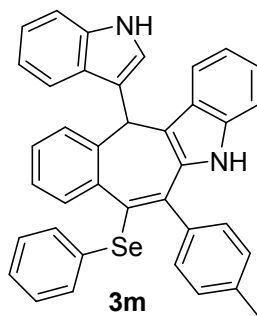
Yield: 64%; Melting point: 139-141°C; IR (neat): 3416, 3056, 3005, 2873, 2776, 2663, 2439, 1456, 1432, 1352, 1314, 1218, 1136, 1011, 910, 814, 742 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (1H, d, *J* = 6.9 Hz), 7.86-7.88 (1H, m), 7.79 (1H, s), 7.69 (1H, d, *J* = 7.3 Hz), 7.58 (1H, s), 7.41 (1H, dd, *J* = 7.6, 6.2 Hz), 7.28 (2H, t, *J* = 8.2 Hz), 7.16-7.22 (5H, m), 7.10 (1H, d, *J* = 8.2 Hz), 7.01 (1H, t, *J* = 7.8 Hz), 6.84 (1H, t, *J* = 7.1 Hz), 6.67 (1H, s), 6.01 (1H, s), 2.41 (3H, s), 0.98 (3H, d, *J* = 6.4 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 138.6, 137.9, 136.6, 136.6, 136.1, 135.3, 133.3, 132.6, 129.9, 128.9, 128.5, 127.3, 126.6, 125.9, 122.9, 122.5, 121.5, 120.1, 119.8, 119.2, 118.3, 115.3, 111.1, 111.0, 40.5, 21.5, 8.8; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 245.1; HRMS (ESI): *m/z* = 531.1339 calcd. For C<sub>33</sub>H<sub>27</sub>N<sub>2</sub>Se, found 531.1324 [M+H]<sup>+</sup>.

**12-(1*H*-Indol-3-yl)-7-(propylselanyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3I)**



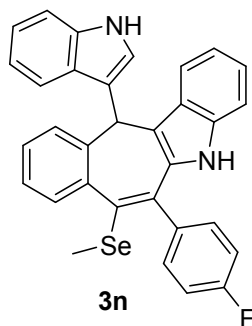
Yield: 58%; Melting point: 132-135°C; IR (neat): 3422, 3020, 2962, 1506, 1455, 1353, 1338, 1312, 1217, 1151, 1089, 1011, 923, 815, 742 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07-8.09 (1H, m), 7.82-7.84 (1H, m), 7.77 (1H, s), 7.71 (1H, d, *J* = 7.8 Hz), 7.53 (1H, s), 7.42 (1H, td, *J* = 7.6, 1.4 Hz), 7.26-7.28 (2H, m), 7.12-7.23 (6H, m), 7.02 (1H, t, *J* = 7.1 Hz), 6.86-6.90 (1H, m), 6.68 (1H, t, *J* = 1.8 Hz), 6.02 (1H, s), 2.43 (3H, s), 1.66-1.69 (1H, m), 1.30-1.36 (1H, m), 0.72 (1H, dd, *J* = 16.0, 6.9 Hz), 0.62 (1H, d, *J* = 7.3 Hz), 0.22 (3H, t, *J* = 7.3 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 144.0, 138.5, 138.2, 136.8, 136.6, 135.3, 134.3, 133.5, 132.7, 129.0, 128.7, 127.5, 126.6, 125.7, 122.8, 122.5, 121.6, 120.0, 119.8, 119.6, 119.3, 118.3, 114.9, 111.0, 110.9, 40.7, 31.0, 22.5, 21.5, 14.1; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 323.0; HRMS (ESI): *m/z* = 559.1652 calcd. For C<sub>35</sub>H<sub>31</sub>N<sub>2</sub>Se, found 559.1672 [M+H]<sup>+</sup>.

