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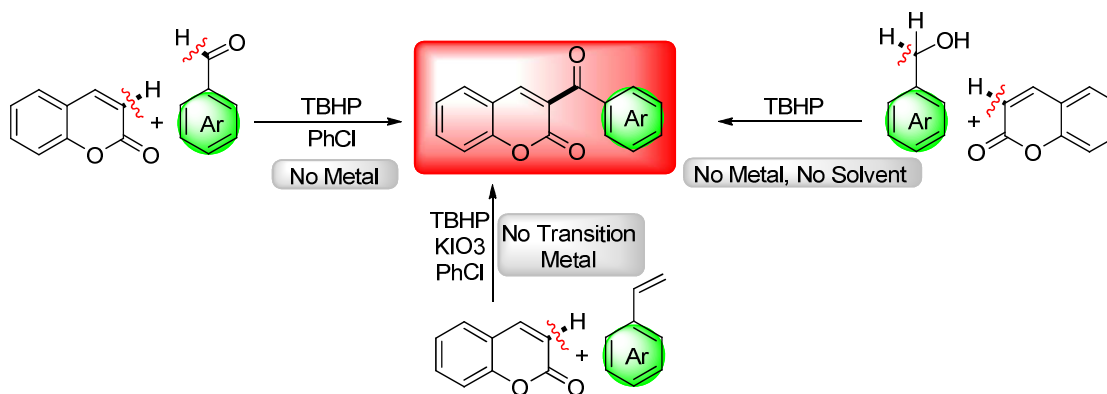
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## A Regioselective Metal-Free Construction of 3-Aroyl Coumarins by Csp<sup>2</sup>-H Functionalization

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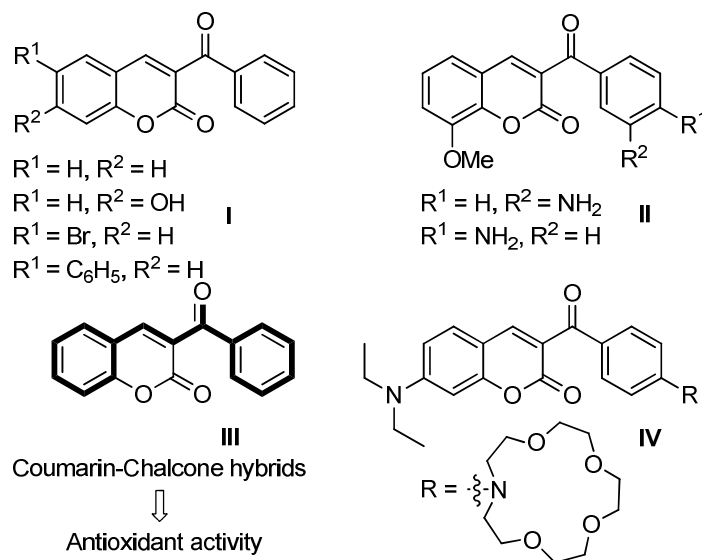
### ABSTRACT

A successive metal-free TBHP-mediated regioselective C-H functionalization of coumarins towards expedient synthesis of 3-arylcoumarins is unveiled. The ongoing method conducted through the reaction of either coumarins or coumarin-3-carboxylic acids with aromatic aldehydes. The optimized reaction condition also worked well with benzyl alcohols and styrenes as surrogates for aldehydes, which bear latent carbonyl functionality.

