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PALLADIUM(0)-ASSISTED SYNTHESIS OF *C*-GLYCOPYRANOSYL COMPOUNDS*

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ABSTRACT

Tetrakis(triphenylphosphine)palladium(0) effects the regio- and stereo-selective alkylation of 2-acetoxy-5,6-dihydro-2*H*-pyrans and 1-*S*-acetyl-1-thiohex-2-enopyranosides. Use of stabilized carbanions resulted in the formation of alkylated dihydropyrans with net retention at the oxygen-bearing carbon atom. Examples include the preparation of 2-[acetamidobis(ethoxycarbonyl)methyl]-5,6-dihydro-2*H*-pyran, 2-[acetamidobis(methoxycarbonyl)methyl]-6-ethoxy-5,6-dihydro-2*H*-pyran, and 2-[acetamidobis(methoxycarbonyl)methyl]-6-methoxymethyl-5,6-dihydro-2*H*-pyran. Use of nonstabilized carbanions, such as arylzinc chlorides, resulted in the formation of alkylated dihydropyrans and *C*-glycosyl compounds with net inversion at the oxygen-bearing carbon atom. Examples include the preparation of 2-[(6-ethoxy-5,6-dihydro-2*H*-pyranyl)methyl]-4,4-dimethyl-2-oxazoline, *trans*-methoxymethyl-2-phenyl-5,6-dihydro-2*H*-pyran, *trans*-methoxymethyl-2-vinyl-5,6-dihydro-2*H*-pyran, *trans*-2-[2,2-bis(ethoxy)ethyl]-6-methoxymethyl-5,6-dihydro-2*H*-pyran, (4,6-di-*O*-methyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)benzene, (2,3-dideoxy-4,6-di-*O*-methyl-β-D-*erythro*-hex-2-enopyranosyl)benzene, 1-(2,3-dideoxy-4,6-di-*O*-methyl-α- and -β-D-*erythro*-hex-2-enopyranosyl)naphthalene, 4-(2,3-dideoxy-4,6-di-*O*-methyl-α- and -β-D-*erythro*-hex-2-enopyranosyl)toluene, and 1-(2,3,6-trideoxy-4-*O*-methyl-α-L-*erythro*-hex-2-enopyranosyl)naphthalene.

INTRODUCTION

C-Glycopyranosyl-containing natural products have been the focus of increasing synthetic interest. Due to the varying complexity of the synthetic targets, methods have been developed which can be categorized by the method used to construct the *C*-glycosyl unit[2]. Some groups have utilized stereocontrolled procedures to construct the pyranoside ring with the requisite carbon bond to C-1 of the eventual pyranosyl residue intact, prior to ring formation. These include the

*Palladium-assisted Reactions, part III. For part II, see ref. 1.
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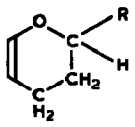
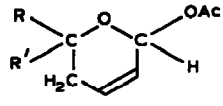
elegant hetero Diels–Alder condensation[3–5], and ring closure methods following Wittig condensations[6] or asymmetric epoxidation[7]. In contrast, the readily available chiral pool of pyranosides has made it increasingly attractive to construct the carbon–carbon bond directly to C-1 of an intact pyranosyl residue. Current examples include the enolate Claisen rearrangement applications[8], glycosyllithium additions[9–13], glycosyl-radical trapping with alkenes[14], nucleophilic displacements on glycal methanesulfonates[15], several variations of Lewis acid or metal-mediated generation of the oxocarbenium ions, followed by nucleophilic addition[16–26], allylstannane coupling with glycosyl halides[27], and organometallic methods utilizing iron[28], manganese[29], and palladium(II) addition–elimination methods[30–32].

As part of our interest in the development of palladium-controlled functionalization of carbohydrates[33], we reasoned that a nucleophilic palladium(0) reagent-controlled, *C*-glycosylation method would offer additional versatility and generality in complementing these above-mentioned methods, whose stereoselectivity depends largely on control by the carbohydrate substrate. A reagent-controlled α or β selective *C*-glycosylation using tetrakis(triphenylphosphine)-palladium(0) [$Pd(PPh_3)_4$] was predicted to be highly stereoselective, based on the elegant work of Trost[34,35] demonstrating that stabilized carbanions react with inversion on carboxylic π-allyl complexes, while Matsushita and Negishi[36] showed that organozinc halides react with carbocyclic π-allylpalladium complexes with retention. Our preliminary studies verified that the same stereoselectivity could be realized in the alkylation of substituted acetoxydihydropyrans, and furthermore the alkylation was completely regioselective, occurring exclusively at the ring oxygen-bearing carbon atom[1].

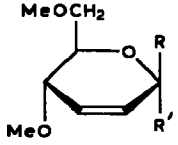
Herein we describe additional details of the alkylation of dihydropyrans and the successful extension of these results to the synthesis of substituted (hex-2-enopyranosyl)arenes. These compounds were chosen as model compounds representing more complex synthetic targets which would be converted to *C*-glycosyl analogs of 11-deoxydaunomycinone and possibly aklavinone[37]. Such a method would allow preparation of these analogs by direct attachment of an intact aglycon nucleophile to a rhamnal-derived palladium complex, as compared to the procedure recently reported by Acton *et al.*[38] in which the D ring was constructed



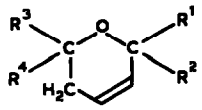
1 R = H
2 R = OEt
3 R = CH_2OMe



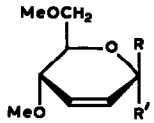
4 R = R′ = H
5 R = OEt, R′ = H
6 R = H, R′ = OEt
7 R = CH_2OMe, R′ = H
8 R = H, R′ = CH_2OMe



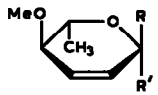
9 R = OAc, R′ = H
10 R = H, R′ = OAc
11 R = SAc, R′ = H



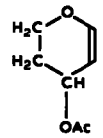
12 R^1 = C(NHAc)$(CO_2Et)_2$, R^2 = R^3 = R^4 = H
13 R^1 = C(NHAc)$(CO_2Me)_2$, R^2 = R^4 = H, R^3 = OEt
14 R^1 = R^4 = H, R^2 = C(NHAc)$(CO_2Me)_2$, R^3 = OEt
15 R^1 = C(NHAc)$(CO_2Me)_2$, R^2 = R^4 = H, R^3 = CH_2OMe
16 R^1 = R^4 = H, R^2 = C(NHAc)$(CO_2Me)_2$, R^3 = CH_2OMe
17 R^1 = R^4 = H, R^2 = Ph, R^3 = OEt
18 R^1 = Ph, R^2 = R^4 = H, R^3 = OEt
19 R^1 = R^4 = H, R^2 = (4,4-dimethyl-2-oxazolin-2-yl)methyl, R^3 = OEt
20 R^1 = (4,4-dimethyl-2-oxazolin-2-yl)methyl, R^2 = R^4 = H, R^3 = OEt
21 R^1 = R^4 = H, R^2 = Ph, R^3 = CH_2OMe
22 R^1 = R^4 = H, R^2 = CH = CH_2, R^3 = CH_2OMe
23 R^1 = R^4 = H, R^2 = $CH_2CH(OEt)_2$, R^3 = CH_2OMe
24 R^1 = $CH_2CH(OEt)_2$, R^2 = R^4 = H, R^3 = CH_2OMe



25 R = H, R′ = Ph
26 R = Ph, R′ = H
27 R = H, R′ = 1-naphthyl
28 R = 1-naphthyl, R′ = H
29 R = H, R′ = *p*-tolyl
30 R = *p*-tolyl, R′ = H



31 R = H, R′ = SAc
32 R = 1-naphthyl, R′ = H



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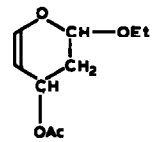

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by use of a Diels–Alder reaction of an ABC ring dienophile with a daunosamine-containing 2,4-pentadiene. Such *C*-glycosyl analogs are resistant to metabolic deactivation by reductive deglycosylation, and, as a result, possibly will have an increased therapeutic potential[39,40].

RESULTS AND DISCUSSION

Initial experiments to effect palladium(0)-catalyzed *C*-glycosylation were attempted on acetylated carbohydrate glycals. Attempts to alkylate the readily avaiable 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol or 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*arabino*-hex-1-enitol in either oxolane or *N,N*-dimethylformamide in the presence of tetrakis(triphenylphosphine)palladium(0)

$[Pd(PPh_3)_4]$ and triphenylphosphine (PPh_3), according to methodology developed by Trost[34], were unsuccessful, with nearly quantitative recovery of the starting glycal. This failure to undergo allylic alkylation was not surprising in view of the lack of examples of alkylation of enolether allylic acetates in which the oxygen atom is attached at the terminus of the allylic double bond. To our knowledge, such allylic acetates do not undergo nucleophilic attack by palladium because they are too electron rich. This result was also consistent with the observation of Trost and Keinan[41] who found a poor yield and, also, that significantly longer reaction times were required to alkylate a 2-ethoxyallylic acetate. Our attention then turned to the alkylation of electron-deficient allylic acetates. Owing to the lack of readily available 1-*O*-acetylhex-2-enopyranoses, initial experiments were carried out on acetoxydihydropyrans in order to define the scope and stereochemical results of the *C*-glycosylation. The dihydropyranyl acetates **4–6** were prepared by a modification of the method of Hurd and Edwards[42] using lead tetraacetate. It was found that the yield of the desired 2-acetoxy-5,6-dihydropyran (**4**) could be increased relative to that of 4-acetoxy-5,6-dihydro-4*H*-pyran when the reaction was carried out at −5–0° in benzene with lead tetraacetate free of residual acetic acid. Thus, the reaction of each dihydropyran **1–3** afforded the corresponding 2-acetoxydihydropyrans **4–6** in the range of 45–50%. When the reaction was performed at −5–0°, the product was usually contaminated with only up to 20% of its allylic isomer. The preponderant stereoisomers formed under these reaction conditions were the *cis* acetoxylated products **5** and **7** with the overall *cis* stereoselectivity greatest for acetoxylation of the methoxymethyldihydropyran **3**. The steric structures were determined by comparison of the ^1H- and ^{13}C-n.m.r. spectra of the *cis* and *trans* isomers. In all cases, the less shielded C-2 and C-6 signals of the ^{13}C-n.m.r. spectrum were assigned to the *cis* isomer in accordance with the expected *γ-gauche* effect previously observed in cyclohexanes and also in *C*-glycopyranosyl compounds[43]. The pertinent spectral data used to identify each stereoisomer are shown in Table I.

