Facile Syntheses of All Possible Diastereomers of Conduritol and Various Derivatives of Inositol Stereoisomers in High Enantiopurity from *myo*-Inositol

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Received October 25, 2001

Phosphoinositide-based signaling processes are crucially important in intracellular signal transduction events. Inositol phosphate analogues have been useful in probing the structure−activity relationships between inositol phosphates and biomacromolecules, and in studying biological functions of newly found inositol phosphates. Thus, a systematic and ready access to inositol stereoisomers is highly desirable. And practical and convenient syntheses of conduritols and related compounds are also important because of their biological activities and their synthetic utilities in the preparation of other bioactive molecules. We herein report the first syntheses of all possible diastereomers of conduritol and various derivatives of eight inositol stereoisomers in high enantiopurity from *myo*-inositol, which involve efficient enzymatic resolution of the intermediates conduritol B and C derivatives, followed by oxidation−reduction or the Mitsunobu reaction, and *cis*-dihydroxylation in stereo- and regioselective manners.

Introduction

Various inositol phosphate derivatives, including D-*myo*-inositol 1,4,5-trisphosphate [D-I(1,4,5)P_3] and D-*myo*-inositol 1,3,4,5-tetrakisphosphate [D-I(1,3,4,5)P_4], and phospholipids play pivotal roles in intracellular signal transduction events.[1] Although the scope of the phosphoinositide-based signaling processes is continually widening, clear understanding of the molecular mechanisms is still lacking. Thus, many research efforts are now being directed toward the structure−activity relationship (SAR) between inositol phosphates and biomacromolecules, which utilizes various regio- and stereoisomers of inositol phosphates (IP_n).[2] There exist nine stereoisomers of inositol: *myo*, *scyllo*, *cis*, D-*chiro*-(+), L-*chiro*-(−), *epi*, *allo*, *muco*, and *neo* (Figure 1). Five stereoisomers (*myo*, *scyllo*, D-*chiro*, L-*chiro*, and *neo*) have been found in nature, and the other four stereoisomers (*cis*, *epi*, *allo*, and *muco*) are unnatural synthetic products.

cis-Inositol, with three *syn*-axial hydroxyl groups in either of its chair conformations, readily forms strong complexes with metal cations and with oxyacid anions.[3] *scyllo*-Inositol with all equatorial hydroxyl groups has been found in animals and plants,[4] and it has been suggested that certain human diseases are associated with *scyllo*-inositol depletion.[5] All inositol stereoisomers have been synthesized in varying efficiencies from halo-

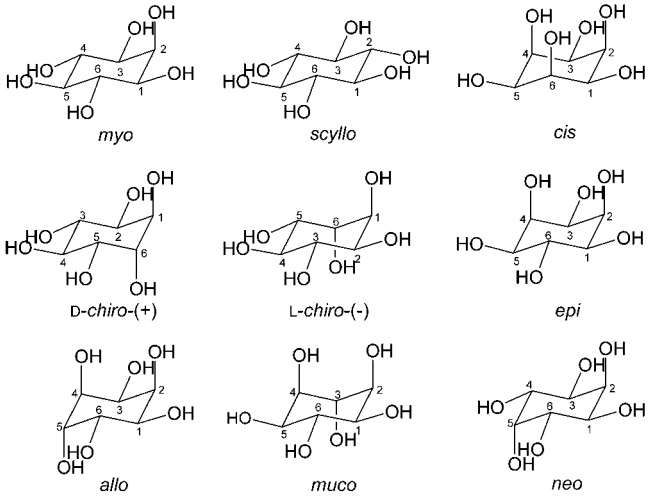

Figure 1. Nine stereoisomeric inositols.

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10.1021/jo016237a CCC: $22.00
Published on Web 04/20/2002

benzenes,[6] benzene,[7] hexahydroxybenzene,[8] tetrahydroxyquinone,[9] sugars,[10] inositols,[11] and others.[12] Yet few reports on general and systematic approaches to all inositol stereoisomers have been made.[10a,c]

Conduritols and their derivatives possess interesting biological properties; for example, conduritol epoxides and aminoconduritols act as inhibitors of glycosidases,[13] cyclophellitols have proven to be potent inhibitors of human immunodeficiency virus (HIV) and glycosidases,[14] and conduritol A analogues modulate the release of insulin from isolated pancreatic islets in the presence of varying concentrations of glucose.[15] A number of conduritol derivatives have also been found to possess antibiotic, antileukemic, and growth-regulating activities.[16] In addition, conduritols have been widely used as intermediates in the chemical syntheses of inositols,[6] quercitols,[17] deoxyinositols,[18] aminoconduritols,[16,19] conduritol epoxides,[16] cyclophellitol,[20] pseudosugars,[21] amino sugar analogues,[22] sugar amino acid analogues, etc. As pointed out in recent reviews,[16] however, a number of difficulties have been encountered in the syntheses of conduritols. Conduritols are cyclohex-5-ene-1,2,3,4-tetrols, and exist as two *meso*-compounds (conduritols A and D) and four enantiomeric pairs (conduritols B, C, E, and F) (Figure 2). Conduritols A and F are naturally occurring. Conduritol isomers have been synthesized by several methods: microbial oxidation of benzene[23] or halobenzenes,[19b,24] followed by epoxidation−ring opening or dihydroxylation, reductive elimination of inositol diols,[25] and others.[18,26] Although considerable progress has been made in the synthesis of optically active conduritols from enantiopure unsaturated cyclic *cis*-diols, obtained by microbial oxidation of halobenzenes,[19b,24] many other approaches have resulted in racemic mixtures. Recently, enantiopure conduritols have been prepared by employing chiral starting materials such as sugar alcohols[27] and diethyl L-tartrate.[28] Enantiopure conduritols have also been obtained by chemical[20,25b,29] or enzymatic[19a,21b,30] resolution of racemic conduritol derivatives or their precursors.

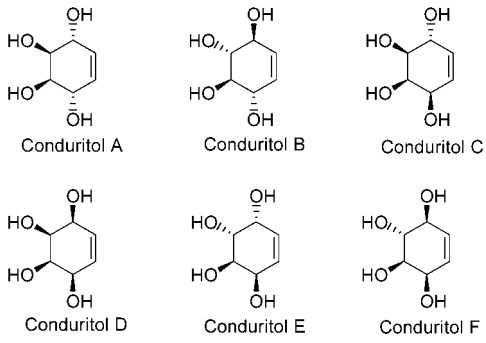

Figure 2. Six stereoisomeric conduritols.

The ready availability of all stereoisomers of IP_n would offer valuable tools for SAR studies of the interactions

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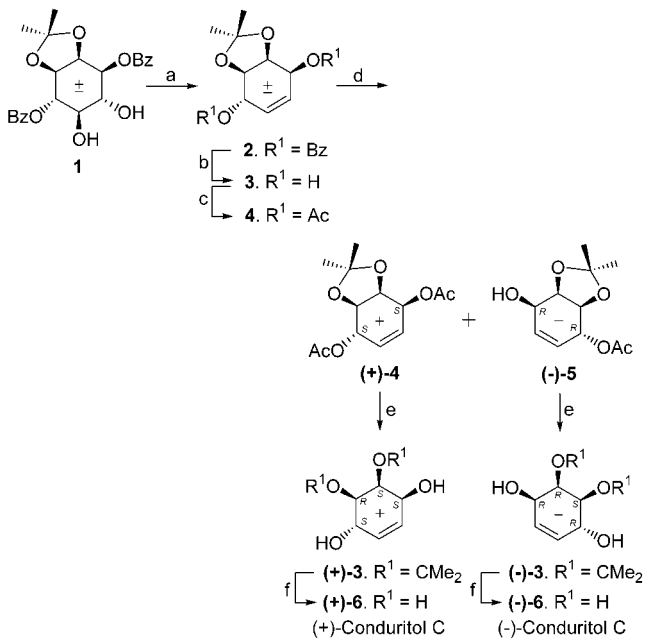
between inositol phosphates and various biomacromolecules. We previously reported the practical and divergent synthesis of all inositol stereoisomers via conduritol derivatives in racemic version.[31] And we also developed facile synthetic routes to all possible enantiomeric pairs of conduritol stereoisomers.[32] We herein report the facile syntheses of all possible diastereomers of conduritol and various derivatives of inositol stereoisomers in high enantiopurity via efficient enzymatic resolution of conduritol B and C derivatives.

Results and Discussion

General Strategy. The major issues in our synthetic schemes for conduritol and inositol stereoisomers are how to efficiently prepare the key intermediates conduritol B and C derivatives from the selectively protected *myo*-inositol diols and how to enantiomerically resolve racemic conduritol derivatives. For the conversion of vicinal diols into olefins, two types of general procedures are known.[31] Generally, the two-step methods via intermediates with activating groups do not work well on cyclic diols, especially cyclic *trans*-diols. Samuelsson et al. reported the one-step conversion of vicinal diols into olefins using triphenylphosphine or chlorodiphenylphosphine, imidazole, and iodine in toluene.[33] We have previously prepared conduritol derivatives from readily available *myo*-inositol derivatives under the Samuelsson conditions.[31] Thus, we have envisioned that conduritol B and C derivatives, whose hydroxyl groups at C-2 and C-3 are protected with acetonides, might easily be prepared under the Samuelsson conditions. Nicolosi et al. and Bäckvall et al. reported the enzymatic resolution of conduritol derivatives or analogues utilizing various lipases.[19a,21b,30] These observations prompted us to examine the enzymatic resolution of conduritol diacetates. Stereochemical inversion of allylic hydroxyl groups in resolved conduritol derivatives would then afford all possible enantiomerically enriched conduritol stereoisomers by the Mitsunobu reaction or oxidation−reduction. The stereocontrolled dihydroxylation of each enantiomerically pure conduritol isomer was expected to yield the chiral inositol stereoisomer derivatives except *cis*-inositol, which is highly symmetric and may not be readily accessible by conduritol routes.

Enzymatic Resolution of Conduritol B and C Derivatives. To obtain enantiomerically enriched conduritol stereoisomers, enantioselective enzyme-catalyzed hydrolysis of conduritol B and C derivatives was explored. First, conduritol C derivative **2** was prepared from *myo*-inositol diol **1**[34] under the Samuelsson conditions.[31,33] The corresponding diacetate **4** was derived from **2**, and exposed to lipase from *Candida rugosa* (CRL; Sigma) in a phosphate buffer (pH 7) according to the Kazlauskas procedure.[35] After 3 h, the conversion reached ca. 50% and the reaction mixture contained the unreacted diacetate (+)-**4** (49%, 95% ee) and the monoacetate (−)-**5** (48%, 95% ee) (Scheme 1). This result was at slight variance with Bäckvall's results, which indicated the enzymatic resolution of the diacetate **4** by CRL produced the unreacted diacetate (+)-**4** and the diol (−)-**3**.[30c] It is clear that the enzyme CRL shows *R* stereopreference and thus recognizes and hydrolyzes preferentially the 1-acetyl group rather than the 4-acetyl group of (−)-**4**. Alkaline methanolysis and successive acid-catalyzed hydroysis of compounds (+)-**4** and (−)-**5** afforded (+)-conduritol C [(+)-**6**] and (−)-conduritol C [(−)-**6**], respectively.[18b,24e,30c] The reaction catalyzed by the lipase from *Pseudomonas cepacia* (PCL; Amano) also gave comparable results in terms of products, enantioselectivity, and reaction rate. However, the alcoholysis of the diacetate **4** with Novozym 435 (CAL, immobilized lipase from *Candida antarctica*; Novo Nordisk) or Lipozyme RM IM (RML, immobilized lipase from *Rhizomucor miehei*; Novo Nordisk) in *tert*-butyl methyl ether (*t*-BME) did not work at all (Table 1).

Scheme 1[a]



[a] Reagents and conditions: (a) PPh_3, imidazole, I_2, toluene, ↑↓, 77%; (b) NaOMe, MeOH, ↑↓, 96%; (c) Ac_2O, pyridine 97.5%; (d) see Table 1; (e) NaOMe, MeOH, quant; (f) 80% aq AcOH, 100 °C, quant.

To obtain enantiomerically enriched conduritol B derivatives, compound **7** was converted to compound **9**,[34] which provided the conduritol B derivative **10** when subjected to Samuelsson's olefination procedure (Scheme 2).[33] The diacetate **12** was prepared by alkaline methanolysis and subsequent acetylation of compound **10**, and then exposed to CRL and PCL in a phosphate buffer (pH 7). The desired optical resolutions were not obtained in this experiment.

