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The iodine-assisted hydroxyselenenylation of alkenes with elemental selenium

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Contents

X-ray crystallographic study

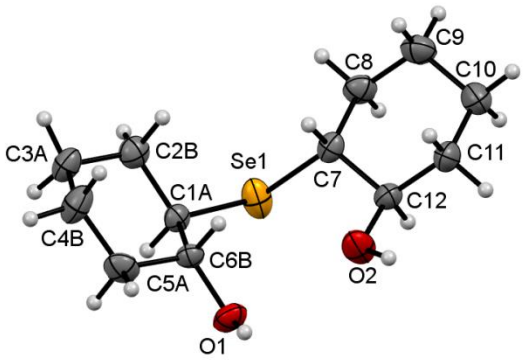

Figure S1. ORTEP plot of compound dl-**4b** at 25% thermal ellipsoid probability.

Data were collected on a Bruker D8 Venture Photon 100 CMOS diffractometer with MoK_{α} radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved and refined by direct methods using the SHELX software [Sheldrick G.M. *Acta Crystallogr*., 2008, **A64**, 112]. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically. The coordinates of the hydrogen atoms were calculated from geometrical positions.

Table S1 contains CCDC reference number of the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk

Selected bond lengths, bond angles and torsion angles are given in Table S2.

Table S1. X-ray crystallographic data, measurement details, and structure refinements for compound *dl*-**4b**

CCDC number	**1982304**
Empirical formula	$C_{12}H_{22}O_2Se$
Formula weight / g·mol^{-1}	277.26
Crystal system	orthorhombic
Space group	Pbca
a / Å	10.3630(12)
b / Å	10.6393(10)
c / Å	23.446(2)
α, β, γ / °	90, 90, 90
Volume / Å^3	2585.0(5)
Z	8
Density (calculated) / g·cm^{-3}	1.425
Absorptions coefficient / mm^{-1}	2.886
Radiation (λ / Å)	MoKα (0.71073)
Temperature / K	293(2)
2Θ range / °	2.62 – 28.00
Crystal size / mm	0.21 × 0.12 × 0.03
Crystal habit	yellow, plate
F(000)	1152
Index ranges	-13<=h<=13, -14<=k<=14, -30<=l<=30
Reflections collected	26284
Independent reflections	3117 [R(int) = 0.0550]
Number of ref. parameters	192
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0548 / 0.1128
R_1 / wR_2 (all data)	0.0904 / 0.1303
Goodness-of-fit on F^2	1.050
Completeness [%]	99.9
Largest diff. peak and hole / e·Å^{-3}	0.623/ -1.287
Weight scheme	w=1/[σ2(Fo2)+(0.0383P)2+3.9381P] where P=(Fo2+2Fc2)/3

Table S2. Selected bond lengths, bond angles and torsion angles for compound *dl*-**4b**

Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
Se1-C1A	1.881(9)	C1A-Se1-C7	113.1(4)	C1A-Se1-C1B-C6A	50.5(10)
Se1-C1B	2.089(9)	C7-Se1-C1B	92.7(3)	C1A-Se1-C1B-C2A	-69.5(16)
O1-C6A	1.424(10)	C6A-C1B-C2A	110.2(10)	C6A-O1-C6B-C5A	67.1(19)
C1B-C2A	1.535(13)	C2A-C1B-Se1	112.1(10)	C1A-Se1-C7-C12	99.2(4)
C2B-C3A	1.487(15)	C3A-C2B-C1A	113.4(16)	C1A-Se1-C7-C8	-137.0(4)
C3B-C4A	1.527(15)	C4A-C3B-C2A	110.0(14)	C12-C7-C8-C9	-54.8(5)
C4B-C5A	1.485(15)	C5A-C4B-C3A	111.2(16)	C7-C8-C9-C10	56.4(6)
C5B-C4A	1.534(15)	C4A-C5B-C6A	107.7(14)	C9-C10-C11-C12	55.0(6)
C6B-C5A	1.490(14)	O1-C6B-C5A	113.9(10)	C10-C11-C12-C7	-53.8(5)
C7-C8	1.515(6)	C5A-C6B-C1A	109.1(12)	Se1-C7-C12-O2	-61.1(4)
C8-C9	1.521(7)	C12-C7-C8	111.6(3)	Se1-C7-C12-C11	176.1(3)
C10-C11	1.513(6)	C8-C7-Se1	109.0(3)	C5A-C6B-C1A-C2B	52.4(18)
Se1-C7	1.967(4)	C7-C8-C9	110.6(4)	C5A-C6B-C1A-Se1	-179.4(13)
O1-C6B	1.407(9)	C10-C9-C8	111.4(4)	C3A-C2B-C1A-Se1	174.9(14)
O2-C12	1.420(5)	C9-C10-C11	110.7(4)	C1B-Se1-C1A-C6B	-57.3(10)
C1B-C6A	1.528(10)	C12-C11-C10	112.1(4)	C1B-Se1-C1A-C2B	72.1(17)
C2B-C1A	1.499(14)	O2-C12-C11	110.7(3)	C6B-O1-C6A-C5B	-77.7(18)
C3B-C2A	1.530(15)	C11-C12-C7	111.7(3)	Se1-C1B-C6A-O1	62.5(8)
C4B-C3A	1.490(13)	C6B-C1A-C2B	112.4(12)	Se1-C1B-C6A-C5B	-178.7(11)
C5B-C6A	1.543(14)	C2B-C1A-Se1	110.1(10)	C4A-C5B-C6A-C1B	62.(2)
C6B-C1A	1.491(10)	O1-C6A-C1B	110.2(7)	O1-C6B-C5A-C4B	-179.5(16)
C7-C12	1.510(5)	C1B-C6A-C5B	110.3(13)	C2A-C3B-C4A-C5B	61.(2)
C9-C10	1.501(6)	C4B-C5A-C6B	116.2(15)	C1A-C2B-C3A-C4B	51.(2)
C11-C12	1.507(6)	C3B-C4A-C5B	109.2(15)	C4A-C3B-C2A-C1B	-56.(2)
		C2B-C3A-C4B	112.5(18)	Se1-C1B-C2A-C3B	171.8(13)
		C3B-C2A-C1B	111.5(15)	C7-Se1-C1B-C6A	-126.6(6)
		C1A-Se1-C1B	20.5(3)	C7-Se1-C1B-C2A	113.4(12)
		C6B-O1-C6A	30.2(4)	C6A-O1-C6B-C1A	-57.7(11)
		C6A-C1B-Se1	105.6(6)	C1B-Se1-C7-C12	100.3(3)
		O1-C6B-C1A	112.4(7)	C1B-Se1-C7-C8	-135.9(3)
		C12-C7-Se1	111.8(3)	Se1-C7-C8-C9	-178.7(3)
		O2-C12-C7	109.3(3)	C8-C9-C10-C11	-56.3(6)
		C6B-C1A-Se1	116.2(6)	C10-C11-C12-O2	-175.8(4)
		O1-C6A-C5B	107.7(8)	C8-C7-C12-O2	176.6(4)
				C8-C7-C12-C11	53.8(5)
				O1-C6B-C1A-C2B	179.7(12)
				O1-C6B-C1A-Se1	-52.1(11)
				C3A-C2B-C1A-C6B	-54.(2)
				C7-Se1-C1A-C6B	-54.1(8)
				C7-Se1-C1A-C2B	75.3(12)
				C6B-O1-C6A-C1B	42.7(9)
				C2A-C1B-C6A-O1	-176.3(12)
				C2A-C1B-C6A-C5B	-57.5(17)
				C4A-C5B-C6A-O1	-178.0(14)
				C3A-C4B-C5A-C6B	52.(3)
				C1A-C6B-C5A-C4B	-53.(3)
				C6A-C5B-C4A-C3B	-63.(2)
				C5A-C4B-C3A-C2B	-49.(2)
				C6A-C1B-C2A-C3B	55.(2)

