Supporting Information-1 (SI and NMR spectra I) for:

Total Synthesis of Agelagalastatin

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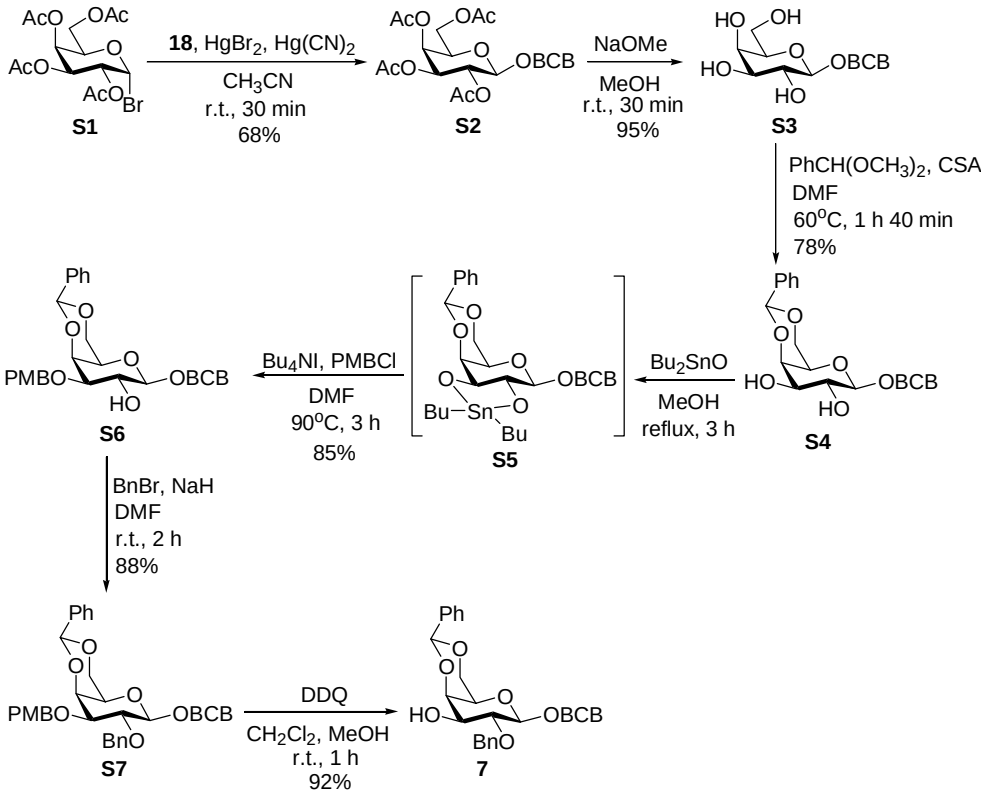
General Methods. All reactions were conducted under a positive pressure of dry argon with dry, freshly distilled solvents unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Dichloromethane and acetonitrile were distilled from calcium hydride and DMF was distilled from barium oxide. Ethyl acetate and toluene were distilled. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization on TLC was achieved by UV light (254 nm) and a typical TLC indication solution (cerium sulfate / molybdic acid solution). NMR spectra were recorded on a 250 or 500 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane (TMS). IR spectra were obtained on a Nicolet Impact 400 spectrometer. MALDI-TOF was performed by the 4700 proteomics analyzer, HRMS-FAB by JEOL, JMS-AX505WA, HP 5890 Series II.



SI-Scheme 1. Preparation of monosaccharide **7**.

2′-(Benzyloxycarbonyl)benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (S2). To a stirred solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**S1**) (5.0 g, 12.16 mmol) in acetonitrile (20 mL) at 0 °C were added mercury (II) bromide (5.26 g, 14.59 mmol), mercury (II) cyanide (3.69 g, 14.61 mmol), and benzyl 2-hydroxymethylbenzoate (**18**) (4.4 g, 18.16 mmol). After stirring at 0 °C for further 30 min, the reaction mixture was filtered and the filtrate was concentrated. The resulting oil was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo and the residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1, v/v) to afford the title compound **S2** (4.74 g, 8.28 mmol,

86%) as a colorless oil.: R_f = 0.25 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 1225, 1713, 1751 cm^{-1}; $[\alpha]_D^{20}$ −27.7 (*c* 1.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 2.00 (s, 3 H), 2.03 (s, 3 H), 2.06 (s, 3 H), 2.17 (s, 3 H), 3.91 (t, *J* = 6.7 Hz, 1 H), 4.11−4.19 (m, 2 H), 4.59 (d, *J* = 7.9 Hz, 1 H), 5.01−5.10 (m, 2 H), 5.31−5.42 (m, 5 H), 7.31−7.65 (m, 8 H), 8.03 (d, *J* = 7.8 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 20.7, 20.8(2), 20.9, 61.2, 66.9, 67.1, 69.1, 69.8, 70.8, 71.0, 101.1, 127.3, 127.5, 128.3, 128.5, 128.8, 130.8, 132.8, 135.9, 139.9, 166.6, 169.6, 170.3, 170.4, 170.5. Anal. calcd for $C_{29}H_{32}O_{12}$: C, 60.83; H, 5.63. Found: C, 60.81; H, 5.72.

2′-(Benzyloxycarbonyl)benzyl β-D-galactopyranoside (S3). To a solution of compound **S2** (3.2 g, 5.59 mmol) in MeOH (100 mL) was added NaOMe (54 mg, 1.0 mmol.) at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode), filtered through Celite®, and concentrated in vacuo. The residue was purified by recrystallization (n-hexane/MeOH) to afford the title compound **S3** (2.15 g, 5.32 mmol, 95%) as a white solid.: m.p.= 92−93 °C; R_f = 0.33 ($CHCl_3$/MeOH, 9:1, v/v); IR (KBr) 1256, 1714, 3353 cm^{-1}; $[\alpha]_D^{20}$ −18.8 (*c* 0.5, DMF); ^1H NMR (500 MHz, DMSO-d_6 + H_2O) δ 3.32 (dd, *J* = 3.0, 9.6 Hz, 1 H), 3.37 (t, *J* = 5.8 Hz, 1 H), 3.42 (t, *J* = 8.6 Hz, 1 H), 3.49 (dd, *J* = 6.1, 10.5 Hz, 1 H), 3.54 (dd, *J* = 6.4, 10.8 Hz, 1 H), 3.67 (brs, 1 H), 4.21 (d, *J* = 7.6 Hz, 1 H), 4.91 and 5.10 (ABq, *J* = 14.8 Hz, 2 H), 5.29 (s, 2 H), 7.31−7.59 (m, 7 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 7.86 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, DMSO-d_6 + H_2O) δ 60.8, 66.9, 68.3, 68.5, 71.1, 73.7, 75.5, 103.6, 127.7, 128.1, 128.3, 128.6, 128.7, 129.1, 130.4, 133.0, 136.4, 140.5, 166.9. Anal. calcd for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.19; H, 5.88.

2′-(Benzyloxycarbonyl)benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside (S4). A solution of the compound **S3** (1.0 g, 2.47 mmol) and benzaldehyde dimethylacetal (408 μL, 2.72 mmol) in the presence of camphor sulfonic acid (172 mg, 0.74 mmol) in DMF (20 mL) was stirred at 60 ^{o}C for 1 h 40 min. After quenched with triethylamine (1 mL), the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (2 × 50 mL) , brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by recrystallization (n-hexane/EtOAc) to afford the title compound **S4** (2.80 g, 70%) as a white solid.: m.p.= 177−178 ^{o}C; R_f = 0.15 (hexane/EtOAc/CH_2Cl_2, 2:4:4, v/v); IR (KBr) 1256, 1715, 3378 cm^{-1}; $[\alpha]_D^{20}$ −32.0 (*c* 0.5, DMF); ^{1}H NMR (250 MHz, DMSO-d_6) δ 3.50−3.52 (m, 3 H), 4.05−4.09 (m, 3 H), 4.34−4.37 (m, 1 H), 4.96−4.98 (m, 1 H), 4.97 and 5.17 (ABq, *J* = 15.0 Hz, 2 H), 5.18−5.21 (m, 1 H), 5.34 (s, 2 H), 5.57 (s, 1 H), 7.35−7.65 (m, 13 H), 7.92 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, DMSO-d_6) δ 66.0,66.3, 67.8, 68.6, 70.2, 71.9, 76.0, 99.8, 103.0, 126.3, 127.1, 127.6, 127.9, 128.1, 128.5, 130.0, 132.5, 136.0, 138.6, 140.3, 166.1. Anal. calcd for $C_{28}H_{28}O_8$: C, 68.28; H, 5.73. Found: C, 68.21; H, 5.87.

2'-(Benzyloxycarbonyl)benzyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (S6). To a solution of compound **S4** (3.63 g, 7.37 mmol) in MeOH (30 mL) was added Bu_2SnO (2.75 g, 11.05 mmol). The resulting solution was heated to reflux for 3 h. The solvent was removed and then concentrated in vacuo. The residue was dissolved in DMF (20 mL), then *p*-methoxybenzyl chloride (1.5 mL, 11.06 mmol) and Bu_4NI (4.08 g, 11.04 mmol) were added. The reaction mixture was stirred at 60 °C for 3 h. The reaction mixture was diluted with EtOAc (50 mL) and quenched with saturated aqueous NH_4Cl (7 mL). The combined organic layer was washed with saturated

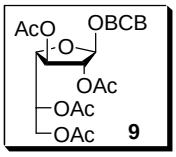
aqueous NH_4Cl (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by recrystallization (n-hexane/EtOAc) to afford the title compound **S6** (3.84 g, 6.27 mmol, 85%) as a white solid.: m.p.= 132−133 °C; R_f = 0.33 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 1255, 1713, 3207 cm^{-1}; $[\alpha]_D^{20}$ +3.7 (*c* 0.6, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 2.77 (brs, 1 H), 3.30 (brs, 1 H), 3.48 (dd, *J* = 3.0, 9.5 Hz, 1 H), 3.77 (s, 3 H), 3.97−4.08 (m, 3 H), 4.28 (d, *J* = 12.2 Hz, 1 H), 4.42 (d, *J* = 7.8 Hz, 1 H), 4.69 (s, 2 H), 5.09 and 5.28 (ABq, *J* = 13.6 Hz, 2 H), 5.32 (s, 2 H), 5.45 (s, 1 H), 6.85 (d, *J* = 8.3 Hz, 2 H), 7.23−7.53 (m, 14 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.3, 66.8, 66.9, 69.3, 70.2, 71.2, 73.3, 78.9, 101.1, 102.8, 113.9, 126.5, 127.4, 128.1, 128.25, 128.3, 128.7, 128.9, 129.5, 130.3, 130.6, 132.6, 135.9, 137.9, 139.8, 159.3, 167.1. Anal. calcd for $C_{36}H_{36}O_9$: C, 70.57; H, 5.92. Found: C, 70.51; H, 6.02.

2′-(Benzyloxycarbonyl)benzyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (S7). To a solution of **S6** (2.18 g, 3.56 mmol) and BnBr (636 µL, 5.35 mmol) in DMF (10 mL) was added NaH (60%, 214 mg, 5.35 mmol) at 0 °C and then the ice bath was removed. After stirring at room temperature for 2 h, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (2 × 50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:1, v/v) to afford the title compound **S7** (2.2 g, 3.13 mmol, 88%) as a white solid.: m.p.= 129−130 °C; R_f = 0.6 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 1255, 1713 cm^{-1}; $[\alpha]_D^{20}$ +1.0 (*c* 1.0, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 3.28 (brs, 1 H), 3.56 (dd, *J* = 3.6, 9.6 Hz, 1 H), 3.78 (s, 3 H), 3.92−4.02 (m, 2

H), 4.09 (d, *J* = 3.4 Hz, 1 H), 4.30 (d, *J* = 12.2 Hz, 1 H), 4.52 (d, *J* = 7.8 Hz, 1 H), 4.71−4.77 (m, 2 H), 4.85 and 4.95 (ABq, *J* = 10.8 Hz, 2 H), 5.13 and 5.41 (ABq, *J* = 15.1 Hz, 2 H), 5.29 (s, 2 H), 5.00 (s, 1 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 7.22−7.59 (m, 19 H), 7.84 (d, *J* = 7.7 Hz, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 55.4, 66.6, 66.7, 69.3, 71.7, 74.0, 75.5, 78.7, 79.1, 101.4, 103.2, 113.8, 126.6, 126.9, 127.4, 127.6, 128.2, 128.21, 128.30, 128.33, 128.7, 129.0, 129.5, 130.5, 130.6, 132.7, 136.1, 138.0, 138.9, 140.9, 159.3, 166.7. Anal. calcd for $C_{43}H_{42}O_9$: C, 73.49; H, 6.02. Found: C, 73.42; H, 6.17.

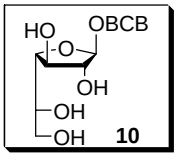
2′-(Benzyloxycarbonyl)benzyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (7). To a solution of compound **S7** (143 mg, 0.203 mmol) in CH_2Cl_2 / H_2O (9.5 mL, 18:1, v/v) was added DDQ (60 mg, 0.264 mmol). After stirring at 0 °C for 1 h, the reaction mixture was quenched with $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:1, v/v) to afford the title compound **7** (109 mg, 0.187 mmol, 92%) as a white solid.: m.p.= 164−165 ^{o}C; R_f = 0.3 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 1262, 1709, 3403 cm^{-1}; $[\alpha]_D^{20}$ −12.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.51−2.54 (m, 1 H), 3.43 (s, 1 H), 3.71−3.80 (m, 2 H), 4.07 and 4.32 (ABq, *J* = 12.4 Hz, 2 H), 4.22 (s, 1 H), 4.55 (d, *J* = 7.3 Hz, 1 H), 4.78 and 5.01 (ABq, *J* = 11.2 Hz, 2 H), 5.15 and 5.41 (ABq, *J* = 14.8 Hz, 2 H), 5.31 (s, 2 H), 5.56 (s, 1 H), 7.25−7.53 (m, 17 H), 7.82 (d, *J* = 7.7 Hz, 1 H), 8.02 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 66.7, 66.8, 69.3, 69.4, 75.2, 75.7, 79.6, 101.5, 103.1, 126.6, 127.1, 127.6, 127.8, 128.2, 128.3, 128.5, 128.7, 129.3, 130.7, 132.7, 136.1,137.7, 138.6, 140.7, 166.8. Anal. calcd for $C_{35}H_{34}O_8$: C, 72.15; H, 5.88.

Found: C, 72.07; H, 5.95.

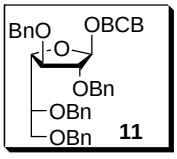


2′-(Benzyloxycarbonyl)benzyl 2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranoside (9). A solution of D-galactofuranosyl pentaacetate (**8**) (3.90 g, 10.0 mmol), thionyl chloride (5 mL), and acetic acid (2 mL) in CH_2Cl_2 (20 mL) was stirred at 0 ^oC for 18 h. Removal of the solvent and then concentration in vacuo gave crude 2,3,5,6-tetra-*O*-acetyl-D-galactofuranosyl chloride. A solution of the crude galactofuranosyl chloride, mercury (II) bromide (4.3 g, 11.93 mmol), mercury (II) cyanide (3.03 g, 11.99 mmol), and benzyl 2-hydroxymethylbenzoate (**18**) (2.91 g, 12.01 mmol) in acetonitrile (30 mL) was stirred at room temperature for 30 min, and the reaction mixture was filtered through Celite®, then the filtrate was concentrated. The resulting oil was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **9** (4.35 g, 7.60 mmol, 76%) as a colorless oil.: R_f = 0.35 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1225, 1370, 1747 cm^{-1}; $[\alpha]_D^{20}$ −40.4 (*c* 1.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 2.02 (s, 3 H), 2.08 (s, 3 H), 2.10 (s, 3 H), 2.13 (s, 3 H), 4.20 (dd, *J* = 7.1, 11.8 Hz, 1 H), 4.28−4.35 (m, 2 H), 4.99 and 5.15 (ABq, *J* = 14.5 Hz, 2 H), 5.05 (dd, J = 1.5, 5.8 Hz, 1 H), 5.18−5.20 (m, 2 H), 5.33 (s, 2 H), 5.38−5.44 (m, 1 H), 7.30−7.56 (m, 7 H), 7.67 (d, *J* = 7.7 Hz, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 20.5(2), 20.6, 20.7, 62.5, 66.6, 67.2, 69.2, 76.5, 80.2, 81.1, 105.2, 127.1, 127.6, 127.9, 128.0, 128.1, 128.5, 130.5, 132.3, 135.8, 139.7, 166.3, 169.4, 169.8, 169.9, 170.3.

Anal. calcd for $C_{29}H_{32}O_{12}$: C, 60.83; H, 5.63. Found: C, 60.87; H, 5.55.

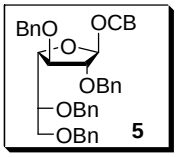


2′-(Benzyloxycarbonyl)benzyl β-D-galactofuranoside (10). To a solution of compound **9** (4.4 g, 7.68 mmol) in MeOH (100 mL) was added NaOMe (54 mg, 1.0 mmol) at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode), filtered through Celite®, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography ($CHCl_3$/MeOH, 9:1, v/v) to afford the title compound **10** (2.86 g, 7.07 mmol, 92%) as a white solid.: m.p.= 77−78 °C; R_f = 0.35 ($CHCl_3$/MeOH, 9:1, v/v); IR ($CHCl_3$ film) 1258, 1711, 3376 cm^{-1}; $[\alpha]_D^{20}$ −75.1 (*c* 2.6, $CHCl_3$); ^1H NMR (250 MHz, CD_3OD) δ 3.59−3.62 (m, 2 H), 3.71−3.74 (m, 1 H), 3.97−4.07 (m, 3 H), 4.90 and 5.08 (ABq, *J* = 14.1 Hz, 2 H), 5.00 (brs, 1 H), 5.33 (s, 2 H), 7.30−7.58 (m, 7 H), 7.70 (d, *J* = 7.4 Hz, 1 H), 7.92 (dd, *J* = 1.2, 7.8 Hz, 1 H); ^{13}C NMR (63 MHz, CD_3OD) δ 64.5, 67.8, 68.6, 72.3, 78.8, 83.5, 84.4, 109.3, 128.3, 129.3, 129.35, 129.6, 131.3, 133.4, 137.5, 141.5, 168.3. Anal. calcd for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.30; H, 5.98.



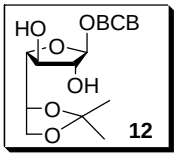
2′-(Benzyloxycarbonyl)benzyl 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranoside (11). To a solution of **10** (615 mg, 1.52 mmol) and BnBr (815 µL, 6.85 mmol) in DMF (10 mL) was added NaH (60%,

274 mg, 6.85 mmol) at 0 °C and then the ice bath was removed. After stirring at room temperature for 1 h, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (2 × 50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 7:1, v/v) to afford the title compound **11** (977 mg, 1.28 mmol, 84%) as a colorless oil.: R_f = 0.55 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1258, 1712 cm^{-1}; $[\alpha]_D^{20}$ −60.5 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.62−3.70 (m, 2 H), 3.77−3.80 (m, 1 H), 4.05−4.07 (m, 1 H), 4.10 (brs 1 H), 4.17−4.19 (m, 1 H), 4.32 (d, *J* = 11.6 Hz, 1 H), 4.44−4.56 (m, 6 H), 4.72 (d, *J* = 11.6 Hz, 1 H), 4.97 and 5.11 (ABq, *J* = 14.3 Hz, 2 H), 5.20 (s, 1 H), 5.30 (s. 2 H), 7.21−7.48 (m, 27 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.96 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.8, 67.5, 71.2, 71.9, 72.2, 73.4, 73.5, 76.5, 81.3, 83.0, 88.6, 105.9, 127.1, 127.7, 127.8, 127.9, 128.0, 128.2, 128.4, 128.7, 130.7, 132.4, 136.1, 137.8, 138.1, 138.5, 138.6, 140.7, 188.6. Anal. calcd for $C_{49}H_{48}O_8$: C, 76.94; H, 6.33. Found: C, 76.92; H, 6.30.



2′-Carboxybenzyl 2,3,5,6-tetra-*O*-benzyl-β-D-galactofuranoside (5). Compound **11** (670 mg, 0.88 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 93 mg) and ammonium acetate (67 mg, 0.87 mmol) in MeOH–EtOAc (1:1 v/v, 10 mL) at room temperature for 1 h. The reaction mixture was filtered through Celite® and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:1, v/v) to afford the title compound **5** (564 mg, 0.84 mmol, 95%) as a colorless

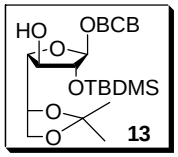
oil.: R_f = 0.50 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 1695, 3157 cm^{-1}; $[\alpha]_D^{20}$ −71.5 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.65−3.71 (m, 2 H), 3.77−3.82 (m, 1 H), 4.08−4.09 (m, 1 H), 4.14 (brs, 1 H), 4.23 (dd, *J* = 3.0, 6.9 Hz, 1 H), 4.33 (d, *J* = 11.7 Hz, 1 H), 4.45−4.49 (m, 4 H), 4.53 and 4.58 (ABq, *J* = 11.9 Hz, 2 H), 4.71 (d, *J* = 11.7 Hz, 1 H), 4.98 and 4.14 (ABq, *J* = 14.4 Hz, 2 H), 5.25 (s, 1 H), 7.21−7.31 (m, 21 H), 7.50 (t, *J* = 7.4 Hz, 1 H), 7.68 (d, *J* = 7.7 Hz, 1 H), 8.04 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 67.5, 70.8, 71.9, 72.1, 73.3, 73.4, 76.3, 81.2, 82.9, 88.5, 105.9, 127.2, 127.6, 127.8, 127.9, 128.0, 128.1, 128.4, 131.5, 133.2, 137.7, 138.0, 138.3, 138.5, 141.3, 172.3. Anal. calcd for $C_{42}H_{42}O_8$: C, 74.76; H, 6.27. Found: C, 74.76; H, 6.31.

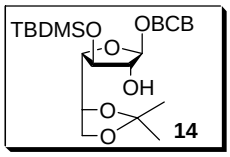


12

2′-(Benzyloxycarbonyl)benzyl 5,6-*O*-isopropylidene-β-D-galactofuranoside (12). A solution of compound **10** (2.03 g, 5.02 mmol) and 2,2-dimethoxypropane (740 μL, 6.02 mmol) in the presence of camphor sulfonic acid (12 mg, 0.05 mmol) in DMF (20 mL) was stirred at room temperature for 1 h. After quenched with triethylamine (1 mL), the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (2 × 50 mL), brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:3, v/v) to afford the title compound **12** (2.80 g, 70%) as a white solid.: m.p.= 62−63 ^oC; R_f = 0.48 (hexane/EtOAc, 1:3, v/v); IR ($CHCl_3$ film) 1258, 1713, 3430 cm^{-1}; $[\alpha]_D^{20}$ −53.8 (*c* 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 3 H), 1.43 (s, 3 H), 3.18 (d, *J* = 11.6 Hz, 1 H), 4.01−4.14 (m, 6 H), 4.36 (t, *J* = 7.1 Hz, 1 H), 4.83 (d, *J* = 13.1 Hz, 1 H), 5.16−5.19 (m, 2 H), 5.31−5.37 (m, 2 H), 7.35−7.55 (m, 7 H), 8.00 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR

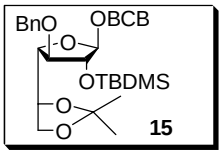
(125 MHz, $CDCl_3$) δ 25.7, 25.8, 65.9, 67.0, 68.0, 75.9, 78.5, 78.9, 85.7, 108.6, 110.3, 127.9, 128.4, 128.5, 128.8, 129.0, 131.0, 132.7, 135.9, 139.4, 166.8. Anal. calcd for $C_{24}H_{28}O_8$: C, 64.85; H, 6.35. Found: C, 64.90; H, 6.26.





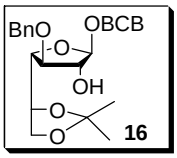
2′-(Benzyloxycarbonyl)benzyl 2-*O*-*t*-buthyldimethylsilyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (13) and 2′-(Benzyloxycarbonyl)benzyl 3-*O*-*t*-buthyldimethylsilyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (14). A solution of compound **12** (212 mg, 0.48 mmol), imidazole (97 mg, 1.42 mmol), and TBDMSCl (79 mg, 0.52 mmol) in DMF (4 mL) was stirred at room temperature for 4 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL), extracted with EtOAc (2 × 30 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **13** (220 mg, 0.43 mmol, 82 %) and compound **14** (21 mg, 0.04 mmol, 8%). Compound **13**: colorless oil, R_f = 0.35 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1255, 1717, 3484 cm^{-1}; $[\alpha]_D^{20}$ −53.4 (*c* 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.11 (s, 3 H), 0.13 (s, 3 H), 0.91 (s, 9 H), 1.40 (s, 3 H), 1.49 (s, 3 H), 3.05 (d, *J* = 10.2 Hz, 1 H), 3.72 (d, *J* = 9.7 Hz, 1 H), 3.91 (t, *J* = 7.3 Hz, 1 H), 4.04 (t, *J* = 7.6 Hz, 1 H), 4.14 (d, *J* = 5.3 Hz, 1 H), 4.17 (s, 1 H), 4.31−4.34 (m, 1 H), 4.88 and 5.20 (ABq, *J* = 13.2 Hz, 2 H), 5.11 (s, 1 H), 5.35 (s, 2 H), 7.33−7.56 (m, 8 H), 7.99 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.9, 17.9, 25.2, 25.6, 26.7, 65.6, 66.7, 67.7, 76.4, 78.8, 81.3, 87.8, 107.9, 109.7, 127.5, 128.2, 128.6, 128.8, 130.7, 132.3, 135.8, 139.5, 166.6. Anal. calcd for

$C_{30}H_{42}O_8Si$: C, 64.49; H, 7.58. Found: C, 64.41; H, 7.63. Compound **14**: colorless oil, R_f = 0.43 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1255, 1717, 3438 cm^{-1}; $[\alpha]_D^{20}$ −50.0 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 3 H), 0.15 (s, 3 H), 0.92 (s, 9 H), 1.40 (s, 3 H), 1.42 (s, 3 H), 3.45 (d, *J* = 10.1 Hz, 1 H), 3.95−4.03 (m, 4 H), 4.12 (s, 1 H), 4.22 (t, *J* = 6.6 Hz, 1 H), 5.00 and 5.16 (ABq, *J* = 15.0 Hz, 2 H), 5.14 (s, 1 H), 5.33 (s, 2 H), 7.25−7.49 (m, 7 H), 7.82 (d, *J* = 7.7 Hz, 1 H), 7.99 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.4, 18.1, 25.8, 65.8, 66.8, 67.5, 76.2, 79.9, 80.8, 85.2, 109.2, 110.0, 126.7, 127.6, 128.4, 128.7, 130.5, 132.5, 136.1, 141.6, 166.8. Anal. calcd for $C_{30}H_{42}O_8Si$: C, 64.49; H, 7.58. Found: C, 64.43; H, 7.67.

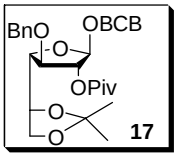


2′-(Benzyloxycarbonyl)benzyl 3-*O*-benzyl-2-*O*-*t*-buthyldimethylsilyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (15). To a solution of **13** (400 mg, 0.716 mmol) and BnBr (103 μL, 0.866 mmol) in DMF (10 mL) was added NaH (60%, 35 mg, 0.875 mmol) at 0 °C and then the ice bath was removed. After stirring at room temperature for 1 h, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (2 × 50 mL). The combined organic layer was washed with saturated aqueous NH_4Cl (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 9:1, v/v) to afford the title compound **15** (441 mg, 0.680 mmol, 95%) as a colorless oil.: R_f = 0.25 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1282, 1728 cm^{-1}; $[\alpha]_D^{20}$ +40.7 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.13 (s, 3 H), 0.17 (s, 3 H), 0.95 (s, 9 H), 1.41 (s, 3 H), 1.46 (s, 3 H), 3.78 (d, *J* = 3.8 Hz, 1 H), 3.87−3.95 (m, 2 H), 4.20 (t, *J* = 5.5 Hz, 1 H), 4.29 (dd, *J* = 6.4, 12.9 Hz, 1 H), 4.43

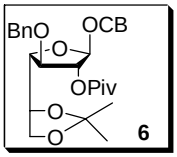
(s, 1 H), 4.61 and 4.74 (ABq, *J* = 11.7 Hz, 2 H), 5.08 (s, 1 H), 5.09 and 5.23 (ABq, *J* = 14.8 Hz, 2 H), 5.38 (s, 2 H), 7.35−7.53 (m, 12 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 8.03 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.6, 18.0, 25.3, 25.8, 26.6, 65.6, 66.7, 67.3, 72.2, 76.1, 81.1, 83.6, 86.3, 108.3, 109.7, 126.9, 127.8, 127.9, 128.3, 128.5, 128.7, 130.6, 132.4, 136.1, 137.9, 141.0, 166.7. Anal. calcd for $C_{37}H_{48}O_8Si$: C, 68.49; H, 7.46. Found: C, 68.43; H, 7.54.



2′-(Benzyloxycarbonyl)benzyl 3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (16). A solution of compound **15** (420 mg, 0.647 mmol) and Bu_4NF (1.0M, 1 mL, 1 mmol) in THF (3 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **16** (339 mg, 0.634 mmol, 98 %) as a colorless oil.: R_f = 0.25 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1260, 1714, 3434 cm^{-1}; $[\alpha]_D^{20}$ −72.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 1.41 (s, 3 H), 3.64 (d, *J* = 10.1 Hz, 1 H), 3.92−3.96 (m, 3 H), 4.15−4.20 (m, 2 H),4.29 (d, *J* = 10.0 Hz, 1 H), 4.54 and 4.70 (ABq, *J* = 11.8 Hz, 2 H), 4.99 and 5.18 (ABq, *J* = 14.8 Hz, 2 H), 5.16 (s, 1 H), 5.30 (s, 2 H), 7.23−7.42 (m, 12 H), 7.72 (d, *J* = 7.7 Hz, 1 H), 7.96 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.7, 25.8, 65.5, 66.6, 67.3, 71.9, 76.3, 77.4, 82.8, 86.0, 108.8, 109.8, 126.7, 127.6, 127.8, 128.2, 128.4, 128.6, 130.4, 132.4, 135.9, 137.7, 141.0, 166.7. Anal. calcd for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.59; H, 6.22.

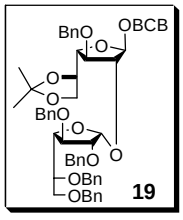


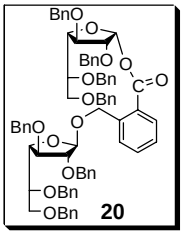
2′-(Benzyloxycarbonyl)benzyl 3-*O*-benzyl-5,6-*O*-isopropylidene-2-*O*-pivaloyl-β-D-galactofuranoside (17). To a solution of compound **16** (3.4 g, 6.36 mmol) and Et_3N (1.8 mL) in CH_2Cl_2 (10 mL) were added pivaloyl chloride (940 μL, 7.63 mmol) and DMAP (233 mg, 1.91 mmol). After stirring at room temperature for 1 h, the reaction mixture was quenched with aqueous NH_4Cl (5 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **17** (3.89 g, 6.29 mmol, 99 %) as a colorless oil.: R_f = 0.53 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1262, 1728 cm^{-1}; $[\alpha]_D^{20}$ −89.8 (*c* 2.1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.22 (s, 9 H), 1.34 (s, 3 H), 1.39 (s, 3 H), 3.72−3.86 (m, 3 H), 4.14−4.22 (m, 2 H), 4.56 and 4.82 (ABq, *J* = 11.9 Hz, 2 H), 5.06 and 5.19 (ABq, *J* = 14.7 Hz, 2 H), 5.17 (s, 1 H), 5.28 (s, 1 H), 5.31 (s, 2 H), 7.24−7.52 (m, 12 H), 7.73 (d, *J* = 7.7 Hz, 1 H), 7.98 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.4, 26.4, 27.0, 38.7, 65.4, 66.7, 67.2, 72.1, 75.8, 80.6, 83.6, 83.7, 105.9, 109.8, 126.9, 127.6, 127.8, 127.9, 128.2, 128.4, 128.6, 130.5, 132.5, 136.0, 137.4, 140.5, 166.6, 177.4. Anal. calcd for $C_{36}H_{42}O_9$: C, 69.88; H, 6.84. Found: C, 69.84; H, 6.76.



2′-Carboxybenzyl 3-*O*-benzyl-5,6-*O*-isopropylidene-2-*O*-pivaloyl-β-D-galactofuranoside (6).

Compound **17** (1.655 g, 2.67 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 284 mg) and ammonium acetate (206 mg, 2.67 mmol) in MeOH–EtOAc (1:1 v/v, 10 mL) at room temperature for 1 h. The reaction mixture was filtered through Celite® and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:1, v/v) to afford the title compound **6** (1.38 g, 2.61 mmol, 98%) as a colorless oil.: R_f = 0.45 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 1694, 1732, 3172 cm^{-1}; $[\alpha]_D^{20}$ −9.4 (*c* 4, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.23 (s, 9 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 3.75−3.85 (m, 3 H), 4.18−4.25 (m, 2 H), 4.58 and 4.84 (ABq, *J* = 11.9 Hz, 2 H), 5.08 and 5.25 (ABq, *J* = 15.1 Hz, 2 H), 5.24 (s, 1 H), 5.31 (s, 1 H), 7.25−7.35 (m, 6 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.80 (d, *J* = 7.7 Hz, 1 H), 7.98 (d, *J* = 7.7 Hz, 1 H), 12.0 (brs, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) 25.3, 26.4, 27.0, 38.6, 65.4, 67.2, 72.0, 75.8, 80.5, 83.5, 83.7, 105.9, 109.8, 126.6, 126.9, 127.3, 127.9, 128.2, 128.3, 131.3, 133.3, 137.3, 141.3, 172.1, 166.4. Anal. calcd for $C_{29}H_{36}O_9$: C, 65.89; H, 6.86. Found: C, 65.86; H, 6.85.





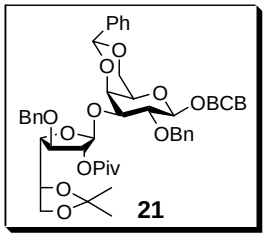
2′-(Benzyloxycarbonyl)benzyl (2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→2) 3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranoside (19).

Method A: A solution of donor **5** (94 mg, 0.139 mmol), acceptor **16** (111 mg, 0.208 mmol) and DTBMP (86 mg, 0.419 mmol) in CH_2Cl_2 (10 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to -78 °C. To the resulting solution was added a

solution of Tf_2O (35 μL, 0.208 mmol) in CH_2Cl_2 (1 mL), and stirred at -78 °C for 1 h. The reaction mixture was allowed to warm to 0 °C over 1 h, quenched with saturated aqueous $NaHCO_3$ (1 mL), and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **19** (100 mg, 0.095 mmol, 68 %, **α only**) as a colorless oil and self-condensed ester **20** (20 mg, 0.033 mmol, 24%) as a colorless oil. Compound **19**: R_f = 0.48 (hexane/EtOAc, 3:1, v/v); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (s, 3 H), 1.39 (s, 3 H), 3.60−3.64 (m, 2 H), 3.68−3.71 (m, 1 H), 3.75−3.79 (m, 2 H), 3.83−3.87 (m, 1 H), 3.97 (dd, *J* = 3.6, 7.6 Hz, 1 H), 4.04−4.09 (m, 2 H), 4.17 (t, *J* = 6.8 Hz, 1 H), 4.26 (d, *J* = 11.7 Hz, 1 H), 4.36−4.50 (m, 7 H), 4.57 (d, *J* = 3.7 Hz, 1 H), 4.61−4.64 (m, 1 H), 4.69 (brs, 1 H), 4.71 (d, *J* = 12.2 Hz, 1 H), 5.03 (d, *J* = 14.3 Hz, 1 H), 5.09 (d, *J* = 4.5 Hz, 1 H), 5.15 (d, *J* = 13.4 Hz, 1 H), 5.18 (brs, 1 H), 5.31 (s, 2 H), 7.16−7.44 (m, 32 H), 7.66 (d, *J* = 7.7 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.5, 26.7, 65.5, 66.7, 67.5, 70.7, 72.1, 72.4(2), 73.2, 73.5, 77.4, 79.6, 80.2,83.5,83.7, 84.6, 84.8, 99.0, 105.7, 109.7, 127.1,127.57, 127.6, 127.7, 127.77,127.8, 127.9, 128.0, 128.2, 128.25, 128.3, 128.36, 128.4, 128.5, 128.6,128.7, 130.6, 132.4, 136.1, 137.6, 138.1, 138.2, 138.5, 140.6, 166.7. Compound **20**: R_f = 0.5 (hexane/EtOAc, 3:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63−3.69 (m, 4 H), 3.76−3.79 (m, 1 H), 3.80−3.84 (m, 1 H), 4.05−4.06 (m, 1 H), 4.09−4.15 (m, 3 H), 4.18−4.20 (m, 1 H), 4.31−4.34 (m, 2 H), 4.39−4.59 (m, 12 H), 4.66 (d, *J* = 11.9 Hz, 1 H), 4.70−4.75 (m, 2 H), 5.01 and 5.12 (ABq, *J* = 14.7 Hz, 2 H), 5.22 (brs, 1 H), 6.48 (brs, 1 H), 7.20−7.31 (m, 41 H), 7.48 (t, *J* = 7.3 Hz, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 67.5, 70.8, 71.2, 72.0, 72.2, 73.4, 73.5, 76.6, 81.4, 83.0, 84.9, 87.0, 88.6, 100.7, 106.1, 127.0, 127.7, 128.0, 128.5, 131.2, 132.9. Anal. calcd for

$C_{76}H_{76}O_{13}$: C, 76.23; H, 6.40. Found: C, 76.32; H, 6.32.

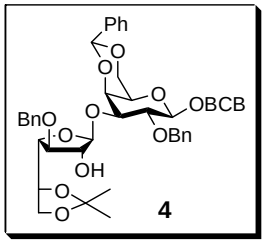
Method B: A solution of the acceptor **16** (116 mg, 0.217 mmol) and DTBMP (89 mg, 0.433 mmol) in CH_2Cl_2 (10 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to -78 °C. To the resulting solution was added a solution of Tf_2O (37 μL, 0.220 mmol) in CH_2Cl_2 (1 mL) and subsequently added dropwise a solution of donor **5** (98 mg, 0.145 mmol) in CH_2Cl_2 (10 mL). After stirring at -78 °C for further 1 h, the reaction mixture was allowed to warm to 0 °C over 1 h, quenched with saturated aqueous $NaHCO_3$ (1 mL), and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes/EtOAc, 3:1, v/v) to afford the title compound **19** (126 mg, 0.119 mmol, 82 %, **α only**).



