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Direct Allylation of Active Methylene Compounds with Allylic Alcohols by Use of Palladium/Phosphine-Borane Catalyst System

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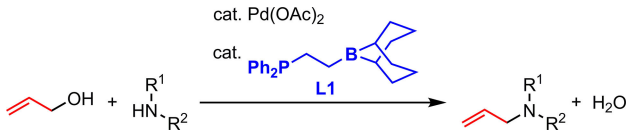
Abstract: The C–C bond formation between active methylene compounds and allylic alcohols has been newly developed by using a palladium complex as a catalyst together with a phosphine-borane ligand. The best phosphine-borane ligand for this direct allylation has been revealed to be $Ph_2P(CH_2)_4$(9-BBN) to produce a variety of desirable allylated products in high yields.

Keywords: palladium; phosphine-borane; allylation; allylic alcohol; active methylene

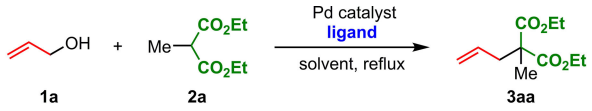
Allylic alcohols often show a low reactivity due to the strong C–O bond and the poor leaving ability of the OH moiety. Still, the study on the usage of allylic alcohols as a direct allylating agent has been developed for many years.[1] One of the effective strategies for the direct allylic substitution is to utilize Lewis acid to activate the hydroxy group. Synthetically important C–C bond formation reactions between allylic alcohols and active methylene compounds by using Lewis acid, such as BEt_3,[1a,d] $InCl_3$,[2] $Yb(OTf)_3$,[3] and $MoO_2(acac)_2$,[4] have been reported by many groups including us. Here, $InCl_3$, $Yb(OTf)_3$, and $MoO_2(acac)_2$ could be used as a catalyst under the neutral condition, while BEt_3 was used together with a palladium catalyst and some base, such as NaH, to deprotonate the pronucleophile. The effect of carboxylic acid and sulfonic acid as an activator was also noted in the direct allylic alkylation catalyzed by palladium[5] and platinum.[6] Furthermore, the study on the activation of allylic alcohols by using an amide acetal was recently reported.[7] The acid-free allylation of 1,3-dicarbonyl compounds with allylic alcohols is also possible by using the transition-metal complexes such as Ir,[8] Pd,[9] Ni,[10] and Mo–Pd cluster.[11] Many other direct allylations of monoketone, aldehyde and so on, have also been reported.[12]

In our laboratory, we have so far developed the direct allylation of a variety of nucleophiles using a combination of a palladium catalyst and BEt_3.[13] In these reactions, allylic alcohols were activated by Lewis acidic BEt_3 to form a π-allylpalladium species as an electrophile, which was attacked by a nucleophile to give the desirable product together with a sole co-product, water. We considered that this allylic substitution could be accelerated by linking the palladium salt with a borane moiety. To produce this type of palladium catalyst, we paid an attention to phosphine-borane ligands. Some useful phosphine-borane ligands have so far been developed by several groups for the transition-metal-catalyzed organic reactions.[14–17] Based on these pioneering works, we studied on the direct allylation of amines with allylic alcohols in the presence of a palladium catalyst and a phosphine-borane ligand. After the screening of many types of phosphine-borane ligands, we found that the $Ph_2PCH_2CH_2$(9-BBN) (**L1**) accelerated this reaction quite well (Scheme 1).[18] The Pd/**L1** catalyst system was much better than the Pd/$EtPPh_2$/*B*-*n*-hexyl-9-BBN system. These results show that the linking between the phosphine and borane is highly effective for the direct allylic substitution. Through this study,

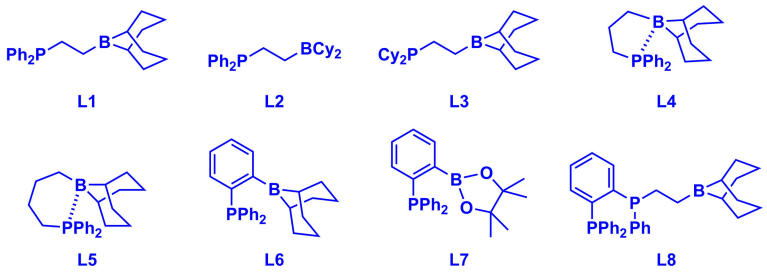


Scheme 1. Palladium-catalyzed direct allylation of amines with allyl alcohol.

