# Synthesis of 3,5-Diarylcyclohex-2-enones by $NH_4Cl$/HCl-Catalyzed Cyclization and Deacetylation of 4-Acetylhexane-1,5-diones

by **Hayreddin Gezegen** and **Mustafa Ceylan***

Department of Chemistry, Faculty of Arts and Sciences, Gaziosmanpasa University, TR-60250 Tokat (phone: +90-356-2521616; fax: +90-356-2521585; e-mail: mustafac.ceylan@gop.edu.tr)

A new route for the synthesis of 3,5-diarylcyclohex-2-enones is reported. The 4-acetyl-1,3-diarylhexane-1,5-diones were obtained by the addition of pentane-2,4-dione to chalcones. The reaction of 4-acetyl-1,3-diarylhexane-1,5-diones with $NH_4Cl$/HCl in EtOH under reflux conditions gave the 3,5-diarylcyclohex-2-enones in good yields. All synthesized compounds were characterized by spectroscopic methods ($^1$H-, $^{13}$C-NMR, and IR), and elemental analyses.

**Introduction.** – Cyclohexenones are rarely found in nature, and isolated from fungi, bacteria, worms, and mushrooms [1]. They have important biological properties such as antibacterial and antitumor activities [2][3]. Several reports have pointed out the importance of cyclohexenones, and their antimicrobial and antitubercular activities [4]. Moreover, cyclohexenone derivatives are also well-known as lead structures for the treatment of inflammation and autoimmune diseases [5][6]. On the other hand, cyclohexenones are useful and important building blocks in synthetic organic chemistry. Therefore, they have been used in the synthesis of many polyfunctional, bioactive compounds and natural products. For example, methyl and ethyl 3,5-diarylcyclohex-2-enone carboxylates are quite important starting compounds [7] for the syntheses of benzoselenadiazoles, benzothiadiazoles [8], benzopyrazoles and benzisoxazoles [9][10], or carbazole derivatives [11].

Generally, 3,5-diarylcyclohexenones are prepared by addition of ethyl and methyl acetoacetate to $\alpha,\beta$-unsaturated compounds (such as chalcone), followed by cyclization and decarboxylation.

Herein, we report a simple and effective procedure for the synthesis of 3,5-diarylcyclohex-2-enones **1a**–**1j** starting from chalcones **2a**–**2j**. The 1,5-dicarbonyl compounds **3a**–**3j** were obtained from the *Michael* addition of pentane-2,4-dione (**4**) to chalcones **2a**–**2j** followed by their conversion to 3,5-diarylcyclohex-2-enones **1a**–**1j**, by catalysis with $NH_4Cl$ in acidic media, in high yields.

**Results and Discussion.** – The chalcone derivatives **2a**–**2j** were easily obtained by the *Claisen–Schmidt* condensation [12][13]. The reaction of substituted acetophenones, furan-2-yl and thiophen-2-yl methyl ketone with substituted benzaldehydes and thiophene-2-carbaldehyde in ethanolic NaOH at room temperature afforded the chalcone derivatives **2a**–**2j** in high yields (> 80%). The structure elucidations of **2a**–**2j** were achieved by $^1$H- and $^{13}$C-NMR spectroscopy in accordance with literature [14–19].

Then, compounds **2a**–**2j** were submitted to *Michael* addition [20] (*Scheme 1*). The addition reaction of pentane-2,4-dione (**4**) with **2a**–**2j** was accomplished with $^t$BuOK (5 mol-%) in the presence of benzyltriethylammonium chloride (PTC; 10 mol-%) as phase transfer catalyst in $CH_2Cl_2$ at room temperature and furnished **3a**–**3j**, respectively, in yields ranging from 75 to 86% (*Table 1*).

First, the synthesis of tetrasubstituted pyridine derivatives has been attempted. Cyclization of 1,5-dicarbonyl compounds with $AcONH_4$ is a well-known procedure for the synthesis of pyridine derivatives [21][22]. Therefore, **3a**–**3j** were reacted with $AcONH_4$ in AcOH under reflux conditions. The reactions resulted in low

Scheme 1. *Synthesis of Cyclohex-2-enone Derivatives* **1a**–**1j**

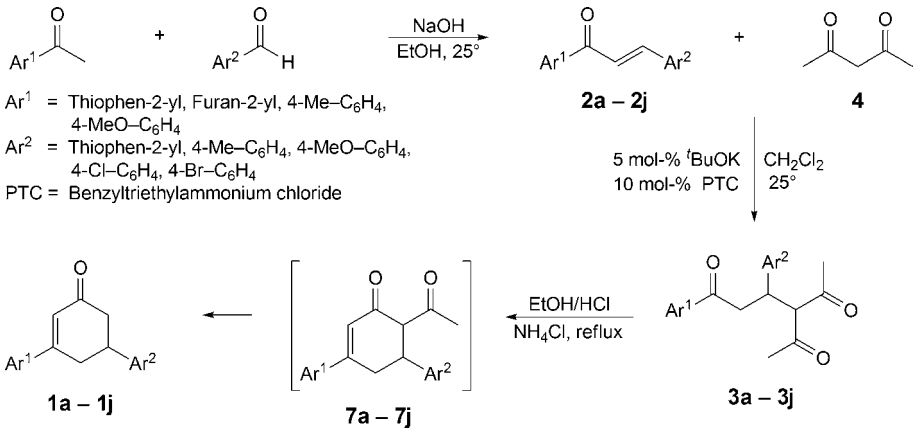
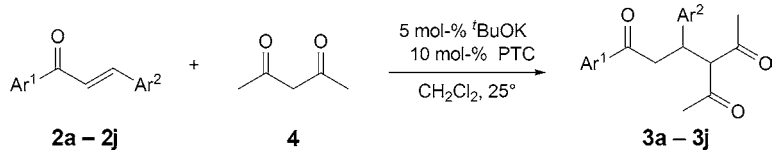



