Ruthenium-Catalyzed *cis*-Dihydroxylation of Alkenes: Scope and Limitations

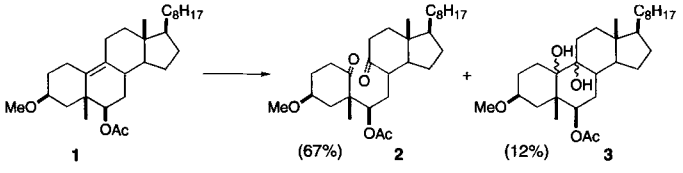
Tony K. M. Shing,* Eric K. W. Tam, Vincent W.-F. Tai, Ivan H. F. Chung, and Qin Jiang

Abstract: Oxidative ruthenium catalysis (0.07 molequiv $RuCl_3 \cdot (H_2O)_3$, 1.5 molequiv $NaIO_4$, $EtOAc/CH_3CN/H_2O$ 3:3:1), beyond the usual C–C bond cleavage to give dicarbonyls, has been shown to *syn*-dihydroxylate a wide range of alkenes (except for strained bicyclic alkenes, sterically hindered trisubstituted alkenes, and most tetrasubstituted alkenes) to give vicinal diols rapidly (within minutes) and efficiently. The minor products are the usual oxidative fission products, namely, ketones and aldehydes or carboxylic acids, and sometimes ketols. Longer reaction times lower the yields of most diols, probably owing to oxidative glycol cleavage. Reactions with substrates containing one or more electron-withdrawing groups in conjugation with or adjacent to the alkene moiety are generally slower but give better yields. The diastereoselectivity of the present "flash" dihydroxylation, *anti* to the existing α-stereogenic center, with cycloalkenes is excellent whereas that with acyclic alkenes is moderate to poor. Sodium metaperiodate is still the best co-oxidant for the catalytic reaction. Aqueous acetonitrile (approximately 86%) as an alternative solvent system was found to give better yields of 1,2-diols than the original solvent system in some cases.

Keywords
alkenes · catalysis · dihydroxylations · electrophilicity · ruthenium compounds

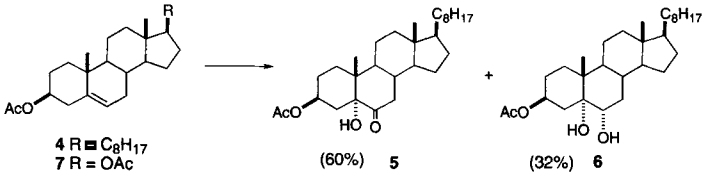
Introduction

The direct addition of hydroxy groups to alkenes to form *syn*-1,2-diols is an important functional-group conversion in organic synthesis and is commonly performed with potassium permanganate or osmium tetroxide.[1] The dihydroxylation protocol involving aqueous potassium permanganate[2] is usually accompanied by problems of overoxidation and alternative α-ketol formation, whereas that involving osmium tetroxide[3] is expensive and toxic. Despite its inherent problems, osmium tetroxide (used in stoichiometric or catalytic amounts) remains the most reliable and popular reagent.[3] Ruthenium and osmium belong to the same group in the periodic table and their oxides are expected to behave similarly. Although the use of ruthenium tetroxide for organic functional group transformations[4] including oxidative fission[5] of olefins to give ketones and aldehydes or carboxylic acids has been well recognized, there are only scattered reports concerning dihydroxylation of olefins mediated by ruthenium tetroxide. For example, Snatzke and Fehlhaber described the reaction of unsaturated steroid **1** with ruthenium tetroxide to give diketone **2** as the major product and a small amount of diol **3** (Scheme 1).[6] Sharpless and Akashi reported on the first successful stereospecific *cis*-dihydroxylation of (*E*)- and (*Z*)-cyclododecene with RuO_4 at −78 °C (ca. 20% yield in each case), but they commented that this was not a practical route to diols because of poor yields.[7] Recently, Sica and co-workers studied the ruthenium tetroxide



Scheme 1. Reaction of unsaturated steroid **1** with RuO_4.

oxidation of a number of trisubstituted steroidal alkenes and observed that the reaction products consisted of a mixture of α-ketols, 1,2-diols, and sometimes epoxides.[8–10] The example that gave the best yield of *vic*-diol is shown in Scheme 2, in which cholesteryl acetate (**4**) was treated with a stoichiometric amount of ruthenium tetroxide (prepared from RuO_2 and $NaIO_4$) in aqueous acetone to give ketol **5**[11] and diol **6** in 60 and 32% yields, respectively.[8]



Scheme 2. Reaction of cholesteryl acetate (**4**) with RuO_4 in aqueous acetone.

In 1981, the Sharpless group reported[12] an improved procedure to cleave alkenes and to oxidize a range of functional groups with a catalytic amount of ruthenium tetroxide and a stoichiometric amount (<2 equiv.) of sodium metaperiodate in a biphasic solvent system (CCl_4/CH_3CN[13]$/H_2O$ in a ratio of

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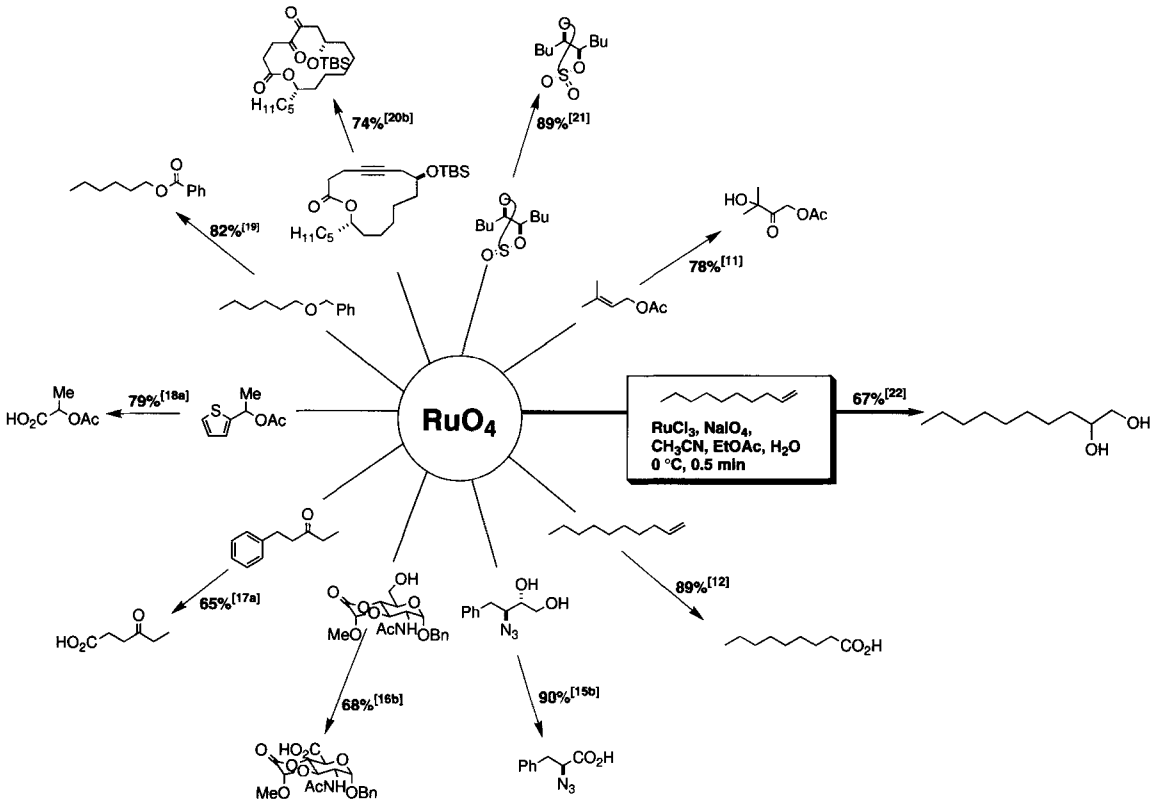


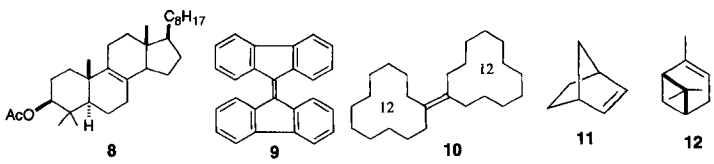
Fig. 1. Reactions of RuO_4 with different substrates.

2:2:3). This experimental protocol has since been employed for the oxidative fission of alkenes[12, 14] and diols,[15] and for the oxidation of primary alcohols,[16] phenyl,[12, 17] furan,[18] and thiophene[18a] rings to carboxylic acids, of ethers to esters,[12, 19] of acetylenes to 1,2-diketones,[20] and of cyclic sulfites to cyclic sulfates[21] (Fig. 1). As an extension of Sharpless's work, we recently communicated the first practical and rapid syntheses of *cis*-vicinal diols from alkenes by ruthenium catalysis.[22] In this paper, we report the scope and limitations of the flash dihydroxylation protocol in detail.

