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Cyclohexenones Through Addition of Ethyl Acetoacetate to 3-Aryl-1-(thiophen-3-yl)prop-2-en-1-one Derivatives

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ABSTRACT

Chalcone derivatives 3a–i containing a thiophene ring were prepared by the condensation of 1-(thiophen-3-yl)ethanone with aromatic aldehydes in excellent yields. The Michael addition of ethyl acetoacetate 4 to chalcone derivatives 3a–i resulted in the formation of nine novel ethyl 6-aryl-4-(3-thienyl)cyclohex-3-en-2-one-1-carboxylate derivatives 6a–i.

KEYWORDS

Michael addition, ethyl acetoacetate, cyclohexenones, cyclocondensation.

1. Introduction

The Michael reaction of chalcones with active methylene compounds such as 1,3-dicarbonyls have been the subject of many investigations.[1–4] It is known that a weak base or acid such as piperidine[5] or phosphorus trichloride[6] often affords open chain adducts, while cyclic products have been obtained in the presence of sodium methoxide[7] or sodium hydroxide.[8] Particularly, the products of these cyclic reactions are of interest in terms of their stereochemistry and as starting materials for the synthesis of compounds with possible biological activity.[3,9] These types of reactions may be exploited with the view of obtaining highly functionalized cyclohexene derivatives,[10] but are more commonly used for the preparation of 3,5-diaryl-6-carbethoxycyclohexenones *via* the Michael addition of ethyl acetoacetate. The cyclohexenones mentioned above are efficient synthons for the synthesis of spiranic compounds[11] or intermediates in the synthesis of fused heterocycles such as benzoselenadiazoles and benzothiadiazoles,[12] benzopyrazoles and benzisoxazoles[13] or carbazole derivatives.[14]

This paper presents the synthesis of the novel ethyl 6-aryl-4-(3-thienyl)cyclohex-3-en-2-one-1-carboxylate derivatives **6a–i**. The synthesized compounds have a variety of chemical functions and are considered as important intermediates in synthetic organic chemistry.

2. Results and Discussion

Firstly, the chalcone derivatives **3a–i** were synthesized employing the general method reported in the literature.[15–17] As shown in Scheme 1, a series of chalcone derivatives (**3a–i**) was prepared through a base-catalyzed reaction. The reaction of 1-(thiophen-3-yl)ethanone (**1**) with benzaldehyde derivatives **2a–i** in ethanolic NaOH resulted in the formation of chalcone derivatives **3a–i** in high yields (93–99 %; see Scheme 1). The structures of the chalcones **3a–i** were evaluated on the basis of spectral data and compared with data from the literature. In the ^{1}H NMR spectra of **3a–i**, the olefinic protons gave an AB system showing characteristic signals for these compounds. A part of the AB system, belonging to the β proton of an α,β-unsaturated system, is shown as a doublet at δ 7.94–7.49 ppm (J = 15.6 Hz). The data were found to be in agreement with the proposed structures. Compounds **3b**,[18–21] **3c**,[18–21] and **3d**[21] were previously reported in the literature and the others are reported for the first time in this paper.

The reactions of **3a–i** with ethyl acetoacetate (**4**) in basic medium resulted in the formation of cyclohexenone derivatives **6a**–**i** respectively (Scheme 2). The reactions were performed employing potassium *tert*-butoxide (KO*t*-Bu) as a base in CH_2Cl_2 at room temperature for 3–4 h.

The crude products were purified on a short silica gel column and recrystallized from CH_2Cl_2/*n*-hexane (1:5). Compounds **6a–i** were obtained as pure products in yields of 83–94 %. Previously, similar compounds to **6a–i** have been prepared through NaOH-catalyzed cyclocondensation of 3-aryl-1-(2-thienyl)prop-2-en-1-ones with ethyl acetoacetate in yields of 43–79 %.[22] In our research, we used KO*t*-Bu as base instead of NaOH. KO*t*-Bu seems to be an efficient base and good results were obtained from the Michael addition of ethyl acetoacetate (**4**) to chalcone derivatives (**3a–i**). The cyclocondensation of ethyl acetoacetate (**4**) with chalcones **3a–i** leads to the formation of a mixture of diastereomers. The diastereomeric cyclohexenones **6a–i** were not separated, and the products were characterized in the form of the mixture originated from the synthesis. The formation of compounds **6a–i** can be explained by base-catalyzed Michael addition conversion of the intermediates **5a–i** into cyclohexenones. This occurs through intramolecular cyclocondensation of the methyl group originating from acetoacetic acid ester and the ketone function of the initial chalcone. The structures of **6a**–**i** were elucidated by means of spectroscopic studies (^{1}H and ^{13}C NMR, IR and elemental analyses) and comparison with spectral data of related compounds.[22] The IR spectra of these compounds revealed two sharp strong absorption bands above 1700 cm^{-1} and near 1660 cm^{-1}. These absorption bands confirm the presence of the ester function and the carbonyl group conjugated with a carbon–carbon double bond, respectively. The characteristic signal in the ^{1}H NMR spectra of compounds **6a–i** is the singlet of the vinylic proton in position 3 of the cyclohexenone ring that occurs at approximately δ 6.5 ppm and confirms that the intramolecular cyclocondensation subsequent to the Michael addition actually took place.

