Supporting Information

Intramolecular Hydrogen Abstraction Reaction Promoted by Alkoxy Radicals in Carbohydrates. Synthesis of Chiral 2,7- Dioxabicyclo[2.2.1]heptane and 6,8-Dioxabicyclo[3.2.1]octane Ring Systems

Cosme G. Francisco, Antonio J. Herrera, and Ernesto Suárez*

Instituto de Productos Naturales y Agrobiología del C.S.I.C., Carretera de La Esperanza
3, 38206 La Laguna, Tenerife, Spain

Contents: Detailed experimental procedures, and spectral and analytical data for
compounds **2-9**, **12-17**, and **19-25**.

Methyl 3,6-Anhydro-7-*O*-[*tert*-butyl(diphenyl)silyl]-2-deoxy-4,5-*O*-isopropylidene-D-*altro*-heptonate (2). To a solution of compound **1**¹ (975 mg, 2.27 mmol) in MeCN (20 mL) was added methyl (triphenylphosphoranylidene)acetate (1.52 g, 4.55 mmol). After stirring under nitrogen at reflux temperature overnight, the mixture was poured into an aqueous solution of hydrochloric acid (5%) and extracted with EtOAc. The organic layer was washed with water, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 9:1) of the residue afforded compound **2** (912 mg, 1.88 mmol, 83%) as an isomeric mixture (β/α , 1:5.5). Compound **2- α** : $[\alpha]_D^{+2.5}$ ($c = 0.748$); IR 3062, 3036, 2933, 2859, 1745, 1428, 1113 cm⁻¹; ¹H NMR 1.06 (9H, s), 1.34 (3H, s), 1.54 (3H, s), 2.63 (1H, dd, $J = 16.0, 7.7$ Hz), 2.68 (1H, dd, $J = 15.8, 5.4$ Hz), 3.68 (3H, s), 3.74 (1H, dd, $J = 11.1, 3.9$ Hz), 3.77 (1H, dd, $J = 11.1, 3.9$

Hz), 4.09 (1H, dd, $J = 7.7, 4.1$ Hz), 4.32 (1H, dd, $J = 12.4, 5.2$ Hz), 4.46 (1H, dd, $J = 5.9, 5.9$ Hz), 4.75 (1H, dd, $J = 6.5, 3.3$ Hz), 7.37 (4H, dd, $J = 7.2, 7.2$ Hz), 7.41 (2H, dd, $J = 7.2, 7.2$ Hz), 7.68 (4H, dd, $J = 6.2, 6.2$ Hz); ^{13}C NMR 19.2 (C), 25.5 (CH_3), 26.8 ($3 \times \text{CH}_3$), 27.4 (CH_3), 38.5 (CH_2), 51.7 (CH_3), 64.1 (CH_2), 80.9 (CH), 81.8 (CH), 84.4 (CH), 84.5 (CH), 114.0 (C), 127.6 ($4 \times \text{CH}$), 129.6 (CH), 129.7 (CH), 133.0 (C), 133.1 (C), 135.6 ($4 \times \text{CH}$), 170.9 (C); MS (EI) m/z (rel intensity) 469 ($\text{M}^+ - \text{Me}$, 3), 453 (6), 427 (100); HRMS calcd for $\text{C}_{26}\text{H}_{33}\text{O}_6\text{Si}$ 469.204625, found 469.207779. Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{O}_6\text{Si}$: C, 66.91; H, 7.49. Found: C, 66.56; H, 7.83. Compound **2- β** : $[\alpha]_{\text{D}} +1.2$ ($c = 1.06$); IR 3062, 3036, 2933, 2859, 1739, 1428, 1113 cm^{-1} ; ^1H NMR 1.05 (9H, s), 1.33 (3H, s), 1.47 (3H, s), 2.69 (1H, dd, $J = 16.3, 7.0$ Hz), 2.75 (1H, dd, $J = 16.5, 6.7$ Hz), 3.66 (1H, dd, $J = 11.1, 3.9$ Hz), 3.69 (3H,), 3.75 (1H, dd, $J = 11.1, 3.9$ Hz), 4.1 (1H, dd, $J = 3.9, 3.9$ Hz), 4.58 (1H, ddd, $J = 6.8, 6.8, 4.0$ Hz), 4.79 (1H, dd, $J = 6.2, 4.1$ Hz), 4.85 (1H, d, $J = 6.2$ Hz), 7.39 (6H, m), 7.65 (4H, dd, $J = 6.7, 6.7$ Hz); ^{13}C NMR 19.0 (C), 24.9 (CH_3), 26.1 (CH_3), 26.7 ($3 \times \text{CH}_3$), 34.7 (CH_2), 51.6 (CH_3), 65.2 (CH_2), 78.3 (CH), 81.7 (CH), 83.1 (CH), 84.1 (CH), 112.3 (C), 127.7 ($4 \times \text{CH}$), 129.7 (CH), 129.8 (CH), 132.7 (C), 132.8 (C), 135.5 ($4 \times \text{CH}$), 171.5 (C); MS (EI) m/z (rel intensity) 469 ($\text{M}^+ - \text{Me}$, 3), 453 (6), 427 (100); HRMS calcd for $\text{C}_{26}\text{H}_{33}\text{O}_6\text{Si}$ 469.204625, found 469.207779. Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{O}_6\text{Si}$: C, 66.91; H, 7.49. Found: C, 66.70; H, 7.86.

