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Resolution and Stereochemistry of *tert*-Butylphenylphosphinous Acid−Borane

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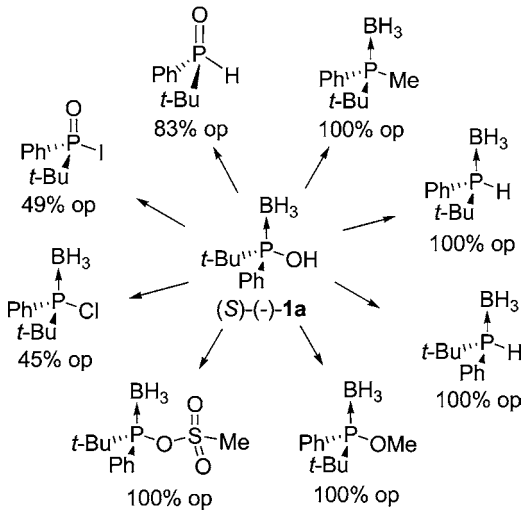

A combined use of ephedrine and cinchonine as resolving agents enabled facile resolution of racemic *tert*-butylphenylphosphinous acid−borane (**1**) into the two enantiomers in ca. 31−32% yield each. The resolved **1** served as a model substrate to study stereoselective synthetic transformations of phosphinous acid−boranes yielding optically active phosphinite−borane, boranatophosphinous−sulfonic anhydride, secondary phosphine−borane, tertiary phosphine−borane, secondary phosphine oxide, and phosphinic halides. By the judicious choice of the reaction paths, either enantiomer of *tert*-butylphenylphosphine−borane and of *tert*-butylmethylphenylphosphine−borane could be stereoselectively obtained from a single enantiomer of **1**.

Introduction

Chiral organophosphorus compounds such as tertiary diphosphines and monophosphines are widely utilized in the field of asymmetric synthesis as chiral ligands and as chiral catalysts.[1] Especially valuable are enantiopure phosphine ligands that possess a chirality center at the phosphorus atom, and the use of such compounds in asymmetric reactions catalyzed by transition metals is continuously growing.[2] Synthesis of such ligands has progressed rapidly in the past two decades due in great part to the development of methodologies based on phosphine−borane chemistry.[3] Among the important intermedi-

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(1) (a) Yamanoi, Y.; Imamoto, T. *Rev. Heteroatom Chem.* **1999**, *20*, 227−248. (b) Lagasse, F.; Kagan, H. B. *Chem. Pharm. Bull.* **2000**, *48*, 315−324.

(2) For recent publications, see: (a) Chen, W.; Mbafor, W.; Roberts, S. M.; Whittall, J. *J. Am. Chem. Soc.* **2006**, *128*, 3922−3923. (b) Imamoto, T.; Itoh, T.; Yamanoi, Y.; Narui, R.; Yoshida, K. *Tetrahedron: Asymmetry* **2006**, *17*, 560−565. (c) Christ, M. L.; Zabłocka, M.; Spencer, S.; Lavender, R. J.; Lemaire, M.; Majoral, J.-P. *J. Mol. Catal. A: Chem.* **2006**, *245*, 210−216. (d) Liu, D.; Zhang, X. *Eur. J. Org. Chem.* **2005**, 646−649. (e) Miller, K. M.; Jamison, T. F. *Org. Lett.* **2005**, *7*, 3077−3080. (f) Hoge, G.; Samas, B. *Tetrahedron: Asymmetry* **2004**, *15*, 2155−2157. (g) Pakulski, Z.; Demchuk, O. M.; Frelek, J.; Luboradzki, R.; Pietrusiewicz, K. M. *Eur. J. Org. Chem.* **2004**, 3913−3918.

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ates in the field are resolved methyl[4] and menthyl[5] phosphinite−boranes, which formally should be viewed as chiral esters of phosphinous acid−boranes. In contrast to the esters, the parent phosphinous acid−boranes have not attracted much attention in the past,[6] and only very recently, the ready access to these compounds has been offered[7,8] and their reactivity profile has been revealed.[9] They can be used as convenient precursors to a large variety of phosphorus compounds such as phosphinite−boranes, *sec*-phosphine−boranes, *tert*-phosphine−boranes, chlorophosphine−boranes, stable boranatophosphinous anhydrides, as well as mixed boranatophosphinous−carboxylic and boranatophosphinous−sulfonic anhydrides, oxaphosphaborolidines, *sec*-phosphine oxides, phosphinic halides, and others.[9] Since the unsymmetrically substituted phosphinous acid−boranes are chiral and bear a stereogenic center at phosphorus, we considered it important to develop a gram-scale access to resolved phosphinous acid−boranes to further expand the synthetic potential of this class of compounds and to study the stereochemistry of their conversions into other optically active phosphorus-stereogenic organophosphorus compounds.