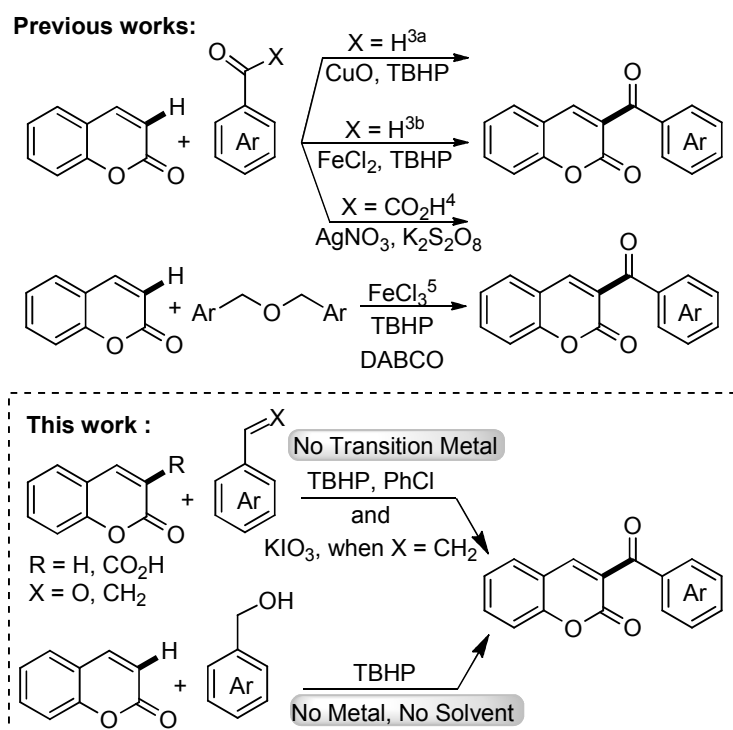
Occurrence of 3-carbonyl coumarins in pharmaceutically active compounds justifies their versatility.<sup>1</sup> 3-Aroyl coumarins in particular, are proved to display varying degrees of  $\alpha$ -glucosidase inhibitory and DPPH scavenging activity (Scheme 1, **I**),<sup>1a</sup> antibacterial (**II**)<sup>1b</sup> and as coumarin-chalcone hybrids, antioxidant activities(**III**).<sup>1c</sup> Furthermore, as a fluorescent chemosensor, compound **IV** has shown a high affinity and selectivity for Pb<sup>2+</sup> which would be helpful in clarifying the cellular role of lead ions in vivo.<sup>1d</sup> Given that, many have made

considerable endeavours towards the synthesis of these motifs. Among the traditional methods,

**Scheme 1.** Interesting compounds with 3-aryl coumarin framework



**Scheme 2.** Methods of direct 3-carbonylation of coumarins

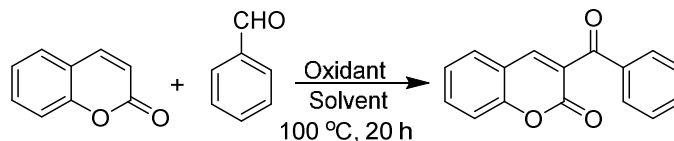


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3 Knoevenagel condensation is the most widely used route in which salicylaldehydes and  $\beta$ -  
4 ketoesters are exploited as the starting materials.<sup>2</sup> However, despite all virtues the  
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6 aforementioned reaction suffers from some drawbacks, namely the necessity of basic or  
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8 acidic conditions and/or a laborious synthetic procedure. Thus, lately efforts have been  
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10 focused on direct acylation of coumarins through metal-catalyzed C-H functionalization  
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12 reactions (Scheme 2).  
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16 To this end, Zhou et al.<sup>3a</sup> and Yuan et al.<sup>3b</sup> individually reported synthetic procedures in  
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18 which coumarins were coupled with aromatic aldehydes through metal catalysed reactions. In  
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20 another effort, Duan and co-workers showed that 3-aryl coumarins could be achieved  
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22 through the reaction of coumarins with phenylglyoxylic acid with the aid of silver catalyst,  
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24 albeit in low yields.<sup>4</sup> 3-Aroyl coumarins were also prepared by the reaction of benzylether  
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26 and oumarins promoted by  $\text{FeCl}_3$  as the catalyst.<sup>5</sup> Nonetheless, a setback relevant to these  
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28 methods, due to the use of metal catalysts, are incompatibility with instructions issued by  
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30 Green Chemistry. Instead, metal-free reactions have recently come of age. Plethora of  
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32 reactions released have now been conducted through metal-free reactions since they offer  
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34 greener approaches which take advantages of cost-effective reaction-promoters.<sup>6</sup> Despite the  
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36 growing prevalence of these reactions, to the best of our knowledge, thus far no metal-free  
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38 cross-dehydrogenative coupling (CDC) reaction for direct functionalization of coumarins has  
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40 been preceded.<sup>7</sup> Herein, we report a state-of-the-art metal-free acylation of this motif via  
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42 cross-dehydrogenative coupling with aromatic aldehydes as well as benzyl alcohols which  
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44 obviates the foregoing impediments of metal-catalyzed reactions. This approach benefits  
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46 from smooth proceedings, is devoid of any kind of metals, and is promoted solely by TBHP.  
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48 Among metal-free reactions, there are rare examples being promoted merely by TBHP as a  
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50 catalyst without any contribution of halide salts or other oxidants.<sup>8</sup> This reaction is notable  
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from another aspect since the competing aldehyde oxidation to its benzoic acid fails to outperform coupling procedure.<sup>9</sup>

