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Brief Communication

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Morita–Baylis–Hillman Reaction of α,β-Unsaturated Ketones with Allylic Acetates by the Combination of Transition-Metal Catalysis and Organomediation

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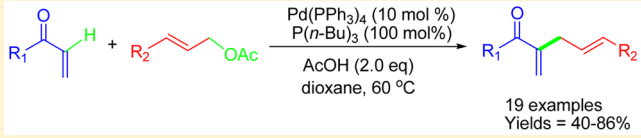
Supporting Information

ABSTRACT: An intermolecular Morita–Baylis–Hillman (MBH) reaction of α,β-unsaturated ketones with allylic acetates under the catalysis of 10 mol % of tetrakis-(triphenylphosphine)palladium(0) and mediation of tributylphosphine has been developed in the presence of acetic acid, affording the desired α-coupling products. The MBH reaction has the advantages of good tolerance to many functional groups, excellent regioselectivity and *E*-stereoselectivity, and moderate to good yields.



The Morita–Baylis–Hillman (MBH) reaction is a very important carbon–carbon bond-forming reaction to provide densely functionalized organic compounds with enormous synthetic application.[1] This reaction was shown to be highly efficient in the coupling of activated alkenes at their α-positions with carbon electrophiles under the influence of organic compounds mainly by the catalysis of amines or phosphines. The activated alkenes can be alkyl vinyl ketones, acrylates, acrylonitrile, vinyl sulfones, acrylamides, allenic esters, vinyl sulfonates, vinyl phosphonates, acrolein, etc.[1a] A broad range of electrophiles, such as aldehydes,[1a] α-keto esters,[1a] 1,2-diketones,[1a] aldimines,[1a] α,β-unsaturated carbonyl compounds,[2] epoxides,[3] and triarylbismuth(V) dichlorides,[4] have been employed in the MBH reaction. In 2005, Krafft and co-workers revealed an intramolecular MBH reaction of α,β-unsaturated ketones with saturated alkyl halides to give five- or six-membered ring enones under the mediation of tertiary phosphine.[5] Until now, the MBH alkylation reaction especially intermolecular alkylation is still a challenging subject. The MBH reaction of α,β-unsaturated carbonyl compounds with allylic halides was developed under organocatalysis or organomediation.[6a−d] In these cases, most α,β-unsaturated carbonyl compounds are cyclic α,β-unsaturated ketones[6a,b] or intramolecular MBH reaction occurs via allylic chloride intermediates.[6c] In general, allylic alcohols and their esters are more easily available as compared to allylic halides. In 2003, Krische et al. reported an intramolecular MBH reaction of the substrates bearing both α,β-unsaturated ketone moieties and allylic carbonate moieties under palladium catalysis and phosphine mediation.[7] However, to the best of our knowledge, there is no systematic results on the intermolecular MBH reaction of α,β-unsaturated carbonyl compounds with allylic esters. Herein we wish to present our recent results on the intermolecular MBH reaction of acyclic α,β-unsaturated ketones with allylic acetates by the combination of transition-metal catalysis and organomediation.

