

Synthesis of methyl 9-phenyl-7*H*-benzocycloheptene-6-carboxylates from Baylis–Hillman adducts: use of intramolecular Friedel–Crafts alkenylation reaction

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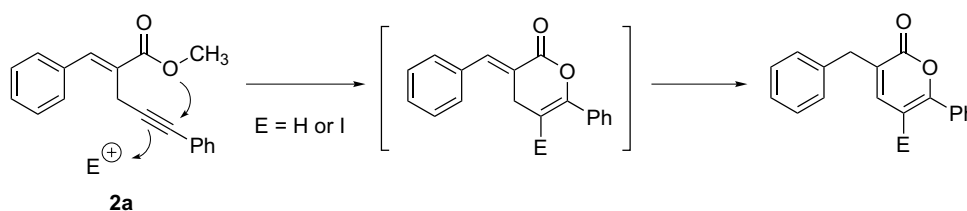
Abstract—We developed a facile synthetic method for 9-phenyl-7*H*-benzocycloheptene derivatives from the Baylis–Hillman adducts. Our method involved intramolecular Friedel–Crafts alkenylation reaction of triple bond-tethered methyl cinnamates. © 2004 Elsevier Ltd. All rights reserved.

Although Friedel–Crafts alkylation reactions have been extensively studied,¹ little has been known about the corresponding Friedel–Crafts alkenylation reaction with either an alkyne² or an alkenyl halide.^{3,4} A substituent that can stabilize the vinyl cation must be attached for the successful alkenylation with alkenyl halide.^{3,4} The reaction involving alkyne itself suffers from side reactions including polymerization.^{2c} Recently, successful intermolecular Friedel–Crafts alkenylation using zeolite HSZ-360,^{2a} GaCl₃,^{4c,d} M(OTf)_n (M = Sc, Zr, In)^{2c} have been reported. More recently, Reetz and Sommer reported the novel gold-catalyzed hydroarylation of alkynes.^{2b}

Low molecular weight α -pyrones have been shown to be potent HIV-1 protease inhibitors.⁵ Recently, Larock and Rossi have reported an elegant synthesis of iso-

coumarins and α -pyrones via electrophilic cyclization.⁶ We were stimulated by their works and envisioned that we could synthesize suitably substituted α -pyrone derivatives starting from the Baylis–Hillman adducts (Scheme 1). The requisite starting material **2a** was prepared from the reaction of Baylis–Hillman acetate **1a** and phenylethyne/magnesium bromide in THF at room temperature in the presence of CuI (10 mol%) in moderate yield.⁷ We expected that benzyl-substituted α -pyrones could be synthesized via the electrophile-promoted (e.g., I⁺ or H⁺) lactonization followed by proton transfer as shown in Scheme 1.

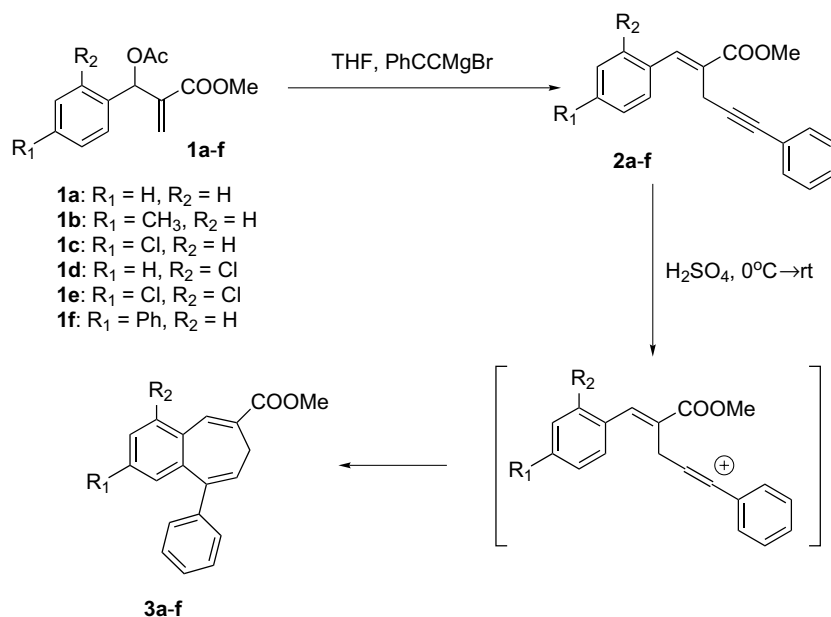
We examined the electrophile-promoted lactonization of **2a** under various reaction conditions including the use of iodine, iodine/LiI/AcOH, LiClO₄ and found that all conditions failed to give the desired pyrone derivative.⁶



Scheme 1.

