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Chemical transformation of Baylis–Hillman adducts: the reaction of methyl 3-arylamino-2-methylene-3-phenylpropanoates in polyphosphoric acid

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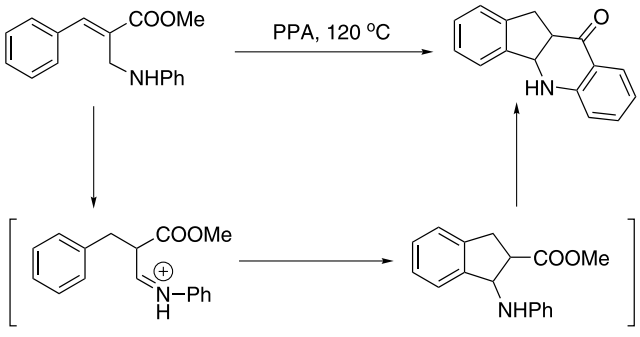
Abstract—We synthesized some interesting compounds including 3-benzylidene-3,4-dihydro-1*H*-quinolin-2-one, 3-benzylquinolin-2-ol, 4-amino-2-benzylideneindan-1-one, and 1-amino-9a,10-dihydro-4b*H*-indeno[1,2-*a*]inden-9-one skeletons starting from Baylis–Hillman adducts.

1. Introduction

Recently, the chemical transformations of the Baylis–Hillman adducts have been studied extensively by us and other groups.[1,2] Among them synthesis of heterocyclic compounds has received much attention including quinolines,[2j,l] dihydroquinolines,[2k] and pyrazoles.[2f] More recently, we reported the synthesis of 4b,5,10a,11-tetrahydroindeno[1,2-*b*]quinolin-10-one derivatives from 2-arylaminomethylcinnamates, which were made from the acetates of the Baylis–Hillman adducts (Scheme 1).[3] In the reaction, treatment of the 2-arylaminomethylcinnamates with polyphosphoric acid (PPA) resulted the formation of 4b,5,10a,11-tetrahydroindeno[1,2-*b*]quinolin-10-one derivatives in moderate yields via the consecutive 1,3-H transfer, protonation, cyclization, and the final Friedel–Crafts reaction sequences.[3]



Scheme 1.

During the investigation we decided to examine the reaction of **2** in PPA as shown in Scheme 2. The synthesis of starting materials **2** was carried out from the acetates of the Baylis–Hillman adducts **1** according to the reported method involving the use of DABCO salt concept.[4] We tried the reaction of **2a** in PPA, and we isolated 3-benzylidene-3,4-dihydro-1*H*-quinolin-2-one (**3a**) in 79% yield. This compound might be generated via the following mechanism as shown in Scheme 3: (1) Claisen rearrangement[5] of the aniline moiety of **2a** to the primary position to give the corresponding intermediate **7** and (2) amide bond formation. Similarly, we prepared some 3-arylidene-3,4-dihydro-1*H*-quinolin-2-one derivatives **3b–d** in good yields as shown in Table 1.[6] During the synthesis of **3a** we observed the formation of trace amounts of 3-benzylquinolin-2-ol (**4a**),[6] which might be formed via double bond isomerization and tautomerization sequences from **3a**. Such conversion of **3a–d** into **4a–d** was carried out effectively in high yields by treatment of **3a–d** with DBU in THF at room temperature in short time (Table 1).

However, when we used **2e** as the starting material we could not detect any appreciable amounts of the expected 3-benzylidene-3,4-dihydro-1*H*-quinolin-2-one compound. Instead, we could isolate two types of major products,