Initially, aryl vinyl ketone **1a** and allylic acetate **2a** were chosen as model substrates to explore and optimize their MBH reaction. When the reaction performed in the presence of $Pd(PPh_3)_4$ (10 mol %) and $P(n\text{-}Bu)_3$ (100 mol %) under nitrogen at 60 °C, we were pleased to find that the desired α-allylic group substituted aryl vinyl ketone **3aa** was formed in 20% yield (entry 1, Table 1). Along with the minor α-allylated product **3aa**, Rauhut–Currier byproduct **4aa** was also formed in 78% yield. We added an equimolecular Brønsted acid, benzoic acid, to the reaction mixture to quench the generation of the Rauhut–Currier byproduct (also see Scheme 2).[8] As expected, the amount of Rauhut–Currier byproduct **4aa** was decreased remarkably, and the yield of α-allylated product **3aa** was increased to 50% (entry 2, Table 1). Other palladium catalysts and other tertiary phosphines or amines were screened, but none of them gave a better yield for **3aa** (compare entries 3–8 with entry 2, Table 1; also see the Supporting Information). Then other Brønsted acids were examined in the MBH reaction, and AcOH proved to be the most efficient among them (entries 9–11, Table 1). Increasing the amount of AcOH from 1.0 to 2.0 equiv resulted in improvement of the yield to 82% (entry 12, Table 1). When the loading of $P(n\text{-}Bu)_3$ was decreased to 50 mol %, the yield of **3aa** was decreased to 37% dramatically. The effect of solvent on this reaction was also studied, and 1,4-dioxane proved to be best for the yield of desired **3aa** (compare entries 13–15 with entry 12, Table 1; also see SI). It is noteworthy that, if either $Pd(PPh_3)_4$ or $P(n\text{-}Bu)_3$ was employed in the MBH reaction, no desired α-coupling product **3aa** was obtained.

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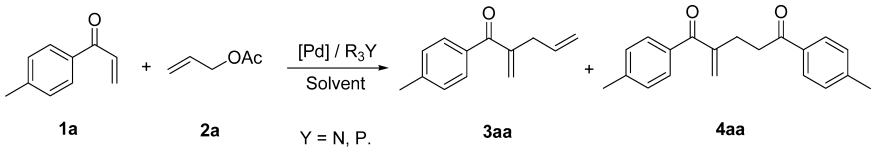
Table 1. Optimization of MBH Reaction of Aryl Vinyl Ketone 1a with Allylic Acetate 2a[a]



1a 2a 3aa 4aa

entry	[Pd]	phosphine	additive	solvent	yield[b] (%) 3aa	4aa
1	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$		dioxane	20	78
2	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	BzOH	dioxane	50	45
3	$Pd(dba)_2$	P(*n*-Bu)$_3$	BzOH	dioxane	39	51
4	$Pd_2(dba)_3.CHCl_3$	P(*n*-Bu)$_3$	BzOH	dioxane	43	50
5	$Pd(OAc)_2$	P(*n*-Bu)$_3$	BzOH	dioxane	45	53
6	$Pd(PPh_3)_4$	P(*t*-Bu)$_3$	BzOH	dioxane		trace
7	$Pd(PPh_3)_4$	P(Cyhex)$_3$	BzOH	dioxane	trace	trace
8	$Pd(PPh_3)_4$	PPh_3	BzOH	dioxane		trace
9	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	*p*-TSA	dioxane		
10	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	PivOH	dioxane	47	51
11	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	AcOH	dioxane	59	40
12[c]	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	AcOH	dioxane	82 (37)[d]	12
13[c]	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	AcOH	toluene	60	31
14[c]	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	AcOH	DME	74	16
15[c]	$Pd(PPh_3)_4$	P(*n*-Bu)$_3$	AcOH	THF	46	39

[a]The mixture of **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (10 mol %), phosphine (100 mol %), and additive (1.0 equiv) was stirred in solvent (2 mL) at 60 °C; under N_2 (1 atm) for 24 h. [b]Isolated yield. [c]2.0 equiv of AcOH. [d]50 mol % of phosphine.

