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Transition metal-free cross-dehydrogenative coupling acylation of coumarins by the $K_2S_2O_8$/Aliquat 336 catalytic system: a versatile strategy towards 4-aroylcoumarin derivatives†

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A new and efficient transition metal-free oxidative cross-dehydrogenative coupling (CDC) reaction is described for the preparation of 4-aroylcoumarin derivatives. In this protocol aldehydes have been used as acylating agents for acylation of 3-substituted coumarins through C(sp^2)–C(sp^2) bond formation using the $K_2S_2O_8$/Aliquat 336 system as an inexpensive and environmentally friendly reagent. The reactions proceeded in acetonitrile at 80 °C for 2–3 h to afford the corresponding 4-aroylcoumarin derivatives in high yields.

The coumarin moiety is a heterocyclic scaffold that exists widely in a variety of biologically active synthetic and natural products.[1] Notably, coumarin derivatives are well documented as therapeutic agents and possess a variety of biological properties such as monoamine oxidase (MAO)[2] as well as lipoxygenase inhibitory activity and accordingly antioxidant,[3] anti-inflammatory,[4] antitumour,[5] antimicrobial,[6] antimalarial,[7] anticoagulant[8] and anti-HIV properties[9] (Fig. 1). Moreover, coumarins have been used as sensitizers in older photovoltaic technologies[10] and also as dyes in laser technology,[11] as well as in the preparation of soaps, sunscreen, cosmetics, perfumes and flavorings.[12]

Due to formation of C–C bonds from two C–H bonds, CDC reactions are applied as a high atom-efficient and step-economic approach for the construction of complex molecules in organic synthesis.[13] Recently the formation of C–C and C–heteroatom bonds by use of CDC technique in the absence of transition metals has been considered significantly.[14]

Transition metal-free synthetic protocols from simplicity point of view as well as reducing adverse environmental consequences are elegant and robust approaches.[15] On the other hand, tetraalkylammonium halides/oxidants as catalytic systems have been found to be highly effective to replace the toxic heavy metal catalysts and have a significant role in development of C–C, C–N, C–O and C–S bonds formation in organic synthesis.[16]

Over the past decade, acylation of heterocyclic scaffolds using acylating agents such as aldehydes and arylmethanes *via* oxidative CDC reactions under transition metal-free conditions has attracted considerable interest.[17]

Recently, acylation of coumarins *via* CDC approaches using aldehydes as acylating agents has been investigated by our group,[18a] Qu[18b] and Zhou.[18c] In addition, Duan and co-workers reported an Ag-catalyzed diacylation of coumarins using α-oxocarboxylic acids as acyl sources.[18d]

As part of our continuing effort to develop efficient methods for the preparation of biologically active heterocyclic

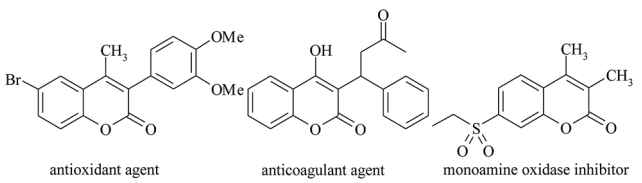
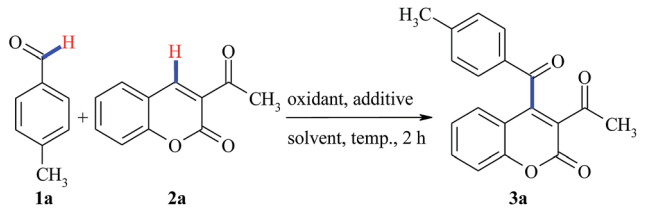


Fig. 1 Examples of pharmacologically active coumarin derivatives.



Scheme 1 Model CDC reaction between 4-methylbenzaldehyde **1a** and 3-acetylcoumarin **2a**.

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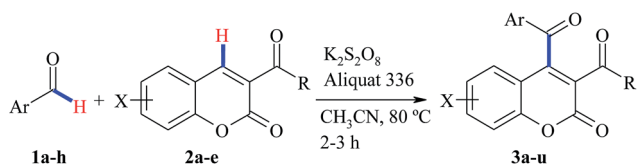
Table 1 Condition screening for the CDC reaction of 4-methylbenzaldehyde **1a** with 3-acetylcoumarin **2a**[a]

