

## Electronic Supplementary Information for

# Synthesis and preliminary antifungal evaluation of a library of phytosphingolipid analogues

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## Compound characterization

### (2*S*,3*S*,4*R*)-2-Aminooctadecane-1,3,4-triol (*D*-ribo phytosphingosine) (**1a**).

Obtained in 82% yield as a white solid from carbamate **1b**.

mp 102-103°C; Lit<sup>1,2</sup> mp 103°C; Lit<sup>3</sup> mp 98.5-101.5; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.78(dd, *J*=11, 4 Hz, 1H, H1a), 3.58(dd, *J*=11, 7 Hz, 1H, H1b), 3.50(td, *J*=8.2, 2.7Hz, 1H, H4), 3.37(dd, *J*=8, 5Hz, 1H, H3), 3.02(ddd, *J*=6.9, 5.3, 4.2 Hz, 1H, H2), 1.74(m, 1H), 1.56(m, 1H), 1.26-1.39(m, 24H), 0.90(t, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 76.1, 74.3, 63.5, 55.9, 34.8, 33.1, 30.9, 30.8, 30.8, 30.8, 30.5, 26.6, 23.7, 14.4. ESI-MS *m/z* 318 [M+H]<sup>+</sup>, 340 [M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=3.98 min.

### (2*S*,3*R*,4*S*)-2-Aminooctadecane-1,3,4-triol (*L*-arabino phytosphingosine) (**2a**).

Obtained in 89% yield from carbamate **2b**.

mp 82-83°C; Lit<sup>2</sup> mp 75°C; Lit<sup>1</sup> mp 86°C; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.60(dd, *J*=11, 6 Hz, 1H, H1a), 3.56(m, 1H, H4), 3.52(dd, *J*=11, 7 Hz, 1H, H1b), 3.37(dd, *J*=7.5, 2.5 Hz, 1H, H3), 3.02(ddd, *J*=7, 6, 2.5 Hz, 1H, H2), 1.74(m, 1H), 1.56(m, 1H), 1.26-1.39(m, 24H), 0.90(t, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 73.7, 73.5, 64.7, 54.2, 34.9, 33.1, 30.9, 30.8, 30.8, 30.5, 26.8, 23.7, 14.4. ESI-MS *m/z* 318 [M+H]<sup>+</sup>, 340 [M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.58 min.

### (2*S*,3*R*,4*R*)-2-Aminooctadecane-1,3,4-triol (*D*-xylo phytosphingosine) (**3a**).

Obtained in 92% yield from carbamate **3b**.

mp 95-96°C; Lit <sup>4</sup> mp 98-99°C; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.65(dd, *J*=11, 5 Hz, 1H, H1a), 3.63(m, 1H, H4), 3.56(dd, *J*=11, 6.5 Hz, 1H, H1b), 3.47(dd, *J*=4.5, 3 Hz, 1H, H3), 3.00(m, 1H, H2), 1.54(m, 2H), 1.47(m, 1H), 1.29-1.38(m, 23H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz): 74.0, 72.8, 63.8, 56.6, 34.8, 33.1, 30.9, 30.8, 30.8, 30.5, 26.9, 23.7, 14.4. ESI-MS *m/z* 318 [M+H]<sup>+</sup>, 340 [M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.65 min.

**(2*S*,3*S*,4*S*)-2-Aminooctadecane-1,3,4-triol (*L*-lyxo phytosphingosine) (4a).**

Obtained in 88% yield from carbamate **4b**.

mp 102-103°C; Lit <sup>5</sup> mp 104.2-105.5; Lit <sup>3</sup> mp 104.8-106.0; Lit <sup>6</sup> mp 96-98; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.74(dd, *J*=11, 4 Hz, 1H), 3.64(m, 1H, H2), 3.54(dd, *J*=11, 7 Hz, 1H, H1b), 3.34(dd, *J*=6.5, 2.5 Hz, 1H, H3), 2.94(td, *J*=6.8, 4.4 Hz, 1H, H2), 1.52(m, 2H), 1.47(m, 1H), 1.25-1.38(m, 23H), 0.87(t, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 74.7, 72.0, 64.1, 55.2, 34.2, 32.6, 30.4, 30.4, 30.3, 30.0, 26.6, 23.3, 14.4. ESI-MS *m/z* 318 [M+H]<sup>+</sup>, 340 [M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT= 4.57 min.

**(2*S*,3*S*,4*R*)-2-Amino-1-azidooctadecane-3,4-diol (5a)**

Obtained in 86% yield from azidocarbamate **5b**.

mp 87-88°C; [α]<sub>D</sub><sup>25</sup> +5.5 (c 0.92, CHCl<sub>3</sub>); IR (film): 3375 3261, 2921, 2851, 2107, 1572, 1468, 1441, 1370, 1313, 1273, 1172, 1131, 1094, 1043, 936. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 3.59(dd, *J*=12.5, 3.5 Hz, 1H), 3.51(m, 1H, H4), 3.57(dd, *J*=12.5, 7.5 Hz, 1H, H1b), 3.43(t, *J*=7 Hz, 1H, H3), 2.94(td, *J*=7, 3.5 Hz, 1H, H2), 1.65(m, 1H), 1.53(m, 1H), 1.50(m, 1H), 1.21-1.40(m, 23H), 0.88(t, *J*=6.7 Hz, 3H). <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1drop CD<sub>3</sub>OD, 500 MHz): 3.59(dd, *J*=12.5, 3.5 Hz, 1H, H1a), 3.51(m, 1H, H4), 3.43(dd, *J*=12.5, 7.5 Hz, 1H, H1b), 3.32(t, *J*=7Hz, 1H, H3), 2.94(td, *J*=7, 3.5 Hz, 1H, H2), 1.62(m, 1H), 1.47(m, 1H), 1.20-1.36(m, 24H), 0.88(t, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 74.4, 74.2, 55.6, 54.4, 33.3, 32.0, 29.9, 29.8, 29.8, 29.5, 25.5, 22.8, 14.2. ESI-MS *m/z* 343 [M+H]<sup>+</sup>; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=3.54 min.

**(2*S*,3*R*,4*S*)-2-Amino-1-azidooctadecane-3,4-diol (6a)**

Obtained in 90% yield, as a white solid, from azidocarbamate **6b**.

mp 75-76°C; [α]<sub>D</sub><sup>25</sup> -11.2 (c 0.87, CHCl<sub>3</sub>); IR (film): 3364, 2917, 2849, 2126, 2102, 1503, 1470. <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 500 MHz): 3.61(m, 1H, H4), 3.44(dd, *J*=12, 5.5 Hz, 1H, H1a), 3.37(dd, *J*=4.5, 2 Hz, 1H, H3), 3.33(dd, *J*=12, 7 Hz, 1H, H1b), 3.09(ddd,

$J=7.8, 5.6, 1.7$  Hz, 1H, H2), 2.70(br s, 4H), 1.45(m, 3H), 1.21-1.34(m, 23H), 0.85(t,  $J=7$  Hz, 3H).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 3.70(dt,  $J=8.4, 4.3$  Hz, 1H, H4), 3.49(dd,  $J=12, 5.5$  Hz, 1H, H1a), 3.41(dd,  $J=4, 1.5$  Hz, 1H, H3), 3.36(dd,  $J=12, 8$  Hz, 1H, H1b), 3.13(m, 1H, H2), 1.45(m, 3H), 1.21-1.34(m, 23H), 0.85(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 125 MHz): 74.9, 72.1, 56.1, 51.0, 34.3, 32.0, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.4, 26.1, 22.8, 14.2. ESI-MS  $m/z$  343  $[\text{M}+\text{H}]^+$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 (0.1%TFA) RT=3.49 min.

