Highly Flexible Synthetic Routes to Functionalized Phospholanes from Carbohydrates

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Highly functionalized phospholanes **15**, **17**, and **26** and the corresponding diastereomers in which the configurations of the phospholane carbon-2 and carbon-5 are inverted can be readily prepared from D-mannitol by displacement of the appropriate dimesylate or cyclic sulfate with dilithium-phosphide reagents. The diols from which these ligands are prepared can also be converted into diarylphosphinite ligands. A route to related monophosphines bearing hemilabile *tert*-butylthio groups is also described. Complexes of these ligands and of related deprotected derivatives are potentially useful for enantioselective catalysis in organic and aqueous media.

Introduction

Carbohydrates with their rich array of stereochemical and functional group diversity have been a popular source of starting materials in organic synthesis. Many mono- and disaccharides are abundantly available in 100% enatiomeric purity, and there is a prolific history of functional group manipulations that dates back to more than a century of carbohydrate chemistry. It is therefore surprising that they have attracted broad attention as ligand precursors for asymmetric catalysis only recently.[1] In previous work from our laboratories, we have shown that carbohydrate-derived diarylphosphinite complexes of transition metals catalyze a wide variety of C−C and C−H bond forming reactions[2] including hydrogenation (Rh), hydroformylation (Rh), hydrocyanation (Ni), hydrovinylation (Ni), and allylation reactions (Ni and Pd). The modular construction of these ligands renders them amenable to electronic and steric tuning, and unprecedented enantioselectivity has been achieved in hydrocyanation and hydrovinylation reactions. One salient property of these complexes that has not been fully exploited is the polyhydroxylic nature of their deprotected derivatives, which should make them water-soluble.[3] Such complexes can now be used as catalysts for organic reactions in water, which can serve as an environmentally friendly solvent if certain stringent criteria for solubility of the products and catalyst can be met. Ideally, water-soluble contaminants and side products should be avoided, and the product(s) should be soluble in an organic medium, and the catalyst, in the aqueous medium. Under these circumstances, the water-soluble catalyst can be separated and reused in subsequent cycles.[4] Yet another approach is the use of supported aqueous phase catalysts.[5] In either of these cases, a catalyst with a very high partition coefficient between water and the appropriate organic solvent is *one of the most critical* components if catalyst recovery is desired.

Pioneering studies by the Selke/Oehme groups[6] have shown that vicinal diarylphosphinite-Rh complexes derived from glucose (**1**) can be used for the asymmetric hydrogenation of acetamidoacrylic acid derivatives in water. Very high enantioselectivities can be obtained, especially in the presence of micelle-forming amphiphiles. The high selectivities of these reactions notwithstanding, anecdotal evidence suggests that the monosaccharide diarylphosphinite ligands have only solubility in water, and quantitative recovery/reuse of the catalyst could be problematic. In an approach to circumvent this problem, we[7] and others[8] have resorted to preparing the vicinal diarylphosphinite complexes (e.g., **2**) from a disaccharide,

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(2) (a) Ni-catalyzed hydrocyanation: Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869. (b) Rh-catalyzed hydrogenations: RajanBabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101. RajanBabu, T. V.; Ayers, T. A.; Halliday, G. A.; You, K. K.; Calabrese, J. C. *J. Org. Chem.* **1997**, *62*, 6012. See also: Kumar, A.; Oehme, G.; Roque, J. P.; Schwarze, M.; Selke, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2197 and references therein. (c) Hydroformylation: RajanBabu, T. V.; Ayers, T. A. *Tetrahedron Lett.* **1994**, *35*, 4295. (d) Hydrovinylation: Park, H.; RajanBabu, T. V. Unpublished results. (e) Pd-catalyzed allylation: Nomura, N.; Mermet-Bouvier, Y. C.; RajanBabu, T. V. *Synlett* **1996**, 745. Clyne, D.; Mermet-Bouvier, Y. C.; Nomura, N.; RajanBabu, T. V. *J. Org. Chem.* **1999**, *64*, 7601. See also: Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gagné, M. R. *J. Org. Chem.* **1999**, *64*, 2994.

(3) For recent reports dealing with the use of carbohydrates for solubilizing organometallic complexes, see: (a) Mitchell, T. N.; Heesche-Wagner, K. *J. Organomet. Chem.* **1992**, *436*, 43. (b) Sawamura, M.; Kitayama, K.; Ito, Y. *Tetrahedron: Asymmetry* **1993**, *4*, 1829. (c) Beller, M.; Krauter, J. G. E.; Zapf, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 772.

(4) (a) Sinou, D. *Bull. Soc. Chim. Fr.* **1986**, 480. (b) Herrmann, W. A.; Kohlpaintner, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (b) Horváth, I. T.; Joó, F. *Aqueous Organometallic Chemistry and Catalysis*; Horváth, I. T., Joó, F., Eds.; Kluwer: Dodrecht, 1995.

(5) (a) Wan, K. T.; Davis, M. E. *Nature* **1994**, *370*, 449. (b) Choplin, A.; Santos, S. D.; Quignard, F.; Sigismondi, S.; Sinou, D. *Catal. Today* **1998**, *42*, 471.