After the reaction conditions were screened, it can be concluded that the optimized reaction should be performed under the catalysis of 10 mol % of $Pd(PPh_3)_4$ and 100 mol % of P(*n*-Bu)$_3$ with 2.0 equiv of AcOH in 1,4-dioxane at 60 °C under nitrogen atmosphere. Under the optimized conditions, we found that various aryl vinyl ketones **1a**−**l**, which bear either electron-donating or electron-withdrawing groups on the benzene ring (in **1a**−**l**), were able to undergo the MBH reaction smoothly with allylic acetate **2a** to give the desired *α*-allylated products **3aa**−**la** in the yields of 65−82% (entries 1−12, Table 2). The MBH reaction tolerated a range of functional groups on the benzene ring in **1a**−**l**, such as fluoro, chloro, bromo, nitro, trifluoromethyl, and methoxyl. A naphthyl group instead of a benzene group in aryl vinyl ketone **1m** also resulted in a good yield of **3ma** in the MBH reaction (entry 13, Table 2). We also found that 3-aryl allylic acetates **2b**−**e** were also able to undergo the MBH reaction with vinyl ketone **1a** smoothly to give 5-aryl *α*-allylated products **3ab**−**ae** in good yields with high *E* selectivity (entries 14−17, Table 2). The MBH reaction of vinyl ketone **1a** with 3-aryl allylic acetates **2b**−**e** also has excellent regioselectivity, and no 3-aryl *α*-allylated product was observed. Moreover, 2-branched allylic acetate **2f** also performed the MBH reaction with vinyl ketone **1a** expediently (entry 18, Table 2). However, when 3-(4-nitrophenyl)allylic acetate was employed, no desired coupling product was observed.

When alkyl vinyl ketone **1n** was employed in the MBH reaction under the optimized conditions, the coupling product **3nb** was also obtained albeit in a lower yield as compared to that of **3aa**−**ma** (Scheme 1, eq 1). If the acetate group in **2a** was switched to phenoxyl group in allylic phenyl ether **5a**, aryl vinyl ketone **1a** was able to perform the MBH reaction readily with ether **5a**, affording the desired *α*-coupling product **3aa** in moderate yield (eq 2). However, no desired product was obtained when allylic bromide was employed instead of allylic acetate (eq 2).

On the basis of the literature[1a,7,9] and our experimental results, a plausible mechanism for the MBH allylation reaction is depicted in Scheme 2. First, aryl vinyl ketone **1** undergoes a nucleophilic addition with tri(*n*-butyl)phosphine followed by protonation with AcOH, generating phosphonium acetate **6**, which was determined by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and MS (see the SI). Then, phosphonium salt **6** may be deprived a proton slowly by acetate anion to give active intermediate **7**. Intermediate **7** nucleophilically attacks *π*-allylpalladium complex **8** to generate phosphonium salt **9** with regenerating palladium(0) for catalytic cycle. Finally, the *β*-hydrogen elimination of phosphonium salt **9** leads to the desired *α*-allylated product **3** with regenerating tri-*n*-butylphosphine.

In conclusion, we have developed a intermolecular MBH reaction of *α*,*β*-unsaturated ketones **1** with allylic acetates **2** under the catalysis of 10 mol % of $Pd(PPh_3)_4$ and mediation of P(*n*-Bu)$_3$ and AcOH, affording the desired *α*-coupling products **3**. The MBH reaction has the advantages of good tolerance to many functional groups, excellent regioselectivity and *E*-stereoselectivity, and moderate to good yields. A plausible mechanism via phosphonium salt **6** was also proposed. Further studies on the intermolecular alkylation of the MBH reaction using Brønsted acid to decrease Rauhut−Currier byproduct are currently underway.

EXPERIMENTAL SECTION

Preparation of Aryl Vinyl Ketone 1.[10] To a mixture of methyl aryl ketone (10.0 mmol) and paraformaldehyde (0.90 g, 30.0 mmol) in THF (20.0 mL) were added diisopropylammonium trifluoroacetate (2.13 g, 10.0 mmol) and trifluoroacetic acid (0.11 g, 1.0 mmol, 10 mol %). After the reaction mixture was stirred at reflux for 1 day, the mixture was cooled to room temperature, and a second addition of paraformaldehyde (0.90 g, 30.0 mmol) was performed. The reaction mixture was then stirred at reflux for an additional 1 day. After the