Table 1. Michael *Addition of Pentane-2,4-dione* (**4**) *to Chalcones* **2a**–**2j**[a])



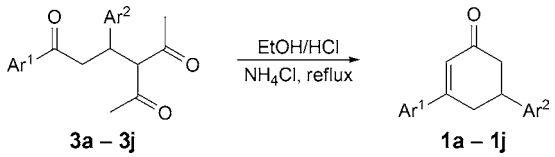

| *Entry* | $Ar^1$ | $Ar^2$ | Product | Yield [%] |
|---|---|---|---|---|
| *1* | Thiophen-2-yl | Thiophen-2-yl | **3a** | 86 |
| *2* | Furan-2-yl | Thiophen-2-yl | **3b** | 76 |
| *3* | Thiophen-2-yl | 4-Me–$C_6H_4$ | **3c** | 84 |
| *4* | Thiophen-2-yl | 4-MeO–$C_6H_4$ | **3d** | 85 |
| *5* | 4-MeO–$C_6H_4$ | Thiophen-2-yl | **3e** | 81 |
| *6* | 4-Me–$C_6H_4$ | Thiophen-2-yl | **3f** | 75 |
| *7* | 4-MeO–$C_6H_4$ | 4-Br–$C_6H_4$ | **3g** | 78 |
| *8* | 4-MeO–$C_6H_4$ | 4-Cl–$C_6H_4$ | **3h** | 77 |
| *9* | 4-MeO–$C_6H_4$ | 4-MeO–$C_6H_4$ | **3i** | 79 |
| *10* | 4-MeO–$C_6H_4$ | 4-Me–$C_6H_4$ | **3j** | 81 |

[a]) Reaction conditions: chalcone **2** (1.0 mmol), pentane-2,4-dione (**4**; 1.2 mmol), $CH_2Cl_2$ (2 ml), 4 h.

conversions and mixtures of products in low yields, whereupon the reactions were run with $NH_4Cl$ in strongly acidic media (*Scheme 1*). Unexpectedly, the reaction of **3a**–**3j** (1 mmol) with $NH_4Cl$ (4 mmol) and HCl (10 ml) in EtOH (5 ml) resulted in the direct formation of 3,5-diarylcyclohex-2-enone derivatives **1a**–**1j** under reflux conditions (*Table 2*).

The proposed mechanism for the formation of **1a**–**1j** is depicted in *Scheme 2*. The 1,3-dicarbonyl moiety of **3a**–**3j** is transformed in the presence of HCl to enol forms **5a**–**5j**, respectively The intramolecular attack of enol form at the C=O group leads to cyclic products **6a**–**6j**, respectively. Loss of $H_2O$ from **6a**–**6j** provides **7a**–**7j**. Finally, **1a**–**1j** are formed by deacetylation of **7a**–**7j**, respectively, *via* the ammonolysis reaction.

Table 2. *Cyclization of 4-Acetyl 1,5-Diones* **3a**–**3j**[a])

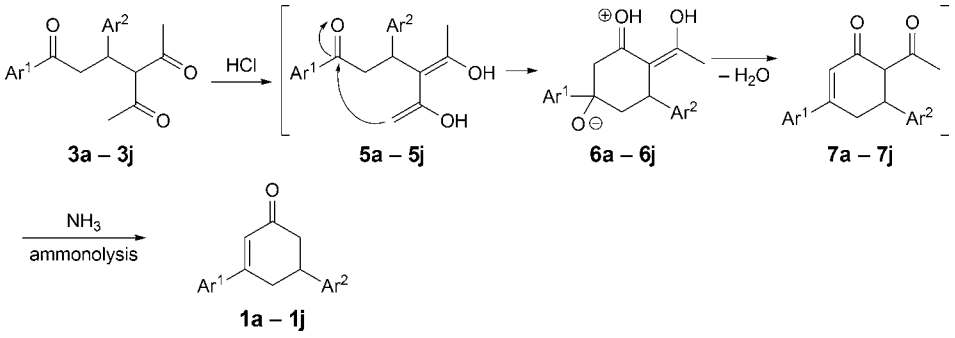



**3a – 3j** **1a – 1j**

| *Entry* | $Ar^1$ | $Ar^2$ | Product | Yield [%][b]) |
|---|---|---|---|---|
| *1* | Thiophen-2-yl | Thiophen-2-yl | **1a** | 94 |
| *2* | Furan-2-yl | Thiophen-2-yl | **1b** | 72 |
| *3* | Thiophen-2-yl | 4-Me–$C_6H_4$ | **1c** | 92 |
| *4* | Thiophen-2-yl | 4-MeO–$C_6H_4$ | **1d** | 90 |
| *5* | 4-MeO–$C_6H_4$ | Thiophen-2-yl | **1e** | 95 |
| *6* | 4-Me–$C_6H_4$ | Thiophen-2-yl | **1f** | 90 |
| *7* | 4-MeO–$C_6H_4$ | 4-Br–$C_6H_4$ | **1g** | 86 |
| *8* | 4-MeO–$C_6H_4$ | 4-Cl–$C_6H_4$ | **1h** | 95 |
| *9* | 4-MeO–$C_6H_4$ | 4-MeO–$C_6H_4$ | **1i** | 83 |
| *10* | 4-MeO–$C_6H_4$ | 4-Me–$C_6H_4$ | **1j** | 89 |

[a]) Reaction conditions: 4-acetyl 1,5-diones **3** (1.0 mmol), $NH_4Cl$ (4 mmol), EtOH (5 ml), conc. HCl (10 ml), 6 h.

