**SUPPORTING INFORMATION FOR:**

# Radical Based Asymmetric Synthesis: An Iterative Approach to 1,3,5...(2n+1) Polyols

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## General Details

All radical addition and auxiliary attachment reactions were performed under an inert, moisture-free atmosphere (Ar). Solvents/reagents were purified beyond reagent grade as follows: THF was distilled from Na/benzophenone; $CH_3CN$, $CH_2Cl_2$ and $Et_3N$ were distilled from $CaH_2$ (0-1 mm grain size, ACROS). All distillations were done in an inert ($N_2$ or Ar), dry environment. Analytical TLC was performed on JT-Baker Si250F plates (0.25 mm). TLC plates were visualized by UV illumination followed by charring with Verghn's reagent (12.5g Ammonium molybdate and 0.5g Ceric sulfate dissolved in 250 mL of 10% aq. $H_2SO_4$). $^1$H-NMR assignments are based on selective homonuclear decoupling experiments. High resolution MS data are reported in units of m/z for $M^+$ or the highest mass fragment derived from $M^+$.

## Procedure for Radical Additions:

A dry THF solution of the acid was added to a foil-covered 2-neck round bottom flask containing a dry $CH_3CN$ solution of HOTT (1.5 equiv) and DMAP (0.1 equiv) (it was later determined that DMAP was <u>not</u> necessary) at room temperature under Ar. The final concentration of the acid was 0.1 M in 3:1 THF-$CH_3CN$. $Et_3N$ was added to the reaction mixture and the resulting solution stirred (in the dark) for 30 min under Ar at room temperature. The reaction was judged to be complete based on IR analysis (the appearance of the Barton ester C=O at 1810-1820 $cm^{-1}$ and the disappearance of the starting acid C=O at 1735-1745 $cm^{-1}$). The trap (3-10 equiv) was added, and the resulting solution cooled to 0 °C. The foil was removed and placed directly under the flask to reflect the light from the sunlamp in the photolysis. The reaction mixture was photolyzed for 25-30 min using a 275W sunlamp. The photolysis was monitored by TLC (40% EtOAc/hexs). Upon completion of the photolysis, the reaction was stopped and the solvent removed via rotary evaporation. To faciliate the determination of diastereomer ratios, the crude product was filtered through a small plug of $SiO_2$ (3-5 cm high x 1.5-3 cm wide) eluting with 50-100 mL 40% EtOAc/hexs. The crude product was purified by column chromatography using EtOAc/hexs.

**1a** → **6a.** A dry THF (11.9 mL) solution of the acid **1a** (0.85 g, 1.6 mmol) was added to a foil-covered 2-neck round bottom flask containing a dry $CH_3CN$ (4 mL) solution of HOTT (0.89 g,.

2.4 mmol) and DMAP (.02 g, 0.16 mmol) to make a 0.1 M solution in 3:1 THF-$CH_3CN$. $Et_3N$ (0.66 mL, 4.8 mmol) was added and the resulting solution stirred under Ar at room temperature for 30 min. IR analysis of an aliquot taken in the dark showed a complete reaction. TLC (40% EtOAc/hexs) of the Barton ester showed one spot at $R_f$ 0.27. The trap (0.81 mL, 4.8 mmol) was added, and the reaction mixture cooled to 0 °C. The foil was removed and placed directly under the flask to reflect the light from the sunlamp. The reaction mixture was photolyzed using a 275 W sunlamp for 25 min. TLC (40% EtOAc/hexs) showed complete disappearance of the Barton ester and a charred UV spot at $R_f$ 0.71. Other components on TLC are UV active but do not char when using Verghn's reagent. The reaction was stopped and the solvent removed. The crude product was dissolved in 3.0 mL $CHCl_3$ and filtered through a short plug (4 cm high x 3 cm wide) of $SiO_2$ (wetted with eluent) and eluted with 75 mL 40% EtOAc/hexs. The filtrate was concentrated. The crude product was purified using column chromatography ($SiO_2$) eluting with 18% EtOAc/hexs to give **6a** as a light yellow oil, 90% yield.

**Procedure for α-ketoester reduction:**

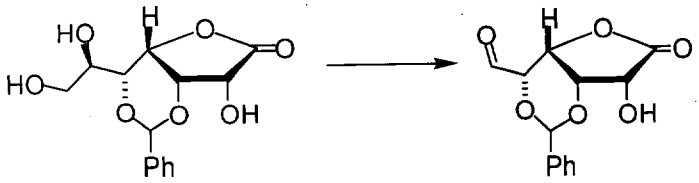
To a 0 °C absolute EtOH solution of the α-keto-ester was added a slightly basic EtOH solution of $NaBH_4$ (0.25 equiv) over a period of 2-3 min. The $NaBH_4$ solution was made basic by adding a couple drops (3 drops per 1.3 mmol) of 1.0 M aq NaOH for stabilization. The reaction was monitored by TLC (30% EtOAc/hexs) and the reduction is complete after 5 min. The reaction was quenched with EtOAc. The reaction mixture was poured into a small amount of saturated aq bicarbonate solution and extracted 3x EtOAc. Depending on the purity of the starting ketoester, the α-hydroxyester product can usually be used without purification in the subsequent protection step.

