(2 H, s, $C_{8a}H_2$), 4.29 (2 H, brm, $C_{13}H$, C_5H), 3.94 (1 H, d, J = 6 Hz, C_6H), 3.74 (1 H, brm, $C_{17}H$), 3.39 (1 H, m, C_2H), 3.19 (1 H, d, J = 8 Hz, $C_{25}H$), 2.90 (1 H, brs, $C_{12}H$), 1.88 (3 H, s, C_4CH_3), 1.27 (3 H, d, J = 7 Hz, $C_{12}CH_3$).

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An Efficient Synthesis of Both Enantiomers of *trans*-1,2-Cyclopentanediol and Their Conversion to Two Novel Bidentate Phosphite and Fluorophosphinite Ligands

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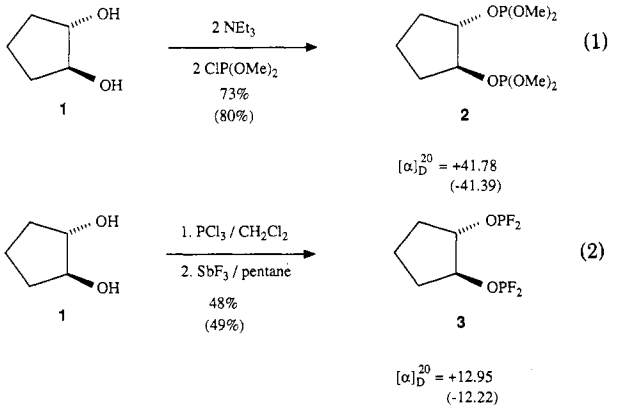
Ancillary ligands occupy a central role in organometallic chemistry as they are used to fine tune the electron density and to modify the steric environment at the metal center. In this capacity trivalent phosphorous ligands have been used extensively because this class of compounds exhibits a wide range of steric and electronic properties.[1] Chiral bidentate ligands in particular have been found to be very useful in asymmetric synthesis via organometallics—primarily in asymmetric catalysis.[2] However, all of the chiral phosphorous ligands known are the relatively electron-rich bis-phosphines and bis-phosphinites.[3] In conjunction with a study of asymmetric induction in the sequential addition of nucleophiles and electrophiles to arene chromium complexes,[4] we required better π-acceptor bidentate ligands. We here describe the synthesis of enantiomerically pure (+)- and (−)-*trans*-1,2-bis(dimethoxyphosphinoxy)cyclopentane (**2**) and *trans*-1,2-bis(difluorophosphinoxy)cyclopentane (**3**), the first examples of chiral chelating phosphite and fluorophosphinite ligands.

Reaction of common diols such as ethylene glycol and 2(*R*),3(*R*)-butanediol with dimethyl phosphorochlorodite[5] led to complex mixtures of products. Material balances were never greater than 45%. This suggested that in addition to the desired intermolecular reaction, polymerization and intramolecular processes were also occurring because of the lability of the P–OMe bond to nucleophilic displacement.

To avoid these side reactions, we employed a diol in which the hydroxyl functionalities were sterically constrained from intramolecular interaction. The reaction of racemic *trans*-1,2-cyclopentanediol (**1**)[6] with dimethyl phosphorochlorodite afforded a 72% yield of the desired bis(dimethylphosphite) **2** (eq 1). A more electron-withdrawing bidentate ligand, bis(difluorophosphite) **3**, was also prepared via a simple two-step procedure (eq 2). First, the



diol **1**, as a solution in CH_2Cl_2/ether (10:1), was slowly added to 10 equiv of PCl_3 in CH_2Cl. After removal of the solvent and excess PCl_3 at room temperature, the residue was treated with SbF_3 in refluxing pentane. Trap-to-trap distillation afforded a 48% yield of the tetrafluoride **3**. Purification of the intermediate tetrachloride by distillation (130 °C, 0.1 mmHg) led to lower yields as this material is prone to polymerization. The direct approach to **3**, involving the condensation of **1** with PF_3 in the presence of pyridine,[7] was unsuccessful.

