 

# Reactions of *t*-Butylphosphine–Borane with Various Electrophiles and Synthesis of Optically Active *t*-Butylmethylphosphine–Borane

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The reactivity of *t*-butylphosphine–borane toward various electrophiles was studied with a focus on alkylation. Monoalkylation of this compound proceeded smoothly in good yields (61–85%). Disubstituted derivatives were also synthesized in good yields (86–99%). Optically active *t*-butylmethylphosphine–borane was prepared from *t*-butylphosphine–borane by resolution of intermediate diastereomers of (1*S*)-*endo*-2-bornyloxycarbonyl(*t*-butyl)methylphosphine-borane.

Optically active phosphines have become increasingly important as chiral ligands in various transition metal-catalyzed asymmetric reactions,[1] and numerous phosphines of this class have been reported.[1,2] Among them, some P-chirogenic trialkyl bisphosphine ligands exhibit high catalytic activity and enantioselectivity.[3]

Although these phosphine ligands are usually conveniently prepared from trichlorophosphine or alkyldichlorophosphines,[4] primary alkylphosphines[5] derived from $PH_3$ may also contribute valuable starting materials for the synthesis of phosphine ligands.

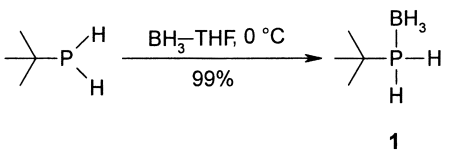
Recently, we have developed a new synthetic route to enantiomerically enriched[6] or pure[7] dialkylphosphine–boranes having a P–H bond, which are useful chiral building blocks for the synthesis of bisphosphine ligands. However, the former method provides only one of the enantiomer ligands and the latter cannot be carried out in large scale separation of the key intermediate diastereomers by recrystallization. Therefore, a new efficient method is still strongly required for the synthesis of both enantiomer ligands.

In this study we prepared *t*-butylphosphine–borane from *t*-butylphosphine and examined its reactivity toward various electrophiles in order to explore a new route to optically active *t*-butylmethylphosphine–borane.

## Results and Discussion

**Synthesis of *t*-Butylphosphine–Borane.** As a representative example of primary alkylphosphine, we selected *t*-butylphosphine, because this phosphine is prepared on industrial scale from phosphine and isobutene.[8] Another reason is that bisphosphine ligands bearing a *t*-butyl substituent exhibit excellent enantioselectivity in transition metal-catalyzed asymmetric reactions.[3a,3b]

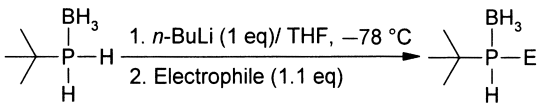
Its borane complex was prepared almost quantitatively by reaction of *t*-butylphosphine with stoichiometric quantities of $BH_3$–THF complex (Scheme 1). This compound can be handled in air, while it gradually decomposes on contact with moisture. A weak P–B bond may be responsible for this sensitiveness to moisture. The strength of this bond can be estimated by the value of the coupling constant between phosphorus and boron in NMR analysis ($J_{PB}$).[9] The values of the $J_{PB}$ in other primary alkylphosphine–boranes were reported (e.g. phenylphosphine–borane (38.4 Hz), methylphosphine–borane (41.8 Hz)).[10] The observed $J_{PB}$ of **1** in this study was 35.2 Hz (literature 32 Hz).[11] These relatively smaller $J_{PB}$ values are compared with larger values of tertiary phosphine–boranes which are more stable than primary phosphine–borane.




**1**

Scheme 1.

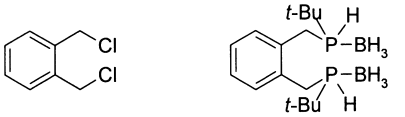
**Synthesis of Monosubstituted Derivatives of 1.** Compound **1** was subjected to deprotonation with 1 equivalent of *n*-BuLi at −78 °C. The generated lithium derivative was allowed to react with 1.1 equivalents of electrophile to give the corresponding monosubstituted derivative (Scheme 2). These results are summarized in Table 1.




Scheme 2.

Reactions with alkyl halides proceeded smoothly to give the corresponding secondary dialkylphosphine-boranes in good

Table 1. Synthesis of Monosubsutituted Derivatives of **1**

| Entry[a)] | Electrophile | Product | Yield%[d)] |
|---|---|---|---|
| 1 | $CH_3I$ | *t*-Bu$CH_3$P$H(BH_3)$ (**2a**) | 85 |
| 2 | *n*-$C_4H_9Cl$ | *t*-Bu(*n*-$C_4H_9$)P$H(BH_3)$ (**2b**) | 65 |
| 3 | *n*-$C_{14}H_{29}Cl$ | *t*-Bu(*n*-$C_{14}H_{29}$)P$H(BH_3)$ (**2c**) | 74 |
| 4 | $PhCH_2Cl$ | t-Bu($PhCH_2$)P$H(BH_3)$ (**2d**) | 61 |
| 5 |  |  | 34 (*rac*) (**2e**)<br>32 (*meso*) (**2f**) |
| 6 | (+)-Men*OCOCl[b)] | *t*-Bu(Men*OCO)$_2$P$BH_3$ (**2g**) | 18[e)] |
| 7 | PhSSPh | *t*-Bu$(PhS)_2$P (**2h**) | 13 |
| 8 | $ClCH_2COOC_2H_5$ | *t*-BuP$H(BH_3)CH_2COOC_2H_5$ (**2i**) | 34 |
| 9 | $ClCH_2$COOMen*[b)] | *t*-BuP$H(BH_3)CH_2$COOMen* (**2j**) | 75 |
| 10 | $ClCH_2$COOBor*[c)] | *t*-BuP$H(BH_3)CH_2$COOBor* (**2k**) | 67 |

a) All the reactions were carried out according to Scheme 2. b) Men = menthyl. c) Bor = bornyl. d) Isolated yield. e) Crude product.

yields (Table 1, entries 1–5, 61–85%) with small amounts of dialkylation products (ca. < 10%). On the other hand, reaction of (+)-menthyl chloroformate or diphenyl disulfide with compound **1** offered no appreciable amount of monosubstituted derivatives but only low yields of disubstituted derivatives (entries 6, 7). TLC analyses of these reaction mixtures showed that disubstitution occurred from the beginning of the reactions, suggesting that the acidity of the P–H bond in monosubstituted derivatives increases with the substitution of the carbonyl or phenylthio component.