We then investigated the system with Novozym 435 and *n*-BuOH in *t*-BME at 45 °C. After 30 min, the reaction mixture was found to contain the unreacted diacetate (+)-**12**, the monoacetate (−)-**13**, and the diol (−)-**11**. The monoacetate (−)-**13** was slowly converted to (−)-**11**. This reveals that this enzyme also has *R* stereopreference and can recognize both acetyl groups since the diacetate (−)-**12** has a C_2 symmetry axis. After 3 h, the reaction mixture contained (+)-**12** (49.5%, 98% ee), and

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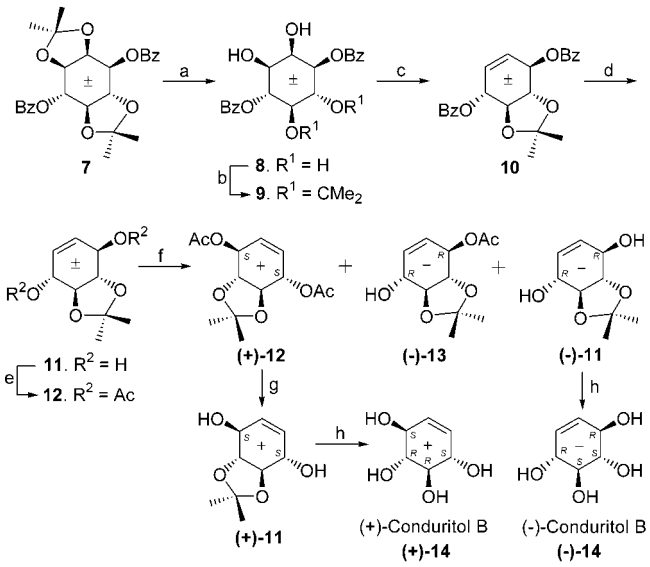
Table 1. Lipase-Catalyzed Resolution of Conduritol B and C Derivatives

substrate	lipase	time (h)[c]	yield (%)	enantioselectivity of products (% ee)[d]
4	CRL[a]	3	48	95 (>99)[e]
4	PCL[a]	3	48	95 (>99)[e]
4	CAL[b]	no rxn.		
4	RML[b]	no rxn.		
12	CRL[a]	no rxn.		
12	PCL[a]	no rxn.		
12	CAL[b]	3	48.5	>99
12	RML[b]	36	48.5	>99

[a] CRL, lipase from *C. rugosa* (Sigma); PCL, lipase from *P. cepacia* (Amano); experimental conditions, enzyme (100 mg/mmol of substrate), 0.5 N buffer (pH 7.0, 5 mL/mmol of substrate), 0.5 N NaOH, rt. [b] CAL, Novozym 435 (immobilized lipase from *C. antarctica*, Novo Nordisk); RML, Lipozyme RM IM (immobilized lipase from *R. miehei*, Novo Nordisk); experimental conditions, enzyme (300 mg/mmol of substrate), *n*-BuOH (10 mmol/mmol of substrate), *t*-BME (15 mL/mmol of substrate), 45 °C. [c] At ca. 50% conversion. [d] Determined by NMR analysis of the diacetates using $Eu(hfc)_3$ as the NMR shift agent. [e] After recrystallization.

Scheme 2[a]



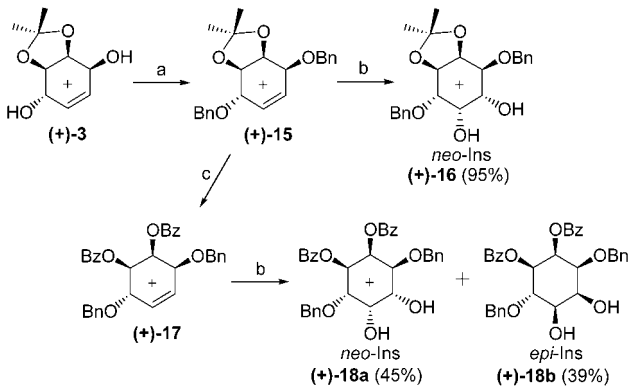
[a] Reagents and conditions: (a) 80% aq AcOH, 100 °C, quant; (b) 2-methoxypropene, TSA, DMF, 43%; (c) PPh_3, imidazole, I_2, toluene, ↑↓, 78%; (d) NaOMe, MeOH, ↑↓, 97.4%; (e) Ac_2O, pyridine 98.8%; (f) see Table 1; (g) NaOMe, MeOH, quant; (h) 80% aq AcOH, 100 °C, quant.

(−)-**11** (48.5%, >99% ee). Compound (+)-**12** was treated with NaOMe in MeOH to give (+)-**11**. The reaction catalyzed by Lipozyme RM IM gave comparable results in terms of products and enantioselectivity but showed a lower reaction rate (Table 1). The enantiomerically enriched *trans*-diols (+)-**11** and (−)-**11** were hydrolyzed in 80% aqueous AcOH to yield (+)-conduritol B [(+)-**14**] and (−)-conduritol B [(−)-**14**], respectively.[18a,25d]

Syntheses of All Possible Diastereomers of Conduritol and Various Derivatives of Inositol Stereoisomers. Conversions of the enantiomeric diols (+)-**3**/(−)-**3** and (+)-**11**/(−)-**11** to diastereomers of conduritol and inositol derivatives in high enantiopurity follow the same procedures except that the corresponding products involved in each route have opposite configurations. Accordingly, the procedures starting from (+)-**3** and (+)-**11** only are described as representative.

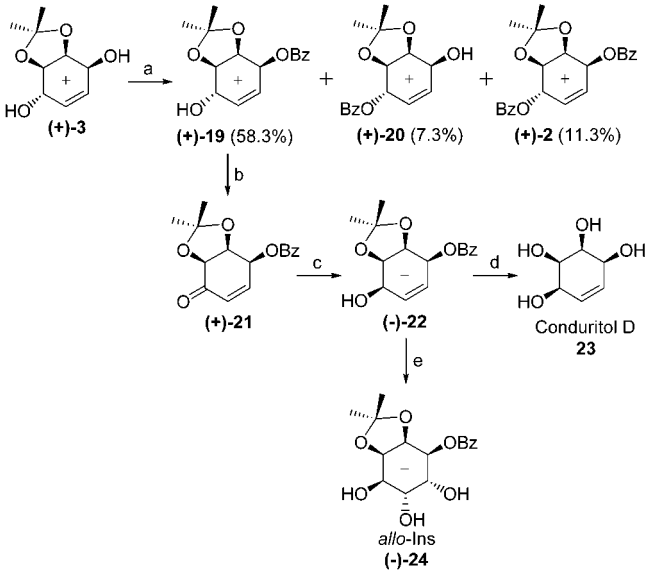
First, we examined *cis*-dihydroxylation of the enantiomerically enriched conduritol C derivative (+)-**15**, which

Scheme 3[a]



[a] Reagents and conditions: (a) BnBr, NaH, DMF, 98.6%; (b) OsO_4, NMO, aq acetone; (c) (i) 80% aq AcOH, 100 °C, (ii) BzCl, pyridine, 96%.

Scheme 4[a]

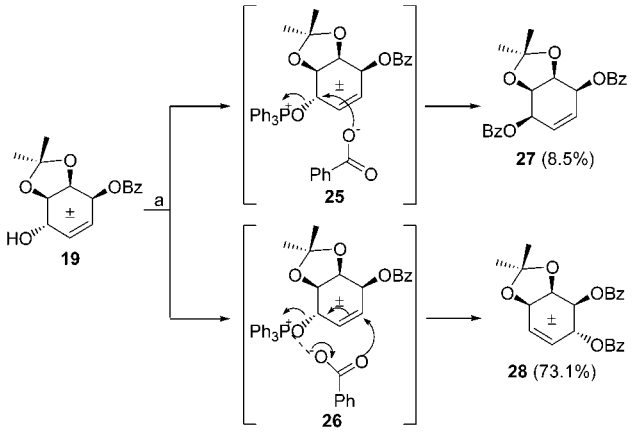


[a] Reagents and conditions: (a) BzCl (1.0 equiv), pyridine; (b) SO_3–pyridine complex, TEA, DMSO; (c) $NaBH_4$, MeOH−CH_2Cl_2, 74.5% from (+)-**19**; (d) (i) NaOMe, MeOH, ↑↓, (ii) 80% aq AcOH, 100 °C, 92%; (e) OsO_4, NMO, aq acetone, 88%.

was derived by benzylation of (+)-**3**. It was expected that the *cis*-dihydroxylation of (+)-**15** might give the *neo*-stereoisomer due to steric reasons, and it was gratifying to find that, under the reaction conditions employing OsO_4 and NMO in aqueous acetone, D-2,3-*O*-(1-methylethylidene)-1,4-bis-*O*-(phenylmethyl)-*neo*-inositol [(+)-**16**] was essentially the sole product (Scheme 3). To obtain an *epi*-inositol derivative, we replaced the acetonide group of (+)-**15** with a benzoyl protecting group by treatment with 80% aqueous AcOH and the subsequent benzoylation of the crude diol with BzCl in pyridine to give compound (+)-**17**; the acetonide group was thought to be the origin of the facial selectivity observed in *cis*-dihydroxylation of (+)-**15**. Compound (+)-**17** was treated with OsO_4 and NMO in aqueous acetone to provide, as expected, D-1,4-bis-*O*-(phenylmethyl)-*neo*-inositol 2,3-dibenzoate [(+)-**18a**] and D-3,6-bis-*O*-(phenylmethyl)-*epi*-inositol 4,5-dibenzoate [(+)-**18b**] in 45% and 39% yields, respectively.

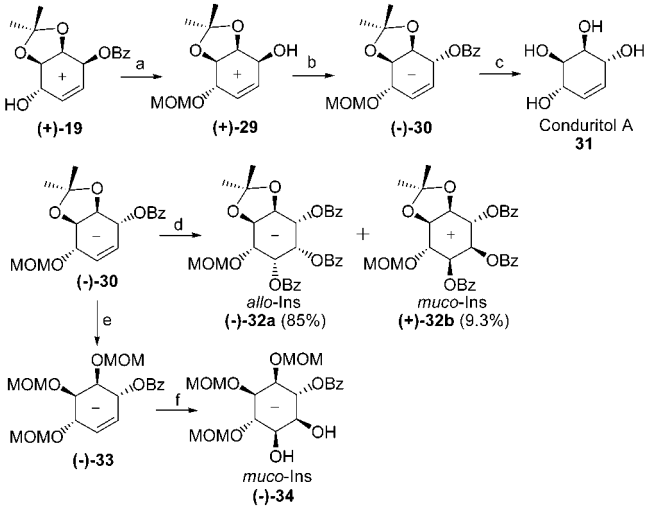
Since our initial synthetic plan for enantiomerically enriched conduritol stereoisomers involved the inversion

Scheme 5[a]



[a] Reagents and conditions: (a) BzOH, Ph_3P, DEAD, toluene, rt.

Scheme 6[a]

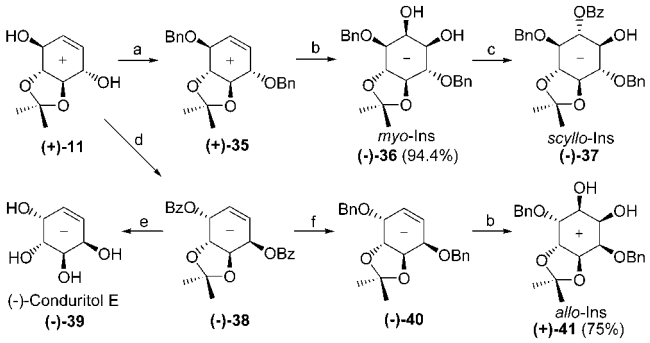


[a] Reagents and conditions: (a) (i) MOMCl, $(i\text{-Pr})_2$NEt, (ii) NaOMe, MeOH, ↑↓, 97.1%; (b) BzOH, Ph_3P, DEAD, toluene, rt, 97.1%; (c) (i) NaOMe, MeOH, ↑↓, (ii) 80% aq AcOH, 100 °C, 89%; (d) (i) OsO_4, NMO, aq acetone, (ii) BzCl, pyridine; (e) (i) 80% aq AcOH, 70 °C, (ii) MOMCl, $(i\text{-Pr})_2$NEt, 97.1%; (f) OsO_4, NMO, aq acetone, 98%.

of the allylic alcohol stereochemistry in the selectively protected conduritol derivatives under the Mitsunobu conditions, the monobenzoate (+)-**19** was preferentially prepared by treatment of (+)-**3** with BzCl (1.0 equiv) in pyridine (Scheme 4). In the preliminary experiments, the racemic monobenzoate **19** was subjected to the Mitsunobu conditions with BzOH, Ph_3P, and DEAD in toluene at room temperature, and it was found that the expected conduritol D derivative **27** (8.5%) was obtained only as the minor product together with the rearranged conduritol C derivative **28** (73.1%) as the major product in stereo- and regioselective fashions (Scheme 5). The reaction proceeded predominantly with both inversion and allylic rearrangement by an S_N2' process, presumably via the intermediate **26**. These unexpected results suggest that the reaction of a carboxylate anion with an alkoxy phosphonium salt is better described as proceeding through an intimate ion pair rather than a free allylic carbonium ion.[36] When the related compounds (3a*S*,4*S*,7*S*,

(36) Grynkiewicz, G.; Burzynska, H. *Tetrahedron* **1976**, *32*, 2109–2111.

Scheme 7[a]



[a] Reagents and conditions: (a) BnBr, NaH, DMF, 96%; (b) OsO_4, NMO, aq acetone; (c) BzOH, Ph_3P, DEAD, toluene, 80 °C, 79%. (d) BzOH, Ph_3P, DEAD, toluene, rt, 90%; (e) (i) NaOMe, MeOH, ↑↓, (ii) 80% aq AcOH, 100 °C, 91%; (f) (i) NaOMe, MeOH, ↑↓, (ii) BnBr, NaH, DMF, 92%.

