was added with stirring at room temperature. After 1.5 h the reaction was judged complete by TLC (25:75 ethyl acetate-hexanes, R_f(15) = 0.62, R_f(16) = 0.17). The mixture was concentrated, taken into 300 mL of dichloromethane, and washed with 200 mL of water. The aqueous layer was back-extracted with 2 × 100 mL of dichloromethane, and the combined organic solutions were dried ($MgSO_4$) and concentrated to a dark oil. This residue was subjected to silica gel chromatography (500 g) made up in 20:80 ethyl acetate-hexanes and eluted with 30:70 of the same to give 17.2 g of 16 (93%) as a clear oil: $[\alpha]^{25}_D$ -77.9° (c 0.43, MeOH), -5.95 (c 1.0, $CHCl_3$); IR (neat) 3413 (br), 1964, 1736, 1420, 1246, 1154, 1057. ^{1}H NMR (500 MHz) 5.37 (m, 2 H), 4.09 (dd, J = 5.7, 3.1, 2 H), 3.69 (s, 3 H), 2.47 (m, 2 H), 2.35 (m, 2 H), 1.88 (br s, 1 H exchanges with D_2O); ^{13}C NMR 23.4, 32.6 (each t), 51.9 (q), 60.3 (T), 92.4, 93.5 (each d), 173.4, 202.9 (each s); MS m/e (relative intensity) 156 (M^+, 6), 138 (18), 110 (100), 97 (22), 79 (43). Anal. Calcd for $C_8H_{12}O_3$: c, 61.53; H, 7.75. Found: C, 61.28; H, 7.82.

Mosher esters 17, 18, and 19 were prepared using the standard procedure[21] and were carefully[39] purified by radial chromatography (15:85 ethyl acetate-hexanes) prior to analysis.

(39) Although no separation of diastereoisomers was observed on TLC, care was taken to avoid discarding any early or late fractions which could have been diastereomerically enriched.

17: ^{13}C NMR (125 MHz) 24.0, 27.5, 33.2 (each t, CH_2), 51.5 (q, CO_2CH_3), 55.5 (q, OCH_3), 64.65 (t, OCH_2, C1),[35] 86.38 (d, HC=, C2), 92.39 (d, =CH, C4), 166.3 (s, CO_2CH_2), 173.8 (s, CO_2CH_3), 206.42 (s, =C=, C3).

18: unlisted data were identical with that of compound 17; ^{13}C NMR (125 MHz) 64.61 (t, OCH_2, C1), 86.42 (d, HC=, C2), 92.47 (d, =CH, C4), 206.29 (s, =C=, C3).

Mosher ester of racemic 16.[36] ^{13}C NMR (125 MHz) 23.2, 32.8 (both t, CH_2), 51.6 (q, CO_2CH_3), 55.5 (q, OCH_3), 64.40 (t, OCH_2, C1), 64.45 (t, OCH_2, C1), 87.34 (d, HC=, C2), 87.37 (d, HC=, C2), 92.13 (d, =CH, C4), 92.20 (d, =CH, C4), 166.3 (s, CO_2CH_2), 173.1 (s, CO_2CH_3), 205.94 (s, =C=, C3), 206.06 (s, =C=, C3).

19: unlisted data were identical with that of the ester of racemic 16 above; ^{13}C NMR (125 MHz) 64.45 (t, OCH_2, C1), 87.31 (d, HC=, C2), 92.11 (d, =CH, C4), 206.03 (s, =C=, C3).

Acknowledgment. We wish to thank Lisa A. Guzzo for conducting the chiral shift study and Janis T. Nelson for performing the ^{13}C NMR analysis of the Mosher esters.

Supplementary Material Available: ^{1}H NMR spectra for compound 6 and ^{13}C NMR spectra for compounds 6, 17, 18, 19, a mixture of 17 and 18, and the Mosher ester of racemic 16 (7 pages). Ordering information is given on any current masthead page.

Enantiomerically Pure Acetals in Organic Synthesis. 1. Chromatographic Separability of Furanoside and Pyranoside Acetals Derived from α-Hydroxy Esters[1]

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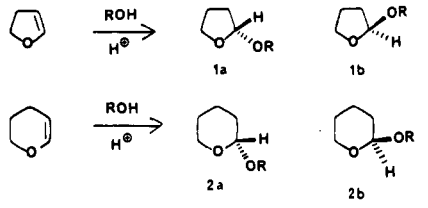
A general chromatographic separation of diastereomeric furanoside and pyranoside acetals derived from α-hydroxy esters is described. Application of this separation methodology is made to rapid syntheses of the diastereomers of (S)-methyl lactyl 4-deoxy-β-*erythro*-pentopyranoside.

Most enantioselective syntheses of uncommon sugars begin with an inexpensive carbohydrate available from the chiral pool.[2] Synthetic routes from such starting materials sometimes require many steps. Routes to carbohydrates from non-carbohydrate precursors have been employed,[3] but normally lead to racemic products. A general and reliable method by which enantiomerically pure carbohydrates might be prepared from achiral or racemic non-carbohydrate precursors could provide a valuable alternative approach, particularly for deoxy and heteroatom-containing carbohydrates.

Tetrahydrofuranyl (THF) and tetrahydropyranyl (THP) ethers such as 1 and 2 represent the simple parent ring systems for carbohydrate furanosides and pyranosides. The anomeric center, a mixed acetal, is stereogenic and usually stereorandom. When R is achiral, **1a** and **1b**, or **2a** and **2b**, are enantiomers. However, if R is chiral, then **1a** and **1b** are diastereomers, as are **2a** and **2b**. Diastereomers are sometimes separable,[4] and so an examination of the chromatographic separability of the diastereomeric THF and THP ethers derived from several commercially available enantiomerically pure alcohols was undertaken.



Separation Studies

Pairs of diastereomeric THP ethers 3-8, derived from the terpenic alcohols (-)-menthol, (+)-isomenthol, (-)-borneol, (-)-isopinocampheol, (-)-nopol, and (-)-myrtenol, respectively, were examined initially. None of these diastereomeric pairs were separable on analytical TLC plates

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† Graduate Fellow of the Division of Organic Chemistry of the American Chemical Society sponsored by Smith-Kline and French Laboratories, 1989-1990.

(1) A portion of this work has previously appeared; see: Mash, E. A.; Arterburn, J. B.; Fryling, J. A. *Tetrahedron Lett.* **1989**, *30*, 7145-7148.

(2) Yoshimura, J. In *Advances in Carbohydrate Chemistry and Biochemistry*; Tipson, R. S., Horton, D., Eds.; Academic Press: 1984; Vol. 42, pp 69-134, and similar chapters in the series.

(3) Zamojski, A.; Grynkeiwicz, G. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley Interscience: New York; Vol. 6, pp 141-235, and references cited therein.

(4) (a) David, S.; Eustache, J. *J. Chem. Soc., Perkin Trans. I* **1979**, 2230-2234. (b) Feringa, B. L.; de Jong, J. C. *J. Org. Chem.* **1988**, *53*, 1125-1127. (c) White, J. D.; Theramongkol, P.; Kuroda, C.; Engebrecht, J. R. *J. Org. Chem.* **1988**, *53*, 5909-5921. (d) Noe, C. R. *Chem. Ber.* **1982**, *115*, 1576-1590. (e) Noe, C. R.; Knollmuller, M.; Wagner, E.; Vollenkle, H. *Chem. Ber.* **1985**, *118*, 3299-3310. (f) Mucha, B.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1989**, *30*, 4489-4492.

