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Triethylborane as an efficient promoter for palladium-catalyzed allylation of active methylene compounds with allyl alcohols

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Abstract—Without prior activation of allyl alcohols, allylation of a variety of active methylene compounds with allyl alcohols proceeds smoothly at rt–50°C in the presence of catalytic amounts of $Pd(OAc)_2$ (1–10 mol%), Et_3B (30–240 mol%), a phosphine ligand (1–20 mol%), and a base (0 to 50–60 mol%).

1. Introduction

Palladium-catalyzed allylation of active methylene compounds is a well-established, efficient method for C–C bond formation.[1] In most cases, carboxylic acid esters,[2] carbonates,[3] phosphates,[1] and related compounds of allyl alcohols have been utilized as substrates. Apparently the direct use of allyl alcohols as substrates is more desirable; however, the poor capability of the hydroxyl group as a leaving group has limited their use.[4]

In 1970, Atkins et al.[5] reported that allyl alcohols themselves reacted with acetylacetone (pK_a=9) to give 3-allylpentane-2,4-dione in good yield when heated at 85°C in the presence of catalytic amounts of $Pd(acac)_2$ [acac=acetylacetonato] and PPh_3. Later, Bergbreiter et al.[6] and Chauvin et al.[7] revealed that even less acidic β-ketoesters (pK_a=ca. 11) and malonates (pK_a=ca. 13) also underwent palladium-catalyzed allylation with allyl alcohols, though under rather harsh conditions (heating at around 100°C). Meanwhile, there have been developed several methods that enable the allylation to proceed under milder conditions (room temperature-refluxing THF), where allyl alcohols are in situ activated through transformation into the esters of inorganic acids, such as As_2O_3,[8] B_2O_3,[9] and CO_2.[10] The effect of $Ti(O\text{-}i\text{-}Pr)_4$ as an additive was also noted.[11] A break through has been brought about by Ozawa et al.,[12] who have succeeded in allylation of amines, malonates, and β-ketoesters at 50°C with allyl alcohols using a sp^2-hybridized bidentate phosphine–palladium complex in the presence of pyridine.

Recently we have demonstrated that a sub-catalytic amount of triethylborane (Et_3B) nicely promotes the palladium-catalyzed allylations of amines,[13a] active methylene compounds (pK_a=5–13),[13b] *o*-hydroxypropiophenones (α-carbon of the ketones),[13c] and even aliphatic aldehydes (pK_a=ca. 16)[14] under mild reaction conditions (room temperature–50°C). In the presence of a stoichiometric amount of Et_3B, on the other hand, allyl alcohols dramatically change the reactivity and undergo nucleophilic allylation of aromatic aldehydes (*umpolung*).[15]

Allylation of malonates with allyl alcohols using a stoichiometric amount of triphenylborane (Ph_3B) has been reported.[16] This method seems to be similar to ours regarding the reagents used. However, these two are essentially different from a mechanistic point of view. Furthermore, in a practical sense, the method using Ph_3B seems not to be very attractive, since it requires Ph_3B (110 mol%) and *n*-butyllithium (250 mol%) and heating at 65°C in THF. Detrimentally, the yields in general are modest.

This paper is a full account of our preliminary communication[13b] and discloses results of a full range of combination of reaction partners: active methylene compounds and allyl alcohols. Only relevant portions are cited from the communication. The catalytic cycles and the catalytic roles that Et_3B and an Pd^0 species play are also discussed in detail.

2. Results and discussion

In a previous communication,[13b] we have disclosed that highly acidic carbo-nucleophiles, such as Meldrum's acid (pK_a=5.2), react with a variety of allyl alcohols to provide diallylation products in 70–90% isolated yields, where Et_3B greatly accelerate the reaction. Less acidic carbo-nucleophiles, such

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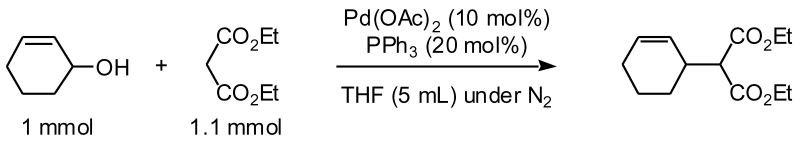


run	Et_3B (mmol)	NaH (mmol)	temp (°C)/ time (h)	% isolated yield
1	1.2	0.5	25/4	74
2	0.0	0.5	50/18	13
3	1.2	0.0	50/41	0

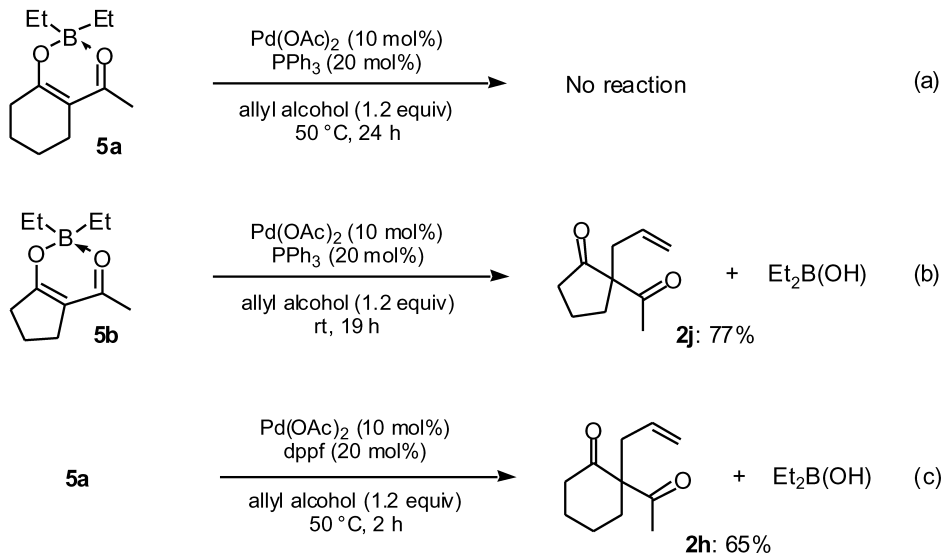
Scheme 1. Pd-catalyzed allylation of diethyl malonate with 2-cyclohexenol.

as malonates (pK_a=ca. 13), required both Et_3B and a base (NaH) for the allylation to proceed at a reasonable rate at room temperature (run 1, Scheme 1). In the absence of the base (run 3), no reaction took place even under energetic conditions: an elevated temperature and a long period of the reaction time. In the absence of Et_3B (run 2), on the other hand, the allylation proceeded slowly at 50°C, yielding an expected product, albeit in low yield.

