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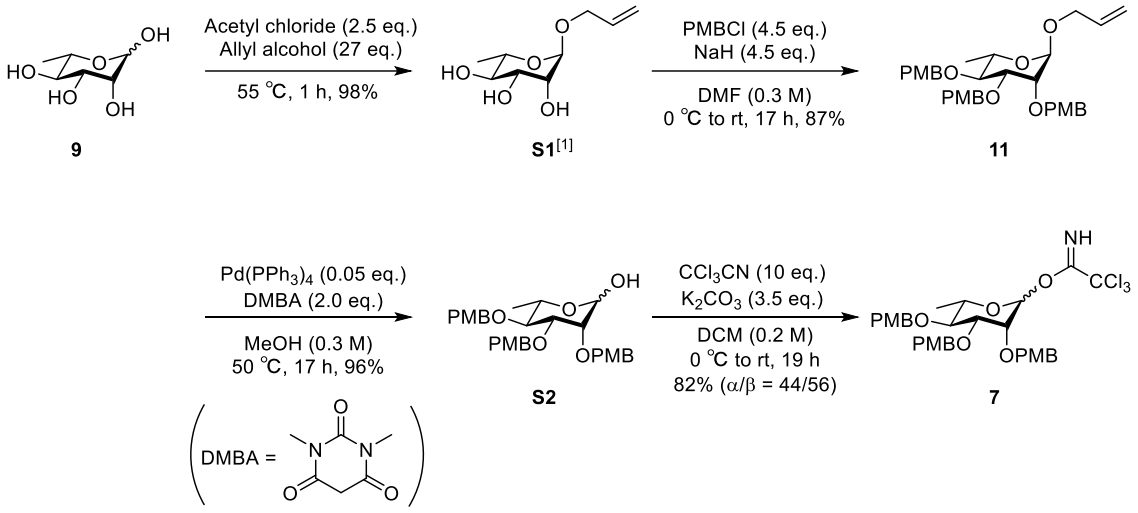
1. General experimental methods

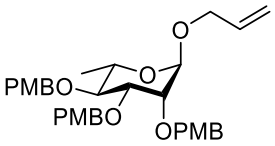
NMR spectra were recorded on JEOL ECZ-400S (400MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. ^{1}H-NMR data are reported as follows; chemical shift in parts per million (ppm) downfield or upfield from $CDCl_3$ (δ 7.26) or CD_3OD (δ 3.31) tetramethyl silane (δ 0.00) integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz).^{13}C-NMR chemical shifts are reported in ppm downfield or upfield from $CDCl_3$ (δ 77.0) or CD_3OD (δ 49.0). ESI-TOF MS spectra were measured on a Waters LCT premier XE**.** Melting points were determined on a micro hot-stage (Yanako MP-S3) and were uncorrected. Optical rotations were measured on a JASCO P-2200 polarimeter. Silica gel TLC was performed on a Merck TLC 60F-254 (0.25 mm). Column chromatography separation was performed on a Silica Gel 60N (spherical, neutral, 63-210 μm or 40-50 μm) (Kanto Chemical Co., Inc.).

2. Synthesis of glycosyl donor 7



Scheme S1. Synthesis of glycosyl donor **7**.

Compound **11**



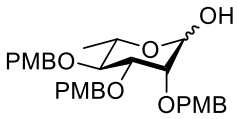
11

To a solution of **S1**[1] (2.77 g, 13.6 mmol) in dry DMF (45 mL) were added 60% NaH (2.50 g, 60.9 mmol, dispersion in paraffin liquid) and PMBCl (8.3 mL, 60 9 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 17 h, the reaction was quenched with water at 0 ℃. The aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (2/1 to 1/1 *n*-haxane/EtOAc) gave **11** (6.59 g, 11.7 mmol, 86% yield).

Data for **11**: Colorless syrup; R_f 0.23 (4/1 *n*-haxane/EtOAc); $[\alpha]^{28}_D$ -29.9° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (6H, m), 6.89-6.82 (6H, m), 5.88-5.76 (1H, m), 5.23-5.16 (1H, m), 5.16-5.10 (1H, m), 4.86 and 4.55 (2H, ABq, J = 10.0 Hz), 4.74 (1H, d, J = 1.6 Hz), 4.69 and 4.64 (2H, ABq, J = 12.0 Hz), 4.58-4.50 (2H, m), 4.13-4.06 (1H, m), 3.92-3.82 (2H, m), 3.82-3.79 (9H, m), 3.77-3.73 (1H, m), 3.71-3.61 (1H, m), 3.56 (1H, dd, J = 9.6 Hz, 9.2 Hz), 1.30 (3H, d, J = 6.0 Hz); ^{13}C-NMR

(100 MHz, $CDCl_3$) δ 159.1, 159.0, 133.8, 130.8×2, 130.3, 129.6, 129.5, 129.1, 116.9, 113.7×2, 97.1, 80.1, 79.8, 75.0, 74.2, 72.3, 71.7, 68.0, 67.5, 55.2, 17.9; HRMS (ESI-TOF) *m/z* 587.2616 (587.2615 calcd for $C_{33}H_{40}O_8Na$ $[M+Na]^+$).

Compound **S2**

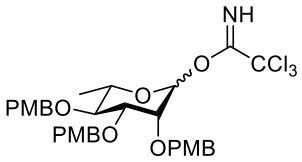


S2

To a solution of **11** (200 mg, 0.354 mmol) in dry MeOH (1.18 mL) were added 1,3-dimethylbarbituric acid (111 mg, 0.708 mmol) and $Pd(PPh_3)_4$ (20.5 mg, 17.7 μmol) at room temperature under Ar atmosphere. After the reaction mixture was stirred at 50 ℃ for 17 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (2/1 to 1/1 *n*-haxane/EtOAc) gave **S2** (179 mg, 0.341 mmol, 96% yield, α/β = 87/13).

Data for **S2**: Colorless syrup; R_f 0.14 (4/1 *n*-haxane/EtOAc); $[\alpha]^{29}_D$ -16.4° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) for α-isomer δ 7.32-7.21 (6H, m), 6.90-6.81 (6H, m), 5.10-5.03 (1H, m), 4.85 (1H, d, *J* = 10.4 Hz), 4.70-4.49 (5H, m), 3.92-3.71 (12H, m), 3.56 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.33 (1H, d, *J* = 3.6 Hz), 1.27 (3H, d, *J* = 6.4 Hz); ^{1}H-NMR for β-isomer δ 7.32-7.21 (6H, m), 6.90-6.81 (6H, m), 5.00 (1H, d, *J* = 11.2 Hz), 4.85 (1H, d, *J* = 10.4 Hz), 4.70-4.49 (4H, m), 3.92-3.71 (12H, m), 3.56 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.33 (1H, d, *J* = 3.6 Hz), 1.30 (3H, d, *J* = 6.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.4, 159.2, 159.1, 159.0, 130.7 × 2, 130.4, 130.3, 130.1 × 2, 129.9, 129.7, 129.6, 129.5, 129.2, 129.1, 113.9, 113.8, 113.7, 113.6, 93.3, 92.8, 82.6, 80.1, 79.5, 79.3, 75.9, 75.0, 74.9, 74.5, 74.3, 72.4, 72.3, 71.7, 71.5, 67.9, 55.2, 17.9, 17.8; HRMS (ESI-TOF) *m/z* 547.2307 (547.2302 calcd for $C_{30}H_{36}O_8Na$ $[M+Na]^+$).

Compound **7**



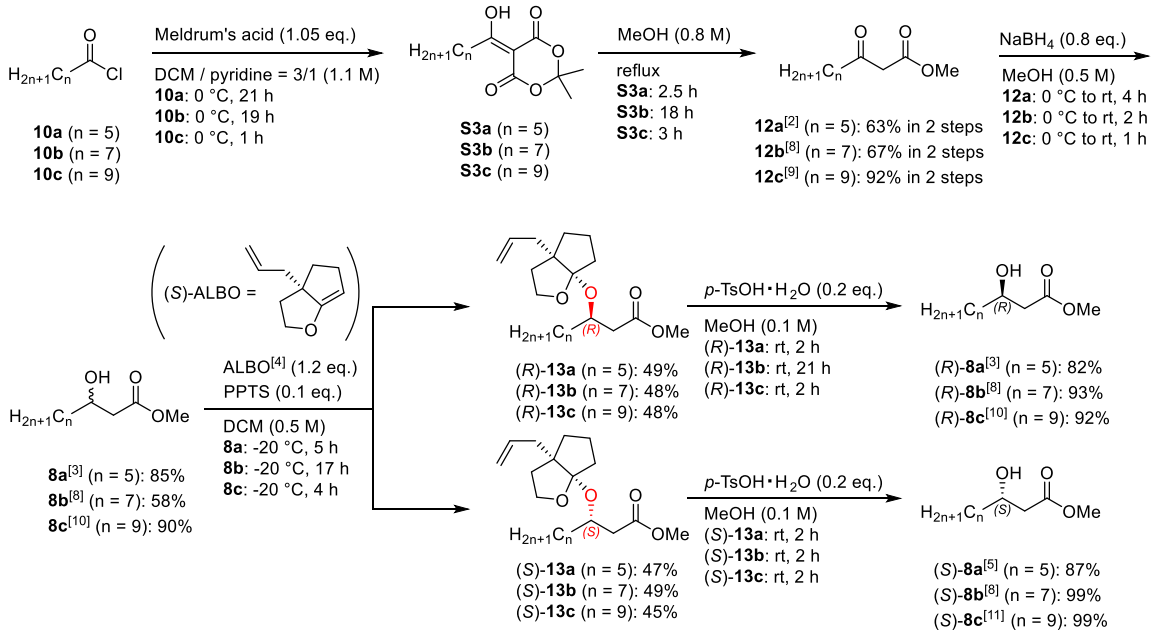
7

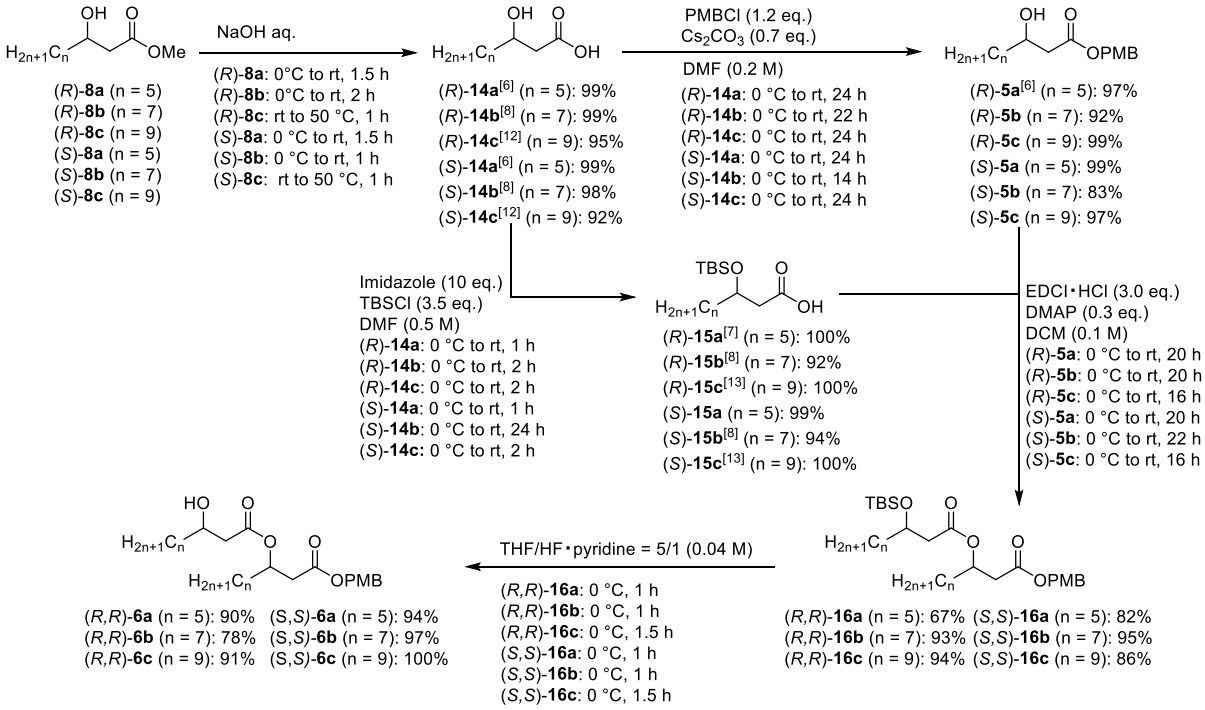
To a solution of **S2** (100 mg, 0.191 mmol) in dry DCM (955 μL) were added K_2CO_3 (92.5 mg, 0.669 mmol) and CCl_3CN (192 μL, 1.91 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 19 h, the resulting mixture was filtered through celite pad, and the filtrate was concentrated in *vacuo*. The purification of the residue by flash silica gel column chromatography (8/1 to 1/1 *n*-hexane/EtOAc with 5% Et_3N) gave **7α** (45.8 mg, 0.0684 mmol, 36% yield) and **7β** (59.4 mg, 0.0888 mmol, 46% yield).

Data for **7α**: Colorless syrup; R_f 0.45 (2/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ -26.1° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.49 (1H, s), 7.36-7.20 (6H, m), 6.90-6.81 (6H, m), 6.20 (1H, d, J = 1.6 Hz), 4.87 and 4.57 (2H, ABq, J = 10.4 Hz), 4.69 (2H, s), 4.56 and 4.51 (2H, ABq, J = 11.6 Hz), 3.90-3.77 (12H, m), 3.65 (1H, dd, J = 9.6 Hz, 9.2 Hz), 1.32 (3H, d, J = 6.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.4, 159.2, 159.1, 130.4, 130.2, 129.8, 129.8, 129.6, 129.4, 113.7, 113.6, 95.9 (J_{CH} = 176 Hz), 91.0, 79.3, 78.3, 75.1, 73.2, 72.2, 71.8, 71.0, 56.1, 17.9.

Data for **7β**: Colorless syrup; R_f 0.32 (2/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ +24.2° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.60 (1H, s), 7.40-7.34 (2H, m), 7.25-7.18 (4H, m), 6.89-6.81 (6H, m), 5.69 (1H, s), 4.94 and 4.81 (2H, ABq, J = 12.0 Hz), 4.85 and 4.58 (2H, ABq, J = 10.4 Hz), 4.49 and 4.44 (2H, ABq, J = 11.2 Hz), 4.09 (1H, d, J = 2.8 Hz), 3.82-3.78 (9H, m), 3.64 (1H, dd, J = 9.2 Hz, 9.2 Hz), 3.54 (1H, dd, J = 8.8 Hz, 2.4 Hz), 3.50-3.41 (1H, m), 1.37 (3H, d, J = 6.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.0, 159.2, 159.1, 130.5, 130.4, 130.2, 129.9, 129.7, 129.1, 113.7, 113.6, 97.2 (J_{CH} = 161 Hz), 90.9, 81.6, 79.1, 75.0, 73.7, 73.1, 72.9, 71.4, 55.2, 17.8.

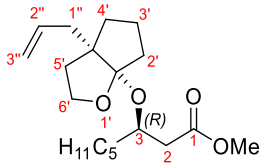
3. Synthesis of glycosyl acceptors 5 and 6



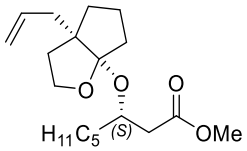


Scheme S2. Synthesis of glycosyl acceptors **5** and **6**.

Compounds (*R*)- and (*S*)-**13a**



(*R*)-**13a**



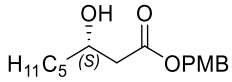
(*S*)-**13a**

To a solution of **8a**[3] (3.66 g, 21.0 mmol) in dry DCM (35 mL) were added (*S*)-5-allyl-2-oxabicyclo[3.3.0]oct-8-ene (ALBO)[4] (4.1 mL, 23.1 mmol) and PPTS (528 mg, 2.10 mmol) at -20 ℃ under Ar atmosphere. After the reaction mixture was stirred at -20 ℃ for 5 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by flash silica gel column chromatography (100/1 to 50/1 toluene/acetone) gave (*R*)-**13a** (3.34 g, 10.3 mmol, 49% yield) and (*S*)-**13a** (3.23 g, 10.0 mmol, 47% yield).

Data for (*R*)-**13a**: Colorless syrup; R_f 0.18 (100/1 toluene/acetone); $[\alpha]^{26}_D$ -26.5° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.90-5.77 (1H, m), 5.09-4.99 (2H, m), 4.14-4.05 (1H, m), 3.85-3.71 (2H, m), 3.66 (3H, s), 2.70 (1H, dd, *J* = 14.8 Hz, 6.0 Hz), 2.43 (1H, dd, *J* =14.4 Hz, 6.4 Hz), 2.28-2.19 (1H, m), 2.19-2.11 (1H, m), 2.09-2.00 (1H, m), 1.95-1.87 (1H, m), 1.73-1.20 (14H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 136.8, 117.9, 116.6, 71.1, 65.8, 54.7, 51.3, 41.6, 40.3, 38.0, 36.6, 35.9, 35.0, 31.8, 25.1, 22.5, 21.4, 14.0; HRMS (ESI-TOF) *m/z* 347.2193 (347.2193 calcd for $C_{19}H_{32}O_4Na$ $[M+Na]^+$).

Data for (*S*)-**13a**: Colorless syrup; R_f 0.24 (100/1 toluene/acetone); $[\alpha]^{27}_D$ -10.0° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.88-5.75 (1H, m), 5.07-4.98 (2H, m), 4.22-4.14 (1H, m), 3.86-3.74 (2H, m), 3.66 (3H, s), 2.49 (1H, dd, *J* = 14.8 Hz, 7.6 Hz), 2.43 (1H, dd, *J* =14.8 Hz, 5.6 Hz), 2.24-2.15 (1H, m), 2.14-2.03 (1H, m), 2.03-1.88 (2H, m), 1.72-1.20 (14H, m), 0.89 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 136.8, 117.8, 116.6, 71.2, 65.9, 54.5, 51.4, 40.5, 40.4, 38.1, 36.4, 35.9, 34.4, 31.9, 24.4, 22.6, 21.4, 14.0; HRMS (ESI-TOF) *m/z* 347.2192 (347.2193 calcd for $C_{19}H_{32}O_4Na$ $[M+Na]^+$).

Compound (*S*)-**5a**

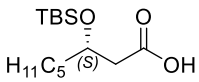


(*S*)-**5a**

To a solution of (*S*)-**14a**[6] (725 mg, 4.53 mmol) in dry DMF (23.0 mL) were added PMBCl (736 μL, 5.43 mmol) and Cs_2CO_3 (1.03 g, 3.17 mmol) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at room temperature for 24 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S*)-**5a** (1.25 g, 4.46 mmol, 99% yield).

Data for (*S*)-**5a**: White solid; R_f 0.43 (2/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +18.4° (c 1.00, $CHCl_3$); mp 37.0-38.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (2H, m), 6.93-6.86 (2H, m), 5.09 (2H, s), 4.05-3.96 (1H, m), 3.81 (3H, s), 2.89 (1H, d, *J* = 4.0 Hz), 2.53 (1H, dd, *J* = 16.8 Hz, 3.2 Hz), 2.43 (1H, dd, *J* = 16.8 Hz, 9.2 Hz), 1.57-1.21 (8H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.9, 159.7, 130.1, 127.6, 113.9, 68.0, 66.2, 55.2, 41.3, 36.4, 31.6, 25.1, 22.5, 14.0; HRMS (ESI-TOF) *m/z* 303.1567 (303.1567 calcd for $C_{16}H_{24}O_4Na$ $[M+Na]^+$).

Compound (*S*)-**15a**



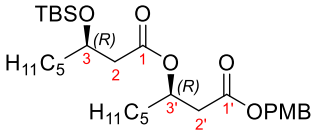
(*S*)-**15a**

To a solution of (*S*)-**14a**[6] (304 mg, 1.90 mmol) in dry DMF (3.8 mL) were added TBSCl (1.00 g, 6.63 mmol) and imidazole (1.29 g, 19.0 mmol) at 0 °C under Ar atmosphere. The mixture was stirred at room temperature for 1 h, then transferred to a separatory funnel. Brine was added to the mixture and the aqueous layer was extracted with a *n*-hexane/Et_2O mixture (3:1 *v/v*). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was dissolved in a mixture of MeOH (36 mL) and THF (18 mL). To a solution of above residue was added a solution of K_2CO_3 (650 mg, 4.70 mmol) in H_2O (8.7 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h after which brine was added. The solution was acidified with 1 M aqueous HCl solution to reach pH 3. The aqueous layer was extracted with a *n*-hexane/Et_2O mixture (3:1 *v/v*), dried over anhydrous Na_2SO_4,

filtered, and concentrated in *vacuo*. The residue was dried under high vacuum overnight to give (*S*)-**15a** (514 mg, 1.87 mmol, 99% yield).

Data for (*S*)-**15a**: Colorless oil; R_f 0.71 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{23}_D$ +2.2° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.14-4.05 (1H, m), 2.55 (1H, dd, *J* = 15.6 Hz, 5.6 Hz), 2.49 (1H, dd, *J* = 15.2 Hz, 5.6 Hz), 1.61-1.45 (2H, m), 1.37-1.22 (6H, m), 0.92-0.86 (12H, m), 0.10-0.08 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.3, 69.4, 42.1, 37.3, 31.8, 25.7, 25.6, 24.7, 22.6, 18.0, 14.0, -4.6, -4.9; HRMS (ESI-TOF) *m/z* 297.1858 (297.1856 calcd for $C_{14}H_{30}O_3SiNa$ $[M+Na]^+$).

Compound (*R,R*)-**16a**

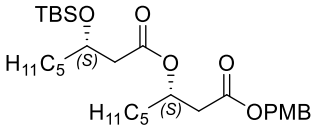


(*R,R*)-**16a**

To a solution of (*R*)-**15a**[7] (49.5 mg, 0.180 mmol) in dry DCM (1.5 mL) were added (*R*)-**5a** (42.1 mg, 0.150 mmol), EDCI·HCl (86.3 mg, 0.450 mmol), and DMAP (5.5 mg, 45.0 μmol) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at room temperature for 20 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 *n*-hexane/EtOAc) gave (*R,R*)-**16a** (53.7 mg, 0.100 mmol, 67% yield).

Data for (*R,R*)-**16a**: Colorless syrup; R_f 0.67 (4/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ -1.4° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.92-6.84 (2H, m), 5.25-5.16 (1H, m), 5.04 (2H, s), 4.12-4.02 (1H, m), 3.81 (3H, s), 2.63 (1H, dd, *J* = 15.2 Hz, 6.8 Hz), 2.54 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 2.42 (1H, dd, *J* = 14.8 Hz, 6.0 Hz), 2.36 (1H, dd, *J* = 14.8 Hz, 6.4 Hz), 1.65-1.18 (16H, m), 0.92-0.82 (15H, m), 0.08-0.03 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 159.6, 130.1, 127.8, 113.8, 70.4, 69.1, 66.1, 55.1, 42.6, 39.1, 37.1, 33.8, 31.8, 31.4, 25.7, 24.7, 24.6, 22.5, 22.4, 17.9, 13.9×2, -4.7; HRMS (ESI-TOF) *m/z* 559.3423 (559.3425 calcd for $C_{30}H_{52}O_6SiNa$ $[M+Na]^+$).

Compound (*S,S*)-**16a**

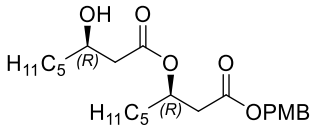


(*S,S*)-**16a**

To a solution of (*S*)-**15a** (141 mg, 0.514 mmol) in dry DCM (4.3 mL) was added (*S*)-**5a** (120 mg, 0.428 mmol), EDCI·HCl (246 mg, 1.28 mmol), and DMAP (15.6 mg, 0.128 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 20 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 *n*-hexane/EtOAc) gave (*S,S*)-**16a** (189 mg, 0.352 mmol, 82% yield).

Data for (*S,S*)-**16a**: Colorless syrup; R_f 0.67 (4/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ +2.4° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.91-6.86 (2H, m), 5.24-5.17 (1H, m), 5.04 (2H, s), 4.10-4.04 (1H, m), 3.81 (3H, s), 2.63 (1H, dd, *J* = 15.2 Hz, 6.8 Hz), 2.54 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 2.42 (1H, dd, *J* = 14.8 Hz, 6.0 Hz), 2.36 (1H, dd, *J* = 14.8 Hz, 6.4 Hz), 1.62-1.18 (16H, m), 0.91-0.83 (15H, m), 0.07-0.03 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 159.6, 130.1, 127.8, 113.8, 70.4, 69.1, 66.1, 55.1, 42.7, 39.1, 37.2, 33.8, 31.8, 31.4, 25.7, 24.7, 24.6, 22.5, 22.4, 17.9, 13.9×2, -4.7; HRMS (ESI-TOF) *m/z* 559.3424 (559.3425 calcd for $C_{30}H_{52}O_6SiNa$ $[M+Na]^+$).

Compound (*R,R*)-**6a**

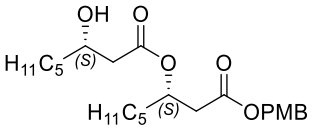


(*R,R*)-**6a**

To a solution of (*R,R*)-**16a** (150 mg, 0.279 mmol) in dry THF (5.8 mL) was added 70% HF·pyridine (1.2 mL) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at 0 ℃ for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*R,R*)-**6a** (106 mg, 0.251 mmol, 90% yield).

Data for (*R,R*)-**6a**: Colorless syrup; R_f 0.25 (4/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ -12.0° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.85 (2H, m), 5.32-5.22 (1H, m), 5.04 (2H, s), 4.00-3.91 (1H, m), 3.81 (3H, s), 2.98 (1H, d, *J* = 3.2 Hz), 2.64-2.53 (2H, m), 2.42 (1H, dd, *J* = 16.0 Hz, 2.8 Hz), 2.30 (1H, dd, *J* = 16.0 Hz, 9.6 Hz), 1.65-1.20 (16H, m), 0.93-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 170.4, 159.6, 130.2, 127.7, 113.8, 70.7, 68.1, 66.3, 55.2, 41.6, 39.1, 36.5, 33.8, 31.6, 31.3, 25.0, 24.7, 22.5, 22.3, 13.9, 13.8; HRMS (ESI-TOF) *m/z* 445.2557 (445.2561 calcd for $C_{24}H_{38}O_6Na$ $[M+Na]^+$).

Compound (*S,S*)-**6a**

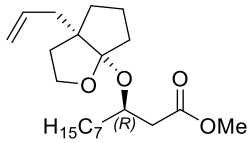


(*S,S*)-**6a**

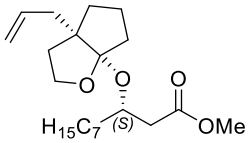
To a solution of (*S,S*)-**16a** (50.1 mg, 93.3 μmol) in dry THF (1.9 mL) was added 70% HF·pyridine (389 μL) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at 0 ℃ for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S,S*)-**6a** (36.9 mg, 87.3 μmol, 90% yield).

Data for (*S,S*)-**6a**: Colorless syrup; R_f 0.22 (4/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +14.3° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.85 (2H, m), 5.31-5.22 (1H, m), 5.04 (2H, s), 4.01-3.91 (1H, m), 3.81 (3H, s), 3.00 (1H, d, *J* = 3.6 Hz), 2.64-2.53 (2H, m), 2.42 (1H, dd, *J* = 15.6 Hz, 2.8 Hz), 2.30 (1H, dd, *J* = 15.6 Hz, 9.2 Hz), 1.66-1.19 (16H, m), 0.93-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 170.4, 159.6, 130.2, 127.7, 113.9, 70.8, 68.1, 66.4, 55.2, 41.7, 39.1, 36.5, 33.9, 31.7, 31.3, 25.1, 24.7, 22.5, 22.4, 13.9×2; HRMS (ESI-TOF) *m/z* 445.2560 (445.2561 calcd for $C_{24}H_{38}O_6Na$ $[M+Na]^+$).

Compounds (*R*)- and (*S*)-**13b**



(*R*)-**13b**



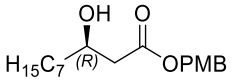
(*S*)-**13b**

To a solution of **8b**[8] (1.40 g, 6.91 mmol) in dry DCM (13.8 mL) was added ALBO (1.27 mL, 8.29 mmol) and PPTS (174 mg, 0.691 mmol) at -20 ℃ under Ar atmosphere. After the reaction mixture was stirred at -20 ℃ for 17 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by flash silica gel column chromatography (toluene only) gave (*R*)-**13b** (1.17 g, 3.32 mmol, 48% yield) and (*S*)-**13b** (1.18 g, 3.35 mmol, 49% yield).

Data for (*R*)-**13b**: Colorless syrup; R_f 0.53 (20/1 toluene/acetone); $[\alpha]^{28}_D$ -25.5° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.89-5.79 (1H, m), 5.08-5.00 (2H, m), 4.13-4.07 (1H, m), 3.81-3.70 (2H, m), 3.66 (3H, s), 2.70 (1H, dd, *J* = 14.8 Hz, 5.6 Hz), 2.43 (1H, dd, *J* = 14.8 Hz, 6.4 Hz), 2.23 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 2.17-2.12 (1H, m), 2.04 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 1.94-1.87 (1H, m), 1.69-1.18 (18H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.3, 136.7, 117.9, 116.6, 71.1, 65.7, 54.6, 51.2, 41.6, 40.3, 38.0, 36.5, 35.9, 35.0, 31.7, 29.5, 29.2, 25.4, 22.6, 21.4, 14.0; HRMS (ESI-TOF) *m/z* 375.2505 (375.2506 calcd for $C_{21}H_{36}O_4Na$ $[M+Na]^+$).

Data for (*S*)-**13b**: Colorless syrup; R_f 0.68 (20/1 toluene/acetone); $[\alpha]^{28}_D$ -11.2° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.87-5.76 (1H, m), 5.09-4.99 (2H, m), 4.21-4.15 (1H, m), 3.85-3.74 (2H, m), 3.66 (3H, s), 2.49 (1H, dd, *J* = 14.8 Hz, 7.6 Hz), 2.43 (1H, dd, *J* = 14.8 Hz, 5.6 Hz), 2.20 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 2.12-2.06 (1H, m), 1.98 (1H, dd, *J* = 13.6 Hz, 7.2 Hz), 1.95-1.89 (1H, m), 1.72-1.20 (18H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 136.7, 117.8, 116.5, 71.1, 65.8, 54.5, 51.3, 40.5, 40.4, 38.1, 36.3, 35.9, 34.3, 31.7, 29.6, 29.2, 24.6, 22.6, 21.4, 14.0; HRMS (ESI-TOF) *m/z* 375.2505 (375.2506 calcd for $C_{21}H_{36}O_4Na$ $[M+Na]^+$).

Compound (*R*)-**5b**

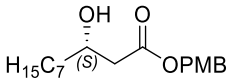


(*R*)-**5b**

To a solution of (*R*)-**14b**[8] (256 mg, 1.36 mmol) in dry DMF (6.8 mL) were added PMBCl (203 μL, 1.50 mmol) and Cs_2CO_3 (310 mg, 0.952 mmol) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at room temperature for 22 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with DCM, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*R*)-**5b** (384 mg, 1.25 mmol, 92% yield).

Data for (*R*)-**5b**: White solid; R_f 0.47 (2/1 *n*-hexane/EtOAc); $[\alpha]^{26}_D$ -15.6° (c 1.00, $CHCl_3$); mp 51.0-52.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.91-6.87 (2H, m), 5.09 (2H, s), 4.04-3.95 (1H, m), 3.81 (3H, s), 2.87 (1H, d, *J* = 3.6 Hz), 2.53 (1H, dd, *J* = 16.4 Hz, 3.2 Hz), 2.43 (1H, dd, *J* = 16.4 Hz, 9.2 Hz), 1.55-1.18 (12H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.9, 159.7, 130.1, 127.7, 113.9, 68.0, 66.2, 55.2, 41.3, 36.5, 31.7, 29.4, 29.2, 25.4, 22.6, 14.0; HRMS (ESI-TOF) *m/z* 331.1878 (331.1880 calcd for $C_{18}H_{28}O_4Na$ $[M+Na]^+$).

Compound (*S*)-**5b**



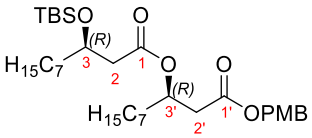
(*S*)-**5b**

To a solution of (*S*)-**14b**[8] (305 mg, 1.62 mmol) in dry DMF (8.1 mL) were added PMBCl (263 μL, 1.94 mmol) and Cs_2CO_3 (368 mg, 1.13 mmol) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at room temperature for 14 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with DCM, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S*)-**5b** (415 mg, 1.35 mmol, 83% yield).

Data for (*S*)-**5b**: White solid; R_f 0.47 (2/1 *n*-hexane/EtOAc); $[\alpha]^{25}_D$ +18.7° (c 1.00, $CHCl_3$); mp 51.5-52.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.86 (2H, m), 5.13-5.04 (2H, m),

4.05-3.95 (1H, m), 3.81 (3H, s), 2.88 (1H, d, J = 4.0 Hz), 2.53 (1H, dd, J = 16.4 Hz, 2.8 Hz), 2.43 (1H, dd, J = 16.4 Hz, 9.2 Hz), 1.57-1.20 (12H, m), 0.88 (3H, t, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.9, 159.7, 130.1, 127.7, 113.9, 68.0, 66.3, 55.2, 41.3, 36.5, 31.7, 29.4, 29.2, 25.4, 22.6, 14.0; HRMS (ESI-TOF) *m/z* 331.1881 (331.1880 calcd for $C_{18}H_{28}O_4Na$ $[M+Na]^+$).

Compound (*R,R*)-**16b**

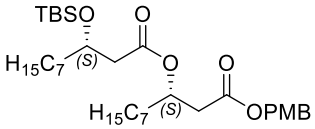


(*R,R*)-**16b**

To a solution of (*R*)-**15b**[8] (76.9 mg, 0.254 mmol) in dry DCM (2.1 mL) were added (*R*)-**5b** (65.4 mg, 0.212 mmol), EDCI·HCl (122 mg, 0.636 mmol), and DMAP (7.8 mg, 63.6 μmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 20 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 *n*-hexane/EtOAc) gave (*R,R*)-**16b** (117 mg, 0.197 mmol, 93% yield).

Data for (*R,R*)-**16b**: Colorless syrup; R_f 0.59 (4/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ -2.0° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (2H, m), 6.90-6.85 (2H, m), 5.24-5.16 (1H, m), 5.08-5.01 (2H, m), 4.11-4.03 (1H, m), 3.81 (3H, s), 2.63 (1H, dd, J = 15.2 Hz, 7.2 Hz), 2.53 (1H, dd, J = 15.2 Hz, 6.0 Hz), 2.45-2.32 (2H, m), 1.62-1.18 (24H, m), 0.90-0.84 (15H, m), 0.08-0.03 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.2, 159.6, 130.1, 127.8, 113.9, 70.5, 69.2, 66.2, 55.2, 42.7, 39.1, 37.3, 33.9, 31.8, 31.7, 29.6, 29.3, 29.2, 29.1, 25.8, 25.1, 25.0, 22.6×2, 18.0, 14.1, -4.7; HRMS (ESI-TOF) *m/z* 615.4052 (615.4051 calcd for $C_{34}H_{60}O_6SiNa$ $[M+Na]^+$).

Compound (*S,S*)-**16b**

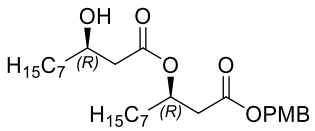


(*S,S*)-**16b**

To a solution of (*S*)-**15b**[8] (118 mg, 0.389 mmol) in dry DCM (3.2 mL) were added (*S*)-**5b** (100 mg, 0.324 mmol), EDCI·HCl (187 mg, 0.973 mmol), and DMAP (11.9 mg, 97.3 μmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 22 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 *n*-hexane/EtOAc) gave (*S,S*)-**16b** (182 mg, 0.307 mmol, 95% yield).

Data for (*S,S*)-**16b**: Colorless syrup; R_f 0.60 (4/1 to 2/1 *n*-hexane/EtOAc); $[\alpha]^{27}_D$ +2.3° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.91-6.85 (2H, m), 5.25-5.16 (1H, m), 5.09-5.00 (2H, m), 4.11-4.03 (1H, m), 3.81 (3H, s), 2.62 (1H, dd, *J* = 15.6 Hz, 7.2 Hz), 2.54 (1H, dd, *J* = 15.6 Hz, 6.0 Hz), 2.46-2.32 (2H, m), 1.65-1.19 (24H, m), 0.91-0.84 (15H, m), 0.08-0.02 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.8, 170.1, 159.5, 130.0, 127.8, 113.8, 70.4, 69.1, 66.1, 55.0, 42.7, 39.1, 37.2, 33.8, 31.8, 31.6, 29.5, 29.2×2, 29.0, 25.7, 25.0, 24.9, 22.5×2, 17.9, 14.0×2, -4.8; HRMS (ESI-TOF) *m/z* 615.4050 (615.4051 calcd for $C_{34}H_{60}O_6SiNa$ $[M+Na]^+$).

Compound (*R,R*)-**6b**

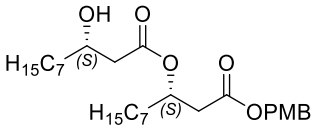


(*R,R*)-**6b**

To a solution of (*R,R*)-**16b** (168 mg, 0.283 mmol) in dry THF (5.8 mL) was added 70% HF·pyridine (1.2 mL) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at 0 ℃ for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*R,R*)-**6b** (107 mg, 0.223 mmol, 79% yield).

Data for (*R,R*)-**6b**: Colorless syrup; R_f 0.34 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ -11.1° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.85 (2H, m), 5.32-5.22 (1H, m), 5.08-5.01 (2H, m), 4.00-3.91 (1H, m), 3.81 (3H, s), 3.00 (1H, d, *J* = 3.6 Hz), 2.64-2.53 (2H, m), 2.42 (1H, dd, *J* = 16.0 Hz, 2.8 Hz), 2.29 (1H, dd, *J* = 16.0 Hz, 9.2 Hz), 1.69-1.18 (24H, m), 0.92-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.5, 170.5, 159.7, 130.3, 127.7, 113.9, 70.8, 68.2, 66.4, 55.2, 41.7, 39.2, 36.6, 34.0, 31.8, 31.7, 29.5, 29.2, 29.1, 25.4, 25.1, 22.6×2, 14.1; HRMS (ESI-TOF) *m/z* 501.3187 (501.3187 calcd for $C_{28}H_{46}O_6Na$ $[M+Na]^+$).

Compound (*S,S*)-**6b**

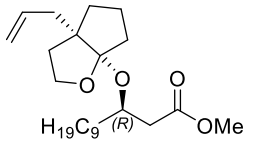


(*S,S*)-**6b**

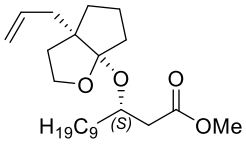
To a solution of (*S,S*)-**16b** (50.1 mg, 93.3 μmol) in dry THF (1.9 mL) was added 70% HF·pyridine (389 μL) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at 0 ℃ for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S,S*)-**6b** (36.9 mg, 87.3 μmol, 94% yield).

Data for (*S,S*)-**6b**: Colorless syrup; R_f 0.32 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ +13.6° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.86 (2H, m), 5.31-5.22 (1H, m), 5.08-5.01 (2H, m), 4.01-3.91 (1H, m), 3.81 (3H, s), 3.00 (1H, d, *J* = 3.6 Hz), 2.64-2.53 (2H, m), 2.42 (1H, dd, *J* = 16.0 Hz, 2.8 Hz), 2.29 (1H, dd, *J* = 16.0 Hz, 10.4 Hz), 1.64-1.19 (24H, m), 0.91-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.6, 170.6, 159.8, 130.4, 127.8, 114.0, 71.0, 68.3, 66.5, 55.3, 41.8, 39.3, 36.7, 34.1, 31.9, 31.8, 29.6, 29.3, 29.2, 25.6, 25.2, 22.7×2, 14.2×2; HRMS (ESI-TOF) *m/z* 501.3186 (501.3187 calcd for $C_{28}H_{46}O_6Na$ $[M+Na]^+$).

Compounds (*R*)- and (*S*)-**13c**



(*R*)-**13c**



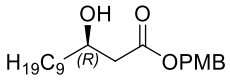
(*S*)-**13c**

To a solution of **8c** (5.02 g, 21.8 mmol) in dry DCM (44.0 mL) were added ALBO (3.67 mL, 24.0 mmol) and PPTS (549 mg, 2.18 mmol) at -20 °C under Ar atmosphere. After the reaction mixture was stirred at -20 °C for 4 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by flash silica gel column chromatography (1/0 to 0/1 Toluene/$CHCl_3$) gave (*S*)-**13c** (3.70 g, 9.73 mmol, 45% yield) and (*R*)-**13c** (4.02 g, 10.6 mmol, 48% yield).

Data for (*R*)-**13c**: Colorless oil; R_f 0.21 (toluene only); $[\alpha]^{25}_D$ -21.3° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.90-5.77 (1H, m), 5.09-4.98 (2H, m), 4.14-4.05 (1H, m), 3.82-3.69 (2H, m), 3.66 (3H, s), 2.69 (1H, dd, *J* = 14.8 Hz, 6.0 Hz), 2.43 (1H, dd, *J* = 14.8 Hz, 6.4 Hz), 2.23 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 2.18-2.10 (1H, m), 2.04 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 1.95-1.86 (1H, m), 1.70-1.17 (22H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 136.8, 118.0, 116.7, 71.1, 65.8, 54.7, 51.3, 41.6, 40.3, 38.0, 36.6, 36.0, 35.0, 31.9, 29.6, 29.5, 29.3, 25.5, 22.7, 21.5, 14.1; HRMS (ESI-TOF) *m/z* 403.2817 (403.2819 calcd for $C_{23}H_{40}O_4Na$ $[M+Na]^+$).

Data for (*S*)-**13c**: Colorless oil; R_f 0.35 (toluene only); $[\alpha]^{26}_D$ -12.5° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.88-5.75 (1H, m), 5.08-4.98 (2H, m), 4.22-4.13 (1H, m), 3.85-3.73 (2H, m), 3.66 (3H, s), 2.49 (1H, dd, *J* = 14.8 Hz, 7.2 Hz), 2.43 (1H, dd, *J* = 14.4 Hz, 5.2 Hz), 2.20 (1H, dd, *J* = 14.0 Hz, 7.2 Hz), 2.15-2.02 (1H, m), 1.98 (1H, dd, *J* = 13.6 Hz, 6.8 Hz), 1.95-1.87 (1H, m), 1.74-1.16 (22H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 136.8, 117.8, 116.6, 71.2, 65.9, 54.5, 51.4, 40.6, 40.4, 38.2, 36.4, 36.0, 34.4, 31.9, 29.7, 29.6, 29.5, 29.3, 24.7, 22.7, 21.4, 14.1; HRMS (ESI-TOF) *m/z* 403.2816 (403.2819 calcd for $C_{23}H_{40}O_4Na$ $[M+Na]^+$).

Compound (*R*)-**5c**

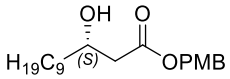


(*R*)-**5c**

To a solution of (*R*)-**14c**[12] (614 mg, 2.84 mmol) in dry DMF (14.2 mL) were added PMBCl (462 μL, 3.41 mmol) and Cs_2CO_3 (648 mg, 1.99 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 24 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*R*)-**5c** (950 mg, 2.82 mmol, 99% yield).

Data for (*R*)-**5c**: White solid; R_f 0.30 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ -17.7° (c 1.00, $CHCl_3$); mp 62.0-63.0 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.87 (2H, m), 5.12-5.05 (2H, m), 4.04-3.96 (1H, m), 3.81 (3H, s), 2.86 (1H, d, *J* = 4.0 Hz), 2.53 (1H, dd, *J* = 16.8 Hz, 3.2 Hz), 2.43 (1H, dd, *J* = 16.8 Hz, 8.8 Hz), 1.56-1.20 (16H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.9, 159.7, 130.1, 127.7, 114.0, 68.0, 66.3, 55.2, 41.3, 36.5, 31.8, 29.5, 29.2, 25.4, 22.6, 14.1; HRMS (ESI-TOF) *m/z* 359.2193 (359.2193 calcd for $C_{20}H_{32}O_4Na$ $[M+Na]^+$).

Compound (*S*)-**5c**



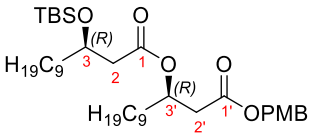
(*S*)-**5c**

To a solution of (*S*)-**14c**[12] (611 mg, 2.82 mmol) in dry DMF (14.1 mL) were added PMBCl (460 μL, 3.39 mmol) and Cs_2CO_3 (642 mg, 1.97 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 24 h, the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S*)-**5c** (924 mg, 2.75 mmol, 97% yield).

Data for (*S*)-**5c**: White solid; R_f 0.30 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ +18.2° (c 1.00, $CHCl_3$); mp 62.0-63.0 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.92-6.86 (2H, m), 5.12-5.05 (2H, m),

4.04-3.96 (1H, m), 3.81 (3H, s), 2.86 (1H, d, J = 4.0 Hz), 2.53 (1H, dd, J = 16.8 Hz, 3.2 Hz), 2.43 (1H, dd, J = 16.8 Hz, 9.2 Hz), 1.56-1.20 (16H, m), 0.88 (3H, t, J = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.9, 159.7, 130.1, 127.7, 113.9, 68.0, 66.2, 55.2, 41.4, 36.5, 31.8, 29.5×2, 29.2, 25.4, 22.6, 14.1; HRMS (ESI-TOF) *m/z* 359.2188 (359.2193 calcd for $C_{20}H_{32}O_4Na$ $[M+Na]^+$).

Compound (*R,R*)-**16c**

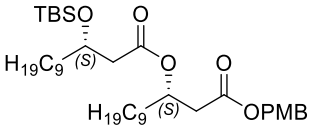


(*R,R*)-**16c**

To a solution of (*R*)-**15c**[13] (23.6 mg, 71.3 μmol) in dry DCM (594 μL) were added (*R*)-**5c** (20.0 mg, 59.4 μmol), EDCI·HCl (34.1 mg, 0.178 mmol), and DMAP (2.2 mg, 17.8 μmol) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at room temperature for 16 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 *n*-hexane/EtOAc) gave (*R,R*)-**16c** (36.3 mg, 55.9 μmol, 94% yield).

Data for (*R,R*)-**16c**: Colorless oil; R_f 0.65 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ -1.7° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.91-6.85 (2H, m), 5.24-5.16 (1H, m), 5.08-5.01 (2H, m), 4.11-4.02 (1H, m), 3.81 (3H, s), 2.62 (1H, dd, J = 15.6 Hz, 2.8 Hz), 2.53 (1H, dd, J = 15.6 Hz, 5.6 Hz), 2.42 (1H, dd, J = 14.4 Hz, 5.6 Hz), 2.36 (1H, dd, J = 14.4 Hz, 6.4 Hz), 1.62-1.19 (32H, m), 0.91-0.84 (15H, m), 0.07-0.03 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.2, 130.1, 127.9, 113.9, 70.5, 69.2, 66.2, 55.2, 42.7, 39.2, 37.3, 33.9, 31.9, 29.7, 29.6, 29.6, 29.5×2, 29.3×3, 25.8, 25.1, 25.0, 22.6, 18.0, 14.1, -4.6; HRMS (ESI-TOF) *m/z* 671.4676 (671.4677 calcd for $C_{38}H_{68}O_6SiNa$ $[M+Na]^+$).

Compound (*S,S*)-**16c**

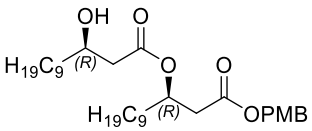


(*S,S*)-**16c**

To a solution of (*S*)-**15c**[13] (354 mg, 1.07 μmol) in dry DCM (8.9 mL) were added (*S*)-**5c** (300 mg, 0.892 mmol), EDCI·HCl (514 mg, 2.68 mmol), and DMAP (32.7 mg, 0.268 mmol) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at room temperature for 16 h, the reaction mixture was diluted with $CHCl_3$ and saturated aqueous $NaHCO_3$. After separation, the aqueous layer was extracted with $CHCl_3$, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (4/1 to 2/1 *n*-hexane/EtOAc) gave (*S,S*)-**16c** (485 mg, 0.747 mmol, 86% yield).

Data for (*S,S*)-**16c**: Colorless oil; R_f 0.62 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ +2.1° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.91-6.85 (2H, m), 5.24-5.16 (1H, m), 5.08-5.00 (2H, m), 4.11-4.03 (1H, m), 3.81 (3H, s), 2.62 (1H, dd, *J* = 15.2 Hz, 2.8 Hz), 2.53 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 2.42 (1H, dd, *J* = 14.4 Hz, 5.6 Hz), 2.36 (1H, dd, *J* = 14.4 Hz, 6.4 Hz), 1.63-1.18 (32H, m), 0.90-0.84 (15H, m), 0.07-0.03 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.2, 130.1, 127.9, 113.9, 70.5, 69.2, 66.2, 55.2, 42.8, 39.2, 37.3, 33.9, 31.9, 29.7, 29.6×2, 29.5×2, 29.4, 29.3×2, 25.8, 25.1, 25.0, 22.7, 18.0, 14.1, -4.6; HRMS (ESI-TOF) *m/z* 671.4676 (671.4677 calcd for $C_{38}H_{68}O_6SiNa$ $[M+Na]^+$).

Compound (*R,R*)-**6c**

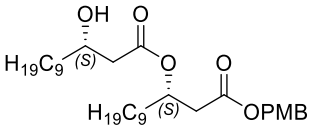


(*R,R*)-**6c**

To a solution of (*R,R*)-**16c** (63.4 mg, 97.7 μmol) in dry THF (2.0 mL) was added 70% HF·pyridine (407 μL) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred at 0 ℃ for 1.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (6/1 to 4/1 *n*-hexane/EtOAc) gave (*R,R*)-**6c** (47.4 mg, 88.6 μmol, 91% yield).

Data for (*R,R*)-**6c**: White solid; R_f 0.37 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ -12.2° (c 1.00, $CHCl_3$); mp 44.0-45.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.91-6.85 (2H, m), 5.31-5.22 (1H, m), 5.08-5.00 (2H, m), 4.00-3.91 (1H, m), 3.81 (3H, s), 3.00 (1H, d, *J* = 3.6 Hz), 2.63-2.52 (2H, m), 2.42 (1H, dd, *J* = 16.0 Hz, 2.8 Hz), 2.29 (1H, dd, *J* = 16.0 Hz, 9.6 Hz), 1.64-1.16 (32H, m), 0.92-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 170.5, 159.7, 130.3, 113.9, 70.8, 68.2, 66.4, 55.2, 41.7, 39.2, 36.6, 34.0, 31.9, 31.8, 29.6, 29.5, 29.4×2, 29.3, 29.2, 25.4, 25.1, 22.6, 14.1; HRMS (ESI-TOF) *m/z* 557.3809 (557.3813 calcd for $C_{32}H_{54}O_6Na$ $[M+Na]^+$).

Compound (*S,S*)-**6c**

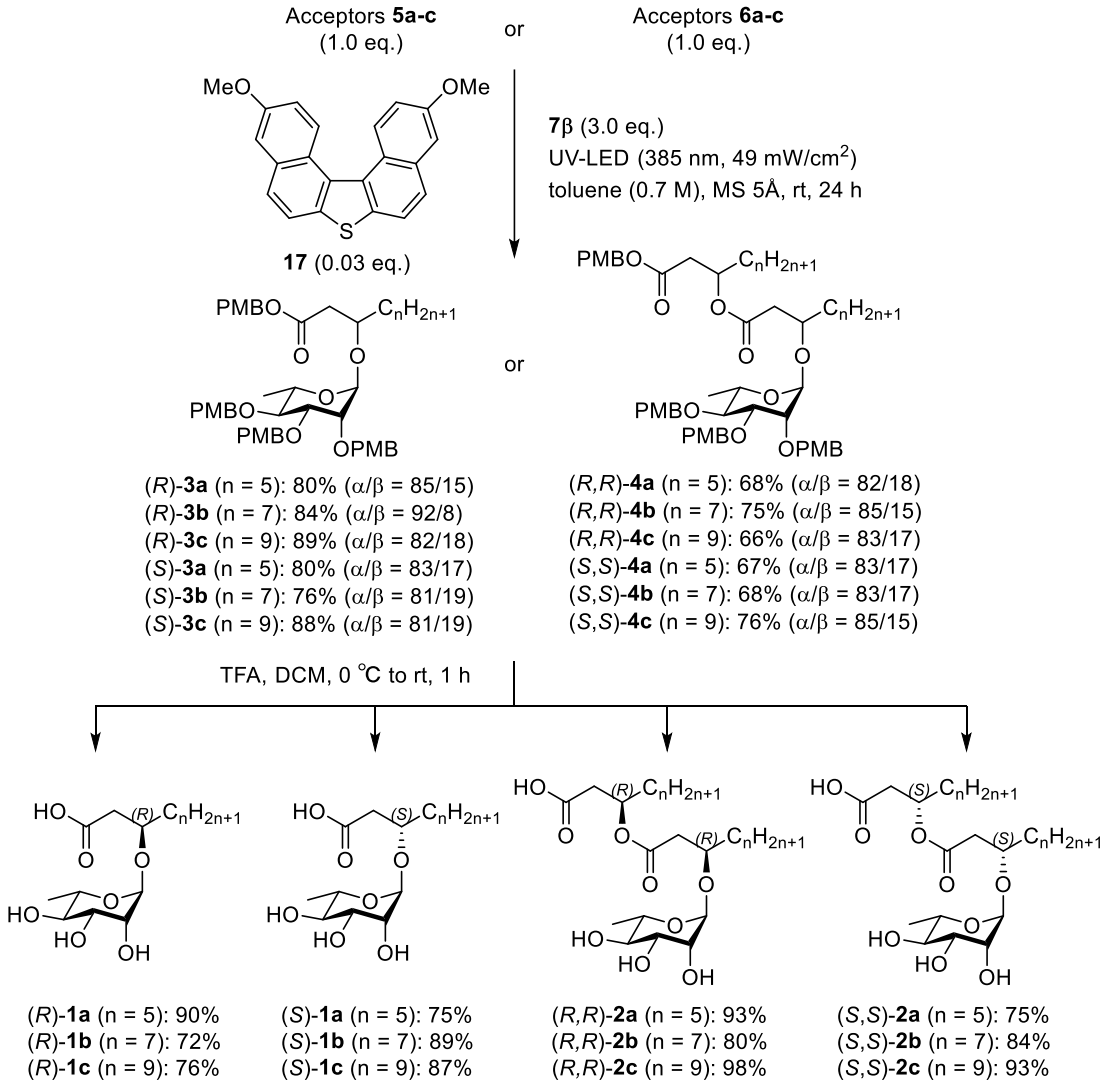


(*S,S*)-**6c**

To a solution of (*S,S*)-**16c** (202 mg, 0.311 mmol) in dry THF (6.5 mL) was added 70% HF·pyridine (1.3 mL) at 0 °C under Ar atmosphere. After the reaction mixture was stirred at 0 °C for 1.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with EtOAc, and then the combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (6/1 to 4/1 *n*-hexane/EtOAc) gave (*S,S*)-**6c** (166 mg, 0.310 μmol, quantitative yield).

Data for (*S,S*)-**6c**: White solid; R_f 0.40 (4/1 *n*-hexane/EtOAc); $[\alpha]^{23}_D$ +12.3° (c 1.00, $CHCl_3$); mp 44.0-45.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (2H, m), 6.91-6.85 (2H, m), 5.31-5.22 (1H, m), 5.08-5.00 (2H, m), 4.00-3.91 (1H, m), 3.81 (3H, s), 2.97 (1H, d, *J* = 3.6 Hz), 2.64-2.52 (2H, m), 2.42 (1H, dd, *J* = 16.0 Hz, 3.2 Hz), 2.29 (1H, dd, *J* = 15.6 Hz, 9.2 Hz), 1.65-1.08 (32H, m), 0.91-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.4, 170.5, 159.7, 130.3, 113.9, 70.8, 68.2, 66.4, 55.2, 41.7, 39.2, 36.6, 34.0, 31.9, 31.8, 29.6, 29.5, 29.4×2, 29.3, 29.2, 25.4, 25.1, 22.6, 14.1; HRMS (ESI-TOF) *m/z* 557.3812 (557.3813 calcd for $C_{32}H_{54}O_6Na$ $[M+Na]^+$).

4. Synthesis of mono-rhamnolipids 1 and 2

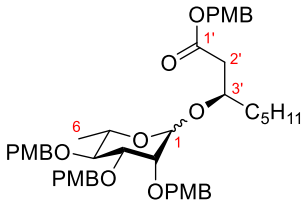


Scheme S3. Synthesis of mono-rhamnolipids **1** and **2**.

General procedure for organophotoacid-catalyzed glycosylation

To a mixture of glycosyl donor (60.0 mg, 3.0 eq.) and MS 5Å (60.0 mg, 100 wt% to glycosyl donor) was added a solution of glycosyl acceptor (1.0 eq.) and 3,11-dimethoxydinaphthothiophene (**17**) (0.03 eq.) in toluene (0.7 M to glycosyl donor). After stirring for 24 h under the photoirradiation using a UV-LED lamp (385 nm, 49 mW/cm^2) (OPTCODE Corporation) at room temperature, the mixture was filtered, and concentrated in *vacuo*. After purification of the residue by column chromatography (8/1 to 2/1 *n*-hexane/EtOAc), followed by preparative TLC (9/1 toluene/EtOAc), the corresponding glycoside was obtained.

Compound (*R*)-**3a**



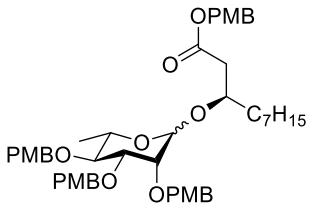
(*R*)-**3a**

(*R*)-**3a** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R*)-**5a** by organophotoacid-catalyzed glycosylation using general procedure in 80% yield (α/β = 85/15).

Data for (*R*)-**3aα**: Colorless syrup; R_f 0.45 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ -26.6° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (8H, m), 6.88-6.79 (8H, m), 5.02 and 4.98 (2H, ABq, *J* = 12.0 Hz), 4.85 and 4.55 (2H, ABq, *J* = 10.4 Hz), 4.74 (1H, d, *J* = 2.0 Hz), 4.68 and 4.59 (2H, ABq, *J* = 12.4 Hz), 4.52 and 4.49 (2H, ABq, *J* = 11.6 Hz), 4.01-3.94 (1H, m), 3.82-3.78 (9H, m), 3.76 (3H, s), 3.72 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.69-3.63 (1H, m), 3.62-3.59 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.55 (1H, dd, *J* = 15.2 Hz, 7.6 Hz), 2.40 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 1.40-1.09 (11H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 159.5, 159.2, 159.1, 159.0, 131.0, 130.8, 130.3, 130.2, 129.6×2, 129.2, 127.8, 113.8, 113.7, 97.0 (J_{CH} = 168 Hz), 80.2, 79.7, 74.9, 74.5, 74.2, 72.3, 71.8, 68.3, 66.2, 55.2×3, 40.4, 33.3, 31.6, 24.3, 22.5, 17.9, 14.0; HRMS (ESI-TOF) *m/z* 809.3870 (809.3871 calcd for $C_{46}H_{58}O_{11}Na$ $[M+Na]^+$).

Data for (*R*)-**3aβ**: Colorless syrup; R_f 0.50 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ +35.4° (c 1.23, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (2H, m), 7.28-7.17 (6H, m), 6.87-6.79 (8H, m), 5.04 and 4.97 (2H, ABq, *J* = 12.0 Hz), 4.83 and 4.52 (2H, ABq, *J* = 10.0 Hz), 4.82 and 4.69 (2H, ABq, *J* = 12.4 Hz), 4.36 (1H, s), 4.34 and 4.29 (2H, ABq, *J* = 11.2 Hz), 4.11-4.01 (1H, m), 3.81-3.77 (9H, m), 3.72 (3H, s), 3.67 (1H, d, *J* = 2.8 Hz), 3.50 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.29 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.24-3.14 (1H, m), 2.57-2.47 (2H, m), 1.77-1.49 (2H, m), 1.41-1.20 (9H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.5, 159.6, 159.1, 159.0, 158.9, 131.1, 130.8, 130.5, 130.1, 129.9, 129.7, 129.0, 127.8, 113.9, 113.7, 113.6, 113.3, 101.3 (J_{CH} = 153 Hz), 82.0, 79.6, 76.5, 74.9, 73.9, 73.4, 71.7, 70.9, 66.0, 55.2×2, 39.9, 35.5, 31.7, 24.6, 22.5, 17.9, 14.0; HRMS (ESI-TOF) *m/z* 809.3868 (809.3871 calcd for $C_{46}H_{58}O_{11}Na$ $[M+Na]^+$).

Compound (*R*)-**3b**



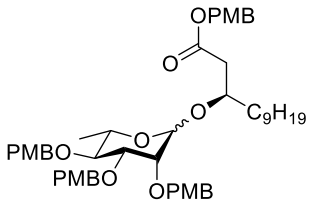
(*R*)-**3b**

(*R*)-**3b** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R*)-**5b** by organophotoacid-catalyzed glycosylation using general procedure in 84% yield (α/β = 92/8).

Data for (*R*)-**3bα**: Colorless syrup; R_f 0.46 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -18.9° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.20 (8H, m), 6.89-6.79 (8H, m), 5.02 and 4.98 (2H, ABq, *J* = 11.6 Hz), 4.84 and 4.55 (2H, ABq, *J* = 10.4 Hz), 4.75 (1H, d, *J* = 1.2 Hz), 4.68 and 4.59 (2H, ABq, *J* = 12.0 Hz), 4.51 and 4.48 (2H, ABq, *J* = 11.6 Hz), 4.02-3.94 (1H, m), 3.83-3.74 (12H, m), 3.74-3.63 (2H, m), 3.63-3.60 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.55 (1H, dd, *J* = 15.2 Hz, 7.2 Hz), 2.40 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 1.43-1.07 (15H, m), 0.89 (3H, t, *J* = 7.2 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 159.6, 159.2, 159.1, 159.0, 131.0, 130.8, 130.3, 130.2, 129.6, 129.2, 127.9, 113.8, 113.7, 97.0 (J_{CH} = 168 Hz), 80.2, 79.7, 74.9, 74.5, 74.2, 72.3, 71.8, 68.3, 66.2, 55.2×2, 40.4, 33.4, 31.8, 29.5, 29.2, 24.7, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 837.4183 (837.4184 calcd for $C_{48}H_{62}O_{11}Na$ $[M+Na]^+$).