7a*R*)-*rel*-3a,4,7,7a-tetrahydro-4-(methoxymethoxy)-2,2-dimethyl-1,3-be nzodioxol-7-ol and (1*S*,4*S*,5*S*,6*R*)-*rel*-4,5,6-tris(methoxymethoxy)-2-cyclohexen-1-ol, derived from the racemic **3**, were subjected to the Mitsunobu conditions (not shown), similar results were obtained, indicating that the nature of the protecting groups made little difference. The stereochemistry of the transformation does not significantly depend on the steric and electronic effects of protecting groups but rather on the substrate structure itself.

Next, the possibility of obtaining conduritol D by way of oxidation of (+)-**19** and subsequent stereoselective reduction was investigated (Scheme 4). Compound (+)-**19** was treated with SO_3–pyridine complex and TEA in DMSO to furnish an enone, (+)-**21**. Although conduritol D itself is a *meso*-compound, reduction of the enone (+)-**21** with $NaBH_4$ gave stereoselectively an enantiomerically enriched conduritol D derivative, (−)-**22**, in 74.5% overall yield from (+)-**19**. Alkaline methanolysis and successive acid-catalyzed hydrolysis of (−)-**22** provided achiral conduritol D (**23**).[18b,23d,24a] *cis*-Dihydroxylation of (−)-**22** with OsO_4 and NMO in aqueous acetone gave stereoselectively D-2,3-*O*-(1-methylethylidene)-*allo*-inositol 1-monobenzoate [(−)-**24**] in 88% yield. The observed facial selectivity might again be attributed to the acetonide group and two neighboring functions, which block the *cis*-approach to the olefinic bond.

On the other hand, the allylic alcohol (+)-**29**, derived from (+)-**19** by treatment with MOMCl and $(i\text{-Pr})_2$NEt in $CHCl_3$, followed by debenzoylation, was treated with BzOH, Ph_3P, and DEAD in toluene to afford in 97.1% yield the conduritol A derivative (−)-**30** with inversion of the stereochemistry but no allylic rearrangement. All protecting groups of (−)-**30** were removed by treatment with NaOMe and subsequent acid-catalyzed hydrolysis to give achiral conduritol A (**31**) (Scheme 6).[23d,26a]

When compound (−)-**30** was subjected to OsO_4 and NMO in aqueous acetone, inseparable multiple products were obtained which appeared to be formed by benzoyl migration catalyzed by 4-methylmorpholine. Thus, we carried out benzoylation of the crude mixtures with BzCl in pyridine to obtain D-4-*O*-(methoxymethyl)-5,6-*O*-(1-methylethylidene)-*allo*-inositol tribenzoate [(−)-**32a**] and D-3-*O*-(methoxymethyl)-1,2-*O*-(1-methylethylidene)-*muco*-inositol tribenzoate [(+)-**32b**] in 85% and 9.3% yields, respectively. The observed products show that the facial selectivity is more strongly influenced by the steric bulk

Table 2. Optical Rotations of Synthetic Conduritol Stereoisomers

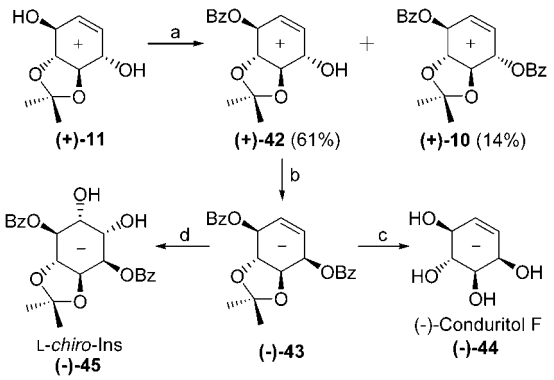
conduritol stereoisomer	$[\alpha]_D^{20}$ (+)-form	$[\alpha]_D^{20}$ (−)-form
conduritol A (**31**)	*meso*	
conduritol B [(+)-**14**/(−)-**14**]	+179.3 (*c* 0.80, CH_3OH)[25d]	−179.2 (*c* 1.08, CH_3OH)[18a]
conduritol C **[(+)-6**/(−)-**6**]	+218.7 (*c* 1.01, H_2O)[24e,30c]	−220.0 (*c* 0.76, H_2O)[18b,24e,30c]
conduritol D (**23**)	*meso*	
conduritol E [(+)-**39**/(−)-**39**]	+331.8 (*c* 1.20, H_2O)	−331.6 (*c* 1.06, H_2O)[19b,27b]
conduritol F **[(+)-44**/(−)-**44**]	+100.2 (*c* 0.77, H_2O)[18a]	−99.7 (*c* 0.60, H_2O)[24d,25d,27b]

Table 3. Optical Rotations of Synthetic Inositol Stereoisomeric Derivatives[a]

inositol stereoisomer derivative		$[\alpha]_D^{20}$ (+)-form	$[\alpha]_D^{20}$ (−)-form
myo	[(+)-**36**/(−)-**36**]	+68.0 (*c* 1.08, $CHCl_3$)	−67.0 (*c* 1.02, $CHCl_3$)
scyllo	[(+)-**37**/(−)-**37**]	+74.7 (*c* 1.01, $CHCl_3$)	−74.0 (*c* 0.88, $CHCl_3$)
chiro[b]	[(+)-**45**/(−)-**45**]	+11.6 (*c* 2.93, $CHCl_3$)	−10.8 (*c* 2.10, $CHCl_3$)
epi	**[(+)-18b**/(−)-**18b**]	+16.7 (*c* 2.56, $CHCl_3$)	−17.2 (*c* 5.25, $CHCl_3$)
allo	**[(+)-24**/(−)-**24**]	+41.8 (*c* 1.16, CH_3OH)	−42.9 (*c* 1.06, CH_3OH)
	[(+)-32a/(−)-**32a**]	+4.82 (*c* 1.66, $CHCl_3$)	−4.23 (*c* 2.00, $CHCl_3$**)**
	[(+)-**41**/(−)-**41**]	+20.4 (*c* 1.00, $CHCl_3$)	−21.3 (*c* 0.57, $CHCl_3$)
muco	[(+)-**32b**/(−)-**32b**]	+89.5 (*c* 1.80, $CHCl_3$)	−88.2 (*c* 2.15, $CHCl_3$)
	[(+)-**34**/(−)-**34**]	+3.58 (*c* 0.43, $CHCl_3$)	−3.29 (*c* 1.11, $CHCl_3$)
neo	[(+)-**16**/(−)-**16**]	+11.7 (*c* 0.75, THF)	−11.4 (*c* 0.77, THF)
	[(+)-**18a**/(−)-**18a**]	+47.7 (*c* 4.60, $CHCl_3$)	−46.4 (*c* 4.24, $CHCl_3$)

[a] *cis*-Inositol, which is highly symmetric and not readily accessible by conduritol routes, was previously synthesized via *myo*-inositol orthoformate as the key intermediate.[31] [b] *chiro*-Inositol exists as an enantiomeric pair. The (+)-form is the D-*chiro*-inositol derivative.

Scheme 8[a]



[a] Reagents and conditions: (a) BzCl (1.05 equiv), pyridine; (b) BzOH, Ph_3P, DEAD, toluene, rt, 98%; (c) (i) NaOMe, MeOH, ⇅, (ii) 80% aq AcOH, 100 °C, 90%; (d) OsO_4, NMO, aq acetone, 97.4%.

of the acetonide group rather than the stereochemistry of two neighboring groups. The acetonide group of (−)-**30**, which appears to block the *cis*-approach to the olefinic bond, was removed in 80% aqueous AcOH, and then the crude mixture was treated with MOMCl and $(i\text{-Pr})_2NEt$ in $CHCl_3$ to give compound (−)-**33**. As expected, *cis*-dihydroxylation of compound (−)-**33** stereoselectively afforded D-1,2,3-tris-*O*-(methoxymethyl)-*muco*-inositol 6-monobenzoate [(−)-**34**] in 98% yield.

cis-Dihydroxylation of compound **(+)-35**,[27b] which was prepared by simple benzylation of (+)-**11** with BnBr and NaH in DMF, gave exclusively D-4,5-*O*-(1-methylethylidene)-3,6-bis-*O*-(phenylmethyl)-*myo*-inositol [(−)-**36**][37] in 94.4% yield (Scheme 7). The vicinal *cis*-diol (−)-**36** was subjected to the Mitsunobu conditions with BzOH, Ph_3P, and DEAD in toluene at 80 °C to give *scyllo*-inositol derivative (−)-**37** with inversion of only the axial hydroxyl group at C-2.[11d] The proton on the benzoyl-bearing carbon appears as a triplet at $\delta = 5.38$ ppm with $J = 8.9$ Hz in the ^1H NMR spectrum, indicating that the substituent is in the equatorial orientation.

The double inversion of two allylic hydroxyl groups of (+)-**11** might be expected to give a conduritol E derivative. Treatment of (+)-**11** with BzOH, Ph_3P, and DEAD in toluene at room temperature indeed provided in 90% yield the (−)-conduritol E derivative (−)-**38** without allylic rearrangement (Scheme 7). The protecting groups of (−)-**38** were removed by successive reactions with NaOMe in MeOH and 80% aqueous AcOH to yield (−)-conduritol E [(−)-**39**].[19b,27b] In the direct dihydroxylation of (−)-**38**, the benzoyl group migration apparently catalyzed by 4-methylmorpholine was encountered. Thus, we switched the protecting group from benzoyl to benzyl. Compound (−)-**40**, which has a symmetry axis, was treated with OsO_4 and NMO in aqueous acetone to afford D-1,6-*O*-(1-methylethylidene)-2,5-bis-*O*-(phenylmethyl)-*allo*-inositol [(+)-**41**] in 75% yield. The dihydroxylation rate of (−)-**40** was very slow compared to that of the conduritol B derivative (+)-**35**.

A conduritol F derivative might be prepared by the inversion of one allylic hydroxyl group of the diol (+)-**11**. Thus, the monobenzoate (+)-**42** was obtained by treatment of the diol (+)-**11** with BzCl (1.05 equiv) in pyridine in 61% yield (Scheme 8). The Mitsunobu reaction of (+)-**42** with BzOH, Ph_3P, and DEAD in toluene provided the conduritol F derivative (−)-**43** in 98% yield. All protecting groups of (−)-**43** were removed by alkaline methanolysis and subsequent acid-catalyzed hydrolysis to yield conduritol F [(−)-**44**].[18a,24d,25d,27b] The conduritol F derivative (−)-**43** was treated with OsO_4 and NMO in aqueous acetone to afford stereoselectively L-2,3-*O*-(1-methylethylidene)-*chiro*-inositol 1,4-dibenzoate [(−)-**45**] in 97.4% yield.

All synthetic conduritol and inositol derivatives were fully characterized and confirmed on the basis of ^1H and ^{13}C NMR spectra, including $^1H-^1H$ homonuclear COSY spectra, and mass spectra. Enantiomeric pairs of conduritol and inositol stereoisomeric derivatives derived from the enantiomeric diols (+)-**3**/(−)-**3** and (+)-**11**/(−)-

(37) Gigg, J.; Gigg, R.; Payne, S.; Conant, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1757−1762.

11 have identical spectral data except opposite optical rotations. The optical rotations of synthetic conduritol stereoisomers and inositol stereoisomeric derivatives are shown in Tables 2 and 3, respectively.

Conclusions

In summary, we successfully developed synthetic routes to all possible diastereomers of conduritol as well as optically enriched inositol derivatives from the easily available *myo*-inositol by efficient enzymatic resolution of conduritol B and C derivatives, followed by oxidation−reduction or the Mitsunobu reaction, and *cis*-dihydroxylation in stereo- and regioselective manners. The *cis*-inositol derivative, which is highly symmetric and may not be readily accessible by conduritol routes, was previously synthesized in five steps via 2-*O*-benzoyl-*myo*-inositol orthoformate as the key intermediate.[31] We are currently examining the utilities of enantiomerically enriched conduritol and inositol stereoisomers in the syntheses of various biologically important cyclitols and IP_n analogues.

Experimental Section

General Methods. All nonhydrolytic reactions were carried out in oven-dried glassware under an inert atmosphere of dry argon or nitrogen. All commercial chemicals were used as obtained without further purification, except for the solvents, which were purified and dried by standard methods prior to use. Melting points were determined on a Thomas−Hoover apparatus and are uncorrected. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness), and visualization was done with UV light, and/or by spraying with a 5% solution of phosphomolybdic acid followed by charring with a heat gun. Column chromatography was performed on Merck 60 silica gel (70−230 mesh or 230−400 mesh). NMR spectra were recorded on a Bruker AM 300, DPX 300, or DRX 500 spectrometer. Tetramethylsilane was used as internal standard for ^{1}H NMR. Mass spectra (EI or FAB) were determined on a micromass PLATFORM II, at the Korea Basic Science Center, Taejeon, or Inter-University Center for Natural Science Research Facilities, Seoul National University, Seoul, Korea. Elemental analyses were carried out on an Elementar Vario-EL system. Optical rotations were measured with a JASCO DIP-360 digital polarimeter.

