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Mixed 1,1-Bisphosphorus Compounds: Synthesis, Alkylation, and Horner−Wadsworth−Emmons Olefination Reactions

Stéphanie Ortial, Dane A. Thompson, and Jean-Luc Montchamp*

Department of Chemistry, Box 298860, Texas Christian University, Fort Worth, Texas 76129, United States

j.montchamp@tcu.edu

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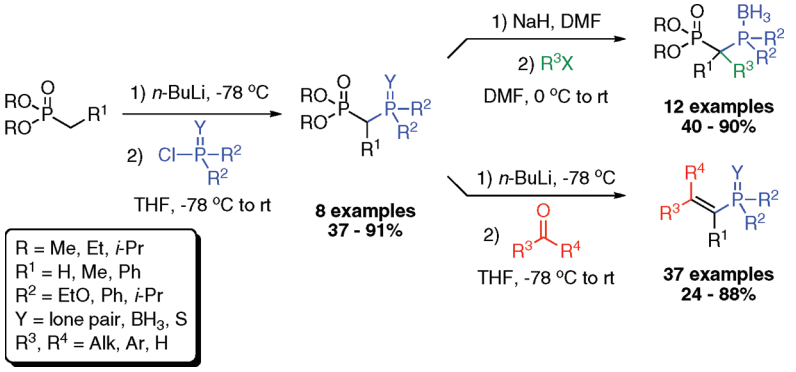

Mixed 1,1-bisphosphorus compounds were prepared by the reaction between a phosphonate diester anion and a P(III) chlorophosphine, or its P(V) borane complex. After deprotonation either in situ or in a separate step, the resulting products can be alkylated or reacted with carbonyl compounds. A variety of olefination products were obtained, generally with high *E*-stereoselectivity. The reaction is competitive with other methods for the synthesis of alkenyl phosphorus compounds, and in the case of trisubstituted alkenes, regio- and stereocontrolled olefination provides products not easily accessible via any other process. The deprotection of phosphine−borane adducts was also demonstrated. Overall, a variety of novel organophosphorus reagents and products were synthesized easily and in good yields.

Introduction

1,1-Bisphosphorus compounds **1** (Figure 1) constitute an important subclass of organophosphorus compounds numbering in the thousands. The most important and common members, 1,1-bisphosphonates **3**, are hydrolytically stable pyrophosphate **2** mimics with useful and broad biological activities. Compounds **3** have been used to treat various bone diseases,[1] such as osteoporosis (loss of bone mass), Paget's disease (a disorder in which hyperactive bone turnover results in weakened and deformed bones), and tumor-associated bone diseases[2] (including breast carcinoma). Like inorganic pyrophosphate **2**, bisphosphonates **3** have a high affinity for divalent metals, such as Ca^{2+} and Mg^{2+}.

When R^1 is OH or NH_2, the calcium affinity is increased through a tridentate mode. Although the exact mechanism of bone resorption activity is still the object of debate, it is believed that bisphosphonates are selectively bound to the hydroxyapatite of the bone, where they interfere with osteoclast (cells that mediate bone resorption) activity. Recent studies have shown that the mode of action of bisphosphonates is complex and that they can act at various biological sites.[3] For example, bisphosphonates can also inhibit various other processes,

*To whom correspondence should be addressed. Phone: (817) 257 6201. Fax: (817) 257 5851.

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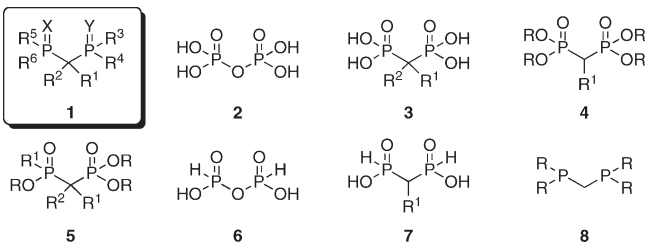

FIGURE 1. General formula of 1,1-bisphosphorus compounds **1** (R^n = C, O, N, F, Cl; X, Y = O, S, BH_3, lone pair), and important examples.

including isoprenoid biosynthesis, leading to cholesterol-lowering activities, and even anticancer activities through the modulation of Ras proteins involved in cell proliferation. Bisphosphonates have also been used to covalently modify a drug (for example an antitumor agent or a steroid) for bone-targeting,[4] or to mimic biologically important pyrophosphate monoesters (such as adenosine diphosphate or phosphoribose pyrophosphate). As a result of their commercial importance and useful biological activities, bisphosphonates **3** have been, and continue to be, intensely investigated.[1−4]

Bisphosphonate esters **4** are another important structural type. Although they are intermediates in the synthesis of the aforementioned **3** through alkylation and deprotection,[5] compounds **4** are also used to prepare vinylphosphonates via Horner−Wadsworth−Emmons (HWE) olefination.[6] Vinylphosphonates are themselves key intermediates in the synthesis of numerous phosphonic acids, and significant research has been devoted to their synthesis and transformations.[7] Mixed phosphonate−phosphinates **5** are less common, but they are important intermediates for the synthesis of pyrophosphate monoester analogues.[8] 1,1-Bis-*H*-phosphinates **7** are a novel class of compounds analogous to the known *H*-pyrophosphonic acid **6** we synthesized via our radical hydrophosphinylation of terminal alkynes.[9] Compounds **7** can be converted to other compounds, particularly **3**. Using **7** as intermediates, we reported the straightforward synthesis of a steroid−bisphosphonate conjugate for potential use in hormone replacement therapy,[9] as well as the synthesis of carbohydrate−bisphosphonate conjugates for the medicinal modification of silicon nanowires.[10]

Lastly, 1,1-bisphosphines **8**, a subset of the extremely important bisphosphines, have found use as supporting ligands in catalysis.[11] 1,1-Bis(diphenylphosphino)methane **8** (R = Ph, dppm), perhaps the best known member of this class, has been applied to important aromatic functionalization processes. 1,1-Bisphosphonites **8** (R = OAlk) have also been reported as intermediates for the synthesis of various other organophosphorus compounds.[12]

In contrast, few mixed 1,1-bisphosphorus compounds **1** ($X \neq Y$) have been reported (note, however, that phosphonate−phosphinates **5** are also mixed functionality compounds even

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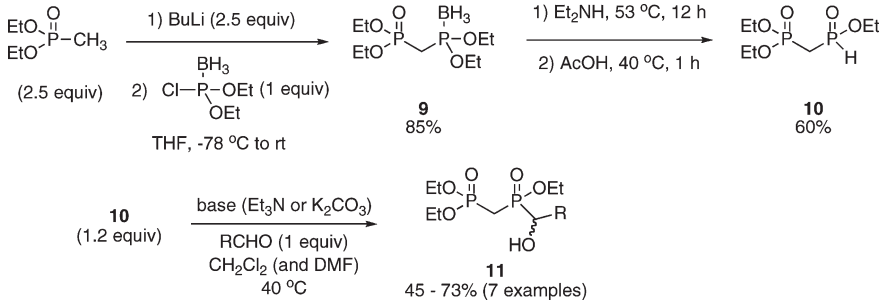
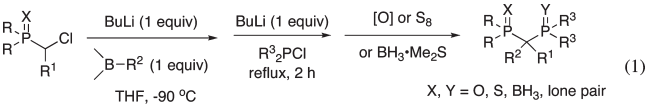
SCHEME 1. Bisseret's Synthesis of Mixed 1,1-Bisphosphorus Reagent 9, and Subsequent Application



if X = Y = O). One important example of mixed 1,1-bisphosphorus compounds is the Bisseret reagent $(EtO)_2P(O)CH_2P(BH_3)(OEt)_2$ **9**.[13] Bisseret and co-workers prepared their reagent using the reaction between the anion derived from diethyl methanephosphonate and $(EtO)_2P(BH_3)Cl$ (Scheme 1).[14] After deprotection of **9**, the resulting phosphonate−phosphinate **10** was reacted with aldehydes to produce pyrophosphate monoester analogues. Other phosphorylations of phosphonate-stabilized anions to produce 1,1-bisphosphorus compounds were pioneered and developed by Lutsenko, Savignac, and others.[15]



(1)

X = O, S, BH_3; R = EtO, Ph; R^1 = Me, Ph, H; R^2 = Alk; R^3 = EtO, Ph

Recently, we discovered and developed a novel P−C−C homologation of organoboranes B−C bonds, using phosphorus-containing carbenoids.[16] As part of our ongoing interest in bisphosphorus compounds and pyrophosphate analogues, we applied this homologation reaction to the preparation of various 1,1-bisphosphorus compounds (eq 1).[17] Realizing that many of the products were either rare or completely unknown, we decided to undertake a study of various compounds **1**, including alternate syntheses, and the reactivity of these species in Horner−Wadsworth−Emmons olefination.[6] As mentioned above, since many 1,1-bisphosphorus compounds **1** already have great utility in medicine, catalysis, and as synthetic intermediates, expanding this chemistry to new compounds is a worthwhile objective.[18]

Results and Discussion

1. Synthesis. Considering our own work, Bisseret's, and the general paucity of reports on mixed 1,1-bisphosphorus compounds, we undertook the present study. While our homologation reaction[16] delivers functionalized compounds in one pot, the preparation of unsubstituted mixed species needed to be examined.

Two major approaches (Scheme 2) can be considered: (a) the reaction of phosphonate-stabilized anions **12** with phosphorus (V or III) electrophiles[15,17] or (b) the displacement of phosphonomethyl electrophiles **13** (where LVG is a leaving group such as halide or sulfonate) with phosphorus(III) nucleophiles. The latter approach (approach b) has been employed successfully,[14,19] but overall, it seemed more complicated and fundamentally less efficient than approach a. Since we also showed that alkylphosphonite−borane complexes can be alkylated at the α-position,[16b] and based on the Savignac/Bisseret precedents, we thought that the phosphorylation of a phosphorus-stabilized anion (Scheme 2, approach a) would be the most general, inexpensive, and straightforward strategy toward the preparation of compounds **1**.

The reaction of phosphonate-stabilized anions **12** with electrophiles is well-precedented, but often not as efficient as might be expected.[20] For example, anions **12** tend to "dimerize" to the phosphonate−phosphinate compound **14**, either through self-condensation, or through incomplete deprotonation during

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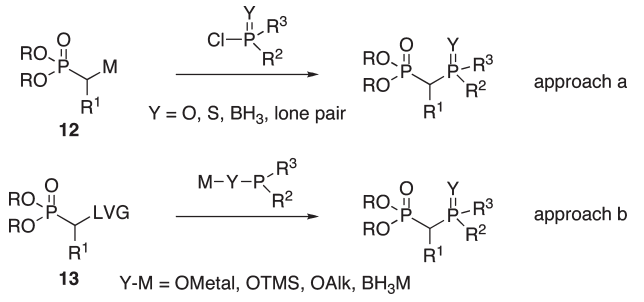
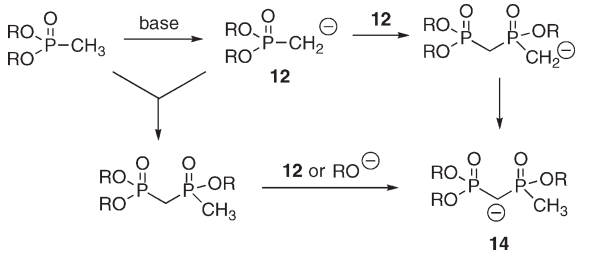
(20) (a) Poindexter, M. K.; Katz, T. J. *Tetrahedron Lett.* **1988**, *29*, 1513. (b) Coutrot, P.; Savignac, P.; Mathey, F. *Synthesis* **1978**, 36. (c) Phillion, D. P.; Andrew, S. S. *Tetrahedron Lett.* **1986**, *27*, 1477. (d) See also ref 15b.

SCHEME 2. Two Complementary Strategies toward Mixed Bisphosphorus Compounds 1



SCHEME 3. The Phospha-Claisen Condensation As a Side Reaction

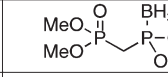
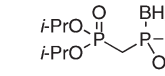
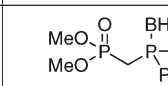
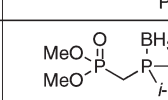
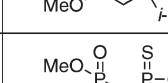
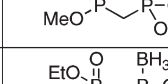
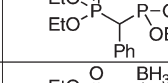
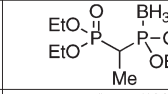
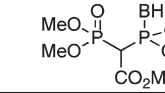


the formation of **12**, when the anion is allowed to reach room temperature (Scheme 3).[15c]

Depending on the R group this side reaction can be significant, even dominant. The best leaving groups such as phenyl esters (R = Ph) will easily form the phosphonate−-phosphinate condensation product **14**. Poorer and bulkier leaving groups, such as isopropyl esters (R = *i*-Pr), lead to significantly more stable phosphonomethyl anion since nucleophilic attack at the phosphorus atom is slower. However, an additional parameter to consider is the cost of the phosphonate precursor, and the cheapest starting material is, by far, dimethyl methanephosphonate (which can be made by catalytic Arbuzov rearrangement of trimethylphosphite), even if self-condensation could be a concern. In the end, the ready availability of cheap dimethyl methanephosphonate $(MeO)_2P(O)CH_3$ seemed to offset any potential reactivity issue. On the basis of these considerations, dimethyl methanephosphonate was deprotonated with *n*-BuLi at low temperature and then treated with various phosphorus electrophiles. The results are shown in Table 1.

Two methods were employed. In method A, where complexation is accomplished after the condensation step (with $BH_3 \cdot Me_2S$ or S_8), the optimum stoichiometry was a 1.0:1.5 ratio of anion **12** (R = Me) to chlorophosphine. However, in a few instances a small amount of disubstitution (ca. 10%) can be observed as expected with an excess of chlorophosphine. In method B, borane precomplexation of the chlorophosphine is conducted prior to the condensation step (or commercially available diethyl chlorothiophosphate is used directly), and in this case the optimum stoichiometry is 2.5:1 since an excess of **12** is required to deprotonate the condensation intermediate. Method B follows the conditions pioneered by Bisseret,[13] and it generally leads to better yields of mixed 1,1-bisphosphorus products.

