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钯催化大位阻芳基异腈作为羰基源的烯丙基羰基化 Negishi 偶联反应

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摘要 利用大位阻芳基异腈作为羰基源, 发展了钯催化下的烯丙基羰基化 Negishi 偶联反应. 大位阻芳基异腈的使用可以有效地避免羰基化反应过程中 β-H 消除副反应的发生, 可专一区域选择性、高立体选择性地实现 β,γ-不饱和酮的精准合成, 解决了传统一氧化碳化学中长期存在的区域选择性较差的难题. 有机锌试剂作为含碳原子亲核试剂, 反应拥有条件温和, 底物适用性广等优点.

关键词 钯催化; 羰基化; 异腈; β,γ-不饱和酮

Palladium-Catalyzed Allylic Carbonylative Negishi Cross-Coupling Reactions with Sterically Bulky Aromatic Isocyanides

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Abstract Herein, the palladium-catalyzed allylic carbonylative Negishi cross-coupling reaction employing sterically bulky aromatic isocyanides as the CO surrogate was disclosed. The leverage of sterically bulky aromatic isocyanide minimizes the side β-H elimination in carboxylation reaction, affords synthetically important β,γ-unsaturated ketones with high regioselectivity and stereoselectivity, thereby tackles the long-standing challenge in Pd-catalyzed allylic carbonylative cross-coupling with CO gas. Moreover, this protocol exhibits the advantage including mild reaction conditions, as well as broad substrate scope due to the utilization of Negishi reagent as the carbon nucleophiles.

Keywords palladium catalysis; carbonylation; isocyanide; β,γ-unsaturated ketones

1 Introduction

Transition metal-catalyzed carbonylation represents a powerful and efficient strategy to achieve the formation of new carbon-carbon bonds in the past few decades[1] since the pioneering work developed by Heck in the 1970s.[2] In particular, the employment of carbon-nucleophiles in the carbonylation would provide a convenient and straightforward protocol to afford various ketones.[3] Furthermore, palladium-catalyzed Tsuji-Trost reaction is one of the most efficient method to construct new carbon-carbon bonds.[4] Numerous transition metal-catalyzed allylic reactions have been developed with different allylic partners and nucleophiles enabled by diverse transition metals.[5] Among the Pd-catalyzed allylic transformations, carbonylative allylic reactions have been widely investigated as this important strategy allows incorporation of alkene and carbonyl functionality in single synthetic protocol which enables the expedient synthesis of the significant building blocks β,γ-unsaturated compounds. However, the nucleophiles employed in the Pd-catalyzed three-component allylic carbonylation were largely restricted on the noncarbon nucleophiles, such as alcohols[6] amines[6f,7] and others.[8] In contract, the carbon-nucleophiles used in this type reactions were relatively underdeveloped while it allows the transformation of versatile β,γ-unsaturated ketones.[9] The Stille and coworkers have reported the elegant Pd-catalyzed allylic carbonylation with organotin reagents under

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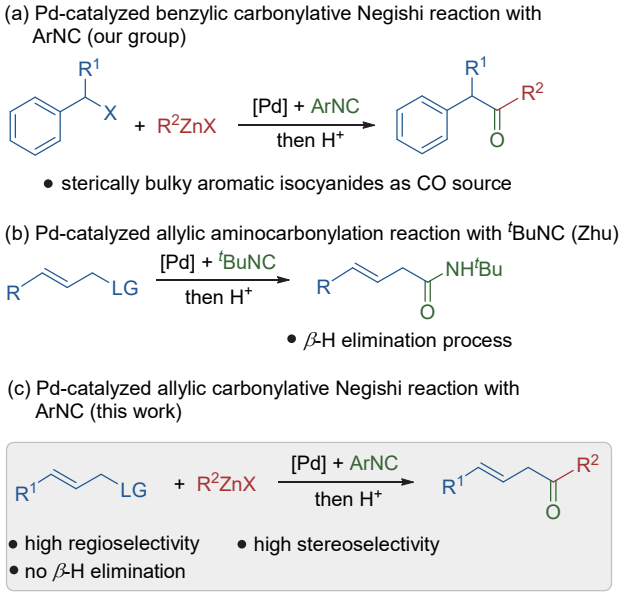
mild conditions while the nucleophiles used were largely limited on aryl, vinyl and allyl stananers.[10] After that, Tamaru group has achieved three-component Pd-catalyzed allylic carbonylative Negishi coupling with sp^3-alkyl zincs. However, this transformation was confronted with selectivity issues which highly depend on the electronics of the alkyl zinc reagents, and the mixture of isomers was usually obtained.[11] Isocyanide is an important C1-synthon which has been widely employed in transition metal-catalyzed carbonylative reactions.[12] Recently, our group has developed the Ni-catalyzed allylic carbonylative coupling of alkyl zinc reagents with *tert*-butyl isocyanide as CO surrogate, which provides a practical and straightforward strategy to generate important *β*,*γ*-unsaturated ketones with high selectivity under mild conditions.[13] Then, the Pd-catalyzed secondary benzylic imidoylative Negishi reaction was also developed using the sterically bulky aromatic isocyanide as imine source[14] (Scheme 1a). Based on continuing research interest on transition metal-catalyzed carbonylation with isocyanides as carbonyl source,[15] we wish to explore an effective Pd-catalyzed three components allylic carbonylative Negishi coupling with suitable isocyanides as CO source. Pd-catalyzed allylic carbonyltions with isocyanide as CO surrogate have been rarely developed. In 2016, an allylic carbonylative reaction of *tert*-butyl isocyanide with allyl carbonates was reported by Zhu and coworker. It was revealed that *β*-H elimination of the allyl imidoylpalladium intermediates was the major process, which could hydrolyze to *β*,*γ*-unsaturated amides[16] (Scheme 1b). In addition, the isomerization of *β*,*γ*-unsaturated ketones to more thermodynamically stable *α*,*β*-unsaturated ketones represents another synthetic obstacle.[17] Herein, we developed a general, one-pot Pd-catalyzed allylic carbonylative coupling with alkyl zinc reagents by the usage of sterically bulky aromatic isocyanides as CO synthon under mild conditions (Scheme 1c). This transformation features high selectivity and good functional group tolerance to afford versatile *β*,*γ*-unsaturated ketones. Notably, this Pd-mediated allylic carbonylation could be a complementary strategy to our former reported Ni-catalyzed allylic carbonylative coupling.