(3a*R*,4*R*,7*R*,7a*S*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate (2). To a stirred solution of compound **1**[34] (2.60 g, 6.07 mmol), imidazole (1.67 g, 24.5 mmol), and triphenylphosphine (6.49 g, 24.5 mmol) in toluene (120 mL) at reflux was added iodine (5.08 g, 20.0 mmol) in portions. The mixture was stirred for 5.5 h. After being cooled to rt, it was poured into excess aq sodium thiosulfate and aq $NaHCO_3$, and diluted with EtOAc. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The product mixture was chromatographed to give compound **2** (1.84 g, 77%): R_f 0.25 (EtOAc:Hex = 1:10); mp 120.5−122 °C; ^{1}H NMR ($CDCl_3$) δ 1.37, 1.43 (2s, 6H), 4.68 (dd, J = 3.1, 7.4 Hz, 1H), 4.83 (dd, J = 4.0, 7.4 Hz, 1H), 5.69 (app t, J = 3.3 Hz, 1H), 5.86 (dd, J = 2.1, 4.0 Hz, 1H), 6.18−6.26 (m, 2H), 7.43−8.14 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 25.1, 26.6, 68.2, 70.3, 74.4, 76.5, 110.5, 128.6−133.7, 166.0, 166.5; MS (FAB) m/z 395 (M^+ + H). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.11; H, 5.72.

(3a*R*,4*S*,7*S*,7a*S*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol (3). To a solution of compound **2** (9.75 g, 24.7 mmol) in MeOH (100 mL) was added sodium methoxide (300 mg, 5.5 mmol). After being stirred for 3 h at reflux, the mixture was filtered through a short pad of silica gel, and the filtrate was evaporated under reduced pressure. The crude product was chromatographed to give compound **3** (4.42 g, 96%) as a solid: R_f 0.12 (EtOAc:Hex = 1:2); mp 95−96 °C; ^{1}H NMR ($CDCl_3$) δ 1.39, 1.46 (2s, 6H), 2.37 (br s, 1H), 2.70 (d, J = 4.7 Hz, 1H), 4.30−4.34 (m, 1H), 4.44−4.47 (m, 2H), 4.52 (br s, 1H), 5.98−6.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.8, 26.7, 64.6, 68.5, 75.6, 79.4, 110.0, 132.2, 133.5; MS (FAB) m/z 187 (M^+ + H). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.86; H, 7.55.

(3a*R*,4*R*,7*R*,7a*S*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Diacetate (4). To a solution of compound **3** (4.29 g, 23.0 mmol) in pyridine (80 mL) at 0 °C was added acetic anhydride (4.4 mL, 46.1 mmol). After 30 min, the mixture was warmed to rt and stirred overnight. The reaction mixture was treated with water and extracted with EtOAc. The organic layer was washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), concentrated, and chromatographed to give compound **4** (6.07 g, 97.5%) as an oil: R_f 0.39 (EtOAc:Hex = 1:4); ^{1}H NMR ($CDCl_3$) δ 1.34, 1.41 (2s, 6H), 2.05, 2.15 (2s, 6H), 4.45 (dd, J = 2.3, 7.2 Hz, 1H), 4.67 (ddd, J = 0.85, 3.9, 7.2 Hz, 1H), 5.25 (dd, J = 2.3, 4.6 Hz, 1H), 5.50−5.53 (m, 1H), 5.98 (ddd, J = 0.85, 2.5, 9.8 Hz, 1H), 6.06 (ddd, J = 1.4, 4.6, 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.7, 20.9, 24.5, 26.0, 67.5, 68.5, 74.0, 75.7, 109.7, 127.8, 131.8, 169.7, 170.3; MS (FAB) m/z 271 (M^+ + H).

Lipase-Catalyzed Resolution of Compound 4. To a solution of racemate **4** (6.65 g, 24.6 mmol) in 0.5 N sodium phosphate buffer (120 mL, pH 7.0) was added lipase (ca. 2.5 g) from *C. rugosa* (Sigma) or *P. cepacia* (Amano). The suspension was vigorously stirred while pH 7.0 was automatically maintained with 0.5 N NaOH by an auto pH titrator. After 3 h conversion was ca. 50%, and EtOAc (40 mL) was added. The suspension was filtered through Celite, and the filtrate was extracted three times with EtOAc. The combined extracts were washed with aq $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated, and chromatographed to give (+)-**4** (3.26 g, 49%, 95% ee by NMR analysis) as an oil, and (−)-**5** (2.70 g, 48%, 95% ee) as a solid whose optical purity could be improved to >99% ee after recrystallization from CH_2Cl_2−Hex. The optical purity of (+)-**4** could also be improved to >99% ee after repeated resolution. After acetylation of the monoacetate (−)-**5**, the optical purities (% ee) were determined by NMR analysis of the diacetates using europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the NMR shift agent. Compounds (+)-**4** and (−)-**5** were treated with NaOMe in MeOH to give compounds (+)-**3** and (−)-**3**, and their optical purities could be improved to >99% ee upon recrystallization from CH_2Cl_2−MeOH.

Data for (3a*R*,4*S*,7*S*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Diacetate [(+)-4]:[30c] $[\alpha]_D^{20}$ +161.0 (*c* 4.60, $CHCl_3$) [lit.[30c] $[\alpha]_D^{20}$ +154.7 (*c* 1.106, $CHCl_3$)]; R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **4**.

Data for (3a*S*,4*R*,7*R*,7a*R*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol 4-Monoacetate [(−)-5]: R_f 0.26 (EtOAc:Hex = 1:2); mp 63−64 °C; $[\alpha]_D^{20}$ −206.7 (*c* 4.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.41 (2s, 6H), 2.04 (s, 3H), 3.07 (br s, 1H), 4.40−4.45 (m, 2H), 4.59 (ddd, J = 1.0, 4.3, 7.3 Hz, 1H), 5.23 (dd, J = 2.8, 4.9 Hz, 1H), 5.97 (ddd, J = 1.4, 4.9, 9.8 Hz, 1H), 6.05 (ddd, J = 1.0, 2.5, 9.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 24.8, 26.4, 65.4, 68.7, 75.9, 76.0, 109.7, 126.7, 136.5, 170.3; MS (FAB) m/z 229 (M^+ + H). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.65; H, 7.20.

Data for (3a*R*,4*S*,7*S*,7a*S*)- and (3a*R*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol [(+)-3 and (−)-3]:[30c] [(+)-**3**] mp 122−123 °C; $[\alpha]_D^{20}$ +88.6 (*c* 1.11, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **3**; [(−)-**3**] mp 122−123 °C; $[\alpha]_D^{20}$ −88.5 (*c* 1.00, $CHCl_3$) [lit.[30c] $[\alpha]_D^{20}$ −157.2 (*c* 0.998, $CHCl_3$)]; R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **3**.

(1*S*,2*R*,3*S*,4*S*)- and (1*R*,2*R*,3*S*,4*R*)-5-Cyclohexene-1,2,3,4-tetrol [(+)- and (−)-Conduritol C, (+)-6 and (−)-6].[18b,24e,30c] A solution of compound (+)-**3** (102 mg, 0.548 mmol) in 80% aq AcOH (5 mL) was heated at 100 °C for 3 h, and then concentrated under reduced pressure to give a crude product, (+)-**6**, quantitatively. Recrystallization from MeOH−Et_2O gave compound (+)-**6** as a solid. Similarly, compound (−)-**6** was prepared from (−)-**3**. Data for (+)-**6**: mp 127−129 °C [lit.[24e]

mp 128−129 °C, lit.[30c] mp 128−129 °C]; $[\alpha]_D^{20}$ +218.7 (*c* 1.01, H_2O) [lit.[24e] $[\alpha]_D^{20}$ +212 (*c* 0.47, H_2O), lit.[30c] $[\alpha]_D^{20}$ +215 (*c* 2.008, H_2O)]; ^{1}H NMR (CD_3OD) δ 3.53 (dd, J = 5.0, 10.5 Hz, 1H), 4.03 (m, 1H), 4.22−4.29 (m, 2H), 5.54−5.59 (m, 1H), 5.65 (td, J = 2.05, 2.05, 10.2 Hz, 1H); ^{13}C NMR (CD_3OD) δ 69.7, 70.8, 74.3, 76.3, 130.2, 131.0. Data for (−)-**6**: mp 128−129 °C [lit.[18b] mp 129−130 °C, lit.[24e] mp 127−128 °C, lit.[30c] mp 128−129 °C,]; $[\alpha]_D^{20}$ −220.0 (*c* 0.76, H_2O) [lit.[18b] $[\alpha]_D^{20}$ −209 (*c* 2, H_2O), lit.[24e] $[\alpha]_D^{20}$ −207 (*c* 0.5, H_2O), lit.[30c] $[\alpha]_D^{20}$ −213 (*c* 1.996, H_2O)]; ^{1}H NMR and ^{13}C NMR data identical to those of (+)-**6**.

***myo*-Inositol 1,4-Dibenzoate (8).** Compound **7**[34] (2.0 g, 4.2 mmol) in 80% aq AcOH (80 mL) was heated at reflux for 3 h, and evaporated to dryness to give a crude product quantitatively. Recrystallization of the crude product from EtOH gave compound **8**: R_f 0.17 (MeOH:CH_2Cl_2 = 1:20); mp 245−249 °C; ^{1}H NMR (CD_3OD) δ 3.62 (app t, J = 9.4 Hz, 1H), 3.84 (dd, J = 2.7, 10.0 Hz, 1H), 4.14 (app t, J = 9.7 Hz, 1H), 4.25 (app t, J = 2.6 Hz, 1H), 4.97 (dd, J = 2.6, 10.2 Hz, 1H), 5.51 (app t, J = 9.8 Hz, 1H), 7.45−8.16 (m, 10H); ^{13}C NMR (CD_3OD) δ 71.6, 72.1, 72.3, 74.7, 76.4, 77.1, 129.5−134.4, 168.0, 168.3; MS (FAB) *m*/*z* 389 (M^+ + H). Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.73; H, 5.49.

5,6-*O*-(1-Methylethylidene)-*myo*-inositol 1,4-Dibenzoate (9). To a solution of **8** (4.0 g, 10.3 mmol) and TSA (100 mg) in DMF (50 mL) at 0 °C was added 2-methoxypropene (2 mL, 20.8 mmol) by syringe. The solution was stirred for 3 h in an ice bath, poured into 1% aq $NaHCO_3$ (350 mL) with vigorous stirring, and extracted with CH_2Cl_2. The organic layer was diluted with ether, and slow evaporation of the solvents gave a crystalline solid precipitate, compound **9** (1.90 g, 43%). The filtrate was evaporated under reduced pressure and boiled in aq AcOH (80%) to give the starting material **8**, quantitatively on the basis of recovered product. Data for **9**: R_f 0.4 (EtOAc:Hex = 1:4); mp 212−215 °C; ^{1}H NMR (DMSO-d_6) δ 1.35, 1.39 (2s, 6H), 3.87 (dd, J = 9.2, 10.2 Hz, 1H), 3.92 (ddd, J = 2.9, 7.3, 9.3 Hz, 1H), 4.20 (ddd, J = 2.8, 2.9, 4.8 Hz, 1H), 4.26 (dd, J = 9.2, 10.7 Hz, 1H), 5.17 (d, J = 7.3 Hz, 1H), 5.23 (dd, J = 2.8, 10.7 Hz, 1H), 5.46 (dd, J = 9.3, 10.2 Hz, 1H), 5.59 (d, J = 4.8 Hz, 1H), 7.54−8.05 (m, 10H); ^{13}C NMR (DMSO-d_6) δ 26.6, 26.7, 70.9, 71.1, 72.3, 72.7, 75.0, 76.1, 111.3, 128.6−133.4, 165.0, 165.1; MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.19; H, 5.69.

(3a*R*,4*S*,7*S*,7a*R*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate (10). Compound **9** (6.98 g, 16.3 mmol) was treated by the same procedure as described for compound **2** to afford compound **10** (5.01 g, 78%): R_f 0.42 (EtOAc:Hex = 1:4); mp 193−194 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6H), 4.04 (dd, J = 2.4, 5.8 Hz, 2H), 5.85−5.90 (m, 4H), 7.26−8.11 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.4 (2C), 73.3 (2C), 78.0 (2C), 112.4, 128.8−133.8, 166.4 (2C); MS (FAB) *m*/*z* 395 (M^+ + H). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 70.22; H, 5.84.

(3a*R*,4*S*,7*S*,7a*R*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol (11). Compound **10** (4.0 g, 12.4 mmol) was hydrolyzed by the same procedure as described for compound **3** to afford compound **11** (1.84 g, 97.4%) as an oil: R_f 0.23 (EtOAc:Hex = 1:1); ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 6H), 2.74 (br s, 2H), 3.55 (dd, J = 2.3, 5.6 Hz, 2H), 4.50 (dd, J = 2.3, 5.6 Hz, 2H), 5.69 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 27.4 (2C), 71.1 (2C), 81.1 (2C), 111.7, 130.9 (2C); MS (FAB) *m*/*z* 187 (M^+ + H).

(3a*R*,4*S*,7*S*,7a*R*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Diacetate (12). Compound **11** (3.25 g, 17.4 mmol) was acetylated by the same procedure as described for compound **4** to afford compound **12** (4.66 g, 98.8%) as a solid: R_f 0.5 (EtOAc:Hex = 1:2); mp 153−154 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H), 2.13 (s, 6H), 3.79 (dd, J = 2.4, 5.9 Hz, 2H), 5.54 (dd, J = 2.4, 5.9 Hz, 2H), 5.70 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.4 (2C), 27.2 (2C), 72.7 (2C), 77.7 (2C), 112.2, 128.9 (2C), 170.7 (2C); MS (FAB) *m*/*z* 271 (M^+ + H). Anal. Calcd for $C_{13}H_{18}O_6$: C, 57,77; H, 6.71. Found: C, 57.39; H, 6.89.

