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Controlled synthesis of 1-vinylnaphthalenes versus (*E*)-α-(1,3-enyn-4-yl)-α,β-unsaturated esters from Morita–Baylis–Hillman bromides: a sequential alkynylation and competitive 6π-electrocyclization versus conjugative transposition of a triple bond

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ABSTRACT

An expedient controlled synthesis of 1-vinylnaphthalenes and various dienyne derivatives has been carried out from the Morita–Baylis–Hillman bromides and propargyl acetate or *p*-nitrophenyl propargyl ether. By judicious choice of base, reaction temperature, and leaving group, a selective synthesis of 1-vinylnaphthalenes and dienynes, (*E*)-α-(1,3-enyn-4-yl)-α,β-unsaturated esters, could be performed.

The synthesis of α-ethynyl-α,β-unsaturated esters has received much attention due to their wide synthetic applicability.[1,2] These compounds have been synthesized in a variety of methods including a palladium-catalyzed alkynylation of α-halo-α,β-unsaturated esters,[1a–d] an iridium complex-catalyzed cross-coupling reaction of terminal alkynes with internal alkynes,[1e] CuI-catalyzed cross-coupling reaction between α-stannyl-α,β-unsaturated esters and alkynyl bromides,[1f] and a DABCO-catalyzed synthesis from allenyl acetates.[1g,h] However, the synthesis of α,β-unsaturated esters bearing a 1,3-enyne tether at the α-position has not been reported, to the best of our knowledge.[3] This prompted us to investigate the synthesis of α-(1,3-enyn-4-yl)-α,β-unsaturated esters starting from the bromides of Morita–Baylis–Hillman (MBH) adducts.[4]

Very recently, we reported an efficient synthesis of 1-benzylnaphthalene derivatives from Morita–Baylis–Hillman bromides via a tandem alkynylation, propargyl–allenyl isomerization, and 6π-electrocyclization sequence, as shown in Scheme 1.[5] As a continuous study, we presumed that 1-vinylnaphthalene **4a** and/or dienyne derivative **5a** could be synthesized from **3a**, which could be prepared from MBH bromide **1a** and propargyl acetate (**2a**). 1-Vinylnaphthalene[6] **4a** could be formed via a sequential propargyl–allenyl isomerization, 6π-electrocyclization, and an elimination of AcOH, while the dienyne derivative **5a** could be produced via propargyl–allenyl isomerization and a following 1,4-elimination of AcOH (vide infra, Scheme 4). We expected that a selective synthesis of **4a** and **5a** could be achieved by judicious choice of reaction conditions such as base or reaction temperature.

At the outset of our experiment, a one-pot reaction of MBH bromide **1a** and propargyl acetate (**2a**) was examined in the presence of CuI (20 mol %) and Cs_2CO_3 (2.0 equiv) in CH_3CN at elevated temperature (50 °C).[5] To our delight, vinylnaphthalene **4a** (41%) and dienyne **5a** (8%) were formed, albeit in low yields, presumably via the intermediate **3a**. Thus, we decided to prepare **3a** and examine the reaction in the presence of a base in order to find an optimum condition, and the results are summarized in Table 1. The starting material **3a** could be prepared from **1a** and **2a** at room temperature in the presence of CuI (20 mol %) and Cs_2CO_3 (1.5 equiv) in CH_3CN in 66% yield according to our previous paper.[5]

As shown in entry 1, the reaction of **3a** in the presence of Cs_2CO_3 in CH_3CN at 50 °C afforded **4a** in moderate yield (56%) along with a low yield of **5a** (9%). The result is similar to that of the one-pot reaction of **1a** and **2a** (vide supra). The reaction of **3a** in the presence of Et_3N showed no reaction at room temperature (entry 2). The reaction was sluggish even at 50 °C (entry 3).

When we carried out the reaction under refluxing conditions (entry 4), **4a** was obtained in good yield (64%). However, the reaction required a long reaction time (72 h). The yield of **4a** increased to 71% by using 3.0 equiv of Et_3N (entry 5), and the reaction time could be shortened. In toluene, the reaction was not completed

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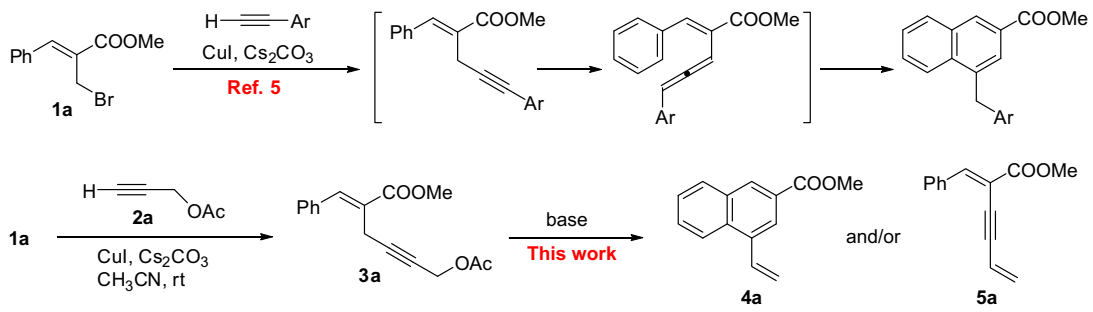


Scheme 1.

