银催化炔烃与有机高价碘(III)试剂的立体选择性加成反应

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摘要 报道了一种银催化功能化炔烃与有机高价碘(III)试剂的立体选择性加成反应。该反应体系底物适用范围广, 可以中等到优秀的收率得到烯基酯类化合物。分子内的控制实验证实, 有机高价碘试剂分子中的芳基显著促进与其相连的 I—O 键优先断裂, 进而参与后续的立体选择性加成反应。

关键词 银催化; 炔烃; 高价碘(III)试剂; 立体选择性加成

Silver-Catalyzed Stereoselective Addition of Organic Hypervalent Iodine(III) Reagents to Alkynes

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Abstract A silver-catalyzed stereoselective addition reaction of functionalized alkynes with organic hypervalent iodine(III) reagents as nucleophiles is reported, providing an approach to vinyl esters in high yields with excellent group tolerance. Intramolecular experiment demonstrates that the presence of aryl group considerably affects the cleavage of I—O bond within hypervalent iodine(III) reagents, which is also responsible for the high stereoselectivity observed in this catalytic system.

Keywords silver catalysis; alkyne; hypervalent(III) iodine reagent; stereoselective addition

1 Introduction

The functionalization of alkynes represents an extremely powerful tool for the construction of chemical bonds, which has widespread application in organic synthesis.^[1] Alkynes usually are used as feedstock to afford a series of valuable commodity chemicals, such as acetaldehydes, ketones, vinyl esters and some unique compounds that are not easy to obtain by conventional synthetic methods.^[2] Particularly, in the case of functionalized alkynes, a number of vinyl esters can be prepared from the addition reaction of carbon-carbon triple bond, in which the pursuit of good selectivity remains a significant challenge. In recent years, considerable effort has been devoted to explore the versatile additions of alkynes toward achieving high selectivity.^[3] For example, Jiang's group^[4] has realized the difunctionalization of terminal alkynes by silver catalysis,

generating a variety of 1-halo-1-alkenes in good yields and selectivity (Scheme 1a). Hou and coworkers^[5] have established the halogenation of internal alkynes using quaternary ammonium salt as mediators. Then it is found that both phenols and 4-hydroxyl coumarins are effective O-containing nucleophiles, which can enable the stereoselective addition of alkynes (Schemes 1b and 1c).^[6] Very recently, Xu *et al.*^[7] reported an efficient addition of sulfonic acids to haloalkynes, in which the reactivity of sulfonic acids can be tuned by varying the hydrogen bonding cluster (Scheme 1, d). Moreover, it should be noted that the direct addition of carboxyl acid to propiolates also proceeds well under palladium catalysis (Scheme 1, e).^[8] Although the reported strategies have been well developed for the alkyne addition, most of which suffer from poor selectivity or critical reaction conditions. Hence, the de-

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Scheme 1 Stereoselective addition reactions of alkynes with O-containing nucleophiles

development of an efficient and alternative methodology for the alkyne addition with good selectivity is highly desirable.

Organic hypervalent iodine reagents (HIRs) have gained increasing interest as coupling partners, oxidants and both of them in organic synthesis, mainly due to their selective, versatile and environment-benign properties.^[9] Several typical organoiodine(III) reagents have been successfully employed for the construction of organic molecules.^[9-10] Among them, [bis(acyloxy)iodo]arenes (DIB) and [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent), belong to one such reagent that has been frequently explored in organic transformations.^[10] For example, we recently have utilized the organoiodine(III) reagents to realize the selective C(sp³)-H acetoxylation of 2*H*-aziridines^[11c] and radical cyclization of unsaturated oximes,^[11d] respectively. During the course of the investigation, it was found that the cleavage of I—O bond could be facilitated by iron(II/III) salts. We then postulated the possible cleavage model of I—O bond mediated by other transition metals, such as silver salts. In this contribution, we will report an example of silver-catalyzed I—O cleavage within HIRs derived from DIB and the corresponding addition to functionalized alkynes (Scheme 1f).

2 Results and discussion

Based on previous work,^[11] we commenced this study with the reaction of (bromoethynyl)benzene **1a** with hypervalent iodine reagent **2a** to evaluate the feasibility of the process, and the results are summarized in Table 1. Initially, Ag₂O was selected as a catalyst for the catalytic system.^[6b] The model reaction proceeded slightly in CH₃CN at 90 °C for 6 h, and the desired product **3a** was generated in 21% isolated yield (Entry 1). It should be noted that the NOSEY spectra of **3a** further supported the observed stereoselectivity. Other silver salts, such as AgOAc, AgOTf and AgNO₃ were then tried for the addition reaction of **1a**, but failed to give the product **3a** (Entries 2~4). Gratifyingly, it was found that Ag₂CO₃ exhibited high efficiency in this reaction system, affording **3a** in 86% yield (Entry 5). Instead of Ag₂CO₃, the use of some other catalysts including CuO and Cu₂O, Fe(acac)₂, Fe(acac)₃ and Pd(OAc)₂ did not promote this addition process (Entries 6~10). No