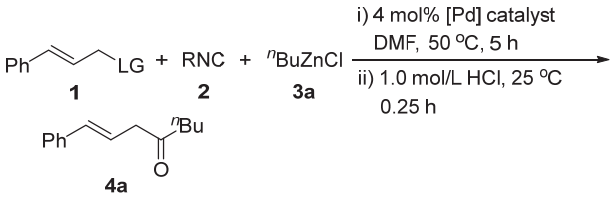
Scheme 1 Pd-catalyzed allylic carbonylative reaction

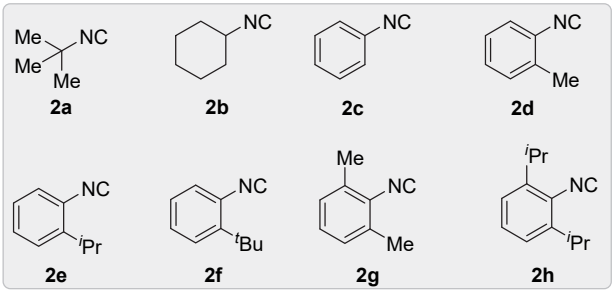
2 Results and discussion

We initiated our investigation with cinnamyl diethyl phosphate **1a** as allylic electrophile, commercially available alkyl isocyanide *tert*-butyl isocyanide as CO source, ^{n}BuZnCl as nucleophile, and $Pd(dba)_2$ as catalyst under 50 ℃ in *N*,*N*-dimethylformamide (DMF). To our delight, after simple acidic work-up, the desired *β*,*γ*-unsaturated ketone **4a** could afford in 52% corrected GC yields with exclusive *trans*-alkene configuration (Table 1, Entry 1). Then the influence of diverse isocyanide species on this Pd-catalyzed three-component allylic carbonylative Negishi coupling was investigated. Alkyl isocyanide CyNC gave inferior result and provided the *β*,*γ*-unsaturated ketone **4a** only in 28% yield (Table 1, Entry 2). Notably, when the isocyanide was changed to aromatic isocyanide **2c**, the yield of **4a** was increased dramatically to 69% yield with high selectivity (Table 1, Entry 3). By introducing the methyl to the *ortho*-position of phenyl isocyanide, the yield of this carbonylative reaction was further improved, and the product **4a** was obtained in 76% yield (Table 1, Entry 4). Encouraged by this result, the isocyanide species were then exchanged to more sterically bulky aromatic isocyanides. The 2-isopropyphenyl isocyanide was proved to the optimal CO surrogate, which gave the desired *trans*-*β*,*γ*-unsaturated ketone **4a** in 85% isolated yield (Table 1, Entry 5). The employment of 2-*tert*-butylphenyl isocyanide **2f** did not give better result (Table 1, Entry 6). Especially, when the more sterically bulky aromatic isocyanides such as **2g** and **2h** were used, the yields were decreased to 21% and 17%, respectively (Table 1, Entries 7～8), which may could be attributed to the increased challenge for the 1,1-insertion of isocyanide. Furthermore, the usage of other leaving groups reduced the yields (Table 1, Entries 9～11). Other palladium catalysts such as $Pd(OAc)_2$ and $Pd(PPh_3)_4$ also could catalyze this transformation albeit with lower yields (Table 1, Entries 12～13).

