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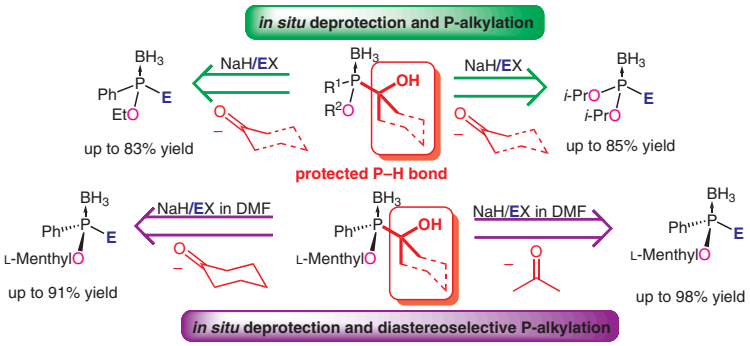
Alkylation of Phosphinite/Phosphonite-Boranes via Temporary Protection of the P–H Bond

Kamil Modzelewski
Sylwia Sowa*

Department of Organic Chemistry, Faculty of Chemistry, Institute of Chemical Sciences, Marie Curie-Sklodowska University in Lublin, 33 Gliniana St., Lublin 20-614, Poland
sylwia.sowa@poczta.umcs.lublin.pl



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Abstract A new alkylation protocol for the synthesis of tertiary phosphonite/phosphinite-boranes is developed. P-Alkylation products are obtained exclusively in moderate to very good yields from easily accessible (1-hydroxy-1-methylethyl)/(1-hydroxy-1-cyclohexyl) phosphonite/phosphinite-boranes upon reaction with a variety of electrophiles under mild conditions. The methodology opens up new synthetic routes for organophosphorus chemistry and offers access to valuable alkyl phosphonite/phosphinite-boranes. In contrast to previously reported oxidative removal–substitution sequences for the preparation of optically active phosphinite-boranes, our protocol provides a one-step procedure that occurs without loss of stereochemical information at phosphorus. This new approach provides a rather advantageous protocol when compared to direct alkylation methods (which may undergo P-epimerization) and occurs in a stereoselective manner even at 0 °C.

Key words alkylation, chemoselectivity, protecting group, in situ deprotection, phosphinite-boranes, phosphonite-boranes, diastereoselectivity

During the last 40 years, methods based on the temporary protection of P–H bonds have slowly been developed into a powerful synthetic strategy for the preparation of organophosphorus compounds.[1] First, Gallagher[2] and others[3] introduced the 'Ciba-Geigy reagents' (in which one P–H bond of hypophosphorous acid is masked temporarily), and these were extensively explored for the syntheses of many phosphonic and phosphinic acid derivatives,[4] some of them for biological purposes.[3c,4d] Later, Hall employed these compounds in an elegant preparation of non-symmetrical secondary phosphine oxides.[5] An interesting example of the deprotection of Ciba-Geigy reagents was presented by Baylis, who proved that removal of a ketal protecting group could be achieved using TMSCl in chloroform, in contrast to acetals which were not reactive under the same conditions.[6]

More recently, Montchamp's group applied an acetal protection–cleavage approach to a wide range of syntheses and transformations of *H*-phosphinates[7] and has also developed parallel chemistry using borane analogues.[8]

On the other hand, and even earlier, Kharasch observed that α-hydroxyalkylphosphonates under basic conditions (10% NaOH solution) underwent a retro-addition reaction enabling recovery of aldehydes.[9] On the basis of this investigation, Baylis developed conditions for an analogous deprotection method for 1-hydroxy-1-methylethylphosphonates/phosphinates and 1-hydroxy-1-methylethyl-*H*-phosphinates.[10] Later, a similar process of deformylation of α-hydroxymethylphosphine-boranes in the presence of KOH or under thermal conditions was described by Imamoto in 2000.[11]

In the same paper, an even more important approach based on oxidative degradation of a hydroxymethyl moiety was presented.[11] The decarboxylation of (*R*)-(adamantyl)hydroxymethyl(methyl)phosphine-borane using $RuCl_3$/$K_2S_2O_8$/KOH enabled access to the corresponding secondary phosphine-borane with excellent enantioselectivity and high yield. Later, a further precedent for the use of this procedure was reported by Buono where oxidative removal of the hydroxymethyl group in the case of adamantyl (hydroxymethyl)phenylphophinous acid-borane was effected with good yield and diastereoselectivity.[12]

An equally significant impact on the field of oxidative degradation processes was reported in a methodology introduced in 2012 by Montchamp's group.[13] They described another useful reagent, (hydroxymethyl)-*H*-phosphinic acid (prepared from H_3PO_2 and paraformaldehyde), the hydroxymethyl moiety of which could be oxidatively unmasked to provide the corresponding *H*-phosphinate. In contrast to Imamotos's decarboxylation process, this protocol features a Kim–Corey removal of the hydroxymethyl group proceeding via decarbonylation. This method

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allowed a large-scale preparation of diastereomerically pure L-menthyl (hydroxymethyl)-*H*-phosphinate [a chiral equivalent of an alkyl phosphinate, ROP(O)H_2],[14] which was shown to be a versatile intermediate for the synthesis of P-stereogenic compounds.[15]

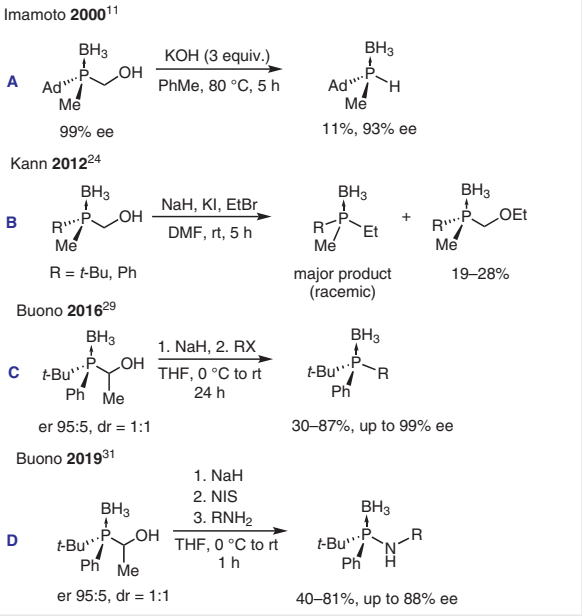
The above examples suggest that temporary masking of a P–H group can solve problems of chemoselectivity during transformations of hypophosphites and other organophosphorus compounds. A further advantage is that the protecting moiety can be re-introduced in a later step. An alternative strategy is to use masked species and cleave them in situ under reaction conditions that allow the typical reactivity of P–H-type compounds to be expressed. In 1977, Whitham and Postle reported the unexpected formation of 1,2-bis(diphenylphosphinoyl)ethane after treatment of diphenyl(hydroxymethyl)phosphine oxide with *n*-BuLi and Br_2.[16] Subsequently, Cristau observed the same retro-formylation process as a step in the reaction of diphenyl-(hydroxymethyl)phosphine oxide with diphenyl-(vinyl)phosphine oxide, also leading to the formation of 1,2-bis(diphenylphosphinoyl)ethane.[17]

Later, in situ deprotection became an intentional synthetic tactic enabling generation of the desired P anions or radicals, which could be smoothly and immediately reacted under the utilized reaction conditions. For example, Yuan showed that 1,1-diethoxyalkylphosphinates could be converted into phosphonates or phosphonamides in one-pot reactions that proceed through the *H*-phosphinate.[18]

During the last few years, a number of organophosphorus compounds possessing the hydroxyalkyl moiety have been used more extensively. α-Hydroxyalkylphosphonates have been employed for palladium-[19] and rhodium-catalyzed[20] phosphonation of C(sp^2)–H bonds. Meanwhile, Hayashi and co-workers have also presented a palladium-catalyzed P–C coupling reaction using (hydroxymethyl)diphenylphosphine sulfide as a $Ph_2P(S)H$ equivalent.[21] Recently, Chen performed a P–C bond cleavage and radical alkynylation of α-hydroxyalkyl/phosphonic/phosphinic acid derivatives and α-hydroxyalkylphosphine oxides.[22]

In early studies, the reverse additions to carbonyl compounds of α-hydroxyphosphine-boranes were observed by Imamoto[11] and others[23] under thermal, basic and oxidative (as mentioned before) conditions, and all of these cases were found to be compatible with the formation of the expected products featuring P–H bonds (Scheme 1, A). Kann and co-workers were the first to employ such reactivity as part of an in situ P-alkylation process, through the reaction of tertiary α-hydroxyphosphine-boranes with an electrophile in the presence of a base (Scheme 1, B).[24]

Pioneered by Köster[25] and continued by Keglevich[26] and others,[27] the employment of borane complexes as reducing agents for P=O bonds has opened new synthetic routes to phosphine-boranes. In the same way, the synthetic access to α-hydroxyphosphine-boranes has been improved recently, which enhances the potential of retro-addition reactions for the functionalization of α-hydroxyphosphine-boranes.[28] Buono[29] has developed an enantioselective alkylation methodology that uses P-stereogenic α-hydroxyalkyl-phosphine-boranes as precursors for a synthetically demanding class of optically active secondary phosphine-boranes[30] (Scheme 1, C).

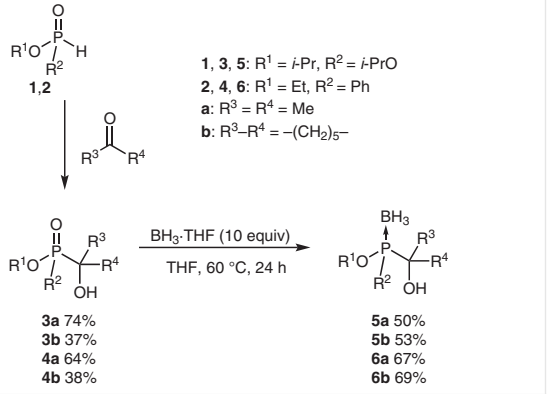


Scheme 1 Reported examples using an α-hydroxyalkyl group as a masking group in the P-alkylation of phosphine-boranes

In 2019 the same group used an analogous synthetic route to allow the synthesis of enantiomerically pure aminophosphine-boranes that involved the umpolung of an in situ generated P-anion (Scheme 1, D).[31]

Herein, we present our results concerning the alkylation of phosphinite-boranes and phosphonite-boranes; these are readily available via a recently reported chemoselective reduction of the P=O bond in α-hydroxyphosphonates and α-hydroxyphosphinates.[12,28b,d,32] To the best of our knowledge, there are only a few precedents for the direct alkylation of $(RO)_2P(BH_3)H$[8] and $(RO)RP(BH_3)H$,[12,33] presumably because of the poor availability of these species. Our method provides a promising pathway for overcoming this problem.

We began our study with the synthesis of a series of α-hydroxyphosphonite-boranes **5a**,**b** and α-hydroxyphosphinite-boranes **6a**,**b**. These are accessible through an Abramov reaction of compounds **1** and **2** with acetone or cyclohexanone leading to the corresponding phosphonates **3a**,**b** and phosphinates **4a**,**b** in moderate yields (see the Supporting Information). A subsequent chemoselective reduction of the P=O bond in presence of ester bonds in **3** and **4** afforded phosphonite/phosphinite-boranes **5** and **6** in good yields (Scheme 2).[32] Unfortunately, the yields achieved on gram scale for **5a**,**b** were lower than those reported

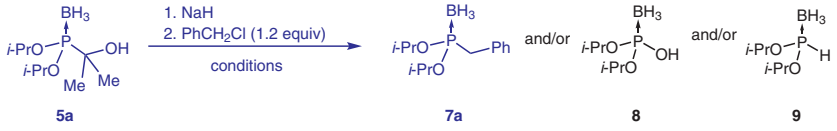


Scheme 2 Synthesis of α-hydroxyphosphonite/phosphinite-boranes

previously[32] due to the instability of these compounds during extraction. Still, our two-step procedure provides precursors **5** and **6** that can be stored at –20 °C for long periods of time. To develop the most selective conditions for the alkylation reaction, an optimization study was undertaken. Compound **5a** was used as the model starting material with benzyl chloride as the electrophile (Table 1).