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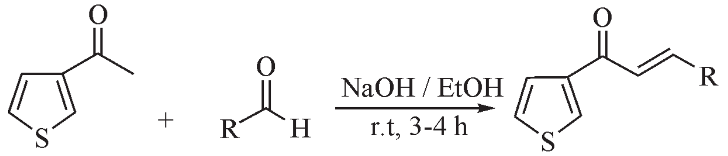


1 **2a-i** **3a-i**

(**a**) R = C_6H_5; (**b**) R = 4-ClC_6H_4; (**c**) R = 4-BrC_6H_4; (**d**) R = 4-$CH_3C_6H_4$; (**e**) R = 4-$OCH_3C_6H_4$;
(**f**) R = 3-BrC_6H_4; (**g**) R = 3-$CH_3C_6H_4$; (**h**) R = 2-$OCH_3C_6H_4$; (**i**) R = 2-thienyl (C_4H_3S).

Scheme 1

3. Experimental

General

Melting points were measured on an Electrothermal 9100 apparatus (Chelmsford, Essex, UK). IR spectra (KBr or liquid) were recorded on a Jasco FT/IR-430 spectrometer (Ahmedabad, India). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III instrument (Faellanden, Switzerland). TMS (δ 0.00 ppm) for ^1H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectroscopy served as internal standards. The multiplicities of the signals in the ^1H NMR spectra are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) and combinations thereof. Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer (New Orleans, LA, USA).

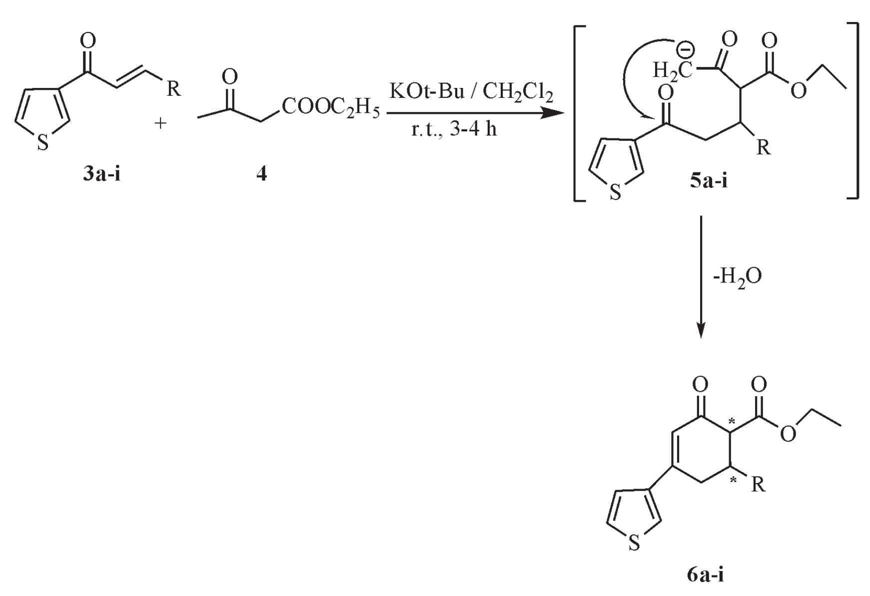
3.1. Synthesis of 3-Aryl-1-(thiophen-3-yl)prop-2-en-1-one Derivatives 3a–i (General Procedure)