Methyl 3,6-Anhydro-2-deoxy-4,5-*O*-isopropylidene-D-*altro*-heptonate (3). To a solution of compound **2** (229 mg, 0.47 mmol) in dry THF (5 mL) was added under nitrogen Bu_4NF in THF (0.57 mL, 0.57 mmol, 1M). The mixture was stirred at room temperature for 2h, poured into an aqueous saturated solution of NaHCO_3 and extracted with CHCl_3 . The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 6:4) gave compound **3** (104 mg, 0.42 mmol, 89%) as a colorless oil: $[\alpha]_{\text{D}} +8$ ($c = 0.376$); IR 3478, 2989, 2952, 1732, 1383,

1210 cm^{-1} ; ^1H NMR 1.27 (3H, s), 1.42 (3H, s), 2.67 (1H, dd, $J = 16.8, 7.0$ Hz), 2.71 (1H, dd, $J = 16.8, 6.5$ Hz), 3.56 (2H, d, $J = 5.7$ Hz), 3.65 (3H, s), 4.06 (1H, dd, $J = 5.4, 5.4$ Hz), 4.34 (1H, ddd, $J = 6.3, 6.3, 4.5$ Hz), 4.63 (1H, d, $J = 6.2$ Hz), 4.71 (1H, dd, $J = 4.4, 5.9$ Hz); ^{13}C NMR 24.8 (CH_3), 26.1 (CH_3), 34.3 (CH_2), 51.7 (CH_3), 61.9 (CH_2), 76.9 (CH), 81.3 (CH), 82.4 (CH), 84.2 (CH), 112.6 (C), 171.8 (C); MS (EI) m/z (rel intensity) 231 ($\text{M}^+ - \text{Me}$, 100), 215 (32), 157 (19), 141 (82); HRMS calcd for $\text{C}_{10}\text{H}_{15}\text{O}_6$ 231.086854, found 231.086655. Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_6$: C, 53.65; H, 7.37. Found: C, 53.61; H, 7.57.

3,6-Anhydro-2-deoxy-4,5-*O*-isopropylidene-D-*altro*-heptitol (4). A suspension of LiAlH_4 (149 mg, 3.93 mmol) in dry THF (4 mL) was stirred at room temperature as a solution of compound **3** (242 mg, 0.984 mmol) in THF (2 mL) was added. The reaction mixture was kept at this temperature for 1 h. The excess hydride was destroyed by adding a saturated aqueous solution of Na_2SO_4 , and the white salts were separated by filtration. Concentration under reduced pressure gave compound **4** (210 mg, 0.96 mmol, 98%) as a colorless oil: $[\alpha]_{\text{D}} +19$ ($c = 0.17$); IR 3383, 2938, 1650, 1381, 1210 cm^{-1} ; ^1H NMR 1.34 (3H, s), 1.5 (3H, s), 1.91 (1H, m), 2.0 (1H, m), 3.61 (2H, d, $J = 5.4$ Hz), 3.81 (2H, dd, $J = 5.5, 5.5$ Hz), 4.15 (2H, m), 4.64 (1H, d, $J = 6.1$ Hz), 4.68 (1H, dd, $J = 4.9, 4.9$ Hz); ^{13}C NMR 24.9 (CH_3), 26.2 (CH_3), 31.7 (CH_2), 60.1 (CH_2), 61.8 (CH_2), 78.9 (CH), 82.0 (CH), 82.3 (CH), 84.4 (CH), 112.5 (C); MS (EI) m/z (rel intensity) 203 ($\text{M}^+ - \text{Me}$, 90), 187 (9), 142 (15); HRMS calcd for $\text{C}_9\text{H}_{15}\text{O}_5$ 203.091939, found 203.089931. Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_5$: C, 55.03; H, 8.31. Found: C, 54.97; H, 8.50.

2,5-Anhydro-6-*O*-[*tert*-butyl(diphenyl)silyl]-3,4-*O*-isopropyliden-D-*altritol* (5). To a suspension of NaH (50 mg, 2.15 mmol) in dry DMSO (5 mL) was added, under nitrogen, trimethylsulfoxonium iodide (461 mg, 1.07 mmol). The mixture was stirred at room temperature for 30 min and the sugar **1** (461 mg, 1.08 mmol) in DMSO (3 mL)

was added. After 2 h at this temperature the solution was poured into water and extracted with EtOAc. The organic extracts were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexanes–EtOAc, 8:2) to give compound **5** (110 mg, 0.25 mmol, 23%) as a colorless oil: $[\alpha]_D -6.4$ ($c = 0.344$); IR (CHCl₃) 3500, 3088, 3063, 3031, 2869, 1766, 1455 cm⁻¹; ¹H NMR 1.06 (9H, s), 1.33 (3H, s), 1.49 (3H, s), 3.69 (1H, dd, $J = 3.7, 11.1$ Hz), 3.77 (1H, dd, $J = 4.1, 11.1$ Hz), 3.87 (2H, m), 4.18 (1H, t, $J = 3.8$ Hz), 4.24 (1H, dd, $J = 5.5, 9.8$ Hz), 4.81 (1H, dd, $J = 4.3, 6.4$ Hz), 4.85 (1H, d, $J = 6.2$ Hz), 7.38 (6H, m), 7.65 (4H, m); ¹³C NMR 19.0 (C), 24.6 (CH₃), 26.1 (CH₃), 26.8 (3 × CH₃), 61.8 (CH₂), 65.2 (CH₂), 81.9 (2 × CH), 83.2 (CH), 84.2 (CH), 112.6 (C), 127.5 (2 × CH), 127.8 (2 × CH), 129.8 (CH), 129.9 (CH), 132.8 (2 × C), 135.5 (2 × CH), 135.5 (2 × CH); MS (EI) m/z (rel intensity) 427 ($M^+ - \text{Me}$, 3), 385 (100); HRMS calcd for C₂₄H₃₁O₅Si 427.194062, found 427.192650. Anal. Calcd for C₂₅H₃₄O₅Si: C, 67.84; H, 7.74. Found: C, 67.90; H, 7.75.

2,5-Anhydro-3,4-O-isopropyliden-D-altritol (6). To a solution of compound **5** (99 mg, 0.224 mmol) in dry THF (2 mL), was added under argon Bu₄NF in THF (0.27 mL, 0.27 mmol, 1M). Workup as described for compound **3** and column chromatography (CH₂Cl₂–MeOH, 95:5) gave compound **6** (45 mg, 0.20 mmol, 94%) as a colorless oil: $[\alpha]_D -7.4$ ($c = 1.8$, EtOH); IR 3418, 2939, 1382, 1211 cm⁻¹; ¹H NMR 1.30 (3H, s), 1.47 (3H, s), 3.58 (1H, dd, $J = 6.7, 11.8$ Hz), 3.62 (1H, dd, $J = 4.2, 11.8$ Hz), 3.80 (2H, d, $J = 5.2$ Hz), 4.10 (1H, dd, $J = 5.1, 10.0$ Hz), 4.16 (1H, dd, $J = 5.1, 6.6$ Hz), 4.63 (1H, d, $J = 6.2$ Hz), 4.75 (1H, dd, $J = 4.4, 6.2$ Hz); ¹³C NMR 24.6 (CH₃), 26.1 (CH₃), 61.5 (CH₂), 61.9 (CH₂), 80.7 (CH), 81.3 (CH), 82.4 (CH), 84.3 (CH), 112.9 (C); MS (EI) m/z (rel intensity) 203 ($M^+ - \text{H}$, 3), 189 (100), 173 (12); HRMS calcd for C₉H₁₅O₅ 203.091939, found 203.092815. Anal. Calcd for C₉H₁₆O₅: C, 52.93; H, 7.90. Found: C, 52.73; H, 8.23.

