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Asymmetric synthesis of P-stereogenic *o*-hydroxyaryl-phosphine (borane) and phosphine-phosphinite ligands†

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Abstract

The first asymmetric synthesis of P-stereogenic 2-hydroxyarylphosphine ligands is described, using borane complexation methodology. This synthesis is based on the highly stereoselective preparation of bromoarylphosphinite boranes, leading to the 2-hydroxyarylphosphine derivatives, by an intramolecular *ortho* Fries-like rearrangement mediated in basic conditions. The *o*-anisyl-2-hydroxynaphthylphenylphosphine borane has been decomplexed in EtOH, affording the P(III)-stereogenic hydroxyarylphosphine ligand with 84% yield. The interest of the hydroxyarylphosphine borane is also demonstrated by the preparation of a new class of phosphine-phosphinite ligands, by trapping the rearrangement products first with chlorodiphenylphosphine, Ph_2PCl, then with borane. The corresponding phosphine-phosphinites are obtained and purified as diborane complexes, with the decomplexation of these borane complexes being achieved by heating with dabco, to afford the free hybrid ligands with retention of the configuration at the P-atom (isolated yield up to 53%).

1. Introduction

During the last three decades, considerable developments have been made for asymmetric transition-metal catalyzed reactions[1] and more precisely in the synthesis of numerous chiral ligands.[2] In this area, the most commonly used P(III)-organophosphorus ligands (diphosphines,[3] diphosphinites, diphosphites,[4] aminophosphine-phosphinites,[5] chelating monophosphines or P(III) derivatives)[6] generally bear the chirality on the carbon backbone. Since the asymmetric

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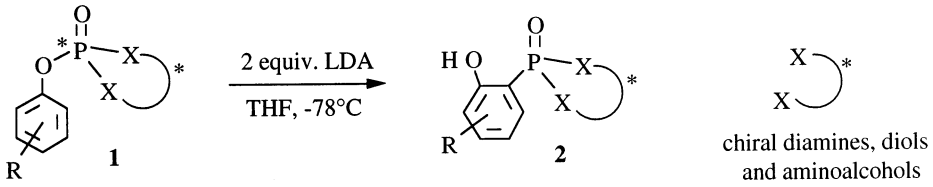
synthesis of P(III)-organophosphorus compounds has made important progress by the use of borane as a protecting group,[7–9] P-stereogenic phosphorus ligands have revived interest in catalysis.[10] Thus, it is now possible to study new kinds of bulky,[11] hybrid or functionalized phosphorus ligands,[12] bearing the chirality close to the metal center, for the study of new catalytic species. Moreover, P-stereogenic centers may amplify the influence of the chiral carbon backbone, to increase the asymmetric induction of the catalyst.[13]

Recently, chiral organophosphorus derivatives bearing an *o*-hydroxyaryl substituent have gained attention because these compounds, could be used either as ligands[14] or catalysts in various asymmetric reactions.[15] The preparation of these compounds could be achieved by demethylation of a methoxy substituent,[15a,16] or by trapping a C,O-phenol dilithium reagent with a chlorophosphine.[17] A more convenient method has been developed on the basis of the *ortho* Fries-like rearrangement of the corresponding aryl phosphoric ester **1**.[18] This method, which proceeds with complete retention of the configuration at the phosphorus center,[19] has been particularly studied by Buono et al. in order to prepare various P-stereogenic *o*-hydroxyaryl phosphonic derivatives **2**[20] (Scheme 1).



Scheme 1.

Continuing our research on asymmetric synthesis of organophosphorus compounds, we have reported the synthesis of chiral chlorophosphine boranes **3**, which are useful electrophilic blocks for the preparation of P-stereogenic cyclopentadienyl methyl phenyl phosphine (borane) **4**,[7f] or aminophosphine-phosphinite ligands **5** (Fig. 1).[13] Herein, we wish to report a convenient synthesis of 2-bromoarylphosphinites (borane) **6** from **3**, and their application in the first preparation of P-stereogenic *o*-hydroxyarylphosphines **7** with high enantiomeric excesses.

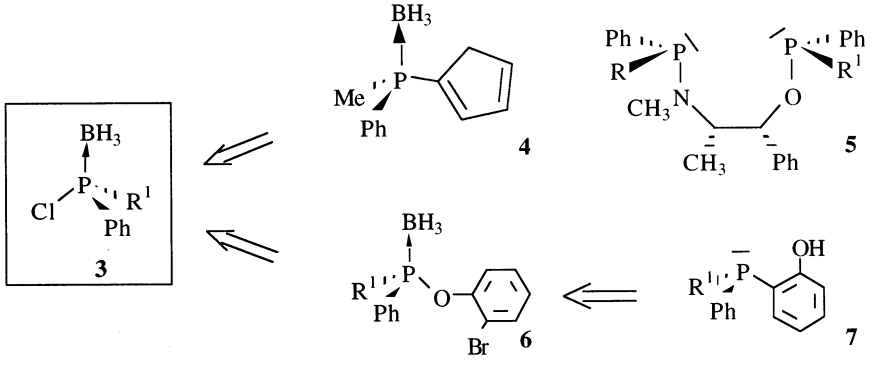
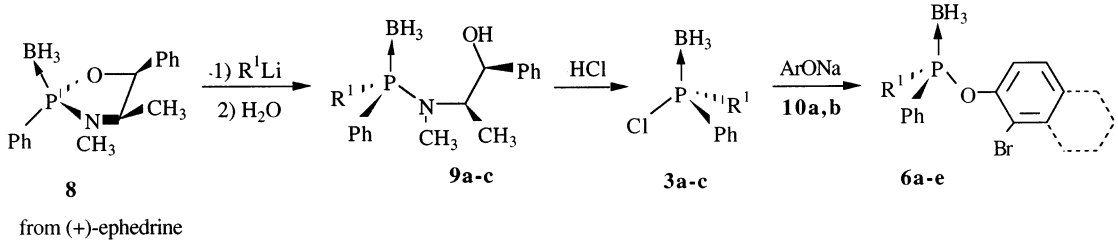


Figure 1.

2. Results and discussion

The chlorophosphine boranes **3** are prepared in two steps from the (+)-ephedrine derived oxazaphospholidine borane **8**, which is the starting complex for the P-stereogenic asymmetric synthesis methodology.[7] Thus, the acidolysis of the aminophosphine boranes **9**, which are prepared as pure diastereomers by reaction of complex **8** with organolithium reagents R^1Li, leads to chlorophosphines **3a–c** (Scheme 2). After simple filtration of the ephedrine hydrochloride, the chlorophosphine boranes **3** are directly used without further purification, and react with the corresponding bromophenate salt **10** to afford the corresponding arylphosphinite boranes **6** in 66–73% overall yields (Table 1). The enantiomeric excesses of the compounds **6** have been determined by HPLC on a chiral column, of their derivative phosphine boranes **11** and **12**, which result from their reaction with *o*-anisyllithium or *t*-butyllithium, respectively (Schemes 2 and 3). The results are summarized in Table 1.



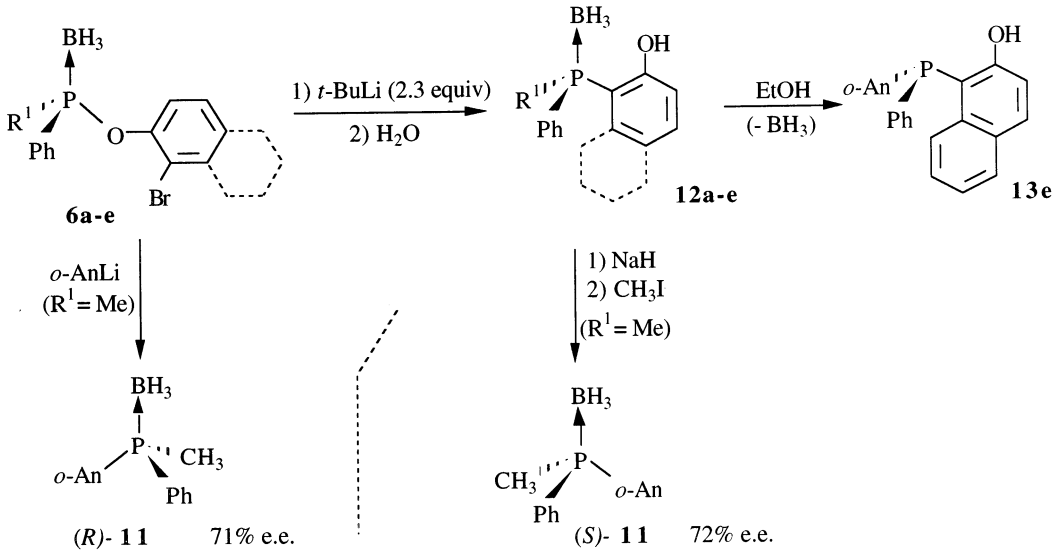
Scheme 2.

