ChemPubSoc Europe

DOI: 10.1002/ejoc.201501251

EurJOC European Journal of Organic Chemistry

Full Paper

C–H Functionalization

Regioselective Coupling Reactions of Coumarins with Aldehydes or Di-*tert*-butyl Peroxide (DTBP) through a C(sp^2)–H Functionalization Process

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Abstract: Coumarin derivatives are highly valuable compounds in drug discovery. Herein, we have developed two new coupling reactions that involve coumarins and either aldehydes or di-*tert*-butyl peroxide (DTBP) in the presence of inexpensive copper or iron catalysts. Both of these reactions proceed through a C(sp^2)–H functionalization process to regioselectivity generate keto- or methyl-substituted coumarin derivatives in moderate to good yields These coupling reactions will enrich current coumarin chemistry.

Introduction

Coumarin derivatives are widely found in nature[1] and are a significant class of natural products because of their remarkable range of biological activities,[2] which include anticancer,[3] antioxidant,[4] monoamine oxidase (MAO) inhibition,[5] HIV protease inhibition,[6] acetylcholinesterase (AChE) inhibition, and anti-hepatitis C virus (HCV) properties.[7] They also have therapeutic effects on cardiovascular system diseases.[8] Despite the fact that coumarins have been extensively investigated, explorations of new coumarin derivative bioactivities are still attractive to researchers in the drug discovery community. This research is somewhat restricted, however, by the availability of and effective modification methods for coumarin derivatives. Therefore, new powerful modification methods that can directly install functionality into coumarin skeletal structures are welcome.[9]

Until now, many methods to synthesize coumarin derivatives have been reported,[10] but traditional methods typically require several steps or used prefunctionalized reactants to generate the target compounds.[11] In recent years, transition-metal-catalyzed C(sp^2 or sp^3)–H functionalization has emerged as a highly efficient and environmentally friendly method to produce coumarin derivatives. However, these methods involve the use of expensive metal catalysts. More recently, direct coupling reactions of coumarins with a partner that proceed through radical mechanisms have attracted increasing attention.[12] Because these C–C bond-forming reactions are straightforward and highly efficient,[13] they provide a better and more practical method for researchers to functionalize coumarin scaffolds.

Herein, aldehydes and di-*tert*-butyl peroxide (DTBP) were selected as coupling partners with coumarins to generate keto- and methyl-substituted coumarin derivatives through a radical mechanism. This new method is different from previously reported approaches, which generate keto- and methyl-substituted coumarin derivatives mainly from 2-hydroxybenzaldehydes[14] (Scheme 1). Although the generation of coumarin derivatives by using radical sequences can be found in the literature,[12] the coupling reactions of coumarins with aldehydes or DTBP by using a C(sp^2)–H functionalization process has not been reported.

Results and Discussion

On the basis of previous reports,[15] we screened various metal catalysts, oxidants, and solvents to find the suitable reaction conditions for the couplings between the coumarins and aldehydes (Table 1). *p*-Methoxybenzaldehyde was selected as the representative aldehyde for our optimization studies. First, TBAI (tetra-*n*-butylammonium iodide, 10.0 mol-%) and TBHP (70 wt.-% in water, 2.0 equiv.) were used in the screening reaction along with an excess amount of *p*-methoxybenzaldehyde (3.0 equiv.) to promote the reaction rate and partially act as a solvent. This reaction, however, afforded only a trace amount of the expected product **3a** (Table 1, Entry 1). A combination of $FeCl_3$/TBHP or $CuBr_2$/TBHP still gave trace amounts of product **3a** (Table 1, Entries 2 and 3), whereas using $CuCl_2$ or CuO as the catalyst in the presence of TBHP generated the expected products in 50 and 61 % yield, respectively (Table 1, Entries 4 and 5). When $Cu(OAc)_2$ was used with TBHP as the oxidant, the reaction only afforded 18 % of the coupling product (Table 1, Entry 6). The combination of CuI/TBHP did not afford coupling

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201501251.