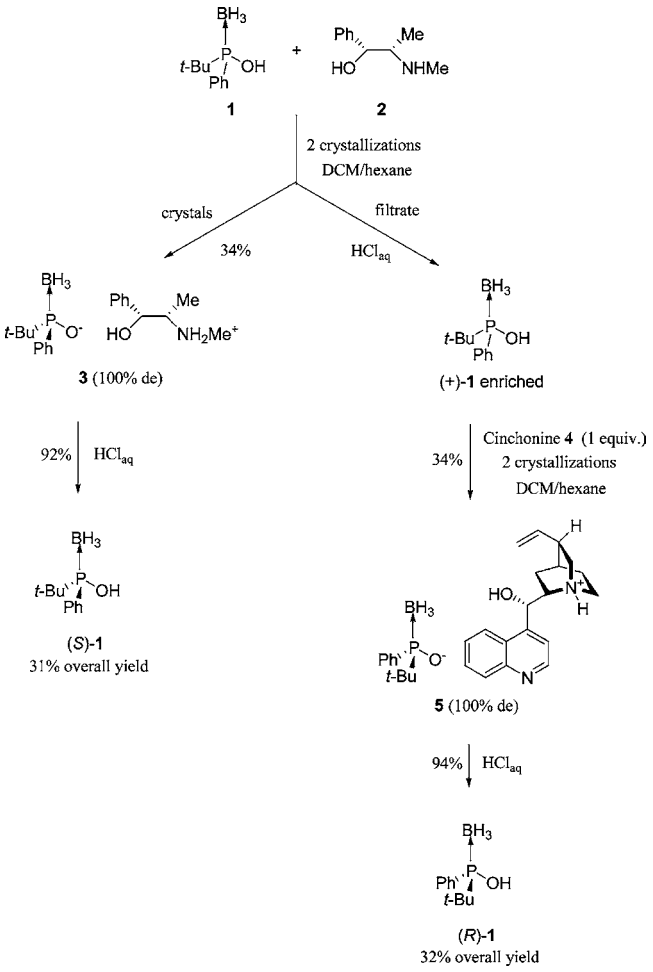
Herein, we report that by taking advantage of the acidic properties of phosphinous acid−boranes, it is possible to resolve them in the classical way by using enantiopure amines as resolving agents. We have selected *tert*-butylphenylphosphinous acid−borane (**1**) for the model study and have succeeded in effectively resolving it through its diastereomeric salts with ephedrine and cinchonine. We will demonstrate that the resolved **1** can be transformed with high stereoselectivity into optically active phosphinite−borane, tertiary phosphine−borane, secondary phosphine−borane, phosphinic halides, and a mixed phosphinous acid−borane sulfonic anhydride.

Results and Discussion

Racemic *tert*-butylphenylphosphinous acid−borane (**1**) was synthesized from *tert*-butylphenylphosphinic chloride by reduction with BH_3−THF in 95% yield as described before.[9a] Separation of *rac*-**1** into enantiomers was carried out according to the protocol shown in Scheme 1.

Dissolving equimolar amounts of *rac*-**1** and (1*R*,2*S*)-ephedrine hemihydrate **2**[10] in DCM and adding hexane until the solution became slightly cloudy resulted in the precipitation of a crystalline salt. After 24 h, the crystals were collected and recrystallized once more from DCM/hexane to yield the ephedrine salt of **1** of high diastereomeric purity as confirmed by ^{1}H NMR. Acidic workup of **3** with aqueous HCl afforded free phosphinous acid borane (*S*)-**1** in 31% overall yield. Attempted crystallizations of the second phosphorus−epimeric ephedrine salt of **1** from the mother liquor were unsuccessful. However, recovering the enriched (*R*)-**1** from the mother liquor and treating it with an equimolar amount of cinchonine **4** in the same solvent system resulted in the precipitation of a crystalline cinchonine salt of **1** that after one additional recrystallization afforded diastereomerically pure **5** (^{1}H NMR). Acidic workup of **5** as before furnished enantiomerically pure (*R*)-**1** in 32% overall yield.

SCHEME 1



The assignment of the absolute configurations to the resolved enantiomers of **1** was originally based on our previous chemical correlation of enriched (*S*)-**1** with (*S*)-*tert*-butylmethylphenylphosphine−borane.[11] It is now unequivocally confirmed by the single-crystal X-ray diffraction data obtained for **5** (Figure 1).

The potential of using the resolved phosphinous acid−boranes as convenient precursors to other synthetically useful enantiopure organophosphorus compounds was demonstrated first by reacting (*S*)-**1** at oxygen in the straightforward conversions of (*S*)-**1** into (*S*)-methyl *tert*-butylphenylphosphinite-borane (**6**)

(3) For recent reviews concerning phosphine−boranes, see: (a) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 665−698. (b) Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391−1415. (c) Carboni, B.; Monnier, L. *Tetrahedron* **1999**, *55*, 1197−1248.

(4) (a) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357−6360. (b) Jugé, S.; Stephan, M.; Merdes, R.; Genêt, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun*. **1993**, 531−533.

(5) Imamoto, T.; Osiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244−5252. (b) Hoge, G. *J. Am. Chem. Soc.* **2003**, *125*, 10219−10227.

(6) (a) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287−306. (b) Köster, R.; Tsay, Y.-H.; Synoradzki, L. *Chem. Ber.* **1987**, *120*, 1117−1124. (c) Uziel, J.; Stéphan, M.; Kaloun, E. B.; Genêt, J. P.; Jugé, S. *Bull. Soc. Chim. Fr.* **1997**, *134*, 379−389. (d) Nagata, K.; Matsukawa, S.; Imamoto, T. *J. Org. Chem.* **2000**, *65*, 4185−4188.

(7) Stankevič, M.; Pietrusiewicz, K. M. *Synlett* **2003**, 1012−1016.

(8) Stankevič, M.; Andrijewski, G.; Pietrusiewicz, K. M. *Synlett* **2004**, 311−315.

(9) (a) Stankevič, M.; Pietrusiewicz, K. M. *Synthesis* **2005**, 1279−1290. (b) Pietrusiewicz, K. M.; Stankevič, M. *Curr. Org. Chem.* **2005**, *9*, 1883−1897.