0022-3263/91/1956-1088$02.50/0

Table I. Separations of Diastereomeric THP Ethers of α-Hydroxy Esters

entry	diastereomeric acetals	R_1	R_2	yield,[a] %	α[b] (solvent)[c]	loading[d] (solvent)[c]
1	9	Me	Me	49, 49	1.18 (20)	10 (15)
2	10	Et	Me	45, 38	1.18 (20)	4.5 (10)
3	11	*i*-Pr	Me	49, 45	1.12 (20)	3.8 (5)
4	12	*t*-Bu	Me	75[e]	1.07 (20)	*f*
5	17	Me	Ph	42, 49	1.10 (20)	1.9 (10)
6	18	Me	CH_2Ph	41, 51	1.11 (20)	3.3 (15)
7	19	Me	*i*-Bu	33, 42	1.18 (20)	4.3 (10)
8	20a, 20b			49, 47	1.40 (20)	11 (20)

[a] Isolated yields of the less and more polar diastereomers, respectively. [b] The separation factor, α, is the ratio of R_f values for diastereomers **a** and **b** on 0.25-mm silica gel 60 plates (Merck, 70–230 mesh). [c] Solvent is given as the percent ethyl acetate used in hexanes. [d] Column loading is given as mg sample loaded per g of silica gel 60 used (Merck, 70–230 mesh). [e] Combined yield of **12a** and **12b**. [f] Not separated.

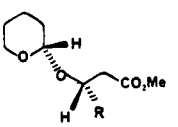
eluted with mixtures of ethyl acetate and hexanes. However, the diastereomeric THP ethers **9a** and **9b** (Table I) derived from (*S*)-(−)-methyl lactate were found to be separable on analytical TLC plates and were also separable by preparative column chromatography. Diastereomeric purity was assayed by 62.9-MHz ^{13}C NMR spectroscopy (limit of detection ≥20:1).[5] The pairs of diastereomeric THP ethers **10a** and **10b**, **11a** and **11b**, and **12a** and **12b** (Table I) derived from (*S*)-(−)-ethyl lactate, (*S*)-(−)-isopropyl lactate, and (*S*)-(−)-*tert*-butyl lactate were similarly separable.

Structures could not be directly assigned to the above pairs of separable diastereomers. Rather, structural assignments for the less and more polar diastereomers have been made throughout in analogy with structures assigned to the less and more polar alkenes **24a** and **24b**, respectively, by their conversion to the enantiomeric forms of 4-deoxy-β-*erythro*-pentopyranose (vide infra).

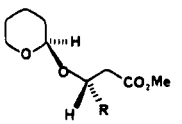
In the hope of deducing the structural features necessary for separability, pairs of diastereomeric THP ethers **13–16**, derived from the secondary alcohols 3-methyl-2-butanol, 1-methoxy-2-propanol, 2-pentanol, and 1-phenylethanol, were examined. As none of these diastereomeric pairs was separable on analytical TLC plates, it seemed reasonable to postulate that the α-hydroxycarbonyl functional group array might be critically important. Thus, pairs of diastereomeric THP ethers **17–20** (Table I), derived from the α-hydroxy esters (*S*)-(+)-methyl mandelate, (*S*)-(+)-methyl 3-phenyllactate, (*S*)-(+)-methyl 2-hydroxy-4-methylvalerate, and (*R*)-(−)-pantolactone were examined next. In each case the pair of diastereomeric THP ethers was separable on analytical TLC plates and also by preparative column chromatography. The α values varied from 1.07 to 1.40, so that some pairs of diastereomers were more readily separable than others. The ease of separation is a function of not only α but also of the scale of the separation and of the equipment employed. In the present work involving gravity driven column chromatography, separations involving diastereomers having an α value <1.1 were tedious. However, separation could be effected in each case to give good to excellent recoveries of roughly equal amounts of the two diastereomeric THP ethers, which were then characterized independently (see Experimental Section).

(5) Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, *18*, 2183–2186.

The observed chromatographic inseparability of diastereomeric THP ethers **21a** and **21b** derived from (*S*)-(+)-methyl 3-hydroxybutyrate was a further indication of the importance of the α-hydroxycarbonyl functional group array to the separability of such THP ethers. At the same time, the observed inseparability of diastereomers **22a** and **22b** derived from (*S*)-(−)-methyl malate demonstrates that this separation is not completely general for all α-hydroxy esters. Having investigated the generality of this separation process for the simple THP ethers of various α-hydroxy esters, we next explored the applicability of this method to more complex THP and THF systems (Table II). The generality of the separability observed for the pairs of diastereomeric (*S*)-methyl lactyl pyranosides (Table I, entry 1, and Table II, entries 1–5) and furanosides (Table II, entries 6–8) examined was most encouraging. Diastereomers **23a** and **23b**, produced under conditions similar to those known to be highly trans selective,[6] were actually more easily separable than unsubstituted diastereomers **9a** and **9b**. Pairs of diastereomers **24a** and **24b**, **25a** and **25b**, and **26a** and **26b**, which contain, respectively, one, one, and two unsaturations in the THP ring, were also more easily separable than the saturated diastereomers **9a** and **9b**. Diastereomers **27a** and **27b** were derived from racemic 2-carbomethoxy-3,4-dihydro-2*H*-pyran.[7] These diastereomers were slightly less separable than **9a** and **9b**.



21a R = Me
22a R = CO_2Me

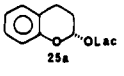
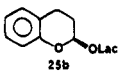
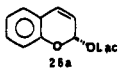
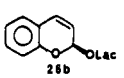
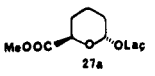
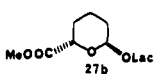


21b R = Me
22b R = CO_2Me

Pairs of diastereomeric (*S*)-methyl lactyl furanosides **28–30** were also chromatographically separable (Table II). Diastereomers **29a** and **29b** were prepared under conditions similar to those known to be highly trans selective.[6] Diastereomers **30a** and **30b** were prepared by acetal exchange from the corresponding methyl furanosides. For steric and/or stereoelectronic reasons, only two of the four possible diastereomers were produced. However, all four possible diastereomers were produced when **31a–d** and

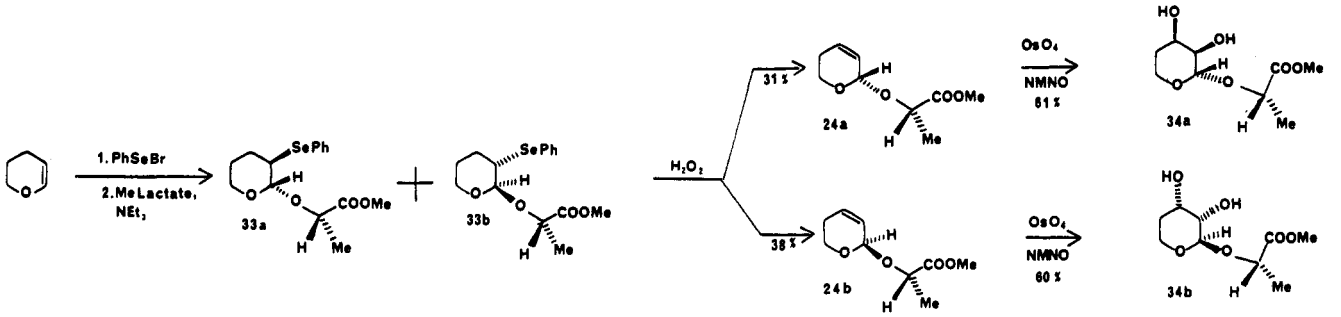
(6) Sweet, F.; Brown, R. K. *Can. J. Chem.* **1968**, *46*, 707–713.
(7) Okada, M.; Sumitomo, H.; Yamada, S.; Atsumi, M.; Hall, H. K.; Chan, R. J. H.; Ortega, R. B. *Macromolecules* **1986**, *19*, 953–959.

