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A Regioselective Approach to C3-Aroylcoumarins via Cobalt-Catalyzed C(sp^2)–H Activation Carbonylation of Coumarins

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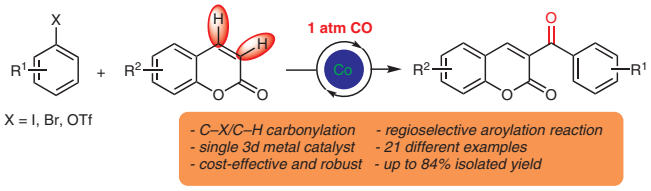

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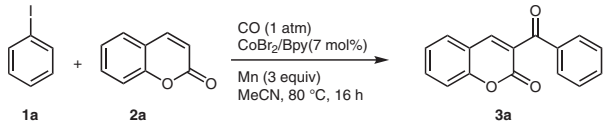
Abstract A new cobalt-catalyzed C–H bond activation of coumarins with aryl halides or pseudohalides and carbon monoxide insertion to give various 3-aroylcoumarin derivatives is described. It is the first time that CO as C1 feedstock is used as the coupling partners in cobalt-catalyzed regioselective coumarin C–H functionalization reactions. Upon activation with manganese powder, the Co catalyzes the C–H bond activation carbonylation reactions of aryl iodides, bromides, and even triflates under mild conditions, providing the regioselective aroylated products in moderate to good yields.

Key words cobalt-catalyzed, C–H activation, carbon monoxide, carbonylation, 3-aroylcoumarin

The direct C–H bond activation and functionalization method has emerged as a straightforward and step-economical synthetic methodology for the sustainable synthesis of diverse organic structures.[1] Construction of C–C bonds is one of the most facile and powerful strategies in organic chemistry, and ether containing compounds are widely employed in the synthesis of complex molecules and functional materials, which this methodology facilitated by using transition metals.[2] Indeed, utilization of metal-catalyzed cross-coupling reactions for the development of new C–C bonds formation is still progressing impressively and is certainly an undeniable strategy for the chemists. In recent years, tremendous breakthroughs have been achieved in transition-metal-catalyzed C–H bond carbonylation with carbon monoxide as C1 feedstock and represents one of the most atom-economic and efficient ways to construct carbonyl compounds.[3] Because cobalt metal is abundant, more

Table 1 Optimization of Cross-Coupling Carbonylation Reaction[a]

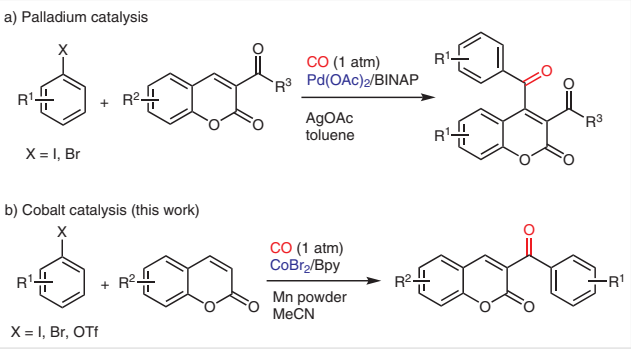


1a 2a 3a

Entry	Catalyst system: Changes from the standard conditions	Yield (%)[b]
1	none	77
2	without $CoBr_2$	ND
3	without 2,2′-bipyridine	23
4	without Mn powder	ND
5	Mn powder (2 equiv)	62
6	CoI_2 in place of $CoBr_2$	43
7	$Co(OAc)_2$ in place of $CoBr_2$	40
8	$Co(OAc)_2{\cdot}4H_2O$ in place of $CoBr_2$	57
9	1,10-phenanthroline in place of 2,2′-bipyridine	65
10	PPh_3 in place of 2,2′-bipyridine	36
11	Cu in place of Mn	46
12	Zn in place of Mn	52
13	toluene in place of MeCN	63
14	1,4-dioxane in place of MeCN	30
15	PhCl in place of MeCN	45
16	DMA in place of MeCN	<5
17	NMP in place of MeCN	21
18	DMSO in place of MeCN	ND

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), catalyst (7.0 mol %), solvent (3 mL), CO (1 atm), at 80 °C for 16 h in a sealed reaction tube.
[b] Isolated yields. ND: Not detected.

