Tetrahedron xxx (2014) 1–7

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Diacylation of coumarins by silver-catalyzed decarboxylative cross-coupling

Hua Wang, Shi-Liu Zhou, Li-Na Guo, Xin-Hua Duan *

Department of Chemistry, School of Science and MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 13 August 2014
Received in revised form 30 November 2014
Accepted 8 December 2014
Available online xxx

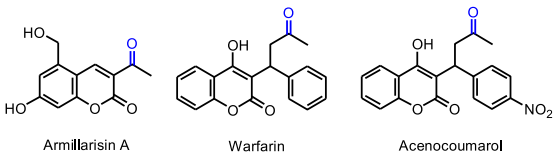
Keywords:
Decarboxylation
Acylation
Radical
Silver-catalyzed
Substituted coumarins

ABSTRACT

A mild silver-catalyzed decarboxylative acylation of coumarins has been developed by using α-oxocarboxylic acids as acyl sources. This protocol provides an efficient and straightforward access to aroyl substituted coumarins in moderate to excellent yields with good selectivities. Furthermore, the reaction conditions were also applicable to quinolinones and naphthoquinones, affording the corresponding acylated heterocyclic compounds.

1. Introduction

Coumarins are widely used in pharmaceuticals, agrochemicals, organic materials, and in other areas due to their remarkable biological activities and optical properties.[1] For examples, Armillarisin A, Warfarin, and Acenocoumarol with containing carbonyl groups in coumarins usually used clinically as antibiotic, anticoagulant, and anticoagulant agents (Scheme 1).[1a] As a result, many effective methods for the synthesis of coumarins have been developed over the past several years.[2] Among these methods, the synthesis of substituted coumarins is more attractive because of their extensive existence as core structures in natural products and pharmaceuticals. Recently, the transition metal-catalyzed direct regioselective C-3 or C-4 functionalization of simple coumarins provided an efficient way to obtain substituted coumarins. For example, palladium-catalyzed C-4 regioselective arylation of coumarins using arylboronic acids and simple arenes was extensively developed by Jafarpour, Li and Hong.[3a–c] Lately, the direct C-3 functionalization of coumarins has also been documented in the literature.[3d–h] However, most of these approaches are mainly focused on monosubstituted coumarins, the corresponding 3,4-disubstituted coumarins are less explored.[4] Therefore, the development of a general procedure for the synthesis of polysubstituted coumarins using environmentally friendly and inexpensive reagents is still highly desirable.



Scheme 1. Biologically active coumarins containing carbonyl groups.

In recent years, the application of readily available and stable carboxylic acids instead of expensive and sensitive organometallic reagents is highly attractive for organic chemists.[5] Up to now, great progress has been made for the construction of C–C and *C*-heteroatom bonds through the transition metal-catalyzed decarboxylative cross-coupling reactions.[6] More recently, Goossen,[7a,b] Ge,[7c,d] and others[7f–j] including our group[7e] have also developed a series of novel palladium-catalyzed decarboxylative acylation reactions using α-oxocarboxylic acids as acyl sources. In this regard, our group recently discovered that silver-catalyzed decarboxylative coupling of α-oxocarboxylic acids with alkenes could also be applied to the synthesis of heterocycles and organofluorine compounds through tandem radical process.[8a–c] Herein we report a mild synthetic method for preparation of monosubstituted and polysubstituted coumarins through direct decarboxylative cross-coupling reactions.

2. Results/discussion

We began our investigation by treatment of coumarin (**1a**) with phenylglyoxylic acid (**2a**) in the presence of $AgNO_3$ (10 mol %) and

* Corresponding author. E-mail address: duanxh@mail.xjtu.edu.cn (X.-H. Duan).

http://dx.doi.org/10.1016/j.tet.2014.12.029
0040-4020/

$K_2S_2O_8$ (2 equiv) in different solvents (Table 1). As expected, the reaction proceeded smoothly at room temperature in DMSO/H_2O (1:1), affording the desired 3,4-diacylcoumarin **3a** in 68% yield, along with 24% yield of 3-acylcoumarin **3a′** (entry 1).[9] Screening of solvents revealed that the reactions were fully suppressed in CH_3CN/H_2O, DCM/H_2O, and acetone/H_2O (entries 2–4). For the different oxidants, both $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$ resulted in satisfactory yields (entries 5 and 6), while oxone was ineffective (entry 7). Various catalysts were also examined, but none of them gave better results than $AgNO_3$ (entries 8–10). Further optimization found that no reaction took place in the absence of catalyst or oxidant (entries 11 and 12).

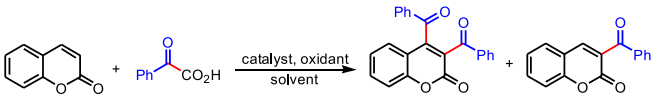
Under the optimal reaction conditions, we explored the scope of the reaction with a variety of α-oxocarboxylic acids **2** (Table 2). Both electron-rich and electron-poor α-oxocarboxylic acids **2** could successfully afford the corresponding products **3** or **3′** in moderate to good yields with excellent functional group tolerance (**3b**–**k**). Phenylglyoxylic acids containing electron-rich groups at the *para* position of the aromatic ring, such as **2b** and **2c** led to the 3,4-diacylcoumarins **3b** and **3c** in moderate yields along with a considerable amount of monoacylcoumarins **3′**. Interestingly, phenylglyoxylic acids with *p*-substituted electron-withdrawing groups gave the 3-acylcoumarins **3d′**–**g′** as major products, which perhaps arises from the nucleophilicities of the in situ generated acyl radicals (vide infra). Notably, when the more sterically congested *o*-substituted phenylglyoxylic acids **2h**–**j** were used, the 3,4-diacylcoumarins were selectively obtained (**3h**–**j**). Furthermore, multisubstituted phenylglyoxylic acid **2k** was also suitable for the reaction, giving the desired diacylated coumarin **3k** in 85% yield. These results demonstrated that the steric effect was of crucial importance for the selectivity of the reaction. Finally, β-naphthyloxoacetic acid and 2-thienylglyoxylic acid were selectively monoacylated in moderated yields (**3l′** and **3m′**).

Next, other coumarins were also investigated with *o*-methylphenylglyoxylic acid **2h** as reactant (Table 3). In general, we found that coumarins with electron-donating groups on the phenyl ring reacted smoothly to give the corresponding diacylated coumarins in high yields (**4a**, **4c**, **4d**, and **4f**). By contrast, coumarins containing electron-withdrawing groups, such as 7-chloro- and 6,8-dichlorocoumarin, led to the desired products **4e** and **4g** in somewhat lower yields. When the 6-nitrocoumarin was used, only a trace amount of the product **4b** was observed. These results implied that the electronic effect of the R group on the phenyl ring of coumarins was quite significant. It is noteworthy that 5,8-dimethylcoumarin only furnished monoacylated product **4h′** probably due to the steric effect. Gratifyingly, coumarin having methyl group on C-4 position afforded the monoacylated product **4i** in 43% yield.