With the optimal conditions in hand, we next turned our attention to investigate the substrate scope of this Pd-catalyzed allylic carbonylative coupling (Table 2). At the beginning, the scope of alkyl zinc reagents was explored. The reaction tolerates various alkylative zinc reagents and a series of highly selective *β*,*γ*-unsaturated ketones could be produced. Simple alkyl zincs such as 2-phenylethyl (**4b**) and *n*-octyl (**4c**) were also tolerated to afford the products in good yields. In addition, a wide range of functional groups including an alkene (**4d**), a fluoride (**4e**), a chloride (**4f**), a nitrile (**4g**), an ester (**4h**) and ethers (**4i**, **4j**) were all compatible to this carbonylative reactions, the desired *β*,*γ*-unsaturated ketones could be obtained in moderate to excellent yields under standard conditions. Notably, more

Table 1 Optimization of Conditions[a]





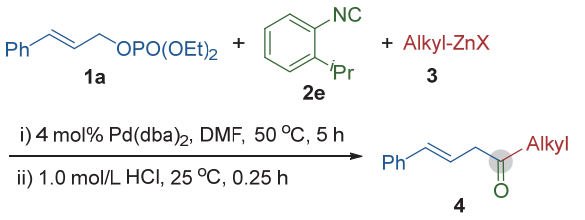
Entry	LG	Isocyanide **2**	[Pd] catalyst	Yield[b]/%
1	$OPO(OEt)_2$	**2a**	$Pd(dba)_2$	52
2	$OPO(OEt)_2$	**2b**	$Pd(dba)_2$	28
3	$OPO(OEt)_2$	**2c**	$Pd(dba)_2$	69
4	$OPO(OEt)_2$	**2d**	$Pd(dba)_2$	76
5	$OPO(OEt)_2$	**2e**	$Pd(dba)_2$	86 (85)[c]
6	$OPO(OEt)_2$	**2f**	$Pd(dba)_2$	70
7	$OPO(OEt)_2$	**2g**	$Pd(dba)_2$	21
8	$OPO(OEt)_2$	**2h**	$Pd(dba)_2$	17
9	OCOOMe	**2e**	$Pd(dba)_2$	41
10	OBoc	**2e**	$Pd(dba)_2$	40
11	OAc	**2e**	$Pd(dba)_2$	53
12	$OPO(OEt)_2$	**2e**	$Pd(OAc)_2$	71
13	$OPO(OEt)_2$	**2e**	$Pd(PPh_3)_4$	45

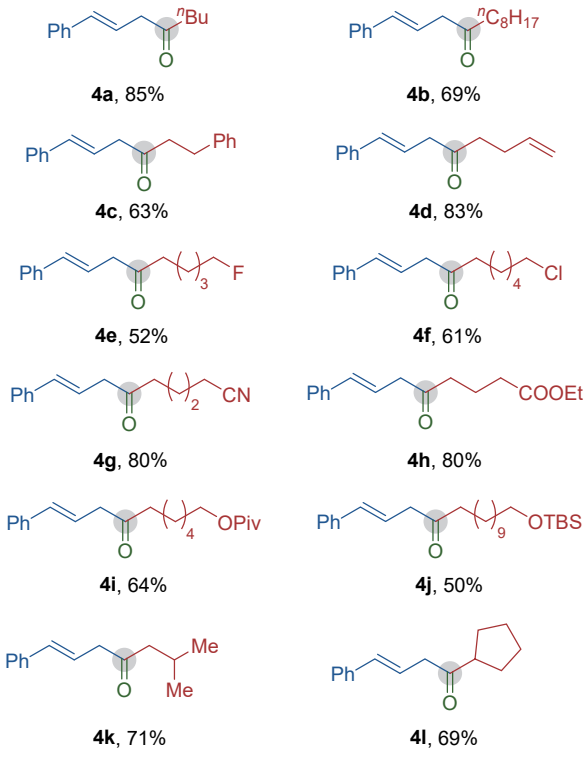
[a] Reaction conditions: **1** (0.1 mmol), **2** (0.15 mmol), **3a** (0.15 mmol), [Pd] catalyst (0.004 mmol), DMF (1 mL), 50 ℃, 5 h, then 1.0 mol/L HCl, 25 ℃, 0.25 h. [b] Corrected GC yield. [c] Isolated yield in the parentheses.

sterically bulky organozincs also could be applied in this reaction including isobutyl zinc bromide (**4k**) and secondary cyclopentyl zinc bromide (**4l**) to provide the corresponding ketones in good yields.

Next, the generality of allylic electrophiles was explored as summarized in Table 3. 2-Methyl (**4m**) and 4-methyl (**4n**) substituted aryl allylic substrates were all tolerated well in this reaction, providing the product in good yields. 2-Naphtyl substituted allylic electrophile (**4o**) was also compatible for this carbonylative reaction, which afforded the *β*,*γ*-unsaturated ketone in moderate yield. It was noteworthy that the Pd-catalyzed three-component allylic carbonylation could serve as a complementary strategy to the Ni-catalyzed allylic carbonylative reaction previously reported. Some substrates that were not tolerated in Ni-catalyzed carbonylation could proceed smoothly in this transformation. Styryl substituted allylic phosphate (**4p**) was tolerated, which furnished the desired ketone in 53% isolated yield albeit with moderate *E*/*Z* selectivity. Particularly, tertiary allylic elctrophile (**4q**) proceeded well in this reaction when the benzyl zinc bromide functioned as nucleophilic partner, affording the target product in excellent yield. Heteroaromatic ring was not limited to thiophene (**4s**), and pyridine (**4r**) also could be applied in this mild allylic carbonylation to provide the product in good yields. Furthermore, C-3 methyl substistuted allylic coupling partner was also tolerated well (**4t**), and the *trans*-*β*,*γ*-unsaturated ketone was successfully generated in 68% yield.

