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P-Heterocyclic Building Blocks: Application to the Stereoselective Synthesis of *P*-Sugars

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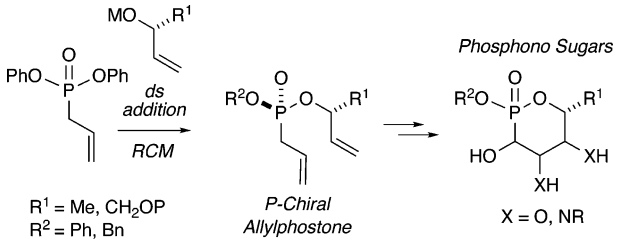

A strategy relying on the utilization of stereoselective additions to allyldiphenylphosphonate esters and subsequent ring-closing metathesis (RCM) to access *P*-chiral *P*-heterocyclic building blocks for the synthesis of phosphono sugars is described. These building blocks possess several attractive components, including the following: (i) P(2) and C(6) stereogenic centers for directing stereoselective transformations; (ii) an activated C(3) methylene group that promotes base-mediated olefin transposition to generate vinyl phosphonates available for further stereoselective reactions; and (iii) a P(2)-stereogenic center containing an exchangeable phosphonate ester armed to attenuate the "stereochemical environment" at phosphorus. Taken collectively, these attributes contribute to a concise method for the stereoselective synthesis of an array of *P*-sugars.

Carbohydrates offer excellent opportunities to exploit stereochemical diversity, since subtle changes in conformation, stereochemistry, and substituents at various positions are all known to illicit biological responses.[1] Recent interest in the development of new carbohydrate-based mimetics has focused on the development of scaffolds that can serve as effective biological probes and/or potential therapeutic agents.[1] A number of innovative synthetic approaches toward this goal have been undertaken,[2] including the development of new phosphorus-based sugars (*P*-sugars).[3] The emergence of *P*-sugars has resulted largely from previous successes with organophosphorus compounds,[4] in both drug[5] and agricultural[6] discovery programs. Most notably, recent successes with anomerically modified *P*-sugars[3f,3h] have validated their utility and warranted the continued screening of new derivatives. Overall, a multitude of *P*-sugar analogues have been constructed starting from naturally occurring

* Corresponding author.

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(2) (a) Kunz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 294−308. (b) Musser, J. H., Ed. Carbohydrates as Drug Discovery Leads. In *Annual Reports in Medical Chemistry*; Academic Press: New York, 1992; Vol. 27, pp 301−310. (b) Danishefsky, S. J.; Roberge, J. Y. *Pure Appl. Chem.* **1995**, *67*, 1647−1662.

(3) (a) Thiem, J.; Günther, M.; Paulsen, H.; Kopf, J. *Chem. Ber.* **1977**, *110*, 3190−3200. (b) Wróblewski, A. E. *Tetrahedron* **1986**, *42*, 3595−3606. (c) Molin, H.; Noren, J. O.; Claesson, A. *Carbohydr. Res.* **1989**, *194*, 209−221. (d) Darrow, J. W.; Drueckhammer, D. G. *J. Org. Chem.* **1994**, *59*, 2976−2985. (e) Hanessian, S.; Galeotti, N.; Rosen, P.; Oliva, G.; Babu, S. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2763−2768. (f) Darrow, J. W.; Drueckhammer, D. G. *Bioorg. Med. Chem.* **1996**, *4*, 1341−1348. (g) Harvey, T. C.; Simiand, C.; Weiler, L.; Withers, S. G. *J. Org. Chem.* **1997**, *62*, 6722−6725. (h) Hanessian, S.; Rogel, O. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2441−2446. (i) Hanessian, S.; Rogel, O. *J. Org. Chem.* **2000**, *65*, 2667−2674.

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(5) For examples of phosphorus compounds as pharmaceuticals, see: (a) Kafarski, P.; Lejczak, B. *Curr. Med. Chem.* **2001**, *1*, 301−312. (b) Colvin, O. M. *Curr. Pharm. Des.* **1999**, *5*, 555−560. (c) Zon, G. *Prog. Med. Chem.* **1982**, *19*, 205−246. (d) Stec, W. *J. Organophosphorus Chem.* **1982**, *13*, 145−174. (e) Mader, M. M.; Bartlett, P. A. *Chem. Rev.* **1997**, *97*, 1281−1301. (f) Kafarski, P.; Lejczak, B. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1991**, *63*, 193-215.

(6) For an example of a phosphorus-containing herbicide, see Franz, J. E.; Mao, M. K.; Sikorski, J. A. *Glyphosate: A Unique Global Herbicide*; American Chemical Society: Washington, DC, 1997.

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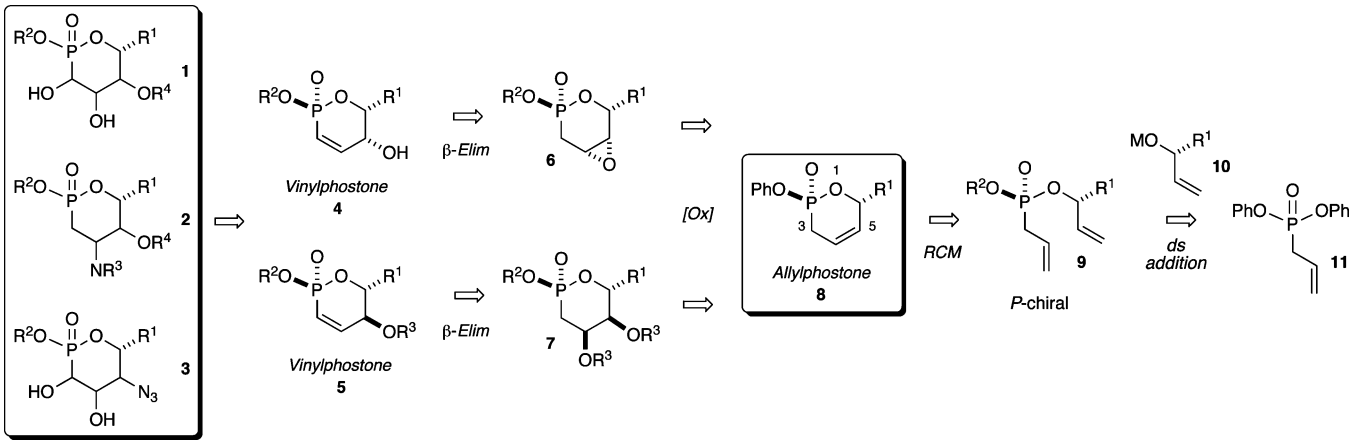
SCHEME 1



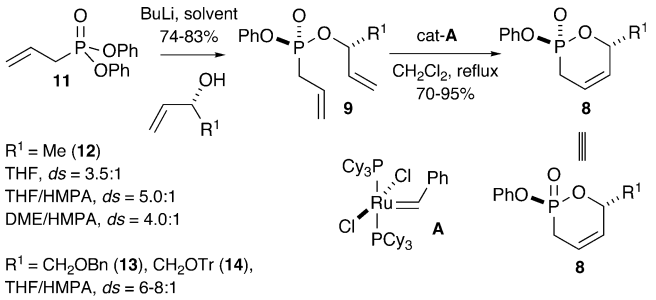
sugars.[3] These routes have mainly employed the Abramov reaction between preformed or commercially available sugar aldehydes and di- or trialkyl phosphites, followed by intramolecular transesterification of the resulting hydroxyphosphonates.[7,4b] As part of our program aimed at the development of synthetic routes to new *P*-heterocycles with biological and synthetic utility,[8] we herein report our continued efforts[9] for the synthesis of novel *P*-sugars.

Our approach hinges on routes emphasizing stereochemical diversity[10] and focuses on the production of a key *P*-chiral allylphostone building block **8**, using ring-closing metathesis (RCM),[9] to generate versatile epimeric vinylphostones **4** and **5**, respectively (Scheme 1). These vinylphostone substrates serve as diverse building blocks for the stereo-controlled synthesis of C(3)−C(5) *O*- and *N*-substituted *P*-sugars (**1**-**3**, Scheme 1). Several attractive features of scaffold **8** are worth mentioning: (i) P(2) and C(6) stereogenic centers (phostone numbering) for directing stereoselective transformations upon the olefin moiety subunit of **8**; (ii) an activated C(3) methylene group that promotes base-mediated olefin transposition to generate vinyl phosphonates **4** and **5** possessing P(2) and C(5) stereocenters for further stereoselective reactions; and (iii) a P(2)-stereogenic center containing an exchangeable phenyl phosphonate ester which allows for attenuation of the "stereochemical environment" at phosphorus. Overall, the method reported herein allows for the generation of an array of stereochemically rich phosphono sugars.

Results and Discussion

Our strategy begins with a stereoselective alkoxide addition of the readily available allylic alcohols **12**, **13**, or **14** to allyl diphenyl phosphonate (**11**) to derive dienes **9** (R^1 = CH_3, CH_2OBn, CH_2OTr) (Scheme 2). This

SCHEME 2



diastereoselective process, first introduced by Moriarty,[11] effectively differentiates the two enantiotopic phenyl esters of **11** (*ds* = 3.5−8:1, selectivities determined by ^{31}P NMR). This procedure has been shown to be successful with the commercially available racemic 3-butene-2-ol (**12**) to yield products possessing a 1,3-*trans*-relationship between the PhO- and Me-groups,[9] or more elaborate allylic alcohols **13** and **14** (vide infra). Subsequent RCM of acyclic precursors **9** using the 1st generation Grubbs metathesis catalyst (cat-**A**)[12] provides allyl phostones **8** in excellent yields.

Elaboration of allylphostone **15**, via the aforementioned stereo-divergent oxidation pathways, is outlined in Scheme 3. As previously reported,[9] both C(5) epimers are available from **15** by employing either OsO_4 or trifluoromethyl dioxirane. Dihydroxylation of substrate **15** provided diol **16a** in high stereoselectivity (*ds* = 15:1) in a process that adheres to the Donohoe/Kishi model,[13] whereby dihydroxylation occurs anti to the C(5) hydroxyl group.[9] Subsequent eliminative opening of the corresponding carbonate or mesylate of the C(4)/C(5) diol subunit in **16a** afforded vinyl phostones **17a** (R^1 = H) and **17b** (R^1 = Ms). Alternatively, epoxidation of **15** led to the C(5) epimer **16b** in modest selectivity (*ds* = 4:1), but in excellent isolated yields. As previously reported, we believe the latter is governed by electrostatic repulsion of the P−OR ester and the incoming dipolar dioxirane reagent.[14]

(7) For some recent examples of the synthesis of nonfunctionalized cyclic phosphonates, see: (a) Tasz, M. K.; Rodriguez, O. P.; Cremer, S. E.; Hussain, M. S.; Haque, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2221−2226. (b) Yokomatsu, T.; Shioya, Y.; Iwasawa, H.; Shibuya, S. *Heterocycles* **1997**, *46*, 463−472. (c) Brel, V. K. *Synthesis* **1998**, 710−712.

(8) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239−2258.

(9) Stoianova, D. S.; Hanson, P. R. *Org. Lett.* **2001**, *3*, 3285−3288.