**(2S,3R,4R)-2-Amino-1-azidooctadecane-3,4-diol (7a)**

Obtained in 98% yield from azidocarbamate **7b**.

mp 74-75°C;  $[\alpha]_{\text{D}}^{25} -1.3$  (c 0.85,  $\text{CHCl}_3$ ); IR (film) 3287, 2916, 2848, 2106, 1584, 1464, 1349, 1261, 1139, 1110.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 3.70(ddd,  $J=7, 6, 1$  Hz, 1H, H4), 3.49(dd,  $J=12, 5.5$  Hz, 1H, H1a), 3.39(m, 1H, H3), 3.34(dd,  $J=12, 8$  Hz, 1H, H1b), 2.93(ddd,  $J=7.8, 5.6, 2.2$  Hz, 1H, H2), 1.57(m, 1H), 1.49(m, 1H), 1.45(m, 1H), 1.21-1.40(m, 23H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 74.4, 71.5, 56.3, 55.1, 33.9, 32.0, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.5, 25.8, 22.8, 14.2. ESI-MS  $m/z$  343  $[\text{M}+\text{H}]^+$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 (0.1%TFA) RT=4.85 min.

**(2S,3S,4S)-2-Amino-1-azidooctadecane-3,4-diol (8a)**

Obtained in 89% yield from azidocarbamate **8b**

mp 87-88°C;  $[\alpha]_{\text{D}}^{25} -12.1$  (c 0.52,  $\text{CHCl}_3$ ); IR (film): 3375, 2954, 2916, 2849, 2134, 2094, 1603, 1470, 1316.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 3.66(m, 1H), 3.57(br d,  $J=12$  Hz, 1H), 3.40(dd,  $J=12, 8$  Hz, 1H), 3.31(m, 1H), 3.04(m, 1H), 1.38-1.54(m, 3H), 1.21-1.32(m, 23H), 0.85(t,  $J=6.3$  Hz, 3H).  $^1\text{H}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 500 MHz): 3.58(m, 1H, H4), 3.55(dd,  $J=12, 3.5$  Hz, 1H, H1a), 3.37(dd,  $J=12, 7.5$  Hz, 1H, H1b), 3.23(dd,  $J=6.5, 2.5$  Hz, 1H, H3), 2.94(td,  $J=7.2, 3.7$  Hz, 1H, H2), 1.38-1.54(m, 3H), 1.21-1.32(m, 23H), 0.85(t,  $J=6.3$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 125 MHz): 73.7, 71.1, 54.9, 53.3, 33.7, 32.0, 29.8, 29.7, 29.7, 29.4, 25.9, 22.8, 14.2. ESI-MS  $m/z$  343  $[\text{M}+\text{H}]^+$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 (0.1%TFA) RT=4.47 min.

**(2R,3Z)-2-Amino-1-octadec-3-en-1-ol ((Z)-13a)**

Obtained in 99% yield (734 mg, 2.59 mmol) as a white solid from **1g** (2.61 mmol) of carbamate **(Z)-13b**.

mp 64-65°C;  $[\alpha]_D^{25}$  -6.25 (c 1.44, CHCl<sub>3</sub>); IR (film): 2922, 2846, 1699, 1610, 1549, 1466, 1371, 1339, 1183, 1160, 1075, 1037, 953. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.50(dt, *J*=10.5, 7.8 Hz, 1 Hz, 1H), 5.23(dd, *J*=10.8, 9.3 Hz, 1H), 3.75(td, *J*=8.4, 5 Hz, 1H), 3.50(dd, *J*=10.5, 5 Hz, 1H), 3.32(dd, *J*=10.5, 7.5 Hz, 1H), 2.06(m, 2H), 1.81(br s, 3H), 1.35(m, 2H), 1.20-1.31(m, 22H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 133.1, 130.5, 66.4, 50.2, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 27.9, 22.8, 14.3. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 5.78(dtd, *J*=11, 7.5, 1 Hz, 1H), 5.33(dtd, *J*=11, 9.5, 1.5 Hz, 1H), 4.02(m, 1H), 3.63(dd, *J*=11.5, 4.5 Hz, 1H), 3.47(dd, *J*=11.5, 8.5 Hz, 1H), 2.16(m, 2H), 1.42(m, 2H), 1.23-1.35(m, 22H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD 125 MHz): 139.0, 123.1, 63.4, 51.8, 33.1, 30.8, 30.8, 30.7, 30.6, 30.5, 30.5, 30.4, 28.8, 23.4, 14.5. ESI-MS *m/z* 284 [M+H]<sup>+</sup>. HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=5.24 min.

**(2*R*,3*E*)-2-Aminooctadec-3-en-1-ol ((*E*)-13a)**

Obtained in 95% yield (316 mg, 1.11 mmol) as a white solid from 450 mg (1.17 mmol) of carbamate (*E*)**13b**.

mp 83-84°C;  $[\alpha]_D^{25}$  -2.9(c 0.87, CHCl<sub>3</sub>); IR (film): 3341, 3284, 3102, 2958, 2924, 2848, 1592, 1462, 382, 1305, 1144, 1111, 1053, 969. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.63(dt, *J*=15, 7 Hz, 1H), 5.36(dd, *J*=15, 6 Hz, 1H), 3.56(m, 1H), 3.40(m, 1H), 3.32(dd, *J*=9.5, 8.5 Hz, 1H), 2.15(br s, 3H), 2.01(m, 2H), 1.34(m, 2H), 1.22-1.32(m, 22H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 132.8, 130.6, 66.7, 55.2, 32.5, 32.1, 29.8, 29.6, 29.5, 29.3, 22.8, 14.3. ESI-MS *m/z* 284 [M+H]<sup>+</sup>; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=5.37 min.

**(2*R*,3*Z*)-1-(Azidomethyl)heptadec-2-enylamine ((*Z*)-14a)**

Obtained in 81% yield as a brown oil from (*Z*)-**14b**.

$[\alpha]_D^{25}$  -37.1 (c 0.92, CHCl<sub>3</sub>); IR (film): 2925, 2855, 2100, 1461, 1274, 827. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.49(dtd, *J*=11, 7.5, 0.7 Hz, 1H), 5.24(dd, *J*=11, 9 Hz, 1H), 3.84(m, 1H), 3.27(dd, *J*=12, 4.5 Hz, 1H), 3.17(dd, *J*=12.8 Hz, 1H), 2.06(m, 2H), 1.36(m, 2H), 1.30-1.20(m, 22H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 133.2, 130.3, 57.8, 48.5, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 27.9, 22.8, 14.2. ESI-MS *m/z* 308 [M+H]<sup>+</sup>, 280 [M-N<sub>2</sub>].

**(2*R*,3*E*)-1-(Azidomethyl)heptadec-2-enylamine ((*E*)-14a)**

Obtained in 85% yield as a brown oil from (*E*)-**14b**.

$[\alpha]_D^{25}$  -2.1 (2.08, CHCl<sub>3</sub>); IR (film): 2925, 2854, 2100, 1590, 1461, 1349, 1271, 970. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.66(dtd, *J*=15, 8.5, 0.8 Hz, 1H), 5.36(ddt, *J*=15, 7, 1.5 Hz, 1H), 3.48(m, 1H), 3.32(dd, *J*=12, 4.5 Hz, 1H), 3.16(dd, *J*=12, 7.5 Hz, 1H), 2.01(m, 2H), 1.34(m, 2H), 1.24(m, 22H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 132.9, 130.4, 57.9, 53.4, 32.3, 31.9, 29.7, 29.6, 29.6, 29.6, 29.6, 29.4, 29.3, 29.1, 29.1, 22.6, 14.1. ESI-MS *m/z* 309 [M+H]<sup>+</sup>.

**(2R,3Z)-Octadec-3-ene-1,2-diamine ((Z)-15a)**

Obtained in 79% yield as a yellow wax from (Z)-15b.

$[\alpha]_D^{25}$  -5.2 (0.38, CHCl<sub>3</sub>/CH<sub>3</sub>OH 10/3); IR (film): 3302, 2928, 2858, 1576, 1473. <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 500 MHz): 5.45(dt, *J*=11, 7.7 Hz, 1H), 5.12(t, *J*=10 Hz, 1H), 3.54(m, 1H), 3.27(m, 2H), 2.52(m, 2H), 2.00(m, 2H), 1.27(m, 2H), 1.18-1.25(m, 22H), 0.80(t, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 125 MHz): 133.2, 130.9, 50.3, 47.6, 31.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 27.8, 22.7, 14.1. ESI-MS *m/z* 283 [M+H]<sup>+</sup>

**(2R,3E)-Octadec-3-ene-1,2-diamine ((E)-15a)**

Obtained in 66% yield as a yellow-brown wax from (E)-15b.

