Asymmetric Synthesis of 2-Amino-1,3-diols and D-*erythro*-Sphinganine

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The asymmetric synthesis of protected 2-amino-1,3-diols (*S*,*R*)-**5** starting from 2,2-dimethyl-1,3-dioxan-5-one is described. The stereogenic centres are generated by α-alkylation using the SAMP/RAMP hydrazone methodology and diastereoselective reduction of the ketones (*S*)-**2** with L-selectride. The resulting alcohols (*S*,*S*)-**3** are converted into the amines (*S*,*R*)-**4** by nucleophilic substitution with sodium azide and subsequent reduction with lithium aluminium hydride. The products are obtained in high diastereomeric and enantiomeric excesses (*de* ≥ 96%, *ee* = 90–94%). By employing this methodology, the ammonium salt of D-*erythro*-sphinganine (*R*,*S*)-**11** was synthesised starting from RAMP-hydrazone (*R*)-**1** in 47% overall yield and with excellent diastereomeric and enantiomeric excess (*de*, *ee* ≥ 96%).

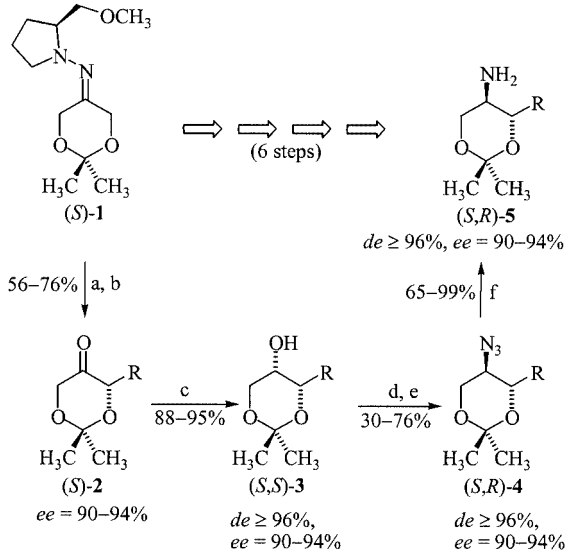
Introduction

The vicinal amino alcohol functionality is a common structural feature in many natural products and biologically active molecules.[1] A broad class of naturally occurring molecules containing the vicinal amino alcohol moiety are the sphingolipids, such as ceramides, cerebrosides and gangliosides. Structurally, these molecules contain a 2-amino-1,3-diol subunit. They are important components of the cell membrane and take part in many physiological processes like cell recognition, signal transduction and cell-growth modulation.[2] Additionally, members of the sphinganine family have been found to be potent inhibitors of the protein kinase C.[3] The key step in the preparation of the sphinganines is the stereoselective synthesis of the aminodiol functionality. In the last few years various methods for the synthesis of sphinganine and its derivatives have been developed.[4]

Our synthetic strategy, employing the SAMP/RAMP-hydrazone methodology[5] starting from the easily available dihydroxy acetone equivalent 1,3-dioxan-5-one, provides a flexible route to 2-amino-1,3-diols and allows a broad range of modifications in the side chain of the sphinganines. In addition, both *anti*-configured enantiomers are accessible by this method.

Results and Discussion

As shown in Scheme 1, our synthesis starts from the SAMP-hydrazone (*S*)-**1**, which was readily prepared on a multigram scale by condensation of (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP) with 2,2-dimethyl-1,3-dioxan-5-one.[6] In the first step the SAMP-hydrazone (*S*)-**1** was alkylated in the α-position.[7] Subsequently, the chiral auxiliary was removed by treatment with a saturated aqueous solution of oxalic acid[8] to afford the acetal-protected



Scheme 1. a) *t*BuLi, THF, −78 °C, then RX, −100 °C; b) aq. oxalic acid; c) L-Selectride®, THF, −78 °C; d) MsCl, CH_2Cl_2, Et_3N, 0 °C → room temp.; e) NaN_3, 18-crown-6, DMF, 100 °C; f) LAH, THF, room temp.

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ketodiols (*S*)-**2** (Scheme 1). After the racemisation-free removal of the auxiliary a variety of α-substituted ketones (*S*)-**2a**−**e** could be obtained in good overall yields (56−76%) and very good enantiomeric excess (*ee* = 90−94%; Table 1).

Table 1. Synthesis of α-substituted ketones (*S*)-**2a**−**e**

(*S*)-**2**	R	X	Yield [%][a]	*ee*[b] [%]	$[\alpha]_D$[c], (c)
(*S*)-**2a**		Br	56	94	−216.0 (1.07)
(*S*)-**2b**	*n*-$C_{10}H_{21}$	Br	76	93	−181.5 (1.03)
(*S*)-**2c**	Bn	Br	72	94	−212.6 (1.06)
(*S*)-**2d**	*p*-$BrC_6H_4CH_2$	Br	71	90	−166.6 (1.08)
(*S*)-**2e**	$BnOCH_2$	Cl	59	94	−171.8 (1.08)

[a] Overall yield starting from (*S*)-**1**. [b] Determined by GC on a chiral stationary phase by comparison with racemic samples. [c] All optical rotations were measured in Uvasol grade $CHCl_3$ at $T = 26 \pm 3$ °C.

The alcohols (*S*,*S*)-**3a**−**e** were prepared by diastereoselective reduction of the ketones (*S*)-**2a**−**e** with L-selectride. The results are shown in Table 2. All compounds could be obtained in very good yields (88−95%) and excellent diastereomeric excess (*de* ≥ 96%).

Table 2. Synthesis of the alcohols (*S*,*S*)-**3a**−**e**

(*S*,*S*)-**3**	R	Yield [%][a]	*de*[b] [%]	$[\alpha]_D$[c], (c)
(*S*,*S*)-**3a**		88	82 (≥ 96)[d]	−2.4 (0.99)
(*S*,*S*)-**3b**	*n*-$C_{10}H_{21}$	89	≥ 96	+5.6 (1.00)
(*S*,*S*)-**3c**	Bn	90	≥ 96	+4.7 (1.28)[e]
(*S*,*S*)-**3d**	*p*-$BrC_6H_4CH_2$	85	80 (≥ 96)[d]	−6.2 (0.98)
(*S*,*S*)-**3e**	$BnOCH_2$	95	≥ 96	+8.9 (1.15)[e]

[a] Based on isolated material after flash chromatography. [b] Determined by ^{13}C NMR spectroscopy. [c] All optical rotations were measured in Uvasol grade $CHCl_3$ at $T = 26 \pm 3$ °C. [d] Numbers in parenthesis indicate the value after column chromatography. [e] Rotations were measured in Uvasol grade C_6H_6 at $T = 26 \pm 3$ °C.

The azides (*S*,*R*)-**4a**−**e** were synthesised by conversion of the hydroxy group into a mesylate and subsequent nucleophilic substitution with sodium azide.[9] The reaction occurred with complete inversion of configuration at the stereogenic centre. The results are summarised in Table 3.

The synthesis of the amines (*S*,*R*)-**5** was carried out by reduction of the azides (*S*,*R*)-**4** with lithium aluminium hydride in THF. The amines (*S*,*R*)-**5a**−**e** could be obtained in very good yields (65−99%) and excellent diastereomeric excess (*de* ≥ 96%) without further purification (Table 4).

Table 3. Synthesis of the azides (*S*,*R*)-**4a**−**e**

(*S*,*R*)-**4**	R	Yield [%][a]	*de*[b] [%]	$[\alpha]_D$[c], (c)
(*S*,*R*)-**4a**		30	≥ 96	−40.7 (1.08)
(*S*,*R*)-**4b**	*n*-$C_{10}H_{21}$	32	≥ 96	−31.0 (1.12)
(*S*,*R*)-**4c**	Bn	48	≥ 96	−39.1 (1.03)
(*S*,*R*)-**4d**	*p*-$BrC_6H_4CH_2$	76	≥ 96	−31.0 (1.06)
(*S*,*R*)-**4e**	$BnOCH_2$	32	≥ 96	−21.8 (0.99)

[a] Overall yield starting from (*S*,*S*)-**3** after flash chromatography. [b] Determined by ^{13}C NMR spectroscopy. [c] All optical rotations were measured in Uvasol grade $CHCl_3$ at $T = 26 \pm 3$ °C.

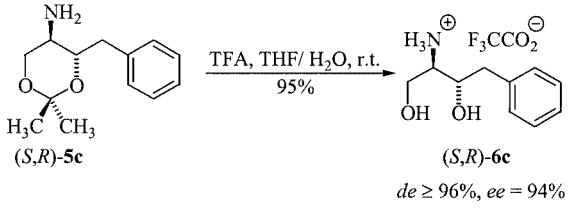
Table 4. Synthesis of the amines (*S*,*R*)-**5a**−**e**

(*S*,*R*)-**5**	R	Yield [%]	*de*[a] [%]	$[\alpha]_D$[b], (c)
(*S*,*R*)-**5a**		65	≥ 96	−33.4 (1.08)
(*S*,*R*)-**5b**	*n*-$C_{10}H_{21}$	99	≥ 96	−30.8 (1.02)
(*S*,*R*)-**5c**	Bn	99	≥ 96	−46.9 (0.98)
(*S*,*R*)-**5d**	*p*-$BrC_6H_4CH_2$	99	≥ 96	−36.4 (0.99)
(*S*,*R*)-**5e**	$BnOCH_2$	97	≥ 96	−12.4 (0.93)

[a] Determined by ^{13}C NMR spectroscopy. [b] All optical rotations were measured in Uvasol grade $CHCl_3$ at $T = 26 \pm 3$ °C.

