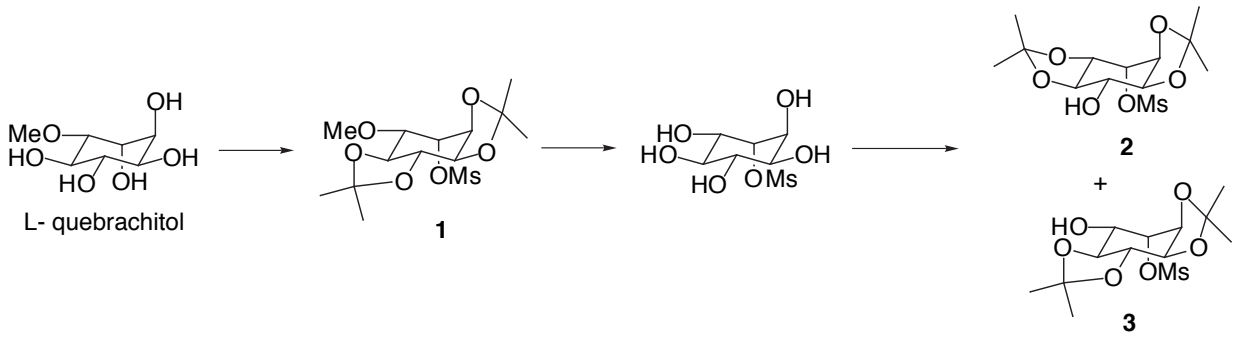
**General Methods:** NMR spectra were acquired at proton frequencies of 300 MHz, using $CDCl_3$ as solvent unless noted otherwise. $^1H$ chemical shifts were reported with $Me_4Si$ ($\delta$ = 0.00 ppm) or $CHCl_3$ ($\delta$ = 7.26 ppm) as internal standards, $^{31}P$ chemical shifts relative to external aqueous 85% $H_3PO_4$ ($\delta$ = 0.00 ppm), and $^{13}C$ chemical shifts with $CHCl_3$ ($\delta$ = 77.00 ppm) or TMS ($\delta$ = 0.00 ppm) as internal standards. Optical rotations were measured at rt.

**Abbreviations:** PMBCl—*para*-methoxybenzyl chloride; CSA—Camphor sulfonic acid; DMF—*N,N*-dimethyl formamide; DMSO—dimethyl sulfoxide.

**General Procedure A** (for benzylation and p-methoxybenzylatioon): At 0 °C, to a well-stirred solution of the substrate in DMF was added NaH (1.2 eq per hydroxyl group). After 30 min, BnBr or PMBCl (1.05 eq per hydroxyl group) and $Bu_4NI$ (1% mol per hydroxyl group) were added. The resulting mixture was stirred for additional 4 h before being poured into ice-water. Ethyl ether or ethyl acetate was used to extract product, and the combined organic layer was washed with dilute aqueous HCl, water, brine, and dried over $Na_2SO_4$. After concentration, the residue was purifed either by column chromatography on silica gel or recrystallization.

**General Procedure B** (for hydrolysis of trans-acetonide): To a well-stirred solution of the substrate (with both trans- and cis-acetonides) in MeOH-$CH_2Cl_2$ (1/4 v/v, 12.5 mL/mol), was added acetyl chloride (2% mol). This reaction was monitored by TLC until no starting material left. Then the reaction was quenched by addition of $Et_3N$ (6% mol). After removal of solvent, the residue was purified either by column chromatography on silica gel or recrystallization.

**Section I**: Experimental procedure and spectral data for the intermediates in the preparation of **PI(3,4)$P_2$**:




To a solution of L-quebrachitol (25.0 g, 0.128mol) and camphor sulfonic acid (600 mg) in DMF (120 mL) at 0°C, was added dropwise 2-methoxypropene (40 mL, 0.42 mol). After addition, the resulting mixture was stirred at rt for 1h and at 60 °C for 4h. DMF was then removed in *vacuo*, and the residue was extracted with ethyl ether (200 mL x 2). The organic layer was washed with water (100 mL x 2), brine (100 mL), and dried over $MgSO_4$. After concentration, 32.17g of yellow oil was obtained as the expected 1,2; 4,5-diacetonide quebrachitol (91%). This intermediate can be used in the next step without any purification.

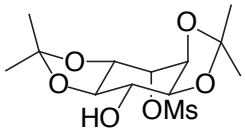
To a solution of the intermediate obtained above (0.116 mol) and $Et_3N$ (24.4 mL, 0.176 mol) in $CH_2Cl_2$ (250 mL) at 0 °C, was added methanesulfonyl chloride (9.9 mL, 0.128 mol). The resulting mixture was warmed to rt and stirred for an additional hour before pouring into 100 mL of ice-water. The organic layer was washed consecutively with dilute HCl, aqueous $NaHCO_3$,

brine, and dried over $MgSO_4$. After filtration, the filtrate (containing compound **1**) was diluted with another 350 mL of $CH_2Cl_2$ and cooled to 0 °C. To this solution with vigorous mechanical stirring, $BBr_3$ (50 mL, 0.53 mol) was added during 1h. Then the stirring was continued for 12 h at rt. The reaction mixture was recooled to 0 °C, and 100 mL of methanol was dropped in slowly. Evaporation of all the solvent left a dark brown oil, which was partitioned in $CH_2Cl_2$ (200 mL) and $H_2O$ (300mL). The aqueous layer was washed by $CH_2Cl_2$ (20 mL x 3), then evaporated to dryness giving about 42 g of crude product as pentol.

