Synthesis of a New Chiral Source, (1*R*,2*S*)-1-Phenylphospholane-2-carboxylic Acid, via a Key Intermediate α-Phenylphospholanyllithium Borane Complex: Configurational Stability and X-ray Crystal Structure of an α-Monophosphinoalkyllithium Borane Complex

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Abstract: A synthetic route to enantiomerically pure (1*R*,2*S*)-1-phenylphospholane-2-carboxylic acid (**1**), which is a phosphorus analogue of proline, has been established. A key step is the deprotonation–carboxylation of the 1-phenylphospholane borane complex **3** by using *s*BuLi/1,2-dipiperidinoethane (DPE). Configurational stability of the key intermediate, the amine-coordinated α-phosphinoalkyllithium borane complex **4**, was investigated by employing lithiodestannylation–carboxylation of both diastereomers of the 1-phenyl-2-trimethylstannylphospholane borane complex **7** in the presence of several kinds of amines, and as a result, **4** was found to be configurationally labile even at −100 °C. The key intermediate, the DPE-coordinated *trans*-1-phenyl-2-phospholanyllithium borane complex **9**, was isolated, and the structure was identified by X-ray crystal structure analysis. This is the first X-ray crystal structure determined for an α-monophosphinoalkyllithium borane complex. Remarkably, the alkyllithium complex is monomeric and tricoordinate at the lithium center with a slightly pyramidalized environment, and the existence of a Li–C bond (2.170 Å) has been confirmed. Moreover, ^{1}H–^{7}Li HOESY and ^{6}Li NMR analyses suggested the structure of **9** in solution as well as the existence of an equilibrium between **9**, its *cis* isomer, and the ion pair **8** at room temperature, which was extremely biased towards **9** at −100 °C. Finally, **1** was used as a chiral ligand in a palladium-catalyzed allylic substitution, and the desired product was obtained in high yield with good enantioselectivity.

Keywords: asymmetric allylic substitution · boranes · carboxylation · chiral phosphine · deprotonation · transmetalation

Introduction

The design and synthesis of chiral phosphine ligands have played significant roles in the development of efficient transition-metal-catalyzed asymmetric reactions.[1] Among them, P-stereogenic tertiary phosphines provide one of the most important and promising ligands.[2] On the other hand, proline is an efficient chiral source because it can be a ligand or a starting material of ligands for metal catalysts in asymmetric reactions,[3] and, in addition, proline itself can be an effective organocatalyst for several asymmetric transformations such as aldol, Mannich, and Michael reactions.[4] In aiming to develop a new chiral source, we designed a new type of P-stereogenic phosphine, (1*R*,2*S*)-1-phenylphospholane-2-carboxylic acid (**1**), which is a phosphorus analogue of proline and is expected to have similar steric factors and different electronic effects than proline.[5] A retrosynthetic route to compound **1** is outlined in Scheme 1, in which **1** would be obtained from its borane complex **2** by deboronation, and **2** would be obtained from the phenylphospholane borane complex **3** by deprotonation–carboxylation through a key intermediate, namely the α-monophosphinoalkyllithium borane complex **4**.

α-Monophosphinoalkyllithium borane complexes are some of the most important intermediates for the synthesis

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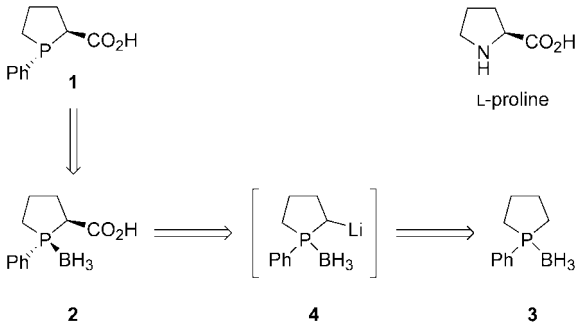


Scheme 1. Design and retrosynthesis of **1**.

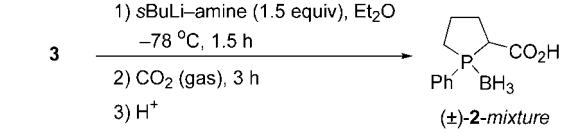
of chiral phosphines including P-stereogenic phosphine ligands.[6] To develop an efficient stereoselective synthetic route to **1**, however, deeper understanding of the stereochemical behavior and structure of the phosphinoalkyllithium borane complexes is desirable. Although there are several papers dealing with the stereochemical behavior of alkyllithium compounds such as α-oxyalkyllithium compounds and α-aminoalkyllithium compounds,[7] only one paper on that of α-phosphinoalkyllithium borane complexes at −20 °C has been reported.[8a] Furthermore, X-ray crystal structural information on these compounds is completely lacking except that of the bis(dimethylphosphino)methyllithium borane complex, which forms an independent anion (with no carbon–lithium bond) stabilized by the two adjacent $Me_2(BH_3)P$ groups.[9] Herein, we report the synthesis of a new chiral source **1**, and the configurational stability and the structure of the key intermediate α-monophosphinoalkyllithium **4**. A preliminary study on the asymmetric catalysis using **1** is also presented.

Results and Discussion

Synthesis of enantiomerically pure 1: To find an efficient method for synthesizing enantiomerically pure **1**, we first investigated deprotonation–carboxylation reactions of **3** in the absence or presence of an amine at −78 °C.[10] The reaction was conducted as follows: to an Et_2O solution of an amine, a hexane–cyclohexane solution of *s*BuLi was added at −78 °C, and after 1 h, an Et_2O solution of **3** was added. After 1.5 h, the mixture was trapped with CO_2 (gas). Accordingly (Table 1), when 1,2-dipiperidinoethane (DPE) was used as the ligand for lithium, the 1-phenylphospholane-2-carboxylic acid borane complex, (±)-**2**-*mixture* (a mixture of the two diastereomers), was obtained in high yield; however, the diastereoselectivity was low (Table 1, entry 3).[11] The use of different amines did not affect the diastereoselectivity.