Scheme 2. *Proposed Reaction Mechanism for the Cyclization*



In summary, we have developed a route for the synthesis of 3,5-diarylcyclohex-2-enones **1a**–**1j** starting from readily available chalcones **2a**–**2j**. Eight new and two known 3,5-diarylcyclohex-2-enone derivatives, **1a**–**1j**, were also prepared in two steps: *1*) addition of pentane-2,4-dione (**4**) to chalcones **2a**–**2j**, and *2*) cyclization of 1,5-dicarbonyl compounds **3a**–**3j** and removal of the acyl groups, in high yields (72–95%). The present method has some advantages such as excellent yields of the products, and simple workup and purification. This process has the potential to be used for the syntheses of biologically and medicinally relevant compounds.

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## Experimental Part

*General.* Anh. $Na_2SO_4$ was used as a drying agent for the org. phase. Column chromatography (CC): silica gel ($SiO_2$, 60–230 mesh; *Merck*). M.p.: *Electrothermal 9100* apparatus. IR Spectra (KBr disc): *Jasco FT/IR-430* spectrometer; $\tilde{\nu}$ in $cm^{-1}$. $^1H$- and $^{13}C$-NMR spectra: *Bruker Avance DPX-400* instrument; in $CDCl_3$; $\delta$ in ppm rel. to $Me_4Si$ ($^1H$) and $CDCl_3$ ($^{13}C$) as internal standard; *J* in Hz. GC/MS: *Perkin–Elmer Clarus 500* GC-MS. Elemental analyses: *LECO CHNS 932* analyzer.

1. *General Procedure for the Synthesis of 4-Acetyl-1,3-diarylhexane-1,5-diones* **3a**–**3j**. To a stirred soln. of chalcone **2a**–**2j** (1 mmol), pentane-2,4-dione (**4**; 1.2 mmol), and benzyltriethylammonium chloride (10 mol-%) in $CH_2Cl_2$ (2 ml) was added $^t$BuOK (5 mol-%). The mixture was stirred at r.t. for 4 h and then extracted with $CHCl_3$ (3 × 10 ml). The combined extracts were dried ($Na_2SO_4$), and the solvent was removed under reduced pressure. The crude product was eluted over a short silica-gel column with $CHCl_3$/hexane 2:1. The products were crystallized from $CCl_4$/hexane 3:1 or EtOH/hexane 2:1, and the yields were determined.

*4-Acetyl-1,3-di(thiophen-2-yl)hexane-1,5-dione* (**3a**). Yield: 86%. White solid. M.p. 108–110°. IR: 3097, 3079, 2954, 2915, 1729, 1697, 1650, 1575, 1515, 1417, 1357, 1243, 1214, 1133, 948, 846, 829, 730, 696, 518. $^1H$-NMR: 7.65 (*dd*, *J* = 4.0, 1.2, 1 H); 7.62 (*dd*, *J* = 5.0, 1.0, 1 H); 7.12 (*dd*, *J* = 4.6, 1.4, 1 H); 7.08 (*dd*, *J* = 4.8, 3.6, 1 H); 6.87–6.83 (*m*, 2 H); 4.53 (*ddd*, *J* = 10.5, 8.3, 4.4, 1 H); 4.42 (*d*, *J* = 10.4, 1 H); 3.27 (*dd*, *J* = 15.8, 8.2, 1 H); 3.20 (*dd*, *J* = 15.8, 4.2, 1 H); 2.29 (s, 3 H); 2.03 (s, 3 H). $^{13}C$-NMR: 202.8; 202.6; 190.3; 144.0; 143.1; 134.1; 132.3; 128.1; 126.8; 126.1; 124.4; 74.0; 44.1; 36.7; 30.0; 29.8. Anal. calc. for $C_{16}H_{16}O_3S_2$ (320.43): C 59.97, H 5.03, S 20.01; found: C 59.93, H 4.99, S 19.98.

*4-Acetyl-1-(furan-2-yl)-3-(thiophen-2-yl)hexane-1,5-dione* (**3b**). Yield: 76%. White solid. M.p. 112–115°. IR: 3118, 3100, 2956, 2925, 2856, 1729, 1697, 1666, 1562, 1467, 1357, 1272, 1251, 1160, 1039, 761, 696, 592. $^1H$-NMR: 7.52 (*s*, 1 H); 7.11 (*d*, *J* = 3.6, 1 H); 7.10 (*d*, *J* = 4.8, 1 H); 6.83 (*s*, 1 H); 6.81 (*d*, *J* = 3.6, 1 H); 6.47 (*t*, *J* = 1.8, 1 H); 4.53–4.48 (*m*, 1 H); 4.37 (*d*, *J* = 10.4, 1 H); 3.21 (*dd*, *J* = 16.0, 8.8, 1 H); 3.05 (*dd*, *J* = 16.0, 4.0, 1 H); 2.27 (*s*, 3 H); 2.00 (*s*, 3 H). $^{13}C$-NMR: 202.7; 202.6; 186.3; 152.4; 146.6; 143.1; 126.8; 126.0; 124.3; 117.7; 112.3; 74.2; 43.2; 36.2; 30.0; 29.8. Anal. calc. for $C_{16}H_{16}O_4S$ (304.36): C 63.14, H 5.30, S 10.54; found: C 63.11, H 5.27, S 10.50.