Results and Discussion

We found that, if we used a biphasic solvent system of ethyl acetate or carbon tetrachloride, acetonitrile, and water in a ratio of 3:3:1 in the presence of 0.07 molequiv of $RuCl_3 \cdot (H_2O)_3$[23] and 1.5 molequiv of $NaIO_4$, and ran the reactions at 0–5 °C, very rapid dihydroxylation (within minutes) of alkenes (except for strained bicyclic alkenes, sterically hindered trisubstituted alkenes, and some tetrasubstituted alkenes, vide infra) gave *syn*-diols in good-to-excellent yields. The minor products were the usual oxidative fission products, that is, ketones and aldehydes or carboxylic acids, and sometimes ketols. Longer reaction times led to more dicarbonyl formation owing to oxidative glycol cleavage[24] by sodium metaperiodate. A loading of 7 mol% of $RuCl_3 \cdot (H_2O)_3$ gave the best yields in most cases. Further decrease in the amount of catalyst (longer reaction times) resulted in competitive glycol cleavage. Like Sharpless,[12] we found that dihydroxylation reactions failed or were incomplete in the absence of acetonitrile,[25] which was crucial in maintaining the catalytic cycle.

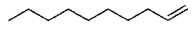
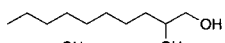
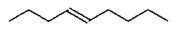
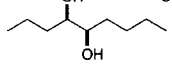
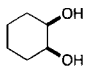
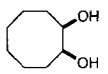
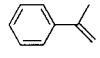
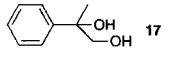
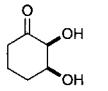
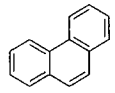
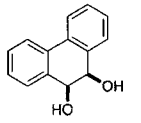
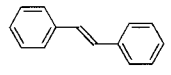
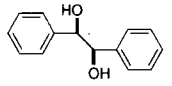
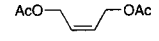
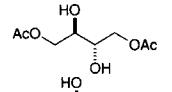
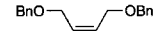
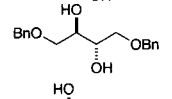
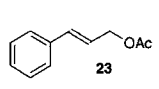
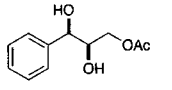
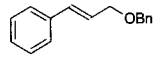
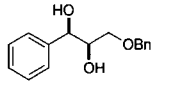
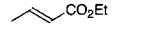
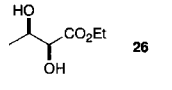
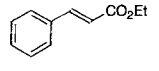
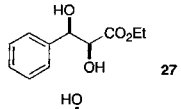
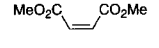
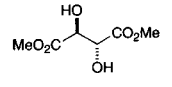
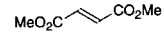
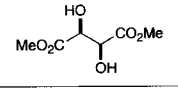
Our results, shown in Tables 1 and 2, indicate that the procedure worked well with a wide range of alkenes. Simple mono- and disubstituted olefins (Table 1, entries 1–5) were particularly reactive and the reactions had to be quenched within 30 s since prolonged reactions led to diminished yields (vide supra). For example, if the reaction of cyclooctene was allowed to run for 3 min, the *cis*-diol was obtained in 42% yield (c.f. Table 1, entry 4), and the by-product was mainly octanedial. Although trisubstituted alkenes (except for some sterically hindered ones) also afforded vicinal diols in good yields within minutes, the dihydroxylation reactions of most tetrasubstituted alkenes were sluggish, and some of them displayed incomplete reactions (Table 2, entries 6–8). Our method of ruthenium-catalyzed dihydroxylation failed to dihydroxylate cholesteryl acetate (**4**), androst-5-en-3β,17β-diol diacetate (**7**), dihydrolanosterol acetate (**8**), bisflurylidene (**9**), and biscyclododecylidene (**10**) (Fig. 2). Reactions of trisubstituted alkenes **4** and **7** stopped after two turnovers, whereas those of **8**, **9**, and **10** gave mainly carbonyls. Strained bicyclic alkenes also afforded appreciable amounts of scission products (Table 2, entries 4, 5), which were sometimes preponderant; for example, norbornene (**11**) gave 14% of the corresponding dial, only 8% of the diol, and 58% of the starting material after 15 min. When the reaction was allowed to continue for longer, the dial was obtained as the only product. (1*S*)-α-Pinene (**12**) furnished only dicarbonyls after 3 min. The oxidative fission pathway in these cases was probably facilitated by the release of the ring-strain energy.



8 9 10 11 12

Fig. 2. Alkenes that showed poor results with RuO_4.

Table 1. Ruthenium-catalyzed *cis*-dihydroxylation of mono- and disubstituted alkenes.

Entry	Alkene	Diol	Time (min)	% Yield[a]
1		 **13**	0.5	67 {54}[b]
2		 **14**	0.5	52 {58}
3		 **15**	0.5	58 {72}
4		 **16**	0.5	58
5		 **17**	0.5	70
6		 **18**	0.5	36 {51}
7		 **19**	3	65
8		 **20**	3	60[c]
9		 **21**	3	68
10		 **22**	3	76
11	 **23**	 **24**	3	69 {65}
12		 **25**	3	68
13		 **26**	3	55 {69}
14		 **27**	3	77 {84}
15		 **28**	3	85
16		 **29**	3	90 {89}

[a] Isolated yields employing Method A. [b] Values in brackets refer to isolated yields employing Method B. [c] Yield based on 33% recovery of starting material.

Another limitation of the present protocol is the poor yield obtained when the diol product is highly water soluble (Table 1, entry 6), probably because of the concomitant oxidative glycol cleavage in the aqueous layer by sodium metaperiodate. This is also reflected in the results in entries 13 and 14; we believe the lower yield in the former case is due to the higher solubility of the diol in water. Other factors that affect yields are the rate of oxidation of the alcohol products to carbonyls by ruthenium catalysis and the rate of oxidative scission by sodium metaperiodate. We also found that ethyl acetate used in the solvent system gave better yields than carbon tetrachloride, probably because of the superior solubility of the diol products in the former solvent. For example, the reaction of cinnamyl acetate (**23**) or isophorone (**31**) in carbon tetrachloride furnished the diol **24** or **32** in 57 and 72% yields, respectively (c.f. Table 1, entry 11 and Table 2, entry 2).

The C=C double bonds in allyl acetates, allyl benzyl ethers, and α,β-unsaturated ketones and esters all underwent facile *cis*-dihydroxylations within minutes. It appears that electron-withdrawing groups conjugated with or adjacent to the alkene moiety tend to slow down the reaction slightly, but these vicinal hydroxylations are still very rapid and hence can be regarded as "flash dihydroxylations". We believe the retardation of the reaction is attributable to the decrease in nucleophilicity of the double bond,[26a] the experimental evidence for which has been obtained for the analogous osmium tetroxide mediated dihydroxylation.[26b] It is noteworthy that most electrophilic alkenes gave excellent yields (Table 1, entries 15, 16; Table 2, entry 2).

The diastereoselectivities of the dihydroxylation of di- and trisubstituted cyclohexenes are shown in Table 3. All the reactions were performed in 3 min except for entry 2 (30 s) and the yields are generally good. Cyclohexenyl acetate and cyclohexenyl benzyl ether (**47**) displayed good diastereoselectivities (entries 1, 2), favoring the diol *anti* to the existing stereogenic center. It is noteworthy that whereas *syn*-selectivity was poor for the homoallylic system in 4-acetyl-1-methylcyclohexene (**49**), the homoallylic isopropyl group in enone **52** directed good *anti*-selectivity[27] (entries 3, 4). Our protocol works well with more complicated systems containing a number of oxygen functionalities (entries 5–8) and exhibits excellent diastereoselectivities that appear to be controlled by the existing stereogenic center α to the double bond (entries 7, 8). The stereochemistries of the products were assigned by ^{1}H NMR spectroscopy. The reaction conditions are compatible with various protecting groups such as esters, acetals, and benzyl and silyl ethers. Entry 8 is particularly noteworthy, since the analogous dihydroxylation reaction with catalytic osmium tetroxide[3] was disappointing and gave β-diol **61**, α-diol **62**, and the starting material **60** in 20, 10, and 60% yields, respectively (Scheme 3).

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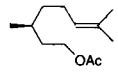
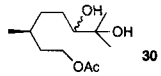
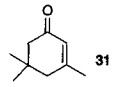
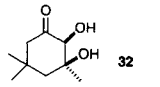
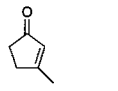
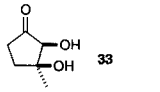
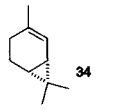
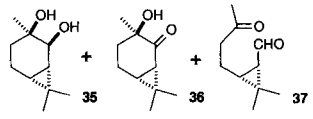
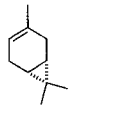
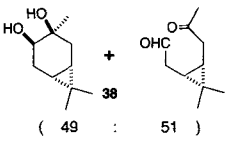
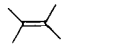
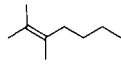
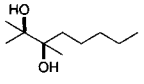
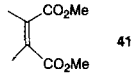
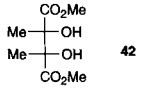
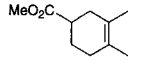
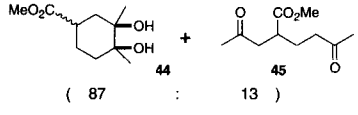
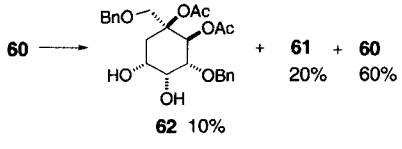
Table 2. Ruthenium-catalyzed *cis*-dihydroxylation of tri- and tetrasubstituted alkenes.