To a solution of 1-(thiophen-3-yl)ethanone (**1**) (0.5 g, 4 mmol) and benzaldehyde derivatives **2a–i** (4 mmol) in EtOH (15 mL), an aqueous solution of sodium hydroxide (NaOH) (5 %, 5 mL) was added. The temperature was kept at *ca.* 25 °C, and the mixture was stirred vigorously for 3–4 h. Then it was neutralized with aqueous HCl. The mixture was extracted with $CHCl_3$ (3 × 15 mL). The combined organic extracts were washed with water (50 mL) and dried (Na_2SO_4). The solvent was evaporated (45 °C, 20 mmHg) and purified by recrystallization from a mixture of *n*-hexane and CH_2Cl_2 (5:1) (yield 93–99 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with benzaldehyde (**2a**) was obtained (*E*)-3-phenyl-1-(thiophen-3-yl)prop-2-en-1-one (**3a**) (98 %) as colourless crystals; m.p. 105–106 °C (CH_2Cl_2–hexane). IR ν (KBr): 3094, 2961, 2840, 1670, 1638, 1617, 1515, 1417, 1229, 1192, 976, 762, 618 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.19–8.18 (1H, m), 7.83 (1H, d, *J* 16 Hz) 7.69 (1H, brd, *J* 5 Hz), 7.65–7.63 (2H, m), 7.44–7.40 (4H, m), 7.37 ppm (1H, dd, *J* 5, 2.8 Hz). δ_C (100 MHz, $CDCl_3$): 183.93, 144.09, 143.10, 134.80, 132.16, 130.55, 128.98, 128.46, 127.47, 126.56, 122.69 ppm. (Found: C, 72.60; H, 4.42; S, 15.14 %. Calc. for $C_{13}H_{10}OS$ (214.28); C, 72.87; H, 4.70; S, 14.96 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 4-chlorobenzaldehyde (**2b**) was obtained (*E*)-3-(4-chlorophenyl)-1-(thiophen-3-yl)prop-2-en-1-one (**3b**) (98 %) as yellowish crystals; m.p. 124–125 °C (CH_2Cl_2–hexane). IR ν (KBr): 3084, 1615, 1564, 1405, 1229, 1197, 1087, 861, 758, 602 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.18–8.17 (1H, m), 7.76 (1H, d, *J* 16 Hz), 7.67 (1H, dd, *J* 5, 0.8 Hz), 7.56 (2H, d, *J* 8.4 Hz), 7.40–7.36 ppm (4H, m). δ_C (100 MHz, $CDCl_3$): 183.60, 142.95, 142.85, 136.38, 133.28, 132.25, 129.58 (2C), 129.24 (2C), 127.41, 126.64, 123.07 ppm. (Found: C, 62.57; H, 3.63; S, 12.59 %. Calc. for $C_{13}H_9ClOS$ (248.73); C, 62.78; H, 3.65; S, 12.89 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 4-bromobenzaldehyde (**2c**) was obtained (*E*)-3-(4-bromophenyl)-1-(thiophen-3-yl)prop-2-en-1-one (**3c**) (98 %) as colourless crystals; m.p. 132–133 °C (CH_2Cl_2-hexane). IR ν (KBr): 3084, 2963, 2846, 1617, 1561, 1484, 1229, 1192, 976, 762, 618 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.18–8.17 (1H, m), 7.74 (1H, d, *J* 15.6 Hz), 7.65–7.63 (1H, m), 7.54 (2H, d, *J* 8.2 Hz), 7.48 (2H, d, *J* 8.2 Hz), 7.41–7.36 ppm (2H, m). δ_C (100 MHz, $CDCl_3$): 183.58, 142.93, 142.63, 133.71, 132.26, 132.19 (2C), 129.77 (2C), 127.41, 126.64,



3a-i **4** **5a-i** **6a-i**

	R
a	C_6H_5
b	4-Cl-C_6H_4
c	4-Br-C_6H_4
d	4- CH_3-C_6H_4
e	4-OCH_3-C_6H_4
f	3-Br-C_6H_4
g	3-CH_3-C_6H_4
h	2-OCH_3-C_6H_4
i	2-thienyl (C_4H_3S)

