General methods

All reactions were conducted under a dried argon stream. Solvents (CH$_2$Cl$_2$ 99.9%, toluene 99.9%) were purchased in capped Pure Solv System-4® bottles and used without further purification and stored under argon. Yields refer to the chromatographically and spectroscopically (¹H and ¹³C) homogeneous materials, unless otherwise stated. All glassware utilized was flame-dried before use. Reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel plates. Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in ethanol/H$_2$SO$_4$ (15:1) and basic solution of permanganate potassium. Flash column chromatography (FCC) was performed using flash silica gel (32–63 μm) and employed a solvent polarity correlated with TLC mobility. Melting points, determined with Reichert apparatus, are uncorrected. Optical rotations were measured at 598 nm on a Jasco DIP-370 digital polarimeter using a 100 mm cell. NMR experiments were conducted on a Varian 400 MHz instrument using CDCl$_3$ (99.9% D) as the solvent, with chemical shifts (δ) reference to internal standards CDCl$_3$ (7.26 ppm ¹H, 77.23 ppm ¹³C) or Me$_4$Si as an internal reference (0.00 ppm)
Chemical shifts are relative to the deuterated solvent peak and are in parts per million (ppm).

**Experimental Procedures**

*(E)-1-bromohexadec-2-ene (6).* Allyl bromide (8) (240 mg, 2 mmol) was dissolved in 40 mL of dry CH₂Cl₂ and then pentadec-1-ene 9 (1.68 g, 8 mmol) and Grubs catalyst B (8 mg, 2%) were added at room temperature. After the addition was completed, the reaction mixture was kept boiling for 8 h under argon atmosphere and then cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane-AcOEt (98:2) as the eluent to give 590 mg of pure 1-bromohexadec-2-ene (6) (97 %) as colourless oil and with *E,Z* selectivity of 52:1.

TLC (Hexane) *R*ₚ 0.60; ¹H NMR (400 MHz, CDCl₃): δ 5.78 (1H, dt, *J*= 14.8, 7.6 Hz), 5.68 (1H, dt, *J*= 14.8, 7.2 Hz), 3.96 (2H, d, *J*= 7.6 Hz), 2.03 (2H, q, *J*= 7.2, Hz), 1.34-1.20 (22H, m), 0.86 (3H, t, *J*= 6.9 Hz); ¹³C NMR (100.6 MHz, CDCl₃): δ 137, 126.3, 34, 32.3, 32.1, 29.8, 29.6, 29.5, 29.3, 29, 22.9, 14.3. Anal. Calcd. for C₁₆H₃₁Br: C, 63.36; H, 10.30. Found: C, 63.34; H, 10.31.

Formylmethyl benzylcarbamate (10). To a solution of 2-hydroxyacetaldehyde 7 (184 mg, 3.06 mmol) in 20 mL of dry Et₂O freshly distilled Et₃N (10.16 mmol) and BnNCO (647 mg, 4.8 mmol) were added. The resulting mixture was heated to 60 °C in a sealed tube for 17 h, cooled to room temperature and quenched with saturate NH₄Cl (10 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane-AcOEt (85:15) as the eluent to give 580 mg of pure formylmethyl benzylcarbamate (10) (98 %) as an oil. TLC (Hexane-AcOEt 80:20) *R*ₚ 0.70; ¹H NMR (400 MHz, CDCl₃): δ 9.67 (1H, t, *J*= 0.7 Hz), 7.35-7.21 (5H, m), 5.08 (1H, br s), 4.89 (2H, d, *J*= 0.7 Hz) 4.4 (2H, d, *J*= 5.5); ¹³C NMR (100.6 MHz, CDCl₃): δ 194.2, 153.6, 136.9, 128.5, 124.4, 121.6, 69.5, 45.2. Anal. Calcd. For C₁₀H₁₁NO₃: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.15; H, 5.75; N, 7.26.
**Sulfonium salt 12.** To a rapidly stirred solution of chiral sulfide 11 (500 mg, 2.0 mmol) and \((E)-1\)-bromohexadec-2-ene (909 mg, 3.0 mmol) in 2 mL dichloromethane was added silver tetrafluoroborate (778 mg, 4.0 mmol) in the dark under an argon atmosphere at room temperature. The reaction was stirred for 48 h and 10 mL of CH\(_2\)Cl\(_2\) was added. Silver bromide precipitate was filtered and the filtrate was concentrated in vacuo. The residual brown oil was recrystallized from CH\(_2\)Cl\(_2\) and Et\(_2\)O to give sulfonium salt 12 as a white precipitate which was used directly into the next step.

