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Synthesis of allenes by double Horner–Wadsworth–Emmons reaction

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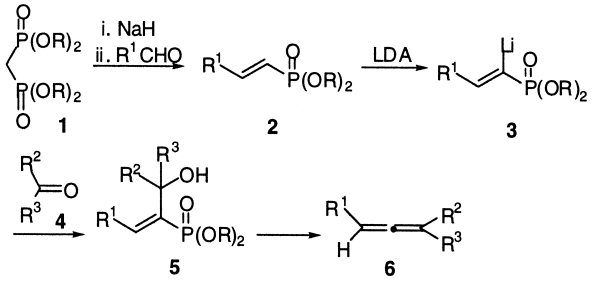
Abstract—LDA treatment of aldehydes or ketone with alkenylphosphonates **2**, prepared by Horner–Wadsworth–Emmons (HWE) reaction of methylenebisphosphonate **1** with aldehydes, afforded Baylis–Hillman reaction-type products **5** in high yields. HWE olefination of **5** with KH or KH-18-crown-6 as a base provided allenes in good yields. One-flask procedure was successfully developed starting from **1** to afford an allene in a reasonably good yield. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Allenes are recent focus of versatile class of intermediates in a variety of organic synthetic processes.[1] The major allene synthesis relies on a S_N2' replacement of propargylic leaving groups[2] and others involve dehydrohalogenation of vinylic halides,[3] reductive elimination of halogenated cyclopropanes,[4] elimination of the enolphosphate,[5] allenation of aldehydes with alkenyltitanocene derivatives,[6] radical β-elimination of vinylsulfoxides[7] and S_N2' reaction of 2-bromo-1,3-butadiene derivatives.[8] Our allene synthesis by the Horner–Wadsworth–Emmons (HWE) reaction[9] of alkenylphosphonates is conceptually different from these and is advantageous in the retrosynthetic simplicity.[10] The cumulated carbon–carbon double bonds of allenes **6** are constructed by the HWE reaction starting from alkenylphosphonates **2**. The sequence of the reaction starts from the formation of vinylanion **3** from **2** by the treatment with LDA, hydroxyalkylation of **3** with a carbonyl compound **4** to hydroxyalkenylphosphonate **5**, and finally HWE olefination of **5** to afford allenes **6** (Scheme 1). Since **2** is also synthesized by the HWE reaction of methylenebisphosphonate **1** with aldehydes, two sp^2 and one sp carbon atoms of an allene functionality are constructed by sequential double HWE olefinations of the three components, **1** and two carbonyl compounds.[11] Realization of this scenario is critically dependent on the efficacy of hydroxyalkylation of **2** giving **5** and the second HWE olefination of **5**, because the first olefination of **1** to **2** is a well-established high yield process.[12] We describe herein the efficient HWE olefination of **2** with a wide range of carbonyl compounds in both stepwise and one-flask manner. Selection of a base for the HWE olefination of **5** was the key to success.



Scheme 1. Three-step and three-components allene synthesis.

2. Results and discussion

2.1. Synthesis of alkenylphosphonates 2 from 1

Methylenebisphosphonates **1** (R=Et, *i*-Pr) are commercially available. Alkenylphosphonates **2** were prepared by the HWE reaction of **1** with aldehydes under the standard conditions in reasonably high yields (Table 1). Aldehydes bearing aryl, tertiary, secondary and methylene carbons at the α-position were possible to be used in the reaction.

2.2. Synthesis of hydroxyalkenylphosphonates 5

The anion formation step of the HWE reaction is generally accomplished by direct deprotonation of alkylphosphonate with appropriate bases or alternatively by conjugate addition of nucleophiles to alkenylphosphonates. The latter procedure using alkenylphosphonates owing another electron-withdrawing group at the α-position has been well established, since such a double-activated olefin is

Keywords: allenes; olefination; alkenylphosphonates.

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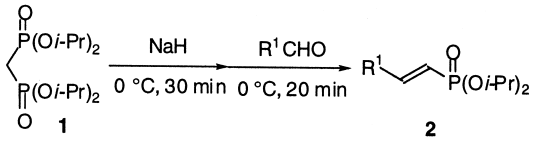
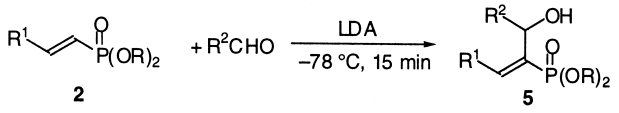
Table 1. Synthesis of alkenylphosphonate **2**



1 **2**

Entry	2	R^1	Yield (%)
1	**a**	Ph	85
2	**b**	*t*-Bu	83
3	**c**	*c*-Hex	81
4	**d**	$Ph(CH_2)_2$	85

Table 2. Synthesis of α,β-unsaturated hydroxyphosphonate **5**

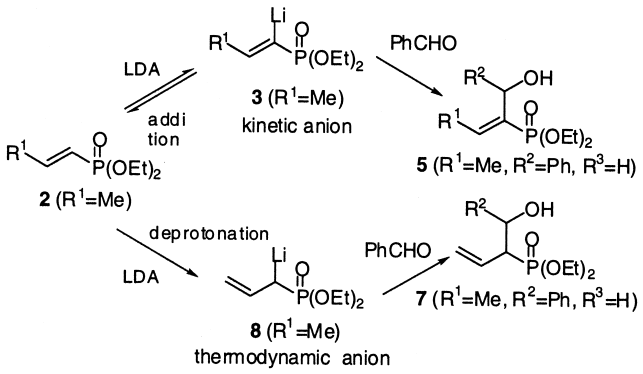


2 **5**

Entry	Method	5	R	R^1	R^2	Yield (%)
1	A	**a**	*i*-Pr	Ph	*t*-Bu	91
2	A	**b**	*i*-Pr	Ph	Ph	97
3	A	**c**	*i*-Pr	Ph	*c*-Hex	99
4	A	**d**	*i*-Pr	Ph	$Ph(CH_2)_2$	97
5	A	**e**	*i*-Pr	*t*-Bu	Ph	100
6	A	**f**	*i*-Pr	*t*-Bu	$Ph(CH_2)_2$	99
7	A	**g**	*i*-Pr	*c*-Hex	$Ph(CH_2)_2$	99
8	A	**h**	*i*-Pr	$Ph(CH_2)_2$	*t*-Bu	44
9	B	**i**	Et	Me	Ph	73
10	B	**j**	Et	Me	*t*-Bu	80
11	B	**k**	Et	H	*t*-Bu	87

