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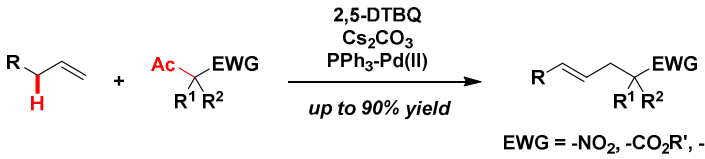
Palladium(II)-Catalyzed Deacylative Allylic C-H Alkylation

Xiao-Le Zhou[†], Lei Ren[‡], Pu-Sheng Wang*[†]

[†] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, China, 230026

[‡] Anhui Therapy Pharmaceutical Co., LTD, China

Supporting Information

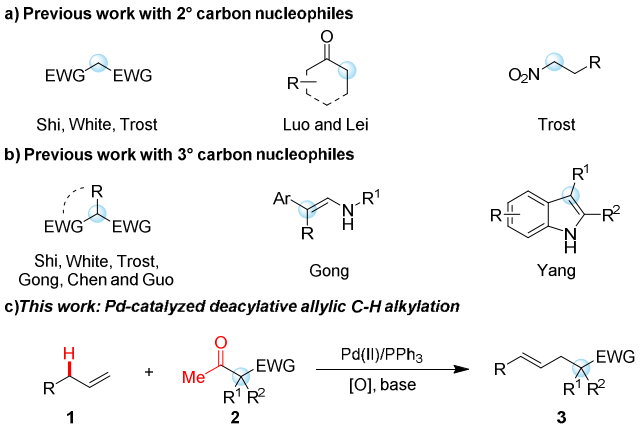


ABSTRACT: The first deacylative allylic C-H alkylation has been established by employing the palladium-catalyzed allylic C-H activation and decarboxylative nucleophile generation. A wide scope of nucleophiles are tolerated and densely functionalized alkylation products turn out to be furnished in moderate to good yield. More importantly, this strategy provides an alternative method for the allylic C-H alkylation with less stabilized carbon nucleophiles, and can be further expanded to the synthesis of unconjugated enynes.

Palladium-catalyzed allylic alkylation[1] is one of the most widely applied transformations for the construction of carbon-carbon bonds, along with predictable high levels of chemo-, regio-, and stereoselectivity.[2] Over the past decades, allylic substrates with a wide range of leaving groups, including acetates, halides, carbonates, epoxides, phosphonates and alcohols, has been introduced into the allylic alkylation.[3] In recent years, the direct palladium-catalyzed allylic C-H[4] alkylation has emerged as a more efficient synthetic approach, which can avoid the installation of the allylic leaving groups. So far, the disubstituted methylene carbon nucleophiles[5] bearing electron-withdrawing groups (Scheme 1a) have been well developed.[6] However, the scope of tertiary carbon nucleophiles for the creation of quaternary carbon centers are still restricted in the nucleophiles bearing two electron-withdrawing groups,[5b,7] aldehyde enamines,[8] and 3,3-disubstituted indolines[9] (Scheme 1b). Owing to the requirement of strong basic condition for enolization, relatively less stabilized tertiary nucleophiles, like nitronates,[5b] acylic ketones and esters, are rarely reported in the allylic C−H alkylation. Therefore, the emergence of new efficient strategy for the allylic C−H alkylation with less stabilized tertiary carbon nucleophiles is highly desired.

Since the last decade, decarboxylative[10] and deacylative[11] nucleophile generation strategy have emerged as a convenient method for the *in situ* formation of less stabilized carbon nucleophiles, which can avoid the demand of stoichiometric organometallic reagents as strong base. In recent years, Tunge and co-workers developed a deacylative allylation reactions[11b-d] by using readily functionalized ketones as the precursor of versatile relatively less stabilized tertiary carbon nucleophiles, where the intermolecular carbon-carbon bond formation was facilitated by a retro-Claisen condensation.[12] Inspired by these leading findings, we envision that the deacylative strategy might be compatible with the oxidative allylic C-H condition.

Scheme 1. Nucleophiles for allylic C-H alkylation.



In the proposed mechanism of the deacylative allylic C-H alkylation (Scheme 2), the π-allyl palladium intermediate **I** was formed from simple terminal olefin **1** in the presence of palladium(0) and oxidant, while the nonstabilized tertiary nucleophile **II** was generated *in situ* from the deacylative retro-Claisen condensation of functionalized ketones **2** with alkoxide anion. Principally, nucleophile **II** could undergo either nucleophilic substitution or protonation, thus theoretically leading to the formation of **3** and **4**. Therefore, the control of reaction conditions to selectively afford the alkylation product would be one of the formidable challenges to the proposed reaction. Herein, we will describe the first deacylative allylic C-H alkylation with less stabilized carbon nucleophiles, enabled by combining palladium-catalyzed allylic C-H activation and decarboxylative nucleophile generation.

Scheme 2. Proposed mechanism for the deacylative allylic C-H alkylation.

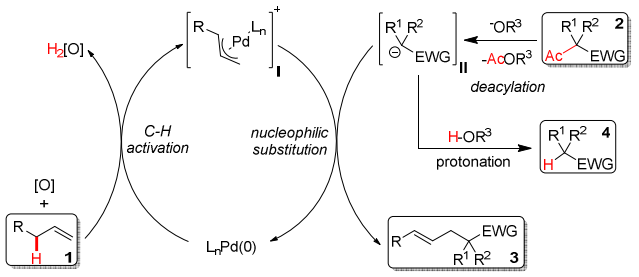
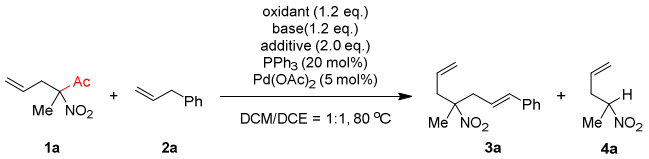


Table 1. Optimization of reaction conditions[a]



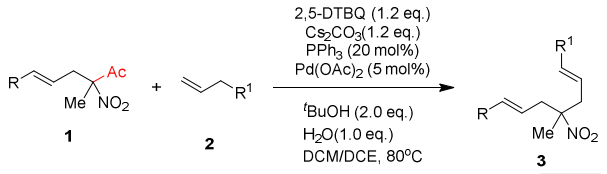
entry	base	additive	oxidant	**1a** conv. (%)[b]	**3a** yield (%)[b]	**4a** yield (%)[b]
1	Cs_2CO_3	^{t}BuOH	2,6-DMBQ	99	6	23
2	Cs_2CO_3	^{t}BuOH	2,5-DMBQ	99	6	33
3	Cs_2CO_3	^{t}BuOH	2,6-DTBQ	82	trace	68
4	Cs_2CO_3	^{t}BuOH	2,5-DTBQ	99	50	26
5	Cs_2CO_3	MeOH	2,5-DTBQ	99	30	19
6	Cs_2CO_3	^{i}PrOH	2,5-DTBQ	99	39	19
7	Cs_2CO_3	Ad-OH	2,5-DTBQ	99	33	34
8	Cs_2CO_3	Ph_3COH	2,5-DTBQ	99	49	11
9	Cs_2CO_3	Ph_3SiOH	2,5-DTBQ	99	45	62
10[c]	Cs_2CO_3	^{t}BuOH	2,5-DTBQ	99	70(60[d])	19
11[c]	K_2CO_3	^{t}BuOH	2,5-DTBQ	85	28	38
12[c]	Na_2CO_3	^{t}BuOH	2,5-DTBQ	26	18	9
13[c]	KOH	^{t}BuOH	2,5-DTBQ	59	19	30
14[c]	CsOH	^{t}BuOH	2,5-DTBQ	98	11	45

[a]Reaction conditions: **1a** (0.125 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), base (1.2 equiv), oxidant (1.2 equiv), additive (2.0 equiv), DCM/DCE=1:1 (0.8 mL), 80 °C, 22 h, under N_2. [b]Based on GC analysis of the crude reaction mixture using methyl benzoate as an internal standard. [c]H_2O (1.0 equiv) was added. [d]Isolated yield.