We examined a scope of the catalytic system, Et_3B/a base/$Pd(OAc)_2$/PPh_3, for a wide range of active methylene and methine compounds (pK_a=5–14) using two typical allyl alcohols: 2-propen-1-ol (allyl alcohol) and *trans*-3-phenyl-2-propen-1-ol (*trans*-cinnamyl alcohol). The results are summarized in Table 1. Table 2 also lists the results of allylation of α-acetyl-γ-butyrolactone examined for the purpose of demonstrating applicability to a wide structural variety of primary and secondary allyl alcohols. In Tables 1 and 2, the relative amounts of each component of the catalytic system were fixed as shown in equation (1), where as a precaution for carbo-nucleophiles and allyl alcohols of low reactivity, the amount of Et_3B was doubled as compared with that in Scheme 1. For active methylene compounds (di-allylation), 240 mol% of an allylic alcohol and 110 mol% of a base were applied (conditions A–C, footnote a, Table 1). For active methine compounds, 110 mol% of an allylic alcohol and 60 mol% of a base were used (conditions D–F).

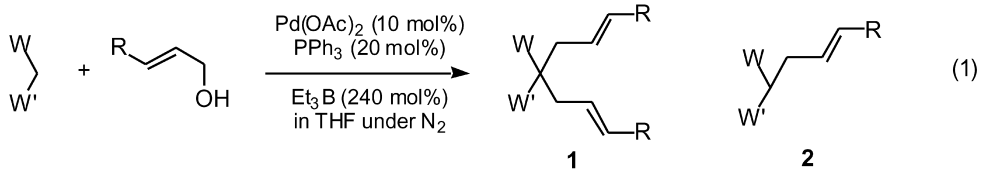
Table 1 reveals that the catalytic system shows quite satisfactory results, giving rise to expected monoallylation products (**2**) for active methine compounds and diallylation products (**1**) for active methylene compounds in good to excellent yields. The following points may be worth mentioning. First, the least acidic ethyl benzenesulfonyl-acetate exclusively provided a monoallylation product **2a**, even in the presence of an excess amount of allyl alcohol (run 1). No diallylation product was produced in any trace amount. Retardation of the second allylation may be attributed to the low acidity and/or steric hindrance associated with the primary product **2a**. Second, as was noted, highly acidic nucleophiles, such as 2-formylcyclo-hexanone (run 14) and Meldrum's acid (run 16),[13b] do not necessitate any base and the reactions are completed within a few hours at room temperature. Finally, and most remarkably, acetylacetone (AA) and 2-acetylcyclohexanone (AC) are exceptionally unreactive, yielding expected products, albeit in poor yields (runs 9–12). Despite close structural similarity, AC and 2-acetylcyclopentanone (run 13) show a distinctive difference in reactivity.

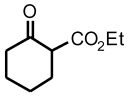
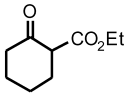
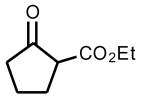
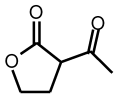
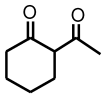
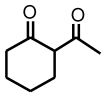
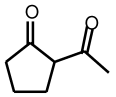
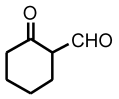
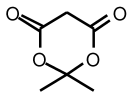
Et_3B is stable toward hydrolysis by water and alcohols,[23] while it undergoes hydrolysis when exposed to some weakly acidic compounds of chelation ability (e.g. 2-hydroxypyr-idine, AA, AC) and forms cyclic diethylboric acid esters (e.g. **5a** and **5b** in Scheme 2).[24] According to the literature,[24]



Scheme 2. Pd-Catalyzed allylation of isolated diethylborates **5** with allyl alcohol.

Table 1. Palladium-catalyzed allylation of active methylene and methine compounds using allyl alcohol and cinnamyl alcohol in the presence of triethylborane



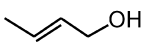
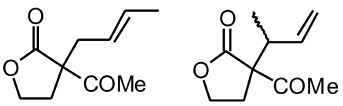
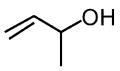
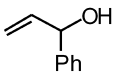
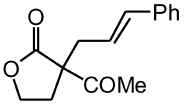
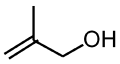
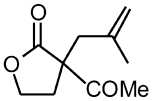
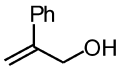
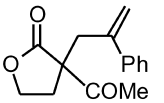
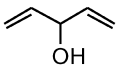
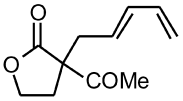
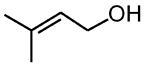
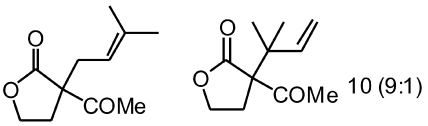
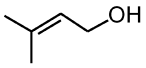
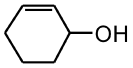
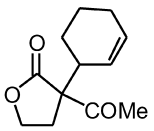
Run	Active methylene compounds	pK_a	R=H		R=Ph	
			Temp (°C), time (h)[a]	% yield isolated	Temp (°C), time (h)[a]	% yield isolated
1	$PhSO_2CH_2CO_2Et$	14[17]	A: rt, 5	**2a**: 74	–	–
2	$CH_2(CO_2Et)_2$	13[18]	A: rt, 2[b]	**1a**: 70	–	–
3	$MeCOCH_2CO_2Me$	11[18]	A: 50, 1	**1b**: 98	B: 50, 1	**1c**: 73
4		–	D: rt, 2	**2b**: 93	D: rt, 1.5	**2c**: 93
5			E: rt, 1	**2b**: 95	E: rt, 1	**2c**: 95
6		12.0[19]	D: rt, 1	**2d**: 88	D: rt, 1.5	**2e**:89
7		–	D: rt, 1.5	**2f**: 92	D: rt, 3	**2g**: 85
8	$CH_2(CN)_2$	11[18]	A: rt, 2	**1d**: 87	–	–
9	$CH_2(COMe)_2$ (AA)	9[18]	–	–	A: 50, 24	**1e**: 7
10	$CH_2(COMe)_2$ (AA)		–	–	B: 50, 48	**1e**: <5
11		9.9[20]	E: rt, 2	**2h**: 24	D: rt, 2	**2i**: 32
12			–	–	E: rt, 3	**2i**: 16
13		8.1[21]	E: rt, 1	**2j**: 85	E: rt, 2	**2k**: 84
14		7.1[19]	–	–	F: rt, 1	**2l**: 85
15	$O_2NCH_2CO_2Et$	5.8[19]	A: rt, 2	**1f**: 64	–	–
16		5.2[22]	C: rt, 2.5	**1g**: 78	C: rt, 2	**1h**: 85

[a] Conditions A: an active methylene compound (1.0 mmol), an allylic alcohol (2.4 mmol), and KHMDS (potassium bis(trimethylsilyl)amide, 1.1 mmol); Conditions B: under the conditions A using Et_3N (1.1 mmol) in place of KHMDS; Conditions C: under the conditions A without the base, Conditions D: an active methine compound (1.0 mmol), an allylic alcohol (1.1 mmol), and KHMDS (0.6 mmol); Conditions E: under the conditions D using Et_3N (0.6 mmol) in place of KHMDS; Conditions F: under the conditions D without the base.