Table II. Separations of (*S*)-Methyl Lactyl Pyranosides and Furanosides[a]

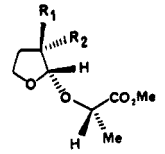
entry	diastereomeric acetals		yields,[b] %	α[c] (solvent)[d]	loading[e] (solvent)[d]
1	 23a	 23b	42, 42	1.30 (20)	14 (15)
2	 24a	 24b	31, 38	1.34 (20)	7 (15)
3	 25a	 25b	48, 23	1.22 (10)	8 (10)
4	 26a	 26b	41, 17	1.58 (5)[f]	5 (5)[f]
5	 27a	 27b	42, 40	1.09 (50)	1 (20)[g]
6	 28a R=H	 28b R=H	45, 48	1.25 (20)	9 (15)
7	29a R=Br	29b R=Br	43, 44	1.10 (20)	7 (10)
8	30a R=OSiMe$_2$-*t*-Bu	30b R=OSiMe$_2$-*t*-Bu	36, 36	1.19 (20)	14 (5)[g]

[a] "OLac" is used as an abbreviation for (*S*)-methyl lactate in the structures in this table. [b] Isolated yields of the less and more polar diastereomers, respectively. [c] The separation factor, α, is the ratio of R_f values for diastereomers **a** and **b** on 0.25-mm silica gel 60 plates (Merck, 70–230 mesh). [d] Solvent is given as the percent ethyl acetate used in hexanes. [e] Column loading is given as mg sample loaded per g of silica gel 60 used (Merck, 70–230 mesh). [f] Silica pretreated with triethylamine. [g] Flash chromatography employed.

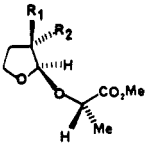
Scheme I



32a–d were prepared by acetal exchange from the corresponding methyl furanosides using (*S*)-(−)-methyl lactate. In both cases, all four diastereomers were chromatographically resolvable.[8]



	R_1	R_2
31a	Me	H
31c	H	Me
32a	CH_2Ph	H
32c	H	CH_2Ph

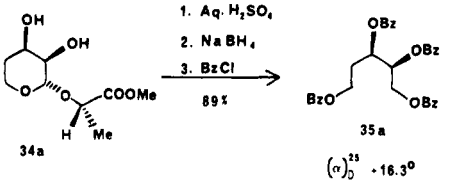


	R_1	R_2
31b	Me	H
31d	H	Me
32b	CH_2Ph	H
32d	H	CH_2Ph

Synthesis of Diastereomeric (*S*)-Methyl Lactyl 4-Deoxy-β-*erythro*-pentopyranosides

As a means of assigning structures to several pairs of separated diastereomers, and as a first test of the potential utility of this methodology, a synthesis of the (*S*)-methyl lactyl pyranosides of D- and L-4-deoxy-β-*erythro*-pentose was undertaken (Scheme I). Reaction of benzeneselenenyl bromide with 3,4-dihyro-2*H*-pyran,[9] followed by reaction with (*S*)-(−)-methyl lactate in the presence of triethylamine, produced phenylselenenyl acetals **33a** and **33b**. Although these acetals were separable (α = 1.17), the mixture of **33a** and **33b** was treated with hydrogen peroxide to give, after chromatographic separation, diastereomeric alkenes **24a** and **24b** in 31% and 38% yields, respectively (from benzeneselenenyl bromide). Each of these alkenes was hydroxylated with use of a catalytic amount of osmium tetraoxide and *N*-methylmorpholine *N*-oxide. From alkene **24a**, diol **34a** was obtained in 61% yield as the only isolable product, while from alkene **24b**, diol **34b** was obtained in 60% yield. No evidence for formation of other diastereomeric diols was observed.[10]

Scheme II



(8) R_f values for **31a–d**: 0.42, 0.38, 0.30, 0.27 (30% EtOAc/hexanes); for **32a–d**: 0.37, 0.33, 0.31, 0.26 (20% EtOAc/hexanes). These diastereomers were not separated.

(9) Kozikowski, A. P.; Sorgi, K. L.; Schmiesing, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 477–479.

(10) Sirivastava, R. M.; Brown, R. K. *Can. J. Chem.* **1971**, *49*, 1339–1342.

Structures were assigned to diols **34a** and **34b** as outlined in Scheme II. Hydrolysis[10,11] of acetal **34a**, followed by reduction[11] with sodium borohydride and perbenzoylation[11] of the resulting tetrol gave the known compound (2*S*,3*R*)-tetra-*O*-benzoyl-1,2,3,5-pentanetetrol[11] (**35a**) in 89% yield (from **34a**). A similar treatment of **34b** produced the enantiomeric pentanetetrol derivative **35b**. For comparison purposes, tetrabenzoate **35b** was also prepared by borohydride reduction and perbenzoylation of commercially available 2-deoxy-D-ribose (**36**). Assuming anti hydroxylation,[10] hydroxylation,[10] it then follows that the structures of compounds **33a**, **33b**, **24a**, **24b**, **34a**, and **34b** are as indicated.[12]

The separation methodology described herein appears to be general for a variety of α-hydroxy esters and substituted THP and THF acetals. Methodological and synthetic studies employing this separation are currently underway in our laboratories.

Experimental Section

Benzene and CH_2Cl_2 were distilled from calcium hydride while diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under an inert atmosphere. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over 3-Å molecular sieves. 2,3-Dihydrofuran, 3,4-dihyro-2*H*-pyran, (*S*)-(−)-methyl lactate, (*S*)-(−)-ethyl lactate, (*S*)-(−)-isopropyl lactate, (S)-(+)-methyl mandelate, (*R*)-(−)-pantolactone, and (*S*)-(+)-methyl 3-hydroxybutyrate were purchased from Aldrich Chemical Company and used as supplied. (*S*)-(−)-*tert*-Butyl lactate, (*S*)-(+)-methyl 3-phenyllactate, (*S*)-(+)-methyl 2-hydroxy-4-methylvalerate, and (*S*)-(−)-methyl malate were prepared by esterification (gaseous HCl, CH_3OH) of the commercially available acids. The purity of all title compounds was judged to be ≥95% by ^1H and ^{13}C NMR spectral determinations. ^1H and ^{13}C NMR spectra were recorded at 250 and at 62.9 MHz, respectively. Mass spectral determinations were performed at the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant CHE-0211164). Thin layer chromatographic analyses were performed on Merck silica gel 60 plates (0.25 mm, 70–230 mesh ASTM). Column chromatography was performed on Merck silica gel 60 (gravity driven, 70–230 mesh ASTM; flash, 230–400 mesh ASTM).