To the resulting pentol and 600 mg of CSA in 100 mL of DMF, was added dropwise 2-methoxypropene (43.2 mL, 0.45mol) at rt. After addition, the resulting mixture was stirred at 80 °C for 4h before removal of DMF *in vacuo*. The residue was dissolved into ethyl acetate (200 mL) and washed with 5% NaOH solution (20 mL), water (20 mL) and brine (20 mL) successively. After drying over $MgSO_4$, the solution was concentrated. The precipitate came out during evaporation. When there was about 40 mL solvent left, 40 mL of hexane was added and the solid was filtered out affording 8.14 g white solid (compound **2**). The mother liquor was then concentrated, and dissloved into 50 mL of DMF with 300mg of CSA. Subsequently 10 mL of 2-methoxypropene was added, and the same procedure was repeated again giving 6.0 g of compound **2**. Totally 14.14 g of desired diacetonide **2** was obtained (36%), the mother liquor mainly contained the isomer **3**.

The mother liquor was concentrated, and the residue was purified by column chromatography on silica gel using Hexane/Ethyl Acetate (v/v 1/1) as eluent giving yellow oil 7.7 g (20%). $^1$H NMR showed the ratio of compound **2** and **3** is about 1/4.26 in mother liquor. This ratio was increased when crystallization was applied in 80 mL of EtOAc/Hexane (1/3 v/v), whereas the precipitate obtained was a mixture of compound **2** and **3**.

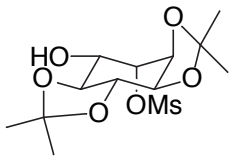
NMR data for compound **2**:




$^1$H NMR δ 5.33 (br s, 1H), 4.43 (dd, 2H, *J* = 2.4, 5.7 Hz), 4.20 (br t, 1H, *J* = 5.7 Hz), 3.86 (br s, 3H), 3.12 (s, 3H), 2.46 (s, 1H), 1.50, 1.49, 1.46, 1.37 (4s, 3H each);

$^{13}$C NMR δ 112.58, 110.48, 80.89, 77.98, 75.72, 75.04, 74.47, 74.04, 38.67, 27.81, 27.07, 26.44, 25.77.

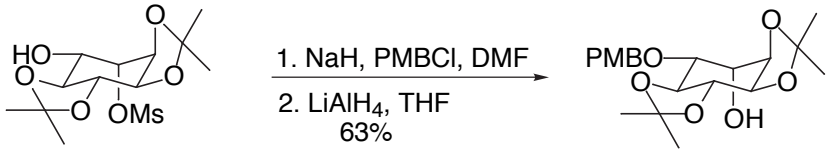
NMR data for compound **3**:




$^1$H NMR δ 4.98 (t, 1H, *J* = 5.4 Hz), 4.49 (t, 1H, *J* = 6.3 Hz), 4.42 (br t, 1H, *J* = 6.6 Hz), 4.30 (m, 1H), 3.71-3.69 (m, 2H), 3.19 (s, 3H), 2.05 (s, 1H), 1.49 (s, 3H), 1.46 (br s, 6H, 2Me), 1.37 (s, 3H).

$^{13}$C NMR δ 111.03, 109.59, 79.19, 77.32, 75.69, 75.57, 74.60, 67.69, 37.29, 26.65, 25.78, 25.71, 24.33.

Preparation of compound **5**:




**3** **5**

Compound **3** (3.8 g, 11.3 mmol) was *p*-methoxybenzylated using General Procedure A. The product in this step was purified by flash column chromatography on silica gel with EtOAc/Hexane (1/3 v/v) as eluent giving compound **4** as a slight yellow foam.

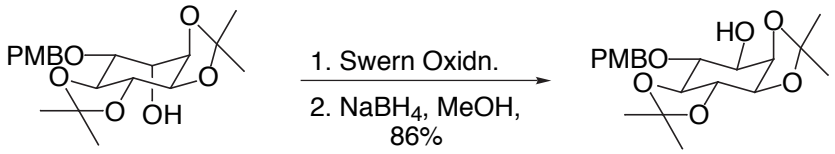
To a well-stirred solution of compound **4** in dry THF (50 mL) at 0 °C, was added $LiAlH_4$ powder (1.3 g) in several portions. The reaction mixture was then warmed to room temperature and kept stirring for another 2 h before being recooled to 0 °C. Water (5 mL) was added dropwise to destroy the excess amount of $LiAlH_4$. When no gas was evolved from the reaction system, anhydrous $MgSO_4$ (20 g) was added. 30 mins later, the reaction mixture was filtered through a Buchner funnel, and the filter cake was washed with EtOAc (200 mL). The combined filtrate was washed with regular bleach (30 mL) and water (100 mL) and dried over $MgSO_4$. After concentration, the residue was purified by flash column chromatography on silica gel with EtOAc/Hexane (1/3 v/v) as eluent giving 2.64 g of compound **5** as colorless semi-solid (63% overall yield for 2 steps).