$[\alpha]_D^{25}$  -4.1 (c 0.14, CH<sub>3</sub>OH/CHCl<sub>3</sub> 10/1); IR (film): 3437, 2930, 2845, 1642, 1458, 1331. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.59(dt, *J*=15.5, 7 Hz, 1H, H4), 5.33(dd, *J*=15.5, 7.5 Hz, 1H, H3), 3.23(m, 1H, H2), 2.66(dd, *J*=12.5, 5.5 Hz, 1H, H1a), 2.58(dd, *J*=12.5, 7 Hz, 1H, H1b), 2.00(m, 2H, H5), 1.72(br s, 4H), 1.34(m, 2H), 1.20-1.30(m, 22H), 0.86(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 132.5, 132.1, 56.2, 48.5, 32.5, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 22.8, 14.3. ESI-MS *m/z* 283 [M+H]<sup>+</sup>.

**(1'S,2'S,3'R)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-2,2-dimethylpropionamide (1c)**

Obtained in 47% yield (20 mg, 0.05 mmol) as a white solid from 1a.

mp 88-89°C;  $[\alpha]_D^{25}$  +0.43(c 1.57, CHCl<sub>3</sub>); IR (film): 3414, 2921, 2853, 1640, 1529, 1464, 1426, 1368, 1232, 1202, 1052. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 6.60(d, *J*=8 Hz, 1H, NH), 4.07(m, 1H, H2), 3.81(dd, *J*=11.5, 2.5 Hz, 1H, H1a), 3.65(dd, *J*=11.5, 6 Hz, 1H, H1b), 3.56(m, 2H, H3, H4), 1.67(m, 1H), 1.46(m, 2H), 1.20-1.36(m, 23H), 1.19(s, 9H), 0.86(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 179.9, 76.2, 72.8, 61.3, 52.6, 52.6, 38.9, 38.9, 33.4, 32.0, 29.8, 29.8, 29.5, 27.6, 27.5, 26.0, 22.8, 14.2. ESI-MS *m/z* 402 [M+H]<sup>+</sup>, 424 [M+Na], 826 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=4.85 min.

**(1'S,2'S,3'R)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]octanamide (1d)**

Obtained in 54% yield (29 mg, 0.07 mmol) as a white solid from **1a**.

mp 82-83°C;  $[\alpha]_D^{25}$  -1.6(c 0.95, CHCl<sub>3</sub>); IR (film): 3328, 2924, 2853, 1614, 1550, 1463, 1375, 1338, 1226, 1121, 1073, 1046. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 4.08(dt, *J*=5.9, 4.4 Hz, H<sub>2</sub>), 3.75(dd, *J*=11.2, 4.3 Hz, 1H, H<sub>1a</sub>), 3.70(dd, *J*=11.2, 5.7 Hz, 1H, H<sub>1b</sub>), 3.58(t, *J*=6 Hz, 1H, H<sub>3</sub>), 3.52(ddd, *J*=9.6, 5.9, 2.4 Hz, 1H, H<sub>4</sub>), 2.22(t, *J*=7.5 Hz, 2H), 1.62(m, 2H), 1.55(m, 1H), 1.41(m, 1H), 1.29-1.37(m, 32H), 0.91(t, *J*=7 Hz, 3H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 176.0, 76.0, 73.3, 62.1, 53.4, 37.3, 33.1, 33.0, 32.9, 30.8, 30.8, 30.5, 30.4, 30.3, 27.1, 27.0, 23.7, 23.7, 14.5. ESI-MS *m/z* 445 [M+H]<sup>+</sup>, 467 [M+Na], 910 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=8.05 min.

**(1'S,2'S,3'R)-4-tert-Butyl-N-[2,3-dihydroxy-1-(hydroxymethyl)heptadecyl]benzamide (1e)**

Obtained in 85% yield (37 mg, 0.08 mmol) as a white solid from **1a**.

mp 80-81°C;  $[\alpha]_D^{25}$  +17.7(c 1.46, CHCl<sub>3</sub>); IR (film): 3594, 3372, 2919, 2852, 1642, 1542, 1506, 1465, 1361, 1312, 1125, 1065, 850. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.73(d, *J*=8 Hz, 2H), 7.43(d, *J*=8 Hz, 2H), 7.16(d, *J*=8 Hz, 1H, NH), 4.35(m, 1H, H<sub>2</sub>), 4.13(br d, *J*=6.5 Hz, 1H, OH), 3.98(dd, *J*=11.5, 2.5 Hz, 1H, H<sub>1a</sub>), 3.82(dd, *J*=11.5, 5.5 Hz, 1H, H<sub>1b</sub>), 3.69(m, 2H, H<sub>3</sub>, H<sub>4</sub>), 1.73(m, 1H), 1.49(m, 2H), 1.32(s, 9H), 1.19-1.29(m, 22H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 168.5, 155.7, 130.8, 127.1, 125.7, 76.6, 72.9, 61.8, 53.6, 35.1, 33.5, 32.1, 313, 29.9, 29.8, 29.5, 25.9, 22.8, 14.3. ESI-MS *m/z* 479 [M+H]<sup>+</sup>, 501 [M+Na], 978 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=7.71 min.

**(3RS,1'S,2'S,3'R)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-3,5,5-trimethylhexanamide (1f)**

Obtained in 77% yield (32 mg, 0.07 mmol, mixture of epimers) as a white solid from **1a**

IR (film): 3411, 3243, 2965, 2855, 1633, 1535, 1464, 1369, 1246, 1223, 1169, 1044, 909, 736. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 6.41(br d, *J*=7 Hz, 1H), 4.15(m, 1H), 4.00(dd, *J*=11.2, 7.2 Hz, 1H), 3.87(dd, *J*=11.5, 2.5 Hz, 1H), 3.71(dd, *J*=11.5, 5.5 Hz, 1H), 3.62(m, 1H), 3.58(m, 1H), 2.24(ddd, *J*=17, 10, 5 Hz, 1H), 2.04(m, 1H), 1.99(ddd, *J*=17, 9, 4.5 Hz, 1H), 1.73(m, 1H), 1.49(m, 2H), 1.21-1.35(m, 23H), 1.12(dd, *J*=14, 5.5 Hz, 1H), 0.97(d, *J*=6.5 Hz, 3H), 0.91(s, 9H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 174.1, 76.8, 72.7, 61.7, 53.3, 50.8, 46.6, 33.5, 33.5, 32.1, 31.2, 30.1, 29.8, 29.8, 29.5, 27.6, 27.6, 25.8, 22.8,

22.7, 14.3. ESI-MS  $m/z$  459  $[M+H]^+$ , 481  $[M+Na]$ , 938  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=8.61 min.

**(2*RS*,1'*S*,2'*S*,3'*R*)-2-(4-Chlorophenyl)-*N*-[2,3-dihydroxy-1-(hydroxymethyl)heptadecyl]-3-methylbutyramide (1g)**

Obtained in 63% (37 mg, 0.05 mmol, mixture of epimers) as a white solid from **1a**.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.28(m, 4H), 6.41(d,  $J=7.5$  Hz, 1H, NH), 4.11(ddt,  $J=8.3, 5.8, 2.8$  Hz, 1H, H2), 3.90(dd,  $J=11.5, 2.5$  Hz, 1H, H1a), 3.72(dd,  $J=11.5, 6$  Hz, 1H, H1b), 3.45(dd,  $J=11.5, 3$  Hz, 1H, H3), 3.30(ddd,  $J=8.9, 6.6, 2.7$  Hz, 1H, H4), 2.85(d,  $J=10.5, 1H, H2'$ ), 2.35 (dq,  $J=13.2, 6.5$  Hz, 1H, H3'), 1.50-1.70(m, 3H), 1.20-1.35 (m, 23H), 1.03(d,  $J=6.5$  Hz, 3H), 0.88(t,  $J=7$  Hz, 3H), 0.69(d,  $J=6.5$  Hz, 3H). ESI-MS  $m/z$  524  $[M+H]^+$ , 535  $[M+Na]$ , 1046  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=8.47+9.02 min.

