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Chemoselective reduction of the P=O bond in the presence of P-O and P-N bonds in phosphonate and phosphinate derivatives

Sylwia Sowa, K. Michał Pietrusiewicz*[a]

Abstract: Chemoselective reduction of the strong P=O bond in the presence of weaker P-O (ester) and P-N (amide) bonds in phosphonic acid derivatives has constituted an unresolved problem in organophosphorus chemistry for years. This long-standing problem is now solved for biologically relevant α-hydroxy and α-amino phosphonic as well as phosphinic acids esters and amides. The reduction of the P=O bond without concomitant scission of the ester and amide bonds is effected by use of BH_3, a mild reducing agent, which affords the corresponding borane protected P(III) phosphonite and phosphinite derivatives in one step. A mechanistic rationale is proposed for the role played by neighboring OH and NHR groups in facilitating the reduction, and for the observed chemo- and stereoselectivity. The reduction methodology described opens up previously unavailable synthetic options in chemistry of α-functionalized phosphonic and phosphinic acids by offering a unique possibility for direct modifications of oxidation level of the P-centre in these compounds.

Introduction

Many strategies for the preparation of phosphines are based on the reduction of a strong P=O bond in the final synthetic step.[1-2] The stability of P-C bond allows for the use of strong reducing agents (metal hydrides,[3] silanes[4]) which usually leads to highly efficient deoxygenation of phosphine oxides. However, these typically harsh reagents are a major drawback when the reductions of compounds possessing other reactive functionalities[5] or chirality centres[3f,6] at the phosphorus need to be performed, though some progress in this field has been made.[7] Nevertheless, these methods are generally useless for the reduction of strong P=O bonds in phosphonic and phosphinic acid derivatives that contain much weaker and more reactive P-O or P-N bonds is to be accomplished. The reaction of various reducing agents (metal hydrides,[8] organoboron hydride,[9] PHMS,[10] Ph_2SiH_2,[10] Ph_2SiH_2/Lewis acid or $PhSiH_3$/Lewis acid[11]) with phosphinates or phosphonates typically leads to the reduction of all phosphorus-oxygen bonds in what constitutes a valuable preparation of secondary and primary phosphines, respectively. Similarly, phosphinic acid amides typically undergo P-N bond[12] cleavage in the presence of reducing agents with two early[13] and one recent[14] reported exceptions. A demand for methods enabling chemoselective reduction of the P=O bond inthe presence of either ester or amide bonds because these could open up completely new possibilities for preparation of various P(III) ester and amide derivatives directly from their usually much more readily available and robust pentavalent P=O counterparts.

Phosphine borane adducts, soon after their introduction[15a] as easily handled and storable equivalents of P(III) compounds, and versatile synthetic reagents *per se*,[15b] quickly started to become preferred targets in synthesis of P(III) compounds replacing sensitive and difficult-to-handle non-protected phosphines. In this context, the direct transformation of phosphine oxides into phosphine-boranes, thus avoiding handling and/or isolation of the free phosphines has become a new challenge in the synthesis of trivalent phosphorus compounds.[14,16] In much the same vein, the development of new reducing procedures that could use BH_3 as the complexing agent and also as the reducing agent is gaining growing attention due character of BH_3.[17-19]

Recently, we[19] and Buono[20] demonstrated that the reduction of P=O bond by BH_3 complexes in functionalized tertiary phosphine oxides bearing neighboring assisting groups, *e.g.*, –OH, -SH, and –NHR, is possible, and that it can be regarded as an attractive alternative to the conventional reduction protocols. Furthermore, earlier observations by Kiełbasiński[17e,21] and more recent work by Buono[20,22] have shown that the phosphinate P=O bond can be also reduced by BH_3 to give the corresponding phosphinite-borane with high chemoselectivity when a hydroxy group is present in the proximity of the phosphoryl group. For the first time, it therefore seems reasonable to assume that there is a really good prospect for successfully addressing a long-sought possibility of reduction of P=O bond in phosphonic acid esters and amides without affecting their P-O and P-N bonds.

Herein, we present our results concerning unprecedented chemoselective BH_3 reductions of phosphonic P=O bond assisted by neighboring –OH and –NHR groups. The reductions lead directly to the formation of the pertinent α-hydroxy and α-amino phosphonite-boranes from their easily available and robust P=O precursors. This seems valuable, given that functionalized α-hydroxy phosphonite-boranes have currently only been obtained through multistep protocols.[23] To the best of our knowledge, α-amino phosphonite-boranes as well as α-amino phosphinite-boranes have been neither studied nor synthesized before, despite their direct structural analogy to biologically highly relevant α-amino phosphonic and α-amino phosphinic acid derivatives.[24]

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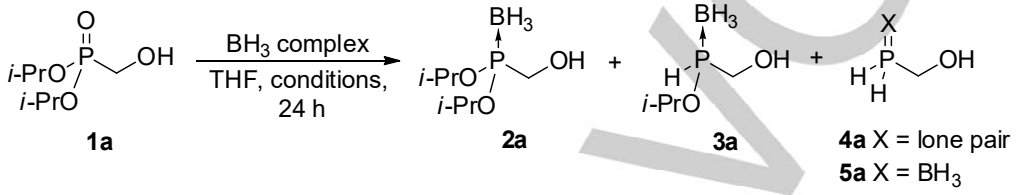
Results and Discussion

The initial experiments were carried out with diisopropyl hydroxymethylphosphonate (**1a**) as a model compound (Table 1). As shown in entries 1 and 4 of Table 1, **1a** was found to be practically unreactive or slowly reacting when exposed to 3 or 10 equiv. of BH_3-THF at room temperature. Increasing the temperature to 60 °C with 3-fold excess of BH_3-THF resulted in the formation of primary phoshine **4a** (Table 1, entry 2). When **1a** was treated with 10 equiv. of BH_3-THF at 60 °C for 24 h, it partially successfully underwent reduction of the P=O bond, the desired phosphonite-borane **2a** was obtained in only 20% yield (isolated) together with two over-reduction products **3a** and **5a** (not isolated) (Table 1, entry 5). Changing the BH_3 source to BH_3-SMe_2 gave promising results according to ^{31}P NMR but the desired **2a** was isolated only in very poor 7% yield (Table 1, entry 6). Increasing the amount of BH_3-SMe_2 to 5 or 10 equivalents under the same conditions gave only traces of **2a** and provided primary phosphine-borane **5a** as the major product (Table 1, entries 7-8). Therefore, for further study we choose the conditions used in entry 5, *i.e.*, BH_3-THF, 60 °C, 24 h, considered as the most appropriate.

Table 1. Attempted optimizing of the reaction conditions for reduction of **1a** with BH_3 complexes.



No	Conditions	Yields of Products (%)[a,b]		
1	BH_3-THF (3.0), rt	**2a** 0 (0)	**3a** 0 (0)	**4a**/**5a** 0 (0)
2	BH_3-THF (3.0), 60 °C	**2a** 0 (0)	**3a** 0 (0)	**4a** 0 (100)
3	BH_3-THF (5.0), 60 °C	**2a** 6 (20)	**3a** 0 (39)	**5a** 0 (40)
4	BH_3-THF (10.0), rt	**2a** traces	**3a** 0 (0)	**5a** 0 (0)
5	BH_3-THF (10.0), 60 °C	**2a** 20 (28)	**3a** 0 (12)	**5a** 0 (60)
6	BH_3-SMe_2 (3.0), 60 °C	**2a** 7 (41)	**3a** 0 (0)	**4a** 0 (59)
7	BH_3-SMe_2 (5.0), 60 °C	**2a** 0 (8)	**3a** 0 (8)	**5a** 0 (77)
8	BH_3-SMe_2 (10.0), 60 °C	**2a** 0 (17)	**3a** 0 (11)	**5a** 0 (74)

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR.

Results of the reductions subsequently carried out with a series of structurally diversified α-hydroxy phosphonates **1b-g** under these conditions are presented in Table 2 and are compared to the reduction of **1a**. Quite unexpectedly, analogous reduction of sterically more demanding di-*t*-butyl phosphonate **1b** failed to give any identifiable product. Instead, complete decomposition of the starting material was observed even at 0 °C (Table 2, entries 2 and 3). This result is in sharp contrast to the earlier observations on similar BH_3 reductions of hydroxymethylphosphinates for which chemoselectivity towards P=O bond cleavage increased with the steric demand of the ester group.[17e,22b]

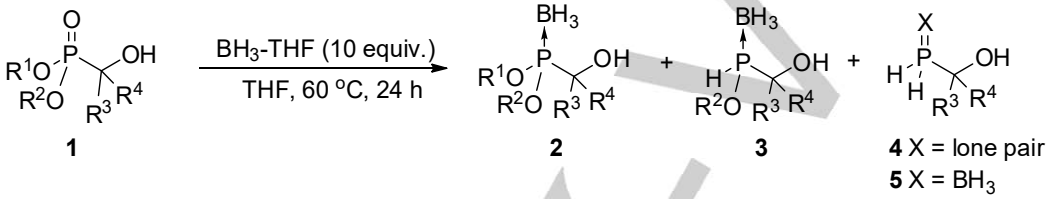
Reduction of a cyclic phosphonate **1c** went faster than for **1a** and was completed with 3 equiv. of BH_3-THF at room temperature within 4 h. Interestingly, it led to complete reduction of not only the P=O bond but also the two P-O bonds (Table 2, entry 3), providing the primary hydroxymethylphosphine (**4a**) as essentially the only product (by ^{31}P NMR of the crude reaction mixture, δ_P = -121.52 ppm). Attempted isolation of **4a**, in either its pure form, or after attempted boranation or oxidation, led to its decomposition. In contrast to analogous BH_3 reductions of α-hydroxy phosphinates,[17e,22b] it seems clear that increased steric demand of the phosphonate ester groups, or their incorporation into a ring, dramatically increases their reactivity under the studied reaction conditions.

We next investigated the effect of α-substitution pattern on the chemoselectivity of P=O bond reduction in α-hydroxy phosphonates. For phosphonate **1d**, which has a single Me substituent at the α carbon the reduction chemoselectivity was slightly higher than for the unsubstituted **1a** and gave α-hydroxy phosphonite-borane **2d** in 25% yield (isolated) with palpably diminished contribution from over-reduction products **3d** and **5d** (not isolated). (Table 2, entry 4). To our delight, use of compounds with double substitution at the α carbon resulted in significantly more selective reduction of the P=O bond. Both **1e** and **1g** underwent reduction with an excess of BH_3-THF (10 equiv.) at room temperature to afford the corresponding phosphonite-boranes **2e** and **2g** as the major products isolated

in 72% and 49% yield, respectively (Table 2, entries 5 and 7). In these cases, small amounts of over-reduction products **3e** and **3g**, from reduction of both phosphoryl P=O and one P-O bond were also isolated in 9% and 6% yield, respectively. Products resulting from complete reduction of all phosphorus-oxygen bonds were also observed in both cases in the ^{31}P NMR spectra of the crude reaction mixtures but their attempted isolation failed. Interestingly, attempted reduction of a cyclic α,α-dimethyl-substituted α-hydroxy phosphonate **1f** failed completely and led to decomposition of the substrate in spite of its apparently promising geminal α,α-disubstitution pattern (Table 2, entry 6). This behaviour of **1f** seems to resemble cyclic hydroxymethylenephosphonate **1c** although in the case of **1f** the primary phosphine product has not been even detected.

The data collected in Table 2 indicate that in favourable cases the P=O bond in α-hydroxy phosphonates can be indeed reduced by BH_3 without simultaneous cleavage of the ester bonds. However, the observed degree of chemoselectivity depends on the substitution pattern in both the ester groups and the chain. Bulky or cyclic ester groups, promote nonselective reduction while increased substitution at the α-carbon leads to selective P=O bond cleavage with chemoselectivity of up to 75% being achieved in the best case. In all cases, both BH_3-THF and BH_3-SMe_2 complexes were evaluated and, generally, the former gave superior results. These results clearly show that the developed protocol can constitute a very practical alternative to the known protocols for the synthesis of α-hydroxy phosphonite-boranes.[23]

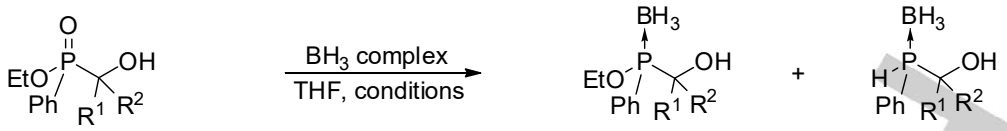
Table 2. Reactivity of α-hydroxy phosphonates **1** towards BH_3-THF.



Entry	Compound	$R^1 = R^2$	R^3	R^4	Yields of Products (%)[a,b]		
1	**1a**	*i*-Pr	H	H	**2a** 20 (28)	**3a** 0 (12)	**5a** 0 (60)
2	**1b**	*t*-Bu	H	H	**2b** 0 (0)	**3b** 0 (0)	-
3[c,d]	**1b**	*t*-Bu	H	H	**2b** 0 (0)	**3b** 0 (0)	-
4	**1c**	-CH(CH$_3$)CH$_2$CH$_2$-	H	H	**2c** 0 (0)	**3c** 0 (0)	**5a** 0 (98)
5[e]	**1c**	-CH(CH$_3$)CH$_2$CH$_2$-	H	H	**2c** 0 (0)	**3c** 0 (0)	**4a** 0 (90)
6	**1d**	*i*-Pr	Me	H	**2d** 31 (60)	**3d** 0 (10)	**5d** 0 (30)
7[f]	**1d**	*i*-Pr	Me	H	**2d** 25 (35)	**3d** 0 (17)	**5d** 0 (33)
8	**1e**	*i*-Pr	Me	Me	**2e** 71 (78)	**3e** 0 (9)	**5e** 0 (10)
9[g,h]	**1e**	*i*-Pr	Me	Me	**2e** 72 (75)	**3e** 9 (11)	**5e** 0 (5)
10	**1f**	-(CH$_2$)$_3$-	Me	Me	**2f** 0 (5)	**3f** 0 (0)	**5e** 0 (95)
11	**1g**	*i*-Pr	-(CH$_2$)$_5$-		**2g** 67 (88)	**3g** 0 (5)	**5g** 0 (7)
12[i]	**1g**	*i*-Pr	-(CH$_2$)$_5$-		**2g** 49 (60)	**3g** 6 (9)	**5g** 0 (10)

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR. [c] BH_3-THF (10.0), 0 °C, 4 h. [d] Complete decomposition of starting material was observed. [e] BH_3-THF (3.0), rt, 4 h. [f] BH_3-SMe_2 (3.0), 60 °C, 16 h (seemingly the best conditions suggested by the optimization study of reductions of **1a**; *Table 1, entry 5*). [g] Reaction was run at rt. [h] **3e** was isolated only in a mixture together with **2e** (9% yield determined by ^{1}H NMR). [i] BH_3-THF (5.0), rt, 16 h.

To check the generality of the influence of α-substitution we also carried out experiments with structurally related α-hydroxy phosphinates **6** possessing single ester group at P and differing in substitution at the α-carbon atom (Scheme 1).



6a (R^1 = H, R^2 = Me)	BH_3-THF (10.0), 60 °C, 24 h	**7a** 47%[a] (61%)[b]	**8a** 10%[a] (28%)[b]
6a (R^1 = H, R^2 = Me)	BH_3-SMe_2 (5.0), rt, 16 h	**7a** 16%[a] (30%)[b]	**8a** 19%[a] (54%)[b]
6b (R^1 = R^2 = Me)	BH_3-THF (10.0), 60 °C, 24 h	**7b** 75%[a] (87%)[b]	**8b** 0%[a] (10%)[b]
6b (R^1 = R^2 = Me)	BH_3-THF (3.0), rt, 24 h	**7b** 74%[a] (91%)[b]	**8b** 0%[a] (0%)[b]
6b (R^1 = R^2 = Me)	BH_3-SMe_2 (3.0), rt, 16 h	**7b** 57%[a] (66%)[b]	**8b** 0%[a] (10%)[b]
6c (R^1 = R^2 = -$(CH_2)_5$-)	BH_3-THF (10.0), 60 °C, 24 h	**7c** 71%[a] (81%)[b]	**8c** 0%[a] (14%)[b]
6c (R^1 = R^2 = -$(CH_2)_5$-)	BH_3-SMe_2, (3.0), 60 °C, 16 h	**7c** 62%[a] (67%)[b]	**8c** 14%[a] (20%)[b]

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR.