Keywords: Baylis–Hillman adducts; Polyphosphoric acid (PPA); Quinolin-2-ones; Quinolin-2-ols; Indan-1-ones; Indeno[1,2-*a*]inden-9-ones.
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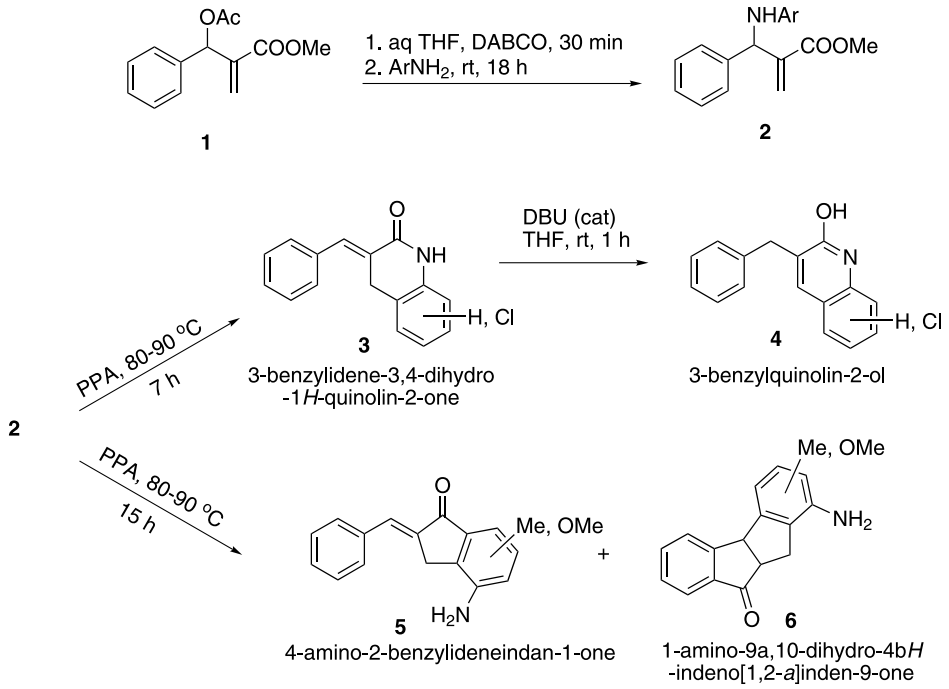
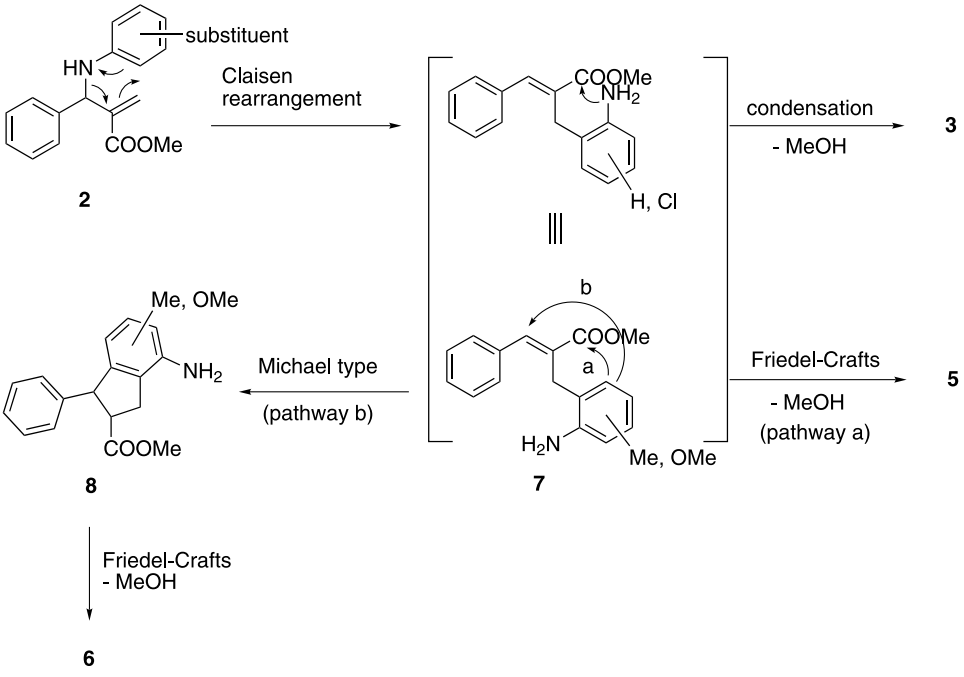


Scheme 2.

