Syntheses and Properties of Enantiomerically Pure Higher \( (n \geq 7) \)

\([n-2]\text{Triangulanedimethanols and } \sigma-[n]\text{Helicenes}\)

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I. Synthesis of (1S,3R,4S,5S,6S,7S,8R,9S)-[9-(hydroxymethyl)hexaspiro-
[2.0.0.0.0.1.1.1.1]pentadec-1-yl]methanol [(1S,3R,4S,5S,6S,7S,8R,9S)-22]

2-[(1S,3R,4S)-5,5-Dibromodispiro[2.0.2.1]hept-1-ylmethoxy]tetrahydro-2H-pyran
[(1S,3R,4S)-20]: The crude compound (1S,3R,4S)-20 (30.4 g, 97%) was obtained from
[(1S,3R,4S)-5,5-dibromo[2.0.2.1]hept-1-yl]methanol [(1S,3R,4S)-19] (24.0 g, 85 mmol),
DHP (12.9 g, 153 mmol) and PPTS (1.3 g, 5.2 mmol) in CH₂Cl₂ (150 mL) according to
GP 2 (20 °C, 2 h) and used without further purification. ¹H NMR (250 MHz, CDCl₃):
δ = 4.82–4.61 (m, 1 H; CHO₂), 3.96–3.74 (m, 2 H; CH₂O), 3.72–3.54 (m, 2 H; CH₂O),
2.13–1.40 (m, 11 H), 1.35–0.98 (m, 1 H; cPr-H), 0.91–0.84 (m, 1 H; cPr-H).

(E)-(3S,3'S,4R,4'R,5S,5'S)-(5'-Hydroxymethyl-[1,1']bi[dispiro[2.0.2.1]heptylidene]-
5-yl)methanol [(E)-(3S,3'S,4R,4'R,5S,5'S)-21]: Compound (1S,3R,4S)-20 (30.4 g, 83.1
mmol) was treated with nBuLi (99.6 mmol, 41.2 mL of a 2.42 M solution in hexane) and
CuCl₂ (2.20 g, 16.4 mmol) in THF/Et₂O 15:1 (256 mL) and the oily residue (19.1 g) was
worked up with MeOH (1000 mL) and PPTS (1.30 g, 5.2 mmol) according to GP 3 (60 °C,
2 h). Column chromatography of the residue (300 g of silica gel, 8 × 50 cm column,
hexane/Et₂O 2:1, Rᵢ = 0.25) followed by recrystallization from hexane/Et₂O furnished
(E)-(3S,3'S,4R,4'R,5S,5'S)-21 (5.20 g, 25% over three steps) as a colorless solid, m.p.
122–127 °C; [α]ᵢ²⁰ = +33.4 (c = 0.500 in CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 3.75
(dd, J = 6.4, 11.2 Hz, 2 H; 2 CH₂O), 3.57 (dd, J = 7.2, 11.2 Hz, 2 H; 2 CH₂O), 1.66 (br s,
2 H; 2 OH), 1.53 (d, J = 5.6 Hz, 2 H; cPr-H), 1.52 (m, 2 H; cPr-H), 1.39 (m, 4 H; cPr-H), 1.30 (d, J = 5.6 Hz, 2 H; cPr-H), 1.10 (dd, J = 7.8, 4.6 Hz, 2 H; cPr-H), 0.81 (dd, J = 4.6, 4.5 Hz, 2 H; cPr-H); 13C NMR (62.9 MHz, CDCl3): δ = 122.4 (2 C), 66.1 (2 CH2), 21.8 (2 C), 19.8 (2 C), 16.3 (2 C), 13.7 (2 CH2), 10.1 (2 CH2), 9.8 (2 CH2); IR (KBr): ν (tilde) = 3244, 3059, 2992, 2963, 2888, 1419, 1330, 1123, 1047, 987, 838 cm⁻¹; MS (Cl): m/z (%): 507/506 (1/4) (2M + NH₄⁺) 264/263/262 (2/16/100) (M + NH₄⁺); elemental analysis calcd (%) for C₁₆H₂₀O₂: C 78.65, H 8.25; found C 78.35, H 7.94. Its structure was also confirmed by X-ray crystal structure analysis.[10]

Scheme 10. Synthesis of (1S,3R,4S,5S,6S,7S,8R,9S)-[9-(hydroxymethyl)hexaspiro[2.0.0.0.0.0.2.1.1.1.1]pentadec-1-yl]methanol [(1S,3R,4S,5S,6S,7S,8R,9S)-22].

Reagents and conditions: a) DHP, PPTS, CH₂Cl₂, 20 °C, 2 h; b) nBuLi, CuCl₂, THF/Et₂O 15:1, −105 to −95 °C, 1 h, then −78 to 20 °C, 2 h; c) MeOH, PPTS, 60 °C, 2 h; d) CH₂N₂ (134 equiv.), CuCl (2.67 equiv.), 20 °C, 3 h.
pentadec-1-yl)methanol [(1S,3R,4S,5S,6S,7S,8R,9S)-22]: Each of three equal portions of the diol (E)-(3S,3'S,4R',5S,5'S)-21 (70 mg, 0.29 mmol) in diethyl ether (50 mL) was treated with CH₂N₂ (29.1 mmol, 10 mL of a 2.9 M solution in Et₂O) in the presence of CuCl (57 mg, 0.58 mmol) according to GP 4, and the combined reaction mixtures were treated with CH₂N₂ (29.1 mmol, 10 mL of a 2.9 M solution in Et₂O) in the presence of CuCl (57 mg, 0.58 mmol) according to GP 4 again. Column chromatography of the residue (20 g of silica gel, 2 × 30 cm column, pentane/Et₂O 1:2, Rᵣ = 0.24) afforded (1S,3R,4S,5S,6S,7S,8R,9S)-22 (40 mg, 18%) as a colorless solid, m.p. 132–135 °C, [α]D²⁰ = −190.8 (c = 0.50 in CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 3.70 (dd, J = 6.3, 11.2 Hz, 2 H; 2 CH₂O), 3.51 (dd, J = 7.5, 11.2 Hz, 2 H; 2 CH₂O), 1.66 (br, 2 H; 2 OH), 1.44 (m, 2 H; cPr-H), 1.18 (m, 4 H, cPr-H), 1.11 (d, J = 3.9 Hz, 2 H; cPr-H), 1.02 (s, 2 H; cPr-H), 0.99 (d, J = 3.9 Hz, 2 H; cPr-H), 0.92 (dd, J = 4.4, 7.7 Hz, 2 H; cPr-H), 0.75 (dd, J = 4.4, 4.5 Hz, 2 H; cPr-H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 66.2 (2 CH₂), 29.6 (2 C), 20.8 (2 CH), 17.9 (2 C), 17.4 (2 C), 13.0 (CH₂), 10.2 (2 CH₂), 9.6 (2 CH₂), 8.7 (2 CH₂); IR (KBr): ν (tilde) = 3244, 3028, 2963, 2887, 1718, 1457, 1419, 1333, 1271, 1152, 1104, 1023, 762, 703 cm⁻¹; MS (Cl): m/z (%): 536/535/534 (1/4/7) (2M + NH₄⁺), 278/277/276 (2/16/100) (M + NH₄⁺); elemental analysis calcd (%) for C₁₇H₂₂O₂: C 79.03, H 8.58; found C 79.05, H 8.53.