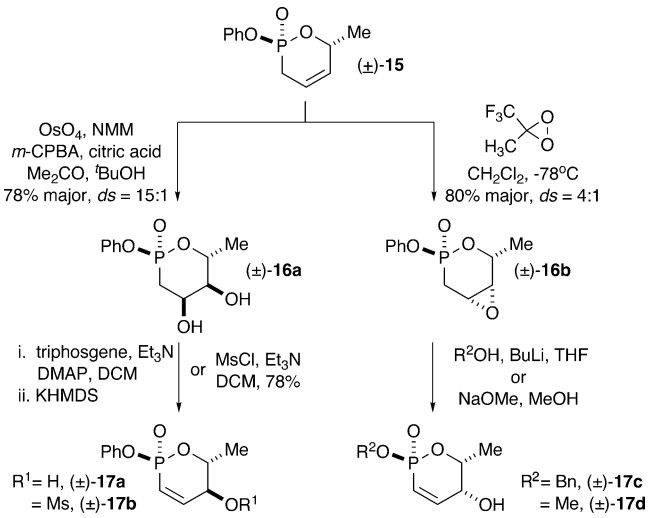
(10) Burke, M. D.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 46−58.

(11) Moriarty, R. M.; Tao, A.; Condeiu, C.; Gilardi, R. *Tetrahedron Lett.* **1997**, *38*, 2597−2600.

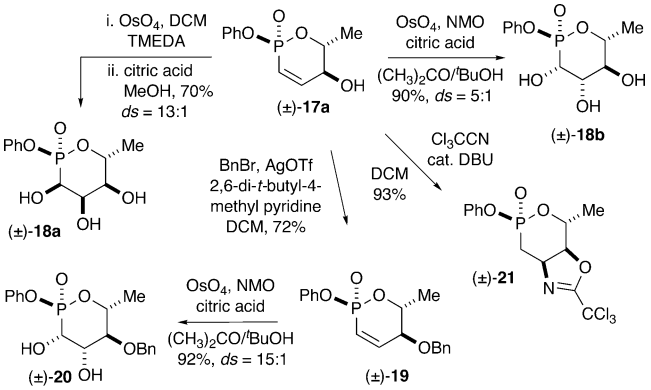
(12) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 8, 100−110.

(13) (a) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3943−3946. (b) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3947−3950. (c) Donohue, T. J.; Moore, P. R.; Beddoes, R. L. *J. Chem. Soc., Perkin Trans. 1* **1997**, 43−51.

SCHEME 3



SCHEME 4



Opening of epoxide **16b** with (nucleophilic) Li-alkoxide bases cleanly afforded the desired vinylphostone **17c** and also promoted phenoxy displacement with retention of configuration at phosphorus in addition to the eliminative opening. The relative stereochemistry of compounds **16b** and **17d** (R^2 = Me) was determined by X-ray crystallographic analysis.[9] It is noteworthy that attempts to open the epoxide with nonnucleophilic bases such as KHMDS or LDA resulted in decomposition.

Functionalization of vinyl phostone intermediate **17a** is highlighted in Scheme 4. Directed dihydroxylation using the Donohoe protocol[15] with stoichiometric amounts of OsO_4/TMEDA provided the C(3)−C(5) all *syn*-triol **18a** with excellent selectivity (*ds* = 13:1). Hydrolysis of the osmate ester was accomplished with citric acid, which has been previously shown to facilitate catalytic osmium-promoted dihydroxylation reactions due to its ability to readily hydrolyze osmate esters.[16] The excellent selectivity of this directed-dihydroxylation reaction is in agreement with the results of Donahoe, showing that substrates possessing equatorial hydroxy-groups are very selective under hydrogen-bonding conditions.[17]

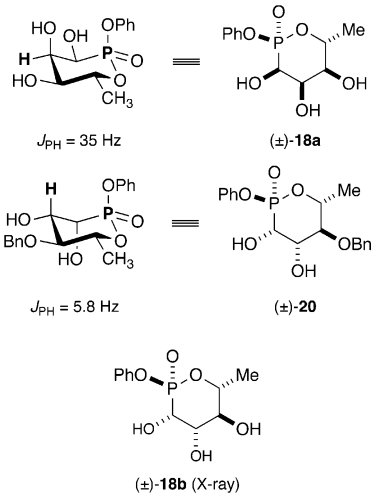


FIGURE 1. Dihedral coupling constant analysis for compounds **18a** and **20**.

Dihydroxylation of **17a** under catalytic OsO_4 conditions was previously shown, by X-ray crystallographic analysis of the product, to occur anti to the C(5) allylic hydroxy group to afford triol **18b** in modest selectivity (*ds* = 5:1).[9] We were able to improve this selectivity by protecting the hydroxy-group as a benzyl ether using in situ formed benzyl triflate to derive **19**. Subsequent dihydroxylation generated triol **20** in excellent yield (92%) and selectivity (15:1).[18]

We assumed that the dihydroxylation of **19** occurred anti to the C(5) benzyloxy group to derive **20**, in an analogous manner to the dihydroxylation of **17a** affording **18b**.[19] This assumption was confirmed by three-bond coupling analysis of coupling constants (J_{HP}) between the C(4) proton and P(1) atoms in the fully dihydroxylated compounds **20** and **18a** as shown in Figure 1. A significantly higher coupling constant (35 Hz) is observed for **18a** when the H−C−C−P dihedral angle is 180°. Alternatively, an H−C−C−P dihedral angle of <90° in **20** affords a much smaller coupling constant (5.8 Hz). This coupling constant data was substantiated by a 5.8 Hz coupling in the previously reported X-ray supported structure **18b**.[19]

Alternatively, introduction of nitrogen at the C(4) position could also be achieved from vinylphosphonate **17a** via treatment with Cl_3CCN to form the corresponding trichloroacetimidate, which underwent facile 1,4-conjugate addition to afford **21** in excellent yield. Attempts at the aminohydroxylation of **17a** have thus far failed.

Introduction of nitrogen nucleophiles at the C(5) position was achieved from the mesylated vinylphosphonate **17b**. Thus, treatment with sodium azide afforded C(5)-inverted azide product **22**. Subsequent dihydroxylation proceeded with complete selectivity to afford **23** as a single diastereomer (Scheme 5). The relative stereochem-

(14) (a) D'Accolti, L.; Fiorentino, M.; Fusco, C.; Rosa, A. M.; Curci, R. *Tetrahedron Lett.* **1999**, *40*, 8023−8027. (b) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811−822. (c) Adam, W.; Paredes, R.; Smerz, A. K.; Veloza, L. A. *Liebigs Ann.* **1997**, 547−551.

(15) Donohoe, T. J. *Synlett* **2002**, 1223−2332.

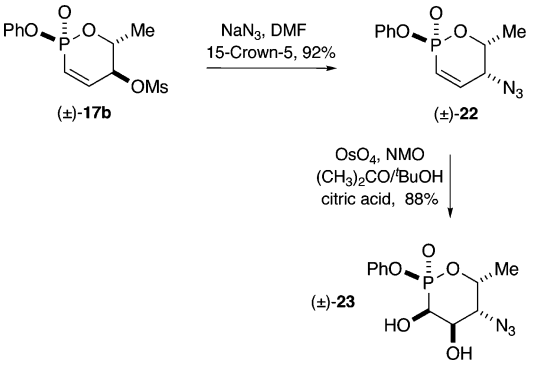
(16) Dupau, P.; Epple, R.; Thomas, A. A.; Fokin, V. A.; Sharpless, B. K. *Adv. Synth. Catal.* **2002**, *344*, 421−433.

(17) Donohoe, T. J.; Blades, K.; Helliwell, M.; Moore, P. R.; Winter, J. J. *J. Org. Chem.* **1999**, *64*, 2980−2981.

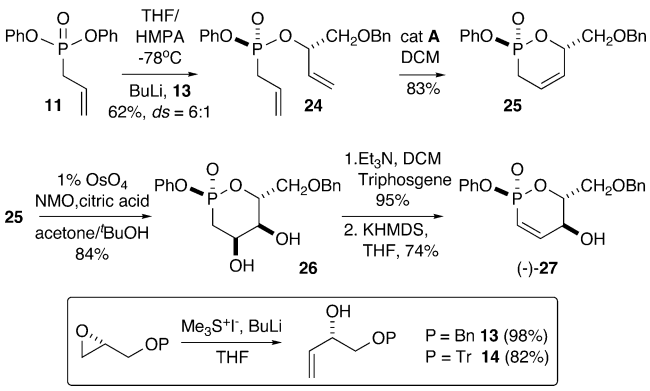
(18) Benzylation with BnBr under basic conditions gave very low yields of the desired product accompanied by some epimerization. For use of BnBr/AgOTf for benzylation of alcohols, see: Burk, R. M.; Gac, T. S.; Roof, M. B. *Tetrahedron Lett.* **1994**, 44, 8111−8112.

(19) We have previously reported the X-ray structure of **18b**; see ref 9.

SCHEME 5



SCHEME 6

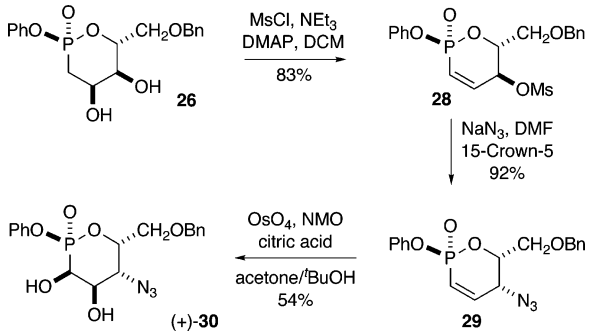


istry of this compound was confirmed by X-ray crystallographic analysis.[20]

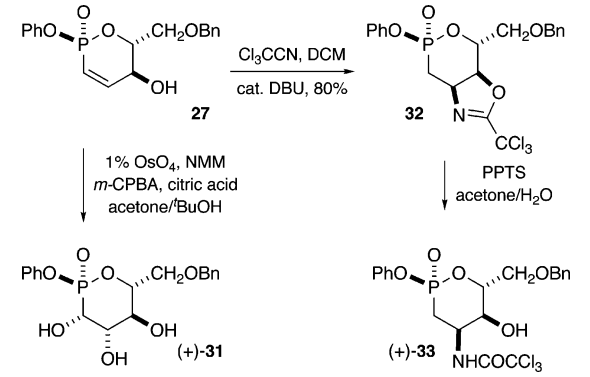
Having established this method with a racemic allylic alcohol, we turned to the use of nonracemic allyl alcohols, which we conveniently derived from commercially inexpensive enantio-enriched (97−99% ee) benzyl- and trityl-protected[21] glycidyl ethers.[22,23] Transformation of these readily available epoxides into corresponding allyl alcohols **13** and **14** was achieved in a single step via addition of trimethylsulfonium ylide (Scheme 6).[24] Diastereoselective addition of benzyl protected (2*S*)-1,2-butenediol **13** proceeded in good yield and selectivity (*ds* = 6:1) to produce phosphonate **24** as a mixture of P(2)-epimers. RCM of **24** provided nonracemic allyl phostone intermediate **25**. Dihydroxylation of substrate **25** provided diol **26** as a single diastereomer using 1% OsO_4, *m*-CPBA and NMM (*N*-methyl morpholine). Noteworthy, reactions with 4% OsO_4, *m*-CPBA/NMM or OsO_4/NMO gave a dramatic decrease in selectivity (*ds* = 2−5:1). Subsequent carbonate formation using the aforementioned triphosgene conditions, and elimination led to vinylphosphonate (−)-**27** in good yield.