TABLE 1. Synthesis of Mixed 1,1-Bisphosphorus Compounds from Dialkyl Methanephosphonate

Entry	Method[a]	Product		Isolated yield (%)[g]
1a 1b	A B		**15**	47 78
2a 2b	A[b] B[b]		**16**	40 83
3a 3b	A B		**17**	63 67
4a 4b	A B		**18**	70 89
5a 5b	A B		**19**	37 15[h]
6	A[c]		**20**	91
7	B[d]		**21**	75
8	A[e]		**22**	70
9	A[f]		**23**	[f]

[a]Method A: (i) $(MeO)_2P(O)CH_3$ (1 equiv), *n*-BuLi (1 equiv), THF, −78 °C; (ii) $ClPR_2$ (1.5 equiv), −78 °C to rt; (iii) $BH_3 \cdot Me_2S$ (1.5 equiv) or S_8 (3 equiv), rt. Method B: (i) $(MeO)_2P(O)CH_3$ (2.5 equiv), *n*-BuLi (2.5 equiv), THF, −78 °C; (ii) $ClP(BH_3)R_2$ (1 equiv) or $ClP(S)(OEt)_2$ (1 equiv), −78 °C to rt. [b]$(i\text{-PrO})_2P(O)CH_3$ was used in the place of $(MeO)_2P(O)CH_3$. [c]$(EtO)_2P(O)CH_2Ph$ was used in the place of $(MeO)_2P(O)CH_3$. [d]$(EtO)_2P(O)CH_2CH_3$ was used in the place of $(MeO)_2P(O)CH_3$, and *sec*-BuLi was used in the place of *n*-BuLi. [e]$(MeO)_2P(O)CH_2CO_2Me$ was used in the place of $(MeO)_2P(O)CH_3$, and NaH was used in the place of *n*-BuLi. [f]Compound **23** was isolated as a byproduct in entry 1a. Yield below 20%, see text. [g]The product was isolated after chromatographic purification over silica gel. [h]^{31}P NMR yield. Savignac already reported similar results with $(EtO)_2P(O)CH_2Li + ClC(S)P(OEt)_2$ (ref 15b).

Although expected, it is interesting to note that the yield for method A directly correlates with decreased electrophilicity of the chlorophosphine or the electron-withdrawing ability of PR_2 (entries 4a > 3a > 1a; electron-withdrawing abilities: *i*-Pr < Ph < OEt). For example, the electron-donating isopropyl group (entry 4a) decreases the acidity of the intermediate $(MeO)_2P(O)CH_2P(i\text{-Pr})_2$ and $ClP(i\text{-Pr})_2$ is also less reactive toward the deprotonated intermediate. In fact, in this reaction, the formation of a triphosphorus species is not observed.

The reactions of other phosphonate precursors were also successful. Diisopropyl methanephosphonate gave results (entry 2) similar to the dimethyl ester (entry 1), even if the corresponding anion is more stable (see Scheme 3). Diethyl benzylphosphonate reacted uneventfully (entry 6), but the less acidic diethyl ethylphosphonate (entry 7) required *sec*-BuLi for deprotonation since *n*-BuLi was unsatisfactory (low yield, complex mixture). Finally, trimethylphosphonoacetate (entry 8) cleanly reacted to afford **22**.[21]

Since triphosphorus compounds can sometimes be observed by using method A (entry 9), compound **23** could be isolated, albeit in low yield. It is interesting to note that this compound does not form at all from isolated **15** or when $ClP(BH_3)(OEt)_2$ is used (method B). All attempts at optimizing the yield of **23** failed. This could be due to a combination of steric effects, and the decreased reactivity of complex **15** over the uncomplexed phosphonate−phosphonite intermediate.

Regardless of the method employed, mixed 1,1-bisphosphorus compounds were obtained easily, in good to moderate yields. Method B was generally superior both in terms of yields and ease of reaction scale-up. One exception is entry 5b failing to give a better yield than method A (entry 5a). Surprisingly, none of the compounds shown in Table 2 have been previously described in the literature (Bisseret's reagent **9** is derived from diethyl methanephosphonate, not the dimethyl ester). In fact, having methyl groups might also be advantageous since phosphonate dimethyl esters can be selectively monodealkylated to the corresponding monoester under mild conditions.[22]

Once the mixed 1,1-bisphosphorus compounds were obtained, their reactivity was studied. Two major reaction types were investigated: (1) alkylation of the stabilized anion and (2) olefination through Horner−Wadsworth−Emmons reaction.

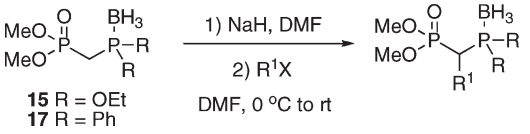
2. Alkylation. The formation of compounds such as **23** obviously suggests the possibility to alkylate the anion derived from the bis-1,1-phosphorus compounds. Compounds **15** and **17** were chosen as representative test cases. Deprotonation with sodium hydride followed by addition of an alkyl halide proceeded well in DMF as the solvent. The results are shown in Table 2.

The alkylation takes place in good to excellent yields with various alkyl halides. Compound **15** is alkylated uneventfully with alkyl iodides, as well as benzylic or allylic bromides (Table 3, entries 1−5). Since analogues of geranyl and farnesyl pyrophosphates have important biological activities, compound **28** was synthesized. The same strategy might be applied to prepare drug-conjugates. As expected, bis-alkylation also occurs smoothly (entries 6−8). Although it was not investigated, it is clear that unsymmetrical 1,1-dialkylbisphosphorus compounds can also be obtained from the monoalkylated intermediate. Compound **17** reacted like **15** to deliver alkylated mixed bisphosphorus compounds **31**−**35** (entries 9−12). It should be noted that although compounds like those in Table 2 are accessible as we described previously (eq 1), the present method is arguably more straightforward and inexpensive, since it is based on widely available reagents. Taken together, the two methods allow for the synthesis of a very broad range of bisphosphorus compounds.

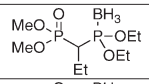
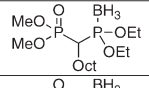
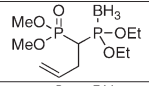
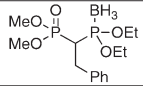
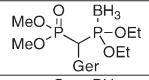
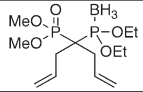
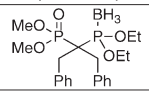
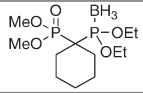
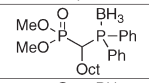
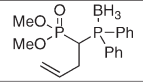
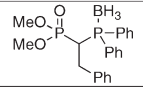
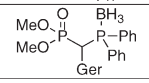
3. Horner−Wadsworth−Emmons (HWE) Olefination. As mentioned in the introduction, tetraalkyl methylenebisphosphonates have been employed in the synthesis of vinyl phosphonates.[6,7] Since the mixed bisphosphorus compounds **15**−**23** (Table 1) can, at least in principle, undergo olefination with carbonyl compounds, this reaction was investigated next. We were delighted to see that various mixed 1,1-bisphosphorus compounds react smoothly with aldehydes and ketones (Table 3). Not unexpectedly, in all cases the dimethyl phosphate is eliminated instead of the second less electrophilic other phosphorus atom.[23]

Reagents **15**, **17**, **18**, and **19** all reacted uneventfully to deliver the corresponding alkenylphosphorus compounds.[24] The *E*/*Z* ratios (when relevant) are high and quite typical of HWE reactions, although the *Z*-isomer is sometimes

TABLE 2. Alkylation of 1,1-Bisphosphorus Compounds 15 and 17[a]



15 R = OEt
17 R = Ph

Entry	Starting Material	Alkyl Halide (equiv)	Product		Isolated yield (%)[b]
1	**15**	EtI (1.05)		**24**	73
2	**15**	OctI (1.05)		**25**	80
3	**15**	H_2C=$CHCH_2Br$ (1.0)		**26**	63
4	**15**	BnBr (1.05)		**27**	81
5	**15**	geranyl bromide (1.05)		**28**	79
6	**15**	H_2C=$CHCH_2Br$ (4.0)		**29**	90
7	**15**	BnBr (4.0)		**30**	89
8	**15**	1,5-dibromopentane (1.0)		**31**	40
9	**17**	OctI (1.05)		**32**	80
10	**17**	H_2C=$CHCH_2Br$ (1.05)		**33**	72
11	**17**	BnBr (1.05)		**34**	81
12	**17**	geranyl bromide (1.05)		**35**	81

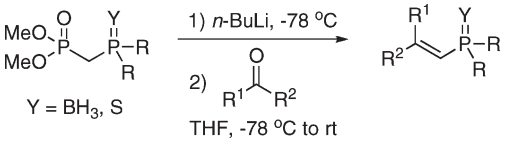
[a]Conditions: (i) $(R^1O)_2P(O)CH_2P(BH_3)R_2$ (1 equiv), NaH (1.05 or 4 equiv), DMF, 0 °C; (ii) R^3X (1.05 or 4 equiv), 0 °C to rt. [b]The product was isolated after chromatographic purification over silica gel.

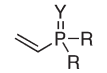
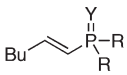
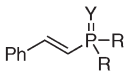
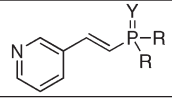
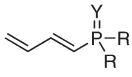
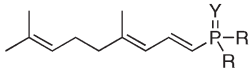
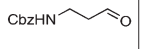
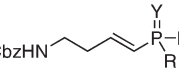
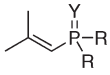
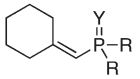
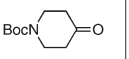
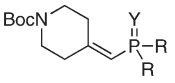
(21) For the reaction of trialkylphosphonoacetate with $ClP(OEt)_2$, see: (a) Novikova, Z. S.; Skorobogatova, S. Y.; Lutsenko, I. F. *J. Gen. Chem. USSR* **1978**, *48*, 694. (b) Lee, K.; Wiemer, D. F. *J. Org. Chem.* **1991**, *56*, 5556. (c) Boekman, R. K., Jr.; Kamenecka, T. M.; Nelson, S. G.; Pruitt, J. R.; Barta, T. E. *Tetrahedron Lett.* **1991**, *32*, 2581. (d) Lee, K.; Wiemer, D. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *75*, 87.

(22) See for example: (a) Boutevin, B.; Hervaud, Y.; Jeanmaire, T.; Boulahna, A.; Elasri, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *174*, 1. (b) Chowdhury, S.; Muni, N. J.; Greenwood, N. P.; Pepperberg, D. R.; Standaert, R. F. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3745. (c) Taylor, S. D.; Mirzaei, F.; Bearne, S. L. *Org. Lett.* **2006**, *8*, 4243 and references cited therein.

(23) Not all 1,1-bisphosphorus compounds undergo olefination satisfactorily: (a) Gilmore, W. F.; Huber, J. W., III *J. Org. Chem.* **1973**, *38*, 1423. (b) Izod, K.; McFarlane, W.; Tyson, B. V. *Eur. J. Org. Chem.* **2004**, 1043.

TABLE 3. Horner−Wadsworth−Emmons Olefinations[a]



Entry	Starting Material	R	Y	Carbonyl Compound	Product		E/Z Ratio[b]	Isolated yield (%)[c]
1a	**15**	OEt	BH_3	$(CH_2O)_n$		**36**	n/a	24
1b	**17**	Ph	BH_3			**37**		77
1c	**18**	*i*-Pr	BH_3			**38**		58
1d	**19**	OEt	S			**39**		52
2a	**15**	OEt	BH_3	pentanal		**40**	90:10	44
2b	**17**	Ph	BH_3			**41**	85:15	78
2c	**18**	*i*-Pr	BH_3			**42**	>98:2	60
2d	**19**	OEt	S			**43**	80:20	71
3a	**15**	OEt	BH_3	benzaldehyde		**44**	>98:2	67
3b	**17**	Ph	BH_3			**45**	>98:2	88[d]
3c	**18**	*i*-Pr	BH_3			**46**	>98:2	81
3d	**19**	OEt	S			**47**	>98:2	75
4a	**15**	OEt	BH_3	3-pyridine carboxaldehyde		**48**	>98:2	51
4b	**18**	*i*-Pr	BH_3			**49**	>98:2	71
4c	**19**	OEt	S			**50**	>98:2	73
5a	**15**	OEt	BH_3	acrolein		**51**	>98:2	59
5b	**17**	Ph	BH_3			**52**	>98:2	64
5c	**18**	*i*-Pr	BH_3			**53**	>98:2	70
5d	**19**	OEt	S			**54**	96:4	67
6a	**15**	OEt	BH_3	geranial		**55**	>98:2	70
6b	**17**	Ph	BH_3			**56**	96:4	74
6c	**18**	*i*-Pr	BH_3			**57**	>98:2	66
6d	**19**	OEt	S			**58**	94:6	65
7a	**15**	OEt	BH_3			**59**	>98:2	59
7b	**17**	Ph	BH_3			**60**	90:10	86
7c	**19**	OEt	S			**61**	93:7	74
8a	**15**	OEt	BH_3	acetone		**62**	n/a	81
8b	**17**	Ph	BH_3			**63**		67
8c	**19**	OEt	S			**64**		75
9a	**15**	OEt	BH_3	cyclohexanone		**65**	n/a	75
9b	**17**	Ph	BH_3			**66**		75
9c	**19**	OEt	S			**67**		73
10a	**15**	OEt	BH_3			**68**	n/a	84
10b	**17**	Ph	BH_3			**69**		65
10c	**19**	OEt	S			**70**		80

[a]Conditions: (i) $(MeO)_2P(O)CH_2P(Y)R_2$ (1 equiv), *n*-BuLi (1 equiv), THF, −78 °C; (ii) R^1R^2CO (1.1 equiv), −78 °C to rt. [b]When only the *E*-isomer is detected by NMR, selectivity is estimated at >98:2. [c]The product was isolated after chromatographic purification over silica gel. [d]Obtained in 67% yield from $(MeO)_2P(O)CH_3$ in a one-pot procedure, using method B.

formed in significant amount. This is consistent with the fact that the transferred groups are less electron-withdrawing than in the corresponding phosphonoacetates or bisphosphonates.