(10) Anhydrous ephedrine failed to provide any crystalline precipitate with *rac*-**1**. However, the addition of a small amount of water to the mixture of *rac*-**1** and anhydrous ephedrine was found effective in promoting the desired fractional crystallization of **2a**.

(11) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075−9076.

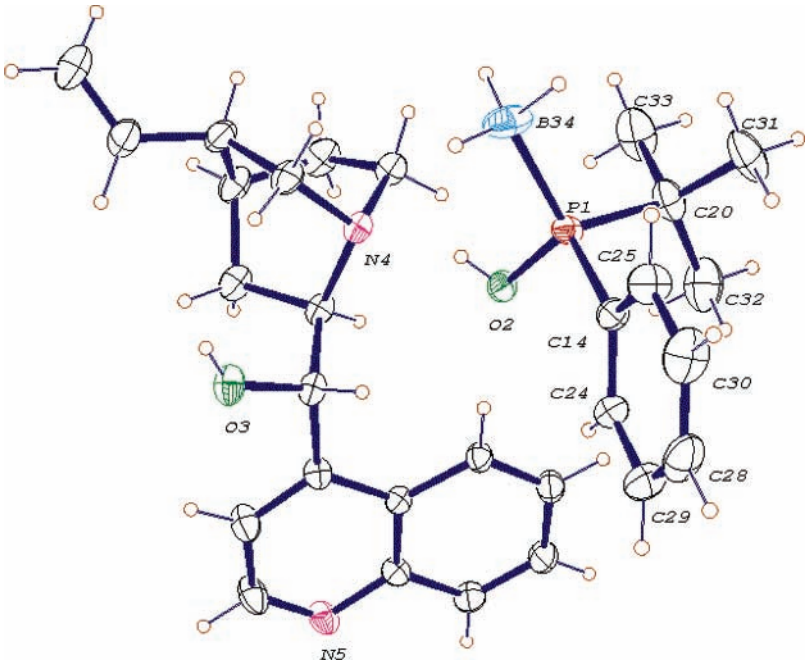
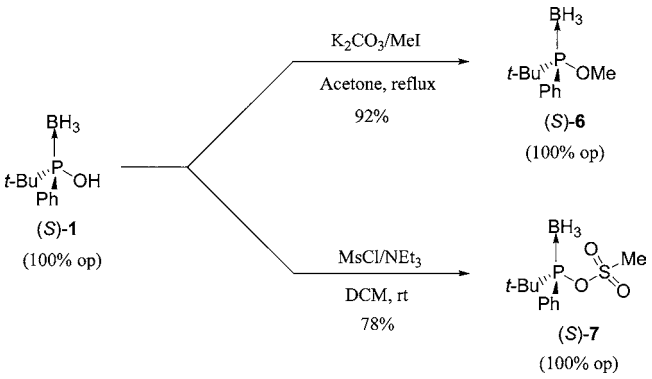


FIGURE 1. ORTEP view of cinchonine salt of (*R*)-**1**.

SCHEME 2



and into (*S*)-*tert*-butylphenylboranatophosphinous methanesulfonic anhydride (**7**) by means of simple alkylation and acylation reactions, respectively (Scheme 2).

O-Methylation of (*S*)-**1** was best achieved with methyl iodide in the presence of potassium carbonate in boiling acetone and afforded the desired ester (*S*)-**6** in 92% isolated yield. In turn, treatment of (*S*)-**1** with mesyl chloride in the presence of triethylamine in DCM gave the mixed anhydride (*S*)-**7** in 78% isolated yield. As the two reactions took place at the oxygen center, the configuration at P remained intact, and the (*S*) absolute configuration was assigned to the two products (i.e., the same as in the starting phosphinous acid−borane).

With the readily available enantiopure **6** and **7** in hand, the fully stereoselective synthesis of the two enantiomers of a secondary phosphine−borane and a tertiary phosphine−borane could then be carried out as delineated in Scheme 3.

Treatment of (*S*)-**6** with lithium in THF/NH_3 at low temperature resulted in the cleavage of the ester bond leading to (*R*)-*tert*-butylphenylphosphine−borane (**8**) in 58% yield. Deprotonation of **8** at low temperature and quenching of the resulting lithiated *sec*-phosphine borane with methyl iodide afforded (*S*)-*tert*-butylmethylphenylphosphine−borane (**9**). The optical purity (op) and the absolute configuration of **8** and **9** were determined by comparison with the known compounds[11] and confirmed the expected full retention of configurations in both steps.[12]

According to the lower track of Scheme 3, anhydride (*S*)-**7** was reduced by sodium borohydride in ethanol with the clean inversion of configuration[13] and afforded enantiomerically pure (*S*)-**8** in 96% yield. Methylation of the lithiated (*S*)-**8** as stated previously gave (*R*)-**9** in 89% yield. Thus, as indicated in Scheme 3, the two synthetic paths are complementary and demonstrate the practical possibility of achieving the fully stereoselective synthesis of either enantiomer of a secondary phosphine−borane and a tertiary phosphine−borane from a single enantiomer of the resolved phosphinous acid−borane.