4,7-Anhydro-8-*O*-[*tert*-butyl(diphenyl)silyl]-1,2,3-trideoxy-D-*altro*-oct-1-enitol (7).

To a solution of 4,7-anhydro-1,2,3-trideoxy-D-*altro*-oct-1-enitol² (514 mg, 2.95 mmol) and imidazol (361 mg, 5.31 mmol) in dry DMF (15 ml), was added *tert*-butyldiphenylsilyl chloride (892 mg, 3.25 mmol). The mixture was stirred at rt for 30 min, poured into ice–water and extracted with EtOAc. The organic layer was dried (Na₂SO₄) and concentrated in vacuo. Column chromatography of the residue (hexanes–EtOAc, 60:40) gave compound **7** (1.03 g, 2.5 mmol, 84.7%): colorless oil; [α]_D +23.8 (*c* = 0.79); IR 3389, 3072, 2931, 2858, 1643, 1428, 1113, 998 cm⁻¹; ¹H NMR 1.06 (9H, s), 2.46 (2H, dd, *J* = 7.0, 7.0 Hz), 2.88 (1H, d, *J* = 4.2 Hz), 2.89 (1H, d, *J* = 6.9 Hz), 3.83 (2H, m), 3.90 (1H, ddd, *J* = 7.4, 3.8, 3.8 Hz), 4.05 (1H, dd, *J* = 7.1, 3.0 Hz), 4.08 (1H, dd, *J* = 6.8, 4.2 Hz), 4.42 (1H, ddd, *J* = 6.9, 6.9, 4.7 Hz), 5.09 (1H, dd, *J* = 10.2, 2.1 Hz), 5.18 (1H, dd, *J* = 17.2, 3.4 Hz), 5.87 (1H, dddd, *J* = 17.4, 10.2, 7.2, 7.2 Hz), 7.37–7.40 (6H, m), 7.67–7.71 (4H, m); ¹³C NMR 19.2 (C), 26.8 (3 × CH₃), 33.9 (CH₂), 64.4 (CH₂), 72.7 (CH), 73.8 (CH), 80.6 (CH), 81.8 (CH), 117 (CH₂), 127.6 (4 × CH), 129.7 (2 × CH), 133.1 (2 × C), 134.5 (CH), 135.5 (4 × CH); MS *m/z* (rel- intensity) 355 (M⁺ – C₄H₉, 8); HRMS calcd for C₂₀H₂₃O₄Si 355.1365512, found 355.13723. Anal. Calcd for C₂₄H₃₂O₄Si: C, 69.86; H, 7.82. Encontrado: C, 69.94; H, 7.78.

4,7-Anhydro-8-*O*-[*tert*-butyl(diphenyl)silyl]-1,2,3-trideoxy-5,6-*O*-(oxomethylene)-D-

***altro*-oct-1-enitol (8).** A solution of triphosgene (172 mg, 0.582 mmol) in CH₂Cl₂ (1.5 mL) was added dropwise to a solution of pyridine (550 mg, 7.0 mmol) and compound **7** (240 mg, 0.582 mmol) in CH₂Cl₂ (2 mL) cooled to –70 °C. Once addition was complete the reaction was allowed to warm to room temperature. The resultant homogenous solution was quenched with saturated aqueous ammonium chloride and the aqueous portion was separated and extracted with CH₂Cl₂. The organic extract was washed with 1N HCl, saturated aqueous NaHCO₃, brine, dried (Na₂SO₄), filtered and concentrated in

vacuo. Column chromatography of the residue (hexanes–EtOAc, 8:2) afforded compound **8** (246 mg, 0.56 mmol, 96%) as a colorless oil: $[\alpha]_D -3.9$ ($c = 0.772$); IR 3069, 2932, 1799, 1081 cm^{-1} ; ^1H NMR 1.06 (9H, s), 2.48 (2H, m), 3.78 (1H, dd, $J = 3.6, 11.3$ Hz), 3.86 (1H, dd, $J = 3.6, 11.3$ Hz), 4.31 (1H, d, $J = 3.6$ Hz), 4.38 (1H, ddd, $J = 3.9, 7.0, 7.0$ Hz), 5.08 (1H, dd, $J = 3.9, 6.9$ Hz), 5.16 (1H, d, $J = 10.2$ Hz), 5.22 (1H, d, $J = 15.7$ Hz), 5.27 (1H, d, $J = 6.9$ Hz), 5.83 (1H, m), 7.41 (4H, m), 7.47 (2H, m), 7.62 (4H, m); ^{13}C NMR (50.4 MHz) 19.0 (C), 26.8 ($3 \times \text{CH}_3$), 33.2 (CH_2), 65.1 (CH_2), 81.5 (CH), 81.7 (CH), 82.3 (CH), 83.4 (CH), 118.2 (CH_2), 127.9 ($2 \times \text{CH}$), 130.1 ($2 \times \text{CH}$), 130.2 ($2 \times \text{CH}$), 132.1 ($2 \times \text{C}$), 132.9 (CH), 135.4 ($4 \times \text{CH}$), 153.4 (C); MS (EI), m/z (rel intensity) 381 ($\text{M}^+ - \text{C}_4\text{H}_9$, 71); HRMS calcd for $\text{C}_{21}\text{H}_{21}\text{O}_5\text{Si}$ 381.1158161, found 381.117538. Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{O}_5\text{Si}$: C, 68.46; H, 6.89. Found: C, 68.13; H, 6.86.