When the lead tetraacetate acetoxylation procedure of Hurd and Edwards[42] was attempted on 3-deoxyglycals, only skeletal rearrangement products were

TABLE I

STEREOCHEMICAL ASSIGNMENTS OF DIHYDROPYRANYLACETATES

Reactant	*Products (ratio)*	*N.m.r. data*[a]			
		Cpd.	*δ ^{13}C-2*	*δ ^{13}C-6*	*δ H-2, multiplicity, $J_{2,3}$ (Hz)*
1	**4**	**4**	87.90	57.27	6.24–6.09 m
2	**5,6** (3:1)	**5**	89.89	94.72	6.401, ddd, 0.8
		6	86.34	94.12	6.34–6.32, m 9 (whh)
3	**7,8** (>20:1)	**7**	89.01	67.98	6.423, ddd, 1.6

[a]For a solution in $CDCl_3$.

isolated. Consequently, the desired 1-*O*-acetylhex-2-enopyranoses **9** and **10** were prepared by a procedure described by Fraser-Reid *et al.*[44]. Thus, either ethyl 2,3-dideoxy-4,6-di-*O*-methyl-α-D-*erythro*-hex-2-enopyranoside or 1,5-anhydro-2-deoxy-3,4,6-tri-*O*-methyl-D-*arabino*-hex-1-enitol were treated with acetic anhydride and boron trifluoride etherate in benzene to afford the 1-*O*-acetyl-2,3-dideoxy-4,6-di-*O*-methyl-D-*erythro*-hex-2-enopyranoses **9** and **10** in a 1:1 ratio. Chromatographic separation of these anomers was not possible without accompanying allylic isomerization. Variation in the reaction temperature and time did not improve the stereoselectivity in favor of either anomer. Consequently, we have developed a method to prepare stereo- and regio-selectively 1-*S*-acetyl-2,3-dideoxy-1-thio-β-D-*erythro*-hex-2-enopyranoses which serve as adequate synthetic equivalents to 1-*O*-acetylhex-2-enopyranoses. They can also be prepared in a more stereo- and regioselective fashion and seem to be stable to silica gel chromatography and amenable to anomer separation[45].

The palladium(0)-catalyzed *C*-glycosylation of dihydropyranyl acetates **4–8** was carried out with a variety of stabilized and nonstabilized carbanions. Several adducts were prepared and the results are summarized in Table II. With a stabilized carbanion and the acetoxydihydropyran in *N,N*-dimethylformamide, the use of 10 moles percent of $Pd(PPh_3)_4$ and 1 mole percent of triphenylphosphine at 60–70° for 12 h led to the formation of the alkylated dihydropyran with net retention of configuration. The yields of isolated products, after chromatography on silica gel, were in the range of 65–98%, based on the allylic acetate. When dihydropyranyl acetate **7** was stirred with *N,N*-dimethylformamide in the presence of 10 moles percent of $Pd(PPh_3)_4$ for 2 h prior to the addition of triphenylphosphine or carbanion, the major project isolated with dimethyl sodio(acetamido)malonate was the *trans* isomer **16**, the product of net inversion. This result suggested that the intermediate

TABLE II

Pd(0)-CATALYZED ALKYLATION OF DIHYDROPYRANYL ACETATES

Reactants	*Carbanion*	*Method*[a]	*Products (ratio)*	*Yield (%)*[b]
4	$NaC(NHAc)(CO_2Et)_2$	*A*	**12**	80
5 + **6** (3:1)	$NaC(NHAc)(CO_2Me)_2$	*A*	**13**, **14** (3:1)	85
7	$NaC(NHAC)(CO_2Me)_2$	*A*	**15**	90
7	$NaC(NHAc)(CO_2Me)_2$	[c]	**16**	88
5 + **6** (3:1)	PhZnCl	*B*	**17** + **18** (3:1)	98
5 + **6** (3:1)	$Me_2C_3H_2NOCH_2ZnCl$	*B*	**19** + **20** (3:1)	42
7	PhZnCl	*B*	**21**	94
7	$CH_2{=}CHZnCl$	*B*	**22**	97
5 + **6** (3:1)	$CH(OEt)_2CH_2ZnCl$	*B*	**23** + **24** (3:1)	79

[a]Method *A*: (a) $Pd(PPh_3)_4$ (0.1 equiv.), PPh_3 (1 equiv.), *N,N*-dimethylformamide, room temperature, 20 min; (b) carbanion, 70°, 18 h. Method *B*: (a) $Pd(PPh_3)_4$ (0.05 equiv.), oxolane, room temperature, 15 min; (b) RZnCl oxolane, room temperature, 6 h. [b]Yield based on acetate, after chromatography. [c]See text.

TABLE III

STEREOCHEMICAL ASSIGNMENTS OF ALKYLATED DIHYDROPYRANS BY N.M.R. SPECTROSCOPY[a]

Compd.	$\delta^{13}C$		$\delta^{1}H$-2	$J_{1,2}$ (Hz)
	C-2	*C-6*		
12	76.81	64.16	4.935–4.914	1.7
13	77.74	98.61	5.059	1.6
14	71.14	95.60	5.030	1.9
15	77.73	69.40	5.105	1.56
16	69.66	69.42	5.084	2.4[b]
17	70.43	95.79	5.220	0.8
19	65.37	95.25	4.56–4.52	[c]
20	71.38	98.32	4.58–4.54	[c]
21	73.99	66.54	5.30	1.83
22	73.19	66.80	4.69	2.16
23	65.08	66.47	4.99	1.5
24	69.43	70.73	[c]	[c]

[a]For solutions in $CDCl_3$. [b]At 318 K. [c]Could not be determined.

palladium–dihydropyranyl complex had isomerized prior to alkylation, a result which had previously been observed for carbocyclic π-allylpalladium complexes. In further experiments, it was verified that the *cis, trans* equilibration of dihydropyranyl acetate **7** only occurred in *N,N*-dimethylformamide, and did not occur in oxolane. There is a possibility that the mechanism of the alkylation in these two solvents is different, but at present no experiments have been performed that verify this postulate. This isomerization in *N,N*-dimethylformamide is an example of reagent-controlled stereoselectivity, and enables the preparation of either stereoisomer from the same starting dihydropyranyl acetate **7**.

The structures of each of the alkylated dihydropyrans were confirmed by n.m.r. spectrometry, primarily on the basis of ^{1}H-chemical shifts and coupling constants associated with H-2 and the gamma-*gauche* effect on C-2 and C-6 in each of the adducts. Comparative spectral data for the various adducts are summarized in Table III. Each *cis* adduct exists primarily in a single conformation, whereas the *trans* adducts equilibrate between their two half-chair forms and show some temperature dependence in their n.m.r. spectra.

When nonstabilized carbanions were used, such as phenylzinc chloride or allylzinc chloride, the products formed resulted from net inversion, which is consistent with transmetallation of the organozinc reagent to palladium, followed by reductive elimination with retention of configuration. Again, the structure of each of these adducts was verified by spectral comparisons with those of previously described compounds, and a good correlation was obtained for the chemical shifts and coupling constants, even in the absence of any minor isomers. These palladium-assisted alkylations of dihydropyranyl acetates are completely regio- and stereo-

TABLE IV

Pd(0)-CATALYZED *C*-GLYCOSYLATION WITH ARYLZINC CHLORIDES

Reactants (ratio)	*ArZnCl*	*Products (ratio)*	*Yield (%)*[a]
9 + **10** (1:1)	Phenyl	**25** + **26** (1:1)	30
11 + **α** (86:14)	1-Naphthyl	**27** + **28** (86:14)	16
11 + **α** (93:7)	*p*-Tolyl	**29** + **30** (94:6)	21
11 + **α** (72:28)	*p*-Tolyl	**29** + **30** (75:25)	21
31	1-Naphthyl	**32**	23

[a]Based on carbohydrate reactant.

selective, and the stereoselectivity thus far observed has been found to be identical with that for alkylations of carboxylic allylic acetates.