**Table 1.** Screening optimal conditions



Entry	Initiator	Additive	Solvent	Yield% <sup>a</sup>
1	TBHP		neat	57
2	DTBP		neat	52
3	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		neat	trace
4	TBHP/DTBP		neat	50
5	AIBN		neat	trace
6	TBHP	TBAI	neat	trace
7	TBHP	TBAB	neat	trace
8	TBHP	TBAC	neat	40
9	TBHP	K <sub>2</sub> CO <sub>3</sub>	neat	trace
10	TBHP		EtOAc	45
11	TBHP		ACN	48
12	TBHP		DCE	35
13	TBHP		H <sub>2</sub> O	25
<b>14</b>	<b>TBHP</b>		<b>PhCl</b>	<b>70</b>
15	TBHP	TEMPO	PhCl	0

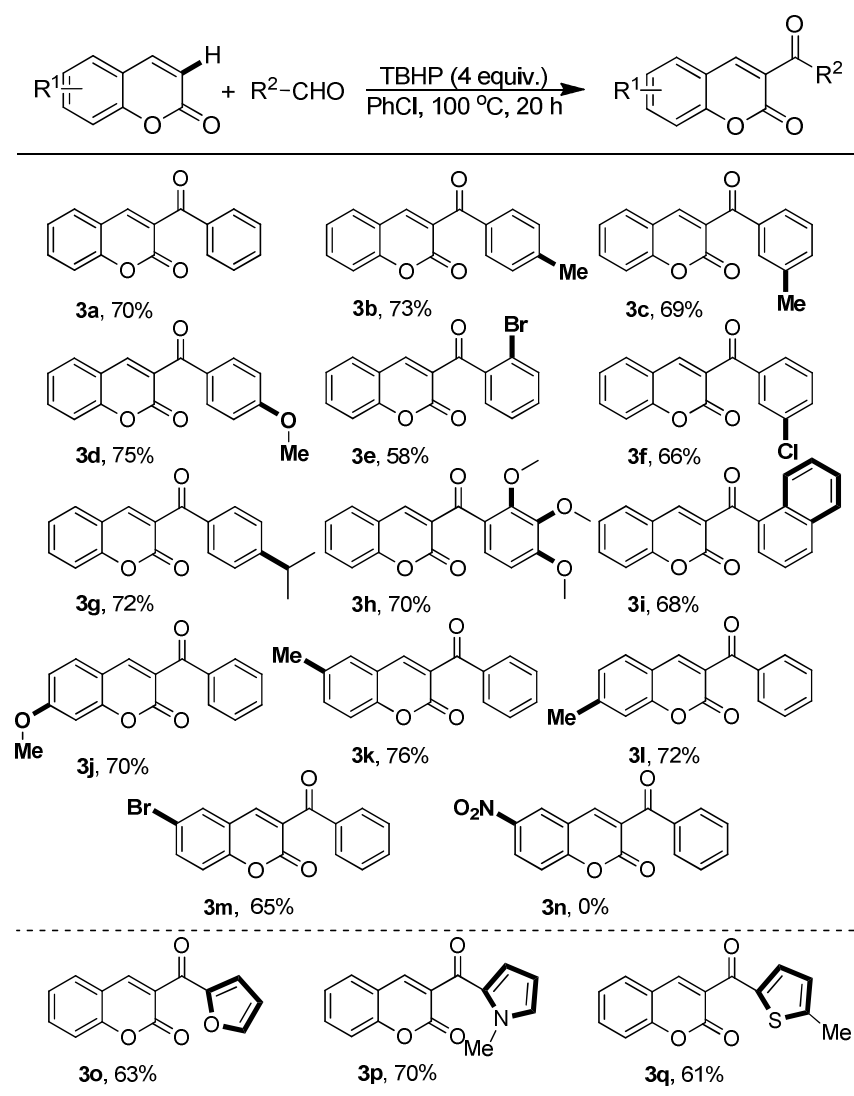
<sup>a</sup> Reaction conditions: Coumarin (0.3 mmol), benzaldehyde (4 equiv.), TBHP (4 equiv., 70% in water) were heated in a sealed tube at 100 °C for 20 h.