Entry	Alkene	Product(s)	Time (min)	% Yield[a]
1		 **30**	3	67[b]
2	 **31**	 **32**	3	81
3		 **33**	3	64
4	 **34**	 **35** + **36** + **37** (55 : 32 : 13)	3	74
5		 **38** (49 : 51)	3	63
6		 **39**	120	85 {81}[c]
7		 **40**	45	49[d] {49}[e]
8	 **41**	 **42**	5	77[f] {73}
9	 **43**	 **44** + **45** (87 : 13)	3	92[b]

[a] Isolated yields employing Method A. [b] Products isolated as a mixture of 1:1 diastereomers. [c] Values in brackets referred to isolated yields employing Method B. [d] Yield based on 36% recovery of starting material. [e] Yield based on 29% recovery of starting material. [f] Yield based on 12% recovery of starting material.



Scheme 3. Dihydroxylation of alkene **60** with OsO_4.

Table 4 shows the diastereoselectivities obtained in the dihydroxylation of acyclic alkenes. Selectivities in general (except for entry 7) are inferior to those displayed by osmium tetroxide mediated dihydroxylation.[28] The stereochemistry between the newly introduced hydroxyl groups in the major product and the existing alkoxy or acetoxy group was confirmed as *erythro* by conversion of the major product into the known D-arabitol or D-ribitol pentaacetate. This result is in accord with the stereochemical outcome of the analogous osmium tetroxide reactions.[28] However, it is noteworthy that, in contrast to osmium tetroxide mediated dihydroxylation,[28] the present protocol shows better diastereoselectivities with *trans*-alkenes than with *cis*-alkenes.

We have been seeking an alternative co-oxidant to sodium metaperiodate, but a satisfactory substitute has not yet been found. Reactions in the presence of co-oxidants *tert*-butyl hydroperoxide, hydrogen peroxide, 4-methylmorpholine *N*-oxide, trimethylamine *N*-oxide, sodium hypochlorite, potassium peroxodisulfate, sodium bromate, potassium hexacyanoferrate(III), or ceric ammonium nitrate did not afford any diols, whereas those listed in Table 5 (except for entry 1) furnished the diol **24** in poor yields. Periodic acid worked as well as sodium metaperiodate (entry 1), but afforded slightly more scission products.

An alternative solvent system of acetonitrile and water in a ratio of 6:1 was found to complement the existing solvent system and gave better results in some cases (see entries 1–3, 6, 11, 13, 14, and 16 in Table 1 and entries 6–8 in Table 2).

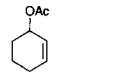
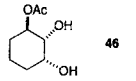
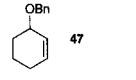
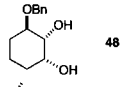
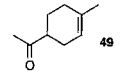
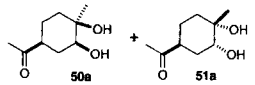
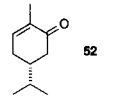
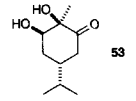
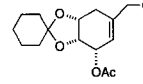
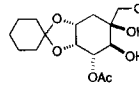
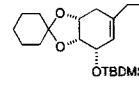
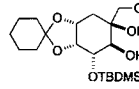
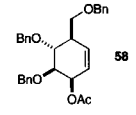
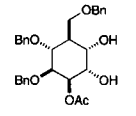
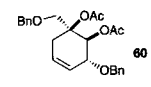
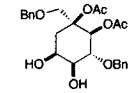
Conclusions

The ruthenium-catalyzed dihydroxylation of a wide range of alkenes with ethyl acetate or carbon tetrachloride, acetonitrile, and water in a ratio of 3:3:1 or with acetonitrile and water in a ratio of 6:1 in the presence of 0.07 molequiv of $RuCl_3 \cdot (H_2O)_3$ and 1.5 molequiv of $NaIO_4$ at 0–5 °C gave *syn*-diols rapidly and efficiently. Reactions with substrates containing electron-withdrawing group(s) conjugated with or adjacent to the alkene moiety were generally slower but gave better yields. Cyclohexene derivatives displayed better diastereoselectivities for *syn*-dihydroxylation *anti* to the existing α-stereogenic center than acyclic alkenes. Sodium metaperiodate is still the co-oxidant of choice and the alternative solvent system, approximately 86% aqueous acetonitrile, was found to give better yields of 1,2-diols than the original solvent system in some cases. Although the mechanism of the ruthenium-catalyzed dihydroxylation is not clear, the *cis*-stereochemistry of the resultant diols derived from cycloalkenes hints at a cyclic intermediate,[7] supported by the isolation[10] of a cyclic ruthenium(VI) diester. Recent density-functional theory calculations on the reaction by Sharpless et al.[29] indicate, but do not prove, the intermediacy of a metallaoxetane in a [2 + 2] mechanism. However, the classical [3 + 2] mechanism cannot be ruled out.[29] Further mechanistic information on the reaction is under active investigation and will be the subject of a future communication. Although there is not much documentation concerning the toxicity of RuO_4, which may well be less potent than OsO_4, RuO_4 is extremely volatile and a very powerful oxidizing agent. Consequently, RuO_4 should be treated as a serious health hazard.

Experimental Procedure

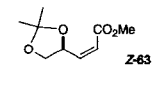
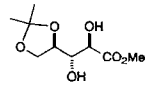
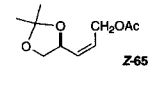
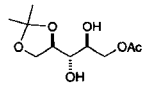
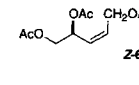
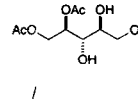
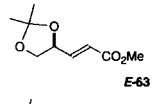
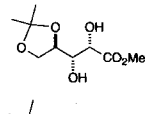
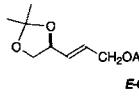
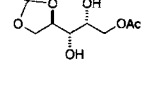
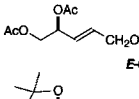
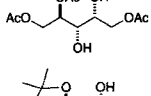
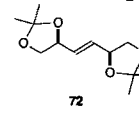
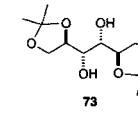
Melting points were determined with a Reichert apparatus and are reported in degrees Celsius (uncorrected). Optical rotations were measured with a JASCO DIP-370 automatic digital polarimeter operating at 589 nm. IR spectra were recorded on a Nicolet 205 FT-IR spectrometer. NMR spectra were measured on a Bruker WM 250 spectrometer at 250.13 MHz (^1H) or 62.89 MHz (^{13}C). All chemical shifts were recorded in ppm downfield from tetramethylsilane on the δ scale. Spin–spin

Table 3. Diastereoselectivity of ruthenium-catalyzed *cis*-dihydroxylation of cylcohexene derivatives [a].

Entry	Alkene	Major Product(s)	% Yield[b]	d.s.[c]
1		 **46**	80	91 : 9
2	 **47**	 **48**	72	95 : 5
3	 **49**	 **50a** + **51a**	82	67 : 33
4	 **52**	 **53**	72	91 : 9
5	 **54**	 **55**	71	>95 : 5
6	 **56**	 **57**	75	>95 : 5
7	 **58**	 **59**	86	>95 : 5
8	 **60**	 **61**	80	>95 : 5

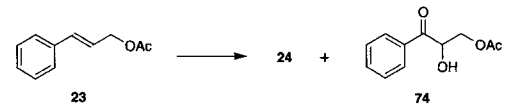
[a] All reactions run in 3 min except for entry 2 (30 s). [b] Isolated yields employing Method A. [c] Diastereoselectivity determined by ^{1}H NMR spectral analysis.

Table 4. Diastereoselectivity of ruthenium-catalyzed *cis*-dihydroxylation of acyclic (*Z*)- and (*E*)-alkenes [a].

Entry	Alkenes	Major product	% Yield	d.s.
1	 **Z-63**	 **64**	75	68 : 32[b]
2	 **Z-65**	 **66**	78	60 : 40[b]
3	 **Z-67**	 **68**	85	52 : 48[c]
4	 **E-63**	 **69**	66	86 : 14[c]
5	 **E-65**	 **70**	62	79 : 21[b]
6	 **E-67**	 **71**	82	72 : 28[b]
7	 **72**	 **73**	70	>95 : 5[b]

[a] All reactions run in 3 min employing Method A. [b] Ratio determined by ^{1}H NMR spectral analysis. [c] Ratio determined by isolation of products.

Table 5. Co-oxidants for ruthenium-catalyzed *cis*-dihydroxylation of cinnamyl acetate (**23**).