The reactivity of the lithium salt of **1** toward substrates bearing a carbonyl group, such as benzophenone and cyclohexanone, was also investigated. However, these reactions proceeded sluggishly, and the corresponding $\alpha$-hydroxyalkylphosphine-borane derivatives could not be obtained.

**Dehydrocoupling Dimer of 1.** In order to obtain phenyl derivative of **1**, we tried cross-coupling reactions with **1** and iodobenzene as well as phenyl triflate using transition-metal catalysts in the presence of base but our efforts were unsuccessful. However, in the process of these trials, we found that an interesting compound was produced in low yield. This compound was isolated and characterized by NMR, HRMS, and X-ray crystallographic analysis as being the dehydrocoupling dimer (**3**) possessing a P–B–P bond linkage as depicted in Fig. 1. The geometry around P1, B2, and P2 is approximately tetrahedral with slightly opened B1–P1–B2 angle and C5–P2–B2 angle (117.3(7)° and 115.3(8)°, respectively) and slightly closed P1–B2–P2 angle (103.0(1)°). In contrast to the bond length of B1–P1 (1.93 Å), which is a typical value of phosphine–borane complexes,[12] P1–B2 (1.97 Å) and B2–P1 (2.00 Å) bond lengths are a little longer.

Recently, Manners and co-workers have reported the synthesis of this type of dehydrocoupling compounds by use of transition-metal catalyzed reactions.[13,14,15] Encouraged by their results, we performed the previous experiment by rhodium-catalyzed reaction using complexes such as $[RhCl(nbd)]_2$, $[Rh(t\text{-BuBisP}^*)(nbd)]^+BF_4^-$. However, this dimer could not be obtained. The best result was realized by employing 10 mol% of $NiCl_2$ (ca. 12%, Scheme 3).

**Synthesis of Disubstituted Derivatives of 1.** The low

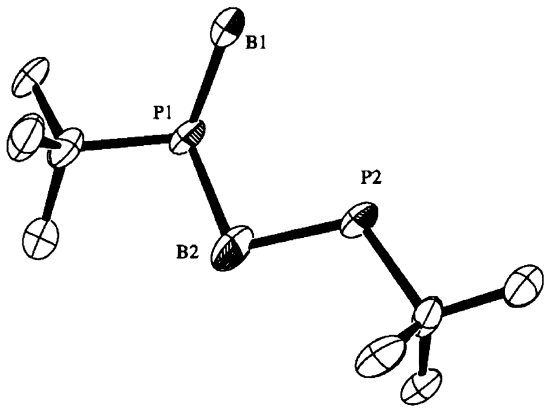
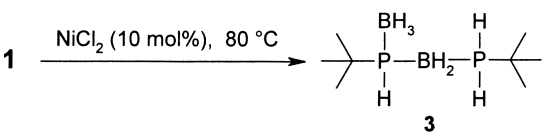
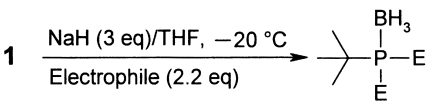



Fig. 1. ORTEP drawing of *t*-Bu$PH_2$–$BH_2$–*t*-BuPH–$BH_3$ (**3**) Hydrogen atoms are omitted for clarity.




Scheme 3.




Scheme 4.

yields of disubstituted compounds (**2g**, **2h**) led us to investigate the syntheses of this type of compounds, as shown in Scheme 4.

Compound **1** was slowly added to a mixture of NaH (3 equivalents) and electrophile (2.2 equivalents) in THF at −20 °C. Upon addition, the reaction mixture was allowed to warm to 0 °C and stirred for several hours until consumption of the starting material was complete.

Results summarized in Table 2 show that the corresponding

Table 2. Synthesis of Disubsutituted Derivatives of **1**

| Entry[a)] | Electrophile | Product | Yield%[c)] |
|---|---|---|---|
| 1 | $CH_3I$ | *t*-Bu$(CH_3)_2PBH_3$ (**4a**) | 94 |
| 2 | *n*-$C_4H_9Cl$ | *t*-Bu$(n$-$C_4H_9)_2PBH_3$ (**4b**) | 88 |
| 3 | *n*-$C_{14}H_{29}Cl$ | *t*-Bu$(n$-$C_{14}H_{29})_2PBH_3$ (**4c**) | 97 |
| 4 | $PhCH_2Cl$ | *t*-Bu$(PhCH_2)_2PBH_3$ (**4d**) | 99 |
| 5 | (+)-Men*OCOCl[b)] | *t*-Bu$(Men^*OCO)_2PBH_3$ (**2g**) | 92[d)] |
| 6 | PhSSPh | *t*-Bu$(PhS)_2P$ (**2h**) | 96 |

a) All the reactions were carried out according to Scheme 4. b) Men = menthyl. c) Isolated yield. d) Crude product.

disubstituted compounds of **1** were isolated in high yields (88–99%). Another notable fact is that *t*-butyldimethylphosphine–borane (**4a**), key intermediate for the preparation of BisP* [3a] and MiniPHOS,[3b] was isolated in excellent 94% yield (Table 2, entry 1).

**Synthesis of Optically Active *t*-Butylmethylphosphine–Borane.** Finally, we examined the synthesis of optically active secondary dialkylphosphine–borane. At first, a one pot synthesis was performed by deprotonation of precursor **1** using *n*-BuLi/(−)-sparteine complex,[16] followed by trapping with benzyl chloride. Specific rotation measurements or chiral-HPLC analyses of these products showed no significant differences as compared to their racemates, indicating that prochiral P–H bonds of primary alkylphosphine–borane cannot be stereoselectively deprotonated by this method.

The dynamic resolution method, reported by Livinghouse et al.[17] was also examined under even more forcing conditions, but afforded no success.

Our attention was turned to the optical resolution of intermediate diastereomers prepared from **1** and chiral auxiliary. Although the yield was only moderate, the successful introduction of alkoxycarbonylmethyl group to phosphorus atom of **1**, as a test experiment (Table 1, entry 8), led us to the synthesis of chiral analogues, namely the (−)-menthyl and (−)-bornyl derivatives.[18] To our surprise, the isolated yields of diastereomers **2j** and **2k** increased to 75% and 67%, respectively (Table 1, entries 9, 10). Unfortunately, their separation by recrystallization proved unsuccessful.[19]

In order to overcome their difficulty, we designed an alternative three step strategy (Scheme 5): (i) conversion of racemic *t*-butylmethylphosphine–borane (**2a**) to diastereomers by introducing chiral auxiliary, (ii) separation of diastereomers by recrystallization, and (iii) hydrolysis and decarboxylation of the separated diastereomer to recover each pure enantiomer.

