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# Catalytic Allylation of Stabilized Phosphonium Ylides with Primary Allylic Amines

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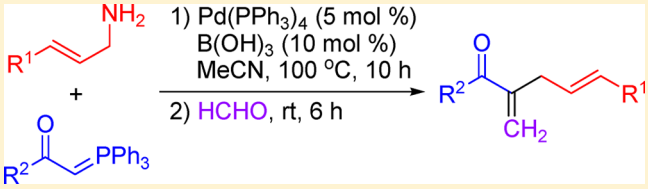
Supporting Information

**ABSTRACT:** A range of ketone-stabilized phosphonium ylides were allylated with high regioselectivity by primary allylic amines in the presence of 5 mol % $Pd(PPh_3)_4$ and 10 mol % $B(OH)_3$, and subsequent one-pot Wittig olefination gave structurally diverse $\alpha,\beta$-unsaturated ketones in good to excellent overall yields with excellent *E* selectivity. The one-pot allylation/olefination reaction was extended to ester- and nitrile-stabilized phosphonium ylides by replacing $B(OH)_3$ with TsOH, and the corresponding $\alpha,\beta$-unsaturated esters and nitriles were obtained in moderate overall yields.




The Tsuji–Trost reaction is powerful for the introduction of the allyl moiety to target compounds, permitting a broad range of transformations such as oxidation, reduction, and addition.[1] While allylic halides and alcohol derivatives frequently serve as electrophilic components in the Tsuji–Trost reaction by exhibiting various reactivities and selectivities,[2] allylic amines have rarely been employed directly as allylic electrophiles because of the poor leaving ability and compatibility of amino groups.[3] However, it would be rewarding to develop the corresponding reactions with allylic amines in regard to the exploration of new reactivity and selectivity. Although in many cases the synthetic routes to allylic amines are not shorter than those to allylic halides and alcohol derivatives, allylic amines can be readily purified in large quantities using simple extractive procedures instead of routine chromatography because of their basicity. Sporadic studies have shown that allylic amines can undergo the Tsuji–Trost reaction with a few carbon,[4] nitrogen,[5] and sulfur nucleophiles.[6,7] In most cases, secondary and tertiary allylic amines have been employed as allylic electrophiles, and only recently has appeared the disclosure of the Tsuji–Trost reaction with primary allylic amines, which exhibits much higher atom economy relative to that with commonly used allylic electrophiles.[4f,g,6b]

The Tsuji–Trost reaction has recently been extended to the allylation of stabilized phosphonium ylides, which affords more highly substituted phosphonium ylides for the synthesis of polysubstituted alkenes through the Wittig reaction.[8,9] In 2010, You and co-workers reported an elegant allylation reaction of ester-stabilized phosphonium ylides with allylic carbonates in the presence of $[Pd(allyl)Cl]_2$/Trost ligand/$Cs_2CO_3$.[10] Inspired by this work, together with our interest in exploring new reactions with allylic amines[4f,g,6b] and phosphonium ylides,[11] we have realized a $Pd(PPh_3)_4/B(OH)_3$-catalyzed allylation of ketone-stabilized phosphonium ylides with primary allylic amines. Importantly, the resulting more highly substituted phosphonium ylides could be subjected to the Wittig reaction to afford a range of structurally diverse $\alpha,\beta$-unsaturated ketones in good to excellent overall yields.

A 5 mol % loading of $Pd(PPh_3)_4$ was employed to catalyze the allylation of phosphonium ylide **2a** with primary allylic amine **1a** in acetonitrile under a nitrogen atmosphere at 100 °C, and subsequently, the resulting mixture was treated with formaldehyde (formalin) at room temperature (Table 1, entry 1). Whereas such a one-pot allylation/olefination sequence did not give $\alpha,\beta$-unsaturated ketone **3a** at all, to our delight, addition of 10 mol % $B(OH)_3$ to the allylation reaction mixture permitted the synthesis of the desired product in 93% overall yield with retention of the alkene geometry (Table 1, entry 2).[4f,6b] A few other palladium catalysts, phosphine ligands, and acids were examined, but none of them gave a better yield (Table 1, entries 3–9). The reaction efficiency was also significantly affected by the solvent, but a survey of common solvents proved fruitless to improve the yield (Table 1, entries 10–15).

In the presence of 5 mol % $Pd(PPh_3)_4$ and 10 mol % $B(OH)_3$, a range of ketone-stabilized phosphonium ylides were smoothly allylated by $\alpha$-unbranched primary allylic amines in an $\alpha$-selective fashion, and subsequent one-pot olefination with formaldehyde gave structurally diverse $\alpha,\beta$-unsaturated ketones in good to excellent overall yields with excellent *E* selectivity (Table 2).[12] It is noteworthy that the $\gamma$-positions of the primary allylic amines could bear aryl, heteroaryl, and alkyl groups and that the reaction tolerated allylic ethers (Table 2, entries 1–10). When the $\gamma$-substituent was a benzyloxymethyl group, *E* to *Z*