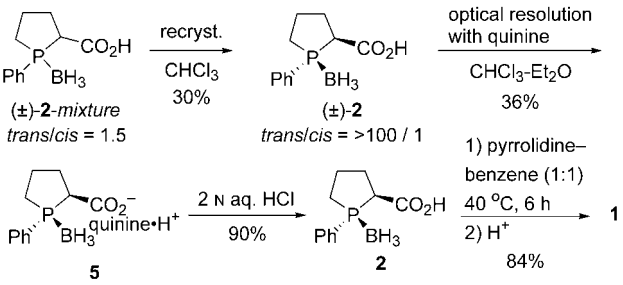
In spite of extensive efforts, it was revealed at this stage that the diastereoselective synthesis of the *trans*-1-phenylphospholane-2-carboxylic acid borane complex ((±)-**2**) was difficult to achieve. We then tried to obtain diastereomerically pure material by fractional recrystallization. Fortunately, (±)-**2** (*trans*/*cis* = >100/1) was obtained by simple recrystallization from $CHCl_3$ (Scheme 2). The relative stereochemistry was determined by X-ray structure analysis of (±)-**2**.[12]

Table 1. Deprotonation–carboxylation of **3**.



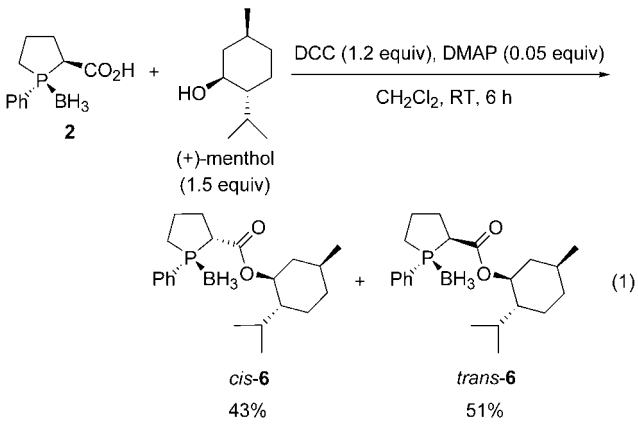
Entry	Amine[a]	Yield [%]	*trans*:*cis*[b]
1	–	39	1.6:1
2	TMEDA	61	1.6:1
3	DPE	91	1.5:1
4	PMDETA	41	1.7:1
5	HMTETA	25	1.6:1

[a] Abbreviations: TMEDA = tetramethylethylenediamine; DPE = 1,2-dipiperidinoethane; PMDETA = pentamethyldiethylenetriamine; HMTETA = hexamethyltriethylenetetramine. [b] Determined by ^1H NMR analysis after converting to the corresponding methyl esters.



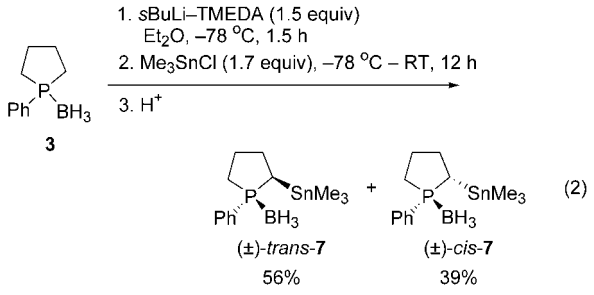
Scheme 2. Synthesis of optically pure **1**.

Furthermore, enantiomerically pure **2** was obtained after optical resolution with quinine in good yield. Esterification with (+)-menthol was performed to determine the absolute configuration of **2** ([Eq. (1); DCC = dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine]). Although significant epimerization occurred at the asymmetric carbon



center, X-ray crystal analysis of *cis*-**6** revealed the 1*R*,2*S* configuration of **2**.[12] The deboronation reaction of **2** proceeded smoothly in the presence of pyrrolidine to afford enantiomerically pure **1**.[13] We have thus established a synthetic route to enantiomerically pure **1**, and it is noted that this procedure is easily applicable to a large-scale preparation of the new chiral source (Scheme 2).

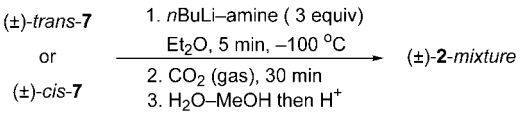
Configurational stability and structure of α-monophosphinoalkyllithium 4: To clarify the origin of the diastereoselectivity in the deprotonation–carboxylation of **3**, we next investigated the configurational stability of the key intermediate **4.** The two diastereomers of **4** would be generated from the corresponding 2-trimethylstannyl derivatives **7** by tin–lithium transmetalation (lithiodestannylation).[14] The preparation of (±)-**7** is outlined in Equation (2). Deprotonation



of **3** with *s*BuLi–tetramethylethylenediamine (TMEDA) followed by trapping with trimethyltin chloride gave (±)-*trans*-**7** and (±)-*cis*-**7**. The relative configuration was determined by X-ray crystal structure analysis of (±)-*cis*-**7**.[12]

Lithiodestannylation–carboxylation of (±)-*trans*-**7** and (±)-*cis*-**7** was conducted as follows: to an Et_2O solution of **7**, a hexane solution of *n*BuLi was added in the absence or presence of an amine at −78 °C or −100 °C. After 5 min, the mixture was trapped with CO_2 (gas). Accordingly (Table 2),

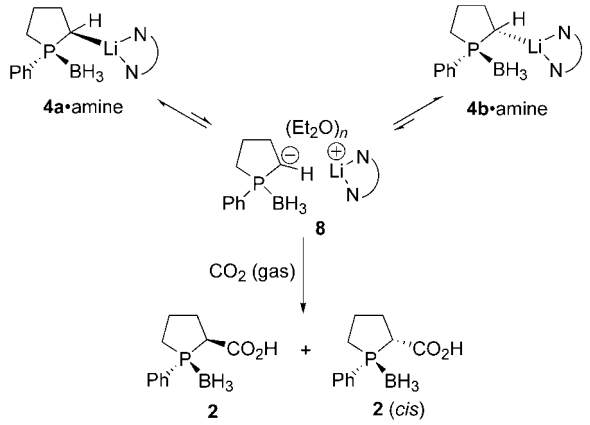
Table 2. Lithiodestannylation–carboxylation of **7**.