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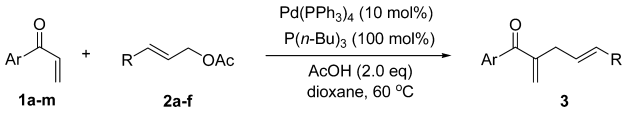
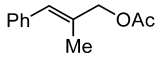
Table 2. Intermolecular MBH Reaction of Aryl Vinyl ketones 1 with Allylic Acetates 2 by the Combination of Transition-Metal Catalysis and Organomediation[a]



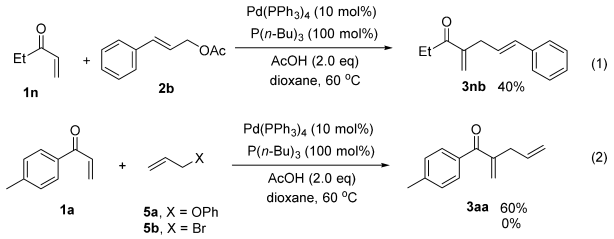
entry	Ar	R	product	yield (%)[b]
1	*p*-MeC_6H_4 **1a**	H **2a**	**3aa**	82
2	*o*-MeC_6H_4 **1b**	H **2a**	**3ba**	71
3	*m*-MeC_6H_4 **1c**	H **2a**	**3ca**	64
4	*m*-$MeOC_6H_4$ **1d**	H **2a**	**3da**	80
5	*p*-$MeOC_6H_4$ **1e**	H **2a**	**3ea**	76
6	Ph **1f**	H **2a**	**3fa**	78
7	*p*-FC_6H_4 **1g**	H **2a**	**3ga**	73
8	*p*-ClC_6H_4 **1h**	H **2a**	**3ha**	72
9	*p*-BrC_6H_4 **1i**	H **2a**	**3ia**	66
10	*m*-$NO_2C_6H_4$ **1j**	H **2a**	**3ja**	69
11	*p*-$NO_2C_6H_4$ **1k**	H **2a**	**3ka**	80
12	*p*-$CF_3C_6H_4$ **1l**	H **2a**	**3la**	65
13	2-naphthyl **1m**	H **2a**	**3ma**	86
14	*p*-MeC_6H_4 **1a**	Ph **2b**	**3ab**	82
15	*p*-MeC_6H_4 **1a**	*o*-$MeOC_6H_4$ **2c**	**3ac**	61
16	*p*-MeC_6H_4 **1a**	*p*-FC_6H_4 **2d**	**3ad**	71
17	*p*-MeC_6H_4 **1a**	*p*-ClC_6H_4 **2e**	**3ae**	77
18	*p*-MeC_6H_4 **1a**	 **2f**	**3af**	50

[a]The mixture of **1a** (0.1 mmol), **2a** (0.3 mmol), $Pd(PPh_3)_4$ (10 mol %), P(*n*-Bu)$_3$ (100 mol %), and AcOH (2.0 equiv) was stirred in dioxane (2 mL) at 60 °C; under N_2 (1 atm) for 24 h. [b]Isolated yield.

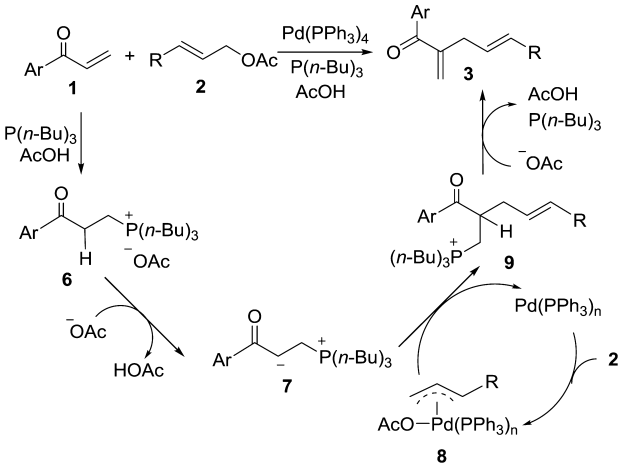
mixture was cooled, solvent was removed under reduced pressure. The residue was dissolved in Et_2O, and the etheric solution was washed with 1 N HCl (200 mL), 1 N NaOH (200 mL), and brine (200 mL), respectively. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/200−1/100 as eluent) to give aryl vinyl ketone **1**.