Finally, a series of other heterocyclic compounds were also examined under the optimal conditions (Table 4). When 1-methyl-2-quinolinones were treated with **2a**, the diacylated quinolinones were obtained in somewhat low yields because of the low conversion (**5a** and **5b**). Moreover, chromone was also suitable for this reaction, affording the desired product **5c** in 36% isolated yield. Unfortunately, 2-phenyl-4-chromone was ineffective in this system (**5d**). 2,6-Dimethylquinone reacted with **2a** to give the **5e** in 56% yield. Notably, substituted 1,4-naphthoquinone performed well, leading to the monoacylated naphthoquinone in high yields (**5f** and **5g**). For 2-hydroxy-1,4-naphthoquinone, the **5h** was obtained, which was formed by acylation of the C=C and C–O bonds of the naphthoquinone.

To further probe the mechanism of the reaction, we conducted the reaction of **3a′** with **2a** under the standard conditions (Scheme 2). The desired product **3a** was isolated in 73% yield, along with 19% of **3a′** was recovered. This result indicated that **3a′** should be an intermediate product in this transformation. Furthermore,

Table 1
Optimization of the reaction conditions[a]

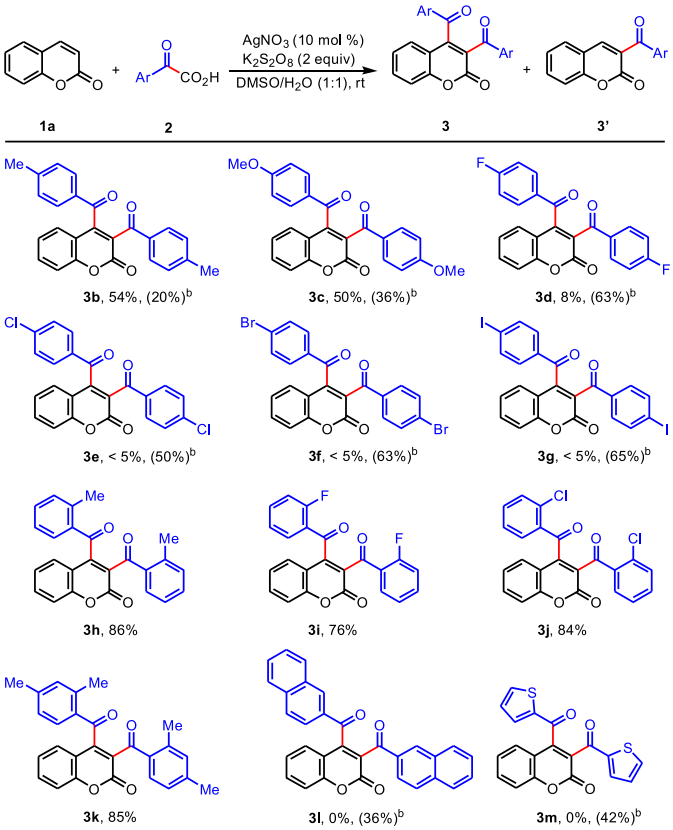


1a 2a 3a 3a'

Entry	Oxidant (equiv)	Solvent	Yield[b] (%)
1	$K_2S_2O_8$ (2)	DMSO/H_2O (1:1)	68 (24)[c]
2	$K_2S_2O_8$ (2)	CH_3CN/H_2O (1:1)	Trace
3	$K_2S_2O_8$ (2)	DCM/H_2O (1:1)	n.r.[d]
4	$K_2S_2O_8$ (2)	Acetone/H_2O (1:1)	Trace
5	$Na_2S_2O_8$ (2)	DMSO/H_2O (1:1)	65 (20)[c]
6	$(NH_4)_2S_2O_8$ (2)	DMSO/H_2O (1:1)	64 (21)[c]
7	Oxone	DMSO/H_2O (1:1)	n.r.[d]
8[e]	$K_2S_2O_8$ (2)	DMSO/H_2O (1:1)	61 (22)[c]
9[f]	$K_2S_2O_8$ (2)	DMSO/H_2O (1:1)	51 (16)[c]
10[g]	$K_2S_2O_8$ (2)	DMSO/H_2O (1:1)	50 (17)[c]
11	—	DMSO/H_2O (1:1)	n.r.[d]
12[h]	$K_2S_2O_8$ (2)	DMSO/H_2O (1:1)	n.r.[d]

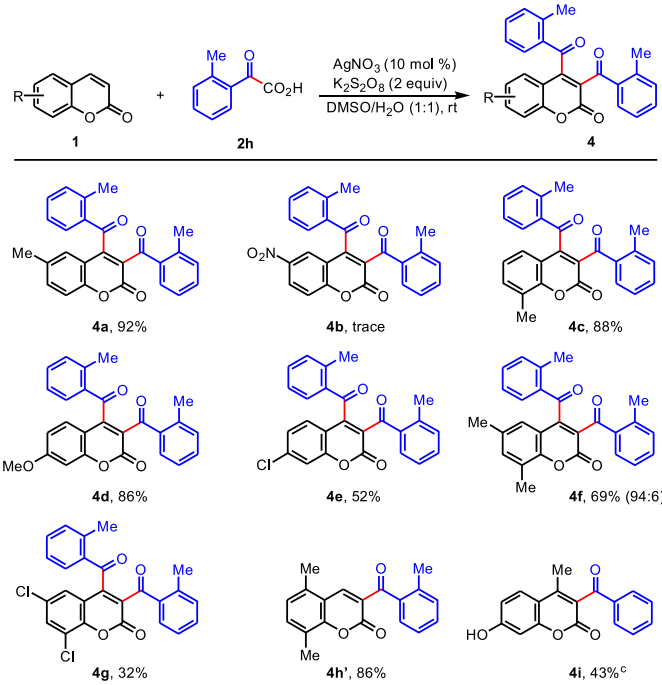
[a] Reaction conditions: $AgNO_3$ (10 mol %), **1a** (0.2 mmol, 1 equiv), **2a** (0.48 mmol, 2.4 equiv), oxidant (0.4 mmol, 2 equiv), solvent (2 mL), room temperature, 24 h.
[b] Yield of isolated product.
[c] Yield of **3a′** is given in parentheses.
[d] n.r.=no reaction.
[e] 10 mol % of Ag_2CO_3 was used.
[f] 10 mol % of AgOAc was used.
[g] 10 mol % of Ag_2O was used.
[h] Without a catalyst.

Table 2
Scope of α-oxocarboxylic acids[a,b]



[a] Reaction conditions: $AgNO_3$ (10 mol %), **1a** (0.2 mmol, 1 equiv), **2** (0.48 mmol, 2.4 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), DMSO/H_2O (1:1, 2 mL), room temperature, 24 h.
[b] Yields of **3′** are given in parentheses.

Table 3
Scope of coumarins[a]



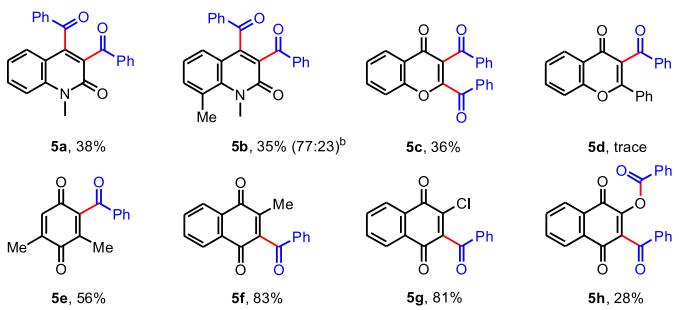
[a] Reaction conditions: $AgNO_3$ (10 mol %), **1** (0.2 mmol, 1 equiv), **2h** (0.48 mmol, 2.4 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), $DMSO/H_2O$ (1:1, 2 mL), room temperature, 24 h.