First, we set out to functionalize coumarin regioselectively at C-3 by benzaldehyde using TBHP which is endowed by the commencement of SET (single electron transfer) reactions. To this end, coumarin was treated with benzaldehyde under TBHP at 100 °C for 20 h as the model reaction. At the outset, the effects of different oxidants were screened as the oxidant seemed to have the key role in conducting the reaction. Hence, an initial reaction was accomplished using 4.0 equiv. of TBHP at 100 °C for 20 h under neat conditions which gave rise to the desired product in 57% yield (Table 1, entry 1). When the oxidant was replaced with DTBP, it still resulted in the favourable product, albeit in a lower yield, but no product was observed when K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was employed (entries 2 and 3, respectively). In the next step, we added some additives in hope of increasing the reaction efficiency but they had conspicuously deleterious effects on the yields (entries 6-9). In continuation, different solvents were taken into account among which chlorobenzene furnished the best yield (entries 10-14). Finally reducing the amount of TBHP to 2 equivs slightly reduced the yield. We were delighted to find that these conditions, afforded aroylated coumarin regioselectively at C-3 with 70% yield (entry 14). Introduction of coumarin to the optimized conditions in the presence of a radical scavenger like TEMPO (10 equiv), suppressed the formation of the desired aroyl compound markedly which indicated that a radical pathway could be involved (entry 15).

Next, to investigate the scope and limitations of the regioselective direct carbonylation process, various aromatic aldehydes and coumarins were exposed to the reaction condition (Table 2). As we expected, *p*- and *m*-methylbenzaldehydes led to good yields (**3b-3c**). Employing highly electron-rich benzaldehyde increased the yield even more (**3d**). Also, halo substituted arenes were tolerated under these circumstances, making the way for further manipulation (**3e-3f**). Cuminaldehyde as a coupling partner also resulted satisfactory yield of the desired product (**3g**). The performance of this approach is also manifest in efficient

conversion of sterically encumbered trimethoxy substituted benzaldehyde as well as naphthaldehyde to their desired ketones (**3h-3i**). Gratifyingly, various alkyl, alkoxy and halo substituted coumarins were also tolerated under the optimized conditions and the reactions proceeded smoothly furnishing the desired products in yields exceeding 65% (**3j-3m**). Unfortunately, electron-deficient *p*-nitro benzaldehyde, did not participate in the cross-coupling reaction.

**Table 1.** Substrate scope for construction of 3-aryl coumarins<sup>a</sup>

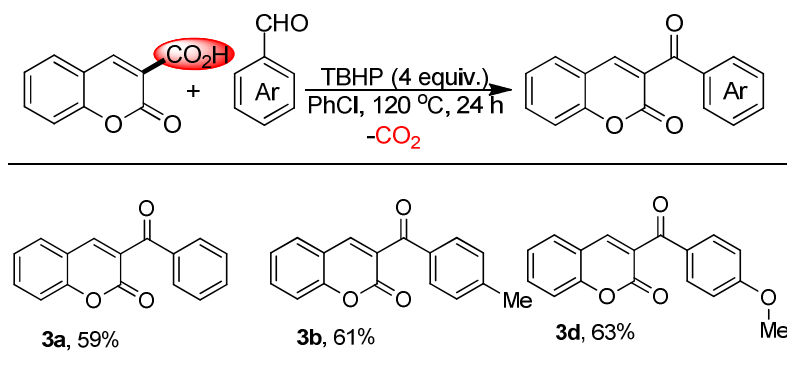


<sup>a</sup> All reactions were proceeded through the following conditions: Coumarin **1** (0.1 mmol), arylaldehyde **2** (4.0 equiv.), TBHP (4 equiv., 70% in water) in 0.5 mL PhCl were heated in a sealed tube at 100 °C for 20 h.

To our delight, the approach was also viable for some heterocyclic carboxaldehydes. When furfural, pyrrole- and thiophene-2-carboxaldehydes were exposed to coumarin under reaction conditions, the desired heteroaroyl coumarins **3o**, **3p** and **3q** were obtained with satisfactory yields, respectively. 1,2-Dihydro derivatives of these motifs which can be readily prepared from reduction of the corresponding coumarins with sodium borohydride, are proved to show a marked selectivity for the inhibition of SIRT2 over SIRT1 (sirtuins' inhibitors).<sup>10</sup>

Surprisingly, when coumarin-3-carboxylic acid was reacted with arene aldehydes, a tandem decarboxylative/oxidative cross-coupling reaction proceeded and good yields of aroyl coumarins were obtained (Scheme 3). Although lately some reports on metal-free decarboxylation have been released,<sup>11</sup> this is the first example of decarboxylation of coumarins under metal free conditions. Previous report in this field was also revealed by our group using palladium catalyst.<sup>12</sup>

