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Borane complexes of the H_3PO_2 P(III) tautomer: useful phosphinate equivalents

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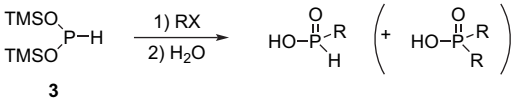
ABSTRACT

The preparation and reactivity of novel $(R^1O)(R^2O)P(BH_3)H$ [R^1, R^2=Et, TIPS] synthons is investigated. The direct alkylation of these compounds with lithium hexamethyldisilazide (LiHMDS) and various electrophiles, provided new series of phosphonite-borane complexes, which can be converted into *H*-phosphinates and boranophosphonates.

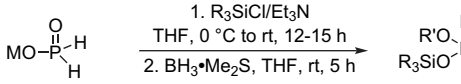
1. Introduction

Synthons, which are equivalent to alkyl phosphinates $ROP(O)H_2$ have found some practical applications in the preparation of *H*-phosphinic acid derivatives. Most notably, the so-called 'Ciba–Geigy reagents' $RC(OEt)_2P(O)(OEt)H$ (R=Me, H; **1** and **2**)[1] have been used extensively to prepare *H*-phosphinic acid and esters under a variety of conditions, and especially base-promoted alkylation (Scheme 1).[2]



3 (1)

Similarly, bis(trimethylsiloxy)phosphine **3** ($(TMSO)_2PH$, also called BTSP)[3] has been employed for a similar purpose, although some problems exist with this approach: the reagent is pyrophoric and it typically requires a large excess of BTSP **3** to favor mono-substitution (Eq. 1).[4] Our group has been involved in the development of methodologies based on hypophosphorous acid (H_3PO_2) and its derivatives (alkyl phosphinates and hypophosphite salts).[5] When successful, these reagents are more desirable than the above alternatives since the desired *H*-phosphinate products are delivered directly in a single step and under simple conditions. We also reported the alkylation of alkyl phosphinates ($ROP(O)H_2$) using butyl lithium, but the approach is limited to the more reactive electrophiles.[6] The alkylation of the Ciba–Geigy reagents using LiHMDS under stoichiometric conditions was also described.[2] However, the Ciba–Geigy synthons are always deprotected to the desired products under acidic conditions.[1] In connection with studies aiming at the preparation of GABA analogs, and other potentially bioactive compounds, we needed a different kind of approach, and we decided to investigate the borane complexes derived from the P(III) form of H_3PO_2. Although secondary phosphine-boranes are well known,[7] the reactivity of dialkoxyphosphine-boranes toward P–C bond formation has never been reported. In fact, there is apparently only one previous example of such a dialkoxyphosphine-borane complex in the literature: $(MeO)_2P(BH_3)H$ (Scheme 2).[8] Knochel described the related reagent $(Et_2N)_2P(BH_3)Li$ as a phosphorus nucleophile.[9] Centofanti described the synthesis of pyrophoric $(MeO)_2P(BH_3)H$, but no further investigation was conducted.[8] We have repeated Centofanti's work and similarly found that the compound is pyrophoric and difficult to purify resulting in a low yield of material, confirming his report. Thus, $(MeO)_2P(BH_3)H$ is ill-suited for use as a practical reagent.



M = Et, $PhNH_3$
R_3 = Ph_2Me, Et_3, *t*-$BuMe_2$, *t*-$BuPh_2$, *i*-Pr_3
R' = Et, *i*-Pr_3Si

4 R = *i*-Pr, R' = *i*-Pr_3Si
5 R = *i*-Pr, R' = Et

(2)

Herein, we report the syntheses and reactivity of novel $(R^1O)(R^2O)P(BH_3)H$ [R^1, R^2=Et, *i*-Pr_3Si (TIPS)][3] reagents as alkyl phosphinate equivalents (Eq. 2). The synthesis of the complexes is straightforward, and reactivities similar to that of the related and well-known dialkyl-*H*-phosphonates $(RO)_2P(O)H$ are observed. One advantage of the method is that the complexes can be employed for the syntheses of both *H*-phosphinate, and of unsymmetrically disubstituted phosphinic derivatives, as well as boranophosphonates. The latter approach is particularly interesting because, at least conceptually, the initial silylation step constitutes both a protection step and formation of a latent phosphonite poised for a sila-Arbuzov[10] reaction upon decomplexation. The Ciba–Geigy reagents

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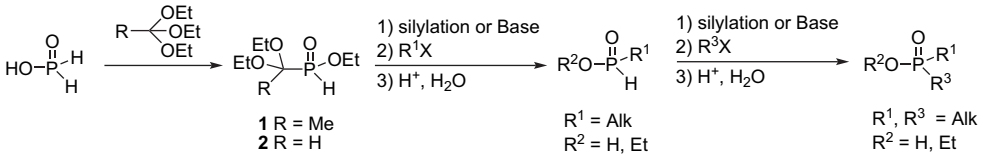
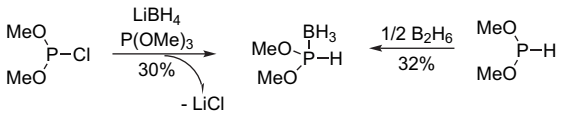


Scheme 1. 'Ciba–Geigy reagents' in the synthesis of phosphinic acid derivatives.



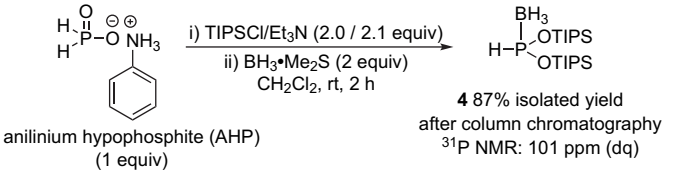
Scheme 2. Centofanti's synthesis of $(MeO)_2P(BH_3)H$.

have also been derivatized using sila-Arbuzov reaction, but this must be performed separately from the initial protection as an acetal. Additionally, in the case of $(TIPSO)_2P(BH_3)H$ **4**, a new synthesis of boranophosphonates,[11] which are phosphonic acid analogs of potential biological value, is readily achieved (vide infra).

Even more surprisingly, we found that the diethoxyphosphine-borane complex is completely stable to air and chromatography on silica gel, unlike what was reported for the dimethoxyphosphine-borane complex.[8] After functionalization through alkylation and related methods, the phosphonite-borane complexes can be directly converted into unsymmetrical disubstituted phosphinic acid derivatives via a one-pot decomplexation/Arbuzov reaction.

2. Results and discussion

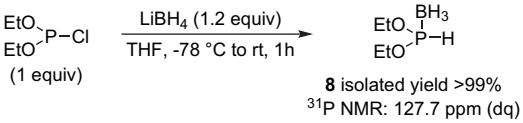
2.1. Synthesis



(3)

Initially, the formation of borane complexes of BTSP **3** and related species was investigated. The borane complex of BTSP is too easily hydrolyzed to be useful. Therefore, a study of more robust silicon groups was undertaken. It was found that the triisopropylsilyl group provided excellent stability of the complex, so much so, in fact, that the complex $(TIPSO)_2P(BH_3)H$ **4** can be isolated uneventfully by chromatography over silica gel, and it is completely stable to air and moisture (Eq. 3). Encouraged by this result, the silylation/borane complex formation with various chlorosilanes was also investigated on ethyl phosphinate $EtOP(O)H_2$ (Table 1). Ethyl phosphinate was prepared and used in situ, as we previously described.[12]

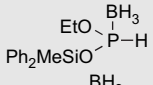
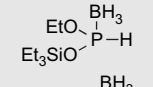
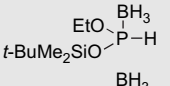
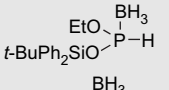
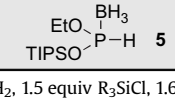
Although some silicon protecting groups provided reasonably stable products **6** and **7** (Table 1, entries 3 and 4), once again the best result was obtained with TIPS[3] both in terms of stability and yield (entry 5, compound **5**). The resulting $(EtO)(TIPSO)P(BH_3)H$ **5** was therefore selected for subsequent reactivity studies.