[b] NaH in place of KHMDS.

acetylacetone (AA), for example, reacts with Et_3B in refluxing THF (3 h) and provides air- and moisture-stable diethylboronium acetylacetonate in 84% isolated yield after distillation. Under our allylation conditions, AA, AC, 2-acetylcyclopentanone, and 2-formylcyclohexanone, all readily reacted with Et_3B at room temperature and provided corresponding cyclic diethylboric acid esters. The hydrolysis may be accelerated by a base, being present in the reaction mixture. The progress of reaction could be monitored conveniently by means of TLC (hexane/EtOAc=4:1 v/v, $R_{f(\text{diethylborates } \mathbf{5})}$=ca. 0.7; $R_{f(\beta\text{-dicarbonyls})}$=ca. 0.6, $R_{f(\text{allylation products})}$=ca. 0.4). Among these diethylborates, the latter two were so reactive that they faded away completely at room temperature within 1–2 h (runs 13 and

Table 2. Et_3B-Promoted, Pd-catalyzed allylation of α-acetyl-γ-butyrolactone with a variety of allyl alcohols

Run	Allyl alcohol	Temp (°C), time (h)	% isolated of products
1		rt, 3	 **3a** **3a'**
2		rt, 2	72 (2.5:1)[b] 73 (2.5:1)[b]
3		rt, 1	 **2g**: 95
4		rt, 1	 **3b**: 82
5		rt, 1	 **3c**: 81
6		rt, 2	 **3d**: 24
7		rt, 12 then 50, 10	 **3e** **3e'** 10 (9:1) **3e**, **3e'**: 82 (20:1)
8		rt, 40[a]	
9		rt, 5	 **3f**:70[c]

Reaction conditions: α-acetyl-γ-butyrolactone (1.0 mmol), an allylic alcohol (1.1 mmol), Et_3B (2.4 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), KHMDS (0.6 mmol) in THF (5 mL) under N_2.
[a] Dppf (20 mol%) in place of PPh_3.
[b] Diastereomeric mixture (1.4:1).
[c] Diastereomeric mixture (1.7:1).

14). The former two, on the other hand, were very reluctant and either remained at a final stage of reactions (runs 11 and 12) or faded away very slowly (runs 9 and 10), probably owing to decomposition.

These results suggest that the formation of boric acid esters might not be a main cause of reluctant reactivity associated with AA and AC. In fact, the reactions of allyl alcohol with boric acid esters of AC (**5a**) and 2-acetylcyclopentanone (**5b**), prepared independently, showed an apparent difference in reactivity (Eq. (a) and (b), Scheme 2). Even under forcing conditions, **5a** did not react with allyl alcohol, while **5b** did react with the same alcohol under usual conditions, though in a somewhat lower yield and at a lower reaction rate compared with the in situ reaction (run 13, Table 1).

From a mechanistic point of view, the results associated with equation (b) seem to be particularly important, which indicate that **5b** is capable of activating an allylic alcohol as a precursor of a π-allylpalladium species, and also **5b** is reactive enough toward the thus-formed π-allylpalladium species (vide infra).

Table 2 summarizes the results for the reactions of α-acetyl-γ-butyrolactone with a wide structural variety of primary and secondary allyl alcohols. The yield and regioselectivity are similar to those reported for diethyl benzylmalonate;[13b] α- and γ-methylallyl alcohols showed the identical product distribution, giving rise to a mixture of straight and branched chain isomers in a ratio of 2.5:1 (runs 1 and 2). α-Phenylallyl alcohol (run 3) and α-vinylallyl alcohol (run 6), on the other hand, provided straight chain products

exclusively. This is presumably due to conjugation stabilization of the double bonds that the straight chain isomers are engaged in.

Under usual conditions, γ,γ-dimethylallyl alcohol was exceptionally unreactive (run 7). Even under energetic conditions, the expected product were obtained in a low yield and with a low regioselectivity. Interestingly, the yield and the regioselectivity were remarkably improved by the use of dppf [1,1′-bis(diphenylphosphino)ferrocene] in place of PPh_3 (run 8).

Encouraged with this, we re-examined the hitherto unsuccessful allylation, the allylation of AA and AC (runs 9–12, Table 1) with bidentate phosphine ligands varying the degrees of bite angle. The results in runs 1–5 (Table 3) clearly indicate that the allylation of AA sharply depends on the kind of phosphine ligands and that the bidentate ligands with bite angle[25] larger than 100°, e.g. dppb and dppf, remarkably increase the yield. Furthermore, dppf greatly accelerates the reaction (run 5, Table 3).

The product **4** was not detected by careful TLC monitoring during a whole course of reaction (runs 2–5, Table 3). Accordingly, **4** is regarded to be formed during a work-up under alkaline conditions (NaOH, H_2O_2), presumably via de-acylation through the retro-Claisen condensation of **1e**: addition of OH^- to one of the acetyl groups of **1e** followed by a bond cleavage giving rise to a mixture of acetic acid and an enolate of **4**.

A remarkable improvement in yields with dppf was also confirmed for the allylation of AC (runs 6–8, Table 3). In accord with this, dppf turned out to promote the allylation of **5a** with allyl alcohol (Eq. (c), Scheme 2). The causes of dramatic differences observed for the two pairs of reactions, equations (a) and (c), i.e. a ligand effect, and equations (a) and (b), i.e. a ring size effect, are not clear at present.

