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TETRAHEDRON: *ASYMMETRY*

# Total, asymmetric synthesis of ethyl D-*ido*-4-heptulosuronate derivatives starting from diethyl 4-oxopimelate

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**Abstract**

Bromination of diethyl 4-oxopimelate, followed by double elimination of HBr and ketalization provided diethyl (*E*,*E*)-4,4-(ethylidenedioxy)hepta-2,5-dienedioate **4**. Sharpless asymmetric dihydroxylation of **4** produced diethyl (2*S*,3*S*)-4,4-(ethylidenedioxy)-2,3-dihydroxyhept-5-enedioate (+)-**5**, with 78% e.e. The corresponding tetrol could not be obtained in one step. Silylation of (+)-**5** and a second asymmetric dihydroxylation, followed by silylation led to 20% of *meso*-diester **9** and 60% of diethyl (2*S*,3*S*,5*S*,6*S*)-2,3,5,6-tetrakis[(*t*-butyl)dimethylsilyloxy]-4,4-(ethylidenedioxy)heptanedioate (−)-**10**. Reductive desymmetrization of (−)-**10** with DIBAL-H furnished, after selective oxidation, ethyl (2*S*,3*S*,5*S*,6*S*)-2,3,5,6-tetrakis-[(*t*-butyl)dimethylsilyloxy]-4,4-(ethylidenedioxy)-7-oxoheptanoate (+)-**13** which was then converted into ethyl 1,2,3,6-*O*-tetraacetyl-4,4-ethylidenedioxy-α- and β-D-*ido*-heptapyranuronate (−)-**15**α,β and into the corresponding 3-(α-D-pyranosyl)propene (−)-**16**. 

## 1. Introduction

Recently we disclosed[1] our approach to the synthesis of the $C_{37}$–$C_{45}$-F-ring fragment of the spongistatins[2] starting from (*R*)-(+)-3-benzyloxy-2-methyl-propan-1-ol. The method generates a 4-deoxy-4-methyl-D-*glycero*-L-*gluco*-heptopyranose intermediate using two sequential Sharpless dihydroxylations as key-steps. With the goal to generate analogues of these rare and powerful antimitotic agents we have explored a route to precursors of 40-nor-40-oxo derivatives. This requires the preparation of D-*ido*-4-heptulosuronate esters which is presented in this report. To our knowledge these sugars have never been described, although heptoses,[3,4] have been derived from hexose,[5] pentose,[6] treose[7] and glyceraldehyde derivatives,[8] or through total synthesis using achiral starting materials.[9]

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## 2. Results and discussion

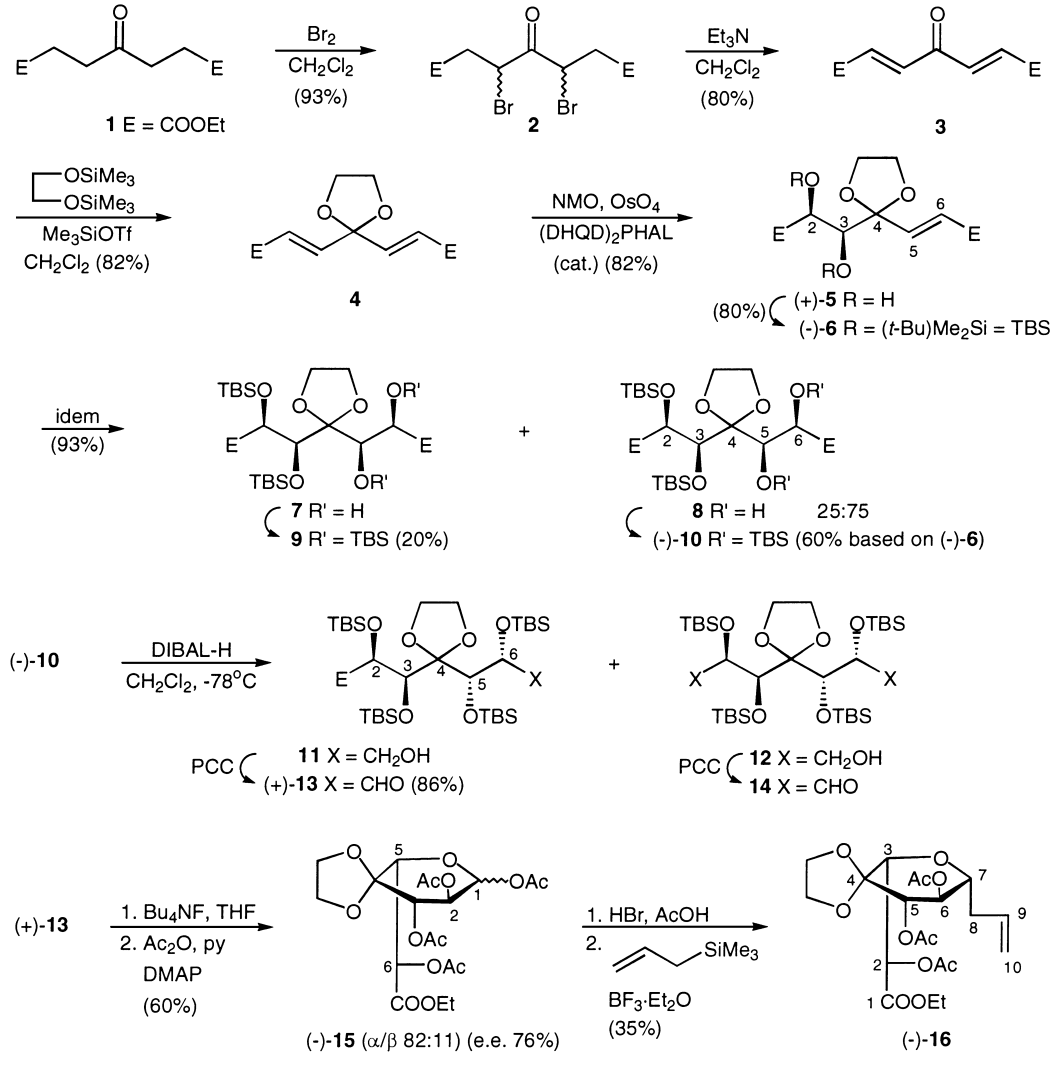
Our initial plan was to carry out a double asymmetric dihydroxylation[10] of a derivative of (*E*,*E*)-4-oxohepta-2,5-dien-1,7-dioic acid which would generate in one step a $C_2$-symmetrical tetrol with the D- or L-*ido* configuration, followed by desymmetrization of the dioic system through reduction[11] into a monoaldehyde or a primary mono-alcohol. Unfortunately, this plan failed as we found that the double dihydroxylation of **3** or **4** could not be achieved in a one-pot operation.