In the light of the previous works on allylic C-H alkylation[5, 7-9], our initial investigation was conducted by the reaction of allylbenzene (**2a**) with 3-methyl-3-nitrohex-5-en-2-one (**1a**) in the presence of 5.0 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 1.2 equivalent 2,6-dimethylbenzoquinone (2,6-DMBQ), 1.2 equivalent Cs_2CO_3, and 2.5 equivalent ^{t}BuOH (Table 1, entry 1). Although the ketone **1a** was converted completely, unfortunately only a small amount of the desired alkylation product **3a** was afforded, and the undesired protonation product **4a** was obtained in 23% yield. In consideration of the possible side reaction between alkylquinone oxidant and tertiary carbon nucleophile intermediate under basic condition[13], then a series of para-benzoquinones with more steric hindrance substituents were examined. Using either 2,5-DMBQ (entry 2) or 2,6-DTBQ (entry 3) as the oxidant gave nearly the same performance as 2,6-DMBQ. To our delight, the desired alkylation product **3a** was obtained in 50% yield, when 2,5-DTBQ was used as external oxidant for the reaction. Then a screen of alcohol additives was evaluated (entries 5-9), and ^{t}BuOH was turned out to be the best alcohol additive with balanced performance to promote the deacylative nucleophile generation and inhibit the allylic ether formation. When less hindered alcohol, like MeOH, was used, the allylic ether was detected.[14] Especially, the yield was able to be greatly improved to 70% by the addition of 1.0 equivalent H_2O (entry 10), which might be caused by the water-assisted dispersion of Cs_2CO_3 in the solvent. Subsequently, a brief screening of bases (entries 11−14) revealed that Cs_2CO_3 was clarified to be essential for the deacylative alkylation process. The yield of **3a** decreased dramatically when the other bases were used.

With the optimized conditions in hand, various 1-ntroacetones **1** and allylarenes **2** were examined (Table 2). Generally, a wide range of allylarenes bearing a phenyl group with substituents at the *para*- and *meta*- position (entries 1-6) were able to provide the desired nitro-substituted 1,6-dienes **3** in moderate yields. However, the reactivity appeared to be greatly influenced by the *ortho*- substitution of allylarenes. For instance, the reaction of **1a** with *ortho*-methyl allylbenzene gave a much lower yield (entry 7), where the *ortho*- substitution might inhibit the formation of π-allyl palladium intermediate. Moreover, 1-ntroacetone **1b** with more steric hindrance substituent could also give product **3i** in 45% yield (entry 8).

Table 2. Scope of 1-nitroacetones and allylarenes[a]

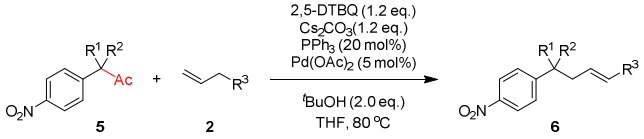


entry	R	**1**	R^1	**2**	**3**	yield (%)[b]
1	H	**1a**	4-Me-C_6H_4	**2b**	**3b**	50
2	H	**1a**	4-^{t}Bu-C_6H_4	**2c**	**3c**	50
3	H	**1a**	4-F-C_6H_4	**2d**	**3d**	40
4	H	**1a**	3-Me-C_6H_4	**2e**	**3e**	56
5	H	**1a**	3,4-$(MeO)_2$-C_6H_4	**2f**	**3f**	53
6	H	**1a**	3,4,5-$(MeO)_3$-C_6H_4	**2g**	**3g**	57
7	H	**1a**	2-Me-C_6H_4	**2h**	**3h**	25
8	C_6H_5	**1b**	3-Me-C_6H_4	**2e**	**3i**	45

[a]Reaction conditions: **1** (0.125 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), Cs_2CO_3 (1.2 equiv), 2,5-DTBQ (1.2 equiv), ^{t}BuOH (2.0 equiv), DCM/DCE=1:1 (0.8 mL), 80 °C, 22 h, under N_2. [b]Isolated yield.

To our delight, the deacylative allylic C-H alkylation proceeded smoothly with acetylacetone substrates (Table 3), which further demonstrated the utility of this strategy to access alkylation products with less stabilized carbon nucleophiles. After fine-tuning of the reaction conditions, the treatment of 3-Methyl-3-(4-nitrophenyl)pentane-2,4-dione **5a** with a wide range of allylarenes **2** bearing either electron-donating or electron-withdrawing groups was nicely tolerated to furnish the alkylation products **6** in good to excellent yield. (entries 1-7). However, allylarenes with *ortho*-electron-withdrawing substitution (entry 8) was less reactive and only resulted in 44% yield. Moreover, 2-allylnaphthalene was compatible with the optimal reaction condition (entry 9), delivering the desired product in moderate yield. Acetylacetone substrate bearing more steric hindrance substituent (entry 10) could successfully deliver the desired product in good yield. In particular, the substituted acetoacetate (entry 11) was also suitable deacylative nucleophile precursor to accomplish the α-allylic alkylation of ester in synthetically useful yield.

Table 3. Scope of alkenes and acetylacetones[a]



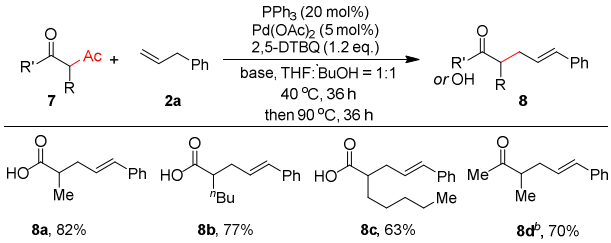
5 2 6

entry	R^1	R^2	5	R^3	2	6	yield (%)[b]
1	Ac	Me	**5a**	4-Me-C_6H_4	**2b**	**6a**	90
2	Ac	Me	**5a**	4-MeO-C_6H_5	**2i**	**6b**	73
3	Ac	Me	**5a**	4-F-C_6H_4	**2d**	**6c**	92
4	Ac	Me	**5a**	3-Me-C_6H_4	**2e**	**6d**	78
5	Ac	Me	**5a**	3,4-$(MeO)_2$-C_6H_4	**2f**	**6e**	89
6	Ac	Me	**5a**	3,4,5-$(MeO)_3$-C_6H_4	**2g**	**6f**	90
7	Ac	Me	**5a**	2-Me-C_6H_4	**2h**	**6g**	71
8	Ac	Me	**5a**	2-F-C_6H_4	**2j**	**6h**	44
9	Ac	Me	**5a**	1-naphthyl	**2k**	**6i**	67
10	Ac	Bn	**5b**	C_6H_5	**2a**	**6j**	77
11	CO_2Et	Me	**5c**	C_6H_5	**2a**	**6k**	58

[a]Reaction conditions: **5** (0.125 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), Cs_2CO_3 (1.2 equiv), 2,5-DTBQ (1.2 equiv), ^{t}BuOH (2.0 equiv), THF (0.8 mL), 80 °C, 22 h, under N_2. [b]Isolated yield.