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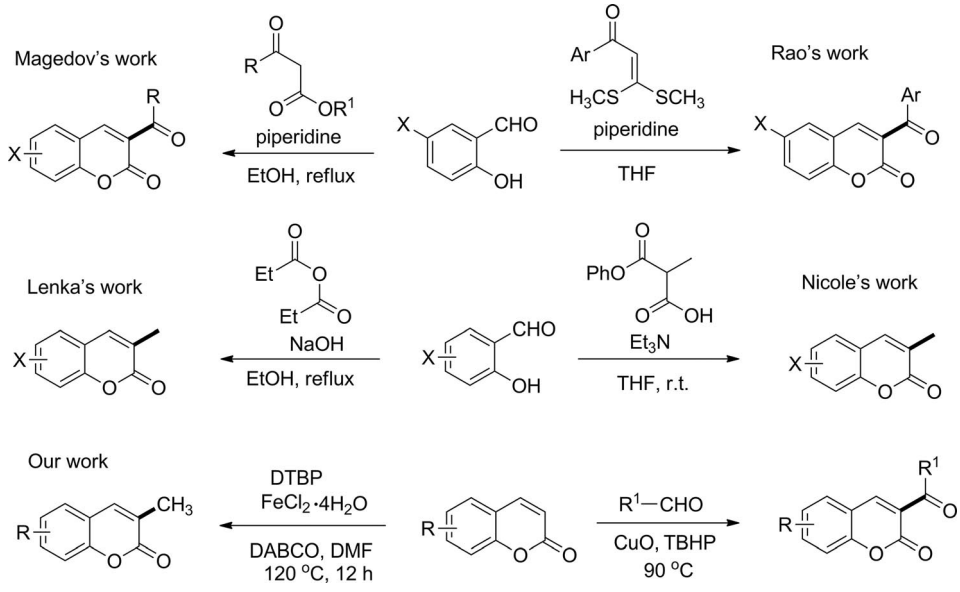
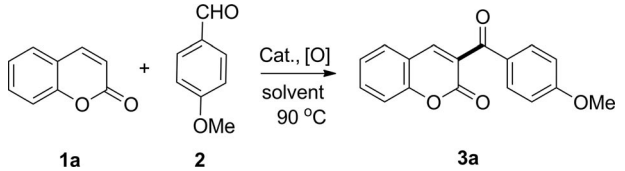


Scheme 1. Previous representative methods to generate keto- and methyl-substituted coumarin derivatives (THF = tetrahydrofuran, DABCO = 1,4-diazabicyclo[2.2.2]octane, DMF = *N*,*N*-dimethylformamide, TBHP = *tert*-butylhydroperoxide).

product **3a** (Table 1, Entry 7). Using $Mn(OAc)_2$ and TBHP together gave only a 14 % isolated product yield (Table 1, Entry 8). Employing DTBP, instead of TBHP, in the presence of $CuCl_2$ generated a trace amount of product (Table 1, Entry 9). Different solvents were also screened, but these coupling reactions gave trace amounts of **3a** (Table 1, Entries 10–12). Using CuO as the catalyst in benzene, DMF, or 1,2-dichloroethane (DCE) as the solvent generated product **3a** either in 15 % yield (Table 1, Entry 13) or in a trace amount (Table 1, Entries 14 and 15). On the basis of these screening results, the suitable conditions for this coupling reaction include the aldehyde (3.0 equiv.), CuO (10 mol-%), and TBHP (2.0 equiv.) at 90 °C for 24 h.

Under the optimized reaction conditions, different aldehydes were then treated with the coumarin derivatives (Table 2). Most of these reactions regioselectively gave keto-substituted coumarin derivatives **3** in moderate to good yields, but when iso-

Table 1. Screening to optimize reaction conditions.[a]

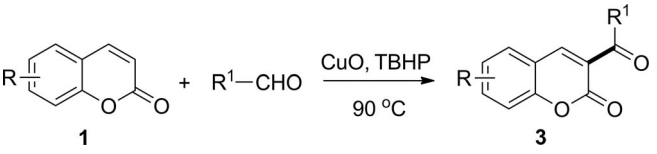


1a **2** **3a**

Entry	Catalyst	Oxidant	Temp. [°C]	Solvent	Yield [%][b]
1	TBAI	TBHP	90	–	trace
2	$FeCl_3$	TBHP	90	–	trace
3	$CuBr_2$	TBHP	90	–	trace
4	$CuCl_2$	TBHP	90	–	50
5	CuO	TBHP	90	–	61
6	$Cu(OAc)_2$	TBHP	90	–	18
7	CuI	TBHP	90	–	trace
8	$Mn(OAc)_2$	TBHP	90	–	14
9	$CuCl_2$	DTBP	90	–	trace
10	$CuCl_2$	TBHP	90	EtOAc	trace
11	$CuCl_2$	TBHP	90	CH_3CN	trace
12	$CuCl_2$	DTBP	90	EtOAc	trace
13	CuO	TBHP	90	benzene	15
14	CuO	TBHP	90	DMF	trace
15	CuO	TBHP	90	DCE	trace

[a] Reagents and conditions: coumarin (1.0 equiv.), catalyst (10 mol-%), *p*-methoxybenzaldehyde (3.0 equiv.), and oxidant such as TBAI (10 mol-%), TBHP (70 wt.-% in water, 2.0 equiv.), or DTBP (2.0 equiv.). [b] Isolated yield of product **3a** was calculated by using the amount of coumarin (**1a**). The reaction was carried out for 24 h.