Installation of nitrogen nucleophiles at the C(5) position within the framework of nonracemic benzyl-protected alcohol **26** was achieved using similar sequences as previously described for **17b** (Scheme 7). Formation of the mesylated diol intermediate followed by elimination provided vinyl phostone **28**. Addition of a single equivalent of azide produced **29** in excellent yield.[25] Dihydroxylation of the vinyl phostone **29** produced azido *P*-sugar (+)-**30** as a single diastereoisomer in modest yield.

SCHEME 7



SCHEME 8



Alternatively, installation of nitrogen at the C(4) position can be accomplished by facile formation of the trichloroacetimidate and subsequent Michael addition in the presence of DBU to yield the bicyclic trichlorooxazoline (Scheme 8). Hydrolysis of this product yielded the trichloroacetamide of the C(4)/C(5) amino alcohol. Dihydroxylation of **27** gave triol **31** with excellent selectivity (*ds* = 15:1), but only moderate yield (53%).

Problems associated with the base lability of phenoxy phosphonate esters led us to develop an alternate route employing BnO-substituted phosphonate esters. Thus, mixed phosphonate ester **34** could be produced by displacement of the PhO-group in the acyclic mixed phosphonate with BnOLi in DME (Scheme 9). This reaction occurs with inversion of the configuration at phosphorus[26] to afford **34**.[27] Subsequent RCM afforded phostone **35** possessing a cis relationship between the C(6) trityloxymethyl group and the P(2)-benzyl phosphonate ester. Dihydroxylation of **35** with OsO_4/NMO in the presence of citric acid yielded diol **36** with excellent selectivity (*ds*

(20) See Supporting Information (*S*-68).

(21) The mixed phosphonate, derived from optically pure Tr-protected (2*S*)-1,2-butenediol, was also prepared as described in our previous paper. Stability issues with the Tr-protected compounds led us to focus on the more robust Bn-protected vinylphosphonate (+)-**27**.

(22) We kindly acknowledge Daiso Co., Ltd., Fine Chemical Department for donating 100 g of each antipode of both the benzyl and trityl protected glycidols (e-mail: akkimura@daiso.co.jp).

(23) Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307−1315.

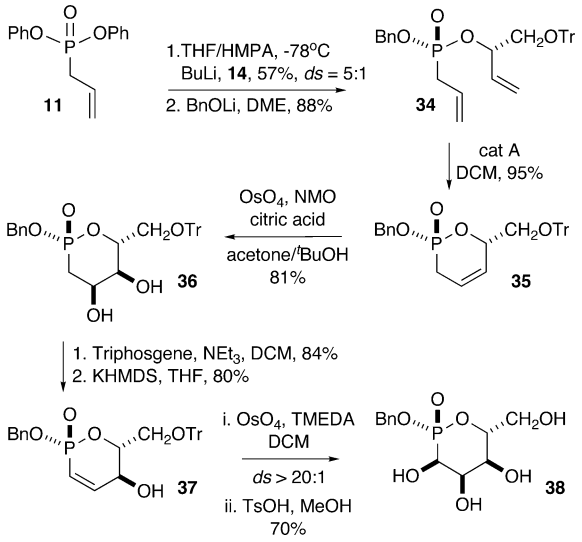
(24) Davoille, R. J.; Rutherford, D. T.; Christie, S. D. R. *Tetrahedron Lett.* **2000**, *41*, 1255−1259.

(25) Displacement of the C(5) mesylate in compound **28** using a slight excess of sodium azide was complicated by the formation of an inseparable side product (5−10 mol %). This side product most likely arose from conjugative addition of a second azide into the vinylphosphonate.

(26) Thatcher, G. R. J.; Kluger, R. *Adv. Phys. Org. Chem.* **1989**, *25*.

(27) Product **34** was contaminated with ~4% of the vinylphosphonate arising from double bond isomerization. Reactions run in THF gave extensive isomerization of the double bond (40%).

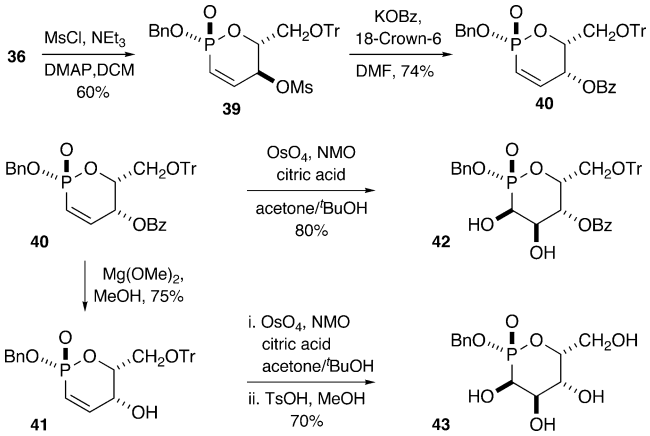
SCHEME 9



= 10−14:1) and in good isolated yields. On the basis of the aforementioned selectivity seen in the dihydroxylation of the C(6)-Me-substituted allylphostone **15**, we tentatively assigned the major product **36** occurring via dihydroxylation anti to the C(6)-trityloxymethyl group.[28] Conversion of diol **36** into the corresponding carbonate and treatment with KHMDS gave vinyl phosphonate **37** (Scheme 9). Dihydroxylation of this compound under standard conditions (cat. OsO_4, NMO, citric acid) proceeded with very low selectivity (*ds* = 2:1), presumably due to the anti relationship between the P(2)-benzyloxy phosphonate ester and the equatorial C(5)−OH which provide opposing factors. Alternatively, directed-dihydroxylation using the Donohoe conditions[15] provided C(3)/C(4)/C(5) all *syn*-triol **38** as a single diastereoisomer (*ds* > 20:1). Attempts to hydrolyze the osmate ester using literature conditions (HCl in MeOH)[8] gave only decomposition of the product. Treatment with citric acid[16] gave clean hydrolysis of the osmate without cleaving the Tr-group. This product was filtered through silica gel[29] and treated with catalytic amount of TsOH to give fully deprotected tetraol **38**.

In our previous work outlined in Scheme 3, we used epoxidation to derive **16b** as an alternative route of functionalizing the RCM product **15**, and ultimately to derive diastereomer **17c**. Unlike the dihydroxylation of **15** (Scheme 3), the major product of the epoxidation resulted from attack syn to the C(6)-methyl group. Unfortunately, all epoxidations of nonracemic phostones **25** and **35** were low yielding and not very selective. Attempts to access a vinyl phosphonate with a syn stereochemical relationship between the C(5) and C(6) substituents using Mitsunobu inversion of the C(5) hydroxy group in **37** gave only starting material. Alternatively, the desired intermediate was accessed by conversion of diol **36** into mesylate **39** and carrying out S_N2-substitution with an alkoxide-containing nucleophile. The best results were seen using KOBz in the presence

SCHEME 10



of 18-Crown-6 in DMF. Use of other reagents (Bu_4NOAc, NaOAc, KO_2, $CH_3CH_2CO_2Cs/CH_3CH_2CO_2H$) led to cleavage of the Bn-group on the P-atom and formation of a substantial amount of the free acid.[30] Dihydroxylation of **40** gave diol **42** in good yields and selectivity, but attempts to deprotect this compound were unsuccessful. Deprotection of the benzoate in **40** using $Mg(OMe)_2$, followed by dihydroxylation, and cleavage of the Tr-group gave desired tetraol **43** (Scheme 10) as a single diastereoisomer.

In conclusion, a facile strategy has been developed that allows for the diastereoselective generation of a number of novel *P*-sugar analogues. Additional stereoselective routes to nonracemic phosphono sugars are currently being pursued as well as the generation of libraries of pertinent analogues. Further synthetic studies, the production of chemical libraries, and biological screening of these *P*-sugars are underway and will be reported in due course.

Experimental Section

Experimental Procedures and Spectral Data for Compounds **17b**, **18**−**42**.

(2S$_P$*,3S*,4R*,5R*,6R*)-6-Methyl-2-phenoxy-1,2-oxaphosphorinane-3,4,5-triol-2-oxide [(±)-18a]. To a solution of **17a** (20 mg, 0.083 mmol) in CH_2Cl_2 (1.5 mL) were added OsO_4 (28 mg, 0.11 mmol) and TMEDA (13 mg, 0.11 mmol) at −60 °C. The reaction mixture was stirred for 2 h at −60 °C and warmed to room temperature. Removal of the solvent under reduced pressure under reduced pressure afforded the crude osmate as a mixture of diastereoisomers (12.5:1 by ^{31}P NMR analysis). The product was dissolved in 1.5 mL MeOH and treated with citric acid overnight. Removal of the solvent under reduced pressure and flash chromatography (EtOAc/4% MeOH) afforded 16 mg (70%) of **18a** as an oil; ^1H NMR δ 7.29−7.09 (m, 5H), 4.63−4.55 (m, 1H), 4.26 (dd, J = 35.2, 3.9, 2.5 Hz, 1H), 4.05 (dd, J = 7.6, 4.0 Hz, 1H), 3.38 (dd, J = 9.4, 2.2 Hz, 1H), 1.38 (dd, J = 6.3, 1.9 Hz, 3H); ^{13}C NMR δ 150.0 (d, J_{CP} = 10.0 Hz), 129.5 (d, J_{CP} = 125.0 Hz), 120.3 (d, J_{CP} = 4.3 Hz), 74.4 (d, J_{CP} = 6.2 Hz), 72.5, 72.3, 66.3 (d, J_{CP} = 146.9 Hz), 18.4 (d, J_{CP} = 8.3 Hz); ^{31}P NMR δ 16.4.

(2S$_P$*,5S*,6R*)-5,6-Dihydro-6-methyl-2-phenoxy-2H-1,2-oxaphosphorinan e-5-methanesulfonate-2-oxide [(±)-17b]. To a solution of the diol **16a** (20 mg, 0.077 mmol) in CH_2Cl_2 (2.0 mL) was added a catalytic amount of DMAP (1.9 mg, 0.015 mmol), MsCl (0.02 mL, 0.26 mmol), and Et_3N (0.04

(28) Exhaustive deprotection of compounds **26** and **36** gave rise to a common free acid, thus confirming that diols **26** and **36** differ only in their substitution at phosphorus.

(29) Attempts to isolate this product led to lower yields due to its instability.