Table 2 Scope of alkyl zinc reagents[a]

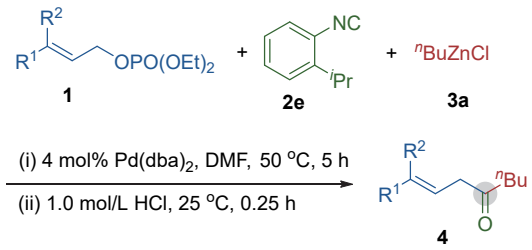


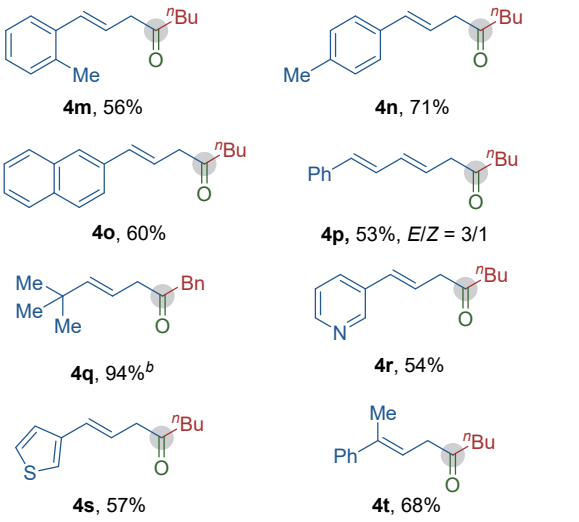


[a] Reaction conditions: **1a** (0.3 mmol), **2e** (0.45 mmol), **3** (0.45 mmol), $Pd(dba)_2$ (0.012 mmol), DMF (3 mL), 50 ℃, 5 h, then 1.0 mol•L^{-1} HCl, 25 ℃, 0.25 h.

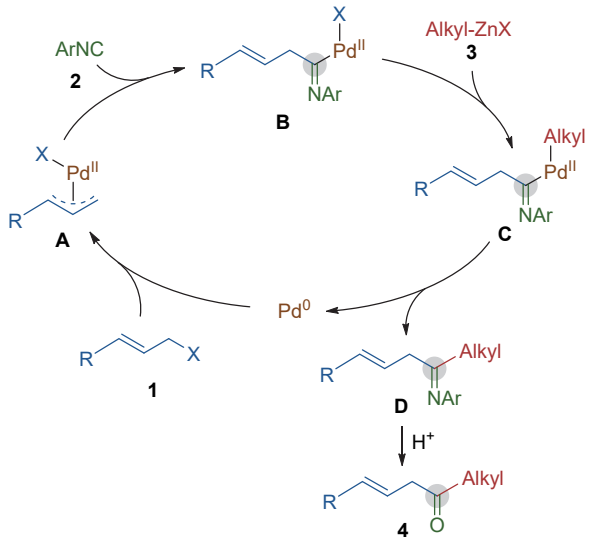
Based on our previous report,[13] a possible reaction pathway is proposed in Scheme 2. The oxidative addition of allyl electrophile **1** with Pd(0) catalyst could afford the π-allylpalladium(II) intermediate **A**. Then, 1,1-insertion of sterically bulky aromatic isocyanide **2** could give allyl imidoylpalladium intermediate **B**, which was prone to proceed *β*-H elimination process to furnish the ketenimine intermediate in Pd-catalyzed allylic carbonylation with *tert*-butyl isocyanide.[16] However, the employment of aromatic isocyanide could suppress this process efficiently and the fast transmetallation of the alkyl zincs **3** with **B** would generate intermediate **C**, which could provide the

Table 3 Scope of allylic phosphates[a]





[a] Reaction conditions: **1** (0.3 mmol), **2e** (0.45 mmol), **3a** (0.45 mmol), $Pd(dba)_2$ (0.012 mmol), DMF (3 mL), 50 ℃, 5 h, then 1.0 mol•L^{-1} HCl, 25 ℃, 0.25 h. [b] BnZnBr was used.



Scheme 2 Proposed mechanism

desired *β*,*γ*-unsaturated imine **D** after reductive elimination. Finally, the desired *β*,*γ*-unsaturated ketone could be obtained after simple acidic hydrolysis.

3 Conclusions

In summary, Pd-catalyzed allyic carbonylative Negishi coupling with sp^3-alkyl zinc reagents has been reported, which employing steric bulkyl aromatic isocyanide 2-isopropyphenyl isocyanide as CO source to afford various versatile *β*,*γ*-unsaturated ketones with excellent regio- and setero-selectivity. This three-component carbonylation features broad substrate scopes and good functional group tolerance under mild conditions. In addition, this method serves as a complementary strategy to the previously reported Ni-catalyzed allylic carbonylative coupling.