Spectral characteristic of compounds 3a-c, 4a,b

NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H) and 100 (^{13}C) MHz. All shifts are reported in ppm relative to residual $CHCl_3$ [7.27 (^{1}H) and 77.1 (^{13}C) ppm].

Bis(2-hydroxyhex-1-yl) selenide **3a**. Yield 75%. Light yellow oil. ^{1}H NMR, δ, ppm: 0.86–0.89 m (6H, CH_3), 1.24–1.51 m (12H, CH_2), 2.60 ddd (2H, $SeCH^A$, J = 13.0, 6.0, 5.2 Hz), 2.82 ddd (2H, $SeCH^B$, J = 12.9, 3.0, 1.9 Hz), 2.96 br.s (2H, OH), 3.66–3.75 m (2H, C<u>H</u>OH). ^{13}C NMR, δ, ppm: 13.94 (CH_3), 22.59 (CH_2), 27.93 (CH_2), 33.40 (CH_2Se), 33.66 (CH_2Se), 36.52, 36.60 (CH_2), 70.47 (CHOH), 70.94 (CHOH). GS-MS: *m/z* (rel. int., %) 282 $[M]^{+\cdot}$(8), 196 (30), 163 (20), 135 (15), 110 (58), 83 (90), 55 (100), 41 (90). Found: C, 51.06; H, 9.14; Se, 28.35. Calcd for $C_{12}H_{26}O_2Se$: C, 51.24; H, 9.32; Se, 28.07.

Bis(2-hydroxyhept-1-yl) selenide **3b**. Yield 81%. Light yellow oil. ^{1}H NMR, δ, ppm: 0.85–0.89 m (6H, CH_3), 1.25–1.52 m (16H, CH_2), 2.60 dd (2H, $SeCH^A$, J = 12.9, 8.2 Hz), 2.84 dd (2H, $SeCH^A$, J = 12.9, 3.4 Hz), 3.66–3.75 m (2H, C<u>H</u>OH). ^{13}C NMR, δ, ppm: 13.94 (CH_3), 22.51 (CH_2), 25.44 (CH_2), 31.71 (CH_2), 33.49 (CH_2Se), 33.76 (CH_2Se), 36.87 (CH_2), 70.48 (CHOH), 70.96 (CHOH). GS-MS: *m/z* (rel. int., %) 310 $[M]^{+\cdot}$(3), 210 (12), 135 (9), 110 (38), 97 (34), 55 (100), 41 (45). Found: C, 54.22; H, 9.68; Se, 25.39. Calcd for $C_{14}H_{30}O_2Se$: C, 54.36; H, 9.77; Se, 25.52.

Bis(2-hydroxyoct-1-yl) selenide **3c**. Yield 83%. Light yellow oil. ^{1}H NMR, δ, ppm: 0.86–0.89 m (6H, CH_3), 1.27–1.54 m (20H, CH_2), 2.59 dd (2H, CH_2Se, 12.9, 8.1 Hz), 2.84 dd (2H, CH_2Se, J = 12.9, 3.4 Hz), 2.92 br.s (2H, OH), 3.67–3.72 m (2H, CHOH). ^{13}C NMR, δ, ppm: 13.96 (CH_3), 22.49 (CH_2), 25.71 (CH_2), 29.18 (CH_2), 31.68 (CH_2), 33.36 (CH_2Se), 33.60 (CH_2Se), 36.82 (CH_2), 36.90 (CH_2), 70.51 (CHOH), 70.95 (CHOH). GS-MS: *m/z* (rel. int., %) 338 $[M]^{+\cdot}$(5), 224 (19), 110 (88), 69 (92), 55 (100), 43 (95). Found: C, 56.80; H, 10.05; Se, 23.45. Calcd for $C_{16}H_{34}O_2Se$ (%): C, 56.96; H, 10.16; Se, 23.40.

Bis(2-hydroxyoct-1-yl) selenide **3c** (single diastereomer). Isolated by double crystallization from hexane. Colorless solid; mp 54–56 °C; ^{1}H NMR, δ, ppm: 0.86–0.89 m (6H, CH_3), 1.29–1.58 m (20H, CH_2), 2.56 br.s (2H, OH), 2.61 dd (2H, CH_2Se, J = 12.8, 8.2 Hz),), 2.85 dd (2H, CH_2Se, J = 12.8, 3.4 Hz), 3.68–3.74 m (2H, CHOH). ^{13}C NMR, δ, ppm: 14.03 (CH_3), 22.56 (CH_2), 25.78 (CH_2), 29.23 (CH_2), 31.74 (CH_2), 33.48 (CH_2Se), 36.87, 70.41 (CHOH). Found: C, 56.87; H. 10.15; Se, 23.43. Calcd for $C_{16}H_{34}O_2Se$: C 56.96; H 10.16; Se 23.40.

Bis(2-hydroxycyclopent-1-yl) selenide **4a**. Purified by column chromatography on Al_2O_3 with hexane/ $CHCl_3$, 4:1. Yield 58%. Light yellow oil. ^{1}H NMR, δ, ppm: 1.49–1.78 m (8H, CH_2), 1.99–2.07 m (2H, CH_2), 1.16–2.25 m (2H, CH_2), 3.02–3.09 m (1H, CHSe in the *dl*-isomer), 3.21 dt (1H, CHSe in the *meso* isomer, J = 4.7, 7.9 Hz), 3.87 br.s (2H, OH), 4.19 q (1H, C<u>H</u>OH in one diastereomer, J = 6.9 Hz), 4.25–4.31 m (1H, C<u>H</u>OH in another diastereomer). ^{13}C NMR, δ, ppm: 21.79, 22.79, 31.74, 32.00, 33.50, 33.72, 44.44 (CH_2Se), 46.76 (CH_2Se), 80.59 (CHOH), 81.60 (CHOH). GS-MS: *m/z* (rel. int., %) 250 $[M]^{+\cdot}$(6), 164 (5), 148 (8), 84 (37), 67 (100), 41 (30). Found: C, 48.16; H, 7.25; Se, 31.84. Calcd for $C_{10}H_{18}O_2Se$: C, 48.20; H, 7.28; Se, 31.68.