In the case of compound **36** (entry 1a), volatility complicated isolation and resulted in a low yield. Since phosphonite−borane complexes can be deprotected to the corresponding *H*-phosphinate esters, the method is interesting, even if not always competitive with our various hydrophosphinylation methodologies. One significant exception is when ketones are used since the corresponding *H*-phosphinates would require palladium-catalyzed cross-coupling reaction of alkenyl halides, which are themselves not readily available. Even more importantly, the HWE olefination reaction of monosubstituted phosphonate−phosphonite−borane complexes can deliver *H*-phosphinate precursors[13,16,17] regiospecifically, and these are not available through alkyne hydrophosphinylation,

(24) Reviews: (a) Alk-1-enylphosphines: Gaumont, A. C.; Gulea, M. *Science of Synthesis, Houben Weyl Methods of Molecular transformations*; Georg Thieme Verlag KG: Stuttgart, Germany, 2007; Vol. 33, pp 711−724. (b) Alk-1-enyl phosphorus compounds: Gaumont, A. C.; Gulea, M. *Science of Synthesis, Houben Weyl Methods of Molecular transformations*; Georg Thieme Verlag KG: Stuttgart, Germany, 2007; Vol. 33, pp 665−694. (c) Alk-1-enylphosphine oxides and derivatives: Gaumont, A. C.; Gulea, M. *Science of Synthesis, Houben Weyl Methods of Molecular transformations*; Georg Thieme Verlag KG: Stuttgart, Germany, 2007; Vol. 33, pp 701−710. (d) Alk-1-enylphosphinic acids and derivatives: Gaumont, A. C.; Gulea, M. *Science of Synthesis, Houben Weyl Methods of Molecular transformations*; Georg Thieme Verlag KG: Stuttgart, Germany, 2007; Vol. 33, pp 695−700. (e) Gilheany, D. G.; Mitchell, C. M. In *Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, U.K., 1990; Vol. 1, pp 151−190. (f) Delacroix, O.; Gaumont, A. C. *Curr. Org. Chem.* **2005**, *9*, 1851. (g) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (h) Promonenkov, V. K.; Ivin, S. Z. *Russ. Chem. Rev.* **1968**, *37*, 670. (i) See also ref 7w.

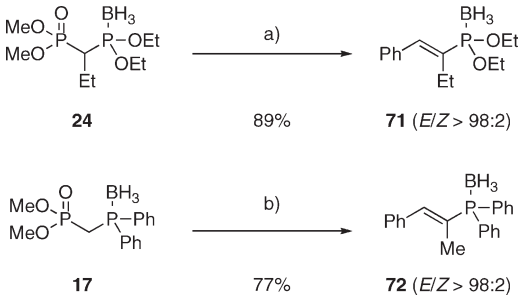
unless a significant steric and/or electronic bias exists on the alkyne.

Perhaps of even greater importance, alkenyl phosphine boranes can be prepared in a straightforward manner. Alkenyl phosphines are important compounds as precursors to ligands for metal catalysis. For example, vinyldiphenylphosphine−borane complex **37** has been prepared previously, but in only 18% yield, through the reaction of vinylmagnesium bromide with chlorodiphenylphosphine and subsequent borane complexation.[25] In general, alkenylphosphine−borane complexes have been prepared through a variety of reactions, including cross-metathesis[25] or transition metal-catalyzed reaction with alkynes.[26] In this field, Gaumont and co-workers have made the major contributions.[26a,b] Our present HWE approach is quite competitive since it employs reagents that are readily available in multigram quantities, and it avoids the use of diphenylphosphine. Reactions with compound **18** show that substituents on phosphorus other than phenyl can be equally easily introduced. Another example is compound **64**, which has been prepared in a multistep sequence from isobutylene, phosphorus pentachloride, and antimony (23% overall yield).[27] Our approach to **64** is obviously quite competitive (Table 3, entry 8c). Actually, most products in Table 3 have not been reported previously. The exceptions are compounds **42**, **64**, and several thiophosphonates (**39**, **43**, **47**, and **54**).[28] At any rate, the present work offers a very competitive (and in most cases superior) access to the same compounds, as well as many others. Furthermore, a one-pot procedure for bisphosphorus synthesis/olefination was successful. For example, compound **45** was prepared in 67% overall yield (actually higher than in the two-step process) by using the one-pot procedure. Since method B produces the intermediate anion, it is ideal for in situ olefination upon addition of a carbonyl compound without intermediate purification.

The formation of trisubstituted alkenes from ketones took place smoothly (Table 3, entries 8a−10c). As an alternate route to trisubstituted alkenes, we also briefly investigated the reaction between alkylated 1,1-bisphosphorus reagents and an aldehyde (Scheme 4). Compound **71** was synthesized in two steps through alkylation and olefination, as in Tables 2 and 3, respectively. A one-pot process was also developed as illustrated for the synthesis of **72**. It was found that dioxane gave slightly better results than when DMF or THF is employed for each step, but this reaction was not optimized.

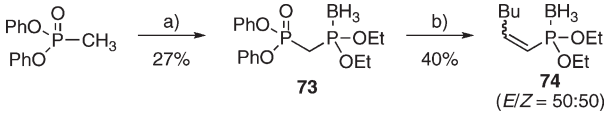
Delighted with the above results, we then turned our attention to the possibility of preparing *Z*-alkenylphosphorus

SCHEME 4. Synthesis of Trisubstituted Alkenes[a]



[a]Reagents and conditions: (a) (i) *n*-BuLi (1 equiv), THF, −78 °C; (ii) PhCHO (1.1 equiv), −78 °C to rt. (b) (i) NaH (2.5 equiv), dioxane, rt; (ii) MeI (1.05 equiv), rt. (iii) PhCHO (1.05 equiv), rt.

SCHEME 5. Attempted *Z*-Selective Olefination[a]



[a]Reagents and conditions: (a) (i) $(PhO)_2P(O)CH_3$ (1 equiv), *n*-BuLi (1 equiv), THF, −78 °C; (ii) $ClP(OEt)_2$ (1.5 equiv), −78 °C to rt; (iii) $BH_3 \cdot Me_2S$ (1.5 equiv), rt [method A in Table 1]. (b) *n*-BuLi (1 equiv), THF, −78 °C; (ii) pentanal (1.1 equiv), −78 °C to rt.

compounds, which are extremely rare. Various *Z*-alkenyl phosphonates have been prepared from alkynylphosphonates by Srebnik and co-workers,[29] and Gaumont reported a very interesting and unusual *Z*-selective synthesis of alkenylphosphine−borane complexes through addition to alkynes.[26b] Taking a cue from the phosphonoacetate literature,[30] the diphenylphosphonate diester **73** (a version of **15**) was synthesized (in low yield, due to phospha-Claisen condensation, Scheme 3) and then treated with pentanal, delivering a 50:50 mixture of stereoisomers **74** (Scheme 5). Since the preparation of the mixed 1,1-bisphosphorus precursor is plagued by the problems discussed in Scheme 3, and the outcome was not satisfactory (yet significantly more *Z*-selective), this was abandoned. Because of the lack of solution to this problem, a different approach to *Z*-alkenylphosphonite−borane complexes will be investigated in the near future.

Although, at least in principle, the present olefination approach could be made asymmetric through the use of chiral ester groups on the phosphonate moiety,[31] this possibility has not been investigated at this time.

4. Deprotection of Phosphine−Borane Complexes. The chemistry of dialkyl- and diarylphosphine−boranes is quite extensive; however, that of dialkoxyphosphine−boranes

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(26) (a) Delacroix, O.; Gaumont, A.-C. *Curr. Org. Chem.* **2005**, *9*, 1851. (b) Mimeau, D.; Gaumont, A.-C. *J. Org. Chem.* **2003**, *68*, 7016. (c) Busacca, C. A.; Farber, E.; De Young, J.; Campbell, S.; Gonnella, N. C.; Grinberg, N.; Haddad, N.; Lee, H.; Ma, S.; Reeves, D.; Shen, S.; Senanayake, C. H. *Org. Lett.* **2009**, *11*, 5594.

(27) Kamai, G.; Tsivunin, V. S.; Nurtdinov, S. Kh. *Zh. Obshch. Khim.* **1965**, *35*, 1817.

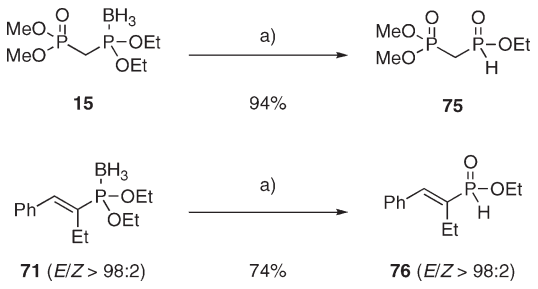
(28) Compound **39**: Kabachnik, M. I.; Medved, T. Y. *Izv. Akad. Nauk SSSR* **1961**, 604. Althoff, W.; Fild, M.; Riek, H.-P.; Schmutzler, R. *Chem. Ber.* **1978**, *111*, 1845. Compound **42**: Miyaji, T.; Xi, Z.; Ogasawara, M.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2007**, *72*, 8737. Compound **43**: Fedorova, G. K.; Anan'eva, L. G.; Kononenko, I. M.; Maksyutina, L. I.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1973**, *43*, 538. Compound **47**: Levin, Y. A.; Galeev, V. S. *Zh. Obshch. Khim.* **1967**, *37*, 1327. Compound **54**: Pudovik, A. N.; Konovalova, I. V.; Ishmaeva, E. A. *Zh. Obshch. Khim.* **1963**, *33*, 2509.

(29) For representative references, see: (a) Sinelnikove, Y.; Rubinstein, A.; Srebnik, M.; Al Quntar, A. A. A. *Tetrahedron Lett.* **2009**, *50*, 867. (b) Quntar, A. A. A.; Rosenthal, D.; Srebnik, M. *Tetrahedron* **2006**, *62*, 5995. (c) Al-Quntar, A. A. A.; Srebnik, M. *J. Organomet. Chem.* **2005**, *690*, 2504. (d) Ben-Valid, S.; Quntar, A. A. A.; Srebnik, M. *J. Org. Chem.* **2005**, *70*, 3554. (e) Rochdi, A.; Taourirte, M.; Lazrek, H. B.; Barascut, J. L.; Imbach, J. L. *Molecules* **2000**, *5*, 1139.

(30) (a) Touchard, F. P.; Capelle, N.; Mercier, M. *Adv. Synth. Catal.* **2005**, *347*, 707. (b) Ando, K.; Oishi, T.; Hirama, M.; Ohno, H.; Ibuka, T. *J. Org. Chem.* **2000**, *65*, 4745. (c) Ando, K. *J. Org. Chem.* **1998**, *63*, 8411.

(31) Examples: (a) Zhang, Y.; Xu, C.; Li, J.; Yuan, C. *Tetrahedron: Asymmetry* **2003**, *14*, 63. (b) Bedekar, A. V.; Watanabe, T.; Tanaka, K.; Fuji, K. *Tetrahedron: Asymmetry* **2002**, *13*, 721. (c) Arai, S.; Hamaguchi, S.; Shioiri, T. *Tetrahedron Lett.* **1998**, *39*, 2997. (d) Mizuno, M.; Fujii, K.; Tomioka, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 515. (e) Hanessian, S.; Beaudoin, S. *Tetrahedron Lett.* **1992**, *33*, 7655.

SCHEME 6. Deprotection of Phosphonite-Borane Complexes with Van der Eycken's Conditions[a]



[a]Reagents and conditions: (a) refluxing absolute EtOH, N_2. Compound **75**, 48 h. Compound **76**, 96 h.

(phosphonite−borane complexes) is not. Bisseret provided one of the earliest examples of cleavage with the conversion of **9** to the corresponding *H*-phosphinate (Scheme 1), via a two-step sequence using diethylamine decomplexation followed by hydrolysis with acetic acid.[13] On the other hand, we have been developing the chemistry of phosphonite−boranes[16,17] and demonstrated both the deprotection and Arbuzov reactions of phosphonite−borane complexes. Still, in order to show that this chemistry is general, two representative examples were secured for the present study (Scheme 6).

In the place of our original $HBF_4 \cdot Et_2O$ or amine-based deprotection conditions, which were modeled after the classical phosphine−borane work,[32] we elected instead to try the recent conditions disclosed by Van der Eycken and coworkers,[33] using ethanol. In their work, no phosphonite−borane complexes were tested, and phosphite−boranes [$(RO)_3P \cdot BH_3$], which are even more electron-poor, failed completely. However, in our situation, we were delighted to see that phosphonite−borane complexes were successfully and cleanly deprotected, even though the reactions were quite slow (the use of higher boiling primary alcohols, like *n*-BuOH, will be investigated in future work). Accordingly, phosphonite complex **15** was treated with refluxing absolute ethanol for 2 days, to deliver *H*-phosphinate **75**, in 94% yield. The synthesis of **75** is both simpler and higher yielding (73% overall) than that of **10** (Scheme 1, 51% overall).

Similarly, decomplexation of phosphonite−borane **71** could also be accomplished uneventfully, although a longer reaction time (4 days) was necessary to obtain a good yield of *H*-phosphinate **76**. This deprotection proves the usefulness of the strategy since **76** and related *H*-phosphinates cannot be easily obtained, even through our own methodologies based on hypophosphorous compounds. Because the preparations of **75** and **76** proceeded well, the conditions described by Hiyama, which employ molecular sieves,[34] were not tried (although in this work, the deprotection of $(PhO)_3P \cdot BH_3$ was accomplished in 100% yield after 3 days at room temperature, using a THF/*t*-BuOH mixture).

We intend to study more extensively the chemistry of phosphonite−borane complexes in the near future. Regardless, the present study clearly illustrates the usefulness of phosphonite (and phosphine)−borane complexes for the preparation of many organophosphorus compounds, and further establishes our olefination approach as a competitive alternative to other methodologies.