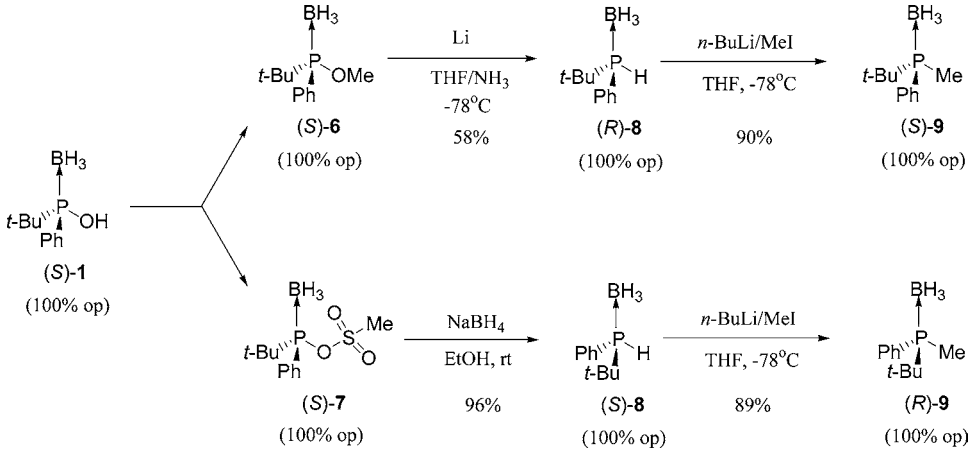
The stereochemistry of the conversions of the resolved **1** into its acid halide derivatives was studied next. The reaction of (*S*)-**1** with mesyl chloride in the presence of an excess of triethylamine hydrochloride gave the optically active chlorophosphine−borane (*R*)-**10** in 56% yield (Scheme 4). This conversion was found to occur with predominant inversion of configuration at P, although it was accompanied by a considerable loss of configurational integrity of the phosphorus center as evidenced by the pertinent chemical correlation with methyl phosphinite−borane (*S*)-**6** obtained previously (Scheme 4).

In turn, reaction of (*S*)-**1** with NaH and hexachloroacetone as the chlorinating agent resulted in the loss of the borane protecting group and led to the exclusive formation of (*S*)-*tert*-butylphenylphosphinic chloride (**11**) (Scheme 5). Comparing the optical rotation of the obtained (*S*)-**11** with the pertinent literature data[14] indicated that the studied conversion occurred with the predominant inversion of configuration and gave the phosphinic chloride of 45% optical purity.

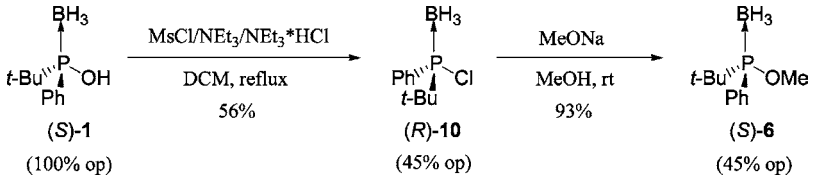
Similarly, treatment of (*S*)-**1** with bromine or iodine as halogenating agents led to the formation of (*S*)-*tert*-butylphe-

(12) Oshiki, T.; Hikosaka, T.; Imamoto, T. *Tetrahedron Lett.* **1991**, *32*, 3371−3374.
(13) Skrzypczyński, Z.; Michalski, J. *J. Org. Chem.* **1988**, *53*, 4549−4551.
(14) Omelańczuk, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1718−1719.

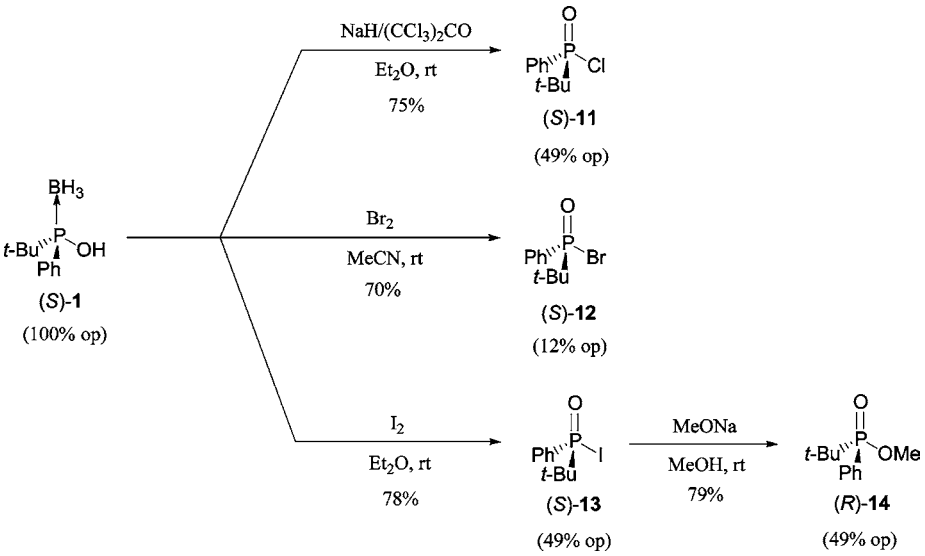
SCHEME 3



SCHEME 4



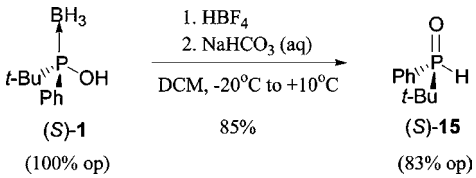
SCHEME 5



nylphosphinic bromide (**12**) and (*S*)-*tert*-butylphenylphosphinic iodide (**13**), respectively (Scheme 5). The absolute configuration and the optical purity of the obtained (*S*)-**12** was determined by comparison of its rotation data with the literature value,[15] whereas for (*S*)-**13**, it was assessed by chemical correlation with (*R*)-**14** obtained previously[16] (Scheme 5).