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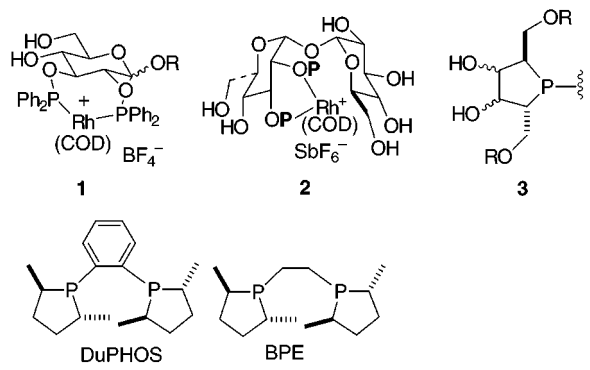
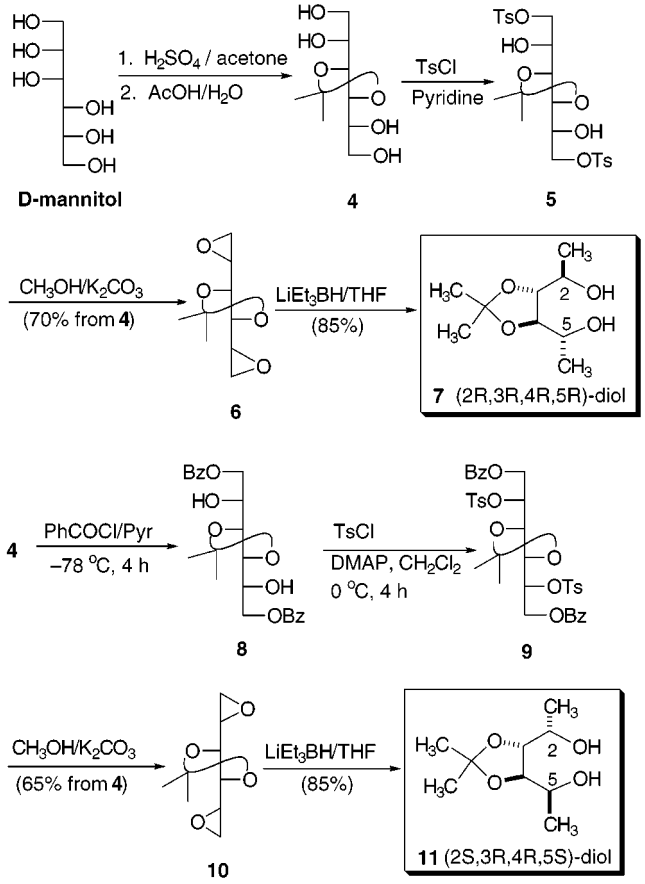
trehalose, with the expectation that the increased number of hydroxyl groups would improve the water solubility. While these studies[8] have shown that with the right glycoside (in this case, the β,β-isomer of trehalose) outstanding enantioselectivity can be achieved, the distribution coefficient for the cationic rhodium complexes between water and organic solvents (determined by the ion-coupled plasma method) is too low to be of practical value.[7] Yet another potential problem with phosphinites could be their long-term hydrolytic instability due to the presence of the P−O bond. As a solution to these problems, we envisioned the design of polyhydroxy *phosphine* ligands (viz., with only P−C bonds) with less hydrophobic P-substituents compared to the commonly encountered P-aryl groups. The P−C bonds in these ligands should be considerably more stable in an aqueous medium.[9] For our initial studies, we chose the C_2-symmetric phospholane system (**3**), which forms the backbone of the enormously successful DuPHOS and bisphospholanoethane (BPE) series of ligands discovered by Burk and co-workers.[10,11] In view of the flurry of activity in this area, most notably from the groups of Börner, Brown, and Zhang, in this paper we report our preliminary findings on a highly versatile route for the synthesis of two classes of appropriately protected C_2-symmetric phospholanes from D-mannitol.[12]



Results and Discussion

We considered the diol **4** as a key intermediate in our synthetic planning (Scheme 1). Depending on the specific sequence of reactions that follow, two diastereomeric bis-

Scheme 1. Synthesis of Diol Precursors from D-Mannitol[13,14]



epoxides **6** and **10** can be prepared. These can be further elaborated into diols **7** and **11**, respectively, via known chemistry.[13] The epoxides **6** and **10** could also serve in the future as electrophiles for copper-mediated ring-opening[14] from which a variety of 1,4-diols can be prepared, allowing sufficient flexibility in steric tuning of the final phospholane ligands (vide infra). In the event, the epoxides were reduced with superhydride in THF to the diols **7** and **11**.

Each of the diols was separately transformed into a number of ligands via the intermediate dimesylates or the cyclic sulfates (Scheme 2). Reaction of **11** with methanesulfonyl chloride in pyridine gave in 97% yield the mesylate **12**, which is a key intermediate for the synthesis of a number of phosphine ligands (Scheme 3). Alternatively, the diol can be transformed into a cyclic sulfate **14**, which can also be used for phospholane synthesis. Two other ligands that are readily prepared from the diol and the respective diarylchlorophosphines are the 1,4-diarylphosphinites **13a** and **13b**.

The mesylate **12** is a versatile intermediate that reacts with various phosphide reagents to give the phospholanes **15** and **17** (Scheme 3). In these reactions, it is important to keep the temperatures low, and to carefully monitor the reaction, to obtain reasonable yields of the product.[15] The ligands were purified by careful column chromatography in an inert atmosphere, and in most cases analyti-

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(11) For other modifications of the bisphospholane scaffolding, see: (a) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 3836. (b) Vedejs, E.; Daugulis, O. *J. Am. Chem. Soc.* **1999**, *121*, 5813.

(12) While our studies were in progress, a number of reports dealing with the synthesis of functionalized bisphospholanes have appeared. (a) Holz, J.; Quirmbach, M.; Schmidt, U.; Heller, D.; Stürmer, R.; Börner, A. *J. Org. Chem.* **1998**, *63*, 8031. (b) Carmichael, D.; Doucet, H.; Brown, J. M. *J. Chem. Soc., Chem. Commun.* **1999**, 261. (c) Li, W.; Zhang, Z.; Xiao, D.; Zhang, X. *Tetrahedron Lett.* **1999**, *40*, 6701. (d) Holz, J.; Heller, D.; Stürmer, R.; Börner, A. *Tetrahedron Lett.* **1999**, *40*, 7059. The earliest report in this area, which appeared in 1992, has received no mention in subsequent papers: Hitchcock, P. B.; Lappert, M. F. Yin, P. *J. Chem. Soc., Chem. Commun.* **1992,** 1598.

(13) Le Merrer, Y.; Duréault, A.; Greck, C.; Micas-Languin, D.; Gravier, C.; Depezay, J.-C. *Heterocycles* **1987**, *25*, 541.

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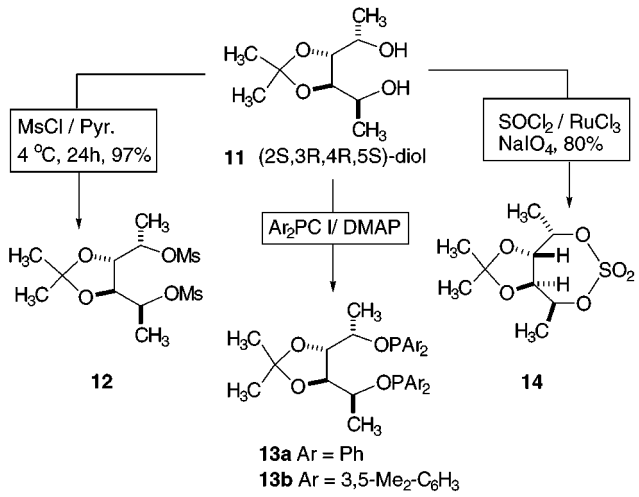
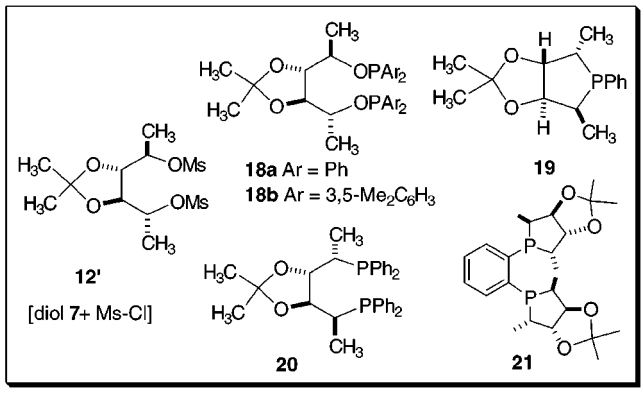
(15) See Experimental Section for details.