[b] The ratio given in parentheses corresponds to 3,4-diacyl coumarin **4f** and 3-acyl coumarin **4f'**, the ratio was determined by ^1H NMR.

[c] **2a** was used.

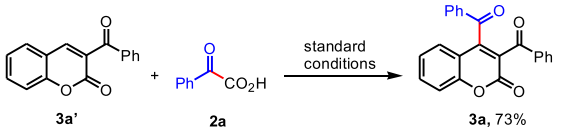
the yields of **3a** were also decreased dramatically by addition of radical scavengers, such as TEMPO and BHT, which implies that the reaction probably proceeded via free radical process. Based on these results and previous studies,[8a,b] a possible reaction mechanism was proposed as shown in Scheme 3. The reaction is initiated by the silver-catalyzed oxidative decarboxylation of **2a** by persulfate to form the acyl radical **I**,[10] which attacks the C=C bond of coumarin **1a** to give the radical intermediate **II**. The radical **II** was then oxidized to the corresponding carbocation followed by the loss of H^+, affording the 3-acylcoumarin **3a'**. Finally, the resulting **3a'** would then readily couple with nucleophilic acyl radical **I**[10] to give the diacylated coumarin **3a** and regenerate the catalyst. In the

Table 4
Scope of heterocyclic compounds[a,b]

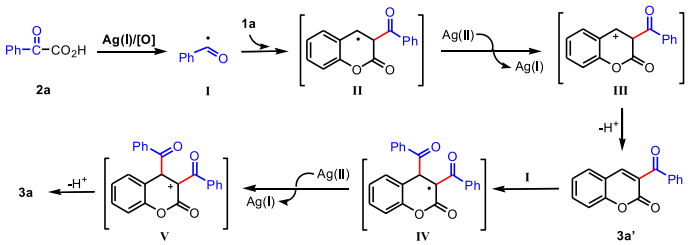


[a] Reaction conditions: $AgNO_3$ (10 mol %), heterocyclic compounds (0.2 mmol, 1 equiv), **2a** (0.48 mmol, 2.4 equiv), $K_2S_2O_8$ (0.4 mmol, 2 equiv), $DMSO/H_2O$ (1:1, 2 mL), room temperature, 24 h.

[b] The ratio given in parentheses corresponds to 3,4-diacyl quinolinone **5b** and 3-acyl quinolinone **5b'**, the ratio was determined by ^1H NMR.



Scheme 2. Direct decarboxylative coupling of 3-acylcoumarin **3a'** with **2a**.



Scheme 3. Proposed mechanism.

cases of acyl radicals having electron-withdrawing groups (Table 2, **2d**–**g**), the corresponding monosubstituted coumarins **3'** were obtained as major products, which might be attributed to the less nucleophilicities of the acyl radical.

3. Conclusion

In summary, we have developed a direct acylation of coumarins by Ag-catalyzed decarboxylative cross-coupling reactions. These methods allow efficient access to various 3,4-diacylcoumarins or 3-acylcoumarins bearing a wide range of functional groups under mild conditions. In addition, the excellent selectivity of the reaction could be controlled by using a series of *o*-substituted α-oxo-carboxylic acids.

4. Experimental section

4.1. General information

All reactions were carried out under an atmosphere of nitrogen with the strict exclusion of air. Column chromatography was carried out on silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz in solvents as indicated. Chemical shift are reported in parts per million (ppm) from $CDCl_3$ using TMS as internal standard. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer. Melting points were determined on a microscopic apparatus and were uncorrected.

4.2. Starting materials

Coumarin **1a** was commercial available and the other coumarin derivatives **1** were synthesized according to the literature, and the NMR spectroscopies were in full accordance with the data in the literature.[2g] Phenylglyoxylic acid **2a** was commercial available. Other α-oxocarboxylic acids **2** were prepared from the corresponding methyl ketones according to the reported procedure.[11]

4.3. General procedure for the decarboxylative acylation of coumarins with α-oxocarboxylic acids

A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (3.4 mg, 10 mol %), coumarin (**1**, 0.2 mmol, 1.0 equiv), and $K_2S_2O_8$ (108 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). α-Oxocarboxylic acids (**2**,

Please cite this article in press as: Wang, H.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.12.029

0.48 mmol, 2.4 equiv) in DMSO/H_2O (1:1) 2 mL were added by syringe. The tube was then sealed and the mixture was stirred for 24 h at room temperature. Upon completion of the reaction, the mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1:30 to 1:15) to give the corresponding products **3** or **4** in yields listed in Tables 2 and 3.

*4.3.1. 3,4-Dibenzoyl-chromen-2-one (**3a**).* A white solid, mp 147–149 °C, R_f 0.2 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.89–7.88 (d, J=7.2 Hz, 2H), 7.82–7.80 (d, J=7.2 Hz, 2H), 7.68–7.56 (m, 3H), 7.50–7.41 (m, 5H), 7.29–7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.9, 191.4, 158.3, 154.1, 153.3, 136.0, 135.3, 135.0, 134.1, 133.7, 129.8, 129.4, 129.0, 128.6, 127.3, 125.2, 124.8, 117.4, 116.8 ppm; IR (KBr): υ_{max} 1727, 1668, 1598, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{14}NaO_4$ [M+Na]$^+$ 377.0784, found 377.0784.

*4.3.2. 3,4-Bis-(4-methyl-benzoyl)-chromen-2-one (**3b**).* A white solid, mp 189–191 °C, R_f 0.2 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.78–7.76 (d, J=8.0 Hz, 2H), 7.73–7.70 (d, J=8.4 Hz, 2H), 7.65–7.61 (m, 1H), 7.48–7.46 (d, J=8.0 Hz, 1H), 7.28–7.21 (m, 6H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.3, 190.8, 158.4, 154.0, 152.8, 146.4, 145.3, 133.5, 133.4, 132.9, 130.0, 129.7, 129.3, 127.3, 125.1, 124.8, 117.4, 116.9, 21.9, 21.8 ppm; IR (KBr): υ_{max} 1728, 1667, 1604, 1562, 1253 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}NaO_4$ [M+Na]$^+$ 405.1097, found 405.1099.

*4.3.3. 3,4-Bis-(4-methoxy-benzoyl)-chromen-2-one (**3c**).* A white solid, mp 202–204 °C, R_f 0.3 (EtOAc/petroleum ether=1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.85–7.79 (m, 4H), 7.64–7.60 (m, 1H), 7.47–7.45 (d, J=8.0 Hz, 1H), 7.30–7.21 (m, 2H), 6.92–6.87 (m, 4H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.9, 189.4, 165.1, 164.5, 158.4, 153.9, 152.0, 133.3, 132.5, 132.2, 128.9, 128.3, 127.2, 125.0, 124.7, 117.3, 116.9, 114.3, 113.9, 55.6, 55.5 ppm; IR (KBr): υ_{max} 1727, 1598, 1506, 1254, 1169 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}NaO_6$ [M+Na]$^+$ 437.0996, found 437.0994.