The relative configuration of the amines (*S*,*R*)-**5a**−**e** was determined to be *anti* by ^1H NMR spectroscopy. For all synthesised amines (*S*,*R*)-**5a**−**e** the coupling constant for the corresponding H atoms is 9.6 Hz. Due to the known (*S*)-configuration of the stereogenic centre generated by α-alkylation, the absolute configuration could be assigned as (*S*,*R*).[7]

Finally, the acetal group of the amine (*S*,*R*)-**5c** was removed by hydrolysis with trifluoroacetic acid (TFA) in a mixture of THF and water at room temperature to afford the ammonium salt (*S*,*R*)-**6c** in excellent yield (Scheme 2). The enantiomeric excess of the final products was based on the diastereomeric excess, as all further reaction steps proceed without racemisation.

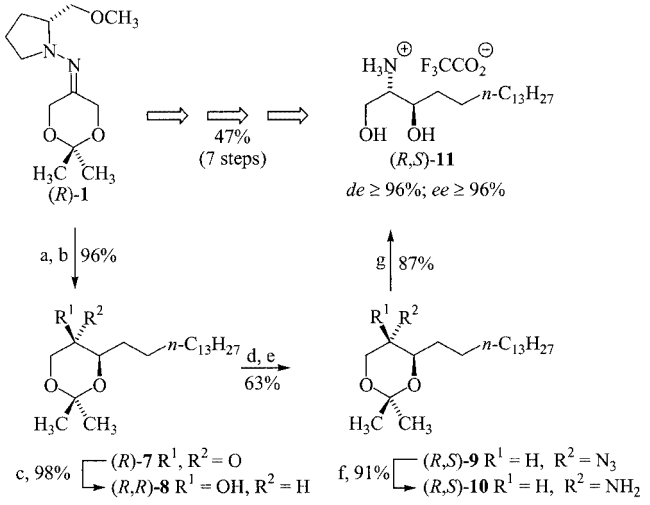


(*S*,*R*)-**5c** (*S*,*R*)-**6c**

de ≥ 96%, *ee* = 94%

Scheme 2. Cleavage of the acetal group by trifluoroacetic acid

We then employed our protocol in the synthesis of the ammonium salt D-*erythro*-sphinganine (*R*,*S*)-**11** (Scheme 3). In this case the RAMP-hydrazone (*R*)-**1** was used instead of the SAMP-hydrazone to afford the correct absolute con-



Scheme 3. a) *t*BuLi, THF, −78 °C, then pentadecyl bromide, −100 °C; b) aq. oxalic acid; c) L-Selectride®, THF, −78 °C; d) MsCl, CH_2Cl_2, Et_3N, 0 °C → room temp.; e) NaN_3, 18-crown-6, DMF, 100 °C; f) LAH, THF, room temp.; g) TFA, THF/H_2O, room temp.

figuration. In the first step the hydrazone (*R*)-**1** was alkylated with pentadecyl bromide. Subsequently the hydrazone was cleaved with a saturated aqueous solution of oxalic acid (Scheme 3). As a result the ketone (*R*)-**7** could be obtained in excellent yield (96%) and enantiomeric excess (*ee* ≥ 96%). As described in the former cases the ketone (*R*)-**7** was reduced with L-Selectride to give the alcohol (*R*,*R*)-**8** in practically quantitative yield (98%) and very high diastereomeric excess (*de* ≥ 96%). Treatment of the alcohol with methanesulfonyl chloride yielded the corresponding mesylate, which was then converted into the azide (*R*,*S*)-**9** by nucleophilic substitution with sodium azide in DMF in the presence of 18-crown-6. Reduction of the azide (*R*,*S*)-**9** with lithium aluminium hydride followed by hydrolytic cleavage of the acetonide group with trifluoroacetic acid in THF and water afforded the ammonium salt (*R*,*S*)-**11** with an overall yield of 47%, a diastereomeric excess of greater than 96% and an enantiomeric excess of greater than 96%.

Conclusion

In summary, a practical method for the diastereo- and enantioselective synthesis of 2-amino-1,3-diols, using the SAMP/RAMP-hydrazone methodology as stereoselective key step, has been developed. This methodology was applied to generate the 2-amino-1,3-diol functionality in the efficient asymmetric synthesis of the D-*erythro*-sphinganine ammonium salt.

Experimental Section

General Remarks: All solvents were dried and purified prior to use. All reactions were carried out under dry argon, using standard Schlenk techniques. THF was freshly distilled under argon from Na/Pb alloy in the presence of benzophenone. Reagents of commercial quality were used from freshly opened containers. Analytical TLC: Silica gel 60 F_{254} plates Merck, Darmstadt. Preparative column chromatography: Silica gel 60, particle size 0.040−0.063 mm, Merck, Darmstadt. Optical rotation values were measured on a Perkin−Elmer P241 (589 nm), solvents used were of Merck Uvasol quality. Microanalyses were obtained with Heraeus, CHN-O-Rapid. All melting points (Büchi 510) are uncorrected. IR: Perkin−Elmer FT/IR 1750. NMR spectra: Varian VXR 300, Varian Gemini 300, Varian Inova 400, TMS as internal standard. MS: Finnigan MAT 212 and Finnigan SSQ 7000 (EI, 70 eV, CI 100 eV). High resolution MS: Finnigan MAT 95. The hydrazones (*S*)-**1** and (*R*)-**1** were prepared according to a published procedure[7] from SAMP or RAMP[10] and 2,2-dimethyl-1,3-dioxan-5-one.[7m,11]

General Procedure for the Preparation of the Ketones (*S*)-2 (GP 1): SAMP-hydrazone (*S*)-**1**, (1.0 equiv.) was dissolved in anhydrous THF (2 mL/mmol hydrazone) and *t*BuLi (15% in *n*-pentane) (1.1 equiv.) was added dropwise at −78 °C. After stirring for 2 h at this temperature, the lithiated hydrazone was cooled to −100 °C and the electrophile (1.1 equiv.) slowly added. After 2 h the mixture was warmed to room temp. over 15 h. The mixture was quenched with pH 7 buffer solution and diluted with diethyl ether. The organic layer was washed with pH 7 buffer solution and brine. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The obtained monoalkylated SAMP-hydrazone was dissolved in diethyl ether (10 mL/mmol) and then a saturated aqueous solution of oxalic acid (2 mL/mmol) was added. After three hours the aqueous layer was extracted with diethyl ether and the combined organic layers were washed with pH 7 buffer solution and brine. After drying ($MgSO_4$) and concentration under reduced pressure, the crude product was purified by flash chromatography to afford the ketones (*S*)-**2**.

General Procedure for the Preparation of the Alcohols (*S*)-3 by Reduction with L-Selectride (GP 2): L-Selectride® (1 M in THF) (1.2 equiv.) was added dropwise to a stirred solution of the ketone (*S*)-**2** (1.0 equiv.) in anhydrous THF (6 mL/mmol ketone) at −78 °C. After stirring for 2 h at this temperature the mixture was warmed to room temp. over 15 h. The reaction was quenched with a saturated solution of aqueous ammonium chloride (2 mL/mmol) followed by a dropwise addition of a H_2O_2 solution (30%, 0.5 mL/mmol) and sodium hydroxide (c = 0.1 mol/L, 0.5 mL/mmol). After stirring at room temp. for 15 min the mixture was extracted with diethyl ether and the combined organic layers dried ($MgSO_4$). Concentration under reduced pressure and flash chromatography afforded the desired product.

General Procedure for the Preparation of the Azides (*S*,*R*)-4 (GP 3): Triethylamine (10.0 equiv.), followed by methanesulfonyl chloride (5.0 equiv.), were added dropwise to a stirred solution of the alcohol (*S*,*S*)-**3** (1.0 equiv.) in CH_2Cl_2 (10 mL/mmol) at 0 °C under argon. The resulting red solution was stirred at room temperature for 10 min then poured into water and extracted with CH_2Cl_2. The combined organic layers were washed with water, brine, dried ($MgSO_4$) and concentrated in vacuo. Sodium azide (10.0 equiv.) and 18-crown-6 ether (1.0 equiv.) were added to a stirred solution of the crude mesylate (1.0 equiv.) in DMF (10 mL/mmol) at room temp. This reaction mixture was heated to 100 °C under argon for 12−48 h. Upon cooling the reaction mixture was poured into water and extracted with diethyl ether. The combined organic extracts were washed with brine (3 x) and dried ($MgSO_4$). Concentration under reduced pressure and flash chromatography afforded the desired azide **4**.

