## **Supplementary Information for:**

## Transition Metal-Free Cross-Dehydrogenative Coupling Acylation of Coumarins by the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Aliquat 336 Catalytic System: A Versatile Strategy towards 4-Aroylcoumarin Derivatives

Mehdi Adib,<sup>a,\*</sup> Rahim Pashazadeh,<sup>a</sup> Saideh Rajai-Daryasarei,<sup>a</sup> Roya Kabiri<sup>b</sup> and Mehdi Jahani<sup>a</sup> <sup>a</sup> School of Chemistry, College of Science, University of Tehran, PO Box 14155-6455, Tehran, Iran

<sup>b</sup> NMR lab, Faculty of Chemistry, Tabriz University, Tabriz, Iran

List of contents	Page
Title, author's name, address and table	S1
General, experimental procedure and characterization data	S2-S10
<sup>1</sup> H NMR spectrum of <b>3a</b>	S11
<sup>13</sup> C NMR spectrum of <b>3a</b>	S12
<sup>1</sup> H NMR spectrum of <b>3b</b>	S13
<sup>13</sup> C NMR spectrum of <b>3b</b>	S14
<sup>1</sup> H NMR spectrum of <b>3c</b>	S15
<sup>13</sup> C NMR spectrum of <b>3c</b>	S16
<sup>1</sup> H NMR spectrum of <b>3d</b>	S17
<sup>13</sup> C NMR spectrum of <b>3d</b>	S18
<sup>1</sup> H NMR spectrum of <b>3</b> e	S19
<sup>13</sup> C NMR spectrum of <b>3e</b>	S20
<sup>1</sup> H NMR spectrum of <b>3</b> f	S21
<sup>13</sup> C NMR spectrum of <b>3f</b>	S22
<sup>1</sup> H NMR spectrum of <b>3</b> g	S23
<sup>13</sup> C NMR spectrum of <b>3</b> g	S24
<sup>1</sup> H NMR spectrum of <b>3h</b>	S25
<sup>13</sup> C NMR spectrum of <b>3h</b>	S26
<sup>1</sup> H NMR spectrum of <b>3</b> i	S27
<sup>13</sup> C NMR spectrum of <b>3i</b>	S28
<sup>1</sup> H NMR spectrum of <b>3</b> j	S29
<sup>13</sup> C NMR spectrum of <b>3</b> j	S30
<sup>1</sup> H NMR spectrum of <b>3</b> k	S31
$^{13}$ C NMR spectrum of <b>3</b> k	S32
<sup>1</sup> H NMR spectrum of <b>3</b> I	S33

<sup>13</sup> C NMR spectrum of <b>3</b> I	S34
<sup>1</sup> H NMR spectrum of <b>3m</b>	S35
<sup>13</sup> C NMR spectrum of <b>3m</b>	S36
<sup>1</sup> H NMR spectrum of <b>3n</b>	S37
<sup>13</sup> C NMR spectrum of <b>3n</b>	S38
<sup>1</sup> H NMR spectrum of <b>3</b> 0	S39
<sup>13</sup> C NMR spectrum of <b>30</b>	S40
<sup>1</sup> H NMR spectrum of <b>3p</b>	S41
<sup>13</sup> C NMR spectrum of <b>3p</b>	S42
<sup>1</sup> H NMR spectrum of <b>3</b> q	S43
<sup>13</sup> C NMR spectrum of <b>3</b> q	S44
<sup>1</sup> H NMR spectrum of <b>3r</b>	S45
<sup>13</sup> C NMR spectrum of <b>3r</b>	S46
<sup>1</sup> H NMR spectrum of <b>3s</b>	S47
<sup>13</sup> C NMR spectrum of <b>3s</b>	S48
<sup>1</sup> H NMR spectrum of <b>3</b> t	S49
<sup>13</sup> C NMR spectrum of $3t$	S50
<sup>1</sup> H NMR spectrum of <b>3u</b>	S51
<sup>13</sup> C NMR spectrum of <b>3u</b>	S52

## General

All chemicals were purchased from Merck (Germany) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured (CDCl<sub>3</sub> solution) with Bruker DRX-500 AVANCE (at 500.1 and 125.8 MHz, resp.), Bruker DRX-400 AVANCE III (at 400.1 and 100.6 MHz, resp.) and Bruker DPX-250 (at 250.1 and 62.8 MHz, resp.) instruments. Chromatography columns were prepared from Merck silica gel 230–240 meshes.