Scheme 2

124.76, 123.18 ppm. (Found: C, 53.02; H, 3.13; S, 10.96 %. Calc. for $C_{13}H_9BrOS$ (293.18); C, 53.26; H, 3.09; S, 10.94 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 4-methylbenzaldehyde (**2d**) was obtained (*E*)-1-(thiophen-3-yl)-3-*p*-tolylprop-2-en-1-one (**3d**) (99 %) as colourless crystals; m.p. 118–119 °C (CH_2Cl_2–hexane). IR ν (KBr): 3103, 2968, 2842, 1638, 1509, 1229, 1180, 1026, 992, 798, 622 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.17– 8.16 (1H, m), 7.81 (1H, d, *J* 15.6 Hz), 7.69–7.67 (1H, m), 7.53 (2H, d, *J* 7.6 Hz), 7.38 (2H, d, *J* 7.6 Hz), 7.23–7.21 (2H, m), 2.39 ppm (3H, s, -CH_3). δ_C (100 MHz, $CDCl_3$): 184.03, 144.17, 143.21, 141.06, 132.07, 131.93, 129.72, 128.47, 127.48, 126.44, 121.71, 21.55 ppm. (Found: C, 73.38; H, 5.13; S, 13.87 %. Calc. for $C_{14}H_{12}OS$ (228.31); C, 73.65; H, 5.30; S, 14.04 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 4-methoxybenzaldehyde (**2e**) was obtained (*E*)-3-(4-methoxyphenyl)-1-(-3-yl)prop-2-en-1-one (**3e**) (98 %) as yellowish crystals; m.p. 47–48 °C (CH_2Cl_2–hexane). IR ν (KBr): 3091, 3001, 2960, 2836, 1654, 1462, 1440, 1353, 1316, 1225, 1183, 1072, 806, 728, 625 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.17–8.15 (1H, m), 7.81 (1H, d, *J* 15.6 Hz), 7.67 (1H, dd, *J* 5, 0.9 Hz), 7.60 (2H, d, *J* 8.6 Hz), 7.37–7.35 (1H, m), 7.31 (1H, d, *J* 15.6 Hz), 6.94 (2H, d, *J* 8.6 Hz), 3.85 ppm (3H, s, -OCH_3). δ_C (100 MHz, $CDCl_3$): 184.02, 161.65, 143.94, 143.30, 131.73, 130.21 (2C), 127.51, 127.41, 126.39, 120.38, 114.42 (2C), 55.41 ppm. (Found: C, 68.61; H, 4.73; S, 13.39 %. Calc. for $C_{14}H_{12}O_2S$ (244.31); C, 68.83; H, 4.95; S, 13.12 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 3-bromobenzaldehyde (**2f**) was obtained (*E*)-3-(3-bromophenyl)-1-(thiophen-3-yl)prop-2-en-1-one (**3f**) (97 %) as colourless crystals; m.p. 91–92 °C (CH_2Cl_2–hexane). IR ν (KBr): 3105, 2970, 2849, 1656, 1600, 1505, 1402, 1300, 1226, 1179, 781, 669, 575 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.19–8.18 (1H, m), 7.76 (1H, brs), 7.70 (1H, d, *J* 15.6 Hz), 7.67 (1H, d, *J* 5.1 Hz), 7.51 (2H, d, *J* 8.1 Hz), 7.40–7.35 (2H, m), 7.27 ppm (1H, t, *J* 7.7 Hz). δ_C (100 MHz, $CDCl_3$): 183.39, 142.86, 142.18, 136.92, 133.19, 132.45, 130.78, 130.46, 127.42, 127.25, 126.68, 123.89, 123.08 ppm. (Found: C, 52.98; H, 3.21; S, 11.06 %. Calc. for $C_{13}H_9BrOS$ (293.18); C, 53.26; H, 3.09; S, 10.94 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 3-methylbenzaldehyde (**2g**) was obtained (*E*)-1-(thiophen-3-yl)-3-*m*-tolylprop-2-en-1-one (**3g**) (99 %) as yellowish crystals; m.p. 80–81 °C (CH_2Cl_2-hexane). IR ν (KBr): 3084, 2968, 2842, 1638, 1616, 1598, 1510, 1412, 1242, 1198, 1033, 984, 782, 714, 681 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.19–8.18 (1H, m), 7.81 (1H, d, *J* 15.6 Hz), 7.69 (1H, dd, *J* 5, 0.9 Hz), 7.45–7.43 (3H, m), 7.39–7.36 (1H, m), 7.32 (1H, t, *J* 7.6 Hz), 7.23 (1H, t, *J* 7.4 Hz), 2.40 ppm (3H, s, -CH_3). δ_C (100 MHz, $CDCl_3$): 183.97, 144.30, 143.15, 138.62, 134.76, 132.04, 131.40, 129.05, 128.86, 127.48, 126.48, 126.69, 122.51, 21.86 ppm. (Found: C, 73.34; H, 5.17; S, 14.33 %. Calc. for $C_{14}H_{12}O_2S$ (244.31); C, 73.65; H, 5.30; S, 14.04 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with 2-methoxybenzaldehyde (**2h**) was obtained (*E*)-3-(2-methoxyphenyl)-1-(thiophen-3-yl)prop-2-en-1-one (**3h**) (93 %) as colourless crystals; m.p. 69–70 °C (CH_2Cl_2–hexane). IR ν (KBr): 3092, 2961, 2845, 1617, 1509, 1414, 1322, 1248, 1186, 1032, 989, 862, 816, 751 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.16–8.15 (1H, m), 7.67–7.66 (1H, brd, *J* 5 Hz), 7.62 (1H, brd, *J* 7.5 Hz), 7.60–7.40 (2H, m), 7.49 (1H, d, *J* 15 Hz), 7.38–7.33 (2H, m), 6.98 (1H, t, *J* 8 Hz), 6.92 (1H, d, *J* 8 Hz), 3.88 ppm (3H, s, -OCH_3). δ_C (100 MHz, $CDCl_3$): 184.54, 164.03, 158.78, 143.34, 139.60, 131.91, 131.77, 129.20, 127.54, 126.35, 123.80, 123.80, 123.50, 120.75, 111.26 ppm. (Found: C, 68.67; H, 4.69; S, 13.41 %. Calc. for $C_{14}H_{12}O_2S$ (244.31); C, 68.83; H, 4.95; S, 13.12 %).