Data for (*R*)-**3bβ**: Colorless syrup; R_f 0.49 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ +36.8° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (2H, m), 7.27-7.17 (6H, m), 6.87-6.79 (8H, m), 5.04 and 4.97 (2H, ABq, *J* = 12.0 Hz), 4.83 and 4.52 (2H, ABq, *J* = 10.4 Hz), 4.82 and 4.69 (2H, ABq, *J* = 12.4 Hz), 4.36 (1H, s), 4.34 and 4.28 (2H, ABq, *J* = 11.6 Hz), 4.09-4.01 (1H, m), 3.81-3.77 (9H, m), 3.72 (3H, s), 3.67 (1H, d, *J* = 2.8 Hz), 3.50 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.29 (1H, dd, *J* = 9.2 Hz, 2.8 Hz), 3.24-3.13 (1H, m), 2.57-2.46 (2H, m), 1.77-1.50 (2H, m), 1.42-1.19 (13H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 159.6, 159.1, 159.0, 158.9, 131.1, 130.8, 130.5, 130.1, 129.9, 129.7, 129.0, 127.8, 113.9, 113.7, 113.6, 113.3, 101.4 (J_{CH} = 154 Hz), 82.0, 79.6, 76.5, 74.9, 73.9, 73.4, 71.7, 70.9, 66.0, 55.2×2, 39.9, 35.6, 31.8, 29.5, 29.2, 25.0, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 837.4183 (837.4184 calcd for $C_{48}H_{62}O_{11}Na$ $[M+Na]^+$).

Compound (*R*)-**3c**



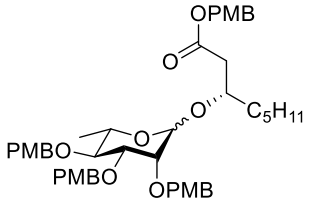
(*R*)-**3c**

(*R*)-**3c** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R*)-**5c** by organophotoacid-catalyzed glycosylation using general procedure in 89% yield (α/β = 82/18).

Data for (*R*)-**3cα**: Yellow syrup; R_f 0.52 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -22.7° (c 1.03, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (8H, m), 6.88-6.79 (8H, m), 5.02 and 4.98 (2H, ABq, *J* = 12.0 Hz), 4.84 and 4.55 (2H, ABq, *J* = 10.8 Hz), 4.75 (1H, d, *J* = 1.6 Hz), 4.68 and 4.60 (2H, ABq, *J* = 12.4 Hz), 4.53-4.46 (2H, m), 4.02-3.94 (1H, m), 3.82-3.78 (9H, m), 3.76 (3H, s), 3.72 (1H, dd, *J* = 9.2 Hz, 3.2 Hz), 3.69-3.63 (1H, m), 3.63-3.60 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.55 (1H, dd, *J* = 14.8 Hz, 7.6 Hz), 2.40 (1H, dd, *J* = 15.2 Hz, 6.0 Hz), 1.41-1.09 (19H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 159.6, 159.2, 159.1, 159.0, 131.0, 130.8, 130.3, 130.2, 129.6, 129.2, 127.9, 113.8, 113.7, 96.9 (J_{CH} = 167 Hz), 80.2, 79.7, 74.9, 74.5, 74.2, 72.3, 71.8, 68.3, 66.2, 55.2×2, 40.4, 33.4, 31.9, 29.5, 29.3, 24.7, 22.7, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 865.4490 (865.4497 calcd for $C_{50}H_{66}O_{11}Na$ $[M+Na]^+$).

Data for (*R*)-**3cβ**: Yellow syrup; R_f 0.55 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ +32.9° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (2H, m), 7.26-7.18 (6H, m), 6.86-6.80 (8H, m), 5.04 and 4.97 (2H, ABq, *J* = 12.0 Hz), 4.83 and 4.52 (2H, ABq, *J* = 10.8 Hz), 4.81 and 4.69 (2H, ABq, *J* = 12.4 Hz), 4.36 (1H, s), 4.34 and 4.28 (2H, ABq, *J* = 12.0 Hz), 4.09-4.01 (1H, m), 3.80-3.78 (9H, m), 3.72 (3H, s), 3.67 (1H, d, *J* = 2.8 Hz), 3.50 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.29 (1H, dd, *J* = 9.2 Hz, 2.8 Hz), 3.23-3.14 (1H, m), 2.54-2.49 (2H, m), 1.77-1.52 (2H, m), 1.39-1.20 (17H, m), 0.88 (3H, t, *J* = 6.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.5, 159.6, 159.2, 159.1, 158.9, 131.1, 130.8, 130.6, 130.1, 129.9, 129.7, 129.0, 127.9, 113.9, 113.7, 113.6, 113.4, 101.4 (J_{CH} = 155 Hz), 82.0, 79.7, 76.5, 74.9, 74.0, 73.4, 71.8, 70.9, 66.0, 55.3, 55.2×2, 40.0, 35.6, 31.9, 29.6, 29.5, 29.3, 25.0, 22.7, 18.0, 14.1; HRMS (ESI-TOF) *m/z* 865.4493 (865.4497 calcd for $C_{50}H_{66}O_{11}Na$ $[M+Na]^+$).

Compound (*S*)-**3a**



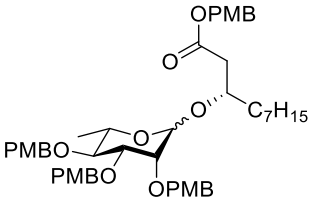
(*S*)-**3a**

(*S*)-**3a** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S*)-**5a** by organophotoacid-catalyzed glycosylation using general procedure in 80% yield (α/β = 83/17).

Data for (*S*)-**3aα**: Colorless syrup; R_f 0.46 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -10.3° (c 1.08, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (8H, m), 6.93-6.79 (8H, m), 5.05-4.92 (2H, m), 4.89 (1H, s), 4.83 and 4.53 (2H, ABq, *J* = 10.8 Hz), 4.64-4.55 (2H, m), 4.50-4.42 (2H, m), 4.03-3.92 (1H, m), 3.83-3.67 (14H, m), 3.64-3.58 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.48-2.34 (2H, m), 1.60-1.13 (11H, m), 0.86 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 159.6, 159.1×2, 159.0, 130.8×2, 130.5, 130.0, 129.7, 129.5, 129.1, 127.9, 113.9, 113.7, 113.6, 97.9 (J_{CH} = 171 Hz), 80.0, 79.6, 75.2, 74.9, 74.7, 72.0, 71.5, 68.4, 66.0, 55.2×2, 39.3, 35.0, 31.6, 24.8, 22.4, 17.8, 14.0; HRMS (ESI-TOF) *m/z* 809.3871 (809.3871 calcd for $C_{46}H_{58}O_{11}Na$ $[M+Na]^+$).

Data for (*S*)-**3aβ**: Colorless syrup; R_f 0.35 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ +39.8° (c 0.45, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (2H, m), 7.31-7.26 (2H, m), 7.25-7.17 (4H, m), 6.89-6.79 (8H, m), 5.07 and 5.00 (2H, ABq, *J* = 12.0 Hz), 4.86 and 4.77 (2H, ABq, *J* = 12.0 Hz), 4.85 and 4.54 (2H, ABq, *J* = 10.4 Hz), 4.42 and 4.36 (2H, ABq, *J* = 11.2 Hz), 4.40 (1H, s), 4.08-3.98 (1H, m), 3.82-3.77 (13H, m), 3.52 (1H, dd, *J* = 9.6 Hz, 8.8 Hz), 3.37 (1H, dd, *J* = 8.8 Hz, 2.8 Hz), 3.25-3.16 (1H, m), 2.93 (1H, dd, *J* = 16.0 Hz, 6.0 Hz), 2.49 (1H, dd, *J* = 16.0 Hz, 6.4 Hz), 1.60-1.19 (11H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 159.5, 159.2, 159.0×2, 130.9, 130.8, 130.4, 130.2, 130.0, 129.7, 129.1, 128.0, 113.9, 113.7×2, 113.4, 101.7 (J_{CH} = 153 Hz), 82.0, 79.7, 75.0, 73.5, 73.2, 71.7, 71.1, 66.0, 55.2×2, 41.2, 34.9, 31.7, 24.9, 22.6, 18.1, 14.0; HRMS (ESI-TOF) *m/z* 809.3880 (809.3871 calcd for $C_{46}H_{58}O_{11}Na$ $[M+Na]^+$).

Compound (*S*)-**3b**



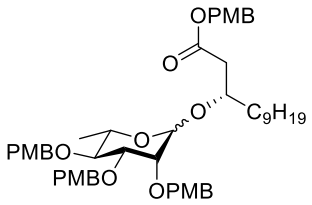
(*S*)-**3b**

(*S*)-**3b** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S*)-**5b** by organophotoacid-catalyzed glycosylation using general procedure in 76% yield (α/β = 81/19).

Data for (*S*)-**3bα**: Colorless syrup; R_f 0.52 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -9.5° (c 1.74, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (8H, m), 6.88-6.81 (8H, m), 5.02-4.94 (2H, m), 4.89 (1H, d, *J* = 1.6 Hz), 4.83 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.63-4.55 (2H, m), 4.49-4.43 (2H, m), 4.02-3.93 (1H, m), 3.82-3.68 (14H, m), 3.62-3.59 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.46-2.35 (2H, m), 1.60-1.18 (15H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.3, 159.6, 159.1, 159.0, 130.8, 130.5, 130.0, 129.7, 129.6, 129.1, 127.9, 113.9, 113.7, 113.6, 97.9 (J_{CH} = 168 Hz), 80.0, 79.7, 75.3, 75.0, 74.7, 72.0, 71.5, 68.4, 66.0, 55.2×2, 39.4, 35.1, 31.8, 29.5, 29.1, 25.1, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 837.4186 (837.4184 calcd for $C_{48}H_{62}O_{11}Na$ $[M+Na]^+$).

Data for (*S*)-**3bβ**: Colorless syrup; R_f 0.47 (9/1 toluene/EtOAc); $[\alpha]^{30}_D$ +45.3° (c 1.10, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (2H, m), 7.31-7.26 (2H, m), 7.25-7.18 (4H, m), 6.88-6.79 (8H, m), 5.07 and 5.00 (2H, ABq, *J* = 12.0 Hz), 4.87 and 4.78 (2H, ABq, *J* = 12.0 Hz), 4.85 and 4.53 (2H, ABq, *J* = 10.8 Hz), 4.41 and 4.35 (2H, ABq, *J* = 12.0 Hz), 4.41 (1H, s), 4.08-3.99 (1H, m), 3.82-3.76 (13H, m), 3.52 (1H, dd, *J* = 9.6 Hz, 8.8 Hz), 3.37 (1H, dd, *J* = 9.6 Hz, 2.4 Hz), 3.26-3.16 (1H, m), 2.93 (1H, dd, *J* = 16.0 Hz, 6.0 Hz), 2.49 (1H, dd, *J* = 16.0 Hz, 6.0 Hz), 1.57-1.18 (15H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 159.5, 159.2, 159.0×2, 130.8×2, 130.4, 130.0, 129.7, 129.0, 128.0, 113.8, 113.7×2, 113.4, 101.7 (J_{CH} = 155 Hz), 82.0, 79.7, 75.0, 73.4, 73.2, 71.6, 71.0, 66.0, 55.2×2, 41.2, 35.0, 31.8, 29.5, 29.2, 25.3, 22.6, 18.0, 14.1; HRMS (ESI-TOF) *m/z* 837.4180 (837.4184 calcd for $C_{48}H_{62}O_{11}Na$ $[M+Na]^+$).

Compound (*S*)-**3c**



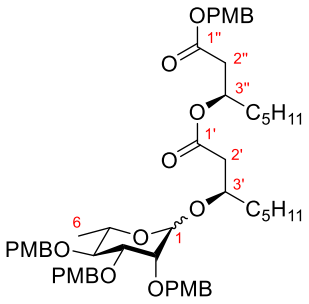
(*S*)-**3c**

(*S*)-**3c** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S*)-**5c** by organophotoacid-catalyzed glycosylation using general procedure in 88% yield (α/β = 81/19).

Data for (*S*)-**3cα**: Colorless syrup; R_f 0.45 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ -10.2° (c 1.05, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (8H, m), 6.88-6.81 (8H, m), 5.03-4.95 (2H, m), 4.89 (1H, d, *J* = 2.0 Hz), 4.82 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.62-4.55 (2H, m), 4.50-4.42 (2H, m), 4.02-3.94 (1H, m), 3.82-3.68 (14H, m), 3.63-3.59 (1H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.47-2.35 (2H, m), 1.61-1.19 (19H, m), 0.87 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.2, 159.6, 159.2, 159.1, 159.0, 130.8, 130.5, 130.0, 129.7, 129.5, 129.1, 127.9, 113.9, 113.7, 113.6, 97.9 (J_{CH} = 170 Hz), 80.0, 79.7, 75.3, 74.9, 74.7, 72.0, 71.5, 68.4, 66.0, 55.2×2, 39.4, 35.1, 31.8, 29.5×2, 29.3, 25.1, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 865.4493 (865.4497 calcd for $C_{50}H_{66}O_{11}Na$ $[M+Na]^+$).

Data for (*S*)-**3cβ**: Colorless syrup; R_f 0.41 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ +34.3° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (2H, m), 7.31-7.26 (2H, m), 7.24-7.17 (4H, m), 6.88-6.79 (8H, m), 5.07 and 5.00 (2H, ABq, *J* = 11.6 Hz), 4.87 and 4.78 (2H, ABq, *J* = 12.0 Hz), 4.85 and 4.53 (2H, ABq, *J* = 10.0 Hz), 4.41 and 4.35 (2H, ABq, *J* = 11.2 Hz), 4.41 (1H, s), 4.08-3.99 (1H, m), 3.82-3.77 (13H, m), 3.52 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.37 (1H, dd, *J* = 9.6 Hz, 2.8 Hz), 3.26-3.15 (1H, m), 2.93 (1H, dd, *J* = 16.0 Hz, 6.0 Hz), 2.49 (1H, dd, *J* = 16.0 Hz, 6.4 Hz), 1.63-1.19 (19H, m), 0.88 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.6, 159.5, 159.2, 159.0×2, 130.8, 130.8, 130.4, 130.0, 129.7, 129.0, 128.0, 113.9, 113.7, 113.7, 113.4, 101.7 (J_{CH} = 154 Hz), 82.0, 79.7, 75.0, 73.5, 73.2, 71.6, 71.0, 66.0, 55.2×2, 41.2, 35.0, 31.9, 29.6, 29.3, 25.3, 22.7, 18.1, 14.1; HRMS (ESI-TOF) *m/z* 865.4493 (865.4497 calcd for $C_{50}H_{66}O_{11}Na$ $[M+Na]^+$).

Compound (*R,R*)-**4a**



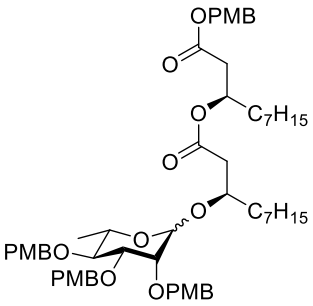
(*R,R*)-**4a**

(*R,R*)-**4a** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R,R*)-**6a** by organophotoacid-catalyzed glycosylation using general procedure in 68% yield (α/β = 82/18).

Data for (*R,R*)-**4aα**: Colorless syrup; R_f 0.36 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -21.1° (c 1.03, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.20 (8H, m), 6.88-6.81 (8H, m), 5.23-5.15 (1H, m), 5.03-4.98 (2H, m), 4.82 and 4.54 (2H, ABq, *J* = 10.4 Hz), 4.74 (1H, d, *J* = 1.2 Hz), 4.68 and 4.60 (2H, ABq, *J* = 12.0 Hz), 4.55 and 4.50 (2H, ABq, *J* = 11.2 Hz), 3.94-3.86 (1H, m), 3.81-3.78 (12H, m), 3.75 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.72-3.66 (1H, m, H-5), 3.65-3.61 (1H, m, H-2), 3.52 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.65-2.47 (3H, m), 2.33 (1H, dd, *J* = 14.8 Hz, 6.8 Hz), 1.61-1.10 (19H, m), 0.91-0.82 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 159.6, 159.2, 159.1, 131.0, 130.8, 130.3, 130.1, 129.6, 129.5, 129.2, 127.9, 113.9, 113.7, 97.6 (J_{CH} = 168 Hz), 80.2, 79.7, 74.8, 74.6, 74.5, 72.3, 71.8, 70.7, 68.3, 66.2, 55.2×2, 40.3, 39.1, 33.7, 33.4, 31.7, 31.4, 24.7, 24.3, 22.5, 22.4, 17.9, 14.0, 13.9; HRMS (ESI-TOF) *m/z* 951.4860 (951.4865 calcd for $C_{54}H_{72}O_{13}Na$ $[M+Na]^+$).

Data for (*R,R*)-**4aβ**: Colorless syrup; R_f 0.42 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ +59.5° (c 0.37, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (2H, m), 7.25-7.16 (6H, m), 6.87-6.79 (8H, m), 5.25-5.16 (1H, m), 5.01 and 4.97 (2H, ABq, *J* = 12.4 Hz), 4.87 and 4.75 (2H, ABq, *J* = 12.4 Hz), 4.84 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.45 (1H, s), 4.39 and 4.32 (2H, ABq, *J* = 11.6 Hz), 4.08-4.00 (1H, m), 3.84 (1H, d, *J* = 3.2 Hz), 3.81-3.75 (12H, m), 3.53 (1H, dd, *J* = 9.2 Hz, 9.2 Hz), 3.41 (1H, dd, *J* = 9.6 Hz, 2.8 Hz), 3.31-3.21 (1H, m), 2.60-2.33 (4H, m), 1.76-1.15 (19H, m), 0.91-0.82 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 170.1, 159.6, 159.1, 159.0, 158.9, 131.2, 130.9, 130.6, 130.1, 129.8, 129.7, 129.0, 127.8, 113.9, 113.7, 113.6, 113.4, 101.1 (J_{CH} = 155 Hz), 82.2, 79.7, 76.0, 74.9, 74.1, 73.5, 71.8, 70.9, 70.7, 66.2, 55.2×2, 39.8, 39.1, 35.5, 33.9, 31.8, 31.5, 29.7, 24.8, 24.5, 22.5×2, 18.0, 14.1, 14.0; HRMS (ESI-TOF) *m/z* 951.4873 (951.4865 calcd for $C_{54}H_{72}O_{13}Na$ $[M+Na]^+$).

Compound (*R,R*)-**4b**



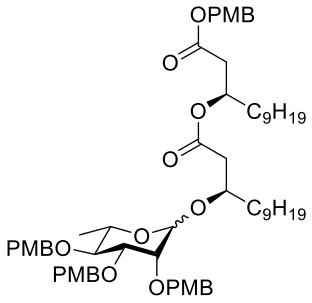
(*R,R*)-**4b**

(*R,R*)-**4b** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R,R*)-**6b** by organophotoacid-catalyzed glycosylation using general procedure in 75% yield (α/β = 85/15).

Data for (*R,R*)-**4bα**: Colorless syrup; R_f 0.43 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -20.8° (c 0.70, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (8H, m), 6.88-6.80 (8H, m), 5.24-5.15 (1H, m), 5.04-4.97 (2H, m), 4.82 and 4.54 (2H, ABq, *J* = 10.4 Hz), 4.75 (1H, d, *J* = 1.2 Hz), 4.68 and 4.60 (2H, ABq, *J* = 12.0 Hz), 4.54 and 4.50 (2H, ABq, *J* = 11.2 Hz), 3.95-3.86 (1H, m), 3.83-3.61 (15H, m), 3.52 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.65-2.46 (3H, m), 2.33 (1H, dd, *J* = 15.2 Hz, 7.2 Hz), 1.74-1.07 (27H, m), 0.92-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 159.6, 159.2, 159.0, 131.0, 130.8, 130.3, 130.1, 129.6, 129.5, 129.2, 127.8, 113.9, 113.7, 97.5 (J_{CH} = 166 Hz), 80.2, 79.7, 74.8, 74.6, 74.5, 72.3, 71.8, 70.7, 68.3, 66.2, 55.2×2, 40.3, 39.1, 33.8, 33.4, 31.8, 31.7, 29.5, 29.2, 29.1, 25.1, 24.7, 22.6×2, 17.9, 14.1×2; HRMS (ESI-TOF) *m/z* 1007.5488 (1007.5491 calcd for $C_{58}H_{80}O_{13}Na$ $[M+Na]^+$).

Data for (*R,R*)-**4bβ**: Colorless syrup; R_f 0.48 (9/1 toluene/EtOAc); $[\alpha]^{30}_D$ +38.3° (c 1.19, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (2H, m), 7.25-7.16 (6H, m), 6.87-6.79 (8H, m), 5.25-5.17 (1H, m), 5.01 and 4.97 (2H, ABq, *J* = 12.0 Hz), 4.87 and 4.75 (2H, ABq, *J* = 12.4 Hz), 4.84 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.45 (1H, s), 4.39 and 4.32 (2H, ABq, *J* = 11.6 Hz), 4.09-4.00 (1H, m), 3.84 (1H, d, *J* = 2.8 Hz), 3.81-3.76 (12H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 8.8 Hz), 3.41 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.31-3.21 (1H, m), 2.59-2.35 (4H, m), 1.74-1.15 (27H, m), 0.90-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 170.1, 159.6, 159.1, 159.0, 158.9, 131.2, 130.9, 130.6, 130.1, 129.8, 129.7, 129.0, 127.7, 113.9, 113.7, 113.6, 113.3, 101.1 (J_{CH} = 153 Hz), 82.1, 79.7, 76.0, 74.9, 74.0, 73.5, 71.8, 70.8, 70.7, 66.2, 55.2×2, 39.7, 39.1, 35.5, 34.0, 31.8, 31.7, 29.6, 29.3, 29.2, 29.1, 25.1, 24.9, 22.7, 22.6, 18.0, 14.1×2; HRMS (ESI-TOF) *m/z* 1007.5487 (1007.5491 calcd for $C_{58}H_{80}O_{13}Na$ $[M+Na]^+$).

Compound (*R,R*)-**4c**



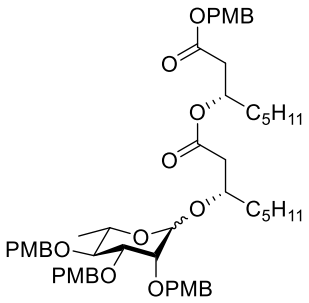
(*R,R*)-**4c**

(*R,R*)-**4c** was obtained from glycosyl donor **7β** and glycosyl acceptor (*R,R*)-**6c** by organophotoacid-catalyzed glycosylation using general procedure in 66% yield (α/β = 83/17).

Data for (*R,R*)-**4cα**: Colorless syrup; R_f 0.54 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -18.7° (c 1.01, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.20 (8H, m), 6.89-6.80 (8H, m), 5.24-5.14 (1H, m), 5.05-4.96 (2H, m), 4.82 and 4.54 (2H, ABq, *J* = 10.4 Hz), 4.76 (1H, d, *J* = 1.2 Hz), 4.68 and 4.60 (2H, ABq, *J* = 12.4 Hz), 4.54 and 4.50 (2H, ABq, *J* = 11.2 Hz), 3.95-3.87 (1H, m), 3.82-3.73 (13H, m), 3.73-3.66 (1H, m), 3.66-3.62 (1H, m), 3.52 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.66-2.46 (3H, m), 2.33 (1H, dd, *J* = 15.2 Hz, 7.2 Hz), 1.64-1.07 (35H, m), 0.92-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 170.2, 159.6, 159.2, 159.0, 131.0, 130.8, 130.3, 130.1, 129.6, 129.5, 129.1, 127.8, 113.9, 113.7, 97.5 (J_{CH} = 168 Hz), 80.2, 79.7, 74.8, 74.6, 74.5, 72.3, 71.8, 70.7, 68.3, 66.2, 55.2×2, 40.3, 39.1, 33.8, 33.4, 31.9, 31.8, 29.6, 29.5, 29.3×3, 25.1, 24.7, 22.7, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 1063.6113 (1063.6117 calcd for $C_{62}H_{88}O_{13}Na$ $[M+Na]^+$).

Data for (*R,R*)-**4cβ**: Colorless syrup; R_f 0.59 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ +39.2° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (2H, m), 7.27-7.16 (6H, m), 6.87-6.79 (8H, m), 5.25-5.16 (1H, m), 5.01 and 4.97 (2H, ABq, *J* = 12.0 Hz), 4.87 and 4.74 (2H, ABq, *J* = 12.8 Hz), 4.84 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.45 (1H, s), 4.39 and 4.32 (2H, ABq, *J* = 11.6 Hz), 4.09-4.00 (1H, m), 3.84 (1H, d, *J* = 3.2 Hz), 3.81-3.76 (12H, m), 3.53 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.41 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.31-3.21 (1H, m), 2.60-2.36 (4H, m), 1.74-1.17 (35H, m), 0.91-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.0, 170.1, 159.6, 159.1, 159.0, 158.9, 131.2, 130.9, 130.6, 130.1, 129.8, 129.7, 129.0, 127.7, 113.9, 113.7, 113.6, 113.4, 101.1 (J_{CH} = 154 Hz), 82.2, 79.7, 76.0, 74.9, 74.1, 73.5, 71.8, 70.8, 70.7, 66.2, 55.2×2, 39.7, 39.1, 35.5, 34.0, 31.9×2, 29.6×2, 29.5, 29.3, 25.2, 24.9, 22.7, 18.0, 14.1; HRMS (ESI-TOF) *m/z* 1063.6116 (1063.6117 calcd for $C_{62}H_{88}O_{13}Na$ $[M+Na]^+$).

Compound (*S,S*)-**4a**



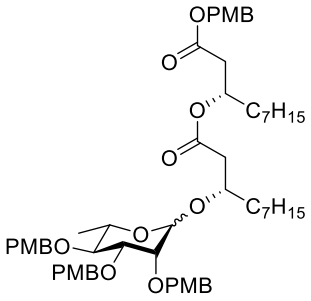
(*S,S*)-**4a**

(*S,S*)-**4a** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S,S*)-**6a** by organophotoacid-catalyzed glycosylation using general procedure in 67% yield (α/β = 83/17).

Data for (*S,S*)-**4aα**: Colorless syrup; R_f 0.49 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -7.7° (c 1.36, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m), 7.26-7.19 (6H, m), 6.88-6.80 (8H, m), 5.25-5.16 (1H, m), 5.05-4.97 (2H, m), 4.91 (1H, d, *J* = 1.6 Hz), 4.83 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.71-4.60 (2H, m), 4.51-4.46 (2H, m), 3.99-3.91 (1H, m), 3.82-3.67 (15H, m), 3.54 (1H, dd, *J* = 9.2 Hz, 9.2 Hz), 2.59 (1H, dd, *J* = 15.6 Hz, 7.6 Hz), 2.51 (1H, dd, *J* = 15.6 Hz, 5.6 Hz), 2.39-2.28 (2H, m), 1.62-1.16 (19H, m), 0.91-0.82 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 159.6, 159.1×2, 159.0, 130.9, 130.6, 130.1, 129.7, 129.5, 129.1, 127.8, 113.9, 113.7, 113.6, 97.6 (J_{CH} = 169 Hz), 80.0, 79.8, 74.9, 74.7, 72.2, 71.4, 70.6, 68.4, 66.2, 55.2, 39.1, 39.0, 34.9, 33.8, 31.7, 31.5, 24.8, 24.7, 22.5, 22.4, 17.9, 14.0, 13.9; HRMS (ESI-TOF) *m/z* 951.4863 (951.4865 calcd for $C_{54}H_{72}O_{13}Na$ $[M+Na]^+$).

Data for (*S,S*)-**4aβ**: Colorless syrup; R_f 0.43 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ +30.2° (c 0.31, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (2H, m), 7.30-7.18 (6H, m), 6.89-6.81 (8H, m), 5.25-5.17 (1H, m), 5.06-5.00 (2H, m), 4.87 and 4.78 (2H, ABq, *J* = 12.0 Hz), 4.84 and 4.52 (2H, ABq, *J* = 10.4 Hz), 4.42 and 4.36 (2H, ABq, *J* = 11.6 Hz), 4.38 (1H, s), 4.00-3.92 (1H, m), 3.81-3.77 (13H, m), 3.51 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.38 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.28-3.19 (1H, m), 2.90 (1H, dd, *J* = 15.6 Hz, 5.2 Hz), 2.66 (1H, dd, *J* = 15.6 Hz, 6.8 Hz), 2.53 (1H, dd, *J* = 15.6 Hz, 6.0 Hz), 2.45 (1H, dd, *J* = 15.2 Hz, 8.8 Hz), 1.70-1.17 (19H, m), 0.91-0.82 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 159.6, 159.2, 159.0×2, 130.8×2, 130.4, 130.2, 130.0, 129.7, 129.0, 127.8, 113.9, 113.7×2, 113.4, 101.7 (J_{CH} = 153 Hz), 82.0, 79.7, 75.0, 73.4, 73.2, 71.8, 71.1, 70.6, 66.2, 55.2×2, 41.2, 39.1, 34.5, 33.8, 31.8, 31.5, 24.7, 22.6, 22.4, 18.0, 14.1, 13.9; HRMS (ESI-TOF) *m/z* 951.4868 (951.4865 calcd for $C_{54}H_{72}O_{13}Na$ $[M+Na]^+$).

Compound (*S,S*)-**4b**



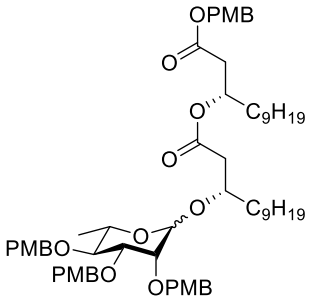
(*S,S*)-**4b**

(*S,S*)-**4b** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S,S*)-**6b** by organophotoacid-catalyzed glycosylation using general procedure in 68% yield (α/β = 83/17).

Data for (*S,S*)-**4bα**: Colorless syrup; R_f 0.52 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -5.5° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (2H, m), 7.27-7.20 (6H, m), 6.88-6.81 (8H, m), 5.25-5.16 (1H, m), 5.05-4.97 (2H, m), 4.91 (1H, s), 4.83 and 4.53 (2H, ABq, *J* = 10.8 Hz), 4.70-4.61 (2H, m), 4.51-4.44 (2H, m), 3.99-3.91 (1H, m), 3.82-3.68 (15H, m), 3.54 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.59 (1H, dd, *J* = 15.6 Hz, 7.2 Hz), 2.51 (1H, dd, *J* = 15.2 Hz, 5.6 Hz), 2.38-2.28 (2H, m), 1.60-1.16 (27H, m), 0.90-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 159.6, 159.1×2, 159.0, 130.9, 130.6, 130.1, 129.7, 129.5, 129.0, 127.8, 113.9, 113.7, 113.6, 97.6 (J_{CH} = 168 Hz), 80.0, 79.8, 74.9, 74.7, 72.2, 71.4, 70.7, 68.4, 66.2, 55.2, 39.2, 39.0, 35.0, 33.9, 31.8, 31.7, 29.5, 29.3, 29.2, 29.1, 25.1, 22.6×2, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 985.5644 (985.5672 calcd for $C_{58}H_{81}O_{13}$ $[M+H]^+$).

Data for (*S,S*)-**4bβ**: Colorless syrup; R_f 0.45 (9/1 toluene/EtOAc); $[\alpha]^{29}_D$ +33.1° (c 0.55, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (2H, m), 7.29-7.18 (6H, m), 6.89-6.80 (8H, m), 5.26-5.16 (1H, m), 5.06-4.99 (2H, m), 4.87 and 4.78 (2H, ABq, *J* = 12.0 Hz), 4.84 and 4.52 (2H, ABq, *J* = 10.8 Hz), 4.42 and 4.36 (2H, ABq, *J* = 11.6 Hz), 4.38 (1H, s), 4.01-3.92 (1H, m), 3.82-3.76 (13H, m), 3.51 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 3.38 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.29-3.18 (1H, m), 2.90 (1H, dd, *J* = 15.6 Hz, 5.2 Hz), 2.65 (1H, dd, *J* = 15.6 Hz, 6.8 Hz), 2.52 (1H, dd, *J* = 15.6 Hz, 5.6 Hz), 2.45 (1H, dd, *J* = 15.2 Hz, 8.4 Hz), 1.66-1.12 (27H, m), 0.91-0.84 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 159.6, 159.2, 159.0, 130.8, 130.5, 130.1, 130.0, 129.7, 129.0, 127.8, 113.9, 113.7×2, 113.4, 101.7 (J_{CH} = 154 Hz), 82.0, 79.7, 75.0, 73.4, 73.2, 71.8, 71.0, 70.6, 66.2, 55.2×2, 41.2, 39.1, 34.6, 33.9, 31.8, 31.7, 29.6, 29.3, 29.1, 25.1, 22.6, 22.6, 18.0, 14.1; HRMS (ESI-TOF) *m/z* 1007.5485 (1007.5491 calcd for $C_{58}H_{81}O_{13}Na$ $[M+Na]^+$).

Compound (*S,S*)-**4c**



(*S,S*)-**4c**

(*S,S*)-**4c** was obtained from glycosyl donor **7β** and glycosyl acceptor (*S,S*)-**6c** by organophotoacid-catalyzed glycosylation using general procedure in 76% yield (α/β = 85/15).

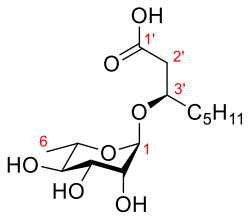
Data for (*S,S*)-**4cα**: Colorless syrup; R_f 0.57 (9/1 toluene/EtOAc); $[\alpha]^{28}_D$ -5.2° (c 0.98, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (2H, m), 7.26-7.20 (6H, m), 6.88-6.81 (8H, m), 5.26-5.16 (1H, m), 5.05-4.96 (2H, m), 4.91 (1H, d, *J* = 1.2 Hz), 4.83 and 4.53 (2H, ABq, *J* = 10.4 Hz), 4.71-4.61 (2H, m), 4.51-4.45 (2H, m), 4.00-3.91 (1H, m), 3.82-3.68 (15H, m), 3.55 (1H, dd, *J* = 9.2 Hz, 9.2 Hz), 2.59 (1H, dd, *J* = 15.6 Hz, 8.0 Hz), 2.51 (1H, dd, *J* = 15.6 Hz, 5.6 Hz), 2.40-2.27 (2H, m), 1.62-1.14 (35H, m), 0.92-0.83 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.6, 170.1, 159.6, 159.1×2, 159.0, 130.9, 130.6, 130.1, 129.7, 129.5, 129.0, 127.8, 113.9, 113.7, 113.6, 97.6 (J_{CH} = 168 Hz), 80.0, 79.8, 74.9, 74.7, 72.2, 71.4, 70.6, 68.4, 66.2, 55.2, 39.1, 39.0, 35.0, 33.9, 31.8, 29.6, 29.5, 29.3×2, 29.2, 25.1, 22.6, 17.9, 14.1; HRMS (ESI-TOF) *m/z* 1063.6116 (1063.6117 calcd for $C_{62}H_{88}O_{13}Na$ $[M+Na]^+$).

Data for (*S,S*)-**4cβ**: Colorless syrup; R_f 0.49 (9/1 toluene/EtOAc); $[\alpha]^{23}_D$ +35.1° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (2H, m), 7.29-7.26 (2H, m), 7.24-7.18 (4H, m), 6.89-6.81 (8H, m), 5.25-5.17 (1H, m), 5.05-5.01 (2H, m), 4.90 and 4.78 (2H, ABq, *J* = 12.4 Hz), 4.84 and 4.52 (2H, ABq, *J* = 10.4 Hz), 4.42 and 4.36 (2H, ABq, *J* = 11.2 Hz), 4.39 (1H, s), 4.01-3.93 (1H, m), 3.82-3.77 (13H, m), 3.51 (1H, dd, *J* = 9.2 Hz, 9.2 Hz), 3.38 (1H, dd, *J* = 9.6 Hz, 3.2 Hz), 3.28-3.19 (1H, m), 2.90 (1H, dd, *J* = 15.6 Hz, 5.2 Hz), 2.65 (1H, dd, *J* = 15.6 Hz, 6.8 Hz), 2.53 (1H, dd, *J* = 15.6 Hz, 6.0 Hz), 2.45 (1H, dd, *J* = 15.6 Hz, 8.4 Hz), 1.62-1.18 (35H, m), 0.90-0.85 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 159.6, 159.2, 159.0, 130.8×2, 130.5, 130.1, 130.0, 129.7, 129.0, 127.8, 113.9, 113.7×2, 113.4, 101.7 (J_{CH} = 154 Hz), 82.1, 79.7, 75.0, 73.5, 73.3, 71.8, 71.0, 70.6, 66.2, 55.2×2, 41.2, 39.1, 34.6, 33.9, 31.9×2, 29.7×2, 29.5×2, 29.4, 29.3, 25.1, 22.7, 18.0, 14.1; HRMS (ESI-TOF) *m/z* 1063.6110 (1063.6117 calcd for $C_{62}H_{88}O_{13}Na$ $[M+Na]^+$).

General procedure for the deprotection of PMB groups

To a solution of each compound **3a-c**, **4a-c** (1.0 eq.) in dry DCM (16mM) was added TFA (40 eq.) at 0 ℃ under Ar atmosphere. After the reaction mixture was stirred for 1 h at 0 ℃, the resulting mixture was concentrated in *vacuo*. The purification of the residue by silica gel column chromatography (50/10/1 $CHCl_3$/MeOH/H_2O) gave mono-rhamnolipids **1a-c**, **2a-c**.

Compound (*R*)-**1a**

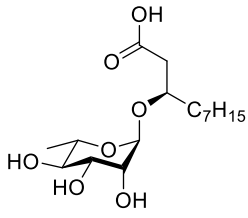


(*R*)-**1a**

(*R*)-**1a** was obtained from (*R*)-**3aα** by the general procedure for the deprotection of PMB groups in 90% yield.

Data for (*R*)-**1a**: Colorless syrup; R_f 0.16 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{25}_D$ -76.3° (c 0.65, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.80 (1H, d, *J* = 1.6 Hz), 4.12-4.04 (1H, m), 3.77-3.73 (1H, m), 3.70-3.59 (2H, m), 3.36 (1H, dd, *J* = 9.6, 9.6 Hz), 2.56-2.44 (2H, m), 1.61-1.50 (2H, m), 1.40-1.23 (9H, m), 0.92 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.3, 100.4 (J_{CH} = 168 Hz), 75.6, 73.9, 72.7, 72.3, 70.2, 41.2, 34.5, 33.0, 25.6, 23.6, 17.9, 14.4; HRMS (ESI-TOF) *m/z* 329.1571 (329.1571 calcd for $C_{14}H_{26}O_7Na$ $[M+Na]^+$).

Compound (*R*)-**1b**

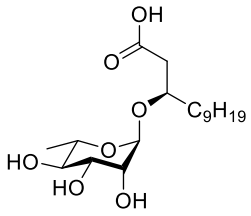


(*R*)-**1b**

(*R*)-**1b** was obtained from (*R*)-**3bα** by the general procedure for the deprotection of PMB groupsin 72% yield.

Data for (*R*)-**1b**: Colorless syrup; R_f 0.17 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{25}_D$ -73.0° (c 0.94, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.80 (1H, d, *J* = 1.2 Hz), 4.13-4.03 (1H, m), 3.79-3.73 (1H, m), 3.72-3.58 (2H, m), 3.36 (1H, dd, *J* = 9.6, 9.6 Hz) 2.57-2.43 (2H, m), 1.64-1.20 (15H, m), 0.91 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.3, 100.4 (J_{CH} = 167 Hz), 75.6, 73.9, 72.7, 72.3, 70.2, 41.3, 34.5, 33.0, 30.7, 30.4, 25.9, 23.7, 17.9, 14.4; HRMS (ESI-TOF) *m/z* 357.1884 (357.1884 calcd for $C_{16}H_{30}O_7Na$ $[M+Na]^+$).

Compound (*R*)-**1c**

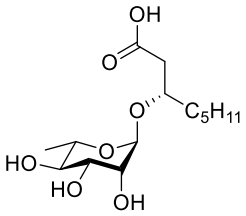


(*R*)-**1c**

(*R*)-**1c** was obtained from (*R*)-**3cα** by the general procedure for the deprotection of PMB groups in 76% yield.

Data for (*R*)-**1c**: Colorless syrup; R_f 0.22 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -74.1° (c 1.13, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.80 (1H, s), 4.12-4.03 (1H, m), 3.79-3.73 (1H, m), 3.71-3.58 (2H, m), 3.36 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.57-2.43 (2H, m), 1.63-1.20 (19H, m), 0.90 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.4, 100.4 (J_{CH} = 167 Hz), 75.6, 73.9, 72.7, 72.3, 70.2, 41.3, 34.5, 33.1, 30.8, 30.7, 30.5, 25.9, 23.7, 17.9, 14.4; HRMS (ESI-TOF) *m/z* 385.2195 (385.2197 calcd for $C_{18}H_{34}O_7Na$ $[M+Na]^+$).

Compound (*S*)-**1a**

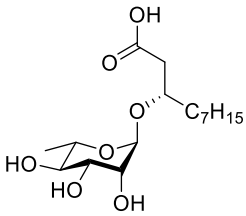


(*S*)-**1a**

(*S*)-**1a** was obtained from (*S*)-**3aα** by the general procedure for the deprotection of PMB groups in 75% yield.

Data for (*S*)-**1a**: Colorless syrup; R_f 0.11 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -25.8° (c 0.92, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.08-3.99 (1H, m), 3.77-3.72 (1H, m), 3.72-3.63 (1H, m), 3.61 (1H, dd, *J* = 9.6Hz, 3.2 Hz), 3.37 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.54-2.41 (2H, m), 1.69-1.20 (11H, m), 0.92 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.4, 101.6 (J_{CH} = 169 Hz), 76.6, 73.9, 72.7, 72.4, 70.3, 40.4, 36.3, 33.0, 26.0, 23.6, 17.9, 14.4; HRMS (ESI-TOF) *m/z* 329.1571 (329.1571 calcd for $C_{14}H_{26}O_7Na$ $[M+Na]^+$).

Compound (*S*)-**1b**

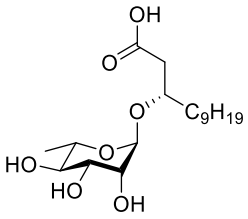


(*S*)-**1b**

(*S*)-**1b** was obtained from (*S*)-**3bα** by the general procedure for the deprotection of PMB groups in 89% yield.

Data for (*S*)-**1b**: Colorless syrup; R_f 0.13 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -23.7° (c 1.17, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.85 (1H, d, *J* = 2.0 Hz), 4.08-3.98 (1H, m), 3.76-3.72 (1H, m), 3.71-3.63 (1H, m), 3.61 (1H, dd, *J* = 9.6Hz, 3.2 Hz), 3.38 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.54-2.41 (2H, m), 1.69-1.22 (15H, m), 0.91 (3H, t, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.3, 101.6 (J_{CH} = 168 Hz), 76.6, 73.8, 72.7, 72.4, 70.3, 40.4, 36.3, 33.0, 30.7, 30.4, 26.3, 23.7, 17.9, 14.4; HRMS (ESI-TOF) *m/z* 357.1884 (357.1884 calcd for $C_{16}H_{30}O_7Na$ $[M+Na]^+$).

Compound (*S*)-**1c**

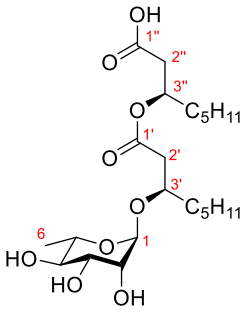


(*S*)-**1c**

(*S*)-**1c** was obtained from (*S*)-**3cα** by the general procedure for the deprotection of PMB groups in 87% yield.

Data for (*S*)-**1c**: Colorless syrup; R_f 0.13 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -21.4° (c 1.05, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 4.85 (1H, d, *J* = 2.0 Hz), 4.09-3.98 (1H, m), 3.77-3.72 (1H, m), 3.71-3.63 (1H, m), 3.61 (1H, dd, *J* = 9.6Hz, 3.6 Hz), 3.38 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.54-2.39 (2H, m), 1.70-1.18 (19H, m), 0.90 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.4, 101.6 (J_{CH} = 167 Hz), 76.6, 73.8, 72.7, 72.4, 70.3, 40.4, 36.3, 33.1, 30.7×2, 30.5, 26.3, 23.7, 18.0, 14.4; HRMS (ESI-TOF) *m/z* 385.2196 (385.2197 calcd for $C_{18}H_{34}O_7Na$ $[M+Na]^+$).

Compound (*R,R*)-**2a**



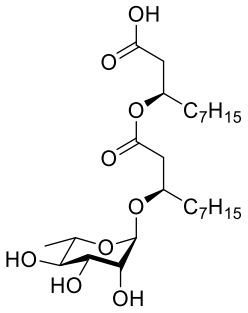
(*R,R*)-**2a**

(*R,R*)-**2a** was obtained from (*R,R*)-**4aα** by the general procedure for the deprotection of PMB groups in 93% yield.

Data for (*R,R*)-**2a**: Colorless syrup; R_f 0.27 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -53.5° (c 1.18, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.31-5.20 (1H, m), 4.79 (1H, d, *J* = 1.2 Hz), 4.11-4.02 (1H, m), 3.78-3.72 (1H, m), 3.71-3.59 (2H, m), 3.36 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.64-2.45 (4H, m), 1.68-1.20 (19H, m), 0.96-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.7, 172.5, 100.6 (J_{CH} = 166

Hz), 75.5, 74.0, 72.6, 72.4, 72.2, 70.1, 41.3, 40.1, 35.1, 34.2, 33.0, 32.7, 25.9, 25.5, 23.6×2, 17.9, 14.4, 14.3; HRMS (ESI-TOF) *m/z* 471.2564 (471.2565 calcd for $C_{22}H_{40}O_9Na$ $[M+Na]^+$).

Compound (*R,R*)-**2b**

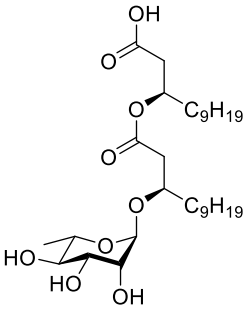


(*R,R*)-**2b**

(*R,R*)-**2b** was obtained from (*R,R*)-**4bα** by the general procedure for the deprotection of PMB groups in 80% yield.

Data for (*R,R*)-**2b**: Colorless syrup; R_f 0.27 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -59.7° (c 0.69, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.30-5.20 (1H, m), 4.79 (1H, d, *J* = 1.2 Hz), 4.11-4.02 (1H, m), 3.78-3.72 (1H, m), 3.70-3.59 (2H, m), 3.36 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.63-2.45 (4H, m), 1.68-1.21 (27H, m), 0.94-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.9, 172.5, 100.5 (J_{CH} = 166 Hz), 75.4, 74.0, 72.6, 72.5, 72.2, 70.1, 41.3, 40.3, 35.1, 34.3, 33.0, 32.9, 30.7, 30.4, 30.4, 30.3, 26.3, 25.9, 23.7, 17.9, 14.5; HRMS (ESI-TOF) *m/z* 527.3190 (527.3191 calcd for $C_{26}H_{48}O_9Na$ $[M+Na]^+$).

Compound (*R,R*)-**2c**

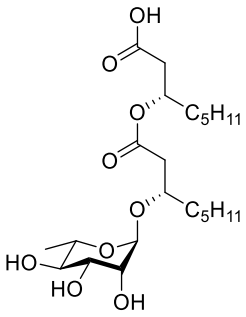


(*R,R*)-**2c**

(*R,R*)-**2c** was obtained from (*R,R*)-**4cα** by the general procedure for the deprotection of PMB groups in 98% yield.

Data for (*R,R*)-**2c**: Colorless syrup; R_f 0.35 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -66.5° (c 1.29, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.30-5.21 (1H, m), 4.79 (1H, d, *J* = 1.2 Hz), 4.10-4.01 (1H, m), 3.77-3.73 (1H, m), 3.70-3.60 (2H, m), 3.36 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.63-2.45 (4H, m), 1.67-1.15 (35H, m), 0.94-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.7, 172.5, 100.6 (J_{CH} = 168 Hz), 75.5, 74.0, 72.6, 72.4, 72.2, 70.1, 41.3, 40.2, 35.1, 34.3, 33.1, 30.8, 30.7×2, 30.5, 26.3, 25.9, 23.8, 17.9, 14.5; HRMS (ESI-TOF) *m/z* 583.3816 (583.3817 calcd for $C_{30}H_{56}O_9Na$ $[M+Na]^+$).

Compound (*S,S*)-**2a**

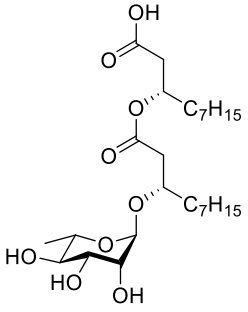


(*S,S*)-**2a**

(*S,S*)-**2a** was obtained from (*S,S*)-**4aα** by the general procedure for the deprotection of PMB groups in 75% yield.

Data for (*S,S*)-**2a**: Colorless syrup; R_f 0.23 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -6.6° (c 1.01, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.32-5.19 (1H, m), 4.83 (1H, s), 4.11-3.98 (1H, m), 3.81-3.73 (1H, m), 3.71-3.57 (2H, m), 3.38 (1H, dd, *J* = 9.6 Hz, 9.6 Hz), 2.62-2.43 (4H, m), 1.68-1.20 (19H, m), 0.97-0.86 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.8, 172.8, 101.1 (J_{CH} = 167 Hz), 75.9, 73.8, 72.8, 72.5, 72.4, 70.2, 40.8, 40.5, 36.3, 35.2, 32.9, 32.7, 26.0×2, 23.6×2, 17.9, 14.4×2; HRMS (ESI-TOF) *m/z* 471.2563 (471.2565 calcd for $C_{22}H_{40}O_9Na$ $[M+Na]^+$).

Compound (*S,S*)-**2b**

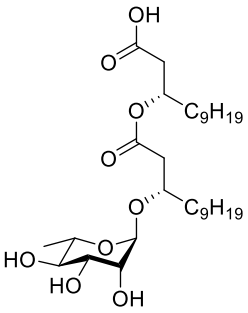


(*S,S*)-**2b**

(*S,S*)-**2b** was obtained from (*S,S*)-**4bα** by the general procedure for the deprotection of PMB groups in 84% yield.

Data for (*S,S*)-**2b**: Colorless syrup; R_f 0.25 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -2.1° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.32-5.22 (1H, m), 4.83 (1H, s), 4.10-4.01 (1H, m), 3.79-3.75 (1H, m), 3.70-3.58 (2H, m), 3.38 (1H, dd, *J* = 10.0 Hz, 9.2 Hz), 2.56-2.43 (4H, m), 1.66-1.21 (27H, m), 0.94-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 176.2, 172.8, 101.0 (J_{CH} = 169 Hz), 75.8, 73.8, 72.9, 72.5, 72.3, 70.2, 41.0, 40.6, 36.3, 35.2, 33.0×2, 30.6, 30.5, 30.4, 30.3, 26.4, 26.3, 23.7×2, 18.0, 14.5; HRMS (ESI-TOF) *m/z* 527.3188 (527.3191 calcd for $C_{26}H_{48}O_9Na$ $[M+Na]^+$).

Compound (*S,S*)-**2c**

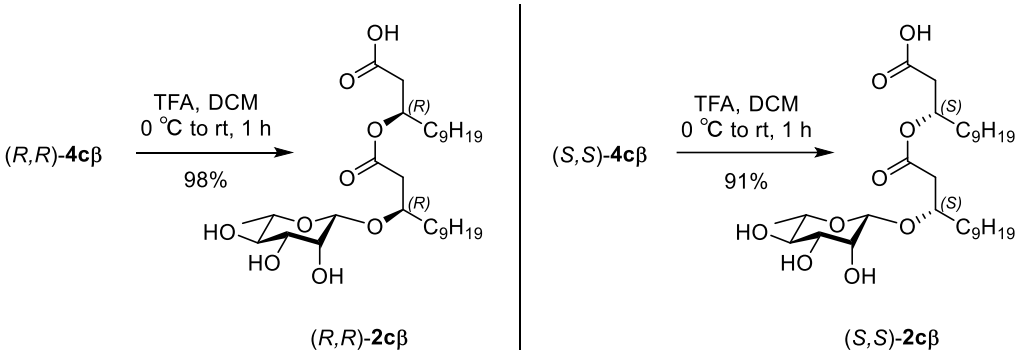


(*S,S*)-**2c**

(*S,S*)-**2c** was obtained from (*S,S*)-**4cα** by the general procedure for the deprotection of PMB groups in 93% yield.

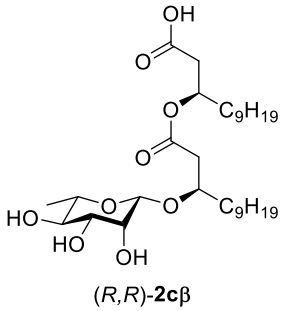
Data for (*S,S*)-**2c**: Colorless syrup; R_f 0.32 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{26}_D$ -0.7° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.32-5.23 (1H, m), 4.83 (1H, d, *J* = 1.2 Hz), 4.10-4.01 (1H, m), 3.81-3.75 (1H, m), 3.70-3.59 (2H, m), 3.39 (1H, dd, *J* = 9.6 Hz, 9.2 Hz), 2.58-2.43 (4H, m), 1.66-1.21 (35H,

m), 0.94-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 176.3, 172.8, 101.0 (J_{CH} = 168 Hz), 75.8, 73.8, 72.9, 72.5, 72.3, 70.2, 41.1, 40.6, 36.3, 35.2, 33.1, 30.8, 30.7, 30.5, 26.4, 26.3, 23.8, 18.0, 14.5; HRMS (ESI-TOF) *m/z* 583.3828 (583.3817 calcd for $C_{30}H_{56}O_9Na$ $[M+Na]^+$).



Scheme S4. Synthesis of (*R*,*R*)-**2cβ** and (*S*,*S*)-2**cβ**.

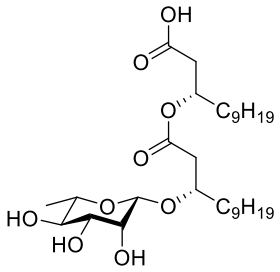
Compound (*R,R*)-**2cβ**



(*R*,*R*)-**2bβ** was obtained from (*R*,*R*)-**4bβ** by the general procedure for the deprotection of PMB groups in 98% yield.

Data for (*R,R*)-**2cβ**: Colorless syrup; R_f 0.25 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{30}_D$ +2.2° (c 1.00, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.31-5.22 (1H, m), 4.57 (1H, s), 4.14-4.05 (1H, m), 3.83 (1H, d, *J* = 3.2 Hz), 3.41 (1H, dd, *J* = 9.2 Hz, 3.6 Hz), 3.26-3.17 (1H, m), 2.58-2.45 (4H, m), 1.72-1.15 (35H, m), 0.93-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.6, 173.0, 101.3 (J_{CH} = 156 Hz), 77.6, 75.0, 73.9, 73.5, 72.8, 72.7, 41.1, 40.7, 36.5, 35.2, 33.1, 30.8, 30.7×2, 30.5×2, 26.3, 26.1, 23.8, 18.1, 14.5; HRMS (ESI-TOF) *m/z* 583.3810 (583.3817 calcd for $C_{30}H_{56}O_9Na$ $[M+Na]^+$).

Compound (*S,S*)-**2cβ**



(*S,S*)-**2cβ**

(*S,S*)-**2bβ** was obtained from (*S,S*)-**4bβ** by the general procedure for the deprotection of PMB groups in 91% yield.

Data for (*S,S*)-**2cβ**: Colorless syrup; R_f 0.22 (50/10/1 $CHCl_3$/MeOH/H_2O); $[\alpha]^{30}_D$ +46.5° (c 0.67, $CHCl_3$); ^{1}H-NMR (400 MHz, CD_3OD) δ 5.28-5.19 (1H, m), 4.57 (1H, s), 4.11-4.02 (1H, m), 3.84 (1H, d, *J* = 3.2 Hz), 3.40 (1H, dd, *J* = 9.6 Hz, 3.6 Hz), 3.26-3.17 (1H, m), 2.84 (1H, dd, *J* = 15.2 Hz, 5.2 Hz), 2.61-2.43 (3H, m), 1.68-1.19 (35H, m), 0.93-0.87 (6H, m); ^{13}C-NMR (100 MHz, CD_3OD) δ 175.5, 172.7, 101.4 (J_{CH} = 157 Hz), 77.6, 75.0, 73.8, 73.6, 72.8, 72.6, 42.1, 40.6, 35.4, 35.1, 33.1, 30.7×2, 30.5, 26.3, 26.2, 23.8, 18.1, 14.5; HRMS (ESI-TOF) *m/z* 583.3813 (583.3817 calcd for $C_{30}H_{56}O_9Na$ $[M+Na]^+$).

5. Antibacterial activity of mono-rhamnolipids

Strains. Reference strains *Micrococcus luteus* IFO 3333, *Staphylococcus. aureus* MS16526, and *Escherichia coli* NIHJ were exploited from the culture collection at the Institute of Microbial Chemistry. *Enterococcus faecalis* JCM5803 and *Enterococcus faecium* JCM5804 were purchased from Japan Collection of Microorganisms. *E. faecalis* NCTC 12201 and *E. faecium* NCTC 12202 purchased from National Collection of Type Cultures.

Determination of the MICs by the agar dilution method against gram-positive and gram-negative bacteria. The MICs were examined by a serial agar dilution method using Nutrient Broth (Difco) with agar (1.8 %, Wako). The test suspension was prepared at approximately 10^4 CFU per spot using a MIC-2000 (Dynatech Laboratories, Inc.) inoculum replicating apparatus. The MIC was defined as the lowest concentration of antibiotic that inhibited the development of visible growth on the agar after 18 h of incubation at 37 °C.

Natural RL (mono-rhamnolipid dominant) was purchased from AGAE Technologies.