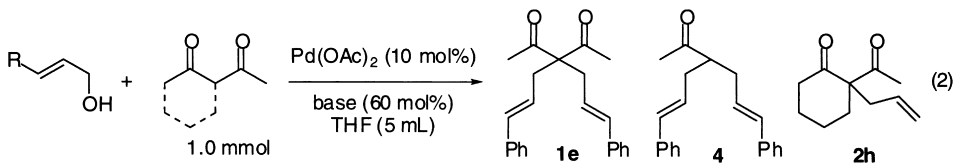
Run 8 in Table 3 indicates that, although we have so far used an excess amount of Et_3B, the amount can be reduced to a sub-catalytic level,[13b] i.e. a smaller amount than that of active methylene compounds. It should be noted that under such conditions, Et_3B is subject to hydrolysis (vide infra) and is completely converted to a boric acid ester **5**. This apparently indicates that under such conditions, allyl alcohol is activated not by Et_3B, but some other species like **5** (cf. Eq. (c), Scheme 2. See also Section 3).

In order to estimate minimum loadings of $Pd(OAc)_2$, phosphine ligands, and Et_3B, the allylation of α-acetyl-γ-butyrolactone and AC was examined (Scheme 3). Runs 1–3 indicate that the amount of Et_3B can be reduced to 30 mol% in a combination of $Pd(OAc)_2$ and PPh_3, 10 and 20 mol% each. Comparison of runs 4 and 5 reveals that the catalyst composition of Et_3B (30 mol%)/$Pd(OAc)_2$ (5 mol%)/PPh_3 (10 mol%) almost reaches the lowest limit of loading. Runs 6–8 indicate that a combination of $Pd(OAc)_2$ and dppf, in 5 mol% each, is almost the lowest limit for successful reaction. Loading the lower amounts of these reagents, e.g. 3 mol% each (run 8), apparently causes a significant decrease in the yield.

Almost at a final stage of the present study, we found by chance that a particular combination $Pd(OAc)_2$ and BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] in 1:1 ratio was marvelous; to our pleasant surprise, the combination of these, 3 mol% each, showed the best record and gave rise to **2h** in 94% isolated yield (run 10, Scheme 3). This observation indicates that allylation of AC sharply depends on not only a bite angle, but also a basicity of bidentate ligands. The bite angle of BINAP is 87°.[25] Relied on a guide-line deduced from Table 3 (vide supra), regrettably, we have ignored this ligand through this study.

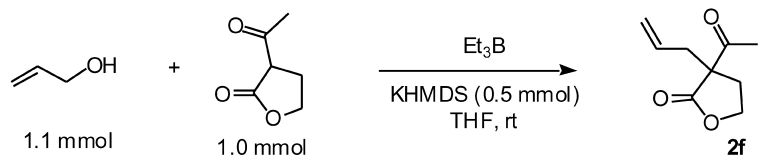
In order to assess the efficiency of BINAP as a ligand for the present Et_3B- and Pd^0-catalyzed allylation, we re-examined the reaction of AC with cinnamyl alcohol (runs 11 and 12 in Table 1) as well as the reaction of α-acetyl-γ-butyrolactone with α-vinylallyl alcohol (run 6 in Table 2), specific combinations of reactants having been so far unsatisfactory. In Scheme 4 are summarized the results. In the same scheme are

Table 3. Effects of ligands and bases on allylation of acetylacetone (AA) and 2-acetylcyclohexanone (AC)

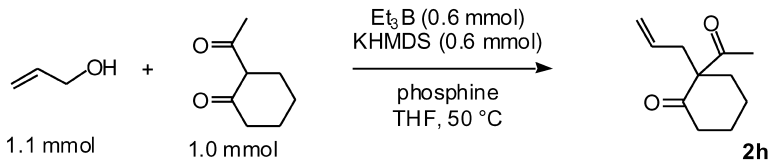


Run	Nu	Ligand (mol%)	Bite angle (°)	Base	Et_3B (equiv.)	Temp (°C), Time (h)	% isolated yield	
1	AA	PPh_3 (20)		Et_3N	2.4	50/48	**1e**: trace	
2	AA	dppe (20)[a]	85	Et_3N	2.4	50/24	**1e**: 36	**4**: 13
3	AA	dppp (20)[b]	95	Et_3N	2.4	50/24	**1e**: 32	**4**: 14
4	AA	dppb (20)[c]	99	Et_3N	2.4	50/20	**1e**: 65	**4**: 22
5	AA	dppf (20)	106	Et_3N	2.4	50/2	**1e**: 78	**4**: 9
6	AC	PPh_3 (20)		KHMDS	2.4	rt/2	**2h**: 32	
7	AC	dppf (20)		KHMDS	2.4	50/1	**2h**: 80	
8	AC	dppf (20)		KHMDS	0.6	50/1	**2h**: 83	

2.4 mmol of an allylic alcohol for AA and 1.1 mmol for AC.
[a] 1,2-Bis(diphenylphosphino)ethane.
[b] 1,3-Bis(diphenylphosphino)propane.
[c] 1,4-Bis(diphenylphosphino)butane.



run	$Pd(OAc)_2$ (mol%)/ PPh_3 (mol%)	Et_3B (mmol)	time (h)	% isolated yield
1	10/20	1.2	2	90
2	10/20	0.6	2	89
3	10/20	0.3	1	86
4	5/10	0.3	1	88
5	5/10	0.1	1	75



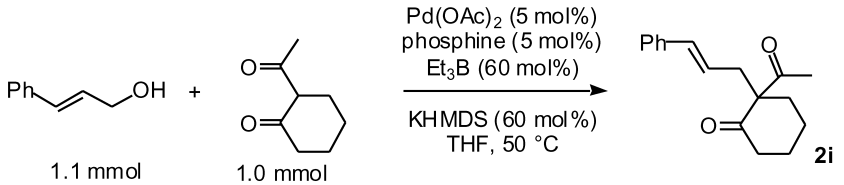
run	$Pd(OAc)_2$ (mol%)/ phosphine (mol%)	time (h)	% isolated yield
6	10/dppf 10	2	80
7	5/dppf 5	2	86
8	3/dppf 3	2	75
9	5/binap 5	2	84
10	3/binap 3	2	94
11	1/binap 1	2	75

Scheme 3. Reactions using reduced amounts of $Pd(OAc)_2$, phosphines, and Et_3B.

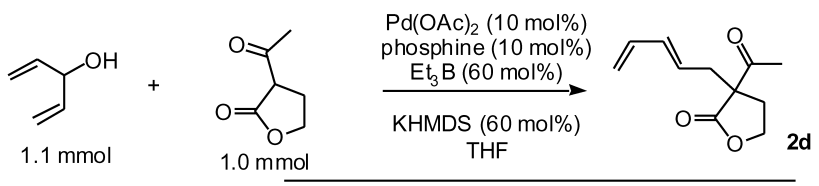
also listed the results examined with dppf as a reference ligand under the identical reaction conditions. From these results, it may be concluded that BINAP is much superior to dppf and any other phosphine ligands examined so far in this study.