Table 1 Optimization of reaction conditions^a

Entry	Catalyst	Solvent	Yield ^b /%
1	Ag ₂ O	CH ₃ CN	21
2	AgOAc	CH ₃ CN	0
3	AgOTf	CH ₃ CN	0
4	AgNO ₃	CH ₃ CN	0
5	Ag ₂ CO ₃	CH ₃ CN	86
6	CuO	CH ₃ CN	0
7	Cu ₂ O	CH ₃ CN	Trace
8	Fe(acac) ₂	CH ₃ CN	0
9	Fe(acac) ₃	CH ₃ CN	0
10	Pd(OAc) ₂	CH ₃ CN	0
11	—	CH ₃ CN	0
12	Ag ₂ CO ₃	EtOH	15
13	Ag ₂ CO ₃	AcOH	22
14	Ag ₂ CO ₃	THF	Trace
15	Ag ₂ CO ₃	DMF	n.r.
16	Ag ₂ CO ₃	DMSO	17
17	Ag ₂ CO ₃	1,4-Dioxane	Trace
18	Ag ₂ CO ₃	PhMe	0
19	Ag ₂ CO ₃	CH ₃ CN	65 ^c
20	Ag ₂ CO ₃	CH ₃ CN	83 ^d
21	Ag ₂ CO ₃	CH ₃ CN	72 ^e
22	Ag ₂ CO ₃	CH ₃ CN	58 ^f
23	Ag ₂ CO ₃	CH ₃ CN	78 ^g
24	Ag ₂ CO ₃	CH ₃ CN	64 ^h

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) and catalyst (2.5 mol%) in CH₃CN (1 mL) at 90 °C under ambient air for 6 h. ^b Isolated yield. ^c Ag₂CO₃ (1 mol%). ^d Ag₂CO₃ (5 mol%). ^e 80 °C. ^f 100 °C. ^g 8 h. ^h 5 h.

product **3a** was isolated in absence of Ag₂CO₃ (Entry 11). Following, it was found that the reaction of **1a** with **2a** was considerably affected by the reaction medium. For instance, using ethanol or acetic acid as a solvent did not remarkably accelerate the addition process, and only 15%

and 22% yields were achieved under the above conditions, respectively (Entries 12 and 13). Moreover, some other polar solvents were also examined in the model reaction, and resulted into inferior yields (Entries 13~17). The reaction did proceed in toluene (Entry 18). Finally, the evaluation of reaction time, temperature and catalyst loading gave the optimal reaction conditions for the addition reaction of **1a** with **2a**. The experiment results indicated that longer reaction time and higher temperature would lead to partial decomposition of **3a** with lower isolated yield (Entries 19~24).

With the optimal conditions in hand, we next investigated the applicability of this method across a series of bromoalkynes, and the result is listed in Table 2. The bromoalkynes bearing aryl group could undergo the reaction with **2a** to deliver the related products in good yields. Notably, the *para*-substituted substrates with an electron-donating group such as Me, ^{*n*}Pr, ^{*n*}Bu, ^{*n*}Pent, MeO and EtO, were well tolerated under the standard conditions (**3b**~**3g**). The incorporation of F and Br into the *para* position did not affect the silver-catalyzed system, generating the desired product in 89% (**3h**) and 86% (**3i**) yields, respectively. We then found that the bromoalkynes with electron-

deficient groups including CN, NO₂ and CF₃ afforded the products in excellent yields (**3j**~**3l**). It was found that 4-(bromoethynyl)-1,1'-biphenyl could react with **2a** to give 76% yield of **3m**. The use of *meta*-substituted bromoalkynes gave the according products in comparable yields, indicating weak steric hindrance exists in this process (**3n** and **3o**). Introducing thienyl group into bromoalkynes still generated the desired products, albeit with moderate yields (**3p**~**3q**). Finally, it was found that 1-bromopent-1-yne still reacted with **2a** to afford the desired product **3r** in 75% isolated yield.

To explore the scope of this method, we next turned our attention to the HIRs, and the result is shown in Table 3. Firstly, a number of PhI(O₂CR)₂ were readily synthesized through a ligand exchange of DIB with carboxylic acids in boiling toluene. Notably, most of the HIRs derived from aryl carboxylic acid reacted with (bromoethynyl)benzene **1a** under optimized conditions to afford the addition products in satisfactory yields (**4a**~**4d**). The scope was also expanded to HIRs derived from alkyl carboxylic acid, and which produced the addition products in lower yields (**4e**~**4f**). This result can be explained by an intramolecular competition experiment of BI-OAc with bromoalkyne **1a**

Table 2 Scope of bromoalkynes^a

^a Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol) and Ag₂CO₃ (2.5 mol%) in CH₃CN (1 mL) at 90 °C under ambient air for 6 h. ^b Isolated yield.

Table 3 Scope of HIRs and alkynes^a

^a Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol) and Ag₂CO₃ (2.5 mol%) in CH₃CN (1 mL) at 90 °C under ambient air for 6 h. ^b Isolated yield. ^c 24 h. ^d 10 h.

under standard reaction conditions, generating **5** as a major product in 76% yield (Scheme 2). It was found that replacing the bromide with Cl or I within alkynes still gave the corresponding products in acceptable yields (**4g** and **4h**).

Scheme 2 Intramolecular competition experiment

Furthermore, methyl 3-phenylpropiolate was employed to react with HIRs under the modified reaction conditions, and which delivered the vinyl esters in excellent yields (**4i**~**4l**). Then, a gram-scale reaction of **1a** with **2a** was performed under standard conditions, which generated **3a** in 72% yield (Scheme 3a). Finally, a transformation of **3i** with 1-phenylethyne by Sonogashira reaction was realized, and produced the product **6** in 70% yield (Scheme 3b).