6. References

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7. NMR spectrum charts

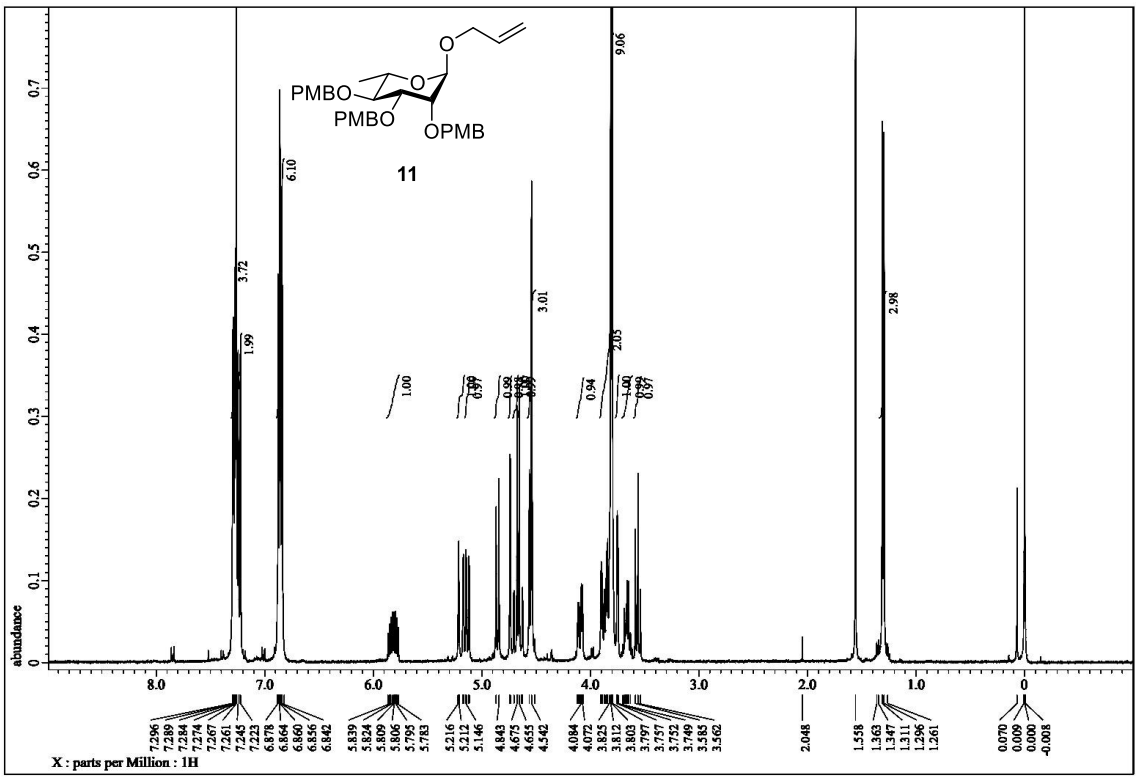

Fig. S1 ^{1}H-NMR spectrum of **11** (400MHz, $CDCl_3$)

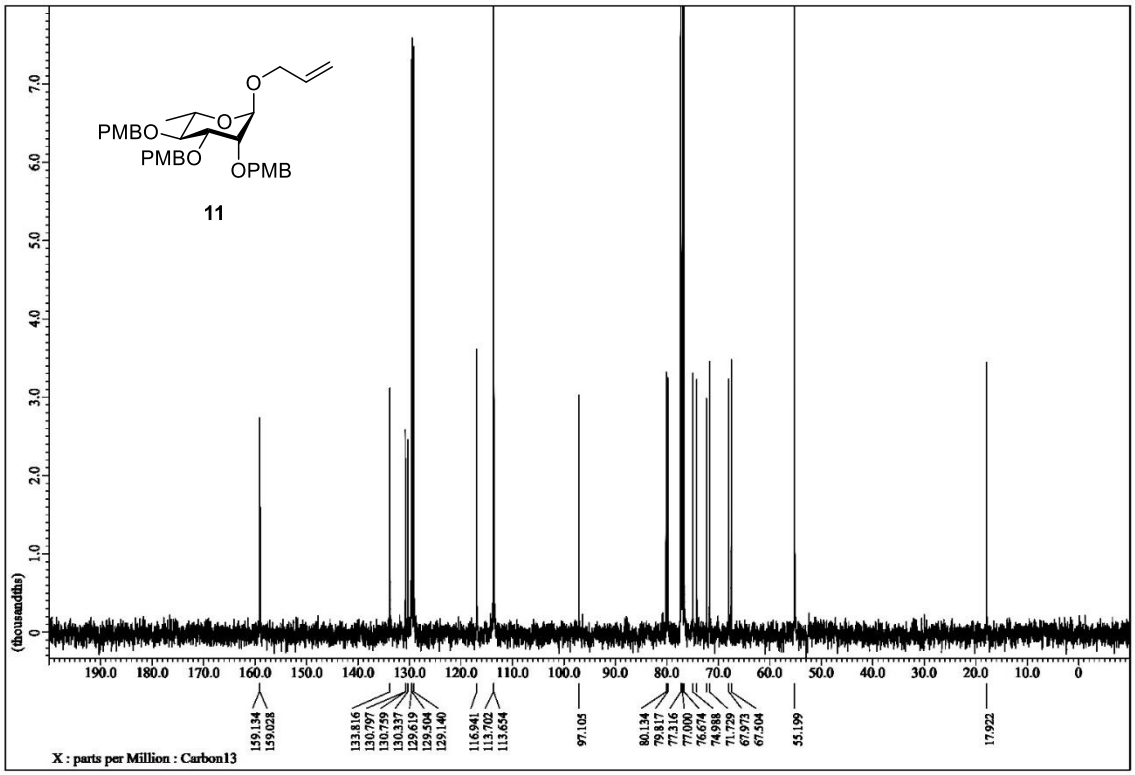

Fig. S2 ^{13}C-NMR spectrum of **11** (100MHz, $CDCl_3$)

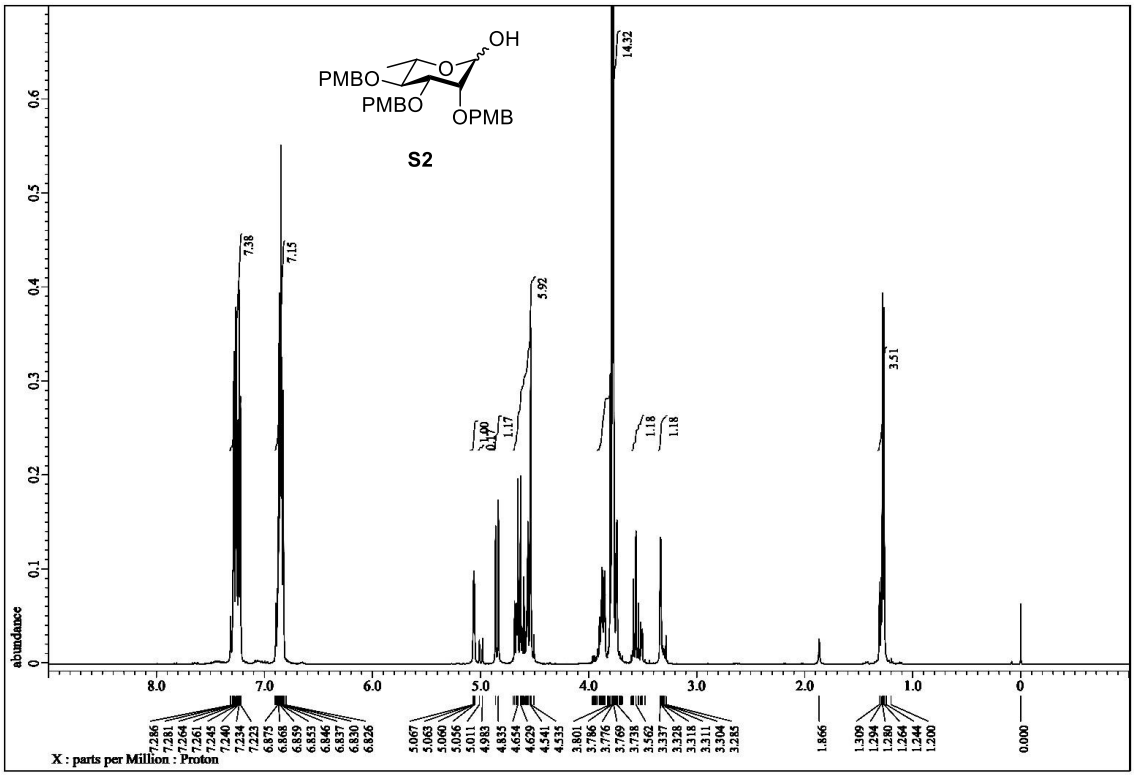

Fig. S3 ^{1}H-NMR spectrum of **S2** (400MHz, $CDCl_3$)

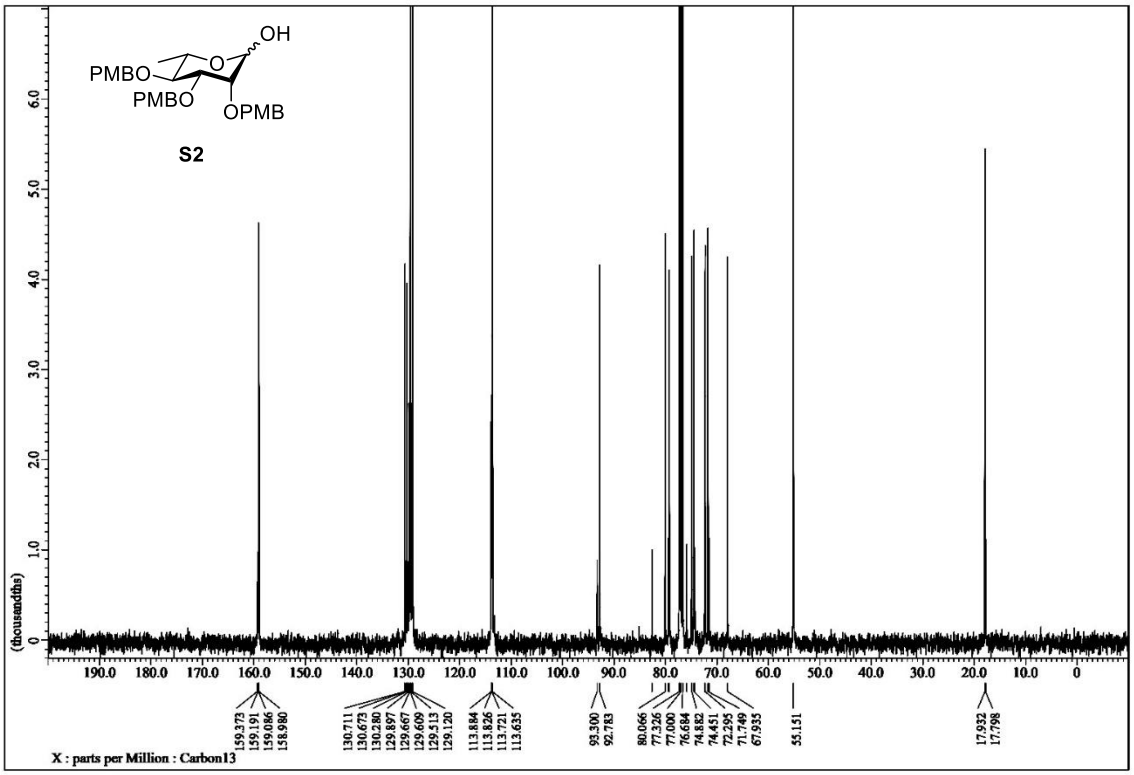

Fig. S4 ^{13}C-NMR spectrum of **S2** (100MHz, $CDCl_3$)

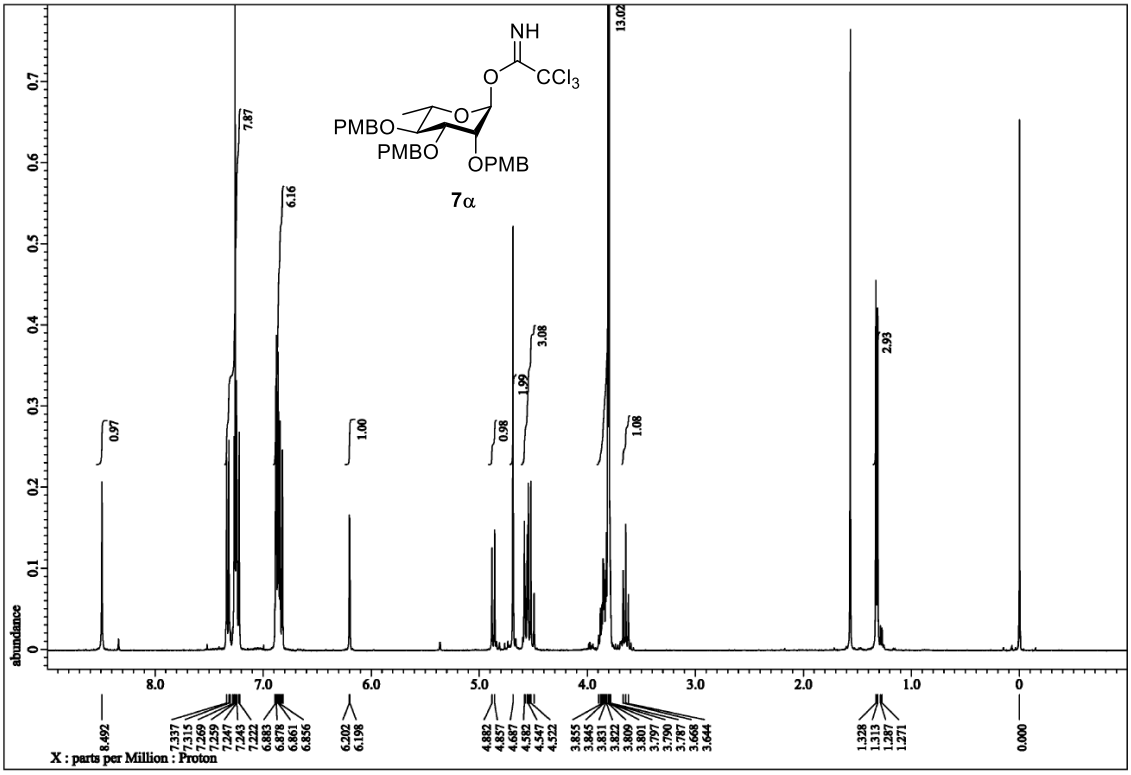

Fig. S5 ^{1}H-NMR spectrum of **7α** (400MHz, $CDCl_3$)

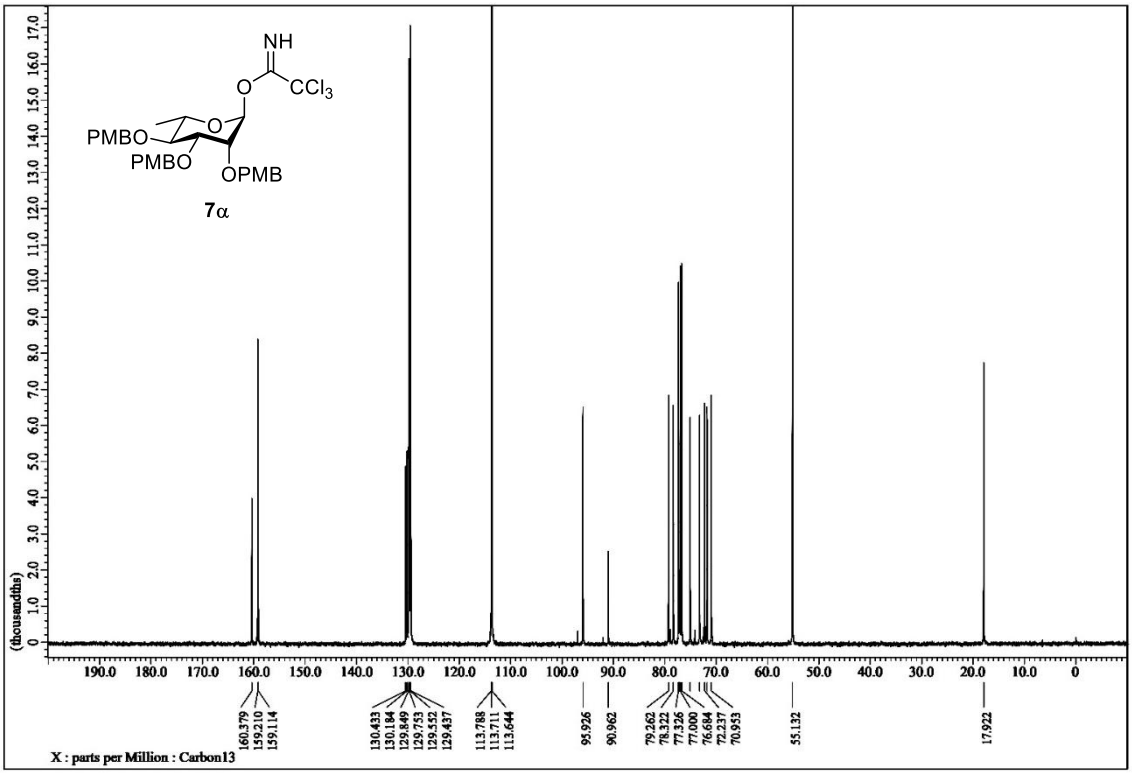

Fig. S6 ^{13}C-NMR spectrum of **7α** (100MHz, $CDCl_3$)

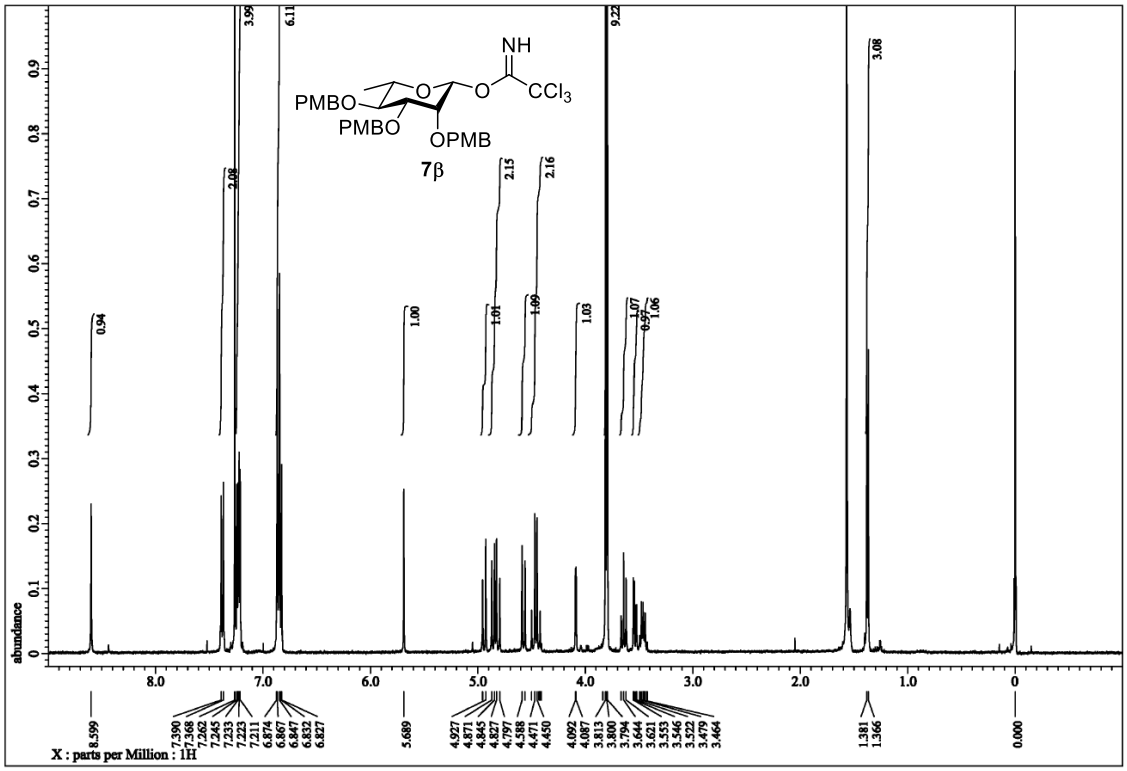

Fig. S7 ^{1}H-NMR spectrum of **7β** (400MHz, $CDCl_3$)

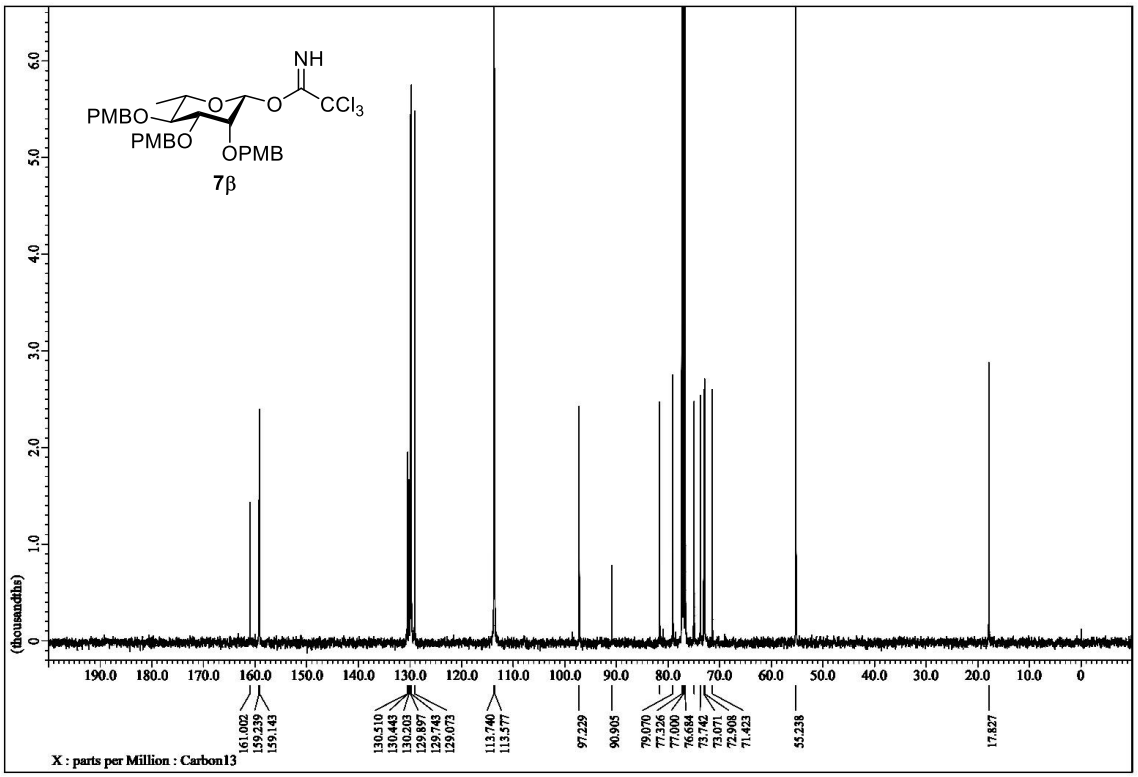

Fig. S8 ^{13}C-NMR spectrum of **7β** (100MHz, $CDCl_3$)

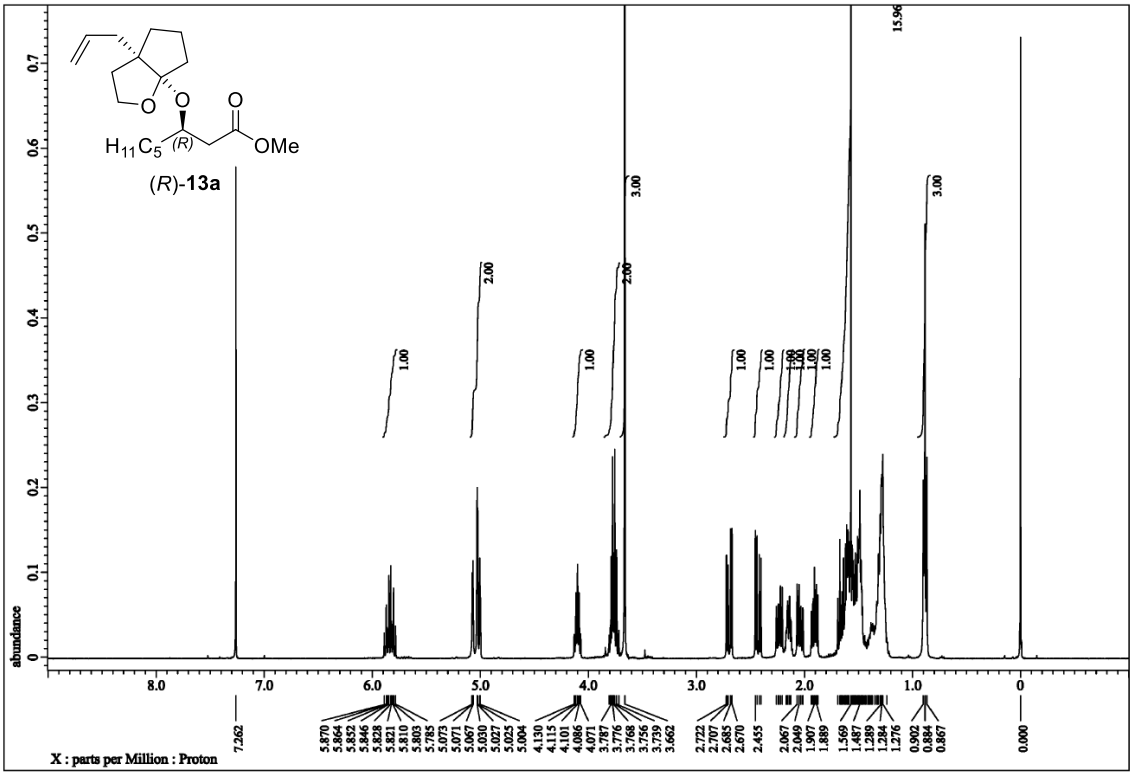

Fig. S9 ^{1}H-NMR spectrum of (*R*)-**13a** (400MHz, $CDCl_3$)

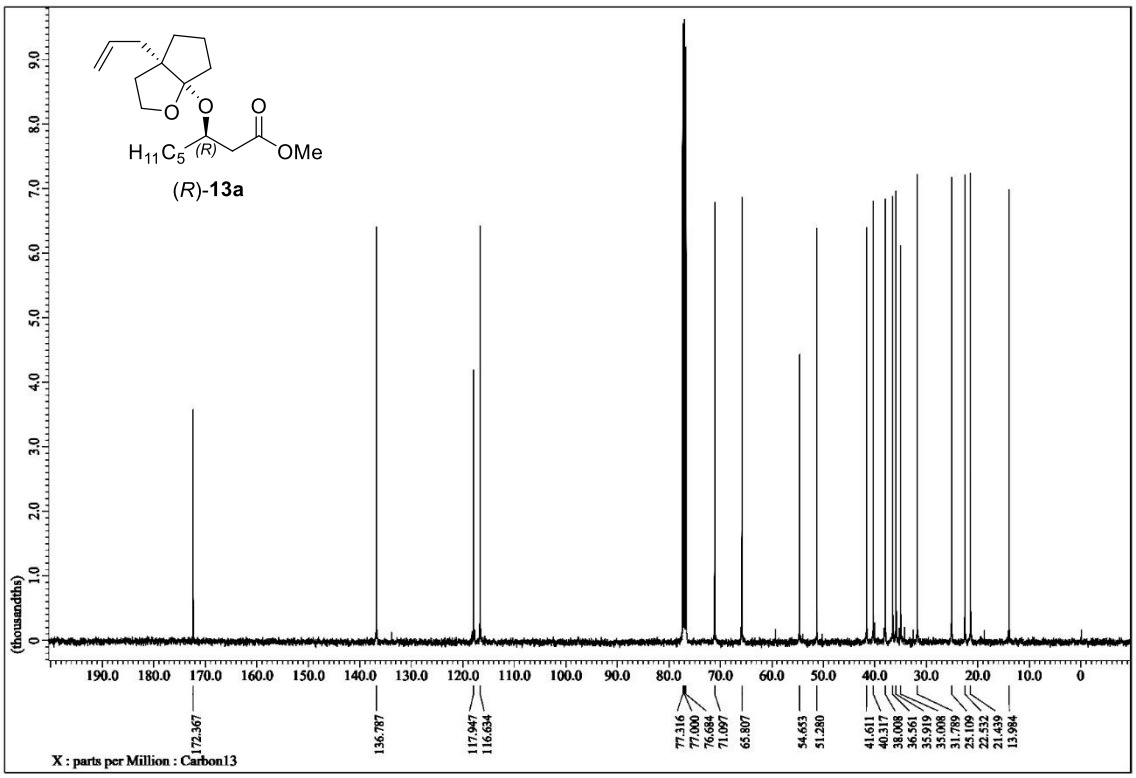

Fig. S10 ^{13}C-NMR spectrum of (*R*)-**13a** (100MHz, $CDCl_3$)

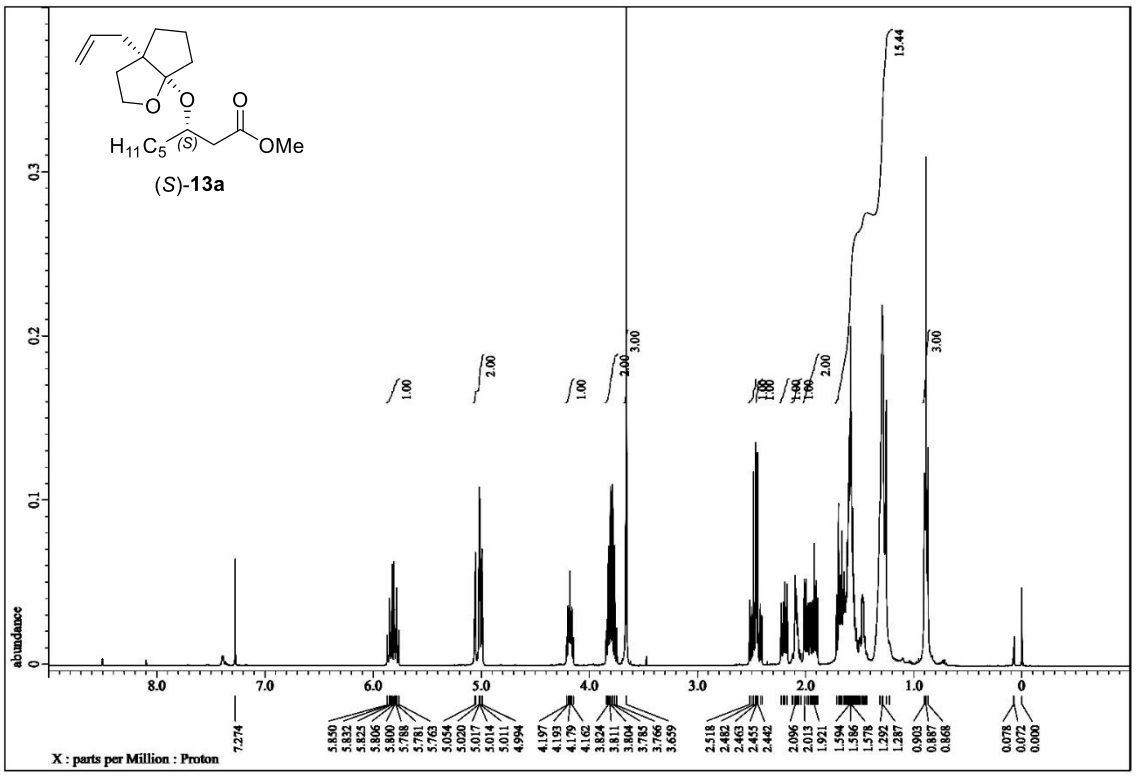

Fig. S11 ^{1}H-NMR spectrum of (*S*)-**13a** (400MHz, $CDCl_3$)

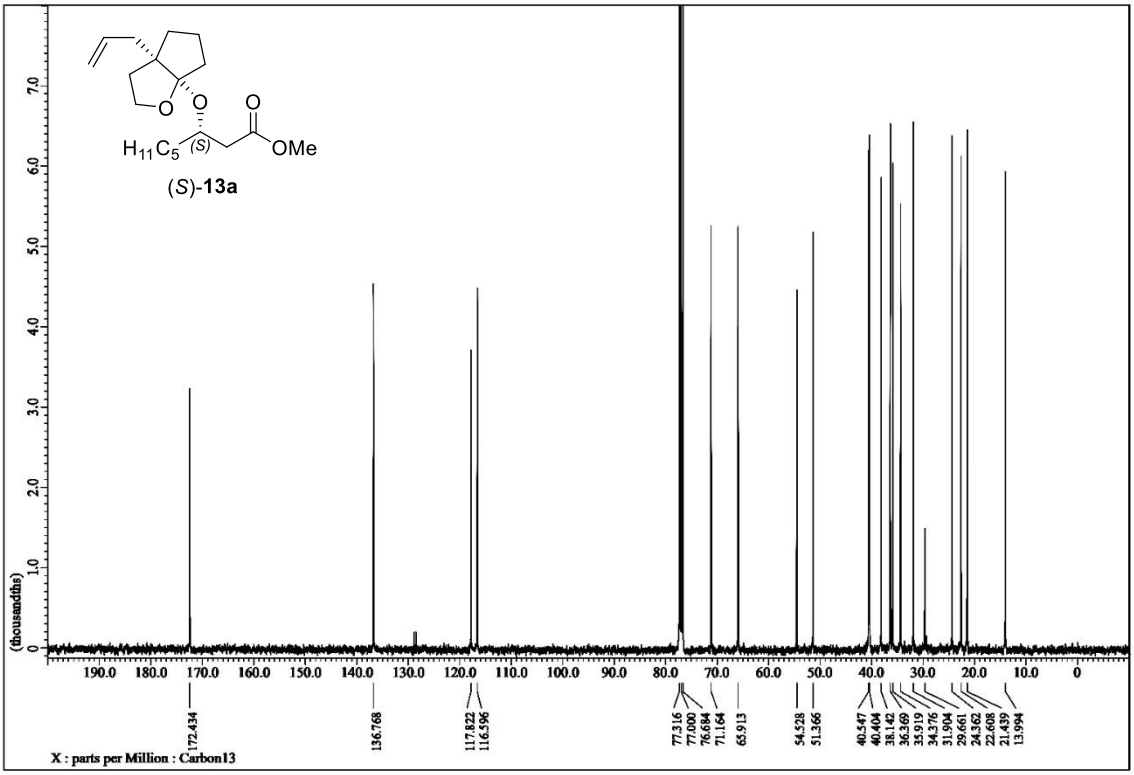

Fig. S12 ^{13}C-NMR spectrum of (*S*)-**13a** (100MHz, $CDCl_3$)

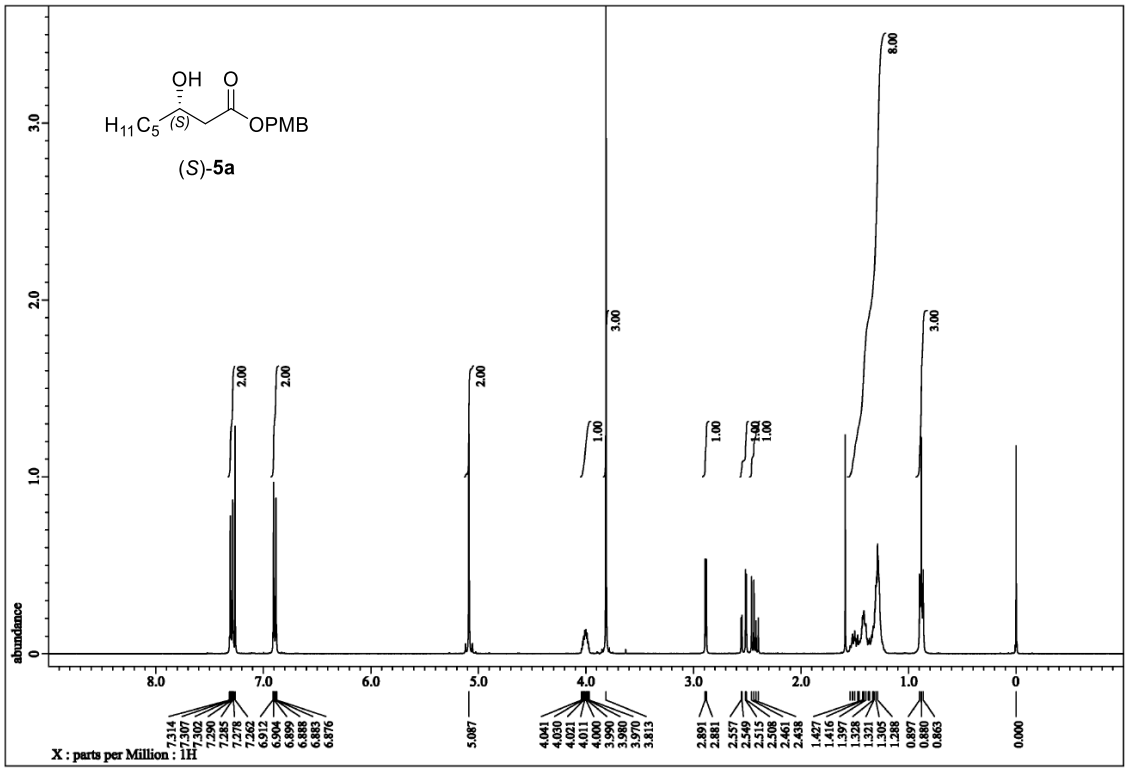

Fig. S13 ^{1}H-NMR spectrum of (*S*)-**5a** (400MHz, $CDCl_3$)

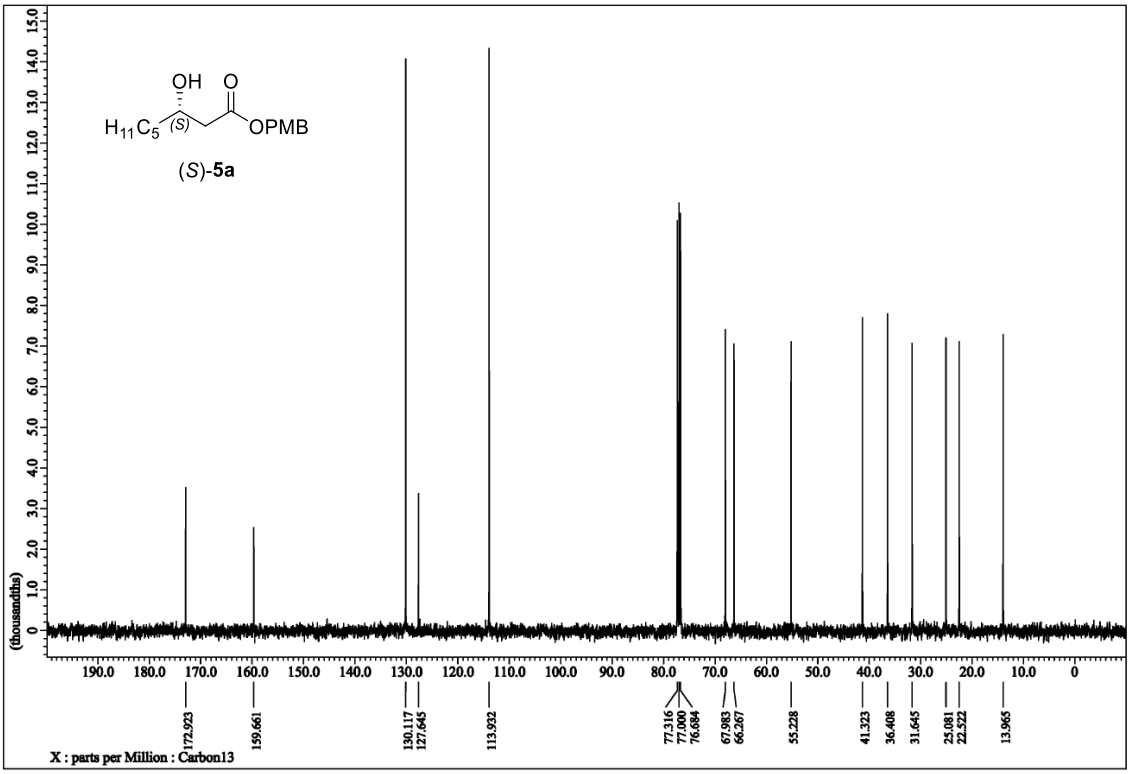

Fig. S14 ^{13}C-NMR spectrum of (*S*)-**5a** (100MHz, $CDCl_3$)

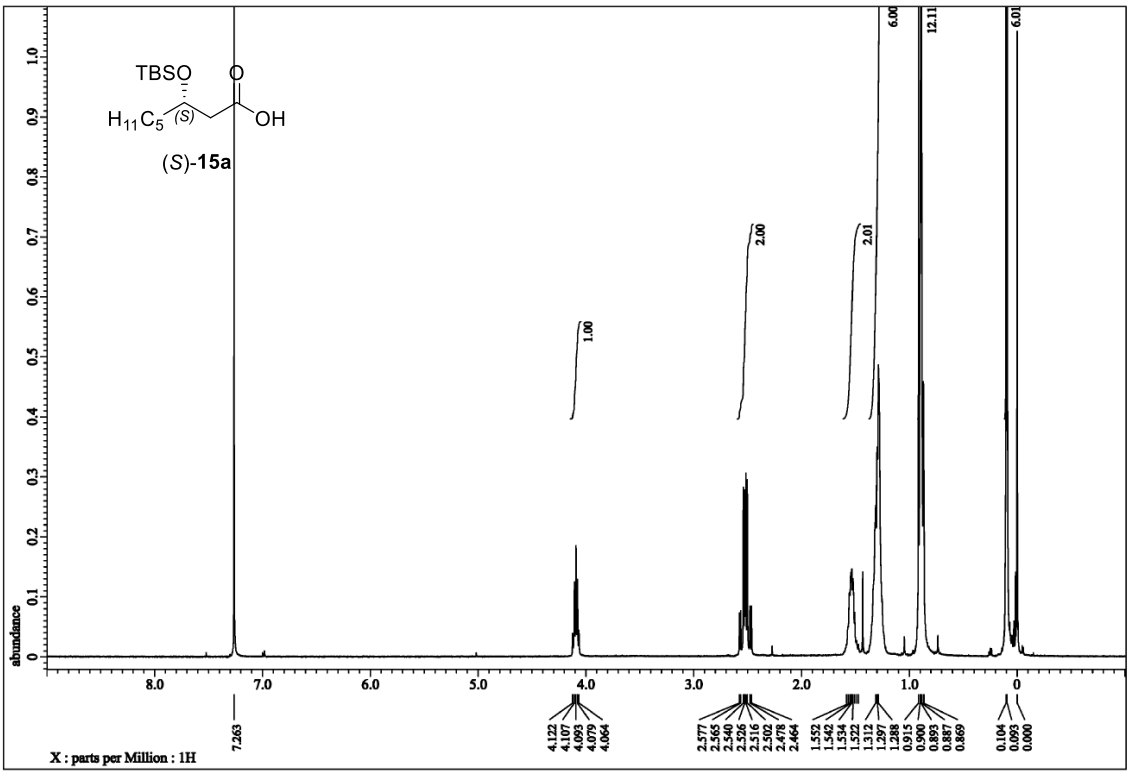

Fig. S15 ^{1}H-NMR spectrum of (*S*)-**15a** (400MHz, $CDCl_3$)

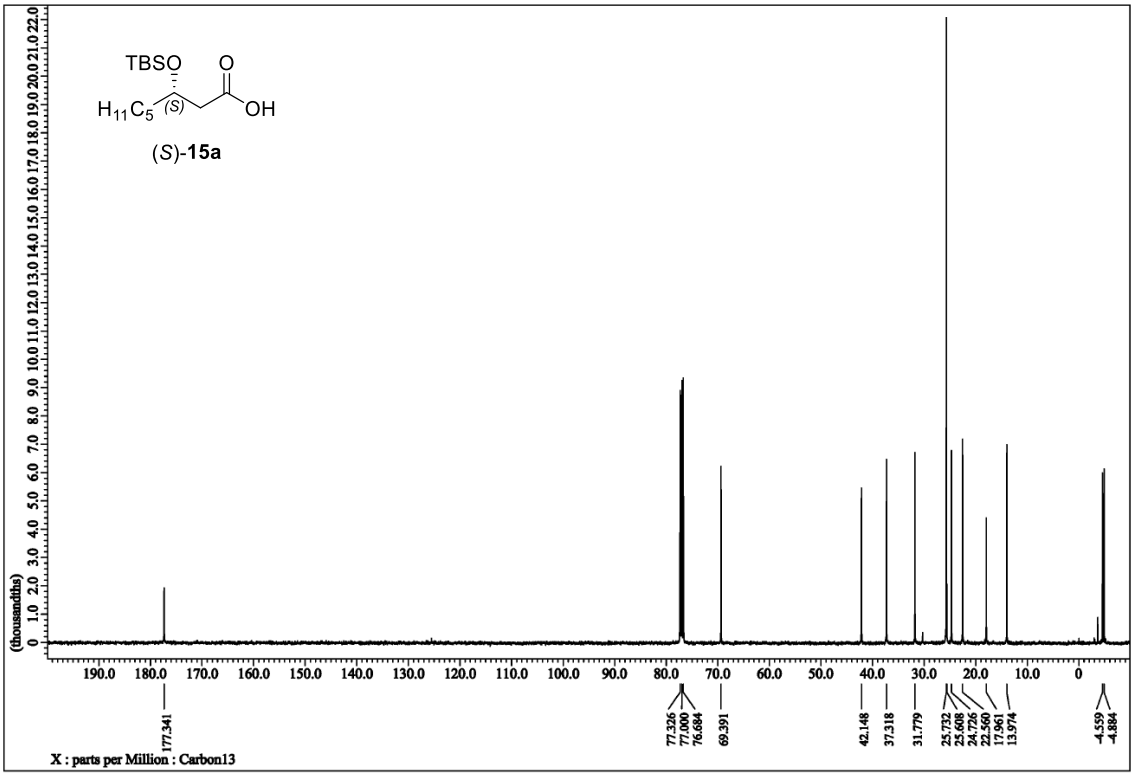

Fig. S16 ^{13}C-NMR spectrum of (*S*)-**15a** (100MHz, $CDCl_3$)

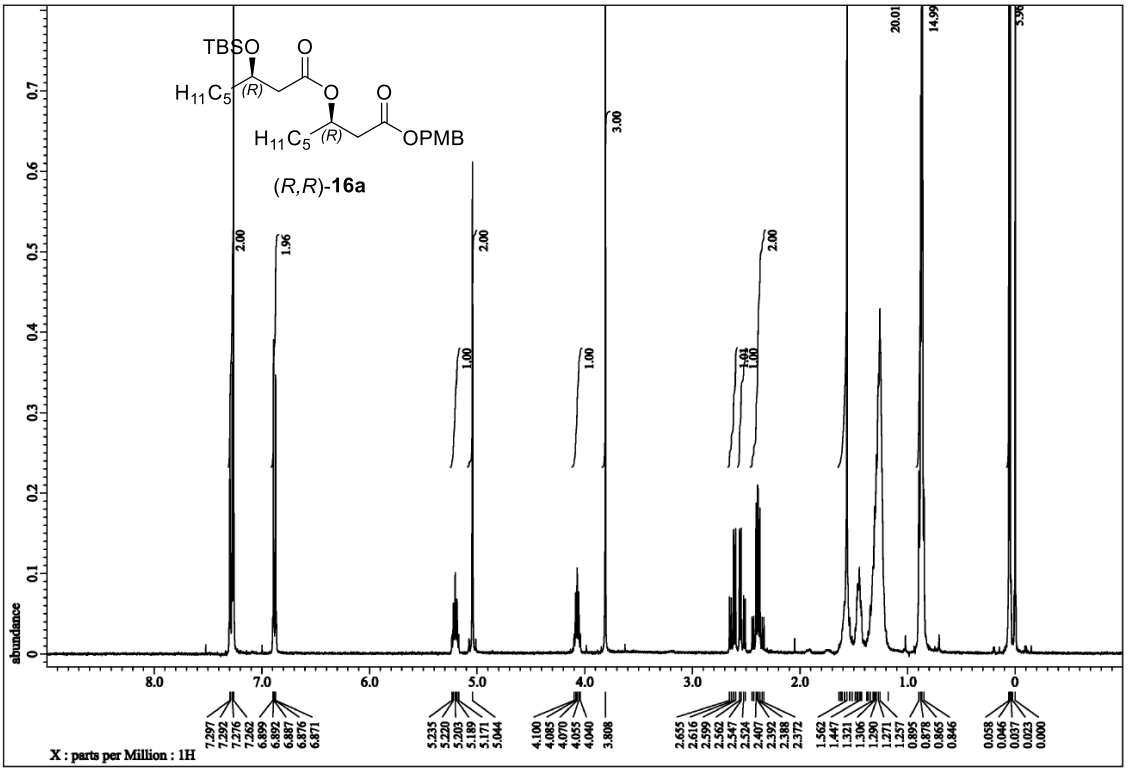

Fig. S17 ^{1}H-NMR spectrum of (*R,R*)-**16a** (400MHz, $CDCl_3$)

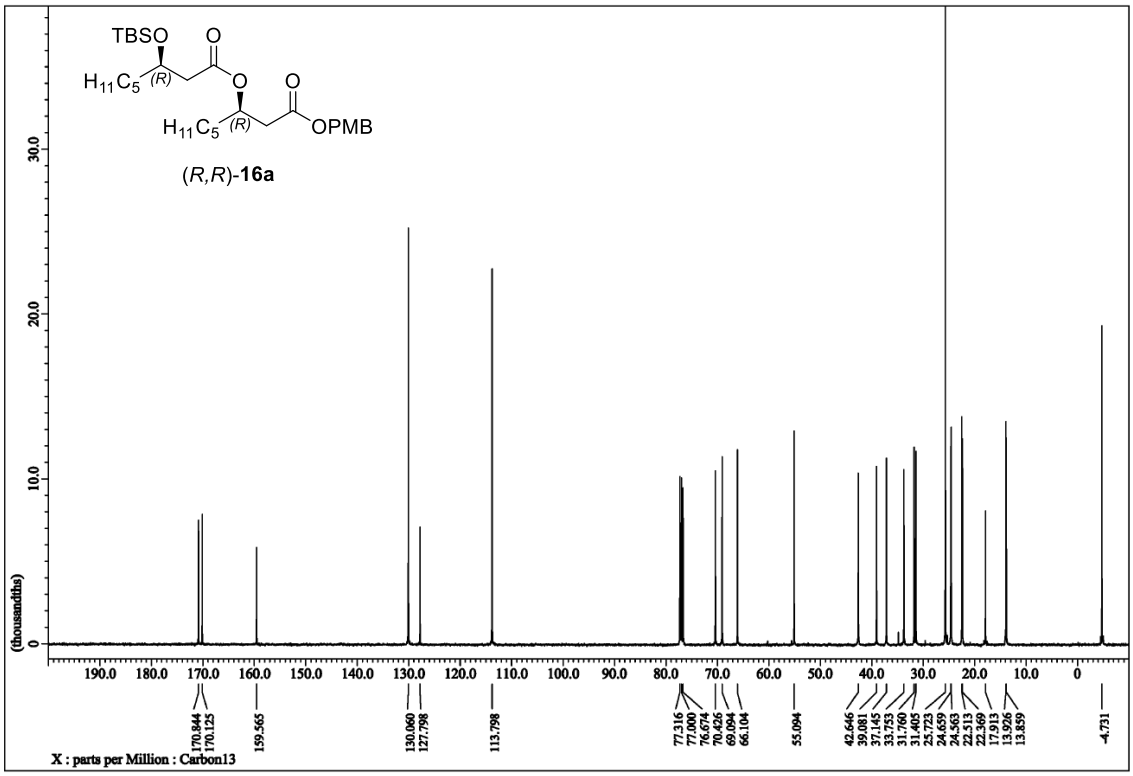

Fig. S18 ^{13}C-NMR spectrum of (*R,R*)-**16a** (100MHz, $CDCl_3$)

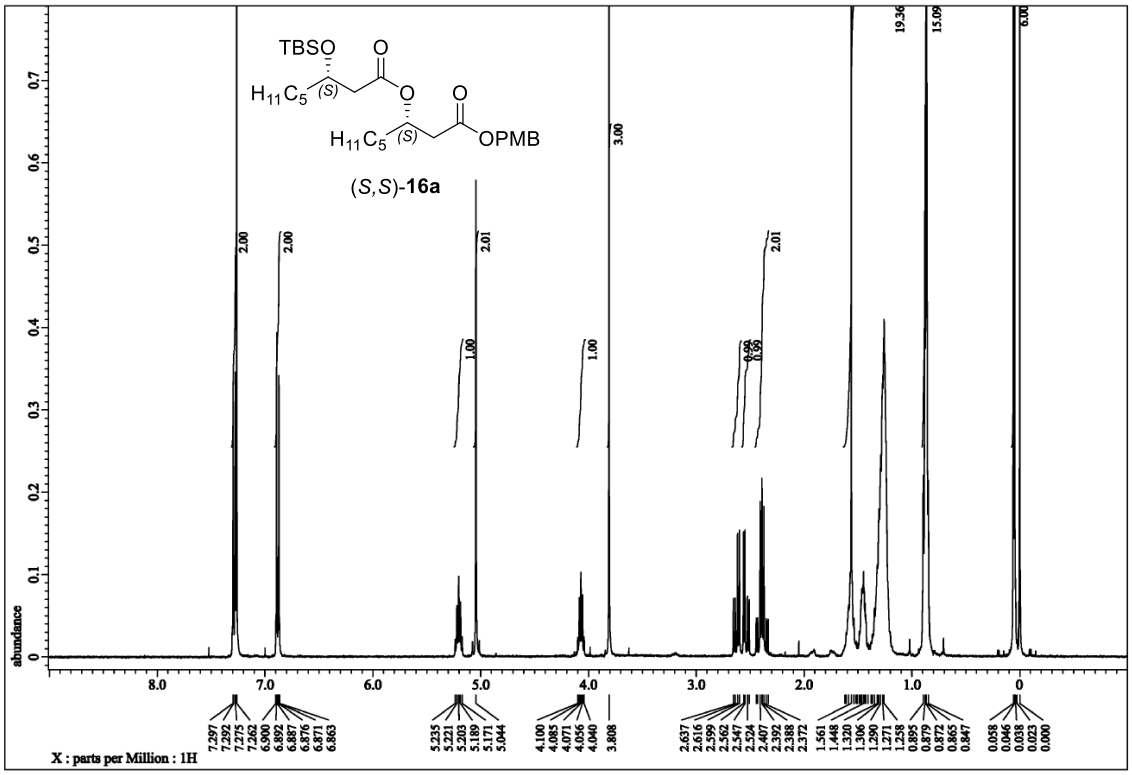

Fig. S19 ^{1}H-NMR spectrum of (*S,S*)-**16a** (400MHz, $CDCl_3$)

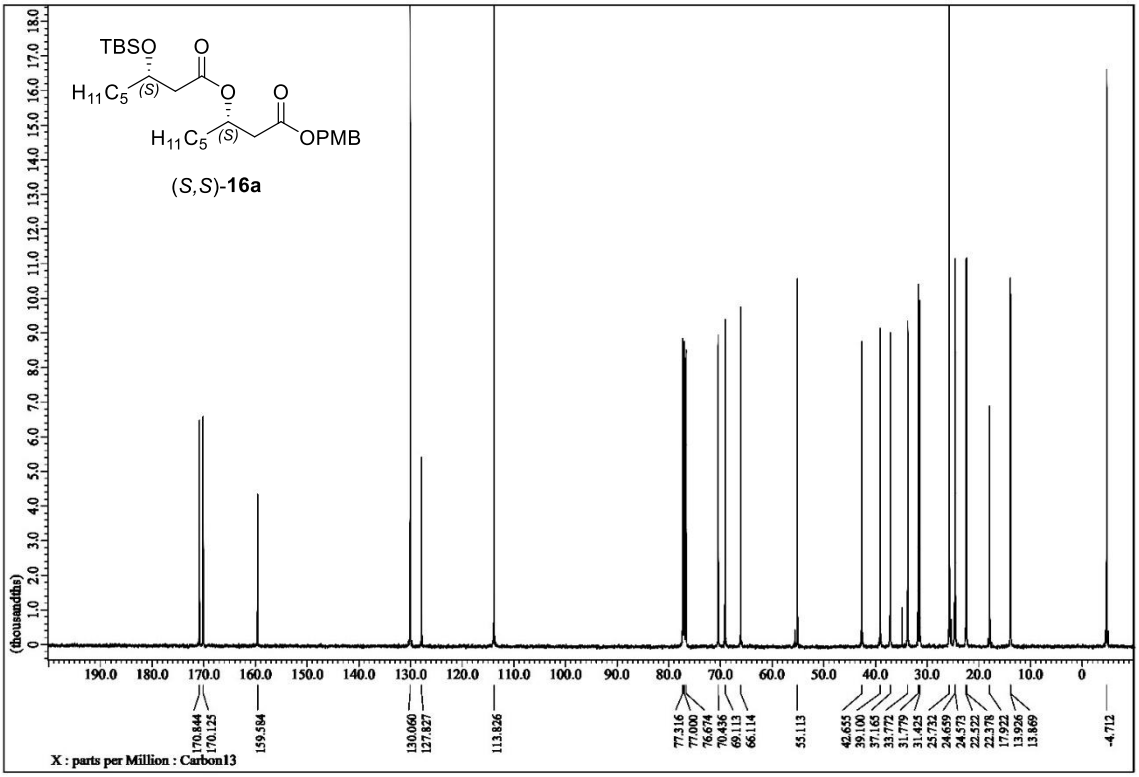

Fig. S20 ^{13}C-NMR spectrum of (*S,S*)-**16a** (100MHz, $CDCl_3$)

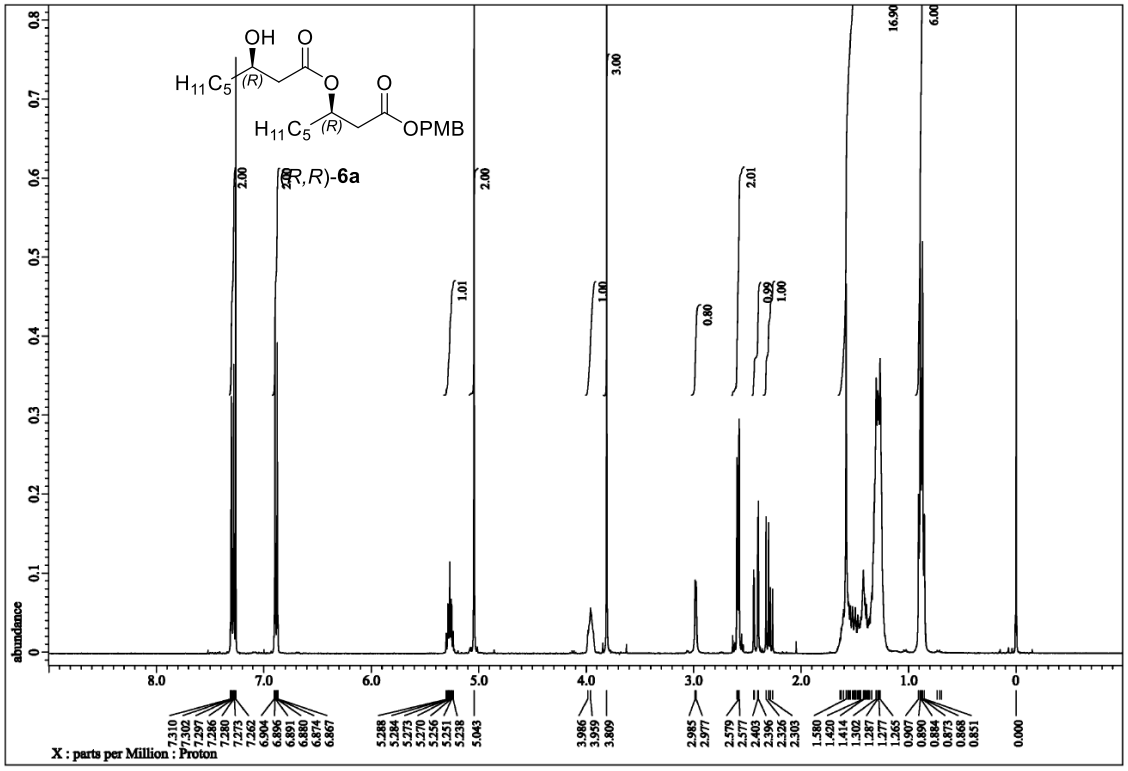

Fig. S21 ^{1}H-NMR spectrum of (*R,R*)-**6a** (400MHz, $CDCl_3$)

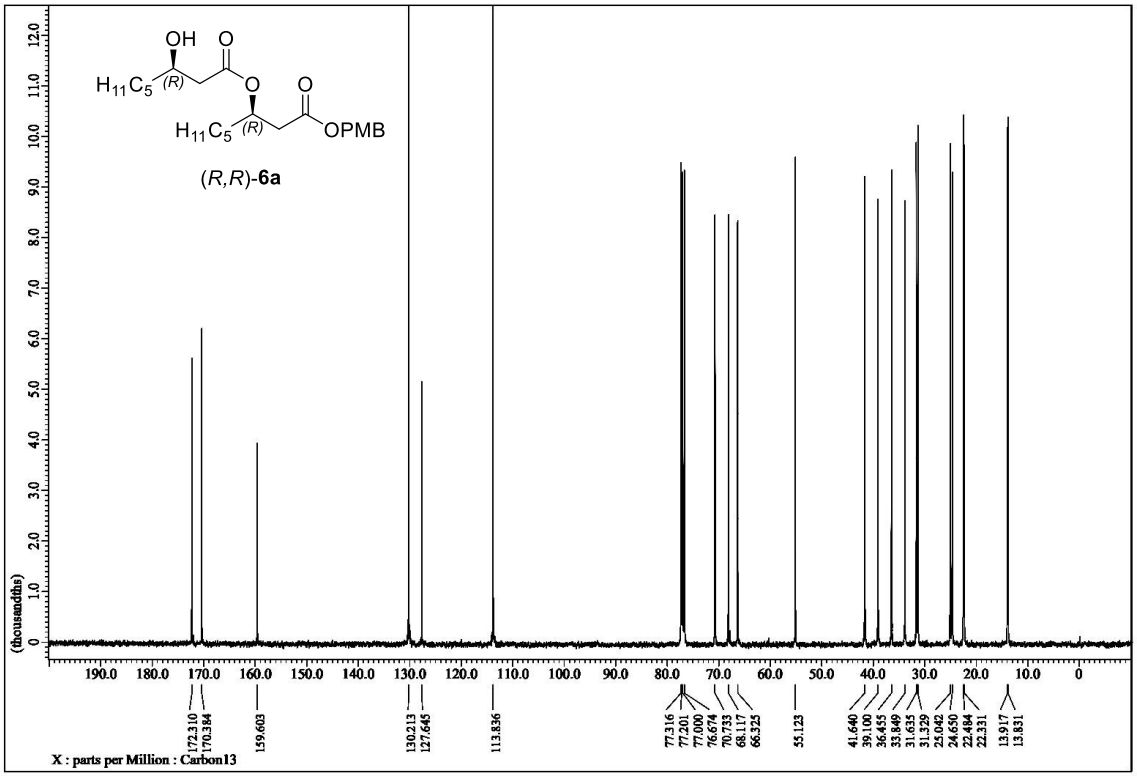

Fig. S22 ^{13}C-NMR spectrum of (*R,R*)-**6a** (100MHz, $CDCl_3$)

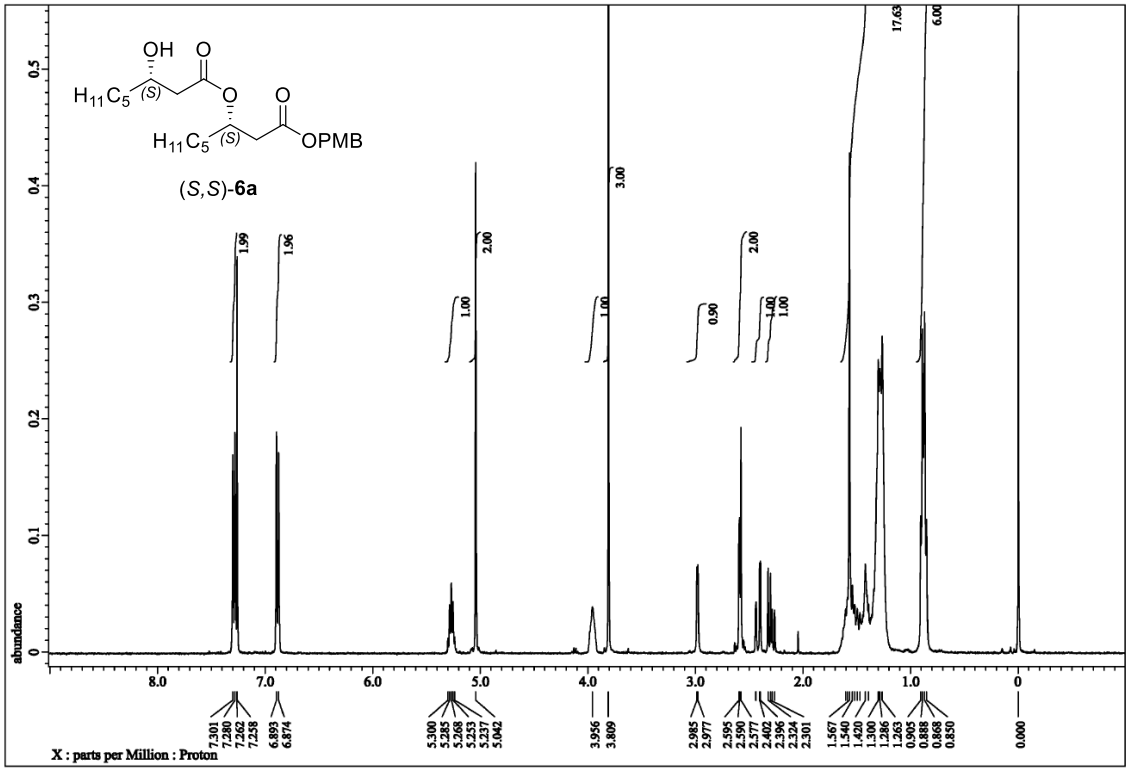

Fig. S23 ^{1}H-NMR spectrum of (*S,S*)-**6a** (400MHz, $CDCl_3$)