General Procedure for the MBH Reaction. To a mixture of aryl vinyl ketone **1** (0.1 mmol) and AcOH (12.0 mg, 0.2 mmol) in 1,4-dioxane (2 mL) was added P(*n*-Bu)$_3$ (20.2 mg, 0.1 mmol, 100 mol %). After the reaction mixture was stirred at room temperature for 1 min, $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 10 mol %) and allylic acetate **2** (0.3 mmol) were added. The reaction mixture was stirred at 60 °C for 24 h under N_2. Then, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/100 as eluent) to give the desired α-allylic group substituted aryl vinyl ketone **3**.

Scheme 1. MBH Reactions of Expanded Scope by the Combination of Transition-Metal Catalysis and Organomediation



Scheme 2. Possible Mechanism for the MBH Reaction of Aryl Vinyl Ketone 1 with Allylic Acetate 2 by the Combination of Transition-Metal Catalysis and Organomediation



2-Methylene-1-(4-tolyl)pent-4-en-1-one (***3aa***)*:* colorless oil (15.3 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.95−5.83 (m, 2H), 5.64 (s, 1H), 5.17−5.09 (m, 2H), 3.22 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 146.5, 143.0, 135.0, 134.9, 129.8, 128.9, 125.5, 117.1, 36.4, 21.6; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{14}O$ 186.1045, found 186.1049.

2-Methylene-1-(2-tolyl)pent-4-en-1-one (***3ba***)*:* colorless oil (13.2 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 1H), 7.25−7.17 (m, 3H), 5.97−5.87 (m, 2H), 5.65 (s, 1H), 5.19−5.11 (m, 2H), 3.21 (d, *J* = 6.8 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 147.8, 138.9, 136.2, 135.1, 130.8, 129.8, 129.7, 127.9, 125.0, 117.1, 34.8, 19.7; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{14}O$ 186.1045, found 186.1048.

2-Methylene-1-(3-tolyl)pent-4-en-1-one (***3ca***)*:* colorless oil (11.9 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2H), 7.36−7.29 (m, 2H), 5.95−5.85 (m, 2H), 5.67 (d, *J* = 0.8 Hz, 1H), 5.18−5.10 (m, 2H), 3.22 (dt, *J* = 6.8, 1.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 146.5, 138.1, 137.7, 135.0, 133.0, 129.9, 128.0, 126.8, 126.4, 117.1, 36.2, 21.3; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{14}O$ 186.1045, found 186.1044.

1-(3-Methoxyphenyl)-2-methylenepent-4-en-1-one (***3da***)*:* colorless oil (16.2 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 3H), 7.09−7.06 (m, 1H), 5.95−5.84 (m, 2H), 5.69 (d, *J* = 0.8 Hz, 1H), 5.17−5.10 (m, 2H), 3.84 (s, 3H), 3.22−3.21 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 159.5, 146.3, 139.0,

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134.9, 129.1, 126.4, 122.2, 118.5, 117.2, 113.9, 55.4, 36.2; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0998.

*1-(4-Methoxyphenyl)-2-methylenepent-4-en-1-one (**3ea**):* colorless oil (15.4 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.79 (m, 2H), 6.94−6.91 (m, 2H), 5.94−5.84 (m, 1H), 5.77 (d, J = 1.2 Hz, 1H), 5.58 (d, J = 0.8 Hz, 1H), 5.16−5.08 (m, 2H), 3.86 (s, 3H), 3.21 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 163.2, 146.5, 135.0, 132.0, 130.1, 124.2, 117.1, 113.5, 55.4, 36.7; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0993.