The starting oxodienedioate **3** was readily obtained from diethyl 4-oxopimelate **1** through selective dibromination with bromine in $CH_2Cl_2$ at 0°C. This gave a major dibromide **2** isolated in 93% yield which was either a *meso*-3,5-dibromo or a racemic *threo*-3,5-dibromo derivative (Scheme 1). Treatment of **2** with triethylamine led to double elimination of HBr ($CH_2Cl_2$, 0°C) with formation of the desired diethyl (*E*,*E*)-4-oxohepta-2,5-diene-1,7-dioate **3** isolated in 80% yield. Attempts to carry out dihydroxylation or double dihydroxylation of dienone **3** under standard conditions[10] failed to furnish the desired diols or tetrols in satisfactory yields because concurrent retroaldolizations led to decomposition. We were forced to convert the ketone moiety into an acetal and we chose for that to generate the corresponding dioxolane **4** on treating **3** with 1,2-bis(trimethylsilyloxy)ethane and trimethylsilyl trifluoromethanesulfonate.[12] Applying the Sharpless dihydroxylation protocol to **4** [$(DHQD)_2PHAL$ 1%, $OsO_4$ 0.2%, *N*-methylmorpholine *N*-oxide in excess, 5 h] gave diol (+)-**5** which was isolated in 82% yield. Under forcing conditions (long reaction times, higher concentrations of catalyst and ligand) expected tetrols were formed very slowly and could not be isolated in reasonable yield (<10%). We thus protected the diol as the disilyl ether (−)-**6** [(*t*-Bu)$Me_2SiOSO_2CF_3$, 2,6-lutidine, $CH_2Cl_2$]. The enantiomeric purity of (+)-**5** was 78% (established as shown below) and could not be improved by varying the concentration or temperature.

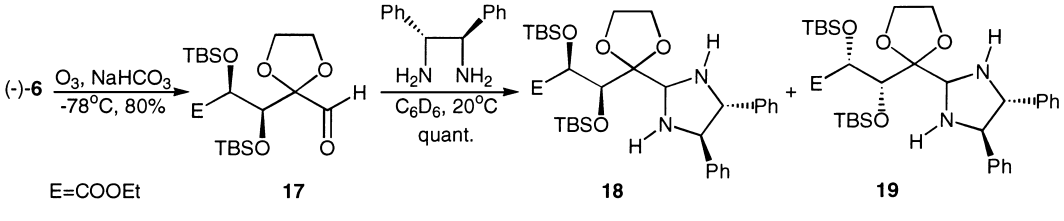
Dihydroxylation of alkene (−)-**6** was a slow reaction that required some higher concentrations of catalyst and ligand than for the dihydroxylation of diene **4**. It led to a 25:75 mixture of two diastereomeric diols **7** and **8** (93%) which was silylated under standard conditions giving a mixture of tetrasilyl ethers **9** and (−)-**10** which was separated by flash chromatography on silica gel, in 20% and 60% yields, respectively (based on (−)-**6**). Selective reduction of (−)-**10** with diisobutylaluminum hydride[13] (DIBAL-H, 4 equivalents) was possible at low temperature and with slow addition of the reducing agent (−78°C, $CH_2Cl_2$) producing a mixture of alcohol **11** and diol **12** which was not purified but directly oxidized with pyridinium chlorochromate (PCC) to give a mixture of monoaldehyde (+)-**13** and dialdehyde **14** which was separated by flash chromatography on silica gel in 86% and 5% yield, respectively (based on (−)-**10**). Desilylation of (+)-**13** with $Bu_4NF$ led to the formation of a mixture of pyranoses which was acetylated under standard conditions to give an 89:11 mixture of α- and β-acetyl pyranosides **15**α and **15**β (60% yield). Treatment of (−)-**15**α,β with allyltrimethylsilane and $BF_3 \cdot Et_2O$[14] generated the α-C-glycoside (−)-**16** in moderate yield (35%).

The enantiomeric excess of (−)-**6** was evaluated in the following fashion (Scheme 2). Ozonolysis of (−)-**6** generated aldehyde **17** (80%) which was reacted with (1*R*,2*R*)-1,2-diphenylethylenediamine[15] which produced a 89:11 mixture of aminals **18** and **19** ($^1$H NMR of the crude) establishing an e.e. of 78%.

The absolute configuration of compounds **5**–**16** was established in the following way (Scheme 3). Diol (+)-**5** was protected with *p*-methoxybenzoyl chloride to give the corresponding diester **20** (72%). Ozonolysis, followed by reduction in situ with $NaBH_4$ afforded primary alcohol **21**. Upon treatment with DBU in THF, at 0°C, lactonization occurred to give lactone **22**. Circular dichroism of this cyclic compound (Fig. 1) gave the absolute configuration (2*S*,3*S*) of diol (+)-**5** as it displayed a typical exciton split type of spectrum.[16]

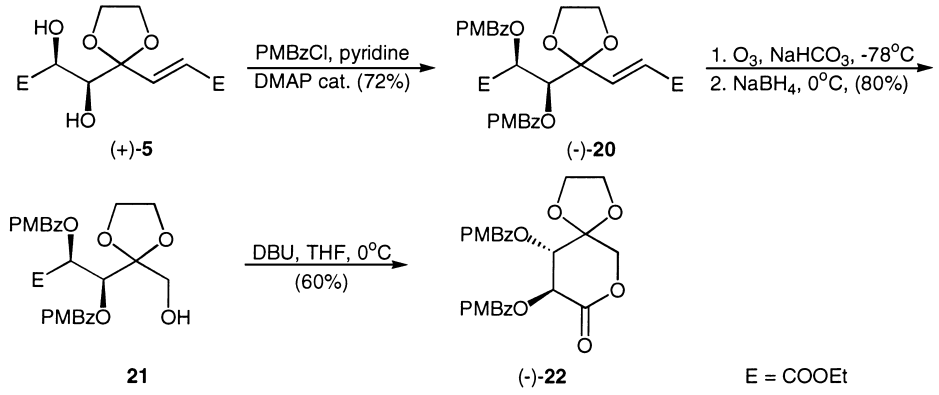



Scheme 1.




Scheme 2.

Distinction between *meso*-diester **9** ($[\alpha]_D^{25}$ 0) and its *threo*-stereomer (−)-**10** ($[\alpha]_D^{25}$ −8.2) was given by their optical rotations. The $^1$H NMR spectrum of **9** showed one quadruplet for the $CH_2$ protons of the ethyl esters whereas the $^1$H NMR spectrum of (−)-**10** showed two quadruplet×doublet for these protons (they are diastereotopic in **10** and enantiotopic in **9**). 2D-$^1$H NMR (COSY, NOESY) confirmed the structures of (−)-**15** and (−)-**16**. Monoaldehyde (+)-**13** was reacted with (1*S*,2*S*)-diphenylethylene




Scheme 3.

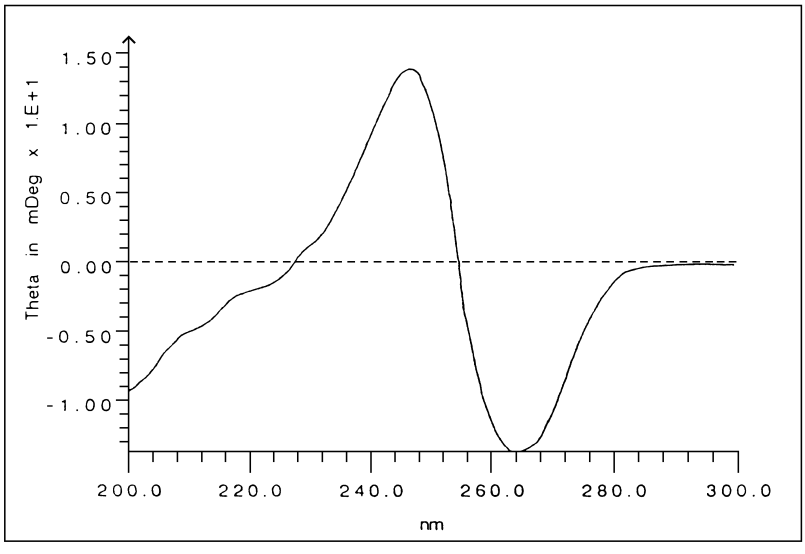



Figure 1.

diamine to give an 88:12 mixture of aminals corresponding to an enantiomeric excess of 76%, showing that there is no modification of the optical purity during the second dihydroxylation and the other steps.