21

2′-(Benzyloxycarbonyl)benzyl (3-*O*-benzyl-5,6-*O*-isopropylidene-2-*O*-pivaloyl-β-D-galactofuranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (21). A solution of acceptor **7** (527 mg, 0.905 mmol) and DTBMP (667 mg, 3.248 mmol) in CH_2Cl_2 (15 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to –45 °C. To the resulting solution was added a solution of Tf_2O (273 μL, 1.623 mmol) in CH_2Cl_2 (3 mL) and subsequently added dropwise a solution of donor **6** (715 mg, 1.353 mmol) in CH_2Cl_2 (10 mL). After stirring at –40 °C for further 1 h, the reaction mixture was allowed to warm to 0 °C over 1 h,

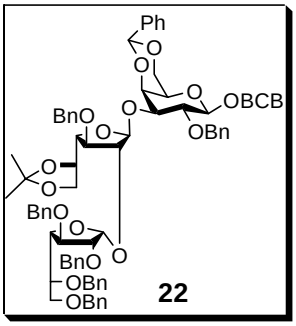
quenched with saturated aqueous $NaHCO_3$ (1 mL), and diluted with CH_2Cl_2 (50 mL) The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1, v/v) to afford the title compound **21** (682 mg, 0.711 mmol, 79%) as a white solid.: m.p.= 81−82 °C; R_f = 0.18 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1258, 1374, 1459, 1717, 1736 cm^{-1}; $[\alpha]_D$ −33.1 (*c* 1.1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.20 (s, 9 H), 1.34 (s, 6 H), 3.41 (brs, 1 H), 3.60 (d, *J* = 5.9 Hz, 1 H), 3.67 (d, *J* = 7.8 Hz, 1 H), 3.72−3.83 (m, 2 H), 3.93−4.15 (m, 3 H), 4.24−4.37 (m, 2 H), 4.41 (d, *J* = 3.4 Hz, 1 H), 4.47 and 4.79 (ABq, *J* = 12.0 Hz, 2 H), 4.55 (d, *J* = 7.7 Hz, 1 H), 4.83 and 4.91 (ABq, *J* = 10.7 Hz, 2 H), 5.14 and 5.41 (ABq, *J* = 15.1 Hz, 2 H), 5.27−5.33 (m, 4 H), 5.59 (s, 1 H), 7.23−7.59 (m, 22 H), 7.83 (d, *J* = 7.7 Hz, 1 H), 8.01 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.5, 26.6, 27.1, 38.7, 65.5, 66.5, 66.7, 69.1, 72.0, 75.5, 76.4, 77.4, 76.5, 78.0, 79.4, 80.7, 83.5, 84.1, 100.8, 103.1, 108.5, 109.9, 126.3, 126.9, 127.4, 127.5, 127.6,128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 130.6, 132.7, 136.0, 137.3, 137.9,138.7, 140.9, 166.7, 177.1. Anal. calcd for $C_{56}H_{62}O_{14}$: C, 70.13; H, 6.52. Found: C, 70.04; H, 6.51.



4

2′-(Benzyloxycarbonyl)benzyl (3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (4). A solution of benzyl alcohol (340 μL, 3.29 mmol) and sodium hydride (60%, 132 mg, 3.30 mmol) in THF (10 mL) was stirred at

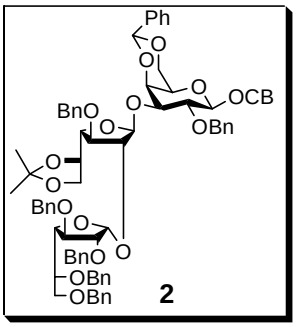
0 °C for 30 min. To the solution was added a solution of **21** (2.11 g, 2.20 mmol) in THF (4 mL) and stirred at 0 °C for 1 h. The reaction mixture was quenched with water (2 mL), diluted with EtOAc (50 mL), washed with brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:1, v/v) to afford the title compound **4** (1.58 g, 1.81 mmol, 82%) as a white solid.: m.p.= 47−48 °C; R_f = 0.38 (hexane/EtOAc, 1:1, v/v); IR ($CHCl_3$ film) 3442, 1717, 1463, 1378, 1262 cm^{-1}; $[\alpha]_D$ −26.2 (*c* 0.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 3 H), 1.37 (s, 3 H), 2.93 (brs, 1 H), 3.38 (brs, 1 H), 3.73−3.80 (m, 2 H), 3.83−3.98 (m, 3 H), 4.00−4.17 (m, 3 H), 4.19−4.24 (m, 1 H), 4.29−4.36 (m, 2 H), 4.47 and 4.65 (ABq, *J* = 11.9 Hz, 2 H), 4.55 (d, *J* = 7.7 Hz, 1 H), 4.73 and 4.92 (ABq, J = 11.2 Hz, *2* H), 5.11 and 5.40 (ABq, *J* = 14.9 Hz, 2 H), 5.27−5.29 (m, 3 H), 5.53 (s, 1 H), 7.16−7.55 (m, 22 H), 7.81 (d, *J* = 7.7 Hz, 1 H), 8.00 (dd, *J* = 1.0, 7.7 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.5, 26.1, 65.6, 66.6, 66.7, 69.1, 69.2, 71.9, 75.4, 76.5, 77.4, 78.4, 78.5, 79.2, 82.8, 86.3, 100.8, 103.1, 109.9, 111.1, 126.3, 126.9, 127.6, 127.7, 127.8, 128.0, 128.1, 128.27, 128.3, 128.4, 128.6, 132.6, 137.8, 138.0, 138.9, 140.8, 166.7. Anal. calcd for $C_{51}H_{54}O_{13}$: C, 70.01; H, 6.22. Found: C, 70.06; H, 6.30.



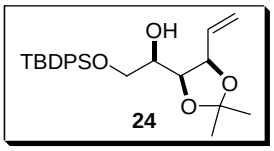
22

2′-(Benzyloxycarbonyl)benzyl (2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→2)-(3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (22). A solution of acceptor **4** (93 mg, 0.106 mmol) and DTBMP (52 mg, 0.253

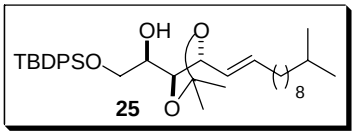
mmol) in CH_2Cl_2 (10 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to –78 °C. To the resulting solution were added a solution of Tf_2O (22 μL, 0.131 mmol) in CH_2Cl_2 (1 mL) and subsequently added dropwise a solution of donor **5** (71 mg, 0.105 mmol) in CH_2Cl_2 (5 mL). After stirring at –78 °C for further 1 h, the reaction mixture was allowed to warm to 0 °C over 1 h, quenched with saturated aqueous $NaHCO_3$ (1 mL), and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1, v/v) to afford the title compound **22** (134 mg, 0.096 mmol, 91%) as a white solid.: m.p.= 43−44 ^oC; R_f = 0.3 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 1713, 1497, 1368, 1261 cm^{-1}; $[\alpha]_D$ +22.1 (*c* 0.8, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 6 H), 3.42 (brs, 1 H), 3.64−3.86 (m, 8 H), 3.91−4.02 (m, 2 H), 4.06−4.24 (m, 5 H), 4.31−4.41 (m, 8 H), 4.53−4.59 (m, 3 H), 4.64−4.70 (m, 2 H), 4.73 (d, *J* = 4.8 Hz, 1 H), 4.92 (d, *J* = 4.6 Hz, 1 H), 4.99 (d, *J* = 10.8 Hz, 1 H), 5.16 and 5.42 (ABq, *J* = 15.0 Hz, 2 H), 5.26 (brs, 1 H), 5.30 (s, 2 H), 5.58 (s, 1 H), 7.20−7.55 (m, 42 H), 7.82 (d, *J* = 7.8 Hz, 1 H), 8.02 (dd, *J* = 1.1, 7.8 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.5, 26.8, 65.4, 66.6, 66.7(2), 69.1, 70.7, 71.8, 72.1, 72.4, 73.2, 73.5,75.3, 76.5, 77.0, 77.4, 78.0, 79.2, 79.3, 80.0, 82.8, 83.8, 84.5, 85.0, 98.5, 100.9, 103.2, 108.4, 109.7, 126.3, 126.9, 127.4, 127.5, 127.6, 127.7. 127.8, 127.87, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 130.7, 132.6, 136.0, 137.6, 137.9, 138.1, 138.2, 138.3, 138.8, 140.8, 166.6. Anal. calcd for $C_{85}H_{88}O_{18}$: C, 73.05; H, 6.35. Found: C, 73.12; H, 6.22.



2′-Carboxybenzyl (2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→2)-(3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (2). Compound **22** (127 mg, 0.91 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 10 mg) and ammonium acetate (7 mg, 0.091 mmol) in MeOH–EtOAc (1:1, v/v, 5 mL) at room temperature for 1 h. The reaction mixture was filtered through Celite® and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 1:2, v/v) to afford the title compound **2** (112 mg, 0.086 mmol, 95%) as a white solid.: m.p.= 48−49 ^{o}C; R_f = 0.3 (hexane/EtOAc, 1:2, v/v); IR ($CHCl_3$ film) 3306, 1715, 1499, 1457, 1376 cm^{-1}; $[\alpha]_D$ +23.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 6 H), 3.48 (brs, 1 H), 3.62−3.86 (m, 8 H), 3.94−4.02 (m, 3 H), 4.07−4.20 (m, 3 H), 4.21−4.24 (m, 1 H), 4.36−4.48 (m, 8 H), 4.54−4.72 (m, 5 H), 4.76 and 5.03 (ABq, *J* = 10.8 Hz, 2 H), 4.92 (d, *J* = 4.5 Hz, 1 H), 5.22 and 5.43 (ABq, *J* = 15.5 Hz, 2 H), 5.27 (brs, 1 H), 5.59 (s, 1 H), 7.20−7.56 (m, 37 H), 7.87 (d, *J* = 7.8 Hz, 1 H), 8.07 (d, *J* = 7.7 Hz, 1 H), 9.77 (brs, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.6, 26.8, 65.4, 66.6, 69.1(2), 70.7, 71.9,72.2, 72.4, 73.3, 73.5(2), 75.4, 76.5, 77.0, 78.1, 79.3(2), 80.0, 82.8, 83.8, 84.5, 85.0, 98.5, 100.9,103.1, 108.4, 109.8, 126.3, 126.6, 127.0, 127.5, 127.6, 127.68, 127.7, 127.8, 127.9, 127.97, 128.0, 128.1, 128.27, 128.3, 128.36, 128.4, 128.5, 128.7, 131.5, 133.4, 137.7, 138.0, 138.15, 138.2, 138.4, 138.8, 141.5, 171.8. Anal. calcd for $C_{78}H_{82}O_{18}$: C, 71.65; H, 6.32. Found: C, 71.60; H, 6.45.

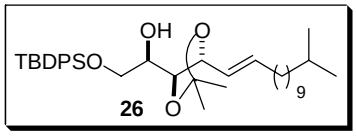


(2*R*,3*S*,4*R*)-1-*O*-*t*-Buthyldiphenylsilyl-3,4-*O*-isopropylidene-5-hexene-1,2,3,4-tetrol (24). To a suspension of trimethylphosphonium bromide (6.0 g, 16.8 mmol) in THF (50 mL) was added dropwise *n*-BuLi (1.6 M, 10.5 mL, 16.8 mmol) at 0 ^{o}C, and the mixture was stirred at 0 ^{o}C for 30 min. To this mixture was added dropwise a solution of **23** (2.3 g, 5.37 mmol) in THF (20 mL) at 0 ^{o}C, and allowed to warm to room temperature, then stirred for 1 h. After the reaction mixture was quenched with methanol, it was dissolved in 80% aqueous methanol and extracted with n-hexane (100 mL), washed with brine (2 × 50 mL) and then concentrated. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 4:1, v/v) to afford the title compound **24** (2.06 g, 4.83 mmol, 90%) as a colorless oil.: R_f = 0.53 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1111, 1429, 3467 cm^{-1}; $[\alpha]_D^{20}$ −15.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (s, 9 H), 1.39 (s, 3 H), 1.51 (s, 3 H), 2.43 (d, *J* = 6.2 Hz, 1 H), 3.63−3.72 (m, 3 H), 4.30 (dd, *J* = 3.6, 6.9 Hz, 1 H), 4.50 (t, *J* = 7.5 Hz, 1 H), 5.18 (brs, 1 H), 5.23 (dd, *J* = 0.8, 6.9 Hz, 1 H), 5.88−6.03 (m, 1 H), 7.34−7.68 (m, 10 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.4, 25.1, 27.0, 27.4, 65.0, 70.1, 77.3, 79.2, 108.8, 119.5, 127.86, 127.9, 129.9, 130.0, 133.3, 134.5, 135.7. Anal. calcd for $C_{25}H_{34}O_4Si$: C, 70.38; H, 8.03. Found: C, 70.24; H, 8.38.



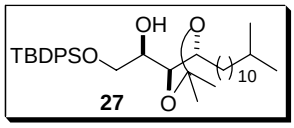
(2*R*,3*S*,4*R*)-1-*O*-*t*-Buthyldiphenylsilyl-3,4-*O*-isopropylidene-5-hexadecene-15-methyl-1,2,3,4-

tetrol (25). To a solution of **24** (320 mg, 0.75 mmol) and 11-methyl-dodec-1-ene (**39**) (1.37 g, 7.51 mmol) in CH_2Cl_2 (25 mL) was added the Grubbs generation II catalyst **41** (127 mg, 0.15 mmol). The reaction mixture was stirred at reflux for 24 h, concentrated and directly purified by silica gel flash column chromatography (hexane/EtOAc, 9:1, v/v) to afford the title compound **25** (327 mg, 0.56 mmol, 75%) as a colorless oil.: R_f = 0.45 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1112, 3483 cm^{-1}; $[\alpha]_D^{20}$ −3.9 (*c* 0.9, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 3 H), 0.87 (s, 3 H), 1.07 (s, 9 H), 1.15−1.35 (m, 15 H), 1.38 (s, 3 H), 1.50 (s, 3 H), 2.00−2.02 (m, 2 H), 2.42 (d, *J* = 4.5 Hz, 1 H), 3.65−3.70 (m, 3 H), 4.26 (dd, *J* = 2.2, 6.2 Hz, 1 H), 4.51 (t, *J* = 7.3 Hz, 1 H), 5.58−5.70 (m, 2 H), 7.36−7.67 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 22.8, 25.0, 27.0, 27.3, 27.5, 28.1, 29.1, 29.3, 29.6, 29.7, 30.0, 32.3, 39.1, 65.0, 70.2, 77.2, 79.1, 108.3, 125.7, 127.8, 129.9, 133.3, 135.7, 137.4. Anal. calcd for $C_{36}H_{56}O_4Si$: C, 74.43; H, 9.72. Found: C, 74.69; H, 9.94.

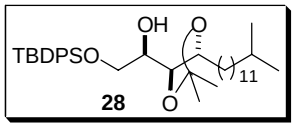


(2*R*,3*S*,4*R*)-1-*O*-*t*-Buthyldiphenylsilyl-3,4-*O*-isopropylidene-5-heptadecene-16-methyl-1,2,3,4-tetrol (26). The title compound **26** was prepared from compound **24** (180 mg, 0.42 mmol) in the same procedure as described for **25**: 190 mg (0.319 mmol, 76%); colorless oil; R_f = 0.45 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1111, 3421 cm^{-1}; $[\alpha]_D^{20}$ −2.8 (*c* 0.9, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 0.87 (s, 3 H), 1.06 (s, 9 H), 1.13−1.35 (m, 14 H), 1.38 (s, 3 H), 1.50 (s, 3 H), 1.53−1.61 (m, 3 H), 1.97−2.04 (m, 2 H), 2.42 (brs, 1 H), 3.62−3.71 (m, 3 H), 4.23−4.27 (m, 1 H), 4.50 (t, *J* = 7.3 Hz, 1 H), 5.54−5.73 (m, 2 H), 7.34−7.68 (m, 10 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.4, 22.8, 25.1, 27.0, 27.4, 27.6, 28.1, 29.1, 29.4, 29.6, 29.8, 29.9, 30.1, 32.4,

39.2, 65.0, 70.2, 77.3, 79.1, 108.4, 125.7, 127.86, 127.9, 129.94, 133.4, 135.7, 137.5. Anal. calcd for $C_{37}H_{58}O_4Si$: C, 74.70; H, 9.83. Found: C, 74.33; H, 9.99.

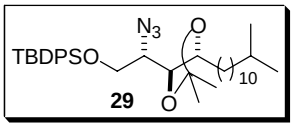


(2*R*,3*S*,4*R*)-1-*O*-*t*-Buthyldiphenylsilyl-3,4-*O*-isopropylidene-15-methyl-1,2,3,4-hexadecanetetrol (27). Compound **25** (236 mg, 0.406 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of $Pd(OH)_2$ (20%, 150 mg) in EtOAc (10 mL) at room temperature for 1.5 h. The reaction mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 9:1, v/v) to afford the title compound **27** (225 mg, 0.386 mmol, 95%) as a colorless oil.: R_f = 0.50 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1112, 3416 cm^{-1}; $[\alpha]_D^{20}$ −10.8 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 3 H), 0.87 (s, 3 H), 1.07 (s, 9 H), 1.15−1.36 (m, 18 H), 1.36 (s, 3 H), 1.47 (s, 3 H), 1.49−1.72 (m, 3 H), 2.35 (brs, 1 H), 3.66−3.71 (m, 3 H), 4.09−4.18 (m, 2 H), 7.36−7.67 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.3, 27.0(m), 27.4, 27.5, 28.1, 29.8(m), 30.0, 30.1, 39.2, 65.4, 70.0, 76.6, 77.6, 107.8, 127.9, 129.9, 133.4, 135.7. Anal. calcd for $C_{36}H_{58}O_4Si$: C, 74.17; H, 10.03. Found: C, 74.12; H, 10.32.



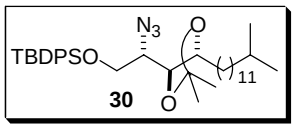
(2*R*,3*S*,4*R*)-1-*O*-*t*-Buthyldiphenylsilyl-3,4-*O*-isopropylidene-16-methyl-1,2,3,4-heptadecanetetrol (28). The title compound **28** was prepared from compound **26** (422 mg, 0.709

mmol) in the same procedure as described for **27**: 398 mg (0.667 mmol, 94%); colorless oil; R_f = 0.35 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1111, 3421 cm^{-1}; $[\alpha]_D^{20}$ −8.6 (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 3 H), 0.87 (s, 3 H), 1.07 (s, 9 H), 1.15−1.32 (m, 20 H), 1.36 (s, 3 H), 1.46 (s, 3 H),1.49−1.53 (m, 2 H), 1.71−1.78 (m, 1 H), 2.35 (brs, 1 H), 3.67−3.71 (m, 3 H), 4.09−4.14 (m, 1 H), 4.16−4.21 (m, 1 H), 7.36−7.68 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 22.8, 25.3, 27.0, 27.4, 27.5, 28.1, 29.8, 30.0, 30.1, 39.2, 65.4, 70.0, 76.6, 77.6, 107.8, 127.9, 129.9, 133.4, 135.7. Anal. calcd for $C_{37}H_{60}O_4Si$: C, 74.44; H, 10.13. Found: C, 74.35; H, 10.34.

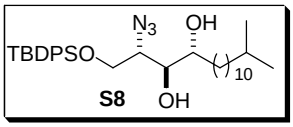


(2*S*,3*S*,4*R*)-2-Azide-1-*O*-*t*-buthyldiphenylsilyl-3,4-*O*-isopropylidene-15-methyl-1,3,4-hexadecanetriol (29). To a stirred solution of **27** (1.04 g, 1.78 mmol) in CH_2Cl_2 (10 mL) at 0 °C, trifluoromethanesulfonic anhydride (450 μL, 2.76 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (567 mg, 2.76 mmol) were added. The resulting solution was stirred at 0 °C for 12 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel quick column chromatography (hexane/EtOAc = 15:1, v/v) to afford the triflate intermediate (R_f = 0.43, hexane/EtOAc, 15:1, v/v). A solution of the triflate intermediate and tetramethylguanidinium azide (1.41 g, 8.91 mmol) in DMF (15 mL) was stirred at 0 °C for 10 min. The reaction mixture was diluted with EtOAc (100 mL), washed with saturated aqueous NH_4Cl (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 15:1, v/v) to afford the title compound

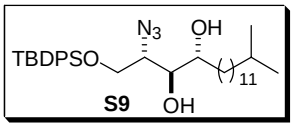
29 (952 mg, 1.57 mmol, 88%) as a colorless oil.: R_f = 0.55 (hexane/EtOAc, 15:1, v/v); IR ($CHCl_3$ film) 1111, 2101 cm^{-1}; $[\alpha]_D^{20}$ +18.3 (*c* 0.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 0.88 (s, 3 H), 1.08 (s, 9 H), 1.14−1.40 (m, 22 H), 1.41−1.59 (m, 5 H), 3.39−3.46 (m, 1 H), 3.85 (dd, *J* = 7.0, 10.8 Hz, 1 H), 3.95 (dd, *J* = 5.5, 9.7 Hz, 1 H), 4.03 (dd, *J* = 2.6, 10.8 Hz, 1 H), 4.09−4.16 (m, 1 H), 7.36−7.75 (m, 10 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.3, 22.8, 25.8, 26.6, 26.8, 27.6, 28.1, 28.3, 29.6, 29.7, 29.8, 29.9, 30.1, 39.2, 61.9, 65.4, 75.4, 78.0, 108.3, 127.8, 127.9, 129.88, 129.9, 133.0, 133.2, 135.76, 135.8. Anal. calcd for $C_{36}H_{57}N_3O_3Si$: C, 71.12; H, 9.45; N, 6.91. Found: C, 71.19; H, 9.72; N, 6.73.



(2*S*,3*S*,4*R*)-2-Azide-1-*O*-*t*-buthyldiphenylsilyl-3,4-*O*-isopropylidene-16-methyl-1,3,4-heptadecanetriol (30). The title compound **30** was prepared from compound **28** (133 mg, 0.223 mmol) in the same procedure as described for **29**: 122 mg (0.196 mmol, 88%); colorless oil; R_f = 0.55 (hexane/EtOAc, 15:1, v/v); IR ($CHCl_3$ film) 1116, 2100 cm^{-1}; $[\alpha]_D^{20}$ +16.8 (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 3 H), 0.87 (s, 3 H), 1.08 (s, 9 H), 1.13−1.42 (m, 24 H), 1.49−1.55 (m, 5 H), 3.42 (t, *J* = 7.3 Hz, 1 H), 3.85 (dd, *J* = 7.0, 10.5 Hz, 1 H), 3.94 (dd, *J* = 5.5, 9.5 Hz, 1 H), 4.03 (dd, *J* = 2.5, 10.5 Hz, 1 H), 4.09−4.15 (m, 1 H), 7.37−7.73 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 22.8, 25.8, 26.6, 26.8, 27.6, 28.1, 28.3, 29.6, 29.8, 30.1, 31.7, 31.9, 39.2, 61.9, 65.4, 75.4, 78.0, 108.3, 127.8, 127.9, 129.9, 133.1, 133.2, 135.77, 135.8. Anal. calcd for $C_{37}H_{59}N_3O_3Si$: C, 71.45; H, 9.56; N, 6.76. Found: C, 71.27; H, 9.77; N, 6.86.

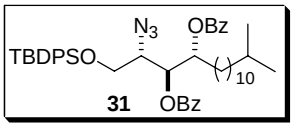


(2*S*,3*S*,4*R*)-2-Azide-1-*O*-*t*-buthyldiphenylsilyl-15-methyl-1,3,4-hexadecanetriol (S8). A solution of **29** (870 mg, 1.43 mmol) and trifluoroacetic acid (1 mL) in H_2O (0.1 mL) and CH_2Cl_2 (9 mL) was stirred at room temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 4:1, v/v) to afford the title compound **S8** (756 mg, 1.33 mmol, 93%) as a colorless oil.: R_f = 0.38 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1122, 2100, 3385 cm^{-1}; $[\alpha]_D^{20}$ +23.5 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (s, 3 H), 0.87 (s, 3 H), 1.08 (s, 9 H), 1.16−1.54 (m, 21 H), 2.14 (brs, 1 H), 2.67 (brs, 1 H), 3.53−3.58 (m, 1 H), 3.63−3.69 (m, 2 H), 3.91 (dd, *J* = 6.0, 10.5 Hz, 1 H), 4.03 (dd, *J* = 3.5, 10.5 Hz, 1 H), 7.38−7.70 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 22.8, 25.8, 26.9, 27.5, 28.1, 29.7, 30.1, 31.9, 39.2, 63.6, 64.3, 72.5, 74.2, 128.0, 130.1, 132.6, 132.7, 135.7. Anal. calcd for $C_{33}H_{53}N_3O_3Si$: C, 69.80; H, 9.41; N, 7.40. Found: C, 69.86; H, 9.08; N, 7.68.



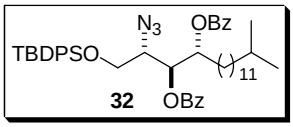
(2*S*,3*S*,4*R*)-2-Azide-1-*O*-*t*-buthyldiphenylsilyl-16-methyl-1,3,4-heptadecanetriol (S9). The title compound **S9** was prepared from compound **30** (57 mg, 0.0916 mmol) in the same procedure as described for **S8**: 49 mg (0.0842 mmol, 92%); colorless oil; R_f = 0.38 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1122, 2100, 3396 cm^{-1}; $[\alpha]_D^{20}$ +17.8 (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ

0.86 (s, 3 H), 0.87 (s, 3 H), 1.08 (s, 9 H), 1.14−1.56 (23 H), 2.07 (brs, 1 H), 2.59 (brs, 1 H), 3.52−3.60 (m, 1 H), 3.64−3.73 (m, 2 H), 3.91 (dd, *J* = 5.5, 10.5 Hz, 1 H), 4.03 (dd, *J* = 3.5, 10.5 Hz, 1 H), 7.40−7.70 (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 22.8, 25.8, 26.9, 27.6, 28.1, 29.7, 30.1, 31.9, 39.2, 63.4, 64.3, 72.5, 74.2, 128.0, 130.2, 132.5, 135.7. Anal. calcd for $C_{34}H_{55}N_3O_3Si$: C, 70.18; H, 9.53; N, 7.22. Found: C, 70.07; H, 9.72; N, 7.52.

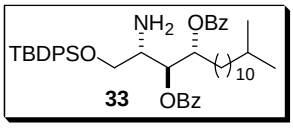


(2*S*,3*S*,4*R*)-2-Azide-3,4-di-*O*-benzoyl-1-*O*-*t*-buthyldiphenylsilyl-15-methyl-1,3,4-hexadecanetriol (31). To a solution of compound **S8** (340 mg, 0.60 mmol) in CH_2Cl_2 (5mL) and pyridine (5 mL) were added benzoyl chloride (209 μL, 1.80 mmol) and 4-(dimethylamino) pyridine (22 mg, 0.18 mmol). After stirring at room temperature for 12 h, the reaction mixture was quenched with NH_4Cl (5 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was washed with 2N HCl (2 × 30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 15:1, v/v) to afford the title compound **31** (418 mg, 0.54 mmol, 90%) as a colorless oil.: R_f = 0.65 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1116, 1265, 1731, 2106 cm^{-1}; $[\alpha]_D^{20}$ +6.6 (*c* 0.65, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 1.05 (s, 9 H), 1.14−1.53 (m, 19 H), 1.75−1.85 (m, 2 H), 3.82−3.91 (m, 2 H), 3.95−4.04 (m, 1 H), 5.51−5.57 (m, 2 H), 7.19−7.67 (m, 16 H), 7.86−7.94 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.1, 22.8, 25.5, 26.7, 27.5, 28.1, 29.45, 29.5, 29.6, 29.7, 29.8, 29.83, 30.0, 39.1, 63.2, 64.2, 72.3, 73.2, 127.8, 127.9, 128.5, 128.6, 129.5, 129.8, 129.86, 129.9, 132.5, 132.8, 133.1, 133.4, 135.6, 135.65, 165.1, 165.7. Anal. calcd for

$C_{47}H_{61}N_3O_5Si$: C, 72.74; H, 7.92; N, 5.41. Found: C, 72.70; H, 7.63; N, 5.68.

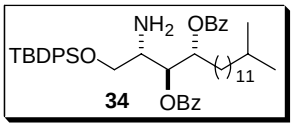


(2*S*,3*S*,4*R*)-2-Azide-3,4-di-*O*-benzoyl-1-*O*-*t*-buthyldiphenylsilyl-16-methyl-1,3,4-heptadecanetriol (32). The title compound **32** was prepared from compound **S9** (38 mg, 0.065 mmol) in the same procedure as described for **31**: 46 mg (0.058 mmol, 89%); colorless oil; R_f = 0.65 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1116, 1265, 1731, 2105 cm^{-1}; $[\alpha]_D^{20}$ +9.4 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 0.86 (s, 3 H), 1.04 (s, 9 H), 1.14−1.42 (m, 20 H), 1.43−1.52 (m, 1 H), 1.77−1.83 (m, 2 H), 3.79−3.90 (m, 2 H), 3.93−4.02 (m, 1 H), 5.44−5.58 (m, 2 H), 7.21−7.65 (m, 16 H), 7.87 (d, *J* = 7.5 Hz, 2 H), 7.91 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2, 22.8, 25.5, 26.8, 27.5, 28.1, 29.5, 29.7, 29.8, 30.1, 39.2, 63.3, 64.3, 72.4, 73.3, 127.9,128.5, 128.6, 129.9, 132.6, 132.9, 133.1, 133.4, 135.7, 165.2, 165.8. Anal. calcd for $C_{48}H_{63}N_3O_5Si$: C, 72.97; H, 8.04; N, 5.32. Found: C, 72.88; H, 8.24; N, 5.16.



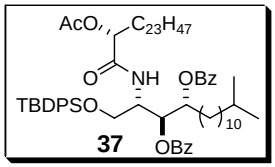
(2*S*,3*S*,4*R*)-2-Amino-3,4-di-*O*-benzoyl-1-*O*-*t*-buthyldiphenylsilyl-15-methyl-1,3,4-hexadecanetriol (33). Compound **31** (355 mg, 0.457 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of $Pd(OH)_2$ (20%, 177 mg) in MeOH–EtOAc (1:1, v/v, 10 mL) at room temperature for 4 h. The reaction mixture was filtered through Celite® and the filtrate was concentrated in vacuo. The residue was purified by silica gel flash column

chromatography (hexane/EtOAc, 4:1, v/v) to afford the title compound **33** (319 mg, 0.425 mmol, 93%) as a colorless oil.: R_f = 0.28 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1116, 1275, 1726, 3375 cm^{-1}; $[\alpha]_D^{20}$ −22.8 (*c* 1.2, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 1.04 (s, 9 H), 1.15−1.55 (m, 19 H), 1.77−1.83 (m, 2 H), 2.09 (brs, 2 H), 3.24−3.31 (m, 1 H), 3.65 (dd, *J* = 6.6, 10.2 Hz, 1 H), 3.84 (dd, *J* = 3.1, 10.2 Hz, 1 H), 5.51 (dd, *J* = 3.5, 7.3 Hz, 1 H), 5.62−5.68 (m, 1 H), 7.15−7.65 (m, 16 H), 7.90−7.93 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.3, 22.8, 25.6, 26.9, 27.5, 28.0, 29.5, 29.6, 29.7, 29.75, 30.0, 39.1, 53.6, 65.7, 73.9, 74.8, 127.7, 127.8, 128.0, 128.37, 128.4, 129.7, 129.8, 130.0, 130.1, 130.2, 132.9, 133.0, 133.1, 133.3, 135.6, 135.63, 165.5, 166.0. Anal. calcd for $C_{47}H_{63}NO_5Si$: C, 75.26; H, 8.47; N, 1.87. Found: C, 75.28; H, 8.25; N, 1.74.

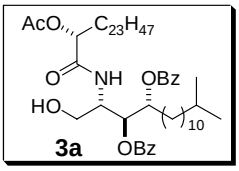


(2*S*,3*S*,4*R*)-2-Amino-3,4-di-*O*-benzoyl-1-*O*-*t*-buthyldiphenylsilyl-16-methyl-1,3,4-heptadecanetriol (34). The title compound **34** was prepared from compound **32** (39 mg, 0.0494 mmol) in the same procedure as described for **33**: 36 mg (0.0471 mmol, 95%); colorless oil; R_f = 0.28 (hexane/EtOAc, 4:1, v/v); IR ($CHCl_3$ film) 1111, 1270, 1726, 3370 cm^{-1}; $[\alpha]_D^{20}$ −14.0 (*c* 0.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 1.03 (s, 9 H), 1.14−1.55 (m, 21 H), 1.75−1.83 (m, 2 H), 1.97 (brs, 2 H), 3.22−3.29 (m, 1 H), 3.63 (dd, *J* = 6.9, 10.2 Hz, 1 H), 3.83 (dd, *J* = 3.2, 10.2 Hz, 1 H), 5.48 (dd, *J* = 3.5, 7.4 Hz, 1 H), 5.59−5.65 (m, 1 H), 7.18−7.65 (m, 16 H), 7.88−7.92 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.3, 22.8, 25.7,27.0, 27.5, 28.1, 29.6, 29.67, 29.7, 29.77, 29.8, 30.1, 39.2, 53.6, 65.8, 74.0,74.9, 127.8, 127.9, 128.4, 128.5, 129.8, 129.84, 130.0,

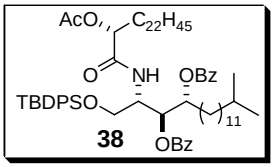
130.1, 130.3, 133.0, 133.1, 133.3, 135.65, 135.7, 165.6, 166.1. HRMS (FAB) calcd for $C_{48}H_{65}NO_5SiNa$ $(M+Na)^+$: *m*/*z* 786.4530. Found: 786.4538.



(2*S*,3*S*,4*R*)-*N*-[(*R*)-2-Acetoxypentacosanoyl]-2-amino-3,4-di-*O*-benzoyl-1-*O*-*t*-buthyldiphenylsilyl-15-methyl-1,3,4-hexadecanetriol (37). A solution of **33** (45 mg, 0.06 mmol), **35** (32 mg, 0.073 mmol), and 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) (23 mg, 0.093 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with EtOAc (50 mL), washed consecutively with aqueous $NaHCO_3$, aqueous 1 N HCl. The organic layer was dried over $MgSO_4$, concentrated in vacuo, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc, 9:1, v/v) to afford the title compound **37** (68 mg, 0.058 mmol, 97%) as a colorless oil.: R_f = 0.33 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1112, 1280, 1690, 1731 cm^{-1}; $[\alpha]_D^{20}$ +34.1 (*c* 0.8, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.2 Hz, 3 H), 0.99 (s, 9 H), 1.07−1.53 (m, 61 H), 1.82−1.96 (m, 4 H), 2.04 (s, 3 H), 3.65 (dd, *J* = 2.9, 10.6 Hz, 1 H), 3.75 (dd, *J* = 2.6, 10.6 Hz, 1 H), 4.47−4.55 (m, 1 H), 5.31−5.37 (m, 2 H), 5.86 (dd, *J* = 2.3, 9.3 Hz, 1 H), 6.99−7.64 (m, 17 H), 7.95−8.00 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.3, 19.3, 21.0, 22.8, 22.83, 25.0, 25.9, 26.7, 26.8, 27.6, 28.1, 28.6, 29.5, 29.6, 29.7, 29.8, 29.9, 30.1, 32.1, 32.4, 39.2, 49.7, 62.2, 72.0, 74.2, 74.3, 127.7, 127.8, 128.0, 128.5, 128.6, 129.9, 129.93, 130.0, 130.4, 132.1, 133.0, 133.3, 134.9, 135.4, 135.6, 165.2, 166.5, 169.7, 169.8. Anal. calcd for $C_{74}H_{113}NO_8Si$: C, 75.79; H, 9.71; N, 1.19. Found: C, 75.74; H, 9.55; N, 1.11.

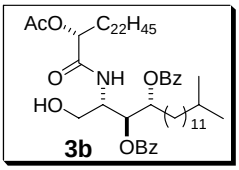


(2*S*,3*S*,4*R*)-*N*-[(*R*)-2-Acetoxypentacosanoyl]-2-amino-3,4-di-*O*-benzoyl-15-methyl-1,3,4-hexadecanetriol (3a). A solution of compound **37** (68 mg, 0.058 mmol) and Bu_4NF (1.0 M, 87 μL, 0.087 mmol) in THF (3 mL) was stirred at room temperature for 1 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 2:1, v/v) to afford the title compound **3a** (52 mg, 0.056 mmol, 97 %) as a colorless oil.: R_f = 0.38 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 1285, 1724, 3361 cm^{-1}; $[\alpha]_D^{20}$ +58.3 (*c* 0.4, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 0.90 (t, *J* = 6.3 Hz, 3 H), 1.04−1.53 (m, 61 H), 1.87−1.89 (m, 2 H), 1.95−2.05 (m, 2 H), 2.18 (s, 3 H), 3.24 (brs, 1 H), 3.45−3.72 (m, 2 H), 4.36−4.43 (m, 1 H), 5.18 (t, *J* = 6.2 Hz, 1 H), 5.36−5.41 (m, 1 H), 5.54 (dd, *J* = 2.3, 9.4 Hz, 1 H), 7.18 (d, *J* = 9.4 Hz, 1 H), 7.32−7.62 (m, 6 H), 7.93−8.05 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.2, 20.9, 22.7, 22.74, 25.0, 25.9, 27.5, 28.0, 28.5, 29.4, 29.5, 29.67, 29.7, 29.8, 30.0, 32.0, 39.1, 50.0, 61.2, 73.2, 74.0, 74.4, 128.4, 128.6, 129.2, 129.7, 129.9, 129.95, 133.1, 133.7, 166.3, 166.7, 170.2, 170.4. HRMS (FAB) calcd for $C_{58}H_{95}NO_8Na$ $(M+Na)^+$: *m*/*z* 956.6955. Found: 956.6971. Anal. calcd for $C_{58}H_{95}NO_8$: C, 74.55; H, 10.25; N, 1.50. Found: C, 74.44; H, 10.45; N, 1.37.



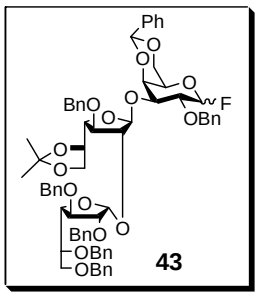
(2*S*,3*S*,4*R*)-*N*-[(*R*)-2-Acetoxypentacosanoyl]-2-amino-3,4-di-*O*-benzoyl-1-*O*-*t*-

buthyldiphenylsilyl-16-methyl-1,3,4-heptadecanetriol (38). The title compound **38** was prepared from compound **34** (33 mg, 0.043 mmol) and compound **36** (22 mg, 0.052 mmol) in the same procedure as described for **37**: 48 mg (0.041 mmol, 95%); colorless oil; R_f = 0.33 (hexane/EtOAc, 9:1, v/v); IR ($CHCl_3$ film) 1112, 1286, 1690, 1731 cm^{-1}; $[\alpha]_D^{20}$ +38 (*c* 0.45, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.2 Hz, 3 H), 0.99 (s, 9 H), 1.08−1.53 (m, 61 H), 1.81−1.96 (m, 4 H), 2.04 (s, 3 H), 3.66 (dd, *J* = 2.4, 10.4 Hz, 1 H), 3.73−3.76 (m, 1 H), 4.51 (t, J = 8.6 Hz, 1 H), 5.29−5.36 (m, 2 H), 5.85 (dd, *J* = 2.3, 8.6 Hz, 1 H), 7.00−7.60 (m, 17 H), 7.91−8.05 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 19.2, 21.0, 22.8, 25.0, 25.9, 26.8, 27.6, 28.1, 28.6, 29.5, 29.6, 29.8, 30.1, 32.1, 32.4, 39.2, 49.7, 62.3, 72.0, 74.2, 74.3, 127.7, 128.0, 128.4, 128.6, 129.9, 130.4, 132.2, 132.8, 133.0, 133.3, 135.4, 135.6, 165.2, 166.5, 169.7, 169.8. Anal. Calcd for $C_{74}H_{113}NO_8Si$: C, 75.79; H, 9.71; N, 1.19. Found: C, 75.81; H, 9.35; N, 1.08.