(4)

Next, we investigated the preparation of diethoxyphosphine-borane complex $(EtO)_2P(BH_3)H$ **8**, from the commercially available chlorodiethoxyphosphine. Reduction with lithium borohydride provided **8** directly and in excellent isolated yield after chromatographic purification (Eq. 4). The yield and stability of **8** are quite remarkable considering the reported low yield and pyrophoric nature of the methyl analog (Scheme 2).[8]

Table 1
Preparation of (ethoxy)(trialkylsiloxy)phosphine-borane complexes[a]

Entry	R_3SiCl	Product	^{31}P NMR chemical shift (δ ppm)	Isolated yield %[b] (NMR yield %[c])
1	$Ph_2MeSiCl$		117.7	(62)
2	Et_3SiCl		114.2	(69)
3	*t*-$BuMe_2SiCl$	 **6**	114.7	79 (81)
4	*t*-$BuPh_2SiCl$	 **7**	114.5	91 (94)
5	TIPSCl	 **5**	116.8	100 (100)

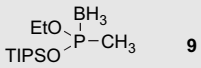
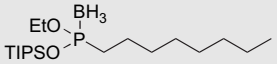
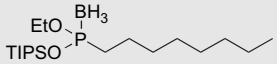
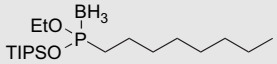
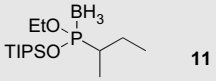
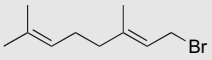
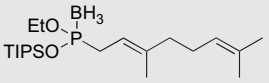
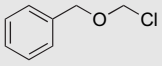
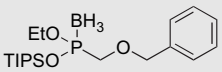
[a] (a) 1 equiv $EtOP(O)H_2$, 1.5 equiv R_3SiCl, 1.6 equiv Et_3N, THF, 0 °C to rt, 15 h; (b) 2 equiv $BH_3 \cdot Me_2S$, THF, rt, 5 h.
[b] Isolated yield of pure compounds after chromatography on silica gel.
[c] NMR yields are determined by integrating all the resonances in the ^{31}P NMR spectra of the reaction mixtures.

2.2. Reactivity of borane complexes 4, 5, and 8: alkylation

Our group recently reported a general alkylation protocol for *H*-phosphinate esters using LiHMDS[3] as a base.[2] The main features are the equimolar ratios of the base, phosphorus nucleophile, and carbon electrophile, and the broad scope of these conditions. We therefore selected LiHMDS as the base of choice in the alkylation studies with borane complexes. As we described for the alkylation of *H*-phosphinates, moderate deoxygenation affords better yields. Alkylation generally took place smoothly under these conditions. Table 2 summarizes the results obtained with complex $(EtO)(TIPSO)P(BH_3)H$ **5**. The alkylation products were isolated in excellent yields. Various alkyl halides and a tosylate reacted uneventfully. Even a secondary iodide (entry 5, compound **11**) could be employed. These results are at least comparable to those we reported with the Ciba–Geigy reagents.[1,2] However, 2-chlorooctane did not react satisfactorily.

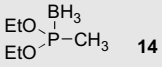
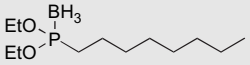
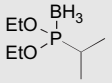
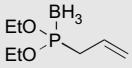
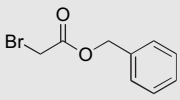
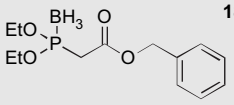
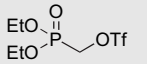
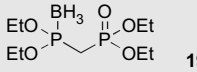
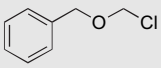
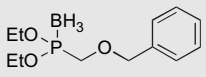
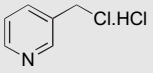
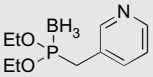
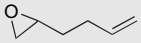
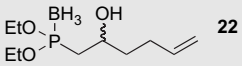
Diethoxyphosphine-borane complex, $(EtO)_2P(BH_3)H$ **8**, was similarly alkylated in moderate to good isolated yields (Table 3). Again, a secondary iodide gave a moderate yield of alkylated product **16** (entry 3). Unfortunately, the reaction with a bromoacetate (entry 5) did not give a good yield of product **18**, even when excess base (>2 equiv) was employed. Bisseret prepared the phosphonate-phosphonite borane complex **19** in entry 6 by a different (and admittedly simpler) route, and he demonstrated its use for the preparation of various pyrophosphate analogs.[13] Complex **8** also reacted with an epoxide, and in this case, the use of a Lewis acid improved the yield significantly (entry 9b vs entry 9a).

Table 2
Scope of the base-promoted alkylation of (TIPSO)(EtO)P(BH$_3$)H **5**[a]

Entry	Electrophile	Temperature	Reaction time	Product	Isolated yield, %[b] (NMR yield, %)[c]
1	CH_3I	−78 °C to rt	4 h	 **9**	100 (100)
2	OctI	−78 °C to rt	2 h	 **10**	100 (100)
3	OctBr	−78 °C to rt	5 h	 **10**	100 (100)
4	OctOTs	−78 °C to reflux	12 h	 **10**	90 (94)
5		−78 °C to rt	4 h	 **11**	85 (100)
6		−78 °C to rt	5 h	 **12**	80 (94)
7		−78 °C to rt	12 h	 **13**	100 (92)

[a] Deoxygenation was conducted by placing a THF solution of the (EtO)(TIPSO)P(BH$_3$)H under vacuum at −78 °C for 5 min, then adding N_2.
[b] Isolated yield of pure compounds after chromatography on silica gel.
[c] NMR yields are determined by integrating all the resonances in the ^{31}P NMR spectra of the reaction mixtures.

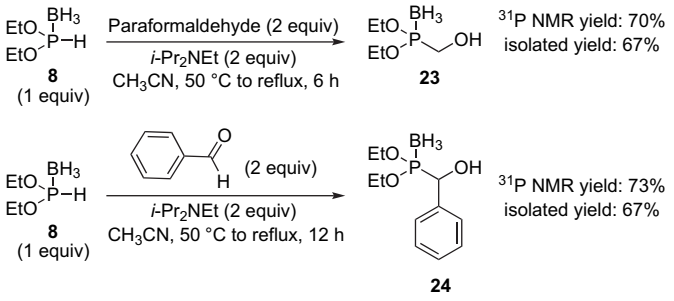
Table 3
Scope of the base-promoted alkylation of (EtO)$_2$P(BH$_3$)H **8**

Entry	Electrophile	Reaction Time	Product	^{31}P NMR chemical shift (ppm)	^{11}B NMR chemical shift (ppm)	Isolated yield, %[a]
1	CH_3I	2 h	 **14**	149.7	−41.8	80
2a 2b	OctI OctBr	4 h 4 h	 **15**	148.9	−42.2	74 77
3		4 h	 **16**	154.8	−45.0	49
4		12 h	 **17**	144.0	−42.9	69
5		12 h	 **18**	139.1	−42.2	25
6		12 h	 **19**	138.8 and 19.9	−41.4	52
7		20 min	 **20**	138.0	−43.0	89
8[b]		12 h	 **21**	143.0	−43.0	69
9a 9b	 $+BF_3\cdot Et_2O$	12 h 12 h	 **22**	146.8	−42.2	36 50

[a] Isolated yield of pure compounds after chromatography on silica gel.
[b] LiHMDS (2 equiv) was used.

2.3. Addition to carbonyl compounds

Borane complex **8** could also be added to carbonyl compounds using *i*-Pr$_2$NEt as the base (Scheme 3). While the direct addition of ROP(O)H$_2$ to carbonyl compounds is superior,[12] the possibility to examine chiral dialkoxyphosphine-borane complexes is intriguing in this context. On the other hand, complex **5** did not add to carbonyl compounds under identical conditions.



Scheme 3. Reaction of complex **8** with carbonyl compounds.

2.4. Radical reactions

The reactivity of borane complexes **5** and **8** in free radical reactions was also briefly investigated. The results are shown in Table 4. Interestingly, the thermal AIBN-initiated reaction was completely unsuccessful, whereas our Et_3B/air protocol for generating P-centered radicals[14] gave good yields of isolated products. Once again, the direct radical reaction of $ROP(O)H_2$ we reported previously is superior to the present reaction.[12,14] However, the possibility to extend this chemistry to chiral borane complexes could provide an approach to asymmetric P–C bond-forming reactions. It is also important to note that the radical reactions of the Ciba–Geigy reagents **1** and **2** are either inefficient or require specialized initiators.[15] Thus, the new synthons described herein provide added flexibility in terms of the range of available reactions.