Finally, decomplexation of (*S*)-**1** by HBF_4 etherate[17] was found to occur with the expected retention of configuration at P and yielded (*S*)-**15** (Scheme 6). Somewhat less expectedly, however, the isolated (*S*)-**15** was found to be not optically pure

SCHEME 6



(83% op) as revealed by the comparison of its specific rotation with the known literature values.[18]

(15) Haynes, R.; Lam, W. W.-L.; Williams, I. D.; Yeung, L.-L. *Chem.—Eur. J.* **1997**, *3*, 2052−2057.

(16) Au-Yeung, T.-L.; Chan, K.-Y.; Chan, W.-K.; Haynes, R. K.; Williams, I. D.; Yeung, L. L. *Tetrahedron Lett.* **2001**, *42*, 453−456.

(17) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319−9322.

(18) (a) Drabowicz, J.; Łyżwa, P.; Omelańczuk, J.; Pietrusiewicz, K. M.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2757−2863. (b) Haynes, R. K.; Au-Yeung, T.-L.; Chan, W.-K.; Lam, W.-L.; Li, Z.-Y.; Yeung, L.-L.; Chan, A. S. C.; Li, P.; Koen, M.; Mitchell, C. R.; Vonwiller, S. C. *Eur. J. Org. Chem.* **2000**, 3205−3216. (c) Leyris, A.; Nuel, D.; Giordano, L.; Achard, M.; Buono, G. *Tetrahedron Lett.* **2005**, *46*, 8677−8680.

Conclusion

The efficient resolution of racemic *tert*-butylphenylphosphinous acid−borane (**1**) through the combined use of cinchonine and ephedrine as the resolving agents has been achieved. Use of the resolved **1** in the model syntheses of optically active phosphinite−borane, boranatophosphinous−sulfonic anhydride, secondary phosphine−borane, tertiary phosphine−borane, secondary phosphine oxide, and phosphinic halides demonstrated the potential of resolved phosphinous acid−boranes as convenient substrates for the synthesis of a variety of other phosphorus-stereogenic compounds. The fully stereoselective syntheses of both enantiomers of *tert*-butylphenylphosphine−borane **8** and of *tert*-butylmethylphenylphosphine−borane **9** from a single enantiomer of the resolved phosphinous acid−borane **1** highlight this potential the best. In the course of these syntheses, the fully regio- and stereoselective reduction of mixed boranatophosphinous−sulfonic anhydride by sodium borohydride was accomplished.

Experimental Procedures

Resolution of Racemic *tert*-Butylphenylphosphinous Acid−Borane (1). A sample of racemic *tert*-butylphenylphosphinous acid−borane (**1**) (0.980 g, 5 mmol) was dissolved in DCM (10 mL), and then (1*R*,2*S*)-ephedrine hemihydrate **2** (0.871 g, 5 mmol) was added. After homogenization of the mixture, hexane was added until the clear solution became slightly cloudy and it was left overnight. The formed precipitate was filtered off and recrystallized from hexane−DCM to give 0.614 g of diastereomerically pure (^{1}H NMR) salt **3** (34%). The mother liquor was evaporated to dryness, and the residue was dissolved in DCM (10 mL). A total of 10 mL of 10% hydrochloric acid was then added, and the mixture was stirred at room temperature for 0.5 h. Then, the two phases were separated, and the aqueous phase was washed 3 times with DCM (20 mL). The collected organic phases were dried over anhydrous $MgSO_4$, filtered, and evaporated on a rotary evaporator. The resulting enriched phosphinous acid−borane **1** was dissolved in 10 mL of DCM, and cinchonine **4** (1.030 g, 3.5 mmol) was added with a few drops of methanol to make all cinchonine dissolved. Then, hexane was added until the mixture became slightly cloudy. The solvents were allowed to evaporate slowly at room temperature in an open flask (24 h). The resulting crystalline precipitate was filtered off and recrystallized from DCM−hexane to afford diastereomerically pure (^{1}H NMR) cinchonine salt **5** (0.833 g, 34%). The diastereomerically pure ephedrine salt (0.666 g, 1.85 mmol) **3** was dissolved in DCM (20 mL), and 10 mL of 10% hydrochloric acid was added. The resulting mixture was extracted 6 times with 20 mL of DCM, and the combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to give 0.333 g of (*S*)-**1** (92%) as a glassy solid. $[\alpha]^{22}_D$ −44.2 (*c* 1.15, $CHCl_3$) (100% op);[8] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.0−1.7 (bm, 3H), 1.1 (d, J_{P-H} = 14.66 Hz, 9H), 4.5 (bs, 1H), 7.4−7.6 (m, 3H), 7.7−7.9 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.9 (d, J_{P-C} = 3.44 Hz), 31.7 (d, J_{P-C} = 41.1 Hz), 127.9 (d, J_{P-C} = 10.1 Hz), 131.2; 131.4 (d, J_{P-C} = 10.4 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 114.4; Anal. Calcd for $C_{10}H_{18}BOP$: C 61.27, H 9.26. Found: C 61.26, H 9.08.

Acid (*R*)-**1** was liberated from the cinchonine salt **5** using the same procedure as described for (*S*)-(−)-**1**. $[\alpha]^{22}_D$ +44.2 (*c* 1.02, $CHCl_3$) (100% op);[8] Anal. Calcd for $C_{10}H_{18}BOP$: C 61.27, H 9.26. Found: C 61.39, H 9.30.