(30) Treatment of the phenoxy substituted *P*-sugar **28** (Scheme 7) with KOBz, 18-Crown-6 in DMF gave almost exclusively the free acid.

mL, 0.29 mmol) at 0 °C. The reaction mixture was warmed to room temperature over 1 h and stirred overnight. Brine was added, and the mixture was extracted with EtOAc (3x) and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (7:3 EtOAc/hexanes) afforded 19 mg (78%) of **17b**; IR (neat) 3028, 2936, 1591, 1490, 1455, 1361, 1270, 1177, 1070, 1023, 931 cm^{-1}; ^1H NMR δ 7.38−7.18 (m, 5H), 6.82 (ddd, J = 46.8, 12.9, 2.0 Hz, 1H), 6.26 (ddd, J = 17.4, 12.9, 2.0 Hz, 1H), 5.17−5.13 (m, 1H), 4.75−4.70 (m, 1H), 3.12 (s, 3H), 1.57 (dd, J = 6.3, 2.0 Hz, 3H); ^{13}C NMR δ 149.6, 146.1, 129.9, 125.4, 120.3, 119.7 (d, J_{CP} = 169.7 Hz), 76.3 (d, J_{CP} = 8.1 Hz), 75.1 (d, J_{CP} = 10.8 Hz), 38.8, 18.9 (d, J_{CP} = 6.9 Hz); ^{31}P NMR δ 5.5. Exact mass: calcd for $C_{12}H_{16}O_6PS$ (M+1) 319.0405; found 319.0405 (FAB).

(2S_P*,5S*,6R*)-5,6-Dihydro-6-methyl-2-phenoxy-2H-1,2-oxaphosphorinan e-5-phenylmethoxy-2-oxide [(±)-19]. To a solution of the alcohol **17a** (10 mg, 0.042 mmol) in CH_2Cl_2 (0.6 mL) were added 2,6-di-*t*-butyl-4-methyl pyridine (55 mg, 0.26 mmol), AgOTf (54 mg, 0.21 mmol), and BnBr (0.03 mL, 0.25 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 3 h and diluted with CH_2Cl_2, and the filtrate was washed with brine. Removal of the solvent under reduced pressure and flash chromatography (4:1 hexanes/EtOAc) afforded 10 mg (72%) of **19** as an oil; IR (neat) 3061, 3031, 2982, 2934, 2871, 1723, 1593, 1490, 1454, 1364, 1270, 1202, 1095, 1067, 982, 928 cm^{-1}; ^1H NMR δ 7.41−7.31 (m, 7H), 7.21−7.15 (m, 3H), 6.83 (ddd, J = 48.2, 12.9, 1.6 Hz, 1H), 6.10 (ddd, J = 18.8, 12.9, 2.1 Hz, 1H), 4.72−4.57 (m, 3H), 4.03−3.99 (m, 1H), 1.49 (dd, J = 6.2, 2.0 Hz, 3H); ^{13}C NMR δ 149.6, 136.6, 129.8, 128.7, 128.5, 125.1, 120.5 (d, J_{CP} = 4.6 Hz), 116.8 (d, J_{CP} = 170.8 Hz), 77.9 (d, J_{CP} = 8.2 Hz), 76.5 (d, J_{CP} = 10.1 Hz), 72.8, 19.1 (d, J_{CP} = 7.5 Hz); ^{31}P NMR δ 7.7. Exact mass: calcd for $C_{18}H_{20}O_4P$ (M+1) 331.1099; found 331.1098 (FAB).

(2S_P*,3R*,4S*,5S*,6R*)-6-Methyl-2-phenoxy-1,2-oxaphosphorinane-3,4-diol-5-phenylmethoxy-2-oxid e [(±)-20]. To a solution of **19** (15 mg, 0.045 mmol) in acetone (0.9 mL) and *t*-BuOH (0.3 mL) were added citric acid (19 mg, 0.10 mmol), NMO·H_2O (12 mg, 0.09 mmol), and OsO_4 (2 drops of a 4% solution in water). The reaction mixture was stirred for 24 h, followed by the addition of Na_2SO_3. Water was added, and the mixture was extracted with EtOAc (3x) and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (EtOAc/1% MeOH) afforded 15 mg (92%) of **20** as an oil; ^1H NMR δ 7.36−7.16 (m, 10H), 5.45 (br. s, 1H), 4.94 (d, J = 10.7 Hz, 1H), 4.65 (t, J = 10.8 Hz, 1H), 4.38 (q, J = 3.8 Hz, 1H), 4.22−4.11 (m, 2H), 3.62 (t, J = 9.2, 1H), 3.24 (d, J = 8.6, 1.6 Hz, 1H), 1.47 (dd, J = 6.2, 1.3 Hz, 3H); ^{13}C NMR δ 149.6, 137.6, 130.0, 128.5, 128.2, 128.1, 125.4, 119.7 (d, J_{CP} = 4.7 Hz), 80.0, 75.7, 75.5 (d, J_{CP} = 5.8 Hz), 73.5 (d, J_{CP} = 6.2 Hz), 65.6 (d, J_{CP} = 144.3 Hz), 19.2 (d, J_{CP} = 9.0 Hz); ^{31}P NMR δ 16.2.

[(±)-21]. To a solution of **17a** (16 mg, 0.067 mmol) in CH_2Cl_2 (0.6 mL) were added Cl_3CCN (0.01 mL) and a catalytic amount of DBU (2.0 mg, 0.013 mmol) at −50 °C, and the solution was warmed to −20 °C over 4 h. The cooling bath was removed, and the stirring was continued at room temperature overnight. The reaction mixture was quenched with NH_4Cl (sat'd aq), extracted with CH_2Cl_2 (3x) and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (EtOAc/1% MeOH) afforded 24 mg (93%) of product **21**; IR (neat) 2918, 1725, 1521, 1486, 1256, 1182, 1039, 1008, 918, 899 cm^{-1}; ^1H NMR δ 7.37−7.18 (m, 5H), 4.97−4.88 (m, 1H), 4.83 (d, J = 9.0 Hz, 1H), 4.49−4.44 (m, 1H), 2.80 (ddd, J = 18.3, 15.6, 6.5 Hz, 1H), 2.29 (ddd, J = 17.8, 15.8, 9.5 Hz, 1H), 1.59 (dd, J = 6.2, 1.0 Hz, 3H); ^{13}C NMR δ 162.4 (d, J_{CP} = 6.6 Hz), 149.4 (d, J_{CP} = 8.9 Hz), 129.9, 125.4, 119.9 (d, J_{CP} = 4.8 Hz), 77.1 (d, J_{CP} = 6.6 Hz), 70.4 (d J_{CP} = 5.5 Hz), 48.8 (d, J_{CP} = 4.0 Hz), 24.6 (d, J_{CP} = 126.9 Hz), 19.0 (d, J_{CP} = 6.2 Hz); ^{31}P NMR δ 20.0.

(2S_P*,5R*,6R*)-5,6-Dihydro-6-methyl-2-phenoxy-2H-1,2-oxaphosphorinan e-5-azido-2-oxide [(±)-22]. To a solution of mesylate **17b** (13 mg, 0.041 mmol) in DMF (0.5 mL) were added NaN_3 (13 mg, 0.20 mmol) and 15-crown-5 (9 mg, 0.041 mmol). The reaction mixture was stirred overnight at room temperature, and the solvent was removed under reduced pressure. Flash chromatography of the residue (1:1 hexanes/EtOAc) afforded 10 mg (92%) of **22**; IR (neat) 3049, 2993, 2938, 2109, 1612, 1596, 1490, 1455, 1358, 1269, 1162, 1028, 968, 921 cm^{-1}; ^1H NMR δ 7.36−7.17 (m, 5H), 6.85 (ddd, J = 46.6, 12.5, 5.5 Hz, 1H), 6.44 (dd, J = 17.3, 12.5 Hz, 1H), 4.92−4.89 (m, 1H), 3.56−3.55 (m, 1H), 1.54 (dd, J = 6.4, 2.0 Hz, 3H); ^{13}C NMR δ 149.8, 142.4, 129.9, 125.2, 121.7 (d, J_{CP} = 169.5 Hz), 120.2 (d, J_{CP} = 4.6 Hz), 76.8 (d, J_{CP} = 7.5 Hz), 57.1 (d, J_{CP} = 10.1 Hz), 18.5 (d, J_{CP} = 7.8 Hz); ^{31}P NMR δ 5.8. Exact mass: calcd for $C_{11}H_{13}N_3O_3P$ (M+1) 266.0695; found 266.0692 (FAB).

(2S_P*,3S*,4R*,5R*,6R*)-6-Methyl-2-phenoxy-1,2-oxaphosphorinane-3,4-diol-5-azido-2-oxide [(±)-23]. To a solution of **22** (5 mg, 0.019 mmol) in acetone (0.6 mL) and *t*-BuOH (0.2 mL) were added citric acid (4 mg, 0.021 mmol), NMO·H_2O (3 mg, 0.022 mmol), and OsO_4 (1 drop 4% solution in water). The reaction mixture was stirred for 24 h, and water was added and extracted with EtOAc (3x). Removal of the solvent under reduced pressure and flash chromatography (4:1 EtOAc/hexanes) afforded 5 mg (88%) of **23**; IR (neat) 3350, 2923, 2110, 1590, 1491, 1255, 1199, 1026, 987 cm^{-1}; ^1H NMR δ 7.33−7.16 (m, 5H), 5.84 (br. s, 1H), 5.10−5.04 (m, 1H), 4.40 (dt, J = 35.2, 4.2 Hz, 1H), 4.25 (t, J = 4.5 Hz, 1H), 3.42 (br. s, 1H), 3.73 (d, J = 4.2 Hz, 1H), 1.47 (dd, J = 6.6, 1.6 Hz, 3H); ^{13}C NMR δ 150.2 (d, J_{CP} = 9.8 Hz), 129.7, 125.1, 120.4 (d, J_{CP} = 4.3 Hz), 73.4 (d, J_{CP} = 7.1 Hz), 71.8 (d, J_{CP} = 2.9 Hz), 65.2 (d, J_{CP} = 2.6 Hz), 63.7 (d, J_{CP} = 145.7 Hz), 18.0 (d, J_{CP} = 9.0 Hz); ^{31}P NMR δ 15.9. Exact mass: calculated for $C_{11}H_{15}N_3O_5P$ (M+1) 300.0749; found 300.0754 (FAB).