(2*S*,3*S*,4*R*)-*N*-[(*R*)-2-Acetoxypentacosanoyl]-2-amino-3,4-di-*O*-benzoyl-16-methyl-1,3,4-heptadecanetriol (3b). The title compound **3b** was prepared from compound **38** (48 mg, 0.0409 mmol) in the same procedure as described above **3a**: 37 mg (0.0396 mmol, 97%); colorless oil; R_f = 0.38 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 1278, 1670, 1732, 3357 cm^{-1}; $[\alpha]_D^{20}$ +54.2 (*c* 0.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 0.88 (t, *J* = 6.2 Hz, 3 H), 1.12−1.56 (m, 61 H), 1.87−1.89 (m, 2 H), 0.98−2.05 (m, 2 H), 2.21 (s, 3 H), 2.76 (brs, 1 H), 3.49−3.71 (m, 2 H), 4.32−4.39 (m, 1 H), 5.19 (t, *J* = 6.1 Hz, 1 H), 5.36−5.40 (m, 1 H), 5.45 (dd, *J* = 2.4, 9.3 Hz, 1 H), 7.03 (d, *J* = 9.3 Hz, 1 H), 7.35−7.67 (m, 6 H), 7.94−8.07 (m, 4 H); ^{13}C NMR (63

MHz, $CDCl_3$) δ 14.3, 21.2, 22.8, 22.83, 25.1, 26.0, 27.6, 28.1, 28.6, 29.45, 29.5, 29.54, 29.6, 29.75, 29.8, 29.85, 30.1, 32.1, 39.2, 50.0, 61.4, 73.6, 73.9, 74.4, 128.5, 128.8, 129.1, 129.8, 130.0, 130.1, 133.3, 134.0, 166.3, 167.2, 170.2, 170.4. MALDI-TOF calcd for $C_{58}H_{95}NO_8Na$ $(M+Na)^+$: *m/z* 956.6955. Found: 956.7050. Anal. calcd for $C_{58}H_{95}NO_8$: C, 74.55; H, 10.25; N, 1.50. Found: C, 74.53; H, 10.30; N, 1.44.

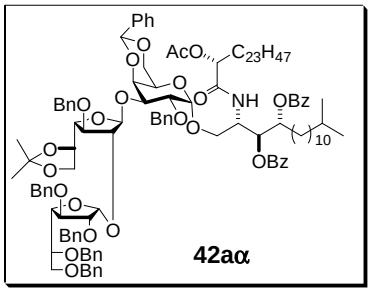


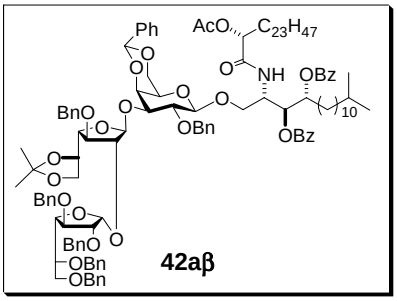
43

2,3,5,6-Tetra-*O*-benzyl-α-D-galactofuranosyl-(1→2)-(3-*O*-benzyl-5,6-*O*-isopropylidene-β-D-galactofuranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-D-galactopyranosyl fluoride (43). A solution of donor **2** (100 mg, 0.077 mmol) and DTBMP (50 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to –78 °C. To the resulting solution was added a solution of Tf_2O (20 μL, 0.12 mmol) and subsequently added hydrogen fluoride (70% in pyridine, 6 μL, 0.23 mmol), then the solution was stirred at –78 °C for further 1 h and allowed to warm to 0 °C over 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc, 2:1, v/v) to afford the title compound **43** (75 mg, 0.064 mmol, 83 %, β/α = 20:1). **43α**: colorless oil, R_f = 0.4 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 2925, 1456, 1125 cm^{-1}; $[\alpha]_D$ +52.0 (*c* 0.1,

$CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.32 (s, 3 H), 1.33 (s, 3 H), 3.62−3.79 (m, 6 H), 3.88−4.01 (m, 4 H), 4.06−4.26 (m, 6 H), 4.31−4.44 (m, 7 H), 4.48−4.58 (m, 3 H), 4.63−4.73 (m, 4 H), 4.96 (d, *J* = 4.6 Hz, 1 H), 5.26 (brs, 1 H), 5.56 (s, 1 H), 5.63 and 5.85 (dd, *J* = 2.3, 53.4 Hz, 1 H), 7.21−7.50 (m, 35 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.6, 26.8, 64.9, 65.5, 69.0, 70.8, 72.0, 72.5(2), 73.3, 73.5, 73.8, 74.2 and 74.6 (d, *J* = 23.9 Hz, C-2), 75.6, 76.3, 77.0, 77.4, 79.4, 80.1, 83.0, 83.9, 84.8, 84.9, 98.8, 100.7, 104.9 and 108.5 (d, *J* = 223.5 Hz, C-1), 108.5, 109.8, 126.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.06, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.63, 128.9, 137.67, 138.0, 138.16, 138.2, 138.3, 138.4. HRMS (FAB) calcd for $(M+Na)^+$: *m*/*z* 1197.4988. Found: 1197.4991. Anal. calcd for $C_{70}H_{75}FO_{15}$: C, 71.53; H, 6.43. Found: C, 71.61; H, 6.26.

43β: colorless oil, R_f = 0.25 (hexane/EtOAc, 2:1, v/v); IR ($CHCl_3$ film) 2929, 1459, 1102 cm^{-1}; $[\alpha]_D$ +68.0 (*c* 0.2, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 1.34 (s, 6 H), 3,51 (brs, 1 H), 3.60−3.78 (m, 7 H), 3.83−3.88 (m, 1 H), 3.96−3.97 (m, 1 H), 3.99−4.01 (m, 1 H), 4.07−4.20 (m, 4 H), 4.23 and 4.55 (ABq, *J* = 11.4 Hz, 2 H), 4.31−4.43 (m, 8 H), 4.52 (d, *J* = 2.0 Hz, 1 H), 4.61−4.72 (m, 3 H), 4.86 (d, *J* = 10.9 Hz, 1 H), 4.90 (d, *J* = 4.7 Hz, 1 H), 5.12 and 5.34 (dd, *J* = 7.2, 53.0 Hz, 1 H), 5.23 (brs, 1 H), 5.56 (s, 1 H), 7.15−7.53 (m, 35 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 25.5, 26.8, 65.4, 66.8, 66.9, 68.7, 70.7, 71.9, 72.2, 72.4, 73.3, 73.5, 75.2, 75.7, 77.0, 77.4 and 77.8 (d, *J* = 30.3 Hz, C-2), 77.9, 79.3, 80.1, 83.2, 83.9, 84.4, 84.9, 98.6, 101.0, 108.3, 108.7 and 112.1 (d, *J* = 215.5 Hz, C-1), 109.8, 126.3, 127.5, 127.6, 127.7, 127.75, 127.8, 127.9, 127.97, 128.0, 128.2, 128.3, 128.4, 128.44, 128.5, 128.9, 137.7, 138.1, 138.16, 138.2, 138.3, 138.4. HRMS (FAB) calcd for $(M+Na)^+$: *m*/*z* 1197.4988. Found: 1197.4987. Anal. calcd for $C_{70}H_{75}FO_{15}$: C, 71.53; H, 6.43. Found: C, 71.28; H, 6.54.





Synthesis of 42a (Glycosylation of ceramide 3a).

Method A: Using CB glycoside **2** as glycosyl donor**.**

A solution of ceramide **3a** (150 mg, 0.161 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (83 mg, 0.404 mmol) in CH_2Cl_2 (20 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to –78 °C. To the resulting solution were added sequentially a solution of Tf_2O (34 µL, 0.202 mmol) and dropwise a solution of CB glycosyl donor **2** (175 mg, 0.134 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for further 1 h at –78 °C, allowed to warm over 1 h to 0 °C, diluted with CH_2Cl_2 (50 mL), and quenched with saturated aqueous $NaHCO_3$ (2 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **42a** (216 mg, 0.103 mmol, 77%, **α/β = 1.4:1**).

Method B: Using glycosyl fluoride **43** as glycosyl donor.

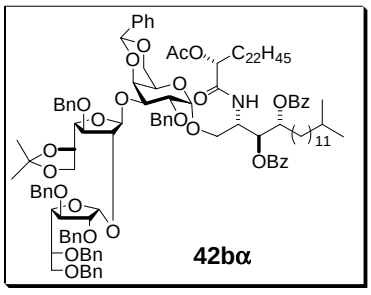
A solution of ceramide **3a** (27 mg, 0.029 mmol), tin(II) chloride (13 mg, 0.069 mmol), silver perchlorate (14 mg, 0.068 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (7 mg, 0.034 mmol) in THF (5 mL) in the presence of 4 Å molecular sieves was stirred for 30 min at room temperature and cooled to –10 °C. To the resulting solution was dropwise added a solution of glycosyl fluoride **43** (52 mg, 0.044 mmol) in THF (2 mL) at –10 °C. The reaction mixture was stirred for further 1 h at –

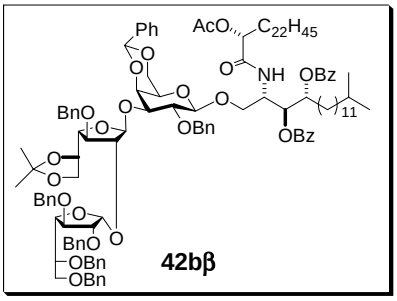
10 °C, allowed to warm over 1 h to room temperature, diluted with diethyl ether (50 mL), and quenched with saturated aqueous $NaHCO_3$ (5 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **42aα** (43 mg, 0.021 mmol, 72%).

42aα : colorless oil, R_f = 0.35 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1262, 1367, 1525, 1679, 1728, 3321 cm^{-1}; $[\alpha]_D^{20}$ +47.6 (*c* 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.5 Hz, 3 H), 1.14−1.51 (m, 67 H), 1.82−1.95 (m, 4 H), 2.15 (s, 3 H), 3.56−3.68 (m, 5 H), 3.72−3.78 (m, 2 H), 3.90−4.04 (m, 6 H), 4.09−4.15 (m, 3 H), 4.22 (d, *J* = 12.0 Hz, 1 H), 4.30 (d, *J* = 11.5 Hz, 1 H), 4.37−4.48 (m, 7 H), 4.50−4.60 (m, 6 H), 4.63−4.69 (m, 2 H), 4.78 (d, *J* = 3.1 Hz, 1 H), 5.01 (d, *J* = 4.0 Hz, 1 H), 5.13 (t, *J* = 5.8 Hz, 1 H), 5.17−5.27 (m, 1 H), 5.21 (brs, 1 H), 5.57 (s, 1 H), 5.70 (d, *J* = 9.5 Hz, 1 H), 7.14−7.55 (m, 41 H), 7.68 (d, *J* = 10.0 Hz, 1 H), 7.93 (d, *J* = 7.5 Hz, 2 H), 7.99 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 21.1, 22.8, 25.3, 25.6, 25.9, 26.7, 27.5, 27.8, 28.1, 29.5, 29.8(m), 30.0, 32.0, 32.3, 39.2, 48.7, 63.8, 65.5, 69.3, 70.8, 71.3, 71.9, 72.3,72.4, 73.3, 73.5, 73.7, 74.2, 74.5, 74.9, 75.9, 76.69, 76.7, 77.3, 79.6, 80.1, 82.5, 83.7, 84.6, 84.8, 98.5, 100.5, 100.8, 107.9, 109.6, 126.1, 127.4, 127.6, 127.7, 127.9, 128.1, 128.25, 128.3, 128.4, 128.6, 129.8, 129.9, 130.2, 133.1, 133.4, 137.7, 138.2, 138.4, 165.1, 166.6, 170.5, 171.1. MALDI-TOF calcd for $C_{128}H_{169}NNaO_{23}$ $(M+Na)^+$: *m/z* 2111.1983. Found: 2111.1982. Anal. calcd for $C_{128}H_{169}NO_{23}$: C, 73.57; H, 8.15; N, 0.67. Found: C, 73.57; H, 8.35; N, 0.62.

42aβ : colorless oil, R_f = 0.18 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1285, 1455, 1690, 1721, 3388 cm^{-1}; $[\alpha]_D^{20}$ +48.6 (*c* 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.0 Hz, 3 H), 1.13−1.51 (m, 67 H), 1.76−2.01 (m, 4 H), 1.85 (s, 3 H), 3.45 (brs, 1 H),

3.56−3.73 (m, 8 H), 3.82−3.91 (m, 2 H), 3.92−4.01 (m, 3 H), 4.05−4.14 (m, 2 H), 4.19 (d, *J* = 12.0 Hz, 1 H), 4.26 (d, *J* = 11.5 Hz, 1 H), 4.28−4.32 (m, 1 H), 4.33−4.44 (m, 8 H), 4.49 (brs, 1 H), 4.55−4.59 (m, 3 H), 4.65 (d, *J* = 12.5 Hz, 1 H), 4.68 (d, *J* = 11.5 Hz, 1 H), 4.77 (d, *J* = 11.0 Hz, 1 H), 4.92 (d, *J* = 4.0 Hz, 1 H), 5.10 (t, *J* = 6.1 Hz, 1 H), 5.19 (brs, 1 H), 5.35−5.39 (m, 1 H), 5.54 (s, 1 H), 5.75 (dd, *J* = 3.1, 8.6 Hz, 1 H), 6.93 (d, *J* = 9.0 Hz, 1 H), 7.15−7.54 (m, 41 H), 7.95 (d, *J* = 7.5 Hz, 2 H), 8.01 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 20.9, 22.8, 25.0, 25.6, 25.7, 26.8, 27.5, 28.1, 28.7, 29.5, 29.8(m), 30.0, 32.0, 39.2, 48.3, 65.5, 66.7, 68.1, 69.0,70.8, 71.9, 72.2, 72.4, 73.0, 73.3, 73.6, 73.9, 74.2, 75.4, 76.3, 76.9, 77.9, 79.2, 79.4, 80.1, 83.0, 83.8, 84.5, 85.1, 98.7, 100.5, 104.4, 108.4, 109.8, 126.1, 127.7, 128.0, 128.1, 128.4, 129.8, 130.0, 130.1, 133.1, 133.4, 137.7, 138.1, 138.2, 138.4, 138.7, 165.5, 166.2, 170.3, 170.5. MALDI-TOF calcd for $C_{128}H_{169}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 2111.1983. Found: 2111.1980. Anal. calcd for $C_{128}H_{169}NO_{23}$: C, 73.57; H, 8.15; N, 0.67. Found: C, 73.65; H, 8.38; N, 0.63.





Synthesis of 42b (Glycosylation of ceramide 3b).

Method A: Using CB glycoside **2** as glycosyl donor**.**

A solution of ceramide **3b** (170 mg, 0.182 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (93 mg, 0.453 mmol) in CH_2Cl_2 (20 mL) in the presence of 4Å molecular sieves was stirred for 10 min at room temperature and cooled to –78 °C. To the resulting solution were added sequentially a solution

of Tf_2O (38 µL, 0.226 mmol) and dropwise a solution of CB glycosyl donor **2** (197 mg, 0.151 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for further 1 h at –78 °C, allowed to warm over 1 h to 0 °C, diluted with CH_2Cl_2 (50 mL), and quenched with saturated aqueous $NaHCO_3$ (2 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 3:1, v/v) to afford the title compound **42b** (237 mg, 0.113 mmol, 75%, **α/β = 1.4:1**).

Method B: Using glycosyl fluoride **43** as glycosyl donor.

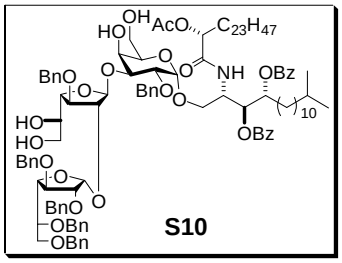
A solution of ceramide **3b** (25 mg, 0.027 mmol), tin(II) chloride (12 mg, 0.063 mmol), silver perchlorate (13 mg, 0.063 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (7 mg, 0.034 mmol) in THF (5 mL) in the presence of 4Å molecular sieves was stirred for 30 min at room temperature and cooled to –10 °C. To the resulting solution was dropwise added a solution of glycosyl fluoride **43** (47 mg, 0.040 mmol) in THF (2 mL) at –10 °C. The reaction mixture was stirred for further 1 h at –10 °C, allowed to warm over 1 h to room temperature, diluted with diethyl ether (50 mL), and quenched with saturated aqueous $NaHCO_3$ (5 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane /EtOAc, 3:1, v/v) to afford the title compound **42bα** (41 mg, 0.020 mmol, 74%).

42bα : colorless oil, R_f = 0.35 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1267, 1456, 1679, 1729, 3330 cm^{-1}; $[\alpha]_D^{20}$ +47.4 (*c* 0.2, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.87 (s, 3 H), 0.88 (t, *J* = 6.3 Hz, 3 H), 1.35−1.55 (m, 67 H), 1.81−1.85 (m, 4 H), 2.15 (s, 3 H), 3.55−3.76 (m, 7 H), 3.88−4.01 (m, 5 H), 4.03−4.19 (m, 4 H), 4.25 (d, *J* = 6.8 Hz, 1 H), 4.29−4.45 (m, 8 H),

4.51−4.53 (m, 3 H), 4.57−4.66 (m, 4 H), 4.68 (d, *J* = 7.7 Hz, 1 H), 4.80 (d, *J* = 3.2 Hz, 1 H), 5.01 (d, *J* = 4.6 Hz, 1 H), 5.10 (d, *J* = 6.0 Hz, 1 H), 5.18−5.27 (m, 2 H), 5.56 (s, 1 H), 5.74 (dd, *J* = 1.9, 10.2 Hz, 1 H), 7.12−7.60 (m, 41 H), 7.83 (d, *J* = 9.8 Hz, 1 H), 7.90−8.01 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.3, 21.1, 22.8, 25.3, 25.6, 25.9, 26.7, 27.6, 27.8, 28.1, 29.5, 29.54, 29.6, 29.78, 29.8(m), 30.1, 32.0, 32.3, 39.2, 48.7, 63.7, 65.5, 69.3, 70.3, 70.8, 71.2, 71.9, 72.2, 72.4, 73.3, 73.5, 73.7, 74.2, 74.5, 75.0, 75.8,77.4, 79.5, 80.1, 82.5, 83.7, 84.5, 84.8, 98.4, 100.4, 100.6, 108.0, 109.7, 126.1, 127.6, 127.7, 128.0, 128.1, 128.2, 128.28, 128.3, 128.36, 128.4, 128.43, 128.5, 129.8, 130.1, 133.1, 133.5, 137.7, 138.1, 138.2, 138.25, 138.26, 138.4, 165.1, 166.6, 170.6, 171.1. MALDI-TOF calcd for $C_{128}H_{169}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 2111.1983. Found: 2111.1982. Anal. calcd for $C_{128}H_{169}NO_{23}$: C, 73.57; H, 8.15; N, 0.67. Found: C, 73.69; H, 8.30; N, 0.62.

42bβ : colorless oil, R_f = 0.18 (hexane/EtOAc, 3:1, v/v); IR ($CHCl_3$ film) 1281, 1686, 1728, 3388 cm^{-1}; $[\alpha]_D^{20}$ +48.4 (*c* 0.1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.3 Hz, 3 H), 1.13−1.55 (m, 67 H), 1.65−2.04 (m, 4 H), 1.86 (s, 3 H), 3.45 (brs, 1 H), 3.59−3.71 (m, 8 H), 3.84−3.99 (m, 5 H), 4.05−4.13 (m, 2 H), 4.17 (d, *J* = 12.0 Hz, 1 H), 4.25 (d, *J* = 11.5, Hz, 1 H), 4.29−4.43 (m, 9 H), 4.50 (d, *J* = 1.7 Hz, 1 H), 4.54−4.66 (m, 4 H), 4.68 (d, *J* = 11.6 Hz, 1 H), 4.78 (d, *J* = 10.9 Hz, 1 H), 4.92 (d, *J* = 4.6 Hz, 1 H), 5.09 (t, *J* = 6.1 Hz, 1 H), 5.19 (brs, 1 H), 5.34−5.38 (m, 1 H), 5.53 (s, 1 H), 5.76 (dd, *J* = 3.3, 8.6 Hz, 1 H), 7.02 (d, *J* = 9.2 Hz, 1 H), 7.12−7.56 (m, 41 H), 7.93−8.02 (m, 4 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.8, 21.0,22.8, 24.4, 25.1, 25.6, 25.8, 26.8, 27.6, 28.1, 28.6, 29.5, 29.6, 29.7, 29.79, 29.8(m), 30.1, 32.1, 39.2, 40.6, 45.9, 48.3, 65.5, 66.6, 68.2, 69.0,70.8, 71.9, 72.2, 72.5, 72.9, 73.3, 73.6, 73.9, 74.2, 75.5, 76.3, 76.9, 77.0, 77.9, 79.1, 79.4, 80.1, 81.9, 83.0, 83.8, 84.4, 85.1, 98.6, 100.5, 104.5, 108.4, 109.8, 126.1, 127.6, 127.7, 127.8, 128.0, 128.03, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.8, 133.1, 133.5, 137.6, 138.0,

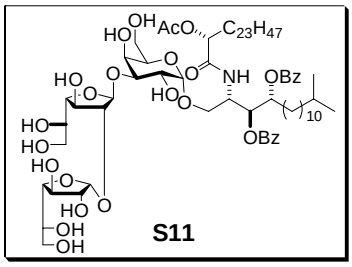
138.2, 138.21, 138.4, 138.7, 165.5, 166.3, 170.4, 170.5. MALDI-TOF calcd for $C_{128}H_{169}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 2111.1983. Found: 2111.1982. Anal. calcd for $C_{128}H_{169}NO_{23}$: C, 73.57; H, 8.15; N, 0.67. Found: C, 73.62; H, 8.42; N, 0.67.



S10

Compound S10. To a solution of **42aα** (110 mg, 0.0526 mmol) in CH_2Cl_2 (8 mL) was added trifluoroacetic acid (2 mL). The resulting solution was stirred at room temperature for 30 min. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous $NaHCO_3$ (2×50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/EtOAc, 1:2, v/v) to afford the title compound **S10** (92 mg, 0.0469 mmol, 89%) as a colorless oil.: R_f = 0.2 (hexane/EtOAc, 1:2, v/v); IR ($CHCl_3$ film) 1285, 1459, 1678, 1740, 3484 cm^{-1}; $[\alpha]_D^{20}$ +47.5 (*c* 0.5, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.83 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.3 Hz, 3 H), 1.05−1.55 (m, 61 H), 1.78−1.97 (m, 4 H), 2.13 (s, 3 H), 2.36 (brs, 1 H), 2.81 (brs, 1 H), 2.95 (brs, 1 H), 3.46−3.72 (m, 8 H), 3.82−4.20 (m, 12 H), 4.33−4.47 (m, 9 H), 4.53−4.57 (m, 4 H), 4.64−4.69 (m, 2 H), 4.88 (d, *J* = 4.2 Hz, 1 H), 5.04 (t, *J* = 6.1 Hz, 1 H), 5.11 (brs, 1 H), 5.19−5.25 (m, 1 H), 5.88 (d, *J* = 9.4 Hz, 1 H), 7.13−7.46 (m, 36 H), 7.89 (d, *J* = 7.4 Hz, 2 H), 7.97 (d, *J* = 7.3 Hz, 2 H), 8.03 (d, *J* = 9.9 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.2, 21.1, 22.76, 22.8, 25.4, 25.8, 27.4, 27.5, 28.0, 29.46, 29.5, 29.6, 29.7, 29.76, 29.8(m), 30.0, 32.0, 32.2, 39.1, 48.7, 62.4, 63.7, 69.7, 70.3, 70.6, 71.4, 72.1, 72.5, 72.6,73.3, 73.6,73.7, 74.8,

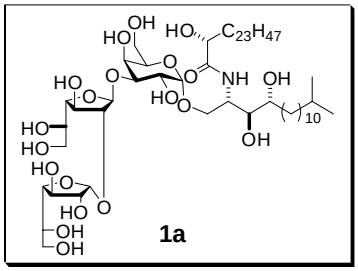
75.4, 75.5, 76.9, 77.4, 79.3, 80.2, 80.4, 83.8, 85.1, 97.9, 100.6, 105.8, 127.6, 127.7, 127.9, 128.0, 128.05, 128.18, 128.2, 128.5, 128.6, 128.65, 128.7, 128.9, 133.3, 133.5, 137.2, 137.7, 138.1, 138.2, 165.3, 167.3, 170.8, 171.2. MALDI-TOF calcd for $C_{118}H_{161}NNaO_{23}$ $(M+Na)^+$: *m/z* 1983.1357. Found: 1983.1356.



S11

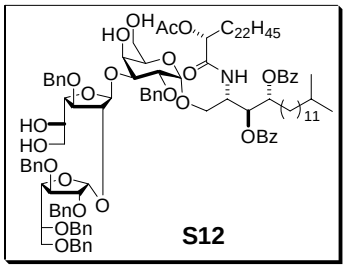
Compound S11. Compound **S10** (38 mg, 0.019 mmol) was stirred under hydrogen atmosphere using a balloon in the presence of Pd/C (10%, 30 mg) in MeOH–CH_2Cl_2–AcOH (5:3:2, v/v/v, 5 mL) at room temperature for 3 h. The reaction mixture was filtered through Celite® and concentrated. The residue was purified by column chromatography on Iatrobeads® ($CHCl_3$/MeOH, 5:1, v/v, to 3:1, v/v) to afford the title compound **S11** (23 mg, 0.016 mmol, 84%) as a colorless oil.: R_f = 0.5 ($CHCl_3$/MeOH, 3:1, v/v); IR ($CHCl_3$ film) 1266, 1678, 1732, 3367 cm^{-1}; $[\alpha]_D^{20}$ +48.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD + $CDCl_3$) δ 0.85 (s, 3 H), 8.6 (s, 3 H), 0.89 (t, *J* = 6.5 Hz, 3 H), 1.08−1.52 (m, 61 H), 1.83−2.06 (m, 4 H), 2.22 (s, 3 H), 3.56−3.77 (m, 10 H), 3.78−3.84 (m, 2 H), 3.85−3.93 (m, 3 H), 3.97 (dd, *J* = 4.5, 8.0 Hz, 1 H), 3.99−4.05 (m, 1 H), 4.05−4.10 (m, 1 H), 4.12 (t, *J* = 7.8 Hz, 1 H), 4.14−4.22 (m, 2 H), 4.71 (d, *J* = 3.5 Hz, 1 H), 5.01 (t, *J* = 6.3 Hz, 1 H), 5.04 (d, *J* = 4.0 Hz, 1 H), 5.19 (brs, 1 H), 5.33−5.35 (m, 1 H), 5.78 (d, *J* = 8.5 Hz, 1 H), 7.39−7.65 (m, 6 H), 7.92 (d, *J* = 7.5 Hz, 2 H), 8.01 (d, *J* = 7.5 Hz, 2 H), 8.32 (d, *J* = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, CD_3OD + $CDCl_3$) δ 14.3, 21.0, 22.9, 23.1, 26.5, 26.1, 27.8, 28.4, 29.8, 30.1(m), 30.3,

32.3, 32.4, 39.5, 62.3, 63.7(2), 63.8(2), 68.2, 69.8, 70.2, 71.3, 71.8, 72.0, 72.6, 74.6, 75.0, 75.4, 75.7, 82.7(2), 88.4, 101.5, 101.8, 108.1, 128.9, 129.1, 129.8, 130.2, 133.8, 134.2, 166.4, 167.3, 172.0, 172.1. MALDI-TOF calcd for $C_{76}H_{125}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 1442.8540. Found: 1442.8540.

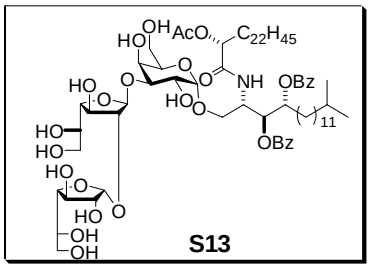


1a

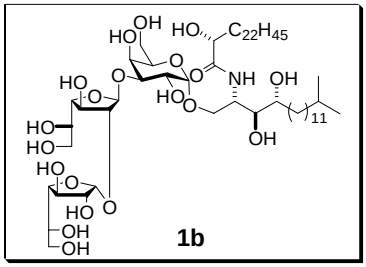
Agelagalastatin 1a (major component). A solution of compound **S11** (18 mg, 0.0127 mmol) and sodium methoxide (10 mg, 0.185 mmol) in CH_2Cl_2−MeOH (1:2, v/v, 6 mL) was stirred at room temperature for 2 h. The reaction mixture was neutralized with DOWEX CCR-3 (H^+ mode) resin, filtered through Celite®, and concentrated. The residue was purified by washing with diethyl ether (2 × 30 mL), and concentrated in vacuo to afford the title compound agelagalastatin **1a** (14 mg, 0.012 mmol, 94%) as a colorless amorphous powder.: R_f = 0.08 ($CHCl_3$/MeOH, 3:1, v/v); $[\alpha]_D^{20}$ +58.8 (*c* 0.65, CH_3OH); ^{1}H NMR (500 MHz, C_5D_5N) δ 0.84−0.85 (m, 9 H), 1.12−1.50 (m, 57 H), 1.63−1.83 (m, 3 H), 1.87−2.08 (m, 3 H), 2.16−2.34 (m, 2 H), 4.12−4.51(m, 13 H), 4.55−4.68 (m, 5 H), 4.69−4.76 (m, 2 H), 5.14 (t, *J* = 8.0 Hz, 1 H), 5.23−5.26 (m, 1 H), 5.47 (d, *J* = 4.0 Hz, 1 H), 5.61 (d, *J* = 4.5 Hz, 1 H), 5.78 (brs, 1 H), 8.58 (d, *J* = 9.5 Hz, 1 H); ^{13}C NMR (125 MHz, C_5D_5N) δ 14.3, 22.8, 22.9, 25.9, 26.5, 27.7, 28.2, 29.6, 30.0(m), 31.17, 30.2, 30.4, 32.1, 34.1, 35.6, 39.2, 51.1, 62.7, 64.4(2), 68.5, 68.9, 70.4, 71.9, 72.5(2), 72.8, 75.2, 75.5, 76.2, 79.1, 80.0, 82.5, 83.3, 88.7, 101.4, 101.7, 108.5, 175.3. HRMS (FAB) calcd for $C_{60}H_{115}NNaO_{20}$ $(M+Na)^+$: *m*/*z* 1192.7910. Found: 1192.7921.



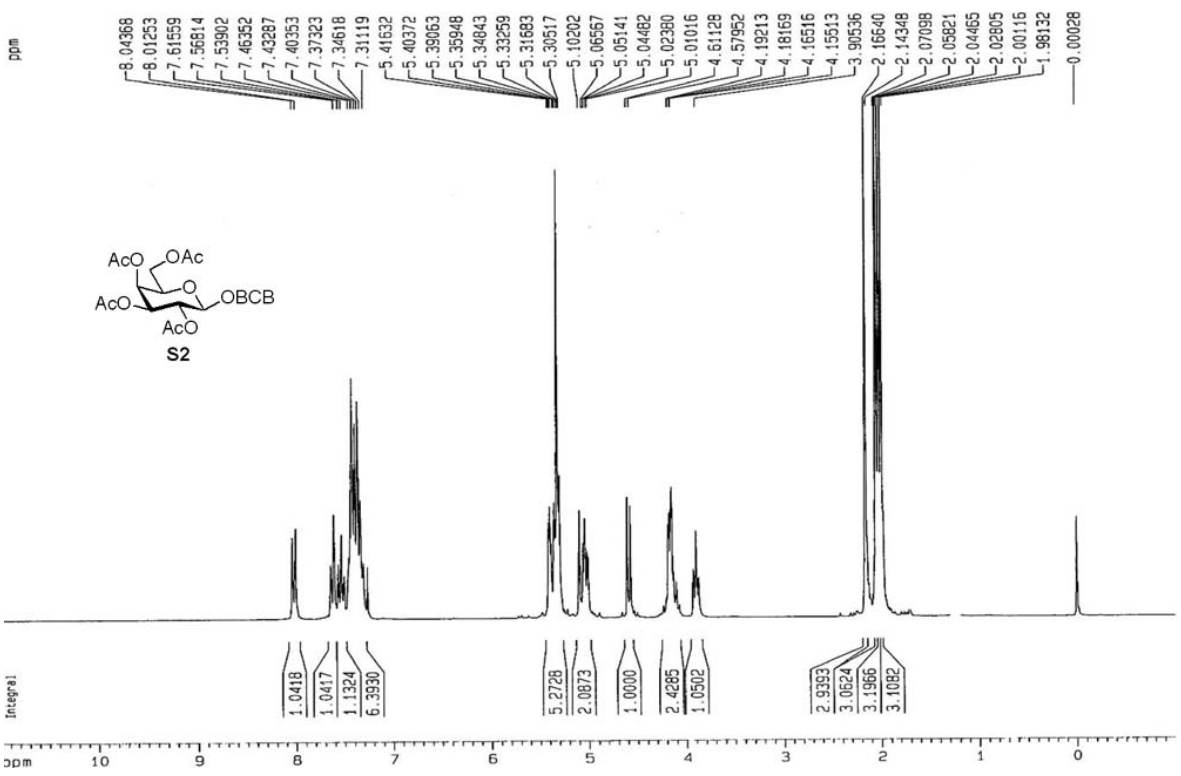
Compound S12. The title compound **S12** was prepared from compound **42bα** (90 mg, 0.043 mmol) in the same procedure as described for **S10**: 74 mg (0.00377 mmol, 88%); colorless oil, R_f = 0.2 (hexane/EtOAc, 1:2, v/v); IR ($CHCl_3$ film) 1285, 1458, 1678, 1741, 3452 cm^{-1}; $[\alpha]_D^{20}$ +45.6 (*c* 0.3, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$) δ 0.84 (s, 3 H), 0.86 (s, 3 H), 0.88 (t, *J* = 6.3 Hz, 3 H), 1.01−1.55 (m, 61 H), 1.72−2.04 (m, 6 H), 2.13 (s, 3 H), 2.78−3.03 (m, 2 H), 3.46−3.71 (m, 8 H), 3.82−3.96 (m, 7 H), 3.97−4.03 (m, 2 H), 4.07−4.16 (m, 3 H), 4.31−4.40 (m, 6 H), 4.42 (brs, 1 H), 4.44−4.49 (m, 2 H), 4.52−4.64 (m, 4 H), 4.66−4.69 (m, 1 H), 4.88 (d, *J* = 4.4 Hz, 1 H), 5.03 (t, *J* = 6.1 Hz, 1 H), 5.13 (brs, 1 H), 5.18−5.23 (m, 1 H), 5.89 (d, *J* = 10.4 Hz, 1 H), 7.10−7.62 (m, 36 H), 7.89 (d, *J* = 7.5 Hz, 2 H), 7.97 (d, *J* = 7.5 Hz, 2 H), 8.09 (d, *J* = 9.9 Hz, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.3, 21.1, 22.8, 25.4, 25.9, 27.4, 27.6, 28.1, 29.5, 29.9(m), 30.1, 32.1, 32.2, 39.2, 48.7, 62.5, 63.7, 69.9, 70.3, 70.6, 71.4, 72.1, 72.6, 73.3, 73.7, 74.9, 75.2, 75.5, 77.4, 79.3, 80.1, 80.4, 83.8, 84.0, 85.2, 97.9,100.5, 105.8, 127.6, 127.8, 127.9, 128.1, 128.3, 128.5, 128.8, 129.6, 129.9, 133.4, 133.6, 137.2, 137.7, 138.1, 165.4, 167.3, 170.8, 171.3. MALDI-TOF calcd for $C_{118}H_{161}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 1983.1357. Found: 1983.1360.



Compound S13. The title compound **S13** was prepared from compound **S12** (42 mg, 0.0214 mmol) in the same procedure as described for **S11**: 26 mg (0.0183 mmol, 86%); colorless oil, R_f = 0.5 ($CHCl_3$/MeOH, 3:1, v/v); IR ($CHCl_3$ film) 1266, 1682, 1731, 3343 cm^{-1}; $[\alpha]_D^{20}$ +49.2 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, CD_3OD + $CDCl_3$) δ 0.85 (s, 3 H), 8.6 (s, 3 H), 0.89 (t, *J* = 6.0 Hz, 3 H), 1.08−1.52 (m, 61 H), 1.81−2.10 (m, 4 H), 2.22 (s, 3 H), 3.57−3.77 (m, 10 H), 3.78−3.84 (m, 2 H), 3.85−3.93 (m, 3 H), 3.97 (dd, *J* = 4.5, 8.0 Hz, 1 H), 3.99−4.04 (m, 1 H), 4.06−4.10 (m, 1 H), 4.12 (t, *J* = 7.5 Hz, 1 H), 4.14−4.21 (m, 2 H), 4.71 (d, *J* = 3.3 Hz, 1 H), 5.00 (t, *J* = 6.0 Hz, 1 H), 5.04 (d, *J* = 4.0 Hz, 1 H), 5.19 (brs, 1 H), 5.33−5.35 (m, 1 H), 5.78 (d, *J* = 9.5 Hz, 1 H), 7.39−7.66 (m, 6 H), 7.92 (d, *J* = 7.5 Hz, 2 H), 8.01 (d, *J* = 7.5 Hz, 2 H), 8.33 (brs, 1 H); ^{13}C NMR (125 MHz, CD_3OD + $CDCl_3$) δ 14.3, 21.0, 22.9, 23.1, 26.7, 26.1, 27.9, 28.4, 29.8, 30.1(m), 30.4, 32.4, 32.5, 39.5, 62.3, 63.7(2), 63.8(2), 68.2, 69.8, 70.1, 71.3, 71.9, 72.0, 72.6, 74.7, 75.0, 75.4, 75.7, 82.7(2), 88.4, 101.6, 101.8, 108.1, 128.9, 129.2, 129.8, 130.2, 133.8, 134.2, 166.4, 167.4, 172.0, 172.1. MALDI-TOF calcd for $C_{76}H_{125}NNaO_{23}$ $(M+Na)^+$: *m*/*z* 1442.8540. Found: 1442.8540.