**(1'*S*,2'*S*,3'*R*)-*N*-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]furan-2-carboxamide (1h)**

Obtained in 47% yield (15 mg, 0.04 mmol) as a white solid from **1a**.

mp 99-100°C;  $[\alpha]_D^{25}$  -13.2 (c 0.73, CHCl<sub>3</sub>); IR (film): 3310, 2918, 2850, 1609, 1564, 1537, 1434, 1371, 1324, 1225, 1129, 1063, 1013. <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 500 MHz): 7.45(dd,  $J=1.75, 0.75$  Hz, 1H, CHar), 7.25(d,  $J=8.5$  Hz, 1H, NH), 7.11(dd,  $J=3.5, 0.5$  Hz, 1H), 6.49(dd,  $J=3.5, 1.5$  Hz, 1H), 4.24(m, 1H, H2), 3.89(dd,  $J=11.5, 3$  Hz, 1H, H1a), 3.75(dd,  $J=11.5, 6$  Hz, 1H, H1b), 3.65(dd,  $J=6.2, 3.2$  Hz, 1H, H3), 3.63(m, 1H, H4), 1.98(br s, 2H, OH), 1.68(m, 1H), 1.51(m, 2H), 1.20-1.40(m, 23H), 0.87(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 75 MHz): 159.1, 147.4, 144.6, 115.0, 112.4, 76.0, 72.7, 61.1, 52.0, 33.4, 32.0, 29.8, 29.8, 29.5, 25.9, 22.8, 14.2. ESI-MS  $m/z$  412  $[M+H]^+$ , 434  $[M+Na]$ , 846  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=3.82 min.

**(1'*S*,2'*S*,3'*R*)-*N*-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]propionamide (1i)**

Obtained in 69% yield (29 mg, 0.08 mmol) as a white solid from **1a**.

mp 91-92°C;  $[\alpha]_D^{25}$  +4.7 (c 0.32, CHCl<sub>3</sub>/CH<sub>3</sub>OH 1/1); IR (film): 2919, 2851, 2462, 2421, 1633, 1615, 1554, 1537, 1470, 1456, 1369, 1069, 1032. <sup>1</sup>H NMR (CDCl<sub>3</sub> + 1 drop CD<sub>3</sub>OD, 500 MHz): 6.68(d,  $J=8$  Hz, 1H), 4.07(m, 1H), 3.79(dd,  $J=11.5, 3.5$  Hz, 1H), 3.65(dd,  $J=11.5, 6$  Hz, 1H), 3.56(m, 2H), 2.23(q,  $J=7.7$  Hz, 2H), 2.17(br s, 2H), 1.63(m, 1H), 1.49(m, 1H), 1.41(m, 1H), 1.22-1.33(m, 22H), 1.13(t,  $J=7.7$  Hz, 3H), 0.86(t,  $J=7$  Hz, 3H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 125 MHz): 175.2, 175.1, 76.0, 72.7, 61.1, 52.2, 33.4, 32.0, 29.8, 29.7, 29.6, 29.5, 25.9, 22.8, 14.2, 9.9. ESI-MS  $m/z$  374  $[\text{M}+\text{H}]^+$ , 396  $[\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  20/80 RT=3.53 min.

**(1'S,2'S,3'R)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-3-methylbutyramide (1j)**

Obtained in 43% yield (19 mg, 0.05 mmol) as a white solid from **1a**.

mp 108-109°C;  $[\alpha]_D^{25} +0.5$  (c 1.01,  $\text{CHCl}_3$ ); IR (film): 3305, 2921, 2853, 2464, 2416, 1631, 1544, 1461, 1071, 1041.  $^1\text{H}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 500 MHz): 6.65(d,  $J=7.5$  Hz, 1H), 4.07(m, 1H), 3.77(dd,  $J=11.5$ , 3 Hz, 1H), 3.64(dd,  $J=11.5$ , 6 Hz, 1H), 3.55(m, 2H), 2.06(m, 3H), 1.65(m, 1H), 1.49(m, 1H), 1.42(m, 1H), 1.22-1.33(m, 22H), 0.93(d,  $J=5.5$  Hz, 6H), 0.85(t,  $J=6.7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 125 MHz): 173.9, 76.1, 72.6, 61.1, 52.3, 45.9, 33.3, 32.0, 29.8, 29.7, 29.5, 26.3, 25.9, 22.8, 22.5, 22.4, 14.2. ESI-MS  $m/z$  402  $[\text{M}+\text{H}]^+$ , 424  $[\text{M}+\text{Na}]$  826  $[\text{2M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  20/80 RT=4.17 min.

**(1'S,2'R,3'S)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-2,2-dimethylpropionamide (2c)**

Obtained in 88% yield (117 mg, 0.29 mmol) as a white solid from **2a**.

$[\alpha]_D^{25} -27.5$  (c 0.52,  $\text{CHCl}_3$ ); IR (film): 3359, 2921, 2851, 1639, 1522, 1452, 1363, 1206, 1063.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.59(d,  $J=8.5$  Hz, 1H), 4.20(m, 1H), 3.89(dd,  $J=11$ , 3, Hz, 1H), 3.78(dd,  $J=11$ , 5 Hz, 1H), 3.65(d,  $J=8.5$  Hz, 1H), 3.19(t,  $J=8$  Hz, 1H), 1.66(m, 1H), 1.55(m, 1H), 1.23-1.38(m, 24H), 1.22(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 180.9, 76.7, 71.3, 64.6, 50.0, 39.1, 32.9, 32.1, 29.9, 29.8, 29.8, 29.5, 27.7, 25.9, 22.8, 14.3. ESI-MS  $m/z$  402  $[\text{M}+\text{H}]^+$ , 424  $[\text{M}+\text{Na}]$ , 826  $[\text{2M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  20/80 RT=5.71 min.

**(1'S,2'R,3'R)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-2,2-dimethylpropionamide (3c)**

Obtained in 89% yield (106 mg, 0.26 mmol) as a white solid from **3a**.

$[\alpha]_D^{25} -0.3$ (c 0.75,  $\text{CHCl}_3$ ); IR (film): 3383, 2924, 2854, 1638, 1521, 1466, 1367, 1206, 1072.  $^1\text{H}$  NMR ( $\text{CDCl}_3 + 1$  drop  $\text{CD}_3\text{OD}$ , 500 MHz): 6.52(d,  $J=8$  Hz, 1H, NH), 3.97(m, 1H, H2), 4.40(br s, 1H, OH), 3.89(dd,  $J=11.2$ , 3.7 Hz, 1H, H1a), 3.70(dd,  $J=7$ , 4.5 Hz, 1H, H3), 3.68(dd,  $J=11.2$ , 4.7 Hz, 1H, H1b), 3.54(m, 1H, H4), 2.42(br s, 2H), 1.55(m, 1H),



1.49(m, 1H), 1.44(m, 1H), 1.23-1.34(m, 23H), 1.21(s, 9H), 0.88(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  + 1 drop  $\text{CD}_3\text{OD}$ , 100 MHz): 179.9, 72.4, 71.4, 61.9, 52.1, 38.9, 33.2, 32.0, 29.7, 29.7, 29.7, 29.6, 29.4, 27.4, 25.7, 22.7, 14.1. ESI-MS  $m/z$  402  $[\text{M}+\text{H}]^+$ , 424  $[\text{M}+\text{Na}]$ , 826  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  20/80 RT=4.94 min.