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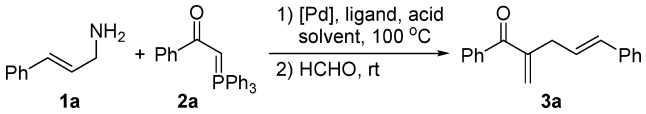
**Table 1. Optimization of the Reaction Conditions**[a]



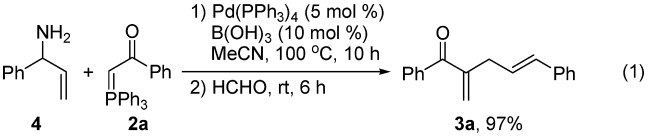

1a 2a 3a

| entry | [Pd] | ligand (mol %) | acid | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | none | none | MeCN | 0 |
| 2 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | MeCN | 93 |
| 3 | $Pd_2(dba)_3$ | none | $B(OH)_3$ | MeCN | 31 |
| 4 | $Pd(OAc)_2$ | $PPh_3$ | $B(OH)_3$ | MeCN | 37 |
| 5 | $[Pd(allyl)Cl]_2$ | $PPh_3$ | $B(OH)_3$ | MeCN | 86 |
| 6 | $[Pd(allyl)Cl]_2$ | dppb | $B(OH)_3$ | MeCN | 83 |
| 7 | $Pd(PPh_3)_4$ | none | $ZnCl_2$ | MeCN | 92 |
| 8 | $Pd(PPh_3)_4$ | none | HOAc | MeCN | 80 |
| 9 | $Pd(PPh_3)_4$ | none | TsOH | MeCN | 87 |
| 10 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | dioxane | 42 |
| 11 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | DMSO | 52 |
| 12 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | DMF | 62 |
| 13 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | $^n$PrOH | trace |
| 14 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | toluene | 69 |
| 15 | $Pd(PPh_3)_4$ | none | $B(OH)_3$ | DCE | trace |

[a]Reaction conditions: (1) amine **1a** (0.36 mmol), phosphonium ylide **2a** (0.30 mmol), [Pd] (5 mol %; for entries 3, 5, and 6, 2.5 mol %), ligand (if any, 20 mol %; for entry 6, 10 mol %), acid (if any, 10 mol %), solvent (0.50 mL), 100 °C (oil bath), 10 h; (2) HCHO (3.0 equiv), rt, 6 h. [b]Isolated yields (two steps).

isomerization of the original allyl carbon−carbon double bond was observed (Table 2, entry 10). Such a geometric isomerization could be attributed to the coordination between the alkoxy group and palladium in the $\pi$-allylpalladium intermediate generated from the palladium catalyst and the allylic amine (see below). Nevertheless, the reaction was not applicable to $\alpha$-unbranched primary allylic amines with $\beta,\gamma$- or $\gamma,\gamma'$-disubstitution because of poor reactivity.[13] On the other hand, suitable nucleophiles include aryl, heteroaryl, alkenyl, and alkyl ketone-stabilized phosphonium ylides (Table 2, entries 12−21).

In contrast, $\gamma$-selectivity was observed with an $\alpha$-substituted terminal allylic amine. For example, phosphonium ylide **2a** was allylated by $\alpha$-phenyl allylamine (**4**) in a $\gamma$-selective fashion, and subsequent one-pot olefination gave $\alpha,\beta$-unsaturated ketone **3a** in 97% overall yield with exclusive *E* selectivity (eq 1). Such

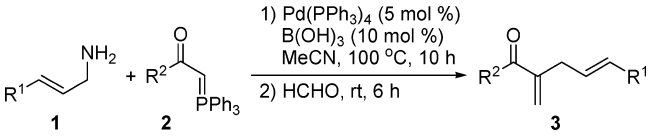



4 2a 3a, 97% (1)

regioisomerization could be attributed to the selective attack of phosphonium ylide **2a** on the $\pi$-allylpalladium intermediate generated from the palladium catalyst and the allylic amine (see below). Probably as a result of steric hindrance, sluggish reactions were observed with $\alpha,\gamma$-disubstituted allylamines such as (*E*)-4-phenylbut-3-en-2-amine.

Replacement of the $NH_2$ group with a bulkier amino group as the leaving group significantly decreased the reaction rate for the allylation of ketone-stabilized phosphonium ylides with allylic amines. As shown in eq 2, either secondary allylic amine **1aa** or tertiary allylic amine **1ab** underwent one-pot allylation/olefination under the same reaction conditions to give $\alpha,\beta$-unsaturated ketone **3a** in a much lower overall yield

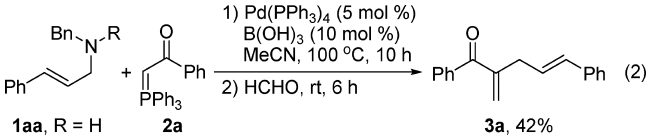
**Table 2. Allylation of Ketone-Stabilized Phosphonium Ylides with Primary Allylic Amines Followed by the Wittig Reaction with Formaldehyde**[a,b]