Table 1
Optimization of reaction conditions with **3a**

Entry	Conditions	**4a** (%)	**5a** (%)
1	Cs_2CO_3 (1.0 equiv), CH_3CN, 50 °C, 24 h	56	9
2	Et_3N (1.5 equiv), CH_3CN, rt, 24 h	0	0
3[a]	Et_3N (1.5 equiv), CH_3CN, 50 °C, 24 h	10	0
4[b]	Et_3N (1.5 equiv), CH_3CN, reflux, 72 h	64	0
5[c]	Et_3N (3.0 equiv), CH_3CN, reflux, 24 h	**71**	0
6[d]	Et_3N (3.0 equiv), toluene, 100 °C, 72 h	56	0
7	DBU (1.0 equiv), CH_3CN, rt, 5 h	0	47
8[e]	DBU (1.5 equiv), CH_3CN, rt, 1 h	0	**51**
9	DBU (1.5 equiv), CH_3CN, 50 °C, 1 h	0	42
10	*t*-BuOK (1.2 equiv), CH_3CN, rt, 2 h	0	36
11[f]	TBAF (1.2 equiv), CH_3CN, 50 °C, 5 h	16	13

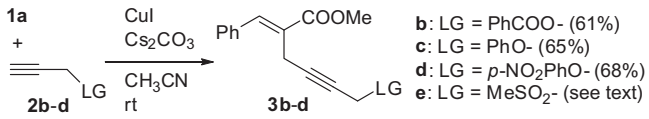
[a] Compound **3a** (75%) was recovered.
[b] Compound **3a** (9%) was recovered.
[c] Selected as condition A.
[d] Compound **3a** (15%) was recovered.
[e] Selected as condition B.
[f] TBAF (1.0 M in THF) was used, and **3a** (45%) was recovered.

even after 72 h (entry 6). In all of the reactions employing Et_3N (entries 2–6), the formation of dienyne **5a** was not observed. The reactions with DBU (entries 7–9) showed completely different results. Dienyne **5a** was formed selectively at room temperature or even at 50 °C in short time; however, the yield was moderate (42–51%). The reactions of **3a** in the presence of *t*-BuOK (entry 10) or TBAF (entry 11) did not improve the yield of **4a** and/or **5a**. Thus, the condition of entry 5 was selected as the best one (condition A) for the synthesis of vinylnaphthalene and the condition of entry 8 (condition B) for dienyne.

As a next experiment, some representative substrates **3b–d** were prepared from **1a** and propargyl benzoate (**2b**), phenyl propargyl ether (**2c**), and *p*-nitrophenyl propargyl ether (**2d**) in order to examine the effect of a leaving group. The results of **3b–d** under the optimized reaction conditions (A and B) are summarized in Table 2 (entries 1–6). The reactions of benzoate **3b** (entries 1 and 2) showed a very similar result to that of the acetate **3a**. The reaction of phenyl ether **3c** also showed a similar result (entries 3 and 4). The yield of **4a** from the reaction of *p*-nitrophenyl ether **3d** under the condition A (entry 5) was not improved; however, the reaction under the condition B (entry 6) afforded good yield of **5a** (62%).[7] In order to prepare the mesylate **3e** the reaction between **1a** and the mesylate of propargyl alcohol was examined; however, compound **3e** was not formed at all. Thus, **3e** was prepared via the hydrolysis of acetate **3a** (K_2CO_3, H_2O/MeOH, rt, 30 min, 85%) and a following mesylation with CH_3SO_2Cl (Et_3N, CH_2Cl_2, 0 °C to rt, 2 h, 94%). The reactions of **3e** and Et_3N (entry 7) or DBU (entry 8) produced the corresponding ammonium salts instantaneously even at room temperature and did not form **4a** and/or **5a** at this temperature for 6 h. When we raised the temperature to 50 °C, both reactions provided **4a** and **5a** as a mixture, unfortunately (entries 7 and 8).