**6a → 7a.** An EtOH (5.0 mL) solution of $NaBH_4$ (18.7 mg, 0.50 mmol, 0.25 equiv) containing 3 drops of 1.0 M aq NaOH was added to a 0 °C EtOH (14.8 mL, 0.13 M) solution of the α-ketoester **6a** (1.20 g, 1.98 mmol) over a period of 5 min. TLC (30% EtOAc/hexs) showed a complete reaction after 5 min. The reaction was quenched with 10 mL EtOAc. The solvent was removed using rotary evaporation and the crude product dissolved in 50 mL EtOAc and washed with 10 mL saturated aq bicarbonate, 10 mL water, and then 15 mL brine. The organic layer was dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by flash chromatography using 28% EtOAc/hexs to give **7a** as an oil, 78% yield.

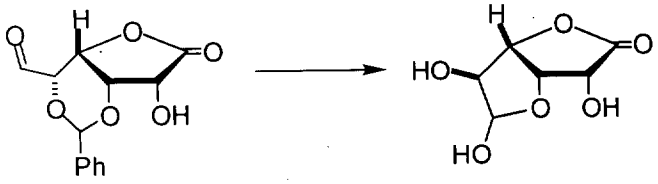
**Procedure for auxiliary introduction:**

The starting α-hydroxyester and appropriate glycal (1.5 equiv) were dissolved in toluene (~10 mL) and the toluene removed via rotary evaporation to azeotrope possible traces of water. The flask contents were concentrated further by vacuum pumping for 30-60 min. The flask was flushed with Ar and covered with foil. Solid $HBr{\cdot}PPh_3$ (3-5 mol%) was added followed by dry $CH_2Cl_2$ to make a 0.2 M solution. The resulting solution was stirred in the dark (2-3 h for initial protection, 24-48 h for subsequent protections) under Ar at room temperature. The reaction was monitored by TLC (25% EtOAc/hexs). Upon completion, the reaction was quenched with saturated aq bicarbonate and extracted 3 x with EtOAc. The organic layers were combined and washed with brine, dried over $Na_2SO_4$, filtered and concentrated.

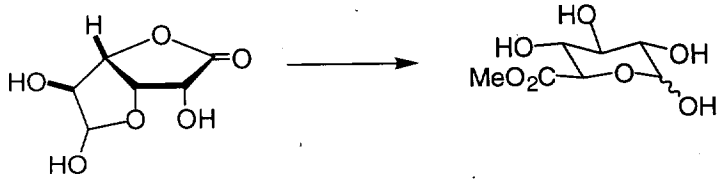
**L-auxiliary synthesis:**



Step 1: 3,5(R)-O-Benzylidene-D-*gulo*-heptono-1,4-lactone (prepared in 95% yield from α-D-glucoheptonic γ-lactone according to the procedure of Fleet *et. al.*[1]) (30.0 g, 101 mmol) was added to a 0 °C solution of $NaIO_4$ (23.5 g, 110 mmol in water (450 mL). The resulting suspension was stirred at 0 °C for 90 min and then slowly warmed for 25 min after removing the ice bath. The reaction was complete according to TLC (10% MeOH/EtOAc). The flask contents were suction-filtered and concentrated using rotary evaporation (water bath 29-31 °C). The filter cake was collected in a 600 mL beaker and 300 mL MeOH added. This suspension was stirred vigorously for 45 min to extract additional aldehyde from the collected solids. The suspension was suction filtered and the filtrate added to the initial (concentrated) filtrate and the solvent removed by rotary evaporation to give a wet, slightly yellow solid.



Step 2: To the crude solid was added 1.0 M aq HCl (300 mL) and the resulting mixture was stirred overnight at room temperature. The next morning, after 12 h, the benzylidene deprotection was not complete. The reaction was heated to 55-60 °C using a hot water bath and the deprotection was complete 2 h after heating as seen by TLC (20% MeOH/EtOAc). The reaction mixture was cooled to room temperature and the reaction contents extracted 3 x 100 mL $Et_2O$ to remove benzaldehyde. The aqueous layer was collected and concentrated using rotary evaporation. Once concentrated, 50 mL water was added and the solution concentrated again. This process was repeated once more to remove additional HCl.

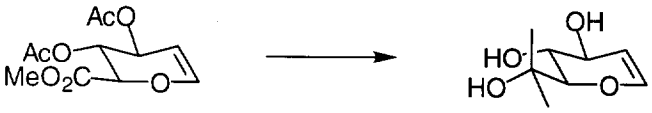


Step 3: In the same flask, 100 mL MeOH was added followed by sufficient NaOMe to make the solution slightly basic (pH ~9) on wet pH paper. The solution turns yellow upon the addition of NaOMe. The reaction mixture was stirred for 1 h at room temperature. TLC showed that the

[1] Bichard, C.J.F.; Bruce, I.; Hughes, D.J.; Girdhar, A.; Fleet, G.W.J.; Watkin, D.J. *Tetrahedron: Asymmetry* **1993**, *4*, 1579-1589.

reaction was nearly complete, however the starting material (L-glucuronolactone) has never disappeared completely in this reaction. The reaction was stopped and the solvent removed using rotary evaporation.