Bis(2-hydroxycyclohex-1-yl) selenide **4b**. Purified as above. Yield 61 %. Colorless crystals, mp 69–70 °C. ^{1}H NMR, δ, ppm: 1.21–1.35 m (6H, CH_2), 1.48–1.77 m (6H, CH_2), 2.08–2.24 m (4H, CH_2), 2.70 ddd (1H, CHSe in the *dl*-isomer, J = 12.5, 10.1, 4.1 Hz), 2.82 ddd (1H, CHSe in the *meso* isomer, J = 12.8, 10.0, 4.1 Hz), 3.09 br.s (1H, OH), 3.35–3.45 m (2H, CHOH), 3.63 br.s (1H, OH). ^{13}C NMR, δ, ppm: 24.60, 27.03, 34.41, 34.92, 34.97, 48.90 (CHSe), 49.65 (CHSe), 73.16 (CHOH), 74.79 (CHOH). GS-MS: *m/z* (rel. int., %) 278 $[M]^{+\cdot}$ (21), 178 (6), 162 (47), 98 (75), 81 (100), 41 (79). Found: C, 51.99; H, 8.00; Se, 28.50. Calcd for $C_{12}H_{22}O_2Se$: C, 51.98; H, 8.00; Se, 28.48.

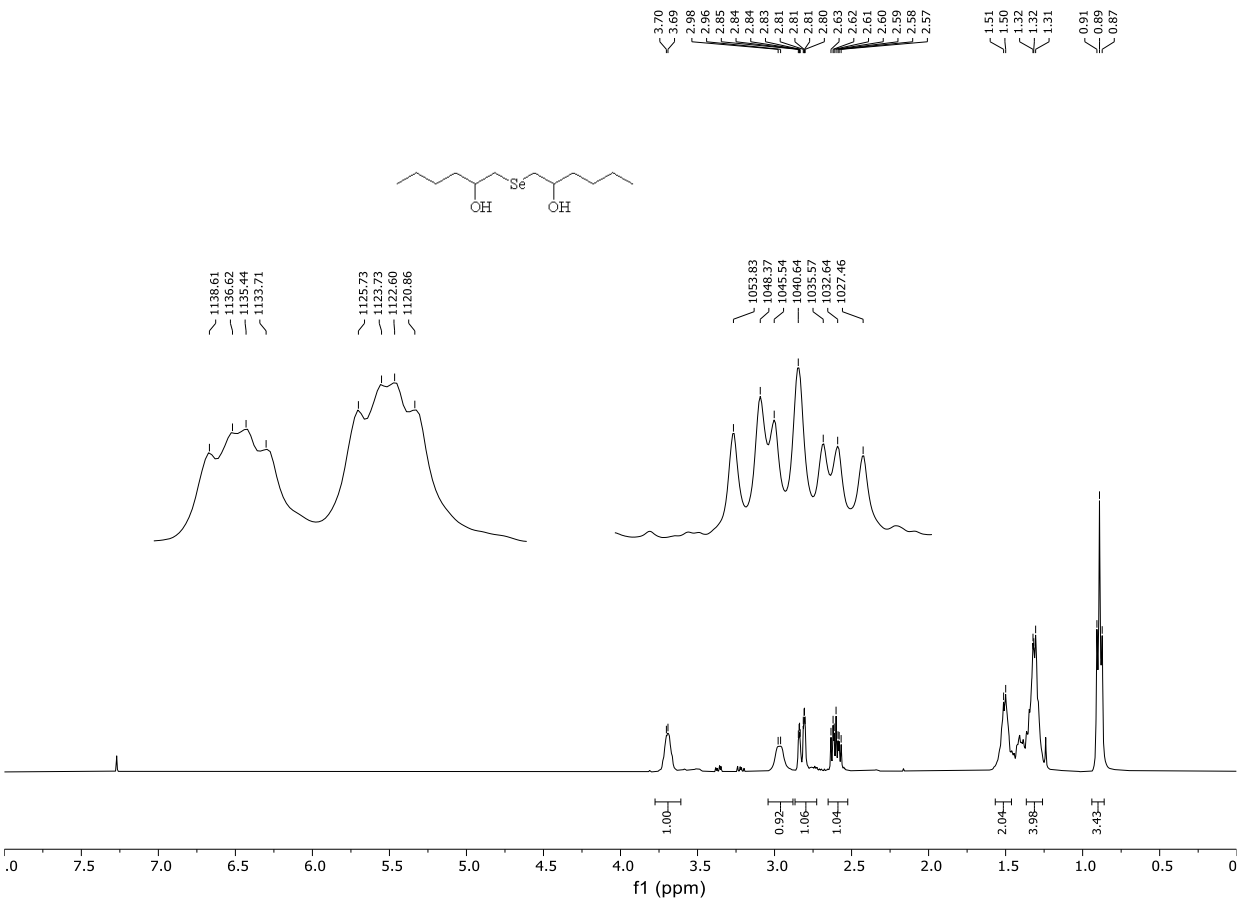

Figure S2. ^{1}H NMR spectrum of bis(2-hydroxyhex-1-yl) selenide (**3a**)