Keywords: Baylis–Hillman adducts; Benzocycloheptene; Friedel–Crafts alkenylation.

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Scheme 2.

However, when we treated the starting material **2a** with H₂SO₄ in CH₂Cl₂ we obtained methyl 9-phenyl-7H-benzocycloheptenecarboxylate (**3a**)^{8,9} as the major product (41%) and hydration product as the minor product (10%).¹⁰ For the hydration reaction, complete regio-

selectivity was observed to produce methyl 2-(3-oxo-3-phenylpropyl)cinnamate.

As shown in Scheme 2 and in Table 1, starting materials **2b–f** and the desired final products **3b–f** were synthesized

Table 1. Synthesis of 9-substituted-7H-benzocycloheptene derivatives 3

Entry	Conditions	2	Conditions	3
1	1a , THF, PhCCMgBr (1.5 equiv), CuI (10 mol%), 0°C → rt, 8 h		CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0°C → rt, 12 h	
2	1b , THF, PhCCMgBr (1.3 equiv), CuI (10 mol%), 0°C → rt, 12 h		CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0°C → rt, 12 h	
3	1c , THF, PhCCMgBr (1.5 equiv), CuI (10 mol%), 0°C → rt, 8 h		CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0°C → rt, 12 h	
4	1d , THF, PhCCMgBr (1.5 equiv), 0°C → rt, 8 h		CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0°C → rt, 9 h	
5	1e , THF, PhCCMgBr (1.3 equiv), CuI (10 mol%), 0°C → rt, 8 h		CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0°C → rt, 8 h	

Table 1 (continued)

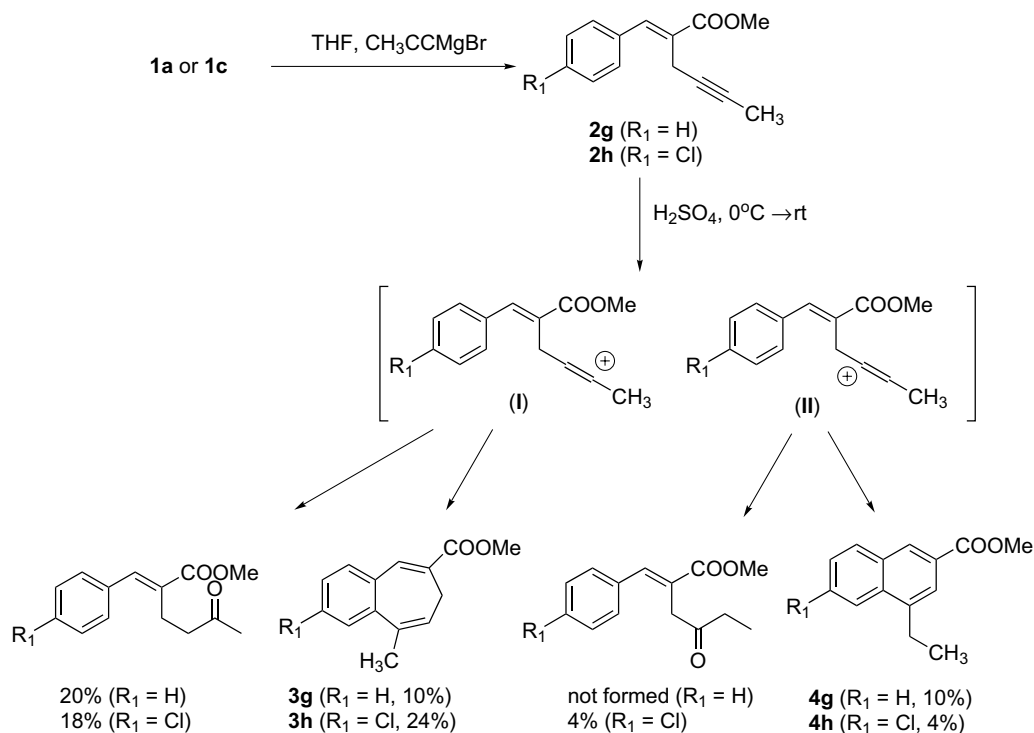
Entry	Conditions	2	Conditions	3
6	1f , THF, PhCCMgBr (1.8 equiv), 0 °C → rt, 8 h	 2f (63%)	CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0 °C → rt, 8 h	 3f (56%)
7	1a , THF, CH ₃ CCMgBr (1.3 equiv), 0 °C → rt, 7 h	 2g (75%)	CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0 °C → rt, 16 h	 3g (10%) ^b
8	1c , THF, CH ₃ CCMgBr (1.4 equiv), 0 °C → rt, 7 h	 2h (60%)	CH ₂ Cl ₂ , H ₂ SO ₄ (1.2 equiv), 0 °C → rt, 12 h	 3h (24%) ^b