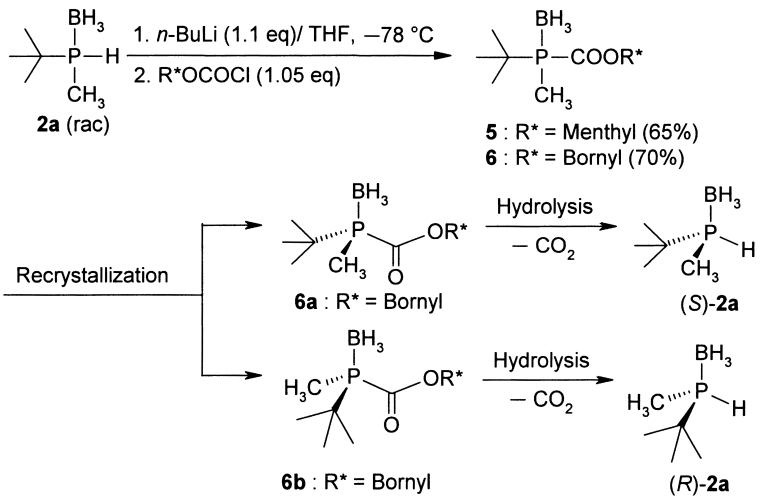
Thus, racemic **2a** was allowed to react with (+)-menthyl chloroformate to give 1:1 mixture of corresponding diastereomers (**5**) in 65% yield. However, attempts to separate these diastereomers by recrystallization failed owing to the fact that **5** was obtained as pasty oil.

On the other hand, the (1*S*)-*endo*-2-bornyl chloroformate derivative (**6**), prepared from (−)-borneol and racemic **2a** in 70% yield, was isolated as a crystalline solid (1:1 mixture of diastereomers). A few recrystallizations from hexane provided (**6a**) (95% de[20]), one of the diastereomers, in 32% yield.[21]

Transformation of diastereomerically enriched **6a** into *t*-butylmethylphosphine-borane was achieved by hydrolysis and decarboxylation. Table 3 shows summarized results. After screening several base/solvents, the best compromise between yield and ee was achieved when the starting material was treated with a large excess of KOH (20 equivalents) at room temperature (Table 3, entry 5). Under these conditions, (*S*)-*t*-butylmethylphosphine–borane was obtained in 75% yield without any loss of enantiomeric purity (95% ee).

## Experimental

**General.** All pieces of glassware were dried in an oven be-




Scheme 5.

Table 3. Hydrolysis–Decarboxylation of **6a**

| Entry | Temp/°C | Conditions | Yield% | ee[f]/% |
|---|---|---|---|---|
| 1[a] | 50 | conc. HCl/MeOH, 1h | trace[d] | — |
| 2[a] | 50 | KOH (5 equiv)/MeOH, 3h | 45 | 84 |
| 3[a] | r.t. | KOH (10 equiv)/$CH_3CN/H_2O$,[c] 1h | —[e] | — |
| 4[b] | r.t. | KOH (15 equiv)/$CH_3CN$/MeOH/$H_2O$, 4h | 64 | 95 |
| 5[b] | r.t. | KOH (20 equiv)/$CH_3CN$/MeOH/$H_2O$, 4h | 75 | 95 |

a) 84% de of **6a** was used. b) 95% de of **6a** was used. c) Reaction was performed under the same conditions that we previously reported,[6] without oxidation reagents. d) TLC analysis. e) Because **6a** was insoluble in this solvent system, the reaction was aborted. f) The ee (%) values were determined by HPLC analysis using Chiral Daicel OD-H column on the corresponding 2-pyridylmethyl derivative.[6,7]

fore use. Dehydrated, stabilizer-free THF was purchased from Kanto Kagaku Co., Ltd., and was used as the reaction solvent. *t*-Butylphosphine (exact 10 wt% solution of hexane) was supplied by Shin-Etsu Chemical Co., Ltd. Reactions were carried out under argon atmosphere. Reaction products were purified by flash column chromatography on silica gel (Wakogel C-200 or C-300), unless otherwise stated. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a JMN-LA300 spectrometer (JEOL). Chemical shifts are referenced to solvent peaks or internal TMS ($^1$H, $^{13}$C), or external 85% $H_3PO_4$ ($^{31}$P). High-resolution mass spectra were obtained on a JMS-DX303 mass spectrometer (JEOL). FT-IR spectra were obtained on a FT/IR-430 spectrometer (JASCO). Melting points were determined with MP-V500 (Yanako) or FP-62 (Mettler Tledo). Specific rotation was obtained on SEPA-300 polarimeter (HORIBA). TLC were performed on glass plates precoated with silica gel 60 F-254 (0.2 mm) from Merck.

***t*-Butylphosphine–Borane (1).** *t*-Butylphosphine was stored in well-sealed SUS bottle as 10 wt% hexane solutions. From this bottle, 91.0 g of this solution (101 mmol) was transferred to 500 mL flask under argon atmosphere via syringe. $BH_3$–THF complex (100 mL of 1.01 M THF solution, 101 mmol) was slowly added at 0 °C and the resulting mixture was stirred for 1 h at this temperature. The solvents were removed under vacuum and the residue was distilled in vacuo to give *t*-butylphosphine–borane as a colorless liquid (10.42 g, 99%). Bp 31–32 °C /6 mmHg; $^1$H NMR (300.4 MHz, $C_6D_6$) $\delta$ 0.93 (d, $^3J_{HP}$ = 15.2 Hz, 9H), 1.04 (br q, $J_{HB}$ = 101.5 Hz, 3H), 3.93 (dm, $J_{HP}$ = 352.7 Hz, 2H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 25.2 (d, $J_{CP}$ = 34.7 Hz), 27.8 (d, $^2J_{CP}$ = 3.1 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $C_6D_6$) $\delta$ −11.9 (br q, $J_{PB}$ = 35.2 Hz); IR (KBr Plate) 2961, 2396, 1461 cm$^{-1}$; HRMS EI *m/z* 103.0845. Calcd for $C_4H_{13}BP$ ($M^+-H$) 103.0848.