4 Experimental section

4.1 General information

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. Tetrahydrofuran (THF) were distilled from sodium/benzophenone. Dichloromethane (DCM) was distilled over CaH_2. $ZnCl_2$ was purchased from Strem; *N*,*N*-Dimethylformamide (DMF) was purchased from Adamas (99.8%, SafeDry, with molecular sieves, water $\leqslant 50\times10^{-6}$ (by KF, SafeSeal); ^{n}BuLi (2.4 mol/L in hexane) was purchased from Acros and Aldrich; Zinc dust (325 mesh) and LiCl were purchased from Greagent. $Pd(dba)_2$ and $Pd(OAc)_2$ were purchased from Sinocompound. $Pd(PPh_3)_4$ was purchased from Adamas (All Negishi reagents were titrated according to Knochel's procedure).[18] Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm Huanghai silica gel plates (HSGF 254) using UV light as the visualizing agent and an acidic solution of phosphomolybdic acid (PMA) and basic solution of potassium permanganate ($KMnO_4$) with heat as the developing agent.

All new compounds were characterized by means of ^{1}H NMR, ^{13}C NMR, and HR-MS. GC analysis was performed on an Agilent Technologies 7820A GC system. GC runs were performed with the following method: GC, HP-5 column, inlet temperature 100 ℃, column temperature 100 ℃ for 1 min, then 50 ℃/min to 280 ℃, then 280 ℃ for 6 min. NMR spectra were recorded using a Bruker AVANCE III 400 MHz NMR spectrometer. HRMS were recorded on an Agilent Technologies 7250 GCQTOF (EI) and a JEOL AccuTOF LC-plus 4G (ESI). All ^{1}H NMR data were calibrated relative to the signals for residual chloroform (δ 7.26) in deuterochloroform ($CDCl_3$). All ^{13}C NMR data were calibrated relative to $CDCl_3$ (δ 77.16) and were obtained with ^{1}H decoupling.

Compounds **1a**,[19] **1m**,[20] **1n**,[21] **1o**,[22] **1p**,[19] **1q**,[23] **1r**,[24] **1s**,[20] **1t**,[20] were synthesized according to the published procedures.

4.2 Preparation of $ZnCl_2$ solution

Zinc chloride (1.0 mol•L^{-1} in THF): Finely powdered anhydrous $ZnCl_2$ (0.68 g, 5.0 mmol) was weighed into a 25 mL flame-dried Schlenk tube in the glove box. The tube was taken out of the glove box and heated with a heat gun for 2 min under vacuum and then back filled with nitrogen (This process was repeated 3 times.). After cooling down to room temperature, the flask was backfilled with N_2, and

THF (anhydrous, 5.0 mL) was added. The suspension was vigorously stirred for 30 min before it was used.

4.3 Preparation of ^{n}BuZnCl

To a solution of $ZnCl_2$ (1.0 mol•L^{-1} in THF, 1.0 mL, 1.0 mmol) in THF (0.6 mL) was added ^{n}BuLi (2.4 mol•L^{-1} in hexane, 0.42 mL, 1.0 mmol) at 0 ℃. The mixture was vigorously stirred at the same temperature for 15 min.

4.4 General procedure for the preparation of organozinc reagents via direct insertion of zinc

This method is modified from the reported literature.[25] Anhydrous LiCl (10 mmol, 2.0 equiv.) was placed in an N_2-flushed sealed tube and dried for 10 min under the vacuum with heat gun. Zinc powder (10 mmol, 2.0 equiv., 325 mesh) was added under N_2 and the heterogeneous mixture of Zn and LiCl was dried again for 10 min under the vacuum with heat gun. The sealed tube was backfilled with N_2 (this process was repeated for three times). THF (5 mL) was added and Zn was activated with $BrCH_2CH_2Br$ (5 mol%) under the reflux condition for 20 min. After cooling, Me_3SiCl (1 mol%) and I_2 (0.5 mol%) were added under N_2, then the mixture was refluxed for another 20 min. Alkyl halide (5 mmol) was then added neat at room temperature and the reaction mixture was stirred at 65 ℃ for 12～72 h (checked by GC analysis of reaction aliquots, the conversion was higher than 98%).

4.5 General procedure for the Pd-catalyzed allylic carbonylative Negishi reactions

An oven-dried Schlenk tube charged with $Pd(dba)_2$ (0.012 mmol, 4 mol%) was evacuated and backfilled with N_2 (This process was repeated for three times). DMF (0.1 mol/L, 3 mL) was added into the reaction mixture. To this solution were subsequently added allylic phosphate (0.3 mmol, 1.0 equiv.), 2-isopropyphenyl isocyanide (0.45 mmol, 1.5 equiv.) and Negishi reagent (0.45 mmol, 1.5 equiv.). The tube was equipped with a balloon filled with N_2 at 50 ℃ for 5 h. The mixture was then added 1 mol•L^{-1} HCl (aq.) and stirred at room temperature for 0.25 h. The mixture was then extracted with EtOAc and the separated organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to yield the crude product, which was purified by silica gel flash column chromatography.