2.5. Decomplexation: conversion into *H*-phosphinates and disubstituted phosphinates

For the strategy to be useful, the ability to deprotect the borane complexes must be available. Thus, we investigated the conversion of the phosphonite complexes to the corresponding *H*-phosphinates. As with the related phosphine-borane complexes,[16] treatment with $HBF_4 \cdot Et_2O$ leads to the *H*-phosphinate ester in excellent yields. The P–O ester bond is not cleaved in this process. With the Ciba–Geigy reagents, only **1** can be deprotected ($TMSCl/CHCl_3$) without cleavage of the phosphorus ester functionality.[1] Compounds derived from **8** can also be decomplexed through treatment with an amine base. Scheme 4 summarizes some of these reactions. We also reported previously a tandem decomplexation/Arbuzov reaction leading to a disubstituted phosphinate ester in one-pot (Scheme 4).[17]

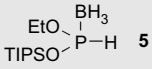
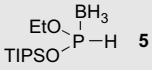
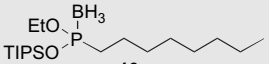
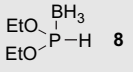
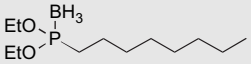
2.6. Boranophosphonate synthesis

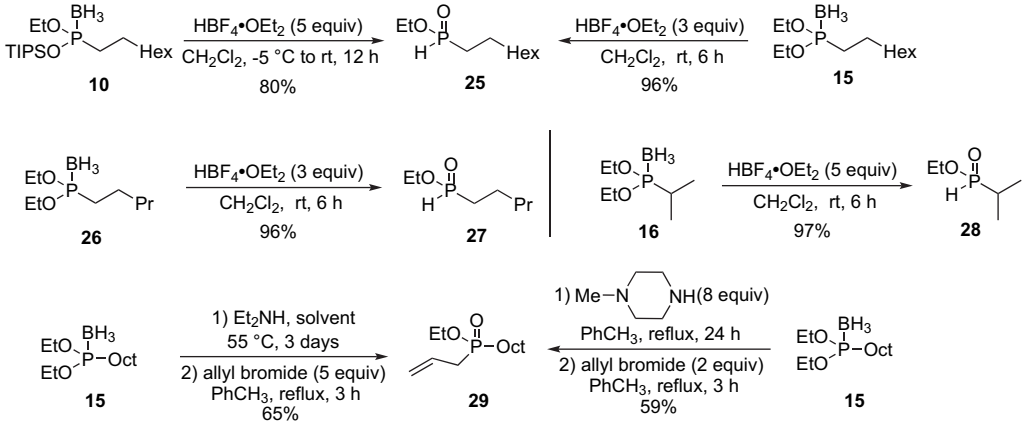
An important application of $(TIPSO)_2P(BH_3)H$ **4** is for the synthesis of boranophosphonates. While the chemistry of boranophosphonates is still limited currently, this class of compounds could constitute biologically active analogs of phosphonates or prodrugs of *H*-phosphinates. Scheme 5 shows an application of our reagent in the preparation of a boranophosphonate.[11] Alternatively, boranophosphonates can be easily prepared from the corresponding *H*-phosphinic acid, via silylation/borane complex formation/hydrolysis. Once again, although this approach is more straightforward than the one which uses **4**, it obviously implies the availability of the *H*-phosphinic acid precursor. Furthermore, the use of **4** provides added flexibility in terms of the variety of compounds, which could be synthesized from the same intermediate (i.e., more divergent).

2.7. Temporary protection of *H*-phosphinates with TIPSCl and BH_3

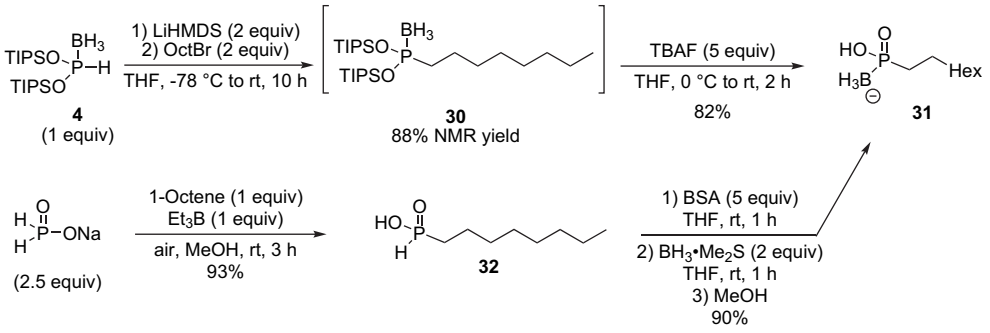
Finally, a similar silylation strategy with TIPSCl can be employed for the temporary protection of *H*-phosphinate esters. This will be

Table 4
Radical reactions

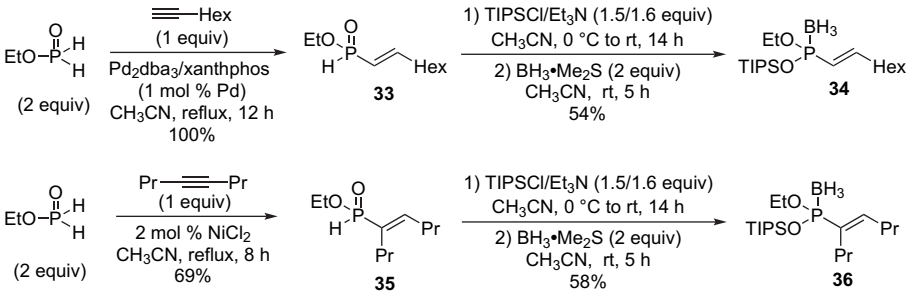
Entry	Substrate	Alkene	Reaction conditions	Product	Isolated yield %
1	 **5**	1-Octene	AIBN (3×0.2 equiv), CH_3CN, under N_2, reflux, 12 h	No product	—
2	 **5**	1-Octene	Et_3B (1 equiv), MeOH/dioxane (5:1), air, rt, 5 h	 **10**	67
3	 **8**	1-Octene	Et_3B (1 equiv), MeOH/dioxane (5:1), air, rt, 4 h	 **15**	66



Scheme 4. Decomplexation of the phosphonite-borane complexes.



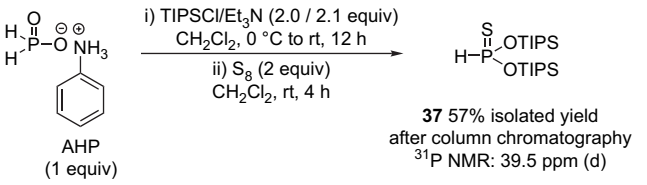
Scheme 5. Boranophosphonate synthesis.



Scheme 6. Protection of *H*-phosphinates as phosphonite-borane complexes.

investigated in the near future as a way to functionalize the carbon chain without affecting the P–H bond in *H*-phosphinates. Examples of protection are shown in Scheme 6. Many reactions are not compatible with the presence of the phosphinylidene group P(O)H, thus temporary protection as the TIPS/borane-phosphonite complex could allow the elaboration of the carbon chain. In the examples shown, various reactions, such as asymmetric dihydroxylation, epoxidation, hydroboration, or hydrogenation can be conceived. This approach will be investigated in future work.