(1S,S_P)-2-Propenyl-1-phenylmethoxymethyl-2-propenyl Phenyl Ester Phosphonic Acid [(+)-24]. To a solution of the 2-benzyl-(2*R*)-1,2-butenediol **13** (69 mg, 0.388 mmol) in dry THF (2 mL) was added BuLi (0.27 mL 1.4 M in hexanes, 0.38 mmol) at −40 °C, and the solution was warmed to room temperature over 2 h and stirred at room temperature for an additional 4 h. This solution was added to the diphenyl allylphosphonate (127 mg, 0.42 mmol) in THF (0.6 mL) and HMPA (0.1 mL) at −78 °C over 30 min. The reaction mixture was stirred overnight at −78 °C, quenched with NH_4Cl (sat'd aq.), extracted with EtOAc (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (4:1 hexanes/EtOAc) afforded 75 mg (54%) of **24** as a mixture of diastereoisomers (6:1 by ^{31}P analysis); $[\alpha]_D$ +5.3 (*c* 0.3, CH_2Cl_2); IR (neat) 3065, 3029, 2982, 2861, 1639, 1593, 1490, 1454, 1364, 1265, 1208, 1091, 1013, 926 cm^{-1}; ^1H NMR (only signals for major isomer) δ 7.36−7.11 (m, 10H), 5.92−5.14 (m, 2H), 5.46−5.14 (m, 5H), 4.64−4.53 (m, 2H), 3.62−3.53 (m, 2H), 2.85−2.75 (m, 2H); ^{13}C NMR (only signals for major isomer) δ 150.3 (d, J_{CP} = 8.9 Hz), 137.5, 129.4, 128.3, 127.7, 127.6, 124.7, 124.63, 120.59, 120.2 (d, J_{CP} = 15.1 Hz), 118.3, 76.5 (d, J_{CP} = 6.6 Hz), 73.0, 72.3 (d, J_{CP} = 4.8 Hz), 32.1 (d, J_{CP} = 140.7 Hz); ^{31}P NMR δ 25.6. Exact mass: calculated for $C_{20}H_{24}O_4P$ (M+1) 359.1412; found 359.1406 (FAB).

(2S_P,6S)-2-Phenoxy-6-[(phenylmethoxymethyl]-2H-1,2-oxaphosphorin-3,6-dihydro-2-oxide [(−)-25]. To a solution of **24** (75 mg, 0.23 mmol, 9:1 mixture) in dry CH_2Cl_2 (20 mL) was added $(PCy_3)_2Cl_2Ru{=}CHPh$ (6 mg, 3 mol %), and the mixture was refluxed overnight. An additional amount of catalyst (3 mg, 0.0036 mmol) was added, and reflux was continued for 14 h. The mixture was diluted with CH_2Cl_2 and flushed with air, 3 drops DMSO were added, and the solution was stirred overnight at room temperature. Removal of the solvent under reduced pressure and flash chromatography (1:1 hexanes/EtOAc) afforded 60 mg (83%) of **25** as an oil; $[\alpha]_D$ −42.1 (*c* 1.2, CH_2Cl_2); IR (neat) 3062, 3033, 2905, 2866, 1592, 1491, 1454, 1297, 1254, 1207, 1083, 1026, 927 cm^{-1}; ^1H NMR δ 7.36−7.13 (m, 10H), 5.88−5.77 (m, 2H), 5.14−5.13 (m, 1H), 4.58 (s, 2H), 3.73−3.62 (m, 2H), 2.68−2.48 (m, 2H); ^{13}C NMR

δ 149.9 (d, J_{CP} = 7.8 Hz), 137.4, 129.7, 128.2, 127.6, 127.5, 126.2 (d, J_{CP} = 16.0 Hz), 124.8, 121.2 (d, J_{CP} = 9.8 Hz), 129.9 (d, J_{CP} = 4.5 Hz), 79.7 (d, J_{CP} = 8.5 Hz), 63.4, 71.6 (d, J_{CP} = 7.4 Hz), 21.4 (d, J_{CP} = 132.4 Hz); ^{31}P NMR δ 17.5. Exact mass: calculated for $C_{18}H_{20}O_4P$ (M+1) 331.1099; found 331.1110 (FAB).

(2S_P,4*R*,5*S*,6*S*)-2-Phenoxy-6-[(phenylmethoxy)methyl]-1,2-oxaphosphorinane-4,5-diol-2-oxide [(+)-26]. To a solution of **25** (12 mg, 0.036 mmol in 1.2 mL acetone and *t*-BuOH (0.4 mL) were added citric acid (10 mg, 0.052 mmol), *m*-CPBA (26 mg 70−75%), NMM (11 mg, 0.11 mmol) and OsO_4 (1 drop of a 1% solution in water). After stirring for 24 h one more drop of OsO_4 was added and the stirring continued for 24 h. The reaction mixture was diluted with $CHCl_3$, solid Na_2SO_3 and water was added, stirred for 30 min and extracted with $CHCl_3$. Removal of the solvent under reduced pressure and flash chromatography (EtOAc/1% MeOH) afforded 11 mg (84%) of **26** as a white solid; mp = 145−148; $[\alpha]_D$ +51.1 (*c* 0.980, CH_2Cl_2); IR (neat) 3341, 3062, 2969, 1591, 1490, 1454, 1251, 1197, 933 cm^{-1}; ^{1}H NMR δ 7.32−7.11 (m, 10H), 4.71−4.68 (m, 1H), 4.55−4.48 (m, 2H), 4.12 (dd, J = 35.8, 1.8 Hz, 1H), 3.85 (br. s, 1H), 3.75−3.71 (m, 4H), 2.32 (ddd, J = 19.4, 15.8, 3.6 Hz, 1H), 2.04−1.94 (m, 1H); ^{13}C NMR δ 149.6 (d, J_{CP} = 8.4 Hz), 137.6, 129.9, 129.6, 128.3, 127.7, 127.5, 125.1, 120.6 (d, J_{CP} = 4.3 Hz), 76.4 (d, J_{CP} = 6.7 Hz), 73,4, 69.9 (d, J_{CP} = 7.8 Hz), 68.0 (d, J_{CP} = 6.5 Hz), 67.1 (d, J_{CP} = 9.1 Hz), 27.2 (d, J_{CP} = 125.9 Hz); ^{31}P NMR δ 20.2. Exact mass: calculated for $C_{18}H_{22}O_6P$ (M+1) 365.1154; found 365.1160 (FAB).

(2S_P,4*R*,5*S*,6*S*)-2-Phenoxy-6-[(phenylmethoxy)methyl]-1,2-oxaphosphorinane-4,5-carbonate-2-oxide. To a solution of **26** (450 mg, 1.24 mmol) in CH_2Cl_2 (20 mL) were added triphosgene (770 mg, 2.59 mmol) and Et_3N (0.80 mL, 5.75 mmol) at −40 °C, and the solution was warmed to 10 °C over 3 h. The reaction mixture was diluted with CH_2Cl_2, quenched with NH_4Cl (sat'd aq.), extracted with CH_2Cl_2 (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (7:3 EtOAc/hexanes) afforded 460 mg (95%) of the carbonate; ^{1}H NMR δ 7.42−7.18 (m, 10H), 5.25 (ddd, J = 25.0, 7.8, 6.2, 4.1 Hz, 1H), 4.94 (dd, J = 8.1, 4.5 Hz, 1H), 4.86−4.85 (m, 1H), 4.65 (d, J = 11.1 Hz, 1H), 4.53 (d, J = 11.5 Hz, 1H), 3.94 (dd, J = 11.1, 2.0 Hz, 1H), 3.80 (dt, J = 11.1, 3.0 Hz, 1H), 2.70 (ddd, J = 18.7, 16.3, 6.2 Hz, 1H), 2.48 (ddd, J = 17.6, 16.3, 4.0 Hz, 1H); ^{13}C NMR δ 152.6, 149.3 (d, J_{CP} = 8.6 Hz), 136.4, 129.6, 128.4, 128.0, 127.7, 125.2, 120.1 (d, J_{CP} = 4.7 Hz), 77.9 (d, J_{CP} = 7.7 Hz), 73,6, 73.0 (d, J_{CP} = 6.1 Hz), 72.7 (d, J_{CP} = 11.9 Hz), 69.6 (d, J_{CP} = 3.8 Hz), 24.3 (d, J_{CP} = 128.2 Hz); ^{31}P NMR δ 15.2.

(2S_P,5*S*,6*R*)-5,6-Dihydro-2-phenoxy-6-[(phenylmethoxy)-methyl]-2H-1,2-oxaphosphorinane-5-ol-2-oxide [(−)-27]. To a solution of the carbonate (430 mg, 1.10 mmol) in THF (20 mL) was added KHMDS (2.5 mL, 0.5 M in toluene, 1.25 mmol) at −50 °C, and the solution was warmed to 0 °C over 2.5 h. The reaction mixture was quenched with NH_4Cl (sat'd aq.), extracted with EtOAc (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (9:1 EtOAc/hexanes) afforded 280 mg (74%) of **27**; $[\alpha]_D$ −4.6 (*c* 0.5, CH_2Cl_2); IR (neat) 3341, 3062, 2869, 1591, 1490, 1454, 1356, 1251, 1198, 1077, 1007, 985, 932 cm^{-1}; ^{1}H NMR δ 7.34−7.12 (m, 10H), 6.68 (ddd, J = 49.4, 12.9, 1.3 Hz, 1H), 5.93−5.85 (m, 1H), 4.70−4.49 (m, 4H), 4.36 (d, J = 1.5 Hz, 1H), 3.83−3.71 (m, 1H); ^{13}C NMR δ 154.0, 149.5 (d, J_{CP} = 8.5 Hz), 137.5, 129.1, 128.3, 127.7, 127.5, 125.3, 120.5 (d, J_{CP} = 4.2 Hz), 114.4 (d, J_{CP} = 171.7 Hz), 81.4, 73.4, 69.7 (d, J_{CP} = 7.5 Hz), 64.3; ^{31}P NMR δ 8.0. Exact mass: calculated for $C_{18}H_{20}O_5P$ (M+1) 347.1048; found 347.1055 (FAB).

(2S_P,5*S*,6*R*)-5,6-Dihydro-2-phenylmethoxy-2H-1,2-oxaphosphorinane-5-methanesulfonate-6-[(triphenylmethoxy)methyl]-2-oxide [(+)-28]. To a solution of the diol (100 mg, 0.27 mmol) in CH_2Cl_2 (8 mL) were added a catalytic amount of DMAP (6.6 mg, 0.054 mmol) and MsCl (0.07 mL, 0.90 mmol) at 0 °C, followed by Et_3N (0.15 mL, 1.08 mmol). The reaction mixture was warmed to room temperature over 1 h and stirred overnight at room temperature. Et_3N (0.10 mL, 0.72 mmol) was added, and the stirring was continued for 6 h. After addition of brine the mixture was extracted with EtOAc (3x) and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (1:1 hexanes/EtOAc) afforded 95 mg (83%) of **28**; $[\alpha]_D$ +30.7 (*c* 0.91, CH_2Cl_2); IR (neat) 3060, 3044, 3023, 2931, 2896, 2865, 1590, 1491, 1454, 1348, 1268, 1204, 1171, 1101, 1018, 985, 939 cm^{-1}; ^{1}H NMR δ 7.37−7.16 (m, 10H), 6.87 (ddd, J = 47.2, 12.9, 1.9 Hz, 1H), 6.24 (ddd, J = 17.9, 12.9, 2.0 Hz, 1H), 5.53−5.49 (m, 1H), 4.76−4.71 (m, 1H), 4.66 (d, J = 11.5 Hz, 1H), 4.60 (d, J = 11.7 Hz, 1H), 3.88−3.80 (m, 2H), 3.00 (s, 3H); ^{13}C NMR δ 149.5 (d, J_{CP} = 8.2 Hz), 146.6, 137.0, 129.9, 128.4, 127.9, 127.8, 125.4, 120.4 (d, J_{CP} = 4.4 Hz), 119.3 (d, J_{CP} = 170.5 Hz), 78.7 (d, J_{CP} = 8.0 Hz), 73.8, 70.7 (d, J_{CP} = 10.7 Hz), 68.0 (d, J_{CP} = 7.1 Hz), 38.1; ^{31}P NMR δ 6.1. Exact mass: calculated for $C_{19}H_{22}O_7PS$ (M+1) 425.0824; found 425.0809 (FAB).

