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Synthesis of Isocoumarins from Cyclic 2-Diazo-1,3-diketones and Benzoic Acids via Rh(III)-Catalyzed C−H Activation and Esterification

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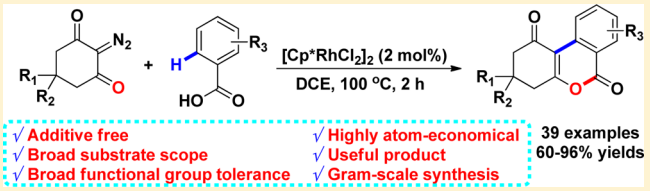
Supporting Information

ABSTRACT: A mild and efficient Rh(III)-catalyzed C−H activation/esterification reaction for the synthesis of isocoumarins has been developed. This procedure uses readily available benzoic acids and cyclic diazo-1,3-diketones as starting materials and involves domino intermolecular C−H activation in combination with intramolecular esterification to give the corresponding isocoumarins in moderate to excellent yields. This process provides a facile approach for the construction of isocoumarins containing various functional groups that does not require any additives.



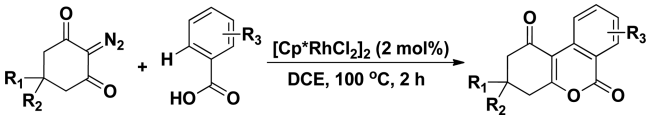
INTRODUCTION

It is well-known that diazo compounds generate metal−carbene species that participate in a variety of transition-metal-catalyzed conversions, including addition,[1] insertion,[2] 1,3-dipolar cycloaddition,[3] rearrangement,[4] cyclization reactions,[5] C−H activation,[6] and other reactions.[7] Rhodium-catalyzed C−H activation/cyclization has emerged as a powerful and promising tool for the construction of diverse heterocyclic systems in organic synthesis.[8] As good partners for C−H activation coupling or cyclization, diazo compounds are easily prepared, stable, and reactive and are therefore widely used in synthetic organic chemistry.[9,10] Cyclic 2-diazo-1,3-diketones are stable diazo compounds that are also polar substrates with high dipole moments. They are easily obtained from the reaction of arylsulfonyl azides and cyclic 1,3-diketones under mild conditions. Recently, several new reactions of cyclic 2-diazo-1,3-diketones, including Wolff rearrangement,[11] 1,3-dipolar cycloadditions,[12] and other reactions,[13] have been developed. To the best of our knowledge, synthesis of isocoumarins via Rh(III)-catalyzed C−H activation/esterification of benzoic acids with cyclic 2-diazo-1,3-diketones has not yet been reported.

Isocoumarins are the key scaffolds in numerous natural products that exhibit a variety of biological activities, such as antifungal, antitumor, antiallergic, antimicrobial, anti-inflammatory, antidiabetic, phytotoxic, and anticancer.[14,15] Because of the interesting biological properties of these natural products, great attention has been focused on the synthesis of isocoumarin derivatives.[16] However, their synthesis frequently requires specific preactivated C−X or C−M reagents as substrates.[17] Oxidative annulations of aryl carboxylic acids and alkynes can be achieved in the presence of Rh,[18] Ru,[19] or Ir[20] catalysts, but these reactions require stoichiometric oxidants and temperatures above 100 °C.

As part of our continuing efforts toward heterocycle construction,[21] we report here a mild procedure for generating various isocoumarins. The process involves Rh(III)-catalyzed C−H activation of benzoic acids and subsequent intermolecular esterification with diazo compounds via C−C/C−O bond formation (Scheme 1).

