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An efficient resolution of phosphinous acid-boranes

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Abstract—A general protocol has been developed for the resolution of racemic P-stereogenic phosphinous acid-boranes. It employs cinchonine as the resolving agent and most frequently gives an access to the pertinent diastereomerically pure cinchoninium salt of the acid in a single crystallization step. The resolved acids were assigned their absolute configurations by chemical correlations with already known enantiomerically pure phosphinite-boranes.

1. Introduction

Enantiomerically pure phosphines possessing a stereogenic center at the phosphorus atom have found growing use as chiral ligands in various asymmetric reactions catalyzed by transition metal complexes.[1] Development of new protocols for the synthesis of resolved organophosphorus compounds, which could serve as convenient precursors to such enantiomerically pure P-stereogenic phosphines have become increasingly important. Recently, Imamoto et al.[2] and Jugé et al.[3] reported that resolved menthyl and methyl phosphinite-boranes can be used to stereoselectively synthesize valuable enantiomerically pure tertiary phosphine-boranes. Both these methodologies have been based on the resolved P-stereogenic phosphinite-boranes which can be viewed as the esters of phosphinous acid-boranes which, in principle, could be readily derived from the parent acid-boranes. Until very recently however, the synthesis and chemistry of phosphinous acid-boranes was practically unexplored. In 2004, we demonstrated that phosphinous acid-boranes could be synthesized readily in a great structural variety starting from secondary phosphine oxides[4] or from phosphinic acid chlorides.[5] In the follow-up study, phosphinous acid-boranes were found to possess a rich reactivity pattern which offered many useful synthetic transformations through the reactions at their P, O, or B, reactivity centers.[5,6] When unsymmetrically substituted phosphinous acid-boranes are P-stereogenic, they can serve as convenient starting materials for the synthesis of other P-stereogenic organophosphorus compounds including the above phosphinite-boranes. We have already demonstrated in a model study[7] that *tert*-butylphenylphosphinous acid-borane could be readily resolved into its two enantiomers by the combined use of ephedrine and cinchonine as the resolving bases. We have also shown that the resolved *tert*-butylphenylphosphinous acid-borane could be stereoselectively transformed into a variety of other enantiomerically pure P-stereogenic compounds including valuable secondary phosphine-boranes and tertiary phosphine-boranes.[7] In order to further expand upon the potential utility of phosphinous acid-boranes **1** for the synthesis of enantiomerically pure compounds we have now developed a general protocol for the resolution of a series of other racemic phosphinous acid-boranes **1** by using cinchonine as the resolving agent of choice.

2. Results and discussion

Racemic *o*-anisylphenylphosphinous acid-borane **1a** was chosen as a model for testing the resolving ability of different chiral organic bases. This acid was chosen because of the potentially easy recognition and quantification of its two diastereomeric salts by ^{1}H NMR. The tested bases are presented in Chart 1.

Prompted by the successful use of ephedrine **2** in our recent resolution of *tert*-butylphenylphosphinous acid-borane,[7] we decided to test first the same base for the resolution of **1a**. However, attempted crystallizations of 1:1 mixtures