Table 2. The coupling reactions of coumarins with aldehydes through C(sp^2)–H functionalization.[a]



1 **3**

Entry	R	R^1	Product	Yield [%][b]
1	H	4-MeO-C_6H_4	**3a**	61
2	6-Me	4-MeO-C_6H_4	**3b**	58
3	H	4-Me-C_6H_4	**3c**	61
4	H	4-*t*Bu-C_6H_4	**3d**	67
5	6-Me	4-*t*Bu-C_6H_4	**3e**	65
6	H	furan	**3f**	65
7	6-Me	furan	**3g**	63
8	6-Me	2-MeO-C_6H_4	**3h**	61
9	H	*i*Bu	**3i**	48
10	H	2-O_2N-C_6H_4	**3j**	trace
11	6-MeO	4-Br-C_6H_4	**3k**	62
12	6-Br	4-*t*Bu-C_6H_4	**3l**	64
13	6-*t*Bu	4-Br-C_6H_4	**3m**	51
14	benzo[*f*]	4-Br-C_6H_4	**3n**	52
15	H	C_6H_5	**3o**	68

[a] Reagents and conditions: coumarin (1.0 equiv.), an aldehyde (3.0 equiv.), TBHP (70 wt.-% in water, 2.0 equiv.), and the catalysts (10 mol-%). [b] Isolated yields of **3a**–**3o** were calculated by using the amount of coumarin derivative **1**. The reaction was carried out for 24 h.

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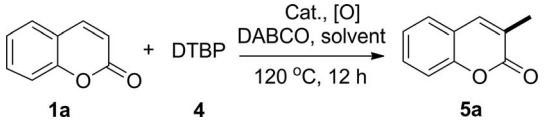
butyraldehyde was used, the reaction only generated a moderate 48 % yield. The coupling of electron-deficient 2-nitrobenzaldehyde with coumarin was then explored, but this reaction failed to give the expected product **3j**. On the basis of the chemical shifts in the ^{1}H NMR spectra, it was clear that the aldehydes were selectively added to the α-position of the double bond of the coumarin ester.

The methyl group is another important functionality in drug discovery. Because its presence can improve the pharmaceutical properties of some bioactive molecules, the addition of a methyl function into these compounds is very popular, and many researchers have spent their efforts exploring efficient methods to incorporate it into bioactive compounds. Until now, various methylation methods have been developed, but the use of DTBP as a methylation reagent in the presence of a copper or iron catalyst is a new approach. Here, we applied this strategy to coumarin to make the corresponding methyl-substituted derivatives.

Hence, we examined the suitable reaction conditions for the coupling between coumarin (**1a**) and DTBP. Different catalysts and solvents were screened for the optimization study. First, various copper catalysts [i.e., CuCl, CuI, CuBr, $CuCl_2$, CuO, and $Cu(OAc)_2$] were employed in DMF, but these reactions only gave trace amounts of product **5a** (Table 3, Entries 1–6). Switching the catalyst from a copper salt to $FeCl_3$ greatly increased the yield of **5a** to 70 % (Table 3, Entry 7). When $FeCl_2{\cdot}4H_2O$ was used as a catalyst in dimethyl sulfoxide (DMSO), a 60 % yield of **5a** was obtained (Table 3, Entry 8). Changing the solvent from DMSO to DMF or dichloromethane (DCM) afforded the expected product **5a** in 72 and 60 % yield, respectively (Table 3, Entries 9 and 10). Using CH_3CN as the solvent generated a trace amount of the expected product (Table 3, Entry 11). On the basis of these screening results, the optimized reaction conditions for the coupling of coumarin with DTBP include $FeCl_2{\cdot}4H_2O$ (10.0 mol-%), coumarin (1.0 equiv.), DTBP (2.0 equiv.), and DABCO (0.1 equiv.) in DMF (1.0 mL) at 120 °C.

Table 3. Screening for suitable reaction conditions for coupling of coumarin (**1a**) with DTBP.[a]

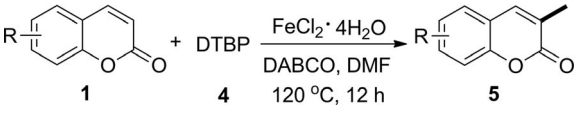


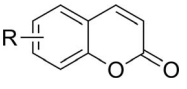
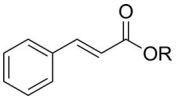
Entry	Catalyst	Temp. [°C]	Solvent	Yield [%][b]
1	CuCl	120	DMF	trace
2	CuI	120	DMF	trace
3	CuBr	120	DMF	trace
4	$CuCl_2$	120	DMF	trace
5	CuO	120	DMF	trace
6	$Cu(OAc)_2$	120	DMF	trace
7	$FeCl_3$	120	DMF	70
8	$FeCl_2{\cdot}4H_2O$	120	DMSO	60
9	$FeCl_2{\cdot}4H_2O$	120	DMF	72
10	$FeCl_2{\cdot}4H_2O$	120	DCM	60
11	$FeCl_2{\cdot}4H_2O$	120	MeCN	trace