Lipase-Catalyzed Resolution of Compound 12. To a solution of racemate **12** (2.71 g, 10.0 mmol) and Novozym 435 (immobilized lipase from *C. antarctica*, Novo Nordisk, 3.0 g) in *tert*-butyl methyl ether (150 mL) was added *n*-BuOH (9.3 mL). The reaction mixture was stirred at 45 °C. After 30 min, the reaction mixture contained (+)-**12**, (−)-**13**, and (−)-**11**. The monoacetate (−)-**13** was slowly converted to (−)-**11**. After 3 h, the enzyme was filtered off, and the filtrate was concentrated and chromatographed to give the unreacted diacetate (+)-**12** (1.34 g, 49.5%, 98% ee), whose optical purity could be improved to >99% ee by recrystallization from EtOAc−petroleum ether, and the diol (−)-**11** (906 mg, 48.5%, >99% ee) as an oil. After acetylation of the diol (−)-**11**, the optical purities (% ee) were determined by NMR analysis of the diacetates using europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as the NMR shift agent. Compound (+)-**12** was treated with NaOMe in MeOH to give the diol (+)-**11**.

Data for (3a*R*,4*S*,7*S*,7a*R*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Diacetate [(+)-12]: mp 94−95 °C; $[\alpha]_D^{20}$ +180.3 (*c* 1.27, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **12**.

Data for (3a*R*,4*S*,7*S*,7a*R*)- and (3a*S*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol [(+)-11 and (−)-11]: [(+)-**11**] $[\alpha]_D^{20}$ +30.4 (*c* 3.98, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **11**; [(−)-**11**] $[\alpha]_D^{20}$ −30.2 (*c* 2.40, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **11**.

(1*S*,2*R*,3*R*,4*S*)- and (1*R*,2*S*,3*S*,4*R*)-5-Cyclohexene-1,2,3,4-tetrol [(+)- and (−)-Conduritol B, (+)-14 and (−)-14].[18a,25d] Compound (+)-**11** (95 mg, 0.51 mmol) was hydrolyzed by the same procedure as described for compound (+)-**6** to give compound (+)-**14** as a solid. Similarly, compound (−)-**14** was prepared from compound (−)-**11**. Data for (+)-**14**: mp 169−171 °C [lit.[25d] mp 177−178 °C]; $[\alpha]_D^{20}$ +179.3 (*c* 0.80, CH_3OH) [lit.[25d] $[\alpha]_D^{20}$ +191 (*c* 1.26, CH_3OH)]; ^{1}H NMR (CD_3OD) δ 3.38 (dd, J = 2.4, 5.3 Hz, 1H), 4.07 (dd, J = 2.4, 5.3 Hz, 1H), 5.58 (s, 2H); ^{13}C NMR (CD_3OD) δ 73.8 (2C), 77.6 (2C), 130.9 (2C). Data for (−)-**14**: mp 171−173 °C [lit.[18a] mp 174−175 °C]; $[\alpha]_D^{20}$ −179.2 (*c* 1.08, CH_3OH) [lit.[18a] $[\alpha]_D^{20}$ −179 (*c* 1.2, CH_3OH)]; ^{1}H NMR and ^{13}C NMR data identical to those of (+)-**14**.

(3a*R*,4*S*,7*S*,7a*S*)- and (3a*R*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-4,7-bis(phenylmethoxy)-1,3-benzodioxole [(+)-15 and (−)-15]. To a solution of compound (+)-**3** (1.866 g, 10.0 mmol) and NaH (1.26 g, 50.0 mmol) in DMF (50 mL) at 0 °C was added BnBr (4.9 mL, 40.4 mmol). After 30 min, the mixture was warmed to rt and stirred overnight. The mixture was diluted with EtOAc and successively washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic phase was dried ($MgSO_4$), concentrated, and chromatographed to give compound (+)-**15** (3.61 g, 98.6%) as an oil. Similarly, compound (−)-**15** was prepared from compound (−)-**3**. Data for (+)-**15**: R_f 0.46 (EtOAc:Hex = 1:4); $[\alpha]_D^{20}$ +123.5 (*c* 3.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.38 (2s, 6H), 4.06 (dd, J = 2.4, 4.8 Hz, 1H), 4.29 (td, J = 2.4, 2.4, 4.2 Hz, 1H), 4.41−4.52 (m, 3H), 4.60 (ddd, J = 1.1, 3.7, 7.1 Hz, 1H), 4.66 (d, J = 12.5 Hz, 1H), 4.72 (d, J = 12.5 Hz, 1H), 6.00 (ddd, J = 1.9, 4.6, 9.8 Hz, 1H), 6.12 (ddd, J = 1.2, 2.4, 9.8 Hz, 1H), 7.18−7.34 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 25.1, 26.6, 71.1, 71.8, 72.6, 73.4, 76.0, 77.6, 109.8, 128.1−138.6; MS (FAB) *m*/*z* 367 (M^+ + H). Data for (−)-**15**: $[\alpha]_D^{20}$ −124.0 (*c* 3.88, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**15**.

D-2,3-*O*-(1-Methylethylidene)-1,4-bis-O-(phenylmethyl)-*neo*-inositol [(+)-16] and D-1,2-*O*-(1-Methylethylidene)-3,6-bis-O-(phenylmethyl)-*neo*-inositol [(−)-16]. To a solution of compound (+)-**15** (450 mg, 1.23 mmol) in a mixture of acetone and water (8:1, 4.5 mL) were added 4-methylmorpholine *N*-oxide (NMO) (690 mg, 5.71 mmol) and then OsO_4 (~25 mg). After being stirred for 12 h at rt, the reaction mixture was quenched with a few drops of 10% $NaHSO_3$, and the solvents were evaporated under reduced pressure. The crude material was dissolved in MeOH and filtered through a short pad of silica gel. After removal of the solvent by evaporation, flash column chromatography on silica gel gave compound (+)-**16** (467 mg, 95%) as a solid. Similarly, compound (−)-**16** was prepared from compound (−)-**15**. Data for (+)-**16**: R_f 0.24 (EtOAc:Hex = 1:1); mp 116−117 °C; $[\alpha]_D^{20}$ +11.7 (*c* 0.75, THF); ^{1}H NMR ($CDCl_3$) δ 1.30, 1.35 (2s, 6H), 2.84 (d, J = 4.3 Hz, 1H), 2.88 (d, J = 2.5 Hz, 1H), 3.43 (dd, J = 2.5, 6.8 Hz, 1H),

3.88 (ddd, J = 3.0, 4.3, 9.4 Hz, 1H), 3.96 (dd, J = 3.7, 9.4 Hz, 1H), 4.14 (app q, J = 2.5 Hz, 1H), 4.25 (app t, J = 6.0 Hz, 1H), 4.31 (dd, J = 3.7, 5.1 Hz, 1H), 4.64−4.77 (m, 4H), 7.28−7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.3, 28.4, 70.4, 70.6, 72.4, 73.2, 73.8, 76.8, 78.5, 79.1, 110.0, 128.3−138.5; MS (FAB) m/z 401 (M^+ + H). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.62; H, 7.09. Data for (−)-**16**: mp 116−117 °C; $[\alpha]_D^{20}$ −11.4 (c 0.77, THF); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**16**.

(1*R*,2*S*,3*S*,6*S*)- and (1*S*,2*R*,3*R*,6*R*)-3,6-Bis(phenylmethoxy)-4-cyclohexene-1,2-diol Dibenzoate [(+)-17 and (−)-17]. A solution of compound (+)-**15** (3.09 g, 8.43 mmol) in 80% aq AcOH (70 mL) was heated at 100 °C for 3 h, and then concentrated under reduced pressure to give a crude product quantitatively. To a solution of the crude product and DMAP (108 mg) in pyridine (60 mL) at 0 °C was added BzCl (4 mL, 34.1 mmol) dropwise. After being stirred for 10 h at rt, the mixture was treated with water (5 mL) for 30 min, diluted with EtOAc, and washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed to afford compound (+)-**17** (4.33 g, 96%) as an oil. Similarly, compound (−)-**17** was prepared from compound (−)-**15**. Data for (+)-**17**: R_f 0.35 (EtOAc:Hex = 1:4); $[\alpha]_D^{20}$ +190.5 (c 1.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.46 (td, J = 2.6, 5.5 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.64−4.73 (m, 3H), 4.74 (d, J = 11.7 Hz, 1H), 5.59 (dd, J = 2.0, 8.0 Hz, 1H), 5.84 (m, 1H), 6.00 (td, J = 2.3, 2.3, 10.4 Hz, 1H), 6.17 (td, J = 1.6, 1.6, 3.3 Hz, 1H), 7.21−8.00 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 70.6, 71.7, 72.4, 73.9, 74.0, 75.0, 128.0−138.3, 166.3, 166.4; MS (FAB) m/z 535 (M^+ + H). Data for (−)-**17**: $[\alpha]_D^{20}$ −192.6 (c 2.34, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**17**.

D-1,4-Bis-*O*-(phenylmethyl)-*neo*-inositol 2,3-Dibenzoate [(+)-18a], D-3,6-Bis-*O*-(phenylmethyl)-*neo*-inositol 1,2-Dibenzoate [(−)-18a], D-3,6-Bis-*O*-(phenylmethyl)-*epi*-inositol 4,5-Dibenzoate [(+)-18b], and D-3,6-Bis-*O*-(phenylmethyl)-*epi*-inositol 1,2-Dibenzoate [(−)-18b]. Compound (+)-**17** (4.29 g, 8.02 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compounds (+)-**18a** (2.01 g, 45%) and (+)-**18b** (1.73 g, 39%). A similar reaction with compound (−)-**17** gave compounds (−)-**18a** and (−)-**18b**. Data for (+)-**18a**: oil; R_f 0.25 (EtOAc:Hex = 1:1); $[\alpha]_D^{20}$ +47.7 (c 4.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.73 (br s, 1H), 2.84 (br s, 1H, 4.03−4.08 (m, 3H, H-3), 4.44 (br s, 1H), 4.48 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.71(d, J = 12.0 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 5.70 (dd, J = 2.4, 10.0 Hz, 1H), 6.13 (br s, 1H), 7.23−7.91 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 68.6, 69.1, 70.3, 71.1, 72.5, 72.8, 76.1, 76.8, 128.4−137.8, 166.0, 166.1; HRMS (FAB) m/z calcd for $C_{34}H_{33}O_8$ 569.2175, found 569.2171 (M^+ + H). Data for (−)-**18a**: $[\alpha]_D^{20}$ −46.4 (c 4.24, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**18a**. Data for (+)-**18b**: oil; R_f 0.4 (EtOAc:Hex = 1:1); $[\alpha]_D^{20}$ +16.7 (c 2.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.97 (br s, 1H), 3.10 (br s, 1H), 3.86 (dd, J = 3.0, 6.3 Hz, 1H), 4.02 (br s, 1H), 4.29−4.32 (m, 2H), 4.67−4.84 (m, 4H), 5.52 (dd, J = 3.1, 6.9 Hz, 1H), 5.96 (br s, 1H), 7.27−8.06 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 70.5, 70.6, 71.7, 73.0, 74.1, 75.0, 77.1, 77.6, 128.5−138.4, 166.1, 166.2; HRMS (FAB) m/z calcd for $C_{34}H_{33}O_8$ 569.2175, found 569.2178 (M^+ + H). (−)-**18b**: $[\alpha]_D^{20}$ −17.2 (c 5.25, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**18b**.

(3a*S*,4*S*,7*S*,7a*R*)- and (3a*R*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol 4-Monobenzoate [(+)-19 and (−)-19], (3a*R*,4*S*,7*S*,7a*S*)- and (3a*S*,4*R*,7*R*,7a*R*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol 4-Monobenzoate [(+)-20 and (−)-20], and (3a*R*,4*S*,7*S*,7a*S*)- and (3a*R*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate [(+)-2 and (−)-2]. To a solution of compound (+)-**3** (1.865 g, 10 mmol) in pyridine (50 mL) at 0 °C was added BzCl (1.2 mL, 10.2 mmol) dropwise. After being stirrred for 5 h at 0−10 °C, the mixture was treated with water (3 mL) for 30 min, diluted with EtOAc, and washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed to afford (+)-**19** (1.69 g, 58.3%), (+)-**20** (211 mg, 7.3%), (+)-**2** (448 mg, 11.3%), and the starting material (+)-**3** (345 mg, 18.5%). A similar reaction with compound (−)-**3** afforded compounds (−)-**19**, (−)-**20**, (−)-**2**, and the starting material (−)-**3**. Data for (+)-**19**: R_f 0.25 (EtOAc:Hex = 1:2); mp 128−129 °C; $[\alpha]_D^{20}$ +190.5 (c 2.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.34, 1.36 (2s, 6H), 2.77 (br s, 1H), 4.37 (dd, J = 4.3, 8.0 Hz, 1H), 4.53 (dd, J = 4.2, 8.0 Hz, 1H), 4.65 (br s, 1H), 5.75 (app t, J = 4.3 Hz, 1H), 6.06 (ddd, J = 1.4, 4.4, 9.4 Hz, 1H), 6.13 (dd, J = 2.8, 9.4 Hz, 1H), 7.37−8.04 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.9, 26.7, 67.3, 69.7, 74.3, 79.9, 110.5, 127.8−136.4, 166.4; MS (FAB) m/z 291 (M^+ + H). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.79; H, 6.28. Data for (−)-**19**: mp 128−129 °C; $[\alpha]_D^{20}$ −190.2 (c 2.15, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**19**. Data for (+)-**20**: R_f 0.32 (EtOAc:Hex = 1:2); mp 124−125 °C; $[\alpha]_D^{20}$ +205.6 (c 1.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.45 (2s, 6H), 2.67 (br s, 1H), 4.50 (br s, 1H), 4.61 (dd, J = 2.8, 7.3 Hz, 1H), 4.68 (dd, J = 4.4, 7.3 Hz, 1H), 5.53 (app q, J = 2.7 Hz, 1H), 6.11 (m, 2H), 7.41−8.00 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.0, 26.6, 65.7, 69.0, 75.9, 76.0, 110.0, 126.9−136.8, 165.9 (*C*OPh); MS (FAB) m/z 291 (M^+ + H). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.89; H, 6.42. Data for (−)-**20**: mp 124−125 °C; $[\alpha]_D^{20}$ −205.5 (c 1.05, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**20**. Data for (+)-**2**: mp 140−141 °C; $[\alpha]_D^{20}$ +175.3 (c 1.66, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **2**. Data for (−)-**2**: mp 140−141 °C; $[\alpha]_D^{20}$ −175.3 (c 1.62, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **2**.

