# Selenochromanes via Tandem Homolytic Addition/Substitution Chemistry

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# **Electronic Supplementary Information**

Characterisation data for all new compounds reported.

*O*-Ethyl-*S*-(2-benzylselenobenzyl)dithiocarbonate (6): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.51 (dd, J = 1.3, 7.7, 1H), 7.43 (dd, J = 1.5, 7.6, 1H), 7.27 – 7.19 (m, 4 H), 7.16 (ddd, J = 3.4, 5.9, 9.0, 3H), 4.65 (q, J = 7.1, 2H), 4.42 (s, 2 H), 4.09 – 4.06 (m, 2 H), 1.42 (t, J = 7.1, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  213.91, 138.74, 138.20, 135.80, 131.75, 130.21, 128.86, 128.42, 128.34, 128.10, 126.96, 69.98, 41.22, 33.21, 13.81; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  327.75; IR (neat) cm<sup>-1</sup>: 2980.1, 1741.6, 1493.7, 1453.0, 1213.12, 1109.7; MS (EI) 382 (1) 291 (28) 201 (17) 119.1 (9) 91.1 (100); HRMS calcd for C<sub>17</sub>H<sub>18</sub>OS<sub>2</sub>Se [M + Ag] 488.90097, found 488.90130.

Methyl 3,4-dihydro-2H-1-benzoselenin-2-carboxylate (1, R=CO<sub>2</sub>Me): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.24 (m, 1H), 7.20 – 7.04 (m, 3H), 4.24 – 4.18 (m, 1H), 3.74 (s, 3H), 2.96 – 2.87 (m, 1H), 2.74 – 2.64 (m, 1H), 2.20 – 2.12 (m, 2H);  $\delta$  <sup>13</sup>C NMR (500 MHz CDCl<sub>3</sub>)  $\delta$  173.13, 138.24, 129.26, 128.77, 128.40, 127.06, 125.83, 52.55, 35.43, 31.32, 25.69; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  305.168; IR (neat) cm<sup>-1</sup>: 2949.1, 1731.0, 1433.6, 1307.4, 1234.7, 1157.6; MS (EI) *m/z* (relative intensity) 256 (66) 195 (31) 169 (23) 115.1 (100) 89.1 (18); HRMS calcd for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>Se [M+Ag] 362.90480, found 362.90491.

**Methyl 3,4-dihydro-2-methyl-2H-1-benzoselenin-2-carboxylate (10)**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (d, J = 7.7, 1H), 7.40 (d, J = 7.6, 1H), 7.32 – 7.22 (m, 5H), 7.21 – 7.13 (m, 3H), 7.12 – 7.06 (m, 3H), 3.75 (s, 3H), 2.98 – 2.88 (m, 1H), 2.81 – 2.71 (m, 1H), 2.46 – 2.37 (m, 1H), 1.86 – 1.81 (m, 3H); <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  425.708; MS (EI) *m/z* (relative intensity) 270.1 (100) 211 (64) 195 (27) 183 (25) 169 (34) 130.1 (65) 115.1 (24) 91.1 (22); HRMS calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>Se [M+Ag] 376.92045, found 376.92053.

**Compound 11**: mp 193 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.40 (m, 1H), 7.28 – 7.05 (m, 6H), 6.71 (d, J = 7.3, 2H), 4.49 (q, J = 14.6, 2H), 4.27 (d, J = 9.5, 1H), 3.60 (dt, J = 4.6, 9.4, 1H), 3.39 (dd, J = 4.2, 13.9, 1H), 2.93 (dd, J = 5.0, 13.9, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  176.81, 176.68, 137.00, 134.86, 131.90, 129.65, 128.47, 128.42, 128.38, 128.18, 127.36, 127.25, 43.28, 42.48, 36.91, 35.20; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  320.312; IR (neat) cm<sup>-1</sup>: 1773.9, 1698.8, 1426.6, 1395.3, 1339.8, 1168.2; MS (EI) *m/z* (relative

intensity) 357.1 (94) 276.1 (12) 195 (75) 186 (30) 168.9 (30) 115 (100) 106.1 (29) 91.1 (100) 89 (24) 65 (21); Anal. Calc. for  $C_{18}H_{15}NO_2Se$ : C 60.68, H 4.24; found C 60.79, H 4.01.