Based on the results, we selected the acetoxy group as a suitable leaving group for the synthesis of vinylnaphthalenes under the

Table 2
The effect of a leaving group (LG)



Entry	Substrate	Condition[a]	**4a** (%)	**5a** (%)
1	**3b**	A	68	0
2	**3b**	B	0	54
3	**3c**	A[b]	52	0
4	**3c**	B[c]	0	58
5	**3d**	A	45	0
6	**3d**	B	0	**62**
7	**3e**	A[d]	36	32
8	**3e**	B[d]	25	29

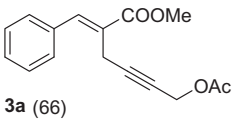
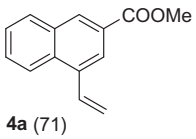
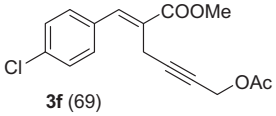
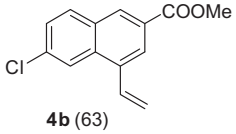
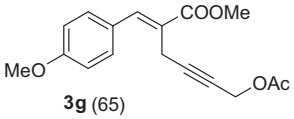
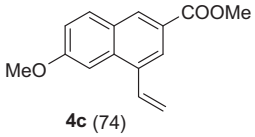
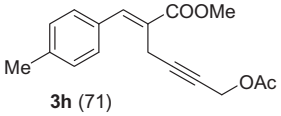
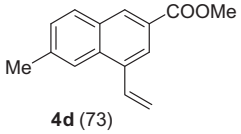
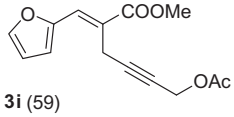
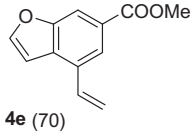
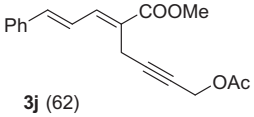
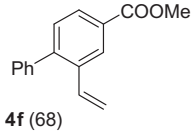
[a] Condition A: substrate **3** (0.5 mmol), Et_3N (3.0 equiv), reflux, 24 h. Condition B: substrate **3** (0.5 mmol), DBU (1.5 equiv), rt, 1 h.
[b] Reaction time was 72 h and **3c** (9%) was recovered.
[c] Reaction time was 3 h.
[d] Reaction time was 12 h at 50 °C.

influence of Et_3N (3.0 equiv) in refluxing CH_3CN solvent (entry 5 in Table 1). For the synthesis of dienyne derivatives, the *p*-nitrophenoxy group was selected as a leaving group in the presence of DBU (1.5 equiv) in CH_3CN at room temperature (entry 6 in Table 2). Accordingly, some representative acetates **3f–j** were prepared from propargyl acetate (**2a**) and the corresponding MBH bromides, and the synthetic results of vinylnaphthalenes **4b–f** are summarized in Table 3.[8] The reaction of 4-chlorophenyl derivative **3f** (entry 2) provided **4b** in moderate yield (63%), while the *p*-methoxyphenyl and *p*-tolyl derivatives produced good yields of **4c** (74%) and **4d** (73%), respectively (entries 3 and 4). The reaction of furan derivative **3i** gave 4-vinylbenzofuran **4e** in 70% yield (entry 5). The cinnamyl-substituted substrate **3j** afforded a styrene derivative **4f** in 68% yield (entry 6).

Next, various *p*-nitrophenoxy derivatives **3k–o** were prepared from *p*-nitrophenyl propargyl ether (**2d**) and the corresponding MBH bromides, and the synthetic results of dienyns **5b–f** are summarized in Table 4.[9] Dienynes **5b–e** were obtained in moderate to good yields (63–75%) from **3k–n** in the presence of DBU at room temperature (entries 2–5). However, the reaction of **3o** (entry 6) showed somewhat different reactivity. Expected compound **5f** was not formed at all, instead a styrene derivative **4f** (entry 6 in Table 3) was obtained in 61% (vide infra, Scheme 2).

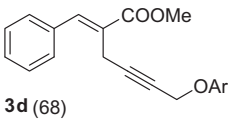
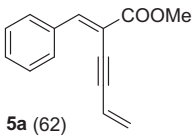
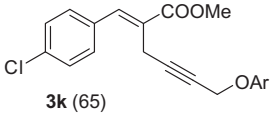
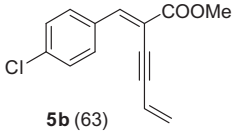
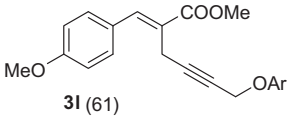
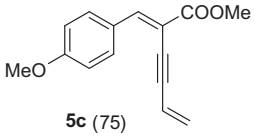
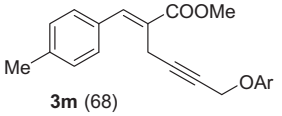
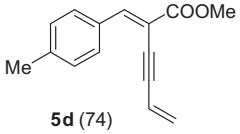
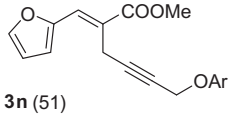
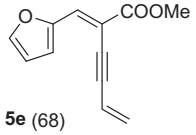
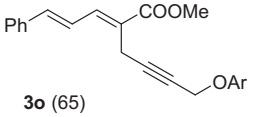
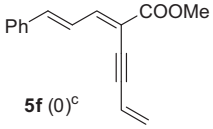
A plausible explanation for the facile formation of a styrene **4f** and a different reactivity between **3a** and **3o** are shown in Scheme 2. The 6π-electrocyclization of allene intermediate **I**, derived from **3o**, proceeded easily under mild condition[10] to form **4f** as a major product. In contrast, the corresponding 6π-electrocyclization of the