environmentally friendly, and less expensive compared with noble metals, cobalt catalysts have received significant attention due to their high activities in C–H functionalizations.[4] In 1956, Murahashi and Horiie showed an elegant method for the carbonylation reactions using a simple, commercially available cobalt(II) precursor via chelation-assisted C–H activation process.[5] In spite of undisputed advances in the cross-coupling reactions field, Co-catalyzed C–H carbonylation has attracted significant fondness due to the wide presence of carbonyl groups in organic and medicinal chemistry.[6] Particularly, C–C bond formation by using low-valent cobalt catalysis in the presence of manganese powder as the reducing agent has witnessed major progress, which illustrates the high importance and application of Co(II)/Mn catalytic system in the cross-coupling reactions.[7] To continue our efforts on metal-free heterocyclic C–H functionalization[8] and palladium-catalyzed carbonylation aroylation of coumarins (Scheme 1a),[9] we disclose here the cobalt-catalyzed C3-aroylation of coumarins with aryl halides and aryl triflates through an sp^2 C–H bond carbonylation functionalization reaction (Scheme 1b). This process represents the first example of aroylation cross-coupling reactions on a coumarin platform via a regioselective sp^2 C–H functionalization process with cobalt catalysis in a carbon monoxide atmosphere (Scheme 1).



Scheme 1 Transition-metal-catalyzed coumarin C(sp^2)–H bond carbonylation

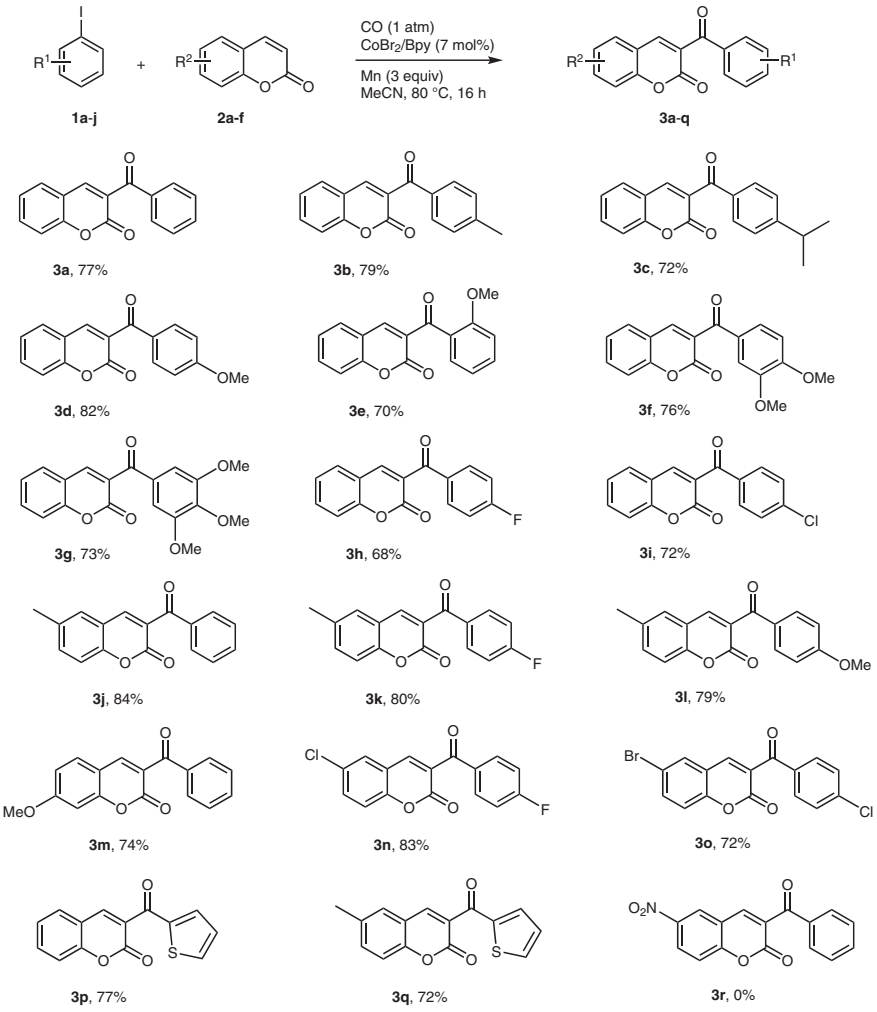
The regioselective aroylation of coumarin (**2a**) was carried out under CO (1 atm) at 80 °C in the presence of $CoBr_2$/Bpy[10] (Bpy = 2,2′-bipyridine) and Mn powder (3.0 equiv) in acetonitrile (Table 1). Under the standard conditions, 3-benzoylcoumarin (**3a**) was obtained in 77% yield (Table 1, entry 1). Without $CoBr_2$, product **3a** was not obtained (entry 2). In the absence of 2,2′-bipyridine, the reaction led to reduced synthesis of product **3a** (entry 3). Without the addition of Mn powder, the C–H activation aroylation did not proceed at all (entry 4). When the amount of manganese powder was reduced to 2.0 equivalents, the yield of **3a** was decreased to 62% (entry 5). Furthermore, use of CoI_2, $Co(OAc)_2$, and $Co(OAc)_2{\cdot}4H_2O$ as the cobalt sources did not give any interesting results (entries 6–8). Upon subsequent screening of 1,10-phenanthroline and PPh_3 ligands (entries 9 and 10), we identified that 1,10-phenanthroline has slightly higher ligand activity (entry 9) but PPh_3 afforded a lower yield of product **3a** (entry 10). Other reducing agents such as Cu and Zn powder gave **3a** in only moderate yields (entries 11 and 12). Low conversion into 3-benzoylcoumarin (**3a**) was observed when other solvents such as toluene, 1,4-dioxane, and PhCl were employed (entries 13–15). It is necessary to mention that the use of different polar aprotic solvents such as DMA, NMP, and DMSO did not increase the yield of the desired product (entries 16–18).