1 2 3

| entry | 1 | $R^1$ | 2 | $R^2$ | 3 | yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** | Ph | **2a** | Ph | **3a** | 93 |
| 2 | **1b** | 4-$MeOC_6H_4$ | **2a** | Ph | **3b** | 83 |
| 3 | **1c** | 4-$Me_2NC_6H_4$ | **2a** | Ph | **3c** | 73 |
| 4 | **1d** | 4-$CF_3C_6H_4$ | **2a** | Ph | **3d** | 95 |
| 5 | **1e** | 2-$MeOC_6H_4$ | **2a** | Ph | **3e** | 97 |
| 6 | **1f** | 1-naphthyl | **2a** | Ph | **3f** | 94 |
| 7 | **1g** | 3-pyridinyl | **2a** | Ph | **3g** | 87 |
| 8 | **1h** | 3-thienyl | **2a** | Ph | **3h** | 97 |
| 9 | **1i** | $^n$Pr | **2a** | Ph | **3i** | 66 |
| 10 | **1j** | $BnOCH_2$ | **2a** | Ph | **3j** | 68[d] |
| 11[e] | **1k** | H | **2a** | Ph | **3k** | 75 |
| 12 | **1a** | Ph | **2b** | 4-$MeOC_6H_4$ | **3l** | 84 |
| 13 | **1a** | Ph | **2c** | 4-$FC_6H_4$ | **3m** | 79 |
| 14 | **1a** | Ph | **2d** | 4-$ClC_6H_4$ | **3n** | 89 |
| 15 | **1a** | Ph | **2e** | 4-$O_2NC_6H_4$ | **3o** | 80 |
| 16 | **1a** | Ph | **2f** | 2-$MeC_6H_4$ | **3p** | 83 |
| 17 | **1a** | Ph | **2g** | 2-naphthyl | **3q** | 80 |
| 18 | **1a** | Ph | **2h** | 2-furyl | **3r** | 84 |
| 19 | **1a** | Ph | **2i** | 2-thienyl | **3s** | 85 |
| 20 | **1a** | Ph | **2j** | (*E*)-PhCH=CH | **3t** | 84 |
| 21[f] | **1a** | Ph | **2k** | $^t$Bu | **3u** | 62 |

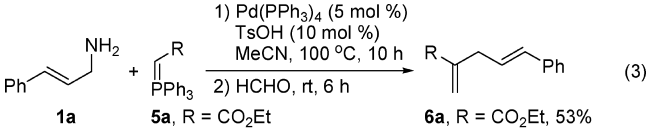
[a]Reaction conditions: (1) amine **1** (0.36 mmol), phosphonium ylide **2** (0.30 mmol), $Pd(PPh_3)_4$ (5 mol %), $B(OH)_3$ (10 mol %), acetonitrile (0.50 mL), 100 °C (oil bath), 10 h; (2) HCHO (3 equiv), rt, 6 h. [b]Unless otherwise stated, the product was obtained with >99:1 *E*/*Z*. [c]Isolated yields (two steps). [d]92:8 *E*/*Z*. [e]The reaction of step 1 was run in a sealed tube. [f]The reaction of step 1 was run at 120 °C.




**1aa**, R = H
**1ab**, R = Bn
**2a**
**3a**, 42%
**3a**, 40% (2)

(42% or 40%) relative to primary allylic amine **1a** (93%; Table 2, entry 1).

The one-pot allylation/olefination sequence was extended to ester- and nitrile-stabilized phosphonium ylides, but the desired electron-poor alkenes were obtained in much lower yields. To our delight, the yields could be significantly improved by replacing $B(OH)_3$ with TsOH, and consequently, the corresponding $\alpha,\beta$-unsaturated esters and nitriles were obtained in moderate overall yields with retention of the alkene geometry (eq 3).




**1a**
**5a**, R = $CO_2Et$
**5b**, R = CN
**6a**, R = $CO_2Et$, 53%
**6b**, R = CN, 58% (3)

On the basis of our experimental results and previous mechanistic studies,[4f,6b,10] we propose the reaction pathway depicted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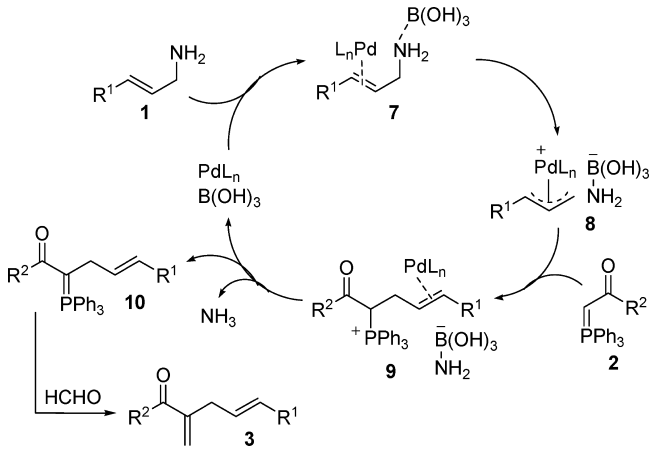
**Scheme 1. Proposed Reaction Pathway**




in Scheme 1 for the allylation of stabilized phosphonium ylides with primary allylic amines. The $NH_2$ group in allylic amine **1** is activated by $B(OH)_3$, and the allylic carbon−nitrogen bond is cleaved by palladium(0) to give $\pi$-allylpalladium **8**,[4f,6b] the allylic carbon of which is selectively attacked by phosphonium ylide **2** to give phosphonium salt **9**. Proton transfer of phosphonium salt **9** gives phosphonium ylide **10** and ammonia[14] and concurrently regenerates palladium(0) and $B(OH)_3$ to continue the catalytic cycle. The subsequent one-pot Wittig reaction of phosphonium ylide **10** with formaldehyde gives $\alpha,\beta$-unsaturated ketone **3**.[8]