^a Hydration product was isolated in about 10% yield.

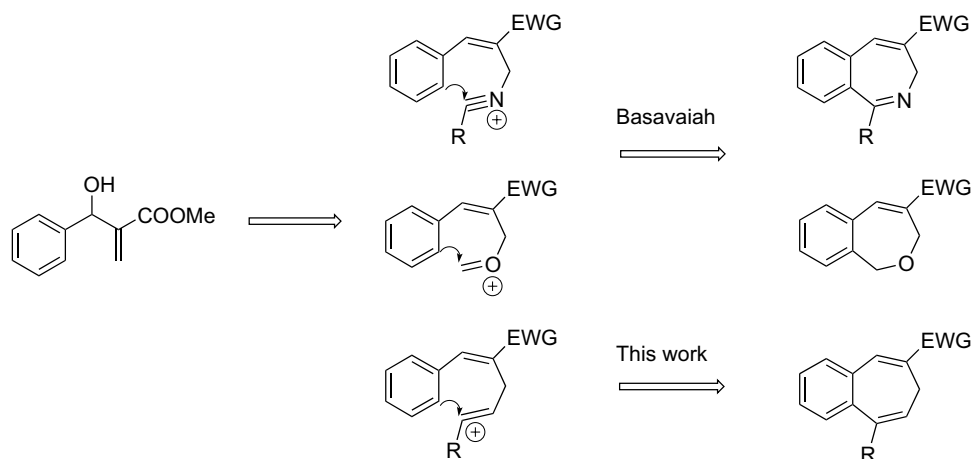
^b See text and Scheme 3.

without any problems in moderate yields.^{9,10} The reaction mechanism (Scheme 2) involved the selective formation of vinyl cation at the benzylic site following intramolecular Friedel–Crafts alkenylation. The arene moieties of **2a–f** are in electron-deficient state due to the electron withdrawing conjugated ester moiety. The highly electron-deficient arene moiety of **2e** underwent the cyclization in a similar yield, very interestingly. In these reactions, we cannot detect nor isolate the corresponding naphthalene derivatives (vide infra), which might be produced via the regioisomeric vinyl cationic

intermediate. In some cases, we isolated the hydration product during the conversion of **2** into **3** (vide supra).¹⁰ But, as mentioned above, one form of regioisomeric hydration product was isolated as the sole product due to the selective formation of vinylic cation at the benzylic site. This meant that the vinylic cation at the benzylic site would be much more stable than the other regioisomeric vinyl cation. As a next trial, we carried out the reaction of **2a** in benzene in order to examine the relative reactivities between the intramolecular seven-membered ring formation and the intermolecular



Scheme 3.



Scheme 4.

Friedel–Crafts alkenylation with benzene. In the reaction, we could isolate the benzocycloheptene derivative **3a** as the sole product although the yield is lower than the reaction in CH_2Cl_2 . When we used $\text{Sc}(\text{OTf})_3$ in dichloroethane^{2c} instead of H_2SO_4 we could obtain similar results (benzocycloheptene derivative as the major product and trace amounts of hydration product).

