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Divergent Syntheses of All Possible Optically Active Regioisomers of *myo*-Inositol Tris- and Tetrakisphosphates

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Since the discovery of D-*myo*-inositol 1,4,5-trisphosphate, which plays a pivotal role as a second messenger in transmembrane signaling, the scope of the phosphoinositide-based signaling processes has been continually expanding. However, the clear understanding of the molecular signal transduction mechanisms including the functions of newly found IP_n is still lacking. As a continuing effort to our previously reported syntheses of all possible 39 optically inactive regioisomers of *myo*-inositol phosphates (IP_n; $n = 1-6$), we synthesized all possible optically active regioisomers of *myo*-IP_3 and *myo*-IP_4 using chiral IBz_3s and IBz_2s, respectively. A series of procedures involving CRL-catalyzed enzymatic resolution of racemic 1,2:5,6-di-*O*-isopropylidene-*myo*-inositol and base-catalyzed benzoyl migration in tri- and dibenzoyl-isopropylidene-*myo*-inositol afforded eight enantiomeric pairs of IBz_3 and six enantiomeric pairs of IBz_2, respectively. Phosphorylation of these intermediates by the phosphitylation and oxidation procedure gave the target products.

Introduction

The phospholipase C catalyzed cleavage of membrane-bound phosphatidylinositol bisphosphate (PIP_2) into two second messengers, D-*myo*-inositol 1,4,5-trisphosphate [$I(1,4,5)P_3$] and diacylglycerol, is a crucially important means of cellular signaling processes. Since the discovery that $I(1,4,5)P_3$ mobilizes calcium ions from the intracellular storage, thus activating many calcium-dependent enzymes in the cell, its interactions with the $I(1,4,5)P_3$ receptor and metabolic enzymes have been extensively studied.[1] One of the major metabolic pathways involves a specific phosphorylation of $I(1,4,5)P_3$ to $I(1,3,4,5)P_4$, by $I(1,4,5)P_3$ 3-kinase [IP3K].[2] It has been suggested that $I(1,3,4,5)P_4$ also acts as a second messenger that mediates the entry of extracellular Ca^{2+} through plasma membrane ion channels[3] and mobilizes Ca^{2+} even from the intracellular calcium stores, although less potently than $I(1,4,5)P_3$.[4] Putative $I(1,3,4,5)P_4$ binding protein, purified from pig platelet, was shown to have a GTPase-activating protein (GAP) activity. This result suggested the possibility of a novel $I(1,3,4,5)P_4$ function to connect between PLC-mediated signaling and the *ras* signaling pathway.[5] The C5-dephosphorylated product $I(1,3,4)P_3$ acts in vivo as a specific regulator of cellular signaling by $I(3,4,5,6)P_4$,[6] which inhibits Ca^{2+}-activated Cl^- channels.[7] $I(1,3,4)P_3$ can be rephosphorylated by 6-kinase to $I(1,3,4,6)P_4$,[8] which has a weak, but distinct Ca^{2+} mobilizing activity.[9] Both $I(1,3,4,5)P_4$ and $I(1,3,4,6)P_4$ can be phosphorylated by 5/6-kinase in animal cells to $I(1,3,4,5,6)P_5$, which is metabolized to three compounds, IP_6 (phytic acid) and the normally inseparable enantiomeric pair $I(3,4,5,6)P_4$ and $I(1,4,5,6)P_4$.[10] $I(1,3,4,5,6)P_5$ can also be synthesized by a 3-kinase from a different precursor, $I(1,4,5,6)P_4$, which was found in avian erythrocytes[11] and Rat-1 fibroblasts.[12] Recently, nuclear inositol phosphates were shown to control mRNA export and transcription.[13] Synthesis of $I(1,4,5,6)P_4$ is also required for gene regula-

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tion. Thus, the phospholipase C pathway produces multiple IP_n messengers that modulate distinct cellular and nuclear processes. These observations suggest that activation of IP_n signaling may control gene expression.

Because of the biological importance as second messengers in the intracellular signal transduction, IP_3, IP_4, and related molecules have been targets of many chemical syntheses.[1] Studies to elucidate the functions of newly found IP_n, including binding affinity to specific proteins, are also in progress in many laboratories. There are 20 (four meso and eight enantiomeric pairs) IP_3 regioisomers and 15 (three meso and six enantiomeric pairs) IP_4 regioisomers. Some of the IP_3s[14]and IP_4s[14k,m,w,15] have been synthesized in the enantiomerically pure forms by optical resolution of racemic *myo*-inositol derivatives with chemical resolving agents and enzymes, or from chiral starting materials.

We previously reported the systematic and divergent syntheses of all possible 39 optically inactive regioisomers of *myo*-inositol phosphates[16] using the acyl migration as the key strategy[17] and utilized them to probe the binding domains of I(1,4,5)P_3 receptors,[18] I(1,3,4,5)P_4 binding proteins,[19] and I(1,4,5)P_3 3-kinase,[20] and as an iron binding motif.[21] Although we could obtain much useful information on the structure−activity relationships (SAR) of these biomacromolecules using optically inactive IP_n isomers, the availability of optically active regioisomers of IP_3 and IP_4 would facilitate obtaining more precise pictures. We report herein the first complete syntheses of all possible optically active regioisomers of IP_3 and IP_4 by employing the CRL-catalyzed enzymatic resolution and the benzoyl migration strategy.

Results and Discussion

Synthesis of Eight Enantiomeric Pairs of *myo*-Inositol Trisphosphates. The key issues in the synthesis of optically active regioisomers of IP_3 and IP_4 are how (1) to obtain enantiomerically pure inositol derivatives and (2) to efficiently prepare IBz_3s and IBz_2s, the key intermediates. Our synthetic approaches to homochiral regioisomers of IP_3 and IP_4 are based on the enzyme-catalyzed asymmetric acetylation of (±)-1,2:5,6-di-*O*-isopropylidene-*myo*-inositol[22] with acetic anhydride in the presence of lipase from *Candida rugosa* (CRL, Sigma), which we previously utilized in the synthesis of two enantiomeric pairs of *myo*-IP_5.[23] The conversions of the enantiomeric diols, **1D** and **1L**, to two enantiomeric pairs of all possible IP_3 and IP_4 regioisomers involve the identical series of reactions except that the corresponding substrates and products along the synthetic route have opposite configurations. Therefore, the procedure starting from **1D** only is described as the representative procedure.

Chiral IBz_3s, the key intermediates for the synthesis of eight enantiomeric pairs of *myo*-IP_3, were prepared as follows. First, benzoylation of the chiral diol **1D**[23] under the conventional conditions with BzCl in pyridine, followed by acid-catalyzed partial solvolysis with a catalytic amount of AcCl in MeOH−CH_2Cl_2 gave the diol **3Da** (59%) and the tetrol **4Da** (32%) (Scheme 1). The tetrol **4Da** was also prepared by direct hydrolysis of **2D** in 80% aq AcOH. To cause the limited benzoyl migration, a series of IBz_3s protected with the acetonide group was prepared. The dibenzoate **3Da** was further benzoylated with BzCl

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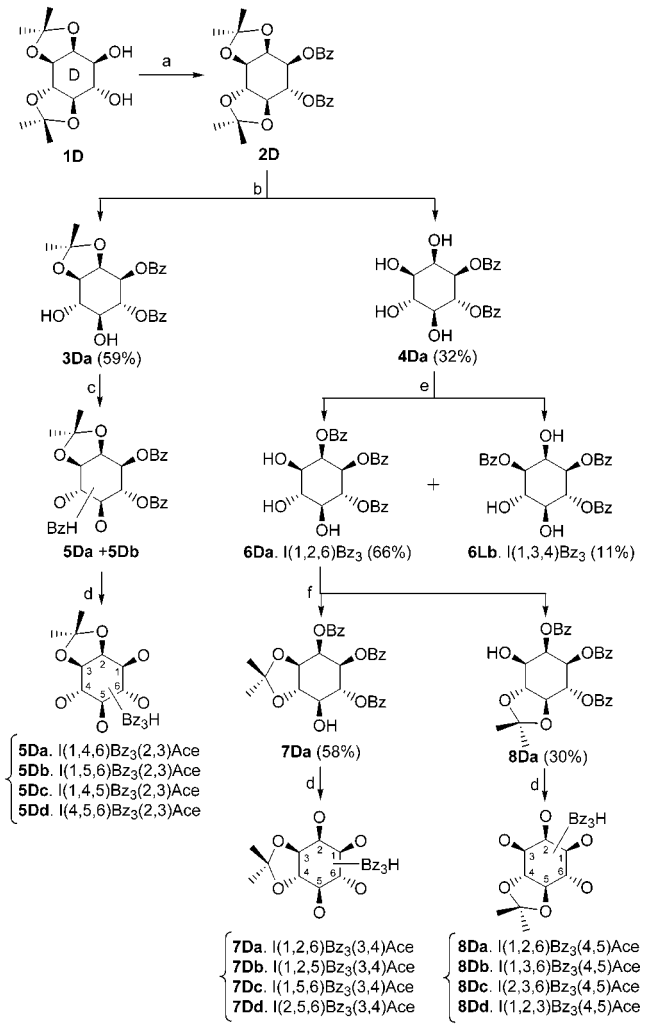
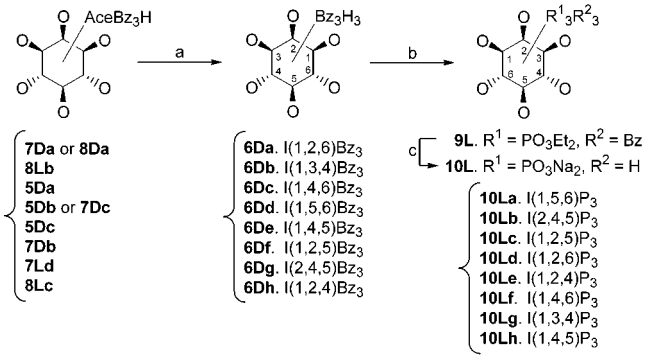
SCHEME 1[a]



[a] Reagents and conditions: (a) BzCl, pyridine, 96%; (b) AcCl, MeOH−CH_2Cl_2, 0 °C; (c) BzCl (1.2 equiv), pyridine, 0 °C; (d) 60% aq pyridine, 100 °C; (e) (i) $(MeO)_3CPh$, TSA, DMF, rt, (ii) H_2O; (f) 2,2-dimethoxypropane, TSA, DMF, rt. (Compounds in D-series only are shown.)

(1.2 equiv) in pyridine to give a mixture of tribenzoylated inositol monoacetonides **5Da** and **5Db** (ca. 1:2). Compound **4Da** was initially transformed to two isomers of the necessary eight IBz_3 regioisomers, **6Da** (66%) and **6Lb** (11%), by treatment with trimethyl orthobenzoate and TSA in THF followed by hydrolysis. In this conversion, no product that could potentially be generated via the 4,5-trans-cyclic orthobenzoate was detected, suggesting that the cis-cyclic orthobenzoate was preferentially formed over the trans-cyclic orthobenzoate. The reaction of tribenzoate **6Da** with 2-dimethoxypropene in the presence of a catalytic amount of TSA afforded additional tribenzoylated inositol monoacetonides **7Da** and **8Da**, which were isolated in 58% and 30% yield, respectively. When these three IBz_3 monoacetonide derivatives were subjected to the acyl migration conditions (60% aqueous pyridine, 100 °C), mixtures of four regioisomers were generated. First, the equilibration of **5Da** or **5Db** produced four regioisomers (**5Da**, **5Db**, **5Dc**, and **5Dd**). Similar reactions of **7Da** and **8Da** afforded another set of four regioisomers (**7Da**, **7Db**, **7Dc**, and **7Dd**) and the third set of regioisomers (**8Da**, **8Db**, **8Dc**, and **8Dd**),

SCHEME 2[a]



[a] Reagents and conditions: (a) 80% aq AcOH, 100 °C, quant.; (b) (i) $(EtO)_2PCl$, *N*,*N*-diisopropylethylamine, (ii) H_2O_2, 65−77%; (c) (i) TMSBr, (ii) 1 N LiOH, (iii) Dowex 50WX8-100 (H^+), (iv) pH 10 (NaOH), ca. 90%.

TABLE 1. Optical Rotations of IBz_3s

	$[\alpha]_D^{25}$	
IBz_3	D-form	L-form
6a [I(1,2,6)Bz_3]	−151.9 (*c* 2.03, $CHCl_3$)	+154.8 (*c* 1.71, $CHCl_3$)
6b [I(1,3,4)Bz_3]	+46.1 (*c* 1.00, MeOH)	−46.2 (*c* 1.07, MeOH)
6c [I(1,4,6)Bz_3]	−46.7 (*c* 1.01, EtOAc)	+46.3 (*c* 1.07, EtOAc)
6d [I(1,5,6)Bz_3]	+5.53 (*c* 1.11, EtOAc)	−3.96 (*c* 1.21, EtOAc)
6e [I(1,4,5)Bz_3]	−49.8 (*c* 0.97, EtOAc)	+50.0 (*c* 1.04, EtOAc)
6f [I(1,2,5)Bz_3]	−63.6 (*c* 2.75, $CHCl_3$)	+62.1 (*c* 1.75, $CHCl_3$)
6g [I(2,4,5)Bz_3]	+9.40 (*c* 1.03, EtOAc)	−9.74 (*c* 1.00, EtOAc)
6h [I(1,2,4)Bz_3]	−5.30 (*c* 0.8, THF)	+5.90 (*c* 1.06, THF)

respectively. Each of these regioisomers was readily separated and purified by silica gel chromatography. Reequilibration of any one isolated regioisomer under the acyl migration conditions was found to provide the other regioisomers found in the initial mixture. For example, additional amounts of **5Da**, **5Db**, and **5Dc** could be obtained by the reequilibration of **5Dd**.

Of the twelve monoacetonide IBz_3s obtained, seven regioisomers (**5Da**, **5Db**/**7Dc**, **5Dc**, **7Db**, **7Dd**, and **8Dc**) were individually hydrolyzed with 80% aqueous AcOH under reflux to afford an additional six IBz_3 regioisomers **6Dc**−**6Df** and **6Lg**−**6Lh**, respectively (Scheme 2). Thus, the complete set of the necessary eight IBz_3 regioisomers (five D-IBz_3 regioisomers and three L-IBz_3 regioisomers) was secured. Similarly, the other set of eight IBz_3 regioisomers with the opposite stereochemistry (five L-IBz_3 regioisomers and three D-IBz_3 regioisomers) was obtained starting from **1L**. All of these IBz_3s were fully characterized by ^1H and ^{13}C NMR spectroscopy and their optical rotation values are listed in Table 1.

Next, all of the enantiomeric IBz_3 regioisomers were converted to the corresponding enantiomeric IP_3 regioisomers (Scheme 2). Phosphorylation of the enantiomeric IBz_3 regioisomers with diethyl chlorophosphite in the presence of *N*,*N*-diisopropylethylamine in DMF, followed by oxidation with 30% hydrogen peroxide, afforded eight enantiomeric pairs of IP'_3Bz_3 derivatives (**9a**−**9h**). The ^{31}P NMR chemical shifts and optical rotations of the eight enantiomeric pairs of IP'_3Bz_3 are shown in Table 2.