Conclusions

The void in the literature concerning the synthesis of mixed 1,1-bisphosphorus compounds, and consequently the lack of studies of their reactivity, prompted the present study. Very few of the compounds described herein have been previously characterized, and our method is either comparable or more often much superior to those literature precedents. Various mixed 1,1-bisphosphorus compounds were synthesized in a straightforward and scaleable manner from inexpensive dimethyl methanephosphonate and related phosphonate diesters. These compounds were then used in two important reactions: alkylation and HWE olefination. Overall, good to excellent yields were achieved in these investigations, delivering numerous novel compounds. While *Z*-selective olefination to produce phosphorus-containing compounds remains somewhat elusive, future work will focus on this problem, and results will be reported in due course.

Since both alkylation and HWE olefination are efficient, many phosphorus functionalities can be accessed easily. For example, the present work provides a competitive alternative to the metal-catalyzed addition of phosphine−borane complexes and other P−H compounds to alkynes as an approach to alkenylphosphorus species.

Because of the great importance of 1,1-bisphosphorus compounds in chemical biology and as synthetic intermediates, the present work should constitute a valuable stepping stone to further contributions to the organophosphorus literature. Our planned future work will focus on additional developments, including Knoevenagel condensation, *Z*-selective preparation of alkenylphosphorus compounds, and the synthesis of molecules displaying potential biological activities. Additionally, the elaboration of the alkenylphosphorus compounds will be investigated through a variety of reactions, such as conjugate addition and asymmetric versions of those.

Virtually no attention has been devoted to the chemistry of phosphonite−borane complexes (unlike phosphine−boranes), even though these compounds offer great synthetic flexibility and are now becoming much more readily available. Since deprotection of phosphonite−borane complexes is established, the preparation of previously inaccessible *H*-phosphinates becomes possible. While not every phosphonite−borane species can compete with our past or current methodological efforts by using hypophosphorous derivatives directly, some have promise for a previously unrealized potential, especially when regiocontrol in the addition to alkynes is contemplated but unsuccessful. In the end, the present paper offers a novel foray into previously ignored functionalities, and it opens up the way for further studies, especially concerning the elaboration of the synthesized alkenylphosphorus products in general, and phosphonite−borane complexes in particular.

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(33) Van Overschelde, M.; Vervecken, E.; Modha, S. G.; Cogen, S.; Van der Eycken, E.; Van der Eycken, J. *Tetrahedron* **2009**, *65*, 6410.

(34) Schroeder, M.; Nozaki, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1931.

Experimental Section

General Chemistry. All starting materials were purchased from commercial sources and used as received. The solvents were distilled under N_2 and dried according to standard procedures (THF and dioxane from Na/benzophenone ketyl; DMF from $MgSO_4$). TLC analyses were performed on sheets precoated with silica gel $60F_{254}$. Compound detection was achieved by exposure to UV light (254 nm), by immersion in anisaldehyde stain (by volume: 93% ethanol, 3.5% H_2SO_4, 1% AcOH, and 2.5% anisaldehyde) followed by heating at 150 °C. Flash chromatography experiments were carried out on Silica Gel Premium Rf grade (40−75 μm). The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts for ^{1}H NMR are given in ppm relative to internal tetramethylsilane (δ = 0.00 ppm), using $CDCl_3$ as solvent. Chemical shifts for ^{13}C NMR are given in ppm relative to $CDCl_3$ (δ = 77.0 ppm). Chemical shifts for ^{31}P NMR spectra are given relative to external 85% phosphoric acid (δ = 0.00 ppm). Abbreviations used for signal patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet.

General Procedure for the Preparation of Mixed 1,1-Bisphosphorus Compounds (Table 1). Method A. In an oven-dried 25-mL round-bottomed flask, a solution of dialkylalkanephosphonate (2.5 mmol, 1 equiv) in anhydrous THF (10 mL) is cooled to −78 °C and degassed under high vacuum for 5 min. The flask is then filled with nitrogen and *n*-BuLi (2.5 mmol, 1 equiv, 2.5 M in hexanes) is added dropwise. The solution is stirred at −78 °C for 30 min and neat chlorophosphine (3.75 mmol, 1.5 equiv) is added quickly via a syringe. After 10 min, the solution is slowly warmed to rt and $BH_3 \cdot Me_2S$ (3.75 mmol, 1.5 equiv, 2 M in THF) is added dropwise. The solution is then stirred at rt for an additional 30 min and concentrated under vacuum. The crude is diluted in EtOAc and washed with brine. Extraction of the aqueous layer with EtOAc, drying over $MgSO_4$, followed by chromatography on silica gel afford the corresponding mixed 1,1-bisphosphorus compound.

Method B. In a first oven-dried 25-mL round-bottomed flask, a solution of dialkylalkanephosphonate (6.25 mmol, 2.5 equiv) in anhydrous THF (10 mL) is cooled to −78 °C and degassed under high vacuum for 5 min. The flask is then filled with nitrogen and *n*-BuLi (6.25 mmol, 2.5 equiv, 2.5 M in hexanes) is added dropwise. The solution is stirred at −78 °C for 30 min. At the same time, a second oven-dried 25- mL round-bottomed flask is charged with the chlorophosphine (2.5 mmol, 1 equiv) and anhydrous THF (10 mL) under nitrogen. $\mathbf{BH_3 \cdot Me_2S}$ (2.5 mmol, 1 equiv, 2 M in THF) is added dropwise and the solution is stirred at rt for 30 min. The protected chlorophosphine is then added slowly to the phosphonate via a syringe. After 10 min, the solution is slowly warmed to rt and stirred at this temperature for an additional 30 min. The extraction and purification procedures described above for Method A afforded the desired mixed 1,1-bisphosphorus compound.

Dimethyl 1-(diethoxyphosphanylborane)methylphosphonate (15): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17−4.06 (m, 4H), 3.79 (d, 6H, J = 11.4 Hz), 2.45 (dd, 2H, J = 20.9 and 10.6 Hz), 1.32 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.0 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 3.5 Hz), 53.0 (d, 2 CH_3, $J_{P(O)OC}$ = 6.3 Hz), 29.7−27.3 (dd, CH_2, $J_{P(O)C}$ = 137 Hz, $J_{P(BH_3)C}$ = 43.8 Hz), 16.4 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 139.0 (q, J_{PB} = 73.5 Hz), 23.0 (s); HRMS (EI^+) calcd for $C_7H_{25}BNO_5P_2$ ($[M + NH_4]^+$) 276.1301, found 276.1294.

Diisopropyl 1-(diethoxyphosphanylborane)methylphosphonate (16): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.64 (m, 2H), 4.06−3.95 (m, 4H), 2.28 (dd, 2H, J = 20.5 and 10.3 Hz), 1.24 (t, 18H, J = 7.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 71.4 (d, 2 CH, $J_{P(O)OC}$ = 6.3 Hz), 63.9 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 3.5 Hz), 31.6−29.8 (dd, CH_2, $J_{P(O)C}$ = 138.2 Hz, $J_{P(BH_3)C}$ = 42.9 Hz), 24.1 (4 CH_3), 16.5 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 138.5 (q, J_{PB} = 70.2 Hz), 17.2 (s); HRMS (EI^+) calcd for $C_{11}H_{28}BO_5P_2$ ($[M - H]^+$) 313.1505, found 313.1515.

Dimethyl 1-(diphenylphosphanylborane)methylphosphonate (17): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80−7.73 (m, 4H), 7.51−7.42 (m, 6H), 3.55 (d, 6H, J = 11.4 Hz), 2.86−2.76 (dd, 2H, J = 20.2 and 11.4 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 132.7 (d, 4 CH, J_{PCC} = 10 Hz), 131.8 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 128.9 (d, C, J_{PC} = 59 Hz), 128.8 (d, C, J_{PC} = 59 Hz), 129.0 (d, 4 CH, J_{PCCC} = 10 Hz), 53.0 (d, 2 CH_2, $J_{P(O)OC}$ = 6.6 Hz), 25.3−23.0 (dd, CH_2, $J_{P(O)C}$ = 139.6 Hz, $J_{P(BH_3)C}$ = 27.6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 23.9 (s) and 13.4 (m); HRMS (EI^+) calcd for $C_{15}H_{20}BO_3P_2$ ($[M - H]^+$) 321.0981, found 321.0975.

Dimethyl 1-(diisopropylphosphanylborane)methylphosphonate (18): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.78 (d, 6H, J = 11.4 Hz), 2.32 (m, 2H), 2.17−2.07 (dd, 2H, J = 20 and 10.3 Hz), 1.24 (dd, 12H, J = 15.2 and 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 52.8 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 22.5 (d, CH, $J_{P(BH_3)C}$ = 2.6 Hz), 22.1 (d, 1CH, $J_{P(BH_3)C}$ = 2.6 Hz), 18.1−16.0 (dd, CH_2, $J_{P(O)C}$ = 139.6 Hz, $J_{P(BH_3)C}$ = 21 Hz), 17.1 (d, 4 CH_3, $J_{P(BH_3)CC}$ = 10.7 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 35.3 (m) and 26.7 (d, J_{PP} = 18.5 Hz); HRMS (EI^+) calcd for $C_9H_{24}BO_3P_2$ ($[M - H]^+$) 253.1294, found 253.1292.

Dimethyl 1-(diethoxyphosphonothioate)methylphosphonate (19): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.23−4.14 (m, 4H), 3.80 (d, 6H, J = 11.4 Hz), 2.75 (dd, 2H, J = 20.5 and 18.8 Hz), 1.33 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.4 (d, 2 CH_2, $J_{P(S)OC}$ = 6.3 Hz), 53.3 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 35.3−32.0 (dd, CH_2, $J_{P(O)C}$ = 136.5 Hz, $J_{P(S)C}$ = 108 Hz), 16.3 (d, 2 CH_3, $J_{P(S)OCC}$ = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 84.0 (s) and 22.1 (s); HRMS (EI^+) calcd for $C_7H_{18}O_5P_2S$ ($[M]^+$) 276.0350, found 276.0347.

Diethyl 1-(diethoxyphosphanylborane)-1-phenylethanephosphonate (20): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46−7.30 (m, 5H), 4.20−3.78 (m, 8H), 3.70 (dd, 1H, J = 24.6 and 14.4 Hz), 1.26 (td, 6H, J = 7 Hz), 1.15 (td, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 131.2 (2 CH), 129.4 (C), 128.5 (2 CH), 127.9 (CH), 64.6 (2 CH_2), 63.5 (d, CH_2, $J_{P(O)OC}$ = 6.9 Hz), 62.6 (d, CH_2, $J_{P(O)OC}$ = 6.6 Hz), 49.6 (dd, CH, $J_{P(O)C}$ = 134 Hz, $J_{P(BH_3)C}$ = 39.2 Hz), 16.4 (m, 4 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 140.1 (m) and 19.4 (s); HRMS (EI^+) calc. for $C_{15}H_{28}BO_5P_2$ ($[M - H]^+$) 361.1505, found 361.1511.

Diethyl 1-(diethoxyphosphanylborane)ethylphosphonate (21): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.22−4.05 (m, 8H), 2.36 (m, 1H), 1.43 (m, 3H), 1.26 (td, 6H, J = 7 Hz), 1.15 (td, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.6 (d, CH_2, $J_{P(BH_3)OC}$ = 3.7 Hz), 63.8 (d, CH_2, $J_{P(BH_3)OC}$ = 3.5 Hz), 62.6 (d, CH_2, $J_{P(O)OC}$ = 6.9 Hz), 62.3 (d, CH_2, $J_{P(O)OC}$ = 6.6 Hz), 34.2 (dd, CH, $J_{P(O)C}$ = 136.8 Hz, $J_{P(BH_3)C}$ = 44.9 Hz), 16.5 (d, 2 CH_3, $J_{P(O)OCC}$ = 5.2 Hz), 16.4 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 6 Hz), 9.5 (d, CH_3, J_{PCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 145.2 (m8) and 24.7 (s); HRMS (EI^+) calcd for $C_{10}H_{26}BO_5P_2$ ($[M - H]^+$) 299.1349, found 299.1347.

Dimethyl 1-(diethoxyphosphanylborane)-1-(methyloxycarbonyl)-methylphosphonate (22): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.25−4.14 (m, 4H), 3.90−3.72 (m, 10H), 1.35 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 163.9 (d, CO, J_{PCC} = 5.5 Hz), 65.4 (m, CH_2), 65.1 (m, CH_2), 54.2 (d, CH_3, $J_{P(O)OC}$ = 6.3 Hz), 54.0 (d, CH_3, $J_{P(O)OC}$ = 6.6 Hz), 53.4 (CH_3), 51.2 (dd, CH, $J_{P(O)C}$ = 129 Hz, $J_{P(BH_3)C}$ = 32.5 Hz), 16.5 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 137.3 (m) and 16.8 (s); HRMS (EI^+) calcd for $C_9H_{22}BO_7P_2$ ($[M - H]^+$) 315.0934, found 315.0941.

Dimethyl 1,1-di(diethoxyphosphanylborane)methylphosphonate (23): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.23−4.00 (m, 8H), 3.79 (d, 6H, J = 11.7 Hz), 3.26 (m, 1H), 1.31 (t, 12H, J = 7 Hz), 1.00−0.00 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.0

(d, 4 CH_2, $J_{P(BH_3)OC}$ = 3.2 Hz), 53.7 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 47.2 (dt, CH, $J_{P(O)C}$ = 122.7 Hz, $J_{P(BH_3)C}$ = 25.6 Hz), 16.5 (d, 4 CH_3, $J_{P(BH_3)OCC}$ = 6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 139.3 (m) and 17.9 (s); HRMS (EI^+) calcd for $C_{11}H_{32}B_2O_7P_3$ ([M − H]$^+$) 391.1551, found 391.1541.