To reveal the reaction mechanism, several control experiments were subsequently designed and performed under given conditions (Scheme 4). It was found that the reaction of 1-phenylethyne with DIB under air condition did not give the desired product **7**, which demonstrated the critical role of halogens (Scheme 4a).^[12] The addition of a radical quencher, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), into the reaction of **1a** with DIB did not

Scheme 3 Gram-scale reaction and late-stage transformation

completely inhibit the process under air atmosphere, generating **4e** in 32% yield, which indicated a radical pathway was not involved therein (Scheme 4b). The model reaction was carried out in CH₃CN at 90 °C under a N₂ atmosphere for 6 h, and generated **4e** in 59% yield, showing the presence of oxygen did not affect the addition event (Scheme 4c). Further, it was found that the selected reaction almost did not proceed in anhydrous CH₃CN (Scheme 4, d). We then treated this reaction with heavy water, and a 1.86 : 1 ratio of (vinylic) D/H was observed by the ¹H

NMR analysis (Scheme 4e). The above result demonstrates that the vinylic hydrogen comes from H₂O and a protonation step also takes part in this catalytic system.

Scheme 4 Mechanistic studies

Based on the above results and previous report,^[4-7] a possible reaction mechanism for the silver-catalyzed stereoselective addition reaction of functionalized alkynes with DIB is depicted in Scheme 5. Initially, in the presence of H₂O, DIB interacts with silver(I) via a I—O bond cleavage to generate species **A** and cationic iodine intermediate **B**.^[12] Then bromoalkyne **1** is activated by weak coordination with **A** or **B** to afford the complex **C** or **C'**,^[4,6b,13] followed by a nucleophilic attack of OAc[−] on the carbon-carbon triple bond to give intermediate **D**.^[13] Finally, the hydrolysis of **D** releases a hypervalent iodine compound **E** and desired product **3**.

Scheme 5 Possible reaction mechanism

3 Conclusions

In summary, a silver-catalyzed stereoselective addition reactions of functionalized alkynes with hypervalent iodine(III) reagents via I—O bond cleavage has been developed, which provides an efficient access to vinyl esters in high yields. The control experiment supports that the presence of aryl group considerably affects the cleavage model of I—O bond within hypervalent iodine(III) reagents. The further exploration of this strategy using HIRs and transition metal catalysis in synthetic chemistry and mechanistic studies is underway in our laboratory.

4 Experimental section

4.1 General information

All ¹H NMR and ¹³C NMR spectra were recorded on 400, 600 MHz Bruker FT-NMR spectrometers (400 MHz and 100 MHz, 600 MHz and 150 MHz, respectively). All chemical shifts are given with reference to tetramethylsilane (TMS) as an internal standard. High resolution mass spectroscopy data of the products were collected on a Thermo Fisher Scientific LTQ FTICR-MS instrument.

The starting materials, such as (bromoethynyl)benzene and hypervalent iodine(III) reagents, are prepared according to the reported methods, respectively.^[1-2] All chemical reagents used in this work were purchased from commercial suppliers, Huawei Ruiké Chemical company, Energy Chemical company, or Shanghai Chemical Company of China and Aldrich of USA. All solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on silica gels with petroleum ether/ethyl acetate (*V* : *V* = 10 : 1 to 20 : 1) as eluent.

4.2 General procedure for the Ag-catalyzed stereoselective addition reaction

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with alkyne **1** (0.20 mmol), HIRs **2** (0.20 mmol), silver carbonate (2.5 mol%), and freshly distilled CH₃CN (1.0 mL) under air atmosphere. The reaction tube was placed in an oil bath and stirred at 90 °C for 6 h. After the reaction was completed, the mixture was cooled to room temperature, detected by thin-layer chromatography (TLC), and extracted with ethyl acetate (5 mL × 3). The organic layers were combined, dried over anhydrous MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, *V*(petroleum ether) : *V*(ethyl acetate) = 10 : 1 to 20 : 1], affording the desired product **3**.

(*Z*)-2-Bromo-1-phenylvinyl 4-methylbenzoate (**3a**): Yellow liquid, 51.8 mg, 82% yield. ¹H NMR (600 MHz, CDCl₃) δ: 8.13 (d, *J* = 8.0 Hz, 2H), 7.49~7.48 (m, 2H), 7.36~7.32 (m, 5H), 6.66 (s, 1H), 2.47 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 163.17, 150.65, 144.81, 133.41, 130.40, 129.39, 129.34, 128.78, 125.96, 124.92, 96.65, 21.77; HRMS (ESI) calcd for C₁₆H₁₃BrNaO₂ [*M* + Na]⁺ 338.9991, found 338.9991.

(Z)-2-Bromo-1-(*p*-tolyl)vinyl 4-methylbenzoate (**3b**): Pale yellow solid, 52.7 mg, 80% yield. m.p. 46.8~47.4 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (t, *J*=8.4 Hz, 2H), 7.36 (dd, *J*=16.0, 8.0 Hz, 4H), 7.16 (d, *J*=8.0 Hz, 2H), 6.60 (s, 1H), 2.47 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.18, 150.69, 144.72, 139.46, 130.62, 130.37, 129.45, 129.36, 126.02, 124.82, 95.61, 21.75, 21.25; HRMS (ESI) calcd for C₁₇H₁₄BrNaO₂ [M+Na]⁺ 353.0148, found 353.0150.