To know the scope of the present cobalt-catalyzed C–H activation functionalization, various substituted aryl iodides **1** and coumarins **2** were tested under the optimized reaction conditions (Scheme 2). Substrates bearing electron-donating groups, such as Me, *i*Pr, and OMe, could participate in the reaction smoothly to give the desired products **3b**, **3c**, and **3d** , respectively, in good yields (72–82%). Steric hindrance was observed for an electron-donating OMe group at *ortho*-position of iodobenzene and relatively lower yield was obtained (**3e**, 70%). Iodobenzenes bearing electron-rich aryl groups **1f** and **1g** behaved similarly generating the 3-aroylcoumarins **3f**,**g** in good yields. The halogen groups (F and Cl) at the *para*-position were also tolerated, and the corresponding C–H activation products **3h** and **3i** were obtained in 68% and 72% yield, respectively. We were pleased to find that coumarins with different substituents such as 6-methyl, 7-methoxy, 6-chloro, and 6-bromo survived well under the reaction conditions (→ **3j–o,** 72–84% yields). Pleasingly, 2-iodothiophene with coumarin (**2a**) and 6-methylcoumarin (**2b**) survived the reaction conditions and were successfully transformed into the corresponding products **3p** and **3q** in good yields. When 6-nitrocoumarin (**2f**) was examined, no desired product **3r** was detected.

Furthermore, we set out to explore the scope with a wide range of aryl bromides and aryl triflates for the carbonylation coupling reaction (Scheme 3). Moderate to good yields of coupled products were obtained with neutral, various electron-donating, and electron-deficient aryl bromides, but aryl triflates proved to be less efficient as double C–C coupling partner, resulting in the aroylated products in low yields. However, 2,6-diisopropylphenyl triflate did not give the 3-aroylcoumarin **3v**.

To test chemoselective carbonylation mediated by CO, we examined the benzene derivative **1k**, which is substituted with two different halogens: iodide and bromide. Selective C–I bond cleavage carbonylation led to product **3w** in 75% yield under the standard reaction conditions (Scheme 4).

Based on the above studies and relevant literature,[7] a plausible regioselective aroylation mechanism is proposed in Scheme 5. Initially, the $CoBr_2$/Bpy as the catalytic system is reduced to the electron-rich Co(0) species by the manga-