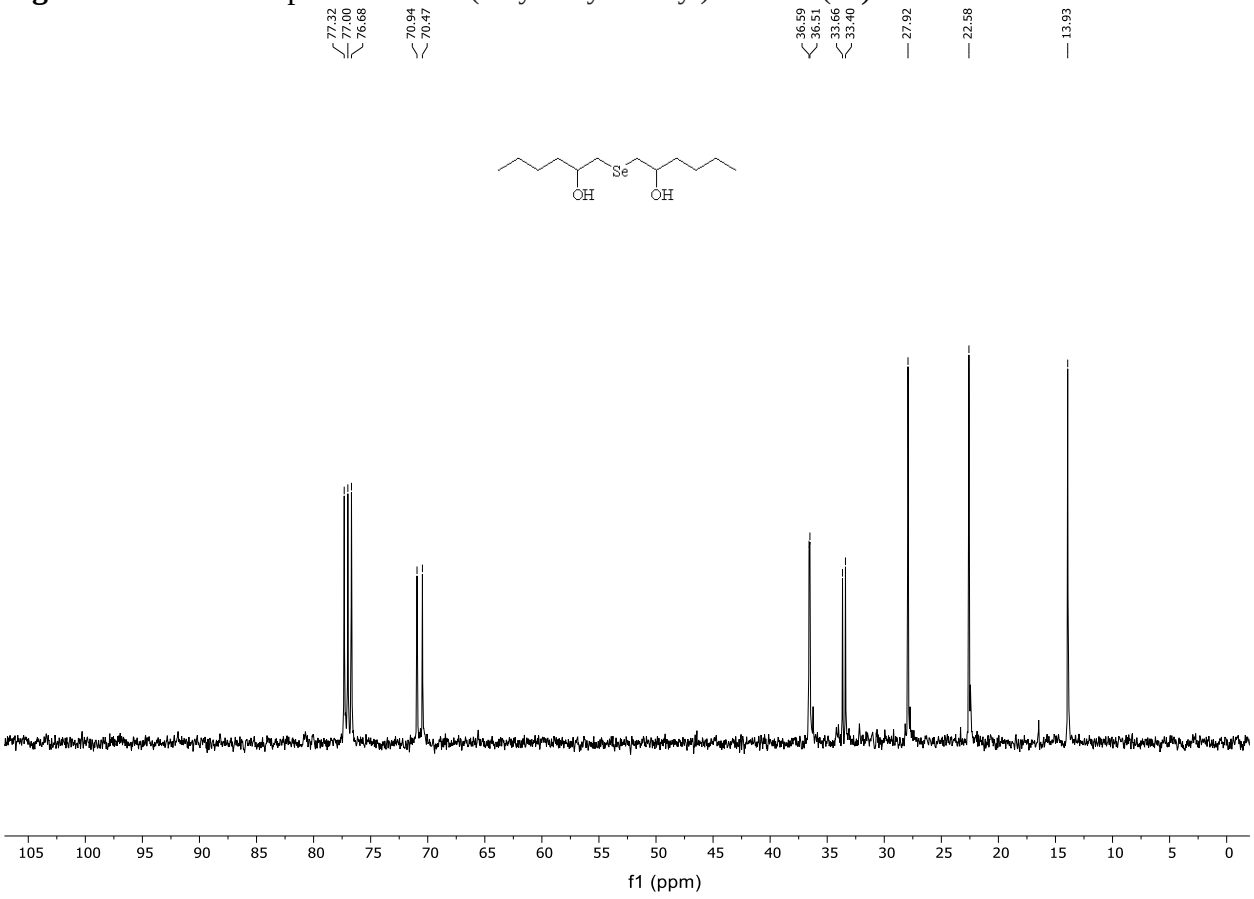

Figure S3. ^{13}C NMR spectrum of bis(2-hydroxyhex-1-yl) selenide (**3a**)

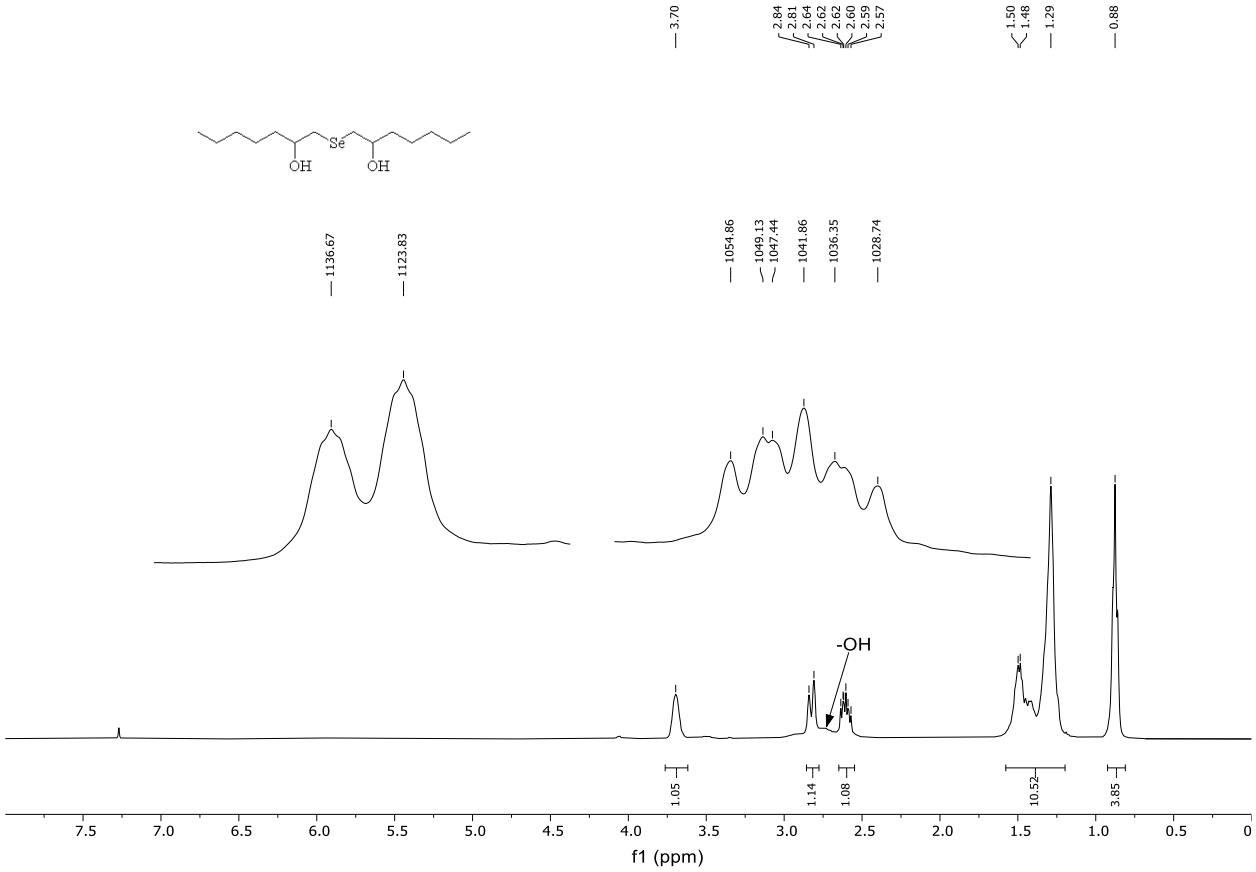

Figure S4. ^{1}H NMR spectrum of bis(2-hydroxyhept-1-yl) selenide (**3b**).