These stereo- and regio-selective alkylation reactions were extended to the preparation of aryl-substituted hex-2-enopyranosides. Thus either 1-*O*- or 1-*S*-acetylhex-2-enopyranosides could be converted into their corresponding *C*-glycosyl arenes by treatment with their respective arylzinc chloride in the presence of $Pd(PPh_3)_4$ in oxolane for 5–6 h at room temperature, affording a moderate yield of their respective (hex-2-enopyranosyl)arenes. These reactions were completely stereoselective, each 1-*S*-acetyl-1-thio-β-D-hex-2-enopyranose being converted into the corresponding α-D-glycosylarene with net inversion of configuration at C-1. The reaction was also completely regioselective in favor of alkylation exclusively at C-1. Although the present yields are only moderate (20–30%) based on thioacetate, they represent the yield after both column and liquid chromatographic separation, and the reaction seems reproducible on both a small and medium scale. We are currently in the process of optimizing the yield with respect to both the catalyst and the ratio of nucleophile to thioacetate. The quality of the palladium catalyst in this reaction was especially crucial to its reproducibility. The results for each of these reactions are summarized in Table IV, and the relevant spectroscopic data on

TABLE V

STEREOCHEMICAL ASSIGNMENTS OF GLYCOSYLARENES

Compd.	*N.m.r. data*[a]				
	^1H δ H-1 ($J_{1,2}$)	*^{13}C δ C-1*	*^{13}C δ C-5*	*$^1J_{C\text{-}1,H\text{-}1}$*	*$[\alpha]_D^{25}$*[b] *(degrees)*
25	5.28 (2.0)	74.06	70.21	145	+19
26	5.16 (1.6)	77.49	72.21	[c]	[c]
27	5.92 ([d])	71.75	70.35	144	+61
29	5.23–5.30 ([d])	74.08	69.89	[c]	+37
32	5.91–5.97 ([d])	77.99	67.36	134	−64

[a]For solutions in (^{2}H)chloroform. *J* values in hertz. [b]For solutions in chloroform. [c]Value unavailable. [d]Broad singlets, whh ~5–10 Hz varying with temperature.

which the stereochemical assignments are based are shown in Table V. In the absence of any crystalline products from this reaction to date, we have based our stereochemical assignments on comparative data including ^{1}H- and ^{13}C-n.m.r. spectrometry and specific rotation. The chemical shifts and coupling constants for H-1 are in accord with each product assigned as the α-D anomer. The $^1J_{C\text{-}1,H}$ data are included in Table V primarily to indicate that the close proximity of the values strongly supports the assignment of the same stereoisomer from each reaction. These coupling-constant values are reasonable for α anomers when compared to other data for substituted pyranosides, considering the differences in the electronegativity of various substituents and the possible effects of the double bond on the dihedral angle between the O–H bond and the oxygen atom lone-pairs[46]. The specific rotation for each α-D anomer agrees with the rotation reported for a comparable α-D-glycosylbenzene prepared by Czernecki and Dechavenne[31]. Our data are consistent with the observation that each *C*-α-D-glycosyl compound exists as a mixture of equilibrating $^OH_5$ and ^5H_O conformers. The observed gamma-*gauche* effect for the phenyl anomers was also useful in helping to assign the steric structure of other α-D-glycosylarenes when only one isomer was formed in the reaction. Thus, we have demonstrated that nucleophilic substituents can be directly attached to C-1 of carbohydrates by a method in which the stereo- and regio-chemical outcome of the reaction is controlled by both the reactant and the substrate.

EXPERIMENTAL

General methods. — Optical rotations were measured with a Rudolph Autopol III polarimeter. I.r. spectra were recorded with a Perkin–Elmer 281 or a Nicolet F.t.i.r. spectrometer. N.m.r. spectra were recorded for solutions in (^{2}H)chloroform with either Varian XL-100, Varian XL-200, Nicolet-200, or Bruker WM-500 spectrometers; ^{1}H-n.m.r. spectra are reported referenced to the signal of internal tetramethylsilane at 100, 200, or 500 MHz; ^{13}C-n.m.r. spectra were recorded at 25.2, 50.3, or 125.7 MHz and are referenced to the signal of (^{2}H)chloroform (δ 77.00); multiplicities from off-resonance decoupling experiments are in agreement with the assignments, and ^1J values were obtained in the gated mode. Mass spectra were obtained with either a Hewlett–Packard 5985 low-resolution or a Kratos MS-80 medium-resolution mass spectrometer in either the low-resolution electron impact (e.i.) or chemical ionization (c.i., methane) mode, or in the high-resolution mode with peak matching to perfluorokerosene. T.l.c. and column chromatography were performed on Silica gel GF_{254} (230–400 mesh, Merck). Analytical l.c. (7 MPa) was performed in a 30-cm Waters 5-μ Microporasil column and semipreparative l.c. with a 50-cm Whatman Magnum 9 silica column. Conventional processing signified the drying of organic solutions (Na_2SO_4), filtration, and concentration under diminished pressure. All solvents were distilled shortly before use from an appropriate drying agent. Ether, oxolane, and benzene were distilled from sodium metal in the presence of diphenylketyl anion. $ZnCl_2$ was

dried by flaming *in vacuo* (1 mm). All air-sensitive reactions were performed under an atmosphere of Ar. Tetrakis(triphenylphosphine)palladium(0) was purchased from Aldrich or prepared according to the procedure of Coulson[47].

*2-Acetoxy-5,6-dihydro-2*H*-pyran* (**4**) *and 4-acetoxy-5,6-dihydro-4*H*-pyran* (**33**). — A modification of the procedure of Hurd and Edwards[42] was used to prepare **4**. Lead tetraacetate (Aldrich) was dried *in vacuo* to a fine (white to beige) powder and stored under strictly anhydrous conditions. To a mechanically stirred solution of 3,4-dihydro-2*H*-pyran (**1**; 9.22 g, 0.11 mol) in dry benzene (110 mL), at −5° under N_2, was added anhydrous lead tetraacetate (44 g, 0.99 mol) in small portions over 1 h during which the reaction temperature was kept at or ~0° with an ice–salt bath. About 15 min after the final portion of lead tetraacetate had been added, the mixture was allowed to warm temperature with stirring continued for an additional 15 min. The mixture was filtered through a bed of Filter Aid and the filter pad rinsed with dry benzene. The combined benzene filtrates were evaporated *in vacuo* to give crude **4** which was purified by vacuum distillation (1.2 Pa) to give a ~9:1 mixture of **4** and **33** (7.04 g, 45%); b.p. 37° (1.2 Pa); $\nu_{max}^{CHCl_3}$ 2990, 2980 (CH), 1750 (C=O), 1360, 1260, and 1070 cm^{-1} (C–O); ^{1}H-n.m.r. (**4**; 100 MHz): δ 6.24–6.09 (m, *J* 10 Hz, H-2,3), 5.82–5.65 (m, *J* 10 Hz, H-4), 3.98–3.86 (m, *J* 10.4 Hz, H-6,6′), 2.65–1.86 (m, H-5,5′), and 2.14 (s, $OCOCH_3$); ^{13}C-n.m.r. (**4**; 25.2 MHz): δ 168.52 (C=O), 129.33 (C-3), 122.98 (C-4), 87.90 (C-2), 57.27 (C-6), 24.78 (C-5), and 21.88 ($COCH_3$); m.s. (e.i.; 200°): *m/z* 142.1 (3.2%; M^+) and 82.1 (39%; M − HOAc); ^{13}C-n.m.r. [**33**; 25.2 MHz, $(CD_3)_2SO$]: δ 169.58 (C=O), 147.88 (C-2), 99.38 (C-3), 61.89, 61.59 (C-4,6), 27.98 (C-5), and 20.86 ($COCH_3$).

*2-Acetoxy-6-ethoxy-5,6-dihydro-2*H*-pyrans* (**5** *and* **6**) *and 4-acetoxy-2-ethoxy-3,4-dihydro-2*H*-pyran* (**34**). — Following the procedure for the preparation of **4**, 2-ethoxy-3,4-dihydro-2*H*-pyran (Aldrich; 47.8 g, 373 mmol) was treated with lead tetraacetate (149 g, 336 mmol) at 0°, followed by vacuum distillation (0.8 Pa) of the crude product to give >20:1 ratio of **5** plus **6** and **34** (32.0 g, 46%, **5**:**6** ~3:1); b.p. 54–58° (0.8 Pa); ν_{max}^{film} 3045 (C=CH), 2980, 2960, 2900 (CH), 1740 (C=O), 1340, 1290, and 1120 cm^{-1} (C–O); ^{1}H-n.m.r. (**5**; 500 MHz): δ 6.401 (ddd, *J* 3.8, 1.6, and 0.8 Hz, H-2); 5.981 (dddd, *J* 10.0, 5.2, 2.8, 1.2 Hz, H-4), 5.714 (dddd, *J* 10.0, 2.8, 2.7, 1.6 Hz, H-3), 4.961 (ddd, *J* 7.8, 3.8, 0.6 Hz, H-6), 3.917 (ddd, *J* 9.6, 7.1, 7.1, 7.1 Hz, OCH), 3.538 (dddd, *J* 9.6, 7.1, 7.1, 7.1 Hz, OCH), ~2.3 (m, H-5b), 2.242 (dddd, *J* 7.8, 2.8, 2.7, 1.5 Hz, H-5a), 2.074 (s, $OCOCH_3$), $J_{2,3}$ 1.6, $J_{2,6}$ 3.8, $J_{2,4}$ 0.8 or 1.2, $J_{3,4}$ 10, $J_{3,4a}$ 2.7 or 2.8, $J_{4,5a}$ 5.2, $J_{4,5b}$ 2.7 or 2.8, and $J_{5a,6}$ 7.8 Hz; ^{13}C-n.m.r. (**5**; 25.2 MHz): δ 168.16 (C–O), 127.19 (C-3), 122.83 (C-4), 94.72 (C-6), 89.89 (C-2), 64.21 (OCH_2), 30.78 (C-5), 21.82 ($COCH_3$), and 15.77 (CH_3); ^{1}H-n.m.r. (**6**; 500 MHz): δ 6.34–6.32 (m, whh 9 Hz, H-2); 6.06–6.02 (m, H-4), 5.77–5.74 (m, H-3), 5.03–5.01 (m, H-6), 3.83–3.77 (m, OCH), 3.52–3.47 (m, OCH), 2.47–2.41 (m, H-5,5′), and 2.029 (s, $OCOCH_3$); ^{13}C-n.m.r. (**6**; 25.2 MHz): δ 168.56 (C=O), 125.34 (C-3), 121.90 (C-4), 94.12 (C-6), 86.34 (C-2), 63.24 (OCH_2), 29.71 (C-5), 21.82 ($COCH_3$), and 15.77 (CH_3); m.s. (c.i., CH_4, 100°; mixture): *m/z* 187 (5%, MH^+) and 127 (100%), MH^+ − HOAc).