(Z)-2-Bromo-1-(4-propylphenyl)vinyl 4-methylbenzoate (**3c**): Pale yellow solid, 60.2 mg, 84% yield. m.p. 98.7~100.4 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (d, *J*=8.0 Hz, 2H), 7.38 (d, *J*=8.0 Hz, 2H), 7.32 (d, *J*=8.0 Hz, 2H), 7.15 (d, *J*=8.0 Hz, 2H), 6.61 (s, 1H), 2.59~2.55 (m, 2H), 2.47 (s, 3H), 1.65~1.59 (m, 2H), 0.93 (t, *J*=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.19, 150.71, 144.72, 144.24, 130.82, 130.39, 129.36, 128.86, 126.04, 124.82, 95.66, 37.75, 24.25, 21.75, 13.73; HRMS (ESI) calcd for C₁₉H₁₉BrNaO₂ [M+Na]⁺ 381.0461, found 381.0460.

(Z)-2-Bromo-1-(4-butylphenyl)vinyl 4-methylbenzoate (**3d**): Pale yellow solid, 61.8 mg, 83% yield. m.p. 89.2~91.3 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (d, *J*=8.4 Hz, 2H), 7.39 (d, *J*=8.0 Hz, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 7.16 (d, *J*=8.0 Hz, 2H), 6.61 (s, 1H), 2.59 (t, *J*=7.6 Hz, 2H), 2.46 (s, 3H), 1.58 (t, *J*=8.0 Hz, 2H), 1.34 (dd, *J*=15.2, 7.6 Hz, 2H), 0.92 (t, *J*=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.19, 150.73, 144.72, 144.48, 130.79, 130.39, 129.36, 128.82, 126.06, 124.84, 95.65, 35.37, 33.30, 22.27, 21.76, 13.87; HRMS (ESI) calcd for C₂₀H₂₁BrNaO₂ [M+Na]⁺ 395.0617, found 395.0617.

(Z)-2-Bromo-1-(4-pentylphenyl)vinyl 4-methylbenzoate (**3e**): Pale yellow solid, 65.6 mg, 85% yield. m.p. 101.4~103.2 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.14 (d, *J*=8.0 Hz, 2H), 7.39 (d, *J*=8.0 Hz, 2H), 7.34 (d, *J*=8.0 Hz, 2H), 7.16 (d, *J*=8.0 Hz, 2H), 6.61 (s, 1H), 2.59 (t, *J*=7.6 Hz, 2H), 2.47 (s, 3H), 1.61~1.58 (m, 2H), 1.36~1.30 (m, 4H), 0.90 (t, *J*=6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 163.25, 150.78, 144.77, 144.56, 130.84, 130.45, 129.42, 128.87, 126.12, 124.90, 95.71, 35.71, 31.45, 30.90, 22.53, 21.81, 14.02; HRMS (ESI) calcd for C₂₁H₂₃BrNaO₂ [M+Na]⁺ 409.0774, found 409.0774.

(Z)-2-Bromo-1-(4-methoxyphenyl)vinyl 4-methylbenzoate (**3f**): Pale yellow solid, 57.5 mg, 83% yield. m.p. 101.6~102.6 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (d, *J*=8.0 Hz, 2H), 7.42 (d, *J*=8.0 Hz, 2H), 7.33 (d, *J*=7.6 Hz, 2H), 6.87 (d, *J*=7.6 Hz, 2H), 6.51 (s, 1H), 3.80 (s, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 164.45, 161.73, 151.68, 145.97, 131.63, 130.62, 127.68, 127.34, 115.44, 95.72, 56.56, 23.00; HRMS (ESI) calcd for C₁₇H₁₆BrNaO₃ [M+Na]⁺ 369.0097, found 369.0097.

(Z)-2-Bromo-1-(4-ethoxyphenyl)vinyl 4-methylbenzoate (**3g**): Pale yellow solid, 61.9 mg, 86% yield. m.p. 102.7~103.2 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.13 (d, *J*=8.0 Hz, 2H), 7.40 (d, *J*=8.8 Hz, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 6.85 (d, *J*=8.8 Hz, 2H), 6.51 (s, 1H), 4.02 (dd, *J*=13.0, 8.4 Hz, 2H), 2.46 (s, 3H), 1.40 (t, *J*=6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.19, 159.85, 150.45,

144.70, 130.38, 129.36, 126.39, 126.08, 125.86, 114.67, 94.35, 63.53, 21.76, 14.70; HRMS (ESI) calcd for C₁₈H₁₇BrNaO₃ [M+Na]⁺ 383.0253, found 383.0253.

(Z)-2-Bromo-1-(4-fluorophenyl)vinyl 4-methylbenzoate (**3h**): Pale yellow solid, 59.5 mg, 89% yield. m.p. 76.2~77.5 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.12 (d, *J*=8.0 Hz, 2H), 7.48~7.45 (m, 2H), 7.33 (d, *J*=7.8 Hz, 2H), 7.04 (t, *J*=9.0 Hz, 2H), 6.59 (s, 1H), 2.46 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 163.25 (d, *J*=249.9 Hz), 162.42, 149.81, 144.95, 130.40, 129.75 (d, *J*=3.2 Hz), 129.43, 126.94 (d, *J*=8.1 Hz), 125.80, 115.89 (d, *J*=21.8 Hz), 96.38, 21.77; ¹⁹F NMR (600 MHz, CDCl₃) δ: -111.2; HRMS (ESI) calcd for C₁₆H₁₂BrFNaO₂ [M+Na]⁺ 356.9897, found 356.9899.