$[\alpha]_D$ = +17.6 (*c* 0.55 in $CHCl_3$);

$^1$H NMR δ 7.30 (d, 2H, *J* = 8.4 Hz), 6.89 (d, 2H, *J* = 8.4 Hz), 4.84, 4.59 (AB q, 2H, *J* = 11.4 Hz), 4.34 (br q, 2H, *J* = 5.7 Hz), 4.20 (br q, 1H, *J* = 3.3 Hz), 4.87 (dd, 1H, *J* = 4.8, 8.1 Hz), 3.81 (s, 3H), 3.78 (dd, 1H, *J* = 3.3, 8.7 Hz), 3.61 (m, 1H), 2.90 (d, 1H, *J* = 3.6 Hz), 1.50 (s, 3H), 1.45 (s, 6H), 1.34 (s, 3H);

$^{13}$C NMR δ 159.42, 129.59 x 2, 129.50, 113.86 x 2, 111.79, 109.67, 78.95, 78.42, 76.89, 76.58, 76.48, 75.84, 71.90, 69.85, 55.21, 27.91, 26.95 x 2, 25.31.

Preparation of compound **6**:




**5** **6**

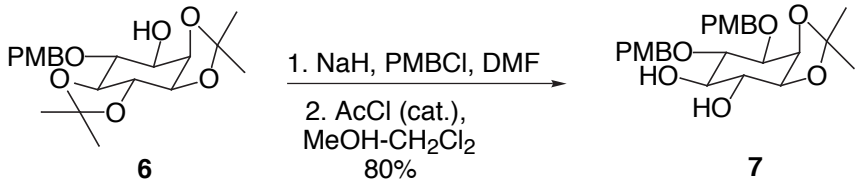
$N_2$, to a stirring solution of oxalyl chloride (750 μL, 8.59 mmol) in 15 mL of anhydrous $CH_2Cl_2$ at -78 °C, was added dropwise DMSO (1.20 mL, 17 mmol). The resulting solution was stirred at this temperature for additional 15 mins followed by addition of compound **5** (2.50 g, 6.61 mmol) in $CH_2Cl_2$ (5 mL). The stirring was continued below -60 °C for another 1.5 h, before 10 mL of *i*-$Pr_2NEt$ was added. The resulting mixture was warmed up to room temperature slowly, then diluted with another 100 mL of $CH_2Cl_2$. The resulting organic layer was washed with water, brine, and dried over $MgSO_4$. After concentration, the residue was redissolved into MeOH (100 mL) and cooled to 0 °C. $NaBH_4$ powder (500 mg) was added in several portions to keep the reaction temperature below 5 °C. One hour later, the reaction was quenched by saturated aqueous $NH_4Cl$ and the reaction mixture was concentrated under reduced pressure to about 30 mL left. Ethyl ether (200 mL) was used to extract the product, and the organic layer was washed with water, brine, and dried over $Na_2SO_4$. After concentration, the residue was purified by flash column chromatography on silica gel with EtOAc/Hexane (1/3 v/v) as eluent giving 2.15 g of compound **6** as colorless oil (86% overall yield for 2 steps).

$[\alpha]_D$ = +20.7 (*c* 0.68 in $CHCl_3$);

$^1$H NMR δ 7.30 (d, 2H, *J* = 8.4 Hz), 6.89 (d, 2H, *J* = 8.4 Hz), 4.72, 4.58 (AB q, 2H, *J* = 11.4 Hz), 4.44 (dd, 1H, *J* = 3.6, 7.2 Hz), 4.34 (t, 1H, *J* = 7.5 Hz), 4.17 (dd, 1H, *J* = 7.5, 10.5 Hz), 4.01 (br s, 1H), 3.89 (dd, 1H, *J* = 2.1, 8.1 Hz), 3.80 (s, 3H), 3.55 (dd, 1H, *J* = 7.8, 10.5 Hz), 2.59 (d, 1H, *J* = 1.5 Hz), 1.54 (s, 3H), 1.45 (s, 6H), 1.38 (s, 3H);

$^{13}$C NMR δ 159.25, 129.89, 129.49 x 2, 113.80 x 2, 112.28, 110.51, 79.64, 79.21, 76.80, 76.78, 75.60, 72.14, 71.56, 55.23, 27.13, 27.02, 26.58, 24.19.

Preparation of compound **7**:




**6** **7**

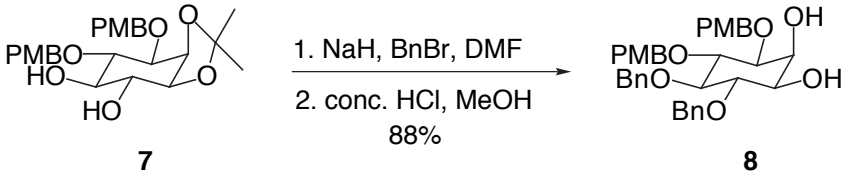
*p*-Methoxybenzylation of compound **6** (2.0 g, 5.29 mmol) was carried out using General Procedure A, and hydrolysis of trans-acetonide was achieved through General Procedure B. Compound **7** was purified by flash column chromatography on silica gel giving colorless oil 2.1 g (80%, 2 steps).