Entry	Substrate	Amine[a]	Yield [%]	*trans*:*cis*[b]
1[c]	*trans*-**7**	–	41	1.6:1
2	*trans*-**7**	TMEDA	79	1.5:1
3	*trans*-**7**	DPE	19	1.7:1
4	*trans*-**7**	PMDETA	79	1.6:1
5	*trans*-**7**	HMTETA	80	1.7:1
6[c]	*cis*-**7**	–	8	1.7:1
7	*cis*-**7**	TMEDA	82	1.5:1
8	*cis*-**7**	DPE	11	1.6:1
9	*cis*-**7**	PMDETA	78	1.6:1
10	*cis*-**7**	HMTETA	83	1.7:1

[a] Abbreviations see Table 1, footnote [a]. [b] Determined by ^1H NMR analysis after converting to the corresponding methyl esters. [c] The reaction was performed at −78 °C.

the carboxylic acid borane complex (±)-**2**-*mixture* was obtained not as a single diastereomer, but as a mixture. Stannanes (±)-*trans*-**7** and (±)-*cis*-**7** gave almost the same *trans*/*cis* ratios. This result indicates that both diastereomers of **4** are configurationally labile even at −100 °C, contrary to many other organolithium compounds, and in equilibrium presumably via ion pair **8** (Scheme 3).[15] It is also worthwhile to mention that, although addition of some different amines improved the yields,[16] the structure of the amine ligands did not affect the diastereoselectivity of the reactions, similar to the examples in Table 1.



Scheme 3. The stereochemical behavior.

Definitive structural information on the lithiated species was obtained from the X-ray crystal structure analysis of the DPE-coordinated *trans*-1-phenyl-2-phospholanyllithium borane complex **9**, which was recrystallized from Et_2O–hexane (Figure 1).[17] In the crystal structure, the tetrahedral carbanionic carbon is directly connected to lithium (Li-C-2 2.170 Å) through a covalent bond, and **9** adopts a *trans* configuration (Li and Ph are *trans* to each other). Interestingly, **9** is monomeric and contains a tricoordinate lithium center with a slightly pyramidalized environment (angle sum at Li 351.9°) presumably due to steric constraints.[18,19] It is noted

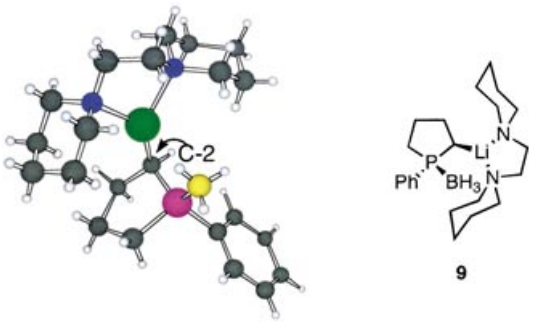


Figure 1. X-ray crystal structure of **9**. P: pink; B: yellow; Li: green; N: blue.

that the structure contrasts with the previously reported crystal structure of a bis(dimethylphosphino)methyllithium borane complex, in which no carbon–lithium bond exists.[9a,b]

To understand the stereochemical behavior of **4** in solution, crystals of **9** were dissolved in $[D_{10}]Et_2O$, and ^1H, ^{13}C, ^{31}P, ^6Li, and ^7Li NMR studies of the solution were performed.[20] The ^1H–^7Li HOESY spectrum[21] of **9** showed strong NOE enhancements of the ^7Li nuclei by the proton at C-2 ($\delta = 0.32$ ppm, d, $J = 4.4$ Hz), BH_3 ($\delta = 0.44$–0.90, m), and some on the DPE ligand at room temperature (Figure 2). Similar strong NOE enhancements were observed at −100 °C. This result strongly suggests the presence of the Li-C−2 bond and the *cis* arrangement of BH_3 and Li as seen in **9**. On the other hand, the ^6Li NMR spectrum of the sample prepared from ^6Li-labeled **9** showed one singlet ($\delta = 0.81$ ppm) at room temperature (Figure 3). At lower temperatures it shifted downfield, broadened, and finally split into a doublet (1.16 ppm, $^2J_{^6Li^{31}P} = 2.3$ Hz).[22] Although we have not obtained conclusive evidence, all these results are consistent with the assumption that a fast equilibrium exists between **4** and the ion pair **8** at room temperature (Scheme 3),[23] and that at −100 °C the equilibrium becomes slower on the NMR time scale and is extremely biased towards the *trans* isomer **4a**.

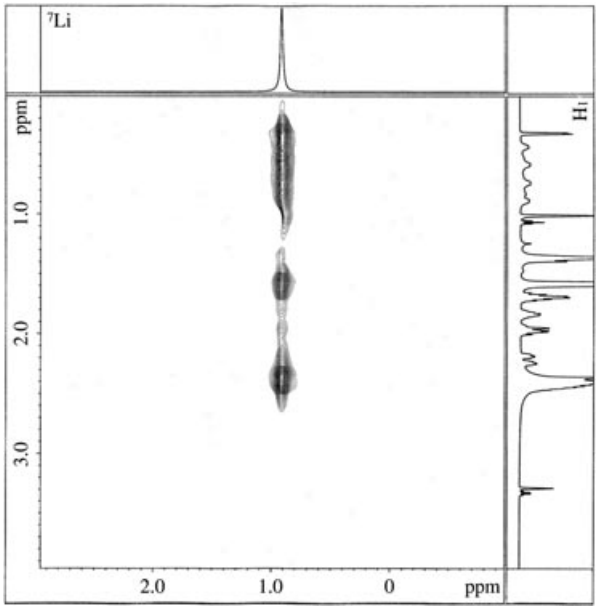


Figure 2. ^1H–^7Li HOESY of **9** in $[D_{10}]Et_2O$.

From these results we assume the mechanism of the carboxylation of **4** as follows. Although there is an equilibrium between **4a**, **4b**, and **8** and the equilibrium is biased to **4a** at low temperature in solution, **4a** and **4b** could react with CO_2 at a different rate to give the ratios observed, but more reasonably, CO_2 would react better with the more reactive independent trigonal anion **8**, and thereby, the different bulkiness of the two substituents (Ph and BH_3 groups) at the phosphorus center would affect the diastereoselectivity.[24] Although further studies are needed to obtain more definitive evidence, this mechanism is in accord with the constant diastereoselectivity regardless of the amines used.