In the final step of the synthesis, all protecting groups of IP'_3Bz_3 derivatives (**9a**−**9h**) were removed by successive treatment with TMSBr and then LiOH. The target products (**10a**−**10h**) were obtained after chromatography on Dowex 50WX8-100 (H^+), pH adjustment to 10 with

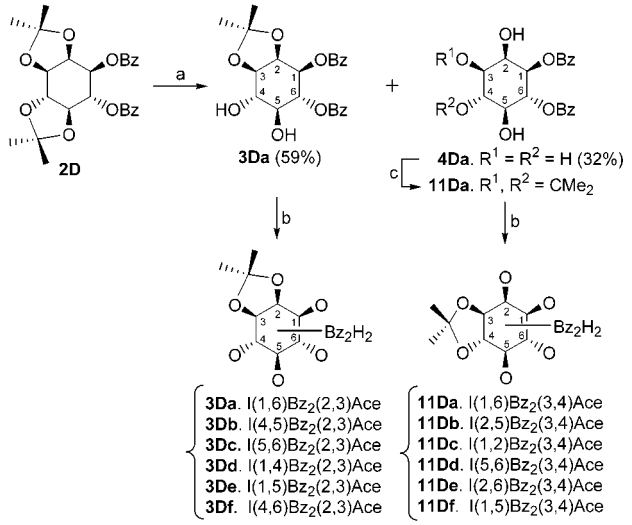
TABLE 2. ^{31}P NMR Chemical Shifts and Optical Rotations of IP′$_3$Bz$_3$s

IP′$_3$Bz$_3$s [P′ = PO(OEt)$_2$]	^{31}P (δ, ppm)	$[\alpha]_D^{25}$ (in $CHCl_3$) D-form	L-form
9a [I(1,5,6)P′$_3$Bz$_3$]	0.02, 0.07, 0.83	+75.8 (*c* 1.06)	−71.1 (*c* 1.89)
9b [I(2,4,5)P′$_3$Bz$_3$]	0.51, 0.52, 1.16	−10.0 (*c* 0.98)	+10.6 (*c* 1.92)
9c [I(1,2,5)P′$_3$Bz$_3$]	0.23, 0.99, 1.19	+11.9 (*c* 1.54)	−12.7 (*c* 1.62)
9d [I(1,2,6)P′$_3$Bz$_3$]	0.21, 0.55, 1.26	−8.13 (*c* 2.48)	+6.04 (*c* 0.86)
9e [I(1,2,4)P′$_3$Bz$_3$]	0.39, 1.07, 1.21	+19.2 (*c* 1.64)	−19.1 (*c* 1.40)
9f [I(1,4,6)P′$_3$Bz$_3$]	0.22, 0.86, 1.03	+38.0 (*c* 1.12)	−42.3 (*c* 1.77)
9g [I(1,3,4)P′$_3$Bz$_3$]	0.44, 0.93, 0.97	−2.53 (*c* 0.75)	+2.59 (*c* 1.02)
9h [I(1,4,5)P′$_3$Bz$_3$]	0.29, 0.72, 0.90	+15.3 (*c* 0.60)	−14.7 (*c* 1.61)

TABLE 3. ^{31}P NMR Chemical Shifts and Optical Rotations of IP$_3$s

IP$_3$s [P = PO(ONa)$_2$]	^{31}P (δ, ppm)	$[\alpha]_D^{25}$ (in H_2O, pH 10) D-form	L-form
10a [I(1,5,6)P$_3$]	6.30, 6.74, 7.24	−2.57 (*c* 1.01)	+4.56 (*c* 0.95)
10b [I(2,4,5)P$_3$]	7.28, 7.46, 7.60	−9.59 (*c* 1.45)	+12.0 (*c* 0.96)
10c [I(1,2,5)P$_3$]	7.02, 7.28, 7.48	+5.94 (*c* 1.62)	−6.41 (*c* 1.58)
10d [I(1,2,6)P$_3$]	7.04, 7.16, 7.80	−16.5 (*c* 1.47)	+15.9 (*c* 0.99)
10e [I(1,2,4)P$_3$]	7.31, 7.34, 7.59	+11.5 (*c* 1.51)	−13.7 (*c* 0.75)
10f [I(1,4,6)P$_3$]	6.05, 7.15, 7.66	−10.1 (*c* 0.78)	+11.2 (*c* 1.14)
10g [I(1,3,4)P$_3$]	6.11, 6.91, 7.61	+10.4 (*c* 0.59)	−9.20 (*c* 0.74)
10h [I(1,4,5)P$_3$]	5.67, 7.30, 7.40	−24.1 (*c* 0.28)	+20.1 (*c* 0.74)

SCHEME 3[a]



[a] Reagents and conditions: (a) AcCl, MeOH−CH_2Cl_2, 0 °C; (b) 60% aq pyridine, 100 °C; (c) 2-methoxypropene, TSA, 0 °C, 73.8%. (Compounds in D-series only are shown.)

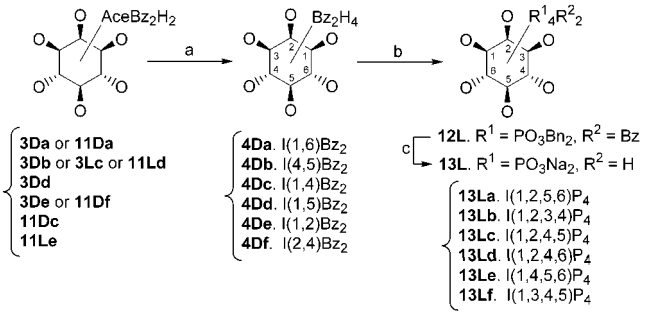
NaOH, and then lyophilization. All products were fully characterized with NMR spectroscopy, and their ^{31}P NMR data and optical rotations are given in Table 3.

Synthesis of Six Enantiomeric Pairs of *myo*-Inositol Tetrakisphosphates. For the conversions of the enantiomeric starting materials **1D** and **1L** to the six enantiomeric pairs of *myo*-IP$_4$, two monoacetonide IBz$_2$s (**3Da** and **11Da**) were prepared in the usual fashion. When **3Da** was subjected to 60% aq pyridine at 100 °C, six possible isomers of chiral I(2,3)AceBz$_2$ (**3Da**−**3Df**) were obtained in substantial amounts (Scheme 3). The kinetically controlled acetonation of chiral tetrol **4Da** with 2-methoxypropene and TSA at 0 °C gave monoacetonated diol **11Da** in 73.8% yields, which was then subjected to the benzoyl migration in 60% aq pyridine

TABLE 4. Optical Rotations of Six Enantiomeric Pairs of IBz$_2$

IBz$_2$	$[\alpha]_D^{25}$ (in MeOH) D-form	L-form
4a [I(1,6)Bz$_2$]	−74.7 (*c* 0.87)	+73.3 (*c* 1.00)
4b [I(4,5)Bz$_2$]	−55.3 (*c* 1.19)	+55.7 (*c* 0.93)
4c [I(1,4)Bz$_2$]	−16.7 (*c* 0.54)	+16.6 (*c* 0.41)
4d [I(1,5)Bz$_2$]	−18.1 (*c* 0.50)	+19.1 (*c* 0.50)
4e [I(1,2)Bz$_2$]	−96.9 (*c* 0.53)	+97.2 (*c* 0.48)
4f [I(2,4)Bz$_2$]	+84.2 (*c* 0.56)	−82.1 (*c* 0.48)

SCHEME 4[a]



[a] Reagents and conditions: (a) 80% aq AcOH, 100 °C, quant.; (b) (i) dibenzyl diisopropylphosphoamidite, 1*H*-tetrazole, CH_2Cl_2, (ii) mCPBA, 82−99%; (c) (i) H_2 (50 psi), Pd/C, (ii) 1 N LiOH, (iii) Dowex 50WX8-100 (H^+), (iv) pH 10 (NaOH), ca. 90%.

at 100 °C to afford the six possible isomers of chiral I(3,4)-AceBz$_2$ (**11Da**−**11Df**). In each case, the individual regioisomers were separated with flash column chromatography in the forms of IAceBz$_2$ with the intact acetonide group or the IBz$_2$ after the acid-catalyzed hydrolysis. The acid-catalyzed hydrolysis of IAceBz$_2$s (**3D**/**3L** and **11D**/**11L**) gave six enantiomeric pairs of IBz$_2$ (**4D**/**4L**) as the key intermediates. Thus, all possible optically active 12 regioisomers of IBz$_2$ were successfully prepared and fully characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Table 4 summarizes the optical rotations of each enantiomeric pairs.

Phosphitylation of the 12 IBz$_2$ regioisomers with dibenzyl diisopropylphosphoamidite and 1*H*-tetrazole in CH_2Cl_2 at room temperature and subsequent oxidation with mCPBA afforded the six enantiomeric pairs of inositol tetrakisphosphate (**12L** and **12D**) in the protected forms in 82−99% yields (Scheme 4). The ^{31}P NMR chemical shifts and optical rotations of the six enantiomeric pairs of IP$_4$Bz$_2$ are shown in Table 5.

In the final steps, all protecting groups were removed by hydrogenolysis and treatment with LiOH to give the desired 12 optically active regioisomers of IP$_4$ (**13L** and **13D**) in good yields (Scheme 4). The ^{31}P NMR data showed reproducible chemical shifts at ca. pH 10 and all the signals were well-resolved. Each enantiomeric pair of the fully deprotected IP$_4$s showed similar optical rotations with opposite signs. The ^{31}P NMR data and optical rotations of six enantiomeric pairs of IP$_4$ are listed in Table 6.

Conclusion

We have successfully carried out the first total syntheses of the complete sets of all enantiomeric pairs of *myo*-IP$_3$ and *myo*-IP$_4$ regioisomers from homochiral in-

TABLE 5. ^{31}P NMR Chemical Shifts and Optical Rotations of IP′$_4$Bz$_2$s

IP′$_4$Bz$_2$ [P′ = PO(OBn)$_2$]	^{31}P (δ, ppm)	$[\alpha]_D^{25}$ (in $CHCl_3$) D-form	$[\alpha]_D^{25}$ (in $CHCl_3$) L-form
12a [I(1,2,5,6)P′$_4$Bz$_2$]	0.37, 0.91, 1.04, 1.53	+21.3 (*c* 1.50)	−20.8 (*c* 1.53)
12b [I(1,2,3,4)P′$_4$Bz$_2$]	0.13, 1.13, 1.18, 1.61	−2.98 (*c* 1.14)	+3.30 (*c* 1.76)
12c [I(1,2,4,5)P′$_4$Bz$_2$]	0.34, 0.99, 1.06, 1.35	−6.06 (*c* 1.40)	+6.33 (*c* 1.24)
12d [I(1,2,4,6)P′$_4$Bz$_2$]	0.39, 1.17, 1.42, 1.53	+2.59 (*c* 1.75)	−2.67 (*c* 1.40)
12e [I(1,4,5,6)P′$_4$Bz$_2$]	0.59, 0.72, 1.26, 1.59	+6.93 (*c* 1.49)	−6.38 (*c* 1.40)
12f [I(1,3,4,5)P′$_4$Bz$_2$]	0.65, 1.03, 1.19, 1.22	−20.6 (*c* 1.45)	+22.0 (*c* 1.35)

TABLE 6. ^{31}P NMR Chemical Shifts and Optical Rotations of IP$_4$s

IP$_4$ [P = PO(ONa)$_2$]	^{31}P (δ, ppm)	$[\alpha]_D^{25}$ (in H_2O, pH 10) D-form	$[\alpha]_D^{25}$ (in H_2O, pH 10) L-form
13a [I(1,2,5,6)P$_4$]	4.93, 6.47, 6.97, 7.28	−4.98 (*c* 1.93)	+4.19 (*c* 2.35)
13b [I(1,2,3,4)P$_4$]	5.84, 7.38, 7.95, 8.12	+19.0 (*c* 2.27)	−19.9 (*c* 2.59)
13c [I(1,2,4,5)P$_4$]	3.98, 4.69, 5.59, 5.69	−13.2 (*c* 1.65)	+14.9 (*c* 2.08)
13d [I(1,2,4,6)P$_4$]	6.87, 6.96, 7.19, 7.82	−15.2 (*c* 2.10)	+14.7 (*c* 1.77)
13e [I(1,4,5,6)P$_4$]	5.03, 5.50, 6.25, 6.99	−8.99 (*c* 1.85)	+10.1 (*c* 2.23)
13f [I(1,3,4,5)P$_4$]	5.80, 6.42, 6.92, 7.38	−4.08 (*c* 2.02)	+4.68 (*c* 2.11)

termediates **1D** and **1L**, which were obtained by the CRL-catalyzed enzymatic resolution. The chiral regioisomers of *myo*-IP$_3$ and *myo*-IP$_4$, together with the available meso compounds,[16c,d] are currently being utilized as molecular probes in the studies of IP$_3$ receptors and metabolic enzymes. These studies are expected to provide more detailed pictures on the structure−activity relationships in the areas of intracellular signal transduction, eventually providing grounds for the rational design of compounds with useful pharmacological activities.

Experimental Section

General Methods. All nonhydrolytic reactions were carried out in oven-dried glassware under dry argon or nitrogen atmosphere. All commercial reagents were used as obtained without further purification. Solvents were purified and dried by standard methods prior to use. Melting points were determined on a Thomas-Hoover apparatus and were uncorrected. NMR spectra were recorded on a Bruker AM 300, DPX 300, or DRX 500 spectrometer. Tetramethylsilane and phosphoric acid (85%) were used as internal and external standards for ^{1}H NMR and ^{31}P NMR, respectively. When necessary, definitive assignments of each proton for new synthetic compounds were based on ^{1}H−^{1}H homonuclear COSY spectra. Mass spectra (EI or FAB) were determined on a micromass PLATFORM II, and were performed by Korea Basic Science Center, Taejeon and Inter-University Center for Natural Science Research Facilities, Seoul National University, Seoul, Korea. Elemental analyses were performed with an Elementar Vario-EL system. Optical rotations were measured with a JASCO DIP-360 digital polarimeter.

D- and L-1,6-Di-*O*-benzoyl-2,3:4,5-Di-*O*-isopropylidene-*myo*-inositol (2D and 2L). Benzoylation of compound **1D**[23] (4.0 g, 15.4 mmol) was carried out with BzCl (8 mL, 65 mmol) in pyridine (50 mL). After being stirred for 6 h at room temperature, the reaction mixture was treated with water (10 mL) for 20 min, diluted with EtOAc, and washed with aq $NaHSO_4$, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), and concentrated to give a solid product that was recrystallized from MeOH−CH_2Cl_2 to give compound **2D** (6.93 g, 96%). Similarly, compound **2L** was prepared from compound **1L**. **2D**: R_f 0.27 (EtOAc:Hex = 1:4); mp 169−171 °C (lit. racemate: mp 197−200 °C,[22a] mp 187−189 °C[22b]); $[\alpha]_D^{25}$ −60.6 (*c* 0.96, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.33, 1.34, 1.48, 1.51 (4s, 12H, C*Me*$_2$), 3.90 (dd, *J* = 8.5, 10.5 Hz, 1H, H-5), 4.32 (dd, *J* = 7.8, 10.5 Hz, 1H, H-4), 4.54 (app. t, *J* = 7.3 Hz, 1H, H-3), 4.73 (dd, *J* = 3.7, 6.7 Hz, 1H, H-2), 5.61−5.66 (m, 2H, H-1 & H-6), 7.39−8.08 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 25.6, 27.1, 27.4, 27.5 (2C*Me*$_2$), 73.1, 74.1, 74.5, 76.8, 76.9, 78.1 (inositol ring carbons), 111.8, 113.6 (2C*Me*$_2$), 128.8−133.8 (2Ph), 165.3, 165.5 (2*C*OPh). **2L**: mp 170−172 °C; $[\alpha]_D^{25}$ +61.2 (*c* 1.00, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **2D**.