Table 1
Preparation of the arylphosphinite borane complexes **6**

Entry	R^1	ArONa **10**	Arylphosphinite BH_3 **6**		
				Yield[a] (%)	E.e. (%)
1	CH_3	2-Bromophenate **10a**	**6a**	71	71[b]
2	*o*-An	"	**6b**	70	80[c]
3	*o*-Tol	"	**6c**	66	–
4	CH_3	1-Bromo-2-naphthoate **10b**	**6d**	66	91[d]
5	*o*-An	"	**6e**	73	100[d]

[a] Isolated yield from **9**.
[b] Determined by HPLC with Chiralcel OK, from the PAMP·BH_3 **11** which results from the reaction with *o*-anisyllithium.
[c] Determined by HPLC with Chiralcel OK from the derivative **12b**.
[d] Determined by HPLC with Chiralcel OK, from the corresponding derivative **12d** or **12e**.

When methyllithium reacts with complex **8**, the aminophosphine borane **9a** is obtained with retention of the configuration at the phosphorus atom.[7e] The reaction of **9a** with dry HCl then gives the methyl phenyl chlorophosphine borane **3a**, which is trapped with the sodium 2-bromophenate **10a** to afford the phosphinite borane **6a** in 71% yield (Table 1, entry 1). The HPLC analysis on a chiral column of the PAMP borane **11**, which results from the reaction of **6a** with *o*-anisyllithium, indicates an *R* absolute configuration and 71% e.e. (Scheme 3, Table 1, entry 1). In the same way, the 2-bromoarylphosphinite borane complexes **6b** and **6c** have been



Scheme 3.

prepared in 70 and 66% yields, respectively, by reaction of the *o*-anisyl or *o*-tolyllithium reagents with complex **8**, and trapping the chlorophosphine borane intermediates **3b** and **3c** with sodium 2-bromophenate **10a** (entries 2, 3). If the chlorophosphine boranes **3a** or **3b** are trapped by the sodium 1-bromo-2-naphthoate **10b**, the phosphinite complexes **6d** or **6e** are obtained in 66 and 73% yields, respectively (entries 4, 5). It should be pointed out that the enantiomeric excesses of **6d**, **6e** (91–100% e.e.) have been determined from the hydroxyarylphosphine boranes **12d** and **12e**, which result from their intramolecular rearrangement, as described below. We think that the variation of stereoselectivity observed for the arylphosphinite boranes **6** prepared must arise either from the aminophosphine borane acidolysis step,[21] or from reaction of the phenates **10a** (or **10b**) with the chlorophosphine boranes **3**, rather than from the reactions leading to their derivatives **11** or **12**.

On the other hand, the absolute configuration of the phosphinite borane **6d** has been established as *S*, by X-ray crystallography, owing to the presence of the bromine atom which results in differences between the intensities of Friedel reflections (Fig. 2). This stereochemistry is in good agreement with an inversion of configuration in the aminophosphine borane **9a** acidolysis step,[21] and for the substitution of the chlorophosphine borane **3a** by the naphthoate salt **10b** (Scheme 2). Moreover, it also confirms that the *o*-anisyllithium reaction of **6d**, leading to the (*R*)-PAMP BH_3 **11**, proceeds with inversion of configuration (entry 4).

We have also studied the rearrangement of these arylphosphinite boranes **6**, after formation of the anion *ortho* to the aryloxy substituent, by halogen–metal exchange (Scheme 3). This rearrangement was realized by reaction of the complex **6a–e** with *t*-BuLi at −78°C, and after increasing the temperature to 0°C, the corresponding *o*-hydroxyphosphine boranes **12a–e** were obtained in 48–96% yields (Table 2).

The rearrangement of the 2-bromophenylphosphinite borane **6a** gives the *o*-hydroxymethylphenylphosphine borane **12a** in 75% yield (Table 2, entry 1). After deprotonation of the

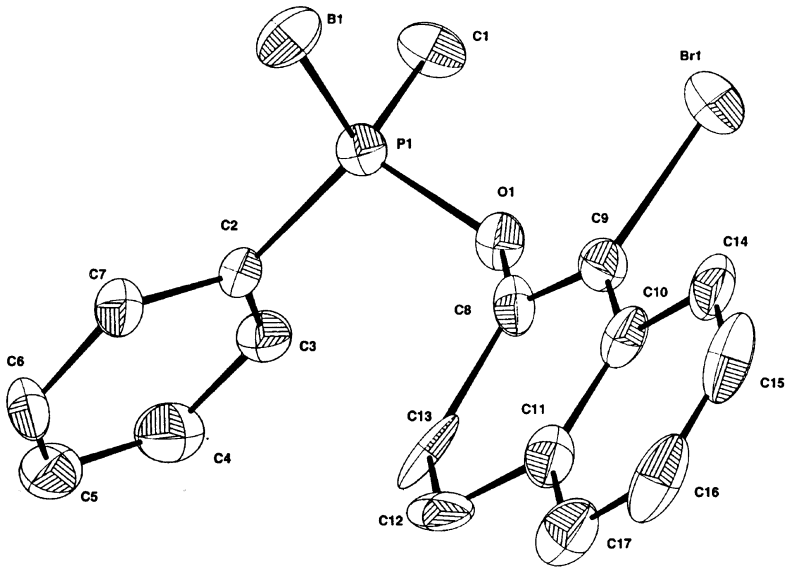
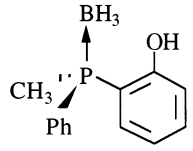
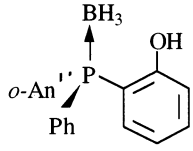
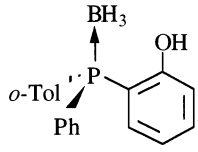
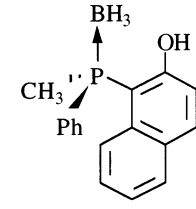
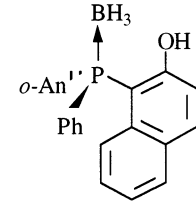


Figure 2. Crystal structure of the 2-bromonaphthylphosphinite borane **6d**. Selected bond lengths (Å) angles (°), dihedral angles (°): P(1)–B(1) 1.92(1), P(1)–O(1) 1.626(8), P(1)–C(1) 1.79(1), P(1)–C(2) 1.77(1), O(1)–C(8) 1.35(2), Br(1)–C(9) 1.90(1); O(1)–P(1)–B(1) 114.3(6), B(1)–P(1)–C(1) 113.9(7), B(1)–P(1)–C(2) 114.6(7), O(1)–P(1)–C(2) 105.4(5), P(1)–O(1)–C(8) 122.8(7); C(3)–C(2)–P(1)–B(1) 15.49, C(9)–Br(1)–P(1)–B(1) 84.33

hydroxy group by NaH, then alkylation with CH_3I, **12a** leads to the (*S*)-PAMP·BH_3 **11** (Scheme 3; entry 1). As the phosphinite borane **6a** leads directly or via the hydroxyphosphine borane **12a** to the two enantiomers of the PAMP·BH_3 **11** with the same enantiomeric purity, this proves the stereospecificity of the rearrangement which proceeds with complete retention of configuration at the P-center (Scheme 3). Consequently, these results show similar stereospecificity of the rearrangement for the phosphinite borane complexes, with respect to the phosphate series.[19] In the case of the *o*-anisyl or *o*-tolylphosphinite borane **6b** or **6c**, the rearrangement leads to the corresponding *o*-hydroxyarylphosphine boranes **12b** and **12c** in good yields (>60%, entries 2, 3). The enantiomeric excess of the hydroxyarylphosphine complex **12b** has been established by HPLC on a chiral column of its (*S*)-(–)-*O*-acetyllactyl derivative (80% e.e., entry 2). Finally, when the 1-bromo-2-naphthylphosphinite borane **6d** or **6e** are treated with *t*-BuLi, the rearrangement affords the corresponding 2-hydroxynapthylphosphine borane **12d** or **12e**, in 96 and 48% yields, respectively, and with enantiomeric excesses up to 100% e.e. (entries 4, 5).

In order to explain the retention of configuration during the rearrangement of the complexes **6**, we have examined the stereochemical pathway of all pentacoordinate intermediates, which result from the intramolecular nucleophilic attack, using the topological representation[22a] shown in Fig. 3. In this topological representation, each top corresponds to the possible pentacoordinate stereoisomers, while the lines represent the stereopermutations (Berry or turnstile rotation), allowing the passage from one stereoisomer to another. It should be pointed out that each pentacoordinate intermediate could isomerize into a maximum of three others stereoisomers by one stereopermutation (Berry or TR).

Table 2
Rearrangement of the arylphosphinites **6** into *o*-hydroxyarylphosphine boranes **12**

entry	phosphinite BH_3	BH_3 complex	yield (%)[a]	e.e. (%)
1	**6a**	 **12a**	75	72[b]
2	**6b**	 **12b**	87	80[c]
3	**6c**	 **12c**	60	-
4	**6d**	 **12d**	96	91[b]
5	**6e**	 **12e**	48	100[b]

[a] Isolated yield [b] Determined by HPLC with Chiracel OK [c] Determined by HPLC with Chiracel OK from the (*S*)-(-)-O-acetyllactyl derivative.