In summary, we have developed an unprecedented allylation reaction of stabilized phosphonium ylides with allylic amines. In the presence of 5 mol % $Pd(PPh_3)_4$ and 10 mol % $B(OH)_3$, a range of ketone-stabilized phosphonium ylides were smoothly allylated by primary allylic amines in a highly regioselective fashion, and subsequent one-pot Wittig olefination gave structurally diverse $\alpha,\beta$-unsaturated ketones in good to excellent overall yields with excellent *E* selectivity. The one-pot allylation/olefination reaction was extended to ester- and nitrile-stabilized phosphonium ylides by replacing $B(OH)_3$ with TsOH, and the corresponding $\alpha,\beta$-unsaturated esters and nitriles were obtained in moderate overall yields.

## EXPERIMENTAL SECTION

**General Information.** $^1H$ NMR and $^{13}C$ NMR spectra were recorded using tetramethylsilane as an internal reference. Chemical shifts ($\delta$) and coupling constants ($J$) were expressed in parts per million and hertz, respectively. High-resolution mass spectrometry (HRMS) was performed on an LC-TOF spectrometer using electron impact (EI) techniques. Melting points were uncorrected. All of the starting allylic amines and phosphonium ylides are known compounds, and they were prepared according to known procedures.[4f,6b,11d]

**General Procedure for the Allylation of Stabilized Phosphonium Ylides with Primary Allylic Amines Followed by the Wittig Reaction with Formaldehyde.** A mixture of primary allylic amine **1** (0.36 mmol), phosphonium ylide **2** (0.30 mmol), $B(OH)_3$ (1.9 mg, 10 mol %), and $Pd(PPh_3)_4$ (17.3 mg, 5 mol %) in acetonitrile (0.50 mL) was heated under nitrogen at 100 °C for 10 h. After the reaction mixture was cooled to room temperature, formalin (37% w/w HCHO in water, 0.068 mL, 0.90 mmol) was added, and the resulting mixture was stirred for 6 h. The solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (0:100−1:5), to give compound **3**.

*(E)-2-Methylene-1,5-diphenylpent-4-en-1-one (**3a**).* Colorless oil (69.4 mg, 93% yield); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78−7.74 (m, 2H), 7.56−7.49 (m, 1H), 7.45−7.40 (m, 2H), 7.37−7.34 (m, 2H), 7.30−7.26 (m, 2H), 7.22−7.16 (m, 1H), 6.50 (d, $J$ = 15.6 Hz, 1H), 6.29 (dt, $J$ = 15.6, 6.8 Hz, 1H), 5.93 (d, $J$ = 0.8 Hz, 1H), 5.70 (d, $J$ = 0.8 Hz, 1H), 3.37 (dd, $J$ = 6.8, 0.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.7, 146.6, 137.7, 137.4, 132.5, 132.3, 129.5, 128.6, 128.3, 127.3, 126.7, 126.6, 126.2, 35.5; HRMS (EI) calcd for $C_{18}H_{16}O$ (M) 248.1201, found 248.1196.

*(E)-5-(4-Methoxyphenyl)-2-methylene-1-phenylpent-4-en-1-one (**3b**).* Colorless oil (69.2 mg, 83% yield); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.76 (dd, $J$ = 8.4, 1.6 Hz, 2H), 7.54−7.49 (m, 1H), 7.44−7.39 (m, 2H), 7.30−7.25 (m, 2H), 6.84−6.80 (m, 2H), 6.44 (d, $J$ = 15.6 Hz, 1H), 6.14 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.91 (d, $J$ = 0.8 Hz, 1H), 5.68 (d, $J$ = 0.8 Hz, 1H), 3.77 (s, 3H), 3.34 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.8, 159.0, 146.9, 137.8, 132.2, 131.9, 130.2, 129.5, 128.2, 127.3, 126.5, 124.3, 114.0, 55.3, 35.5; HRMS (EI) calcd for $C_{19}H_{18}O_2$ (M) 278.1307, found 278.1301.