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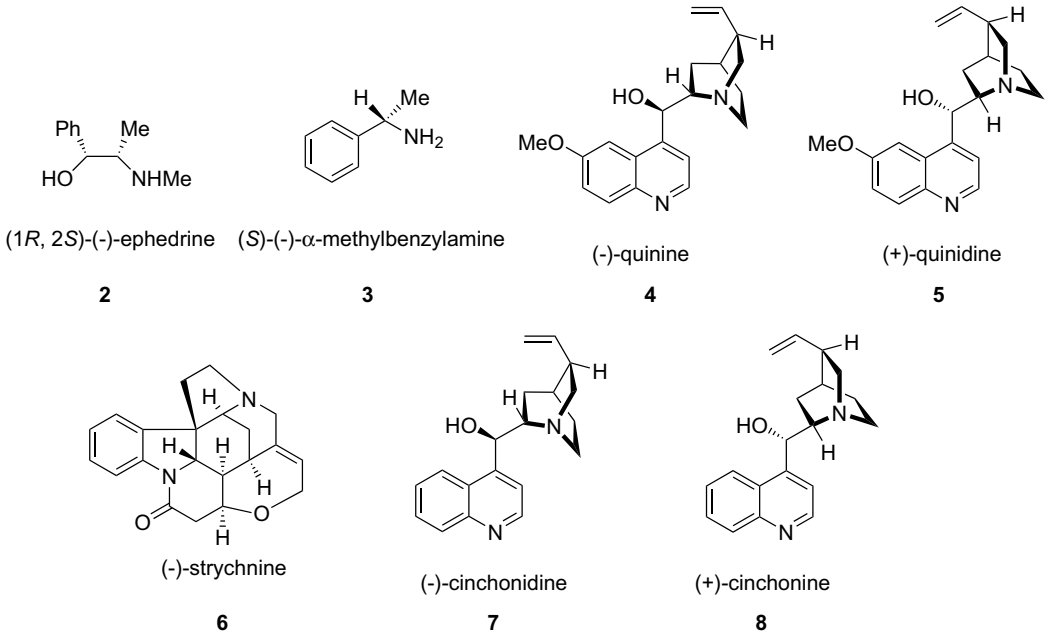


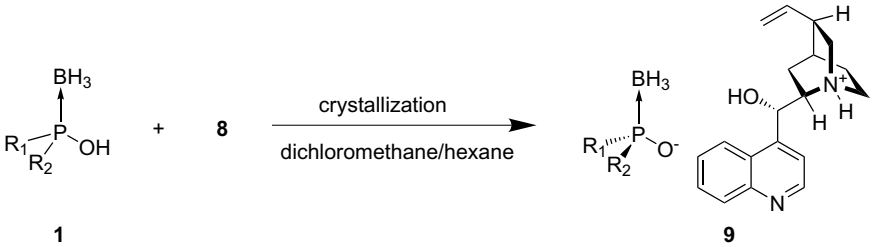
Chart 1.

of *rac*-**1a** and (−)-**2** from a variety of solvents failed and gave the expected diastereomeric salts as an oil. Also, only oily salts were obtained upon treatment of **1a** with equimolar amounts of (*S*)-(−)-α-methylbenzylamine **3**, quinine **4**, and quinidine **5**. Strychnine **6** formed crystalline salts with **1a**, but they were found to crystallize out always as a ca. 1:1 mixture of the two diastereomers. The first promising results were obtained with cinchonidine **7**, which with **1b** gave crystalline diastereomeric salts showing 27% de (^{1}H NMR) after the first crystallization from dichloromethane admixed with the small amounts of hexane. Still better results were obtained with cinchonine **2**, which afforded the corresponding salts of **1a** in 68% de (^{1}H NMR) in the first crop from the same solvent system.

Following this lead, a series of four other racemic phosphinous acid-boranes **1a**–**e** were next subjected to analogous resolutions with cinchonine under the conditions developed. The results obtained are summarized in Table 1.

As can be seen from the data collected in Table 1, cinchonine **8** appeared to be the base of choice for the resolution of phosphinous acid-boranes. The three phosphinous acid-boranes bearing mixed alkyl and aryl substituents at P (**1b**,**c**,**e**) gave with this base the diastereomerically pure crystalline salts in the first crop. Interestingly, in the case of phosphinous acid-borane **1c** repeated crystallization of the mother liquor gave the second crop of crystals which were found to contain the other diastereomeric salt of **1c**

Table 1. Resolution of racemic phosphinous acid-boranes **1a**–**e** by cinchonine



1 + **8** → **9**

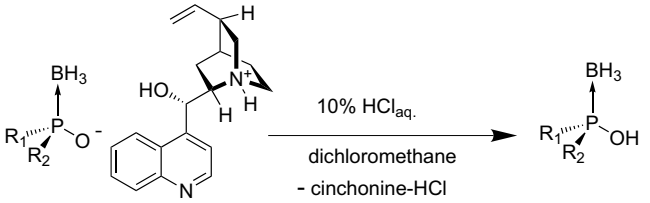
Nr	Acid	Substituents		Number of crystallizations	**9** % yield	**9** % de
		R_1	R_2			
1	**1a**	*o*-An	Ph	4	34	96
2	**1b**	Bn	Ph	1	32	100
3	**1c**	2-NphthCH$_2$[a]	Ph	1	26	100
4	**1d**	1-Nphth[a]	Ph	2	28	100
5	**1e**	Me	Ph	1	16	100