Having developed facile syntheses of the racemic bidentate ligands **2** and **3**, their preparation in optically pure form was undertaken. When we began our work, neither (1*R*,2*R*)-(−)- nor (1*S*,2*S*)-(+)-cyclopentanediol ((−)-**1** or (+)-**1**) was available in optically pure form. In a preparation of *trans*-1,2-bis(diphenylphosphinoxy)cyclopentane[8] (which shows some promise as a ligand in asymmetric homogeneous hydrogenation), (+)-**1** was obtained with an enantiomeric excess of 67% from repeated crystallizations of the strychnine salt of its bis-hydrogensulfate.[9] Schneider and co-workers have reported an enzymatic hydrolysis of racemic *trans*-1,2-diacetoxycyclopentane which furnished the monoacetate of (−)-**1** with 63% ee and the diacetate of (+)-**1** with 50% ee.[10] A very recent report by Sakai and co-workers[11] described an enzymatic hydrolysis that afforded the same compounds with >99% ee and 95% ee, respectively. We have accomplished the synthesis of enantiomerically pure (1*R*,2*R*)- and (1*S*,2*S*)-cyclopentanediol ((−)-**1** and (+)-**1**) from the corresponding diethyl tartrates (Scheme I). This creates easy access to both pure enantiomers of ligands **2** and **3**.

The dibenzyl ether of L-(+)-diethyl tartrate (**4**) was prepared via the procedure described by Seebach et al.[12,13] Reduction of **4** with LAH in refluxing ether for 4 h afforded the diol **5** in a yield of 87%. Longer reaction periods resulted in lower yields due to reduction of the benzyl ether functionalities. Ditosylation of **5** under standard conditions led to **6** (86%) which was treated with 3 equiv of LiBr in DMSO to give the dibromide **7** (91%). It should be noted that **7** contains four of the five carbons of (1*S*,2*S*)-(+)-cyclopentanediol ((+)-**1**) and the proper stereochemistry of the vicinal hydroxyl functionalities. The addition of the fifth carbon and ring closure by cy-

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.3.
(2) *Asymmetric Synthesis*; Morrison, J., Ed.; Academic Press: New York, 1985, Vol. 5 (Chiral Catalysis).
(3) For a recent review, see: Kagan, H. B. "Chiral Ligands for Asymmetric Catalysis", in ref 2, p 1.
(4) (a) Kündig, E. P.; Simmons, D. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1320. (b) Kündig, E. P. *Pure Appl. Chem.* **1985**, *57*, 1855. (c) Cunningham, A. F., Jr.; Dupré, C.; Kündig, E. P., manuscript in preparation.
(5) Ramirez, F.; Chaw, Y. F.; Maracek, J. F.; Ugi, I. *J. Am. Chem. Soc.* **1974**, *96*, 2429.
(6) Owen, L. N.; Smith, P. N. *J. Chem. Soc.* **1952**, 4026.
(7) (a) Centofanti, L. F.; Lines, L. *Inorg. Synth.* **1976**, *16*, 166. (b) Lines, L.; Centofanti, L. F. *Inorg. Chem.* **1973**, *12*, 2111.
(8) Hayashi, T.; Tanaka, M.; Ogata, I. *Tetrahedron Lett.* **1977**, 295.
(9) Derx, H. G. *Recl. Trav. Chim. Pays-Bas* **1922**, *41*, 312.
(10) Crout, D. H. G.; Gaudet, V. S. B.; Laumen, K.; Schneider, M. F. *J. Chem. Soc., Chem. Commun.* **1986**, 808.
(11) Xie, Z.-F.; Suemune, H.; Sakai, K. *J. Chem. Soc., Chem. Commun.* **1987**, 838.
(12) Kalinowski, H.-O.; Crass, G.; Seebach, D. *Chem. Ber.* **1981**, *114*, 477.
(13) Yields and optical rotations for the (−) enantiomers prepared from D-(−)-diethyl tartrate are reported in parentheses in Scheme I.