*4-Acetyl-3-(4-methylphenyl)-1-(thiophen-2-yl)hexane-1,5-dione* (**3c**). Yield: 84%. White solid. M.p. 115–117°. IR: 3087, 3033, 2942, 2917, 1691, 1658, 1646, 1517, 1415, 1355, 1261, 1153, 935, 821, 727, 532. $^1H$-NMR: 7.62 (br. *d*, *J* = 4.0, 1 H); 7.57 (br. *d*, *J* = 5.2, 1 H); 7.10 (*d*, *J* = 8.0, 2 H); 7.07–7.02 (*m*, 3 H); 4.34 (*d*, *J* = 11.2, 1 H); 4.16 (*m*, 1 H); 3.19 (*dd*, *J* = 15.6, 8.8, 1 H); 3.12 (*dd*, *J* = 15.6, 4.4, 1 H); 2.29 (*s*, 3 H); 2.24 (*s*, 3 H); 1.89 (*s*, 3 H). $^{13}C$-NMR: 203.3; 202.9; 190.7; 144.1; 136.9; 136.8; 133.9; 132.2; 129.4 (2 C); 128.1; 127.9 (2 C); 74.1; 43.8; 41.2; 30.0; 29.7; 21.0. Anal. calc. for $C_{19}H_{20}O_3S$ (328.43): C 69.48, H 6.14, S 9.76; found: C 69.42, H 6.10, S 9.69.

*4-Acetyl-3-(4-methoxyphenyl)-1-(thiophen-2-yl)hexane-1,5-dione* (**3d**). Yield: 85%. White solid. M.p. 118–121°. IR: 3079, 3006, 2973, 2938, 2844, 1691, 1644, 1612, 1517, 1415, 1253, 1182, 1025, 827, 728, 547. $^1H$-NMR: 7.63 (*d*, *J* = 3.6, 1 H); 7.59 (*d*, *J* = 4.8, 1 H); 7.13 (*d*, *J* = 8.6, 2 H); 7.07 (*t*, *J* = 4.4, 1 H); 6.77 (*d*, *J* = 8.6, 2 H); 4.33 (*d*, *J* = 10.8, 1 H); 4.19–4.12 (*m*, 1 H); 3.74 (*s*, 3 H); 3.16 (*dd*, *J* = 15.4, 8.8, 1 H);

3.10 (*dd*, *J* = 15.4, 4.4, 1 H); 2.30 (*s*, 3 H); 1.90 (*s*, 3 H). $^{13}$C-NMR: 203.3; 203.0; 190.7; 158.6; 144.1; 133.9; 132.2; 131.8; 129.1 (2 C); 128.1; 114.1 (2 C); 74.2; 55.1; 43.9; 40.8; 30.0; 29.7. Anal. calc. for $C_{19}H_{20}O_4S$ (344.42): C 66.26, H 5.85, S 9.31; found: C 66.22, H 5.81, S 9.28.

*4-Acetyl-1-(4-methoxyphenyl)-3-(thiophen-2-yl)hexane-1,5-dione* (**3e**). Yield: 81%. White solid. M.p. 88–91°. IR: 3087, 3056, 2962, 2906, 2840, 1720, 1697, 1670, 1606, 1575, 1511, 1419, 1355, 1259, 1172, 844, 723, 603, 516. $^1$H-NMR: 7.86 (*d*, *J* = 9.0, 2 H); 7.12 (*dd*, *J* = 4.4, 1.6, 1 H); 6.90 (*d*, *J* = 9.0, 2 H); 6.85–6.84 (*m*, 2 H); 4.59–4.53 (*m*, 1 H); 4.39 (*d*, *J* = 10.4, 1 H); 3.87 (*s*, 3 H); 3.32 (*dd*, *J* = 16.4, 8.8, 1 H); 3.19 (*dd*, *J* = 16.4, 4.0, 1 H); 2.29 (*s*, 3 H); 2.03 (*s*, 3 H). $^{13}$C-NMR: 203.0; 202.8; 196.0; 163.6; 143.6; 130.4 (2 C); 129.7; 126.8; 126.0; 124.2; 113.7 (2 C); 74.3; 55.4; 43.1; 36.6; 30.0; 29.9. Anal. calc. for $C_{19}H_{20}O_4S$ (344.42): C 66.26, H 5.85, S 9.31; found: C 66.20, H 5.82, S 9.29.

*4-Acetyl-1-(4-methylphenyl)-3-(thiophen-2-yl)hexane-1,5-dione* (**3f**). Yield: 75%. White solid. M.p. 101–104°. IR: 3104, 3068, 2906, 2821, 1720, 1698, 1673, 1606, 1415, 1357, 1253, 1241, 1184, 1143, 979, 850, 809, 700. $^1$H-NMR: 7.77 (*d*, *J* = 8.0, 2 H); 7.23 (*d*, *J* = 8.0, 2 H); 7.12 (*dd*, *J* = 4.8, 1.6, 1 H); 6.87–6.84 (*m*, 2 H); 4.59–4.54 (*m*, 1 H); 4.39 (*d*, *J* = 10.4, 1 H); 3.35 (*dd*, *J* = 16.6, 8.6, 1 H); 3.22 (*dd*, *J* = 16.6, 3.8, 1 H); 2.40 (*s*, 3 H); 2.28 (*s*, 3 H); 2.03 (*s*, 3 H). $^{13}$C-NMR: 203.0; 202.8; 197.1; 144.1; 143.6; 134.2; 129.3 (2 C); 128.2 (2 C); 126.8; 126.0; 124.3; 74.4; 43.3; 36.4; 30.0; 29.9; 21.6. Anal. calc. for $C_{19}H_{20}O_3S$ (328.42): C 69.48, H 6.14, S 9.76; found: C 69.39, H 6.07, S 9.65.