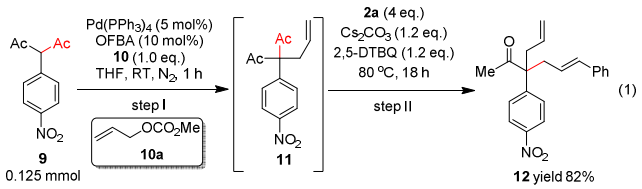
Particularly, the tertiary carbon centers were also accessible via a one-pot stepwise allylic C-H alkylation and deacylation under the basic oxidation condition (Scheme 3). Various tertiary α-acetyl carbonyl compounds smoothly underwent the formal deacylative allylic C-H alkylation in high conversion and gave the tertiary carbon products with good yields. However, due to the unstability of ethyl esters under the basic condition, the α-substituted ethyl acetylacetates would result in the formation of aliphatic acids (**8a-c**). The α-methyl acetylacetone was also suitable substrate to afford aliphatic ketone (**8d**) in 70% yield with the employment of Cs_2CO_3, as a relatively weaker base.

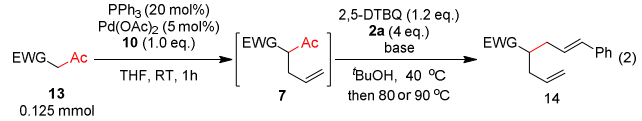
Scheme 3. Scope of tertiary carbon nucleophiles[a]



[a]Reaction conditions: **7** (0.125 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), 20 M NaOH (4 equiv), 2,5-DTBQ (1.2 equiv), THF (0.4 mL), ^{t}BuOH (0.4 mL), 40 °C, 36 h, under N_2, then 90 °C, 36 h. [b]Cs_2CO_3 (1.2 equiv) was used as base, THF (0.8 mL), 40 °C, 24 h, under N_2, then 80 °C, 24 h.

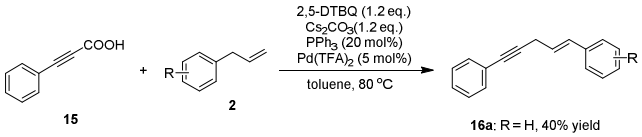
Notably, a one pot tandem catalytic process involving Pd-catalyzed allylic alkylation[7e] and deacylative allylic C-H alkylation was feasible to afford 1,6-dienes. In the presence of catalytic amount of $Pd(PPh_3)_4$ and OFBA (2-fluorobenzoic acid), α-aryl acetylacetone **9** could react smoothly with allyl methyl carbonate **10** to give allylic alkylation intermediate **11**, which further underwent deacylative allylic C-H alkylation to give the desired 1,6-diene **12** in 82% yield (eq. 1). Similarly, either α-acetyl ketone or ester **13** was also able to conduct the tandem catalytic process, providing the 1,6-diene **14** in moderate to good yield (eq. 2).





base = Cs_2CO_3 (1.2 eq.), 40 °C, 24 h then 80 °C, 24 h, EWG = -COMe, 47% yield, **14a**
base = 20 M NaOH (4 eq.), 40 °C, 24 h then 90 °C, 24 h, EWG = -$CO_2{}^t$Bu, 69% yield, **14b**

Moreover, the catalytic system of deacylative allylic C-H alkylation was applicable for the combination of decarboxylative process.[15] For instance, when 3-phenylpropiolic acid (**15**) was treated with substituted allylbenzenes, the unconjugated enyne products **16** could be generated in the presence of $Pd(TFA)_2$, PPh_3, Cs_2CO_3 and 2,5-DTBQ, albeit in the unsatisfying yields.



In conclusion, we have established a novel catalytic system for the combination of allylic C-H activation and deacylation manner, giving the α-allylic alkylation of nitroalkanes, ketones and esters with tertiary or quaternary carbon center. This strategy not only provides an alternative approach for the allylic C-H alkylation with less stabilized carbon nucleophiles, but also can be used in a tandem catalytic process with the Tsuji–Trost allylation to access the unsymmetrical 1,6-diene through a three-component coupling. Moreover, the catalytic system can be expanded to the decarboxylative allylic C-H functionalization for the synthesis of unconjugated enynes.

EXPERIMENTAL SECTION

General Information: NMR spectra were recorded on a Brucker-400 MHz spectrometer. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI$^+$) or water XEVO G2 Q-TOF (Waters Corporation). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer.

Materials: All starting materials, reagents and solvents were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas, etc.) and used as supplied unless otherwise stated. The nitroketones[11c] and acetylacetones[11b] were prepared following the procedures reported in literatures.

General procedure A for the deacylative allylation with nitroketones

To a flame-dried schlenk tube (25 mL) were added nitroketone **1** (0.125 mmol), allylarene **2** (0.5 mmol), $Pd(OAc)_2$ (5 mol%, 0.00625 mmol, 1.4 mg), PPh_3 (20 mol%, 0.025 mmol, 6.5 mg), Cs_2CO_3 (1.2 equiv, 0.15 mmol, 48.9 mg), 2,5-DTBQ (1.2 equiv, 0.15 mmol, 33.1 mg), ^{t}BuOH (2.0 equiv, 0.25 mmol, 24 μL), H_2O (1 equiv, 0.125 mmol, 2.3 μL), DCM/DCE=1:1 (0.8 mL) and a stir bar. The solution was stirred at 80 °C for 22 h, under N_2. After the vial was cooled down to room temperature, the reaction mixture was directly subjected on flash chromatography (SiO_2, Petroleum ether:EtOAc = 50:1) to provide the allylation product **3**.

General procedure B for the deacylative allylation with acetylacetones

To a flame-dried schlenk tube (25 mL) were added acetylacetone **5** (0.125 mmol), allylarene **2** (0.5 mmol), $Pd(OAc)_2$ (5 mol%, 0.00625 mmol, 1.4 mg), PPh_3 (20 mol%, 0.025 mmol, 6.5 mg), Cs_2CO_3 (1.2 equiv, 0.15 mmol, 48.9 mg), 2,5-DTBQ (1.2 equiv, 0.15 mmol, 33.1 mg), ^{t}BuOH (2.0 equiv, 0.25 mmol, 24 μL), THF (0.8 mL) and a stir bar. The solution was stirred at 80 ^{o}C for 22 h, under N_2. After the vial was cooled down to room temperature, the reaction mixture was directly subjected on flash chromatography (SiO_2, Petroleum ether/EtOAc = 10:1) to provide the allylation product **6**.