*4.3.4. 3,4-Bis-(4-fluoro-benzoyl)-chromen-2-one (**3d**).* A white solid, mp 176–178 °C, R_f 0.2 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.94–7.91 (m, 2H), 7.87–7.83 (m, 2H), 7.69–7.65 (m, 1H), 7.50–7.48 (d, J=8.4 Hz, 1H), 7.29–7.23 (m, 2H), 7.18–7.09 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.2, 189.8, 166.8 (d, J_{C-F}=257.5 Hz), 166.4 (d, J_{C-F}=255.4 Hz), 158.1, 154.1, 153.1, 133.9, 132.6 (d, J_{C-F}=9.8 Hz), 132.3 (d, J_{C-F}=9.6 Hz), 131.8 (d, J_{C-F}=2.8 Hz), 127.2, 125.3, 124.5, 117.6, 116.6 (d, J_{C-F}=22.3 Hz), 116.5, 116.0 (d, J_{C-F}=22.0 Hz) ppm; IR (KBr): υ_{max} 1728, 1669, 1597, 1245, 1155 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{12}F_2NaO_4$ [M+Na]$^+$ 413.0596, found 413.0596.

*4.3.5. 3,4-Bis-(2-methyl-benzoyl)-chromen-2-one (**3h**).* A white solid, mp 147–149 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.66–7.62 (m, 1H), 7.58–7.56 (d, J=8.0 Hz, 1H), 7.51–7.49 (d, J=7.6 Hz, 1H), 7.46–7.41 (m, 2H), 7.38–7.32 (m, 2H), 7.29–7.18 (m, 5H), 2.50 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.2, 193.1, 158.3, 154.2, 153.3, 141.2, 139.5, 136.1, 134.2, 133.7, 133.6, 132.9, 132.5, 132.4, 131.8, 130.7, 127.4, 126.0, 125.6, 125.1, 125.0, 117.4, 117.1, 21.5, 20.7 ppm; IR (KBr): υ_{max} 1731, 1668, 1600, 1242 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}O_4$ [M+H]$^+$ 383.1278, found 383.1291.

*4.3.6. 3,4-Bis-(2-fluoro-benzoyl)-chromen-2-one (**3i**).* A white solid, mp 163–165 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.09–8.05 (td, J=7.6, 2.0 Hz, 1H), 7.72–7.50 (m, 4H), 7.47–7.45 (dd, J=8.4, 0.4 Hz, 1H), 7.35–7.26 (m, 3H), 7.24–7.19 (m, 1H), 7.10–7.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=189.3, 188.1, 162.2 (d, J_{C-F}=257.8 Hz), 161.5 (d, J_{C-F}=253.3 Hz), 158.5 (d, J_{C-F}=2.7 Hz), 155.7, 154.5, 136.7 (d, J_{C-F}=9.1 Hz), 135.2 (d, J_{C-F}=8.9 Hz), 134.0, 130.6, 127.0, 125.9 (d, J_{C-F}=11.7 Hz), 125.1, 124.9 (d, J_{C-F}=3.5 Hz), 124.5 (d, J_{C-F}=3.4 Hz), 124.4, 123.7 (d, J_{C-F}=2.7 Hz), 117.5, 117.0 (d, J_{C-F}=21.7 Hz), 116.6 (d, J_{C-F}=2.1 Hz), 116.1 (d, J_{C-F}=22.4 Hz) ppm; IR (KBr): υ_{max} 1732, 1663, 1609, 1455, 1239 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{12}F_2NaO_4$ [M+Na]$^+$ 413.0596, found 413.0599.

*4.3.7. 3,4-Bis-(2-chloro-benzoyl)-chromen-2-one (**3j**).* A white solid, mp 158–160 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.92–7.89 (dd, J=8.0, 1.6 Hz, 1H), 7.69–7.65 (m, 1H), 7.53–7.27 (m, 10H), ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.5, 190.9, 158.2, 156.0, 154.6, 137.4, 134.4, 134.3, 134.1, 134.0, 132.8, 132.6, 131.9, 131.7, 130.4, 130.0, 127.7, 127.1, 125.3, 122.9, 117.5, 117.3 ppm; IR (KBr): υ_{max} 1737, 1605, 1239 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{12}Cl_2NaO_4$ [M+Na]$^+$ 445.0005, found 445.0007.

*4.3.8. 3,4-Bis-(2,4-dimethyl-benzoyl)-chromen-2-one (**3k**).* A white solid, mp 137–139 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.58 (m, 1H), 7.48–7.42 (m, 3H), 7.32–7.30 (dd, J=8.4, 1.6 Hz, 1H), 7.24–7.20 (m, 1H), 7.07 (s, 1H), 7.01–6.99 (m, 3H), 2.43 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.6, 192.4, 158.4, 154.0, 152.6, 144.8, 143.3, 141.1, 139.9, 133.4, 133.3, 133.2, 132.6, 131.7, 131.6, 127.3, 126.7, 125.1, 125.0, 117.2, 117.1, 21.6, 21.5, 21.4, 20.8 ppm; IR (KBr): υ_{max} 1731, 1665, 1607, 1248 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}NaO_4$ [M+Na]$^+$ 433.1410, found 433.1411.

*4.3.9. 3-Benzoyl-chromen-2-one (**3a′**).*[2c] R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.09 (s, 1H), 7.90–7.88 (d, J=7.2 Hz, 2H), 7.68–7.60 (m, 3H), 7.51–7.47 (t, J=8.0 Hz, 2H), 7.43–7.41 (d, J=8.4 Hz, 1H), 7.38–7.34 (td, J=7.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.7, 158.4, 154.8, 145.4, 136.2, 133.8, 133.6, 129.6, 129.2, 128.6, 127.0, 125.0, 118.2, 117.0 ppm.

*4.3.10. 3-(4-Methyl-benzoyl)-chromen-2-one (**3b′**).*[2c] R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.06 (s, 1H), 7.80–7.78 (d, J=8.0 Hz, 2H), 7.67–7.58 (m, 2H), 7.42–7.40 (d, J=8.4 Hz, 1H), 7.37–7.33 (m, 1H), 7.29–7.27 (d, J=8.0 Hz, 2H), 2.43 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.2, 158.5, 154.7, 145.0, 144.9, 133.6, 133.5, 129.8, 129.3, 129.1, 127.3, 124.9, 118.2, 116.9, 21.8 ppm; IR (KBr): υ_{max} 1726, 1662, 1607, 1241 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{13}O_3$ [M+H]$^+$ 265.0859, found 265.0862.

*4.3.11. 3-(4-Methoxy-benzoyl)-chromen-2-one (**3c′**).*[12a] R_f 0.4 (EtOAc/petroleum ether=1:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03 (s, 1H), 7.90–7.88 (d, J=9.2 Hz, 2H), 7.66–7.58 (m, 2H), 7.42–7.40 (d, J=8.4 Hz, 1H), 7.37–7.30 (td, J=7.6, 0.8 Hz, 1H), 6.97–6.95 (d, J=8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.0, 164.3, 158.6, 154.6, 144.6, 133.3, 132.2, 129.0, 127.6, 124.9, 118.3, 116.9, 113.9, 55.6 ppm; IR (KBr): υ_{max} 1716, 1606, 1246, 1174 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{12}NaO_4$ [M+Na]$^+$ 303.0628, found 303.0624.