II. Esterification of diols (P)-(+)→14, (1S,3R,4S,5S,6S,7S,8R,9S)-22 and (P)-(+)→22

General procedure GP 10: To a solution of the respective diol, the respective acid and DMAP in anhydrous CH₂Cl₂ (2 mL) was added DCC at 0 °C. The reaction mixture was
stirred at ambient temp. for an additional 12 h and then concentrated under reduced pressure. The product was purified by column chromatography on silica gel (12.5 g of silica gel, 2 × 30 cm column, hexane/Et₂O 20:1).

(1S,3R,4R,5R,6R,7S)-{7-[(4-n-Pentylbenzoyl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]-undec-1-yl)methyl} 4-n-pentylbenzoate (43a): Column chromatography (R₁ = 0.25) of the reaction mixture obtained from diol (P)-(+)−14 (31 mg, 0.15 mmol), 4-n-pentylbenzoic acid (88 mg, 0.46 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 43a (39 mg, 47%) as a colorless powder, m.p. 49.0–52.9 °C, [α]D²⁰ = +190.3 (c = 0.3 in CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 7.96 (d, J = 8.1 Hz, 4 H; Ar -H), 7.24 (d, J = 8.1 Hz, 4 H; Ar-H), 4.32 (d, J = 7.0 Hz, 4 H; 2 CH₂O), 2.66 (t, J = 7.4 Hz, 4 H; 2 CH₃), 1.63 (m, 4 H), 1.52 (m, 2 H; cPr-H), 1.34–1.07 (m, 16 H), 0.89 (t, J = 5.2 Hz, 6 H; 2 CH₃), 0.83 (t, J = 4.4 Hz, 2 H; cPr-H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 166.8 (2 C), 148.4 (2 C), 129.6 (4 CH), 128.4 (2 C), 127.9 (4 CH), 68.4 (2 CH₂), 35.9 (2 CH₂), 31.4 (2 CH₂), 30.8 (2 CH₂), 22.5 (2 CH₂), 18.5 (2 CH), 18.2 (2 C), 15.0 (2 C), 14.0 (2 CH₃), 11.5 (CH₂), 9.8 (2 CH₂), 8.7 (2 CH₂); IR (KBr): ν(tilde) = 3041, 2930, 2857, 1720, 1611, 1462, 1445, 1415, 1383, 1309, 1271, 1177, 1106, 963, 857, 764 cm⁻¹; MS (EI): m/z (%): 554 (1) (M⁺), 363 (8), 175 (100), 171 (21), 155 (14), 91 (17), 41 (6); HRMS (CI): calcd for C₃₇H₅₉NO₄: M⁺ + NH₄ 572.3734; found 572.3735.

(1S,3R,4R,5R,6R,7S)-{7-[(4-trans-n-Pentylcyclohexanecarbonyl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]-undec-1-yl)methyl} (4-trans-n-pentyl)cyclohexanecarboxylate
(43b): Column chromatography (Rf = 0.24) of the reaction mixture obtained from diol (P)-(+)−14 (31 mg, 0.15 mmol), 4-trans-n-pentylcyclohexanecarboxylic acid (89 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 43b (54 mg, 63%) as a colorless powder, m.p. 77.3–78.8 °C, [α]20D = +180.0 (c = 0.50 in CHCl3); 1H NMR (250 MHz, CDCl3): δ = 4.06 (d, J = 7.2 Hz, 4 H; 2 CH2O), 2.22 (tt, J = 3.4, 12.1 Hz, 2 H; cHex-H), 1.94 (d, J = 11.7 Hz, 4 H; 2 CH2), 1.79 (d, J = 12.0 Hz, 4 H; 2 CH2), 1.51–0.99 (m, 36 H), 0.87 (t, J = 7.0 Hz, 6 H; 2 CH3), 0.70 (t, J = 4.5 Hz, 2 H; cPr-H); 13C NMR (CDCl3, 62.9 MHz): δ = 176.4 (2 C), 67.7 (2 CH2), 43.6 (2 CH2), 37.2 (2 CH2), 36.9 (2 CH), 32.3 (2 CH2), 32.1 (2 CH2), 29.1 (4 CH2), 26.5 (2 CH2), 22.7 (4 CH2), 18.4 (2 CH), 18.2 (2 C), 14.9 (2 C), 14.1 (2 CH3), 11.4 (CH2), 9.6 (2 CH2), 8.6 (2 CH2); IR (KBr): ν (tilde) = 3046, 2953, 2923, 2852, 1729, 1450, 1371, 1272, 1180, 1141, 1035, 997, 900, 866, 763 cm−1; MS (EI): m/z (%): 566 (1) (M+), 222 (32), 99 (100), 55 (64), 41 (6); HRMS (CI): calcd for C37H62NO4: M+ + NH4 584.4673; found 584.4674.