[a] Nphth = naphthyl.

of 100% de. However, this resolution pattern did not occur again in any of the repeated resolutions of **1c**, even though the first diastereomeric salt of 100% de was always reliably obtained in the first crystallization in ca. 24–26% yield. For diaryl substituted phosphinous acid-boranes **1a** and **1d** more than one crystallization was needed to afford the corresponding salts in high diastereomeric purity (Table 1).

To liberate the resolved phosphinous acid-boranes from the diastereomerically pure salts **9a**–**e** the salts were dissolved in dichloromethane and treated with 10% aqueous hydrochloric acid. Extraction and evaporation of the solvent directly afforded pure phosphinous acid-boranes. The results of these experiments are presented in Table 2.

Table 2. Liberation of the resolved phosphinous acid-boranes **1a**–**e**



9 **1**

Nr	Salt	Substituents		**1** % yield	$[\alpha]_D$ ($CHCl_3$)
		R_1	R_2		
1	**9a**	*o*-An	Ph	81	−19.2 (*c* 1.04)
2	**9b**	Bn	Ph	73	+57.9 (*c* 1.06)
3	**9c**	2-NphthCH_2[a]	Ph	95	+57.8 (*c* 1.04)
4	**9d**	1-Nphth[a]	Ph	87	−40.8 (*c* 1.04)
5	**9e**	Me	Ph	95	−21.7 (*c* 1.06)

In order to assign the absolute configurations of the resolved phosphinous acid-boranes they were converted into their methyl esters of which the absolute configurations and optical purities were already known. These conversions were conveniently achieved by O-alkylation of the resolved phosphinous acid-boranes with methyl iodide in acetone in the presence of potassium carbonate as a base[5] (Scheme 1). Based on the known configurations of the esters **10a**,[3a,b] **10d**,[8] and **10e**,[9] thus obtained it was possible to assign the absolute configurations of phosphinous acid-boranes **1a**, **1d**, and **1e**, to be (*R*), (*R*), and (*S*), respectively.

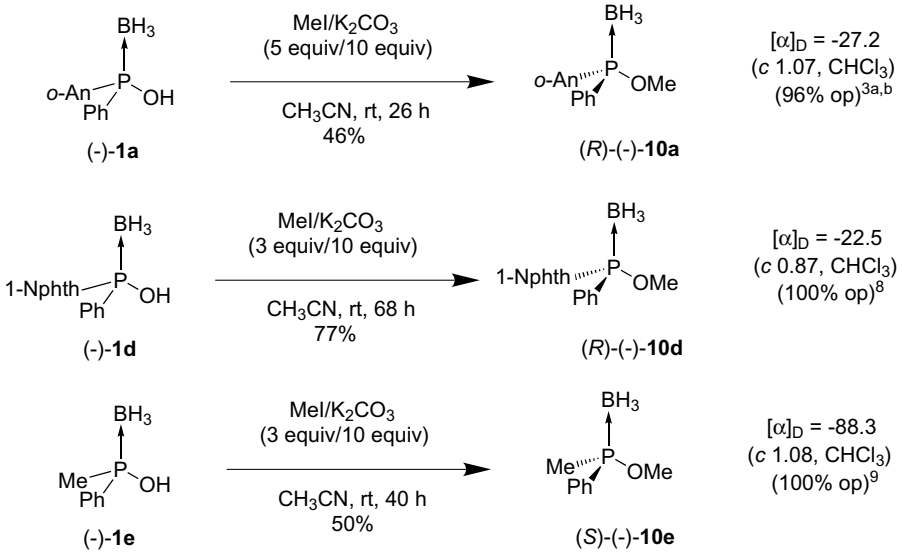
The results of these chemical correlations also revealed an interesting feature of the developed resolution procedure. It turned out that the diastereomeric salts, which crystallized out first, that is, **9a**, **9d**, and **9e**, contained the acid-borane of the same stereochemical arrangement of the R, Ph, OH, and BH_3 substituents around phosphorus regardless of the nature of the R substituent. By this token, the configuration of (+)-**1b** and (+)-**1c** could be tentatively expected to be (*S*), although the definite assignments for these acids must await an unequivocal confirmation.