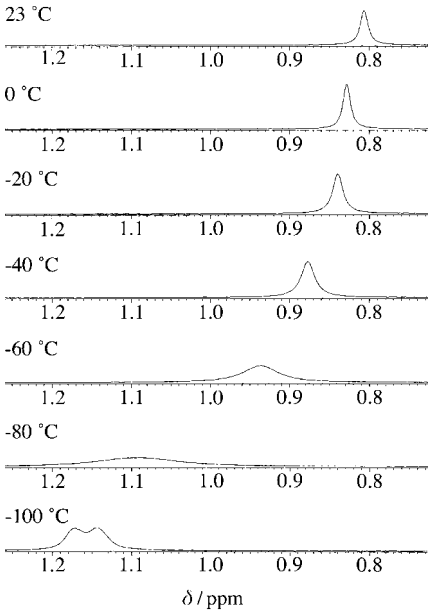
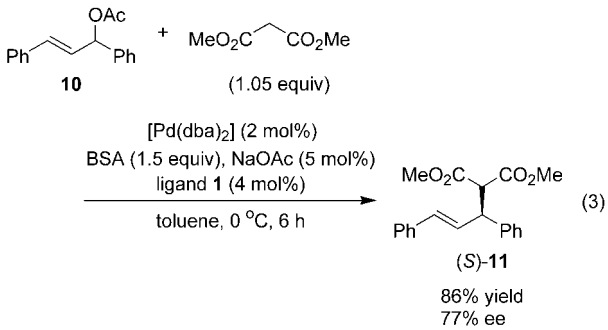


Figure 3. Variable-temperature ^6Li NMR of ^6Li-**9** in $[D_{10}]Et_2O$.

Application of 1 for asymmetric catalysis: With enantiomerically pure **1** in hand, we applied it to asymmetric catalysis. A preliminary study revealed that when **1** was used in the palladium-catalyzed allylic substitution[1a,b] of **10** in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and sodium acetate, the desired product **11** was obtained in high yield with relatively good enantioselectivity ([Eq. (3)]; dba = dibenzylideneacetone). Although further optimization is needed, this result indicates that **1** can construct an effective asymmetric environment around the palladium atom, and will be a useful chiral source.



(3)

Conclusion

A synthetic route to the new chiral source **1** has been established. It has been also shown that the 1-phenyl-2-phospholanyllithium borane complex **4** is configurationally labile

even at −100 °C. Furthermore, the crystal structure of the DPE-coordinated phospholanyllithium borane complex **9** has been determined by X-ray analysis, showing the existence of a Li–C bond. This is the first X-ray crystal structure of an α-monophosphinoalkyllithium borane complex, and interestingly, the complex is monomeric and contains a three-coordinate lithium center. Furthermore, ^{1}H–^{7}Li HOESY and ^{6}Li NMR analyses of **9** were conducted. It was suggested that a DPE-coordinated phospholanyllithium borane complex such as **9** also existed in solution, and that an equilibrium between **4** and the ion pair **8** existed at room temperature and was biased towards the *trans* isomer **4a** at −100 °C. This work provides valuable stereochemical and structural information towards gaining a better understanding of the chemistry of α-phosphinoalkyllithium borane complexes, and will contribute to the development of useful methods for the synthesis of chiral phosphines. Finally, **1** was successfully used as a ligand in a palladium-catalyzed allylic substitution reaction.

Experimental Section

General methods: Tetramethylsilane ($\delta=0$) was used as an internal standard for the ^{1}H NMR spectra and $CDCl_3$ ($\delta=77.0$) for the ^{13}C NMR spectra. H_3PO_4 ($CDCl_3$ solution) was used as an external standard for the ^{31}P NMR spectra. LiCl (H_2O solution) was used as an external standard for the ^{6}Li and ^{7}Li NMR spectra. [D_{10}]Et_2O distilled from sodium benzophenone ketyl was used as a solvent for the NMR study. Commercially available dry Et_2O was used as a solvent for the deprotonation–carboxylation, for the lithiodestannylation–carboxylation, and for the preparation of the 1-phenyl-2-trimethylstannylphospholane borane complex.

Preparation of the 1-phenyl-2-phospholane borane complex 3: 1,4-Dibromobutane (48 mL, 0.40 mol) was slowly added to a stirred suspension of Mg (24 g, 0.99 mol) in THF at 0 °C under an argon atmosphere over a period of 30 min, and the mixture was allowed to warm to room temperature. After the mixture was stirred for 4 h, the flask was immersed in an ice-bath and dichlorophenylphosphine (0.40 mol in THF (100 mL)) was added over 30 min. The ice-bath was removed and the mixture was stirred for 12 h at ambient temperature. The flask was again immersed in an ice-bath. After BH_3–THF complex (400 mL of 1.0 M THF solution, 0.40 mol) was added over 1 h, the ice-bath was removed and the mixture was stirred for 12 h. The flask was immersed in an ice-bath, and 1 N aq. HCl (100 mL) was slowly added. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The combined extracts were washed with brine, dried over Na_2SO_4, concentrated, and purified by column chromatography (SiO_2, hexane/AcOEt = 10:1–6:1). Distillation under reduced pressure (b.p. 157–160 °C/6 mmHg) gave **3** (29 g, 40 %). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.81$ (br q, $J=96.6$ Hz, 3H), 1.97–2.09 (m, 8H), 7.41–7.49 (m, 3H), 7.69–7.72 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=26.74$ (d, $J=37.2$ Hz), 27.42, 128.69 (d, $J=9.0$ Hz), 130.96 (d, $J=2.5$ Hz), 131.16 (d, $J=43.8$ Hz), 131.27 ppm (d, $J=8.2$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=27.82$ ppm (q, $J=51.3$ Hz); IR (KBr): $\tilde{\nu}=2930$, 2871, 2374, 1635, 1438, 1111, 1054 cm^{-1}; MS (ESI): *m/z*: 179 ([$M+H^+$]); elemental analysis calcd (%) for $C_{10}H_{16}BP$: C 67.47, H 9.06; found: C 67.48, H 9.17.