**(1'S,2'S,3'S)-N-[2,3-Dihydroxy-1-(hydroxymethyl)heptadecyl]-2,2-dimethylpropionamide (4c)**

Obtained in 89% yield (97 mg, 0.24 mmol) as a white solid from **4a**.

mp 82-83°C;  $[\alpha]_D^{25} +10.9$  (c 0.80,  $\text{CHCl}_3$ ); IR (film): 3432, 3332, 3232, 2919, 2851, 1619, 1532, 1470, 1342, 1203, 1064.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.49(d,  $J=8.5$  Hz, 1H), 4.20(d,  $J=4$  Hz, 1H), 4.07(ddd,  $J=10, 4, 2.5$  Hz, 1H), 3.78(m, 1H), 3.68(dt,  $J=10, 5$  Hz, 1H), 3.45(m, 1H), 3.43(dd,  $J=10, 8.5$  Hz, 1H), 3.01(t,  $J=5.2$  Hz, 1H), 2.88(d,  $J=10$  Hz, 1H), 1.64(m, 1H), 1.47(m, 1H), 1.41(m, 1H), 1.23-1.32(m, 23H), 1.22(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 180.6, 72.1, 69.7, 61.4, 52.8, 39.0, 32.8, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 27.6, 26.3, 22.8, 14.3. ESI-MS  $m/z$  402  $[\text{M}+\text{H}]^+$ , 424  $[\text{M}+\text{Na}]$ , 826  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  20/80 RT=6.49 min.

**(1'S,2'S,3'R)-N-(1-Azidomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (5c)**

Obtained in 75% yield (72 mg, 0.17 mmol) as a colourless wax from **5a**.

$[\alpha]_D^{25} +19.0$  (c 0.77,  $\text{CHCl}_3$ ); IR (film): 3344, 3291, 2962, 2917, 2853, 2111, 1636, 1516, 1464, 1286, 1224.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.30(d,  $J=8.5$  Hz, 1H), 4.13(m, 1H), 3.76(dd,  $J=12.5, 5.5$  Hz, 1H), 3.53-3.61(m, 3H), 2.75(d,  $J=5.5$  Hz, 1H), 1.63(m, 1H), 1.49(m, 1H), 1.40(m, 1H), 1.22-1.34(m, 23H), 1.21(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 179.4, 75.1, 73.2, 51.4, 50.9, 39.0, 33.1, 32.0, 29.8, 29.8, 29.8, 29.7, 29.5, 27.5, 26.0, 22.8, 14.2. ESI-MS  $m/z$  427  $[\text{M}+\text{H}]^+$ , 449  $[\text{M}+\text{Na}]$ , 876  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 RT=3.96 min.

**(1'S,2'S,3'R)-N-(1-Azidomethyl-2,3-dihydroxyheptadecyl)octanamide (5d)**

Obtained in 80% yield (274 mg, 0.58 mmol) as a colourless wax from **5a**.

$[\alpha]_D^{25} +13.6$  (c 1.61,  $\text{CHCl}_3$ ); IR (film): 3315, 3021, 2925, 2855, 2104, 1644, 1534, 1462, 1284, 1276, 1049, 763.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.07(d,  $J=8.5$  Hz, 1H), 4.13(m, 1H), 3.79(dd,  $J=12.5, 5.5$  Hz, 1H), 3.58-3.64(m, 3H), 3.28(d,  $J=6.5$  Hz, 1H), 2.27(d,  $J=6$  Hz, 1H), 2.21(td,  $J=7.5, 1.2$  Hz, 2H), 1.63(m, 2H), 1.50(m, 1H), 1.42(m, 1H), 1.25-1.31(m,

32H), 0.88(m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 174.1, 75.2, 73.3, 51.5, 50.7, 36.9, 33.2, 32.1, 31.8, 29.8, 29.8, 29.7, 29.5, 29.3, 29.1, 26.0, 25.8, 22.8, 22.7, 14.3, 14.2. ESI-MS  $m/z$  470  $[\text{M}+\text{H}]^+$ , 493  $[\text{M}+\text{Na}]$ , 960  $[2\text{M}+\text{Na}]$ .

**(1'S,2'R,3'S)-N-(1-Azidomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (6c)**

Obtained in 59% yield (37 mg, 0.09 mmol) as a colourless wax from **6a**.

$[\alpha]_{\text{D}}^{25}$  -16.2 (c 0.97,  $\text{CHCl}_3$ ); IR (film): 3371, 2916, 2851, 2105, 1645, 1520, 1455, 1280, 1225.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.19(d,  $J=8.5$  Hz, 1H), 4.35(ddd,  $J=14.5$ , 7, 1.5 Hz, 1H), 3.73(m, 1H), 3.58(dd,  $J=12.5$ , 7 Hz, 1H), 3.52(dd,  $J=12.5$ , 6.5 Hz, 1H), 3.48(br d,  $J=8.5$  Hz, 1H), 3.22(t,  $J=8.2$  Hz, 1H), 2.84(br s, 1H), 1.65(m, 1H), 1.54(m, 1H), 1.37(m, 2H), 1.24-1.32(m, 22H), 1.23(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 180.8, 75.1, 71.4, 53.0, 49.4, 39.2, 33.0, 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.8, 29.5, 27.6, 25.9, 22.8, 14.3. ESI-MS  $m/z$  427  $[\text{M}+\text{H}]^+$ , 449  $[\text{M}+\text{Na}]$ , 876  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 RT=4.64 min.

**(1'S,2'R,3'R)-N-(1-Azidomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (7c)**

Obtained in 79% yield (71 mg, 0.17 mmol) as a colourless wax from **7a**.

$[\alpha]_{\text{D}}^{25}$  +18.2 (0.66,  $\text{CHCl}_3$ ); IR (film): 3343, 2926, 2855, 2100, 1637, 1505, 1459, 1276, 1082.  $^1\text{H}$  NMR ( $\text{CDCl}_3$  + drop  $\text{CD}_3\text{OD}$ , 500 MHz): 6.33(d,  $J=8$  Hz, 1H), 4.06(dd,  $J=14$ , 7 Hz, 1H), 3.51(d,  $J=6$  Hz, 1H), 3.46(dd,  $J=12$ , 6 Hz, 1H), 3.43(dd,  $J=12$ , 6 Hz, 1H), 3.40(m, 1H), 1.49(m, 1H), 1.38(m, 2H), 1.20-1.32(m, 23H), 1.17(s, 9H), 0.85(t,  $J=6.7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  + drop  $\text{CD}_3\text{OD}$ , 125 MHz): 179.5, 73.1, 72.0, 52.2, 50.2, 39.0, 33.2, 32.0, 29.8, 29.7, 29.7, 29.6, 29.4, 27.5, 25.5, 22.8, 14.2. ESI-MS  $m/z$  427  $[\text{M}+\text{H}]^+$ , 449  $[\text{M}+\text{Na}]$ , 876  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 RT=4.36 min.

**(1'S,2'S,3'S)-N-(1-Azidomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (8c)**

Obtained in 72% yield (56 mg, 0.13 mmol) as a white solid from **8a**.

mp 69-70°C;  $[\alpha]_{\text{D}}^{25}$  +41.2 (c 1.00,  $\text{CHCl}_3$ ); IR (film): 3374, 2914, 2849, 2108, 1617, 1533, 1459, 1290, 1226.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 6.10(d,  $J=8.5$  Hz, 1H), 3.98(dd,  $J=12.5$ , 3.5 Hz, 1H), 3.94(d,  $J=4$  Hz, 1H), 3.89(ddd,  $J=9$ , 8, 3.5 Hz, 1H), 3.57(dd,  $J=12.2$ , 3.7 Hz, 1H), 3.38(m, 1H), 3.26(t,  $J=9.5$  Hz, 1H), 1.63(m, 1H), 1.42(m, 2H), 1.22-1.32(m, 23H),

1.21(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 180.5, 72.5, 69.1, 51.7, 50.9, 39.0, 32.6, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 27.6, 26.2, 22.8, 14.3. ESI-MS  $m/z$  427  $[\text{M}+\text{H}]^+$ , 449  $[\text{M}+\text{Na}]$ , 876  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  10/90 RT=5.09 min.