Steps 4-6: The subsequent peracetylation, bromination, and reductive elimination intersect the procedure of Fehlhaber *et. al.*[2] with the addition of using copper sulfate (10 wt% based on zinc) in the elimination. Data for triester: $[\alpha]^{23}_D$ +61.9° (c 1.77, $CHCl_3$); literature data for D-isomer[2,3]: $[\alpha]^{25}_D$ –61.3° (c 0.87, $CHCl_3$); $^1$H-NMR (300 MHz, $CDCl_3$) matched the spectra of the D-isomer.




Step 7: A dry THF (17 mL, 0.44 M) solution of the triacetate (1.89 g, 7.4 mmol) was added to a 0 °C 3.0 M THF solution of MeMgCl (17 mL, 7 equiv) over a period of 5 min under Ar. The resulting solution was allowed to warm to room temperature and stirred for 90 min. TLC (70% EtOAc/hexs) showed a complete reaction. The reaction was quenched at 0 °C with the careful addition of 5 mL saturated aq $NH_4Cl$ solution. The reaction mixture was poured onto 25 mL $H_2O$ and extracted 4 x 40 mL EtOAc. The organic layers were combined and washed with 50 mL brine, dried over $Na_2SO_4$, filtered and concentrated. No purification, 87% crude yield.


**10**

Step 8: A dry THF (10 mL) solution of the crude triol (5 mmol) was added dropwise to a dry THF (10mL) suspension of NaH (1.0 g of a 60 wt% oil dispersion, 5 equiv) over a period of 5 min at room temperature. The resulting mixture was stirred under Ar at room temperature for 20 min. The reaction mixture was cooled to 0 °C and methyl iodide (25 mmol) added dropwise over a period of 5 min. The resulting mixture was warmed to room temperature and stirred vigorously overnight under Ar. After 12 h, the TLC (15% EtOAc/hexs) showed a clean formation of a new product and that the triol had been consumed. The reaction was quenched by pouring the reaction mixture onto ice (25 mL) and then extracted 3 x 35 mL $Et_2O$. The organic layers were combined and washed with brine (10 mL), dried over $Na_2SO_4$, filtered and concentrated by rotary evaporation. Purified using column chromatography ($SiO_2$) eluting with 12% EtOAc/hexs to give a clear oil, 74%. $R_f$ 0.30, 15% EtOAc/ hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 6.41 (m, 1H, H-1), 4.82 (dd, $J_1$ = 6.0 Hz $J_2$ = 2.3 Hz, 1H, H-2), 3.97 (ddd, $J_1$ = 7.0 Hz $J_2$ = $J_3$ = 1.6 Hz, 1H, H-3),

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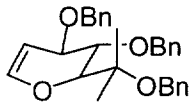
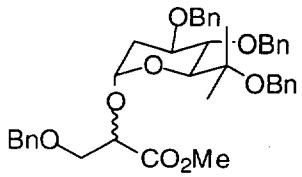
[2] Wyss, P.C.; Kiss, J.; Arnold, W. *Helv. Chim. Acta* **1975**, *58*, 1847-1864.
[3] Fehlhaber, H.W.; Snatzke, G.; Vlahov, I. *Liebigs Ann. Chem.* **1987**, 637-638.

3.68 ( d, J = 9.5 Hz, 1H, H-5), 3.58 (s, 3H, -$OCH_3$) 3.50 (dd, $J_1$ = 9.6 Hz $J_2$ = 6.9 Hz, 1H, H-4), 3.41 (s, 3H, $OCH_3$), 3.28 (s, 3H, $OCH_3$), 1.30 (s, 6H, 2 x $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$) δ 144.81, 99.81, 79.69, 77.75, 75.99, 59.29, 55.64, 49.52, 22.98, 22.34; EIMS (m/z): $M^+$ calcd for $C_{11}H_{20}O_4$, 216.1362; found, 216.1362.

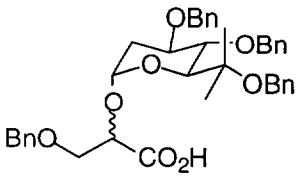



**2**

$R_f$ 0.29, 10% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.35-7.20 (15H, 3 x Ph), 6.44 (d, J = 4.6 Hz, 1H, H-1), 4.90 (2H, H-2 + ½ C$H_2$Ph), 4.76-4.52 (5H, 2½ C$H_2$Ph), 4.31 (m, 1H, H-3), 3.99 (dd, $J_1$ = 9.2 Hz, $J_2$ = 6.7 Hz, H-4), 3.84 (d, J = 9.2 Hz, H-5), 1.42 (s, 3H, $CH_3$), 1.40 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): δ 145.16, 139.65, 138.43, 138.31, 128.38, 128.24, 128.17, 127.95, 127.84, 127.61, 127.45, 127.28, 127.02, 100.28, 82.30, 78.33, 76.76, 76.53, 73.92, 70.78, 64.27, 24.59, 23.41; EIMS (m/z): [M - $CH_2Ph$]$^+$ calcd for $C_{22}H_{25}O_4$, 353.1753; found, 353.1730.