**Benzyl 3,4-dihydro-2H-1-benzoselenin-2-carboxylate (13)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.25 (m, 6H), 7.13 – 7.04 (m, 3H), 5.23 – 5.12 (m, 2H), 4.29 – 4.20 (m, 1H), 2.96 – 2.85 (m, 1H), 2.74 – 2.62 (m, 1H), 2.24 – 2.11 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 172.431, 138.255, 135.515, 129.209, 128.762, 128.528, 128.447, 128.271, 128.088, 127.019, 125.803, 67.031, 35.499, 31.288, 25.604; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  305.785; IR (neat) cm<sup>-1</sup>: 2928.6, 1732.4, 1454.8, 1441.1; MS (EI) *m/z* (relative intensity) 332.1 (30) 241 (18) 195 (54) 169 (12) 116.1 (80) 91.1 (100) 65.1 (13); HRMS calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>Se [M+Ag] 438.93610, found 438.93622.

**Compound 14**: mp 210-211 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, J = 7.3, 1H), 7.36 – 7.21 (m, 3H), 4.45 (d, J = 10.5, 1H), 3.89 – 3.82 (m, 1H), 3.37 (dd, J = 4.5, 14.2, 1H), 2.96 (dd, J = 4.9, 14.2, 1H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  171.72, 171.26, 136.10, 131.89, 129.87, 128.89, 128.77, 127.66, 44.08, 35.25, 34.93; IR (neat) cm<sup>-1</sup>: 1849.4, 1787.5, 1693.7, 1464.3, 1443.5, 1423.0.

*O*-Ethyl-*S*-(2-benzylseleno-5-nitrobenzyl)dithiocarbonate (15): mp 77-78 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (d, J 2.4, 1H), 8.01 (dd, J 2.5, 8.6, 1H), 7.58 (d, J 8.6, 1H), 7.34 – 7.22 (m, 5H), 4.66 (q, J 7.1, 2H), 4.43 (s, 2H), 4.26 – 4.22 (m, 2H), 1.46 – 1.42 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 212.81, 146.84, 143.01, 139.27, 136.79, 133.03, 129.38, 129.17, 128.02, 124.97, 122.98, 70.95, 40.44, 33.18, 14.17; <sup>77</sup>Se NMR (CDCl<sub>3</sub>) δ 342.222; IR (neat) cm<sup>-1</sup>: 3063.0, 2981.2, 1569.9, 1512.3, 1453.8, 1338.2, 1216.3, 1037.4. HRMS calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>S<sub>2</sub>Se [M+Ag] 533.88605, found 533.79749.

*O*-Ethyl-*S*-(2-benzylseleno-3-pyridyl)dithiocarbonate (16): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.41 (dd, J 1.7, 4.8, 1H), 7.60 (dd, J 1.8, 7.6, 1H), 7.37 (d, J 7.3, 2H), 7.26 (t, J 7.3, 2H), 7.19 (t, J 7.3, 1H), 7.03 (dd, J 4.8, 7.6, 1H), 4.62 (q, J 7.1, 2H), 4.54 (d, J 4.3, 2H), 4.31 (s, 2 H), 1.38 (t, J 7.1, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 213.31, 156.44, 148.66, 138.98, 136.67,

131.72, 129.15, 128.48, 126.89, 120.20, 70.32, 38.41, 30.02, 13.78.;  $^{77}$ Se NMR (CDCl<sub>3</sub>)  $\delta$  388.103; IR (neat) cm-1: 2980.4, 1573.15, 1493.5, 1397.5, 1212.4, 1109.4; MS (EI) 383 (1) 291.9 (18) 201.9 (24) 182.1 (18) 91.1 (100); HRMS calcd for C<sub>16</sub>H<sub>17</sub>NOS<sub>2</sub>Se [M+Ag] 489.89622, found 489.89647.

**Compound 17**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.25 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.13 (m, 2H), 7.10 – 7.06 (m, 2H), 4.42 (dd, J = 1.1, 4.5, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.47 (dd, J = 11.2, 16.2, 1H), 3.31 (dd, J = 2.7, 16.5, 1H), 3.06 – 3.00 (m, 1H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  172.06, 135.57, 130.41, 129.00, 128.55, 127.78, 127.21, 125.68, 52.58, 52.44, 41.82, 33.48, 30.64; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  318.029; MS (EI) *m/z* (relative intensity) 314.1 (40) 254 (12) 195 (100) 115.1 (46); HRMS calcd for C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>Se [M+Ag] 420.91028, found 420.91040.