**Synthesis of Monosubstituted Derivatives of 1. *t*-Butyl(methyl)phosphine–Borane (2a).** A representative experimental procedure is described for *t*-butylmethylphosphine–borane.

To a stirred, cooled (−78 °C) solution of **1** (3.91 g, 37.7 mmol) in THF (120 mL) was slowly added *n*-BuLi (26 mL of 1.50 M hexane solution, 39 mmol) under argon atmosphere. After 10 min, $CH_3I$ (5.88 g, 41.4 mmol) was slowly added at −78 °C. The resulting mixture was stirred for 1 h at this temperature then at room temperature. To this reaction mixture was carefully added iced water containing HCl. The organic layer was separated and the aqueous layer was extracted with $Et_2O$ three times. The combined extracts were washed with water and brine, dried ($Na_2SO_4$), and concentrated. The residue was distilled in vacuo to give *t*-butylmethylphosphine–borane as a white solid (3.78 g, 85%). Mp 33–37 °C; bp 90–91 °C /15 mmHg; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.49 (br q, $J_{HB}$ = 98.6 Hz, 3H), 1.21 (d, $^3J_{HP}$ = 14.7 Hz, 9H), 1.33 (dd, $^2J_{HP}$ = 10.7 Hz, $J$ = 6.0 Hz, 3H), 4.41 (dm, $J_{HP}$ = 354.8 Hz, 1H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 2.1 (d, $J_{CP}$ = 34.8 Hz), 26.0 (d, $J_{CP}$ = 34 Hz), 26.2 (d, $^2J_{CP}$ = 3.0); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ −12.1 (br q, $J_{PB}$ = 51.4 Hz); IR (KBr) 2970, 2380, 1463 cm$^{-1}$; HRMS EI *m/z* 117.1009. Calcd for $C_5H_{15}BP$ ($M^+-H$) 117.1005.

**Butyl(*t*-butyl)phosphine–Borane (2b).** This compound was prepared from **1** and butyl chloride in 65% yield (2 mmol scale) and isolated as colorless oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.47 (br q, $J_{HB}$ = 98.7 Hz, 3H), 0.94 (t, $J$ = 6.8 Hz, 3H), 1.22 (d, $^3J_{HP}$ = 14.1 Hz, 9H), 1.34–1.60 (m, 4H), 1.58–1.90 (m, 2H), 4.23 (dm, $J_{HP}$ = 350.5 Hz, 1H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 13.7, 17.4 (d, $J_{CP}$ = 31 Hz), 24.2 (d, $^3J_{CP}$ = 12.5 Hz), 26.4 (d, $J_{CP}$ = 35.4 Hz), 26.6 (d, $^2J_{CP}$ = 1.9 Hz), 27.2 (d, $^3J_{CP}$ = 1.9 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 23.4 (br q, $J_{PB}$ = 48.6 Hz); IR (KBr) 2958, 2383, 1465 cm$^{-1}$; HRMS EI *m/z* 146.1201. Calcd for $C_8H_{19}P$ ($M^+-BH_3$) 146.1224.

***t*-Butyl(tetradecyl)phosphine–Borane (2c).** This compound was prepared from **1** and tetradecyl chloride in 74% yield (2 mmol scale) and isolated as white pasty oil. $^1$H NMR (300.4 MHz, $C_6D_6$) $\delta$ 0.93 (d, $^3J_{HP}$ = 9.3 Hz, 9H), 0.96 (t, $J$ = 6.8 Hz, 3H), 1.1–1.7 (m, 29 H), 3.92 (dm, $J_{HP}$ = 346.4 Hz, 1H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 14.4, 17.7 (d, $J_{CP}$ = 31.0 Hz), 23.1, 25.2, 26.1, 26.6 (d, $^2J_{CP}$ = 1.9 Hz), 29.6, 29.86, 29.94, 30.10, 30.17, 30.20, 31.2, 31.3, 32.4; $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $C_6D_6$) $\delta$ 22.7–23.8 (m); IR (KBr) 2933, 2853, 2384, 1464 cm$^{-1}$; HRMS EI *m/z* 286.2826. Calcd for $C_{18}H_{39}P$ ($M^+-BH_3$) 286.2790.

**Benzyl(*t*-butyl)phosphine–Borane (2d).** This compound was prepared from **1** and benzyl chloride in 61% yield (2 mmol scale) and isolated as white pasty oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.50 (br q, $J_{HB}$ = 98.2 Hz, 3H), 1.24 (d, $^3J_{HP}$ = 9.6 Hz, 9H), 2.9–3.3 (m, 2 H), 4.73 (dm, $J_{HP}$ = 357.3 Hz, 1H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 25.9 (d, $J_{CP}$ = 28.6 Hz), 26.8 (d, $^2J_{CP}$ = 1.9 Hz), 31.0 (d, $^2J_{CP}$ = 31.0 Hz), 127.0 (d, $J$ = 2.5 Hz), 128.8 (d, $J$ = 2.5 Hz), 129.4 (d, $J$ = 4.4 Hz), 130.2 (d, $J$ = 4.4 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 31.2 (br q, $J_{PB}$ = 55.9 Hz); IR (KBr) 3030, 2956, 2389, 1457, 1368 cm$^{-1}$; HRMS EI *m/z* 194.1402. Calcd for $C_{11}H_{20}BP$ ($M^+$) 194.1396.

**1,2-Bis{[boranato(*t*-butyl)phosphino]methyl}benzene.** This compound was prepared from **1** and 1,2-bis(chloromethyl)benzene dichloride in 34% yield (racemic), 32% yield (meso) (5 mmol scale) and isolated as colorless cubes. Racemate compound (**2e**). Mp 136.0–137.0 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.44 (br q, $J_{HB}$ = 110.7 Hz, 6H), 1.32 (d, $^3J_{HP}$ = 14.4 Hz, 18H), 3.19–3.36 (m, 4H), 4.32 (dm, $J_{HP}$ = 357.4 Hz, 2H), 7.11–7.20 (m, 4H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 22.6 (d, $J_{CP}$ = 26.7 Hz), 26.7

(d, $^2J_{CP}$ = 1.9 Hz), 27.5 (d, $^2J_{CP}$ = 31.0 Hz), 127.4–127.6 (m), 130.4–130.5 (m), 133.3–133.5 (m); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 31.0–33.0 (m); IR (KBr) 3030, 2954, 2867, 2386, 1461, 1367 cm$^{-1}$; HRMS EI *m/z* 304.1850. Calcd for $C_{16}H_{28}B_2P_2$ ($M^+-6H$) 304.1852.