$[\alpha]_D$ = -33.0 (*c* 0.66 in $CHCl_3$);

$^1$H NMR δ 7.32 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 6.89 (d, 2H, *J* = 8.4 Hz), 6.87 (d, 2H, *J* = 8.4 Hz), 4.92, 4.62 (AB q, 2H, *J* = 10.8 Hz), 4.73, 4.68 (AB q, 2H, *J* = 11.7 Hz), 4.23 (t, 1H, *J* = 7.8 Hz), 3.89 (dd, 1H, *J* = 5.4, 7.5 Hz), 3.81 (s, 6H), 3.75-3.63 (m, 3H), 3.25 (t, 1H, *J* = 9.3 Hz), 2.63 (br s, 2H), 1.56 (s, 3H), 1.35 (s, 3H);

$^{13}$C NMR δ 159.41 x 2, 130.47, 129.84, 129.72 x 2, 129.67 x 2, 113.98 x 2, 113.86 x 2, 110.01, 79.97, 78.48, 77.36, 74.91, 74.83, 74.11, 72.91, 72.44, 55.27 x 2, 28.18, 25.91.

Preparation of compound **8**:




**7** **8**

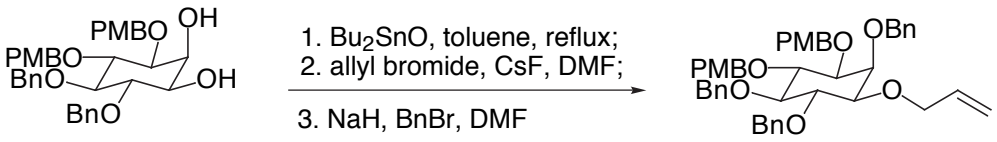
Benzylation of compound **7** (1.4 g, 3.06 mmol) was carried out using General Procedure A, and hydrolysis of cis-acetonide was achieved using 3 drops of concentrated HCl in 30 mL of MeOH overnight. The compound **8** was crystallized from MeOH, giving white solid 1.60 g (88%, 2 steps).

$[\alpha]_D$ = -25.4 (*c* 0.62 in $CHCl_3$);

$^1$H NMR δ 7.32-7.21 (m, 14H), 6.87 (d, 2H, *J* = 8.4 Hz), 6.85 (d, 2H, *J* = 8.4 Hz), 4.96-4.60 (m, 8H), 4.16 (br s, 1H), 3.93 (t, 1H, *J* = 9.3 Hz), 3.81 (br s, 4H), 3.80 (s, 3H), 3.45 (br t, 2H, *J* = 9.6 Hz), 2.50 (s, 1H), 2.42 (d, 1H, *J* = 4.5 Hz);

$^{13}$C NMR δ 159.39, 159.16, 138.56, 138.46, 130.83, 129.89, 129.59 x 2, 129.51 x 2, 128.55 x 2, 128.38 x 2, 127.95 x 2, 127.85, 127.72 x 2, 127.57, 113.91 x 2, 113.76 x 2, 83.22, 81.40, 81.28, 79.73, 75.60, 72.42, 71.73, 69.19, 55.26.

Preparation of compound **9**:




**8** **9**

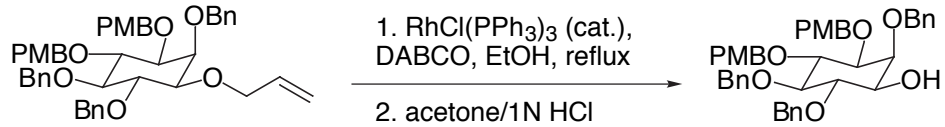
Under $N_2$, a solution of compound **8** (2.0 g, 3.48 mmol) and $Bu_2SnO$ (1.04 g, 4.17 mmol) in toluene (60 mL) was refluxed azeotropically for 2 h until no water was distilled out in Dean-Stark trap. After evaporation of toluene, the resulting solid was dried in vacuo for 2 h and then suspended into 20 mL of dry DMF. At 0 °C, anhydrous CsF (608 mg, 4.0 mmol) was added to the solution followed by addition of allyl bromide (451 μL, 5.2 mmol). The resulting mixture was stirred at rt for 18 h before addition of 100 mL of ethyl ether. The reaction mixture was filtered through a celite pad, and the filtrate was washed with water, brine, and dried over $Na_2SO_4$. After concentration, the residue was benzylated using General Procedure **A**. Compound **9** (2.24 g, colorless oil) was obtained after flash column chromatography on silica gel with EtOAc/Hexane (1/7 to 1/5 v/v) as eluents (92%, 3 steps).