The possible pentacoordinate intermediates are defined by the substituents in the apical positions following the normal convention.[23] Usually, the substituents are numbered arbitrarily or by taking into account their electronegativity[22b] or the existence of a ring.[22a] Here, the

substituents of the phosphorus atom are ranked from *1* to *5* following their 'relative stereo-apicophilicity'.[24] This ranking considers the apicophilicity[25] and steric hindrance of the five substituents, including the nucleophile, around the phosphorus center, thus leading to the increasing order of the series: OAr>Ar>Ph>R>BH_3. Consequently, this ranking corresponds to the relative aptitude of the substituents to occupy an apical position in the P-stereogenic pentacoordinate intermediate. As the substituents ranked 1 and 2 are borne by the same group, the formation of the two pentacoordinate intermediates {12} and {$\overline{12}$} could not be observed and are not represented in Fig. 3.

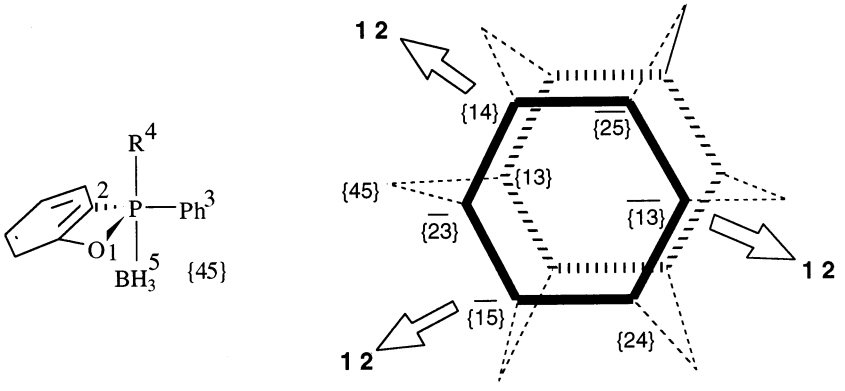
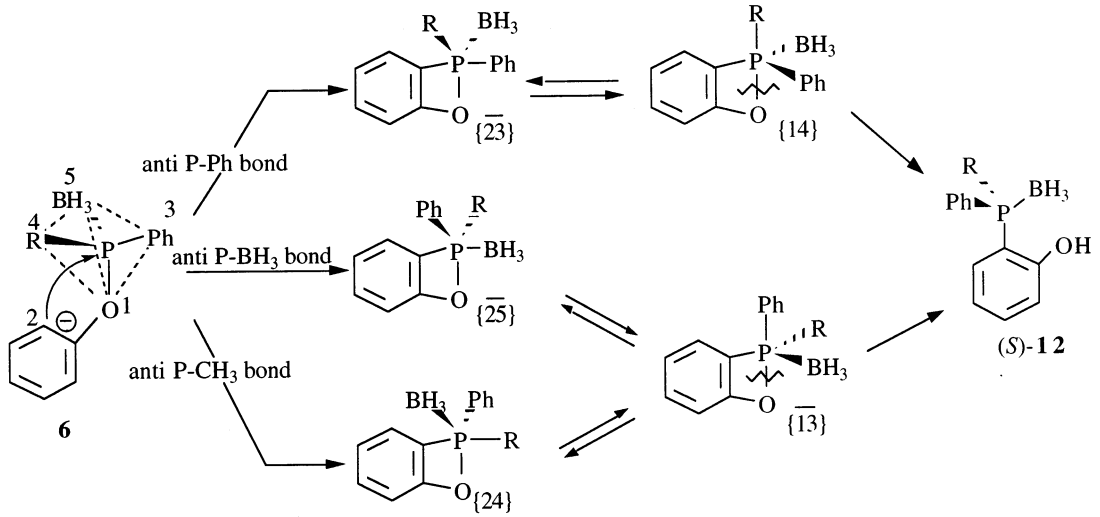


Figure 3.

On this basis, the three initial pentacoordinate intermediates which could arise from the intramolecular nucleophilic attack of the *ortho*-anion on the accessible side faces of the tetrahedral phosphorus center of **6** are {$\overline{23}$}, {$\overline{25}$} and {24} (Scheme 4).



Scheme 4.

Although it was generally assumed that the nucleophilic attack on the edges of the tetrahedral phosphorus center requires higher energy,[26] three other early pentacoordinate intermediates could also be envisaged from this approach (i.e. {14}, {$\overline{13}$}, {$\overline{15}$}). If we examine Fig. 3, we

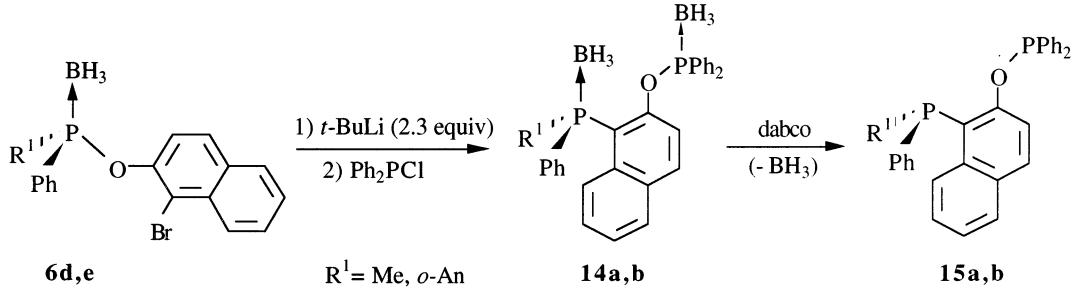
notice that the six possible early pentacoordinate intermediates occupy the same side of the topological representation. Consequently, a minimum of low energy permutations leads to the last intermediate {$\overline{13}$}, which affords the hydroxyarylphosphine borane **12** with retention of configuration, by P–O bond cleavage (Scheme 4). The same stereochemistry is also obtained, if we consider {14} (or {$\overline{15}$}), as the last pentacoordinate intermediates with a P–O bond in the axial position (Fig. 3).

On the contrary, a reverse stereochemistry for the rearrangement requires the formation of the pentacoordinate enantiomer {13}, which is located on the other side of the topological representation (Fig. 3). The interconversion could not occur easily, since the permutation of the early pentacoordinate species toward {13} get through isomers as {45}. This last one is energetically unfavorable due to the presence of a four-membered ring in the equatorial position, and electron donor substituents in the apical position (Fig. 3).

We can see that the stereospecificity of the rearrangement arises from the impossibility of making a four-membered ring pentacoordinate intermediate, which locks the racemization.

On the other hand, the borane could not be removed from the hydroxyaryl borane complexes **12** by exchange with dabco,[13] because numerous by-products arise during the reaction. However, we have succeeded in obtaining the free *o*-hydroxyarylphosphine **13e** in 84% isolated yield, by stirring the corresponding borane complex **12e** in ethanol during 24 h at room temperature (Scheme 3).

Finally, the 2-hydroxyarylphosphine boranes **12d**, **12e** have been used for the preparation of a new class of phosphine-phosphinite ligand **14a**,**b** (Scheme 5). Thus, when the rearrangement products of **6d** (or **6e**) are trapped with chlorodiphenylphosphine Ph_2PCl, then with borane, the corresponding phosphine-phosphinites **14a** (or **14b**) are obtained in 54 or 25% yields, respectively, as diborane complexes (Scheme 5). Decomplexation of borane complex **14a** or **14b** is achieved by heating with dabco,[27] giving the free phosphine-phosphinites **15a** (R^1 = Me) (or **15b**, R^1 = *o*-An) in 80 (or 85%) isolated yields, respectively, with retention of the configuration at the P-center (Scheme 5).



6d,e R^1 = Me, *o*-An **14a,b** **15a,b**

Scheme 5.

3. Conclusion

We have described herein, the first asymmetric synthesis of P-stereogenic 2-hydroxyaryl phosphine ligands **13**, using borane complexation methodology. This synthesis is based on two key steps: firstly, the highly stereoselective preparation of a chlorophosphine borane which allows the preparation of the arylphosphinite borane derivatives **6a**–**e**; secondly, the intramolec-

ular rearrangement of the complexes **6**, affording the 2-hydroxyarylphosphine boranes **12a–e** without loss of enantiomeric purity. The *o*-anisyl-2-hydroxynaphthylphenylphosphine borane **12e** has been decomplexed in EtOH, affording the first example of a P-stereogenic hydroxyarylphosphine ligand **13e**. The interest of the hydroxyarylphosphine boranes **12** is also demonstrated by the preparation of a new class of phosphine-phosphinite ligand **15**, by trapping the rearrangement products first with chlorodiphenylphosphine Ph_2PCl, then with borane. The corresponding phosphine-phosphinites **14a**,**b** are then obtained and purified as diborane complexes. When necessary, the decomplexation was achieved by heating with dabco, to afford the free phosphine-phosphinite hybrid ligands **15a**,**b** with retention of the configuration at the P-center (yield up to 85%). Studies of these new classes of ligands in asymmetric catalysis are under way in our laboratory.