Meso compound (**2f**). Mp 130.8–133.2 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.45 (br q, $J_{HB}$ = 104.2 Hz, 6H), 1.32 (d, $^3J_{HP}$ = 14.4 Hz, 18H), 2.82–2.93 (m, 2H), 3.46–3.57 (m, 2H), 4.31 (dm, $J_{HP}$ = 348.0 Hz, 2H), 7.19–7.23 (s, 4H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 22.9 (d, $J_{CP}$ = 27.3 Hz), 26.8 (d, $^2J_{CP}$ = 1.9 Hz), 27.7 (d, $^2J_{CP}$ = 31.0 Hz), 127.6–127.8 (m), 131.4–131.5 (m), 132.1–132.3 (m); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 29.0–30.8 (m); IR (KBr) 3030, 2961, 2384, 1463, 1368 cm$^{-1}$; HRMS EI *m/z* 306.1969. Calcd for $C_{16}H_{30}B_2P_2$ ($M^+-4H$) 306.2008.

**X-ray Crystallographic Analysis of 2e.** Lattice constants and intensity data for **2e** were measured using graphite monochromated Cu $K\alpha$ radiation on a Rigaku AFC7S diffractometer. A well-shaped monoclinic crystal was obtained by recrystallization from ethyl acetate: $C_{16}H_{34}B_2P_2$; space group $C2/c$ (#15); $a$ = 17.430(4) Å, $b$ = 14.045 (2) Å, $c$ = 18.093(2) Å, $\beta$ = 107.74(1)°, $V$ = 4218(1) Å$^3$; $Z$ = 8, $D$ = 0.976 g/cm$^3$; $F(000)$ = 1360; $\mu$(Cu $K\alpha$) = 17.66 cm$^{-1}$; $\lambda$(CuK$\alpha$) = 1.54178 Å; 3997 reflections measured, 3251 observed ($I > 1.00\sigma(I)$); 182 variables; $R$ = 0.091, $R\omega$ = 0.146, GOF = 1.62.

**Ethyl Boranato(*t*-butyl)phosphinoacetate (2i).** This compound was prepared from **1** and ethyl chloroacetate in 34% yield (2 mmol scale) and isolated as colorless oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.52 (br q, $J_{HB}$ = 100.1 Hz, 3H), 1.25 (d, $^3J_{HP}$ = 15.2 Hz, 9H), 1.30 (t, $J$ = 7.0 Hz, 3H), 2.6–2.9 (m, 2 H), 4.20 (q, $J$ = 7.0 Hz, 2H), 4.78 (dm, $J_{HP}$ = 369.1 Hz, 1H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.0, 25.8 (d, $J_{CP}$ = 26.1 Hz), 26.5 (d, $^2J_{CP}$ = 1.9 Hz), 27.1 (d, $^2J_{CP}$ = 32.9 Hz), 167.7 (d, $^2J_{CP}$ = 5.0 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 19.5–21.0 (m); IR (KBr) 2963, 2870, 2391, 1733, 1464, 1368, 1283 cm$^{-1}$; HRMS EI *m/z* 189.1228. Calcd for $C_8H_{19}BO_2P$ ($M^+-H$) 189.1216.

**Menthyl [Boranato(*t*-butyl)phosphino]acetate (2j, Diastereomeric Mixture).** This compound was prepared from **1** and menthyl chloroacetate in 75% yield (2 mmol scale) and isolated as colorless pasty oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.50 (br q, $J_{HB}$ = 90.0 Hz, 6H), 0.74–0.78 (m, 6H), 0.8–0.9 (m, 2H), 0.88–0.94 (m, 12H), 0.92–1.14 (m, 4H), 1.25 (d, $^3J_{HP}$ = 15.2 Hz, 18H), 1.30–1.52 (m, 4H), 1.64–1.73 (m, 4 H), 1.83–1.98 (m, 2H), 1.98–2.09 (m, 2H), 2.63–2.95 (m, 4H), 4.72 (m, 2H), 4.77 (dm, $J_{HP}$ = 368.6 Hz, 2H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 16.0, 16.1, 20.7, 21.9, 23.14, 23.16, 26.0 (d, $J_{CP}$ = 26.7 Hz), 26.5–26,6 (m), 27.1 (d, $J_{CP}$ = 32.3 Hz), 31.3–31.4 (m), 34.0, 40.5– 40.6 (m), 46.7–46.8 (m), 76.1, 76.2, 167.2– 167.4 (m); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 18.8–20.4 (m); IR (KBr) 2956, 2870, 2393, 1725, 1462, 1370, 1288 cm$^{-1}$; HRMS EI *m/z* 299.2308. Calcd for $C_{16}H_{33}BO_2P$ ($M^+-H$) 299.2312.

**Bornyl [Boranato(*t*-butyl)phosphino]acetate (2k, Diastereomeric Mixture).** This compound was prepared from **1** and bornyl chloroacetate in 67% yield (25 mmol scale) and isolated as a white pasty solid. Mp 110–112 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.53 (br q, $J_{HB}$ = 96.2 Hz, 6H), 0.86–0.87 (m, 6H), 0.88 (m, 6H), 0.90 (6H), 1.02–1.13 (2H), 1.21–1.30 (m, 18H), 1.20–1.40 (m, 2H), 1.66–1.73 (m, 2H), 1.70–1.83 (m, 2H), 1.86–2.03 (m, 2H), 2.30–2.45 (m, 2H), 2.68–3.18 (m, 4H), 4.76 (dm, $J_{HP}$ = 368.8 Hz, 2H), 4.84–4.97 (m, 2H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 13.5–13.8 (m), 18.8, 19.6, 25.5, 25.6, 27.1, 27.2, 27.9, 29.5 (d, $J_{CP}$ = 28.6 Hz), 36.4–36.6 (m), 44.8, 47.9, 48.6–48.9 (m), 82.1–82.2 (m), 168.0–168.1 (m); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 19.9–20.5 (m); IR (KBr) 2956, 2880, 2394, 2360, 1726, 1474, 1391, 1369, 1284 cm$^{-1}$; HRMS EI *m/z* 284.1915. Calcd for $C_{16}H_{29}O_2P$ ($M^+$–$BH_3$) 284.1905.

