Reactivity of allyl anions of allylphosphine-boranes towards electrophiles

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This paper is dedicated to Prof. William F. Bailey on the occasion of his 65th birthday

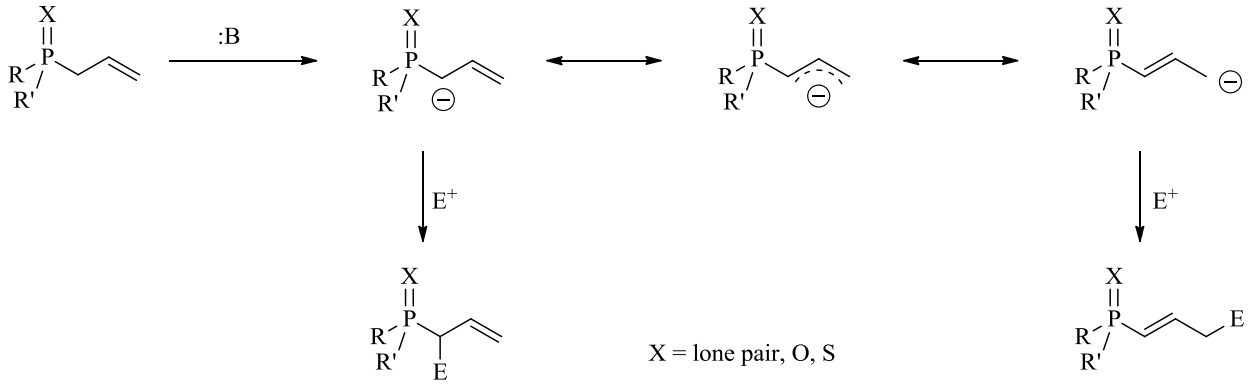
Abstract
The reactivity of mesomeric carbanions derived from allylphosphine-boranes varies as a function of electrophile. Small sp^3-electrophiles react predominantly at the α carbon atom whereas bulky sp^3-electrophiles and carbonyl compounds react mainly at the γ carbon. In the case of electron-deficient aldehydes reduction of carbonyl group and formation of the corresponding alcohols is observed. This is attributed to the weakly reducing properties of carbanions derived from allylphosphine-boranes, whose mesomeric form resembles the structure of a modified borohydride.

Keywords: Phosphine-boranes, allyl, carbanion, alkylation, reduction

Introduction

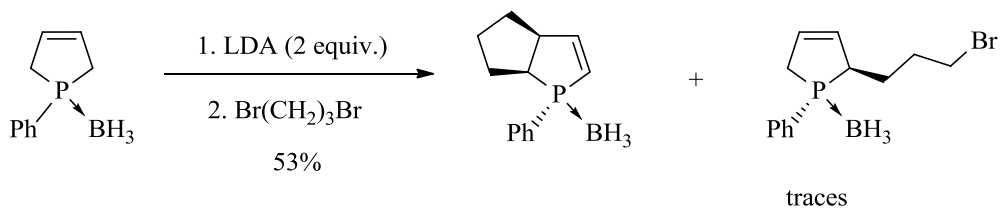
The presence of a multiple carbon-carbon bond in close proximity to phosphorus atom provides a wide the spectrum of reactivity for modifying organophosphorus compounds. Those possessing a P-vinyl substituent can be utilised in Michael addition reactions to provide precursors of P-P[1] or P-N-type[2] ligands. Ruthenium-catalysed metathesis of vinylphosphine oxides and boranes has been used by several research groups for the synthesis of ethylene-bridged diphosphine derivatives.[3] The Diels-Alder reaction between vinyl-substituted organophosphorus compounds and P-heterocycles in the presence of an organometallic template can also provide norbornene-like bicyclic diphosphines.[4] In the case of allyl-substituted organophosphorus compounds, most of the known functionalisation chemistry concerns the α-carbanions which are formed upon abstraction of a proton from the allyl moiety by a strong base. When such anions are generated from triphenylphosphonium salts, reaction with carbonyl compounds leads to the formation of a conjugated alkene through a Wittig reaction, and its reactivity has been widely explored in the

synthesis of natural compounds like callystatin A,[5] astaxanthin analogues,[6] ratjadone,[7] epolactaene,[8] viridenomycin[9] or superstolide A.[10] In such cases, however, the loss of the phosphorus moiety is necessary to complete the synthesis. In the cases where the phosphorus moiety is retained in the final product, the mesomeric nature of phosphorus-substituted allyl anion means that the formation of two isomeric compounds is to be expected (Scheme 1).



Scheme 1. Mesomeric forms of allyl anion derived from P-allyl compounds.

The outcome of such a reaction is influenced by the nature of the substrates employed and the reaction conditions, with less sterically demanding electrophiles generally preferring the α-position, whilst more sterically encumbered electrophiles favour the γ-position. Results obtained so far for allylphosphonates show that *sp*^{3}-electrophiles and aldehydes react preferentially at the α-position[11] whereas ketones react at both the α- and the γ-carbon.[12] On the other hand, α,β-unsaturated carbonyls react mainly at the γ-carbon atom of the allyl moiety.[13] Surprisingly little is known about the reactivity of other classes of allyl-substituted organophosphorus compounds,[14] including phosphine-boranes, which are very attractive substitutes for free phosphines because they are devoid of many typical shortcomings of free phosphines such as sensitivity to oxygen and moisture. These features explain why phosphine-boranes are often used in the synthesis of phosphine ligands for transition metal-catalysed reactions.[15] Surprisilgly, the only known application of phosphine-borane-derived allyl carbanions can be found in one of our recent studies,[16] which demonstrated that the alkylation of a 3-phospholene-borane with dihaloalkanes in the presence of an excess of base can lead to the formation of a bicyclic phosphine-borane as the major reaction product (Scheme 2)



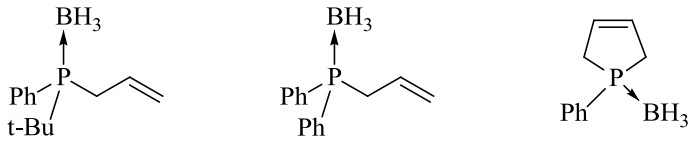
Scheme 2. Cyclopentannulation of 1-phenylphosphol-3-ene-borane.

The usefulness and generality of these allyl anion-induced annulations was further confirmed by the synthesis of *P,C*-chiral bicyclic monophosphine ligands which showed enantioselectivities up to 95% ee in palladium-catalysed allylic substitution reactions.[17]

The structural complexity of the bicyclic phosphine-borane formed from simple allylphosphine-boranes nicely illustrates the ambivalent reactivity of phosphorus-substituted allyl anions and suggests that, if controlled appropriately, this could be used in the synthesis of a wide range of useful compounds. To achieve this, a basic understanding of the reactivity of such systems is needed. Here, we present our results concerning the reactivity of allyl carbanions derived from allyphosphine-boranes or phosphol-3-ene-boranes.

Results and Discussion

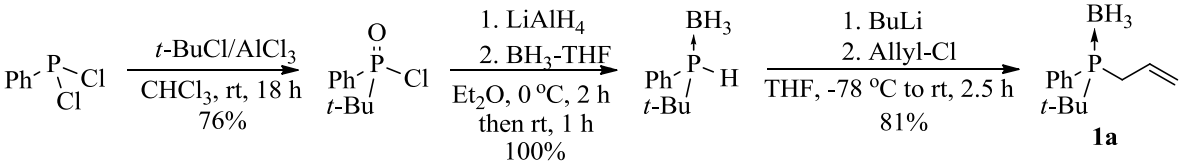
Three model phosphine-boranes: allyl-*t*-butylphenylphosphine-borane **1a**, allyldiphenyl-phosphine-borane **1b** and 1-phenylphosphol-3-ene-borane **1c** (Chart 1), were chosen for test reactions because they present different structural motifs having diaryl, arylalkyl and arylcycloalkyl substitution patterns at phosphorus.



1a **1b** **1c**

Chart 1. Model phosphine-boranes.

Allyl-*t*-butylphenylphosphine-borane **1a** was synthesized in three steps from phenyldichlorophosphine as shown in Scheme 3.

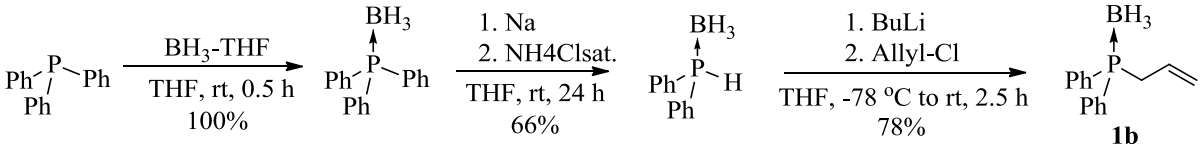


1a

Scheme 3. The synthesis of allyl(*t*-butyl)phenylphosphine-borane **1a**.

Treatment of $PhPCl_2$ with *t*-butyl chloride in the presence of $AlCl_3$ followed by hydrolysis gave *t*-butylphenylphosphinic chloride. Subsequent reduction with $LiAlH_4$ and *in situ* trapping with BH_3 afforded the corresponding secondary phosphine-borane, which was in turn allylated in the presence of butyllithium.

Allyldiphenylphosphine-borane **1b** was prepared in three steps starting from commercially available triphenylphosphine (Scheme 4).



Scheme 4. The synthesis of allyldiphenylphosphine-borane **1b**.

Triphenylphosphine was treated with the BH_3-THF complex to give the corresponding phosphine-borane quantitatively. Removal of one phenyl group from the phosphorus atom was accomplished by treatment with sodium and the resulting secondary phosphine-borane was converted to allylphosphine-borane by allylation with BuLi/Allyl-Cl.

1-Phenylphosphol-3-ene-borane **1c** was prepared from the corresponding phosphine oxide in two steps[16b] through reduction of P=O bond with $LiAlH_4$ and *in situ* complexation of tertiary phosphine with BH_3-THF.

With these three model compounds in hands, we started our studies of the alkylation of P-allyl carbanions with a range of alkyl halides (Table 1).

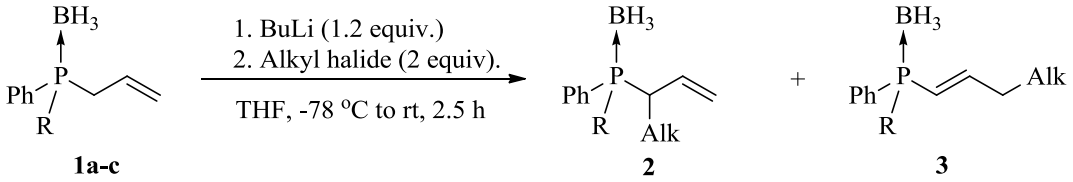


Table 1. Reactivity of **1a-b** towards alkylating agents

Entry	Electrophile	Phosphine-borane	Products (%)			
1	MeI (**a**)	**1a**	**2aa**	68	**3aa**	15
2		**1b**	**2ba**	88		-
3	BnCl (**b**)	**1a**	**2ab**	29*	**3ab**	21
4		**1b**	**2bb**	76	**3bb**	13
5	AllylCl (**c**)	**1a**	**2ac**	13	**3ac**	62
6		**1b**	**2bc**	42	**3bc**	42
7	c-HexBr (**d**)	**1a**		-	**3ad**	47
8		**1b**	**2bd**	22	**3bd**	47
9	TMSCl (**e**)	**1a**		-	**3ae**	91
10	$BrCH_2COOEt$ (**f**)	**1a**		-	**3af**	20
11	$BrCH_2COOEt$ (**f**)	**1a**	**2af**	23**		-

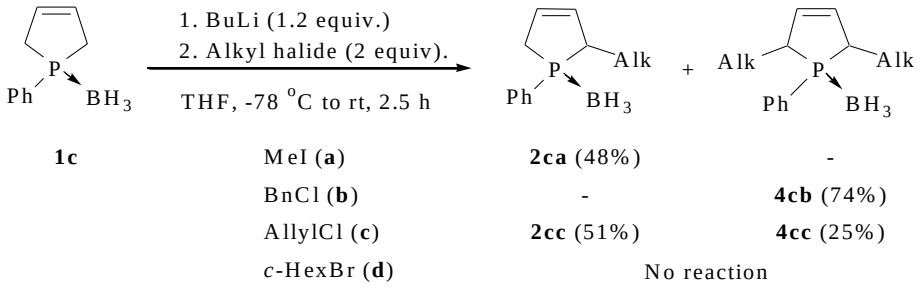
* - when performed in Et_2O, the reaction afforded **2ab** as the sole product in 58% yield.