General procedure for synthesis of 3-acetyl-4-(4-methylbenzoyl)-2*H*-chromen-2-one (3a): A 10 mL oven-dried scintillation vial equipped with a magnetic stir bar was charged with a mixture of 3-acetyl coumarin 2a (0.5 mmol, 0.094 g), 4-methylbenzaldehyde 1a (1.0 mmol, 0.120 g),  $K_2S_2O_8$  (0.6 mmol, 0.162 g), Aliquat 336 (30 mol%, 0.060 g) and CH<sub>3</sub>CN (2.0 mL). The vial was capped, and the reaction mixture was stirred at 80 °C for 2 h. Upon completion, saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 mL) and distilled H<sub>2</sub>O (7 mL) was added, and the mixture was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with

saturated aqueous solution of NaCl, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by SiO<sub>2</sub> column chromatography to afford 3-acetyl-4-(4-methyl benzoyl)-2*H*-chromen-2-one **3a** as a lemon solid; mp 180–182 °C (recrystallized from 8:1 *n*-hexane-EtOAc); yield: 0.133 g (87%).



**3-Acetyl-4-(4-methylbenzoyl)-2***H***-chromen-2-one (3a)**: yield 0.133 g, 87%; pale yellow solid, m.p. 180–182 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.44 (s, 3H), 2.67 (s, 3H), 7.24 (td, *J* = 7.6, 0.8 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 20.8, 29.9, 116.0, 116.1, 120.3, 124.1, 127.4, 127.6, 128.7, 132.1, 133.6, 144.4, 153.5, 156.3, 157.7, 192.1, 195.0.



**3-Acetyl-4-(4-isopropylbenzoyl)-***2H***-chromen-2-one** (**3b**): yield 0.134 g, 80%; pale yellow solid, m.p. 188–190 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.29$  (d, J = 6.9 Hz, 6H), 2.68 (s, 3H), 2.99 (sept, J = 6.9 Hz, 1H), 7.25 (td, J = 7.3 Hz, 1H), 7.32 (dd, J = 8.0, 1.5 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 1H), 7.68 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 22.5$ , 30.0, 33.3, 116.0, 116.1, 120.2, 124.2, 126.2, 127.5, 127.7, 132.3, 133.7, 153.5, 155.0, 156.5, 157.8, 192.1, 195.0.



**3-Acetyl-4-(3-methoxybenzoyl)-2***H***-chromen-2-one (3c)**: yield 0.137 g, 85%; pale yellow solid, m.p. 120–121 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.68 (s, 3H), 3.89 (s, 3H), 7.18 (ddd, *J* = 8.1, 2.2, 0.6 Hz, 1H), 7.23–7.31 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.68 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 29.9, 54.4, 111.0, 116.0, 119.7, 120.1, 120.4, 124.2, 127.4, 129.0, 133.8, 135.7, 153.7, 156.4, 157.6, 159.1, 192.2, 194.9.



**3-Acetyl-4-(4-methoxybenzoyl)-2***H***-chromen-2-one (3d)**: yield 0.137 g, 85%; pale yellow solid, m.p. 150–152 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.67 (s, 3H), 3.90 (s, 3H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.24 (td, *J* = 7.6, 0.7 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.67 (td, *J* = 8.6, 1.5 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 29.9, 54.5, 112.6, 113.3, 116.0, 120.4, 124.1, 127.4, 129.9, 131.2, 133.6, 153.5, 156.1, 157.8, 163.4, 191.0, 195.1.



**3-Acetyl-4-(4-chlorobenzoyl)-2***H***-chromen-2-one (3e**): yield 0.129 g, 79%; pale yellow solid, m.p. 204–206 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.70 (s, 3H), 7.25–7.28 (m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.69–7.73 (m, 1H), 7.81 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 30.0, 115.8, 116.2, 120.1, 124.3, 127.2, 128.5, 128.7, 132.8, 134.0, 139.7, 153.6, 156.0, 157.5, 191.4, 195.0.



**3-Acetyl-4-benzoyl-2***H***-chromen-2-one (3f)**: yield 0.123 g, 84%; pale yellow solid, m.p. 130– 132 °C. <sup>1</sup>H NMR (250.1 MHz, CDCl<sub>3</sub>): δ = 2.88 (s, 3H), 7.15–7.22 (m, 2H), 7.34–7.44 (m, 3H), 7.52–7.62 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 2H). <sup>13</sup>C NMR (62.8 MHz, CDCl<sub>3</sub>): δ = 30.9, 117.0, 117.1, 125.3, 128.4, 128.5, 129.1, 134.2, 134.8, 135.5, 154.6, 157.5, 158.7, 193.5, 196.0.