D- and L-1,6-Di-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (3Da and 3La) and D- and L-1,6-Di-*O*-benzoyl-*myo*-inositol (4Da and 4La). To a solution of compound **2D** (5 g, 10.5 mmol) in MeOH (15 mL) and CH_2Cl_2 (45 mL) at 0 °C was added acetyl chloride (4 drops). After 5 h, the reaction mixture was quenched with TEA (1 mL), evaporated, and chromatographed on silica gel to give oily compound **3Da** (2.65 g, 59%) and crystalline compound **4Da** (1.30 g, 32%). A similar reaction with compound **2L** was carried out to give compounds **3La** and **4La**. **3Da**: R_f 0.3 (EtOAc:Hex = 1:1); $[\alpha]_D^{25}$ −79.8 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.35, 1.51 (2s, 6H, C*Me*$_2$), 2.99 (d, *J* = 2.6 Hz, 1H, O*H*-4), 3.25 (d, *J* = 3.8 Hz, 1H, O*H*-5), 3.72 (ddd, *J* = 3.8, 7.6, 9.6 Hz, 1H, H-5), 4.09 (ddd, *J* = 2.6, 7.2, 9.6 Hz, 1H, H-4), 4.24 (dd, *J* = 5.9, 7.2 Hz, 1H, H-3), 4.66 (dd, *J* = 3.7, 5.9 Hz, 1H, H-2), 5.54 (dd, *J* = 7.6, 7.9 Hz, 1H, H-6), 5.60 (dd, *J* = 3.7, 7.9 Hz, 1H, H-1), 7.35−8.02 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 25.9, 28.0 (C*Me*$_2$), 70.5, 73.7, 73.8, 74.8, 74.9, 78.6 (inositol ring carbons), 111.2 (*C*Me$_2$), 126.3−134.0 (2Ph), 166.1, 167.2 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.59; H, 5.99. **3La**: $[\alpha]_D^{25}$ +78.9 (*c* 1.70, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **3Da**. **4Da**: R_f 0.2 (EtOAc); mp 108−111 °C; $[\alpha]_D^{25}$ −74.7 (*c* 0.87, MeOH); ^{1}H NMR (CD_3OD) δ 3.62 (dd, *J* = 2.8, 9.6 Hz, 1H, H-3), 3.67 (app. t, *J* = 9.5 Hz, 1H, H-5), 3.87 (app. t, *J* = 9.5 Hz, 1H, H-4), 4.30 (app. t, *J* = 2.6 Hz, 1H, H-2), 5.20 (dd, *J* = 2.6, 10.4 Hz, 1H, H-1), 5.83 (app. t, *J* = 10.0 Hz, 1H, H-6), 7.36−7.96 (m, 10H, 2Ph); ^{13}C NMR (CD_3OD) δ 71.8, 73.0, 74.4, 74.4, 74.9, 74.8 (inositol ring carbons), 129.5−134.5 (2Ph), 167.5, 167.9 (2*C*OPh); MS (FAB) *m*/*z* 411 (M^+ + Na), 389 (M^+ + H). Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.61; H, 5.54. **4La**: mp 107−110 °C; $[\alpha]_D^{25}$ +73.3 (*c* 1.00, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4Da**.

D- and L-1,4,6-Tri-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (5Da and 5La) and D- and L-1,5,6-Tri-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (5Db and 5Lb). Monobenzoylation of **3Da** (2 g, 2. 4 mmol) in pyridine (25 mL) was carried out by dropwise addition of BzCl (0.66 mL, 5.8 mmol). After being stirred for 3 h at room temperature, the reaction mixture was treated with water (5 mL) for 5 min, diluted with EtOAc, and washed with aq $NaHSO_4$, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated,

and chromatographed to give **5Da** (640 mg, 25%) and **5Db** (1.18 g, 46%). Similarly, compounds **5La** and **5Lb** were prepared from **3La**. **5Da**: R_f 0.5 (EtOAc:CH_2Cl_2:Hex = 1:10:5); mp 220−221 °C; $[\alpha]_D^{25}$ −54.3 (*c* 0.99, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.65 (2s, 6H, C*Me*$_2$), 2.92 (d, *J* = 6.3 Hz, 1H, O*H*-5), 4.01 (app. q, *J* = 7.2 Hz, 1H, H-5), 4.55 (app. t, 6.1 Hz, 1H, H-3), 4.79 (dd, *J* = 3.7, 5.8 Hz, 1H, H-2), 5.63 (dd, *J* = 6.4 8.1 Hz, 1H, H-4), 5.71 (dd, *J* = 3.7, 9.7 Hz, 1H, H-1), 5.80 (dd, *J* = 7.5, 9.7 Hz, 1H, H-6), 7.26−8.12 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 25.7, 27.6 (C*Me*$_2$), 70.0, 73.5, 73.9, 74.4, 75.6, 76.4 (inositol ring carbons), 111.5 (*C*Me$_2$), 128.8−133.9 (3Ph), 166.7, 166.8, 167.3 (3*C*OPh); MS (FAB) *m*/*z* 555 (M^+ + Na), 533 (M^+ + H). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.44; H, 5.30. **5La**: mp 221−222 °C; $[\alpha]_D^{25}$ +52.8 (*c* 1.10, CH_2Cl_2); identical ^{1}H NMR and ^{13}C NMR data to those of **5Da**. **5Db**: R_f 0.2 (EtOAc:CH_2Cl_2:Hex = 1:10:5); mp 106−107 °C; $[\alpha]_D^{25}$ +0.78 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (CD_3OD) δ 1.39, 1.64 (2s, 6H, C*Me*$_2$), 4.13 (dd, *J* = 6.5, 8.3 Hz, 1H, H-4), 4.39 (app. t, *J* = 6.0 Hz, 1H, H-3), 4.61 (s, 1H, O*H*-4), 4.81 (dd, *J* = 4.0, 5.5 Hz, 1H, H-2), 5.49 (app. t, *J* = 8.6 Hz, 1H, H-5), 5.82 (dd, *J* = 3.9, 10.2 Hz, 1H, H-1), 5.97 (dd, *J* = 8.8, 10.1 Hz, 1H, H-6), 7.30−7.95 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 24.7, 27.0 (C*Me*$_2$), 70.3, 71.0, 72.6, 74.1, 74.6, 79.1 (inositol ring carbons), 110.7 (*C*Me$_2$), 126.3−133.6 (3Ph), 165.9, 166.2, 166.3 (3*C*OPh); MS (FAB) *m*/*z* 533 (M^+ + H). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.36; H, 5.34. **5Lb**: mp 109−110 °C; $[\alpha]_D^{25}$ −0.91 (*c* 1.00, CH_2Cl_2); identical ^{1}H NMR and ^{13}C NMR data to those of **5Db**.

Generation and Separation of IBz_3 Regioisomers from 5Da/5Db or 5La/5Lb. Compound **5Da** or **5Db** (1.40 g) in the solvent mixture of pyridine−water (6:4, 60 mL) was heated at 100 °C for 3 h. The solution was cooled and concentrated under reduced pressure. Addition of acetone to the reaction mixture followed by evaporation of the solvents was repeated twice. The crude mixture, which contained almost equal amounts of **5Da**, **5Db**, **5Dc**, and **5Dd**, was chromatographed on silica gel (EtOAc:CH_2Cl_2:Hex = 1:10:10 → 1:10:0 gradient). The eluting sequence of the isomers was **5Da**, **5Dc**, **5Dd**, and **5Db** with the R_f value of 0.5, 0.4, 0.3, and 0.2 (EtOAc:CH_2Cl_2:Hex = 1:10:5), respectively. Compounds **5Dd** and **5Db** could not be cleanly separated, thus the mixture of **5Dd** and **5Db** was hydrolyzed in 80% aq AcOH (100 °C, 3h) and chromatographed (MeOH:CH_2Cl_2 = 1:20) on silica gel to give meso compound 4,5,6-tri-*O*-benzoyl-*myo*-inositol[16c] and compound **6Dd**, respectively. Compound **6Dd** could also be obtained by direct hydrolysis of compound **5Db**. Each isomer (**5Da** and **5Dc**) was hydrolyzed in 80% aq AcOH (100 °C, 1 h) and concentrated to give the corresponding IBz_3 products **6Dc** and **6De** in quantitative yield. Compounds **6Lc**, **6Ld**, and **6Le** were similarly prepared from a mixture of **5La/5Lb**.

D- and L-1,4,5-Tri-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (5Dc and 5Lc). 5Dc: R_f 0.4 (EtOAc:CH_2Cl_2:Hex = 1:10:5); mp 170−171 °C; $[\alpha]_D^{25}$ −51.3 (*c* 0.98, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.37, 1.57 (2s, 6H, C*Me*$_2$), 3.09 (d, *J* = 4.1 Hz, 1H, O*H*-6), 4.43 (dt, *J* = 4.2, 7.3 Hz, 1H, H-6), 4.57 (app. t, 6.7 Hz, 1H, H-3), 4.78 (dd, *J* = 3.8, 6.1 Hz, 1H, H-2), 5.23 (dd, *J* = 7.0, 9.8 Hz, 1H, H-5), 5.58 (dd, *J* = 3.7, 7.7 Hz, 1H, H-1), 5.98 (dd, *J* = 7.2, 9.8 Hz, 1H, H-4), 7.26−8.18 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 25.7, 27.4 (C*Me*$_2$), 71.7, 72.2, 72.9, 73.7, 76.6, 76.7 (inositol ring carbons), 111.4 (*C*Me$_2$), 128.8−133.9 (3Ph), 166.3, 166.6, 167.5 (3*C*OPh); MS (FAB) *m*/*z* 533 (M^+ + H). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.34; H, 5.42. **5Lc**: mp 170−171 °C; $[\alpha]_D^{25}$ +53.6 (*c* 0.77, CH_2Cl_2); identical ^{1}H NMR and ^{13}C NMR data to those of **5Dc**.

D- and L-1,4,6-Tri-*O*-benzoyl-*myo*-inositol (6Dc and 6Lc). 6Dc: R_f 0.56 (EtOAc:Hex = 2:1); mp 111−112 °C; $[\alpha]_D^{25}$ −46.7 (*c* 1.01, EtOAc); ^{1}H NMR (CD_3OD) δ 3.96−4.12 (m, 2H, H-3 & H-5), 4.36 (app. t, *J* = 2.5 Hz, 1H, H-2), 5.31 (dd, *J* = 2.5, 10.4 Hz, 1H, H-1), 5.66 (app. t, *J* = 9.8 Hz, 1H, H-4), 5.96 (app. t, *J* = 10.0 Hz, 1H, H-6), 7.34−8.13 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 70.2, 70.8, 71.2, 73.3, 73.5, 75.9 (inositol ring carbons), 128.4−133.4 (3Ph), 166.3, 166.6, 166.9 (3*C*OPh); MS (FAB) *m*/*z* 515 (M^+ + Na), 493 (M^+ + H). Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 65.56; H, 5.06. **6Lc**: mp 112−113 °C; $[\alpha]_D^{25}$ +46.3 (*c* 1.07, EtOAc); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **6Dc**.

D- and L-1,5,6-Tri-*O*-benzoyl-*myo*-inositol (6Dd and 6Ld). 6Dd: R_f 0.39 (EtOAc:Hex = 2:1, 2 times); mp 197−198 °C; $[\alpha]_D^{25}$ +5.53 (*c* 1.11, EtOAc); ^{1}H NMR (CD_3OD) δ 3.79 (dd, *J* = 2.7, 9.7 Hz, 1H, H-3), 4.15 (app. t, *J* = 9.7 Hz, 1H, H-4), 4.38 (app. t, *J* = 2.6 Hz, 1H, H-2), 5.38 (dd, *J* = 2.6, 10.5 Hz, 1H, H-1), 5.52 (app. t, *J* = 9.8 Hz, 1H, H-5), 6.09 (app. t, *J* = 10.2 Hz, 1H, H-6), 7.24−7.96 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 68.9, 69.7 (2C), 70.3, 71.7, 73.0 (inositol ring carbons), 126.8−131.9 (3Ph), 164.6, 164.7, 164.9 (3*C*OPh); MS (FAB) *m*/*z* 515 (M^+ + Na), 493 (M^+ + H). Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 65.47; H, 4.97. **6Ld**: mp 201−202 °C; $[\alpha]_D^{25}$ −3.96 (*c* 1.21, EtOAc) [lit.[24] $[\alpha]_D$ +10.2 (*c* 2.8, $CHCl_3$)]; identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **6Dd**.

D- and L-1,4,5-Tri-*O*-benzoyl-*myo*-inositol (6De and 6Le). 6De: R_f 0.6 (EtOAc:Hex = 2:1); mp 118−119 °C; $[\alpha]_D^{25}$ −49.8 (*c* 0.97, EtOAc); ^{1}H NMR (CD_3OD) δ 4.06 (dd, *J* = 2.5, 10.0 Hz, 1H, H-3), 4.35 (app. t, *J* = 2.5 Hz, 1H, H-2), 4.45 (app. t, *J* = 9.9 Hz, 1H, H-6), 5.16 (dd, *J* = 2.4, 10.2 Hz, 1H, H-1), 5.50 (app. t, *J* = 9.7 Hz, 1H, H-5), 5.80 (app. t, *J* = 9.9 Hz, 1H, H-4), 7.34−8.17 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 67.6, 68.5, 69.2, 72.1, 73.2, 73.5 (inositol ring carbons), 126.8−131.8 (3Ph), 164.9, 165.0, 165.1 (3*C*OPh); MS (FAB) *m*/*z* 515 (M^+ + Na), 493 (M^+ + H). Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 65.52; H, 5.06. **6Le**: mp 117−119 °C; $[\alpha]_D^{25}$ +50.0 (*c* 1.04, EtOAc); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **6De**.