General Procedure for the Preparation of the Amines (*S*,*R*)-5 (GP 4): A solution of the azide (*S*,*R*)-**4** (1.0 equiv.) in THF (3 mL/mmol)

was added dropwise to a stirred suspension of lithium aluminium hydride (2.0 equiv.) in THF (3 mL/mmol) at room temp. under argon. The reaction mixture was stirred for 20 min and then a 10% aq. NaOH solution (3.6 equiv.) was added dropwise, and diluted with CH_2Cl_2. This biphasic system was stirred for 5 min and then separated. The aqueous phase was further extracted with CH_2Cl_2 and the combined organic phases were washed with brine and dried ($MgSO_4$). Concentration under reduced pressure afforded the expected amine **5** without need for further purification.

(4*S*)-4-(2-Bromoallyl)-2,2-dimethyl-1,3-dioxane-5-one [(*S*)-2a]: According to GP 1, (*S*)-**2a** was obtained as a yellow oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:5). Yield: 0.70 g (56%). R_t = 8.32 min (CP-Sil-8, 60−10−300). R_f = 0.53 (pentane/Et_2O, 5:1). $[\alpha]_D^{24}$ = −216.0 (*c* = 1.07, $CHCl_3$). *ee* = 94%. IR (film): $\tilde{\nu}$ = 2988 (s), 2939 (m), 2883 (m), 1750 (vs, C=O), 1634 (s), 1423 (m), 1378 (s), 1273 (m), 1244 (s), 1222 (s), 1176 (m), 1162 (m), 1109 (s), 1069 (m), 1030 (m), 965 (m), 898 (s), 837 (m), 526 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CCH_3), 1.50 (s, 3 H, CCH_3), 2.57 (m, 1 H, C*H*H), 3.03 (m, 1 H, CH*H*), 4.04 (dd, *J* = 1.4/17.3 Hz, 1 H, OCH*H*), 4.29 (dd, *J* = 1.4/17.3 Hz, 1 H, OC*H*H), 4.60 (m, 1 H, C*H*), 5.51 (m, 1 H, CBr=CH*H*), 5.71 (m, 1 H, CBr=C*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.6, 23.7, 40.0, 66.3, 72.2, 101.1, 119.5, 128.7, 207.8 ppm. MS (EI): *m*/*z* (%) = 250 (1) [M^+ + 1], 169 (9), 129 (10), 111 (99), 100 (13), 83 (13), 81 (11), 73 (10), 72 (100), 59 (39), 58 (11), 55 (13), 53 (31), 51 (9). $C_9H_{13}BrO_3$ (249.10): calcd. C 43.40, H 5.26; found C 43.53, H 5.54.

(4*S*)-4-Decyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-2b]: According to GP 1, (*S*)-**2b** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:10). Yield: 2.04 g (76%). R_t = 8.45 min (CP-Sil-8, 120−10−300). R_f = 0.62 (pentane/Et_2O, 10:1). $[\alpha]_D^{24}$ = −181.5 (*c* = 1.03, $CHCl_3$). *ee* = 93%. IR (film): $\tilde{\nu}$ = 2987 (s), 2925 (vs), 2855 (vs), 1750 (vs, C=O), 1466 (m), 1375 (s), 1251 (m), 1225 (s), 1103 (s), 870 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, CH_2CH_3), 1.26 [m, 16 H, $CH_2(CH_2)_8CH_3$], 1.43 (s, 3 H, CCH_3), 1.45 (s, 3 H, CCH_3), 1.53 (m, 1 H, CHCH*H*), 1.86 (m, 1 H, CHC*H*H), 3.97 (d, *J* = 16.8 Hz, 1 H, OCH*H*), 4.20 (m, 1 H, C*H*), 4.25 (dd, *J* = 1.4/16.8 Hz, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 23.5, 24.0, 25.1, 28.4, 29.3, 29.4, 29.4, 29.6, 31.9, 66.5, 74.6, 100.5, 209.5 ppm. MS (EI): *m*/*z* (%) = 255 (1) [$M^+ - CH_3$], 101 (14), 100 (31), 96 (7), 86 (13), 82 (7), 72 (100), 69 (6), 59 (26), 58 (10), 55 (17). $C_{16}H_{30}O_3$ (270.41): calcd. C 71.07, H 11.18; found C 71.18, H 11.05.

(4*S*)-Benzyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-2c]: According to GP 1, (*S*)-**2c** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:20). Yield: 1.59 g (72%). R_t = 7.23 min (CP-Sil-8, 100−10−300). R_f = 0.31 (pentane/Et_2O, 20:1). $[\alpha]_D^{24}$ = −212.6 (*c* = 1.06, $CHCl_3$). *ee* = 94%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 2.79 (dd, *J* = 9.1/14.8 Hz, 1 H, HC*H*C_6H_5), 3.24 (dd, *J* = 3.3/14.8 Hz, 1 H, *H*CHC$_6H_5$), 4.01 (d, *J* = 17.0 Hz, 1 H, OHC*H*), 4.26 (dd, *J* = 1.7/17.0 Hz, 1 H, O*H*CH), 4.46 (m, 1 H, C*H*), 7.27 (s, 5 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 23.9, 34.4, 66.5, 75.5, 100.8, 126.2, 128.0, 129.0, 137.5, 208.6 ppm. For further analytical data see ref.[7]

(4*S*)-(4-Bromobenzyl)-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-2d]: According to GP 1, (*S*)-**2d** was obtained as a green oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:5). Yield: 1.08 g (71%). R_t = 10.64 min (CP-Sil-8, 100−10−300). R_f = 0.38 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −166.6 (*c* = 1.08, $CHCl_3$). *ee* = 90%. IR (film): $\tilde{\nu}$ = 2988 (s), 2937 (m), 2881 (m), 1748 (vs, C=O), 1489 (s), 1378 (s), 1224 (s), 1173 (m), 1102 (s), 1069 (s),1014 (s), 901 (m), 806 (m), 634 (w), 536 (m), 519 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CCH_3), 1.41 (s, 3 H, CCH_3), 2.75 (dd, *J* = 9.0/14.8 Hz, 1 H, CHCH*H*), 3.16 (dd, *J* = 3.3/14.8 Hz, 1 H, CHC*H*H), 3.99 (d, *J* = 17.0 Hz, 1 H, OCH*H*), 4.23 (dd, *J* = 1.4/17.0 Hz, 1 H, OC*H*H), 4.40 (m, 1 H, C*H*), 7.13 [d, *J* = 8.8 Hz, 2 H, CH_{meta}), 7.39 (d, *J* = 8.5 Hz, 2 H, CH_{ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 23.8, 33.1, 66.5, 75.1, 100.8, 120.2, 130.8, 131.1, 136.4, 208.1 ppm. MS (EI): *m*/*z* (%) = 300 (17) [M^+ + 1], 298 (16), 201 (7), 200 (80), 199 (9), 198 (85), 184 (6), 182 (5), 171 (46), 171 (20), 169 (39), 161 (5), 131 (12), 130 (5), 129 (67), 103 (12), 102 (10), 101 (5), 100 (5), 91 (11), 90 (18), 89 (14), 77 (11), 73 (10), 72 (100), 59 (20), 58 (6), 55 (7), 51 (5). $C_{13}H_{15}BrO_3$ (299.16): calcd. C 52.19, H 5.05; found C 52.63, H 5.38.

(4*S*)-Benzyloxymethyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-2e]: According to GP 1, (*S*)-**2e** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:3). Yield: 1.48 g (59%). R_t = 9.93 min (CP-Sil-8, 100−10−300). R_f = 0.48 (pentane/Et_2O, 3:1). $[\alpha]_D^{24}$ = −171.8 (*c* = 1.08, $CHCl_3$). *ee* = 94%. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.47 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 3.73 (dd, *J* = 6.3/11.0 Hz, 1 H, CHHC*H*O), 3.88 (dd, *J* = 2.8/11.0 Hz, 1 H, CH*H*CHO), 3.98 (d, *J* = 16.8 Hz, 1 H, OHC*H*), 4.28 (dd, *J* = 1.7/16.8 Hz, 1 H, O*H*CH), 4.46 (m, 1 H, C*H*), 4.57 (d, *J* = 5.5 Hz, 2 H, OC$H_2C_6H_5$), 7.32 (s, 5 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 24.1, 66.6, 67.8, 73.5, 75.1, 100.7, 127.5, 128.2, 137.7, 207.1 pm. For further analytical data see ref.[7]

(4*R*)-2,2-Dimethyl-4-pentadecyl-1,3-dioxan-5-one [(*R*)-7]: According to GP 1 [starting with (*R*)-**1**], (*R*)-**7** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:10). Yield: 3.26 g (96%). R_t = 7.48 min (CP-Sil-8, 180−10−300). R_f = 0.62 (pentane/Et_2O, 10:1). $[\alpha]_D^{25}$ = +127.9 (*c* = 1.21, $CHCl_3$). *ee* = 96%. IR (film): $\tilde{\nu}$ = 2987 (m), 2925 (vs), 2854 (s), 1750 (s, C=O), 1464 (m), 1377 (m), 1224 (s), 1172 (w), 1104 (m), 864 (w), 722 (ww) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [t, *J* = 6.9 Hz, 3 H, $(CH_2)_{14}CH_3$], 1.26 [m, 26 H, $(CH_2)_{13}CH_3$], 1.41 (s, 3 H, CCH_3), 1.43 (s, 3 H, CCH_3), 1.53 (m, 1 H, OCHCH*H*), 1.85 (m, 1 H, OCHC*H*H), 3.94 (d, *J* = 16.8 Hz, 1 H, OCH*H*), 4.18 (m, 1 H, OC*H*), 4.22 (dd, *J* = 1.7/16.8 Hz, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.8, 23.6, 24.0, 25.2, 28.5, 29.49, 29.6, 29.8, 29.8, 29.8, 32.0, 66.5, 74.6, 100.5, 209.0 ppm. MS (EI): *m*/*z* (%) = 325 (2) [$M^+ - CH_3$], 170 (6), 156 (6), 142 (7), 128 (7), 114 (10), 101 (28), 100 (34), 98 (5), 97 (7), 96 (10), 95 (7), 86 (12), 85 (5), 83 (9), 82 (9), 81 (6), 73 (6), 72 (100), 71 (7), 69 (9), 67 (6), 59 (31), 58 (9), 57 (18), 55 (24). $C_{21}H_{40}O_3$ (340.54): calcd. C 74.07, H 11.84; found C 73.87, H 11.63.