Method A: to a solution of LDA was added the phosphonate and to the mixture was added aldehyde. Method B: LDA was added to a mixture of the phosphonate and aldehyde.

the excellent Michael acceptor, and moreover, the resulting α-anion is thermodynamically stabilized by delocalization and is readily acceptable by carbonyl compounds.[13] However, little has been known about the HWE reaction starting from a non-activated alkenylphosphonate **2**[14] that should be a central component in our allene synthesis. We carried out this step by the direct deprotonation with LDA[15] and then treatment with aldehydes gave **5** in high yields as shown in Table 2 (method A, entries 1–7).[16] However, this procedure was not applicable to **2** (R^1=$Ph(CH_2)_2$, Me) giving the products in low or miserable yields (entry 8). In particular, reaction of **2** (R^1=Me) with benzaldehyde failed to give the expected product and the only isolable product was **7** (Scheme 2). These suggested formation of



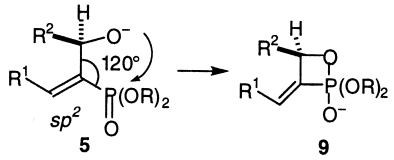
Scheme 2. Formation of **5** through kinetic anion **3**.

the thermodynamically stabilized allylic anion **8** via isomerization of **3**. Addition of LDA to a mixture of **2** and benzaldehyde overcame the problem and gave **5** in a good yield (method B, entry 9). This procedure is operative for **2** that has a deprotonatable proton at the γ-position. This is because the initially formed vinyl anion **3** (R^1=Me) may react rapidly with benzaldehyde before the isomerization.[17]

Since it has been shown that enolizable aldehydes and ketones are not an obstacle in this reaction, **5** with variety of substituents are available. Conversion of **2** to **5** is equivalent to DABCO-catalyzed Baylis–Hillman reaction.[18] However, the reaction was reported to require a long time to completion, besides, alkenylphosphonates were limited to vinyl and propenyl-**2** (R^1=H, Me). Our direct method B completed the reaction within a few minutes and was applicable to a wide range of carbonyl compounds.

2.3. HWE olefination of 5 to allenes 6

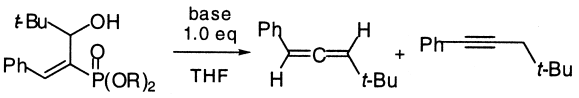
Since a variety type of **5** in hand, conversion of **5** to an allene **6** was the next target.[19] In our previous report, NaH was used as a base for HWE olefination of **5** to provide **6** in utmost 72% yield.[17] The low efficiency was ascribable to an unfavorable phosphooxetane **9** that involves one sp^2 carbon in the four-membered ring, and furthermore, the 120° bond angle by the sp^2 carbon as shown in Scheme 3. These are significantly unfavorable factors in intramolecular nucleophilic attack of an alcoholic oxygen to a P=O phosphorous electrophile to form **9**. The analysis suggested that olefination of **5** requires efficient activation of a nucleophilic alcoholic oxygen. However, a strong base is likely to deprotonate allene protons resulting in isomerization into an alkyne. We studied to find an appropriate base for olefination of **5**.



Scheme 3. Formation of phosphooxetane.

We set **5a** (R^1=Ph, R^2=*t*-Bu, R=Et or *i*-Pr) as an olefination testing hydroxyphosphonate to allene **6a** (R^1=Ph, R^2=*t*-Bu), because **5a** and **6a** are the most simple alcohol and allene with regard to deprotonatable protons (Table 3). The lithium alkoxide, generated by treating **5a** (R=Et) with 1 equiv. of BuLi in THF, was the least reactive alkoxide to afford **6a** in 30% yield along with concomitant formation of inseparable complex mixture after 5 h under reflux (entry 1). Reaction of the sodium alkoxide, prepared with NaH, was more efficient and gave **6a** in moderate 72% yield at 50°C for 0.5 h (entry 2). The excellent conversion was achieved by treating the potassium alkoxide, generated with KH, at 60°C for 5 min in THF to give **6a** in 92% yield with concomitant formation of the isomerized alkyne **10a** in 2% yield (entry 3). Upon addition of 0.1 equiv. of 18-crown-6, the reaction of **5a** (R=*i*-Pr)[20] underwent at 0°C for 0.5 h to give **6a** in the same 92% yield and trace amount of **10a**

Table 3. Base dependency of olefination efficacy of **5a**



5a **6a** **10a**

Entry	R	Base	18-crown-6 (equiv.)	Temp (°C)	Time (min)	**6a** yield (%)	**10a** yield (%)
1	Et	BuLi	0	Reflux	300	30	Trace
2	Et	NaH	0	50	30	72	Trace
3	Et	KH	0	60	5	92	2
4	*i*-Pr	KH	1.0	60	5	25	75
5	*i*-Pr	KH	1.0	0	15	89	2
6	*i*-Pr	KH	0.1	0	30	92	Trace
7	Et	KDA	0	60	60	41	5
8	Et	KHMDS	0	25	15	88	Trace
9	Et	KOH[a]	0	150	80	55	0
10	Et	*t*-BuOK[b]	0	40	15	62	Trace
11	Et	*t*-BuOCs	0	60	10	70	Trace

[a] DMSO was used as a solvent.
[b] 1.5 equiv.

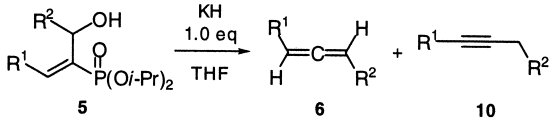
(entry 6). At the higher temperature (60°C) and in the presence of 1 equiv. of 18-crown-6 for 5 min, alkyne **10a** was the major product in 75% yield (entry 4). Isomerization of **6a** to **10a** was prevented at the lower reaction temperature of 0°C affording **6a** in 89% yield (entry 5). The effects of 18-crown-6 are apparent and favorable for the olefination through nucleophilic activation of the potassium alkoxide. Other potassium bases such as potassium diisopropylamide (KDA),[21] *t*-BuOK, and KOH were less effective than KH, although KHMDS[22] was almost equally effective to give **6a** in 88% yield (entries 7–10). The softer base, *t*-BuOCs[23] was less effective than KH (entry 11). Thus we learned KH and KH-18-crown-6 as suitable olefination bases for **6a**.