[a] Reagents and conditions: coumarin (1.0 equiv.), DTBP (2.0 equiv.), DABCO (0.1 equiv.), the catalysts (10 mol-%), solvent (1.0 mL), 120 °C. [b] Isolated yield of product **5a** was calculated by using the amount of coumarin (**1a**). The reaction time was 12 h.

Under the optimized reaction conditions, different coumarin derivatives were then treated with DTBP, and the expected products **5a**–**5g** were produced in yields of 60–72 % (Table 4, Entries 1–7). All reactions gave the substituted coumarin derivatives with the methyl group at the α-position. Besides coumarins, cinnamate esters were also used as a reactant. These reactions proceeded well and regioselectively generated the methyl-substituted products **5h**–**5j** in isolated yields of 60–70 % (Table 4, Entries 8–10).

Table 4. The coupling reactions of coumarins and cinnamate esters with DTBP through C(sp^2)–H functionalization.[a]



Entry	R	Product	Yield [%][b]
			
1	H	**5a**	72
2	6-Me	**5b**	60
3	6-MeO	**5c**	65
4	6-*t*Bu	**5d**	65
5	6-Br	**5e**	60
6	benzo[*f*]	**5f**	65
7	6-O_2N	**5g**	70
			
8	Me	**5h**	60
9	Et	**5i**	70
10	Bn	**5j**	65

[a] Reagents and conditions: coumarin (1.0 equiv.), DTBP (2.0 equiv.), DABCO (0.1 equiv.), and $FeCl_2{\cdot}4H_2O$ (10 mol-%). [b] Isolated yields of **5a**–**5j** were calculated by using the amount of coumarin derivative **1**.

To determine if the two coupling reactions proceed through a radical process, TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] was used as a radical scavenger. In the presence of TEMPO, **3a** and **5a** were not formed, which indicates that a radical process is involved. On the basis of these and previously reported results,[15f,16] we propose the mechanism as shown in Scheme 2.

Upon initial heating, TBHP can split into two radicals, which could then extract a hydrogen atom from the aldehyde functional group to generate radical **A**. Possible attack at the α- and β-position of the olefin moiety of coumarin then generates radical intermediates **B** and **C**. As benzylic radical **B** is more stable than radical **C**, only keto-substituted coumarin derivative **3** is regioselectively obtained after the loss of one electron to the Cu catalyst. In the second coupling reaction, a methyl radical is generated upon heating DTBP. Possible attack by this radical to the α- and β-position of the olefin unit of coumarin generates radical intermediates **D** and **E**, respectively. Because benzylic radical **D** is more stable than radical **E**, only methyl-

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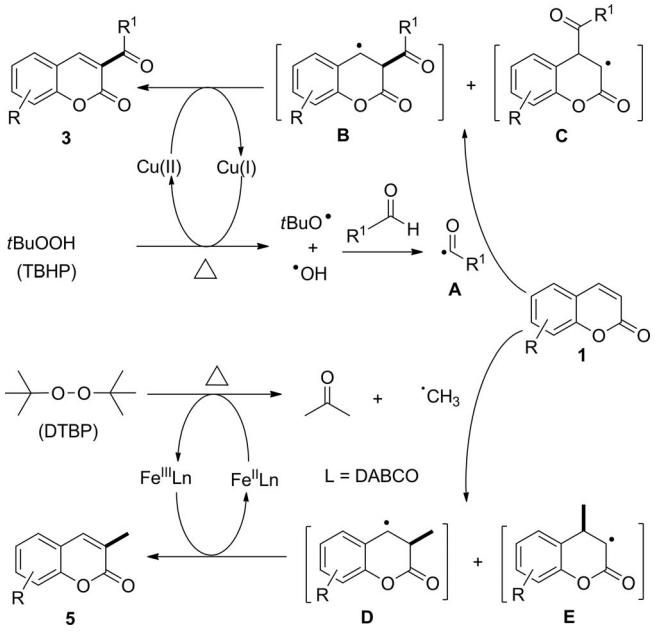

Scheme 2. Plausible reaction mechanism.

substituted coumarin derivative **5** is regioselectively generated after the loss of one electron to the Fe catalyst.