(4*S*,5*S*)-(2-Bromoallyl)-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-3a]: According to GP 2, (*S*,*S*)-**3a** was obtained as a red oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:2). Yield: 0.46 g (88%). R_t = 7.07 min (CP-Sil-8, 80−10−300). R_f = 0.24 (pentane/Et_2O, 2:1). $[\alpha]_D^{24}$ = −2.4 (*c* = 0.99, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3449 (vs, OH), 2992 (vs), 2939 (s), 1795 (w), 1633 (vs), 1456 (s), 1382 (vs), 1271 (s), 1246 (s), 1201 (s), 1166 (s), 1128 (s), 1052 (vs), 979 (s), 941 (m), 898 (vs), 847 (s), 817 (s), 776 (w), 749 (m), 626 (m), 560 (m), 537 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.70 (m, 2 H, CHCH_2), 3.18 (s, 1 H, O*H*), 3.40 (s, 1 H, C*H*OH), 3.87 (dd, *J* = 1.9/12.4 Hz, 1 H, OCH*H*), 4.10 (d, *J* = 12.4 Hz, 1 H, OC*H*H), 4.22 (m, 1 H, OC*H*), 5.50 (m, 1 H, CBrCH*H*), 5.73 (m, 1 H, CBrC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4,

29.3, 43.0, 64.2, 65.9, 69.8, 99.3, 119.8, 129.6 ppm. MS (EI): *m*/*z* (%) = 236 ($M^+ - CH_3$, 1), 235 (9), 131 (8), 102 (10), 74 (12), 59 (100), 45 (18). $C_9H_{15}BrO_3$ (251.12): calcd. C 43.05, H 6.02; found C 43.29, H 6.18.

(4*S*,5*S*)-Decyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-3b]: According to GP 2, (*S*,*S*)-**3b** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:1). Yield: 1.68 g (89%). R_t = 5.57 min (CP-Sil-8, 160−10−300). R_f = 0.47 (pentane/Et_2O, 1:1). $[\alpha]_D^{27}$ = +5.6 (*c* = 1.00, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3435 (m, OH), 2992 (s), 2925 (vs), 2855 (vs), 1463 (m), 1378 (s), 1270 (m), 1227 (m), 1201 (s), 1167 (m), 1140 (w), 1112 (w), 1072 (s), 977 (m), 898 (w), 853 (m), 752 (w), 722 (w), 521 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H/7.1; $(CH_2)_9CH_3$], 1.25 (m, 16 H, $CH_2(CH_2)_8CH_3$], 1.42 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.56 (m, 2 H, OCHCH_2), 2.58 (s, 1 H, O*H*), 3.31 (s, 1 H, C*H*OH), 3.82 (m, 2 H, COC*H*; COCH*H*), 4.03 (dd, *J* = 1.4/12.1, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 18.4, 22.7, 24.8, 29.29, 29.5, 29.6, 29.7, 31.3, 31.8, 65.0, 66.2, 72.1, 98.7 ppm. MS (EI): *m*/*z* (%) = 257 ($M^+ - CH_3$, 9), 229 (8), 102 (13), 83 (5), 69 (5), 59 (100), 57 (6), 55 (7). $C_{16}H_{32}O_3$ (272.43): calcd. C 70.54, H 11.84; found C 70.35, H 11.66.

(4*S*,5*S*)-Benzyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-3c]: According to GP 2, (*S*,*S*)-**3c** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:1). Yield: 1.31 g (90%). R_t = 8.16 min (CP-Sil-8, 100−10−300). R_f = 0.36 (pentane/Et_2O, 1:1). $[\alpha]_D^{24}$ = +4.7 (*c* = 1.28, C_6H_6). *de* = 96%. IR (film): $\tilde{\nu}$ = 3437 (s, OH), 3085 (vw), 3062 (w), 3028 (w), 2992 (s), 2939 (s), 2873 (s), 1604 (w), 1496 (s), 1455 (s), 1380 (vs), 1270 (s), 1227 (w), 1202 (s), 1162 (s), 1127 (s), 1073 (vs), 963 (s), 895 (s), 867 (w), 829 (s), 778 (vw), 751 (s), 701 (vs), 593 (w), 552 (w), 522 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 2.82 (m, 1 H, CH*H*C_6H_5), 2.96 (m, 1 H, C*H*HC_6H_5), 3.22 (s, 1 H, C*H*OH), 3.82 (d, *J* = 12.3 Hz, 1 H, OCH*H*), 3.95 (d, *J* = 12.3 Hz, 1 H, OC*H*H), 4.02 (m, 1 H, C*H*), 7.23 (s, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 29.4, 37.5, 63.6, 66.0, 73.3, 99.1, 126.2, 128.2, 129.3, 137.0 ppm. MS (EI): *m*/*z* (%) = 222 (M, 1), 207(7), 179 (28), 147 (5), 131 (38), 129 (10), 121 (5), 105 (5), 103 (6), 102 (8), 92 (9), 91 (20), 59 (100). $C_{13}H_{18}O_3$ (222.28): calcd. C 70.24, H 8.16; found C 70.02, H 8.17.

(4*S*,5*S*)-(4-Bromobenzyl)-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-3d]: According to GP 2, (*S*,*S*)-**3d** was obtained as a colourless solid after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:2). Yield: 0.67 g (85%). R_t = 11.83 min (CP-Sil-8, 100−10−300). R_f = 0.22 (pentane/Et_2O, 2:1). $[\alpha]_D^{24}$ = −6.2 (*c* = 0.98, $CHCl_3$). m.p. 75 °C. *de* = 96%. IR (film): $\tilde{\nu}$ = 3431 (vs, OH), 2992 (vs), 2938 (s), 2873 (s), 1899 (w), 1642 (w), 1592 (w), 1488 (vs), 1402 (m), 1380 (vs), 1270 (s), 1227 (s), 1201 (vs), 1161 (s), 1126 (s), 1071 (vs), 1013 (s), 964 (s), 901 (s), 869 (s), 830 (vs), 805 (s), 736 (s), 635 (m), 559 (m), 536 (m), 521 (s), cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.77 (dd, *J* = 6.4/13.4 Hz, 2 H, HC$H_2C_6H_4$Br, O*H*), 2.89 (dd, *J* = 7.9/13.4 Hz, 1 H, *H*CHC_6H_4Br), 3.20 (s, 1 H, C*H*OH), 3.80 (dd, *J* = 2.0/12.4 Hz, 1 H, OHC*H*), 3.96 (m, 2 H, O*H*CH; OC*H*), 7.12 (d, *J* = 8.4 Hz, 2 H, C_6H_{meta}Br), 7.40 (d, *J* = 8.4 Hz, 2 H, C_6H_{ortho}Br) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 29.6, 37.1, 63.6, 66.0, 73.0, 98.9, 120.1, 131.1, 131.2, 136.2 ppm. MS (EI): *m*/*z* (%) = 301 (4) [M^+], 286 ($M^+ - CH_3$, 9), 285 (8), 171 (9), 169 (8), 131 (45), 128 (10), 103 (7), 102 (16), 90 (5), 59 (100). $C_{13}H_{17}BrO_3$ (301.18): calcd. C 51.99, H 5.87; found C 51.84, H 5.69.