**Scheme 3.** The reaction of coumarin-3-carboxylic acid and benzaldehydes

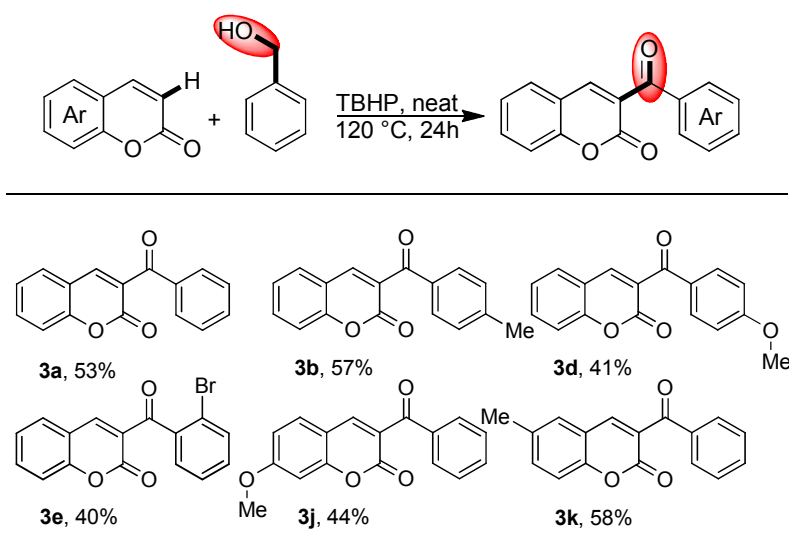


Next our thoughts were stimulated about other approaches for construction of 3-aroyl coumarins. Gratifyingly, when benzylalcohol was utilized as an acyl source for coupling with coumarin, the corresponding carbonylated coumarin was obtained albeit in low yield. A slightly altered reaction condition with increasing amounts of TBHP and a higher reaction temperature, afforded the desired products in moderate yields (Scheme 4).



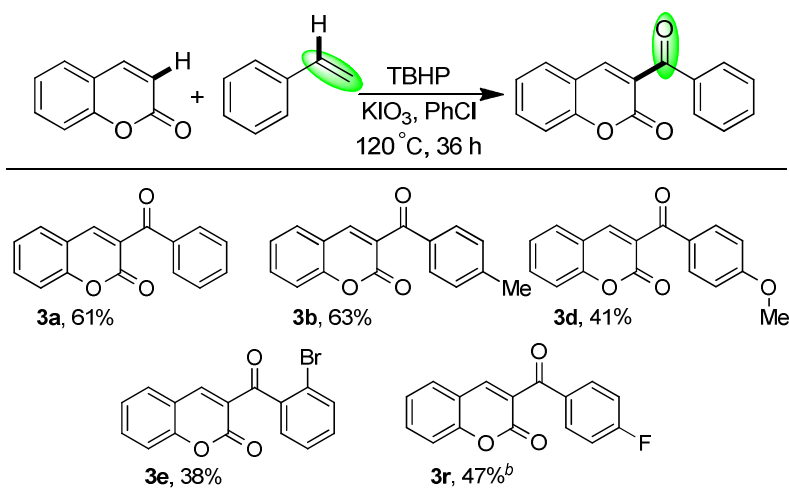
As a final step, inspired by Patel, Bhanage, Pan and Shah's work,<sup>13</sup> we set out to gain the desired product through the reaction of styrene with benzaldehyde (Scheme 5). Using slightly altered reaction conditions the desired ketones were obtained, delightfully (See Table S2, Supporting Information). Although the reaction yields are moderate to good, this is the first report of acylation of a heterocycle via reaction with styrene.

**Scheme 4.** Oxidative coupling of benzylalcohols and coumarins<sup>a</sup>



<sup>a</sup> Reaction conditions: Coumarin (0.1 mmol), benzylalcohol (0.1 mL), TBHP (8 equiv., 70% in water) were heated in a sealed tube at 120 °C for 24 h.

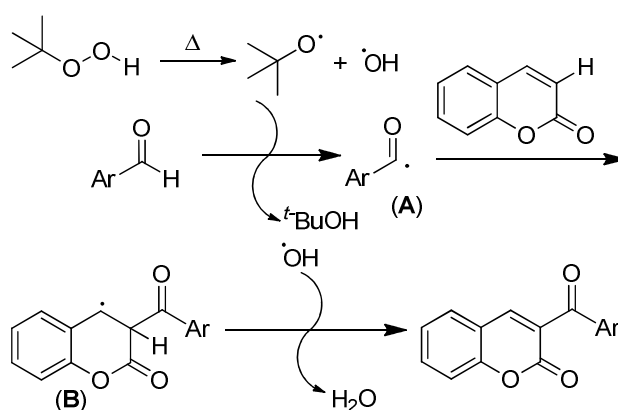
**Scheme 5.** Acylation of coumarin via the reaction with styrene<sup>a</sup>



<sup>a</sup> Reaction conditions: Coumarin **1** (0.1 mmol), styrene (4.0 equiv.), TBHP (8 equiv., 70% in water), KIO<sub>3</sub> (2 equiv.) in 0.5 mL PhCl were heated in a sealed tube at 120 °C for 36 h. <sup>b</sup> Due to difficulties in purification a rough yield is given.