Table 1. Reaction of diethyl methylmalonate (**2a**) with allyl alcohol (**1a**).[a]



1a 2a 3aa



L1 L2 L3 L4 L5 L6 L7 L8

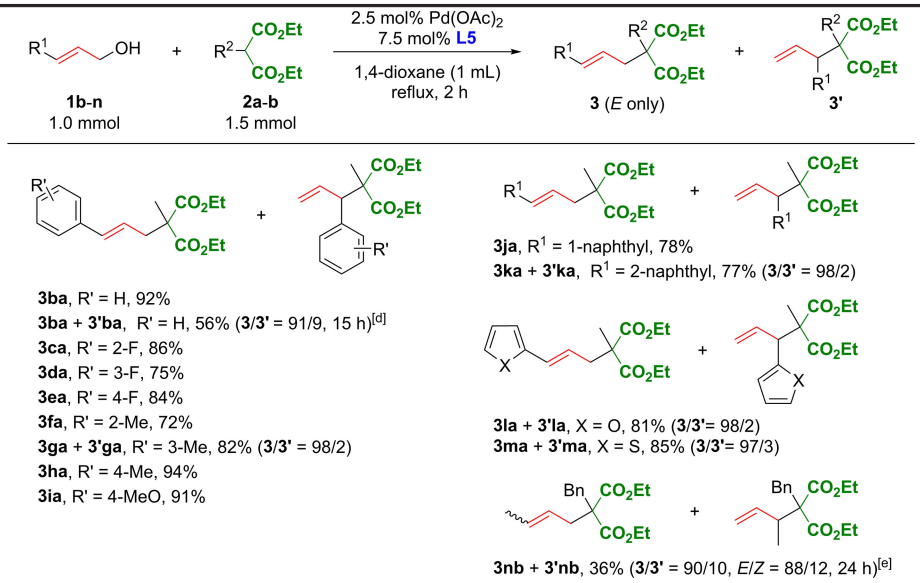
Entry	Pd catalyst (mol%)	Ligand (mol%)	Solvent	Time [h]	Yield [%][b]
1	$Pd(OAc)_2$ (2.5)	**L1** (7.5)	Toluene	15	93
2	$Pd(OAc)_2$ (2.5)	**L1** (7.5)	THF	15	48
3	$Pd(OAc)_2$ (2.5)	**L1** (7.5)	1,4-Dioxane	15	99
4	$Pd(OAc)_2$ (2.5)	**L1** (7.5)	1,4-Dioxane	5	99
5	$Pd(OAc)_2$ (2.5)	**L1** (7.5)	1,4-Dioxane	1	69
6	$Pd(OAc)_2$ (2.5)	**L1** (5.0)	1,4-Dioxane	15	74
7	$Pd(OAc)_2$ (2.5)	**L1** (2.5)	1,4-Dioxane	15	2
8	$PdCl_2$ (2.5)	**L1** (7.5)	1,4-Dioxane	15	0
9	$Pd_2(dba)_3$ (1.25)	**L1** (7.5)	1,4-Dioxane	15	25
10	$Pd(OAc)_2$ (2.5)	**L2** (7.5)	1,4-Dioxane	15	78
11	$Pd(OAc)_2$ (2.5)	**L3** (7.5)	1,4-Dioxane	15	0
12	$Pd(OAc)_2$ (2.5)	**L4** (7.5)	1,4-Dioxane	15	57
13	$Pd(OAc)_2$ (2.5)	**L5** (7.5)	1,4-Dioxane	1	98
14	$Pd(OAc)_2$ (2.5)	**L6** (7.5)	1,4-Dioxane	15	2
15	$Pd(OAc)_2$ (2.5)	**L7** (7.5)	1,4-Dioxane	15	7
16	$Pd(OAc)_2$ (2.5)	**L8** (5.0)	1,4-Dioxane	15	83

[a] A mixture of **1a** (2.0 mmol), **2a** (1.0 mmol), Pd catalyst, ligand, and solvent (1 mL) was stirred under N_2.
[b] Determined by GLC, based on calibration curve and using cyclododecane as an internal standard.