23 → **24** + **74**

Entry	Co-oxidant	Conditions [a]	Products (% yield) [b] 23	24	74
1	1.5 equiv H_5IO_6	0 °C, 3 min	0	64	0
2	1.5 equiv Dess–Martin periodinane	0 °C–RT, 12 h	70	3	10
3	1 equiv diacetoxyiodobenzene	0 °C–RT, 12 h	56	25	0
4	1 equiv Oxone®	0 °C, 1.5 h	64	6	10
5	3 equiv 85% MCPBA, 3 equiv 30% H_2O_2	0 °C, 1.5 h	61	7	4

[a] All reactions carried out in 1 mmol scale employing Method A. [b] All reactions showed a trace amount of benzaldehyde.

coupling constants (*J*) were measured directly from the spectra. EIMS were recorded on a VG 7070 F mass spectrometer. HRMS or carbon and hydrogen elemental analyses were carried out at either the Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences (China) or MEDAC Ltd, Department of Chemistry, Brunel University, Uxbridge (UK). All reactions were monitored by analytical thin-layer chromatography (TLC) on aluminum precoated with silica gel 60 F_{254} (E. Merck) and compounds were visualized with a 5% w/v spray of dodecamolybdophosphoric acid in ethanol and subsequent heating. All columns were packed wet with E. Merck silica gel 60 (230–400 mesh) as the stationary phase and eluted by flash chromatography [29]. All solvents were reagent grade. Ruthenium trichloride was purchased from Aldrich or MTM. Sodium metaperiodate was purchased from BDH. Cholesteryl acetate (**4**), androst-5-en-3β,17β-diol diacetate (**7**), dihydrolanosterol acetate (**8**), bisflurylidene (**9**), biscyclododecylidene (**10**), and 2,3-dimethyl-2-octene were kindly provided as gifts by Prof. K. B. Sharpless and Dr. B. King. Other reagents were purchased from commercial suppliers and used without further purification.

General procedure for dihydroxylation of alkenes:

Method A: To a vigorously stirred solution of the alkene (1.0 mmol) in EtOAc/CH_3CN (6 mL/6 mL) at 0–5 °C (ice/water bath) was added a solution of $RuCl_3\cdot(H_2O)_3$ (0.07 mmol) and $NaIO_4$ (1.5 mmol) in distilled water (2 mL). The two-phase mixture was stirred vigorously for 3 min and quenched with a saturated aqueous solution of $Na_2S_2O_3$ (10 mL). The aqueous phase was separated and extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and filtered. Concentration of the filtrate followed by flash chromatography afforded the diol.

Method B: To a vigorously stirred solution of the alkene (1.0 mmol) in CH_3CN (12 mL) at 0–5 °C (ice/water bath) was added a solution of $RuCl_3\cdot(H_2O)_3$ (0.07 mmol) and $NaIO_4$ (1.5 mmol) in distilled water (2 mL). The mixture was stirred vigorously for 3 min, during which white inorganics precipitated. The suspension was filtered through a thin pad of silica gel, which then was washed with EtOAc (30 mL). Concentration of the filtrate followed by flash chromatography gave the diol.

(±)-1,2-Decanediol (13): M.p. 41–42 °C (ref. [30] M.p. 48–49 °C).

(±)-*threo*-4,5-Nonanediol (14): R_f = 0.64 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 2872, 2958, 3398 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.88–0.97 (m, 6H), 1.35–1.70 (m, 10H), 2.11 (brs, 2H), 3.41 (brs, 2H); ^{13}C NMR ($CDCl_3$): δ = 13.9 (× 2), 18.8, 22.6, 27.8, 33.1, 35.6, 74.1, 74.4; MS (EI): *m/e*: 160 ([M^+], 3), 142 (2), 86 (100); $C_9H_{20}O_2$ (160.3): calcd C 67.45, H 12.58; found C 67.16, H 12.61.

***cis*-1,2-Cyclohexanediol (15)**: M.p. 95–97 °C (ref. [31] M.p. 95–96.5 °C).

***cis*-1,2-Cyclooctanediol (16)**: M.p. 75–77 °C (ref. [32] M.p. 76.5–78 °C).

(±)-2-Phenyl-1,2-propanediol (17) [33]: R_f = 0.30 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1444, 1494, 3380 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.45 (s, 3H), 3.06 (brs, 1H), 3.40 (brs, 1H), 3.52 and 3.67 (ABq, *J* = 11.3 Hz, 2H), 7.20–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 25.8, 70.6, 74.7, 125.0, 126.9, 128.1, 145.0; MS (EI) *m/e*: 121 ([M^+ −31], 41), 43 (100).

(±)-*cis*-2,3-Dihydroxycyclohexanone (18): M.p. 75–77 °C; R_f = 0.29 (EtOAc); IR ($CHCl_3$): $\tilde{\nu}$ = 1716, 3416 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.86–2.15 (m, 4H), 2.29–2.42 (m, 1H), 2.50–2.60 (m, 1H), 2.67 (brs, 1H), 3.93 (d, *J* = 2.7 Hz, 1H), 4.15

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(brs, 1H), 4.41 (brs, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.0, 28.9, 39.0, 72.6, 77.4, 209.8; MS (EI) *m/e*: 130([M^+], 19), 112 (32), 42 (100); $C_6H_{10}O_3$ (130.1): calcd C 55.37, H 7.74; found: C 55.32, H 7.80.

***cis*-9,10-Dihydro-9,10-phenanthrenediol (19)**: M.p. 175–176 °C (ref. [34] M.p. 178–179 °C).

(±)-*threo*-Hydrobenzoin (20): M.p. 147–149 °C (ref. [35] M.p. 117–118 °C).

(±)-1,4-Di-*O*-acetylerythritol (21): M.p. 91–93 °C; R_f = 0.40 (EtOAc); IR (KBr): $\tilde{\nu}$ = 1711, 1739, 3347 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 6H), 3.25 (brs, 2H), 3.82 (s, 2H), 4.27–4.32 (m, 4H); ^{13}C NMR ([D_6]acetone): δ = 21.2, 67.0, 70.9, 172.2; MS (EI) *m/e*: 207 ([M^+ + 1], 1), 189 (12), 43 (100).

(±)-1,4-Di-*O*-benzylerythritol (22): M.p. 56–58 °C; R_f = 0.44 (50% EtOAc/hexanes); IR (KBr): $\tilde{\nu}$ = 1453, 3286, 3453 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.72 (d, J = 3.6 Hz, 2H), 3.62–3.65 (m, 4H), 3.83 (m, 2H), 4.54 (s, 4H), 7.28–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$): δ = 71.1, 71.5, 73.5, 127.7, 128.4, 137.8; MS (EI) *m/e*: 302 ([M^+], 0.5), 211 (47), 91 (100); $C_{18}H_{22}O_4$ (302.4): calcd C 71.50, H 7.33; found: C 71.58, H 7.33.

(±)-*threo*-3-*O*-Acetyl-1-phenylpropane-1,2,3-triol (24): R_f = 0.26 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1722, 1724, 3450 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.06 (s, 3H), 3.03–3.07 (m, 2H), 3.06 (d, J = 4.1 Hz, 1H), 3.89–3.97 (m, 2H), 4.04–4.14 (m, 1H), 4.61 (dd, J = 3.4, 6.1 Hz, 1H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 20.6, 65.1, 73.8, 74.5, 126.6, 128.1, 128.5, 140.2, 171.2; MS (EI) *m/e*: 211 ([M^+ + 1], 2), 193 (19), 107 (100).

(±)-*threo*-3-*O*-Benzyl-1-phenylpropane-1,2,3-triol (25): M.p. 60–62 °C; R_f = 0.44 (50% EtOAc/hexanes); IR (KBr): $\tilde{\nu}$ = 1373, 1452, 3363, 3453 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 2.80 (brs, 1H), 3.10 (brs, 1H), 3.41 (dd, J = 5.1, 9.8 Hz, 1H), 3.51 (dd, J = 3.4, 9.8 Hz, 1H), 3.79–3.87 (m, 1H), 4.47 and 4.55 (ABq, J = 11.8 Hz, 2H), 4.72 (dd, J = 2.8, 6.4 Hz, 1H), 7.25–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$): δ = 71.1, 73.6, 74.7, 74.8, 126.7, 127.8, 128.0, 128.5, 137.7, 140.6; MS (EI) *m/e*: 241 ([M^+ −17], 2), 215 (64), 198 (100); $C_{16}H_{18}O_3$ (258.3): calcd C 74.40, H 7.02; found: C 74.34, H 7.03.

(±)-*threo*-Ethyl 2,3-dihydroxybutanoate (26) [31]: R_f = 0.22 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1734, 3436 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.28 (d, J = 6.4 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 2.57 (brs, 1H), 3.41 (brs, 1H), 4.02 (brs, 1H), 4.06 (brd, J = 6.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.0, 19.3, 61.8, 68.6, 74.6, 173.2; MS (EI) *m/e*: 148 ([M^+], 44), 128 (25), 76 (100).

