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):** $^1$H NMR (CDCl$_3$) $\delta$ 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); $^{13}$C NMR (CDCl$_3$) $\delta$ 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; $^{77}$Se NMR (CDCl$_3$) $\delta$ 327.75; IR (neat) cm$^{-1}$: 2980.1, 1741.6, 1493.7, 1453.0, 1213.1, 1109.7; MS (EI) m/z (relative intensity) 382 (1) 291 (28) 201 (17) 119.1 (9) 91.1 (100); HRMS calcd for C$_{17}$H$_{18}$O$_2$Se [M + Ag] 488.90097, found 488.90130.

**Methyl 3,4-dihydro-2H-1-benzoselenin-2-carboxylate (1, R=CO$_2$Me):** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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); $\delta$ $^{13}$C NMR (CDCl$_3$) $\delta$ 173.13, 138.24, 129.26, 128.77, 128.40, 127.06, 125.83, 52.55, 35.43, 31.32, 25.69; $^{77}$Se NMR (CDCl$_3$) $\delta$ 305.168; IR (neat) cm$^{-1}$: 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$_{11}$H$_{12}$O$_2$Se [M+Ag] 362.90480, found 362.90491.

**Methyl 3,4-dihydro-2-methyl-2H-1-benzoselenin-2-carboxylate (10):** $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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); $^{77}$Se NMR (CDCl$_3$) $\delta$ 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$_{12}$H$_{14}$O$_2$Se [M+Ag] 376.92045, found 376.92053.

**Compound 11:** mp 193 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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); $^{13}$C NMR (CDCl$_3$) $\delta$ 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; $^{77}$Se NMR (CDCl$_3$) $\delta$ 320.312; IR (neat) cm$^{-1}$: 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 (100) 106.1 (29) 91.1 (100) 89 (24) 65 (21); Anal. Calc. for C_{18}H_{15}NO_{2}Se: C 60.68, H 4.24; found C 60.79, H 4.01.

**Benzyl 3,4-dihydro-2H-1-benzoseolenin-2-carboxylate (13):** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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); \(^{13}\)C NMR (CDCl\(_3\)) 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; \(^{77}\)Se NMR (CDCl\(_3\)) \(\delta\) 305.785; IR (neat) cm\(^{-1}\): 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_{17}H_{16}O_{2}Se \([M+Ag]\) 438.93610, found 438.93622.

**Compound 14:** mp 210-211 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 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\(^{-1}\): 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; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 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; \(^{77}\)Se NMR (CDCl\(_3\)) \(\delta\) 342.222; IR (neat) cm\(^{-1}\): 3063.0, 2981.2, 1569.9, 1512.3, 1453.8, 1338.2, 1216.3, 1037.4. HRMS calcd for C_{17}H_{17}NO_{3}S_{2}Se \([M+Ag]\) 533.88605, found 533.79749.

**O-Ethyl-S-(2-benzylseleno-3-pyridyl)dithiocarbonate (16):** \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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, 2H), 1.38 (t, \(J = 7.1\), 3H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 213.31, 156.44, 148.66, 138.98, 136.67,
Compound 17: $^1$H NMR (500 MHz, CDCl$_3$) δ 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); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 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; $^{77}$Se NMR (CDCl$_3$) δ 318.029; MS (EI) m/z (relative intensity) 314.1 (40) 254 (12) 195 (100) 115.1 (46); HRMS calcd for C$_{13}$H$_{14}$O$_4$Se [M+Ag] 420.91028, found 420.91040.

Compound 18: mp 212-214 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 2.4, 1H), 7.89 (d, 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); $^{13}$C NMR (400 MHz) CDCl$_3$ δ 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; $^{77}$Se NMR (CDCl$_3$) δ 344.802; IR (neat) cm$^{-1}$: 1769.1, 1699.4, 1509.4, 1395.5, 1332.9; HRMS calcd for C$_{18}$H$_{14}$N$_2$O$_4$Se [M+Ag] 508.91642, found 508.91652.

Compound 19: mp 162 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 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); $^{13}$C NMR (500 MHz, CDCl$_3$) δ 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; $^{77}$Se NMR (CDCl$_3$) δ 372.290; IR (neat) cm$^{-1}$: 2916.8, 1775.6, 1703.6, 1561.8, 1421.3, 1400.1, 1341.6; HRMS calcd for C$_{17}$H$_{14}$N$_2$O$_2$Se [M+Ag] 464.92659, found 464.92680.
Std proton

File: xp

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 °C / 298.1 K
Operator: chc
INOVA-500 "Bio500"

Pulse 45.0 degrees
Aqa. time 4.000 sec
Width 8003.2 Hz
4 repetitions
OBSERVE H1, 500.205682 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 16 sec

[Chemical Structure Image]
Supplementary Material (ESI) for Chemical Communications
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File: xp

Pulse Sequence: s2pu1
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
31488 repetitions
OBSERVE C13, 125.778656 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
File: home/chs/chs_data/Maree/final NMR for chem comm/MS-48formicro.fid

[Chemical structure image]

Pulse Sequence: s2pu1
Solvent: CDCl3
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
Std carbon

File: xp

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: chs
INOVA-500 "bi600"