3. Mechanistic consideration

Scheme 5 illustrates the most probable catalytic cycles with respect to an Pd^0 species and Et_3B. Catalytic cycle A might

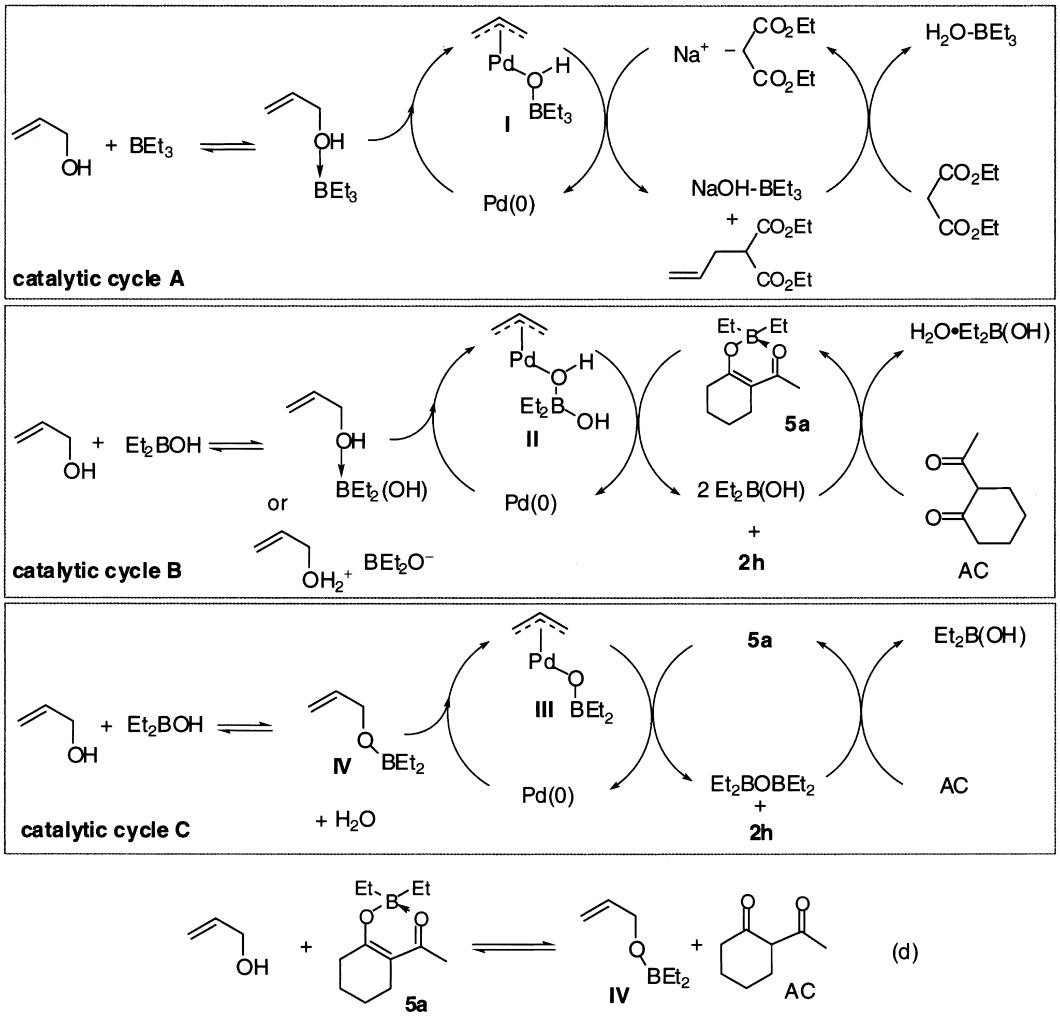


run	phosphine	time (h)	% isolated
1	dppf	3	36
2	BINAP	2	80



run	phosphine	temp (°C)	time (h)	% isolated
3	dppf	25	4	39
4	BINAP	50	4	54

Scheme 4. Remarkable improvement in yields by the use of BINAP as a ligand.



Scheme 5. Plausible catalytic cycles with respect to Pd^0 and Et_3B and boric acid derivatives.

be applied to reactions that do not involve hydrolysis of Et_3B, where an essential role of Et_3B is to activate an allyl alcohol by coordination to the hydroxy group, through which oxidative addition of Pd^0 into the C–O bond might proceed with ease. Use of a base is essential to activate weakly acidic nucleophiles as their conjugate bases.

According to this scheme, one molecule of water is generated for every one catalytic cycle, and in principle, Et_3B and a base (NaOH from NaH, KOH from KHMDS) as well as an Pd^0 species remain intact and the reaction should be catalytic with respect to all these reagents. In practice, however, Et_3B may be damaged partially by air and some other side reactions and the base may be neutralized by the thus-formed boric acids.

Catalytic cycles B and C might be applied to reactions that involve hydrolysis of Et_3B to **5**. The cycles B and C differ in that in cycle B, diethylhydroxyborane (Et_2BOH) serves as either a Lewis acid or a Brønsted acid to activate an allylic alcohol, while in cycle C, it serves as an acid portion of an allyl ester **IV**.[9] Catalytic cycle B illustrates only the case that Et_2BOH plays as a Lewis acid; the case that Et_2BOH as a Brønsted acid might be accounted for in a similar way. In catalytic cycles B and C, not only Et_2BOH, but also an intermediate **5a** might also contribute to activate an allylic alcohol through an equilibrium shown in equation (d) (Scheme 5). As was demonstrated by equations (b) and (c) in Scheme 2, cyclic diethylborates **5** might serve as potent nucleophiles toward a π-allylpalladium species (**II** or **III**) under certain conditions.

In Schemes B and C, the participation of a base is not referred to explicitly. Indeed, allylation of some highly acidic nucleophiles, e.g. 2-formylcyclohexanone (run 14, Table 1) and Meldrum's acid (run 16, Table 1) proceed smoothly even in the absence of a base. For less acidic nucleophiles, however, a base might help them react with Et_3B and/or Et_2BOH to form reactive cyclic diethyl borates **5** (vide supra).

In all catalytic cycles A–C, one molecule of water is generated for every catalytic cycle, i.e. the present Et_3B–Pd catalyzed allylation may be regarded as the condensation reaction between active methylene compounds (H^+ donors) and allyl alcohols (OH^- donors).