(1S,3R,4R,5R,6R,7S)-7-[(4-n-Propylbenzoyl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]-undec-1-yl)methyl] 4-n-propylbenzoate (43c): Column chromatography (Rf = 0.23) of the reaction mixture obtained from diol (P)-(+)−14 (31 mg, 0.15 mmol), 4-n-propylbenzoic acid (74 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 43c (30 mg, 40%) as a colorless powder, m.p. 73–77 °C, [α]20D = +213.8 (c = 0.50 in CHCl3); 1H NMR (250 MHz, CDCl3): δ = 7.97 (d, J = 8.1 Hz, 4 H; Ar-H), 7.24 (d, J = 8.1 Hz, 4 H; Ar-H), 4.33 (d, J = 7.0 Hz, 4 H; 2 CH2O), 2.64 (t, J = 8.0 Hz, 4 H; 2 CH2), 1.73–1.50 (m, 6 H), 1.25–1.07 (m, 8 H), 0.94 (t, J = 7.3
Hz, 6 H; 2 CH3), 0.82 (t, J = 4.5 Hz, 2 H; cPr-H); 13C NMR (62.9 MHz, CDCl3): δ = 166.8 (2 C), 148.1 (2 C), 129.6 (4 CH), 128.4 (2 C), 128.0 (4 CH), 68.4 (2 CH2), 38.0 (2 CH2), 24.3 (2 CH2), 18.5 (2 CH), 18.3 (2 C), 15.0 (2 C), 13.7 (2 CH3), 11.5 (CH2), 9.8 (2 CH2), 8.7 (2 CH2); IR (KBr): nu(tilde) = 3042, 2961, 2963, 2872, 1717, 1610, 1559, 1457, 1309, 1271, 1178, 1057, 1019, 851, 761, 703 cm⁻¹; MS (EI): m/z (%): 498 (1) (M⁺), 147 (100), 91 (19), 57 (46), 41 (16); HRMS (CI): calcd for C33H42NO4: M⁺ + NH₄ 516.3108; found 516.3108.

(1S,3R,4R,5R,6R,7S)-{7-[(4-trans-n-Propylcyclohexanecarbonyl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1]undec-1-yl)methyl} (4-trans-n-propyl)cyclohexanecarboxylate (43d): Column chromatography (Rf = 0.26) of the reaction mixture obtained from diol (P)-(+)–14 (31 mg, 0.15 mmol), 4-trans-n-propylecyclohexanecarboxylic acid (77 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 43d (53 mg, 69%) as a colorless powder, m.p. 90–95 ºC, [α]D₀ = +197.4 (c = 0.50 in CHCl3); 1H NMR (250 MHz, CDCl3): δ = 4.06 (d, J = 7.2 Hz, 4 H; 2 CH2O), 2.22 (tt, J = 12.2, 3.6 Hz, 2 H; cHex-H), 1.94 (d, J = 11.0 Hz, 4 H; 2 CH2), 1.78 (d, J = 11.0 Hz, 4 H; 2 CH2), 1.51–0.85 (m, 28 H), 0.86 (t, J = 7.2 Hz, 6 H; 2 CH3), 0.70 (t, J = 4.5 Hz, 2 H; cPr-H); 13C NMR (62.9 MHz, CDCl3): δ = 176.4 (2 C), 67.7 (2 CH2), 43.6 (2 CH2), 39.5 (2 CH2), 36.6 (2 CH), 32.3 (4 CH2), 29.1 (4 CH2), 19.9 (2 CH2), 18.4 (2 CH), 18.2 (2 C), 14.9 (2 C), 14.3 (2 CH3), 11.4 (CH2), 9.6 (2 CH2), 8.6 (2 CH2); IR (KBr): nu(tilde) = 3048, 2915, 2856, 1722, 1559, 1457, 1374, 1315, 1253, 1223, 1186, 1143, 1092, 1037, 996, 948, 737 cm⁻¹; MS (EI): m/z (%): 510 (1) (M⁺), 239 (14), 222 (23), 207 (35), 125 (37), 69 (100),
(1S,3R,4R,5R,6R,7S)-7-[4-n-Pentyloxybenzoyl]oxymethyl]tetraspiro[2.0.0.0.2.1.1.1.undec-1-yl]methyl) 4-n-pentyloxybenzoate (43e): Column chromatography (RF = 0.09) of the reaction mixture obtained from diol (P)-(+) \textbf{14} (31 mg, 0.15 mmol), 4-n-pentyloxybenzoic acid (94 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 43e (30 mg, 34%) as a colorless powder, m.p. 86.3–88.7 °C, [α]D20 = +178.8 (c = 0.50 in CHCl3); ¹H NMR (250 MHz, CDCl3): δ = 8.00 (d, J = 8.9 Hz, 4 H; Ar-H), 6.91 (d, J = 8.9 Hz, 4 H; Ar-H), 4.28 (dd, J = 7.3, 2.2 Hz, 4 H; 2 CH₂O), 4.00 (t, J = 6.6 Hz, 4 H; 2 CH₂O), 1.80 (m, 4 H), 1.54–1.06 (m, 18 H), 0.93 (t, J = 7.3 Hz, 6 H; 2 CH₃), 0.81 (t, J = 4.5 Hz, 2 H; cPr-H); ¹³C NMR (62.9 MHz, CDCl3): δ = 166.6 (2 C), 162.8 (2 C), 131.5 (4 CH), 122.6 (2 C), 114.0 (4 CH), 68.21 (2 CH₂), 68.19 (2 CH₂), 28.8 (2 CH₂), 28.1 (2 CH₂), 22.4 (2 CH₂), 18.5 (2 CH), 18.2 (2 C), 15.0 (2 C), 14.0 (2 CH₃), 11.5 (CH₂), 9.8 (2 CH₂), 8.7 (2 CH₂); IR (KBr): ν(tilde) = 3048, 2955, 2933, 2871, 1717, 1606, 1507, 1457, 1419, 1387, 1313, 1272, 1254, 1167, 1102, 1052, 846, 770, 696, 649 cm⁻¹; MS (EI): m/z (%): 586 (1) (M⁺), 363 (8), 175 (100), 171 (21), 155 (14), 91 (17); HRMS (CI): calcd for C₃₇H₅₀NO₆: M⁺ + NH₄ 604.3633; found 604.3632.

(1S,3R,4R,5R,6R,7S)-7-[(n-Hexanoyl)oxymethyl]tetraspiro[2.0.0.0.2.1.1.1.undec-1-yl]methyl) n-hexanoate (43f): Column chromatography (RF = 0.36) of the reaction mixture obtained from diol (P)-(+) \textbf{14} (31 mg, 0.15 mmol), n-hexanoic acid (52 mg, 0.45...
mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 45f (24 mg, 40%) as a colorless oil, $[\alpha]_{D}^{20} = +244.0 (c = 0.3 \text{ in CHCl}_3)$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 4.07$ (dd, $J = 4.2$, 7.0 Hz, 4 H; 2 CH$_2$O), 2.31 (t, $J = 7.6$ Hz, 4 H; 2 CH$_2$), 1.63 (m, 4 H), 1.41–1.25 (m, 10 H), 0.90 (t, $J = 6.8$ Hz, 6 H; 2 CH$_3$), 0.70 (t, $J = 4.5$ Hz, 2 H; cPr-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 174.1$ (2 C), 67.9 (2 CH$_2$), 34.4 (2 CH$_2$), 31.3 (2 CH$_2$), 24.7 (2 CH$_2$), 22.3 (2 CH$_2$), 18.5 (2 CH), 18.2 (2 C), 14.9 (2 C), 13.9 (2 CH$_3$), 11.5 (CH$_2$), 9.6 (2 CH$_2$), 8.6 (2 CH$_2$); IR (Film): $\nu$(tilde) = 3048, 2957, 2937, 2860, 1734, 1653, 1540, 1457, 1362, 1275, 1243, 1172, 1095, 1026, 991, 889, 734 cm$^{-1}$; MS (EI): m/z (%): 402 (1) ($M^+$), 303 (8), 115 (23), 99 (100); HRMS (CI): calcd for C$_{25}$H$_{42}$NO$_4$: $M^+$ + NH$_4$ 420.3108; found 420.3109.