Scheme 2. Sulfonate, Phosphinite, and Sulfate Precursors from a 1,4-Diol



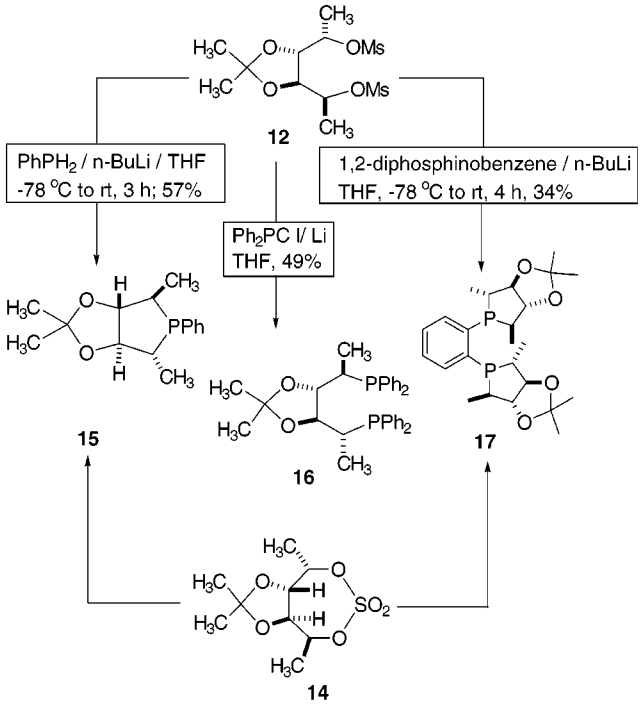
cally pure ligands could be obtained. The mesylate reacts with 2 equiv of lithium diphenylphosphide to give **16**, an analogue of the well-known DIOP (2,2-dimethyl-1,3-dioxalane-4,5-diylbismethylene)bisdiphenylphosphine) ligand.[16] The monophosphine **15** and the diphosphine **17** can also be prepared by the recipe originally prescribed by Burk using the cyclic sulfate **14**.

The diastereomeric diol **7** readily forms the mesylate **12′**, which is useful for the synthesis of a new set of ligands **19**, **20**, and **21**. Dimethyl DIOP analogue **20** has been described in the literature.[17] 1,4-Bis-diarylphosphinites **18a** and **18b** are also readily prepared from **7**.



Yet another application of this chemistry is in the synthesis of "hemilabile" ligands containing the phospholano moiety. It has been known for some time that the use of hemilabile ligands can improve the efficiency and selectivity of certain transition-metal-catalyzed reactions.[18] Selectivities of many allylation and Heck-type reactions catalyzed by Pd(0) complexes are also improved by judicious choice of unsymmetrical ligands carrying P/N, N/S, or P/S chelating atoms.[19] Synthesis of a phospholane ligand **26** carrying a potentially hemilabile *tert*-butylthioether functionality at the γ−position is shown in Scheme 4. The anticipated problem with the benzylic sulfur in the Pd-catalyzed P−C bond formation did not materialize, and we expect this scheme to be generally applicable for the synthesis of phospholane ligands bearing other hemilabile atoms. Dimesylate derived from alcohol **7** likewise yielded the ligand **27**.

Scheme 3. Utility of a Dimesylate and a 1,4-Cyclic Sulfate for the Synthesis of Mono- and Diphosphine Ligands



In summary, we have discovered a versatile route for the synthesis of various functionalized mono and bis-phospholane ligands. The starting materials are readily available, and the transformations highly diastereoselective, ensuring enantiomeric purity of the final products. The synthetic scheme is characterized by sufficient flexibility to allow fine tuning of the final phospholane ligands. Utility of these ligands in asymmetric catalysis and also for the synthesis of water-soluble transition-metal catalysts will be reported in due course.[20]

Experiemental Section

General. All anaerobic reactions were carried out an inert atmosphere of nitrogen in a Vacuum Atmospheres drybox, or

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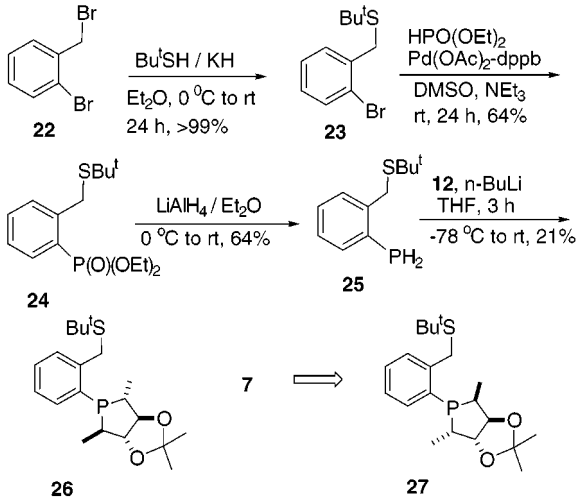
(20) **Note added in proof:** Applications of these ligands for a prototypical Pd(0)-catalyzed allylation (yields up to 99% and ee's >99% in selected cases) have been reported. Yan, Y.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 199.

Scheme 4. Synthesis of a Phospholane with a Hemilabile Thioether



using Schlenk techniques. Methylene chloride was distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen from sodium/benzophenone ketyl. All chemicals were purchased from Aldrich Chemical Co. unless otherwise noted. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted by using silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). ^{1}H NMR spectra were recorded in $CDCl_3$ unless otherwise mentioned. Gas chromatographic analyses were performed using HP-ultra-1 cross-linked methyl silicone capillary column (25 m length × 0.2 mm i.d.).