*4-Acetyl-3-(4-bromophenyl)-1-(4-methoxyphenyl)hexane-1,5-dione* (**3g**). Yield: 78%. White solid. M.p. 170–172°. IR: 3066, 2958, 2836, 1695, 1668, 1604, 1575, 1509, 1490, 1419, 1363, 1261, 1245, 1172, 1105, 1029,1012, 831, 815, 653, 588. $^1$H-NMR: 7.81 (*d*, *J* = 9.0, 2 H); 7.36 (*d*, *J* = 8.4, 2 H); 7.12 (*d*, *J* = 8.4, 2 H); 6.88 (*d*, *J* = 9.0, 2 H); 4.29 (*d*, *J* = 11.2, 1 H); 4.19 (*td*, *J* = 10.0, 4.0, 1 H); 3.84 (*s*, 3 H); 3.23 (*dd*, *J* = 16.4, 9.2, 1 H); 3.13 (*dd*, *J* = 16.4, 4.0, 1 H); 2.27 (*s*, 3 H); 1.91 (*s*, 3 H). $^{13}$C-NMR: 203.0; 202.7; 163.6; 139.5; 131.8(2 C); 130.3 (2 C); 129.9 (2 C); 129.6; 121.1; 113.7 (2 C); 55.5; 42.3; 40.6; 30.0; 29.9. Anal. calc. for $C_{21}H_{21}BrO_4$ (417.29): C 60.44, H 5.07; found: C 60.38, H 5.01.

*4-Acetyl-3-(4-chlorophenyl)-1-(4-methoxyphenyl)hexane-1,5-dione* (**3h**). Yield: 77%. White solid. M.p. 148–151°. IR: 3066, 3054, 2958, 2927, 2836, 1697, 1668, 1604, 1575, 1509, 1494, 1419, 1361, 1261, 1245, 1172, 1091, 1031, 1014, 950, 831, 815, 671, 528. $^1$H-NMR: 7.82 (*d*, *J* = 9.0, 2 H); 7.22 (*d*, *J* = 8.4, 2 H); 7.18 (*d*, *J* = 8.4, 2 H); 6.89 (*d*, *J* = 9.0, 2 H); 4.30 (*d*, *J* = 10.8, 1 H); 4.25–4.18 (*m*, 1 H); 3.86 (*s*, 3 H); 3.23 (*dd*, *J* = 16.3, 9.2, 1 H); 3.13 (*dd*, *J* = 16.3, 4.2, 1 H); 2.29 (*s*, 3 H); 1.93 (*s*, 3 H). $^{13}$C-NMR: 203.1; 202.7; 195.9; 163.6; 138.9; 132.9 (2 C); 130.4 (2 C); 129.6 (2 C); 129.5; 128.9; 113.7 (2 C); 74.2; 55.4; 42.3; 40.6; 29.9; 29.8. Anal. calc for $C_{21}H_{21}ClO_4$ (372.84): C 67.65, H 5.68; found: C 67.58, H 5.61.

*4-Acetyl-1,3-bis(4-methoxyphenyl)hexane-1,5-dione* (**3i**). Yield: 79%. White solid. M.p. 135–138°. IR: 3062, 3018, 2962, 2898, 2840, 1693, 1671, 1602, 1575, 1513, 1421, 1355, 1257, 1241, 1176, 1153, 1025, 983, 835, 738, 541. $^1$H-NMR: 7.83 (*d*, *J* = 8.8, 2 H); 7.14 (*d*, *J* = 8.8, 2 H); 6.89 (*d*, *J* = 8.8, 2 H); 6.78 (*d*, *J* = 8.8, 2 H); 4.30 (*d*, *J* = 10.8, 1 H); 4.17 (*td*, *J* = 10.0, 4.0, 1 H); 3.86 (*s*, 3 H); 3.74 (*s*, 3 H); 3.22 (*dd*, *J* = 15.9, 9.2, 1 H); 3.13 (*dd*, *J* = 15.9, 4.0, 1 H); 2.29 (*s*, 3 H); 1.89 (*s*, 3 H). $^{13}$C-NMR: 203.5; 203.2; 196.4; 163.4; 158.5; 132.1; 130.4 (2 C); 129.8; 129.1 (2 C); 114.0 (2 C); 113.7 (2 C); 74.6; 55.4; 55.1; 42.9; 40.7; 29.9 (2 C). Anal. calc. for $C_{22}H_{24}O_5$ (368.42): C 71.72, H 6.57; found: C 71.68, H 6.49.