(*S*)-*tert*-Butylphenylphosphinous Acid−Borane Methyl Ester (6). In a flask equipped with a magnetic stirrer, argon inlet, and reflux condenser was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of acetone. Then, anhydrous potassium carbonate (0.414 g, 3 mmol) was added. After 5 min, methyl iodide (0.426 g, 3 mmol) was added, and the reaction mixture was heated under reflux for 3 h. The reaction mixture was allowed to cool to room temperature, inorganic salt was filtered off, and the filtrate was evaporated to dryness. The residue was subjected to separation by flash chromatography with hexane/ethyl acetate (6:1) as an eluent and yielded 0.058 g of (*S*)-**6** (92%) as a white solid. $[\alpha]^{22}_D$ −119.2 (*c* 1.02, $CHCl_3$) (100% op);[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.1−1.6 (bm, 3H), 1.1 (d, J_{P-H}= 14.2 Hz, 9H), 3.7 (d, J_{P-H}= 11.1 Hz, 3H), 7.4−7.6 (m, 3H), 7.6−7.8 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.2 (d, J_{P-C} = 3.0 Hz); 32.1 (d, J_{P-C} = 43.5 Hz); 54.7 (d, J_{P-C} = 4.3 Hz); 128.1 (d, J_{P-C} = 9.4 Hz); 131.4 (d, J_{P-C} = 2.7 Hz); 131.8 (d, J_{P-C} = 9.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 127.6; HRMS for $C_{11}H_{20}BONaP$ ($M + Na^+$): Calcd: 233.1237. Found: 233.1235.

(*S*)-*tert*-Butylphenylphosphinous Acid−Borane Methanesulfonyl Anhydride (7). In a flask equipped with magnetic stirrer and a drying tube ($CaCl_2$) (*S*)-**1** (0.059 g, 0.3 mmol) was placed 15 mL of DCM. Then was added triethylamine (0.036 g, 0.36 mmol) and after 5 min, mesyl chloride (0.069 g, 0.60 mmol). The reaction mixture was stirred at room temperature for 3 h. Then, the mixture was filtered to remove triethylammonium salt, the filtrate was evaporated to dryness, and the residue was purified by flash chromatography using hexane/ethyl acetate 6:1 as eluent to give 0.064 g of (*S*)-**7** (78%) as a waxy solid. $[\alpha]^{22}_D$ −130.6 (*c* 1.10, $CHCl_3$) (100% op);[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.2−1.9 (bm, 3H), 1.2 (d, J_{P-H}= 15.6 Hz, 9H), 3.5 (s, 3H), 7.5−7.7 (m, 3H), 7.8−7.9 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.0 (d, J_{P-C} = 3.5 Hz); 33.8 (d, J_{P-C} = 33.7 Hz); 47.2; 126.7 (d, J_{P-C} = 47.6 Hz); 128.4 (d, J_{P-C} = 10.4 Hz); 131.8 (d, J_{P-C} = 10.9 Hz); 132.6 (d, J_{P-C} = 2.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 144.7; Anal. Calcd for $C_{11}H_{20}BO_3PS$: C 48.20, H 7.35, S 11.70. Found: C 48.09, H 7.37, S 11.57.

Conversion of (*S*)-*tert*-Butylphenylphosphinous Acid−Borane Methyl Ester (6) to (*R*)-*tert*-Butylphenylphosphine−Borane (8) and to (*S*)-*tert*-Butylmethylphenylphosphine−Borane (9). A flask equipped with magnetic stirrer, argon inlet, and a dry ice condenser was cooled to − 78 °C. Then, 20 mL of ammonia was condensed, and lithium (0.12 g, 1.66 mmol) was added. After lithium was dissolved, (*S*)-**6** (0.058 g, 0.28 mmol) in 5 mL of THF was added, and the reaction mixture was allowed to stir at this temperature for 1 h. Then, acetic acid (2 mL) was added, and ammonia was evaporated. The residue was washed with DCM, the inorganic phase was filtered off, and the filtrate was evaporated to dryness. The residue was purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to yield 0.029 g of (*R*)-**8** (58%) as an oil. $[\alpha]^{22}_D$ −6.4 (*c* 1.12, $CHCl_3$) (100% op);[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.1−1.7 (bm, 3H), 1.2 (d, J_{P-H}= 14.8 Hz, 9H), 5.1 (dq, J_{P-H} = 368 Hz, 1H), 7.4−7.7 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.5 (d, J_{P-C} = 2.9 Hz); 28.5 (d, J_{P-C} = 32.5 Hz); 124.7 (d, J_{P-C} = 51.0 Hz); 128.5 (d, J_{P-C} = 9.7 Hz); 131.5 (d, J_{P-C} = 3.5 Hz); 133.9 (d, J_{P-C} = 7.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.0; Anal. Calcd for $C_{10}H_{18}BP$: C 66.71, H 10.08. Found: C 66.83, H 10.21. In a flask equipped with magnetic stirrer and argon inlet was placed (*S*)-**8** (0.029 g, 0.16 mmol) in 15 mL of dry THF. Then, the mixture was cooled to −78 °C, and 1.6 M *n*-BuLi (0.1 mL, 0.48 mmol) was added. After 15 min, methyl iodide (0.068 g, 0.48 mmol) was added, and the reaction mixture was allowed to stir at this temperature for 2 h. Then, 0.5 mL of 10% hydrochloric acid was added, and the reaction mixture was allowed to warm to room temperature. The mixture was extracted 3 times with DCM (20 mL), and the combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash chromatography using hexane/ethyl acetate (6:1) as eluent to yield 0.028 g of (*S*)-**9** (89%) as a glassy solid. $[\alpha]^{22}_D$ +10.6 (*c*

(19) Correlated within this study.