(*E*)-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3a)

Yield: 17 mg, 60%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 6.55 – 6.43 (m, 1H), 6.03 (dt, *J* = 15.4, 7.5 Hz, 1H), 5.70 (ddt, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.28 – 5.12 (m, 2H), 2.90 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.79 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.70 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.59 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.6, 135.4, 130.9, 128.6, 127.8, 126.3, 122.1, 120.7, 90.9, 43.5, 42.65, 22.11. **IR (KBr)** γ 3446, 1537, 1449, 1387, 1352, 969, 927, 748, 693 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{14}H_{18}NO_2$, 232.1332; found, 232.1335.

(*E*)-1-methyl-4-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3b)

Yield: 15.4 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.11 – 5.95 (m, 1H), 5.70 (td, *J* = 17.2, 7.4 Hz, 1H), 5.21 (d, *J* = 6.5 Hz, 1H), 5.18 (d, *J* = 13.7 Hz, 1H), 2.89 (dd, *J* = 14.3, 7.2 Hz, 1H), 2.79 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.69 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.59 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.34 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.7, 135.3, 133.8, 130.9, 129.3, 126.2, 121.0, 120.7, 90.9, 43.5, 42.7, 22.1, 21.2. **IR (KBr)** γ 3456, 2921, 1642, 1538, 1455, 1387, 1352, 996, 969, 926, 775, 692 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{15}H_{20}NO_2$, 246.1494; found, 246.1494.

(*E*)-1-(tert-butyl)-4-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3c)

Yield: 18.0 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.07 – 5.93 (m, 1H), 5.70 (td, *J* = 17.2, 7.5 Hz, 1H), 5.25 – 5.12 (m, 2H), 2.88 (dd, *J* = 14.3, 7.2 Hz, 1H), 2.78 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.70 (dd, *J* = 14.1, 7.9 Hz, 1H), 2.58 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.57 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.0, 135.2, 133.9, 130.9, 126.1, 125.5, 121.2, 120.7, 90.9, 43.5, 42.7, 34.6, 31.3, 22.1. **IR (KBr)** γ 3465, 2963, 1540, 1460, 1387, 1352, 1269, 995, 971, 926, 855, 831, 553 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{18}H_{26}NO_2$, 288.1958; found, 288.1972.

(*E*)-1-fluoro-4-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3d)

Yield: 12.5 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 6.44 (d, *J* = 15.7 Hz, 1H), 5.95 (dt, *J* = 15.5, 7.6 Hz, 1H), 5.70 (td, *J* = 17.2, 7.6 Hz, 1H), 5.27 – 5.12 (m, 2H), 2.89 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.79 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.68 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.59 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, J = 247.2 Hz), 134.2, 132.8 (d, J = 3.4 Hz), 130.8, 127.86 (d, J = 8.0 Hz), 121.79 (d, J = 2.2 Hz), 120.78, 115.5 (d, J = 21.6 Hz), 90.9, 43.5, 42.6, 22.1. **IR (KBr)** γ 3465, 2921, 1601, 1538, 1508, 1387, 1351, 1228, 1158, 970, 927 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{14}H_{17}FNO_2$, 250.1238; found, 250.1254.

(*E*)-1-methyl-3-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3e)

Yield: 17.2 mg, 56%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.04 – 5.91 (m, 1H), 5.70 (td, *J* = 17.0, 7.3 Hz, 1H), 5.20 (d, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 14.4 Hz, 1H), 2.88 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.78 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.69 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.58 (dd, *J* = 14.1, 7.5 Hz, 1H), 2.33 (s, 3H), 1.57 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 136.5, 135.5, 130.9, 128.6, 128.5, 127.0, 123.5, 121.8, 120.7, 90.9, 43.5, 42.7, 22.1, 21.4. **IR (KBr)** γ 3462, 2922, 1538, 1513, 1456, 1387, 1352, 995, 971, 926, 853, 818, 795 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{15}H_{20}NO_2$, 246.1494; found, 246.1492.

(*E*)-1,2-dimethoxy-4-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3f)

Yield: 19.3 mg, 53%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.88 (dt, *J* = 15.4, 7.5 Hz, 1H), 5.71 (td, *J* = 17.2, 7.5 Hz, 1H), 5.25 – 5.14 (m, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 2.89 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.80 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.67 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.59 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 149.0, 135.1, 130.9, 129.8, 120.7, 120.0, 119.5, 111.1, 108.9, 91.0, 56.0, 55.9, 43.5, 42.8, 22.1. **IR (KBr)** γ 2938, 1602, 1538, 1515, 1464, 1266, 1140, 1027, 969, 857 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{16}H_{22}NO_4$, 292.1543; found, 292.1560.

(*E*)-1,2,3-trimethoxy-5-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3g)

Yield: 22.9 mg, 57%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.55 (s, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.94 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.71 (td, *J* = 17.2, 7.5 Hz, 1H), 5.26 – 5.14 (m, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 2.90 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.80 (dd, *J* = 14.2, 7.1 Hz, 1H), 2.68 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.59 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.3, 138.0, 135.4, 132.3, 130.8, 121.4, 120.8, 103.4, 90.9, 60.9, 56.1, 43.6, 42.7, 22.0. **IR (KBr)** γ 3453, 2938, 1582, 1537, 1506, 1455, 1417, 1388, 1349, 1326, 1240, 1127, 1007, 969, 926, 854 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{17}H_{24}NO_5$, 322.1802; found, 322.1805.

(*E*)-1-methyl-2-(4-methyl-4-nitrohepta-1,6-dien-1-yl)benzene (3h)

Yield: 7.7 mg, 25%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 1H), 7.21 – 7.10 (m, 3H), 6.68 (d, *J* = 15.7 Hz, 1H), 5.97 – 5.84 (m, 1H), 5.71 (td, *J* = 17.2, 7.8 Hz, 1H), 5.21 (d, *J* = 5.4 Hz, 1H), 5.18 (d, *J* = 13.0 Hz, 1H), 2.91 (dd, *J* = 14.2, 7.4 Hz, 1H), 2.80 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.73 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.61 (dd, *J* = 14.2, 7.6 Hz, 1H), 2.32 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0, 135.3, 133.6, 130.9, 130.3, 127.7, 126.1, 125.8, 123.6, 120.7, 91.0, 43.5, 42.9, 22.11, 19.80. **IR (KBr)** γ 3463, 2921, 2852, 1642, 1538, 1386, 1352, 969, 927, 749 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{15}H_{20}NO_2$, 246.1494; found, 246.1466.

1-methyl-3-((1*E*,6*E*)-4-methyl-4-nitro-7-phenylhepta-1,6-dien-1-yl)benzene (3i)

Yield: 18.1 mg, 45%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (q, *J* = 7.3 Hz, 4H), 7.25 (d, *J* = 3.9 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.16 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.57 – 6.40 (m, 2H), 6.05 (dq, *J* = 14.9, 7.3 Hz, 2H), 2.99 – 2.89 (m, 2H), 2.74 (dd, *J* = 14.2, 7.8 Hz, 2H), 2.34 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2, 136.6, 136.5, 135.6, 135.5, 128.6, 128.5, 127.8, 127.0, 126.4, 123.6, 122.1, 121.8, 91.19, 42.8, 42.8, 22.3, 21.4. **IR (KBr)** γ 3462, 3028, 2921, 1598, 1536, 1492, 1450, 1387, 1349, 969, 746, 692 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{21}H_{24}NO_2$, 322.1802; found, 322.1805.