(1S,3R,4S,5S,6S,7S,8R,9S)-9-[(4-n-Pentylbenzoyl)oxymethyl]hexaspiro-
[2.0.0.0.0.2.1.1.1.1]pentadec-1-yl)methyl] 4-n-pentylbenzoate (44a): Column chromatography ($R_f = 0.41$) of the reaction mixture obtained from diol (1S,3R,4S,5S,6S,7S,8R,9S)-22 (50 mg, 0.2 mmol), 4-n-pentylbenzoic acid (115 mg, 0.6 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (136 mg, 0.66 mmol) according to GP 10 gave 44a (37 mg, 31%) as a colorless powder, m.p. 68.3–70.8 °C, $[\alpha]_{D}^{20} = -139.7 (c = 0.35 \text{ in CHCl}_3)$; $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.92$ (d, $J = 8.3$ Hz, 4 H; Ar-H), 7.22 (d, $J = 8.3$ Hz, 4 H; Ar-H), 4.48 (dd, $J = 8.2$, 11.1 Hz, 2 H; CH$_2$O), 4.12 (dd, $J = 8.2$, 11.1 Hz, 2 H; CH$_2$O), 2.65 (t, $J = 8.0$ Hz, 4 H; 2 CH$_2$), 1.64 (m, 6 H), 1.39–1.25 (m, 8 H), 1.22 (d, $J = 3.7$ Hz, 2 H; cPr-H), 1.15 (d, $J = 3.7$ Hz, 2 H; cPr-H), 1.06–0.86 (m, 16 H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 166.7$ (2 C), 148.4 (2 C), 129.5 (4 CH), 128.3 (2 C), 127.9 (4 CH),
68.6 (2 CH₂), 35.9 (2 CH₂), 31.4 (2 CH₂), 30.9 (2 CH₂), 22.5 (2 CH₂), 18.5 (2 CH), 17.9 (2 C), 17.4 (2 C), 14.1 (2 CH₃), 14.0 (2 CH₂), 10.3 (2 CH₂), 10.1 (2 CH₂), 8.7 (2 CH₂), 8.6 (CH₂); IR (KBr): ν̃ = 3041, 2957, 2930, 2857, 1716, 1611, 1510, 1462, 1415, 1329, 1353, 1309, 1272, 1177, 1105, 1019, 985, 939, 857, 763, 703, 637 cm⁻¹; MS (EI): m/z (\%): 606 (1) (M⁺), 207 (18), 175 (100), 91 (21), 41 (6); HRMS (CI): calcd for C₄₁H₅₄NO₄: M⁺ + NH₄ 624.4047; found 624.4045.

(1S,3R,4S,5S,6S,7S,8R,9S)-[9-[(4-trans-n-Pentylcyclohexanecarbonyl)oxymethyl]-hexaspiro[2.0.0.0.0.1.1.1.1]pentadec-1-yl)methyl] (4-trans-n-pentyl)cyclohexanecarboxylate (44b): Column chromatography (Rf = 0.41) of the reaction mixture obtained from diol (1S,3R,4S,5S,6S,7S,8R,9S)-22 (50 mg, 0.2 mmol), 4-trans-n-pentylcyclohexanecarboxylic acid (119 mg, 0.6 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (136 mg, 0.66 mmol) according to GP 10 gave 44b (47 mg, 39%) as a colorless powder, m.p. 63–70 °C, [α]₂₀^D = −146.4 (c = 0.50 in CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 4.21 (dd, J = 8.1, 11.2 Hz, 2 H; CH₂O), 3.89 (dd, J = 8.1, 11.2 Hz, 2 H; CH₂O), 2.18 (tt, J = 3.4, 12.1 Hz, 2 H; cHex-H), 1.92 (d, J = 12.5 Hz, 4 H; 2 CH₂), 1.77 (d, J = 12.5 Hz, 4 H; 2 CH₂), 1.53–1.11 (m, 30 H), 1.00–0.80 (m, 18 H); ¹³C NMR (CDCl₃, 62.9 MHz): δ = 176.2 (2 C), 67.8 (2 CH₂), 43.7 (2 CH₂), 37.1 (2 CH₂), 36.9 (2 CH), 32.3 (2 CH₂), 32.1 (2 CH₂), 29.0 (4 CH₂), 26.5 (2 CH₂), 22.7 (4 CH₂), 18.5 (2 CH), 17.9 (2 C), 17.4 (2 C), 14.2 (2 CH₃), 14.1 (2 C), 10.02 (2 CH₂), 9.96 (2 CH₂), 8.8 (2 CH₂), 8.6 (CH₂); IR (KBr): ν̃ = 3042, 2921, 2853, 1725, 1448, 1316, 1279, 1171, 1135, 1035, 993, 904 cm⁻¹; MS (EI): m/z (\%): 618 (1) (M⁺), 239 (43), 207 (53), 99 (100), 55 (54); HRMS (CI): calcd
for C\textsubscript{43}H\textsubscript{66}NO\textsubscript{4}: \(M^+\)+NH\textsubscript{4} 636.4986; found 636.4985.