D- and L-1,2,6-Tri-*O*-benzoyl-*myo*-inositol (6Da and 6La) and D- and L-1,3,4-Tri-*O*-benzoyl-*myo*-inositol (6Db and 6Lb). To a solution of compound **4Da** (2.50 g, 6.44 mmol) and TSA (300 mg) in dry DMF (25 mL) at room temperature was added trimethyl orthobenzoate (16 mL, 94 mmol). After being stirred for 18 h, the reaction mixture was treated with 80% aq AcOH (10 mL) for 2 h at room temperature, diluted with EtOAc, and then washed with aq $NaHCO_3$ and water. The organic layer was dried ($MgSO_4$), evaporated, and chromatographed to provide **6Da** (2.09 g, 66%) and **6Lb** (349 mg, 11%). A similar reaction with **4La** provided **6La** and **6Db**. **6Da**: oil; R_f 0.17 (MeOH:CH_2Cl_2 = 1:20); $[\alpha]_D^{25}$ −151.9 (*c* 2.03, $CHCl_3$); ^{1}H NMR (CD_3OD) δ 3.81 (app. t, *J* = 9.0 Hz, 1H, H-5), 3.92−4.03 (m, 2H, H-3 & H-4), 5.48 (dd, *J* = 2.7, 10.5 Hz, 1H, H-1), 5.87 (app. t, *J* = 10.0 Hz, 1H, H-6), 5.96 (app. t, *J* = 2.5 Hz, 1H, H-2), 7.21−8.29 (m, 15H, Ph); ^{13}C NMR (CD_3OD) δ 68.6, 69.9, 71.1, 71.5, 71.8, 72.3 (inositol ring carbons), 126.9−132.0 (3Ph), 164.3, 164.9, 165.1 (3*C*OPh); HRMS (FAB) *m*/*z* calcd for $C_{27}H_{25}O_9$ 493.1499, found 493.1494 (M^+ + H). **6La**: oil; $[\alpha]_D^{25}$ +154.8 (*c* 1.71, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **6Da**. **6Db**: R_f 0.28 (MeOH:CH_2Cl_2 = 1:20); mp 195−196 °C; $[\alpha]_D^{25}$ +46.1 (*c* 1.00, MeOH); ^{1}H NMR (CD_3OD) δ 3.81 (app. t, *J* = 9.4 Hz, 1H, H-5), 4.23 (app. t, *J* = 9.7 Hz, 1H, H-6), 4.54 (app. t, *J* = 2.5 Hz, 1H, H-2), 5.14 (dd, *J* = 2.6, 10.2 Hz, 1H, H-1), 5.35 (dd, *J* = 2.5, 10.4 Hz, 1H, H-3), 5.90 (app. t, *J* = 10.0 Hz, 1H, H-4), 7.32−8.17 (m, 15H, Ph); ^{13}C NMR (CD_3OD) δ 66.6, 69.5, 71.6 (3C), 73.1 (inositol ring carbons), 126.8−131.8 (3Ph), 164.6, 165.1 (2C) (3*C*OPh); MS (FAB) *m*/*z* 493 (M^+ + H); Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 65.60; H, 4.98. **6Lb**: mp 195−196 °C (lit.[14e] mp 184−194 °C); $[\alpha]_D^{25}$ −46.2 (*c* 1.07, MeOH) [lit.[14e] $[\alpha]_{546}$ 546−38.3 (dioxane)]; Identical R_f, ^{1}H NMR and ^{13}C NMR data to those of **6Db**.

D- and L-1,2,6-Tri-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (7Da and 7La) and D- and L-1,2,6-Tri-*O*-benzoyl-4,5-*O*-isopropylidene-*myo*-inositol (8Da and 8La). To a

(24) Bruzik, K. S.; Tsai, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 6361−6374.

solution of compound **6Da** (1.80 g, 3.65 mmol) and TSA (150 mg) in THF (50 mL) at room temperature was added 2-methoxypropene (1.1 mL, 11.1 mmol) in portions with vigorous stirring. After 5 h, the reaction mixture was quenched with TEA (1 mL), poured into saturated aq $NaHCO_3$ solution, and extracted with EtOAc. The extract was dried ($MgSO_4$), evaporated, and chromatographed on silica gel (EtOAc:CH_2Cl_2:Hex = 1:5:5) to give **7Da** (1.13 g, 58%) and **8Da** (583 mg, 30%). Compounds **7La** and **8La** were similarly prepared from **6La**. 7**Da**: R_f 0.5 (EtOAc:CH_2Cl_2 = 1:10); mp 205−206 °C; $[\alpha]_D^{25}$ −184.0 (*c* 1.05, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.42, 1.51 (2s, 6H, C*Me*$_2$), 2.85 (d, *J* = 4.4 Hz, 1H, O*H*-5), 3.92 (dd, *J* = 2.5, 9.3 Hz, 1H, H-3), 4.21 (ddd, *J* = 4.4, 8.7, 10.0 Hz, 1H, H-5), 4.37 (dd, *J* = 9.3, 10.0 Hz, 1H, H-4), 5.61 (dd, *J* = 3.1, 10.0 Hz, 1H, H-1), 5.82 (dd, *J* = 8.7, 10.0 Hz, 1H, H-6), 6.19 (dd, *J* = 2.5, 3.1 Hz, 1H, H-2), 7.22−8.09 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 27.1, 27.6 (C*Me*$_2$), 67.5, 72.2, 72.5, 75.6, 75.9, 77.2 (inositol ring carbons), 134.0 (*C*Me$_2$), 129.0−134.2 (3Ph), 166.0, 166.1, 167.2 (3*C*OPh); MS (FAB) *m*/*z* 533 (M^+ + H). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.51; H, 5.28. **7La**: mp 203−204 °C; $[\alpha]_D^{25}$ +185.2 (*c* 0.54, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **7Da**. **8Da**: R_f 0.3 (EtOAc:CH_2Cl_2 =1:10); mp 113−114 °C; $[\alpha]_D^{25}$ −138.1 (*c* 0.54, EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.51, 1.56 (2s, 6H, C*Me*$_2$), 2.46 (d, *J* = 4.8 Hz, 1H, O*H*-3), 3.86 (dd, *J* = 9.3, 10.3 Hz, 1H, H-5), 4.21 (app. t, *J* = 9.8 Hz, 1H, H-4), 4.35 (ddd, *J* = 3.4, 4.7, 10.4 Hz, 1H, H-3), 5.52 (dd, *J* = 3.4, 9.6 Hz, 1H, H-1), 6.04 (app. t, *J* = 3.3 Hz, 1H, H-2), 6.04 (dd, *J* = 9.6, 10.3 Hz, 1H, H-6), 7.24−8.06 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 27.2, 27.3 (C*Me*$_2$), 69.6, 71.1, 72.5, 73.0, 76.8, 78.3 (inositol ring carbons), 113.4 (*C*Me$_2$), 128.8−134.1 (3Ph), 165.9, 166.0, 166.7 (3*C*OPh); MS (FAB) *m*/*z* 533 (M^+ + H). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.64; H, 5.32. **8La**: mp 113−114 °C; $[\alpha]_D^{25}$ +136.0 (*c* 0.99, EtOAc); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **8Da**.

Generation and Separation of IBz_3 Regioisomers from 7Da and 7La. Compound **7Da** (850 mg) in a solvent mixture of pyridine−water (6:4, 100 mL) was heated at 100 °C for 3 h. The solution was cooled and concentrated under reduced pressure. The serial operation of adding acetone to the reaction mixture followed by evaporation of the solvents was repeated twice. The crude mixture, which contained almost equal amounts of **7Da**, **7Db**, **7Dc**, and **7Dd**, was concentrated and chromatographed on silica gel (EtOAc:Hex = 1:4 → 1:2 gradient) to give two fractions. The first fraction contained **7Db** and **7Dc**, the second **7Da** and **7Dd** with the R_f values of 0.4 and 0.2 (EtOAc:Hex = 1:2), respectively. Each fraction was treated with 80% aq AcOH (100 °C, 1 h) to give (**6Df** and **6Dd**) and (**6Da** and **6Lg**) mixtures, which were separately chromatographed (EtOAc−CH_2Cl_2 gradient) to give four IBz_3 isomers with R_f values of 0.6, 0.4, 0.35, and 0.5 for **6Df**, **6Dd, 6Da**, and **6Lg** (EtOAc:CH_2Cl_2 = 1:2, 3 times). Compounds **6Lf**, **6Ld**, **6La**, and **6Dg** were similarly prepared from **7La**.

D- and L-1,2,5-Tri-*O*-benzoyl-*myo*-inositol (6Df and 6Lf). 6Df: oil; $[\alpha]_D^{25}$ −63.6 (*c* 2.75, $CHCl_3$); ^{1}H NMR (CD_3OD) δ 4.02 (dd, *J* = 2.9, 9.9 Hz, 1H, H-3), 4.17 (app. t, *J* = 9.8 Hz, 1H, H-4), 4.36 (app. t, *J* = 10.0 Hz, 1H, H-6), 5.33−5.40 (m, 2H, H-1 & H-5), 5.97 (app. t, *J* = 2.8 Hz, 1H, H-2), 7.31−8.18 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 68.4, 68.7, 70.3, 71.0, 71.7, 75.3 (inositol ring carbons), 126.9−132.1 (3Ph), 164.7, 164.9, 165.4 (3*C*OPh); HRMS (FAB) *m*/*z* calcd for $C_{27}H_{25}O_9$ 493.1499, found 493.1414 (M^+ + H). **6Lf**: oil; $[\alpha]_D^{25}$ +62.1 (*c* 1.75, $CHCl_3$); identical ^{1}H NMR and ^{13}C NMR data to those of **6Df**.

D- and L-2,4,5-Tri-*O*-benzoyl-*myo*-inositol (6Dg and 6Lg). 6Dg: mp 123−124 °C; $[\alpha]_D^{25}$ +9.40 (*c* 1.03, EtOAc); ^{1}H NMR (CD_3OD) δ 3.93 (dd, *J* = 2.9, 9.8 Hz, 1H, H-1), 4.14 (app. t, *J* = 9.7 Hz, 1H, H-6), 4.22 (dd, *J* = 2.9, 10.2 Hz, 1H, H-3), 5.47 (app. t, *J* = 9.8, 1H, H-5), 5.8 (app. t, *J* = 10.1 Hz, 1H, H-4), 5.85 (app. t, *J* = 2.9 Hz, 1H, H-2), 7.35−8.16 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 68.8, 70.8, 71.8, 73.9, 74.8, 75.3 (inositol ring carbons), 128.4−133.3 (3Ph), 166.6, 166.7, 166.8 (3*C*OPh); MS (FAB) *m*/*z* 515 (M^+ + Na), 493 (M^+ + H). Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 65.54; H, 5.03. **6Lg**: mp 122−123 °C; $[\alpha]_D^{25}$ −9.74 (*c* 1.00, EtOAc) [lit.[24] $[\alpha]_D$ −8.6 (*c* 2.5, $CHCl_3$)]; identical ^{1}H NMR and ^{13}C NMR data to those of **6Dg**.

Generation and Separation of IBz_3 Regioisomers from 8Da and 8La. Compound **8Da** (550 mg) in pyridine−water (6:4, 100 mL) was heated at 100 °C, for 3 h. The solution was cooled and concentrated under reduced pressure. The serial operation of adding acetone to the reaction mixture followed by evaporation of the solvents was repeated twice. The crude mixture which contained 4 regioisomers with the R_f value of 0.6, 0.5, 0.3, and 0.2 was concentrated and chromatographed on silica gel (EtOAc:CH_2Cl_2:Hex = 1:2:6 → 1:10:2 gradient) to give two fractions. The first fraction, which contained **8Db** and **8Dc**, was treated with 80% aq AcOH (100 °C, 3 h), concentrated, and chromatographed on silica gel to give **6Lb** and **6Lh**, respectively. **6Lb** was also obtained from **4Da**. The second fraction was the mixture of **8Dd** and **8Da**. Similarly, **6Db** and **6Dh** were prepared from **8La**.

D- and L-1,2,4-Tri-*O*-benzoyl-*myo*-inositol (6Dh and 6Lh). 6Dh: R_f 0.4 (EtOAc:CH_2Cl_2 = 1:3); mp 187−189 °C (lit.[14e] mp 186−190 °C); $[\alpha]_D^{25}$ −5.3 (*c* 0.8, THF) [lit.[14e] $[\alpha]_{546}$ −6.5 (THF)]; ^{1}H NMR (CD_3OD) δ 3.77 (dd, *J* = 9.2, 9.8 Hz, 1H, H-5), 4.17 (dd, *J* = 9.2, 10.5 Hz, 1H, H-6), 4.20 (dd, *J* = 2.6, 9.8 Hz, 1H, H-3), 5.23 (dd, *J* = 2.6, 10.5 Hz, 1H, H-1), 5.66 (app. t, *J* = 9.8 Hz, 1H, H-4), 5.93 (app. t, *J* = 2.6 Hz, 1H, H-2), 7.33−8.13 (m, 15H, 3Ph); ^{13}C NMR (CD_3OD) δ 69.8, 73.0, 74.3, 74.5, 74.7, 77.1 (inositol ring carbons), 129.7−134.8 (3Ph), 167.6, 167.7, 168.3 (3*C*OPh); MS (FAB) *m*/*z* 515 (M^+ + Na), 493 (M^+ + H). **6Lh**: mp 186−187 °C (lit.[14e] mp 188−191 °C); $[\alpha]_D^{25}$ +5.9 (*c* 1.06, THF) [lit. $[\alpha]_{546}$ +5.4 (THF),[14e] $[\alpha]_D^{20}$ +5.9 (*c* 2.5, THF)[24]]; identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **6Dh**.

Phosphorylation of IBz_3 Regioisomers (6Da−6Dh and 6La−6Lh): General Procedure. To a solution of each IBz_3 regioisomer (0.20 mmol) in DMF (5 mL) at −42 °C were added dropwise *N*,*N*-diisopropylethylamine (1 mL, 5.7 mmol) and then diethyl chlorophosphite (0.3 mL, 2.1 mmol) with vigorous stirring. After 20 min, the reaction mixture was allowed to slowly warm to room temperature and stirred for an additional 12 h. The mixture was cooled in an ice bath, and sodium phosphate buffer (1 N, pH 7, 5 mL) and excess 30% H_2O_2 (5 mL) were added. After being stirred overnight at room temperature, the mixture was diluted with EtOAc, and washed with aq $NaHSO_4$, aq $NaHCO_3$, and brine. The organic layer was separated, dried ($MgSO_4$), concentrated, and chromatographed to give IP'_3Bz_3 regioisomers (**9La**−**9Lh** and **6Da**−**6Dh**) in 65−77% yields.

D- and L-2,3,4-Tri-*O*-benzoyl-*myo*-inositol 1,5,6-tris-(diethyl phosphate) (9Da and 9La) were prepared from compounds **6La** and **6Da**, respectively. **9Da**: oil; $[\alpha]_D^{25}$ +75.8 (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.78−1.37 (m, 18H, 6CH_2CH_3), 3.54−4.32 (m, 12H, 6CH_2CH_3), 4.69 (dt, *J* = 2.8, 8.9 Hz, 1H, H-1), 4.89 (q, *J* = 9.3 Hz, 1H, H-5), 5.11 (q, *J* = 9.5 Hz, 1H, H-6), 5.42 (dd, *J* = 2.8, 10.4 Hz, 1H, H-3), 6.04 (app. t, *J* = 10.0 Hz, 1H, H-4), 6.28 (app. t, *J* = 2.8 Hz, 1H, H-2), 7.25−8.05 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.7−16.4 (6CH_2CH_3), 64.2−65.1 (6CH_2CH_3), 69.3, 70.1, 70.4, 73.7, 76.3, 76.6 (inositol ring carbons), 126.3−134.0 (3Ph), 165.4, 165.6, 165.7 (3*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.02, 0.07, 0.83; HRMS (FAB) *m*/*z* calcd for $C_{39}H_{52}O_{18}P_3$ 901.2367, found 901.2373 (M^+ + H). **9La**: oil; $[\alpha]_D^{25}$ −71.1 (*c* 1.89, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Da**.