4,7-Anhydro-1,2,3-trideoxy-5,6-*O*-(oxomethylene)-D-*altro*-oct-1-enitol (9). To a solution of compound **8** (205 mg, 0.467 mmol) in dry THF (7 mL) was added under argon Bu_4NF in THF (0.56 mL, 0.56 mmol, 1M). Workup as described for compound **3** and column chromatography (hexanes–EtOAc, 6:4) gave compound **9** (80 mg, 0.4 mmol, 86%) as a crystalline solid: mp 84 °C (from *n*-hexane–EtOAc); $[\alpha]_D -43$ ($c = 0.63$); IR 3444, 2948, 1790, 1080 cm^{-1} ; ^1H NMR 2.47 (2H, m), 3.79 (2H, d, $J = 4.4$ Hz), 4.24 (1H, ddd, $J = 3.8, 3.8, 7.0$ Hz), 4.33 (1H, t, $J = 4.4$ Hz), 5.09 (1H, dd, $J = 3.84, 6.9$ Hz), 5.14 (1H, dd, $J = 1.2, 10.2$ Hz), 5.21 (1H, d, $J = 6.8$ Hz), 5.22 (1H, dd, $J = 1.5, 17.1$ Hz), 5.82 (1H, m); ^{13}C NMR 32.4 (CH_2), 62.2 (CH_2), 80.4 (CH), 80.8 (CH), 81.3 (CH), 82.5 (CH), 117.6 (CH_2), 131.9 (CH), 153.6 (C); MS (EI), m/z (rel intensity) 200 (M^+ , <1), 159 (100); HRMS calcd for $\text{C}_9\text{H}_{12}\text{O}_5$ 200.0684657, found 200.076763. Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_5$: C, 54.00; H, 6.04. Found: C, 54.37; H, 5.74.

(7Z)- and (7E)-1,3,4,5-Tetra-*O*-acetyl-2,6-anhydro-7,8,9-trideoxy-D-*glycero*-L-*galacto*-non-7-enitol (12). A solution of 1,3,4,5-tetra-*O*-acetyl-2,6-anhydro-7,8,9-

trideoxy-D-*glycero*-L-*galacto*-non-8-enitol³ (2.41 g, 6.48 mmol) in dry benzene (60 mL) containing a catalytic amount of bis(benzonitrile)dichloropalladium(II) (240 mg, 10 mol %) was refluxed under nitrogen for 24 h. The reaction mixture was then filtered and concentrated in vacuo. Purification of the residue by chromatography (hexanes–EtOAc, 7:3) on silver nitrate impregnated silica gel gave the olefin **12** as an isomeric mixture (1.76 g, 4.73 mmol, 73%, *Z/E*, 1:4): oil; IR 2969, 1754, 1667, 1434, 1372, 1224, 1048 cm⁻¹; ¹H NMR (major isomer *E*) 1.98 (3H, s), 2.01 (6H, s), 2.11 (3H, s), 2.74 (3H, d, *J* = 6.6 Hz), 4.06 (2H, dd, *J* = 11.6, 5.0), 4.13 (1H, ddd, *J* = 6.5, 6.5, 1.3 Hz), 4.70 (1H, dd, *J* = 6.0, 6.0 Hz), 5.13 (1H, dd, *J* = 10.5, 3.4 Hz), 5.24 (1H, dd, *J* = 10.5, 5.9 Hz), 5.37 (1H, brs), 5.60 (1H, ddd, *J* = 15.5, 4.4, 1.6 Hz), 5.85 (1H, m); ¹³C NMR (major isomer *E*) 18.2 (CH₃), 20.7 (3 × CH₃), 20.8 (CH₃), 61.8 (CH₂), 67.8 (CH), 68.1 (2 × CH), 68.3 (CH), 73.9 (CH), 122.5 (CH), 133.2 (CH), 169.9 (C), 170.1 (C), 170.2 (C), 170.4 (C); MS (EI) *m/z* (rel intensity) 373 (M⁺ + H, <1), 329 (2), 313 (<1), 270 (5); HRMS calcd for C₁₇H₂₅O₉ 373.149842, found 373.149475. Anal. Calcd for C₁₇H₂₄O₉: C, 54.83; H, 6.50. Found: C, 54.91; H, 6.67.

(7Z)- and (7E)-2,6-Anhydro-7,8,9-trideoxy-1,3,4,5-tetra-O-methyl-D-glycero-L-galacto-non-7-enitol (13). A solution of the mixture of olefins **12** (1.6 g, 4.3 mmol) in MeOH (50 mL) containing KOH (1.5 g, 26.8 mmol) was stirred at room temperature for 1h. The reaction mixture was then neutralized with Dowex 50X8 acid resin, filtered and concentrated in vacuo to give an oil which was used in the following reaction without purification. To a suspension of NaH (825 mg, 34.4 mmol) in dry DMF (50 mL) was added the crude tetrol previously obtained in DMF (50 mL) and the mixture stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (2.06 mL, 33.1 mmol) was added dropwise and stirring continued at room temperature for 3 h. Excess reagent was destroyed by slow addition of MeOH and the

solution poured into water and extracted with EtOAc. The organic extracts were dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 8:2) of the residue afforded **13** (852 mg, 3.27 mmol, 76%) as an oil: IR 2979, 2914, 2826, 1449, 1364, 1196, 1107 cm⁻¹; ¹H NMR (major isomer *E*) 1.71 (3H, d, *J* = 6.4 Hz), 3.31 (1H, dd, *J* = 8.0, 2.5 Hz), 3.34 (3H, s), 3.40 (3H, s), 3.47 (3H, s), 3.48 (2H, m), 3.50 (3H, s), 3.65 (1H, brs), 3.66 (1H, m), 3.84 (1H, dd, *J* = 6.2, 6.2 Hz), 4.53 (1H, dd, *J* = 5.5, 5.5 Hz), 5.62 (1H, dd, *J* = 14.4, 5.7 Hz), 5.82 (1H, dq, *J* = 14.4, 5.7 Hz); ¹³C NMR (major isomer *E*) 18.1 (CH₃), 57.9 (CH₃), 58.3 (CH₃), 59.0 (CH₃), 60.5 (CH₃), 70.8 (CH), 70.9 (CH₂), 72.8 (CH), 75.9 (CH), 77.9 (CH), 80.2 (CH), 124.4 (CH), 130.7 (CH); MS (EI) *m/z* (rel intensity) 260 (M⁺, <1), 228 (0.8), 197 (1); HRMS calcd for C₁₃H₂₄O₅ 260.162361, found 260.159859. Anal. Calcd for C₁₃H₂₄O₅: C, 59.98; H, 9.29. Found: C, 59.92; H, 9.34.