When the reaction was performed in toluene at −40° (with warming to 0° before filtration), none of the allylic isomer **34** was detected by ^{1}H-n.m.r. The *cis*-to-*trans* ratio was unaltered and the yield of distilled compound was 42%; b.p. 53° (0.1 Pa).

cis-(**7**) *and* trans-*2-Acetoxy-6-methoxymethyl-5,6-dihydro-2*H*-pyran* (**8**). — According to the procedure for the preparation of **4**, **3** (15.3 g, 120 mmol) was treated with lead tetraacetate (47.6 g, 107 mmol) at 0°, followed by vacuum distillation (2.4 Pa) of the crude product to give a ~6:1 ratio of **7** and **8** (10.1 g, 46%); b.p. 64–67° (1.0 Pa); ν_{max}^{film} 3010 (C=CH), 2930, 2900 (CH), 1740 (C=O), 1245, 1200, and 1140 cm^{-1} (C–O); ^{1}H-n.m.r. (**7**; 500 MHz): δ 6.243 (ddd, J 3.2, 1.6, 1.6 Hz, H-2), 6.079 (dddd, J 10.0, 6.0, 1.6, 1.6 Hz, H-3), 5.711 (dddd, J 10.0, 3.1, 2.9, 1.4 Hz, H-4), 4.044 (dddd, J 11.3, 5.5, 3.6, 3.6 Hz, H-6), 3.430 (ddd, J 16.4, 11.3, 6.0 Hz, CH_2), 3.338 (s, OCH_3), 2.144 (ddddd, J 17.9, 11.3, 2.8, 1.9, 1.9 Hz, H-5b), 2.028 (s, $OCOCH_3$), 1.963 (dddd, J 17.9, 5.9, 3.5, 1.4 Hz, H-5a); irradiation at δ 6.243 caused H-3 to collapse to a ddd minus, $J_{2,3}$ 1.6 Hz, H-4 to collapse to a ddd minus, $J_{2,4}$ 3.1 Hz, and H-5b to collapse to a ddd minus $J_{2,5}$ 1.9 Hz, and no change at H-5a; thus, for **7**: $J_{2,3}$ 1.6, $J_{2,4}$ 3.1, $J_{2,5a}$ 1.9, $J_{2,5a}$ 0, $J_{3,4}$ 10.0, $J_{3,5a}$ 6.0, $J_{3,5b}$ 1.6 or 1.9, $J_{4,5a}$ 1.4, $J_{4,5b}$ 2.8 or 2.9, $J_{5a,5b}$ 17.9, $J_{5b,6}$ 11.3, $J_{5a,6}$ 3.5 or 3.6, $J_{6,7a}$, $J_{6,7b}$ 3.6, 5.5 or 6.0, and $J_{7a,7b}$ 16.4 Hz; ^{13}C-n.m.r. (**7**; 25.2 MHz): δ 168.27 (C=O), 128.54 (C-2), 122.73 (C-4), 89.01 (C-2), 74.43 (C-7), 67.98 (C-6), 59.32 (OCH_3), 26.86 (C-5), and 21.87 ($COCH_3$); ^{1}H-n.m.r. (**8**; 500 MHz): δ 6.542 (d, J 6.1 Hz, H-2), 5.090 (ddd, J 5.8, 3.6, and 2.1 Hz, H-3), 4.936 (ddd, J 5.8, 5.8, 1.7 Hz, H-4), 4.06 (m, H-6), 3.504 (m, OCH_2), 3.373 (s, OCH_3), 2.017 (s, $OCOCH_3$), and ~1.83 (m, H-5,5′); ^{13}C-n.m.r. (**8**; 25.2 MHz): δ 169.04 (C=O), 147.19 (C-2), 98.70 (C-3), 74.44 (C-7), 70.70 (C-6), 62.95 (C-4), 59.46 (OCH_3), 30.98 (C-5), and 21.92 ($COCH_3$); m.s. (c.i., CH_4, 100°; mixture): m/z 187 (6%, MH^+) and 127 (100%, MH^+ − HOAc).

Anal. (h.r.e.i.m.s.) Calc. for $C_7H_{11}O_2$ (M^+ − OAc): 127.0759. Found: 127.0759.

*1-*O*-Acetyl-2,3-dideoxy-4,6-di-*O*-methyl-α-* (**9**) *and* -β-D-erythro-*hex-2-eno-pyranose* (**10**). — The procedure described is an adaptation of that described by Fraser-Reid *et al.*[44]. 1,5-Anhydro-2-deoxy-3,4,6-tri-*O*-methyl-D-*arabino*-hex-1-enitol (1 g, 5.3 mmol) was dissolved in a solution of acetic anhydride (6.71 g, 65.7 mmol) in dry benzene (13.8 mL, 0.4M) with stirring at room temperature. BF_3·diethyl ether complex (16 mg, 0.1 mmol, commercial grade) was then added and the mixture stirred for 6 h. It was then poured into ice-cold 0.63M $NaHCO_3$ (50 mL) with vigorous stirring for 30 min. The mixture was transferred to a separatory funnel and extracted with ether (3 × 50 mL). The combined ether extracts were washed with water (1 × 50 mL), dried (Na_2SO_4), and evaporated *in vacuo*. Methanol was evaporated from the residue several times to remove traces of acetic acid from the crude product (630 mg, 57%); t.l.c. (30%, v/v, ethyl acetate–hexane) indicated the presence of two main products (R_F 0.55 and 0.45) with a minor decomposition product (R_F 0.11); ^{1}H-n.m.r. (100 MHz): δ 6.51 (d), 6.28 (br. s),

6.25 (br. s), 6.14 (br. s), 6.05–6.01 (m), 5.88–5.44 (m), 4.96 (br. s), 4.90 (br. s), 3.89–3.83 (m), 3.75–3.48 (m), 3.46 (s, OCH_3), 3.44 (s, OCH_3), 3.42 (s, OCH_3), 2.26 (s, OAc), 2.12 (s, OAc), and 2.11 (s, OAc). A repetition of this procedure starting from ethyl 2,3-dideoxy-4,6-di-*O*-methyl-α-D-*erythro*-hex-2-enopyranoside (1 g, 5 mmol) produced a similar mixture of products (650 mg, 60%). The mixture was used directly without purification for the synthesis of **25** and **26**.

General procedure for Pd(0)-catalyzed C-glycosylation. — This is a modification of the procedure developed by Trost and coworkers for allylic alkylation[48]. A dihydropyranyl acetate (1 equiv.) was dissolved in an appropriate solvent (dry oxolane or *N,N*-dimethylformamide, Ar saturated, 0.15M total volume). With stabilized carbanions (Method *A*), triphenylphosphine (1 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) were then added with stirring under Ar. Carbanions (1.05 equiv.) were prepared and added, within 5 min, either as solids or in solution. The mixture was heated to 60–70° over a 12–18 h period, and then cooled to room temperature, partitioned between equal volumes of water and ether, and the aqueous layer extracted with additional ether (3 times). The combined extracts were washed with saturated NaCl solution (water when *N,N*-dimethylformamide was used), dried (Na_2SO_4), and evaporated *in vacuo*. Chromatography of the crude residue on silica gel afforded the corresponding *C*-glycosyl compounds in good yields (65–90% based on the dihydropyranyl acetate). With nonstabilized carbanions (Method *B*) only oxolane was used. $Pd(PPh_3)_4$ (0.25–0.50 equiv.), without added PPh_3, was then added, followed immediately by a preformed (0°) solution of carbanion in oxolane. The mixture was stirred for 3–6 h at room temperature and then worked up as described in Method *A* (yield, 85–98%, based on the dihydropyranyl acetate).

2-[Acetamidobis(ethoxycarbonyl)methyl]-5,6-dihydro-2H-pyran (**12**). — 2-Acetoxy-5,6-dihydro-2*H*-pyran (**4**; 200 mg, 1.41 mmol) and diethyl sodioacetamidomalonate (345 mg, 1.44 mmol) in *N,N*-dimethylformamide (20 mL) were treated according to Method *A* to afford **12** as a pale-yellow oil after chromatography (270 mg, 80%); R_F (30%, v/v, EtOAc–hexane) 0.5; $\nu_{max}^{CHCl_3}$ 3420 (NH), 3015 (C=CH), 2980, 2920, 2860 (CH), 1755, 1740 (C=O ester), 1680 (C=O amide), 1655 (C=C), 1280 and 1085 cm^{-1} (C–O); ^{1}H-n.m.r. (500 MHz): δ 6.076–6.043 (dddd, *J* 10.5, 4.1, 1.6, 1.6 Hz, H-3), 5.899–5.856 (dddd, *J* 10.5, 4.3, 2.3, 1.2 Hz, H-4), 4.935–4.914 (dddd, *J* 4.8, 1.7, 1.7, 1.7 Hz, H-2), 4.303–4.113 (m, 4 H, CO_2CH_2), 3.922–3.882 (m, H-6*e*), 3.617–3.567 (m, H-6*a*), 2.244–2.099 (m, H-5*e*), 1.972 (s, $OCOCH_3$), 1.857–1.795 (m, H-5*a*), 1.23 (t, *J* 7.0 Hz, CH_3), and 1.202 (t, *J* 7.0 Hz, CH_3); ^{13}C-n.m.r. (25.2 MHz): δ 168.8 (NC=O), 167.00 (C=O), 165.41 (C=O), 126.45 (C-3), 126.21 (C-4), 76.81 (C-2), 68.62 (C-1'), 64.16 (C-5), 62.76, 61.94 (OCH_2), 24.82 (C-5), 23.13 ($OCOCH_3$), and 14.02 (CH_3).