** - the reaction was performed at 0 °C.

It can be seen from Table 1 that only methyl iodide, the smallest electrophile, gave completely regioselective alkylation at the α-carbon of the P-allyl carboanion (entries 1 and 2, Table 1). Other electrophiles react with phosphine-boranes **1a** and **1b** at both the α- and γ-carbanionic sites. The course of the reaction seems to be governed by the steric hindrance at the reaction centre; this control is more pronounced for **1a** which possesses a bulky *tert*-butyl group attached to the phosphorus atom than for **1b** which features a smaller phenyl substituent. Steric crowding at the phosphorus atom impedes the approach of the electrophile at the α-carbon atom thus favouring its reaction through the γ-carbocation. This is clearly seen in the reactions of **1a** with different electrophiles (entries 1,3,5,7,9), where replacement of methyl iodide with the more bulky benzyl chloride gives less clean α-alkylation and no α-alkylation at all is found when cyclohexyl bromide or trimethylsilyl chloride are used as electrophiles. An interesting effect was observed in the reaction of **1a** with ethyl bromoacetate. When performed at -78 ^{o}C, the reaction afforded the γ-alkylation product **3af** in 20% yield (Table 1, entry 10) whilst changing the temperature to 0 ^{o}C gave only α-alkylation product **2af** in 23% yield (Table 1, entry 11).

Being sterically less demanding than a *t*-butyl substituent, the phenyl group gives higher yields of α-alkylation products (entries 2,4,6,8, Table 1). Even with cyclohexyl bromide the formation of α-alkylation product was still observed at a reasonable level.

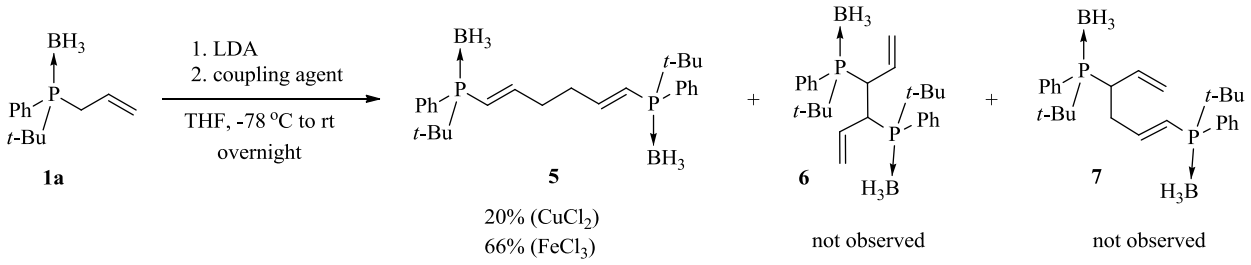
Unlike **1a** and **1b**, phosphine-borane **1c** gave only α-alkylation products, regardless of the electrophile used. Another striking observation for **1c** was the formation of bis-α,α'-alkylated products in the reaction with benzyl and allyl chlorides (Scheme 5).



Scheme 5. Reaction of **1c** with various alkyl halides.

The same type of behaviour has previously been observed by Pakulski *et al.* in the reactions of 3-phospholene oxides and sulphides with alkylating agents (Scheme 2).[16] Another potentially useful application of P-allyl anions is their homocoupling, which provides diphosphines having two double bonds in the carbon skeleton linking the two phosphorus atoms. Given the two mesomeric forms of phosphorus-substituted allyl anion, three isomeric α,α-, γ,γ- and α,γ-coupling products **5**, **6** or **7** can theoretically be formed (Scheme 6). Each of them appears to have a potentially useful unsaturation pattern: activated double bonds for Michael addition or Diels-Alder reaction in **5**, or non-activated allylic double bonds for radical reactions or polymerisation in **6** and **7**. In the event, treatment of the allyl anion generated from phosphine-

borane **1a** and LDA with $CuCl_2$ or $FeCl_3$ led to the formation of only the γ,γ-coupled product in 20% and 66% yields, respectively (Scheme 6).



Scheme 6. Homocoupling of **1a**.

We next turned our attention to sp^2-type electrophiles and explored their reactivity towards the P-allyl anions derived from **1a-c** (Table 2). The results collected in the Table 2 clearly show that, under basic conditions, phosphine-boranes **1a,b** react as γ-carbon nucleophiles towards carbonyl compounds to give the corresponding δ-hydroxy-α-alkenylphosphine-boranes **8** exclusively, in good to excellent yields. Formaldehyde however, failed to give clean conversion and instead yielded a complex product mixtures. With acetophenone as the electrophile (Table 2, entry 11), the allyl anion of **1a** afforded a mixture of two γ-addition products: **8al** and **9al**, the latter possibly arising from isomerisation of the double bond in **8al**. Another striking observation was the reaction of methyl vinyl ketone **m** with the allyl anions of **1a** and **1b** (Table 2, entries 13, 14). In this case, the allyl anions reacted exclusively through 1,2-addition to form the corresponding γ-alcohols in good yields. This stands in sharp contrast to previous observations of the reactivity of phosphoryl-substituted allyl anions with α,β-unsaturated carbonyl compounds where exclusively 1,4-addition products were observed in the reaction mixture.[13] Reactions with methyl vinyl ketone also revealed a sensitivity to steric demands. In the case of allyl-*t*-butylphenylphosphine-borane **1a**, the only product isolated from the reaction mixture resulted from γ-addition, whereas in the case of **1b** substantial quantities of α-addition product were observed (Table 2, entry 14). With ethyl acetate as the electrophile, the only compound isolated from the reaction mixture was the tertiary alcohol **8an**, an evolution product which results from the addition of butyllithium to the carbonyl group of the first-formed γ-acyl product (Table 2, entry 15).

In the case of borane **1a**, addition of the allyl anion to carbonyl compound possessing a prochiral C=O group created additional chirality at the centre δ to the phosphorus atom. However, as there was no steric differentiation in the proximity of the γ carbon atom, the reaction of **1a** with prochiral carbonyl reagents prodeeded with low diatereoselectivity in all cases (Table 2, entries 1, 3, 5, 11 and 13).

Addition of carbon dioxide to the allyl anion of **1a**,**b** yielded the corresponding (4-boranatophosphinyl)but-3-enoic acids in 76 and 92% yields, respectively (Table 2, entries 16 and 17).

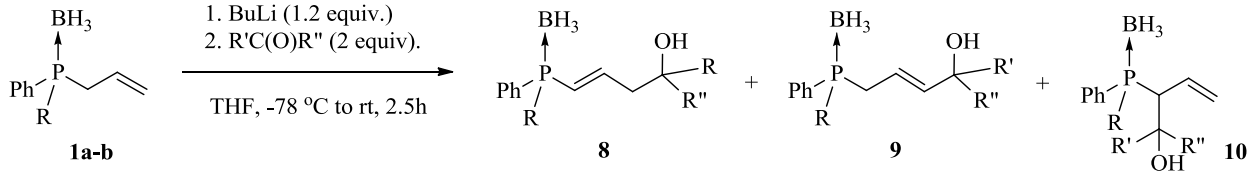
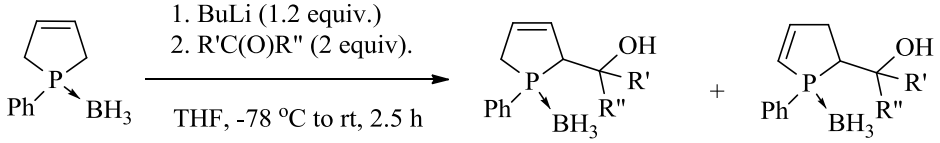


Table 2. Reactivity of **1a-b** towards carbonyl compounds

Entry	Electrophile	Phosphine-borane	Products (%)	
1	benzaldehyde (**g**)	**1a**	**8ag**	97 (61:39 d.r.)
2		**1b**	**8bg**	77
3	p-tolulaldehyde (**h**)	**1a**	**8ah**	64 (50:50 d.r.)
4		**1b**	**8bh**	65
5	o-tolulaldehyde (**i**)	**1a**	**8ai**	67 (53:47 d.r.)
6		**1b**	**8bi**	73
7	acetone (**j**)	**1a**	**8aj**	99
8		**1b**	**8bj**	73
9	cyclohexanone (**k**)	**1a**	**8ak**	71
10		**1b**	**8bk**	53
11	acetophenone (**l**)	**1a**	**8al** **9al**	36 (56:44 d.r.) 24 (62:38 d.r.)
12		**1b**	**8bl**	67
13	methyl vinyl ketone (**m**)	**1a**	**8am**	84 (58:42 d.r.)
14		**1b**	**8bm**:**10bm**	91 (45:55)
15	ethyl acetate (**n**)	**1a**	**8an** (R' - Me, R" - *n*-Bu)	81
16	carbon dioxide (**o**)	**1a**	**8ao**	76
17		**1b**	**8bo**	92

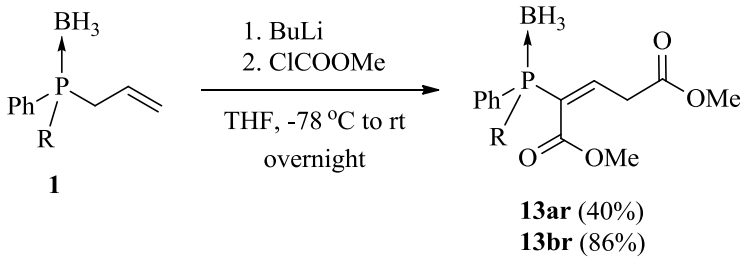
Unlike phosphine-boranes **1a** and **1b**, the cyclic phosphine-borane **1c** reacted only as an α-nucleophiles but isomerisation of the double bond was observed in some cases. This may reflect strongly basic conditions present in the reaction mixture (Scheme 7).



benzaldehyde (**g**)	-	**12cg** (41% (59:41 dr))
cyclohexanone (**k**)	**11ck** (31%)	-
acetophenone (**l**)	-	**12cl** (76%)

Scheme 7. Reactivity of **1c** towards carbonyl compounds.

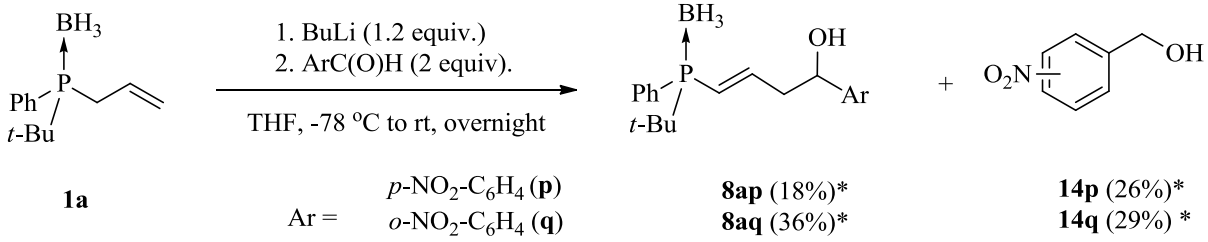
Interesting results were obtained in the reaction between P-allyl anions derived from **1a** and **1b** and methyl chloroformate (Scheme 8).



Scheme 8. Reaction of **1a** with methyl chloroformate.

In both cases, the formation of α,γ-disubstitution products was observed, in 40% and 86% yields for **1a** and for **1b**, respectively. It seems likely, that the formation of these unusual products can be explained in terms of an enhanced reactivity of the intermediate monosubstitution product with respect to the parent P-allyl anion.

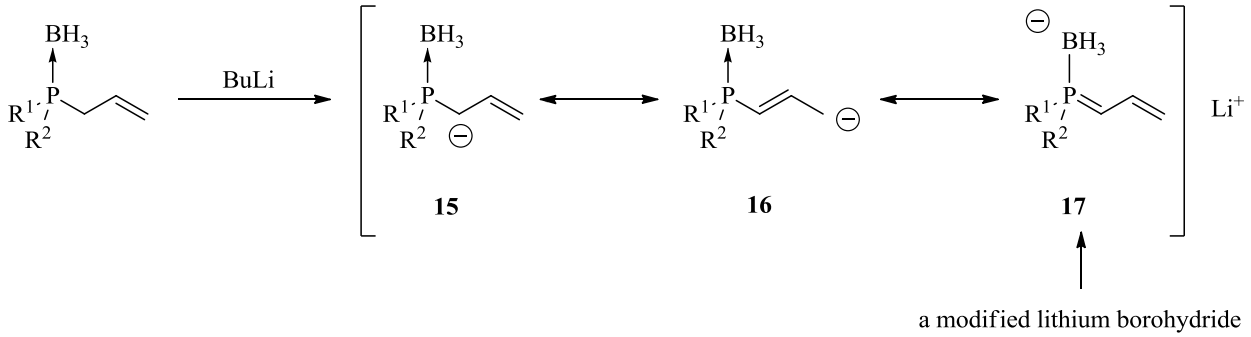
An interesting feature of the reactions of allylphosphine-borane anions with some electron deficient carbonyl electrophiles was the reduction of the carbonyl compounds (Scheme 9).