(2S_P,5*R*,6*R*)-5,6-Dihydro-2-phenoxy-2H-1,2-oxaphosphorinane-5-azido-6-[(phenylmethoxy)methyl]-2-oxide [(−)-29]. Mesylated alcohol **28** (63 mg, 0.148 mmol) was taken up in DMF (0.3 mL) at room temperature, followed by the subsequent addition of 15-crown-5 ether (33 mg, 0.148 mmol) and sodium azide (9 mg, 0.140 mmol). Upon completion (2.5−3 h), removal of solvent under reduced pressure followed by flash chromatography (1:1 EtOAc/hexanes) afforded 45 mg (82%) of compound **29**; $[\alpha]_D$ −316.3 (*c* 0.4, CH_2Cl_2); IR (neat) 3062, 2106, 1590, 1488, 1271, 1198 cm^{-1}; ^{1}H NMR δ 7.12−7.39 (m, 10H), 6.85 (ddd, J_{HP} = 46.4, J = 12.5, 5.6 Hz, 1H), 6.44 (dd, J = 17.4, J = 12.9 Hz, 1H), 4.93 (ddd, J = 11.4, 6.9, 3.3 Hz, 1H), 4.59 (s, 2H), 3.89 (m, 1H), 3.84 (d, J = 6.39 Hz, 2H); ^{13}C NMR δ 149.5 (J_{CP} = 8.3 Hz), 142.2, 137.3, 129.8 (J_{CP} = 11.0 Hz), 128.6 (J_{CP} = 10.1 Hz), 128.1 (J_{CP} = 5.7 Hz), 127.8, 125.4, 121.8 (J_{CP} = 171.2 Hz), 120.4 (J_{CP} = 4.5 Hz), 78.3 (J_{CP} = 7.1 Hz), 73.9, 69.1 (J_{CP} = 9.3 Hz), 54.2 (J_{CP} = 11.1 Hz); ^{31}P NMR δ 5.72. Exact mass: calcd for $C_{18}H_{19}N_3O_4P$ (M+1) 372.1113; found 372.2313 (FAB).

(2S_P,3*S*,4*R*,5*R*,6*R*)-2-Phenoxy-6-[(phenylmethoxy)-methyl]-1,2-oxaphosphorinane-3,4-diol-5-azido-2-oxide [(+)-30]. To a solution of **29** (12 mg, 0.032 mmol) in acetone (0.9 mL) and *t*-BuOH (0.3 mL) were added citric acid (6 mg, 0.031 mmol), NMO·H_2O (5 mg, 0.037 mmol), and OsO_4 (1 drop of a 4% solution in water). After stirring for 24 h at room temperature, one more drop OsO_4 was added, and the stirring was continued for 8 h. Water was added to the reaction mixture and extracted with EtOAc (3x). Removal of the solvent under reduced pressure and flash chromatography (3:2 EtOAc/hexanes) afforded **30** (7 mg, 54%) as an oil; $[\alpha]_D$ +41.1 (*c* 0.0072, CH_2Cl_2); IR (neat) 3343, 3065, 2922, 2113, 1590, 1491, 1454, 1256, 1201, 1024, 981, 938 cm^{-1}; ^{1}H NMR δ 7.38−7.11 (m, 10H), 5.07−5.05 (m, 1H), 4.56 (s, 2H), 4.50−4.39 (m, 2H), 4.06 (d, J = 3.7 Hz, 1H), 3.78−3.70 (m, 2H); ^{13}C NMR δ 150.0 (d, J_{CP} = 10.3 Hz), 137.2, 129.7, 128.5, 127.9, 125.2, 120.4 (d, J_{CP} = 4.2 Hz), 74.8 (d, J_{CP} = 6.8 Hz), 73.6, 71.7 (d, J_{CP} = 3.2 Hz), 68.1 (d, J_{CP} = 11.0 Hz), 64.3 (d, J_{CP} = 146.7 Hz), 61.6; ^{31}P NMR δ 16.2. Exact mass: calcd for $C_{18}H_{21}N_3O_6P$ (M+1) 406.1168; found 406.1159 (FAB).

(2S_P,3*R*,4*S*,5*S*,6*R*)-2-Phenoxy-6-[(phenylmethoxy)-methyl]-1,2-oxaphosphorinane-3,4,5-triol-5−2-oxide [(+)-31]. To a solution of **27** (65 mg, 0.187 mmol) in acetone (5.2 mL) and *tert*-butyl alcohol (2.1 mL) were added citric acid (72 mg, 0.374 mmol), NMM (100 μl, 0.560 mmol), and a 1% solution of OsO_4 in water (24 μL). A solution of *m*-CPBA (137 mg, 0.560 mmol) in acetone (1 mL) was added over 30 min. After 24 h of stirring, additional amounts of OsO_4 (0.024 mL) and *m*-CPBA (70 mg) were added, and the reaction was stirred for an additional 24 h. The reaction was quenched with Na_2SO_3 (sat'd aq.) and extracted with CH_2Cl_2 (3x), and the combined organic layers were dried (Na_2SO_4). ^{31}P analysis of the crude reaction mixture showed a diastereomeric ratio of 15:1. Subsequent flash chromatography (9:1 EtOAc/MeOH) afforded 38 mg (53%) of **31** as the major isomer; $[\alpha]_D$ +21.6 (*c* 0.94, CH_2Cl_2); IR ($CHCl_3$) 3352, 2922, 1590, 1491, 1267, 1196,

736, 690 cm^{-1}; ^1H NMR δ 7.31−7.13 (m, 10H), 4.52−4.49 (m, 2H), 4.47−4.43 (m, 1H), 4.21−4.18 (m, 1H), 4.03 (dd, J_{HP} = 9.53, 9.53 Hz, 1H), 3.96 (dd, J_{HP} = 11.3, 1.81 Hz, 1H), 3.86−3.84 (m, 1H), 3.76 (dd, J_{HP} = 10.9, 5.81 Hz); ^{13}C NMR δ 149.5 (d, J_{CP} = 9.6 Hz), 137.8, 130.0, 128.4, 127.6, 127.6, 125.5, 120.0 (d, J_{CP} = 4.4 Hz), 78.7 (d, J_{CP} = 3.6 Hz), 73.4, 73.3 (d, J_{CP} = 7.2 Hz), 69.8 (d, J_{CP} = 12.6 Hz), 66.8, 65.7 (d, J_{CP} = 145.9 Hz); ^{31}P NMR δ 17.1. Exact mass: calcd for $C_{18}H_{22}O_7P$ (M+1) 381.1025; found 381.1103 (FAB).

Trichlorooxazoline-Containing Phosphonate [(−)-32]. To a solution of **27** (32 mg, 0.092 mmol) in CH_2Cl_2 (2 mL) were added Cl_3CCN (0.01 mL) and a catalytic amount of DBU at −50 °C. The solution was allowed to warm to −20 °C over 5 h. The reaction mixture was quenched with NH_4Cl (sat'd aq.), extracted with CH_2Cl_2 (3x) and dried (Na_2SO_4). Removal of solvent under reduced pressure and flash chromatography (1:1 hexanes/EtOAc) afforded 36 mg (80%) of **32**; $[\alpha]_D$ −1.88 (*c* 2.6, CH_2Cl_2); IR (neat) 3063, 3030, 2927, 2868, 1716, 1664, 1591, 1491 1454, 1271, 1203, 985, 930 cm^{-1}; ^1H NMR δ 7.38−7.15 (m, 10H), 5.12−5.08 (m, 1H), 4.99−4.89 (m, 1H), 4.70−4.57 (m, 3 H), 3.92 (d, J = 11.2 Hz, 1H), 3.82 (dd, J = 11.1, 4.6 Hz, 1H), 2.75 (dd, J = 18.2, 15.9, 7.0 Hz, 1H), 2.32 (dd, J = 17.0, 7.5 Hz, 1H); ^{13}C NMR δ 162.3, 149.5 (d, J_{CP} = 8.5 Hz), 137.1, 129.8, 128.5, 128.0, 127.8, 120.7 (d, J_{CP} = 4.3 Hz), 85.8, 79.2 (d, J_{CP} = 7.6 Hz), 77.4, 73,8, 69.8 (d, J_{CP} = 5.9 Hz), 63.1 (d, J_{CP} = 3.7 Hz), 24.9 (d, J_{CP} = 126.3 Hz); ^{31}P NMR δ 19.5. Exact mass: calcd for $C_{20}H_{20}Cl_3NO_5P$ (M+1) 490.0145; found 490.0145 (FAB).

Trichloroacetimidate-Containing Phosphonate [(+)-33]. Compound **32** (15 mg, 0.031 mmol) was dissolved in acetone (0.6 mL), followed by the addition of H_2O (0.1 mL). PPTS (2 mg, 0.0093 mmols) was added, and the reaction was stirred at room-temperature overnight. Concentration under reduced pressure and flash chromatography (3:2 EtOAc/hexanes), provided 12 mg (76% yield) of the **33** as an oil; $[\alpha]_D$ +36.0 (*c* 1.6, CH_2Cl_2); ^1H NMR δ 7.70 (d, J = 7.5 Hz, 1H), 7.37−7.19 (m, 10H), 4.17 (dddd, J = 33.6, 8.0, 8.0, 4.0 Hz, 1H), 4.62 (d, J = 11.8 Hz, 1H), 4.57 (d, J = 11.8 Hz, 1H), 4.48 (ddd, J = 8.8, 8.8, 4.4 Hz, 1H), 4.17 (dd, J = 9.0, 3.6 Hz, 1H), 3.85 (m, 2H), 2.61 (dd, J = 15.9, 15.9, 4.6 Hz, 1H), 2.41 (ddd, J = 19.1, 15.9, 4.6 Hz, 1H); ^{13}C NMR δ 163.2, 149.4 (d, J_{CP} = 9.3 Hz), 137.2, 130.2, 128.6, 128.1, 127.8, 125.8, 120.0 (d, J_{CP} = 4.6 Hz), 95.2, 73.9, 72.2, 70.0 (d, J_{CP} = 8.0 Hz), 68.5 (d, J_{CP} = 6.1 Hz), 49.4 (d, J_{CP} = 7.8 Hz), 25.3 (d, J_{CP} = 126.3 Hz); ^{31}P NMR δ 18.7.