\(((2R,3R)-3-((E)-pentadec-1-enyl)oxiran-2-yl)methyl benzylcarbamate (13).** To a stirred solution of sulfonium salt 12 (465 mg, 0.83 mmol) in 5 mL of CH\(_2\)Cl\(_2\) \(N,N,N',N''\)-tetramethyl-N\''-[tris(dimethylamino)phos-phoralidene]phosphoric triamide ethylimine (415 mg, 1.22 mmol) was added at \(-78^\circ\) C under argon. After 30 min, a mixture of 20 mL of CH\(_2\)Cl\(_2\) and formylmethyl benzylcarbamate 10 (240 mg, 1.25 mmol) was added to the solution. The reaction mixture was stirred for 2 h and then was warmed up to room temperature and a saturated NaCl solution (10 mL) was added. The phases were separated and the aqueous layer was extracted with AcOEt (2 x 10 mL). The organic layer was dried over MgSO\(_4\) and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane-AcOEt (85:15) as the eluent to give 192 mg of pure epoxide 13 (60 %). Compound 11 (180 mg, 87% was also recovered). TLC (Hexane-AcOEt 70:30) \(R_f 0.60\); \([\alpha]_D \ +15.0\ (c 0.5 \text{ in CHCl}_3); \ ^1\text{H NMR (400 MHz, CDCl}_3): \delta 7.37-7.26 \ (5H, m), \ 5.73 \ (1H, dt, J=14.8, 6.5 Hz), \ 5.10 \ (1H, dd, J=14.8, 9.1 Hz), \ 5.01 \ (1H, br s), \ 4.47 \ (1H, dd, J=12.2, 3.1 Hz), \ 4.39 \ (2H, d, J=6), \ 4.05 \ (1H, dd, J=12.2, 6.3 Hz), \ 3.30 \ (1H, dd, J=9.1, \ 2.4), \ 3.15 \ (1H, ddd, J=6.3, \ 3.1, \ 2.4 Hz), \ 2.03 \ (2H, q, J=6.5 Hz), \ 1.37-1.20 \ (22H, m), \ 0.81 \ (3H, t, J=6.8 Hz); \ ^13\text{C NMR (100.6 MHz, CDCl}_3): \delta 156.0, \ 138.4, \ 134.6, \ 128.8, \ 127.7, \ 127.6, \ 120.3, \ 64.9, \ 57.6, \ 56.5, \ 45.2, \ 32.5, \ 32.1, \ 29.8, \ 29.6, \ 29.5, \ 29.4, \ 29.3, \ 22.8, \ 14.3. \ \text{Anal. Calcd. for C}_{26}H_{41}NO_3: \ C, 75.14; \ H, 9.94; \ N, 3.37. \ \text{Found: C, 75.12; H, 9.95, N, 3.36.}