Agelagalastatin 1b (minor component). The title compound **1b** was prepared from compound **S13** (16 mg, 0.0113 mmol) in the same procedure as described for **1a**: 13 mg (0.0111 mmol, 98%); colorless amorphous powder, R_f = 0.08 ($CHCl_3$/MeOH, 3:1, v/v); $[\alpha]_D^{20}$ +59.8 (*c* 0.45, CH_3OH); ^1H NMR (500 MHz, C_5D_5N) δ 0.84−0.85 (m, 9 H), 1.12−1.50 (m, 57 H), 1.63−1.83 (m, 3 H), 1.87−2.08 (m, 3 H), 2.16−2.34 (m, 2 H), 4.12−4.51(m, 13 H), 4.55−4.68 (m, 5 H), 4.69−4.76 (m, 2 H), 5.14 (t, *J* = 8.0 Hz, 1 H), 5.23−5.26 (m, 1 H), 5.47 (d, *J* = 4.0 Hz, 1 H), 5.61 (d, *J* = 4.5 Hz, 1 H), 5.78 (brs, 1 H), 8.58 (d, *J* = 9.5 Hz, 1 H); ^{13}C NMR (125 MHz, C_5D_5N) δ 14.2, 22.7, 22.9, 25.9, 26.5, 27.7, 28.2, 29.6, 30.0(m), 30.4, 32.1, 34.0, 35.6, 39.2, 51.1, 62.7, 64.4(2), 68.5, 68.9, 70.4, 71.9, 72.4, 72.5, 72.8, 75.2, 75.4, 76.2, 79.0, 80.0, 82.4, 83.2, 88.7, 101.3, 101.7, 108.5, 175.3. HRMS (FAB) calcd for $C_{60}H_{115}NNaO_{20}$ $(M+Na)^+$: *m*/*z* 1192.7910. Found: 1192.7914.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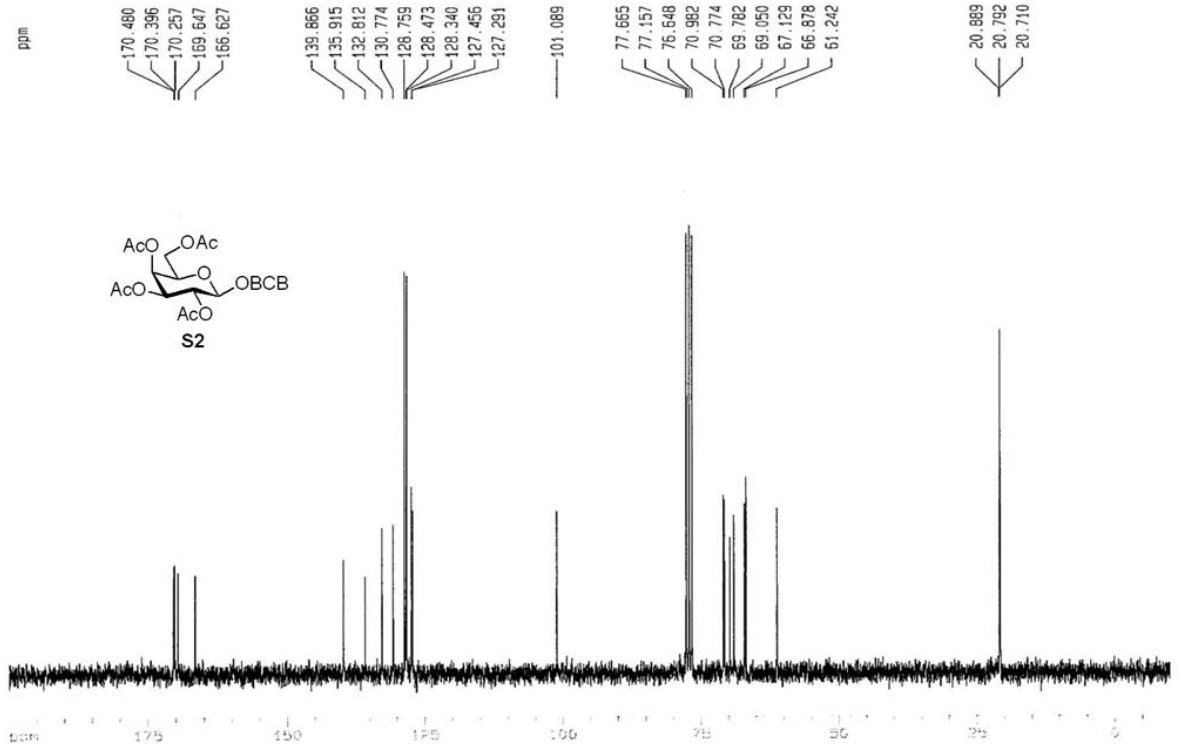
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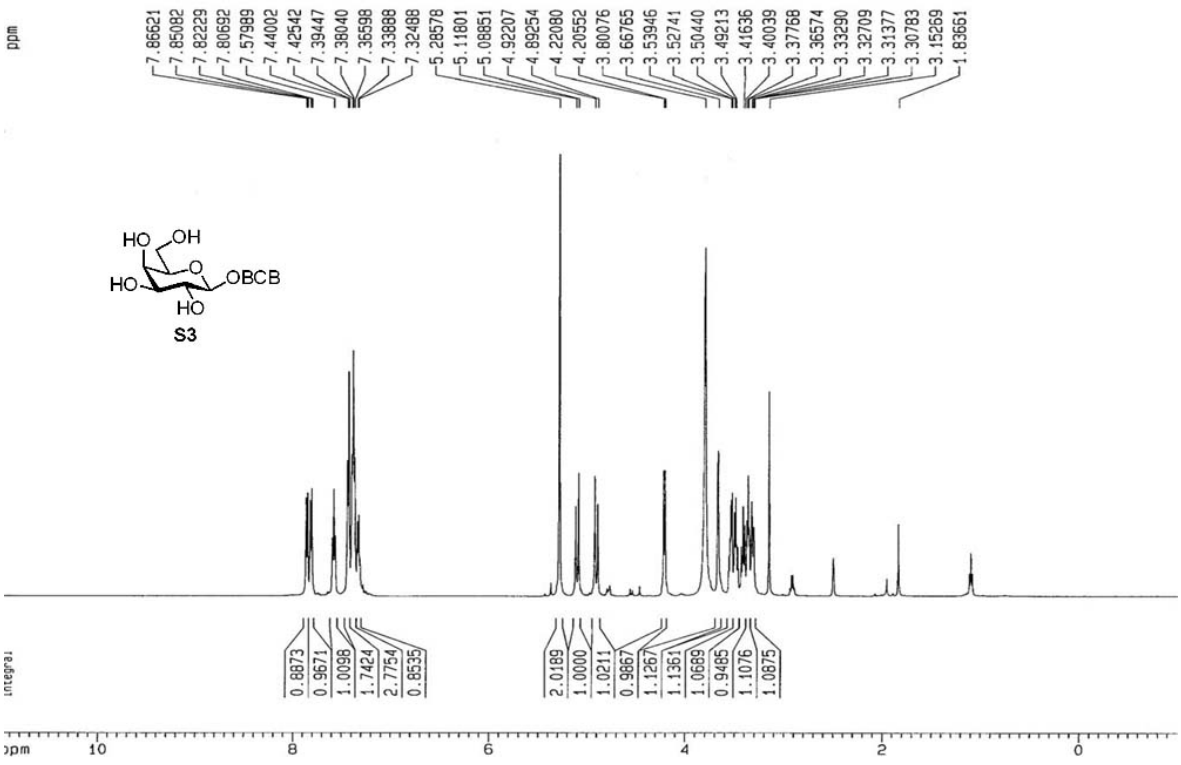
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3.32709
3.31377
3.30783
3.15269
1.83661
HO
OH
O
OBCB
HO
HO
S3
integral
0.8873
0.9671
1.0098
1.7424
2.7754
0.8535
2.0189
1.0000
1.0211
0.9867
1.1267
1.1361
1.0689
0.9485
1.1076
1.0875
ppm
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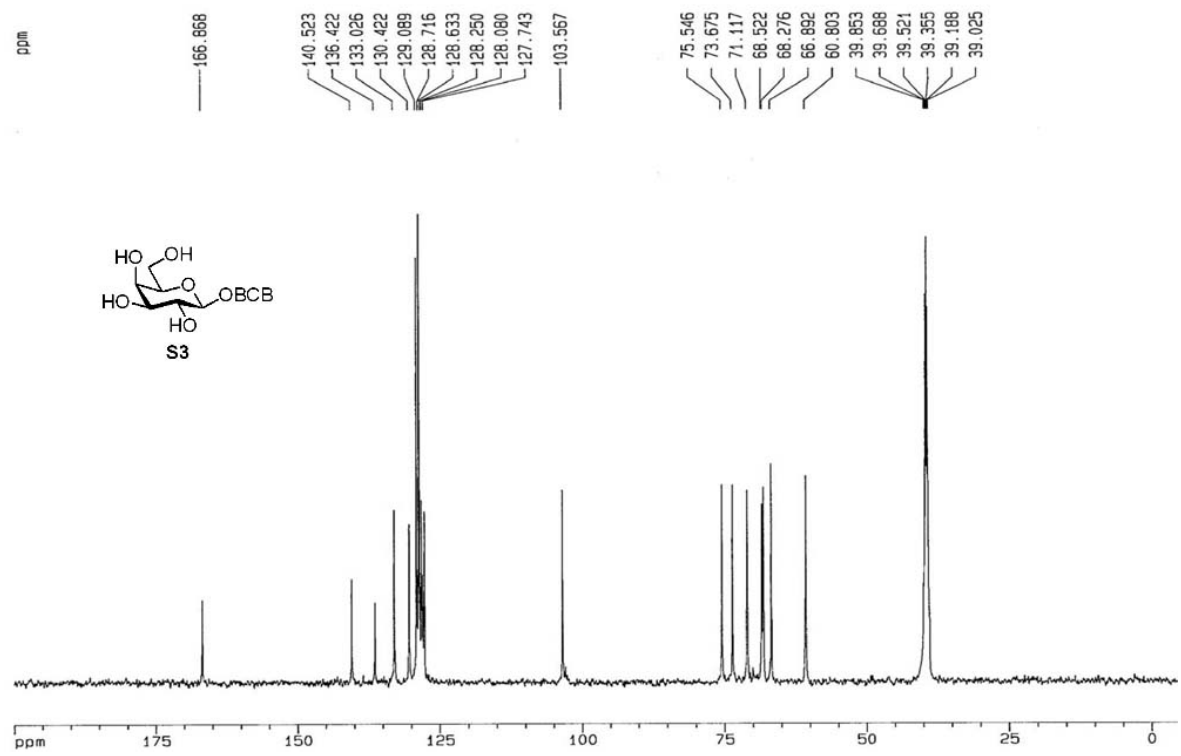
2
0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133.026
130.422
129.089
128.716
128.633
128.250
128.080
127.743
103.567
75.546
73.675
71.117
68.522
68.276
66.892
60.803
39.853
39.688
39.521
39.355
39.188
39.025
HO
OH
O
OBCB
HO
HO
S3
ppm
175
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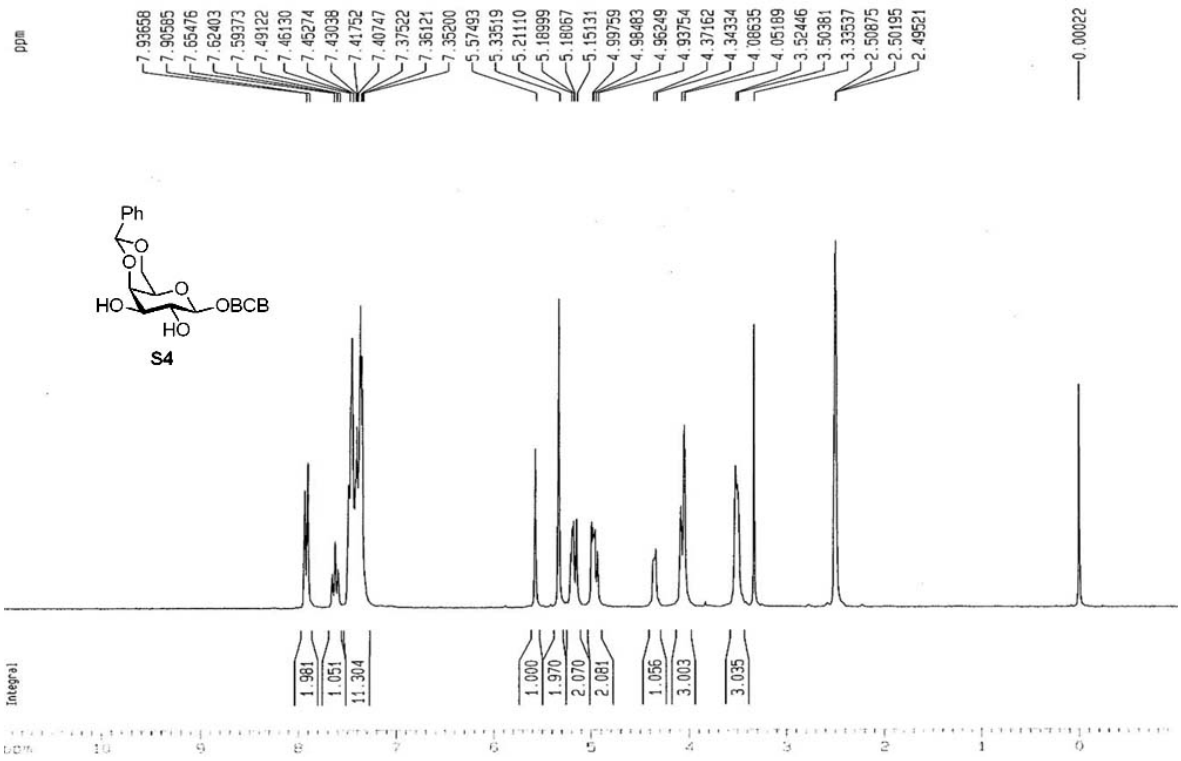
125
100
75
50
25
0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7.62403
7.59373
7.49122
7.46130
7.45274
7.43038
7.41752
7.40747
7.37522
7.36121
7.35200
5.57493
5.33519
5.21110
5.18999
5.18067
5.15131
4.99759
4.98483
4.96249
4.93754
4.37162
4.34334
4.08635
4.05189
3.52446
3.50381
3.33537
2.50875
2.50195
2.49521
0.00022
Ph
O
O
O
HO
OBCB
HO
S4
Integral
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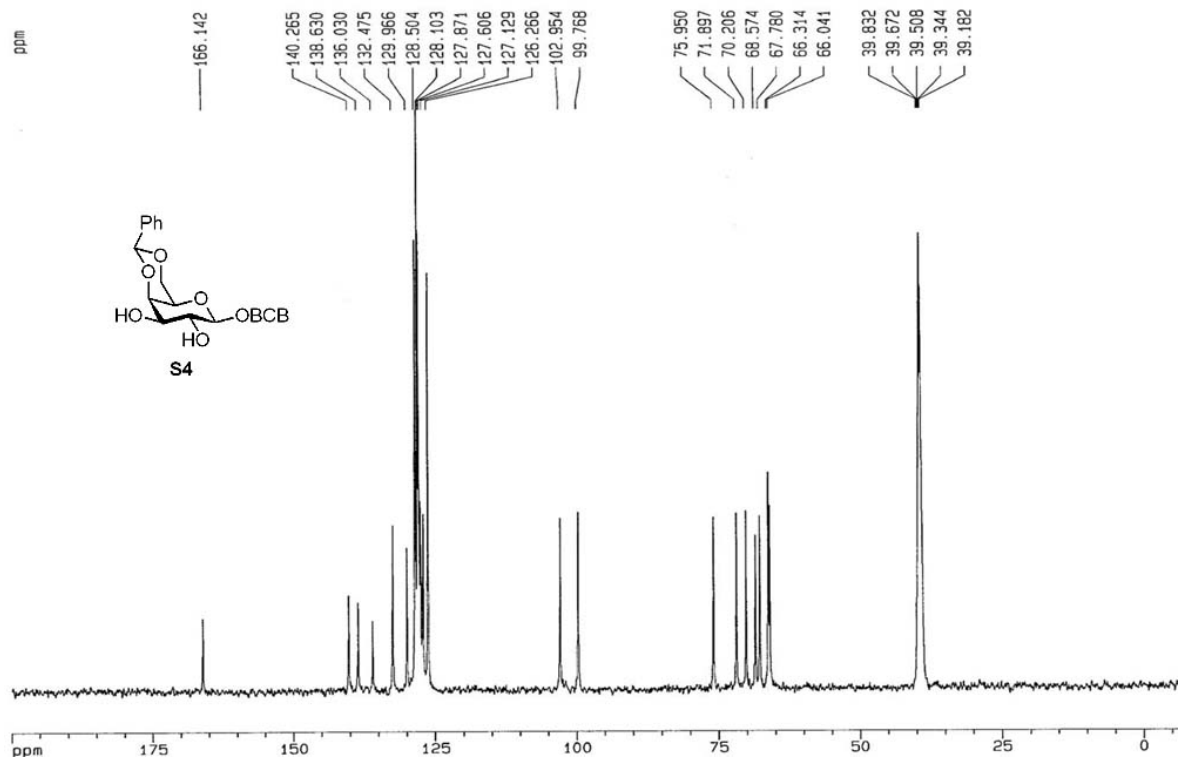
1.051
11.304
1.000
1.970
2.070
2.081
1.056
3.003
3.035
ppm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166.142
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138.630
136.030
132.475
129.966
128.504
128.103
127.871
127.606
127.129
126.266
102.954
99.768
75.950
71.897
70.206
68.574
67.780
66.314
66.041
39.832
39.672
39.508
39.344
39.182
Ph
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O
O
HO
OBCB
HO
S4
ppm
175
150
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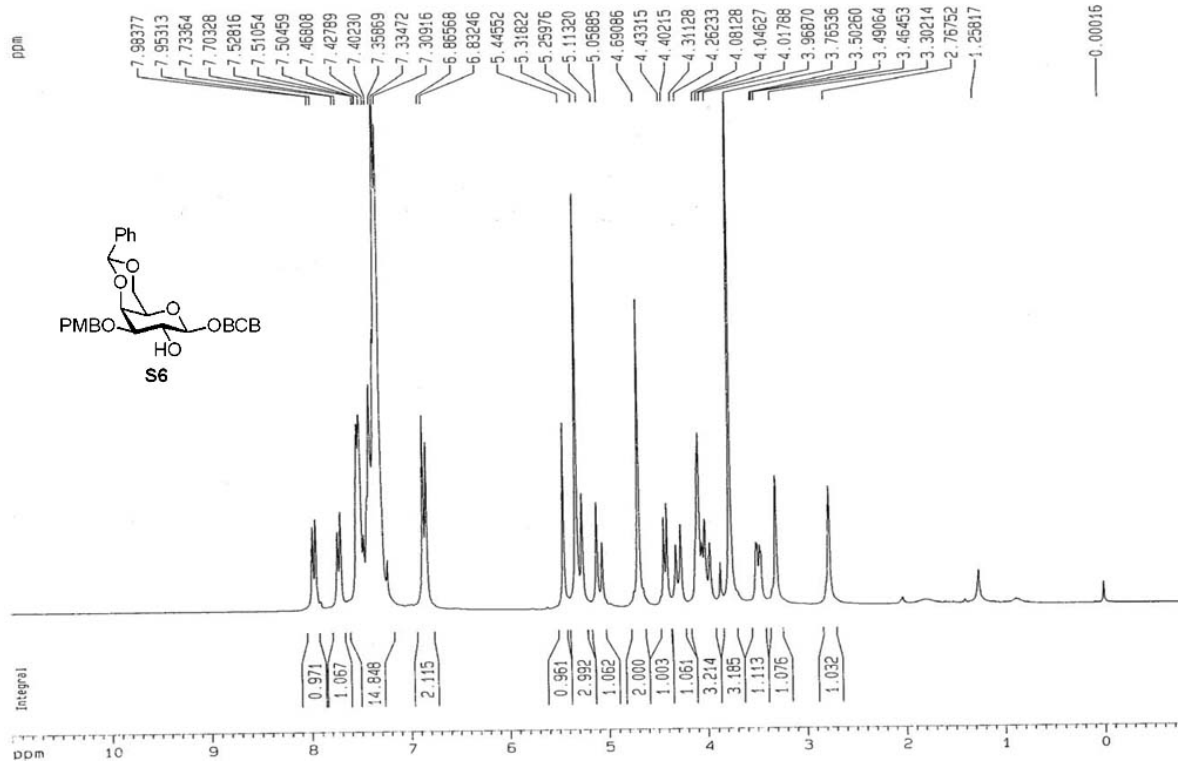
100
75
50
25
0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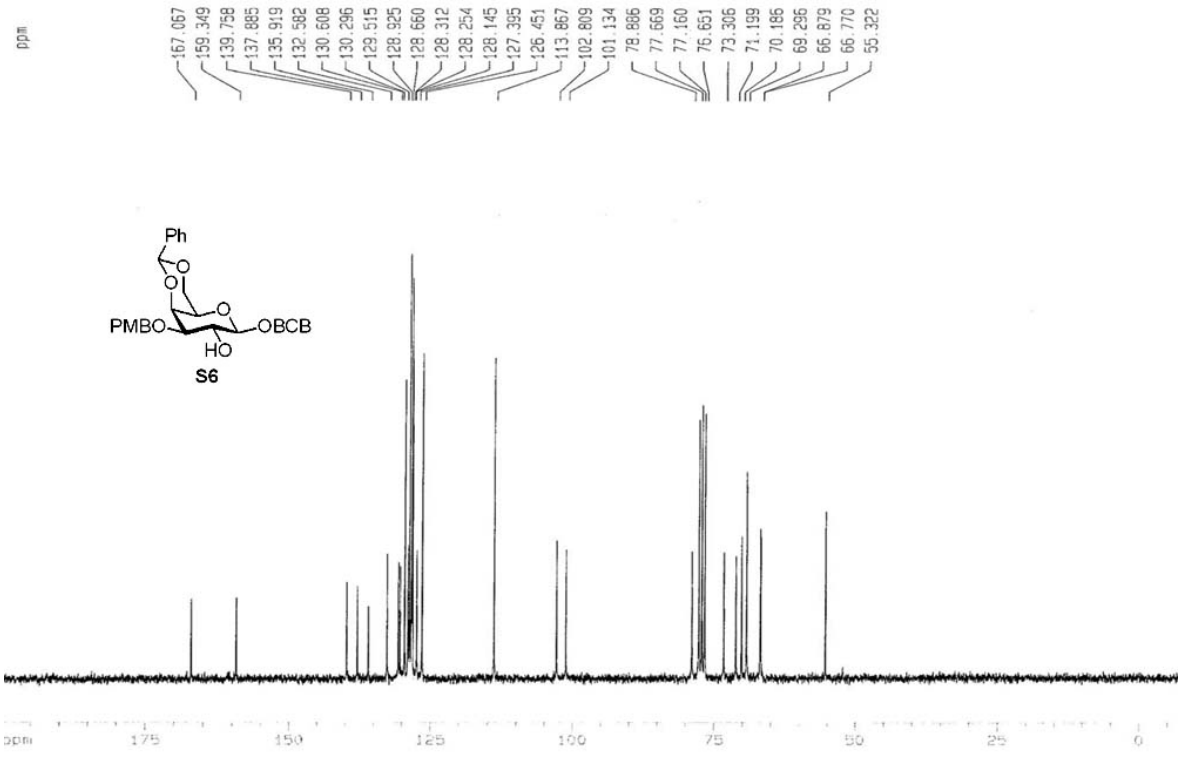
7.46808
7.42789
7.40230
7.35869
7.33472
7.30916
6.86568
6.83246
5.44552
5.31822
5.25976
5.11320
5.05685
4.69086
4.43315
4.40215
4.31128
4.26233
4.08128
4.04627
4.01788
3.96870
3.76536
3.50260
3.49064
3.46453
3.30214
2.76752
1.25817
0.00016
Ph
PMBO
OBCB
HO
S6
Integral
0.971
1.067
14.848
2.115
0.961
2.992
1.062
2.000
1.003
1.061
3.214
3.185
1.113
1.076
1.032
ppm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137.885
135.919
132.582
130.608
130.296
129.515
128.925
128.660
128.312
128.254
128.145
127.395
126.451
113.867
102.809
101.134
78.806
77.669
77.160
76.651
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70.185
69.296
66.879
66.770
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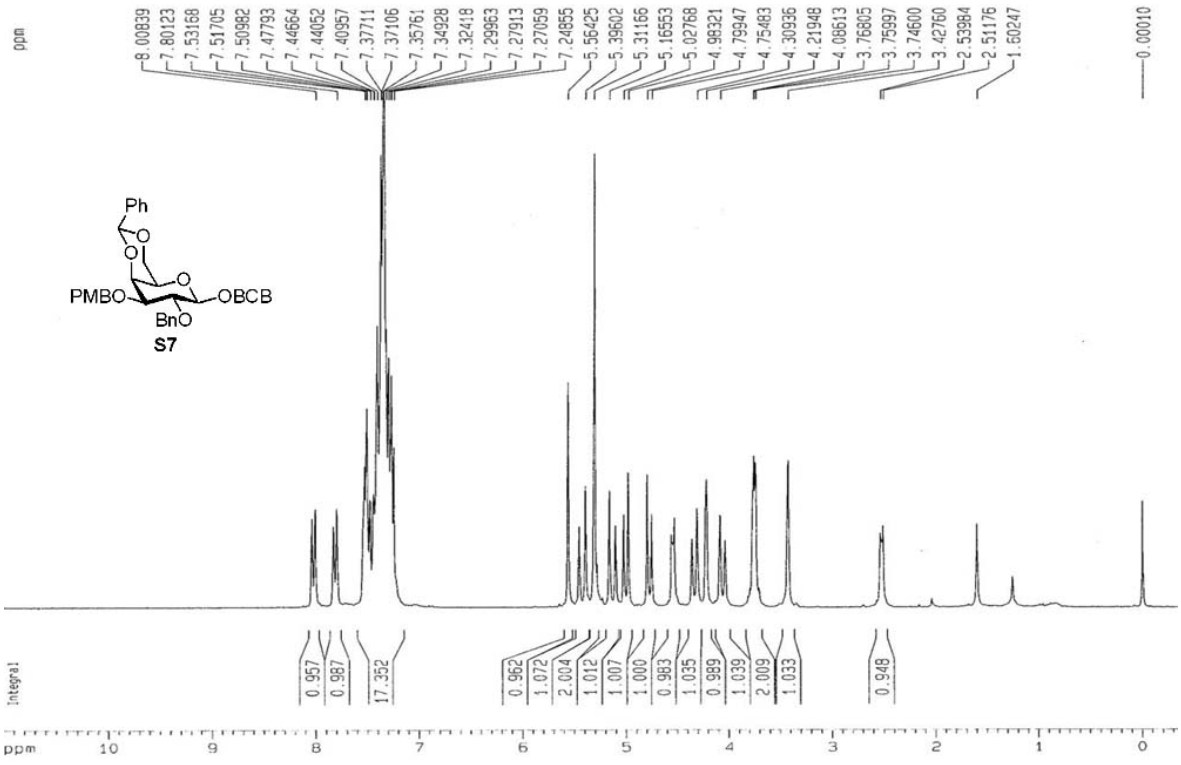
Ph
PMBO
OBCB
HO
S6
ppm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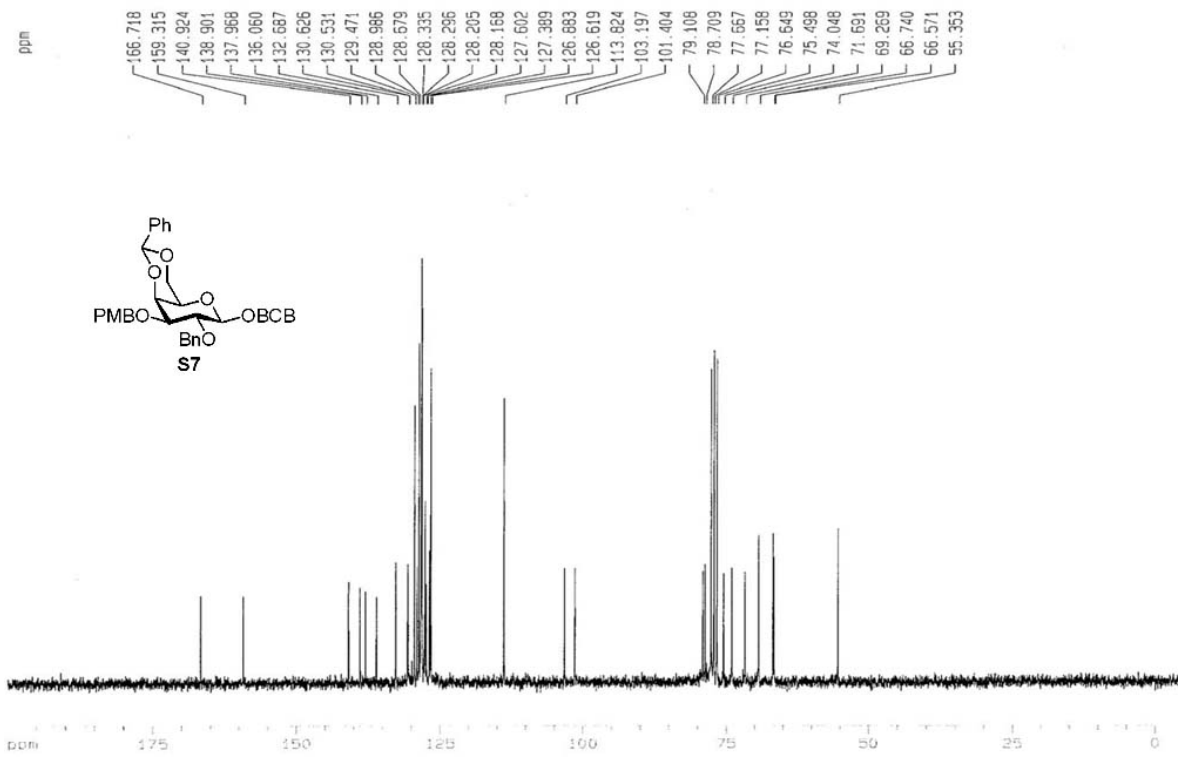
7.53168
7.51705
7.50982
7.47793
7.44664
7.44052
7.40957
7.37711
7.37106
7.35761
7.34928
7.32418
7.29963
7.27913
7.27059
7.24855
5.56425
5.39602
5.31166
5.16553
5.02768
4.98321
4.79947
4.75483
4.30936
4.21948
4.08613
3.76805
3.75997
3.74600
3.42760
2.53984
2.51176
1.60247
0.00010
Ph
PMBO
OBCB
BnO
S7
Integral
0.957
0.987
17.352
0.962
1.072
2.004
1.012
1.007
1.000
0.983
1.035
0.989
1.039
2.009
1.033
0.948
ppm
10
9
8
7
6
5
4
3
2
1
0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138.901
137.968
136.060
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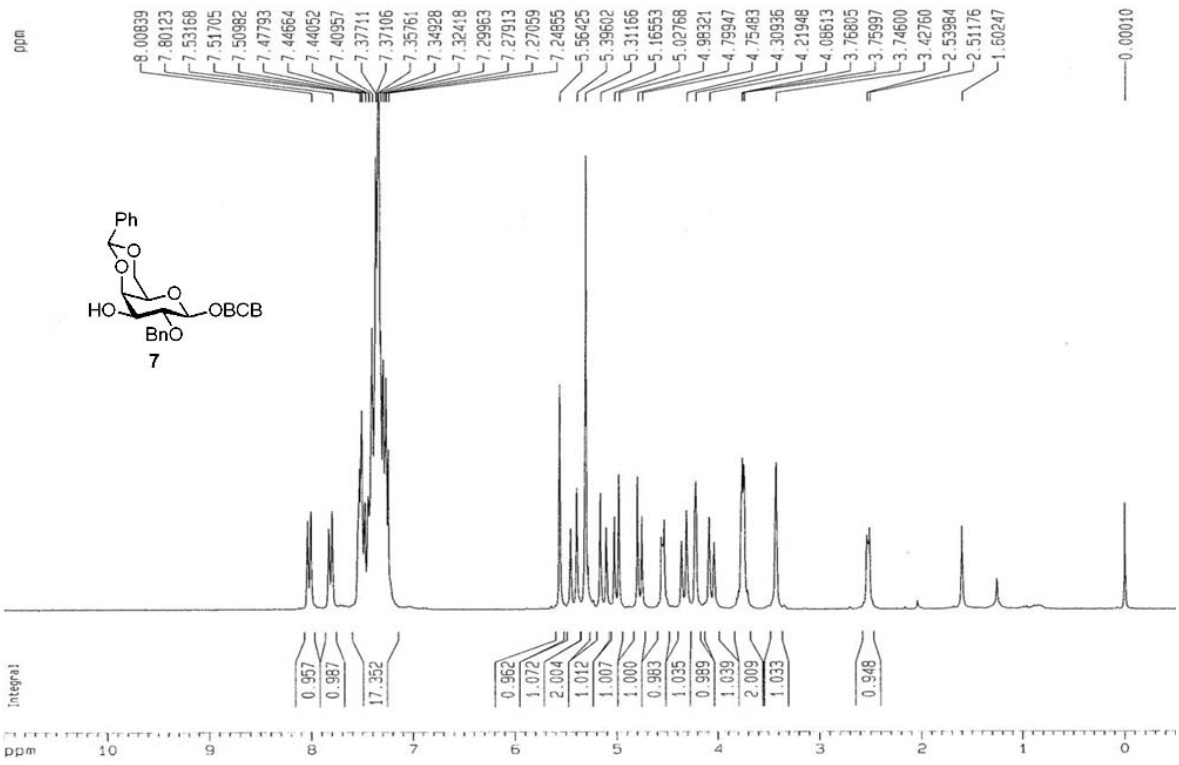
130.626
130.531
129.471
128.986
128.679
128.335
128.296
128.205
128.168
127.602
127.389
126.883
126.619
113.824
103.197
101.404
79.106
78.709
77.667
77.158
76.649
75.498
74.048
71.691
69.269
66.740
66.571
55.353
Ph
PMBO
OBCB
BnO
S7
ppm
175
150
125
100
75
50
25
0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7.53168
7.51705
7.50982
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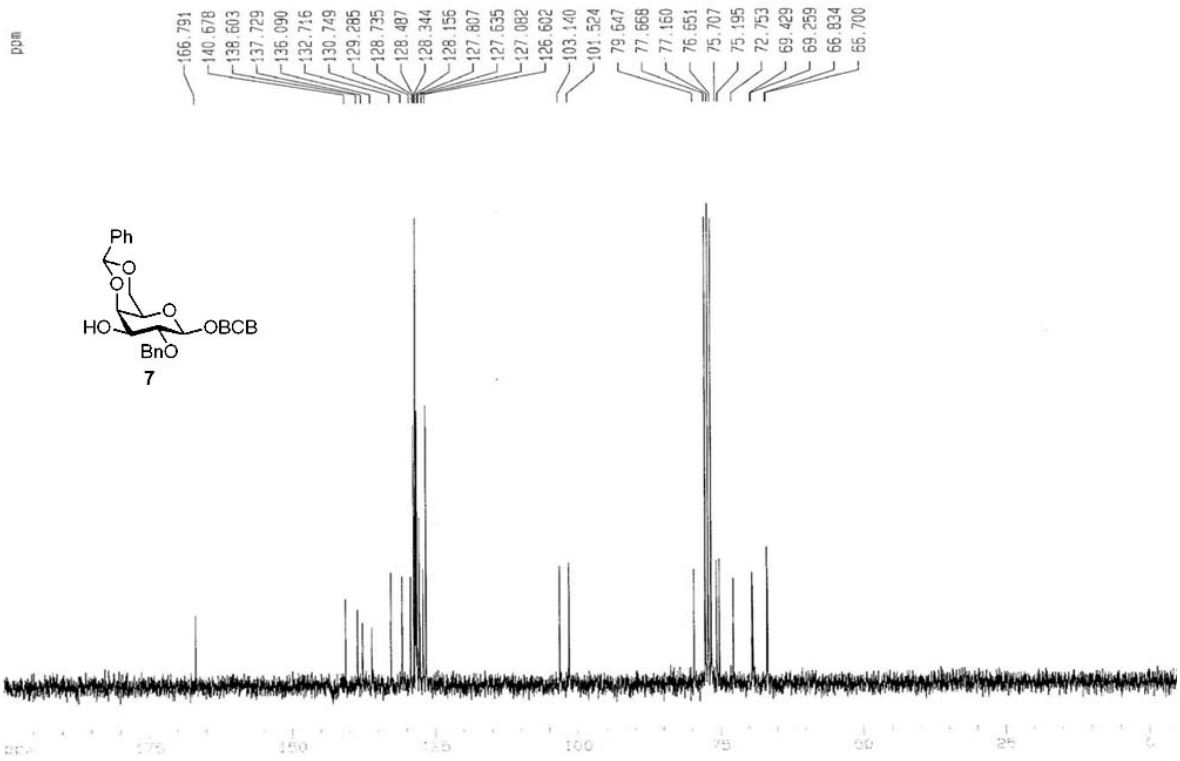
7.44664
7.44052
7.40957
7.37711
7.37106
7.35761
7.34928
7.32418
7.29963
7.27913
7.27059
7.24855
5.56425
5.39602
5.31166
5.16553
5.02768
4.98321
4.79947
4.75483
4.30936
4.21948
4.08613
3.76805
3.75997
3.74600
3.42760
2.53984
2.51176
1.60247
0.00010
Integral
0.957
0.987
17.352
0.962
1.072
2.004
1.012
1.007
1.000
0.983
1.035
0.989
1.039
2.009
1.033
0.948
ppm
10
9
8
7
6
5
4
3
2
1
0
Ph
HO
OBCB
BnO
7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128.487
128.344
128.156
127.807
127.635
127.082
126.602
103.140
101.524
79.647
77.668
77.160
76.651
75.707
75.195
72.753
69.429
69.259
66.834
66.700
175
150
125
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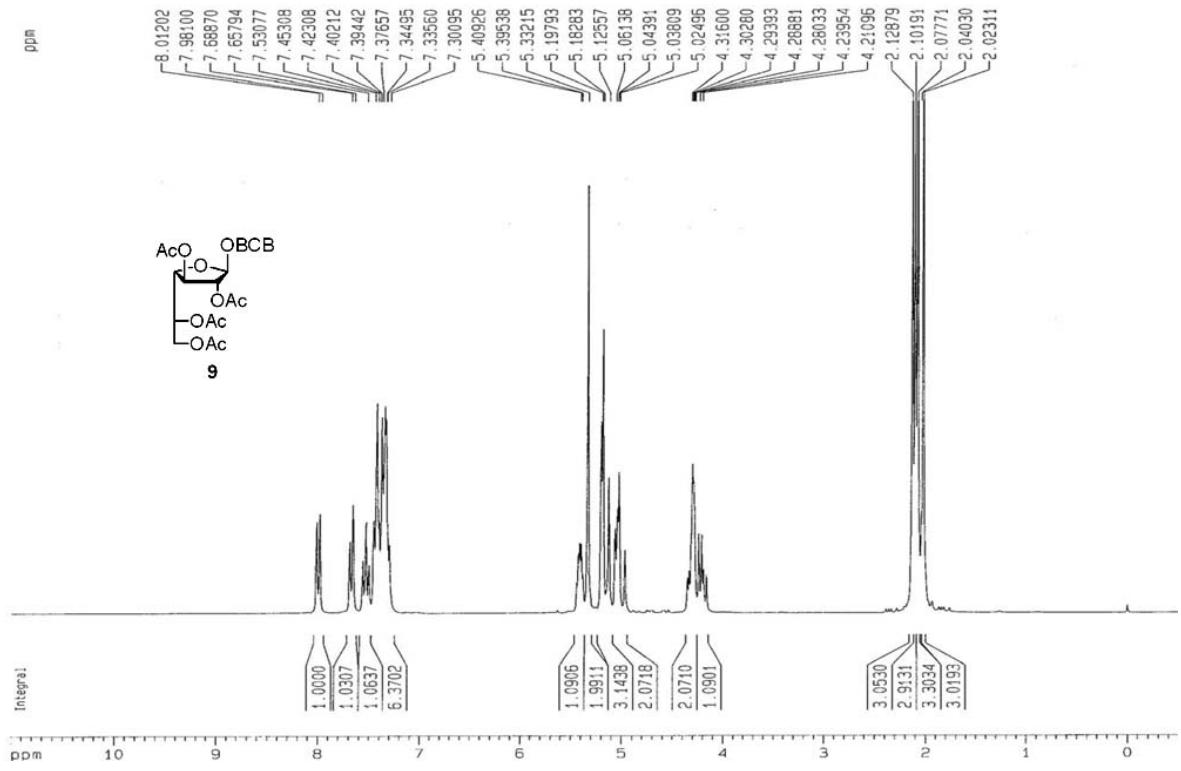
75
50
25
0
Ph
HO
OBCB
BnO
7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7.39442
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7.34495
7.33560
7.30095
5.40926
5.39538
5.33215
5.19793
5.18283
5.12557
5.06138
5.04391
5.03809
5.02496
4.31600
4.30280
4.29393
4.28881
4.28033
4.23954
4.21096
2.12879
2.10191
2.07771
2.04030
2.02311
AcO
OBCB
OAc
OAc
OAc
9
Integral
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1.0307
1.0637
6.3702
1.0906
1.9911
3.1438
2.0718
2.0710
1.0901
3.0530
2.9131
3.3034
3.0193
ppm
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8
7
6
5
4
3
2
1
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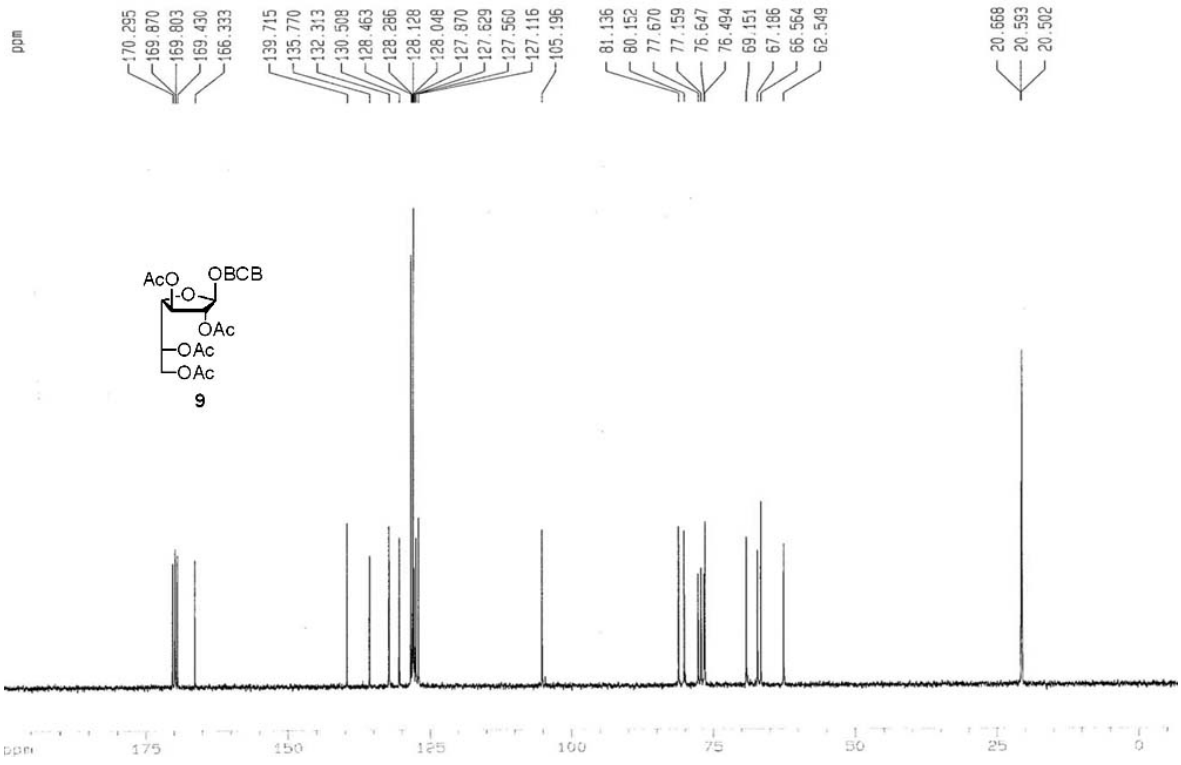
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128.128
128.048
127.870
127.629
127.560
127.116
105.196
81.136
80.152
77.670
77.159
76.647
76.494
69.151
67.186
66.564
62.549
20.668
20.593
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AcO
OBCB
OAc
OAc
OAc
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ppm
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75
50
25
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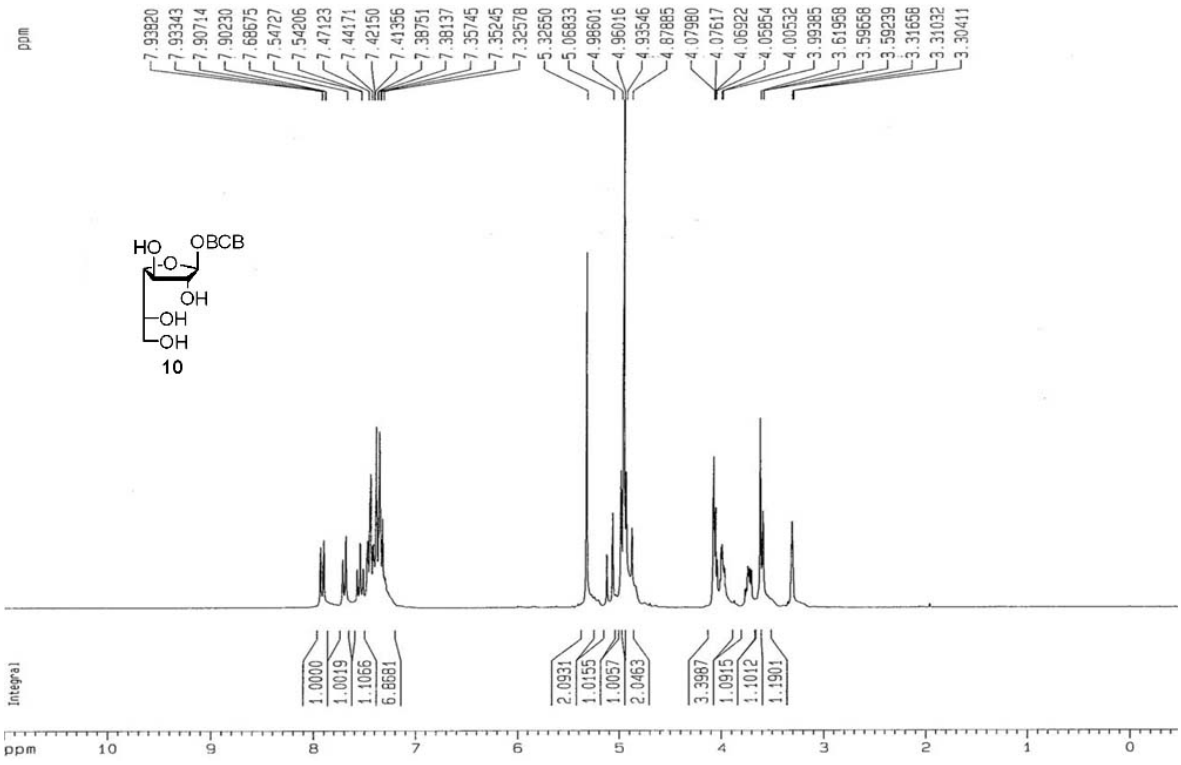
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7.47123
7.44171
7.42150
7.41356
7.38751
7.38137
7.35745
7.35245
7.32578
5.32650
5.06833
4.98601
4.96016
4.93546
4.87885
4.07980
4.07617
4.06922
4.05854
4.00532
3.99385
3.61958
3.59658
3.59239
3.31658
3.31032
3.30411
HO
OBCB
OH
OH
OH
10
Integral
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1.0019
1.1066
6.8681
2.0931
1.0155
1.0057
2.0463
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1.1012
1.1901
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7
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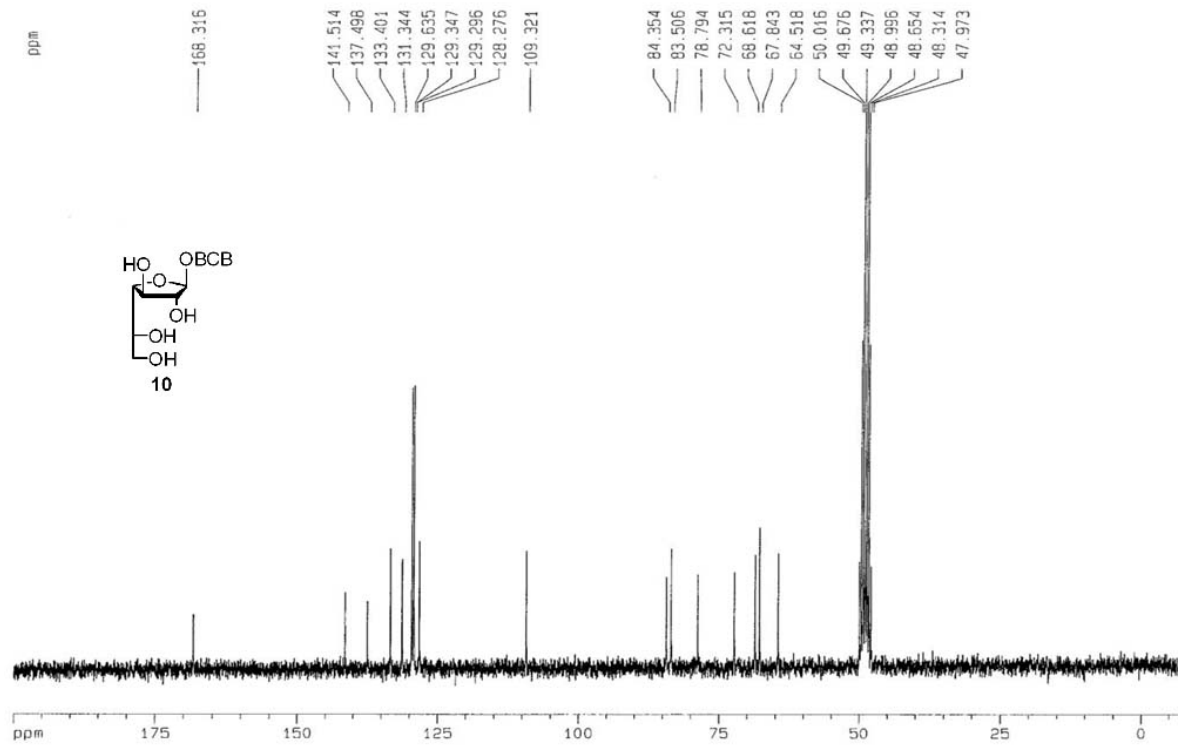
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129.296
128.276