(*E*)-1-Phenyloct-1-en-4-one (**4a**):[26] Colorless oil (34.4 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.21 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.32 (dt, J=16.0, 6.8 Hz, 1H), 3.32 (dd, J=6.8, 1.2 Hz, 2H), 2.49 (t, J=7.6 Hz, 2H), 1.58 (quin, J=7.6 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.1, 137.1, 133.7, 128.7, 127.6, 126.4, 122.3, 47.1, 42.3, 25.9, 22.4, 14.0.

(*E*)-1-Phenyldodec-1-en-4-one (**4b**):[27] Pale yellow oil (56.1 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.21 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.31 (dt, J=15.6, 7.2 Hz, 1H), 3.32 (dd, J=7.2, 1.2 Hz, 2H), 2.48 (t, J=7.2 Hz, 2H), 1.59 (quin, J=7.2 Hz, 2H), 1.27～1.22 (m, 10H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.2, 137.0, 133.7, 128.7, 127.6, 126.4, 122.3, 47.1, 42.6, 31.9, 29.5, 29.3, 29.3, 23.8, 22.8, 14.2.

(*E*)-1,6-Diphenylhex-5-en-3-one (**4c**):[28] Pale yellow solid (47,1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.34 (m, 2H), 7.32～7.28 (m, 3H), 7.26～7.22 (m, 2H), 7.21～7.18 (m, 3H), 6.44 (d, J=15.6 Hz, 1H), 6.28 (dt, J=15.6, 7.2 Hz, 1H), 3.30 (dd, J=7.2, 1.2 Hz, 2H), 2.94～2.90 (m, 2H), 2.85～2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.9, 141.0, 136.9, 133.9, 128.7, 128.6, 128.5, 127.7, 126.4, 126.3, 121.9, 47.3, 44.1, 29.8.

(*E*)-1-Phenylocta-1,7-dien-4-one (**4d**):[13] Pale yellow oil (49.6 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.22 (m, 1H), 6.48 (d, J=15.6 Hz, 1H), 6.31 (dt, J=15.6, 7.2 Hz, 1H), 5.87～5.77 (m, 1H), 5.08～4.98 (m, 2H), 3.33 (dd, J=6.8, 1.2 Hz, 2H), 2.60 (t, J=7.2 Hz, 2H), 2.38～2.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.0, 137.1, 137.0, 133.9, 128.7, 127.7, 126.4, 122.1, 115.5, 47.1, 41.6, 27.8.

(*E*)-9-Fluoro-1-phenylnon-1-en-4-one (**4e**):[13] Pale yellow solid (36.8 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.21 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.31 (dt, J=16.0, 7.2 Hz, 1H), 4.49 (t, J=6.0 Hz, 1H), 4.37 (t, J=6.0 Hz, 1H), 3.32 (dd, J=7.2, 1.2 Hz, 2H), 2.52 (t, J=7.2 Hz, 2H), 1.77～1.70 (m, 2H), 1.68～1.61 (m, 2H), 1.45～1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.7, 137.0, 133.9, 128.7, 127.7, 126.4, 122.2, 84.0 (d, J=163.4 Hz), 47.1, 42.3, 30.3 (d, J=19.4 Hz), 24.9 (d, J=5.2 Hz), 23.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −218.4 (tt, J=46.9, 25.6 Hz, 1F).

(*E*)-10-Chloro-1-phenyldec-1-en-4-one (**4f**)[13]: Colorless oil (47.8 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.20 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.31 (dt, J=16.0, 7.2 Hz, 1H), 3.52 (t, J=6.8 Hz, 2H), 3.31 (dt, J=7.2, 1.2 Hz, 2H), 1.80～1.73 (m, 2H), 1.65～1.57 (m, 2H), 1.48～1.40 (m, 2H), 1.35～1.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.7, 136.8, 134.1, 128.7, 127.8, 126.4, 121.8, 119.6, 47.1, 41.2, 24.9, 22.7, 17.3.

(*E*)-6-*oxo*-9-Phenylnon-8-enenitrile (**4g**):[13] Colorless oil (54.2 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.26～7.22 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.29 (dt, J=15.6, 7.2 Hz, 1H), 3.32 (dd, J=7.2, 0.8 Hz, 2H), 2.56 (t, J=7.2 Hz, 2H), 2.35 (t, J=7.2 Hz, 2H), 1.78～1.73 (m, 2H), 1.68～1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.7, 136.8, 134.1, 128.7, 127.8, 126.4, 121.8, 119.6, 47.1, 41.2, 24.9, 22.7, 17.3.

Ethyl (*E*)-5-*oxo*-8-phenyloct-7-enoate (**4h**):[11] Pale yellow oil (62.4 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.35 (m, 2H), 7.32～7.28 (m, 2H), 7.24～7.20 (m, 1H), 6.46 (d, J=16.0 Hz, 1H), 6.29 (dt, J=16.0, 6.8 Hz, 1H), 4.11 (q, J=7.2 Hz, 2H), 3.31 (dd, J=7.2, 1.2 Hz, 2H), 2.57 (t, J=7.2 Hz, 2H), 2.33 (t, J=7.2 Hz, 2H), 1.91 (quin, J=7.2 Hz, 2H), 1.23 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.1, 173.3, 136.9, 133.9, 128.6,

127.7, 126.3, 122.0, 60.5, 47.1, 41.3, 33.3, 18.9, 14.3.