1.10, $CHCl_3$) (100% op);[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.3−1.8 (bm, 3H), 1.1 (d, J_{P-H} = 14.0 Hz, 9H), 1.6 (d, J_{P-H} = 9.6 Hz, 3H), 7.4−7.6 (m, 3H), 7.7−7.8 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.2 (d, J_{P-C} = 37.0 Hz); 25.1 (d, J_{P-C} = 2.5 Hz); 28.5 (d, J_{P-C} = 32.8 Hz); 127.6 (d, J_{P-C} = 50.9 Hz); 128.2 (d, J_{P-C} = 9.5 Hz); 131.0 (d, J_{P-C} = 2.6 Hz); 132.8 (d, J_{P-C} = 8.7 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 25.1; HRMS for $C_{11}H_{20}BNaP$ (M + Na^+): Calcd: 217.1288 Found: 217.1299.

Conversion of (*S*)-*tert*-Butylphenylphosphinous Acid−Borane Methanesulfonyl Anhydride (7) to (*S*)-*tert*-Butylphenylphosphine−Borane (8) and to (*R*)-*tert*-Butylmethylphenylphosphine−Borane (9). In a flask equipped with a magnetic stirrer and argon inlet was placed (*S*)-**7** (0.064 g, 0.23 mmol) in 10 mL of anhydrous ethanol. Then, $NaBH_4$ (0.089 g, 2.34 mmol) was added, and the reaction mixture was stirred at room temperature for 45 min. Then, 1 mL of 10% hydrochloric acid was added, and the reaction mixture was extracted with DCM (3 × 20 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash chromatography using hexane/ethyl acetate 6:1 as eluent to give 0.040 g of (*S*)-**8** (96%) as an oil. $[\alpha]^{22}_D$ +6.5 (*c* 1.14, $CHCl_3$) (100% op);[19] Anal. Calcd for $C_{10}H_{18}BP$: C 66.71, H 10.08. Found: C 66.74, H 10.05.

(*S*)-**8** (0.040 g, 0.22 mmol) was converted into (*R*)-**9** using the same prorocol as described previously. The yield of (*R*)-**9** was 83%. $[\alpha]_D$ −10.8 (*c* 1.09, $CHCl_3$) (100% op).[20]

Conversion of (*S*)-*tert*-Butylphenylphosphinous Acid−Borane (1) into (*R*)-*tert*-Butylphenylchlorophosphine−Borane (10) and (*S*)-*tert*-Butylphenylphosphinous Acid−Borane Methyl Ester (6). In a flask equipped with a magnetic stirrer, reflux condenser, and a drying tube ($CaCl_2$) was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of DCM. Then was added triethylamine (0.036 g, 0.36 mmol) and, after 5 min, mesyl chloride (0.069 g, 0.60 mmol). After an additional 30 min, triethylammonium chloride (0.206 g, 1.5 mmol) was added, and the reaction mixture was heated under reflux for 3.5 h. Then, the mixture was cooled to room temperature, inorganic salts were filtered off, the filtrate was evaporated to dryness, and the residue was purified by flash chromatography using hexane/ethyl acetate 6:1 as eluent to yield 0.036 g of (*R*)-**10** (56%) as an oil. $[\alpha]^{22}_D$ +56.9 (*c* 1.10, $CHCl_3$) (45% op);[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.3−2.0 (bm, 3H), 1.3 (d, J_{P-H} = 16.5 Hz, 9H), 7.4−7.7 (m, 3H), 7.8−8.0 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.5 (d, J_{P-C} = 4.6 Hz); 35.3 (d, J_{P-C} = 20.9 Hz); 128.3 (d, J_{P-C} = 10.4 Hz); 132.3 (d, J_{P-C} = 2.8 Hz); 132.5 (d, J_{P-C} = 10.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 121.9. In a flask equipped with magnetic stirrer and argon inlet, 10 mL of methanol was placed, and then sodium (0.046 g, 2 mmol) was added. After sodium was dissolved, (*R*)-**10** (0.036 g, 0.17 mmol) was added, and the mixture was stirred at room temperature for 16 h. Then, methanol was evaporated, and 2 mL of 10% hydrochloric acid was added. The resulting mixture was extracted with DCM (3 × 20 mL), and the combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash chromatography using hexane/ethyl acetate 6:1 as eluent to give 0.033 g of (*S*)-**6 (**93%) as a white solid. $[\alpha]^{22}_D$ +24.4 (*c* 0.99, $CHCl_3$) (49% op).[19]

Conversion of (S)-*tert*-Butylphenylphosphinous Acid−Borane (1) into (*S*)-*tert*-Butylphenylphosphinic Acid Chloride (11). In a flask equipped with magnetic stirrer and argon inlet was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of dry Et_2O. Then was added sodium hydride (0.009 g, 0.36 mmol) and, after 15 min, hexachloroacetone (0.398 g, 1.5 mmol). After 3 h, the reaction mixture was evaporated to dryness, and the residue was purified by flash chromatography using hexane/ethyl acetate 2:1 as eluent to yield 0.049 g of (*S*)-**11** (75%) as a wacky solid. $[\alpha]^{22}_D$ +24.4 (*c* 0.99, $CHCl_3$) (49% op);[14] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3 (d, J_{P-H} = 19.1 Hz, 9H), 7.5−7.7 (m, 3H), 7.8−8.0 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.1; 38.9 (d, J_{P-C} = 77.4 Hz); 128.3 (d, J_{P-C} = 12.8 Hz); 132.5 (d, J_{P-C} = 10.0 Hz); 132.8 (d, J_{P-C} = 2.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 74.3.