(*E*)-3-methyl-3-(4-nitrophenyl)-6-(p-tolyl)hex-5-en-2-one (6a)

Yield: 36.4 mg, 90%. **^{1}H NMR** (400 MHz, CDCl3) δ 8.23 (d, J = 7.8 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 6.33 (d, J = 15.7 Hz, 1H), 5.87 – 5.69 (m, 1H), 2.94 – 2.70 (m, 2H), 2.31 (s, 3H), 1.98 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.7, 149.9, 147.0, 137.3, 134.2, 134.0, 129.2, 127.5, 126.0, 124.0, 123.4, 56.5, 41.8, 26.3, 21.3,

21.2. **IR (KBr)** γ 3025, 2975, 2922, 1710, 1604, 1519, 1457, 1347, 1111, 1075, 970, 858, 793, 700, 505 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_3$, 324.1594; found, 324.1621.

(*E*)-6-(4-methoxyphenyl)-3-methyl-3-(4-nitrophenyl)hex-5-en-2-one (6b)

Yield: 30.8 mg, 73%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.74 – 5.60 (m, 1H), 3.78 (s, 3H), 2.88 – 2.74 (m, 2H), 1.98 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.7, 159.1, 149.9, 147.0, 133.5, 129.8, 127.5, 127.3, 124.0, 122.1, 113.9, 56.5, 55.3, 41.8, 26.3, 21.3. **IR (KBr)** γ 3443, 2935, 1709, 1605, 1511, 1463, 1346, 1246, 1112, 1037, 857, 750, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_4$, 340.1543; found, 340.1549.

(*E*)-6-(4-fluorophenyl)-3-methyl-3-(4-nitrophenyl)hex-5-en-2-one (6c)

Yield: 37.7 mg, 92%. **^{1}H NMR** (400 MHz, CDCl3) δ 8.24 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.25 – 7.15 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.33 (d, J = 15.7 Hz, 1H), 5.82 – 5.68 (m, 1H), 2.91 – 2.73 (m, 2H), 1.98 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.6, 162.2(d, 246.73), 149.7, 147.0, 133.1 (d, *J* = 3.3 Hz), 132.9, 127.59 (d, *J* = 7.9 Hz), 127.48, 124.27 (d, *J* = 2.2 Hz), 124.02, 115.4 (d, *J* = 21.6 Hz)., 56.4, 41.8, 26.2, 21.2. **IR (KBr)** γ 3446, 2979, 1710, 1602, 1520, 1509, 1348, 1227, 1158, 970, 858, 700, 514 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{19}H_{19}FNO_3$, 328.1343; found, 328.1363.

(*E*)-3-methyl-3-(4-nitrophenyl)-6-(m-tolyl)hex-5-en-2-one (6d)

Yield: 31.5 mg, 78%. **^{1}H NMR** (400 MHz, CDCl3) δ 8.24 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.09 – 6.97 (m, 3H), 6.34 (d, J = 15.8 Hz, 1H), 5.82 (dt, J = 15.2, 7.4 Hz, 1H), 2.97 – 2.73 (m, 2H), 2.31 (s, 3H), 1.98 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.7, 149.8, 147.0, 138.2, 136.8, 134.3, 128.5, 128.3, 127.5, 126.8, 124.2, 124.0, 123.3, 56.5, 41.9, 26.3, 21.4, 21.3. **IR (KBr)** γ 3463, 2923, 1710, 1604, 1519, 1347, 1110, 968, 855, 776, 754, 698 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_3$, 324.1594; found, 324.1616.

(*E*)-6-(3,4-dimethoxyphenyl)-3-methyl-3-(4-nitrophenyl)hex-5-en-2-one (6e)

Yield: 41.1 mg, 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 6.83 – 6.72 (m, 3H), 6.29 (d, J = 15.6 Hz, 1H), 5.78 – 5.63 (m, 1H), 3.85 (s, 6H), 2.85 (dd, J = 14.2, 7.9 Hz, 1H), 2.76 (dd, J = 14.1, 6.9 Hz, 1H), 1.98 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.8, 149.9, 149.0, 148.7, 147.0, 133.9, 130.1, 127.5, 124.0, 122.4, 119.1, 111.1, 108.8, 56.5, 55.9, 55.9, 41.9, 26.3, 21.3. **IR (KBr)** γ 3452, 2935, 1709, 1603, 1516, 1464, 1347, 1265, 1158, 1139, 1026, 968, 857, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{21}H_{24}NO_5$, 370.1649; found, 370.1661.

(*E*)-3-methyl-3-(4-nitrophenyl)-6-(3,4,5-trimethoxyphenyl)hex-5-en-2-one (6f)

Yield: 45.0 mg, 90%. **^{1}H NMR** (400 MHz, CDCl3) δ 8.26 – 8.20 (m, 2H), 7.49 – 7.40 (m, 2H), 6.45 (s, 2H), 6.27 (d, J = 15.7 Hz, 1H), 5.84 – 5.68 (m, 1H), 3.83 (s, 6H), 3.81 (s, 3H), 2.86 (dd, J = 14.2, 7.7 Hz, 1H), 2.74 (dd, J = 14.1, 7.2 Hz, 1H), 1.98 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.7, 153.3, 149.8, 147.0, 137.7, 134.2, 132.7, 127.5, 124.02, 123.95, 103.2, 60.9, 56.5, 56.1, 41.9, 26.3, 21.3. **IR (KBr)** γ 3459, 2939, 1581, 1519, 1456, 1418, 1347, 1239, 1158, 1127, 1009, 967, 857, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{22}H_{26}NO_6$, 400.1755; found, 400.1761.

(*E*)-3-methyl-3-(4-nitrophenyl)-6-(o-tolyl)hex-5-en-2-one (6g)

Yield: 28.8 mg, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 6.7 Hz, 1H), 7.15 – 7.06 (m, 3H), 6.55 (d, *J* = 15.6 Hz, 1H), 5.70 (dt, *J* = 15.2, 7.4 Hz, 1H), 2.94 – 2.77 (m, 2H), 2.23 (s, 3H), 1.99 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.6, 149.8, 147.0, 136.2, 135.0, 132.3, 130.2, 127.6, 127.4, 126.1, 125.9, 125.7, 124.0, 56.5, 42.0, 26.3, 21.3, 19.7. **IR (KBr)** γ 3458, 2975, 1710, 1604, 1520, 1485, 1460, 1347, 1111, 969, 857, 749, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_3$, 324.1594; found, 324.1616.

(*E*)-6-(2-fluorophenyl)-3-methyl-3-(4-nitrophenyl)hex-5-en-2-one (6h)

Yield: 17.8 mg, 44%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.17 (dd, J = 13.4, 6.4 Hz, 1H), 7.09 – 6.93 (m, 2H), 6.51 (d, J = 15.9 Hz, 1H), 5.99 – 5.83 (m, 1H), 2.97 – 2.77 (m, 2H), 1.99 (s, 3H), 1.61 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.5, 159.9 (d, *J* = 248.9 Hz), 149.6, 147.0, 128.7 (d, *J* = 8.3 Hz), 127.49, 127.36 (d, *J* = 4.7 Hz), 127.17 (d, *J* = 3.8 Hz), 126.53 (d, *J* = 3.5 Hz), 124.69 (d, *J* = 12.3 Hz), 124.07, 124.03, 115.7 (d, *J* = 22.2 Hz), 56.4, 42.2, 26.2, 21.2. **IR (KBr)** γ 3452, 2927, 1710, 1604, 1520, 1487, 1456, 1347, 1229, 1110, 970, 856, 754, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{19}H_{19}FNO_3$, 328.1343; found, 328.1367.