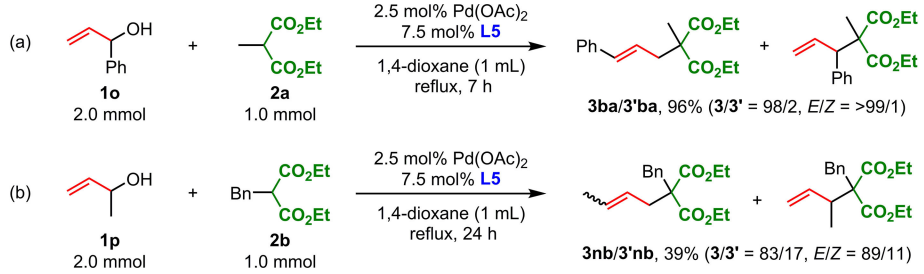
we have learned that the Lewis acidity of borane moiety and the length of linkage between phosphorus and boron were important for improving the catalytic activity. This successful application of a Pd/phosphine-borane system led us to study the C–C bond formation using allylic alcohols. We have now found that the butylene-linked phosphine-borane $Ph_2P(CH_2)_4$(9-BBN) (**L5**) works much better than **L1** in the direct allylation of active methylene compounds to afford the expected C–C bond formation products. In contrast, **L5** was far less effective than **L1** in the direct allylation of amines, and the yield of the corresponding allylamine was extremely low after the same reaction time.[19] Herein, we report this new finding as a communication form.

Results of palladium-catalyzed allylation of diethyl methylmalonate (**2a**) with allyl alcohol (**1a**) using a variety of phosphine-borane ligands are summarized in Table 1. The reaction using **L1** (7.5 mol%), the best ligand for the so-far disclosed allylation of amines, proceeded in refluxing toluene to give diethyl 2-allyl-2-methylmalonate (**3aa**) in 93% yield after 15 h (entry 1). When THF was used as a solvent instead of toluene, the product yield was lower (entry 2). By use of 1,4-dioxane, the reaction provided **3aa** in quantitative yield even after 5 h (entries 3 and 4). The ratio of **L1** to Pd was then investigated. Although the use of two equivalents of **L1** to Pd gave the product in a good yield, an equimolar amount of **L1** to Pd was not effective for this reaction (entries 6 and 7). These results suggest that one equivalent of **L1** can be used as the reductant of $Pd(OAc)_2$ to form Pd(0) species. In contrast to $Pd(OAc)_2$, $PdCl_2$ and $Pd_2(dba)_3$ was not a suitable catalyst precursor for this reaction (entries 8 and 9). We next screened a variety of phosphine-borane ligands in this direct allylation. Ligand **L2** bearing a dicyclohexylboryl group decreased the yield (entry 10), and ligand **L3** bearing a dicyclohexylphosphino group inhibited the reaction (entry 11). The propylene-linked phosphine-borane ligand **L4** was less

Table 2. Reactions of diethyl methylmalonate (**2a**) and diethyl benzylmalonate (**2b**) with γ-substituted allylic alcohols **1b–n**.[a–c]



[a] A mixture of **1**, **2**, $Pd(OAc)_2$ (0.025 mmol), **L5** (0.075 mmol), and 1,4-dioxane (1 mL) was stirred under N_2.
[b] Isolated yield.
[c] Regio- and stereoisomers were not separated and the ratios were determined by ^1H NMR and GLC.
[d] **L1** (0.075 mmol) was used instead of **L5**.
[e] *E*/*Z* mixture of **1n** (*E*/*Z* = 83/17) was used.