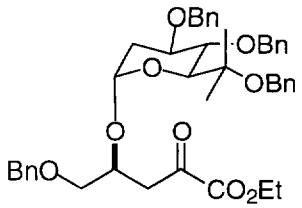

Mixture of diastereomers: $R_f$ 0.23, 20%EtOAc/hexs; $R_f$ 0.28, 20% EtOAc/hexs; Data for the more polar diastereomer: $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.32-7.20 (20H, 4 x Ph), 5.12-5.07 (m, 1H, H-1'), 4.82 (d, J = 11.0 Hz, 1H, ½ C$H_2$Ph), 4.68-4.47 (8H, 3½ C$H_2$Ph, H-2), 4.06-3.96 (m, 1H, H-3'), 3.80-3.64 (7H, H-4', H-5', -$OCH_3$, H-3), 2.40 (ddd, $J_1$ = 13.7 Hz, $J_2$ = 4.4 Hz, $J_3$ = 2.7 Hz, 1H, H-2' eq), 1.91 (ddd, $J_1$ = 13.7 Hz $J_2$ = 9.3 Hz $J_3$ = 4.4 Hz, 1H, H-2' ax), 1.33 (s, 3H, $CH_3$), 1.31 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): δ 170.85, 139.94, 138.62, 138.49, 137.66, 128.54, 128.34, 128.16, 128.09, 127.80, 127.67, 127.52, 127.28, 127.07, 126.85, 95.85, 78.52, 77.33, 77.19, 76.65, 75.90, 73.61, 73.47, 71.64, 70.20, 64.26, 52.11, 33.80, 24.68, 23.26; EIMS (m/z): [M - $CH_2Ph$]$^+$ calcd for $C_{33}H_{39}O_8$, 563.2645; found, 563.2650.




**1b**

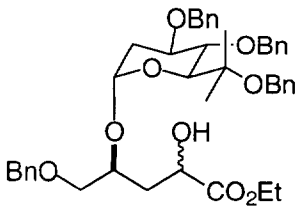
Mixture of diastereomers: $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.36-7.19 (20H, 4 x Ph), 5.22-5.19 (m, ½ H, H-1'), 5.13 (m, ½ H, H-1'), 4.82-4.44 (9H, 4 x C$H_2$Ph, H-2), 4.02-3.94 (m, 1H, H-3'), 3.87-3.69 (4H, H-4', H-5', H-3), 2.40-2.21 (m, 1H, ½ H-2'), 2.05-1.87 (m, 1H, ½ H-2'), 1.43-1.30 (6H,

2 x $CH_3$); IR (neat): 1730 $cm^{-1}$ (C=O); EIMS (m/z): calcd $[M - BnOCH_2CHCO_2H]^+$ for $C_{29}H_{33}O_5$, 461.2328; found, 461.2332.



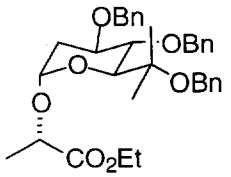

**6b**

$R_f$ (major diastereomer, shown) 0.35, 25%EtOAc/hexs; $R_f$ (minor diastereomer) 0.40, 25%EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.33-7.18 (20H, 4 x Ph), 5.16 (m, 1H, H-1'), 4.79-4.54 (6H, 3 x C$H_2$Ph), 4.45 (d, J = 12.1 Hz, 1H, ½ C$H_2$Ph), 4.38 (d, J = 12.1 Hz, 1H, ½ C$H_2$Ph), 4.32-4.28 (m, 1H, H-4), 4.24 (q, J = 7.1 Hz, 2H, OC$H_2$CH$_3$), 3.92-3.86 (m, 1H, H-3') 3.79-3.67 (2H, H-4' H-5') 3.61 (dd, $J_1$ = 9.5 Hz, $J_2$ = 4.7 Hz, 1H, ½ H-5), 3.41 (dd, $J_1$ = 9.5 Hz $J_2$ = 6.8 Hz, 1H, ½ H-5), 3.18 (dd, $J_1$ = 16.4 Hz, $J_2$ = 6.2 Hz, 1H, ½ H-3), 3.05 (dd, $J_1$ = 16.4 Hz, $J_2$ = 6.4 Hz, 1H, ½ H-3), 2.11 (ddd, $J_1$ = 13.3 Hz, $J_2$ = $J_3$ = 4.0 Hz, 1H, H-2' eq), 1.81 (ddd, $J_1$ = 13.6 Hz, $J_2$ = 9.5 Hz $J_3$ = 4.3 Hz, 1H, H-2' ax), 1.36-1.29 (9H, OCH$_2$C$H_3$, 2 x $CH_3$); $^{13}$C-NMR (APT) (75 MHz, $CDCl_3$): δ 191.96 (+), 160.72 (+), 139.96 (+), 138.56 (+), 138.46 (+), 137.62 (+), 128.34 (-), 128.30 (-),128.17 (-), 128.14 (-), 128.13 (-), 128.07 (-), 127.64 (-), 127.51 (-), 127.49 (-), 127.24 (-), 127.16 (-), 127.13 (-), 127.10 (-), 126.84 (-), 96.47 (-), 78.36 (-), 77.12 (-), 76.71 (+), 76.22 (-), 73.33 (+), 73.18 (+), 72.02 (-), 71.64 (+), 71.52 (+), 64.36 (+), 62.38 (+), 41.61 (+), 33.98 (+), 24.88 (-), 23.21 (-), 13.91 (-); EIMS (m/z): $[M - CH_2Ph]^+$ calcd for $C_{36}H_{43}O_9$, 619.29071; found, 619.29270; $[M - OCH_2Ph]^+$ calcd for $C_{36}H_{43}O_8$, 603.2958; found, 603.2896.