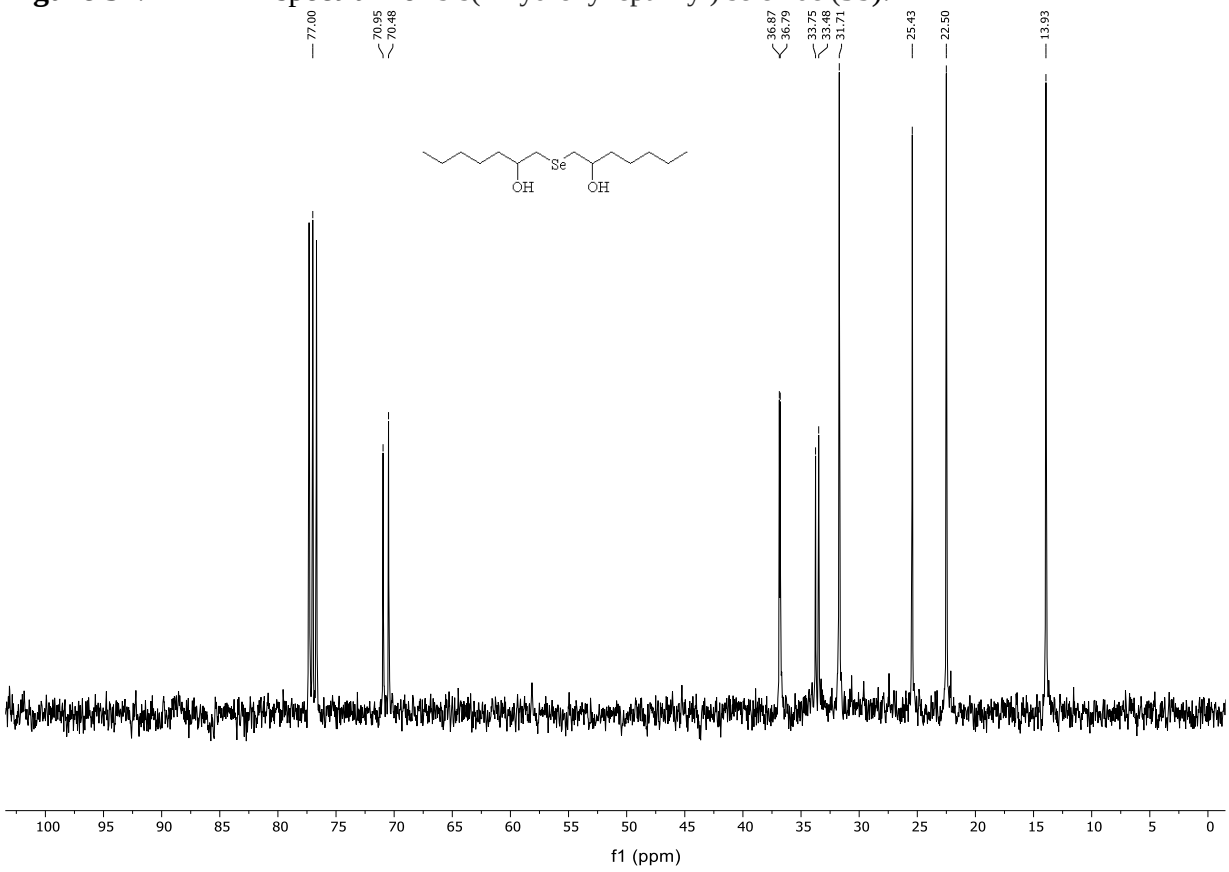

Figure S5. ^{13}C NMR spectrum of bis(2-hydroxyhept-1-yl) selenide (**3b**)