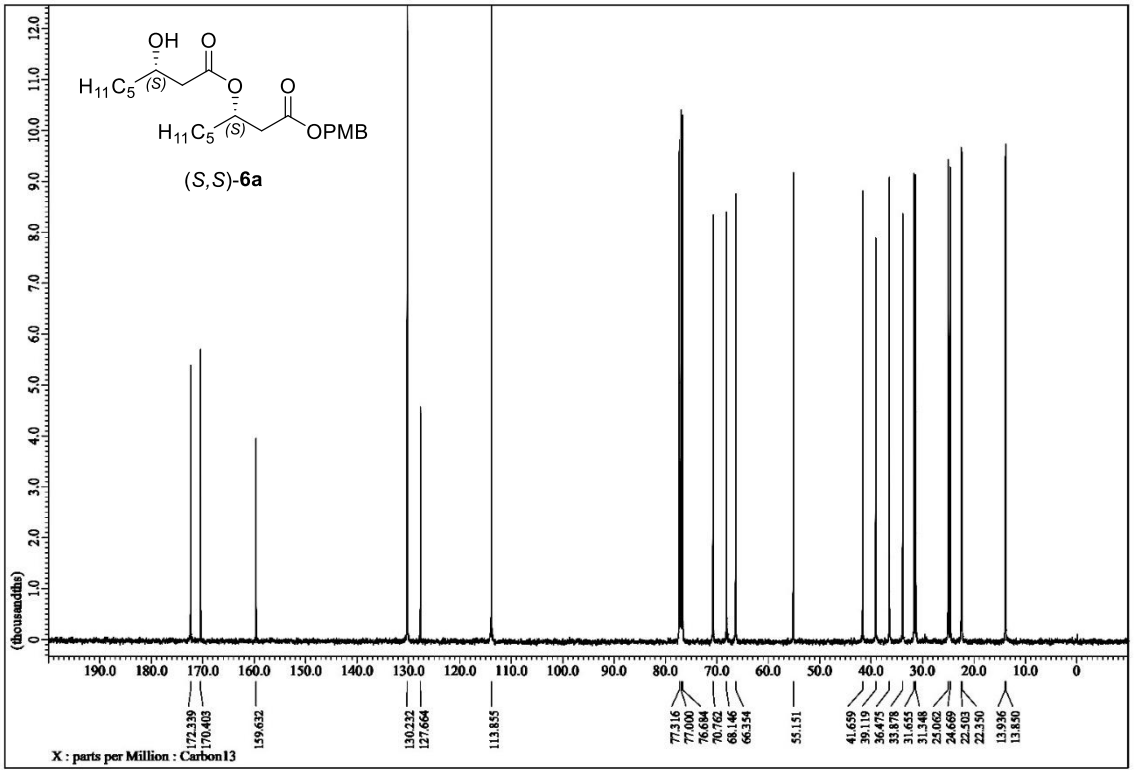

Fig. S24 ^{13}C-NMR spectrum of (*S,S*)-**6a** (100MHz, $CDCl_3$)

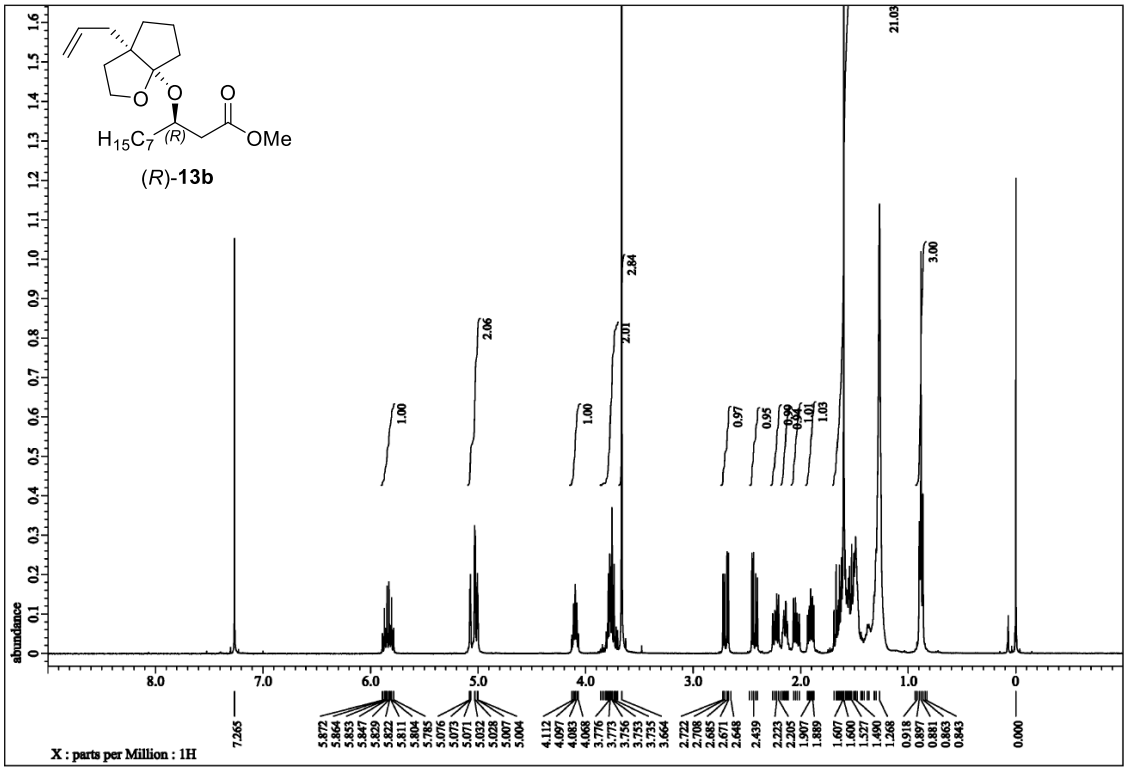

Fig. S25 ^{1}H-NMR spectrum of (*R*)-**13b** (400MHz, $CDCl_3$)

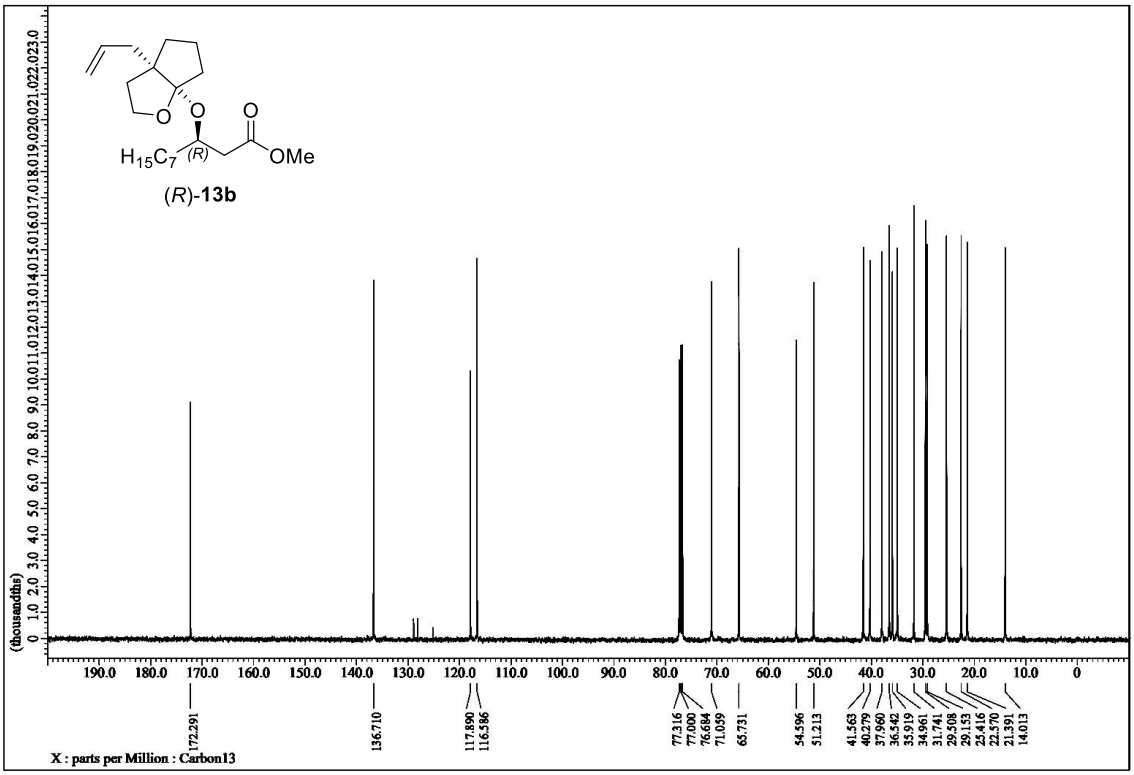

Fig. S26 ^{13}C-NMR spectrum of (*R*)-**13b** (100MHz, $CDCl_3$)

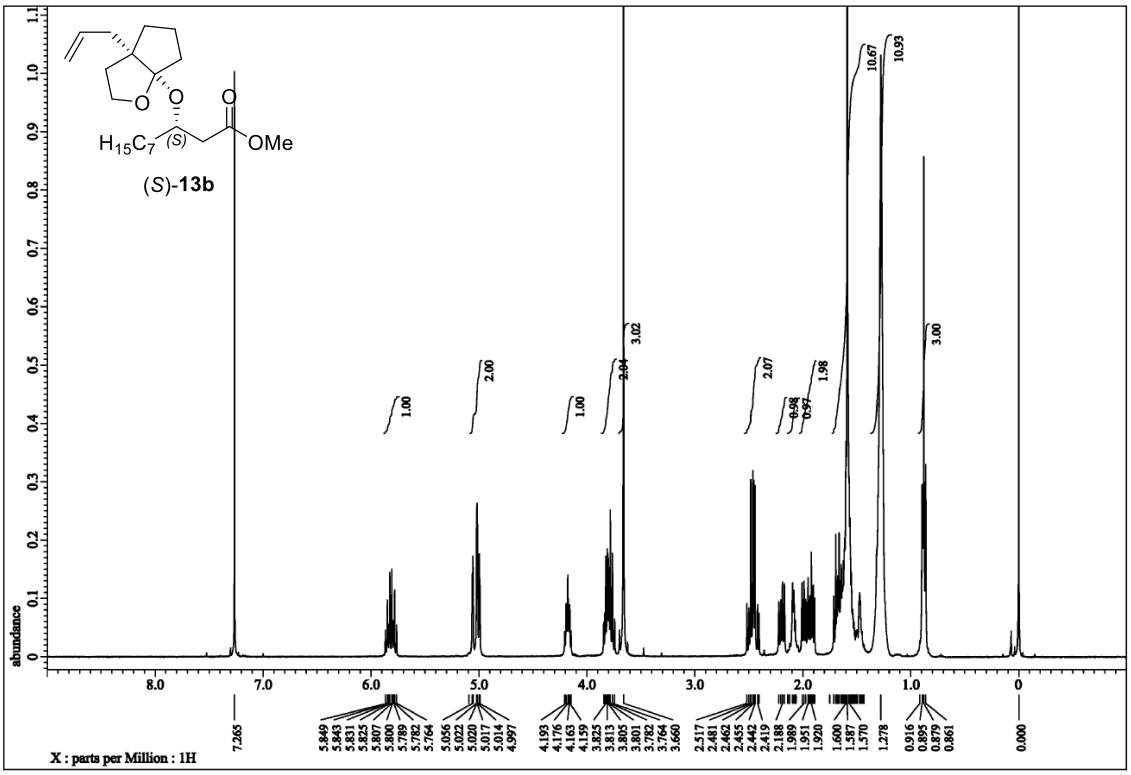

Fig. S27 ^{1}H-NMR spectrum of (*S*)-**13b** (400MHz, $CDCl_3$)

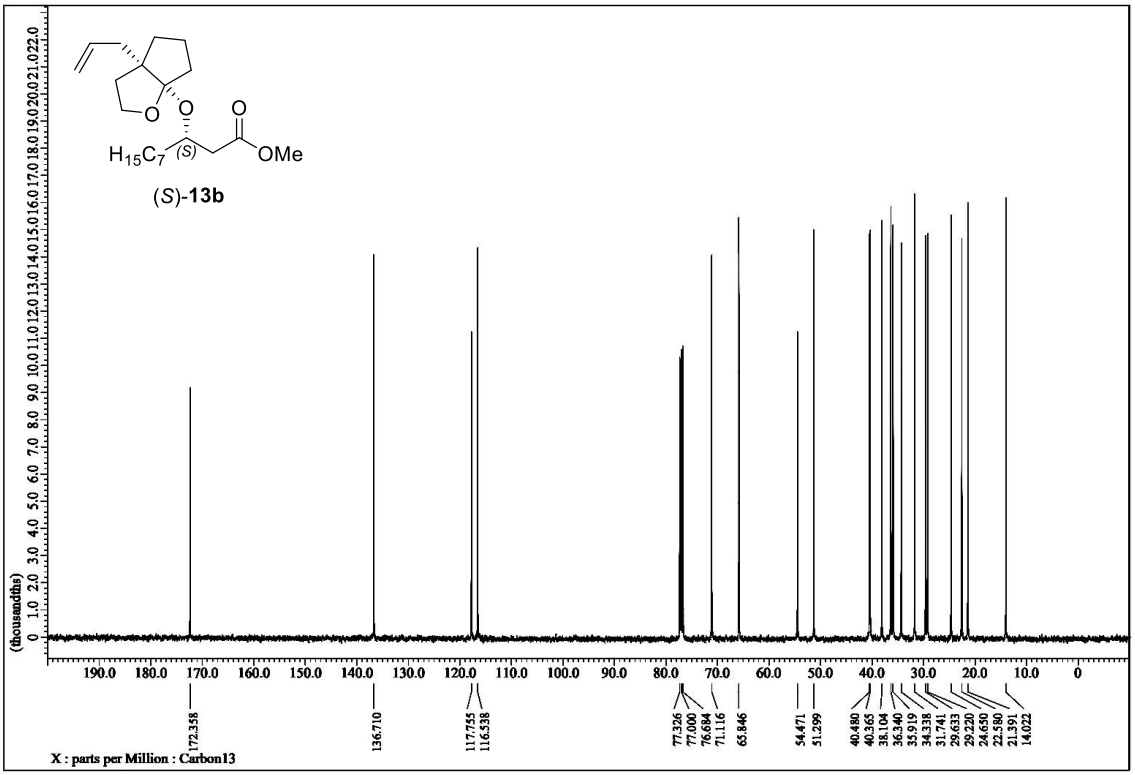

Fig. S28 ^{13}C-NMR spectrum of (*S*)-**13b** (100MHz, $CDCl_3$)

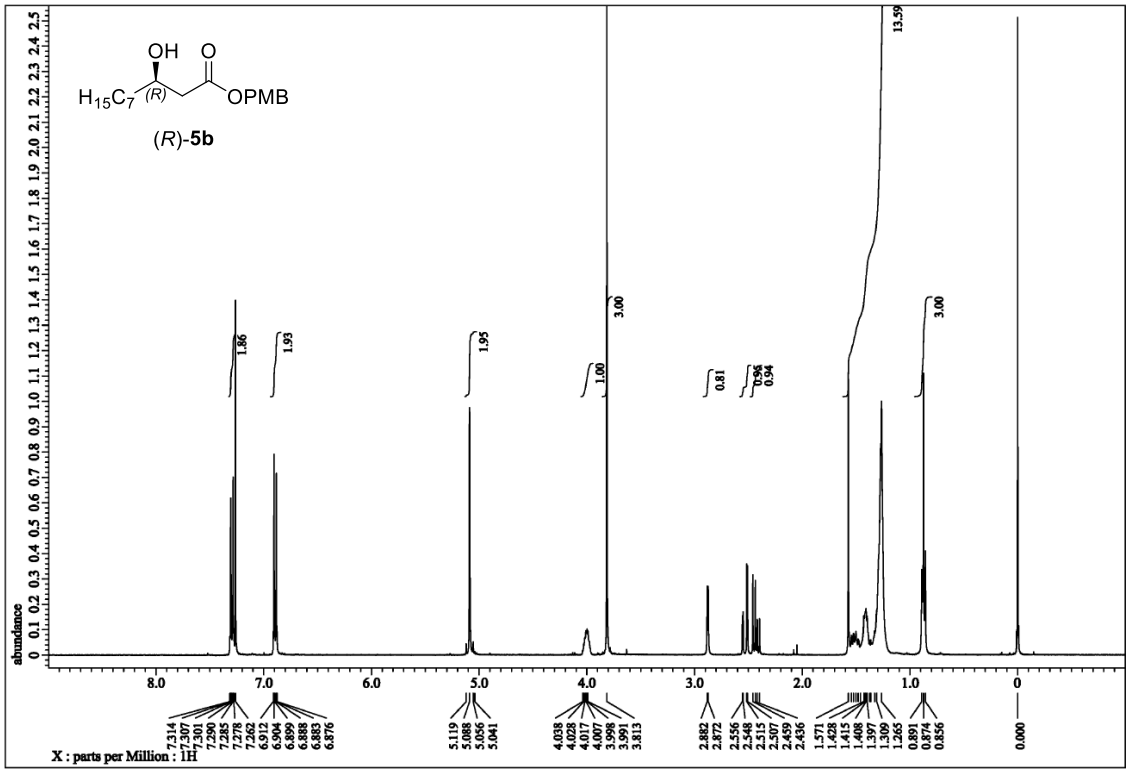

Fig. S29 ^{1}H-NMR spectrum of (*R*)-**5b** (400MHz, $CDCl_3$)

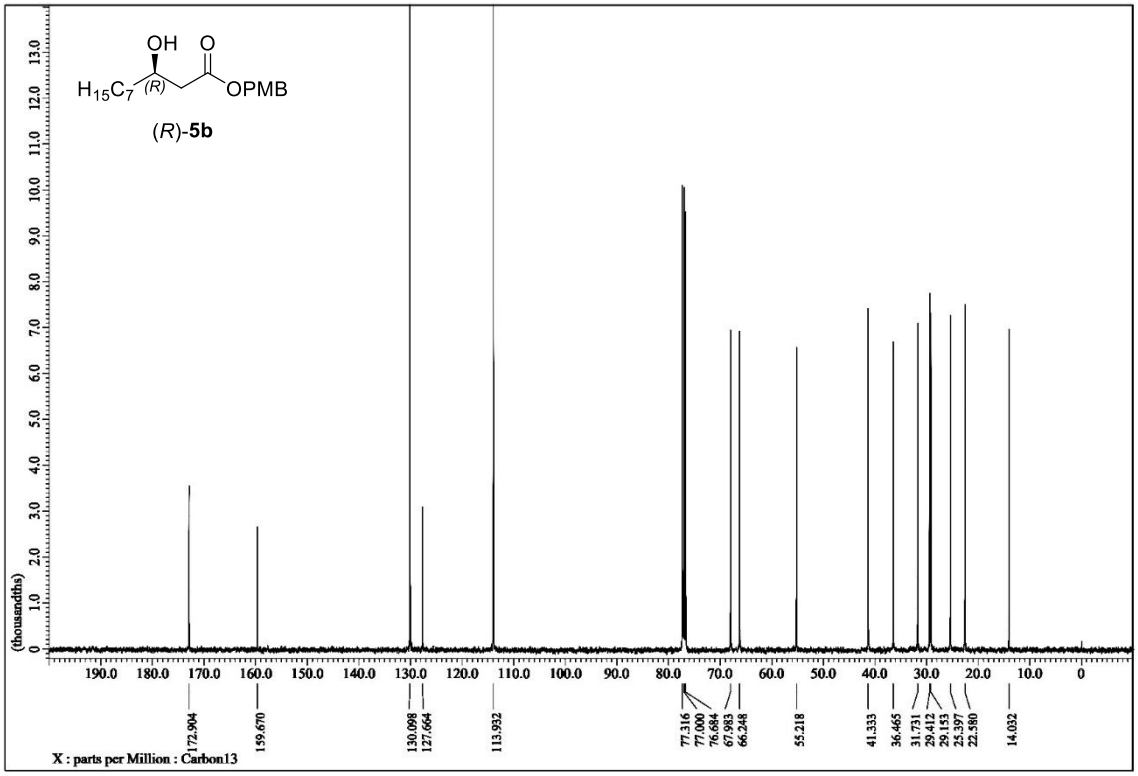

Fig. S30 ^{13}C-NMR spectrum of (*R*)-**5b** (100MHz, $CDCl_3$)

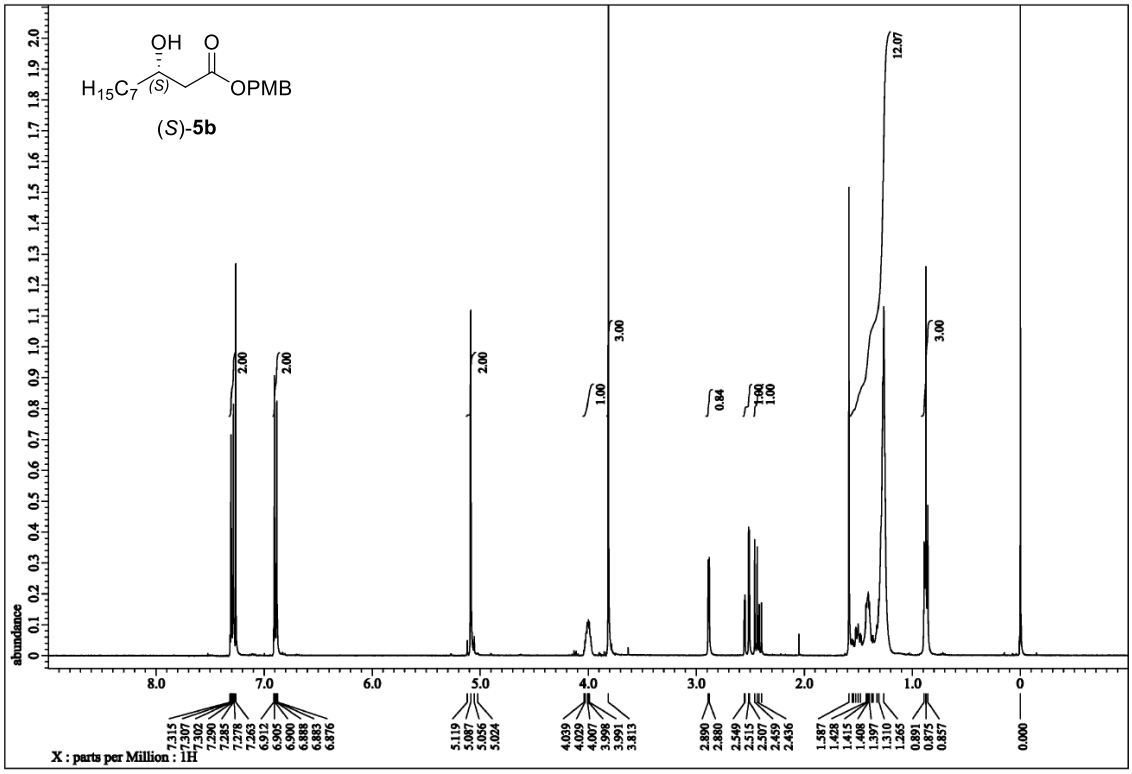

Fig. S31 ^{1}H-NMR spectrum of (*S*)-**5b** (400MHz, $CDCl_3$)

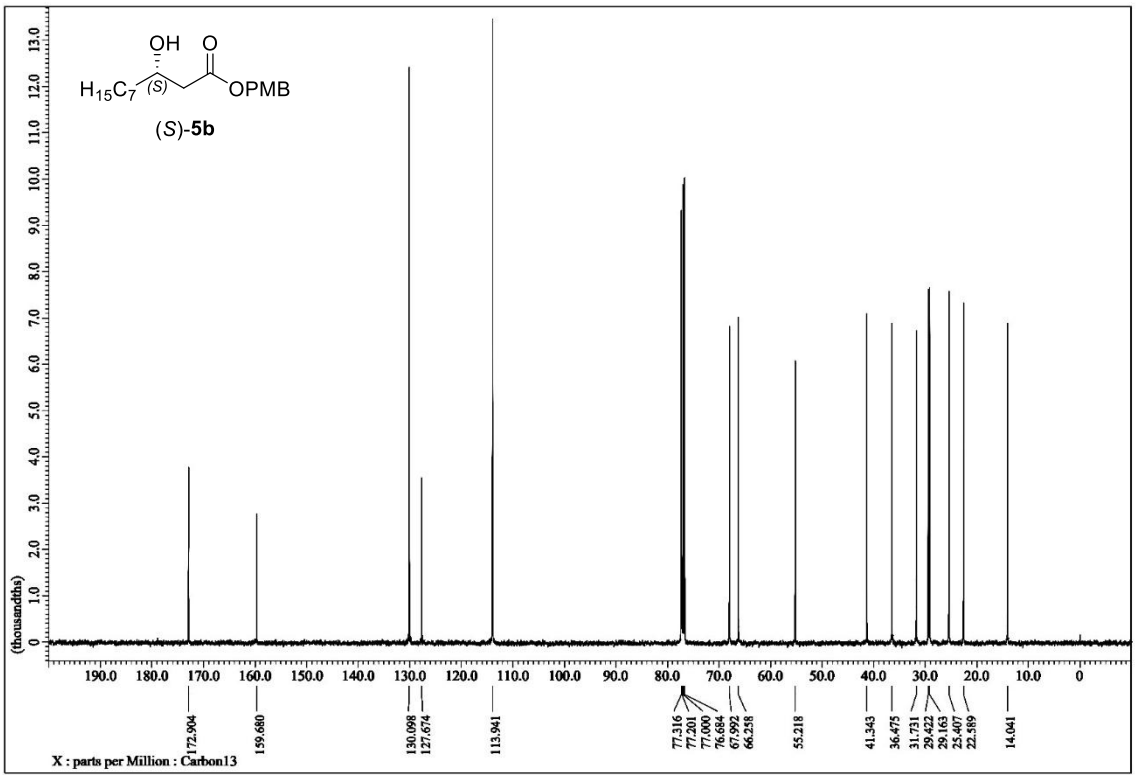

Fig. S32 ^{13}C-NMR spectrum of (*S*)-**5b** (100MHz, $CDCl_3$)

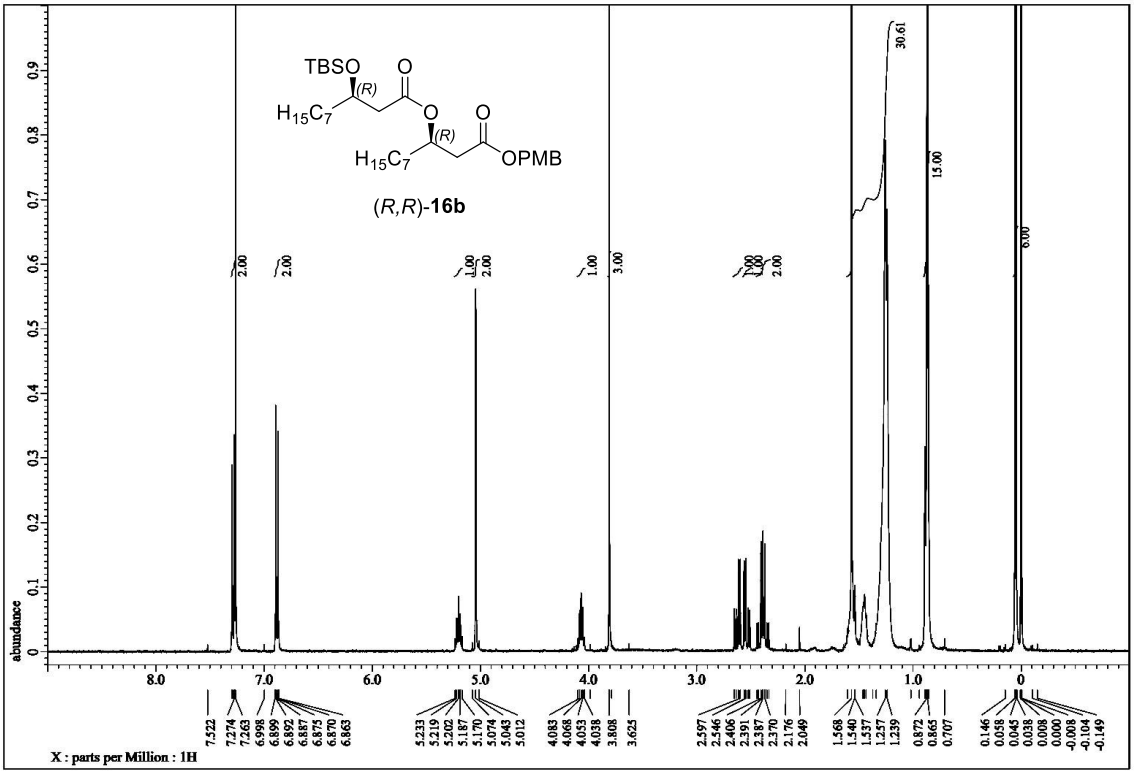

Fig. S33 ^{1}H-NMR spectrum of (*R,R*)-**16b** (400MHz, $CDCl_3$)

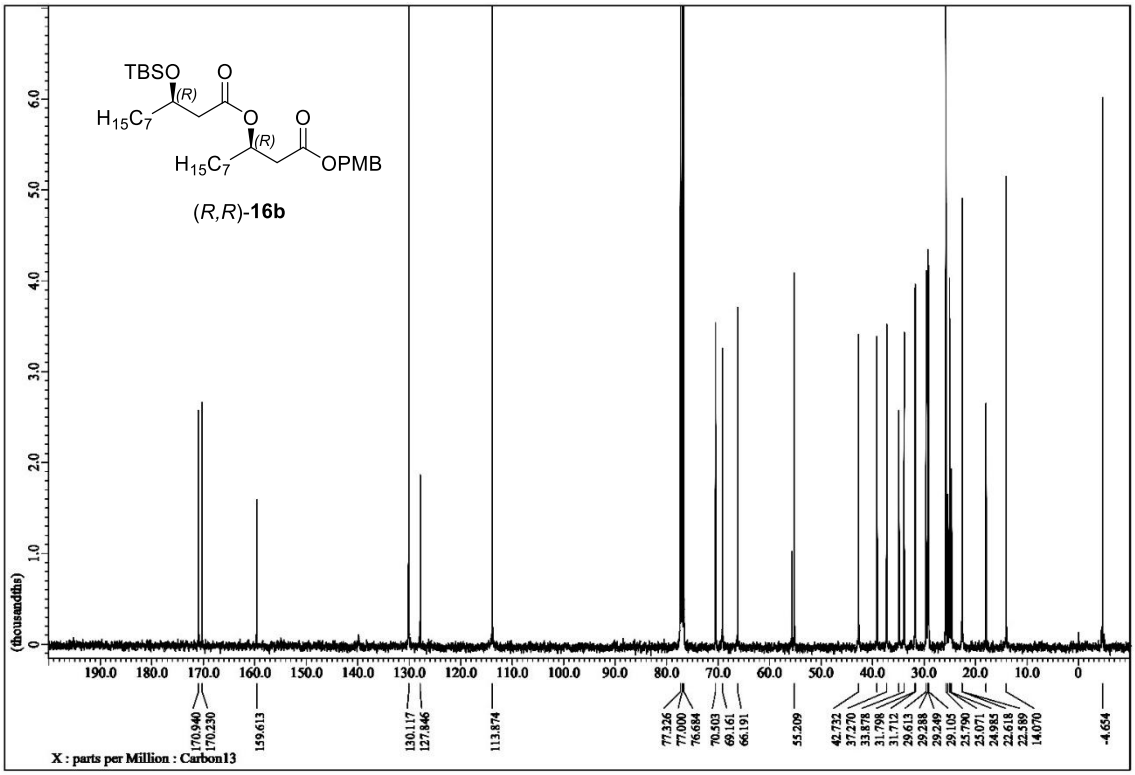

Fig. S34 ^{13}C-NMR spectrum of (*R,R*)-**16b** (100MHz, $CDCl_3$)

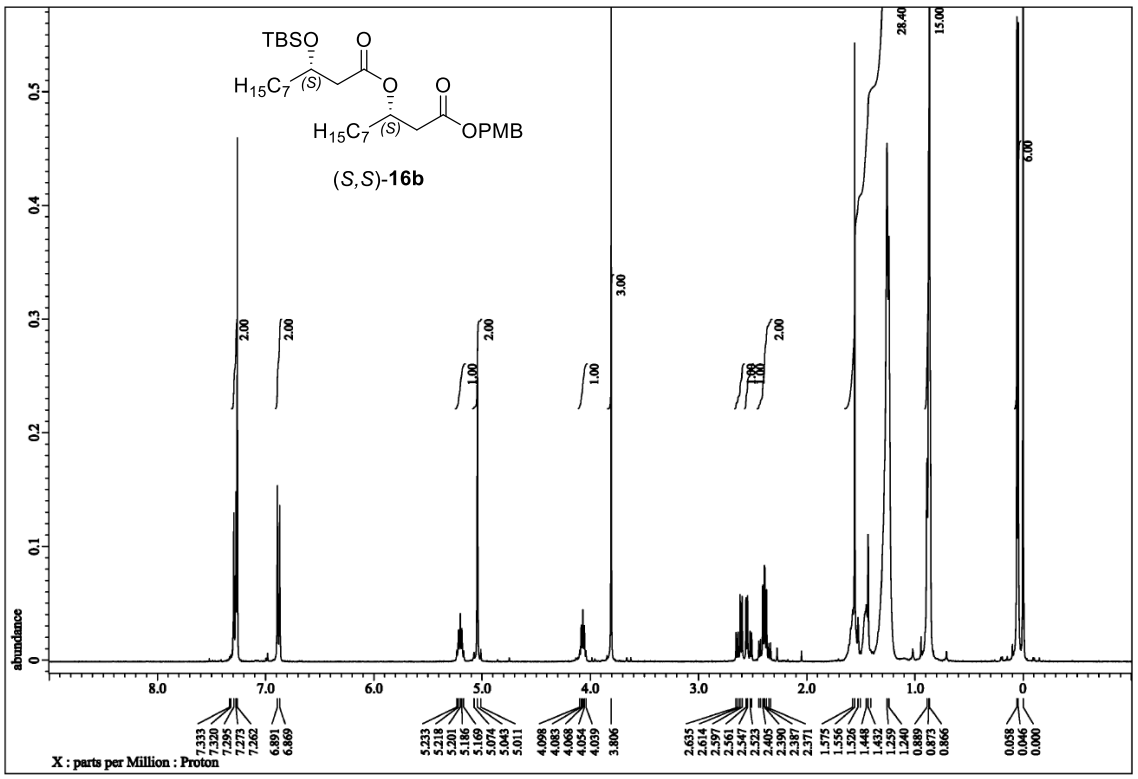

Fig. S35 ^{1}H-NMR spectrum of (*S,S*)-**16b** (400MHz, $CDCl_3$)

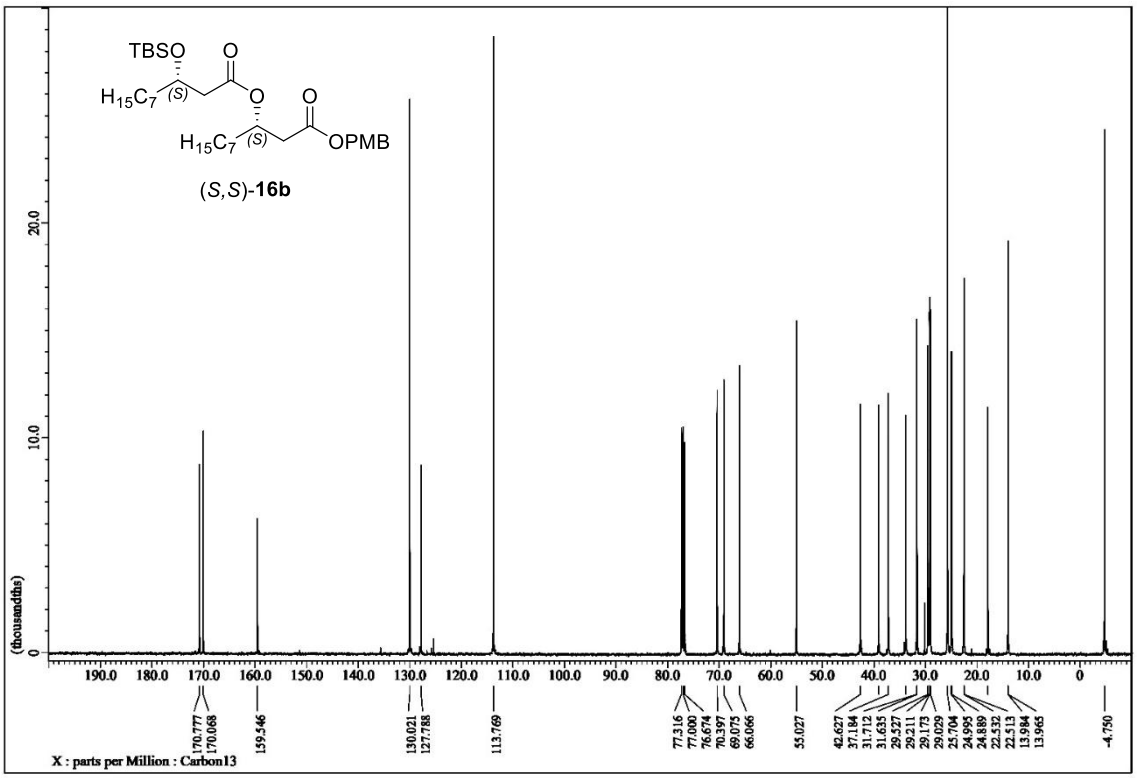

Fig. S36 ^{13}C-NMR spectrum of (*S,S*)-**16b** (100MHz, $CDCl_3$)

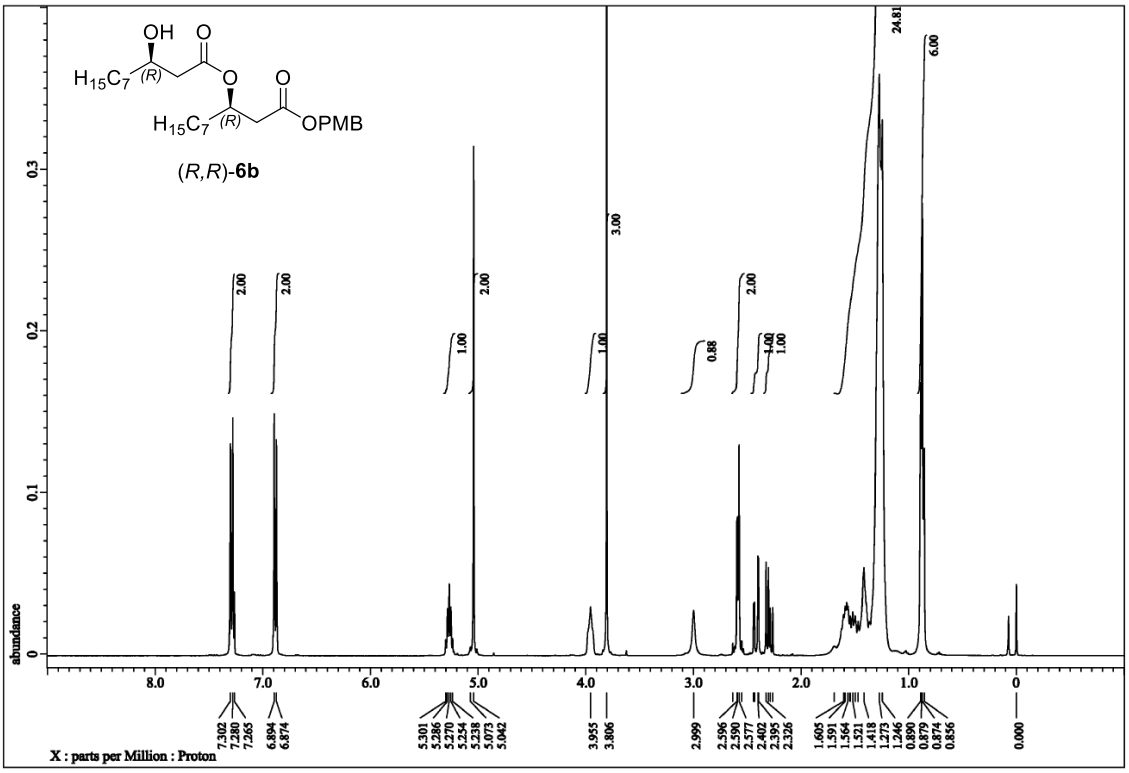

Fig. S37 ^{1}H-NMR spectrum of (*R,R*)-**6b** (400MHz, $CDCl_3$)

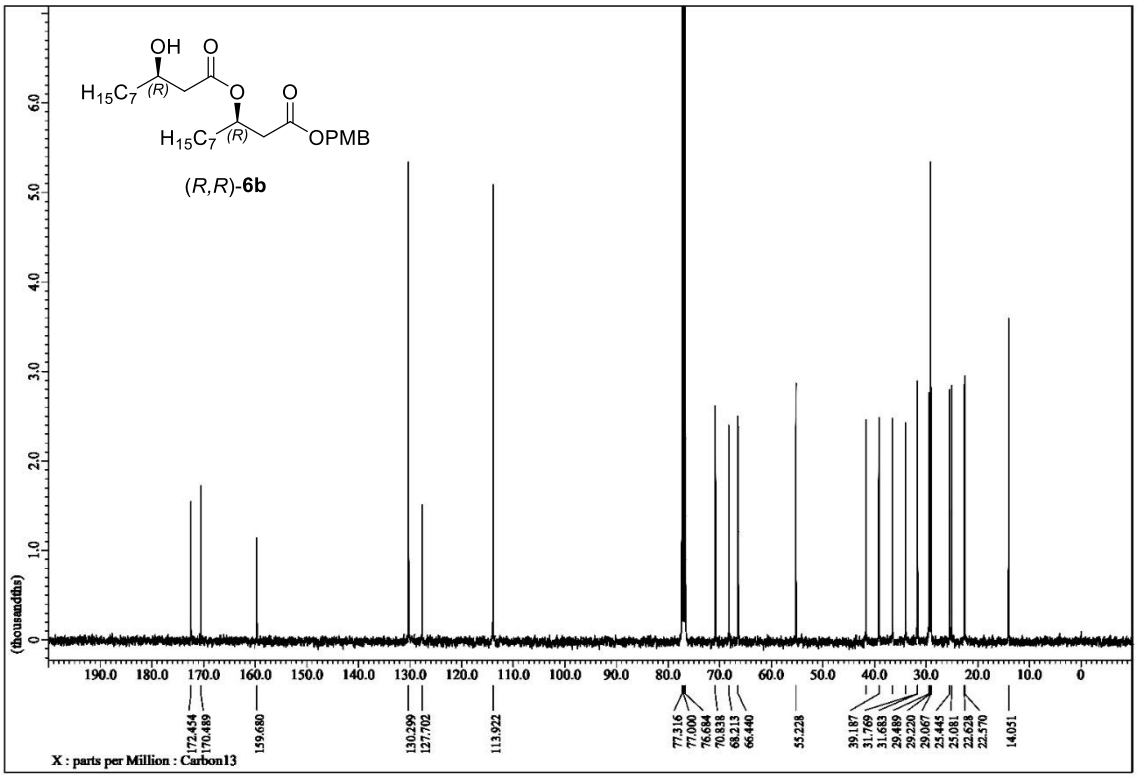

Fig. S38 ^{13}C-NMR spectrum of (*R,R*)-**6b** (100MHz, $CDCl_3$)

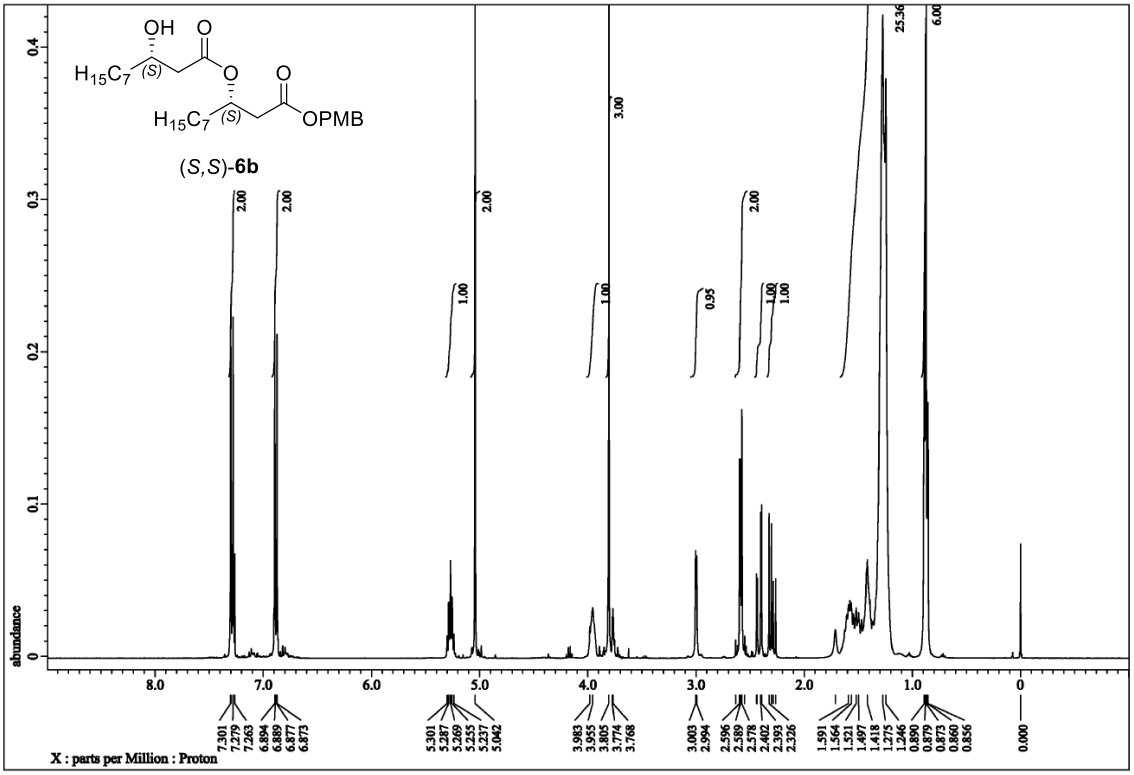

Fig. S39 ^{1}H-NMR spectrum of (*S,S*)-**6b** (400MHz, $CDCl_3$)

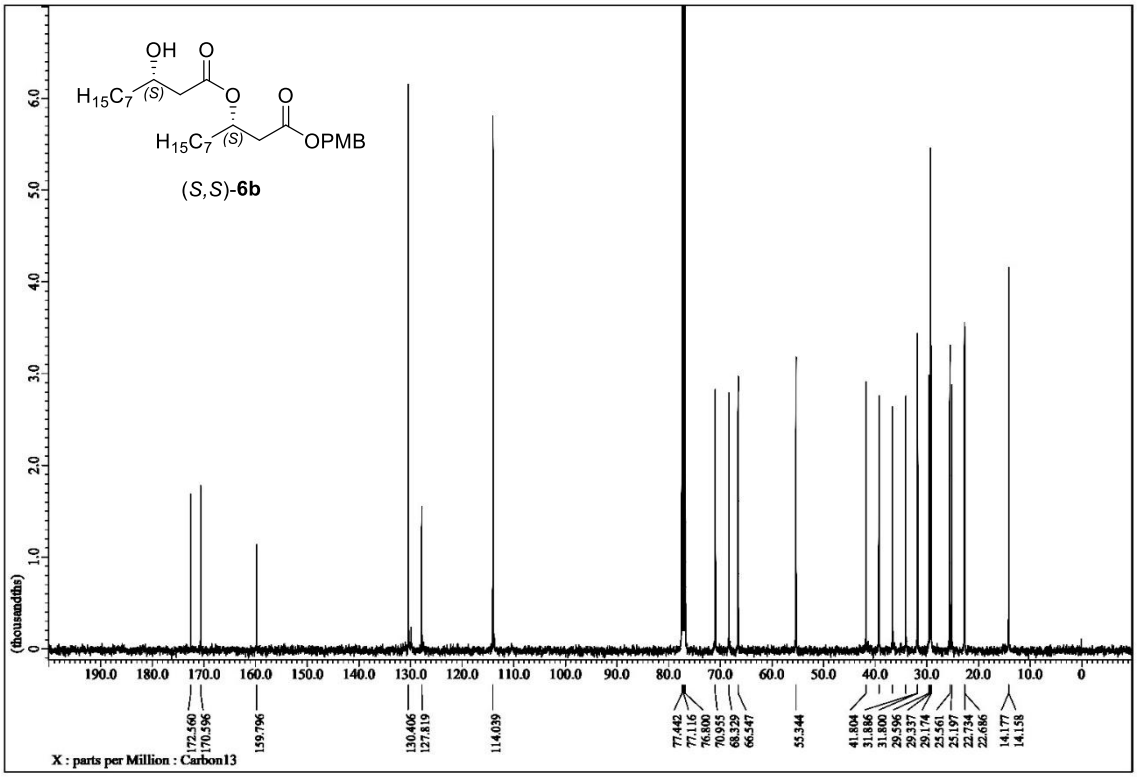

Fig. S40 ^{13}C-NMR spectrum of (*S,S*)-**6b** (100MHz, $CDCl_3$)

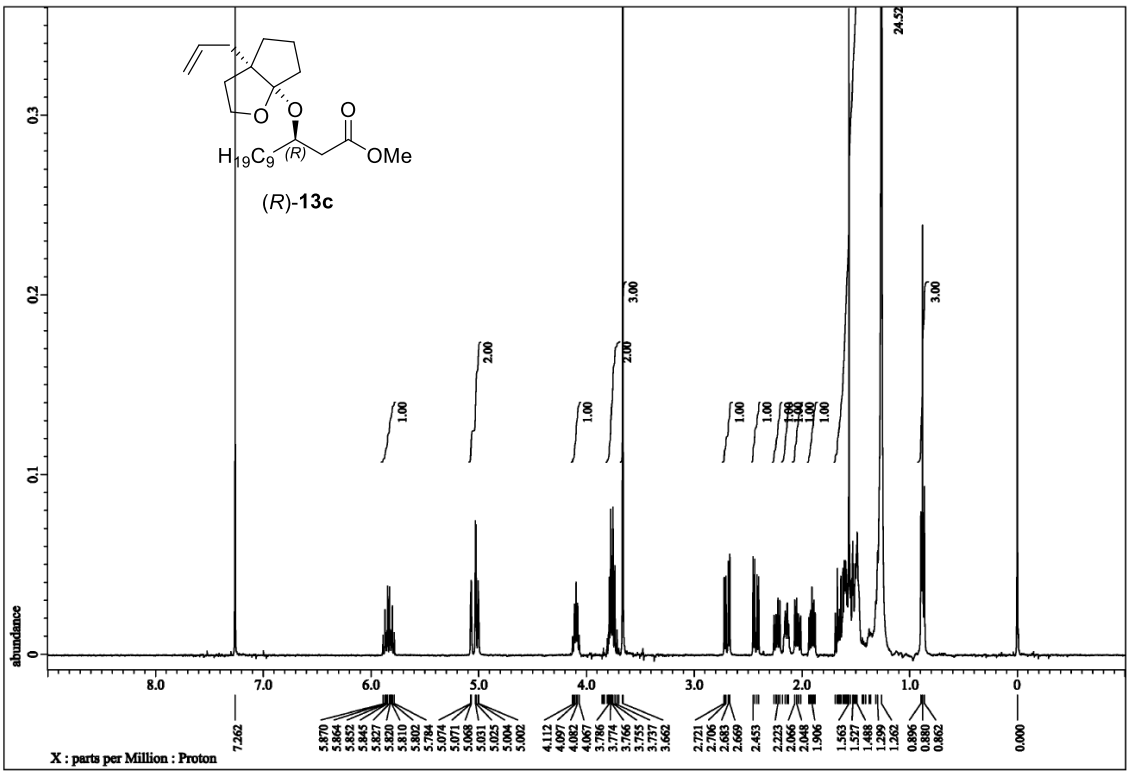

Fig. S41 ^{1}H-NMR spectrum of (*R*)-**13c** (400MHz, $CDCl_3$)

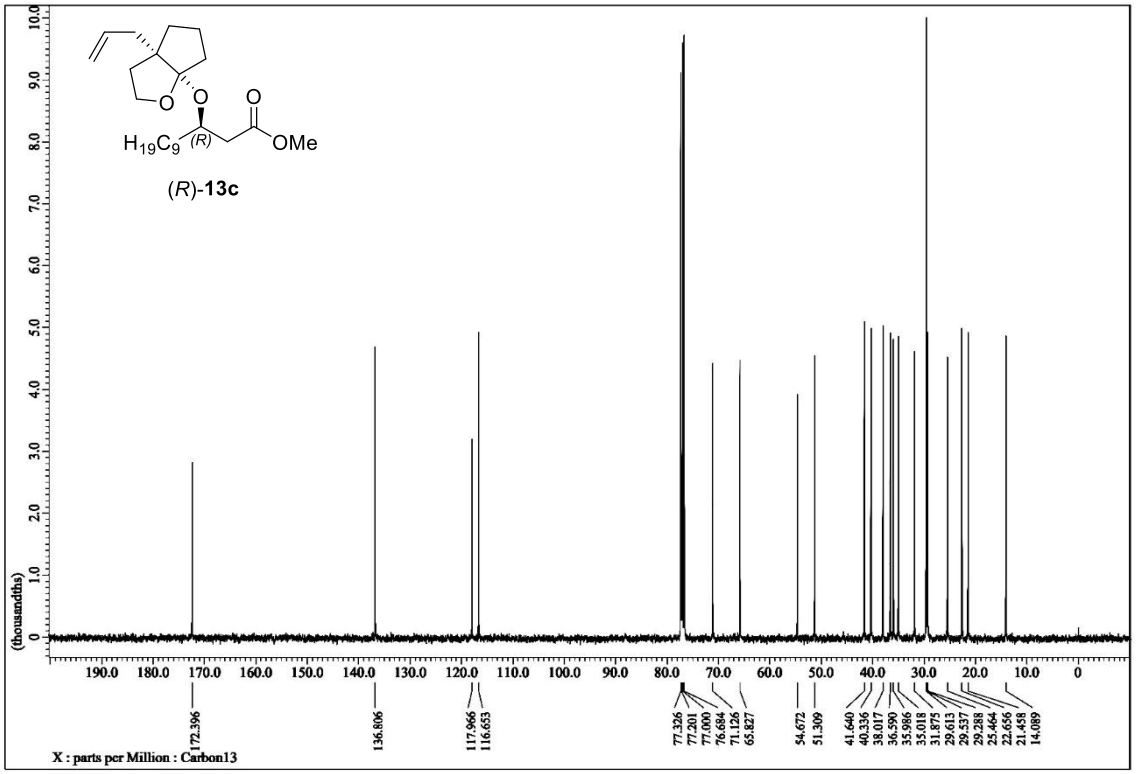

Fig. S42 ^{13}C-NMR spectrum of (*R*)-**13c** (100MHz, $CDCl_3$)

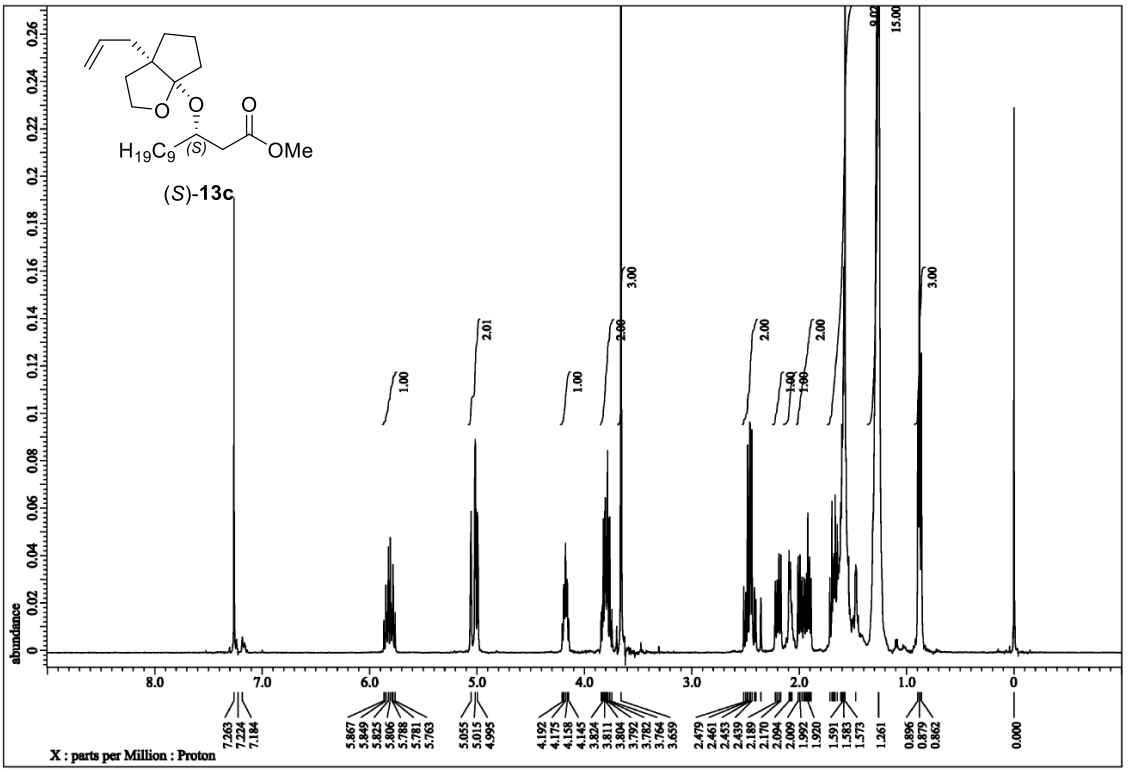

Fig. S43 ^{1}H-NMR spectrum of (*S*)-**13c** (400MHz, $CDCl_3$)

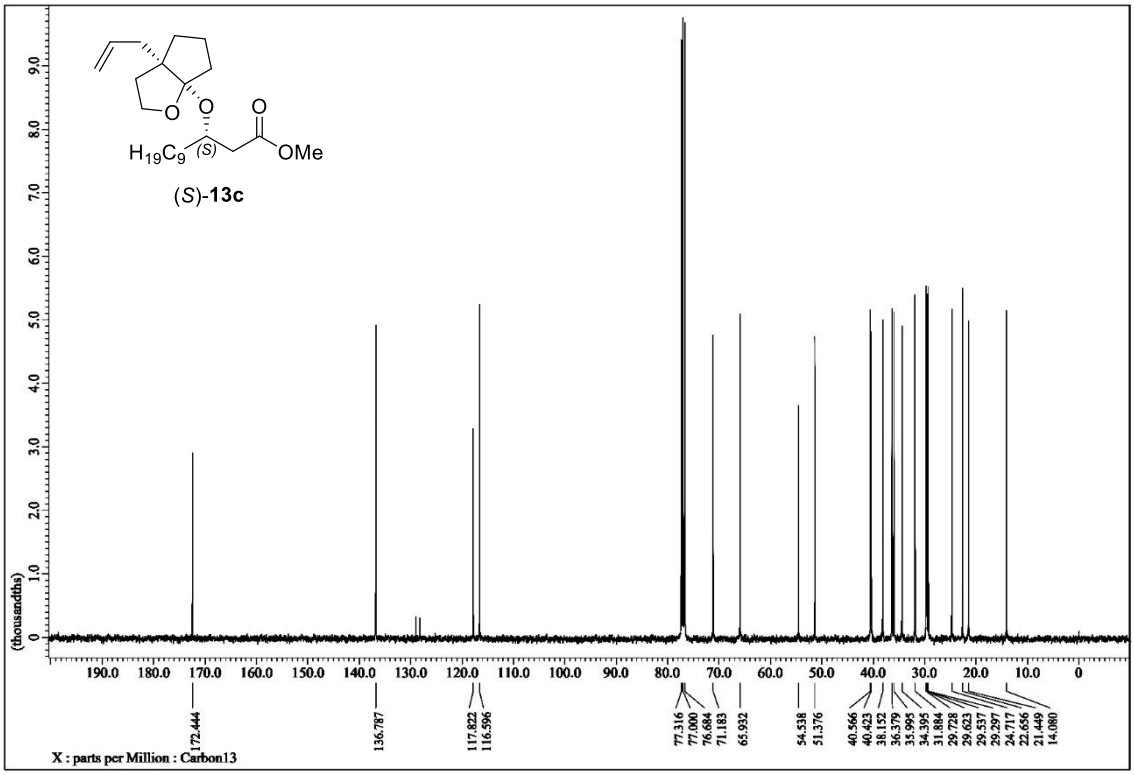

Fig. S44 ^{13}C-NMR spectrum of (*S*)-**13c** (100MHz, $CDCl_3$)

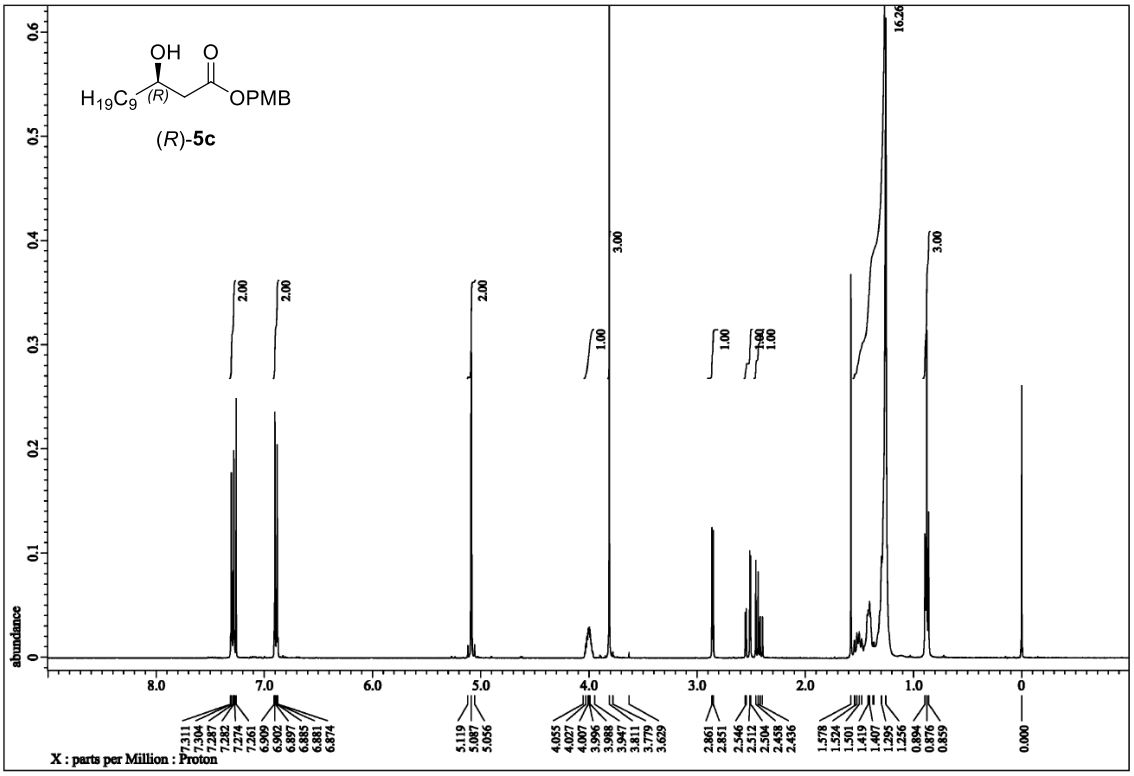

Fig. S45 ^{1}H-NMR spectrum of (*R*)-**5c** (400MHz, $CDCl_3$)