4. Experimental section

4.1. General

All reactions were carried out under an argon or nitrogen atmosphere in dried glassware. Solvents were dried and freshly distilled under a nitrogen atmosphere over sodium/benzophenone for THF, toluene and benzene, P_2O_5 for CH_2Cl_2 and sodium ethoxide for EtOH. Hexane, ethanol and isopropanol for HPLC were of chromatographic grade and used without further purification. Methyllithium, *t*-butyllithium, chlorodiphenylphosphine, 2-bromoanisole, 2-bromotoluene, 1-bromo-2-naphthol, 2-bromophenol, $BH_3{\cdot}S(CH_3)_2$ and dabco were purchased from Aldrich, Acros and Avocado. Commercially available 2-bromoanisole and 2-bromotoluene were distilled before use. The toluenic HCl solution was obtained by bubbling gas, and the titration of the resulting solution was realized with NaOH and phenolphthalein as indicator. HPLC analyses were performed on a Gilson 305/306 chromatograph equipped with an UV 116 detector. The enantiomeric excess of the borane complexes **6**, **11**, **12** was determined using a Chiralcel OK column (Daicel), with a hexane/iPrOH or EtOH mixture as the mobile phase (flow rate 1 mL min^{-1}), and the UV detection at $\lambda = 254$ nm. Flash chromatography was performed on silica gel (60ACC, 35–70 μm; SDS) or neutral aluminum oxide (Carlo Erba; ref. 417241). All NMR spectra data were obtained on Bruker DPX 250 spectrometer using TMS as internal reference for ^1H (250 MHz) and ^{13}C NMR (62.9 MHz) and 85% phosphoric acid as external reference for ^{31}P NMR (101.3 MHz). Melting points were measured on a Büchi melting point apparatus and are uncorrected. Optical rotation values were determined at 20°C on a Perkin–Elmer 241 polarimeter. Infrared spectra were recorded on a Bruker Equinox 55. Mass spectral analyses were performed on a JEOL MS 700 at the Mass Spectroscopy Laboratories of ENS Paris. The major peak m/z is mentioned with the intensity as a percentage of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratories of P. & M. Curie University (Paris).

4.2. Synthesis of phosphinite boranes *6*

4.2.1. Preparation of phenate reagents

In a two-necked flask equipped with a magnetic stirrer and an argon inlet, 288 mg of NaH (12 mmol) was added and washed several times with small amounts of pentane. 10 mL of dry THF

was then added. The mixture was allowed to cool to 0°C, a solution of one equivalent (12 mmol) of phenol in a minimum of dry THF was slowly added with a syringe and the reaction was stirred during 2 hours at 0°C. Then, the phenate was used after solubilization of the possible precipitate in a minimum of anhydrous THF.

4.2.2. Preparation of the phosphinite boranes

*4.2.2.1. Typical procedure for the methylphosphinite boranes **6a**, **6d**.* In a 250 mL three-necked flask equipped with a magnetic stirrer and an argon inlet, 4 mmol of aminophosphine borane **9a** (or **9d**) were dissolved in anhydrous toluene. Then, 8.4 mmol (2.1 equiv.) of a freshly titrated toluene solution of dry HCl was added at room temperature under stirring (the final concentration of aminophosphine borane **9a** or **9d**, must be 20 mM). The reaction was stirred at room temperature for one hour and the ephedrine hydrochloride precipitate was filtered off using a Millipore 4 μm filter. The resulting solution of chlorophosphine borane **3a** (or **3d**) was then collected in a 500 mL flask and cooled at −78°C. The flask was then put under an argon atmosphere and 3 equivalents (12 mmol) of previously prepared phenate (Section 4.2.1) were added to the solution. The resulting mixture was then stirred for 2 hours and warmed to room temperature. The reaction was monitored by TLC over silica (toluene), and was hydrolyzed with 20 mL of water. The aqueous phase was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed. The residue was purified by chromatography on silica gel using toluene as eluent yielding the phosphinite borane **6a**, **6d** in 66–73% yield. When the separation between the phenol and the phosphinite borane is quite difficult, a washing of the organic layer with a 0.5 M solution of KOH can be carried out without alteration of the phosphinite borane.

The enantiomeric excess and the absolute configuration of the aryl phosphinite boranes **6a** have been determined by HPLC analysis on a Chiralcel OK Daicel column of the crude PAMP borane **11**, which results from their reaction at low temperature (<−50°C), with *o*-anisyllithium; eluent: hexane/EtOH 70:30; (*R*) enantiomer $t_R = 11.1$ min; (*S*) enantiomer $t_R = 21.4$ min.

*4.2.2.2. Typical procedure for the phosphinite boranes **6b**, **6c**, and **6e**.* In a 250 mL three-necked flask equipped with a magnetic stirrer and an argon inlet, 24 mmol (6 equiv.) of freshly titrated toluene solution of dry HCl were added to 4 mmol of aminophosphine borane **9b** (or **9c**). The reaction was stirred at room temperature for 1 hour, and the ephedrine hydrochloride precipitate was filtered off using a Millipore 4 μm filter. The resulting solution of chlorophosphine borane **3b**,**c**, was collected in a 250 mL flask and cooled at −78°C. The flask was then put under an argon atmosphere and 28 mmol of phenate (7 equiv.), previously prepared according to the procedure described in Section 4.2.1, was added. The resulting mixture was then stirred for 2 hours, warmed to room temperature and monitored by TLC over silica (toluene). After hydrolysis with 20 mL of water, the mixture was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed. The residue was purified by chromatography on silica gel using toluene as eluent, yielding the phosphinite borane **6b** (or **6c**, **6e**) in 66–73% yield. The excess of phenol could be recovered from the residue by extracting the organic layer with a 0.5 M solution of KOH, without alteration of the phosphite borane.

4.2.2.3. (S)-(−)-Methyl-(2-bromophenyl)phenylphosphinite borane ***6a***. Yield = 71%; white oil; $R_f = 0.75$ (toluene); $[\alpha]_D^{20} = -32.3$ (*c* 1.7, $CHCl_3$) for 71% e.e.; IR (neat, *v* cm^{-1}): 3061–2920 (w), 2381 (m, B–H), 1578 (w), 1472 (s), 1438 (m), 1225 (s), 1119 (m), 1046 (w), 905 (s), 747 (m); ^1H NMR ($CDCl_3$): δ 0.2–1.60 (3H, br, BH_3), 1.93 (3H, d, $^2J_{HCP} = 8.8$, CH_3), 6.80–6.90 (1H, m, *H* arom.), 7.07–7.20 (3H, m, *H* arom.), 7.40–7.55 (4H, m, *H* arom.), 7.80–7.95 (1H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 16.9 (d, $^1J_{CP} = 44.2$, CH_3), 115.3 (d, $J_{CP} = 4.2$, *C*Br), 121.7 (d, $J_{CP} = 4.2$, *C* arom.), 125.6 (*C* arom.), 128.2 (*C* arom.), 128.8 (d, $J_{CP} = 10.3$, *C* arom.), 130.9 (d, $J_{CP} = 12.1$, *C* arom.), 131.6 (*C* arom.), 132.6 (d, $J_{CP} = 1.8$, *C* arom.), 133.3 (*C* arom.), 149.5 (d, $J_{CP} = 5.5$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +121.2 (q, $^1J_{PB} = 63.6$); MS (DCI, CH_4) *m*/*z* (relative intensity): 309 (M^+–H; 80), 307 (M^+–H; 100), 305 (M^+–3H; 20), 227 (90), 217 (40), 173 (30), 141 (35), 125 (70), 107 (70); HRMS (DCI, CH_4) calcd for $C_{13}H_{14}BBrOP$ [M^+–H]: 307.0061; found: 307.0060.

*4.2.2.4. (S)-(−)-*o*-Anisyl-(2-bromophenyl)phenylphosphinite borane* ***6b***. Yield = 70%; white powder; mp = 122°C; $R_f = 0.6$ (toluene); $[\alpha]_D^{20} = -12.5$; (*c* 1, $CHCl_3$) for 80% e.e.; IR (neat, *v* cm^{-1}): 3071–2838 (w), 2403 (m, B–H), 2347 (m, B–H), 1588 (m), 1575 (m), 1474 (s), 1438 (s), 1430 (s), 1279 (m), 1267 (m), 1252 (m), 1229 (s), 1109 (m), 1045 (m), 1018 (m), 911 (s), 742 (s); ^1H NMR ($CDCl_3$): δ 0.2–1.60 (3H, br, BH_3), 3.52 (3H, s, OCH_3), 6.77–6.91 (2H, m, *H* arom.), 7.00–7.12 (3H, m, *H* arom.), 7.30–7.50 (5H, m, *H* arom.), 7.84–7.93 (2H, ddd, $J = 1.7$, $J = 7.8$, $^3J_{HP} = 12.6$, *H* arom.), 8.03–8.11 (1H, ddd, $J = 1.7$, $J = 7.6$, $^3J_{HP} = 11.4$, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.4 (s, CH_3O), 111.6 (d, $J_{CP} = 5.0$, *C* arom.), 115.4 (d, $J_{CP} = 5.3$, *C* arom.), 119.0 (d, $J_{CP} = 60.4$, *C* arom.), 120.9 (d, $J_{CP} = 11.4$, *C* arom.), 121.4 (d, $J_{CP} = 4.4$, *C* arom.), 125.1 (*C* arom.), 128.0 (d, $J_{CP} = 7.4$, *C* arom.), 128.3 (*C* arom.), 131.3 (d, $J_{CP} = 12.1$, *C* arom.), 131.6 (d, $J_{CP} = 2.3$, *C* arom.), 132.4 (*C* arom.), 133.4 (*C* arom.), 134.4 (d, $J_{CP} = 12.1$, *C* arom.), 134.6 (d, $J_{CP} = 1.7$, *C* arom.), 150.0 (d, $J_{CP} = 3.9$, *C* arom.), 160.9 (d, $J_{CP} = 3.2$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +112.1 (q, $^1J_{PB} = 73.3$); MS (DCI, CH_4) *m*/*z* (relative intensity): 401 (M^+–H; 90), 399 (M^+–H; 100), 389 (M^++H–BH_3; 30), 387 (M^++H–BH_3; 30), 281 (10), 279 (10), 215 (35); HRMS (DCI, CH_4) calcd for $C_{19}H_{18}PBO_2Br$ [M^+–H]: 399.0321; found: 399.0303; anal. calcd for $C_{19}H_{19}BBrO_2P$: C, 56.90; H, 4.78; found: C, 56.91; H 4.78.