(*E*)-3-methyl-6-(naphthalen-1-yl)-3-(4-nitrophenyl)hex-5-en-2-one (6i)

Yield: 29.9 mg, 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.83 (dd, *J* = 9.3, 7.2 Hz, 2H), 7.74 (t, *J* = 4.7 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.38 (d, *J* = 5.0 Hz, 2H), 7.04 (d, *J* = 15.5 Hz, 1H), 5.85 (dt, *J* = 15.3, 7.6 Hz, 1H), 2.95 (d, *J* = 7.5 Hz, 2H), 2.01 (s, 3H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.6, 149.7, 147.0, 134.9, 133.5, 131.8, 130.9, 128.5, 127.9, 127.9, 127.6, 126.0, 125.8, 125.6, 124.0, 123.8, 123.6, 56.6, 42.2, 26.3, 21.3. **IR (KBr)** γ 3451, 1709, 1621, 1604, 1519, 1346, 1289, 1111, 1074, 1039, 970, 855, 777, 700 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{23}H_{22}NO_3$, 360.1594; found, 360.1598.

(*E*)-3-benzyl-3-(4-nitrophenyl)-6-phenylhex-5-en-2-one (6j)

Yield: 32.7 mg, 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.24 (m, 7H), 7.19 – 7.07 (m, 3H), 6.66 (d, *J* = 6.9 Hz, 2H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.12 – 5.99 (m, 1H), 3.38 (d, *J* = 14.1 Hz, 1H), 3.25 (d, *J* = 14.2 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.03 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.9, 148.9, 147.1, 136.7, 136.1, 134.8, 130.2, 128.7, 128.2, 128.0, 127.8, 126.8, 126.3, 123., 123.3, 61.2, 40.6, 35.6, 27.1. **IR (KBr)** γ 3462, 2959, 1737, 1521, 1403, 1386, 1370, 1348, 1208, 1176, 1121, 1020, 915, 855, 701 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{25}H_{23}NO_3Na$, 408.1570; found, 408.1579.

Ethyl (*E*)-2-methyl-2-(4-nitrophenyl)-5-phenylpent-4-enoate (6k)

Yield: 24.5 mg, 58%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.14 (m, 5H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.04 – 5.88 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.98 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.83 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.63 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 150.8, 146.8, 137.0, 134.4, 128.6, 127.5, 127.3, 126.2, 124.4, 123.6, 61.4, 50.9, 43.0, 22.8, 14.1. **IR (KBr)** γ 2981, 1728, 1604, 1521, 1496, 1449, 1348, 1229, 1114, 1015, 969, 856, 742, 694 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}NO_4$, 340.1543; found, 340.1563.

General procedure C for the deacylative allylation with alkyl acetylacetates

To a flame-dried schlenk tube (25 mL) were added alkyl acetylacetate **7** (0.125 mmol), allylarene **2** (0.5 mmol), $Pd(OAc)_2$ (5 mol%, 0.00625 mmol, 1.4 mg), PPh_3 (20 mol%, 0.025 mmol, 6.5 mg), NaOH solution (4.0 equiv, 0.5 mmol, 20 M, 25 μL), 2,5-DTBQ (1.2 equiv, 0.15 mmol, 33.1 mg), ^{t}BuOH (0.4 mL), THF (0.4 mL) and a stir bar. The solution was stirred at 40 ^{o}C for 36 h, under N_2. The solution was warmed up to 90 ^{o}C and stirred for another 36 h. Then the vial was cooled down to room temperature, the reaction mixture was directly subjected on flash chromatography (SiO_2, EtOAc/EtOH = 1:1) to provide the allylation product **8**.

(*E*)-2-methyl-5-phenylpent-4-enoic acid (8a)
Yield: 19.5 mg, 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.23 – 7.17 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.21 – 6.11 (m, 1H), 2.78 – 2.54 (m, 2H), 2.45 – 2.29 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.3, 137.3, 132.4, 128.5, 127.2, 126.8, 126.2, 39.3, 36.7, 16.5. **IR (KBr)** γ 3461, 3027, 2976, 2930, 1706, 1494, 1461, 1416, 1285, 1238, 965, 741, 693 cm^{-1}. **HRMS (ESI)** (m/z): $[M-H]^-$ calcd for $C_{12}H_{13}O_2$, 189.0910; found, 189.0931.

(*E*)-2-cinnamylhexanoic acid (8b)
Yield: 22.2 mg, 77 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.23 – 6.08 (m, 1H), 2.62 – 2.47 (m, 2H), 2.46 – 2.34 (m, 1H), 1.79 – 1.48 (m, 2H), 1.43 – 1.27 (m, 4H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.5, 137.4, 132.2, 128.5, 127.2, 127.0, 126.2, 45.4, 35.3, 31.3, 29.4, 22.6, 13.9. **IR (KBr)** γ 3027, 2957, 2930, 2859, 1705, 1494, 1452, 1417, 1285, 1239, 964, 740, 692 cm^{-1}. **HRMS (ESI)** (m/z): $[M-H]^-$ calcd for $C_{15}H_{19}O_2$, 231.1380; found, 231.1402.

(*E*)-2-cinnamylheptanoic acid (8c)
Yield: 19.5 mg, 63 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.24 – 6.07 (m, 1H), 2.61 – 2.47 (m, 2H), 2.47 – 2.34 (m, 1H), 1.74 – 1.61 (m, 1H), 1.60 – 1.48 (m, 1H), 1.40 – 1.19 (m, 6H), 0.88 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.1, 137.4, 132.2, 128.5, 127.2, 127.0, 126.1, 45.4, 35.3, 31.7, 31.6, 26.9, 22.5, 14.0. **IR (KBr)** γ 3457, 3027, 2955, 2928, 2857, 1706, 1447, 1411, 1280, 1240, 964, 740, 692 cm^{-1}. **HRMS (ESI)** (m/z): $[M-H]^-$ calcd for $C_{16}H_{21}O_2$, 245.1536; found, 245.1559.

(*E*)-3-methyl-6-phenylhex-5-en-2-one (8d)
Yield: 16.5 mg, 70 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.7, 7.2 Hz, 1H), 2.76 – 2.61 (m, 1H), 2.56 (dtd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.17 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.9, 137.3, 132.1, 128.5, 127.3, 127.2, 126.1, 47.1, 36.2, 28.5, 16.1. **IR (KBr)** γ 3461, 3199, 2923, 2852, 1712, 1657, 1632, 1454, 1405, 1359, 966, 742, 693 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{13}H_{17}O$, 189.1274; found, 189.1271.