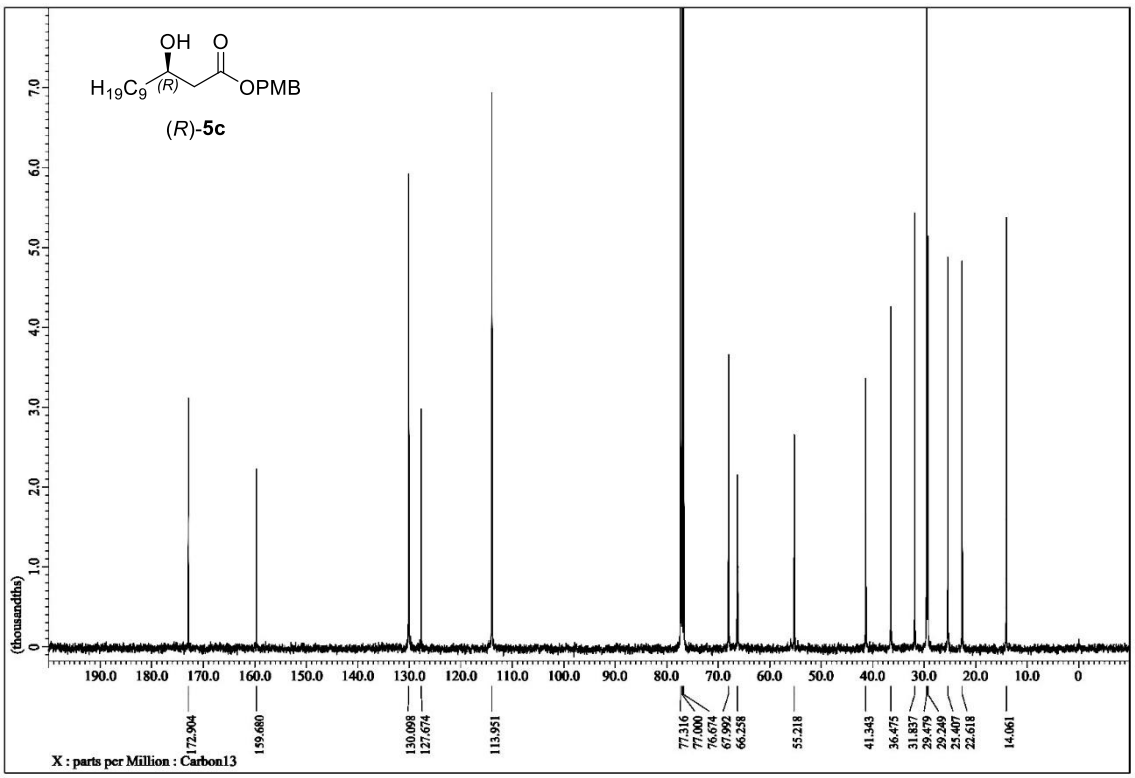

Fig. S46 ^{13}C-NMR spectrum of (*R*)-**5c** (100MHz, $CDCl_3$)

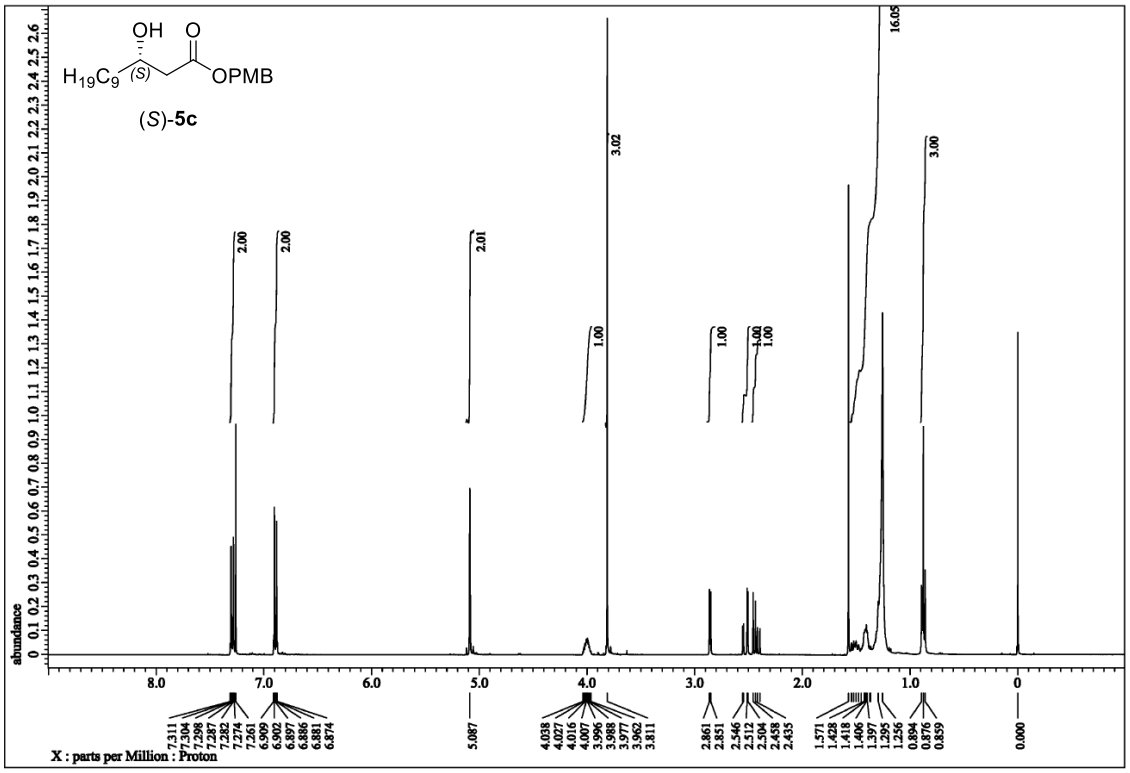

Fig. S47 ^{1}H-NMR spectrum of (*S*)-**5c** (400MHz, $CDCl_3$)

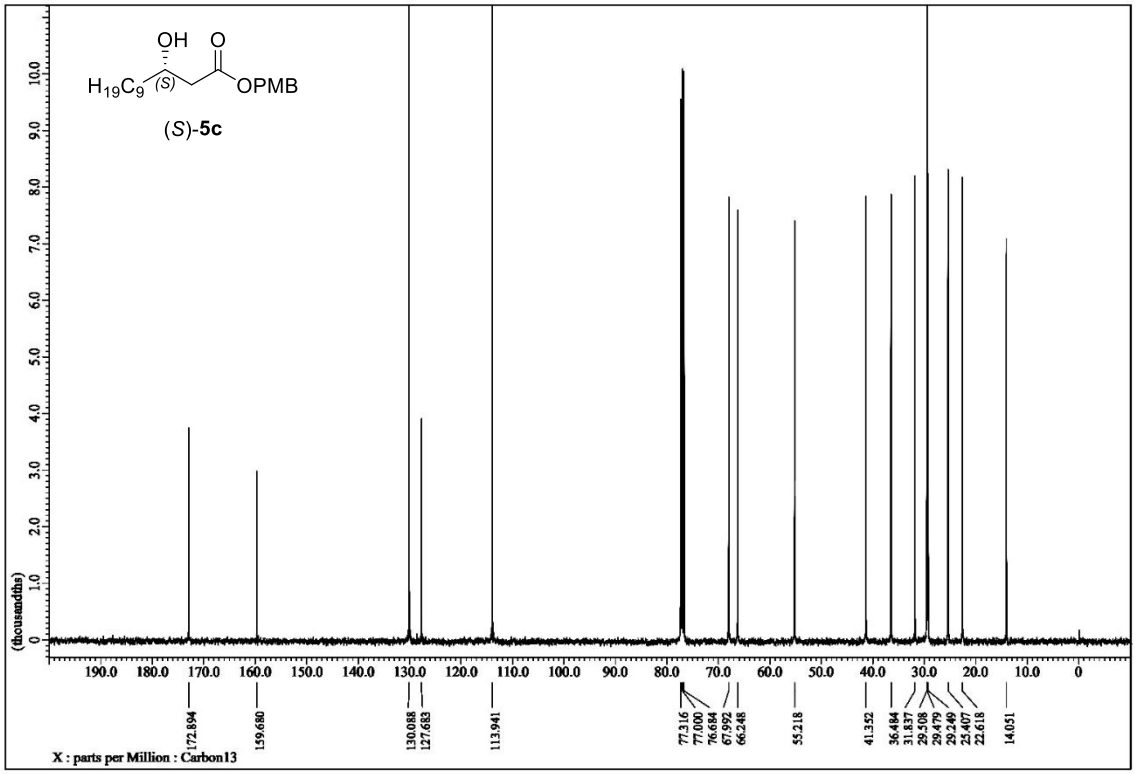

Fig. S48 ^{13}C-NMR spectrum of (*S*)-**5c** (100MHz, $CDCl_3$)

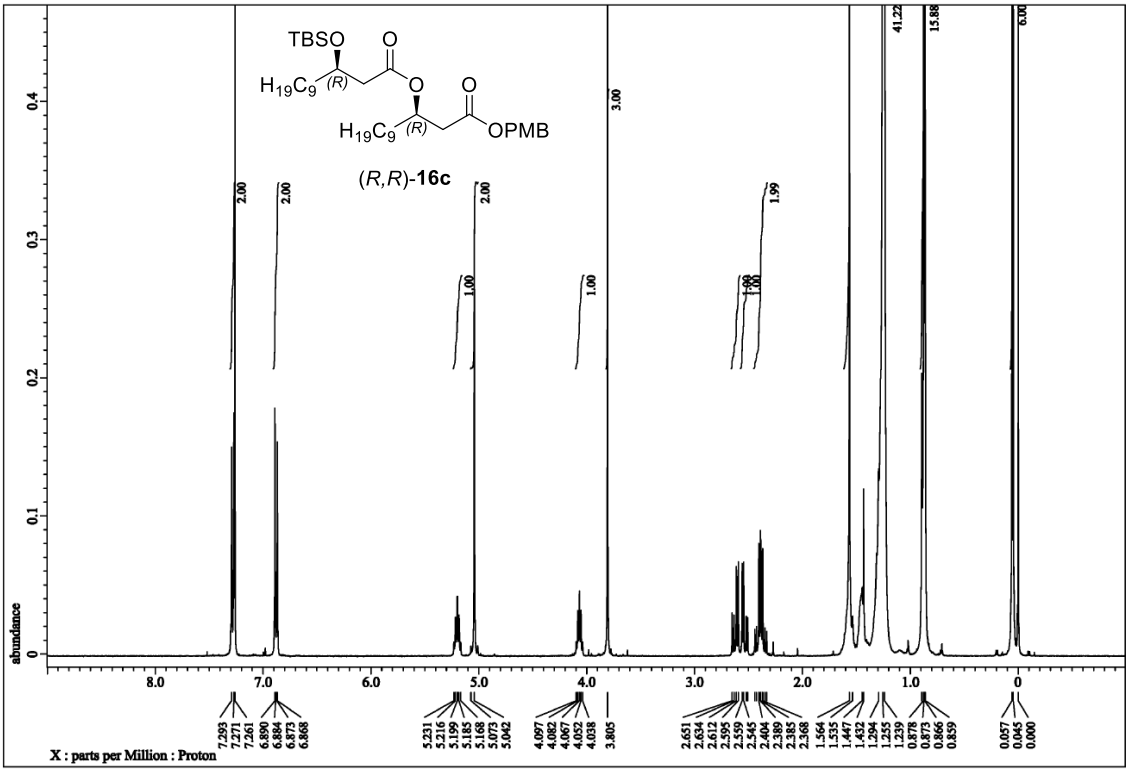

Fig. S49 ^{1}H-NMR spectrum of (*R,R*)-**16c** (400MHz, $CDCl_3$)

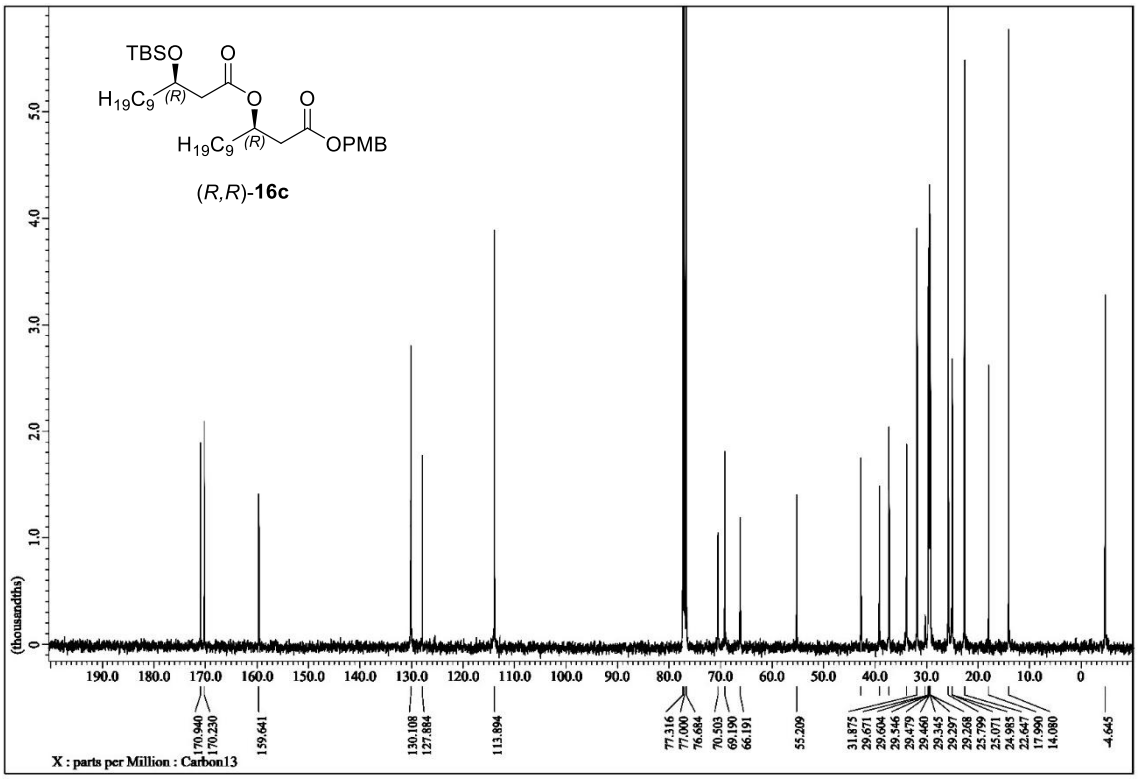

Fig. S50 ^{13}C-NMR spectrum of (*R,R*)-**16c** (100MHz, $CDCl_3$)

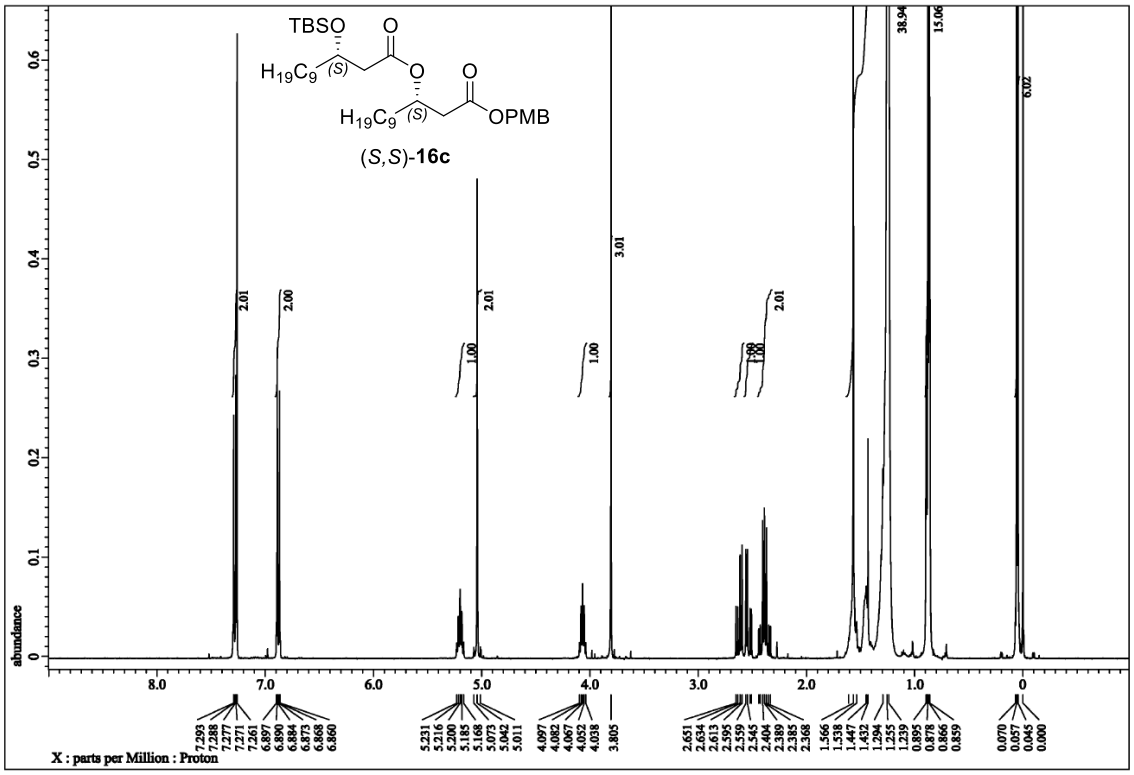

Fig. S51 ^{1}H-NMR spectrum of (*S,S*)-**16c** (400MHz, $CDCl_3$)

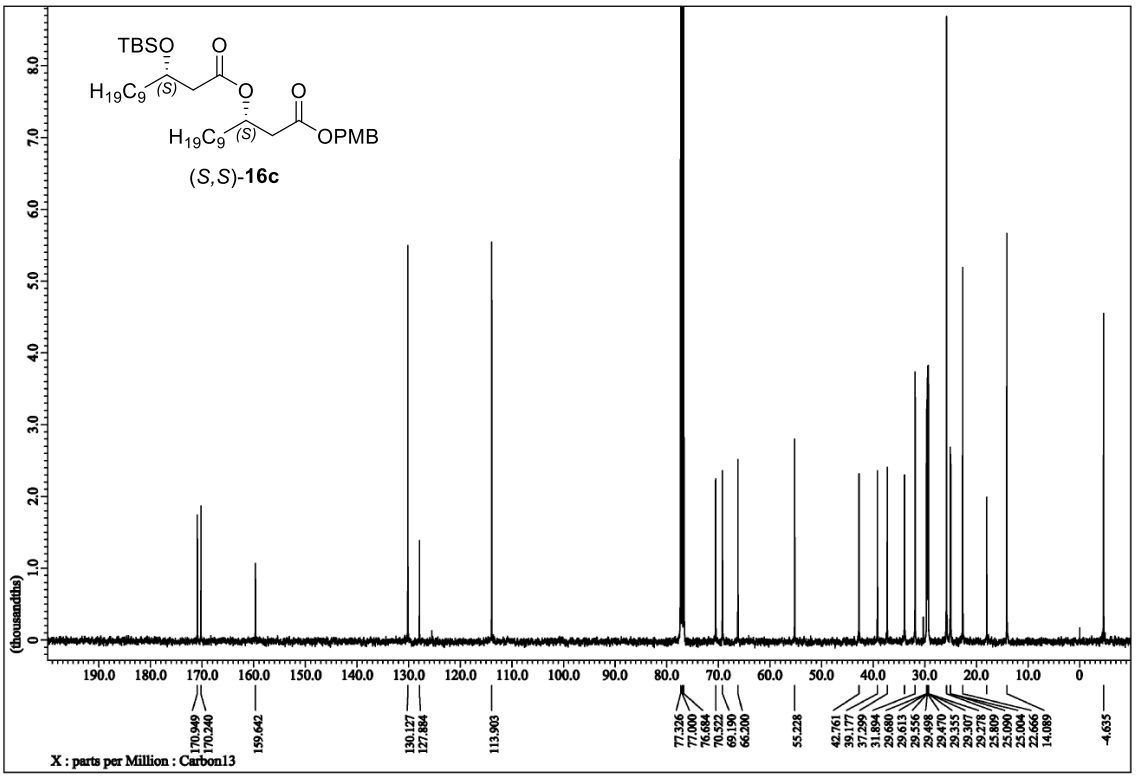

Fig. S52 ^{13}C-NMR spectrum of (*S,S*)-**16c** (100MHz, $CDCl_3$)

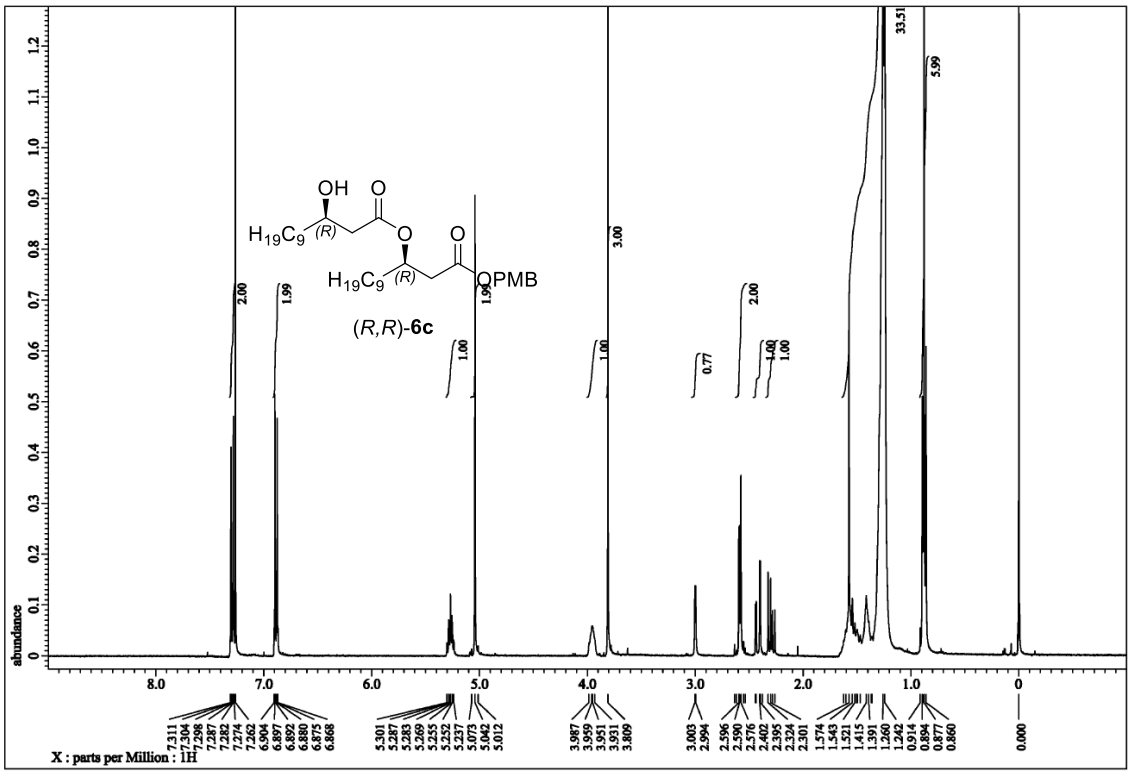

Fig. S53 ^{1}H-NMR spectrum of (*R,R*)-**6c** (400MHz, $CDCl_3$)

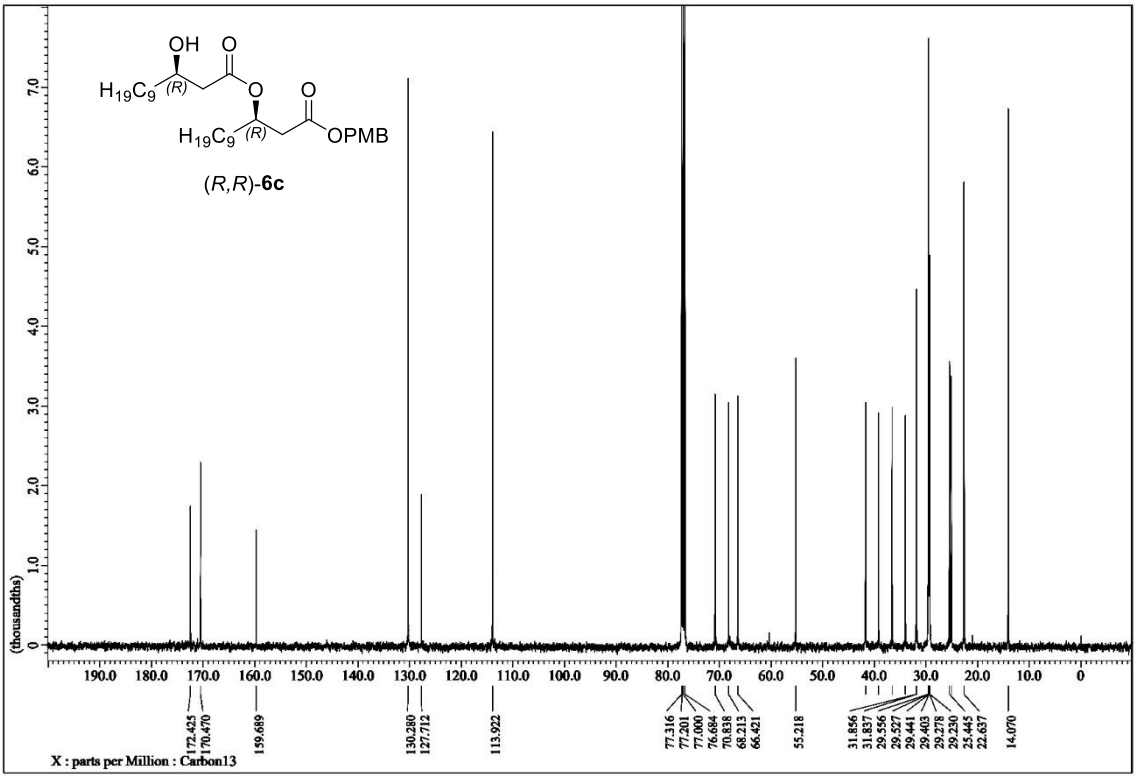

Fig. S54 ^{13}C-NMR spectrum of (*R,R*)-**6c** (100MHz, $CDCl_3$)

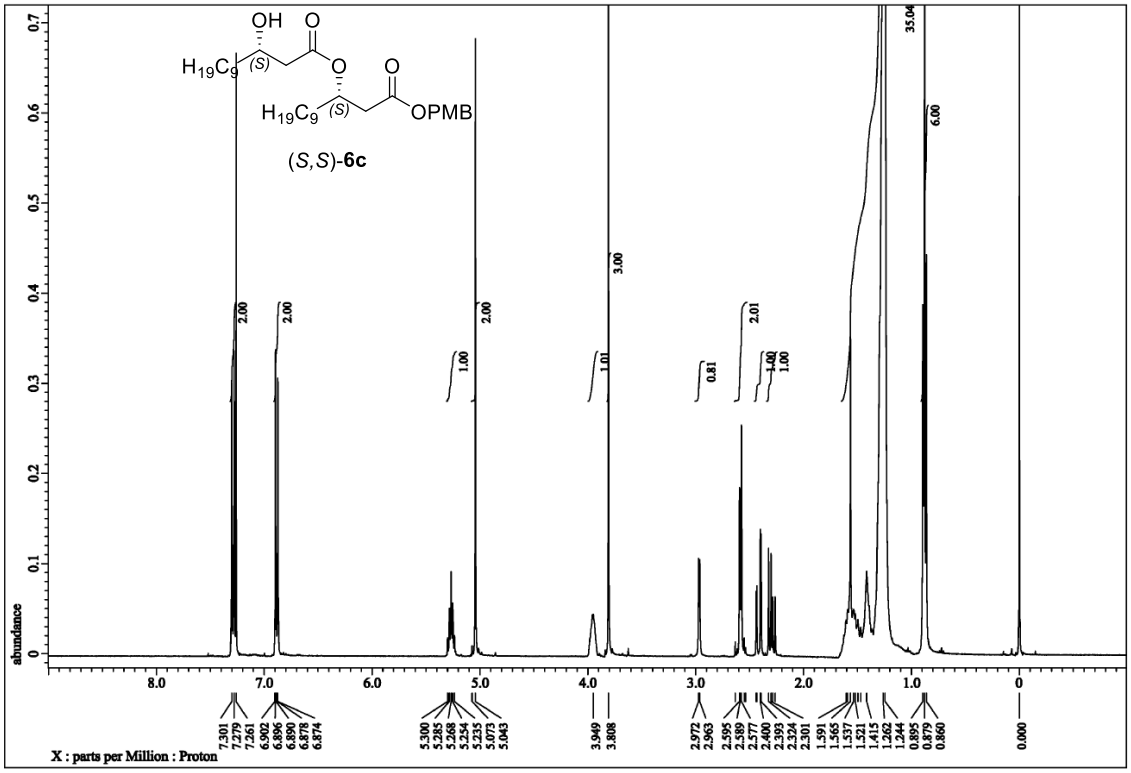

Fig. S55 ^{1}H-NMR spectrum of (*S,S*)-**6c** (400MHz, $CDCl_3$)

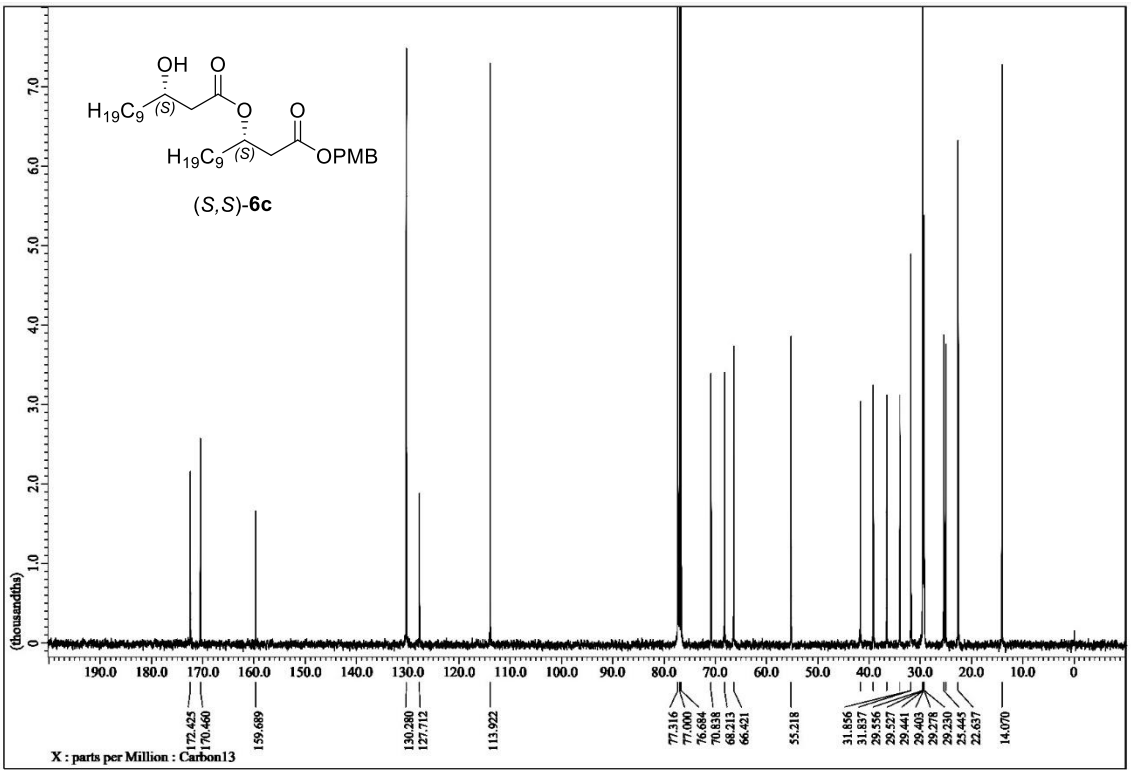

Fig. S56 ^{13}C-NMR spectrum of (*S,S*)-**6c** (100MHz, $CDCl_3$)

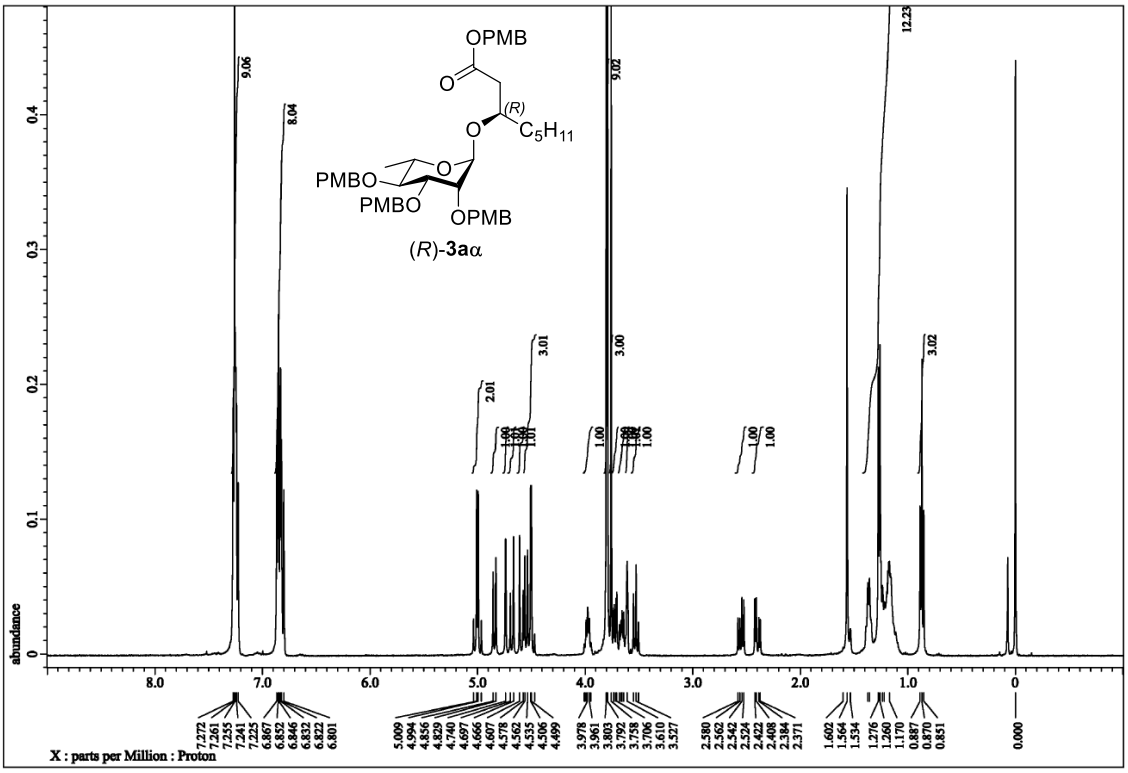

Fig. S57 ^{1}H-NMR spectrum of (*R*)-**3aα** (400MHz, $CDCl_3$)

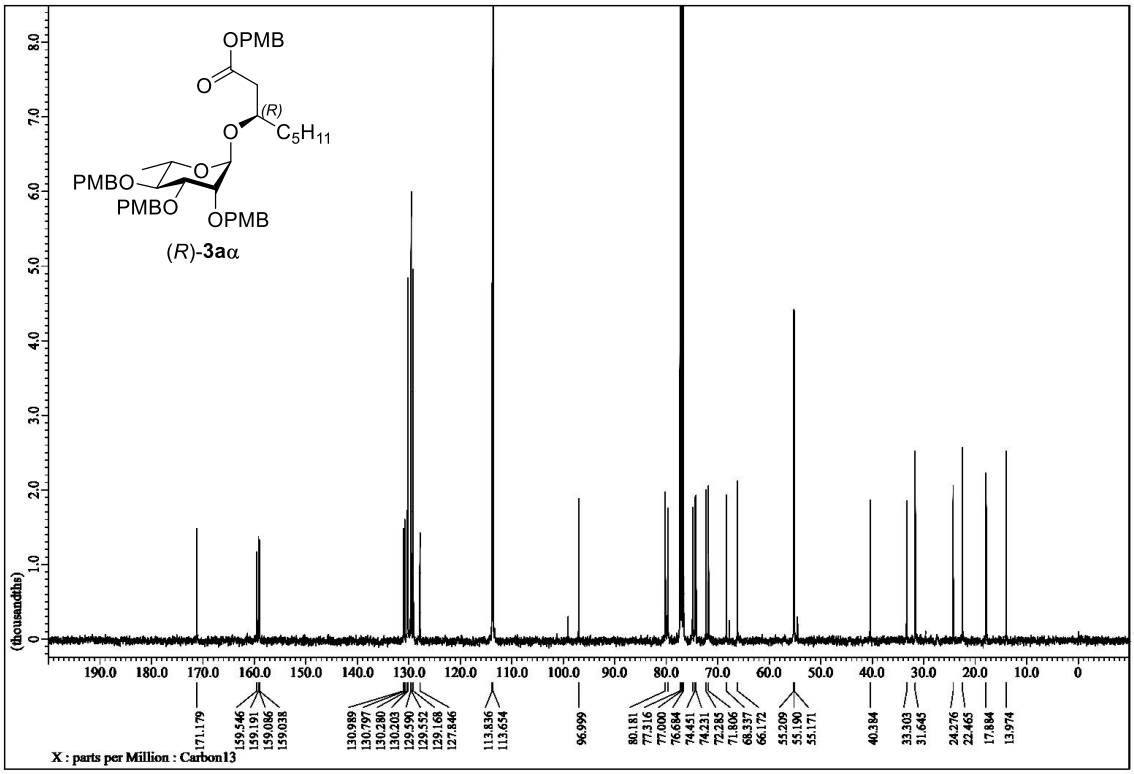

Fig. S58 ^{13}C-NMR spectrum of (*R*)-**3aα** (100MHz, $CDCl_3$)

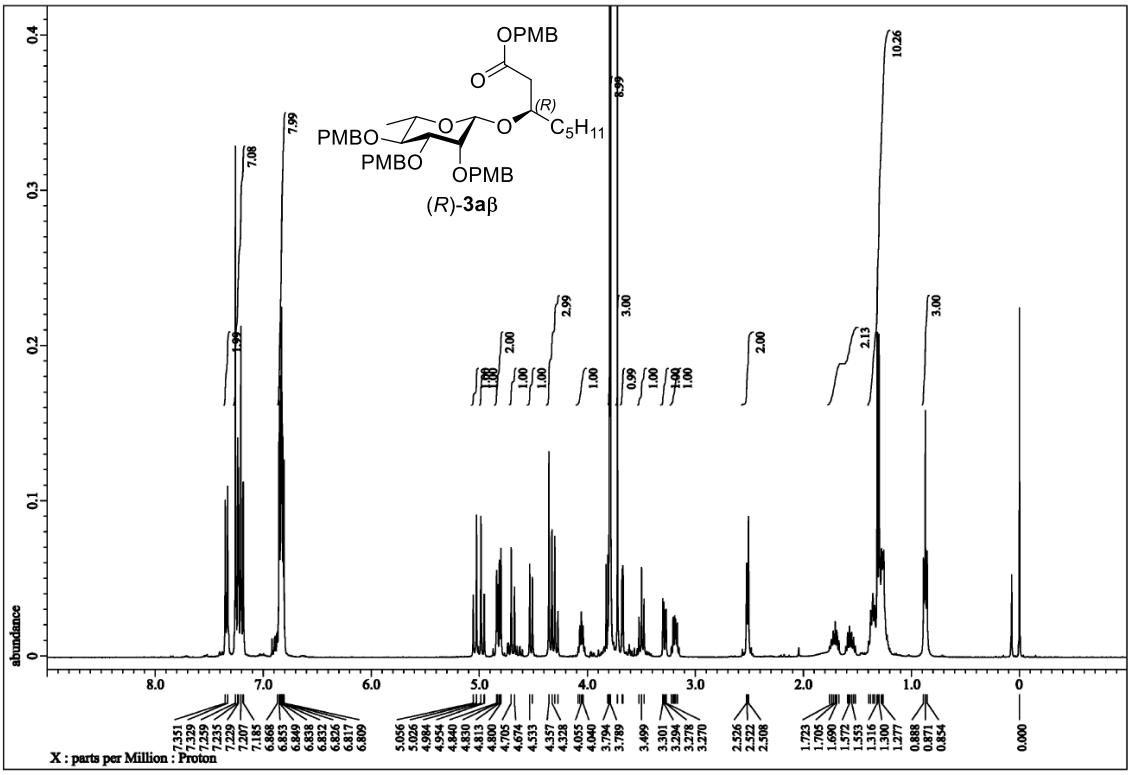

Fig. S59 ^{1}H-NMR spectrum of (*R*)-**3aβ** (400MHz, $CDCl_3$)

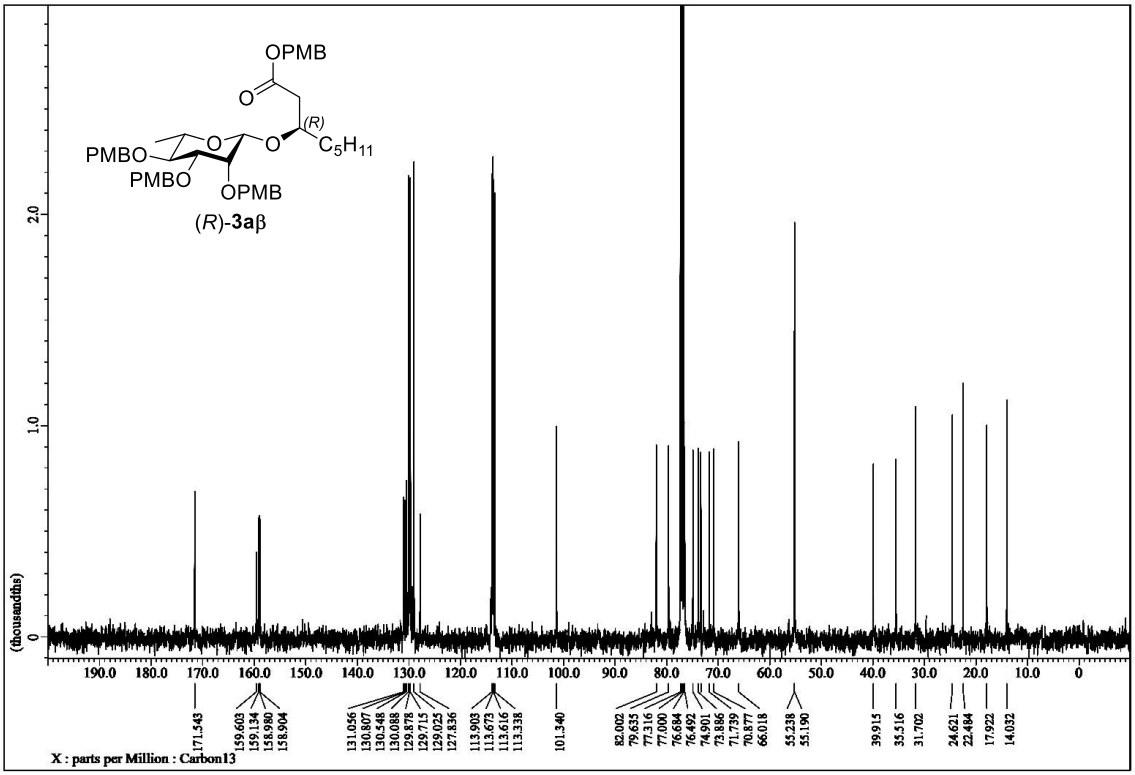

Fig. S60 ^{13}C-NMR spectrum of (*R*)-**3aβ** (100MHz, $CDCl_3$)

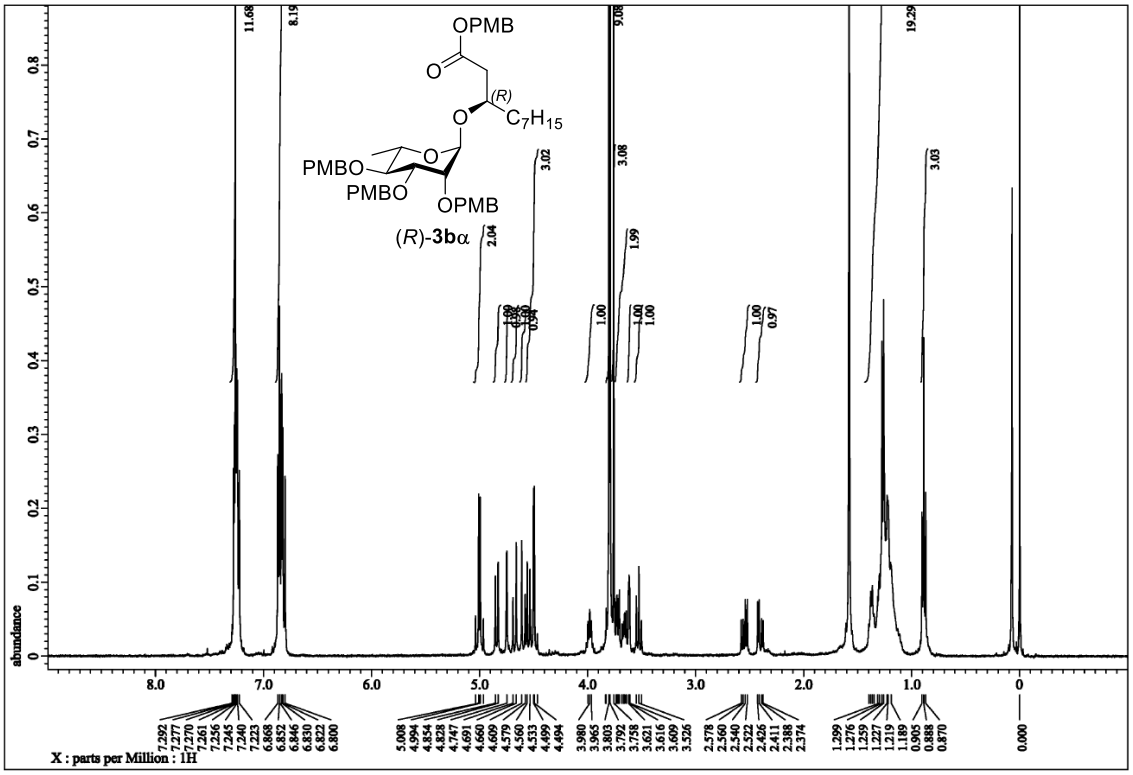

Fig. S61 ^{1}H-NMR spectrum of (*R*)-**3bα** (400MHz, $CDCl_3$)

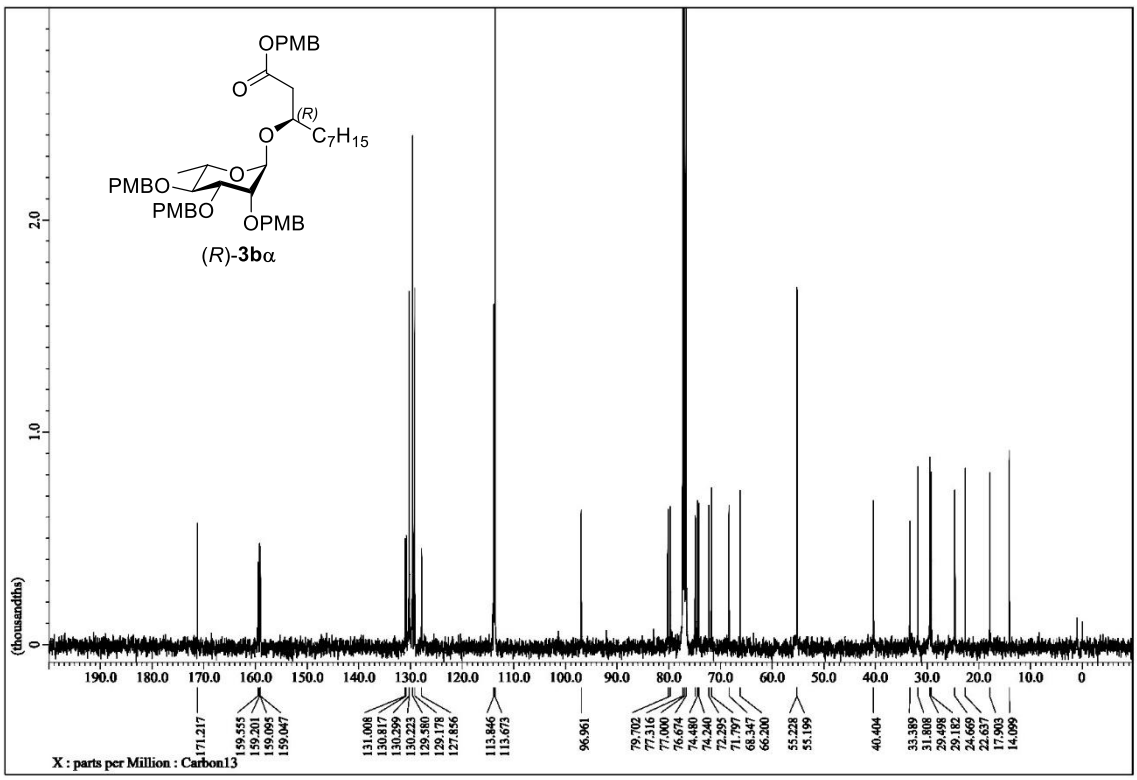

Fig. S62 ^{13}C-NMR spectrum of (*R*)-**3bα** (100MHz, $CDCl_3$)

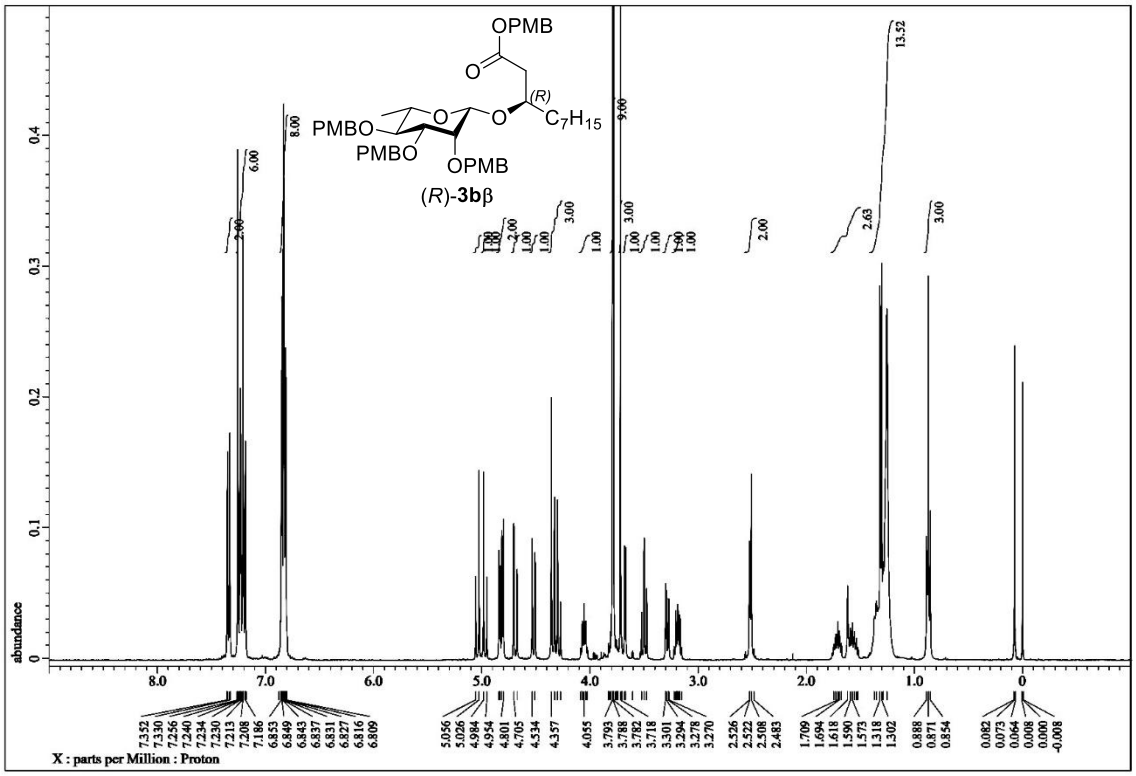

Fig. S63 ^{1}H-NMR spectrum of (*R*)-**3bβ** (400MHz, $CDCl_3$)

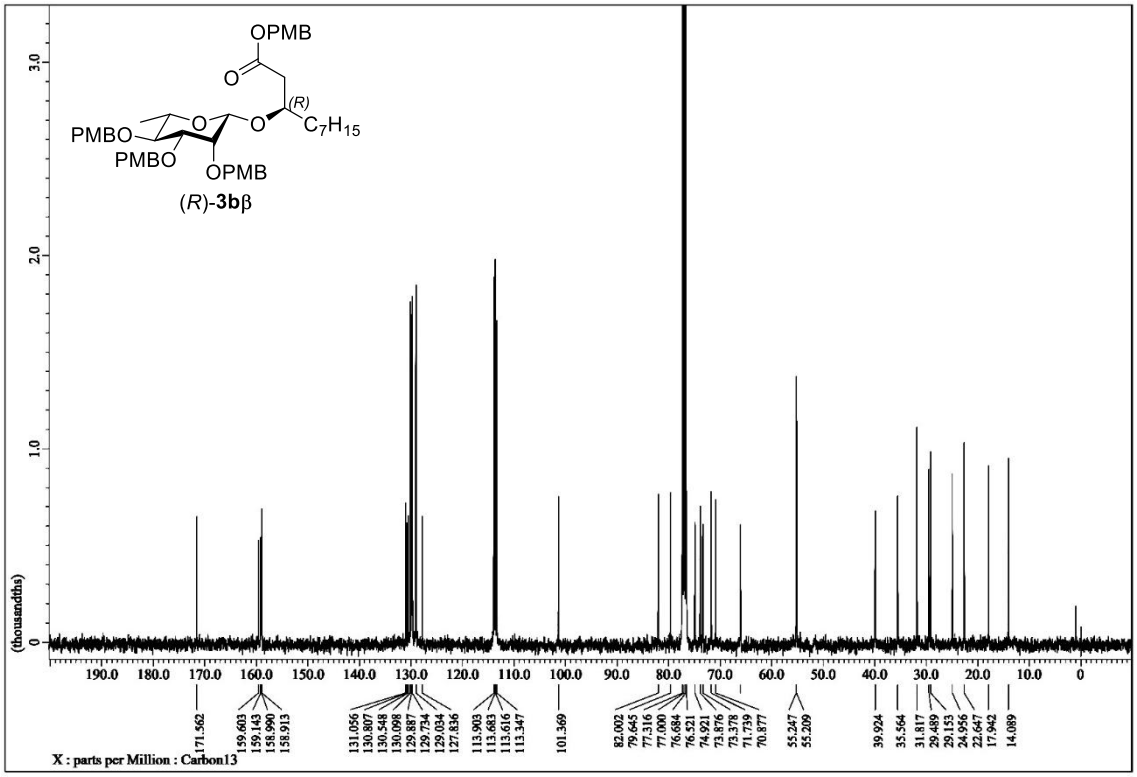

Fig. S64 ^{13}C-NMR spectrum of (*R*)-**3bβ** (100MHz, $CDCl_3$)

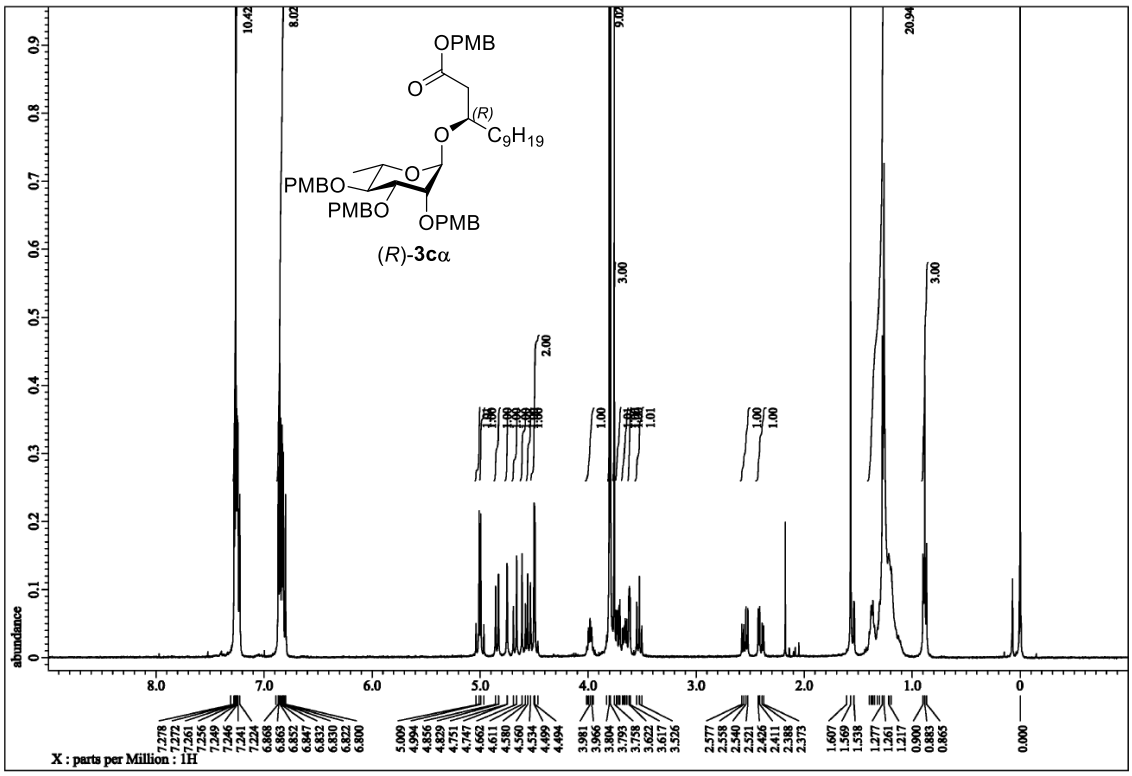

Fig. S65 ^{1}H-NMR spectrum of (*R*)-**3cα** (400MHz, $CDCl_3$)

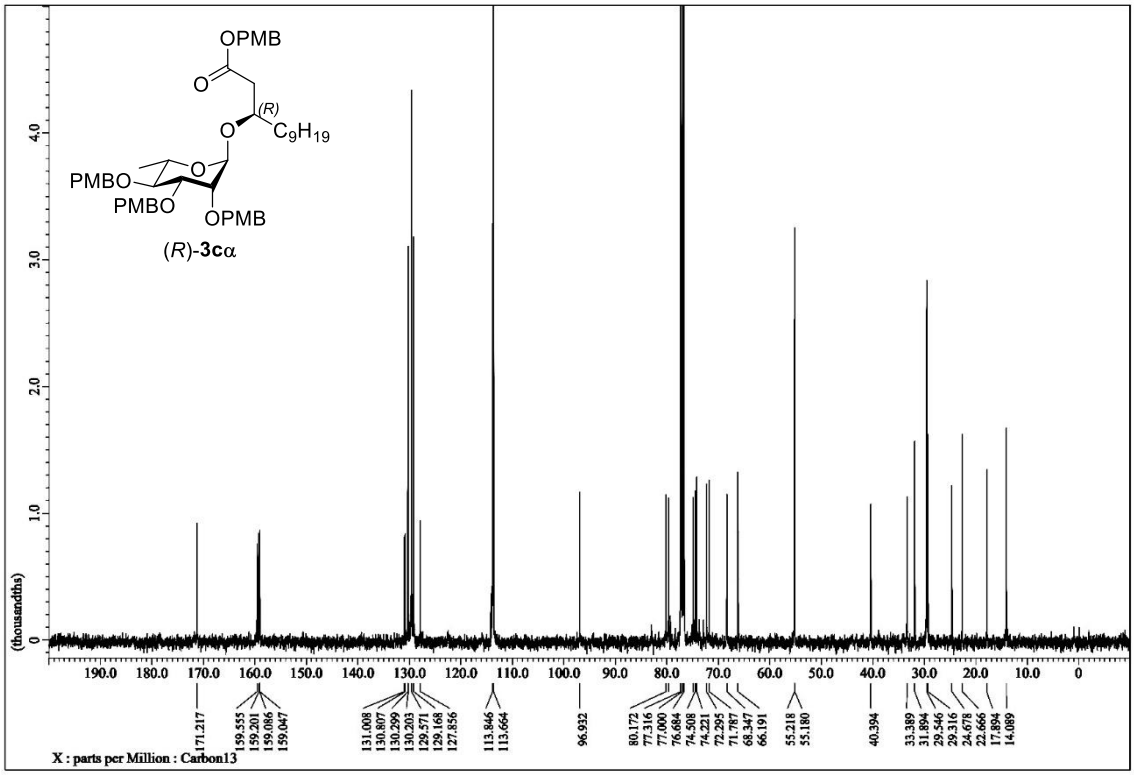

Fig. S66 ^{13}C-NMR spectrum of (*R*)-**3cα** (100MHz, $CDCl_3$)

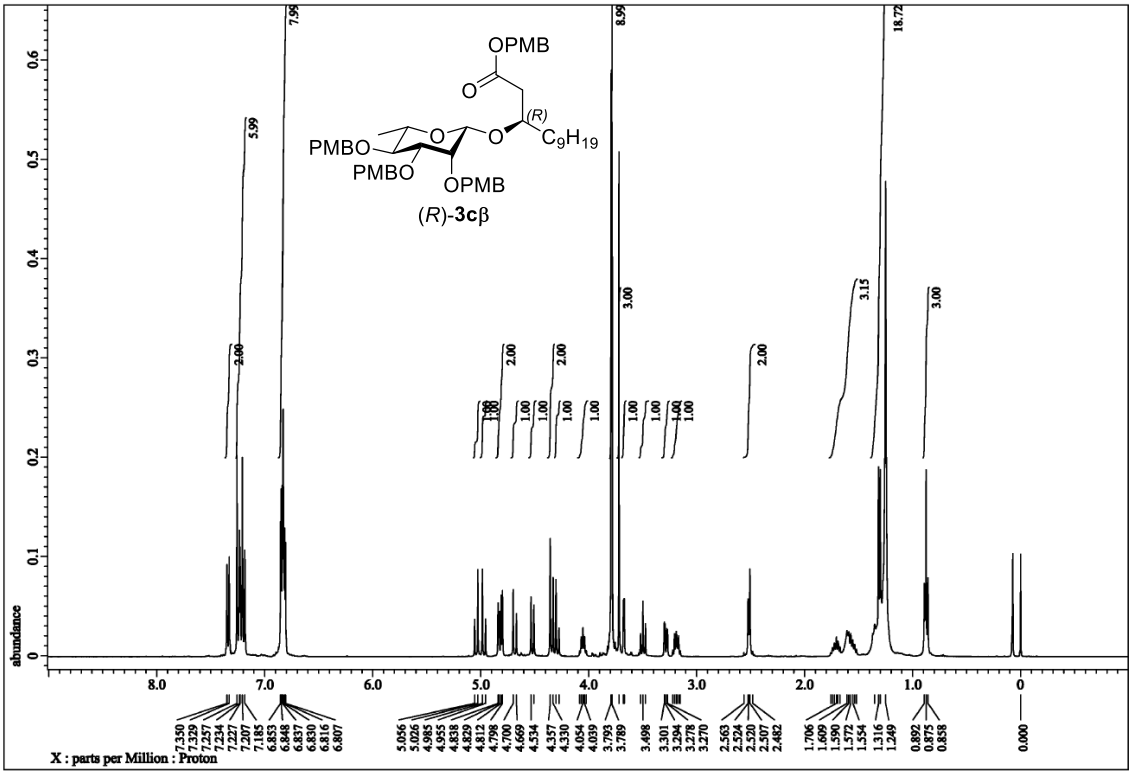

Fig. S67 ^{1}H-NMR spectrum of (*R*)-**3cβ** (400MHz, $CDCl_3$)