**Compound 18:** mp 212-214 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 2.4, 1H), 7.89 (dd, J = 2.5, 8.4, 1H), 7.51 (d, J = 8.4, 1H), 7.13 (t, J = 7.3, 1H), 7.05 (t, J = 7.5, 2H), 6.88 (d, J = 7.3, 2H), 4.52 – 4.40 (m, 2H), 4.34 (d, J = 9.5, 1H), 3.71 – 3.62 (m, 1H), 3.49 (dd, J = 4.0, 14.0, 1H), 2.92 (dd, J = 5.1, 14.0, 1H); <sup>13</sup>C NMR (400 MHz) CDCl<sub>3</sub>  $\delta$  175.807, 175.722, 147.508, 138.150, 137.770, 134.975, 132.485, 128.401, 128.105, 127.856, 123.878, 122.750, 42.864, 42.739, 37.539, 35.576; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  344.802; IR (neat) cm<sup>-1</sup>: 1769.1, 1699.4, 1509.4, 1395.5, 1332.9; HRMS calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub> [M+Ag] 508.91642, found 508.91652

**Compound 19**: mp 162 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 (dd, J = 1.4, 4.8, 1H), 7.43 (dd, J = 1.4, 7.6, 1H), 7.21 – 7.10 (m, 3H), 7.04 (dd, J = 4.8, 7.5, 1H), 6.92 (dt, J = 2.4, 4.0, 2H), 4.51 (q, J = 14.4, 2H), 4.38 (d, J = 9.4, 1H), 3.58 (dt, J = 4.8, 9.5, 1H), 3.30 (dd, J = 4.7, 14.2, 1H), 2.92 (dd, J = 4.8, 14.2, 1H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 176.577, 176.496, 153.925, 149.384, 136.903, 135.240, 133.529, 128.790, 127.948, 127.893, 122.887, 42.956, 42.799, 37.316, 34.448; <sup>77</sup>Se NMR (CDCl<sub>3</sub>)  $\delta$  372.290; IR (neat) cm<sup>-1</sup>: 2916.8, 1775.6, 1703.6, 1561.8, 1421.3, 1400.1, 1341.6; HRMS calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Se [M+Ag] 464.92659, found 464.92680. Std proton

File: xp

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Pulse Sequence: s2pul

Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs INOVA-500 "bio500"

Pulse 45.0 degrees Acq. time 4.000 sec Width 8003.2 Hz 4 repetitions OBSERVE H1, 500.2058682 MHz DATA PROCESSING FT size 65536 Total time 0 min, 16 sec SeBn S



#### Std carbon

File: xp

Pulse Sequence: s2pul

Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs INOVA-500 "bio500"

Pulse 45.0 degrees Acq. time 1.500 sec Width 30188.7 Hz 31488 repetitions OBSERVE C13, 125.77686556 MHz DECOUPLE H1, 500.2083693 MHz Power 48 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 25 hr, 8 min, 51 sec

SeBn

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Std proton

# Supplementary Material (ESI) for Chemical Communications

File: home/chs/chs\_data/Maree/final NMR for chem comm/MS-48formicro.fid

Pulse Sequence: s2pul Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs File: MS-48formicro INOVA-400 "chem400"

Pulse 45.0 degrees Acq. time 4.000 sec Width 8003.2 Hz 4 repetitions OBSERVE H1, 500.2058849 MHz DATA PROCESSING FT size 65536 Total time 0 min, 16 sec





-48

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#### Std carbon

File: xp

- Pulse Sequence: s2pul Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs INOVA-500 "bio500"
- Pulse 45.0 degrees Acq. time 1.500 sec Width 30188.7 Hz 32912 repetitions OBSERVE C13, 125.7768656 MHz DECOUPLE H1, 500.2083693 MHz Power 48 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total'time 29 hr, 20 min, 19 sec



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220	200	180	160	140	120	100	80	60	40	20	0 ppm



MS3\_79.1 after column

## Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009

#### File: home/chs/chs\_data/Maree/final NMR for chem comm/MS3\_79.1C13.fid

Pulse Sequence: s2pul Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs File: MS3\_79.1C13 INOVA-400 "chem400"

Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.300 sec Width 24125.5 Hz 256 repetitions OBSERVE C13, 100.5173750 MHz DECOUPLE H1, 399.7526414 MHz Power 44 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 9 min, 51 sec



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220		180	160	120	100	80		40	20	m

#### STANDARD 1H OBSERVE

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Pulse Sequence: s2pul Solvent: CDC13 Ambient temperature Operator: chs INOVA-400 "inova400"

Pulse 36.0 degrees Acq. time 3.744 sec Width 6000.6 Hz 16 repetitions OBSERVE H1, 399.7571552 MHz DATA PROCESSING Gauss window 0.500 sec center at 0.200 sec FT size 65536 Total time 1 min, 0 sec Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009