(4*S*,5*S*)-Benzyloxymethyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-3e]: According to GP 2, (*S*,*S*)-**3e** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:1). Yield: 1.49 g (95%). R_t = 10.75 min (CP-Sil-8, 100−10−300). R_f = 0.24 (pentane/Et_2O, 1:1). $[\alpha]_D^{24}$ = +8.9 (*c* = 1.15, C_6H_6). *de* = 96%. IR (film): $\tilde{\nu}$ = 3382 (vs, OH), 3063 (m), 3030 (m), 2992 (vs), 2939 (vs), 2874 (vs), 1497 (m), 1455 (vs), 1382 (vs), 1278 (s), 1236 (m), 1200 (vs), 1171 (s), 1143 (s), 1070 (vs), 1028 (w), 976 (s), 904 (s), 849 (vs), 747 (vs), 700 (vs) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 1.17 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 3.25 (m, 1 H, C*H*OH), 3.55−3.74 (m, 4 H, OCH_2; CH_2O), 3.88 (m, 1 H, OC*H*), 4.41 (s, 2 H, OCH_2), 7.10−7.31 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 18.4, 29.5, 63.9, 65.7, 70.3, 71.5, 73.5, 98.9, 127.6, 127.8, 128.1, 138.6 ppm. MS (EI): *m*/*z* (%) = 252 (1) [M^+], 237 (4) [$M^+ - CH_3$], 194 (10), 176 (8), 149 (5), 133 (8), 131 (9), 107 (14), 105 (6), 92 (12), 91 (100), 65 (6), 59 (42). $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.99; found C 66.64, H 8.24.

(4*R*,5*R*)-2,2-Dimethyl-4-pentadecyl-1,3-dioxan-5-ol [(*R*,*R*)-8]: According to GP 2, (*RR*)-**8** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:2). Yield: 1.68 g (98%). R_t = 8.05 min (CP-Sil-8, 180−10−300). R_f = 0.34 (pentane/Et_2O, 2:1). $[\alpha]_D^{24}$ = −3.32 (*c* = 0.91, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3420 (m, OH), 2991 (m), 2921 (vs), 2852 (vs), 1471 (s), 1381 (m), 1274 (m), 1247 (m), 1199 (s), 1170 (m), 1139 (m), 1076 (m), 1025 (w), 976 (m), 948 (w), 904 (m), 850 (m), 802 (w), 720 (m), 622 (w), 561 (w), 519 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 [t, 3 H, $(CH_2)_{14}CH_3$], 1.26 [m, 28 H, $(CH_2)_{14}CH_3$], 1.42 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 2.57 (d, *J* = 11.5 Hz, 1 H, O*H*), 3.32 (dd, *J* = 0.8/11.5 Hz, 1 H, C*H*OH), 3.82 (m, 1 H, OC*H*), 3.84 (dd, *J* = 1.9/12.0 Hz, 1 H, OCH*H*), 4.04 (dd, *J* = 1.1/12.0 Hz, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 18.4, 22.7, 24.9, 29.3, 29.5, 29.6, 29.6, 29.7, 31.3, 31.9, 65.0, 66.2, 72.0, 98.7 ppm. MS (EI): *m*/*z* (%) = 327 (100) [$M^+ - CH_3$], 311 (12), 123 (6), 111 (8), 109 (11), 101 (34), 97 (19), 95 (17), 85 (9), 83 (18), 82 (5), 81 (12), 73 (6), 71 (12), 70 (5), 69 (15), 67 (9), 60 (5), 59 (82), 57 (33), 56 (6), 55 (26), 45 (7). $C_{21}H_{42}O_3$ (342.56): calcd. C 73.63, H 12.36; found C 73.49, H 12.66.

(4*S*,5*R*)-5-Azido-4-(2-bromoallyl)-2,2-dimethyl-1,3-dioxane [(*S*,*R*)-4a]: According to GP 3, (*S*,*R*)-**4a** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:10). Yield: 167 mg (30%). R_t = 8.23 min (CP-Sil-8, 80−10−300). R_f = 0.49 (pentane/Et_2O, 10:1). $[\alpha]_D^{27}$ = −40.7 (*c* = 1.08, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 2994 (m), 2943 (m), 2874 (m), 2108 (vs, N_3), 1633 (m), 1459 (w), 1382 (s), 1329 (w), 1295 (s), 1266 (s), 1240 (m), 1200 (s), 1165 (s), 1123 (s), 1070 (m), 1030 (m), 975 (w), 962 (w), 900 (m), 844 (w), 829 (m), 749 (w), 645 (w), 554 (w), 521 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 2.59 (m, 1 H, CHCH*H*), 2.87 (m, 1 H, CHC*H*H), 3.28 (dt, *J* = 5.5/9.6 Hz, 1 H, C*H*N_3), 3.74 (dd, *J* = 9.6/11.5 Hz, 1 H, OCH*H*), 3.93 (m, 1 H, OC*H*), 4.00 (dd, *J* = 5.5/11.5 Hz, 1 H, OC*H*H), 5.52 (m, 1 H, CBrCH*H*), 5.69 (m, 1 H, CBrC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 28.3, 44.6, 58.1, 62.3, 69.9, 99.1, 119.3, 128.5 ppm. MS (EI): *m*/*z* (%) = 261 (27) [$M^+ - CH_3$], 260 (27), 234 (5), 110 (15), 84 (17), 82 (11), 80 (16), 73 (5), 72 (28), 70 (7), 69 (28), 65 (5), 59 (100), 56 (8), 55 (7), 54 (8), 53 (28), 45 (15). $C_9H_{14}BrN_3O_2$ (276.13): calcd. C 39.15, H 5.11, N 15.23; found C 39.34, H 5.38, N 15.64.

(4*S*,5*R*)-5-Azido-4-decyl-2,2-dimethyl-1,3-dioxane [(*S*,*R*)-4b]: According to GP 3, (*S*,*R*)-**4b** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:40). Yield: 192 mg (32%). R_t = 7.72 min (CP-Sil-8, 140−10−300). R_f = 0.40 (pentane/Et_2O, 40:1). $[\alpha]_D^{27}$ = −31.0 (*c* =

1.12, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 2994 (m), 2926 (vs), 2855 (s), 2107 (vs, N_3), 1684 (w), 1465 (m), 1381 (m), 1370 (m), 1266 (s), 1227 (m), 1201 (s), 1166 (w), 1140 (w), 1111 (w), 1079 (w), 982 (m), 866 (w), 699 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [m, 3 H, $(CH_2)_9CH_3$], 1.27 [m, 16 H, $CHCH_2(CH_2)_8CH_3$], 1.37 (s, 3 H, CCH_3), 1.42 (s, 3 H, CCH_3), 1.69 [m, 1 H, $CHCHH(CH_2)_8CH_3$], 1.73 [m, 1 H, $CHCHH(CH_2)_8CH_3$], 3.21 (ddd, *J* = 5.5/9.6/15.5 Hz, 1 H, CHN_3), 3.57 (m, 1 H, COCH), 3.67 (dd, *J* = 9.6/15.5 Hz, 1 H, COCHH), 3.95 (dd, *J* = 5.5/15.5 Hz, 1 H, COCHH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 19.4, 22.7, 24.8, 28.5, 29.3, 29.4, 29.5, 29.6, 31.9, 32.9, 59.0, 62.4, 72.0, 98.8 ppm. MS (EI): *m*/*z* (%) = 282 (27) [$M^+ - CH_3$], 169 (14), 156 (5), 98 (6), 97 (12), 95 (11), 85 (6), 84 (69), 83 (9), 82 (6), 81 (7), 72 (43), 70 (10), 69 (100), 68 (6), 67 (8), 59 (95), 57 (15), 56 (25), 55 (28), 54 (6). HRMS: [$C_{16}H_{31}N_3O_2 - CH_3$] calcd. 282.2182; found 282.2183.

(4*S*,5*R*)-5-Azido-4-benzyl-2,2-dimethyl-1,3-dioxane [(*S*,*R*)-4c]: According to GP 3, (*S*,*R*)-**4c** was obtained as a yellow oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:20). Yield: 229 mg (48%). R_t = 8.70 min (CP-Sil-8, 100−10−300). R_f = 0.41 (pentane/Et_2O, 20:1). $[\alpha]_D^{26}$ = −39.1 (*c* = 1.03, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3086 (w), 3063 (w), 3029 (w), 2994 (m), 2942 (m), 2873 (m), 2234 (w), 2107 (vs, N_3), 1604 (w), 1496 (m), 1455 (m), 1435 (w), 1379 (s), 1265 (s), 1225 (m), 1202 (s), 1162 (m), 1126 (m), 1105 (m), 1082 (m), 1031 (w), 981 (m), 955 (w), 894 (w), 829 (m), 797 (w), 751 (m), 700 (s), 544 (w), 521 (w), 494 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CCH_3), 1.36 (s, 3 H, CCH_3), 2.80 (dd, *J* = 7.4/14.3 Hz, 1 H, $CHHC_6H_5$), 3.02 (dd, *J* = 3.0/14.3 Hz, 1 H, $CHHC_6H_5$), 3.22 (ddd, *J* = 5.7/9.6 Hz, 1 H, CHN_3), 3.69 (dd, *J* = 9.6/11.6, 1 H, OCHH), 3.82 (ddd, *J* = 3.0/7.4/9.6 Hz, 1 H, OCH), (3.93 (dd, *J* = 5.7/11.6 Hz, 1 H, COCHH), 7.25 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1, 28.4, 38.8, 57.7, 62.2, 72.5, 98.7, 126.2, 127.9, 129.4, 137.1 ppm. MS (EI): *m*/*z* (%) = 247 (1) [M^+], 233 (5), 232 (41) [$M^+ - CH_3$], 190 (6), 189 (48), 162 (5), 156 (20), 146 (8), 144 (9), 133 (8), 132 (6), 131 (6), 130 (29), 129 (17), 121 (32), 120 (23), 119 (30), 118 (7), 117 (16), 115 (8), 105 (20), 104 (35), 103 (29), 99 (12), 92 (38), 91 (97), 84 (34), 78 (15), 77 (15), 74 (17), 73 (8), 72 (47), 70 (7), 69 (37), 65 (16), 61 (5), 59 (100), 58 (40), 57 (7), 56 (17), 55 (13), 51 (7), 46 (8), 45 (36). HRMS: [$C_{13}H_{17}N_3O_2 - CH_3$] calcd. 232.1086; found 232.1087.