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83.506
78.794
72.315
68.618
67.843
64.518
50.016
49.676
49.337
48.996
48.654
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HO
OBCB
OH
OH
OH
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ppm
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100
75
50
25
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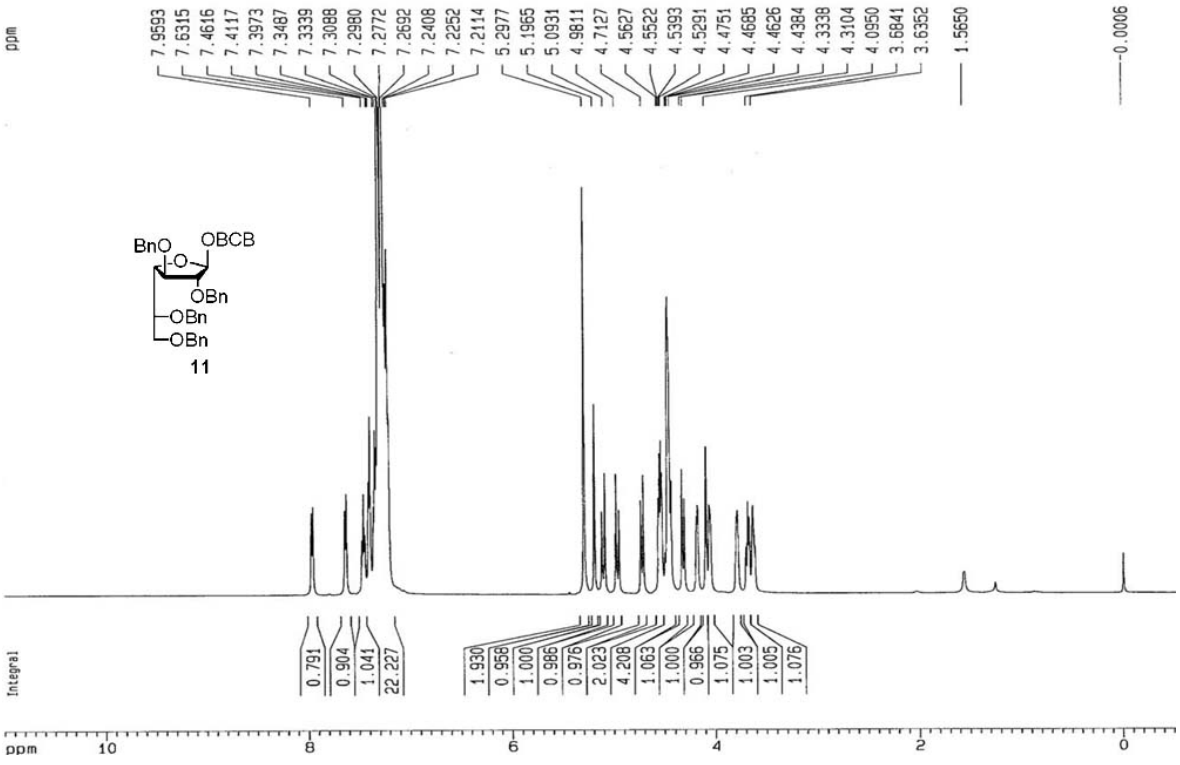
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7.2692
7.2408
7.2252
7.2114
5.2977
5.1965
5.0931
4.9811
4.7127
4.5627
4.5522
4.5393
4.5291
4.4751
4.4685
4.4626
4.4384
4.3338
4.3104
4.0950
3.6841
3.6352
1.5650
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BnO
OBCB
OBn
OBn
OBn
11
Integral
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22.227
1.930
0.958
1.000
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0.976
2.023
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0.966
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1.003
1.005
1.076
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6
4
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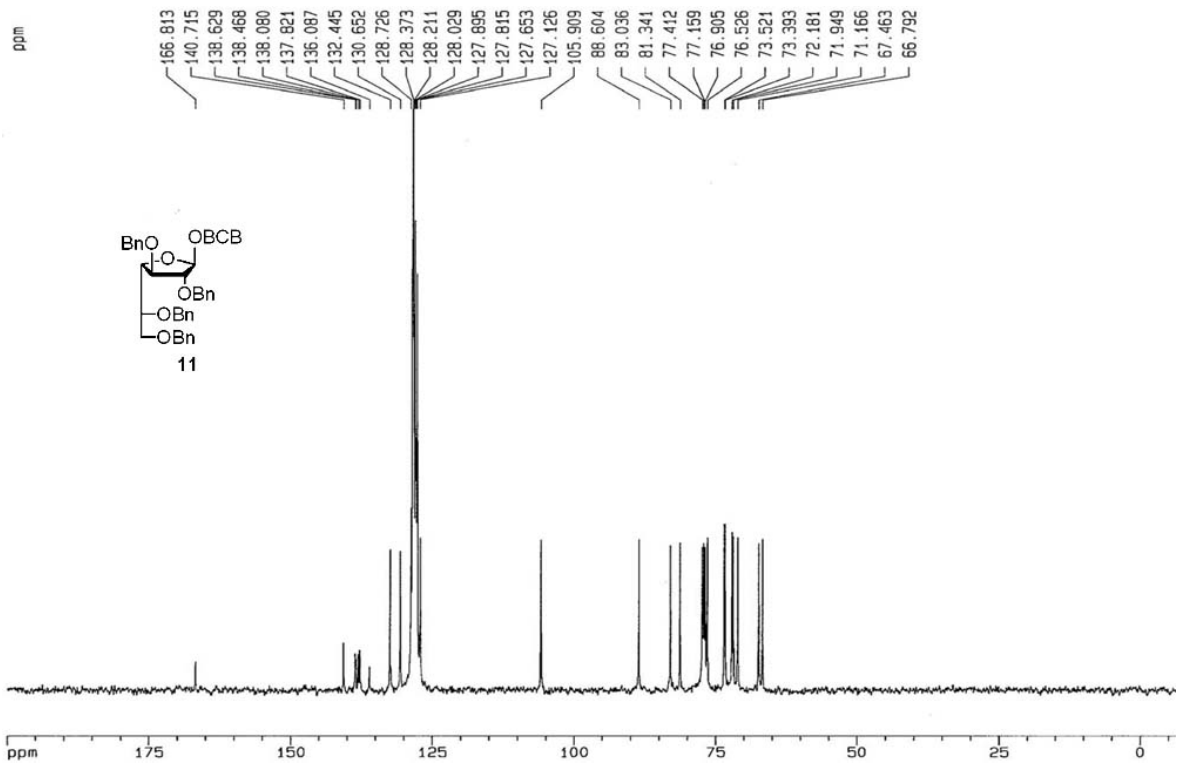
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128.726
128.373
128.211
128.029
127.895
127.815
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127.126
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77.159
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76.526
73.521
73.393
72.181
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71.166
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OBCB
OBn
OBn
OBn
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ppm
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75
50
25
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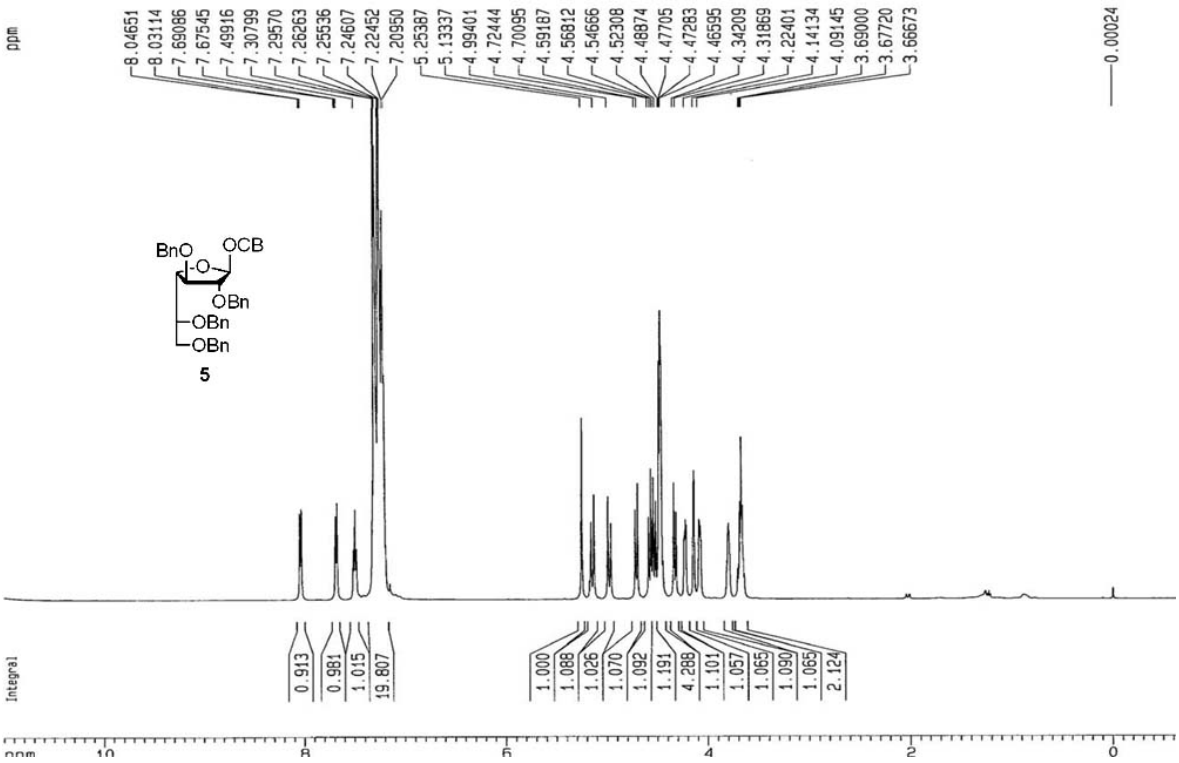
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7.22452
7.20950
5.25387
5.13337
4.99401
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4.70095
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4.56812
4.54666
4.52308
4.48874
4.47705
4.47283
4.46595
4.34209
4.31869
4.22401
4.14134
4.09145
3.69000
3.67720
3.66673
0.00024
BnO
OCB
OBn
OBn
OBn
5
Integral
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0.981
1.015
19.807
1.000
1.088
1.026
1.070
1.092
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4.288
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1.057
1.065
1.090
1.065
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6
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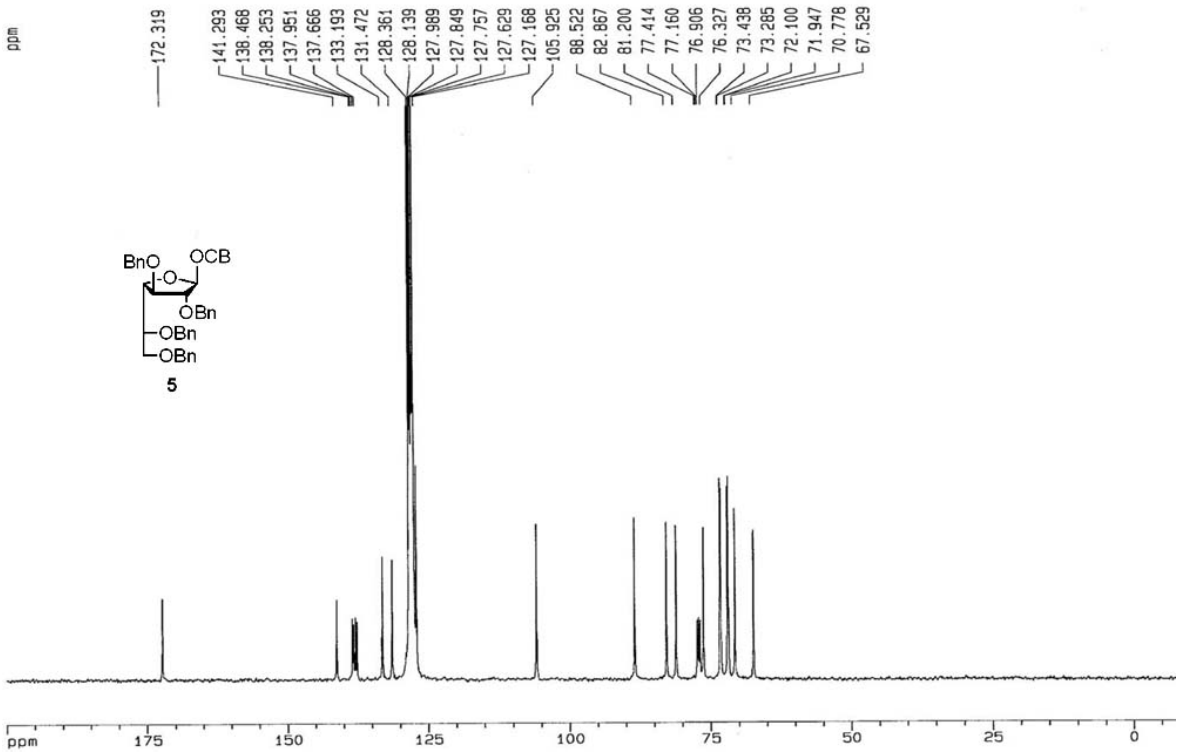
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127.849
127.757
127.629
127.168
105.925
88.522
82.867
81.200
77.414
77.160
76.906
76.327
73.438
73.285
72.100
71.947
70.778
67.529
BnO
OCB
OBn
OBn
OBn
5
ppm
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100
75
50
25
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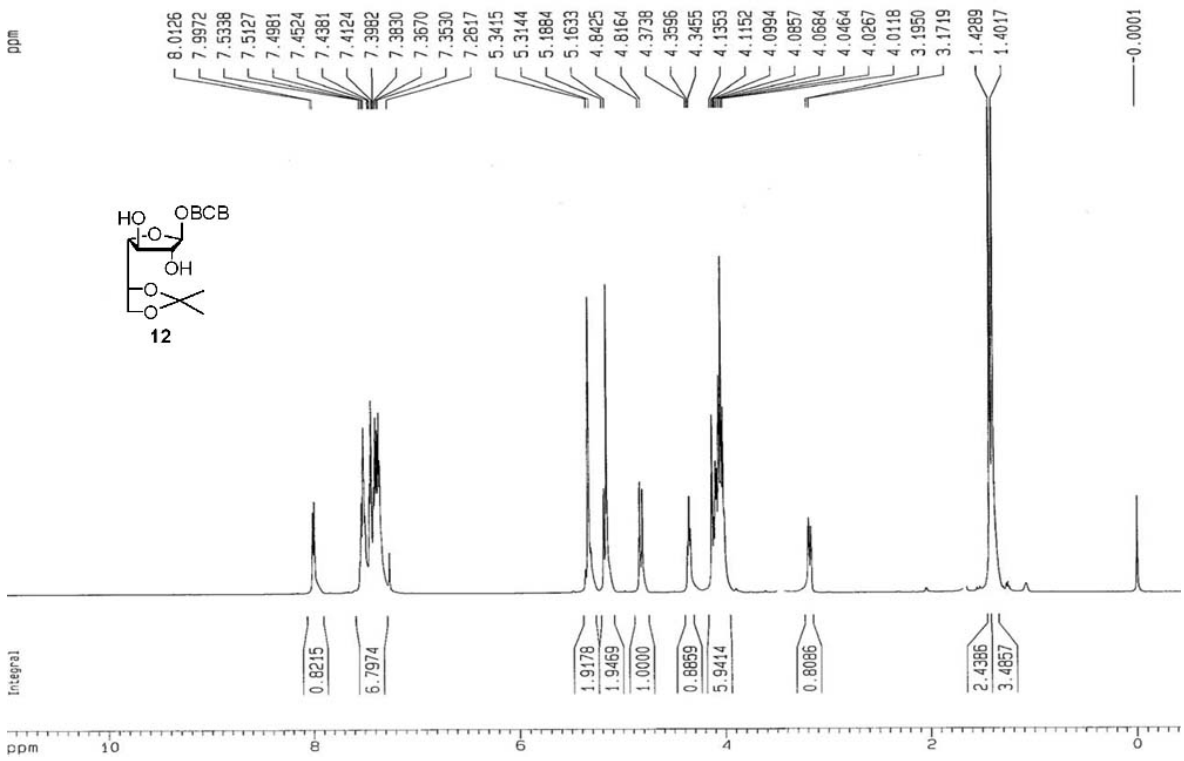
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7.3982
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7.3670
7.3530
7.2617
5.3415
5.3144
5.1884
5.1633
4.8425
4.8164
4.3738
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4.3455
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4.1152
4.0994
4.0857
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4.0464
4.0267
4.0118
3.1950
3.1719
1.4289
1.4017
0.0001
HO
OBCB
OH
O
O
12
Integral
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1.9178
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1.0000
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5.9414
0.8086
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ppm
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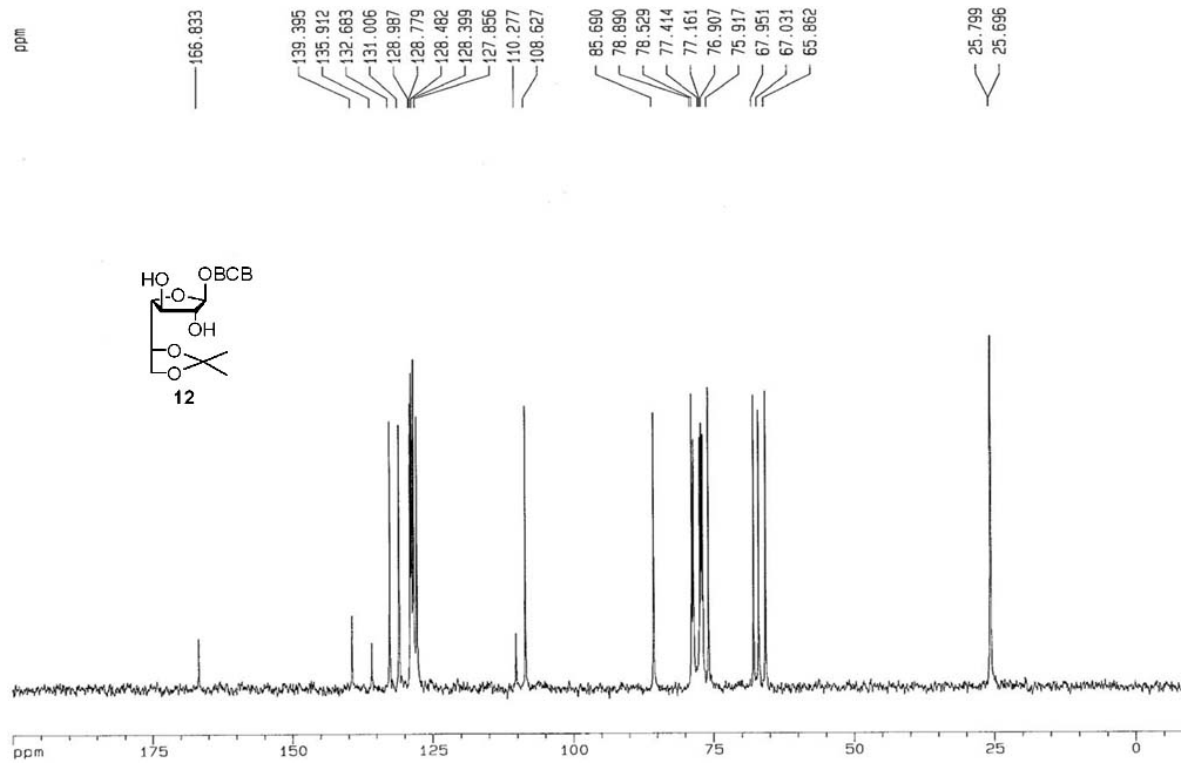
6
4
2
0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128.482
128.399
127.856
110.277
108.627
85.690
78.890
78.529
77.414
77.161
76.907
75.917
67.951
67.031
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HO
OBCB
OH
O
O
12
ppm
175
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75
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25
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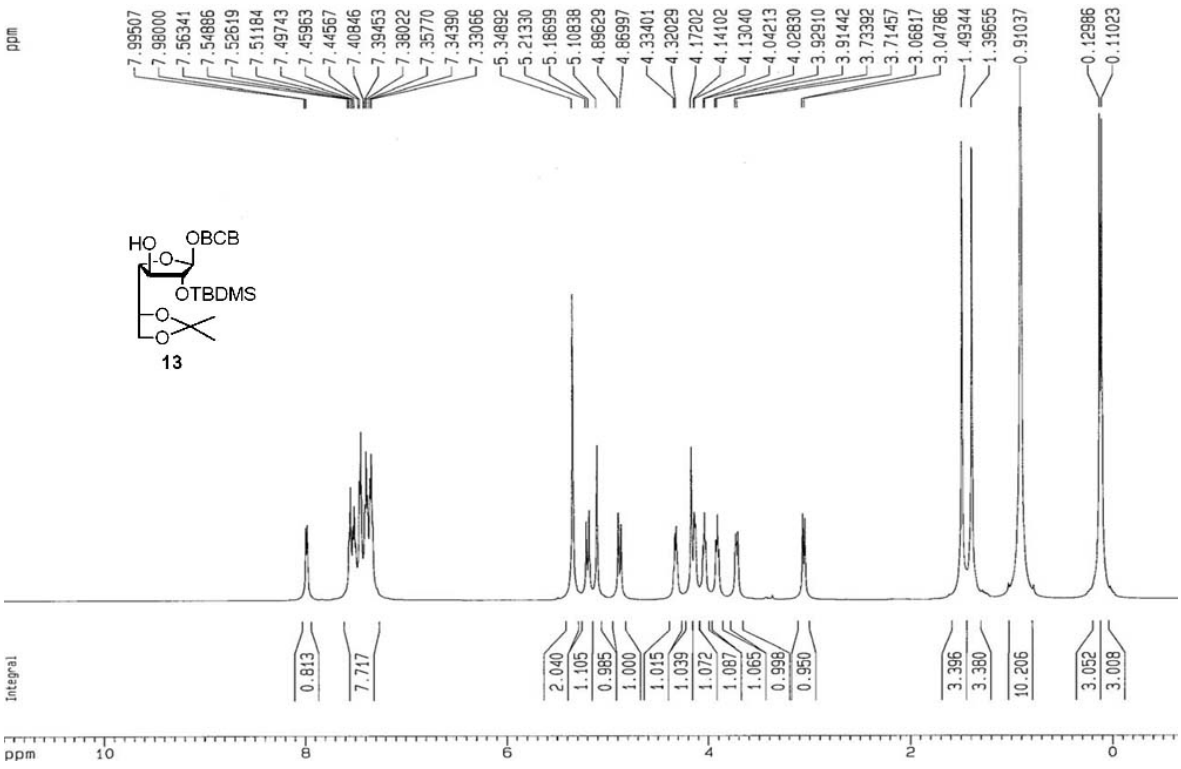
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7.44567
7.40846
7.39453
7.38022
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5.21330
5.18699
5.10838
4.89629
4.86997
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4.17202
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4.13040
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3.71457
3.06817
3.04786
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1.39655
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0.12986
0.11023
HO
OBCB
OTBDMS
13
Integral
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7.717
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1.105
0.985
1.000
1.015
1.039
1.072
1.087
1.065
0.998
0.950
3.396
3.380
10.206
3.052
3.008
ppm
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8
6
4
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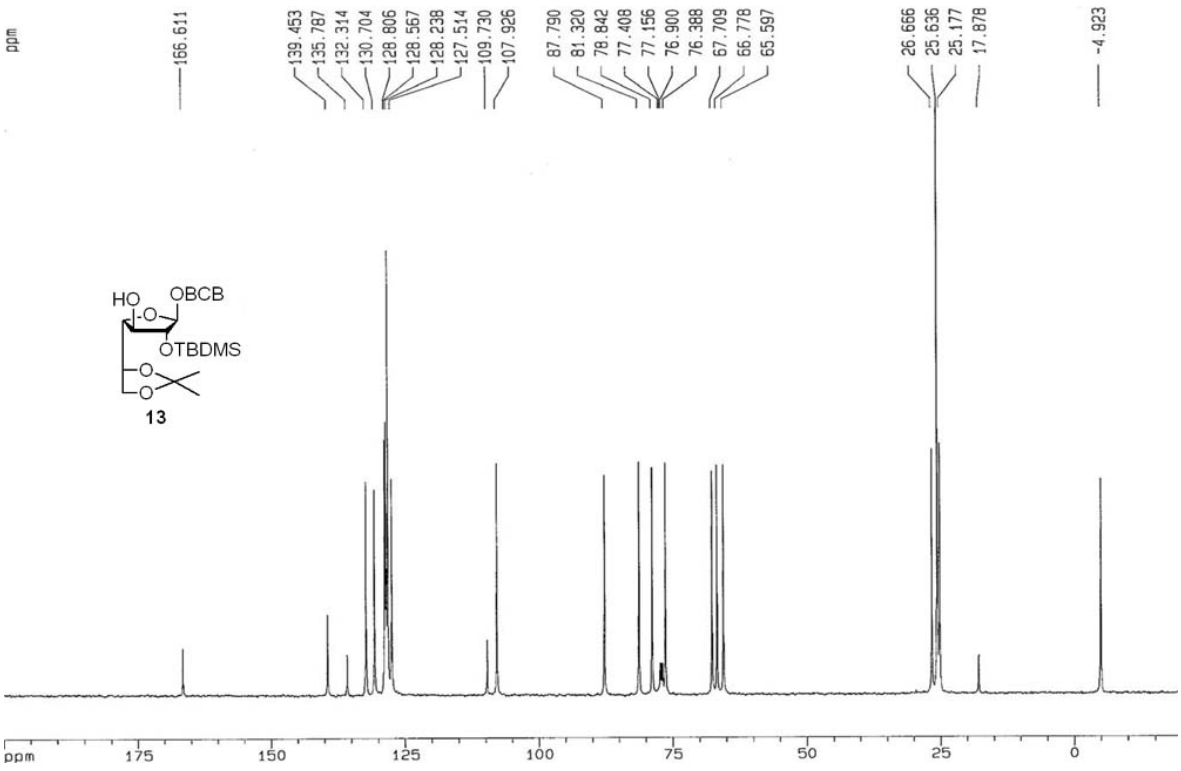
0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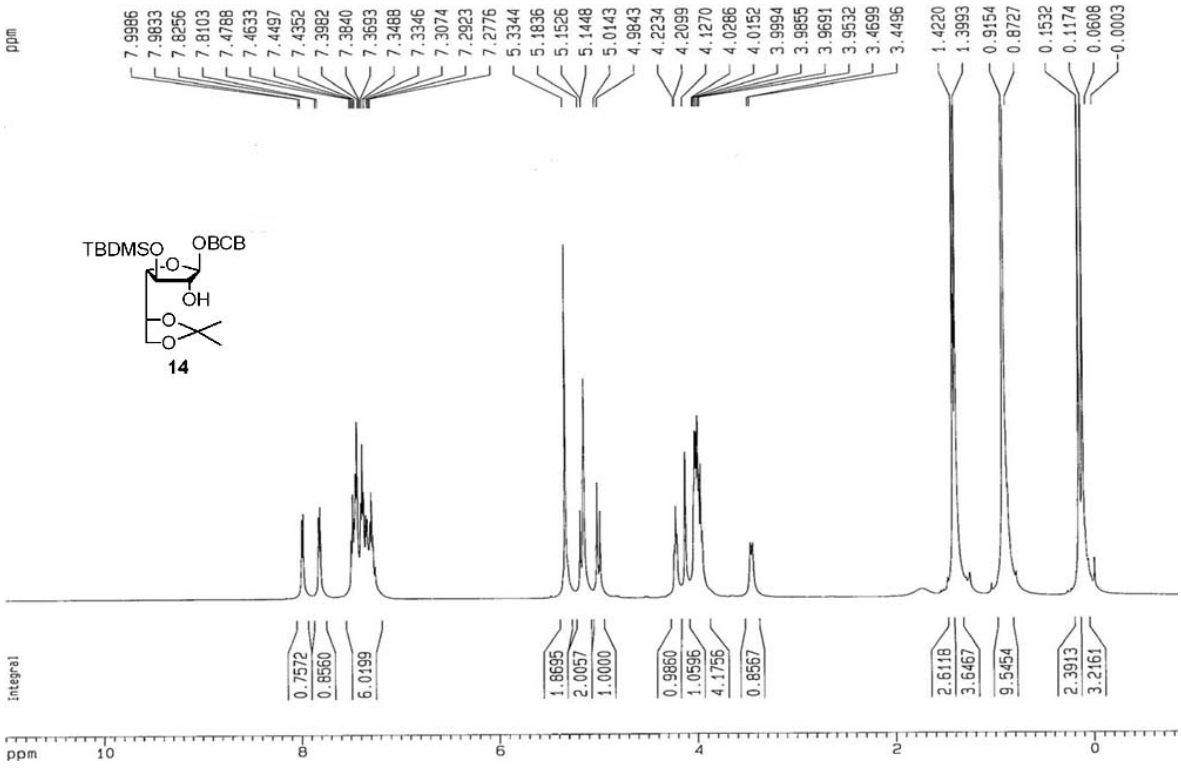
132.314
130.704
128.806
128.567
128.238
127.514
109.730
107.926
87.790
81.320
78.842
77.408
77.156
76.900
76.388
67.709
66.778
65.597
26.666
25.636
25.177
17.878
-4.923
HO
OBCB
OTBDMS
13
ppm
175
150
125
100
75
50
25
0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7.4633
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7.3982
7.3840
7.3693
7.3488
7.3346
7.3074
7.2923
7.2776
5.3344
5.1836
5.1526
5.1448
5.0143
4.9843
4.2234
4.2099
4.1270
4.0286
4.0152
3.9994
3.9855
3.9691
3.9532
3.4699
3.4496
1.4220
1.3993
0.9154
0.8727
0.1532
0.1174
0.0608
-0.0003
TBDMSO
OBCB
OH
14
integral
0.7572
0.8560
6.0199
1.8695
2.0057
1.0000
0.9860
1.0596
4.1756
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3.6467
9.5454
2.3913
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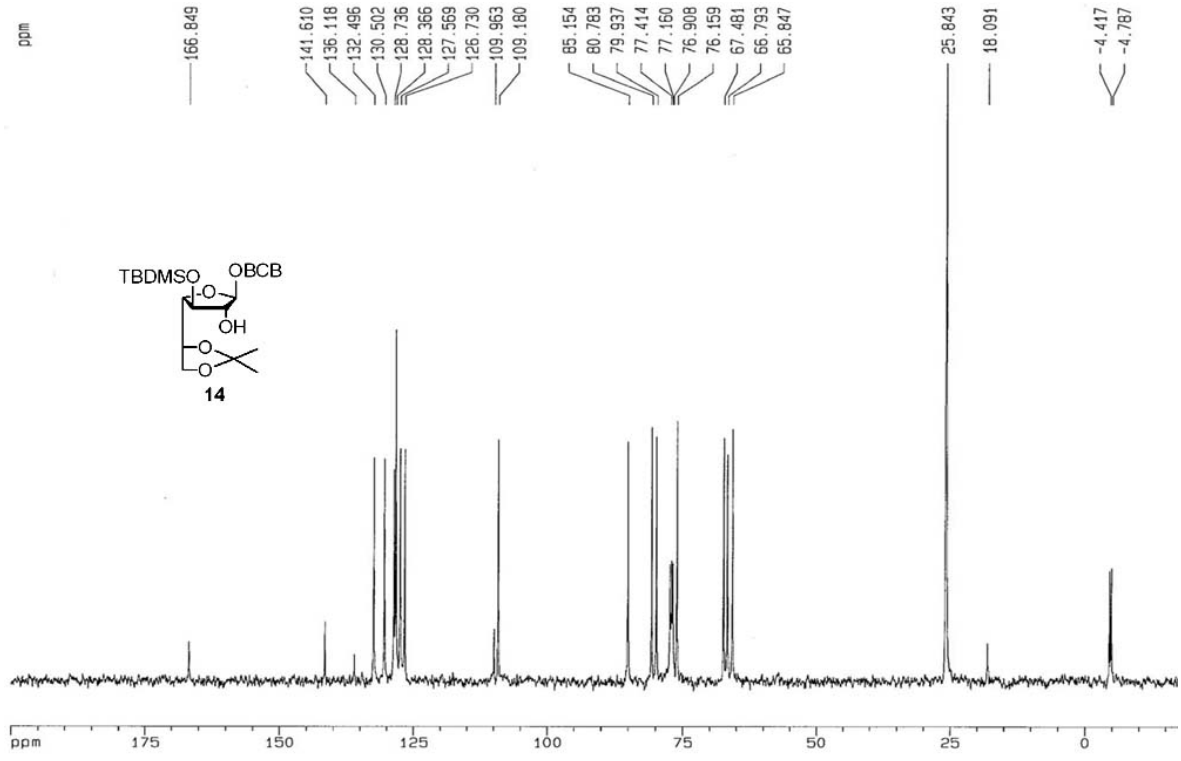
ppm
10
8
6
4
2
0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132.496
130.502
128.736
128.366
127.569
126.730
109.963
109.180
85.154
80.783
79.937
77.414
77.160
76.908
76.159
67.481
66.793
65.847
25.843
18.091
-4.417
-4.787
TBDMSO
OBCB
OH
14
ppm
175
150
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100
75
50
25
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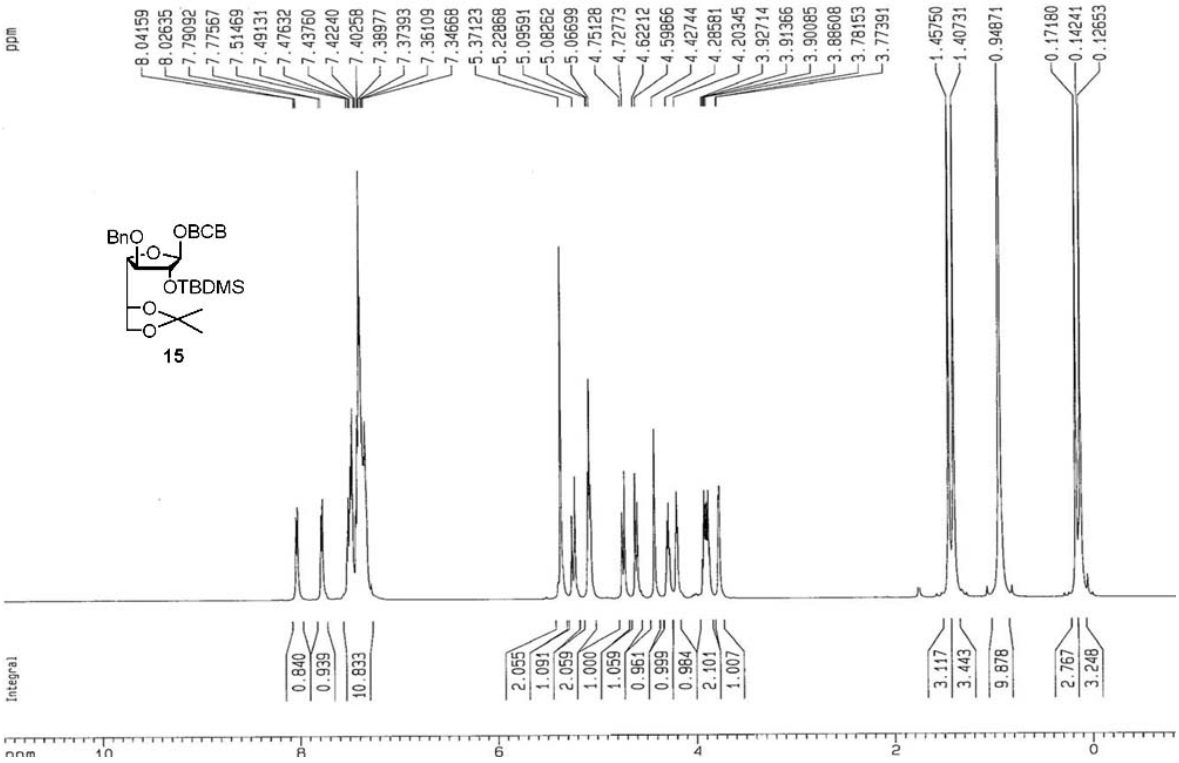
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7.51469
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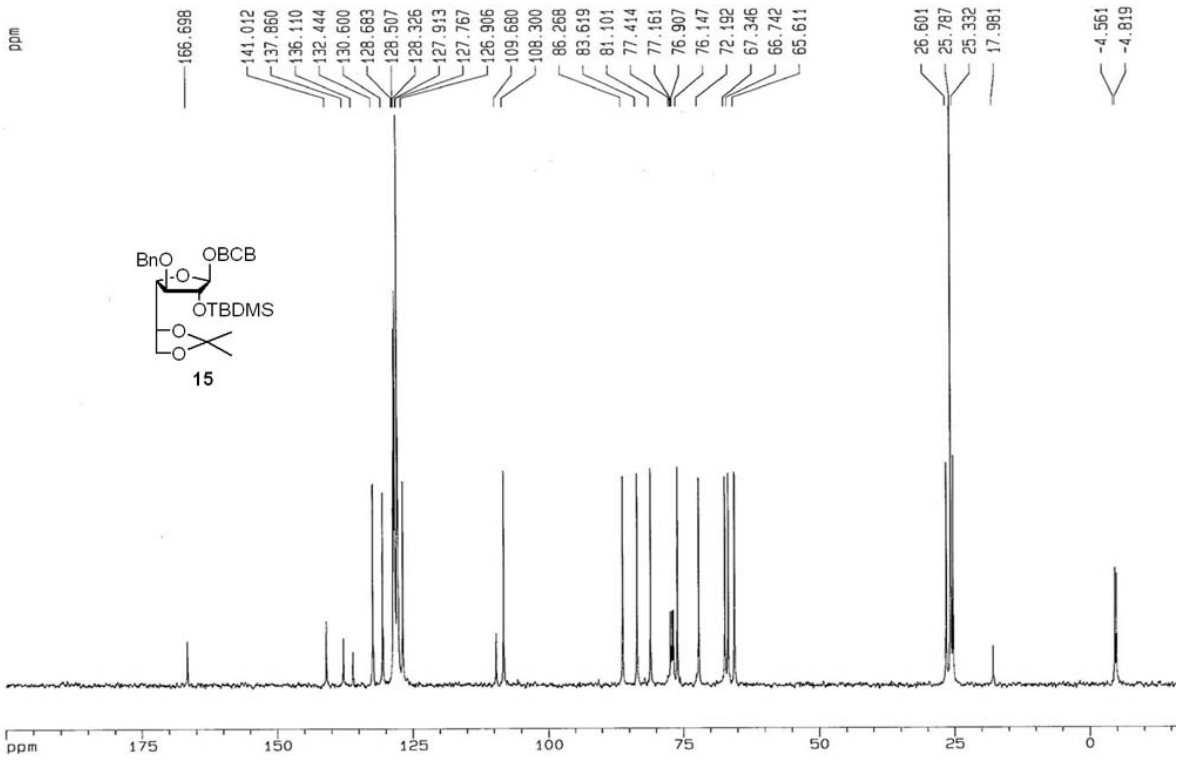
7.43760
7.42240
7.40258
7.38977
7.37393
7.36109
7.34668
5.37123
5.22868
5.09591
5.08262
5.06699
4.75128
4.72773
4.62212
4.59866
4.42744
4.28581
4.20345
3.92714
3.91366
3.90085
3.88608
3.78153
3.77391
1.45750
1.40731
0.94871
0.17180
0.14241
0.12653
BnO
OBCB
OTBDMS
15
Integral
0.840
0.939
10.833
2.055
1.091
2.059
1.000
1.059
0.961
0.999
0.984
2.101
1.007
3.117
3.443
9.878
2.767
3.248
ppm
10
8
6
4
2
0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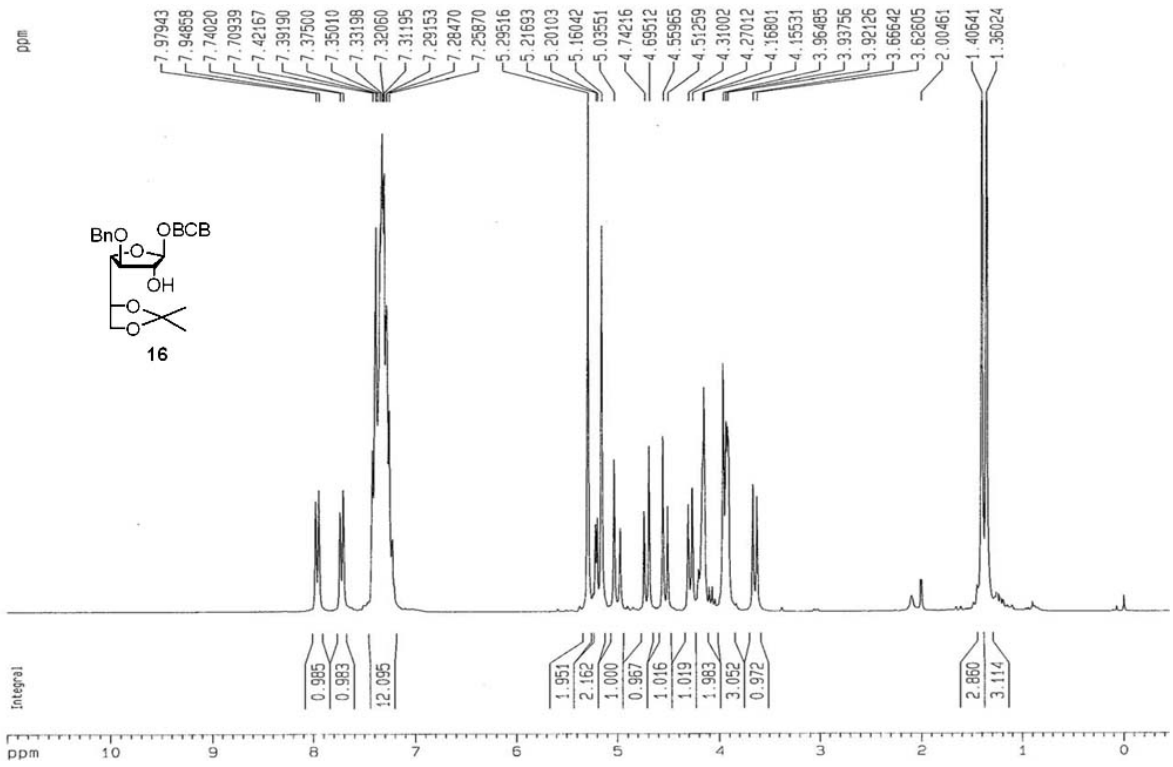
136.110
132.444
130.600
128.683
128.507
128.326
127.913
127.767
126.906
109.680
108.300
86.268
83.619
81.101
77.414
77.161
76.907
76.147
72.192
67.346
66.742
65.611
26.601
25.787
25.332
17.981
-4.561
-4.819
BnO
OBCB
OTBDMS
15
ppm
175
150
125
100
75
50
25
0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7.94858
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7.70939
7.42167
7.39190
7.37500
7.35010
7.33198
7.32060
7.31195