When we tried the same reaction with methyl group-substituted starting materials **2g** and **2h** (prepared by 1-propynylmagnesium bromide), competitions were observed. Two types of vinyl cations might be formed (**I** and **II** in Scheme 3), and the reactions produced mixtures of products, namely, benzocycloheptene derivatives (**3g** and **3h**) and naphthalene derivatives (**4g** and **4h**) and two kinds of hydration products in a variable ratio.¹¹ These results can be expected generally when we consider the comparable stabilities of two vinyl cations **I** and **II**.

Recently, Basavaiah and co-workers have reported the synthesis of 2-benzazepines and 2-benzoxepines from the Baylis–Hillman adducts.¹² Our synthesis of 7H-benzocycloheptene derivatives is a carbon surrogate of Basavaiah's syntheses (Scheme 4) as well as a new achievement of our chemical transformations of the Baylis–Hillman adducts.¹³

In summary, we developed a facile synthetic method of 7H-benzocycloheptene derivatives. Our synthetic scheme involved the novel intramolecular Friedel–Crafts alkenylation reaction with electron-deficient arene moiety. We are currently studying the feasibility for the synthesis of further-reduced benzocycloheptene derivatives by the reaction of Baylis–Hillman acetate and styrene under the similar reaction conditions.

Acknowledgements

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data was obtained from the Korea Basic Science Institute, Kwangju branch.

References and notes

- For reviews of Friedel–Crafts alkylation reactions, see: (a) Olah, G. A. In *Friedel–Crafts and Related Reactions*; Wiley-Interscience: New York, 1964; Vol. II, part 1; (b) Olah, G. A.; Krishnamurti, R.; Prakash, G. K. S. In *Friedel–Crafts Alkylations in Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991.
- Friedel–Crafts alkenylation of arenes using alkynes, see: (a) Sartori, G.; Bigi, F.; Pastorio, A.; Porta, C.; Arienti, A.; Maggi, R.; Moretti, N.; Gnappi, G. *Tetrahedron Lett.* **1995**, 36, 9177; (b) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485; (c) Tsuchimoto, T.; Maeda, T.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* **2000**, 1573; (d) Asao, N.; Shimada, T.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2001**, 123, 10899; (e) Inoue, H.; Chatani, N.; Murai, S. *J. Org. Chem.* **2002**, 67, 1414; (f) Martin-Matute, B.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, 125, 5757, and references cited therein.
- For alkenylation of arenes via vinyl cation trapping, see: (a) Takeda, T.; Kanamori, F.; Matsusita, H.; Fujiwara, T. *Tetrahedron Lett.* **1991**, 32, 6563; (b) Gronheid, R.; Lodder, G.; Okuyama, T. *J. Org. Chem.* **2002**, 67, 693; (c) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Rappoport, Z. *J. Org. Chem.* **1982**, 47, 5003.
- For other alkenylation of arenes, see: (a) Ishikawa, T.; Okano, M.; Aikawa, T.; Saito, S. *J. Org. Chem.* **2001**, 66, 4635; (b) Sangu, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2004**, 6, 353; (c) Yamaguchi, M.; Kido, Y.; Hayashi, A.; Hiram, M. *Angew. Chem., Int. Ed.* **1997**, 36, 1313; (d) Kido, Y.; Yoshimura, S.; Yamaguchi, M.; Uchimar, T. *Bull. Chem. Soc. Jpn.* **1999**, 72, 1445; (e) Barluenga, J.; Rodriguez, M. A.; Gonzalez, J. M.; Campos, P. J. *Tetrahedron Lett.* **1990**, 31, 4207.
- Vara Prasad, J. V. N.; Para, K. S.; Lunney, E. A.; Ortwine, D. F.; Dunbar, J. B.; Ferguson, D.; Tummino, P. J.; Hupe, D.; Tait, B. D.; Domagala, J. M.; Humblet, C.; Bhat, T. N.; Liu, B.; Guerin, D. A. M.; Baldwin, E. T.; Erickson, J. W.; Sawyer, T. K. *J. Am. Chem. Soc.* **1994**, 116, 6989.
- Synthesis of isocoumarins and α -pyrones from acetylenic compounds, see: (a) Rossi, R.; Carpita, A.; Bellina, F.;