*4.3.12. 3-(4-Fluoro-benzoyl)-chromen-2-one (**3d′**).*[12b] R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.11 (s, 1H), 7.94–7.90 (m, 2H), 7.69–7.61 (m, 2H), 7.43–7.41 (d, J=8.4 Hz, 1H), 7.39–7.35 (td, J=7.6, 0.8 Hz, 1H), 7.18–7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.1, 166.2 (d, J_{C-F}=254.7 Hz), 158.5, 154.8, 145.7, 133.8, 132.6 (d, J_{C-F}=2.9 Hz), 132.3 (d, J_{C-F}=9.5 Hz), 129.2, 126.8, 125.1, 118.1, 117.0, 116.0, 115.8 (d, J_{C-F}=22.0 Hz) ppm; IR (KBr): υ_{max} 1708, 1661, 1598, 1244, 1160 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_9FNaO_3$ [M+Na]$^+$ 291.0428, found 291.0430.

*4.3.13. 3-(4-Chloro-benzoyl)-chromen-2-one (**3e′**).*[2c] R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.13 (s, 1H),

7.83–7.81 (d, J=8.8 Hz, 2H), 7.69–7.61 (m, 2H), 7.47–7.45 (d, J=8.8 Hz, 2H), 7.43–7.41 (d, J=8.4 Hz, 1H), 7.39–7.35 (td, J=8.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.5, 158.4, 154.8, 146.0, 140.3, 134.6, 133.9, 130.9, 129.3, 128.9, 126.6, 125.1, 118.1, 117.0 ppm; IR (KBr): υ_{max} 1714, 1662, 1608, 1242 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{10}ClO_3$ $[M+H]^+$ 285.0313, found 285.0320.

*4.3.14. 3-(4-Bromo-benzoyl)-chromen-2-one (**3f**′).*[9c] R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, DMSO-d_6): δ=8.47 (s, 1H), 7.89–7.86 (m, 3H), 7.77–7.73 (m, 3H), 7.51–7.49 (d, J=8.4 Hz, 1H), 7.45–7.41 (t, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=191.0, 158.1, 154.3, 146.1, 135.3, 133.8, 131.8, 131.5, 129.9, 128.1, 125.9, 125.0, 118.3, 116.4 ppm; IR (KBr): υ_{max} 1713, 1663, 1608, 1243 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_9BrNaO_3$ $[M+Na]^+$ 350.9627, found 350.9634.

*4.3.15. 3-(4-Iodo-benzoyl)-chromen-2-one (**3g**′).* A white solid, mp 206–208 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.13 (s, 1H), 7.86–7.84 (d, J=8.4 Hz, 2H), 7.69–7.61 (m, 2H), 7.59–7.57 (d, J=8.4 Hz, 2H), 7.43–7.41 (d, J=8.4 Hz, 1H), 7.39–7.35 (td, J=7.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.1, 158.4, 154.9, 146.1, 137.9, 135.6, 133.9, 130.8, 129.3, 126.5, 125.1, 118.1, 117.0, 102.0 ppm; IR (KBr): υ_{max} 1713, 1664, 1607, 1579, 1242 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_9INaO_3$ $[M+Na]^+$ 398.9489, found 398.9502.

*4.3.16. 3-(Naphthalene-2-carbonyl)-chromen-2-one (**3l**′).*[2c] R_f 0.3 (EtOAc/petroleum ether=1:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.36 (s, 1H), 8.14 (s, 1H), 8.01–7.89 (m, 4H), 7.70–7.60 (m, 3H), 7.57–7.53 (m, 1H), 7.46–7.44 (d, J=8.4 Hz, 1H), 7.40–7.36 (dd, J=7.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.6, 158.5, 154.8, 145.3, 136.0, 133.6, 132.3, 132.0, 129.7, 129.2, 128.9, 128.6, 127.9, 127.3, 126.9, 125.0, 124.6, 118.2, 117.0 ppm; IR (KBr): υ_{max} 1719, 1653, 1609, 1196 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{12}NaO_3$ $[M+Na]^+$ 323.0679, found 323.0688.

*4.3.17. 3-(Thiophene-2-carbonyl)-chromen-2-one (**3m**′).*[12a] R_f 0.1 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.10 (s, 1H), 7.78–7.76 (d, J=5.2 Hz, 1H), 7.74–7.73 (d, J=4.0 Hz, 1H), 7.68–7.64 (td, J=8.4, 1.2 Hz, 1H), 7.61–7.59 (dd, J=8.0, 1.2 Hz, 1H), 7.42–7.40 (d, J=8.0 Hz, 1H), 7.38–7.34 (t, J=7.6 Hz, 1H), 7.18–7.16 (t, J=4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=182.9, 158.2, 154.6, 144.7, 142.8, 135.7, 135.1, 133.7, 129.1, 128.4, 126.9, 125.0, 118.1, 116.9 ppm; IR (KBr): υ_{max} 1726, 1635, 1607, 1410, 1245 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_8NaO_3S$ $[M+Na]^+$ 279.0086, found 279.0089.

*4.3.18. 6-Methyl-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4a**).* A white solid, mp 182–184 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–7.54 (d, J=7.6 Hz, 1H), 7.47–7.41 (m, 3H), 7.37–7.33 (m, 2H), 7.28–7.26 (d, J=7.6 Hz, 1H), 7.23–7.16 (m, 3H), 7.12 (s, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.3, 193.1, 158.5, 153.2, 152.4, 141.2, 139.4, 136.2, 135.1, 134.8, 134.2, 133.7, 132.8, 132.4, 132.3, 131.7, 130.6, 127.0, 126.0, 125.6, 124.5, 117.1, 116.8, 21.4, 20.9, 20.7 ppm; IR (KBr): υ_{max} 1723, 1677, 1560, 1242 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{20}NaO_4$ $[M+Na]^+$ 419.1254, found 419.1254.

*4.3.19. 8-Methyl-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4c**).* A white solid, mp 167–169 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.58–7.56 (dd, J=7.6, 0.8 Hz, 1H), 7.52–7.47 (m, 2H), 7.44–7.40 (td, J=7.6, 1.2 Hz, 1H), 7.38–7.34 (td, J=7.6, 1.2 Hz, 1H), 7.28–7.27 (d, J=7.6 Hz, 1H), 7.22–7.14 (m, 5H), 2.52 (s, 3H), 2.50 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.5, 193.3, 158.4, 153.7, 152.5, 141.1, 139.4, 136.2, 134.8, 134.2, 133.6, 133.0, 132.4, 131.7, 130.7, 127.0, 126.0, 125.6, 125.1, 124.6, 116.8, 21.5, 20.7, 15.6 ppm; IR (KBr): υ_{max} 1731, 1669, 1569, 1243 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{21}O_4$ $[M+H]^+$ 397.1434, found 397.1435.

*4.3.20. 7-Methoxy-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4d**).* A white solid, mp 173–175 °C, R_f 0.3 (EtOAc/petroleum ether=1:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.57–7.55 (d, J=7.6 Hz, 1H), 7.45–7.41 (m, 2H), 7.36–7.32 (t, J=7.6 Hz, 1H), 7.30–7.16 (m, 5H), 6.91 (d, J=2.4 Hz, 1H), 6.83–6.80 (dd, J=8.8, 2.4 Hz, 1H), 3.91 (s, 3H), 2.56 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.6, 193.6, 164.5, 158.7, 156.6, 154.9, 141.1, 138.7, 137.0, 134.2, 133.5, 132.6, 132.5, 131.9, 131.5, 129.9, 128.7, 125.9, 125.5, 120.9, 113.8, 110.6, 101.0, 56.0, 21.5, 20.5 ppm; IR (KBr): υ_{max} 1724, 1669, 1615, 1258 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{20}NaO_5$ $[M+Na]^+$ 435.1203, found 435.1202.