(*S*)-Methyl Lactyl Tetrahydropyranyl Ethers 9a and 9b. To a well-stirred solution of 3,4-dihyro-2*H*-pyran (2 mL, 1.84 g, 22 mmol) in dry CH_2Cl_2 (5 mL) were added (*S*)-methyl lactate (1.0 mL, 1.09 g, 10.5 mmol) and pyridinium *p*-toluenesulfonate (ca. 50 mg, 0.2 mmol). After 16 h at room temperature, the mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated $NaHCO_3$ solution (25 mL), then dried (Na_2SO_4), and filtered, and the volatiles were removed in vacuo. The residue was chromatographed twice on silica gel 60 (200 g) eluted with 15% ethyl acetate/hexanes, affording 970 mg (5.16 mmol, 49%) each of the less polar diastereomer **9a** (R_f 0.32, 20% EtOAc/hexanes) and of the more polar diastereomer **9b** (R_f 0.27). Spectral data for **9a**: an oil, $[\alpha]^{24}_D$ −144° (*c* 3.04, EtOAc); IR (neat) cm^{-1} 2944, 1741; ^1H NMR ($CDCl_3$) δ 1.45 (3, d, *J* = 6.9 Hz), 1.40–2.90 (6, m), 3.45–3.54 (1, m), 3.74 (3, s), 3.75–3.90 (1, m), 4.43 (1, q, *J* = 6.9 Hz), and 4.70 (1, m, *J* < 4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.54 (CH_3), 18.90 (CH_2), 25.13 (CH_2), 30.12 (CH_2), 51.62 (CH_3), 62.15 (CH_2), 69.65 (CH), 97.31 (CH), and 173.54 (C).

For **9b**: an oil, $[\alpha]^{24}_D$ +70.1° (*c* 3.90, EtOAc); ^1H NMR ($CDCl_3$) δ 1.40 (3, d, *J* = 6.7 Hz), 1.50–1.95 (6, m), 3.40–3.50 (1, m), 3.74 (3, s), 3.85–4.00 (1, m), 4.22 (1, q, *J* = 6.7 Hz) and 4.71 (1, m, *J* < 4 Hz); ^{13}C NMR ($CDCl_3$) δ 17.87 (CH_3), 19.04 (CH_2), 25.10 (CH_2), 30.30 (CH_2), 51.75 (CH_3), 62.27 (CH_2), 72.24 (CH), 98.17 (CH), and 173.55 (C); mass spectrum (70 eV) *m/z* (rel intensity) 187 (0.4), 133 (2), 130 (3), 129 (3), 101 (16), 86 (7), and 85 (100); exact mass calcd for $C_9H_{15}O_4$ ($M^+ - H^\bullet$) 187.0970, obsd 187.0975.

(*S*)-Methyl Mandelyl Tetrahydropyranyl Ethers 17a and 17b. These diastereomers were similarly prepared and separated. Spectral data for the less polar diastereomer **17a**: a solid, mp 49.8–52.7 °C (R_f 0.360, 20% EtOAc/hexanes); $[\alpha]^{21}_D$ −45.17° (*c* 4.10, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3015, 2946, 1744, 1212, 1122; ^1H NMR ($CDCl_3$) δ 1.45–1.90 (6, m), 3.47–3.53 (1, m), 3.71 (3, s), 3.65–3.75 (1, m), 4.89 (1, t, *J* = 2.5 Hz), 5.33 (1, s), 7.26–7.51 (5, m); ^{13}C NMR ($CDCl_3$) δ 18.60 (CH_2), 25.26 (CH_2), 30.10 (CH_2), 52.18 (CH_3), 61.85 (CH_2), 75.50 (CH), 97.05 (CH), 127.16 (CH), 128.35 (CH), 128.47 (CH), 136.70 (C), 171.81 (C).

Spectral data for the more polar diastereomer **17b** (R_f 0.326): an oil, $[\alpha]^{20}_D$ +169.3° (*c* 2.83 $CHCl_3$); IR ($CHCl_3$) cm^{-1} 2949, 1742, 1208, 1122, 1079; ^1H NMR ($CDCl_3$) δ 1.50–2.00 (6, m), 3.45–3.55 (1, m), 3.704 (3, s), 3.90–4.00 (1, m), 4.58 (1, t, *J* = 3.5 Hz), 5.245 (1, s), 7.26–7.48 (5, m); ^{13}C NMR ($CDCl_3$) δ 18.98 (CH_2), 25.21 (CH_2), 30.16 (CH_2), 52.15 (CH_3), 62.25 (CH_2), 76.65 (CH), 96.47 (CH), 127.43 (CH), 128.53 (CH), 136.20 (C), 171.10 (C).

(*S*)-Methyl 3-Phenyllactyl Tetrahydropyranyl Ethers 18a and 18b. These diastereomers were similarly prepared from (*S*)-(+)-methyl 3-phenyllactate, $[\alpha]^{25}_D$ +5.88° (*c* 1.23, CH_3OH), and separated. Spectral data for the less polar diastereomer **18a**: a solid, mp 37–39 °C (R_f 0.30, 20% EtOAc/hexanes); $[\alpha]^{25}_D$ −149.0° (*c* 1.87, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3009, 2949, 2869, 2851, 1743, 1602; ^1H NMR ($CDCl_3$) δ 1.20–1.80 (6, m), 2.81–3.23 (4, m), 3.72 (3, s), 4.44–4.52 (1, dd, *J* = 9.11 and 4.42 Hz), 4.71–4.77 (1, m), 7.15–7.32 (5, m); ^{13}C NMR ($CDCl_3$) δ 18.0 (CH_2), 25.2 (CH_2), 30.0 (CH_2), 39.2 (CH_2), 51.8 (CH_3), 60.6 (CH_2), 74.3 (CH), 95.9 (CH), 126.6 (CH), 128.1 (CH), 129.7 (CH), 137.3 (C), 172.7 (C).

Spectral data for the more polar diastereomer **18b**: an oil (R_f 0.27); $[\alpha]^{25}_D$ +63.1° (*c* 2.46, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3011, 2949, 2851, 1745, 1602; ^1H NMR ($CDCl_3$) δ 1.20–1.92 (6, m), 2.99–3.08 (2, m), 3.36–3.47 (1, m), 3.71 (3, s), 3.83–3.95 (1, m), 4.18–4.28 (1, m), 4.34–4.49 (1, m), 7.17–7.33 (5, m); ^{13}C NMR ($CDCl_3$) δ 18.9 (CH_2), 25.1 (CH_2), 30.0 (CH_2), 39.1 (CH_2), 51.8 (CH_3), 62.2 (CH_2), 78.4 (CH), 99.8 (CH), 126.6 (CH), 128.2 (CH), 129.3 (CH), 136.8 (C), 172.7 (C).

(*S*)-Methyl 2-Hydroxy-4-methylvaleryl Tetrahydropyranyl Ethers 19a and 19b. These diastereomers were similarly prepared from (*S*)-(+)-methyl 2-hydroxy-4-methylvalerate, $[\alpha]^{25}_D$ +3.72° (*c* 2.48, $CHCl_3$), and separated. Spectral data for the less polar diastereomer **19a**: an oil (R_f 0.33, 20% EtOAc/hexanes); $[\alpha]^{24}_D$ −186.4° (*c* 1.61, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3009, 2952, 2869, 1742; ^1H NMR ($CDCl_3$) δ 0.92–1.03 (6, 2 d), 1.47–2.00 (9, m), 3.42–3.58 (1, m), 3.74 (3, s), 3.77–3.90 (1, m), 4.35–4.44 (1, dd, *J* = 4.3 and 9.5 Hz), 4.62–4.67 (1 m); ^{13}C NMR ($CDCl_3$) δ 19.0 (CH_2), 21.4 (CH_3), 23.2 (CH_3), 24.4 (CH), 25.3 (CH_2), 30.3 (CH_2), 41.8 (CH_2), 51.6 (CH_3), 62.2 (CH_2), 72.4 (CH), 97.0 (CH), 173.8 (C).