## 3. Conclusion

The as yet unknown D-*ido*-4-heptulosuronic acid derivatives can be obtained from diethyl 4-oxopimelate with an enantiomeric excess of 76%. The L-*ido* enantiomers can also be obtained since the method used relies upon the Sharpless asymmetric dihydroxylation.

## 4. Experimental

General, see literature.[17] FC=flash chromatography on silica gel. All $^1$H NMR signal assignments were confirmed by 2D-$^1$H NMR (COSY, NOESY).

### 4.1. *Diethyl (3*RS,*5*RS*)- or (3*RS,*5*SR*)-3,5-dibromo-4-oxoheptadioate* **2**

Bromine (13.4 ml, 0.26 mol) in soln in anhydrous $CH_2Cl_2$ (30 ml) was added dropwise to a stirred soln of diethyl 4-oxopimelate (30 g, 0.13 mol, Fluka) in anhydrous $CH_2Cl_2$ cooled to 0°C. After the addition, the soln was stirred at 20°C for 5 min and $CH_2Cl_2$ (250 ml) was added. The soln was washed with 1 M $Na_2S_2O_3$ in $H_2O$, then dried ($MgSO_4$) and concentrated in vacuo. Recrystallization from light petroleum at −18°C: 47 g (93%), white crystals, m.p. 48–49°C, $R_f$: 0.57 (2:1, light petroleum:$Et_2O$). IR (KBr): 2985, 2940, 1725, 1460, 1375, 1200, 1030, 960, 940, 865, 830, 785, 665. $^1$H NMR (400 MHz, $CDCl_3$): 5.34 (*dd*, $^3J$=6.9, H-3, H-5), 4.19 (*q*, $^3J$=7.2, 2 $CH_2$(Et)), 3.27, 3.01 (2*dd*, $^2J$=17.1, $^3J$=6.9, $H_2C$(2), $H_2C$(6)), 1.27 (*t*, $^3J$=7.2, 2 Me(Et)). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 194.3 (C-4), 169.3 (C-1, C-7), 61.3 ($CH_2$(Et)), 49.5 (C-3, C-5), 38.2 (C-2, C-6), 14.1 (Me). CI-MS ($NH_3$): 389 (1, M+H$^+$), 343 (17, M$^{\cdot+}$−OEt), 315 (7), 263, 261 (33, M$^{\cdot+}$−OEt−Br), 209, 207 (90), 183, 181 (28), 127 (100), 99 (63).

### 4.2. *Diethyl (*E,E*)-4-oxohepta-2,5-dienedioate* **3**

Triethylamine (35 ml, 0.248 mol) was added dropwise to a stirred soln of **2** (47 g, 0.121 mol) in anhydrous $CH_2Cl_2$ (400 ml) cooled to 0°C. After stirring at 0°C for 30 min, $H_2O$ (400 ml) and $CH_2Cl_2$ (300 ml) were added and the mixture was shaken vigorously. The organic phase was washed with $H_2O$ (700 ml, twice). After drying ($MgSO_4$), the solvent was evaporated and the residue crystallized from 96% EtOH: 21.8 g (80%), yellow needles, m.p. 49–50°C, $R_f$: 0.47 (1:2, light petroleum:$Et_2O$). UV (MeCN): 246 (15 000). IR (KBr): 3070, 2985, 1725, 1675, 1285, 1195, 1090, 1000, 865, 805, 775, 705, 635. $^1$H NMR (400 MHz, $CDCl_3$): 7.23 (*d*, $^3J$=15.9, H-3, H-5), 6.81 (*d*, $^3J$=15.9, H-2, H-6), 4.29 (*q*, $^3J$=7.2, 2 $CH_2$), 1.34 (*t*, $^3J$=7.2, 2 Me). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 188.2 (*s*, C-4), 165.1 (*s*, C-1, C-7), 137.5 (*d*, *J*=163, C-3, C-5), 133.2 (*d*, *J*=167, C-2, C-6), 61.6 (*t*, *J*=148), 14.1 (*q*, *J*=127). CI-MS ($NH_3$): 226 (34, M$^{\cdot+}$), 197 (16, M$^{\cdot+}$−Et), 181 (56, M$^{\cdot+}$−OEt), 153 (29, M$^{\cdot+}$−COOEt), 127 (70), 99 (100). Anal. calcd for $C_{11}H_{14}O_5$ (226.23): C 58.41, H 6.19; found: C 58.31, H 6.19.

### 4.3. *Diethyl (*E,E*)-4,4-(ethylidenedioxy)hepta-2,5-dienedioate* **4**

Trimethylsilyl trifluoromethanesulfonate (0.8 ml, 4.43 mmol) was added dropwise to a stirred soln of **3** (10 g, 44.3 mmol) and 1,2-bis(trimethylsilyloxy)ethane (16.3 ml, 66.4 mmol) in anhydrous $CH_2Cl_2$ (100 ml) cooled to −78°C. After stirring at −78°C for 1 h, the mixture was stirred at 20°C for 18 h. Pyridine (0.9 ml, 11.2 mmol) was added and the mixture poured into a sat. aq. soln of $NaHCO_3$ (250 ml). The aq. layer was extracted with $CH_2Cl_2$ (250 ml, three times). The combined organic extracts were washed with brine (100 ml) and dried (1:1, $MgSO_4$:$K_2CO_3$). The solvent was evaporated and the residue was purified by FC (1:3, light petroleum:$Et_2O$): 9.8 g (82%), pale yellow oil, $R_f$: 0.27 (2:1, light petroleum:$Et_2O$). UV (MeCN): 203 (10 000). IR (film): 3060, 2980, 2900, 1720, 1660, 1270, 1180, 1035, 980, 950, 865, 710, 665. $^1$H NMR (400 MHz, $CDCl_3$): 6.78 (*d*, $^3J$=15.7, H-3, H-5), 6.17 (*d*, $^3J$=15.7, H-2, H-6), 4.21 (*q*, $^3J$=7.2, 2 $CH_2$), 4.00 (*s*, 4H), 1.29 (*t*, $^3J$=7.2, 2 Me). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 165.8 (*s*, C-1, C-7), 143.0 (*d*, *J*=163, C-2, C-6), 123.0 (d, *J*=166, C-3, C-5), 105.1, (*s*, C-4), 65.3 (*t*, *J*=150), 60.8 (*t*, *J*=148), 14.1 (*q*, *J*=127). CI-MS ($NH_3$): 217 (25, M+H$^+$), 241 (2), 224 (52), 197 (100), 171 (86), 143 (13), 97 (24). Anal. calcd for $C_{13}H_{18}O_6$ (270.28): C 57.78, H 6.67; found: C 57.88, H 6.66.