3. Conclusion

In conclusion, we have developed a general procedure for the resolution of racemic phosphinous acid-boranes **1** by means of cinchonine as the base of choice. The procedure opens ready access to enantiomerically pure phosphinous acid-boranes, which constitute a new valuable class of resolved P-stereogenic phosphorus acids. Their use as chiral substrates for the synthesis of other P-stereogenic compounds as well as chiral acidic catalysts is under investigation.

4. Experimental

All solvents were purified prior to use. Commercially available cinchonine was recrystallized before use. ^{1}H, ^{13}C, and ^{31}P NMR were measured with a Varian AC-200 (200 MHz) and Bruker AM-500 (500 MHz). Phosphinous acid-bor-



Scheme 1.

anes **1** were prepared by the reported method.[4,5] Melting points of the compounds were uncorrected.

5. General procedure for the resolution of racemic phosphine acid-boranes with cinchonine

In a round bottom flask, phosphinous acid-borane (5 mmol) was dissolved in 20 mL of dichloromethane. Cinchonine **8** (1.47 g, 5 mmol) was then added to the solution after which, methanol (ca. 5 mL) was added in small portions until all the cinchonine had dissolved. The mixture was evaporated to dryness and ^{1}H NMR spectra of equimolar mixture of two diastereomeric salts was taken. The mixture was then dissolved again in 20 mL of dichloromethane and hexane (ca. 50 mL) was added until the mixture became slightly cloudy. The solvents were allowed to evaporate slowly at room temperature to aid the crystallization. The crystalline salts formed were filtered off and their diastereomeric purity was checked by ^{1}H NMR and, if needed, crystallization of the salts was repeated.

Cinchonine salt of *o*-anisylphenylphosphinous acid-borane **9a**. Yield 0.92 g (34%), white solid, mp 173–176 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88–1.05 (m, 1H), 1.50–1.77 (m, 2H), 2.17–2.34 (m, 2H), 2.35–2.50 (m, 1H), 2.84–3.05 (m, 1H), 3.05–3.34 (m, 2H), 3.57 (s, 3H), 3.89–4.05 (m, 1H), 5.10–5.22 (m), 5.95–6.16 (m, 1H), 6.37 (br s), 6.73–8.17 (m, 14H), 8.75 (d, 1H).

Cinchonine salt of benzylphenylphosphinous acid-borane **9b**. Yield 0.84 g (32%), white solid, mp 127–130 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85–1.10 (m, 2H), 1.43–1.76 (m, 2H), 1.82–1.91 (m, 1H), 2.12–2.41 (m, 2H), 2.56–2.85 (m, 2H), 3.05–3.27 (m, 3H), 3.76–3.90 (m, 1H), 5.10–5.22 (m, 2H), 5.88–6.09 (m, 1H), 6.36 (br s, 1H), 7.05–7.92 (m, 13H), 8.05–8.16 (m, 2H), 8.88 (d, 1H).

Cinchonine salt of (2-naphthylmethyl)phenylphosphinous acid-borane **9c**. Yield 0.75 g (26%), white solid, mp 142–145 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.79–0.97 (m, 2H), 1.40–1.61 (m, 2H), 1.85–2.33 (m, 4H), 2.48–2.62 (m, 1H), 3.02–3.23 (m, 2H), 3.28–3.47 (m, 2H), 3.61–3.79 (m, 1H), 4.94–5.18 (m, 2H), 5.72–5.95 (m, 1H), 6.16 (br s, 1H), 7.21–8.19 (m, 17H), 8.85 (d, 1H).