General Procedure for the Preparation of Alkylated 1,1-Bisphosphorus Compounds. In an oven-dried 25-mL round-bottomed flask, sodium hydride (17 mg, 1.05 equiv, 60% in mineral oil) is suspended in anhydrous DMF (3 mL) under nitrogen. The suspension is cooled to 0 °C and the bisphosphorus (100 mg, 1 equiv) in anhydrous DMF (1 mL) is added dropwise. After 10 min, the alkyl halide (1.05 equiv) in anhydrous DMF (1 mL) is added dropwise. The resulting solution is warmed to rt and stirred for an additional hour. The mixture is then diluted with EtOAc (10 mL) and the organic layer is washed with water (3 × 50 mL) and brine. Drying over $MgSO_4$ followed by chromatography on silica gel afford the corresponding alkylated mixed 1, 1-bisphosphorus compound.

Dimethyl 1-(diethoxyphosphanylborane)propylphosphonate (24): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.23−4.03 (m, 4H), 3.81 (d, 6H, J = 11.1 Hz), 2.26 (m, 1H), 1.99 (m, 2H), 1.35 (t, 6H, J = 6.7 Hz), 1.16 (t, 3H, J = 7.6 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.6 and 64.0, (d, 2 CH_2, $J_{P(BH_3)OC}$ = 3.7 Hz), 53.1 and 53.0 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 39.8 (dd, CH, $J_{P(O)C}$ = 134.2 Hz, $J_{(PH3)C}$ = 42.9 Hz), 18.6 (d, CH_2, J_{PCC} = 5.2 Hz), 16.6 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.8 Hz), 14.5 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 145.4 (m) and 27.4 (s); HRMS (EI^+) calcd for $C_9H_{24}BO_5P_2$ ([M − H]$^+$) 285.1192, found 285.1190.

Dimethyl 1-(diethoxyphosphanylborane)nonylphosphonate (25): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.21−4.05 (m, 4H), 3.80 (d, 6H, J = 11.1 Hz), 2.24 (m, 1H), 1.89 (m, 2H), 1.53 (m, 2H), 1.34 (t, 6H, J = 7 Hz), 1.28 (m, 10H), 0.89 (t, 3H, J = 6.5 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 65.2, 64.7 (CH_2), 53.2 and 53.1 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 39.8 (dd, CH, $J_{P(O)C}$ = 134.2 Hz, $J_{P(BH_3)C}$ = 42.3 Hz), 32.0, 29.6, 29.5, 29.4, 29.3, 24.7, 22.8 (CH_2), 16.6 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.8 Hz), 14.3 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 145.5 (m) and 27.6 (s); HRMS (EI^+) calcd for $C_{15}H_{36}BO_5P_2$ ([M − H]$^+$) 369.2131, found 369.2129.

Dimethyl 1-(diethoxyphosphanylborane)-1-allylmethylphosphonate (26): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.91 (m, 1H), 5.19 (m, 2H), 4.22−4.04 (m, 4H), 3.82 (d, 6H, J = 11.1 Hz), 2.69 (m, 2H), 2.39 (m, 1H), 1.35 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 136.0 (CH), 116.9 (CH_2), 64.7, 64.1 (CH_2), 53.1 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 40.1 (dd, CH, $J_{P(O)C}$ = 135.9 Hz, $J_{P(BH_3)C}$ = 36.3 Hz), 29.1 (CH_2), 16.6 (2 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 144.7 (m) and 26.5 (s); HRMS (EI^+) calcd for $C_{10}H_{24}BO_5P_2$ ([M − H]$^+$) 297.1192, found 297.1197.

Dimethyl 1-(diethoxyphosphanylborane)-1-phenylethylphosphonate (27): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (m, 5H), 4.16 and 4.02 (m, 4H), 3.68 and 3.64 (d, 6H, J = 11.1 Hz), 3.37−3.08 (m, 2H), 2.68 (m, 1H), 1.32 and 1.24 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 139.5 (C), 128.8 (2 CH), 128.3 (2 CH), 126.5 (CH), 64.4 (d, CH_2, $J_{P(BH_3)OC}$ = 3.7 Hz), 63.9 (CH_2), 52.9 and 52.8 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 41.9 (dd, CH, $J_{P(O)C}$ = 134.2 Hz, $J_{P(BH_3)C}$ = 41.2 Hz), 30.1 (d, CH_2, J_{PCC} = 4.6 Hz), 16.4 and 16.2 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 6.1 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 144.8 (m) and 26.4 (s); HRMS (EI^+) calcd for $C_{14}H_{26}BO_5P_2$ ([M − H]$^+$) 347.1349, found 347.1355.

Dimethyl 1-(diethoxyphosphanylborane)-1-geranylmethylphosphonate (28): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.27 (t, 1H, J = 6.7 Hz), 5.1 (m, 1H), 4.22− 4.05 (m, 4H), 3.78 (d, 6H, J = 11.1 Hz), 2.63 (m, 2H), 2.31 (m, 1H), 2.03 (m, 4H), 1.69 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H), 1.33 (td, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.2, 131.6 (C), 124.4, 121.9 (CH), 64.5, 64.0 (CH_2), 53.1 and 53.0 (d, 2 CH_3, $J_{P(O)OC}$ = 6.6 Hz), 40.6 (dd, C, $J_{P(O)C}$ = 133.9 Hz, $J_{P(BH_3)C}$ = 41.5 Hz), 39.8, 26.7 (CH_2), 25.8 (CH_3), 23.4 (d, CH_2, J_{PCC} = 4.9 Hz), 17.8 (CH_3), 16.6 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.8 Hz), 16.3 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 145.0 (m) and 27.2 (s); HRMS (EI^+) calcd for $C_{17}H_{36}BO_5P_2$ ([M − H]$^+$) 393.2131, found 393.2140.

Dimethyl 1-(diethoxyphosphanylborane)-1,1-diallylmethylphosphonate (29): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.97 (m, 2H), 5.12 (m, 4H), 4.20−4.11 (m, 4H), 3.79 (d, 6H, J = 10.8 Hz), 2.69 (m, 2H), 2.69 (m, 2H), 1.33 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 133.4 (d, CH, J_{PCCC} = 7.4 Hz), 133.2 (d, CH, J_{PCCC} = 7.2 Hz), 118.6 (2 CH_2), 64.5 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 3.7 Hz), 53.1 (d, 2 CH_3, $J_{P(O)OC}$ = 7.2 Hz), 47.4 (dd, C, $J_{P(O)C}$ = 133 Hz, $J_{P(BH_3)C}$ = 42 Hz), 34.2 (d, 2 CH_2, J_{PCC} = 3.5 Hz), 16.6 (2 CH_3, $J_{P(O)OCC}$ = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 149.1 (m) and 28.9 (s); HRMS (EI^+) calcd for $C_{13}H_{28}BO_5P_2$ ([M − H]$^+$) 337.1505, found 337.1509.

Dimethyl 1-benzyl-1-(diethoxyphosphanylborane)-1-(phenylethyl)-phosphonate (30): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (m, 4H), 7.27 (m, 6H), 4.00−3.90 (m, 4H), 3.56 (d, 6H, J = 11.1 Hz), 3.45−3.23 (m, 4H), 1.10 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 136.8 (d, C, J_{PCCC} = 6.1 Hz), 136.7 (d, C, J_{PCCC} = 6.1 Hz), 132.0 (4 CH), 127.6 (4 CH), 126.9 (2 CH), 64.4 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 4.3 Hz), 52.6 (d, 2 CH_3, $J_{P(O)OC}$ = 7.5 Hz), 50.3 (dd, C, $J_{P(O)C}$ = 133 Hz, $J_{P(BH_3)C}$ = 40.9 Hz), 37.1 (2 CH_2), 16.3 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 6.1 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 149.5 (m) and 27.6 (s); HRMS (EI^+) calcd for $C_{21}H_{33}BO_5P_2$ ([M]$^+$) 438.1896, found 438.1899.

Dimethyl 1-(diethoxyphosphanylborane)cyclohexylphosphonate (31): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17−4.08 (m, 4H), 3.79 (d, 6H, J = 10.8 Hz), 2.20−1.80 (m, 6H), 1.61 (m, 4H), 1.31 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.6 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 4 Hz), 53.2 (d, 2 CH_3, $J_{P(O)OC}$ = 7.2 Hz), 43.9 (dd, C, $J_{P(O)C}$ = 132.4 Hz, $J_{P(BH_3)C}$ = 42 Hz), 25.9 (d, 2 CH_2, J_{PCCC} = 3.5 Hz), 24.9 (CH_2), 21.7 (d, 2 CH_2, J_{PCC} = 5.9 Hz), 21.6 (d, 2 CH_2, J_{PCC} = 5.9 Hz), 16.7 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 149.3 (m) and 30.6 (s); HRMS (EI^+) calcd for $C_{12}H_{28}BO_5P_2$ ([M − H]$^+$) 325.1505, found 325.1506.

Dimethyl 1-(diphenylphosphanylborane)nonylphosphonate (32): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (m, 2H), 7.79 (m, 2H), 7.46 (m, 6H), 3.50 and 3.48 (d, 6H, J = 11.1 Hz), 2.87 (m, 1H), 1.94 (m, 2H), 1.62 (m, 2H), 1.16 (m, 10H), 0.86 (t, 3H, J = 6.7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 133.5 and 132.8 (d, 4 CH, J_{PCC} = 9.8 Hz), 131.5 and 131.4 (d, 2 CH, J_{PCCCC} = 2.6 Hz), 129.4 (C), 128.8 and 128.6 (d, 4 CH, J_{PCCC} = 10.4 Hz), 128.5 (C), 52.9 and 52.8 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 34.6 (dd, CH, $J_{P(O)C}$ = 137.9 Hz, $J_{P(BH_3)C}$ = 23.6 Hz), 31.9, 30.2, 29.3, 26.6, 22.8 (CH_2), 14.3 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 27.4 (s) and 23.2 (m); HRMS (EI^+) calcd for $C_{23}H_{36}BO_3P_2$ ([M − H]$^+$) 433.2233, found 433.2239.

Dimethyl 1-(diethoxyphosphanylborane)-1-allylmethylphosphonate (33): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95 (m, 2H), 7.80 (m, 2H), 7.47 (m, 6H), 5.86 (m, 1H), 4.99 (m, 2H), 3.50 and 3.49 (d, 6H, J = 11.1 Hz), 2.97 (m, 1H), 2.69 (m, 1H), 2.43(m, 1H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 136.0 (d, CH, J_{PCCC} = 9.2 Hz), 133.5 and 132.9 (d, 4 CH, J_{PCC} = 9.8 Hz), 131.7 and 131.6 (d, 2 CH, J_{PCCCC} = 2.6 Hz), 128.8 and 128.6 (d, 4 CH, J_{PCCC} = 10.1 Hz), 127.9 (d, 2 C, J_{PC} = 55.6 Hz), 117.2 (CH_2), 53.0 and 52.8 (d, 2 CH_3, $J_{P(O)OC}$ = 7.2 Hz), 34.7 (dd, CH, $J_{P(O)C}$ = 138.5 Hz, $J_{P(BH_3)C}$ = 23.3 Hz), 30.8 (CH_2); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 27.6 (s) and 22.9 (m); HRMS (EI^+) calcd for $C_{18}H_{24}BO_3P_2$ ([M − H]$^+$) 361.1294, found 361.1292.

Dimethyl 1-(diphenylphosphanylborane)-1-phenylethylphosphonate (34): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.07 (m, 2H), 7.82 (m, 2H), 7.52 (m, 6H), 7.15(m, 5H), 3.28 and 3.26 (d, 6H, J =

11.1 Hz), 3.18 (m, 3H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 138.3 (d, CH, J_{PCCC} = 9.2 Hz), 132.5 and 131.2 (d, 4 CH, J_{PCC} = 9.8 Hz), 130.5 and 130.3 (d, 2 CH, J_{PCCCC} = 2.6 Hz), 127.7 (2 CH), 127.5 (d, 4 CH, J_{PCCC} = 10.4 Hz), 127.2 (2 CH), 126.0 (d, 2 C, J_{PC} = 55.9 Hz), 125.5 (CH), 51.6 and 51.2 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 36.0 (dd, CH, $J_{P(O)C}$ = 137.2 Hz, $J_{P(BH_3)C}$ = 23.0 Hz), 30.9 (CH_2); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 27.4 (s) and 23.2 (m); HRMS (EI^+) calcd for $C_{22}H_{26}BO_3P_2$ ($[M - H]^+$) 411.1450, found 411.1453.

Dimethyl 1-(diphenylphosphanylborane)-1-geranylmethylphosphonate (35): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.97 (m, 2H), 7.80 (m, 2H), 7.46 (m, 6H), 5.14 (t, 1H, J = 6.4 Hz), 5.05 (m, 1H), 3.52 (d, 6H, J = 11.1 Hz), 2.94 (m, 1H), 2.75−2.42 (m, 2H), 2.01−1.89 (m, 4H), 1.68 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.4 (CH), 133.2 and 132.8 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.5 (C), 131.4, 131.2 (CH), 129.2 (2 C), 128.5 and 128.3 (d, 4 CH, J_{PCCC} = 10.7 Hz), 124.0 (CH), 121.6 (dd, CH, J_{PCC} = 8.9 Hz), 52.7 and 52.5 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 39.6 (CH_2), 34.9 (dd, CH, $J_{P(O)C}$ = 137.9 Hz, $J_{P(BH_3)C}$ = 23.0 Hz), 26.4 (CH_2), 25.6 (CH_3), 24.9 (CH_2), 17.6, 15.9 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 28.7 (s) and 22.9 (m); HRMS (EI^+) calcd for $C_{25}H_{36}BO_3P_2$ ($[M - H]^+$) 457.2233, found 457.2234.

General Procedure for HWE Olefination (Table 3). In an oven-dried 25-mL round-bottomed flask, a solution of bisphosphorus compound (100 mg, 1 equiv) in anhydrous THF (4 mL) is cooled to −78 °C and degassed under high vacuum for 5 min. The flask is then filled with nitrogen and *n*-BuLi (1 equiv, 2.5 M in hexanes) is added dropwise. The solution is stirred at −78 °C for 10 min, and the carbonyl compound (1.1 equiv) in anhydrous THF (1 mL) is added dropwise. After 10 min, the solution is warmed to −60 °C for an additional 10 min and then to −40 °C for the same amount of time. After that, the ice bath is removed and the solution allowed to reach rt and stirred at this temperature for an additional hour. The crude is then diluted in EtOAc and washed with brine. Extraction of the aqueous layer with EtOAc, drying over $MgSO_4$, followed by chromatography on silica gel afford the corresponding olefin.