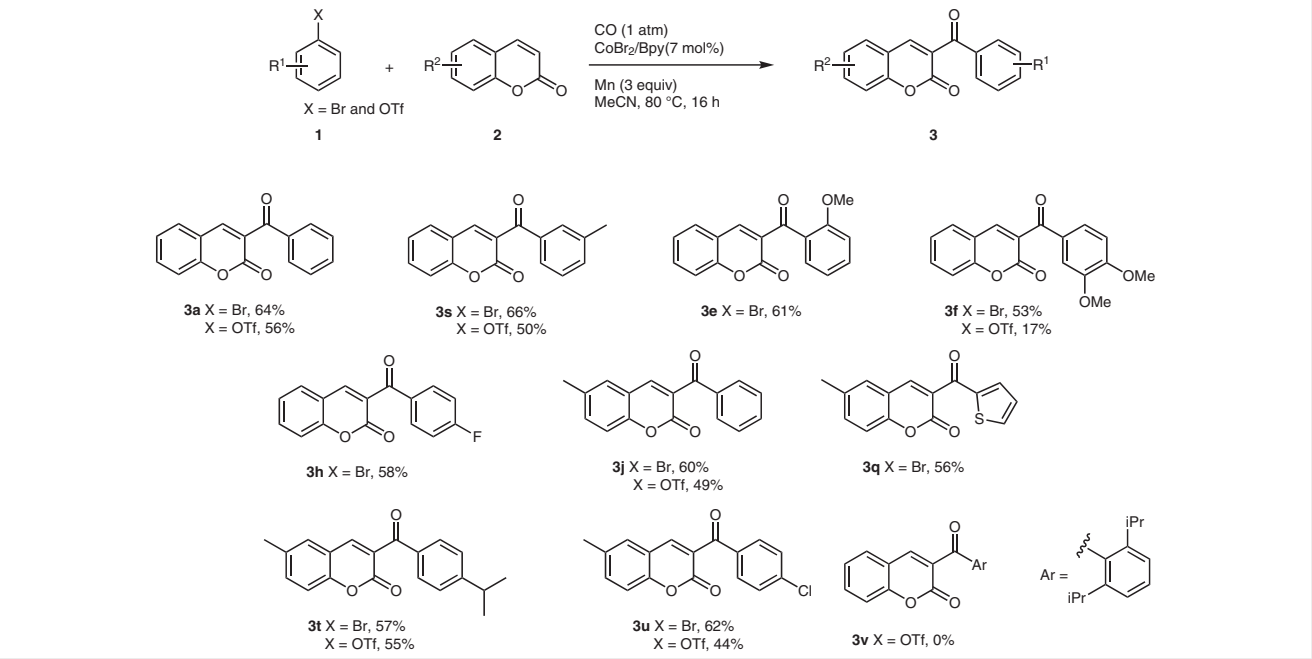


Scheme 2 Carbonylation of aryl iodides with a range of coumarin derivatives. *Reagents and conditions*: **1** (0.6 mmol), **2** (0.5 mmol), catalyst (7.0 mol%), MeCN (3 mL), CO (1 atm), at 80 °C for 16 h in a sealed reaction tube. Isolated yields are given.

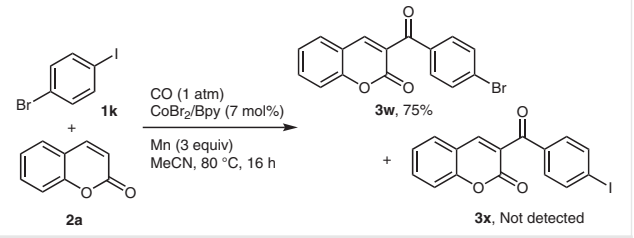
nese reductant. The oxidative addition of the C–I bond to low-valent cobalt occurs to form organocobalt species **A**, followed by coordination and the migratory insertion of a carbonyl moiety to generate the benzoylcobalt intermediate **C**. Then, the subsequent addition of Co-complex **C** into the C3(sp^2)–H bond of coumarin (**2a**) through migratory insertion takes place to give rise to a coumarincobalt(II) complex **D**, which the undergoes the β-hydride elimination to generate the aroylated product **3a** and liberate the H–Co(II)–I species **E**. The reduction of Co(II) **E** to Co(0) by Mn continues the cycle. Finally, reduction of **E** with manganese affords the corresponding zerovalent cobalt catalytic species for regeneration.

In summary, we have established an efficient and convenient approach for the regioselective C(sp^2)–H bond carbonylation of coumarins using stable, inexpensive, and commercially available $CoBr_2$ as the catalyst, Mn powder as the best reducing agent, and easily handling carbon monoxide as the carbonyl source. This protocol could significantly simplify provide new insight into Co-catalyzed C–H functionalization for the formation of two C–C bonds, which paves the way for other Co-catalyzed carbon–carbon bond cross-coupling carbonylation reactions.

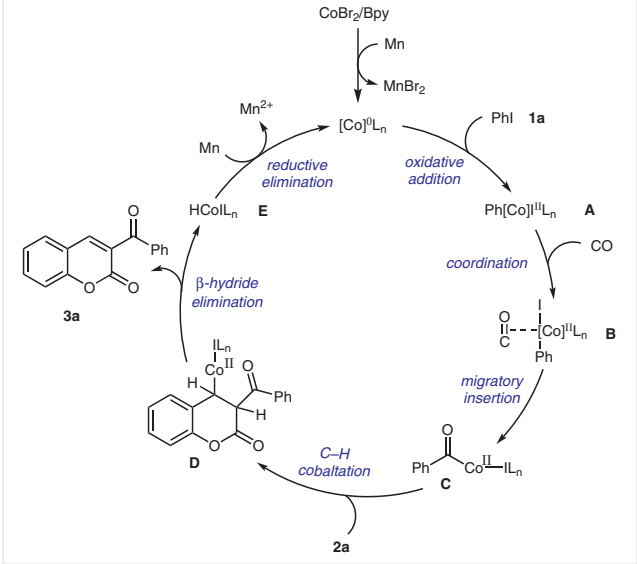
All reactions were carried out in oven-dried Schlenk tubes under a CO atmosphere using a balloon filled with CO. All chemicals were purchased from Merck (Germany) and were used without further purification. Mn powder (≥99%) was purchased from Sigma-Aldrich and stored under a N_2 atmosphere. $CoBr_2$/Bbpy was prepared according to a published method.[10] Aryl triflates were synthesized according to literature procedures.[11] Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were obtained on a Unicom Galaxy Series FT-IR 5000 spectrophotometer. High-resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. ^1H and ^{13}C NMR spectra were recorded ($CDCl_3$ solution with TMS as an internal standard) on a Bruker DRX-