Scheme 2. Reactions of diethyl methylmalonate (**2a**) and diethyl benzylmalonate (**2b**) with α-substituted allylic alcohols **1o** and **1p**.

effective than **L1** (entry 12). On the other hand, the butylene-linked phosphine-borane ligand **L5** was the best ligand and the reaction was completed within only 1 h (entry 13; compare with the result using **L1** as the ligand (entry 5)). Phenylene-linked phosphine-borane ligands **L6** and **L7** gave only a trace amount of the product (entries 14 and 15). The diphosphine-borane **L8** was effective in some extent (entry 16).

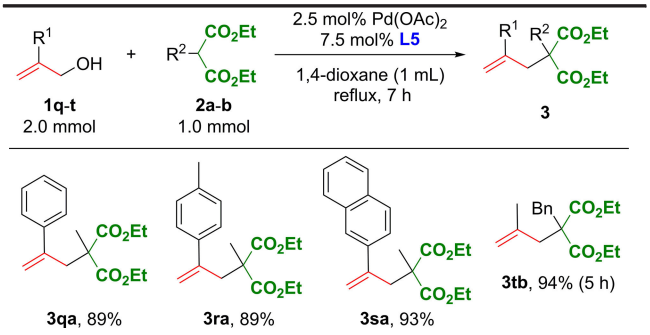
Various allylic alcohols **1** could be used in this allylic alkylation. Results of the reactions of diethyl methylmalonate (**2a**) and diethyl benzylmalonate (**2b**) with a variety of γ-substituted allylic alcohols **1b–n** are summarized in Table 2. Cinnamyl alcohol (**1b**) gave the corresponding product **3ba** as a single product in 92% after 2 h. In this reaction, we also confirmed that **L5** was more effective than **L1**. When **L1** was used as a ligand instead of **L5**, a mixture of **3ba** and **3'ba** was obtained in 56% yield (**3ba**/**3'ba** = 91/9) after 15 h and dicinnamyl ether was also formed as a byproduct. Other cinnamyl alcohol derivatives **1c–i** reacted to afford the corresponding allylated products **3ca–3ia** in high yields with almost complete regio- and stereoselectivities. Some other 3-aryl- and 3-heteroaryl-2-propen-1-ols **1j–m** reacted with **2a** to give the corresponding products **3ja–3ma** in good to high yields. When crotyl alcohol (**1n**) was used in the reaction with **2b**, a mixture of the corresponding products **3nb** and **3'nb** was obtained in 36% in the ratio of 90/10.

Next, we investigated the allylation using α-substituted allylic alcohols **1o** and **1p** (Scheme 2). Allylated products **3ba** and **3'ba** (98/2) were obtained by

the reaction of **2a** with 1-phenyl-2-propen-1-ol (**1o**) in high yield (Scheme 2a). The reaction of **2b** with 3-buten-2-ol (**1p**) gave the products as a mixture of **3nb** and **3'nb** (83/17) in 39% yield (Scheme 2b), the result of which is similar to that of the reaction of **2b** with crotyl alcohol (**1n**, R^1 = Me) shown in Table 2. Together with the fact that the reaction with either **1o** or **1p** gave mainly the linear products **3**, these results indicated that this allylation proceeded via a π-allylpalladium intermediate.

Furthermore, we tried the allylation using some β-substituted allylic alcohols **1q–t** (Table 3). The reaction of **2a** with β-aryl-substituted allylic alcohols **1q–s** provided the corresponding products in high yields. The allylation of **2b** with 2-methyl-2-propen-1-ol (**1t**) also proceeded successfully. Unfortunately, α,γ-, α,α- and γ,γ-disubstituted allylic alcohols were revealed to be not applicable to this reaction system.