Diethyl vinylphosphoniteborane (36): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.29−6.14 (m, 2H), 6.11−6.05 (m, 1H), 4.14−3.99 (m, 4H), 1.32 (t, 6H, J = 7.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 134.4 (d, CH_2, J_{PCC} = 8.6 Hz), 130.0 (d, CH, J_{PC} = 76.6 Hz), 63.0 (d, 2 CH_2, J_{POC} = 4.9 Hz), 16.5 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 130.9 (q, J_{PB} = 83.2 Hz); HRMS (EI^+) calcd for $C_6H_{20}BNO_2P$ ($[M + NH_4]^+$) 180.1325, found 180.1326.

Diphenyl(vinyl)phosphineborane (37):[1]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67−7.42 (m, 10H), 6.61−6.32 (m, 1H), 6.23−6.05 (m, 2H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 135.3 (d, CH_2, J_{PCC} = 4.6 Hz), 132.7 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.5 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 129.1 (d, 4 CH, J_{PCCC} = 10 Hz), 129.6−128.7 (d, 2 C, J_{PC} = 59 Hz), 128.8−128.1 (d, CH, J_{PC} = 54.4 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 16.4 (m); HRMS (EI^+) calcd for $C_{14}H_{15}BP$ ($[M - H]^+$) 225.1004, found 225.1000.

Diisopropyl(vinyl)phosphineborane (38): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.36−6.19 (m, 2H), 6.10−6.00 (m, 1H), 2.06 (m, 2H), 1.12 (m, 12H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.7 (d, CH_2, J_{PCC} = 6 Hz), 124.0 (d, CH, J_{PC} = 46.1 Hz), 21.5 (d, 2 CH, J_{PC} = 35.7 Hz), 16.5 (4 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 33.2 (q, J_{PB} = 59.5 Hz); HRMS (EI^+) calcd for $C_8H_{19}BP$ ($[M - H]^+$) 157.1317, found 157.1316.

***O,O*-Diethyl vinylthiophosphonate (39):**[2]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.40−6.15 (m, 2H), 6.00 (m, 1H), 4.16−4.04 (m, 4H), 1.32 (t, 6H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 133.7 (d, CH_2, J_{PCC} = 5.2 Hz), 131.4 (d, CH, J_{PC} = 147.7 Hz), 62.5 (d, 2 CH_2, J_{POC} = 6 Hz), 16.1 (d, 2 CH_3, J_{POCC} = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 86.3 (s); HRMS (EI^+) calcd for $C_6H_{13}O_2PS$ ($[M]^+$) 180.0374, found 180.0375.

(*Z*/*E*)-Diethyl hex-1-enylphosphoniteborane (*Z*/*E*: 10/90) (40): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.80−6.68 (m, 1H), 5.82 (m, 1H *E*-isomer), 5.63 (m, 1H, *Z*-isomer), 4.13−3.99 (m, 4H), 2.45 (m, 2H *Z*-isomer), 2.25 (q, 2H *E*-isomer, J = 7 Hz), 1.45 (m, 4H), 1.33 (t, 6H, J = 7 Hz), 0.93 (t, 3H, J = 7.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 153.2 (d, CH, J_{PCC} = 11.5 Hz), 121.1 (d, CH, J_{PC} = 79.7 Hz), 62.8 (d, 2 CH_2, J_{POC} = 4.9 Hz), 34.2 (d, CH_2, J_{PCCC} = 16.7 Hz), 30.0, 22.4 (CH_2), 16.6 (d, 2 CH_3, J_{POCC} = 5.8 Hz), 14.0 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 131.4 (q, J_{PB} = 86.5 Hz, *E*- and *Z*-isomers); HRMS (EI^+) calcd for $C_{10}H_{28}BNO_2P$ ($[M + NH_4]^+$) 236.1951, found 236.1943.

(*Z*/*E*)-Hex-1-enyldiphenylphosphineborane (*Z*/*E*: 15/85) (41): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71−7.40 (m, 10H), 6.74−6.52 (m, 1H), 6.18−6.08 (m, 1H *E*-isomer), 6.04−5.90 (m, 1H *Z*-isomer), 2.32 (q, 2H *E*-isomer, J = 6.5 Hz), 2.20 (q, 2H *Z*-isomer, J = 6.5 Hz), 1.50−1.29 (m, 4H), 0.92 (t, 3H *E*-isomer, J = 7 Hz), 0.80 (t, 3H *Z*-isomer, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 153.7 (d, CH, J_{PCC} = 7.5 Hz), 132.5 (d, 4 CH, J_{PCC} = 9.8 Hz), 131.2 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 130.4 (d, 2 C, J_{PC} = 59 Hz), 128.9 (d, 4 CH, J_{PCCC} = 10.4 Hz), 118.3 (d, CH, J_{PC} = 58.4 Hz); 34.9 (d, CH_2, J_{PCCC} = 15.3 Hz), 30.3, 22.5 (CH_2), 14.1 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 13.9 (m, *E*-isomer) and 8.4 (m, *Z*-isomer); HRMS (EI^+) calcd for $C_{18}H_{23}BP$ ($[M - H]^+$) 281.1630, found 281.1632.

(*E*)-Hex-1-enyldiisopropylphosphineborane (42): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.65 (m, 1H), 5.54 (dd, 1H, J = 16.7 and 7 Hz), 2.25 (q, 2H, J = 7.3 Hz), 2.00 (m, 2H), 1.49−1.20 (m, 4H), 1.08 (m, 12H), 0.90 (t, 3H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 155.4 (d, CH, J_{PCC} = 7.5 Hz), 113.7 (d, CH, J_{PC} = 50.4 Hz), 34.8 (d, CH_2, J_{PCCC} = 14.1 Hz), 30.3, 22.1 (CH_2), 21.7 (d, 2 CH, J_{PC} = 36.6 Hz), 16.6 (d, 4 CH_3, J_{PCC} = 2.9 Hz), 13.8 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 30.5 (q, J_{PB} = 59.8 Hz); HRMS (EI^+) calcd for $C_{12}H_{27}BP$ ($[M - H]^+$) 213.1943, found 213.1945.

(*Z*/*E*)-*O,O*-Hex-1-enylthiophosphonate (*Z*/*E*: 20/80) (43):[3]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89−7.73 (m, 1H), 5.92−5.77 (m, 1H, *E*- and *Z*-isomers), 4.11 (m, 4H), 2.52 (q, 2H *Z*-isomer, J = 5.9 Hz), 2.24 (q, 2H *E*-isomer, J = 6.4 Hz), 1.55−1.22 (m, 10H), 0.90 (t, 3H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.8 (d, CH, J_{PCC} = 7.5 Hz), 122.6 (d, CH, J_{PC} = 151.4 Hz), 62.2 (d, 2 CH_2, J_{POC} = 5.8 Hz), 33.3 (d, CH_2, J_{PCCC} = 22.5 Hz), 29.9, 22.2 (CH_2), 16.1 (d, 2 CH_3, J_{POCC} = 7.5 Hz), 13.8 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 87.7 (s, *E*-isomer) and 81.8 (s, *Z*-isomer); HRMS (EI^+) calcd for $C_{10}H_{21}O_2PS$ ($[M]^+$) 236.1000, found 236.0995.

(*E*)-Diethyl(styryl)phosphoniteborane (44): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53−7.37 (m, 6H), 6.44 (dd, 1H, J = 17.6 and 12.6 Hz), 4.17−4.06 (m, 4H), 1.37 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.8 (d, CH, J_{PCC} = 13.2 Hz), 135.1 (d, C, J_{PCCC} = 17.9 Hz), 130.4 (CH), 129.0 (2 CH), 127.9 (2 CH), 118.6 (d, CH, J_{PC} = 80 Hz), 63.2 (d, 2 CH_2, J_{POC} = 4.9 Hz), 16.7 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 132.3 (q, J_{PB} = 82.3 Hz); HRMS (EI^+) calcd for $C_{12}H_{24}BNO_2P$ ($[M + NH_4]^+$) 256.1638, found 256.1634.

(*E*)-Diphenyl(styryl)phosphineborane (45): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71−7.65 (m, 4H), 7.53−7.25 (m, 12H), 6.76 (dd, 1H, J = 17.3 and 10 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 148.2 (d, CH, J_{PCC} = 9.5 Hz), 135.4 (d, C, J_{PCCC} = 17 Hz), 132.4 (d, 4 CH, J_{PCC} = 8.8 Hz), 131.8 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 130.2−129.4 (d, 2 C, J_{PC} = 59.3 Hz), 129.9 (CH), 128.9 (d, 4 CH, J_{PCCC} = 7.2 Hz), 128.7 (2 CH), 127.5 (2 CH), 116.4 (d, CH, J_{PC} = 59.3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 15.8 (m); HRMS (EI^+) calcd for $C_{20}H_{19}BP$ ($[M - H]^+$) 301.1317, found 301.1312.

(*E*)-Diisopropyl(styryl)phosphineborane (46):[4]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (m, 6H), 6.26 (dd, 1H, J = 17 and 4.7 Hz), 2.11

(m, 2H), 1.15 (m, 12H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.3 (d, CH, J_{PCC} = 9.5 Hz), 135.7 (d, C, J_{PCCC} = 15.5 Hz), 129.8 (CH), 128.7 (2 CH), 127.3 (2 CH), 112.6 (d, CH, J_{PC} = 50.7 Hz), 22.1 (d, 2 CH, J_{PC} = 36.3 Hz), 16.7 (d, 4 CH_3, J_{PCC} = 1.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 32.6 (m); HRMS (EI$^+$) calcd for $C_{16}H_{23}BP$ ([M − H]$^+$) 233.1630, found 233.1624.

(*E*)-*O*,*O*-Diethyl styrylthiophosphonate (47):[5]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.36 (m, 6H), 6.47 (t, 1H, J = 17 Hz), 4.15 (m, 4H), 1.34 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.8 (d, CH, J_{PCC} = 10.7 Hz), 134.6 (d, C, J_{PCCC} = 24.2 Hz), 130.1 (CH), 128.8 (2 CH), 127.9 (2 CH), 119.9 (d, CH, J_{PC} = 155.2 Hz), 62.5 (d, 2 CH_2, J_{POC} = 5.8 Hz), 16.7 (d, 2 CH_3, J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 88.1 (s); HRMS (EI$^+$) calcd for $C_{12}H_{17}O_2PS$ ([M]$^+$) 256.0687, found 256.0685.

(*E*)-Diethyl 2-(pyridin-3-yl)vinylphosphoniteborane (48): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.73 (d, 1H, J = 2.3 Hz), 8.61 (dd, 1H, J = 4.7 and 1.5 Hz), 7.82 (dd, 1H, J = 7.9 and 5.9 Hz), 7.46−7.32 (m, 2H), 6.53 (dd, 1H, J = 17.9 and 12.6 Hz), 4.18−4.06 (m, 4H), 1.36 (t, 6H, J = 6.9 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 151.2, 149.6 (CH), 143.9 (d, CH, J_{PCC} = 13.2 Hz), 134.2 (CH), 130.8 (d, C, J_{PCCC} = 17.6 Hz), 123.9 (CH), 121.5 (d, CH, J_{PC} = 80.6 Hz), 63.5 (d, 2 CH_2, J_{POC} = 4.3 Hz), 16.7 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 131.5 (q, J_{PB} = 80.3 Hz); HRMS (EI$^+$) calcd for $C_{11}H_{20}BNO_2P$ ([M + H]$^+$) 240.1328, found 240.1325.

(*E*)-Diisopropyl-2-(pyridyn-3-yl)vinyl)phosphineborane (49): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.74 (d, 1H, J = 2.1 Hz), 8.60 (dd, 1H, J = 4.7 and 1.5 Hz), 7.79 (dt, 1H, J = 7.6 and 1.8 Hz), 7.49−7.25 (m, 2H), 6.38 (dd, 1H, J = 17 and 4.1 Hz), 2.14 (m, 2H), 1.16 (m, 12H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.4, 148.9 (CH), 146.9 (d, CH, J_{PCC} = 9.8 Hz), 133.8 (CH), 131.3 (d, C, J_{PCCC} = 15.5 Hz), 123.6 (CH), 115.8 (d, CH, J_{PC} = 48.4 Hz), 22.1 (d, 2 CH, J_{PC} = 36 Hz), 16.7 (d, 4 CH_3, J_{PCC} = 3.2 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 33.6 (m); HRMS (EI$^+$) calcd for $C_{13}H_{22}BP$ ([M − H]$^+$) 234.1583, found 234.1587.

(*E*)-*O*,*O*-Diethyl 2-(pyridyn-3-yl)vinylthiophosphonate (50): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.74 (d, 1H, J = 2.1 Hz), 8.61 (dd, 1H, J = 4.7 and 1.5 Hz), 7.82 (dd, 1H, J = 7.9 and 1.8 Hz), 7.52 (dd, 1H, J = 25.2 and 17.3 Hz), 7.33 (dd, 1H, J = 7.6 and 5 Hz), 6.53 (t, 1H, J = 17 Hz), 4.22−4.11 (m, 4H), 1.35 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.9, 149.5 (CH), 143.7 (d, CH, J_{PCC} = 10.7 Hz), 134.1 (CH), 130.4 (d, C, J_{PCCC} = 24.2 Hz), 123.6 (CH), 122.7 (d, CH, J_{PC} = 155.5 Hz), 62.7 (d, 2 CH_2, J_{POC} = 5.8 Hz), 16.2 (d, 2 CH_3, J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 86.3 (s); HRMS (EI$^+$) calcd for $C_{11}H_{16}NO_2PS$ ([M]$^+$) 257.0639, found 257.0636.