(4*S*,5*R*)-5-Azido-4-(4-bromobenzyl)-2,2-dimethyl-1,3-dioxane [(*S*,*R*)-4d]: According to GP 3, (*S*,*R*)-**4d** was obtained as a colourless solid after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:5). Yield: 419 mg (76%). R_t = 10.07 min (CP-Sil-8, 120−10−300). R_f = 0.49 (pentane/Et_2O, 5:1). $[\alpha]_D^{25}$ = −31.0 (*c* = 1.06, $CHCl_3$). M.p. 53 °C. *de* = 96%. IR (KBr): $\tilde{\nu}$ = 2998 (m), 2945 (m), 2920 (m), 2878 (m), 2226 (w), 2106 (vs, N_3), 1488 (m), 1440 (w), 1404 (w), 1379 (s), 1303 (w), 1271 (s), 1204 (m), 1165 (m), 1125 (m), 1104 (m), 1062 (s), 1010 (m), 978 (m), 955 (w), 922 (w), 901 (m), 831 (s), 800 (m), 747 (w), 714 (w), 695 (w), 647 (w), 548 (m), 523 (m), 498 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 [s, 6 H, $(CH_3)_2$], 2.75 (dd, *J* = 7.7/14.3 Hz, 1 H, CHCHH), 2.98 (dd, *J* = 3.0/14.3 Hz, 1 H, CHCHH), 3.70 (dd, *J* = 9.6/11.5 Hz, 1 H, OCHH), 3.77 (ddd, *J* = 3.0/7.7/9.9 Hz, 1 H, OCH), 3.95 (dd, *J* = 5.5/11.5 Hz, 1 H, OCHH), 3.22 (ddd, *J* = 5.5/9.6/9.9 Hz, 1 H, CHN_3), 7.13 (d, *J* = 8.5 Hz, 2 H, $C_6H_{ortho}Br$), 7.40 (d, *J* = 8.5 Hz, 2 H, $C_6H_{meta}Br$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 28.5, 38.2, 57.6, 62.2, 72.4, 99.0, 120.4, 131.22, 131.4, 136.3 ppm. MS (EI): *m*/*z* (%) = 327 (3) [M^+ + 1], 312 (29), 310 (27), 269 (14), 267 (15), 201 (10), 200 (51), 199 (12), 198 (53), 185 (5), 184 (13), 183 (7), 182 (13), 172 (6), 171 (44), 170 (7), 169 (46), 156 (19), 143 (9), 130 (17), 129 (10), 128 (13), 116 (11), 115 (7), 104 (10), 103 (19), 102 (13), 99 (14), 98 (6), 91 (12), 90 (23), 89 (20), 86 (8), 84 (35), 77 (16), 72 (49), 69 (33), 63 (10), 59 (100), 58 (25). $C_{13}H_{16}BrN_3O_2$ (326.19): calcd. C 47.87, H 4.94, N 12.88; found C 47.95, H 5.11, N 12.88.

(4*S*,5*R*)-5-Azido-4-benzyloxymethyl-2,2-dimethyl-1,3-dioxane [(*S*,*R*)-4e]: According to GP 3, (*S*,*R*)-**4e** was obtained as a colourless oil after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:10). Yield: 177 mg (32%). R_t = 11.24 min (CP-Sil-8, 100−10−300). R_f = 0.30 (pentane/Et_2O, 10:1). $[\alpha]_D^{25}$ = −21.8 (*c* = 0.99, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3030 (w), 2993 (m), 2941 (M), 2870 (m), 2109 (vs, N_3), 1497 (w), 1454 (m), 1381 (m), 1308 (w), 1270 (s), 1224 (m), 1201 (s), 1168 (m), 1131 (m), 1098 (s), 1061 (m), 1028 (w), 986 (m), 913 (w), 845 (m), 738 (m), 689 (s), 521 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.41 (s, 3 H, CCH_3), 1.43 (s, 3 H, CCH_3), 3.60−3.70 (kB, 4 H, CHN_3, OCH, $CHCH_2O$), 3.76 (m, 1 H, OCH), 3.96 (dd, *J* = 5.0/11.= Hz, 1 H, OCHH), 4.57 (d, *J* = 12.0 Hz, 1 H, $OCHHC_6H_5$), 4.64 (d, *J* = 12.0 Hz, 1 H, $OCHHC_6H_5$), 7.34 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.3, 28.4, 54.9, 62.2, 70.0, 72.2, 73.6, 99.1, 127.7, 127.8, 128.3, 138.0 ppm. MS (EI): *m*/*z* (%) = 262 (6) [$M^+ - CH_3$], 234 (11), 149 (11), 132 (8), 131 (22), 130 (7), 107 (28), 106 (5), 105 (6), 104 (18), 100 (19), 92 (8), 91 (100), 84 (8), 77 (6), 72 (14), 69 (9), 65 (11), 59 (22), 58 (7), 56 (7), 51 (5). HRMS: [$C_{14}H_{19}N_3O_3-CH_3$] calcd. 262.1192; found 262.1193.

(4*R*,5*S*)-5-Azido-2,2-dimethyl-4-pentadecyl-1,3-dioxane [(*R*,*S*)-9]: According to GP 3, (*R*,*S*)-**9** was obtained as a colourless solid after purification by column chromatography (SiO_2, diethyl ether/pentane, 1:40). Yield: 0.70 g (63%). GC: decomposition. R_f = 0.37 (pentane/Et_2O, 40:1). $[\alpha]_D^{25}$ = +32.5 (*c* = 0.80, $CHCl_3$). M.p. 35 °C. *de* = 96%. IR (KBr): $\tilde{\nu}$ = 2920 (vs), 2852 (s), 2229 (m), 2105 (N_3, vs), 1469 (m), 1379 (m), 1316 (m), 1266 (s), 1200 (s), 1166 (m), 1116 (m), 1091 (m), 1060 (m), 984 (m), 942 (w), 890 (m), 864 (m), 836 (w), 805 (w), 722 (w), 700 (m), 524 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 [t, *J* = 6.7 Hz, 3 H, $(CH_2)_{14}CH_3$], 1.26 [m, 26 H, $(CH_2)_{13}CH_3$], 1.38 (s, 3 H, CCH_3), 1.43 (s, 3 H, CCH_3), 1.49 (m, 1 H, CHCHH), 1.71 (m, 1 H, CHCHH), 3.21 (ddd, *J* = 5.4/9.4/9.7 Hz, 1 H, CHN_3), 3.57 (m, 1 H, OCH), 3.67 (dd, *J* = 9.4/11.4 Hz, 1 H, OCHH), 3.95 (dd, *J* = 5.4/11.4 Hz, 1 H, OCHH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 19.4, 22.7, 24.8, 28.5, 29.4, 29.5, 29.6, 29.6, 29.7, 32.0, 33.0, 59.1, 62.5, 72.1, 98.9 ppm. MS (EI): *m*/*z* (%) = 352 (53) [$M^+ - CH_3$], 282 (8), 239 (14), 113 (5), 111 (6), 109 (6), 99 (6), 98 (5), 97 (15), 96 (5), 95 (12), 91 (7), 85 (15), 84 (90), 83 (19), 82 (6), 81 (9), 74 (21), 73 (11), 72 (37), 71 (12), 70 (11), 69 (99), 68 (5), 67 (10), 60 (5), 59 (100), 58 (5), 57 (36), 56 (32), 55 (33), 54 (6). $C_{21}H_{41}N_3O_3$ (367.57): calcd. C 68.62, H 11.24, N 11.43; found C 68.45, H 11.02, N 11.31.

