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借助有机催化去共轭-羟醛缩合反应来获得 α-乙烯基-β-炔基取代的烯醛

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摘要 发展了一种从 α,β-不饱和醛和炔醛出发来获取 α-乙烯基-β-炔基取代的烯醛的新绿色合成路线. 该方法体现出较为广泛的底物适用范围, 且反应条件温和. 此外, 还对反应过程中共轭-羟醛缩合的催化过程进行了详细讨论.
关键词 α-乙烯基-β-炔基取代的烯醛; 共轭-羟醛缩合; 有机催化; 烯胺

Access to α-Vinyl β-Alkynyl Enals via an Organocatalytic Deconjugation-Aldol Condensation Sequence

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Abstract A new green synthetic route to α-vinyl β-alkynyl enals from α,β-unsaturated aldehydes and ynals is developed. This protocol allows a broad substrate scope and mild conditions. Furthermore, a proposed mechanism of a deconjugation-aldol condensation process is discussed in detail.
Keywords α-vinyl β-alkynyl enal; deconjugation-aldol condensation; organocatalysis; enamine

1 Introduction

α-Vinyl enal, as a kind of unsaturated aldehydes, has been found in natural products and utilized to construct many other useful molecules.[1] For example, onchidal is a substrate for acetylcholinesterase and has been identified as the main component of the defensive secretions of the mollusk *Onchidella binneyi*, responsible for the chemical protection of onchidella.[2]

Moreover, various multi-substituted enals have been found as flavors or fragrance molecules.[3] Therefore, the main interest in the synthesis of these compounds and other studies rely heavily on the fact that many unsaturated aldehydes, as potential Michael receptors, exhibit relatively large toxicity.[3] The palladium catalyzed Suzuki coupling of α-bromo enals with boronic acids has been successfully applied to assembly these α-vinyl enals directly (Scheme 1, a).[4] However, α-bromo enal, which is a key precursor, needs to be prepared in advance. Therefore, there is still a high demand for the development of other efficient but greener catalytic systems for the rapid preparation of α-vinyl enal derivatives.

Organocatalysis has become a powerful tool in organic synthesis.[5] Aminocatalysis,[6-11] as one of the most efficient organocatalytic strategies, has attracted much attention. Under aminocatalysis, substrates are normally motivated via the highest occupied molecular orbital (HOMO)-,[6-9] lowest unoccupied molecular orbital (LUMO)-,[10] or singly occupied molecular orbital (SOMO)-activation.[11] In particular, the HOMO activation of α,β-unsaturated aldehydes via dienamine catalysis has made significant progresses in this field, contributed by Jørgensen, Chen, Melchiorre, Uria, Liao, and others.[12]

It should be noted that our group[13] successfully developed the first dienamine-mediated enantioselective 1,3-dipolar [3+2] cycloaddition of α,β-unsaturated aldehyde with C,N-cyclic azomethine imines. Moreover, our group[14] also developed the dienamine catalyzed 1,3-dipolar cycloaddition reaction of azides and α,β-unsaturated aldehydes. Building upon the significance of ynal in organo-