4. Conclusion

In this paper, we have disclosed that without prior activation of allyl alcohols, allylation of a variety of combination of

active methylene compounds (pK_a 5–14) and allyl alcohols proceeds smoothly at rt–50°C in the presence of $Pd(OAc)_2$ (1–10 mol%), Et_3B (30–240 mol%), a phosphine ligand (1–20 mol%), and a base (0 to 50–60 mol%). Et_3B serves as a unique co-catalyst and plays many roles to promote the reaction depending on the kind of β-dicarbonyl compounds. (1) The primary role is to activate an allylic alcohol by coordinating to the hydroxy group, through which oxidative addition of an Pd^0 species to the C–O bond takes place easily at room temperature–50°C. (2) Neither being verified, nor pursued in detail, Et_3B might be responsible for reduction of $Pd(OAc)_2$ to an Pd^0 species, which is maintained active as long as organoborane species that possess B–Et bonds of reducing ability persist. (3) Et_3B activates some β-dicarbonyl compounds, such as acetylacetone and 2-acetylcyclohexanone, by forming cyclic diethylborates **5**, which in the presence of an appropriate bidentate ligand, such as dppf and BINAP, not only serves as a nucleophile, but also as a promoter of oxidative addition of an Pd^0 species to the C–O bond of an allylic alcohol.

5. Experimental

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with 230–400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ±0.4 %.

5.1. Solvents and reagents

THF (tetrahydrofuran) was distilled from sodium/benzophenone ketyl under N_2 prior to use. Triethylamine was distilled from CaH_2 under N_2. KHMDS (potassium bis(trimethylsilyl)amide, 0.5 M in toluene, Aldrich), Et_3B (1.0 M in hexane, Kanto Kagaku), allyl alcohols, active methylene compounds, phosphine ligands, and $Pd(OAc)_2$ were used as received from commercial sources. 2-Formylcyclohexanone was prepared according to the literature procedure.[26]

The structures of trivial allylation products were determined by spectral means (IR, HRMS) especially by comparison of the ^1H NMR data with those of authentic samples: diethyl diallylmalonate (**1a**),[27] methyl diallylacetoacetate (**1b**),[28] diallylmalononitrile (**1d**),[29] 3,3-bis-(trans-cinnamyl)pentane-2,4-dione (**1e**),[30] ethyl 2,2-diallyl-2-nitroacetate (**1f**),[31] 5,5-diallyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**1g**),[32] 5,5-bis-cinnamyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**1h**),[32] ethyl 2-benzenesulfonyl-4-pentenoate (**2a**),[33] ethyl 1-allyl-2-oxocyclohexanecarboxylate (**2b**),[34] ethyl 1-allyl-2-oxocyclopentanecarboxylate (**2d**),[35] ethyl 1-*trans*-cinnamyl-2-oxocyclopentanecarboxylate (**2e**),[36] α-acetyl-α-allyl-γ-butyrolactone (**2f**),[37] α-acetyl-α-*trans*-cinnamyl-γ-butyrolactone (**2g**),[37] 2-acetyl-2-allylcyclohexanone (**2h**),[38] 5-phenyl-3-trans-cinnamylhex-5-en-2-one (**4**).[39]

5.2. General procedure for palladium-catalyzed allylation of active methylene compounds

(1) Allylation of 2-acetylcyclohexanone (run 10, Scheme 3): Into a two-necked flask equipped with a reflux condenser at the top of which was attached a N_2 balloon were placed $Pd(OAc)_2$ (6.75 mg, 0.03 mmol) and *rac*-BINAP (18.6 mg, 0.03 mmol). The flask was purged with N_2 and then THF (5 mL), 2-acetylcyclohexanone (140.1 mg, 1.0 mmol), allyl alcohol (61.8 mg, 1.1 mmol), KHMDS (1.2 mL, 0.5 M in toluene), and Et_3B (0.60 mL, 1.0 M in hexane) were added successively at room temperature via syringe. The mixture was stirred and heated at 50°C for 2 h, during which the mixture was colored red. The mixture was diluted with EtOAc (20 mL) and washed with 2N HCl, sat. $NaHCO_3$, and then brine. The extract was dried ($MgSO_4$) and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (gradient: hexane to hexane/EtOAc=16/1, v/v) to give 2-acetyl-2-allylcyclohexanone (**2g**, 169.5 mg, R_f=0.5, hexane/EtOAc=4/1) in 94% yield.

(2) Cinnamylation of acetylacetone (run 5, Table 3): Into a solution of $Pd(OAc)_2$ (12.0 mg, 0.1 mmol) and dppf (110.8 mg, 0.2 mmol) in THF (5 mL) were successively introduced cinnamyl alcohol (322.0 mg, 2.4 mmol), acetylacetone (100.1 mg, 1.0 mmol), Et_3N (60 mg, 0.6 mmol), and Et_3B (2.4 mL, 1 M in hexane). The mixture was heated at 50°C for 2 h under N_2. Into the mixture were added 6N NaOH (1 mL) and 30% H_2O_2 (2 mL) and the mixture was heated at 50°C for 2 h. After dilution with EtOAc (20 mL), the mixture was worked up in an usual way similar to the procedure (1). 3,3-Bis-(*trans*-cinnamyl)pentane-2,4-dione (**1e**, 259.5 mg, 78% isolated yield; R_f=0.40, hexane/EtOAc=4/1, v/v) and 5-phenyl-3-(*trans*-cinnamyl)hex-5-en-2-one (**4**, 26.3 mg, 9% isolated yield, R_f=0.55) were isolated as spectroscopically homogeneous materials.

5.3. New compounds appeared in Table 1

5.3.1. Methyl 2,2-di(*trans*-cinnamyl)acetoacetate (1c). IR (neat) 1745 (s), 1712 (s), 1198 (m), 1107 (s), 968 (s) cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 2.19 (s, 3H), 2.78 (br dd, *J*=7.5, 14.5 Hz, 2H), 2.84 (br dd, *J*=7.5, 14.5 Hz, 2H), 3.75 (s, 3H), 6.00 (dt, *J*=15.6, 7.5 Hz, 2H), 6.45 (br d, *J*=15.6 Hz, 2H), 7.19 – 7.33 (m, 10H). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 78.91; H, 7.00.