*4.3.21. 7-Chloro-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4e**).* A white solid, mp 168–170 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54–7.52 (d, J=7.6 Hz, 1H), 7.49–7.41 (m, 3H), 7.39–7.35 (td, J=7.6, 1.2 Hz, 1H), 7.29–7.18 (m, 6H), 2.47 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.7, 192.6, 157.7, 154.4, 152.5, 141.3, 139.8, 139.6, 135.9, 134.0, 133.9, 132.8, 132.6, 132.5, 131.8, 130.7, 128.3, 126.1, 125.8, 125.6, 124.8, 117.7, 115.6, 21.4, 20.7 ppm; IR (KBr): υ_{max} 1737, 1670, 1599, 1256 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{17}ClNaO_4$ $[M+Na]^+$ 439.0708, found 439.0706.

*4.3.22. 6,8-Dimethyl-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4f**).* A white solid, mp 209–211 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55–7.53 (d, J=8.0 Hz, 1H), δ=7.47–7.45 (d, J=7.6 Hz, 1H), 7.43–7.40 (t, J=7.6 Hz, 1H), 7.36–7.26 (m, 3H), 7.22–7.16 (m, 3H), 6.95 (s, 1H), 2.48 (s, 6H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.6, 193.3, 158.6, 153.7, 150.8, 141.2, 139.4, 136.3, 136.2, 134.4, 134.3, 133.6, 132.8, 132.4, 132.3, 131.7, 130.6, 126.5, 125.9, 125.5, 124.6, 124.1, 116.5, 21.5, 20.8, 20.7, 15.5 ppm; IR (KBr): υ_{max} 1734, 1669, 1572, 1236 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}NaO_4$ $[M+Na]^+$ 433.1410, found 433.1412.

*4.3.23. 6,8-Dichloro-3,4-bis-(2-methyl-benzoyl)-chromen-2-one (**4g**).* A white solid, mp 185–187 °C, R_f 0.2 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70–7.69 (d, J=2.4 Hz, 1H), 7.50–7.43 (m, 3H), 7.40–7.37 (t, J=7.2 Hz, 1H), 7.29–7.18 (m, 5H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.0, 191.8, 156.7, 150.8, 148.5, 141.5, 140.2, 135.2, 134.2, 133.7, 133.4, 133.0, 132.9, 132.6, 132.0, 131.3, 130.4, 126.5, 126.1, 125.7, 125.1, 123.4, 119.0, 21.3, 20.8 ppm; IR (KBr): υ_{max} 1745, 1671, 1555, 1228 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{16}Cl_2NaO_4$ $[M+Na]^+$ 473.0318, found 473.0317.

*4.3.24. 5,8-Dimethyl-3-(2-methyl-benzoyl)-chromen-2-one (**4h**′).* A white solid, mp 156–158 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.40 (s, 1H), 7.46–7.40 (m, 2H), 7.37–7.35 (d, J=7.6 Hz, 1H), 7.32–7.30 (d, J=7.6 Hz, 1H), 7.25–7.22 (t, J=7.6 Hz, 1H), 7.07–7.05 (d, J=8.0 Hz, 1H), 2.54 (s, 3H), 2.53 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.2, 158.2, 154.0, 143.9, 138.3, 137.1, 135.5, 135.0, 131.7, 129.5, 125.9, 125.6, 125.4, 124.0, 117.0, 20.7, 18.1, 15.3 ppm; IR (KBr): υ_{max} 1736, 1594, 1232 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{17}O_3$ $[M+H]^+$ 293.1172, found 293.1178.

*4.3.25. 3-Benzoyl-7-hydroxy-4-methyl-chromen-2-one (**4i**).* A white solid, mp 200–202 °C, R_f 0.2 (EtOAc/petroleum ether=1:5); ^{1}H NMR (400 MHz, acetone-d_6): δ=8.00–7.98 (m, 2H), 7.78–7.76 (dd, J=8.8, 1.2 Hz, 1H), 7.70–7.66 (td, J=8.0, 1.2 Hz, 1H), 7.56–7.52 (t, J=7.6 Hz, 2H), 6.96–6.93 (dd, J=8.8, 2.4 Hz, 1H), 6.83–6.82 (d, J=2.4 Hz, 1H), 3.00 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=194.3, 162.6, 159.4, 156.0, 151.4, 137.8, 134.7, 130.0, 129.8, 128.2, 123.1, 114.1, 113.2, 103.3, 15.9 ppm; IR (KBr): υ_{max} 3271, 1666,

Please cite this article in press as: Wang, H.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.12.029

1598, 1563, 1261 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{12}NaO_4$ $[M+Na]^+$ 303.0628, found 303.0635.

4.4. General procedure for the decarboxylative acylation of heterocyclic compounds with 2a

A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (3.4 mg, 10 mol %), heterocyclic compounds (**6**, 0.2 mmol, 1.0 equiv), and $K_2S_2O_8$ (108 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with nitrogen (three times). Phenylglyoxylic acid (**2a**, 0.48 mmol, 2.4 equiv) in DMSO/H_2O (1:1) 2 mL was added by syringe. The tube was then sealed and the mixture was stirred for 24 h at room temperature. Upon completion of the reaction, the mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1:30 to 1:15) to give the corresponding products **5** in yields listed in Table 4.

*4.4.1. 3,4-Dibenzoyl-1-methyl-1H-quinolin-2-one (**5a**).* A pale yellow solid, mp 175–177 °C, R_f 0.2 (EtOAc/petroleum ether=1:5); ^1H NMR (400 MHz, $CDCl_3$): δ=7.87–7.79 (m, 4H), 7.69–7.65 (m, 1H), 7.59–7.55 (m, 1H), 7.53–7.49 (m, 2H), 7.44–7.35 (m, 5H), 7.21–7.17 (td, J=8.0, 0.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.7, 193.6, 159.6, 148.2, 140.3, 136.8, 136.1, 134.5, 133.6, 132.3, 129.9, 129.5, 129.3, 128.8, 128.4, 127.9, 122.9, 117.8, 114.8, 29.8 ppm; IR (KBr): υ_{max} 1643, 1595, 1451, 1235 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{17}NNaO_3$ $[M+Na]^+$ 390.1101, found 390.1101.

*4.4.2. Isolated as unseparable mixture of **5b** and **5b′** (ratio 77:23).* ^1H NMR (400 MHz, $CDCl_3$): δ=7.88–7.84 (m, 2H), 7.81–7.79 (dd, J=8.0, 1.2 Hz, 2H), 7.59–7.50 (m, 2H), 7.44–7.37 (m, 4H), 7.29–7.22 (m, 3H), 7.01–6.99 (dd, J=0.8, 8.4 Hz, 1H), 3.88 (s, 0.7H), 3.79 (s, 2H), 2.77 (s, 0.7H), 2.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=194.9, 193.9, 159.8, 148.4, 143.5, 140.5, 137.0, 136.6, 136.1, 134.4, 133.4, 129.9, 129.8, 129.3, 128.8, 128.4, 128.3, 127.8, 126.1, 124.4, 123.3, 115.6, 115.0, 37.3, 29.8, 23.9, 22.4 ppm.