2.8. Preparation of $(TIPSO)_2P(S)H$



(5)

Based on the unique stabilities observed with the TIPS-borane complexes, the preparation of the sulfur equivalent to complex **4** was investigated (Eq. 5). As expected, compound **37** was stable even to chromatography on silica gel. Although Voronkov described the spectral properties of $(TMSO)_2P(S)H$, no synthesis, yield, nor discussion of its chemical properties were included.[18]

3. Conclusions

The straightforward preparation of three novel phosphorus synthons displaying remarkable stabilities was described. When available, the direct reaction of alkyl phosphinates $(RO)P(O)H_2$ is always superior to this protecting group strategy, as we have demonstrated in the past. However, limitations still exist for the direct synthesis of *H*-phosphinate esters, especially through alkylation with alkyl halides. While the 'Ciba–Geigy' reagents have solved a number of problems, these always require acidic conditions to unmask a P–H bond, and the preparation of the reagents is not shorter. The advantages of the borane complexes described herein are: (1) possible unmasking under either basic or acidic conditions, (2) the possibility for tandem decomplexation/Arbuzov functionalization to disubstituted phosphinates, and (3) the preparation of boranophosphonates. Therefore, the novel borane complexes, which are derived from the $HP(OH)_2$ tautomer, provide added flexibility for the preparation of organophosphorus compounds. Preliminary reactivity studies indicate a broad range of applications. The trapping of *H*-phosphinates as P(III) borane complexes is also potentially useful to modify the carbon chain under conditions, which might otherwise not be compatible with the P(O)–H functionality, and this strategy will be explored further. The present strategy should be useful for the preparation of functionalized phosphinates and applications are currently underway in our laboratory. Synthons **4**, **5**, and **8** represent additional tools for the synthesis of various organophosphorus compounds. Extension to chiral versions of **5** and **8** will be investigated. In addition, the protection of *H*-phosphinates as stable TIPS/borane-phosphonite complexes opens up the possibility for functionalizing the carbon chain of *H*-phosphinate precursors.

While much work remains to be explored, the chemistry described herein provides a platform for numerous extensions and applications. For example, the direct conversion of the phosphonite-borane complexes into phosphonothioates is also a possibility, which needs to be considered.

4. Experimental section

4.1. General

General experimental procedures and the preparation of anilinium hypophosphite (AHP)[19] and alkyl phosphinates[12] have been described elsewhere. The NMR yields are determined by integration of all the resonances in the ^{31}P NMR spectra. The yields determined by ^{31}P NMR are accurate within ~10% of the value

indicated and are reproducible. Some experiments with internal standards and gas chromatography also confirmed the validity of the method.[20] In many cases, the isolated yields are very close to the NMR yields. Mass spectrometry was provided by the Mass Spectrometry Facility of the University of South Carolina.

4.2. Experimental procedures

*4.2.1. Bis(triisopropylsilyloxy)phosphine-borane **4** (Eq. 3)*

Triisopropylchlorosilane (4.27 mL, 20 mmol) was added into a flame-dried two-neck round bottom flask and cooled to 0 °C, under N_2. Then, Et_3N (2.93 mL, 21 mmol) was added dropwise and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate flame-dried three-neck round bottom flask, a solution of anilinium hypophosphite (1.54 g, 10 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C, under N_2. The TIPSCl/Et_3N mixture was slowly added to the hypophosphite solution via syringe and the temperature maintained at 0 °C for 10–15 min, at which time the reaction was allowed to warm up to room temperature and stirred for 12 h under N_2. The reaction mixture was treated with $BH_3\cdot Me_2S$ (1.0 M in CH_2Cl_2, 20 mL, 20 mmol) by dropwise addition at room temperature. After 2 h, the reaction mixture was concentrated under reduced pressure and the residue partitioned between DI H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×150 mL) and the combined organic phases washed with brine (1×20 mL), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (hexanes) afforded complex **4** as a pale yellowish syrup (3.46 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 (d, J=417.2 Hz, 1H), 1.28–1.12 (m, 6H), 1.10 (d, J=6.4 Hz, 36H), 0.96–0.05 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 17.7, 12.6; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 100.9 (dq, J_{PB}=90 Hz, J_{PH}=422 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −36.8 (dq, J_{BP}=88 Hz, J_{BH}=92 Hz); HRMS (EI) calcd for $C_{18}H_{46}BO_2PSi_2$ $(M+NH_4)^+$: 410.3211, found: 410.3196.

*4.2.2. Ethoxy(tert-butyldimethylsilyloxy)phosphine-borane **6** (Table 1, entry 3)*

Yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.85 (d, J=432.1 Hz, 1H), 3.96–3.70 (m, 2H), 1.09 (t, J=7.0 Hz, 3H), 0.68 (s, 9H), 0.01 (s, 6H), 0.59–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 69.0 (d, J_{POC}= 9 Hz), 29.0, 21.8 (d, J_{POSiC}=2 Hz), 20.1 (d, J_{POCC}=6 Hz), 0.03 (d, J_{POSiC}=4 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 115.7 (dq, J_{PB}=81 Hz, J_{PH}=430 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −39.3 (dq, J_{BP}=76 Hz, J_{BH}=91 Hz); HRMS (EI) calcd for $C_8H_{24}BO_2PSi$ $(M+NH_4)^+$: 240.1720, found: 240.1722.

*4.2.3. Ethoxy(tert-butyldiphenylsilyloxy)phosphine-borane **7** (Table 1, entry 4)*

Yield: 91%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17 (d, J=433.2 Hz, 1H), 7.70–7.63 (m, 4H), 7.52–7.25 (m, 6H), 4.11–3.79 (m, 2H), 1.19 (t, J=6.9 Hz, 3H), 1.13 (s, 9H), 0.90–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 135.5 (d, J_{POSiC}=3 Hz), 131.6 (d, $J_{POSiCCCC}$=3 Hz), 130.9 (d, J_{POSiCC}=1 Hz), 128.3 (d, $J_{POSiCCC}$=3 Hz), 65.3 (d, J_{POC}=7 Hz), 26.7, 19.8, 16.5 (d, J_{POCC}=6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 114.7 (dq, J_{PB}=89 Hz, J_{PH}=428 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −40.2 (dq, J_{BP}=89 Hz, J_{BH}=89 Hz); HRMS (EI) calcd for $C_{18}H_{28}BO_2PSi$ $(M+NH_4-H_2)$: 362.1877, found: 362.1869.

*4.2.4. Ethoxy(triisopropylsilyloxy)phosphine-borane **5** (Table 1, entry 5)*

Triisopropylchlorosilane (12.11 mL, 56.7 mmol) was added into a flame-dried two-neck round bottom flask and cooled to 0 °C, under N_2. Then, Et_3N (8.43 mL, 60.5 mmol) was added dropwise and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate flame-dried three-neck round bottom flask, a solution of ethyl hypophosphite (0.5 M in CH_3CN, 75.7 mL, 37.8 mmol) was cooled to 0 °C, under N_2. The mixture TIPSCl/Et_3N was slowly added to the hypophosphite solution via syringe and the reaction mixture maintained at 0 °C for 10–15 min, at which time the reaction was allowed to warm up to room temperature, then stirred for 12 h under N_2. The reaction mixture was treated with $BH_3\cdot Me_2S$ (2.0 M in THF, 37.8 mL, 75.6 mmol) by dropwise addition at room temperature. After 1 h, the reaction mixture was concentrated under reduced pressure and the residue partitioned between DI H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×250 mL) and the combined organic phases washed with brine (1×50 mL), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (petroleum ether) afforded **5** as a colorless oil (9.98 g, 100%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20 (d, J=429.9 Hz, 1H), 4.26–3.98 (m, 2H), 1.34 (t, J=7.2 Hz, 3H), 1.22–1.12 (m, 3H), 1.08 (d, J=6.9 Hz, 18H), 0.90–0.05 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 65.1 (d, J_{POC}=8 Hz), 17.6, 16.5 (d, J_{POCC}=6 Hz), 12.5; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 116.7 (dq, J_{PB}=78 Hz, J_{PH}=425 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −39.2 (dq, J_{BP}=79 Hz, J_{BH}=92 Hz); HRMS (FAB) calcd for $C_{11}H_{30}BO_2PSi$ $(M+NH_4)^+$: 282.2190, found: 282.2196.

*4.2.5. Diethoxyphosphine-borane **8** (Eq. 4)*

In a flame-dried three-neck round-bottomed flask was placed diethyl chlorophosphite (10 g, 63.9 mmol) in THF (100 mL) under N_2 and this was cooled to −78 °C. $LiBH_4$ (1.67 g, 76.7 mmol) was then added (quickly in air) at −78 °C and the reaction mixture was stirred at this temperature for 10 min, then allowed to warm up to room temperature and stirred for 1 h. The reaction mixture was poured directly into a beaker containing a mixture of concentrated HCl (12 N, 28 mL) and ice (200 g). The resulting mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated to afford the crude compound. Purification over silica gel (hexanes/EtOAc, 80:20, v/v) afforded **8** (8.65 g, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.99 (d, J_{PH}= 444.1 Hz, 1H), 4.25–4.01 (m, 4H), 1.37 (dt, J=7.0 Hz, 6H), 1.18–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 65.1 (d, J_{POC}=7 Hz), 16.4 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 128.3 (dq, J_{PB}=74 Hz, J_{PH}=450 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −41.0 (dq, J_{BP}=75 Hz, J_{BH}=97 Hz); HRMS (EI) calcd for $C_4H_{14}BO_2P$ $(M+NH_4)^+$: 154.1168, found: 154.1165.