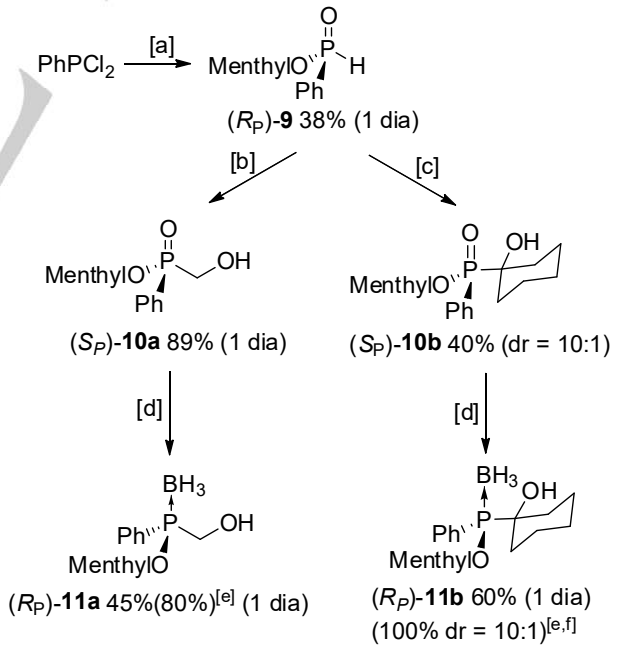
Scheme 1. Reduction of P=O bond in α-substituted α-hydroxy phosphinates **6.**

As with the reductions of α-hydroxy phosphonates **1** discussed above, the best results were obtained for the phosphinates **6b** and **6c** which have double substitution at the α carbon atom. The target phosphinite-boranes **7b** and **7c** were isolated as major products in 74% and 62% isolated yield, respectively. In two cases, small amounts of over-reduction products were observed and the corresponding secondary phosphine-boranes **8a** and **8c** were isolated in 19% and 14% yield, respectively. The use of BH_3-THF was again found to be more appropriate than BH_3-SMe_2.

Next, in order to address the stereoselectivity of the reductions of the P=O bond in the presence of an ester P-O bond, we turned our attention to P-resolved stereogenic (*L*)-menthyl α-hydroxy phosphinates (S_P)-**10a** and (S_P)-**10b** whose relatively ready availability contrasts with the potentially very inaccessible, and probably currently unknown, resolved P-stereogenic α-hydroxy phosphonates. The P-resolved phosphinates were obtained from (R_P)-**9** which had been prepared in 38% yield according to the procedure reported by Mislow,[6c] Letsinger[6d] and Han,[25] (Scheme 2, step *a*). (R_P)-**9** was reacted with formaldehyde and with cyclohexanone (Scheme 2, steps *b* and *c*) to afford the requisite α-hydroxy phosphinates (S_P)-**10a** and (S_P)-**10b**, respectively, in good yields and with excellent stereoselectivity (Scheme 2, steps *d*).

Reduction of (S_P)-**10a** (Scheme 2, step *d*) with 5 equivalents of BH_3-SMe_2 at 60 °C for 24 h led to the complete conversion of the substrate. The expected formation of the desired phosphinite-borane (R_P)-**11a** (45% yield, isolated; 80% by ^{31}P NMR) was accompanied by the formation of the corresponding secondary phosphine-borane **12** (15% yield, isolated), in good accord with the previously reported reduction of (S_P)-**10a**.[22b]

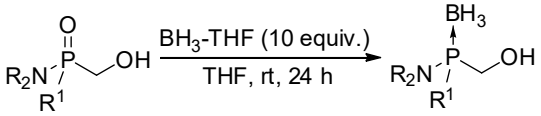
In turn, reduction of (S_P)-**10b** (dr = 10:1) under the same conditions (Scheme 2, step *d*) proceeded with complete chemoselectivity and afforded phosphinite-borane (R_P)-**11b** (dr = 10:1) as the sole product (100% by ^{31}P NMR) isolated in 60% yield in the form of a pure diastereoisomer. The latter result confirms again that geminal substitution at the α carbon markedly enhances chemoselectivity of the reduction towards reduction of the P=O bond. Importantly also, the studied reductions occur with clean inversion of configuration at the P-center as already established[21] and as implied by the proposed mechanisms.[19,22b] Such a chemo- and stereoselective transformation is thus likely to gain considerable importance in the field of synthesis of optically active P-stereogenic P(III) compounds since the starting P-resolved α-hydroxy phosphinates can be easily obtained from (R_P)-**9** and a rich variety of carbonyl compounds based on cheap *L*-menthol as the chiral auxiliary (*cf.* Scheme 2).



[a] According to reported procedures.[6c,25]
[b] DBU (0.01 equiv.), $(CH_2O)_n$ (3 equiv.), THF, rt, 6 d.
[c] Cyclohexanone (4 equiv.), 60 °C, 48 h.
[d] BH_3-SMe_2 (5 equiv.), 60 °C, 24 h. [e] Numbers in parentheses indicate yields according to ^{31}P NMR spectrum of crude reaction mixture. [f] Only major diastereoisomer was isolated.

Scheme 2. Synthesis of P-stereogenic (*L*)-menthyl α-hydroxy phosphinates **10a** and **10b** and their reactivity towards BH_3-SMe_2 complexes.

The next classes of hydroxymethylphosphonic acid derivatives used for test reactions were represented by phosphonic acid monoester monoamide **13** and bis(amides) **14** and **15** (Scheme 3).



13 R = Et, R^1 = *i*-PrO
14 R = Et, R^1 = Et_2N
15 R = *i*-Pr, R^1 = *i*-Pr_2N

16-18

16 60%[a] (100%)[b] **17** 20%[a] (30%)[b] **18** 78%[a] (100%)[b,c]

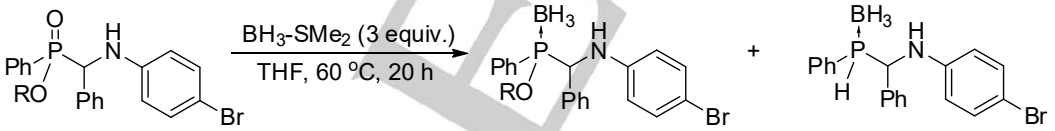
[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR. [c] Reaction was run at 60 °C.

Scheme 3. Reduction of monoester monoamide **13** and bis(amides) **14** and **15** by BH_3-THF.

It was rewarding to find that two of these three compounds underwent completely chemoselective α-OH-assisted reduction of P=O bonds by BH_3 complexes. In case of monoester monoamide **13** and *N*,*N*-diisopropyl bis(amide) **15** the only products observed in the crude reaction mixture were the desired borane-protected P(III) derivatives **16** and **18**. Their isolated yields were moderate to good (60% and 78%, respectively) probably because of decomposition during purification on silica. Intriguingly, *N*,*N*-diethyl bis(amide) **14** appeared to be less stable under the reaction conditions and the desired product **17** was obtained in an unexpectedly low yield (22%).

The utility of BH_3 as a mild and highly chemoselective reducing agent for the direct reductive conversion of α-hydroxy phosphinates and α-hydroxy phosphonates into the pertinent α-hydroxy phosphinite-boranes and α-hydroxy phosphonite-boranes described above prompted us to check if α-amino phosphinates and α-amino phosphonates could also undergo an analogous chemoselective reduction of their P=O bonds by BH_3 complexes. These compounds are important classes of organophosphorus compounds which function in biology, medicine, pharmacology, agriculture, as well as in synthetic chemistry as phosphorus analogues of naturally occurring α-amino acids.[24] The chemoselective reduction of their P=O bonds would enable access to their new borane protected P(III) derivatives and, by extension,[26] to other P(V) chalcogenide counterparts.

First, we checked the possibility of chemoselective P=O bond reduction assisted by NH group in α-amino phosphinates **19** differing in size of the ester group (Scheme 4).



19a R = *i*-Pr dr = 1:0.9
19b R = Et dr = 1:0.8

20a R = *i*-Pr 84%[a] (100%)[b] dr = 1:0.7
20b R = Et 60%[a] (64%)[b] dr = 1:0.8 **21** 0%[a] (36%)[b] dr = 1: 0.7

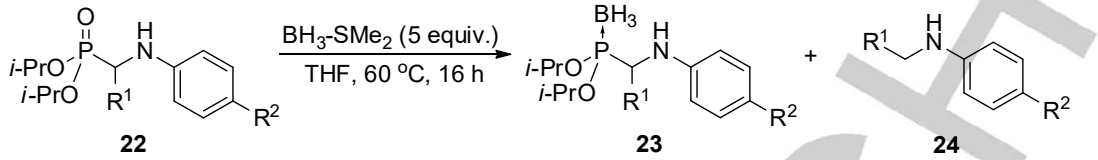
[a] Isolated yields of the product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR.

Scheme 4. Reaction of α-amino phosphinates **19a** and **19b** with BH_3-SMe_2.

As found in a preliminary experiment, **19a** remained unchanged upon reaction with 10 equiv. of BH_3-THF at 60 °C for 24 h, *i.e.*, under conditions used above in reductions of α-hydroxy phosphinates (*cf.* Scheme 1). On the other hand, treatment of **19a** and **19b** with 3 equiv. of BH_3-SMe_2 at 60 °C for 20 h led to complete conversion of the substrates and afforded the target phosphinite-boranes **20a** and **20b** in 84% and 60% isolated yield, respectively. Reduction of isopropyl phosphinate **19a** was *completely* chemoselective and occurred with full preservation of the ester P-O bond. Under the same conditions, reduction of phosphinate **19b** possessing the smaller ethyl ester group was markedly less selective and gave a 2:1 mixture of the desired phosphinite-borane **20b** (major) and a secondary phosphine-borane **21** (minor) according to the ^{31}P NMR spectrum of the crude reaction mixture.

Encouraged by these promising results we turned to examine the reactivity of α-amino phosphonates **22a-l**[27] towards BH_3 complexes (Table 3). Given the higher stability of isopropyl esters in the previous reactions we decided to focus only on diisopropyl α-amino phosphonates **22a-l** which were all readily prepared by Kabachnik-Fields reaction (see: *Supplementary Information*).

Table 3. Reduction of *N*-aryl substituted α-amino phosphonates **22** by BH_3-SMe_2.



Entry	Compound	R^1	R^2	Yields of Products (%)[a,b,c]	
1	**22a**	Ph	Br	**23a** 77 (100)	
2[d]	**22b**	*p*-Br-C_6H_4	Br	**23b** 47 [67]	**24b** 7
3[e]	**22b**	*p*-Br-C_6H_4	Br	**23b** 85 [100]	**24b** 10
4[d]	**22c**	*o*-Br-C_6H_4	Br	**23c** 38 [100]	**24c** 45
5[f]	**22d**	*m*-NO_2-C_6H_4	Br	**23d** 60 (96)	
6	**22e**	*p*-NO_2-C_6H_4	Br	**23e** 79 (100)	
7	**22f**	*p*-An	Br	**23f** 64 [100]	traces
8[e,h]	**22g**	H	Br	**23g** 50 (90)	
9	**22h**	Ph	OH	**23h** 67 (90)	
10	**22i**	Ph	OMe	**23i** 63 (100)	
11	**22j**	Ph	Me	**23j** 70 [100]	traces
12	**22k**	*t*-Bu	Me	**23k** 24 [100]	traces
13[e,g]	**22l**	H	Me	**23l** 49 (77)	

[a] Isolated yields. [b] Numbers in parentheses indicate yields according to ^{31}P NMR of the crude reaction mixture. [c] Numbers in brackets indicate conversion of the starting material. [d] Reaction run for 72 h. [e] Reaction run with 10 equiv. of BH_3-SMe_2. [f] Reaction run for 48 h. [g] Reaction run for 4 h; longer reaction time led to lower yield of **23l**.

Preliminary reduction attempts revealed that complete conversion of **22** can be best achieved using 5 equiv. of reducing agent at 60 °C for 16 h, and that BH_3-SMe_2 performed better than BH_3-THF.The results of reductions performed on **22** are presented in Table 3.

In almost all cases the only product isolated from the reaction mixture was the desired α-amino phosphonite-borane **23**. Importantly, no traces of any products resulting from ester bond scission were detected even in cases when the reduction was slow and required use of a larger excess of BH_3-SMe_2 and/or prolonged heating for 72 h.

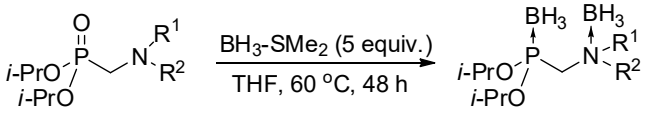
Although, in general, the reduction of α-amino phosphonates was found to be little affected by substitution at the *N*-phenyl group, the highest isolated yields of phosphonite-boranes were achieved for α-amino phosphonates possessing the *N*-*p*-bromophenyl group, *e.g.*, **22a**,**b**, and **e**, respectively, (Table 3, entries 1, 3 and 6). Similarly, the near quantitative ^{31}P NMR yields and conversions that were observed in most cases show that, the substituents at the α carbon atom did not interfere with the reduction process. Somewhat lower yields of isolated products bearing either bulky aryl or bulky alkyl α-substituent (*e.g.*, **23c,k**) or of those not having α-substituent, (*e.g.*, **23g,l**) probably reflect their lower stability during workup (Table 3, entries 4, 8, 12, 13).

The formation of small amounts of secondary amines **24** was observed in reductions of **22b**,**c** and **22j**,**k** (Table 3, entries 2-4,7,11,12). Of those substrates, **22c** decomposed most extensively under the reduction conditions and gave secondary amine **24c** as the main reaction product (Table 3, entry 4). The reaction of **22c** was very slow and heating for 72 h was necessary to make conversion of this substrate complete. Under the same conditions, **22b** was even less reactive and full conversion was not achieved under the standard reduction conditions. However, use of 10-fold amount of reducing agent led eventually to complete conversion and to production of the

desired phosphonite-borane **23b** in 85% yield together with 10% of amine byproduct **24b** (Table 3, entry 2,3).

The observed formation of amine byproducts in these reactions can be attributed to an instability of α-amino phosphinates **22b**,**c** which underwent a retro-Kabachnik-Fields process under the reaction conditions to give secondary phosphite and an imine. These decomposition products reacted further with BH_3 to give the observed amine and, most probably, $(i\text{-PrO})_2P(BH_3)OH$ (δ 90.15 ppm according to ^{31}P NMR, not isolated).[28] It is also worth noting that **21c** was checked to have been thermally stable while heated without BH_3 at 60 °C for 24 h. Apparently, the reaction conditions under study allow BH_3 to act also as a Lewis acid and facilitate the observed retro-Kabachnik-Fields reaction in the more susceptible cases. It seems that the substitution pattern and stability with respect to Lewis acid have the biggest impact on the observed degradation of **22** by the retro-Kabachnik-Fields process.

For comparison, we also briefly checked the reactivity of *N*-alkyl substituted α-amino phosphonates **25** and **26** under the same reaction conditions (Scheme 5).



25 $R^1 = CH_2Ph$, $R^2 = H$ — **27** 24%[a](67%)[b]

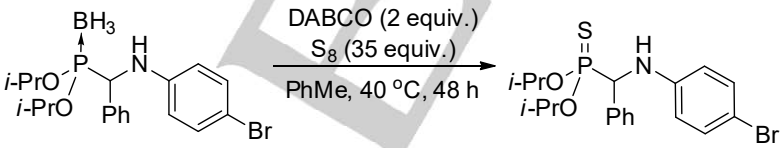
26 $R^1 = R^2 = Et$ — **28** 0%[a](traces)[b]

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR of crude reaction mixture.