The conditions above were successfully applied to olefination of other **5** (Table 4). Even when methine, methylene, and methyl groups (R^2) were adjacent to the allene function, olefination proceeded smoothly to give the corresponding allenes **6b–d** in good yields (entries 2–5). Especially, KH-crown base improved the yield from 40 to 73% even when R^2 is a methyl group that is readily deprotonatable (entry 5). When both ends of an allene are phenyl groups (**6e**: R^1=R^2=Ph), deprotonation of the allene proton and isomerization to **10e** (32%) was the major pathway (entry 6). When methylene is at one end of the allene such as **6f–h** (R^2=$Ph(CH_2)_2$), the reaction proceeded smoothly to afford the allenes in relatively high yields (entries 7–9). It is noteworthy that R^1 is possible to be a proton as shown in the conversion of **5** to **6h** in 42% yield (entry 9). The isomeric alcohol **5e** to **5a** gave the same allene **6a** in 55% yield together with retro-aldol product **2** (R^1=*t*-Bu) in 24% yield (entry 10).

2.4. One-flask allene synthesis from 1

The stepwise double olefination method of allene synthesis was successfully extended to a semi-one-flask process from **2** (Table 5). Since the direct conversion of intermediate lithium alkoxide **Li-5a** to **6** was not efficient, activation of **Li-5a** was critical for success. At first, we examined the addition of KH that was the most effective base for the allene synthesis from **5a**. KH was added to **Li-5a**, which was prepared by treatment of **5a** with BuLi in THF at −78°C, and the mixture was heated at 60°C for 3 h to afford **6a** in only 37% yield (entry 2). On the other hand, the addition of metal *t*-butoxides worked effectively for the activation of lithium alkoxide to afford **6** in improved 64–83% yield (entries 3–5). Judging from the reaction times,

Table 4. Synthesis of allenes **6** by treatment of **5** with KH

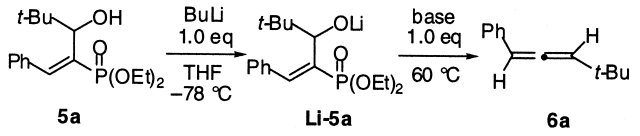


5 **6** **10**

Entry	**6**	R^1	R^2	18-crown-6 (equiv.)	Temp (°C)	Time (min)	**6a** yield (%)	**10a** yield (%)
1	**a**	Ph	*t*-Bu	0.1	0	30	92	
2	**b**	Ph	*c*-Hex	0	60	10	61	10
3	**c**	Ph	$Ph(CH_2)_2$	0	60	20	71	
4	**d**	Ph	Me	0	60	20	40	
5	**d**	Ph	Me	0.1	0	60	73	
6	**e**	Ph	Ph	0	60	40	17	32
7	**f**	*t*-Bu	$Ph(CH_2)_2$	0	60	20	79	
8	**g**	*c*-Hex	$Ph(CH_2)_2$	0.1	60	60	77	
9	**h**	H	$Ph(CH_2)_2$	1.0	60	10	42	38[a]
10	**a**	*t*-Bu	Ph	0	60	60	55[b]	

[a] Alkyne **10** (R^1=Me, R^2=Bn) was obtained.
[b] Retro-aldol product **2** (R^1=*t*-Bu) was obtained in 24% yield.

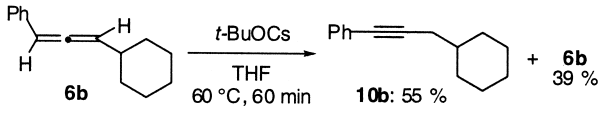
Table 5. Effect of additional bases on conversion efficiency of **Li-5a** to **6a**



5a Li-5a 6a

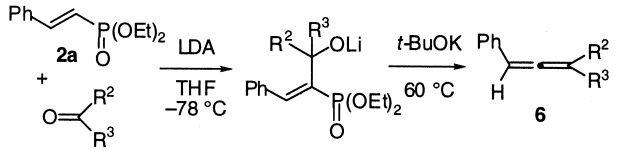
Entry	Base	Time (min)	**6a** yield (%)	**10a** yield (%)
1	None	5	30	
2	KH	3	37	
3	*t*-BuONa	2	64	
4	*t*-BuOK	0.5	83	5
5	*t*-BuOCs	0.2	76	15

the reactivity was increased in accordance with the order of counter metal cation, Na<K<Cs. It is interesting to learn that the *t*-BuOCs-mediated conversion of **Li-5a** to **6a** proceeded much more smoothly than that of **5a** to **6a** mediated by *t*-BuOCs (Table 3, entry 11). However, the addition of *t*-BuOCs caused the contamination of alkyne, which resulted in the decrease of allene production (entry 5). Formation of the alkyne would be due to isomerization of allenes. Indeed treatment of **6b** (R^1=Ph, R^2=*c*-Hex) with *t*-BuOCs in THF at 60°C for 1 h resulted in the formation of an alkyne **10b** (R^1=Ph, R^2=*c*-Hex) in 55% yield together with recovery of **6b**.



Formation of alkyne was diminished by the use of *t*-BuOK. Therefore, we chose *t*-BuOK as an activating co-base of **Li-5**. A semi-one-flask allene synthesis was carried out by the reaction of **2a** (R^1=Ph, R=Et) with aldehydes and ketone, and desired allenes **6a**,**c**,**i** were obtained in 47–85% yield (Table 6). Thus we succeeded in the synthesis of **6** by the HWE reaction starting from **2**. Since **2** was also prepared by HWE reaction of **1** with aldehydes, next target was a real one-flask procedure starting from **1**.

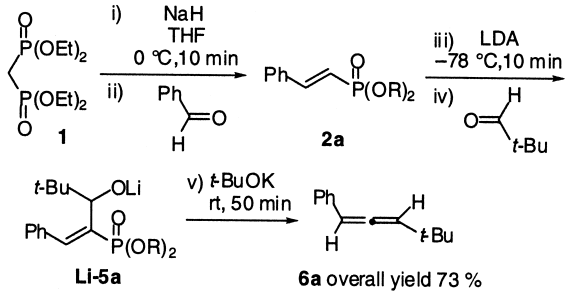
Table 6. One-pot synthesis of allenes **6** from **2** (R^1=Ph) and **4**



Entry	**6**	R^2	R^3	Yield (%)
1	**a**	*t*-Bu	H	85
2	**c**	$Ph(CH_2)_2$	H	55
3	**i**	Et	Me	47

The real one-flask process was initiated by the treatment of **1** with NaH followed by addition of benzaldehyde to produce **2a**, then LDA treatment followed by addition of pivalaldehyde at −78°C giving **Li-5a**, finally addition of *t*-BuOK to afford, after workup and chromatography, allene **6a** in 73% overall yield (Scheme 4).