*4-Acetyl-1-(4-methoxyphenyl)-3-(4-methylphenyl)hexane-1,5-dione* (**3j**). Yield: 81%. White solid. M.p. 110–113°. IR: 3035, 2958, 2902, 2836, 1693, 1670, 1604, 1575, 1513, 1421, 1357, 1265, 1247, 1174, 1155, 1025, 981, 950, 827, 813, 592, 532. $^1$H-NMR: 7.83 (*d*, *J* = 9.0, 2 H); 7.11 (*d*, *J* = 8.0, 2 H); 7.05 (*d*, *J* = 8.0, 2 H); 6.89 (*d*, *J* = 9.0, 2 H); 4.32 (*d*, *J* = 11.2, 1 H); 4.21–4.17 (*m*, 1 H); 3.86 (*s*, 3 H); 3.23 (*dd*, *J* = 15.9, 9.2, 1 H); 3.13 (*dd*, *J* = 15.9, 4.2, 1 H); 2.29 (*s*, 3 H); 2.26 (*s*, 3 H); 1.89 (*s*, 3 H). $^{13}$C-NMR: 203.6; 203.2; 163.4; 137.2; 136.8; 130.4 (2 C); 129.8; 129.4 (2 C); 127.9 (2 C); 113.6 (2 C); 74.6; 55.4; 42.8; 41.0; 29.9 (2 C); 21.0. Anal. calc. for $C_{22}H_{24}O_4$ (352.42): C 74.98, H 6.86; found: C 74.87, H 6.77.

2. *General Procedure for the Synthesis of 3,5-Diarylcyclohex-2-en-1-ones* **1a**–**1j**. To a soln. of **3a**–**3j** (1 mmol) in EtOH (5 ml) were added $NH_4Cl$ (4 mmol) and conc. HCl (10 ml). The mixture was heated at reflux for 6 h, then extracted with $CHCl_3$ (3 × 10 ml), and the org. layer was dried ($Na_2SO_4$). The solvent was removed under reduced pressure. The crude products were purified by crystallization from $CCl_4$/hexane 3:1 or $Et_2O$/hexane 3:1.

*3,5-Di(thiophen-2-yl)cyclohex-2-en-1-one* (**1a**). Yield: 94%. Yellow solid. M.p. 87–89°. IR: 3087, 2946, 2908, 2819, 1646, 1579, 1508, 1409, 1278, 908, 840, 717. $^1$H-NMR: 7.46 (*d*, *J* = 4.8, 1 H); 7.42 (*d*, *J* = 3.2, 1 H); 7.22 (*dd*, *J* = 4.8, 0.8, 1 H); 7.11 (*dd*, *J* = 4.8, 4.0, 1 H); 6.99 (*dd*, *J* = 5.0, 3.4, 1 H); 6.94 (br. *d*,

$J$ = 2.8, 1 H); 6.50 (br. *d*, $J$ = 1.2, 1 H); 3.79–3.69 (*m*, 1 H); 3.23 (*dd*, $J$ = 17.2, 4.0, 1 H); 2.97–2.85 (*m*, 2 H); 2.68 (*dd*, $J$ = 16.4, 12.4, 1 H). $^{13}$C-NMR: 197.6; 150.9; 146.9; 142.1; 129.2; 128.5; 127.8; 127.0; 123.7; 123.6; 122.5; 45.0; 36.7; 35.9. Anal. calc. for $C_{14}H_{12}OS_2$ (260.37): C 64.58, H 4.65, S 24.63; found: C 64.45, H 4.57, S 24.55. GC/MS: 260 ($M^+$, 36.84), 232 (17.05), 150 (100), 122 (69.66), 110 (41.01).

*3-(Furan-2-yl)-5-(thiophen-2-yl)cyclohex-2-en-1-one* (**1b**). Yield: 72%. Yellow solid. M.p. 59–62°. IR: 3108, 2954, 2823, 1652, 1604, 1540, 1473, 1402, 1270, 1033, 881, 779, 703. $^1$H-NMR: 7.58 (br. *s*, 1 H); 7.24 (*dd*, $J$ = 5.0, 1.0, 1 H); 7.07 (*dd*, $J$ = 5.2, 3.6, 1 H); 6.95 (br. *d*, $J$ = 3.2, 1 H); 6.81 (*d*, $J$ = 3.6, 1 H); 6.58 (br. *s*, 1 H); 6.54 (*dd*, $J$ = 3.4, 1.8, 1 H); 3.80–3.71 (*m*, 1 H); 3.14 (*dd*, $J$ = 17.4, 4.2, 1 H); 2.92 (*dd*, $J$ = 16.4, 4.0, 1 H); 2.84 (*ddd*, $J$ = 14.5, 10.8, 2.0, 1 H); 2.71 (*dd*, $J$ = 16.4, 12.4, 1 H). $^{13}$C-NMR: 197.8; 151.7; 147.0; 145.6; 145.3; 126.9; 123.6; 123.5; 120.8; 113.0; 112.5; 45.2; 35.8; 34.1. Anal. calc. for $C_{14}H_{12}O_2S$ (244.31): C 68.83, H 4.95, S 13.12; found: C 68.69, H 4.87, S 13.02. GC/MS: 244 ($M^+$, 31.45), 216 (16.18), 134 (100), 78 (61.08).

*5-(4-Methylphenyl)-3-(thiophen-2-yl)cyclohex-2-en-1-one* (**1c**). Yield: 92%. Yellowish solid. M.p. 101–104° ([23]: yield: 70%; m.p. 116–117°). IR: 3104, 3018, 2962, 2910, 1644, 1590, 1515, 1415, 1286, 1251, 1133, 819, 727, 505. $^1$H-NMR: 7.48 (*dd*, $J$ = 5.0, 1.0, 1 H); 7.41 (*dd*, $J$ = 3.6, 1.2, 1 H); 7.22 (*s*, 4 H); 7.12 (*dd*, $J$ = 5.0, 3.8, 1 H); 6.54 (*d*, $J$ = 2.4, 1 H); 3.49–3.41 (*m*, 1 H); 3.12 (*dd*, $J$ = 17.4, 4.2, 1 H); 2.90 (*ddd*, $J$ = 17.4, 11.2, 2.2, 1 H); 2.80–2.66 (*m*, 2 H); 2.39 (*s*, 3 H). $^{13}$C-NMR: 198.8; 151.5; 142.4; 140.0; 136.8; 129.5 (2 C); 129.0; 128.3; 127.5; 126.7 (2 C); 122.4; 44.1; 40.3; 36.2; 21.0. Anal. calc. for $C_{17}H_{16}OS$: C 76.08, H 6.01, S 11.95; found: C 75.96, H 5.98, S 11.87. GC/MS: 268 ($M^+$, 26.34), 150 (100), 122 (63.39).