2,6-Anhydro-1,3,4,5-tetra-*O*-methyl-D-glycero-L-galacto-heptitol (14). A solution of compound **13** (596 mg, 2.29 mmol) in dry CH₂Cl₂/MeOH (25 mL, 1:2) was cooled to –78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess of ozone, dimethyl sulfide (853 mg, 13.7 mmol) was added and the mixture was heated to 0 °C for 30 min. Afterward, NaBH₄ (346 mg, 9.15 mmol) was added and the solution stirred for 20 min at room temperature. The reaction mixture was then poured into water and extracted with CH₂Cl₂, dried over Na₂SO₄, and concentrated. Column chromatography (CHCl₃–MeOH, 95:5) of the residue afforded compound **14** (545 mg, 2.18 mmol, 95%) as a colorless oil: [α]_D +37 (*c* = 0.89); IR 3454, 2934, 2829, 1647, 1463, 1366, 1196, 1098 cm⁻¹; ¹H NMR 3.37 (3H, s), 3.45 (3H, s), 3.47 (3H, s), 3.48 (3H, s), 3.49 (1H, m), 3.51 (1H, m), 3.63 (1H, dd, *J* = 7.1, 4.3 Hz), 3.69 (1H, m), 3.71 (1H, m), 3.72 (1H, m), 3.82 (1H, dd, *J* = 11.0, 8.0 Hz), 3.98 (1H, ddd, *J* = 7.7, 7.7, 4.0 Hz), 4.10 (1H, ddd, *J* = 8.1, 8.1, 4.4

Hz); ^{13}C NMR 58.2 (CH_3), 59.0 ($2 \times \text{CH}_3$), 59.5 (CH_3), 60.2 (CH_2), 69.8 (CH_2), 71.4 (CH), 72.3 (CH), 75.4 (CH), 77.5 (CH), 78.4 (CH); MS (EI) m/z (rel intensity) 251 ($\text{M}^+ + \text{H}$, <1), 232 (3), 220 (2); HRMS calcd for $\text{C}_{11}\text{H}_{23}\text{O}_6$ 251.149450, found 251.150509. Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_6$: C, 52.78; H, 8.86. Found: C, 52.42; H, 9.08.

(7Z)- and (7E)-1,3,4,5-Tetra-O-acetyl-2,6-anhydro-7,8,9-trideoxy-D-glycero-D-manno-non-7-enitol (15). A solution of 1,3,4,5-tetra-*O*-acetyl-2,6-anhydro-7,8,9-trideoxy-D-glycero-D-manno-non-8-enitol⁴ (2.8 g, 7.52 mmol) in dry benzene (12 mL) containing a catalytic amount of bis(benzonitrile)dichloropalladium(II) (280 mg, 10 mol %) was refluxed under nitrogen for 24 h. The reaction mixture was then filtered and concentrated in vacuo. Purification of the residue by chromatography (hexanes–EtOAc, 7:3) on silver nitrate impregnated silica gel gave the olefin **15** as an isomeric mixture (1.72 g, 4.62 mmol, 61.4%, *Z/E*, 1:5): colorless oil; IR 2967, 1747, 1435, 1371, 1228, 1051 cm^{-1} ; ^1H NMR (major isomer *E*) 1.79 (3H, d, $J = 1.8$ Hz), 2.00 (3H, s), 2.04 (3H, s), 2.10 (3H, s), 2.15 (3H, s), 3.92 (1H, ddd, $J = 8.9, 5.9, 2.9$ Hz), 4.09 (1H, dd, $J = 12.0, 2.6$ Hz), 4.29 (1H, dd, $J = 12.0, 5.6$ Hz), 4.49 (1H, dd, $J = 4.7, 2.1$ Hz), 5.19 (2H, dd, $J = 9.5, 3.4$ Hz), 5.35 (1H, d, $J = 3.4$ Hz), 5.38 (1H, dd, $J = 2.8, 2.8$ Hz), 5.54 (1H, ddd, $J = 15.9, 4.7, 1.7$ Hz), 5.92 (1H, dq, $J = 6.5, 1.8$ Hz); ^{13}C NMR (major isomer *E*) 18.2 (CH_3), 20.7 ($2 \times \text{CH}_3$), 20.8 (CH_3), 21.0 (CH_3), 62.8 (CH_2), 66.8 (CH), 69.4 (CH), 70.5 (CH), 70.5 (CH), 75.6 (CH), 124.7 (CH), 132.1 (CH), 169.7 (C), 170.2 (C), 170.4 (C), 170.8 (C); MS (EI) m/z (rel intensity) 373 ($\text{M}^+ + \text{H}$, 1), 331 (1); HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}_9$ 373.149842, found 373.146179. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_9$: C, 54.83; H, 6.50. Found: C, 55.09; H, 6.60.

(7Z)- and (7E)-2,6-Anhydro-7,8,9-trideoxy-1,3,4,5-tetra-O-methyl-D-glycero-D-manno-non-7-enitol (16). A solution of the mixture of olefins **15** (1.55 g, 4.16 mmol) in MeOH (50 mL) containing KOH (1.5 g, 26.8 mmol) was stirred at room temperature

for 1h. The reaction mixture was then neutralized with Dowex 50X8 acid resin, filtered and concentrated in vacuo to give an oil which was used in the following reaction without purification. To a suspension of NaH (798 mg, 33.3 mmol) in dry DMF (75 mL) was added the crude tetrol previously obtained in DMF (50 mL) and the mixture stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (2.0 mL, 32.1 mmol) was added dropwise and stirring continued at room temperature for 2 h. Excess reagent was destroyed by slow addition of MeOH and the solution poured into water and extracted with EtOAc. The organic extracts were dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 8:2) of the residue afforded **16** (790 mg, 3.03 mmol, 72.8%) as a colorless oil: IR 2979, 2931, 2826, 1451, 1192, 1111 cm⁻¹; ¹H NMR (major isomer *E*) 1.71 (3H, br d, *J* = 6.4 Hz), 3.37 (3H, s), 3.40–3.65 (6H, m), 3.43 (3H, s), 3.47 (3H, s), 3.48 (3H, s), 4.52 (1H, brs), 5.51 (1H, ddd, *J* = 15.9, 4.7, 1.7 Hz), 5.75 (1H, m); ¹³C NMR (major isomer *E*) 18.1 (CH₃), 57.5 (CH₃), 57.8 (CH₃), 59.1 (CH₃), 60.2 (CH₃), 72.0 (CH), 72.8 (CH₂), 73.2 (CH), 76.9 (CH), 78.6 (CH), 80.61 (CH), 126.4 (CH), 130.2 (CH); MS (EI) *m/z* (rel intensity) 219 (M⁺ – C₃H₅, 6), 187 (13); HRMS calcd for C₁₀H₁₉O₅ 219.123238, found 219.118572. Anal. Calcd for C₁₃H₂₄O₅: C, 59.98; H, 9.29. Found: C, 59.85; H, 9.48.