A tentative mechanism of the foregoing reaction has been shown below (Scheme 6). First, the aryl carbonyl radical **A** may be generated with the aid of TBHP. Then this radical would selectively attack coumarins at C-3 position and produce intermediate **B** which upon a hydrogen radical loss would deliver the target molecule.

**Scheme 6.** Plausible mechanism for regioselective C-3 acylation of coumarins



In summary, a regioselective direct carbonylation of coumarins via metal-free cross-dehydrogenative coupling of coumarins and aromatic aldehydes has been developed which provides an expedient access to 3-aryl coumarins. Benzylalcohol and styrene derivatives can also be used in this term enabling one to reach the same products with various reagents. Another privilege offered by this approach is that an in situ decarboxylation takes place simultaneously over the coupling process allowing this procedure to be extended for coumarin-3-carboxylic acids. Good tolerance towards different functional groups renders this method efficient and provides a simple alternative to its precedents.

## EXPERIMENTAL SECTION

**Typical Experimental Procedure for Metal-Free Direct Carbonylation of Coumarins.** A vial equipped with a stir bar was charged with coumarin (0.1 mmol), arylaldehyde (4 equiv)

and TBHP (4 equiv). Chlorobenzene (0.5 mL) was added and the vial was capped. The resulting mixture was heated in an oil bath at 100 °C for 20 h. Removal of the solvent gave a crude mixture which was purified by flash column chromatography (hexane/EtOAc gradient) and recrystallization was conducted either using diethyl ether or a mixture of diethyl ether/hexane.

**3-Benzoyl-2H-chromen-2-one (3a).** White crystal (18 mg, 70%), mp 131-133 °C (Ref.<sup>2c</sup> 134-136 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.07 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.58-7.66 (m, 3H), 7.31-7.49 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 191.7, 158.5, 154.7, 145.5, 136.2, 133.9, 133.7, 129.6, 129.2, 128.8, 128.6, 125.0, 118.2, 116.9. Anal. Calcd for C<sub>16</sub>H<sub>10</sub>O<sub>3</sub>: C, 76.79; H, 4.03. Found: C, 77.07; H, 4.16.

**3-(4-Methylbenzoyl)-2H-chromen-2-one (3b).** White Crystal (19 mg, 73%), mp 127-129 °C (Ref.<sup>2c</sup> 132-134 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.79(d, *J* = 8.1 Hz, 1H), 7.62 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 2H), 7.26-7.40 (m, 4H), 2.43 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 191.3, 158.5, 154.7, 145.1, 144.9, 133.6, 133.5, 129.8, 129.4, 129.2, 127.2, 124.9, 118.2, 116.8, 21.8. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>: C, 77.26; H, 4.58. Found: C, 77.53; H, 4.68.

**3-(3-Methylbenzoyl)-2H-chromen-2-one (3c).** White Crystal (18 mg, 69%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.07 (s, 1H), 7.60-7.74 (m, 4H), 7.27-7.44 (m, 4H), 2.42 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 191.9, 158.5, 154.7, 138.5, 136.2, 134.7, 133.6, 129.9, 129.2, 128.4, 127.9, 127.2, 126.9, 125.0, 118.2, 116.9, 21.3. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>: C, 77.26; H, 4.58. Found: C, 77.57; H, 4.72.

**3-(4-Methoxybenzoyl)-2H-chromen-2-one (3d).** White Crystal (21 mg, 75%), mp 174-175 °C (Ref.<sup>2d</sup> 174-175 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.02 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.65 (td, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.58 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 190.0, 164.3, 157.4, 154.7, 144.6, 133.3, 132.2, 129.0, 127.7, 124.9, 118.3, 116.9, 113.9, 55.6. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>: C, 72.85; H, 4.32. Found: C, 73.10; H, 4.42.