*5-(4-Methoxyphenyl)-3-(thiophen-2-yl)cyclohex-2-en-1-one* (**1d**). Yellow solid. Yield: 90%. M.p. 86–89°. IR: 3083, 2998, 2929, 2832, 1646, 1589, 1513, 1421, 1294, 1247, 1180, 1035, 827, 711. $^1$H-NMR: 7.46 (*d*, $J$ = 5.2, 1 H); 7.40 (*d*, $J$ = 3.2, 1 H); 7.24 (*d*, $J$ = 8.4, 2 H); 7.11 (*t*, $J$ = 4.4, 1 H); 6.94 (*d*, $J$ = 8.4, 2 H); 6.52 (*d*, $J$ = 1.2, 1 H); 3.80 (*s*, 3 H); 3.46–3.36 (*m*, 1 H); 3.12 (*dd*, $J$ = 17.6, 4.0, 1 H); 2.86 (*ddd*, $J$ = 17.4, 11.2, 1.8, 1 H); 2.73 (*dd*, $J$ = 16.6, 4.6, 1 H); 2.67 (*dd*, $J$ = 16.2, 13.0, 1 H). $^{13}$C-NMR: 198.8; 158.6; 151.5; 142.4; 135.1; 129.0; 128.4; 127.8 (2 C); 127.6; 122.4; 114.2 (2 C); 55.3; 44.3; 39.9; 36.3. Anal. calc. for $C_{17}H_{16}O_2S$ (284.37): C 71.80, H 5.67, S 11.28; found: C 71.74, H 5.55, S 11.12. GC/MS: 284 ($M^+$, 14.31), 134 (100), 91 (16.85).

*3-(4-Methoxyphenyl)-5-(thiophen-2-yl)cyclohex-2-en-1-one* (**1e**). Yield: 95%. Yellow solid. M.p. 94–97°. IR: 3083, 2998, 2954, 2832, 1646, 1589, 1513, 1421, 1294, 1247, 1180, 1035, 827, 711. $^1$H-NMR: 7.56 (br. *d*, $J$ = 8.8, 2 H); 7.23 (*dd*, $J$ = 5.2, 1.2, 1 H); 7.00 (*dd*, $J$ = 5.0, 3.4, 1 H); 6.98–6.93 (*m*, 3 H); 6.50 (*d*, $J$ = 2.0, 1 H); 3.86 (*s*, 3 H); 3.80–3.71 (*m*, 1 H); 3.22 (*dd*, $J$ = 17.6, 4.0, 1 H); 2.98–2.89 (*m*, 2 H); 2.71 (*dd*, $J$ = 16.2, 12.6, 1 H). $^{13}$C-NMR: 198.2; 161.4; 157.6; 147.3; 130.2; 127.8 (2 C); 126.9; 123.59; 123.53; 123.4; 114.2 (2 C); 55.4; 44.9; 36.8; 36.2. Anal. calc. for $C_{17}H_{16}O_2S$ (284.37): C 71.80, H 5.67, S 11.28; found: C 71.69, H 5.59, S 11.15. GC/MS: 284 ($M^+$, 13.04), 134 (100), 91 (16.29).

*3-(4-Methylphenyl)-5-(thiophen-2-yl)cyclohex-2-en-1-one* (**1f**). Yield: 90%. Yellow solid. M.p. 92–95° (74%, 72–73°) [23]. IR: 3102, 3068, 2942, 2913, 1722, 1671, 1606, 1571, 1415, 1355, 1253, 1241, 1182, 1141, 1006, 850, 809, 700. $^1$H-NMR: 7.49 (*d*, $J$ = 8.0, 2 H); 7.27–7.22 (*m*, 3 H); 7.00 (*dd*, $J$ = 5.0, 3.4, 1 H); 6.96 (*d*, $J$ = 3.2, 1 H); 6.52 (*d*, $J$ = 2.0, 1 H); 3.81–3.74 (*m*, 1 H); 3.22 (*dd*, $J$ = 17.2, 4.4, 1 H); 3.01–2.91 (m, 2 H); 2.72 (*dd*, $J$ = 16.4, 12.8, 1 H); 2.41 (*s*, 3 H). $^{13}$C-NMR: 198.3; 158.2; 147.2; 140.7; 135.2; 129.6 (2 C); 126.9; 126.1 (2 C); 124.5; 123.6; 123.4; 44.9; 36.9; 36.2; 21.3. Anal. calc. for $C_{17}H_{16}OS$ (268.37): C 76.08, H 6.01, S 11.95; found: C 75.91, H 5.91, S 11.86.