$[\alpha]_D$ = 0.0 (*c* 1.31 in $CHCl_3$);

$^1$H NMR δ 7.44-7.20 (m, 19H), 6.86 (d, 1H, *J* = 8.4 Hz), 6.79 (d, 1H, *J* = 8.4 Hz), 5.90 (m, 1H), 5.30 (dd, 1H, *J* = 1.5, 17.4 Hz), 5.18 (br d, 1H, *J* =10.5 Hz), 4.93-4.72 (m, 8H), 4.57 (AB q, 2H, *J* = 11.1 Hz), 4.10-3.97 (m, 5H), 3.81 (s, 3H), 3.78 (s, 3H), 3.43 (t, 1H, *J* = 9.3 Hz), 3.33 (dd, 1H, *J* = 1.8, 9.9 Hz), 3.27 (dd, 1H, *J* = 1.8, 9.6 Hz).

$^{13}$C NMR δ 159.09, 159.05, 138.98, 138.91, 138.82, 134.89, 131.04, 130.53, 129.70 x 2, 129.12 x 2, 128.28 x 2, 128.23 x 2, 128.11 x 2, 128.08 x 2, 127.76 x 2, 127.68 x 2, 127.49, 127.39, 127.26, 116.58, 113.69 x 2, 113.66 x 2, 83.63, 81.62, 81.34, 80.66, 75.81, 75.47, 74.27, 73.97, 72.45, 71.60, 55.23, 55.20.

Preparation of compound **10**:




**9** **10**

Under $N_2$, a solution of compound **9** (2.25 g, 3.2 mmol), $RhCl(PPh_3)_3$ (148 mg, 0.16 mmol, 5% mol), and DABCO (900 mg, 8 mmol) in EtOH (20 mL) was refluxed about 6 h until no compound **9** left (monitored by TLC, toluene/EtOAc = 9/1 v/v). After concentration, the reaction mixture was extracted with 100 mL of ethyl ether, washed with 3N HCl, water, and brine. The organic layer was concentrated again, then dissolved in Acetone/1N HCl (50 mL, v/v 9/1). The solution was refluxed for about 30 min until TLC showed that the nonpolar material has been transformed completely into a polar product. Acetone was then removed under reduced pressure, the residue was extracted with EtOAc, washed with aq. $NaHCO_3$, brine, and dried over $Na_2SO_4$. After concentration, compound **10** was purified by column chromatography on silica gel with EtOAc/Hexane (1/2 v/v) as eluent, giving 1.91 g of colorless oil (90%).

$[\alpha]_D$ = -9.35 (*c* 1.19 in $CHCl_3$);

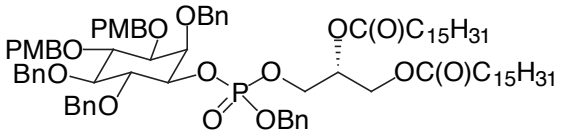
$^{1}$H NMR δ 7.40-7.20 (m, 19H), 6.85 (d, 2H, *J* = 8.4 Hz), 6.81 (d, 2H, *J* = 8.4 Hz), 5.00-4.60 (m, 10H), 4.02 (t, 1H, *J* = 9.6 Hz), 3.98 (br s, 1H), 3.80 (s, 3H), 3.78 (br s, 4H), 3.48-3.40 (m, 3H), 2.21 (d, 1H, *J* = 6.3 Hz);

$^{13}$C NMR δ 159.17, 159.10, 138.71, 138.68, 138.55, 130.92, 130.37, 129.67 x 2, 129.21 x 2, 128.43 x 2, 128.35 x 2, 128.30 x 2, 128.03 x 2, 127.74 x 4, 127.55, 127.51, 113.79 x 2, 113.71 x 2, 83.56, 82.13, 81.57, 80.83, 77.14, 75.68, 75.50, 74.68, 72.64, 72.34, 55.23 x 2.

For the preparation of compounds **11**, **12** and **PI(3,4)P$_2$**, please refer to the published full papers:

a) Kozikowski, A. P.; Qiao, L.; Tückmantel, W.; Powis, G. *Tetrahedron* **1997**, *53*, 14903-14914.
b) Painter, G. F.; Grove, S. J. A.; Gilbert, I. H.; Holmes, A. B.; Raithby, P. R.; Hill, M. L.; Hawkins, P. R.; Stephens, L. R. *J. Chem. Soc.; Perkin Trans. I* **1999**, 923-935.

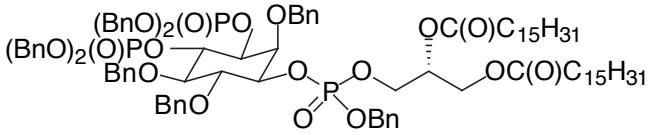
Compound **11**:




$^{1}$H NMR δ 7.40-7.20 (m, 24H), 6.86 (d, 1H, *J* = 8.4 Hz), 6.79 (d, 1H, *J* = 8.4 Hz), 5.10-4.52 (m, 13H), 4.32-3.84 (m, 8H), 3.80 (s, 3H), 3.78 (s, 3H), 3.50-3.39 (m, 2H), 2.20 (m, 4H), 1.55 (m, 4H), 1.32-1.18 (br s, 48H), 0.88 (t, 6H, *J* = 6.9 Hz).

$^{31}$P NMR δ -1.08 (major), -1.11 (minor).