Cinchonine salt of (1-naphthyl)phenylphosphinous acid-borane **9d**. Yield 0.78 g (28%), white solid, mp 190–193 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.81–1.02 (m, 2H), 1.44–1.89 (m, 3H), 2.21–2.57 (m, 2H), 2.88–3.13 (m, 1H), 3.13–3.44 (m, 3H), 4.04–4.23 (m, 1H), 5.09–5.28 (m, 2H), 5.89–6.13 (m, 1H), 6.63 (br s, 1H), 7.12–7.55 (m, 8H), 7.55–7.94 (m, 5H), 8.00–8.32 (m, 3H), 8.57–8.81 (m, 2H).

Cinchonine salt of methylphenylphosphinous acid-borane **9e**. Yield 0.36 g (16%), white solid, mp 105–109 °C (dec). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83–1.12 (m, 2H), 1.52 (d, 3H, $J_{P-H} = 9.38$ Hz), 1.55–1.91 (m, 2H), 2.34–2.66 (m, 2H), 3.05–3.41 (m, 3H), 3.46–3.68 (m, 1H), 4.21–4.39 (m, 1H), 5.15–5.30 (m, 2H), 6.00–6.21 (m, 1H), 6.54 (br s, 1H), 6.90–7.25 (m, 4H), 7.52–7.70 (m, 4H), 7.82–8.03 (m, 2H), 8.79 (d, 1H).

6. General procedure for the liberation of phosphinous acid-boranes 1 from their cinchonine salts 9

A sample of cinchonine salt of phosphinous acid-borane **9** (0.3 mmol) was dissolved in 50 mL of dichloromethane and 10 mL of 10% hydrochloric acid was added. The mixture was allowed to stir for 0.5 h at room temperature and then transferred to a separation funnel. The organic phase was separated, and the aqueous phase washed three times with 20 mL of dichloromethane. The combined organic phases were then dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent on a rotary evaporator afforded chemically pure phosphinous acid-borane **1**.

o-Anisylphenylphosphinous acid-borane *o*-AnPhP(BH_3)-OH **1a**. Yield 0.061 g (81%), waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.20–1.96 (br m, 3H), 3.81 (s, 3H), 5.11 (br s, 1H), 6.91–7.04 (m, 1H), 7.10–7.22 (m, 1H), 7.38–7.76 (m, 6H), 7.83–8.00 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.98, 111.33 (d, $J_{P-C} = 4.00$ Hz), 121.61 (d, $J_{P-C} = 12.55$ Hz), 128.23 (d, $J_{P-C} = 10.50$ Hz), 130.16 (d, $J_{P-C} = 11.40$ Hz), 131.12 (d, $J_{P-C} = 2.35$ Hz), 134.04 (d, $J_{P-C} = 2.45$ Hz), 134.22 (d, $J_{P-C} = 10.90$ Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 98.00 ppm (m). Anal. Elem. for $C_{13}H_{16}BO_2P$: Calcd: C, 63.46; H, 6.55. Found. C, 63.44; H, 6.57. $[\alpha]_D = -19.2$ (*c* 1.04, $CHCl_3$) (96% ee).

Benzylphenylphosphinous acid-borane BnPhP(BH_3)OH **1b**. Yield 0.052 g (73%), waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.07–1.65 (br m, 3H), 3.38 (d, $J_{P-H} = 10.22$ Hz, 2H), 4.90 (br s, 1H), 7.01–7.13 (m, 2H), 7.21–7.34 (m, 3H), 7.40–7.75 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.76 (d, $J_{P-C} = 36.70$ Hz), 126.71 (d, $J_{P-C} = 2.95$ Hz), 128.03 (d, $J_{P-C} = 4.80$ Hz), 128.15 (d, $J_{P-C} = 12.55$ Hz), 129.98 (d, $J_{P-C} = 4.45$ Hz), 130.30 (d, $J_{P-C} = 11.15$ Hz), 131.53 (d, $J_{P-C} = 2.50$ Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 101.64 ppm (m). Anal. Elem. for $C_{13}H_{16}BOP$: Calcd: C, 68.87; H, 7.01. Found. C, 68.95; H, 7.10. $[\alpha]_D = +57.9$ (*c* 1.06, $CHCl_3$) (100% ee).