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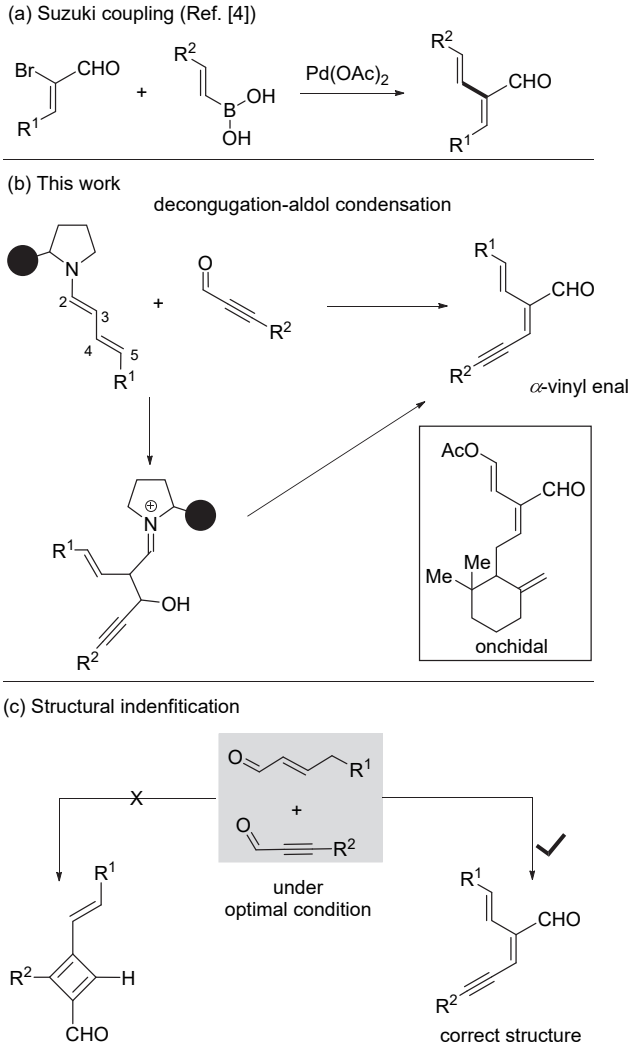
catalytic reactions,[15] we envisioned that a reaction between α,β-unsaturated aldehyde and ynal might provide a novel route to construct a diverse set of the α-vinyl enals. As part of our continued interest in this field, we herein reported our new discovery regarding the organocatalytic deconjugation-aldol condensation reaction of ynals and α,β-unsaturated aldehydes, to efficiently assemble various α-vinyl enals (Scheme 1, b). Notably, the groups of Hudlicky[16] and Sarotti[17] respectively provided conclusive evidences [*e.g.* X-ray crystal structure and extensive density functional theory (DFT) calculations of NMR shifts] to assist in identifying the absolute and geometry structure of our product (Scheme 1, c).

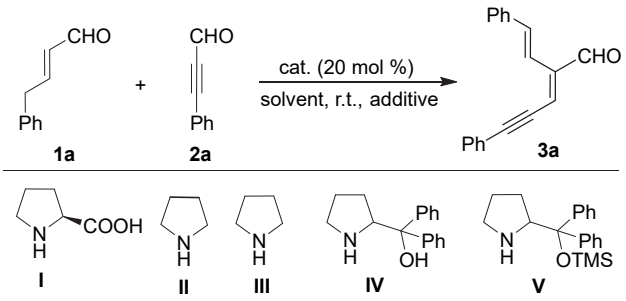


Scheme 1 Strategies for the synthesis of α-vinyl enals

2 Results and discussion

Our preliminary study with the model reaction of α,β-unsaturated aldehyde **1a** and phenylpropargyl aldehyde **2a** in the presence of *L*-proline as catalyst and K_2CO_3 as base was initiated. However, almost no desired product was obtained (Table 1, Entry 1). With the initial experimental results in hand, then our attention to other catalysts was turned. The assessment of other catalysts indicated that catalyst **V** showed the highest conversion and gave the desired product **3a** in 65% yield (Table 1, Entry 5). Further investigations revealed that the additive played a key role in this transformation. If the reaction was conducted in the absence of K_2CO_3, the yield would decrease to 13% remarkably (Table 1, Entry 6). Other bases afforded **3a** in only moderate yields (Table 1, Entries 7～11). Notably, only 14% yield was observed if acetic acid was utilized as the additive (Table 1, Entry 12). After identifying base K_2CO_3 as the best additive, then the role of solvent in this process was investigated. The experimental results showed that toluene was the best medium in stabilizing and promoting the efficiency of the reaction (Table 1, Entry 15). To further optimize the reaction conditions, the reaction temperature was changed and 78% yield was obtained when the reaction was conducted at 50 ℃ for 48 h (Table 1, Entry 17).