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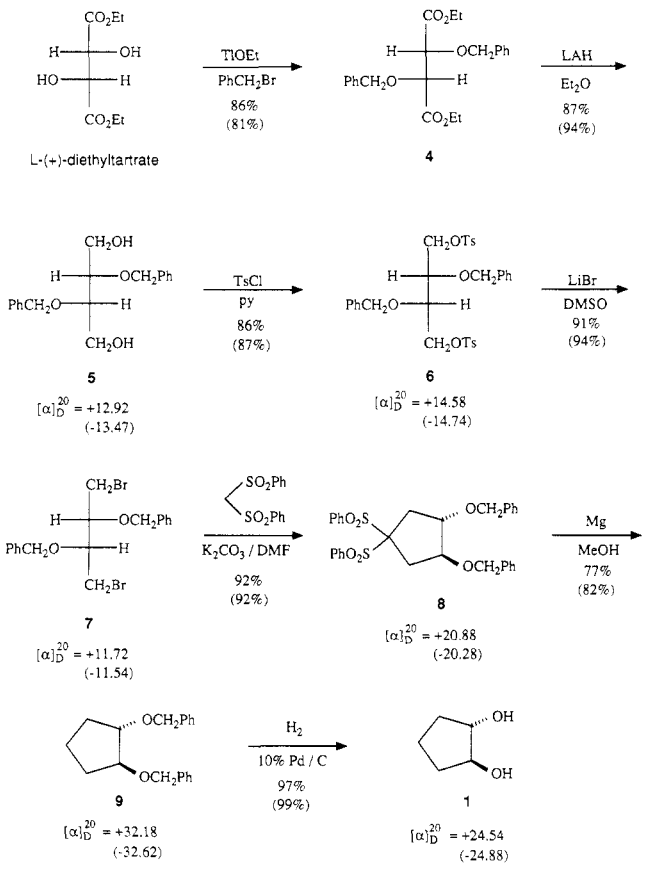
Scheme I



cloalkylation of bis(phenylsulfonyl)methane completes the synthesis of the diol.

Attempted cycloalkylation under phase-transfer conditions (50% NaOH/toluene/NBu_4I[14]) resulted in complete recovery of the starting materials. Heating the dibromide **7** with 2 equiv of the sodium salt of bis(phenylsulfonyl)methane in DMF at 75 °C[15] resulted in the loss of **7** without yielding the desired cyclic product **8**.

However, when a 1:1 mixture of **7** and bis(phenylsulfonyl)methane was stirred in a suspension of K_2CO_3 in DMF at 75 °C for 20 h,[16] a 76% yield (based on bis(phenylsulfonyl)methane) of **8** was obtained. The purification of this reaction mixture by column chromatography was somewhat tedious due to the similar polarities of **8** and the unreacted bis(phenylsulfonyl)methane. This problem was circumvented by using a 10% excess of the dibromide, allowing the preparation of **8** in 92% yield and nearly quantitative recovery of the dibromide **7** (the yield based on **7** is 99%). The remaining bis(phenylsulfonyl)methane (8%) was apparently lost during workup as its potassium salt.

The phenylsulfonyl groups of **8** were reductively cleaved by magnesium in methanol[17] to afford the dibenzyl ether **9** in 77% yield. The major byproduct of this reaction was also a benzyl ether as evidenced by ^1H NMR. The lack of SO_2 absorptions in the IR spectrum as well as its pungent odor suggested this compound to be a sulfide. However, treatment of this unidentified byproduct with Raney nickel in methanol did not furnish either the dibenzyl ether **9** or the diol (+)-**1**.

Hydrogenolysis of **9** over 10% palladium on charcoal led to the desired diol (+)-**1** in nearly quantitative yield. The ^1H NMR and IR spectra of (+)-**1** were identical with those of the racemic diol prepared in two steps from cyclopentene.[6] Its enantiomeric purity was determined to be >96%[18] by a ^1H NMR experiment in CD_3CN with the chiral shift reagent tris(((trifluoromethyl)hydroxymethylene)-*d*-camphorato)europium(III).[19,20] The overall yield of (+)-**1** from L-(+)-diethyl tartrate was 40%. The corresponding enantiomer, (−)-**1**, was prepared analogously in 46% yield from D-(−)-diethyl tartrate.[13]

The enantiomerically pure bidentate phosphite derivatives were prepared from (+)-**1** and (−)-**1** as described above (eq 1 and 2).