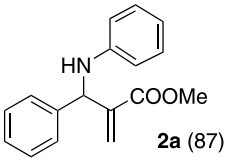
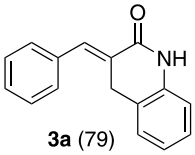
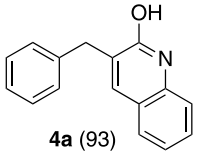
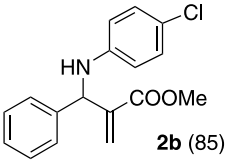
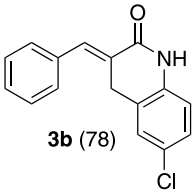
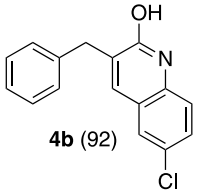
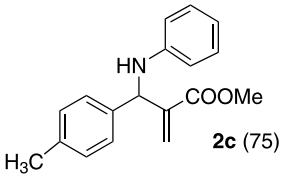
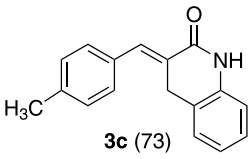
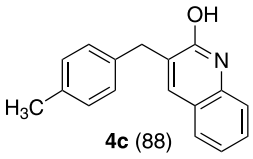
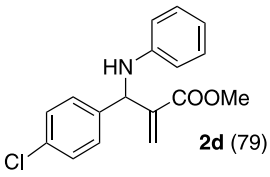
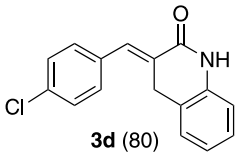
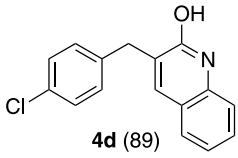


Scheme 3.

which have the structures of **5a** and **6a** based on their spectroscopic data. The formation of 4-amino-2-benzylidene-7-methylindan-1-one (**5a**, 57%)[7] and 1-amino-4-methyl-9a,10-dihydro-4b*H*-indeno[1,2-*a*]inden-9-one (**6a**, 18%, NOE results of **6a** was summarized in Fig. 1)[8] could be explained as shown in Scheme 3. The compound **5a** was generated from the Claisen rearrangement intermediate **7** via intramolecular Friedel–Crafts acylation (pathway a). The compound **6a** might be produced from the same intermediate **7** via Michael type addition (pathway b)[9] and the following Friedel–Crafts reaction. Similarly, when we used **2f–h** as the starting materials we obtained similar results (Table 2). The reaction mechanism for the formation of **6** was further confirmed indirectly by the isolation of the corresponding intermediate **8** in low yield (29% of **8** together with 59% of **5d** and 6% of **6d** when we stopped the reaction after 3 h) when we carried out the reaction with **2h**, fortunately.

The intermediate **7** has two major nucleophilic sites (amino

Table 1. Synthesis of quinolones **3** and quinolinols **4**

Entry	Substrate (%)[a]	Quinolone **3** (%)[b]	Quinolinol **4** (%)[c]
1	 **2a** (87)	 **3a** (79)	 **4a** (93)
2	 **2b** (85)	 **3b** (78)	 **4b** (92)
3	 **2c** (75)	 **3c** (73)	 **4c** (88)
4	 **2d** (79)	 **3d** (80)	 **4d** (89)

[a] The corresponding Baylis–Hillman acetate, aq THF, DABCO (1.1 equiv), 30 min, then aniline derivative (1 equiv), rt, 18 h.
[b] PPA, 80–90 °C, 7 h.
[c] DBU (0.1 equiv), THF, rt, 1 h.

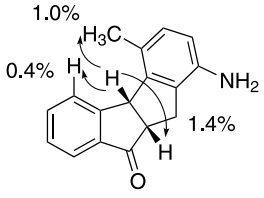


Figure 1. NOE results of compound **6a**.

group and the *ortho*-position of the aniline moiety) and two major electrophilic sites (ester moiety and the β-position of the methyl cinnamate backbone). For the intermediates **7** derived from **2a–d**, the major pathway is the attack of the amino group toward ester moiety.[10] For the intermediates **7** derived from **2e–h**, the major route is the attack of the *ortho*-position of aniline moiety to ester group (pathway a) and the minor is the attack of the *ortho*-position to the vinyl carbon at the β-position of cinnamate skeleton (pathway b).[11] The subtle difference of the electron density at the aniline moiety caused such a strikingly different results. For the reason, however, we cannot explain definitively at this point.