Table 1 Optimization of the reaction conditions[a]



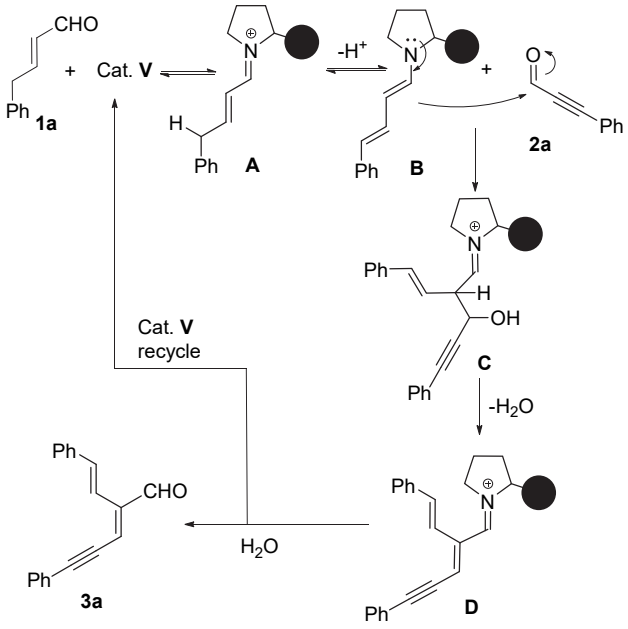
Entry	Cat.	Solvent	Base	Yield[b]/%
1	**I**	CH_2Cl_2	K_2CO_3	<5
2	**II**	CH_2Cl_2	K_2CO_3	55
3	**III**	CH_2Cl_2	K_2CO_3	58
4	**IV**	CH_2Cl_2	K_2CO_3	16
5	**V**	CH_2Cl_2	K_2CO_3	65
6	**V**	CH_2Cl_2	—	13
7	**V**	CH_2Cl_2	Cs_2CO_3	63
8	**V**	CH_2Cl_2	Na_2CO_3	37
9	**V**	CH_2Cl_2	NaOAc	32
10	**V**	CH_2Cl_2	Et_3N	56
11	**V**	CH_2Cl_2	DBU	54
12	**V**	CH_2Cl_2	AcOH	14
13	**V**	$CHCl_3$	K_2CO_3	73
14	**V**	THF	K_2CO_3	52
15	**V**	Toluene	K_2CO_3	87
16	**V**	DMSO	K_2CO_3	<5
17[c]	**V**	Toluene	K_2CO_3	78

[a] Reaction conditions: a mixture of **1a** (0.15 mmol), **2a** (0.10 mmol), catalyst (20 mol%) and additive (20 mol%) in solvent (0.3 mL) was stirred at room temperature for 72 h. [b] Isolated yield. [c] The reaction was conducted at 50 ℃ for 48 h.

With the optimized reaction conditions in hand, the scope of α,β-unsaturated aldehydes **1** was next examined. As indicated in Table 2, various substrates **1** bearing either electron-withdrawing or electron-donating groups in different positions of the phenyl ring were all tolerated to give

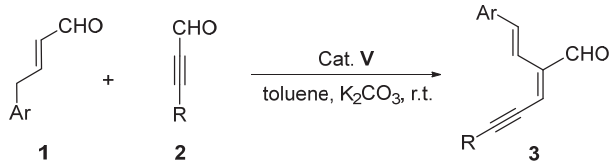
the corresponding products **3b**～**3e** in high to excellent yields (83%～92%). Moreover, the *α*,*β*-unsaturated aldehydes, which contained a naphthyl or thiophenyl ring, also participated in this process smoothly and yielded the corresponding products **3f** and **3g** (89% and 87%, respectively). The generality of ynals **2** was also evaluated. To our delight, no matter whether the substitution patterns of ynals have electron-donating or electron-withdrawing groups on the aromatic ring, the corresponding products **3h**～**3n** could be obtained in good to excellent yields (82%～93%). Ynals, having an alkyl or heterocyclic ring, also efficiently yielded their corresponding *α*-vinyl enals **3o**～**3k** (83%～90%). A dimethyl(phenyl)silyl group contained substrate was also compatible with the standard reaction conditions and afforded the desired *α*-vinyl enal **3r** in 78% yield.