(±)-*threo*-Ethyl 2,3-dihydroxy-3-phenylpropanoate (27): M.p. 55–57 °C; R_f = 0.40 (50% EtOAc/hexanes); IR (KBr): $\tilde{\nu}$ = 1697, 3453 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, J = 7.1 Hz, 3H), 3.07 (brd, J = 6.5 Hz, 1H), 3.34 (brd, J = 5.9 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.32 (brs, 1H), 4.97 (brs, 1H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 14.0, 62.1, 74.6, 74.8, 126.3, 128.0, 128.4, 140.0, 172.7; MS (EI) *m/e*: 210 ([M^+], 21), 193 (74), 77 (100).

***meso*-Dimethyl tartrate (28)**: M.p. 112–3 °C (ref. [35] M.p. 114 °C).

(±)-Dimethyl tartrate (29): M.p. 78–80 °C (ref. [35] M.p. 90 °C).

(±)-8-Acetoxy-2,3-dihydroxy-2,6-dimethyloctane (30) [31]: R_f = 0.23 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1717, 1741, 3426 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.92 (d, J = 6.1 Hz, 3H) and 0.93 (d, J = 6.1 Hz, 3H) are the C6 methyl groups of the diastereomers; ^{13}C NMR ($CDCl_3$): δ = 19.2, 19.5, 20.8, 23.1, 26.3, 28.7, 28.9, 29.6, 29.9, 33.6, 33.9, 35.2, 35.5, 62.8, 73.0, 78.4, 78.8, 171.2; MS (EI) *m/e*: 233 ([M^+ + 1], 3), 70 (100).

(±)-*cis*-2,3-Dihydroxy-3,5,5-trimethylcyclohexanone (32): R_f = 0.50 (50% EtOAc/hexanes); IR (KBr): $\tilde{\nu}$ = 1709, 3411 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.09 (s, 3H), 1.11 (s, 3H), 1.36 (s, 3H), 1.79 (d, J = 15.0 Hz, 1H), 1.93 (dd, J = 2.2, 15.0 Hz, 1H), 2.33–2.36 (m, 3H), 3.85 (brs, 1H), 3.97 (brs, 1H); ^{13}C NMR ($CDCl_3$): δ = 27.4, 29.0, 33.5, 36.5, 47.6, 51.6, 76.9, 79.5, 209.3; MS (EI) *m/e*: 173 ([M^+], 2), 114 (32), 43 (100); $C_9H_{16}O_3$ (172.2): calcd C 62.77, H 9.36; found: C 62.61, H 9.31.

(±)-*cis*-2,3-Dihydroxy-3-methylcyclopentanone (33): M.p. 83–84 °C; R_f = 0.19 (80% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1750, 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 3H), 1.89 (dt, J = 10.4, 14.0 Hz, 1H), 2.15 (ddd, J = 3.5, 8.0, 14.0 Hz, 1H), 2.34–2.42 (m, 2H), 2.74 (brs, 1H), 3.60 (brs, 1H), 3.91 (d, J = 0.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 25.0, 30.5, 31.7, 75.3, 81.6, 216.1; MS (EI) *m/e*: 130 ([M^+], 18), 58 (100); $C_6H_{10}O_3$ (130.1): calcd C 55.37, H 7.74; found: C 55.15, H 7.68.

[1*S*-(1α,2α,3α,4α)]-3,7,7-trimethylbicyclo[4.1.0]heptane-2,3-diol (35): 2-Carene (**34**) (272.1 mg, 2 mmol) gave diol **35** as a white solid (139.4 mg, 41%) together with a mixture of inseparable ketol **36** and keto-aldehyde **37** (110.5 mg, 33%). The ratio of **37** to **36** was determined by ^{1}H NMR to be approx. 1:2.5. Data for diol **35**: M.p. 59–61 °C; R_f = 0.33 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 3400 cm^{-1}; $[\alpha]_D^{20}$ = −37.3 (c = 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 0.56 (dd, J = 2.6, 9.1 Hz, 1H), 0.77 (t, J = 9.1 Hz, 1H), 0.95 (s, 3H), 1.06 (s, 3H), 1.02–1.16 (m, 1H), 1.22 (s, 3H), 1.54–1.69 (m, 2H), 1.82–2.00 (m, 2H), 2.14 (d, J = 8.0 Hz, 1H), 3.17 (dd, J = 2.6, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.8, 15.0, 16.5, 20.0, 25.7, 26.5, 29.0, 34.2, 70.0, 70.9; MS (EI) *m/e*: 170 ([M^+], 1); $C_{10}H_{18}O_2$ (170.3): calcd C 70.55, H 10.66; found: C 70.43, H 10.72.

[1*S*-(1α,3α,4α,6α)]-3,7,7-trimethylbicyclo[4.1.0]heptane-3,4-diol (38): M.p. 68–70 °C (ref. [36] M.p. 70–71 °C); R_f = 0.21 (50% EtOAc/hexanes); $[\alpha]_D^{24}$ = +18.1 (c = 1.66, $CHCl_3$) (ref. [36] $[\alpha]_D^{24}$ = +12.6 (c = 0.5, $CHCl_3$)); IR ($CHCl_3$): $\tilde{\nu}$ = 3380 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.61 (dt, J = 4.8, 9.5 Hz, 1H), 0.81 (d, J = 8.3 Hz, 1H), 0.88 (s, 3H), 0.98 (s, 3H), 1.18 (s, 3H), 1.24 (d, J = 4.4 Hz, 1H), 1.66 (ddd, J = 8.3, 9.5, 14.5 Hz, 1H), 1.90 (brs, 2H), 2.02 (dd, J = 7.3, 14.5 Hz, 1H), 2.11 (dd, J = 4.4, 14.5 Hz, 1H), 3.15 (dd, J = 7.3, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 15.3, 16.4, 17.5, 21.1, 25.5, 27.0, 28.6, 29.7, 33.3, 70.2, 73.2; MS (EI) *m/e*: 170 ([M^+], 3), 152 (51), 109 (100).

Pinacol (39): M.p. 34–35 °C (ref. [37] M.p. 38 °C).

2,3-Dihydroxy-2,3-dimethyloctane (40) [31]: R_f = 0.55 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 3441 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, J = 6.9 Hz, 3H), 1.16 (s, 3H), 1.21 (s, 3H), 1.22 (s, 3H), 1.29–1.59 (m, 8H), 2.00 (brs, 1H), 2.21 (brs, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.0, 20.9, 22.7, 23.5, 24.6, 25.0, 32.6, 36.2, 75.5, 76.7; MS (EI) *m/e*: 117 ([M^+ − 57], 60).

***meso*-Dimethyl 2,3-dimethyltartrate (42)**: Dimethyl 2,3-dimethylmaleate [38] (**41**) (172 mg, 1 mmol) gave diol **42** (132 mg, 73% based on 12% recovery of starting material) as colorless needles: M.p. 47–48 °C; R_f = 0.25 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1737, 3450 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.50 (s, 6H), 3.55 (brs, 2H), 3.78 (s, 6H); ^{13}C NMR ($CDCl_3$): δ = 20.2, 52.8, 78.6, 174.5; MS (EI) *m/e*: 207 ([M^+ + 1], 1), 43 (100); $C_8H_{14}O_6$ (206.2): calcd C 46.60, H 6.84; found: C 46.38, H 6.81.

(±)-Methyl *cis*-3,4-dihydroxy-3,4-dimethylcyclohexane-1-carboxylate (44) and **(±)-methyl 2,7-dioxo-4-octanoate (45)**: (±)-Methyl 3,4-dimethyl-3-cyclohexene-1-carboxylate [39] (**43**) (359.3 mg, 2.14 mmol) gave diol **44** (345.8 mg, 80%) and bisketone **45** (50.1 mg, 12%), both as colorless oils.

Diol **44**: R_f = 0.24 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1722, 3443 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 3.65 (s, 3H) and 3.67 (s, 3H) are the methoxy groups of the two diastereomers; ^{13}C NMR ($CDCl_3$): δ = 22.6, 22.9, 23.4, 23.8, 24.0, 26.2, 35.0, 35.9, 38.2, 38.4, 38.5, 40.3, 51.5, 51.6, 72.9, 73.37 (×2), 73.44, 175.7, 176.2; MS (EI) *m/e*: 203 ([M^+ + 1], 85), 185 (90), 153 (100); $C_{10}H_{18}O_4$ (202.3): calcd C 59.39, H 8.97; found: C 59.33, H 9.04.

Bisketone **45**: R_f = 0.24 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.79 (brq, J = 6.4 Hz, 2H), 2.12 (s, 3H), 2.14 (s, 3H), 2.44–2.55 (m, 3H), 2.77–2.86 (m, 1H), 2.90 (dd, J = 8.9, 16.6 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 25.3, 29.6, 39.2, 40.6, 45.0, 51.5, 174.9, 205.9, 207.1; MS (EI) *m/e*: 201 ([M^+ + 1], 3), 168 (15), 43 (100); $C_{10}H_{16}O_4$ (200.2): calcd C 59.98, H 8.05; found: C 59.80, H 8.06.