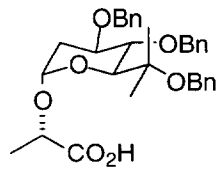



**7b**

Mixture of diastereomers: $R_f$ 0.30, 30% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.36-7.18 (20H, 4 x Ph), 5.17-5.12 (m, ½ H, ½ anomeric-H), 5.09-5.04 (m, ½ H, ½ anomeric-H), 4.83-4.74 (m, 1H, ½ C$H_2$Ph), 4.69-4.43 (7H, 3½ C$H_2$Ph), 4.30-4.15 (3H), 4.09-3.88 (2H), 3.80-3.74 (2H), 3.67-3.44 (2H), 3.15-2.85 (br, OH), 2.26-1.76 (4H), 1.33-1.27 (9H); EIMS (m/z): $[M - CH_2Ph]^+$ calcd for $C_{36}H_{45}O_9$, 621.3064; found, 621.3075; $[M - OCH_2Ph]^+$ calcd for $C_{36}H_{45}O_8$, 605.3114; found, 605.3117.

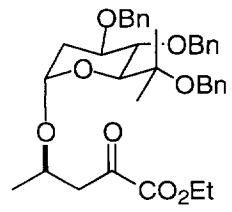



$R_f$ 0.47, 25% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.34-7.19 (15H, 3 x Ph), 5.07 (m, 1H, H-1'), 4.81-4.58 (6H, 3 x C*H*$_2$Ph), 4.27 (q, J = 6.8 Hz, 1H, $CH_3CHOCO_2Et$), 4.23-4.13 (2H, $OCH_2CH_3$), 4.04-3.97 (m, 1H, H-3'), 3.87-3.79 (2H, H-4', H-5'), 2.25 (ddd, $J_1$ = 13.4 Hz, $J_2$ = $J_3$ = 4.3 Hz, 1H, H-2' eq), 1.88 (ddd, $J_1$ = 13.9 Hz, $J_2$ = 9.6, Hz $J_3$ = 4.5 Hz, 1H, H-2' ax), 1.40-1.38 (9H, 2 x $CH_3$, $CH_3CHOCO_2Et$), 1.27 (t, J = 7.1 Hz, 3H, $OCH_2CH_3$); $^{13}$C-NMR (75MHz, $CDCl_3$): δ 172.42, 140.04, 138.72, 138.57, 128.32, 128.10, 127.80, 127.64, 127.51, 127.18, 127.09, 126.84, 95.72, 78.55, 77.36, 76.65, 76.13, 73.28, 71.81, 71.20, 64.34, 60.84, 34.24, 25.08, 23.09, 17.45, 14.17; EIMS (m/z): calcd $[M - CH_2Ph]^+$ for $C_{27}H_{35}O_7$, 471.2383; found, 471.2379; calcd $[M - C(CH_3)_2OCH_2Ph]^+$ for $C_{24}H_{29}O_6$, 413.1964; found, 413.1962.