Conclusions

In summary, we have developed two new coupling reactions that proceed through a C(sp^2)–H functionalization process. The reactions between coumarins and aldehydes and coumarins and DTBP regioselectively generated keto- and methyl-substituted coumarin derivatives, respectively, in moderate to good yields in the presence of an inexpensive copper or iron catalyst. The couplings will enrich current coumarin chemistry, as these derivatives are highly valuable in drug discovery. All compounds synthesized will be screened for a variety of biological activities at the medical school of Jiangsu University.

Experimental Section

General Methods: All reactions were carried out in sealed tubes. An oven-dried magnetic stirring bar was used to stir the reaction mixtures. Solvents were purified by standard methods, unless otherwise noted. Commercially available reagents were purchased from the Aladdin Company in China and used without further purification than that detailed below. Flash column chromatography was performed on silica gel (200–300 mesh). All reactions were monitored by TLC analysis. Deuterated solvents were purchased from Cambridge Isotope Laboratories. The ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Bruker DRX-400 spectrometer that operated at 400 and 100 MHz, respectively. HRMS [liquid chromatography (LC)–HRMS] was recorded on a LXQ Spectrometer (Thermo Scientific) with ESI-TOF (MeOH as a solvent). Coumarins derivatives were synthesized according to the literature.

General Procedure for the Syntheses of Compounds 3a–3o: To a dry sealed tube were added coumarin (1.0 equiv.) and *p*-methoxybenzaldehyde (3.0 equiv.) followed by the addition of TBHP (2.0 equiv., 70 wt.-% in water). The mixture was stirred at 90 °C for 24 h (monitored by TLC). Then the reaction was quenched with water, and the resulting solution was extracted with dichloromethane. The combined organic layers were washed by brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 15:1) to provide the desired product **3a** in 64 % yield as well as compounds **3b**–**3o**.

General Procedure for the Synthesis of Compounds 5a–5j: To a dry sealed tube were added coumarin (1.0 equiv.) and DTBP (2.0 equiv.) followed by the addition of $FeCl_2{\cdot}4H_2O$ (10.0 mol-%), DABCO (0.1 equiv.), and DMF (1.0 mL). The mixture was stirred at 120 °C for 12 h (monitored by TLC). Then the reaction was quenched with water, and the resulting solution was extracted with ethyl acetate. The combined organic layers were washed by brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 20:1) to provide the desired product **5a** in 72 % yield as well as compounds **5b**–**5j**.

3-(4-Methoxybenzoyl)-2*H*-chromen-2-one (3a): FTIR: $\tilde{\nu}$ = 3083, 2919, 1716, 1647, 1607, 1260, 1176, 759 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.91 (d, J = 8.8 Hz, 2 H), 7.68–7.60 (m, 2 H), 7.44–7.35 (m, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.0, 164.3, 158.6, 154.7, 144.6, 133.3, 132.2, 129.0, 129.0, 127.6, 124.9, 118.3, 116.9, 113.9, 55.6 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{12}NaO_4^+$ [M + Na]$^+$ 303.0628; found 303.0626.

3-(4-Methoxybenzoyl)-6-methyl-2*H*-chromen-2-one (3b): FTIR: $\tilde{\nu}$ = 2919, 2843, 1720, 1650, 1618, 1574, 1256, 1175, 790 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.88 (d, J = 8.4 Hz, 2 H), 7.45–7.43 (m, 1 H), 7.37 (s, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 6.95 (d, J = 8.0 Hz, 2 H), 3.88 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 164.2, 158.8, 152.8, 144.7, 134.7, 134.5, 132.2, 129.1, 128.7, 127.5, 118.0, 116.6, 113.9, 55.6, 20.8 ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_{14}NaO_4^+$ [M + Na]$^+$ 317.0784; found 317.0783.

3-(4-Methylbenzoyl)-2*H*-chromen-2-one (3c): FTIR: $\tilde{\nu}$ = 3060, 2919, 1713, 1658, 1608, 1265, 1184, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.79 (d, J = 8.0 Hz, 2 H), 7.64–7.58 (m, 2 H), 7.40 (d, J = 8.4 Hz, 1 H), 7.37–7.33 (m, 1 H), 7.28 (d, J = 8.0 Hz, 2 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 158.5, 154.7, 145.1, 145.0, 133.7, 133.5, 129.8, 129.3, 129.1, 127.3, 124.9, 118.2, 116.9, 21.8 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{12}NaO_3^+$ [M + Na]$^+$ 287.0679; found 287.0680.