2-[Acetamidobis(methoxycarbonyl)methyl]-6-ethoxy-5,6-dihydro-2H-pyrans (**13** *and* **14**). — Compounds **5** and **6** (574 mg, 3.08 mmol) in *N,N*-dimethylformamide (20 mL) were treated with dimethyl sodio(acetamido)malonate (720 mg, 3.4 mmol) according to Method *A* to afford a yellow oil (660 mg, 85% based on **5** and **6** of 80% purity), **13** and **14** in the ratio 3:1, which were partially separated

by chromatography. Mixture of **13** and **14**: R_F 0.36 (**5**), 0.28 (**6**) (40%, v/v, ethyl acetate–petroleum ether); $\nu_{max}^{CHCl_3}$ 3420 (NH), 3040 (C=CH), 2980, 2950, 2910, 2870 (CH), 1740, 1670 (C=O), 1620 (C=C), 1270–1180, 1115, 1040, 1020, and 980 cm^{-1} (C–O); ^{1}H-n.m.r. (**13**; 500 MHz): δ 6.673 (br. s, 1 H, NH), 6.019 (dddd, *J* 10.4, 2.1, 1.9, 1.6 Hz, H-5), 5.763–5.722 (m, H-4), 5.059 (ddd, *J* 7.0, 3.6, 1.6 Hz, H-2), 4.646 (dd, *J* 6.4, 5.2 Hz, H-6), 3.790 (s, CO_2CH_3), 3.725 (s, CO_2CH_3), 3.75–3.70 (m, 1 H, OCH), 2.146–1.906 (m, H-3,3′), 1.976 (s, $COCH_3$), and 1.172 (t, *J* 7.1 Hz, CH_3); ^{13}C-n.m.r. (**13**, 25.2 MHz): δ 124.87 (C-5), 124.48 (C-6), 98.61 (C-2), 77.74 (C-6), 64.50 (OCH_2), 53.80 (CO_2CH_3), 27.31 (CO_2CH_3), 42 (C-2), 23.72 ($NHCOCH_3$), and 16.11 (OCH_2CH_3); the C=O and C-1′ signals could not be assigned; ^{1}H-n.m.r. (**14**; 500 MHz): δ 6.557 (br. s, 1 H, NH), 6.094 (dddd, *J* 10.4, 1.9, 1.0, 1.0 Hz, H-5), 5.756 (dddd, *J* 10.4, 4.6, 2.4 Hz, H-4), 5.030 (ddd, whh 8 Hz, *J* 4.6, 3.7, 1.9 Hz, H-2), 4.636 (dd, *J* 6.4, 5.2 Hz, H-6), 3.806 (s, CO_2CH_3), 3.746 (s, CO_2CH_3), 3.667 (q, 1 H, *J* 9.6, 7.1 Hz, OCH), 3.431 (q, *J* 9.6, 7.1 Hz, OCH), 2.006 (s, $COCH_3$), and 1.202 (t, *J* 7.1 Hz, CH_3); ^{13}C-n.m.r. (**14**; 25.2 MHz): δ 167.65 (C=O), 166.00 (C=O), 164.45 (C=O), 123.76 (C-5), 122.40 (C-4), 95.60 (C-2), 71.14 (C-6), 68.24 (C-1), 62.96 (OCH_2), 53.66 (CO_2CH_3), 53.13 (CO_2CH_3), 30.12 (C-3), 23.62 ($COCH_3$), and 15.87 (OCH_2CH_3); an upfield shift in the signals corresponding to the *cis* isomer of approximately 0.15 p.p.m. was observed in the fraction from which this ^{13}C-n.m.r. spectrum was recorded; m.s. (c.i., CH_4, 100°): *m/z* 316 (44%, MH^+), 344 (12%, $MC_2H_5^+$), 356 (9%, $MC_3H_5^+$), and 270 (100%, MH − EtOH).

Anal. (h.r.c.i.m.s.) Calc. for $C_{12}H_{16}NO_6$: 270.0977. Found: 270.0978.

cis-*2-[Acetamidobis(methoxycarbonyl)methyl]-6-methoxymethyl-5,6-dihydro-2H-pyran* (**15**). — Compound **7** (560 mg, 3 mmol) in *N,N*-dimethylformamide (20 mL) was treated with dimethyl sodio(acetamido)malonate (700 mg, 3.3 mmol) according to Method *A* to afford **15** as a pale-yellow oil after chromatography (680 mg, 90%, based on **7** of 80% purity), R_F (30%, v/v, ethyl acetate–petroleum ether) 0.15; $\nu_{max}^{CHCl_3}$ 3400 (NH), 3030 (C=CH), 1740, 1680 (C=O), 1645 (C=C), 1280, 1220, 1120, and 1060 cm^{-1} (C–O); ^{1}H-n.m.r. (500 MHz): δ 6.626 (br. s, NH), 6.056 (dddd, *J* 10.5, 2.6, 2.6, 1.6 Hz, H-3), 5.909 (dddd, *J* 10.5, 5.0, 3.0, 2.0 Hz, H-4), 5.105 (ddd, *J* 4.8, 2.6, 2.0 Hz, H-2), 3.960 (dddd, *J* 8.0, 5.7, 4.8, 4.3 Hz, H-6), 3.811 (s, CO_2CH_3), 3.714 (s, CO_2CH_3), 3.370 (dd, *J* 10.1, 5.7 Hz, $CHOCH_3$), 3.332 (s, 3 H, OCH_3), 3.313 (dd, *J* 10.1, 4.8 Hz, $CHOCH_3$), 2.05–1.92 (m, H-5,5′), and 1.987 (s, $COCH_3$); ^{13}C-n.m.r. (25.2 MHz): δ 167.45 ($NCOCH_3$), 165.95, 164.94 (CO_2CH_3), 124.38 (C-3), 123.86 (C-4), 77.73 (C-2, tentative), 74.53 (CH_2OCH_3), 69.55 [$CNHAc(CO_2CH_3)_2$], 69.40 (C-6), 53.85, 53.03 (CO_2CH_3), 59.37 (OCH_3), 26.77 (C-5), and 23.67 ($NHCOCH_3$); m.s. (c.i., CH_4, 100°): *m/z* 316 (98%, MH^+) and 190 [39%, $MH^+ - C(CO_2Me)_2NHAc$].

Anal. (h.r.c.i.m.s.) Calc. for $C_{14}H_{22}NO_7$: 316.1390. Found: 316.1399.

trans-*2-[Acetamidobis(methoxycarbonyl)methyl]-6-methoxymethyl-5,6-dihydro-2H-pyran* (**16**). — Compound **7** (500 mg, 2.7 mmol) was stirred with $Pd(PPh_3)_4$ (310 mg, 0.37 mmol) in *N,N*-dimethylformamide (20 mL) for 2 h, and

then dimethyl sodio(acetamido)malonate (580 mg, 2.74 mmol) and PPh_3 (704 mg, 2.7 mmol) were added according to Method *A*. Chromatography afforded **16** as a yellow oil (599 mg, 88% based on **7** of 80% purity) which was shown by ^{1}H-n.m.r. spectroscopy to be an equilibrium mixture of conformers which coalesced at 318 K, R_F (30%, v/v, ethyl acetate–petroleum ether) 0.15; $\nu_{max}^{CHCl_3}$ 3400 (NH), 3030 (C=CH), 2980, 2950, 2880 (CH), 1740, 1680 (C=O), 1645 (C=C), 1280, 1220, 1120, and 1060 cm^{-1} (C–O); ^{1}H-n.m.r. (500 MHz, 298 K): δ 6.784 (br. s, NH), 6.022–5.983 (m, H-3), 5.877–5.831 (m, H-4), 5.603–5.040 (m, H-2), 3.943–3.893 (m, H-6), 3.759, 3.755 (2 s, CO_2CH_3), 3.662, 3.657 (2 s, CO_2CH_3), 3.338–3.296 (m, OCH_2), 3.283, 3.728 (2 s, OCH_3), 2.0–1.8 (m, 2 H, C-5,5′), 1.941, and 1.937 (2 s, $COCH_3$); ^{1}H-n.m.r. (500 MHz, 318 K): δ 6.708 (br. s, 1 H, NH), 6.058 (dddd, *J* 10.5, 4.1, 2.3, 1.7 Hz, H-3), 5.889 (dddd, *J* 10.5, 5.1, 2.7, 2.5 Hz, H-4), 5.084 (ddd, *J* 4.6, 2.5, 2.4 Hz, H-2), 3.951 (m, H-6), 3.795 (s, CO_2CH_3), 3.705 (s, CO_2CH_3), 3.39–3.30 (m, OCH_2), 3.325 (s, 3 H, OCH_3), 2.06–1.86 (m, H-5,5′), and 1.979 (s, $COCH_3$); ^{13}C-n.m.r. (50.2 MHz, 298 K): δ 169.00 ($NCOCH_3$), 167.47, 166.40 (CO_2CH_3), 125.22 (C-3), 124.64 (C-4), 74.49 (CH_2OCH_3), 69.66 (C-2), 69.42 [$CNHCOCH_3(CO_2CH_3)_2$], 59.20 (OCH_3), 53.67, 52.82 (CO_2CH_3), 26.08 (C-5), and 22.95 ($COCH_3$); m.s. (c.i., CH_4, 100°): *m/z* 316 (4.5%, MH^+) and 127 [100%, $MH^+ - C(CO_2Me)_2NHAc$].