Scheme 1. Rh(III)-Catalyzed Domino C−H Activation/Esterification for the Synthesis of Isocoumarins



RESULTS AND DISCUSSION

To evaluate the feasibility of our proposed synthetic pathway, 2-diazo-5,5-dimethylcyclohexane-1,3-dione **1a** and benzoic acid **2a** were chosen as model substrates and were initially treated with $[Cp^*RhCl_2]_2$ (2 mol %) in MeCN at reflux for 3 h (Table 1, entry 3). However, only a trace product was detected by TLC. We then carried out the reaction in other solvents, including dimethylformamide (DMF), dichloromethane (DCM), toluene, H_2O, EtOH, and 1,2-dichloroethane (DCE) (Table 1, entries 1, 2, and 4−7). Among these solvents, DCE and toluene were found to be capable of providing the desired product **3aa**, with DCE giving the highest yield (Table 1, entry 7). Subsequent studies on the effect of various transition-metal catalysts showed that $Rh_2(OAc)_4$, $Rh(PPh_3)Cl$, $Ru(PPh_3)Cl_2$, and $[(p\text{-cymene})RuCl_2]_2$ were less efficient than $[Cp^*RhCl_2]_2$ in promoting this reaction (Table 1, entries 9−12). No reaction

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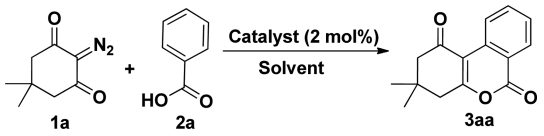
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	temp (°C)	time (h)	yield[b] (%)
1	$[Cp^*RhCl_2]_2$	DMF	100	3	trace
2	$[Cp^*RhCl_2]_2$	DCM	reflux	3	trace
3	$[Cp^*RhCl_2]_2$	MeCN	reflux	3	trace
4	$[Cp^*RhCl_2]_2$	toluene	100	3	75
5	$[Cp^*RhCl_2]_2$	H_2O	100	3	trace
6	$[Cp^*RhCl_2]_2$	EtOH	reflux	3	trace
7	$[Cp^*RhCl_2]_2$	DCE	100	3	88
8	—	DCE	100	3	NR
9	$Rh_2(OAc)_4$	DCE	100	3	trace
10	$Rh(PPh_3)Cl$	DCE	100	3	trace
11	$Ru(PPh_3)Cl_2$	DCE	100	3	trace
12	$[(p\text{-cymene})RuCl_2]_2$	DCE	100	3	trace
13[c]	$[Cp^*RhCl_2]_2$	DCE	100	3	60
14[d]	$[Cp^*RhCl_2]_2$	DCE	100	3	75
15[e]	$[Cp^*RhCl_2]_2$	DCE	100	3	88
16	$[Cp^*RhCl_2]_2$	DCE	rt	3	trace
17	$[Cp^*RhCl_2]_2$	DCE	20	3	trace
18	$[Cp^*RhCl_2]_2$	DCE	40	3	trace
19	$[Cp^*RhCl_2]_2$	DCE	60	3	40
20	$[Cp^*RhCl_2]_2$	DCE	80	3	60
21	$[Cp^*RhCl_2]_2$	DCE	120	3	88
22	$[Cp^*RhCl_2]_2$	DCE	100	0.5	65
23	$[Cp^*RhCl_2]_2$	DCE	100	1	78
24	$[Cp^*RhCl_2]_2$	DCE	100	2	88
25	$[Cp^*RhCl_2]_2$	DCE	100	5	88

[a]Reaction conditions: 2-diazo-5,5-dimethylcyclohexane-1,3-dione **1a** (0.5 mmol), benzoic acid **2a** (0.5 mmol), solvent (2 mL), catalyst (2 mol %), 100 °C, 2 h. [b]Isolated yield. [c]1 mol % of catalyst was used. [d]1.5 mol % of catalyst was used. [e]5 mol % of catalyst was used.

occurred in the absence of catalyst (Table 1, entry 8). We later found that reducing the loading of $[Cp^*RhCl_2]_2$ led to a decrease in the product yield (Table 1, entries 13 and 14), although increasing the amount of $[Cp^*RhCl_2]_2$ did not give further enhancement of the yield (Table 1, entry 15). In addition, the effects of temperature and reaction time were also investigated (Table 1, entries 16–25). It was found that the highest yield was obtained from a reaction time of 2 h (Table 1, entry 24), and neither decreasing nor increasing the reaction temperature or time improved the yield. To summarize the optimization study, isocoumarin **3aa** was obtained in 88% yield through treatment of **1a** and **2a** with $[Cp^*RhCl_2]_2$ (2 mol %) in DCE at 100 °C for 2 h (Table 1, entry 24).