* - yields calculated from ^{1}H NMR spectra

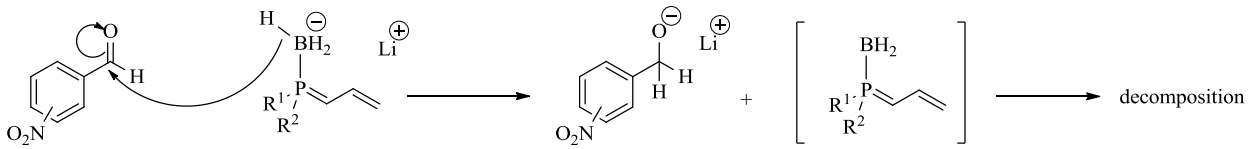
Scheme 9. Reaction of **1a** with nitro-substituted benzaldehydes under basic conditions.

In the reaction of **1a** with *p*-nitrobenzaldehyde the yield of the expected adduct **8ap** was only 18% (^{1}H NMR) while the yield of *p*-nitrobenzyl alcohol **12p** was 26% based on consumed aldehyde. When *o*-nitrobenzaldehyde was used as the reactant, the yield of expected **8aq** was estimated to be 36% (^{1}H NMR), whereas the yield of *o*-nitrobenzyl alcohol **12q** was 29% as based on aldehyde consumption. The formation of such benzyl alcohols in reactions, where no reducing agent was added to the reaction mixture, points to the allylphosphine-borane anions as potential reducing agents.



Scheme 10. Formulation of an allylphosphine-borane anion as amodified lithium borohydride.

As depicted in Scheme 10, deprotonation of allylphosphine-borane leads to the formation of an anion whose structure can be drawn in three mesomeric forms **15-17**. Form **17** localises some anionic electron density at boron and can be regarded as a modified borohydride anion. Borohydrides are known to reduce carbonyl groups in aldehydes and ketones easily but is apparently less reactive and exhibits its reducing properties only towards electron deficient aldehydes (Scheme 11).



Scheme 11. Plausible mechanism for the reduction of carbonyl groups by a modified borohydride.

Conclusions

In conclusion, the reactivity of mesomeric allylphosphine-borane-derived anions derived from allylphosphine-boranes towards electrophiles depends strongly on the structure of the starting allylphosphine-borane and on the electrophile. Small sp^3-electrophiles react predominantly at the α-carbon atom, whereas sterically demanding sp^3-electrophiles react mostly at the γ-carbon. On the other hand, sp^2-electrophiles react with such allyl anions at γ-carbon atom to give δ-hydroxy-α-alkenylphosphine-boranes in good yields, except in the case of electron deficient carbonyl compounds which are reduced by the phosphine-borane anions to the corresponding alcohols instead of being attacked by the allyl anion. Homodimerisation of allylphosphine-borane-derived anions provides 1,6-diphosphine-diboranes possessing a 1,5-hexadienyl linker.

Experimental Section

General. All reactions were conducted under inert atmosphere and with anhydrous and oxygen-free solvents. THF was dried under sodium/benzophenone, diethyl ether was dried under metallic sodium and chloroform was dried under P_2O_5. All electrophiles used in reactions were commercially available and were used as received. The course of reaction was followed by TLC (Merck, silica 60 F_{254}, aluminium plates) and iodine/SiO_2 was used as the developing agent. Flash chromatography was performed using silica gel (Merck, 20-230 mesh) with hexane:ethyl acetate 2-50:1 as eluents. NMR analyses were performed on Bruker Avance 300 in $CDCl_3$ with TMS as internal standard and elementary analysis was performed on PERKIN ELMER CHN 2400 at the Department of Organic Chemistry, Marie Curie-Skłodowska University, Lublin, Poland.

Synthesis of allyl-*t*-butylphenylphosphine-borane (1a)

***t*-Butylphenylphosphinic chloride.** In a two-necked flask (500 mL) equipped with magnetic stirrer, argon inlet and dropping funnel was placed 200 mL of chloroform, 23 mL (0.17 mol) dichlorophosphine, and 25 g (0.188 mol) of $AlCl_3$ and the mixture was stirred at room temperature for 30 min until all $AlCl_3$ dissolved. Then, the flask was immerced in the ice-water bath and 25 mL (0.226 mol) of *t*-butyl chloride was slowly added via dropping funnel. After complete addition of *t*-BuCl the reaction mixture was stirred at room temperature for overnight. Then, diluted hydrochloric acid (10%, 150 mL) was added and mixture was extracted with DCM (5x100 mL). Combined organic phases were dried over magnesium sulfate, filtered and evaporated and the residue was distilled under low pressure yielding *t*-butylphenylphosphinic chloride as colorless oil which solidified upon standing in refrigerator (24.3 g, 66%). b.p. 156 ^{o}C/15 mm Hg. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (d, J_{P-H} 19.1 Hz, *t*-Bu, 9H), 7.45-7.70 (m, Ph, 3H), 7.79-7.96 (m, Ph, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.12, 38.93 (d, J_{P-C} 77.4 Hz), 128.25 (d, J_{P-C} 12.8 Hz), 132.45 (d, J_{P-C} 10.0 Hz), 132.81 (d, J_{P-C} 2.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 74.3 ppm. Elem. anal. for $C_{10}H_{14}ClOP$: calc. C 55.44, H 6.51; found C 55.59, H 6.82.

***t*-Butylphenylphosphine-borane.** In a 500 mL two-necked flask equipped with magnetic stirrer, ice-water bath and argon inlet was placed 150 mL of diethyl ether and 2.40 g (11 mmol) of *t*-butylphenylphosphinic chloride. Reaction mixture was cooled to 0 ^{o}C and 0.84 g (22 mmol) of lithium aluminum hydride was added in one portion and reaction was stirred at 0 ^{o}C for two hours. Then, excess of $LiAlH_4$ was removed by slow addition of water until no bubbling was observed. The formed solids were removed by filtration through 2 cm layer of silica gel under argon and the solid was washed with DCM (100 mL). The solution was then placed in the two-necked flask equipped with magnetic stirrer and argon inlet and 22 mL (22 mmol) of 1M BH_3-THF complex was added. Reaction was stirred at room temperature for an hour and then was evaporated and the residue was dissolved in 50 mL of DCM and filtered. Evaporation yielded 1.98 g (100%) of *t*-butylphenylphosphine-borane as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ –0.05-1.65 (bm, BH_3, 3H); 1.21 (d, J_{P-H} 14.8 Hz, *t*-Bu, 9H), 5.13 (dq, J_{P-H} 368.0 Hz, 1H, P-H);

7.41-7.73 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.54 (d, J_{P-C} 2.9 Hz), 28.46 (d, J_{P-C} 32.5 Hz), 124.74 (d, J_{P-C} 51.0 Hz), 128.54 (d, J_{P-C} 9.7 Hz). 131.50 (d, J_{P-C} 3.5 Hz), 133.88 (d, J_{P-C} 7.7 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 31.99 ppm (m). Elem. anal. for $C_{10}H_{15}BP$: calc. C 66.83, H 10.21; found C 67.15, H 10.48.

Allyl-*t*-butylphenylphosphine-borane (1a). In a 250 mL two-necked flask equipped with magnetic stirrer, dry ice-acetone bath, and argon inlet was placed 100 mL of THF and 1.98 g (11 mmol) of *t*-butylphenylphosphine-borane. Then, 10 mL (16.5 mmol) of 1.6 M butyllithium was added and mixture was stirred at -78 ^{o}C for 30 minutes. Then, 1.8 mL (22 mmol) of allyl chloride was added and reaction mixture was left at room temperature for overnight. Then, 10 mL of 5% HCl was added with subsequent 30 mL of distilled water and the mixture was extracted with DCM (3x50 mL). Organic phases were dried over magnesium sulfate, filtered and evaporated. The residue was purified by flash chromatography using hexane/EtOAc 6:1 as eluent yielding 2.0 g (83%) of allyl-*t*-butylphenylphosphine-borane **1a** as pasty white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.13-1.29 (bm, BH_3, 3H), 1.12 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 2.72-2.86 (m, 1H), 2.88-3.04 (m, 1H), 5.05-5.21 (m, 2H), 7.40-7.53 (m, 3H), 7.66-7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.74 (d, J_{P-C} 33.1 Hz), 25.04 (d, J_{P-C} 2.3 Hz), 28.89 (d, J_{P-C} 30.8 Hz), 119.18 (d, J_{P-C} 10.6 Hz), 125.19 (d, J_{P-C} 48.3 Hz), 127.76 (d, J_{P-C} 9.2 Hz), 128.76 (d, J_{P-C} 4.6 Hz), 130.73 (d, J_{P-C} 2.3 Hz), 133.16 (d, J_{P-C} 7.6 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 30.36 (m). Elem. anal. for $C_{13}H_{19}BP$: calc. C 70.93, H 10.09; found C 70.18, H 10.01.

Synthesis of allyldiphenylphosphine-borane (1b)

Diphenylphosphine-borane. In a 250 mL two-necked flask equipped with magnetic stirrer and argon inlet was placed 100 mL of THF, 10 g (38 mmol) of triphenylphosphine and 38 mL (38 mmol) of 1M BH_3-THF was added. After one hour the mixture was evaporated yielding pure triphenylphosphine-borane which was used directly in the next step.

In 250 mL two-necked flask equipped with magnetic stirrer and argon inlet was placed 100mL of THF, 5.0 g (18 mmol) of triphenylphosphine-borane and 0.83 g (36 mmol) of metallic sodium was added. After stirring for 24h at rt reaction was finished by adding saturated ammonium chloride solution (50 mL). The formed mixture was extracted with DCM (3x100 mL) dried over anhydrous magnesium sulfate, filtered and evaporated. The residue was purified on silica gel using hexane/EtOAc 6:1 as eluent yielding 5.02 g (66%) of diphenylphosphine-borane as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.25-1.95 (bm, BH_3, 3H), 6.35 (dq, J_{P-H} 380.0 Hz, 1H), 7.41-7.79 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 126,11 (d, J_{P-C} 56.9 Hz), 128.98 (d, J_{P-C} 10.6 Hz), 131.56 (d, J_{P-C} 2.4 Hz). 132.85 (d, J_{P-C} 9.3 Hz, P-Ph). ^{31}P NMR ($CDCl_3$, 121.5 MHz): d 2.89 (m). Elem. anal. for $C_{12}H_{14}BP$: calc. C 71.93, H 6.90; found C 72.15, H 7.09.

Preparation of allyldiphenylphosphine-borane (1b). In a Schlenk flask equipped with magnetic stirrer and argon inlet was placed diphenylphosphine-borane (2.34g, 11.7 mmol) in 80 mL of dry THF. Then, reaction was cooled to -78 ^{o}C and 1.6 M BuLi (11 mL, 17.6 mmol) was added and the mixture was stirred at -78 ^{o}C for 0.5 h. Then, the bath was taken out and allyl chloride(1.91 mL, 22 mmol) was added and the mixture was allowed to stir for overnight. Then,

reaction mixture was quenched with saturated ammonium chloride solution and extracted three times with DCM (3x30 mL). Combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The residue was purified by flash chromatography using hexane/EtOAc 6:1 as eluent yielding allyldiphenylphosphine-borane **1b** (2.20 g, 78%) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.30-1.40 (bm, BH_3, 3H); 3.04-3.13 (m, 2H), 5.03-5.11 (m, 2H), 5.72-5.89 (m, 1H), 7.42-7.55 (m, 6H), 7.65-7.74 (m 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 26.18 (d, J_{P-C} 40.2 Hz), 120.02 (d, J_{P-C} 11.5 Hz), 128.18 (d, J_{P-C} 9.8 Hz), 128.99 (d, J_{P-C} 5.5 Hz), 129.36 (d, J_{P-C} 54.6 Hz), 130.74 (d, J_{P-C} 2.6 Hz), 133.05 (d, J_{P-C} 8.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 15.88 (m). Elem. anal. for $C_{15}H_{18}BP$: calc. C 75.04, H 7.56; found C 74.80, H 7.27.

General procedure for reaction between allylphosphine-boranes 1 and *sp*^{3} electrophiles

In a Schlenk flask equipped with magnetic stirrer and argon inlet was placed allylphosphine-borane **1** (0.19-0.76 mmol) in 10 mL of dry THF. Then, reaction was cooled to -78 ^{o}C and BuLi (1.6 M in hexanes) (0.28-1.142 mmol) was added and the resulting mixture was stirred at -78 ^{o}C temperature for 0.5 h. Then, an electrophile (0.38-1.52 mmol) was added and the reaction mixture was allowed to warm to room temperature overnight. Then, the reaction was quenched with saturated NH_4Cl solution and extracted with DCM (3x15 mL). Combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The residue was purified by flash chromatography using hexane/EtOAc 2:1 to 50:1 as eluent to give product.