Conversion of (S)-*tert*-Butylphenylphosphinous Acid−Borane (1) into (*S*)-*tert*-Butylphenylphosphinic Acid Bromide (12). In a flask equipped with magnetic stirrer and argon inlet was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of dry acetonitrile. Then, bromine (0.192 g, 1.2 mmol) was added, and the resulting mixture was stirred at room temperature for 23 h. The mixture was evaporated to dryness, and the residue was dissolved in a mixture of ethyl acetate and hexane (1:1, 10 mL). The formed precipitate was filtered off, and the residue was evaporated to dryness. The residue was purified by flash chromatography using hexane/ethyl acetate 2:1 as eluent to give (*S*)-**12** (0.055 g, 70%) as a slightly yiellow solid. $[\alpha]^{22}_D$ −5.6 (*c* 1.22, $CHCl_3$) (12% op);[15] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3 (d, J_{P-H} = 19.7 Hz, 9H), 7.5−7.7 (m, 3H), 7.8−8.0 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.3; 40.7 (d, J_{P-C} = 69.5 Hz); 128.2 (d, J_{P-C} = 12.6 Hz); 132.5 (d, J_{P-C} = 10.2 Hz); 132.9 (d, J_{P-C} = 3.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 73.7.

Stereochemistry of Conversion of (*S*)-*tert*-Butylphenylphosphinous Acid−Borane (1) into (*S*)-*tert*-Butylphenylphosphinic Acid Iodide (13). In a flask equipped with magnetic stirrer and argon inlet was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of dry Et_2O. Then, iodine (0.076 g, 1.2 mmol) was added, and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was evaporated to dryness, and the residue was purified by flash chromatography using hexane/ethyl acetate 2:1 as eluent to yield 0.040 g of (*S*)-**13** (78%) as a yiellow solid. $[\alpha]^{22}_D$ +57.3 (*c* 1.07, $CHCl_3$) (49% op);[19] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3 (d, J_{P-H} = 20.3 Hz, 9H), 7.5−7.7 (m, 3H), 7.8−8.0 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.3; 42.1 (d, J_{P-C} = 59.6 Hz); 128.0 (d, J_{P-C} = 12.2 Hz); 132.2 (d, J_{P-C} = 10.0 Hz); 132.8 (d, J_{P-C} = 3.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 63.1. In a flask equipped with magnetic stirrer and argon inlet was placed 10 mL of methanol, and then sodium (0.046 g, 2 mmol) was added. After sodium was dissolved, (*S*)-**13** (0.040 g, 0.13 mmol) in 2 mL of methanol was added, and the resulting mixture was stirred at room temperature for 16 h. Then, solvent was evaporated, 2 mL of 10% hydrochloric acid was added to the residue, and the resulting mixture was extracted with DCM (3 × 20 mL), and the combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash chromatography using ethyl acetate−methanol 20:1 as eluent to give 0.022 g of (*R*)-methyl *tert*-butylphenylphosphinate (**14)** (79%) as a white solid. $[\alpha]^{22}_D$ −28.5 (*c* 1.08, $CHCl_3$) (49% op);[16] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2 (d, J_{P-H} = 15.9 Hz, 9H), 3.8 (d, J_{P-H} = 10,9 Hz, 3H), 7.4−7.6 (m, 3H), 7.8−7.9 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.2; 32.6 (d, J_{P-C} = 100.0 Hz); 51.9 (d, J_{P-C} = 7.1 Hz); 128.3 (d, J_{P-C} = 12.0 Hz); 132.2 (d, J_{P-C} = 2.6 Hz); 133.2 (d, J_{P-C} = 9.6 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ 55.1; HRMS for $C_{11}H_{17}O_2NaP$ (M + Na^+): Calcd: 235.0858; Found: 235.0844.

Conversion of (*S*)-*tert*-Butylphenylphosphinous Acid−Borane (1) into (*S*)-*tert*-Butylphenylphosphine Oxide (15). In a flask equipped with magnetic stirrer and argon inlet was placed (*S*)-**1** (0.059 g, 0.3 mmol) in 15 mL of DCM. Then, tetrafluoroboric acid diethyl etherate (0.206 mL, 1.5 mmol) was added, and the mixture was stirred at 0 °C for 1 h. Then, 1 mL of saturated aqueous solution of $NaHCO_3$ was added, and the resulting mixture was extracted with DCM (3 × 20 mL), and the combined extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash chromatography using ethyl acetate−methanol 20:1 as eluent to give 0.046 g of (*S*)-**15** (85%) as a white solid. $[\alpha]^{22}_D$ −35.3 (*c* 1.21, $CHCl_3$) (83% op);[18] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.2 (d, J_{P-H} = 16.6 Hz, 9H), 7.0 (d, J_{P-H} = 454 Hz), 7.4−7.8 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.5 (d, J_{P-C} = 2.0 Hz); 32.0 (d, J_{P-C} = 68.7 Hz); 128.4 (d, J_{P-C} = 11.6 Hz); 130.8 (d, J_{P-C} = 10.0 Hz); 132.4 (d, J_{P-C} = 2.6 Hz); ^{31}P NMR

(20) Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116−5117.

(161 MHz, $CDCl_3$) δ 47.7; HRMS for $C_{10}H_{15}ONaP$ ($M + Na^+$): Calcd: 205.0777. Found: 205.0755.

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Supporting Information Available: General experimental methods and crystallographic information file for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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