\([1S,3R,4S,5S,6S,7S,8R,9S]-\{9-[(4-n-Propylbenzoyl)oxy\textsubscript{methyl}]\text{hexaspiro-}\[2.0.0.0.0.2.1.1.1.1.1]\text{pentadec-1-yl}methyl\} 4-n-propy\textsubscript{b}eno\text{zoate} (44c): Column chromatography (\(R_f = 0.36\)) of the reaction mixture obtained from diol \([1S,3R,4S,5S,6S,7S,8R,9S]-22\) (40 mg, 0.155 mmol), 4-\(n\)-propy\text{b}eno\text{z}ic acid (77 mg, 0.47 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 44c (24 mg, 28%) as a colorless powder, m.p. 74–93 °C. \([\alpha]_D^{20} = -151.4\) (c = 0.35 in CHCl\textsubscript{3}); \(\text{\textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3})}: \delta = 7.92\) (d, \(J = 8.2\) Hz, 4 H; Ar-H), 7.22 (d, \(J = 8.2\) Hz, 4 H; Ar-H), 4.47 (dd, \(J = 8.0, 11.5\) Hz, 2 H; CH\textsubscript{2}O), 4.11 (dd, \(J = 8.0, 11.5\) Hz, 2 H; CH\textsubscript{2}O), 2.64 (t, \(J = 8.0\) Hz, 4 H; 2 CH\textsubscript{2}), 1.73–1.55 (m, 6 H), 1.29 (d, \(J = 3.7\) Hz, 2 H; cPr-H), 1.22 (d, \(J = 4.0\) Hz, 2 H; cPr-H), 1.15 (d, \(J = 3.7\) Hz, 2 H; cPr-H), 0.98–0.92 (m, 8 H), 0.94 (t, \(J = 7.4\) Hz, 6 H; 2 CH\textsubscript{3}); \(\text{\textsuperscript{13}C NMR (62.9 MHz, CDCl\textsubscript{3})}: \delta = 166.7\) (2 C), 148.1 (2 C), 129.5 (4 CH), 128.4 (2 C), 127.9 (4 CH), 68.6 (2 CH\textsubscript{2}), 38.0 (2 CH\textsubscript{2}), 24.3 (2 CH\textsubscript{2}), 18.5 (2 CH), 17.9 (2 C), 17.4 (2 C), 14.1 (2 C), 13.7 (2 CH\textsubscript{3}), 10.3 (2 CH\textsubscript{2}), 10.1 (2 CH\textsubscript{2}), 8.7 (2 CH\textsubscript{2}), 8.6 (CH\textsubscript{2}); IR (KBr): nu(\text{tilde}) = 3041, 2966, 2930, 2871, 1717, 1653, 1559, 1506, 1457, 1419, 1308, 1271, 1178, 1104, 1074, 1019, 761, 703 cm\textsuperscript{-1}; MS (EI): \(m/z\) (%): 550 (1) (\(M^+\)), 207 (13), 147 (100), 119 (15), 91 (19), 57 (12), 41 (17); HRMS (CI): calcd for C\textsubscript{37}H\textsubscript{46}NO\textsubscript{4}: \(M^+\) + NH\textsubscript{4} 568.3421; found 568.3421.

\([1S,3R,4S,5S,6S,7S,8R,9S]-\{9-[(4-trans-\text{n-Propylcyclohexanecarbonyl)oxy\text{methyl}]\text{hexaspiro-}\[2.0.0.0.0.2.1.1.1.1.1]\text{pentadec-1-yl}methyl\} 4-trans-\text{n-propy\text{c}lohexa-}
necarboxylate (44d): Column chromatography ($R_f = 0.36$) of the reaction mixture obtained from diol (1S,3R,4S,5S,6S,7S,8R,9S)-22 (40 mg, 0.15 mmol), 4-trans-$n$-propylcyclohexanecarboxylic acid (94 mg, 0.55 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 44d (30 mg, 34%) as a colorless powder, m.p. 79–87 °C, $[\alpha]_D^{20} = -151.4$ ($c = 0.50$ in CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 4.21$ (dd, $J = 6.5, 11.3$ Hz, 2 H; CH$_2$O), 3.88 (dd, $J = 8.1, 11.3$ Hz, 2 H; CH$_2$O), 2.18 (tt, $J = 3.5, 12.2$ Hz, 2 H; cHex-H), 1.92 (d, $J = 12.2$ Hz, 4 H; 2 CH$_2$), 1.77 (d, $J = 12.2$ Hz, 4 H; 2 CH$_2$), 1.50–1.11 (m, 24 H), 1.02–0.94 (m, 6 H), 0.89 (t, $J = 7.0$ Hz, 6 H; 2 CH$_3$), 0.89–0.78 (m, 4 H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 176.2$ (2 C), 67.8 (2 CH$_2$), 43.6 (2 CH$_2$), 39.4 (2 CH$_2$), 36.6 (2 CH), 32.2 (4 CH$_2$), 29.0 (4 CH$_2$), 19.8 (2 CH$_2$), 18.4 (2 C), 17.9 (2 C), 17.4 (2 C), 14.3 (2 CH$_3$), 14.2 (2 C), 10.1 (2 CH$_2$), 10.0 (2 CH$_2$), 8.7 (2 CH$_2$), 8.5 (CH$_2$); IR (KBr): $\nu$ (tilde) = 3048, 1743, 1653, 1617, 1559, 1506, 1457, 1419, 1393, 1176, 1038, 908, 668 cm$^{-1}$; MS (EI): $m/z$ (%): 562 (1) ($M^+$), 222 (31), 207 (35), 125 (42), 69 (100), 55 (14); HRMS (CI): calcd for C$_{37}$H$_{58}$NO$_5$: $M^+$ + NH$_4$ 580.4360; found 580.4360.

(1S,3R,4S,5S,6S,7S,8R,9S)-[9-[(4-$n$-Pentyloxybenzoyl)oxymethyl]hexaspiro-
[2.0.0.0.0.2.1.1.1.1]pentadec-1-yl)methyl] 4-$n$-pentyloxybenzoate (44e): Column chromatography ($R_f = 0.20$) of the reaction mixture obtained from diol (1S,3R,4S,5S,6S,7S,8R,9S)-22 (40 mg, 0.15 mmol), 4-$n$-pentyloxybenzoic acid (94 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 44e (57 mg, 58%) as a colorless powder, m.p. 69–85 °C, $[\alpha]_D^{20} = -162.0$ ($c = 0.50$)
in CHCl₃; ¹H NMR (250 MHz, CDCl₃): δ = 7.94 (d, J = 8.8 Hz, 4 H; Ar-H), 6.88 (d, J = 8.8 Hz, 4 H; Ar-H), 4.45 (dd, J = 6.7, 11.2 Hz, 2 H; CH₂O), 4.10 (dd, J = 6.7, 11.2 Hz, 2 H; CH₂O), 4.00 (t, J = 6.6 Hz, 4 H; 2 CH₂O), 1.80 (m, 4 H), 1.60–1.14 (m, 14 H), 1.09–1.04 (m, 4 H), 0.99–0.85 (m, 6 H), 0.93 (t, J = 6.9 Hz, 6 H; 2 CH₃); ¹³C NMR (62.9 MHz, CDCl₃): δ = 166.4 (2 C), 162.8 (2 C), 131.4 (4 CH), 122.6 (2 C), 113.9 (4 CH), 68.4 (2 CH₂), 68.1 (2 CH₂), 28.8 (2 CH₂), 28.1 (2 CH₂), 22.4 (2 CH₂), 18.4 (2 CH), 17.9 (2 C), 17.4 (2C), 14.1 (2 CH₃), 14.0 (2 C), 10.3 (2 CH₂), 10.1 (2 CH₂), 8.7 (2 CH₂), 8.6 (CH₂); IR (KBr): ν(tilde) = 3044, 2957, 2936, 2872, 1714, 1607, 1559, 1511, 1457, 1313, 1273, 1254, 1168, 1101, 1020, 989, 846, 770, 697, 646 cm⁻¹; MS (EI): m/z (%): 638 (1) (M⁺), 363 (32), 175 (100), 171 (21), 155 (14), 91 (17); HRMS (CI): calcd for C₄₁H₅₄NO₆: M⁺ + NH₄ 656.3946; found 656.3945.