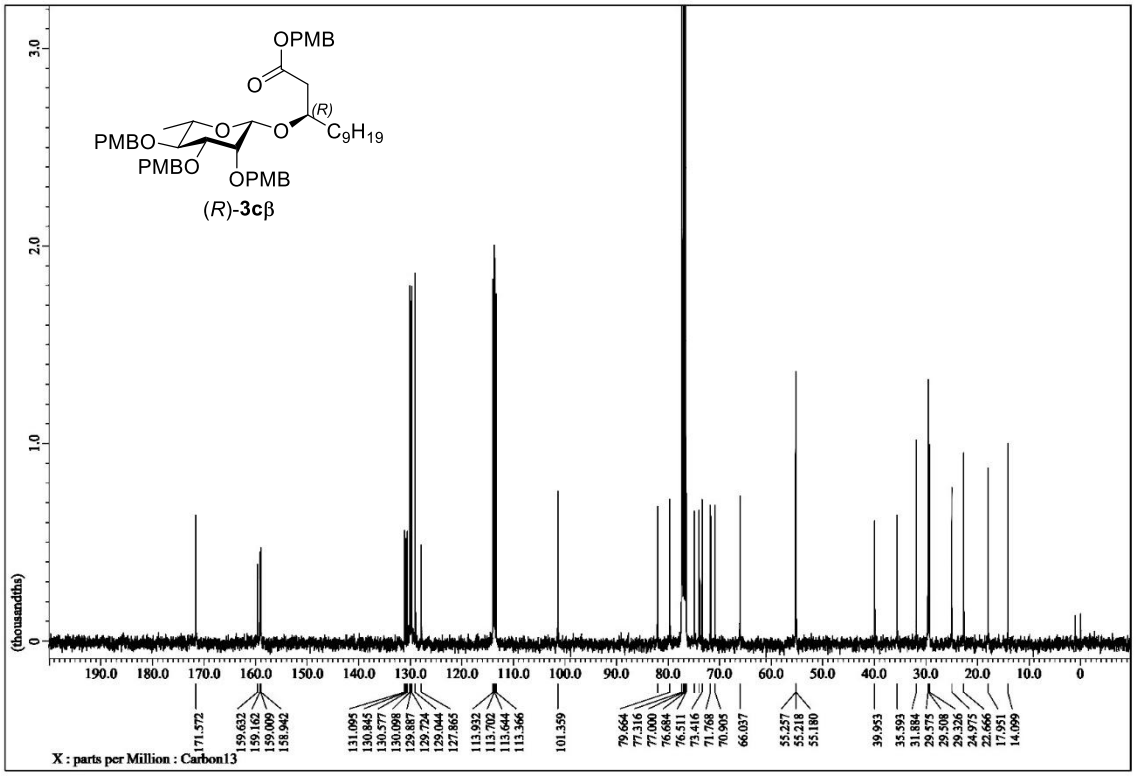

Fig. S68 ^{13}C-NMR spectrum of (*R*)-**3cβ** (100MHz, $CDCl_3$)

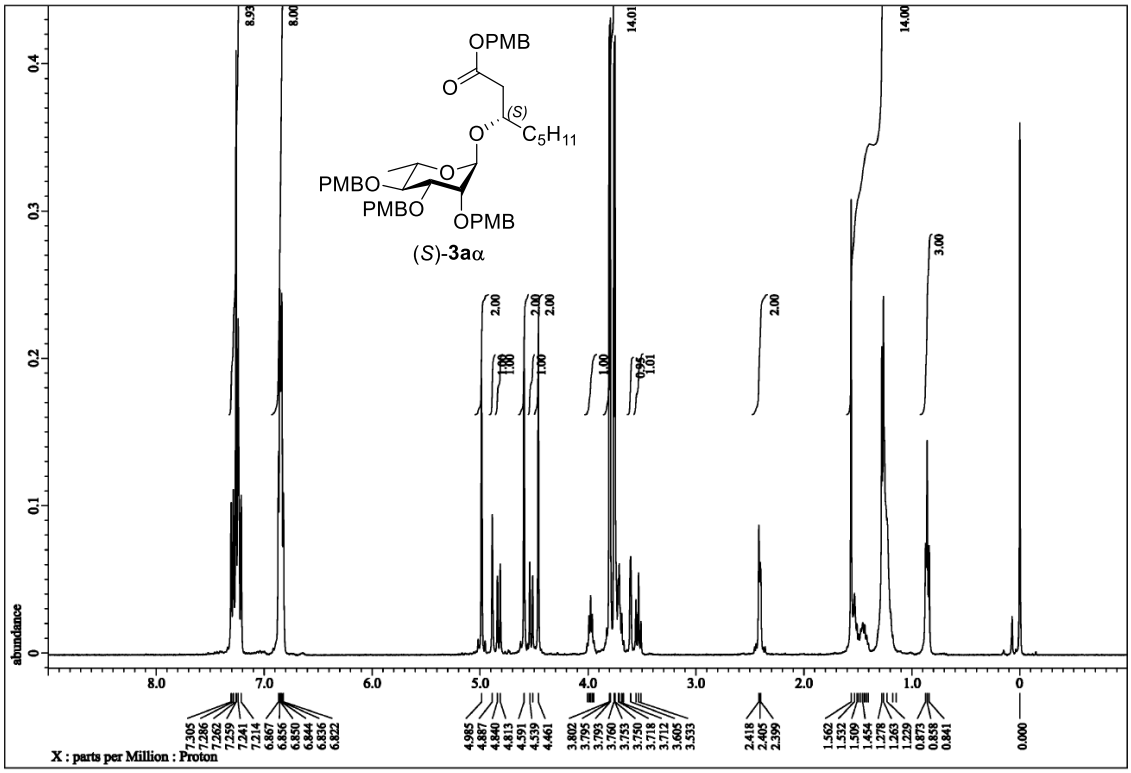

Fig. S69 ^{1}H-NMR spectrum of (*S*)-**3aα** (400MHz, $CDCl_3$)

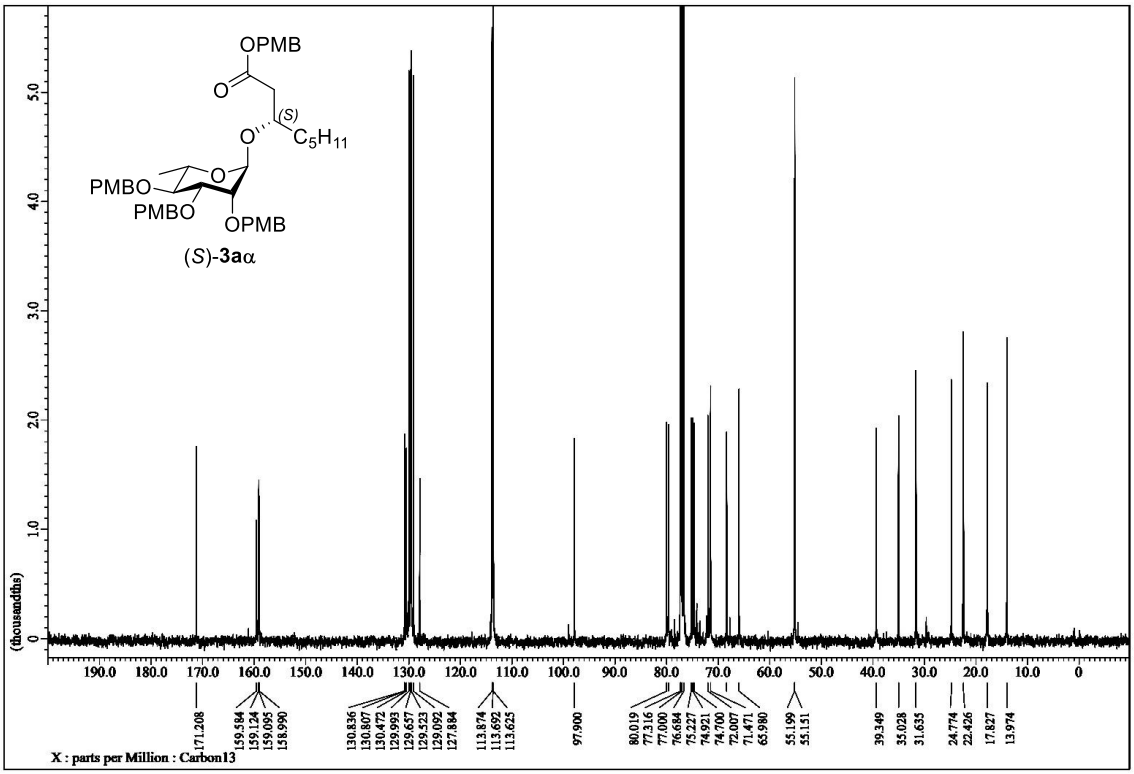

Fig. S70 ^{13}C-NMR spectrum of (*S*)-**3aα** (100MHz, $CDCl_3$)

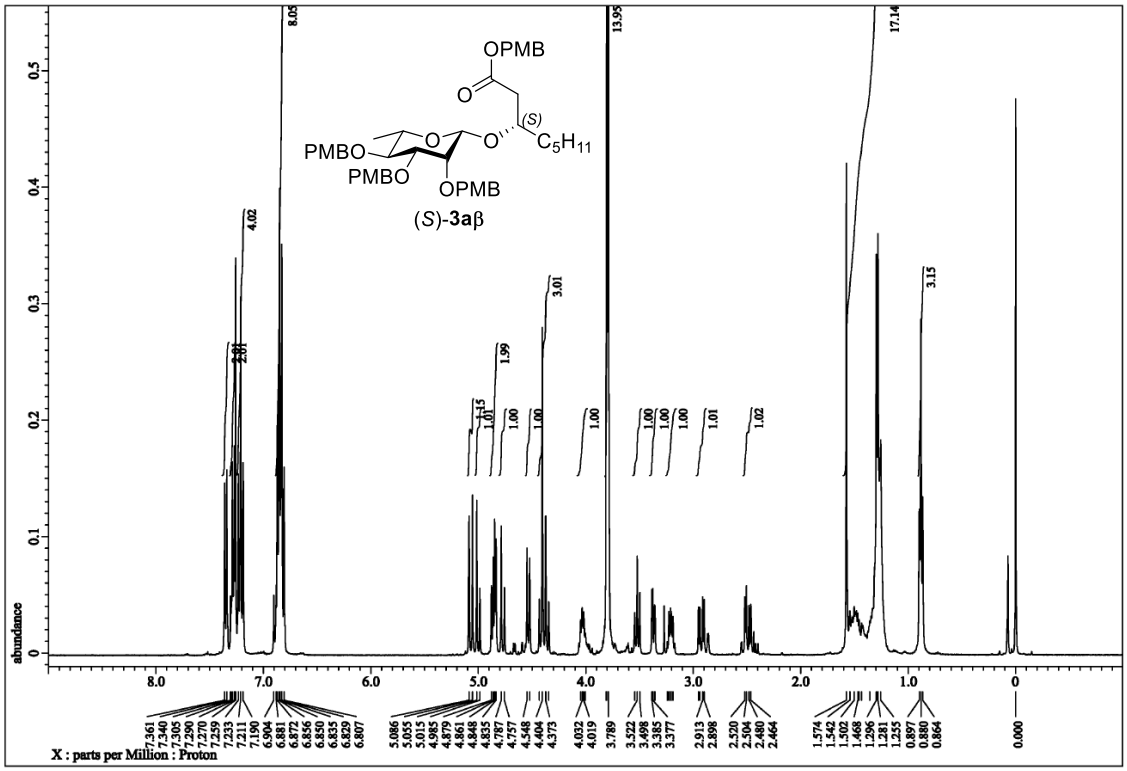

Fig. S71 ^{1}H-NMR spectrum of (*S*)-**3aβ** (400MHz, $CDCl_3$)

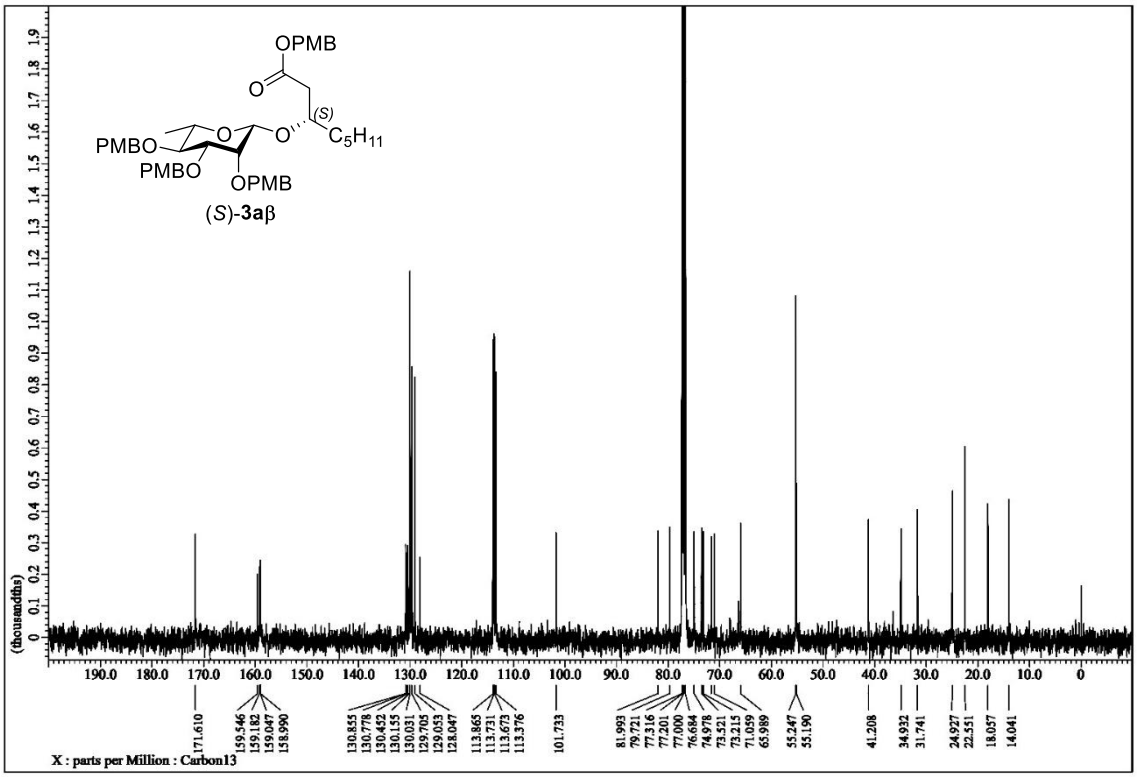

Fig. S72 ^{13}C-NMR spectrum of (*S*)-**3aβ** (100MHz, $CDCl_3$)

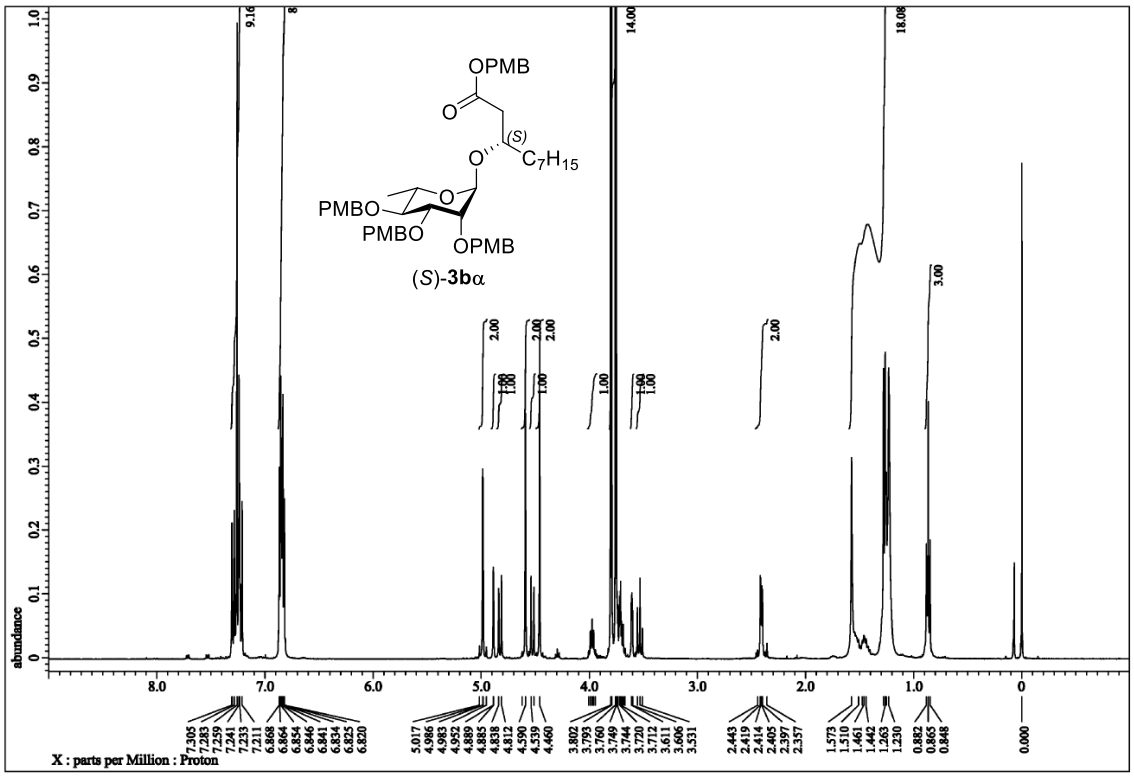

Fig. S73 ^{1}H-NMR spectrum of (*S*)-**3bα** (400MHz, $CDCl_3$)

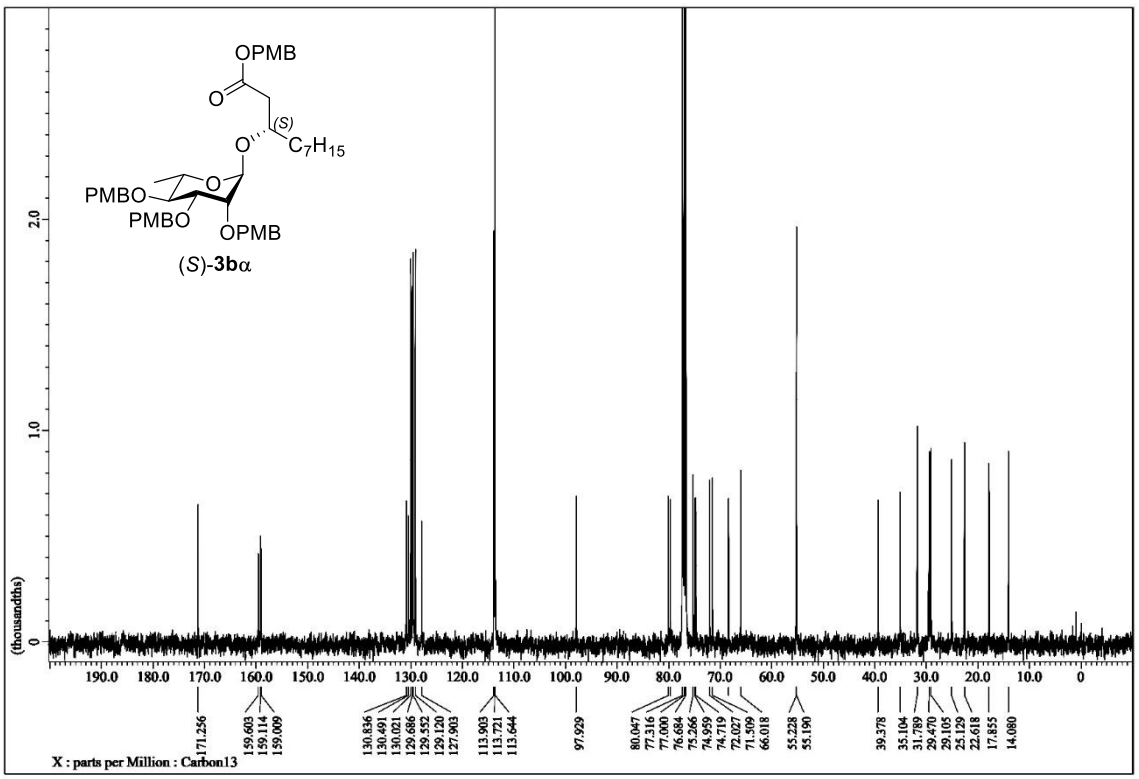

Fig. S74 ^{13}C-NMR spectrum of (*S*)-**3bα** (100MHz, $CDCl_3$)

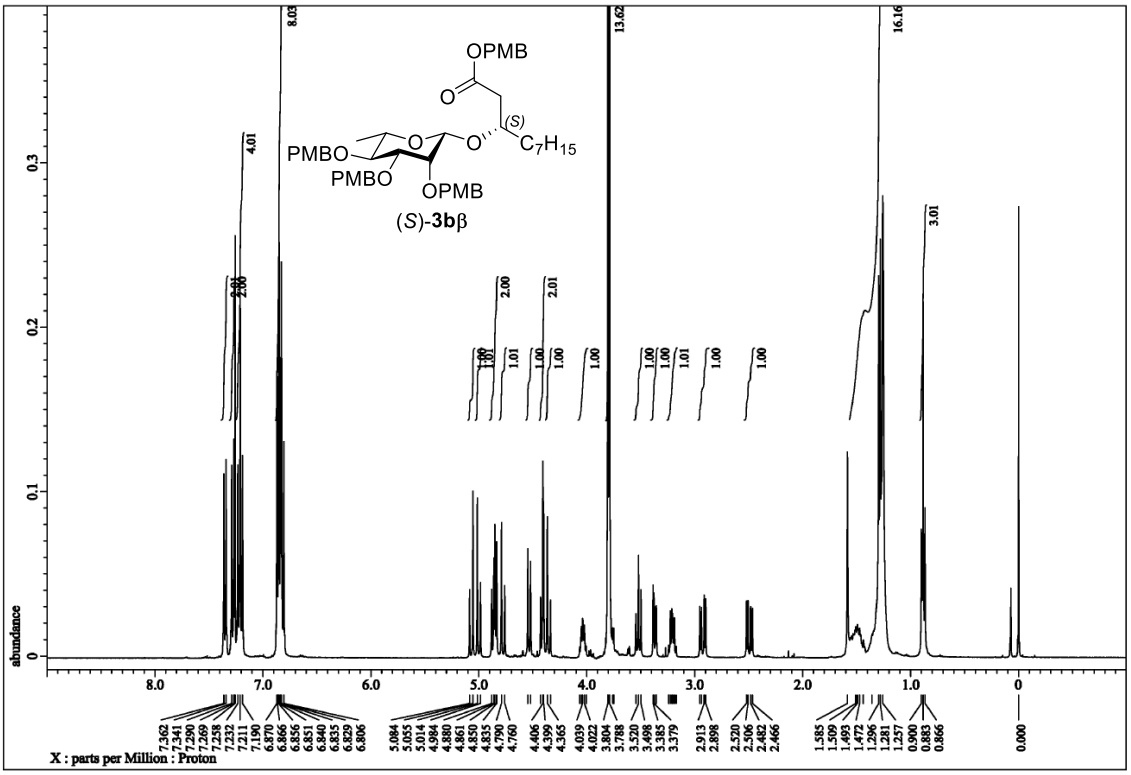

Fig. S75 ^{1}H-NMR spectrum of (*S*)-**3bβ** (400MHz, $CDCl_3$)

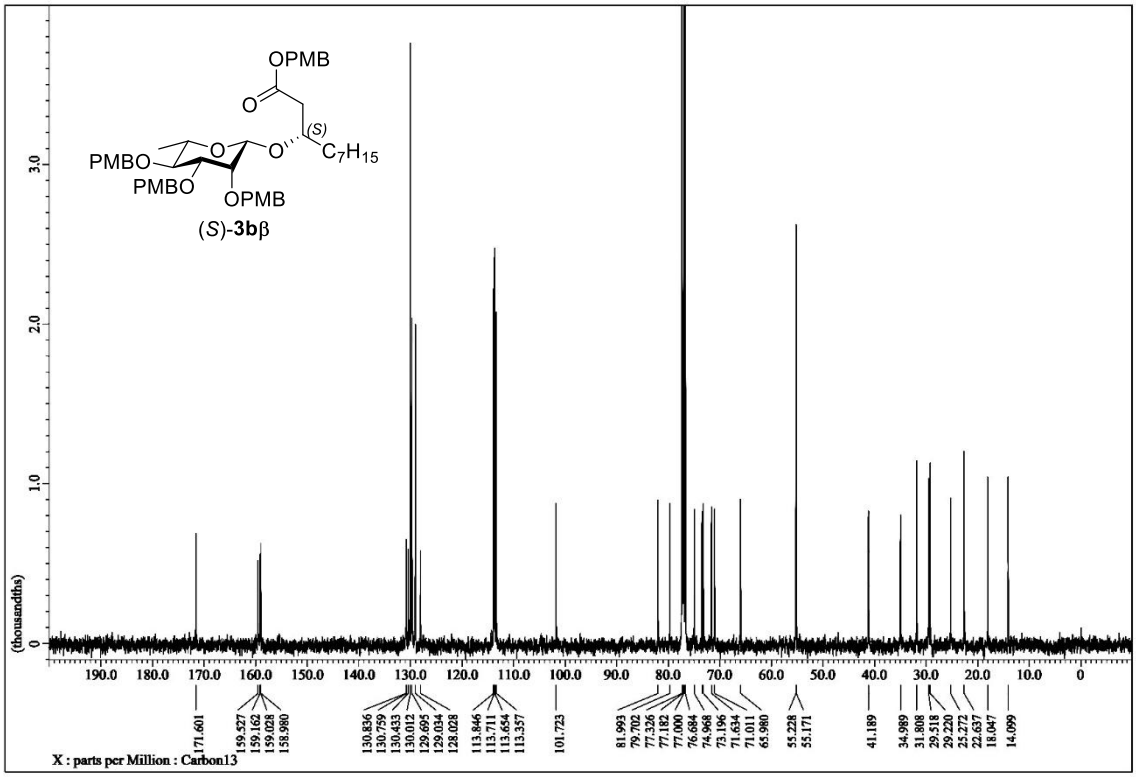

Fig. S76 ^{13}C-NMR spectrum of (*S*)-**3bβ** (100MHz, $CDCl_3$)

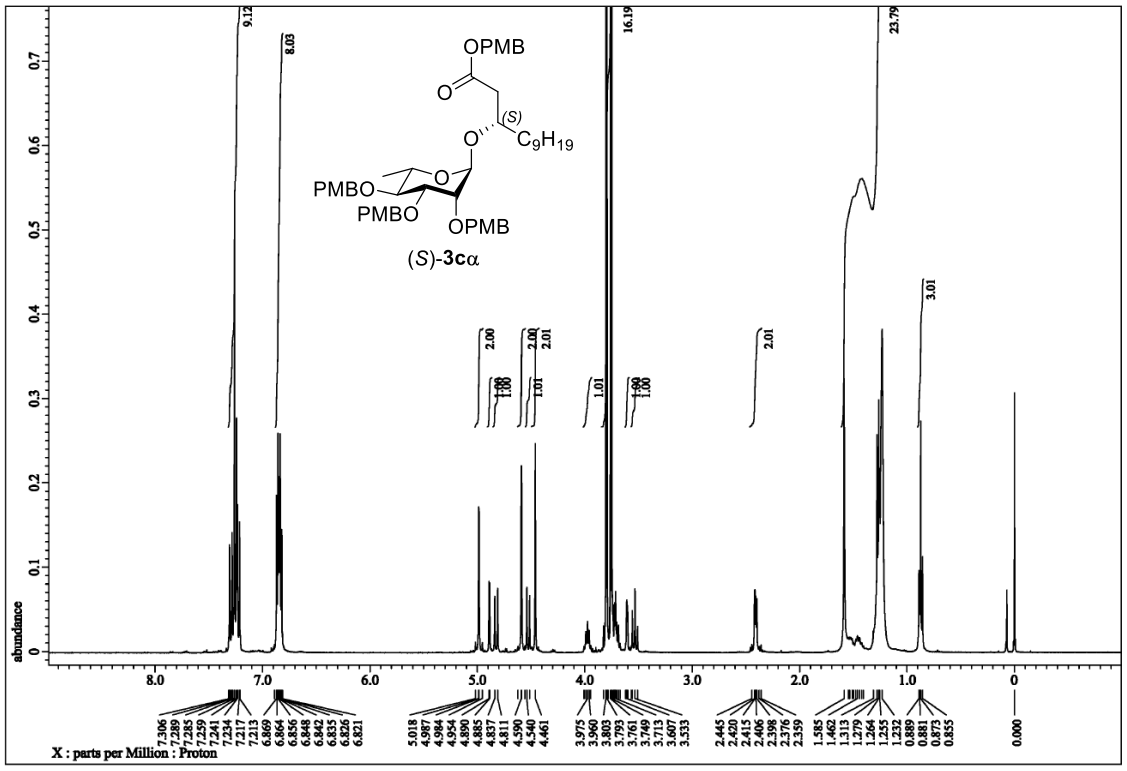

Fig. S77 ^{1}H-NMR spectrum of (*S*)-**3cα** (400MHz, $CDCl_3$)

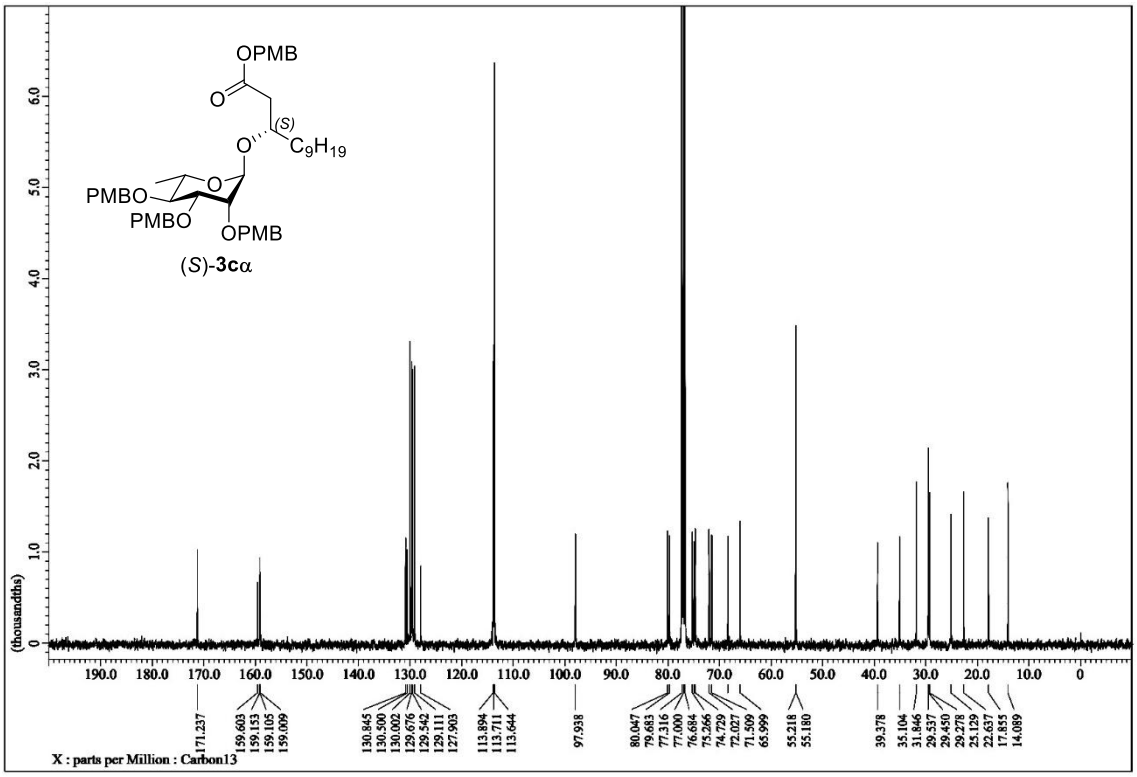

Fig. S78 ^{13}C-NMR spectrum of (*S*)-**3cα** (100MHz, $CDCl_3$)

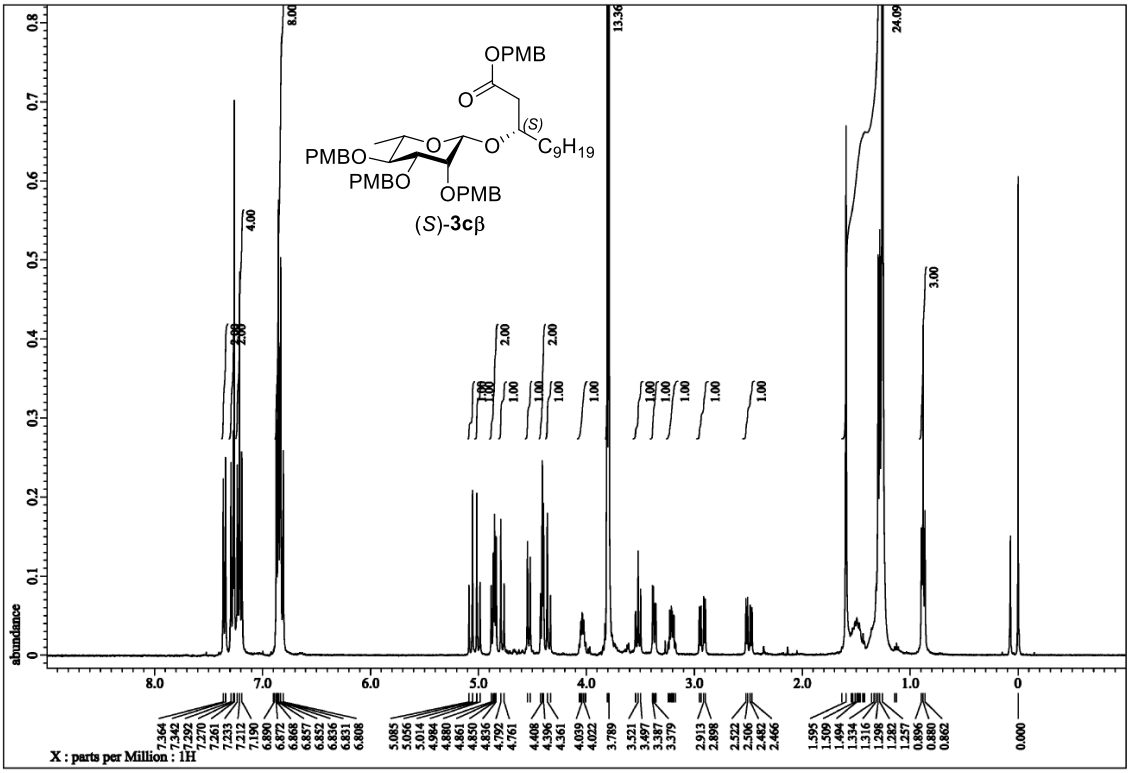

Fig. S79 ^{1}H-NMR spectrum of (*S*)-**3cβ** (400MHz, $CDCl_3$)

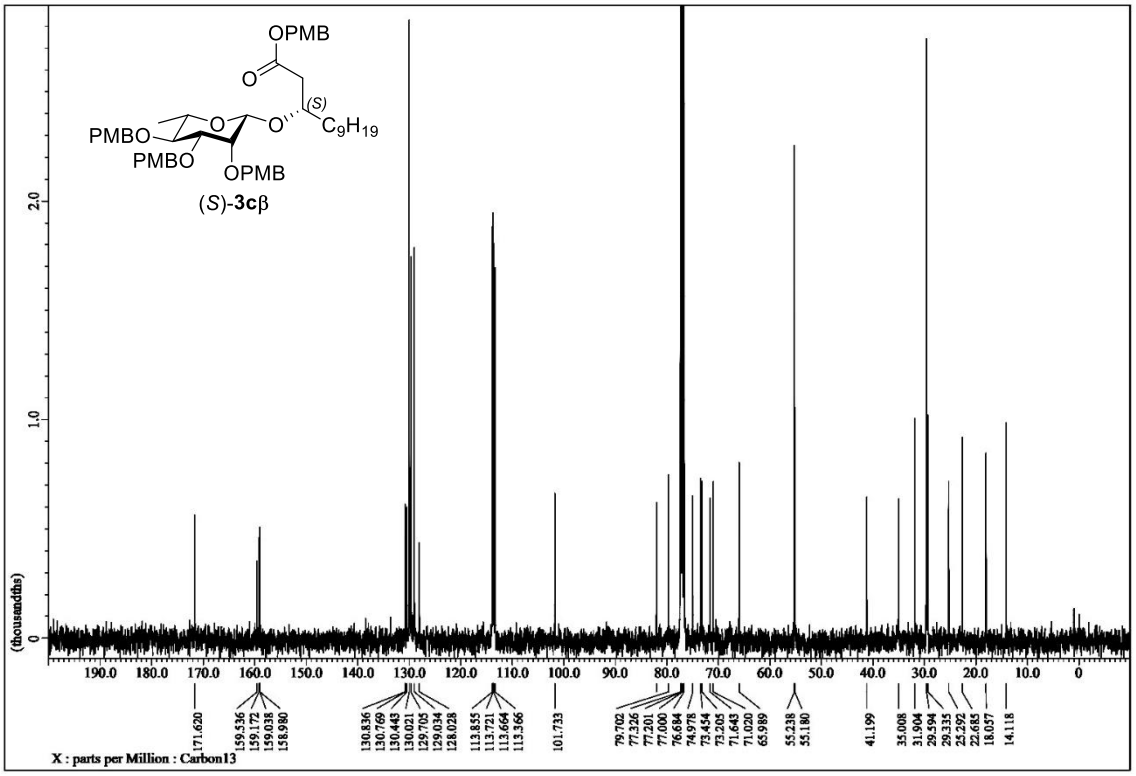

Fig. S80 ^{13}C-NMR spectrum of (*S*)-**3cβ** (100MHz, $CDCl_3$)

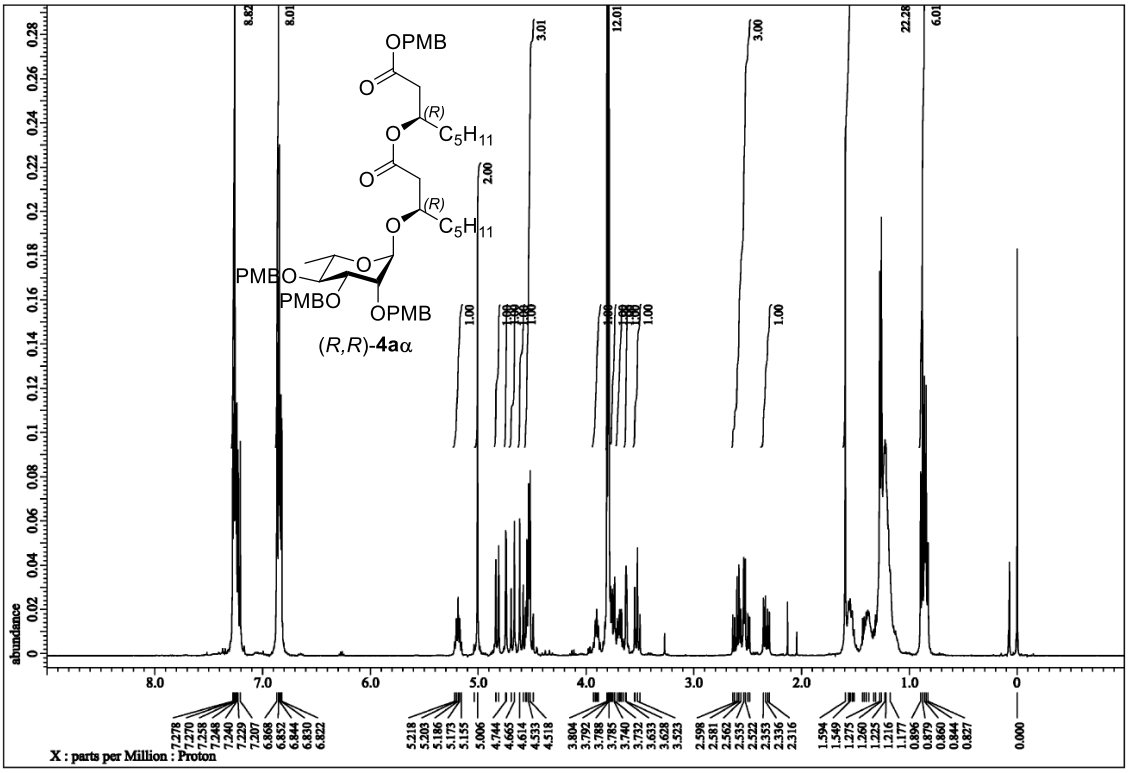

Fig. S81 ^{1}H-NMR spectrum of (*R,R*)-**4aα** (400MHz, $CDCl_3$)

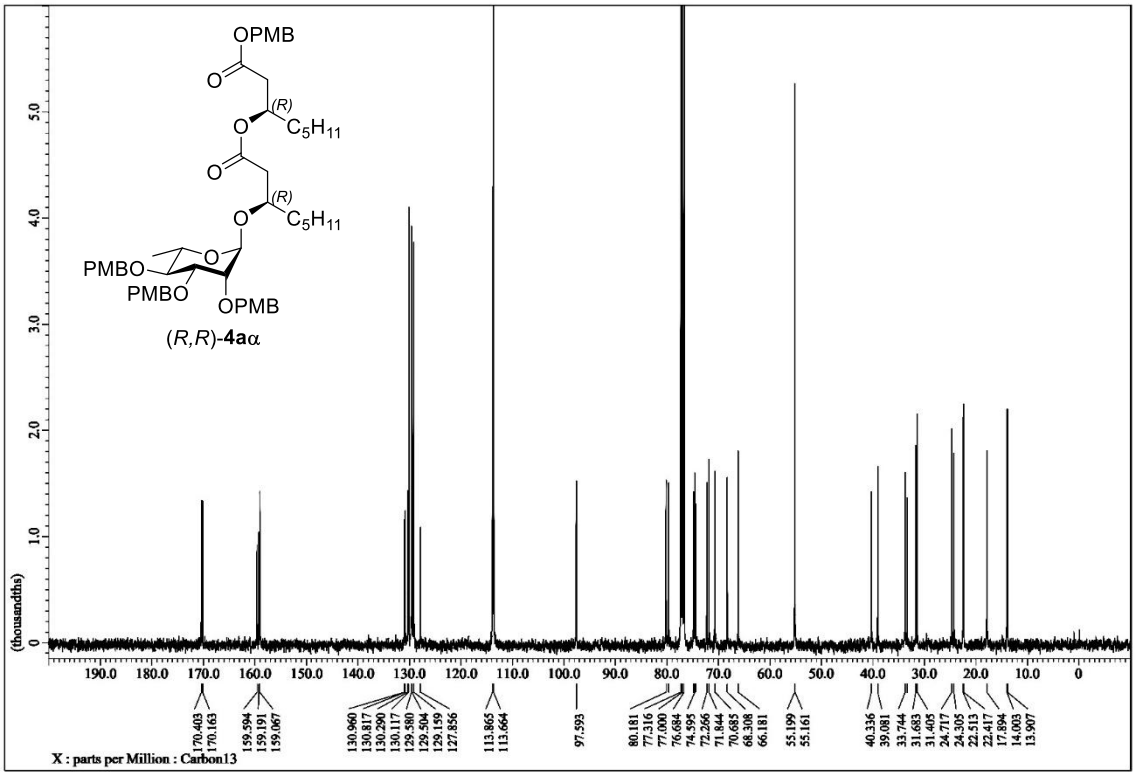

Fig. S82 ^{13}C-NMR spectrum of (*R,R*)-**4aα** (100MHz, $CDCl_3$)

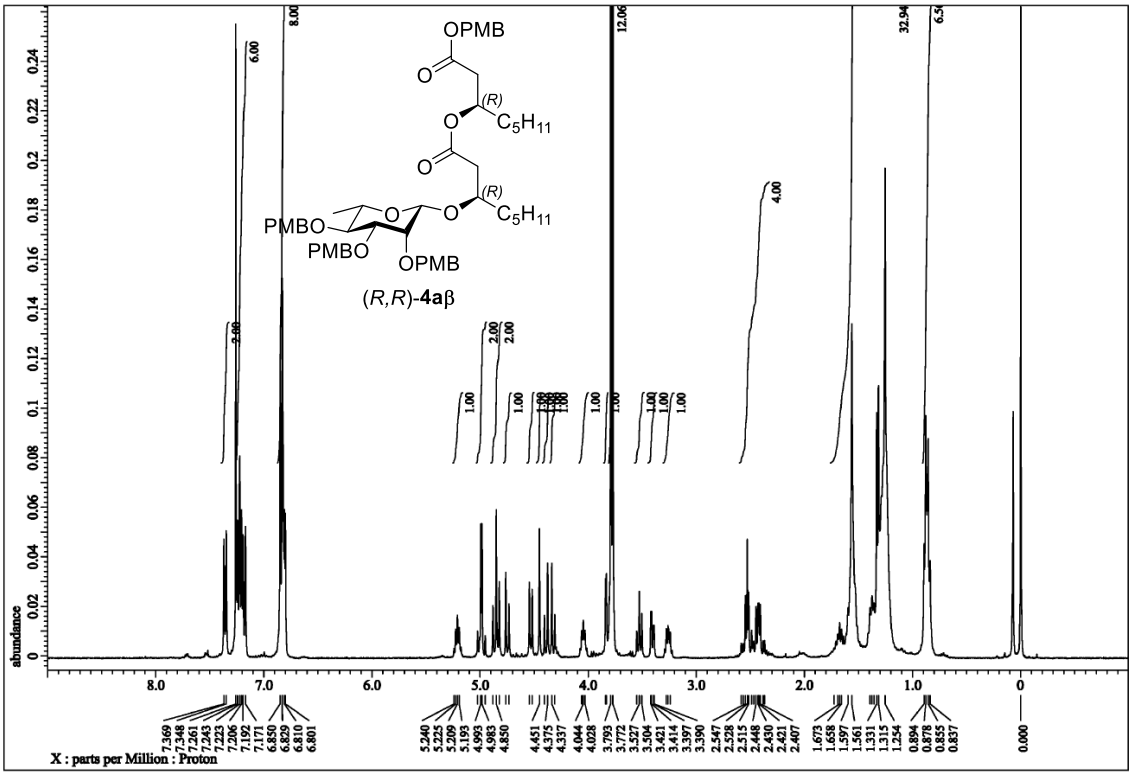

Fig. S83 ^{1}H-NMR spectrum of (*R,R*)-**4aβ** (400MHz, $CDCl_3$)

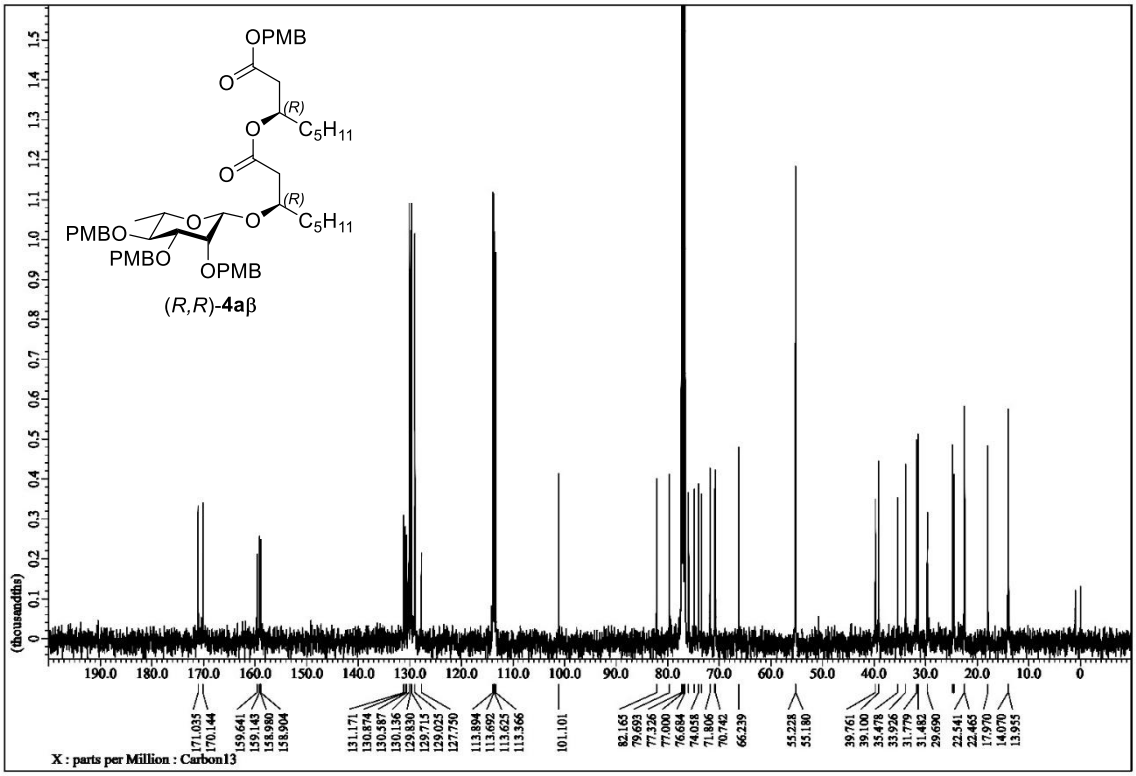

Fig. S84 ^{13}C-NMR spectrum of (*R,R*)-**4aβ** (100MHz, $CDCl_3$)

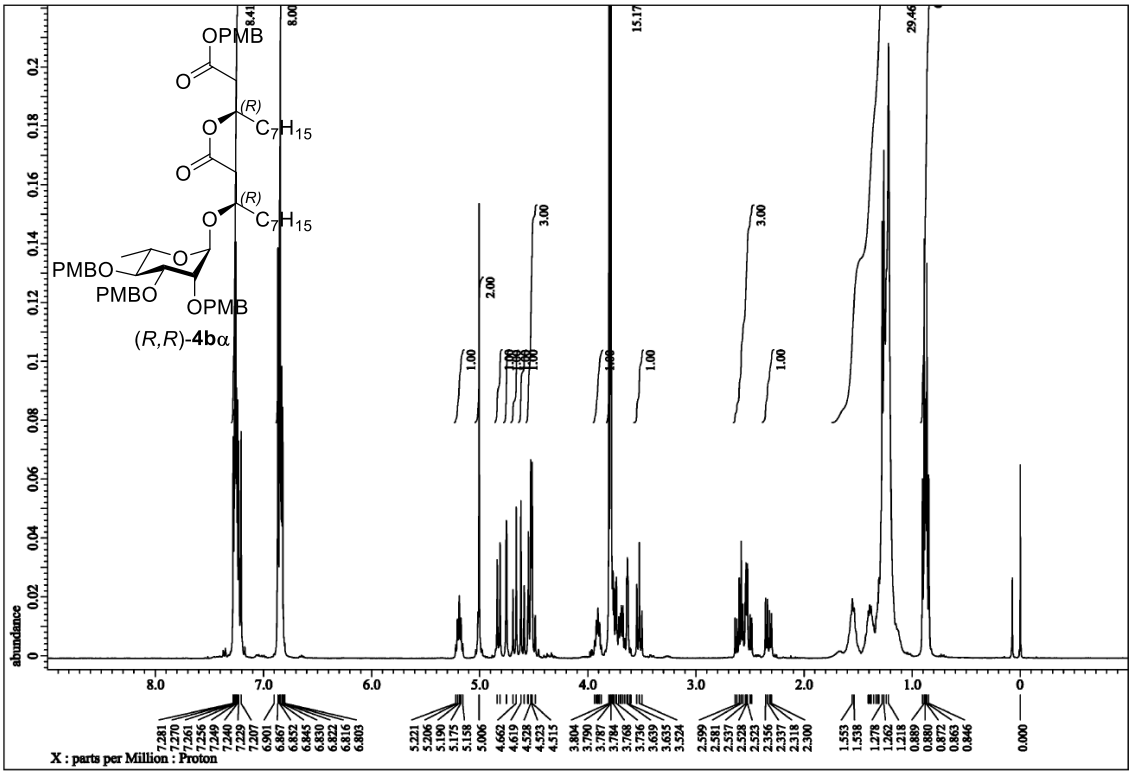

Fig. S85 ^{1}H-NMR spectrum of (*R,R*)-**4bα** (400MHz, $CDCl_3$)

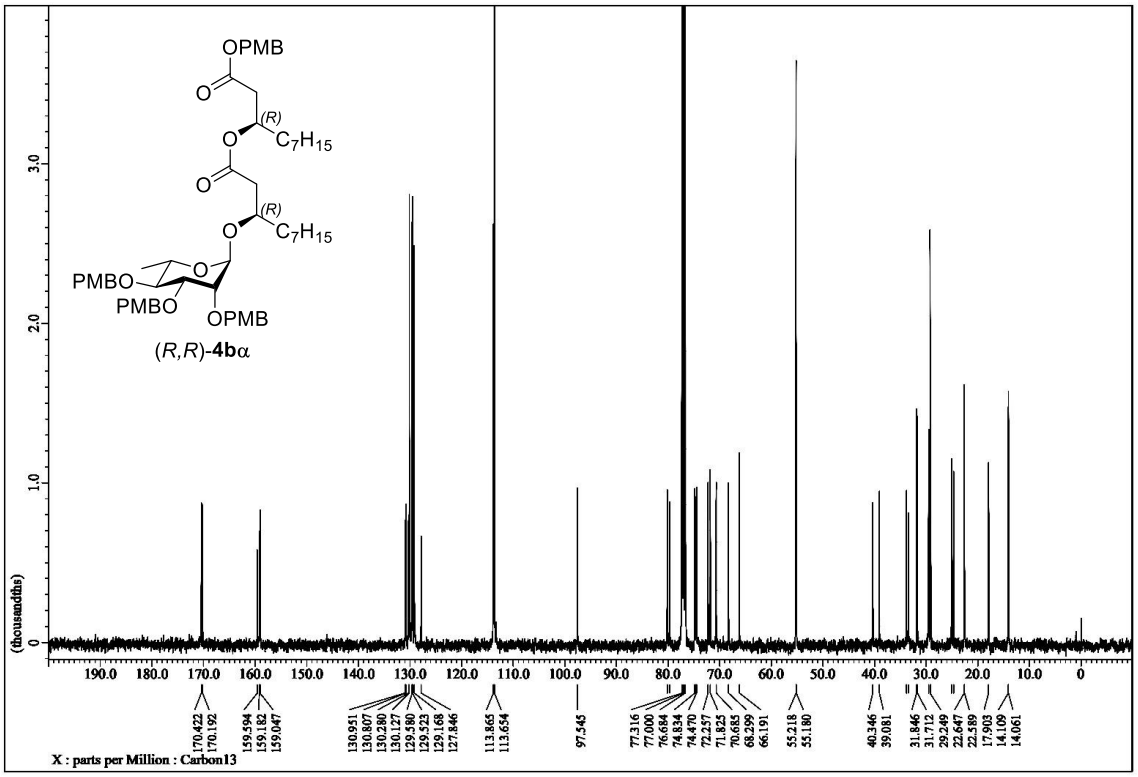

Fig. S86 ^{13}C-NMR spectrum of (*R,R*)-**4bα** (100MHz, $CDCl_3$)

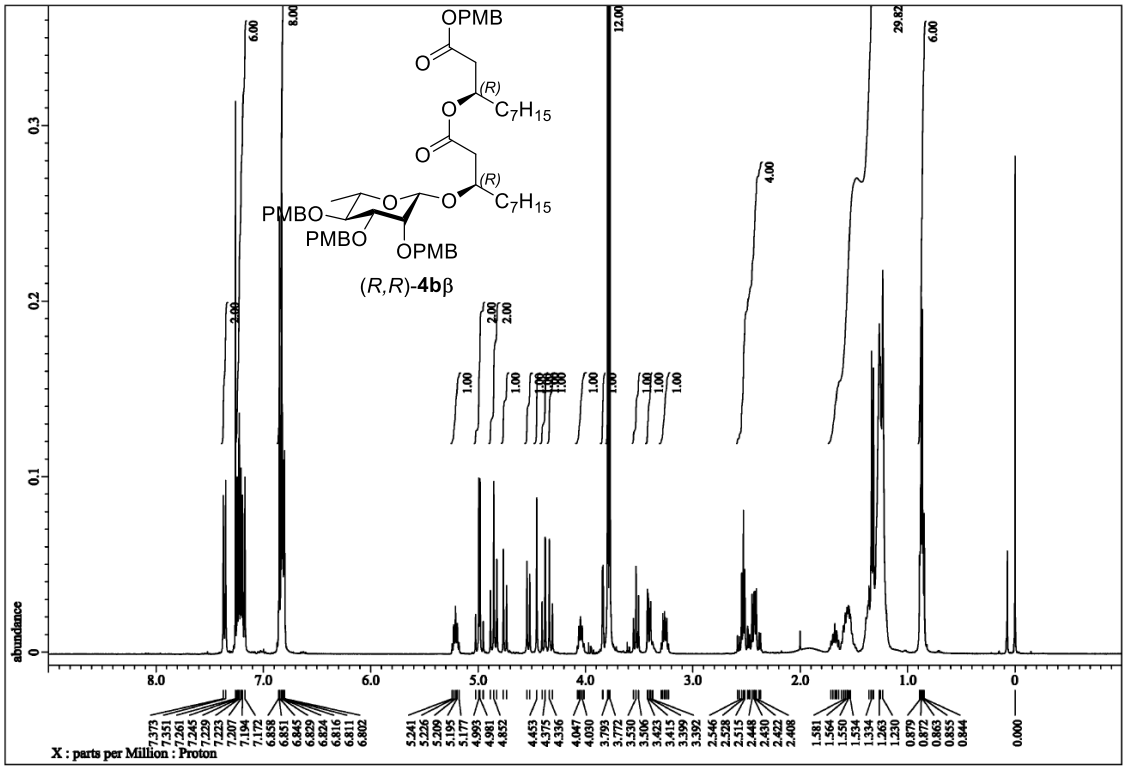

Fig. S87 ^{1}H-NMR spectrum of (*R,R*)-**4bβ** (400MHz, $CDCl_3$)

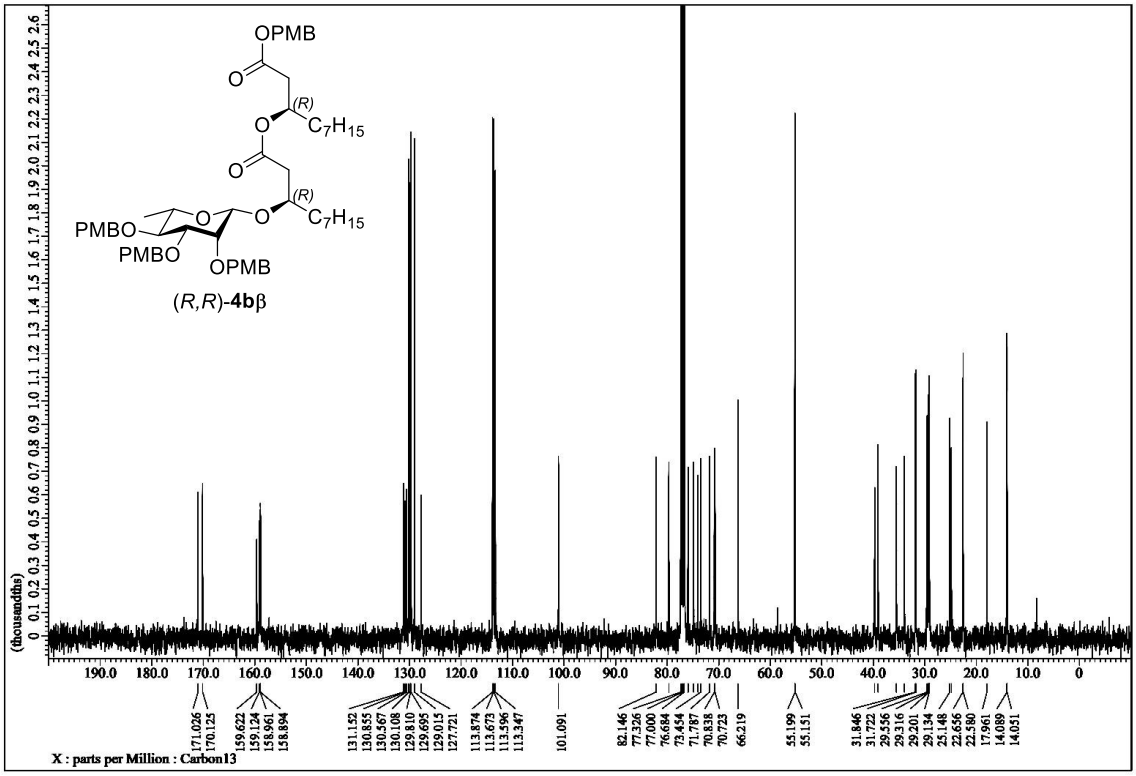

Fig. S88 ^{13}C-NMR spectrum of (*R,R*)-**4bβ** (100MHz, $CDCl_3$)

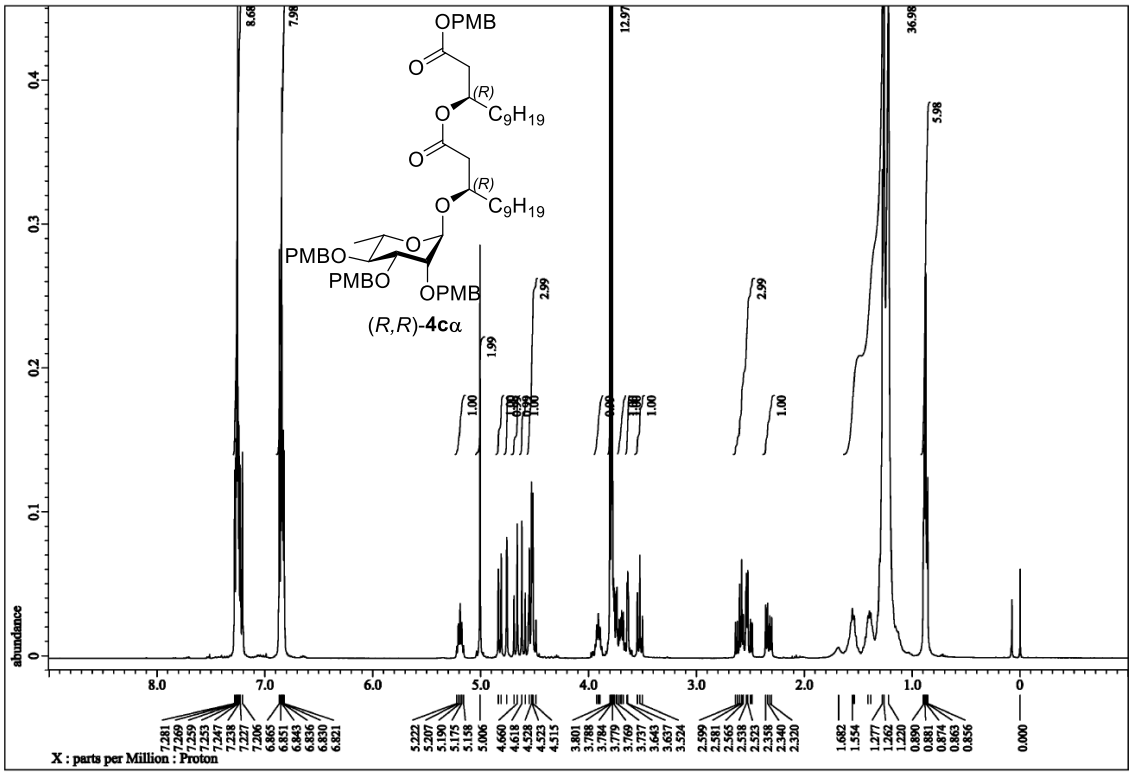

Fig. S89 ^{1}H-NMR spectrum of (*R,R*)-**4cα** (400MHz, $CDCl_3$)