4.3. Typical alkylation procedure (Tables 2 and 3)

Neat phosphine-borane (EtO)(TIPSO)P(BH_3)H **5** or $(EtO)_2$-P(BH_3)H **8** (1 equiv, 1.89 mmol and 3.68 mmol, respectively) was placed under vacuum in a flame-dried two-neck flask, during 5 min before use. Anhydrous THF (6 mL or 10 mL, respectively) was then added under N_2. The flask was then placed at −78 °C and deoxygenated under high vacuum for 5 min. The reaction flask was back-filled with N_2 and LiHMDS (1.0 M in THF, 1 equiv) was added at −78 °C. After 15 min, the electrophile (1 equiv) was added under N_2 as a neat liquid or as a THF solution (0.5 M) for solids. After the addition of the electrophile, the reaction mixture was slowly allowed to reach room temperature then stirring was continued (see Tables 2 and 3 for reaction times). The reaction mixture was quenched with a saturated solution of NH_4Cl/brine and extracted with EtOAc (3×). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The resulting crude mixture was purified by column chromatography over silica gel.

*4.3.1. Ethoxy(triisopropylsilyloxy)methylphosphine-borane **9** (Table 2, entry 1)*

Yield: 100%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17–3.97 (m, 2H), 1.51 (d, J=8.2 Hz, 3H), 1.31 (t, J=7.0 Hz, 3H), 1.18–1.11 (m, 3H), 1.10 (d, J=5.6 Hz, 18H), 0.95–0.02 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz)

δ 62.7 (d, J_{POC}=3 Hz), 18.8 (d, J_{PC}=53 Hz), 17.6, 16.6 (d, J_{POCC}=6 Hz), 12.6; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 132.4 (q, J_{PB}=93 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −39.2 (dq, J_{BP}=95 Hz, J_{BH}=98 Hz); HRMS (EI) calcd for $C_{12}H_{32}BO_2PSi$ $(M+NH_4)^+$: 296.2346, found: 296.2336.

4.3.2. Ethoxy(triisopropylsilyloxy)octylphosphine-borane ***10*** *(Table 2, entries 2–4)*

Yields: 90–100%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13–4.00 (m, 2H), 1.73–1.60 (m, 2H), 1.62–1.46 (m, 2H), 1.37–1.23 (m, 13H), 1.17–1.02 (m, 21H), 0.87 (t, J=7.0 Hz, 3H), 0.75–0.05 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.1 (d, J_{POC}=3 Hz), 33.1 (d, J_{PC}=53 Hz), 32.0, 31.0 (d, J_{PCC}=14 Hz), 29.3 (d, J_{PCCC}=3 Hz), 22.8, 22.0, 17.7, 16.7 (d, J_{POCC}=6 Hz), 14.2, 12.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 135.6 (q, J_{PB}=83 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −40.6 (dq, J_{BP}=83 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{19}H_{46}BO_2PSi$ $(M+NH_4)^+$: 394.4761, found: 394.3442.

4.3.3. Ethoxy(triisopropylsilyloxy)(1-methylpropyl)phosphine-borane ***11*** *(Table 2, entry 5)*

Yield: 85%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.21–4.00 (m, 2H), 1.90–1.74 (m, 2H), 1.29 (t, J=6.9 Hz, 3H), 1.20–1.13 (m, 3H), 1.12–1.03 (m, 26H), 1.02–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.6 (d, J_{POC}=3 Hz), 33.4 (d, J_{PC}=56 Hz), 17.7, 16.7 (d, J_{POCC}=6 Hz), 15.7, 15.4, 12.9; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 139.9 (q, J_{PB}=87 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.3 (dq, J_{BP}=88 Hz, J_{BH}=89 Hz); MS *m/e* 306 $(M-BH_3)^+$, 277 $(M-Pr)^+$.

4.3.4. Ethoxy(triisopropylsilyloxy)geranylphosphine-borane ***12*** *(Table 2, entry 6)*

Yield: 80%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.30–5.12 (m, 1H), 5.12–5.05 (m, 1H), 4.18–3.95 (m, 2H), 2.55 (dd, J=11.2, 7.8 Hz, 2H), 2.14–2.02 (m, 4H), 1.78–1.61 (m, 9H), 1.28 (t, J=6.9 Hz, 3H), 1.18–1.04 (m, 21H), 0.90–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 140.3 (d, J_{PCCC}=12 Hz), 131.7, 124.2, 112.9 (d, J_{PCC}=5 Hz), 63.4, 40.1, 33.6 (d, J_{PC}=52 Hz), 26.6, 25.9, 17.8, 16.7 (d, J_{POCC}=7 Hz), 12.7; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 135.6 (q, J_{PB}=87 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −40.0 (dq, J_{BP}=82 Hz, J_{BH}=89 Hz); HRMS (EI) calcd for $C_{21}H_{46}BO_2PSi$ $(M+NH_4)^+$: 418.3442, found: 418.3432.

4.3.5. Ethoxy(triisopropylsilyloxy)benzyloxymethylphosphine-borane ***13*** *(Table 2, entry 7)*

Yield: 100%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.25 (m, 5H), 4.64 (s, 2H), 4.22–4.08 (m, 2H), 3.72 (s, 2H), 1.31 (t, J=7.0 Hz, 3H), 1.23–1.10 (m, 3H), 1.10–1.02 (m, 18H), 0.95–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.4, 128.6, 128.2, 128.1, 75.4 (d, J_{PCOC}=9 Hz), 69.8 (d, J_{PC}=66 Hz), 63.8 (d, J_{POC}=4 Hz), 17.7, 16.8 (d, J_{POCC}=6 Hz), 12.7; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 124.8 (q, J_{PB}=78 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −45.0 (dq, J_{BP}=74 Hz, J_{BH}=90 Hz); HRMS (EI) calcd for $C_{19}H_{38}BO_3PSi$ $(M+NH_4)^+$: 402.2765, found: 402.2769.

4.3.6. Diethoxy methylphosphine-borane ***14*** *(Table 3, entry 1)*

Yield: 80%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13–3.96 (m, 4H), 1.50 (d, J=8.5 Hz, 3H), 1.32 (t, J=7.0 Hz, 6H), 0.90–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.1 (d, J_{POC}=5 Hz), 16.71 (d, J_{POCC}=6 Hz), 15.7 (d, J_{PC}=56 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 149.7 (q, J_{PB}=83 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −41.8 (dq, J_{BP}=83 Hz, J_{BH}=91 Hz); HRMS (EI) calcd for $C_5H_{16}BO_2P$ $(M+NH_4)^+$: 168.1325, found: 168.1321.

4.3.7. Diethoxy octylphosphine-borane ***15*** *(Table 3, entry 2)*

Yield: 74–77%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17–3.95 (m, 4H), 1.79–1.68 (m, 2H), 1.62–1.48 (m, 2H), 1.42–1.24 (m, 16H), 0.88 (t, J=6.4 Hz, 3H), 0.80–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.1 (d, J_{POC}=5 Hz), 32.0, 30.9 (d, J_{PCC}=14 Hz), 29.9 (d, J_{PC}=56 Hz), 29.2, 22.8, 21.7, 16.7 (d, J_{POCC}=6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 148.9 (q, J_{PB}=86 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.2 (dq, J_{BP}=83 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{12}H_{30}BO_2P$ $(M+NH_4)^+$: 266.2420, found: 266.2418.

4.3.8. Diethoxy-1-methylethylphosphine-borane ***16*** *(Table 3, entry 3)*

Yield: 48%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.15–3.99 (m, 4H), 1.96–1.86 (m, 1H), 1.39 (t, J=7.0 Hz, 6H), 1.14 (dd, J=16.7, 7.0 Hz, 6H), 1.00–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.5 (d, J_{POC}=5 Hz), 28.9 (t, J_{PC}=59 Hz), 16.8 (d, J_{POCC}=5 Hz), 15.4; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 154.8 (q, J_{PB}=75 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −45.0 (dq, J_{BP}=74 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_7H_{20}BO_2P$ $(M+NH_4)^+$: 196.1638, found: 196.1629.