**3-(2-Bromobenzoyl)-2H-chromen-2-one (3e).** White Crystal (19 mg, 58%), mp 120-121 °C (Ref.<sup>3b</sup> 127-128 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.41 (s, 1H), 7.66 (m, 2H), 7.65-7.74 (d, *J* = 7.8 Hz, 1H), 7.27-7.51 (m, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 191.8, 158.0, 155.3, 147.7, 140.3, 134.5, 133.1, 132.2, 130.0, 129.8, 127.7, 125.5, 125.0, 119.7, 118.4, 117.0. Anal. Calcd for C<sub>16</sub>H<sub>9</sub>BrO<sub>3</sub>: C, 58.38; H, 2.76. Found: C, 58.66; H, 2.90.

**3-(3-Chlorobenzoyl)-2H-chromen-2-one (3f).** White Crystal (19 mg, 66%), mp 124-125 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.15 (s, 1H), 7.82 (d, *J* = 1.5 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.36-7.46 (m, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 190.6, 158.4, 154.9, 146.2, 137.9, 134.9, 134, 133.7, 129.9, 129.4, 129.3, 127.6, 126.3, 125.1, 118.1, 117.0. Anal. Calcd for C<sub>16</sub>H<sub>9</sub>ClO<sub>3</sub>: C, 67.50; H, 3.19. Found: C, 67.80; H, 3.32.

**3-(4-Isopropylbenzoyl)-2H-chromen-2-one (3g).** White Crystal (21 mg, 72%), mp 135-136 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.03 (s, 1H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.58-7.65 (m, 2H), 7.32-7.40 (m, 4H), 2.95-3.00 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 191.1, 158.5, 155.6, 154.7, 144.9, 134.0, 133.5, 130.0, 129.1, 127.4, 126.8, 125.0, 118.3, 116.9, 34.4, 23.6. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>: C, 78.06; H, 5.52. Found: C, 78.30; H, 5.63.

**3-(2, 3, 4-Trimethoxybenzoyl)-2H-chromen-2-one (3h).** Red Solid (24 mg, 70%), mp 228-230 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.04 (s, 1H), 7.55-7.60 (m, 3H), 7.27-7.37 (m, 2H), 7.76 (d,  $J$  = 8.8 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3 H), 3.72 (s, 3 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.7, 158.7, 158.4, 154.5, 154.0, 142.1, 141.4, 133.0, 130.2, 129.2, 126.1, 125.0, 124.7, 118.6, 116.8, 107.3, 61.6, 60.9, 56.2. Anal. Calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_6$ : C, 67.05; H, 4.74. Found: C, 67.33; H, 4.87.

**3-Naphthoyl-2H-chromen-2-one (3i).** White Crystal (21 mg, 68%), mp 251-252 °C (Ref.<sup>3b</sup> 252-253 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 8.56 (d,  $J$  = 8.5 Hz, 1H), 8.23 (s, 1H), 8.04 (d,  $J$  = 8.2 Hz, 1H), 7.93 (d,  $J$  = 7.9 Hz, 1H), 7.76 (d,  $J$  = 7.1 Hz, 1H), 7.56-7.68 (m, 5H), 7.48 (t,  $J$  = 7.5 Hz, 1H), 7.41 (d,  $J$  = 8.3 Hz, 1H), 7.36 (t,  $J$  = 7.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 193.2, 158.1, 155.1, 146.6, 134.6, 134.0, 133.4, 130.7, 129.6, 129.5, 128.6, 128.2, 126.7, 125.5, 124.9, 124.3, 118.3, 116.9. Anal. Calcd for  $\text{C}_{20}\text{H}_{12}\text{O}_3$ : C, 79.99; H, 4.03. Found: C, 80.31; H, 4.16.

**3-Benzoyl-7-methoxy-2H-chromen-2-one (3j).** White Crystal (20 mg, 70%), mp 159-160 °C (Ref.<sup>3b</sup> 150-151 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.11 (s, 1H), 7.88 (d,  $J$  = 7.2 Hz, 2H), 7.61 (t,  $J$  = 7.2 Hz, 1H), 7.47-7.53 (m, 3H), 6.93 (dd,  $J$  = 8.7 Hz, 2.4 Hz, 1H), 6.89 (d,  $J$  = 2.4 Hz, 1H), 3.94 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.0, 163.6, 157.7, 156.1, 145.4, 135.8, 132.4, 129.4, 128.5, 127.4, 121.9, 112.5, 110.9, 99.7, 55.0. Anal. Calcd for  $\text{C}_{17}\text{H}_{12}\text{O}_4$ : C, 72.85; H, 4.32. Found: C, 73.12; H, 4.44.