1,6-Dideoxy-3,4-*O*-isopropylidene-D-mannitol (7). To an oven-dried 250 mL flask was introduced 68 mL of a 1.0 M solution in THF of $LiEt_3BH$, followed by 4.22 g (22.66 mmol) of the diepoxide **6** in 40 mL of THF at 0 °C (ice bath). After the mixture was stirred at room temperature for 2 h, the excess hydride was decomposed with water and the organoborane was oxidized with H_2O_2 (15 mL of 30% aqueous solution) and NaOH (15 mL of 3 N aqueous solution) at 0 °C for 1 h. Then the THF layer was separated, and the aqueous layer was extracted with diethyl ether−hexane (1:1, v/v). The combined organic extract was washed with sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. Column chromatography (silica gel; 1:3 of ethyl acetate:hexanes) gave 3.66 g (85%) of **7**.[14] ^{1}H NMR ($CDCl_3$): δ 1.28 (d, J = 6.1 Hz, 6 H), 1.35 (s, 6 H), 3.56 (m, 2 H), 3.72 (m, 2 H), 4.21 (s, 2 H). ^{13}C NMR (CD_3OD): δ 20.41, 26.81, 69.19, 84.20, 108.73.

1,6-Dideoxy-3,4-*O*-isopropylidene-L-iditol (11). The title compound was prepared by a route similar to the previous experiment. To an oven-dried 250 mL flask was introduced 53 mL of a 1.0 M solution in THF of $LiEt_3BH$, followed by 3.275 g (17.58 mmol) of diepoxide (**10**)[13] in 40 mL of THF at 0 °C (ice bath). After the mixture was stirred at room temperature for 2 h, the excess hydride was decomposed with water and the organoborane was oxidized with H_2O_2 (10 mL of 30% aqueous solution) and NaOH (10 mL of 3 N aqueous solution) at 0 °C for 1 h. Then the THF layer was separated, and the aqueous layer was extracted with diethyl ether−hexane (1:1, v/v). The combined organic extracts were washed with sodium bicarbonate solution, dried ($MgSO_4$), and evaporated. Column chromatography (silica gel; 1:3 of ethyl acetate:hexanes) gave 2.847 g (85%) of the expected product. ^{1}H NMR ($CDCl_3$): δ 1.21 (d, J = 6.4 Hz, 6 H), 1.40 (s, 6 H), 2.39 (m, 2 H), 3.72 (m, 2 H), 3.77 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 20.01, 27.36, 66.97, 81.25, 109.33.

(2*S*,3*S*,4*S*,5*S*)-2,5-Di-*O*-methanesulfonyl-3,4-*O*-isopropylidenehexanetetraol (1,6-Dideoxy-3,4-*O*-isopropylidene-L-iditol Dimethanesulfonate) (12). To a solution of 0.44 g (2.3 mmol) of the diol **11** in 8 mL of pyridine was added 1.0 mL (5.5 equiv) of methanesulfonyl chloride. The mixture was stirred at 0 °C for 2 h and was kept in the refrigerator overnight. The mixture was poured into 30 mL of ice-cold water and extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were successively washed with 20 mL each of 3 N HCl and saturated NaCl solution and dried with anhydrous $MgSO_4$. Removal of the solvent on the evaporator gave the crude product, which was purified by chromatography eluting with ethyl acetate/hexane (3:7), to give 0.779 g (97%) of the dimesylate (**12**). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 6 H), 1.46 (d, J = 10.0 Hz, 6 H), 3.04 (s, 6 H), 4.00 (m, 2H), 4.81 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 17.69, 26.79, 38.60, 76.19, 78.14, 110.19.

1,6-Dideoxy-3,4-*O*-isopropylidene-D-mannitol Dimethanesulfonate (12′). To a solution of 0.76 g (4.0 mmol) of diol **7** in 10 mL of pyridine was added 1.5 mL (5 equiv) of methanesulfonyl chloride. The mixture was stirred at 0 °C for 2 h and kept in the refrigerator overnight. The mixture was poured into 30 mL of ice-cold water and extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were successively washed with 20 mL of 3 N HCl and saturated NaCl solution and dried with anhydrous $MgSO_4$. Removal of the solvent on the evaporator gave the crude product, which was purified by column chromatography on silica gel (elution with ethyl acetate/hexane 3:7) to give 1.29 g (93%) of the dimesylate **12′**. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 6 H), 1.49 (d, J = 6.4 Hz, 6 H), 3.07 (s, 6 H), 4.03 (m, 2 H), 4.81 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 17.28, 27.01, 38.77, 78.02, 80.01, 111.20.

1,6-Dideoxy-3,4-*O*-isopropylidene-L-iditol Bis(diphenylphosphinite) (13a). In a drybox, to a stirring solution of 0.285 g (1.498 mmol) of **11** and 18 mg of DMAP in 5 mL of pyridine was added 0.727 g (2.2 equiv) of chlorodiphenylphosphine in 5 mL of CH_2Cl_2. After stirring overnight, the mixture was filtered and concentrated. The residue was purified by flash chromatography eluting with ether/hexane (1:9), to obtain 0.553 g (66%) of (**13a**). ^{1}H NMR ($CDCl_3$): δ 1.26 (d, J = 6.4 Hz, 6 H), 1.39 (s, 6 H), 3.96 (m, 2 H), 4.03 (m, 2 H); 7.34 (m, 12 H); 7.50 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 18.68 (d, J = 5.1 Hz), 27.37, 75.67 (d, J = 19.5 Hz), 80.08 (d, J = 6.5 Hz) 109.43, 128.12, 128.18, 128.25, 128.99, 129.36, 130.01, 130.22, 130.81, 131,03, 142.08 (d, J = 17.5 Hz), 142.76 (d, J = 16.2 Hz). ^{31}P NMR ($CDCl_3$): δ 112.54. Elemental analysis for $C_{33}H_{36}O_4P_2$. Calcd: C, 70.96; H, 6.50. Found: C, 71.22; H, 6.68.

1,6-Dideoxy-3,4-*O*-isopropylidene-L-iditol Bis(3,5-dimethylphenyl)phosphinite (13b). In a drybox, to a stirring solution of 0.197 g (1.035 mmol) of (**11**) and 12 mg of DMAP in 4 mL of pyridine was added 0.633 g (2.2 equiv) of bis(3,5-dimethylphenyl)chlorophosphine in 4 mL of CH_2Cl_2. After stirring overnight, the mixture was filtered and concentrated. The residue was purified by flash chromatography eluting with ether/hexane (1:9) to give 0.295 g (42%) of (**13b**). ^{1}H NMR ($CDCl_3$): δ 1.29 (d, J = 6.3 Hz, 6 H), 1.48 (s, 6 H); 2.31 (s, 12 H), 2.33 (s, 12 H); 4.03 (m, 4 H), 7.05 (m, 4 H); 7.19 (s, 4 H), 7.21 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 18.76 (d, J = 5.0 Hz), 21.25, 21.29, 27.34, 75.11 (d, J = 19.8 Hz), 80.19 (d J = 6.5 Hz), 109.17, 127.62, 127.84, 128.42, 128.64, 130.70, 131.05, 137.40, 137.44, 137.46, 137.52, 141.81 (d, J = 17.1 Hz), 142.47 (d, J = 15.9). ^{31}P NMR ($CDCl_3$): δ 114.12 (s). Elemental analysis for $C_{41}H_{52}O_4P_2$. Calcd: C, 73.41; H, 7.81. Found: C, 72.66; H, 7.97.