(*E*)-Diethyl buta-1,3-dienylphosphoniteborane (51): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.04 (m, 1H), 6.44 (m, 1H), 5.90 (dd, 1H, J = 17 and 13.8 Hz), 5.49 (m, 2H), 4.13−3.98 (m, 4H), 1.32 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.7 (d, CH, J_{PCC} = 12.4 Hz), 135.9 (d, CH, J_{PCCC} = 20.4 Hz), 124.9 (CH_2), 122.5 (d, CH, J_{PC} = 80.3 Hz), 62.8 (d, 2 CH_2, J_{POC} = 4.6 Hz), 16.5 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 131.4 (q, J_{PB} = 83.7 Hz); HRMS (EI$^+$) calcd for $C_8H_{22}BNO_2P$ ([M + NH_4]$^+$) 206.1481, found 206.1477.

(*E*)-Buta-1,3-dienyldiphenylphosphineborane (52): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.61 (m, 4H), 7.51−7.43 (m, 6H), 7.06−6.91 (m, 1H), 6.58−6.46 (m, 1H), 6.32−6.23 (dd, 1H, J = 16.7 and 10.6 Hz), 5.54−5.42 (m, 2H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 148.7 (d, CH, J_{PCC} = 8.6 Hz), 136.4 (d, CH, J_{PCCC} = 18.7 Hz), 132.6 (d, 4 CH, J_{PC} = 9.8 Hz), 131.4 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 129.9 (d, 2 CH, J_{PC} = 59.6 Hz), 129.0 (d, 4 CH, J_{PCCC} = 10.4 Hz), 124.1 (CH_2), 120.9 (d, CH, J_{PC} = 59 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 14.8 (m); HRMS (EI$^+$) calcd for $C_{14}H_{15}BP$ ([M − H]$^+$) 251.1161, found 251.1159.

(*E*)-Buta-1,3-dienyldiisopropylphosphineborane (53): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (m, 1H), 6.44 (m, 1H), 5.72 (dd, 1H, J = 16.7 and 5.3 Hz), 5.47 (m, 2H), 2.04 (m, 2H), 1.12 (m, 12H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.7 (d, CH, J_{PCC} = 8.6 Hz), 136.3 (d, CH, J_{PCCC} = 17.3 Hz), 123.0 (CH_2), 116.9 (d, CH, J_{PC} = 50.4 Hz), 22.0 (d, 2 CH, J_{PC} = 36.6 Hz), 16.7 (4 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 31.7 (q, J_{PB} = 59.8 Hz); HRMS (EI$^+$) calcd for $C_{10}H_{21}BP$ ([M − H]$^+$) 183.1474, found 183.1476.

(*Z*/*E*)-*O*,*O*-Diethyl buta-1,3-dienylthiophosphonate (*Z*/*E*: 4/96) (54):[6]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20−7.03 (m, 1H), 6.47 (m, 1H), 5.95 (dd, 1H, J = 18.5 and 16.4 Hz), 5.58 (d, 1H, J = 17 Hz), 5.49 (m, 1H), 4.17−4.05 (m, 4H), 1.33 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.7 (d, CH, J_{PCC} = 9.2 Hz), 135.3 (d, CH, J_{PCCC} = 27.6 Hz), 125.0 (CH_2), 124.0 (d, CH, J_{PC} = 155.8 Hz), 62.3 (d, 2 CH_2, J_{POC} = 5.8 Hz), 16.2 (d, 2 CH_3, J_{POCC} = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 86.9 (s, *E*-isomer), 80.8 (s, *Z*-isomer); HRMS (EI$^+$) calcd for $C_8H_{15}O_2PS$ ([M]$^+$) 206.0531, found 206.0531.

Diethyl (1*E*,3*E*)-4,8-dimethylnona-1,3,7-trienylphosphoniteborane (55): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33 (m, 1H), 5.96 (d, 1H, J = 11.1 Hz), 5.74 (dd, 1H, J = 16.7 and 13.5 Hz), 5.08 (m, 1H), 4.12−3.99 (m, 4H), 2.13 (m, 4H), 1.88 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.32 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 148.9 (C), 144.2 (d, CH, J_{PCC} = 13.8 Hz), 132.2 (C), 124.4 (d, CH, J_{PCCC} = 20.2 Hz), 123.3 (CH), 118.3 (d, CH, J_{PC} = 82.3 Hz), 62.6 (d, 2 CH_2, J_{POC} = 4.9 Hz), 40.1, 26.2 (CH_2), 25.6, 17.7, 17.3 (CH_3), 16.4 (d, 2 CH_3 J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 132.7 (q, J_{PB} = 84.3 Hz); HRMS (EI$^+$) calcd for $C_{15}H_{34}BNO_2P$ ([M + NH_4]$^+$) 302.2420, found 302.2418.

((1*Z*/*E*,3*E*)-4,8-Dimethylnona-1,3,7-trienyl)diphenylphosphineborane (*Z*/*E*: 4/96) (56): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.67−7.60 (m, 4H), 7.50−7.40 (m, 6H), 7.39−7.24 (m, 1H), 6.12−6.03 (m, 2H), 5.08 (m, 1H), 2.12 (s, 4H), 1.83 (s, 3H), 1.69 (s, 3H), 1.60 (s, 3H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.7 (C), 145.1 (d, CH, J_{PCC} = 10.4 Hz), 132.3 (d, 4 CH, J_{PCC} = 9.5 Hz), 132.1 (C), 130.9 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 130.5 (d, 2 C, J_{PC} = 56 Hz), 128.6 (d, 4 CH, J_{PCCC} = 10.1 Hz), 124.7 (d, CH, J_{PCCC} = 19 Hz), 123.4 (CH), 116.1 (d, CH, J_{PC} = 61.6 Hz), 40.0, 26.3 (CH_2), 25.7, 17.7, 17.3 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 14.8 (m, *E*-isomer) and 10.0 (m, *Z*-isomer); HRMS (EI$^+$) calcd for $C_{14}H_{15}BP$ ([M]$^+$) 348.2178, found 348.2174.

((1*E*,3*E*)-4,8-Dimethylnona-1,3,7-trienyl)diisopropylphosphineborane (57): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.23 (m, 1H), 6.01 (d, 1H, J = 11.7 Hz), 5.52 (dd, 1H, J = 16.1 and 5.6 Hz), 5.10 (m, 1H), 2.13 (s, 4H), 2.03 (m, 2H), 1.88 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H), 1.14 (m, 12H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 147.0 (d, CH, J_{PCC} = 9.8 Hz), 146.2, 132.1 (C), 124.9 (d, CH, J_{PCCC} = 17.6 Hz), 123.5 (CH), 112.5 (d, CH, J_{PC} = 52.7 Hz), 40.0, 26.3 (CH_2), 25.6 (CH_3), 22.0 (d, 2 CH, J_{PC} = 36.9 Hz), 17.7, 17.3 (CH_3), 16.6 (d, 4 CH_3, J_{PCC} = 2.3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 31.6 (m); HRMS (EI$^+$) calcd for $C_{17}H_{33}BP$ ([M − H]$^+$) 279.2413, found 279.2416.

***O*,*O*-Diethyl (1*Z*/*E*,3*E*)-4,8-dimethylnona-1,3,7-trienylthiophosphonate (*Z*/*E*: 6/94) (58):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52−7.35 (m, 1H), 6.00 (d, 1H, J = 11.1 Hz), 5.79 (dd, 1H, J = 35.5 and 16.1 Hz), 5.07 (m, 1H), 4.14−4.04 (m, 4H), 2.15 (d, 4H, J = 9.1 Hz), 1.89 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.32 (t, 6H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 149.1 (C), 144.5 (d, CH, J_{PCC} = 10.4 Hz), 132.2 (C), 123.9 (d, CH, J_{PCCC} = 27.1 Hz), 123.3 (CH), 120.0 (d, CH, J_{PC} = 155.5 Hz), 62.2 (d, 2 CH_2, J_{POC} = 5.8 Hz), 40.1, 26.2 (CH_2), 25.6, 17.7, 17.4 (CH_3), 16.2 (d, 2 CH_3 J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 89.2 (s, *E*-isomer) and 82.6 (s, *Z*-isomer); HRMS (EI$^+$) calcd for $C_{15}H_{27}O_2PS$ ([M]$^+$) 302.1469, found 302.1461.

(*E*)-Diethyl 4-(*N*-benzyloxycarbonyl)but-1-en-2-ylphosphoniteborane (59): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (m, 5H), 6.63 (m, 1H), 5.89 (m, 1H), 5.10 (s, 2H), 4.81 (m, 1H), 4.13−3.97 (m, 4H), 3.35 (q, 2H, J = 6.5 Hz), 2.46 (q, 2H, J = 6.7 Hz), 1.30 (t, 6H, J = 7.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 156.2 (CO), 148.4 (d, CH, J_{PCC} = 10.9 Hz), 136.3 (C), 128.1 (3 CH), 128.0 (2 CH), 123.8 (d, CH, J_{PC} = 77.2 Hz), 66.5 (CH_2), 62.8 (d, 2 CH_2, J_{POC} = 5 Hz), 39.2 (CH_2), 34.7 (d, CH_2, J_{PCCC} = 17 Hz), 16.4 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 130.6 (m); HRMS (EI^+) calcd for $C_{16}H_{31}BN_2O_4P$ ($[M + NH_4]^+$) 357.2115, found 357.2109.

(*Z*/*E*)-4-(*N*-Benzyloxycarbonyl)but-1-en-2-yldiphenylphosphineborane (*Z*/*E*: 10/90) (60): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.26 (m, 15H), 6.63−6.49 (m, 1H), 6.25 (dd, 1H *E*-isomer, J = 16.1 and 11.1 Hz), 6.10 (m, 1H *Z*-isomer), 5.08 (s, 2H), 4.79 (m, 1H), 3.37 (q, 2H *E*-isomer, J = 6.4 Hz), 3.27 (q, 2H *Z*-isomer, J = 6.4 Hz), 2.52 (q, 2H, J = 6.4 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 156.5 (CO), 149.1 (d, CH, J_{PCC} = 7.8 Hz), 136.6 (C), 132.3 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.3 (d, 2 CH, J_{PCCCC} = 2.6 Hz), 129.9 (d, 2 C, J_{PC} = 59 Hz), 129.0 (d, 4 CH, J_{PCCC} = 10.4 Hz), 128.7 (3 CH), 128.4, 128.3 (CH), 122.1 (d, CH, J_{PC} = 57.6 Hz), 67.0, 39.0 (CH_2), 35.4 (d, CH_2, J_{PCCC} = 15.3 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 13.9 (m, *E*-isomer) and 8.4 (m, *Z*-isomer); HRMS (EI^+) calcd for $C_{24}H_{26}BNO_2P$ ($[M - H]^+$) 402.1794, found 402.1786.

(*Z*/*E*)-*O*,*O*-Diethyl 4-(*N*-benzyloxycarbonyl)but-1-en-2-ylthiophosphonate (*Z*/*E*: 7/93) (61): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36 (m, 5H), 6.72 (m, 1H), 5.95 (t, 1H, J = 19.6 Hz), 5.11 (s, 2H), 4.80 (m, 1H), 4.17−4.02 (m, 4H), 3.36 (q, 2H, J = 6.2 Hz), 2.48 (q, 2H, J = 6.5 Hz), 1.31 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 156.2 (CO), 148.2 (d, CH, J_{PCC} = 7.5 Hz), 136.4 (C), 128.1 (3 CH), 128.0 (2 CH), 125.4 (d, CH, J_{PC} = 151.4 Hz), 66.7 (CH_2), 62.4 (d, 2 CH_2, J_{POC} = 6 Hz), 39.3 (CH_2), 34.0 (d, CH_2, J_{PCCC} = 22.5 Hz), 16.1 (d, 2 CH_3, J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 86.1 (s, *E*-isomer) and 80.6 (s, *Z*-isomer); HRMS (EI^+) calcd for $C_{16}H_{24}NO_4PS$ ($[M]^+$) 357.1164, found 357.1163.

Diethyl 2-methylprop-1-enylphosphoniteborane (62): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.43 (d, 1H, J = 12.9 Hz), 4.13−3.97 (m, 4H), 2.03 (m, 3H), 1.94 (m, 3H), 1.32 (t, 6H, J = 7.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 158.6 (d, C, J_{PCC} = 10.7 Hz), 116.5 (d, CH, J_{PC} = 81.5 Hz), 62.2 (d, 2 CH_2, J_{POC} = 6 Hz), 28.4 (d, CH_3, J_{PCCC} = 16.1 Hz), 21.8 (d, CH_3, J_{PCCC} = 6.6 Hz), 16.5 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 129.5 (m); HRMS (EI^+) calcd for $C_8H_{24}BNO_2P$ ($[M + NH_4]^+$) 208.1638, found 208.1636.

(2-Methylprop-1-enyl)diphenylphosphineborane (63): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71−7.65 (m, 4H), 7.46−7.38 (m, 6H), 5.70 (d, 1H, J = 12 Hz), 2.00 (m, 3H), 1.84 (m, 3H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 158.1 (C), 132.4 (d, 4 CH, J_{PCC} = 9.2 Hz), 131.6 (d, 2 CH, J_{PC} = 58.2 Hz), 131.1 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 129.0 (d, 4 CH, J_{PCCC} = 10.1 Hz), 113.6 (d, CH, J_{PC} = 59.9 Hz), 29.1 (d, CH_3, J_{PCCC} = 14.4 Hz), 22.6 (d, CH_3, J_{PCCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 8.7 (m); HRMS (EI^+) calcd for $C_{14}H_{15}BP$ ($[M + NH_4 - H_2]^+$) 270.1583, found 270.1575.

***O*,*O*-Diethyl 2-methylprop-1-enylthiophosphonate (64):**[7]**.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.64 (d, 1H, J = 23.7 Hz), 4.18−4.01 (m, 4H), 2.06 (d, 3H, J = 2.9 Hz), 1.91 (s, 3H), 1.32 (t, 6H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 156.8 (C), 119.0 (d, CH, J_{PC} = 154 Hz), 61.8 (d, 2 CH_2, J_{POC} = 6 Hz), 28.2 (d, CH_3, J_{PCCC} = 23.6 Hz), 21.3 (d, CH_3, J_{PCCC} = 7.5 Hz), 16.1 (d, 2 CH_3, J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 82.5 (s); HRMS (EI^+) calcd for $C_8H_{17}O_2PS$ ($[M]^+$) 208.0687, found 208.0689.