Table 3
Synthesis of 1-vinylnaphthalene derivatives

Entry	Acetates **3**[a] (%)	Products **4**[b] (%)
1	 **3a** (66)	 **4a** (71)
2	 **3f** (69)	 **4b** (63)
3	 **3g** (65)	 **4c** (74)
4	 **3h** (71)	 **4d** (73)
5	 **3i** (59)	 **4e** (70)
6	 **3j** (62)	 **4f** (68)

[a] Conditions: MBH bromide (1.0 mmol), propargyl acetate (1.1 equiv), Cs_2CO_3 (1.5 equiv), CuI (20 mol %), CH_3CN, 20 °C, 12–24 h.
[b] Conditions: acetate **3** (0.5 mmol), Et_3N (3.0 equiv), CH_3CN, reflux, 24 h.

Table 4
Synthesis of dienyne derivatives

Entry	*p*-Nitrophenyl ethers **3**[a] (%)	Products **5**[b] (%)
1	 **3d** (68)	 **5a** (62)
2	 **3k** (65)	 **5b** (63)
3	 **3l** (61)	 **5c** (75)
4	 **3m** (68)	 **5d** (74)
5	 **3n** (51)	 **5e** (68)
6	 **3o** (65)	 **5f** (0)[c]

[c] Compound **4f** was obtained in 61% yield.
[a] Conditions: MBH bromide (1.0 mmol), *p*-nitrophenyl propargyl ether (1.1 equiv), Cs_2CO_3 (1.5 equiv), CuI (20 mol %), CH_3CN, 20 °C, 12–24 h. Ar is *p*-nitrophenyl.
[b] Conditions: *p*-nitrophenyl ether **3** (0.5 mmol), DBU (1.5 equiv), CH_3CN, 20 °C, 1 h.

allene intermediate **III**, derived from **3a**, to form **IV**, required somewhat higher activation energy due to loss of the stabilizing resonance energy of the benzene ring. Thus we expected that 6π-electrocyclization of the corresponding allene intermediate of **3p** would also be facile, because only one of the two benzene rings of naphthalene loses its resonance energy. As expected, 1-vinylphenanthrene **4g** was formed as a major product (43%) even at room temperature (condition B) along with a low yield of dienyne **5g** (19%).[11] The vinylphenanthrene **4g** was prepared in good yield (80%) using the acetate **3q** under the condition A (18 h).

In order to show the generality of the reaction we prepared **3r** and **3s** by the reaction of MBH bromide **1a** with **2f** and **2g**, as shown in Scheme 3. Compound **2f** was prepared by acetylation of 3-butyn-2-ol and compound **2g** from *p*-nitrophenol by Mitsunobu reaction in the presence of DEAD and PPh_3. Introduction of **2f** and **2g** at the primary position of the MBH adduct was carried out similarly to obtain **3r** and **3s** in moderate yields. The reaction of **3r** under the condition A afforded 1-(2-propenyl)naphthalene **4h** in good yield (71%). The stereochemistry of 2-propenyl moiety of **4h** was *E*. The corresponding *Z* isomer was not formed at all. The reaction of **3s** under the condition B gave dienyne derivative **5h** in 61% yield, and the *E*/*Z* ratio was about 2:1 (*E*-isomer 40%, *Z*-isomer 21%).

The plausible mechanism for the formation of vinylnaphthalene **4a** and dienyne **5a**, as an example, is proposed in Scheme 4. As in our previous paper,[5] a base-mediated propargyl–allenyl isomerization[5,10,12] of **3a** could produce an allenyl intermediate **III**. A subsequent 6π-electrocyclization would afford an intermediate **IV**, which was converted into vinylnaphthalene **4a** by an aromatization-driven 1,4-elimination of AcOH. Dienyne **5a** could be formed from **III** via a direct 1,4-elimination of AcOH[1g,l,2a,13] or via a 1,3-H shift to form **6a** and a following elimination of AcOH. Compounds **4a** and **5a** could also be produced via the [3]-cumulene intermediate **V**,[10,14] which could be formed by 1,4-elimination of AcOH from **3a**.[13] Although the formations of plausible intermediates **III**–**V** were not observed during the reaction, the involvement of **6a** could be confirmed when we carried out the reaction of **3a** in the presence of a limited amount of DBU (0.3 equiv) at room temperature for 6 h.[15] Under the condition compound **6a** was isolated in 9% along with **5a** (17%), and **3a** was recovered (40%).