1,6-Dideoxy-3,4-*O*-isopropylidene-L-iditol Cyclic Sulfate (14). The preparation of the cyclic sulfate is based upon the method used by Burk et al. to prepare similar compounds.[10b] The mixture that resulted by addition of 0.63 mL of thionyl chloride to a solution of 1.32 g (6.93 mmol) of (2*S*,3*R*,4*R*,5*S*)-diol **11** in 10 mL of CCl_4 was stirred under reflux for 1.5 h. After cooling, the solvent was evaporated to dryness in a rotary evaporator. The cyclic sulfite, obtained as a brown oil, was dissolved in 6 mL of CCl_4, 6 mL of CH_3CN, and 9 mL of H_2O. After cooling to 0 °C, 12.3 mg of $RuCl_3 \cdot 3H_2O$ and 2.95 g (13.7 mmol) of $NaIO_4$ were added with stirring. Two yellow layers formed, which gradually became black. Later, a yellow precipitate appeared, and the solution became yellow again. After the solution was stirred for 1 h, 40 mL of water and 20 mL of diethyl ether were added. The two layers were separated, and the aqueous phase was extracted with 3 × 20 mL of the ether. The combined organic extracts were washed with 2 × 10 mL of saturated aqueous solution of NaCl and dried over $MgSO_4$.

The solution was filtered through silica gel, and the volume was reduced to 3 mL. The addition of hexane (7 mL) and cooling to −10 °C afforded 1.40 g (80%) of **14** as a colorless, crystalline solid. ^{1}H NMR ($CDCl_3$): δ 1.35 (d, J = 6.0 Hz, 3 H), 1.40 (s, 3 H), 1.43 (s, 3 H), 1.59 (d, J = 6.2 Hz, 3 H), 3.63 (dd, J = 1.6, 8.2 Hz, 1 H), 4.23 (m, 1 H), 4.48 (dd, J = 1.6, 8.7 Hz, 1 H), 5.14 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 16.94, 17.33, 25.97, 27.28, 72.55, 78.19, 80.75, 84.51, 110.05.

(3a*S*,4*R*,6*R*,6a*S*)-Tetrahydro-2,2,4,6-tetramethyl-5-phenyl-4*H*-phospholo[3,4-*d*]-1,3-dioxole (15). To phenylphosphine (0.110 g, 1.0 mmol) in THF (10 mL) was added *n*-BuLi (0.88 mL of 2.5 M solution in hexane, 2.2 equiv) via syringe at −78 °C over 5 min. Then the orange solution was warmed to room temperature, and stirring was continued for 1 h. To the resulting yellow suspension was added a solution of dimesylate **12** (0.346 g, 1.0 mmol) in THF (5 mL) over 5 min, and the mixture was stirred for an additional 3 h at room temperature. A few drops of methanol were added to quench any excess BuLi. The solvent was distilled off. The residue was purified by flash chromatography on silica gel (elution with ether−hexane, 1:9, v/v, in the drybox) to obtain 0.150 g (57%) of monophosphine **15** as an oil. ^{1}H NMR ($CDCl_3$): δ 0.75 (dd, J = 6.9, 10.1 Hz, 3 H), 1.40 (dd, J = 6.8, 18.7 Hz, 3 H), 1.50 (s, 3 H), 1.52 (s, 3 H), 2.32 (m, 1 H), 2.66 (m, 1 H), 3.85 (m, 1 H), 3.98 (m, 1 H), 7.37 (m, 3 H), 7.58 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 12.81, 17.12 (d, J = 31.5 Hz), 27.46, 27.50, 29.15 (d J = 18.3 Hz), 30.15 (d, J = 12.9 Hz), 87.50 (d, J = 10.6 Hz), 88.83, 118.48, 128.17, 128.24, 129.38, 133.21 (d, J = 27.5 Hz), 134.51, 134.72. ^{31}P NMR ($CDCl_3$): δ 44.24 (s). Elemental analysis for $C_{15}H_{21}O_2P$. Calcd: C, 68.17; H, 8.01. Found: C, 67.92; H, 7.99.

(3a*S*,4*S*,6*S*,6a*S*)-Tetrahydro-2,2,4,6-tetramethyl-5-phenyl-4*H*-phospholo[3,4-*d*]-1,3-dioxole (19). To phenylphosphine (180 mg, 1.63 mmol) in THF (10 mL) was added *n*-BuLi (1.43 mL of 2.5 M solution in hexane, 2.2 equiv) via syringe at −78 °C over 5 min. Then the orange solution was warmed to room temperature, and stirring was continued for 1 h. To the resulting yellow suspension was added a solution of dimesylate **12′** (566.3 mg, 1.63 mmol) in THF (5 mL) over 5 min, and the mixture was stirred for 3 h at room temperature. A few drops of methanol were added to quench any excess BuLi. The solvent was distilled off. The residue was purified by flash chromatography on silica gel (elution with ether−hexane, 1:9, v/v, in the drybox) to give 0.217 g (50%) of monophosphine **19** as an oil. ^{1}H NMR ($CDCl_3$): δ 0.62 (t, J = 7.2 Hz, 3 H), 1.34 (dd, J = 7.5, 20.0 Hz, 3 H), 1.48 (s, 3 H), 1.50 (s, 3 H), 2.49 (m, 1 H), 2.62 (m, 1 H), 4.20 (m, 1 H), 4.52 (m, 1 H), 7.39 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 10.96 (d, J = 4.3 Hz), 13.54 (d, J = 30.4 Hz), 24.42 (d, J = 14.2 Hz), 25.44 (d, J = 20.2 Hz), 27.21, 27.25, 81.24 (d, J = 10 Hz), 81.55, 117.71, 128.22, 128.33, 128.70, 133.02, 133.34, 134.32 (d, J = 26.1 Hz). ^{31}P NMR ($CDCl_3$): δ 50.95 (s). Elemental analysis for $C_{15}H_{21}O_2P$. Calcd: C, 68.17; H, 8.01. Found: C, 67.87; H, 7.98.