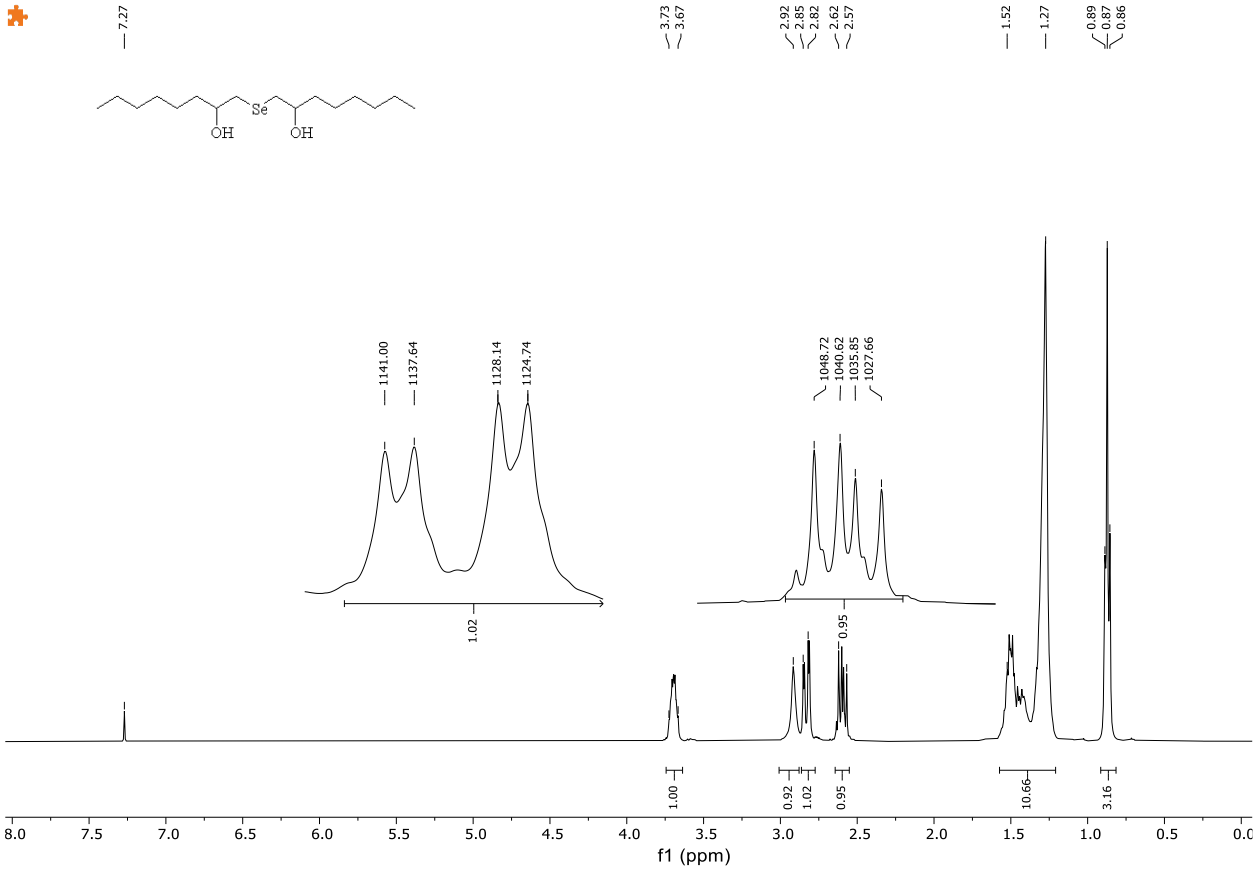

Figure S6. ^{1}H NMR spectrum of bis(2-hydroxyoct-1-yl) selenide (**3c)**

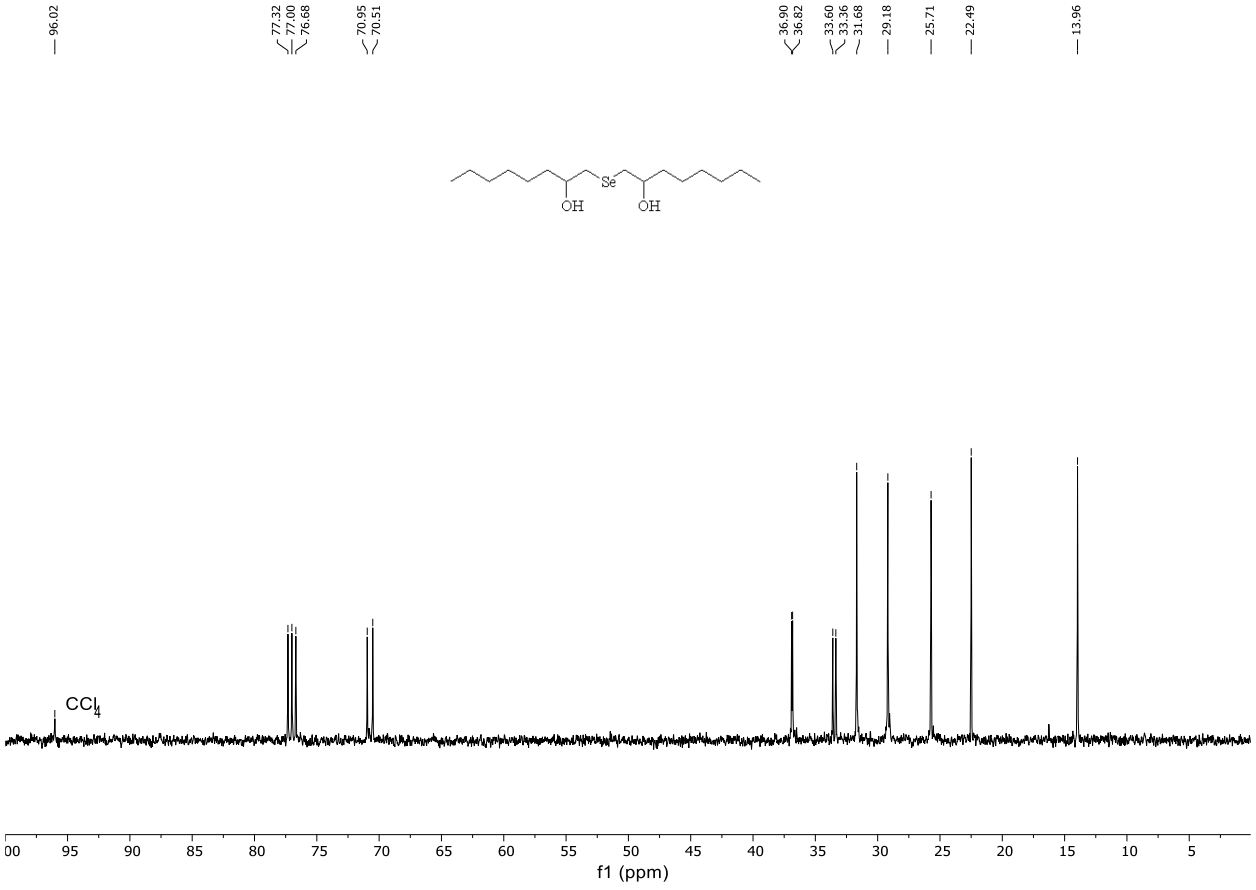

Figure S7. ^{13}C NMR spectrum of bis(2-hydroxyoct-1-yl) selenide (**3c**).

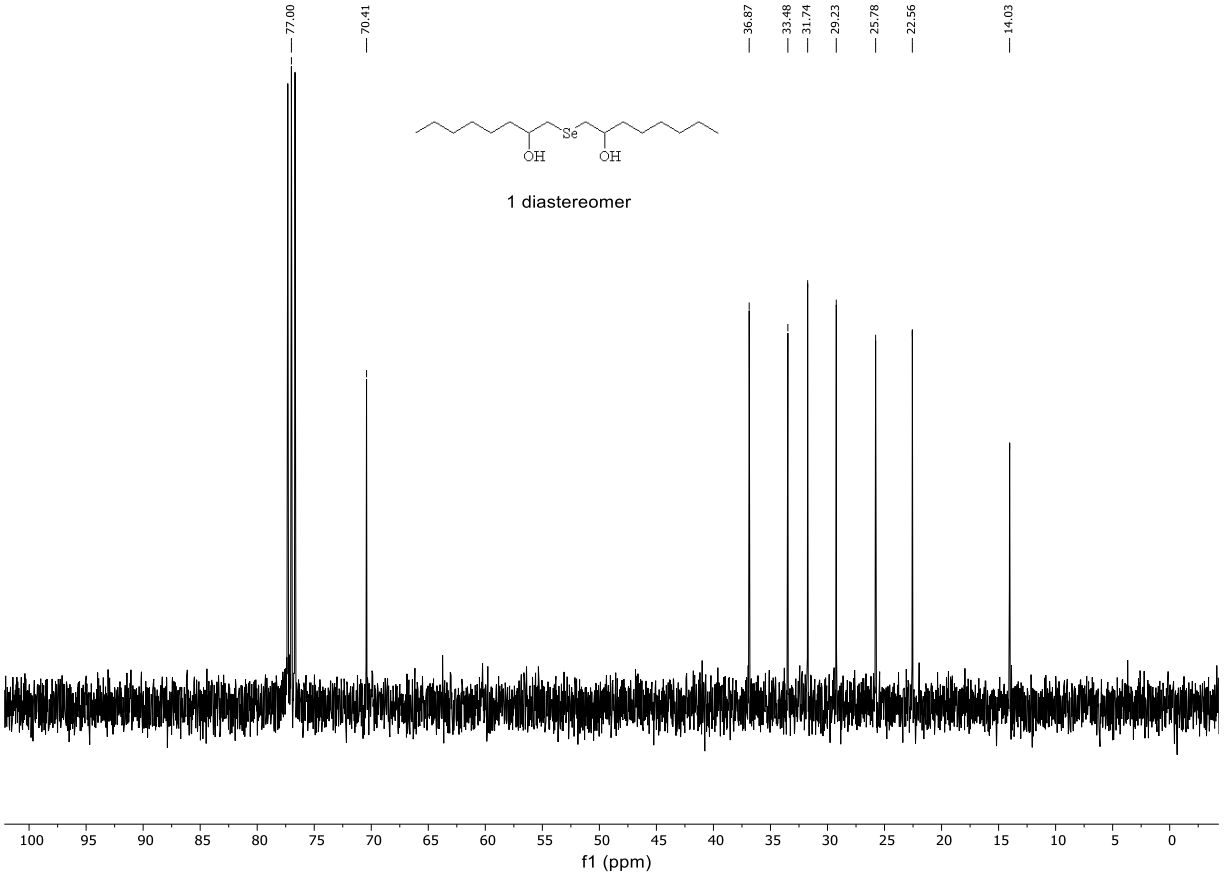

Figure S8. ^{13}C NMR spectrum of bis(2-hydroxyoct-1-yl) selenide (**3c)** (single diastereomer).