Diethyl cyclohexylidenemethylphosphoniteborane (65): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.36 (d, 1H, J = 13.2 Hz), 4.11−3.96 (m, 4H), 2.52 (t, 2H, J = 6.2 Hz), 2.26 (t, 2H, J = 5.6 Hz), 1.67 (m, 6H), 1.33 (t, 6H, J = 5.9 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 166.3 (d, C, J_{PCC} = 10.7 Hz), 113.1 (d, CH, J_{PC} = 80.9 Hz), 62.3 (d, 2 CH_2, J_{POC} = 5.8 Hz), 39.2 (d, CH_2, J_{PCCC} = 15.5 Hz), 32.7 (d, CH_2, J_{PCCC} = 6.9 Hz), 28.7, 27.9, 25.9 (CH_2), 16.6 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 129.6 (q, J_{PB} = 85.0 Hz); HRMS (EI^+) calcd for $C_{11}H_{28}BNO_2P$ ($[M + NH_4]^+$) 248.1951, found 248.1958.

(Cyclohexylidenemethyl)diphenylphosphineborane (66): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73−7.66 (m, 4H), 7.46−7.39 (m, 6H), 5.62 (d, 1H, J = 13.5 Hz), 2.34−2.25 (dt, 4H, J = 5.9 Hz), 1.69−1.43 (m, 6H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 165.6 (C), 132.4 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.9 (d, 2 C, J_{PC} = 57.6 Hz), 130.9 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 128.9 (d, 4 CH, J_{PCCC} = 10.1 Hz), 110.4 (d, CH, J_{PC} = 59.6 Hz), 39.8 (d, CH_2, J_{PCCC} = 13.8 Hz), 33.3 (d, CH_2, J_{PCCC} = 8.3 Hz), 28.8, 27.3, 25.9 (CH_2); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 7.8 (m); HRMS (EI^+) calcd for $C_{14}H_{15}BP$ ($[M + NH_4 - H_2]^+$) 310.1896, found 310.1894.

***O*,*O*-Diethyl cyclohexylidenemethylthiophosphonate (67):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.58 (d, 1H, J = 24.9 Hz), 4.16−4.05 (m, 4H), 2.59 (t, 2H, J = 4.4 Hz), 2.21 (t, 2H, J = 5.3 Hz), 1.60 (m, 6H), 1.33 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 164.3 (d, C, J_{PCC} = 5.5 Hz), 115.6 (d, CH, J_{PC} = 152.6 Hz), 61.8 (d, 2 CH_2, J_{POC} = 6.3 Hz), 38.8 (d, CH_2, J_{PCCC} = 22.5 Hz), 31.9 (d, CH_2, J_{PCCC} = 8.1 Hz), 28.4, 27.5, 25.8 (CH_2), 16.1 (d, 2 CH_3, J_{POCC} = 7.5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 83.0 (s); HRMS (EI^+) calcd for $C_{11}H_{21}O_2PS$ ($[M]^+$) 248.1000, found 248.0999.

Diethyl 1-(4-*N*-Boc-piperidinyl)meth-1-en-2-ylphosphoniteborane (68): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.51 (d, 1H, J = 12.6 Hz), 4.14−3.96 (m, 4H), 3.51 (q, 4H, J = 5.9 Hz), 2.59 (t, 2H, J = 5.6 Hz), 2.31 (t, 2H, J = 5.6 Hz), 1.48 (s, 9H), 1.32 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 160.5 (d, C, J_{PCC} = 10.4 Hz), 154.5 (CO), 115.8 (d, CH, J_{PC} = 79.5 Hz), 79.9 (C), 62.4 (d, 2 CH_2, J_{POC} = 5.47 Hz), 44.6 (2 CH_2), 37.7 (d, CH_2, J_{PCCC} = 13.5 Hz), 31.8 (CH_2), 28.3 (3 CH_3), 16.4 (d, 2 CH_3, J_{POCC} = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 129.4 (m); HRMS (EI^+) calcd for $C_{15}H_{32}BNO_4P$ ($[M + H]^+$) 332.2162, found 332.2162; HRMS (EI^+) calcd for $C_{15}H_{35}BN_2O_4P$ ($[M + NH_4]^+$) 349.2428, found 349.2416.

Diphenyl 1-(4-*N*-Boc-piperidinyl)meth-1-ene-2-ylphosphineborane (69): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73−7.67 (m, 4H), 7.49−7.41 (m, 6H), 5.81 (d, 1H, J = 11.7 Hz), 3.53 (t, 2H, J = 5.6 Hz), 3.34 (t, 2H, J = 5.6 Hz), 2.37 (q, 4H, J = 5.6 Hz), 1.45 (s, 9H), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 159.9 (C), 154.5 (CO), 132.1 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.0 (d, 2 CH, J_{PCCCC} = 2.3 Hz), 130.9 (d, 2 C, J_{PC} = 58.2 Hz), 128.8 (d, 4 CH, J_{PCCC} = 10.1 Hz), 113.4 (d, CH, J_{PC} = 58.2 Hz), 79.8 (C), 44.9 (2 CH_2), 38.2 (d, CH_2, J_{PCCC} = 13.4 Hz), 32.3 (CH_2), 28.3 (3 CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 8.0 (m); HRMS (EI^+) calcd for $C_{23}H_{28}NO_2P$ ($[M - BH_3]^+$) 381.1858, found 381.1848.

***O*,*O*-Diethyl 1-(4-*N*-Boc-piperidinyl)meth-1-en-2-ylthiophosphonate (70):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.73 (d, 1H, J = 23.2 Hz), 4.19−4.04 (m, 4H), 3.51 (q, 4H, J = 5.9 Hz), 2.71 (t, 2H, J = 7 Hz), 2.28 (t, 2H, J = 5.3 Hz), 1.48 (s, 9H), 1.33 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 158.4 (C), 154.5 (CO), 118.4 (d, CH, J_{PC} = 154 Hz), 79.9 (C), 62.1 (d, 2 CH_2, J_{POC} = 6.3 Hz), 44.8 (2 CH_2), 37.4 (d, CH_2, J_{PCCC} = 22.5 Hz), 31.3 (CH_2), 28.3 (3 CH_3), 16.2 (d, 2 CH_3, J_{POCC} = 7.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 81.3 (s); HRMS (EI^+) calcd for $C_{15}H_{28}NO_4PS$ ($[M]^+$) 349.1477, found 349.1467.

Synthesis of Trisubstituted Olefins (Scheme 4). (*E*)-Diethyl 1-phenylbut-1-en-2-ylphosphoniteborane (71): Compound **71** has been synthesized from the mixed 1,1-bisphosphorus **24** following the procedure for the preparation of olefins. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.26 (m, 6H), 4.17−4.04 (m, 4H), 2.5 (m, 2H), 1.35 (t, 6H, J = 7 Hz), 1.21 (t, 6H, J = 7.6 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 141.7

(d, CH, J_{PCC} = 19.8 Hz), 136.7 (d, CH, J_{PC} = 70.5 Hz), 135.7 (d, C, J_{PCCC} = 19.3 Hz), 129.3 (2 CH), 129.2 (CH), 128.6 (2 CH), 63.4 (d, 2 CH_2, J_{POC} = 4.3 Hz), 20.6 (d, CH_2, J_{PCC} = 9.2 Hz), 16.7 (d, 2 CH_3, J_{POCC} = 5.8 Hz), 14.2 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 137.3 (q, J_{PB} = 81.2 Hz); HRMS (EI^+) calcd for $C_{14}H_{28}BNO_2P$ ($[M + NH_4]^+$) 284.1951, found 284.1943.

(*E*)-Diphenyl(1-phenyllprop-1-en-2-yl)phosphineborane (72): In an oven-dried 25-mL round-bottomed flask, sodium hydride (0.78 mmol, 2.5 equiv, 60% in mineral oil) is suspended in anhydrous dioxane (3 mL) under nitrogen. Compound **17** (0.31 mmol, 1.05 equiv) in anhydrous dioxane (1 mL) is added dropwise. After 10 min, ethyl iodide (0.33 mmol, 1.05 equiv) in anhydrous dioxane (1 mL) is added and the resulting solution is stirred at rt for an additional hour before the addition of benzaldehyde (0.33 mmol, 1.05 equiv) diluted in anhydrous dioxane (1 mL). After 1 h at rt, EtOAc (10 mL) is added and the organic layer is washed with water (3 × 50 mL) and brine. Drying over $MgSO_4$ followed by chromatography on silica gel afford the trisubstituted olefin **72** in 77% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74−7.24 (m, 15H), 6.93 (d, 1H, J = 20 Hz), 2.11 (d, 3H, J = 12.3 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 143.2 (d, CH, J_{PCC} = 11.2 Hz), 136.3 (d, C, J_{PCCC} = 16.1 Hz), 133.5 (d, 4 CH, J_{PCC} = 9.5 Hz), 131.5 (d, 2 CH, J_{PCCCC} = 2.0 Hz), 129.4 (2 CH), 129.0 (d, 4 CH, J_{PCCC} = 10.1 Hz), 128.6 (2 CH), 128.4 (CH), 128.2 (d, 2 C, J_{PC} = 58.4 Hz), 128.1 (d, C, J_{PC} = 49.2 Hz), 16.5 (d, CH_3, J_{PCC} = 10.4 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 30.2 (m); HRMS (EI^+) calcd for $C_{21}H_{21}BP$ ($[M - H]^+$) 315.1474, found 315.1477.

Attempted *Z*-Selective Olefination (Scheme 5). Diphenyl 1-(diethoxyphosphanylborane)methylphosphonate (73): Compound **73** has been synthesized following the general procedure for the preparation of mixed 1,1-bisphosphorus compounds and using method A. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34−7.14 (m, 10H), 4.22−4.09 (m, 4H), 2.75 (dd, 2H, J = 21.1 and 10 Hz), 1.30 (t, 6H, J = 7 Hz), 1.00−0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.3 (d, 2 C, $J_{P(O)OC}$ = 8.9 Hz), 130.0 (4 CH), 125.6 (2 CH), 120.7 (d, 4 CH, $J_{P(O)OCC}$ = 4.6 Hz), 64.5 (d, 2 CH_2, $J_{P(BH_3)OC}$ = 3.5 Hz), 30.9−28.7 (dd, CH_2, $J_{P(O)C}$ = 139.3 Hz, $J_{P(BH_3)C}$ = 42.6 Hz), 16.6 (d, 2 CH_3, $J_{P(BH_3)OCC}$ = 5.8 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 138.5 (m) and 13.1 (s); HRMS (EI^+) calcd for $C_{17}H_{29}BNO_5P_2$ ($[M + NH_4]^+$) 400.1614, found 400.1616.

(*Z*/*E*)-Diethyl hex-1-enylphosphoniteborane (*Z*/*E*: 50/50) (74): Compound **74** has been synthesized from the mixed 1,1-bisphosphorus **15** following the procedure for the preparation of olefins. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.73 (m, 1H, *E*-isomer), 6.53−6.40 (m, 1H, *Z*-isomer), 5.81 (m, 1H *E*-isomer), 5.62 (m, 1H, *Z*-isomer), 4.15−3.97 (m, 4H), 2.44 (m, 2H *Z*-isomer, J = 7 Hz), 2.26 (q, 2H *E*-isomer, J = 7 Hz), 1.46 (m, 4H), 1.33 (t, 6H, J = 7 Hz), 0.93 (t, 3H, J = 6.7 Hz), 1.00−0.00 (m, 3H); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 130.8 (m, *E*- and *Z*-isomers).

General Procedure for Deprotection of Phosphonite−Borane Complexes (Scheme 6). An oven-dried 25-mL round-bottomed flask equipped with a condenser is charged with a 0.1 M solution of phosphite−borane in EtOH. The solution is cooled to −78 °C and degassed for 5 min under high vacuum. The flask is filled with nitrogen and warmed to rt for 10 min. This degas/thaw procedure is repeated three times and the solution is then refluxed until completion of the reaction. Concentration under vacuum followed by chromatography on silica gel afford the corresponding deprotected product.

Dimethyl 1-(ethoxyphosphinyl)methylphosphonate (75): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33 (d, 1H, J = 581.6 Hz), 4.28−4.12 (m, 4H), 3.82 (d, 6H, J = 11.4 Hz), 2.48 (m, 1H), 1.40 (t, 6H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.3 (d, CH_2, $J_{P(O)C}$ = 6.3 Hz), 53.3 and 53.4 (d, 2 CH_3, $J_{P(O)OC}$ = 6.9 Hz), 27.7 (dd, CH_2, $J_{P(O)C}$ = 133.6 Hz, $J_{P(O)C}$ = 133.6 Hz), 16.4 (d, CH_3, $J_{P(BH_3)OCC}$ = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 26.5 (d, J_{PP} = 6.1 Hz), 22.4 (d, d, J_{PP} = 6.1 Hz); HRMS (EI^+) calcd for $C_3H_9O_5P_2$ ($[M - Et]^+$) 186.9925, found 186.9924.

(*E*)-Ethyl 1-phenylbut-1-en-2-ylphosphinate (76): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23 (d, 1H, J = 547 Hz), 7.50−7.28 (m, 6H), 4.23−4.10 (m, 2H), 2.58 (m, 2H), 1.41 (t, 3H, J = 6.7 Hz), 1.24 (t, 3H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 142.4 (d, CH, J_{PCC} = 15.8 Hz), 135.2 (d, C, J_{PCC} = 22.5 Hz), 134.6 (d, C, J_{PC} = 124.4 Hz), 129.4 (2 CH), 129.0 (CH), 128.8 (2 CH), 62.3 (d, 2 CH_2, J_{POC} = 6.6 Hz), 20.6 (d, CH_2, J_{PCC} = 11.5 Hz), 16.6 (d, 2 CH_3, J_{POCC} = 6.3 Hz), 13.8 (CH_3); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 32.7 (s); HRMS (EI^+) calcd for $C_{12}H_{17}O_2P$ ($[M]^+$) 224.0966, found 224.0965.

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Supporting Information Available: Spectral data and additional experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.