Pulse 45.0 degrees
Acq. time 1.500 sec
Width 30188.7 Hz
32812 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
Sample: MS3_79.1
Sample ID: study02007120446
File: home/chs/chs_data/Maree/final NMR for chem comm/MS3_79.1_Proton-Std_01.fid

Pulse Sequence: s2pul
Solvent: dce13
Temp. 25.0 °C / 288.1 K
Sample #45, Operator: chs-mks
File: MS3_79.1_Proton-Std_01
INOVA-400 "chem400"

Pulse 45.0 degrees
Acq. time 3.995 sec
Width 7995.2 Hz
16 repetitions

OBSERVE M1, 6853785 MHz
DATA PROCESSING
FT size 85536
Total time 1 min, 14 sec
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
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Operator: chs
INOMA-400 "inova400"

Pulse 36.0 degrees
Acq. time 3.744 sec
Width 8080.6 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
File: home/chs/NMR for chem comm/MS1_6.14F12-31C13.fld

Pulse Sequence: s2pul
Solvent: CDCl3
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 sec
Sample: MS1_209-40C13
Pulse Sequence: s2pul
Solvent: cdCl3
Ambient temperature
Operator: chs
INOVA-400 localhost.localdomain

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24125.5 Hz
122 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

File: home/chs/NMR for chem comm/MS1-32-1C2F8-15.fid

Pulse Sequence: s2pul
Solvent: CDC13
Temp. 25.9 C / 298.1 K
Operator: chs
File: MS1-32-1C2F8-15
INOVA-400 “Chem400”

Pulse 45.0 degrees
Acq. time 4.000 sec
Width 8008.2 Hz
16 repetitions
OBSERVE H1 500.2058810 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 4 sec
Supplementary Material (ESI) for Chemical Communications
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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 131972
Total time 2 min, 8 sec

![N-Benzyl-2-seco-3-oxo-1,2-dihydrobenzofuran-3-carbonyl](image)
pad=10 run with findz0 before acquisition
pad=10 run with gradshim before acquisition

Sample ID: study02008050804
File: home/chs/NMR for chem comm/MS4_53.7carbonlong.fid

Pulse Sequence: s2pul
Solvent: ccdcl3
Temp. 25.0 °C / 298.1 K
Sample #36, Operator: chs-mks
File: MS4_53.7carbonlong
INOVA-400 "chem400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 30154.5 Hz
2000 repetitions
OBSERVE C13, 125.6458844 MHz
DECUPLE H1, 499.6875700 MHz
Power 42 dB
Continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 151072
Total time 1 hr, 23 min, 47 sec
Supplementary Material (ESI) for Chemical Communications
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pad=10 run with find2o before acquisition
pad=10 run with gradshim before acquisition

Sample: MS4_55.7recrystccl3
Sample ID: Study02608090759
File: home/chs/NMR for chem comm/MS4_55.7recrystccl3_Proton-Std_02.fld

Pulse Sequence: s2p1
Solvent: ccl3
Temp. 25.0 C / 298.1 K
Sample #37, Operator: chs-mks
File: MS4_55.7recrystccl3_Proton-Std_02
INova-600 "chem600"

Pulse 45.0 degrees
Acq. time 9.995 sec
Width 7995.2 Hz
18 repetitions

OBSErve H1, 499.6853765 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 14 sec
Sample: MS4_55.7carbonlonger
Sample ID: study02009050910
File: home/chs/NMR for chem comm/MS4_55.7carbonlonger_Carbon-Long_01.fid

Pulse Sequence: s2pul
Solvent: cdc13
Temp. 25.0 C / 298.1 K
Sample #30, Operator: chs-mks
File: MS4_55.7carbonlonger_Carbon-Long_01
INOVA-400 "chem400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.500 sec
Width 3015â„¢5 Hz
8000 repetitions
OBSERVE C13, 125.6459638 MHz
DECOUPLE H1, 498.6675700 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 5 hr, 34 min, 40 sec
Supplementary Material (ESI) for Chemical Communications
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Solvent: dce13
Temp. 25.0 °C / 298.1 K
Sample #29, Operator: chs-mks
INOVA-500 "chem500"

Pulse 45.0 degrees
Acq. time 3.995 sec
Width 7095.2 Hz
16 repetitions
OBSERVE H1, 499.6853768 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 4 sec

![NMR Spectrum](image-url)
Pulse Sequence: ss2pul
Solvent: CDCl3
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
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 30186.7 Hz
1184 repetitions
OBSERVE C13, 125.7781724 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 2 hr, 5 min, 44 sec
Supplementary Material (ESI) for Chemical Communications
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Sample: MS3.81.1f6to13
Sample ID: Study020712434
File: home/chs/NMR for chm comm/MS3.81.1f6to13_Proton-Std_03.fid

Pulse Sequence: s2pul
Solvent: ddc13
Temp. 25.0 C / 298.1 K
Sample #25, Operator: chs-mks
File: MS3.81.1f6to13_Proton-Std_03
INNOVA-400 "chem400"

Pulse 45.0 degrees
Acq. time 3.985 sec
Width 7955.2 Hz
16 repetitions
OBSERVE $^{1}H$, 499.6853741 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 4 sec
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 30186.7 Hz
352 repetitions
OBSERVE C13, 125.7781460 MHz
DECOUPLE H1, 500.2140810 MHz
Power 40 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 min, 52 sec