In summary, we have presented an efficient and short synthesis of enantiomerically pure *trans*-1,2-cyclopentanediol (**1**) and have introduced two novel chiral bidentate phosphite ligands, **2** and **3**. As bidentate phosphine ligands occupy a prominent position in asymmetric organometallic chemistry,[4] we believe that **2** and **3**, having electronic properties quite different from the classic bidentate ligands, should offer new possibilities to fine tune metal-mediated transformations.

Experimental Section

General. The solvents used were dried and/or distilled as follows: from sodium/potassium–benzophenone ketyl, ether, THF; from CaH_2, pyridine, DMSO, pentane; from phosphorus pentoxide, CH_2Cl_2. Methanol, ethanol, and DMF were used as supplied. Reagents were purified by standard procedures when deemed appropriate. ^1H and ^{19}F NMR spectra were recorded on a Varian T-60 (60 MHz) or a Varian XL-200 (200-MHz) spectrometer. ^{19}F chemical shifts are reported in ppm relative to internal C_6F_6. IR spectra were recorded on a Mattson Instruments Polaris spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Mass spectra were measured on a Varian CH 4 or SM 1 spectrometer at 70 eV. Melting points were determined on a Büchi 510 apparatus and are not corrected. Elementary analyses were performed by H. Eder, Institute of Pharmaceutical Chemistry, University of Geneva.

(2*S*,3*S*)-2,3-Bis(phenylmethoxy)-1,4-butanediol (5). A solution of 19.87 g (51.6 mmol) of diethyl 2(*R*),3(*R*)-bis(benzyloxy)tartrate (**4**) in ether (100 mL) was added dropwise, during 1 h, to a stirred suspension of 4.11 g (108.4 mmol) of LAH in ether (100 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was then heated under reflux for 4 h and allowed to stir at room temperature overnight. The excess hydride was destroyed by the slow, sequential addition of 4.1 mL of H_2O, 4.1 mL of 15% NaOH, and 12.3 mL of H_2O at 0 °C. The reaction mixture was filtered through Celite, washing the aluminium salts thoroughly with ether. Concentration of the filtrate gave an opaque oil. Column chromatography (1:1 ether/pentane, followed by ether) afforded 13.60 g (45.0 mmol, 87%) of the pure diol which solidified upon storage at 0 °C for several weeks: mp 39–41 °C; IR (CH_2Cl_2) 3600, 3450 (br), 2825, 1500, 1462, 1400, and 1075 cm^{-1}, ^1H NMR (60 MHz, $CDCl_3$) δ 7.43 (s, 10), 4.70 (s, 4), 3.77 (br s, 6), and 3.03 (br s, 2, exchange with D_2O); $[\alpha]^{20}_D$ +20.88° (ethanol, *c* 4.9); high resolution mass spectrum, calcd for $C_{18}H_{22}O_4$ 302.1519, found 302.1519.

(2*S*,3*S*)-2,3-Bis(phenylmethoxy)-1,4-bis[[(4-methylphenyl)sulfonyl]oxy]butane (6). To a stirred solution of 13.26 g (43.9 mmol) of **5** in pyridine (50 mL) at −5 °C was added 17.84

(14) Nantz, M. H.; Radisson, X.; Fuchs, P. L. *Synth. Commun.* **1987**, *17*, 55.
(15) (a) Li, C.; Sammes, M. P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2193. (b) Li, C.; Sammes, M. P. *Ibid.* **1983**, 1303.
(16) White, D. A. *Synth. Commun.* **1977**, *7*, 559.
(17) Brown, A. C.; Carpino, L. A. *J. Org. Chem.* **1985**, *50*, 1749.
(18) Detection level of the method. As the chiral centers are not involved in the reaction sequence, the enantiomeric purity is not expected to be different from that of the starting material (diethyl tartrate).
(19) Sweeting, L. M.; Crans, D. C.; Whitesides, G. M. *J. Org. Chem.* **1987**, *52*, 2273.
(20) We experienced great difficulty in preparing the 0.2 M solution of the shift reagent in CD_3CN. Even though the shift reagent was dried at 100 °C under vacuum for 15 h and the CD_3CN was freshly distilled from phosphorus pentoxide, there was a substantial amount of insoluble white solid. Use of the filtered solution, however, led to excellent results.