Scheme 3 Carbonylation of aryl bromides and aryl triflates with a range of coumarins. *Reagents and conditions*: **1** (0.6 mmol), **2** (0.5 mmol), catalyst (7.0 mol%), MeCN (3 mL), CO (1 atm), at 80 °C for 16 h in a sealed reaction tube. Isolated yields are given.



Scheme 4 Chemoselectivity on a single substrate. *Reagents and conditions*: **1k** (0.6 mmol), **2a** (0.5 mmol), catalyst (7.0 mol%), MeCN (3 mL), CO (1 atm), at 80 °C for 16 h in a sealed reaction tube. Isolated yields are given.



Scheme 5 Proposed mechanism of Co-catalyzed carbonylation reaction

500 Avance (at 500.1 and 125.8 MHz) or a Bruker DRX-300 Avance III (at 300.1 and 75.4 MHz) instrument. Elemental analyses for C and H were performed using an ECS 4010 CHNSO analyzer. Chromatography columns were prepared from Merck silica gel (230–240 mesh).

3-Aroylcoumarins 3; General Procedure

In an oven-dried Schlenk tube equipped with a stir bar, $CoBr_2$/Bpy (7 mol%, 13.1 mg), and Mn powder (1.5 mmol, 82 mg) were placed in MeCN (1.5 mL). The reaction mixture was activated by a trace of trifluoroacetic acid (0.1 mmol, 7.6 μL). Then, the mixture was stirred for 10 min at r.t. In a vial, aryl halide **1** or aryl triflate **1** (0.6 mmol, 1.2 equiv) and coumarin **2** (0.5 mmol, 1.0 equiv) were dissolved in MeCN (1.5 mL) and added to the Schlenk tube. Next, a balloon filled with CO (1 atm) was connected to the Schlenk tube by the side tube and the system was purged three times. The Schlenk tube was heated at 80 °C for 16 h. When the reaction was completed (detected by TLC), the mixture was cooled to r.t. The reaction was quenched with aq 2 N HCl or NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (anhyd Na_2SO_4) and evaporated in vacuum. The residue was purified by column chromatography (*n*-hexane/EtOAc 6:1) on silica gel to afford the corresponding **3**.

3-Benzoyl-2*H*-chromen-2-one (3a)[12a]

Yield: 0.096 g (77%); white solid; mp 132–134 °C (Lit.[12a] mp 134–136 °C).

IR (KBr): 3054, 1715, 1601, 1491, 1240, 1045, 798 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 7.90 (d, *J* = 7.4 Hz, 2 H), 7.55–7.76 (m, 3 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.28–7.46 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.7, 158.5, 154.8, 145.6, 136.2, 133.9, 133.7, 129.6, 129.3, 128.6, 126.9, 125.0, 118.2, 116.9.

3-(4-Methylbenzoyl)-2*H*-chromen-2-one (3b)[12b]

Yield: 0.104 g (79%); colorless crystals; mp 130–132 °C (Lit.[12b] mp 132–133 °C).

IR (KBr): 3064, 1710, 1662, 1608, 1567, 1240, 1095, 758 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.80 (d, *J* = 7.9 Hz, 2 H), 7.59–7.67 (m, 2 H), 7.27–7.42 (m, 4 H), 2.43 (s, 3 H, CH_3).

^{13}C NMR (75.4 MHz, $CDCl_3$): 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, 116.9, 21.8.

3-(4-Isopropylbenzoyl)-2*H*-chromen-2-one (3c)[12c]

Yield: 0.105 g (72%); white solid; mp 134–136 °C (Lit.[12c] mp 135–136 °C).

IR (KBr): 3068, 3042, 2889, 1721, 1659, 1603, 1549, 1252, 1141, 770 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.04 (s, 1 H), 7.83 (d, *J* = 8.2 Hz, 2 H), 7.63 (t, *J* = 7.9 Hz, 1 H), 7.59 (d, *J* = 7.7 Hz, 1 H), 7.29–7.36 (m, 4 H), 2.97 (sept, *J* = 6.9 Hz, 1 H, CH), 1.27 (d, *J* = 6.9 Hz, 6 H, 2 × CH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.2, 158.6, 155.6, 154.7, 145.0, 134.0, 133.5, 130.0, 129.2, 127.3, 126.8, 125.0, 118.2, 116.9, 34.4, 23.7.