Typical experimental procedure for the deprotonation–carboxylation of 3 in Et_2O: *s*BuLi (0.87 M in hexane–cyclohexane solution, 1.5 mmol) was added at −78 °C over 5 min to a stirred solution of an amine (1.5 mmol) in Et_2O (2 mL). After 60 min, **3** (1 mmol in Et_2O (2 mL)) was added within 5 min, and then after 90 min, CO_2 (gas) was bubbled through the mixture for 3 h. After addition of aqueous 1 N HCl (5 mL), the mixture was extracted with CH_2Cl_2 three times and purified by column chromatography (SiO_2, hexane/AcOEt = 6:1 to 1:1, then AcOEt). The yields and the diastereomer ratios of 1-phenylphospholane-2-carboxylic acid ((±)-**2**-*mixture*) are listed in Table 1. The diastereomeric ratio was determined by ^{1}H NMR spectroscopy after converting **2** to the corresponding methyl ester. The relative stereochemistry was determined by X-ray structure analysis of the *trans*-1-phenylphospholane-2-carboxylic acid borane complex ((±)-**2**), which was obtained by recrystallization of (±)-**2**-*mixture* from $CHCl_3$. *trans*-1-Phenylphospholane-2-carboxylic acid borane complex ((±)-**2**): white solid; m.p. 131.0–131.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.77$ (br q, $J=116$ Hz, 3H), 1.90–2.02 (m, 1H), 2.14–2.39 (m, 5H), 3.26–3.33 (m, 1H), 7.46–7.55 (m, 3H), 7.74–7.79 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=26.24$ (d, $J=1.7$ Hz), 26.38 (d, $J=37$ Hz), 29.96 (d, $J=5$ Hz), 46.45 (d, $J=25.5$ Hz), 129.13 (d, $J=10.7$ Hz), 129.82 (d, $J=46$ Hz), 131.38 (d, $J=9$ Hz) 131.73 (d, $J=2.5$ Hz), 175.39 ppm (d, $J=3.2$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=38.72$ ppm (d, $J=47.4$ Hz); IR (KBr): $\tilde{\nu}=2940$, 2378, 1707, 1422, 1067 cm^{-1}; MS (ESI): *m/z* 245 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{11}H_{16}BO_2P$: C 59.50, H 7.26; found: C 59.41, H 7.34.

Methyl 1-phenylphospholane-2-carboxylate borane complex: Me_3SiCHN_2 (0.75 mmol, 2 M hexane solution) was added at 0 °C to a stirred solution of (±)-**2**-*mixture* (0.5 mmol) in MeOH–benzene (4.5 mL). After 10 min, the reaction mixture was diluted with MeOH (10 mL) and then further stirred until the color completely disappeared. The crude ester was concentrated, and was purified by PTLC (SiO_2, hexane/AcOEt = 4:1). Yield: 96 % (*trans*:*cis* = 1.5:1). The diastereomer ratio was determined by ^{1}H NMR spectroscopy (*trans*: $\delta=3.74$, 3H, s; *cis*: $\delta=3.10$, 3H, s).

***trans*-Form**: white solid; m.p. 80.1–81.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.71$ (q, $J=102$ Hz, 3H), 1.93–2.38 (m, 6H), 3.24–3.34 (m, 1H), 3.74 (s, 3H), 7.45–7.56 (m, 3H), 7.73–7.79 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=26.26$, 26.48 (d, $J=36.6$ Hz), 29.89 (d, $J=5.0$ Hz), 46.04 (d, $J=26.0$ Hz), 52.12, 128.99 (d, $J=9.9$ Hz), 130.01 (d, $J=46.6$ Hz), 131.24 (d, $J=9.4$ Hz), 131.54 (d, $J=2.5$ Hz), 170.26 ppm (d, $J=3.1$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=39.31$ ppm (d, $J=59.5$ Hz); IR (KBr): $\tilde{\nu}=3064$, 2959, 2937, 2922, 2365, 2334, 1746, 1439, 1205, 1152, 1066, 1051 cm^{-1}; MS (ESI): *m/z* 259 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{12}H_{18}BO_2P$: C 61.06, H 7.69; found: C 60.79, H 7.67.

***cis*-Form**: white solid; m.p. 76.1–77.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.95$ (q, $J=94.7$ Hz, 3H), 1.98–2.46 (m, 6H), 3.10 (s, 3H), 3.31–3.39 (m, 1H), 7.42–7.55 (m, 3H), 7.67–7.74 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.77$ (d, $J=36.0$ Hz), 26.02, 30.13 (d, $J=3.1$ Hz), 46.01 (d, $J=26.63$ Hz), 51.60, 126.67 (d, $J=44.1$ Hz), 128.49 (d, $J=9.4$ Hz), 131.93 Hz (d, $J=2.5$ Hz), 132.57 Hz (d, $J=9.3$ Hz), 170.15 ppm (d, $J=5.0$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=36.5$ ppm (d, $J=60.8$ Hz); IR (KBr): $\tilde{\nu}=$ 2959, 2390, 2365, 2332, 1735, 1434, 1202, 1061 cm^{-1}; MS (ESI): *m/z* 259 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{12}H_{18}BO_2P$: C 61.06, H 7.69; found: C 60.97, H 7.79.

Enantiomeric resolution with quinine: Quinine (54.27 g, 167.3 mmol) and Et_2O (300 mL) were added at room temperature to a stirred solution of *trans*-1-phenylphospholane-2-carboxylic acid (±)-**2** (37.14 g, 167.3 mmol) in $CHCl_3$ (600 mL). The solution was stirred at room temperature for 3 h and then at 0 °C for 2 h. The white precipitate was collected and dissolved in $CHCl_3$, and Et_2O ($CHCl_3/Et_2O \approx 2:1$) was then added. The solution was stirred at room temperature for 3 h and then at 0 °C for 2 h, and the resulting white precipitates were collected. After repeating this dissolution–precipitation–collection procedure four more times, a white cotton-like solid **5** was obtained in 36 % yield (33.21 g). $[\alpha]_D^{25}=-143.6°$ ($c=1.00$ in $CHCl_3$).