(1S,3R,4S,5S,6S,7S,8R,9S)-{9-[(n-Hexanoyl)oxy)methyl]hexaspiro[2.0.0.0.0.0.2.1.1.1.1.-pentadec-1-yl)methyl} n-hexanoate (44f): Column chromatography (Rₛ = 0.43) of the reaction mixture obtained from diol (1S,3R,4S,5S,6S,7S,8R,9S)-22 (60 mg, 0.23 mmol), n-hexanoic acid (80 mg, 0.69 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (156 mg, 0.76 mmol) according to GP 10 gave 44f (68 mg, 65%) as a colorless oil, [α]₂⁰⁰ = –151.0 (c = 0.50 in CHCl₃); ¹H NMR (250 MHz, CDCl₃): δ = 4.03 (dd, J = 4.2, 7.2 Hz, 4 H; 2 CH₂O), 2.26 (t, J = 7.4 Hz, 4 H; 2 CH₂), 1.53 (m, 4 H), 1.41–1.11 (m, 14 H), 0.99 (m, 6 H), 0.90–0.79 (m, 10 H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 173.8 (2 C), 67.9 (2 CH₂), 34.3 (2 CH₂), 31.3 (2 CH₂), 24.6 (2 CH₂), 22.2 (2 CH₂), 18.3 (2 CH), 17.9 (2 C), 17.4 (2 C), 14.2 (2 CH₃), 13.9 (2 C), 10.11 (2 CH₂), 10.09 (2 CH₂), 8.62 (2 CH₂), 8.58 (CH₂); IR
(Film): $\nu$(tilde) = 3043, 2959, 2933, 2872, 2864, 1735, 1457, 1363, 1276, 1243, 1173, 1096, 1007, 996, 907, 865, 734 cm$^{-1}$; MS (EI): $m/z$ (%): 454 (1) ($M^+$), 303 (12), 115 (21), 99 (100); HRMS (CI): calcd for C$_{29}$H$_{46}$NO$_4$: $M^+$ + NH$_4$ 472.3421; found 472.3421.

(1S,3R,4R,5R,6R,7R,8R,9S)-(9-[(4-$n$-Pentylbenzoyl)oxymethyl]hexaspiro-
[2.0.0.0.0.2.1.1.1.1]pentadec-1-yl)methyl] 4-$n$-pentylbenzoate (45a): Column chromatography ($R_f= 0.28$) of the reaction mixture obtained from diol ($P$)-(+)–22 (50 mg, 0.2 mmol), 4-$n$-pentylbenzoic acid (115 mg, 0.6 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (136 mg, 0.66 mmol) according to GP 10 gave 45a (61 mg, 52%) as a colorless powder, m.p. 71–76 °C, $[\alpha]_D^{20} = +270.0$ ($c = 0.50$ in CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 7.97$ (d, $J = 8.3$ Hz, 4 H; Ar-H), 7.25 (d, $J = 8.3$ Hz, 4 H; Ar-H), 4.34 (d, $J = 6.9$ Hz, 4 H; 2 CH$_2$O), 2.66 (t, $J = 7.4$ Hz, 4 H; 2 CH$_2$), 1.63 (t, $J = 7.4$ Hz, 4 H), 1.54 (m, 2 H; cPr-H), 1.32 (m, 8 H), 1.25 (d, $J = 3.9$ Hz, 4 H; cPr-H), 1.10 (m, 8 H), 0.89 (t, $J = 6.7$ Hz, 6 H; 2 CH$_3$), 0.83 (t, $J = 4.5$ Hz, 2 H; cPr-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 166.8$ (2 C), 148.3 (2 C), 130.0 (4 CH), 128.4 (2 C), 128.0 (4 CH), 68.4 (2 CH$_2$), 35.9 (2 CH$_2$), 31.4 (2 CH$_2$), 30.8 (2 CH$_2$), 22.5 (2 CH$_2$), 18.5 (2 CH), 18.1 (2 C), 17.6 (2 C), 15.0 (2 C), 14.0 (2 CH$_3$), 10.4 (2 CH$_2$), 9.8 (2 CH$_2$), 8.9 (CH$_2$), 8.8 (2 CH$_2$); IR (KBr): $\nu$(tilde) = 3042, 2967, 2857, 1718, 1457, 1419, 1363, 1271, 1177, 1104, 1020, 762, 703 cm$^{-1}$; MS (EI): $m/z$ (%): 606 (1) ($M^+$), 222 (11), 207 (13), 175 (100), 91 (19), 41 (7); HRMS (CI): calcd for C$_{41}$H$_{54}$NO$_4$: $M^+$ + NH$_4$ 624.4047; found 624.4047.