*6-Ethoxy-2-phenyl-5,6-dihydro-2*H*-pyrans* (**17** *and* **18**). — Compounds **5** and **6** (280 mg, 1.5 mmol; ratio **5** to **6**, 3:1) in oxolane (10 mL) were treated with phenylzinc chloride [prepared by adding M phenylmagnesium bromide in oxolane (1.6 mL) to anhydrous $ZnCl_2$ (210 mg, 1.55 mmol) in oxolane (3.4 mL)] at 0° according to Method *B*. Chromatography on silica gel afforded **17** and **18** as a pale-yellow oil (245 mg, 98% based on **5** and **6** of 80% purity; ratio **17** to **18**, 3:1); R_F (20%, v/v, ethyl acetate–petroleum ether) 0.94; $\nu_{max}^{CHCl_3}$ 3070, 3030 (C=CH), 2980, 2920 (CH), 1590 (C=C), 1130, 1050, and 1025 cm^{-1} (C–O); ^{1}H-n.m.r. (**17**; 500 MHz): δ 5.84–5.83 (m, H-3,4), 5.220 (ddd, *J* 3.5, 3.5, 0.8 Hz, H-6), 5.056 (ddd, *J* 4.6, 0.8, 0.8 Hz, H-2), 3.911 (dddd, *J* 9.8, 7.1, 7.1, 7.1 Hz, $OCHCH_3$), 3.559 (dddd, *J* 9.8, 7.1, 7.1, 7.1 Hz, $OCHCH_3$), 2.564–2.509 (m, 1 H, H-5*e*), 2.184–2.132 (m, 1 H, H-5*a*), and 1.271 (dd, *J* 7.1, 7.1 Hz, CH_3); ^{13}C-n.m.r. (**17**; 125.6 MHz): δ 140.98, 128.65, 128.43, 127.77 (C-3), 127.33, 121.75 (C-4), 95.79 (C-6), 70.43 (C-2), 63.12 (OCH_2), 29.98 (C-5), and 15.21 (CH_3); ^{13}C-n.m.r. (**18**; 125.7 MHz, tentative): δ 128.66 (C-2), 125.55 (C-4), 95.88 (C-6), 30.76 (C-5), and 15.32 (CH_3).

*2-[6-Ethoxy-5,6-dihydro-2*H*-pyranyl)methyl]-4,4-dimethyl-2-oxazolines* (**19** *and* **20**). — Compounds **5** and **6** (1.383 g, 7.4 mmol) in oxolane (35 mL) were treated with 5,5-dimethyl-2-oxazolinozinc chloride (1.2 g, 8.2 mmol) in oxolane according to Method *B*. Chromatography on silica gel afforded **19** and **20** in two major fractions as an orange oil (600 mg, 42% based on **5** and **6** of 80% purity). The first fraction was substantially enriched in **20**, and the latter in **19**, as determined by the ^{1}H-n.m.r. spectra. The two fractions were combined and a ^{13}C-n.m.r. spectrum was recorded, which allowed a determination of the *cis, trans* ratio; ratio **19** to **20**, 3:1; R_F (30%, v/v, ethyl acetate–petroleum ether) 0.4 (**20**) and 0.3 (**19**);

ν_{max}^{film} 3020 (C=CH), 2970, 2930, 2900 (CH), 1670 (C=N), and 1060 cm^{-1} (C–O); ^{1}H-n.m.r. (**20**; 500 MHz): δ 5.726–5.648 (m, H-3′,4′), 4.681 (dd, J 6.3, 4.9 Hz, H-6′), 4.57–4.54 (m, H-2), 3.9808 (ddddd, J 9.6, 7.1, 7.1, 7.1 Hz, OCH), 3.878 (s, OCH_2), 3.494 (dddd, J 9.6, 7.1, 7.1, 7.1 Hz, OCH), 2.610 (dd, J 14.9, 7.0 Hz, CH–C-2), 2.423 (dd, J 14.9, 7.6 Hz, CH–C-2), 2.42–1.99 (m, 2 H, H-5′a,5′b), 1.237 (s, 6 H, CH_3), and 1.196 (dd, J 7.1, 7.1 Hz, CH_3); ^{13}C-n.m.r. (**20**; 125.7 MHz): δ 162.79 (C-2), 128.17 (C-3′), 123.52 (C-4′), 98.32 (C-6′), 78.76 (C-5), 71.38 (C-2′), 66.93 (C-4), 62.77 (OCH_2), 34.19 (C–C-2), 30.87 (C-3), 28.22 (CH_3), and 15.01 (OCH_2CH_3); m.s. (c.i., CH_4, 100°): m/z 240 (75%, MH^+), 268 (14%, $MC_2H_5^+$), 280 (7%, $MC_3H_5^+$), 194.1 (100%, MH^+ – EtOH) and 166 (4%, MH^+ – EtOH – C≡O).

Anal. (h.r.c.i.m.s.) Calc. $C_{13}H_{22}NO_3$: 240.1600. Found: 240.1600.

^{1}H-n.m.r. (**19**; 500 MHz): δ 5.726–5.648 (m, H-3′,4′), 4.955 (dd, J 4.6, 1.7 Hz, H-5′), 4.56–4.52 (m, H-2′), 3.802 (dddd, J 9.8, 7.1, 7.1, 7.1 Hz, OCH), 3.89 (s, OCH_2), 3.500 (dddd, J 9.8, 7.1, 7.1, 7.1 Hz, OCH), 2.536 (dd, 1 H, J 14.2, 8.1 Hz, CH–C-2), 2.433 (dd, J 14.2, 6.1 Hz, CH–C-2), 2.42–1.99 (m, 2 H, H-5′), 1.240 (s, CH_3), 1.234 (s, CH_3), and 1.193 (dd, J 7.1, 7.1 Hz, CH_3); ^{13}C-n.m.r. (**19**; 125.7 MHz): δ 162.98 (C-2), 127.42 (C-3′), 122.26 (C-4′), 95.25 (C-6′), 78.89 (C-5), 66.93 (C-4), 65.37 (C-6), 63.85 (OCH_2), 33.82 (C–C-2), 29.82 (C-3), 28.22 (CH_3), and 15.0 (OCH_2CH_3).

trans-*6-Methoxymethyl-2-phenyl-5,6-dihydro-2H-pyran* (**21**). — Compound **7** (280 mg, 1.5 mmol) in oxolane (10 mL) was treated with phenylzinc chloride [prepared by adding phenylmagnesium bromide (1.6 mL, 1.6 mmol) to anhydrous $ZnCl_2$ chloride (211 mg, 1.55 mmol) in oxolane (5 mL) at 0°] according to Method *B*. Chromatography afforded **21** as a yellow oil (230 mg, 94% based on **7** of 80% purity), R_F (20%, v/v, ethyl acetate–petroleum ether) 0.8; ν_{max}^{film} 3030, 3020 (C=CH), 2990, 2930, 2890, 2820 (CH), 1600 (C=C), 1120, and 1090 cm^{-1} (C–O); ^{1}H-n.m.r. (500 MHz): δ 7.43–7.25 (m, 5 H, Ph), 6.042 (dddd, J 10.3, 4.7, 1.8, 1.8 Hz, H-3), 6.008 (dddd, J 10.3, 3.0, 1.3, 1.3 Hz, H-4), 5.301 (m, whh 6 Hz, H-2), 3.77 (dddd, J 9.9, 5.7, 4.0, 3.9 Hz, H-6), 3.439 (dd, J 10.2, 5.7 Hz, $CHOCH_3$), 3.380 (dd, J 10.2, 4.1 Hz, $CHOCH_3$), 3.323 (s, OCH_3), 2.244–2.177 (m, H-5b), and 2.008–1.953 (m, H-5a), irradiation at δ 5.301 caused $J_{2,3}$ 1.8 Hz to disappear from δ 6.042, $J_{2,4}$ 3.0 Hz to disappear from δ 6.008, and δ 2.210 to collapse into a dddd pattern (J 17.3, 10.0, 1.8, 1.3 Hz); $J_{3,4}$ 10.3, $J_{2,4}$ 3.0, $J_{2,3}$ 1.8, $J_{5b,6}$ 10.0, $J_{5a,6}$ 3.9, $J_{3,5b}$ 4.7, $J_{3,5a}$ 1.8, and $J_{4,5a} = J_{4,5b}$ 1.3 Hz; ^{13}C-n.m.r. (50.2 MHz): δ 140.87 (C-3), 128.24, 127.86, 127.53, 127.45, 125.26 (C-4), 75.16 (CH_2OCH_3), 73.99 (C-2), 66.54 (C-6), 59.16 (OCH_3), and 27.04 (C-5).

Anal. (h.r.c.i.m.s.) Calc. for $C_{13}H_{17}O_2$: 205.1229. Found: 205.1222.

trans-*6-Methoxymethyl-2-vinyl-5,6-dihydro-2H-pyran* (**22**). — Compound **7** (280 mg, 1.5 mmol) in oxolane (10 mL) was treated with vinylzinc chloride [prepared by the addition of vinylmagnesium bromide (1.55 mL, 1.55 mmol) to anhydrous $ZnCl_2$ (211 mg, 1.55 mmol) in oxolane (5 mL) at 0°] according to Method *B*. Chromatography afforded **22** as a yellow oil (180 mg, 97% based on **7** of