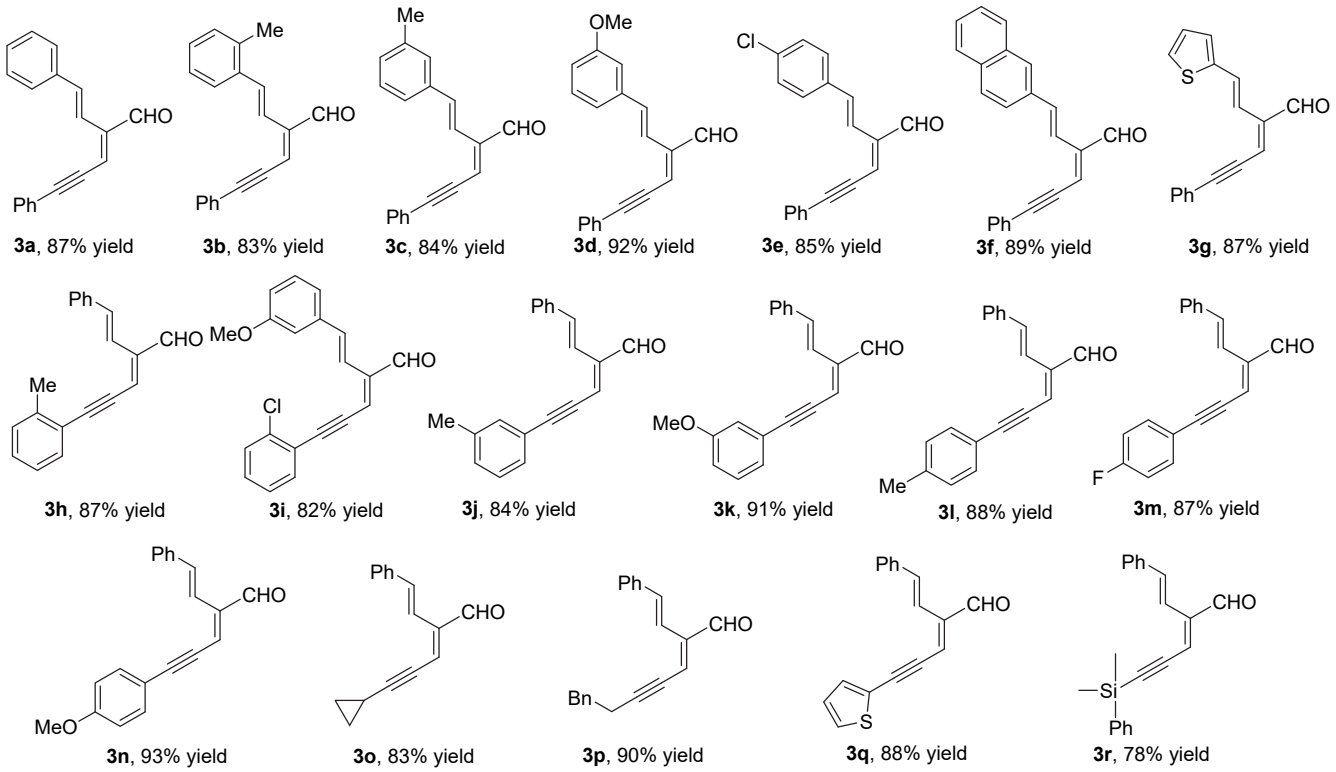
Our postulated reaction pathway is summarized in Scheme 2. First, the condensation of *α*,*β*-unsaturated aldehyde **1a** and catalyst **V** generates iminium ion **A**, which then converts to the dienamine intermediate **B** via a proton transfer.[12] Subsequently, the aldol reaction of intermediate **B** with **2a** leads to the formation of key intermediate **C**, followed by a dehydration to generate intermediate **D**.



Scheme 2 Plausible mechanism

Table 2 Substrate scope[a]





[a] Reaction conditions: a mixture of **1** (0.15 mmol), **2** (0.10 mmol), catalyst **V** (20 mol%) and K_2CO_3 (20 mol%) in toluene (0.3 mL) was stirred at room temperature for 72 h.