Using the optimal reaction conditions, we then explored the substrate scope with various cyclic 2-diazo-1,3-diketones (**1a–d**) and benzoic acids (**2a–p,s,t**). The results of these studies are summarized in Table 2. The results indicated that benzoic acids bearing a variety of substituents on the phenyl ring reacted effectively to give **3aa–at** in reasonable to excellent yields. Functional groups such as chloro, bromo, methyl, methoxyl, hydroxyl, nitro, *tert*-butyl, trifluoromethyl, cyano, and acetyl on the phenyl ring of the benzoic acid were tolerated well, and the electronic and steric nature of the substituents did not show obvious effects on the yield of **3**. In contrast to benzoic acids, when aromatic acids such as picolinic acid, thiophene-2-carboxylic acid, and furan-3-carboxylic acid were used for this reaction, no desired product was obtained. Different cyclic 2-diazo-1,3-diketones were then examined. Both alkyl (e.g., CH_3) and aryl (e.g., phenyl) R_1 groups were well tolerated under the reaction conditions, leading to the final products in satisfactory yields.

Furthermore, we carried out a gram-scale reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**1a**, 5 mmol) and 4-bromobenzoic acid (**2j**, 5 mmol) under the standard conditions, and the product **3aj** was isolated in 84% (1.35 g) yield (Scheme 2), which showed promise for this synthetic method as a useful tool in practical synthetic contexts.

Interestingly, when sterically hindered substrates, such as 2-diazo-4,4-dimethylcyclohexane-1,3-dione (**1e**), were used for this reaction (Scheme 3), two desired products **3ee** and **3ee′** were obtained in 44% and 43% yield, respectively.

Subsequently, substrate 3-diazopentane-2,4-dione **1f** was prepared and then subjected to the optimized reaction conditions (Scheme 4). Only three of the benzoic acid substrates reacted to give the desired products **3fh**, **3fj**, and **3fq** in 60%, 65%, and 63% yield, respectively. Interestingly, all of the reactions required a reaction time of 5 h, indicating that the activation of 3-diazopentane-2,4-dione is slower than cyclic 2-diazo-1,3-diketones. To further demonstrate the versatility of the present method, other noncyclic diazo components, such as ethyl 2-diazoacetate and ethyl 2-diazo-3-oxobutanoate, were also used as substrates under standard reaction conditions, but no desired product was obtained.

We next explored the scope and limitations of aromatic acid substrates with this method (Scheme 5). Although the reaction proceeded smoothly when 2-naphthoic acid was used as the substrate to give the desired products **3ar–dr** in 85–88% yield, an additive such as cesium acetate (CsOAc) was found to be necessary, illustrating that the poorer reactivity of C–H bond on the naphthalene ring and a higher activity catalyst $[Cp^*Rh(OAc)_2]_2$ should be first formed via ligand exchange with CsOAc and $[Cp^*RhCl_2]_2$.

In addition, all of the products were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy and HRMS analysis, and the structures of novel isocoumarin products **3ah**, **3fj**, and **3ar** were also unambiguously confirmed by X-ray crystallographic analysis (see the SI).

On the basis of the experimental results obtained above and those described in previous reports, a plausible mechanism was proposed (Scheme 6). First, benzoic acid **2** reacts with the catalyst $[Cp^*RhCl_2]_2$ through directed C–H cleavage to form the intermediate **A**, which is followed by generation of the intermediate Rh(III)–carbene **B**. Subsequent migratory insertion of the carbene into the Rh–C bond yields the six-membered rhodacycle intermediate **C**, which can be protonated by HCl to generate the intermediate **D** and release the Rh(III) catalyst, which starts a new catalytic cycle. Finally, tautomerization of intermediate **D** generates the enol intermediate **E** in situ, which then undergoes lactonization via elimination of water to give the final product **3**.