In conclusion, we synthesized 3-benzylidene-3,4-dihydro-1*H*-quinolin-2-one, 3-benzylquinolin-2-ol, 4-amino-2-benzylideneindan-1-one, and 1-amino-9a,10-dihydro-4b*H*-indeno[1,2-*a*]inden-9-one skeletons starting from Baylis–Hillman adducts. We also found that the slight differences in the electron density of the aniline moiety may cause strikingly different reaction pathways.

2. Experimental

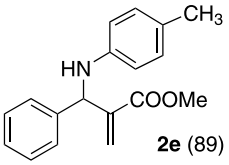
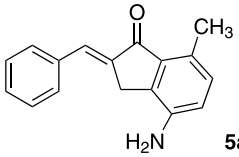
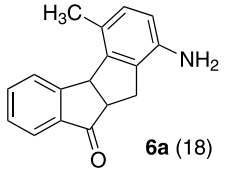
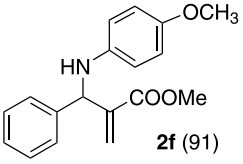
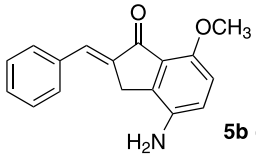
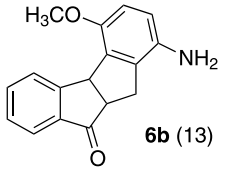
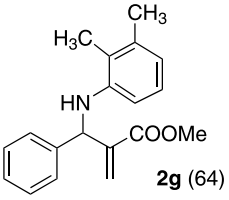
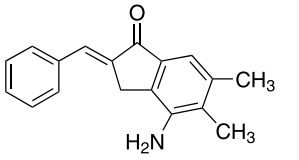
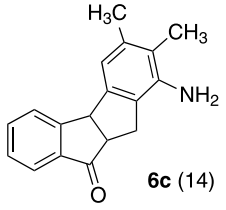
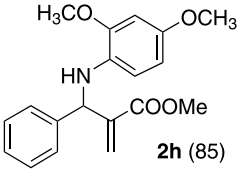
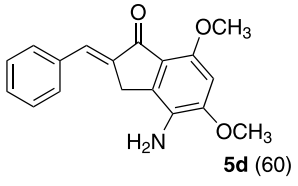
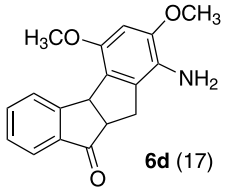
2.1. General procedure

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ or in $CDCl_3$+DMSO-d_6. The signal positions are reported in ppm relative to TMS (δ scale) used as an internal standard. The separations were carried out by flash column chromatography over silica gel (230–400 mesh ASTM). Organic extracts were dried over anhydrous $MgSO_4$ and the solvents were evaporated on a rotary evaporator under water aspirator pressure. IR spectra are reported in cm^{-1}. Mass spectra were obtained from the Korea Basic Science Institute (Gwangju branch). Melting points are uncorrected. The combustion analyses were carried out at Korea Research Institute of Chemical Technology, Taejon, Korea. The starting materials **2a–h** were prepared according to the published method from the acetates of the Baylis–Hillman adducts and aniline derivatives via the corresponding DABCO salts.[4] Identification of starting materials was carried out with their ^{1}H NMR and/or ^{13}C NMR spectra simply.

2.2. Typical procedure for the synthesis of quinolone 3a

A stirred mixture of **2a** (174 mg, 0.65 mmol) in PPA (2 g) was heated to 80–90 °C for 7 h. The reaction mixture was poured into cold water, extracted with EtOAc, washed with $NaHCO_3$ solution, drying with $MgSO_4$, removal of solvent, and after column chromatographic purification process

Table 2. Synthesis of indanones **5** and indenoindenones **6**

Entry	Substrate (%)[a]	Indanone **5** (%)[b]	Indenoindenone **6** (%)[b]
1	 **2e** (89)	 **5a** (57)	 **6a** (18)
2	 **2f** (91)	 **5b** (61)	 **6b** (13)
3	 **2g** (64)	 **5c** (59)	 **6c** (14)
4	 **2h** (85)	 **5d** (60)	 **6d** (17)

[a] The corresponding Baylis–Hillman acetate, aq THF, DABCO (1.1 equiv), 30 min, then aniline derivative (1 equiv), rt, 18 h.
[b] PPA, 80–90 °C. 15 h.