### 4.4. Diethyl (2S,3S)-4,4-(ethylidenedioxy)-2,3-dihydroxyhept-5-enedioate (+)-**5**

A mixture of compound **4** (5 g, 18.5 mmol), *tert*-butanol (60 ml), $(DHQD)_2PHAL$ (145 mg, 0.185 mmol), 60% *N*-methylmorpholine-*N*-oxide (NMO) in $H_2O$ (7.14 ml, 27.8 mmol) and 0.1 M $OsO_4$ in $CCl_4$ (0.37 ml) was stirred at 20°C for 5 h. Aqueous 1 N HCl (100 ml) was added and the mixture was extracted with EtOAc (150 ml, three times). The combined organic extracts were washed with a sat. aq. soln of $NaHCO_3$, and then dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue purified by FC (1:1, light petroleum:$Et_2O$): 4.62 g (82%), colorless oil, $R_f$: 0.24 (1:1, light petroleum:EtOAc). $[\alpha]_D^{25}$ +10.3, $[\alpha]_{577}^{25}$ +8.4, $[\alpha]_{546}^{25}$ +9.3, $[\alpha]_{435}^{25}$ +10.7, $[\alpha]_{405}^{55}$ +11.0 (*c*=1.0, $CH_2Cl_2$). UV (MeCN): 206 (9800). IR (film): 3470, 2985, 2900, 1720, 1660, 1470, 1445, 1270, 1075, 1030, 950, 865, 715, 665. $^1$H NMR (400 MHz, $CDCl_3$): 6.90, (*d*, $^3J$=15.6, H-5), 6.21 (*d*, $^3J$=15.6, H-6), 4.41 (*d*, $^3J$=1.3, H-2), 4.30 (*q*, $^3J$=7.0, $CH_2$), 4.22 (*q*, $^3J$=7.1, $CH_2$), 4.06 (*d*, $^3J$=1.3, H-3), 4.13–4.15 (2*m*, $CH_2$–$CH_2$ of dioxolane), 2.31 (br. *s*, HO–C(2), HO–C(3′)), 1.32 (*t*, $^3J$=7.0, $CH_3$), 1.31 (*t*, $^3J$=7.1, $CH_3$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 172.7, 165.8 (2*s*, C-1, C-7), 143.0 (*d*, *J*=162, C-6), 123.6 (*d*, *J*=166, C-5), 107.9 (*s*, C-4), 74.2 (*d*, *J*=147, C-2), 69.9 (*d*, *J*=148, C-3), 65.9, 65.0 (2*t*, *J*=152, dioxolane), 60.7, 60.4 (2*t*, *J*=157, 2 $CH_2$), 14.1 (*q*, *J*=126, 2 Me). CI-MS ($NH_3$): 305 (5, M+$H^+$), 241 (4, $M^{\cdot+}$−OEt−$H_2O$), 205 (71), 171 (100), 157 (9), 143 (23), 99 (26). Anal. calcd for $C_{13}H_{20}O_8$ (304.29): C 51.32, H 6.58; found: C 51.15, H 6.60.

### 4.5. Diethyl (2S,3S)-2,3-bis[(t-butyl)dimethylsilyloxy]-4,4-(ethylidenedioxy)hept-5-enedioate (−)-**6**

(*t*-Butyl)dimethylsilyl trifluoromethanesulfonate (15.1 ml, 65.8 mmol) was added dropwise to a stirred soln of (+)-**5** (4 g, 13.16 mmol) in 2,6-lutidine (9.17 ml) and anhydrous $CH_2Cl_2$ (70 ml) cooled to 0°C. After stirring at 0°C for 30 min, the mixture was stirred at 20°C for 6 h. Aqueous 2 N NaOH (150 ml) was added and the phases were separated. The aq. layer was extracted with EtOAc (150 ml, three times). The combined organic extracts were washed with aq. 1 N HCl (100 ml), then with brine (100 ml) and then dried ($MgSO_4$). The solvent was evaporated in vacuo and the residue was purified by FC (15:1, light petroleum:EtOAc): 5.6 g (80%), colorless oil, $R_f$: 0.58 (4:1, light petroleum:EtOAc). $[\alpha]_D^{25}$ −4.5, $[\alpha]_{577}^{25}$ −8.1, $[\alpha]_{546}^{25}$ −8.6, $[\alpha]_{435}^{25}$ −13.9, $[\alpha]_{405}^{25}$ −17.2 (*c*=1.2, $CH_2Cl_2$). UV (MeCN): 204 (9700). IR (film): 3080, 2950, 2930, 2885, 2845, 1720, 1460, 1355, 1265, 1160, 840, 740. $^1$H NMR (400 MHz, $CDCl_3$): 7.05 (*d*, $^3J$=15.8, H-6), 6.03 (*d*, $^3J$=15.8, H-5), 4.45 (*d*, $^3J$=2.6, H-2), 4.20–4.14 (*m*, 2 $CH_2$), 4.00 (*d*, $^3J$=2.6, H-3), 4.02–3.86 (*m*, $CH_2$–$CH_2$ of dioxolane), 1.31–1.25 (*m*, 2 Me), 0.92, 0.88 (2*s*, 2 *t*-Bu), 0.09, 0.04, 0.03, 0.00 (4*s*, 2 $Me_2Si$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 172.3, 166.3 (2*s*, C-1, C-7), 144.3 (*d*, *J*=164, C-6), 121.6 (*d*, *J*=166, C-5), 108.0 (*s*, C-4), 78.1, 72.9 (2*d*, *J*=147, 144, C-2, C-3), 65.4, 64.8 (2*t*, 2 $CH_2$, dioxolane), 60.8, 60.2 (2*t*, 2 $CH_2$), 25.7, 25.6 (2*q*, 2 *t*-Bu), 18.1 (*s*, *C*$(Me)_3$), 14.1, 14.0 (2*q*, 2 Me (EtO)), −4.4, −4.8, −5.1, −5.4 (4*q*, 2 $Me_2Si$). CI-MS ($NH_3$): 551 (34, M+$NH_4^+$), 533 (24, M+$H^+$), 475 (30, $M^{\cdot+}$−*t*-Bu), 401 (4), 373 (15), 343 (22), 286 (72). Anal. calcd for $C_{25}H_{48}O_8Si_2$ (532.82): C 56.39, H 9.02, Si 10.53; found: C 56.49, H 9.12, Si 10.48.