*(E)-5-(4-(Dimethylamino)phenyl)-2-methylene-1-phenylpent-4-en-1-one (**3c**).* Colorless oil (63.6 mg, 73% yield); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.77−7.74 (m, 2H), 7.55−7.50 (m, 1H), 7.45−7.40 (m, 2H), 7.25 (d, $J$ = 8.8 Hz, 2H), 6.67 (d, $J$ = 8.8 Hz, 2H), 6.41 (d, $J$ = 15.6 Hz, 1H), 6.07 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.91 (d, $J$ = 0.8 Hz, 1H), 5.66 (d, $J$ = 0.8 Hz, 1H), 3.33 (dd, $J$ = 7.2, 0.8 Hz, 2H), 2.93 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 198.0, 149.9, 147.2, 137.8, 132.4, 132.2, 129.5, 128.2, 127.1, 126.3, 122.2, 112.6, 40.6, 35.5; HRMS (EI) calcd for $C_{20}H_{21}NO$ (M) 291.1623, found 291.1625.

*(E)-2-Methylene-1-phenyl-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (**3d**).* White solid (90.3 mg, 95% yield); mp 72−73 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78−7.74 (m, 2H), 7.57−7.52 (m, 3H), 7.48−7.42 (m, 4H), 6.54 (d, $J$ = 15.6 Hz, 1H), 6.40 (dt, $J$ = 15.6, 6.4 Hz, 1H), 5.95 (d, $J$ = 0.8 Hz, 1H), 5.74 (d, $J$ = 0.8 Hz, 1H), 3.41 (d, $J$ = 6.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.5, 146.1, 140.8, 137.6, 132.3, 131.2, 129.6, 129.5, 128.3, 127.1, 126.3, 125.5 (q, $J$ = 7.6 Hz), 35.5; HRMS (EI) calcd for $C_{19}H_{15}OF_3$ (M) 316.1075, found 316.1061.

*(E)-5-(2-Methoxyphenyl)-2-methylene-1-phenylpent-4-en-1-one (**3e**).* Colorless oil (80.9 mg, 97% yield); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.79−7.76 (m, 2H), 7.55−7.50 (m, 1H), 7.45−7.40 (m, 3H), 7.21−7.16 (m, 1H), 6.92−6.81 (m, 3H), 6.29 (dt, $J$ = 16.0, 6.8 Hz, 1H), 5.94 (d, $J$ = 0.8 Hz, 1H), 5.69 (d, $J$ = 0.8 Hz, 1H), 3.83 (s, 3H), 3.39 (dd, $J$ = 6.8, 0.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 198.0, 156.6, 147.0, 137.9, 132.3, 129.7, 128.4, 128.3, 127.3, 126.8, 126.5, 120.8, 111.0, 55.6, 35.9; HRMS (EI) calcd for $C_{19}H_{18}O_2$ (M) 278.1307, found 278.1310.

*(E)-2-Methylene-5-(naphthalen-1-yl)-1-phenylpent-4-en-1-one (**3f**).* White solid (84.1 mg, 94% yield); mp 68−69 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (dd, $J$ = 6.8, 2.4 Hz, 1H), 7.83−7.72 (m, 4H), 7.56−7.38 (m, 7H), 7.24 (d, $J$ = 15.6 Hz, 1H), 6.29 (dt, $J$ = 15.6, 6.8 Hz, 1H), 5.98 (s, 1H), 5.73 (s, 1H), 3.50 (d, $J$ = 6.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.8, 146.7, 137.7, 135.2, 133.7, 132.3, 131.2, 129.9, 129.6, 128.5, 128.3, 127.7, 126.7, 126.0, 125.8, 125.7, 124.0, 123.8, 35.9; HRMS (EI) calcd for $C_{22}H_{18}O$ (M) 298.1358, found 298.1352.

*(E)-2-Methylene-1-phenyl-5-(pyridin-3-yl)pent-4-en-1-one (**3g**).* White solid (65.1 mg, 87% yield); mp 51−52 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.59 (s, 1H), 8.45 (d, $J$ = 3.6 Hz, 1H), 7.77 (dd, $J$ = 8.4, 1.2 Hz, 2H), 7.68 (d, $J$ = 8.0 Hz, 1H), 7.58−7.53 (m, 1H), 7.47−7.42 (m, 2H), 7.25−7.21 (m, 1H), 6.50 (d, $J$ = 16.0 Hz, 1H), 6.38 (dt, $J$ = 16.0, 6.8 Hz, 1H), 5.96 (d, $J$ = 0.8 Hz, 1H), 5.75 (d, $J$ = 0.8 Hz, 1H), 3.41 (dd, $J$ = 6.8, 0.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.5, 148.2, 148.0, 146.0, 137.6, 132.8, 132.3, 129.5, 129.4, 129.2, 128.8, 128.3, 127.1, 123.5, 35.6; HRMS (EI) calcd for $C_{17}H_{15}NO$ (M) 249.1154, found 249.1142.

*(E)-2-Methylene-1-phenyl-5-(thiophen-3-yl)pent-4-en-1-one (**3h**).* Colorless oil (74.2 mg, 97% yield); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.77−7.73 (m, 2H), 7.55−7.50 (m, 1H), 7.45−7.40 (m, 2H), 7.24−7.16 (m, 2H), 7.10−7.08 (m, 1H), 6.52 (d, $J$ = 15.6 Hz, 1H), 6.14 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.92 (d, $J$ = 0.8 Hz, 1H), 5.70 (d, $J$ = 0.8 Hz, 1H), 3.34 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.7, 146.6, 139.9, 137.7, 132.2, 129.5, 128.3, 126.8, 126.5, 125.9,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125.0, 121.3, 35.4; HRMS (EI) calcd for $C_{16}H_{14}OS$ (M) 254.0765, found 254.0763.