(3a*S*,7*S*,7a*S*)- and (3a*R*,7*R*,7a*R*)-7-(Benzoyloxy)-7,7a-dihydro-2,2-dimethyl-1,3-benzodioxol-4(3aH)-one [(+)-21 and (−)-21]. To a solution of compound (+)-**19** (581 mg, 2 mmol) and TEA (3 mL, 21.4 mmol) in DMSO (6 mL) at −15 °C, was added sulfur trioxide−pyridine complex (1.136 g, 7 mmol) in DMSO (4 mL). After being stirred for 3 h at rt, the mixture was poured into cold brine, and extracted with EtOAc three times. The organic extracts were washed with 0.1 N HCl and brine, dried ($MgSO_4$), and concentrated to afford the enone (+)-**21**, which was used in the next step without further purification. Similarly, compound (−)-**21** was prepared from compound (−)-**19**. Data for (+)-**21**: R_f 0.41 (EtOAc:Hex = 1:2); ^{1}H NMR ($CDCl_3$) δ 1.38, 1.40 (2s, 6H), 4.44 (d, J = 4.7 Hz, 1H), 4.91 (dt, J = 2.2, 4.4, 4.4 Hz, 1H), 6.16 (td, J = 2.4, 2.4, 4.1 Hz, 1H), 6.22 (dd, J = 2.5, 10.4 Hz, 1H), 6.90 (td, J = 2.2, 2.2, 10.4, 9.4 Hz, 1H), 7.45−8.15 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.4, 27.8, 67.7, 74.9, 75.8, 111.6, 128.8−146.4, 166.1, 195.6. Data for (−)-**21**: R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**21**.

(3a*S*,4*S*,7*R*,7a*R*)- and (3a*R*,4*R*,7*S*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol 4-Monobenzoate [(−)-22 and (+)-22]. To a solution of the crude enone (+)-**21** in MeOH−CH_2Cl_2 (1:5, 12 mL) at 0 °C was added $NaBH_4$ (193 mg, 5 mmol). After being stirred at rt for 2.5 h, the mixture was treated with water (2 mL), evaporated, and diluted with EtOAc. The organic layer was washed with water and brine, dried ($MgSO_4$), concentrated, and chromatographed to afford compound (−)-**22** (433 mg, 74.5% from (+)-**19**). Similarly, compound (+)-**22** was prepared from compound (−)-**19** via compound (−)-**21**. Data for (−)-**22**: R_f 0.24 (EtOAc:Hex = 1:2); mp 108−109 °C; $[\alpha]_D^{20}$ −42.6 (c 1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.35, 1.42 (2s, 6H), 2.66 (br s, 1H), 4.10 (br s, 1H), 4.60 (ddd, J = 1.6, 4.8, 7.4 Hz, 1H), 4.82 (ddd, J = 1.7, 3.7, 7.4 Hz, 1H), 5.33−5.36 (m, 1H), 5.76−5.81 (m, 1H), 5.83−5.88 (m, 1H), 7.44−8.14 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.2, 26.2, 67.0, 70.0, 74.1, 75.7, 110.6, 126.7−133.7, 166.6; MS (FAB) m/z 291 (M^+ + H). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.87; H, 6.34. Data for **(+)-22**: mp 108−109 °C; $[\alpha]_D^{20}$ +42.5 (c 0.74, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**22**.

(1*R*,2*R*,3*S*,4*S*)-*rel*-5-Cyclohexene-1,2,3,4-tetrol (Conduritol D, 23).[18b,23d,24a] To a solution of compound (+)-**22** or (−)-**22** (145 mg, 0.50 mmol) in MeOH (3 mL) was added 25 wt % sodium methoxide (in MeOH, 3 drops). After being stirred for 1.5 h at reflux, the mixture was filtered through a short pad of silica gel, and the solvent was evaporated under reduced pressure. The crude product in 80% aq AcOH (5 mL) was

heated at 100 °C for 3 h, and then concentrated under reduced pressure to give a crude product which was chromatographed (MeOH:CH_2Cl_2 = 1:15) to give the pure conduritol D (**23**)[18b,23d,24a] (67 mg, 92%) as an oil: ^{1}H NMR (CD_3OD) δ 3.77 (d, J = 4.6 Hz, 2H), 4.06 (d, J = 3.4 Hz, 2H), 5.76 (d, J = 1.5 Hz, 2H); ^{13}C NMR (CD_3OD) δ 69.2 (2C), 71.1 (2C), 130.5 (2C).

D-2,3-*O*-(1-Methylethylidene)-*allo*-inositol 1-Monobenzoate [(−)-24] and D-2,3-*O*-(1-Methylethylidene)-*allo*-inositol 4-Monobenzoate [(+)-24]. Compound (−)-**22** (290 mg, 1.0 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compound (−)-**24** (285 mg, 88%) as a solid. A similar reaction with compound (+)-**22** gave compound (+)-**24**. Data for (−)-**24**: R_f 0.22 (MeOH:CH_2Cl_2 = 1:20); mp 173−175 °C; $[\alpha]_D^{20}$ −42.9 (*c* 1.06, CH_3OH); ^{1}H NMR (CD_3OD) δ 1.32, 1.43 (2s, 6H), 3.92 (dd, J = 4.1, 8.4 Hz, 1H), 4.09 (dd, J = 5.1, 8.4 Hz, 1H), 4.25 (dd, J = 5.1, 8.2 Hz, 1H), 4.55 (dd, J = 4.1, 6.8 Hz, 1H), 4.67 (dd, J = 4.2, 6.8 Hz, 1H), 5.30 (dd, J = 4.2, 8.2 Hz, 1H), 7.45−8.10 (m, 5H); ^{13}C NMR (CD_3OD) δ 24.9, 26.3, 69.1, 70.4, 71.1, 73.4, 74.5, 77.0, 111.1, 129.6, 130.9, 131.4, 134.5, 167.7; MS (FAB) *m*/*z* 325 (M^+ + H). Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 58.99; H, 6.42. Data for (+)-**24**: mp 174−175 °C; $[\alpha]_D^{20}$ +41.8 (*c* 1.16, CH_3OH); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**24**.

(3a*R*,4*R*,7*S*,7a*S*)-*rel*-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4, 7-diol Dibenzoate (27) and (3a*R*,4*S*,5*R*,7a*R*)-rel-3a,4,5,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,5-diol Dibenzoate (28). To a solution of the racemate **19** (mp 132−133 °C; 790 mg, 2.72 mmol), which was prepared from racemate **3** by the same procedure as described for compound (+)-**19**, Ph_3P (1.80 g, 6.79 mmol), and benzoic acid (839 mg, 6.79 mmol) in toluene (25 mL) was added dropwise diethyl azodicarboxylate (1.1 mL, 6.79 mmol). After being stirred at rt for 3 h, the mixture was filtered through silica gel (EtOAc:Hex = 1:4), concentrated, and chromatographed to afford compounds **27** (91 mg, 8.5%) and **28** (785 mg, 73.1%). Data for **27**: R_f 0.6 (EtOAc:Hex = 1:2); mp 201−202 °C; ^{1}H NMR ($CDCl_3$) δ 1.33, 1.44 (2s, 6H), 4.88 (app t, J = 1.2 Hz, 2H), 5.42 (dd, J = 2.4 Hz, 2H), 5.96 (s, 2H), 7.45−8.16 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 24.9, 25.9, 69.8 (2C), 73.9 (2C), 110.7, 127.6−133.5, 166.3 (2C); MS (FAB) *m*/*z* 395 (M^+ + H). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.83; H, 5.66. Data for **28**: R_f 0.61 (EtOAc:Hex = 1:2); mp 108−110 °C; ^{1}H NMR ($CDCl_3$) δ 1.36, 1.45 (2s, 6H), 4.71 (dd, J = 2.3, 8.4 Hz, 1H), 4.78−4.80 (m, 1H), 5.58 (dd, J = 2.3, 8.9 Hz, 1H), 5.83 (m, 2H), 6.13 (br d, J = 8.9 Hz, 1H), 7.33−8.06 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.2, 28.2, 69.4, 72.8, 74.0, 74.9, 111.1, 127.2−133.7, 166.4, 166.6; MS (FAB) *m*/*z* 395 (M^+ + H). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.79; H, 5.84.

(3a*S*,4*S*,7*S*,7a*R*)- and (3a*R*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-7-(methoxymethoxy)-2,2-dimethyl-1,3- benzodioxol-4-ol [(+)-29 and (−)-29]. To a solution of compound (+)-**19** (900 mg, 3.10 mmol) in chloroform (12 mL) were added *N*,*N*-diisopropylethylamine (2.2 mL, 12.6 mmol) and chloromethyl methyl ether (0.71 mL, 9.35 mmol). After being stirred at rt overnight, the reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$ and brine, dried, and concentrated to dryness. The crude mixture was treated with 25 wt % sodium methoxide (in MeOH, 0.2 mL) in MeOH (12 mL). The resulting mixture was stirred under reflux for 3 h and filtered through a short pad of silica gel, and the solvent was evaporated under reduced pressure. Column chromatography gave compound (+)-**29** (693 mg, 97.1%) as an oil. Similarly, compound (−)-**29** was prepared from (−)-**19**. Data for (+)-**29**: R_f 0.22 (EtOAc:Hex = 1:2); $[\alpha]_D^{20}$ +111.3 (*c* 1.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.41 (2s, 6H), 2.99 (br s, 1H), 3.36 (s, 3H), 4.29 (app t, J = 3.4 Hz, 1H), 4.38−4.44 (m, 2H), 4.51 (dd, J = 4.1, 7.5 Hz, 1H), 4.65 (d, J = 6.7 Hz, 1H), 4.68 (d, J = 6.7 Hz, 1H), 5.97−6.03 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.8, 26.5, 55.7, 65.3, 71.4, 76.1, 77.5, 95.3, 109.5, 129.4, 134.7; MS (FAB) *m*/*z* 231 (M^+ + H). Data for (−)-**29**: $[\alpha]_D^{20}$ −111.5 (*c* 2.25, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**29**.

(3a*S*,4*R*,7*S*,7a*R*)- and (3a*R*,4*S*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-7-(methoxymethoxy)-2,2-dimethyl-1,3-benzodioxol-4-ol Monobenzoate [(−)-30 and (+)-30]. Mitsunobu reaction of compound (+)-**29** (665 mg, 2.89 mmol) was accomplished by the same procedure as described for compound **19** to give compound (−)-**30** (938 mg, 97.1%) as an oil. Similarly, compound (+)-**30** was prepared from compound (−)-**29**. Data for (−)-**30**: R_f 0.55 (EtOAc:Hex = 1:4); $[\alpha]_D^{20}$ −91.7 (*c* 4.37, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.51 (2s, 6H), 3.34 (s, 3H), 4.26−4.31 (m, 2H), 4.39−4.44 (m, 1H), 4.79 (d, J = 6.7 Hz, 1H), 4.90 (d, J = 6.7 Hz, 1H), 5.47−5.51 (m, 1H), 5.78 (td, J = 2.1, 2.1, 10.0 Hz, 1H), 5.91 (td, J = 2.2, 2.2, 10.0 Hz, 1H), 7.42−8.11 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.5, 27.6, 56.0, 73.3, 74.9, 76.4, 77.9, 96.2, 110.0, 128.0−133.6, 166.3; HRMS (FAB) *m*/*z* calcd for $C_{18}H_{23}O_6$ 335.1495, found 335.1511 (M^+ + H). Data for (+)-**30**: $[\alpha]_D^{20}$ +91.3 (*c* 4.16, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**30**.

(1*R*,2*S*,3*R*,4*S*)-*rel*-5-Cyclohexene-1,2,3,4-tetrol (Conduritol A, 31).[23d,26a] Compound (−)-**30** or (+)-**30** (151 mg, 0.45 mmol) was hydrolyzed by the same procedure as described for compound **23** to give conduritol A (**31**) (40 mg, 89%) as a solid: mp 140−142 °C [lit.[23d] mp 141−143 °C, lit.[26a] mp 140−141 °C]; ^{1}H NMR (CD_3OD) δ 3.64 (d, J = 4.6 Hz, 2H), 3.99 (d, J = 4.1 Hz, 2H), 5.56 (d, J = 1.2 Hz, 2H); ^{13}C NMR (CD_3OD) δ 70.6 (2C), 74.2 (2C), 130.7 (2C).