**Dehydrocoupling Dimer of 1 (3).** $NiCl_2$ (38.8 mg, 10 mol%) was added to neat **1** (311.8 mg, 3 mmol) under argon atmosphere. The mixture was allowed to warm slowly and gas evolution was observed at about 80 °C. After 1 h, the mixture could no longer be stirred. It was then diluted with MeOH and passed through a selite pad to remove insoluble materials. The filtrate was concentrated, and purified by flash chromatography on silica gel to give a colorless needle (38.1 mg, 12% yield). Mp 97.8–98.6 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.44 (br q, $J_{HB}$ = 97.2 Hz, 3H), 1.18 (d, $^3J_{HP}$ = 14.3 Hz, 9H), 1.34 (d, $^3J_{HP}$ = 16.4 Hz, 9H), 3.50 (dm, $J_{HB}$ = 340 Hz, 1H), 4.75 (dm, 2H); $^{13}$C NMR (75.45 MHz, $CDCl_3$) $\delta$ 26.0 (dd, $J_{CP}$ = 32.3 Hz, $^3J_{CP}$ = 8.7 Hz), 26.5 (dd, $J_{CP}$ = 37.2 Hz, $^3J_{CP}$ = 6.9 Hz), 27.7 (d, $^2J_{CP}$ = 2.5), 28.1 (d, $^2J_{CP}$ = 1.8); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ −24.5 to −20.0 (m), −14 to −11 (m); IR (KBr) 2965, 2897, 2865, 2362,1469, 1364 cm$^{-1}$; HRMS EI *m/z* 206.1694. Calcd for $C_8H_{26}B_2P_2$ ($M^+$) 206.1696.

**X-ray Crystallographic Analysis of 3.** Lattice constants and intensity data for **3** were measured using graphite monochromated Mo $K\alpha$ radiation on a Rigaku RAXIS-II Imaging Plate diffractometer. A well-shaped triclinic crystal was obtained by recrystallization from diethyl ether: $C_8H_{26}B_2P_2$; space group $P\bar{1}$(#2); $a$ = 13.93(6) Å, $b$ = 17.6(1) Å, $c$ = 6.13(2) Å, $\beta$ = 102.5(2)°, $V$ = 1433(12) Å$^3$; $Z$ = 4, $D$ = 0.953 g/cm$^3$; $F(000)$ = 456; $\mu$(MoK$\alpha$) = 2.62 cm$^{-1}$; $\lambda$(MoK$\alpha$) = 0.71070 Å; 3450 reflections measured, 2581 observed ($I > 5.00\sigma(I)$); 217 variables; $R$ = 0.220, $R\omega$ = 0.292, GOF = 7.03.

**Synthesis of Disubstituted Derivatives of 1. *t*-Butylbis(phenylthio)phosphine (2h).** A representative experimental procedure is described for *t*-butylbis(phenylthio)phosphine.

NaH (260 mg (60% in oil), 6 mmol) was washed with dried THF three times and then dispersed in 4 mL of THF. Diphenyl disulfide (960 mg, 4.4 mmol) was added and the solution was cooled to −20 °C. Compound **1** (208 mg, 2 mmol) was slowly added and the reaction mixture was allowed to warm to 0 °C in 30 min. The mixture was stirred at this temperature until complete consuming of the starting material (TLC analysis). This solution was carefully poured onto ice/water containing HCl, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (three times). The combined extracts were washed with water and brine, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was purified by flash chromatography on silica gel eluting with hexane/ethyl acetate to give *t*-butylbis(phenylthio)phosphine as white needles (592 mg, 96% yield). Mp 44–45 °C; $^1$H NMR (300.4 MHz, $C_6D_6$) $\delta$ 1.34 (d, $^3J_{HP}$ = 13.5 Hz, 9H), 6.85–7.02 (m, , 6H), 7.48–7.60 (m, 4H); $^{13}$C NMR (75.4 MHz, $C_6D_6$) $\delta$ 27.9 (d, $^2J_{CP}$ = 16.1 Hz), 36.7 (d, $J_{CP}$ = 27.9 Hz), 127.7, 129.5, 133.9, 135.0; $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $C_6D_6$) $\delta$ 132.8 (s); IR (KBr) 3057, 2965, 2858, 1576, 1474 cm$^{-1}$; HRMS EI *m/z* 306.0680. Calcd for $C_{16}H_{19}PS_2$ ($M^+$) 306.0664.

***t*-Butyl(dimenthyloxycarbonyl)phosphine–Borane (2g).** The compound was prepared from **1** and (+)-menthyl chloroformate (2 mmol scale). After workup, the crude product was purified by flash chromatography on silica gel eluting with hexane/ethyl acetate to give **2g** as colorless oil (873 mg, 92% yield). Unfortunately, **2g** rapidly decomposed during this process, making full characterization by NMR impossible. IR (KBr) 2955, 2884, 1709, 1455, 1370 cm$^{-1}$; HRMS EI *m/z* 454.3256. Calcd for $C_{26}H_{47}O_4P_2$ ($M^+-BH_3$) 454.3312.

***t*-Butyl(dimethyl)phosphine–Borane (4a).** This compound was prepared from **1** and methyl iodide in 94% yield (10 mmol scale). After workup, the crude product was filtered by a short column on silica gel. The filtrate was concentrated on a rotary evaporator to give virtually pure *t*-butyl(dimethyl)phosphine–borane as a white solid. Mp 165.0–166.0 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.45 (br q, $J_{HB}$ = 98.2 Hz, 3H), 1.16 (d, $^3J_{HP}$ = 13.8 Hz, 9H), 1.23 (d, $^2J_{HP}$ = 9.8 Hz, 6H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 7.3 (d, $J_{CP}$ = 35.4 Hz), 24.7 (d, $^2J_{CP}$ = 2.5 Hz), 26.5 (d, $J_{CP}$ = 35.3 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 20.9 (br q, $J_{PB}$ = 64.4 Hz); IR (KBr) 2971, 2869, 2369, 1474, 1366 cm$^{-1}$; HRMS EI *m*/*z* 131.1138. Calcd for $C_6H_{17}BP$ ($M^+-H$) 131.1151.