*2-Methylene-1-phenylpent-4-en-1-one (**3fa**):*[11] colorless oil (13.4 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.74(m, 2H), 7.55−7.51 (m, 1H), 7.45−7.41 (m, 2H), 5.95−5.85 (m, 2H), 5.67 (d, J = 0.8 Hz, 1H), 5.18−5.09 (m, 2H), 3.22 (dt, J = 6.8, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 146.4, 137.7, 135.0, 132.2, 129.5, 128.2, 126.5, 117.2, 36.2; MS (EI) m/z 172.1 (M^+), 171.1, 129.1, 128.1, 105.1, 77.1, 51.1, 39.1.

*1-(4-Fluorophenyl)-2-methylenepent-4-en-1-one (**3ga**):* colorless oil (13.9 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.79 (m, 2H), 7.14−7.09 (m, 2H), 5.94−5.83 (m, 2H), 5.63 (d, J = 0.8 Hz, 1H), 5.17−5.10 (m, 2H), 3.21 (dt, J = 6.8, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 165.5 (d, J = 252.1 Hz,), 146.3, 134.8, 133.8 (d, J = 3.0 Hz), 132.1 (d, J = 8.9 Hz), 125.9, 117.3, 115.3 (d, J = 21.5 Hz), 36.3; HR-MS (EI-TOF) (M^+) calcd for $C_{12}H_{11}FO$ 190.0794, found 190.0795.

*1-(4-Chlorophenyl)-2-methylenepent-4-en-1-one (**3ha**):* colorless oil (14.9 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.69 (m, 2H), 7.43−7.40 (m, 2H), 5.93−5.83 (m, 2H), 5.65 (d, J = 0.8 Hz, 1H), 5.17−5.10 (m, 2H), 3.21 (dt, J = 6.8, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 146.3, 138.7, 136.0, 134.7, 130.9, 128.6, 126.5, 117.4, 36.2; HR-MS (EI-TOF) (M^+) calcd for $C_{12}H_{11}ClO$ 206.0498, found 206.0498.

*1-(4-Bromophenyl)-2-methylenepent-4-en-1-one (**3ia**):* yellow oil (16.6 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.57 (m, 4H), 5.93−5.83 (m, 2H), 5.65 (s, 1H), 5.17−5.11 (m, 2H), 3.21 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 146.2, 136.4, 134.7, 131.5, 131.0, 127.2, 126.6, 117.4, 36.1; HR-MS (EI-TOF) (M^+) calcd for $C_{12}H_{11}BrO$ 249.9993, found 249.9995.

*2-Methylene-1-(3-nitrophenyl)pent-4-en-1-one (**3ja**):* colorless oil (15.0 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, J = 1.8 Hz, 1H), 8.40 (ddd, J = 8.4, 2.2, 1.0 Hz, 1H), 8.08 (dt, J = 7.6, 1.2 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 6.03 (t, J = 1.4 Hz, 1H), 5.96−5.85 (m, 1H), 5.72 (s, 1H), 5.21−5.14 (m, 2H), 3.25 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 148.0, 145.9, 139.2, 134.9, 134.3, 129.6, 128.1, 126.5, 124.2, 117.8, 35.9; HR-MS (EI-TOF) (M^+) calcd for $C_{12}H_{11}NO_3$ 217.0739, found 217.0742.

*2-Methylene-1-(4-nitrophenyl)pent-4-en-1-one (**3ka**):* colorless oil (17.4 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dt, J = 8.8, 2.1 Hz, 2H), 7.86 (dt, J = 9.2, 2.0 Hz, 2H), 6.04 (t, J = 1.4 Hz, 1H), 5.95−5.85 (m, 1H), 5.71 (s, 1H), 5.20−5.14 (m, 2H), 3.24 (dt, J = 6.8, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 149.7, 146.2, 143.1, 134.4, 130.1, 128.8, 123.5, 117.7, 35.7; HR-MS (EI-TOF) (M^+) calcd for $C_{12}H_{11}NO_3$ 217.0739, found 217.0742.