From the reaction of 1-(thiophen-3-yl)ethanone (**1**) with thiophene-2-carbaldehyde (**2i**) was obtained (*E*)-3-(thiophen-2-yl)-1-(thiophen-3-yl)prop-2-en-1-one (**3i**) (96 %) as yellowish crystals; m.p. 82–83 °C (CH_2Cl_2–hexane). IR ν (KBr): 3100, 3088, 2975, 2849, 1640, 1616, 1602, 1572, 1508, 1499, 1409, 1313, 1225, 1183, 1020, 806, 728, 702, 635 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 8.18–8.15 (1H, m), 7.94 (1H, d, *J* 15.6 Hz), 7.67 (1H, brd, *J* 5 Hz), 7.43 (1H, d, *J* 3.9 Hz), 7.38–7.34 (2H, m), 7.21 (1H, d, *J* 15.6 Hz), 7.11–7.07 ppm (1H, m). δ_C (100 MHz, $CDCl_3$): 183.38, 143.02, 140.27, 136.49, 132.03, 131.97, 128.73, 128.36, 127.40, 126.50, 121.49 ppm. (Found: C, 59.71; H, 3.57; S, 29.41 %. Calc. for $C_{11}H_8OS_2$ (220.31); C, 59.97; H, 3.66; S, 29.11 %).