In conclusion, we have developed allene synthesis through double HWE reaction in both stepwise and one-flask manner. Activation of an oxygen nucleophile of **5** or **Li-5** with properly selected bases was the key to success.



Scheme 4. One-pot synthesis of allene **6a** in three step procedure.

3. Experimental

3.1. General

^{1}H, ^{13}C and ^{31}P NMR spectra were taken at 500.0, 125.7 and 202.4 Hz in $CDC1_3$. Chemical shift values are expressed in ppm relative to internal tetramethylsilane. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Purification was carried out using silica gel column chromatography unless otherwise noted.

3.1.1. Synthesis of diisopropyl (*E*)-2-phenylethenylphosphonate (2a: R^1=Ph, R=*i*-Pr) (Table 1, entry 1). Tetraisopropyl methylenebisphosphonate **1** (12.8 mL, 40 mmol) was added to a suspension of NaH (2.4 g, 60 mmol) in THF (100 mL) at 0°C. After being stirred for 0.5 h, benzaldehyde (4.2 mL, 41 mmol) was added. The mixture was stirred for 30 min at 0°C, and was quenched with satd NH_4Cl, extracted with EtOAc, washed with brine, and dried over Na_2SO_4. Concentration and distillation gave **2a** as a colorless oil. ^{1}H NMR: 1.32 and 1.37 (each 6H, d, *J*=6.1 Hz, CH_3), 4.72 (2H, m, CH), 6.27 (1H, t, *J*=17.4 Hz, CH), 7.36–7.52 (6H, m, CH, Ph). ^{13}C NMR: 23.9 (d, *J*=4.1 Hz), 24.0 (d, *J*=4.1 Hz), 70.3 (d, *J*=5.2 Hz), 115.6 (d, *J*=192.4 Hz), 127.5, 128.7, 129.9, 135.0 (d, *J*=23.8 Hz), 147.6 (d, *J*=7.2 Hz). ^{31}P NMR: 17.4. IR (neat): 1615, 1240 cm^{-1}. EIMS *m*/*z*: 268 (M^+). Anal. calcd for $C_{14}H_{21}O_3P$: C, 62.67; H, 7.89. Found: C, 62.71; H, 8.16.

3.1.2. Diisopropyl (*E*)-3,3-dimethyl-1-butenylphosphonate (2b). A colorless oil. ^{1}H NMR: 1.06 (9H, s, *t*-Bu), 1.29 and 1.33 (6H, d, *J*=6.1 Hz, CH_3), 4.65 (2H, m, CH), 5.55 (1H, dd, *J*=17.4, 19.8 Hz, CH), 6.75 (1H, dd, *J*=17.4, 23.2 Hz, CH). ^{13}C NMR: 23.9 (d, *J*=4.1 Hz), 24.0 (d, *J*=4.1 Hz), 28.4, 34.7 (d, *J*=19.7 Hz), 70.0 (d, *J*=5.2 Hz), 113.4 (d, *J*=189.3 Hz), 162.1 (d, *J*=4.1 Hz). ^{31}P NMR: 18.4. IR (nujor): 1620 cm^{-1}. EIMS *m*/*z*: 248 (M^+). HRMS calcd for $C_{12}H_{25}O_3P$: 248.1541. Found: 248.1535.

3.1.3. Diisopropyl (*E*)-2-cyclohexylethenylphosphonate (2c). A colorless oil. ^{1}H NMR: 1.09–2.15 (11H, m), 1.29 (6H, d, *J*=6.1 Hz, CH_3), 1.33 (6H, d, *J*=6.1 Hz, CH_3), 4.64 (2H, m, CH), 5.59 (1H, ddd, *J*=1.5, 17.1, 20.4 Hz, CH), 6.70 (1H, ddd, *J*=6.4, 17.1, 22.6 Hz, CH). ^{13}C NMR: 23.9 (d, *J*=4.1 Hz), 24.0 (d, *J*=4.1 Hz), 25.7, 25.9, 31.4, 41.8 (d, *J*=20.7 Hz), 70.0 (d, *J*=6.2 Hz), 115.7 (d, *J*=188.3 Hz),

157.5 (d, J=4.1 Hz). ^{31}P NMR: 17.8. IR (nujor): 1625 cm^{-1}. EIMS m/z: 274 (M^+). Anal. calcd for $C_{14}H_{27}O_3P$: C, 61.29; H, 9.92. Found: C, 61.01; H, 10.12.

3.1.4. Diisopropyl (*E*)-4-phenyl-1-butenylphosphonate (2d). A colorless oil. ^{1}H NMR: 1.25 and 1.33 (each 6H, d, J=6.1 Hz, CH_3), 2.54 and 2.78 (each 2H, m), 4.59 (2H, m), 5.56 (1H, ddt, J=20.4, 17.1, 1.5 Hz, CH), 6.77 (1H, ddt, J=22.0, 17.1, 6.4 Hz, CH), 7.16–7.29 (5H, m, Ph). ^{13}C NMR: 23.8 (d, J=4.1 Hz), 24.0 (d, J=4.1 Hz), 33.9, 35.5 (d, J=22.8 Hz), 70.0 (d, J=4.1 Hz), 119.1 (d, J=188.3 Hz), 126.0, 128.2, 128.3, 140.6, 151.3 (d, J=4.1 Hz). ^{31}P NMR: 16.5. IR (neat): 1630 cm^{-1}. EIMS m/z: 296 (M^+). Anal. calcd for $C_{16}H_{25}O_3P$: C, 64.85; H, 8.50. Found: C, 64.70; H, 8.68.