- Stabile, P.; Mannina, L. *Tetrahedron* **2003**, *59*, 2067; (b) Yao, T.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5936; (c) Yao, T.; Larock, R. C. *Tetrahedron Lett.* **2002**, *43*, 7401; (d) Larock, R. C.; Doty, M. J.; Han, X. *J. Org. Chem.* **1999**, *64*, 8770; (e) Biagetti, M.; Bellina, F.; Carpita, A.; Stabile, P.; Rossi, R. *Tetrahedron* **2002**, *58*, 5023; (f) Oliver, M. A.; Gandour, R. D. *J. Org. Chem.* **1984**, *49*, 558.
7. In some cases, the purified compounds **2** have some inseparable impurities and made the next step problematic. In those cases (entries 1–3 and entry 5) we used CuI (10 mol%) during the preparation of **2** and we could obtain pure compounds.
8. For the chemistry of benzocycloheptene and related systems, see: (a) Perron-Sierra, F.; Dizier, D. S.; Bertrand, M.; Genton, A.; Tucker, G. C.; Casara, P. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 3291; (b) Kirmse, W.; Sluma, H.-D. *J. Org. Chem.* **1988**, *53*, 763; (c) Bonvallet, P. A.; Todd, E. M.; Kim, Y. S.; McMahan, R. J. *J. Org. Chem.* **2002**, *67*, 9031; (d) Ewing, G. D.; Paquette, L. A. *J. Org. Chem.* **1975**, *40*, 2965; (e) Battye, P. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1458; (f) Saito, K.; Ishihara, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2664; (g) Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 6798; (h) Saito, K.; Ishihara, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4447; (i) Kryczka, B.; Descotes, G. *Bull. Pol. Acad. Sci.* **1986**, *33*, 475; (j) Buu-Hoi, N. P.; Jacquignon, P.; Roussel, O. *Bull. Soc. Chim. Fr.* **1962**, 1652; (k) Huisgen, R.; Juppe, G. *Chem. Ber.* **1961**, *94*, 2332.
9. Synthesis of **2a** as a typical procedure: To a stirred solution of the Baylis–Hillman acetate **1a** (234 mg, 1 mmol) in dry THF (2 mL) was added CuI (20 mg, 10 mol%). To the reaction mixture was added dropwise the solution of phenylethynylmagnesium bromide (1 M solution in THF, 1.5 mL, 1.5 mmol) at 0 °C and stirred further at room temperature for 8 h. After usual aqueous workup process and column chromatographic purification process (hexanes/ether, 99:1) we obtained the desired products **2a** as an oil, 141 mg (51%). The other compounds were synthesized similarly and the spectroscopic data are as follows. **2a**: IR (neat) 2950, 1712, 1273, 1219 cm⁻¹; ¹H NMR (CDCl₃) δ 3.61 (s, 2H), 3.88 (s, 3H), 7.24–7.61 (m, 10H), 7.81 (s, 1H); ¹³C NMR (CDCl₃) δ 18.76, 52.35, 80.94, 87.09, 123.59, 127.69, 127.79, 128.14, 128.63, 129.04, 129.72, 131.71, 134.94, 140.72, 167.73; Mass (70 eV) *m/z* (rel. intensity) 115 (56), 202 (47), 215 (100), 261 (30), 276 (M⁺, 19). **2b**: ¹H NMR (CDCl₃) δ 