Finally, the hydrolysis of intermediate **D** delivers final prouct **3a** and releases catalyst **V**. Based on the proposed mechanism, we can explain why *L*-proline (cat. **I**) just provides sluggish yield (Table 1, Entry 1). Under basic condition, the carboxyl group of the catalyst **I** will lose their acidic function, which will detract from the dehydration step of the reaction. Meanwhile, the solubility of the catalyst will be greatly reduced, which will eventually lead to slow progress of the reaction.

3 Conclusions

In summary, an organocatalytic deconjugation-aldol condensation reaction between *α*,*β*-unsaturated aldehydes and ynals has been developed. The reaction was catalyzed by a secondary amine and generated *α*-vinyl *β*-alkynyl enals in high to excellent yields. It is noteworthy that this chemistry includes a unique deconjugation-aldol condensation sequence. We believe that this work will draw more research interests in green synthesis of other biologically active compounds. Further extensions of this chemistry are underway in our laboratory and more results will be reported in due course.

4 Experimental section

4.1 General information

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported with tetramethylsilane as internal standard and are referenced to residual protium in the NMR solvent ($CDCl_3$: *δ* 7.26). Chemical shifts for carbon are reported referenced to the carbon resonances of the solvent ($CDCl_3$: *δ* 77.16). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on a Merck 60 (0.040～0.063 mm) mesh silica gel. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Alkyne aldehydes were prepared following the literature procedures.

4.2 General procedure for the synthesis of *α*-vinyl *β*-alkynyl enals **3**

To a solution of toluene (0.3 mL) were added *α*,*β*-unsaturated aldehydes **1** (0.15 mmol), alkyne aldehydes **2** (0.10 mmol), catalyst (0.02 mmol) and K_2CO_3 (0.02 mmol). The reaction mixture was stirred at room temperature for 72 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography (hexane/ethyl acetate, *V*∶*V*=30∶1～20∶1) to yield the desired product *α*-vinyl *β*-alkynyl enals **3**.

(*E*)-2-Phenyl-3-styrylcyclobuta-1,3-dienecarbaldehyde (**3a**): Yellow oil, 22.4 mg, 87% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.66 (s, 1H), 8.01～7.92 (m, 2H), 7.61～7.55 (m, 3H), 7.43～7.42 (m, 1H), 7.40～7.37 (m, 1H), 7.33～7.30 (m, 1H), 7.25～7.24 (m, 2H), 7.16～7.15 (m, 2H), 6.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.3, 143.3, 137.2, 136.4, 131.9, 129.8, 128.8, 128.7, 127.2, 127.0, 122.3, 119.5, 109.6, 86.9; HRMS (EI) calcd for $C_{19}H_{14}O$ 258.1045, found 258.1039.

(*E*)-5-Phenyl-2-((*E*)-styryl)pent-2-en-4-ynal (**3b**): Yellow oil, 22.6 mg, 83% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.69 (s, 1H), 8.27 (d, *J*=16.5 Hz, 1H), 7.67～7.65 (m, 1H), 7.57～7.56 (m, 2H), 7.43～7.42 (m, 3H), 7.26～7.21 (m, 3H), 7.19～7.16 (m, 1H), 6.56 (s, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.3, 143.5, 136.8, 136.3, 134.2, 131.9, 130.5, 129.7, 128.6, 128.5, 127.1, 126.2, 125.3, 122.2, 120.5, 109.5, 86.9, 19.9; HRMS (EI) calcd for $C_{20}H_{16}O$ 272.1201, found 272.1195.

(*E*)-2-((*E*)-3-Methylstyryl)-5-phenylpent-2-en-4-ynal (**3c**): Yellow oil, 22.8 mg, 84% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.67 (s, 1H), 7.99 (d, *J*=16.5 Hz, 1H), 7.60～7.59 (m, 2H), 7.45～7.42 (m, 3H), 7.39～7.38 (m, 2H), 7.31～7.29 (m, 1H), 7.28～7.24 (m, 1H), 7.16～7.15 (m, 1H), 6.53 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.3, 143.4, 138.3, 137.1, 136.5, 131.9, 129.8, 129.6, 128.7, 128.6, 127.8, 126.9, 124.1, 122.3, 119.3, 109.5, 87.0, 21.4; HRMS (EI) calcd for $C_{20}H_{16}O$ 272.1201, found 272.1196.