(*E*)-7-*oxo*-10-Phenyldec-9-en-1-yl pivalate (**4i**):[13] Pale yellow oil (63.5 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.35 (m, 2H), 7.31～7.28 (m, 2H), 7.24～7.19 (m, 1H), 6.46 (d, J=16.0 Hz, 1H), 6.30 (dt, J=16.0, 7.2 Hz, 1H), 4.03 (t, J=6.8 Hz, 2H), 3.30 (dd, J=7.2, 1.2 Hz, 2H), 2.48 (t, J=7.2 Hz, 2H), 1.63～1.57 (m, 4H), 1.36～1.31 (m, 4H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.9, 178.7, 137.7, 133.7, 128.6, 127.6, 126.3, 122.2, 64.3, 47.1, 42.4, 38.8, 28.8, 28.5, 27.3, 25.8, 23.6.

(*E*)-15-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpentadec-1-en-4-one (**4j**):[13] Pale yellow oil (64 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.36 (m, 2H), 7.32～7.29 (m, 2H), 7.25～7.20 (m, 1H), 6.47 (d, J=15.6 Hz, 1H), 6.31 (dt, J=15.6, 7.2 Hz, 1H), 3.60 (t, J=6.8 Hz, 2H), 3.31 (dd, J=7.2, 1.2 Hz, 2H), 2.48 (t, J=7.2 Hz, 2H), 1.61～1.56 (m, 2H), 1.52～1.47 (m, 2H), 1.26 (s, 14H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.0, 137.0, 133.7, 128.7, 127.6, 126.4, 122.3, 63.5, 47.1, 42.6, 33.0, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 26.1, 25.9, 23.9, 18.5, －5.1.

(*E*)-6-Methyl-1-phenylhept-1-en-4-one (**4k**):[27] Pale yellow oil (42.8 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.21 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.31 (dt, J=16.0, 6.8 Hz, 1H), 3.30 (dd, J=7.2, 1.2 Hz, 2H), 2.37 (d, J=6.8 Hz, 2H), 2.22～2.12 (m, 1H), 0.93 (d, J=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.7, 137.0, 133.7, 128.7, 127.6, 126.4, 122.2, 51.6, 47.6, 24.6, 22.7.

(*E*)-1-Cyclopentyl-4-phenylbut-3-en-1-one (**4l**):[13] Pale yellow oil (44.2 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.36 (m, 2H), 7.33～7.29 (m, 2H), 7.25～7.20 (m, 1H), 6.47 (d, J=16.0 Hz, 1H), 6.34 (dt, J=16.0, 6.8 Hz, 1H), 3.38 (dd, J=7.2, 1.2 Hz, 2H), 2.98 (quin, J=8.0 Hz, 1H), 1.88～1.74 (m, 4H), 1.69～1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 211.2, 137.1, 133.4, 128.7, 127.6, 126.3, 122.6, 51.2, 46.1, 29.0, 26.2.

(*E*)-1-(*o*-Tolyl)oct-1-en-4-one (**4m**): Colorless oil (36.3 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46～7.43 (m, 1H), 7.18～7.13 (m, 3H), 6.68 (d, J=15.6 Hz, 1H), 6.19 (dt, J=15.6, 7.2 Hz, 1H), 3.34 (dd, J=7.2, 1.2 Hz, 2H), 2.51 (t, J=7.2 Hz, 2H), 2.34 (s, 3H), 1.59 (quin, J=7.6 H_Z, 2H), 1.33 (sext, J=7.2 Hz, 2H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.3, 136.2, 135.3, 131.6, 130.3, 127.6, 126.2, 125.8, 123.6, 47.4, 42.3, 25.9, 22.4, 19.9, 14.0. HRMS (EI) calcd for $C_{15}H_{20}O$: 216.1514; found 216.1509.

(*E*)-1-(*p*-Tolyl)oct-1-en-4-one (**4n**): Yellow oil (45.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) found: 7.18 (d, J=8.0 Hz, 2H), 7.03 (d, J=8.0 Hz, 2H), 6.35 (d, J=16.0 Hz, 1H), 6.17 (dt, J=16.0, 6.8 Hz, 1H), 3.21 (dd, J=7.2, 0.8 Hz, 2H), 2.40 (t, J=7.2 Hz, 2H), 2.25 (s, 3H), 1.49 (quin, J=7.6 H_Z, 2H), 1.24 (sext, J=7.6 Hz, 2H), 0.83 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) found 209.3, 137.4, 134.3, 133.6, 129.3, 126.2, 121.2, 47.1, 42.2, 25.9, 22.4, 21.3, 14.0; HRMS (ESI) calcd for $C_{15}H_{20}NaO$ $[M+Na]^+$: 239.1412; found 239.1402.