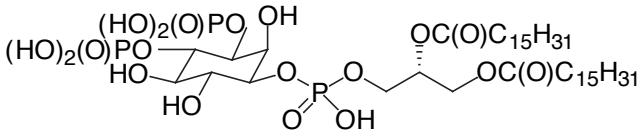
Compound **12**:




$^{1}$H NMR δ 7.32-7.00 (m, 40H), 5.10-4.68 (m, 18H), 4.61 (br s, 1H), 4.34-3.82 (m, 8H), 3.47 (q, 1H, *J* = 9.3 Hz), 2.20 (m, 4H), 1.55 (m, 4H), 1.32-1.18 (br s, 48H), 0.88 (t, 6H, *J* = 6.9 Hz);

$^{31}$P NMR δ -0.69, -0.93 (minor), -0.98 (major), -1.32 (major), -1.36 (minor).

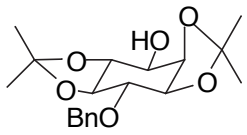
**PI(3,4)P$_2$**:




$^{1}$H NMR ($CDCl_3$/$CD_3OD$ 1/1 v/v, TMS) δ 5.27 (m, 1H), 4.50 (q, 1H, *J* = 8.7 Hz), 4.43 (dd,1H, *J* = 3.3, 12.6 Hz), 4.41 (br s, 1H), 4.21 (m, 4H), 4.06 (br t, 1H, *J* = 9.9 Hz), 3.90 (t, 1H, *J* = 9.0 Hz), 3.48 (t, 1H, *J* = 9.0 Hz), 2.34 (q, 4H, *J* = 7.8 Hz), 1.60 (br s, 4H), 1.40-1.20 (br s, 48H), 0.88 (t, 6H, *J* = 6.9 Hz);

$^{31}$P NMR ($CDCl_3$/$CD_3OD$ 1/1 v/v) δ 1.42, 0.73, -0.50.

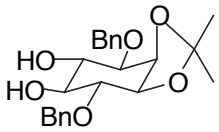
**Section II**: Spectral data for the intermediates for the preparation of **PI(4,5)$P_2$**:




$[\alpha]_D$ = -67.9 (*c* 1.1 in $CHCl_3$);

$^1$H NMR δ 7.40 (m, 5H), 4.82 (s, 2H), 4.47 (t, 1H, *J* = 4.8 Hz), 4.20 (t, 1H, *J* = 6.0 Hz), 3.99 (dt, 1H, *J* = 4.5, 9.9 Hz), 3.80 (t, 1H, *J* = 9.9 Hz), 3.68 (dd, 1H, *J* = 6.3, 10.5 Hz), 3.41 (t, 1H, 9.9 Hz), 2.33 (dd, 1H, *J* = 2.7, 9.0);

$^{13}$C NMR δ 138.04, 128.19 x 2, 127.93 x 2, 127.34, 112.34, 109.94, 81.27, 80.27, 78.40, 77.81, 77.57, 71.92, 69.74, 27.74, 26.96 x 2, 25.82.

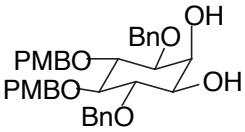



$[\alpha]_D$ = + 4.8 (*c* 1.0 in $CHCl_3$);

$^1$H NMR δ 7.35 (m, 10H), 4.92, 4.67 (AB q, 2H, *J* = 11.6 Hz), 4.77 (s, 2H), 4.28 (t, 1H, *J* = 4.2 Hz), 4.06 (dd, 1H, *J* = 6.6, 5.4 Hz), 3.92 (t, 1H, *J* = 9.4 Hz), 3.52 (m, 2H), 3.35 (t, 1H, *J* = 9.6 Hz), 2.96 (s, 1H), 2.92 (s, 1H), 1.48 (s, 3H), 1.33 (s, 3H);

$^{13}$C NMR δ 138.09, 137.80, 128.46, 128.33, 128.06, 127.98, 127.72, 109.88, 81.92, 79.18, 76.95, 73.99, 73.28, 72.96, 72.60, 71.51, 27.98, 25.90;

Anal. calcd. for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05; Found: C, 69.01 ; H, 6.93.



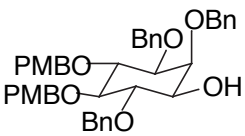

m.p. 126-128 ºC;

$[\alpha]_D$ = -32.2 (*c* 2.5 in $CHCl_3$);

$^1$H NMR δ 7.34-7.21 (m, 14H), 6.86 (d, 2H, *J* = 8.4 Hz), 6.82 (d, 2H, *J* = 8.4 Hz), 4.95 (d, 1H, *J* = 11.4 Hz), 4.87-4.70 (m, 7H), 4.17 (m, 1H), 3.94 (t, 1H, *J* = 9.6 Hz), 3.81 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.44 (m, 3H), 2.58 (s, 1H), 2.50 (s, 1H);

$^{13}$C NMR δ 159.39, 138.75, 138.05, 131.08, 130.94, 129.81, 129.68, 128.80, 128.74, 128.17, 128.13, 128.08, 114.01, 83.20, 81.65, 81.52, 80.27, 75.85, 75.79, 75.61, 72.96, 71.94, 69.93, 55.50;

Anal. calcd. for $C_{36}H_{40}O_8$: C, 71.98; H, 6.71; Found: C, 71.64 ; H, 6.88.