Spectral data for the more polar diastereomer **19b**: an oil (R_f 0.28); $[\alpha]^{24}_D$ +51.3° (*c* 1.68, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3024, 3013, 2954, 2869, 1742; ^1H NMR ($CDCl_3$) δ 0.89–1.00 (6, 2 d, *J* = 6.19 and 6.20 Hz), 1.44–1.96 (9, m), 3.39–3.51 (1, m), 3.74 (3, s), 3.85–3.98 (1, m), 4.01–4.08 (1, dd, *J* = 8.6 and 5.1 Hz), 4.63–4.68 (1, m); ^{13}C NMR ($CDCl_3$) δ 19.2 (CH_2), 22.0 (CH_3), 22.9 (CH_3), 24.3 (CH), 25.2 (CH_2), 30.3 (CH_2), 41.7 (CH_2), 51.7 (CH_3), 62.5 (CH_2), 76.5 (CH), 100.3 (CH), 173.9 (C).

(*R*)-Pantolactyl Tetrahydropyranyl Ethers 20a and 20b. These diastereomers were similarly prepared and separated. Spectral data for the less polar diastereomer **20a**: an oil (R_f 0.21, 20% EtOAc/hexanes); $[\alpha]^{26}_D$ +211° (*c* 3.42, EtOAc); IR (neat) cm^{-1} 3543, 2939, 1767, 1234; ^1H NMR ($CDCl_3$) δ 1.14 (3, s), 1.22 (3, s), 1.50–1.90 (6, m), 3.50–3.60 (1, m), 3.80–3.90 (1, m), 3.93 (1, d, *J* = 11 Hz), 4.00 (1, d, ^2J = 11 Hz), 4.15 (1, s), 5.16 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.74 (CH_2), 19.36 (CH_3), 23.10 (CH_3), 25.21 (CH_2), 30.00 (CH_2), 39.95 (C), 62.02 (CH_2), 76.15 (CH_2), 77.14 (CH), 97.03 (CH), 175.51 (C).

Spectral data for the more polar diastereomer **20b**: an oil (R_f 0.15); $[\alpha]^{26}_D$ −175° (*c* 3.42, EtOAc); IR (neat) cm^{-1} 3557, 2939, 1789, 1735, 1202; ^1H NMR ($CDCl_3$) δ 1.11 (3, s), 1.21 (3, s), 1.50–2.00 (6, m), 3.49–3.61 (1, m), 3.91 (1, d, *J* = 9 Hz), 3.98 (1, d, *J* = 9 Hz), 4.09–4.11 (1, m), 4.23 (1, s), 4.86 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.07 (CH_2), 19.36 (CH_3), 23.57 (CH_3), 25.10 (CH_2), 29.92 (CH_2), 40.38 (C), 61.41 (CH_2), 75.61 (CH_2), 78.06 (CH), 98.23 (CH), 174.78 (C).

(*S*)-Methyl Lactyl 3-Bromotetrahydropyranyl Ethers 23a and 23b. To a well-stirred mixture of 3,4-dihydro-2*H*-pyran (1 mL, 922 mg, 11 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added

(11) Verheyden, J. P. H.; Moffatt, J. G. *J. Org. Chem.* **1969**, *34*, 2643–2645.

(12) Hydrogenation of **24a** gave the saturated acetal **9a**, while elimination of the elements of HBr from **23a** using diazabicyclo[5.4.0]undec-7-ene in DMSO at 100 °C gave alkene **24a**.

dropwise Br_2 (540 μL, 1.675 g, 10.5 mmol) neat. Decolorization was instantaneous. A mixture of (*S*)-methyl lactate (1 mL, 1.09 g, 10.5 mmol) and triethylamine (1.5 mL, 1.09 g, 10.8 mmol) was then added. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was then diluted with CH_2Cl_2 (100 mL), washed with water (100 mL) and saturated $NaHCO_3$ solution (100 mL), dried ($MgSO_4$), and filtered, and the volatiles were removed in vacuo. The residue was chromatographed twice on silica gel 60 (200 g) eluted with 15% ethyl acetate/hexanes, affording 1.17 g (4.38 mmol, 42%) of the less polar diastereomer **23a** (R_f 0.33, 20% EtOAc/hexanes) and 1.18 g (4.41 mmol, 42%) of the more polar diastereomer **23b** (R_f 0.25) as oils. Spectral data for **23a**: ^1H NMR ($CDCl_3$) δ 1.46 (3, d, J = 6.9 Hz), 1.50–1.60 (1, m), 1.88–2.12 (2, m), 2.35–2.40 (1, m), 3.56–3.66 (1, m), 3.75 (3, s), 3.82–3.95 (1, m), 4.09–4.16 (1, m), 4.41 (1, q, J = 6.9 Hz), and 4.80 (1, d, J = 3.3 Hz); ^{13}C NMR ($CDCl_3$) δ 18.45 (CH_3), 21.84 (CH_2), 28.30 (CH_2), 48.38 (CH), 51.81 (CH_3), 61.61 (CH_2), 70.41 (CH), 98.88 (CH), and 172.72 (C).

Spectral data for **23b**: ^1H NMR ($CDCl_3$) δ 1.43 (3, d, J = 6.9 Hz), 1.49–2.02 (1, m), 2.35–2.50 (1, m), 3.49–3.61 (1, m), 3.75 (3, s), 3.91–4.10 (2, m), 4.23 (1, q, J = 6.9 Hz), and 4.71 (1, d, J = 4.2 Hz); ^{13}C NMR ($CDCl_3$) δ 17.77 (CH_3), 22.75 (CH_2), 29.66 (CH_2), 48.83 (CH), 51.90 (CH_3), 62.68 (CH_2), 73.24 (CH), 100.74 (CH), and 172.80 (C).

(*S*)-Methyl Lactyl 5,6-Dihydropyranyl Acetals 24a and 24b. To a well-stirred solution of 3,4-dihydro-2*H*-pyran (2.1 mL, 1.9 g, 23 mmol) in dry CH_2Cl_2 (10 mL) at −78 °C was added dropwise a solution of benzeneselenenyl bromide prepared in situ by adding Br_2 (0.57 mL, 1.77 g, 11 mmol) to diphenyl diselenide (3.382 g, 10.8 mmol) in dry CH_2Cl_2 (10 mL).[9] Decolorization occurred immediately. Decolorization a solution of (*S*)-methyl lactate (2.1 mL, 2.3 g, 22 mmol) and triethylamine (3.3 mL, 2.41 g, 24 mmol) was added slowly. The mixture was allowed to warm to room temperature slowly. After filtration the mixture was washed with water, saturated $NaHCO_3$ solution, and brine (50 mL each), then dried (Na_2SO_4), and filtered, and the volatiles were removed in vacuo leaving a yellow oil.