(Z)-2-Bromo-1-(4-bromophenyl)vinyl 4-methylbenzoate (**3i**): Pale yellow solid, 67.7 mg, 86% yield. m.p. 83.3~84.8 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.11 (d, *J*=8.0 Hz, 2H), 7.48 (d, *J*=8.8 Hz, 2H), 7.34 (dd, *J*=8.5, 2.5 Hz, 4H), 6.67 (s, 1H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.08, 149.81, 144.99, 132.45, 131.98, 130.40, 129.44, 126.44, 125.73, 123.53, 97.33, 21.77; HRMS (ESI) calcd for C₁₆H₁₂Br₂NaO₂ [M+Na]⁺ 416.9096, found 416.9097.

(Z)-2-Bromo-1-(4-cyanophenyl)vinyl 4-methylbenzoate (**3j**): Pale yellow solid, 61.4 mg, 90% yield. m.p. 156.3~157.7 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.11 (d, *J*=8.0 Hz, 2H), 7.64 (d, *J*=8.4 Hz, 2H), 7.57 (d, *J*=8.4 Hz, 2H), 7.34 (d, *J*=8.0 Hz, 2H), 6.84 (s, 1H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.02, 149.14, 145.30, 137.62, 132.62, 130.44, 129.53, 125.38, 118.24, 112.80, 100.42, 21.78; HRMS (ESI) calcd for C₁₇H₁₂BrNNaO₂ [M+Na]⁺ 363.9944, found 363.9942.

(Z)-2-Bromo-1-(4-nitrophenyl)vinyl 4-methylbenzoate (**3k**): Pale yellow solid, 66.4 mg, 92% yield. m.p. 148.0~149.9 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.21 (d, *J*=8.8 Hz, 2H), 8.12 (d, *J*=8.4 Hz, 2H), 7.64 (d, *J*=9.2 Hz, 2H), 7.35 (d, *J*=8.0 Hz, 2H), 6.91 (s, 1H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 163.00, 148.91, 147.92, 145.35, 139.34, 130.43, 129.54, 125.58, 125.30, 124.12, 101.10, 21.78; HRMS (ESI) calcd for C₁₆H₁₂BrNNaO₄ [M+Na]⁺ 383.9842, found 383.9842.

(Z)-2-Bromo-1-(4-(trifluoromethyl)phenyl)vinyl 4-methylbenzoate (**3l**): Pale yellow solid, 66.8 mg, 87% yield. m.p. 75.3~77.2 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.12 (d, *J*=8.0 Hz, 2H), 7.63~7.57 (m, 4H), 7.35 (d, *J*=8.0 Hz, 2H), 6.79 (s, 1H), 2.47 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 163.11, 149.53, 145.17, 136.83, 131.12 (q, *J*=32.4 Hz), 130.78, 130.44, 129.50, 123.79 (q, *J*=270.4 Hz), 125.85 (q, *J*=3.0 Hz), 125.188, 99.15, 21.79; ¹⁹F NMR (600 MHz, CDCl₃) δ: -62.8; HRMS (ESI) calcd for C₁₇H₁₃BrF₃NaO₂ [M+Na]⁺ 406.9865, found 406.9865.

(Z)-1-([1,1'-Biphenyl]-4-yl)-2-bromovinyl 4-methylbenzoate (**3m**): Pale yellow solid, 59.9 mg, 76% yield. m.p. 123.3~124.6 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.16 (d, *J*=8.4 Hz, 2H), 7.60~7.54 (m, 6H), 7.44 (t, *J*=7.2 Hz, 2H), 7.36 (t, *J*=8.8 Hz, 3H), 6.72 (s, 1H), 2.48 (s,

3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.24, 150.42, 144.86, 142.16, 140.18, 132.26, 130.44, 129.43, 128.84, 127.68, 127.49, 127.00, 125.96, 125.31, 96.62, 21.78; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{17}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 415.0304, found 415.0306.

(Z)-2-Bromo-1-(*m*-tolyl)vinyl 4-methylbenzoate (**3n**): Pale yellow solid, 52.1 mg, 79% yield. m.p. 45.8~47.9 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.18 (d, $J=8.4$ Hz, 2H), 7.38 (d, $J=8.0$ Hz, 2H), 7.33 (d, $J=6.4$ Hz, 2H), 7.29 (d, $J=7.6$ Hz, 1H), 7.21 (d, $J=7.2$ Hz, 1H), 6.68 (s, 1H), 2.51 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.19, 150.79, 144.75, 138.47, 133.36, 130.39, 130.18, 129.37, 128.66, 126.01, 125.53, 122.09, 96.38, 21.74, 21.39; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 353.0148, found 353.0148.