(hexanes/EtOAc = 3:2), we obtained **3a** as a yellow solid, 121 mg (79%). The spectroscopic data of prepared compounds are as follows.

2.2.1. Compound 3a. Yield 79%; yellow solid, mp 174–175 °C; IR (CH_2Cl_2) 3197, 1666, 1593, 1377 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.11 (d, J = 2.4 Hz, 2H), 6.88–7.19 (m, 4H), 7.34–7.47 (m, 5H), 7.90 (t, J = 2.4 Hz, 1H), 9.27 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 30.58, 115.52, 121.39, 123.12, 127.29, 127.69, 128.36, 128.71, 128.85, 130.16, 135.65, 136.31, 137.64, 166.30. Mass (70 eV) *m/z* (rel. intensity) 77 (32), 89 (27), 117 (32), 204 (16), 216 (36), 218 (32), 234 (100), 235 (M^+, 89). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.60; H, 5.61; N, 5.92.

2.2.2. Compound 3b. Yield 78%; yellow solid, mp 205–206 °C; IR (KBr) 1666, 1500 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 4.06 (d, J = 2.1 Hz, 2H), 6.89 (d, J = 8.4 Hz, 1H), 7.05 (m, 2H), 7.38–7.49 (m, 5H), 7.78 (t, J = 2.4 Hz, 1H), 10.01 (br s, 1H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 29.66, 116.05, 122.12, 126.21, 126.34, 126.62, 127.23, 128.01, 128.12, 129.27, 134.70, 135.08, 136.19, 164.39. Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 13.14. Found: C, 71.38; H, 4.59; N, 13.02.

2.2.3. Compound 3c. Yield 73%; yellow solid, mp 187–188 °C; IR (CH_2Cl_2) 3398, 1651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 4.11 (d, J = 2.1 Hz, 2H), 6.81 (dd, J = 7.8, 0.6 Hz, 1H), 6.96 (td, J = 7.8, 1.5 Hz, 1H), 7.12–7.38 (m, 6H), 7.86 (t, J = 2.4 Hz, 1H), 8.50 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.63, 30.65, 115.33, 121.46, 123.13, 127.62, 128.02, 128.43, 129.47, 130.29, 132.78, 136.18, 137.81, 139.16, 166.19. Mass (70 eV) *m/z* (rel. intensity) 116 (17), 232 (32), 249 (M^+, 100).

2.2.4. Compound 3d. Yield 80%; pale yellow solid, mp 207–208 °C; IR (KBr) 3359, 3186, 1674, 1597, 1493 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 4.05 (d, J = 2.7 Hz, 2H), 6.89–6.96 (m, 2H), 7.09–7.16 (m, 2H), 7.36–7.44 (m, 4H), 7.75 (t, J = 2.7 Hz, 1H), 9.66 (s, 1H); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 29.97, 114.92, 120.23, 122.12, 126.97, 127.56, 127.82, 128.27, 130.69, 133.55, 133.84, 134.66, 136.07, 164.54.

2.3. Typical procedure for the conversion of quinolone 3a into quinolinol 4a

To a stirred solution of **3a** (146 mg, 0.62 mmol) in THF (2 mL) was added DBU (9 mg, 0.06 mmol) and the reaction mixture was stirred at room temperature for 1 h. After the usual workup and column chromatographic purification process (hexanes/EtOAc = 1:1), desired **4a** was obtained, 136 mg (93%). The spectroscopic data of prepared compounds are as follows.

2.3.1. Compound 4a. Yield 93%; white solid, mp 196–197 °C (Lit.[6f] 199–200 °C); IR (CH_2Cl_2) 3467, 1658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03 (d, J = 0.9 Hz, 2H), 7.15 (td, J =

7.2, 1.2 Hz, 1H), 7.22–7.35 (m, 6H), 7.41–7.46 (m, 3H), 11.85 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.39, 115.78, 120.38, 122.64, 126.61, 127.50, 128.77, 129.64, 129.83, 133.70, 137.70, 137.73, 139.38, 164.22. Mass (70 eV) *m/z* (rel. intensity) 76 (25), 116 (35), 216 (27), 234 (100), 235 (M^+, 91). Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.85; H, 5.73; N, 5.87.