7.29153
7.28470
7.25870
5.29516
5.21693
5.20103
5.16042
5.03551
4.74216
4.69512
4.55965
4.51259
4.31002
4.27012
4.16801
4.15531
3.96485
3.93756
3.92126
3.66642
3.62605
2.00461
1.40641
1.36024
BnO
OBCB
OH
O
O
16
Integral
0.985
0.983
12.095
1.951
2.162
1.000
0.967
1.016
1.019
1.983
3.052
0.972
2.860
3.114
ppm
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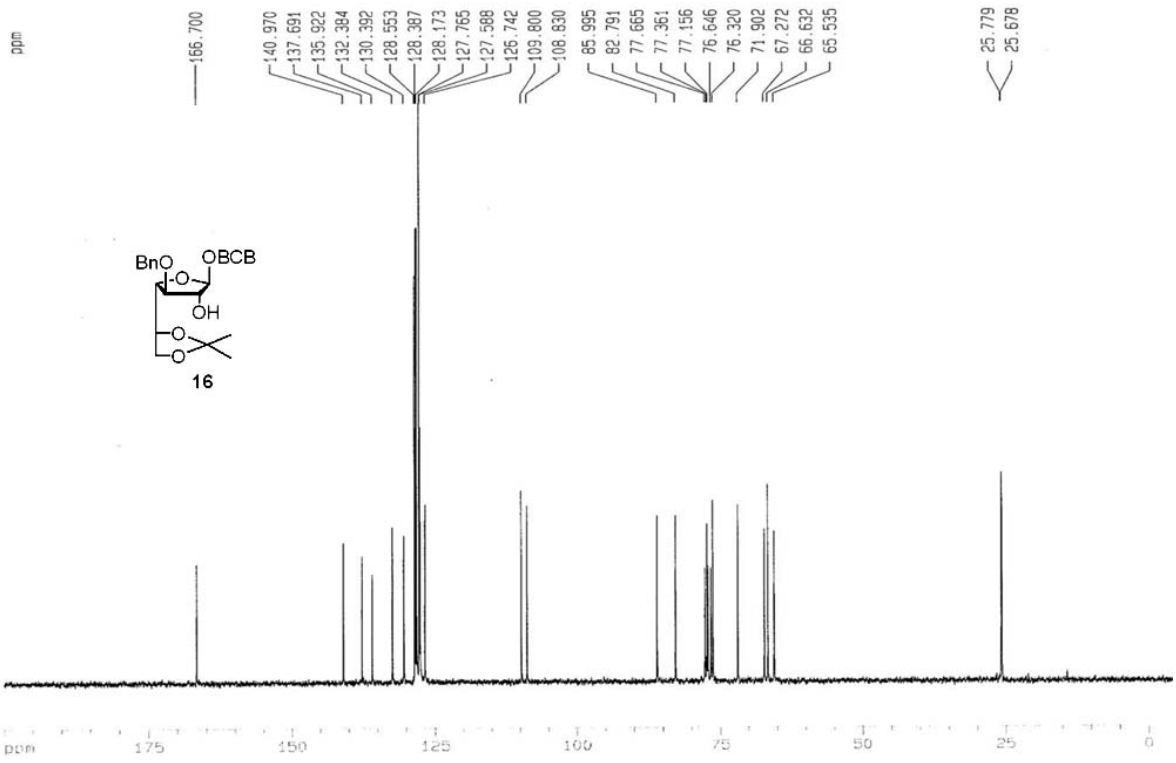
9
8
7
6
5
4
3
2
1
0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166.700
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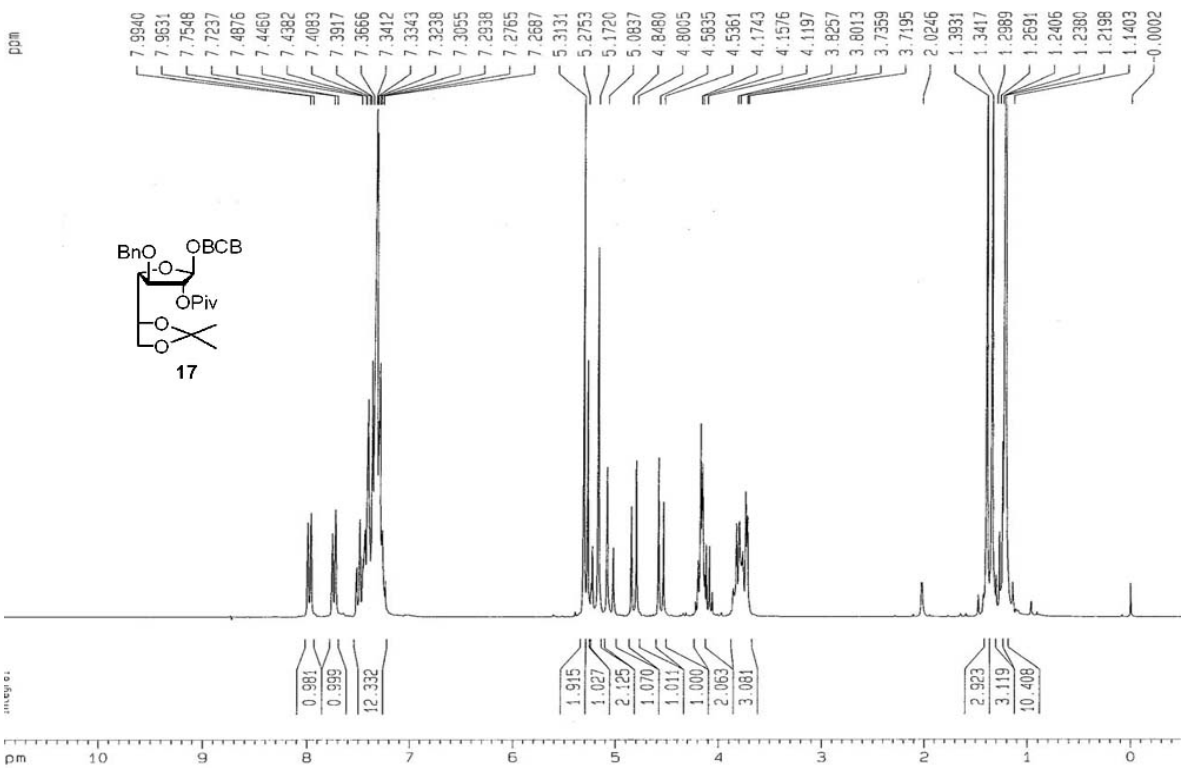
137.691
135.922
132.384
130.392
128.553
128.387
128.173
127.765
127.588
126.742
109.800
108.830
85.995
82.791
77.665
77.361
77.156
76.646
76.320
71.902
67.272
66.632
65.535
25.779
25.678
BnO
OBCB
OH
O
O
16
ppm
175
150
125
100
75
50
25
0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7.9631
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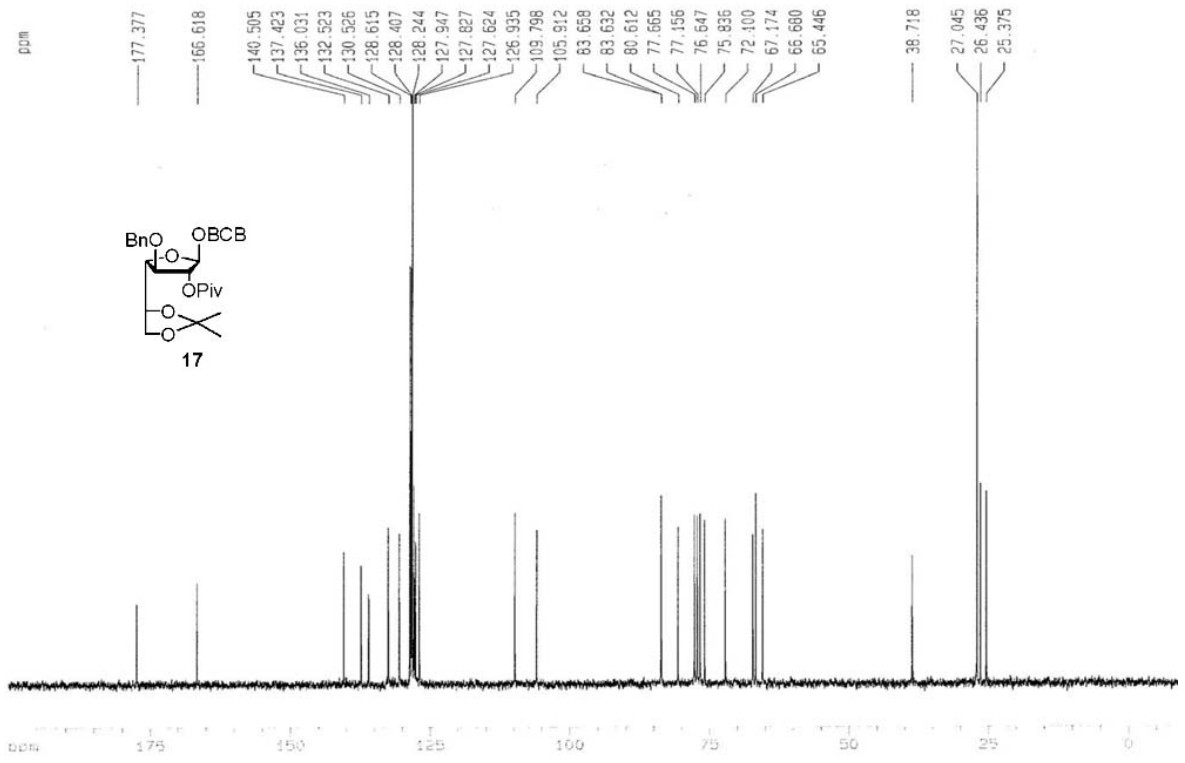
7.4876
7.4460
7.4382
7.4083
7.3917
7.3666
7.3412
7.3343
7.3238
7.3055
7.2938
7.2765
7.2687
5.3131
5.2753
5.1720
5.0837
4.8480
4.8005
4.5835
4.5361
4.1743
4.1576
4.1197
3.8257
3.8013
3.7359
3.7195
2.0246
1.3931
1.3417
1.2989
1.2691
1.2406
1.2380
1.2198
1.1403
-0.0002
BnO
OBCB
OPiv
17
0.981
0.999
12.332
1.915
1.027
2.125
1.070
1.011
1.000
2.063
3.081
2.923
3.119
10.408
pm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137.423
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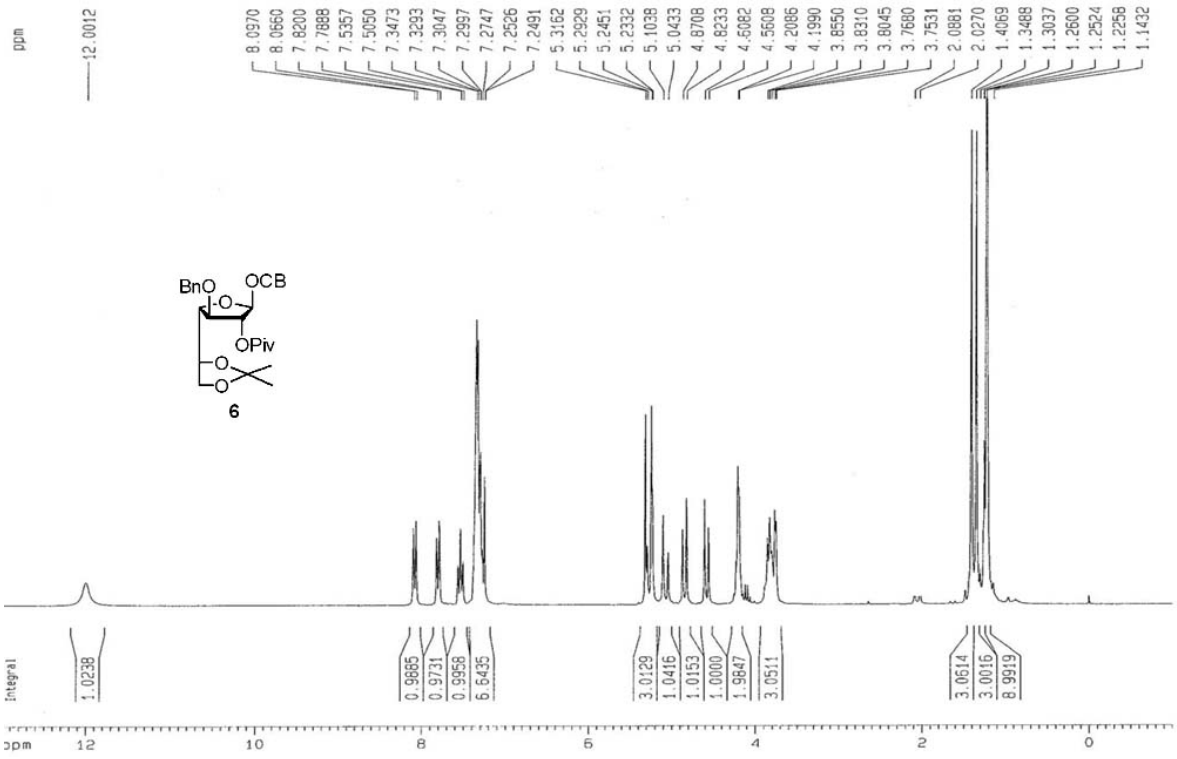
130.526
128.615
128.407
128.244
127.947
127.827
127.624
126.935
109.798
105.912
83.658
83.632
80.612
77.665
77.156
76.647
75.836
72.100
67.174
66.680
65.446
38.718
27.045
26.436
25.375
BnO
OBCB
OPiv
17
ppm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7.5050
7.3473
7.3293
7.3047
7.2997
7.2747
7.2526
7.2491
5.3162
5.2929
5.2451
5.2332
5.1038
5.0433
4.8708
4.8233
4.6082
4.5608
4.2086
4.1990
3.8550
3.8310
3.8045
3.7680
3.7531
2.0881
2.0270
1.4069
1.3488
1.3037
1.2600
1.2524
1.2256
1.1432
BnO
OCB
OPiv
6
Integral
1.0238
0.9685
0.9731
0.9958
6.6435
3.0129
1.0416
1.0153
1.0000
1.9847
3.0511
3.0614
3.0016
8.9919
ppm
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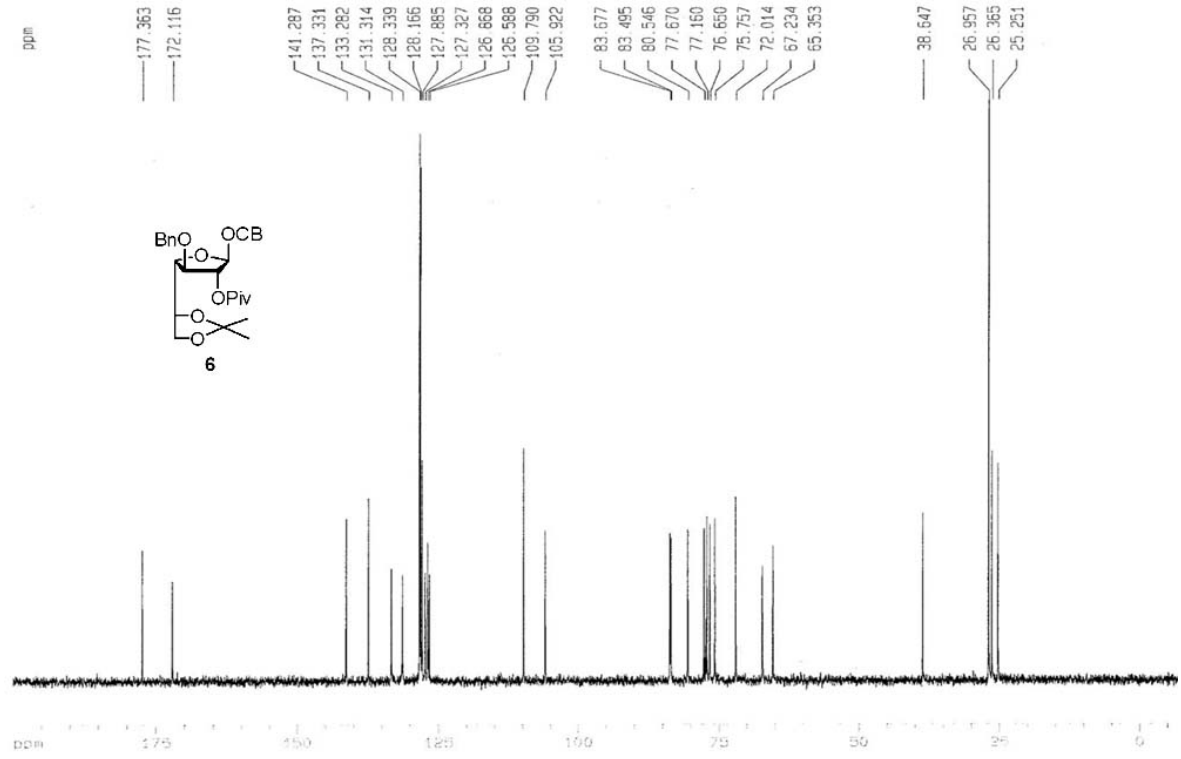
10
8
6
4
2
0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137.331
133.282
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128.166
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127.327
126.868
126.588
109.790
105.922
83.677
83.495
80.546
77.670
77.160
76.650
75.757
72.014
67.234
65.353
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26.365
25.251
BnO
OCB
OPiv
6
ppm
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125
100
75
50
25
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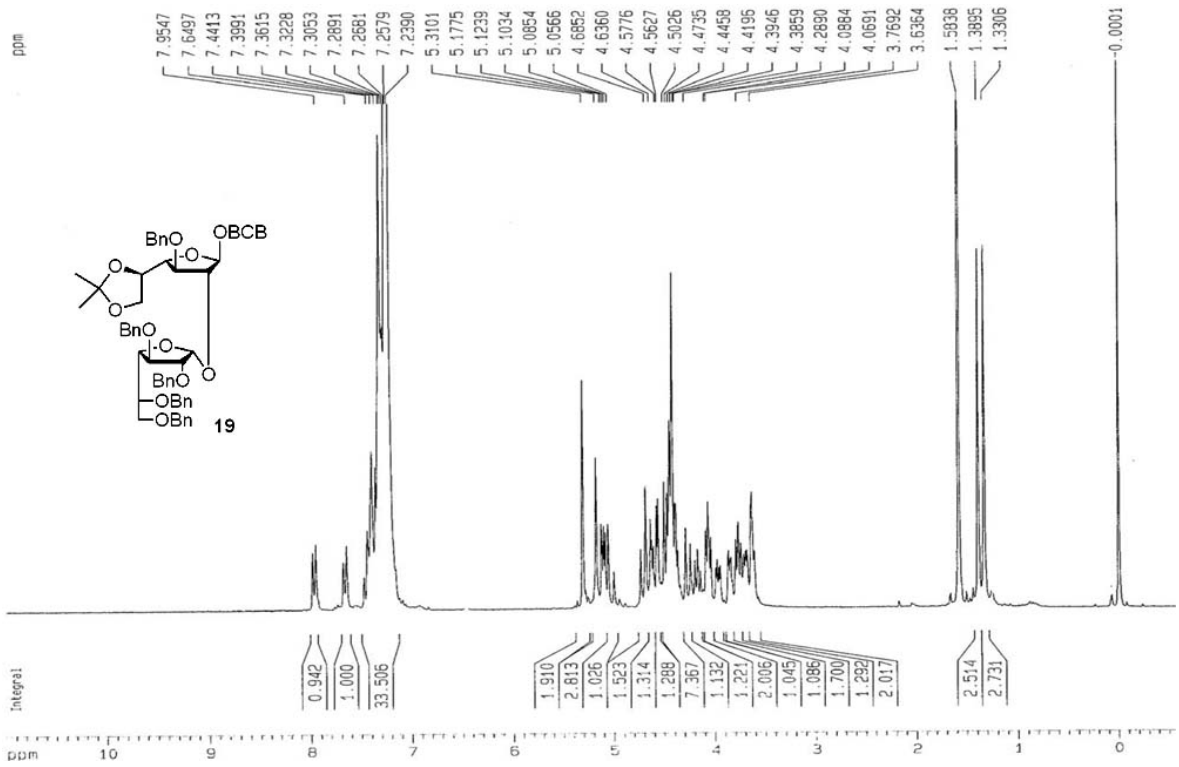
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7.3615
7.3228
7.3053
7.2891
7.2681
7.2579
7.2390
5.3101
5.1775
5.1239
5.1034
5.0854
5.0566
4.6852
4.6360
4.5776
4.5627
4.5026
4.4735
4.4458
4.4196
4.3946
4.3859
4.2890
4.0884
4.0691
3.7692
3.6364
1.5938
1.3895
1.3306
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OBCB
BnO
BnO
OBn
OBn
19
Integral
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33.506
1.910
2.813
1.026
1.523
1.314
1.288
7.367
1.132
1.221
2.006
1.045
1.086
1.700
1.292
2.017
2.514
2.731
ppm
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9
8
7
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5
4
3
2
1
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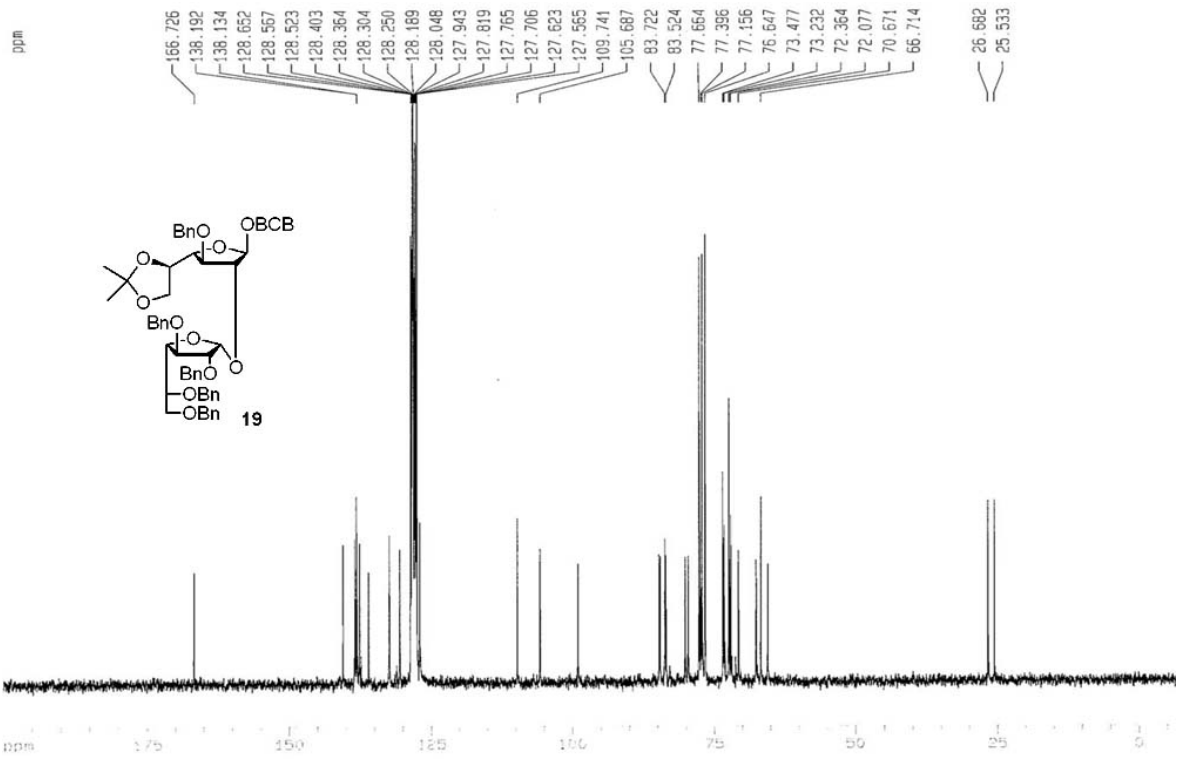
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128.364
128.304
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128.048
127.943
127.819
127.765
127.706
127.623
127.565
109.741
105.687
83.722
83.524
77.664
77.396
77.156
76.647
73.477
73.232
72.364
72.077
70.671
66.714
26.682
25.533
BnO
OBCB
BnO
BnO
OBn
OBn
19
ppm
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150
125
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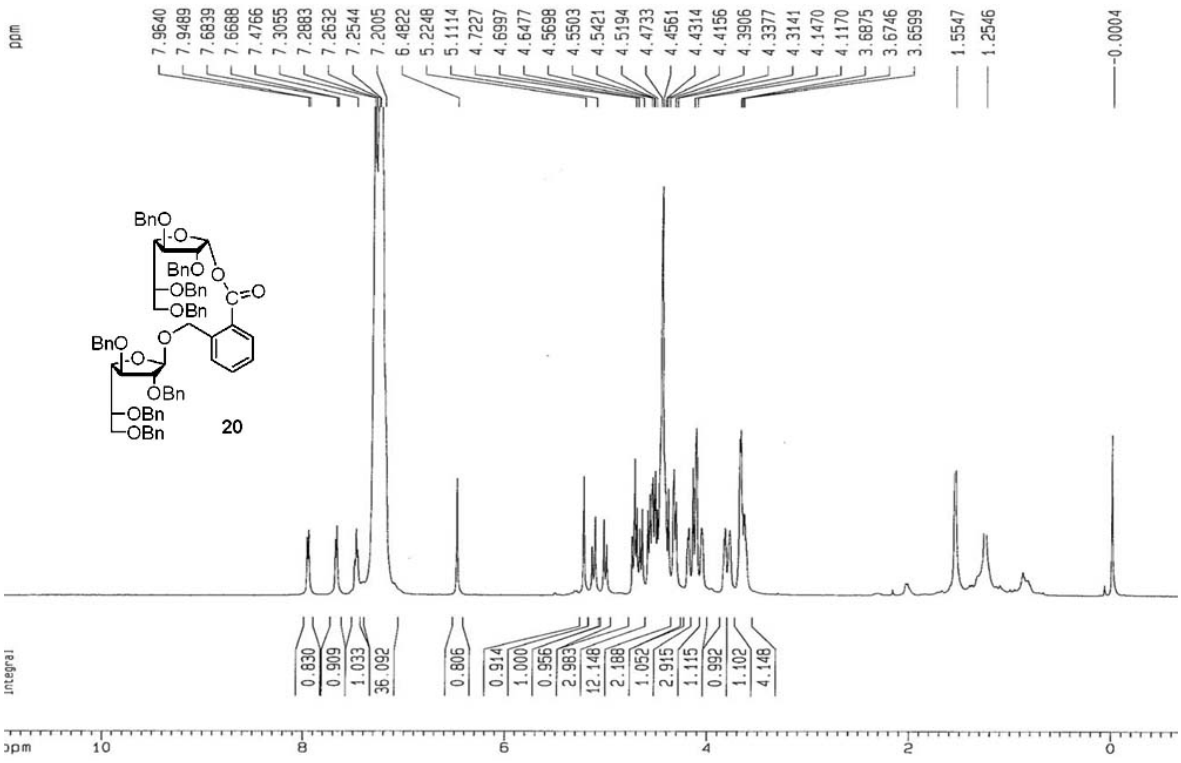
75
50
25
0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7.2632
7.2544
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5.2248
5.1114
4.7227
4.6997
4.6477
4.5698
4.5503
4.5421
4.5194
4.4733
4.4561
4.4314
4.4156
4.3906
4.3377
4.3141
4.1470
4.1170
3.6875
3.6746
3.6599
1.5547
1.2546
0.0004
BnO
BnO
OBn
OBn
C=O
BnO
OBn
OBn
OBn
20
integral
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0.909
1.033
36.092
0.806
0.914
1.000
0.956
2.983
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2.915
1.115
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6
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2
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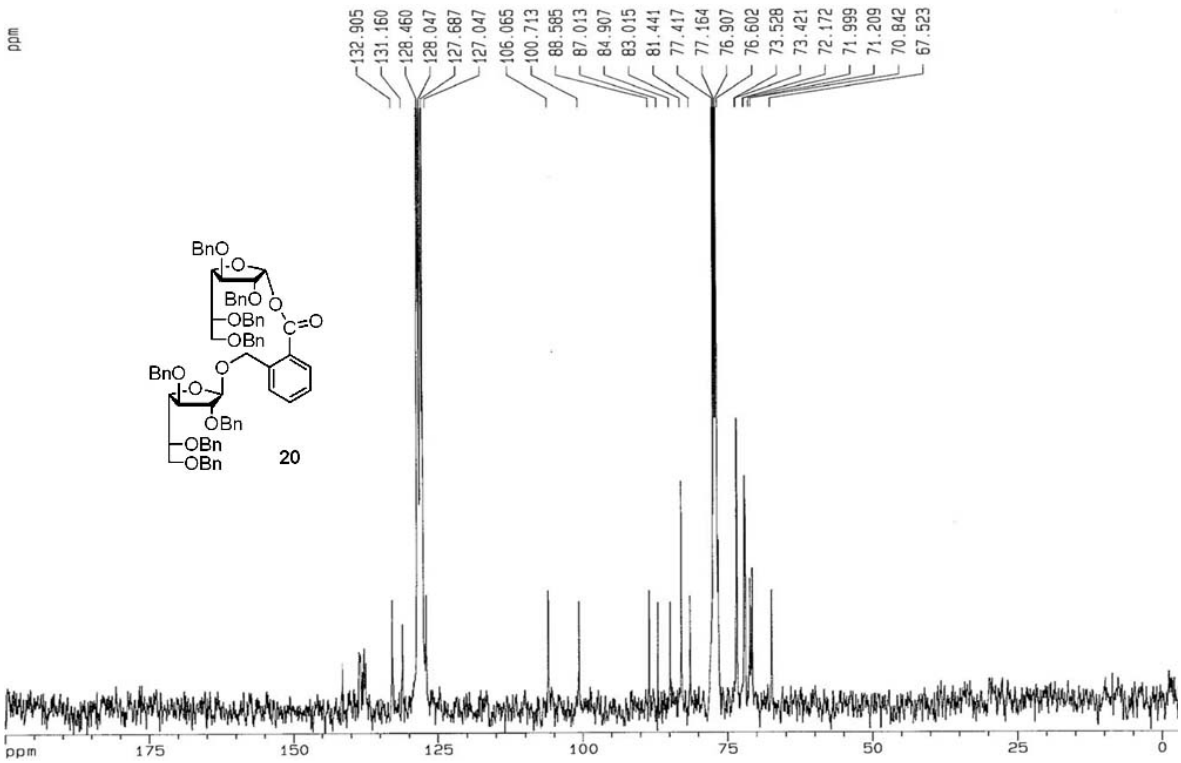
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127.047
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88.585
87.013
84.907
83.015
81.441
77.417
77.164
76.907
76.602
73.528
73.421
72.172
71.999
71.209
70.842
67.523
BnO
BnO
OBn
OBn
C=O
BnO
OBn
OBn
OBn
20
ppm
175
150
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100
75
50
25
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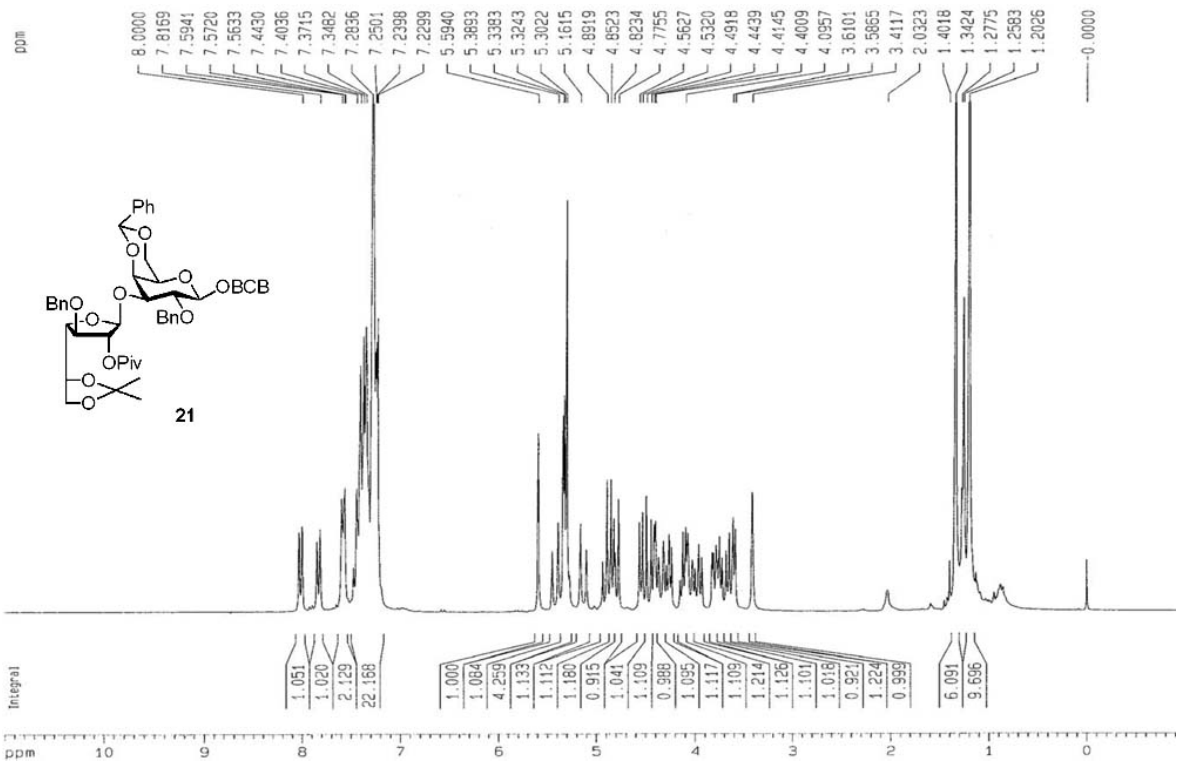
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7.3482
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7.2398
7.2299
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5.3893
5.3383
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5.3022
5.1615
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4.8523
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4.7755
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4.5320
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4.4439
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3.5865
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2.0323
1.4018
1.3424
1.2775
1.2583
1.2026
0.0000
Integral
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1.020
2.129
22.168
1.000
1.084
4.259
1.133
1.112
1.180
0.915
1.041
1.109
0.988
1.095
1.117
1.109
1.214
1.126
1.101
1.018
0.921
1.224
0.999
6.091
9.696
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7
6
5
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3
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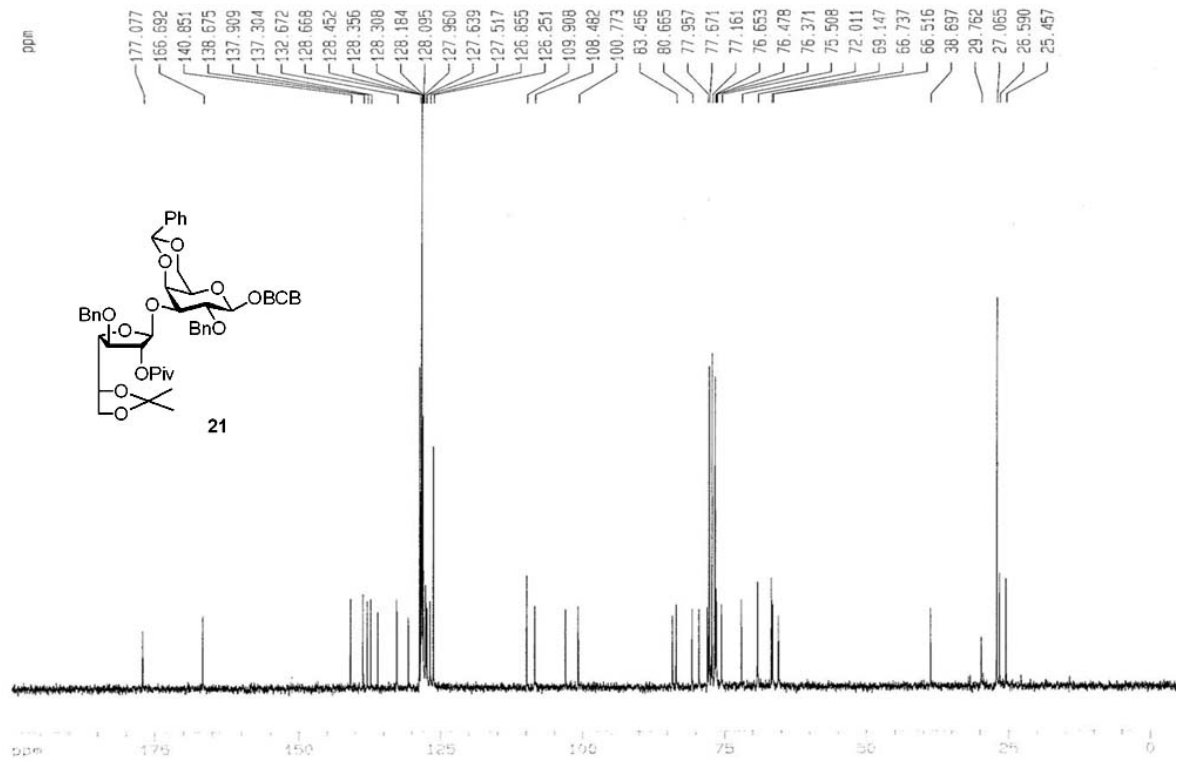
Ph
OBCB
BnO
BnO
OPiv
21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137.909
137.304
132.672
128.668
128.452
128.356
128.308
128.184
128.095
127.960
127.639
127.517
126.855
126.251
109.908
108.482
100.773
83.456
80.665
77.957
77.671
77.161
76.653
76.478
76.371
75.508
72.011
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66.737
66.516
38.697
29.762
27.065
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25.457
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125
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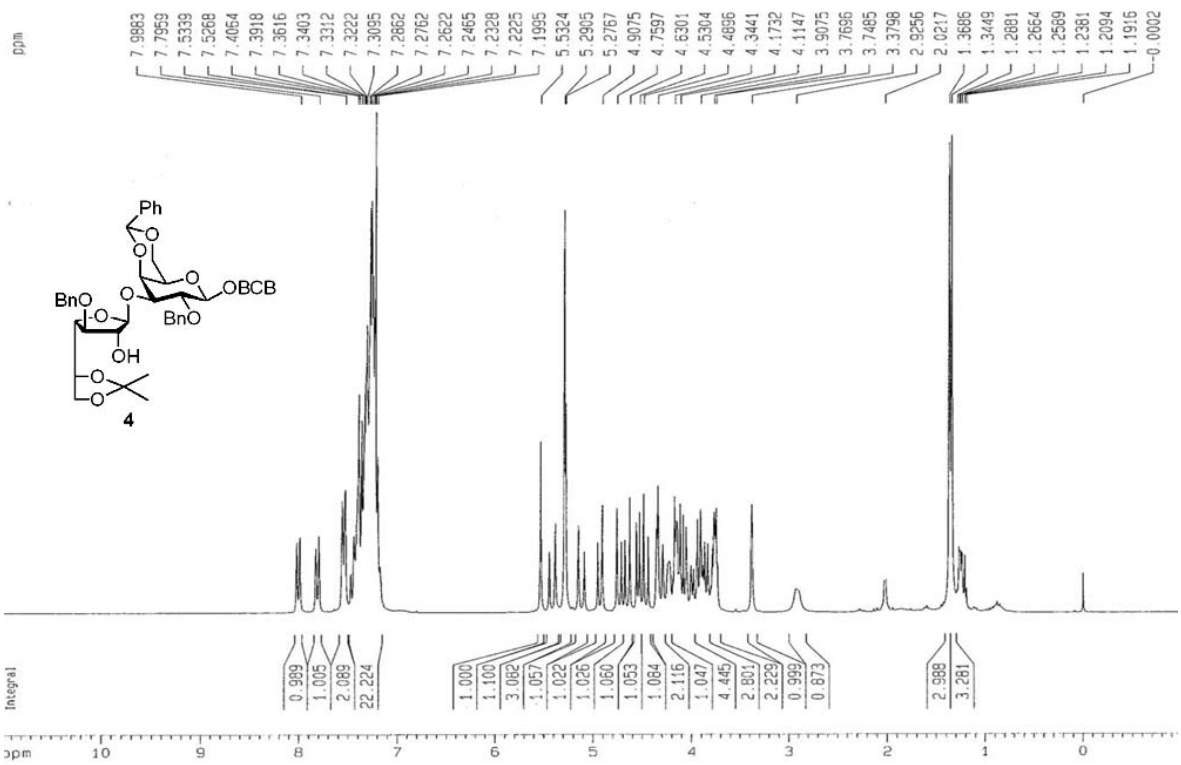
Ph
OBCB
BnO
BnO
OPiv
21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7.3616
7.3403
7.3312
7.3222
7.3095
7.2862
7.2762
7.2622
7.2465
7.2328
7.2225
7.1995
5.5324
5.2905
5.2767
4.9075
4.7597
4.6301
4.5304
4.4896
4.3441
4.1732
4.1147
3.9075
3.7696
3.7485
3.3798
2.9256
2.0217
1.3686
1.3449
1.2881
1.2664
1.2569
1.2381
1.2094
1.1916
-0.0002
Ph
BnO
OBCB
BnO
OH
4
Integral
0.989
1.005
2.089
22.224
1.000
1.100
3.082
1.057
1.022
1.026
1.060
1.053
1.084
2.116
1.047
4.445
2.801
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0.999
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2.988
3.281
ppm
10
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7