4.3.9. Diethoxy allylphosphine-borane ***17*** *(Table 3, entry 4)*

Yield: 69%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.83–5.72 (m, 1H), 5.24–5.23 (m, 1H), 5.21–5.17 (m, 1H), 4.18–4.11 (m, 4H), 2.62 (dd, J=11.7, 7.6 Hz, 2H), 1.31 (dt, J=7.0, 2.4 Hz, 6H), 1.05–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 127.3 (d, J_{PCC}=5 Hz), 120.2 (d, J_{PCCC}=11 Hz), 63.3 (d, J_{POC}=4 Hz), 35.9 (d, J_{PC}=54 Hz), 16.6 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 144.0 (q, J_{PB}=81 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.9 (dq, J_{BP}=86 Hz, J_{BH}=95 Hz); HRMS (EI) calcd for $C_7H_{18}BO_2P$ $(M+NH_4)^+$: 194.1481, found: 194.1483.

4.3.10. Benzyl diethoxyphosphinylacetate-borane ***18*** *(Table 3, entry 5)*

Yield: 25%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.33 (m, 5H), 5.17 (s, 2H), 4.11–4.03 (m, 4H), 3.01 (d, J=10.3 Hz, 2H), 1.28 (t, J=7.0 Hz, 6H), 0.95–0.001 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 165.7, 128.9, 128.8, 67.6, 64.3 (d, J_{POC}=4 Hz), 38.6 (d, J_{PCC}=44 Hz), 16.6 (d, J_{POCC}=6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 139.1 (q, J_{PB}=72 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.2 (dq, J_{BP}=76 Hz, J_{BH}=95 Hz); HRMS (EI) calcd for $C_{15}H_{22}BO_4P$ $(M+NH_4)^+$: 302.1693, found: 302.1695.

4.3.11. Diethoxy(diethoxyphosphinoylmethyl)phosphine-borane ***19*** *(Table 3, entry 6)*

Yield: 52%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.22–4.08 (m, 8H), 2.46 (dd, J=20.8, 10.6 Hz, 2H), 1.38–1.31 (m, 12H), 1.20–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.9 (d, J_{POC}=4 Hz), 62.5 (d, J_{POC}=6 Hz), 29.3 (dd, J_{PCP}=137 Hz, J_{PC}=43 Hz), 16.4 (d, J_{POCC}=6 Hz), 16.3 (d, J_{POCC}=6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 138.8 (q, J_{PB}=80 Hz), 19.9 (s); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −41.4 (dq, J_{BP}=80 Hz, J_{BH}=95 Hz); HRMS (EI) calcd for $C_9H_{25}BO_5P_2$ (M−H): 285.1192, found: 285.1191.

4.3.12. Diethoxy benzyloxymethylphosphine-borane ***20*** *(Table 3, entry 7)*

Yield: 89%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.24 (m, 5H), 4.66 (s, 2H), 4.20–4.04 (m, 4H), 3.77 (s, 2H), 1.32 (dt, J=7.0 Hz, 6H), 1.10–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 137.3, 128.7, 128.2, 75.4 (d, J_{PCOC}=8 Hz), 67.7 (d, J_{PC}=70 Hz), 63.9 (d, J_{POC}=5 Hz), 16.8 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 138.0 (q, J_{PB}=83 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −43.0 (dq, J_{BP}=81 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{12}H_{22}BO_3P$ $(M+NH_4)^+$: 274.1743, found: 274.1749.

4.3.13. Diethoxy 3-pyridylmethylphosphine-borane ***21*** *(Table 3, entry 8)*

Yield: 69%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.52–8.47 (m, 2H), 7.63–7.60 (m, 1H), 7.28–7.25 (m, 1H), 4.08–3.90 (m, 4H), 3.14 (d, J=11.4 Hz, 2H), 1.25 (t, J=7.2 Hz, 6H), 1.00–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 150.9 (d, J_{PCC}=5 Hz), 148.3 (d, J_{PCCCNC}=3 Hz), 138.0 (d, J_{PCCC}=4 Hz), 123.5 (d, J_{PCCCC}=3 Hz), 64.2 (d, J_{POC}=4 Hz), 35.8 (d, J_{PC}=53 Hz), 16.7 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 143.0 (q, J_{PB}=76 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz)

δ −43.0 (dq, J_{BP}=76 Hz, J_{BH}=87 Hz); HRMS (EI) calcd for $C_{10}H_{19}BNO_2P$ (M+H): 228.1325, found: 228.1325.

*4.3.14. Diethoxy (2-hydroxy-hex-5-enyl)phosphine-borane **22** (Table 3, entry 9)*

Yield: 36–50%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85–5.74 (m, 1H), 5.10–4.92 (m, 2H), 4.22–3.90 (m, 4H), 2.57 (s, 1H), 2.39–2.10 (m, 2H), 2.04–1.94 (m, 2H), 1.74–1.58 (m, 2H), 1.33 (t, J=7.0 Hz, 6H), 1.20–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 138.1, 115.1 (d, $J_{PCCCCCC}$=2 Hz), 65.8, 63.5, 38.4 (d, J_{PC}=54 Hz), 37.5 (d, J_{PCCC}=9 Hz), 29.8, 16.7 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 146.8 (q, J_{PB}=86 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.2 (dq, J_{BP}=81 Hz, J_{BH}=90 Hz); HRMS (EI) calcd for $C_{10}H_{24}BO_3P$ $(M+NH_4)^+$: 252.1900, found: 252.1907.

*4.3.15. Reaction of **8** with carbonyl compounds (Scheme 3). Diethoxy (hydroxymethyl)phosphine-borane **23***

To diethoxyphosphine-borane **8** (0.408 g, 3 mmol) in CH_3CN (5 mL) were added diisopropylethylamine (1.05 mL, 6 mmol) and paraformaldehyde (0.184 g, 6 mmol) at room temperature. The solution was stirred at reflux for 6 h. The reaction mixture was then concentrated in vacuo, and the resulting residue was partitioned between H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×20 mL) and the combined organic layers washed with brine. Drying over $MgSO_4$ and concentration afforded the crude compound. Purification over silica gel (hexanes–EtOAc, 100:0 to 80:20, v/v) produced the expected compound **23** (0.334 g, 67%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.22–4.08 (m, 4H), 3.91 (s, 2H), 2.54 (s, 1H), 1.34 (dt, J=7.2 Hz, 6H), 1.10–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 64.0 (d, J_{POC}=5 Hz), 60.8 (d, J_{PC}=67 Hz), 16.7 (d, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 138.8 (q, J_{PB}=80 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −43.8 (dq, J_{BP}=80 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{10}H_{24}BO_3P$ $(M+NH_4)^+$: 184.1274, found: 184.1271.

*4.3.16. Diethoxy-hydroxyphenyl phosphine-borane **24** (Scheme 3)*

To diethoxyphosphine-borane **8** (0.408 g, 3 mmol) in CH_3CN (5 mL) were added diisopropylethylamine (1.05 mL, 6 mmol) and benzaldehyde (0.637 g, 6 mmol) at room temperature. The solution was stirred at reflux for 12 h. The reaction mixture was then concentrated in vacuo, and the resulting residue was partitioned between H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×20 mL) and the combined organic layers washed with brine. Drying over $MgSO_4$ and concentration afforded the crude compound. Purification over silica gel (hexanes–EtOAc, 100:0 to 90:10, v/v) produced the expected compound **24** (0.487 g, 67%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43–7.25 (m, 5H), 4.95 (s, 1H), 4.12–3.96 (m, 4H), 2.74 (s, 1H, OH), 1.24 (dt, J=14.1, 7.2 Hz, 6H), 1.01–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 135.5 (d, J_{PCC}=2 Hz), 128.5 (d, J_{PCCCCC}=3 Hz), 128.3 (d, J_{PCCCC}=2 Hz), 127.6 (d, J_{PCCC}=4 Hz), 74.4 (d, J_{PC}=64 Hz), 64.7 (dd, J_{POC}=4 Hz, J_{POC}=5 Hz), 16.7 (t, J_{POCC}=5 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 139.2 (q, J_{PB}=66 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −45.6 (dq, J_{BP}=69 Hz, J_{BH}=79 Hz); HRMS (EI) calcd for $C_{11}H_{20}BO_3P$ $(M+NH_4)^+$: 260.1587, found: 260.1585.