*5-(4-Bromophenyl)-3-(4-methoxyphenyl)cyclohex-2-en-1-one* (**1g**). Yield: 86%. Yellowish solid. M.p. 106–109°. IR: 3075, 3006, 2935, 2838, 1639, 1594, 1513, 1488, 1421, 1369, 1282, 1257, 1178, 1027, 1008, 977, 815, 509. $^1$H-NMR: 7.52 (*d*, $J$ = 8.8, 2 H); 7.48 (*d*, $J$ = 8.4, 2 H); 7.18 (*d*, $J$ = 8.4, 2 H); 6.93 (*d*, $J$ = 8.8, 2 H); 6.48 (*d*, $J$ = 1.6, 1 H); 3.83 (*s*, 3 H); 3.42–3.36 (*m*, 1 H); 3.02 (*dd*, $J$ = 17.5, 4.2, 1 H); 2.83 (*ddd*, $J$ = 17.5, 11.2, 2.2, 1 H); 2.72 (*dd*, $J$ = 16.3, 4.4, 1 H); 2.64 (*dd*, $J$ = 16.3, 13.0, 1 H). $^{13}$C-NMR: 198.6; 161.4; 157.9; 142.3; 131.9 (2 C); 130.8; 130.1; 128.6 (2 C); 127.7 (2 C); 123.2; 114.2 (2 C); 55.4; 43.7; 40.4; 35.7. Anal. calc. for $C_{19}H_{17}BrO_2$ (357.24): C 63.88, H 4.80; found: C 63.76, H 4.71.

*5-(4-Chlorophenyl)-3-(4-methoxyphenyl)cyclohex-2-en-1-one* (**1h**). Yield: 95%. Yellow solid. M.p. 117–120°. IR: 3077, 2967, 2904, 2838, 1650, 1594, 1565, 1511, 1490, 1423, 1280, 1253, 1186, 1089, 1025, 885, 827, 684, 501. $^1$H-NMR: 7.52 (*d*, $J$ = 8.8, 2 H); 7.33 (*d*, $J$ = 8.8, 2 H); 7.24 (*d*, $J$ = 8.8, 2 H); 6.93 (*d*, $J$ = 8.8, 2 H); 6.48 (*d*, $J$ = 2.0, 1 H); 3.84 (*s*, 3 H); 3.43–3.37 (*m*, 1 H); 3.03 (*dd*, $J$ = 17.6, 3.6, 1 H); 2.83 (*ddd*, $J$ = 17.6, 11.0, 2.2, 1 H); 2.72 (*dd*, $J$ = 16.1, 4.8, 1 H); 2.64 (*dd*, $J$ = 16.1, 12.8, 1 H). $^{13}$C-NMR: 198.7; 161.4;

157.8; 141.8; 132.7; 130.1; 128.9; 128.2; 127.7; 123.3; 114.2; 55.4; 43.7; 40.3; 35.8. Anal. calc. for $C_{19}H_{17}ClO_2$ (312.79): C 72.96, H 5.48; found: C 72.82, H 5.34.

*3,5-Bis(4-methoxyphenyl)cyclohex-2-en-1-one* (**1i**). Yield: 83%. Yellow solid. M.p. 116–118°. IR: 3066, 3046, 2996, 2956, 2898, 2834, 1654, 1598, 1565, 1511, 1457, 1419, 1367, 1280, 1245, 1180, 1029, 823, 740, 522. $^1$H-NMR: 7.56 (*d*, *J* = 8.8, 2 H); 7.25 (*d*, *J* = 8.8, 2 H); 6.96–6.92 (*m*, 4 H); 6.50 (*d*, *J* = 2.0, 1 H); 3.86 (*s*, 3 H); 3.84 (*s*, 3 H); 3.45–3.37 (*m*, 1 H); 3.05 (*dd*, *J* = 17.5, 4.2, 1 H); 2.86 (*ddd*, *J* = 17.5, 11.2, 2.0, 1 H); 2.75 (*dd*, *J* = 16.3, 4.6, 1 H); 2.71 (*dd*, *J* = 16.3, 12.8, 1 H). $^{13}$C-NMR: 199.4; 161.3; 158.5; 158.2; 135.5; 130.3; 127.8 (4 C); 123.2; 114.2 (4 C); 55.4; 55.3; 44.2; 40.2; 36.3. Anal. calc. for $C_{20}H_{20}O_3$ (308.37): C 77.90, H 6.54; found: C 77.78, H 6.41.

*3-(4-Methoxyphenyl)-5-(4-methylphenyl)cyclohex-2-en-1-one* (**1j**). Yield: 89%. Yellow solid. M.p. 149–151°. IR: 3075, 3021, 2971, 2937, 2900, 2840, 1652, 1592, 1565, 1511, 1425, 1367, 1280, 1253, 1186, 1132, 1025, 887, 827, 634, 565, 501. $^1$H-NMR: 7.56 (*d*, *J* = 8.8, 2 H); 7.22 (s, 4 H); 6.95 (*d*, *J* = 8.8, 2 H); 6.52 (*d*, *J* = 2.0, 1 H); 3.89 (*s*, 3 H); 3.45–3.40 (*m*, 1 H); 3.06 (*dd*, *J* = 17.6, 4.0, 1 H); 2.87 (*ddd*, *J* = 17.6, 11.3, 2.4, 1 H); 2.80–2.67 (*m*, 2 H); 2.39 (*s*, 3 H). $^{13}$C-NMR: 199.5; 161.3; 158.3; 140.4; 136.7; 130.3; 129.5 (2 C); 127.8 (2 C); 126.7 (2 C); 123.2; 114.2 (2 C); 55.4; 44.0; 40.6; 36.2; 21.1. Anal. calc. for $C_{20}H_{20}O_2$ (292.37): C 82.16, H 6.89; found: C 82.02, H 6.76.

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