**Dibutyl(*t*-butyl)phosphine–Borane (4b).** This compound was prepared from **1** and butyl chloride in 88% yield (2 mmol scale) and isolated as colorless oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.37 (br q, $J_{HB}$ = 96.6 Hz, 3H), 0.93 (t, $J$ = 7.2 Hz, 6H), 1.16 (d, $^3J_{HP}$ = 12.8 Hz, 9H), 1.3–1.7 (m, 12H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 13.6 , 20.4 (d, $J_{CP}$ = 20.4 Hz), 24.8 (d, $^2J_{CP}$ = 12.4 Hz), 25.8 (d), 25.9, 28.1 (d, $J_{CP}$ = 33.5 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 30.3 (br q, $J_{PB}$ = 69.3 Hz); IR (KBr) 2957, 2378, 1464, 1365 cm$^{-1}$; HRMS EI *m*/*z* 202.1837. Calcd for $C_{12}H_{27}P$ ($M^+-BH_3$) 202.1850.

***t*-Butyl(ditetradecyl)phosphine–Borane (4c).** This compound was prepared from **1** and tetradecyl chloride in 97% yield (2 mmol scale) and isolated as white pasty oil. $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.74 (br q, $J_{HB}$ = 114 Hz, 3H), 0.85 (t, $J$ = 7.0 Hz, 6H), 1.12 (d, $^3J_{HP}$ = 12.9 Hz, 9H), 1.2–1.4 (m, 44H), 1.4–1.6 (m, 8H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.1 , 20.6 (d, $J_{CP}$ = 31.0 Hz), 22.7, 23.8, 25.7, 28.1 (d, $^2J_{CP}$ = 32.9 Hz), 29.0–29.9 (m), 31.6–31.8 (m), 31.9; $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 30.3 (m, $J_{PB}$ = 69 Hz); IR (KBr) 2925, 2853, 2377, 1465, 1367 cm$^{-1}$; HRMS EI *m*/*z* 489.4970. Calcd for $C_{32}H_{67}P$ ($M^+-BH_3$) 482.4980.

**Dibenzyl(*t*-butyl)phosphine–Borane (4d).** This compound was prepared from **1** and benzyl chloride in 99% yield (2 mmol scale) and isolated as white needles. Mp 147.2–148.0 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.59 (br q, $J_{HB}$ = 104.4 Hz, 3H), 1.12 (d, $^3J_{PH}$ = 13.5 Hz, 9H), 2.8–3.1 (m, 4H), 7.2–7.3 (m, 10H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.1 , 25.7 (d), 28.9 (d, $J_{CP}$ = 27.3), 29.5 (d, $J_{CP}$ = 28.0), 126.8–126.9 (m), 128.2–128.3 (m), 130.1–130.2 (m), 133.0–133.1 (m); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 33.1–34.8 (m); IR (KBr) 3030, 2979, 2394, 1455, 1366 cm$^{-1}$; HRMS EI *m*/*z* 284.1837. Calcd for $C_{18}H_{26}BP$ ($M^+$) 284.1865.

**Derivation of *t*-Butyl(methyl)phosphine–Borane. *t*-Butyl-(menthyloxycarbonyl)methylphosphine–Borane (5, Diastereomeric Mixture).** To a stirred, cooled (−78 °C) solution of *t*-butyl(methyl)phosphine–borane (236 mg, 2 mmol) in THF (2 mL) was slowly added *n*-BuLi (1.3 mL of 1.50 M hexane solution, 2 mmol) under argon atmosphere. After 10 min, (+)-menthyl chloroformate (481 mg, 2.2 mmol) was slowly added at −78 °C. The solution was stirred for 1 h and then allowed to warm to room temperature. Iced water containing HCl was carefully added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with water and brine, dried ($Na_2SO_4$), and concentrated. The residue was purified by flash chromatography on silica gel eluting with hexane/ethyl acetate. The eluent was concentrated to give a 1:1 diastereomeric mixture of *t*-butyl(methyloxycarbonyl)methylphosphine–borane as colorless pasty oil (412 mg, 67% yield). $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.56 (br q, $J_{HB}$ = 85.0 Hz, 6H), 0.74–0.77 (m, 6H), 0.8–0.9 (m, 2H), 0.89–0.97 (m, 12H), 0.98–1.17 (m, 4H), 1.21–1.33 (m, 18H), 1.42–1.49 (m, 6H), 1.46–1.56 (m, 4H), 1.65–1.77 (m, 4H), 1.86–2.07 (m, 4H), 4.84–4.97 (m, 2H) ; $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 4.5 (d, $J_{CP}$ = 34.8 Hz), 4.7 (d, $J_{CP}$ = 34.8 Hz), 15.7, 15,9 20.7, 20.8, 21.9, 22.0, 22,9 23.1, 25.4–25.6 (m), 25.9, 26.1, 28.6 (d, $J_{CP}$ = 28.6 Hz), 28.7 (d, $J_{CP}$ = 28.6 Hz), 31.4–31.5 (m), 33.9, 34.0, 40.6, 40.8, 46.7, 47.0, 77.2, 77,4 171.3, 172.3; $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 40.4–42.4 (m); IR (KBr) 2957, 2871, 2402, 2343, 1702, 1459, 1370 cm$^{-1}$; HRMS EI *m*/*z* 299.2281. Calcd for $C_{16}H_{33}BP$ ($M^+-H$) 299.2312.

**(1*S*)-*endo*-2-Bornyl Chloroformate.** To a stirred, cooled (0 °C) solution of triphosgene (15.1 g, 50.8 mmol) in toluene (150 mL) was slowly added a solution of (−)-borneol (23.1 g, 149 mmol) and quinoline (19.3 g, 149 mmol) in toluene (150 mL) for 1 h under argon atmosphere. After 1 h, the reaction mixture was allowed to warm to 60 °C slowly and stirred for 3 h at this temperature. The reaction mixture was filtered off to remove the quinoline salt. The filtrate was concentrated and distilled under reduced pressure to give (1*S*)-*endo*-2-bornyl chloroformate as a colorless liquid (28.1 g, 87% yield). Bp 54–55 °C/0.2 mmHg; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.86 (6H), 0.87 (3H), 1.11–1.19 (m, 1H), 1.20–1.40 (m, 2H), 1.66–1.80 (m, 2H), 1.80–1.94 (m, 1H), 2.30–2.44 (m, 1H), 4.95 (dm, 1H); $^{13}$C NMR (75.45 MHz, $CDCl_3$) $\delta$ 18.7, 19.6, 26.7, 27.8, 36.0, 44.6, 48.0, 49.3, 89.3, 150.6; IR (KBr) 2958, 1777, 1171, 1151 cm$^{-1}$; HRMS EI *m*/*z* 216.0899. Calcd for $C_{11}H_{17}ClO_2$ ($M^+$) 216.0917.