To a well-stirred solution of the above crude phenyl selenides **33a** and **33b** and pyridine (2.9 mL, 2.8 g, 36 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added dropwise an aqueous H_2O_2 solution (1.62 g, 47.5 mmol, 9.9 mL of H_2O). After being stirred at room temperature for 6 days, the mixture was diluted with CH_2Cl_2 (40 mL), washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL), then dried (Na_2SO_4), and filtered, and the volatiles were removed in vacuo. The residue was chromatographed on silica gel 60 (400 g) deactivated with 1% Et_3N and eluted with 10% EtOAc/hexanes; the overlap fraction was similarly rechromatographed (200 g), affording 1.233 g (6.62 mmol, 31%) of the less polar diastereomer **24a** (R_f 0.29, 20% EtOAc/hexanes) and 1.540 g (8.27 mmol, 38%) of the more polar diastereomer **24b** (R_f 0.22) as oils.

Spectral data for **24a**: $[\alpha]^{22}_D$ −40.37° (*c* 2.72, $CHCl_3$); IR (neat) cm^{-1} 2936, 1746; ^1H NMR ($CDCl_3$) δ 1.45 (3, d, J = 7 Hz), 1.90 (1, dm, J = 17 Hz), 2.23–2.41 (1, m), 3.68–3.78 (1, m), 3.83 (3, s), 3.92 (1, dt, J = 11 Hz, J = 4 Hz), 4.47 (1, q, J = 7 Hz), 5.00 (1, m), 5.82 (1, dm, J = 10 Hz), and 6.07 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.83 (CH_3), 24.51 (CH_2), 51.80 (CH_3), 57.32 (CH_2), 70.23 (CH), 92.77 (CH), 125.30 (CH), 129.15 (CH), and 173.51 (C).

Spectral data for **24b**: $[\alpha]^{21}_D$ −77.4° (*c* 2.65, $CHCl_3$); IR (neat) cm^{-1} 3043, 2890, 1753; ^1H NMR ($CDCl_3$) δ 1.42 (3, d, J = 6.8 Hz), 1.85–2.01 (1, m), 2.20–2.40 (1, m), 3.61 (1, dd, J = 11.6 Hz, J = 6.2 Hz), 3.75 (3, s), 3.96 (1, dt, J = 11.6 Hz, J = 3.5 Hz), 4.18 (1, q, J = 6.8 Hz), 4.98 (1, m), 5.75 (1, dm, J = 10.2 Hz), and 6.05–6.15 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.40 (CH_3), 24.38 (CH_2), 51.71 (CH_3), 57.47 (CH_2), 73.12 (CH), 94.20 (CH), 124.78 (CH), 129.70 (CH), and 173.89 (C); mass spectrum (70 eV) m/z (rel intensity) 186 (0.05), 185 (0.5), 156 (1), 142 (1), 127 (2), 115 (2), 100 (2), 99 (8), 84 (10), 83 (100), 55 (22); high resolution peak matching calcd for $C_9H_{14}O_4$ (M^+) 186.0892, obsd 186.0882.

(*S*)-Methyl Lactyl Dihydrocoumarin Acetals 25a and 25b. A solution of 2-methoxydihydro-2*H*-coumarin (1.129 g, 6.876 mmol), (*S*)-methyl lactate (2.7 mL, 2.9 g, 28 mmol), and *p*-toluenesulfonic acid (250 mg, 1.3 mmol) in benzene (300 mL) was refluxed overnight under argon in a Dean–Stark apparatus. After being cooled to room temperature, the mixture was washed with saturated $NaHCO_3$ (50 mL), dried (Na_2SO_4), and filtered, and the volatiles were removed in vacuo. The residue was chromatographed twice on silica gel 60 (200 g) eluted with 10% EtOAc/hexanes, affording 782 mg (3.31 mmol, 48%) of the less polar diastereomer **25a** (R_f 0.22, 10% EtOAc/hexanes) and 382 mg (1.62 mmol, 23%) of the more polar diastereomer **25b** (R_f 0.18) as oils. Spectral data for **25a**: $[\alpha]^{23}_D$ −177.3° (*c* 1.85, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3022, 3011, 2951, 1743; ^1H NMR ($CDCl_3$) δ 1.33 (3, d, J = 7.0 Hz), 1.88–2.08 (1, m), 2.10–2.25 (1, m), 2.56–2.73 (1, m), 2.95–3.12 (1, m), 3.76 (3, s), 4.58 (1, q, J = 7.0 Hz), 5.36 (1, m), 6.78–6.98 (2, m), 7.02–7.19 (2, m); ^{13}C NMR ($CDCl_3$) δ 18.63 (CH_3), 19.89 (CH_2), 26.00 (CH_2), 51.98 (CH_3), 70.32 (CH), 95.41 (CH), 116.79 (CH), 120.79 (CH), 122.61 (C), 127.19 (CH), 129.25 (CH), 151.66 (C), 173.31 (C).

For **25b**: $[\alpha]^{23}_D$ +67.2° (*c* 1.80, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3017, 2938, 1731; ^1H NMR ($CDCl_3$) δ 1.42 (3, d, J = 6.8 Hz), 1.83–2.02 (1, m), 2.06–2.21 (1, m), 2.56–2.70 (1, m), 2.95–3.16 (1, m), 3.43 (3, s), 4.34 (1, q, J = 6.8 Hz), 5.35 (1, m), 6.66–6.78 (1, m), 6.82–6.93 (1, m), 7.01–7.16 (2, m); ^{13}C NMR δ 18.84 (CH_3), 19.90 (CH_2), 25.96 (CH_2), 51.62 (CH_3), 73.37 (CH), 96.70 (CH), 116.49 (CH), 120.73 (CH), 122.35 (C), 127.08 (CH), 129.17 (CH), 151.66 (C), 173.31 (C).

(*S*)-Methyl Lactyl Coumarin Acetals 26a and 26b. These diastereomers were similarly prepared from 2-methoxycoumarin and separated.

Spectral data for **26a**: an oil; $[\alpha]^{28}_D$ −30.10° (*c* 1.96, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3028, 3013, 2952, 1736; ^1H NMR ($CDCl_3$) δ 1.33 (3, d, J = 7.0 Hz), 3.71 (3, s), 4.63 (1, q, J = 7.0 Hz), 5.78 (1, d, J = 3.8 Hz), 5.93 (1, dd, J = 9.6 Hz and 3.8 Hz), 6.71 (1, d, J = 9.6 Hz), 6.86–6.99 (2, m), 7.04–7.26 (2, m); ^{13}C NMR ($CDCl_3$) δ 18.39 (CH_3), 51.71 (CH_3), 70.20 (CH), 93.64 (CH), 116.17 (CH), 119.39 (CH), 120.46 (C), 121.43 (CH), 126.43 (CH), 126.85 (CH), 129.07 (CH), 150.75 (C), 172.84 (C).

For **26b**: an oil; $[\alpha]^{27}_D$ −90.1° (*c* 0.69, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3153, 2951, 1732; ^1H NMR ($CDCl_3$) δ 1.42 (3, d, J = 6.9 Hz), 3.60 (3, s), 4.36 (1, q, J = 6.9 Hz), 6.76–6.90 (2, m), 7.72–8.28 (5, m); ^{13}C NMR ($CDCl_3$) δ 18.51 (CH_3), 51.83 (CH_3), 73.25 (CH), 95.04 (CH), 116.22 (CH), 118.63 (CH), 120.02 (C), 121.55 (CH), 127.12 (2 × CH), 129.23 (CH), 150.92 (C), 173.13 (C).