(*E*)-2-((*E*)-3-Methoxystyryl)-5-phenylpent-2-en-4-ynal (**3d**): Yellow oil, 26.5 mg, 92% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.68 (s, 1H), 7.99 (d, *J*=16.5 Hz, 1H), 7.60～7.58 (m, 2H), 7.45～7.43 (m, 3H), 7.34～7.30 (m, 1H), 7.28～7.24 (m, 1H), 7.19～7.18 (m, 1H), 7.11 (s, 1H), 6.91～6.89 (m, 1H), 6.55 (s, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.3, 159.9, 143.2, 138.6, 136.2, 131.9, 129.8, 129.7, 128.7, 127.4, 122.3, 119.7, 119.6, 114.6, 112.1, 109.7, 86.9, 55.2; HRMS (EI) calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1142.

(*E*)-2-((*E*)-4-Chlorostyryl)-5-phenylpent-2-en-4-ynal (**3e**): Yellow oil, 24.8 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.67 (s, 1H), 7.97 (d, *J*=16.5 Hz, 1H), 7.59～7.57 (m, 2H), 7.50～7.49 (m, 2H), 7.46～7.42 (m, 2H), 7.38～7.36 (m, 2H), 7.24～7.21 (m, 2H), 6.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.2, 143.0, 135.7, 135.0, 134.4, 131.9, 129.9, 129.0, 128.7, 128.1, 127.8, 122.2, 120.0, 109.9, 86.7; HRMS (EI) calcd for $C_{19}H_{13}OCl$ 292.0655, found 292.0652.

(*E*)-2-((*E*)-2-(Naphthalen-2-yl)vinyl)-5-phenylpent-2-en-4-ynal (**3f**): Yellow oil, 27.4 mg, 89% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.71 (s, 1H), 8.20 (d, *J*=16.5 Hz, 1H), 7.94 (s, 1H), 7.88～7.84 (m, 3H), 7.80～7.78 (m, 1H), 7.64～7.62 (m, 2H), 7.51～7.46 (m, 5H), 7.41～7.38 (m, 1H), 6.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ*: 193.3, 143.3, 136.4, 134.6, 133.6, 131.9, 129.8, 128.7, 128.5, 128.3, 128.1, 127.7, 126.4, 123.2, 122.3, 119.8, 109.7, 87.0; HRMS (EI) calcd for $C_{23}H_{16}O$ 308.1201, found 308.1203.

(*E*)-5-Phenyl-2-((*E*)-2-(thiophen-2-yl)vinyl)pent-2-en-4-ynal (**3g**): Yellow oil, 23.0 mg, 87% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) *δ*: 9.64 (s, 1H), 8.16 (d, *J*=16.5 Hz, 1H), 7.61～7.60 (m, 2H), 7.45～7.44 (m, 3H), 7.32～7.30

(m, 1H), 7.19～7.18 (m, 1H), 7.13～7.10 (m, 1H), 7.07～7.05 (m, 1H), 6.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.2, 143.1, 143.0, 131.9, 129.8, 129.4, 128.7, 128.2, 127.9, 127.0, 126.1, 122.3, 119.1, 110.0, 86.9; HRMS (EI) calcd for $C_{17}H_{12}OS$ 264.0609, found 264.0603.

(*E*)-2-((*E*)-Styryl)-5-(*o*-tolyl)pent-2-en-4-ynal (**3h**): Yellow oil, 23.7 mg, 87% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.70 (s, 1H), 8.02 (d, J=16.5 Hz, 1H), 7.57～7.56 (m, 3H), 7.41～7.38 (m, 2H), 7.35～7.29 (m, 3H), 7.27～7.24 (m, 2H), 6.60 (s, 1H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.2, 143.0, 140.7, 137.2, 136.2, 132.5, 129.9, 129.8, 128.7, 128.6, 127.7, 127.1, 125.9, 122.2, 119.7, 108.8, 90.6, 20.9; HRMS (EI) calcd for $C_{20}H_{16}O$ 272.1201, found 272.1196.