(Z)-2-Bromo-1-(3-fluorophenyl)vinyl 4-methylbenzoate (**3o**): pale yellow solid, 54.1 mg, 81% yield. m.p. 78.0~79.2 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (d, $J=8.0$ Hz, 2H), 7.42 (td, $J=7.7$, 1.6 Hz, 1H), 7.36~7.29 (m, 3H), 7.14~7.09 (m, 2H), 6.91 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.08, 159.48 (d, $J=250.3$ Hz), 145.07 (d, $J=4.3$ Hz), 144.86, 130.58 (d, $J=8.7$ Hz), 130.40, 129.39, 127.72 (d, $J=1.7$ Hz), 125.80, 124.36 (d, $J=3.5$ Hz), 121.26 (d, $J=11.4$ Hz), 116.39 (d, $J=22.5$ Hz), 101.81 (d, $J=13.7$ Hz), 21.75; ^{19}F NMR (600 MHz, CDCl_3) δ : -111.9; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{BrFNaO}_2$ $[\text{M} + \text{Na}]^+$ 356.9897, found 356.9897.

(Z)-2-Bromo-1-(thiophen-2-yl)vinyl 4-methylbenzoate (**3p**): Pale yellow solid, 43.8 mg, 68% yield. m.p. 86.1~87.9 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (d, $J=8.4$ Hz, 2H), 7.33 (d, $J=8.0$ Hz, 2H), 7.28 (dd, $J=4.8$, 0.8 Hz, 1H), 7.15 (dd, $J=4.0$, 0.8 Hz, 1H), 6.98 (dd, $J=5.2$, 4.0 Hz, 1H), 6.59 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 162.87, 145.65, 144.91, 136.56, 130.44, 129.39, 127.57, 126.36, 125.74, 125.15, 95.51, 21.77; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{BrNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 344.9555, found 344.9556.

(Z)-2-Bromo-1-(thiophen-3-yl)vinyl 4-methylbenzoate (**3q**): Pale yellow solid, 39.3 mg, 61% yield. m.p. 88.6~89.3 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (d, $J=8.4$ Hz, 2H), 7.34~7.31 (m, 4H), 7.19 (dd, $J=4.8$, 1.2 Hz, 1H), 6.61 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.03, 146.88, 144.85, 135.01, 130.39, 129.39, 126.93, 125.87, 124.20, 122.36, 96.27, 21.76; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{BrNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 344.9555, found 344.9555.

(Z)-1-Bromohept-1-en-2-yl 4-methylbenzoate (**3r**): Pale yellow liquid, 46.5 mg, 75% yield. ^1H NMR (600 MHz, CDCl_3) δ : 8.03 (d, $J=8.4$ Hz, 2H), 7.29 (d, $J=7.8$ Hz, 2H), 5.91 (s, 1H), 2.44 (s, 3H), 2.42~2.39 (m, 2H), 1.53~1.51 (m, 2H), 1.33~1.31 (m, 4H), 0.90~0.87 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 163.19, 153.27, 144.48, 130.20, 129.26, 126.31, 93.70, 33.66, 31.09, 25.85, 22.30, 21.73, 13.91; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 333.0461, found 333.0463.

For the synthesis of compound **4**, see the general procedure for compound **3**.

(Z)-2-Bromo-1-phenylvinyl benzoate (**4a**):^[14] Pale yellow solid, 44.7 mg, 74% yield. m.p. 45.8~47.3 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.25 (dd, $J=8.0$, 0.8 Hz, 2H), 7.67 (t, $J=7.6$ Hz, 1H), 7.54 (t, $J=7.8$ Hz, 2H), 7.51~7.48 (m, 2H), 7.38~7.36 (m, 3H), 6.68 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.10, 150.63, 133.86, 133.31, 130.33, 129.39, 128.79, 128.74, 128.67, 124.92, 96.71.

(Z)-2-Bromo-1-phenylvinyl 4-(*tert*-butyl)benzoate (**4b**): White solid, 58.0 mg, 81% yield. m.p. 82.4~83.7 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.17 (d, $J=8.8$ Hz, 2H), 7.55 (d, $J=8.4$ Hz, 2H), 7.50~7.47 (m, 2H), 7.36~7.33 (m, 3H), 6.66 (s, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.09, 157.76, 150.68, 133.46, 130.29, 129.35, 128.78, 125.95, 125.70, 124.95, 96.64, 35.24, 31.09; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 381.0461, found 381.0461.

(Z)-2-Bromo-1-phenylvinyl 3-chlorobenzoate (**4c**): Pale yellow solid, 51.7 mg, 77% yield. m.p. 79.9~80.9 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.23 (t, $J=1.6$ Hz, 1H), 8.13 (dt, $J=8.0$ Hz, 1.2 Hz, 1H), 7.66~7.63 (m, 1H), 7.50~7.46 (m, 3H), 7.37 (dd, $J=6.0$, 2.4 Hz, 3H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 161.91, 150.47, 134.87, 133.90, 133.01, 130.44, 130.26, 130.01, 129.51, 128.83, 128.42, 124.89, 96.89; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{BrClNaO}_2$ $[\text{M} + \text{Na}]^+$ 358.9445, found 358.9445.

(Z)-2-Bromo-1-phenylvinyl 2-methylbenzoate (**4d**): Pale yellow solid, 50.5 mg, 80% yield. m.p. 47.8~48.3 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.29 (d, $J=8.0$ Hz, 1H), 7.54~7.50 (m, 3H), 7.38~7.33 (m, 5H), 6.67 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.50, 150.68, 141.66, 133.51, 132.97, 131.98, 131.33, 129.34, 128.80, 127.75, 125.96, 124.92, 96.63, 21.86; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{13}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 338.9991, found 338.9990.