General procedure D for the deacylative allylation with acetylacetones under tandem catalysis process

To a flame-dried schlenk tube (25 mL) were added acetylacetone **9** (0.125 mmol), o-FBA (10% mol), $Pd(PPh_3)_4$ (5% mol), allyl methyl carbonate (1.0 equiv., 14μL), THF (0.4 mL) and a stir bar. The solution was stirred at room temperature for 1 h, under N_2. After that time, Cs_2CO_3 (1.2 equiv, 0.15 mmol, 48.9 mg), 2,5-DTBQ (1.2 equiv, 0.15 mmol, 33.1 mg), **2a** (4.0 equiv, 0.5 mmol), and another 0.4 mL THF was added into the solution. And the mixture was stirred at 80 °C for 18 hours. After the vial was cooled down to room temperature, the reaction mixture was subjected directly on flash chromatography (SiO_2, Petroleum ether/EtOAc = 10:1) to provide the allylation product **9**.

(*E*)-3-allyl-3-(4-nitrophenyl)-6-phenylhex-5-en-2-one (12)
Yield: 34.4 mg, 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.32 – 7.17 (m, 5H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.80 – 5.68 (m, 1H), 5.50 (dt, *J* = 16.2, 7.3 Hz, 1H), 5.18 – 5.08 (m, 2H), 2.92 (d, *J* = 7.5 Hz, 2H), 2.83 (d, *J* = 7.2 Hz, 2H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.7, 148.8, 147.1, 136.8, 134.5, 132.0, 128.6, 127.8, 127.6, 126.1, 124.0, 123.5, 119.7, 59.9, 37.7, 37.1, 26.6. **IR (KBr)** γ 3081, 3027, 2925, 2854, 1709, 1597, 1495, 1447, 1347, 1188, 1165, 1111, 1014, 968, 924, 857, 746, 695 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{21}H_{22}NO_3$, 336.1594; found, 336.1618.

General procedure E for the deacylative allylation with Dicarbonyl compounds to construct tertiary center under tandem catalysis process

To a flame-dried schlenk tube (25 mL) were added dicarbonyl compounds **13** (0.125 mmol), allylarene **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%, 0.00625 mmol, 1.4 mg), PPh_3 (20 mol%, 0.025 mmol, 6.5 mg), allyl methyl carbonate (1.0 equiv., 14 μL), THF (0.4 mL) and a stir bar. The solution was stirred at room temperature for 1 h, under N_2. After that time, base, 2,5-DTBQ (1.2 equiv, 0.15 mmol, 33.1 mg) and ^{t}BuOH (0.4 mL) were added. The solution was stirred at 40 °C for 24 h, under N_2. The solution was warmed up to 80 or 90 °C and stirred for another 24 h. Then the vial was cooled down to room temperature, the reaction mixture was directly subjected on flash chromatography (SiO_2, PE/DCM = 2:1) to provide the allylation product **14**.

(*E*)-3-allyl-6-phenylhex-5-en-2-one (14a)
Yield: 12.2 mg, 47 %. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.23 – 7.16 (m, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.7, 7.3 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.11 – 5.01 (m, 2H), 2.77 – 2.68 (m, 1H), 2.51 (dtd, *J* = 8.7, 7.4, 1.3 Hz, 1H), 2.45 – 2.32 (m, 2H), 2.30 – 2.21 (m, 1H), 2.15 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.1, 137.2, 135.2, 132.3, 128.5, 127.3, 126.9, 126.1, 117.2, 52.4, 35.3, 34.39, 29.78. **IR (KBr)** γ 3462, 3079, 3026, 2925, 2852, 1711, 1641, 1493, 1442, 1356, 1162, 1026, 966, 916, 743, 693 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{15}H_{19}O$, 215.1430; found, 215.1429.

tert-butyl (*E*)-2-allyl-5-phenylpent-4-enoate (14b)
Yield: 23.5 mg, 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.15 (dt, *J* = 15.7, 6.9 Hz, 1H), 5.78 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.15 – 4.97 (m, 2H), 2.54 – 2.43 (m, 2H), 2.43 – 2.32 (m, 2H), 2.30 – 2.21 (m, 1H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 137.5, 135.5, 131.9, 128.5, 127.3, 127.1, 126.1, 116.7, 80.4, 46.0, 36.1, 35.3, 28.2. **IR (KBr)** γ 3445, 3027, 2977, 2930, 1727, 1643, 1441, 1368, 1237, 1151, 965, 916, 847, 741, 693 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{18}H_{25}O_2$, 273.1849; found, 273.1847.

General procedure F for the decarboxylative allylation with alkynyl acids

To a flame-dried schlenk tube (25 mL) were added alkynyl acids **11** (0.25 mmol), $Pd(TFA)_2$ (10 mol%, 0.025 mmol, 8.3 mg), PPh_3 (40 mol%, 0.10 mmol, 26.2 mg), Cs_2CO_3 (2 equiv, 0.5 mmol, 163.0 mg), 2,5-DTBQ (2 equiv, 0.5 mmol, 110.2 mg), 2 (4.0 equiv, 1.0 mmol), *o*-FBA (1 equiv, 0.25mmol, 35.0 mg), toluene (3.0 mL) and a stir bar. The solution was subjected to three freeze-pump-thaw cycles using liquid nitrogen to degas, then the mixture was stirred at 75 °C for 22 h. After the vial was cooled down to room temperature, the reaction mixture was subjected directly on flash chromatography (SiO_2, Petroleum ether/EtOAc = 100:1) to provide the allylation product **12**.

(*E*)-pent-1-en-4-yne-1,5-diyldibenzene (16a)
Yield: 22.0 mg, 40%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 3.7 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.27 (m, 5H), 7.27 – 7.19 (m, 1H), 6.71 (d, *J* = 15.7 Hz, 1H), 6.25 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.36 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 131.65, 131.43, 128.56, 128.27, 127.85, 127.4, 126.29, 124.26, 123.65, 86.8, 82.9, 23.0. **IR (KBr)** γ 3080, 3028, 2878, 1750, 1653, 1598, 1574, 1490, 1444, 1414, 1341, 1310, 1269, 1177, 1070, 1027, 964, 840, 795, 755, 690 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{17}H_{15}$, 219.1168; found, 219.1171.

(*E*)-1-methyl-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (16b)
Yield: 14.2 mg, 24%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.0 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.20 (dt, *J* = 15.6, 5.6 Hz, 1H), 3.35 (d, *J* = 5.4 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 134.3, 131.6, 131.3, 129.2, 128.3, 127.8, 126.2, 123.7, 123.2,

86.9, 82.5, 23.0, 21.2. **IR (KBr)** γ 3454, 2962, 2924, 1621, 1512, 1490, 1412, 1384, 1261, 1096, 1027, 869, 799, 755, 691 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{18}H_{17}$, 233.1325; found, 233.1315.

(*E*)-1-methyl-3-(5-phenylpent-1-en-4-yn-1-yl)benzene (16c)

Yield: 16.4 mg, 28%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 7.24 – 7.16 (m, 3H), 7.10 – 6.99 (m, 1H), 6.68 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.29 – 6.19 (m, 1H), 3.36 (dd, *J* = 5.6, 1.7 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 137.0, 131.7, 131.5, 128.5, 128.2, 128.2, 127.8, 127.1, 124.0, 123.7, 123.4, 86.8, 82.8, 23.0, 21.4. **IR (KBr)** γ 3465, 3031, 2920, 1599, 1489, 1442, 1415, 1274, 1070, 964, 775, 755, 690 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{18}H_{17}$, 233.1325; found, 233.1345.