In summary, an expedient synthetic method of 1-vinylnaphthalene and dienyne derivatives was developed from the MBH bromides and propargyl acetate or *p*-nitrophenyl propargyl ether. 1-Vinylnaphthalenes were obtained selectively from the acetates in the presence of Et_3N in CH_3CN under refluxing conditions, while dienynes from the *p*-nitrophenyl ethers under the influence of DBU at room temperature. Further studies on the reaction mechanism[16] and synthetic application of prepared dienynes are under progress.

Acknowledgments

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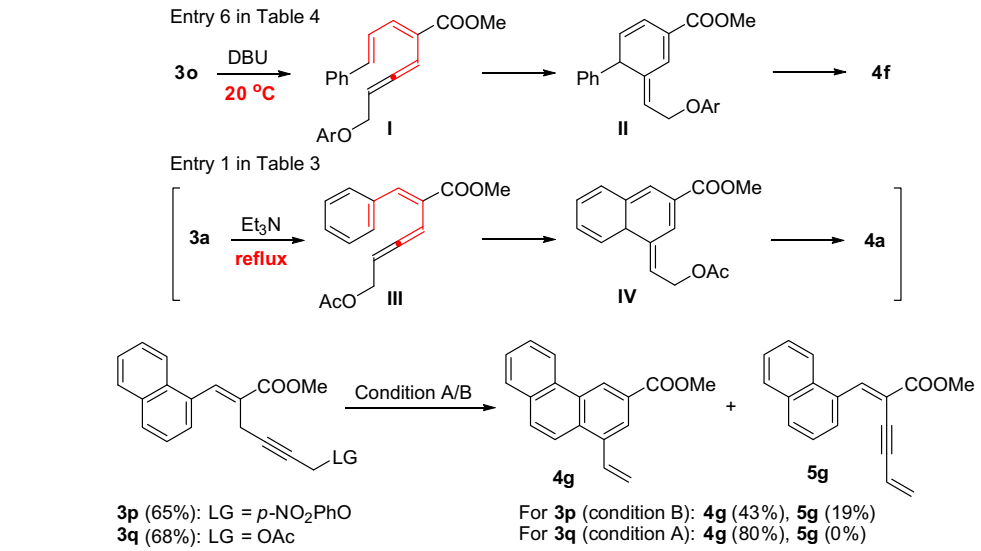
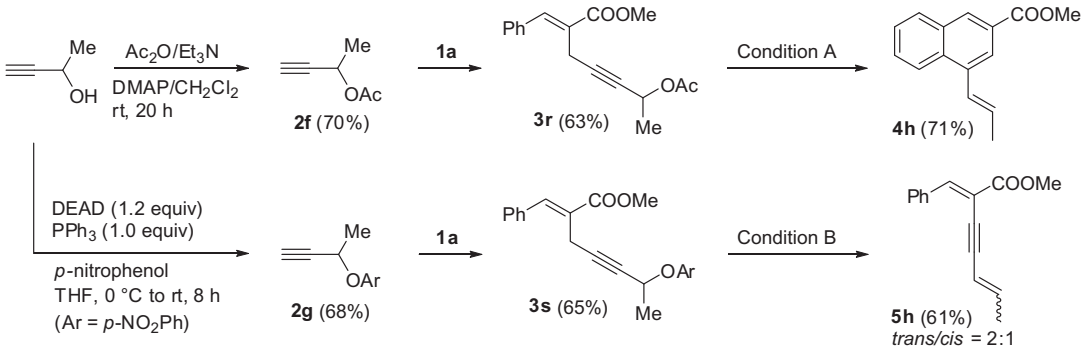
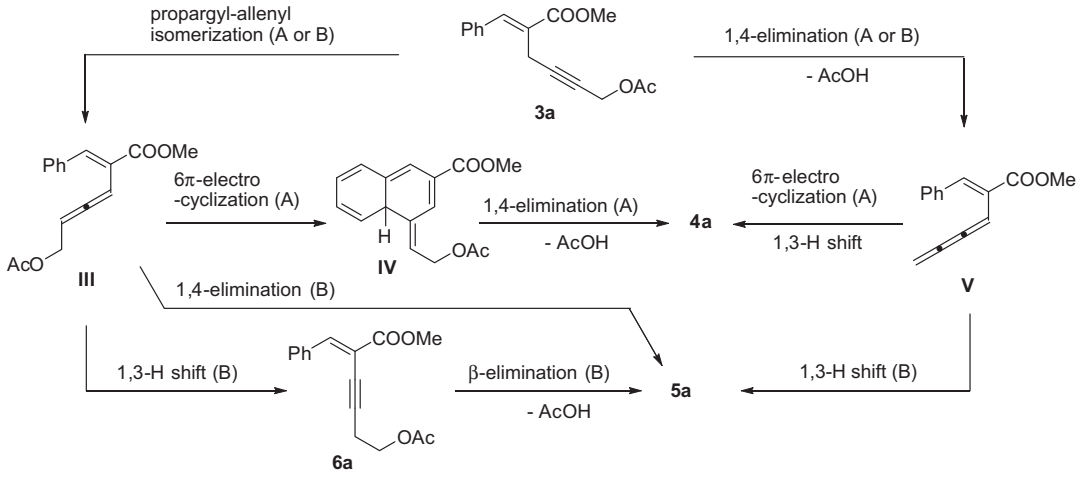