(But-1-en-3-yl)-*t*-butylphenylphosphine-borane (**2aa).** Yield 68% from 0.076 g (0.35 mmol) of **1**, purified with hexane/EtOAc (10/1), white solid, m.p. 42-44 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.02-1.11 (bm, BH_3, 3H), 0.97 (d, J_{P-H} 7.0 Hz, 3H, CH_3), 1.04 (d, J_{P-H} 13.5 Hz, 9H, *t*-Bu), 3.17-3.35 (m, 1H), 5.07-5.14 (m, 1H), 5.17-5.27 (m, 1H), 5.99-6.20 (m, 1H), 7.30-7.45 (m, 3H), 7.62-7.73 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.22, 26.15 (d, J_{P-C} 2.0 Hz), 30.36 (d, J_{P-C} 30.2 Hz), 32.39 (d, J_{P-C} 31.9 Hz), 116.70 (d, J_{P-C} 10.4 Hz), 126.90 (d, J_{P-C} 48.0 Hz), 128.26 (d, J_{P-C} 8.9 Hz), 130.97 (d, J_{P-C} 2.3 Hz), 133.23 (d, J_{P-C} 7.2 Hz), 138.01. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 37.80 (m). Elem. anal. for $C_{14}H_{24}BP$: calc. C 71.82, H 10.33; found C 71.99, H 10.50.

(But-1-en-1-yl)-*t*-butylphenylphosphine-borane (**3aa).** Yield 15% from 0.076 g (0.35 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.10-1.17 (bm, BH_3, 3H), 1.08 (d, J_{P-H} 13.7 Hz, 9H, *t*-Bu), 1.09 (t, J_{H-H} 6.9 Hz, 1H), 2.25-2.35 (m, 2H), 6.16-6.26 (m, 1H), 6.78-7.00 (m, 1H), 7.43-7.53 (m, 3H), 7.69-7.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.28 (d, J_{P-C} 1.2 Hz), 25.33 (d, J_{P-C} 2.9 Hz), 27.96 (d, J_{P-C} 36.5 Hz), 35.16 (d, J_{P-C} 14.7 Hz), 112.47 (d, J_{P-C} 56.0 Hz), 128.08 (d, J_{P-C} 9.5 Hz), 130.71 (d, J_{P-C} 2.6 Hz), 133.00 (d, J_{P-C} 7.8 Hz), 156.32 (d, J_{P-C} 9.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 24.83 (m). Elem. anal. for $C_{14}H_{24}BP$: calc. C 71.82, H 10.33; found C 71.78, H 10.61.

(But-1-en-3-yl)-diphenylphosphine-borane (**2ba).** Yield 88% from 0.077 g (0.32 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24-1.32 (bm, BH_3, 3H), 1.18 (dd, J_{H-H} 7.0 Hz, J_{P-H} 16.28 Hz, CH_3, 3H), 3.13-3.32 (m, 1H), 4.84-5.01 (m, 2H), 5.65-5.82 (m, 1H), 7.23-7.43 (m, 6H), 7.60-7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.33 (d,

J_{P-C} 1.5 Hz), 34.89 (d, J_{P-C} 34.5 Hz), 117.76 (d, J_{P-C} 10.1 Hz), 127.90 (d, J_{P-C} 54.0 Hz), 128.26 (d, J_{P-C} 50.9 Hz), 128.42 (d, J_{P-C} 9.8 Hz), 128.70 (d, J_{P-C} 10.1 Hz), 131.10 (d, J_{P-C} 2.3 Hz), 131.12 (d, J_{P-C} 2.0 Hz), 132.58 (d, J_{P-C} 8.3 Hz), 133.00 (d, J_{P-C} 8.3 Hz), 135.15 (d, J_{P-C} 2.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 23.29 (m). Elem. anal. for $C_{16}H_{20}BP$: calc. C 75.62, H 7.93; found C 75.80, H 7.95.

2-Methyl-1-phenyl-3-phospholene-borane (**2ca).** Yield 48% from 0.050 g (0.28 mmol) of **1c**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.13-1.32 (bm, BH_3, 3H), 1.27 (dd, J_{P-H} 16.7 Hz, J_{P-H} 7.3 Hz, CH_3, 3H), 2.61-2.88 (m, 2H), 2.90-3.03 (m, 1H), 5.79-5.92 (m, 2H), 7.31-7.46 (m, 3H), 7.61-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.04 (d, J_{P-C} 4.9 Hz), 32.86 (d, J_{P-C} 35.6 Hz), 39.62 (d, J_{P-C} 34.5 Hz), 126.73 (d, J_{P-C} 0.9 Hz), 128.77 (d, J_{P-C} 9.8 Hz), 131.10 (d, J_{P-C} 8.6 Hz), 131.35 (d, J_{P-C} 2.6 Hz), 131.38 (d, J_{P-C} 52.3 Hz), 135.98 (d, J_{P-C} 4.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 32.20 (m). Elem. anal. for $C_{11}H_{16}BP$: calc. C 69.52, H 8.49; found C 69.40, H 8.40.

***t*-Butylphenyl-(4-phenylbut-1-en-3-yl)phosphine-borane** (**2ab).** Yield 29% from 0.051 g (0.23 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.11-1.28 (bm, BH_3, 3H), 1.06 (d, J_{P-H} 13.6 Hz, *t*-Bu, 9H), 2.44-2.66 (m, 2H), 3.15-3.30 (m, 1H), 4.74-4.83 (m, 1H), 5.03-5.09 (m, 1H), 5.91-6.07 (m, 1H), 6.85-6.91 (m, 2H), 7.04-7.19 (m, 3H), 7.41-7.50 (m, 3H), 7.77-7.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.20 (d, J_{P-C} 1.7 Hz), 30.69 (d, J_{P-C} 29.6 Hz), 36.23 (d, J_{P-C} 2.3 Hz), 40.95 (d, J_{P-C} 30.8 Hz), 119.51 (d, J_{P-C} 10.9 Hz), 126.19, 126.98 (d, J_{P-C} 47.7 Hz), 128.02, 128.54 (d, J_{P-C} 9.2 Hz), 129.20, 131.29 (d, J_{P-C} 2.3 Hz), 133.33 (d, J_{P-C} 7.2 Hz), 134.79, 139.12 (d, J_{P-C} 12.6 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 36.96 (m). Elem. anal. for $C_{20}H_{28}BP$: calc. C 77.43, H 9.10; found C 77.70, H 9.31.

***t*-Butylphenyl-(4-phenylbut-1-en-1-yl)phosphine-borane (3ab).** Yield 21% from 0.051 g (0.23 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07-1.28 (bm, BH_3, 3H), 0.95 (d, J_{P-H} 13.9 Hz, *t*-Bu, 9H), 2.51-2.61 (m, 2H), 2.71-2.79 (m, 2H), 6.01-6.12 (m, 1H), 6.71-6.89 (m, 1H), 7.04-7.15 (m, 3H), 7.15-7.24 (m, 2H), 7.28-7.40 (m, 3H), 7.51-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.31 (d, J_{P-C} 2.6 Hz), 29.45 (d, J_{P-C} 35.4 Hz), 34.29 (d, J_{P-C} 1.4 Hz), 36.75 (d, J_{P-C} 14.7 Hz), 114.82 (d, J_{P-C} 54.9 Hz), 126.04, 128.11 (d, J_{P-C} 9.5 Hz), 128.43, 128.45, 128.90 (d, J_{P-C} 43.7 Hz), 130.73 (d, J_{P-C} 2.6 Hz), 133.03 (d, J_{P-C} 8.3 Hz), 140.71, 153.58 (d, J_{P-C} 9.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25,28 ppm (m). Elem. anal. for $C_{20}H_{28}BP$: calc. C 77.43, H 9.10; found C 77.25, H 9.00.

Diphenyl-(4-phenylbut-1-en-3-yl)phosphine-borane (**2bb).** Yield 76% from 0.081 g (0.33 mmol) of **1b**, purified with hexane/EtOAc (50/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.33-1.63 (bm, BH_3, 3H), 2.66-2.92 (m, 2H), 3.22-3.37 (m, 1H), 4.49-4.61 (m, 1H), 4.83-4.90 (m, 1H), 5.57-5.74 (m, 1H), 7.00-7.23 (m, 5H), 7.24-7.48 (m, 6H), 7.60-7.71 (m, 2H), 7.75-7.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 35.14 (d, J_{P-C} 3.6 Hz), 43.26 (d, J_{P-C} 32.5 Hz), 120.48 (d, J_{P-C} 10.3 Hz), 126.29, 128.03 (d, J_{P-C} 54.3 Hz), 128.06 (d, J_{P-C} 56.0 Hz), 128.20, 128.41 (d, J_{P-C} 9.8 Hz), 128.89 (d, J_{P-C} 10.1 Hz), 128.92, 131.13 (d, J_{P-C} 2.3 Hz), 131.38 (d, J_{P-C} 2.6 Hz), 132.69 (d, J_{P-C} 8.9 Hz), 132.76 (d, J_{P-C} 2.6 Hz), 132.92 (d, J_{P-C} 8.6 Hz), 139.18 (d, J_{P-C} 13.8 Hz). ^{31}P

NMR ($CDCl_3$, 121.5 MHz): δ 21.96 (m). Elem. anal. for $C_{22}H_{24}BP$: calc. C 80.02, H 7.33; found C 79.91, H 7.14.

Diphenyl-(4-phenylbut-1-en-1-yl)phosphine-borane (**3bb).** Yield 13% from 0.081 g (0.33 mmol) of **1b**, purified with hexane/EtOAc (50/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.33-1.63 (bm, BH_3, 3H), 2.23-2.34 (m, 2H), 2.60-2.71 (m, 2H), 6.02-6.15 (m, 1H), 6.57-6.76 (m, 1H), 7.05-7.27 (m, 5H), 7.34-7.48 (m, 6H), 7.61-7.77 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 34.20 (d, J_{P-C} 1.2 Hz), 36.44 (d, J_{P-C} 15.2 Hz), 119.40 (d, J_{P-C} 57.8 Hz), 126.05, 128.16, 128.62 (d, J_{P-C} 10.1 Hz), 128.49, 130.90 (d, J_{P-C} 2.3 Hz), 132.32 (d, J_{P-C} 9.5 Hz), 151.77 (d, J_{P-C} 7.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.35 (m). Elem. anal. for $C_{22}H_{24}BP$: calc. C 80.02, H 7.33; found C 80.24, H 7.50.

2,5-Dibenzyl-3-phospholene-borane (**4cb).** Yield 73% from 0.051 g (0.29 mmol) of **1c**, purified with hexane/EtOAc (50:1), white solid, m.p. 100-102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.12-1.63 (bm, BH_3, 3H), 2.57-2.72 (m, 2H), 3.08-3.31 (m, 4H), 5.65-5.79 (m, 2H), 7.04-7.28 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 38.08 (d, J_{P-C} 5.2 Hz), 46.62 (d, J_{P-C} 32.2 Hz) 126.38, 128.24, 128.44, 128.83, 128.84 (d, J_{P-C} 9.5 Hz), 131.20 (d, J_{P-C} 8.6 Hz), 131.26 (d, J_{P-C} 48.6 Hz), 131.49 (d, J_{P-C} 2.3 Hz), 132.60 (d, J_{P-C} 4.3 Hz), 139.97 (d, J_{P-C} 13.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 38.66 (m). Elem. anal. for $C_{24}H_{26}BP$: calc. C 80.91, H 7.36; found C 80.92, H 7.50.

***t*-Butyl-(hexa-1,5-dien-3-yl)phenylphosphine-borane** (**2ac).** Yield 13% from 0.148 g (0.76 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07-1.20 (bm, BH_3, 3H), 1.04 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 1.81-1.95 (m, 1H), 2.07-2.22 (m, 1H), 3.00-3.14 (m, 1H), 4.72-4.91 (m, 2H), 5.12-5.25 (m, 2H), 5.48-5.64 (m, 1H), 5.86-6.02 (m, 1H), 7.31-7.47 (m, 3H), 7.62-7.74 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 36.69 (m). Elem. anal. for $C_{16}H_{26}BP$: calc. C 73.87, H 10.07; found C 74.15, H 10.34.

***t*-Butyl-(hexa-1,5-dien-1-yl)phenylphosphine-borane (3ac).** Yield 62% from 0.148 g (0.76 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.08-1.23 (bm, BH_3, 3H), 1.02 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H), 2.13-2.23 (m, 2H), 2.29-2.39 (m, 2H), 4.90-5.03 (m, 2H), 5.64-5.81 (m, 1H), 6.10-6.22 (m, 1H), 6.69-6.87 (m, 1H), 7.29-7.45 (m, 3H), 7.60-7.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.36 (d, J_{P-C} 2.9 Hz), 29.36 (d, J_{P-C} 35.1 Hz), 32.10 (d, J_{P-C} 1.2 Hz), 34.39 (d, J_{P-C} 14.9 Hz), 114.28 (d, J_{P-C} 55.8 Hz), 115.54, 128.11 (d, J_{P-C} 9.5 Hz), 128.30 (d, J_{P-C} 52.6 Hz), 130.77 (d, J_{P-C} 2.3 Hz), 133.06 (d, J_{P-C} 8.3 Hz), 137.13, 153.97 (d, J_{P-C} 8.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.19 (m). Elem. anal. for $C_{16}H_{26}BP$: calc. C 73.87, H 10.07; found C 73.99, H 10.00.