Entry	Oxidant[b] (equiv.)	Additive[b] (equiv.)	Solvent	t (°C)	Yield[c] (%)
1	$K_2S_2O_8$ (1)	Aliquat 336 (15)	CH_3CN	r.t.	NR[d]
2	$K_2S_2O_8$ (1)	Aliquat 336 (15)	CH_3CN	50	NR
3	$K_2S_2O_8$ (1)	Aliquat 336 (15)	CH_3CN	80	65
4	$K_2S_2O_8$ (1)	Aliquat 336 (30)	CH_3CN	80	78
5	$K_2S_2O_8$ (1)	Aliquat 336 (40)	CH_3CN	80	78
6	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	CH_3CN	80	87
7	$K_2S_2O_8$ (1.5)	Aliquat 336 (30)	CH_3CN	80	83
8	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	CH_3CN	100	82
9	$K_2S_2O_8$ (1.2)	TBAB[e] (30)	CH_3CN	80	NR
10	$K_2S_2O_8$ (1.2)	TBPB[f] (30)	CH_3CN	80	NR
11	$K_2S_2O_8$ (1.2)	NBS[g] (30)	CH_3CN	80	NR
12	$K_2S_2O_8$ (1.2)	I_2 (30)	CH_3CN	80	NR
13	$K_2S_2O_8$ (1.2)	KI (30)	CH_3CN	80	NR
14	$K_2S_2O_8$ (1.2)	CuI (30)	CH_3CN	80	NR
15	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	Toluene	80	50
16	$K_2S_2O_8$ (1.2)	Aliquat 336 (40)	Chlorobenzene	80	50
17	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	1,4-Dioxane	80	30
18	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	DCE	80	NR
19	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	DMSO : H_2O (1 : 1)	80	65
20	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	DMSO	80	55
21	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	H_2O	80	40
22	$K_2S_2O_8$ (1.2)	Aliquat 336 (30)	CH_3CN : H_2O (1 : 1)	80	82
23	$(NH_4)_2S_2O_8$ (1.2)	Aliquat 336 (30)	CH_3CN	80	40
24	TBHP[h] (1.2)	Aliquat 336 (30)	CH_3CN	80	60
25	H_2O_2[i] (1.2)	Aliquat 336 (30)	CH_3CN	80	NR
26	DDQ (1.2)	Aliquat 336 (30)	CH_3CN	80	NR
27	—	Aliquat 336 (30)	CH_3CN	80	NR
28	$K_2S_2O_8$ (1.2)	—	CH_3CN	80	NR

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.5 mmol), solvent (2 mL) for 2 h. [b] In respect to **2a**. [c] Isolated yield. [d] NR = no reaction. [e] Tetrabutylammonium bromide. [f] Tetrabutylphosphonium bromide. [g] *N*-Bromosuccinimide. [h] 70 wt% ^{t}BuOOH in H_2O. [i] 30 wt% H_2O_2 in H_2O.

compounds from readily available precursors,[19] and in continuation of our recent studies on CDC reactions,[20] herein, we describe an efficient approach for the intermolecular double C_{sp^2}–H functionalization between aromatic aldehydes and 3-acetylcoumarins through C_{sp^2}–C_{sp^2} bond formation leading to 4-aroylcoumarin derivatives.

To verify this theory, 4-methylbenzaldehyde **1a** and 3-acetylcoumarin **2a** were chosen as model substrates to optimize the CDC reaction conditions (Scheme 1 and Table 1). In this optimization, the effect of several oxidants, solvents, additives, reaction temperature and time as well as various equivalents of oxidants and additives were investigated. Initially, we tested this reaction in the presence of $K_2S_2O_8$ (1.0 equiv.) as oxidant and Aliquat 336 (tricaprylmethylammonium chloride)[21] (15 mol%) as additive in acetonitrile at room temperature or 50 °C for 2 h, but no product was detected (entries 1 and 2). By rising the temperature to 80 °C, 4-aroylcoumarin **3a** was obtained in 65% yield (entry 3). Subsequently, different quantities of $K_2S_2O_8$ and Aliquat 336 were evaluated to improve the yields (entries 4–7). Increasing the amount of additive to 30 mol%, led to the desired product **3a** in 78% yield (entry 4). However, increasing the amount of Aliquat 336 to 40 mol% had no effect on the yield (entry 5). Then we employed 1.2 and 1.5 equiv. of $K_2S_2O_8$ in the presence of 30 mol% Aliquat 336. Thus the desired product **3a** was obtained in 87% and 83% yields, respectively (entries 6 and 7). However, rising the temperature to 100 °C decreased efficiency of the reaction (entry 8). Some other additives including TBAB, TBPB, NBS (see footnotes in Table 1), I_2, KI and CuI were also screened in this study, but all were inert to this CDC reaction (entries 9–14). Next, the effect of different solvents such as toluene, chlorobenzene, 1,4-dioxane, DCE, DMSO/H_2O (1 : 1, v/v), DMSO and H_2O on the efficiency of the reaction were investigated. However, carrying out the reaction in these solvents **3a** was obtained in 40–65% yields and in DCE **3a** was not detected (entries 15–21). Also, the reaction was performed in CH_3CN/H_2O (1 : 1, v/v), but the yield decreased to 82% (entry 22). More experiments indicated that by use of $(NH_4)_2S_2O_8$ and TBHP as oxidant the yield of **3a** decreased to 60% and 40%, respectively (entries 23 and 24). Furthermore, oxidants such as H_2O_2 and DDQ were ineffective in this reaction (entries 25 and 26). Without $K_2S_2O_8$ as oxidant and Aliquat 336 as additive, the CDC reaction could not proceed in CH_3CN at 80 °C after 2 h (entries 27 and 28). Thus, the optimal conditions for the metal-