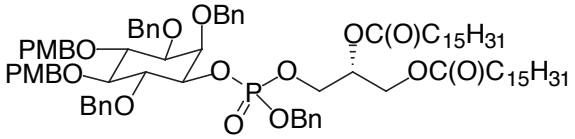


$[\alpha]_D$ = -13.9 (*c* 3.4 in $CHCl_3$);

$^1$H NMR δ 7.33-7.22 (m, 19H), 6.86 (d, 2H, *J* = 8.4 Hz), 6.82 (d, 2H, *J* = 8.4 Hz), 4.98 (d, 1H, *J* = 11.4 Hz), 4.90-4.69 (m, 9H), 4.03 (m, 2H), 3.81 (s, 1H), 3.79 (s, 6H), 3.45 (m, 3H), 2.19 (d, 1H, *J* = 6.0 Hz);

$^{13}$C NMR δ 159.10, 138.68, 138.59, 138.25, 130.93, 130.83, 129.61, 129.41, 128.44, 128.38, 128.27, 127.97, 127.71, 127.62, 127.52, 113.76, 113.71, 83.30, 82.14, 81.62, 81.12, 76.98, 75.49, 75.46, 74.65, 72.93, 72.33, 55.22;

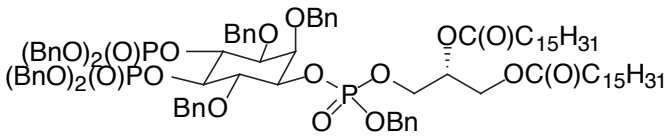
Anal. calcd. for $C_{43}H_{46}O_8$: C, 74.76; H, 6.71; Found: C, 74.61 ; H, 6.78.




$^1$H NMR δ 7.36-7.15 (m, 24H), 6.86 (d, 2H, *J* = 8.4 Hz), 6.82 (d, 2H, *J* = 8.4 Hz), 5.10-4.64 (m, 13H), 4.32 (m, 1H), 4.24-3.91 (m, 7H), 3.78 (s, 3H), 3.77 (s, 3H), 3.45 (m, 2H), 2.21 (m, 4H), 1.54 (m, 5H), 1.24 (br, 47H), 0.88 (t, 6H, *J* = 6.9 Hz);

$^{31}$P NMR δ -1.07 (major), -1.12 (minor);

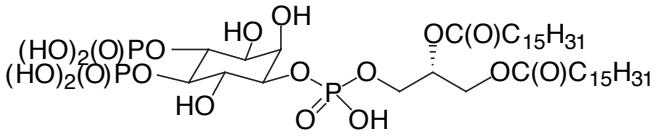
Anal. calcd. for $C_{85}H_{119}O_{15}P$ (1411.82) C, 72.31; H, 8.50; Found: C, 72.34 ; H, 8.46.




$^1$H NMR δ 7.34-6.94 (m, 40H), 5.09-4.50 (m, 19H), 4.34 (m, 1H), 4.29-3.73 (m, 6H), 3.52 (dd, 1H, *J* = 17.7, 8.7 Hz,), 2.21 (m, 4H), 1.54 (m, 4H), 1.25 (br, 48H), 0.88 (t, 6H, *J* = 6.3 Hz);

$^{31}$P NMR δ -1.00, -1.22, -1.35 (0.5 P), -1.40 (0.5 P).

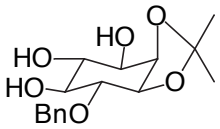
**PI(4,5)$P_2$**




$^1$H NMR ($CDCl_3$/$CD_3OD$ 1/1 v/v, TMS) δ 5.35 (m, 1H), 4.60 (m, 1H), 4.40 (dd, *J* = 12.0, 3.0 Hz), 4.29-4.12 (m, 7H), 3.72 (d, 1H, *J* = 7.8 Hz), 2.42 (q, 4H, *J* = 7.8 Hz), 1.70 (m, 4H), 1.45 (br s, 48H), 0.97 (t, 6H, *J* = 6.9 Hz);

$^{31}$P NMR ($d_6$-DMSO) δ 1.74, 1.06, –0.81.

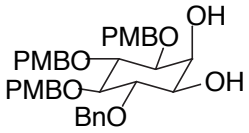
**Section III**: Spectral data for the intermediates for the preparation of **PI(3,4,5)$P_3$**:



$[\alpha]_D$ = -18.0 (*c* 1.13 in $CHCl_3$);

$^1$H NMR δ 7.40-7.20 (m, 5H), 4.79 (AB q, 2H, *J* = 11.7 Hz), 4.72 (br s, 1H), 4.29 (t, 1H, *J* = 4.2 Hz), 4.08 (t, 1H, *J* = 6.0 Hz), 4.00 (br s, 1H), 3.81 (br s, 1H), 3.64-3.78 (m, 2H), 3.48 (dd, 1H, *J* = 9.6, 7.1 Hz), 3.36 (t, 1H, *J* = 8.4 Hz), 1.43 (s, 3H), 1.34 (s, 3H);

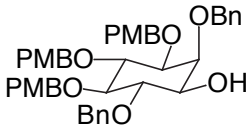
$^{13}$C NMR δ 138.11, 128.27, 128.04, 127.66, 109.89, 82.39, 79.16, 76.12, 73.26, 72.86, 72.24, 70.15, 27.97, 26.03.