**3-Benzoyl-6-methyl-2H-chromen-2-one (3k).** White Crystal (21 mg, 76%), mp 163-164 °C (Ref.<sup>14</sup> 157.7-158.9 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (s, 1H), 7.89 (d,  $J$  = 7.5 Hz, 2H),

7.63 (t,  $J = 7.5$  Hz, 1H), 7.28-7.52 (m, 5H), 2.45 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 157.6, 151.9, 144.5, 135.3, 133.7, 132.7, 129.9, 128.6, 127.8, 127.6, 125.8, 116.9, 115.6, 19.7. Anal. Calcd for  $\text{C}_{17}\text{H}_{12}\text{O}_3$ : C, 77.26; H, 4.58. Found: C, 77.55; H, 4.71.

**3-Benzoyl-7-methyl-2H-chromen-2-one (3l).** White Crystal (19 mg, 72%), mp 156-158 °C (Ref.<sup>14</sup> 157-158 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (s, 1H), 7.85 (d,  $J = 8.1$  Hz, 2H), 7.59 (t,  $J = 8.1$  Hz, 1H), 7.44-7.48 (m, 3H), 7.14-7.18 (m, 2H), 2.48 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.8, 158.6, 155.0, 145.7, 136.5, 133.6, 129.5, 128.9, 128.5, 126.3, 125.6, 117.0, 115.8, 22.0. Anal. Calcd for  $\text{C}_{17}\text{H}_{12}\text{O}_3$ : C, 77.26; H, 4.58. Found: C, 77.58; H, 4.71.

**3-(Furan-2-carbonyl)-2H-chromen-2-one (3o).** Brown Solid (15 mg, 63%), mp 155-156 °C (Ref.<sup>3b</sup> 157-158 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 7.67-7.60 (m, 3H), 7.40 (d,  $J = 8.4$  Hz, 1H), 7.37-7.33 (m, 2H), 6.61 (dd,  $J = 3.6$  Hz, 1.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  178.0, 154.8, 151.8, 147.7, 145.5, 133.8, 129.3, 128.8, 126.3, 125.0, 120.7, 118.1, 117.0, 112.7. Anal. Calcd for  $\text{C}_{14}\text{H}_8\text{O}_4$ : C, 70.00; H, 3.36. Found: C, 70.26; H, 3.47.

**3-(1-Methyl-1H-pyrrole-2-carbonyl)-2H-chromen-2-one (3p).** Brown Solid (18 mg, 70%), mp 148-150 °C (Ref.<sup>15</sup> 162-163 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.95 (s, 1H), 7.56-7.65 (m, 2H), 7.28-7.41 (m, 2H), 6.98 (s, 1H), 6.83 (d,  $J = 2.1$  Hz, 1H), 6.19 (d,  $J = 2.1$  Hz, 1H), 4.1 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 179.8, 158.6, 154.3, 142.6, 133.2, 132.9, 130.9, 128.8, 127.9, 124.8, 123.3, 118.2, 116.9, 108.9, 37.7. Anal. Calcd for  $\text{C}_{15}\text{H}_{11}\text{NO}_3$ : C, 71.14; H, 4.38; N, 5.53. Found: C, 71.42; H, 4.50; N, 5.70.

**3-(5-Methyl-thiophene -2-carbonyl)-2H-chromen-2-one (3q).** Brown Solid (16 mg, 61%), mp 150-151 °C (Ref.<sup>3b</sup> 153-154 °C). <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 2.6 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 182.4, 158.3, 154.6, 152.3, 144.3, 140.6, 136.0, 133.5, 129.1, 127.2, 127.0, 125.0, 118.2, 116.9, 16.2. Anal. Calcd for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>S: C, 66.65; H, 3.73; S, 11.86. Found: C, 66.94; H, 3.87; S, 12.07.

**3-(4-Fluorobenzoyl)-2H-chromen-2-one (3r).** White Solid (13 mg, 47%), mp 165-166 °C (Ref.<sup>3b</sup> 167-168 °C). <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>): δ: 8.11- 8.15 (m, 2H), 7.91-7.94 (m, 2H), 7.66-7.68 (m, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.14-7.18 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ: 190.2, 166.2 (d, *J*<sub>C-F</sub> = 254.7 Hz), 158.5, 154.9, 145.7, 133.8, 132.3 (d, *J*<sub>C-F</sub> = 9.5 Hz), 129.3, 126.9, 125.1, 118.2, 117.0, 115.8 (d, *J*<sub>C-F</sub> = 21.9 Hz, CH). Anal. Calcd for C<sub>16</sub>H<sub>9</sub>FO<sub>3</sub>: C, 71.64; H, 3.38. Found: C, 71.90; H, 3.49.

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## Supporting Information

Copies of <sup>1</sup>H and <sup>13</sup>C spectra of all synthesized compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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