1a-h 2a-e 3a-u

Scheme 2 CDC reaction between aldehydes **1** and coumarins **2**.

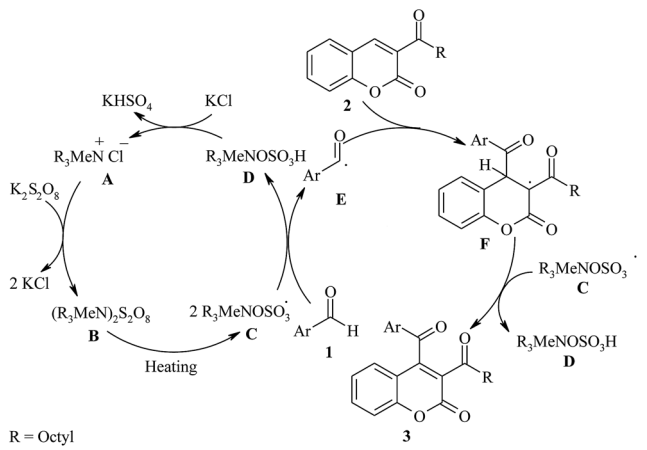
Table 2 Cross-dehydrogenative coupling of aldehydes **1** with 3-substituted coumarins **2**[a]

Entry	1	Ar	2	X	R	3	Yield[b] (%)
1[c]	**1a**	4-$CH_3C_6H_4$	**2a**	H	CH_3	**3a**	87
2	**1b**	4-iPrC_6H_4	**2a**	H	CH_3	**3b**	80
3	**1c**	3-$CH_3OC_6H_4$	**2a**	H	CH_3	**3c**	85
4	**1d**	4-$CH_3OC_6H_4$	**2a**	H	CH_3	**3d**	88
5	**1e**	4-ClC_6H_4	**2a**	H	CH_3	**3e**	79
6	**1f**	C_6H_5	**2a**	H	CH_3	**3f**	84
7	**1g**	2-Thienyl	**2a**	H	CH_3	**3g**	73
8[d]	**1f**	C_6H_5	**2b**	8-OMe	CH_3	**3h**	71
9	**1c**	3-$CH_3OC_6H_4$	**2b**	8-OMe	CH_3	**3i**	75
10	**1a**	4-$CH_3C_6H_4$	**2c**	6-Br	CH_3	**3j**	77
11	**1b**	4-iPrC_6H_4	**2c**	6-Br	CH_3	**3k**	73
12	**1c**	3-$CH_3OC_6H_4$	**2c**	6-Br	CH_3	**3l**	77
13	**1e**	4-ClC_6H_4	**2c**	6-Br	CH_3	**3m**	75
14	**1g**	2-Thienyl	**2c**	6-Br	CH_3	**3n**	72
15	**1f**	C_6H_5	**2d**	H	OEt	**3o**	82
16	**1a**	4-$CH_3C_6H_4$	**2d**	H	OEt	**3p**	79
17	**1e**	4-ClC_6H_4	**2d**	H	OEt	**3q**	82
18	**1f**	C_6H_5	**2e**	6-Cl	CH_3	**3r**	83
19	**1h**	3-$CH_3C_6H_4$	**2e**	6-Cl	CH_3	**3s**	80
20	**1b**	4-*i*PrC_6H_4	**2e**	6-Cl	CH_3	**3t**	78
21	**1d**	4-$CH_3OC_6H_4$	**2e**	6-Cl	CH_3	**3u**	77
22	**1i**	4-$O_2NC_6H_4$	**2a**	H	CH_3	**3v**	NR
23	**1f**	C_6H_5	**2f**	6-NO_2	CH_3	**3w**	NR
24	**1a**	4-$CH_3C_6H_4$	**2f**	6-NO_2	CH_3	**3x**	NR
25	**1j**	*n*-C_4H_9	**2a**	H	CH_3	**3y**	NR
26	**1k**	$C_6H_5CH_2$	**2a**	H	CH_3	**3z**	NR