5.3.2. 2-*trans*-Cinnamyl-2-ethoxycarbonylcyclohexanone (2c). IR (neat) 1741 (s), 1714 (s), 1647 (s), 1616 (s), 1450 (s), 1404 (s), 1369 (s), 1298 (s), 1259 (s), 1218 (s), 1193 (s), 1176 (s), 1130 (s), 1082 (s), 1060 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J*=7.6 Hz, 3H), 1.48–1.79 (m, 4H), 2.02 (m, 1H), 2.46–2.55 (m, 3H), 2.49 (dd, *J*=13.7, 7.0 Hz, 1H), 2.74 (br dd, *J*=13.7, 7.0 Hz, 1H), 4.17 (q,

J=7.6 Hz, 2H), 6.17 (ddd, J=15.5, 7.7, 7.0 Hz, 1H), 6.37 (d, J=15.5 Hz, 1H), 7.17–7.33 (m, 5H); HRMS, calcd for $C_{18}H_{22}O_3$: 286.1569. Found m/z (relative intensity): 286.1571 (M^+, 100).

5.3.3. 2-*trans*-Cinnamyl-2-acetylcyclohexanone (2i). IR (neat) 1697 (s), 1598 (m), 1433 (s), 1359 (s), 970 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (m, 4H), 2.13 (s, 3H), 2.26–2.34 (m, 2H), 2.50 (br dd, J=14.3, 7.7 Hz, 2H), 2.60 (J=14.3, 7.5 Hz, 1H), 2.72 (dd, J=14.3, 7.5 Hz, 1H), 6.02 (dt, J=15.8, 7.5 Hz, 1H), 6.39 (d, J=15.8 Hz, 1H), 7.18–7.33 (m, 5H); HRMS, calcd for $C_{17}H_{20}O_2$: 256.1463. Found m/z (relative intensity): 256.1466 (M^+, 100).

5.3.4. 2-Acetyl-2-allylcyclopentanone (2j). IR (neat) 1737 (s), 1703 (s), 1355 (s), 1130 (s), 921 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (dt, J=12.8, 7.8 Hz, 1H), 1.82–1.92 (m, 3H), 2.21 (s, 3H), 2.31 (ddd, J=8.4, 5.8, 1.3 Hz, 1H), 2.42 (ddt, J=14.4, 7.4, 1.3 Hz, 1H), 2.64 (br dt, J=12.8, 5.8 Hz, 1H), 2.69 (ddt, J=14.4, 7.4, 1.3 Hz, 1H), 5.10 (tq, J=10.3, 1.3 Hz, 1H), 5.11 (br d, J=16.9 Hz, 1H), 5.57 (ddt, J=16.9, 10.3, 7.4 Hz, 1H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.34; H, 8.44.

5.3.5. 2-Acetyl-2-*trans*-cinnamylcyclopentanone (2k). IR (neat) 3026 (s), 1732 (s), 1703 (s), 1577 (s), 1450 (s), 1357 (s), 1141 (s), 970 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.81–1.93 (m, 3H), 2.25 (s, 3H), 2.28–2.40 (m, 2H), 2.60 (ddd, J=14.4, 7.0, 1.5 Hz, 1H), 2.46–2.70 (m, 1H), 2.82 (ddd, J=14.4, 7.7, 1.5 Hz, 1H), 5.94 (dt, J=15.8, 7.7 Hz, 1H), 6.44 (d, J=15.8 Hz, 1H), 7.21–7.31 (m, 5H). Anal. Calcd for $C_{16}H_{18}O_2$:C, 79.31; H, 7.49. Found: C, 79.34; H, 7.55.

5.3.6. 2-*trans*-Cinnamyl-2-formylcyclohexanone (2l). IR (neat) 1728 (s), 1699 (s), 1598 (w), 1132 (m), 970 (m), 748 (m), 694 (m) cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 1.67 – 1.97 (m, 5H), 2.23 – 2.53 (m, 3H), 2.66 (br dd, J=7.6, 14.3 Hz, 1H), 2.70 (br dd, J=7.6, 14.3 Hz, 1H), 6.06 (dt, J=15.8, 7.6 Hz, 1H), 6.43 (br d, J=15.8 Hz, 1H), 7.18 – 7.32 (m, 5H), 9.57 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 21.5, 26.3, 31.8, 35.8, 41.1, 65.0, 123.5, 126.2, 127.5, 128.5, 134.2, 136.8, 200.9, 208.8; HRMS, calcd for $C_{16}H_{18}O_2$: 242.1307. Found m/z (relative intensity): 242.1292 (M^+, 28), 213 (100).

5.4. New compounds appeared in Table 2

5.4.1. α-Acetyl-α-(*trans*-crotyl)-γ-butyrolactone (3a). IR (neat) a mixture with **3a′** 1766 (s), 1712 (s), 1436 (s), 1375 (s), 1359 (s), 1166 (s), 1028 (s), 972 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.66 (dd, J=6.2, 1.1 Hz, 3H), 2.09 (ddt, J=13.2, 8.8, 6.6 Hz, 1H), 2.34 (s, 3H), 2.56 (ddt, J=14.3, 6.6, 1.5 Hz, 1H), 2.70 (dd, J=14.3, 7.3 Hz, 1H), 2.85 (ddd, J=13.2, 7.3, 3.7 Hz, 1H), 4.17 (dt, J=8.8, 7.3 Hz, 1H), 4.26 (td, J=8.8, 3.7 Hz, 1H), 5.20 (br dq, J=15.2, 1.1 Hz, 1H), 5.61 (br dq, J=15.2, 6.2 Hz, 1H). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.08; H, 7.75.

5.4.2. α-Acetyl-α-(α-methylallyl)-γ-butyrolactone (3a′). a mixture of diastereomers in a ratio of 1.4:1; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.91 (d, J=7.0 Hz, 3H), 2.16 (m, 1H), 2.36 (s, 3H), 2.85 (m, 1H), 3.26 (qm, J=7.0 Hz, 1H), 4.06 – 4.25 (m, 2H), 5.20 (dm, J=10.6 Hz, 1H), 5.22 (d, J=16.9 Hz, 1H), 5.76 (ddm, J=10.6, 16.9 Hz, 1H). ^1H NMR (400 MHz, $CDCl_3$, minor isomer) δ 1.11 (d, J=7.0 Hz, 3H), 2.16 (m, 1H), 2.40 (s, 3H), 2.85 (m, 1H), 3.26 (qm, J=7.0 Hz, 1H), 4.06 – 4.25 (m, 2H), 5.07 (br d, J=10.6 Hz, 1H), 5.13 (br d, J=16.9 Hz, 1H), 5.47 (ddm, J=10.6, 16.9 Hz, 1H).