Table 3. Reactions of diethyl methylmalonate (**2a**) and diethyl benzylmalonate (**2b**) with β-substituted allylic alcohols **1q–t**.[a,b]

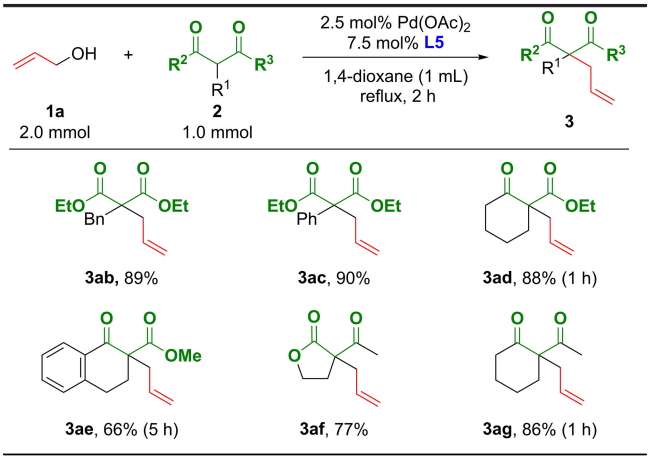


[a] A mixture of **1**, **2**, $Pd(OAc)_2$ (0.025 mmol), **L5** (0.075 mmol), and 1,4-dioxane (1 mL) was stirred under N_2.
[b] Isolated yield.

Results of allylation of 2-substituted 1,3-dicarbonyl compounds **2b–g** with allyl alcohol (**1a**) under the optimized reaction conditions (Table 1, entry 12) are summarized in Table 4. Reactions of 2-substituted malonic esters **2b** and **2c** proceeded smoothly to give the products **3ab** and **3ac**, respectively, in high yields. A variety of cyclic β-ketoesters **2d–f** afforded the corresponding products **3ad–3af** in good yields, and the allylation of the cyclic diketone **2g** successfully underwent to give **3ag** in 86%.

We next examined the scope of 2-unsubstituted 1,3-dicarbonyl compounds **2h–l** (Table 5). Both mono- and diallylated products were produced from unsubstituted malonic ester, because the monoallylated product could be used as a pronucleophile under these reaction conditions. When 2 equiv. of 2-phenyl-2-propene-1-ol (**1q**) to diethyl malonate (**2h**) was used,

Table 4. Reactions of 2-substituted 1,3-dicarbonyl compounds **2b–g** with allyl alcohol (**1a**).[a,b]



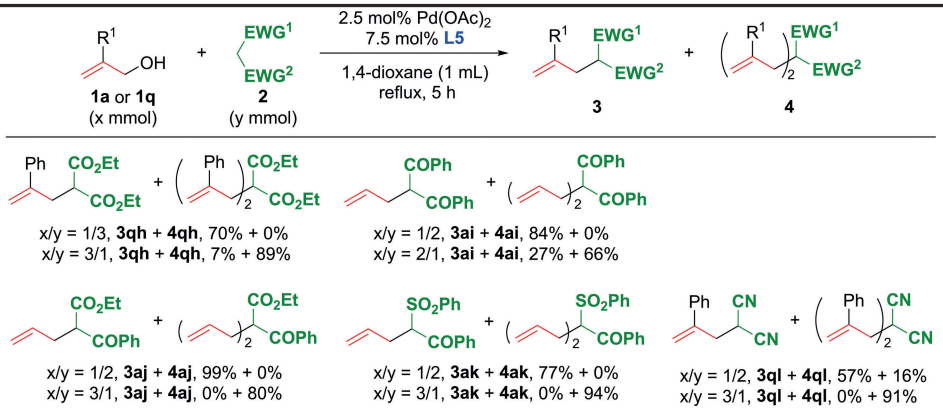
[a] A mixture of **1a**, **2**, $Pd(OAc)_2$ (0.025 mmol), **L5** (0.075 mmol), and 1,4-dioxane (1 mL) was stirred under N_2.
[b] Isolated yield.