We used sodium hydride as the base for the initial test reactions because it has been used regularly in earlier decarbonylative eliminations.[24,30,31] When compound **5a** was treated with an equimolar amount of NaH, even after 16 hours, it appeared that the starting material was not fully consumed in typical solvents (Et_2O, PhMe, THF) (Table 1, entries 1, 3 and 5). In Et_2O and PhMe, we observed the formation of an inseparable mixture of **8** (with a shift of 94.24 ppm in the ^{31}P NMR spectrum) and the *H*-phosphonite-borane **9** (with a shift of 121.8 ppm) rather than the expected product **7a** or its O-alkylation product (Table 1, entries 1 and 3). However, products **8** and **9** are both derived from the desired P-anion: acid **8** is presumably formed through its oxidation, whilst **9** is its protonation product. In THF, **5a** underwent partial deprotection–alkylation but the desired phosphonite-borane **7a** was obtained in only 10% yield (isolated) along with **8** and **9** (not isolated). Nonetheless, these preliminary results suggested that compound **5a** was a potentially good precursor of the P-anion, and that the P–C bond in α-hydroxyphosphonite-borane **5a** may be far more labile than has been found for other phosphine-boranes.[21] Using 1.5 equivalents of base in PhMe, Et_2O and THF led to complete conversion of **5a** and shifted the selectivity of the reaction towards the formation of **7a** (Table 1, entries 2, 4 and 6). It should be noted, however, that the desired

Table 1 Optimization of the Conditions for the Reaction of **5a** with Base and Benzyl Chloride



Entry	Base (equiv)	Conditions	Yield (%)[a,b] 7a	8	9
1[c]	NaH (1.0)	Et_2O, 0 °C to 25 °C, 16 h	–	0 (44)	0 (11)
2	NaH (1.5)	Et_2O, 0 °C to 25 °C, 16 h	15 (25)	0 (62)	0 (11)
3[c]	NaH (1.0)	PhMe, 0 °C to 25 °C, 16 h	–	0 (36)	0 (15)
4	NaH (1.5)	PhMe, 0 °C to 25 °C, 16 h	40 (51)	–	0 (49)
5[c]	NaH (1.0)	THF, 0 °C to 25 °C, 16 h	10 (25)	0 (60)	0 (11)
6	NaH (1.5)	THF, 0 °C to 25 °C, 16 h	58 (90)	–	–
7	NaH (1.0)	DMF, 0 °C to 25 °C, 40 min	28 (60)	0 (20)	0 (15)
8	NaH (1.5)	DMF, 0 °C to 25 °C, 40 min	38 (60)	0 (30)	trace
9[d]	NaH (1.5)	DMF, 0 °C to 25 °C, 40 min	37 (64)	0 (34)	trace
10[e]	NaH (1.5)	DMF, 0 °C to 25 °C, 40 min	72 (90)	–	–
11	DIPEA (1.5)	MeCN, 25 °C, 4 h	–	–	–
12	DBU (1.0)	THF, 25 °C, 24 h	–	–	–

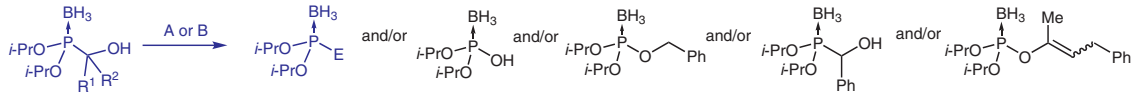
[a] Yields of isolated products.
[b] Numbers in parentheses indicate yields according to ^{31}P NMR spectroscopy.
[c] Starting material **1a** was still present in the reaction mixture.
[d] Pure NaH (95%) was used.
[e] The base was added after addition of the electrophile

compound **7a** was the major product only in THF and could only be isolated in moderate yield (58%) (Table 1, entry 6). Given these results, and the earlier work of Kann et al. showing the beneficial effect of DMF on the P-alkylation of phosphidoboranes that are transiently generated from hydroxymethylphosphine-boranes (Scheme 1, B),[24] we were led to screen this solvent. When the reaction was carried out in DMF, total conversion of the starting material was observed after 40 minutes, even when a stoichiometric amount of base was used, and subsequent reaction with the electrophile led predominantly to **7a** (Table 1, entry 7).

Increasing the amount of base to 1.5 equivalents resulted in a higher yield of the P-alkylation product (38%) (Table 1, entry 8), although byproducts **8** and **9** were still observed. Even using dry NaH did not limit the formation of **8** (Table 1, entry 9). After a number of further unsuccessful attempts to prevent the partial oxidation of the in situ generated anion, we reversed our standard procedure and added the base *after* the addition of the electrophile. This provided the product in 72% yield without the formation of significant amounts of acid **8** (Table 1, entry 10). Unfortunately, in both protocols, purification of the crude reaction mixture was accompanied with partial loss of **7a** that was even more severe when extraction was involved (Table 1, entries 6 and 10). It should be noted that reactions carried out with organic bases such as DBU or DIPEA[7] did not give any product, and in these cases the starting material was recovered unchanged (Table 1, entries 11 and 12). Subsequent studies therefore employed the conditions used for entries 6 and 10, in THF and DMF respectively. These appear to be the most appropriate solvents for the transformation.

Once optimization had been completed, we decided to check the reactivity of **5a** towards other electrophiles using both sets of conditions (Table 2) (see Table 1, entry 6 for conditions A and entry 10 for conditions B). The use of a more hindered benzyl halide (Table 2, entry 2) showed no influence upon the reaction selectivity in DMF and provided **7c** in 83% yield. When **5a** was treated with MeI according to conditions B, the main observed reaction product was **7b** that was isolated in 53% yield (Table 2, entry 8). The same excellent chemoselectivity was observed when the reaction was carried out in DMF (Table 2, entry 3). However, in this

Table 2 Reactivity of Compounds **5a**,**b** under Optimized Reaction Conditions



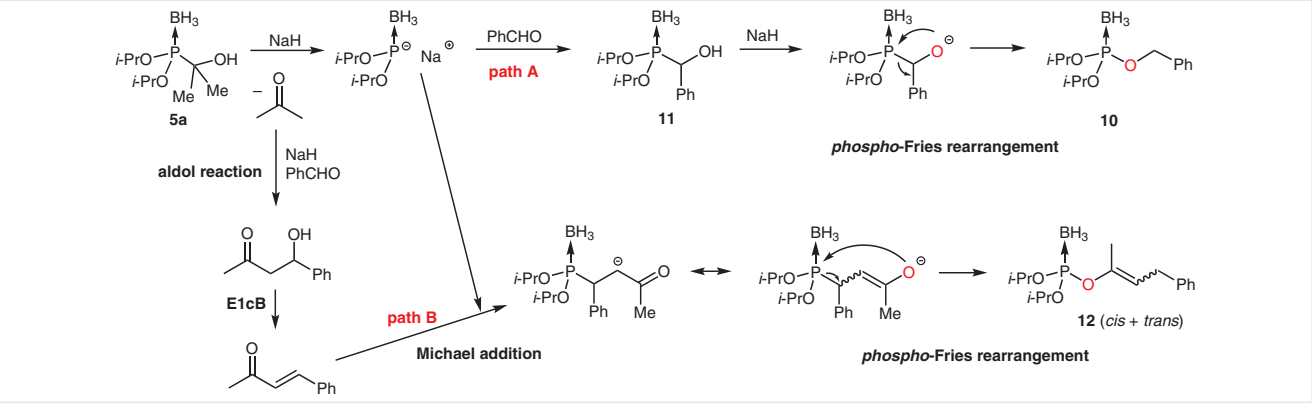
5a $R^1 = R^2 = Me$
5b $R^1–R^2 = –(CH_2)_5–$

7a–c **8** **10** **11** **12**

A: EX (1.2 equiv), NaH (1.5 equiv), DMF, 0 °C, 3 min, then 0–25 °C, 40 min
B: EX (1.2 equiv), NaH (1.5 equiv), THF, 0 °C, 3 min, then 0–25 °C, 16 h

Entry	Reactant	EX	Conditions	Product	Yield (%)[a,b]
1	**5a**	$PhCH_2Cl$	A	**7a**	72 (90)
2	**5a**	$2\text{-}MeC_6H_4CH_2Cl$	A	**7b**	83 (90)
3[c]	**5a**	MeI	A	**7c**	0 (100)
4	**5a**	PhCHO	A	**10** **8**	54 (70) 0 (30)
5	**5b**	$PhCH_2Cl$	A	**7a**	85 (93)
6	**5b**	PhCHO	A	**10** **8**	49 (59) 0 (41)
7	**5a**	$PhCH_2Cl$	B	**7a**	58 (90)
8	**5a**	MeI	B	**7c**	53 (90)
9[d]	**5a**	PhCHO	B	**10** **12**	16 31
10	**5b**	$PhCH_2Cl$	B	**7a** **8**	37 (59) 0 (41)
11[c]	**5b**	PhCHO	B	**11** **10**	61 33

[a] Yields of isolated products.
[b] Numbers in parentheses indicate the yields according to ^{31}P NMR spectroscopy.
[c] EX (1.5 equiv) was used.
[d] Yields according to ^1H NMR spectroscopy. Compounds **10** and **12** were isolated as a mixture.The major isomer (7%) was separated from a mixture of **10** and **12**. Compound **12** was obtained as mixture of geometric isomers (ratio = 1:0.81). The stereochemistry of the geometric isomers of **12** was not defined. The appearance of the C=CH group in the ^1H NMR spectra of both diastereoisomers is very similar and did not give clear insight in the stereochemistry of the structure of geometric isomers.

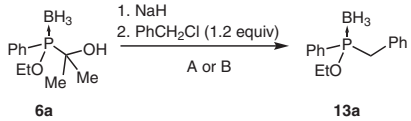


Scheme 3 Proposed mechanism of the formation of products **10** and **12**

case, because **7b** is volatile, the product was completely lost during removal of the solvent. Attempted alkylation of the more hindered phosphonite-borane **5b** with benzyl chloride was achieved successfully in DMF with the same selectivity as for **5a** (85% yield of **7a**) (Table 2, entry 5). However, when the solvent was changed to THF, compound **7a** was obtained as a mixture with **8**, of which **7a** was isolated in only 37% yield (Table 2, entry 10). Finally, we wanted to check the addition of an in situ generated P-anion to a carbonyl group. Unexpectedly, the outcome of the reaction with benzaldehyde appeared to depend on both the reaction conditions and the structure of the ketone leaving from **5** (Table 2, entries 4, 6, 9 and 11). When compound **5a** was subjected to reaction with a base and subsequently with benzaldehyde in THF, a mixture of **10** and **12** was obtained (16% and 31%, respectively, according to the ^{1}H NMR spectrum) (Table 2, entry 9). Compound **10** results from the expected P-anion addition to the carbonyl group and a subsequent *phospho*-Fries rearrangement (Scheme 3, path A).[34] Formation of product **12** (as a mixture of *cis*/*trans* isomers) was unexpected (Scheme 3, path B); it seems that 4-phenylbut-3-en-2-one was formed in an initial aldol condensation of acetone with benzaldehyde, and this Michael acceptor then reacted with the P-anion to form an adduct that also underwent *phospho*-Fries rearrangement[34] to give the two isomers of the phosphorus ester **12** (Scheme 3, path B). Subjecting **5a** to the same reaction under conditions A led predominantly to **10** (in a mixture with **8**), which was isolated in 54% yield (Table 2, entry 4). An analogous reaction sequence from **5b** revealed similar selectivity and provided **10** (49%) in a mixture with **8** (not isolated) (Table 2, entry 6). Surprisingly, when **5b** was treated with benzaldehyde under conditions B, the selectivity changed dramatically. In this case the major species observed in the crude NMR spectrum was the desired product **11** (~90%) along with traces of ester **10** (Table 2, entry 11). However, an aqueous work-up promoted the transformation of product **11** into **10**, so that **11** and **10** were finally isolated in respective yields of 61% and 33%.

Next, we investigated the structurally similar α-hydroxyphosphinite-boranes **6** possessing a single ester group at phosphorus. Initially, we decided to check both protocols to choose the most appropriate set of conditions for the reaction of **6a** (Table 3). Compound **6a** proved to be more prone to unmasking and in situ alkylation with benzyl chloride than **5a**, and it reacted well in the presence of a stoichiometric amount of base (Table 3, entries 1 and 3). The use of 1.5 equivalents of sodium hydride lowered the reaction selectivity in both THF and DMF (Table 3, entries 2 and 4). Thus, the best chemoselectivity towards P-alkylation was observed when a 1:1 ratio of **6a**/NaH was used, with the reaction of benzyl chloride with **6a** leading exclusively to **13a**, which was isolated in 76% yield (Table 3, entry 1).