5.4.3. α-Acetyl-α-(β-methylallyl)-γ-butyrolactone (3b). IR (neat) 1768 (s), 1712 (s), 1375 (s), 1359 (s), 1159 (s), 1029 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ?1.70 (s, 3H), 2.14 (dt, J=13.2, 9.0 Hz, 1H), 2.34 (s, 3H), 2.60 (d, J=15.6 Hz, 1H), 2.91 (d, J=15.6 Hz, 1H), 3.00 (ddd, J=13.2, 7.1, 2.9 Hz, 1H), 4.19 (dt, J=7.1, 9.0 Hz, 1H), 4.31 (dt, J=2.9, 9.0 Hz, 1H), 4.69 (s, 1H), 4.89 (s, 1H); HRMS, calcd for $C_{10}H_{14}O_3$: 182.0943. Found m/z (relative intensity): 182.0957 (M^+, 3.9), 140.0825 (100).

5.4.4. α-Acetyl-α-(β-phenylallyl)-γ-butyrolactone (3c). IR (neat) 3057 (s), 1766 (s), 1712 (m), 1629 (s), 1494 (s), 1444 (s), 1357 (s), 1218 (s), 1159 (s), 1028 (s), 958 (s), 912 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (dt, J=13.2, 8.8 Hz, 1H), 2.28 (s, 3H), 2.76 (ddd, J=13.2, 7.3, 3.1 Hz, 1H), 3.05 (dd, J=15.4, 1.1 Hz, 1H), 3.39 (dd, J=15.4, 1.1 Hz, 1H), 4.07 (dt, J=7.3, 8.8 Hz, 1H), 4.16 (td, J=8.8, 3.1 Hz, 1H), 5.10 (d, J=1.1 Hz, 1H), 5.33 (s, 1H), 7.29–7.33 (m, 5H). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.78; H, 6.82.

5.4.5. α-Acetyl-α-(*trans*-2,4-pentadienyl)-γ-butyrolactone (3d). ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (dt, J=13.2, 8.8 Hz, 1H), 2.35 (s, 3H), 2.69 (dd, J=14.7, 6.8 Hz, 1H), 2.78 (dd, J=14.7, 6.8 Hz, 1H), 2.87 (ddd, J=13.2, 7.3, 3.7 Hz, 1H), 4.18 (dt, J=8.8, 8.2 Hz, 1H), 4.28 (ddd, J=9.0, 8.8, 3.3 Hz, 1H), 5.09 (d, J=9.5 Hz, 1H), 5.19 (d, J=16.1 Hz, 1H), 5.45 (dt, J=15.0, 7.5 Hz, 1H), 6.16 (dd, J=15.0, 10.4 Hz, 1H), 6.27 (dt, J=16.8, 10.4 Hz, 1H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.23; H, 7.39.

5.4.6. α-Acetyl-α-(γ,γ-dimethylallyl)-γ-butyrolactone (3e). IR (neat) a mixture with **3e′** 1770 (s), 1674 (m), 1440 (s), 1377 (s), 1359 (s), 1163 (s), 1029 (s), 954 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 3H), 1.71 (s, 3H), 2.04 (dt, J=12.8, 8.8 Hz, 1H), 2.33 (s, 3H), 2.57 (dd, J=14.8, 6.6 Hz, 1H), 2.77 (dd, J=14.8, 8.1 Hz, 1H), 2.87 (ddd, J=12.8, 7.3, 3.7 Hz, 1H), 4.17 (dt, J=7.3, 8.8 Hz, 1H), 4.27 (td, J=8.8, 3.7 Hz, 1H), 4.29 (br dd, J=8.8, 6.6 Hz, 1H); HRMS, calcd for $C_{11}H_{16}O_3$: 196.1099. Found m/z (relative intensity): 196.1087 (M^+, 65.5), 178.1020 (100).

5.4.7. α-Acetyl-α-(α,α-dimethylallyl)-γ-butyrolactone (3e′). ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.22 (s, 3H), 2.35 (s, 3H), 5.05 (d, J=17.4 Hz, 1H), 5.12 (d, J=10.8 Hz, 1H), 7.25 (dd, J=17.4, 10.8 Hz, 1H).

5.4.8. α-Acetyl-α-(2-cyclohexenyl)-γ-butyrolactone (3f). A mixture of diastereomers in a ratio of 1.7:1; IR (neat) 1761 (s), 1711 (s), 1165 (s), 1026 (s), 951 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.03 (dtm, J=10.3, 13.2 Hz, 1H), 1.48 – 2.08 (m, 6H), 2.36 (s, 3H), 2.82 (dm, J=7.2 Hz, 1H), 3.26 (dm, J=13.2 Hz, 1H), 4.08 (ddd, J=7.2, 9.2, 10.3 Hz, 1H), 4.26 (dm, J=9.2 Hz, 1H),

5.34 (dm, J=10.3 Hz, 1H), 5.93 (dm, J=10.3 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer) 1.22 (m, 1H), 1.48 – 2.08 (m, 6H), 2.41 (s, 3H), 2.88 (dm, J=8.5 Hz, 1H), 3.19 (m, 1H), 4.16 (q, J=8.5 Hz, 1H), 4.25 (dm, J=8.5 Hz, 1H), 5.14 (dm, J=10.3 Hz, 1H), 5.85 (dm, J=10.3 Hz, 1H). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.50; H, 7.71.

5.4.9. Diethylboron acetylacetonate. IR (neat) 1589 (s), 1539 (s), 1386 (s), 1365 (s), 1064 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.41 (q, J=7.8 Hz, 4H), 0.76 (s, J=7.8 Hz, 6H), 5.41 (s, 1H); ^{11}B NMR (125 MHz, $CDCl_3$, relative to H_3BO_3) δ −5.16; HRMS, calcd for $C_9H_{17}BO_2$: 168.1322. Found m/z (relative intensity): 168.1324 (M^+, 1), 167 (1), 139 (100).

5.4.10. Diethylboron 2-acetyl-1-cyclohexenolate (5a). IR (neat) 1595 (s), 1492 (m), 1460 (m), 1379 (m), 1363 (s), 1058 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (q, J=7.8 Hz, 4H), 0.76 (t, J=7.8 Hz, 6H), 1.68–1.71 (m, 4H), 2.06 (s, 3H), 2.26–2.34 (m, 4H); ^{11}B NMR (125 MHz, CDCl3, relative to H_3BO_3) δ −6.45; HRMS, calcd for $C_{12}H_{21}BO_2$: 208.1635. Found m/z (relative intensity): 207.1496 (M^+, 4), 179 (100).

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