(1S,3R,4R,5R,6R,7R,8R,9S)-(9-[(4-$trans$-$n$-Pentylcyclohexanecarbonyl)oxymethyl]oxymethyl]-
hexaspiro[2.0.0.0.0.2.1.1.1.1]pentadec-1-yl)methyl} (4-trans-n-pentyl)cyclohexanecarboxylate (45b): Column chromatography ($R_f = 0.18$) of the reaction mixture obtained from diol ($P$)-(+)\textbf{-22} (50 mg, 0.2 mmol), 4\textit-trans-n\textit-pentylcyclohexanecarboxylic acid (119 mg, 0.6 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (136 mg, 0.66 mmol) according to GP 10 gave 45b (70 mg, 58%) as a colorless powder, m.p. 65–72 °C, $\alpha$\textbf{-20} = +217.0 (c = 0.50 in CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 4.07 (d, $J = 7.1$ Hz, 4 H; 2 CH$_2$O), 2.23 (tt, $J = 3.4$, 12.1 Hz, 2 H; cHex-H), 1.95 (d, $J = 11.7$ Hz, 4 H; 2 CH$_2$), 1.79 (d, $J = 11.7$ Hz, 4 H; 2 CH$_2$), 1.22 (m, 38 H), 1.02 (m, 2 H), 0.87 (t, $J = 7.0$ Hz, 6 H; 2 CH$_3$), 0.72 (t, $J = 4.4$ Hz, 2 H; cPr-H); $^{13}$C NMR (CDCl$_3$, 62.9 MHz): $\delta$ = 176.4 (2 C), 67.8 (2 CH), 43.7 (2 CH$_2$), 37.2 (2 CH$_2$), 36.9 (2 CH), 32.3 (2 CH$_2$), 32.1 (2 CH$_2$), 29.1 (4 CH$_2$), 26.5 (2 CH$_2$), 22.7 (4 CH$_2$), 18.4 (2 CH), 18.1 (2 C), 17.5 (2 C), 14.9 (2 C), 14.1 (2 CH$_3$), 10.3 (2 CH$_2$), 9.7 (2 CH$_2$), 8.9 (CH$_2$), 8.8 (2 CH$_2$); IR (KBr): ν(tilde) = 3043, 2923, 2854, 1729, 1450, 1377, 1316, 1246, 1172, 1140, 1077, 1029, 1000, 900, 725 cm$^{-1}$; MS (EI): $m/z$ (%): 618 (1) ($M^+$), 239 (12), 207 (53), 99 (100), 55 (62); HRMS (CI): calcd for C$_{41}$H$_{66}$NO$_4$: $M^+$ + NH$_4$ 636.4986; found 636.4986.

\vspace{2em}

(1S,3R,4R,5R,6R,7R,8R,9S)-(9-[(4-n-Propylbenzoyl)oxymethyl]hexaspiro-
[2.0.0.0.0.2.1.1.1.1]pentadec-1-yl)methyl} 4-n-propylbenzoate (45c): Column chromatography ($R_f = 0.21$) of the reaction mixture obtained from diol ($P$)-(+)\textbf{-22} (50 mg, 0.2 mmol), 4-n-propylbenzoic acid (99 mg, 0.6 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (136 mg, 0.66 mmol) according to GP 10 gave 45c (53 mg, 50%) as a colorless powder, m.p. 72–76 °C, $\alpha$\textbf{-20} = +300.0 (c = 0.50 in CHCl$_3$); $^1$H NMR (250 MHz,
CDCl$_3$: $\delta = 7.97$ (d, $J = 8.1$ Hz, 4 H; Ar-H), 7.25 (d, $J = 8.1$ Hz, 4 H; Ar-H), 4.34 (d, $J = 7.4$ Hz, 4 H; 2 CH$_2$O), 2.64 (t, $J = 7.3$ Hz, 4 H; 2 CH$_2$), 1.66 (q, $J = 7.5$ Hz, 4 H; 2 CH$_2$), 1.54 (m, 2 H; cPr-H), 1.25 (d, $J = 4.0$ Hz, 4 H; cPr-H), 1.18 (d, $J = 4.0$ Hz, 2 H; cPr-H), 1.07 (m, 2 H; cPr-H), 0.94 (t, $J = 7.3$ Hz, 6 H; 2 CH$_3$), 0.83 (t, $J = 4.5$ Hz, 2 H; cPr-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 166.8$ (2 C), 148.1 (2 C), 130.0 (4 CH), 128.4 (2 C), 128.0 (4 CH), 68.4 (2 CH$_2$), 38.0 (2 CH$_2$), 24.3 (2 CH$_2$), 18.5 (2 CH), 18.1 (2 C), 17.6 (2 C), 15.0 (2 C), 13.7 (2 CH$_3$), 10.4 (2 CH$_2$), 9.8 (2 CH$_2$), 8.92 (CH$_2$), 8.88 (2 CH$_2$); IR (KBr): $\nu (\tilde{\nu}) = 3042, 2967, 2932, 2872, 1717, 1610, 1457, 1416, 1380, 1272, 1178, 1104, 1076, 1019, 961, 872, 853, 761, 703, 563$ cm$^{-1}$; MS (EI): $m/\text{z}$ (%): 550 (1) ($M^+$), 222 (11), 207 (9), 147 (100), 119 (15), 91 (19), 41 (8); HRMS (CI): calcd for C$_{37}$H$_{46}$NO$_4$: $M^+$ + NH$_4$ 568.3421; found 568.3422.

$(1S,3R,4R,5R,6R,7R,8R,9S)$-9-[(4-trans-Propylcyclohexane-2-carboxylic acid)oxymethyl]-hexaspiro[2.0.0.0.0.2.1.1.1.1]pentadec-1-yilmethyl (4-trans-Propyl)cyclohexane-2-carboxylate (45d): Column chromatography ($R_f = 0.25$) of the reaction mixture obtained from diol (P)-(+-)22, (40 mg, 0.15 mmol), 4-trans-n-propylcyclohexanecarboxylic acid (77 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 45d (61 mg, 70%) as a colorless powder, m.p. 101–113 $^\circ$C, $[\alpha]_D^{20} = +267.4$ (c = 0.50 in CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 4.08$ (d, $J = 7.2$ Hz, 4 H; 2 CH$_2$O), 2.23 (tt, $J = 3.6$, 12.2 Hz, 2 H; cHex-H), 1.96 (d, $J = 11.0$ Hz, 4 H; 2 CH$_2$), 1.79 (d, $J = 11.0$ Hz, 4 H; 2 CH$_2$), 1.44–0.84 (m, 38 H), 0.72 (t, $J = 4.5$ Hz, 2 H; cPr-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 176.5$ (2 C), 67.8 (2 CH$_2$), 43.7 (2 CH$_2$), 25.5 (2 CH$_2$), 15.0 (2 C), 13.7 (2 CH$_3$), 10.4 (2 CH$_2$), 9.8 (2 CH$_2$), 8.92 (CH$_2$), 8.88 (2 CH$_2$).
39.5 (2 CH$_2$), 36.6 (2 CH), 32.3 (4 CH$_2$), 29.1 (4 CH$_2$), 19.9 (2 CH$_2$), 18.4 (2 CH), 18.1 (2 C), 17.5 (2 C), 14.9 (2 C), 14.3 (2 CH$_3$), 10.4 (2 CH$_2$), 9.7 (2 CH$_2$), 8.9 (CH$_2$), 8.8 (2 CH$_2$); IR (KBr): $\tilde{\nu} = 3044, 2956, 2935, 2872, 1714, 1607, 1511, 1472, 1400, 1394, 1313, 1273, 1254, 1168, 1101, 1075, 1050, 1019, 1010, 990, 963, 846, 770, 697, 649, 632, 614, 603$ cm$^{-1}$; MS (EI): $m/\zeta$ (%): 562 (1) ($M^+$), 239 (14), 222 (21), 207 (33), 125 (47), 83 (59), 69 (100), 55 (14); HRMS (CI): calcd for C$_{37}$H$_{58}$NO$_4$: $M^+$ + NH$_4$ 580.4360; found 580.4360.