(*E*)-1-fluoro-4-(5-phenylpent-1-en-4-yn-1-yl)benzene (16d)

Yield: 24.6 mg, 42%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.39 – 7.27 (m, 5H), 7.06 – 6.93 (m, 2H), 6.67 (d, *J* = 15.7 Hz, 1H), 6.16 (dt, *J* = 15.7, 5.6 Hz, 1H), 3.35 (dd, *J* = 5.6, 1.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ162.2 (d, *J* = 246.2 Hz), 133.3 (d, *J* = 3.3 Hz), 131.7, 130.3, 128.3, 127.9, 127.8 (d, *J* = 7.9 Hz), 124.00 (d, *J* = 2.2 Hz), 123.58, 115.4 (d, *J* = 21.6 Hz), 86.6, 83.0, 23.0. **IR (KBr)** γ 3455, 3036, 1600, 1508, 1499, 1229, 1158, 1070, 965, 840, 756, 691 cm^{-1}. **HRMS (ESI)** (m/z): $[M+H]^+$ calcd for $C_{17}H_{14}F$, 237.1074; found, 237.1079.

AUTHOR INFORMATION

Corresponding Author

pusher@ustc.edu.cn

Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C NMR spectra for compounds **3**, **6**, **8**, **12**, **14**, **16**.

REFERENCES

(1) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387. (b) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292.

(2) (a) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195. (b) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203. (c) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1. (d) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813. (e) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747.

(3) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Dai, L. X.; Tu, T.; You, S. L.; Deng, W. P.; Hou, X. L. *Acc. Chem. Res.* **2003**, *36*, 659. (c) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (d) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258.

(4) (a) Jensen, T.; Fristrup, P. *Chem. Eur. J.* **2009**, *15*, 9632. (b) Liu, G.; Wu, Y. *Top. Curr. Chem.* **2010**, *292*, 195. (c) Engelin, C. J.; Fristrup, P. *Molecules* **2011**, *16*, 951. (d) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (e) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (f) Li, B. J.; Shi, Z. J. *Chem. Soc. Rev.* **2012**, *41*, 5588. (g) Liron, F.; Oble, J.; Lorion, M. M.; Poli, G. *Eur. J. Org. Chem.* **2014**, 5863. (h) Zheng, C.; You, S. L. *RSC Adv.* **2014**, *4*, 6173.

(5) (a) Lin, S.; Song, C. X.; Cai, G. X.; Wang, W. H.; Shi, Z. J. *J. Am. Chem. Soc.* **2008**, *130*, 12901. (b) Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 14090. (c) Young, A. J.; White, M. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 6824. (d) Trost, B. M.; Hansmann, M. M.; Thaisrivongs, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4950. (e) Tang, S.; Wu, X.; Liao, W.; Liu, K.; Liu, C.; Luo, S.; Lei, A. *Org. Lett.* **2014**, *16*, 3584.

(6) (a) Tao, Z. L.; Zhang, W. Q.; Chen, D. F.; Adele, A.; Gong, L. Z. *J. Am. Chem. Soc.* **2013**, *135*, 9255. (b) Li, L. L.; Tao, Z. L.; Han, Z. Y.; Gong, L. Z. *Org. Lett.* **2016**.

(7) (a) Trost, B. M.; Thaisrivongs, D. A.; Hansmann, M. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 11522. (b) Li, L.; Chen, Q. Y.; Guo, Y. *Chem. Commun.* **2013**, *49*, 8764. (c) Trost, B. M.; Thaisrivongs, D. A.; Donckele, E. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 1523. (d) Howell, J. M.; Liu, W.; Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 5750. (e) Lin, H. C.; Wang, P. S.; Tao, Z. L.; Chen, Y. G.; Han, Z. Y.; Gong, L. Z. *J. Am. Chem. Soc.* **2016**, *138*, 14354.

(8) Wang, P. S.; Lin, H. C.; Zhai, Y. J.; Han, Z. Y.; Gong, L. Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 12218.

(9) Zhang, H.; Hu, R. B.; Liu, N.; Li, S. X.; Yang, S. D. *Org. Lett.* **2016**, *18*, 28.

(10) (a) Tunge, J. A.; Burger, E. C. *Eur. J. Org. Chem.* **2005**, 1715. (b) You, S.-L.; Dai, L.-X. *Angew. Chem., Int. Ed.* **2006**, *45*, 5246. (c) Mohr, J. T.; Stoltz, B. M. *Chem. Asian J.* **2007**, *2*, 1476. (d) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846. (e) Rodriguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030. (f) Cornella, J.; Larrosa, I. *Synthesis* **2012**, *44*, 653. (g) Dzik, W. I.; Lange, P. P.; Goossen, L. J. *Chem. Sci.* **2012**, *3*, 2671. (h) Park, K.; Lee, S. *RSC Adv.* **2013**, *3*, 14165. (i) Wang, Z.-L. *Adv. Synth. Catal.* **2013**, *355*, 2745. (j) Braun, M. *Modern Enolate Chemistry. From Preparation to Applications in Asymmetric Synthesis*; Wiley-VCH: Weinheim, **2016**.

(11) (a) Brodsky, B. H.; Du Bois, J. *Org. Lett.* **2004**, *6*, 2619. (b) Grenning, A. J.; Tunge, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 14785. (c) Grenning, A. J.; Tunge, J. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1688. (d) Grenning, A. J.; Van Allen, C. K.; Maji, T.; Lang, S. B.; Tunge, J. A. *J. Org. Chem.* **2013**, *78*, 7281. (e) Ye, F.; Wang, C.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 11625. (f) Yong, W.-S.; Park, S.; Yun, H.; Lee, P. H. *Adv. Synth. Catal.* **2016**, *358*, 1958. (g) Zhu, Y.; Zhang, L.; Luo, S. *J. Am. Chem. Soc.* **2016**, *138*, 3978.

(12) (a) Kawata, A.; Takata, K.; Kuninobu, Y.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7793. (b) Jukic, M.; Sterk, D.; Casar, Z. *Curr. Org. Synth.* **2012**, *9*, 488. (c) Xie, F.; Yan, F.; Chen, M.; Zhang, M. *RSC Adv.* **2014**, *4*, 29502.

(13) Mori-Quiroz, L. M.; Clift, M. D. *Org. Lett.* **2016**, *18*, 3446.

(14) 30% yield of cinnamyl methyl ether was obtained when MeOH was used.

(15) (a) Tsuda, T.; Chujo, Y.; Nishi, S.; Tawara, K.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6381. (b) Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510. (c) Zhang, W. W.; Zhang, X. G.; Li, J. H. *J. Org. Chem.* **2010**, *75*, 5259. (d) Choe, J.; Yang, J.; Park, K.; Palani, T.; Lee, S. *Tetrahedron Lett.* **2012**, *53*, 6908. (e) Yang, Y.; Lim, Y. H.; Robins, E. G.; Johannes, C. W. *RSC Adv.* **2016**, *6*, 72810.