3-(4-Methoxybenzoyl)-2*H*-chromen-2-one (3d)[12d]

Yield: 0.114 g (82%); white solid; mp 171–173 °C (Lit.[12d] mp 174–175 °C).

IR (KBr): 3075, 1714, 1643, 1605, 1587, 1256, 1166, 755 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.89 (d, *J* = 8.8 Hz, 2 H), 7.59–7.67 (m, 2 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H, OCH_3).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.0, 164.3, 158.6, 154.6, 144.7, 133.4, 132.2, 129.1, 128.9, 127.5, 124.9, 118.3, 116.9, 113.9, 55.6.

3-(2-Methoxybenzoyl)-2*H*-chromen-2-one (3e)[12b]

Yield: 0.098 g (70%); white solid; mp 155–156 °C (Lit.[12b] mp 158–159 °C).

IR (KBr): 3032, 2923, 2856, 1737, 1642, 1618, 1563, 1239, 745 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.18 (s, 1 H). 7.78 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.57–7.63 (m, 2 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.32–7.40 (m, 2 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 6.95 (d, *J* = 8.3 Hz, 1 H), 3.75 (s, 3 H, OCH_3).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.8, 158.9, 158.7, 154.7, 143.7, 134.4, 133.2, 130.7, 129.5, 129.4, 127.6, 124.7, 121.1, 118.7, 116.7, 111.4, 55.8.

3-(3,4-Dimethoxybenzoyl)-2*H*-chromen-2-one (3f)[12b]

Yield: 0.117 g (76%); white solid; mp 196–198 °C (Lit.[12b] mp 193–194 °C).

IR (KBr): 3069, 3046, 1701, 1652, 1605, 1580, 1243, 1066, 782 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.66 (td, *J* = 8.7, 1.6 Hz, 1 H), 7.61 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.43 (d, *J* = 8.3 Hz, 1 H), 7.37 (td, *J* = 7.7, 1.0 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 3.98 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 190.1, 158.7, 154.7, 154.2, 149.3, 144.5, 133.4, 129.2, 129.0, 127.6, 125.6, 125.0, 118.3, 116.9, 111.0, 109.9, 56.2, 56.1.

3-(3,4,5-Trimethoxybenzoyl)-2*H*-chromen-2-one (3g)

Yield: 0.127 g (73%); white solid; mp 208–210 °C.

IR (KBr): 3012, 2876, 1692, 1651, 1603, 1512, 1238, 1065, 790 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.08 (s, 1 H), 7.68 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.62 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.38 (td, *J* = 7.7, 0.8 Hz, 1 H), 7.16 (s, 2 H), 3.96 (s, 3 H, OCH_3), 3.89 (s, 6 H, 2 × OCH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 190.5, 158.5, 154.7, 153.1, 145.2, 143.5, 133.7, 131.2, 129.2, 127.2, 125.1, 118.2, 117.0, 107.3, 61.0, 56.4.

Anal. Calcd for $C_{19}H_{16}O_6$: C, 67.06; H, 4.74. Found: C, 67.21; H, 4.69.

3-(4-Fluorobenzoyl)-2*H*-chromen-2-one (3h)[12b]

Yield: 0.091 g (68%); white solid; mp 162–164 °C (Lit.[12b] mp 167–168 °C).

IR (KBr): 3054, 1710, 1658, 1601, 1597, 1240, 1162, 761 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.86 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{F,H}$ = 5.4 Hz, 2 H), 7.67 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.62 (d, *J* = 7.8, 1.5 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.37 (td, *J* = 7.7, 1 Hz, 1 H), 7.11 (t, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 190.2, 166.3 (d, $^1J_{C,F}$ = 288.0 Hz, C), 158.5, 154.8, 145.8, 133.9, 132.3 (d, $^3J_{C,F}$ = 9.6 Hz, 2 × CH), 129.3, 126.8, 125.1, 118.2, 116.9, 115.9 (d, $^2J_{C,F}$ = 22.2 Hz, 2 × CH).

3-(4-Chlorobenzoyl)-2*H*-chromen-2-one (3i)[12b]

Yield: 0.102 g (72%); white solid; mp 205–207 °C (Lit.[12b] mp 205–206 °C).

IR (KBr): 3069, 1715, 1659, 1607, 1571, 1231, 1074, 752 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.83 (dd, *J* = 7.4, 2.5 Hz, 2 H), 7.62–7.70 (m, 2 H), 7.32–7.57 (m, 4 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 190.6, 158.1, 154.8, 146.2, 140.3, 134.6, 133.9, 130.9, 129.4, 128.9, 126.5, 125.1, 118.1, 116.9.