2.3.2. Compound 4b. Yield 92%; white solid, mp 235–236 °C; IR (KBr) 3155, 1674, 1485 cm^{-1}; ^{1}H NMR ($CDCl_3$+DMSO-d_6) δ 3.94 (s, 2H), 7.21–7.39 (m, 9H), 11.66 (s, 1H); ^{13}C NMR ($CDCl_3$+DMSO-d_6) δ 35.89, 116.69, 120.72, 126.12, 126.33, 126.80, 128.47, 129.24, 129.25, 135.10, 135.53, 136.26, 138.65, 162.71. Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 13.14. Found: C, 71.33; H, 4.45; N, 13.32.

2.3.3. Compound 4c. Yield 88%; white solid, mp 197–198 °C; IR (CH_2Cl_2) 1655, 1570, 1431 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 3.98 (s, 2H), 7.12–7.25 (m, 5H), 7.32–7.46 (m, 4H), 11.97 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.29, 35.93, 115.84, 120.42, 122.57, 127.44, 129.46, 129.52, 129.72, 133.90, 136.08, 136.23, 137.59, 137.70, 164.34. Mass (70 eV) *m/z* (rel. intensity) 77 (98), 123 (13), 216 (10), 232 (35), 249 (M^+, 100).

2.3.4. Compound 4d. Yield 89%; white solid, mp 221–222 °C; IR (KBr) 3302, 3155, 1670, 1570, 1489 cm^{-1}; ^{1}H NMR ($CDCl_3$+DMSO-d_6) δ 3.92 (s, 2H), 7.09–7.49 (m, 9H), 11.59 (s, 1H); ^{13}C NMR ($CDCl_3$+DMSO-d_6) δ 35.18, 115.05, 119.44, 121.70, 126.85, 128.19, 129.18, 130.31, 131.55, 132.68, 136.78, 137.63, 137.64, 162.62.

2.4. Typical procedure for the preparation of indanone 5a and indenoindenone 6a

A mixture of **2e** (218 mg, 0.78 mmol) and PPA (2 g) was heated to 80–90 °C for 15 h. The reaction mixture was poured into cold water, extracted with EtOAc, washed with $NaHCO_3$ solution, drying with $MgSO_4$, removal of solvent and after column chromatographic purification process (hexanes/EtOAc=2:1), we obtained **5a** (110 mg, 57%) and **6a** (35 mg, 18%). The spectroscopic data of prepared compounds are as follows.

2.4.1. Compound 5a. Yield 57%; yellow solid, mp 169–170 °C; IR (KBr) 3413, 3332, 1689, 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 3.72 (br s, 2H), 3.74 (d, J=1.8 Hz, 2H), 6.80 (d, J=7.8 Hz, 1H), 6.99 (dd, J=8.1, 0.9 Hz, 1H), 7.36–7.48 (m, 3H), 7.54 (t, J=2.4 Hz, 1H), 7.66 (d, J=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.83, 29.24, 119.82, 129.08, 129.30, 129.61, 130.67, 130.76, 133.24, 135.04, 135.56, 135.80, 135.93, 141.16, 193.66. Mass (70 eV) *m/z* (rel. intensity) 77 (12), 102 (28), 117 (47), 144 (29), 172 (26), 206 (30), 220 (24), 232 (27), 249 (M^+, 100). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.79; H, 6.13; N, 5.57.

2.4.2. Compound 5b. Yield 61%; yellow solid, mp 212–213 °C; IR (KBr) 3413, 3344, 1685, 1631, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.57 (br s, 2H), 3.76 (d, J=2.1 Hz, 2H), 3.92 (s, 3H), 6.73 (d, J=8.4 Hz, 1H), 6.91 (d, J=8.7 Hz, 1H), 7.36–7.48 (m, 3H), 7.61–7.68 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 29.56, 56.31, 111.04, 122.17, 126.71, 129.07, 129.58, 130.75, 133.17, 134.82, 135.78, 136.48, 136.97, 152.20, 192.53. Mass (70 eV) *m/z* (rel. intensity) 66 (10), 77 (30), 110 (32), 174 (100), 236 (41), 265 (M^+, 87). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.93; H, 5.92; N, 5.33.