*(E)-2-Methylene-1-phenyloct-4-en-1-one (**3i**).* Colorless oil (42.7 mg, 66% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77−7.73 (m, 2H), 7.55−7.51 (m, 1H), 7.45−7.41 (m, 2H), 5.85 (d, $J$ = 0.8 Hz, 1H), 5.62 (d, $J$ = 0.8 Hz, 1H), 5.57−5.42 (m, 2H), 3.15 (d, $J$ = 6.4 Hz, 2H), 2.03−1.96 (m, 2H), 1.43−1.35 (m, 2H), 0.88 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 198.1, 147.5, 137.9, 133.6, 132.2, 129.6, 128.3, 126.3, 125.8, 35.2, 34.7, 22.6, 13.7; HRMS (EI) calcd for $C_{15}H_{18}O$ (M) 214.1358, found 214.1364.

*(E)-6-(Benzyloxy)-2-methylene-1-phenylhex-4-en-1-one (**3j**).* Obtained as a 92:8 mixture of $E$ and $Z$ isomers; colorless oil (59.6 mg, 68% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.76−7.73 (m, 2H), 7.55−7.50 (m, 1H), 7.44−7.40 (m, 2H), 7.36−7.25 (m, 5H), 5.89−5.65 (m, 4H), 4.50 (s, 2H), 4.01 (dd, $J$ = 6.4, 0.8 Hz, 2H), 3.24 (d, $J$ = 6.4 Hz, 2H); partial $^1$H NMR for the minor $Z$ isomer $\delta$ 4.53 (s, 2H), 4.15 (d, $J$ = 6.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.6, 146.4, 138.4, 137.7, 132.2, 130.3, 129.5, 129.2, 128.4, 128.2, 127.8, 127.6, 126.6, 72.0, 70.5, 34.9; HRMS (EI) calcd for $C_{20}H_{20}O_2$ (M) 292.1463, found 292.1467.

*2-Methylene-1-phenylpent-4-en-1-one (**3k**).*[15] Colorless oil (38.9 mg, 75% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77−7.74 (m, 2H), 7.56−7.51 (m, 1H), 7.46−7.42 (m, 2H), 5.97−5.81 (m, 2H), 5.67 (s, 1H), 5.17−5.07 (m, 2H), 3.22 (d, $J$ = 6.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.8, 146.5, 137.8, 135.0, 132.3, 129.6, 128.3, 126.5, 117.2, 36.3.

*(E)-1-(4-Methoxyphenyl)-2-methylene-5-phenylpent-4-en-1-one (**3l**).* White solid (70.4 mg, 84% yield); mp 38−39 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84−7.79 (m, 2H), 7.36−7.33 (m, 2H), 7.30−7.25 (m, 2H), 7.21−7.17 (m, 1H), 6.94−6.90 (m, 2H), 6.49 (d, $J$ = 15.6 Hz, 1H), 6.28 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.82 (d, $J$ = 0.8 Hz, 1H), 5.61 (d, $J$ = 0.8 Hz, 1H), 3.84 (s, 3H), 3.36 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 196.5, 163.2, 146.8, 137.4, 132.4, 132.0, 130.1, 128.5, 127.3, 126.7, 126.2, 124.5, 113.6, 55.5, 35.9; HRMS (EI) calcd for $C_{19}H_{18}O_2$ (M) 278.1307, found 278.1305.

*(E)-1-(4-Fluorophenyl)-2-methylene-5-phenylpent-4-en-1-one (**3m**).* Colorless oil (63.0 mg, 79% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84−7.78 (m, 2H), 7.38−7.34 (m, 2H), 7.31−7.26 (m, 2H), 7.23−7.18 (m, 1H), 7.14−7.08 (m, 2H), 6.50 (d, $J$ = 15.6 Hz, 1H), 6.27 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.91 (s, 1H), 5.66 (s, 1H), 3.36 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 196.2, 165.3 (d, $J$ = 252.2 Hz), 146.6, 137.3, 133.8 (d, $J$ = 3.1 Hz), 132.6, 132.1 (d, $J$ = 9.0 Hz), 128.6, 127.3, 126.3, 126.2, 126.1, 115.4 (d, $J$ = 21.7 Hz), 35.6; HRMS (EI) calcd for $C_{18}H_{15}FO$ (M) 266.1107, found 266.1108.

*(E)-1-(4-Chlorophenyl)-2-methylene-5-phenylpent-4-en-1-one (**3n**).* White solid (75.0 mg, 89% yield); mp 51−52 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73−7.68 (m, 2H), 7.44−7.18 (m, 7H), 6.50 (d, $J$ = 15.6 Hz, 1H), 6.26 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.94 (s, 1H), 5.67 (d, $J$ = 0.4 Hz, 1H), 3.36 (dd, $J$ = 6.8, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 196.4, 146.5, 138.7, 137.3, 135.9, 132.7, 130.9, 128.6, 127.4, 126.7, 126.3, 126.2, 35.4; HRMS (EI) calcd for $C_{18}H_{15}OCl$ (M) 282.0811, found 282.0815.