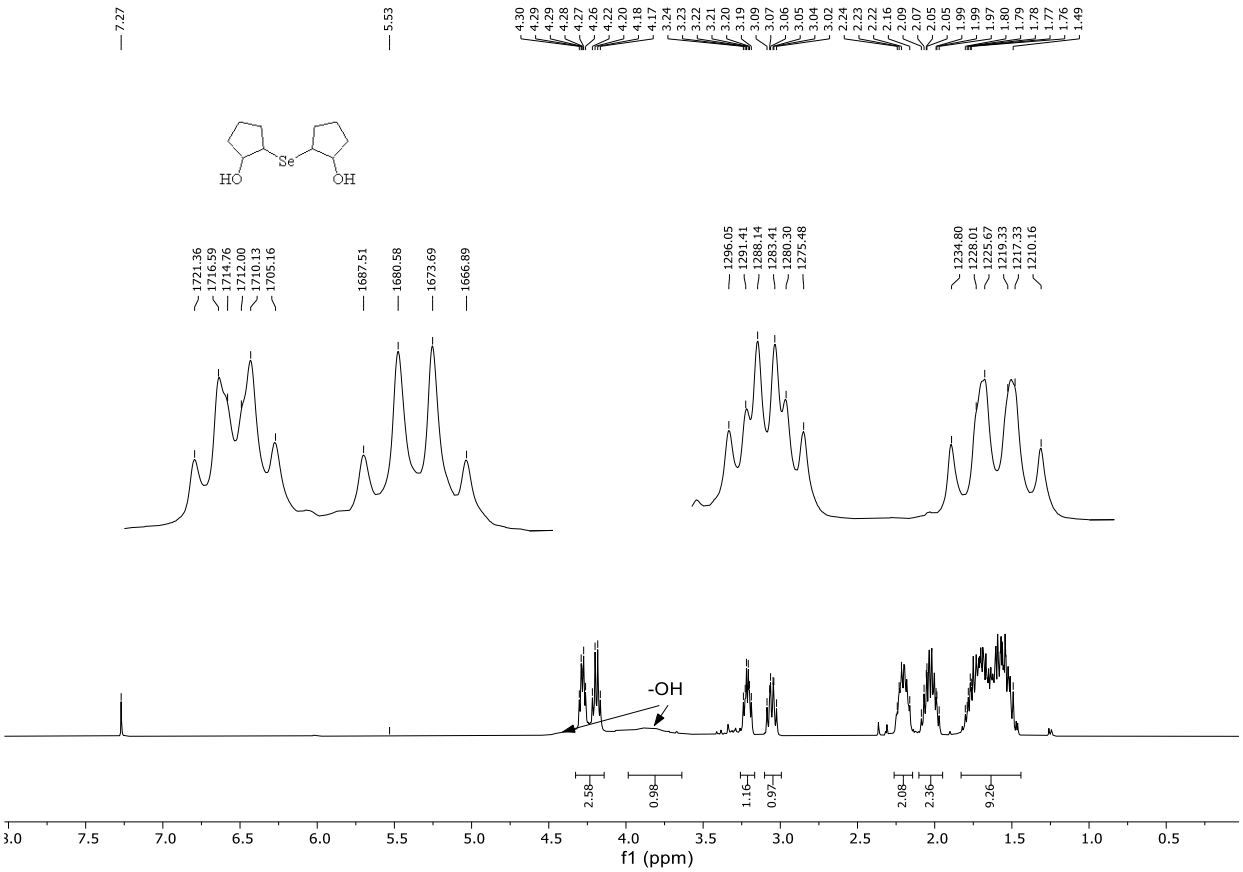

Figure S9. ^{1}H NMR spectrum of bis(2-hydroxycyclopent-1-yl) selenide (**4a)**

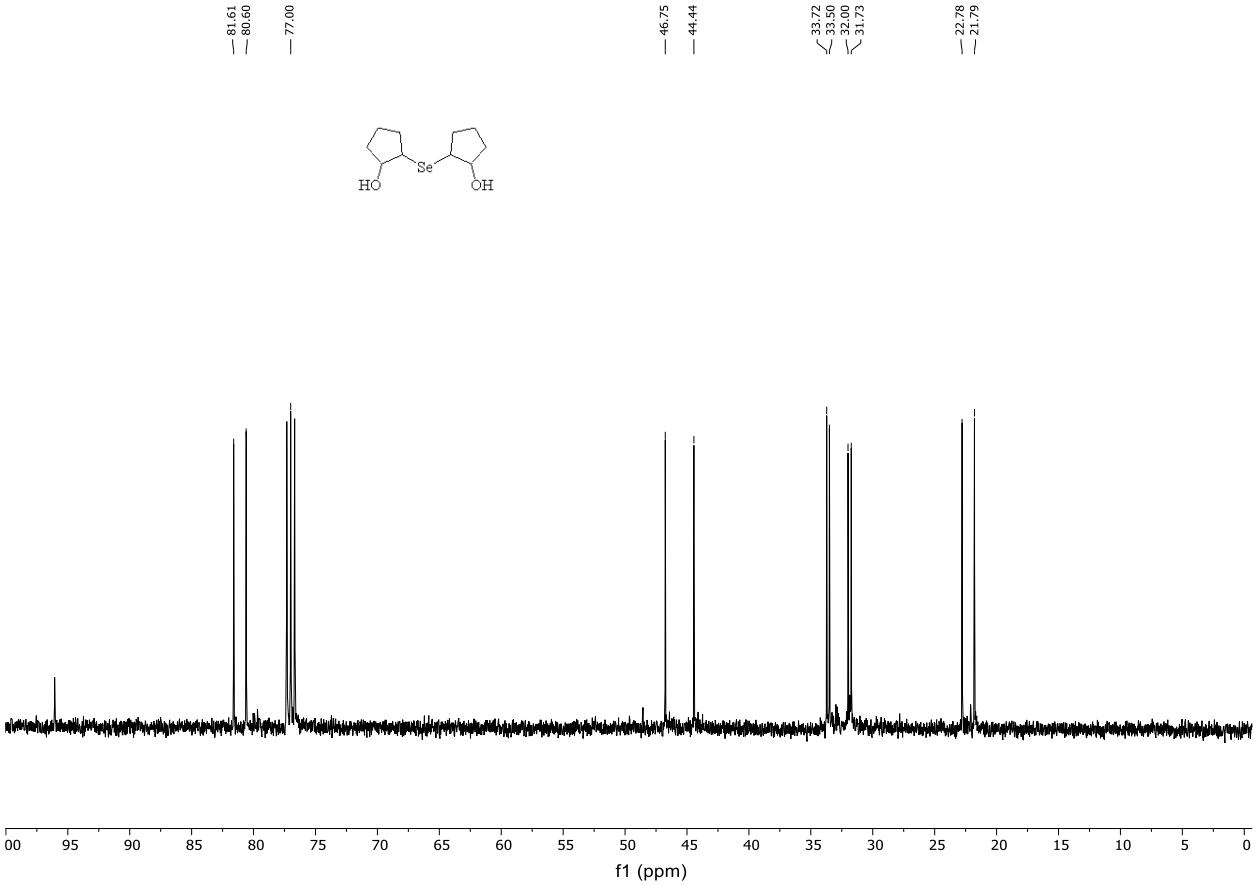

Figure S10. ^{13}C NMR spectrum of bis(2-hydroxycyclopent-1-yl) selenide (**4a)**