**(1'R,2'Z)-N-[1-(Hydroxymethyl)heptadec-2-enyl]-2,2-dimethylpropionamide ((Z)-13c)**

Obtained in 43% yield (75 mg, 0.20 mmol) as a white solid from (Z)13a.

mp 57-58°C;  $[\alpha]_D^{25} +19.0$  (c 0.77,  $\text{CHCl}_3$ ); IR (film): 3347, 2957, 2924, 2857, 1642, 1533, 1470, 1366, 1215, 1068.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 5.79(d,  $J=5.5$  Hz, 1H), 5.61(dt,  $J=10.5$ , 7.5 Hz, 1H), 5.30(dd,  $J=10.5$ , 9 Hz, 1H), 4.73(m, 1H), 3.64(dd,  $J=11$ , 4 Hz, 1H), 3.59(dd,  $J=11$ , 7 Hz, 1H), 2.10(m, 2H), 1.35(m, 2H), 1.24(m, 22H), 1.19(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 179.6, 135.6, 125.4, 67.0, 50.1, 38.7, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.3, 29.3, 28.0, 27.5, 22.7, 14.1. ESI-MS  $m/z$  368  $[\text{M}+\text{H}]^+$ , 390  $[\text{M}+\text{Na}]$ , 758  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  5/95 RT=5.26 min.

**(1'R,2'E)-N-[1-(Hydroxymethyl)heptadec-2-enyl]-2,2-dimethylpropionamide ((E)-13c)**

Obtained in 63% yield (72 mg, 0.20 mmol) as a white solid from (E)13a.

mp 63-64°C;  $[\alpha]_D^{25} -9.7$  (c 0.66,  $\text{CHCl}_3$ ); IR (film): 3360, 2954, 2922, 2851, 1636, 1529, 1465, 1366, 1206, 1077, 967.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 5.90(d,  $J=5.5$  Hz, 1H), 5.66(dt,  $J=15.5$ , 7 Hz, 1H), 5.40(dd,  $J=15.5$ , 6 Hz, 1H), 4.47(m, 1H), 3.68(br d,  $J=10.5$  Hz, 1H), 3.61(dd,  $J=10.5$ , 5.5 Hz, 1H), 2.03(m, 2H), 1.35(m, 2H), 1.23-1.31(m, 22H), 1.21(s, 9H), 0.87(t,  $J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 179.3, 134.2, 126.3, 66.4, 53.5, 38.9, 32.5, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 27.7, 22.7, 14.3. ESI-MS  $m/z$  368  $[\text{M}+\text{H}]^+$ , 390  $[\text{M}+\text{Na}]$ , 758  $[2\text{M}+\text{Na}]$ ; HPLC >95% pure  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  5/95 RT=5.72 min.

**(1'R,2'Z)-N-[1-(Hydroxymethyl)heptadec-2-enyl]octanamide ((Z)-13d)**

Obtained in 86% yield (250 mg, 0.61 mmol) as a white solid from (Z)13a.

mp 72-73°C;  $[\alpha]_D^{25} +18.1$  (c 0.75,  $\text{CHCl}_3$ ); IR (film): 3298, 2954, 2921, 2850, 1646, 1545, 1464, 1065, 753.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 5.70(d,  $J=6.3$  Hz, 1H), 5.61(dtd,  $J=10.5$ , 7.5, 0.9 Hz, 1H), 5.29(ddt,  $J=10.5$ , 9, 1.5 Hz, 1H), 4.76(m, 1H), 3.64(dd,  $J=10.8$ , 3.9 Hz, 1H), 3.59(dd,  $J=10.8$ , 6.3 Hz, 1H), 2.18(t,  $J=7.5$  Hz, 2H), 2.11(m, 2H), 1.62(m, 2H), 1.21-1.34(m, 32H), 0.87(m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 174.2, 135.6, 125.4, 67.0, 50.2, 36.9, 32.1, 31.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.2, 25.8, 22.8, 22.7,

14.3, 14.2. ESI-MS  $m/z$  410  $[M+H]^+$ , 842  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 5/95 RT=12.01 min.

**(1'R,3'Z)-N-[(1-Azidomethyl)heptadec-2-enyl]-2,2-dimethylpropionamide ((Z)-14c)**

Obtained in 90% (266 mg, 0.68 mmol) yield as a white solid from (Z)14a

mp 46-47°C;  $[\alpha]_D^{25}$  -1.88 (c 0.69, CHCl<sub>3</sub>); IR (film): 3321, 2954, 2923, 2853, 2097, 16376, 1524, 1441, 878. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.63(m, 2H), 5.42(ddt,  $J=11, 9, 1.5$  Hz, 1H), 4.89(dtd,  $J=8.7, 4.9, 1$  Hz, 1H), 3.51(dd,  $J=12.5, 5$  Hz, 1H), 3.34(dd,  $J=12, 4.5$  Hz, 1H), 2.09(m, 2H), 1.34(m, 2H), 1.24-1.29(m, 22H), 1.20(s, 9H), 0.88(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 177.9, 136.0, 125.8, 55.0, 46.8, 38.9, 32.5, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 28.2, 22.8, 14.3. ESI-MS  $m/z$  393  $[M+H]^+$ , 415  $[M+Na]$ , 808  $[2M+Na]$ .

**(1'R,3'E)-N-[(1-Azidomethyl)heptadec-2-enyl]-2,2-dimethylpropionamide ((E)-14c)**

Obtained in 94% (386 mg, 0.61 mmol) yield as a white solid from (E)14a.

mp 43-44°C;  $[\alpha]_D^{25}$  +3.6 (c 1.09, CHCl<sub>3</sub>); IR (film): 3321, 2957, 2921, 2852, 2097, 1636, 1528, 1463, 1363, 1303, 1226, 967. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.73(d,  $J=7.5$  Hz, 1H), 5.67(dtd,  $J=15.5, 6.7, 1$  Hz, 1H), 5.42(ddt,  $J=15.5, 6.2, 1.5$  Hz, 1H), 4.59(m, 1H), 3.48(dd,  $J=12.5, 4.5$  Hz, 1H), 3.38(dd,  $J=12, 4.5$  Hz, 1H), 2.03(m, 2H), 1.35(m, 2H), 1.24-1.30(m, 22H), 1.21(s, 9H), 0.87(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 178.0, 134.5, 126.5, 54.9, 50.7, 38.9, 32.5, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 27.6, 22.8, 14.2. ESI-MS  $m/z$  393  $[M+H]^+$ , 415  $[M+Na]$ , 808  $[2M+Na]$ .

**(2S,3S,4R)-1,2-Diaminooctadecane-3,4-diol (9a)**

Obtained in 99% yield from 5a.

mp 104-106°C;  $[\alpha]_D^{25}$  +4.7 (c 0.15, CH<sub>3</sub>OH); IR (neat): 3351, 2917, 2851, 1578, 1475, 1378, 1324, 1059. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.49(td,  $J=8, 2.5$  Hz, 1H, H4), 3.29(dd,  $J=7.5, 5$  Hz, 1H, H3), 2.88(dd,  $J=12.5, 4$  Hz, 1H, H1a), 2.85(m, 1H, H2), 2.66(dd,  $J=12.5, 6$  Hz, 1H, H1b), 1.75(m, 1H), 1.55(m, 1H), 1.24-1.42(m, 24H), 0.90(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz): 77.7, 74.5, 55.9, 44.6, 34.9, 33.1, 31.0, 30.8, 30.8, 30.5, 26.6, 23.8, 14.5. ESI-MS  $m/z$  317  $[M+H]^+$ , 339  $[M+Na]$ . HRMS: Calculated: 317.3168; Found 317.3170; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=3.58 min.

**(1'S,2'S,3'R)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)carbamic acid *tert*-butyl ester (9b)**

Obtained in 82% yield from 5b.

$[\alpha]_D^{25} +13.4$  (c 1.24, CHCl<sub>3</sub>); IR (film): 3342, 2924, 2873, 2850, 1691, 1522, 1461, 1365, 1244, 1165. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.74(m, 1H), 3.47(m, 2H), 2.94(dd, *J*=13, 4 Hz, 1H), 2.74(dd, *J*=13, 7.5 Hz, 1H), 1.67(m, 1H), 1.56(m, 1H), 1.45(s, 9H), 1.45(m, 2H), 1.27-1.38(m, 24H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 158.1, 80.3, 77.3, 73.2, 54.4, 42.4, 33.5, 33.1, 30.8, 30.8, 30.5, 28.8, 27.0, 23.7, 14.5. ESI-MS *m/z* 417 [M+H]<sup>+</sup>, 856 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 20/80 RT=1.17 min.