### 4.6. Diethyl (2S,3S,5R,6R)-**9** and (2S,3S,5S,6S)-2,3,5,6-tetrakis[(t-butyl)dimethylsilyloxy]-4,4-(ethylidenedioxy)heptanedioate (−)-**10**

A mixture of (−)-**6** (3 g, 5.64 mmol), *tert*-butanol (30 ml), $(DHQD)_2PHAL$ (440 mg, 0.564 mmol), 60% NMO in $H_2O$ (2.8 ml, 14.1 mmol) and 0.1 M $OsO_4$ in $CCl_4$ (2.8 ml, 0.28 mmol) was stirred at 20°C for 20 h. Aqueous 1 N HCl (60 ml) was added and the two phases were separated. The aq. layer was extracted with EtOAc (80 ml, three times). The combined organic extracts were washed with sat. aq. soln of $NaHSO_3$ (100 ml), then with brine (100 ml) and dried ($MgSO_4$). The solvent was evaporated

in vacuo to afford 2.97 g (93%): 1:2 mixture of diols **7** and **8**. The pale yellow oil was dissolved in anhydrous $CH_2Cl_2$ (45 ml), and 2,6-lutidine (3.7 ml, 31.5 mmol) and (*t*-Bu)$Me_2SiOSO_3CF_3$ (6.7 ml, 29.4 mmol) were added at 0°C. After stirring at 0°C for 30 min, the mixture was allowed to stay at 20°C for 6 h. Aqueous 2 N NaOH (150 ml) was added and the two phases were separated. The aq. layer was extracted with EtOAc (150 ml, three times). The combined organic extracts were washed with aqueous 1 N HCl (200 ml), then with brine (200 ml) and dried ($MgSO_4$). The solvent was evaporated in vacuo and the oily residue purified by FC (30:1, light petroleum:EtOAc): 895 mg (20%) of **9** and 2.69 g (60%) of **10**. Data for **9**: $R_f$: 0.83 (15:1, light petroleum:EtOAc), colorless oil. $[\alpha]_D^{25}=[\alpha]_{405}^{25}=0$ (*c* 1.3, $CH_2Cl_2$). UV (MeCN): 192 (8600). IR (film): 2950, 2930, 2895, 2855, 1750, 1470, 1465, 1390, 1360, 1250, 1160, 1135, 1100, 1070, 1035, 1005, 995, 970, 940, 815, 680, 665. $^1$H NMR (400 MHz, $CDCl_3$): 4.41 (*d*, $^3J$=2.0, H-2, H-6), 4.30 (*d*, $^3J$=2.0, H-3, H-5), 4.16 (*q*, $^3J$=7.1, 2 $CH_2$(EtO)), 3.88 (*m*, $CH_2$–$CH_2$ (dioxolane)), 1.69 (*t*, $^3J$=7.1, 2 $CH_3$), 0.93, 0.89 (2*s*, 2 *t*-Bu), 0.13, 0.07, 0.05, 0.03 (4*s*, 4 $Me_2Si$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 172.4 (*s*, C-1, C-7), 110.0 (*s*, C-4), 75.5 (*d*, *J*=142, C-2, C-6), 73.6 (*d*, *J*=142, C-3, C-5), 66.6 (*t*, *J*=149, $CH_2$–$CH_2$ ($C_2$-symmetrical dioxolane)), 60.6 (*t*, *J*=145, $CH_2$(EtO)), 25.8, 25.7 (2*q*, *J*=127, 2 *t*-Bu), 18.4, 18.1 (2*s*, 2 *C*$Me_2$), 14.1 (*q*, $CH_3$(EtO)), −4.1, −4.4, −5.0, −5.7 (4*q*, *J*=118, 4 $Me_2Si$). CI-MS ($NH_3$): 795 (100, M+H$^+$), 737 (16, M$^{\cdot+}$−*t*-Bu), 606 (3), 531 (1), 491 (8), 433 (56), 303 (61). Anal. calcd for $C_{37}H_{78}O_{10}Si_4$ (795.36): C 55.92, H 9.82, Si 14.11; found: C 55.95, H 9.74, Si 14.05.

Data for (−)-**10**: $R_f$: 0.73 (15:1, light petroleum:EtOAc), colorless oil. $[\alpha]_D^{25}$ −08.2, $[\alpha]_{577}^{25}$ −10.4, $[\alpha]_{546}^{25}$ −11.0, $[\alpha]_{535}^{25}$ −14.5, $[\alpha]_{405}^{25}$ −20 (*c* 1.4, $CH_2Cl_2$). IR (film): 2950, 2930, 2895, 2860, 1745, 1470, 1465, 1390, 1360, 1110, 1030, 1005, 950, 940, 900, 815, 735, 665. $^1$H NMR (400 MHz, $CDCl_3$): 4.37 (*d*, $^3J$=4.6, H-2, H-6), 4.28 (*d*, $^3J$=4.6, H-3, H-5), 4.16, 4.02 (2*dq*, $^2J$=10.8, $^3J$=7.1, 2 $CH_2$(EtO)), 3.94, 3.78 (2*m*, AA′BB′, $CH_2$–$CH_2$ of dioxolane), 1.27 (*t*, $^3J$=7.1, 2 $CH_3$(EtO)), 0.94, 0.91 (2*s*, 4 *t*-Bu), 0.16, 0.09, 0.07, 0.06 (4*s*, 4 $Me_2Si$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 172.6 (*s*, C-1, C-7), 110.3 (*s*, C-4), 75.9 (*d*, *J*=146, C-2, C-6), 72.6 (*d*, *J*=143, C-3, C-5), 65.9, 64.5 (2*t*, *J*=151, 2 $CH_2$ of $C_2$-symmetrical dioxolane), 60.3 (*t*, *J*=144, 2 $CH_2$(EtO)), 26.1, 25.9 (2*q*, *J*=126, 4 *t*-Bu), 18.3 (*q*, 4 *C*$Me_2$), 14.0 (*q*, *J*=127, Me(OEt)), −4.0, −4.2, −4.3, −4.8 (4*q*, *J*=117, 4 $Me_2Si$). CI-MS ($NH_3$): 812 (42, M+$NH_4^+$), 795 (87, M+H$^+$), 738 (13), 491 (4), 433 (64), 303 (46), 229 (21), 90 (100). Anal. calcd for $C_{37}H_{78}O_{10}Si_4$ (795.36): C 55.92, H 9.82, Si 14.11; found: C 55.88, H 9.75, Si 13.88.

### *4.7. Ethyl (2S,3S,5S,6S)-2,3,5,6-tetrakis[(t-butyl)dimethylsilyloxy]-4,4-ethylidenedioxy-7-oxoheptanoate (+)-**13** and (2S,3S,5S,6S)-2,3,5,6-tetrakis[(t-butyl)dimethylsilyloxy-4,4-ethylidenedioxyheptadial **14***

A solution of 1 M diisobutylaluminum hydride in $CH_2Cl_2$ (12.6 ml, 12.6 mmol) was added dropwise (over 20 min) to a stirred soln of (−)-**10** (2.5 g, 3.15 mmol) in anhydrous $CH_2Cl_2$ (40 ml) cooled to −78°C. After stirring for 5 min at −78°C, MeOH (5 ml) was added, followed by aq. 1 N HCl (100 ml). The phases were separated and the aq. layer was extracted with EtOAc (150 ml, three times). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was taken in anhydrous $CH_2Cl_2$ (40 ml). 4 Å molecular sieves (2 g) and pyridinium chlorochromate (1.7 g, 7.87 mmol) were added whilst stirring the solution at 20°C. After 4 h at 20°C, the mixture was filtered through a pad of silica gel (EtOAc) and the solvent was evaporated in vacuo. The pale brownish oil was purified by FC (40:1, petroleum ether:EtOAc): 111 mg (5%) of **14** and 2.03 g (86%) of (+)-**13**.