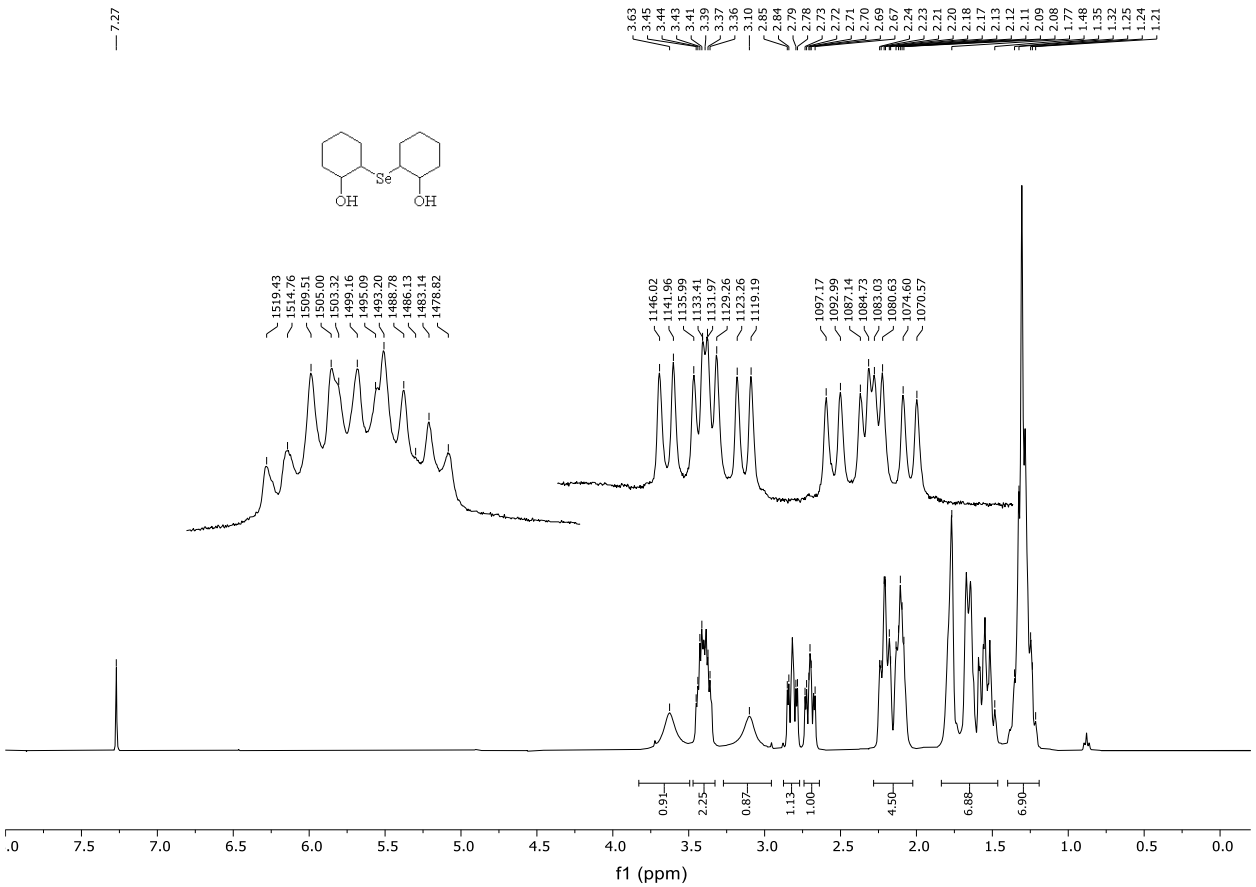

Figure S11. ^{1}H NMR spectrum of bis(2-hydroxycyclohex-1-yl) selenide (**4b)**

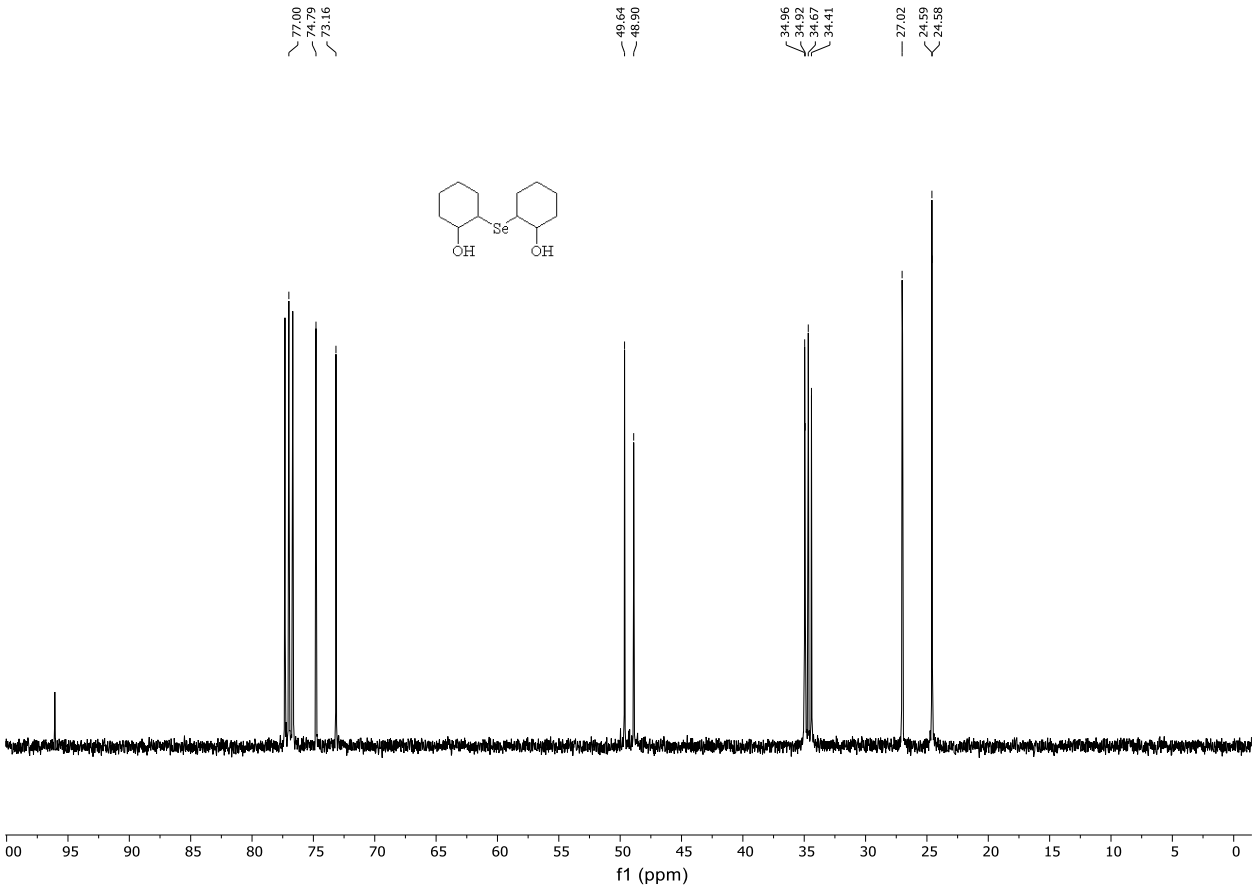

Figure S12. ^{1}H NMR spectrum of bis(2-hydroxycyclopent-1-yl) selenide (**4b)**