D- and L-1,3,6-Tri-*O*-benzoyl-*myo*-inositol 2,4,5-tris-(diethyl phosphate) (9Db and 9Lb) were prepared from compounds **6Lb** and **6Db**, respectively. **9Db**: oil; $[\alpha]_D^{25}$ −10.0 (*c* 0.98, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.84−1.31 (m, 18H, 6CH_2CH_3), 3.57−4.23 (m, 12H, 6CH_2CH_3), 4.94 (app. q, *J* = 9.2 Hz, 1H, H-5), 5.22 (app. q, *J* = 9.3 Hz, 1H, H-4), 5.34−5.40 (m, 2H, H-1 & H-2), 5.44 (br d, *J* = 10.1 Hz, 1H, H-3), 6.08 (app. t, *J* = 10.0 Hz, 1H, H-6), 7.28−8.26 (m, 15H, 3Ph);

^{13}C NMR ($CDCl_3$) δ 15.7−16.4 ($6CH_2\mathit{C}H_3$), 64.2−64.8 ($6\mathit{C}H_2CH_3$), 70.1, 70.5, 70.6, 73.8, 76.0, 77.1 (inositol ring carbons), 128.7−133.9 (3Ph), 165.7, 165.8, 165.9 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.51, 0.52, 1.16; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Lb**: oil; $[\alpha]_D^{25}$ +10.6 (*c* 1.92, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Db**.

D- and L-3,4,6-Tri-*O*-benzoyl-*myo*-inositol 1,2,5-tris(diethyl phosphate) (9Dc and 9Lc) were prepared from compounds **6Lc** and **6Dc**, respectively. **9Dc**: oil; $[\alpha]_D^{25}$ +11.9 (*c* 1.54, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.76−1.37 (m, 18H, $6CH_2C\mathit{H}_3$), 3.54−3.82 (m, 12H, $6C\mathit{H}_2CH_3$), 4.88 (br t, *J* = 10.1 Hz, 1H, H-1), 5.06 (app. q, *J* = 9.5 Hz, 1H, H-5), 5.34 (br d, *J* = 10.5 Hz, 1H, H-3), 5.39 (br d, *J* = 9.1 Hz, 1H, H-2), 6.02 (app. t, *J* = 10.0 Hz, 1H, H-6), 6.13 (app. t, *J* = 10.1 Hz, 1H, H-4), 7.30−8.21 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.7−16.4 ($6CH_2\mathit{C}H_3$), 64.2−64.9 ($6\mathit{C}H_2CH_3$), 70.3, 70.5, 70.9, 73.9, 75.5, 76.0 (inositol ring carbons), 128.7−133.8 (3Ph), 165.7, 165.9, 166.0 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.23, 0.99, 1.19; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Lc**: oil; $[\alpha]_D^{25}$ −12.7 (*c* 1.62, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Dc**.

D- and L-3,4,5-Tri-*O*-benzoyl-*myo*-inositol 1,2,6-tris(diethyl phosphate) (9Dd and 9Ld) were prepared from compounds **6Ld** and **6Dd**, respectively. **9Dd**: oil; $[\alpha]_D^{25}$ −8.13 (*c* 2.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.84−1.41 (m, 18H, $6CH_2C\mathit{H}_3$), 3.63−4.31 (m, 12H, $6C\mathit{H}_2CH_3$), 4.70 (br t, *J* = 9.5 Hz, 1H, H-1), 5.22 (app. q, *J* = 9.6 Hz, 1H, H-6), 5.39 (br d, *J* = 10.5 Hz, 1H, H-3), 5.50 (br d, *J* = 9.1 Hz, 1H, H-2), 5.78 (app. t, *J* = 9.8 Hz, 1H, H-5), 6.09 (app. t, *J* = 10.3 Hz, 1H, H-4), 7.28−8.05 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 16.0−16.8 ($6CH_2\mathit{C}H_3$), 64.5−65.6 ($6\mathit{C}H_2CH_3$), 70.2, 70.9, 71.7, 74.7, 75.4, 75.8 (inositol ring carbons), 128.9−134.0 (3Ph), 166.1, 166.2 (2C) ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.21, 0.55, 1.26; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Ld**: oil; $[\alpha]_D^{25}$ +6.04 (*c* 0.86, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Dd**.

D- and L-3,5,6-Tri-*O*-benzoyl-*myo*-inositol 1,2,4-tris(diethyl phosphate) (9De and 9Le) were prepared from compounds **6Le** and **6De**, respectively. **9De**: oil; $[\alpha]_D^{25}$ +19.2 (*c* 1.64, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.74−1.37 (m, 18H, $6CH_2C\mathit{H}_3$), 3.44−4.21 (m, 12H, $6C\mathit{H}_2CH_3$), 4.96 (app. t, *J* = 1.9, 10.1 Hz, 1H, H-1), 5.31−5.43 (m, 3H, H-2, H-3 & H-4), 5.75 (app. t, *J* = 9.5 Hz, 1H, H-5), 5.99 (app. t, *J* = 10.1 Hz, 1H, H-6), 7.33−8.24 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.7−16.4 ($6CH_2\mathit{C}H_3$), 64.1−64.9 ($6\mathit{C}H_2CH_3$), 70.4, 70.9, 71.5, 73.9, 75.0, 75.7 (inositol ring carbons), 128.7−133.9 (3Ph), 165.6, 165.7, 165.8 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.39, 1.07, 1.21; HRMS (FAB) *m*/*z* calcd for $C_{39}H_{52}O_{18}P_3$ 901.2367, found 901.2352 ($M^+ + H$). **9Le**: oil; $[\alpha]_D^{25}$ −19.1 (*c* 1.40, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Dd**.

D- and L-2,3,5-Tri-*O*-benzoyl-*myo*-inositol 1,4,6-tris(diethyl phosphate) (9Df and 9Lf) were prepared from compounds **6Lf** and **6Df**, respectively. **9Df**: oil; $[\alpha]_D^{25}$ +38.0 (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.72−1.30 (m, 18H, $6CH_2C\mathit{H}_3$), 3.48−4.15 (m, 12H, $6C\mathit{H}_2CH_3$), 4.76 (ddd, *J* = 3.0, 7.8, 10.2 Hz, 1H, H-1), 5.16−5.27 (m, 2H, H-4 & H-6), 5.47 (dd, *J* = 3.0, 10.2 Hz, 1H, H-3), 5.67 (app. t, *J* = 9.9 Hz, 1H, H-5), 6.25 (app. t, *J* = 2.9 Hz, 1H, H-2), 7.35−8.27 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.8−16.6 ($6CH_2\mathit{C}H_3$), 64.3−65.4 ($6\mathit{C}H_2CH_3$), 69.6, 70.8, 71.9, 74.1, 75.4, 76.0 (inositol ring carbons), 128.9−134.2 (3Ph), 165.7, 165.8, 166.1 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.22, 0.86, 1.03; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Lf**: oil; $[\alpha]_D^{25}$ −42.3 (*c* 1.77, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Df**.

D- and L-2,5,6-Tri-*O*-benzoyl-*myo*-inositol 1,3,4-tris(diethyl phosphate) (9Dg and 9Lg) were prepared from compounds **6Lg** and **6Dg**, respectively. **9Dg**: oil; $[\alpha]_D^{25}$ −2.53 (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.70−1.27 (m, 18H, $6CH_2C\mathit{H}_3$), 3.56−4.12 (m, 12H, $6C\mathit{H}_2CH_3$), 4.64 (dt, *J* = 2.7, 9.2 Hz, 1H, H-3), 4.91 (dt, *J* = 2.9, 9.99 Hz, 1H, H-1), 5.14 (q, *J* = 9.5 Hz, 1H, H-4), 5.61 (app. t, *J* = 9.9 Hz, 1H, H-5), 5.91 (app. t, *J* = 10.2 Hz, 1H, H-6), 6.25 (app. t, *J* = 2.7 Hz, 1H, H-2), 7.27−8.09 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.9−16.7 ($6CH_2\mathit{C}H_3$), 64.5−65.4 ($6\mathit{C}H_2CH_3$), 71.0 (2C), 71.5, 73.9, 74.3, 76.1 (inositol ring carbons), 128.9−134.2 (3Ph), 165.6, 165.9, 166.1 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.44, 0.93, 0.97; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Lg**: oil; $[\alpha]_D^{25}$ +2.59 (*c* 1.02, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Dg**.

D- and L-2,3,6-Tri-*O*-benzoyl-*myo*-inositol 1,4,5-tris(diethyl phosphate) (9Dh and 9Lh) were prepared from compounds **6Lh** and **6Dh**, respectively. **9Dh**: oil; $[\alpha]_D^{25}$ +15.3 (*c* 0.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.77−1.26 (m, 18H, $6CH_2C\mathit{H}_3$), 3.56−4.20 (m, 12H, $6C\mathit{H}_2CH_3$), 4.87 (app. q, *J* = 9.4 Hz, 1H, H-4), 4.93 (ddd, *J* = 2.9, 9.8, 10.1 Hz, 1H, H-1), 5.16 (app. q, *J* = 9.3 Hz, 1H, H-5), 5.47 (dd, *J* = 2.9, 10.1 Hz, 1H, H-3), 6.04 (app. t, *J* = 10.0 Hz, 1H, H-6), 6.12 (app. t, *J* = 2.9 Hz, 1H, H-2), 7.33−8.21 (m, 15H, 3Ph); ^{13}C NMR ($CDCl_3$) δ 15.9−16.6 ($6CH_2\mathit{C}H_3$), 64.4−65.1 ($6\mathit{C}H_2CH_3$), 70.2, 70.5, 71.2, 73.6, 76.5, 77.1 (inositol ring carbons), 128.9−134.3 (3Ph), 165.7, 165.9, 166.1 ($3\mathit{C}OPh$); ^{31}P NMR ($CDCl_3$) δ 0.29, 0.72, 0.90; MS (FAB) *m*/*z* 901 ($M^+ + H$). **9Lh**: oil; $[\alpha]_D^{25}$ −14.7 (*c* 1.61, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **9Dh**.

Preparation of Sodium Salts of *myo*-Inositol Trisphosphate (10Da−10Dh and 10La−10Lh): General Procedure. To each compound of **9Da**-−**Dh** and **9La**−**9Lh** (60 mg, 0.066 mmol) in CH_2Cl_2 (1 mL) at room temperature was added excess bromotrimethylsilane (0.5 mL), and the solution was stirred overnight. The solvent and excess reagent were evaporated and the residue was redissolved in MeOH (3 mL), and then treated with drops of water at 0 °C. After standing at room temperature for 10 min, the reaction mixture was evaporated to dryness, treated with 1 M LiOH (3 mL), and stirred at 80 °C for 3 h. The basic solution was cooled and loaded on Dowex 50WX8-100 (H^+ form) and eluted with water. The acidic effluent was collected, washed with CH_2Cl_2 three times, and lyophilized to dryness. The residue was redissolved in a small amount of water (1 mL) and pH was adjusted to 10 with NaOH and lyophilized again to give sodium salts of *myo*-inositol trisphosphate **10Da**−**10Dh** and **10La**−**10Lh** in approximately 90% yields.

D- and L-*myo*-Inositol 1,5,6-trisphosphate sodium salt (10Da and 10La) were prepared from compounds **9Da** and **9La**, respectively. **10Da**: $[\alpha]_D^{25}$ −2.57 (*c* 1.01, H_2O) [lit. $[\alpha]_D^{20}$ +2.2 (*c* 2.3, H_2O, free acid),[14v] $[\alpha]_D^{20}$ −2.8 (*c* 1.43, H_2O, sodium salt)[14q]; ^{1}H NMR (D_2O, pH 10) δ 3.63 (dd, *J* = 3.4, 8.4 Hz, 1H, H-3), 3.86−3.92 (m, 2H, H-4 & H-5), 3.98 (br t, *J* = 6.8 Hz, 1H, H-5), 4.33 (br q, *J* = 8.9 Hz, 1H, H-6), 4.45 (br s, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 70.3, 71.6, 73.5, 74.4 (2C), 77.3; ^{31}P NMR (D_2O, pH 10) δ 6.30, 6.74, 7.24. **10La**: $[\alpha]_D^{25}$ +4.56 (*c* 0.95, H_2O) [lit.[14v] $[\alpha]_D^{20}$ −4.6 (*c* 1.4, H_2O, free acid)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Da**.

D- and L-*myo*-Inositol 2,4,5-trisphosphate sodium salt (10Db and 10Lb) were prepared from compounds **9Db** and **9Lb**, respectively. **10Db**: $[\alpha]_D^{25}$ −9.59 (*c* 1.45, H_2O) [lit.[14h] $[\alpha]_{546}$ −8.05 (H_2O, cyclohexylammonium salt)]; ^{1}H NMR (D_2O, pH 10) δ 3.46 (dd, *J* = 1.9, 9.8 Hz, 1H, H-1), 3.69 (dt, *J* = 2.4, 9.7 Hz, 1H, H-3), 3.80 (q, *J* = 8.3 Hz, 1H, H-6), 3.92 (app. t, *J* = 9.3 Hz, 1H, H-5), 4.19 (q, *J* = 8.7 Hz, 1H, H-4), 4.43 (br d, *J* = 7.3 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 72.1, 72.3, 74.0, 75.0, 75.6, 77.8; ^{31}P NMR (D_2O, pH 10) δ 7.28, 7.46, 7.60. **10Lb**: $[\alpha]_D^{25}$ +12.0 (*c* = 0.96, H_2O) [lit.[14h] $[\alpha]_{546}$ +9.5 (H_2O, cyclohexylammonium salt)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Db**.

D- and L-*myo*-Inositol 1,2,5-trisphosphate sodium salt (10Dc and 10Lc) were prepared from compounds **9Dc** and **9Lc**, respectively. **10Dc**: $[\alpha]_D^{25}$ +5.94 (*c* 1.62, H_2O); ^{1}H NMR (D_2O, pH 10) δ 3.51 (br d, *J* = 9.6 Hz, 1H, H-3), 3.77−3.94 (m, 3H, H-4, H-5 & H-6), 4.01 (br t, *J* = 9.4 Hz, 1H, H-1), 4.65 (br d, *J* = 7.2 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 72.2, 72.4,

73.8 (2C), 75.4, 79.0; ^{31}P NMR (D_2O, pH 10) δ 7.02, 7.28, 7.48. **10Lc**: $[\alpha]_D^{25}$ −6.41 (*c* 1.58, H_2O); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Dc**.