Scheme 2.



Scheme 3.



Scheme 4.

(2012R1A1B3000541). Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

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8. *Typical procedure for the synthesis of 1-vinylnaphthalene (**4a**)*: To a stirred solution of MBH bromide **1a** (255 mg, 1.0 mmol) and propargyl acetate (**2a**, 108 mg, 1.1 mmol) in CH_3CN (1.5 mL) was added CuI (38 mg, 0.2 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) at room temperature (20 °C), and the reaction mixture was stirred for 12 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/ether, 6:1), starting material **3a** was obtained as a white solid, 180 mg (66%). A mixture of **3a** (136 mg, 0.5 mmol) and Et_3N (152 mg, 1.5 mmol) in CH_3CN (1.5 mL) was heated to reflux for 24 h. After removal of volatile materials, the crude product was purified by column chromatographic purification process (hexanes/ether, 15:1) to afford **4a** as colorless oil, 75 mg (71%). Other compounds were synthesized similarly, and the selected spectroscopic data of **3a**, **4a,** and **4e**-**h** are as follows. *Compound **3a***: 66%; white solid, mp 74–76 °C; IR (KBr) 2239, 1748, 1715 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.02 (s, 3H), 3.35 (t, J = 2.4 Hz, 2H), 3.79 (s, 3H), 4.61 (t, J = 2.4 Hz, 2H), 7.26–7.45 (m, 5H), 7.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.11, 20.74, 52.29, 52.71, 74.47, 84.43, 127.09, 128.59, 129.07, 129.56, 134.70, 140.90, 167.49, 170.26; ESIMS m/z 295 [M+Na]$^+$. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.38; H, 5.98. *Compound **4a***: 71%; colorless oil; IR (film) 1721, 1436, 1309, 1282 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.91 (s, 3H), 5.46 (dd, J = 11.1 and 1.5 Hz, 1H), 5.80 (dd, J = 17.4 and 1.5 Hz, 1H), 7.36 (dd, J = 17.4 and 11.1 Hz, 1H), 7.42–7.49 (m, 1H), 7.50–7.57 (m, 1H), 7.87 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 8.11 (s, 1H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.24, 118.25, 122.86, 123.79, 126.49, 127.09, 128.36, 129.96, 130.78, 132.78, 133.14, 133.63, 136.06, 167.21; ESIMS m/z 213 [M+H]$^+$. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.03; H, 5.96. *Compound **4e***: 70%; white solid, mp 78–80 °C; IR (KBr) 1724, 1296, 1241 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H), 5.39 (dd, J = 11.1 and 0.9 Hz, 1H), 5.86 (dd, J = 17.7 and 0.9 Hz, 1H), 6.91 (dd, J = 17.7 and 11.1 Hz, 1H), 6.91 (d, J = 2.1 Hz, 1H), 7.69 (d, J = 2.1 Hz, 1H), 7.97 (s, 1H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.26, 105.53, 112.10, 116.87, 121.35, 126.42, 129.67, 130.85, 133.68, 147.94, 154.77, 167.21; ESIMS m/z 203 [M+H]$^+$. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.44; H, 5.06. *Compound **4f***: 68%; colorless oil; IR (film) 1719, 1297, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.87 (s, 3H), 5.18 (dd, J = 11.1 and 2.1 Hz, 1H), 5.73 (dd, J = 17.7 and 1.2 Hz, 1H), 6.62 (dd, J = 17.7 and 11.1 Hz, 1H), 7.23–7.37 (m, 6H), 7.88 (dd, J = 8.1 and 1.8 Hz, 1H), 8.23 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.15, 115.90, 127.16, 127.59, 128.14, 128.42, 129.18, 129.52, 130.23, 135.03, 135.97, 139.82, 145.06, 166.95; ESIMS m/z 239 [M+H]$^+$. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.39; H, 5.88. *Compound **4g***: 80%; white solid, mp 104–106 °C; IR (KBr) 1722, 1437, 1269 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.97 (s, 3H), 5.52 (dd, J = 10.8 and 1.5 Hz, 1H), 5.83 (dd, J = 17.4 and 1.5 Hz, 1H), 7.44 (dd, J = 17.4 and 10.8 Hz, 1H), 7.54–7.68 (m, 2H), 7.79–7.87 (m, 2H), 7.98 (d, J = 9.0 Hz, 1H), 8.26 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H), 9.32 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.32, 118.55, 122.04, 123.11, 124.46, 124.56, 127.11, 127.28, 127.35, 128.58, 129.49, 129.98, 130.70, 131.68, 132.19, 134.12, 136.54, 167.36; ESIMS m/z 285 [M+Na]$^+$. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.18; H, 5.52. *Compound **4h***: 71%; colorless oil; IR (film) 1719, 1301, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.93 (dd, J = 6.6 and 1.8 Hz, 3H), 3.90 (s, 3H), 6.27 (dq, J = 15.3 and 6.6 Hz, 1H), 7.02 (dd, J = 15.3 and 1.8 Hz, 1H), 7.41–7.55 (m, 2H), 7.85 (d, J = 8.1 Hz, 1H), 8.04 (s, 1H), 8.05 (d, J = 10.8 Hz, 1H), 8.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.95, 52.20, 122.67, 123.97, 126.34, 127.05, 127.43, 128.08, 129.89, 129.92, 130.19, 132.77, 133.12, 136.21, 167.34; ESIMS m/z 227 [M+H]$^+$. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.81; H, 6.23.