*2-Methylene-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (**3la**):* colorless oil (15.6 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 5.98 (s, 1H), 5.95−5.85 (m, 1H), 5.69 (s, 1H), 5.19−5.13 (m, 2H), 3.23 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 146.2, 140.9, 134.6, 133.5 (q, J = 32.5 Hz), 129.6, 128.0, 125.3 (q, J = 3.7 Hz), 123.7 (q, J = 270.9 Hz), 117.5, 35.8; HR-MS (EI-TOF) (M^+) calcd for $C_{13}H_{11}F_3O$ 240.0762, found 240.0764.

*2-Methylene-1-(naphthalen-2-yl)pent-4-en-1-one (**3ma**):* colorless oil (19.1 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.93−7.85 (m, 4H), 7.60−7.51 (m, 2H), 6.00−5.90 (m, 2H), 5.73 (d, J = 0.8 Hz, 1H), 5.22−5.12 (m, 2H), 3.28 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 146.6, 135.2, 135.0, 134.9, 132.3, 131.1, 129.4, 128.2, 128.1, 127.8, 126.8, 126.2, 125.5, 117.3, 36.4; HR-MS (EI-TOF) (M^+) calcd for $C_{16}H_{14}O$ 222.1045, found 222.1042.

*(E)-2-Methylene-5-phenyl-1-(4-tolyl)pent-4-en-1-one (**3ab**):* colorless oil (21.5 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 2H), 7.37−7.20 (m, 7H), 6.50 (d, J = 16.0 Hz, 1H), 6.32−6.25 (m, 1H), 5.89 (s, 1H), 5.67 (s, 1H), 3.37 (d, J = 6.8 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 146.7, 143.1, 137.4, 134.9, 132.4, 129.8, 128.9, 128.5, 127.2, 126.7, 126.2, 125.8, 35.6, 21.6; HR-MS (EI-TOF) (M^+) calcd for $C_{19}H_{18}O$ 262.1358, found 262.1359.

*(E)-5-(2-Methoxyphenyl)-2-methylene-1-(4-tolyl)pent-4-en-1-one (**3ac**):* colorless oil (17.8 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.24−7.16 (m, 3H), 6.91−6.80 (m, 3H), 6.32−6.27 (m, 1H), 5.88 (s, 1H), 5.65 (s, 1H), 3.82 (s, 3H), 3.38 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 156.4, 146.9, 143.0, 135.0, 129.8, 128.9, 128.2, 127.3, 127.0, 126.6, 126.4, 125.6, 120.6, 110.9, 55.5, 36.0, 21.6; HR-MS (EI-TOF) (M^+) calcd for $C_{20}H_{20}O_2$ 292.1463, found 292.1467.

*(E)-5-(4-Fluorophenyl)-2-methylene-1-(4-tolyl)pent-4-en-1-one (**3ad**):* white solid (19.9 mg, 71% yield); Mp: 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.33−7.23 (m, 4H), 7.00−6.95 (m, 2H), 6.46 (d, J = 16.0 Hz, 1H), 6.23−6.16 (m, 1H), 5.88 (s, 1H), 5.67 (s, 1H), 3.35 (d, J = 6.8 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 162.1 (d, J = 244.8 Hz), 146.6, 143.1, 134.9, 133.5, 131.2, 129.8, 129.0, 127.6 (d, J = 7.8 Hz), 126.4 (d, J = 2.1 Hz), 125.8, 115.4 (d, J = 21.0 Hz), 35.6, 21.6; HR-MS (EI-TOF) (M^+) calcd for $C_{19}H_{17}FO$ 280.1263, found 280.1262.