(*E*)-5-(2-Chlorophenyl)-2-((*E*)-3-methoxystyryl)pent-2-en-4-ynal (**3i**): Yellow oil, 26.4 mg, 82% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.69 (s, 1H), 8.00～7.97 (m, 1H), 7.60～7.58 (m, 1H), 7.49～7.48 (m, 1H), 7.37～7.27 (m, 4H), 7.17～7.16 (m, 1H), 7.09 (s, 1H), 6.88～6.86 (m, 1H), 6.54 (s, 1H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.2, 159.9, 143.9, 138.6, 136.7, 136.4, 133.7, 130.7, 129.7, 129.6, 126.8, 126.6, 120.1, 119.9, 114.9, 111.9, 91.4, 55.3; HRMS (EI) calcd for $C_{20}H_{15}O_2Cl$ 322.0761, found 322.0756.

(*E*)-2-((*E*)-Styryl)-5-(*m*-tolyl)pent-2-en-4-ynal (**3j**): Yellow oil, 22.8 mg, 84% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.67 (s, 1H), 8.02 (d, J=16.5 Hz, 1H), 7.59～7.58 (m, 2H), 7.41～7.39 (m, 4H), 7.34～7.31 (m, 2H), 7.28～7.26 (m, 2H), 6.54 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.3, 143.2, 138.5, 137.2, 136.2, 132.4, 130.7, 129.0, 128.7, 128.6, 128.5, 127.3, 127.0, 122.1, 119.5, 110.0, 86.6, 21.2; HRMS (EI) calcd for $C_{20}H_{16}O$ 272.1201, found 272.1194.

(*E*)-5-(3-Methoxyphenyl)-2-((*E*)-styryl)pent-2-en-4-ynal (**3k**): Yellow oil, 26.2 mg, 91% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.68 (s, 1H), 8.02 (d, J=16.5 Hz, 1H), 7.59～7.57 (m, 2H), 7.41～7.38 (m, 2H), 7.35～7.33 (m, 2H), 7.28～7.25 (m, 1H), 7.20～7.19 (m, 1H), 7.10 (s, 1H), 7.02～7.00 (m, 1H), 6.53 (s, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.3, 159.5, 143.4, 137.2, 136.4, 129.7, 128.8, 128.7, 127.0, 124.4, 123.2, 119.5, 116.6, 116.4, 109.5, 86.7, 55.3; HRMS (EI) calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1144.

(*E*)-2-((*E*)-Styryl)-5-(*p*-tolyl)pent-2-en-4-ynal (**3l**): Yellow oil, 23.9 mg, 88% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.67 (s, 1H), 8.02 (d, J=16.5 Hz, 1H), 7.59～7.57 (m, 2H), 7.50～7.48 (m, 2H), 7.42～7.39 (m, 2H), 7.35～7.32 (m, 1H), 7.29～7.28 (m, 1H), 7.26～7.24 (m, 2H), 6.54 (s, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.3, 142.9, 140.4, 137.3, 136.1, 131.8, 129.5, 128.7, 128.6, 127.5, 127.0, 119.5, 119.3, 110.3, 86.6, 21.7; HRMS (EI) calcd for $C_{20}H_{16}O$ 272.1201, found 272.1193.

(*E*)-5-(4-Fluorophenyl)-2-((*E*)-styryl)pent-2-en-4-ynal (**3m**): Yellow oil, 24.0 mg, 87% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.68 (s, 1H), 8.00 (d, J=16.5 Hz, 1H), 7.60～7.56 (m, 4H), 7.43～7.39 (m, 2H), 7.36～7.34 (m, 1H), 7.27～7.22 (m, 1H), 7.16～7.12 (m, 2H), 6.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.2, 163.4 (d, J=252.7 Hz), 143.3, 137.1, 136.4, 134.0 (d, J=8.7 Hz), 128.8, 128.7, 127.0, 126.9, 119.4, 118.4 (d, J=3.6 Hz), 116.2 (d, J=22.3 Hz), 108.4, 86.7; HRMS (EI) calcd for $C_{19}H_{13}OF$ 276.0950, found 276.0948.