(1*S*,*S*$_P$)-2-Propenyl-1-triphenylmethoxymethyl-2-propenyl Phenylmethoxymethyl Ester Phosphonic Acid [(−)-34]. To a solution of benzyl alcohol (0.51 mL, 4.93 mmol) in dry DME (25 mL) was added BuLi (3.2 mL 1.3 M in hexanes) at −30 °C, and the solution was warmed to room temperature over 1 h and stirred for an additional 4 h. This solution was added to the mixed phosphonate (1.320 g, 2.59 mmol) in DME (15 mL) at −50 °C over 1 h. The resulting mixture was transferred back to the alkoxide flask at −50 °C and allowed to warm to room temperature overnight. This mixture was stirred for 8 h at room temperature, quenched with NH_4Cl (sat'd aq.), extracted with EtOAc (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (7:3 hexanes/EtOAc) afforded 1.20 g (88%) of **34** as an oil; $[\alpha]_D$ −4.6 (*c* 0.16, CH_2Cl_2); IR (neat) 3059, 3032, 2931, 1638, 1490, 1448, 1257, 1215, 1078, 990 cm^{-1}; ^1H NMR δ 7.49−7.19 (m, 20H), 5.94−5.78 (m, 2H), 5.43−5.01 (m, 7H), 3.30−3.21 (m, 2H), 2.68 (dd, J = 21.1, 7.3 Hz, 2H); ^{13}C NMR δ 143.6, 136.3 (d, J_{CP} = 6.9 Hz), 134.2 (d, J_{CP} = 3.1 Hz), 128.6, 128.3, 128.0, 127.7, 127.6,127.3 (d, J_{CP} = 11.5 Hz), 127.0, 120.0 (d, J_{CP} = 14.8 Hz), 118.4, 86.7, 76.7 (d, J_{CP} = 15.6 Hz), 66.9 (d, J_{CP} = 6.4 Hz), 66.3 (d, J_{CP} = 5.2 Hz), 32.6 (d, J_{CP} = 139.6 Hz); ^{31}P NMR δ 28.3. Exact mass: calcd for $C_{33}H_{34}O_4P$ (M+1) 525.2116; found 525.2195 (FAB).

(2*S*$_P$,6*S*)-2-Phenylmethoxy-6-[(triphenylmethoxy)-methyl]-2H-1,2-oxaphosphorin-3,6-dihydro-2-oxide, [(−)-35]. To a solution of the **34** (70 mg, 0.13 mmol) in dry CH_2Cl_2 (13 mL) was added catalyst A (3 mg, 3 mol %), and the mixture was refluxed for 6 h, diluted with CH_2Cl_2, flushed with air, and stirred overnight at room temperature. Removal of the solvent under reduced pressure and flash chromatography (7:3 EtOAc/hexanes) afforded 63 mg (98%) of **35** as white solid; mp 153−155 °C; $[\alpha]_D$ −38.4 (*c* 0.56, CH_2Cl_2); IR (neat) 3058, 3032, 2929, 1490, 1448, 1279, 1248, 1077, 1001, 899 cm^{-1}; ^1H NMR δ 7.45−7.21 (m, 20H), 5.82−5.72 (m, 2H), 5.19−5.14 (m, 2H), 4.19 (dd, J = 11.9, 8.3 Hz, 1H), 3.37 (dd, J = 9.5, 6.3 Hz, 1H), 3.26 (dd, J = 9.6, 5.3 Hz, 1H), 2.50−2.04 (m, 2H); ^{13}C NMR δ 143.5, 136.0 (d, J_{CP} = 6.3 Hz), 128.6, 128.5, 128.3, 127.8, 127.8, 127.1, 126.7 (d, J_{CP} = 16.9 Hz), 121.0 (d, J_{CP} = 9.5 Hz), 86.7, 78.8 (d, J_{CP} = 7.4 Hz), 67.1 (d, J_{CP} = 6.0 Hz), 65.6 (d, J_{CP} = 5.0 Hz), 22.3 (d, J_{CP} = 132.3 Hz); ^{31}P NMR δ 21.4. Exact mass: calcd for $C_{31}H_{30}O_4P$ (M+1) 497.1882; found 497.1883 (FAB).

(2*S*$_P$,4*R*,5*S*,6*S*)-2-Phenylmethoxy-6-[(triphenylmethoxy)-methyl]-1,2-oxapho sphorinane-4,5-diol-2-oxide [(+)-36]. To a solution of **35** (61 mg, 0.12 mmol) in acetone (2 mL) and *t*-BuOH (0.8 mL) were added citric acid (30 mg, 0.16 mmol), NMO (18 mg, 0.13 mmol) and OsO_4 (1 drop 4% solution in water). The reaction mixture was stirred for 48 h, solid Na_2SO_3 and 3% aq. $NaHSO_4$ were added, and the mixture was stirred for 30 min and extracted with EtOAc (3x). Removal of the solvent under reduced pressure and flash chromatography (EtOAc/4% MeOH) afforded 51 mg (81%) of **36** as an oil; $[\alpha]_D$ +26.0 (*c* 0.19, CH_2Cl_2); IR (neat) 3363, 3059, 3033, 2934, 1490, 1449, 1226, 1079, 1022, 983 cm^{-1}; ^1H NMR δ 7.44−7.19 (m, 20H), 5.13−5.01 (m, 2H), 4.70−4.64 (m, 1H), 4.26 (br. d, J = 31.6 Hz, 1H), 3.89 (d, J = 7.8 Hz, 1H), 3.39 (d, J = 2.8 Hz, 2H), 2.31 (ddd, J = 15.6, 15.2, 5.7 Hz, 1H), 1.98 (ddd, J = 18.1, 14.9, 3.4 Hz, 1H); ^{13}C NMR δ 143.6, 135.6 (d, J_{CP} = 5.8 Hz), 128.6, 128.5, 127.9, 128.8, 127.1, 86.7, 76.5 (dd, J_{CP} = 4.9 Hz), 68.8 (d, J_{CP} = 5.4 Hz), 67.6 (d, J_{CP} = 6.4 Hz), 67.3 (d, J_{CP} = 7.1 Hz), 63.2 (d, J_{CP} = 6.4 Hz), 28.6 (d, J_{CP} = 124.6 Hz); ^{31}P NMR δ 26.6.

(2*S*$_P$,4*R*,5*S*,6*S*)-2-Phenylmethoxy-6-[(triphenylmethoxy)-methyl]-1,2-oxaphosphorinane-4,5-carbonate-2-oxide. To a solution of **36** (23 mg, 0.043 mmol) and triphosgene (27 mg, 0.09 mmol) in CH_2Cl_2 (1.0 mL) was added Et_3N (0.03 mL, 0.22 mmol) at −40 °C, and the solution was warmed to room temperature over 5 h. The reaction mixture was diluted with CH_2Cl_2, quenched with NH_4Cl (sat'd aq.), extracted with CH_2Cl_2, and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (3:2 EtOAc/hexanes) afforded 20 mg (84%) of the carbonate as a white solid; mp 162−164 °C; $[\alpha]_D$ +43.0 (*c* 3.6, CH_2Cl_2); IR (neat) 3059, 3032, 2929, 1817, 1599, 1491, 1448, 1354, 1272, 1170, 1069, 1034, 965 cm^{-1}; ^1H NMR δ 7.46−7.26 (m, 20H), 5.25−5.19 (m, 2H), 5.07 (t, J = 8.7 Hz, 1H), 5.00−4.91 (m, 1H), 4.47−4.44 (m, 1H), 3.63 (dd, J = 11.0, 2.3 Hz, 1H), 3.36 (dt, J = 11.0, 3.0 Hz, 1H), 2.62−2.52 (m, 1H), 2.32 (ddd, J = 18.3, 15.8, 9.5 Hz, 1H); ^{13}C NMR δ 152.5, 143.0, 135.2 (d, J_{CP} = 5.6 Hz), 128.9, 128.8, 128.4, 128.0, 127.9, 127.2, 86.9, 75.0 (d, J_{CP} = 5.7 Hz), 71.7, 71.1 (d, J_{CP} = 6.5 Hz), 68.3 (d, J_{CP} = 6.1 Hz), 61.9 (d, J_{CP} = 7.6 Hz), 24.7 (d, J_{CP} = 121.7 Hz); ^{31}P NMR δ 21.6. Exact mass: calcd for $C_{32}H_{30}O_8P$ (M+1) 557.1729; found 557.1705 (FAB).

(2*S*$_P$,5*S*,6*R*)-5,6-Dihydro-2-phenylmethoxy-6-[(triphenylmethoxy)methyl]2 H-1,2-oxaphosphorinane-5-ol-2-oxide [(+)-37]. To a solution of the carbonate (150 mg, 0.27 mmol) in THF (10.0 mL) was added KHMDS (0.71 mL 0.5 M in toluene, 0.35 mmol) at −40 °C, and the solution was warmed to 0 °C over 3 h. The reaction mixture was quenched with NH_4Cl (sat'd aq.), extracted with EtOAc (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (4:1 EtOAc/hexanes) afforded 110 mg (80%) of **37**; $[\alpha]_D$ +82.9 (*c* 1.64, CH_2Cl_2); IR (neat) 3325, 3058, 3032, 2930, 1597, 1490, 1448, 1362, 1228, 1193, 1079, 1019, 982 cm^{-1}; ^1H NMR δ 7.40−7.17 (m, 20H), 6.69 (ddd, J = 47.7, 12.9, 1.5 Hz, 1H), 5.72 (ddd, J = 18.8, 12.9, 2.2 Hz, 1H), 5.08−4.97 (m, 2H), 4.55−4.51 (m, 2H), 3.70 (br. s, 1H), 3.44 (d, J =

1.8 Hz, 2H); ^{13}C NMR δ 153.1, 143.4, 135.6,128.5, 127.9, 127.8, 127.1, 115.7 (d, J_{CP} = 166.2 Hz), 86.8, 79.5 (d, J_{CP} = 5.6 Hz), 68.5 (d, J_{CP} = 5.7 Hz), 65.6 (d, J_{CP} = 10.0 Hz), 63.1 (d, J_{CP} = 7.7 Hz); ^{31}P NMR δ 12.7. Exact mass: calcd for $C_{31}H_{30}O_5P$ (M+1) 513.1831; found 513.1812 (FAB).

(2S_P,3S,4R,5S,6R)-2-Phenylmethoxy-6-[hydroxymethyl]-1,2-oxaphosphorinane-3,4,5-triol-2-oxide) (38). To a solution of OsO_4 (43 mg, 0.017 mmol) in CH_2Cl_2 (0.6 mL) was added TMEDA (22 mg, 0.19 mmol) followed by the starting alcohol (68 mg, 0.13 mmol) in CH_2Cl_2 (1.0 mL) and at −78 °C. The reaction mixture was stirred for 3 h at −78 °C, warmed to room temperature, and stirred for 15 min. Removal of the solvent under reduced pressure afforded the crude osmate ester, which was dissolved in 1.0 mL MeOH and treated with citric acid (40 mg, 0.21 mmol) for 24 h. The solvent was removed, the residue was dissolved in a small amount of MeOH, and the solvent was filtered through silica gel with EtOAc/10%MeOH. The crude product was dissolved in 1.0 mL MeOH and treated with catalytic amount of TsOH·H_2O for 8 h. Removal of the solvent under reduced pressure and flash chromatography (EtOAc/10% MeOH) afforded 28 mg (71%) of **38**; ^{1}H NMR δ 7.44−7.31 (m, 5H), 5.21−5.11 (m, 2H), 4.55−4.50 (m, 1H), 4.24 (dt, J = 33.7, 2.7 Hz, 1H), 4.01 (dd, J = 9.8, 3.4 Hz, 1H), 3.90 (ddd, J = 12.5, 4.4, 2.9 Hz, 1H), 3.75 (dd, J = 9.8, 2.1 Hz, 1H); ^{13}C NMR δ 137.7 (d, J_{CP} = 6.4 Hz), 129,7, 129.6, 129.2, 78.4 (d, J_{CP} = 4.4 Hz), 75.5 (d), 71.4, 69.6 (dt, J_{CP} = 6.4 Hz), 69.0 (d), 67.7 (d, J_{CP} = 144.5 Hz), 62.8 (dt, J_{CP} = 8.0 Hz); ^{31}P NMR δ 24.5. Exact mass: calcd for $C_{38}H_{36}O_8P$ (M+1) 651.2148; found 651.2131 (FAB).