Data for (+)-**13**: $R_f$: 0.52 (10:1, light petroleum:EtOAc), colorless oil. $[\alpha]_D^{25}$ +3.4, $[\alpha]_{577}^{25}$ −1.6, $[\alpha]_{546}^{25}$ −4.4, $[\alpha]_{435}^{25}$ −9.1, $[\alpha]_{405}^{25}$ −10.1 (*c* 1.2, $CH_2Cl_2$). UV (MeCN): 193 (13 200). IR (film): 3030, 2950, 2930, 2895, 2855, 1730, 1470, 1360, 1265, 1160, 1100, 1005, 915, 835, 780, 740, 705, 666. $^1$H NMR (400 MHz, $CDCl_3$): 9.77 (*s*, CHO), 4.51 (*d*, $^3J$=7.2, H-6), 4.50 (*d*, $^3J$=4.7, H-2), 4.10, 4.00 (2*dq*, $^2J$=10.1, $^3J$=7.2, $CH_2$(EtO)), 4.02 (*d*, *J*=7.2, H-5), 3.90 (*d*, $^3J$=4.7, H-3), 3.85, 3.79 (2*m*, $CH_2$–$CH_2$ of dioxolane),

1.25 (*t*, $^3J$=7.2, $CH_3$(EtO)), 0.97, 0.93, 0.90, 0.89 (4*s*, 4 *t*-Bu), 0.26, 0.20, 0.15, 0.10, 0.07, 0.06, 0.03, 0.01 (8*s*, 4 $Me_2Si$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 198.7 (*d*, *J*=178, CNO), 172.7 (*s*, C-1), 110.6 (*s*, C-4), 79.1 (*d*, *J*=139, C-6), 77.2 (*d*, *J*=146, C-5), 76.3 (*d*, *J*=145, C-2), 73.3 (*d*, *J*=150, C-3), 64.9, 63.6 (2*t*, *J*=150, $CH_2$–$CH_2$ of dioxolane), 60.3 (*t*, *J*=146, $CH_2$(EtO)), 26.3, 25.9, 25.6 (4*q*, *J*=125, 4 *t*-Bu), 18.8, 18.1 (4*s*, 4 *C*$Me_3$), 13.9 (*q*, *J*=126, $CH_3$(EtO)), −3.3, −3.6, −3.8, −4.7, −4.8, −4.9, −5.7 (8*q*, *J*=118, 4 $Me_2Si$). CI-MS ($NH_3$): 752 (1, M+1+$H^+$), 694 (1), 620 (2), 561 (3), 487 (2), 433 (71), 389 (73), 301 (34), 229 (33), 133 (10), 73 (100). Anal. calcd for $C_{35}H_{74}O_9Si_4$ (751.30): C 56.00, H 9.87, Si 14.93; found: C 56.10, H 9.79, Si 14.96.

Data for **14**: $R_f$ 0.58 (10:1, light petroleum:EtOAc), colorless oil. UV (MeCN): 192 (11 700). IR (film): 3030, 2950, 2930, 2895, 2855, 1730, 1470, 1360, 1265, 1095, 1005, 910, 835, 780, 740. $^1$H NMR (400 MHz, $CDCl_3$): 9.69 (*s*, H-1, H-7), 4.34 (*d*, $^3J$=4.9, H-2, H-6), 4.09 (*d*, $^3J$=4.9, H-3, H-5), 3.76, 3.71 (2*m*, $CH_2$–$CH_2$ of dioxolane), 0.93 (*s*, 4 *t*-Bu), 0.18, 0.15, 0.07, 0.05 (4*s*, 4 $Me_2Si$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 199.1 (*d*, C-1, C-7), 110.2 (*s*, C-4), 79.1 (*d*, C-2, C-6), 77.2 (*d*, C-3, C-5), 65.5, 64.6 (2*t*, $CH_2$–$CH_2$ of dioxolane), 25.90, 25.89 (2*q*, 4 *t*-Bu), 18.3, 18.1 (2*s*, 4 *C*$Me_4$), −4.0, −4.5, −4.8 (4*q*, 4 $Me_2Si$). CI-MS ($NH_3$): 724 (1, M+$NH_4^+$), 649 (2), 576 (3), 517 (5), 389 (81), 303 (20), 229 (22), 73 (100).

### *4.8. Ethyl 1,2,3,6-*O*-tetraacetyl-4-deoxy-4,4-ethylidenedioxy-α- and β-*D*-ido-heptapyranuronate (−)-**15**α,β*

A 1 M soln of tetrabutylammonium fluoride in THF (9 ml, 9 mmol) was added dropwise to a stirred soln of (+)-**13** (1.5 g, 2 mmol) in anhydrous THF (20 ml) cooled to −20°C. After 5 min at −20°C, the solvent was evaporated in vacuo and the residue dried in vacuo (20°C, 1 h). It was taken up in pyridine (10 ml), and acetic anhydride (10 ml) and 4-dimethylaminopyridine (2 mg) were added. After stirring at 20°C for 6 h, the solvent was evaporated and the residue was purified by FC (3:2, light petroleum:EtOAc): 554 mg (60%), pale yellow oil that solidifies at −20°C, m.p. 112–113°C, 89:11 mixture of β- and α-anomers. $R_f$: 0.39 (3:2, light petroleum:EtOAc). $[\alpha]_D^{25}$ −3.6, $[\alpha]_{577}^{25}$ −1.0, $[\alpha]_{546}^{25}$ −10.2, $[\alpha]_{435}^{25}$ −22.0, $[\alpha]_{405}^{25}$ −31.3 (*c* 1.0, $CH_2Cl_2$). IR (KBr): 2895, 2870, 1750, 1375, 1225, 1145, 1075, 1050, 940, 915, 730, 665. $^1$H NMR (400 MHz, $CDCl_3$) of β-anomer **15**β: 6.24 (*d*, $^3J$=3.6, H-1), 5.85 (*d*, $^3J$=9.6, H-3), 5.43 (*d*, $^3J$=4.5, H-5), 5.29 (*dd*, $^3J$=9.6, 3.6, H-2), 4.42 (*d*, $^3J$=4.5, H-6), 4.20 (*q*, $^3J$=7.2, $CH_2$(EtO)), 4.14, 4.00 (2*m*, $CH_2$–$CH_2$ of dioxolane), 2.29, 2.18, 2.10, 2.05 (4*s*, 4 AcO), 1.26 (*t*, $^3J$=7.2, $CH_3$(EtO)); α-anomer **15**α: 6.15 (*d*, $^3J$=4.6, H-1), 5.50 (*d*, $^3J$=2.7, H-5), 5.49 (*d*, $^3J$=7.5, H-3), 5.13 (*dd*, $^3J$=7.5, 4.6, H-2), 4.52 (*d*, $^3J$=2.7, H-6), 4.20 (*q*, $^3J$=7.2, $CH_2$(EtO)), 4.23, 3.92 (2*m*, 2 $CH_2$(dioxolane)), 2.27, 2.10, 2.07, 2.05 (4*s*, 4 Ac), 1.27 (*t*, *J*=7.2, $CH_3$(OEt)). $^{13}$C NMR (100.6 MHz, $CDCl_3$) of α-anomer **15**α: 169.7, 169.6, 169.4 (4*s*, 4 Ac), 166.9 (*s*, C-7), 105.6 (*s*, C-4), 88.8 (*d*, *J*=176, C-1), 77.2 (*d*, *J*=156, C-6), 70.9 (*d*, *J*=150, C-5), 68.7 (*d*, *J*=153, C-3), 67.9 (*d*, *J*=132, C-2), 66.8, 65.5 (2*t*, *J*=150, 2 $CH_2$ of dioxolane), 61.9 (*t*, *J*=149, $CH_2$(EtO)), 21.1, 20.8, 20.6 (4*q*, *J*=130, 4 Me(Ac)), 14.0 (*q*, Me(EtO)). CI-MS ($NH_3$): 480 (0.3, M+$NH_4^+$), 462 (0.1, $M^{\cdot+}$), 403 (7), 360 (22), 301 (14), 241 (40), 143 (28), 115 (100), 87 (76). Anal. calcd for $C_{19}H_{26}O_{13}$ (462.40): C 49.35, H 5.63; found: C 49.23, H 5.74.