3-[4-(*tert*-Butyl)benzoyl]-2*H*-chromen-2-one (3d): FTIR: $\tilde{\nu}$ = 3056, 2968, 1736, 1657, 1605, 1263, 1166, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.84 (d, J = 8.0 Hz, 2 H), 7.65–7.58 (m, 2 H), 7.50 (d, J = 8.0 Hz, 1 H), 7.41 (d, J = 8.0 Hz, 2 H), 7.37–7.33 (m, 1 H), 7.33 (s, 1 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 158.5, 157.8, 154.7, 145.0, 144.8, 133.5, 129.7, 129.1, 127.4, 125.6, 124.9, 118.3, 116.9, 35.3, 31.3, 31.0, 30.8 ppm. HRMS (ESI-TOF): calcd. for $C_{20}H_{18}NaO_3^+$ [M + Na]$^+$ 329.1148; found 329.1144.

3-[4-(*tert*-Butyl)benzoyl]-6-methyl-2*H*-chromen-2-one (3e): FTIR: $\tilde{\nu}$ = 2966, 1754, 1662, 1603, 1361, 1255, 864, 786 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.83 (dd, J = 6.8, 2.0 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.46–7.44 (m, 1 H), 7.37 (s, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 2.44 (s, 3 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 158.7, 152.9, 145.0, 134.7, 134.6, 133.6, 129.7, 128.8, 127.3, 125.6, 118.0, 116.6, 35.3, 31.1, 20.7 ppm. HRMS (ESI-TOF): calcd. for $C_{21}H_{20}NaO_3^+$ [M + Na]$^+$ 343.1305; found 343.1308.

3-(Furan-2-carbonyl)-2*H*-chromen-2-one (3f): FTIR: $\tilde{\nu}$ = 3132, 3114, 1717, 1652, 1607, 1462, 1176, 960, 762 cm^{-1}. ^{1}H NMR

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(400 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.68–7.61 (m, 3 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.38–7.36 (m, 2 H), 6.62 (dd, *J* = 3.6, 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0, 158.0, 154.8, 151.8, 147.7, 145.5, 133.8, 129.3, 126.3, 125.0, 120.7, 118.1, 116.9, 112.8 ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_8NaO_4^+$ $[M + Na]^+$ 263.0315; found 263.0312.

3-(Furan-2-carbonyl)-6-methyl-2*H*-chromen-2-one (3g): FTIR: $\tilde{\nu}$ = 3131, 3114, 1714, 1650, 1575, 1462, 1183, 962, 766 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.68 (d, *J* = 1.2 Hz, 1 H), 7.45 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.39 (s, 1 H), 7.36–7.35 (m, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 6.62 (dd, *J* = 3.6, 1.6 Hz, 1 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.2, 158.2, 153.0, 151.8, 147.7, 145.6, 134.9, 128.9, 126.1, 120.7, 117.9, 116.6, 112.7, 20.7 ppm. HRMS (ESI-TOF): calcd. for $C_{15}H_{10}NaO_4^+$ $[M + Na]^+$ 277.0471; found 277.0455.

3-(2-Methoxybenzoyl)-6-methyl-2*H*-chromen-2-one (3h): FTIR: $\tilde{\nu}$ = 2930, 1840, 1726, 1653, 1620, 1575, 1258, 1172, 792 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.0 (s, 1 H), 7.90 (d, *J* = 8.8 Hz, 2 H), 7.46 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.39 (s, 1 H), 7.32 (d, *J* = 8.8 Hz, 1 H), 6.97 (d, *J* = 9.2 Hz, 2 H), 3.91 (s, 3 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 164.2, 158.8, 152.8, 144.7, 134.7, 134.5, 132.2, 129.1, 128.7, 127.5, 118.0, 116.6, 113.9, 55.6, 20.8 ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_{14}NaO_4^+$ $[M + Na]^+$ 317.0784; found 317.0783.

3-Isobutyryl-2*H*-chromen-2-one (3i): FTIR: $\tilde{\nu}$ = 2955, 1866, 1776, 1653, 1322, 1172, 865, 792 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1 H), 7.68–7.64 (m, 2 H), 7.40–7.34 (m, 2 H), 3.91–3.84 (m, 1 H), 1.20 (d, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 158.8, 155.2, 147.6, 134.1, 129.9, 124.9, 124.8, 118.4, 116.7, 38.6, 18.3 ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_{12}NaO_3^+$ $[M + Na]^+$ 239.0679; found 239.0688.

3-(4-Bromobenzoyl)-6-methoxy-2*H*-chromen-2-one (3k): FTIR: $\tilde{\nu}$ = 2988, 2361, 1745, 1659, 1331, 1116, 868, 783 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.75 (d, *J* = 8.8 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 9.2 Hz, 1 H), 7.25 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.02 (d, *J* = 2.8 Hz, 1 H), 3.88 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 158.6, 156.5, 149.4, 145.9, 135.1, 131.9, 131.0, 129.1, 126.8, 122.1, 118.4, 118.0, 110.67, 55.95 ppm. HRMS (ESI-TOF): calcd. for $C_{13}H_{12}NaO_3^+$ $[M + Na]^+$ 380.9733; found 380.9725.