**12-(1*H*-Indol-3-yl)-7-(phenylselanyl)-6-(*p*-tolyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3m)**



Yield: 49%; Melting point: 125-127°C; IR (neat): 3424, 3055, 2873, 1576, 1507, 1430, 1438, 1432, 1313, 1176, 1151, 1090, 970, 815, 739, 690 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (1H, d, *J* = 6.7 Hz), 7.87 (1H, s), 7.79 (1H, d, *J* = 7.6 Hz), 7.67 (1H, d, *J* = 6.7 Hz), 7.52-7.56 (2H, m), 7.28-7.33 (4H, m), 7.10-7.20 (4H, m), 7.03 (1H, t, *J* = 7.0 Hz), 6.96 (1H, t, *J* = 7.2 Hz), 6.81 (1H, s), 6.62 (1H, t, *J* = 7.4 Hz), 6.16 (2H, d, *J* = 7.2 Hz), 6.04-6.09 (3H, m), 2.46 (3H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 143.2, 138.9, 137.9, 137.0, 136.9, 135.8, 135.4, 134.6, 133.8, 132.8, 132.3, 131.8, 129.1, 128.9, 128.2, 127.5, 126.6, 126.1, 125.5, 123.1, 122.7, 121.9, 120.2, 119.8, 119.6, 118.8, 118.5, 114.2, 111.3, 110.9, 40.8, 21.6; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 448.0; HRMS (ESI): *m/z* = 593.1496 calcd. For C<sub>38</sub>H<sub>29</sub>N<sub>2</sub>Se, found 593.1484 [M+H]<sup>+</sup>.

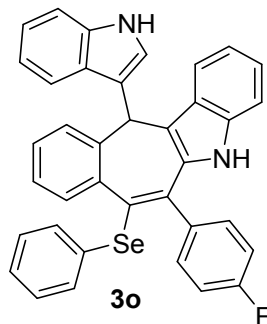
**6-(4-Fluorophenyl)-12-(1*H*-indol-3-yl)-7-(methylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3n)**



Yield: 45%; Melting point: 126-128°C; IR (neat): 3420, 3057, 3008, 2928, 1601, 1505, 1456, 1432, 1354, 1312, 1219, 1155, 1137, 1093, 1012, 847, 831, 744, 667 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (1H, d, *J* = 6.9 Hz), 7.87 (1H, d, *J* = 8.2 Hz), 7.77 (1H, s), 7.67 (1H, d, *J* = 6.9 Hz), 7.48 (1H, s), 7.42 (1H, t, *J* = 6.9 Hz), 7.29 (1H, t, *J* = 7.1 Hz), 7.17-7.21 (4H, m), 7.09 (2H, s), 7.02 (2H, t, *J* = 8.5 Hz), 6.83 (1H, t, *J* = 7.1 Hz), 6.60 (1H, s), 6.00 (1H, s), 1.03 (3H, t, *J* = 6.2 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 136.7, 136.6, 135.9, 135.9, 133.2, 133.1, 132.3, 129.2, 128.6, 127.2, 126.6, 126.0, 123.1, 122.4, 121.6, 120.4, 120.2, 120.0, 119.3, 118.3, 115.4, 111.2, 111.1, 40.5, 8.9; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 245.3; HRMS (ESI): *m/z* = 535.1089 calcd. For C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>SeF, found 535.1091 [M+H]<sup>+</sup>.



**6-(4-Fluorophenyl)-12-(1*H*-indol-3-yl)-7-(phenylselanyl)-5,12-dihydrobenzo[4,5]cyclohepta[1,2-*b*]indole (3o)**



Yield: 47%; Melting point: 114-116°C; IR (neat): 3426, 3057, 3009, 2875, 1601, 1576, 1505, 1476, 1456, 1439, 1354, 1311, 1219, 1156, 1092, 999, 831, 740, 690 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (1H, d, *J* = 7.8 Hz), 7.89 (1H, s), 7.82 (1H, d, *J* = 7.8 Hz), 7.67 (1H, d, *J* = 7.8 Hz), 7.49 (1H, s), 7.44 (1H, d, *J* = 8.2 Hz), 7.27-7.35 (2H, m), 7.15-7.22 (6H, m), 7.01 (2H, td, *J* = 7.0, 3.8 Hz), 6.74 (1H, s), 6.67 (1H, t, *J* = 7.1 Hz), 6.12-6.20 (4H, m), 6.08 (1H, s); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 143.2, 136.9, 135.9, 133.5, 132.5, 132.4, 131.6, 129.3, 128.9, 128.2, 127.4, 126.3, 125.6, 123.3, 122.6, 122.0, 120.2, 120.0, 119.7, 119.2, 118.5, 114.5, 111.3, 111.0, 40.8; <sup>77</sup>Se-NMR (75 MHz, CDCl<sub>3</sub>) δ 447.9; HRMS (ESI): *m/z* = 597.1245 calcd. For C<sub>37</sub>H<sub>26</sub>N<sub>2</sub>SeF, found 597.1246 [M+H]<sup>+</sup>.