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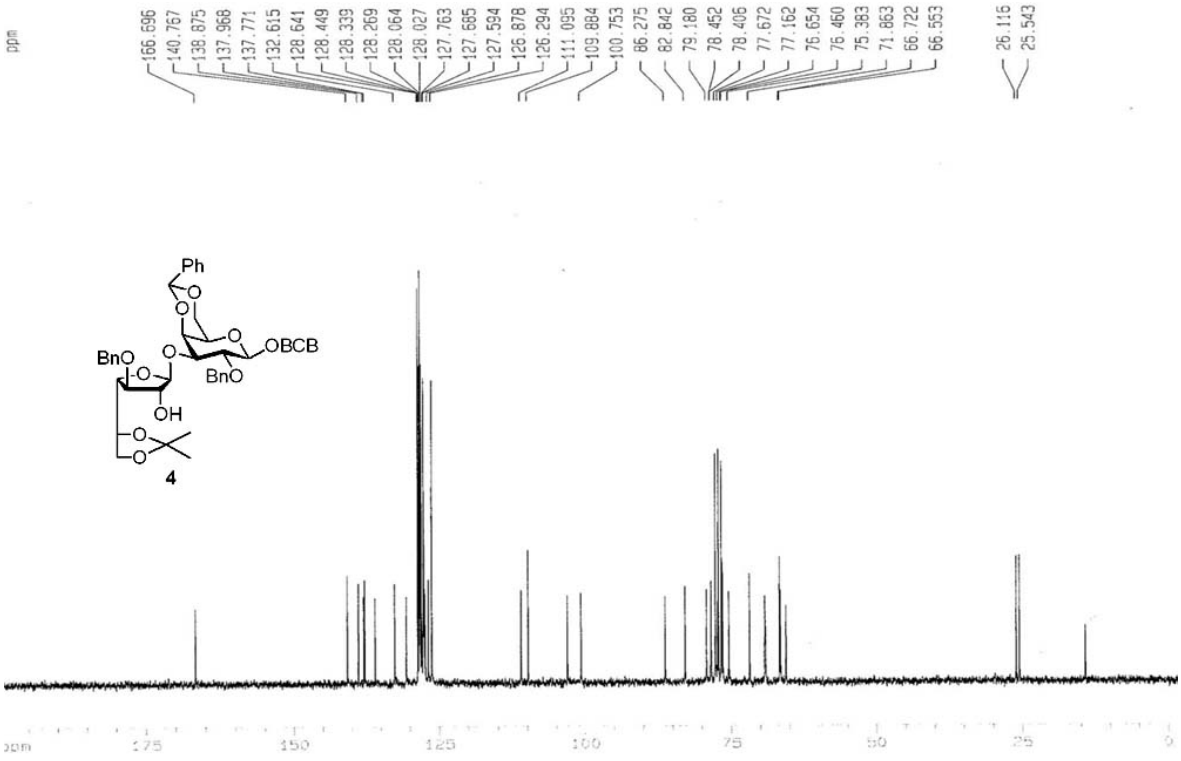
3
2
1
0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128.339
128.269
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128.027
127.763
127.685
127.594
126.878
126.294
111.095
109.884
100.753
86.275
82.842
79.180
78.452
78.406
77.672
77.162
76.654
76.460
75.383
71.863
66.722
66.553
26.116
25.543
Ph
BnO
OBCB
BnO
OH
4
ppm
175
150
125
100
75
50
25
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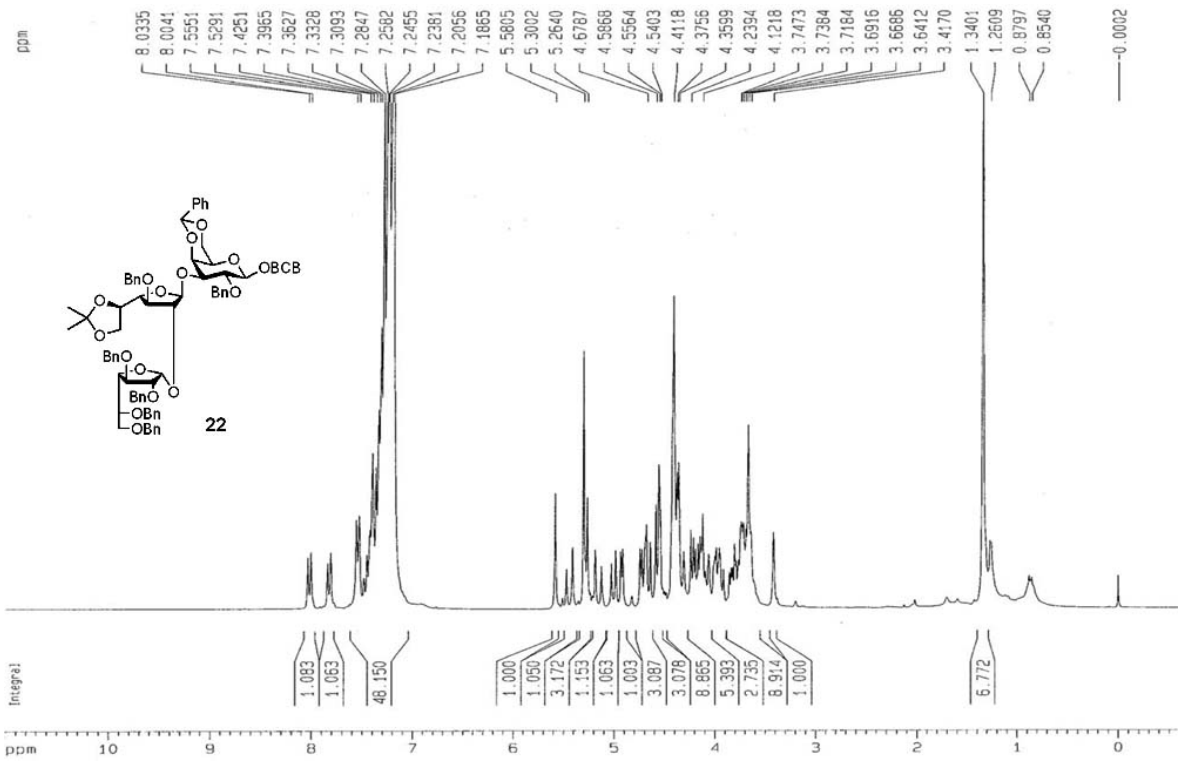
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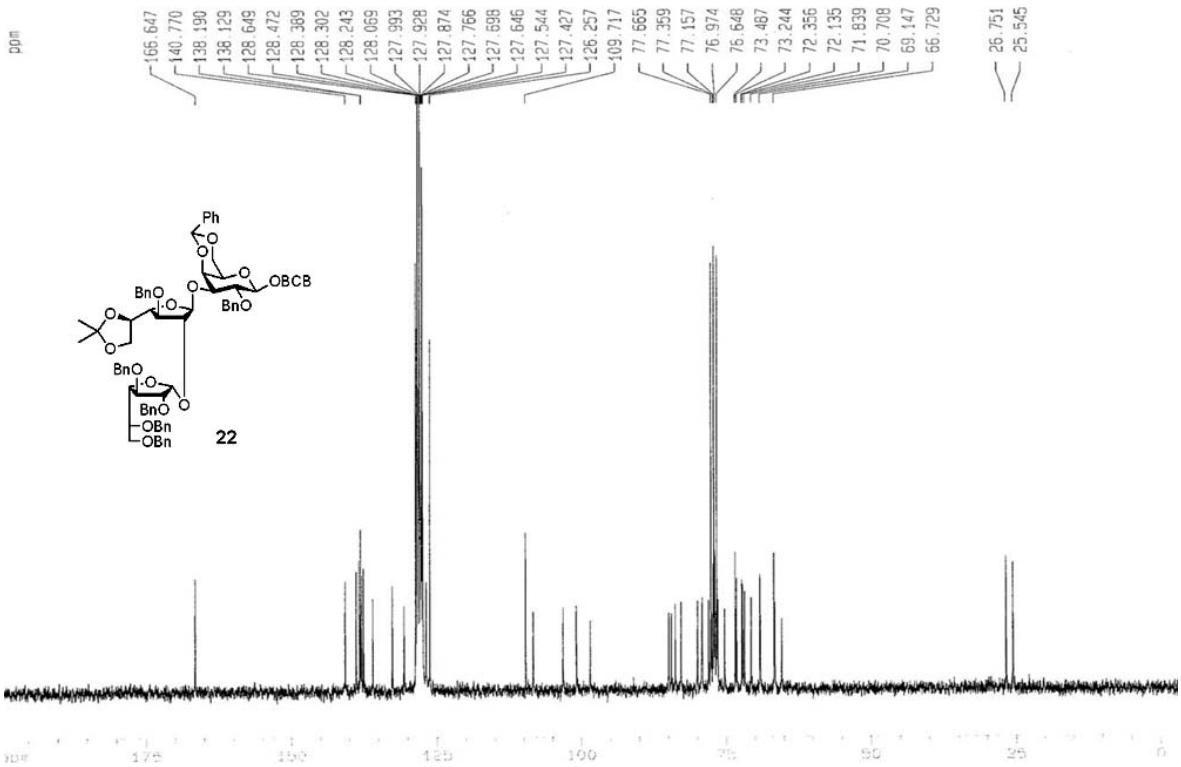
7.5291
7.4251
7.3965
7.3627
7.3328
7.3093
7.2847
7.2582
7.2455
7.2381
7.2056
7.1865
5.5805
5.3002
5.2640
4.6787
4.5868
4.5564
4.5403
4.4118
4.3756
4.3599
4.2394
4.1218
3.7473
3.7384
3.7184
3.6916
3.6686
3.6412
3.4170
1.3401
1.2609
0.8797
0.8540
-0.0002
Integral
1.083
1.053
48.150
1.000
1.050
3.172
1.153
1.063
1.003
3.087
3.078
8.865
5.393
2.735
8.914
1.000
6.772
ppm
10
9
8
7
6
5
4
3
2
1
0
Ph
OBCB
BnO
BnO
BnO
BnO
OBn
OBn
22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128.649
128.472
128.369
128.302
128.243
128.069
127.993
127.928
127.874
127.766
127.698
127.646
127.544
127.427
126.257
109.717
77.665
77.359
77.157
76.974
76.648
73.487
73.244
72.356
72.135
71.839
70.708
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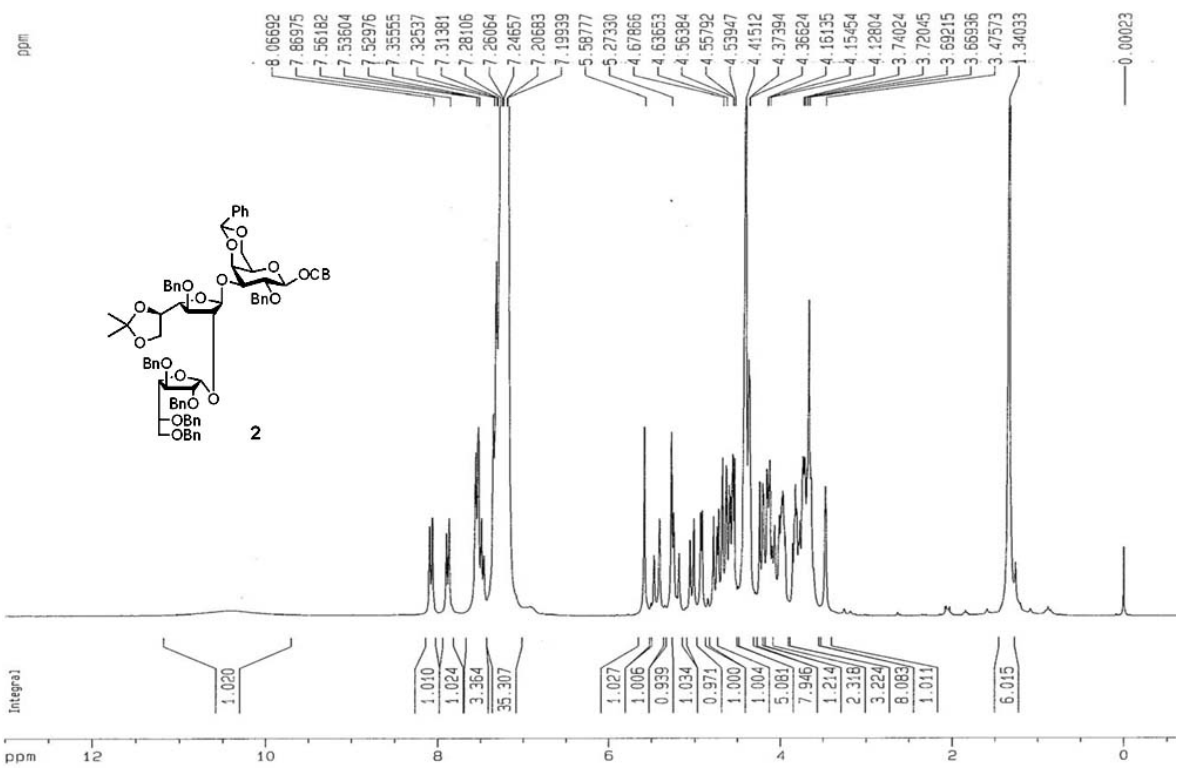
26.751
25.545
Ph
OBCB
BnO
BnO
BnO
BnO
OBn
OBn
22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7.86975
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7.52976
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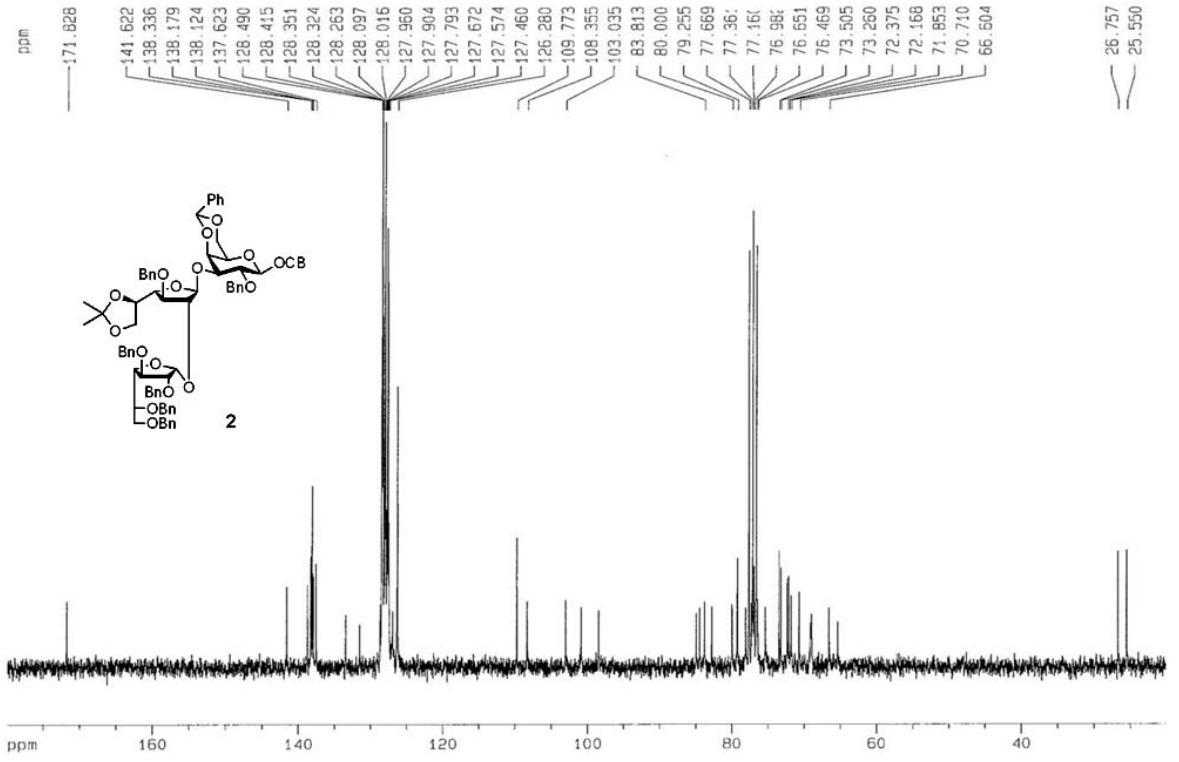
7.31381
7.28106
7.26064
7.24657
7.20683
7.19939
5.58777
5.27330
4.67866
4.63653
4.56384
4.55792
4.53947
4.41512
4.37394
4.36624
4.16135
4.15454
4.12804
3.74024
3.72045
3.69215
3.66936
3.47573
1.34033
0.00023
Integral
1.020
1.010
1.024
3.364
35.307
1.027
1.006
0.939
1.034
0.971
1.000
1.004
5.081
7.946
1.214
2.318
3.224
8.083
1.011
6.015
ppm
12
10
8
6
4
2
0
Ph
OCB
BnO
BnO
BnO
BnO
BnO
OBn
OBn
2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171.828
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138.124
137.623
128.490
128.415
128.351
128.324
128.263
128.097
128.016
127.960
127.904
127.793
127.672
127.574
127.460
126.280
109.773
108.355
103.035
83.813
80.000
79.255
77.669
77.36
77.16
76.98
76.651
76.469
73.505
73.260
72.375
72.168
71.853
70.710
66.604
26.757
25.550
ppm
160
140
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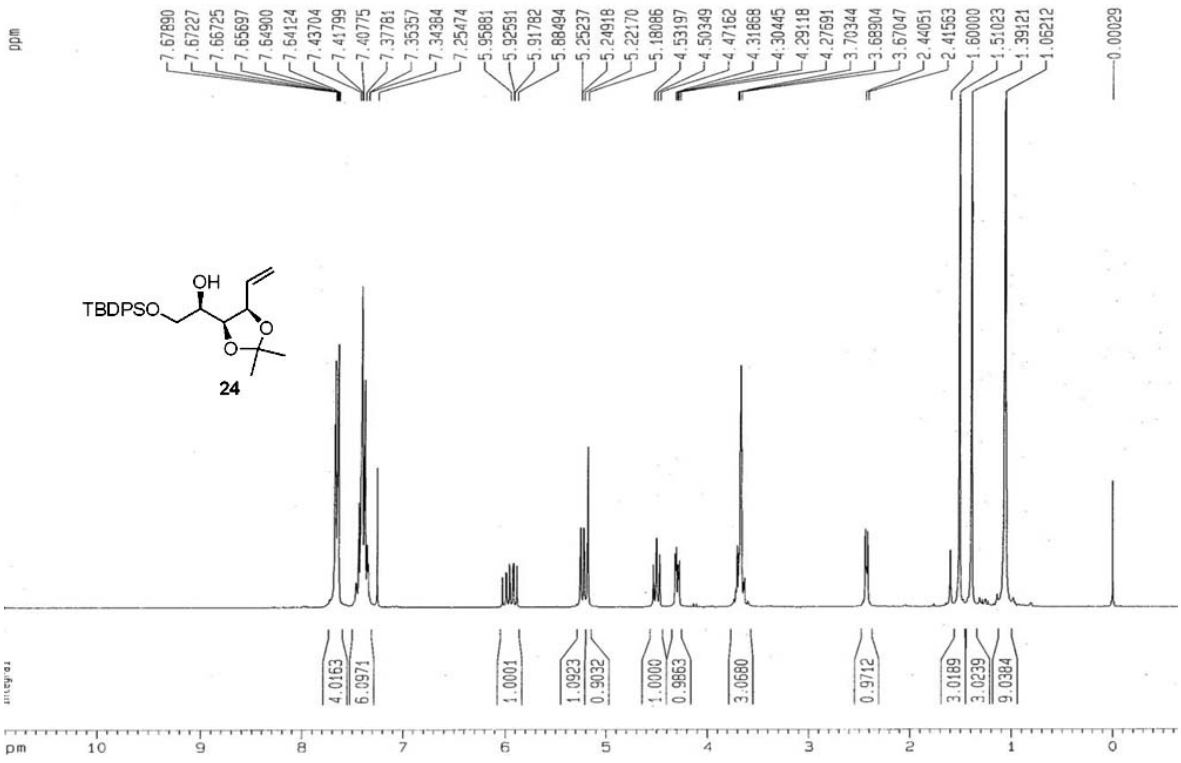
60
40
Ph
OCB
BnO
BnO
BnO
BnO
BnO
OBn
OBn
2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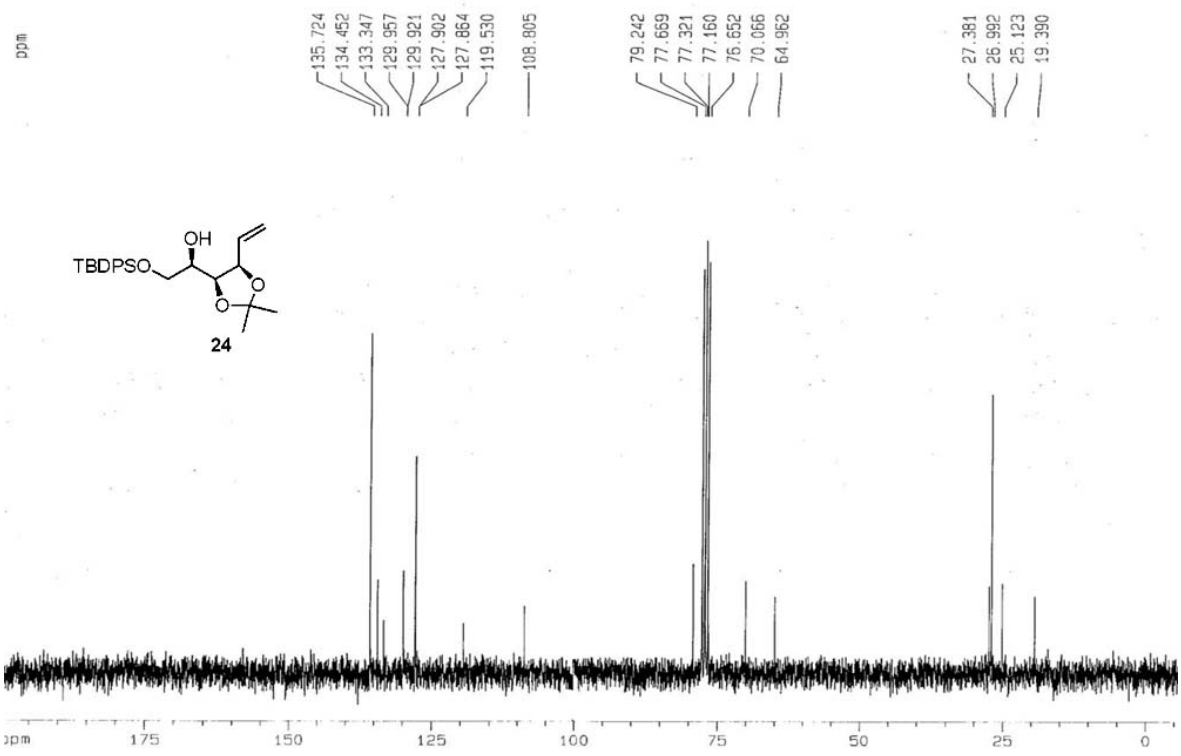
7.64900
7.64124
7.43704
7.41799
7.40775
7.37781
7.35357
7.34384
7.25474
5.95881
5.92591
5.91782
5.88494
5.25237
5.24918
5.22170
5.18086
4.53197
4.50349
4.47162
4.31868
4.30445
4.29118
4.27691
3.70344
3.68904
3.67047
2.44051
2.41563
1.60000
1.51023
1.39121
1.06212
0.00029
OH
TBDPSO
O
O
24
4.0163
6.0971
1.0001
1.0923
0.9032
1.0000
0.9863
3.0680
0.9712
3.0189
3.0239
9.0384
pm
10
9
8
7
6
5
4
3
2
1
0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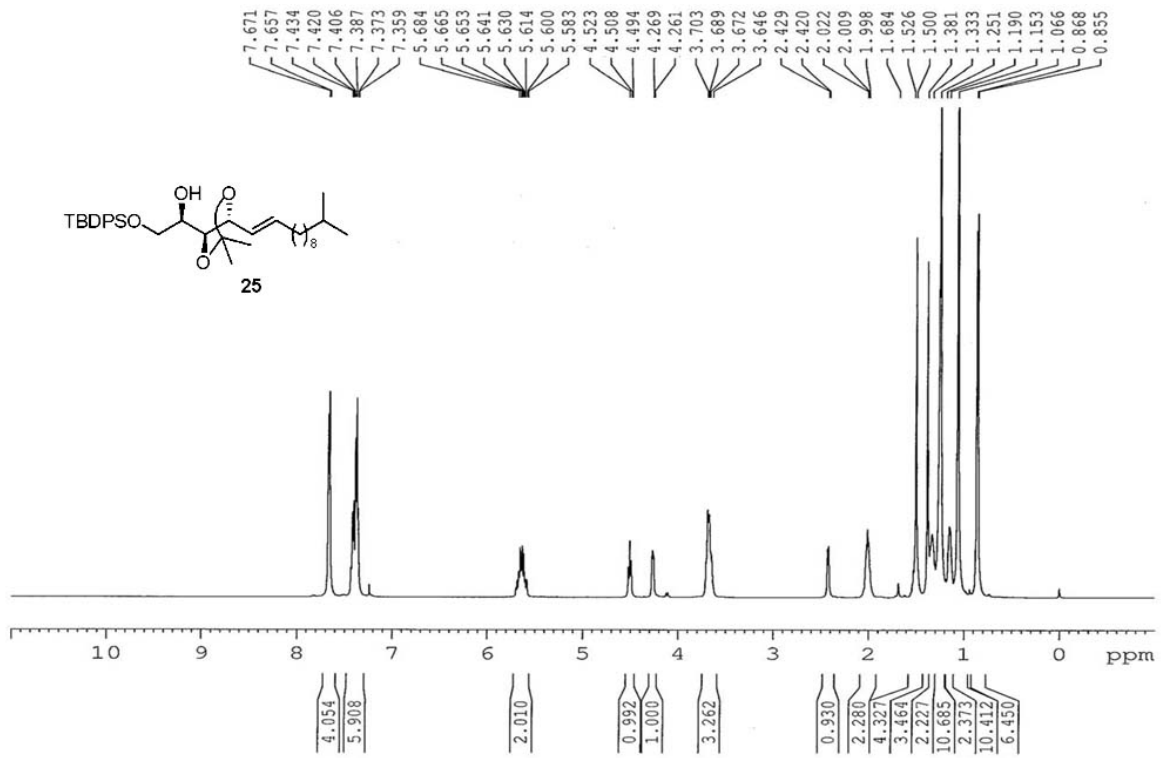
134.452
133.347
129.957
129.921
127.902
127.864
119.530
108.805
79.242
77.669
77.321
77.160
76.652
70.066
64.962
27.381
26.992
25.123
19.390
OH
TBDPSO
O
O
24
ppm
175
150
125
100
75
50
25
0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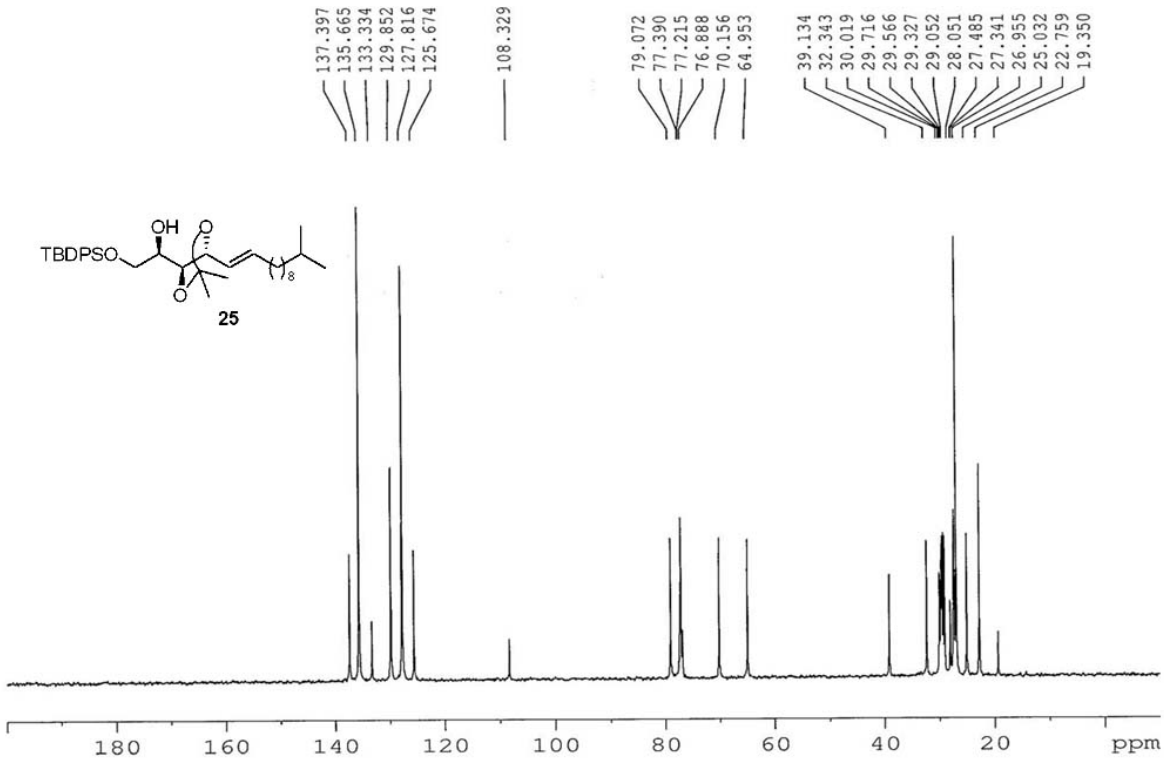
7.657
7.434
7.420
7.406
7.387
7.373
7.359
5.684
5.665
5.653
5.641
5.630
5.614
5.600
5.583
4.523
4.508
4.494
4.269
4.261
3.703
3.689
3.672
3.646
2.429
2.420
2.022
2.009
1.998
1.684
1.526
1.500
1.381
1.333
1.251
1.190
1.153
1.066
0.868
0.855
OH
O
TBDPSO
O
8
25
10
9
8
7
6
5
4
3
2
1
0
ppm
4.054
5.908
2.010
0.992
1.000
3.262
0.930
2.280
4.327
3.464
2.227
10.685
2.373
10.412
6.450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133.334
129.852
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125.674
108.329
79.072
77.390
77.215
76.888
70.156
64.953
39.134
32.343
30.019
29.716
29.566
29.327
29.052
28.051
27.485
27.341
26.955
25.032
22.759
19.350
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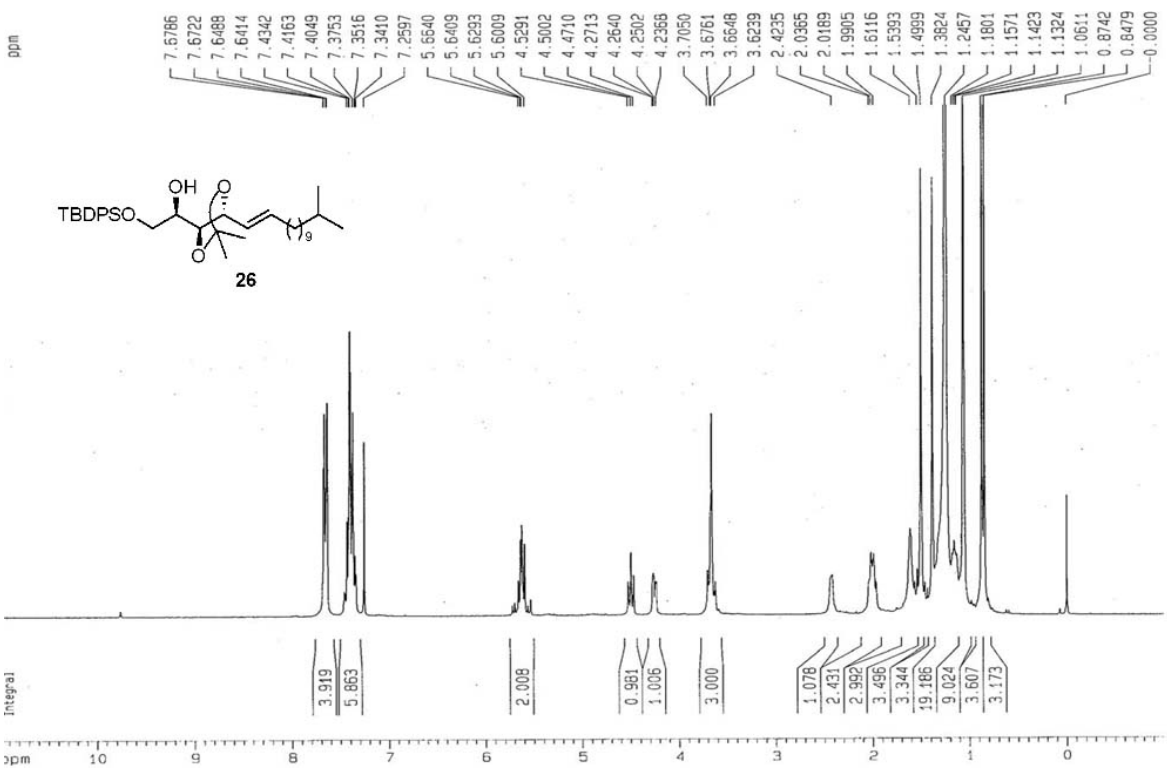
O
TBDPSO
O
8
25
180
160
140
120
100
80
60
40
20
ppm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7.4342
7.4163
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7.3753
7.3516
7.3410
7.2597
5.6640
5.6409
5.6293
5.6009
4.5291
4.5002
4.4710
4.2713
4.2640
4.2502
4.2368
3.7050
3.6761
3.6648
3.6239
2.4235
2.0365
2.0189
1.9905
1.6116
1.5393
1.4999
1.3824
1.2457
1.1801
1.1571
1.1423
1.1324
1.0611
0.8742
0.8479
0.0000
OH
O
TBDPSO
O
9
26
Integral
3.919
5.863
2.008
0.981
1.006
3.000
1.078
2.431
2.992
3.496
3.344
19.186
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3.607
3.173
ppm
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9
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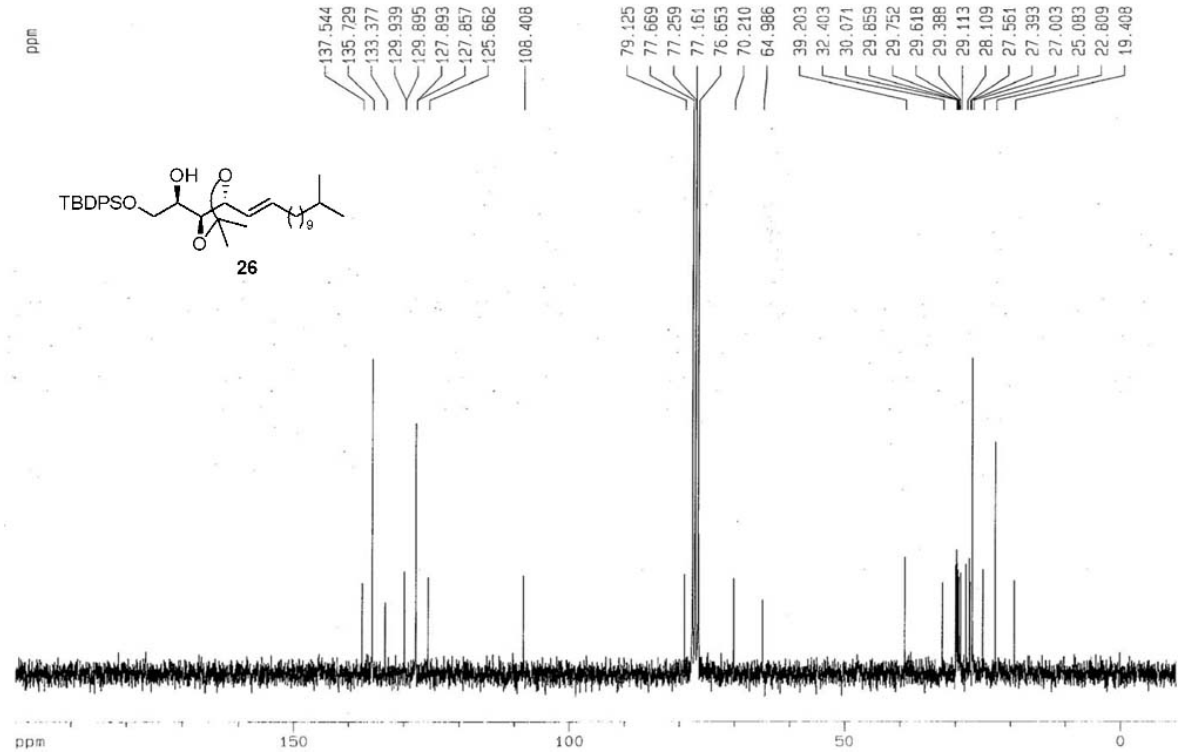
7
6
5
4
3
2
1
0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129.939
129.895
127.893
127.857
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108.408
79.125
77.669
77.259
77.161
76.653
70.210
64.986
39.203
32.403
30.071
29.859
29.752
29.618
29.388
29.113
28.109
27.561
27.393
27.003
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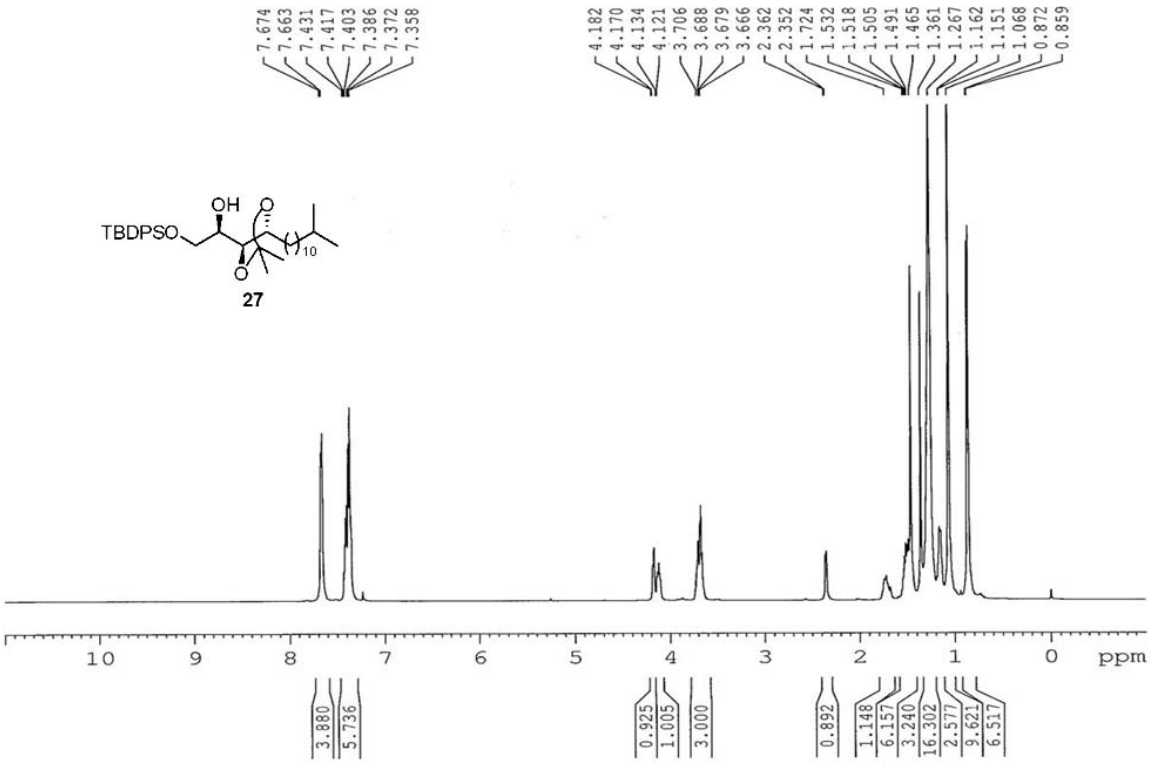
22.809
19.408
OH
O
TBDPSO
O
9
26
ppm
150
100
50
0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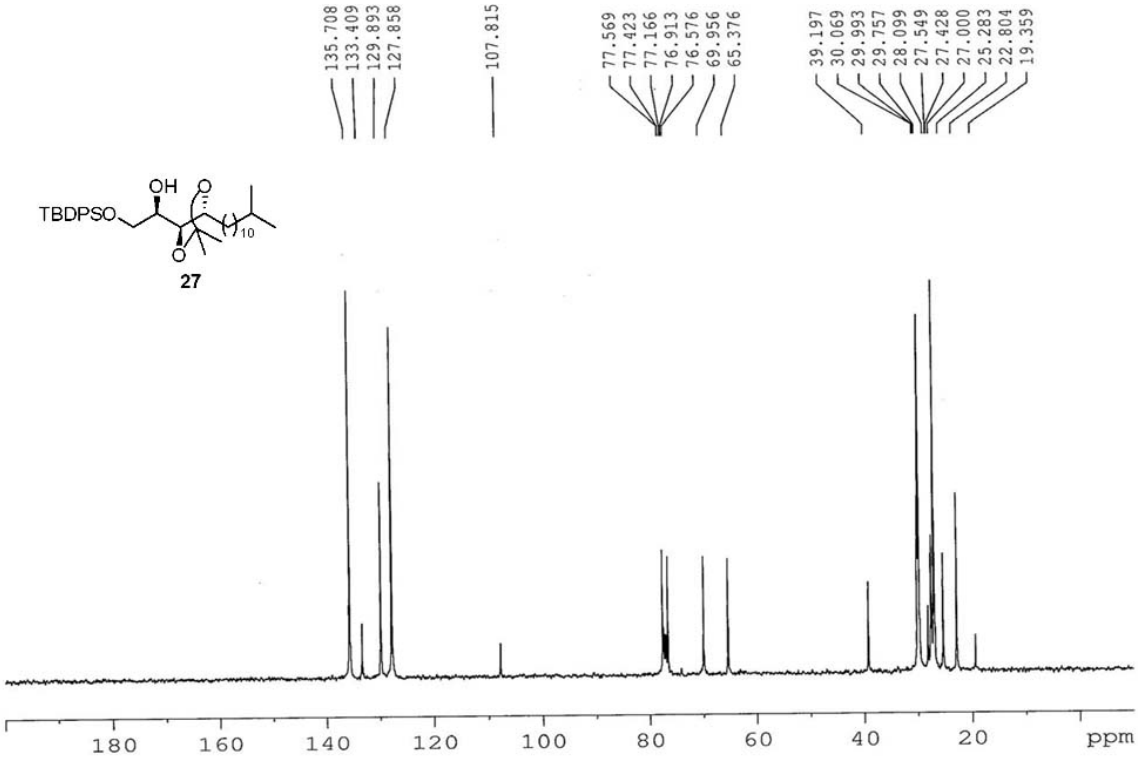
7.417
7.403
7.386
7.372
7.358
4.182
4.170
4.134
4.121
3.706
3.688
3.679
3.666
2.362
2.352
1.724
1.532
1.518
1.505
1.491
1.465
1.361
1.267
1.162
1.151
1.068
0.872
0.859
OH
O
TBDPSO
10
O
27
10
9
8
7
6
5
4
3
2
1
0
ppm
3.880
5.736
0.925
1.005
3.000
0.892
1.148
6.157
3.240
16.302
2.577
9.621
6.517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77.423
77.166
76.913
76.576
69.956
65.376
39.197
30.069
29.993
29.757
28.099
27.549
27.428
27.000
25.283
22.804
19.359
OH
O
TBDPSO
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O
27
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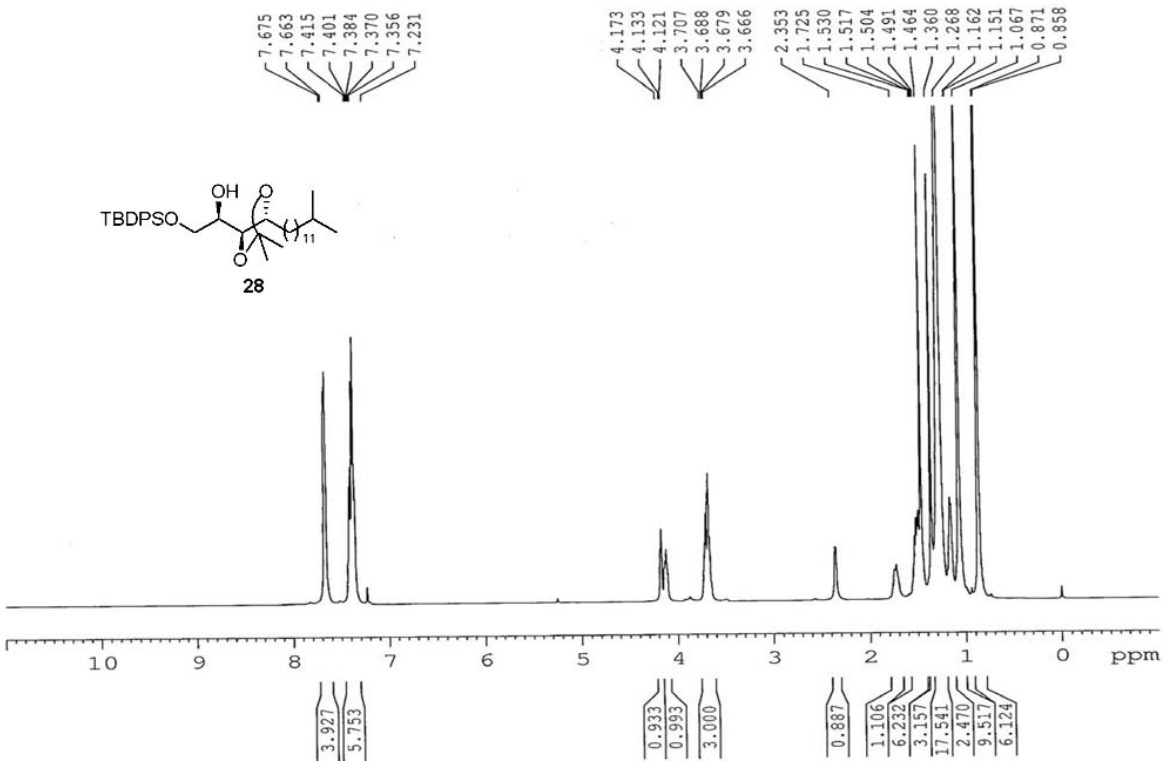
140
120
100
80
60
40
20
ppm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7.415
7.401
7.384
7.370
7.356
7.231
4.173
4.133
4.121
3.707
3.688
3.679
3.666
2.353
1.725
1.530
1.517
1.504
1.491
1.464
1.360
1.268
1.162
1.151
1.067
0.871
0.858
OH
O
TBDPSO
11
O
28
10
9
8
7
6
5
4
3
2
1
0
ppm
3.927
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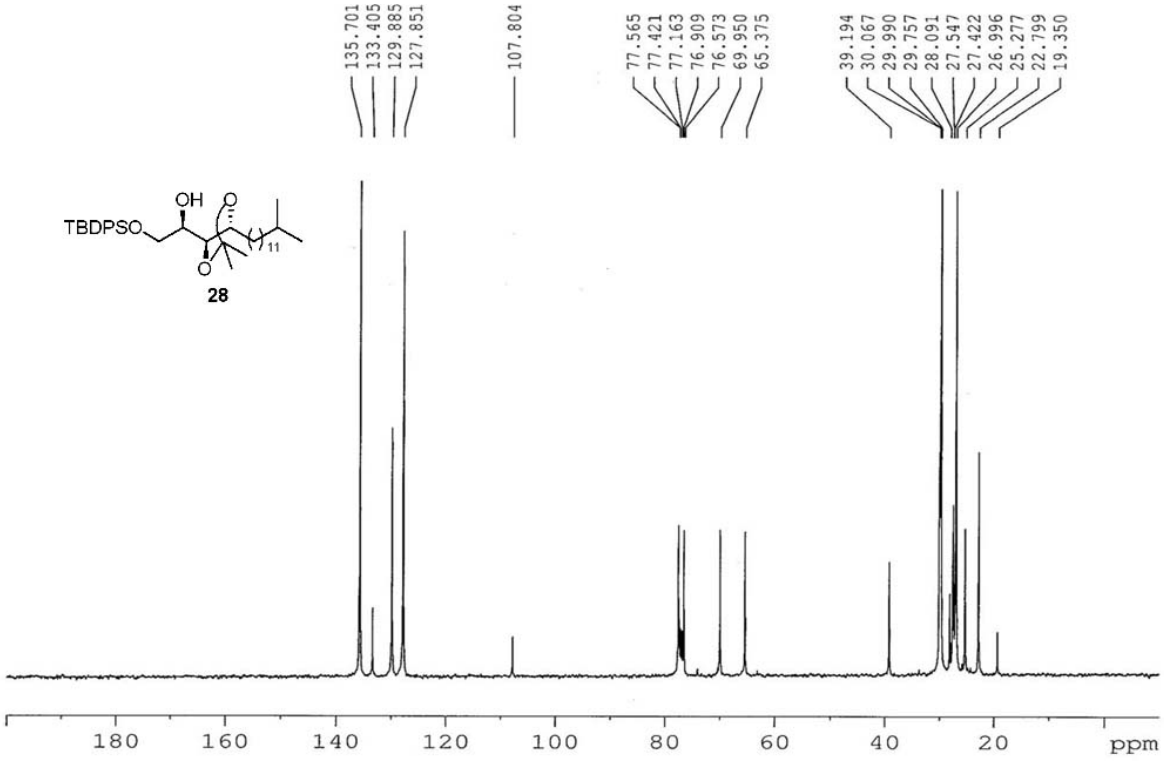
3.000
0.887
1.106
6.232
3.157
17.541
2.470
9.517
6.124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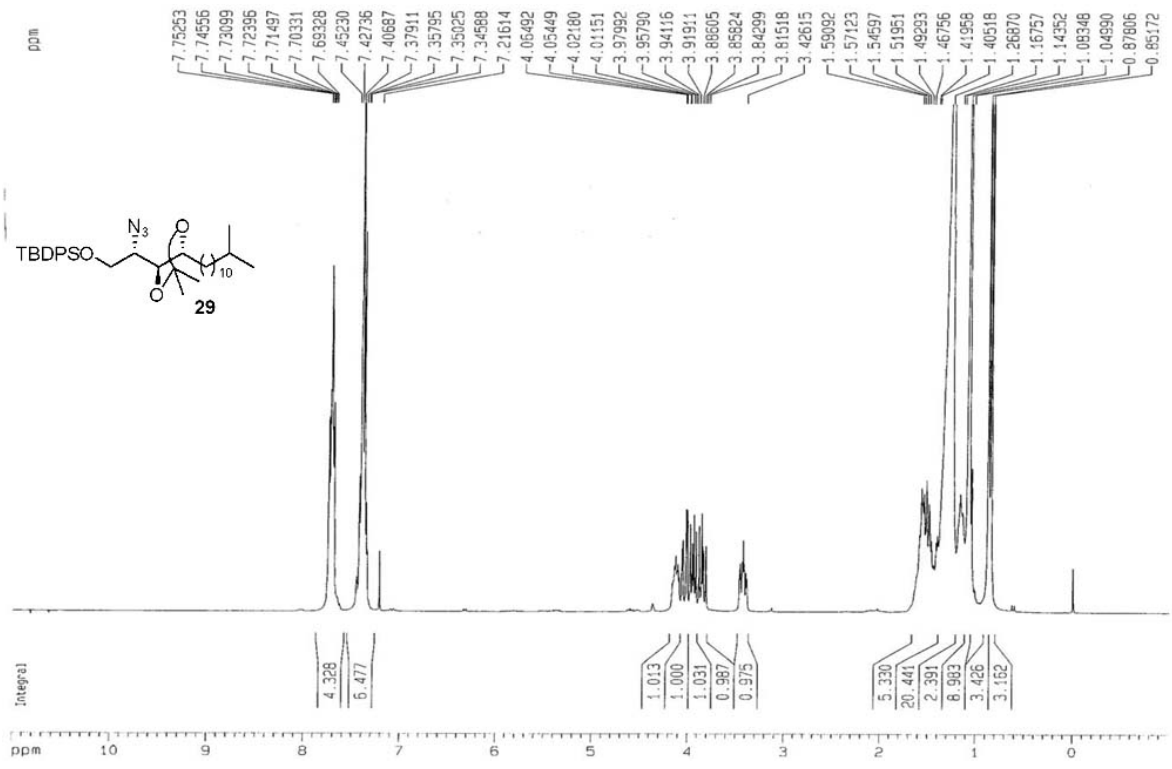
77.163
76.909
76.573
69.950
65.375
39.194
30.067
29.990
29.757
28.091
27.547
27.422
26.996
25.277
22.799
19.350
OH
O
TBDPSO
11
O
28
180
160
140
120
100
80
60
40
20
ppm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7.69328
7.45230
7.42736
7.40687
7.37911
7.35795
7.35025
7.34588
7.21614
4.06492
4.05449
4.02180
4.01151
3.97992
3.95790
3.94416
3.91911
3.88605
3.85824
3.84299
3.81518
3.42615
1.59092
1.57123
1.54597
1.51951
1.49293
1.46756
1.41958
1.40518
1.26870
1.16757
1.14352
1.08348
1.04990
0.87806
0.85172
TBDPSO
N3
O
O
10
29
Integral
4.328
6.477
1.013
1.000
1.031
0.987
0.975
5.330
20.441
2.391
8.983
3.426
3.162
ppm
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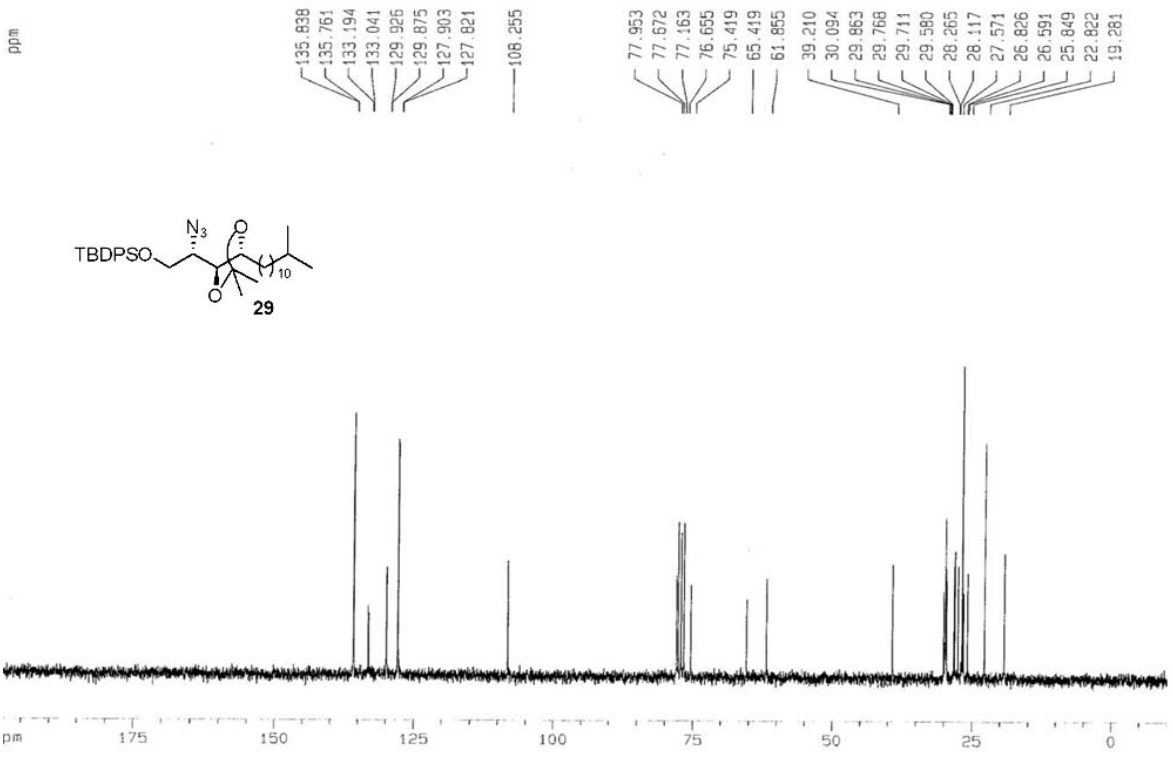
9
8
7
6
5
4
3
2
1
0