(2-Naphthylmethyl)phenylphosphinous acid-borane (2-NphthCH$_2$)PhP(BH_3)OH **1c**. Yield 0.079 g (95%), waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.05–1.72 (br m, 3H), 3.52 (d, $J_{P-H} = 9.98$ Hz, 2H), 3.60 (br s, 1H), 7.11–7.21 (m, 1H), 7.36–7.56 (m, 5H), 7.56–7.89 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 39.99 (d, $J_{P-C} = 35.99$ Hz), 125.86 (d, $J_{P-C} = 15.65$ Hz), 127.50, 127.68, 128.12, 128.36 (d, $J_{P-C} = 10.65$ Hz), 128.64, 128.83 (d, $J_{P-C} = 6.05$ Hz), 130.37 (d, $J_{P-C} = 11.05$ Hz), 131.75 (d, $J_{P-C} = 2.35$ Hz), 132.20 (d, $J_{P-C} = 2.00$ Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 103.16 ppm (m). Anal. Elem. for $C_{15}H_{18}BOP$: Calcd: C, 72.99; H, 6.48. Found. C, 73.04; H, 6.53. $[\alpha]_D = +57.8$ (*c* 1.04, $CHCl_3$) (100% ee).

(1-Naphthyl)phenylphosphinous acid-borane (1-$C_{10}H_7$)-PhP(BH_3)OH **1d**. Yield 0.069 g (87%), waxy solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.30–1.90 (br m, 3H), 4.73 (br s, 1H), 7.35–7.55 (m, 5H), 7.55–7.81 (m, 3H), 7.85–7.96 (m, 1H), 8.02–8.21 (m, 2H), 8.26–8.42 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 124.67 (d, $J_{P-C} = 13.55$ Hz), 126.21, 126.55 (d, $J_{P-C} = 5.60$ Hz), 126.88, 128.53 (d, $J_{P-C} = 10.55$ Hz), 128.93, 130.59 (d, $J_{P-C} = 11.75$ Hz),

131.43 (d, $J_{P-C} = 2.40$ Hz), 133.33 (d, $J_{P-C} = 2.55$ Hz), 133.67 (d, $J_{P-C} = 16.00$ Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ 96.10 ppm (m). HRMS for $C_{16}H_{15}BOP$ [M−H$^+$]: Calcd: 265.0948. Found: 265.0947. $[\alpha]_D = -40.8$ (*c* 1.04, $CHCl_3$) (100% ee).

Methylphenylphosphinous acid-borane $MePhP(BH_3)OH$ **1e**. Yield 0.044 g (95%), an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.05–1.65 (br m, 3H), 1.73 (d, $J_{P-H} = 9.34$ Hz, 3H), 6.20 (br s, 1H), 7.43–7.60 (m, 3H), 7.75–7.90 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.76 (d, $^1J_{P-C} = 44.38$ Hz, P–*CH*$_3$), 128.47 (d, $^3J_{P-C} = 10.40$ Hz, P–*Ph*), 129.84 (d, $^2J_{P-C} = 11.45$ Hz, P–*Ph*), 131.45. ^{31}P NMR (160 MHz, $CDCl_3$): δ 99.61 ppm (m). Anal. Elem. for $C_7H_{12}BOP$: Calcd: C, 54.61; H, 7.96; Found. C, 55.04; H 7.86. $[\alpha]_D = -21.7$ (*c* 1.06, $CHCl_3$) (100% ee).

7. General procedure for the conversion of phosphinous acid-boranes 1a, 1d, and 1e to their methyl esters 10a, 10d, and 10e

In a flask equipped with magnetic stirrer and argon inlet was placed phosphinous acid-borane **1** (0.3 mmol) in 15 mL of acetonitrile. Then, anhydrous potassium carbonate (0.41 g, 3 mmol) was added. After 5 min, methyl iodide (0.056–0.093 mL, 0.9–1.5 mmol) was added and the reaction mixture stirred at room temperature for 26–68 h. After that, the inorganic salt was filtered off and the filtrate was evaporated to dryness. The residue was purified using flash chromatography with hexane/ethyl acetate (6:1) as eluent.