Preparation of 15 via the Cyclic Sulfate 14. To phenylphosphine (0.083 g, 0.75 mmol) in THF (5 mL) was added *n*-BuLi (0.5 mL of 1.6 M solution in hexane) via syringe at −78 °C. Then the orange solution was warmed to room temperature, and stirring was continued for 1 h. To the resulting yellow suspension was added a solution of cyclic sulfate **14** (0.190 g, 0.75 mmol) in THF (5 mL), and the mixture was stirred for 2 h at room temperature. Then 1 equiv of *n*-BuLi (0.5 mL) was added dropwise at 0 °C, and the orange suspension was stirred for 3 h. A few drops of methanol were added to quench any excess BuLi. The solvent was distilled off. The residue was purified by flash chromatography on silica gel (elution with ether−hexane, 1:9, v/v, in the drybox) to obtain the monophosphine **15** as an oil, identical to the sample prepared earlier from the corresponding dimesylate **12**.

(3a*S*,3′a*S*,4*R*,4′*R*,6*R*,6′*R*,6a*S*,6′a*S*)-5,5′-*o*-Phenylene-bis[tetrahydro-2,2,4,6-tetramethyl-4*H*-phospholo[3,4-*d*]1,3-dioxole] (17). To a solution of 1,2-bis-phosphinobenzene (0.226 g, 1.59 mmol) in 10 mL of THF was added via syringe *n*-BuLi (2 mL of 1.6 M solution in hexane, 2.0 equiv) at −78 °C. The solution was warmed to room temperature and stirred for an additional 1 h. After the mixture was cooled to 0 °C, the dimesylate **12** (1.101 g, 3.18 mmol) was added, and the mixture was stirred for 2 h. Then 2.2 equiv of *n*-BuLi (2.2 mL) were added dropwise at 0 °C, and the orange suspension was stirred overnight. After 14 h, 8 mL of water was added to the suspension, and the THF layer was separated. The water phase was extracted with Et_2O (2 × 15 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The crude was purified by flash chromatography on silica gel (elution with ether−hexane, 5:95, v/v, in the drybox) to obtain 0.246 g (34%) of the diphosphine **17** as a white powder. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 6 H), 1.35 (m, 6 H), 1.50 (s, 6 H), 1.51 (s, 6 H), 2.44 (m, 2 H), 2.71 (m, 2H), 3.83 (m, 4 H), 7.44 (m 2 H), 7.71 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 15.23, 17.11 (t, J = 17.0 Hz), 27.52, 27.60, 28.98, 29.40 (t, J = 11.0 Hz), 86.74 (t, J = 7.0 Hz), 89.09, 118.39, 129.39, 132.70, 140.29. ^{31}P NMR ($CDCl_3$): δ 33.71 (s). Elemental analysis for $C_{24}H_{36}O_4P_2$. Calcd: C, 63.99; H, 8.05. Found: C, 62.76; H, 8.03.

(3a*S*,3′a*S*,4*S*,4′*S*,6*S*,6′*S*,6a*S*,6′a*S*)-5,5′-*o*-Phenylene-bis-[tetrahydro-2,2,4,6-tetramethyl-4*H*-phospholo[3,4-*d*]1,3-dioxole] (21). To a solution of 1,2-bis-phosphinobenzene (0.085 g, 0.6 mmol) in 5 mL of THF was added *n*-BuLi (0.8 mL of 1.6 M solution in hexane) via syringe at −78 °C. Then the solution was warmed to room temperature and was stirred for an additional 1 h. After the solution was cooled to 0 °C, a solution of (2*R*,3*S*,4*S*,5*R*)-3,4-*O*-isopropylidene-2,5-di-*O*-methanesulfonyloxyhexanediol (**12′**, 0.416 g, 1.2 mmol) in 4 mL of THF was added, and the mixture was stirred for 2 h. Then 2.2 equiv of *n*-BuLi (0.8 mL) were added dropwise at 0 °C, and the orange suspension was stirred overnight. After 14 h, 8 mL of water was added to the suspension, and the THF layer was separated. The water phase was extracted with Et_2O (2 × 15 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The crude was purified by flash chromatography on silica gel (elution with ether−hexane, 5:95, v/v, in the drybox) to obtain 0.081 g (30%) of the diphosphine **21** as a white powder. ^{1}H NMR ($CDCl_3$): δ 0.70 (m, 6 H), 1.31.(m, 6 H), 1.46 (s, 6 H), 1.49 (s, 6 H), 2.53 (m, 2 H), 2.86 (m, 2 H), 4.40 (m, 4 H), 7.35 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 12.14, 13.72 (t, J = 16.4 Hz), 24.16, 24.99 (t, J = 8.7 Hz), 27.28, 27.31, 80.47 (t, J = 5.5 Hz), 81.37, 117.41, 128.98, 130.56, 140.49 (t, J = 4.7 Hz). ^{31}P NMR ($CDCl_3$): δ 45.92 (s). Elemental analysis for $C_{24}H_{36}O_4P_2$. Calcd: C, 63.99; H, 8.05. Found: C, 62.00; H, 7.79.

Bisphospholane (17) from Cyclic Sulfate 14. To a solution of 1,2-bisphosphanobenzene (64 mg, 0.45 mmol) in 5 mL of THF was added *n*-BuLi (0.6 mL of 1.6 M solution in hexane, 2.0 equiv) via syringe at −78 °C. Then the solution was warmed to room temperature and stirred for an additional 1 h. After the mixture was cooled to 0 °C, the cyclic sulfate **14** (0.229 g, 0.9 mmol) was added, and the mixture was stirred for 2 h. Then 2.2 equiv of *n*-BuLi (0.7 mL) were added dropwise at 0 °C, and the orange suspension was stirred overnight. After 14 h, 8 mL of water was added to the suspension, and the THF layer was separated. The water phase was extracted with Et_2O (2 × 15 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The crude product was purified by flash chromatography eluting with ether−hexane (5:95, v/v, in the drybox) to obtain the diphosphine **17** as a white powder, identical in all respects to the sample prepared in the previous experiment.