D-4-*O*-(Methoxymethyl)-5,6-*O*-(1-methylethylidene)-*allo*-inositol Tribenzoate [(−)-32a], D-1-*O*-(Methoxymethyl)-5,6-*O*-(1-methylethylidene)-*allo*-inositol Tribenzoate [(+)-32a], D-3-*O*-(Methoxymethyl)-1,2-*O*-(1-methylethylidene)-*muco*-inositol Tribenzoate [(+)-32b], and D-6-*O*-(Methoxymethyl)-1,2-*O*-(1-methylethylidene)-*muco*-inositol Tribenzoate [(−)-32b]. To a solution of compound (−)-**30** (418 mg, 1.25 mmol) in a mixture of acetone and water (8:1, 9 mL) were added NMO (630 mg, 5.22 mmol) and then OsO_4 (∼30 mg). After being stirred for 15 h at rt, the reaction mixture was quenched with a few drops of 10% $NaHSO_3$, and the solvents were evaporated under reduced pressure. The crude mixture was diluted with MeOH−CH_2Cl_2 (1:20) and filtered through a short pad of silica gel. After removal of the solvent by evaporation, TLC showed 3−4 products which were thought to be benzoyl-migrated products. Direct benzoylation of the crude mixture was carried out with BzCl (0.7 mL, 5.97 mmol) and DMAP (25 mL) in pyridine (7 mL). After being stirred at rt overnight, the mixture was treated with water (2 mL) for 20 min, diluted with EtOAc, and washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed to afford compounds (−)-**32a** (613 mg, 85%) and (+)-**32b** (75 mg, 9.3%). A similar reaction with compound (+)-**30** was carried out to give compounds (+)-**32a** and (−)-**32b**. Data for (−)-**32a**: oil; R_f 0.16 (CH_2Cl_2); $[\alpha]_D^{20}$ −4.23 (*c* 2.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.44, 1.62 (2s, 6H), 3.37 (s, 3H), 4.25 (dd, J = 3.0, 6.7 Hz, 1H), 4.58−4.66 (m, 2H), 4.74 (d, J = 6.9 Hz, 1H), 4.80 (d, J = 6.9 Hz, 1H), 5.76 (dd, J = 2.8, 4.2 Hz, 1H), 5.95−5.97 (m, 2H), 7.13−8.06 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 26.7, 28.5, 56.2, 68.8, 69.4, 70.4, 74.1, 76.1, 76.4, 96.0, 110.1, 128.6−133.6, 165.6, 166.1, 166.2; HRMS (FAB) *m*/*z* calcd for $C_{32}H_{33}O_{10}$ 577.2074, found 577.2101 (M^+ + H). Data for (+)-**32a**: $[\alpha]_D^{20}$ +4.82 (*c* 1.66, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**32a**. Data for (+)-**32b**: oil; R_f 0.25 (CH_2Cl_2); $[\alpha]_D^{20}$ +89.5 (*c* 1.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42, 1.72 (2s, 6H), 3.50 (s, 3H), 4.46 (dd, J = 3.2, 5.0 Hz, 1H), 4.53 (app. t, J = 3.9 Hz, 1H), 4.57 (app t, J = 6.0 Hz, 1H), 4.89 (s, 2H), 5.76 (dd, J = 2.8, 9.3 Hz, 1H), 5.80 (app t, J = 3.5 Hz, 1H), 6.14 (dd, J = 6.8, 9.3 Hz, 1H), 7.28−8.12 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 26.5, 28.3, 56.6, 69.7, 71.2, 71.4, 72.8, 77.3, 77.8, 97.3, 110.4, 128.8−133.8, 166.0 (2C), 166.1; HRMS (FAB) *m*/*z* calcd for $C_{32}H_{32}O_{10}Na$ 599.1893, found 599.1901 (M^+ + Na). Data for (−)-**32b**: $[\alpha]_D^{20}$ −88.2 (*c* 2.15, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**32b**.

(1*R*,4*S*,5*R*,6*S*)- and (1*S*,4*R*,5*S*,6*R*)-4,5,6-Tris(methoxymethoxy)-2-cyclohexen-1-ol Monobenzoate [(−)-33 and (+)-33]. Compound (−)-**30** (475 mg, 1.42 mmol) in 80% aq AcOH (8 mL) was heated at 70 °C for 3 h, and then concentrated to dryness. To a solution of the crude mixture in

chloroform (10 mL) were added *N*,*N*-diisopropylethylamine (4.5 mL, 25.8 mmol) and chloromethyl methyl ether (1.8 mL, 23.5 mmol). After being stirred at rt overnight, the reaction mixture was diluted with CH_2Cl_2, washed with aq $NaHCO_3$ and brine, dried, and concentrated. Column chromatography afforded compound (−)-**33** (474 mg, 97.1%) as an oil. Similarly, compound (+)-**33** was prepared from compound (+)-**30**. Data for (−)-**33**: R_f 0.4 (EtOAc:Hex = 1:2); $[\alpha]_D^{20}$ −132.3 (*c* 1.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 3.36, 3.42, 3.44 (3s, 9H), 4.14 (dd, J = 2.2, 5.0 Hz, 1H), 4.23 (dd, J = 2.2, 6.0 Hz, 1H), 4.32 (app t, J = 4.0 Hz, 1H), 4.75−4.84 (m, 6H), 5.77 (dd, J = 2.8, 6.0 Hz, 1H), 5.90 (dd, J = 2.8, 10.0 Hz, 1H), 5.96 (dd, J = 3.1, 10.0 Hz, 1H), 7.42−8.07 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 56.0 (3C), 71.3, 74.3, 74.8, 76.1, 96.5, 96.9, 97.2, 128.8−133.5, 166.3; MS (FAB) *m*/*z* 383 (M^+ + H). Data for (+)-**33**: $[\alpha]_D^{20}$ +131.9 (*c* 3.43, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**33**.

D-1,2,3-Tris-*O*-(methoxymethyl)-*muco*-inositol 6-Monobenzoate [(−)-34] and D-1,2,6-Tris-*O*-(methoxymethyl)-*muco*-inositol 3-Monobenzoate [(+)-34]. Compound (−)-**33** (285 mg, 0.745 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compound (−)-**34** (304 mg, 98%) as an oil. Similarly, compound (+)-**34** was prepared from compound (+)-**33**. Data for (−)-**34**: R_f 0.21 (EtOAc:Hex = 1:1); $[\alpha]_D^{20}$ −3.29 (*c* 1.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.86 (br s, 1H), 3.31, 3.44, 3.45 (3s, 9H), 3.61 (br s, 1H), 3.95−4.00 (m, 2H), 4.07 (app t, J = 4.6 Hz, 1H), 4.16 (dd, J = 2.8, 8.7 Hz, 1H), 4.20 (app t, J = 3.4 Hz, 1H), 4.67−4.84 (m, 6H), 5.63 (app t, J = 8.3 Hz, 1H), 7.42−8.09 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 56.3, 56.4, 56.6, 71.9, 72.8, 73.1, 75.1, 76.1, 76.9, 96.9, 97.7, 97.8, 128.8, 129.1, 130.2, 133.5, 166.2; HRMS (FAB) *m*/*z* calcd for $C_{19}H_{28}O_{10}Na$ 439.1580, found 439.1587 (M^+ + Na). Data for (+)-**34**: $[\alpha]_D^{20}$ +3.58 (*c* 0.43, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**34**.

(3a*R*,4*S*,7*S*,7a*R*)- and (3a*S*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-4,7-bis(phenylmethoxy)-1, 3-benzodioxole [(+)-35 and (−)-35].[27b] Compound (+)-**11** (345 mg, 1.85 mmol) was benzylated by the same procedure as described for compound (+)-**15** to give compound (+)-**35** (651 mg, 96%) as an oil. Similarly, compound (−)-**35** was prepared from compound (−)-**11**. Data for (+)-**35**: R_f 0.54 (EtOAc:Hex = 1:6); $[\alpha]_D^{20}$ +19.0 (*c* 2.29, $CHCl_3$) [lit.[27b] $[\alpha]_D^{20}$ +6.1 (*c* 1.46, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H), 3.64 (dd, J = 2.2, 5.3 Hz, 2H), 4.25 (dd, J = 2.2, 5.3 Hz, 2H), 4.66 (d, J = 11.8 Hz, 2H), 4.84 (d, J = 11.8 Hz, 2H), 5.70 (s, 2H), 7.27−7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.6 (2C), 72.2 (2C), 77.6 (2C), 80.8 (2C), 111.4, 128.0, 128.2, 128.8, 129.5, 138.7; MS (FAB) *m*/*z* 367 (M^+ + H). Data for (−)-**35**: $[\alpha]_D^{20}$ −18.9 (*c* 1.61, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**35**.

D-4,5-*O*-(1-Methylethylidene)-3,6-bis-*O*-(phenylmethyl)-*myo*-inositol [(−)-36] and D-5,6-*O*-(1-Methylethylidene)-1,4-bis-*O*-(phenylmethyl)-*myo*-inositol [(+)-36].[37] Compound (+)-**35** (602 mg, 1.64 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compound (−)-**36** (621 mg, 94.4%) as a solid. Similarly, compound (+)-**36** was prepared from compound (−)-**35**. Data for (−)-**36**: R_f 0.2 (EtOAc:Hex = 1:2); mp 125−126 °C [lit.[37] mp 149−151 °C (racemate)]; $[\alpha]_D^{20}$ −67.0 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.47, 1.49 (2s, 6H), 2.60 (br s, 2H), 3.39 (app t, J = 9.6 Hz, 1H), 3.55 (dd, J = 3.1, 8.7 Hz, 1H), 3.60 (dd, J = 3.0, 10.1 Hz, 1H), 3.82 (app t, J = 9.2 Hz, 1H), 4.05 (app t, J = 9.9 Hz, 1H), 4.22 (app t, J = 3.1 Hz, 1H), 4.68−4.97 (m, 4H), 7.27−7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.4 (2C), 71.7, 72.2, 73.4, 74.0, 76.6, 78.0, 78.6, 79.7, 112.3, 128.1−138.4; MS (FAB) *m*/*z* 401 (M^+ + H). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.65; H, 7.21. Data for (+)-**36**: mp 125−126 °C; $[\alpha]_D^{20}$ +68.0 (*c* 1.08, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**36**.

D-4,5-*O*-(1-Methylethylidene)-3,6-bis-*O*-(phenylmethyl)-*scyllo*-inositol 1-Monobenzoate [(−)-37] and D-3,4-*O*-(1-Methylethylidene)-2,5-bis-O-(phenylmethyl)-*scyllo*-inositol 1-Monobenzoate [(+)-37]. To a solution of compound (−)-**36** (401 mg, 1.0 mmol), Ph_3P (477 mg, 1.8 mmol), and benzoic acid (222 mg, 1.8 mmol) in toluene (12 mL) was added dropwise diethyl azodicarboxylate (0.30 mL, 1.85 mmol). After being stirred at 80 °C overnight, the mixture was filtered through silica gel (EtOAc:Hex = 1:2), concentrated, and chromatographed to afford compound (−)-**37** (399 mg, 79%) as a solid. Similarly, compound (+)-**37** was prepared from compound (+)-**36**. Data for (−)-**37**: R_f 0.5 (EtOAc:Hex = 1:2); mp 199−201 °C; $[\alpha]_D^{20}$ −74.0 (*c* 0.88, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.50, 1.51 (2s, 6H), 2.55 (br s, 1H), 3.59 (app t, J = 9.3 Hz, 1H), 3.65 (app t, J = 7.5 Hz, 1H), 3.71 (app t, J = 8.0 Hz, 1H), 3.75 (m, 2H), 4.64−4.98 (m, 4H), 5.38 (app t, J = 8.9 Hz, 1H), 7.14−8.02 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 27.4 (2C), 72.6, 73.3, 75.0, 76.5, 76.7, 79.1, 79.3, 79.5, 113.3, 127.8−138.5, 166.5; MS (FAB) *m*/*z* 505 (M^+ + H). Anal. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.39. Found: C, 71.28; H, 6.59. Data for (+)-**37**: mp 200−202 °C; $[\alpha]_D^{20}$ +74.7 (*c* 1.01, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**37**.

(3a*R*,4*R*,7*R*,7a*R*)- and (3a*S*,4*S*,7*S*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate [(−)-38 and (+)-38]. To a solution of compound (+)-**11** (295 mg, 1.58 mmol), Ph_3P (2.91 g, 11.0 mmol), and benzoic acid (1.35 g, 10.9 mmol) in toluene (20 mL) was added dropwise diethyl azodicarboxylate (1.9 mL, 11.7 mmol). After being stirred for 6 h at rt, the mixture was filtered through silica gel (EtOAc:Hex = 1:2), concentrated, and chromatographed to afford compound (−)-**38** (562 mg, 90%) as a solid. Similarly, compound (+)-**38** was prepared from compound (−)-**11**. Data for (−)-**38**: R_f 0.59 (EtOAc:Hex = 1:2); mp 119−120 °C; $[\alpha]_D^{20}$ −452.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 6H), 4.33 (d, J = 1.1 Hz, 2H), 5.96 (d, J = 1.1 Hz, 2H), 6.26 (m, 2H), 7.43−8.07 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.1 (2C), 66.7 (2C), 72.9 (2C), 111.5, 126.3−133.6, 166.3 (2C); MS (FAB) *m*/*z* 395 (M^+ + H). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.74; H, 5.73. Data for (+)-**38**: mp 119−120 °C; $[\alpha]_D^{20}$ +453.2 (*c* 1.24, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**38**.