3.2. Synthesis of Ethyl 2-oxo-6-aryl-4-(thiophen-3-yl)cyclohex-3-enecarboxylate Derivatives 6a-i (General Procedure)

A solution of chalcone derivatives (1 mmol) **3a–i** and ethyl acetoacetate (**4**) (1 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3–4 h in the presence of potassium tert-butoxide (KO*t*-Bu) (1 mmol). The reaction mixture was extracted with CH_2Cl_2 and the extract was washed with H_2O and dried (Na_2SO_4). The solvent was evaporated (45 °C, 20 mmHg). The crude product was purified on a short silica gel column eluting with CH_2Cl_2/*n*-hexane (7:3) to obtain a pure solid product which was recrystallized from CH_2Cl_2 and *n*-hexane (5:1), (yield 83–94 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-phenyl-1-(thiophen-3-yl)prop-2-en-1-one (**3a**) was obtained ethyl 2-oxo-6-phenyl-4-(thiophen-3-yl)cyclohex-3-enecarboxylate (**6a**) (92 %) as white crystals; m.p. 116–117 °C (CH_2Cl_2–hexane). IR ν (KBr): 3097, 2979, 1733 ($\nu_{C=O}$ ester), 1652 ($\nu_{C=O}$ ketone), 1218, 771 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.56 (1H, s), 7.38–7.31 (6H, m), 7.29–7.25 (1H, m), 6.51 (1H, s, =CHCO-), 4.03 (2H, q, *J* 7.2 Hz, -CH_2CH_3), 3.79–3.76 (2H, m, -CH_2CHAr-), 3.10 (1H, dd, J_{trans} 3.6 Hz, J_{cis} 18 Hz, >$CHCOOC_2H_5$), 2.94–2.88 (1H, m, >CHAr), 1.02 ppm (3H, t, *J* 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 194.34, 169.28, 152.47, 141.01, 139.71, 128.86, 127.55, 127.14, 127.04, 126.07, 125.12, 122.49, 60.91, 59.65, 43.82, 35.77, 13.99 ppm. (Found: C, 69.88; H, 5.59; S, 9.77 %. Calc. for $C_{19}H_{18}O_3S$ (326.41); C, 69.91; H, 5.56; S, 9.82 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(4-chlorophenyl)-1-(thiophen-3-yl) prop-2-en-1-one (**3b**) was obtained ethyl 6-(4-chlorophenyl)-2-oxo-4-(thiophen-3-yl) cyclohex-3-enecarboxylate (**6b**) (93 %) as white crystals; m.p. 145–146 °C (CH_2Cl_2–hexane). IR ν (KBr): 3100, 2979, 1735 ($\nu_{C=O}$ ester), 1654 ($\nu_{C=O}$ ketone), 1243, 1147, 769 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.58 (1H, s), 7.40–7.38 (1H, m), 7.34–7.31 (3H, m), 7.27–7.25 (2H, m), 6.51 (1H, s, =CHCO-), 4.07 (2H, q, *J* 7.2 Hz, -CH_2CH_3), 3.77–3.73 (m, -CH_2CHAr-, 2H), 3.14 (1H, dd, J_{trans} 3.6 Hz, J_{cis} 18 Hz, >$CHCOOC_2H_5$), 2.92–2.85 (1H, m, >CHAr), 1.07 ppm (3H, t, *J* 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 193.90, 167.07, 152.21, 139.53, 133.26, 129.01, 128.85, 128.77, 127.19, 12.55, 126.07, 122.51, 61.10, 59.48, 43.15, 35.60, 14.10 ppm. (Found: C, 63.41; H, 4.63; S, 8.76 %. Calc. for $C_{19}H_{17}ClO_3S$ (360.85); C, 63.24; H, 4.75; S, 8.89 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(4-bromophenyl)-1-(thiophen-3-yl) prop-2-en-1-one (**3c**) was obtained ethyl 6-(4-bromophenyl)-2-oxo-4-(thiophen-3-yl) cyclohex-3-enecarboxylate (**6c**) (94 %) as white crystals; m.p. 113–114 °C (CH_2Cl_2–hexane). IR ν (KBr): 3102, 2979, 1740 ($\nu_{C=O}$ ester), 1654 ($\nu_{C=O}$ ketone), 1147, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.58 (1H, s), 7.41–7.36 (2H, m), 7.27 (1H, t, $J_{1,2}$ 8.0 Hz, $J_{1,2}$ 7.2 Hz, Ar-H), 7.14–7.10 (3H m), 6.55 (1H, s, =CHCO-), 4.07 (2H, q, *J* 7.2 Hz, -CH_2CH_3), 3.77–3.75 (2H, m, -CH_2CHAr-), 3.14 (1H, dd, J_{trans} 3.6 Hz, J_{cis} 17.8 Hz, >$CHCOOC_2H_5$), 2.97–2.91 (1H, m, >CHAr), 1.06 ppm (3H, t, *J* 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 194.49, 169.30, 152.45, 140.91, 139.76, 138.47, 128.73, 128.28, 128.13, 127.06, 125.09, 122.55, 60.94, 59.63, 43.73, 35.93, 13.96 ppm. (Found: C, 56.38; H, 4.18; S, 7.87 %. Calc. for $C_{19}H_{17}BrO_3S$ (405.31); C, 56.30; H, 4.23; S, 7.91 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-1-(thiophen-3-yl)-3-*p*-tolylprop-2-en-1-one (**3d**) was obtained ethyl 2-oxo-4-(thiophen-3-yl)-6-*p*-tolylcyclohex-3-enecarboxylate (**6d**) (91 %) as white crystals; m.p. 147-148 °C (CH_2Cl_2–hexane). IR ν (KBr): 3097, 2979, 1733 ($\nu_{C=O}$ ester), 1652 ($\nu_{C=O}$ ketone), 1218, 1145, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.57–7.56 (1H, m), 7.40–7.34 (2H, m), 7.23–7.16 (4H, m), 6.54 (1H, s, =CHCO-), 4.06 (2H, q, J 7.2 Hz, -CH_2CH_3), 3.77–3.75 (2H, m, -CH_2CHAr-), 3.13 (1H, dd, J_{trans} 3.6 Hz, J_{cis} 18 Hz, >CHCOOC_2H_5), 2.94–2.88 (1H, m, >CHAr), 2.35 (3H, s, -CH_3), 1.08 ppm (3H, t, J 6.8 