(1/2,3)-1-Acetoxy-2,3-dihydroxycyclohexane (46) [28]: R_f = 0.23 (50% EtOAc/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 1722, 3450 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.23–1.55 (m, 3H), 1.64–2.06 (m, 3H), 2.07 (s, 3H), 2.86 (brs, 1H), 3.21 (brs, 1H), 3.55 (dd, J = 2.9, 9.0 Hz, 1H), 4.06 (brs, 1H), 4.98 (dt, J = 4.5, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 18.0, 21.1, 28.8, 29.9, 69.8, 73.7, 74.0, 171.5. The diastereoselectivity (*anti*:*syn* ≈ 91:9) was determined by ^{1}H NMR spectral analysis of the corresponding triacetate in C_6D_6. The reported ratio with osmium tetroxide was 5:1 [28].

(1/2,3)-1-Benzyloxy-2,3-dihydroxycyclohexane (48) [40]: 1-Benzyloxy-2-cyclohexene (**47**) (188 mg, 1 mmol) gave diol **48** (158.7 mg, 72%) together with its *cis*-diastereomer (8.4 mg, 3%), both as colorless oils. Data for diol **48**: R_f = 0.20 (50% Et_2O/hexanes); IR ($CHCl_3$): $\tilde{\nu}$ = 3420 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.22–1.64 (m, 4H), 1.81–1.88 (m, 1H), 2.05–2.11 (m, 1H), 2.65 (brs, 1H), 2.95 (brs, 1H), 3.51 (dd, J = 2.9, 8.6 Hz, 1H), 3.63 (ddd, J = 4.1, 8.6, 10.1 Hz, 1H), 4.08 (dd, J = 2.9, 6.8 Hz, 1H), 4.45 and 4.67 (ABq, J = 11.5 Hz, 2H), 7.25–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$): δ = 18.1, 27.8, 29.5, 69.1, 70.6, 74.2, 78.1, 127.2, 127.3, 128.0, 138.4; MS (EI) *m/e*: 212 ([M^+], 1), 91 (100).

(1,2,4)-4-Acetyl-1-methylcyclohexane-1,2-diol (50a) and **(1,2/4)-4-acetyl-1-methylcyclohexane-1,2-diol (51a)**: 4-Acetyl-1-methylcyclohexene (**49**) (138.2 mg, 1 mmol) gave a mixture of inseparable diols **50a** and **51a** (140.0 mg, 81%). The diastereoselectivity (**50a**:**51a** = 67:33) was determined by ^{1}H NMR spectra analysis of the crude mixture. These diols (120 mg, 0.70 mmol) were acetylated under standard conditions to give their corresponding acetates **50b** (77.4 mg, 52%) and **51b** (51.6 mg, 34%), both as colorless oils.

Compound **50b**: R_f = 0.52 (EtOAc); IR ($CHCl_3$): $\tilde{\nu}$ = 1689, 1708, 3453 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.20 (s, 3H), 1.45 (ddd, J = 7.5, 10.0, 13.8 Hz, 1H), 1.61–1.99 (m, 6H), 2.11 (s, 3H), 2.16 (s, 3H), 2.45 (m, 1H), 4.69 (dd, J = 4.9, 11.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 20.9, 23.0, 26.9, 27.7, 28.3, 36.8, 49.4, 69.8, 170.1, 209.2; MS (EI) *m/e*: 214 ([M^+], 2.4), 196 (8.4), 43 (100); $C_{11}H_{18}O_4$ (214.3): calcd C 61.66, H 8.47; found: C 61.32, H 8.51.

Compound **51b**: $R_f = 0.44$ (EtOAc); IR ($CHCl_3$): $\tilde{\nu} = 1708$, 1739, 3466 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.21$ (s, 3H), 1.51–2.00 (m, 7H), 2.09 (s, 3H), 2.17 (s, 3H), 2.67 (m, 1H), 4.81 (dd, $J = 3.5$, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 21.2$, 23.8, 25.4, 28.1, 28.7, 34.2, 45.8, 70.5, 75.4, 170.3, 210.2; MS (EI) *m/e*: 215 ([$M^+ + 1$], 26), 197 (100); $C_{11}H_{18}O_4$ (214.3): calcd C 61.66, H 8.47; found: C 61.31, H 8.57.

(2*R*,3*R*,5*R*)-2,3-Dihydroxy-2-methyl-5-(methylethyl)-1-cyclohexanone (53) [27]: Enone **52** [41] (304 mg, 2 mmol) gave diol **53** (232 mg, 62%) together with its diastereomer (23.4 mg, 6%). $R_f = 0.50$ (25% EtOAc/hexanes); $[\alpha]_D^{20} = +30$ ($c = 0.8$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1715$, 3400 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.90$ (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H), 1.36 (s, 3H), 1.56–1.65 (m, 1H), 1.70–1.76 (m, 1H), 2.06 (ddd, $J = 3.5$, 5.8, 14.4 Hz, 1H), 2.10 (m, 1H), 2.30 (t, $J = 13.2$ Hz, 1H), 2.45 (ddd, $J = 2.4$, 4.1, 13.2 Hz, 1H), 2.99 (d, $J = 1.8$ Hz, 1H), 4.03 (t, $J = 3.0$ Hz, 1H), 4.27 (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 19.0$, 19.5, 23.3, 31.4, 32.1, 39.4, 40.0, 76.1, 78.3, 210.0; MS (EI) *m/e*: 186 ([M^+], 19), 169 (14), 143 (57), 43 (100); HRMS (EI) calcd for $C_{10}H_{18}O_3$: 186.1256, found: 186.1298.

(1*R*,2*R*,3*S*)-3-*O*-Acetyl-5-benzoyloxymethyl-1,2-*O*-cyclohexylidene-4-cyclohexen-1,2,3-triol (54): Selective benzoylation of the known (1*R*,2*R*,3*S*)-1,2-*O*-cyclohexylidene-5-hydroxymethyl-4-cyclohexen-1,2,3-triol [42] at the primary alcohol followed by acetylation gave compound **54**: M.p. 81–82 °C; $R_f = 0.26$ (25% Et_2O/hexanes); $[\alpha]_D^{20} = +6.9$ ($c = 0.7$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1723$, 2936 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.24$–1.72 (m, 10H), 2.07–2.17 (m, 1H), 2.17 (s, 3H), 2.50 (dd, $J = 11.9$, 16.3 Hz, 1H), 4.58–4.65 (m, 2H), 4.78 (brs, 2H), 5.19 (brs, 1H), 5.84 (brs, 1H), 7.40–7.46 (m, 2H), 7.52–7.59 (m, 1H), 8.04–8.07 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.9$, 23.6, 23.8, 25.1, 29.7, 33.9, 35.6, 66.6, 69.7, 72.1, 74.2, 109.6, 124.2, 128.1, 129.6, 130.0, 132.8, 133.8, 166.0, 170.4; MS (EI) *m/e*: 386 ([M^+], 38), 343 (82), 179 (48), 124 (100); $C_{22}H_{26}O_6$ (386.4): calcd C 68.38, H 6.78; found: C 68.51, H 6.79.

(1*R*,2*S*,3*S*,4*R*,5*R*)-3-*O*-Acetyl-1-benzoyloxymethyl-4,5-*O*-cyclohexylidene-1,2,3,4,5-cyclohexanepentanol (55): Alkene **54** (53.2 mg, 0.138 mmol) gave diol **55** (39.2 mg, 71%) as a white solid: M.p. 162–164 °C; $R_f = 0.47$ (20% Et_2O/hexanes); $[\alpha]_D^{20} = -46.9$ ($c = 1.0$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1722$, 3450 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.35$–1.73 (m, 10H), 1.90 (dd, $J = 7.9$, 14.4 Hz, 1H), 2.12–2.21 (m, 1H), 2.18 (s, 3H), 2.85 (s, 1H), 2.98 (d, $J = 4.8$ Hz, 1H), 3.99 (dd, $J = 4.8$, 9.9 Hz, 1H), 4.20 (d, $J = 11.2$ Hz, 1H), 4.44–4.49 (m, 3H), 5.29 (dd, $J = 3.8$, 9.9 Hz, 1H), 7.42–7.48 (m, 2H), 7.56–7.62 (m, 1H), 8.02–8.07 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 21.2$, 23.6, 24.1, 25.1, 35.1, 35.2, 37.9, 68.8 (×2), 71.9 (×2), 73.6, 73.9, 110.3, 128.5, 129.8, 133.5, 117.0, 171.2; MS (EI) *m/e*: 420 ([M^+], 37), 377 (100); $C_{22}H_{28}O_8$ (420.5): calcd C 62.85, H 6.71; found: C 62.92, H 6.29.