2.38 (s, 3H), 3.61 (s, 2H), 3.86 (s, 3H), 7.23–7.51 (m, 9H), 7.78 (s, 1H); ¹³C NMR (CDCl₃) δ 18.79, 21.41, 52.29, 80.87, 87.25, 123.68, 126.78, 127.77, 128.15, 129.39, 129.86, 131.73, 132.12, 139.34, 140.81, 167.89; Mass (70 eV) *m/z* (rel. intensity) 43 (100), 115 (8), 215 (10), 290 (M⁺, 1). **2c**: ¹H NMR (CDCl₃) δ 3.58 (s, 2H), 3.88 (s, 3H), 7.25–7.55 (m, 9H), 7.75 (s, 1H); ¹³C NMR (CDCl₃) δ 18.71, 52.43, 81.25, 86.63, 123.41, 127.91, 128.18, 128.26, 128.91, 131.02, 131.69, 133.35, 135.10, 139.37, 167.47. **2d**: IR (neat) 2951, 1720, 1288, 1211 cm⁻¹; ¹H NMR (CDCl₃) δ 3.50 (s, 2H), 3.88 (s, 3H), 7.23–7.70 (m, 9H), 7.90 (s, 1H); ¹³C NMR (CDCl₃) δ 18.82, 52.29, 81.18, 86.75, 123.39, 126.72, 127.75, 128.06, 129.52 (2C), 130.01, 130.36, 131.56, 133.42, 134.17, 137.42, 166.98; Mass (70 eV) *m/z* (rel. intensity) 107 (52), 115 (73), 215 (100), 275 (29), 310 (M⁺, 10), 312 (M⁺+2, 3). **2e**: ¹H NMR (CDCl₃) δ 3.48 (s, 2H), 3.89 (s, 3H), 7.19–7.41 (m, 6H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.82 (s, 1H); ¹³C NMR (CDCl₃) δ 18.95, 52.54, 81.58, 86.45, 123.35, 127.27, 127.98, 128.22, 129.58, 130.19, 131.27, 131.68, 132.10, 135.07, 135.43, 136.41, 166.93. **2f**: IR (neat) 1712, 1277, 1208 cm⁻¹; ¹H NMR (CDCl₃) δ 3.66 (s, 2H), 3.89 (s, 3H), 7.24–7.64 (m, 10H), 7.68 (s, 4H), 7.85 (s, 1H); ¹³C NMR (CDCl₃) δ 18.86, 52.36, 81.05, 87.06, 123.58, 127.06, 127.27, 127.57, 127.74, 127.81, 128.16, 128.88, 130.35, 131.72, 133.88, 140.23, 140.33, 141.82, 167.74; Mass (70 eV) *m/z* (rel. intensity) 115 (100), 165 (50), 293 (66), 337 (37), 352 (M⁺, 30). **2g**: ¹H NMR (CDCl₃) δ 1.82 (t, *J* = 2.4 Hz, 3H), 3.32 (q, *J* = 2.4 Hz, 2H), 3.86 (s, 3H), 7.32–7.56 (m, 5H), 7.73 (s, 1H); ¹³C NMR (CDCl₃) δ 3.70, 18.06, 52.25, 76.22, 76.25, 128.43, 128.54, 128.90, 129.67, 135.02, 140.04, 167.86. **2h**: IR (neat) 1716, 1281, 1219 cm⁻¹; ¹H NMR (CDCl₃) δ 1.81 (t, *J* = 2.7 Hz, 3H), 3.28 (q, *J* = 2.7 Hz, 2H), 3.86 (s, 3H), 7.37–7.50 (m, 4H), 7.66 (s, 1H); ¹³C NMR (CDCl₃) δ 3.67, 18.00, 52.33, 75.85, 76.58, 128.80, 128.93, 130.98, 133.39, 134.91, 138.69, 167.59; Mass (70 eV) *m/z* (rel. intensity) 43 (100), 153 (79), 189 (35), 213 (23), 248 (M⁺, 22). Synthesis of **3a** as a typical procedure: To a stirred solution of the acetylenic compound **2a** (276 mg, 1 mmol) in CH₂Cl₂ (5 mL) was added H₂SO₄ (12 mg, 1.2 mmol) at 0 °C and stirred at room temperature for 8 h. After usual aqueous workup process and column chromatographic purification process (hexanes/ether, 99:1) we obtained the desired products **3a** as an oil, 113 mg (41%). The other compounds were synthesized similarly and the spectroscopic data are as follows. **3a**: IR (neat) 1712, 1277, 