(4*S*,5*R*)-4-(2-Bromoallyl)-2,2-dimethyl-1,3-dioxan-5-amine [(*S*,*R*)-5a]: According to GP 4, (*S*,*R*)-**5a** was obtained as a colourless oil. A further purification by column chromatography was not necessary. Yield: 70 mg (65%). R_t = 7.58 min (CP-Sil-8, 80−10−300). $[\alpha]_D^{22}$ = −33.4 (*c* = 1.08, $CHCl_3$). *de* = 96%. IR ($CHCl_3$): $\tilde{\nu}$ = 3375 (m, NH), 3298 (m), 2991 (vs), 2938 (s), 2864 (s), 1632 (s), 1460 (m), 1422 (w), 1379 (vs), 1316 (w), 1265 (s), 1200 (vs), 1164 (vs), 1070 (vs), 964 (m), 899 (s), 831 (s), 748 (w), 673 (w), 643 (w), 565 (m), 521 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (br. s, 2 H, NH_2), 1.38 (s, 3 H, CCH_3), 1.47 (s, 3 H, CCH_3), 2.54 (dd, *J* = 8.8/15.11 Hz, 1 H, CHCHH), 2.69 (dt, *J* = 5.5/9.6 Hz, 1 H, $CHNH_2$), 2.92 (dd, *J* = 2.8/11.5 Hz, 1 H, CHCHH), 3.48 (dd, *J* = 9.9/11.5 Hz, 1 H, OCHH), 3.77 (dt, *J* = 2.8/9.6 Hz, 1 H, OCH), 3.84 (dd, *J* = 5.5/11.5 Hz, 1 H, OCHH), 5.50 (m, 1 H, CBrCHH), 5.70 (m, 1 H, CBrCHH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 28.9, 44.4, 49.3, 66.2, 73.8, 98.5, 118.8, 130.0 ppm. MS (EI): *m*/*z*

(%) = 234 (30) [$M^+ - CH_3$], 193 (11), 191 (10), 176 (19), 174 (22), 171 (8), 170 (83), 161 (5), 112 (27), 101 (33), 100 (6), 95 (18), 94 (20), 83 (9), 82 (100), 81 (6), 80 (20), 73 (6), 72 (26), 67 (12), 65 (7), 60 (15), 59 (38), 58 (8), 56 (31), 55 (17), 54 (14), 53 (17), 51 (7). HRMS: $C_9H_{16}NO_2Br - CH_3$: calcd. 234.0130; found 234.0130.

(4*S*,5*R*)-4-Decyl-2,2-dimethyl-1,3-dioxan-5-amine [(*S*,*R*)-5b]: According to GP 4, (*S*,*R*)-**5b** was obtained as a colourless oil. A further purification by column chromatography was not necessary. Yield: 110 mg (99%). R_t = 7.21 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{23}$ = −30.8 (*c* = 1.02, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3375 (w, NH), 2992 (m), 2925 (vs), 2864 (vs), 1610 (w), 1463 (m), 1378 (s), 1268 (m), 1201 (s), 1166 (m), 1140 (w), 1075 (m), 1013 (w), 976 (w), 872 (w), 621 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [t, *J* = 6.9 Hz, 3 H, $(CH_2)_9CH_3$], 1.13 (br. s, 2 H, NH_2), 1.27 [m, 16 H, $(CH_2)_8CH_3$], 1.38 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 1.50 (m, 1 H, CHC*H*H), 1.73 (m, 1 H, OCHC*H*H), 2.63 (dt, *J* = 5.5/9.6 Hz, 1 H, C*H*NH_2), 3.40 (dt, *J* = 2.5/9.0 Hz, 1 H, OC*H*), 3.45 (dd, *J* = 9.6/11.5 Hz, 1 H, OCH*H*), 3.80 (dd, *J* = 5.5/11.5 Hz, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 19.3, 22.7, 25.1, 29.1, 29.3, 29.6, 31.9, 32.3, 49.7, 66.14, 75.5, 98.2 ppm. MS (EI): *m*/*z* (%) = 257 (14) [$M^+ - CH_3 + 1$], 256 (97) [$M^+ - CH_3$], 213 (8), 197 (9), 196 (59), 182 (7), 138 (6), 126 (5), 112 (8), 109 (6), 102 (17), 101 (100), 98 (5), 97 (6), 95 (13), 85 (5), 83 (14), 82 (9), 81 (12), 73 (7), 72 (14), 71 (7), 70 (24), 69 (84), 868 (6), 67 (14), 61 (23), 60 (24), 59 (36), 58 (15), 57 (26), 56 (97), 55 (45), 54 (9), 45 (10). HRMS: [$C_{16}H_{33}NO_2 - CH_3$] calcd. 256.2277; found 256.2275.

(4*S*,5*R*)-4-Benzyl-2,2-dimethyl-1,3-dioxan-5-amine [(*S*,*R*)-5c]: According to GP 4, (*S*,*R*)-**5c** was obtained as a colourless oil. A further purification by column chromatography was not necessary. Yield: 160 mg (99%). R_t = 8.21 min (CP-Sil-8, 100−10−300). $[\alpha]_D^{27}$ = −46.9 (*c* = 0.98, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3377 (m, NH), 3320 (m), 3085 (m), 3062 (m), 3028 (s), 2993 (vs), 2938 (s), 2857 (s), 1605 (s, NH), 1496 (s), 1455 (s), 1378 (vs), 1267 (s), 1202 (vs), 1161 (vs), 1131 (s), 1079 (vs), 1030 (s), 961 (s), 898 (s), 830 (s), 797 (m), 750 (s), 701 (vs), 676 (w), 636 (w), 592 (w), 550 (w), 522 (s), 501 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (br.s, 2 H, NH_2), 1.37 [m, 6 H, $C(CH_3)_2$], 2.66 (ddd, *J* = 5.5/9.6/10.0 Hz, 1 H, C*H*NH_2), 2.78 (dd, *J* = 7.7/14.3 Hz, 1 H, CHCH*H*), 3.02 (dd, *J* = 3.3/14.3 Hz, 1 H, CHC*H*H), 3.43 (dd, *J* = 10.0/11.5 Hz, 1 H, OCH*H*), 3.67 (ddd, *J* = 3.3/7.7/9.6 Hz, 1 H, OC*H*), 3.77 (dd, *J* = 5.5/11.5 Hz, 1 H, OC*H*H), 7.26 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 29.0, 38.8, 49.2, 66.0, 76.3, 98.2, 125.9, 127.9, 129.2, 138.4 ppm. MS (EI): *m*/*z* (%) = 206 (42) [$M^+ - CH_3$], 164 (7), 163 (53), 156 (10), 147 (6), 146 (45), 144 (7), 135 (6), 134 (6), 133 (44), 132 (71), 131 (6), 130 (23), 129 (38), 128 (6), 127 (10), 117 (17), 116 (17), 115 (26), 106 (7), 105 (29), 104 (9), 103 (17), 102 (20), 101 (88), 92 (11), 91 (100), 89 (6), 79 (6), 78 (8), 77 (18), 73 (8), 72 (47), 70 (7), 69 (65), 65 (30), 63 (8), 61 (62), 60 (35), 59 (33), 58 (15), 56 (42), 55 (19), 54 (26), 51 (17), 45 (34). HRMS: [$C_{13}H_{19}NO_2 - CH_3$] calcd. 206.1181; found 206.1182.

(4*S*,5*R*)-4-(4-Bromobenzyl)-2,2-dimethyl-1,3-dioxane-5-amine [(*S*,*R*)-5d]: According to GP 4, (*S*,*R*)-**5d** was obtained as a colourless oil. A further purification by column chromatography was not necessary. Yield: 210 mg (99%). R_t = 11.62 min (CP-Sil-8, 100−10−300). $[\alpha]_D^{27}$ = −36.4 (*c* = 0.99, $CHCl_3$). *de* = 96%. IR ($CHCl_3$): $\tilde{\nu}$ = 3376 (m, NH), 3319 (m), 2991 (vs), 2926 (vs), 2856 (vs), 1594 (m, NH), 1488 (vs), 1458 (m), 1436 (m), 1404 (m), 1378 (vs), 1267 (s), 1202 (vs), 1160 (s), 1131 (m), 1072 (vs), 1032 (m), 1012 (s), 962 (s), 901 (s), 831 (vs), 802 (s), 748 (m), 702 (w), 676 (w), 634 (w), 555 (w), 522 (s), 504 (m), 474 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (br. s, 2 H, NH_2), 1.36 [s, 6 H, $C(CH_3)_2$], 2.64 (dt, *J* = 5.5/9.6 Hz, 1 H, C*H*NH_2), 2.71 (dd, *J* = 8.0/14.3 Hz, 1 H, CHCH*H*), 3.01 (dd, *J* = 2.8/14.3 Hz, 1 H, CHC*H*H), 3.44 (m, 1 H, OCH*H*), 3.62 (dt, *J* = 2.8/9.6 Hz, 1 H, OC*H*), 3.78 (dd, *J* = 5.5/11.5 Hz, 1 H, OC*H*H), 7.14 (m, 2 H, $C_6H_{ortho}Br$), 7.38 (m, 2 H, $C_6H_{meta}Br$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 28.9, 37.9, 49.0, 66.1, 76.0, 98.2, 119.8, 130.9, 131.1, 137.4 ppm. MS (EI): *m*/*z* (%) = 301 (2) [$M^+ + 1$], 286 (32), 284 (32), 243 (27), 241 (19), 241 (16), 226 (6), 226 (16), 223 (22), 213 (9), 212 (19), 211 (7), 210 (17), 184 (9), 182 (9), 170 (28), 168 (28), 163 (6), 156 (11), 145 (14), 133 (8), 132 (48), 130 (34), 130 (6), 129 (7), 128 (19), 116 (12), 115 (20), 104 (9), 103 (6), 102 (21), 101 (100), 91 (18), 90 (24), 89 (19), 83 (6), 77 (10), 73 (10), 72 (60), 71 (5), 70 (6), 69 (41), 65 (11), 64 (5), 63 (9), 61 (13), 60 (29), 59 (23), 58 (13), 57 (10), 56 (29), 55 (14), 54 (16), 51 (10), 45 (12). $C_{13}H_{18}BrNO_2$ (300.19): calcd. C 52.01, H 6.04, N 4.67; found C 52.01, H 5.91, N 4.67.