(1*R*,2*S*)-1-Phenylphospholane-2-carboxylic acid borane complex (2): To a suspension of the quinine salt **5** (3.32 g, 6.1 mmol) in CH_2Cl_2 was added 2 N aq. HCl (25 mL), and the mixture was stirred for 30 min. The product was extracted with CH_2Cl_2, concentrated, and purified by column chromatography (SiO_2, hexane/AcOEt = 2:1 to 1:1) to afford **2** (1.22 g, 90 % yield, 100 % *ee*). The *ee* was determined by chiral HPLC (chiralpak AD, hexane/2-PrOH = 100:1, 1.0 mL min^{-1}, $RT_{1R,2S}=30$ min; $RT_{1S,2R}=25$ min) after converting to the methyl ester. White solid; m.p. 112.5–113.5 °C; $[\alpha]_D^{27}=-163.6°$ ($c=1.12$ in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.73$ (br d, $J=88.7$ Hz, 3H), 1.90–2.37 (m, 6H), 3.23–3.33 (m, 1H), 7.45–7.55 (m, 3H), 7.72–7.78 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=26.22$ (d, $J=1.9$ Hz), 26.25 (d, $J=37.2$ Hz), 29.95 (d, $J=5.6$ Hz), 46.64 (d, $J=$

25.4 Hz), 129.08 (d, $J=10.0$ Hz), 129.77 (d, $J=46.6$ Hz), 131.33 (d, $J=10.0$ Hz), 131.68 (d, $J=2.4$ Hz), 175.49 ppm (d, $J=3.8$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=38.77$ ppm (d, $J=40.1$ Hz); IR (KBr): $\tilde{\nu}=$ 2952, 2398, 2355, 1699, 1418, 1300, 1063 cm^{-1}; MS (ESI): *m/z*: 245.1 ([$M+Na^+$]); elemental analysis calcd for $C_{11}H_{16}BO_2P$: C 59.50, H 7.26; found: C 59.33, H 7.24.

Methyl (*1R,2S*)-1-phenylphospholane-2-carboxylate borane complex: Colorless prisms; m.p. 109–111 °C; $[\alpha]_D^{28}=-166.6°$ ($c=1.17$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.70$ (q, $J=107.1$ Hz, 3H), 1.95–2.04 (m, 1H), 2.12–2.38 (m, 5H), 3.23–3.34 (m, 1H), 3.76 (s, 3H), 7.45–7.56 (m, 3H), 7.73–7.79 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=26.37$ (d, $J=1.3$ Hz), 26.55 (d, $J=36.6$ Hz), 29.97 (d, $J=5.0$ Hz), 46.14 (d, $J=26.0$ Hz), 52.27, 129.06 (d, $J=9.9$ Hz), 130.11 (d, $J=46.6$ Hz), 131.32 (d, $J=9.4$ Hz), 131.61 (d, $J=2.5$ Hz), 170.36 ppm (d, $J=3.1$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=39.23$ ppm (d, $J=60.8$ Hz); IR (KBr): $\delta=3064$, 2959, 2875, 2373, 1741, 1438, 1206 cm^{-1}; MS (ESI): *m/z*: 259.1 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{12}H_{18}BO_2P$: C 61.06, H 7.69; found: C 61.07, H 7.77.

Determination of the absolute configuration of 2: The absolute configuration of **2** was determined by X-ray crystal structure analysis of the (+)-menthyl ester of the (1*R*,2*R*)-1-phenylphospholane-2-carboxylic acid borane complex *cis*-**6**. (+)-Menthol (234.4 mg, 1.5 mmol), DMAP (7.8 mg, 0.05 mmol) in CH_2Cl_2 (5 mL), and DCC (247.4 mg, 1.2 mmol) were added to a solution of (1*R*,2*S*)-1-phenylphospholane-2-carboxylic acid borane complex **2** (222.0 mg, 1 mmol). The mixture was stirred for 6 h at room temperature, quenched with 1 N aq. HCl (3 mL), extracted with CH_2Cl_2, concentrated, and purified by PTLC (SiO_2, hexane/AcOEt = 10:1) to afford *trans*-**6** (51%) and *cis*-**6** (43%).

(+)-Menthyl (*1R,2S*)-1-phenylphospholane-2-carboxylate borane complex (*trans*-6): More polar than *cis*-**6**, colorless needles; m.p. 94.5–95.5 °C; $[\alpha]_D^{20}=+69.9°$ ($c=1.00$ in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.30$–2.36 (m, 27H), 3.16–3.26 (m, 1H), 4.69–4.78 (m, 1H), 7.45–7.56 (m, 3H), 7.73–7.80 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=16.37$, 20.73 , 22.01, 23.46, 26.07 (d, $J=23.61$ Hz), 26.33 (d, $J=36.6$ Hz), 30.10 (d, $J=5.6$ Hz), 31.47, 34.19, 40.85, 46.24 (d, $J=26.7$ Hz), 47.04, 75.81, 128.97 (d, $J=11.3$ Hz), 130.58 (d, $J=49.3$ Hz), 131.31 (d, $J=9.4$ Hz), 131.42 (d, $J=2.4$ Hz), 169.24 ppm (d, $J=3.1$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=37.17$ ppm (d, $J=52.3$ Hz); IR (KBr): $\tilde{\nu}=2957$, 2872, 2397, 2360, 1724, 1443 cm^{-1}; MS (ESI): *m/z* 383.2 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{21}H_{34}BO_2P$: C 70.01, H 9.51; found: C 69.82, H 9.29.

(+)-Menthyl (*1R,2R*)-1-phenylphospholane-2-carboxylate borane complex (*cis*-6): Less polar than *trans*-**6**, colorless needles; m.p. 128.2–128.3 °C; $[\alpha]_D^{20}=+32.3°$ ($c=1.00$ in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.20$–2.39 (m, 27H), 3.24–3.33 (m, 1H), 4.23–4.31 (m, 1H), 7.43–7.51 (m, 3H), 7.72–7.79 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=15.46$, 20.87, 21.89, 22.70, 25.23 (d, $J=7.5$ Hz), 27.78 (d, $J=36.0$ Hz), 31.20, 31.77 (d, $J=1.9$ Hz), 33.95, 40.42, 46.23, 46.54 (d, $J=27.3$ Hz), 127.18 (d, $J=43.5$ Hz), 128.68 (d, $J=10.0$ Hz), 131.97 (d, $J=2.5$ Hz), 133.23 (d, $J=10.0$ Hz), 169.13 ppm (d, $J=3.7$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=35.24$ ppm (d, $J=55.9$ Hz); IR (KBr): $\tilde{\nu}=2957$, 2863, 2397, 1716, 1439 cm^{-1}; MS (ESI): *m/z*: 383.2 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{21}H_{34}BO_2P$: C 70.01, H 9.51; found: C 69.88, H 9.30.