1203 cm⁻¹; ¹H NMR (CDCl₃) δ 2.78 (d, *J* = 7.5 Hz, 2H), 3.83 (s, 3H), 6.12 (t, *J* = 7.5 Hz, 1H), 7.13–7.59 (m, 9H), 7.77 (s, 1H); ¹³C NMR (CDCl₃) δ 24.93, 52.13, 126.58, 127.16, 127.21, 127.58, 128.09, 129.01, 130.24, 131.15, 132.38, 136.11, 137.65, 139.57, 141.78, 142.91, 166.65; Mass (70 eV) *m/z* (rel. intensity) 43 (100), 202 (1), 215 (2), 275 (M⁺-1, 1). **3b**: IR (neat) 1709, 1277, 1200 cm⁻¹; ¹H NMR (CDCl₃) δ 2.29 (s, 3H), 2.77 (d, *J* = 7.5 Hz, 2H), 3.82 (s, 3H), 6.09 (t, *J* = 7.5 Hz, 1H), 7.07–7.41 (m, 8H), 7.75 (s, 1H); ¹³C NMR (CDCl₃) δ 21.38, 24.96, 52.05, 127.07, 127.38, 127.76, 128.07, 128.98, 130.25, 131.32, 131.36, 133.58, 137.23, 137.79, 139.46, 141.68, 143.03, 166.72; Mass (70 eV) *m/z* (rel. intensity) 43 (100), 107 (53), 215 (45), 231 (24), 290 (M⁺, 25). **3c**: ¹H NMR (CDCl₃) δ 2.78 (d, *J* = 7.5 Hz, 2H), 3.83 (s, 3H), 6.14 (t, *J* = 7.5 Hz, 1H), 7.12–7.45 (m, 8H), 7.71 (s, 1H); ¹³C NMR (CDCl₃) δ 24.91, 52.20, 126.93, 127.48, 128.30, 128.54, 128.94, 130.68, 131.60, 132.65, 133.07, 134.53, 136.58, 140.93, 141.10, 142.14, 166.38; Mass (70 eV) *m/z* (rel. intensity) 94 (59), 107 (92), 251 (23), 310 (M⁺, 21), 312 (M⁺+2, 8). **3d**: IR (neat) 1712, 1269, 1203 cm⁻¹; ¹H NMR (CDCl₃) δ 2.75 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 6.22 (t, *J* = 7.5 Hz, 1H), 7.11–7.44 (m, 8H), 7.97 (s, 1H); ¹³C NMR (CDCl₃) δ 25.12, 52.25, 127.32, 127.64, 127.73, 128.17, 128.88, 129.56, 129.64, 133.20, 133.54, 133.90, 134.40, 141.20, 141.36, 142.46, 166.25; Mass (70 eV) *m/z* (rel. intensity) 94 (55), 107 (100), 215 (99), 251 (26), 310 (M⁺, 18), 312 (M⁺+2, 8). **3e**: IR (neat) 2962, 1716, 1265, 1092 cm⁻¹; ¹H NMR (CDCl₃) δ 2.75 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 6.24 (t, *J* = 7.5 Hz, 1H), 7.10–7.45 (m, 7H), 7.89 (s, 1H); ¹³C NMR (CDCl₃) δ 25.15, 52.36, 127.65, 127.72, 128.40, 128.85, 129.34, 130.53, 132.42, 132.47, 132.93, 133.81, 135.18, 140.46, 141.75, 142.31, 166.04; Mass (70 eV) *m/z* (rel. intensity) 106 (81), 215 (100), 249 (53), 285 (36), 344 (M⁺, 41), 346 (M⁺+2, 29). **3f**: IR (neat) 1709, 1277, 1207 cm⁻¹; ¹H NMR (CDCl₃) δ 2.83 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 6.16 (t, *J* = 7.5 Hz, 1H), 7.18–7.58 (m, 13H), 7.81 (s, 1H); ¹³C NMR (CDCl₃) δ 25.04, 52.13, 125.41, 127.13, 127.23, 127.58, 127.66, 128.17, 128.75, 128.95, 129.63, 130.84, 132.20, 135.15, 137.42, 139.84, 139.96, 140.24, 141.78, 142.77, 166.62; Mass (70 eV) *m/z* (rel. intensity) 91 (56), 144 (67), 215 (49), 293 (82), 352 (M⁺, 100). **3g**: ¹H NMR (CDCl₃) δ 2.13 (s, 3H), 2.61 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 5.86 (t, *J* = 7.2 Hz, 1H), 7.31–7.63 (m, 4H), 7.66 (s, 1H). **3h**: ¹H NMR (CDCl₃) δ