Scheme 5. Reactivity of *N*-alkyl α-aminophosphonates **24** and **25** towards BH_3-SMe_2.

It was found that *N*-alkyl substituted phosphonate **25** underwent complexation at nitrogen prior to reduction. Subsequent reduction of P=O bond in this α-amino phosphonate by 5 equiv. of BH_3-SMe_2 was incomplete even after 48 h at 60 °C. Nevertheless, we were able to isolate the expected *P,N*-diborane **27** in 24% yield and, importantly, no traces of any products with reduced ester bonds were detected. Increasing of the amount of BH_3-SMe_2 to 10 equiv. did not lead to any progress in the conversion of the substrate. Apparently, lowered N-H acidity effectively slows down evolution of hydrogen and an apparently prerequisite[19] formation of an N-BH_2 bond. In this context, it was not too surprising that compound **26** possessing tertiary amine substituent failed to yield the reduction product **28** under the same reaction conditions. It should be noted however, that a single precedent for BH_3 reduction of P=O bond in a tertiary phosphine oxide assisted by tertiary amine substituent at the α position is on record.[20]

To check the possibility of deprotection of phosphonite-boranes **23** to their P(III) counterparts we subjected **23a** to the reaction conditions reported by Jugé and co-workers (Scheme 6).[26b] To simplify the isolation process the deprotected phosphonite was sulfurized *in situ* with S_8 to give **29**. It turned out that use of a twofold excess of DABCO secures practically quantitative conversion of **23a** to **29** without detectable traces of oxidation or decomposition.



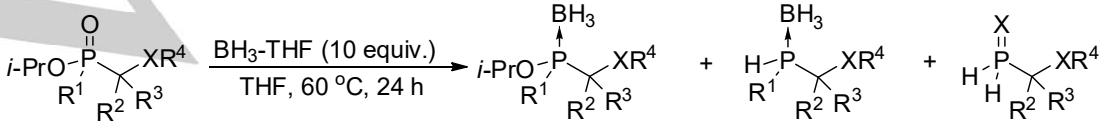
23a — **29** 88%[a](100%)[b]

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR of crude reaction mixture.

Scheme 6. Deprotection of α-amino phosphonite **23a.**

Finally, in order to compare the reactivity of different classes of phosphonate compounds towards BH_3-THF complex we have collected in Table 4 the results of reductions of **1a,d,g,e** and **19a**, **22b**, **25** under unified conditions. While α-hydroxy phosphonates **1a,d,g,e** underwent the expected reduction by BH_3-THF (Table 4, entries 1-4), the α-amino phosphonates **19a**, **22b**, **25** were all found to be inert to BH_3-THF under these conditions, regardless of their substitution pattern (Table 4, entries 5-7). These results confirm again that BH_3-SMe_2 complex should be considered as the reagent of choice for reduction of the P=O bond in α-amino phosphonates as already demonstrated above in Table 3.

Table 4. Comparison of reductions of different classes of phosphonate compounds under unified conditions.



No	Compound	Structure	Yields of Products (%)[a,b]		
1	**1a**	R^1 = *i*-PrO, R^2 = R^3 = H, R^4 = H, X = O	**2a** 20 (28)	**3a** 0 (12)	**5a** 0 (60)
2	**1d**	R^1 = *i*-PrO, R^2 = H, R^3 = Me, R^4 = H, X = O	**2d** 31 (60)	**3a** 0 (10)	**4a** 0 (30)
3	**1g**	R^1 = *i*-PrO, R^1 = R^2 = -$(CH_2)_5$-, R^4 = H, X = O	**2g** 67 (88)	**3g** 0 (5)	**5d** 0 (7)
4	**1e**	R^1 = *i*-PrO, R^1 = R^2 = Me, R^4 = H, X = O	**2e** 71 (78)	**3e** 0 (9)	**5c** 0 (10)
5[c]	**19a**	R^1 = Ph, R^2 = Ph, R^3 = H, R^4 = *p*-Br-C_6H_4-, X = N	**20a** 0 (0)	-	-
6[c]	**22b**	R^1 = *i*-PrO, R^2 = *o*-Br-C_6H_4-, R^3 = H, R^4 = *p*-Br-C_6H_4-, X = N	**23** 0 (0)	-	-
7[c]	**25**	R^1 = *i*-PrO, R^2 = R^3 = H, R^4 = $PhCH_2$, X = N	**27** 0 (0)	-	-

[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR. [c] Unreacted starting material present in the reaction mixture.

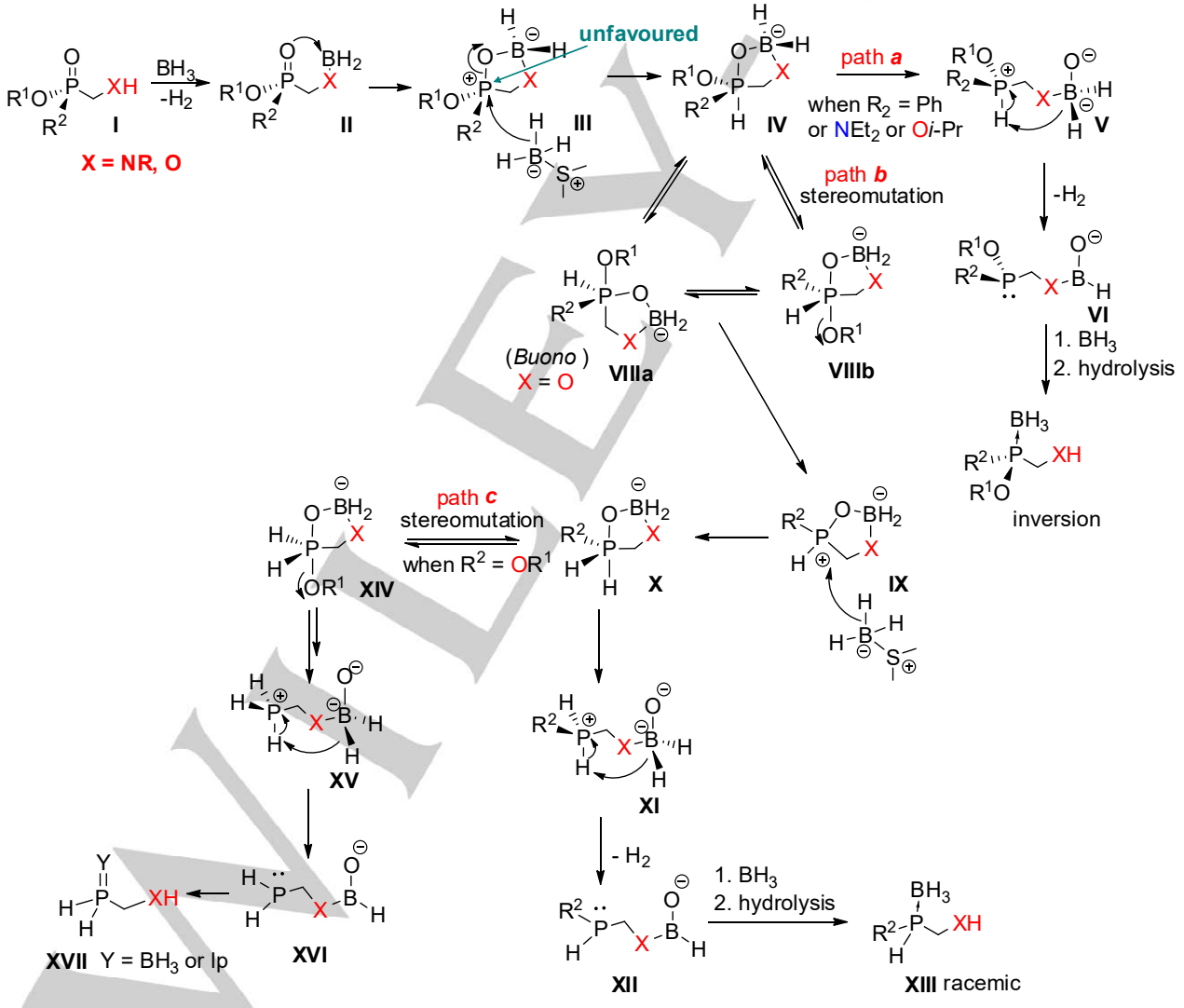


Figure 1. Unified mechanism for reduction of α-hydroxy and α-aminophosphinates/phosphonates by BH_3 complexes.

In light of the above data, our earlier work[19] and previous mechanistic proposals[20-22] we would like to propose a unified mechanistic picture which addresses all the reaction paths and current observations (Figure 1).

In the first step, BH_3 undergoes reaction with the XH group of **I** affording **II** along with evolution of a hydrogen molecule. The formation of intermediate **II** is prerequisite for the coordination of the resulting proximal boron functionality to the phosphoryl oxygen which leads to a cyclic zwitterionic intermediate **III**. Such a facile intramolecular coordination is made possible by the presence of an assisting group at the α position which promotes the formation of a five-membered dioxaboraphospholane ring. The incorporation of the phosphoryl oxygen into a boronic acid moiety makes it now a leaving group that is good enough to compete for departure with the alkoxy ester groups. The subsequent reduction entails a hydride attack *trans*-to the ring P-O bond and allows a five-membered ring in trigonal bipyramide (TBP) **IV** to be made between the favored apical (for P-O) and equatorial (for P-C) positions.[29] This lowers its energy and greatly facilitates the reduction process. The apical position of the activated P-O bond allows its prompt stereoinvertive departure in an S_N2-like process that affords protonated phosphine **V**; this promptly liberates a hydrogen molecule to give a free phosphine **VI**. Finally, complexation and hydrolytic deprotection of the activating group in **VI** yields the product phosphine-borane **VII** (Figure 1, path ***a***).

Any competing BH_3 attack on **III** *trans*- to the OR^1 group would require the five-membered ring to adopt a diequatorial span and this is energetically disfavored.[29] Thus, the cleavage of the P-OR bond in α-hydroxy phosphinates that leads to formation of the observed secondary phosphine-boranes must require stereomutation[30] of TBP **IV** to place the OR group in the apical position suitable for its departure.

Such a sequence of events has already been proposed by Buono and coworkers[22b] in their recent mechanistic analysis of the BH_3 reduction of α-hydroxy phosphinates.[20] As these authors argued,[22b] the stereomutation of **IV** to **VIIIa** to place OR^1 in the (leaving) apical position requires the migration of the apicophilic O-B substituent from its leaving apical position into a less favored and non-leaving equatorial position. Simultaneously, the CH_2-X substituent is forced into adopting an unfavorable apical position.[29b,c] This will raise energy of the resulting TBP **VIIIa** (Figure 1, path ***b***) relative to **IV** but maybe not to the extent which could effectively prevent its formation.

Based on our results we have become more inclined to also consider stereomutation of **IV** to **VIIIb** where OR^1 adopts the leaving apical position and the five-membered ring retains a favored apical-O equatorial-C configuration. If this configuration becomes competitive, the departure of the OR^1 is likely to be preferred, in that it probably constitutes a better leaving group than the OB^- group whose initially vacant boron p orbital is already filled. Thus, to make the preferential departure of the ring oxygen possible, and to avoid ester bond cleavage, the stereomutation of TBP **IV** should be impeded.

It seems reasonable to expect[29a] that as the CH_2-X ligand becomes bulkier or quaternary, its preference for the equatorial position should increase; this can be expected to stabilize the critical α-substituted TBP **IV** significantly and therefore make it less prone to stereomutation. Indeed, under these circumstances, we were able to achieve much greater selectivity for the direct departure of the phosphoryl oxygen (cf. Scheme 1 and Table 1, entries 5,7). Ultimately, by combining quaternary substitution at the α-carbon with a bulky, and therefore less apicophilic[29] menthyl ester group in (S_P)-**10b**, it was possible to achieve the complete suppression of path ***b*** and allow fully chemoselective reduction of the P=O bond *via* path ***a***; this whilst leaving the ester bond intact. Similar success was achieved with the isopropyl α-amino phosphinate **19a** which bears a single α-phenyl substituent and with α-aryl substituted diisopropyl α-amino phosphonates **22** (Scheme 4, and Table 2, respectively).

It is clear that when the α-carbon is unsubstituted or bears small (*e.g.,* single methyl) substituent or, equally, if the ester group is small, path ***b*** can become either competitive or dominant. Thus, after departure of the OR^1 group from **VIIIb** (or **VIIIa**), the protonated cyclic intermediate **IX** picks up a hydride from another molecule of BH_3 to form TBP **X**. Subsequent opening of the five-membered ring leads to **XI** which is stabilized by evolution of a hydrogen molecule yielding free secondary phosphine **XII** (or *H*-phosphinite, when $R^2 = OR^1$) which undergoes complexation with BH_3 (Figure 1).

For phosphonates where two single P-O bonds are present, stereomutation[30] of **X** into **XIV** (path ***c***) can again occur and this places the second OR^1 group in an apical position that enables its departure. This path concludes with the observed formation of a primary phosphine or phosphine-borane **XVII**.

In summary, it can be assumed that substitution at the α-position of the five-membered ring of **III** and/or the presence of bulky ester or amide substituents (the latter constituting less apicophilic and very poor leaving groups) aid the reduction pathway that passes through ***a*** by making stereomutation of **IV** less favorable. This proposal is nicely aligned with our experimental results (*vide supra*) except in the case of cyclic hydroxymethylphosphonate **1c**, which was found to undergo cleavage of all phosphorus-oxygen bonds upon treatment with BH_3. This result may reflect a swift stereomutation of TBP **IV** (R^1,R^2 = -$CH(CH_3)CH_2CH_2O$-) into a TBP of type **VIIIb**, which allows both the six-membered dioxaphosphorinane ring and the five-membered dioxaboraphospholane ring to adopt their energetically favored apical-equatorial positions. Subsequent preferential cleavage of an apical P-O ester bond starts a sequence of events according to path ***b*** and ***c*** (Figure 1) that leads to the formation of the primary phosphine **XVII** (X = lone pair).

It can be also concluded that the reduction of the ester P-O bonds, when observed, must precede reduction of the P=O bond because such bonds, albeit less directly than the P=O, have to benefit from the activating presence of the five-membered ring in **III** and **IX**, as described in paths ***b*** and ***c***.

The proposed reduction mechanism seems to be general regardless of the type of the activating group, *e.g.*, OH or NH present in the starting phosphinate or phosphonates. Importantly, it also implies that the reductive conversion of the P=O bond into a P-BH_3must operate according to path ***a*** in these compounds; this implies an inversion of configuration at P as has already been confirmed in the closely related reductions of hydroxymethylphosphinates.[17e,20,21-22]

Conclusions

In summary, a general and efficient method has been developed for the chemoselective reduction of P=O bond by commercially

available BH_3 complexes for phosphinates and phosphonates bearing either ester or amide functionaiities that have an activating group (OH or NH) in close proximity to the phosphorus atom. The key role of the α functional groups in the reduction process is to assure the formation of a five-membered dioxaboraphospholane ring that converts the robust phosphoryl oxygen into a leaving group. The method nicely complements known synthetic protocols for the synthesis of α-hydroxy phosphonite-boranes and α-hydroxy phosphinite-boranes, and provides possibly the most straightforward procedure for their synthesis in a one-step reaction from the requisite (and readily available) P=O precursors. The same simple route is now also available for the first time for the preparation of α-amino phosphonite-boranes and α-amino phosphinite-boranes. A detailed mechanistic proposal of the reduction process accounting for the observed chemoselectivity and stereoselectivity of the reduction process has also been presented.

An important implication that arises from the stereochemical course of the developed reduction methodology deserves attention. Once the direct reduction of P-stereogenic α-hydroxy phosphinates and α-amino phosphinates to phosphinite-boranes with clean inversion of configuration has been achieved, a subsequentand straightforward stereoretentive oxidation[26] provides the prospect of a two-step sequence for configurational inversion at P. It also provides a route to P-stereogenic P=S analogues.