80% purity), R_F (20%, v/v, ethyl acetate–petroleum ether) 0.9; $\nu_{max}^{CHCl_3}$ 3060, 3010 (C=CH), 2980, 2930, 2880 (CH), 1650, 1620 (C=C), 1220, 1130, 1100, 1050 (C–O), 980, and 910 cm^{-1} (–CH=CH_2); ^{1}H-n.m.r. (500 MHz): δ 5.905 (ddd, J 17.2, 10.5, 5.0 Hz, H-X), 5.867 (dddd, J 10.2, 5.6, 2.2, 2.1 Hz, H-3), 5.711 (dddd, J 10.2, 3.5, 2.6, 1.5 Hz, H-4), 5.211 (ddd, J 9.6, 1.6, 1.6 Hz, H-B), 5.183 (ddd, J 3.6, 1.5, 1.5 Hz, H-A), 4.688 (dddddd, whh 9 Hz, J 5.0, 3.5, 2.6, 2.1, 1.6, 1.5 Hz, H-2, measured indirectly from decoupling H-2), 3.848 (dddd, J 10.2, 6.3, 3.7, 3.4 Hz, H-6), 3.437 (dd, 1 H, J 10.2, 6.3 Hz, $CHOCH_3$), 3.381 (dd, J 10.2, 3.7 Hz, $CHOCH_3$), 3.357 (s, OCH_3), 2.062 (ddddd, J 17.3, 10.3, 2.6, 2.5, 2.5 Hz, H-5b), 1.876 (ddddd, J 17.3, 5.5, 2.3, 2.3, 1.2 Hz, H-5a); irradiation at 2344.6 Hz (δ 4.688) caused loss of J 5.0 Hz from δ 5.905, of J 2.1 Hz from δ 5.867, of J 3.5 Hz from δ 5.711, of J 1.6 Hz from δ 5.211, of J 1.5 Hz from δ 5.183 Hz, and of J 2.6 Hz from δ 2.062, and also caused δ 1.876 to change its coupling pattern to dddd, J 17.3, 5.5, 3.5, 1.4 Hz, suggesting it to be first order by agreement with the same J values from the coupled protons, respectively; J_{BX} 17.2, J_{AX} 10.5 or 9.6, $J_{A,B}$ 1.5 or 1.6, J_{2X} 5.0, $J_{2,3}$ 2.1, $J_{2,4}$ 3.5, $J_{2,B}$ 1.6, $J_{2,A}$ 1.5, $J_{5a,6}$ 10.2 or 10.3, $J_{6,CH}$ 6.3, $J_{6,CH}$ 3.7, $J_{5a,6}$ 3.4 or 3.5, $J_{5a,5b}$ 17.3, $J_{3,4}$ 10.2, $J_{3,5a}$ 5.6 or 5.5, $J_{4,5b}$ 2.6 or 2.3, $J_{4,5a}$ 1.4 or 1.5, and $J_{3,5b}$ 2.5, 2.6, or 2.2 Hz; ^{13}C-n.m.r. (50.2 MHz): δ 136.85 (CH=CH_2), 127.29 (C-3), 124.66 (C-4), 116.85 (CH=CH_2), 75.38 (CH_2OCH_3), 73.19 (C-2), 66.80 (C-6), 59.18 (CH_2OCH_3), and 26.97 (C-5); m.s. (c.i., CH_4, 100°): m/z 155 (67%, MH^+) and 153 (20%, $MH^+ - H_2$).

Anal. (h.r.c.i.m.s.) Calc. for $C_9H_{15}O_2$: 155.1072. Found: 155.1072.

*2-[2,2-Bis(ethoxy)ethyl]-6-methoxymethyl-5,6-dihydro-2*H*-pyrans* (**23** *and* **24**). — Compound **7** (560 mg, 3 mmol) in oxolane (12 mL) was treated with 2,2-diethoxyethylzinc chloride [prepared by adding M 2,2-diethoxyethylmagnesium bromide (3.15 mL) in oxolane to anhydrous $ZnCl_2$ (430 mg, 3.15 mmol) in oxolane (5 mL) at 0°] according to Method *B*. Chromatography on silica gel afforded **23** and **24** (ratio **23** to **24**, 3:1) as a colorless oil (460 mg, 79% based on **7** of 80% purity).

Compound **23**. R_F (20%, v/v, ethyl acetate–petroleum ether) 0.75; ν_{max}^{film} 3020 (C–CH), 2970, 2930, 2900, 2880 (CH), 1650 (C=C), 1185, 1120, 1100, 1050, and 1010 cm^{-1} (C–O); ^{1}H-n.m.r. (500 MHz): δ 5.989 (dddd, J 10.1, 5.6, 1.5, 1.5 Hz, H-3), 5.725 (dddd, J 10.1, 2.9, 2.9, 1.5 Hz, H-4), 4.999 (m, H-2), 4.712 (dd, J 3.1, 3.4 Hz, H-2′), 4.091 (dddd, J 11.5, 4.0, 4.0, 4.0 Hz, H-6), 3.843 (dddd, 2 H, J 9.7, 7.1, 7.1, 7.1 Hz, OCH), 3.524 (dddd, 2 H, J 9.7, 7.1, 7.1, 7.1 Hz, OCH), 3.46 (dd, J 5.8, 10.6 Hz, $CHOCH_3$), 3.370 (m, $CHOCH_3$), 3.386 (s, OCH_3), 2.137 (ddddd, J 17.7, 11.4, 2.3, 2.3, 2.2 Hz, H-5b), 1.894 (dddd, J 17.7, 5.5, 3.7, 1.5 Hz, H-5a), 1.221 (dd, 6 H, J 7.1, 7.1 Hz, CH_3), and 1.182 [m, 2 H, $CH_2CO(Et)_2$], irradiation at δ 4.999 caused a loss of J 1.5 Hz from δ 5.989, of J 2.9 Hz from δ 5.725, and of J 2.2 Hz from δ 2.137; ^{13}C-n.m.r. (125.7 MHz): δ 128.17 (C-3), 125.36 (C-4), 94.33 [$C(OC_2H_5)_2$], 74.86 (CH_2OCH_3), 66.47 (C-6), 65.08 (C-2), 63.04 (OCH_2CH_3), 59.05 (OCH_3), 37.89 (C-5), 26.51 [$CH_2C(OC_2H_5)_2$], and 15.20 (CH_3).

Compound **24**. ^{13}C-n.m.r. (125.7 MHz, 20% based on ^{13}C-n.m.r.): δ 129.30 (C-3), 123.42 (C-4), 100.29 [$C(OC_2H_5)_2$], 75.07 (CH_2OCH_3), 70.73 (C-6), 69.43

(C-2), 62.28 (OCH_2CH_3), 60.47 (OCH_3), 28.70 (C-5), 26.82 [$CH_2C(OC_2H_5)_2$], and 15.20 (CH_3); m.s. (c.i., CH_4, 100°): *m/z* 199.0 (20.1%, MH^+ − EtOH), 127.0 (100%), 103 (17.1%), and 170.9 (1.3%).

Anal. (h.r.c.i.m.s.) Calc. for $C_{13}H_{25}O_4$: 245.1753. Found: 245.1700. Calc. for $C_{11}H_{19}O_3$ (MH^+ − HOEt): 199.1330. Found: 199.1300.

(2,3-Dideoxy-4,6-di-O-methyl-α- (**25**) *and -β-*D-erythro-*hex-2-enopyranosyl)-benzene* (**26**). — Compounds **9** and **10** (5 mmol) in oxolane (25 mL) were treated with phenylzinc chloride [prepared from M phenylmagnesium bromide (5.5 mmol) in oxolane and anhydrous $ZnCl_2$ (715 mg, 5.25 mmol in oxolane (5 mL) at 0°] according to Method *B*. Silica gel chromatography afforded **25** and **26** as a pale-yellow oil (371 mg, 30% overall based on **9** and **10**) which was shown by ^{1}H-n.m.r. to be an ~1.0:1.0 mixture of **25** and **26**, R_F (30%, v/v, ethyl acetate–petroleum ether) 0.66 and 0.59; ν_{max}^{film} 3060, 3030 (C=CH), 2980, 2930, 2880, 2820 (CH), 1600 (C=C), and 1090 cm^{-1} (C–C); ^{1}H-n.m.r. (**25**; 500 MHz): δ 7.59–7.26 (m, 5 H, Ph), 6.140 (ddd, *J* 10.4, 2.0, 2.0 Hz, H-2′), 6.084 (ddd, *J* 10.4, 3.0, 1.6 Hz, H-3′), 5.28 (ddd, *J* 3.0, 2.0, 2.0 Hz, H-1′), 3.905 (dddd, *J* 7.5, 2.0, 2.0, 2.0 Hz, H-4′), 3.75–3.41 (m, 3 H, H-5′,6′,6″), 3.356 (s, OCH_3), and 3.425 (s, OCH_3); ^{1}H-n.m.r. (**26**; 500 MHz): δ 7.59–7.26 (m, 5 H, Ph), 5.996 (ddd, *J* 10.3, 2.4, 1.8 Hz, H-2′), 5.850 (ddd, *J* 10.3, 1.6, 1.5 Hz, H-3′), 5.157 (ddd, *J* 3.0, 2.4, 1.6 Hz, H-1′), 3.853 (dddd, 1 H, *J* 9, 3.0, 1.5, 1.5 Hz, H-4′), 3.75–3.41 (m, H-5′,6′,6′a,6′b), 3.438 (s, OCH_3), and 3.402 (s, OCH_3); ^{13}C-n.m.r. (**25**; 125.7 MHz, tentative assignments): δ 139.40, 129.61, 128.65, 128.27, 127.06, 126.46, 74.06 (C-1′), 71.88 (C-5′), 71.68 (C-4′), 70.21 (C-6′), 59.16 (OCH_3), and 56.46 (OCH_3); ^{13}C-n.m.r. (**26**; 125.7 MHz, tentative assignments): δ 141.15, 131.74, 128.37, 127.97, 127.15, 125.30, 77.49 (C-1′), 76.56 (C-5′), 72.67 (C-4′), 72.21 (C-6′), 59.39 (OCH_3), and 59.16 (OCH_3); m.s. (c.i., CH_4, 100°): *m/z* 235 (9%, MH^+), 263 (1.0%, $MC_2H_5^+$), 275 (1.0%, $MC_3H_5^+$), 203 (81%, MH^+ − MeOH), 161 (100%, $MH^+ - H_3COCH_2CHO$), and 157 (23%, $MH^+ - C_6H_6$).

