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Supporting Information for

An unexpected access to a new sphingoid base containing a vinyl sulfide unit

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Experimental Section

General: Solvents were distilled prior to use and dried by standard methods. ^{1}H and ^{13}CNMR spectra were obtained in $CDCl_3$ solutions, unless otherwise indicated. Chemical shifts were reported in delta (δ units, parts per million (ppm) relative to the singlet at 7.24 ppm of $CDCl_3$ for ^{1}H and in ppm relative to the center line of a triplet at 77.0 ppm of $CDCl_3$ for ^{13}C. ESI/HRMS spectra were recorded on a Waters LCT Premier Mass spectrometer. Analytical samples were homogeneous as confirmed by TLC and afforded spectroscopic results consistent with the assigned structures. Elemental analyses were carried out at CID-CSIC (Barcelona) in an Elemental Microanalyzer (A5) model Flash 1112.

Epoxide **1** and its epimeric counterpart at the C-O bond were obtained in two steps from Garner's aldehyde, by Wittig olefination and DMDO oxidation, as described in Koviach, J. L.; Chappell, M. D.; Halcomb, R. L. *J. Org. Chem.* **2001**, *66*, 2318-2326.

Analytical and spectroscopic data for compounds shown in Table 2
Compounds were obtained and *E/Z* mixtures and were used as such (with the exception of **3A**) for characterization purposes. R_f values also refer to the *E/Z* mixture. For the sake of clarity, only spectroscopic data for major *E*-isomers are shown.

(*R*,*E*)-2-amino-4-(tridecylthio)but-3-en-1-ol (3A)
Oil, yield 61% (40:1 *E/Z* ratio); R_f = 0.24 (CH_2Cl_2/MeOH 9:1). *E*-isomer: $[\alpha]_D$ = -1.1 (c = 0.96, $CHCl_3$). Elemental analysis, calculated for $C_{17}H_{35}NOS$: C, 67.72; H, 11.70; N, 4.65; Found: C, 67.78; H, 11.69; N, 4.39. HRMS: Calculated for $C_{17}H_{33}OS$ (M-NH_3)+1: 285.2252; Found: 285.2264. ^{1}HNMR (500 MHz): δ = 6.32 (d, *J* = 14.9 Hz, 1H), 5.45 (dd, *J* = 14.9, 6.4 Hz, 1H), 3.63 (m, 2H), 3.45 (m, 1H), 2.67 (t, *J* = 6.7 Hz, 2H), 1.61 (m, 2H), 1.37 (m, 2H), 1.25 (s, 18 H), 0.87 (t, *J* = 5.7 Hz, 3H). ^{13}CNMR (100 MHz): δ = 129.0 (CH), 124.4 (CH), 65.2 (CH_2), 55.8 (CH), 32.4 (CH_2), 32.1 (CH_2), 29.8 (CH_2) 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 22.8 (CH_2), 14.3 (CH_3).

(*R*,*E*)-2-amino-4-(cyclohexylthio)but-3-en-1-ol (3B)
Oil, yield 79% (10:1 *E/Z* ratio). R_f = 0.61 (CH_2Cl_2/MeOH 8:2). HRMS: Calculated for $C_{10}H_{17}OS$ (M-NH_3)+1: 185.1000; Found: 185.1001. ^{1}HNMR (400 MHz): δ = 6.24 (d, *J* = 15.3 Hz, 1H), 5.59 (dd, *J* = 15.3, 6.9 Hz, 1H), 3.70 (m, 1H), 3.58 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.35 (dd, *J* = 10.4, 7.7 Hz, 1H), 2.85 (m, 1H), 1.80 (m, 4 H), 1.35 (m, 6 H) ^{13}CNMR (100 MHz): δ = 129.7 (CH), 125.2 (CH), 66.3 (CH_2), 55.8 (CH), 44.9 (CH), 33.5 (2 x CH_2), 26.1 (2 x CH_2), 25.7 (CH_2).

(*R*,*E*)-2-amino-4-(*tert*-butylthio)but-3-en-1-ol (3C)
Oil, yield 78% (6:1 *E/Z* ratio). R_f = 0.39 (CH_2Cl_2/MeOH 8:2). HRMS: Calculated for $C_8H_{15}OS$ (M-NH_3)+1: 159.0844; Found: 159.0921. ^{1}HNMR (400 MHz): δ = 6.65 (d, *J* = 15.2 Hz, 1H), 5.67 (dd, *J* = 15.6, 8.5 Hz, 1H), 3.97 (m, 1H), 3.73 (m, 2H), 1.35 (s, 9 H). ^{13}CNMR (100 MHz): δ = 131.4 (CH), 121.4 (CH), 62.4 (CH_2), 55.8 (CH), 44.4 (C), 31.1 (CH_3).