D- and L-*myo*-Inositol 1,2,6-trisphosphate sodium salt (10Dd and 10Ld) were prepared from compounds **9Dd** and **9Ld**, respectively. **10Dd**: $[\alpha]_D^{25}$ −16.5 (*c* 1.47, H_2O) [lit. $[\alpha]_D^{25}$ −19.5 (c 1.1, H_2O, free acid),[14r] $[\alpha]_D^{29}$ −16.9 (c 0.56, H_2O, lithium salt)[14t]; ^{1}H NMR (D_2O, pH 10) δ 3.46 (br q, *J* = 10.4 Hz, 2H, H-3 & H-5), 3.82 (app. t, *J* = 9.6 Hz, 1H, H-4), 3.91 (br t, *J* = 9.7 Hz, 1H, H-1), 4.21 (q, *J* = 8.6 Hz, 1H, H-6), 4.66 (br d, *J* = 5.9 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 72.5, 72.8, 73.9, 75.9 (3C); ^{31}P NMR (D_2O, pH 10) δ 7.04, 7.16, 7.80. **10Ld**: $[\alpha]_D^{25}$ +15.9 (*c* 0.99, H_2O); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Dd**.

D- and L-*myo*-Inositol 1,2,4-trisphosphate sodium salt (10De and 10Le) were prepared from compounds **9De** and **9Le**, respectively. **10De**: $[\alpha]_D^{25}$ +11.5 (*c* 1.51, H_2O); ^{1}H NMR (D_2O, pH 10) δ 3.47 (q, *J* = 8.2 Hz, 2H, H-3 & H-5), 3.83−3.98 (m, 2H, H-1 & H-6), 4.15 (q, *J* = 8.6 Hz, 1H, H-4), 4.52 (br d, *J* = 7.4 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 71.8, 72.9, 73.6, 75.8 (2C), 77.27; ^{31}P NMR (D_2O, pH 10) δ 7.31, 7.34, 7.59. **10Le**: $[\alpha]_D^{25}$ −13.7 (*c* 0.75, H_2O); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10De**.

D- and L-*myo*-Inositol 1,4,6-trisphosphate sodium salt (10Df and 10Lf) were prepared from compounds **9Df** and **9Lf**, respectively. **10Df**: $[\alpha]_D^{25}$ −10.1 (*c* 0.78, H_2O) [lit.[14o] $[\alpha]_D^{20}$ −8.9 (*c* 0.90, H_2O, sodium salt)]; ^{1}H NMR (D_2O, pH 10) δ 3.56 (app. t, *J* = 9.1 Hz, 1H, H-5), 3.70 (dd, *J* = 2.6, 9.6 Hz, 1H, H-3), 3.92 (br t, *J* = 7.5 Hz, 1H, H-1), 4.13−4.26 (m, 2H, H-4 & H-6), 4.36 (br s, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 71.2, 71.8, 73.8, 74.8, 75.7, 76.7; ^{31}P NMR (D_2O, pH 10) δ 6.05, 7.15, 7.66. **10Lf**: $[\alpha]_D^{25}$ +11.2 (*c* 1.14, H_2O) [lit.[14o] $[\alpha]_D^{20}$ +9.4 (*c* 0.85, H_2O, sodium salt)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Df**.

D- and L-*myo*-Inositol 1,3,4-trisphosphate sodium salt (10Dg and 10Lg) were prepared from compounds **9Dg** and **9Lg**, respectively. **10Dg**: $[\alpha]_D^{25}$ +10.4 (*c* 0.59, H_2O) [lit. $[\alpha]_D^{22}$ −6 (*c* 0.5, H_2O, ammonium salt),[14c] $[\alpha]_D$ +13.6 (*c* 2, H_2O, pH 8.2, potasium salt),[14k] $[\alpha]_D^{26}$ +37 (*c* 0.42, H_2O, pH 7.8, triethylammonium salt)[14p]]; ^{1}H NMR (D_2O, pH 10) δ 3.54 (app. t, *J* = 9.0 Hz, 1H, H-5), 3.81 (app. t, *J* = 9.5 Hz, 1H, H-6), 3.95 (m, 2H, H-1 & H-3), 4.16 (q, *J* = 8.5 Hz, 1H, H-4), 4.45 (br s, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 71.4, 72.8, 73.6, 74.1, 75.4 (2C); ^{31}P NMR (D_2O, pH 10) δ 6.11, 6.91, 7.61. **10Lg**: $[\alpha]_D^{25}$ −9.20 (*c* 0.74, H_2O) [lit.[14p] $[\alpha]_D^{26}$ −40 (*c* 0.42, H_2O, pH 7.8, triethylammonium salt)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Dg**.

D- and L-*myo*-Inositol 1,4,5-trisphosphate sodium salt (10Dh and 10Lh) were prepared from compounds **9Dh** and **9Lh**, respectively. **10Dh**: $[\alpha]_D^{25}$ −24.1 (*c* 0.28, H_2O), [lit. $[\alpha]_D^{22}$ −24 (*c* 0.15, H_2O, pH 6.9),[14g] $[\alpha]_D$ −24 (*c* 0.5, H_2O, pH 9.3, potasium salt),[14k] $[\alpha]_D^{24}$ −20 (*c* 0.05, H_2O, pH 9, sodium salt),[14s] $[\alpha]_D^{24}$ −3.19 (*c* 0.26, H_2O, sodium salt)[14w]; ^{1}H NMR (D_2O, pH 10) δ 3.58 (dd, *J* = 2.8, 9.6 Hz, 1H, H-3), 3.66−3.79 (m, 3H, H-1, H-5 & H-6), 4.03 (q, *J* = 8.5 Hz, 1H, H-4), 4.21 (s, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 70.8, 72.0, 72.7, 74.8, 75.3, 77.3; ^{31}P NMR (D_2O, pH 10) δ 5.67, 7.30, 7.40. **10Lh**: $[\alpha]_D^{25}$ +20.1 (*c* 0.74, H_2O), [lit. $[\alpha]_D^{22}$ +27 (*c* 0.15, H_2O, pH 6.4),[14g] $[\alpha]_D^{24}$ +17 (*c* 0.03, H_2O, pH 10, sodium salt)[14s]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **10Dh**.

Generation and Separation of IBz_2 Regioisomers from 3Da and 3La. Compound **3Da** (1.26 g, 2.94 mmol) in pyridine−water (6:4, 50 mL) was heated at 100 °C for 3 h. The reaction mixture was cooled and concentrated under reduced pressure. The serial operation of EtOH addition and evaporation was repeated twice. The oily residue was triturated with CH_2Cl_2 and precipitated solid (**3Dd**, 110 mg) was filtered off. The filtrate was concentrated and chromatographed on silica gel (EtOAc:CH_2Cl_2:Hex = 1:4:5). The first-eluted material was compound **3Df** (120 mg), and the second-eluted fraction contained **3De** (185 mg). The third and fourth-eluted materials could not be cleanly separated but contained compounds **3Dd** and **3Dc** (245 mg). The mixture of **3Dd** and **3Dc** was treated with 80% aq AcOH (100 °C, 3h), concentrated, and chromatographed (MeOH:CH_2Cl_2 = 1:20) on silica gel to give compound **4Dc** and the more polar compound **4Lb**, respectively. The fifth- and sixth-eluted materials were compounds **3Db** (165 mg) and **3Da** (290 mg). Each isomer (**3Da**, **3Db**, **3Dd**, and **3De**) was treated with 80% aq AcOH (100 °C, 3 h) and concentrated to give the corresponding IBz_2 products **4Da**, **4Db**, **4Dc**, and **4Dd** in quantitative yield. Compounds **4La**, **4Lb**, **4Db**, **4Lc**, and **4Ld** were similarly prepared from compound **3La.**

D- and L-4,5-Di-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (3Db and 3Lb). 3Db: oil; R_f 0.23 (EtOAc:CH_2Cl_2 = 1:3); $[\alpha]_D^{25}$ −38.5 (*c* 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.38, 1.65 (2s, 6H, C*Me*$_2$), 3.74 (br s, 1H, O*H*), 4.03−4.08 (m, 2H, H-1 & O*H*), 4.18 (app. t, *J* = 8.7 Hz, 1H, H-6), 4.40 (dd, *J* = 5.6, 7.3 Hz, 1H, H-3), 4.51 (app. t, *J* = 4.6 Hz, 1H, H-2), 5.25 (app. t, *J* = 9.2 Hz, 1H, H-5), 5.73 (dd, *J* = 7.3, 9.8 Hz, 1H, H-4), 7.26−7.96 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 26.1, 27.9 (C*Me*$_2$), 70.8, 72.4, 73.8, 74.8, 75.9, 76.8 (inositol ring carbons), 111.2 (*C*Me$_2$), 128.7−133.7 (2Ph), 166.0, 167.2 (2*C*OPh); HRMS (FAB) *m*/*z* calcd for $C_{23}H_{25}O_8$ 429.1491, found 429.1442 (M^+ + H). **3Lb**: $[\alpha]_D^{25}$ +38.8 (*c* 1.25, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **3Db**.

D- and L-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (3Dd and 3Ld). 3Dd: R_f 0.39 (EtOAc:CH_2Cl_2 = 1:3); mp 231−234 °C; $[\alpha]_D^{25}$ +8.44 (*c* 0.54, $CHCl_3$:MeOH = 5:1); ^{1}H NMR (DMSO-d_6) δ 1.24, 1.45 (2s, 6H, C*Me*$_2$), 3.54 (ddd, *J* = 5.4, 8.5, 10.4 Hz, 1H, H-5), 3.84 (ddd, *J* = 5.1, 8.4, 8.5 Hz, 1H, H-4), 4.44 (dd, *J* = 5.5, 7.9 Hz, 1H, H-1), 4.54 (dd, *J* = 3.9, 5.5 Hz, 1H, H-2), 5.27 (dd, *J* = 3.9, 8.4 Hz, 1H, H-3), 5.35 (dd, *J* = 7.9, 10.4 Hz, 1H, H-6), 5.36 (d, *J* = 5.4 Hz, 1H, O*H*-5), 5.52 (d, *J* = 5.1 Hz, 1H, O*H*-4), 7.53−8.07 (m, 10H, 2Ph); ^{13}C NMR (DMSO-d_6) δ 25.7, 27.3 (C*Me*$_2$), 70.9, 71.2, 72.5, 73.4, 76.0, 76.1 (inositol ring carbons), 109.3 (*C*Me$_2$), 128.5−133.4 (2Ph), 165.0, 165.1 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H); Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.29; H, 5.92. **3Ld**: mp 232−234 °C; $[\alpha]_D^{25}$ −6.82 (*c* 0.52, $CHCl_3$:MeOH = 5:1); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **3Dd**.

D- and L-1,5-Di-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (3De and 3Le). 3De: R_f 0.45 (EtOAc:CH_2Cl_2 = 1:3); mp 85−88 °C; $[\alpha]_D^{25}$ −44.6 (*c* 0.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.49 (2s, 6H, C*Me*$_2$), 3.45 (br s, 1H, O*H*-4), 3.58 (br s, 1H, O*H*-6) 0.4.22−4.36 (m, 3H, H-3, H-4 & H-6), 4.65 (dd, *J* = 3.9, 6.1 Hz, 1H, H-3), 5.14 (dd, *J* = 7.0, 9.0 Hz, 1H, H-5), 5.56 (dd, *J* = 3.9, 7.7 Hz, 1H, H-1), 7.34−8.08 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 25.5, 27.7 (C*Me*$_2$), 71.4, 72.4, 73.2, 73.6, 78.8, 79.1 (inositol ring carbons), 110.8 (*C*Me$_2$), 128.8−133.9 (2Ph), 166.4, 167.9 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.18; H, 5.83. **3Le**: mp 85−88 °C; $[\alpha]_D^{25}$ +44.6 (*c* 0.55, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **3De**.

D- and L-4,6-Di-*O*-benzoyl-2,3-*O*-isopropylidene-*myo*-inositol (3Df and 3Lf). 3Df: R_f 0.58 (EtOAc:CH_2Cl_2 = 1:3); mp 98−100 °C; $[\alpha]_D^{25}$ −15.7 (*c* 0.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.39, 1.64 (2s, 6H, C*Me*$_2$), 2.73 (br s, 1H, O*H*-1), 2.92 (br s, 1H, O*H*-5), 3.88 (app. t, *J* = 7.9 Hz, 1H, H-5), 4.13 (dd, *J* = 3.8, 9.0 Hz, 1H, H-1), 4.45 (app. t, *J* = 6.2 Hz, 1H, H-3), 4.58 (dd, *J* = 4.2, 5.8 Hz, 1H, H-2), 5.50 (dd, *J* = 8.0, 9.1 Hz, 1H, H-6), 5.55 (dd, *J* = 6.7, 7.8 Hz, 1H, H-4), 7.40−8.08 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 25.7, 27.6 (C*Me*$_2$), 69.3, 73.0, 75.8, 76.1 (2C), 76.9 (inositol ring carbons), 111.2 (*C*Me$_2$), 128.8−133.8 (2Ph), 166.5, 167.5 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.39; H, 5.65. **3Lf**: mp 99−101 °C; $[\alpha]_D^{25}$ +13.3 (*c* 0.67, $CHCl_3$); identical R_f,, ^{1}H NMR, and ^{13}C NMR data to those of **3Df**.

D- and L-4,5-Di-*O*-benzoyl-*myo*-inositol (4Db and 4Lb). 4Db: oil: R_f 0.17 (MeOH:CH_2Cl_2 = 1:10); $[\alpha]_D^{25}$ −55.3 (*c* 1.19, MeOH); ^{1}H NMR (CD_3OD) δ 3.69 (dd, *J* = 2.7, 9.7 Hz, 1H,

H-3), 3.94 (dd, J = 2.7, 10.0 Hz, 1H, H-3), 4.13 (app. t, J = 9.7 Hz, 1H, H-6), 4.17 (app. t, J = 2.7 Hz, 1H, H-2), 5.41 (app. t, J = 9.8 Hz, 1H, H-5), 5.77 (app. t, J = 10.0 Hz, 1H, H-4), 7.31−7.92 (m, 10H, 2Ph); ^{13}C NMR (CD_3OD) δ 71.5, 72.4, 73.3, 74.2, 75.1, 76.1 (inositol ring carbons), 129.4−134.2 (2Ph), 167.7, 167.9 (2*C*OPh); HRMS (FAB) *m*/*z* calcd for $C_{20}H_{21}O_8$ 389.1236, found 389.1229 (M^+ + H). **4Lb**: oil; $[\alpha]_D^{25}$ +55.7 (*c* 0.93, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4Db**.

D- and L-1,4-Di-*O*-benzoyl-*myo*-inositol (4Dc and 4Lc). 4Dc: R_f 0.17 (MeOH:CH_2Cl_2 = 1:20); mp 222−225 °C; $[\alpha]_D^{25}$ −16.7 (*c* 0.54, MeOH); ^{1}H NMR (CD_3OD) δ 3.62 (app. t, J = 9.4 Hz, 1H, H-5), 3.84 (dd, J = 2.7, 10.0 Hz, 1H, H-3), 4.14 (app. t, J = 9.7 Hz, 1H, H-6), 4.25 (app. t, J = 2.6 Hz, 1H, H-2), 4.97 (dd, J = 2.6, 10.2 Hz, 1H, H-1), 5.51 (app. t, J = 9.8 Hz, 1H, H-4), 7.45−8.16 (m, 10H, 2Ph); ^{13}C NMR (CD_3OD) δ 71.5, 72.1, 72.3, 74.7, 76.4, 77.1 (inositol ring carbons), 129.5−134.4 (2Ph), 168.0, 168.3 (2*C*OPh); 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. **4Lc**: mp 223−225 °C; $[\alpha]_D^{25}$ +16.6 (*c* 0.41, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4Dc**.