Table 3 Optimization of the Ratio of **6a**/NaH in the Reaction of **6a** with Benzyl Chloride



6a **13a**

A: DMF, 0 °C, 3 min, then 0 to 25 °C, 40 min
B: THF, 0 °C, 3 min, then 0 to 25 °C, 16 h

Entry	NaH (equiv)	Conditions	Yield of **13a** (%)[a,b]
1	1.0	A	76 (100)
2	1.5	A	44 (48)
3	1.0	B	59 (72)
4	1.5	B	48 (52)

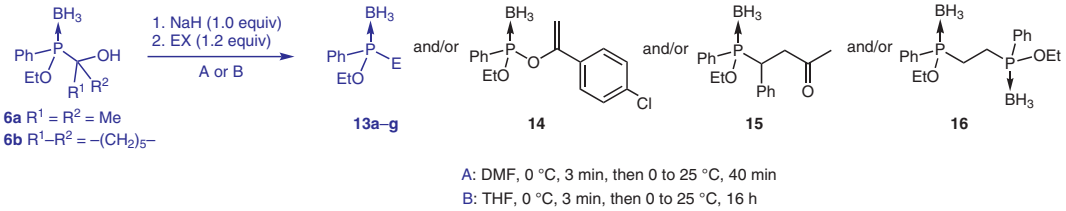
[a] Yield of isolated product.
[b] Numbers in parentheses indicate the yields according to ^{31}P NMR spectroscopy.

The data collected in Table 4 indicates that most alkyl halides are highly reactive in the alkylation of P-anions that are formed in situ from **6a** under the optimized conditions. In most cases, conversion is high, and moderate to high yields of **13a–f** were obtained (Table 4, entries 1–9). Inter-

estingly, when 2,4′-dichlorobenzophenone was used as the electrophile with **6a**, two products, **13g** and **14**, were isolated in yields of 24% and 64%, respectively. Once again, the formation of **14** (Table 4, entry 10) can be attributed to a *phospho*-Fries rearrangement[34] analogous to those observed in the case of **5a** and benzaldehyde (see Table 2, entries 4, 6, 9 and 11). We also checked the reactivity of inactivated electrophiles in the P-alkylation reaction. When *i*-PrBr was used in the reaction with **6a**, the selectivity of the reaction decreased, although complete conversion of **6a** was achieved and the expected product **13d** was isolated in a modest yield (Table 4, entry 6). In sharp contrast to *i*-PrBr, subjecting *i*-PrOTs to the reaction with **6a** resulted in a complex mixture (Table 4, entry 7). In this case, product **13d** was formed in poor conversion (12%) according to the ^{31}P NMR spectrum of the crude reaction mixture.

Subsequently, we increased the steric crowding around the α carbon of the nucleophile precursor to investigate any potential effect upon the reaction outcome. It was found that the cleavage of cyclohexanone from **6b** and subsequent alkylation with benzyl chloride was as efficient as the corresponding acetone elimination from **6a**; thus, phosphinite-borane **13a** was obtained in 70% yield (Table 4, entry 13). However, when *i*-PrI was chosen as the electrophile, the starting material was not fully consumed and the product **13d** was isolated in a much lower 44% yield (Table 4, entry 14). Furthermore, the reaction of **6a** with benzaldehyde under these conditions showed lower selectivity (Table 4, entry 11) than was observed with **5a** and **5b** (see Table 2, entries 4, 6, 9 and 11). The only product detected was **15**; this again must be assumed to arise from the Michael addition of the P-anion to in situ generated 4-phenylbut-3-en-2-one (from the aldol condensation of acetone and benzaldehyde)

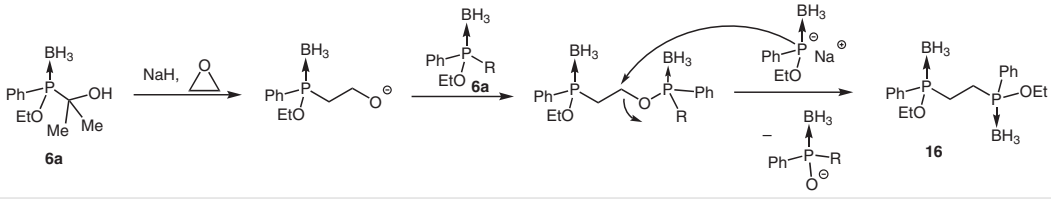
Table 4 Scope of the P-Alkylation of Compounds **6a**,**b**



A: DMF, 0 °C, 3 min, then 0 to 25 °C, 40 min
B: THF, 0 °C, 3 min, then 0 to 25 °C, 16 h

Entry	Reactant	EX	Conditions	Product	Yield (%)[a,b]
1	**6a**	$PhCH_2Cl$	A	**13a**	76 (100)
2	**6a**	$2\text{-}MeC_6H_4CH_2Cl$	A	**13b**	62 (100)
3	**6a**	MeI	A	**13c**	83 (100)
4[c]	**6a**	*i*-PrI	A	**13d**	63 (100)
5	**6a**	*i*-PrI	A	**13d**	55 (90)
6	**6a**	*i*-PrBr	A	**13d**	43 (82)
7[d]	**6a**	*i*-PrOTs	A	**13d**	0 (12)
8[d]	**6a**	$CH_2{=}CHCH_2Br$	A	**13e**	79 (90)
9[c]	**6a**	$MeOCH_2Cl$	A	**13f**	65 (100)
10[e]	**6a**	$ClCH_2C(O)C_6H_4Cl\text{-}p$	A	**13g**	24
11[f]	**6a**	PhCHO	A	**15**	7 (10)
12	**6a**	ethylene oxide	A	**16**	13
13	**6b**	$PhCH_2Cl$	A	**13a**	70 (100)
14[c,d]	**6b**	*i*-PrI	A	**13d**	44 (85)
15[g]	**6a**	PhCHO	B	**15**	30 (33)
16	**6a**	ethylene oxide	B	**16**	26

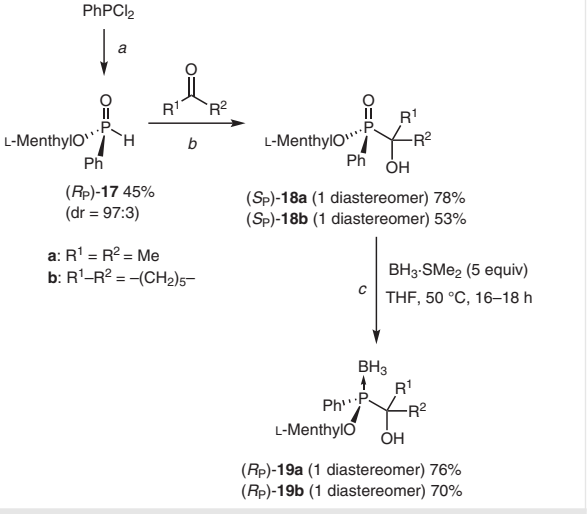
[a] Yield of isolated product.
[b] Numbers in parentheses indicate the yields according to ^{31}P NMR spectroscopy.
[c] EX (1.5 equiv) was used.
[d] Starting material **6a** was still present in the reaction mixture.
[e] Compound **13g** was obtained in a mixture with **14** (isolated in 64% yield).
[f] Compound **15** was obtained and isolated as a mixture of diastereoisomers (dr = 1:0.53 according to the ^{1}H NMR spectrum).
[g] Compound **15** was obtained and isolated as a mixture of diastereoisomers (dr = 1:0.48 according to the ^{1}H NMR spectrum).



Scheme 4 A plausible mechanism for the formation **16** via a β-hydroxyphosphinite-borane; R = $C(Me)_2OH$

and was isolated in 7% yield. The use of conditions B increased the yield of **15** to 30% (Table 4, entry 15). Attempted reaction of **6a** with ethylene oxide failed to afford the expected β-hydroxyethyl-substituted product. Instead, we observed the formation of **16** which was isolated in 13% (when using DMF as the solvent) and 26% (using THF) yields (Table 4, entries 12 and 16). We propose that compound **16** is formed according to the mechanism depicted in Scheme 4. First, the in situ formed P-anion undergoes reaction with ethylene oxide to give the corresponding alkoxide anion, subsequent reaction of which with another molecule of **6a** leads transiently to a diphosphorus-containing intermediate. This reacts with a further P-anion to afford the isolated product **16**.

P-Stereogenic phosphinates were obtained from (R_P)-**17**, which had been prepared in 45% yield (dr = 97:3) according to the procedure reported by Mislow[35] and Han[36] (Scheme 5, step *a*) (see the Supporting Information). (R_P)-**17** then reacted with acetone and with cyclohexanone (Scheme 5, step *b*) to afford the α-hydroxyphosphinates (S_P)-**18a** and (S_P)-**18b**, respectively, in good yields and with excellent stereoselectivity.[32b]



Scheme 5 Synthesis of α-hydroxyphosphonite/phosphinite-boranes

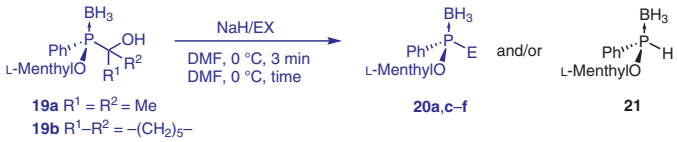
Reduction of (S_P)-**18a** and (S_P)-**18b** (Scheme 5, step *c*) with 5 equivalents of $BH_3{\cdot}SMe_2$ at 50 °C for 16–18 hours proceeded with complete chemoselectivity and led to the complete conversion of the starting material in both cases. The expected phosphinite-boranes (R_P)-**19a** and (R_P)-**19b** were isolated as single diastereoisomers (determined on the basis of ^{31}P NMR spectroscopy) in 76% and 70% isolated yields, respectively. Their configurations were estimated on the basis of previous reports which described the reduction with BH_3 complexes as a stereoinvertive process.[12,28b,d,32]

Having in hand P-stereogenic α-hydroxyphosphinite-boranes (R_P)-**19a** and (R_P)-**19b**, we turned our attention to address the important question of diastereoselectivity in the P-alkylation process (Table 5). Diastereoselective transformations of these molecules would provide a valuable alternative to literature methods, which involve either direct alkylation[33] or oxidation–substitution[12] approaches. Despite the fact that compounds of type **19** are achieved in a three-step synthesis (Scheme 5), their advantage is that they can be stored at –20 °C for prolonged periods without loss of stereochemical information, and this makes them good precursors for other key P-stereogenic compounds.

It was reassuring to find that **19a** provided product **20a** in a completely chemo- and diastereoselective fashion within 40 minutes at 0 °C after treatment with benzyl chloride (Table 5, entry 1). For comparison, an analogous synthesis was attempted in THF over 16 hours. In the presence of one equivalent of base, it was found that the selectivity of the P-alkylation reaction was dramatically lower, and a mixture containing **19a** and **20a** (isolated in 43% yield) along with two other undetermined products was obtained (Table 5, entry 2). Increasing the quantity of NaH to 1.5 equivalents in the same solvent allowed the chemoselectivity to be shifted towards **20a**, but it was still obtained as a mixture of diastereoisomers in a 1:0.28 ratio and in 98% yield (Table 5, entry 3). These results appear to confirm that the reactions carried out in DMF provide the most appropriate conditions for obtaining products **20** diastereoselectively.

When methyl iodide was used as the electrophile in reactions with **19a** under the optimized conditions, the conversion of the starting material was lower and product **20c** was isolated in a modest 63% yield (Table 5, entry 4). However, nearly quantitative formation of **20c** (83% isolated

Table 5 Diastereoselective P-Alkylation of Compounds **19a**,**b**



19a $R^1 = R^2 = Me$
19b $R^1–R^2 = –(CH_2)_5–$

20a,**c**–**f** **21**

Entry	Reactant	NaH (equiv)/EX (equiv)	Time	Product	Yield (%)[a,b]
1	(R_P)-**19a**	NaH (1.0)/$PhCH_2Cl$ (1.2)	40 min	(S_P)-**20a**	98 (100)
2[c]	(R_P)-**19a**	NaH (1.0)/$PhCH_2Cl$ (1.2)	16 h	(S_P)-**20a**	43 (45)
3[c]	(R_P)-**19a**	NaH (1.5)/$PhCH_2Cl$ (1.2)	16 h	**20a**	98 (100, dr = 1:0.28)
4[d]	(R_P)-**19a**	NaH (1.0)/MeI (1.2)	40 min	(S_P)-**20c**	63 (70)
5[d]	(R_P)-**19a**	NaH (1.0)/MeI (2.0)	40 min	(S_P)-**20c**	83 (93)
6[d]	(R_P)-**19a**	NaH (1.0)/*i*-PrI (1.5)	40 min	(S_P)-**20d**	68 (70)
7	(R_P)-**19a**	NaH (1.05)/*i*-PrI (2.5)	2 h	(S_P)-**20d**	80 (100)
8[d]	(R_P)-**19a**	NaH (1.05)/*i*-PrBr (2.5)	2 h	(S_P)-**20d**	45 (77)
9	(R_P)-**19a**	NaH (1.05)/*i*-PrOTs (2.5)	2 h	(S_P)-**20d**	0 (10)
10[d]	(R_P)-**19a**	NaH (1.05)/CH_2=$CHCH_2Br$ (1.5)	2 h	(S_P)-**20e**	80 (90)
11[d,e,f]	(R_P)-**19a**	NaH (1.0)/$MeOCH_2Cl$ (1.2)	40 min	(R_P)-**20f** **21**	20 (30) 11 (15)
12[d,g]	(R_P)-**19a**	NaH (1.05)/$MeOCH_2Cl$ (2.5)	2 h	(R_P)-**20f**	44 (57)
13	(R_P)-**19b**	NaH (1.0)/$PhCH_2Cl$ (1.2)	40 min	(S_P)-**20a**	85 (100)
14[d]	(R_P)-**19b**	NaH (1.05)/MeI (2.5)	1 h	(S_P)-**20c**	91 (98)
15[d]	(R_P)-**19b**	NaH (1.05)/*i*-PrI (2.5)	2 h	(S_P)-**20d**	66 (71)
16[d]	(R_P)-**19b**	NaH (1.05)/CH_2=$CHCH_2Br$ (2.5)	2 h	(S_P)-**20e**	66 (75)