4.4. Representative procedure for radical reactions (Table 4)

To a solution of (EtO)(TIPSO)P(BH_3)H **5** (0.793 g, 3 mmol, 1 equiv) or $(EtO)_2P(BH_3)H$ **8** (0.500 g, 3.68 mmol, 1 equiv) in a mixture of methanol (12.5 mL) and dioxane (2.5 mL) were added 1-octene (1 equiv) and triethylborane (1.0 M in hexane, 1 equiv). The solution was stirred at room temperature in a flask open to air (6 h and 4 h, respectively). The reaction mixture was then concentrated in vacuo and the crude directly purified by column chromatography over silica gel (hexanes/EtOAc, 100:0 to 90:10, v/v) produced the expected compounds as colorless oil.

*4.4.1. Ethoxy(triisopropylsilyloxy)octylphosphine-borane **10** (Table 4, entry 2)*

Yield: 67%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.12–4.00 (m, 2H), 1.73–1.60 (m, 2H), 1.62–1.46 (m, 2H), 1.37–1.23 (m, 13H), 1.17–1.02 (m, 21H), 0.87 (t, J=7.0 Hz, 3H), 0.75–0.05 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.1 (d, J_{POC}=3 Hz), 33.1 (d, J_{PC}=53 Hz), 32.0, 31.0 (d, J_{PCC}=14 Hz), 29.3 (d, J_{PCCC}=3 Hz), 22.8, 22.0, 17.7, 16.7 (d, J_{POCC}=6 Hz), 14.2, 12.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 135.6 (q, J_{PB}=83 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −40.6 (dq, J_{BP}=83 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{19}H_{46}BO_2PSi$ $(M+NH_4)^+$: 394.4761, found: 394.3442.

*4.4.2. Diethoxy octylphosphine-borane **15** (Table 4, entry 3)*

Yield: 66%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.17–3.95 (m, 4H), 1.79–1.68 (m, 2H), 1.62–1.48 (m, 2H), 1.42–1.24 (m, 16H), 0.88 (t, J=6.2 Hz, 3H), 0.80–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 63.1 (d, J_{POC}=5 Hz), 32.0, 30.9 (d, J_{PCC}=14 Hz), 29.9 (d, J_{PC}=56 Hz), 29.2, 22.8, 21.7, 16.7 (d, J_{POCC}=6 Hz); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 148.9 (q, J_{PB}=86 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −42.2 (dq, J_{BP}=83 Hz, J_{BH}=94 Hz); HRMS (EI) calcd for $C_{12}H_{30}BO_2P$ $(M+NH_4)^+$: 266.2420, found: 266.2418.

4.5. Representative procedure for the deprotection of the phosphonite-borane complexes (EtO)(TIPSO)P(BH_3)Oct (Scheme 4)

Neat phosphine-borane (EtO)(TIPSO)P(BH_3)Oct **10** (0.188 g, 0.5 mmol) was placed in a flame-dried two-neck flask under argon and distilled/degassed CH_2Cl_2 (2 mL) was added. The solution was placed at −5 °C and $HBF_4{\cdot}OEt_2$ (0.5 mL, 2.5 mmol) was slowly added via syringe. The reaction mixture was allowed to warm to room temperature then stirred for 12 h. The reaction mixture was concentrated in vacuo. An aqueous solution of $NaHCO_3$ was added to the residue and the resulting mixture was extracted with EtOAc (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (hexanes–EtOAc, 1:1, v/v) afforded the desired product **25** as a colorless oil (0.082 g, 80%).

4.6. Representative procedure for the deprotection of the phosphonite-borane complexes (Scheme 4)

To a 0.2 M solution of phosphinite-borane in dry dichloromethane at 0 °C was added tetrafluoroboric acid diethyl ether complex (3.0 equiv). An exothermic reaction ensued and gas evolved. The reaction was then warmed to room temperature and stirred for additional 6 h. Subsequently, the mixture was cooled to 0 °C and saturated aqueous $NaHCO_3$ was slowly added. The resulting biphasic mixture was stirred vigorously for 5–10 min and poured into separatory funnel. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo to afford the *H*-phosphinate.

*4.6.1. Ethyl octyl-H-phosphinate **25**[17,19]*

The title compound was prepared from diethoxy octylphosphinite-borane (1.6 mmol, 400 mg, 1.0 equiv) and tetrafluoroboric acid diethyl ether complex (4.8 mmol, 0.777 g, 653 μL, 3.0 equiv) in 96% yield (1.54 mmol, 0.317 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (d, J=527 Hz, 1H), 4.03–4.23 (m, 2H), 1.27–1.80 (m, 14H), 1.37 (t, J=7.2 Hz, 3H), 0.88 (t, J=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 62.5 (d, J_{POC}=7 Hz), 31.8, 30.4 (d, J_{PCCC}=15 Hz), 29.1, 29.0, 28.6 (d, J_{PC}=93 Hz), 22.6, 20.7, 16.2 (d, J_{POCC}=6 Hz), 14.0; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 40.7 (dm, J=530 Hz).

*4.6.2. Ethyl pentyl-H-phosphinate **27***

The title compound was prepared from diethoxy pentylphosphinite-borane **26** (1.6 mmol, 330 mg, 1.0 equiv) and tetrafluoroboric acid diethyl ether complex (4.8 mmol, 777 mg, 653 μL, 3.0 equiv) in 96% yield (1.54 mmol, 253 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.09 (d, J=526 Hz, 1H), 4.01–4.26 (m, 2H), 1.26–1.83 (m, 8H), 1.37 (t, J=6.9 Hz, 3H), 0.91 (t, J=6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 62.4 (d, J_{POC}=7 Hz), 32.5 (d, J_{PCCC}=16 Hz), 28.1 (d, J_{PC}=94 Hz), 22.2, 20.3 (d, J_{PCCC}=3 Hz), 16.3 (d, J_{POCC}=6 Hz), 13.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 40.3 (dm, J=527 Hz); HRMS (EI^+) calcd for $C_7H_{18}O_2P$ ($[M]^+$): 165.1044, found: 165.1043.

*4.6.3. Ethyl isopropyl-H-phosphinate **28**[22]*

The title compound was prepared from diethoxy-1-methylethylphosphine-borane **16** (0.88 mmol, 157 mg, 1.0 equiv) and tetrafluoroboric acid diethyl ether complex (4.4 mmol, 623 mg, 5.0 equiv) in 97% yield (0.85 mmol, 116 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.88 (d, J=519.9 Hz, 1H), 4.25–4.05 (m, 2H), 2.01–1.85 (m, 1H), 1.37 (t, J=6.9 Hz, 3H), 1.17 (dd, J=7.0, 19.6 Hz, 6H); ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 47.1 (dm, J=531 Hz).

4.7. Representative procedure for preparation of boranophosphonates (Scheme 5)

Method A. Neat $(TIPSO)_2P(BH_3)H$ **4** (507 mg, 1.29 mmol) was placed under vacuum in a flame-dried two-neck flask, during 5 min before use. Anhydrous THF (5 mL) was then added under N_2. The flask was then placed at −78 °C and deoxygenated under high vacuum for 5 min. The reaction flask was back-filled with N_2 and LiHMDS (1.0 M in THF, 2.58 mL, 2.58 mmol) was added at −78 °C. After 15 min, 1-bromooctane (0.45 mL, 2.58 mmol) was added under N_2. After the addition of the electrophile, the temperature of the solution was slowly allowed to warm to room temperature, and stirred for 10 h. The reaction mixture was quenched with a saturated solution of NH_4Cl/brine and extracted with EtOAc (3×). The combined organic layers were then dried over $MgSO_4$ and concentrated in vacuo to afford the crude compound as a brownish viscous oil. This was dissolved in petroleum ether and filtered through a pad of silica gel. The solvent was evaporated in vacuo, giving the product **30** as a pale yellowish oil (0.227 g, 35% isolated, 88% of purity in ^{31}P NMR).