Experimental Section

General information. All reactions were performed under an argon atmosphere using Schlenk techniques. Only dry solvents were used and glassware was heated under vacuum prior use. All chemicals were used as received unless noted otherwise. Solvents for chromatography and crystallization were distilled once before use and the solvents for extraction were used as received. THF and toluene were distilled from sodium/benzophenone ketyl under argon. Water work-up of the reductions run in up to 300-400 mg scale was intentionally omitted to minimize the vast loss of ester products usually observed when hydrolytic reaction work-up preceded the column chromatography. **Caution**: All reactions and column chromatography have to be carried out under efficient fume hood because of irritating odour accompanying isolation of products.

Equipment. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on Bruker Advance 500 or 400 or 300 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Chemical shifts (δ) are reported chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ 7.27 ppm for ^{1}H and 77 ppm for ^{13}C, DMSO 2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C). Mass spectra were recorded on Shimadzu GC-MS QP2010S in electron ionization (EI). IR spectra were recorded on Thermo Scientific Nicolet iS50 FT-IR ATR mode with diamond prism (4000 - 400 cm^{-1} window) as solids or thin films. In the IR spectra, only the strongest/structurally most important peaks (cm^{-1}) are listed. Melting points were determined on Büchi Melting Point M-560 in a capillary tube and were uncorrected. HPLC-HRMS was performed on Shimazu HRMS ESI-IT-TOF using reverse phase stationary phase with water/MeCN 65:35 as eluent, electrospray ionization (ESI), and IT-TOF detector. Optical rotations were measured on Perkin Elmer 341LC using a 1 mL cell with a 10 mm path length and are reported as follows: $[\alpha]^{25}_D$ (c: g/100 mL, in solvent). Elementary analyses were performed on PERKIN ELMER CHN 2400.Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution or iodide on silica gel. The reaction mixtures were purified by column chromatography over silica gel (60−240 mesh) or basic Al_2O_3 (70-230 mesh).

A. General procedure for the reaction of α-hydroxy phosphonates 1 and α-hydroxy phosphinates 6 with BH_3-THF: In the two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet α-hydroxy phosphonate **1** (0.5 mmol) or α-hydroxy phosphinate **6** (0.5 mmol) in anhydrous THF (5 mL) was placed. Then, BH_3-THF complex (5 mL, 5 mmol, 1M solution in THF) was slowly added via syringe to avoid uncontrolled bubbling. After addition of BH_3 complex the reaction mixture was stirred and heated at 60 °C for 24 h. Then, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on basic Al_2O_3 using hexane/AcOEt (v/v = 10:1) or hexane/AcOEt (v/v = 6:1) as eluent.

Hydroxymethylphosphonous acid-borane diisopropyl ester (2a). **1a** (0.098 g, 0.5 mmol) was reacted according to general procedure **A** to afford **2a** (0.0194 g, 0.1 mmol, 20%) as an oil: R_f = 0.93 (hexane/AcOEt 2:1). IR (ATR, thin film): 3446, 2979, 2384, 1375, 972 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.63-4.73 (m, 2H), 3.83 (s, 2H), 1.99 (bs, 1H), 1.34 (d, $^3J_{P-C}$ = 6.31 Hz, CH_3), 1.31 (d, $^3J_{P-C}$ = 6.31 Hz, CH_3), 0.20-0.86 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.7 (d, $^2J_{P-C}$ = 4.5 Hz, *C*H), 61.7 (d, $^1J_{P-C}$ = 68.1 Hz, *C*H), 24.1 (d, $^3J_{P-C}$ = 3.6 Hz, CH_3), 24.0 (d, $^3J_{P-C}$ = 4.5 Hz, CH_3).^{31}P NMR (202 MHz, $CDCl_3$) δ 134.58 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.70 (bm). GC-MS m/z (rel. int. %): 180 [(M-BH_3)$^+$, 18]. HRMS (ESI/TOF) Found m/z: 247.1062; $C_9H_{24}BO_3PNa$ ([M-BH_3+O+Et+Na])$^+$ requires m/z: 247.1070. Anal. Calcd for $C_7H_{20}BO_3P$: C, 43.33; H, 10.39. Found: C, 43.70; H, 10.55.

Hydroxymethylphosphine-borane (5a). **1c** (0.083 g, 0.5 mmol) was reacted according to general procedure **A** to afford **5a** (98%, according to ^{31}P NMR spectrum of crude reaction mixture, not isolated). ^{31}P NMR (202 MHz, $CDCl_3$) δ -46.88 (bm). {^{1}H}^{31}P NMR (202 MHz, $CDCl_3$) δ -46.82 (t, J_{P-H} = 340.83 Hz).

Hydroxymethylphosphine (4a). **1c** (0.083 g, 0.5 mmol) was reacted with BH_3-THF (1.5 mL, 1.5 mmol, 1M solution in THF) at rt for 4 h according to procedure **A** to afford **4a** (90%, according to ^{31}P NMR spectrum of crude reaction mixture, not isolated). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -121.52 (s). {^{1}H}^{31}P NMR (121.5 MHz, $CDCl_3$) δ -125.32 (t, J_{P-H} = 202.71 Hz).

1-Hydroxy-ethylphosphonous acid-borane diisopropyl ester (2d).**1d** (0.106 g, 0.5 mmol) was reacted according to general **A** procedure to afford **2d** (0.032 g, 0.155 mmol, 31%) as a volatile oil: R_f = 0.28 (hexane/AcOEt 10:1). IR (ATR, thin film): 3502, 2979, 2386, 1374, 1103, 970, 787 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.62-4.72 (m, 2H), 3.89-3.91 (m, 1H), 1.90 (bs, 1H), 1.39 (dd, J_{H-H} = 6.94 Hz, J_{P-H} = 15.45 Hz, 3H), 1.34 (d, J_{H-H}= 2.52 Hz, 3H), 1.33 (d, J = 2.52 Hz, 6H), 1.31 (d, J_{H-H}= 3.78 Hz, 3H), 1.30 (d, J_{H-H}= 4.10 Hz, 3H), 0.15-0.83 (bm, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.8 (d, $^2J_{P-C}$ = 4.6 Hz, *C*H), 72.7 (d, $^2J_{P-C}$ = 6.9 Hz, *C*H), 67.3 (d, $^1J_{P-C}$ = 70.5 Hz, *C*H), 24.1 (d, $^3J_{P-C}$ = 2.3 Hz, CH_3), 24.0 (d, $^3J_{P-C}$ = 4.6 Hz, CH_3), 16.1 (d, $^3J_{P-C}$ = 4.6 Hz, CH_3).^{31}P NMR (202 MHz, $CDCl_3$) δ 137.58 (bm); ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -44.94 (bm). GC-MS m/z (rel. int. %): 194 ([M-BH]$^+$, 13); HRMS (ESI/TOF): Found m/z: 248.1580; $C_{10}H_{24}O_3BPN$ ([M-O+NAc])$^+$ requires m/z: 248.1579.

1-Hydroxy-1-methylethylphosphonous acid-borane diisopropyl ester (2e). **1e** (0.112 g, 0.5 mmol) was reacted according to general procedure **A** to afford **2e** (0.079 g, 0.355 mmol, 71%) as an oil. R_f = 0.28 (hexane/AcOEt 10:1). IR (ATR, thin film): 3502, 2978, 2385, 1374, 973, 774 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64-4.74 (m, 2H), 1.79 (bs, 1H), 1.38 (d, J_{H-P} = 13.56 Hz, 6H), 1.33 (d, J = 5.99 Hz, 6H), 1.31 (d, J = 5.99 Hz, 6H), 0.18-0.84 (bm, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 72.8 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 71.0 (d, $^1J_{P-C}$ = 70.8 Hz), 24.1 (d, $^2J_{P-C}$ = 1.8 Hz, CH_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, CH_3), 23.7 (d, $^3J_{P-C}$ = 9.1 Hz, CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 138.91 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -45.50 (bm). GC-MS m/z (rel. int. %): 208 ([M-BH_3]$^+$, 1), 191 ([M-BH_3-OH]$^+$, 2), 150 [(M-

BH_3-C_3H_6O)$^+$] (37). HRMS (ESI/TOF) Found m/z: 262.1730; $C_{11}H_{26}O_3BPN$ ([M-O+NAc])$^+$ requires m/z: 262.1735. Anal. Calcd for $C_9H_{24}BO_3P$: C, 48.68; H, 10.89; Found: C, 49.01; H, 11.00.

1-Hydroxy-1-methylethyl-H-phosphinous acid-borane isopropyl ester(3e). **1e** (0.112 g, 0.5 mmol) was reacted with BH_3-THF (5 mL, 1.5 mmol, 1M solution in THF) at rt for 24 h according to procedure **A** to afford **2e** (0.08 g, 0.36 mmol, 72%) and **3e** (9%, according to ^{1}H NMR spectrum). **3e** (isolated in a mixture with **2e**): R_f = 0.5 (hexane/AcOEt 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (dm, $J_{H\text{-}P}$= 384.62 Hz, 1H), 4.51-4.57 (m, 1H), 2.18 (bs, 1H), 1.47 (t, $J_{H\text{-}P}$= 15.13 Hz, 6H), 1.32 (d, $J_{H\text{-}P}$= 7.41 Hz, 6H), 0.16-0.91 (bm, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 111.89 (bm).

1-Hydroxy-1-methylethylphosphine-borane (5e). **1f** (0.09 g, 0.5 mmol) was reacted according to general procedure **A** to afford **5a** (95%, according to ^{31}P NMR spectrum of crude reaction mixture, not isolated). ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.28 (bm). {^{1}H}^{31}P NMR (202 MHz, $CDCl_3$) δ-18.05(t, $J_{P\text{-}H}$ = 365.71 Hz).

1-Hydroxy-1-cyclohexylphosphonous acid-borane diisopropyl ester (2g). **1g** (0.083 g, 0.5 mmol) was reacted according to general procedure **A** to afford **2g** (0.0885 g, 0.335 mmol, 67%) as an oil. R_f = 0.46 (hexane/AcOEt 10:1). IR (ATR, thin film): 3503, 2978, 2934, 2959, 2385, 1449, 1385, 1260, 1177, 1140, 974, 883 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 61-4.70 (m, 2H), 1.73-1.80 (m, 2H), 1.54-1.71 (m, 8H), 1.31 (d, $J_{H\text{-}P}$ = 6.31 Hz, 6H), 1.28 (d, $J_{H\text{-}P}$ = 6.15 Hz, 6H), 0.12-0.85 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.6 (d, $^2J_{P\text{-}C}$ = 5.5 Hz, *C*H), 72.4 (d, $^1J_{P\text{-}C}$ = 72.7 Hz, *C*), 30.3 (d, $J_{P\text{-}C}$ = 6.4 Hz, *C*H$_2$), 25.4 (s, *C*H$_2$), 24.2 (d, $^{3\text{-}}J_{P\text{-}C}$ = 1.8 Hz, *C*H$_3$), 23.9 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, *C*H$_3$), 20.1 (d, $J_{P\text{-}C}$ = 9.9 Hz, *C*H$_2$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 138.00 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -45.29 (bm). HRMS (ESI/TOF) Found m/z: 23=1.1497; $C_{12}H_{24}O_2P$ ([M-BH_3-OH])$^+$ requires m/z: 231.1508. Anal. Calcd for $C_{12}H_{28}BO_3P$: C, 54.98; H, 10.77. Found: C, 54.59; H, 10.27.

1-Hydroxy-1-cyclohexyl-H-phosphinous acid-borane isopropyl ester(3g).**1g** (0.083 g, 0.5 mmol) was reacted with BH_3-THF (2.5 mL, 2.5 mmol, 1M solution in THF) at rt for 16 h according to procedure **A** to afford **2g** (0.0642 g, 0.245 mmol, 49%) and **3g** (0.0061 g, 0.03 mmol, 6%). **3g**: an oil. R_f = 0.31 (hexane/AcOEt 10:1). IR (ATR, thin film): 3495, 2977, 2933, 2956, 2384, 1449, 1375, 1104, 936, 754 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (dq,$^1J_{P\text{-}H}$ = 384.03 Hz, $J_{H\text{-}H}$ = 5.04 Hz, 1H), 4.45-4.56 (m, 1H), 1.57-1.80 (m, 11H), 1.31 (d, J = 6.15 Hz, 6H), 0.20-0.92 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.7 (d, $^2J_{P\text{-}C}$ = 5.5 Hz, O*C*H), 71.4 (d, $^1J_{P\text{-}C}$ = 52.7 Hz, *C*), 32.3 (d, $J_{P\text{-}C}$ = 6.4 Hz, *C*H$_2$), 31.3 (d, $J_{P\text{-}C}$ = 7.2 Hz, *C*H$_2$), 25.6 (s, *C*H$_2$), 24.0 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, *C*H$_3$), 23.3 (d, $^3J_{P\text{-}C}$ = 3.6 Hz, *C*H$_3$), 20.4 (d, $J_{P\text{-}C}$ = 7.2 Hz, *C*H$_2$), 20.2 (d, $J_{P\text{-}C}$ = 9.1 Hz, *C*H$_2$).^{31}P NMR (202 MHz, $CDCl_3$)δ 109.97 (bm). {^{1}H}^{31}P NMR (202 MHz, $CDCl_3$) δ 109.86 (dq, $J_{P\text{-}H}$ = 395.64 Hz). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.81 (bm). HRMS (ESI/TOF) Found m/z: 407.2824; $C_{18}H_{43}O_4B_2P_2$ [2M-H]$^+$requires m/z: 407.2812.

(1-Hydroxy-ethyl)phenylphosphinous acid-borane ethyl ester (7a). **6a** (0.107 g, 0.5 mmol) was reacted according to general procedure **A** to afford **7a** as a mixture of diastereoisomers (0.05 g, 0.235 mmol, 47% dr = 59:41) and **8a** as a mixture of diastereoisomers (0.084 g, 0.05 mmol, 10%, dr = 50:50).

7a: a volatile oil with an irritating odour. R_f = 0.34 and 0.29 (hexane/AcOEt 4:1). IR (ATR, liquid): 3502, 2978, 2379, 1437, 1025, 946, 772, 733, 693 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.85 (m, 4H), 7.59-7.59 (m, 2H), 7.43-7.58 (m, 4H), 4.23-4.29 (m, 1H, minor), 4.15-4.20 (m, 1H, major), 4.08-4.16 (m, 2H, minor), 3.93-4.02 4.23-4.29 (m, 2H, major), 2.00 (bs, 2H), 1.33 (t, $J_{H\text{-}P}$ = 6.94 Hz, 3H, major), 1.33 (t, $J_{H\text{-}P}$ = 6.94 Hz, 3H, minor), 1.33 (dd, $J_{H\text{-}P}$ = 7.09 Hz, $J_{H\text{-}H}$ = 3.31 Hz, 3H, minor), 1.30 (dd, $J_{H\text{-}P}$ = 7.09 Hz, $J_{H\text{-}H}$ = 2.36 Hz, 3H, major), 0.40-1.10 (bm, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 132.3 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H, minor), 132.2 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H, major), 131.8 (d, $^2J_{P\text{-}C}$ = 10.9 Hz, *C*H, minor), 131.5 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H, major), 128.1 (d, $^1J_{P\text{-}C}$ = 53.6 Hz, *C*, major), 128.5 (d, $^1J_{P\text{-}C}$ = 52.7 Hz, *C*, minor), 128.7 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H, major), 128.6 (d, $^3J_{P\text{-}C}$ = 9.1 Hz, *C*H, minor), 68.4 (d, $^1J_{P\text{-}C}$ = 50.9 Hz, *C*H, major), 68.0 (d, $^1J_{P\text{-}C}$ = 50.0 Hz, *C*H, minor), 64.5 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H$_2$, major), 64.3 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H$_2$, minor), 16.8 (d, $^2J_{P\text{-}C}$ = 5.5 Hz, *C*H$_3$, major), 16.74 (d, $^3J_{P\text{-}C}$ = 2.7 Hz, *C*H$_3$, major), 16.69 (d, $^3J_{P\text{-}C}$ = 2.7 Hz, *C*H$_3$, major), 16.1 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, *C*H$_3$, minor). ^{31}P NMR (202 MHz, $CDCl_3$) δ 112.97 (bm, major), 111.97 (bm, minor). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.70 (bm). GC-MS m/z (rel. int. %): 154 [(*M-BH_3-C_2H_5O)$^+$] (45), 126 (10), 109 (22), 108 (12), 107 (17), 79 (100), 78 (25), 77 (39), 58 (23), 57 (10). Anal. Calcd for $C_{10}H_{18}BO_2P$: C, 56.65; H, 8.56. Found: C, 56.80; H, 8.65.