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File: home/chs/NMR for chem comm/MS1\_6.14F12-31C13.fid

Pulse Sequence: s2pul Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs File: MS1\_6.14F12-31C13 INOVA-400 "chem400"

Relax. delay 1.700 sec Pulse 45.0 degrees Acq. time 1.300 sec Width 24125.5 Hz 240 repetitions OBSERVE C13, 100.5190184 MHz DECOUPLE H1, 399.7591558 MHz Power 36 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 65536 Total time 16 hr, 42 min, 58 set





07.02.06



24.2 Sample: MS1\_2<del>5-2</del>729-40C13 Pulse Sequence: s2pul Solvent: cdc13 Ambient temperature Operator: chs INOVA-400 "localhost.localdomain"

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Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.300 sec Width 24125.5 Hz 192 repetitions OBSERVE C13, 100.5190238 MHz DECOUPLE H1, 399.7591558 MHz Power 38 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 9 min, 51 sec Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009



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Std proton



Sample: MS-53 Sample ID: Aug14\_18\_01 File: /home/walkup/chs-mks\_data09/Aug09/MS-53\_Proton-Std-01.fid

Pulse Sequence: s2pul

Solvent: cdc13 Temp. 25.0 C / 298.1 K Sample #18, Operator: chs-mks File: MS-53\_Proton-Std-01 INOVA-500 "chem500"

Pulse 45.0 degrees Acq. time 4.000 sec Width 7995.2 Hz 32 repetitions OBSERVE H1, 499.6853768 MHz DATA PROCESSING FT size 131072 Total time 2 min, 8 sec

0 NBn Se 0





pad=10 run with finds0 before acquisition pad=10 run with gradshim before acquisition

Sample: MS4\_55.7recrystcdc13 Sample ID: study02008050759 File: home/chs/NMR for chem comm/MS4\_55.7recrystcdc13\_Proton-Std\_02.fid

Pulse Sequence: s2pul

Solvent: cdc13 Temp. 25.0 C / 298.1 K Sample #37, Operator: chs-mks File: MS4\_55.7recrystcdc13\_Proton-Std\_02 INOVA-400 "chem400"

Pulse 45.0 degrees Acq. time 3.995 sec Width 7995.2 Hz 16 repetitions OBSERVE H1, 499.6853765 MHz DATA PROCESSING FT size 65536 Total time 1 min, 14 sec

0 Se O





pad=10 run with findz0 before acquisition pad=10 run with gradshim before acquisition

Solvent: cdcl3 Temp. 25.0 C / 298.1 K Sample #29, Operator: chs-mks Mbde: M54:95:114 Proton Std\_01' INOVA-500 "chem500"

Pulse 45.0 degrees Acq. time 3.995 sec Width 7995.2 Hz 16 repetitions OBSERVE H1, 499.6853768 MHz DATA PROCESSING FT size 65536 Total time 1 min, 4 sec

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MS3\_80.1 F12-15

File: home/chs/NMR for chem comm/MS3\_80.1F12-15.fid

Pulse Sequence: s2pul

Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs File: MS3\_80.1F12-15 INOVA-400 "chem400"

Pulse 45.0 degrees Acq. time 4.000 sec Width 6395.9 Hz 16 repetitions OBSERVE H1, 399.7506296 MHz DATA PROCESSING FT size 65536 Total time 1 min, 4 sec





MS3\_80.1 F12-15

220

200

180

160

120

140

80

60

100

File: Carbon

Pulse Sequence: s2pul Solvent: CDCl3 Temp. 25.0 C / 298.1 K Operator: chs INOVA-500 "bio500"

Pulse 45.0 degrees Acq. time 1.500 sec Width 30188.7 Hz 1184 repetitions OBSERVE C13, 125.7781724 MHz DECOUPLE H1, 500.2140810 MHz Power 48 dB continuously on WALT2-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 2 hr, 5 min, 44 sec Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009



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MS3\_81.1 F6-13

File: Carbon

Pulse Sequence: s2pul

Solvent: CDC13 Temp. 25.0 C / 298.1 K Operator: chs INOVA-500 "bio500"

Pulse 45.0 degrees Acq. time 1.500 sec Width 30188.7 Hz 352 repetitions OBSERVE C13, 125.7781460 MHz DECOUPLE H1, 500.2140810 MHz Power 48 dB continuously on WALTZ-16 modulated DATA PROCESSING Line broadening 1.0 Hz FT size 131072 Total time 12 min, 52 sec