*4.2.2.5. (R)-(+)-(2-Bromophenyl)phenyl-(*o*-tolyl)phosphinite borane* ***6c***. Yield: 66%; uncrystallized, white; $R_f = 0.75$ (toluene); $[\alpha]_D^{20} = +21.7$ (*c* 1.5, $CHCl_3$); IR (neat, *v* cm^{-1}): 2383–2338 (s, B–H), 1622, 153, 1561, 1497, 1458, 1437, 1398, 1353, 1326, 1314, 1295, 1251, 1228, 1154, 1131, 1115, 1058, 994, 951, 905; ^1H NMR ($CDCl_3$): δ 0.3–1.8 (br, 3H, BH_3), 2.30 (3H, s, CH_3), 6.80–7.20 (5H, m, *H* arom.), 7.30–7.60 (5H, m, *H* arom.), 7.70–7.90 (2H, m, *H* arom.), 8.10–8.30 (1H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 21.4 (d, $J_{CP} = 4.2$, CH_3), 115.3 (d, $J_{CP} = 5.3$, *C* arom.), 121.2 (d, $J_{CP} = 4.7$, *C* arom.), 125.4 (*C* arom.), 126.0 (d, $J_{CP} = 12.4$, *C* arom.), 128.7 (d, $J_{CP} = 10.8$, *C* arom.), 131.2 (d, $J_{CP} = 11.6$,*C* arom.), 131.9 (*C* arom.), 132.9 (d, $J_{CP} = 2.3$, *C* arom.), 133.6, 134.2 (d, $J_{CP} = 17.5$, *C* arom.), 142.0 (d, $J_{CP} = 7$, *C* arom.), 149.6 (d, $J_{CP} = 3.6$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +115.9 (q, $^1J_{PB} = 68.3$); MS (DCI, CH_4) *m*/*z* (relative intensity): 383 (M^+–H; 100), 373 (60), 371 (60), 295 (25), 293 (25), 281 (25), 279 (25), 199 (65); HRMS (DCI, CH_4) calcd for $C_{19}H_{18}BBrOP$, [M^+–H]: 383.0372; found: 383.0307; calcd for $C_{19}H_{17}OBrP$, [M^++H–BH_3]: 371.0200; found: 371.0213.

4.2.2.6. (S)-(−)-Methyl-(1-bromo-2-naphthyl)phenylphosphinite borane ***6d***. Yield = 66%; white powder; mp = 67–68°C; $R_f = 0.7$ (toluene); $[\alpha]_D^{20} = -38.4$ (*c* 2.0, $CHCl_3$) for 91% e.e.; IR (neat, *v* cm^{-1}): 2410, 2383, 2338 (m, B–H), 1622 (w), 1593 (m), 1497 (m), 1458 (m), 1437 (m), 1353 (m),

1251 (m), 1228 (s), 1115 (m), 1058 (m), 994 (s), 951 (s), 905 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–1.8 (br, 3H, BH_3), 1.99 (3H, d, $^2J_{HP}=8.8$, PCH_3), 7.10–7.20 (1H, m, *H* arom.), 7.25–7.63 (7H, m, *H* arom.), 7.9–8.0 (2H, m, *H* arom.), 8.1–8.2 (1H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 17.1 (d, $^1J_{CP}=44$, *C*H_3), 113.8 (d, $J_{CP}=5.4$, *C* arom.), 120.7 (d, $J_{CP}=3.7$, *C* arom.), 126.3 (d, $J_{CP}=64$, *C* arom.), 127.9 (d, $J_{CP}=19.6$, *C* arom.), 128.5 (*C* arom.), 128.8 (d, $J_{CP}=10.6$, *C* arom.), 130.9 (*C* arom.), 131.0 (d, $J_{CP}=14.8$, *C* arom.), 131.4 (*C* arom.), 131.8 (*C* arom.), 132.7 (d, $J_{CP}=2.2$, *C* arom.), 147.7 (d, $J_{CP}=5.6$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +121.3 (q, $^1J_{PB}=68.3$); MS (DCI, NH_3) *m*/*z* (relative intensity): 378 (M+NH_4^+; 5), 376 (M+NH_4^+; 5), 158 (30), 141 (10), 125 (100); HRMS (DCI, CH_4) calcd for $C_{17}H_{16}BBrOP$ [M^+–H]: 357.0218; found: 357.0219; anal. calcd for $C_{17}H_{17}BBrOP$ (359.0): C, 56.88; H, 4.77; found C, 56.74; H 4.81.

Crystal data for compound **6d**: formula $C_{17}H_{17}Br_1P_1O_1B_1$; F.W. 359.01; crystal system: orthorhombic; *a* (Å)=6.593(2); *b* (Å)=6.336(3); *c* (Å)=34.912(9); α (°)=90; β (°)=90, γ (°)=90; *V* (Å^3)=1688.5(9); *Z*=4; space group: $P2_12_12_1$; crystal shape: parallelepiped; linear absorption coefficient μ (cm^{-1}): 24.98; density ρ (g cm^3)=1.41; diffractometer: CAD4-Enraf Nonius; radiation: Mo Kα (λ=0.71069 Å); scan type: $\omega/2\theta$; scan range (°): 0.8+0.345 tgθ; θ limits (°): 1–30; temp.: rt; octants collected: 0.9; 0.10; 0.49; Nb of data collected: 2883; Nb of unique data used for refinement: 999 $(F_o)^2>3\sigma(F_o)^2$; decay of standard reflections%: 3.2; $R=\Sigma IF_o-IF_cII/\Sigma F_o$: 0.0686; $R_w^*=[\Sigma w(F_o-IF_cI)^2/\Sigma wF_o^2]^{1/2}=0.0782$; secondary extinction coefficient: 980.8; goodness of fit: 1.12; Nb of variables: 192; $\Delta\rho_{min}$ (e Å^{-3}): −0.45; $\Delta\rho_{max}$ (e Å^{-3}): 0.79.

4.2.2.7. (R)-(+)-o-*Anisyl-(1-bromo-2-naphthyl)phenyl phosphinite borane* ***6e***. Yield=73%; yellow solid; mp=102°C; R_f=0.67 (toluene); $[\alpha]_D^{20}=+40.8$ (*c* 1, $CHCl_3$); IR (ν cm^{-1}): 3066 (w), 2923 (s), 2403 (s, B–H), 1623 (m), 1588 (s), 1576 (s), 1501 (m), 1477 (s), 1457 (s), 1437 (s), 1354 (m), 1280 (s), 1253 (s), 1228 (s), 1110 (s), 1083 (m), 1063 (m), 1017 (m), 994 (s), 946 (m), 821 (s), 805 (s), 793 (s), 753 (s), 744 (s), 69 (s); ^{1}H NMR ($CDCl_3$): δ 0.2–1.8 (br, 3H, BH_3), 3.37 (3H, s, OCH_3), 6.85–6.90 (1H, dd, *H* arom.), 7.09–7.77 (10H, m, *H* arom.), 7.96–8.04 (2H, m, *H* arom.), 8.15–8.24 (2H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.3 (s, O–*C*H_3), 111.7 (d, $J_{CP}=4.9$, *C* arom.), 113.7 (d, $J_{CP}=5.5$, *C* arom.), 119.3 (d, $J_{CP}=60.6$, *C* arom.) 120.7 (d, $J_{CP}=4$, *C* arom.), 121.0 (d, $J_{CP}=11.4$, *C* arom.), 126.2 (d, $J_{CP}=81.1$, *C* arom.), 127.9 (d, $J_{CP}=26$, *C* arom.), 128.1–128.5 (*C* arom.), 128.7 (d, $J_{CP}=92.8$, *C* arom.), 131.3 (d, $J_{CP}=12.1$, *C* arom.), 131.4 (d, $J_{CP}=19$, *C* arom.), 131.7 (d, $J_{CP}=17.8$, *C* arom.), 134.3 (d, $J_{CP}=12$, *C* arom.), 134.7 (d, $J_{CP}=1.6$, *C* arom.), 148.3 (d, $J_{CP}=4.1$, *C* arom.), 161.0 (d, $J_{CP}=3.2$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +112.6 (q, $^1J_{PB}=51$); MS (DCI, CH_4) *m*/*z* (relative intensity): 439 (M^+; 55), 437 (M^+; 55), 359 (20), 357 (20), 331 (15), 329 (15), 217 (80), 215 (100), 172 (20), 154 (50), 144 (50); HRMS (DCI, CH_4) calcd for $C_{23}H_{19}BrO_2P$ [M^++H–BH_3]: 439.0286; found: 439.0293.