9. *Typical procedure for the synthesis of dienyne **5a***: To a stirred solution of MBH bromide **1a** (255 mg, 1.0 mmol) and *p*-nitrophenyl propargyl ether (**2d**, 193 mg, 1.1 mmol) in CH_3CN (1.5 mL) was added CuI (38 mg, 0.2 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) at room temperature (20 °C), and the reaction mixture was stirred for 12 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/ether, 6:1), a starting material **3d** was obtained as a pale yellow oil, 239 mg (68%). To a stirred solution of **3d** (176 mg, 0.5 mmol) in CH_3CN (1.5 mL) was added DBU (114 mg, 0.75 mmol), and the reaction mixture was stirred at room temperature for 1 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/ether, 15:1), dienyne **5a** was obtained as colorless oil, 66 mg (62%). Other compounds were synthesized similarly, and the selected spectroscopic data of **3d**, **5a**, **5b**, **5e,** and **5g** are as follows. *Compound **3d***: 68%; pale yellow oil; IR (film) 1720, 1596, 1439, 1263 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.35 (t, J = 2.1 Hz, 2H), 3.76 (s, 3H), 4.73 (t, J = 2.1 Hz, 2H), 6.96 (d, J = 9.3 Hz, 2H), 7.24–7.36 (m, 5H), 7.69 (s, 1H), 8.11 (d, J = 9.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.15, 52.34, 56.92, 74.10, 86.64, 115.06, 125.70, 126.75, 128.59, 129.21, 129.50, 134.52, 141.02, 162.55, 167.40 (one carbon is overlapped); ESIMS m/z 352 [M+H]$^+$. Anal. Calcd for $C_{20}H_{17}NO_5$: C, 68.37; H, 4.88; N, 3.99; Found: C, 68.60; H, 4.96; N, 3.68. *Compound **5a***: 62%; colorless oil; IR (film) 1722, 1435, 1261, 1208 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.81 (s, 3H), 5.56 (dd, J = 11.1 and 2.1 Hz, 1H), 5.72 (dd, J = 17.7 and 2.1 Hz, 1H), 6.03 (dd, J = 17.7 and 11.1 Hz, 1H), 7.32–7.37 (m, 3H), 7.84 (s, 1H), 7.90–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.84, 85.56, 96.83, 112.58, 117.02, 128.05, 128.51, 130.43, 130.68, 134.28, 145.80, 166.10; ESIMS m/z 213 [M+H]$^+$. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.50; H, 5.82. *Compound **5b***: 63%; white solid, mp 82–84 °C; IR (KBr) 2217, 1722, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3H), 5.58 (dd, J = 11.1 and 2.1 Hz, 1H), 5.72 (dd, J = 17.7 and 2.1 Hz, 1H), 6.02 (dd, J = 17.7 and 11.1 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.77 (s, 1H), 7.86 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.93, 85.27, 97.47, 113.14, 116.87, 128.38, 128.82, 131.55, 132.76, 136.49, 144.18, 165.88; ESIMS m/z 247 [M+H]$^+$, 249 [M+H+2]$^+$. Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.49. Found: C, 68.03; H, 4.71. *Compound **5e***: 68%; white solid, mp 60–62 °C; IR (KBr) 1719, 1436, 1267 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 3H), 5.57 (dd, J = 11.4 and 2.1 Hz, 1H), 5.74 (dd, J = 17.7 and 2.1 Hz, 1H), 6.06 (dd, J = 17.7 and 11.4 Hz, 1H), 6.48–6.51 (m, 1H), 7.28 (d, J = 3.6 Hz, 1H), 7.51 (d, J = 1.8 Hz, 1H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.76, 85.70, 98.08, 109.14, 112.87, 116.25, 117.05, 127.96, 132.77, 145.10, 151.34, 165.73; ESIMS m/z 203 [M+H]$^+$. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.55; H, 5.12. *Compound **5g***: 19%; pale yellow oil; IR (film) 1722, 1435, 1241 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86 (s, 3H), 5.49 (dd, J = 11.1 and 2.1 Hz, 1H), 5.59 (dd, J = 17.7 and 2.1 Hz, 1H), 5.93 (dd, J = 17.7 and 11.1 Hz, 1H), 7.42–7.54 (m, 3H), 7.79–7.86 (m, 2H), 8.05 (d, J = 8.1 Hz, 1H), 8.32 (d, J = 7.2 Hz, 1H), 8.64 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.92, 85.37, 95.59, 114.83, 116.97, 123.47, 125.05, 126.15, 126.86, 127.66, 128.14, 128.78, 130.83, 130.88, 131.84, 133.47, 143.23, 165.99; ESIMS m/z 263 [M+H]$^+$. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.29; H, 5.53.