D- and L-1,5-Di-*O*-benzoyl-*myo*-inositol (4Dd and 4Ld). 4Dd: R_f 0.18 (MeOH:CH_2Cl_2 = 1:15); mp 183−185 °C; $[\alpha]_D^{25}$ −18.0 (*c* 0.50, MeOH); ^{1}H NMR (CD_3OD) δ 3.30 (dd, J = 2.7, 9.8 Hz, 1H, H-3), 3.98 (app. t, J = 9.7 Hz, 1H, H-4), 4.26 (app. t, J = 2.5 Hz, 1H, H-2), 4.29 (app. t, J = 9.9 Hz, 1H, H-6), 5.02 (dd, J = 2.7, 10.3 Hz, 1H, H-1), 5.17 (app. t, J = 9.6 Hz, 1H, H-5), 7.45−8.14 (m, 10H, 2Ph); ^{13}C NMR (CD_3OD) δ 70.5, 71.7, 72.5, 73.1, 76.4, 78.4 (inositol ring carbons), 129.6−134.4 (2Ph), 167.8, 168.0 (2*C*OPh); MS (FAB) *m*/*z* 389 (M^+ + H). Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.55; H, 5.47. **4Ld**: mp 183−185 °C; $[\alpha]_D^{25}$ +19.1 (*c* 0.50, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4Dd**.

D- and L-1,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (11Da and 11La). To a solution of compound **4Da** (1.24 g, 3.20 mmol) and TSA (72 mg) in DMF (12 mL) at 0 °C was added 2-methoxypropene (0.8 mL, 8.1 mmol). After 30 min, the reaction mixture was warmed to room temperature, stirred for additional 6 h, poured into aq $NaHCO_3$ at 0 °C with vigorous stirring, and extracted with EtOAc. The organic layer was dried ($MgSO_4$), concentrated, and chromatographed on silica gel to give **11Da** (1.01 g, 73.8%). The byproducts including compound **2D** and the monoacetonated IBz_2 derivatives were treated in boiling aq AcOH (80%) to give the starting material **4Da**, quantitatively. Similarly, compound **11La** was prepared from compound **4La**. **11Da**: R_f 0.46 (EtOAc:CH_2Cl_2 = 1:3); mp 219−221 °C; $[\alpha]_D^{25}$ −73.1 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.48, 1.50 (2s, 6H, C*Me*$_2$), 2.79 (br s, 1H, O*H*-2), 2.89 (br s, 1H, O*H*-5), 3.71 (dd, J = 2.0, 9.7 Hz, 1H, H-3), 4.09 (app. t, J = 9.3, H, H-5), 4.32 (app. t, J = 9.8 Hz, 1H, H-4), 4.69 (br s, 1H, H-2), 5.36 (dd, J = 2.9, 10.0 Hz, 1H, H-1), 5.81 (dd, J = 9.1, 10.0 Hz, 1H, H-6), 7.29−7.97 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 26.9, 27.4 (C*Me*$_2$), 66.4, 72.2, 74.0, 75.2, 75.9, 76.9 (inositol ring carbons), 113.3 (*C*Me$_2$), 128.8−133.9 (2Ph), 166.1, 167.1 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.60; H, 6.02. **11La**: mp 218−220 °C; $[\alpha]_D^{25}$ +71.8 (*c* 0.32, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **11Da**.

Generation and Separation of IBz_2 Regioisomers from 11Da and 11La. Compound **11Da** (1.036 g, 2.42 mmol) in a mixed solvent of pyridine−water (6:4, 50 mL) was heated at 100 °C for 3 h. The reaction mixture was cooled and concentrated under reduced pressure. The serial operation of EtOH addition and evaporation were repeated twice. The crude mixture, which contained almost equal amounts of six regioisomers, was chromatographed on silica gel (EtOAc:Hex = 1:5 → EtOAc gradient). The eluted sequence of the isomers was **11Df**, **11De**, **11Da**, **11Dd**, **11Dc**, and **11Db** with the R_f value of 0.67, 0.53, 0.33, 0.25, 0.22, and 0.21 (EtOAc:CH_2Cl_2 = 1:3). Of the six isomers, compound **11Db** was not separated from compound **11Dc** completely. Each isomer (**11Da**, **11Dc**, **11Dd**, **11De**, and **11Df**) was treated with 80% aq AcOH (100 °C, 3 h) and concentrated to give the corresponding IBz_2 products (**4Da**, **4De**, **4Lb, 4Lf**, and **4Dd**) in quantitative yield, respectively. Compounds **4La**, **4Le**, **4Db, 4Df**, and **4Ld** were similarly prepared from compound **11La**.

D- and L-1,2-Di-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (11Dc and 11Lc). 11Dc: R_f 0.22 (EtOAc:CH_2Cl_2 = 1:3); mp 168−170 °C; $[\alpha]_D^{25}$ −81.7 (*c* 0.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.38, 1.46 (2s, 6H, C*Me*$_2$), 3.12 (br s, 1H, O*H*), 3.50 (br s, 1H, O*H*), 3.82 (dd, J = 2.1, 9.7 Hz, 1H, H-3), 3.96 (app. t, J = 9.2 Hz, 1H, H-4), 4.15 (app. t, J = 9.6 Hz, 1H, H-5), 4.23 (app. t, J = 9.8 Hz, 1H, H-6), 5.34 (dd, J = 3.1, 9.9 Hz, 1H, H-1), 6.10 (app. t, J = 2.6 Hz, 1H, H-2), 7.26−8.03 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 26.8, 27.2 (C*Me*$_2$), 67.7, 72.8, 73.7, 74.6, 75.3, 76.5 (inositol ring carbons), 113.3 (*C*Me$_2$), 128.7−133.8 (2Ph), 165.8, 166.4 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.41; H, 5.98. **11Lc**: mp 169−170 °C; $[\alpha]_D^{25}$ +81.8 (*c* 0.52, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **11Dc**.

D- and L-5,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (11Dd and 11Ld). 11Dd: R_f 0.25 (EtOAc:CH_2Cl_2 = 1:3); mp 122−125 °C; $[\alpha]_D^{25}$ +58.6 (*c* 0.23, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6H, C*Me*$_2$), 2.94 (d, J = 1.4 Hz, 1H, O*H*-2), 3.22 (d, J = 8.1 Hz, 1H, O*H*-1), 3.73 (dd, J = 1.9, 9.6 Hz, 1H, H-3), 3.97 (app. dt, J = 3.0, 8.4, 8.4 Hz, 1H, H-1), 4.42 (app. t, J = 9.7 Hz, 1H, H-4), 4.50 (br s, 1H, H-2), 5.61 (app. t, J = 9.7 Hz, 1H, H-6), 5.69 (app. t, J = 9.4 Hz, 1H, H-5), 7.32−7.97 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 26.9, 27.4 (C*Me*$_2$), 67.9, 71.8, 73.4, 73.6, 76.5, 77.6 (inositol ring carbons), 113.3 (*C*Me$_2$), 128.7−133.8 (2Ph), 166.1, 167.7 (2*C*OPh); MS (FAB) *m*/*z* 451 (M^+ + Na), 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.15; H, 5.95. **11Ld**: mp 122−124 °C; $[\alpha]_D^{25}$ −57.3 (*c* 0.24, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **11Dd**.

D- and L-2,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (11De and 11Le). 11De: R_f 0.53 (EtOAc:CH_2Cl_2 = 1:3); mp 197−198 °C; $[\alpha]_D^{25}$ −62.8 (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.30, 1.43 (2s, 6H, C*Me*$_2$), 2.95 (br s, 1H, O*H*), 3.16 (br s, 1H, O*H*), 3.69 (dd, J = 2.0, 9.6 Hz, 1H, H-3), 4.03−4.11 (m, 2H, H-1 & H-5), 4.19 (app. t, J = 9.8 Hz, 1H, H-4), 5.45 (app. t, J = 9.2 Hz, 1H, H-6), 5.93 (app. t, J = 2.6 Hz, 1H, H-2), 7.40−8.08 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$) δ 26.7, 27.2 (C*Me*$_2$), 69.6, 71.6, 71.9, 75.6, 76.8, 78.7 (inositol ring carbons), 113.4 (*C*Me$_2$), 128.9−134.0 (2Ph), 166.4, 167.8 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.55; H, 5.90. **11Le**: mp 199−201 °C; $[\alpha]_D^{25}$ +62.2 (*c* 0.50, $CHCl_3$); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **11De**.

D- and L-1,5-Di-*O*-benzoyl-3,4-*O*-isopropylidene-*myo*-inositol (11Df and 11Lf). 11Df: R_f 0.67 (EtOAc:CH_2Cl_2 = 1:3); mp 191−192 °C; $[\alpha]_D^{25}$ −13.0 (*c* 0.29, $CHCl_3$:MeOH = 5:1); ^{1}H NMR ($CDCl_3$, with a few drops of CD_3OD) δ 1.47 (s, 6H, C*Me*$_2$), 3.78 (dd, J = 1.9, 9.6 Hz, 1H, H-3), 4.30 (app. t, J = 9.7 Hz, 1H, H-6), 4.36 (app. t, J = 9.9 Hz, 1H, H-4), 4.60 (app. t, J = 2.4 Hz, 1H, H-2), 5.14 (dd, J = 3.0, 9.9 Hz, 1H, H-1), 5.44 (dd, J = 9.1, 10.0 Hz, 1H, H-5), 7.42−8.14 (m, 10H, 2Ph); ^{13}C NMR ($CDCl_3$, with a few drops of CD_3OD) δ 26.5, 27.0 (C*Me*$_2$), 65.5, 71.5, 73.5, 74.5, 76.2, 77.2 (inositol ring carbons), 112.7 (*C*Me$_2$), 128.5−133.5 (2Ph), 166.6, 166.7 (2*C*OPh); MS (FAB) *m*/*z* 429 (M^+ + H). Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.15; H, 5.97. **11Lf**: mp 191−193 °C; $[\alpha]_D^{25}$ +15.1 (*c* 0.26, $CHCl_3$:MeOH = 5:1); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **11Df**.

D- and L-1,2-Di-*O*-benzoyl-*myo*-inositol (4De and 4Le). 4De: R_f 0.19 (MeOH:CH_2Cl_2 = 1:10); mp 219−222 °C; $[\alpha]_D^{25}$ −96.9 (*c* 0.53, MeOH); ^{1}H NMR (CD_3OD) δ 3.43 (app. t, J = 9.1 Hz, 1H, H-5), 3.78−3.88 (m, 2H, H-3 & H-4), 4.02 (app. t, J = 9.8 Hz, 1H, H-6), 5.11 (dd, J = 2.8, 10.2 Hz, 1H, H-1), 5.85 (app. t, J = 2.6 Hz, 1H, H-2), 7.32−8.01 (m, 10H, 2Ph);

^{13}C NMR (CD_3OD) δ 71.4, 72.8, 73.9, 74.6, 74.7, 76.5 (inositol ring carbons), 129.5−134.6 (2Ph), 167.5 (2C) (2*C*OPh); MS (FAB) *m*/*z* 389 ($M^+ + H$). Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.90; H, 5.43. **4Le**: mp 220−222 °C; $[\alpha]_D^{25}$ +97.2 (*c* 0.48, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4De**.

D- and L-2,4-Di-*O*-benzoyl-*myo*-inositol (4Df and 4Lf). 4Df: R_f 0.24 (MeOH:CH_2Cl_2 = 1:10); mp 191−193 °C; $[\alpha]_D^{25}$ +84.2 (*c* 0.56, MeOH); ^{1}H NMR (CD_3OD) δ 3.60 (app. t, *J* = 9.4 Hz, 1H, H-5), 3.73 (dd, *J* = 2.7, 9.8 Hz, 1H, H-1), 3.85 (app. t, *J* = 9.5 Hz, 1H, H-6), 4.01 (dd, *J* = 2.8, 10.1 Hz, 1H, H-3), 5.53 (app. t, *J* = 9.9 Hz, 1H, H-4), 5.75 (app. t, *J* = 2.8 Hz, 1H, H-2), 7.43−8.14 (m, 10H, 2Ph); ^{13}C NMR (CD_3OD) δ 70.2, 72.0, 74.8, 75.0, 76.8, 77.4 (inositol ring carbons), 129.5−134.3 (2Ph), 168.0, 168.2 (2*C*OPh); MS (FAB) *m*/*z* 389 ($M^+ + H$). Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.49; H, 5.42. **4Lf**: mp 196−199 °C; $[\alpha]_D^{25}$ −82.1 (*c* 0.48, MeOH); identical R_f, ^{1}H NMR, and ^{13}C NMR data to those of **4Df**.

Phosphorylation of IBz_2 Regioisomers (4Da−4Df and 4La−4Lf): General Procedure. To a solution of each IBz_2 regioisomer (0.1 mmol) and 1*H*-tetrazole (142 mg, 2 mmol) in CH_2Cl_2 (5 mL) at room temperature was added dibenzyl diisopropylphosphoramidite (0.34 mL, 1 mmol). After 7 h, an excess amount of mCPBA (800 mg) was added to the mixture at 0 °C. After being stirred overnight at room temperature, the mixture was diluted with CH_2Cl_2 and washed with aq Na_2SO_3, aq $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$), concentrated, and chromatographed to give IP'_4Bz_2 regioisomers (**12La−12Lf** and **12Da−12Df**) in 82−99% yields.

D- and L-3,4-Di-*O*-benzoyl-*myo*-inositol 1,2,5,6-tetrakis-(dibenzyl phosphate) (12Da and 12La) were prepared from compounds **4La** and **4Da**, respectively. **12Da**: oil; $[\alpha]_D^{25}$ +21.3 (*c* 1.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.34 (dd, *J* = 9.1, 11.8 Hz, 1H, C*H*$_a$H$_b$Ph), 4.59 (br t, *J* = 9.4 Hz, 1H, H-1), 4.68 (dd, *J* = 7.3, 11.8 Hz, 1H, CH$_a$*H*$_b$Ph), 4.82−5.27 (m, 17H, H-3, H-5, H-6 & 7C*H*$_2$Ph), 5.64 (br d, *J* = 9.0 Hz, 1H, H-2), 6.16 (app. t, *J* = 10.1 Hz, 1H, H-4), 6.83−7.96 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.5, 69.6, 70.0, 70.1, 70.2, 70.4, 70.5 (8*C*H$_2$Ph), 70.4, 74.2, 75.2, 75.3, 75.9, 76.9 (inositol ring carbons), 127.9−136.3 (10Ph), 165.7, 165.8 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.37, 0.91, 1.04, 1.53; MS (FAB) *m*/*z* 1451 ($M^+ + Na$), 1429 ($M^+ + H$). **12La**: oil; $[\alpha]_D^{25}$ −20.8 (*c* 1.53, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12Da**.