[a] Yield of isolated product.
[b] Numbers in parentheses indicate the yields according to ^{31}P NMR spectroscopy.
[c] Reaction was carried out in THF.
[d] Starting material was still present in the reaction mixture.
[e] Compounds **20e** and **21** were isolated as a mixture.
[f] Yield according to ^1H NMR spectroscopy.
[g] Traces of **21** were observed in the crude reaction mixture but not isolated.

yield) was achieved upon treatment of **19a** with 2 equivalents of MeI (Table 5, entry 5). Difficulties in effecting full conversion of the starting material were also observed with other electrophiles. The use of a secondary alkyl iodide (*i*-PrI) in the reaction with **20a** led to only 70% of the product in the crude reaction mixture (according to ^{31}P NMR spectroscopy), from which the desired product **20d** was isolated as a single diastereoisomer in 68% yield (Table 5, entry 6). To obtain complete conversion of **19a** in the reaction with isopropyl iodide, we increased the amount of base and electrophile; this allowed us to prepare **20d** as the sole product in 80% isolated yield (Table 5, entry 7). In turn, when *i*-PrBr was used as the electrophile in the reaction with **19a** under the same conditions, the conversion of the starting material was not complete and the product **20d** was isolated in 45% yield (Table 5, entry 8). The worst performance of compound **19a** in an alkylation was observed with *i*-PrOTs. In this reaction 10% of **20d** was observed in the ^{31}P NMR spectrum of the crude reaction mixture (Table 5, entry 9). An analogous reaction of **19a** with allyl bromide afforded **20e** in 80% yield in the presence of 1.5 equivalents of the electrophile (Table 5, entry 10). Poor performance in the alkylation of **19a** was evident in the reaction with $MeOCH_2Cl$ (MOMCl). In this case, our standard conditions gave a mixture containing unreacted compound **19a** along with products **20f** and **21**, isolated as a mixture that provided 20% and 11% yields, respectively (according to the ^1H NMR spectrum) (Table 5, entry 11). Unfortunately, even under improved conditions, compound **19a** provided **20f** in only 44% yield (Table 5, entry 12). However, compound **19b** showed good selectivity in the in situ alkylation process; prior addition of benzyl chloride along with one equivalent of the base allowed the desired product **20a** to be isolated in 85% yield (Table 5, entry 13). Reactions of **19b** with other electrophiles were also performed under the modified conditions (Table 5, entries 14–16). In the reaction of **19b** with MeI, the starting material was nearly fully consumed after 1 hour and product **20c** was obtained in a very high 91% yield (Table 5, entry 14). Unlike **19a**, treatment of **19b** with isopropyl iodide or allyl bromide led to only a 71–75%

conversion of the starting material after 2 hours, and both **20d** and **20e** were obtained in moderate yields (Table 5, entries 15 and 16). These results suggest that the basic cleavage of cyclohexanone from **19b** is slower than that of acetone from **19a** (Table 5, entries 6 and 15). It appears also that overall ketone cleavage reflects the reactivity of the electrophile used in the P-alkylation reaction.

It is noteworthy that all the products of the reactions carried out in DMF were obtained as single diastereoisomers, both observed in the crude reaction mixtures and isolated as the sole diastereoisomers (determined on basis of ^{31}P NMR spectroscopy).

According to the literature, direct alkylation of Ph(MenthylO)P(BH_3)H at phosphorus proceeds with retention of configuration, with the P-anion being responsible for the attack at the electrophile.[33a] It is also important to note that removal of the hydroxymethyl group under oxidative conditions from a P-stereogenic adamantyl (hydroxymethyl)-phenylphophinous acid-borane had no influence on the configuration at the phosphorus atom.[12]

Overall, it appears reasonable to expect that a P-anion is generated slowly during our protocols and that it is gradually alkylated with the electrophile. This is supported by the presence of starting material in some cases after quenching the reaction mixture. The dramatic differences in the reaction times in THF and DMF might be explained by their solvating properties. Less polar THF slowed the P-alkylation process, which in turn resulted in longer reaction times. This presumably allows side reactions to take place (e.g., protonation, oxidation). DMF is more polar than THF, which leads to an increased rate of the alkylation process, even with more bulky electrophiles (e.g., *i*-PrI).

In sharp contrast to the partial or complete racemization of α-hydroxyphosphine-boranes in DMF,[24,30] (R_P)-**19a** and (R_P)-**19b** exhibited enhanced configurational stability of the in situ generated P-anion. This is consistent with earlier observations from the Imamoto group; these showed that this type of anion, generated via direct deprotonation of Ph(MenthylO)P(BH_3)H in the presence of an excess of base, is stable in THF at 0 °C and undergoes diastereoselective alkylation with MeI.[33a] It seems possible that the bulky menthoxy substituent is responsible for the enhanced stability of these species.

In summary, we have presented an efficient method for the in situ P-alkylation of α-hydroxyphosphinite/phosphonite-boranes in which the P–H bond is temporarily protected as a hydroxyalkyl derivative. Two protocols for the synthesis of alkyl phosphinite/phosphonite-boranes using a range of electrophiles have been presented. A straightforward and new diastereoselective approach allowing the alkylation of P-stereogenic α-hydroxyphosphinite-boranes under mild conditions via a retro-Abramov reaction in the presence of a base has also been demonstrated. The configurational stability of P-stereogenic α-hydroxyphosphinite-boranes under the described reaction conditions makes them useful precursors that can be converted into key P-stereogenic species with high stereospecificity.

All reactions were performed under an argon atmosphere using Schlenk techniques. Anhydrous 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, Et_2O and toluene were distilled from sodium/benzophenone ketyl under argon. Caution! All reactions and column chromatography must be carried out in an efficient fume hood because of the irritating odor accompanying the isolation process. Thin-layer chromatography (TLC) was performed with Merck precoated silica gel plates and samples were visualized under UV light or with $KMnO_4$ solution or iodine. The reaction products were purified by column chromatography over Fluka silica gel (60–240 mesh), Merck basic Al_2O_3 (70–230 mesh) or Merck neutral Al_2O_3 (70–230 mesh).

Melting points were determined on a Büchi Melting Point M-560 apparatus in a capillary tube and are uncorrected. Optical rotations were measured on a Perkin Elmer 341LC polarimeter using a 1 mL cell with a 10 mm path length and are reported as follows: $[\alpha]_D^{25}$ (*c*: g/100 mL, in solvent). IR spectra were recorded as solids or thin films on a Thermo Scientific Nicolet iS50 FT-IR ATR fitted with a diamond prism (4000–400 cm^{-1} window); only the strongest/structurally most important peaks (cm^{-1}) are listed. ^{1}H NMR, ^{11}B NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker Avance 500 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Chemical shifts (δ) are reported in ppm from tetramethylsilane with the solvent as an internal standard ($CDCl_3$: 7.27 ppm for ^{1}H and 77 ppm for ^{13}C). Mass spectra were recorded on a Shimadzu GC-MS QP2010S mass spectrometer in electron ionization (EI) mode. HPLC-HRMS was performed on a Shimadzu HRMS ESI-IT-TOF instrument using a reverse-phase stationary phase with water/MeCN (65:35) as eluent, electrospray ionization (ESI), and an IT-TOF detector. Elemental analyses were recorded on a PERKIN ELMER CHN 2400.

Alkylation of α-Hydroxyphosphinite-Boranes and α-Hydroxyphosphonite-Boranes in THF; General Procedure B

To a Schlenk tube (25 mL) equipped with a magnetic stir bar and an argon inlet was added α-hydroxyphosphonite-borane **5** (0.25 mmol) or α-hydroxyphosphinite-borane **6** (0.25 mmol) in anhydrous degassed THF (2 mL) and the resulting mixture was cooled to 0 °C using an ice bath. NaH (15 mg, 0.375 mmol, 60% in mineral oil or 10 mg, 0.25 mmol, 60% in mineral oil) was added and the mixture was stirred at the same temperature for 3 min. The electrophile (0.3 mmol) was then added and the ice bath was removed. The reaction mixture was stirred at room temperature for 16 h and then quenched by addition of saturated NH_4Cl solution (1 mL) and extracted with $CHCl_3$ (5 × 5 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by short (5 cm) column chromatography on neutral Al_2O_3 using hexane/EtOAc (40:1 v/v) or *n*-pentane/EtOAc (100:1 v/v) as the eluent.

Benzylphosphonous Acid-Borane Diisopropyl Ester (7a) (Table 2, entry 7), General Procedure B

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **7a** (0.0368 g, 0.145 mmol, 58%) as a colorless oil.

R_f = 0.36 (hexane/EtOAc, 40:1).

IR (ATR, thin film): 2978, 2929, 2484, 1104, 974, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.30 (m, 5 H), 4.51–4.60 (m, 2 H), 3.11 (d, J_{P-H} = 11.82 Hz, 2 H), 1.28 (d, J_{H-H} = 6.15 Hz, 6 H), 1.13 (d, J_{H-H} = 6.15 Hz, 6 H), 0.15–0.82 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.4 (d, $^2J_{P-C}$ = 3.6 Hz, *C*), 130.4 (d, $^3J_{P-C}$ = 5.5 Hz, *C*H), 128.4 (d, $^1J_{P-C}$ = 83.6 Hz, *C*), 128.1 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 126.7 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 72.3 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 39.5 (d, $^1J_{P-C}$ = 55.4 Hz, *C*H_2), 24.1 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 139.44 (br m).[8]

^{11}B NMR (160 MHz, $CDCl_3$): δ = –42.71 (br m).[8]

MS (EI, 70 eV): *m*/*z* (%) = 254 (1) $[M]^+$, 240 (10) $[M - BH_3]^+$, 149 (37), 139 (14), 121 (10), 107 (100), 92 (35), 91 (64), 65 (54).

HRMS (ESI): *m*/*z* $[2\ M - H]^+$ calcd for $C_{26}H_{47}B_2O_4P_2$: 507.3125; found: 507.3134.

Anal. Calcd for $C_{13}H_{24}BO_2P$: C, 61.44; H, 9.52. Found: C, 61.33; H, 9.42.

Methylphosphonous Acid-Borane Diisopropyl Ester (7c) (Table 2, entry 8), General Procedure B

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with MeI (0.3 mmol, 18.7 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **7c** (0.0236 g, 0.133 mmol, 53%) as a colorless oil.

R_f = 0.47 (*n*-pentane/EtOAc, 100:1).

IR (ATR, thin film): 2955, 2917, 2848, 1462, 1091, 608 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.57–4.67 (m, 2 H), 1.47 (d, J_{P-H} = 8.51 Hz, 3 H), 1.30 (d, J_{P-H} = 5.99 Hz, 6 H), 1.29 (d, J_{P-H} = 5.99 Hz, 6 H), 0.23–0.83 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 71.6 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 24.11 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 24.08 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 17.3 (d, $^1J_{P-C}$ = 59.0 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 140.71 (br m).[8]

^{11}B NMR (160 MHz, $CDCl_3$): δ = –45.28 (br m).[8]

MS (EI, 70 eV): *m*/*z* (%) = 164 (28) $[M - BH_3]^+$, 94 (11), 93 (11), 91 (12), 81 (10), 80 (100).

Anal. Calcd for $C_7H_{20}BO_2P$: C, 47.23; H, 11.32. Found: C, 47.43; H, 11.45.

Phosphorous Acid-Borane Diisopropyl (3-Phenyl-1-methyl-prop-1-enyl) Ester (12) (Table 2, entry 9), General Procedure B

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with PhCHO (0.3 mmol, 30.5 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **12** (as a mixture of isomers, ratio = 1:0.81) and phosphorous acid-borane diisopropyl benzyl ester (**10**) as a mixture in 31% and 16% yield, respectively (according to the ^1H NMR spectrum).