2,6-Anhydro-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-heptitol (17). A solution of compound **16** (621 mg, 2.39 mmol) in dry CH₂Cl₂/MeOH (15 mL, 1:2) was ozonized as described for compound **14** and the ozonide reduced with dimethyl sulfide (890 mg, 14.3 mmol) and NaBH₄ (542 mg, 14.3 mmol). Column chromatography (CHCl₃–MeOH, 95:5) of the residue afforded compound **17** (521 mg, 2.08 mmol, 87.2%) as a colorless oil: [α]_D +31.5 (*c* = 0.27); IR 3445, 2934, 2825, 1455, 1192, 1109 cm⁻¹; ¹H NMR 3.38 (3H, s), 3.42 (3H, s), 3.44 (3H, s), 3.46 (1H, dd, *J* = 4.3, 4.3 Hz), 3.49 (3H,

s), 3.53 (2H, m), 3.64 (1H, dd, $J = 4.8, 3.2$ Hz), 3.71 (1H, dd, $J = 10.5, 7.5$ Hz), 3.73 (1H, d, $J = 4.1$ Hz), 3.76 (1H, dd, $J = 5.6, 11.6$ Hz), 3.89 (1H, m), 3.92 (1H, m); ^{13}C NMR 57.2 (CH₃), 58.3 (CH₃), 58.4 (CH₃), 59.1 (CH₃), 61.8 (CH₂), 70.6 (CH), 70.8 (CH₂), 73.4 (CH), 75.0 (CH), 76.1 (CH), 76.9 (CH); MS (EI) m/z (rel intensity) 251 ($\text{M}^+ + \text{H}$, 0.3), 232 (2), 220 (1), 205 (11), 187 (17); HRMS calcd for C₁₁H₂₂O₆ 250.141626, found 250.139385. Anal. Calcd for C₁₁H₂₂O₆: C, 52.78; H, 8.86. Found: C, 52.65; H, 8.69.

2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-D-galacto-non-8-enitol

(19). A solution of **18**⁵ (3.6 g, 11.46 mmol) in MeOH (25 mL) containing KOH (0.75 g, 13.4 mmol) was stirred at room temperature for 1h. The reaction mixture was then neutralized with Dowex 50X8 acid resin, filtered and concentrated in vacuo to give an oil which was used in the following reaction without purification. To a suspension of NaH (1.65 g, 68.7 mmol) in dry DMF (50 mL) was added the crude tetrol previously obtained in DMF (50 mL) and the mixture stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (4.35 mL, 69.9 mmol) was added dropwise and stirring continued at room temperature for 2 h. Excess reagent was destroyed by slow addition of MeOH and the solution poured into water and extracted with EtOAc. The organic extracts were dried over Na₂SO₄ and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 7:3) of the residue afforded **19** (1.81 g, 7.87 mmol, 68.6%) as a colorless oil: $[\alpha]_{\text{D}} -87$ ($c = 0.82$); IR 2978, 2933, 2826, 1643, 1360, 1193, 1104 cm⁻¹; ^1H NMR 1.27 (3H, d, $J = 6.6$ Hz), 2.30 (1H, m), 2.37 (1H, m), 3.44 (3H, s), 3.48 (3H, s), 3.49 (3H, s), 3.51 (3H, m), 3.92 (1H, dq, $J = 6.5, 3.3$ Hz), 4.03 (1H, ddd, $J = 9.1, 5.3, 3.8$ Hz), 5.05 (1H, d, $J = 10.2$ Hz), 5.10 (1H, dd, $J = 17.0, 1.5$ Hz), 5.81 (1H, ddd, $J = 17.0, 10.2, 6.8$ Hz); ^{13}C NMR 15.0 (CH₃), 31.9 (CH₂), 58.3 (CH₃), 58.5 (CH₃), 59.5 (CH₃), 68.2 (CH), 70.0 (CH), 77.5 (CH), 77.6 (CH), 78.4 (CH),

116.6 (CH₂), 135.2 (CH); MS (EI) m/z (rel intensity) 230 (M⁺, 21), 189 (29); HRMS calcd for C₁₂H₂₂O₄ 230.151798, found 230.151928. Anal. Calcd for C₁₂H₂₂O₄: C, 62.58; H, 9.63. Found: C, 62.49; H, 9.65.

(7Z)- and (7E)-2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-O-methyl-L-glycero-D-galacto-non-7-enitol (20). A solution of the olefin **19** (1.76 g, 7.65 mmol) in dry benzene (60 mL) containing a catalytic amount of bis(benzonitrile)dichloropalladium (II) (210 mg, 7 mol %) was refluxed under nitrogen for 24 h. The reaction mixture was then filtered and concentrated in vacuo. Purification of the residue by chromatography (hexanes–EtOAc, 7:3) on silver nitrate impregnated silica gel gave the olefin **20** as an isomeric mixture (1.06 g, 4.6 mmol, 60%, *Z/E*, 1:8): colorless oil; IR 2977, 2933, 2826, 1722, 1446, 1362, 1195, 1104 cm⁻¹; ¹H NMR (major isomer *E*) 1.23 (3H, d, *J* = 6.4 Hz), 1.72 (3H, d, *J* = 6.5 Hz), 3.35 (1H, m), 3.38 (1H, m), 3.40 (3H, s), 3.48 (3H, s), 3.52 (3H, s), 3.65 (1H, m), 3.84 (1H, m), 4.50 (1H, dd, *J* = 5.6, 5.6 Hz), 5.6 (1H, m), 5.80 (1H, m); ¹³C NMR (major isomer *E*) 16.3 (CH₃), 18.1 (CH₃), 58.0 (CH₃), 58.2 (CH₃), 60.7 (CH₃), 67.9 (CH), 72.4 (CH), 77.8 (CH), 78.7 (CH), 80.3 (CH), 125.0 (CH), 130.4 (CH); MS (EI) m/z (rel intensity) 230 (M⁺, <1), 198 (2), 189 (4), 157 (2); HRMS calcd for C₉H₁₇O₄ 189.112675, found 189.104923. Anal. Calcd for C₁₂H₂₂O₄: C, 62.58; H, 9.63. Found: C, 62.91; H, 9.31.