g (93.6 mmol) of tosyl chloride in one portion. After all the chloride had dissolved, the reaction mixture was allowed to stand at 0 °C for 15 h. The reaction mixture was then diluted with H_2O (200 mL) and extracted with CH_2Cl_2 (3 x 75 mL). The combined organic extracts were washed with 1 M HCl (3 × 100 mL) and saturated NaCl (100 mL), then dried ($MgSO_4$), and concentrated to give an off-white solid. Recrystallization from ethanol (600 mL) gave 22.78 g (38.0 mmol, 86%) of white needles: mp 121 °C; IR (CH_2Cl_2) 3050, 2900, 1600, 1462, 1375, 1188, 1100, 938, and 825 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.90 (d, 4 J = 8 Hz), 7.2–7.6 (m, 14), 3.65–4.80 (m, 10), and 2.50 (s, 6); $[\alpha]^{20}_D$ +14.58° ($CHCl_3$, c 4.8).

Anal. Calcd for $C_{32}H_{34}O_8S_2$: C, 62.93; H, 5.61; S, 10.50. Found: C, 62.89; H, 5.64; S, 10.43.

(2*S*,3*S*)-1,4-Dibromo-2,3-bis(phenylmethoxy)butane (7). A solution of 9.77 g (112.5 mmol) of dry LiBr and 22.6 g (37.5 mmol) of **6** in DMSO (95 mL) was heated at 60 °C for 15 h. The reaction mixture was then diluted with H_2O (500 mL) and extracted with ether (5 × 100 mL). The combined ethereal extracts were washed with H_2O (3 × 100 mL) and saturated NaCl (100 mL), then dried ($MgSO_4$), and concentrated to yield a yellow oil. Column chromatography (pentane, followed by 10:1 pentane/ether) gave 14.66 g (34.0 mmol, 91%) of a clear oil: IR (CH_2Cl_2) 3025, 2875, 1462, 1225, and 1075 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.38 (s, 10), 4.72 (d, 2, J = 11.5 Hz), 4.59 (d, 2, J = 11.5 Hz), 3.96 (m, 2), and 3.38–3.62 (m, 4); $[\alpha]^{20}_D$ +11.72° ($CHCl_3$, c 5.8); high resolution mass spectrum, calcd for $C_{18}H_{20}{}^{79}Br_2O_2$ 425.9810, found 425.9830.

(1*S*,2*S*)-1,2-Bis(phenylmethoxy)-4,4-bis(phenylsulfonyl)cyclopentane (8). A mixture of 7.94 g (26.8 mmol) of bis(phenylsulfonyl)methane, 12.62 g (29.5 mmol) of **7**, and 8.89 g (64.3 mmol) of K_2CO_3 in DMF (35 mL) was stirred at 75 °C for 20 h. The solid/oil residue was dissolved in CH_2Cl_2 (100 mL) and filtered through Celite. Concentration gave an orange oil. Column chromatography (10:1 pentane/CH_2Cl_2, followed by CH_2Cl_2) afforded 1.88 g (4.4 mmol) of **7** and 13.92 g (24.7 mmol, 92%) of a gummy white solid: mp 45–55 °C; IR (CH_2Cl_2) 3050, 2870, 1450, 1330, 1310, 1150, 1110, and 1080 cm^{-1}, ^1H NMR (200 MHz, $CDCl_3$) δ 8.00 (d, 4, J = 8 Hz), 7.63 (m, 6), 7.30 (br s, 10), 4.65 (d, 2, J = 12 Hz), 4.53 (d, 2, J = 12 Hz), 3.88–4.04 (m, 2), 2.68–2.86 (m, 2), and 2.24–2.44 (m, 2); $[\alpha]^{20}_D$ +20.88 (CH_2Cl_2, c 4.4).