*4.4.3. 2,3-Dibenzoyl-chromen-4-one (**5c**).* R_f 0.2 (EtOAc/petroleum ether=1:10); ^1H NMR (400 MHz, $CDCl_3$): δ=8.29–8.26 (dd, J=7.6, 1.2 Hz, 1H), 7.96–7.94 (m, 2H), 7.91–7.89 (m, 2H), 7.82–7.78 (m, 1H), 7.69–7.64 (m, 1H), 7.59–7.49 (m, 5H), 7.46–7.43 (t, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.6, 187.3, 175.9, 158.5, 155.1, 136.8, 135.1, 134.7, 134.2, 133.7, 130.1, 129.2, 128.8, 128.6, 126.5, 126.3, 126.0, 124.2, 118.4 ppm; IR (KBr): υ_{max} 1680, 1648, 1464, 1377, 1239 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{14}NaO_4$ $[M+Na]^+$ 377.0784, found 377.0786.

*4.4.4. 2-Benzoyl-3,5-dimethyl-[1,4]benzoquinone (**5e**).* A pale yellow solid, mp 74–76 °C, R_f 0.4 (EtOAc/petroleum ether=1:10); ^1H NMR (400 MHz, $CDCl_3$): δ=7.86–7.83 (m, 2H), 7.64–7.60 (t, J=7.6 Hz, 1H), 7.50–7.46 (t, J=7.6 Hz, 2H), 6.62 (d, J=1.6 Hz, 1H), 2.12 (d, J=1.2 Hz, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.1, 187.6, 185.6, 146.3, 142.0, 141.5, 135.6, 134.5, 132.8, 129.1, 129.0, 16.1, 13.2 ppm; IR (KBr): υ_{max} 1676, 1652, 1323, 1241 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}NaO_3$ $[M+Na]^+$ 263.0679, found 263.0672.

*4.4.5. 2-Benzoyl-3-methyl-[1,4]naphthoquinone (**5f**).* A pale yellow solid, mp 139–141 °C, R_f 0.4 (EtOAc/petroleum ether=1:10); ^1H NMR (400 MHz, $CDCl_3$): δ=8.17–8.15 (m, 1H), 8.07–8.05 (m, 1H), 7.92–7.90 (m, 2H), 7.81–7.41 (m, 2H), 7.65–7.61 (t, J=7.6 Hz, 1H), 7.52–6.48 (t, J=7.6 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=193.7, 184.8, 183.4, 144.3, 143.9, 135.6, 134.5, 134.2, 134.1, 131.8, 131.5, 129.1, 126.7, 126.4, 13.6 ppm; IR (KBr): υ_{max} 1664, 1595, 1290 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{12}NaO_3$ $[M+Na]^+$ 299.0679, found 299.0687.

*4.4.6. 2-Benzoyl-3-chloro-[1,4]naphthoquinone (**5g**).* A pale yellow solid, mp 151–153 °C, R_f 0.4 (EtOAc/petroleum ether=1:10); ^1H NMR (400 MHz, $CDCl_3$): δ=8.24–8.22 (m, 1H), 8.12–8.10 (m, 1H), 7.94–7.91 (m, 2H), 7.84–7.82 (m, 2H), 7.68–7.64 (t, J=7.6 Hz, 1H), 7.53–7.49 (t, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=189.6, 181.2, 177.3, 144.2, 141.6, 134.9, 134.6, 134.5, 131.2, 131.0, 129.3, 129.1, 127.6, 127.1 ppm; IR (KBr): υ_{max} 1685, 1658, 1594, 1277 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{10}ClO_3$ $[M+H]^+$ 297.0313, found 297.0314.

*4.4.7. Benzoic acid 3-benzoyl-1,4-dioxo-1,4-dihydro-naphthalen-2-yl ester (**5h**).* A pale yellow solid, mp 142–144 °C, R_f 0.3 (EtOAc/petroleum ether=1:10); ^1H NMR (400 MHz, $CDCl_3$): δ=8.22–8.19 (m, 1H), 8.17–8.15 (m, 1H), 7.99–7.96 (m, 4H), 7.86–7.83 (m, 2H), 7.62–7.58 (td, J=7.6, 1.2 Hz, 2H), 7.49–7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=189.4, 182.9, 178.0, 163.4, 151.0, 135.5, 134.8, 134.7, 134.6, 134.4, 131.5, 130.9, 130.6, 129.3, 128.9, 128.7, 127.2, 127.0 ppm; IR (KBr): υ_{max} 1751, 1682, 1659, 1289, 1227 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{14}NaO_5$ $[M+Na]^+$ 405.0733, found 405.0731.

4.5. Investigation of the reaction mechanism

When the TEMPO was added to the reaction of **1a** with phenylglyoxylic acid **2a** under the standard condition, the yield of **3a** was isolated in 41%. This result indicates that the radical intermediate might be involved in the catalytic cycle of the reaction; When the BHT was added to the reaction of **1a** with phenylglyoxylic acid **2a** under the standard condition, the yield of **3a** was isolated in 38%. This result indicates that the radical intermediate might be involved in the catalytic cycle of the reaction.

Acknowledgements

Financial support from National Natural Science Foundation of China (Nos. 21102110, 21102111) and the Fundamental Research Funds of the Central Universities (Nos. 2012jdhz28, xjj2012100) are greatly appreciated.

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.12.029.

References and notes

1. For review, see: (a) Sandhu, S.; Bansal, Y.; Silakari, O.; Bansal, G. *Bioorg. Med. Chem.* **2014**, *22*, 3806 For recent examples, see: (b) Li, B.; Pai, R.; Di, M.; Aiello, D.; Barnes, M. H.; Butler, M. M.; Tashjian, T. F.; Peet, N. P.; Bowlin, T. L.; Moir, D. T. *J. Med. Chem.* **2012**, *55*, 10896; (c) Anand, P.; Singh, B.; Singh, N. *Bioorg. Med. Chem.* **2012**, *20*, 1175; (d) Zou, Q.; Fang, Y.; Zhao, Y.; Zhao, H.; Wang, Y.; Gu, Y.; Wu, F. *J. Med. Chem.* **2013**, *56*, 5288; (e) Jagtap, A. R.; Satam, V. S.; Rajule, R. N.; Kanetkar, V. R. *Dyes Pigment* **2009**, *82*, 84; (f) Chang, C.-H.; Cheng, H.-C.; Lu, Y.-J.; Tien, K.-C.; Lin, H.-W.; Lin, C.-L.; Yang, C.-J.; Wu, C.-C. *Org. Electron.* **2010**, *11*, 247.
2. For selected examples, see: (a) Joule, J. A.; Mills, K. In *Heterocyclic Chemistry Blackwell: Oxford, UK, 2000*; (b) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992; (c) Rao, H. S. P.; Sivakumar, S. *J. Org. Chem.* **2006**, *71*, 8715; (d) Yamamoto, Y.; Kirai, N. *Org. Lett.* **2008**, *10*, 5513; (e) Xia, X.-F.; Shu, X.-Z.; Ji, K.-G.; Shaukat, A.; Liu, X.-Y.; Liang, Y.-M. *J. Org. Chem.* **2011**, *76*, 342; (f) Kim, D.; Min, M.; Hong, S. *Chem. Commun.* **2013**, 4021; (g) Wei, J.; Wang, P.; Jia, Q.; Huang, J.; Du, Z.; Zhang, K.; Wang, J. *Eur. J. Org. Chem.* **2013**, 4499; (h) Mi, X.; Wang, C.; Huang, M.; Zhang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 3356.
3. (a) Khoobi, M.; Alipour, M.; Zarei, S.; Jafarpour, F.; Shafiee, A. *Chem. Commun.* **2012**, 2985; (b) Li, Y.; Qi, Z.; Wang, H.; Fu, X.; Duan, C. *J. Org. Chem.* **2012**, *77*, 2053; (c) Min, M.; Hong, S. *Chem. Commun.* **2012**, 9613; (d) Min, M.; Kim, Y.; Hong, S. *Chem. Commun.* **2013**, 196; (e) Mi, X.; Huang, M.; Zhang, J.; Wang, C.; Wu, Y. *Org. Lett.* **2013**, *15*, 6266; (f) Jafarpour, F.; Hazrati, H.; Mohasselyazdi, N.; Khoobi, M.; Shafiee, A. *Chem. Commun.* **2013**, 10935; (g) Cao, X.-H.; Pan, X.;