2,6-Anhydro-1-deoxy-3,4,5-tri-O-methyl-L-glycero-D-galacto-heptitol (21). A solution of compound **20** (248 mg, 1.08 mmol) in dry CH₂Cl₂ (6 mL) was ozonized as described for compound **14** and the ozonide reduced with dimethyl sulfide (402 mg, 6.48 mmol) and NaBH₄ (122 mg, 3.23 mmol). Chromatotron chromatography (hexanes–EtOAc, 1:1 → 1:3) of the residue afforded compound **21** (160 mg, 0.73 mmol, 68%) as a colorless oil: [α]_D –55 (*c* = 0.32, CH₂Cl₂); IR 3460, 2935, 2828, 1463, 1365, 1194, 1102 cm⁻¹; ¹H NMR 1.30 (3H, d, *J* = 6.7 Hz), 3.46 (3H, s), 3.49 (3H, s),

3.51 (3H, s), 3.52 (1H, d, $J = 3.1$ Hz), 3.53 (1H, dd, $J = 2.9, 2.9$ Hz), 3.65 (1H, dd, $J = 6.7, 4.5$ Hz), 3.73 (1H, dd, $J = 11.7, 4.9$ Hz), 3.82 (1H, dd, $J = 11.4, 7.9$ Hz), 3.96 (1H, dq, $J = 6.7, 3.1$ Hz), 4.10 (1H, ddd, $J = 8.1, 8.1, 4.3$ Hz); ^{13}C NMR 15.4 (CH_3), 58.3 (CH_3), 59.0 (CH_3), 59.9 (CH_3), 60.6 (CH_2), 68.9 (CH), 70.9 (CH), 77.6 ($2 \times \text{CH}$), 79.0 (CH); MS (EI) m/z (rel intensity) 220 (M^+ , <1), 202 (1), 189 (14), 157 (8); HRMS calcd for $\text{C}_{10}\text{H}_{20}\text{O}_5$ 220.131062, found 220.125153. Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_5$: C, 54.53; H, 9.15. Found: C, 54.27; H, 9.53.

2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-non-8-enitol (22). To a solution of 1-*O*-acetyl-6-deoxy-2,3,4-tri-*O*-methyl-L-mannopyranose⁶ (476 mg, 1.92 mmol) in dry MeCN (14 mL) were added allyltrimethylsilane (658 mg, 5.75 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (1.36 g, 9.58 mmol) at 0 °C. After 30 min at room temperature, the reaction mixture was poured into ice–water and extracted with EtOAc. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography (hexanes–EtOAc, 6:4) of the residue afforded compound **22** (390 mg, 1.69 mmol, 88.3%) as a colorless oil: $[\alpha]_{\text{D}} -8$ ($c = 0.73$); IR 3077, 2977, 2933, 2825, 1644, 1455, 1382, 1196, 1102 cm^{-1} ; ^1H NMR 1.28 (3H, d, $J = 6.3$ Hz), 2.27 (1H, m), 2.42 (1H, m), 3.16 (1H, dd, $J = 7.7, 7.7$ Hz), 3.43 (1H, m), 3.45 (1H, m), 3.56 (1H, m), 4.02 (1H, dq, $J = 6.5, 3.3$ Hz), 5.09 (1H, dd, $J = 17.0, 1.5$ Hz), 5.12 (1H, d, $J = 10.0$ Hz), 5.79 (1H, ddd, $J = 17.0, 10.2, 6.8$ Hz); ^{13}C NMR (50.3 MHz) 17.8 (CH_3), 34.1 (CH_2), 57.6 ($2 \times \text{CH}_3$), 60.2 (CH_3), 69.1 (CH), 71.9 (CH), 77.7 (CH), 80 (CH), 81.8 (CH), 117.1 (CH_2), 134.2 (CH); MS (EI) m/z (rel intensity) 189 ($\text{M}^+ - \text{C}_3\text{H}_5$, 44), 157 (13); HRMS calcd for $\text{C}_9\text{H}_{17}\text{O}_4$ 189.112675, found 189.115547. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_4$: C, 62.58; H, 9.63. Found: C, 62.61; H, 9.64.

(7Z)- and (7E)-2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-non-7-enitol (23). A solution of the olefin **22** (390 mg, 1.69 mmol) in dry

benzene (12 mL) containing bis(benzonitrile)dichloropalladium(II) (39 mg, 6 mol %) was refluxed under nitrogen for 24 h. The reaction mixture was then filtered and concentrated in vacuo. Purification of the residue by chromatography (hexanes–EtOAc, 1:1) on silver nitrate impregnated silica gel gave the olefin **23** as an isomeric mixture (265 mg, 1.15 mmol, 68%, *Z/E*, 1:4): colorless oil; IR 2975, 2932, 2825, 1450, 1103 cm^{-1} ; ^1H NMR (major isomer *E*) 1.23 (3H, d, $J = 10.1$ Hz), 1.69 (3H, d, $J = 6.5$ Hz), 3.12 (1H, dd, $J = 8.7, 8.7$ Hz), 3.34 (1H, dd, $J = 3.2, 8.8$ Hz), 3.42 (3H, s), 3.43 (3H, s), 3.44 (3H, s), 3.49 (3H, s), 3.53 (1H, dq, $J = 9.2, 6.2$ Hz), 4.43 (1H, m), 5.51 (1H, m), 5.72 (1H, m); ^{13}C NMR (major isomer *E*) 18.0 ($2 \times \text{CH}_3$), 57.5 (CH_3), 57.8 (CH_3), 60.5 (CH_3), 69.4 (CH), 73.3 (CH), 79.0 (CH), 80.8 (CH), 82.2 (CH), 126.6 (CH), 130.0 (CH); MS (EI) m/z (rel intensity) 230 (M^+ , 5), 199 (15), 101 (100); HRMS calcd for $\text{C}_{12}\text{H}_{22}\text{O}_4$ 230.151798, found 230.148285. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_4$: C, 62.58; H, 9.63. Found: C, 62.46; H, 9.92.