\((S)-4-((R,E)-1-hydroxyhexadec-2-enyl)oxazolidin-2-one (14).** To a stirred solution of epoxide 13 (220 mg, 0.57 mmol) in 5 mL of THF at \(-15^\circ\) C was added dropwise NaHMDS (0.57 mmol, 1 M in THF). The resulting mixture was slowly allowed to reach 0 \(^\circ\) C (5 h)
and then quenched by addition of a saturate solution of NH₄Cl (10 mL). The phases were separated and the aqueous layer was extracted with AcOEt (2 x 10 mL). The organic layer was dried over MgSO₄ and concentrated in vacuo. The residue was used directly into next step. Thus, to a stirred mixture of Li (excess) and freshly EtNH₂ (15 mL) under argon at −78 °C was added a solution of first residue in dry 2 mL of Et₂O via syringe. The reaction mixture was stirred at −78 °C for 4 h and then carefully quenched with saturate NHCl₄. The phases were separated and the aqueous layer was extracted with AcOEt (2 X 10 mL). The organic layer was dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using hexane-AcOEt-MeOH (85:10:5) as the eluent to give 154 mg of pure oxazolidinone 14 (82 %). TLC (Hexane-AcOEt-MeOH 60:30:10) Rf 0.70; m.p. 71-73 °C; [α]D −1.3 (c 1.75 in CHCl₃); ¹H NMR (400, MHz, CDCl₃): δ 5.82 (1H, dtd, J =15.4, 6.8, 0.8 Hz), 5.46 (1H, dd, J=15.4, 6.8, 1.2 Hz), 4.41 (1H, dd, J=8.8, 8.5 Hz), 4.31 (1H, dd, J=8.8, 4.9 Hz), 4.06 (1H, dd, J=6.8, 5.2 Hz), 3.82 (1H, ddd, J=8.5, 5.2, 4.9 Hz), 2.18 (1H, br s), 2.04 (2H, q, J=7.0 Hz), 1.37-1.2 (22H, m), 0.81 (3H, t, J=6.7 Hz); ¹³C NMR (100.6 MHz, CDCl₃): δ 160.5, 136.6, 126.6, 73.3, 66.4, 56.4, 32.5, 32.1, 29.81, 29.79, 29.74, 29.6, 29.5, 29.4, 29.1, 22.8, 14.2. Anal. Calcd. For C₁₉H₃₅NO₃: C, 70.11; H, 10.84; N, 4.30. Found: C, 70.19; H, 10.80; N, 4.32.

D-erythro-sphingosine (1). The mixture of oxazolidinone 14 (32.5 mg, 0.1 mmol) and 1 M KOH (2 mL, H₂O:EtOH 1:1) was heated to reflux for 2.5 h, cooled to room temperature and then 2 M HCl (10 mL) was added. The mixture was extracted with EtOAc (3 x 20 mL) and the combined organic layers were dried over MgSO₄ and concentrated in vacuo giving 30 mg of pure D-erythro-sphingosine (1) (100 %). TLC (Hexane-AcOEt-MeOH 60:30:10) Rf 0.70; m.p. 72–74 °C; [α]D −1.6 (c 1 in CHCl₃); ¹H NMR (400, MHz, CDCl₃): δ 5.76 (ddt, 1H, J=15.4, 6.7, 1.2 Hz), 5.47 (ddt, 1H, J=15.4, 7.2, 1.6 Hz), 4.04 (dd, 1H, J=7.2, 6 Hz), 3.70 (dd, 1H, J=10.8, 4.8 Hz), 3.61 (dd, 1H, J=10.8, 6 Hz), 2.88 (ddd, 1H, 6, 6, 4.8), 2.05 (td, 2H, J=7.6, 6.7 Hz), 1.74 (4H, br s), 1.37 (m, 2H), 1.20–1.40 (m, 20H), 0.88 (t, 3H, J=6.8 Hz); ¹³C NMR (100.6 MHz, CDCl₃): δ 135.1, 129.4, 75.8, 64.5, 56.3, 32.5, 32.1, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 22.9, 14.3. Anal. Calcd. For C₁₈H₃₇NO₂: C, 72.19; H, 12.45; N, 4.68. Found: C, 72.21; H, 12.41; N, 4.70.
$^1$H NMR of 13

$^{13}$C NMR of 13
$^1$H NMR of 1

$^{12}$C NMR of 1