(*E*)-5-(4-Methoxyphenyl)-2-((*E*)-styryl)pent-2-en-4-ynal (**3n**): Yellow oil, 26.8 mg, 93% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.64 (s, 1H), 8.03 (d, J=16.5 Hz, 1H), 7.60～7.53 (m, 4H), 7.43～7.39 (m, 2H), 7.35～7.33 (m, 1H), 7.30～7.25 (m, 1H), 6.97～6.94 (m, 2H), 6.53 (s, 1H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.4, 161.0, 142.3, 137.3, 135.8, 133.7, 128.8, 128.6, 127.9, 127.0, 119.6, 114.5, 114.3, 110.8, 86.6, 55.4; HRMS (EI) calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1148.

(*E*)-5-Cyclopropyl-2-((*E*)-styryl)pent-2-en-4-ynal (**3o**): Yellow oil, 18.4 mg, 83% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.56 (s, 1H), 7.91 (d, J=16.5 Hz, 1H), 7.53～7.52 (m, 2H), 7.40～7.37 (m, 2H), 7.32～7.31 (m, 1H), 7.13～7.10 (m, 1H), 6.29 (s, 1H), 1.65～1.61 (m, 1H), 1.09～1.07 (m, 2H), 0.98～0.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.7, 142.8, 137.3, 135.3, 129.2, 128.7, 128.5, 126.9, 119.5, 116.8, 74.2, 10.1, 1.5; HRMS (EI) calcd for $C_{16}H_{14}O$ 222.1045, found 222.1046.

(*E*)-7-Phenyl-2-((*E*)-styryl)hept-2-en-4-ynal (**3p**): Yellow oil, 25.7 mg, 90% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.60 (s, 1H), 7.90 (d, J=16.5 Hz, 1H), 7.48～7.47 (m, 2H), 7.39～7.26 (m, 8H), 7.09～7.06 (m, 1H), 6.31 (s, 1H), 3.02～2.99 (m, 2H), 2.93～2.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.7, 143.3, 140.0, 137.2, 135.8, 129.0, 128.7, 128.6, 128.5, 128.4, 127.1, 126.6, 119.5, 111.6, 79.0, 34.7, 22.6; HRMS (EI) calcd for $C_{21}H_{18}O$ 286.1358, found 286.1347.

(*E*)-2-((*E*)-Styryl)-5-(thiophen-2-yl)pent-2-en-4-ynal (**3q**): Yellow oil, 23.2 mg, 88% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.66 (s, 1H), 8.01 (d, J=16.5 Hz, 1H), 7.69～7.88 (m, 1H), 7.59～7.56 (m, 2H), 7.42～7.39 (m, 3H), 7.35～7.33 (m, 1H), 7.25～7.22 (m, 2H), 6.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.3, 143.0, 137.2, 136.2, 130.1, 129.6, 128.8, 128.7, 127.2, 127.0, 126.2, 121.5, 119.5, 104.9, 86.9; HRMS (EI) calcd for $C_{17}H_{12}OS$ 264.0609, found 264.0605.

(*E*)-5-(Dimethyl(phenyl)silyl)-2-((*E*)-styryl)pent-2-en-4-ynal (**3r**): Yellow oil, 24.6 mg, 78% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.64 (s, 1H), 8.00 (d, J=16.5 Hz, 1H), 7.75～7.73 (m, 2H), 7.48～7.46 (m, 5H), 7.38～7.34 (m, 3H), 7.26～7.21 (m, 1H), 6.34 (s, 1H), 0.61 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 193.4, 144.8, 137.0, 136.8, 135.8, 133.7, 129.9, 128.8, 128.7, 128.2, 127.1, 126.4, 119.3, 114.8, 102.8, 1.2; HRMS (EI) calcd for $C_{21}H_{20}OSi$ 315.1205, found 315.1198.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **3a**～**3r**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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