**1a**

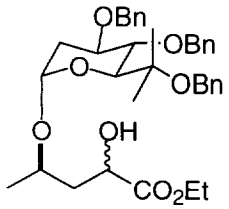
$^1$H-NMR (300 MHz, $CDCl_3$): δ 7.33-7.18 (15H, 3 x Ph), 5.11 (m, 1H, H-1'), 4.73-4.56 (6H, 3 x C*H*$_2$Ph), 4.32 (q, J = 6.9 Hz, 1H, $CH_3CHOCO_2H$), 3.94 (m, 1H, H-3'), 3.87-3.77 (2H, H-4', H-5'), 2.19 (ddd, $J_1$ = 13.7 Hz, $J_2$ = $J_3$ = 4.0 Hz, 1H, H-2' eq), 1.99 (ddd, $J_1$ = 13.3 Hz, $J_2$ = 8.2 Hz, $J_3$ = 5.0 Hz, 1H, H-2' ax), 1.43 (d, J = 6.8 Hz, 3H, $CH_3CHOCO_2H$), 1.36 (s, 3H, $CH_3$), 1.33 (s, 3H, $CH_3$); $^{13}$C-NMR (APT) (75 MHz, $CDCl_3$): δ 176.92 (+), 139.84 (+), 138.33 (+), 128.36 (-), 128.20 (-), 128.13 (-), 127.66 (-), 127.36 (-), 127.14 (-), 126.92 (-), 95.87 (-), 77.93 (-), 76.59 (-), 73.07 (+), 71.66 (+), 71.08 (-), 64.36 (+), 33.42 (+), 24.69 (-), 22.85 (-), 17.35 (-); IR (neat): 1745 cm$^{-1}$ (C=O); EIMS (m/z): $[M - CH_2Ph]^+$ calcd for $C_{25}H_{31}O_7$, 444.2070; found 444.2099.




**6a**

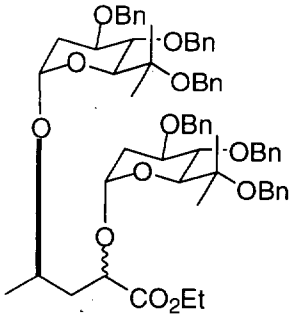
$R_f$ (major diastereomer, shown) 0.32, 25% EtOAc/hexs; $R_f$ (minor diastereomer) 0.38, 25% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.35-7.19 (15H, 3 x Ph), 5.12 (m, 1H, H-1'), 4.79 (d, J = 10.7 Hz, 1H, ½ C*H*$_2$Ph), 4.65-4.55 (5H, 2½ C*H*$_2$Ph), 4.30 (q, J = 7.1 Hz, 2H, $OCH_2CH_3$), 4.24 (q, J = 6.0 Hz, 1H, H-4), 3.94-3.87 (m, 1H, H-3'), 3.81-3.70 (1H, H-4', H-5'), 3.07 (dd, $J_1$ =

16.7, Hz $J_2$ = 6.7 Hz, 1H, ½ H-3), 2.92 (dd, $J_1$ = 16.8 Hz, $J_2$ = 5.5 Hz, 1H, ½ H-3), 2.08 (ddd, $J_1$ = 13.2 Hz, $J_2$ = $J_3$ = 4.2 Hz, 1H, H-2' eq), 1.79 (ddd, $J_1$ = 13.9 Hz, $J_2$ = 9.6 Hz, $J_3$ = 4.4 Hz, 1H, H-2' ax), 1.41-1.33 (9H, 2 x $CH_3$, $OCH_2CH_3$), 1.26 (d, J = 6.3 Hz, 3H, H-5); $^{13}$C-NMR (75MHz, $CDCl_3$): δ 192.71, 168.87, 139.95, 138.52, 128.27, 128.12, 128.05, 127.68, 127.60, 127.44, 127.23, 127.07, 126.81, 96.70, 78.48, 77.33, 76.75, 76.22, 73.41, 71.51, 69.67, 64.38, 62.46, 45.79, 34.19, 25.10, 23.33, 21.68, 13.93; EIMS (m/z): $M^+$ calcd for $C_{36}H_{44}O_8$, 604.3036; found, 604.3039.

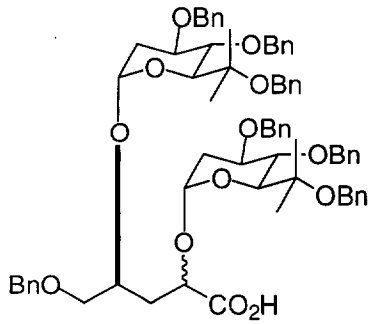



**7a**

Mixture of diastereomers: $R_f$ 0.45, 30% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$): δ 7.39-7.14 (15H, 3 x Ph), 5.13-5.09 (m, ½ H, ½ anomeric-H), 5.07-5.00 (m, ½ H, ½ anomeric-H), 4.85-4.73 (m, 1H, ½ $CH_2Ph$), 4.71-4.50 (5H, 2½ $CH_2Ph$), 4.31-4.09 (3H), 4.06-3.85 (2H), 3.85-3.63 (2H), 3.08-2.84 (br, OH), 2.25-2.04 (m, 1H), 2.04-1.72 (m, 1H), 1.72-1.56 (m, 1H), 1.49-1.09 (12H); EIMS (m/z): $[M - CH_2Ph]^+$ calcd for $C_{29}H_{39}O_8$, 515.2645; found. 515.2650.

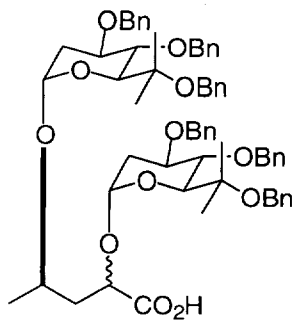



Mixture of diastereomers: $R_f$ 0.42, 20% EtOAc/hexs; HRMS-MALDI-TOF (2,5-dihydrobenzoic acid matrix, m/z): $[M + Na]^+$ calcd for $C_{65}H_{78}O_{12}Na$, 1074.32; found, 1074.32; $[M + K]^+$ calcd for $C_{65}H_{78}O_{12}K$, 1090.43; found, 1090.17.