Anal. Calcd for $C_{31}H_{30}O_6S_2$: C, 66.17; H, 5.37; S, 11.40. Found: C, 66.05; H, 5.43; S, 11.29.

(1*S*,2*S*)-1,2-Bis(phenylmethoxy)cyclopentane (9). To a solution of 13.92 g (24.7 mmol) of **8** in methanol (625 mL) at 50 °C under a nitrogen atmosphere was added 4.33 g (178 mmol) of activated magnesium. Once evolution of hydrogen began, the heating source was removed and the reaction was maintained, over a period of ~6 h, by the addition of two supplementary portions of 4.33 g (total of 535 mmol) of magnesium. It was occasionally necessary to cool the reaction mixture with a 15 °C water bath during this time. After all the magnesium had reacted, the cloudy gray solution was concentrated, diluted with H_2O (300 mL), and then acidified with concentrated HCl at 0 °C until all the magnesium salts were dissolved. The resulting clear solution was extracted with ether (3 × 200 mL). The combined ethereal extracts were washed with 1 M KOH (3 × 200 mL) and saturated NaCl (200 mL), dried ($MgSO_4$), and concentrated to give a pungent oil. Column chromatography (20:1 pentane/ether) afforded 5.37 g (19.0 mmol, 77%) of a clear, fragrant oil: IR (CH_2Cl_2) 3030, 2950, 1500, 1450, 1360, 1340, 1220, and 1100 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.34 (s, 10), 4.52 (2 d, 4, J = 12.5 Hz), 3.92–4.03 (m, 2), 1.87–2.10 (m, 2), and 1.60–1.82 (m, 4); $[\alpha]^{20}_D$ +32.18° ($CHCl_3$, c 5.6).

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.42; H, 8.03.

(1*S*,2*S*)-1,2-Cyclopentanediol ((+)-1). A mixture of 5.11 g (18.1 mmol) of **9** and 1.35 g of 10% palladium on charcoal in ethanol (35 mL) was degassed three times and then hydrogenated under 6 atm pressure of H_2 for 5 h. The reaction mixture was filtered and concentrated to afford 1.79 g (17.5 mmol, 97%) of a fragrant, highly hygroscopic, white solid: mp 47.0–48.0 °C (lit.[6] mp 50 °C); IR (CH_2Cl_2) 3600, 3390 (br), 2920, 1450, 1280, 1075, 1040, and 970 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.93–4.06 (m, 2), 2.24 (s, 2, exchanges with D_2O), 1.86–2.12 (m, 2), 1.63–1.80 (m, 2), and 1.42–1.62 (m, 2); $[\alpha]^{20}_D$ +24.54° (ethanol, c 5.4).

(1*R*,2*R*)-1,2-Cyclopentanediol ((−)-1): 2.24 g (21.9 mmol, 47% overall yield from D-(−)-diethyl tartrate); mp 48.0–48.5 °C; $[\alpha]^{20}_D$ −24.88° (ethanol, c 6.0).

(1*S*,2*S*)-1,2-Bis(dimethoxyphosphinoxy)cyclopentane (2). To a stirred solution of 0.74 g (7.25 mmol) of **1** and 1.62 g (2.23 mL, 16.0 mmol) of triethylamine in ether (50 mL) at 0 °C under a nitrogen atmosphere was added, dropwise during 15 min, 2.05 g (1.80 mL, 16.0 mmol) of dimethyl phosphorochlorodite. This caused the immediate precipitation of triethylamine hydrochloride. The reaction mixture was stirred for 15 h at 0 °C. The reaction mixture was filtered through Celite under a nitrogen atmosphere to afford, after concentration, a pale yellow oil. Bulb-to-bulb distillation at 120 °C (0.1 mm) afforded 1.52 g (5.31 mmol, 73%) of a clear oil: IR (CH_2Cl_2) 2970, 2830, 1465, 1180, 1020, 970, and 725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.39–4.53 (m, 2), 3.50 (d, 6, J = 9.2 Hz), 3.50 (d, 6, J = 10.6 Hz), 1.90–2.15 (m, 2), and 1.60–1.83 (m, 4); MS, m/e (70 eV) 286 (parent), 255 (−OCH_3), 203, 172, 111, 93 (base), 79, and 67; $[\alpha]^{20}_D$ +41.78° (CH_2Cl_2, c 4.8); high resolution mass spectrum, calcd for $C_9H_{20}O_6P_2$ 286.0735, found 286.0730.