12 (Major Isomer) (Table 2, entry 9), General Procedure B

Yield: 5.4 mg, 0.0175 mmol (7%); colorless oil; R_f = 0.69 (hexane/EtOAc, 6:1).

IR (ATR, thin film): 2980, 2394, 1685, 1141, 972, 784 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.27–7.30 (m, 2 H), 7.20–7.23 (m, 3 H), 4.96–5.00 (m, 1 H), 4.70–4.77 (m, 2 H), 3.45 (d, J_{P-H} = 7.25 Hz, 2 H), 2.01–2.03 (m, 3 H), 1.35 (d, J_{P-H} = 5.99 Hz, 6 H), 1.29 (d, J_{P-H} = 6.31 Hz, 6 H), 0.25–0.85 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.8 (d, $^2J_{P-C}$ = 7.3 Hz, *C*), 140.3 (s, *C*), 128.4 (d, J_{P-C} = 6.4 Hz, *C*H), 126.0 (s, CH), 113.9 (d, J_{P-C} = 6.4 Hz, *C*H), 72.2 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 31.8 (s, CH_2), 23.9 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 21.2 (s, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 109.26 (br m).

Anal. Calcd for $C_{16}H_{28}BO_3P$: C, 61.96; H, 9.10. Found: C, 62.23; H, 9.32.

12 (Minor Isomer) (Table 2, entry 9), General Procedure B

Isolated together with the major diastereoisomer and **10**. Yield established for both forms of 12–31% according to 1H NMR. 17% of **12 major** and 14% of **12 minor**. R_f = 0.68 (hexane/EtOAc, 6:1).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.36 (m, 2 H), 7.20–7.23 (m, 3 H), 5.40–5.50 (m, 1 H), 4.46–4.77 (m, 2 H), 3.37 (d, J_{P-H} = 8.04 Hz, 2 H), 2.00 (br s, 3 H), 1.36 (d, J_{P-H} = 5.83 Hz, 6 H), 1.33 (d, J_{P-H} = 6.31 Hz, 6 H), 0.25–0.85 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.8 (d, $^2J_{P-C}$ = 7.3 Hz, *C*), 140.1 (s, *C*), 128.4 (d, J_{P-C} = 10.0 Hz, *C*H), 126.1 (s, *C*H), 114.1 (d, J_{P-C} = 5.5 Hz, *C*H), 72.1 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 32.9 (s, CH_2), 23.79 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3), 23.76 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 16.7 (d, J_{P-C} = 2.7 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 109.38 (br m).

Phosphorous Acid-Borane Diisopropyl Benzyl Ester (10) (Table 2, entry 9), General Procedure B

^1H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.39 (m, 4 H), 7.32–7.38 (m, 1 H), 5.02 (d, J_{P-H} = 7.41 Hz, 2 H), 4.63–4.71 (m, 2 H), 1.31 (d, J_{H-H} = 6.31 Hz, 6 H), 1.30 (d, J_{H-H} = 6.15 Hz, 6 H), 0.22–0.95 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.3 (d, $^3J_{P-C}$ = 6.4 Hz, *C*), 128.5 (d, J_{P-C} = 7.3 Hz, *C*H), 128.3 (d, J_{P-C} = 10.0 Hz, *C*H), 127.6 (s, *C*H), 125.5 (s, *C*H), 71.7 (d, $^2J_{P-C}$ = 2.7 Hz, *C*HO), 67.4 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H_2O), 23.82 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_3), 23.79 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 111.80 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –43.67 (br m).

1-Hydroxy-1-phenylmethylphosphonous Acid-Borane Diisopropyl Ester (11) (Table 2, entry 11), General Procedure B

α-Hydroxyphosphonite-borane **5b** (0.066 g, 0.25 mmol) reacted with PhCHO (0.375 mmol, 38.1 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **11** (0.041 g, 0.153 mmol, 61%) as a colorless oil.

R_f = 0.38 (hexane/EtOAc, 10:1).

IR (ATR, thin film): 3377, 2978, 2929, 2391, 1374, 974, 715 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.44 (m, 2 H), 7.30–7.39 (m, 3 H), 4.89 (d, J_{P-H} = 3.15 Hz, 1 H), 4.54–4.64 (m, 2 H), 2.61 (br s, 1 H), 1.30 (d, J_{H-H} = 6.31 Hz, 3 H), 1.29 (d, J_{H-H} = 6.15 Hz, 3 H), 1.21 (d, J_{H-H} = 6.15 Hz, 3 H), 1.11 (d, J_{H-H} = 6.15 Hz, 3 H), 0.14–0.87 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.2 (s, *C*), 128.2 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 127.9 (d, $^3J_{P-C}$ = 2.7 Hz, *C*H), 127.6 (d, $^4J_{P-C}$ = 4.5 Hz, *C*H), 74.6 (d, $^1J_{P-C}$ = 67.2 Hz, *C*HO), 72.4 (d, $^2J_{P-C}$ = 4.5 Hz, *C*HO), 72.4 (d, $^2J_{P-C}$ = 5.5 Hz, *C*HO), 24.1 (br s, 2 × *C*H_3), 23.8 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3), 23.6 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 134.61 (br m).[8]

^{11}B NMR (160 MHz, $CDCl_3$): δ = –44.78 (br m).[8]

MS (EI, 70 eV): *m*/*z* (%) = 214 (1) [M – BH_3 – C_3H_7]$^+$, 172 (1) [M – BH_3 – C_6H_{14}]$^+$, 155 (3), 149 (8), 108 (18), 107 (100), 106 (22), 105 (34), 91 (14).

Anal. Calcd for $C_{13}H_{24}BO_3P$: C, 57.81; H, 8.96. Found: C, 57.63; H, 8.86.

Benzyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13a) (Table 3, entry 3), General Procedure B

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure B to afford **13a** (0.038 g, 0.148 mmol, 59%) as a colorless oil.

R_f = 0.53 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2925, 2379, 1064, 1037, 772, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.62 (m, 2 H), 7.50–7.53 (m, 1 H), 7.39–7.41 (m, 2 H), 7.20–7.24 (m, 3 H), 6.98–7.03 (m, 2 H), 3.95–4.05 (m, 1 H), 3.83–3.91 (m, 1 H), 3.31 (d, J_{P-H} = 10.09 Hz, 2 H), 1.27 (t, J_{H-H} = 6.94 Hz, 3 H), 0.46–1.10 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.8 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 131.3 (d, $^2J_{P-C}$ = 6.4 Hz, *C*), 131.2 (d, $^1J_{P-C}$ = 55.4 Hz, *C*), 130.9 (d, $^2J_{P-C}$ = 10.9 Hz, *C*H), 130.1 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H), 128.3 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 128.0 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 126.8 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 63.8 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H_2O), 39.4 (d, $^1J_{P-C}$ = 40.0 Hz, *C*H_2), 16.6 (d, $^3J_{P-C}$ = 6.3 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 110.30 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –45.28 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 258 (M)$^+$ (1), 244 (M – BH_3)$^+$ (25), 154 (10), 153 (100), 141 (11), 125 (88), 109 (34), 91 (56).

HRMS (ESI): *m*/*z* [2 M – H] calcd for $C_{30}H_{39}B_2O_2P_2$: 515.2600; found: 515.2617.

Anal. Calcd for $C_{15}H_{20}BOP$: C, 69.80; H, 7.81. Found: C, 69.63; H, 7.72.

3-Oxo-1-phenylbutyl(phenyl)phosphinous Acid-Borane Ethyl Ester (15) (Table 4, entry 15), General Procedure B

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with PhCHO (0.3 mmol, 30.5 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure B to afford **15** (0.024 g, 0.075 mmol, 30%) isolated as a mixture of two diastereoisomers (dr = 1:0.48).

^{1}H NMR (500 MHz, $CDCl_3$): δ (mixture of diastereoisomers) = 7.47–7.53 (m, 2 H), 7.42–7.47 (m, 4 H), 7.33–7.39 (m, 4 H), 7.19–7.22 (m, 2 H), 7.10–7.13 (m, 4 H), 7.06–7.11 (m, 2 H), 6.92–6.95 (m, 2 H), 4.02–4.10 (m, 1 H), 3.84–3.92 (m, 4 H), 3.77–3.82 (m, 1 H), 3.17–3.21 (m, 2 H), 3.12–3.16 (m, 1 H), 2.97–3.03 (m, 1 H), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.29 (t, J_{H-H} = 7.25 Hz, 3 H), 1.18 (t, J_{H-H} = 7.25 Hz, 3 H), 0.42–0.95 (br m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (mixture of diastereoisomers) = 205.1 (d, $^3J_{P-C}$ = 11.8 Hz, *C*=O, major), 204.7 (d, $^3J_{P-C}$ = 12.7 Hz, *C*=O, minor), 135.2 (d, $^2J_{P-C}$ = 5.5 Hz, *C*, minor), 134.4 (s, *C*, major), 131.95 (d, J_{P-C} = 3.6 Hz, C, minor), 131.93 (d, J_{P-C} = 2.7 Hz, *C*, major), 131.25 (d, $^2J_{P-C}$ = 10.5 Hz, *C*H, major), 131.24 (d, $^2J_{P-C}$ = 10.5 Hz, *C*H, minor), 130.5 (d, $^1J_{P-C}$ = 55.4 Hz, *C*, minor), 130.0 (d, $^1J_{P-C}$ = 53.6 Hz, *C*, major), 129.6 (d, J_{P-C} = 3.6 Hz, *C*H, minor), 129.5 (d, J_{P-C} = 4.5 Hz, *C*H, major), 128.3 (d, $^3J_{P-C}$ = 10.5 Hz, *C*H, minor), 128.2 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H, major), 128.0 (d, J_{P-C} = 1.8 Hz, *C*H, minor), 127.9 (d, J_{P-C} = 2.7 Hz, *C*H, major), 127.3 (d, J_{P-C} = 2.7 Hz, *C*H, minor), 127.2 (d, J_{P-C} = 2.7 Hz, *C*H, major), 64.2 (d, $^2J_{P-C}$ = 3.6 Hz, O*C*H_2, minor), 64.0 (d, $^2J_{P-C}$ = 3.6 Hz, O*C*H_2, major), 43.2 (d, $^1J_{P-C}$ = 41.8 Hz, major/minor), 42.7 (d, $^3J_{P-C}$ = 3.6 Hz, *C*H_2, major), 42.3 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H_2, minor), 30.5 (s, *C*H_3, major), 30.3 (s, *C*H_3, minor), 16.7 (d, $^3J_{P-C}$ = 6.4 Hz, *C*H_3, major), 16.4 (d, $^3J_{P-C}$ = 6.4 Hz, *C*H_3, minor).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 115.65 (br m, major), 113.89 (br m, minor).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –42.93 (br m).

Anal. Calcd for $C_{18}H_{24}BO_2P$: C, 68.81; H, 7.70. Found: C, 68.73; H, 7.86.

1,2-Bis(ethoxyphenylboranatophosphinyl)ethane (16) (Table 4, entry 16), General Procedure B

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with ethylene oxide (103.4 μL, 0.3 mmol, 2.5–3.3 M in THF) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure B to afford **16** (0.0254 g, 0.065 mmol, 26%) as a waxy solid.

R_f = 0.33 (hexane/EtOAc, 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.76 (m, 4 H), 7.52–7.57 (m, 2 H), 7.43–7.53 (m, 4 H), 3.93–4.02 (m, 2 H), 3.77–3.87 (m, 2 H), 1.96–2.15 (m, 4 H), 1.26 (t, J_{H-H} = 7.25 Hz, 3 H), 1.24 (t, J_{H-H} = 7.25 Hz, 3 H), 0.3–1.04 (br m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.3 (s, *C*H), 130.8–131.0 (m, *C*H), 128.8–129.9 (m, *C*H), 63.7 (s, *C*H_2O), 23.6 (dd, *J* = 8.6 Hz, *J* = 43.1 Hz, *C*H_2), 16.6 (d, J_{P-C} = 3.7 Hz, *C*H_3), 16.5 (d, J_{P-C} = 3.1 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 114.05 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –44.78 (br m).

Anal. Calcd for $C_{18}H_{30}B_2O_2P_2$: C, 59.72; H, 8.35. Found: C, 59.88; H, 8.55.