8a: ***(1-Hydroxy-ethyl)phenylphosphine-borane***. Volatile oil with irritating odour. R_f = 0.17 (hexane/AcOEt 4:1). IR (ATR, thin film): 3216, 2381, 1436, 1061, 772, 692, 642 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.81 (m, 4H), 7.52-7.60 (m, 2H), 7.42-7.52 (m, 4H), 5.45 (dm, $J_{P\text{-}H}$ = 372.81 Hz, 1H), 5.41 (dm, 372.81 Hz, 1H), 4.42-4.48 (m, 1H), 4.36-4.42 (m, 1H), 2.24 (bs, 2H), 1.46 (dd, $J_{H\text{-}P}$ = 16.08 Hz, $J_{H\text{-}H}$ = 6.94 Hz, 3H), 1.43 (dd, $J_{H\text{-}P}$ = 15.45 Hz, $J_{H\text{-}H}$ = 6.94 Hz, 3H), 0.39-1.15 (bm, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.9 (d, $^2J_{P\text{-}C}$ = 8.18 Hz, *C*H), 133.7 (d, $^2J_{P\text{-}C}$ = 8.17 Hz, *C*H), 132.2 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H), 129.1 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H), 129.0 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H), 122.8 (d, $^1J_{P\text{-}C}$ = 52.7 Hz, *C*), 122.2 (d, $^1J_{P\text{-}C}$ = 53.6 Hz, *C*), 65.1 (d, $^1J_{P\text{-}C}$ = 40.0 Hz, *C*H), 64.8 (d, $^1J_{P\text{-}C}$ = 40.0 Hz, *C*H), 19.02 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, *C*H$_3$), 18.98 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, *C*H$_3$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 12.65 (bm). {^{1}H}^{31}P NMR (202 MHz, $CDCl_3$) δ 12.81 (dm, $J_{P\text{-}H}$ = 355.76 Hz). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.32 (bm). GC-MS m/z (rel. int. %): 154 ([*M-BH_3*]$^+$, 2), 138 ([*M-BH_3-OH*]$^+$, 6).

(1-Hydroxy-1-methylethyl)phenylphosphinous acid-borane ethyl ester (7b). **6b** (0.083 g, 0.5 mmol) was reacted according to general procedure **A** to afford **7b** (0.0848 g, 0.375 mmol, 75%) as an oil with irritating odour. R_f = 0.60 (hexane/AcOEt 2:1). IR (ATR, thin film): 3502, 2976, 2383, 1436, 1025, 730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.84 (m, 2H), 7.44-7.58 (m, 3H), 4.07-4.23 (m, 1H), 3.95-4.07 (m, 1H), 2.18 (bs, 1H), 1.39 (d, $J_{H\text{-}P}$ = 12.81 Hz, 3H), 1.34 (t, $J_{H\text{-}P}$ = 7.04 Hz, 3H), 1.30 (d, $J_{H\text{-}P}$ = 13.72 Hz, 3H), 0.18-1.08 (bm, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.96 (d, $^2J_{P\text{-}C}$ = 10.1 Hz, *C*H), 131.92 (d, $^4J_{P\text{-}C}$ = 2.6 Hz, *C*H), 128.9 (d, $^1J_{P\text{-}C}$ = 51.2 Hz, *C*), 128.3 (d, $^3J_{P\text{-}C}$ = 10.1 Hz, *C*H), 71.4 (d, $^1J_{P\text{-}C}$ = 50.6 Hz, *C*), 64.5 (d, $^2J_{P\text{-}C}$ = 4.0 Hz, *C*H$_2$), 24.8 (d, $^2J_{P\text{-}C}$ = 9.5 Hz, *C*H$_3$), 23.8 (d, $^2J_{P\text{-}C}$ = 9.8 Hz, *C*H$_3$), 16.7 (d, $^3J_{P\text{-}C}$ = 5.8 Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 116.35 (bm); ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.21 (bm). GC-MS m/z (rel. int. %): 154 [(*M-BH_3-C_2H_5O)$^+$] (30), 125 (99). Anal. Calcd for $C_{11}H_{20}BO_2P$: C, 58.44; H, 8.92. Found: C, 58.61; H, 8.39.

(1-Hydroxy-1-cyclohexyl)phenylphosphinous acid-borane ethyl ester (7c). **6c** (0.134 g, 0.5 mmol) was reacted with BH_3-THF complex (1.5 mL, 1.5 mmol, 1M solution in THF) at 60 °C for 24 h according to general procedure **A** to afford **7c** (0.0944 g, 0.355 mmol, 71%).

7c: a colourless oil with an irritating odour. R_f = 0.45 (hexane/AcOEt 6:1). IR (ATR, thin film): 3502, 2934, 2380, 1436, 1113, 1067, 1024, 1024, 967, 945, 896, 844, 728, 692, 621, 609 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.78 (m, 2H), 7.52-7.55 (m, 1H), 7.45-7.50 (m, 2H), 4.08-4.17 (m, 1H), 3.94-4.02 (m, 1H), 1.80 (bs, 1H), 1.49-1.75 (m, 9H), 1.34 (t, $J_{H\text{-}P}$ = 6.94 Hz, 3H), 1.11-1.25 (m, 1H), 0.03-1.19 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.2 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H), 131.8 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H), 128.7 (d, $^1J_{P\text{-}C}$ = 51.2 Hz, *C*), 128.2 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H), 72.7 (d, $^1J_{P\text{-}C}$ = 52.7 Hz, *C*), 64.4 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, *C*H$_2$), 31.1 (d, $^2J_{P\text{-}C}$ = 6.4 Hz, *C*H$_2$), 30.5 (d, $^2J_{P\text{-}C}$ = 8.2 Hz, *C*H$_2$), 25.2 (d, $^4J_{P\text{-}C}$ = 1.1 Hz, *C*H$_2$), 20.2 (d, $^3J_{P\text{-}C}$ = 9.1 Hz, *C*H$_2$), 20.1 (d, $^3J_{P\text{-}C}$ = 10.0 Hz), 16.7 (d, $^3J_{P\text{-}C}$ = 5.75 Hz, *C*H$_3$).^{31}P NMR (202 MHz, $CDCl_3$) δ 114.89 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -43.27 (bm). HRMS (ESI/TOF) Found m/z: 235.1242 $C_{14}H_{20}OP$ ([M-BH_3-OH]$^+$) requires m/z: 235.1246. Anal. Calcd for $C_{14}H_{24}BO_2P$: C, 63.18; H, 9.09; Found: C, 62.88; H, 9.19.

Reduction of 6a-c by BH_3-SMe_2 complex. In the two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet was placed α-hydroxy phosphonite **6** (0.5 mmol) in anhydrous THF (5

mL). Then, BH_3-SMe_2 complex (0.142 mL, 1.5 mmol) or (0.237 mL, 2.5 mmol) was slowly added via syringe to avoid uncontrolled bubbling. After addition of BH_3 complex the reaction mixture was stirred for indicated time and temperature. Then, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel using hexane/AcOEt (v/v = 10:1) or hexane/AcOEt (v/v = 6:1) as eluent.

(1-Hydroxy-ethyl)phenylphosphinous acid-borane ethyl ester (7a). **6a** (0.107 g, 0.5 mmol) was reacted with BH_3-SMe_2 (0.237 mL, 2.5 mmol) at rt for 16 h according to general procedure **A** to afford **7a** as a mixture of diastereoisomers (0.0169 g, 0.08 mmol, 16% dr = 56:45) and **8a** as a mixture of diastereoisomers (0.016 g, 0.095 mmol, 19%, dr = 50:50).

1-Hydroxy-1-cyclohexyl)phenylphosphinous acid-borane ethyl ester (7b). **6b** (0.083 g, 0.5 mmol) was reacted with BH_3-SMe_2 (0.142 mL, 1.5 mmol) at rt for 16 h according to general procedure to afford **7b** (0.064 g, 0.285 mmol, 57%).

(1-Hydroxy-1-cyclohexyl)phenylphosphinous acid-borane ethyl ester (7c). **6c** (0.134 g, 0.5 mmol) was reacted with BH_3-SMe_2 (0.142 mL, 1.5 mmol) at 60 °C for 24 h according to general procedure **A** to afford **7c** (0.082 g, 0.31 mmol, 62%) and **8c** (0.0155 g, 0.07 mmol, 14%).

8c: (1-Hydroxy-1-cyclohexyl)phenylphosphine-borane. A colourless oil. R_f = 0.34 (hexane/AcOEt 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.72 (m, 2H), 7.54-7.59 (m, 1H), 7.45-7.51 (m, 2H), 5.29 (dq, $J_{P\text{-}H}$ = 371.38 Hz, 1H), 1.50-1.89 (m, 11H), 0.42-1.10 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3 (d, $^2J_{P\text{-}C}$ = 7.3 Hz, *C*H), 132.0 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H), 128.9 (d, $^3J_{P\text{-}C}$ = 9.1 Hz, *C*H),123.0 (d, $^1J_{P\text{-}C}$ = 51.8 Hz, *C*), 71.4 (d,$^1J_{P\text{-}C}$ = 40.0 Hz, *C*), 33.63 (d, $^2J_{P\text{-}C}$ = 7.3 Hz, *C*H$_2$), 30.56 (d, $^2J_{P\text{-}C}$ = 6.4 Hz, *C*H$_2$), 25.0 (d, $^4J_{P\text{-}C}$ = 1.0 Hz, *C*H$_2$), 20.7 (d, $^3J_{P\text{-}C}$ = 8.2 Hz, *C*H$_2$), 20.6 (d, $^3J_{P\text{-}C}$ = 7.3 Hz, *C*H$_2$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.05 (bm). {^{1}H}^{31}P NMR (202 MHz, $CDCl_3$) δ 23.86 (dm, $J_{P\text{-}H}$ = 355.37 Hz). HRMS (ESI/TOF) Found m/z: 225.1046; $C_{12}H_{17}O_2P$ ([M-BH_3+O+H]$^+$) requires m/z: 225.1039.

Hydroxymethylphosphonous acid-borane isopropyl ester N,N-diethylamide (16). **13** (0.105 g, 0.5 mmol) was reacted with 10 equiv. of BH_3-THF at rt for 24 h according to general procedure **A** to afford **16** (0.062 g, 0.3 mmol, 60%) as an oil. R_f = 0.6 (hexane/AcOEt 2:1). IR (ATR, thin film): 3502, 2974, 2380, 1381, 969, 791 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41-4.50 (m, 1H), 3.82 (bs, 1H), 3.14-3.25 (m, 2H), 3.05-3.25 (m, 2H), 1.85 (bs, 1H), 1.25 (d, $J_{H\text{-}H}$= 5.99 Hz, 3H), 1.23 (d, $J_{H\text{-}H}$= 6.15 Hz, 3H), 1.12 (t, $J_{H\text{-}P}$ = 7.09 Hz, 6H), 0.12-0.86 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.4 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H), 59.7 (d, $^1J_{P\text{-}C}$ = 73.6 Hz, *C*H$_2$), 39.5 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H$_2$), 24.0 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, *C*H), 23.9 (d, $^3J_{P\text{-}C}$ = 3.6 Hz, *C*H), 23,94; 14.4 (d, $^3J_{P\text{-}C}$ = 1.8 Hz, *C*H$_3$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 111.56 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -42.57 (bm). HRMS (ESI/TOF) Found m/z: 194.1307; $C_8H_{21}O_3P$ ([(M-BH_3)+H]$^+$) requires m/z: 194.1304. Anal. Calcd for $C_8H_{23}BNO_2P$: C, 46.41; H, 11.20; N, 6.76; Found: C, 46.11; H, 11.00; N, 6.50.

Hydroxymethylphosphonous acid-borane N,N,N',N'-tetraethyldiamide (17). **14** (0.111 g, 0.5 mmol) was reacted with 10 equiv. of BH_3-THF at rt for 24 h according to general procedure **A** to afford **17** (0.0242 g, 0.11 mmol, 22%) as an oil. R_f = 0.77 (hexane/AcOEt 2:1); IR (ATR, thin film): 2972, 2345, 1377, 1015 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 2H), 2.97-3.15 (m, 8H), 1.97 (s, 1H), 1.08 (t, $J_{P\text{-}H}$ = 7.09 Hz, 12H), 0.19-0.88 (bm, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 58.2 (d, $^1J_{P\text{-}C}$ = 65.4 Hz, *C*H$_2$), 40.0 (d, $^2J_{P\text{-}C}$ = 2.7 Hz, *C*H$_2$), 14.3 (d, $^3J_{P\text{-}C}$ = 1.8 Hz, *C*H$_2$); ^{31}P NMR (202 MHz, $CDCl_3$) δ 86.70 (bm); ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -40.76 (bm); HRMS (ESI/TOF) Found m/z: 207.1615; $C_9H_{24}OPN_2$ [(M-BH_3)+H]$^+$requires m/z: 207.1621. Anal. Calcd for $C_9H_{26}OPBN_2$: C, 49.11; H, 11.91; N, 12.73. Found: C, 48.80; H, 11.55; N, 12.88.

Hydroxymethylphosphonous acid-borane N,N,N',N'-tetraisopropyldiamide (18). **15** (0.184 g, 0.5 mmol) was reacted with 10 equiv. of BH_3-THF at 60 °C for 24 h according to general procedure **A** to afford **18** (0.108 g, 0.39 mmol, 78%) as a white solid, m.p. 77.7-78.8 °C. R_f = 0.47 (hexane/AcOEt 10:1). IR (ATR, solid): 3308, 2969, 2394, 1366, 1177, 1012, 973, 541 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (d, $J_{H\text{-}H}$= 4.41 Hz, 2H), 3.57-3.69 (m, 4H), 2.32 (bs, 1H), 1.31 (d, $J_{H\text{-}H}$ = 6.94 Hz, 12H), 1.27 (d, $J_{H\text{-}H}$ = 6.94 Hz, 12H), 0.51-1.19 (bm, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 59.9 (d, $^1J_{P\text{-}C}$ = 61.8 Hz, *C*H$_2$), 47.7 (d, $^2J_{P\text{-}C}$ = 4.5 Hz, *C*H), 24.5 (d, $^3J_{P\text{-}C}$ = 1.8 Hz, *C*H$_3$), 23.5 (d, $^3J_{P\text{-}C}$ = 1.8 Hz, *C*H$_3$). ^{31}P NMR (202 MHz, $CDCl_3$) δ 83.69 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -35.79 (bm). GC-MS m/z (rel. int. %): 232 [(*M-BH$_3$-CH$_2$O)*$^+$] (2), 148 (39), 106 (100), 88 (11), 86 (68), 78 (12), 77 (11), 58 (31). Anal. Calcd for $C_{13}H_{34}BN_2OP$: C, 56.53; H, 12.41; N, 10.14. Found: C, 56.20; H, 12.11; N, 9.98.

B. General procedure for reduction of P-stereogenic α-hydroxyphosphinates 10 by BH_3-SMe_2. In the two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet was placed α-hydroxyphosphinate **10** (0.3 mmol) in anhyd. THF (5 mL). Then, BH_3-SMe_2 (142 μL, 1.5 mmol) was slowly added via syringe to avoid uncontrolled bubbling. After addition of BH_3 complex the reaction mixture was stirred and heated at 60 °C for 16 h. Then, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on basic Al_2O_3 using hexane/AcOEt (v/v = 10:1) and hexane/AcOEt (v/v = 6:1) as eluent.