3-Benzoyl-6-methyl-2*H*-chromen-2-one (3j)[12a]

Yield: 0.110 g (84%); white solid; mp 171–172 °C (Lit.[12a] mp 174 °C).

IR (KBr): 3094, 1726, 1659, 1612, 1490, 1250, 1152, 701 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.87–7.89 (m, 2 H), 7.30–7.61 (m, 6 H), 2.43 (s, 3 H, CH_3).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.9, 158.7, 152.9, 145.6, 145.5, 136.3, 134.9, 133.8, 129.6, 128.9, 128.6, 126.7, 117.9, 116.6, 20.8.

3-(4-Fluorobenzoyl)-6-methyl-2*H*-chromen-2-one (3k)[12a]

Yield: 0.112 g (80%); white solid; mp 161–163 °C (Lit.[12a] mp 158–160 °C).

IR (KBr): 3051, 1712, 1647, 1601, 1247, 1154, 775 cm^{-1}.

^1H NMR (300.1 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.38 (s, 1 H), 7.20–7.31 (m, 3 H), 2.44 (s, 6 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 191.4, 158.8, 152.9, 145.2, 144.9, 134.8, 134.7, 133.7, 129.8, 129.3, 128.8, 127.1, 117.9, 116.6, 21.8, 20.8.

3-(4-Methoxybenzoyl)-6-methyl-2*H*-chromen-2-one (3l)[9]

Yield: 0.116 g (79%); white solid; mp 204–206 °C (Lit.[9] mp 206–207 °C).

IR (KBr): 3028, 1724, 1657, 1570, 1532, 1244, 1209, 738 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 6.96 (d, *J* = 8.9 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 1 H), 7.38 (s, 1 H), 7.45 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 2 H), 7.99 (s, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 190.3, 164.3, 158.9, 152.9, 144.9, 134.9, 134.6, 132.3, 129.2, 128.8, 127.4, 118.1, 116.7, 113.9, 55.7, 20.9.

3-Benzoyl-7-methoxy-2*H*-chromen-2-one (3m)[12d]

Yield: 0.103 g (74%); white solid; mp 150–152 °C (Lit.[12d] mp 152–153 °C).

IR (KBr): 3093, 1713, 1654, 1373, 1227, 867, 765 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.09 (s, 1 H), 7.85 (dd, *J* = 8.2, 1.1 Hz, 2 H), 7.60 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.50 (d, *J* = 8.7 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 6.91 (dd, *J* = 8.7, 2.4 Hz, 1 H), 6.86 (d, *J* = 2.3 Hz, 1 H), 3.92 (s, 3 H, OCH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 192.1, 164.7, 158.8, 157.1, 146.6, 136.8, 133.5, 130.6, 129.6, 128.5, 122.8, 113.6, 111.9, 100.7, 56.1.

6-Chloro-3-(4-fluorobenzoyl)-2*H*-chromen-2-one (3n)[12a]

Yield: 0.117 g (83%); white solid; mp 160–162 °C (Lit.[12a] mp 162–164 °C).

IR (KBr): 3073, 1723, 1651, 1239, 1227, 685 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.00 (s, 1 H), 7.88 (dd, *J* = 8.4, 1.3 Hz, 2 H), 7.65 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.58–7.62 (m, 2 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.37 (d, *J* = 9.7 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.2, 157.9, 153.1, 143.9, 135.9, 134.1, 133.5, 130.3, 129.7, 128.8, 128.3, 128.2, 119.2, 118.4.

6-Bromo-3-(4-chlorobenzoyl)-2*H*-chromen-2-one (3o)[12e]

Yield: 0.118 g (72%); white solid; mp 170–172 °C (Lit.[12e] mp 171.2–172.1 °C).

IR (KBr): 3073, 1717, 1658, 1563, 1239, 828 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.87 (dd, *J* = 7.3, 1.2 Hz, 2 H), 7.72–7.74 (m, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.49 (t, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 8.6 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.2, 157.8, 153.5, 143.9, 136.3, 135.9, 134.1, 131.4, 129.7, 128.8, 128.1, 119.7, 118.7, 117.6.

3-(Thiophene-2-carbonyl)-2*H*-chromen-2-one (3p)[12d]

Yield: 0.098 g (77%); white solid; mp 146–148 °C (Lit.[12d] mp 148–150 °C).

IR (KBr): 3091, 1724, 1630, 1609, 1402, 1238, 758 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.1 (s, 1 H), 7.77 (dd, *J* = 4.9, 0.9 Hz, 1 H), 7.72 (dd, *J* = 3.9, 1.0 Hz, 1 H), 7.66 (td, *J* = 8.6, 1.5 Hz, 1 H), 7.62 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.36 (td, *J* = 7.6, 0.8 Hz, 1 H), 7.16 (dd, *J* = 4.8, 4.0 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 183.0, 158.3, 154.6, 144.8, 142.9, 135.9, 135.3, 133.8, 129.3, 128.5, 126.7, 125.1, 118.0, 116.9.