4.2.3. Preparation of the hydroxyphosphine boranes ***12a–e*** *by rearrangement of the arylphosphinite boranes* ***6a–e***

In a 100 mL three-necked flask equipped with a magnetic stirrer and an argon inlet, 3 mmol of phosphinite borane **6a–e** was dissolved in 30 mL of anhydrous THF. The mixture was then cooled at −78°C and 2.7 equiv. of *t*-BuLi (1.5 M in pentane) was slowly added. The resulting mixture was then stirred for 1 hour and warmed to 0°C. The reaction was monitored by TLC over silica (toluene/petroleum ether 7:3), and finally was hydrolyzed with 3 mL of water. The THF was removed under reduced pressure and the aqueous layer was extracted several times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The residue was purified by chromatography on silica gel, using a mixture of

toluene/petroleum ether as eluent, yielding the hydroxyphosphine boranes **12a–d** in 60–90% yield.

4.2.3.1. (S)-*(–)-Methyl-(2-hydroxyphenyl)phenylphosphine borane* ***12a***. Yield = 75%; white solid; mp = 49–50°C; R_f = 0.3 (toluene); $[\alpha]_D^{20}$ = –16.1 (*c* 1.8, $CHCl_3$) for e.e. = 72%; IR (neat, *v* cm^{-1}): 3415 (s, O–H), 3078 (w), 2922 (s), 2852 (s), 2374 (m, B–H), 2347 (s, B–H), 1595 (s), 1581 (m), 1444 (s), 1337 (m), 1290 (m), 1195 (m), 1076 (s), 896 (s), 836 (m), 757 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–1.9 (3H, br, BH_3), 1.86 (3H, d, $^2J_{HP}$ = 10.4, CH_3), 6.80–7.00 (2H, m, *H* arom.), 7.30–7.55 (5H, m, *H* arom.); 7.60–7.85 (2H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 11.8 (d, $^1J_{CP}$ = 43, *C*H_3), 112.9 (d, J_{CP} = 56.6, *C* arom.), 117.9 (d, J_{CP} = 5.7, *C* arom.), 120.9 (d, J_{CP} = 8.5, *C* arom.), 128.8 (d, J_{CP} = 10.4, *C* arom.), 130.1 (d, J_{CP} = 60, *C* arom.), 131.1 (d, J_{CP} = 9.7, *C* arom.), 133.0 (d, J_{CP} = 5.4, *C* arom.), 133.8 (d, J_{CP} = 2.1, *C* arom.), 159.9 (d, J_{CP} = 6.8, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +5.0 (q, $^1J_{PB}$ = 68); MS (EI) *m*/*z* (relative intensity): 227 (M^+–3H; 100), 216 (M^+–BH_3; 70), 215 (25), 183 (55), 169 (10), 149 (15), 121 (20), 107 (30), 91 (15), 77 (30), 69 (10), 51 (15); HRMS (EI) calcd for $C_{13}H_{13}OP$, [M^+–BH_3]: 216.0704; found: 216.0707.

The enantiomeric excess of the *o*-hydroxyphenylphosphine borane **12a** was determined by HPLC on a Chiralcel OK Daicel column, with hexane/EtOH 75:25 as eluent (flow rate 1 mL min^{-1}; major (*S*)-enantiomer t_R = 15.45 min; minor (*R*)-enantiomer t_R = 8.87 min).

4.2.3.2. (S)-*(+)*-o-*Anisyl-(2-hydroxyphenyl)phenylphosphine borane* ***12b***. Yield = 87%; white powder; mp = 103–104°C; R_f = 0.35 (toluene); $[\alpha]_D^{20}$ = +3.3 (*c* 0.5, $CHCl_3$) for e.e. = 80%; IR (neat, *v* cm^{-1}): 3304 (s, O–H), 3058 (w), 2933 (m), 2837 (w), 2396 (m, B–H), 2348 (m, B–H), 1615 (s), 1601 (m), 1588 (s), 1570 (m), 1564 (m), 1512 (s), 1477 (s), 1461 (s), 1436 (s), 1428 (s), 1396 (s), 1280 (s), 1265 (m), 1250 (s), 1221(s), 1209 (m), 1163 (m), 1132 (s), 1076 (m), 1060 (s), 1017 (s), 821 (s), 800 (m), 777 (m), 750 (s), 704 (m); ^{1}H NMR ($CDCl_3$): δ 0.5–1.8 (3H, br, BH_3), 3.56 (3H, s, OCH_3), 6.70–7.05 (5H, m, *H* arom.), 7.20–7.70 (8H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.6 (d, J_{CP} = 4.4, O*C*H_3), 111.9 (d, J_{CP} = 4.8, *C* arom.), 112.1 (d, J_{CP} = 60, *C* arom.), 115.6 (d, J_{CP} = 60.7, *C* arom.), 118.2 (d, J_{CP} = 6, *C* arom.), 120.3 (d, J_{CP} = 8, *C* arom.), 121.3 (d, J_{CP} = 11.1, *C* arom.), 128.1 (d, J_{CP} = 64.9, *C* arom.), 128.6 (d, J_{CP} = 10.6, *C* arom.), 131.0 (d, J_{CP} = 2.5, *C* arom.), 132.6 (d, J_{CP} = 9.9, *C* arom.), 133.4 (d, J_{CP} = 2, *C* arom.), 134.2 (*C* arom.), 135.2 (d, J_{CP} = 2.8, *C* arom.), 160.1 (d, J_{CP} = 8.9, *C* arom.), 161.4 (*C* arom.); ^{31}P NMR ($CDCl_3$): δ +11.9 (q, $^1J_{PB}$ = 69.9); MS (EI) *m*/*z* (relative intensity): 319 (M^+–3H; 90), 317 (M^+–BH_3; 100), 291 (15), 277 (15), 199 (50), 183 (75), 152 (20), 107 (20), 91 (20), 77 (20), 63 (15); HRMS (EI) calcd for $C_{19}H_{17}O_2P$, [M^+–BH_3]: 308.0966; found: 308.0969.

The enantiomeric excess of the *o*-hydroxyphenylphosphine borane **12b** was determined by derivatization with (*S*)-(–)-*O*-acetyllactyl chloride. This derivative was prepared by trapping the rearrangement product with (*S*)-*O*-acetyllactyl chloride, before hydrolysis of the reaction mixture: R_f = 0.55 (toluene); ^{1}H NMR ($CDCl_3$): δ 0.5–1.8 (3H, br, BH_3), 0.95 (3H, d, J_{HH} = 7, CH_3), 2.0 (3H, s, CH_3CO), 3.4 (3H, s, CH_3O), 4.8 (1H, q, J_{HH} = 7, C*H*), 6.8–7.9 (13H, m, *H* arom.); ^{31}P NMR ($CDCl_3$): δ +17.6; ^{13}C NMR ($CDCl_3$): major stereoisomer δ 15.7 (*C*H_3CH), 20.6 (*C*H_3CO), 55.0, 68.5, 111.5, 116.3 (d), 121.0–133.9 (*C* arom.), 151.8 (d, J_{CP} = 3.5, *C* arom.), 161.0, 168.3, 170.2; minor stereoisomer δ 16.7, 20.6, 55.4, 68.1, 111.5, 116.3 (d), 121.0–133.9, 151.0 (d), 160.9, 168.2, 170.3.

The diastereoisomeric ratio of the (*S*)-*O*-acetyllactyl derivative was determined by HPLC analysis on a Chiralcel OK Daicel column, with hexane/*i*-PrOH 98:2 as eluent (flow rate 1 mL min^{-1}; major stereoisomer t_R = 17.8 min; minor stereoisomer t_R = 8.9 min). The minor stereoiso-

mer has been identified by comparison with the corresponding derivative of (*S*)-*o*-anisyl-(2-hydroxyphenyl)phenylphosphine borane **12b**, prepared from (−)-ephedrine.

*4.2.3.3. (*R*)-2-Hydroxyphenyl-phenyl(*o*-tolyl)phosphine borane **12c***. Yield = 60%; white powder; R_f = 0.35 (toluene); IR (ν cm^{-1}): 3367 (s, O–H), 3062–2923 (m), 2408 (m, B–H), 2379 (m, B–H), 2296 (m, B–H), 1601 (m), 1588 (m), 1575 (s), 1473 (s), 1453 (s), 1435 (s), 1299 (m), 1279 (m), 1255 (m), 1214 (m), 1128 (m), 1067 (m), 742 (m), 692 (m); ^{1}H NMR ($CDCl_3$): δ 0.5–1.8 (3H, br, BH_3), 2.26 (3H, s, CH_3), 6.70–7.60 (13H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 22.5 (d, $^3J_{CP}$ = 5, *C*H$_3$), 111.8 (d, J_{CP} = 58.4, *C* arom.), 118.7 (d, J_{CP} = 6, *C* arom.), 120.7 (d, J_{CP} = 7.8, *C* arom.), 125.8–133.9 (*C* arom.), 142.9 (d, J_{CP} = 11.6, *C* arom.), 160.5 (d, J_{CP} = 9.1, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +14.2 (q, $^1J_{PB}$ = 67); MS (DCI, CH_4) *m*/*z* (relative intensity): 305 (M^+–H; 100), 293 (100), 215 (15), 201 (15); HRMS (DCI, CH_4): calcd for $C_{19}H_{19}BOP$, [M^+–H]: 305.1267; found *m*/*z*: 305.1270.