(R_P)-Hydroxymethyl(phenyl)phosphinous acid-borane (L)-menthyl ester (R_P)-(11a).[22b] (***S*$_P$**)-**10a** (0.093 g, 0.3 mmol) was reacted according to general procedure **B** to afford (***R*$_P$**)-(**11a**) as a single diastereoisomer (0.0416 g, 0.135 mmol, 45%) and **12** (0.007 g, 0.045 mmol, 15%).

(*R*$_P$)-(**11a**): a colourless oil. R_f= 0.78 (hexane/AcOEt 2:1). [α]$_D$= -69.52 (c 1.25, $CHCl_3$). IR (ATR, thin film): 3482, 2954, 2379, 1437, 980, 844, 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.89 (m, 2H), 7.54-7.58 (m, 1H), 7.47-7.51 (m, 2H), 4.05-4.12 (m, 2H), 2.23-2.29 (m, 1H), 1.72-1.78 (m, 2H), 1.61-1.70 (m, 2H), 1.42-1.53 (m, 1H), 1.30-1.40 (m, 1H), 1.11-1.14 (m, 1H), 0.95 (d, $J_{H\text{-}H}$ = 6.62 Hz, 3H), 0.83-1.00 (m, 2H), 0.80 (d, $J_{H\text{-}H}$ = 6.94 Hz, 3H), 0.50-0.89 (m, 3H), 0.50 (d, $J_{H\text{-}H}$ = 6.94 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.2 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H), 131.3 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H), 129.5 (d, $^1J_{P\text{-}C}$ = 61.7 Hz, *C*), 128.6 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H), 80.4 (d, $^2J_{P\text{-}C}$ = 4.5 Hz), 63.5 (d, $^1J_{P\text{-}C}$ = 49.1 Hz, *C*H$_2$), 48.8, 43.5, 34.0, 31.5, 25.5, 22.7, 22.1, 20.9, 15.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ 105.87 (bm). Anal. Calcd for $C_{17}H_{30}BO_2P$: C, 66.25; H, 9.81. Found: C, 66.20; H, 9.80.

12: (Hydroxymethyl)phenylphosphine-borane.[22b] A colourless oil. R_f = 0.49 (hexane/AcOEt 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.78 (m, 2H), 7.48-7.60 (m, 3H), 5.59 (dm, $J_{H\text{-}P}$ = 375.40 Hz, 1H), 4.23-4.31 (m, 2H), 1.93 (bs, 1H), 0.37-1.11 (bm, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 133.5 (d, $^2J_{P\text{-}C}$ = 8.17 Hz, *C*H), 132.3 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H), 129.2 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H), 122.6 (d, $^1J_{P\text{-}C}$ = 55.4 Hz, *C*), 58.5 (d, $^1J_{P\text{-}C}$ = 55.4 Hz, *C*H$_2$). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.24 (bm). HRMS (ESI/TOF) Found m/z: 313.0755; $C_{14}H_{19}O_4P_2$ [2(M-BH_3+O)+H]$^+$requires m/z: 313.0753.

(R_P)-1-Hydroxy-1-cyclohexyl(phenyl)phosphinous acid-borane (L)-menthyl ester (R_P)-(11b). (***S*$_P$**)-**10b** (0.114 g, 0.3 mmol) was reacted according to general procedure **B** (0.0677 g, 60%) as an oil. R_f= 0.83 (hexane/AcOEt 2:1). [α]$_D$= -114 (c 0.505, $CHCl_3$). IR (ATR, thin film): 2930, 2862, 2392, 1448, 978, 751, 693 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.89 (m, 2H), 7.49-7.54 (m, 1H), 7.40-7.46 (m, 2H), 4.06-4.14 (m, 1H), 2.31-2.38 (m, 1H), 1.92 (bs, 1H), 1.78-1.80 (m, 1H), 1.76-1.80 (m, 1H), 1.40-1.79 (m, 10H), 1.08-1.15 (m, 2H), 0.93 (d, $J_{H\text{-}H}$ = 6.62 Hz, 3H), 0.82-0.91 (m, 2H), 0.75 (d, $J_{H\text{-}H}$ = 7.09 Hz, 3H), 0.44-0.80 (bm, 3H), 0.34 (d, $J_{H\text{-}H}$ = 6.94 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.6 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H), 131.7 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H), 129.5 (d, $^1J_{P\text{-}C}$ = 54.5 Hz, *C*), 127.9 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H), 80.6 (d, $J_{P\text{-}C}$ = 5.5 Hz, *C*H), 73.3 (d, $^1J_{P\text{-}C}$ = 51.8 Hz, *C*), 48.9 (d, $J_{P\text{-}C}$ = 4.3 Hz, *C*H), 43.6 (s, *C*H$_2$), 34.1 (s, *C*H$_2$), 31.9 (d, $J_{P\text{-}C}$ = 7.3 Hz, *C*H$_2$), 31.6 (s, *C*H), 30.3 (d, $J_{P\text{-}C}$ = 6.4 Hz, *C*H$_2$), 25.4 (s, *C*H), 25.2 (d, $J_{P\text{-}C}$ = 1.2 Hz, *C*H$_2$), 22.6 (s, *C*H$_2$), 22.2 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 20.3 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H$_2$), 20.1 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H$_2$),

15.0 (s, CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 112.93 (bm). GC-MS m/z (rel. int. %): 127 [(*PhPH(OH)*)$^+$] (100), 126 (55), 109 (22), 95 (25), 83 (24). Anal. Calcd for $C_{22}H_{38}BO_2P$: C, 70.22; H, 10.18. Found: C, 69.95; H, 10.00.

C. General procedurefor reduction of α-amino phosphinates 19 and α-amino phosphonates 22 by BH_3-SMe_2. In the two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet was placed α-amino phosphonate **22** (0.25 mmol) or α-amino phosphinate **19** in anhydrous THF (5 mL). Then, BH_3-SMe_2 (71.2 μL, 0.75 mmol for **19a-b**) or BH_3-SMe_2 (118.6 μL, 1.25 mmol for **22a**,**c-f**, **22h-k, 25**) or BH_3-SMe_2 (0.237 mL, 2.5 mmol for **22b**, **22g**, **22l**) was slowly added via syringe to avoid uncontrolled bubbling. After addition of BH_3 complex the reaction mixture was stirred and heated at 60 °C for indicated time (4-24 h). Then, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel using hexane/AcOEt (v/v = 6:1) or hexane/AcOEt (v/v = 4:1) as eluent.

[(4-Bromophenylamino)(phenyl)methyl]phenylphosphinous acid-borane isopropyl ester (20a). **19a** (0.111 g, 0.25 mmol) was reacted with BH_3-SMe_2 (71.2 μL, 0.75 mmol) for 20 h according to general procedure **C** to afford **20a** as a mixture of diastereoisomers isolated as a mixture (0.093 g, 0.21 mmol, 84%, dr = 59:41) as an oil. R_f = 0.7 (hexane/AcOEt 6:1). IR (ATR, thin film): 3395, 2978, 2383, 1590, 1493, 982, 807, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.74 (m, 2H), 7.43-7.53 (m, 6H), 7.33-7.36 (m, 2H), 7.27-7.52 (m, 6H), 7.10-7.18 (m, 2H), 7.15-7.20 (m, 2H, minor), 7.10-7.13 (m, 2H, major), 7.01-7.03 (m, 1H, major), 6.99-7.03 (m, 1H, minor), 6.45-6.49 (m, 2H, minor), 6.39-6.40 (m, 2H, major), 4.76 (d, $J_{P\text{-}H}$ = 14.19 Hz, 1H, major), 4.73 (d, $J_{P\text{-}H}$ = 14.82 Hz, 1H, minor), 4.61-4.68 (m, 1H, minor), 4.39-4.41 (m, 1H, major), 4.02 (bs, 1H), 1.32 (d, $J_{P\text{-}H}$ = 6.22 Hz, 3H, minor), 1.23 (d, $J_{H\text{-}H}$ = 6.22 Hz, 3H, minor), 1.16 (d, $J_{H\text{-}H}$ = 6.31 Hz, 3H, major), 0.92 (d, $J_{P\text{-}H}$ = 6.31 Hz, 3H, major), 0.45-0.99 (bm, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, N*C*, minor), 145.3 (d, $^3J_{P\text{-}C}$ = 11.8 Hz, N*C*, major), 134.9 (s, *C*, major), 134.5 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*, minor), 132.10 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, *C*H, major), 132.06 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H, minor), 131.83 (s, *C*H, minor), 131.76 (s, *C*H, major), 131.6 (s, *C*, minor) 131.5 (s, *C*, major), 131.2 (d, $^2J_{P\text{-}C}$ = 10.0 Hz, *C*H), 131.0 (d, $^2J_{P\text{-}C}$ = 10.9 Hz, *C*H), 130.0 (d, $^1J_{P\text{-}C}$ = 59.0 Hz, *C*), 128.8 (d, $J_{P\text{-}C}$ = 3.6 Hz, *C*H), 128.5 (d, $^3J_{P\text{-}C}$ = 10.5 Hz, *C*H), 128.47 (d, $J_{P\text{-}C}$ = 3.6 Hz, *C*H), 128.63 (d, $^3J_{P\text{-}C}$ = 10.9 Hz, *C*H), 128.11 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H), 128.08 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H), 128.01 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H), 127.98 (d, $J_{P\text{-}C}$ = 1.52 Hz, *C*H), 127.8 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H), 115.6 (s, *C*H, major), 115.5 (s, *C*H, minor), 110.3 (s, *C*, major), 110.1 (s, *C*, minor), 74.3 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H, major), 74.2 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H, minor), 61.1 (d, $^1J_{P\text{-}C}$ = 46.3 Hz, minor), 59.9 (d, $^1J_{P\text{-}C}$ = 49.1 Hz, major), 24.2 (d, $^3J_{P\text{-}C}$ = 2.7 Hz, CH_3), 24.17 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, CH_3), 23.6 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 107.53 (bm, major), 111.70 (bm, minor). HRMS (ESI/TOF) Found m/z: 442.1099; $C_{22}H_{27}BBrNOP$ ([M+H]$^+$) requires m/z: 442.1098. Anal. Calcd for $C_{22}H_{26}BBrNOP$: C, 59.76; H, 5.93; N, 3.17; Found: C, 59.79; H, 5.85; N, 3.10.

[(N-4-Bromophenyl)amino](phenyl)methyl]phenylphosphinous acid-borane ethyl ester (20b). **19b** (0.107 g, 0.25 mmol) was reacted with BH_3-SMe_2 (71.2 μL, 0.75 mmol) for 20 h according to general procedure **C** to afford **20b** as a mixture of diastereoisomers isolated as a mixture (0.064 g, 0.15 mmol, 60%, dr = 51:49, ^{31}P NMR). An oil. IR (ATR, thin film): 3395, 3059, 2384, 1591, 1488, 1042, 810, 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.73 (m, 2H); 7.50-7.56 (m, 1H), 7.43-7.50 (m, 4H), 7.28-7.38 (m, 9H), 7.11-7.20 (m, 2H), 7.15-7.19 (m, 2H, minor), 7.11-7.14 (m, 2H, major), 7.01-7.04 (m, 1H, major), 6.90-7.01 (m, 1H, minor), 6.45-6.49 (m, 2H, minor), 6.38-6.41 (m, 2H, major), 4.94 (bs, 1H), 4.77-4.80 (m, 2H), 4.09-4.18 (m, 1H, minor), 4.00-4.08 (m, 1H, minor), 3.80-3.90 (m, 1H, major), 3.64-3.71 (m, 1H, major), 1.31 (t, $J_{P\text{-}H}$ = 7.04 Hz, 3H, minor), 1.14 (t, $J_{P\text{-}H}$ = 6.94 Hz, 3H, major), 0.05-1.10 (bm, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, N*C*, minor), 145.3 (d, $^3J_{P\text{-}C}$ = 11.8 Hz, N*C*, major), 134.8 (s, *C*, major), 134.3 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*, minor), 132.3 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, major), 132.2 (d, $^4J_{P\text{-}C}$ = 2.7 Hz, minor), 132.0, 138.1 (s, *C*H, minor), 138.8 (s, *C*H, major), 131.2 (d, $^2J_{P\text{-}C}$ = 10.9 Hz, *C*H, minor), 131.0 (d, $^2J_{P\text{-}C}$ = 10.9 Hz, *C*H, major), 130.2 (d, $^1J_{P\text{-}C}$ = 59.0 Hz, *C*, major), 130.2 (d, $^1J_{P\text{-}C}$ = 59.0 Hz, *C*, major), 128.9 (d, $^1J_{P\text{-}C}$ = 57.2 Hz, *C*, major), 128.7, 128.5 (d, $^3J_{P\text{-}C}$ = 10.9 Hz, *C*H, major), 128.3 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, *C*H, minor), 128.2 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H), 128.18 (d, $J_{P\text{-}C}$ = 3.6 Hz, *C*H), 128.17 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H), 128.1 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H), 127.95 (d, $J_{P\text{-}C}$ = 3.6 Hz, *C*H), 127.88 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H), 127.7 (d, $J_{P\text{-}C}$ = 2.7 Hz, *C*H), 115.62 (s, *C*H, major), 115.58 (s, *C*H, minor), 110.3 (s, *C*, major), 110.2 (s, *C*, minor), 65.11 (d, $^2J_{P\text{-}C}$ = 2.7 Hz, CH_2, minor), 65.01 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, CH_2, major), 60.7 (d, $^1J_{P\text{-}C}$ = 44.5 Hz, minor), 59.4 (d, $^1J_{P\text{-}C}$ = 46.3 Hz, major), 16.7 (d, $^3J_{P\text{-}C}$ = 6.4 Hz, CH_3, minor), 16.4 (d, $^3J_{P\text{-}C}$ = 5.5 Hz, CH_3, major). ^{31}P NMR (202 MHz, $CDCl_3$) δ 109.74 (bm, major), 114.53 (bm, minor). HRMS (ESI/TOF) Found m/z: 428.0952; $C_{21}H_{25}BBrNOP$ ([M+H]$^+$) requires m/z: 428.0942. Anal. Calcd for $C_{21}H_{24}BBrNOP$: C, 58.92; H, 5.65; N, 3.27. Found: C, 58.79; H, 5.85; N, 3.10.

[1-(N-p-Bromophenylamino)]-1-phenylmethylphosphonous acid-borane diisopropyl ester (23a). **22a** (0.107 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23a** (0.0816 g, 0.193 mmol, 77%) as an oil. R_f = 0.64 (hexane/AcOEt 10:1). IR (ATR, thin film): 3404, 2978, 2386, 1593, 1493, 1101, 973, 808, 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.41 (m, 5H), 7.16-7.22 (m, 2H), 6.44-6.52 (m, 2H), 4.60-4.69 (m, 1H), 4.59 (d, $J_{P\text{-}H}$ = 17.02 Hz, 1H), 4.46-4.54 (m, 1H), 1.30 (d, $J_{H\text{-}H}$ = 6.15 Hz, 3H), 1.28 (d, $J_{H\text{-}H}$ = 6.31 Hz, 3H), 1.20 (d, $J_{H\text{-}H}$ = 5.99 Hz, 3H), 0.91 (d, $J_{H\text{-}H}$ = 6.15 Hz, 3H), 0.15-0.85 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6 (d, $^3J_{P\text{-}C}$ = 10.9 Hz, N*C*), 135.0 (d,$^2J_{P\text{-}C}$ = 3.6 Hz, *C*), 131.9 (s, *C*H), 128.3 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, *C*H), 128.2 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H), 128.0 (d, $^5J_{P\text{-}C}$ = 2.7 Hz, *C*H), 115.4 (s, *C*H), 110.0 (s, *C*), 73.8 (d, $^2J_{P\text{-}C}$ = 3.6 Hz, *C*H), 73,20 (d, $^2J_{P\text{-}C}$ = 5.5 Hz, *C*H), 59.8 (d, $^1J_{P\text{-}C}$ = 63.6 Hz, *C*H), 24.13 (d, $^3J_{P\text{-}C}$ = 2.7 Hz, CH_3), 24.10 (d,$^3J_{P\text{-}C}$ = 2.7 Hz, CH_3), 23.7 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, CH_3), 23.8 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 135.95 (bm). HRMS (ESI/TOF) Found m/z: 410.0887: $C_{19}H_{26}BrNO_2P$ ([M-BH_3+H]$^+$) requires m/z: 410.0879. Anal. Calcd for $C_{19}H_{28}BrNO_2PB$: C, 53.81; H, 6.65; N, 3.30. Found: C, 53.90; H, 6.78; N, 3.50.