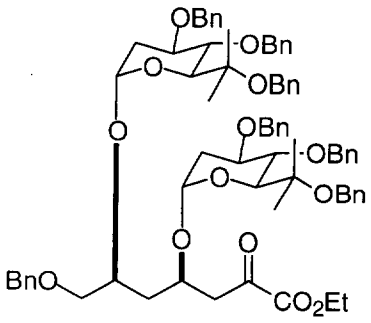
**8b**

Mixture of diastereomers: HRMS-MALDI-TOF (2,5-dihydrobenzoic acid matrix, m/z): $[M + Na]^+$ calcd for $C_{70}H_{80}O_{13}Na$, 1152.39; found, 1152.54; $[M + K]^+$ calcd for $C_{70}H_{80}O_{13}K$, 1168.50; found, 1168.68.



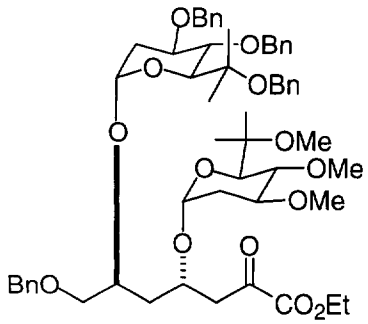
**8a**

Mixture of diastereomers: HRMS-MALDI-TOF (2,5-dihydrobenzoic acid matrix, m/z): $[M + Na]^+$ calcd for $C_{63}H_{74}O_{12}Na$, 1046.26; found, 1045.93; $[M + K]^+$ calcd for $C_{63}H_{74}O_{12}K$, 1062.37; found, 1062.12.



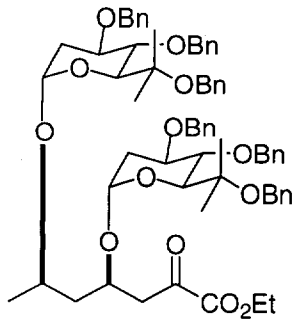
**9b**

$R_f$ (major diastereomer, shown) 0.37, 25% EtOAc/hexs; $R_f$ (minor diastereomer, anti) 0.44, 25% EtOAc/hexs; Diagnostic peaks in $^1$H-NMR (300 MHz, $CDCl_3$): (major) δ 3.08 (2H, H-3); (minor) δ 3.33 (dd, $J_1$ = 15.9 Hz, $J_2$ = 6.6 Hz, 1H, ½ H-3), 2.97 (dd, $J_1$ = 15.9 Hz, $J_2$ = 6.0 Hz, 1H, ½ H-3); HRMS-MALDI-TOF (2,5-dihydrobenzoic acid matrix, m/z): $[M + Na]^+$ calcd for $C_{74}H_{86}O_{14}Na$, 1222.48; found, 1223.44.



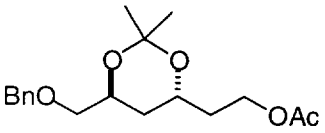

**12**

$R_f$ (major diastereomer, shown) 0.30, 30% EtOAc/ hexs; Diagnostic peaks in $^1$H-NMR (300 MHz, $CDCl_3$): (major diastereomer, anti) δ 3.05 (2H, H-3); (minor diastereomer, syn) δ 2.68 (dd, $J_1$ = 15.9 Hz, $J_2$ = 5.5 Hz, 1H, ½ H-3), 2.55 (dd, $J_1$ = 15.9 Hz, $J_2$ = 7.1 Hz, 1H, ½ H-3); HRMS-FAB (m-nitrobenzyl alcohol matrix + NaI, m/z): $[M + Na]^+$ calcd for $C_{56}H_{74}O_{14}Na$, 993.4976; found, 993.4960.




**9a**

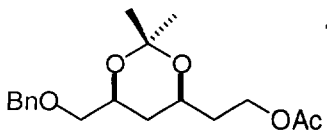
$R_f$ (major diastereomer, shown) 0.21, 20% EtOAc/hexs; $R_f$ (minor diastereomer, anti) 0.28, 20% EtOAc/hexs; Diagnostic peaks in $^1$H-NMR (300 MHz, $CDCl_3$): (major, syn) δ 3.12 (dd, $J_1$ = 17.0 Hz, $J_2$ = 4.9 Hz, 1H, ½ H-3), 3.00 (dd, $J_1$ = 16.9 Hz, $J_2$ = 6.6 Hz, 1H, ½ H-3); (minor, anti) δ 3.29 (dd, $J_1$ = 16.5 Hz, $J_2$ = 6.6 Hz, 1H, ½ H-3), 2.95 (dd, $J_1$ = 16.5 Hz, $J_2$ = 6.0 Hz, 1H, ½ H-3); HRMS-MALDI-TOF (2,5-dihydrobenzoic acid matrix, m/z): $[M + Na]^+$ calcd for $C_{67}H_{80}O_{13}Na$, 1116.35; found, 1116.15; $[M + K]^+$ calcd for $C_{67}H_{80}O_{13}K$, 1132.46; found, 1132.46.