3.1.5. Synthesis of diisopropyl (*E*)-1-(1-hydroxy-2,2-dimethylpropyl)-2-phenylethenylphosphonate (5a): method A. Phosphonate **2a** (536 mg, 2.0 mmol) in THF (5 mL) was added to a solution of LDA (2.4 mmol) in THF (5 mL) at −78°C. After being stirred for 15 min, pivalaldehyde (0.3 mL, 2.8 mmol) was added. The mixture was stirred for 15 min and was quenched with satd NH_4Cl, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Concentration and subsequent chromatography (EtOAc/hexane=3:7) gave **5a** (R^1=Ph, R^2=*t*-Bu, R^3=H, R=*i*-Pr, 643 mg, 91%) as a colorless oil. ^{1}H NMR: 0.86 (9H, s, *t*-Bu), 1.32 and 1.39 (each 3H, d, J=6.4 Hz, CH_3), 1.40 (6H, d, J=6.4 Hz, CH_3), 4.66 (1H, dd, J=11.0, 33.6 Hz, CH), 4.76 (1H, d, J=11.0 Hz, OH), 4.71–4.87 (2H, m), 7.28–7.40 (6H, m, CH, Ph). ^{13}C NMR: 23.4 (d, J=5.2 Hz), 23.80 (d, J=5.2 Hz), 23.84 (d, J=5.2 Hz), 24.1 (d, J=5.2 Hz), 26.5, 37.1, 70.9 (d, J=6.2 Hz), 71.3 (d, J=6.2 Hz), 77.2, 128.0, 128.2, 128.5, 136.0, 133.9 (d, J=167.6 Hz), 145.1 (d, J=7.2 Hz). ^{31}P NMR: 19.7. IR (neat): 3400, 1590 cm^{-1}. FABMS m/z: 355 ($M+H^+$). Anal. calcd for $C_{19}H_{31}O_4P$: C, 64.39; H, 8.82. Found: C, 64.64; H, 9.09.

3.1.6. Diisopropyl (*E*)-1-[hydroxy(phenyl)methyl]-2-phenylethenylphosphonate (5b). Colorless plates of mp 87–88°C (AcOEt/hexane=5:95). ^{1}H NMR: 0.98, 1.21, 1.29 and 1.35 (each 3H, d, J=6.1 Hz, CH_3), 4.36 (1H, m), 4.73 (1H, m), 4.77 (1H, d, J=11.0 Hz, OH), 5.96 (1H, dd, J=11.0, 31.4 Hz, CH), 7.22–7.45 (10H, m, Ph), 7.49 (1H, d, J=24.1 Hz, CH). ^{13}C NMR: 23.5 (d, J=6.2 Hz), 23.6 (d, J=6.2 Hz), 23.9 (d, J=6.2 Hz), 24.1 (d, J=5.2 Hz), 70.3 (d, J=7.2 Hz), 70.9 (d, J=6.2 Hz), 71.4 (d, J=6.2 Hz), 126.1, 127.1, 128.1, 128.7, 128.8, 128.9, 134.4 (d, J=172.8 Hz), 134.6, 134.8, 142.2, 142.9 (d, J=8.3 Hz). ^{31}P NMR: 18.2. IR (nujor): 3200, 1610 cm^{-1}. FABMS m/z: 375 ($M+H^+$). Anal. calcd for $C_{21}H_{27}O_4P$: C, 67.37; H, 7.27. Found: C, 67.21; H, 7.15.

3.1.7. Diisopropyl (*E*)-1-[cyclohexyl(hydroxy)methyl]-2-phenylethenylphosphonate (5c). Colorless plates of mp 81–82°C (AcOEt/hexane=5:95). ^{1}H NMR: 1.35 and 1.41 (each 3H, d, J=6.4 Hz, CH_3), 1.39 (6H, d, J=6.4 Hz, CH_3), 0.59–2.23 (11H, m), 3.67 (1H, d, J=10.7 Hz, OH), 4.29 (1H, ddd, J=10.4, 10.7, 33.9 Hz, CH), 4.80 (2H, m), 7.30–7.39 (5H, m, Ph), 7.37 (1H, d, J=24.7 Hz, CH). ^{13}C NMR: 23.6 (d, J=4.1 Hz), 24.0 (d, J=4.1 Hz), 24.1 (d, J=4.1 Hz), 24.2 (d, J=4.1 Hz), 25.8, 25.9, 26.3, 29.5, 29.7, 43.0, 70.7 (d, J=6.2 Hz), 71.5 (d, J=6.2 Hz), 74.1, 128.2, 128.4, 128.6, 134.6 (d, J=151.0 Hz), 135.3, 143.4 (d, J=9.3 Hz). ^{31}P NMR: 19.3. IR (nujor): 3250, 1620 cm^{-1}. FABMS m/z: 381 ($M+H^+$). Anal. calcd for $C_{21}H_{33}O_4P$: C, 66.30; H, 8.74. Found: C, 66.12; H, 8.82.

3.1.8. Diisopropyl (*E*)-1-(1-hydroxy-3-phenylpropyl)-2-phenylethenylphosphonate (5d). Colorless plates of mp 64–65°C (AcOEt/hexane=5:95). ^{1}H NMR: 1.347, 1.352, 1.38 and 1.41 (each 3H, d, J=6.2 Hz, CH_3), 1.98 (1H, ddt, J=4.0, 8.2, 13.1 Hz, CH_2), 2.32 (1H, m), 2.73–2.85 (2H, m), 3.84 (1H, d, J=10.1 Hz, OH), 4.73 (1H, ddt, J=4.0, 10.1, 32.0 Hz, CH), 4.78 (2H, m), 7.07–7.27 (11H, m, CH, Ph). ^{13}C NMR: 23.4 (d, J=4.1 Hz), 23.7 (d, J=4.1 Hz), 23.9 (d, J=4.1 Hz), 31.6, 38.4, 67.7 (d, J=6.2 Hz), 70.7 (d, J=6.2 Hz), 71.0 (d, J=6.2 Hz), 125.5, 128.0, 128.1, 128.2, 128.4, 128.7, 134.6, 134.4, 135.0 (d, J=191.4 Hz), 141.3, 141.7 (d, J=8.3 Hz). ^{31}P NMR: 19.0. IR (nujor): 3350, 1610 cm^{-1}. FABMS m/z: 403 ($M+H^+$). HRMS Anal. calcd for $C_{23}H_{31}O_4P$: C, 68.64; H, 7.76. Found: C, 68.38; H, 7.86.