A portion of this intermediate (60 mg, 0.17 mmol) was dissolved in anhydrous THF (2 mL) in a flame-dried three-neck flask, at 0 °C, under N_2. TBAF (1.0 M solution in THF, 0.83 mL, 0.83 mmol) was added via syringe at 0 °C and the reaction mixture was allowed to warm to room temperature, then stirred under N_2 for 2 h. The mixture was concentrated in vacuo and the residue partitioned between DI H_2O and EtOAc. The organic layer was washed with DI H_2O (3×) and the aqueous layers were combined and concentrated in vacuo to afford the boranophosphonate **31** as a colorless and viscous oil (26.3 mg, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.31 (s, 1H, OH), 3.24–3.19 (m, 2H), 1.72–1.58 (m, 2H), 1.51–1.39 (m, 2H), 1.32–1.19 (m, 3H), 1.12–0.94 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 35.0, 32.1, 29.6, 22.8, 14.3, 13.1; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 108.9 (q, J_{PB}=137 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −38.2 (br s); HRMS (EI) calcd for $C_8H_{21}BO_2P$ (M): 191.1372, found: 191.1364.

Method B. A solution of octyl-*H*-phosphinic acid **32**[17,23] (1.0 g, 5.61 mmol) in anhydrous THF (20 mL) was treated with BSA (6.94 mL, 28 mmol) at room temperature for 1 h, under N_2. A solution of $BH_3\cdot Me_2S$ (2.0 M in THF, 5.61 mL, 11.22 mmol) was then added at room temperature, and the resulting mixture stirred for 1 h. After addition of MeOH (20 mL), the mixture was stirred for an additional 2 h and then concentrated in vacuo. The residue was partitioned between $CHCl_3$ and H_2O and the organic phase was washed with H_2O (3×). The combined aqueous layers were concentrated in vacuo, affording the desired product **31** (0.965 g, 90%) as a colorless gel. HRMS (EI) calcd for $C_8H_{21}BO_2P$ (M): 191.1371, found: 191.1373.

*4.7.1. Ethoxy(triisopropylsilyloxy)-(trans-hex-1-enyl)phosphine-borane **34** (Scheme 6)*

Triisopropylchlorosilane (4.22 mL, 19.76 mmol) was placed into a flame-dried two-neck round bottom flask and cooled to 0 °C, under N_2. Et_3N (2.94 mL, 21.08 mmol) was then added dropwise and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate flame-dried three-neck round bottom flask, a solution of ethyl (*trans*-hex-1-enyl)phosphinate **33**[20,21a] (2.87 g, 14.05 mmol) in CH_3CN (28 mL) was cooled to 0 °C, under N_2. The mixture TIPSCl/Et_3N was slowly added to the *H*-phosphinate solution via syringe and the reaction mixture maintained at 0 °C for 10–15 min, at which time the reaction was allowed to warm up to room temperature and stirred for 14 h under N_2. The reaction mixture was treated with $BH_3\cdot Me_2S$ (2.0 M in THF, 14.05 mL, 28.1 mmol) by dropwise addition at room temperature. After 5 h, the reaction mixture was concentrated under reduced pressure, and the residue partitioned between DI H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×) and the combined organic layers washed with brine (1×), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (hexanes–toluene, 100:0 to 90:10, v/v) afforded the desired product **34** as a colorless oil (2.84 g, 54%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.72 (ddt, J=6.6, 17.3, 2.5 Hz, 1H), 5.81 (dd, J=17.1, 6.0 Hz, 1H), 4.03 (m, 2H), 2.21 (d, J=6.9 Hz, 2H), 1.46–1.40 (m, 2H), 1.32–1.25 (m, 10H), 1.19–1.02 (m, 15H), 0.90–0.83 (m, 8H), 0.65–0.00 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 151.9 (d, J_{PCC}=14 Hz), 124.4 (d, J_{PC}=75 Hz), 62.4 (d, J_{POC}=4 Hz), 34.4 (d, J_{PCCC}=17 Hz), 31.8, 29.0, 28.0, 22.8, 17.8, 16.7, 14.3, 12.8; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 119.7 (q, J_{PB}=90 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −41.5 (dq, J_{BP}=90 Hz, J_{BH}=92 Hz); HRMS (EI) calcd for $C_{19}H_{44}BO_2PSi$ $(M+NH_4)^+$: 390.3129, found: 390.3119.

*4.7.2. Ethoxy(triisopropylsilyloxy)-allyl-(1-propyl-pent-1-enyl)phosphine-borane **36** (Scheme 6)*

Triisopropylchlorosilane (7.84 mL, 36.7 mmol) was added into a flame-dried two-neck round bottom flask and cooled to 0 °C, under N_2. Et_3N (5.46 mL, 39.17 mmol) was then added dropwise and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate flame-dried three-neck round bottom flask, a solution of ethyl (1-propyl-pent-1-enyl)phosphinate **35**[18,21] (5 g, 24.48 mmol) in CH_3CN (49 mL) was cooled to 0 °C, under N_2. The TIPSCl/Et_3N mixture was slowly added to the *H*-phosphinate solution via syringe and the reaction mixture was kept at 0 °C for 10–15 min, at which time the reaction was allowed to warm up to room temperature and stirred for 14 h under N_2. The reaction mixture was treated with $BH_3\cdot Me_2S$ (2.0 M in THF, 14.05 mL, 28.1 mmol) by dropwise addition at room temperature. After 5 h, the reaction mixture was concentrated under reduced pressure and the residue partitioned between DI H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×) and the combined organic layers washed with brine (1×), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (hexanes–toluene, 100:0 to 90:10, v/v) afforded the desired product **36** as a colorless oil (5.32 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.47 (dt, J=6.9, 22.2 Hz, 1H), 4.05–3.95 (m, 2H), 2.25–2.12 (m, 4H), 1.58–1.40 (m, 3H), 1.31–1.25 (m, 4H), 1.22–1.14 (m, 3H), 1.09 (d, J=8.1 Hz, 18H), 0.94 (t, J=7.2 Hz, 6H), 0.95–0.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 154.4 (d, J_{PCC}=21 Hz), 135.8 (d, J_{PC}=71 Hz), 62.4, 30.7 (d, J_{PCC}=17 Hz), 28.6 (d, J_{PCCC}=8 Hz), 23.3, 22.3, 17.8, 16.6, 14.3 (d, J_{POCC}=42 Hz), 12.9; ^{31}P NMR ($CDCl_3$, 121.47 MHz) δ 124.4 (q, J_{PB}=100 Hz); ^{11}B NMR ($CDCl_3$, 28.88 MHz) δ −43.7 (dq, J_{BP}=100 Hz, J_{BH}=103 Hz); HRMS (EI) calcd for $C_{19}H_{44}BO_2PSi$ $(M-H_2+NH_4)^+$: 390.3129, found: 390.3133.

4.7.3. Bistriisopropylthiophosphonite ***37*** *(Eq. 5)*

Triisopropylchlorosilane (2.14 mL, 10 mmol) was placed into a flame-dried two-neck round bottom flask and cooled to 0 °C, under N_2. Et_3N (1.47 mL, 10.5 mmol) was then added dropwise and the reaction mixture was stirred for approximately 10 min at 0 °C. In a separate flame-dried three-neck round bottom flask, a solution of anilinium hypophosphite (771 mg, 5 mmol) in CH_3CN (20 mL) was cooled to 0 °C, under N_2. The mixture TIPSCl/Et_3N was slowly added to the anilinium hypophosphite solution via syringe and the reaction mixture maintained at 0 °C for 10–15 min, at which time the reaction was allowed to warm up to room temperature and stirred for 12 h under N_2. The reaction mixture was treated with S_8 (321 mg, 10 mmol) by direct addition into the flask at room temperature. After 4 h, the reaction mixture was concentrated under reduced pressure, and the residue partitioned between DI H_2O and EtOAc. The aqueous layer was extracted with EtOAc (3×) and the combined organic layers washed with brine (1×), dried over $MgSO_4$, and concentrated in vacuo to afford the crude compound. Purification by column chromatography over silica gel (100% hexanes) afforded the desired product **37** as a pale green oil (1.17 g, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, J=637.5 Hz, 1H), 1.30–1.18 (m, 6H), 1.10 (d, J=6.9 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 17.8, 12.6; ^{31}P NMR ($CDCl_3$, 36.441 MHz) δ 39.5 (d, J=636 Hz); HRMS (EI) calcd for $C_{18}H_{43}O_2PSSi$ $(M+H)^+$: 411.2338, found: 411.2345.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.07.054.

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