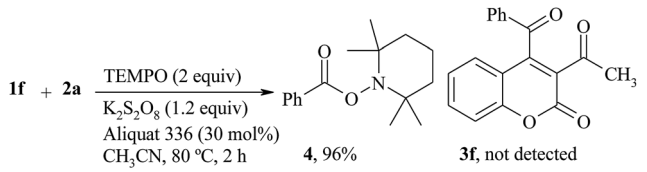
[a] Reaction conditions: aldehyde (**1**, 1 mmol), coumarin (**2**, 0.5 mmol), $K_2S_2O_8$ (1.2 mmol), Aliquat 336 (30 mol%), CH_3CN (2 mL). [b] Isolated yields (in respect to **2**). [c] Reaction time for entries 1–7: 2 h. [d] Reaction time for entries 8–26: 3 h.

free CDC acylation of **2a** by **1a** were determined: $K_2S_2O_8$ (1.2 equiv.), Aliquat 336 (30 mol%), in acetonitrile at 80 °C for 2 h.

With the optimized conditions available, we investigated the substrate scope (Scheme 2 and Table 2). Aromatic aldehydes with electron-donating alkyl or methoxy groups **1a–d** and **1h** those having electron-withdrawing chlorine group **1e** regardless of their position(s) on the aryl ring as well as benzaldehyde **1f**



Scheme 3 A putative reaction mechanism for the synthesis of 4-aroylcoumarins *via* CDC reactions mediated by $K_2S_2O_8$/Aliquat 336.



Scheme 4 Investigation on the reaction mechanism in the presence of TEMPO.

were coupled with 3-acetylcoumarin, affording the corresponding products **3a–f** in 84–88% yields (entries 1–6). Also, with methoxy, chlorine or bromine substituents on acetylcoumarin reaction time was increased and the desired products **3h–m** and **3r–u** were obtained in 71–83% yields after 3 h (entries 8–13 and 18–21). Heteroaromatic aldehyde thiophene-2-carbaldehyde **1g** was also employed in this CDC reaction, and gave the desired products **3g** and **3n** in 73 and 72% yields, respectively (entries 7 and 14). To extend the scope of our studies, ethyl-2-oxo-2*H*-chromen-3-carboxylate **2d** was also successfully reacted under the same conditions with aromatic aldehydes to yield the corresponding products **3o–q** after 3 h in 79–82% yields (entries 15–17). Furthermore, the reaction was tested using 6-nitro-3-acetylcoumarin (**2f**), 4-nitrobenzaldehyde (**1i**) as well as aliphatic aldehydes including *n*-butyraldehyde (**1j**) and phenylacetaldehyde (**1k**) under the optimum conditions, but, the acylation reaction did not take place (entry 22–26).

Based on the above observations and previous reports on the acylating agents and the heterocycle involved in the reaction,[17b–d] we proposed and outlined a plausible mechanism, as shown in Scheme 3. Initially, Aliquat 336 **A** may be converted to methyltrioctylammonium persulfate **B** by potassium peroxodisulfate ($K_2S_2O_8$). Heating would lead to sulfate radical **C** which could abstract "H" atom of aldehyde **1** to generate the corresponding acyl radical **E**. Next, the acyl radical **E** reacts with coumarin **2** at β-position to give radical **F**. Finally, a hydrogen atom may be removed from radical **F** by another sulfate radical **C** to afford 4-aroylcoumarin **3**.

To gather further insight into our novel $K_2S_2O_8$/Aliquat 336 promoted acylation, the reaction between benzaldehyde **1f** and 3-acetylcoumarin **2a** was performed in the presence of 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (TEMPO) as a radical scavenger (Scheme 4). Under this condition, 2,2,6,6-tetramethylpiperidino benzoate **4** was isolated in 96% yield and the desired acylated product **3f** was not detected. Thus an acyl radical is involved in the catalytic cycle of the transformation.

Conclusions

In summary, we have successfully disclosed an expedient and economical approach for 4-aroylcoumarin derivatives without using expensive transition-metal catalysts. In this paper, $K_2S_2O_8$/Aliquat 336 system has been reported as a ubiquitous and inexpensive catalytic combination at moderate temperature for the C4–H acylation of C3-substituted coumarins with aldehydes as acylating agents through oxidative cross-dehydrogenative coupling reaction. This new protocol

represents an attractive route for a straightforward access to a diverse range of substituted coumarins, a privileged motif found in a number of natural and designed compounds with important biological and physical implications.

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