2,6-Anhydro-1-deoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-heptitol (24). A solution of compound **23** (74 mg, 0.32 mmol) in dry $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (3 mL, 1:1) was ozonized as described for compound **14** and the ozonide reduced with dimethyl sulfide (119 mg, 1.93 mmol) and NaBH_4 (24 mg, 0.642 mmol). Column chromatography (CHCl_3 –MeOH, 95:5) of the residue afforded compound **24** (57 mg, 0.26 mmol, 81%) as a colorless oil: $[\alpha]_{\text{D}} -36$ ($c = 1.0$); IR 3444, 2933, 2829, 1455, 1099 cm^{-1} ; ^1H NMR 1.30 (3H, d, $J = 6.8$ Hz), 3.22 (1H, dd, $J = 5.4, 5.4$ Hz), 3.38 (3H, s), 3.41 (3H, s), 3.44 (3H, s), 3.45 (1H, dd, $J = 3.3, 6.8$ Hz), 3.54 (1H, dd, $J = 3.3, 5.6$ Hz), 3.65 (1H, dd, $J = 4.2, 11.5$ Hz), 3.72 (1H, dd, $J = 6.4, 11.4$ Hz), 3.81 (1H, ddd, $J = 6.8, 11.3, 11.3$ Hz), 3.91 (1H, ddd, $J = 4.3, 6.5, 6.5$ Hz); ^{13}C NMR 16.9 (CH_3), 57.3 (CH_3), 58.0 (CH_3), 58.9 (CH_3), 61.7 (CH_2), 70.1 (CH), 70.3 (CH), 75.6 (CH), 77.7 (CH), 80.0 (CH); MS (EI) m/z (rel intensity) 220 (M^+ , 1), 189 (29), 157 (31), 101 (100); HRMS calcd for $\text{C}_{10}\text{H}_{20}\text{O}_5$

220.131062, found 220.131981. Anal. Calcd for C₁₀H₂₀O₅: C, 54.53; H, 9.15. Found: C, 54.51; H, 9.21.

(7R)- and (7S)-2,6-Anhydro-7-C-cyano-1-deoxy-3,4,5-tri-O-methyl-L-glycero-D-galacto-heptitol (25). A solution of compound **20** (143 mg, 0.621 mmol) in dry CH₂Cl₂/MeOH (5 mL, 1:1) was cooled to -78 °C and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess of ozone, dimethyl sulfide (231 mg, 3.73 mmol) was added and the mixture was heated to room temperature overnight. The reaction mixture was concentrated in vacuo and the residue used in the following reaction without purification. To a solution of the crude residue (170 mg) in toluene (3 mL), was added diethylaluminum cyanide (1.3 mL, 1.3 mmol, 1M in toluene) at 0 °C and the mixture stirred for 10 min at this temperature. Afterward, EtOAc (10 mL) and an aqueous saturated solution of Rochelle's salt (3 mL) were added and the stirring continued for 30 min. The organic layer was separated, washed with brine and water, dried over Na₂SO₄ and concentrated under reduced pressure. Chromatotron chromatography (hexanes-EtOAc, 7:3) of the residue afforded both cyanohydrins **25** (87 mg, 0.35 mmol, 56.4%, *R/S*; 1:1) as a colorless oil (only isomer **25-S** could be isolated in pure state). Compound **25-R**: IR 3417, 2940, 2834, 2358, 1732, 1652, 1463, 1368, 1195, 1104 cm⁻¹; ¹H NMR 1.32 (3H, d, *J* = 7.2 Hz), 3.45 (3H, s), 3.47 (3H, s), 3.48 (3H, s), 3.57 (1H, dd, *J* = 5.3, 3.3 Hz), 3.68 (1H, dd, *J* = 5.4, 3.6 Hz), 3.73 (1H, m), 4.08 (1H, dd, *J* = 6.7, 3.4 Hz), 4.21 (1H, dq, *J* = 6.3, 3.5 Hz), 4.70 (1H, d, *J* = 7.2 Hz); ¹³C NMR 14.1 (CH₃), 58.6 (CH₃), 58.7 (CH₃), 59.0 (CH₃), 70.1 (CH), 70.9 (CH), 76.2 (CH), 76.6 (CH), 76.8 (CH), 77.0 (CH), 118.1 (C); MS (EI) *m/z* (rel intensity) 245 (M⁺, 1), 189 (39), 157 (8); HRMS calcd for C₁₁H₁₉O₅N 245.126311, found 245.124493. Anal. Calcd for C₁₁H₁₉O₅N: C, 53.86; H, 7.81; N, 5.71. Found: C, 54.06; H, 8.15; N, 5.32. Compound **25-S**: [α]_D -42 (*c* = 0.38,

CH₂Cl₂); IR 3418, 2986, 2938, 2358, 1455, 1368, 1195, 1103 cm⁻¹; ¹H NMR 1.32 (3H, d, *J* = 6.7 Hz), 3.43 (3H, s), 3.47 (3H, s), 3.50 (3H, s), 3.58 (1H, dd, *J* = 4.9, 3.1 Hz), 3.75 (1H, dd, *J* = 4.7, 2.9 Hz), 3.75 (1H, m), 4.08 (1H, dd, *J* = 7.2, 2.7 Hz), 4.21 (1H, dq, *J* = 6.7, 2.8 Hz), 4.62 (1H, d, *J* = 7.2 Hz); ¹³C NMR 13.7 (CH₃), 58.4 (CH₃), 58.7 (CH₃), 58.9 (CH₃), 61.7 (CH), 68.6 (CH), 70.8 (CH), 75.9 (CH), 76.6 (2 × CH), 119.0 (C); MS (EI) *m/z* (rel intensity) 245 (M⁺, <1), 189 (26), 157 (7); HRMS calcd for C₁₁H₁₉NO₅ 245.126311, found 245.128075. Anal. Calcd for C₁₁H₁₉O₅N: C, 53.86; H, 7.81; N, 5.71. Found: C, 53.92; H, 7.87; N, 5.52.

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