6-Bromo-3-[4-(*tert*-butyl)benzoyl]-2*H*-chromen-2-one(3l): FTIR: $\tilde{\nu}$ = 2988, 2361, 1745, 1659, 1331, 1116, 868, 783 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.76–7.72 (m, 3 H), 7.65–7.63 (m, 2 H), 7.59 (d, *J* = 2.4 Hz, 1 H), 7.37 (d, *J* = 8.8 Hz, 1 H), 1.39 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 158.1, 157.8, 153.5, 143.3, 136.1, 133.2, 131.2, 129.7, 128.5, 125.7, 119.7, 118.7, 117.5, 35.3, 31.0 ppm. HRMS (ESI-TOF): calcd. for $C_{20}HBrNaO_3^+$ $[M + Na]^+$ 407.0253; found 407.0257.

3-(4-Bromobenzoyl)-6-(*tert*-butyl)-2*H*-chromen-2-one (3m): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1323, 1116, 885, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1 H), 7.83 (d, *J* = 8.8 Hz, 2 H), 7.73 (dd, *J* = 6.8, 2.0 Hz, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 9.6 Hz, 1 H), 1.37 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 158.7, 153.0, 148.4, 146.7, 135.2, 131.9, 131.8, 131.0, 129.0, 126.1, 125.5, 117.6, 116.6, 34.7, 31.3 ppm. HRMS (ESI-TOF): calcd. for $C_{20}H_{17}BrNaO_3^+$ $[M + Na]^+$ 407.0253; found 407.0257.

2-(4-Bromobenzoyl)-3*H*-benzo[*f*]chromen-3-one (3n): FTIR: $\tilde{\nu}$ = 2988, 2361, 1745, 1659, 1244, 1116, 868, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 8.30 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.81–7.75 (m, 3 H), 7.67–7.63 (m, 3 H), 7.54 (d, *J* = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 158.6, 155.7, 142.6, 135.8, 135.4, 131.9, 131.0, 130.4, 129.4, 129.3, 129.2, 129.0, 126.7, 124.8, 121.5, 116.7, 112.7 ppm. HRMS (ESI-TOF): calcd. for $C_{20}H_{11}BrNaO_3^+$ $[M + Na]^+$ 400.9784; found 400.9784.

3-Benzoyl-2*H*-chromen-2-one (3o): FTIR: $\tilde{\nu}$ = 3063, 1717, 1607, 1493, 1243, 1055, 813 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.90, (d, *J* = 7.2 Hz, 2 H), 7.62–7.70 (m, 3 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.36–7.49 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 151.2, 137.4, 134.0, 132.0, 130.7, 127.7, 119.1, 116.1, 74.6, 69.1, 32.2, 26.0, 23.6, 20.8 ppm. HRMS (ESI-TOF): calcd. for $C_{16}H_{10}NaO_3^+$ $[M + Na]^+$ 273.0522; found 273.0519.

3-Methyl-2*H*-chromen-2-one (5a): FTIR: $\tilde{\nu}$ = 3072, 2361, 1745, 1659, 1414, 1116, 885, 552 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1 H), 7.50–7.43 (m, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.27–7.25 (m, 1 H), 2.23 (d, *J* = 1.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 153.2, 139.3, 130.4, 127.0, 125.7, 124.3, 119.5, 116.4, 29.7, 17.1 ppm. HRMS (ESI-TOF): calcd. for $C_9H_5NaO_2^+$ $[M + Na]^+$ 183.0417; found 183.0422.

3,6-Dimethyl-2*H*-chromen-2-one (5b): FTIR: $\tilde{\nu}$ = 3072, 2361, 1745, 1659, 1323, 1244, 868, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 1 H), 7.26 (d, *J* = 1.6 Hz, 1 H), 7.22–7.20 (m, 2 H), 2.40 (s, 3 H), 2.21 (d, *J* = 0.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 151.4, 139.9, 131.4, 126.8, 125.6, 119.3, 116.2, 29.7, 20.8, 17.2 ppm. HRMS (ESI-TOF): calcd. for $C_{11}H_{10}NaO_2^+$ $[M + Na]^+$ 197.0753; found 197.0576.

6-Methoxy-3-methyl-2*H*-chromen-2-one (5c): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1244, 1116, 868, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 1 H), 7.23 (d, *J* = 9.2 Hz, 1 H), 7.03 (dd, *J* = 8.8, 2.8 Hz, 1 H), 6.85 (d, *J* = 2.8 Hz, 1 H), 3.84 (s, 3 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 156.0, 147.6, 139.1, 126.2, 119.9, 118.0, 117.4, 109.3, 55.8, 17.3 ppm. HRMS (ESI-TOF): calcd. for $C_{11}H_{10}NaO_3^+$ $[M + Na]^+$ 213.0522; found 213.0525.