2.4.3. Compound 5c. Yield 59%; yellow solid, mp 205–206 °C; IR (KBr) 3448, 3363, 1685, 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3H), 2.29 (s, 3H), 3.64 (s, 2H), 3.73 (br s, 2H), 7.20 (s, 1H), 7.34–7.47 (m, 3H), 7.59–7.65 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.65, 21.03, 29.45, 115.62, 127.12, 129.06, 129.62, 130.76, 133.04, 133.22, 135.31, 135.73, 136.04, 137.48, 141.40, 194.67. Mass (70 eV) *m/z* (rel. intensity) 123 (13), 220 (37), 263 (M^+, 100).

2.4.4. Compound 5d. Yield 60%; yellow solid, mp 166–167 °C; IR (KBr) 3397, 3328, 1685, 1631, 1504 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.54 (br s, 2H), 3.69 (s, 2H), 3.91 (s, 3H), 3.92 (s, 3H), 6.35 (s, 1H), 7.31–7.63 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 29.44, 56.14, 56.42, 94.61, 119.46, 125.55, 128.94, 129.20, 130.56, 131.68, 135.77, 135.91, 136.06, 153.14, 153.40, 191.24. Mass (70 eV) *m/z* (rel. intensity) 204 (32), 236 (12), 266 (68), 295 (M^+, 100).

2.4.5. Compound 6a. Yield 18%; yellow solid, mp 177–178 °C; IR (CH_2Cl_2) 3429, 3352, 1708, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 3H), 2.90–3.24 (m, 2H), 3.44 (br s, 2H), 3.60–3.68 (m, 1H), 5.01 (d, J=7.2 Hz, 1H), 6.48 (d, J=8.1 Hz, 1H), 6.89 (dd, J=7.8, 0.6 Hz, 1H), 7.34–7.39 (m, 1H), 7.54–7.60 (m, 1H), 7.74 (d, J=1.2 Hz, 1H), 7.77 (d, J=0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.44, 31.78, 51.47, 51.80, 114.45, 123.91, 124.53, 127.05, 127.24, 128.06, 130.22, 135.12, 136.28, 140.86, 142.45, 156.47, 208.59. Mass (70 eV) *m/z* (rel. intensity) 76 (18), 102 (32), 206 (30), 234 (28), 249 (M^+, 100). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.95; H, 6.00; N, 5.78.

2.4.6. Compound 6b. Yield 13%; yellow solid, mp 163–164 °C; IR (KBr) 3460, 3410, 3359, 1712, 1601, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.01–3.26 (m, 2H), 3.13–3.34 (br s, 2H), 3.58–3.66 (m, 1H), 3.87 (s, 3H), 5.11 (d, J=7.2 Hz, 1H), 6.50 (dd, J=8.4, 0.6 Hz, 1H), 6.58–6.61 (m, 1H), 7.34 (t, J=7.5 Hz, 1H), 7.57 (td, J=7.2, 1.2 Hz, 1H), 7.71 (d, J=7.5 Hz, 1H), 8.04 (dd, J=8.1, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.01, 50.22, 51.11, 55.65, 110.48, 114.83, 123.97, 127.94, 128.47, 129.48, 131.42, 135.17, 136.13, 136.55, 149.85, 157.27, 209.22. Mass (70 eV) *m/z* (rel. intensity) 76 (12), 83 (46), 96 (53), 110 (49), 165 (18), 204 (19), 222 (27), 250 (83), 265 (M^+, 100). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.03; H, 5.68; N, 5.31.

2.4.7. Compound 6c. Yield 14%; yellow solid, mp 173–174 °C; IR (KBr) 1712, 1647, 1466 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 3H), 2.25 (s, 3H), 3.05–3.24 (m, 2H), 3.54 (br s, 2H), 3.57–3.64 (m, 1H), 4.90 (d, J=7.5 Hz, 1H), 6.77 (s, 1H), 7.31–7.37 (m, 1H), 7.59–7.77 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 12.72, 21.10, 31.51, 51.31, 51.48, 115.96, 119.26, 124.19, 124.38, 125.90, 128.02, 135.45, 135.99, 136.69, 140.92, 141.02, 157.65, 209.36. Mass (70 eV) *m/z*

(rel. intensity) 108 (12), 202 (11), 220 (31), 246 (48), 263 (M^+, 100).