Reversed Alkylation of α-Hydroxyphosphinite-Boranes and α-Hydroxyphosphonite-Boranes in DMF; General Procedure A

To a Schlenk tube (25 mL) equipped with a magnetic stir bar and an argon inlet were added anhydrous degassed DMF (2 mL), α-hydroxyphosphonite-borane **5** (0.25 mmol) or α-hydroxyphosphinite-borane **6** (0.25 mmol) and the electrophile (0.3 mmol). The resulting mixture was cooled to 0 °C using an ice bath and then NaH (15 mg, 0.375 mmol, 60% in mineral oil or 10 mg, 0.25 mmol, 60% in mineral oil) was added and the mixture was stirred at the same temperature for 3 min. The ice bath was removed and the reaction mixture was quenched by the addition of anhydrous NH_4Cl (~300 mg), filtered and evaporated under reduced pressure. The residue was purified by short (5–10 cm) column chromatography on neutral Al_2O_3 using hexane/EtOAc (40:1 v/v) or hexane/EtOAc (10:1 v/v) as the eluent.

Benzylphosphonous Acid-Borane Diisopropyl Ester (7a) (Table 2, entry 1), General Procedure A

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 μL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **7a** (0.046 g, 0.18 mmol, 72%) as a colorless oil.

2-Methylbenzylphosphonous Acid-Borane Diisopropyl Ester (7b) (Table 2, entry 2), General Procedure A

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with 2-$MeC_6H_4CH_2Cl$ (0.3 mmol, 39 μL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure B to afford **7b** (0.056 g, 0.208 mmol, 83%) as a colorless oil.

R_f = 0.48 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2978, 2385, 1386, 1064, 1002, 886, 772 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.26 (m, 1 H), 7.13–7.18 (m, 3 H), 4.54–4.63 (m, 2 H), 3.15 (d, J_{P-H} = 12.30 Hz, 2 H), 2.38 (s, 3 H), 1.29 (d, J_{H-H} = 6.15 Hz, 6 H), 1.13 (d, J_{H-H} = 6.15 Hz, 6 H), 0.14–0.84 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.3 (d, $^2J_{P-C}$ = 5.5 Hz, *C*), 131.3 (d, J_{P-C} = 4.5 Hz, *C*H), 130.1 (d, J_{P-C} = 2.7 Hz, *C*H), 129.9 (d, $^3J_{P-C}$ = 3.6 Hz, *C*), 126.9 (d, J_{P-C} = 3.6 Hz, *CH*), 125.5 (d, J_{P-C} = 2.7 Hz, *C*H), 72.3 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 36.4 (d, $^1J_{P-C}$ = 55.4 Hz, CH_2), 24.2 (d, $^3J_{P-C}$ = 2.7 Hz, CH_3), 23.7 (d, $^3J_{P-C}$ = 4.5 Hz, CH_3), 20.3 (s, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 140.71 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –42.55 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 254 (3) [M – BH_3]$^+$, 153 (12) [M – BH_3 – C_3H_7]$^+$, 149 (25), 135 (7), 107 (100), 106 (34), 105 (65), 103 (18), 91 (13).

Anal. Calcd for $C_{14}H_{26}BO_2P$: C, 62.71, H, 9.77. Found: C, 62.98; H, 9.99.

Methylphosphonous Acid-Borane Diisopropyl Ester (7c) (Table 2, entry 3), General Procedure A

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with MeI (0.3 mmol, 18.7 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure A to afford **7c** (100%, according to the ^{31}P NMR spectrum).

Phosphorous Acid-Borane Diisopropyl Benzyl Ester (10) (Table 2, entry 4), General Procedure A

α-Hydroxyphosphonite-borane **5a** (0.056 g, 0.25 mmol) reacted with PhCHO (0.3 mmol, 30.5 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure A to afford **10** (0.365 g, 0.135 mmol, 54%) as a yellowish oil.

R_f = 0.68 (hexane/EtOAc, 6:1).

IR (ATR, thin film): 2980, 2390, 1375, 975, 784 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 214 (2) [M – BH_3 – C_3H_7]$^+$, 173 (4) [M – BH_3 – C_6H_{14}]$^+$, 172 (6) [M – BH_3 – C_6H_{14}]$^+$, 123 (13), 91 (100), 77 (8), 65 (26).

Anal. Calcd for $C_{13}H_{24}BO_3P$: C, 57.81; H, 8.96. Found: C, 57.90; H, 8.99.

Benzylphosphonous Acid-Borane Diisopropyl Ester (7a) (Table 2, entry 5), General Procedure A

α-Hydroxyphosphonite-borane **5b** (0.066 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure A to afford **7a** (0.054 g, 0.213 mmol, 85%) as a colorless oil.

Phosphorous Acid-Borane Diisopropyl Benzyl Ester (10) (Table 2, entry 6), General Procedure A

α-Hydroxyphosphonite-borane **5b** (0.066 g, 0.25 mmol) reacted with PhCHO (0.3 mmol, 30.5 µL) and NaH (15 mg, 0.375 mmol, 60% in mineral oil) according to general procedure A to afford **10** (0.033 g, 0.123 mmol, 49%) as a yellowish oil.

Benzyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13a) (Table 4, entry 1), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 µL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13a** (0.049 g, 0.19 mmol, 76%) as a colorless oil.

2-Methylbenzyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13b) (Table 4, entry 2), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with 2-$MeC_6H_4CH_2Cl$ (0.3 mmol, 39 µL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure B to afford **13b** (0.0422 g, 0.155 mmol, 62%) as a colorless oil.

R_f = 0.57 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2978, 2383, 1036, 711 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49–7.61 (m, 3 H), 7.37–7.45 (m, 2 H), 7.02–7.15 (m, 3 H), 6.94–6.99 (m, 1 H), 3.93–4.03 (m, 1 H), 3.80–3.87 (m, 1 H), 3.33 (d, J_{P-H} = 10.09 Hz, 2 H), 2.08 (s, 3 H), 1.25 (t, J_{H-H} = 6.94 Hz, 3 H), 0.47–1.10 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.8 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 131.3 (d, $^2J_{P-C}$ = 6.4 Hz, *C*), 131.2 (d, $^1J_{P-C}$ = 55.4 Hz, *C*), 130.9 (d, $^2J_{P-C}$ = 10.9 Hz, *C*H), 130.1 (d, $^3J_{P-C}$ = 4.5 Hz, *C*H), 128.3 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 128.0 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 126.8 (d, $^5J_{P-C}$ = 2.7 Hz, *C*H), 63.8 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H_2O), 39.4 (d, $^1J_{P-C}$ = 40.0 Hz, *C*H_2), 16.6 (d, $^3J_{P-C}$ = 6.3 Hz, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 110.98 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.12 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 259 (6), 258 (32) [M – BH_3]$^+$, 153 (100), 125 (93), 109 (34), 105 (41), 104 (8), 103 (11).

HRMS (ESI): *m*/*z* [2 M – H]$^+$ calcd for $C_{32}H_{43}B_2O_2P_2$: 543.2940; found: 543.2925.

Anal. Calcd for $C_{16}H_{22}BOP$: C, 70.62; H, 8.15. Found: C, 70.88; H, 8.33.

Methyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13c) (Table 4, entry 3), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with MeI (0.3 mmol, 18.7 µL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13c** (0.038 g, 0.208 mmol, 83%) as a colorless oil.

R_f = 0.37 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2980, 2925, 2378, 1437, 1032, 742 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.82 (m, 2 H), 7.52–7.57 (m, 1 H), 7.48–7.51 (m, 2 H), 3.95–4.03 (m, 1 H), 3.76–3.84 (m, 1 H), 1.70 (d, J_{P-H} = 9.46 Hz, 3 H), 1.26 (t, J_{H-H} = 6.94 Hz, 3 H), 0.48–1.13 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.6 (d, $^1J_{P-C}$ = 56.3 Hz, C), 131.9 (d, $^4J_{P-C}$ = 2.7 Hz, CH), 130.5 (d, $^2J_{P-C}$ = 11.8 Hz, CH), 128.7 (d, $^3J_{P-C}$ = 10.0 Hz, CH), 63.1 (d, $^2J_{P-C}$ = 2.7 Hz, CH_2O), 16.7 (d, $^1J_{P-C}$ = 47.3 Hz, CH_3), 16.6 (d, $^3J_{P-C}$ = 6.4 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 108.11 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.29 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 168 (36), [M - BH_3]$^+$, 141 (13), 140 (27), 139 (100), 125 (62), 124 (14), 121 (14).

HRMS (ESI): *m*/*z* [2(M – BH_3+O) + Na]$^+$ calcd for $C_{18}H_{26}O_4P_2$: 391.1199; found: 391.1192.

Anal. Calcd for $C_9H_{16}BOP$: C, 59.39; H, 8.86. Found: C, 58.99; H, 8.47.

Isopropyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13d) (Table 4, entry 4), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with *i*-PrI (0.375 mmol, 37.5 µL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13d** (0.033 g, 0.158 mmol, 63%) as a colorless oil.

R_f = 0.49 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2976, 2929, 2378, 1437, 1023, 732, 694 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.76 (m, 2 H), 7.46–7.56 (m, 3 H), 4.00–4.10 (m, 1 H), 3.82–3.89 (m, 1 H), 2.07–2.17 (m, 1 H), 1.29 (t, J_{H-H} = 7.25 Hz, 3 H), 1.16 (dd, J_{H-H} = 7.25 Hz, J_{P-H} = 15.76 Hz, 3 H), 1.01 (dd, J_{H-H} = 6.94 Hz, J_{P-H} = 16.39 Hz, 3 H), 0.35–0.95 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 131.2 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H), 131.0 (d, $^1J_{P-C}$ = 49.1 Hz, *C*), 128.4 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 63.5 (d, $^2J_{P-C}$ = 3.6 Hz, CH_2O), 29.3 (d, $^1J_{P-C}$ = 45.4 Hz, *C*H), 16.6 (d, $^3J_{P-C}$ = 6.4 Hz, CH_3), 15.7 (s, CH_3), 15.3 (d, $^2J_{P-C}$ = 1.8 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 119.19 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –43.51 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 210 (5) $[M]^+$ 197 (11), 196 (91) $[M - BH_3]^+$, 167 (13), 154 (25), 153 (74), 152 (15), 151 (11), 126 (18), 125 (100), 110 (10), 109 (71), 108 (13), 107 (14), 105 (14), 104 (21).

Anal. Calcd for $C_{11}H_{20}BOP$: C, 62.90; H, 9.60. Found: C, 63.21; H, 9.98.

Allyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13e) (Table 4, entry 8), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with allyl bromide (0.3 mmol, 26 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13e** (0.041 g, 0.198 mmol, 79%) as a colorless oil.

R_f = 0.41 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2961, 2925, 2378, 1260, 1017, 798 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.77 (m, 2 H), 7.44–7.57 (m, 3 H), 5.64–5.75 (m, 1 H), 5.01–5.15 (m, 2 H), 4.00–4.10 (m, 1 H), 3.86–3.94 (m, 1 H), 2.72–2.84 (m, 2 H), 1.29 (t, J_{H-H} = 6.94 Hz, 3 H), 0.48–1.47 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.9 (d, $^4J_{P-C}$ = 1.8 Hz, *C*H), 131.3 (d, $^1J_{P-C}$ = 55.4 Hz, *C*), 130.9 (d, $^2J_{P-C}$ = 11.0 Hz, *C*H), 128.5 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 127.3 (d, $^2J_{P-C}$ = 6.4 Hz, *C*H), 120.3 (d, $^3J_{P-C}$ = 11.0 Hz, CH_2), 63.7 (d, $^2J_{P-C}$ = 2.7 Hz, CH_2O), 37.0 (d, $^1J_{P-C}$ = 42.7 Hz, CH_2), 16.6 (d, $^3J_{P-C}$ = 6.4 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 110.30 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.43 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 194 $[M - BH_3]^+$, 193 (5), 154 (9), 153 (96), 141 (9), 126 (7), 125 (100), 109 (41).

HRMS (ESI): *m*/*z* [2 M – H]$^+$ calcd for $C_{22}H_{35}B_2O_2P_2$: 415.2287; found: 415.2297.

Anal. Calcd for $C_{11}H_{18}BOP$: C, 63.50; H, 8.72. Found: C, 63.61; H, 8.98.

Methoxymethyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13f) (Table 4, entry 9), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with MOMCl (0.375 mmol, 28 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13f** (0.034 g, 0.163 mmol, 65%) as a colorless oil.