(1*R*,2*R*,3*S*)-3-*O*-*tert*-Butyldimethylsilyl-5-benzoyloxymethyl-1,2-*O*-cyclohexylidene-4-cyclohexen-1,2,3-triol (56): Selective benzoylation of the known (1*R*,2*R*,3*S*)-1,2-*O*-cyclohexylidene-5-hydroxymethyl-4-cyclohexen-1,2,3-triol [42] at the primary alcohol followed by silylation gave compound **56** as an oil: $R_f = 0.57$ (20% Et_2O/hexanes); $[\alpha]_D^{26} = +13.7$ ($c = 1.7$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1722$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.13$ (s, 6H), 0.93 (s, 9H), 1.36–1.60 (m, 10H), 2.02 (d, $J = 16.0$ Hz, 1H), 2.44 (d, $J = 16.0$ Hz, 1H), 4.20 (s, 1H), 4.41 (m, 1H), 4.51 (m, 1H), 4.76 (s, 2H), 5.89 (brs, 1H), 7.42 (m, 2H), 7.54 (m, 1H), 8.06 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 4.5$ (×2), 18.3, 23.6, 23.9, 25.3, 25.8, 25.9, 29.9, 33.9, 35.7, 67.1, 69.3, 72.5, 77.2, 109.1, 128.2, 129.5, 129.6, 129.9, 130.2, 131.7, 132.7, 166.1; MS (EI) *m/e*: 458 ([M^+], 4.3); $C_{26}H_{38}O_5Si$ (458.7): calcd C 68.09, H 8.35; found: C 67.85, H 8.27.

(1*R*,2*S*,3*S*,4*R*,5*R*)-3-*O*-*tert*-Butyldimethylsilyl-1-benzoyloxymethyl-4,5-*O*-cyclohexylidene-1,2,3,4,5-cyclohexanepentanol (57): Alkene **56** (60.9 mg, 0.133 mmol) gave diol **57** (49.3 mg, 75%) as a white solid: M.p. 116–117 °C; $R_f = 0.31$ (33% Et_2O/hexanes); $[\alpha]_D^{26} = -22.2$ ($c = 1.6$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1724$, 3473 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.15$ (s, 3H), 0.16 (s, 3H), 0.94 (s, 9H), 1.38–1.75 (m, 10H), 1.83 (ddd, $J = 1.8$, 8.5, 14.2 Hz, 1H), 2.13 (dd, $J = 6.2$, 14.2 Hz, 1H), 2.60 (d, $J = 1.8$, 1H), 2.62 (d, $J = 2.3$ Hz, 1H), 3.91 (dd, $J = 2.3$, 9.5 Hz, 1H), 4.07 (dd, $J = 3.75$, 9.5 Hz, 1H), 4.25 (d, $J = 11.2$ Hz, 1H), 4.27–4.40 (m, 3H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 6.0$ Hz, 1H), 8.05 (d, $J = 5.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = -4.3$, −4.4, 18.2, 23.7, 24.1, 25.1, 25.9, 35.0, 35.5, 38.2, 68.8, 70.5, 71.2, 72.0, 73.3, 76.3, 109.9, 128.4, 129.7, 130.0, 133.1, 166.5; $C_{26}H_{40}O_7Si$ (492.7): calcd C 63.38, H 8.18; found: C 63.38, H 8.21.

(1*R*,2*S*,3*R*,4*S*,5*S*,6*S*)-3-*O*-Acetyl-1,2-di-*O*-benzyl-6-benzyloxylmethyl-1,2,3,4,5-cyclohexanepentanol (59): Alkene **58** [42] (86.6 mg, 0.184 mmol) gave diol **59** (80.2 mg, 86%) as a colorless oil: $R_f = 0.30$ (67% Et_2O/hexanes); $[\alpha]_D^{21} = +13.9$ ($c = 1.4$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1746$, 3450 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.10$ (s, 3H), 2.28 (m, 1H), 3.51 (dd, $J = 9.4$, 10.1 Hz, 1H), 3.60 (dd, $J = 8.6$, 8.7 Hz, 1H), 3.92–4.02 (m, 4H), 4.42 and 4.84 (ABq, $J = 11.0$ Hz, 2H), 4.51 and 4.69 (ABq, $J = 11.1$ Hz, 2H), 4.50 (s, 2H), 5.58 (dd, $J = 3.5$, 3.7 Hz 1H), 7.17–7.43 (m, 15H); ^{13}C NMR ($CDCl_3$): $\delta = 20.9$, 42.7, 69.4, 69.8, 70.4, 70.9, 72.3, 73.5, 74.7, 75.7, 79.0, 127.6, 127.7, 127.86, 127.93, 128.1, 128.3, 128.5, 137.7, 138.1, 138.5, 169.8; MS (EI) *m/e*: 416 ([$M^+ - 90$], 3), 310 (23), 91 (100); $C_{30}H_{34}O_7$ (506.6): calcd C 71.13, H 6.76; found: C 70.89, H 6.78.

(1*S*,2*S*,3*S*,4*S*,5*S*)-1,2-Di-*O*-acetyl-3-*O*-benzyl-1-benzyloxymethyl-1,2,3,4,5-cyclohexanepentanol (61): Alkene **60** [43] (15 mg, 0.035 mmol) gave diol **61** (13 mg, 80%) as a white solid: m.p. 127–128 °C; $R_f = 0.30$ (67% Et_2O/hexanes); $[\alpha]_D^{25} = +21.9$ ($c = 1.0$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1737$, 3450 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.73$ (dd, $J = 2.8$, 16.0 Hz, 1H), 1.96 (s, 3H), 2.03 (s, 3H), 2.54 (brs, 1H), 2.75 (brs, 1H), 3.13 (dd, $J = 2.7$, 16.0 Hz, 1H), 3.48 and 3.97 (ABq, $J = 8.8$ Hz, 2H), 3.62 (dd, $J = 3.2$, 9.2 Hz, 1H), 4.04 (dd, $J = 9.7$, 9.9 Hz, 1H), 4.1–4.2 (m, 1H), 4.36 and 4.47 (ABq, $J = 11.7$ Hz, 2H), 4.67 and 4.77 (ABq, $J = 11.5$ Hz, 2H), 5.27 (d, $J = 9.9$ Hz, 1H), 7.20–7.45 (m, 10H); MS (EI) *m/e*: 367 ([$M^+ - 91$], 18), 261 (100); $C_{25}H_{30}O_8$ (458.5): calcd C 65.49, H 6.60; found: C 65.03, H 6.44.

(*Z*)-(*S*)- and (*E*)-(*S*)-Methyl 2,3-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-pent-2-enonate ((*Z*)-63) and ((*E*)-63) [44]: Wittig reaction of D-glyceraldehyde acetonide [45] with $Ph_3P{=}CHCO_2Me$ in CH_2Cl_2 gave 76% yield of compounds (*Z*)-**63** and (*E*)-**63** in the ratio 3:2. Compound (*Z*)-**63**: $[\alpha]_D^{24} = +126$ ($c = 2.4$, $CHCl_3$) (ref. [44c] $[\alpha]_D^{25} = +122$ ($c = 1.3$, $CHCl_3$)). Compound (*E*)-**63**: $[\alpha]_D^{23} = +45$ ($c = 3.0$, $CHCl_3$) (ref. [44c] $[\alpha]_D^{25} = +45$ ($c = 1.1$, $CHCl_3$)).

Methyl 4,5-*O*-isopropylidene-D-ribonate (64): $R_f = 0.40$ (10% EtOH/$CHCl_3$); $[\alpha]_D^{24} = +10.6$ ($c = 10.5$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1750$, 3425 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.36$ (s, 3H), 1.42 (s, 3H), 2.81 (d, $J = 8.0$ Hz, 1H), 3.23 (d, $J = 8.6$ Hz, 1H), 3.75 (m, 1H), 3.83 (s, 3H), 3.87 (m, 1H), 4.05 (dd, $J = 6.6$, 8.0 Hz, 1H), 4.19–4.25 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 25.2$, 26.2, 52.4, 65.9, 72.3, 72.7, 75.5, 109.7, 172.7; MS (EI) *m/e*: 205 ([$M^+ - 15$], 6), 101 (37), 43 (100).

(*Z*)-1-*O*-Acetyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-pent-2-enitol ((*Z*)-65): The allylic alcohol (3.72 g, 23.6 mmol) obtained from the DIBAL-H reduction [46] of compound (*Z*)-**63** was acetylated under standard conditions to give allyl acetate (*Z*)-**65** (4.33 g, 92%) as a colorless oil: $R_f = 0.26$ (20% Et_2O/hexanes); $[\alpha]_D^{19} = -3.0$ ($c = 8.8$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1741$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.36$ (s, 3H), 1.40 (s, 3H), 2.03 (s, 3H), 3.52 (t, $J = 8.2$ Hz, 1H), 4.08 (dd, $J = 6.4$, 8.2 Hz, 1H), 4.63–4.66 (m, 2H), 4.84 (dd, $J = 7.4$, 13.8 Hz, 1H), 5.58–5.74 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.7$, 25.7, 26.6, 59.9, 69.3, 71.8, 109.4, 127.5, 132.1, 170.3; MS (EI) *m/e*: 185 ([$M^+ - 15$], 14), 43 (100); $C_{10}H_{16}O_4$ (200.2): calcd C 59.98, H 8.05; found: C 59.96, H 8.02.