**3-Acetyl-4-(thiophene-2-carbonyl)-2***H***-chromen-2-one (3g)**: yield 0.109 g, 73%; pale yellow solid, m.p. 151–153 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.69 (s, 3H), 7.14 (dd, *J* = 4.8, 3.9 Hz, 1H), 7.29 (td, *J* = 7.2, 1.0 Hz, 1H), 7.42–7.47 (m, 3H), 7.70 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.82 (dd, *J* = 4.9, 1.0 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 30.0, 115.7, 116.1, 120.4, 124.3, 127.3, 127.5, 133.0, 133.8, 134.4, 141.3, 153.5, 154.4, 157.7, 184.2, 194.9.



**3-Acetyl-4-benzoyl-8-methoxy-2***H***-chromen-2-one (3h)**: yield 0.114 g, 71%; yellow solid, m.p. 188–190 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.69 (s, 3H), 4.03 (s, 3H), 6.85 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 30.0, 55.3, 115.0, 116.5, 118.3, 120.3, 124.0, 127.4, 128.0, 133.1, 134.4, 143.4, 146.2, 156.7, 157.2, 192.5, 195.1.



**3-Acetyl-8-methoxy-4-(3-methoxybenzoyl)-2***H***-chromen-2-one (<b>3i**): yield 0.132 g, 75%; pale yellow solid, m.p. 174–176 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.68 (s, 3H), 3.88 (s, 3H), 4.01 (s, 3H), 6.85 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.14–7.22 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.52 (s, 1 H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 29.9, 54.4, 55.3, 110.9, 115.0, 116.6, 118.3, 119.7, 120.3, 120.4, 124.0, 129.0, 135.7, 143.4, 146.2, 156.6, 157.2, 159.0, 192.2, 195.0.



**3-Acetyl-6-bromo-4-(4-methylbenzoyl)-2***H***-chromene-2-one (3j)**: yield 0.148 g, 77%; pale yellow solid, m.p. 180–182 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.43$  (s, 3H), 2.63 (s, 3H), 7.24–7.38 (m, 4H), 7.70–7.80 (m, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 20.8$ , 29.8, 116.9, 117.5, 117.7, 121.1, 127.6, 128.9, 129.3, 131.6, 136.4, 144.8, 152.3, 154.8, 157.0, 191.3, 194.6.



**3-Acetyl-6-bromo-4-(4-isopropylbenzoyl)-***2H***-chromen-2-one** (**3k**): yield 0.151 g, 73%; white solid, m.p. 188–190 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$  (d, J = 6.9 Hz, 6H), 2.67 (s, 3H), 3.01 (sept, J = 6.9 Hz, 1H), 7.36 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 2.2 Hz, 1H), 7.75–7.79 (m, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 22.5$ , 29.9, 33.4, 117.0, 117.5, 117.7, 121.0, 126.4, 127.7, 129.4, 131.9, 136.5, 152.4, 155.0, 155.3, 157.1, 191.4, 194.7.



**3-Acetyl-6-bromo-4-(3-methoxybenzoyl)-2***H***-chromen-2-one (31)**: yield 0.154 g, 77%; pale yellow solid, m.p. 162–164 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.67$  (s, 3H), 3.92 (s, 3H), 7.21 (ddd, J = 8.3, 2.6, 0.7 Hz, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.37–7.41 (m, 2H), 7.53 (t, J = 1.9 Hz, 1H), 7.77 (dd, J = 8.9, 2.3 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 29.9$ , 54.5, 111.1, 117.0, 117.5, 117.8, 120.1, 120.4, 129.2, 129.4, 135.4, 136.6, 152.4, 154.9, 157.0, 159.2, 191.6, 194.6.



**3-Acetyl-6-bromo-4-(4-chlorobenzoyl)-2***H***-chromen-2-one (3m**): yield 0.152 g, 75%; pale yellow solid, m.p. 197–200 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>): δ = 2.68 (s, 3H), 7.35–7.37 (m, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.76–7.81 (m, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 29.9, 117.1, 117.2, 117.9, 121.0, 128.6, 128.7, 129.1, 132.5, 136.7, 140.1, 152.5, 154.4, 156.9, 190.6, 194.7.



**3-Acetyl-6-bromo-4-(thiophene-2-carbonyl)-2***H***-chromen-2-one (<b>3n**): yield 0.136 g, 72%; pale yellow solid, m.p. 183–185 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.67$  (s, 3H), 7.17 (dd, J = 4.4, 4.4 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 3.8, 0.9 Hz, 1H) 7.52 (d, J = 2.2 Hz, 1H), 7.77 (dd, J = 8.8, 2.2 Hz, 1H), 7.85 (dd, J = 4.8, 0.8 Hz, 1H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 29.9$ , 117.1, 117.7, 121.5, 127.7, 129.2, 133.1, 133.1, 135.0, 136.5, 141.0, 152.3, 152.7, 157.0, 183.3, 194.6.