(*S*)-Methyl Lactyl 6-(Methoxycarbonyl)tetrahydropyranyl Ethers 27a and 27b. These diastereomers were prepared and separated similarly to **9**, starting from racemic 2-(methoxycarbonyl)-3,4-dihydro-2*H*-pyran.[7] Spectral data for the less polar diastereomer **27a**: an oil (R_f 0.46, 50% EtOAc/hexanes); $[\alpha]^{19}_D$ −111.6° (*c* 5.0, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 2953, 1750; ^1H NMR ($CDCl_3$) δ 1.45 (3, d, J = 7 Hz), 1.55–2.04 (6, m), 3.77 (3, s), 3.73 (3, s), 4.39 (1, dd, J = 2.1 Hz and 11.2 Hz), 4.44 (1, q, J = 7 Hz), 5.05 (1, bs); ^{13}C NMR ($CDCl_3$) δ 17.22 (CH_2), 18.51 (CH_3), 27.97 (CH_2), 28.65 (CH_2), 51.69 (CH_3), 51.89 (CH_3), 68.68 (CH), 69.73 (CH), 96.34 (CH), 171.92 (C), 173.19 (C).

Spectral data for the more polar diastereomer **27b**: an oil (R_f 0.42, 50% EtOAc/hexanes); $[\alpha]^{20}_D$ +25.88° (*c* 5.0, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 2956, 1750; ^1H NMR ($CDCl_3$) δ 1.40 (3, d, J = 7 Hz), 1.25–2.08 (6, m), 3.75 (3, s), 3.76 (3, s), 4.22 (1, q, J = 7 Hz), 4.61 (1, bd, J = 11.8 Hz), 5.05 (1, bs); ^{13}C NMR ($CDCl_3$) δ 17.50 (CH_2), 17.85 (CH_3), 27.77 (CH_2), 28.93 (CH_2), 51.70 ($2CH_3$), 68.54 (CH), 72.80 (CH), 97.62 (CH), 171.98 (C), 173.32 (C).

(*S*)-Methyl Lactyl Tetrahydrofuranyl Ethers 28a and 28b. These diastereomers were prepared from 2,3-dihydrofuran and separated similarly to **9a** and **9b**. Spectral data for the less polar diastereomer **28a**: an oil (R_f 0.25, 20% EtOAc/hexanes); $[\alpha]^{25}_D$ −192° (*c* 4.48, EtOAc); IR (neat) cm^{-1} 2952, 2886, 1751, 1207; ^1H NMR ($CDCl_3$) δ 1.38 (3, d, J = 7 Hz), 1.80–2.05 (4, m), 3.74 (3, s), 3.85 (2, m), 4.36 (1, q, J = 7 Hz), and 5.21 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.71 (CH_3), 22.92 (CH_2), 32.12 (CH_2), 51.59 (CH_3), 66.89 (CH_2), 69.54 (CH), 102.35 (CH), 173.55 (C).

Spectral data for the more polar diastereomer **28b**: an oil (R_f 0.20); $[\alpha]^{20}_D$ +73.9° (*c* 7.30, EtOAc); ^1H NMR ($CDCl_3$) δ 1.37 (3, d, J = 6.8 Hz), 1.75–2.20 (4, m), 3.73 (3, s), 3.75–3.92 (2, m), 4.09 (1, q, J = 6.8 Hz), and 5.20 (1, m); ^{13}C NMR ($CDCl_3$) δ 18.9 (CH_3), 23.21 (CH_2), 32.17 (CH_2), 51.57 (CH_3), 67.20 (CH_2), 71.87 (CH), 103.94 (CH), and 174.19 (C); mass spectrum (70 eV) m/z (rel intensity) 115 (3), 88 (3), 87 (4), 85 (2), 71 (100); high resolution peak matching calcd for $C_8H_{14}O_4$ (M^+) 174.0892, obsd 174.0889.

3-Bromo 2(*S*)-Methyl Lactyl Tetrahydrofuranyl Acetals 29a and 29b. To a solution of 2,3-dihydrofuran (500 μL, 463 mg, 6.62 mmol) in dry CH_2Cl_2 (5 mL) at −78 °C under argon was added dropwise Br_2 (325 μL, 1.008 g, 6.30 mmol) followed by a solution

of (*S*)-methyl lactate (600 μL, 654 mg, 6.29 mmol) and Et_3N (1 mL, 700 mg, 7 mmol). After 30 min the reaction was allowed to attain room temperature and stirred for two h. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (100 mL) and saturated $NaHCO_3$ (100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Chromatography (200 g of silica gel 60, 10% EtOAc/hexanes eluent) and rechromatography of the overlap fraction gave the less polar diastereomer **29a** (679 mg, 43% yield) and the more polar diastereomer **29b** (698 mg, 44% yield) as colorless oils.

Spectral data for **29a**: R_f 0.34 (20% EtOAc/hexanes); IR ($CHCl_3$) cm^{-1} 3026, 2989, 1729; ^1H NMR ($CDCl_3$) δ 1.38 (3, d, J = 7 Hz), 2.17–2.28 (1, m), 2.62–2.71 (1, m), 3.75 (3, s), 4.01–4.09 (1, m), 4.18 (1, q, J = 7 Hz), 4.30–4.39 (2, m), 5.33 (1, s); ^{13}C NMR ($CDCl_3$) δ 18.69 (CH_3), 33.52 (CH_2), 49.83 (CH), 51.97 (CH_3), 66.94 (CH_2), 70.11 (CH), 107.24 (CH), 173.01 (C).

Spectral data for **29b**: R_f 0.31 (20% EtOAc/hexanes); IR ($CHCl_3$) cm^{-1} 3025, 3016, 3013, 2989, 1743; ^1H NMR ($CDCl_3$) δ 1.37 (3, d, J = 6.8 Hz), 2.15–2.26 (1, m), 2.68–2.81 (1, m), 3.73 (3, s), 3.96–4.17 (3, m), 4.27–4.30 (1, m), 5.30 (1, s); ^{13}C NMR ($CDCl_3$) δ 18.22 (CH_3), 33.75 (CH_2), 49.83 (CH), 51.89 (CH_3), 67.33 (CH_2), 71.56 (CH), 108.20 (CH), 173.62 (C).

(*S*)-Methyl Lactyl 2-*O*-(*tert*-Butyldimethylsilyl)-2-hydroxyfuranosides 30a and 30b. To a stirred solution of methyl 2-hydroxyfuranoside[13] (1.565 g, 13.25 mmol) and imidazole (2.02 g, 29.7 mmol) in 15 mL of DMF at 0 °C was added a solution of *tert*-butyldimethylsilyl chloride (2.2275 g, 14.78 mmol) in 5 mL of DMF. The reaction was allowed to warm to room temperature and stirred overnight. The solution was then diluted with 150 mL of Et_2O and washed with water (3 × 15 mL). The ether solution was dried with $MgSO_4$ and filtered, and the solvent was removed in vacuo. The concentrate was chromatographed on silica gel 60 (200 g) using 5% EtOAc/hexanes to give the silyl ether as a colorless oil (R_f 0.53, 20% EtOAc/hexanes), 1.91 g (62%).

Spectral data: ^{13}C NMR ($CDCl_3$) δ −4.88 (CH_3), 18.04 (C), 25.74 (CH_3), 33.15 (CH_2), 54.36 (CH_3), 66.74 (CH_2), 76.35 (CH), 109.59 (CH).