Zhou, P.-J.; Zou, J.-P.; Asekun, O. T. *Chem. Commun.* **2014**, 3359; (h) Zhou, S.-L.; Guo, L.-N.; Duan, X.-H. *Eur. J. Org. Chem.* **2014**, 8094.

4. For selected examples leading to 3,4-disubstituted coumarins, see: (a) Kadnikov, D. V.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3643; (b) Kadnikov, D. V.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 9423; (c) Zhang, L.; Meng, T.; Fan, R.; Wu, J. *J. Org. Chem.* **2007**, *72*, 7279; (d) Sun, H.; Zhang, Y.; Guo, F.; Yan, Y.; Wan, C.; Zha, Z.; Wang, Z. *Eur. J. Org. Chem.* **2012**, 480; (e) Kim, S.; Kang, D.; Lee, C.-H.; Lee, P. H. *J. Org. Chem.* **2012**, *77*, 6530.
5. For recent reviews, see: (a) Baudoin, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373; (b) Goossen, L. J.; Rodríguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100; (c) Satoh, T.; Miura, M. *Synthesis* **2010**, 3395; (d) Rodríguez, N.; Goossen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030; (e) Shang, R.; Liu, L. *Sci. China Chem.* **2011**, *54*, 1670; (f) Dzik, W. I.; Lange, P. P.; Goossen, L. J. *Chem. Sci.* **2012**, *3*, 2671; (g) Cornella, J.; Larrosa, I. *Synthesis* **2012**, 653.
6. For selected examples, see: (a) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250; (b) Goossen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662; (c) Forgione, P.; Brochu, M.-C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350; (d) Miyasaka, M.; Fukushima, A.; Satoh, T.; Hirano, K.; Miura, M. *Chem.—Eur. J.* **2009**, *15*, 3674; (e) Zhang, F.; Greaney, M. F. *Org. Lett.* **2010**, *12*, 4745; (f) Dai, J.-J.; Liu, J.-H.; Luo, D.-F.; Liu, L. *Chem. Commun.* **2011**, 677; (g) Messaoudi, S.; Brion, J.-D.; Alami, M. *Org. Lett.* **2012**, *14*, 1496; (h) Zhang, Y.; Patel, S.; Mainolfi, N. *Chem. Sci.* **2012**, *3*, 3196.
7. For some selected examples, see: (a) Goossen, L. J.; Rudolphi, F.; Oppel, C.; Rodríguez, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 3043; (b) Goossen, L. J.; Zimmermann, B.; Knauber, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7103; (c) Fang, P.; Li, M.; Ge, H. *J. Am. Chem. Soc.* **2010**, *132*, 11898; (d) Li, M.; Ge, H. *Org. Lett.* **2010**, *12*, 3464; (e) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Lett.* **2012**, *14*, 4358; (f) Yang, Z.; Chen, X.; Liu, J.; Gui, Q.; Xie, K.; Li, M.; Tan, Z. *Chem. Commun.* **2013**, 1560; (g) Park, J.; Kim, M.; Sharma, S.; Park, E.; Kim, A.; Lee, S. H.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2013**, 1654; (h) Li, H.; Li, P.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, 9170; (i) Yao, J.; Feng, R.; Wu, Z.; Liu, Z.; Zhang, Y. *Adv. Synth. Catal.* **2013**, *355*, 1517; (j) Li, Z.-Y.; Li, D.-D.; Wang, G.-W. *J. Org. Chem.* **2013**, *78*, 10414.
8. (a) Wang, H.; Guo, L.-N.; Duan, X.-H. *Adv. Synth. Catal.* **2013**, *355*, 2222; (b) Yang, H.; Guo, L.-N.; Duan, X.-H. *RSC Adv.* **2014**, *4*, 52986; (c) Wang, H.; Guo, L.-N.; Duan, X.-H. *Chem. Commun.* **2014**, 7382 For other related examples reported in our group, see: (d) Zhang, S.; Guo, L.-N.; Wang, H.; Duan, X.-H. *Org. Biomol. Chem.* **2013**, *11*, 4308; (e) Wang, H.; Guo, L.-N.; Duan, X.-H. *Org. Biomol. Chem.* **2013**, *11*, 4573; (f) Wang, H.; Yang, H.; Li, Y.; Duan, X.-H. *RSC Adv.* **2014**, *4*, 8720.
9. Aroyl substituted coumarins were useful biologically active molecules and useful synthetic intermediates in organic synthesis. For selected examples, see: (a) Pérez-Cruz, F.; Vazquez-Rodriguez, S.; Matos, M. J.; Herrera-Morales, A.; Villamena, F. A.; Das, A.; Gopalakrishnan, B.; Olea-Azar, C.; Santana, L.; Uriarte, E. *J. Med. Chem.* **2013**, *56*, 6136; (b) Wang, Y.; Yu, Z.-H.; Zheng, H.-F.; Shi, D.-Q. *Org. Biomol. Chem.* **2012**, *10*, 7739; (c) Jian, T.-Y.; Chen, X.-Y.; Sun, L.-H.; Ye, S. *Org. Biomol. Chem.* **2013**, *11*, 158.
10. For the pioneering work on the decarboxylation of α-oxocarboxylic acids under Ag (I)/persulfates, see: (a) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 1651; (b) Anderson, J. M.; Kochi, J. K. *J. Org. Chem.* **1970**, *35*, 986; (c) Fontana, F.; Minisci, F.; Claudia, M.; Barbosa, N.; Vismara, E. *J. Org. Chem.* **1991**, *56*, 2866.
11. Wadhwa, K.; Yang, C.; West, P. R.; Deming, K. C.; Chemburkar, S. R.; Reddy, R. E. *Synth. Commun.* **2008**, *38*, 4434.
12. (a) Verma, R. K.; Verma, G. K.; Shukla, G.; Singh, M. S. *RSC Adv.* **2012**, *2*, 2413; (b) Dnyanoba, N.; Nagahama, M.; Inaba, T.; Nishino, Y.; Miura, K.; Kosaka, S.; Fukao, J.; Kawasaki, I.; Ohta, S. *Heterocycles* **2005**, *65*, 2411.

Please cite this article in press as: Wang, H.; et al., Tetrahedron (2014), http://dx.doi.org/10.1016/j.tet.2014.12.029