3.1.9. Diisopropyl (*E*)-1-[hydroxy(phenyl)methyl]-3,3-dimethyl-1-butenylphosphonate (5e). Colorless plates. ^{1}H NMR: 0.88, 1.14, 1.24 and 1.30 (each 3H, d, J=6.1 Hz, CH_3), 1.29 (9H, s, CH_3), 4.23 (1H, m), 4.62 (1H, m), 4.85 (1H, d, J=11.0 Hz, OH), 6.09 (1H, dd, J=11.0, 34.2 Hz, CH), 6.50 (1H, dd, J=0.9, 26.6 Hz, CH), 7.21–7.48 (5H, m, Ph). ^{13}C NMR: 23.35 (d, J=3.1 Hz), 23.40 (d, J=3.1 Hz), 23.8 (d, J=3.1 Hz), 24.1 (d, J=3.1 Hz), 31.1, 34.9 (d, J=18.6 Hz), 69.2 (d, J=8.3 Hz), 70.4 (d, J=6.2 Hz), 71.0 (d, J=6.2 Hz), 126.2, 126.8, 127.9, 131.9 (d, J=170.7 Hz), 142.3, 154.9 (d, J=6.2 Hz). ^{31}P NMR: 19.7. IR (nujor): 3350, 1620 cm^{-1}. FABMS m/z: 355 ($M+H^+$). Anal. calcd for $C_{19}H_{31}O_4P$: C, 64.39; H, 8.82. Found: C, 64.37; H, 9.09.

3.1.10. Diisopropyl (*E*)-1-(1-hydroxy-3-phenylpropyl)-3,3-dimethyl-1-butenylphosphonate (5f). A pale yellow oil. ^{1}H NMR: 1.05 (9H, s, CH_3), 1.28, 1.29, 1.33 and 1.36 (each 3H, d, J=6.1 Hz, CH_3), 1.81 (1H, m), 2.25 (1H, m), 2.73 (1H, m), 2.89 (1H, m), 4.00 (1H, d, J=11.0 Hz, OH), 4.67 (2H, m), 4.78 (1H, ddt, J=3.7, 11.0, 34.2 Hz, CH), 6.26 (1H, dd, J=0.9, 26.9 Hz, CH), 7.15–7.29 (5H, m, Ph). ^{13}C NMR: 23.5 (d, J=4.1 Hz), 23.9 (d, J=4.1 Hz), 24.1 (d, J=4.1 Hz), 30.7, 32.3, 34.4 (d, J=19.7 Hz), 39.3, 67.7 (d, J=8.3 Hz), 70.6 (d, J=6.2 Hz), 71.0 (d, J=6.2 Hz), 125.7, 128.3, 128.7, 133.2 (d, J=166.6 Hz), 141.8, 154.3 (d, J=6.2 Hz). ^{31}P NMR: 20.3. IR (nujor): 3400, 1620 cm^{-1}. FABMS m/z: 383 ($M+H^+$). HRMS calcd for $C_{21}H_{36}O_4P$: 383.2351. Found: 383.2347.

3.1.11. Diisopropyl (*E*)-2-cyclohexyl-1-(1-hydroxy-3-phenylpropyl)ethenylphosphonate (5g). A colorless oil. ^{1}H NMR: 1.02–2.18 (11H, m), 1.27, 1.29, 1.32 and 1.34 (each 3H, d, J=6.1 Hz, CH_3), 1.83 (1H, m), 2.22 (1H, m), 2.76 (2H, m), 3.92 (1H, d, J=9.8 Hz, OH), 4.49 (1H, ddt, J=4.9, 9.8, 29.3 Hz, CH), 4.67 (2H, m), 6.13 (1H, dd, J=10.1, 24.4 Hz, CH), 7.15–7.32 (5H, m, Ph). ^{13}C NMR: 23.3 (d, J=5.2 Hz), 23.6 (d, J=5.2 Hz), 23.7 (d, J=5.2 Hz), 23.8 (d, J=5.2 Hz), 25.0, 25.4, 31.7, 31.8, 31.9, 37.1 (d, J=16.6 Hz), 39.3, 68.2 (d, J=9.3 Hz), 70.2 (d, J=6.2 Hz), 70.5 (d, J=6.2 Hz), 125.5, 128.0, 128.2, 131.5 (d,

J=169.7 Hz), 141.5, 150.6 (d, J=6.2 Hz). ^{31}P NMR: 19.3. IR (nujor): 3375, 1630 cm^{-1}. FABMS *m/z*: 409 (M+H$^+$). Anal. calcd for $C_{23}H_{37}O_4P$: C, 67.62; H, 9.13. Found: C, 67.61; H, 9.37.

3.1.12. Diisopropyl (*E*)-1-(hydroxy-2,2-dimethylpropyl)-4-phenyl-1-butenylphosphonate (5h). A colorless oil. ^{1}H NMR: 0.97 (9H, s, CH_3), 1.16, 1.31, 1.32 and 1.33 (each 3H, d, J=6.1 Hz, CH_3), 2.41 (1H, m), 2.64–2.81 (3H, m), 4.28 (1H, dd, J=10.7, 31.7 Hz, CH), 4.55 (1H, m), 4.71 (1H, m), 4.89 (1H, d, J=10.7 Hz, OH), 6.43 (1H, ddd, J=5.5, 8.5, 24.1 Hz, CH), 7.18–7.32 (5H, m, Ph). ^{13}C NMR: 23.3 (d, J=4.1 Hz), 23.79 (d, J=4.1 Hz), 23.83 (d, J=4.1 Hz), 24.1 (d, J=4.1 Hz), 26.5, 31.2 (d, J=17.6 Hz), 34.8, 37.3, 70.6 (d, J=6.2 Hz), 71.0 (d, J=6.2 Hz), 78.1 (d, J=10.3 Hz), 126.3, 128.3, 128.6, 132.2 (d, J=168.0 Hz), 140.6, 147.3 (d, J=6.2 Hz). ^{31}P NMR: 19.7. IR (nujor): 3400, 1620 cm^{-1}. FABMS *m/z*: 383 (M+H$^+$). HRMS calcd for $C_{21}H_{36}O_4P$: 383.2351. Found: 383.2346.