D- and L-5,6-Di-*O*-benzoyl-*myo*-inositol 1,2,3,4-tetrakis-(dibenzyl phosphate) (12Db and 12Lb) were prepared from compounds **4Lb** and **4Db**, respectively. **12Db**: oil; $[\alpha]_D^{25}$ −2.98 (*c* 1.14, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.36−4.73 (m, 5H, H-3 & 2C*H*$_2$Ph), 4.83−5.31 (m, 13H, H-1 & 6C*H*$_2$Ph), 5.34 (app. q, *J* = 9.6 Hz, 1H, H-4), 5.67 (m, 2H, H-2 & H-5), 6.09 (app. t, *J* = 10.1 Hz, 1H, H-6), 6.82−7.93 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.6, 69.7, 70.0, 70.1, 70.6, 70.7 (8*C*H$_2$Ph), 71.1 (2C), 74.2 (2C), 75.7, 77.1 (inositol ring carbons), 127.9−136.1 (10Ph), 165.8, 165.9 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.13, 1.13, 1.18, 1.61; MS (FAB) *m*/*z* 1451 ($M^+ + Na$), 1429 ($M^+ + H$). **12Lb**: oil; $[\alpha]_D^{25}$ +3.30 (*c* 1.76, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12Db**.

D- and L-3,6-Di-*O*-benzoyl-*myo*-inositol 1,2,4,5-tetrakis-(dibenzyl phosphate) (12Dc and 12Lc) were prepared from compounds **4Lc** and **4Dc**, respectively. **12Dc**: oil; $[\alpha]_D^{25}$ −6.06 (*c* 1.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.33−5.15 (m, 18H, H-1, H-5 & 8C*H*$_2$Ph), 5.35−5.46 (m, 3H, H-2, H-3 & H-4), 6.12 (app. t, *J* = 9.9 Hz, 1H, H-6), 6.79−8.15 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.7, 69.7, 69.9, 70.0, 70.1 (8*C*H$_2$Ph), 70.3, 70.5, 74.1, 76.1 (2C), 77.1 (inositol ring carbons), 128.0−136.1 (10Ph), 165.7, 165.9 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.34, 0.99, 1.06, 1.35; MS (FAB) *m*/*z* 1451 ($M^+ + Na$), 1429 ($M^+ + H$). **12Lc**: oil; $[\alpha]_D^{25}$ +6.33 (*c* 1.24, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12Dc**.

D- and L-3,5-Di-*O*-benzoyl-*myo*-inositol 1,2,4,6-tetrakis-(dibenzyl phosphate) (12Dd and 12Ld) were prepared from compounds **4Ld** and **4Dd**, respectively. **12Dd**: oil; $[\alpha]_D^{25}$ +2.59 (*c* 1.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.26−5.17 (m, 17H, H-1 & 8C*H*$_2$Ph), 5.25−5.47 (m, 3H, H-3, H-4 & H-6), 5.60 (br d, *J* = 9.2 Hz, 1H, H-2), 5.71 (app. t, *J* = 9.5 Hz, 1H, H-5), 6.71−8.12 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.5, 69.5, 69.6, 69.7, 70.0, 70.1, 70.2, 70.4, 70.4, 70.6 (8*C*H$_2$Ph), 70.6, 71.7, 74.2, 75.2, 75.6 (2C) (inositol ring carbons), 127.7−136.1 (10Ph), 165.7, 165.9 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.39, 1.17, 1.42, 1.53; MS (FAB) *m*/*z* 1429 ($M^+ + H$). **12Ld**: oil; $[\alpha]_D^{25}$ −2.67 (*c* 1.40, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12Dd**.

D- and L-2,3-Di-*O*-benzoyl-*myo*-inositol 1,4,5,6-tetrakis-(dibenzyl phosphate) (12De and 12Le) were prepared from compounds **4Le** and **4De**, respectively. **12De**: oil; $[\alpha]_D^{25}$ +6.93 (*c* 1.49, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.37−5.12 (m, 18H, H-1, H-5 & 8C*H*$_2$Ph), 5.15−5.28 (m, 2H, H-4 & H-6), 5.42 (dd, *J* = 2.9, 9.8 Hz, 1H, H-3), 6.25 (app. t, *J* = 2.8 Hz, 1H, H-2), 6.79−8.00 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.5, 69.6, 69.9, 70.0, 70.1, 70.1, 70.2 (8*C*H$_2$Ph), 69.2 (2C), 73.7, 75.8, 76.0, 76.4 (inositol ring carbons), 127.9−136.3 (10Ph), 165.4, 165.5 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.59, 0.72, 1.26, 1.59; MS (FAB) *m*/*z* 1429 ($M^+ + H$). **12Le**: oil; $[\alpha]_D^{25}$ −6.38 (*c* 1.40, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12De**.

D- and L-2,6-Di-*O*-benzoyl-*myo*-inositol 1,3,4,5-tetrakis-(dibenzyl phosphate) (12Df and 12Lf) were prepared from compounds **4Lf** and **4Df**, respectively. **12Df**: oil; $[\alpha]_D^{25}$ −20.6 (*c* 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.30 (dd, *J* = 9.9, 11.7 Hz, 1H, C*H*$_a$H$_b$Ph), 4.43 (dd, *J* = 9.5, 11.8 Hz, 1H, C*H*$_c$H$_d$Ph), 4.56−4.71 (m, 3H, H-3, CH$_a$*H*$_b$Ph & CH$_c$*H*$_d$Ph), 4.79−5.10 (m, 14H, H-1, H-5 & 6C*H*$_2$Ph), 5.18 (app. q, *J* = 9.6 Hz, 1H, H-4), 6.03 (app. t, *J* = 9.9 Hz, 1H, H-6), 6.41 (app. t, *J* = 2.7 Hz, 1H, H-2), 6.82−8.08 (m, 50H, 10Ph); ^{13}C NMR ($CDCl_3$) δ 69.6, 69.7, 69.8, 69.9, 70.1, 70.4 (8*C*H$_2$Ph), 70.5, 70.9, 73.8, 73.9, 76.2, 76.6 (inositol ring carbons), 128.0−136.2 (10Ph), 165.4, 165.7 (2*C*OPh); ^{31}P NMR ($CDCl_3$) δ 0.65, 1.03, 1.19, 1.22; MS (FAB) *m*/*z* 1429 ($M^+ + H$). **12Lf**: oil; $[\alpha]_D^{25}$ +22.0 (*c* 1.35, $CHCl_3$); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **12Df**.

Preparation of Sodium Salts of *myo*-Inositol Tetrakisphosphate (13Da−13Df and 13La-13Lf): General Procedure. To a solution of each IBz_2P_4 regioisomer, **12Da−12Df** and **12La−12Lf** (100 mg, 0.07 mmol) in a solvent mixture of EtOH−MeOH (1:1, 8 mL), was added 10% Pd/C (45 mg). The mixture was stirred under H_2 (50 psi) for 1 day. The catalyst was filtered off and the solution was concentrated under reduced pressure and treated with 1 N LiOH (6 mL) at 80 °C for 5 h. The basic solution was cooled and loaded on Dowex 50WX8-100 (H^+ form) and eluted with water. The acidic effluent was collected, washed with CH_2Cl_2 three times, and lyophilized to dryness. The residue was redissolved in a small amount of water (1 mL) and the pH was adjusted to 10 with NaOH and lyophilized again to give the sodium salts of *myo*-inositol tetrakisphosphate (**13Da−13Df** and **13La−13Lf)** in approximately 90% yields.

D- and L-*myo*-Inositol 1,2,5,6-tetrakisphosphate sodium salt (13Da and 13La) were prepared from compounds **12Da** and **12La**, respectively. **13Da**: $[\alpha]_D^{25}$ −4.98 (*c* 1.93, H_2O, pH 9.5); ^{1}H NMR (D_2O, pH 10) δ 3.49 (br d, *J* = 9.5 Hz, 1H, H-3), 3.84−3.95 (m, 2H, H-4 & H-5), 4.01 (br t, *J* = 10.0 Hz, 1H, H-1), 4.36 (app. q, *J* = 9.2 Hz, 1H, H-6), 4.57 (br d, *J* = 6.9 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 72.1, 73.7, 74.0, 75.3, 76.0, 78.2 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 4.93, 6.47, 6.97, 7.28. **13La**: $[\alpha]_D^{25}$ +4.19 (*c* 2.35, H_2O, pH 8.6); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13Da**.

D- and L-*myo*-Inositol 1,2,3,4-tetrakisphosphate sodium salt (13Db and 13Lb) were prepared from compounds **12Db** and **12Lb**, respectively. **13Db**: $[\alpha]_D^{25}$ +19.0 (*c* 2.27, H_2O, pH 9.2) [lit.[15i] $[\alpha]_D^{20}$ −6.6 (*c* 3.95, H_2O, free acid)]; ^{1}H NMR (D_2O, pH 10) δ 3.52 (app. t, *J* = 8.3 Hz, 1H, H-5), 3.87−3.97 (m, 3H, H-1, H-3 & H-6), 4.21 (app. q, *J* = 8.6 Hz, 1H, H-4), 4.69 (br

d, J = 8.8 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 73.0, 73.2, 74.1, 75.5, 76.2, 76.5 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 5.84, 7.34, 7.95, 8.12. **13Lb**: $[\alpha]_D^{25}$ −19.9 (*c* 2.59, H_2O, pH 9.0) [lit.[15i] $[\alpha]_D^{20}$ +4.8 (c 1.73, H_2O, free acid)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13Db**.

D- and L-*myo*-Inositol 1,2,4,5-tetrakisphosphate sodium salt (13Dc and 13Lc) were prepared from compounds **12Dc** and **12Lc**, respectively. **13Dc**: $[\alpha]_D^{25}$ −13.2 (*c* 1.65, H_2O, pH 9.8) [lit. $[\alpha]_D$ −13.3 (*c* 1.0, H_2O, pH 10, sodium salt),[15h] $[\alpha]_D$ −27.2 (*c* 0.50, H_2O, pH 8.6, triethylammonium hydrogen carbonate salt)[15g]]; ^{1}H NMR (D_2O, pH 10) δ 3.59 (br d, J = 8.7 Hz, 1H, H-3), 3.88−3.97 (m, 3H, H-1, H-5 & H-6), 4.28 (app. q, J = 8.9 Hz, 1H, H-4), 4.61 (br d, J = 8.1 Hz, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 71.1, 72.1, 74.5, 74.8, 77.3, 78.3 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 3.98, 4.69, 5.59, 5.69. **13Lc**: $[\alpha]_D^{25}$ +14.9 (*c* 2.08, H_2O, pH 9.8) [lit. $[\alpha]_D$ +12.1 (c 1.0, H_2O, pH 10, sodium salt),[15h] $[\alpha]_D$ +25.8 (*c* 0.31, H_2O, pH 8.6, triethylammonium hydrogen carbonate salt)[15g]]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13Dc**.

D- and L-*myo*-Inositol 1,2,4,6-tetrakisphosphate sodium salt (13Dd and 13Ld) were prepared from compounds **12Dd** and **12Ld**, respectively. **13Dd**: $[\alpha]_D^{25}$ −15.2 (*c* 2.10, H_2O, pH 9.5); ^{1}H NMR (D_2O, pH 10) δ 3.49−3.55 (m, 2H, H-3 & H-5), 3.88 (app. t, J = 9.6 Hz, 1H, H-1), 4.19−4.30 (m, 2H, H-4 & H-6), 4.64 (br d, J = 7.1 Hz, H-2); ^{13}C NMR (D_2O, pH 10) δ 72.1, 72.6, 75.5 (2C), 75.8, 77.9 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 6.87, 6.96, 7.19, 7.82. **13Ld**: $[\alpha]_D^{25}$ +14.7 (*c* 1.77, H_2O, pH 9.5); identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13Dd**.

D- and L-*myo*-Inositol 1,4,5,6-tetrakisphosphate sodium salt (13De and 13Le) were prepared from compounds **12De** and **12Le**, respectively. **13De**: $[\alpha]_D^{25}$ −8.99 (*c* 1.85, H_2O, pH 9.5) [lit.[15e] $[\alpha]_D^{24}$ −10.2 (*c* 2.46, H_2O, pH 10.7, sodium salt, adjusted by addition of cyclohexylammine)]; ^{1}H NMR (D_2O, pH 10) δ 3.82 (br s, 1H, H-2), 4.05−4.11 (m, 2H, H-4 & H-6), 4.25−4.45 (m, 3H, H-1, H-3 & H-5); ^{13}C NMR (D_2O, pH 10) δ 72.3, 74.0 (2C), 75.2 (2C), 75.5 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 5.03, 5.50, 6.25, 6.99. **13Le**: $[\alpha]_D^{25}$ +10.1 (*c* 2.23, H_2O, pH 8.9) [lit. $[\alpha]_D^{24}$ +9.8 (*c* 1.43, H_2O, pH 11.1, sodium salt, adjusted by addition of cyclohexylammine),[15e] $[\alpha]_D$ −6.2 (*c* 2.15, H_2O, pH 9.5, sodium salt)[15c]]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13De**.

D- and L-*myo*-Inositol 1,3,4,5-tetrakisphosphate sodium salt (13Df and 13Lf) were prepared from compounds **12Df** and **12Lf**, respectively. **13Df**: $[\alpha]_D^{25}$ −4.08 (*c* 2.02, H_2O, pH 9.7) [lit. $[\alpha]_D^{24}$ −13 (*c* 1.0, H_2O, ammonium salt),[15a] $[\alpha]_D^{23}$ −3.5 (*c* 5.5, H_2O, pH 8.3, potassium salt),[14k,m] $[\alpha]_D^{25}$ −2.5 (*c* 1, H_2O, cyclohexylammonium salt),[15b] $[\alpha]_D^{24}$ −4.51 (*c* 0.13, H_2O, sodium salt)[14w]]; ^{1}H NMR (D_2O, pH 10) δ 3.84−3.95 (m, 4H, H-1, H-3, H-5 & H-6), 4.30 (app. q, J = 9.3 Hz, 1H, H-4), 4.66 (br s, 1H, H-2); ^{13}C NMR (D_2O, pH 10) δ 70.1, 73.0, 73.7, 74.2, 74.5, 78.0 (inositol ring carbons); ^{31}P NMR (D_2O, pH 10) δ 5.80, 6.42, 6.92, 7.38. **13Lf**: $[\alpha]_D^{25}$ +4.68 (*c* 2.11, H_2O, pH 8.9) [lit.[15b] $[\alpha]_D^{25}$ +2.6 (*c* 1, H_2O, cyclohexylammonium salt)]; identical ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR data to those of **13Df**.

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Supporting Information Available: ^{1}H spectra of compounds **6Da**, **6Df**, **9Da**−**9Dh**, **10Dc**, **10De**, **3Db**, **4Db**, **12Da**−**12Df**, **13Da**, and **13Dd**. This material is available free of charge via the Internet at http://pubs.acs.org.

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