**15**

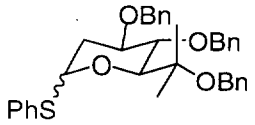
$R_f$ 0.32, 20% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.37-7.27 (5H, Ph), 4.62 (d, J = 12.1 Hz, 1H, ½ C$H_2$Ph), 4.55 (d, J = 12.1 Hz, 1H, C$H_2$Ph), 4.15 (t, J = 6.6 Hz, 2H, H-6), 4.11-4.00 (m, 1H, H-2), 3.97-3.86 (m, 1H, H-3), 3.51 (dd, $J_1$ = 10.4 Hz, $J_2$ = 6.0 Hz, 1H, ½ H-1), 3.43 (dd, $J_1$ = 10.4 Hz $J_2$ = 4.4 Hz, 1H, ½ H-1), 2.04 ( s, 3H, OAc), 1.79 (q, J = 6.6 Hz, 2H, H-5), 1.74-1.64

(1H, ½ H-3), 1.62-1.51 (m, 1H, ½ H-3), 1.37 (s, 3H, $CH_3$), 1.35 (s, 3H, $CH_3$); $^{13}$C-NMR (75MHz, $CDCl_3$) δ 171.42, 137.70, 128.33, 127.68, 127.59, 100.51, 73.31, 72.52, 66.14, 63.32, 61.03, 34.61, 24.66, 20.94; EIMS (m/z): $[M - CH_3]^+$ calcd for $C_{17}H_{23}O_5$, 307.1546; found, 307.1539.



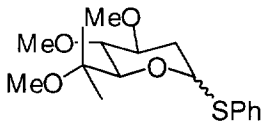

**13**

$R_f$ 0.32, 20% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (5H, Ph), 4.60 (d, J = 12.1 Hz, 1H, ½ C$H_2$Ph), 4.54 (d, J = 12.1 Hz, 1H, ½ C$H_2$Ph), 4.16 (t, J = 6.6 Hz, 2H, H-6), 4.13-4.03 (m, 1H, H-2), 4.03-3.89 (m, 1H, H-4), 3.51 (dd, $J_1$ = 9.9 Hz, $J_2$ = 6.0 Hz, 1H, ½ H-1), 3.37 (dd, $J_1$ = 9.9 Hz, $J_2$ = 4.9 Hz, 1H, ½ H-1), 2.05 (s, 3H, OAc), 1.85-1.70 (2H, H-5), 1.59-1.51 (apparent dt, 1H, ½ H-3), 1.45 (s, 3H, $CH_3$), 1.40 (s, 3H, $CH_3$), 1.29-1.20 (m, 1H, ½ H-3); $^{13}$C-NMR (75MHz, $CDCl_3$) δ 171.18, 138.19, 128.36, 127.73, 127.63, 98.70, 73.52, 73.45, 68.44, 65.61, 60.85, 35.38, 33.78, 30.05, 20.97, 19.67; EIMS (m/z): $[M - CH_3]^+$ calcd for $C_{17}H_{23}O_5$, 307.1546; found, 307.1548.




**14**

Mixture of anomers (α/β 2:1); $R_f$ 0.61, 25% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.55-7.44 (m), 7.44-7.20 (m), 5.83 (t, J = 5.7 Hz), 4.93-4.54 (m), 4.05 (d, J = 8.2 Hz), 3.98-3.85 (m), 3.81-3.69 (m), 3.35 (d, J = 8.8 Hz), 2.51-2.43 (m), 2.36-2.19 (m), 1.88-1.74 (m), 1.42 (s), 1.40 (s), 1.37 (s), 1.27 (s); EIMS (m/z): $M^+$ calcd for $C_{35}H_{38}O_4S$, 554.2491; found, 554.2494.




**16**

Mixture of anomers(α/β ~5:1); Data for α-anomer: $R_f$ 0.26, 20% EtOAc/hexs; $^1$H-NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (2H, 2/5 x Ph), 7.40-7.18 (3H, 3/5 x Ph), 5.77 (dd, $J_1 = J_2$ = 5.7 Hz, H-1), 3.79 (d, J = 8.7 Hz, H-5), 3.56-3.52 (m, H-3), 3.49-3.41 (2 x OMe, H-4), 3.48 (s, $OCH_3$), 3.45 (s, $OCH_3$), 3.24 (s, 3H, $OCH_3$), 2.17 (ddd (app t), $J_1 = J_2$ = 5.9 Hz, $J_3$ = 0 Hz, 2H, H-2), 1.22 (s, $CH_3$), 1.11 (s, $CH_3$); EIMS (m/z): $[M - SPh]^+$ calcd for $C_{11}H_{21}O_4$, 217.1440; found, 217.1450.