*4.2.3.4. (*S*)-(+)-Methyl-1-(2-hydroxynaphthyl)phenylphosphine borane **12d***. Yield = 96%; white powder; mp = 125°C; R_f = 0.5 (toluene); $[\alpha]_D^{20}$ = +1.47 (*c* 0.7, $CHCl_3$) for e.e. = 91%; IR (neat, ν cm^{-1}): 3323 (s, O–H), 2412 (s, B–H), 2382 (s, B–H), 1616 (m), 1603 (m), 1568 (m), 1512 (m), 1463 (m), 1436 (m), 1397 (m), 1266 (m), 1219 (s), 1131 (s), 1107, 1065 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–2.0 (3H, br, BH_3), 2.08 (3H, d, $^2J_{HP}$ = 10.2, PCH_3), 7.1–7.5 (9H, m, *H* arom.), 7.70 (1H, d, J_{HH} = 9, *H* arom.), 7.87 (1H, d, J_{HH} = 9, *H* arom.), 9.12 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$): δ 12.4 (d, $^1J_{CP}$ = 43.4, *C*H$_3$), 98.8 (d, J_{CP} = 55.7, *C* arom.), 120.3 (d, J_{CP} = 7.5), 123.5 (*C* arom.), 125.1 (d, J_{CP} = 5.2, *C* arom.), 127.1 (*C* arom.), 129.0–130.5 (*C* arom.), 131.7 (d, J_{CP} = 62.6, *C* arom.), 133.5 (*C* arom.), 135.9 (*C* arom.), 163.4 (d, J_{CP} = 11.7, *C* arom.); ^{31}P NMR ($CDCl_3$): δ −0.46 (q, $^1J_{PB}$ = 64); MS (EI) *m*/*z* (relative intensity): 277 (M^+–3H; 75), 266 (M^+–BH_3; 50), 233 (20), 83 (100); HRMS (DCI, CH_4) calcd for $C_{17}H_{17}OPB$, [M^+-H]: 279.1113; found: 279.1121; anal. calcd. for $C_{17}H_{18}OPB$ (280.1134): C, 72.89; H, 6.48; found C, 72.76; H, 6.62.

The enantiomeric excess of the *o*-hydroxyphenylphosphine borane **12d** was determined by HPLC on a Chiralcel OK Daicel column, with hexane/EtOH 75:25 as eluent (flow rate 1 mL min^{-1}; minor enantiomer t_R = 10.5 min; major enantiomer t_R = 20.2 min).

*4.2.3.5. (*R*)-(+)-o-Anisyl-1-(2-hydroxynaphthyl)phenylphosphine borane **12e***. Yield = 48%; white powder; mp = 118–120°C; R_f = 0.26 (toluene/cyclohexane, 1:1); $[\alpha]_D^{20}$ = +94.5 (*c* 1, $CHCl_3$); IR (ν cm^{-1}): 3304 (s, O–H), 3059–2837 (w), 2396 (m, B–H), 2350 (m, B–H), 1615 (m), 1601 (m), 1588 (m), 1564 (m), 1512 (m), 1476 (s), 1462 (s), 1436 (s), 1428 (s), 1396 (m), 1280 (m), 1265 (m), 1250 (s), 1221 (s), 1163 (m), 1132 (m), 1060 (m), 1016 (s), 821 (s), 777 (m), 751 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–1.9 (3H, br, BH_3), 3.50 (3H, s, OCH_3), 6.78–7.86 (1H, m, *H* arom.), 6.93–7.07 (2H, m, *H* arom.), 7.10–7.30 (2H, m, *H* arom.), 7.35–7.58 (6H, m, *H* arom.), 7.60–7.78 (3H, m, *H* arom.), 7.90 (1H, d, J_{HH} = 9, *H* arom.), 9.30 (1H, s, O*H*); ^{13}C NMR ($CDCl_3$): δ 55.2 (s, O*C*H$_3$), 99.1 (d, J_{CP} = 58.2, *C* arom.), 111.8 (d, J_{CP} = 5.3, *C* arom.), 117.4 (d, J_{CP} = 62.4, *C* arom.), 119.9 (d, J_{CP} = 7.7, *C* arom.), 120.5 (d, J_{CP} = 9.8, *C* arom.), 122.7 (*C* arom.), 125.5 (d, J_{CP} = 5.3, *C* arom.), 125.8 (*C* arom.), 126.6 (*C* arom.), 127.7 (*C* arom.), 128.0 (d, J_{CP} = 10.6, *C* arom.), 128.5 (*C* arom.), 128.8 (d, J_{CP} = 5.2, *C* arom.), 130.3 (d, J_{CP} = 2.4, *C* arom.), 131.7 (d, J_{CP} = 5.5, *C* arom.), 132.5 (*C* arom.), 132.8 (d, J_{CP} = 9.4, *C* arom.), 133.7 (s, *C* arom.), 134.7 (d, J_{CP} = 1.7, *C* arom.), 160.5 (d, J_{CP} = 5, *C* arom.), 162.4 (d, J_{CP} = 11.9, *C* arom.); ^{31}P NMR ($CDCl_3$): δ +6.07 (br); MS (EI) *m*/*z* (relative intensity): 369 (M^+–3H; 100), 358 (M^+–BH_3; 90), 327 (20), 249 (55), 233 (45), 202 (45), 183 (30), 157 (35), 127 (25), 91 (25), 84 (70); HRMS (EI): calcd for $C_{23}H_{19}O_2PB$, [M-3H]: 369.1220; found *m*/*z*: 369.1227.

The enantiomeric excess of the *o*-hydroxynaphthylphosphine borane **12e** was determined by HPLC on a Chiralcel OK Daicel column, with hexane/EtOH 90:10 as eluent (flow rate 1 mL min^{-1}; minor enantiomer $t_R = 36.6$ min; major enantiomer $t_R = 48.9$ min).

4.2.4. Typical procedure for the preparation of phosphine-phosphinite diborane ligands ***14***

In a 100 mL two-necked flask equipped with a magnetic stirrer and an argon inlet, 2.8 mmol of phosphinite borane **6d** (or **6e**) was dissolved in 28 mL of anhydrous toluene. The mixture was then cooled at −78°C and 2.7 equivalents of *t*-BuLi (7.56 mmol, 1.5 M in pentane) were slowly added. The resulting mixture was then stirred for 1 hour, warmed to 0°C, and the reaction was monitored by TLC over silica (toluene). Then, 2.7 equivalents of chlorodiphenylphosphine (7.56 mmol, 1.67 g, 1.36 mL) were slowly added at 0°C, and the resulting mixture was stirred 1 hour and warmed to room temperature. After addition of 10 equivalents of borane dimethylsulfide (27.8 mmol, 2.78 mL), the mixture was stirred for 1 hour, and the THF was removed under reduced pressure. The residue was hydrolyzed with 10 mL of water, and the mixture extracted several times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by chromatography on silica gel using a mixture of toluene/petroleum ether 1:1 as eluent, yielding the phosphine-phosphinite diborane ligand **14a** (or **14b**) in 54 (or 25%) isolated yield.

*4.2.4.1. (*S*)-(+)-Methyl-1-[2-(diphenylphosphinito borane)naphthyl]phenylphosphine borane* ***14a***. Yield = 54%; white powder; mp = 154–156°C; $R_f = 0.5$ (toluene); $[\alpha]_D^{20} = +17.6$ (*c* 0.96, $CHCl_3$); IR (neat, *v* cm^{-1}): 3434 (m, O–H), 3054–2800 (w), 2395 (s, B–H), 2340 (s, B–H), 1590 (m), 1507 (m), 1460 (s), 1436 (s), 1319 (m), 1221 (s), 1213 (s), 1150 (m), 1114 (m), 1061 (s), 1009 (s), 965 (s), 820 (s), 811 (s), 738 (s), 694 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–2.0 (6H, br, B*H*$_3$), 1.64 (3H, d, $^2J_{HP} = 10.1$, C*H*$_3$), 7.00–7.90 (20H, m, *H* arom.), 8.75 (1H, d, $J = 12.1$, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 16.0 (d, $^1J_{CP} = 42.2$, *C*H$_3$), 125.4–134 (*C* arom.); ^{31}P NMR ($CDCl_3$): δ +8.9 (br, PhMe*P*), +111.0 (br, Ph$_2$*P*O); MS (DCI, CH_4) *m*/*z* (relative intensity): 477 (M^+−H; 5), 465 (20), 451 (20), 339 (25), 294 (35), 279 (90), 277 (100), 267 (90), 216 (55), 187 (90), 125 (30), 109 (50); HRMS (DCI, CH_4): calcd for $C_{29}H_{29}OP_2B_2$, [M^+−H]: 477.1880; found: 477.1890; Anal. calcd for $C_{29}H_{30}OP_2B_2$ (478.125): C, 72.85; H, 6.32; found C, 72.85; H, 6.33.