(1*R*,2*S*)-1-Phenylphospholane-2-carboxylic acid (1): Pyrrolidine (8 mL) was added to a solution of (1*R*,2*S*)-1-phenylphospholane-2-carboxylic acid borane complex **2** (0.90 g, 4.0 mmol) in benzene (8 mL). The solution was stirred for 6 h at 40 °C, and concentrated, and the residue was dissolved in CH_2Cl_2 (2 mL). 1 N aq. HCl (15 mL) was added to decompose the pyrrolidine–borane complex, and then the product was extracted with CH_2Cl_2 and purified by column chromatography (SiO_2, hexane/AcOEt = 1:1) to afford **1** (84%). White solid; m.p. 69.8–69.9 °C; $[\alpha]_D^{28}=-120.5°$ ($c=0.60$ in EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=1.72$–2.26 (m, 6H), 3.10–3.16 (m, 1H), 7.25–7.52 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=26.80$ (d, $J=14.26$ Hz), 28.69 (d $J=3.77$ Hz), 31.16, 48.97 (d, $J=21.1$ Hz), 128.09, 128.55 (d, $J=5.6$ Hz), 130.32 (d, $J=16.2$ Hz), 140.07 (d, $J=24.8$ Hz), 182.42 ppm (q, $J=16.8$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=9.72$ ppm; IR (KBr): $\tilde{\nu}=3184$, 2945, 1718, 1433, 1142 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{11}H_{13}O_2P$ ([$M+H^+$]) 209.0731, found 209.0735.

Preparation of 1-phenyl-2-trimethylstannylphospholane borane complex (7): To a stirred solution of TMEDA (11.89 g, 102 mmol) in Et_2O, *s*BuLi (115.7 mL of 0.88 M hexane–cyclohexane solution, 102 mmol) was added at −78 °C, and then after 1 h, **3** (12.14 g in 130 mL of Et_2O) was added. After 1.5 h, trimethylstannyl chloride (23.10 g in Et_2O (70 mL)) was added, and the mixture was further stirred for 12 h and allowed to warm to room temperature slowly. Then, 1 N aq. HCl (200 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The combined extracts were washed with water twice, dried over Na_2SO_4, concentrated, and purified by column chromatography (SiO_2, hexane/Et_2O = 10:1–6:1). The two diastereomers were separated by fractional recrystallization (*trans*-**7** from hexane first, *cis*-**7** from Et_2O), followed by the column chromatography of the mother liquor (SiO_2, hexane/Et_2O = 50:1). Yields: 56% (*trans*-**7**), 39% (*cis*-**7**).

***trans*-1-Phenyl-2-trimethylstannylphospholane borane complex (*trans*-7)**: colorless prisms; m.p. 90.5–90.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 0.11–1.30 (m, 13H), 1.72–2.45 (m, 6H), 7.40–7.50 (m, 3H), 7.69–7.77 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-8.37$, 22.40 (d, $J=18.0$ Hz), 27.48 (d, $J=34.1$ Hz), 28.79 (d, $J=2.5$ Hz), 31.92 (d, $J=1.9$ Hz), 128.70 (d, $J=9.9$ Hz), 130.81 (d, $J=2.5$ Hz), 131.41 (d, $J=9.4$ Hz), 133.08 ppm (d, $J=42.8$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=32.83$ (q, $J=65.6$ Hz); IR (KBr): $\tilde{\nu}=2952$, 2373, 1436, 1059 cm^{-1}; MS (ESI): *m/z*: 363 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{13}H_{24}BPSn$: C 45.81, H 7.10; found: C 45.59, H 7.15.

***cis*-1-Phenyl-2-trimethylstannylphospholane borane complex (*cis*-7)**: colorless prisms; m.p. 103.6–104.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ −0.17 (s, 9H), 0.38–1.37 (m, 4H), 1.63–1.85 (m, 2H), 2.03–2.41 (m, 4H), 7.37–7.49 (m, 3H), 7.65–7.72 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-9.77$, 23.51 (d, $J=23.6$ Hz), 26.50 (d, $J=34.7$ Hz), 28.53 (d, $J=$ 1.9 Hz), 32.58, 128.59 (d, $J=9.3$ Hz), 131.21 (d, $J=2.5$ Hz), 132.32 (d, $J=$ 9.3 Hz), 132.34 ppm (d, $J=47.2$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$): $\delta=$ 34.75 ppm (q, $J=36.2$ Hz); IR (KBr): $\tilde{\nu}=3049$, 2970, 2945, 2858, 2370, 2332, 1437, 1061 cm^{-1}; MS (ESI): *m/z*: 363 ([$M+Na^+$]); elemental analysis calcd (%) for $C_{13}H_{24}BPSn$: C 45.81, H 7.10; found: C 45.71, H 7.02.

Typical experimental procedure for the lithiodestannylation–carboxylation in Et_2O: *n*BuLi (1.49 M hexane solution, 1.5 mmol) was added to a stirred solution of an amine (1.5 mmol) in Et_2O (4 mL) at −100 °C over 5 min. After 5 min, 1-phenyl-2-trimethylstannylphospholane borane complex **7** (0.5 mmol in 5 mL of Et_2O solution) was added over 5 min, and then after 5 min CO_2 (gas) was bubbled through the mixture for 30 min. H_2O–MeOH (1:1, 5 mL) followed by 1 N aq. HCl (5 mL) were added. The mixture was extracted with CH_2Cl_2 three times, and purified by PTLC (SiO_2, hexane/Et_2O = 20:1, then hexane/AcOEt = 1:1). The yields and the diastereomer ratios of **2**-*mixture* are listed in Table 2.