6-(*tert*-Butyl)-3-methyl-2*H*-chromen-2-one (5d): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1244, 1116, 885, 662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.50 (m, 2 H), 7.40 (d, *J* = 2.0 Hz, 1 H), 7.26 (d, *J* = 8.8 Hz, 1 H), 2.22 (d, *J* = 1.2 Hz, 3 H), 1.36 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 151.2, 147.3, 139.8, 128.1, 125.4, 123.3, 119.0, 116.0, 34.5, 31.4, 17.2 ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_{17}O_2$ $[M + H]^+$ 239.1043; found 239.1046.

6-Bromo-3-methyl-2*H*-chromen-2-one (5e): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1456, 1116, 860, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2 H), 7.46 (s, 1 H), 7.23–7.21 (m, 1 H), 2.25 (d, *J* = 0.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 152.1, 137.8, 133.3, 129.3, 127.3, 121.1, 118.2, 116.8, 17.3 ppm. HRMS (ESI-TOF) *m/z* calculated for $C_{10}H_7NaO_2^+$ $[M + Na]^+$ 260.9522; found 260.9527.

2-Methyl-3*H*-benzo[*f*]chromen-3-one (5f): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1414, 1244, 868, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 1.6 Hz, 1 H), 8.22 (d, *J* = 8.4 Hz, 1 H), 7.92–7.89 (m, 2 H), 7.70–7.65 (m, 1 H), 7.59–7.55 (m, 1 H), 7.44 (d, *J* = 9.2 Hz, 1 H), 2.34 (d, *J* = 1.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.3, 152.5, 135.1, 131.6, 130.3, 129.0, 128.7, 127.9, 125.8, 125.0, 121.4, 116.80, 113.5, 17.6 ppm. HRMS (ESI-TOF): calcd. for $C_{14}H_{10}NaO_2^+$ $[M + Na]^+$ 233.0573; found 233.0575.

3-Methyl-6-nitro-2*H*-chromen-2-one (5g): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1244, 1107, 837, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.39–8.34 (m, 2 H), 7.62 (s, 1 H), 7.46 (d, *J* = 9.2 Hz, 1 H), 2.30 (d, *J* = 0.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 156.7, 137.8, 128.7, 128.6, 125.4, 122.8, 119.6, 117.6 ppm. HRMS (ESI-TOF) calcd. for $C_{10}H_7NNaO_4^+$ $[M + Na]^+$ 228.0267; found 228.0273.

Methyl (*E*)-2-Methyl-3-phenylacrylate (5h): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1414, 1244, 885, 789 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 1.2 Hz, 1 H), 7.42 (t, *J* = 4.4 Hz, 4 H), 7.37–7.33 (m,

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1 H), 3.85 (s, 3 H), 2.15 (d, J = 1.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 139.0, 135.9, 129.7, 128.4, 128.3, 77.4, 77.0, 76.7, 52.1, 14.1 ppm. HRMS (ESI-TOF): calcd. for $C_{11}H_{12}NaO_2^+$ $[M + Na]^+$ 199.0730; found 199.0740.

Ethyl (*E*)-2-Methyl-3-phenylacrylate (5i): FTIR: $\tilde{\nu}$ = 2988, 2361, 1745, 1659, 1323, 1116, 868, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 1.6 Hz, 1 H), 7.44–7.40 (m, 4 H), 7.36–7.33 (m, 1 H), 4.30 (dd, J = 14.4, 7.2 Hz, 2 H), 2.14 (d, J = 1.6 Hz, 3 H), 1.38 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 138.7, 136.0, 129.6, 128.7, 128.4, 128.3, 60.9, 14.3, 14.1 ppm. HRMS (ESI-TOF): calcd. for $C_{11}H_{11}NaO_2^+$ $[M + Na]^+$ 213.0886; found 213.0736.

Benzyl (*E*)-2-Methyl-3-phenylacrylate (5j): FTIR: $\tilde{\nu}$ = 2932, 2361, 1745, 1659, 1298, 1116, 885, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 1.6 Hz, 1 H), 7.47–7.35 (m, 10 H), 5.30 (s, 2 H), 2.18 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 139.3, 136.3, 135.9, 129.7, 128.5, 128.4, 128.3, 128.2, 128.1, 66.7, 14.1 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{16}NaO_2^+$ $[M + Na]^+$ 275.1043; found 275.1048.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of compounds.

Acknowledgments

A. Z. acknowledges Jiangsu University for the financial support (grant number 1281290006).

Keywords: Natural products · Oxygen heterocycles · Aldehydes · C–C coupling · Regioselectivity

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Received: September 29, 2015
Published Online: November 24, 2015

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