R_f = 0.32 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2957, 2922, 2853, 1258, 1105, 1026, 774 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.86 (m, 2 H), 7.54–7.59 (m, 1 H), 7.52–7.58 (m, 2 H), 4.06–4.13 (m, 1 H), 3.96–4.02 (m, 1 H), 3.91–4.03 (m, 2 H), 3.44 (s, 3 H), 1.32 (t, J_{H-H} = 6.94 Hz, 3 H), 0.44–1.09 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.3 (d, $^4J_{P-C}$ = 1.8 Hz, *C*H), 131.4 (d, $^2J_{P-C}$ = 11.0 Hz, *C*H), 129.5 (d, $^1J_{P-C}$ = 58.1 Hz, *C*), 128.5 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 72.4 (d, $^1J_{P-C}$ = 53.6 Hz, CH_2O), 64.0 (d, $^2J_{P-C}$ = 2.7 Hz, CH_2O), 61.8 (d, $^3J_{P-C}$ = 8.2 Hz, OCH_3), 16.7 (d, $^3J_{P-C}$ = 6.4 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.65 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –42.19 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 198 (17) $[M - BH_3]^+$, 168 (23), 153 (77), 141 (7), 140 (5), 125 (100), 124 (20), 21 (11), 109 (42), 108 (5), 107 (10), 104 (8), 91 (16).

HRMS (ESI): *m*/*z* [2 M – H]$^+$ calcd for $C_{20}H_{35}B_2O_4P_2$: 423.2187; found: 423.2186.

Anal. Calcd for $C_{10}H_{18}BO_2P$: C, 56.65; H, 8.56. Found: C, 56.61; H, 8.86.

Phenylphosphonous Acid-Borane Ethyl [1-(4-Chlorophenyl)vinyl] Ester (14) and 1-(4-Chlorophenyl)-2-[ethoxy(phenyl)boranato-phosphinyl]-1-ethanone (13g) (Table 4, entry 10), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with $ClCH_2C(O)C_6H_4Cl$-*p* (0.3 mmol, 56.7 mg) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford compounds **14** and **13g**.

Compound 14

Yield: 0.051 g, 0.16 mmol (64%); colorless oil; R_f = 0.63 (hexane/EtOAc, 6:1).

IR (ATR, thin film): 3212, 2981, 2389, 1489, 1262, 1263, 1096, 988 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83–7.88 (m, 2 H), 7.55–7.60 (m, 1 H), 7.47–7.51 (m, 2 H), 7.44–7.48 (m, 2 H), 7.28–7.32 (m, 2 H), 5.21 (dd, J_{H-H} = 2.05 Hz, J_{P-H} = 2.99 Hz, 1 H), 4.98 (dd, J_{H-H} = 2.36 Hz, J_{P-H} = 2.86 Hz, 1 H), 4.23–4.31 (m, 1 H), 4.09–4.17 (m, 1 H), 1.39 (t, J_{H-H} = 7.05 Hz, 3 H), 0.51–1.13 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6 (d, $^2J_{P-C}$ = 10.0 Hz, *C*), 134.9 (s, *C*), 133.3 (d, $^3J_{P-C}$ = 3.6 Hz, *C*), 132.7 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 130.7 (d, $^2J_{P-C}$ = 12.7 Hz, *C*H), 130.4 (d, $^1J_{P-C}$ = 65.4 Hz, *C*), 128.6 (d, $^3J_{P-C}$ = 11.0 Hz, *C*H), 128.6 (s, *C*H), 126.6 (s, *C*H), 99.0 (d, $^3J_{P-C}$ = 5.4 Hz, CH_2), 64.6 (d, $^2J_{P-C}$ = 4.5 Hz, CH_2O), 16.3 (d, $^3J_{P-C}$ = 5.5 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 131.34 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.21 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 308 (7), 307 (12), 306 $[M - BH_3]^+$, 277 (12), 170 (19), 153 (19), 143 (9), 142 (30), 141 (94), 139 (40), 138 (11), 137 (69), 136 (11), 126 (8), 125 (86), 124 (10).

HRMS (ESI): *m*/*z* [M – BH_3 + O + Na]$^+$ calcd for $C_{16}H_{16}ClO_3PNa$: 345.0418; found: 345.0420.

Anal. Calcd for $C_{16}H_{19}BClO_2P$: C, 59.95; H, 5.97. Found: C, 59.99; H, 6.12.

Compound 13g

Yield: 0.0192 g, 0.06 mmol (24%); colorless oil; R_f = 0.45 (hexane/EtOAc, 6:1).

IR (ATR, thin film): 3060, 2979, 2928, 2384, 1676, 1578, 1268, 1027, 997, 771 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.80 (m, 2 H), 7.71–7.76 (m, 2 H), 7.52–7.56 (m, 1 H), 7.43–7.49 (m, 2 H), 7.37–7.40 (m, 2 H), 4.02–4.10 (m, 1 H), 3.89–3.99 (m, 1 H), 3.79–3.82 (m, 1 H), 3.63–3.70 (m, 1 H), 1.25 (t, J_{H-H} = 6.94 Hz, 3 H), 0.49–1.15 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.3 (d, $^2J_{P-C}$ = 4.5 Hz, *C*), 140.1 (s, *C*), 135.3 (s, *C*), 132.4 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 130.8 (d, $^2J_{P-C}$ = 11.8 Hz, *C*H), 130.6 (d, $^1J_{P-C}$ = 58.1 Hz, *C*), 130.3 (s, *C*H), 128.8 (s, *C*H), 128.7 (d, $^3J_{P-C}$ = 10.8 Hz, *C*H), 64.4 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H), 42.6 (d, $^1J_{P-C}$ = 31.8 Hz, CH_2), 16.5 (d, $^3J_{P-C}$ = 6.4 Hz, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 108.42 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –40.28 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 308 (6), 307 (12) [M – BH_3]$^+$, 279 (12), 170 (19), 153 (19), 142 (60), 141 (94), 139 (38), 138 (11), 137 (69), 126 (8), 125 (86), 124 (9), 111 (30), 109 (21), 107 (21).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}BClO_2PNa$: 343.0794; found: 343.0789.

Anal. Calcd for $C_{16}H_{19}BClO_2P$: C, 59.95; H, 5.97. Found: C, 60.11; H, 6.05.

3-Oxo-1-phenylbutyl(phenyl)phosphinous Acid-Borane Ethyl Ester (15) (Table 4, entry 11), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with PhCHO (0.3 mmol, 30.5 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **15** (0.006 g, 0.018 mmol, 7%, dr = 1:0.53).

1,2-Bis(ethoxyphenylboranatophosphinyl)ethane (16) (Table 4, entry 12), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with ethylene oxide (103.4 μL, 0.3 mmol, 2.5–3.3 M in THF) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **16** (0.0127 g, 0.033 mmol, 13%) as a waxy solid.

R_f = 0.33 (hexane/EtOAc, 10:1).

Isopropyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13d) (Table 4, entry 6), General Procedure A

α-Hydroxyphosphinite-borane **6a** (0.057 g, 0.25 mmol) reacted with *i*-PrBr (0.3 mmol, 28.2 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13d** (0.023 g, 0.108 mmol, 43%).

Benzyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13a) (Table 4, entry 13), General Procedure A

α-Hydroxyphosphinite-borane **6b** (0.067 g, 0.25 mmol) reacted with $PhCH_2Cl$ (0.3 mmol, 34.5 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13a** (0.045 g, 0.175 mmol, 70%).

Isopropyl(phenyl)phosphinous Acid-Borane Ethyl Ester (13d) (Table 4, entry 14), General Procedure A

α-Hydroxyphosphinite-borane **6b** (0.067 g, 0.25 mmol) reacted with *i*-PrI (0.375 mmol, 37.5 μL) and NaH (10 mg, 0.25 mmol, 60% in mineral oil) according to general procedure A to afford **13d** (0.035 g, 0.11 mmol, 44%).

Stereoselective Alkylation of α-Hydroxy Phosphite-Boranes 19a,b; General Procedure C (Table 5)

To a Schlenk tube (25 mL) equipped with a magnetic stir bar and an argon inlet was added (R_P)-**19a** (0.05 g, 0.149 mmol) or (R_P)-**19b** (0.056 g, 0.149 mmol) in anhydrous DMF (1.5 mL) and the resulting mixture was cooled to 0 °C using an ice bath. NaH (6 mg, 0.149 mmol, 60% in mineral oil or 6.3 mg, 0.156 mmol, 60% in mineral oil) was added and the mixture was stirred at the same temperature for 3 min. The electrophile (0.179 mmol or 0.373 mmol) was then added and the mixture was stirred at the same temperature for 40 min or 1–2 h. The reaction mixture was quenched by the addition of anhydrous NH_4Cl (~300 mg), filtered and evaporated under reduced pressure. The residue was purified by short (5–10 cm) column chromatography on neutral Al_2O_3 using hexane/EtOAc (40:1 v/v) or hexane/EtOAc (20:1 v/v) as the eluent.

(S_P)-Benzyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20a] (Table 5, entry 1), General Procedure C

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with $PhCH_2Cl$ (0.179 mmol, 20.6 μL) and NaH (6 mg, 0.149 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20a** (0.054 g, 0.146 mmol, 98%) as a colorless oil.

$[\alpha]_D^{25}$ –110.5 (*c* 1.02, $CHCl_3$); R_f = 0.66 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2979, 2862, 2382, 1436, 997, 693 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63–7.69 (m, 2 H), 7.47–7.51 (m, 1 H), 7.37–7.42 (m, 2 H), 7.18–7.23 (m, 3 H), 7.00–7.05 (m, 2 H), 4.01–4.09 (m, 1 H), 3.26–3.36 (m, 2 H), 1.92–1.98 (m, 1 H), 1.71–1.79 (m, 1 H), 1.57–1.67 (m, 2 H), 1.35–1.42 (m, 1 H), 1.25–1.34 (m, 2 H), 0.95–1.04 (m, 1 H), 0.88 (d, J_{P-H} = 6.62 Hz, 3 H), 0.78–0.94 (m 1 H), 0.76 (d, J_{P-H} = 7.25 Hz, 3 H), 0.55–1.22 (br m, 3 H), 0.42 (d, J_{P-H} = 6.94 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.8 (d, $^1J_{P-C}$ = 60.9 Hz, *C*), 131.75 (d, $^2J_{P-C}$ = 6.4 Hz, *C*), 131.7 (d, $^4J_{P-C}$ = 1.8 Hz, *CH*), 131.0 (d, $^2J_{P-C}$ = 10.9 Hz, *CH*), 130.3 (d, $^3J_{P-C}$ = 4.5 Hz, *CH*), 128.1 (d, $^3J_{P-C}$ = 10.0 Hz, *CH*), 127.9 (d, $^4J_{P-C}$ = 2.7 Hz, *CH*), 126.7 (d, $^5J_{P-C}$ = 3.6 Hz, *CH*), 80.4 (d, $^2J_{P-C}$ = 3.6 Hz, *CHO*), 48.7 (d, J_{P-C} = 5.5 Hz, *CH*), 43.7 (s, CH_2), 40.8 (d, $^1J_{P-C}$ = 39.9 Hz, CH_2), 34.0 (s, CH_2), 31.4 (s, *CH*), 25.4 (s, *CH*), 22.6 (s, CH_2), 22.1 (s, CH_3), 20.9 (s, CH_3), 15.1 (s, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.76 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.16 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 218 (9), 217 (67) [M – BH_3 – $C_{10}H_{19}$]$^+$, 216 (42), 215 (10), 126 (7), 125 (100), 123 (15), 121 (10), 96 (13), 95 (66).

Anal. Calcd for $C_{23}H_{34}BOP$: C, 75.01; H, 9.30. Found: C, 75.22; H, 9.40.

(S_P)-Methyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20c] (Table 5, entry 5), General Procedure C[33a]

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with MeI (0.298 mmol, 18.6 μL) and NaH (6 mg, 0.149 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20c** (0.036 g, 0.124 mmol, 83%) as a colorless oil.

$[\alpha]_D^{25}$ –121.1 (*c* 0.52, $CHCl_3$); R_f = 0.67 (hexane/EtOAc, 20:1).

IR (ATR, thin film): 2951, 2932, 2869, 2374, 1438, 986, 749 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.85 (m, 2 H), 7.51–7.55 (m, 1 H), 7.45–7.50 (m, 2 H), 3.39–4.02 (m, 1 H), 2.22–2.26 (m, 1 H), 1.71–1.79 (m, 1 H), 1.73 (d, J_{P-H} = 9.14 Hz, 3 H), 1.57–1.67 (m, 2 H), 1.42–1.49 (m, 1 H), 1.23–1.29 (m, 2 H), 1.06–1.13 (m, 1 H), 0.79–0.97 (m 1 H), 0.93 (d, J_{P-H} = 6.62 Hz, 3 H), 0.77 (d, J_{P-H} = 6.94 Hz, 3 H), 0.54–1.20 (br m, 3 H), 0.41 (d, J_{P-H} = 6.94 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.0 (d, $^1J_{P-C}$ = 61.7 Hz, *C*), 131.8 (d, $^4J_{P-C}$ = 1.8 Hz, *CH*), 130.6 (d, $^2J_{P-C}$ = 10.9 Hz, *CH*), 128.4 (d, $^3J_{P-C}$ = 10.0 Hz, CH), 79.3 (d, $^2J_{P-C}$ = 3.6 Hz, CHO), 48.8 (d, J_{P-C} = 5.5 Hz, CH), 43.6 (s, CH_2), 34.1 (s, CH_2), 31.4 (s, CH), 25.4 (s, CH_3), 22.7 (s, CH_2), 22.1 (s, CH_3), 20.9 (s, CH_3), 17.8 (d, $^1J_{P-C}$ = 46.3 Hz, CH_3), 15.2 (s, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 106.17 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –39.70 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 156 ($C_6H_{20}O$) (7), 142 (6), 141 (80), 140 (M – BH_3 – $C_{10}H_{19}$) (100), 139 (25), 138 (25), 125 (45), 123 (26), 96 (18), 95 (97).