(Hexa-1,5-dien-3-yl)diphenylphosphine-borane (**2bc).** Yield 42%, from 0.072 g (0.30 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.30-1.58 (bm, BH_3, 3H), 2.11-2.20 (m, 2H), 3.02-3.18 (m, 1H), 4.72-5.04 (m, 2H), 5.52-5.79 (m, 1H), 5.98-6.13 (m, 1H), 6.44-6.64 (m, 1H), 7.26-7.45 (m, 6H), 7.58-7.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.04 (d, J_{P-C} 3.2 Hz), 41.01 (d, J_{P-C} 33.9 Hz), 115.60, 119.94 (d, J_{P-C} 10.6 Hz), 128.39 (d, J_{P-C} 9.8 Hz), 128.80 (d, J_{P-C} 10.1 Hz), 130.00 (d, J_{P-C} 59.2 Hz), 131.11 (d, J_{P-C} 2.3 Hz), 131.27 (d, J_{P-C} 2.3 Hz), 132.60 (d, J_{P-C} 8.6 Hz), 132.94 (d, J_{P-C} 8.6 Hz), 133.09 (d, J_{P-C} 2.9 Hz),

135.50 (d, J_{P-C} 14.1 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 21.99 (m). Elem. anal. for $C_{18}H_{22}BP$ (as a mixture with **3bc**): calc. C 77.17, H 7.92; found C 77.30, H 7.80.

(Hexa-1,5-dien-1-yl)diphenylphosphine-borane (**3bc).** Yield 42%, from 0.072 g (0.30 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.30-1.58 (bm, BH_3, 3H), 2.01-2.38 (m, 4H), 4.72-5.04 (m, 4H), 5.52-5.79 (m, 2H), 7.26-7.45 (m, 6H), 7.47-7.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.04 (d, J_{P-C} 1.2 Hz), 34.00 (d, J_{P-C} 15.2 Hz), 116.74, 118.87 (d, J_{P-C} 58.3 Hz), 128.07 (d, J_{P-C} 63.2 Hz), 128.67 (d, J_{P-C} 10.1 Hz), 130.96 (d, J_{P-C} 2.6 Hz), 132.35 (d, J_{P-C} 9.8 Hz), 137.01, 152.21 (d, J_{P-C} 7.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.46 (m). Elem. anal. for $C_{18}H_{22}BP$ (as a mixture with **2bc**): calc. C 77.17, H 7.92; found C 77.30, H 7.80.

2-Allyl-1-phenyl-3-phospholene-borane (**2cc).** Yield 51% from 0.051 g (0.29 mmol) of **1c**, purified with hexane/EtOAc (50:1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.09-1.31 (bm, BH_3, 3H), 2.10-2.29 (m, 2H), 2.50-2.69 (m, 2H), 2.84-2.92 (m, ,-*CH*-P-CH_2, 1H), 2.83-3.01 (m, 1H), 4.91-5.06 (m 2H), 5.68-5.86 (m, 1H), 5.86-6.00 (m, 2H), 7.29-7.48 (m, 3H), 7.58-7.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 33.04 (d, J_{P-C} 35.9 Hz), 35.39 (d, J_{P-C} 6.0 Hz), 44.79 (d, J_{P-C} 33.6 Hz), 116.85, 127.56 (d, J_{P-C} 0.6 Hz), 128.83 (d, J_{P-C} 9.8 Hz), 131.15 (d, J_{P-C} 8.9 Hz), 131.24 (d, J_{P-C} 48.3 Hz), 131.90 (d, J_{P-C} 2.6 Hz, P-Ph), 133.76 (d, J_{P-C} 5.2 Hz), 135.89 (d, J_{P-C} 11.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 31.44 (m). Elem. anal. for $C_{13}H_{18}BP$: calc. C 72.26, H 8.40; found C 72.40, H 8.45.

2,5-Diallyl-1-phenyl-3-phospholene-borane (**4cc).** Yield 25% from 0.051 g (0.29 mmol) of **1c**, purified with hexane/EtOAc (50:1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.06-1.27 (bm, BH_3, 3H), 2.10-2.27 (m, 2H), 2.50-2.66 (m, 2H), 2.88-3.00 (m, 2H), 4.92-5.05 (m, 4H), 5.67-5.84 (m, 2H), 5.88-6.01 (m, 2H), 7.31-7.47 (m, 3H), 7.61-7.73 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 35.85 (d, J_{P-C} 4.3 Hz), 44.75 (d, J_{P-C} 33.1 Hz), 116.86, 128.83 (d, J_{P-C} 9.5 Hz), 131.23 (d, J_{P-C} 8.6 Hz), 131.41 (d, J_{P-C} 2.6 Hz), 131.51 (d, J_{P-C} 48.9 Hz), 132.62 (d, J_{P-C} 4.3 Hz), 135.85 (d, J_{P-C} 11.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 38.54 (m). Elem. anal. for $C_{16}H_{22}BP$: calc. C 75.03, H 8.66; found C 74.95, H 8.60.

***t*-Butyl-(3-cyclohexylprop-1-en-1-yl)phenylphosphine-borane** (**3ad).** Yield 47% from 0.043 g (0.2 mmol) of **1a**, purified with hexane/EtOAc (10/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.08-1.24 (bm, BH_3, 3H), 1.02 (d J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.09-1.20 (bm, 4H), 1.30-1.44 (bm, 1H), 1.50-1.70 (bm, 6H), 2.10-2.17 (m, 2H), 6.06-6.17 (m, 1H), 6.67-6.86 (m, 1H), 7.30-7.45 (m, 3H), 7.60-7.71 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.36 (d, J_{P-C} 2.9 Hz), 26.12, 26.30, 29.33 (d, J_{P-C} 35.1 Hz), 30.85, 33.02, 33.11, 37.22 (d, J_{P-C} 1.2 Hz), 43.43 (d, J_{P-C} 14.4 Hz), 114.50 (d, J_{P-C} 54.9 Hz), 128.07 (d, J_{P-C} 9.5 Hz), 128.44 (d, J_{P-C} 55.2 Hz), 130.70 (d, J_{P-C} 2.6 Hz), 133.00 (d, J_{P-C} 8.1 Hz), 154.08 (d, J_{P-C} 9.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 24.85 (m). Elem. anal. for $C_{18}H_{30}BP$: calc. C 75.01, H 10.49; found C 74.75, H 10.22.

(3-Cyclohexylpropen-3-yl)diphenylphosphine-borane (**2bd).** Yield 22% from 0.076 g (0.32 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.36-1.65 (bm, BH_3, 3H), 1.31-1.49 (m, 3H), 1.50-1.71 (m, 8H), 2.89-3.04 (m, 1H), 4.71-5.00 (m, 2H), 5.64-5.83 (m, 1H), 7.24-7.47 (m, 6H), 7.5-7.80 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ

25.92, 26.45, 30.64 (d, J_{P-C} 2.9 Hz), 33.59 (d, J_{P-C} 9.5 Hz), 37.19, 47.43 (d, J_{P-C} 31.9 Hz), 120.03 (d, J_{P-C} 11.8 Hz), 128.19 (d, J_{P-C} 9.8 Hz), 128.66 (d, J_{P-C} 9.8 Hz), 129.35 (d, J_{P-C} 58.3 Hz), 129.39 (d, J_{P-C} 52.9 Hz), 130.24 (d, J_{P-C} 2.6 Hz), 130.98 (d, J_{P-C} 2.6 Hz), 132.15 (d, J_{P-C} 2.9 Hz), 132.40 (d, J_{P-C} 7.8 Hz), 133.07 (d, J_{P-C} 8.1 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 19.36 (m). Elem. anal. for $C_{21}H_{28}BP$ (as a mixture with 9d): calc. C 78.27, H 8.76; found C 78.45, H 8.70.

(3-Cyclohexylpropen-1-yl)diphenylphosphine-borane (3bd). Yield 47% from 0.076 g (0.32 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.36-1.65 (bm, BH_3, 3H), 1.31-1.49 (m, 3H), 1.50-1.71 (m, 8H), 2.08-2.18 (m, 2H), 5.97-6.13 (m, 1H), 6.47-6.68 (m, 1H), 7.24-7.47 (m, 6H), 7.49-7.62 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.12, 26.29, 33.07, 38.24 (d, J_{P-C} 2.9 Hz), 43.00 (d, J_{P-C} 15.2 Hz), 119.05 (d, J_{P-C} 58.3 Hz), 128.7 (d, J_{P-C} 9.77 Hz), 130.24 (d, J_{P-C} 63.2 Hz), 130.90 (d, J_{P-C} 2.3 Hz), 132.29 (d, J_{P-C} 9.2 Hz), 152.33 (d, J_{P-C} 7.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.13 (m). Elem. anal. for $C_{21}H_{28}BP$ (as a mixture with **8d**): calc. C 78.27, H 8.76; found C 78.45, H 8.70.

***t*-Butylphenyl-(3-trimethylsilylprop-1-en-1-yl)phosphine-borane (3ae).** Yield 91% from 0.049 g (0.22 mmol) of **1a**, purified with hexane/EtOAc (6/1), white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.05 (s, 9H, TMS), 0.57-1.30 (bm, BH_3, 3H), 1.09 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 1.84-1.89 (m, 2H), 5.95-6.05 (m, 1H), 6.80-6.99 (m, 1H), 7.36-7.47 (m, 3H), 7.68-7.77 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ -1.83, 25.35 (d, J_{P-C} 2.9 Hz), 28.00 (d, J_{P-C} 14.1 Hz), 29.32 (d, J_{P-C} 36.2 Hz), 110.24 (d, J_{P-C} 58.3 Hz), 127.98 (d, J_{P-C} 8.9 Hz), 128.94 (d, J_{P-C} 52.3 Hz), 130.55 (d, J_{P-C} 2.9 Hz), 132.95 (d, J_{P-C} 8.3 Hz), 153.11 (d, J_{P-C} 10.1 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 24.90 (m). Elem. anal. for $C_{16}H_{30}BPSi$: calc. C 65.75, H 10.35; found C 66.02, H 10.20.

3-(*t*-Butylphenylboranatophosphinyl)-pent-4-enoic acid ethyl ester (2af). Yield 23% from 0.101 g (0.46 mmol) of **1a**, 3:1 inseparable mixture of diastereoisomers, purified with hexane/EtOAc (6/1), colorless oil.

Major: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.15-1.56 (bm, BH_3, 3H), 1.15 (d, J_{P-H} 13.9 Hz, *t*-Bu, 9H), 1.28 (t, J_{H-H} 7.0 Hz, 3H), 2.34 (ddd, J_{H-H} 9.8 Hz, J_{H-H} 12.0 Hz, J_{P-H} 2.5 Hz, 2H), 3.71-3.87 (m, 1H), 3.99-4.12 (m, 3H), 5.23-5.30 (m, 1H), 5.35-5.44 (m, 1H), 5.99-6.15 (m, 1H), 7.43-7.53 (m, 3H), 7.75-7.83 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 37.20 (m).

Minor: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.15-1.56 (bm, BH_3, 3H), 1.04 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H), 1.10 (t, J_{H-H} 6.9 Hz, 3H), 2.15-2.28 (m, 1H), 2.42-2.57 (m, 1H), 3.14-3.29 (m, 1H), 4.15-4.33 (m, 2H), 5.05-5.22 (m, 2H), 5.88-6.06 (m, 1H), 7.39-7.50 (m, 3H), 7.64-7.74 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 36.87 (m). Elem. anal. for $C_{17}H_{28}BO_2P$: calc. C 66.69, H 9.22; found C 66.40, H 9.35.

3-(*t*-Butylphenylboranatophosphinyl)pent-3-enoic acid ethyl ester (3af). Yield 20% from 0.041 g (0.19 mmol) of **1a**, colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24-1.32 (bm, BH_3, 3H), 1.08 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H), 1.23 (t, J_{H-H} 7.2 Hz, 3H), 2.46-2.54 (m, 2H), 2.58-2.68 (m, 2H), 4.12 (q, J_{H-H} 7.2 Hz, 2H), 6.25-6.35 (m, 1H), 6.75-6.92 (m, 1H), 7.39-7.49 (m, 3H), 7.67-7.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ .14.17, 25.35 (d, J_{P-C} 2.6 Hz), 29.68, 32.64 (d, J_{P-C} 1.2 Hz), 60.62, 115.39 (d, J_{P-C} 54.3 Hz), 128.20 (d, J_{P-C} 9.8 Hz), 130.89 (d, J_{P-C} 2.0 Hz), 133.08

(d, J_{P-C} 8.1 Hz), 152.24 (d, J_{P-C} 11.5 Hz), 172.36. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.30 (m). Elem. anal. for $C_{17}H_{28}BO_2P$: calc. C 66.69, H 9.22; found C 66.74, H 9.10.