*(E)-2-Methylene-1-(4-nitrophenyl)-5-phenylpent-4-en-1-one (**3o**).* Light-yellow solid (70.3 mg, 80% yield); mp 78−79 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.29 (dd, $J$ = 6.8, 2.0 Hz, 2H), 7.86 (dd, $J$ = 6.8, 2.0 Hz, 2H), 7.40−7.20 (m, 5H), 6.53 (d, $J$ = 15.6 Hz, 1H), 6.27 (dt, $J$ = 15.6, 7.2 Hz, 1H), 6.09−6.07 (m, 1H), 5.73 (s, 1H), 3.39 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 195.7, 149.7, 146.4, 143.1, 137.1, 133.0, 130.2, 128.9, 128.6, 127.5, 126.2, 125.8, 123.5, 34.9; HRMS (EI) calcd for $C_{18}H_{15}NO_3$ (M) 293.1052, found 293.1053.

*(E)-2-Methylene-5-phenyl-1-(o-tolyl)pent-4-en-1-one (**3p**).* Colorless oil (65.0 mg, 83% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41−7.17 (m, 9H), 6.51 (d, $J$ = 15.6 Hz, 1H), 6.30 (dt, $J$ = 15.6, 7.2 Hz, 1H), 6.00 (d, $J$ = 0.8 Hz, 1H), 5.68 (d, $J$ = 0.8 Hz, 1H), 3.36 (dd, $J$ = 7.2, 0.8 Hz, 2H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 199.9, 148.0, 138.8, 137.4, 136.2, 132.5, 130.8, 129.9, 129.8, 128.6, 128.0, 127.3, 126.7, 126.2, 125.1, 34.0, 19.7; HRMS (EI) calcd for $C_{19}H_{18}O$ (M) 262.1358, found 262.1367.

*(E)-2-Methylene-1-(naphthalen-2-yl)-5-phenylpent-4-en-1-one (**3q**).* White solid (71.3 mg, 80% yield); mp 56−57 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.27 (s, 1H), 7.95−7.84 (m, 4H), 7.61−7.49 (m, 2H), 7.37 (d, $J$ = 7.6 Hz, 2H), 7.31−7.27 (m, 2H), 7.23−7.17 (m, 1H), 6.55 (d, $J$ = 15.6 Hz, 1H), 6.34 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.97 (s, 1H), 5.76 (s, 1H), 3.43 (d, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 197.7, 146.8, 137.4, 135.3, 134.9, 132.6, 132.3, 131.1, 129.4, 128.6, 128.3, 128.2, 127.8, 127.3, 126.8, 126.6, 126.5, 126.2, 125.5, 35.6; HRMS (EI) calcd for $C_{22}H_{18}O$ (M) 298.1358, found 298.1365.

*(E)-1-(Furan-2-yl)-2-methylene-5-phenylpent-4-en-1-one (**3r**).* Colorless oil (60.0 mg, 84% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (dd, $J$ = 1.6, 0.8 Hz, 1H), 7.36−7.14 (m, 6H), 6.53 (dd, $J$ = 3.2, 1.6 Hz, 1H), 6.46 (d, $J$ = 15.6 Hz, 1H), 6.24 (dt, $J$ = 15.6, 7.2 Hz, 1H), 6.06 (d, $J$ = 0.8 Hz, 1H), 5.84 (d, $J$ = 0.8 Hz, 1H), 3.34 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 183.6, 152.0, 147.1, 146.3, 137.3, 132.5, 128.5, 127.3, 126.4, 126.2, 124.7, 119.9, 112.0, 35.4; HRMS (EI) calcd for $C_{16}H_{14}O_2$ (M) 238.0994, found 238.1007.

*(E)-2-Methylene-5-phenyl-1-(thiophen-2-yl)pent-4-en-1-one (**3s**).* Colorless oil (64.8 mg, 85% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.70−7.63 (m, 2H), 7.37−7.17 (m, 5H), 7.13−7.09 (m, 1H), 6.48 (d, $J$ = 15.6 Hz, 1H), 6.26 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.88 (d, $J$ = 0.8 Hz, 1H), 5.81 (d, $J$ = 0.8 Hz, 1H), 3.35 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 189.1, 147.0, 143.4, 137.3, 134.1, 133.9, 132.6, 128.5, 127.9, 127.3, 126.3, 126.2, 123.9, 35.8; HRMS (EI) calcd for $C_{16}H_{14}OS$ (M) 254.0765, found 254.0772.