### *4.9. Ethyl 2,5,6-*O*-triacetyl-3,7-anhydro-4-deoxy-4,4-(ethylidenedioxy)-*D*-glycero-*D*-ido-dec-9-eno-pyranuronate (−)-**16***

Pyranoside (−)-**15** (100 mg, 0.216 mmol) was dissolved in 3 ml of 33% HBr in AcOH. After stirring for 2 h at 0°C, evaporation of the solvent afforded the corresponding bromopyranoside as a pale brown oil (81 mg, 78% yield). To a solution of this crude material (62 mg, 0.128 mmol) in 1 ml of anhydrous $CH_2Cl_2$, $ZnBr_2$ (2 equiv. 58 mg, 0.256 mmol) and allyltrimethylsilane (3 equiv. 61 μl, 0.384 mmol) were

added. After stirring for 8 h at 20°C and 12 h at 30°C, the mixture was diluted with EtOAc (10 ml). After washing with a sat. aq. soln of $NaHCO_3$ (5 ml, three times) and with brine (5 ml), the organic layer was dried ($MgSO_4$). Evaporation of the solvent and purification of the residue by FC (3:2, light petroleum:EtOAc) afforded a colorless oil: 34 mg (35%), $R_f$: 0.32 (1:2, light petroleum:EtOAc). $[\alpha]_D^{25}$ −4.7, (*c* 1.1, $CH_2Cl_2$). IR (film): 3100, 2980, 2945, 2915, 1755, 1645, 1430, 1375, 1225, 1130, 1075, 1035, 950, 915, 860. $^1$H NMR (400 MHz, $CDCl_3$): 5.79 (*d*, $^3J$=9.8, H-5), 5.74 (*m*, CH(allyl)), 5.42 (*d*, $^3J$=3.6, H-3), 5.08, 5.02 (*m*, H-6, $CH_2$(allyl)), 4.27, 4.18 (*m*, H-2, $CH_2$(EtO)), 4.12 (*td*, $^3J$=8.7, 4.7, H-7), 4.03, 3.89 (*m*, $CH_2$ of dioxolane), 2.32, 2.08, 2.04 (3*s*, 3 AcO), 2.20, 2.00 (*m*, $CH_2$(allyl)), 1.29 (*t*, $^3J$=7.2, $CH_3$(EtO)). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 170.1, 169.1, 169.2 (3*s*, 3 Ac), 163.0 (*s*, C-1), 133.4 (*d*, *C*H(allyl)), 117.3 (*t*, *C*$H_2$(allyl)), 105.7 (*s*, C-4), 77.5 (*d*, C-3), 73.9 (*d*, C-5), 72.8, 72.5, 72.2 (3 *d*, C-3, C-6, C-7), 66.8, 65.8 (2*t*, 2 $CH_2$ of dioxolane), 61.8 (*t*, $CH_2$(EtO)), 36.6 (*t*, $CH_2$(allyl)), 20.8 (*q*, 3 $CH_3$(Ac)), 14.1 (*q*, $CH_3$(EtO)). CI-MS ($NH_3$): 462 (66, M+$NH_4^+$), 402 (18, M+Ac+1), 325 (11), 215 (12), 173 (16), 102 (100). Anal. calcd for $C_{20}H_{28}O_{11}$ (444.43): C 54.05, H 6.35; found: C 54.16, H 6.32.

### 4.10. *Ethyl 2,2-(ethylidenedioxy)-3,4-*O*-bis[(*t*-butyl)dimethylsilyl]-*D-threo*-penturonate (−)-**17**

Diol (−)-**6** (80 mg, 0.150 mmol) was dissolved in 1:1, $CH_2Cl_2$:MeOH (1.2 ml) and cooled to −78°C. Ozone was bubbled through the solution for 45 min. Three drops of $Me_2S$ were added and the mixture was allowed to warm to 20°C over 1 h. After an additional hour at 20°C $H_2O$ (6 ml) was added. The mixture was extracted with EtOAc (10 ml, three times). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. FC (15:1, light petroleum:EtOAc): 55 mg (80%) colorless oil, $R_f$: 0.71 (4:1, light petroleum:EtOAc). $[\alpha]_D^{20}$ −78 (*c*=0.9, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): 9.68 (*s*, H-5); 4.50 (*d*, $^3J$=2.2, H-2), 4.21 (*dq*, $^2J$=12.8, $^3J$=7.1, $CH_2$(OEt)), 4.15 (*dq*, $^2J$=12.8, $^3J$=7.1, $CH_2$(OEt)), 4.14 (*d*, $^3J$=2.2, H-3), 4.07, 3.99 (*m*, $CH_2$ of dioxolane), 1.30 (*t*, $^3J$=7.1, $CH_3$(OEt)), 0.92, 0.87 (2*s*, $CH_3$(*t*-Bu)), 0.12, 0.03, 0.02, 0.01 (4*s*, $CH_3(SiMe_2)$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 195.5 (C-5), 171.6 (C-1), 105.4 (C-4), 77.9 (C-2), 72.8 (C-3), 66.5, 65.3 (*C*$H_2$ of dioxolane), 61.0 ($CH_2$(OEt)), 25.8, 25.4 ($CH_3$(*t*-Bu)), 18.1, 18.0 ($C(CH_3)_3$), 14.0 ($CH_3$(OEt)), −4.5, −5.0, −5.2, −5.6 ($CH_3(SiMe_2)$). CI-MS ($NH_3$): 480 (100, M+$NH_4^+$), 463 (34, M+$H^+$), 433 (19), 405 (7), 303 (6), 90 (15). Anal. calcd for $C_{21}H_{42}O_7Si_2$ (462.73): C 54.51, H 9.15, Si 12.14; found: C 54.62, H 8.99, Si 12.02.

### 4.11. *Aminals **18** and **19***

Aldehyde **17** (26 mg, 0.056 mmol) was dissolved in $C_6D_6$ (0.5 ml) in an NMR tube. (1*R*,2*R*)-Diphenylethylenediamine (13 mg, 0.062 mmol) was added. After 10 h at 20°C, transformation to the diastereoisomeric aminals **18** and **19** was complete. $^1$H NMR (400 MHz, $C_6D_6$) of **18** (major): 7.43–7.03 (*m*, Har), 5.26 (*s*, H-5), 4.91 (*d*, $^3J$=5.1, H-2), 4.54 (*d*, $^3J$=5.1, H-3), 4.20, 3.96 (*m*, $CH_2$(OEt) and $CH_2$ of dioxolane), 1.11 (*t*, $^3J$=8.1, $CH_3$(OEt)), 1.10, 1.08 (2*s*, $CH_3$(*t*-Bu)), 0.30, 0.28, 0.25, 0.21 ($CH_3(SiMe_2)$).