**(1'S,2'S,3'R)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (9c)**

Obtained in 78% yield from **5c**.

$[\alpha]_D^{25} +20.0$  (c 0.81, CHCl<sub>3</sub>); IR (film): 3361, 2927, 2851, 1634, 1525, 1460, 1363, 1205. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 4.08(dt, *J*=7.2, 5.2 Hz, 1H, H2), 3.51(dd, *J*=11.5, 5.8 Hz, 1H, H3), 3.46(m, 1H, H4), 2.96(dd, *J*=13.2, 4.7 Hz, 1H, H1a), 2.81(dd, *J*=13.2, 7.2 Hz, 1H, H1b), 1.65(m, 1H), 1.56(m, 1H), 1.26-1.44(m, 24H), 1.21(s, 9H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>+ 1drop CD<sub>3</sub>OD, 100 MHz): 179.1, 179.0, 76.1, 72.9, 50.8, 50.7, 40.6, 38.8, 38.8, 33.7, 32.0, 30.0, 29.8, 29.8, 29.5, 27.5, 27.5, 26.2, 22.8, 14.2. Rotamers were observed. ESI-MS *m/z* 401 [M+H]<sup>+</sup>, 824 [2M+Na]; HPLC >95% pure.

**(1'S,2'S,3'R)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)octanamide (9d)**

Obtained in 80% yield from **5d**.

mp 116-117°C;  $[\alpha]_D^{25} +17.4$  (c 0.85, CHCl<sub>3</sub>); IR (film): 3304, 2926, 2849, 1632, 1539, 1467, 1058. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 4.06(dt, *J*=7.4, 4.8 Hz, 1H, H2), 3.49(m, 1H, H3), 3.46(m, 1H, H4), 2.94(dd, *J*=13.2, 4.2 Hz, 1H), 2.74(dd, *J*=13.2, 7.7 Hz, 1H), 2.24(t, *J*=7.5 Hz, 2H), 1.63(m, 3H), 1.55(m, 1H), 1.29-1.42(m, 32H), 0.91(t, *J*=7 Hz, 3H), 0.90(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 176.3, 77.0, 73.2, 53.7, 42.4, 37.3, 33.4, 33.1, 32.9, 30.8, 30.8, 30.5, 30.4, 30.3, 27.1, 27.0, 23.7, 23.7, 14.4. ESI-MS *m/z* 443 [M+H]<sup>+</sup>; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=7.04 min.

**(2S,3R,4S)-1,2-Diaminooctadecane-3,4-diol (10a)**

Obtained in 90% yield from **6a**

mp 116-118°C;  $[\alpha]_D^{25} -13.3$  (c 0.09, CH<sub>3</sub>OH); IR (neat): 3359, 2917, 2850, 1634, 1469, 1434, 1329, 1074. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.53 (m, 1H, H4), 3.30(m, 1H, H3), 2.98(m, 1H, H2), 2.74(dd, *J*=13, 5.5Hz, 1H, H1a), 2.67(dd, *J*=13, 7.5 Hz, 1H, H1b), 1.71(m, 1H), 1.56(m, 1H), 1.32(m, 24H), 0.90(t, *J*=6.7z, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125

MHz): 75.5, 73.3, 54.3, 46.3, 35.0, 33.0, 30.9, 30.8, 30.7, 30.4, 26.8, 23.7, 14.4. ESI-MS  $m/z$  317  $[M+H]^+$ , 339  $[M+Na]$ . HRMS: Calculated: 317.3168; Found 317.3170; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.83 min.

**(1'S,2'R,3'S)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (10c)**

Obtained in 75% yield from **6c**

$[\alpha]_D^{25}$  -26.3 (c 0.60, CHCl<sub>3</sub>); IR (film): 3347, 2924, 2853, 1635, 1518, 1458, 1366, 1205. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 4.14(dt,  $J=6.8, 1.3$  Hz, 1H, H2), 3.38(dd,  $J=8.5, 1.5$  Hz, 1H, H3), 3.24(dt,  $J=8.4, 2.4$  Hz, 1H, H4), 2.85(d,  $J=6.8$  Hz, 2H, H1a, H1b), 1.75(m, 1H), 1.55(m, 1H), 1.26-1.44(m, 24H), 1.21(s, 9H), 0.90(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz): 182.6, 75.1, 72.4, 53.6, 44.0, 40.0, 34.2, 33.1, 30.8, 30.8, 30.8, 30.6, 30.6, 30.5, 27.9, 27.8, 26.7, 23.8, 14.5. ESI-MS  $m/z$  401  $[M+H]^+$ , 423  $[M+Na]$ , 824  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=5.45 min.

**(2S,3R,4R)-1,2-Diaminooctadecane-3,4-diol (11a)**

Obtained in 83% yield from **7a**

mp 116-118°C;  $[\alpha]_D^{25}$  +5.4 (c 0.11, CH<sub>3</sub>OH); IR (neat): 3349, 2923, 2859, 1673, 1590, 1468, 1384, 1339, 1139, 1069. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.62(dt,  $J=6.5, 3.3$  Hz, 1H, H4), 3.34 (t,  $J=3.5$  Hz, 1H, H3), 2.83 (m, 1H, H2), 2.78 (dd,  $J=12.8, 5.1$  Hz, 1H, H1a), 2.64 (dd,  $J=12.8, 7.2$  Hz, 1H, H1b), 1.52(m, 2H), 1.47(m, 1H), 1.31(m, 23H), 0.90 (t,  $J=6.9$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz): 74.4, 74.4, 56.7, 46.1, 34.8, 33.1, 30.9, 30.8, 30.8, 30.5, 26.9, 23.8, 14.5. ESI-MS  $m/z$  317  $[M+H]^+$ , 339  $[M+Na]$ . HRMS: calculated: 317.3168; found: 317.3170; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.54 min.

**(1'S,2'R,3'R)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (11c)**

Obtained in 70% yield from **7c**

$[\alpha]_D^{25}$  +3.7 (c 0.78, CHCl<sub>3</sub>); IR (film): 3358, 2924, 2854, 1638, 1518, 1466, 1366, 1206. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 4.01(m, 1H, H2), 3.52(dd,  $J=6.2, 2.2$  Hz, 1H, H3), 3.40(m, 1H, H4), 2.86(dd,  $J=13, 6$  Hz, 2H, H1a), 2.78(dd,  $J=13, 7$  Hz, 1H, H1b), 1.52(m, 2H), 1.24-1.38(m, 24H), 1.21(s, 9H), 0.90(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 181.2, 74.7, 73.4, 53.4, 44.3, 39.5, 35.1, 33.9, 33.1, 30.8, 30.8, 30.7, 30.5, 27.8, 26.8, 23.7, 14.5.

ESI-MS  $m/z$  401  $[M+H]^+$ , 423  $[M+Na]$ , 824  $[2M+Na]$  HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=5.12 min.

**(2S,3S,4S)-1,2-Diaminooctadecane-3,4-diol (12a)**

Obtained in 97% yield from **8a**.

mp 105-107°C;  $[\alpha]_D^{25}$  - 8.0 (c 0.15, CH<sub>3</sub>OH); IR (neat): 3412, 2923, 2856, 1608, 1467, 1316, 1046, 1009, 962, 916. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.66(m, 1H, H4), 3.28 (dd,  $J=6.9, 2.5$  Hz, 1H, H3), 2.89(dd,  $J=13, 4.5$  Hz, 1H, H1a), 2.81(dt,  $J=6.8, 4.7$  Hz, 1H, H2), 2.65(dd,  $J=13, 7$ Hz, 1H, H1b), 1.46-1.60(m, 3H), 1.24-1.40(m, 23H), 0.90 (t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz): 76.8, 72.3, 55.7, 45.5, 34.7, 33.1, 30.9, 30.8, 30.8, 30.5, 27.1, 23.8, 14.5. ESI-MS  $m/z$  317  $[M+H]^+$ , 339  $[M+Na]$ . HRMS: calculated: 317.3168; found: 317.3170; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.84 min.