Anal. Calcd for $C_{17}H_{30}BOP$: C, 69.88; H, 10.35. Found: C, 69.93; H, 10.22.

(S_P)-Isopropyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20d] (Table 5, entry 7), General Procedure C

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with *i*-PrI (0.373 mmol, 37.3 µL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20d** (0.038 g, 0.119 mmol, 80%) as a colorless oil.

$[\alpha]_D^{25}$ –137.9 (*c* 1.25, $CHCl_3$); R_f = 0.69 (hexane/EtOAc, 10:1).

IR (ATR, thin film): 2958, 2934, 2864, 2385, 1453, 1110, 978, 794 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.82 (m, 2 H), 7.49–7.53 (m, 1 H), 7.42–7.47 (m, 2 H), 3.99–4.06 (m, 1 H), 2.25–2.29 (m, 1 H), 2.18–2.29 (m, 1 H), 1.67–1.74 (m, 1 H), 1.56–1.67 (m, 2 H), 1.40–1.49 (m, 1 H), 1.25–1.39 (m, 2 H), 1.21 (dd, J_{H-H} = 6.94 Hz, J_{H-H} = 16.08 Hz, 3 H), 1.05–1.12 (m, 1 H), 0.94 (dd, J_{H-H} = 7.25 Hz, J_{H-H} = 16.71 Hz, 3 H), 0.93 (d, J_{H-H} = 6.62 Hz, 3 H), 0.78–0.99 (m, 1 H), 0.75 (d, J_{H-H} = 7.25 Hz, 3 H), 0.42–1.00 (br m, 3 H), 0.31 (d, J_{H-H} = 6.94 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6 (d, $^4J_{P-C}$ = 2.7 Hz, *C*), 131.5 (d, $^2J_{P-C}$ = 10.9 Hz, *C*H), 131.3 (d, $^1J_{P-C}$ = 56.3 Hz, *C*H), 130.6 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 79.5 (d, $^2J_{P-C}$ = 4.5 Hz, *C*HO), 48.8 (d, J_{P-C} = 5.5 Hz, *C*H), 43.6 (s, *C*H_2), 34.1 (s, *C*H_2), 31.4 (s, *C*H), 29.6 (d, $^1J_{P-C}$ = 46.3 Hz, *C*H), 25.4 (s, *C*H_3), 22.6 (s, *C*H_2), 22.1 (s, *C*H_3), 20.9 (s, *C*H_3), 16.1 (s, *C*H_3), 15.6 (d, $^2J_{P-C}$ = 2.7 Hz, *C*H_3), 15.0 (s, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 117.14 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –39.70 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 170 (10), 169 (100), 168 (82) [M – BH_3 – $C_{10}H_{12}]^+$, 138 (12), 126 (54), 125 (68), 109 (21), 96 (10), 95 (48).

HRMS (ESI): *m*/*z* [(M – BH_3 + O) + Na]$^+$ calcd for $C_{19}H_{31}O_2PNa$: 345.1954; found: 345.1953.

Anal. Calcd for $C_{19}H_{34}BOP$: C, 71.26; H, 10.70. Found: C, 71.56; H, 10.80.

(S_P)-Allyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20e] (Table 5, entry 10), General Procedure C

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with allyl bromide (0.224 mmol, 19.3 µL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20e** (0.038 g, 0.119 mmol, 80%) as a colorless oil.

$[\alpha]_D^{25}$ –105 (*c* 1.215, $CHCl_3$); R_f = 0.67 (hexane/EtOAc, 6:1).

IR (ATR, thin film): 2926, 2866, 2379, 1437, 984, 772 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.82 (m, 2 H), 7.50–7.54 (m, 1 H), 7.44–7.48 (m, 2 H), 5.62–5.74 (m, 1 H), 5.00–5.12 (m, 2 H), 4.01–4.10 (m, 1 H), 2.75–2.87 (m, 2 H), 2.20–2.27 (m, 1 H), 1.72–1.79 (m, 1 H), 1.57–1.67 (m, 2 H), 1.42–1.51 (m, 1 H), 1.26–1.35 (m, 1 H), 1.06–1.13 (m, 1 H), 0.82–0.97 (m, 2 H), 0.94 (d, J_{H-H} = 6.31 Hz, 3 H), 0.77 (d, J_{H-H} = 6.94 Hz, 3 H), 0.51–1.13 (br m, 3 H), 0.44 (d, J_{H-H} = 6.94 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.7 (d, $^4J_{P-C}$ = 2.7 Hz, *C*H), 131.6 (d, $^1J_{P-C}$ = 60.9 Hz, *C*), 131.0 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H), 128.3 (d, $^3J_{P-C}$ = 10.0 Hz, *C*H), 127.8 (d, $^2J_{P-C}$ = 6.4 Hz, *C*H), 120.1 (d, $^3J_{P-C}$ = 10.9 Hz, *C*H_2), 79.8 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 48.8 (d, J_{P-C} = 5.5 Hz, *C*H), 43.7 (s, *C*H_2), 38.1 (d, $^1J_{P-C}$ = 41.8 Hz, *C*H_2), 34.1 (s, *C*H), 34.5 (s, *C*H), 25.5 (s, *C*H), 22.7 (s, *C*H_2), 22.2 (s, *C*H_3), 20.9 (s, *C*H_3), 15.2 (s, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 107.82 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.16 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 168 (6), 167 (52), 166 (33) [M – BH_3 – $C_{10}H_{19}]^+$, 139 (12), 126 (6), 125 (100), 123 (12), 95 (49).

Anal. Calcd for $C_{19}H_{32}BOP$: C, 71.71; H, 10.14.; Found: C, 71.80; H, 10.26.

(R_P)-Methoxymethyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(R_P)-20f] (Table 5, entry 12), General Procedure C

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with MOMCl (0.373 mmol, 27.8 µL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (R_P)-**20f** (0.021 g, 0.066 mmol, 44%) as a colorless oil.

$[\alpha]_D^{25}$ –105 (*c* 0.71, $CHCl_3$); R_f = 0.52 (hexane/EtOAc, 10:1).

IR (ATR, thin film): 2954, 2626, 2868, 2378, 1437, 1111, 1009, 984, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.88 (m, 2 H), 7.52–7.56 (m, 1 H), 7.46–7.50 (m, 2 H), 4.06–4.15 (m, 1 H), 3.89–3.98 (m, 2 H), 3.43 (s, 3 H), 2.22–2.28 (m, 1 H), 1.80–1.87 (m, 1 H), 1.59–1.69 (m, 2 H), 1.44–1.52 (m, 1 H), 1.32–1.40 (m, 1 H), 1.12–1.19 (m, 1 H), 0.83–1.00 (m, 2 H), 0.95 (d, J_{H-H} = 6.62 Hz, 3 H), 0.80 (d, J_{H-H} = 6.94 Hz, 3 H), 0.51 (d, J_{H-H} = 6.94 Hz, 3 H), 0.47–1.18 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.0 (d, $^4J_{P-C}$ = 1.8 Hz, *C*H), 131.4 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H), 130.1 (d, $^1J_{P-C}$ = 63.8 Hz, *C*), 128.4 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H), 80.2 (d, $^2J_{P-C}$ = 3.6 Hz, *C*HO), 70.3 (d, $^1J_{P-C}$ = 52.7 Hz, *C*H_2), 61.8 (d, $^3J_{P-C}$ = 8.2 Hz, O*C*H_3), 48.7 (d, J_{P-C} = 4.4 Hz, *C*H), 43.4 (s, *C*H_2), 34.1 (s, *C*H_2), 31.5 (s, *C*H), 25.5 (s, *C*H), 22.7 (s, *C*H_2), 22.2 (s, *C*H_3), 20.9 (s, *C*H_3), 15.3 (s, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 104.62 (br m).

^{11}B NMR (160 MHz, $CDCl_3$): δ = –41.75 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 172 (11), 171 (74) [M – BH_3 – $C_{10}H_{19}]^+$, 141 (12), 140 (100), 138 (12), 134 (25), 125 (52), 121 (21), 95 (49).

Anal. Calcd for $C_{18}H_{32}BO_2P$: C, 67.09; H, 10.01. Found: C, 67.15; H, 10.18.

L-Menthoxy(phenyl)phosphine-Borane (21) (Table 5, entry 11), General Procedure C[33]

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with MOMCl (0.179 mmol, 17.9 µL) and NaH (6 mg, 0.149 mmol, 60% in mineral oil) according to general procedure C to afford an inseparable mixture of (R_P)-**20f** (20%) and **21** (11%) (yields determined from the ^1H NMR spectrum).

R_f = 0.45 (hexane/EtOAc, 10:1).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.83 (m, 2 H), 7.55–7.62 (m, 2 H), 7.51–7.55 (m, 1 H), 7.14 (dq, J_{P-H} = 340.68 Hz, J_{H-H} = 5.67 Hz, 1 H), 3.99–4.06 (m, 1 H), 2.03–2.10 (m, 1 H), 1.91–1.99 (m, 1 H), 1.59–1.66 (m, 2 H), 1.41–1.51 (m, 1 H), 1.31–1.40 (m, 1 H), 1.05–1.12 (m, 1 H), 0.83–1.00 (m, 2 H), 0.92 (d, J_{H-H} = 6.62 Hz, 3 H), 0.85 (d, J_{H-H} = 7.09 Hz, 3 H), 0.71 (d, J_{H-H} = 6.94 Hz, 3 H), 0.50–1.15 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.6 (d, $^4J_{P-C}$ = 1.8 Hz, *C*H), 132.0 (d, $^2J_{P-C}$ = 9.1 Hz, *C*H), 129.0 (d, $^1J_{P-C}$ = 66.3 Hz, *C*), 128.8 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H), 80.3 (d, $^2J_{P-C}$ = 6.4 Hz, *C*HO), 48.7 (d, J_{P-C} = 5.5 Hz, *C*H), 42.0 (d, J_{P-C} = 1.8 Hz, *C*H_2), 34.0 (s, *C*H_2), 31.4 (s, *C*H), 25.5 (s, *C*H), 22.9 (s, *C*H_2), 22.0 (s, *C*H_3), 20.9 (s, *C*H_3), 15.8 (s, *C*H_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 93.17 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 126 (100) [M – BH_3 – $C_{10}H_{19}]^+$, 125 (52), 123 (13), 109 (33), 95 (12), 83 (31), 81 (21).

(S_P)-Isopropyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20d] (Table 5, entry 8), General Procedure C

(R_P)-**19a** (0.05 g, 0.149 mmol) reacted with *i*-PrBr (0.373 mmol, 34.9 µL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20d** (0.021 g, 0.061 mmol, 45%).

(S_P)-Benzyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20a] (Table 5, entry 13), General Procedure C

(R_P)-**19b** (0.056 g, 0.149 mmol) reacted with $PhCH_2Cl$ (0.179 mmol, 20.6 μL) and NaH (6 mg, 0.149 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20a** (0.047 g, 0.127 mmol, 85%).

(S_P)-Methyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20c] (Table 5, entry 14), General Procedure C[33a]

(R_P)-**19b** (0.056 g, 0.149 mmol) reacted with MeI (0.373 mmol, 23.2 μL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20c** (0.039 g, 0.136 mmol, 91%).

(S_P)-Isopropyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20d] (Table 5, entry 15), General Procedure C

(R_P)-**19b** (0.056 g, 0.149 mmol) reacted with *i*-PrI (0.373 mmol, 37.3 μL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20d** (0.031 g, 0.098 mmol, 66%).

(S_P)-Allyl(phenyl)phosphinous Acid-Borane L-Menthyl Ester [(S_P)-20e] (Table 5, entry 16), General Procedure C

(R_P)-**19b** (0.056 g, 0.149 mmol) reacted with allyl bromide (0.373 mmol, 32.3 μL) and NaH (6.3 mg, 0.156 mmol, 60% in mineral oil) according to general procedure C to afford (S_P)-**20e** (0.031 g, 0.098 mmol, 66%).

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Supporting Information

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