**Ethyl-4-benzoyl-2-oxo-2***H***-chromen-3-carboxylate (30)**: yield 0.132 g, 82%; white solid, m.p. 111–112 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.07$  (t, J = 7.2 Hz, 3H), 4.14 (q, J = 7.1 Hz, 2H), 7.24–7.30 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.54 (t, J = 8.1 Hz, 2H), 7.65–7.69 (m, 2H), 7.94 (dd, J = 8.4, 1.3 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 12.4$ , 61.3, 115.3, 116.2, 124.0, 126.6, 128.0, 128.1, 129.0, 133.4, 133.7, 134.1, 153.2, 154.3, 155.4, 161.3, 191.1.



**Ethyl-4-(4-methylbenzoyl)-2-oxo-***2H***-chromene-3-carboxylate** (**3p**): yield 0.133 g, 79%; white solid, m.p. 121–123 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.06$  (t, J = 7.1 Hz, 3H), 2.44 (s, 3H), 4.12 (q, J = 7.1 Hz, 2H), 7.21 (t, J = 7.7 Hz, 1H), 7.26 (dd, J = 8.6, 1.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.3 Hz, 1H), 7.63 (td, J = 8.5, 1.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 12.4$ , 20.8, 61.3, 115.3, 115.4, 116.2, 124.0, 126.6, 128.2, 128.8, 131.7, 133.3, 145.1, 153.2, 154.3, 155.5, 161.3, 190.6.



**Ethyl-4-(4-chlorobenzoyl)-2-oxo-2***H***-chromene-3-carboxylate (3q)**: yield 0.146 g, 82%; white solid, m.p. 137–139 °C. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.10$  (t, J = 7.1 Hz, 3H), 4.15 (q, J = 7.1 Hz, 2H), 7.18–7.26 (m, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.64 (ddd, J = 8.6, 6.2, 2.6 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta = 12.5$ , 61.4, 115.2, 115.4, 116.4, 124.1, 126.4, 128.6, 129.3, 132.6, 133.5, 140.4, 153.3, 154.0, 155.2, 161.3, 189.9.



**3-Acetyl-4-benzoyl-6-chloro-2***H***-chromen-2-one (3r)**: yield 0.135 g, 83%; white solid; m.p. 186–188 °C. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>): δ = 2.72 (s, 3H), 7.31 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.68 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>): δ = 31.0, 118.1, 118.7, 122.4, 127.5, 128.6, 129.3, 130.9, 134.7, 134.9, 135.3, 153.1, 156.0, 158.2, 192.9, 195.8.



**3-Acetyl-6-chloro-4-(3-methylbenzoyl)-2***H***-chromen-2-one (3s)**: yield 0.136 g, 80%; pale yellow solid; m.p. 192–194 °C. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.50$  (s, 3H), 2.72 (s, 3H), 7.31 (d, J = 2.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.68 (dd, J = 8.9, 2.4 Hz, 1H), 7.78 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 21.5$ , 31.0, 118.2, 118.7, 122.3, 126.0, 127.5, 128.8, 129.2, 130.9, 134.8, 135.3, 135.6, 139.4, 153.1, 156.2, 158.3, 193.1, 195.8.



**3-Acetyl-6-chloro-4-(4-isopropylbenzoyl)-2***H***-chromen-2-one (<b>3t**): yield 0.143 g, 78%; pale yellow solid; m.p. 162–164 °C. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.36$  (d, J = 6.9 Hz, 6H), 2.72 (s, 3H), 3.07 (sept, J = 6.9 Hz, 1H), 7.32 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.9 Hz, 1H), 7.67 (dd, J = 8.8, 2.3 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 23.6$ , 31.0, 34.6, 118.2, 118.6, 122.3, 127.5, 127.6, 128.9, 130.8, 133.2, 134.8, 153.1, 156.1, 156.5, 158.3, 192.5, 195.9.