(Z)-2-Bromo-1-phenylvinyl acetate (**4e**):^[4a] Yellow liquid, 25.4 mg, 53% yield. ^1H NMR (400 MHz, CDCl_3) δ : 7.44~7.40 (m, 2H), 7.38~7.35 (m, 3H), 6.55 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.23, 150.50, 133.29, 129.39, 128.77, 124.91, 96.55, 20.57.

(Z)-2-Bromo-1-(*p*-tolyl)vinyl heptanoate (**4f**): Yellow liquid, 23.9 mg, 37% yield. ^1H NMR (400 MHz, CDCl_3) δ : 7.32 (d, $J=8.8$ Hz, 2H), 6.85 (d, $J=8.8$ Hz, 2H), 6.39 (s, 1H), 4.03 (q, $J=7.2$ Hz, 2H), 2.59 (t, $J=7.6$ Hz, 2H), 1.78 (q, $J=7.2$ Hz, 2H), 1.44~1.34 (m, 7H), 0.93 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 170.11, 159.83, 150.28, 126.37, 125.89, 114.62, 94.17, 63.53, 33.99, 31.25, 24.52, 22.27, 14.70, 13.87; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{BrNaO}_2$ $[\text{M} + \text{Na}]^+$ 347.0617, found 347.0616.

(Z)-2-Chloro-1-phenylvinyl acetate (**4g**):^[4a] Pale yellow liquid, 21.5 mg, 55% yield. ^1H NMR (600 MHz, CDCl_3) δ : 7.39~7.36 (m, 5H), 6.45 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 167.33, 148.41, 132.76, 129.35, 128.76, 124.70, 107.98, 20.46.

(Z)-2-Iodo-1-phenylvinyl acetate (**4h**):^[4a] Pale yellow liquid, 35.7 mg, 62% yield. ^1H NMR (600 MHz, CDCl_3) δ : 7.42 (s, 2H), 7.35 (s, 3H), 6.63 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 167.33, 155.04, 133.66,

129.39, 128.73, 125.15, 68.28, 20.98.

(*Z*)-Methyl-3-acetoxy-3-phenylacrylate (**4i**): Pale yellow liquid, 41.8 mg, 95% yield. ^1H NMR (600 MHz, CDCl_3) δ : 7.59 (d, $J=7.8$ Hz, 2H), 7.44 (d, $J=6.6$ Hz, 1H), 7.41 (t, $J=7.2$ Hz, 2H), 6.28 (s, 1H), 3.74 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 168.12, 164.60, 158.31, 133.20, 131.06, 128.80, 125.90, 105.57, 51.49, 20.92; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{O}_4$ $[\text{M} + \text{H}]^+$ 221.0808, found 221.0808.

(*Z*)-3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl butyrate (**4j**): Pale yellow liquid, 45.6 mg, 92% yield. ^1H NMR (600 MHz, CDCl_3) δ : 7.58 (d, $J=7.2$ Hz, 2H), 7.45~7.39 (m, 3H), 6.28 (s, 1H), 3.74 (s, 3H), 2.68 (t, $J=7.8$ Hz, 2H), 1.86~1.80 (m, 2H), 1.06 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 170.64, 164.56, 158.29, 133.46, 130.95, 128.77, 125.89, 105.73, 51.43, 36.01, 18.04, 13.70; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{O}_4$ $[\text{M} + \text{H}]^+$ 249.1121, found 249.1120.

(*Z*)-3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl 3-chlorobenzoate (**4k**): White solid, 60.7 mg, 96% yield. m.p. 146.1~147.4 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ : 7.74 (s, 1H), 7.73 (d, $J=7.8$ Hz, 1H), 7.25~7.22 (m, 2H), 7.10~7.00 (m, 5H), 6.02 (s, 1H), 3.30 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 164.29, 162.61, 158.03, 134.73, 133.69, 132.91, 131.15, 130.71, 130.24, 129.95, 128.85, 128.41, 125.86, 106.00, 51.51; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_4$ $[\text{M} + \text{H}]^+$ 317.0575, found 317.0576.

(*Z*)-3-Methoxy-3-oxo-1-phenylprop-1-en-1-yl 4-(*tert*-butyl)benzoate (**4l**): White solid, 60.8 mg, 90% yield. m.p. 149.1~149.8 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ : 8.18 (d, $J=7.8$ Hz, 2H), 7.66 (d, $J=7.8$ Hz, 2H), 7.55 (d, $J=7.8$ Hz, 2H), 7.43 (d, $J=6.6$ Hz, 1H), 7.40 (t, $J=7.8$ Hz, 2H), 6.41 (s, 1H), 3.68 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ : 164.46, 163.80, 158.38, 157.44, 133.41, 130.97, 130.24, 128.79, 126.17, 125.95, 125.68, 106.04, 51.49, 35.16, 31.06; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_4$ $[\text{M} + \text{H}]^+$ 339.1591, found 339.1590.