Preparation of the single crystals of DPE-coordinated *trans*-1-phenyl-2-phospholanyllithium (9): *s*BuLi (0.87 M hexane–cyclohexane solution, 1.53 mmol) was added at −78 °C to a stirred solution of 1,2-dipiperidinoethane (DPE, 0.33 g, 1.70 mmol) in Et_2O (2 mL). After 30 min, **3** (1.13 mmol in Et_2O (2 mL)) was added, and the reaction mixture became turbid yellow over 1.5 h. After warming to about 40 °C, the turbid solution became clear, and the mixture was filtered through a glass filter (G4). After about 12 h at −48 °C, light yellow crystals appeared. The light yellow crystals were washed with Et_2O and then hexane (twice), and were stored in a mineral oil. **9**: ^{1}H NMR (600 MHz, $[D_{10}]Et_2O$, 0.147 M): $\delta=0.32$ (d, $J=4.4$ Hz, 1H), 0.80 (q, $J=250$ Hz, 3H), 1.37 (s, 4H), 1.58 (t, $J=5.5$ Hz, 8H), 1.66–1.72 (m, 2H), 1.82–1.85 (m, 1H), 1.95–2.00 (m, 1H), 2.17–2.25 (m, 1H), 2.37–2.47 (m, 13H), 7.10–7.17 (m, 3H), 7.57–7.60 ppm (m, 2H); ^{13}C NMR (125 MHz, $[D_{10}]Et_2O$, 0.147 M): $\delta=$ 13.8, 25.07, 26.10, 27.37 (d, $J=2.1$ Hz), 30.55 (d, $J=43.39$ Hz), 34.73 (d, $J=5.1$ Hz), 56.16, 57.00, 128.02 (d, $J=7.3$ Hz), 128.45 (d, $J=2.1$ Hz), 131.29 ppm (d, $J=8.3$ Hz), another signal of a carbon was covered by the other's signal; ^{31}P NMR (122 MHz, $[D_{10}]Et_2O_0$): $\delta=28.67$ ppm (q, $J=$ 91.1 Hz); ^{6}Li NMR (88 MHz, $[D_{10}]Et_2O$, 0.0938 M): $\delta=0.81$ (rt), 1.16 ppm ($^2J(^6Li,^{31}P)=2.3$ Hz, −100 °C); ^{7}Li NMR (233 MHz, $[D_{10}]Et_2O$, 0.147 M): $\delta=0.91$ (s, rt), 1.22 ppm (s, −100 °C). ^{6}Li-labeled **9** was prepared by using *s*Bu^{6}Li (0.66 M hexane solution) instead of *s*BuLi according to the same procedure.

Typical experimental procedure for the palladium-catalyzed allylic substitution in toluene: Dimethylmalonate (0.06 mL, 0.525 mmol) was added to a mixture of 1,3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol), [Pd(dba)$_2$] (5.8 mg, 0.01 mmol), chiral phosphine **1** (4.2 mg, 0.02 mmol), and sodium acetate (2.1 mg, 0.025 mmol) in toluene (1 mL). The mixture was stirred for 5 min at room temperature, further stirred for 5 min at 0 °C, and then BSA (185 μL, 0.75 mmol) was added. After the reaction mixture had been stirred for 6 h at 0 °C, the reaction was quenched with water (2 mL), and the product was extracted with CH_2Cl_2 and purified by PTLC (SiO_2, hexane/AcOEt = 6:1). The *ee* was determined by chiral HPLC, and the absolute configuration was determined by comparison of the elution order of the chiral HPLC assay with literature values (chiralpak AD, hexane/2-PrOH = 19:1, 1.0 mL min^{-1}).[25] Yield: 86 %, 77 % *ee* (*S*).

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[10] Although we previously reported an asymmetric synthesis of **2** using sparteine as a chiral amine,[5] this method was found to be unsuitable for practical synthesis because of the low yield and difficulty in purification.

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[12] CCDC-240905 ((±)-**2**), CCDC-240906 ((±)-*cis*-**7**), CCDC-240907 (*cis*-**6**), and CCDC-227521 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] The deboronation of a P-stereogenic phosphine borane complex has been proven to proceed in a stereospecific manner with retention of the configuration.[6c] Furthermore, ^{13}C NMR and ^{31}P NMR spectra only gave one set of signals, indicating that no epimerization occurred during the deboronation.

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[16] The low yields in the reactions using DPE are probably due to the low solubility of the DPE complex of *s*BuLi at −100 °C.

[17] X-ray crystal structure analysis of **6**: A crystal of **6** was obtained from an Et_2O–hexane solution: formula $C_{22}H_{39}BLiN_2P$, formula weight 380.29, crystal dimensions 0.35 × 0.10 × 0.07 mm, monoclinic, space group *C*2/*c*, a = 29.81(1), b = 9.235(3), c = 20.445(7) Å, β = 125.76(3)°, V = 4567(2) Å^3, Z = 8, ρ_{calcd} = 1.106 g cm^{-3}, μ = 1.29 cm^{-1}, $2\theta_{max}$ = 60.1°; 27124 reflections measured, 6634 unique reflections; R_1 = 0.057, Rw = 0.119. Rigaku RAXIS-RAPID Imaging Plate diffractometer (93 K, radiation λ(Mo$_{K\alpha}$) = 0.71075 Å). The structure was solved by direct methods (SHELXS-86).[12]

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[20] a) The NMR spectra of **9** were consistent with those of the deprotonated **3** in the presence of DPE in [D$_{10}$]Et$_2$O. b) Low-temperature ^{1}H, ^{13}C, and ^{31}P NMR analyses did not give useful information to discuss here.

[21] a) L. D. Field, M. G. Gadiner, C. H. L. Kennard, B. A. Messerle, C. L. Raston, *Organometallics* **1991**, *10*, 3167; for a ^{6}Li–^{1}H HOESY study on an α-phosphorus-stabilized anion, see reference [9d].

[22] We assume that these two peaks constitute a doublet, because the coupling constant (2.3 Hz) is within a typical range of $^2J(^6\text{Li},^{31}\text{P})$ = 5 Hz. A broad singlet was observed in ^{31}P NMR spectrum at −100 °C because the phosphorus not only coupled with ^{6}Li but also coupled with B. a) H. J. Reich, D. P. Green, *J. Am. Chem. Soc.* **1989**, *111*, 8729; b) F. E. Romesberg, M. P. Bernstein, J. H. Gilchrist, A. T.

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[23] The chemical shift of **8** was deduced from the ^{6}Li NMR spectrum of DPE-coordinated lithium tetrakis(pentafluorophenyl)borate in $[D_{10}]Et_2O$ at room temperature. A signal appeared at higher field ($\delta = 0.53$ ppm) than the time-averaged signal of ^{6}Li-**9** ($\delta = 0.81$ ppm). We could not distinguish the NMR signals of the *cis* isomer **4b**.

[24] Use of *t*Bu- instead of Ph-substituted phospholanes resulted in high selectivity. a) A. Ohashi, T. Imamoto, *Acta Crystallogr. Sect. C* **2000**, *56*, 723; See also, b) W. Tang, W. Wang, X. Zhang, *Angew. Chem.* **2003**, *115*, 973; *Angew. Chem. Int. Ed.* **2003**, *42*, 943.

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