[1-(N-p-Bromophenylamino)]-[1-(p-bromophenyl)methyl]phosphorous acid-borane diisopropyl ester (23b). **22b** (0.126 g, 0.25 mmol) was reacted with BH_3-SMe_2 (0.237 mL, 2.5 mmol) for 28 h according to general procedure **C** to afford **23b** (0.107 g, 0.213 mmol, 85%) and **24b** (0.0083 g, 0.025 mmol, 10%).

23b: Colourless oil. R_f = 0.62 (hexane/AcOEt 10:1). IR (ATR, thin film): 3403, 2978, 2386, 1487, 972, 810 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.47 (m, 2H), 7.25-7.29 (m, 2H), 7.18-7.21 (m, 2H), 6.43-6.46 (m, 2H), 4.72 (bs, 1H), 4.60-4.68 (m, 2H), 4.54 (d, $J_{P\text{-}H}$ = 16.55 Hz, 1H), 4.49-4.58 (m, 1H), 1.30 (d, $J_{H\text{-}H}$ = 6.31 Hz, 3H), 1.29 (d, $J_{H\text{-}H}$ = 6.15 Hz, 3H), 1.21 (d, $J_{H\text{-}H}$ = 6.15 Hz, 3H), 0.99 (d, $J_{H\text{-}H}$ = 6.15 Hz, 3H),0.10-0.87 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2 (d, $^3J_{P\text{-}C}$ = 11.8 Hz, N*C*), 134.3 (d, $^2J_{P\text{-}C}$ = 2.7 Hz, *C*), 131.9 (s, *C*H), 128.5 (d, $^4J_{P\text{-}C}$ = 1.8 Hz, *C*H),130.0 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, *C*H), 121.8 (d, $^5J_{P\text{-}C}$ = 3.6 Hz, *C*), 115.4 (s, *C*H), 110.4 (s, *C*), 74.0 (d, $^2J_{P\text{-}C}$ = 3.7 Hz, *C*H), 73.5 (d, $^2J_{P\text{-}C}$ = 4.9 Hz, *C*H), 59.4 (d, $^1J_{P\text{-}C}$ = 62.7 Hz, *C*H), 24.12 (d, $^3J_{P\text{-}C}$ = 2.7 Hz, CH_3), 24.09 (d, $^3J_{P\text{-}C}$ = 3.6 Hz, CH_3), 23.8 (d, $^3J_{P\text{-}C}$ = 4.5 Hz, CH_3), 23.3 (d, $^3J_{P\text{-}C}$ = 5.4 Hz, CH_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 134.81 (bm). HRMS (ESI/TOF) Found m/z: 487.9997;$C_{19}H_{25}Br_2NO_2P$ ([M-BH_3]+H$^+$) requires m/z: 487.9984. Anal. Calcd for $C_{19}H_{27}Br_2NO_2PB$: C, 45.37; H, 5.41; N, 2.78; Found: C, 45.50; H, 5.79; N, 3.00.

24b*: *4-bromo-N-(-4-bromobenzyl)aniline.[31] Waxy white solid. R_f = 0.45 (hexane/AcOEt 10:1). IR (ATR, solid): 3397, 2390, 1589, 1487, 1010, 810 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.48 (m, 2H), 7.25-7.30 (m, 2H), 7.21-7.25 (m, 2H), 6.51-6.61 (m, 2H), 4.28 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 138.1, 132.1, 131.8, 129.4, 121.6, 116.0, 48.7. HRMS (ESI/TOF) Found: m/z: 339.9323 $C_{13}H_{12}Br_2N$ ([M+H]$^+$) requires m/z: 339.9331.

[1-(N-p-Bromophenylamino)]-[1-(o-bromophenyl)methyl]phosphonous acid-borane diisopropyl ester (23c). **22c** (0.126 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 72 h according to general procedure **C** to afford **23c** (0.0567 g, 0.113 mmol, 45%) and **24c** (0.0322 g, 0.095 mmol, 38%).

23c: Colourless oil. R_f = 0.57 (hexane/AcOEt 10:1). IR (ATR, thin film): 3405, 2978, 2408, 1497, 987, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.55-7.57 (m, 1H), 7.44-7.47 (m, 1H), 7.26-7.28 (m, 1H), 7.20-7.22 (m, 2H), 7.12-7.14 (m, 1H), 6.47-6.50 (m 2H), 5.31 (d, J_{H-H} = 18.34 Hz, 1H), 4.89 (bs, 1H), 4.70-4.77 (m, 1H), 4.45-4.50 (m, 1H), 1.30 (d, J_{H-H} = 6.05 Hz, 3H), 1.29 (d, J_{H-H} = 6.05 Hz, 3H), 1.27 (d, J_{H-H} = 6.24 Hz, 3H), 0.80 (d, J_{H-H} = 6.05 Hz, 3H), 0.23-0.74 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0 (d,$^3J_{P-C}$ = 12.6 Hz, N*C*), 135.1 (d, J_{P-C} = 4.4 Hz, *C*), 132.6 (s, *C*H), 132.0 (s, *C*H), 129.4 (d, J_{P-C} = 2.2 Hz, *C*H), 127.6 (d, $^4J_{P-C}$ = 3.2 Hz, *C*H), 125.5 (d, $^3J_{P-C}$ = 5.5 Hz, *C*), 115.2 (s, *C*H), 110.2 (s, *C*), 74.2 (d, $^2J_{P-C}$ = 4.2 Hz, *C*H), 73.0 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 59.1 (d, $^1J_{P-C}$ = 65.2 Hz, *C*H), 24.10 (d, $^3J_{P-C}$ = 2.2 Hz, *C*H_3), 24.08 (d, $^3J_{P-C}$ = 2.2 Hz, *C*H_3), 24.0 (d, $^3J_{P-C}$ = 4.2 Hz, *C*H_3), 22.8 (d, $^3J_{P-C}$ = 4.2 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 136.64 (bm). HRMS (ESI/TOF) Found m/z: 487.9983; $C_{19}H_{25}Br_2NO_2P$ ([M-BH_3+H]$^+$) requires m/z: 487.9984. Anal. Calcd for $C_{19}H_{27}Br_2NO_2PB$: C, 45.37; H, 5.41; N, 2.78. Found: C, 45.50; H, 5.79; N, 3.00.

24c: N-(2-Bromobenzyl)-4-bromoaniline). A colourless oil. R_f = 0.46 (hexane/AcOEt 10:1). IR (ATR, solid): 3426, 2921, 1593, 1495, 1023, 809, 745 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.58-7.59 (m, 1H), 7.35-7.38 (m, 1H), 7.29-7.30 (m, 1H), 7.23-7.27 (m, 2H), 7.14-7.17 (m, 1H), 6.48-6.51(m, 2H), 4.39 (bs, 2H), 4.25 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6 (s, *C*), 137.6 (s, *C*), 132.9 (s, *C*H), 132.0 (s, *C*H), 129.1 (s, *C*H), 128.9 (s, *C*H), 127.6 (s, *C*H), 123.3 (s, *C*), 114.6 (s, *C*H), 109.4 (s, *C*), 48.4 (s, *C*H_2). GC-MS m/z (rel. int. %): 343 ([*M*]$^+$, 17), 342 (8), 341 (37), 340 (8), 339 (19). HRMS (ESI/TOF) Found m/z: 339.9327; $C_{13}H_{12}NBr_2$([M+H]$^+$) requires m/z: 339.9934.

[1-(N-p-Bromophenylamino)]-1-(m-nitrophenyl)methylphosphonous acid-borane diisopropyl ester (23d).**22d** (0.118 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 48 h according to general procedure **C** to afford **23d** (0.0704 g, 0.15 mmol, 60%) as a yellow oil. R_f = 0.40 (hexane/AcOEt 10:1). IR (ATR, thin film): 3400, 2979, 2390, 1527, 1360, 975, 810 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$):δ 8.28-8.29 (m, 1H), 8.15-8.18 (m, 1H), 7.43-7.73 (m, 1H), 7.50-7.53 (m, 1H), 7.20-7.23 (m, 2H), 6.44-6.48 (m, 2H), 4.78 (bs, 1H), 4.69 (d, J_{P-H} = 15.92 Hz, 1H), 4.69-4.63 (m, 1H), 4.59-4.63 (m, 1H), 1.31 (d, J_{H-H} = 6.15 Hz, 3H), 1.30 (d, J_{H-H} = 6.15 Hz, 3H), 1.23 (d, J_{H-H} = 6.15 Hz, 3H), 1.01 (d, J_{H-H} = 6.15 Hz, 3H), 0.10-0.87 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1 (d,$^4J_{P-C}$ = 2.7 Hz, N*C*), 144.9 (d, $^3J_{P-C}$ = 11.8 Hz, N*C*), 137.9 (d, J_{P-C} = 2.7 Hz, *C*), 134.1 (d, J_{P-C} = 3.6 Hz, *C*H), 132.1 (s, *C*H), 129.2 (d, J_{P-C} = 1.8 Hz, *C*H), 123.3 (d, J_{P-C} = 3.6 Hz, *C*H), 123.1 (d, J_{P-C} = 2.7 Hz, *C*H), 115.4 (s, *C*H), 110.8 (s, *C*), 72.4 (d, $^2J_{P-C}$ = 3.6 Hz, *C*H), 73.9 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 59.4 (d, $^1J_{P-C}$ = 61.8 Hz, *C*H), 24.0 (s, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 23.4 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 134.81 (bm). HRMS (ESI/TOF) Found m/z: 503.9927; $C_{19}H_{28}BrN_2O_4PB$ ([M+H]$^+$) requires m/z: 503.9933. Anal. Calcd for $C_{19}H_{27}BrN_2O_4PB$: C, 48.65 H, 5.80 N, 5.97. Found: C, 48.90, H, 5.75, N, 5.90.

[1-(N-p-Bromophenylamino)]-1-(p-nitrophenyl)methylphosphonous acid-borane diisopropyl ester (23e). **22e** (0.118 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23e** (0.093 g, 0.198 mmol, 79%) as a yellow solid, m.p. 85.9-86.9 °C. R_f = 0.40 (hexane/AcOEt 10:1). IR (ATR, solid): 3401, 2976, 2401, 1592, 1499, 1348, 1105, 733, 499 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18-8.21 (m, 2H), 7.55-7.60 (m, 2H), 7.18-7.21 (m, 2H), 6.41-6.43 (m, 2H), 4.79 (bs, 1H), 4.68 (d, J_{P-H} = 15.76 Hz, 1H), 4.63-4.70 (m, 1H), 4.53-4.60 (m, 1H), 1.31 (d, J_{H-H} = 6.18 Hz, 3H), 1.30 (d, J_{H-H} = 6.31 Hz, 3H), 1.23 (d, J_{H-H} = 5.99 Hz, 3H), 1.02 (d, J_{H-H} = 6.31 Hz, 3H), 0.10-0.90 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6 (d, $^5J_{P-C}$ = 2.7 Hz, N*C*), 144.91 (d, $^3J_{P-C}$ = 10.9 Hz, N*C*), 143.2 (d, $^2J_{P-C}$ = 2.30 Hz, *C*), 132.1 (s, *C*H), 129.1 (d, J_{P-C} = 3.6 Hz, *C*H), 123.3 (d, J_{P-C} = 2.7 Hz, *C*H), 115.3 (s, *C*H), 110.8 (s, *C*), 74.2 (d,$^2J_{P-C}$ = 3.6 Hz, *C*H), 73.9 (d, $^2J_{P-C}$ = 4.5 Hz, *C*H), 59.7 (d,$^1J_{P-C}$ = 60.9 Hz, *C*H), 24.1 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 3.60 Hz, *C*H_3), 23.4 (d, J_{P-C} = 4.5 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 134.81 (bm). HRMS (ESI/TOF) Found: m/z: 455.0722; $C_{19}H_{25}BrN_2O_4P$ ([M-BH_3+H]$^+$) requires m/z: 455.0730. Anal. Calcd for $C_{19}H_{27}BrN_2O_4PB$: C, 48.65; H, 5.80; N, 5.97. Found: C, 48.82; H, 6.20; N, 5.58.

[1-(N-p-Bromophenylamino)]-[1-(p-anisyl)methyl]phosphonous acid-borane diisopropyl ester (23f). **22f** (0.114 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23f** (0.0727 g, 0.16 mmol, 64%) as an oil. R_f = 0.89 (hexane/AcOEt 2:1). IR (ATR, thin film): 3402, 2978, 2386, 1594, 1494, 1247, 1102, 972, 811 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.31 (m, 2H); 7.17-7.20 (m, 2H), 6.84-6.87 (m, 2H), 6.45-6.50 (m, 2H), 4.60-4.67 (m, 1H), 4.54 (d, J_{P-H} = 17.02 Hz, 1H), 4.47-4.52 (m, 1H), 3.79 (s, 3H), 1.29 (d, J_{H-H} = 6.15 Hz, 3H), 1.28 (d, J_{H-H} = 6.47 Hz, 3H), 1.20 (d, J_{H-H} = 6.15 Hz, 3H), 0.96 (d, J_{H-H} = 6.15 Hz, 3H), 0.12-0.83 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4 (d, $^5J_{P-C}$ = 2.7 Hz, O*C*), 145.7 (d, $^3J_{P-C}$ = 11.8 Hz, N*C*), 131.9 (s, *C*H), 129.5 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H), 126.8 (d, $^2J_{P-C}$ = 2.7 Hz, *C*), 115.5 (s, *C*H), 113.6 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 110.0 (s, Br*C*), 73.8 (d, $^2J_{P-C}$ = 3.6 Hz, *C*H), 73.2 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 59.1 (d, $^1J_{P-C}$ = 64.5 Hz, *C*H), 55.2 (s, *C*H_3), 24.18 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 24.12 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.9 (d, J_{P-C} = 4.5 Hz, *C*H_3), 23.3 (d, J_{P-C} = 5.5 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 135.27 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -44.76 (bm). GC-MS m/z (rel. int. %): 292 [(*p-AnCH$_2$NHC$_6$H$_4$-Br*$^+$] (15), 291 (99), 290 (98), 289 (100), 288 (83), 167 [(*i*-PrO)$_2$POH$^+$] (26), 166 (16), 156 (25), 155 (26). Anal. Calcd for $C_{20}H_{30}BBrNO_3P$: C, 52.89; H, 6.66; N, 3.08. Found: C, 52.70; H, 6.16; N, 2.88.

N-p-Bromophenylaminomethylphosphonous acid-borane diisopropyl ester (23g). **22g** (0.0875 g, 0.25 mmol) was reacted with BH_3-SMe_2 (0.237 mL, 2.5 mmol) for 4 h according to general procedure **C** to afford **23g** (0.0435 g, 0.125 mmol, 50%) as an oil. R_f = 0.51 (hexane/AcOEt 6:1). IR (ATR, thin film): 3403, 2978, 2384, 1497, 971, 809 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25-7.28 (m, 2H), 6.54-6.55 (m, 2H), 4.60-4.71 (m, 2H), 3.91 (bs, 1H), 3.42 (d, J_{P-H} = 4.41 Hz, 2H), 1.32 (d, J_{H-H} = 6.15 Hz, 6H), 1.25 (d, J_{H-H} = 6.15 Hz, 6H), 0.20-0.91 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5 (d, J_{P-C} = 7.3 Hz, N*C*), 131.8 (s, *C*H), 114.9 (s, *C*H), 109.9 (s, *C*), 72.9 (d, $^2J_{P-C}$ = 4.5 Hz, *C*H), 44.8 (d, $^1J_{P-C}$ = 67.2 Hz, *C*H_2), 24.12 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.97 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 136.33 (bm). GC-MS m/z (rel. int. %): 335 (*[M-BH$_3$]*$^+$, 6), 333 (6). HRMS (ESI/TOF) Found m/z: 334.0573; $C_{13}H_{22}BrNO_2P$ ([M-BH_3+H]$^+$) requires m/z: 334.0566. Anal. Calcd for $C_{13}H_{24}BBrNO_2P$: C, 44.86; H, 6.95; N, 4.02. Found: C, 44.90; H, 6.80; N, 3.99.