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 194.48, 169.33, 152.46, 139.77, 138.00, 137.19, 129.51, 127.20, 127.08, 125.89, 125.10, 122.55, 60.94, 59.76, 43.41, 35.97, 21.09, 14.00 ppm. (Found: C, 70.23; H, 4.35; S, 9.65 %. Calc. for $C_{20}H_{20}O_3S$ (340.44); C, 70.56; H, 5.92; S, 9.42 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(4-methoxyphenyl)-1-(3-yl)prop-2-en-1-one (**3e**) was obtained ethyl 6-(4-methoxyphenyl)-2-oxo-4-(thiophen-3-yl)cyclohex-3-enecarboxylate (**6e**) (85 %) as white crystals; m.p. 106–107 °C (CH_2Cl_2-hexane). IR ν (KBr): 3100, 2979, 1733 ($\nu_{C=O}$ ester), 1654 ($\nu_{C=O}$ ketone), 1251, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.57 (1H, m), 7.40–7.35 (2H, m), 7.27–7.24 (2H, m), 6.90–6.88 (2H, m), 6.53 (1H, s, =CHCO-), 4.07 (2H, q, J 6.8 Hz, -CH_2CH_3), 3.81 (3H, m, -OCH_3), 3.75–3.71 (2H, m, -CH_2CHAr-), 3.08 (1H, dd, J_{trans} 5.2 Hz, J_{cis} 18 Hz, >CHCOOC_2H_5), 2.96.2.87 (1H, m, >CHAr), 1.07 ppm (3H t, J 6.8 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 194.49, 169.35, 158.86, 152.48, 139.77, 133.06, 128.38, 127.08, 125.89, 125.10, 122.56, 114.17, 60.93, 60.01, 55.29, 43.07, 36.02, 14.01 ppm. (Found: C, 67.11; H, 5.42; S, 9.10 %. Calc. for $C_{20}H_{20}O_4S$ (356.44) C, 67.39; H, 5.66; S, 9.00 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(3-bromophenyl)-1-(thiophen-3-yl) prop-2-en-1-one (**3f**) was obtained ethyl 6-(3-bromophenyl)-2-oxo-4-(thiophen-3-yl) cyclohex-3-enecarboxylate (**6f**) (87 %) as white crystals; m.p. 139–140 °C (CH_2Cl_2-hexane). IR ν (KBr): 3097, 2979, 1733 ($\nu_{C=O}$ ester), 1652 ($\nu_{C=O}$ ketone), 1218, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): δ 7.58 (1H, s), 7.48 (1H, s), 7.43–7.39 (2H, m), 7.36–7.35 (1H, m), 7.27–7.21 (2H, m), 6.53 (1H, s, =CHCO-), 4.08 (2H, q, J 7.2 Hz, -CH_2CH_3), 3.77–3.71 (2H, m, -CH_2CHAr-), 3.12 (1H, dd, J_{trans} 3.6 Hz, J_{cis} 17.8 Hz, >CHCOOC_2H_5), 2.95–2.88 (1H, m, >CHAr), 1.08 ppm (3H, t, J 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): δ 193.78, 168.98, 152.14, 143.29, 139.52, 130.72, 130.59, 130.48, 127.20, 126.06, 126.01, 125.07, 122.83, 122.52, 61.15, 59.34, 43.38, 35.53, 14.01 ppm. (Found: C, 56.23; H, 4.28; S, 7.95 %. Calc. for $C_{19}H_{17}BrO_3S$ (405.31); C, 56.30; H, 4.23; S, 7.91 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-1-(thiophen-3-yl)-3-*m*-tolylprop-2-en-1-one (**3g**) was obtained ethyl 2-oxo-4-(thiophen-3-yl)-6-*m*-tolylcyclohex-3-enecarboxylate (**6g**) (85 %) as white crystals; m.p. 111–112 °C (CH_2Cl_2–hexane). IR ν (KBr): 3097, 2983, 1733 ($\nu_{C=O}$ ester), 1652 ($\nu_{C=O}$ ketone), 1218, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.56 (1H, s), 7.39–7.34 (2H, m), 7.29–7.23 (1H, m), 7.14–7.09 (3H, m), 6.52 (1H, s, =CHCO-), 4.05 (2H, q, J 7.2 Hz, -CH_2CH_3), 3.79–3.74 (2H, m, -CH_2CHAr-), 3.28 (1H dd, J_{trans} 3.6 Hz, J_{cis} 18 Hz, >CHCOOC_2H_5), 3.02–2.97 (1H m, >CHAr), 1.59 (3H, s, -CH_3), 1.14 ppm (3H, t, J 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 194.48, 169.33, 152.51, 140.95, 139.74, 138.43, 128.74, 128.29, 128.17, 127.11, 126.00, 125.11, 124.31, 122.48, 60.90, 59.63, 43.75, 35.88, 21.49, 14.00 ppm. (Found: C, 70.48; H, 5.96; S, 9.34 %. Calc. for $C_{20}H_{20}O_3S$ (340.44); C, 70.56; H, 5.92; S, 9.42 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(2-methoxyphenyl)-1-(thiophen-3-yl) prop-2-en-1-one (**3h**) was obtained ethyl 6-(2-methoxyphenyl)-2-oxo-4-(thiophen-3-yl) cyclohex-3-enecarboxylate (**6h**) (86 %) as white crystals; m.p. 99–100 °C (CH_2Cl_2-hexane). IR ν (KBr): 3100, 2979, 1735 ($\nu_{C=O}$ ester), 1654 ($\nu_{C=O}$ ketone), 1243, 1147, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.56 (1H, m), 7.39–7.35 (2H, m), 7.28–7.21 (2H, m), 6.95–6.91 (2H, m), 6.52 (1H, s, =CHCO-), 4.05 (2H, q, J 6.8 Hz, -CH_2CH_3), 3.87 (3H, m, -OCH_3), 3.85–3.83 (2H, m, -CH_2CHAr-), 3.09 (1H, dd, J_{trans} 5.2 Hz, J_{cis} 18 Hz, >CHCOOC_2H_5), 3.04–3.03 (1H, m, >CHAr), 1.03 ppm (3H, t, J 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 195.27, 169.64, 157.56, 153.28, 140.02, 128.90, 128.62, 128.38, 126.94, 125.79, 125.12, 122.42, 120.80, 111.17, 60.74, 57.61, 55.43, 39.83, 33.40, 13.98 ppm. (Found: C, 67.46; H, 5.59; S, 9.07 %. Calc. for $C_{20}H_{20}O_4S$ (356.44); C, 67.39; H, 5.66; S, 9.00 %).