*(E)-5-(4-Chlorophenyl)-2-methylene-1-(4-tolyl)pent-4-en-1-one (**3ae**):* white solid (22.9 mg, 77% yield); Mp: 76−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.29−7.23 (m, 6H), 6.47 (d, J = 16.8 Hz, 1H), 6.30−6.22 (m, 1H), 5.88 (s, 1H), 5.68 (s, 1H), 3.36 (d, J = 7.2 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 146.4, 143.1, 135.8, 134.9, 132.8, 131.2, 129.7, 129.0, 128.6, 127.5, 127.4, 125.9, 35.6, 21.6; HR-MS (EI-TOF) (M^+) calcd for $C_{19}H_{17}ClO$ 296.0968, found 296.0968.

*(E)-4-Methyl-2-methylene-5-phenyl-1-(4-tolyl)pent-4-en-1-one (**3af**):* colorless oil (13.8 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.31−7.17 (m, 7H), 6.38 (s, 1H), 5.86 (s, 1H), 5.68 (s, 1H), 3.34 (s, 2H), 2.41 (s, 3H), 1.90 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 146.3, 143.1, 138.2, 135.8, 134.9, 129.8, 129.0, 128.8, 128.1, 127.8, 126.2, 125.8, 42.9, 21.6, 17.9; HR-MS (EI-TOF) (M^+) calcd for $C_{20}H_{20}O$ 276.1514, found 276.1517.

*(E)-4-Methylene-7-phenylhept-6-en-3-one (**3nb**):* colorless oil (8.0 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 5H), 6.42 (d, J = 15.6 Hz, 1H), 6.25−6.17 (m, 1H), 6.06 (s, 1H), 5.80 (s, 1H), 3.18 (d, J = 7.2 Hz, 2H), 2.74 (q, J = 7.3 Hz, 2H), 1.11 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 147.1, 137.4, 132.0, 128.5, 127.3, 127.2, 126.1, 124.5, 34.3, 30.9, 8.4; HR-MS (EI-TOF) (M^+) calcd for $C_{14}H_{16}O$ 200.1201, found 200.1202.

*2-Methylene-1,5-di-4-tolylpentane-1,5-dione (**4aa**):*[12] white solid (22.8 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.26−7.22 (m, 4H), 5.90 (s, 1H), 5.63 (s, 1H), 3.20 (t, J = 7.2 Hz, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H); MS (EI) m/z 292.1 (M^+), 277.1, 264.1, 173.1, 119.0, 91.0, 65.0.

*Phosphonium Acetate **6**.* To a mixture of aryl vinyl ketone **1a** (14.6 mg, 0.1 mmol) and AcOH (12.0 mg, 0.2 mmol) in 1,4-dioxane (2 mL) was added P(n-Bu)$_3$ (20.2 mg, 0.1 mmol). After the reaction mixture was stirred at room temperature for 1 min, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/methanol = 3/1 as eluent) to give the desired phosphonium acetate **6**.

*Tributyl(3-oxo-3-(4-tolyl)propyl)phosphonium acetate (**6**):* Colorless oil (38.8 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.76−3.68 (m, 2H), 2.76−2.70 (m, 2H), 2.43−2.36 (m, 9H), 2.00 (s, 3H), 1.53−1.51 (m, 12H), 0.96 (t, J = 6.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7 (d, J = 6.5 Hz), 176.1, 145.1, 132.9, 129.6, 128.7, 31.6 (d, J = 4.1 Hz), 24.0 (d, J = 15.7 Hz), 23.8 (d, J = 4.6 Hz), 23.2, 21.8, 19.2 (d, J = 47.2 Hz), 13.9 (d, J = 51.4 Hz), 13.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.6 (s); MS-ESI m/z 349.3 [M − OAc]$^+$. Because phosphonium acetate **6** decomposes gradually, it is not pure enough for elemental analysis although it is pure enough for NMR.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00684.

Optimization of reaction conditions and ^{1}H NMR, ^{13}C NMR, and HRMS spectra for new products (PDF)

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Notes

The authors declare no competing financial interest.

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