ppm
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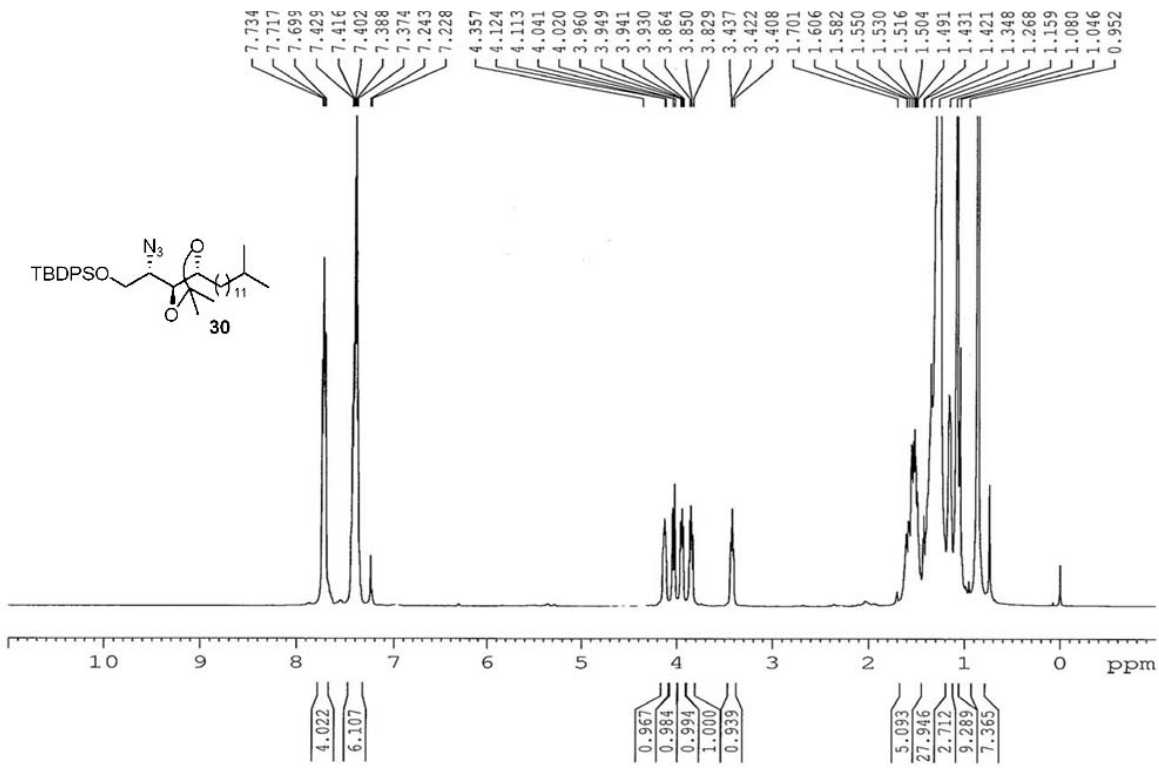
129.875
127.903
127.821
108.255
77.953
77.672
77.163
76.655
75.419
65.419
61.855
39.210
30.094
29.863
29.768
29.711
29.580
28.265
28.117
27.571
26.826
26.591
25.849
22.822
19.281
TBDPSO
N3
O
O
10
29
ppm
175
150
125
100
75
50
25
0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7.699
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7.416
7.402
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7.374
7.243
7.228
4.357
4.124
4.113
4.041
4.020
3.960
3.949
3.941
3.930
3.864
3.850
3.829
3.437
3.422
3.408
1.701
1.606
1.582
1.550
1.530
1.516
1.504
1.491
1.431
1.421
1.348
1.268
1.159
1.080
1.046
0.952
TBDPSO
N3
O
O
11
30
10
9
8
7
6
5
4
3
2
1
0
ppm
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0.994
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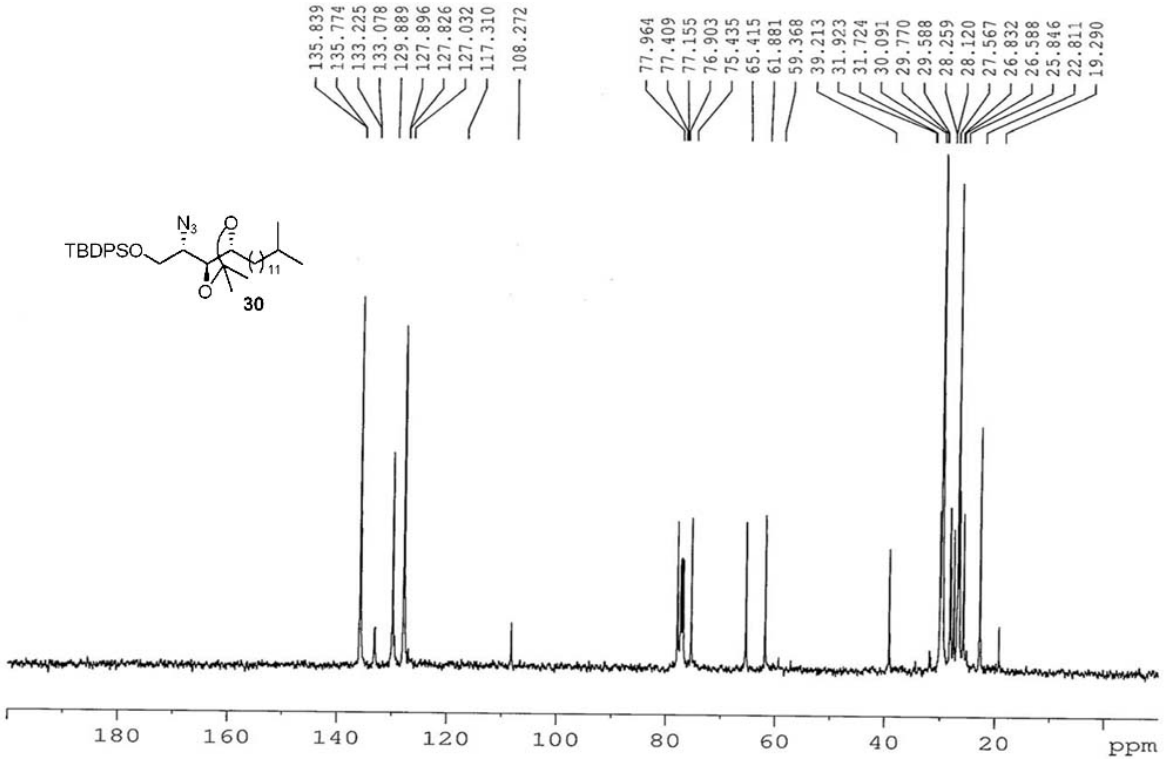
2.712
9.289
7.365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133.078
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127.896
127.826
127.032
117.310
108.272
77.964
77.409
77.155
76.903
75.435
65.415
61.881
59.368
39.213
31.923
31.724
30.091
29.770
29.588
28.259
28.120
27.567
26.832
26.588
25.846
22.811
19.290
TBDPSO
N3
O
O
11
30
180
160
140
120
100
80
60
40
20
ppm