(*R*,*E*)-2-amino-4-(benzylthio)but-3-en-1-ol (3D)
Oil, yield 76 % (13:1 *E/Z* ratio). R_f = 0.32 (CH_2Cl_2/MeOH 8:2). HRMS: Calculated for $C_{11}H_{13}OS$ (M-NH_3)+1: 193.0687; Found: 193.0696. ^{1}HNMR (400 MHz): δ = 7.33 (m,

5H), 6.19 (d, *J* = 15.3 Hz, 1H), 5.55 (dd, *J* = 15.3, 6.7 Hz, 1H), 3.89 (s, 2 H), 3.53 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.45 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.31 (m, 1H). ^{13}CNMR (100 MHz): δ = 136.6(C), 129.0 (2 x CH), 128.8 (2 x CH), 127.6 (CH), 121.2 (CH), 119.8 (CH), 62.9 (CH_2), 55.7 (CH), 36.7 (CH_2).

(*R*,*E*)-2-amino-4-(phenylthio)but-3-en-1-ol (3E)
Oil, yield 67% (9:1 *E/Z* ratio). R_f = 0.52 (CH_2Cl_2/MeOH 8:2). HRMS: Calculated for $C_{10}H_{11}OS$ (M- NH_3)+1: 179.0531; Found: 179.0533. ^{1}HNMR (400 MHz): δ = δ 7.31 (m, 5H), 6.41 (dd, *J* = 15.2, 1.1 Hz, 1H), 5.80 (dd, *J* = 15.2, 6.7 Hz, 1H), 3.63 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.55 (m, 1H), 3.38 (dd, *J* = 10.3, 7.5 Hz, 1H). ^{13}CNMR (100 MHz): δ = 134.9 (C), 133.6 (2 x CH), 130.0 (2 x CH), 129.3 (CH), 127.1 (CH), 125.0 (CH), 66.5 (CH_2), 55.5 (CH).

(*R*,*E*)-2-amino-4-(2-naphthylthio)but-3-en-1-ol (3F)
Oil, yield 59 % (9:1 *E/Z* ratio). R_f = 0.59 (CH_2Cl_2/MeOH 9:1). HRMS: Calculated for $C_{14}H_{13}OS$ (M-NH_3)+1: 229.0687; Found: 229.0695. ^{1}HNMR (300 MHz): δ = 7.72 – 7.53 (m, 4H), 7.36 (m, 3H), 6.60 (d, *J* = 15.2 Hz, 1H), 5.70 (dd, *J* = 15.2, 7.4 Hz, 1H), 3.84 (m, 1H), 3.62 (m, 2H). ^{13}CNMR (100 MHz): δ = 133.7 (C), 132.3 (C), 131.2 (C), 130.4 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 126.3 (CH), 125.4 (CH), 63.4 (CH_2), 55.4 (CH).

(*S*)-tert-butyl 4-[(*S*)-2-(cyclohexylthio)-1-hydroxyethyl]-2,2-dimethyloxazolidine-3-carboxylate (2B)
Oil, yield 58 % (Table 2). R_f = 0.35 (Hexanes/EtOAc 9:1). HRMS: Calculated for $C_{18}H_{33}NNaO_4S$ (M+Na): 382.2028; Found: 382.1978 ^{1}HNMR (400 MHz): δ = 3.87 (m, 4 H), 2.75 (m, 1H), 2.61 (m, 1H), 2.49 (m, 1H), 1.93 (m, 2H), 1.73 (m, 2H), 1.54 (s, 6 H), 1.46 (s, 9 H), 1.30 (m, 6H). ^{13}CNMR (100 MHz): δ = 153.7 (C), 94.2 (C), 80.9 (C), 71.5 (CH), 64.9 (CH_2), 61.4 (CH), 43.7 (CH), 34.6 (CH_2), 33.8 (2 x CH_2), 28.5 (3 x CH_3), 26.2 (2 x CH_2), 25.9 (2 x CH_2), 24.3 (2 x CH_3).