10. For the examples on 6π-electrocyclization at room temperature, see: (a) Zhou, H.; Xing, Y.; Yao, J.; Chen, J. *Org. Lett.* **2010**, *12*, 3674–3677; (b) Zhou, H.; Xing, Y.; Yao, J.; Lu, Y. *J. Org. Chem.* **2011**, *76*, 4582–4590.

11. When we carried out the reaction of **3p** under the influence of DBU (1.5 equiv) in CH_3CN at 0 °C, the yield of **5g** increased up to 45%. The yield of **4g** decreased to 24% under the condition.

12. For the selected examples on propargyl–allenyl isomerization, see: (a) Xing, Y.; Wei, Y.; Zhou, H. *Curr. Org. Chem.* **2012**, *16*, 1594–1608. and further references cited therein; (b) Xu, J.; Wang, Y.; Burton, D. *J. Org. Lett.* **2006**, *8*, 2555–2558; (c) Shen, R.; Zhu, S.; Huang, X. *J. Org. Chem.* **2009**, *74*, 4118–4123; (d) Huang, X.; Zhu, S.; Shen, R. *Adv. Synth. Catal.* **2009**, *351*, 3118–3122.

13. For the 1,4-elimination of acetic acid from allenylmethyl acetate (or tosylate), see: (a) Trost, B. M.; Tour, J. M. *J. Org. Chem.* **1989**, *54*, 484–486; (b) Bridges, A. J.; Fischer, J. W. *J. Chem. Soc., Chem. Commun.* **1982**, 665–666; (c) Back, T. G.; Lai, E. K. Y.; Muralidharan, K. R. *J. Org. Chem.* **1990**, *55*, 4595–4602; (d) Kitagaki, S.; Teramoto, S.; Mukai, C. *Org. Lett.* **2007**, *9*, 2549–2552.

14. For the isomerization of propargyl amides to ynamides via the corresponding allenyl amides, see: Huang, J.; Xiong, H.; Hsung, R. P.; Rameshkumar, C.; Mulder, J. A.; Grebe, T. P. *Org. Lett.* **2002**, *4*, 2417–2420.

15. *Compound **6a***: 9%; colorless oil; IR (film) 2225, 1748, 1722, 1262 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.01 (s, 3H), 2.80 (t, J = 6.6 Hz, 2H), 3.79 (s, 3H), 4.23 (t, J = 6.6 Hz, 2H), 7.31–7.36 (m, 3H), 7.82 (s, 1H), 7.90–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.48, 20.89, 52.79, 62.02, 77.57, 95.12, 112.71, 128.43, 130.23, 130.58, 134.29, 145.62, 166.32, 170.84; ESIMS m/z 273 [M+H]$^+$. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.76; H, 6.05.

16. During the evaluation process one of the referees suggested the possibility for the conversion of **5a**–**4a**. However, the reaction of **5a** in refluxing CH_3CN (24 h) in the presence of Et_3N did not produce any trace amounts of **4a**.