a mixture of monoallylated product **3qh** (15%) and diallylated product **4qh** (76%) was obtained. When the amount of **1q** was increased to 3 equiv., diallylated product **4qh** was obtained in 89% yield as expected together with a small amount of monoallylated product **3qh**. In contrast, when 3 equiv. of **2h** to **1q** was used to avoid diallylation, only monoallylated product **3qh** was formed in 70% yield. Similarly, allylation was also applicable to 1,3-diphenyl-1,3-propanedione (**2i**) to give the corresponding products **3ai** and **4ai**. In the case of ethyl benzoylacetate (**2j**) and 2-(phenylsulfonyl)acetophenone (**2k**), the monoallylation and diallylation were completely controlled. Thus, the monoallylated products (**3aj** and **3ak**) and the diallylated products (**4aj** and **4ak**) were obtained in high yields, respectively. Similarly, although allylation of malononitrile (**2l**) with **1q** gave a mixture of mono- and diallylated products by using 2 equiv. of **2l** to **1q**, the reaction with 3 equiv. of **1q** to **2l** proceeded to give only diallylated product **4ql** in 91% yield. In these reactions, the ratio of allylic alcohols to active methylene compounds was important for the selectivity of mono- and diallylation.

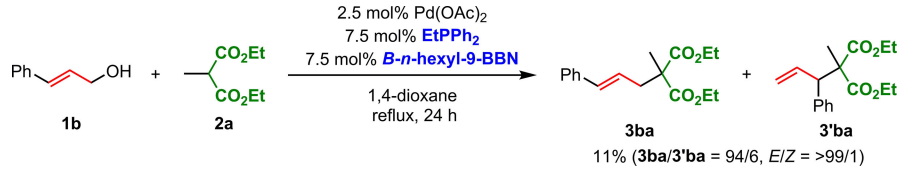
The remarkable effect of linking between the phosphine and borane moiety was observed in the allylation of **2a**. When both $EtPPh_2$ and *B*-*n*-hexyl-9-BBN were used instead of **L5**, the reaction of **2a** with **1b** gave a mixture of **3ba** and **3'ba** in only 11% yield (**3ba**/**3'ba** = 94/6) even after 24 h (Scheme 3). These results indicated that the linking between the phosphine and borane group is critical for obtaining the high catalytic activity.

Plausible reaction pathway is shown in Scheme 4. In this reaction, the borane group of the phosphine-

Table 5. Reactions of active methylene compounds **2h–l** with allyl alcohol (**1a**) and 2-phenyl-2-propen-1-ol (**1q**).[a,b]

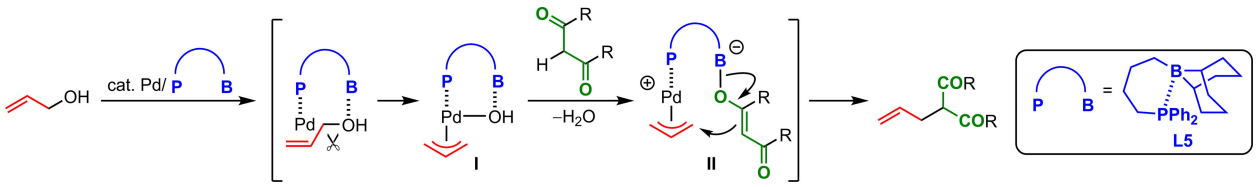


[a] A mixture of **1**, **2**, $Pd(OAc)_2$ (0.025 mmol), **L5** (0.075 mmol), and 1,4-dioxane (1 mL) was stirred under N_2.
[b] Isolated yield.



Scheme 3. Reaction of diethyl methylmalonate (**2a**) with cinnamyl alcohol (**1b**) by using $EtPPh_2$ and *B-n*-hexyl-9-BBN.

borane ligand **L5** acts as a Lewis acid to activate the hydroxy group of allyl alcohol. Successive intramolecular oxidative addition proceeds immediately to give a π-allylpalladium intermediate **I** which can be attacked by an active methylene compound. In this reaction system, a hydroxide anion deprotonates the pronucleophile. Then, a boryl enolate species **II** might be formed and the intramolecular nucleophilic attack proceeds smoothly to give the allylated product along with 1 equiv. of water. The length and the flexibility of butylene linker in **L5** might be well matched for this large-membered ring transition state **II**. On the other hand, in the case of ethylene-linked phosphine-borane ligand **L1**, the transition state might be an unstable medium-membered ring which causes the reaction to be slow, although the details are not yet known.



Scheme 4. Plausible reaction pathway of the direct allylation with allyl alcohol catalyzed by Pd/**L5**.