*(1E,6E)-4-Methylene-1,7-diphenylhepta-1,6-dien-3-one (**3t**).* White solid (69.3 mg, 84% yield); mp 75−76 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 (d, $J$ = 15.6 Hz, 1H), 7.60−7.55 (m, 2H), 7.41−7.17 (m, 9H), 6.47 (d, $J$ = 15.6 Hz, 1H), 6.26 (dt, $J$ = 15.6, 7.2 Hz, 1H), 6.13 (s, 1H), 5.88 (t, $J$ = 1.6 Hz, 1H), 3.31 (dd, $J$ = 7.2, 0.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.4, 148.4, 144.0, 137.4, 134.9, 132.3, 130.4, 128.9, 128.5, 128.4, 127.2, 127.0, 126.2, 124.4, 121.7, 34.8; HRMS (EI) calcd for $C_{20}H_{18}O$ (M) 274.1358, found 274.1366.

*(E)-2,2-Dimethyl-4-methylene-7-phenylhept-6-en-3-one (**3u**).* Colorless oil (42.4 mg, 62% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.36−7.18 (m, 5H), 6.42 (d, $J$ = 15.6 Hz, 1H), 6.17 (dt, $J$ = 15.6, 7.2 Hz, 1H), 5.53 (s, 1H), 5.48 (t, $J$ = 1.2 Hz, 1H), 3.14 (dd, $J$ = 7.2, 1.2 Hz, 2H), 1.25 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 210.8, 146.9, 137.4, 132.5, 128.5, 127.3, 126.6, 126.1, 118.3, 44.1, 37.5, 27.8; HRMS (EI) calcd for $C_{16}H_{20}O$ (M) 228.1514, found 228.1519.

*(E)-Ethyl 2-Methylene-5-phenylpent-4-enoate (**6a**).*[10] Colorless oil (34.4 mg, 53% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.37−7.18 (m, 5H), 6.44 (d, $J$ = 16.0 Hz, 1H), 6.23 (dt, $J$ = 16.0, 7.2 Hz, 1H), 6.22 (s, 1H), 5.61 (d, $J$ = 0.8 Hz, 1H), 4.22 (q, $J$ = 7.2 Hz, 2H), 3.21 (dd, $J$ = 7.2, 0.8 Hz, 2H), 1.30 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 167.0, 139.6, 137.5, 132.2, 128.6, 127.3, 126.9, 126.2, 125.4, 60.8, 35.2, 14.3.

*(E)-2-Methylene-5-phenylpent-4-enenitrile (**6b**).*[16] Colorless oil (29.4 mg, 58% yield); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40−7.22 (m, 5H), 6.53 (d, $J$ = 15.6 Hz, 1H), 6.15 (dt, $J$ = 15.6, 6.8 Hz, 1H), 5.92 (s, 1H), 5.80 (t, $J$ = 1.6 Hz, 1H), 3.14 (dd, $J$ = 6.8, 1.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 136.6, 134.2, 130.8, 128.6, 127.8, 126.4, 123.2, 121.8, 118.5, 37.7.

**Isolation of Phosphonium Ylide 10a.** A mixture of primary allylic amine **1a** (47.9 mg, 0.36 mmol), phosphonium ylide **2a** (114.0 mg, 0.30 mmol), $B(OH)_3$ (1.9 mg, 10 mol %), and $Pd(PPh_3)_4$ (17.3 mg, 5 mol %) in acetonitrile (0.50 mL) was heated under nitrogen at 100 °C for 10 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography, eluting with methanol/dichloromethane (0:100 to 1:10), to give compound **10a** (80.3 mg, 54% yield) as a white solid. Mp 168−169 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 (dd, $J$ = 12.4, 8.0 Hz, 6H), 7.62 (d, $J$ = 7.6 Hz, 2H), 7.54−7.50 (m, 3H), 7.45−7.41 (m, 6H), 7.35−7.22 (m, 5H), 7.14 (dd, $J$ = 17.2, 7.6 Hz, 3H), 6.01 (dt, $J$ = 15.6, 5.2 Hz, 1H), 5.92 (d, $J$ = 15.6 Hz, 1H), 2.98 (dd, $J$ = 22.0, 5.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.8 (d, $J$ = 5.6 Hz), 142.7 (d, $J$ = 12.5 Hz), 138.0, 133.7 (d, $J$ = 9.6 Hz), 133.0, 131.6 (d, $J$ = 2.8 Hz), 129.1, 128.6 (d, $J$ = 12.1 Hz), 128.4, 128.1, 127.8, 127.7, 127.4, 126.7 (d, $J$ = 13.3 Hz), 126.0,


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64.0 (d, $J$ = 102.4 Hz), 31.8 (d, $J$ = 13.1 Hz); HRMS (EI) calcd for $C_{35}H_{29}OP$ (M) 496.1956, found 496.1980.

## ■ ASSOCIATED CONTENT

### Supporting Information

Copies of $^1$H NMR and $^{13}$C NMR spectra for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(12) Replacing formaldehyde with benzaldehyde only gave trace amounts of $\alpha,\beta$-unsaturated ketones.

(13) Sluggish reactions were observed with (*E*)-2-methyl-3-phenyl-prop-2-en-1-amine and (*E*)-3,7-dimethylocta-2,6-dien-1-amine under the standard conditions.

(14) Phosphonium ylide **10a** ($R^1$ = $R^2$ = Ph) was isolated in 54% yield from the reaction mixture of phosphonium ylide **2a** and allylic amine **1a**.

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