[[(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]di(*R*)-ethylidene]bis[diphenylphosphine] (16). In 100 mL of Schlenk tube was charged 105 mg of lithium strips, 20 mL of anhydrous THF, and 1.433 g (6.49 mmol) of chlorodiphenylphosphine. The mixture was stirred at room temperature for 1 h. The excess of lithium strips was fetched out by a spatula. The resultant deep red solution was added to a solution of the dimesylate (**12**) (0.75 g, 2.16 mmol) in 10 mL of the same solvent over a period of 15 min at 0 °C. The mixture was stirred for 6 h at room temperature. The solvent was distilled off, and the residue was partitioned between 30 mL of CH_2Cl_2 and 20 mL of saturated and degassed NaCl solution. The organic phase was separated, and the water layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were worked-up to afford crude, which was purified by flash chromatography

on silica gel (elution with ether−hexane, 5:95, v/v, in the drybox) to give 0.561 g (49%) of the diphosphine **16** as a white powder. ^{1}H NMR ($CDCl_3$): δ 0.88 (d, J = 6.9 Hz, 3 H), 0.92 (d, J = 6.9 Hz, 3H), 1.36 (s, 6 H), 2.48 (m, 2 H), 3.78 (m, 2 H), 7.35 (m, 12 H), 7.54 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 10.51 (d, J = 17.2 Hz), 26.86, 31.07 (d, J = 13.9 Hz), 76.80 (t J = 6.1 Hz), 108.00, 128.26, 128.33, 128.85, 128.87, 133.49, 133.58, 133.69, 133.78, 136.20 (d, J = 15.0 Hz), 136.73 (d, J = 15.2 Hz). ^{31}P NMR ($CDCl_3$): δ −5.42 (s). Elemental analysis for $C_{33}H_{36}O_2P_2$. Calcd: C, 75.27; H, 6.89. Found: C, 75.36; H, 6.90.

[[(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]di(*S*)-ethylidene]bis[diphenylphosphine] (20). To a solution of diphenylphosphine (0.409 g, 2.2 mmol) in 10 mL of THF at 0 °C was added 0.9 mL of *n*-BuLi (2.5 M in hexane) dropwise. The mixture was stirred for 1 h at room temperature. To the resulting deep red solution was added a solution of (2*R*,3*S*,-4*S*,5*R*)-3,4-*O*-isopropylidene-2,5-di-*O*-methanesulfonyloxyhexanediol (**12′**, 0.416 g, 1.2 mmol) in 5 mL of THF. The mixture was stirred overnight at room temperature. After 14 h, 5 mL of water was added to the suspension, and the THF layer was separated. The water phase was extracted with Et_2O (2 × 10 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was distilled off under reduced pressure. The crude was purified by flash chromatography eluting with ether−hexane (5:95, v/v, in the drybox) to obtain 0.332 g (63%) of the diphosphine **20** as a white powder. ^{1}H NMR ($CDCl_3$): δ 1.16 (m, 6 H), 1.51 (s, 6 H), 2.95 (m, 2 H), 4.37 (m, 2 H), 7.31 (m, 12 H), 7.48 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 14.71 (d, J = 7.6 Hz), 27.37, 32.35 (dd, J = 5.8, 15.7 Hz), 80.84, 108.13, 127.81, 127.87, 127.93, 128.25, 128.36, 128.42, 133.00, 133.32, 133.97, 134.29, 136.63 (d, J = 3.4 Hz), 136.86 (d, J = 8.5 Hz). ^{31}P NMR ($CDCl_3$): δ −10.75 (s). Elemental analysis for $C_{33}H_{36}O_2P_2$. Calcd: C, 75.27; H, 6.89. Found: C, 75.13; H, 6.98.

2-[2-(2-Methylpropyl)thiomethyl]bromobenzene (23). To a solution of 2-methyl-2-propanethiol (2.5 mL, 22.2 mmol) in 100 mL of THF was slowly added KH (0.89 g, 1 equiv) at 0 °C, which was stirred for an additional 2 h. Then a solution of 2-bromobenzylbromide (5.0 g, 20 mmol) in 10 mL of THF was added. The suspension solution was stirred overnight at room temperature. After the solution was cooled to 0 °C, a saturated NH_4Cl solution (100 mL) was added, and the organic phase was separated. The water phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (elution with EtOAc/hexane, 4:96, v/v) to give 5.18 g (99$^+$%) of **23** as an oil. ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 9 H), 3.89 (s, 2 H), 7.08 (m, 1 H), 7.25 (m, 1 H), 7.44 (dd, J = 1.6, 7.6 Hz, 1 H), 7.53 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 30.79, 33.45, 43.16, 124.31, 127.49, 128.41, 130.98, 132.88, 137.83.

2-(*tert*-Butylthiomethyl)phosphinobenzene (25). To a mixture of **23** (3.00 g, 11.57 mmol), diethyl phosphite (3.19 g, 23.14 mmol), palladium diacetate (130 mg, 0.58 mmol), and 1,4-bis(diphenylphosphino)butane (247 mg, 0.58 mmol) were added 50 mL of dimethyl sulfoxide and diisopropylethylamine (5.98 g, 46.28 mmol), and the mixture was heated with stirring at 100 °C for 12 h. After the mixture was cooled to room temperature, the reaction mixture was concentrated under reduced pressure to give a dark brown residue. The residue was diluted with EtOAc, washed twice with water, dried over $MgSO_4$, and concentrated on the evaporator. The residue was chromatographed on silica gel (elution with EtOAc/hexane, 40:60, v/v) to give 2.34 g, 64%) of **24** as an oil. ^{1}H NMR ($CDCl_3$): δ 1.32 (t, J = 7.1 Hz, 6 H), 1.35 (s, 9 H), 4.12 (m, 6 H), 7.28 (m, 1 H), 7.46 (m, 1 H), 7.60 (t, J = 6.6 Hz, 1 H), 7. 86 (m, 1 H). ^{13}CNMR ($CDCl_3$): δ 16.26 (d, J = 6.5 Hz), 30.79, 30.87 (d, J = 3.8 Hz), 43.06, 62.07 (d, J = 5.5 Hz), 126.30 (d, J = 14.3 Hz), 126.51 (d, J = 183.4 Hz), 131.10 (d J = 14.1 Hz), 132.42 (d, J = 2.9 Hz), 133.83 (d, J = 9.6 Hz), 142.16 (d, J = 10. 1 Hz). ^{31}P NMR ($CDCl_3$): δ 20.03 (s).