$[\alpha]_D$ = -25.0 (*c* 1.07 in $CHCl_3$);

$^1$H NMR δ 7.40-7.20 (m, 11H), 6.90-6.80 (m, 6H), 5.00-4.60 (m, 8H), 4.18 (br s, 1H), 3.95 (t, 1H, *J* =9.3 Hz), 3.87-3.81 (m, 1H), 3.84 (s, 6H), 3.83 (s, 3H), 3.50-3.43 (m, 3H), 2.59 (br s, 1H), 2.50 (d, 1H, *J* =4.2 Hz);

$^{13}$C NMR: δ 159.36, 159.13, 138.52, 130.90, 130.72, 129.89, 129.51, 129.49, 129.42, 128.52, 127.87, 127.80, 113.88, 113.77, 113.75, 82.95, 81.42, 81.28, 79.72, 75.53, 75.34, 72.38, 71.72, 69.17, 55.24.

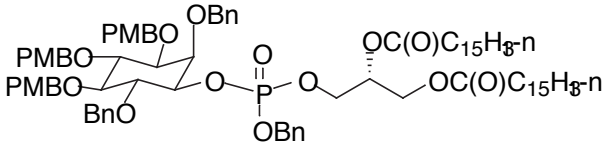



$[\alpha]_D$ = -10.9 (*c* 0.75 in $CHCl_3$);

$^1$H NMR δ 7.40-7.20 (m, 16H), 6.90-6.80(m, 6H), 5.00-4.60 (m, 10H), 4.02 (t, 1H, *J* = 9.6 Hz), 3.98 (d, 1H, *J* = 2.4 Hz), 3.81 (s, 3H), 3.79 (s, 6H), 3.77 (m, 1H), 3.47-3.40 (m, 3H), 2.20 (br d, 1H, *J* =5.1 Hz);

$^{13}$C NMR δ 159.18, 159.11, 138.73, 138.62, 131.01, 130.87, 130.36, 129.60, 129.43, 129.22, 128.45, 128.28, 127.98, 127.72, 127.53, 113.79, 113.77, 113.72, 83.32, 82.15, 81.63, 80.85, 77.13, 75.46, 75.40, 74.66, 72.63, 72.35, 55.24;

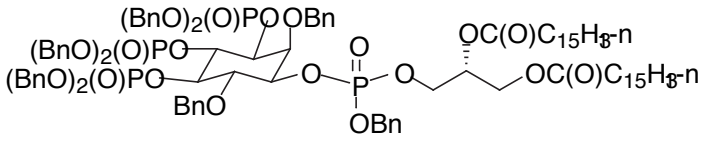
Anal. calcd. for $C_{44}H_{48}O_9$: C, 73.31; H, 6.67; Found: C, 73.04 ; H, 6.40.




$^1$H NMR δ 7.40-7.10 (m, 21H), 6.90-6.76 (m, 6H), 5.10-4.50 (m, 13H), 4.35-3.81 (m, 8H), 3.80 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.50-3.36 (m, 2H), 2.30-2.10 (m, 4H), 1.60-1.50 (m, 4H), 1.24 (br s, 48H), 0.88 (t, 6H, *J* = 6.0 Hz);

$^{31}$P NMR δ -1.14 (major), -1.17 (minor).

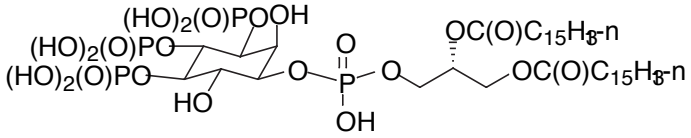
Anal. calcd. for $C_{86}H_{121}O_{16}P$ (1441.85) : C, 71.64; H, 8.46; Found: C, 71.65 ; H, 8.58.




$^{1}$H NMR δ 7.36-6.95 (m, 45H), 5.05-3.64 (m, 29H), 2.28-2.10 (m, 4H), 1.65-1.45 (m, 4H), 1.25 (br s, 48H), 0.88 (t, 6H, *J* =6.3 Hz);

$^{31}$P NMR δ -0.66, -0.87, -1.05, -1.16 (minor), -1.20 (minor), -1.39, -1.42 (minor).

**PI(3,4,5)P$_3$**:




$^{1}$H NMR ($CDCl_3$/$CD_3OD$ 1/1 v/v, TMS) δ 5.26 (m, 1H), 4.40 (m, 2H), 4.30-4.00 (m, 8H), 2.35 (q, 4H, *J* = 7.8 Hz), 1.70 (br s, 4H), 1.45 (br s, 48H), 0.97 (t, 6H, *J* = 6.9 Hz);

$^{31}$P NMR ($d_6$-DMSO) δ 0.54, 0.27, –0.19, –0.95.