(*E*)-1-(Naphthalen-2-yl)oct-1-en-4-one (**4o**):[13] Pale yellow solid (45.3 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81～7.78 (m, 3H), 7.71 (s, 1H), 7.61 (dd, J=8.8, 1.6 Hz, 1H), 7.49～7.42 (m, 2H), 6.63 (d, J=16.0 Hz, 1H), 6.45 (dt, J=16.0, 7.2 Hz, 1H), 3.37 (dd, J=7.2, 1.2 Hz, 2H), 2.52 (t, J=7.6 Hz, 2H), 1.61 (quin, J=7.2 H_Z, 2H), 1.43 (sext, J=7.2 Hz, 2H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.1, 134.6, 133.8, 133.7, 133.1, 128.3, 128.1, 127.8, 126.4, 126.2, 125.9, 123.6, 122.7, 47.1, 42.4, 25.9, 22.4, 14.0.

(1*E*,3*E*)-1-Phenylnona-1,3-dien-5-one (**4p**): Pale yellow oil (34.0 mg, 53%). The ratio of *E*/*Z* was detected to be 3/1 based on the ^{1}H NMR spectrum. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44～7.36 (m, 2H), 7.35～7.29 (m, 2H), 7.24～7.20 (m, 1H), 6.78 (dd, J=15.6, 10.4 Hz, 1H), 6.50 (d, J=15.6 Hz, 1H), 6.31～6.25 (m, 1H), 5.90 (dt, J=15.2, 7.2 Hz, 1H), 3.25 (d, J=7.6 Hz, 2H), 2.46 (t, J=7.2 Hz, 2H), 1.57 (quin, J=7.2 H_Z, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.0, 137.3, 134.3, 132.0, 128.7, 128.6, 127.6, 126.4, 126.3, 46.9, 42.3, 25.9, 22.4, 14.0. HRMS (EI): calcd for $C_{16}H_{20}O$: 228.1514; found 228.1509.

(*E*)-6,6-Dimethyl-1-phenylhept-4-en-2-one (**4q**): Pale yellow oil (61.1 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.31 (m, 2H), 7.28～7.26 (m, 1H), 7.21～7.19 (m, 2H), 5.54 (dt, J=15.6, 1.2 Hz, 1H), 5.41 (dt, J=15.6, 6.4 Hz, 1H), 3.71 (s, 2H), 3.13 (dd, J=6.8, 1.2 Hz, 2H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.1, 146.4, 134.3, 129.6, 128.8, 127.1, 116.7, 49.4, 46.2, 33.3, 29.6; HRMS (ESI) calcd for $C_{15}H_{20}NaO$ $[M+Na]^+$: 239.1412; found 239.1410.

(*E*)-1-(Pyridin-3-yl)oct-1-en-4-one (**4r**): Pale yellow oil (32.4 mg, 54%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (d, J=1.6 Hz, 1H), 8.46 (dd, J=4.8, 1.2 Hz, 1H), 7.73 (dt, J=8.0, 2.0 Hz, 1H), 7.26 (dd, J=7.2, 4.8 Hz, 1H), 6.47～6.37 (m, 2H), 3.36 (d, J=5.6 Hz, 2H), 2.49 (t, J=7.2 Hz, 2H), 1.58 (quin, J=7.6 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.5, 148.1, 147.8, 133.3, 132.9, 129.8, 125.3, 123.8, 46.8, 42.6, 25.9, 22.4, 14.0; HRMS (ESI) calcd for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1388; found 204.1390.

(*E*)-1-(Thiophen-3-yl)oct-1-en-4-one (**4s**)[13]: Colorless oil (37.4 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27～7.25 (m, 1H), 7.21 (dd, J=5.2, 1.4 Hz, 1H), 7.12 (dd, J=3.2, 0.8 Hz, 1H), 6.48 (d, J=16.0 Hz, 1H), 6.15 (dt, J=16.0, 7.2 Hz, 1H), 3.28 (dd, J=7.2, 1.2 Hz, 2H), 2.48 (t, J=7.2 Hz, 2H), 1.57 (quin, J=7.6 Hz, 2H), 1.32 (sext, J=7.6 Hz, 2H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.3, 139.7, 127.9, 126.1, 125.0, 122.1, 121.9, 46.9, 42.3, 25.9, 22.4, 14.0.

(*E*)-2-Phenylnon-2-en-5-one (**4t**): Pale yellow oil (43.6 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33～7.30 (m, 2H), 7.26～7.22 (m, 2H), 7.18～7.14 (m, 1H), 5.89 (tq, J=7.2, 1.2 Hz, 1H), 3.24 (d, J=7.2 Hz, 2H), 2.40 (t, J=7.2 Hz, 2H), 1.97 (d, J=1.2 Hz, 3H), 1.51 (quin, J=7.6 Hz, 2H), 1.25 (sext, J=7.6 Hz, 2H), 0.83 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 209.0, 143.3, 138.3,

128.3, 127.2, 125.9, 119.5, 43.2, 42.4, 26.0, 22.5, 16.4, 14.0. HRMS (EI): calcd for $C_{15}H_{20}O$: 216.1514; found 216.1506.

Supporting Information NMR spectra of products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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