(*S*)-tert-butyl 4-[(*S*)-2-(*tert*-butylthio)-1-hydroxyethyl]-2,2-dimethyloxazolidine-3-carboxylate (2C)
Oil, yield 61 % (Table 2). R_f = 0.48 (Hexanes/EtOAc 7:3). HRMS: Calculated for $C_{16}H_{31}NNaO_4S$ (M+Na): 356.1872; Found: 356.1860. ^{1}HNMR (400 MHz): δ = 3.80 (m, 3 H), 3.70 (m, 1 H), 2.76 (dd, *J* = 13.0, 3.3 Hz, 1H), 2.58 (dd, *J* = 13.0, 9.7 Hz, 1H), 1.72 (s, 3H), 1.58 (s, 6H), 1.49 (s, 9H), 1.45 (s, 3H), 1.33 (s, 3H). ^{13}CNMR (100 MHz): δ = 153.8 (C), 94.2 (C), 81.0 (C), 72.1 (CH), 64.9 (CH_2), 61.6 (CH), 46.3 (C), 33.2 (CH_2), 30.9 (3 x CH_3), 28.5 (3 x CH_3), 27.1 (2 x CH_3).

(*S*)-tert-butyl 4-[(*S*)-2-(benzylthio)-1-hydroxyethyl]-2,2-dimethyloxazolidine-3-carboxylate (2D)
Oil, yield 74 % (Table 2). R_f = 0.57 (Hexanes/EtOAc 7:3). HRMS: Calculated for $C_{19}H_{29}NNaO_4S$ (M+Na): 390.1715; Found: 390.1722. ^{1}HNMR (400 MHz): δ = 7.26 (m, 5 H), 4.10 (m, 2 H), 3.77 (m, 3 H), 3.70 (s, 2 H), 2.56 (m, 1H), 2.41 (m, 1H), 1.50 (s, 6H), 1.46 (s, 9H). ^{13}CNMR (100 MHz): δ = 155.2 (C), 138.7 (C), 129.2 (2 x CH), 128.8 (2 x CH), 127.1 (C), 94.3 (C), 81.2 (C), 71.5 (CH), 65.0 (CH), 62.5 (CH_2), 37.6 (CH_2), 36.2 (CH_2), 28.4 (3 x CH_3), 27.00 (2 x CH_3).

(*S*)-tert-butyl 4-[(*S*)-2-(phenylthio)-1-hydroxyethyl]-2,2-dimethyloxazolidine-3-carboxylate (2E)

Oil, yield 47 % (Table 2). R_f = 0.18 (Hexanes/EtOAc 9:1). HRMS: Calculated for $C_{36}H_{54}N_2NaO_8S_2$ (2M+Na): 729.3220; Found: 729.3219. ^{1}HNMR (300 MHz): δ = 7.37 (m, 2 H), 7.28 (m, 2 H), 7.19 (m, 1H), 3.90 (m, 4H), 3.19 (m, 1H), 2.89 (m, 1H), 1.52 (s, 6H), 1.49 (s, 9H). ^{13}CNMR (75 MHz): δ = 152.9 (C), 129.9 (C), 129.6 (2 x CH), 129.0 (2 x CH), 126.3 (C), 94.3 (C), 81.2 (C), 71.4 (CH), 65.0 (CH_2), 61.3 (CH), 38.5 (CH_2), 28.4 (3 x CH_3), 26.9 (2 x CH_3).

(*S*)-tert-butyl 4-[(*S*)-2-(2-naphthylthio)-1-hydroxyethyl]-2,2-dimethyloxazolidine-3-carboxylate (2F)

Oil, yield 18 % (Table 2). R_f =0.18 (Hexanes/EtOAc 9:1). HRMS: Calculated for $C_{44}H_{58}N_2NaO_8S_2$ (2M+Na): 829.3532; Found: 829.3537. ^{1}HNMR (300 MHz): δ = 7.76 (m, 4H), 7.47 (m, 3H), 4.16 (m, 1H), 3.88 (m, 3H), 3.32 (m, 1H), 3.01 (m, 1H), 1.55 (s, 6H), 1.50 (s, 9H). ^{13}CNMR (100 MHz): δ = 153.4 (C), 134.5 (2 x C), 130.3 (C), 128.8 (CH), 128.4 (4 x CH), 126.3 (2 x CH), 124.1 (CH), 94.5 (C), 79.7 (C), 71.5 (CH), 65.1 (CH), 62.6 (CH_2), 40.6 (CH_2), 28.5 (3 x CH_3), 25.1 (2 x CH_3)