(2S_P,5S,6R)-5,6-Dihydro-2-phenylmethoxy-2H-1,2-oxaphosphorinane-5-methanesulfonate-6-[(triphenylmethoxy)-methyl]-2-oxide [(+)-39]. To a solution of diol **36** (180 mg, 0.339 mmol) in CH_2Cl_2 (10 mL) were added a catalytic amount of DMAP (8.3 mg, 0.068 mmol), MsCl (0.087 mL, 1.13 mmol) at 0 °C followed by Et_3N (0.191 mL, 1.36 mmol). The reaction mixture was warmed to room temperature over 1 h and stirred overnight at room temperature. Et_3N (0.034 mL, 0.339 mmol) was added, and the stirring was continued for 6 h. After addition of brine the mixture was extracted with EtOAc (3x) and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (1:1 hexanes/EtOAc) afforded 120 mg (60%) of **39**; $[\alpha]_D$ +105.2 (*c* 1.9, CH_2Cl_2); IR (neat) 3032, 2933, 1490, 1449, 1364, 1259, 1180, 985, 961, 853 cm^{-1}; ^{1}H NMR δ 7.44−7.24 (m, 20H), 6.81 (ddd, J = 45.9, 12.9, 2.1 Hz, 1H), 6.03 (ddd, J = 17.2, 12.9, 2.1 Hz, 1H), 5.64−5.60 (m, 1H), 5.20−5.18 (m, 2H), 4.75−4.71 (m, 1H), 3.70 (dd, J = 11.0, 2.8 Hz, 1H), 3.30 (dt, J = 11.0, 3.0 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR δ 145.9, 142.8, 135.4 (d, J_{CP} = 5.9 Hz), 128.7, 128.69, 128.6, 128.0, 127.9, 127.4, 119.9 (d, J_{CP} = 165.8 Hz), 87.1, 76.9 (d, J_{CP} = 6.1 Hz), 70.9 (d, J_{CP} = 10.6 Hz), 68.7 (d, J_{CP} = 6.2 Hz), 61.4 (dt, J_{CP} = 6.3 Hz), 38.1; ^{31}P NMR δ 10.9. Exact mass: calcd for $C_{32}H_{32}O_7PS$ (M+1) 591.1606; found 591.1591 (FAB).

(2S,5R,6R)-5,6-Dihydro-2-phenylmethoxy-2H-1,2-oxaphosphorinane-5-ol-b enzoate-6-[(triphenylmethoxy)-methyl]-2-oxide, [(−)-40]. To a solution of **39** (24 mg, 0.044 mmol) in DMF (0.5 mL) was added KOBz (10 mg, 0.062 mmol) and 18-Crown-6 (27 mg, 10 mmol). The resulting reaction mixture was stirred overnight at room temperature, quenched with NH_4Cl (sat'd aq.), extracted with EtOAc, and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (7:3 hexanes/EtOAc) afforded 20 mg (74%) of **40**; $[\alpha]_D$ −100.0 (*c* 0.51, CH_2Cl_2); ^{1}H NMR δ 7.82 (dd, J = 8.2, 1.2 Hz, 2H), 7.61 (t, J = 1.2 Hz, 1H), 7.52−7.12 (m, 22H), 7.03 (ddd, J = 45.5, 12.5, 5.7 Hz, 1H), 6.12 (dd, J = 17.2, 12.5 Hz, 1H), 5.72−5.69 (m, 1H), 5.15−4.97 (m, 3H), 3.56 (dd, J = 8.7, 5.5 Hz, 1H), 3.40 (t, J = 8.8 Hz, 1H); ^{13}C NMR δ 165.0, 143.0, 142.8, 135.5 (d, J_{CP} = 6.2 Hz), 133.4, 129.8, 129.0, 128.53, 128.48, 128.45, 128.3, 127.8, 127.6, 127.1, 122.5 (d, J_{CP} = 164.1 Hz), 87.0, 75.9 (d, J_{CP} = 5.1 Hz), 68.7 (dt, J_{CP} = 6.1 Hz), 63.9 (d, J_{CP} = 10.9 Hz), 61.0 (dt, J_{CP} = 10.5 Hz); ^{31}P NMR δ 10.3. Exact mass: calcd for $C_{38}H_{34}O_6P$ (M+1) 617.2093; found 617.2082 (FAB).

(2S_P,5R,6R)-5,6-Dihydro-2-phenylmethoxy-2H-1,2-oxaphosphorinane-5-ol-6 [(triphenylmethoxy)methyl]-2-oxide [(+)-41]. To a solution of **40** (40 mg, 0.065 mmol) in MeOH (1.0 mL) was added $Mg(OMe)_2$ (0.06 mL 7−8% solution in MeOH) the mixture was stirred overnight at room temperature, quenched with NH_4Cl (sat'd aq.). MeOH was removed, the residue extracted with EtOAc (3x), and dried (Na_2SO_4). Removal of the solvent under reduced pressure and flash chromatography (7:3 EtOAc/hexanes) afforded 25 mg (75%) of **41**; $[\alpha]_D$ +1.27 (*c* 0.63, CH_2Cl_2); ^{1}H NMR δ 7.45−7.24 (m, 20H), 6.82 (ddd, J = 45.9, 12.5, 5.5 Hz, 1H), 5.09 (dd, J = 17.7, 12.5 Hz, 1H), 5.16−5.02 (m, 2H), 4.79−4.75 (m, 1H), 4.28 (br.s, 1H), 3.56−3.45 (m, 2H); ^{13}C NMR δ 146.1, 143.1, 135.8 (d, J_{CP} = 6.0 Hz), 128.5, 128.4, 128.1, 127.9, 127.3, 119.9 (d, J_{CP} = 165.5 Hz), 87.3, 76.9 (d, J_{CP} = 4.9 Hz), 68.7 (dt, J_{CP} = 6.1 Hz), 63.4 (d, J_{CP} = 10.4 Hz), 62.7 (dt, J_{CP} = 9.6 Hz); ^{31}P NMR δ 12.1.

(2S_P,3S,4R,5R,6R)-2-Phenylmethoxy-6-[(triphenylmethoxy)methyl]-1,2-oxaphosphorinane-3,4-diol-5-ol-benzoate-2-oxide) [(−)-42]. To a solution of **40** (33 mg, 0.054 mmol) in acetone (1.5 mL) and *t*-BuOH (0.5 mL) were added citric acid (13 mg, 0.068 mmol), NMO·H_2O (9 mg, 0.067 mmol) and OsO_4 (1 drop 4% solution in water). After stirring for 24 h at room temperature,one more drop of OsO_4 was added, and the stirring was continued for 24 h. Water was added to the reaction mixture and extracted with EtOAc (3x). Removal of the solvent under reduced pressure and flash chromatography (EtOAc/1% MeOH) afforded 28 mg (80%) of **42** as an oil; $[\alpha]_D$ −36.4 (*c* 1.3, CH_2Cl_2); IR (neat) 3325, 3061, 3033, 2926, 1728, 1600, 1491, 1449, 1264, 1241, 1093, 999, 967 cm^{-1}; ^{1}H NMR δ 7.81−7.80 (m, 2H), 7.60−7.56 (m, 1H), 7.40−7.29 (m, 13H), 7.16−7.08 (m, 9H), 5,74 (d, J = 4.5 Hz, 1H), 5.38 (dd, J = 6.5, 6.5 Hz, 1H), 5.20−5.17 (m, 2H), 4.68 (ddd, J = 33.5, 3.8, 3.8 Hz, 1H), 4.19 (dd, J = 10.7, 2.7 Hz, 1H), 3.46 (dd, J = 8.5, 6.0 Hz, 1H), 3.22 (dd, J = 8.6, 8.6 Hz, 1H); ^{13}C NMR δ 164.5, 143.1, 135.5 (d, J_{CP} = 6.0 Hz), 133.4, 129.8, 129.0, 128.6, 128.5, 128.4, 128.0, 127.8, 127.0, 86.9, 74.6 (d, J_{CP} = 4.7 Hz), 71.5, 71.4, 68.9 (dt, J_{CP} = 6.1 Hz), 66.6 (d, J_{CP} = 140.9 Hz), 60.7 (dt, J_{CP} = 11.6 Hz); ^{31}P NMR δ 24.3. Exact mass: calcd for $C_{38}H_{36}O_8P$ (M+1) 651.2148; found 651.2131 (FAB).

(2S_P,3S,4R,5R,6R)-2-Phenylmethoxy-6-[hydroxymethyl]-1,2-oxaphosphorinane-3,4-diol-5-ol-2-oxide (43). To a solution of **42** (24 mg, 0.047 mmol) in acetone (0.9 mL) and *t*-BuOH (0.3 mL) were added citric acid (10 mg, 0.052 mmol), NMO·H_2O (7 mg, 0.052 mmol) and OsO_4 (1 drop 4% solution in water). The reaction was stirred for 24 h. Upon completion water was added to the reaction mixture and extracted with EtOAc (3x). The crude mixture was taken up in MeOH (1 mL), followed by the addition of catalytic TsOH, and stirred for an additional 24 h. Removal of the solvent under reduced pressure and flash chromatography (EtOAc/1% MeOH) afforded 10 mg (70%) of **43** as an oil; IR (neat) 3350, 3025, 2970, 1211, 1045 cm^{-1}; ^{1}H NMR δ 7.31−7.44 (m, 5H), 5.10−5.49 (m, 2H), 4.77 (dt, J = 5.9, 2.4 Hz, 1H), 4.29 (dd, J = 9.7, 3.7 Hz, 1H), 4.22 (ddd, J = 33.4, 4.0, 4.0 Hz, 1H), 3.96 (d, J = 4.4 Hz, 1H), 3.76−3.84 (m, 2H); ^{13}C NMR δ 136.7, 128.6, 128.4, 127.9, 77.6 (d, J_{CP} = 5.4 Hz), 70.5 (d, J_{CP} = 2.3 Hz), 68.5 (d, J_{CP} = 6.6 Hz), 64.5 (d, J_{CP} = 144.9 Hz), 61.5 (d, J_{CP} = 10.1 Hz); ^{31}P NMR δ 20.8.

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Supporting Information Available: We have previously published on compounds **15**−**17a**.[9] ^{1}H, ^{13}C, and ^{31}P NMR spectra for compounds **17b** and **18**−**42**, and X-ray crystallographic data for compound **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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