(*E*)-1-*O*-Acetyl-2,3-dideoxy-4,5-*O*-isopropylidene-D-*glycero*-pent-2-enitol (*E*)-65): Similarly, the allylic alcohol (1.92 g, 12.1 mmol) obtained from the DIBAL-H reduction [46] of compound (*E*)-**63** was acetylated to give allyl acetate (*E*)-**65** (2.33 g, 96%) as a colorless oil: $R_f = 0.27$ (20% Et_2O/hexanes); $[\alpha]_D^{19} = +32.2$ ($c = 8.2$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1742$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.35$ (s, 3H), 1.39 (s, 3H), 2.03 (s, 3H), 3.57 (t, $J = 8.0$ Hz, 1H), 4.06 (dd, $J = 6.2$, 8.0 Hz, 1H), 4.45–4.54 (m, 3H) 5.71 (dd, $J = 6.9$, 15.5 Hz, 1H), 5.86 (dt, $J = 5.5$, 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.4$, 25.5, 26.3, 63.5, 69.0, 75.8, 109.1, 127.3, 131.5, 170.0; MS (EI) *m/e*: 185 ([$M^+ - 15$], 21), 43 (100); $C_{10}H_{16}O_4$ (200.2): calcd C 59.98, H 8.05; found: C 60.20, H 8.09.

1-*O*-Acetyl-4,5-*O*-isopropylidene-D-ribitol (66): $R_f = 0.29$ (60% EtOAc/hexanes); $[\alpha]_D^{23} = +9.3$ ($c = 9.2$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1780$, 3430 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.35$ (s, 3H), 1.43 (s, 3H), 2.12 (s, 3H), 3.01 (d, $J = 4.1$ Hz, 1H), 3.23 (d, $J = 3.3$ Hz, 1H), 3.58 (m, 1H), 3.85 (m, 1H), 3.97 (dd, $J = 5.7$, 8.3 Hz, 1H), 4.08–4.27 (m, 3H), 4.39 (dd, $J = 5.7$, 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.8$, 25.1, 26.5, 65.7, 66.4, 71.3, 72.2, 76.6, 109.5, 172.0; MS (EI) *m/e*: 219 ([$M^+ - 15$], 30), 201 (10), 101 (100).

(*Z*)-1,4,5-Tri-*O*-acetyl-2,3-dideoxy-D-*glycero*-pent-2-enitol ((*Z*)-67) [47]: Ice-cold 50% aqueous acetic acid (40 mL) was added to compound (*Z*)-**65** (0.8 g, 4 mmol) in one portion and the mixture was stirred for 12 h at RT. The solvent was evaporated in vacuo and the residue flash-chromatographed (67% EtOAc/hexanes) to give the corresponding diol (595.2 mg, 93%) which was then acetylated in CH_2Cl_2 (50 mL), pyridine (1.6 mL, 19.7 mmol), acetic anhydride (0.89 mL, 9.5 mmol), and a catalytic amount of DMAP. After aqueous workup and purification by flash chromatography (33% Et_2O/hexanes), compound (*Z*)-**67** (862.2 mg, 95%) was obtained as a colorless oil: $R_f = 0.57$ (67% Et_2O/hexanes); $[\alpha]_D^{24} = -18.6$ ($c = 8.7$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1745$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.98$ (s, 9H), 4.02 (dd, $J = 6.9$, 11.9 Hz, 1H), 4.12 (dd, $J = 4.0$, 10.6 Hz, 1H), 4.58–4.74 (m, 2H), 5.45 (m, 1H), 5.63–5.75 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.4$, 20.5, 20.7, 60.0, 64.4, 67.8, 127.6, 129.4, 169.6, 170.2 (×2); MS (EI) *m/e*: 244 ([M^+], 0.5), 185 (3), 142 (100).

(*E*)-1,4,5-Tri-*O*-acetyl-2,3-dideoxy-D-*glycero*-pent-2-enitol ((*E*)-67) [47]: Following the same procedure as described in the previous experiment, compound (*E*)-**65** (0.8 g, 4 mmol) was hydrolyzed to give the corresponding diol (631.7 mg, 99%) which was then acetylated to give compound (*E*)-**67** (905.5 mg, 94%) as a colorless oil: $R_f = 0.52$ (67% Et_2O/hexanes); $[\alpha]_D^{24} = +25.5$ ($c = 16.2$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1745$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.04$ (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 4.04 (dd, $J = 7.0$, 11.8 Hz, 1H), 4.21 (dd, $J = 3.7$, 11.8 Hz, 1H), 4.52 (brd, $J = 5.4$ Hz, 2H), 5.49 (m, 1H), 5.69 (dd, $J = 6.2$, 14.3 Hz, 1H), 5.83 (dt, $J = 5.4$, 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.3$, 20.5, 20.6, 63.3, 64.4, 70.8, 127.6, 128.5, 169.5, 170.1, 170.2; MS (EI) *m/e*: 244 ([M^+], 0.5), 185 (37), 142 (100).

1,4,5-Tri-*O*-acetyl-D-ribitol (68): $R_f = 0.61$ (75% EtOAc/hexanes); $[\alpha]_D^{23} = +3.2$ ($c = 5.7$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1729$, 3450 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.05$ (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 3.26 (brs, 1H), 3.42 (brs, 1H), 3.78–3.90 (m,

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2H), 4.17 (dd, $J = 5.9$, 11.8 Hz, 1H), 4.24–4.32 (m, 2H), 4.43 (dd, $J = 3.0$, 12.0 Hz, 1H), 5.20 (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.7$ (×2), 20.8, 62.6, 65.4, 70.2, 71.0, 72.1, 170.4, 171.2, 171.6; MS (EI) *m/e*: 279 ([$M^+ + 1$], 17), 261 (100).

Methyl 4,5-*O*-isopropylidene-D-arabinonate (69): $R_f = 0.43$ (80% EtOAc/hexanes); $[\alpha]_D^{22} = +8.0$ ($c = 2.0$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1740$, 3420 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 3H), 1.40 (s, 3H), 2.96 (br s, 1H), 3.58 (br s, 1H), 3.79 (s, 3H), 3.81 (m, 1H), 3.98–4.12 (m, 3H), 4.43 (br d, $J = 4.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 25.1$, 26.8, 52.7, 66.8, 70.5, 73.0, 75.1, 109.4, 173.8; MS (EI) *m/e*: 205 ([$M^+ - 15$], 16), 187 (18), 43 (100).

1-*O*-Acetyl-4,5-*O*-isopropylidene-D-arabitol (70): $R_f = 0.30$ (60% EtOAc/hexanes); $[\alpha]_D^{23} = +6.6$ ($c = 6.4$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1740$, 3425 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.34$ (s, 3H), 1.38 (s, 3H), 2.09 (s, 3H), 2.73 (br d, $J = 6.8$ Hz, 1H), 2.86 (br d, $J = 4.7$ Hz, 1H), 3.53 (br s, 1H), 3.95–4.01 (m, 2H), 4.06–4.15 (m, 2H), 4.19–4.25 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 20.8$, 25.2, 26.7, 66.0, 66.6, 69.1, 71.6, 76.0, 109.3, 171.3; MS (EI) *m/e*: 219 ([$M^+ - 15$], 6.3), 201 (21), 101 (100).

1,4,5-Tri-*O*-acetyl-D-arabitol (71): $R_f = 0.60$ (75% EtOAc/hexanes); $[\alpha]_D^{24} = +1.5$ ($c = 9.3$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 1729$, 3450 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.03$ (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 3.38–3.43 (m, 2H), 3.62 (m, 1H), 3.76 (m, 1H), 4.12–4.16 (m, 2H), 4.23 (dd, $J = 5.4$, 12.3 Hz, 1H), 4.47 (dd, $J = 2.5$, 12.3 Hz, 1H), 5.02 (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.6$, 20.7, 20.9, 62.9, 65.5, 67.7, 69.1, 71.3, 170.8, 171.05, 171.1; MS (EI) *m/e*: 279 ([$M^+ + 1$], 5), 261 (35), 43 (100).

1,2:5,6-Di-*O*-isopropylidene-D-mannitol (73): Alkene **72** [48] (228.0 mg, 1 mmol) gave diol **73** (183 mg, 76%) as colorless needles: M.p. 113–115 °C (ref. [49] M.p. 119–120 °C).

Structural proof for the dihydroxylation products 64, 66, 68, 69, 70, and 71: The major products from the dihydroxylation of compounds (*E*)-**63**, (*E*)-**65**, and (*E*)-**67** were transformed into the same pentaacetate, which was equivalent to synthetic D-arabitol pentaacetate by the usual criteria. Similarly, the major products from the dihydroxylation of compounds (*Z*)-**63**, (*Z*)-**65**, and (*Z*)-**67** were proved to yield D-ribitol pentaacetate. Transformation of **64** and **69** into the pentaacetate was carried out in three steps: i) DIBAL-H THF, −40 °C; ii) $AcOH/H_2O$ (1:1), RT; and iii) Ac_2O, pyridine, DMAP (cat.), CH_2Cl_2, RT. Transformation of **66** and **70** into the pentaacetate was carried out in two steps: i) $AcOH/H_2O$ (1:1), RT; and ii) Ac_2O, pyridine, DMAP (cat.), CH_2Cl_2, RT. Transformation of **68** and **71** into the pentaacetate was carried out in a single step: Ac_2O, pyridine, DMAP (cat.), CH_2Cl_2, RT.

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