(1*S*,2*S*)-1,2-Bis(difluorophosphinoxy)cyclopentane (3). To a stirred solution of 31.48 g (20 mL, 230 mmol) of freshly distilled PCl_3 in CH_2Cl_2 (20 mL) was added, dropwise during 1 h, a solution of 0.717 g (7.02 mmol) of **1** in 10:1 CH_2Cl_2/ether (5 mL). This caused the evolution of HCl. Immediately after the addition was completed, the reaction mixture was concentrated at room temperature to give a pale yellow residue. The residue was dissolved in pentane (10 mL) and added to a suspension of 2.53 g (14.2 mmol) of dry, freshly sublimed SbF_3 in pentane (10 mL), and the resulting mixture was heated under reflux for 1.5 h. At this time, the crude reaction mixture was transferred to a high vacuum line, degassed three times, and distilled at a pressure of ~5×10^{-2} mm, through a series of three traps: −35 °C, −78 °C, and −196 °C. The −35 °C trap contained primarily antimony salts and the −196 °C trap, pentane. The −78 °C trap contained 0.807 g (3.38 mmol, 48%) of a mobile liquid: bp 58 °C (80 mm); IR (CH_2Cl_2) 2980, 1440, 1375, 1070, 1010, 1025, 815, and 770 cm^{-1}; ^1H NMR (200 MHz, CD_2Cl_2) δ 4.78–4.92 (m, 2), 1.90–2.25 (m, 2), and 1.65–2.25 (m, 4); ^{19}F NMR (CD_2Cl_2) 115.51 (d, J = 1298.5 Hz); $[\alpha]^{20}_D$ +12.95° (CH_2Cl_2, c 5.5).

Anal. Calcd for $C_5H_8F_4O_2P_2$: C, 25.23; H, 3.39. Found: C, 25.50; H, 3.46.

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Registry No. (1*S*,2*S*)-(+)-**1**, 107492-82-0; (1*R*,2*R*)-(−)-**1**, 930-46-1; *trans*-(±)-**1**, 86703-52-8; (1*S*,2*S*)-(+)-**2**, 113303-27-8; (1*R*,2*R*)-(−)-**2**, 113350-86-0; *trans*-(±)-**2**, 113427-41-1; (1*S*,2*S*)-(+)-**3**, 113303-28-9; (1*R*,2*R*)-(−)-**3**, 113303-35-8; *trans*-(±)-**3**, 113350-88-2; (2*R*,3*R*)-**4**, 77312-71-1; (2*S*,3*S*)-**4**, 113321-58-7; (2*S*,3*S*)-(+)-**5**, 113427-43-3; (2*R*,3*R*)-(−)-**5**, 113350-84-8; (2*S*,3S)-(+)-**6**, 113303-29-0; (2*R*,3*R*)-(−)-**6**, 113321-59-8; (2*S*,3*S*)-(+)-**7**, 113303-30-3; (2*R*,3*R*)-(−)-**7**, 113321-60-1; (1*S*,2*S*)-(+)-**8**, 113303-31-4; (1*R*,2*R*)-(−)-**8**, 113303-32-5; (1*S*,2*S*)-(+)-**9**, 113350-83-7; (1*R*,2*R*)-(−)-**9**, 113350-85-9; (1*S*,2*S*)-$C_5H_8(OPCl_2)_2$, 113303-33-6; (1*R*,2*R*)-$C_5H_8(OPCl_2)_2$, 113303-34-7; *trans*-(±)-$C_5H_8(OPCl_2)_2$, 113350-87-1; $CH_2(SO_2Ph)_2$, 3406-02-8; $ClP(OMe)_2$, 3743-07-5; L-(+)-diethyl tartrate, 87-91-2; D-(−)-diethyl tartrate, 13811-71-7.