A solution of **24** (0.418 g, 1.32 mmol) in 5 mL of Et_2O was added dropwise to an ice-cold suspension of $LiAlH_4$ (0.15 g, 3.96 mmol) in 10 mL of the same solvent under nitrogen. The mixture was stirred for 6 h at room temperature. The reaction was quenched by careful addition of 10 mL of H_2O (degassed). The organic layer was separated, and the aqueous phase was extracted with three 10 mL portions of Et_2O. The combined organic extracts were washed with saturated NaCl solution and dried over Na_2SO_4. Removal of the solvent afforded the crude, which was purified by flash chromatography on silica gel. Elution with hexane afforded 0.179 g (64%) of **25.** ^{1}H NMR ($CDCl_3$): δ 1.42 (s, 9 H), 3.62 (b s, 1 H), 3.97 (s, 2 H), 4.44 (b s, 1 H), 7.14 (t, J = 7.3 Hz, 1 H), 7.25 (ddd, J = 1.1, 7.4, 14.8 Hz, 1 H), 7.35 (dd, J = 1.5, 7.5 Hz, 1 H), 7.50 (t, J = 7.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 30.71, 33.44 (d, J = 11.7 Hz), 43.18, 126.95 (d, J = 4.1 Hz), 128.74, 129.18 (d, J = 10.0 Hz), 130.00 (d, J = 2.8 Hz), 136.26 (d, J = 9.6 Hz), 141.07 (d, J = 12.5 Hz). ^{31}PNMR ($CDCl_3$): δ −129.64 (s).

(3a*S*,4*R*,6*R*,6a*S*)-5-[α-(*tert*-Butylthio)-*o*-tolyl]-tetrahydro-2,2,4,6-tetramethyl-4*H*-phospholo[3,4-*d*]-1,3-dioxole (26). To a solution of **25 (**0.145 g, 0.68 mmol) in THF (5 mL) was added *n*-BuLi (0.9 mL of 1.6 M solution in hexane, 2.1 equiv) via syringe at −78 °C. Then the solution was warmed to room temperature and continued stirring for 1 h. To the resulting brownish solution was added a solution of dimesylate **12** (0.236 g, 0.68 mmol) in THF (3 mL), and the mixture was stirred for 3 h at room temperature. A few drops of methanol were added to quench any excess BuLi. The solvent was distilled off. The residue was purified by flash chromatography on silica gel (elution with ether−hexane, 1:9, v/v, in the drybox) to give 53 mg (21%) of **26** as an oil. ^{1}H NMR ($CDCl_3$): δ 0.85 (m, 3 H), 1.35 (m, 3 H), 1.37 (s, 9 H), 1.52 (s, 3 H), 1.55 (s, 3 H), 2.51 (m, 2 H), 3.88 (m, 1 H), 4.08 (m, 3 H), 7.28 (m, 2 H), 7.39 (m, 1 H), 7.67 (m, 1 H). ^{31}P NMR ($CDCl_3$): δ 28.17 (s).

(3a*S*,4*S*,6*S*,6a*S*)-5-[α-(*tert*-Butylthio)-*o*-tolyl]-tetrahydro-2,2,4,6-tetramethyl-4*H*-phospholo[3,4-*d*]-1,3-dioxole (27). This ligand was prepared in 24% yield by a similar route from the phosphine **25** and the dimesylate **12′**. ^{1}H NMR ($CDCl_3$): δ 0.70 (t, J = 7.1 Hz, 3 H), 1.32 (m, 3 H), 1.38 (s, 9 H), 1.50 (s, 6 H), 2.43 (m, 1 H), 2.68 (m, 1 H), 3.82 (dd, J = 1.7, 11.2 Hz, 1 H), 4.19 (dd, J = 4.2, 11.2 Hz, 1 H), 4.44 (dd, J = 4.4, 6.4 Hz, 1 H), 4.54 (m, 1 H), 7.26 (m, 2 H), 7.38 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 11.24 (d, J = 4.0 Hz), 14.10 (d, J = 33.3 Hz), 25.00 (d, J = 15.2 Hz), 26.66 (d, J = 19.4 Hz), 27.29, 27.33, 30.84, 32.44 (d, J = 27.5 Hz), 43.46, 80.95 (d, J = 12.3 Hz), 81.61, 117.42, 126.95, 129.13, 130.25 (d, J = 4.5 Hz), 132.28 (d, J = 2.4 Hz). ^{31}P NMR ($CDCl_3$): δ 39.45 (s).

1,6-Dideoxy-3,4-*O*-isopropylidene-D-mannitol Bis(diphenylphosphinite) (18a). In a drybox, to a stirring solution of 0.120 g (0.63 mmol) of **7** and 15 mg of DMAP in 4 mL of pyridine was added 0.306 g (2.2 equiv) of diphenylchlorophosphine in 3 mL of CH_2Cl_2. After stirring overnight, the mixture was filtered and concentrated. The residue was purified by flash chromatography on silica gel (elution with ether/hexane 1:9, v/v) to obtain 0.327 g (93%) of **18a** as an oil. ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J = 6.0 Hz, 6 H), 1.36 (s, 6 H), 4.12 (m, 4 H), 7.29 (m, 6 H), 7.36 (m, 6 H), 7.53 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 18.40 (d, J = 5.5 Hz), 27.82, 77.64 (d, J = 19.7 Hz), 82.11 (d, J = 7.5 Hz), 110.00, 128.10, 128.21, 129.09, 129.17, 130.21, 130.47, 130.57, 130.83, 141.84 (d, J = 16.1 Hz), 142.69 (d, J = 17.9 Hz). ^{31}P NMR ($CDCl_3$): δ 111.89 (s).

1,6-Dideoxy-3,4-*O*-isopropylidene-D-mannitol Bis(3,5-dimethylphenyl)phosphinite (18b). In a drybox, to a stirring solution of 0.120 g (0.63 mmol) of **7** and 15 mg of DMAP in 4 mL of pyridine was added 0.383 g (2.2 equiv) of bis(3,5-dimethylphenyl)chlorophosphine in 3 mL of CH_2Cl_2. After stirring overnight, the mixture was filtered and concentrated. The residue was purified by flash chromatography on silica gel (elution with ether/hexane 1:9, v/v) to give 0.186 g (44%) of **18b** as a white powder. ^{1}H NMR ($CDCl_3$): δ 1.33 (d, J = 5.5 Hz, 6 H), 1.37 (s, 6 H), 2.25 (s, 12 H), 2.27 (s, 12 H), 4.13 (m, 4 H), 6.93 (s, 2 H), 6.96 (s, 2 H), 7.16 (s, 4 H), 7.19 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 18.24 (d, J = 5.7 Hz), 21.20, 27.75, 77.29, 82.03 (d, J = 7.2 Hz), 109.75, 127.85, 128.02, 128.21, 128.38, 130.84, 130.92, 137.42, 137.54, 141.85 (d, J = 16.4 Hz), 142.51 (d, J = 17.0 Hz). ^{31}P NMR ($CDCl_3$): δ 112.75 (s).

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