A stirred solution of the above methyl 2-*O*-(*tert*-butyldimethylsilyl)-2-hydroxyfuranoside (0.8028 g, 3,454 mmol), (*S*)-methyl lactate (0.8070 g, 7.752 mmol), and TsOH (50 mg) in 20 mL of benzene was heated to reflux and the benzene/methanol azeotrope removed a via a Dean–Stark trap. After 6 h the reaction mixture was cooled to room temperature, diluted with 100 mL of Et_2O, washed with 10 mL of saturated $NaHCO_3$, dried ($MgSO_4$), and filtered, and the volatiles were removed in vacuo. The concentrate was separated on 70 g of flash silica eluted with 5% EtOAc/hexanes, affording recovered starting material (93.9 mg) and 368 mg (1.21 mmol, 36%) each of the less polar diastereomer **30a** (R_f 0.44, 20% EtOAc/hexanes) and the more polar diastereomer **30b** (R_f 0.37) as oils.

Spectral data for **30a**: $[\alpha]^{23}_D$ −99.12° (*c* 2.85, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 2951, 1743, 1122; ^1H NMR ($CDCl_3$) δ 0.099 (6, s), 0.890 (9, s), 1.371 (3, d, J = 7 Hz), 1.72–1.84 (1, m), 2.12–2.28 (1, m), 3.738 (3, s), 3.90–3.99 (1, m), 4.092 (1, q, J = 7.8 Hz), 4.307 (1, dd, J = 1.5 Hz, 5.2 Hz), 4.346 (1, q, J = 7 Hz), 4.944 (1, s); ^{13}C NMR ($CDCl_3$) δ −4.98 (CH_3), −4.90 (CH_3), 18.00 (C), 18.80 (CH_3), 25.71 (CH_3), 32.83 (CH_2), 51.81 (CH_3), 67.08 (CH_2), 69.61 (CH), 76.27 (CH), 107.05 (CH), 173.43 (C).

For **30b**: $[\alpha]^{24}_D$ +23.8° (*c* 7.38, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 2953, 1745, 1126; ^1H NMR ($CDCl_3$) δ 0.078 (6, s), 0.880 (9, s), 1.368 (3, d, J = 6.9 Hz), 1.70–1.85 (1, m), 2.20–2.35 (1, m), 3.72 (3, s), 3.86–3.96 (1, m), 4.02 (1, q, J = 7.7 Hz), 4.09 (1, q, J = 6.8 Hz), 4.29 (1, dd, J = 1.9 Hz, 5.30 Hz), 4.91 (1, s); ^{13}C NMR ($CDCl_3$) δ −4.88 (CH_3), 17.98 (C), 18.18 (CH_3), 25.69 (CH_3), 33.15 (CH_2), 51.77 (CH_3), 67.41 (CH_2), 71.44 (CH), 76.44 (CH), 108.23 (CH), 174.00 (C); mass spectrum (70 eV) m/z (rel intensity) 247 (1), 233 (3), 203 (4), 202 (6), 201 (45), 185 (1), 175 (4), 172 (4), 171 (2), 162 (7), 161 (59), 145 (7), 133 (6), 129 (6), 116 (10), 115 (100), 100 (12), 89 (20), 75 (23), 73 (48), 59 (11); high resolution calcd for $C_{10}H_{19}O_5Si$ (M^+ − tBu) 247.1002, obsd 247.0997.

(*S*)-Methyl Lactyl 4-Deoxy-β-*erythro*-pentopyranosides 34b and 34a. To a solution of the more polar (*S*)-methyl lactyl 5,6-dihydropyranoside (**24b**) (516 mg, 2.77 mmol) and 4-methylmorpholine *N*-oxide (650 mg, 5.5 mmol) in dry THF (20 mL) at 0 °C was added 0.1 M OsO_4/THF (2.8 mL, 0.28 mmol). The mixture was stirred at room temperature overnight and then quenched with sodium bisulfite (600 mg, 5.76 mmol) in H_2O (1 mL). After removal of volatiles in vacuo, the residue was chromatographed on silica gel 60 (200 g) eluted with EtOAc, affording 364 mg (1.65 mmol, 60%) of **34b** (R_f 0.26, EtOAc) as an oil.

Spectral data for **34b**: $[\alpha]^{26}_D$ +38.09 (*c* 1.15, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3570, 3457, 3021, 2954, 1740; ^1H NMR ($CDCl_3$) δ 1.42 (3, d, J = 6.8 Hz), 1.65–1.97 (2, m), 3.54 (1, s), 3.62–3.89 (6, m), 3.99 (1, s), 4.06–4.18 (1, m), 4.28 (1, q, J = 6.8 Hz), 4.81 (1, d, J = 4.4 Hz); ^{13}C NMR ($CDCl_3$) δ 17.48 (CH_3), 29.41 (CH_2), 51.97 (CH_3), 59.70 (CH_2), 66.03 (CH), 69.86 (CH), 72.15 (CH), 99.47 (CH), 173.40 (C).

Similarly the less polar (*S*)-methyl lactyl 5,6-dihydropyranoside (**24a**) (625 mg, 3.35 mmol) was converted to the diol **34a**: 448 mg (2.03 mmol, 61%) (R_f 0.31, EtOAc).

Spectral data for **34a**: an oil; $[\alpha]^{26}_D$ −98.34° (*c* 1.14, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3561, 3020, 2928, 1730; ^1H NMR ($CDCl_3$) δ 1.46 (3, d, J = 7.0 Hz), 1.67–1.98 (2, m), 3.45–3.87 (7, m), 4.03–4.28 (2, m), 4.41 (1, q, J = 7.0 Hz), 4.70 (1, d, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 18.46 (CH_3), 29.46 (CH_2), 51.98 (CH_3), 59.73 (CH_2), 65.74 (CH), 70.14 (CH), 71.26 (CH), 99.97 (CH), 173.81 (C); mass spectrum (70 eV) m/z (rel intensity) 133 (28), 117 (86), 101 (53), 88 (39), 70 (66), 60 (100); (M + H) ion identified using FAB 221.1027; exact mass calcd for $C_9H_{17}O_6$ 221.1049.

(2*S*,3*R*)-1,2,3,5-Tetra-*O*-benzoyl-1,2,3,5-pentanetetrol (35a). Using the procedure described by Verheyden and Moffatt,[11] **34a** (97 mg, 0.44 mmol) was converted to **35a** (216 mg, 0.39 mmol, 89%): mp 129–130 °C; $[\alpha]^{25}_D$ +16.25° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.30–2.58 (2, m), 4.37–4.90 (4, m), 5.81–5.98 (2, m), 7.25–7.65 (12, m), 7.93–8.14 (8, m); ^{13}C NMR ($CDCl_3$) δ 29.77 (CH_2), 60.98 (CH_2), 62.55 (CH_2), 70.05 (CH), 72.30 (CH), 128.21 (CH), 128.42 (CH), 129.37 (C), 129.52 (CH), 129.67 (CH), 129.73 (CH), 132.84 (CH), 133.14 (CH), 133.30 (CH), 165.47 (C), 165.54 (C), 166.04 (C), 166.27 (C).

For comparison the tetrabenzoate was prepared similarly from 2-deoxy-D-ribose: mp 129–130 °C; $[\alpha]^{25}_D$ −16.7° (*c* 1.91, $CHCl_3$).

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Supplementary Material Available: Spectral data for compounds **10**, **11**, **12**, **21**, and **22** and ^1H NMR and ^{13}C NMR spectra of all new compounds (75 pages). Ordering information is given on any current masthead page.

(13) Sweet, F.; Brown, R. K. *Can. J. Chem.* **1966**, *44*, 1571–1576.