**3-Acetyl-6-chloro-4-(4-methoxybenzoyl)-2***H***-chromen-2-one (<b>3u**): yield 0.137 g, 77%; yellow solid; m.p. 199–201 °C. <sup>1</sup>H NMR (500.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.71$  (s, 3H), 3.97 (s, 3H), 7.05 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 2.3 Hz, 1H), 7.46 (d, J = 8.9 Hz, 1H), 7.66 (dd, J = 8.9, 2.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H). <sup>13</sup>C NMR (125.8 MHz, CDCl<sub>3</sub>):  $\delta = 31.0$ , 55.8, 114.7, 118.2, 118.6, 122.6, 127.5, 128.5, 130.8, 131.2, 134.6, 153.0, 155.7, 158.3, 164.9, 191.3, 196.0.



<sup>1</sup>H NMR spectrum of 3-acetyl-4-(4-methylbenzoyl)-2*H*-chromen-2-one (**3a**)





<sup>1</sup>H NMR spectrum of 3-acetyl-4-(4-isopropylbenzoyl)-2*H*-chromen-2-one (**3b**)

<sup>13</sup>C NMR spectrum of 3-acetyl-4-(4-isopropylbenzoyl)-2*H*-chromen-2-one (**3b**)







<sup>13</sup>C NMR spectrum of 3-acetyl-4-(3-methoxybenzoyl)-2*H*-chromen-2-one (**3**c)





<sup>1</sup>H NMR spectrum of 3-acetyl-4-(4-methoxybenzoyl)-2*H*-chromen-2-one (**3d**)





<sup>1</sup>H NMR spectrum of 3-acetyl-4-(4-chlorobenzoyl)-2*H*-chromen-2-one (**3e**)







<sup>1</sup>H NMR spectrum of 3-acetyl-4-benzoyl-2*H*-chromen-2-one (**3f**)



<sup>1</sup>H NMR spectrum of 3-acetyl-4-(thiophene-2-carbonyl)-2*H*-chromen-2-one (**3g**)



<sup>13</sup>C NMR spectrum of 3-acetyl-4-(thiophene-2-carbonyl)-2*H*-chromen-2-one (**3g**)





<sup>13</sup>C NMR spectrum of 3-acetyl-4-benzoyl-8-methoxy-2*H*-chromen-2-one (**3h**)





udd





<sup>13</sup>C NMR spectrum of 3-acetyl-8-methoxy-4-(3-methoxybenzoyl)-2*H*-chromen-2-one (**3i**)



<sup>1</sup>H NMR spectrum of 3-acetyl-6-bromo-4-(4-methylbenzoyl)-2*H*-chromene-2-one (**3j**)



<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(4-methylbenzoyl)-2*H*-chromene-2-one (**3**j)







<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(4-isopropylbenzoyl)-2*H*-chromen-2-one (**3**k)







<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(3-methoxybenzoyl)-2*H*-chromen-2-one (**3**I)



<sup>1</sup>H NMR spectrum of 3-acetyl-6-bromo-4-(4-chlorobenzoyl)-2*H*-chromen-2-one (**3m**)



<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(4-chlorobenzoyl)-2*H*-chromen-2-one (**3m**)







<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(thiophene-2-carbonyl)-2*H*-chromen-2-one (**3n**)



<sup>1</sup>H NMR spectrum of ethyl-4-benzoyl-2-oxo-2*H*-chromene-3-carboxylate (**3o**)







<sup>1</sup>H NMR spectrum of ethyl-4-(4-methylbenzoyl)-2-oxo-2*H*-chromene-3-carboxylate (**3p**)

<sup>13</sup>C NMR spectrum of ethyl-4-(4-methylbenzoyl)-2-oxo-2*H*-chromene-3-carboxylate (**3p**)





<sup>13</sup>C NMR spectrum of ethyl-4-(4-chlorobenzoyl)-2-oxo-2*H*-chromene-3-carboxylate (**3**q)





<sup>1</sup>H NMR spectrum of 3-acetyl-6-chloro-4-benzoyl-2*H*-chromen-2-one (**3r**)



<sup>13</sup>C NMR spectrum of 3-acetyl-6-chloro-4-benzoyl-2*H*-chromen-2-one (**3r**)

Т







<sup>13</sup>C NMR spectrum of 3-acetyl-6-chloro-4-(3-methylbenzoyl)-2*H*-chromen-2-one (**3s**)







<sup>13</sup>C NMR spectrum of 3-acetyl-6-chloro-4-(4-isopropylbenzoyl)-2*H*-chromen-2-one (**3**t)



<sup>1</sup>H NMR spectrum of 3-acetyl-6-bromo-4-(4-methoxybenzoyl)-2*H*-chromen-2-one (**3u**)



<sup>13</sup>C NMR spectrum of 3-acetyl-6-bromo-4-(4-methoxybenzoyl)-2*H*-chromen-2-one (**3u**)