From the reaction of ethyl acetoacetate (**4**) with (*E*)-3-(thiophen-2-yl)-1-(thiophen-3-yl)prop-2-en-1-one (**3i**) was obtained ethyl 2-oxo-6-(thiophen-2-yl)-4-(thiophen-3-yl)cyclohex-3-enecarboxylate (**6i**) (83 %) as white crystals; m.p. 93–94 °C (CH_2Cl_2–hexane). IR ν (KBr): 3102, 2979, 1735 ($\nu_{C=O}$ ester), 1654 ($\nu_{C=O}$ ketone), 1147, 773 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.63–7.62 (1H, m), 7.42–7.35 (2H, m), 7.27–7.22 (2H, m), 6.97–6.95 (1H, m), 6.54 (1H, s, =CHCO-), 4.16 (2H, q, J 7.2 Hz, -CH_2CH_3), 3.76–3.71 (2H, m, -CH_2CHAr-), 3.13 (1H, dd, J_{trans} 4.6 Hz, J_{cis} 17.8 Hz, >CHCOOC_2H_5), 3.05–3.02 (1H, m), 1.08 ppm (3H, t, J 7.2 Hz, -CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 193.47, 169.05, 151.99, 144.51, 139.61, 127.15, 126.88, 126.03, 125.09, 124.88, 124.16, 122.73, 61.23, 38.89, 36.27, 29.68, 14.10 ppm. (Found: C, 61.33; H, 4.92; S, 19.36 %. Calc. for $C_{17}H_{16}O_3S_2$ (332.44); C, 61.42; H, 4.85; S, 19.29 %).

4. Conclusions

Nine novel cyclohexenone derivatives (**6a**–**i**) were synthesized by the reaction of chalcone derivatives (**3a–i**) and ethyl acetoacetate (**4**) in the presence of KO*t*-Bu in CH_2CI_2 in high yields and mild reaction conditions (room temperature). The synthesized compounds have important functional groups in terms of various reactivities in organic synthesis.

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