1-[N-p-Hydroxyphenylamino]-(1-phenyl)methylphosphonous acid-borane diisopropyl ester (23h). **22h** (0.0908 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23h** (0.0605 g, 0.168 mmol, 67%) as a solid, m.p. 78.5-79.0 °C. R_f = 0.27 (hexane/AcOEt 6:1). IR (ATR, solid): 3247, 2980, 2394, 1511, 1103, 975, 696 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.40 (m, 2H), 7.24-7.31 (m, 3H), 6.60-6.64 (m, 2H), 6.48-6.51 (m, 2H), 4.61-4.64 (m, 1H), 4.58 (d, J_{P-H} = 16.71 Hz, 1H), 4.47-4.51 (m, 1H), 4.33 (bs, 1H), 1.29 (d, J_{H-H} = 6.31 Hz, 3H), 1.28 (d, J_{H-H} = 6.15 Hz, 3H), 1.21 (d, J_{H-H} = 6.15 Hz, 3H), 0.93 (d, J_{H-H} = 6.15 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2 (s, O*C*), 140.6 (d, $^3J_{P-C}$ = 11.8 Hz, N*C*), 145.6 (d, $^2J_{P-C}$ = 3.6 Hz, *C*), 128.5 (d, $^4J_{P-C}$ = 4.5 Hz, *C*H), 128.1 (d, $^3J_{P-C}$ = 1.8 Hz, *C*H), 127.8 (d, $^5J_{P-C}$ = 1.8 Hz, *C*H), 116.0 (s *C*H), 115.3 (s *C*H), 73.6 (d, $^2J_{P-C}$ = 4.5 Hz, *C*H), 73.1 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 60.8 (d, $^1J_{P-C}$ = 63.6 Hz, *C*H), 24.1 (d, $^3J_{P-C}$ = 1.8 Hz,*C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz,*C*H_3), 23.8 (d, $^3J_{P-C}$ = 5.5 Hz,*C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 136.02 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -44.58 (bm). HRMS (ESI/TOF) Found m/z: 362.2050; $C_{19}H_{30}BNO_3P$ ([M+H]$^+$) requires m/z: 362.2048. Anal. Calcd for $C_{19}H_{29}BNO_3P$: C, 63.18; H, 8.09; N, 3.88; Found: C, 63.45; H, 8.20; N, 4.00.

[1-(N-p-Anisylamino)-(1-phenyl)methyl]phosphonous acid-borane diisopropyl ester (23i). **22i** (0.0944 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23i** (0.059 g, 0.158 mmol, 63%) as an oil. R_f = 0.51 (hexane/AcOEt 10:1). IR (ATR, thin film): 3399, 2978, 2386, 1509, 1236, 1102, 977, 815 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.40 (m, 2H), 7.30-7.33 (m, 2H), 7.24-7.27 (m, 1H), 6.69-6.72 (m, 2H), 6.54-6.58 (m, 2H), 4.62-4.69 (m, 1H), 4.59 (d, J_{H-H} = 6.31 Hz, 1H), 4.47-4.55 (m, 1H), 3.70 (s, 3H), 1.30 (d, J_{H-H} = 6.15 Hz, 3H), 1.28 (d, J_{H-H} = 6.15 Hz, 3H), 1.22 (d, J_{H-H} = 6.15 Hz, 3H), 0.93 (d, J_{H-H} = 6.15 Hz, 3H), 0.17-0.81 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5 (s, O*C*), 140.7 (d, $^3J_{P-C}$ = 11.8 Hz, N*C*), 139.7 (d, $^2J_{P-C}$ = 2.7 Hz, *C*), 128.5 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H), 128.1 (d, $^4J_{P-C}$ = 1.8 Hz, *C*H), 127.4 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 115.2 (s, *C*H), 114.7 (s, *C*H), 73.6 (d,$^2J_{P-C}$ = 4.5 Hz, *C*H), 73.1 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 60.7 (d, $^1J_{P-C}$ = 63.6 Hz, *C*H), 55.8 (s, *C*H_3), 24.1 (d, $^3J_{P-C}$ = 1.8 Hz, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 23.2 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3).^{31}P NMR (202 MHz, $CDCl_3$) δ 136.02 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -44.62 (bm). HRMS (ESI/TOF) Found m/z: 362.1895; $C_{20}H_{29}NO_3P$ ([M-BH_3+H]$^+$)requires m/z: 362.1880. Anal. Calcd for $C_{20}H_{31}BNO_2P$: C, 64.01; H, 8.33; N, 3.73. Found: C, 64.30; H, 8.50; N, 3.68.

[1-(N-p-Tolylamino)-1-phenylmethyl]phosphonous acid-borane diisopropyl ester (23j). **22j** (0.0903 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 16 h according to general procedure **C** to afford **23j** (0.0629 g, 0.175 mmol, 70%) as an oil. R_f = 0.56 (hexane/AcOEt 10:1). IR (ATR, thin film): 3404, 2978, 2386, 1517, 1236, 1102, 976, 803 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.47 (m, 2H), 7.30-7.37 (m, 2H), 7.24-7.26 (m, 1H), 6.92-6.95 (m, 2H), 6.50-6.54 (m, 2H), 4.62-4.69 (m, 1H), 4.65 (d, J_{P-H} = 16.55 Hz, 1H), 4.49-4.57 (m, 1H), 2.20 (s, 3H), 1.31 (d, J_{H-H} = 6.78 Hz, 3H), 1.29 (d, J_{H-H} = 6.78 Hz, 3H), 1.22 (d, J_{H-H} = 6.15 Hz, 3H), 0.94 (d, J_{H-H} = 6.15 Hz, 3H),0.12-0.84 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3 (d, $^3J_{P-C}$ = 11.8 Hz, N*C*), 135.6 (d, $^2J_{P-C}$ = 3.6 Hz, *C*), 129.6 (s, *C*H), 128.4 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H), 128.1 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 127.7 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 127.4 (s, *C*), 113.9 (s, *C*H), 73.6 (d,$^2J_{P-C}$ = 3.6 Hz, *C*H), 73.0 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 60.0 (d, $^1J_{P-C}$ = 63.6 Hz, *C*H), 24.1 (d, $^3J_{P-C}$ = 1.8 Hz, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 23.2 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 20.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ 136.02 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -44.66 (bm). HRMS (ESI/TOF) Found m/z: 360.2245; $C_{20}H_{32}BNO_2P$([M+H]$^+$) requires m/z: 360.2255. Anal. Calcd for $C_{20}H_{31}BNO_2P$: C, 66.87; H, 8.70; N, 3.90. Found: C, 66.99; H, 8.85; N, 4.00.

[1-(N-p-Tolylamino)-(1-t-butyl)-methyl]phosphonous acid-borane diisopropyl ester (23k). **22k** (0.0853 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 72 h according to general procedure **C** to afford **23k** (0.0203 g, 0.06 mmol, 24%) as an oil. R_f = 0.72 (hexane/AcOEt 10:1). IR (ATR, thin film): 2976, 2384, 1518, 970, 753 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.95-6.99 (m, 2H), 6.56-6.59 (m, 2H), 4.48-4.71 (m, 2H), 3.93 (bs, 1H), 3.46 (dd, J_{H-H} = 10.40 Hz, J_{P-H} = 15.29 Hz, 1H), 2.24 (s, 3H), 1.29 (d, J_{H-H} = 6.15 Hz, 3H), 1.28 (d, J_{H-H} = 6.15 Hz, 3H), 1.27 (d, J_{H-H} = 6.15 Hz, 3H), 1.12 (s, 9H), 1.00 (d, J_{H-H} = 6.15 Hz, 3H), 0.29-0.85 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1 (d, $^3J_{P-C}$ = 3.6 Hz, N*C*), 129.5 (s, *C*H), 126.5 (s, *C*), 113.2 (s, *C*H), 72.8 (d, $^2J_{P-C}$ = 5.5 Hz, *C*H), 72.3 (d, $^2J_{P-C}$ = 6.4 Hz, *C*H), 64.1 (d, $^1J_{P-C}$ = 59.9 Hz, *C*H), 36.5 (d, $^2J_{P-C}$ = 11.8 Hz, *C*), 28.1 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 24.4 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 24.2 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.9 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 23.6 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 20.3 (s, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 139.14 (bm). HRMS (ESI/TOF) Found m/z: 340.2565; $C_{18}H_{36}BNO_2P$ [M+H]$^+$requires m/z: 340.2568. Anal. Calcd for $C_{18}H_{35}BNO_2P$: C, 63.72; H, 10.40; N, 4.13. Found: C, 63.45; H, 10.68; N, 4.38.

N-p-Tolylaminomethylphosphonous acid-borane diisopropyl ester (23l). **22l** (0.111 g, 0.25 mmol) was reacted with BH_3-SMe_2 (0.237 mL, 2.5 mmol) for 4 h according to general procedure **C** to afford **23l** (0.0311 g, 0.11 mmol, 44%) as an oil. R_f = 0.59 (hexane/AcOEt 10:1). IR (ATR, thin film): 3404, 2978, 2381, 1519, 1236, 1104, 971, 805 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.99-7.03 (m, 2H), 6.59-6.64 (m, 2H), 4.63-4.72 (m, 2H), 3.75 (bs, 1H), 3.44 (d, J_{P-H} = 4.57 Hz, 2H), 2.26 (s, 3H), 1.33 (d, J_{H-H} = 6.15 Hz, 6H), 1.27 (d, J_{H-H} = 6.15 Hz, 6H), 0.22-0.94 (bm, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2 (d, $^3J_{P-C}$ = 8.2 Hz, *C*), 129.6 (s, *C*H), 127.6 (s, *C*), 113.5 (s, *C*H), 72.7 (d, $^2J_{P-C}$ = 4.5 Hz, *C*H), 45.1 (d,$^1J_{P-C}$ = 66.3 Hz, *C*H_2), 24.1 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 24.0 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 20.4 (s, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 136.86 (bm).GC-MS m/z (rel. int. %): 269 ([*M-BH*$_3^+$], 3), 150 (5), 121 (10), 120 (100). HRMS (ESI/TOF) Found m/z: 270.1616; $C_{14}H_{25}NO_2P$ ([M-BH_3+H]$^+$) requires m/z: 270.1617. Anal. Calcd for $C_{14}H_{27}BNO_2P$: C, 59.38; H, 9.61; N, 4.95. Found: C, 59.45; H, 9.80; N, 4.90.

N-Phenylmethylaminomethylphosphonous acid-P,N-bisborane diisopropyl ester (27). **25** (0.0713 g, 0.25 mmol) was reacted with BH_3-SMe_2 (118.6 μL, 1.25 mmol) for 48 h according to general procedure **C** to afford **27** (0.178 g, 0.06 mmol, 24%) as an oil. R_f = 0.58 (hexane/AcOEt 4:1). IR (ATR, thin film): 2930, 2383, 1374, 969, 784, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$)δ 7.34-7.51 (m, 5H), 4.63-4.71 (m, 2H), 4.18 (bs, 1H), 3.95-4.15 (m, 2H), 3.03-3.26 (m, 2H), 1.42-2.07 (bm, 3H), 1.35 (d, J_{H-H}= 6.31 Hz, 3H), 1.34 (d, J_{H-H}= 6.15 Hz, 3H), 1.31 (d, J_{H-H}= 6.15 Hz, 3H), 1.27 (d, J_{H-H}= 5.99 Hz, 3H), 0.22-0.95 (bm, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4 (s, *C*), 130.0 (s, *C*H), 129.9 (s, *C*H), 128.8 (s, *C*H), 74.0 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H), 73.7 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H), 60.8 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_2), 54.9 (d, $^1J_{P-C}$ = 55.4 Hz, *C*H_2), 24.1 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 24.05 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 23.91 (d, $^3J_{P-C}$ = 1.8 Hz, *C*H_3), 23.88 (d, $^3J_{P-C}$ = 1.8 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 134.86 (bm). ^{11}B NMR (160.5 MHz, $CDCl_3$) δ -42.76 (bm), -12.94 (bm). HRMS (ESI/TOF) Found m/z: 270.1610; $C_{14}H_{25}NO_2P$ ([M-2BH_3+H]$^+$) requires m/z: 270.1617. Anal. Calcd for $C_{14}H_{30}B_2NO_2P$: C, 56.62, H, 10.18; N, 4.72. Found: C, 56.40, H, 10.30; N, 4.50.

Diisopropyl [1-(N-p-Bromophenylamino)]-1-phenylmethylthiophosphonate (29). In a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet was placed α-aminophosphonite-borane **23a** (0.0323 g, 0.076 mmol) in anhydrous toluene (2 mL). Then, was added DABCO (0.0172 mg, 0.152 mmol) and sulfur (0.068 g, 0.266 mmol). The resulting mixture was heated at 40 °C for 48 h. Then, the reaction mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel using hexane/AcOEt (v/v = 10:1) as eluent to afford **29** (0.03 g, 0.068 mmol, 88%). A colourless oil. R_f = 0.61 (hexane/AcOEt 6:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41-7.44 (m, 2H); 7.28-7.31 (m, 3H), 7.15-7.19 (m, 2H), 6.48-6.52 (m, 2H), 4.80-4.89 (m, 1H), 4.70 (d, J_{P-H} = 23.96 Hz, 1H), 4.45-4.52 (m, 1H), 1.31 (d, J_{H-H} = 6.31 Hz, 3H), 1.25(d, J_{H-H} = 6.31 Hz, 3H), 1.23(d, J_{H-H} = 5.99 Hz, 3H), 0.77(d, J_{H-H} = 6.31 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3 (d, $^3J_{P-C}$ = 15.4 Hz, N*C*), 131.5 (s, *C*), 131.9 (s, *C*H), 128.4 (d, $^4J_{P-C}$ = 5.5 Hz, *C*H), 128.1 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H), 128.0 (d, $^5J_{P-C}$ = 3.6 Hz, *C*H), 115.5 (s, *C*H), 109.9 (s, Br*C*), 73.3 (d, $^2J_{P-C}$ = 8.2 Hz, *C*H), 73.2 (d, $^2J_{P-C}$ = 7.3 Hz, *C*H), 60.4 (d, $^1J_{P-C}$ = 123.5 Hz, *C*H), 24.0 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.97 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.5 (d, J_{P-C} = 6.4 Hz, *C*H_3), 22.6 (d, J_{P-C} = 7.3 Hz, *C*H_3). ^{31}P NMR (202 MHz, $CDCl_3$) δ 89.59 (bm). GC-MS m/z (rel. int. %): 262 [(*C*$_6$*H*$_4$-*CH*$_2$*NH*-*C*$_6$*H*$_4$-*Br*)$^+$] (13), 261 (92, 259 (91), 258 (100), 257 (79), 228 (63), 226 (25), 183 [(*i*-PrO)$_2$P$^+$] (10) 182 (10). Anal. Calcd for $C_{19}H_{25}BrNO_2PS$: C, 51.59; H, 5.70; N, 3.17. Found: C, 51.99; H, 5.88; N, 3.05.

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FULL PAPER

The chemoselective reduction of P=O bond in α-hydroxy and α-amino phosphonic/phosphinic acid derivatives can be achieved without concomitant scission of their ester and amide bonds by the use of commercially available BH_3 complexes. The reduction involves an intramolecular assistance by the proximal OH or NH groups enabling preferential removal of the phosphoryl oxygen.

Chemoselective reduction

*Sylwia Sowa and K. Michał Pietrusiewicz**

1 – 16

Chemoselective reduction of the P=O bond in the presence of P-O and P-N bonds in phosphonate and phosphinate derivatives