**[(1*S*)-*endo*-2-Bornyloxycarbonyl](*t*-butyl)methylphosphine–Borane (6, Diastereomeric Mixture).** To a stirred, cooled (−78 °C) solution of *t*-butyl(methyl)phosphine–borane (3.76 g, 31 mmol) in THF (80 mL) was slowly added *n*-BuLi (23 mL of 1.50 M hexane solution, 34 mmol) under argon atmosphere. After 30 min, (1*S*)-*endo*-2-bornyl chloroformate (7.1 g, 33 mmol, 1.05 equivalent) in THF (25 mL) was slowly added at −78 °C and the mixture was stirred for 1 h. The mixture was allowed to warm to room temperature and stirred for 3 h. Iced water containing HCl was carefully added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined extracts were washed with water and brine, dried ($Na_2SO_4$), and concentrated. The residue was purified by flash chromatography on silica gel eluting with hexane/ethyl acetate to give a 1:1 diastereomeric mixture of bornyloxycarbonyl(*t*-butyl)methylphosphine–borane as a white solid (6.49 g, 70% yield). This compound was also obtained from one pot treatment of *t*-butylphosphine–borane in 64% yield. Mp 50–65 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.60 (br q, $J_{HB}$ = 88.6 Hz, 6H), 0.87 (3H), 0.874 (3H), 0.90 (6H), 0.91 (6H), 1.0–1.1 (m, 2H), 1.22–1.33 (m, 18H), 1.22–1.44 (m, 4H), 1.47 (d, $^2J_{HP}$ = 9.6 Hz, 6H), 1.70–1.86 (m, 4H), 1.93–2.20 (m, 2H), 5.0–5.17 (m, 2H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 4.5 (d, $J_{CP}$ = 35.4 Hz), 13.3, 13.6, 18.8, 19.6, 25.5 (m), 27.1, 27.8, 27.9, 28.6 (d, $J_{CP}$ = 28.4 Hz), 28.7 (d, $J_{CP}$ = 28.4 Hz ), 36.7, 36.8, 44.7, 44.8, 48.9, 49.2, 82.8, 83.3, 172.3 (d, $J_{CP}$ = 70.0 Hz), 172.4 (d, $J_{CP}$ = 69.5 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 40.8–43.0 (m); IR (KBr) 2956, 2880, 2378, 1704, 1475, 1368 cm$^{-1}$; HRMS EI *m*/*z* 297.2155. Calcd for $C_{16}H_{31}BP$ ($M^+-H$) 297.2155.

**($R_P$)-[(1*S*)-*endo*-2-Bornyloxycarbonyl](*t*-butyl)methylphosphine–Borane (6a, 95% de).** A solution of bornyloxycarbonyl(*t*-butyl)methylphosphine–borane (9.96 g, 33.4 mmol) in hexane (60 mL) was allowed to warm to 60 °C. The mixture was slowly cooled to 0 °C and stirred at this temperature for 3 h. The mixture was filtered and the residue recrystallized from hexane. The collected filtrates were concentrated and recrystallized 3 times. The

diastereomeric excess value of the obtained crystalline solid (3.2 g, 32%) was determined by $^1$H NMR analysis (95% de). Mp 97.6–99.0 °C; $^1$H NMR (300.4 MHz, $CDCl_3$) $\delta$ 0.60 (br q, $J_{HB}$ = 90.0 Hz, 3H), 0.87 (3H), 0.89 (3H), 0.90 (3H), 1.01–1.09 (m, 1H), 1.28 (d, $^3J_{HP}$ = 14.4 Hz, 9H), 1.27–1.43 (m, 2H), 1.47 (d, $^2J_{HP}$ = 9.8 Hz, 3H), 1.69–1.86 (m, 2H), 1.93–2.01 (m, 2H), 2.33–2.50 (m, 2H), 5.00–5.09 (m, 1H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 4.5 (d, $J_{CP}$ = 35.1 Hz), 13.6, 18.8, 19.6, 25.5 (d, $^2J_{CP}$ = 1.9 Hz), 27.1, 27.8, 28.6 (d, $J_{CP}$ = 28.6 Hz), 36.8, 44.8, 48.0, 49.0, 83.4, 172.4 (d, $J_{CP}$ = 69.5 Hz); $^{31}$P NMR (121.5 MHz, $^1$H decoupled, $CDCl_3$ ) $\delta$ 41.0–43.0 (m); IR (KBr) 2956, 2880, 2377, 1702, 1474, 1368 cm$^{-1}$; HRMS EI *m/z* 297.2143. Calcd for $C_{16}H_{31}BP$ ($M^+-H$) 297.2155.

**(*S*)-*t*-Butyl(methyl)phosphine–Borane (95% ee).** To a stirred solution of **6a** (596 mg, 2 mmol, 95% de) in $CH_3CN$(10 mL)/$CH_3OH$(3 mL) was added KOH (2.24 g, 40 mmol) in water (6 mL) at room temperature. The mixture was vigorously stirred until complete consuming of the starting material (TLC analysis, ca. 4 h). The reaction mixture was treated with 1 M HCl, and extracted with $Et_2O$. The aqueous layer was extracted with $Et_2O$. The combined extracts were washed with water and brine, dried ($Na_2SO_4$), and concentrated at low pressure (20–30 mmHg). The residue was purified by flash chromatography on silica gel eluting with hexane/ethyl acetate to give (*S*)-*t*-butylmethylphosphine–borane as a colorless solid (177 mg, 75% yield, 95% ee). The absolute configuration and ee value were determined by HPLC analysis using Chiral Daicel AD-H column (10% 2-propanol/hexane, 1 mL/min) on the corresponding 2-pyridylmethyl derivative.[6,7]

$[\alpha]_D^{20}$ +3.4 (*c* 1.18, $CHCl_3$); Other spectroscopic properties were identical to those given for *t*-butylmethylphosphine–borane.

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