2.4.8. Compound 6d. Yield 17%; yellow solid, mp 179–180 °C; IR (KBr) 3433, 3359, 1705, 1600, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (br s, 2H), 3.03–3.10 (m, 1H), 3.18–3.27 (m, 1H), 3.59–3.67 (m, 1H), 3.82 (s, 3H), 3.89 (s, 3H), 5.07 (d, $J=7.2$ Hz, 1H), 6.37 (s, 1H), 7.33 (t, $J=7.2$ Hz, 1H), 7.57 (td, $J=7.2$, 1.23 Hz, 1H), 7.70 (d, $J=7.8$ Hz, 1H), 7.79–8.02 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 31.91, 49.60, 511.62, 56.00, 56.43, 95.73, 123.09, 124.01, 125.84, 127.87, 128.34, 129.46, 135.17, 136.08, 147.63, 149.00, 157.72, 209.29. Mass (70 eV) *m/z* (rel. intensity) 220 (11), 252 (14), 277 (82), 295 (M^+, 100).

2.4.9. Spectroscopic data of the intermediate 8 derived from 2h. Yield 29%, mp 68–69 °C; IR (CH_2Cl_2) 3448, 3363, 1732, 1597, 1504 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.12–3.16 (m, 1H), 3.18 (br s, 2H), 3.20–3.26 (m, 2H), 3.49 (s, 3H), 3.70 (s, 3H), 3.84 (s, 3H), 4.44 (d, $J=4.5$ Hz, 1H), 6.34 (s, 1H), 7.09–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 32.45, 52.22, 52.46, 53.71, 56.29, 56.62, 96.92, 124.52, 125.53, 126.37, 127.42, 128.41, 129.33, 145.04, 147.67, 148.92, 175.46. Mass (70 eV) *m/z* (rel. intensity) 133 (14), 165 (11), 252 (40), 327 (M^+, 100).

2.4.10. Spectroscopic data of the Claisen rearrangement intermediate 7 derived from 2b. The corresponding Claisen rearrangement intermediate **7** could be isolated in 40% yield, fortunately, when we carried out the reaction of **2b** in PPA (90 °C) in short time (60 min). This compound was prepared more effectively in 95% isolated yield when we carried out the reaction at low temperature in PPA (60 °C) for 80 min as a pale yellow solid,[10] mp 124–125 °C; IR (KBr) 3460, 3383, 3190, 1670, 1597, 1496 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.66 (s, 2H), 3.70 (br s, 2H), 3.79 (s, 3H), 6.61 (d, $J=8.4$ Hz, 1H), 6.87 (d, $J=2.4$ Hz, 1H), 6.99 (dd, $J=8.4$, 2.4 Hz, 1H), 7.25–7.43 (m, 5H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.75, 52.51, 116.97, 123.64, 125.57, 127.28, 128.07, 128.94, 129.21, 129.38, 129.52, 135.15, 142.04, 143.19, 168.59.

2.4.11. Spectroscopic data of the Claisen rearrangement intermediate 7 derived from 2e. The corresponding Claisen rearrangement intermediate **7** could be isolated in 39% yield when we carried out the reaction at low temperature in PPA (60 °C) for 60 min as a yellow solid,[11] mp 210–211 °C; IR (KBr) 1712, 1628, 1504 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3H), 3.57 (br s, 2H), 3.69 (s, 2H), 3.77 (s, 3H), 6.61 (d, $J=7.8$ Hz, 1H), 6.73 (s, 1H), 6.90 (d, $J=7.8$ Hz, 1H), 7.30–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.83, 28.74, 52.43, 116.07, 123.98, 127.89, 128.25, 128.74, 128.84, 128.99, 129.49, 130.46, 135.46, 141.38, 141.98, 168.95.

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10. The corresponding Claisen rearrangement intermediate **7** was prepared in 95% isolated yield when we carried out the reaction of **2b** in PPA at 60 °C for 80 min (see Section 2). This compound was converted to **3b** in 90% yield under the typical experimental conditions (PPA, 80–90 °C, 7 h).
11. The corresponding Claisen rearrangement intermediate **7** could be also prepared from **2e** in 39% yield (PPA, 60 °C, 60 min) together with **5a** (58%). For the spectroscopic data of the intermediate **7**, please see Section 2. This intermediate **7** was converted into **5a** (60%) and **6a** (15%) under the typical experimental conditions (PPA, 80–90 °C, 15 h).