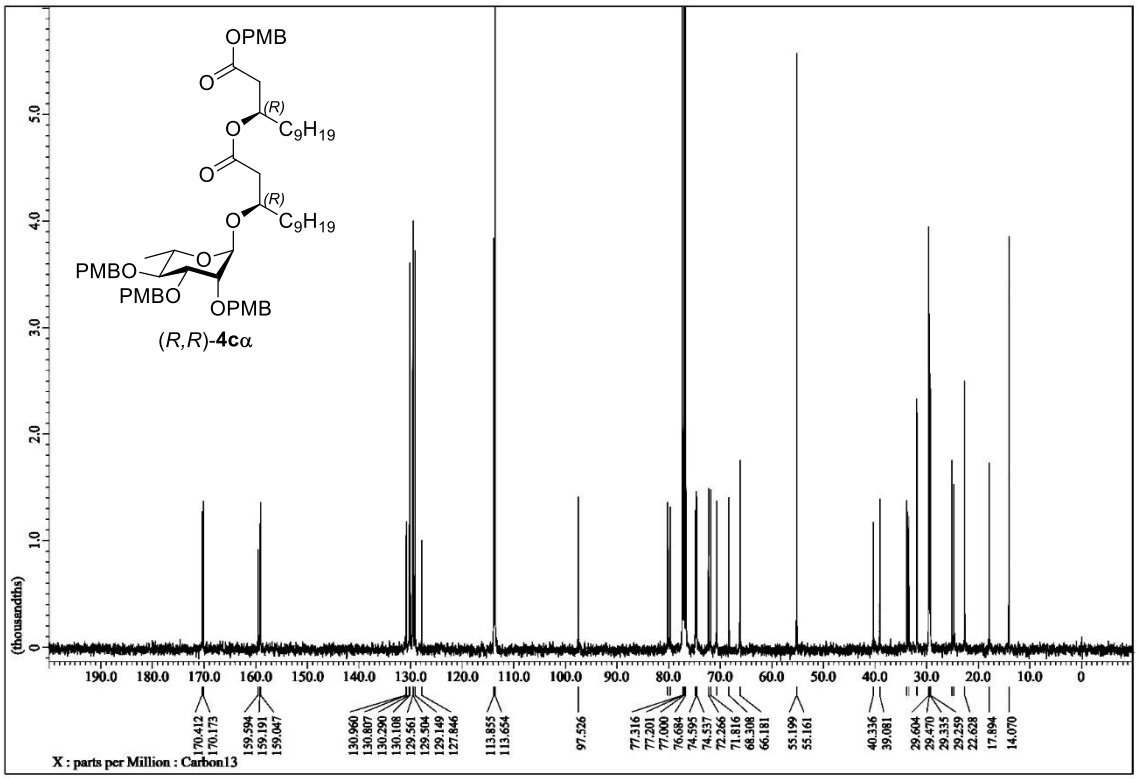

Fig. S90 ^{13}C-NMR spectrum of (*R,R*)-**4cα** (100MHz, $CDCl_3$)

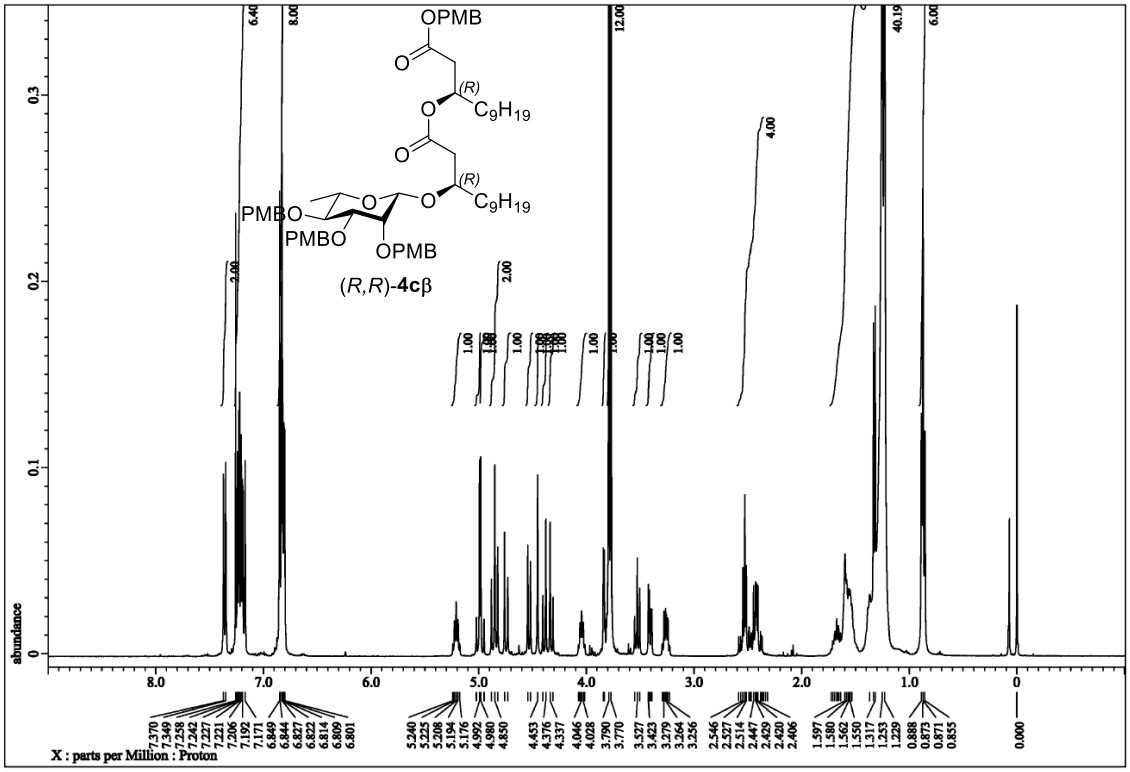

Fig. S91 ^{1}H-NMR spectrum of (*R,R*)-**4cβ** (400MHz, $CDCl_3$)

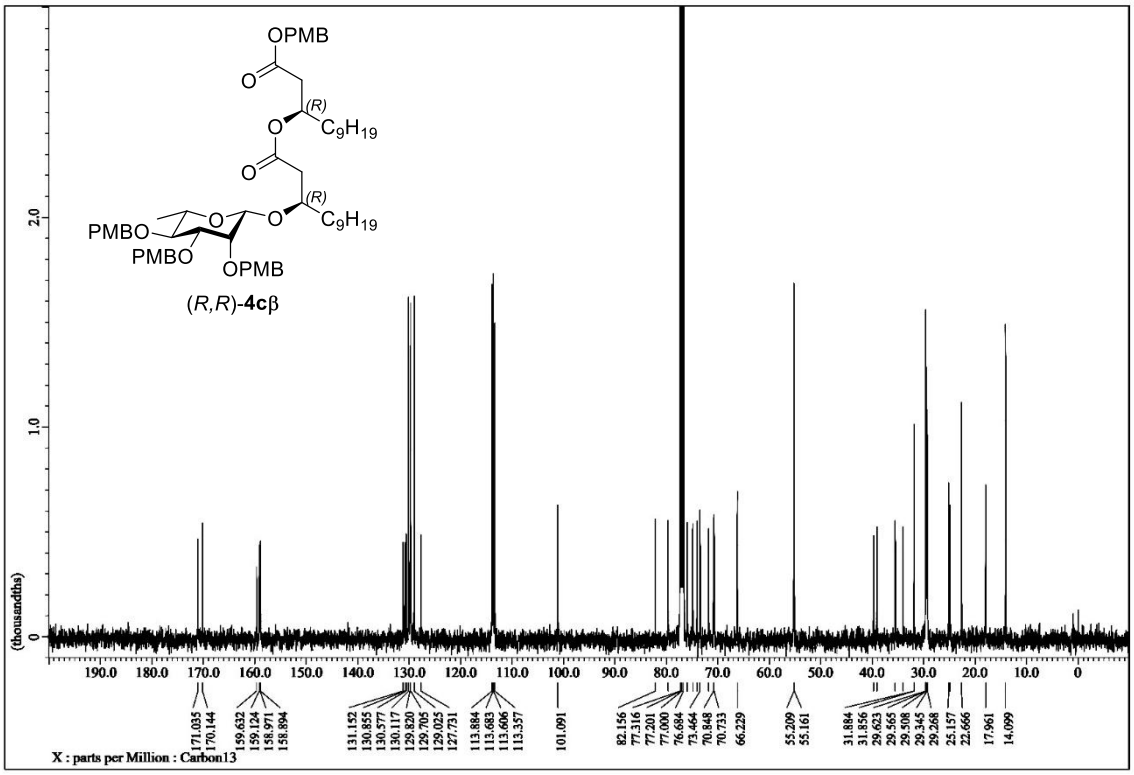

Fig. S92 ^{13}C-NMR spectrum of (*R,R*)-**4cβ** (100MHz, $CDCl_3$)

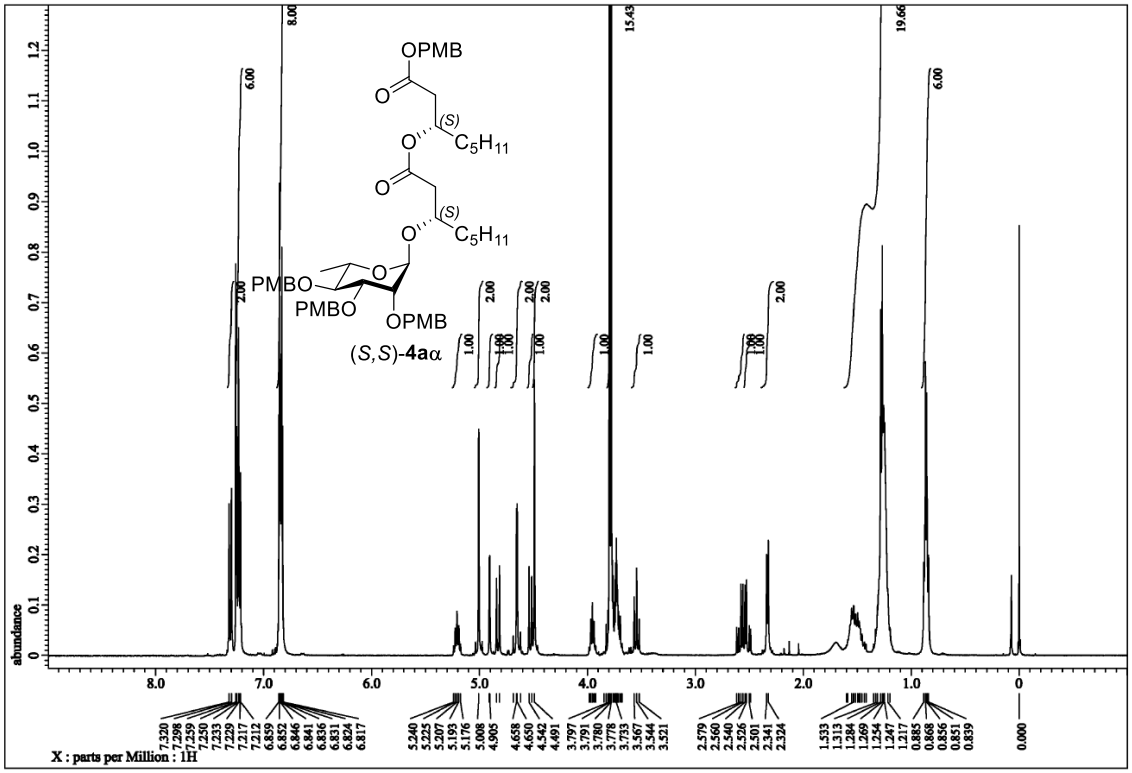

Fig. S93 ^{1}H-NMR spectrum of (*S,S*)-**4aα** (400MHz, $CDCl_3$)

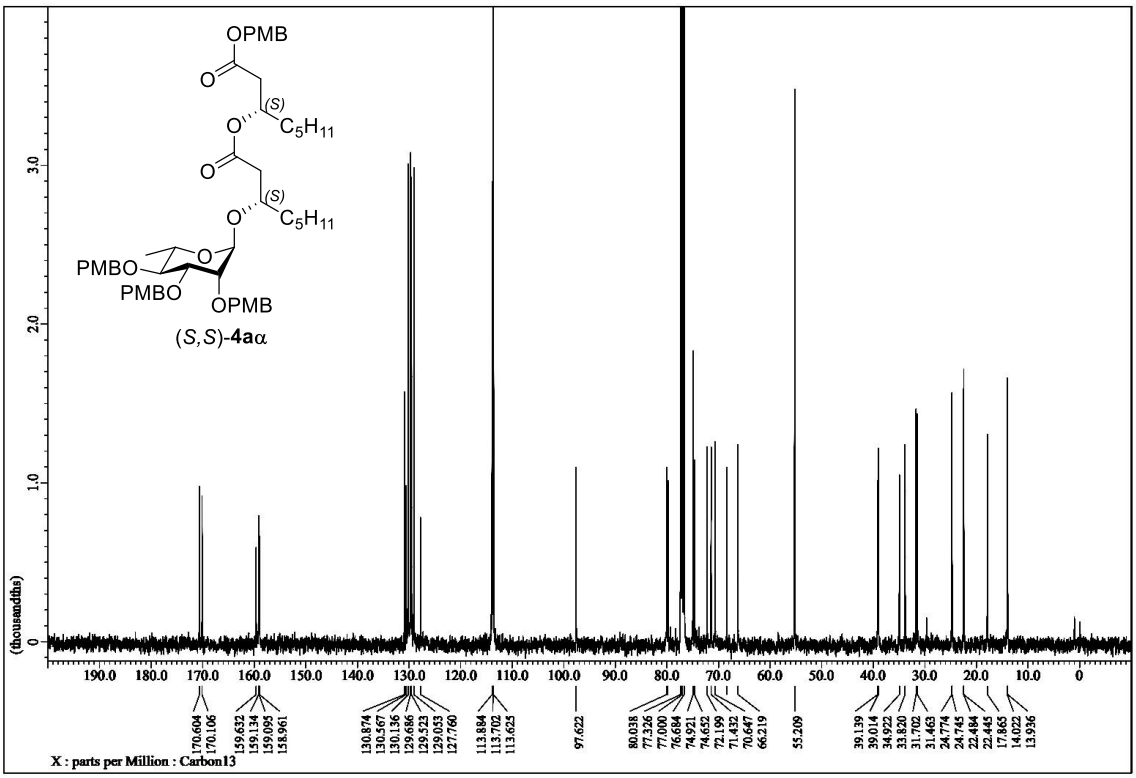

Fig. S94 ^{13}C-NMR spectrum of (*S,S*)-**4aα** (100MHz, $CDCl_3$)

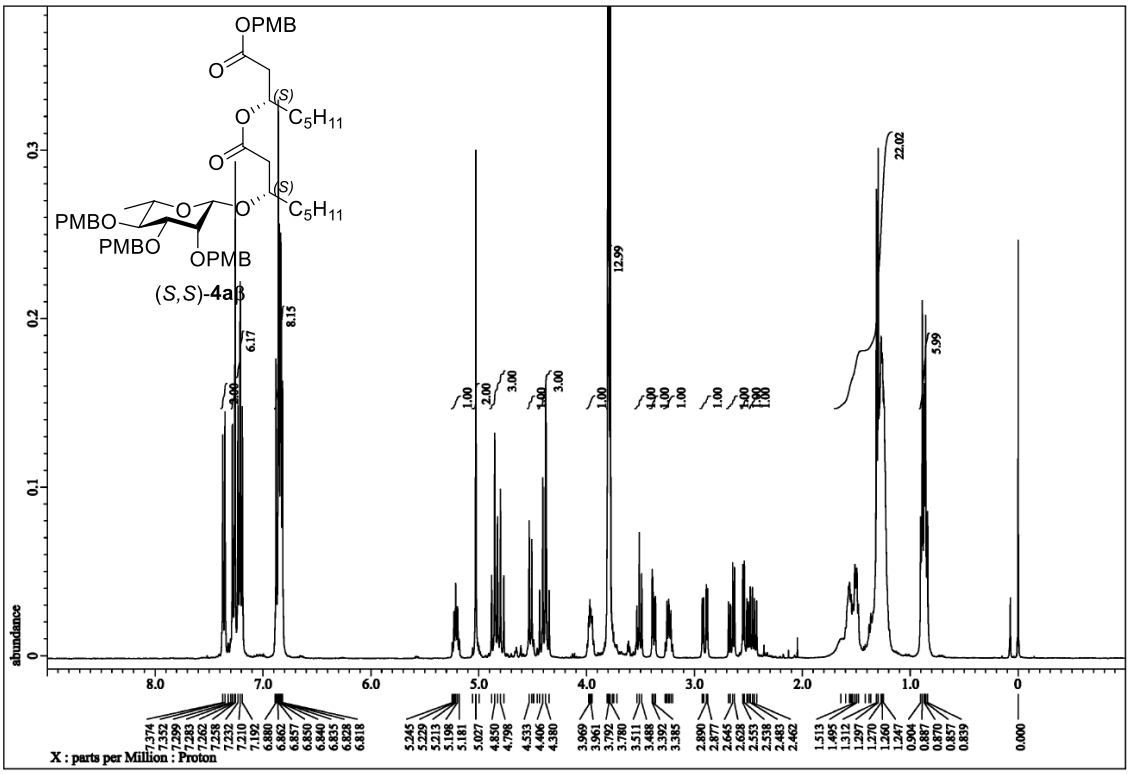

Fig. S95 ^{1}H-NMR spectrum of (*S,S*)-**4aβ** (400MHz, $CDCl_3$)

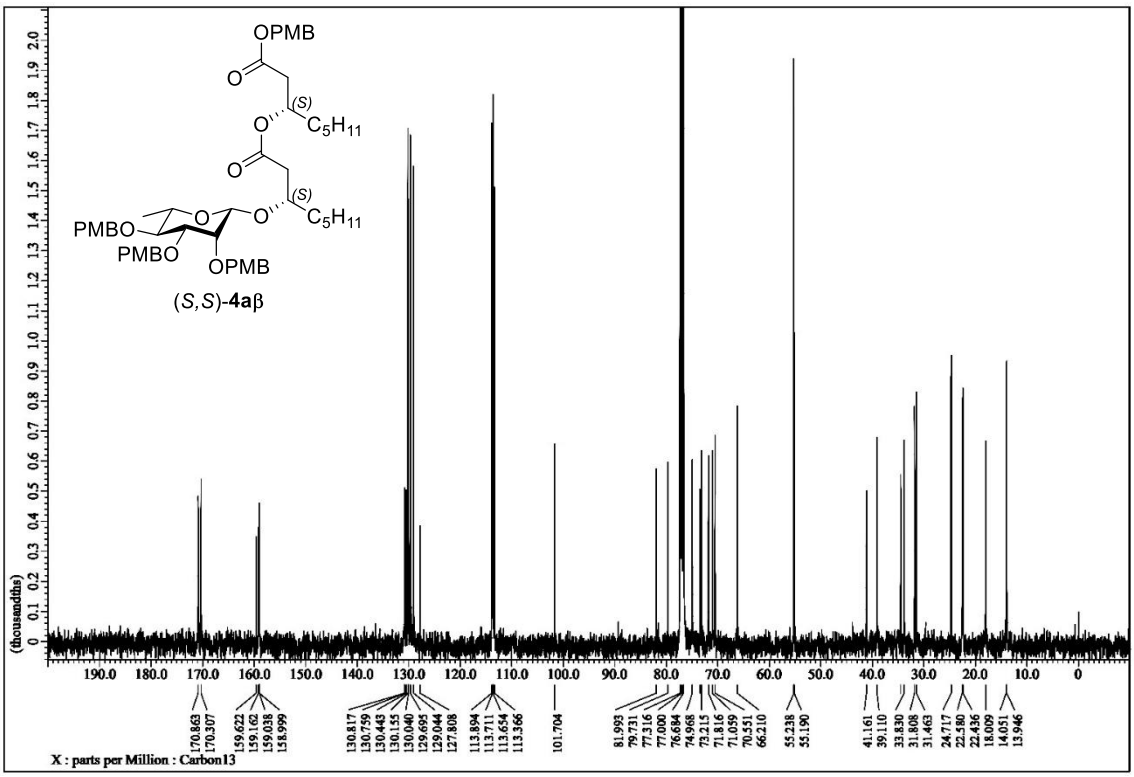

Fig. S96 ^{13}C-NMR spectrum of (*S,S*)-**4aβ** (100MHz, $CDCl_3$)

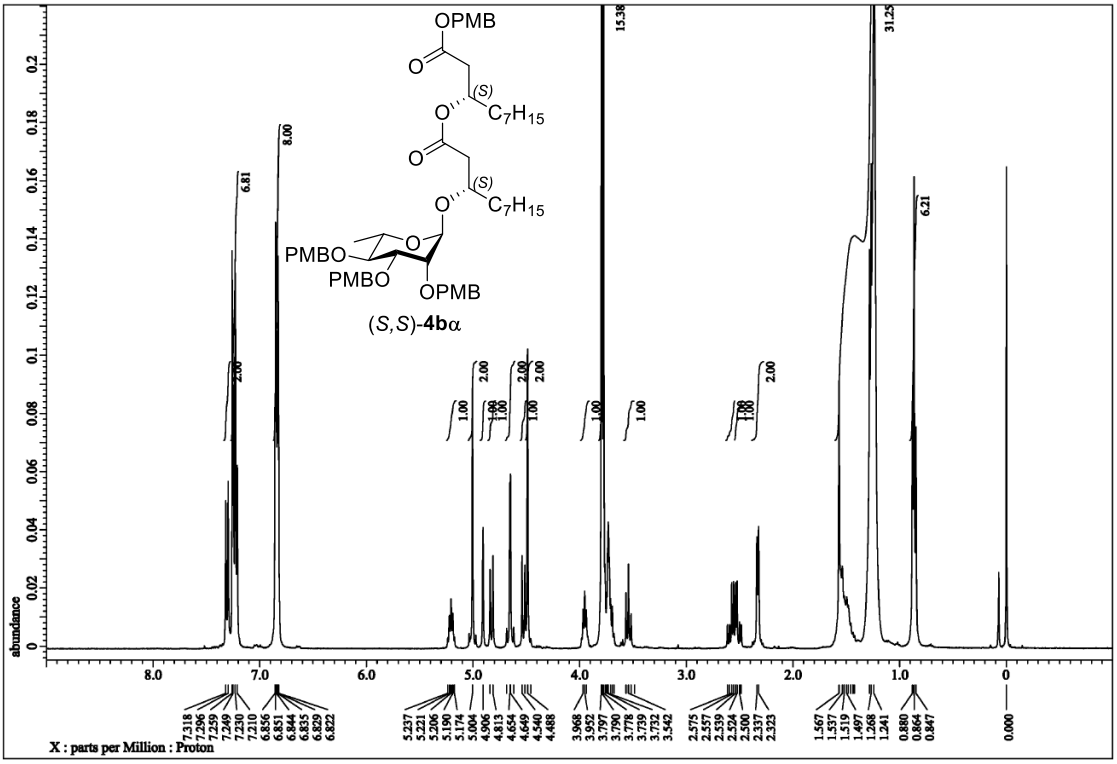

Fig. S97 ^{1}H-NMR spectrum of (*S,S*)-**4bα** (400MHz, $CDCl_3$)

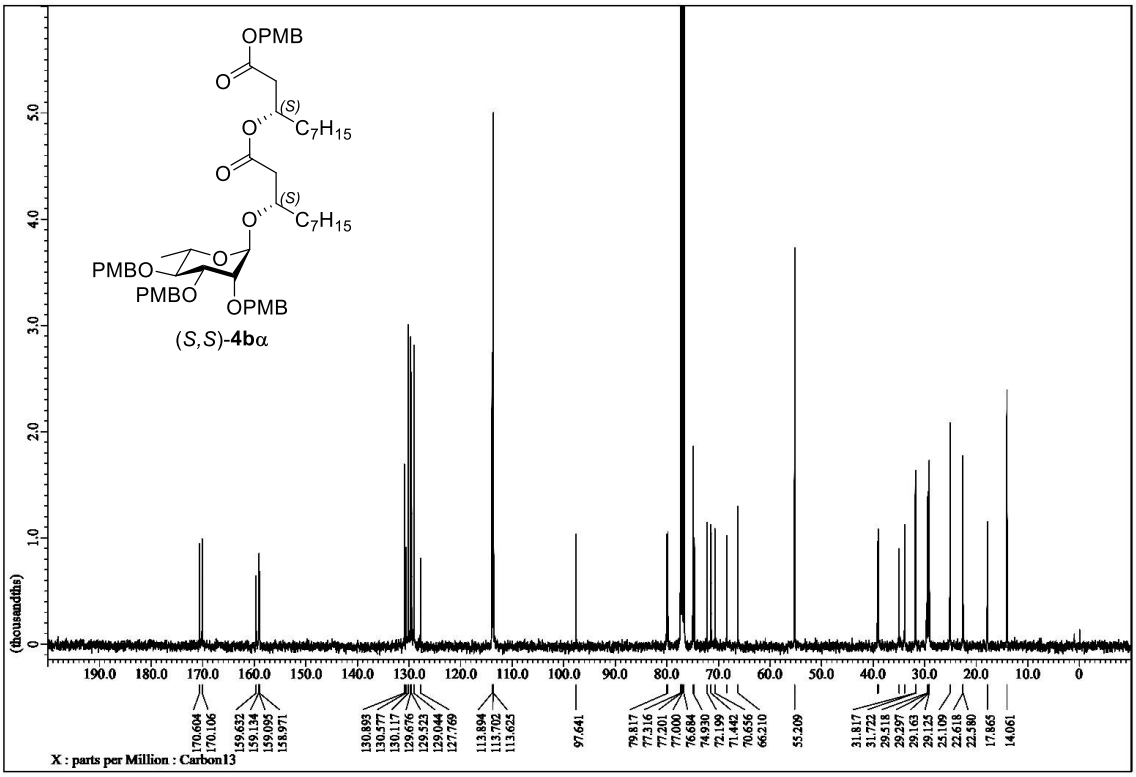

Fig. S98 ^{13}C-NMR spectrum of (*S,S*)-**4bα** (100MHz, $CDCl_3$)

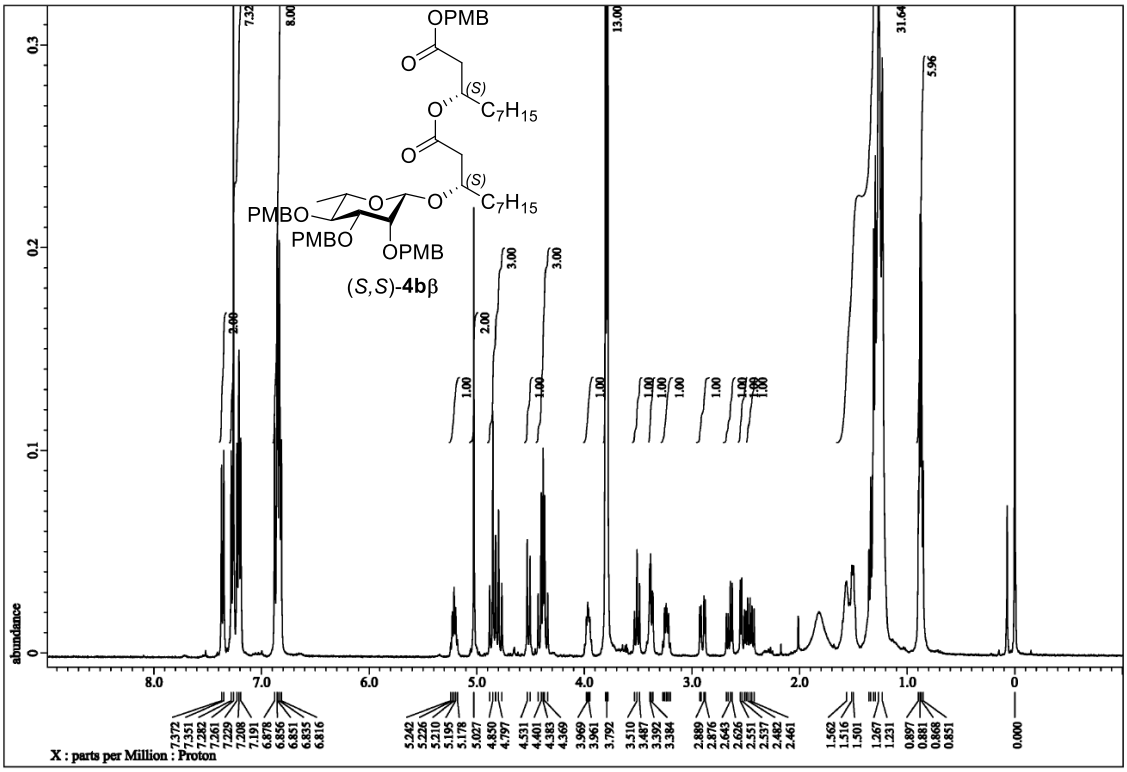

Fig. S99 ^{1}H-NMR spectrum of (*S,S*)-**4bβ** (400MHz, $CDCl_3$)

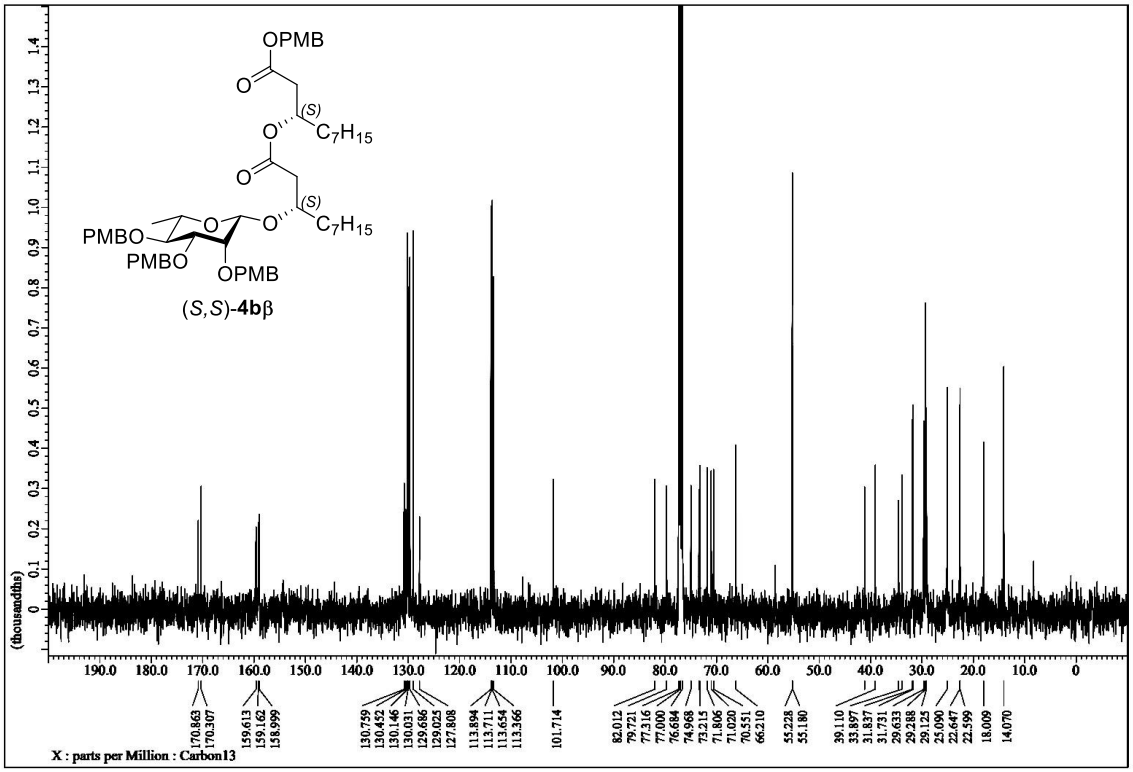

Fig. S100 ^{13}C-NMR spectrum of (*S,S*)-**4bβ** (100MHz, $CDCl_3$)

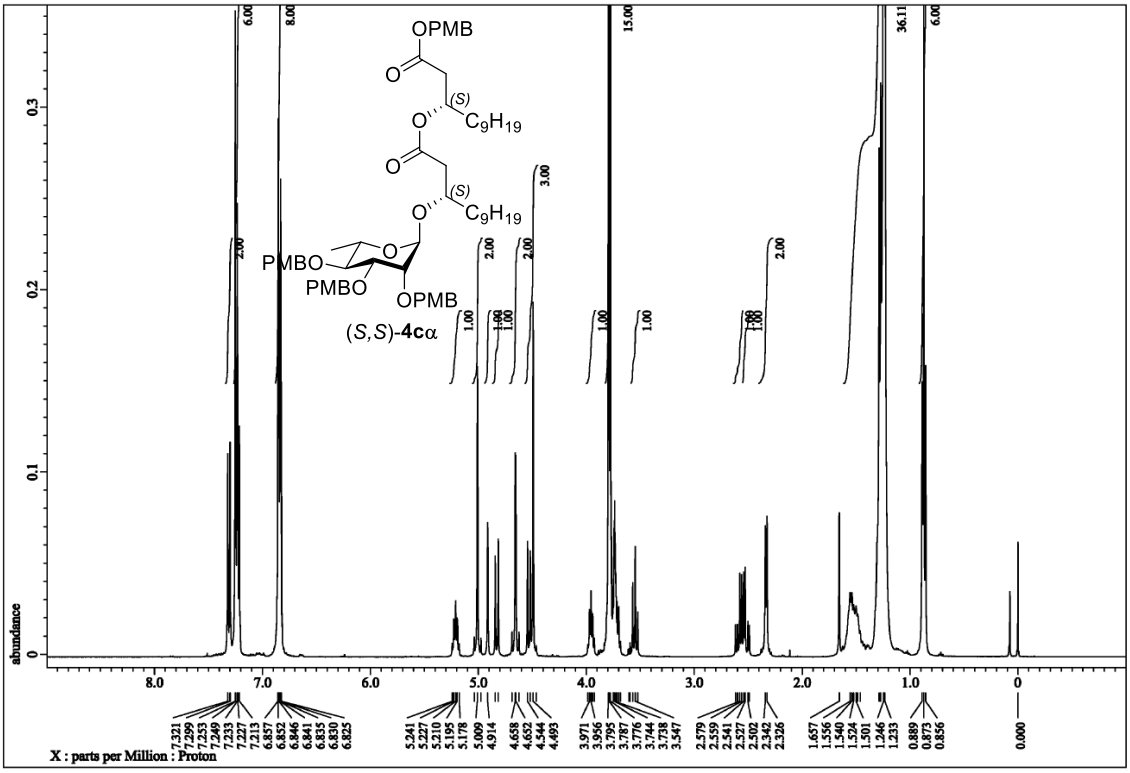

Fig. S101 ^{1}H-NMR spectrum of (*S,S*)-**4cα** (400MHz, $CDCl_3$)

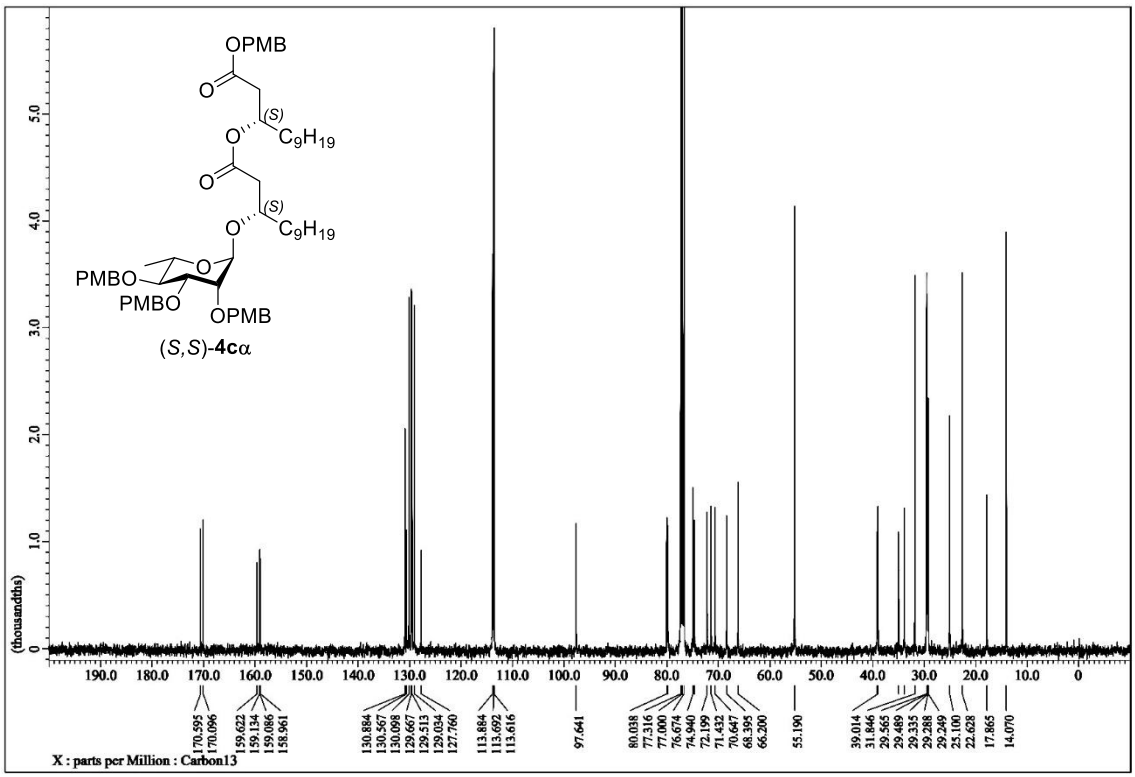

Fig. S102 ^{13}C-NMR spectrum of (*S,S*)-**4cα** (100MHz, $CDCl_3$)

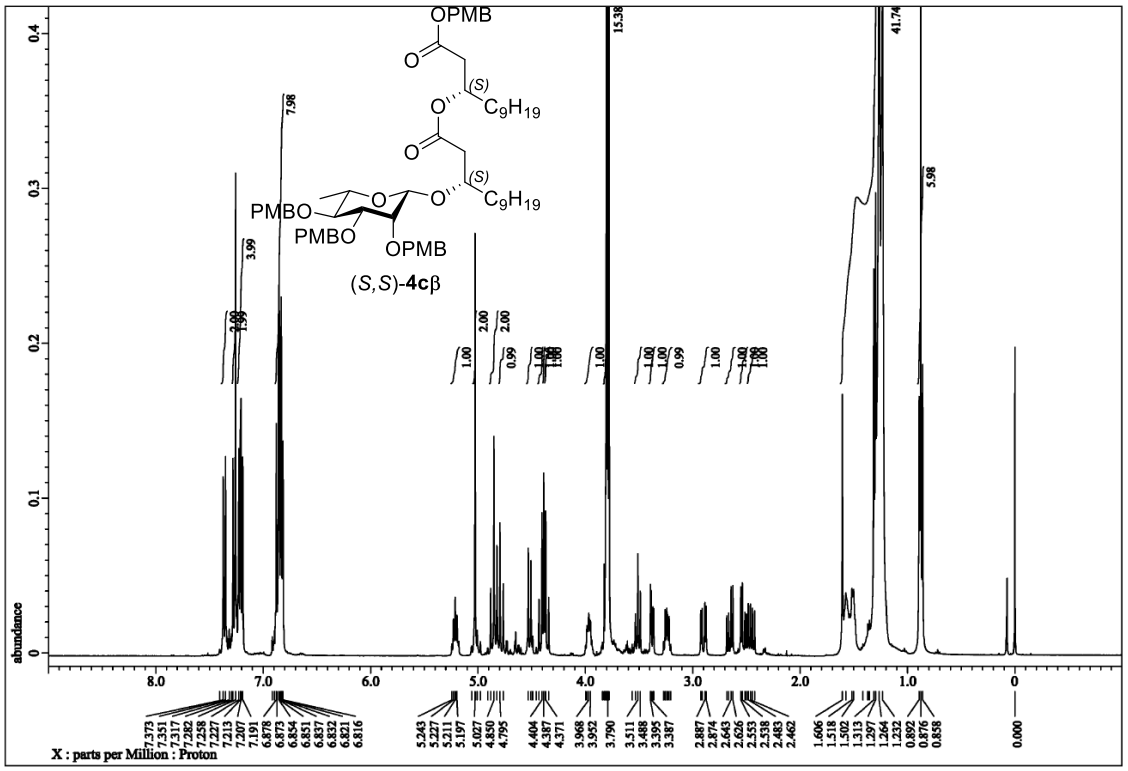

Fig. S103 ^{1}H-NMR spectrum of (*S,S*)-**4cβ** (400MHz, $CDCl_3$)

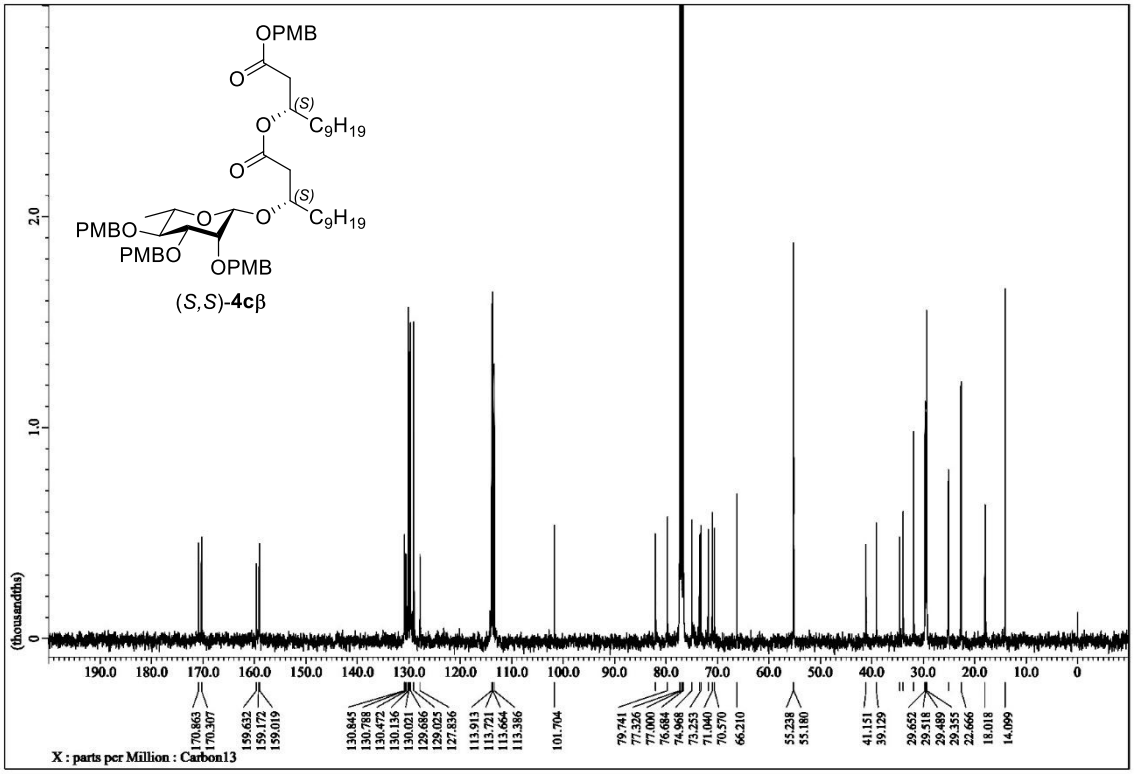

Fig. S104 ^{13}C-NMR spectrum of (*S,S*)-**4cβ** (100MHz, $CDCl_3$)

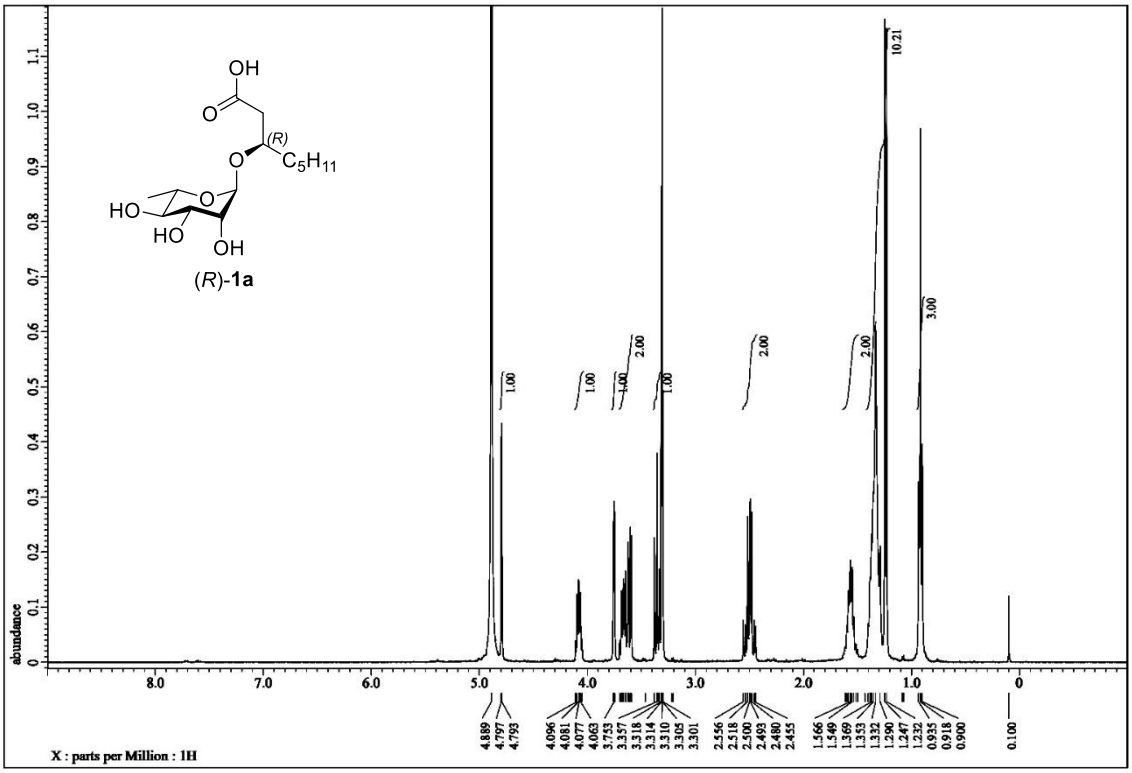

Fig. S105 ^{1}H-NMR spectrum of (*R*)-**1a** (400MHz, CD_3OD)

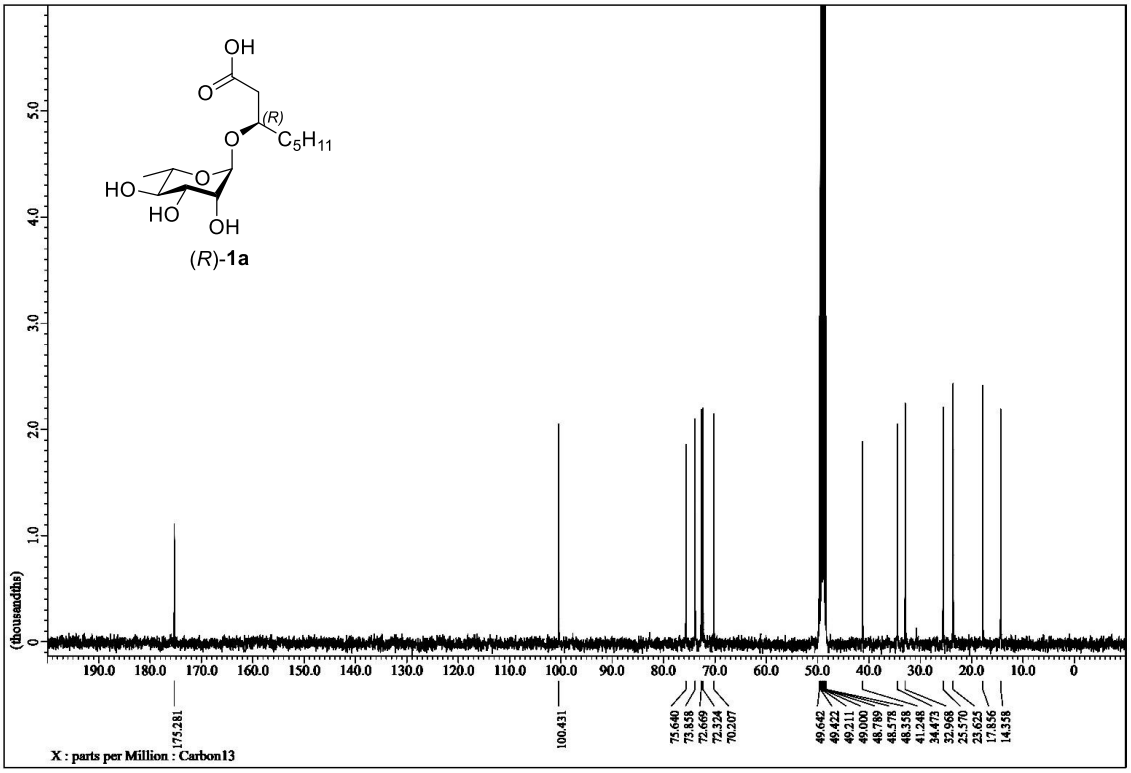

Fig. S106 ^{13}C-NMR spectrum of (*R*)-**1a** (100MHz, CD_3OD)

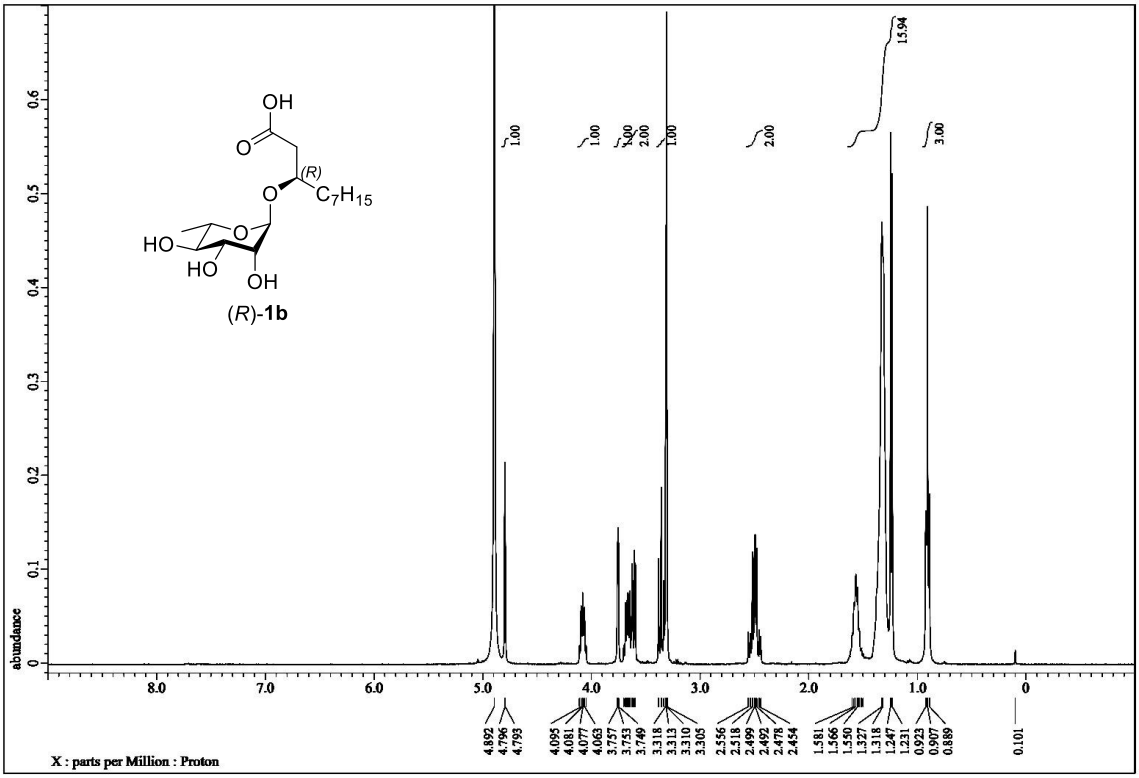

Fig. S107 ^{1}H-NMR spectrum of (*R*)-**1b** (400MHz, CD_3OD)

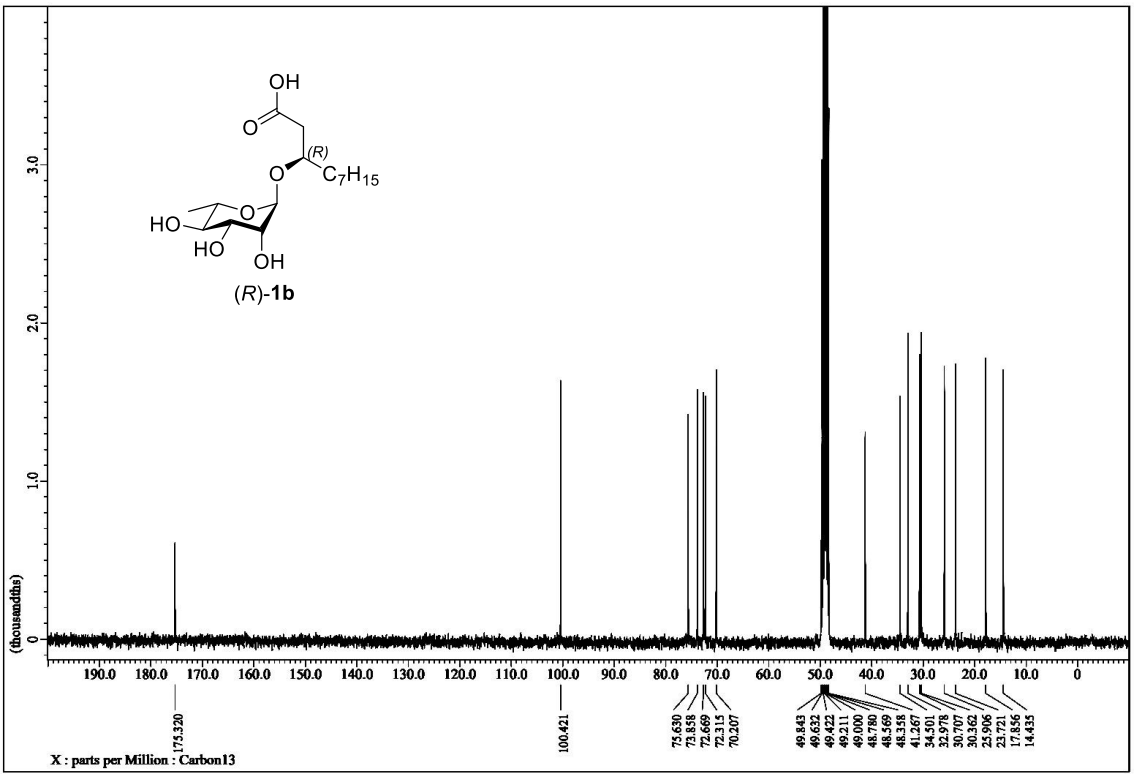

Fig. S108 ^{13}C-NMR spectrum of (*R*)-**1b** (100MHz, CD_3OD)

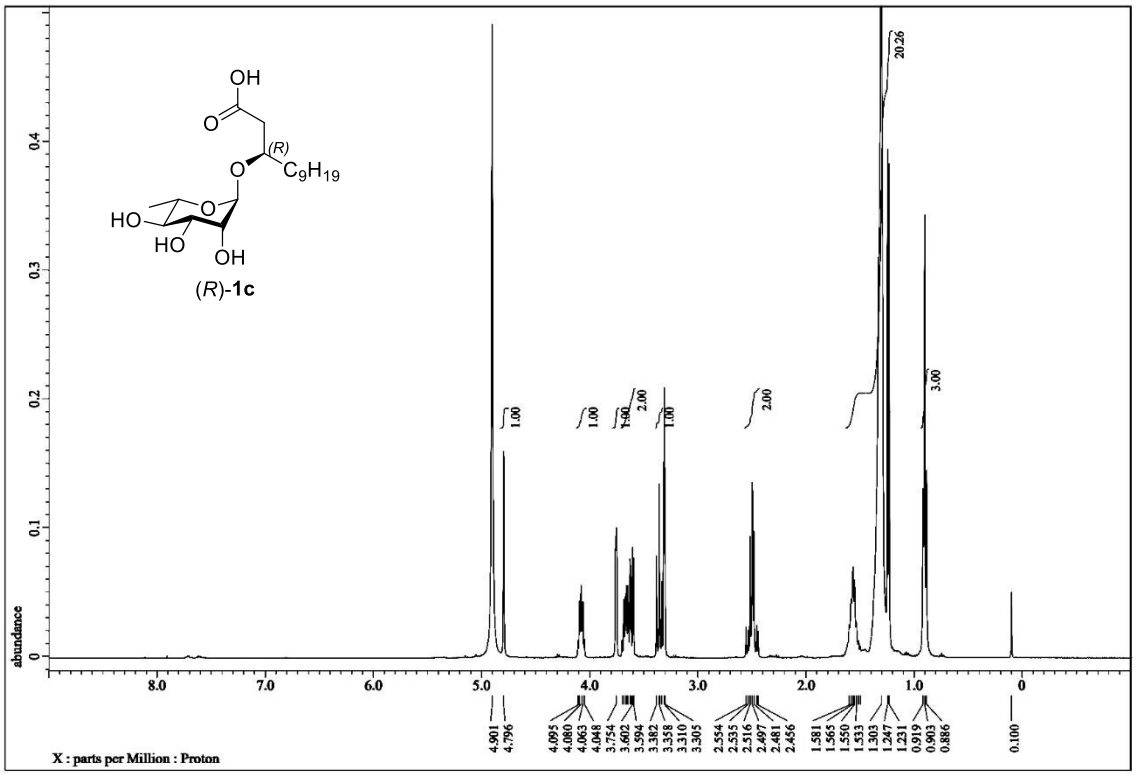

Fig. S109 ^{1}H-NMR spectrum of (*R*)-**1c** (400MHz, CD_3OD)

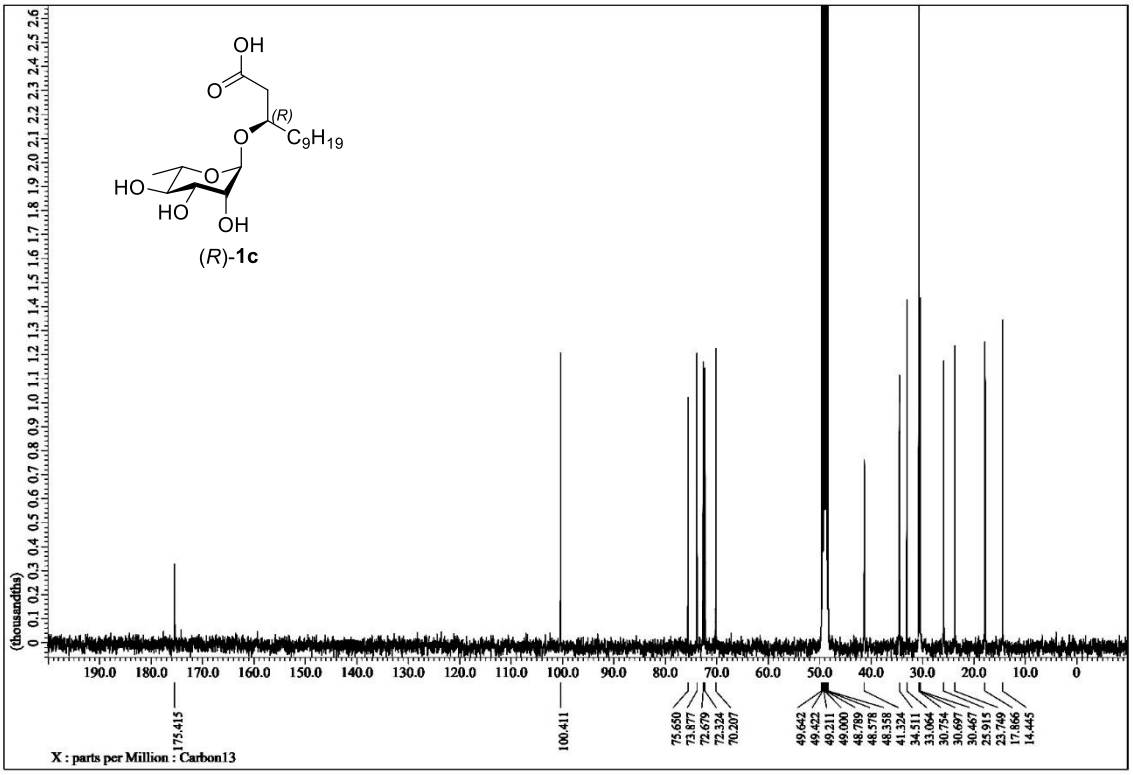

Fig. S110 ^{13}C-NMR spectrum of (*R*)-**1c** (100MHz, CD_3OD)