1,6-Bis(*t*-butylphenylboranatophosphinyl)-hexa-1,5-diene (5). Mixture of two diastereoisomers dr 50:50, yield 66% from 0.110g (0.50 mmol) of **1a**, purified with hexane/EtOAc (6/1), pasty white solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.13-1.34 (bm, BH_3, 3H), 1.02 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.08 (d, J_{H-H} 14.0 Hz, 9H), 2.50-2.55 (m, 4H), 6.24-6.34 (m, 2H), 6.75-6.93 (m, 2H), 7.39-7.50 (m, 6H), 7.66-7.76 (m, 4H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.39 (m). Elem. anal. for $C_{26}H_{42}B_2OP_2$: calc. C 71.27, H 9.66; found C 71.45, H 9.32.

General procedure for reaction between allylphosphine-borane 1 and carbonyl compounds

In a Schlenk flask equipped with magnetic stirrer and argon inlet was placed allylphosphine-borane **1** (0.040-0.193g, 0.18-0.88 mmol) in 10 mL of dry THF. Then, reaction was cooled to -78 ^{o}C and 1.6 M BuLi solution in hexanes (0.17-0.83 mL, 0.27-1.32 mmol) was added and the resulting mixture was stirred at -78 ^{o}C for 0.5h. Then, the bath was taken out and electrophile (0.36-1.76 mmol) was added. The mixture was stirred for overnight then was quenched with saturated NH_4Cl solution and formed mixture was extracted with DCM (3x15 mL). Combined organic phases were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The residue was purified by flash chromatography using hexane/EtOAc 2:1 to 50:1 as eluent to give product.

***t*-Butyl-(4-hydroxy-4-phenyl-but-1-en-1-yl)phenylphosphine-borane (8ag).** Mixture of two diastereoisomers, dr 61:39, yield 97% from 0.193 g (0.88 mmol) of **1a**, purified with hexane/EtOAc (6/1), yellow oil.

Major: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.11-1.26 (bm, BH_3, 3H), 0.99 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H), 2.64-2.84 (m, 2H), 2.85 (bs, OH, 1H), 4.79-4.86 (m, 1H), 6.17-6.28 (m, 1H), 6.71-6.90 (m, 1H), 7.29-7.36 (m, 5H), 7.36-7.49 (m, 3H), 7.56-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.24 (d, J_{P-C} 2.9 Hz), 29.32 (d, J_{P-C} 35.1 Hz), 44.86 (d, J_{P-C} 14.1 Hz), 72.90 (d, J_{P-C} 1.2 Hz), 117.50 (d, J_{P-C} 54.0 Hz), 125.83, 127.69, 128.10 (d, J_{P-C} 9.5 Hz), 128.48, 130.77 (d, J_{P-C} 2.6 Hz), 133.02 (d, J_{P-C} 7.8 Hz), 143.34, 149.95 (d, J_{P-C} 9.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.59 (bm).

Minor: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.11-1.26 (bm, BH_3, 3H), 1.04 (d, J_{P-H} 14.2 Hz, *t*-Bu, 9H), 2.64-2.84 (m, 2H), 2.85 (bs, OH, 1H), 4.79-4.86 (m, 1H), 6.17-6.28 (m, 1H), 6.71-6.90 (m, 1H), 7.29-7.36 (m, 5H), 7.36-7.49 (m, 3H), 7.56-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.30 (d, J_{P-C} 2.9 Hz), 29.35 (d, J_{P-C} 35.1 Hz), 44.83 (d, J_{P-C} 14.1 Hz), 72.85 (d, J_{P-C} 1.2 Hz), 117.46 (d, J_{P-C} 54.3 Hz), 125.74, 127.64, 128.08 (d, J_{P-C} 9.5 Hz), 128.46, 130.73 (d, J_{P-C} 3.2 Hz), 133.00 (d, J_{P-C} 8.1 Hz), 143.41, 150.03 (d, J_{P-C} 8.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.59 (bm). Elem. anal. for $C_{20}H_{28}BOP$: calc. C 73.64, H 8.65; found C 73.78, H 8.80.

(4-Hydroxy-4-phenyl-but-1-en-1-yl)diphenylphosphine-borane (8bg). Yield 77% from 0.049 g (0.20 mmol) of **1b**, purified with hexane/EtOAc (2:1), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.31-1.49 (bm, BH_3, 3H), 2.08 (bs, OH, 1H), 2.53-2.76 (m, 2H), 4.70-4.79 (m, 1H), 5.94-6.10 (m, 1H), 6.36-6.57 (m, 1H), 7.14-7.49 (m, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 44.40 (d, J_{P-C} 15.2 Hz), 72.93 (d, J_{P-C} 1.2 Hz), 121.85 (d, J_{P-C} 57.5 Hz), 125.80, 127.75, 128.54, 128.63 (d, J_{P-C}

10.1 Hz), 128.66 (d, J_{P-C} 10.4 Hz), 129.59 (d, J_{P-C} 58.9 Hz), 129.64 (d, J_{P-C} 59.2 Hz), 130.94 (d, J_{P-C} 2.6 Hz), 130.99 (d, J_{P-C} 2.3 Hz), 132.31 (d, J_{P-C} 9.5 Hz), 132.37 (d, J_{P-C} 9.8 Hz), 143.25, 148.15 (d, J_{P-C} 7.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.55 (m). Elem. anal. for $C_{22}H_{24}BOP$: calc. C 76.32, H 6.99; found C 76.50, H 7.04.

5-(1-Hydroxy-1-phenylmethyl)-2-phospholene-borane (12cg). Yield 41% from 0.049 g (0.28 mmol) of **1c**, purified with hexane/EtOAc (6:1) mixture of two diastereoisomers, dr 59:41, as a mixture with benzyl alcohol (29%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.14-1.30 (bm, BH_3, 3H), 2.14-2.41 (m, 3H), 3.36-3.48 (bs, OH, 1H), 4.39-4.65 (m, 1H), 5.96-6.11 (m, 1H), 6.02-6.20 (m, 1H), 6.27-6.45 (m, 1H), 6.95-7.11 (m, 1H), 7.19-7.44 (m, 8H), 7.48-7.60 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 26.58 and 28.89 (m).

***t*-Butyl-(4-hydroxy-4-(*p*-tolyl)-but-1-en-1-yl)phenylphosphine-borane (8ah).** Mixture of two diastereoisomers, dr 50:50, yield 64% from 0.042 g (0.19 mmol) of **1a**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07-1.18 (bm, BH_3, 3H), 0.92 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H) and 0.97 (d, J_{P-H} =14.2 Hz, *t*-Bu, 9H), 2.03 (bs, OH, 1H), 2.23 (s, 3H), 2.54-2.73 (m, 2H), 4.95-5.03 (m, 1H), 6.09-6.22 (m, 1H), 6.66-6.86 (m, 1H), 6.95-7.18 (m, 4H), 7.27-7.42 (m, 3H), 7.56-7.64 (m, 2H) and 7.48-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.55 and 21.57, 25.75 (d, J_{P-C} 2.9 Hz) and 2.83 (d, J_{P-C} 2.6 Hz), 29.85 (d, J_{P-C} 35.1 Hz) and 29.9 (d, J_{P-C} 35.1 Hz), 45.30 (d, J_{P-C} 14.1 Hz), 73.26 (d, J_{P-C} 1.2 Hz) and 73.29 (d, J_{P-C} 1.2 Hz), 117.86 (d, J_{P-C} 54.0 Hz) and 117.90 (d, J_{P-C} 54.3 Hz), 126.22 and 126.31, 128.54 (d, J_{P-C} 52.3 Hz) and 128.60 (d, J_{P-C} 52.3 Hz), 128.57 (d, J_{P-C} 8.9 Hz) and 128.62 (d, J_{P-C} 9.3 Hz), 129.64 and 129.65, 131.24 (d, J_{P-C} 2.3 Hz) and 131.30 (d, J_{P-C} 2.6 Hz), 133.54 (d, J_{P-C} 7.8 Hz) and 133.55 (d, J_{P-C} 7.8 Hz), 137.73 and 138.36, 150.61 (d, J_{P-C} 9.2 Hz) and 150.70 (d, J_{P-C} 9.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.43 (m). Elem. anal. for $C_{21}H_{30}BOP$: calc. C 74.13, H 8.89; found C 74.00, H 8.70.

(4-Hydroxy-4-(*p*-tolil)-but-1-en-1-yl)diphenylphosphine-borane (8bh). Yield 65% from 0.066 g (0.28 mmol) of **1b**, purified with hexane/EtOAc (6:1), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24-1.63 (m, BH_3, 3H), 1.90 (bs, OH, 1H), 2.26 (s, 3H), 2.48-2.75 (m, 2H), 4.69-4.76 (m, 1H), 5.95-6.08 (m, 1H), 6.38-6.58 (m, 1H), 7.01-7.18 (m, 4H), 7.23-7.50 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.10, 44.34 (d, J_{P-C} 14.9 Hz), 72.78 (d, J_{P-C} 0.9 Hz), 121.58 (d, J_{P-C} 57.2 Hz), 125.75, 128.59 (d, J_{P-C} 10.4 Hz), 128.63 (d, J_{P-C} 10.1 Hz), 129.17, 129.63 (d, J_{P-C} 58.9 Hz), 129.70 (d, J_{P-C} 58.9 Hz), 130.90 (d, J_{P-C} 2.6 Hz), 130.97 (d J_{P-C} 2.9 Hz), 132.31 (d, J_{P-C} 9.5 Hz), 132.37 (d, J_{P-C} 9.5 Hz), 147.40, 140.26, 148.33 (d, J_{P-C} 7.5 Hz. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.56 (m). Elem. anal. for $C_{23}H_{26}BOP$: calc. C 76.68, H 7.27; found C 76.84, H 7.20.

***t*-Butyl-(4-hydroxy-4-(*o*-tolyl)-but-1-en-1-yl)phenylphosphine-borane (8ai).** Mixture of two diastereoisomers, dr 53:47, yield 67% from 0.065 g (0.29 mmol) of **1a**, purified with hexane/EtOAc (6/1), pale yellow oil.

Major: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.06-1.11 (bm, BH_3, 3H), 0.92 (d, J_{P-H} 14.2 Hz, *t*-Bu, 9H), 1.86 (bs, OH, 1H), 2.23 (s, 3H), 2.58-2.68 (m, 2H), 4.96-5.02 (m, 1H), 6.10-6.22 (m, 1H), 6.67-6.86 (m, 1H), 6.95-7.18 (m, 4H), 7.27-7.42 (m, 3H), 7.56-7.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.08, 25.24 (d, J_{P-C} 2.6 Hz), 29.31 (d, J_{P-C} 35.4 Hz), 44.00 (d, J_{P-C} 14.4 Hz), 68.97

(d, J_{P-C} 1.4 Hz), 117.52 (d, J_{P-C} 54.0 Hz), 125.23, 127.40, 128.08 (d, J_{P-C} 52.0 Hz), 128.12 (d, J_{P-C} 9.5 Hz), 128.14, 130.43, 130.78 (d, J_{P-C} 2.6 Hz), 133.00 (d, J_{P-C} 7.8 Hz), 134.33, 141.33, 150.06 (d, J_{P-C} 9.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.44 (m).

Minor: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.06-1.11 (bm, BH_3, 3H), 0.98 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.86 (bs, OH, 1H), 2.17 (s, 3H), 2.58-2.68 (m, 2H), 4.96-5.02 (m, 1H), 6.10-6.22 (m, 1H), 6.67-6.86 (m, 1H), 6.95-7.18 (m, 4H), 7.27-7.42 (m, 3H), 7.48-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.01, 25.32 (d, J_{P-C} 2.9 Hz), 29.37 (d, J_{P-C} 35.1 Hz), 43.96 (d, J_{P-C} 14.1 Hz), 68.97 (d, J_{P-C} 1.4 Hz), 117.36 (d, J_{P-C} 54.0 Hz), 125.17, 127.35, 128.00 (d, J_{P-C} 52.3 Hz), 128.22 (d, J_{P-C} 9.5 Hz), 128.94, 130.41, 130.73 (d, J_{P-C} 2.6 Hz), 132.96 (d, J_{P-C} 8.1 Hz), 134.29, 141.45, 150.15 (d, J_{P-C} 9.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.44 (m). Elem. anal. for $C_{21}H_{30}BOP$: calc. C 74.13, H 8.89; found C 74.38, H 8.99.