(4*S*,5*R*)-4-Benzyloxymethyl-2,2-dimethyl-1,3-dioxan-5-amine [(*S*,*R*)-5e]: According to GP 4, (*S*,*R*)-**5e** was obtained as a colourless oil. A further purification by column chromatography was not necessary. Yield: 160 mg (97%). R_t = 6.99 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{27}$ = −12.4 (*c* = 0.93, $CHCl_3$). *de* = 96%. IR (film): $\tilde{\nu}$ = 3374 (m, NH), 3302 (m), 3063 (m), 3030 (m), 2992 (s), 2938 (s), 2863 (vs), 1603 (m, NH), 1496 (m), 1455 (s), 1376 (vs), 1271 (s), 1225 (s), 1200 (vs), 1167 (s), 1088 (vs), 1057 (s), 1028 (m), 975 (m), 909 (s), 844 (s), 741 (s), 700 (s), 614 (w), 521 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.28 (br. s, 2 H, NH_2), 1.40 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 2.87 (m, 1 H, C*H*NH_2), 3.47 (dd, *J* = 10.1/10.4 Hz, 1 H, OCH*H*), 3.64 (m, 3 H, $CHCH_2$, OC*H*), 3.80 (dd, *J* = 5.5/11.5 Hz, 1 H, OC*H*H), 4.58 (m, 2 H, $OCH_2C_6H_5$), 7.34 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 28.9, 47.3, 65.6, 71.4, 73.4, 74.7, 98.2, 127.5, 127.5, 128.2, 137.9 ppm. MS (EI): *m*/*z* (%) = 236 (19) [$M^+ - CH_3$], 194 (5), 193 (37), 160 (5), 145 (6), 101 (8), 100 (16), 92 (11), 91 (100), 87 (6), 83 (6), 72 (23), 65 (11), 60 (5), 59 (13), 58 (11), 57 (23), 56 (23), 45 (5). HRMS: [$C_{14}H_{21}NO_3 - CH_3$] calcd. 236.1286; found 236.1285.

(4*R*,5*S*)-2,2-Dimethyl-4-pentadecyl-1,3-dioxan-5-amine [(*R*,*S*)-10]: According to GP 4, (*S*,*R*)-**10** was obtained as a colourless solid. A further purification by column chromatography was not necessary. Yield: 110.0 mg (91%). R_t = 11.92 min (CP-Sil-8, 140−10−300). $[\alpha]_D^{23}$ = +27.6 (*c* = 1.06, $CHCl_3$). M.p. 36 °C. *de* = 96%. IR (KBr): $\tilde{\nu}$ = 2995 (m), 2919 (vs), 2852 (vs), 1624 (w), 1469 (m), 1379 (m), 1267 (w), 1203 (m), 1167 (m), 1113 (m), 1095 (m), 1074 (m), 1000 (w), 916 (w), 892 (m), 864 (w), 835 (w), 721 (w), 524 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [m, 3 H, $(CH_2)_{14}CH_3$], 1.26 [m, 26 H, $(CH_2)_{13}CH_3$], 1.38 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.50 [m, 1 H, CH*H*$(CH_2)_{13}CH_3$], 1.72 [m, 1 H, C*H*H$(CH_2)_{13}CH_3$], 2.64 (ddd, *J* = 5.5/9.6/9.6 Hz, 1 H, C*H*NH_2), 3.40 (m, 1 H, OC*H*), 3.45 (dd, *J* = 9.6/11.3 Hz, 1 H, OCH*H*), 3.81 (dd, *J* = 5.5/11.3 Hz, 1 H, OC*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 19.4, 22.8, 25.2, 29.2, 29.5, 29.8, 29.8, 32.1, 32.4, 49.9, 66.3, 75.7, 98.4 ppm. MS (EI): *m*/*z* (%) = 342 (3) [$M^+ + 1$], 327 (16), 326 (72) [$M^+ - CH_3$], 283 (7), 267 (8), 266 (36), 252 (6), 102 (10), 101 (100), 95 (8), 83 (11), 82 88), 81 (8), 72 (9), 71 88), 70 (9), 69 (12), 67 (11), 60 (14), 59 (19), 58 (9), 57 (25), 56 (54), 55 (39). $C_{21}H_{43}NO_2$ (341.58): calcd. C 73.84, H 12.69, N 4.10; found C 74.27, H 12.20, N 3.80.

2-Hydroxy-1-hydroxymethyl-3-phenylpropylammonium Trifluoroacetate [(*S*,*R*)-6c]: 1.5 Equivalents of trifluoroacetic acid was added dropwise to a stirred solution of amine (*S*,*R*)-**5c** (0.10 g) in THF (15.0 mL/mmol) and water (7.5 mL/mmol). After stirring for 20 min at room temp. the solvent was removed in vacuo to give the product as a colourless solid. Yield: 130 mg (95%). $[\alpha]_D^{23}$ = +10.7

(*c* = 1.02, acetone). M.p. 132 °C. *de* = 96%. IR (KBr): $\tilde{\nu}$ = 3220 (m), 3092 (m), 3036 (m), 2948 (m), 2901 (m), 2397 (s), 2268 (s), 1666 (vs), 1499 (w), 1454 (m), 1437 (m), 1376 (w), 1338 (w), 1308 (w), 1186 (vs), 1134 (vs), 1091 (m), 1054 (m), 998 (w), 964 (w), 903 (w), 840 (m), 801 (m), 762 (m), 725 (m), 700 (m), 634 (w), 532 (w), 488 (w) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 2.86 (dd, *J* = 1.7/6.2 Hz, 2 H, $CH_2C_6H_5$), 3.25 (ddd, *J* = 4.0/7.9/8.2 Hz, 1 H, $CHNH_3^+$), 3.86 (dd, *J* = 8.5/11.9 Hz, 1 H, HC*H*OH), 4.02 (dd, *J* = 4.0/11.9 Hz, 1 H, *H*CHOH), 4.14 (ddd, *J* = 1.7/6.2/7.9 Hz, 1 H, C*H*OH), 7.34 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 39.3, 56.3, 57.4, 70.5, 126.3, 128.2, 128.9, 137.7 ppm. MS (FAB) [DTE/DTT/Sul]: Cation: *m*/*z* (%) = 183 (11) [M^+ + 1], 182 (100) [M^+], 91 (7), 60 (8), anion: *m*/*z* (%) = 113 (100) [M^+], 69 (5). $C_{12}H_{16}F_3NO_4$ (295.26): calcd. C 48.82, H 5.46, N 4.74; found C 48.92, H 5.68, N 4.76.

2-Hydroxy-1-(hydroxymethyl)heptadecylammonium Trifluoroacetate [(*R*,*S*)-11]: 1.5 Equivalents of trifluoroacetic acid was added dropwise to a stirred solution of amine (*R*,*S*)-**10** (80.0 mg) in THF (15.0 mL/mmol) and water (7.5 mL/mmol),. After stirring for 20 min at room temp. the solvent was removed in vacuo to give the product as a colourless solid. Yield: 90 mg (87%). $[\alpha]_D^{23}$ = −7.9 (*c* = 0.96, acetone). M.p. 100 °C. *de* = 96%. IR (KBr): $\tilde{\nu}$ = 3345 (m), 3075 (s), 2922 (vs), 2851 (s), 2298 (w), 1656 (s), 1526 (w), 1469 (m), 1445 (w), 1346 (w), 1212 (s), 1185 (s), 1157 (s), 1053 (m), 844 (m), 806 (m), 726 (m) cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 0.93 [t, *J* = 6.7 Hz, 3 H, $(CH_2)_{13}CH_3$], 1.32 [m, 26 H, $(CH_2)_{13}CH_3$], 1.52 [m, 2 H, $CH_2(CH_2)_{13}CH_3$], 3.23 (m, 1 H, $CHNH_3^+$), 3.74 (dd, *J* = 8.4/11.6 Hz, 1 H, HC*H*OH), 3.82 (m, 1 H, C*H*OH), 3.87 (dd, *J* = 4.2/11.8 Hz, 1 H, *H*CHOH) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 13.1, 22.4, 25.6, 29.1, 29.2, 29.3, 29.4, 31.7, 32.8, 57.0, 57.5, 68.5 ppm. MS (FAB) [DTE/DTT/Sul]: cation: *m*/*z* (%) = 303 (14) [M^+ + 1], 302 (100) [M^+], 300 (11), 284 (15), 67 (6), 60 (45), 56 (6), 55 (12), anion: *m*/*z* (%) = 113 (100) [M^+], 69 (5). $C_{20}H_{40}F_3NO_4$ (415.53): calcd. C 57.81, H 9.70, N 3.37; found C 58.04, H 9.92, N 3.13.

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