$(1S,3R,4R,5R,6R,7R,8R,9S)-[9-[(4-n-Pentyloxybenzoyl)oxymethyl]hexaspiro-
[2.0.0.0.0.0.1.1.1.1.1.1]pentadec-1-yl)methyl] 4-n-pentyloxybenzoate (45e): Column chromatography ($R_f = 0.09$) of the reaction mixture obtained from diol (P)-(+)22, (40 mg, 0.15 mmol), 4-n-pentyloxybenzoic acid (94 mg, 0.45 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (103 mg, 0.50 mmol) according to GP 10 gave 45e (60 mg, 61%) as a colorless powder, m.p. 82–85 °C, $[\alpha]^{20}_D = +263.0$ (c = 0.50 in CHCl$_3$); $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 8.00$ (d, $J = 8.9$ Hz, 4 H; Ar-H), 6.90 (d, $J = 8.9$ Hz, 4 H; Ar-H), 4.31 (d, $J = 7.1$ Hz, 4 H; 2 CH$_2$O), 4.00 (t, $J = 6.5$ Hz, 4 H; 2 CH$_2$O), 1.80 (m, 4 H), 1.58–1.34 (m, 10 H), 1.24 (d, $J = 3.9$ Hz, 4 H; cPr-H), 1.17 (d, $J = 3.9$ Hz, 2 H; cPr-H), 1.13–1.01 (m, 6 H), 0.93 (t, $J = 7.1$ Hz, 6 H; 2 CH$_3$), 0.82 (t, $J = 4.5$ Hz, 2 H; cPr-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta = 166.5$ (2 C), 162.8 (2 C), 131.5 (4 CH), 122.6 (2 C), 114.0 (4 CH), 68.3 (2 CH$_2$), 68.1 (2 CH$_2$), 28.8 (2 CH$_2$), 28.0 (2 CH$_2$), 22.4 (2 CH$_2$), 18.4 (2 CH), 18.1 (2 C), 17.6 (2 C), 15.0 (2 C), 14.0 (2 CH$_3$), 10.4 (2 CH$_2$), 9.8 (2 CH$_2$), 8.9 (CH$_2$), 8.8 (2 CH$_2$); IR (KBr): $\tilde{\nu} = 3044, 2956, 2935, 2872, 1714, 1607, 1511, 1472, 1457, 1420, 1394, 1313, 1273, 1254, 1168, 1101, 1075, 1050, 1019, 1010, 990, 963, 846, 770, 697, 649, 632,
612 cm\(^{-1}\); MS (EI): \(m/z\) (%): 638 (1) (\(M^+\)), 363 (24), 175 (100), 171 (27), 155 (11), 91 (12); HRMS (CI): calcd for C\(_{41}\)H\(_{54}\)NO\(_6\): \(M^+ + \text{NH}_4\) 656.3946; found 656.3945.

\((1S,3R,4R,5R,6R,7R,8R,9S)-9-[(n\text{-hexanoyl})\text{oxymethyl}]\text{hexaspiro}[2.0.0.0.0.0.2.1.1.1.1]\text{pentadec}-1-\text{yl})\text{methyl} \text{n-hexanoate (45f)}\): Column chromatography (\(R_f = 0.43\)) of the reaction mixture obtained from diol \((P)-(+)\)-22 (46 mg, 0.18 mmol), \(n\)-hexanoic acid (63 mg, 0.54 mmol), DMAP (2.4 mg, 0.02 mmol) and DCC (122 mg, 0.59 mmol) according to GP 10 gave 45f (40 mg, 49\%) as a colorless oil, \(\alpha_{D}^{20} = +378.0\) (\(c = 0.50\) in CHCl\(_3\)); \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 4.08\) (dd, \(J = 4.2, 7.0\) Hz, 4 H; 2 CH\(_2\)), 2.31 (t, \(J = 7.4\) Hz, 4 H; 2 CH\(_2\)), 1.63 (m, 4 H), 1.41–1.21 (m, 12 H), 1.17 (d, \(J = 3.9\) Hz, 2 H; cPr-H), 1.12 (d, \(J = 3.9\) Hz, 2 H; cPr-H), 1.06–0.98 (m, 6 H), 0.89 (t, \(J = 6.7\) Hz, 6 H; 2 CH\(_3\)), 0.71 (t, \(J = 4.4\) Hz, 2 H; cPr-H); \(^{13}\)C NMR (62.9 MHz, CDCl\(_3\)): \(\delta = 174.1\) (2 C), 67.9 (2 CH\(_2\)), 34.4 (2 CH\(_2\)), 31.3 (2 CH\(_2\)), 24.7 (2 CH\(_2\)), 22.3 (2 CH\(_2\)), 18.4 (2 CH), 18.0 (2 C), 17.5 (2 C), 14.9 (2 C), 13.9 (2 CH\(_3\)), 10.3 (2 CH\(_2\)), 9.7 (2 CH\(_2\)), 8.9 (CH\(_2\)), 8.7 (2 CH\(_2\)); IR (Film): \(\nu(\text{tilde}) = 3043, 2958, 2932, 2872, 2861, 1753, 1653, 1559, 1540, 1506, 1457, 1363, 1315, 1276, 1243, 1173, 1109, 1098, 1076, 1032, 1007, 971, 874, 731, 874 cm\(^{-1}\); MS (EI): \(m/z\) (%): 454 (1) (\(M^+\)), 303 (17), 115 (32), 99 (100), 49 (23); HRMS (CI): calcd for C\(_{29}\)H\(_{46}\)NO\(_4\): \(M^+ + \text{NH}_4\) 472.3421; found 472.3422.