(4-Hydroxy-4-(*o*-tolil)-but-1-en-1-yl)diphenylphosphine-borane (8bi). Yield 68% from 0.066 g (0.27 mmol) of **1b**, purified with hexane/EtOAc (6:1), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32-1.61 (bm, BH_3, 3H), 1.75 (bs, 1H, OH), 2.22 (s, 3H), 2.57-2.73 (m, 2H), 4.99-5.08 (m, 1H), 5.98-6.16 (m, 1H), 6.43-6.62 (m, 1H), 7.00-7.20 (m, 4H), 7.24-7.52 (bm, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.12, 43.49 (d, J_{P-C} 15.2 Hz), 69.12 (d, J_{P-C} 1.2 Hz), 121.87 (d, J_{P-C} 57.2 Hz), 125.29, 126.42, 127.48, 128.67 (d, J_{P-C} 10.4 Hz), 128.70 (d, J_{P-C} 10.1 Hz), 129.68 (d, J_{P-C} 59.2 Hz), 129.70 (d, J_{P-C} 58.9 Hz), 130.48, 130.96 (d, J_{P-C} 2.6 Hz), 131.01 (d, J_{P-C} 2.3 Hz), 132.33 (d, J_{P-C} 9.5 Hz), 132.39 (d, J_{P-C} 9.5 Hz), 134.36, 141.34, 148.25 (d, J_{P-C} 7.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.37 (m). Elem. anal. for $C_{23}H_{26}BOP$: calc. C 76.68, H 7.27; found C 76.70, H 7.25.

***t*-Butyl-(4-hydroxy-4-methylpent-1-en-1-yl)phenylphosphine-borane (8aj).** Yield 99% from 0.045 g (0.2 mmol) of **1a**, purified with hexane/EtOAc (1/1), pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.11-1.20 (bm, BH_3, 3H), 1.30 (d, J_{P-H} 14.2 Hz, *t*-Bu, 9H), 1.18 (s, 6H), 1.77 (bs, OH, 1H), 2.39-2.44 (m, 2H), 6.20-6.30 (m, 1H), 6.73-6.90 (m, 1H), 7.31-7.41 (m, 3H), 7.62-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.30 (d, J_{P-C} 2.6 Hz), 29.16, 29.25, 29.35 (d, J_{P-C} 35.1 Hz), 49.52 (d, J_{P-C} 14.4 Hz), 70.57 (d, J_{P-C} 1.2 Hz), 117.68 (d, J_{P-C} 54.0 Hz). 128.06 (d, J_{P-C} 52.3 Hz), 128.11 (d, J_{P-C} 9.5 Hz), 130.80 (d, J_{P-C} 2.6 Hz), 132.98 (d, J_{P-C} 8.1 Hz), 150.51 (d, J_{P-C} 8.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.43 (m). Elem. anal. for $C_{16}H_{28}BOP$: calc. C 69.08, H 10.15; found C 69.00, H 9.99.

(4-Hydroxy-4-methylpent-1-en-1-yl)diphenylphosphine-borane (8bj). Yield 73% from 0.046 g (0.19 mmol) of **1b**, purified with hexane/EtOAc (6:1), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.33-1.62 (bm, BH_3, 3H), 1.16 (s, 6H), 1.82 (bs, OH, 1H), 2.35-2.41 (m, 2H), 6.09-6.21 (m, 1H), 6.50-6.69 (m, 1H), 7.29-7.43 (m, 6H), 7.50-7.59 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.34, 49.11 (d, J_{P-C} 14.1 Hz), 70.66 (d, J_{P-C} 1.2 Hz), 122.18 (d, J_{P-C} 57.2 Hz), 128.73 (d, J_{P-C} 10.4 Hz), 129.82 (d, J_{P-C} 58.9 Hz), 131.04 (d, J_{P-C} 2.6 Hz), 132.43 (d, J_{P-C} 9.5 Hz), 148.70 (d, J_{P-C} 7.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.36 (m). Elem. anal. for $C_{18}H_{24}BOP$: calc. C 72.51, H 8.11; found C 72.74, H 7.99.

***t*-Butyl-(4-cyclohexylidene-4-hydroxy-but-1-en-1-yl)phenylphosphine-borane (8ak).** Yield 71% from 0.047 g (0.21 mmol) of **1a**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR

($CDCl_3$, 300 MHz): δ 0.08-1.29 (bm, BH_3, 3H), 1.02 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.30-1.59 (m, 10H), 2.37-2.43 (m, 2H), 6.19-6.30 (m, 1H), 6.75-6.92 (m, 1H), 7.31-7.44 (m, 3H), 7.62-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.99, 22.01, 25.37 (d, J_{P-C} 2.9 Hz), 25.51, 29.40 (d, J_{P-C} 35.1 Hz), 37.41, 37.50, 48.35 (d, J_{P-C} 13.8 Hz), 71.44 (d, J_{P-C} 0.9 Hz), 117.81 (d, J_{P-C} 53.7 Hz), 128.16 (d, J_{P-C} 9.2 Hz), 128.19 (d, J_{P-C} 51.7 Hz), 130.83 (d, J_{P-C} 2.6 Hz), 133.04 (d, J_{P-C} 7.8 Hz), 150.21 (d, J_{P-C} 9.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.32 (m). Elem. anal. for $C_{19}H_{32}BOP$: calc. C 71.71, H 10.14; found C 71.79, H 9.97.

(4-Cyclohexylidene-4-hydroxy-but-1-en-1-yl)diphenylphosphine-borane (8bk). Yield 53% from 0.038 g (0.16 mmol) of **1b**, purified with hexane/EtOAc (6:1), colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.30-1.48 (bm, BH_3, 3H), 1.27-1.58 (m, 10H), 2.34-2.41 (m, 2H), 6.08-6.21 (m, 1H), 6.54-6.73 (m, 1H), 7.30-7.44 (m, 6H), 7.49-7.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.02, 25.50, 37.52, 47.99 (d, J_{P-C} 15.5 Hz), 71.45, 122.09 (d, J_{P-C} 56.9 Hz), 128.74 (d, J_{P-C} 10.1 Hz), 131.01 (d, J_{P-C} 2.6 Hz), 132.34 (d, J_{P-C} 9.5 Hz), 148.50 (d, J_{P-C} 7.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.29 (m). Elem. anal. for $C_{21}H_{28}BOP$: calc. C 74.57, H 8.34; found C 74.59, H 8.40.

5-(1'-Hydroxycyclohexyl)-3-phospholene-borane (11ck). Yield 31% from 0.050 g (0.28 mmol) of **1c**, purified with hexane/EtOAc (6:1), colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.39-1.76 (bm, BH_3, 3H), 1.13-1.68 (m, 10H), 1.77-1.89 (m, 2H), 2.68 (bs, OH, 1H), 3.08-3.18 (m, 1H), 5.89-6.12 (m, 2H), 7.31-7.48 (m, 3H), 7.61-7.74 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.44, 21.71, 25.43, 32.56 (d, J_{P-C} 38.2 Hz), 35.16 (d, J_{P-C} 4.6 Hz), 37.39 (d, J_{P-C} 5.5 Hz), 74.19 (d, J_{P-C} 2.6 Hz), 128.29 (d, J_{P-C} 9.5 Hz), 129.76, 130.41 (d, J_{P-C} 47.1 Hz), 131.06 (d, J_{P-C} 9.2 Hz), 131.32 (d, J_{P-C} 11.5 Hz), 131.41 (d, J_{P-C} 2.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.38 (m). Elem. anal. for $C_{16}H_{24}BOP$: calc. C 70.10, H 8.82; found C 70.35, H 8.90.

***t*-Butyl-(4-hydroxy-4-phenylpent-1-en-1-yl)phenylphosphine-borane (8al).** Mixture of two diastereoisomers, dr 56:44, yield 36% from 0.084 g (0.38 mmol) of **1a**, purified with hexane/EtOAc (6/1), colorless oil.

Major: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.05-1.23 (bm, BH_3, 3H), 0.90 (d, J_{P-H} 14.2 Hz, *t*-Bu, 9H), 1.53 (s, 3H), 1.93 (bs, OH, 1H), 2.68-2.75 (m, 2H), 6.03-6.13 (m, 1H), 6.56-6.74 (m, 1H), 7.11-7.41 (m, 8H), 7.47-7.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.28 (d, J_{P-C} 3.2 Hz), 29.32 (d, J_{P-C} 35.3 Hz), 29.80, 49.95 (d, J_{P-C} 14.1 Hz), 74.26 (d, J_{P-C} 1.1 Hz), 118.32 (d, J_{P-C} 54.0 Hz), 124.65, 126.80, 127.95 (d, J_{P-C} 52.0 Hz), 128.07 (d, J_{P-C} 9.5 Hz), 128.23, 130.73 (d, J_{P-C} 2.3 Hz), 133.00 (d, J_{P-C} 7.8 Hz), 146.71, 149.42 (d, J_{P-C} 8.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.74 (m).

Minor: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.05-1.23 (bm, BH_3, 3H), 0.94 (d, J_{P-H} 14.0 Hz, *t*-Bu, 9H), 1.54 (s, 3H), 1.93 (bs, OH, 1H), 2.68-2.75 (m, 2H), 6.03-6.13 (m, 1H), 6.56-6.74 (m, 1H), 7.11-7.41 (m, 8H), 7.47-7.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.24 (d, J_{P-C} 2.9 Hz), 29.28 (d, J_{P-C} 35.1 Hz), 29.59, 49.98 (d, J_{P-C} 14.1 Hz), 74.20 (d, J_{P-C} 1.1 Hz), 118.41 (d, J_{P-C} 54.0 Hz), 124.67, 126.85, 127.95 (d, J_{P-C} 52.0 Hz), 128.07 (d, J_{P-C} 9.5 Hz), 128.23, 130.73 (d, J_{P-C} 2.3 Hz), 133.04 (d, J_{P-C} 7.8 Hz), 146.76, 149.42 (d, J_{P-C} 8.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.74 (m). Elem. anal. for $C_{21}H_{30}BOP$: calc. C 74.13, H 8.89; found C 74.01, H 8.70.

***t*-Butyl-(4-hydroxy-4-phenylpent-2-en-1-yl)phenylphosphine-borane (9al).** Mixture of two diastereoisomers, dr 62:38, yield 24% from 0.084 g (0.38 mmol) of **1a**, purified with hexane/EtOAc (6/1), colorless oil.

Major: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07-1.24 (bm, BH_3, 3H), 1.05 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 1.40 (s, 3H), 1.69 (bs, OH, 1H), 2.64-2.76 (m, 1H), 2.82-2.96 (m, 1H), 5.52-5.83 (m, 2H), 7.01-7.20 (m, 5H), 7.30-7.46 (m, 3H), 7.58-7.67 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.64 (d, J_{P-C} 32.5 Hz), 25.49 (d, J_{P-C} 2.0 Hz), 29.20, 74.32 (d, J_{P-C} 1.7 Hz), 119.49 (d, J_{P-C} 54.0 Hz), 124.88, 126.63, 127.98, 128.19 (d, J_{P-C} 9.8 Hz), 131.13 (d, J_{P-C} 2.6 Hz), 133.78 (d, J_{P-C} 8.1 Hz), 141.66 (d, J_{P-C} 10.6 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 32.13 (m).

Minor: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07-1.24 (bm, BH_3, 3H), 1.04 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 1.44 (s, 3H), 1.69 (bs, OH, 1H), 2.64-2.76 (m, 1H), 2.82-2.96 (m, 1H), 5.52-5.83 (m, 2H), 7.01-7.20 (m, 5H), 7.30-7.46 (m, 3H), 7.58-7.67 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.56 (d, J_{P-C} 33.1 Hz), 25.49 (d, J_{P-C} 2.0 Hz), 29.20, 74.22 (d, J_{P-C} 1.7 Hz), 119.14 (d, J_{P-C} 4.6 Hz), 125.09, 126.82, 128.05, 128.19 (d, J_{P-C} 9.8 Hz), 131.13 (d, J_{P-C} 2.6 Hz), 133.73 (d, J_{P-C} 8.1 Hz), 141.97 (d, J_{P-C} 10.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 32.13 (m). Elem. anal. for $C_{21}H_{30}BOP$: calc. C 74.13, H 8.89; found C 74.01, H 8.70.

Diphenyl-(4-hydroxy-4-phenylpent-1-en-1-yl)phosphine-borane (8bl). Yield 67% from 0.058 g (0.24 mmol of **1b**, purified with hexane/EtOAc (6:1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24-1.43 (bm, BH_3, 3H), 1.53 (s, 3H), 1.77 (bs, OH, 1H), 2.65-2.71 (m, 2H), 5.88-6.01 (m, 1H), 6.26-6.44 (m, 1H), 7.15-7.41 (m, Ph, 15H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.88, 49.69 (d, J_{P-C} 14.7 Hz), 74.32 (d, J_{P-C} 0.9 Hz), 122.55 (d, J_{P-C} 56.9 Hz), 124.71, 126.87, 128.30, 128.62 (d, J_{P-C} 10.4 Hz), 128.64 (d, J_{P-C} 10.1 Hz), 129.54 (d, J_{P-C} 58.9 Hz), 130.93 (d, J_{P-C} 2.6 Hz), 130.97 (d, J_{P-C} 2.3 Hz), 132.35 (d, J_{P-C} 9.5 Hz), 132.37 (d, J_{P-C} 9.8 Hz), 146.61, 147.79 (d, J_{P-C} 6.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.66 (m). Elem. anal. for $C_{23}H_{26}BOP$: calc. C 76.68, H 7.27; found C 76.50, H 7.10.