(*R*)-(−)-*o*-Anisylphenylphosphinous acid-borane methyl ester *o*-AnPhP(BH_3)OMe (*R*)-(−)-**10a**. Yield 0.036 g (46%), an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.20–1.90 (br m, 3H), 3.67 (s, 3H, OMe), 3.78 (d, $J_{P-H} = 12.10$ Hz, 3H, P–O–*CH*$_3$), 6.82–7.17 (m, 3H), 7.22–7.34 (m, 1H), 7.40–7.60 (m, 3H), 7.71–7.91 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 53.98, 55.53, 111.57 (d, $J_{P-C} = 4.95$ Hz), 120.77 (d, $J_{P-C} = 10.80$ Hz), 128.04 (d, $J_{P-C} = 10.70$ Hz), 131.03 (d, $J_{P-C} = 11.55$ Hz), 131.17 (d, $J_{P-C} = 3.35$ Hz), 133.85 (d, $J_{P-C} = 11.60$ Hz), 133.97. ^{31}P NMR (160 MHz, $CDCl_3$): δ 107.34 ppm (m). HRMS for $C_{14}H_{18}BO_2NaP$ [M+Na$^+$]: Calcd: 283.1030. Found: 283.1051. $[\alpha]_D = -27.2$ (*c* 1.07, $CHCl_3$) (96% ee).[10]

(*R*)-(−)-(1-Naphthyl)phenylphosphinous acid-borane methyl ester (1-$C_{10}H_7$)PhP(BH_3)OMe (*R*)-(−)-**10d**. Yield 0.065 g (77%), an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.35–2.05 (br m, 3H), 3.83 (d, $J_{P-H} = 12.18$ Hz, 3H), 7.37–7.75 (m, 8H), 7.90–7.97 (br d, 1H), 8.05–8.21 (m, 2H), 8.23–8.39 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 54.00, 124.66 (d, $J_{P-C} = 13.75$ Hz), 126.23, 126.27 (d, $J_{P-C} = 3.95$ Hz), 127.02, 128.51 (d, $J_{P-C} = 10.40$ Hz), 128.98, 130.81 (d, $J_{P-C} = 11.00$ Hz), 131.49 (d, $J_{P-C} = 2.20$ Hz), 133.61 (d, $J_{P-C} = 2.45$ Hz), 135.13 (d, $J_{P-C} = 17.10$ Hz). ^{31}P NMR (160 MHz, $CDCl_3$): δ 111.01 ppm (m). HRMS for $C_{17}H_{18}BONaP$ [M+Na$^+$]: Calcd: 303.1081. Found: 303.1100. $[\alpha]_D = -22.5$ (*c* 0.87, $CHCl_3$) (100% ee).

(*S*)-(-)-Methylphenylphosphinous acid-borane methyl ester $MePhP(BH_3)OMe$ (*S*)-(−)-**10e**. Yield 0.025 g (50%), an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.05–1.65 (br m, 3H), 1.74 (d, $J_{P-H} = 9.36$ Hz, 3H), 3.60 (d, $J_{P-H} = 12.24$ Hz), 7.46–7.67 (m, 3H), 7.76–7.91 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.00 (d, $J_{P-C} = 46.81$ Hz), 53.57 (d, $J_{P-C} = 3.03$ Hz), 128.71 (d, $J_{P-C} = 10.10$ Hz), 130.62 (d, $J_{P-C} = 11.20$ Hz), 132.13 (d, $J_{P-C} = 2.45$ Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 114.55 ppm (m). HRMS for $C_8H_{14}BONaP$ (M+Na$^+$): Calcd: 191.0768. Found: 191.0759. $[\alpha]_D = -88.3$ (*c* 1.08, $CHCl_3$) (100% ee).

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