6-Methyl-3-(thiophene-2-carbonyl)-2*H*-chromen-2-one (3q)

Yield: 0.097 g (72%); white solid; mp 140–142 °C.

IR (KBr): 3092, 2990, 2786, 1725, 1631, 1601, 1416, 1250, 726 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.05 (s, 1 H), 7.76 (dd, *J* = 4.9, 1.0 Hz, 1 H), 7.72 (dd, *J* = 3.9, 1.0 Hz, 1 H), 7.45 (dd, *J* = 8.5, 2 Hz, 1 H), 7.39 (s, 1 H), 7.28 (d, *J* = 8.5 Hz, 1 H), 7.16 (dd, *J* = 4.9, 3.9 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 183.2, 158.5, 152.8, 144.9, 142.9, 135.8, 135.3, 134.9, 134.8, 128.9, 128.5, 126.6, 117.8, 116.6, 20.8.

Anal. Calcd for $C_{15}H_{10}O_3S$: C, 66.65; H, 3.72; S, 11.86. Found: C, 66.79, H, 3.61; S, 11.95.

3-(3-Methylbenzoyl)-2*H*-chromen-2-one (3s)[9]

Yield: 0.087 g (66%); white solid; mp 110–112 °C (Lit.[9] mp 111–112 °C).

IR (KBr): 3041, 2930, 2855, 1731, 1650, 1612, 1567, 1242, 757 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.09 (s, 1 H). 7.72 (s, 1 H), 7.68 (td, *J* = 8.6, 1.5 Hz, 2 H), 7.62 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.36–7.46 (m, 4 H), 2.43 (s, 3 H, CH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.9, 158.5, 154.8, 145.3, 138.6, 136.3, 134.8, 133.6, 130.0, 129.2, 128.5, 127.3, 126.9, 125.0, 118.2, 117.0, 21.4.

3-(4-Isopropylbenzoyl)-6-methyl-2*H*-chromen-2-one (3t)

Yield: 0.087 g (57%); white solid; mp 110–112 °C.

IR (KBr): 3060, 1723, 1652, 1599, 1546, 1248, 1141, 773 cm^{-1}.

^1H NMR (500.1 MHz, $CDCl_3$): δ = 8.01 (s, 1 H), 7.84 (d, *J* = 8.3 Hz, 2 H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1 H), 2.45 (s, 3 H), 7.38 (s, 1 H), 7.30–7.35 (m, 3 H), 3.00 (sept, *J* = 6.9 Hz, 1 H, CH), 1.29 (d, *J* = 6.9 Hz, 6 H, 2 × CH_3).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 191.4, 158.8, 155.6, 152.9, 145.1, 134.8, 134.6, 134.0, 130.0, 128.8, 127.2, 126.8, 118.0, 116.7, 34.4, 23.7, 20.8.

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.59; H, 5.81.

3-(4-Chlorobenzoyl)-6-methyl-2*H*-chromen-2-one (3u)[12a]

Yield: 0.092 g (62%); white solid; mp 217–219 °C (Lit.[12a] mp >200 °C].

IR (KBr): 3065, 1711, 1662, 1698, 1512, 1238, 759 cm^{-1}.

^1H NMR (300.1 MHz, DMSO-d_6): δ = 8.38 (s, 1 H), 7.94 (d, *J* = 8.2 Hz, 2 H), 7.45–7.75 (m, 4 H), 7.39 (d, *J* = 8.1 Hz, 1 H), 2.38 (s, 3 H, CH_3).

^{13}C NMR (75.4 MHz, DMSO-d_6): δ = 191.3, 158.7, 152.9, 146.4, 139.2, 135.9, 135.4, 134.7, 131.9, 129.9, 129.3, 126.3, 118.4, 116.6, 20.7.

3-(4-Bromobenzoyl)-2*H*-chromen-2-one (3w)

Yield: 0.123 g (75%); white solid; mp 236–238 °C.

IR (KBr): 3058, 1713, 1670, 1610, 1515, 1232, 766 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.89–7.86 (m, 3 H), 7.77–7.73 (m, 3 H), 7.44–7.46 (d, *J* = 8.8 Hz, 1 H), 7.34–7.36 (t, *J* = 8.8 Hz, 1 H).

HRMS (ESI): *m*/*z* calcd for $C_{16}H_9BrO_3$ [M^+]: 327.9735; found: 327.9746.

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Supporting Information

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