5-(1'-Hydroxy-1'-phenylethyl)-2-phospholene-borane (12cl). Yield 76% from 0.050 g (0.28 mmol) of **1c**, purified with hexane/EtOAc (6:1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.23-1.29 (bm, BH_3, 3H), 1.63 (s, 3H), 2.01-2.08 (m, 2H), 3.56-3.64 (m, 1H), 6.06-6.22 (m, 1H), 6.75-6.92 (m, 1H), 7.24-7.44 (m, 8H), 7.50-7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.86 (d, J_{P-C} 39.4 Hz), 27.69, 58.74, 75.46 (d, J_{P-C} 5.2 Hz), 125.05, 125.25 (d, J_{P-C} 49.1 Hz), 127.19, 128.34, 128.70 (d, J_{P-C} 9.8 Hz), 130.01 (d, J_{P-C} 46.8 Hz), 131.33 (d, J_{P-C} 2.6 Hz), 131.55 (d, J_{P-C} 9.8 Hz), 150.42 (d, J_{P-C} 7.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 45.15 (m). Elem. anal. for $C_{18}H_{22}BOP$: calc. C 73.00, H 7.49; found C 73.11, H 7.54.

***t*-Butyl-(4-hydroxy-4-methyl-hexa-1,5-dien-1-yl)phenylphosphine-borane (8am).** Mixture of two diastereoisomers, dr 58:42, yield 84% from 0.074 g (0.33 mmol) of **1a**, purified with hexane/EtOAc (6:1), colorless oil.

Major: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.12-1.42 (bm, BH_3, 3H), 1.07 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.29 (s, 3H, Me), 2.50-2.54 (m, 2H), 5.05 (dd, J_{H-H} 1.0 Hz, J_{H-H} 10.7 Hz, 1H), 5.20 (dd, J_{H-H} 1.0 Hz, J_{H-H} 17.3 Hz, 1H), 5.91 (dd, J_{H-H} 10.7 Hz, J_{H-H} 17.3 Hz, 1H), 6.29-6.34 (m, 1H), 6.71-6.88 (m, 1H), 7.35-7.49 (m, 3H), 7.65-7.75 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.44 (m).

Minor: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 012-1.42 (bm, BH_3, 3H), 1.07 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 1.29 (s, 3H, Me), 2.50-2.54 (m, 2H), 5.04 (dd, J_{H-H} 1.0 Hz, J_{H-H} 10.8 Hz, 1H), 5.18 (dd, J_{H-H} 1.0 Hz, J_{H-H} 17.4 Hz, 1H), 5.90 (dd, J_{H-H} 10.8 Hz, J_{H-H} 17.4 Hz, 1H), 6.24-6.28 (m, 1H), 6.71-6.88 (m, 1H), 7.35-7.49 (m, 3H), 7.65-7.75 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.92 (m). Elem. anal. for $C_{17}H_{28}BOP$: calc. C 70.36, H 9.73; found C 70.69, H 9.49.

(4-Hydroxy-4-methyl-hexa-1,5-dien-1-yl)diphenylphosphine-borane (8bm) and **(4-hydroxy-4-methyl-hexa-1,5-dien-3-yl)diphenylphosphine-borane (10bm).** Product ratio 45:55, yield 91% from 0.084 g (0.35 mmol) of **1b**, purified with hexane/EtOAc (6/1), colorless oil.

Compound **8bm**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.12-1.25 (bm, BH_3, 3H), 1.23 (s, 3H), 2.46-2.52 (m, 2H), 5.01 (dd, J_{H-H} 1.4 Hz, J_{H-H} 10.8 Hz, 1H), 5.18 (dd, J_{H-H} 1.4 Hz, J_{H-H} 17.3 Hz, 1H), 5.90 (dd, J_{H-H} 1.4 Hz, J_{H-H} 10.8 Hz, 1H), 6.12-6.29 (m, 1H), 6.55-6.71 (m, 1H), 7.34-7.51 (m, 6H), 7.55-7.71 (m, 4H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.21 (m).

Compound **12bm** (mixture of diastereomers). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.12-1.25 (bm, BH_3, 6H), 1.25 (s, 3H), 1.26 (s, 3H), 2.99-3.08 (m, 1H), 3.22-3.33 (m, 1H), 4.79-4.86 (m, 1H), 4.81-4.88 (m, 1H), 5.03-5.05 (m, 1H), 5.06-5.08 (m, 1H), 5.56-5.71 (m, 4H), 6.08-6.14 (m, 1H), 6.14-6.20 (m, 1H), 6.51-6.73 (m, 2H), 7.34-7.51 (m, 12H), 7.55-7.71 (m, 8H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 21.39 and 21.81 (m).

***t*-Butyl-(4-hydroxy-4-methyl-oct-1-en-1-yl)phenylphosphine-borane (8an).** Yield 81% from 0.047 g (0.21 mmol) of **1a**, purified with hexane/EtOAc (6/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.17-1.30 (bm, BH_3, 3H), 0.89 (t, J_{H-H} 6.95 Hz, 3H), 1.10 (d, J_{P-H} 13.7 Hz, *t*-Bu, 9H), 1.19 (s, 3H), 1.27-1.35 (m, 4H), 1.42-1.49 (m, 2H), 1.53 (bs, 1H), 2.47 (bd, J_{H-H} 7.31 Hz), 6.27-6.39 (m, 1H), 6.79-6.97 (m, 1H), 7.38-7.51 (m, 3H), 7.69-7.77 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 25.40 ppm (m). Elem. anal. for $C_{19}H_{34}BOP$: calc. C 71.26, H 10.70; found C 71.35, H 10.92.

4-(*t*-Butylphenylboranatophosphinyl)buten-3-oic acid (8ao). Yield 76% from 0.062 g (0.29 mmol) of **1a**, purified with hexane/EtOAc (1/1), colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.08-1.29 (bm, BH_3, 3H), 1.03 (d, J_{P-H} 14.4 Hz, *t*-Bu, 9H), 3.28-3.33 (m, 2H), 6.33-6.43 (m, 1H), 6.73-6.90 (m, 1H), 7.32-7.43 (m, 3H), 7.62-7.70 (m, 2H), 9.84 (bs, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 25.37 (d, J_{P-C} 2.9 Hz), 29.42 (d, J_{P-C} 34.8 Hz), 47.72 (d, J_{P-C} 14.4 Hz), 117.78 (d, J_{P-C} 54.0 Hz), 128.18 (d, J_{P-C} 9.5 Hz), 128.19 (d, J_{P-C} 51.7 Hz), 130.86 (d, J_{P-C} 2.6 Hz), 133.05 (d, J_{P-C} 7.8 Hz), 150.42 (d, J_{P-C} 8.62 Hz), 207.12. ^{31}P NMR ($CDCl_3$, 121.5 MHz): 26.40 ppm (m). Elem. anal. for $C_{14}H_{22}BO_2P$: calc. C 63.67, H 8.40; found C 63.50, H 8.36.

4-(Diphenylboranatophosphinyl)buten-3-oic acid (8bo). Yield 92% from 0.125 g (0.52 mmol) of **1b**, purified with EtOAc as eluent), white solid, m.p. 145-147 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.25-1.58 (bm, BH_3, 3H), 3.20-3.27 (m, 2H), 3.37 (bs, 1H), 6.17-6.30 (m, 1H), 6.48-6.66 (m, 1H), 7.31-7.45 (m, 6H), 7.50-7.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.49 (d, J_{P-C} 15.8 Hz), 122.69 (d, J_{P-C} 57.2 Hz), 128.70 (d, J_{P-C} 10.1 Hz), 129.09 (d, J_{P-C} 59.5 Hz), 131.13 (d, J_{P-C} 2.3 Hz), 132.36 (d, J_{P-C} 9.8 Hz), 143.53 (d, J_{P-C} 8.3 Hz), 172.10. ^{31}P NMR ($CDCl_3$, 121.5 MHz): 13.84 (m). Elem. anal. for $C_{16}H_{18}BO_2P$: calc. C 67.64, H 6.39; found C 67.70, H 6.50.

2-(*t*-Butylphenylboranatophosphinyl)pent-2-eno-1,5-dicarboxylic acid dimethyl ester (13ar). Yield 40% from 0.051 g (0.23 mmol) of **1a**, purified with hexane/EtOAc (6/1) as eluent, colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.08-1.23 (bm, 3H, BH_3), 1.06 (d, J_{P-H} 14.4 Hz, *t*-Bu, 9H), 2.99-3.11 (m, 1H), 3.34-3.48 (m, 1H), 3.65 (s, 3H), 3.79 (s, 3H), 7.01-7.10 (m, 1H), 7.34-7.48 (m, 3H), 7.61-7.69 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.28 (d, J_{P-C} 2.6 Hz), 29.84 (d, J_{P-C} 30.5 Hz), 30.91, 52.39, 52.47, 118.24 (d, J_{P-C} 50.6 Hz), 128.41 (d, J_{P-C} 9.5 Hz), 129.45 (d, J_{P-C} 52.0 Hz), 131.62 (d, J_{P-C} 2.9 Hz), 133.47 (d, J_{P-C} 8.6 Hz), 150.27 (d, J_{P-C} 8.9 Hz), 206.93, 210.14. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 34.60 ppm (m). Elem. anal. for $C_{17}H_{26}BO_4P$: calc. C 60.74, H 7.80; found C 60.47, H 7.62.

2-(Diphenylboranatophosphinyl)pent-2-eno-1,5-dicarboxylic acid dimethyl ester (13br). Yield 86% from 0.106 g (0.44 mmol) of **1a**, purified with hexane/EtOAc (6/1) as eluent, colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32-1.58 (bm, BH_3, 3H), 3.36-3.45 (m, 2H), 3.63 (s, 3H), 3.67 (s, 3H), 6.07-7.06 (m, 1H), 7.34-7.48 (m, 6H), 7.56-7.64 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.29, 52.51, 127.66 (d, J_{P-C} 54.3 Hz), 128.93 (d, J_{P-C} 10.1 Hz), 128.66 (d, J_{P-C} 52.3 Hz Ph), 131.67 (d, J_{P-C} 2.6 Hz), 132.28 (d, J_{P-C} 9.2 Hz), 1541.30 (d, J_{P-C} 2.9 Hz), 163.76 (d, J_{P-C} 2.0 Hz), 134.76 (d, J_{P-C} 2.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): 18.49 (m). Elem. anal. for $C_{19}H_{22}BO_4P$: calc. C 64.07, H 6.23; found C 64.30, H 6.40.

***t*-Butyl-1-(4-hydroxy-4-(*p*-nitrophenyl)but-1-en-1-yl)phenylphosphine-borane (8ap).** Mixture of two diastereoisomers, yield 18% based on ^{1}H NMR spectra of the isolated fraction from 0.040 g (0.18 mmol) of **1a**, purified with hexane/EtOAc (6/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.22-1.16 (bm, BH_3, 3H), 0.95 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H) and 0.97 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H), 2.23 (bs, OH, 1H), 2.55-2.78 (m, 2H), 4.83-5.02 (m, 1H), 6.07-6.24 (m, 1H), 6.62-6.86 (m, 1H), 7.26-7.49 (m, 5H), 7.96-8.06 (m, 2H), 8.08-8.15 (m, 2H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.57 (bm).

***p*-Nitrobenzyl alcohol (14p).** Yield 26%, based on ^{1}H NMR spectra of the isolated fraction. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.25 (bs, OH, 1H), 4,74 (s, 2H), 7.42-7.47 (m, 2H), 8.10-8.14 (m, 2H).

***t*-Butyl-1-(4-hydroxy-4-(*o*-nitrophenyl)but-1-en-1-yl)phenylphosphine-borane (8aq).** Mixture of two diastereoisomers, yield 36% based on ^{1}H NMR spectra of the isolated fraction from 0.050 g (0.23 mmol) of **1a**, purified with hexane/EtOAc (6/1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.06-1.20 (bm, BH_3, 3H), 0.97 (d, J_{P-H} 14.1 Hz, *t*-Bu, 9H) and 1.00 (d, J_{P-H} 13.8 Hz, *t*-Bu, 9H), 2.46 (bs, OH, 1H), 2.48-2.73 (m, 2H), 5.10-5.20 (m, 1H), 6.20-6.35 (m, 1H), 6.78-6.96 (m, 1H), 7.26-7.47 (m, 5H), 7.50-7.75 (m, 3H), 7.98-8.05 (m, 1H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 25.57 (m).

***o*-Nitrobenzyl alcohol (14q).** Yield 29%, based on ^{1}H NMR spectra of the isolated fraction. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.46 (bs, OH, 1H), 4.89 (s, 2H), 7.30-7.44 (m, 1H), 7.50-7.75 (m, 1H), 7.77-7.88 (m, 1H).

Acknowledgements

Authors are grateful to Dr Duncan Carmichael (École Polytechnique, Palaiseau, France) for his guidance during the preparation of manuscript.

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