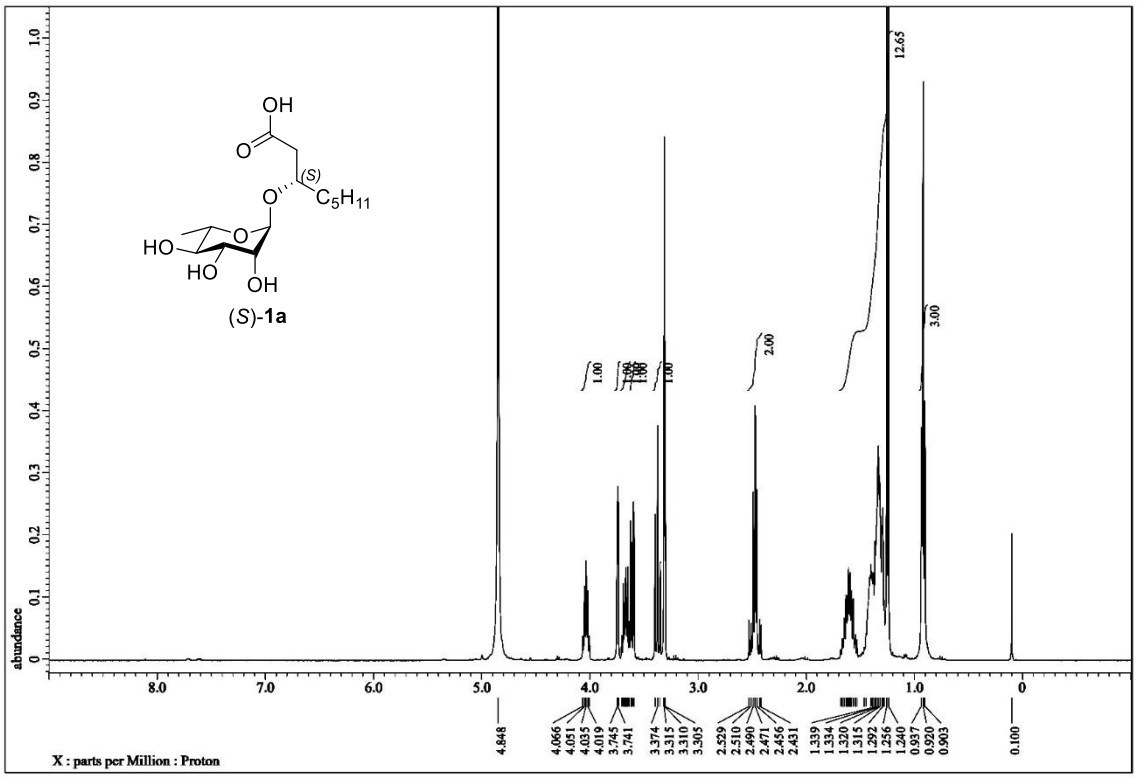

Fig. S111 ^{1}H-NMR spectrum of (*S*)-**1a** (400MHz, CD_3OD)

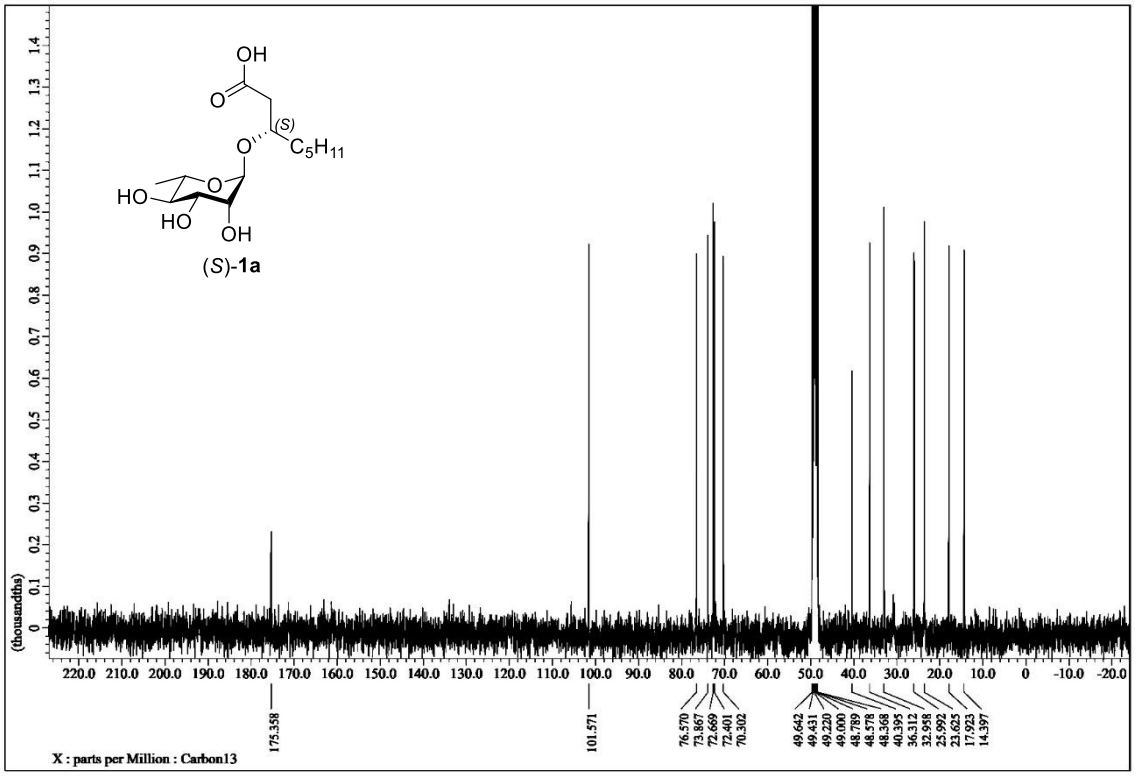

Fig. S112 ^{13}C-NMR spectrum of (*S*)-**1a** (100MHz, CD_3OD)

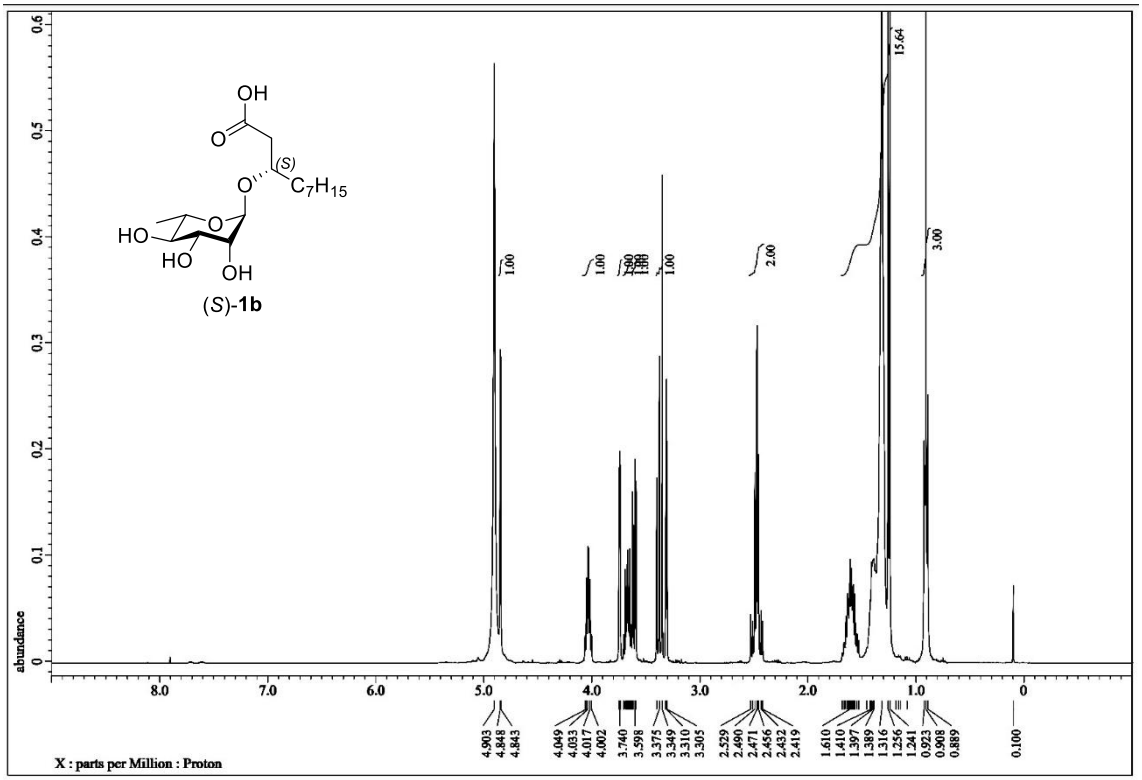

Fig. S113 ^{1}H-NMR spectrum of (*S*)-**1b** (400MHz, CD_3OD)

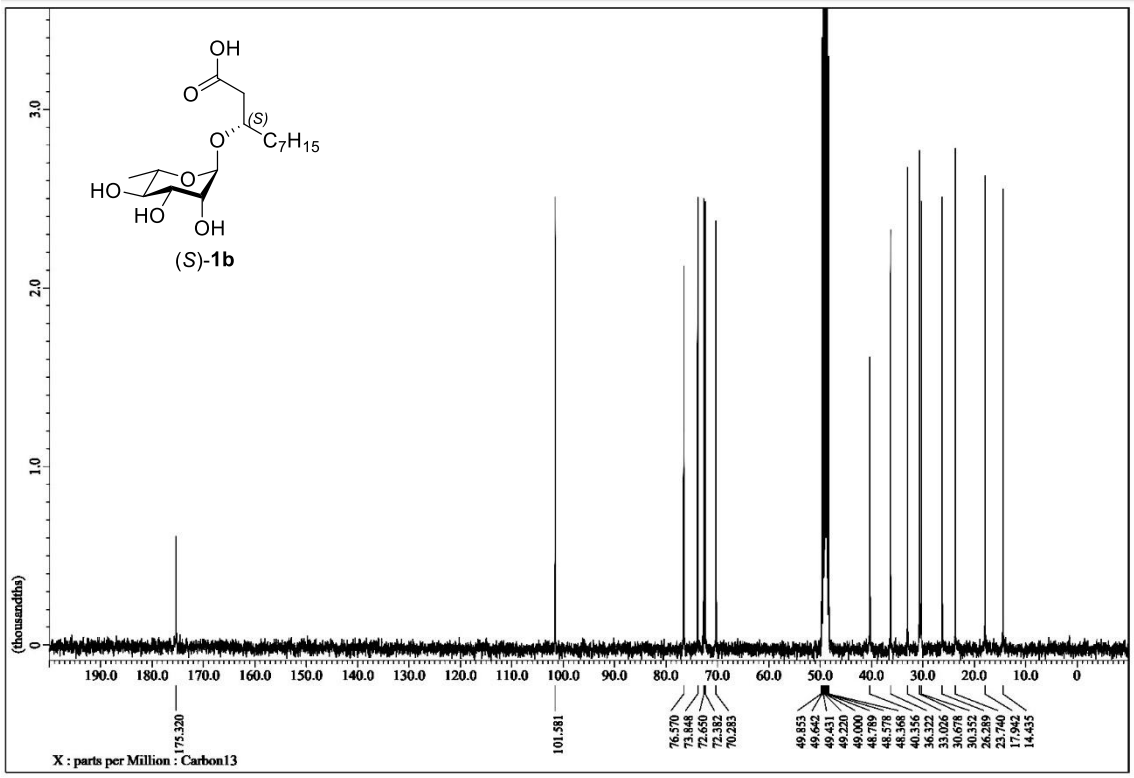

Fig. S114 ^{13}C-NMR spectrum of (*S*)-**1b** (100MHz, CD_3OD)

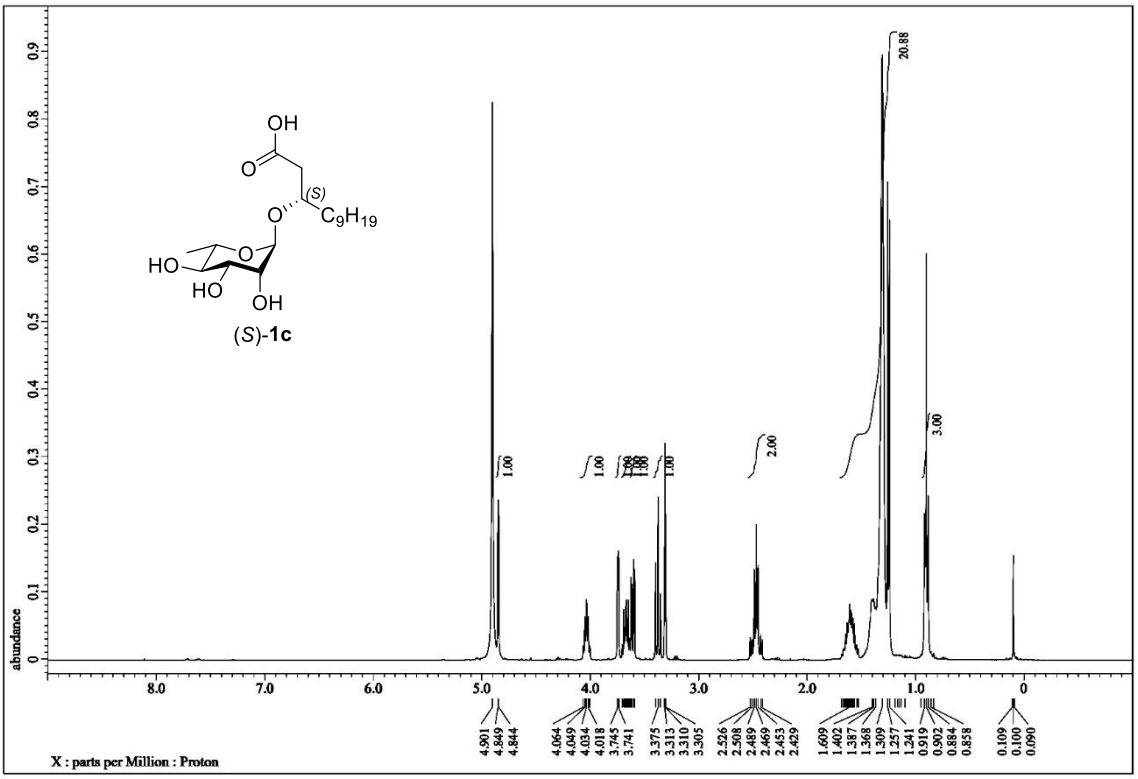

Fig. S115 ^{1}H-NMR spectrum of (*S*)-**1c** (400MHz, CD_3OD)

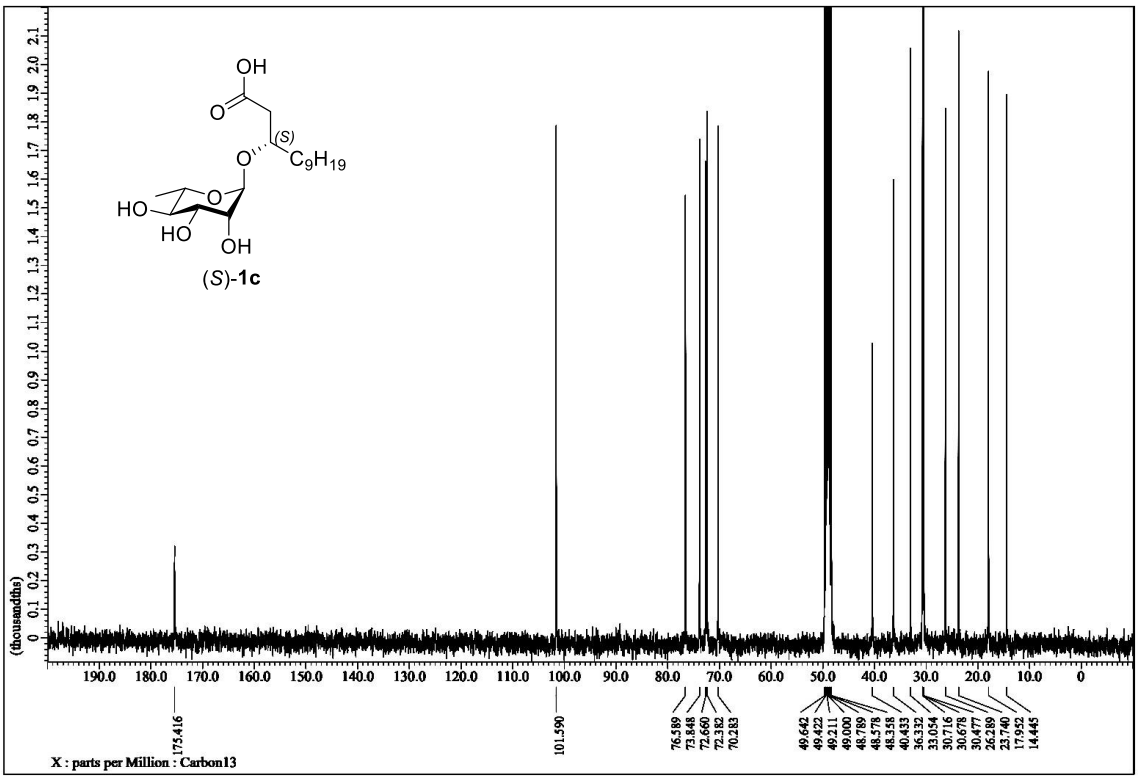

Fig. S116 ^{13}C-NMR spectrum of (*S*)-**1c** (100MHz, CD_3OD)

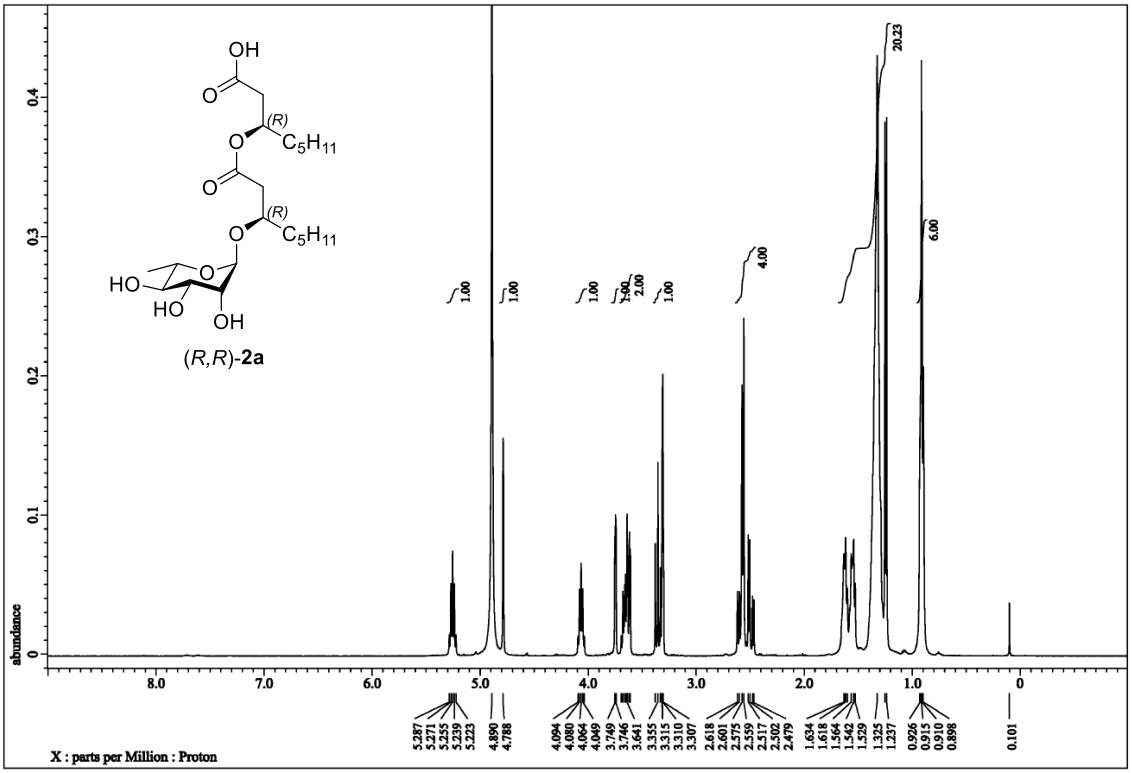

Fig. S117 ^{1}H-NMR spectrum of (*R,R*)-**2a** (400MHz, CD_3OD)

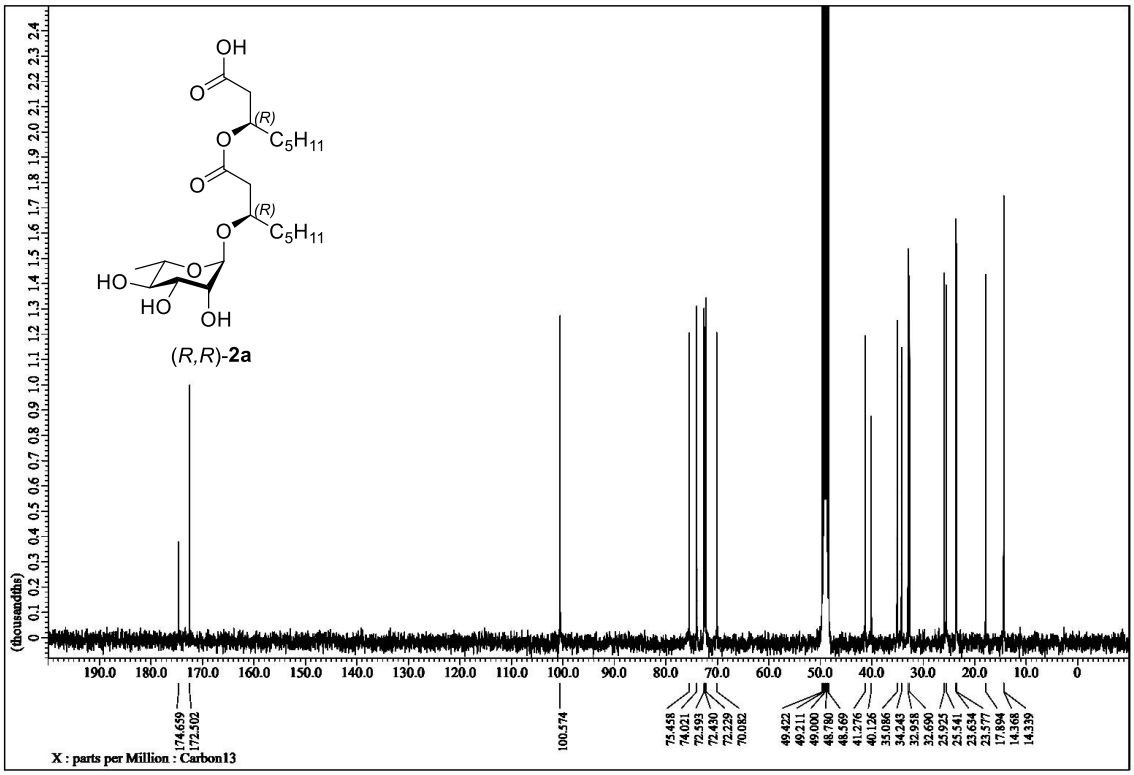

Fig. S118 ^{13}C-NMR spectrum of (*R,R*)-**2a** (100MHz, CD_3OD)

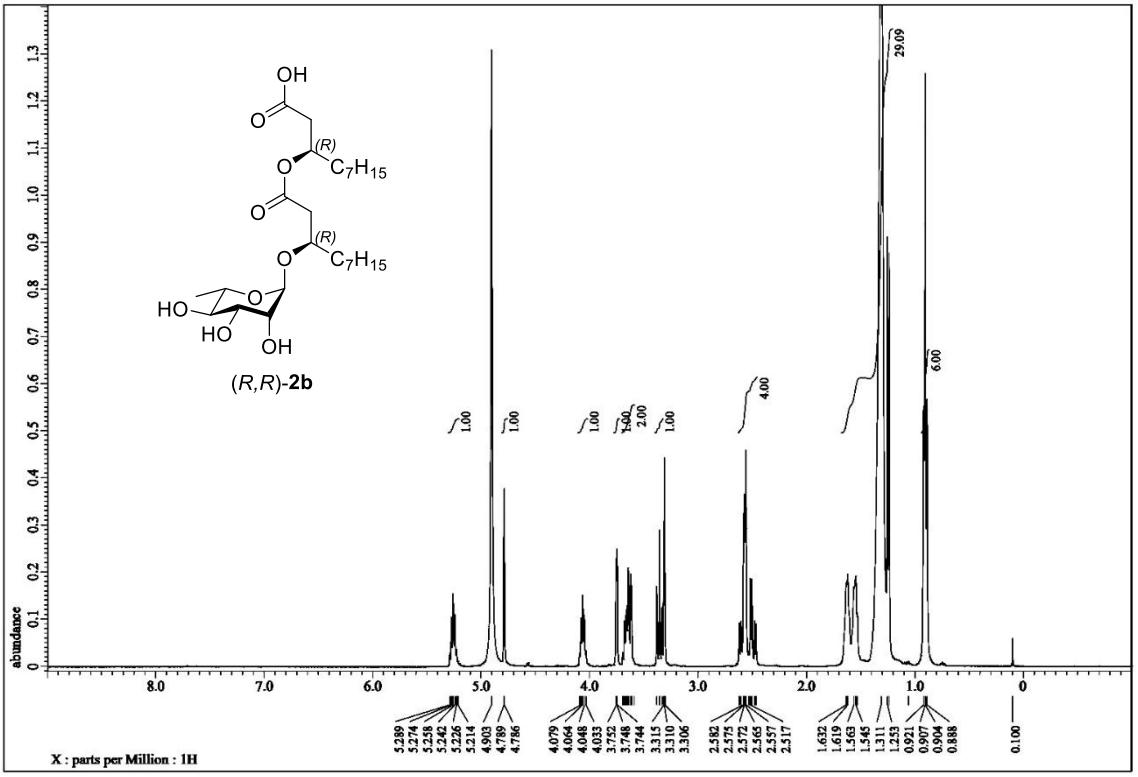

Fig. S119 ^{1}H-NMR spectrum of (*R,R*)-**2b** (400MHz, CD_3OD)

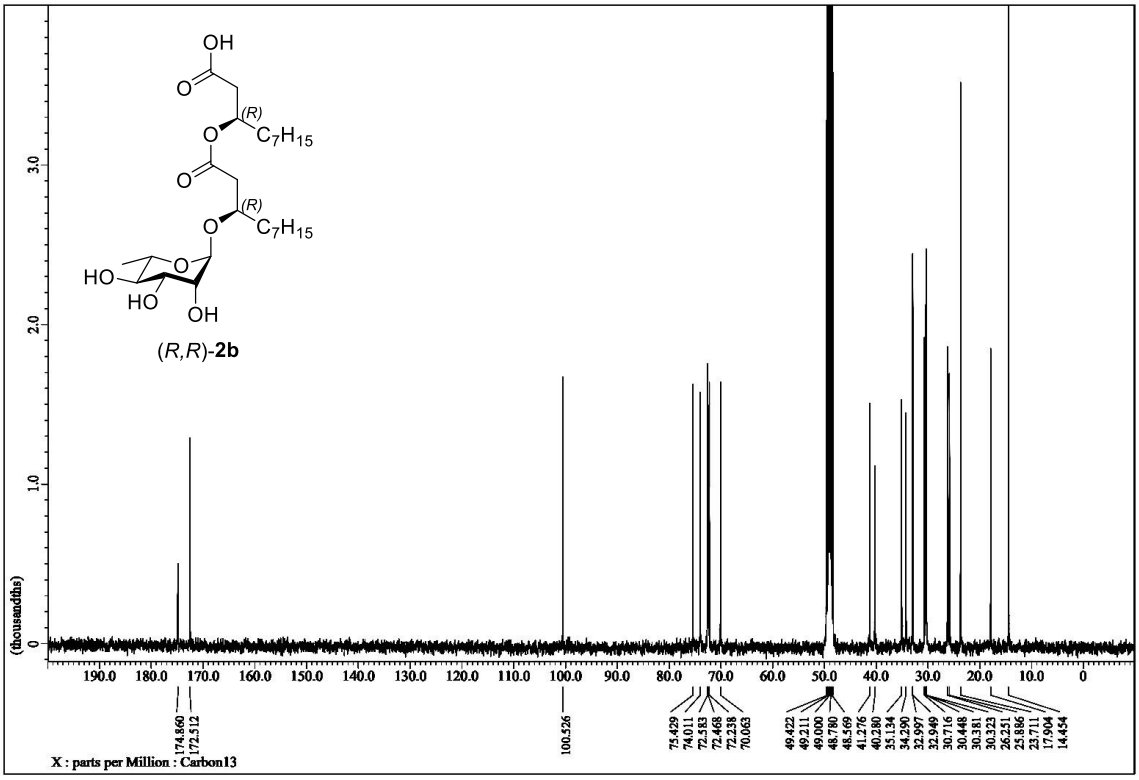

Fig. S120 ^{13}C-NMR spectrum of (*R,R*)-**2b** (100MHz, CD_3OD)

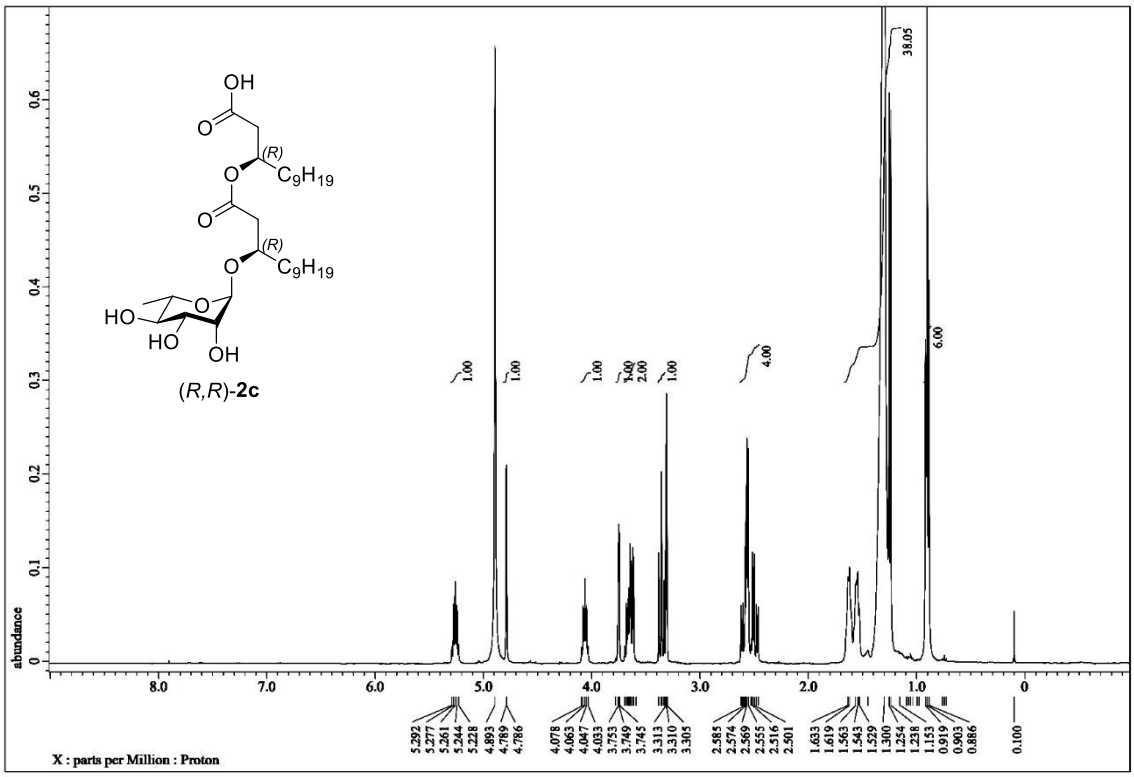

Fig. S121 ^{1}H-NMR spectrum of (*R,R*)-**2c** (400MHz, CD_3OD)

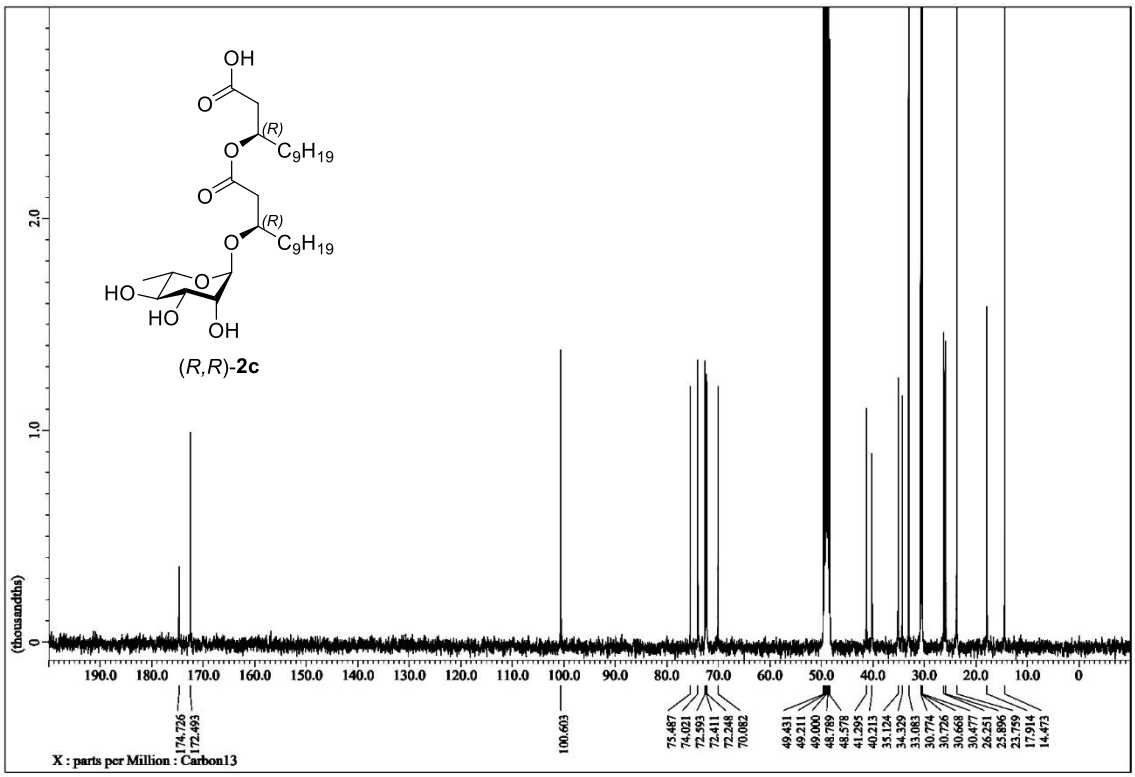

Fig. S122 ^{13}C-NMR spectrum of (*R,R*)-**2c** (100MHz, CD_3OD)

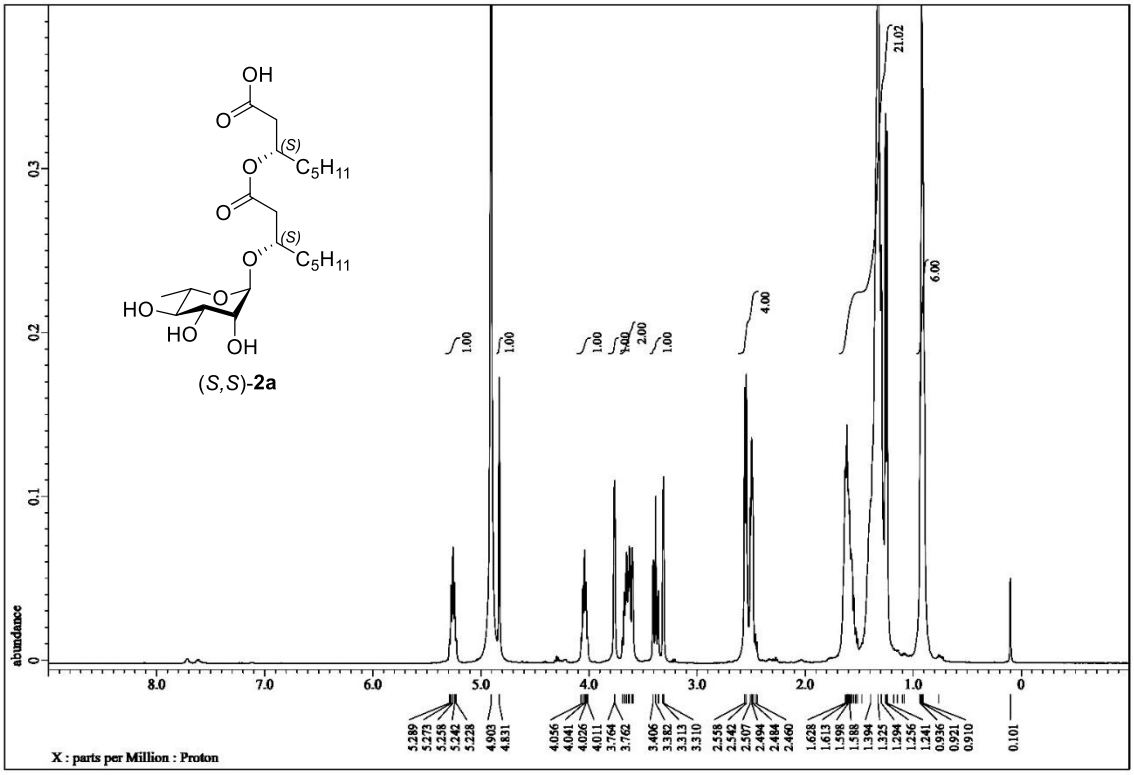

Fig. S123 ^{1}H-NMR spectrum of (*S,S*)-**2a** (400MHz, CD_3OD)

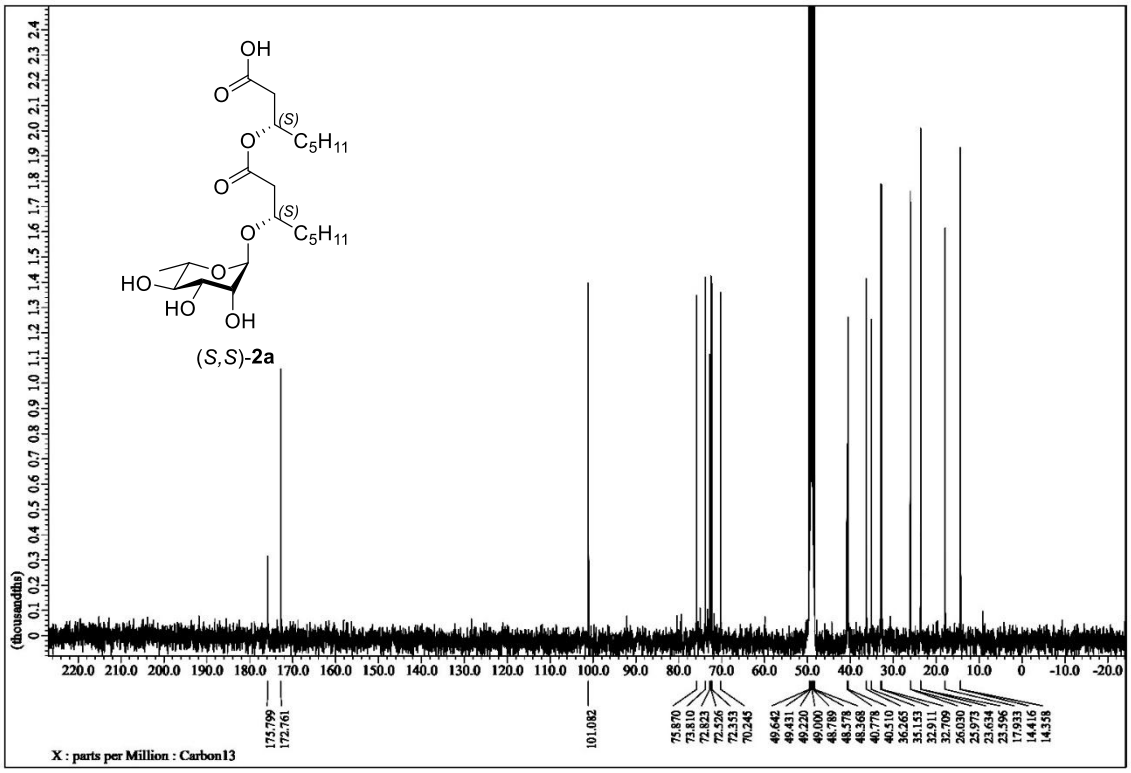

Fig. S124 ^{13}C-NMR spectrum of (*S,S*)-**2a** (100MHz, CD_3OD)

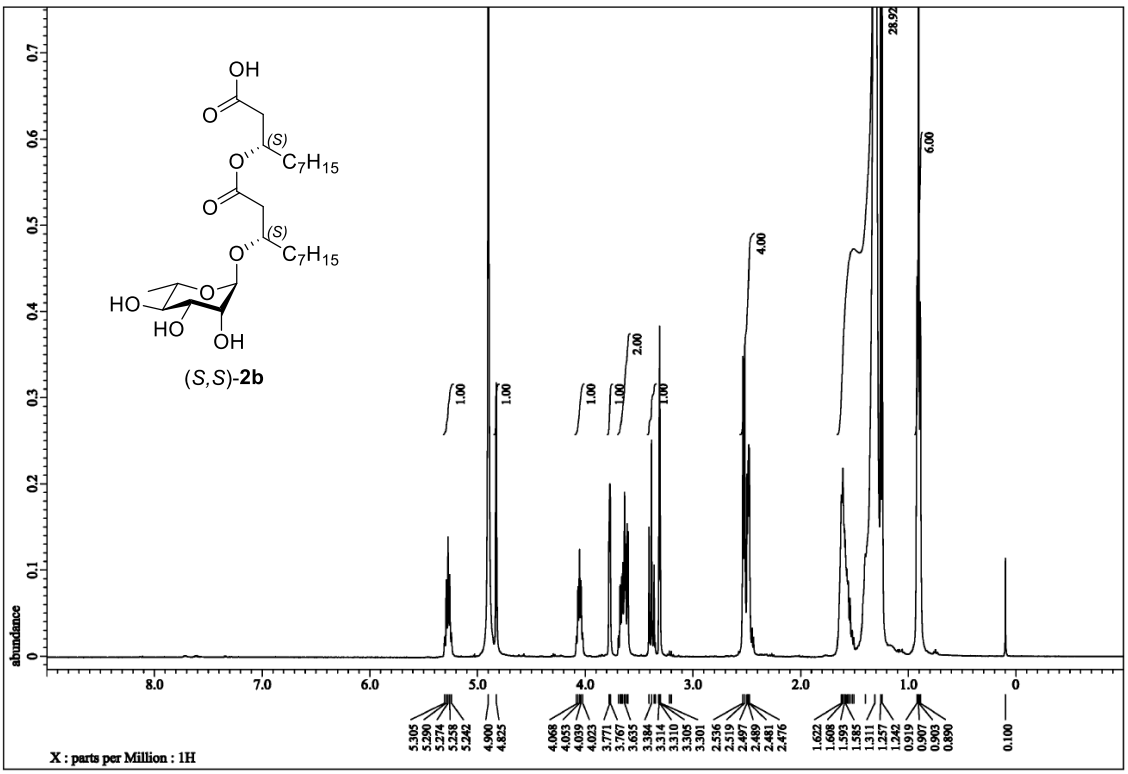

Fig. S125 ^{1}H-NMR spectrum of (*S,S*)-**2b** (400MHz, CD_3OD)

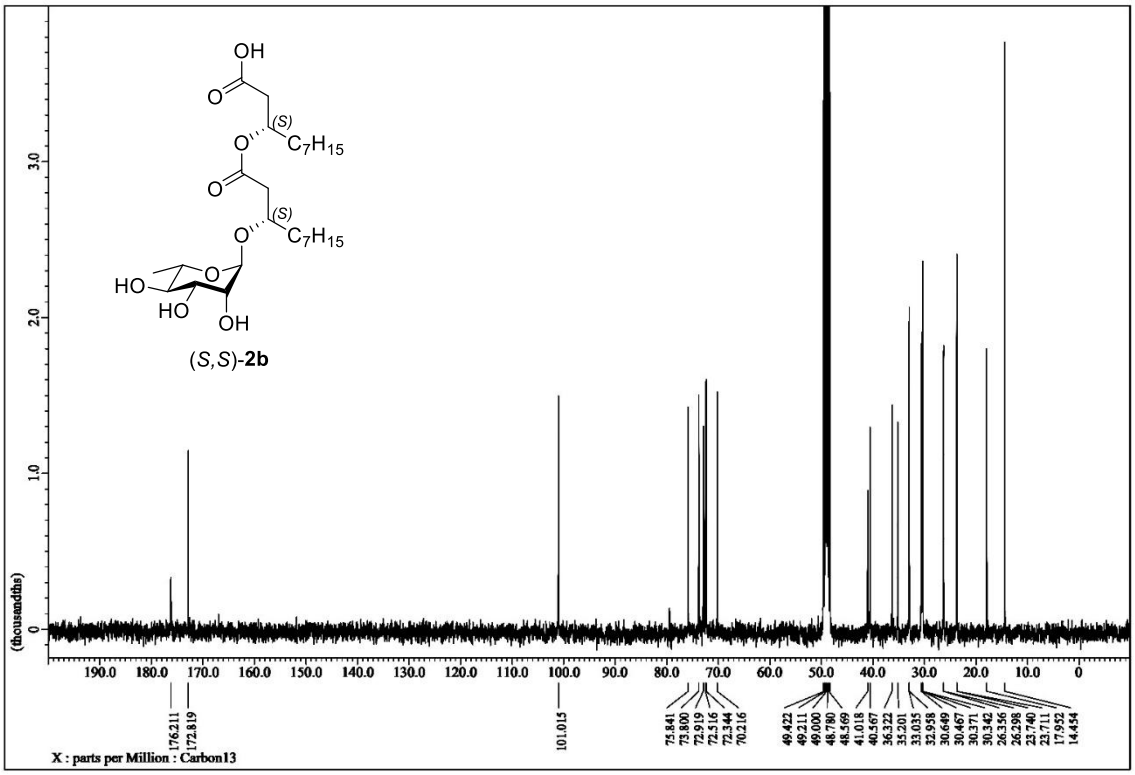

Fig. S126 ^{13}C-NMR spectrum of (*S,S*)-**2b** (100MHz, CD_3OD)

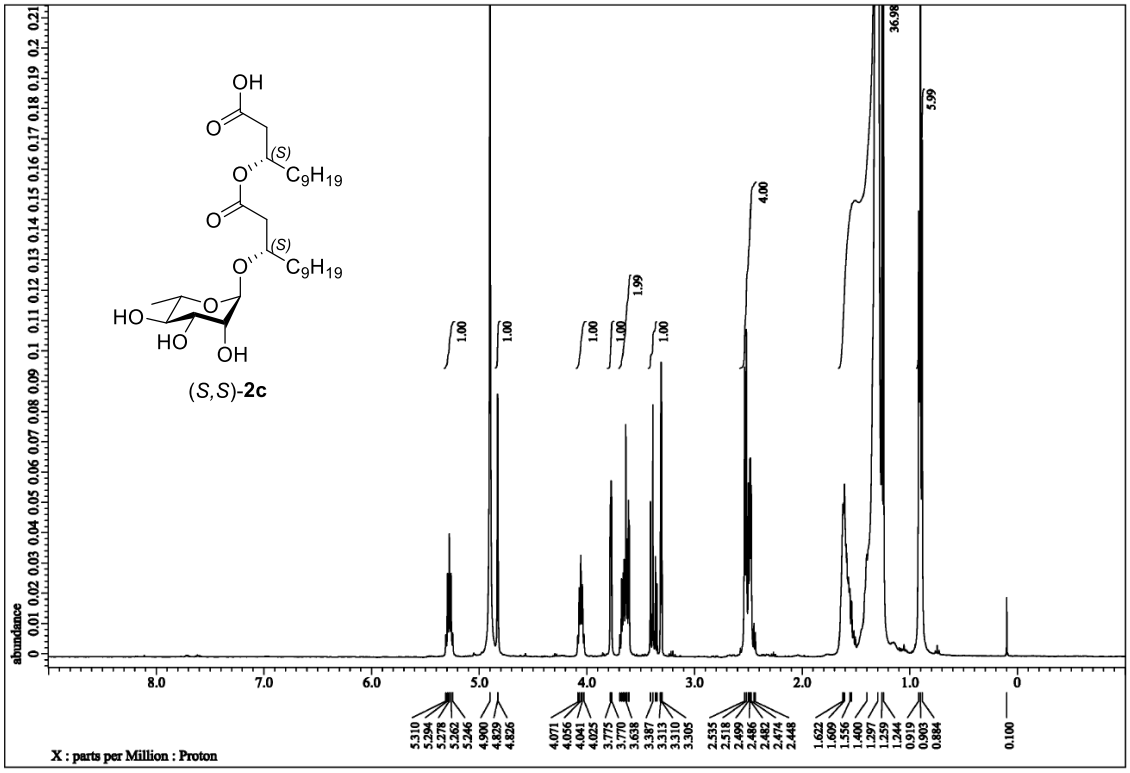

Fig. S127 ^{1}H-NMR spectrum of (*S,S*)-**2c** (400MHz, CD_3OD)

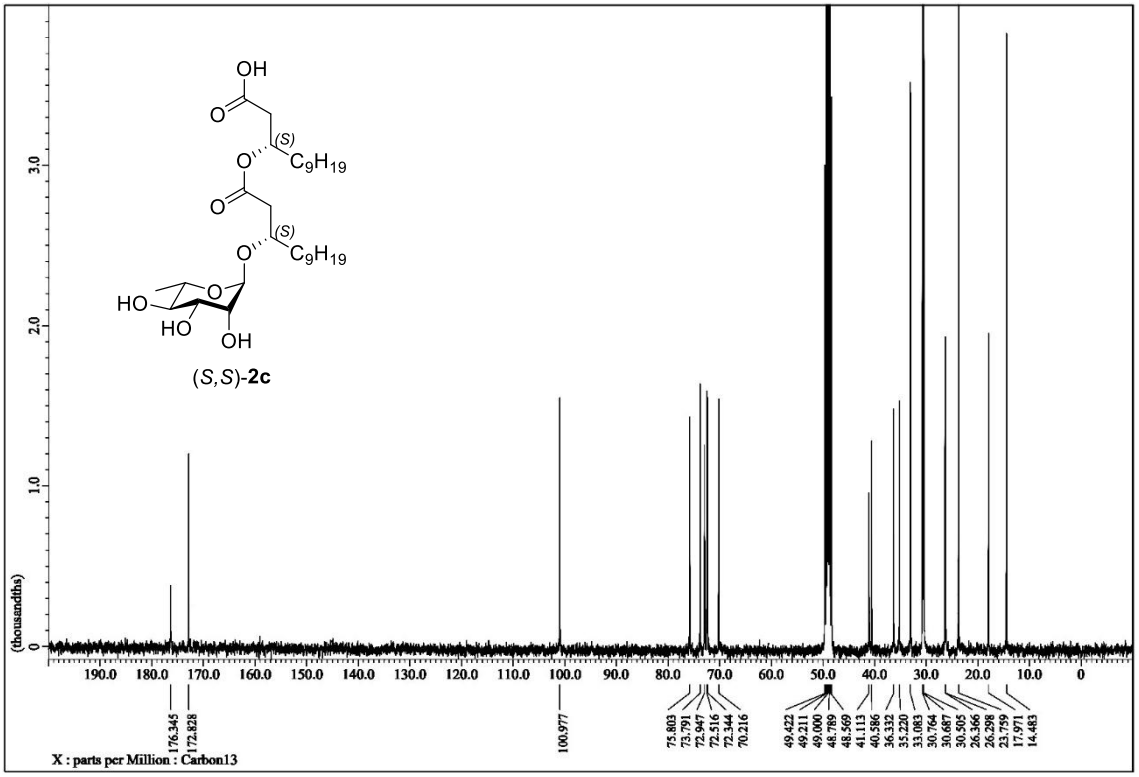

Fig. S128 ^{13}C-NMR spectrum of (*S,S*)-**2c** (100MHz, CD_3OD)

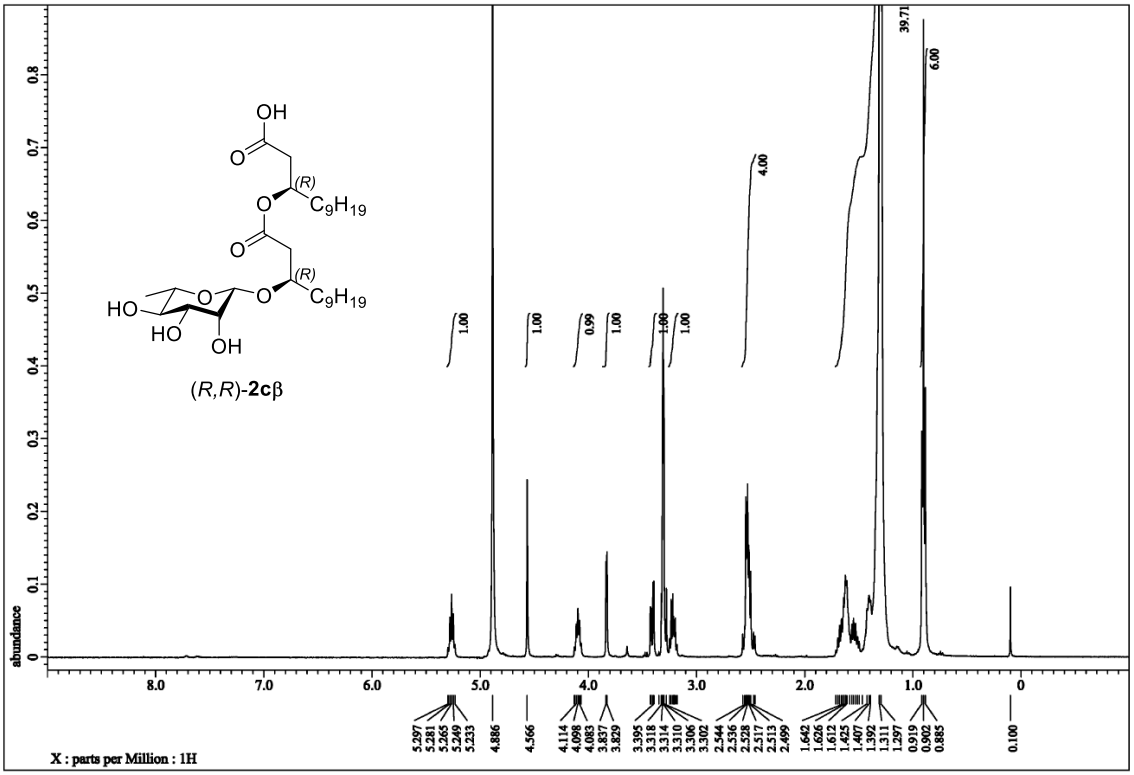

Fig. S129 ^{1}H-NMR spectrum of (*R,R*)-**2cβ** (400MHz, CD_3OD)

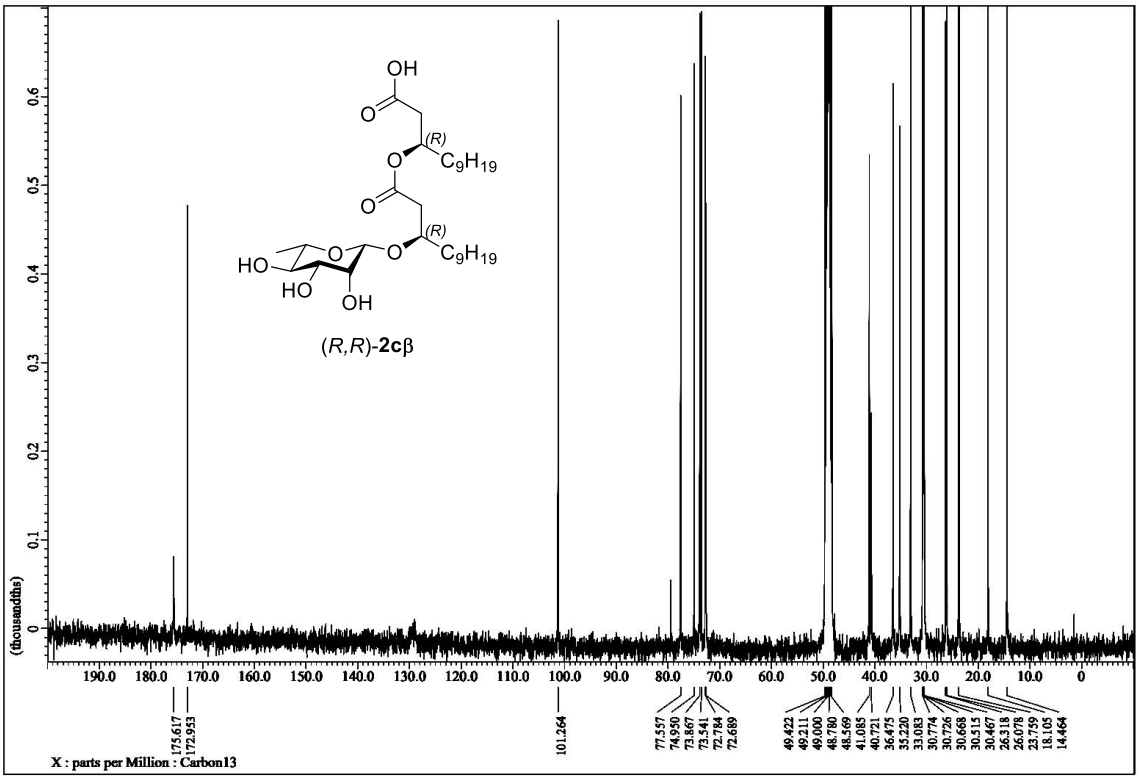

Fig. S130 ^{13}C-NMR spectrum of (*R,R*)-**2cβ** (100MHz, CD_3OD)

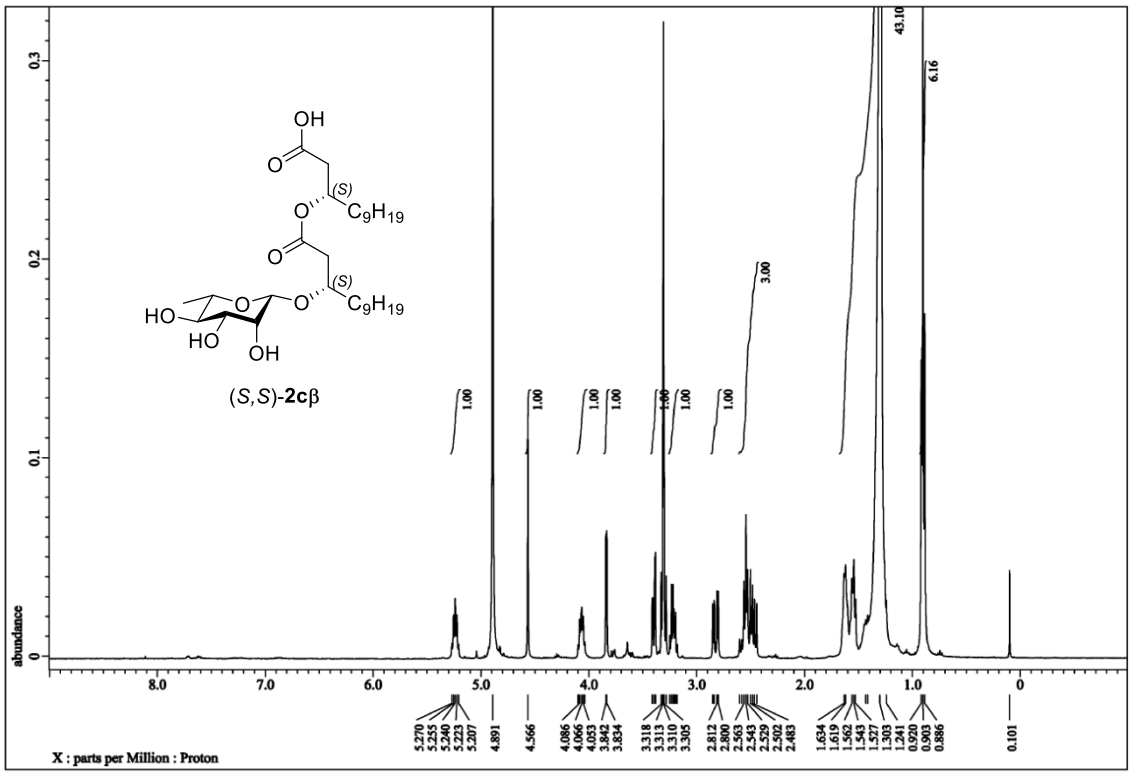

Fig. S131 ^{1}H-NMR spectrum of (*S,S*)-**2cβ** (400MHz, CD_3OD)

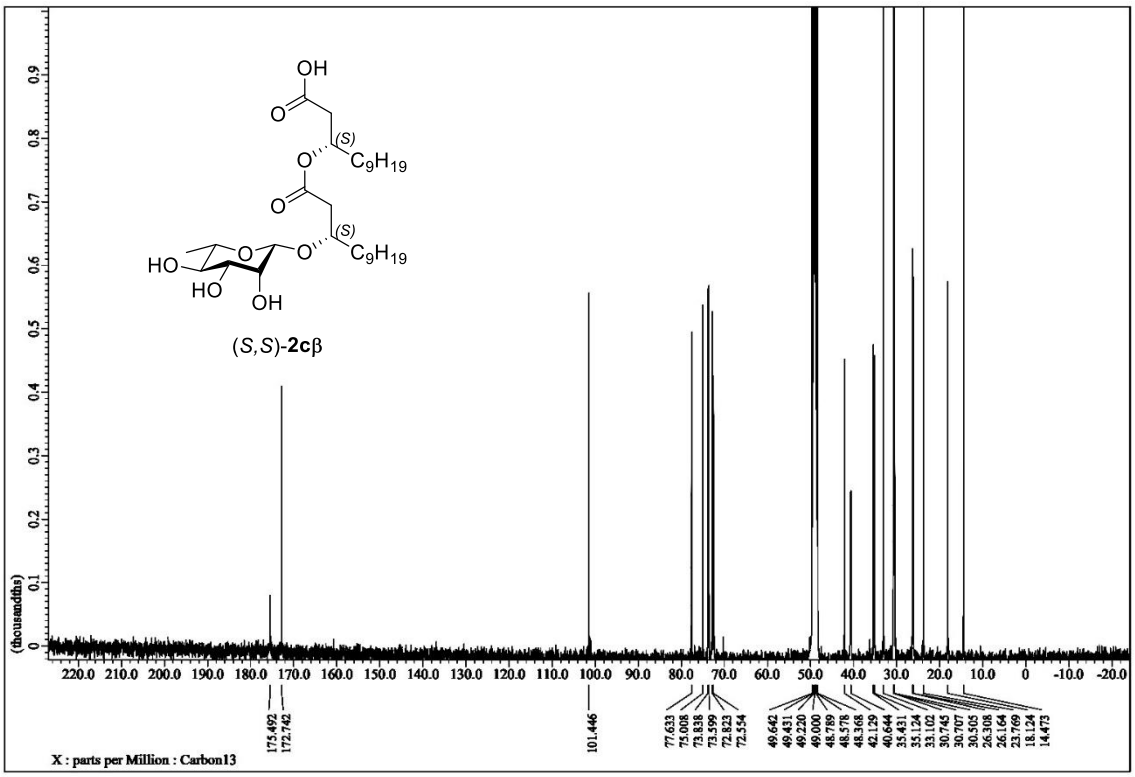

Fig. S132 ^{13}C-NMR spectrum of (*S,S*)-**2cβ** (100MHz, CD_3OD)