- 2.11 (s, 3H), 2.61 (d, $J = 7.2$ Hz, 2H), 3.83 (s, 3H), 5.87 (t, $J = 7.2$ Hz, 1H), 7.28–7.56 (m, 3H), 7.59 (s, 1H).
10. During the synthesis of **3a**, the corresponding acid-catalyzed hydration product, methyl 2-(3-oxo-3-phenylpropyl)cinnamate, was isolated in about 10% yield; ^1H NMR (CDCl_3) δ 2.95–3.01 (m, 2H), 3.20–3.26 (m, 2H), 3.84 (s, 3H), 7.30–7.59 (m, 8H), 7.77 (s, 1H), 7.98 (d, $J = 8.4$ Hz, 2H).
11. Spectroscopic data of naphthalenes **4g–h** and hydration products are as follows. The R_f values of benzocycloheptenes and naphthalenes were similar, thus we separated them together. The two types of hydration products also have similar R_f values and we separated them together. **4g**: ^1H NMR (CDCl_3) δ 1.41 (t, $J = 7.5$ Hz, 3H), 3.14 (q, $J = 7.5$ Hz, 2H), 3.98 (s, 3H), 7.50–7.65 (m, 2H), 7.93 (s, 1H), 7.96 (d, $J = 8.7$ Hz, 1H), 8.80 (d, $J = 8.1$ Hz, 1H), 8.47 (s, 1H). **4h**: ^1H NMR (CDCl_3) δ 1.40 (t, $J = 7.2$ Hz, 3H), 3.10 (q, $J = 7.2$ Hz, 2H), 3.98 (s, 3H), 7.50–8.05 (m, 4H), 8.43 (s, 1H). Methyl 2-(3-oxobutyl)cinnamate: ^1H NMR (CDCl_3) δ 2.15 (s, 3H), 2.65–2.71 (m, 2H), 2.77–2.84 (m, 2H), 3.82 (s, 3H), 7.30–7.42 (m, 5H), 7.72 (s, 1H).
- Methyl *p*-chloro-2-(3-oxobutyl)cinnamate: ^1H NMR (CDCl_3) δ 2.15 (s, 3H), 2.63–2.70 (m, 2H), 2.75–2.81 (m, 2H), 3.82 (s, 3H), 7.25–7.42 (m, 5H), 7.65 (s, 1H). Methyl *p*-chloro-2-(2-oxobutyl)cinnamate: ^1H NMR (CDCl_3) δ 1.10 (t, $J = 7.5$ Hz, 3H), 2.57 (q, $J = 7.5$ Hz, 2H), 3.56 (s, 2H), 3.80 (s, 3H), 7.21–7.37 (m, 4H), 7.86 (s, 1H).
12. For the construction of fused seven-membered rings from the Baylis–Hillman adducts, see: (a) Basavaiah, D.; Satyanarayana, T. *Chem. Commun.* **2004**, 32; (b) Basavaiah, D.; Sharada, D. S.; Veerendhar, A. *Tetrahedron Lett.* **2004**, 45, 3081.
13. For our recent publications on the Baylis–Hillman reaction, see: (a) Kim, J. M.; Lee, K. Y.; Lee, S.-K.; Kim, J. N. *Tetrahedron Lett.* **2004**, 45, 2805; (b) Lee, K. Y.; Kim, J. M.; Kim, J. N. *Tetrahedron Lett.* **2003**, 44, 6737; (c) Kim, J. N.; Kim, J. M.; Lee, K. Y. *Synlett* **2003**, 821; (d) Im, Y. J.; Lee, C. G.; Kim, H. R.; Kim, J. N. *Tetrahedron Lett.* **2003**, 44, 2987; (e) Lee, K. Y.; Kim, J. M.; Kim, J. N. *Synlett* **2003**, 357; (f) Kim, J. N.; Lee, H. J.; Lee, K. Y.; Gong, J. H. *Synlett* **2002**, 173; (g) Lee, K. Y.; Kim, J. M.; Kim, J. N. *Tetrahedron* **2003**, 59, 385, and references cited therein.