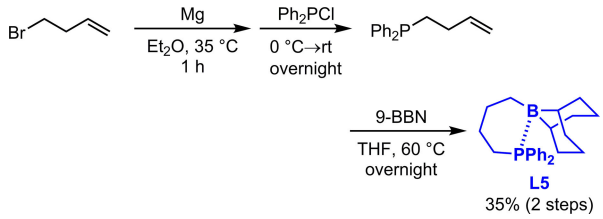
In summary, we have developed the direct allylation of active methylene compounds with allylic alcohols catalyzed by Pd/phosphine-borane. By using the phosphine-borane ligand **L5**, the corresponding allylated products were obtained in high yields under base-free conditions. Further synthetic application and investigation of mechanistic details are currently in progress.

Experimental Section

Preparation of 4-(9-Borabicyclo[3.3.1]Nonanyl) Butyldiphenylphosphine (L5)

The ligand **L5** was synthesized by a similar method as described in the literature (Scheme 5).[18,20,21] To a two-necked 200 mL round bottom flask fitted with a septum and reflux condenser under a nitrogen atmosphere were added magnesium turnings (1.8 g, 75 mmol, 2.5 equiv.). Dry diethyl ether (60 mL) was added to the flask, and 4-bromobutene (3.1 mL,

30 mmol, 1.0 equiv.) was then added dropwise. The solution, refluxed gently during addition, was stirred for 1 h at 40 °C. The resulting solution was allowed to cool to room temperature. Chlorodiphenylphosphine (3.6 mL, 20 mmol) was added slowly at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The solvent was removed under vacuum. To this residue was added hexane and the mixture was filtered. The filtrate was concentrated under vacuum to afford 3-butenyldiphenylphosphine. As a next step, to a THF (50 mL) solution of 3-butenyldiphenylphosphine (4.8 g, 20 mmol) was added 0.5 M 9-BBN in THF solution (40 mL, 20 mmol) at room temperature and the mixture was stirred at 60 °C for overnight. The solvent was removed under vacuum to afford a white solid. The solid was washed with hexane and methanol and dried under vacuum, affording 4-(9-borabicyclo[3.3.1]nonanyl)butyldiphenylphosphine (**L5**) as a white solid in 35% yield (2.5 g, 7.0 mmol, 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.9–1.0 (m, 2H), 1.3 (s, 4H), 1.6–1.9 (m, 14H), 2.3–2.4 (m, 2H), 7.3–7.4 (m, 6H), 7.5–7.6 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.1, 23.9, 24.0 (br), 24.9, 25.0 (d, J = 2.2 Hz), 32.3, 128.6 (d, J = 6.0 Hz), 130.1, 133.0 (d, J = 6.8 Hz), 133.6 (d, J = 26.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ −3.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ −23.1; High-resolution MS (EI^+), calcd for $C_{24}H_{32}PB$: 362.2335, Found: m/z 362.2336 (M^+). Due to the high sensitivity of **L5** towards moisture and oxygen, melting point cannot be obtained.



Scheme 5. Synthesis of **L5**.

General Procedure for Allylation of Active Methylene Compound with Allylic Alcohol (Table 1, Entry 1-2)

Phosphine-borane ligand **L5** (28.4 mg, 0.078 mmol) and $Pd(OAc)_2$ (5.8 mg, 0.026 mmol) were dissolved in 1,4-dioxane (1.0 mL) under nitrogen. The mixture was stirred at room temperature for 1 h during which period it changed to a yellow solution. To the solution were added allyl alcohol (**1a**, 120.2 mg, 2.1 mmol) and diethyl methylmalonate (**2a**, 174.7 mg, 1.0 mmol). The mixture was stirred under reflux. The progress of the reaction was monitored by TLC. After 1 h, the resulting solution was concentrated and purified with column chromatography over silica gel (hexane/AcOEt = 95/5 v/v) to give **3aa** as a colorless oil (211.4 mg, 98%, R_f = 0.7; hexane/ AcOEt = 80/20 v/v).

Acknowledgements

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