*4.2.4.2. (*R*)-(+)-*o*-Anisyl-1-[2-(diphenylphosphinito borane)naphthyl]phenylphosphine borane* ***14b***. Yield = 25%; white powder; mp = 165–168°C; $R_f = 0.26$ (toluene); $[\alpha]_D^{20} = +72.9$ (*c* 1, $CHCl_3$); IR (neat, *v* cm^{-1}): 3050–2850 (w), 2440–2330 (s), 1625 (w), 1590 (s), 1508 (s), 1474 (s), 1462 (s), 1437 (s), 1435 (m), 1429 (m), 1320 (w), 1275 (m), 1245 (m), 1215 (s), 1210 (s), 1110 (m), 1060 (m), 1000 (s), 960 (s), 808 (s), 778 (m), 757 (m), 700 (s); ^{1}H NMR ($CDCl_3$): δ 0.3–2.0 (6H, br, B*H*$_3$), 3.22 (3H, s, OC*H*$_3$), 6.40–6.65 (m, 2H, *H* arom.), 7.05–7.90 (22H, m, *H* arom.), 7.91 (1H, d, $J = 8.8$, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.0 (s, O*C*H$_3$), 110.7 (d, $J_{CP} = 4.8$, *C* arom.), 118.3–120.2 (*C* arom.), 121.0 (d, $J_{CP} = 13.0$, *C* arom.), 124.7 (*C* arom.), 126.2 (*C* arom.), 126.5 (d, $J_{CP} = 6.7$, *C* arom.), 128.1 (d, $J_{CP} = 11.0$, *C* arom.), 128.4–133.0 (*C* arom.), 153.7 (d, $J_{CP} = 4.4$, *C* arom.), 159.9 (*C* arom.); ^{31}P NMR ($CDCl_3$): δ +12.8 (br, AnPh*P*–Ar), +106.9 (br, Ph$_2$*P*–O); MS (DCI, CH_4) *m*/*z* (relative intensity): 555 (M^+−BH_3−H; 55), 443 (M^+−2BH_3+H; 100), 465 (10), 436 (10), 422 (10), 369 (45), 359 (60), 340 (25), 215 (20), 187 (40), 109 (20); HRMS (DCI, CH_4): calcd for $C_{35}H_{30}O_2P_2B_2$, [M^+−BH_3−H]: 555.1820; found: 555.1819; calcd for $C_{35}H_{29}O_2P_2$, [M^+−2BH_3+H]: 543.1643; found: 543.1648.

4.2.5. Typical procedure for the decomplexation of phosphine-phosphinite diboranes ***14a,b***

In a three-necked flask equipped with a reflux condenser, a magnetic stirrer and an argon inlet, 1 equivalent of phosphine-phosphinite diborane ligand **14a,b** (0.075 mmol) was charged. Diazabicyclooctane (4 equivalents, 0.3 mmol) was added, the flask was purged with three cycles of argon and 3 mL of dry toluene were added. The mixture was heated at 60°C for 15 h. The crude product was rapidly filtered off on a neutral alumina column (15 cm height, 2 cm diameter) using toluene/AcOEt, 9:1, as eluent. Phosphine-phosphinite **15a,b** was recovered in 80–84% isolated yields.

4.2.5.1. (S)-(−)-Methyl-1-[2-(diphenylphosphinito)naphthyl]phenylphosphine ***15a***. Yield = 80%; uncrystallized; $[\alpha]_D^{20} = -4.0$ (*c* 0.25, $CHCl_3$); IR (neat, *v* cm^{-1}): 3050 (w), 2970–2850 (w), 1457 (w), 1436 (w), 1261 (s), 1096 (s), 1026 (s), 806 (s); ^1H NMR ($CDCl_3$): δ 1.50 (3H, d, $^2J_{HP} = 4.3$, CH_3), 6.90–7.40 (18H, m, *H* arom.), 7.75 (2H, m, *H* arom.), 8.85 (1H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 9.1 (d, $^1J_{CP} = 13.5$, CH_3), 117.9 (d, $J_{CP} = 23.1$, *C* arom.), 124.0 (d, $J_{CP} = 2.1$, *C* arom.), 126.2 (*C* arom.), 126.5–127.2 (*C* arom.), 127.9–132.4 (*C* arom.), 138.7–139.4 (*C* arom.), 141.9 (d, $J_{CP} = 10.9$, *C* arom.), 158.5 (d, $J_{CP} = 9.5$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ −44.3 (s, MePh*P*–C), +111.7 (s, Ph_2P–O); MS (EI) *m*/*z* (relative intensity): 450 (M^+, 20), 465 (M^+-CH_3, 100), 373 (55), 358 (10), 281 (20), 265 (30), 249 (15), 201 (30), 183 (40); HRMS (EI): calcd for $C_{29}H_{24}OP_2$ [M]: 450.1302; found: 450.1300.

4.2.5.2. (R)-(−)-o-Anisyl-1-[2-(diphenylphosphinito)naphthyl]phenylphosphine ***15b***. Yield = 84%; uncrystallized; $[\alpha]_D^{20} = -6.3$ (*c* 0.26, $CHCl_3$); IR (neat, *v* cm^{-1}): 3050–2850 (w), 1264 (s), 1095 (s), 1022 (s), 809 (s), 696 (m); ^1H NMR ($CDCl_3$): δ 3.53 (3H, s, OCH_3), 6.50–7.75 (m, 24H, *H* arom.), 8.75 (1H, m, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.5 (s, OCH_3), 110.2 (*C* arom.), 117.9 (d, $J_{CP} = 23.9$, *C* arom.), 121.0 (*C* arom.), 123.9–132.8 (*C* arom.), 161.0 (d, $J_{CP} = 16.6$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ −33.0 (d, $J_{PP} = 3.1$, AnPh*P*), +113.3 (Ph_2PO); MS (EI) *m*/*z* (relative intensity): 542 (M^+; 40), 465 (100), 435 (30), 358 (40), 357 (20), 327 (10), 249 (35), 201 (40), 183 (40), 169 (15), 108 (10), 84 (20), 77 (10); HRMS (DCI): calcd for $C_{35}H_{28}O_2P_2$, [M]: 542.1565; found: 542.1561.

4.2.6. (R)-(−)-o-Anisyl-1-(2-hydroxynaphtyl)phenylphosphine ***13e*** *by decomplexation of* ***12e***

In a two-necked flask equipped with a reflux condenser, a magnetic stirrer and an argon inlet, 1 equivalent (0.075 mmol) of hydroxyphosphine borane ligand **6e** was charged. The flask was purged with three cycles of argon and 3 mL of dry ethanol were added. The mixture was stirred at room temperature for 24 h. The crude product was rapidly filtered off on silica column using toluene/AcOEt, 9:1, as eluent to yield the hydroxyphosphine **13e**.

Yield = 80%; white solid; $[\alpha]_D^{20} = -1.7$ (*c* 0.9, $CHCl_3$); IR (neat, *v* cm^{-1}): 3446 (m), 3301 (m), 3064–2833 (m), 1616 (w), 1567 (w), 1464 (m), 1457 (s), 1429 (s), 1261 (m), 1241 (m), 1127 (m), 1100 (m), 1067 (m), 1019 (s), 822 (m), 801 (m), 742 (m); ^1H NMR ($CDCl_3$): δ 3.70 (3H, s, OCH_3), 6.70–8.10 (m, 15H, *H* arom.); ^{13}C NMR ($CDCl_3$): δ 55.7 (s, OCH_3), 110.6 (d, $J_{CP} = 1.9$, *C* arom.), 118.0 (d, $J_{CP} = 1.8$, *C* arom.), 121.1 (d, $J_{CP} = 6.2$, *C* arom.), 121.3 (d, $J_{CP} = 1.8$, *C* arom.), 123.2 (*C* arom.), 126.4–126.8 (*C* arom.), 128.1 (*C* arom.), 128.6 (d, $J_{CP} = 6.3$, *C* arom.), 128.7 (*C* arom.), 129.6 (d, $J_{CP} = 4$, *C* arom.), 130.8 (*C* arom.), 131.0 (d, $J_{CP} = 17$, *C* arom.), 132.7 (d, $J_{CP} = 3$, *C* arom.), 133.6 (*C* arom.), 133.7 (d, $J_{CP} = 6$, *C* arom.), 136.5 (d, $J_{CP} = 10$, *C* arom.), 160.4 (d, $J_{CP} = 13.0$, *C* arom.), 161.2 (d, $J_{CP} = 15.0$, *C* arom.); ^{31}P NMR ($CDCl_3$): δ −45.9; MS (EI) *m*/*z* (relative intensity): 358 (M^+; 100), 327 (20), 249 (60), 220 (20), 202 (40), 183 (20), 157

(25), 127 (20), 115 (25), 77 (10); HRMS (EI): calcd for $C_{23}H_{19}O_2P$, [M]: 358.1123; found: 358.1132.

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