3.1.13. Synthesis of diethyl (*E*)-1-[hydroxy(phenyl)-methyl]-1-propenylphosphonate (5i: R^1=Me, R^2=Ph, R^3=H, R=Et): method B. A solution of LDA (0.55 mmol) in THF (5 mL) was added dropwise to a mixture of propenylphosphonate (89 mg, 0.5 mmol) and benzaldehyde (0.05 mL, 0.5 mmol) in THF (5 mL) at −78°C. The mixture was stirred for 0.5 h at −78°C and was quenched with satd NH_4Cl, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Concentration and chromatography (EtOAc/hexane=2:3) gave **5i** as a colorless oil (208 mg) in 73% yield. ^{1}H NMR: 1.05 and 1.26 (each 3H, t, J=6.9 Hz, CH_3), 1.99 (3H, dd, J=6.9, 7.3 Hz, CH_3), 3.57–3.79 (2H, m), 3.90–4.15 (2H, m), 4.53 (1H, d, J=9.9 Hz, CH), 5.73 (0.5H, d, J=9.9 Hz, OH), 5.84 (0.5H, d, J=9.9 Hz, OH), 6.65 (1H, ddq, J=1.0, 6.9, 30.4 Hz, CH), 7.22–7.44 (5H, m, Ph). ^{13}C NMR: 14.9 (d, J=18.3 Hz), 15.9 (d, J=7.3 Hz), 16.1 (d, J=7.4 Hz), 61.8 (d, J=6.1 Hz), 62.1 (d, J=4.9 Hz), 69.8 (d, J=9.8 Hz), 125.6, 127.1, 128.1, 133.3 (d, J=174.5 Hz), 141.6 (d, J=8.5 Hz), 142.3. IR (neat): 3300 cm^{-1}. FABMS *m/z*: 285 (M+H$^+$). Anal. calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.45. Found: C, 59.44; H, 7.48.

3.1.14. Diethyl (*E*)-1-(1-hydroxy-2,2-dimethylpropyl)-1-propenylphosphonate (5j). Colorless oil. ^{1}H NMR: 0.98 (9H, s, *t*-Bu), 1.25–1.36 (6H, m), 1.86 (3H, dd, J=3.6, 6.9 Hz, CH_3), 3.93–4.18 (4H, m), 4.31 (1H, dd, J=10.2, 30.6 Hz, CH), 4.73 (1H, d, J=10.2 Hz, OH), 6.56 (1H, ddq, J=1.0, 24.1, 6.9 Hz, CH). ^{13}C NMR: 15.6 (d, J=18.4 Hz), 15.9 (d, J=7.3 Hz), 26.2, 37.2, 61.9 (d, J=4.8 Hz), 77.1 (d, J=9.8 Hz), 131.0 (d, J=169.7 Hz), 143.5 (d, J=7.3 Hz). IR (neat): 3350 cm^{-1}. FABMS *m/z*: 265 (M+H$^+$). Anal. calcd for $C_{12}H_{25}O_4P$: C, 54.53; H, 9.53. Found: C, 54.27; H, 9.80.

3.1.15. Diethyl 1-(1-hydroxy-2,2-dimethylpropyl)-vinylphosphonate (5k). Colorless oil. ^{1}H NMR: 0.96 (9H, s, *t*-Bu), 1.35 (6H, dt, J=6.7, 7.3 Hz, CH_3), 4.05–4.21 (5H, m), 4.22 (1H, d, J=8.5 Hz, OH), 6.08 (1H, dd, J=1.2, 50.0 Hz, CH), 6.34 (1H, dd, J=1.2, 24.4 Hz, CH). ^{13}C NMR: 16.3 (d, J=6.2 Hz), 26.3, 35.9, 62.3 (d, J=6.1 Hz), 75.7 (d, J=9.8 Hz), 133.2 (d, J=6.2 Hz), 139.5 (d, J=160.5 Hz). IR (neat): 3370 cm^{-1}. FABMS *m/z*: 251 (M+H$^+$). Anal. calcd. for $C_{11}H_{23}O_4P$: C, 52.79; H, 9.26. Found: C, 52.86; H, 9.11.

3.1.16. Synthesis of (4,4-dimethyl-1,2-pentadienyl)benzene (6a: R^1=Ph, R^2=*t*-Bu, R^3=H).[24] A solution of **5a** (R^1=Ph, R^2=*t*-Bu, R^3=H, R=*i*-Pr) (354 mg, 1.0 mmol) in THF (4.5 mL) was added to a suspension of KH (30% dispersion in oil, 115 mg, 1.0 mmol) in THF (4 mL) at −78°C. After being stirred for 20 min, a solution of 18-crown-6 (26 mg, 0.1 mmol) in THF (1.5 mL) was added. The mixture was stirred for 0.5 h at 0°C and was quenched with brine (20 mL) and extracted with benzene. The organic layer was dried over Na_2SO_4. Concentration and chromatography (hexane) afforded **6a** as a colorless oil (158 mg) in 92% yield. ^{1}H NMR: 1.13 (9H, s, *t*-Bu), 5.57 and 6.18 (each 1H, d, J=6.3 Hz, CH), 7.29 (5H, m, Ph). ^{13}C NMR: 30.3, 32.7, 96.2, 106.9, 126.4, 126.6, 128.5, 135.3, 202.4. IR (neat): 1950, 1580 cm^{-1}. EIMS *m/z*: 172 (M$^+$).

3.1.17. (3-Cyclohexyl-1,2-propadienyl)benzene (6b).[25] A colorless oil. ^{1}H NMR: 1.14–2.16 (11H, m), 5.56 (1H, dd, J=6.1, 6.4 Hz, CH), 6.15 (1H, dd, J=3.1, 6.4 Hz, CH), 7.15–7.29 (5H, m, Ph). ^{13}C NMR: 26.0, 26.1, 33.1, 33.2, 37.6, 95.4, 101.0, 126.4, 126.6, 128.5, 135.2 (Ph), 204.1. IR (neat): 1945 cm^{-1}. EIMS *m/z*: 198 (M$^+$).

3.1.18. (5-Phenyl-1,2-pentadienyl)benzene (6c).[26] A colorless oil. ^{1}H NMR: 2.43–2.54 (2H, m), 2.84 (2H, t, J=8.1 Hz, CH_2), 5.60 (1H, m), 6.11–6.20 (1H, m), 7.15–7.40 (10H, m, Ph). IR (neat): 1945 cm^{-1}. EIMS *m/z*: 220 (M$^+$).