### 4.12. *(2*S*,3*S*)-Diethyl 2,3-di[(*p*-methoxybenzoyl)oxy]-4,4-ethylenedioxyhept-5-ene-1,7-dioate (−)-**20***

Diol (+)-**5** (1 g, 3.29 mmol) was dissolved in dry pyridine (16 ml) and the solution was cooled to 0°C. *p*-Methoxybenzoyl chloride (2.24 g, 13.2 mmol) and DMAP (50 mg) were added. After 30 min, the mixture was allowed to warm to 20°C and stirred for 4 h. Pyridine was removed in vacuo (oil, pump). The residue was diluted with AcOEt (70 ml), washed successively with aq. 1 N HCl (30 ml), sat. aq. soln of $NaHCO_3$ (30 ml) and brine (30 ml). Drying ($MgSO_4$) and concentration in vacuo afforded a yellow oil which was purified by FC (3:2, light petroleum:EtOAc): 1.35 g (72%), colorless oil, $R_f$: 0.41 (1:2, EtOAc:light petroleum). $[\alpha]_D^{25}$ −15.1, $[\alpha]_{577}^{25}$ −16.1, $[\alpha]_{546}^{25}$ −18.2, $[\alpha]_{435}^{25}$ −19.0, $[\alpha]_{405}^{25}$ −22.0 (*c* 1.0,

$CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$): 8.04 (*m*, 4 Har), 7.03 (*d*, $^3J$=15.7, H-6), 6.95 (*d*, $^3J$=9.0, Har), 6.92 (*d*, $^3J$=9.0, Har), 6.12 (*d*, $^3J$=15.7, H-5), 5.83 (*d*, $^3J$=2.6, H-2), 5.71 (*d*, $^3J$=2.6, H-3), 4.19 (*q*, $^3J$=7.2, $CH_2$(OEt)), 4.14–4.10 (*m*, $CH_2$ dioxolane), 4.06 (*dq*, $^2J$=11.2, $^3J$=7.2, $CH_2$(OEt)), 3.98–3.95 (*m*, $CH_2$ of dioxolane), 3.87, 3.86 (2*s*, $CH_3$(PMBz)), 1.23 (*t*, $^3J$=7.2, $CH_3$(OEt)), 1.16 (*t*, $^3J$=7.2, $CH_3$(OEt)). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 167.3, 165.7, 165.0, 164.7 (4*s*, C=O), 163.8, 163.7 (2*s*, Car), 142.0 (*d*, C-6), 132.2, 132.1 (2*d*, Car), 122.8 (*d*, C-5), 121.5, 121.3 (2*s*, Car), 113.8, 113.6 (2*d*, Car), 106.5 (C-4), 73.4 (*d*, C-2), 70.4 (*d*, C-3), 66.1, 65.1 (2*t*, $CH_2$ of dioxolane), 61.9, 60.5 (2*t*, $CH_2$(OEt)), 55.4 (*q*, $CH_3$(OMe)), 14.0, 13.9 (2*q*, $CH_3$(OEt)). IR (film): 2980, 2905, 2840, 1720, 1605, 1510, 1165, 1370, 1255, 1170, 1095, 1030, 850, 770, 615. Anal. calcd for $C_{29}H_{32}O_{12}$ (572.56): C 60.84, H 5.63; found: C 60.64, H 5.60.

### *4.13. (2S,3S)-2,3-Di[(*p*-methoxybenzoyl)oxy]-4,4-ethylenedioxypentano-1,5-lactone (−)-**22***

Compound (−)-**20** (200 mg, 0.35 mmol) was ozonolyzed for 10 min in 1:6, $CH_2Cl_2$:MeOH (14 ml) at −78°C. $Me_2S$ (64 μl, 0.875 mmol) was added and the mixture was warmed to 0°C. After 15 min, $NaBH_4$ (40 mg, 1.05 mmol) was introduced and the mixture was stirred at 0°C for 25 min, AcOH (100 μl) was added and the solution was poured into a sat. aq. soln of $NaHCO_3$ (20 ml). The aq. layer was extracted with EtOAc (25 ml, three times). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo: 140 mg (80%) of **21**. The oily alcohol **21** was dissolved in 3 ml of anhydrous THF (3 ml), and DBU (125 μl, 0.833 mmol) was added at 0°C. After 2 h at 0°C, the solution was poured into water. The aq. layer was extracted with EtOAc (20 ml, three times). The combined extracts were washed with aq. 1 N HCl (20 ml), then with brine, dried ($MgSO_4$) and concentrated in vacuo. FC (3:1, light petroleum:EtOAc): 77 mg (60%) of (−)-**22**, colorless oil, $R_f$: 0.57 (1:2, EtOAc:light petroleum). $[\alpha]_D^{25}$ −33.4, $[\alpha]_{577}^{25}$ −36.0, $[\alpha]_{546}^{25}$ −42.8, $[\alpha]_{435}^{25}$ −70.9, $[\alpha]_{405}^{25}$ −95.1 (*c* 1.1). CD (MeCN, $2.27\times10^{-4}$ M): $\Delta\varepsilon$=18.7 (246 nm), $\Delta\varepsilon$=−18.4 (264 nm). IR (film): 2980, 2900, 2885, 1760, 1610, 1515, 1475, 1370, 1250, 1170, 1035, 850, 780. $^1$H NMR (400 MHz, $CDCl_3$): 8.05 (*d*, $^3J$=9.0, Har), 8.03 (*d*, $^3J$=9.0, Har), 6.94 (*d*, $^3J$=9.0, 2 Har), 6.87 (*d*, $^3J$=2.8, H-2), 6.55 (*d*, $^3J$=2.8, H-3), 4.20–4.05 (*m*, $CH_2$ of dioxolane), 4.31 (*d*, $^2J$=11.5, H-5), 4.02 (*d*, $^2J$=11.5, H-5), 3.85, 3.83 (2*s*, $CH_3$(OMe)). $^{13}$C NMR (100.6 MHz, $CDCl_3$): 164.8, 164.1, 164.0 (4*s*, 4 C=O), 159.6, 158.9 (2*s*, 2 Car), 132.5, 131.6 (2*d*, *J*=163, Car), 120.6, 119.2 (2*s*, 2 Car), 113.8, 113.7 (2*d*, *J*=162, Car), 105.9 (*s*, C-4), 72.2, 71.0 (2*t*, *J*=150, 148, C-2, C-3), 69.6 (*t*, C-5), 55.5, 55.2 (2*q*, *J*=144, 145, $CH_3$(OMe)). CI-MS ($NH_3$): 476 (51, M+$NH_4^+$), 459 (100, M+$H^+$), 427 (26, M−$OMe^+$). Anal. calcd for $C_{23}H_{22}O_{10}$ (458.42): C 60.26, H 4.84; found: C 59.98, H 4.86.

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