**(1'S,2'S,3'S)-N-(1-Aminomethyl-2,3-dihydroxyheptadecyl)-2,2-dimethylpropionamide (12c)**

Obtained in 75% yield from **8c**.

$[\alpha]_D^{25}$  +17.1 (c 1.05, CHCl<sub>3</sub>); IR (film): 3346, 2924, 2853, 1637, 1533, 1466, 1367, 1207. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz): 3.93(dt,  $J=7.4, 5$  Hz, 1H, H2), 3.46(m, 1H, H4), 3.40(dd,  $J=8, 1.5$  Hz, 1H, H3), 2.98(dd,  $J=13.2, 4.7$  Hz, 1H, H1a), 2.85(dd,  $J=13.2, 7.2$  Hz, 1H, H1b), 1.58(m, 1H), 1.49(m, 1H), 1.44(m, 1H), 1.25-1.38(m, 23H), 1.21(s, 9H), 0.90(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 125 MHz): 182.3, 74.5, 71.6, 54.6, 43.4, 39.9, 34.2, 33.1, 30.8, 30.8, 30.8, 30.7, 30.5, 27.9, 27.8, 27.1, 23.8, 14.5. ESI-MS  $m/z$  401  $[M+H]^+$ , 423  $[M+Na]$ , 824  $[2M+Na]$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=4.68 min.

**(1'R,2'Z)- N-[(1-Aminomethyl)heptadec-2-enyl]carbamic acid *tert*-butyl ester ((Z)-15b)**

Obtained in 84% yield as a colourless oil from (Z)-**14b**.

$[\alpha]_D^{25}$  +19.3 (c 1.80, CHCl<sub>3</sub>); IR (film): 3361, 2925, 2855, 1706, 1514, 1461, 1385, 1368, 1248, 1172. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.54(dt,  $J=10.5, 7.7$  Hz, 1H), 5.18(dd,  $J=10.5, 9$  Hz, 1H), 4.68(br s, 1H), 4.30(m, 1H), 2.73(dd,  $J=12.2, 6.3$  Hz, 1H), 2.65(dd,  $J=12.7, 5.2$  Hz, 1H), 2.09(m, 2H), 1.42(s, 9H), 1.33(m, 2H), 1.23-1.30(m, 22H), 0.86(t,  $J=7$  Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 155.6, 134.3, 128.1, 79.4, 50.8, 46.9, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 28.5, 28.1, 22.8, 14.2. ESI-MS  $m/z$  383  $[M+H]^+$ ; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=7.53 min.

**(1'R,3'Z)-N-[(1-Aminomethyl)heptadec-2-enyl]2,2-dimethylpropionamide ((Z)-15c)**

Obtained in 79% yield as a colourless oil from (Z)-14c.

$[\alpha]_D^{25} +11.9$  (c 0.47, CHCl<sub>3</sub>); IR (film): 3358, 2959, 2930, 2851, 1642, 1525, 1457, 1359, 1193. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.85(d, *J*=8.5 Hz, 1H), 5.59(dtd, *J*=10, 7.5 0.7 Hz, 1H), 5.25(dd, *J*=10.5, 9 Hz, 1H), 4.65(m, 1H), 2.82(dd, *J*=12.7, 5.7 Hz, 1H), 2.71(dd, *J*=12.7, 5.7 Hz, 1H), 2.12(m, 2H), 1.35(m, 2H), 1.22-1.32(m, 22H), 1.19(s, 9H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 178.0, 135.0, 127.2, 49.0, 46.5, 38.8, 32.0, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 29.5, 28.2, 27.7, 22.8, 14.3. ESI-MS *m/z* 367 [M+H]<sup>+</sup>, 756 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=6.89 min.

**(1'R,3'Z)-N-[(1-Aminomethyl)heptadec-2-enyl]octanamide ((Z)-15d)**

Obtained in 84% yield as a white solid from (Z)-14d.

mp 66-67°C;  $[\alpha]_D^{25} +11.3$  (c 1.03, CHCl<sub>3</sub>); IR (film): 3290, 2926, 2855, 1644, 1544, 1462, 1374, 1269, 1119, 724. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.64(d, *J*=8 Hz, 1H), 5.58(dtd, *J*=10.7, 7.2, 1 Hz, 1H), 5.23(ddt, *J*=11, 9.5, 1.5 Hz, 1H), 4.69(m, 1H), 2.80(dd, *J*=13, 5.5 Hz, 1H), 2.69(dd, *J*=13, 6.5 Hz, 1H), 2.15(t, *J*=7.7 Hz, 2H), 2.13(m, 2H), 1.61(m, 2H), 1.31-1.37(m, 4H), 1.30-1.24(m, 30H), 0.87(t, *J*=7 Hz, 3H), 0.86(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 173.3, 172.5, 134.8, 132.6, 131.3, 127.2, 48.9, 47.9, 46.4, 45.2, 36.9, 36.8, 31.9, 31.6, 29.7, 29.6, 29.6, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 29.2, 29.0, 28.0, 27.7, 25.7, 22.7, 22.6, 22.5, 14.1, 14.0. (rotamers observed) ESI-MS *m/z* 409 [M+H]<sup>+</sup>, 432 [M+Na], 841 [2M+Na].

**(1'R,2'E)-N-[(1-Aminomethyl)heptadec-2-enyl]carbamic acid *tert*-butyl ester ((E)-15b)**

Obtained in 85% yield as a colourless oil from (E)-14b.

$[\alpha]_D^{25} -3.6$  (c 0.42, CHCl<sub>3</sub>); IR (film): 3352, 2923, 2853, 1685, 1527, 1472, 1390, 1365, 1247, 1173. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 5.61(dt, *J*=15, 7 Hz, 1H), 5.29(dd, *J*=15.5, 6 Hz, 1H), 4.77(m, 1H), 4.03(br s, 1H), 2.65(d, *J*=5.5 Hz, 1H), 2.01(m, 2H), 1.43(s, 9H), 1.34(m, 2H), 1.21-1.30(m, 22H), 0.86(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 155.7, 133.1, 132.9, 128.4, 79.4, 54.6, 46.4, 46.3, 32.6, 32.5, 32.4, 32.0, 29.8, 29.6, 29.5, 29.3, 29.3, 28.7, 28.6, 28.5, 28.3, 22.8, 14.2. ESI-MS *m/z* 383 [M+H]<sup>+</sup>.

**(1'R,3'E)-N-[(1-Aminomethyl)heptadec-2-enyl]-2,2-dimethylpropionamide ((E)-15c)**



Obtained in 82% yield as a colourless oil from (*E*)-**14c**.

$[\alpha]_D^{25}$  -14.6 (c 0.59, CHCl<sub>3</sub>); IR (film): 3332, 2960, 2925, 2854, 1639, 1528, 1459. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 6.02(d, *J*=8 Hz, 1H), 5.60(dtd, *J*=15.5, 6.5, 1 Hz, 1H), 5.33(dd, *J*=11.5, 6 Hz, 1H), 4.40(m, 1H), 2.84(dd, *J*=12.2, 5.2 Hz, 1H), 2.74(dd, *J*=12.5, 5 Hz, 1H), 2.02(m, 2H), 1.35(m, 2H), 1.23-1.32(m, 22H), 1.21(s, 9H), 0.87(t, *J*=7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 178.1, 133.1, 127.8, 52.3, 45.7, 38.9, 32.5, 32.1, 29.8, 29.6, 29.5, 29.3, 27.8, 22.8, 14.3. ESI-MS *m/z* 367 [M+H]<sup>+</sup>, 756 [2M+Na]; HPLC >95% pure H<sub>2</sub>O/CH<sub>3</sub>CN 10/90 (0.1%TFA) RT=7.33 min.

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