(1*R*,2*R*,3*R*,4*R*)- and (1*S*,2*S*,3*S*,4*S*)-5-Cyclohexene-1,2,3,4-tetrol [(−)- and (+)-Conduritol E, (−)-39 and (+)-39].[19b,27b] Compound (−)-**38** (146 mg, 0.37 mmol) was hydrolyzed by the same procedure as described for compound **23** to give compound (−)-**39** (49 mg, 91%) as a solid. Similarly, compound (+)-**39** was prepared from compound (+)-**38**. Data for (−)-**39**: mp 190−192 °C [lit.[27b] mp 191−193 °C, lit.[19b] mp 192−193 °C]; $[\alpha]_D^{20}$ −331.6 (*c* 1.06, H_2O) [lit.[27b] $[\alpha]_D^{20}$ −330.0 (*c* 1.90, H_2O), lit.[19b] $[\alpha]_D^{20}$ −330 (*c* 4.5, H_2O)]; ^{1}H NMR (D_2O) δ 3.93 (s, 2H), 4.31 (s, 2H), 5.88 (d, J = 2.3 Hz, 2H); ^{13}C NMR (D_2O) δ 66.8 (2C), 69.3 (2C), 129.9 (2C). Data for (+)-**39**: mp 191−193 °C; $[\alpha]_D^{20}$ +331.8 (*c* 1.20, H_2O); ^{1}H NMR and ^{13}C NMR data identical to those of (−)-**39**.

(3a*R*,4*R*,7*R*,7a*R*)- and (3a*S*,4*S*,7*S*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-4,7-bis(phenylmethoxy)-1,3-benzodioxole [(−)-40 and (+)-40].[27b] To a solution of compound (−)-**38** (382 mg, 0.97 mmol) in MeOH (6 mL) was added 25 wt % sodium methoxide (in MeOH, 0.05 mL). The resulting mixture was stirred under reflux. After 4 h, the solvent was evaporated under reduced pressure. To a solution of the crude mixture and NaH (150 mg, 5.9 mmol) in DMF (5 mL) at 0 °C was added BnBr (0.5 mL, 4.05 mmol). After 30 min, the mixture was warmed to rt and stirred overnight. The mixture was diluted with EtOAc and successively washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), and concentrated. Column chromatography gave compound (−)-**40** (327 mg, 92%) as a solid. Similarly, compound (+)-**40** was prepared from compound (+)-**38**. Data for (−)-**40**: R_f 0.35 (EtOAc:Hex = 1:10); mp 49−50 °C [lit.[27b] mp 66−68 °C]; $[\alpha]_D^{20}$ −206.7 (*c* 1.21, $CHCl_3$) [lit.[27b] $[\alpha]_D^{20}$ −192.3 (*c* 0.87, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 6H), 4.20 (s, 2H), 4.33 (m, 2H), 4.63 (d, J = 11.6 Hz, 2H), 4.97 (d, J = 11.6 Hz, 2H), 5.90 (dd, J = 1.2, 3.0 Hz, 2H), 7.27−7.38 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.3 (2C), 72.4 (2C), 73.9 (2C), 75.3 (2C), 110.5, 127.9, 128.1, 128.7, 129.8, 139.2; MS (FAB) *m*/*z* 367 (M^+ + H). Data for (+)-**40**: mp 48−49 °C; $[\alpha]_D^{20}$ +206.0 (*c* 1.52, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**40**.

D-1,6-*O*-(1-Methylethylidene)-2,5-bis-*O*-(phenylmethyl)-*allo*-inositol [(+)-41] and D-4,5-*O*-(1-Methylethylidene)-3,6-bis-*O*-(phenylmethyl)-*allo*-inositol [(−)-41]. Compound

(−)-**40** (240 mg, 0.655 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compound (+)-**41** (197 mg, 75%) as a solid. Similarly, compound (−)-**41** was prepared from compound (+)-**40**. Data for (+)-**41**: R_f 0.38 (EtOAc:Hex = 1:2); mp 87−88 °C; $[\alpha]_D^{20}$ +20.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.53, 1.55 (2s, 6H), 3.04 (d, J = 9.6 Hz, 1H), 3.11 (d, J = 10.0 Hz, 1H), 3.87−3.90 (m, 1H), 3.99−4.02 (m, 1H), 4.08 (dd, J = 1.8, 10.1 Hz, 1H), 4.19 (app t, J = 2.9 Hz, 1H), 4.32 (dd, J = 2.4, 10.1 Hz, 1H), 4.36 (br s, 1H), 4.64 (d, J = 11.2 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.88 (d, J = 11.8 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1H), 7.28−7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.23 (2C), 68.4, 73.8, 73.9, 74.7, 75.5, 75.6, 75.7, 79.7, 111.24, 127.9−138.8; MS (FAB) *m*/*z* 401 (M^+ + H). Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.70; H, 7.22. Data for (−)-**41**: mp 87−88 °C; $[\alpha]_D^{20}$ −21.3 (*c* 0.57, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**41**.

(3a*R*,4*S*,7*S*,7a*R*)- and (3a*S*,4*R*,7*R*,7a*S*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol 4-Monobenzoate [(+)-42 and (−)-42] and (3a*S*,4*R*,7*R*,7a*S*)- and (3a*R*,4*S*,7*S*,7a*R*)-3a,4,7,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate [(+)-10 and (−)-10]. To a solution of (+)-**11** (620 mg, 3.3 mmol) in pyridine (15 mL) at 0 °C was added BzCl (0.41 mL, 3.50 mmol) dropwise. After being stirred for 5 h at 0−5 °C, the mixture was treated with water (2 mL) for 20 min, diluted with EtOAc, and washed with 1 N HCl, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed to afford the monobenzoate (+)-**42** (590 mg, 61%), the dibenzoate (+)-**10** (184 mg, 14%), and the starting material (+)-**11** (58 mg, 9.4%). A similar reaction with compound (−)-**11** was carried out to afford the monobenzoate (−)-**42**, the dibenzoate (−)-**10**, and the starting material (−)-**11**. Data for (+)-**42**: R_f 0.27 (EtOAc:Hex = 1:2); mp 123−124 °C; $[\alpha]_D^{20}$ +172.1 (*c* 1.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 6H), 3.46 (br s, 1H), 3.71 (dd, J = 8.3, 9.8 Hz, 1H), 3.88 (app t, J = 9.2 Hz, 1H), 4.55 (br d, J = 7.1 Hz, 1H), 5.71−5.83 (m, 3H), 7.41−8.09 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 27.3, 27.4, 70.9, 73.7, 77.8, 81.3, 112.0, 127.2, 128.8, 130.1, 130.3, 132.9, 133.7, 166.4; MS (FAB) *m*/*z* 291 (M^+ + H). Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 65.94; H, 6.54. Data for (−)-**42**: mp 123−124 °C; $[\alpha]_D^{20}$ −172.9 (*c* 1.41, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (+)-**42**. Data for (+)-**10**: mp 182−184 °C; $[\alpha]_D^{20}$ +208.2 (*c* 1.12, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **10**. Data for (−)-**10**: mp 182−184 °C; $[\alpha]_D^{20}$ −207.8 (*c* 1.13, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of **10**.

(3a*R*,4*R*,7*S*,7a*R*)- and (3a*S*,4*S*,7*R*,7a*S*)-3a,4,5,7a-Tetrahydro-2,2-dimethyl-1,3-benzodioxole-4,7-diol Dibenzoate [(−)-43 and (+)-43]. Mitsunobu reaction of compound (+)-**42** (420 mg, 1.45 mmol) was carried out by the same procedure as described for compound **19** to give compound (−)-**43** (560 mg, 98%) as an oil. Similarly, compound (+)-**43** was prepared from (−)-**42**. Data for (−)-**43**: R_f 0.55 (EtOAc:Hex = 1:2); $[\alpha]_D^{20}$ −56.3 (*c* 3.29, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.43, 1.50 (2s, 6H), 3.86 (dd, J = 3.7, 10.0 Hz, 1H), 4.39 (dd, J = 8.9, 10.0 Hz, 1H), 5.79 (br d, J = 9.1 Hz, 1H), 5.93 (app t, J = 4.3 Hz, 1H), 6.00 (dd, J = 1.8, 10.0 Hz, 1H), 6.13 (ddd, J = 1.8, 5.0, 10.0 Hz, 1H), 7.44−8.13 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.0, 27.4, 66.4, 73.7, 74.6, 75.7, 112.0, 126.6−133.7, 166.2, 166.3; HRMS (FAB) *m*/*z* calcd for $C_{23}H_{22}O_6Na$ 417.1314, found 417.1294 (M^+ + Na). Data for (+)-**43**: $[\alpha]_D^{20}$ +55.0 (*c* 3.10, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**43**.

(1*R*,2*R*,3*R*,4*S*)- and (1*R*,2*S*,3*S*,4*S*)-5-Cyclohexene-1,2,3,4-tetrol [(−)- and (+)-Conduritol F, (−)-44 and (+)-44].[18a,24d,25d,27b] Compound (−)-**43** (140 mg, 0. 35 mmol) was hydrolyzed by the same procedure as described for compound **23** to give compound (−)-**44** (46.5 mg, 90%) as a solid. Similarly, compound **(+)-44** was prepared from compound (+)-**43**. Data for (−)-**44**: mp 129−130 °C [lit. mp[24d] 126 °C, lit.[25d] mp 131−132 °C, lit.[27b] mp 128−130 °C]; $[\alpha]_D^{20}$ −99.7 (*c* 0.60, H_2O) [lit.[24d] $[\alpha]_D^{20}$ −102 (*c* 1.5, H_2O), lit.[25d] $[\alpha]_D^{20}$ −71 (*c* 0.75, CH_3OH), lit.[27b] $[\alpha]_D^{20}$ −84.0 (*c* 0.71, CH_3OH)]; ^{1}H NMR (CD_3OD) δ 3.44 (dd, J = 4.3, 10.3 Hz, 1H), 3.64 (dd, J = 7.6, 10.3 Hz, 1H), 3.95 (br d, J = 7.5 Hz, 1H), 4.18 (app t, J = 4.4 Hz, 1H), 5.73 (dd, J = 1.8, 10.0 Hz, 1H), 5.81 (ddd, J = 1.8, 4.7, 10.0 Hz, 1H); ^{13}C NMR (CD_3OD) δ 67.1, 71.7, 72.9, 73.1, 127.1, 132.9. Data for (+)-**44**: mp 128−129 °C [lit.[18a] mp 129−130 °C]; $[\alpha]_D^{20}$ +100.2 (*c* 0.77, H_2O) [lit.[18a] $[\alpha]_D^{20}$ +97.4 (*c* 0.7, H_2O)]; ^{1}H NMR and ^{13}C NMR data identical to those of (−)-**44**.

L-2,3-*O*-(1-Methylethylidene)-*chiro*-inositol 1,4-Dibenzoate [(−)-45] and D-2,3-*O*-(1-Methylethylidene)-*chiro*-inositol 1,4-Dibenzoate [(+)-45]. Compound (−)-**43** (395 mg, 1.0 mmol) was dihydroxylated by the same procedure as described for compound (+)-**16** to give compound (−)-**45** (418 mg, 97.4%) as an oil. A similar reaction with compound (+)-**43** was carried out to give compound (+)-**45**. Data for (−)-**45**: R_f 0.31 (EtOAc:Hex = 1:2); $[\alpha]_D^{20}$ −10.8 (*c* 2.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.47 (2s, 6H), 3.64 (d, J = 6.7 Hz, 1H), 3.78 (d, J = 3.3 Hz, 1H), 4.00−4.07 (m, 1H), 4.18−4.31 (m, 3H), 5.56 (app t, J = 9.3 Hz, 1H), 5.75 (app t, J = 2.3 Hz, 1H), 7.41−8.13 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 27.0, 27.3, 69.5, 71.9, 73.3, 74.5, 75.5, 75.6, 112.6, 128.8−133.9, 165.8, 168.0; HRMS (FAB) *m*/*z* calcd for $C_{23}H_{25}O_8$ 429.1549, found 429.1573 (M^+ + H). Data for (+)-**45**: $[\alpha]_D^{20}$ +11.6 (*c* 2.93, $CHCl_3$); R_f, ^{1}H NMR, and ^{13}C NMR data identical to those of (−)-**45**.

Acknowledgment. This work was financially supported by POSTECH/POSCO and the Ministry of Education/Basic Science Research Institute fund. We also thank Novo Nordisk Co. for kindly providing Novozym 435 and Lipozyme RM IM and Amano Co. for a generous gift of PCL.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds (+)-**11**, (+)-**15**, (+)-**17**, (+)-**18a**, (+)-**18b**, (+)-**29**, (−)-**30**, (−)-**32a**, (+)-**32b**, (−)-**33**, (−)-**34**, (−)-**43**, and (−)-**45**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016237A