Anal. (h.r.c.i.m.s.) Calc. for $C_{14}H_{19}O_3$: 235.1335. Found: 235.1300.

The mixture was separated by l.c. to afford pure **25**, R_T 24 min (20%, v/v, ethyl acetyl–hexane), $[\alpha]_D^{25}$ +19° (*c* 0.053, chloroform).

1-(2,3-Dideoxy-4,6-di-O-methyl-α- (**27**) *and -β-*D-erythro-*hex-2-enopyranosyl)naphthalene* (**28**). — 1-Naphthylzinc chloride was prepared by adding a solution of 0.298M 1-naphthylmagnesium bromide (6.0 mL) in 1:1 ether–benzene to anhydrous $ZnCl_2$ (0.236 g, 1.73 mmol) in oxolane (4.0 mL) at 0°, and the mixture was stirred for 30 min and then warmed to room temperature. To a solution of 1-*S*-acetyl-2,3-dideoxy-4,6-di-*O*-methyl-1-thio-*α*- and -*β*-D-*erythro*-hex-2-enopyranosides (**11**) (ratio of *α* to *β*, 7:43; 0.209 g, 0.900 mmol) in oxolane (50 mL) was added $Pd(PPh_3)_4$ (1.00 g, 0.866 mmol), and the mixture stirred at room temperature for 15 min. To this was added the solution of 1-naphthylzinc chloride and the mixture stirred for 6 h at room temperature, and then partitioned between water (10 mL) and ether. The aqueous layer was extracted with ether, followed by conventional workup to give a mixture of **27** and **28**, which was filtered through

silica gel and eluted with an ethyl acetate–hexane gradient. Pure **27** and **28** were obtained by semipreparative l.c. (0.040 g, 16%; ratio of **27** to **28**, 43:7); R_F (30%, v/v, ethyl acetate–hexane) 0.66, R_T 16.4 min (10%, v/v, ethyl acetate–hexane); $\nu_{max}^{CHCl_3}$ 3080 (C=CH), 3000, 2920, 2890, 2830 (CH), 1620 (C=C), 1110, and 1090 cm^{-1} (C–C).

Compound **27**. $[\alpha]_D^{25}$ +61° (*c* 0.0095, chloroform); ^{1}H-n.m.r. (200 MHz): δ 8.32–7.29 (m, 7 H, $C_{10}H_7$), 6.35–6.25 (ddd, *J* 10.3, 1.7, 1.7 Hz, H-2′), 6.23–6.13 (ddd, *J* 10.3, 3.1, 1.5 Hz, H-3′), 6.06–6.00 (m, H-1′), 4.13–4.02 (dd, *J* 8.0, 1.7 Hz, H-4′), 3.59–3.36 (m, H-5′,6′a,6′b), 3.48 (s, OCH_3), and 3.31 (s, OCH_3); ^{13}C-n.m.r. (**27**; 50.3 MHz): δ 134.3, 134.1, 132.3, 129.08, 127.64, 126.82, 126.29, 125.74, 127.71, 124.57 ($C_{10}H_7$), 129.71 (C-3′), 128.2 (C-2′), 71.75 (C-1′), 71.57 (C-5′), 71.26 (C-4′), 70.35 (C-6′), 59.26 (OCH_3), and 56.79 (OCH_3); m.s.e.i.: *m/z* 284 (18%, M^+), 210 (78%), 207 (78%), 179 (100%), and 127 (19%, $C_{10}H_7$).

Anal. (h.r.e.i.m.s.) Calc. for $C_{18}H_{20}O_3$: 284.1413. Found: 284.1407.

Compound **28**. ^{1}H-n.m.r. (200 MHz): δ 5.85–5.81 (m, H-1′); remaining peaks were buried under those of **27**.

*4-(2,3-Dideoxy-4,6-di-*O*-methyl-α-* (**29**) *and -β-*D-erythro-*hex-2-enopyranosyl)toluene* (**30**). — *p*-Tolylzinc chloride was prepared by adding 0.768M *p*-tolylmagnesium bromide (0.54 mL) in oxolane to anhydrous $ZnCl_2$ (0.056 g, 0.413 mmol) in oxolane (10 mL) at 0°, and the mixture stirred for 30 min, and then warmed to room temperature. To a solution of **11** (ratio of α to β, 7:93; 0.080 g, 0.344 mmol) in oxolane (10 mL) was added $Pd(PPh_3)_4$ (0.398 g, 0.344 mmol) and the mixture stirred at room temperature for 15 min. To this was added the solution of *p*-tolylzinc chloride and the resulting mixture stirred for 6 h at room temperature. Workup and chromatography as described for the prepration of **27** and **28** afforded **29** and **30** (0.045 g, 21%), $[\alpha]_D^{25}$ +37° (*c* 0.0095, chloroform); R_F (30%, v/v, ethyl acetate–hexane) 0.65, R_T (30%, v/v, ethyl acetate–hexane, 1.0 mL/min) 6.5 min; $\nu_{max}^{CHCl_3}$ 3050 (C=CH), 3000, 2920, 2890, 2820 (CH), 1620 (C=C), and 1100 cm^{-1} (C–C); ^{1}H-n.m.r. (**29**; 200 MHz): δ 7.35–7.08 (m, 4 H, Ph), 6.20–6.12 (ddd, *J* 10.4, 2.0, 1.8 Hz, H-2′), 6.12–6.02 (ddd, *J* 10.4, 2.6, 1.3 Hz, H-3′), 5.30–5.23 (br. s, H-1′), 3.87–3.86 (ddd, *J* 7.0, 1.7, 1.7 Hz, H-4′), 3.65–3.50 (m, H-5′,6′a,6′b), 3.43 (s, OCH_3), 3.36 (s, OCH_3), and 2.33 (s, CH_3); ^{1}H-n.m.r. (**30**; 200 MHz): δ 7.35–7.08 (m, 4 H, Ph), 6.05–5.96 (ddd, *J* 10.4, 2.0, 1.8 Hz, H-2′), 5.88–5.81 (ddd, *J* 10.4, 2.0, 1.5 Hz, H-3′), 5.17–5.12 (br. s, H-1′), 3.88–3.78 (m, H-4′), 3.78–3.60 (m, H-5,6′a,6′b), 3.44 (s, OCH_3), 3.40 (s, OCH_3), and 2.32 (s, CH_3); ^{13}C-n.m.r. (**29**; 50.3 MHz): δ 137.62, 136.44, 129.73, 129.00, 128.17, 126.46 (Ph), 74.08 (C-1′), 71.87 (C-5′), 71.72 (C-4′), 69.89 (C-6′), 59.24 (OCH_3), 56.56 (OCH_3), and 21.15 (CH_3); m.s.e.i.: *m/z* 248 (0.6%, M^+), 217 (1.2%), 203 (1.5%), 174 (100%), 159 (41%), and 143 (54%).

Anal. (h.r.e.i.m.s.) Calc. for $C_{15}H_{20}O_3$: 248.1413. Found: 248.1422.

*1-(2,3,6-Trideoxy-4-*O*-methyl-α-*L-erythro-*hex-2-enopyranosyl)-naphthalene* (**32**). — 1-Naphthylzinc chloride was prepared by adding 0.65M 1-naphthylmagnesium bromide (17.0 mL) in 12:5 oxolane–benzene to anhydrous $ZnCl_2$ (1.18

g, 8.66 mmol) in oxolane (7.0 mL) at 0°, and the mixture stirred for 30 min and then warmed to room temperature. To a solution of 1-*S*-acetyl-2,3,6-trideoxy-4-*O*-methyl-1-thio-β-L-*erythro*-hex-2-enopyranoside (**31**; 0.876 g, 4.33 mmol) in oxolane (50 mL) was added $Pd(PPh_3)_4$ (1.0 g, 0.866 mmol) and the mxiture stirred at room temperature for 15 min. To this was added the solution of 1-naphthylzinc chloride and the mixture stirred for 5 h, followed by partitioning with water (10 mL) and ether and exhaustive extraction of the aqueous layer with ether. Conventional processing was followed by chromatography of crude **32** on silica gel and elution with ethyl acetate–hexane, and then further purification by semipreparative l.c. afforded pure **32** (0.250 g, 23% based on **31**), $[\alpha]_D^{25}$ −64° (*c* 0.0060, chloroform); R_F (30%, v/v, ethyl acetate–hexane) 0.74, R_T (10%, v/v, ethyl acetate–hexane, 4.0 mL/min) 16 min; $\nu_{max}^{CHCl_3}$ 3080 (C=CH), 3000, 2920, 2890, 2830 (CH), 1620 (C=C), and 1110 cm^{-1} (C–O); ^{1}H-n.m.r. (200 MHz): δ 8.79–7.35 (m, 7 H, $C_{10}H_7$), 6.31–6.22 (d, *J* 10.1 Hz, H-2′), 6.22–6.15 (dd, *J* 10.1, 2.6 Hz, H-3′), 5.97–5.91 (br. s, whh 5.5 Hz, H-1′), 3.69–3.51 (m, 2 H, H-4′,5′), 3.48 (s, OCH_3), and 1.22–1.14 (d, *J* 5.61 Hz, CH_3); ^{13}C-n.m.r. (50.3 MHz): δ 132.99, 132.32, 130.30, 128.91, 128.60, 128.02, 126.27, 125.97, 124.29 ($C_{10}H_7$), 128.51 (C-3′), 128.36 (C-2′), 77.99 (C-1′), 70.53 (C-4′), 67.36 (C-5′), 56.52 (OCH_3), and 18.29 (C-6′); m.s.e.i.: *m/z* 254 (7.8%, M^+), 222 (1.3%), and 210 (100%).

Anal. (h.r.e.i.m.s.) Calc. for $C_{17}H_{18}O_2$: 254.1307. Found: 254.1309.

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