3.1.19. 1,2-Butadienylbenzene (6d).[27] A colorless oil. ^{1}H NMR: 1.78 (3H, dd, J=3.4, 7.0 Hz, CH_3), 5.54 (1H, dd, J=6.7, 7.0 Hz, CH), 6.09 (1H, dd, J=3.4, 6.7 Hz, CH), 7.16–7.31 (5H, m, Ph). ^{13}C NMR: 14.1, 89.6, 94.0, 126.6, 128.5, 135.0, 206.0. IR (neat): 1940 cm^{-1}. EIMS *m/z*: 130. (M$^+$).

3.1.20. (3-Phenyl-1,2-propadienyl)benzene (6e).[24] A colorless oil. ^{1}H NMR: 6.60 (2H, s, CH), 7.20–7.36 (10H, m, Ph). ^{13}C NMR: 98.0, 127.0, 127.3, 128.6, 133.2, 208.1. IR (neat): 1940 cm^{-1}. EIMS *m/z*: 192 (M$^+$).

3.1.21. (6,6-Dimethyl-3,4-heptadienyl)benzene (6f).[25] A colorless oil. ^{1}H NMR: 1.01 (9H, s, *t*-Bu), 2.30 (2H, m), 2.72 (2H, t, J=7.9 Hz, CH_2), 5.11 (1H, dt, J=3.1, 6.1 Hz, CH), 5.20 (1H, dt, J=6.1, 6.4 Hz, CH), 7.16–7.29 (5H, m, Ph). ^{13}C NMR: 30.2, 30.9, 31.7, 35.5, 92.1, 103.5, 125.8, 128.3, 128.5, 142.0, 201.1. IR (neat): 1960 cm^{-1}. EIMS *m/z*: 200 (M$^+$). HRMS calcd for $C_{15}H_{20}$: 200.1565. Found: 200.1570.

3.1.22. (5-Cyclohexyl-3,4-pentadienyl)benzene (6g).[25] A colorless oil. ^{1}H NMR: 0.99–1.93 (11H, m), 2.30 (2H, m), 2.71 (2H, m), 5.08 (1H, ddd, J=3.1, 6.1, 9.2 Hz, CH), 5.16 (1H, ddd, J=2.7, 6.1, 6.4 Hz, CH), 7.16–7.29 (5H, m, Ph). ^{13}C NMR: 26.02, 26.04, 26.2, 30.8, 33.0, 33.1, 35.5, 37.2, 91.1, 97.6, 125.8, 128.2, 128.5, 142.0, 202.8. IR (neat): 1960 cm^{-1}. EIMS *m/z*: 226 (M$^+$).

3.1.23. (3,4-Pentadienyl)benzene (6h). A colorless oil. ^{1}H NMR: 2.32 (2H, m), 2.73 (2H, m), 4.67 (2H, dt, J=3.4,

6.7 Hz, CH_2), 5.15 (1H, dq, J=6.7, 6.7 Hz, CH), 7.17–7.30 (5H, m, Ph). ^{13}C NMR: 30.0, 35.4, 75.1, 89.4, 125.9, 128.3, 128.5, 141.7, 208.6. IR (neat): 1940 cm^{-1}. EIMS m/z: 144 (M^+).

3.1.24. (3-Methyl-1,2-pentadienyl)benzene (6i).[28] A colorless oil. ^1H NMR: 1.06 (3H, t, J=7.3 Hz, CH_3), 1.82 (3H, d, J=3.1 Hz, CH_3), 2.09 (2H, dq, J=3.1, 7.3 Hz, CH_2), 6.08 (1H, m), 7.37 (5H, m, Ph). IR (neat): 1940 cm^{-1}. EIMS m/z: 158 (M^+).

3.1.25. (4,4-Dimethyl-1-pentynyl)benzene (10a). A colorless oil. ^1H NMR: 1.05 (9H, s, t-Bu), 2.28 (2H, s, CH_2), 7.24–7.41 (5H, m, Ph). ^{13}C NMR: 29.1, 31.4, 34.4, 82.1, 88.8, 124.2, 127.4, 128.2, 131.5. IR (neat): 2200 cm^{-1}. EIMS m/z: 172 (M^+). Anal. calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.65; H, 9.58.

3.1.26. (3-Cyclohexyl-1-propynyl)benzene (10b). A colorless oil. ^1H NMR: 1.02–1.88 (11H, m), 2.29 (2H, d, J=6.7 Hz, CH_2), 7.24–7.40 (5H, m, Ph). ^{13}C NMR: 26.2, 26.3, 27.2, 32.8, 37.5, 81.5, 89.3, 124.2, 127.4, 128.1, 131.5. IR (neat): 2200 cm^{-1}. EIMS m/z: 198 (M^+).

3.1.27. Synthesis of 6a from 2a (R^1=Ph, R=Et) (Table 6, entry 1). To a mixture of **2a** (240 mg, 1 mmol) and pivalaldehyde (0.13 mL, 1.2 mmol) in THF (2.5 mL) was added a solution of LDA (1.5 mmol) in THF (2.5 mmol) at −78°C for 20 min. The mixture was warmed to 0°C for 5 min. t-BuOK (168 mg, 1.5 mmol) was added at 0°C for 5 min and the mixture was allowed to warm up gradually to 60°C and stirred for 20 min. The mixture was diluted with benzene, washed with brine, and dried over Na_2SO_4. Concentration and chromatography (EtOAc/hexane=0:10–10:0) gave **6a** (148 mg, 85%).

3.1.28. One-flask synthesis of 6a from 1 (Scheme 3). To a suspension of NaH (88 mg, 2.2 mmol) in THF (3 mL) cooled to 0°C was added **1** (0.5 mL, 2 mmol) in THF (2 mL) for 5 min. The solution was warmed to room temperature for 0.5 h and cooled to 0°C for 5 min. Benzaldehyde (0.22 mL, 2.2 mmol) was added at 0°C for 5 min. The mixture was allowed to warm up to room temperature for 50 min and cooled to −78°C for 5 min. After addition of pivalaldehyde (0.33 mL, 3.0 mmol), LDA (3.3 mmol) was added during 10 min and the mixture was stirred at −78°C for 0.5 h. A suspension of t-BuOK (3.3 mmol) in THF (3 mL) was added at −78°C for 10 min. The mixture was heated up to 60°C for 50 min. The mixture was diluted with benzene, washed with brine, and dried over Na_2SO_4. Concentration and chromatography (EtOAc/hexane=0:10–10:0) gave **6a** (286 mg, 73%).

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