4.3 General procedure for the intramolecular competition experiment

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with bromoalkyne **1a** (0.20 mmol), BI-OAc (0.20 mmol), silver carbonate (5 mol%) and freshly distilled CH_3CN (1.0 mL) under air atmosphere. The reaction tube was placed in an oil bath and stirred at 90 $^\circ\text{C}$ for 6 h. After the reaction was completed (detected by TLC), the mixture was cooled to room temperature, and extracted with ethyl acetate (5 mL $\times$ 3). The organic layers were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, $V(\text{petroleum ether}) : V(\text{ethyl acetate}) = 10 : 1$ to $20 : 1$], affording the desired product (*Z*)-2-bromo-1-phenylvinyl 2-iodobenzoate (**5**) as white solid (65.0 mg, 76% yield). m.p. 61.4~62.8 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ : 8.26 (dd, $J=7.8, 1.8$ Hz, 1H), 8.11 (d, $J=7.8$ Hz, 1H), 7.54~7.52 (m, 3H), 7.41~7.39 (m,

3H), 7.28 (t, $J=7.8$ Hz, 1H), 6.70 (s, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ : 162.40, 150.40, 141.91, 133.59, 132.92, 132.74, 131.85, 129.48, 128.81, 128.08, 124.99, 96.98, 95.11; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{10}\text{BrINaO}_2$ $[\text{M} + \text{Na}]^+$ 450.8801, found 450.8801.

4.4 General procedure for the gram-scale synthesis of 3a

A 25 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with **1a** (5.0 mmol), HIRs **2a** (5.00 mmol), silver carbonate (2.5 mol%) and freshly distilled CH_3CN (10 mL) under air atmosphere. The reaction tube was placed in an oil bath and stirred at 90 $^\circ\text{C}$ for 10 h. After the reaction was completed, the mixture was cooled to room temperature, and extracted with ethyl acetate (20 mL $\times$ 3). The organic layers were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, $V(\text{petroleum ether}) : V(\text{ethyl acetate}) = 10 : 1$ to $20 : 1$], affording the desired product **3a** as pale yellow liquid (1.14 g, 72%).

4.5 General procedure for the late-stage transformation

Under nitrogen atmosphere, a 10 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with **3i** (0.40 mmol), 1-phenylethyne (0.84 mmol), $\text{Pd}(\text{dppf})_2\text{Cl}_2$ (1 mol %), CuI (10 mol %), triethylamine (2.0 mol) and anhydrous *N,N*-dimethylformamide (DMF, 1.0 mL). The reaction tube was placed in an oil bath and stirred at 80 $^\circ\text{C}$ for 12 h. After the reaction was completed, the mixture was cooled to room temperature, and extracted with ethyl acetate (5 mL $\times$ 3). The organic layers were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, $V(\text{petroleum ether}) : V(\text{ethyl acetate}) = 9 : 1$], affording the desired product (*Z*)-4-phenyl-1-(4-(phenylethynyl)phenyl)but-1-en-3-yn-1-yl 4-methylbenzoate (**6**) as white solid (122.7 mg, 70%). m.p. 185.1~186.3 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ : 8.19 (d, $J=7.8$ Hz, 2H), 7.56~7.51 (m, 6H), 7.36~7.34 (m, 5H), 7.24~7.14 (m, 6H), 6.30 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ : 163.93, 155.42, 144.70, 133.22, 131.91, 131.80, 131.66, 131.41, 130.45, 129.42, 128.48, 128.37, 128.32, 128.16, 126.31, 124.49, 123.04, 123.00, 98.61, 98.04, 91.37, 89.05, 84.39, 21.80; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$ 439.1693, found 439.1693.

4.6 General procedure for the radical trapping experiments with TEMPO

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with **1a** (0.20 mmol), (diacetoxyiodo)benzene (DIB, 0.20 mmol), silver carbonate (2.5 mol%), TEMPO (0.40 mmol) and freshly distilled CH_3CN (1.0 mL) under air atmosphere. The reaction tube was placed in an oil bath and stirred at 90 $^\circ\text{C}$ for 6 h. After that, the reaction mixture was cooled to room tem-

perature, and extracted with ethyl acetate (5 mL $\times$ 3). The organic layers were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, $V(\text{petroleum ether}) : V(\text{ethyl acetate}) = 10 : 1$ to $20 : 1$], affording the desired product **4e** in 32% yield. Therefore, a radical pathway can be ruled out for this silver-catalyzed system.

4.7 General procedure for deuterium-labeled experiments

A 10 mL oven-dried reaction tube equipped with a magnetic stirrer bar was charged with **1a** (0.20 mmol), (diacetoxyiodo)benzene (DIB, 0.20 mmol), silver carbonate (2.5 mol%), D_2O (0.20 mmol) and freshly distilled CH_3CN (1.0 mL) under N_2 atmosphere. The reaction tube was placed in an oil bath and stirred at 90°C for 6 h. After the reaction was completed, the mixture was cooled to room temperature, and extracted with ethyl acetate (5 mL $\times$ 3). The organic layers were combined, dried over anhydrous MgSO_4 , and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography [silica gel, $V(\text{petroleum ether}) : V(\text{ethyl acetate}) = 10 : 1$ to $20 : 1$], affording the desired product **4e**/[**D**]-**4e** (ca. 29% total yield). The ratio of mixture ([**D**]-**4e**/**4e** = 1.86) was determined by ^1H NMR analysis of the obtained mixture, which indicates the pronation step was involved therein.

Supporting Information ^1H NMR and ^{13}C NMR spectra of new compounds **3**~**6**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

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