CONCLUSION

In summary, a novel and efficient route for the synthesis of isocoumarins via Rh(III)-catalyzed C–H activation/esterification of benzoic acids with cyclic 2-diazo-1,3-diketones under mild conditions has been developed. The described protocol is superior to previous methods due to several advantageous features, including (i) readily available starting materials, (ii) a

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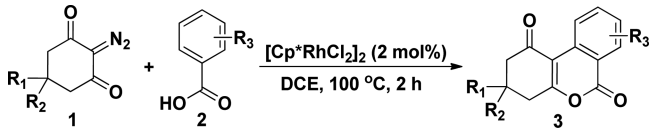
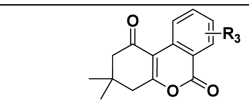
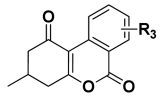
Table 2. Rh(III)-Catalyzed C−H Activation/Esterification of Cyclic 2-Diazo-1,3-diketones and Benzoic Acids[a]

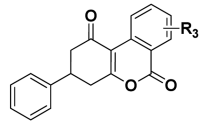




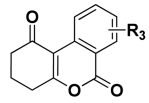
3aa: R_3 = H, 88%
3ab: R_3 = 2-CH_3, 83%
3ac: R_3 = 3-CH_3, 82%
3ad: R_3 = 4-CH_3, 84%
3ae: R_3 = 4-OCH_3, 85%
3af: R_3 = 3-NO_2, 80%
3ag: R_3 = 2-OH, 90%
3ah: R_3 = 2-Br, 93%
3ai: R_3 = 3-Br, 92%
3aj: R_3 = 4-Br, 96%
3ak: R_3 = 4-CF_3, 95%
3al: R_3 = 4-^{t}Bu, 85%
3as: R_3 = 4-CH_3CO, 88%
3at: R_3 = 4-CN, 85%



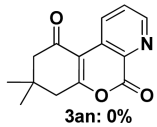
3ba: R_3 = H, 86%
3bd: R_3 = 4-CH_3, 84%
3be: R_3 = 4-OCH_3, 85%
3bh: R_3 = 2-Br, 84%
3bi: R_3 = 3-Br, 89%
3bj: R_3 = 4-Br, 88%
3bk: R_3 = 4-CF_3, 90%



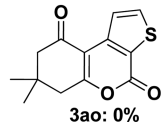
3ca: R_3 = H, 87%
3cb: R_3 = 2-CH_3, 85%
3cd: R_3 = 4-CH_3, 84%
3ce: R_3 = 4-OCH_3, 83%
3ci: R_3 = 3-Br, 86%
3cj: R_3 = 4-Br, 88%
3ck: R_3 = 4-CF_3, 92%
3cl: R_3 = 4-^{t}Bu, 86%



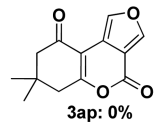
3da: R_3 = H, 87%
3dd: R_3 = 4-CH_3, 85%
3dj: R_3 = 4-Br, 90%
3dk: R_3 = 4-CF_3, 92%
3dm:R_3 = 2-Cl, 89%



3an: 0%



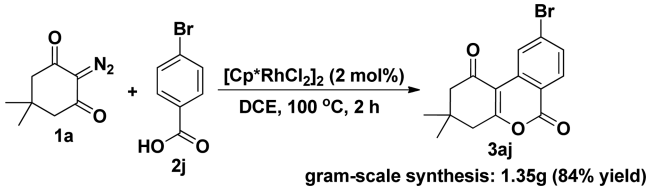
3ao: 0%



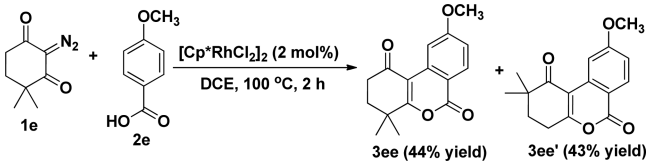
3ap: 0%

[a]Reaction conditions: cyclic 2-diazo-1,3-diketones **1** (0.5 mmol), benzoic acids **2** (0.5 mmol), DCE (2 mL), $[Cp^*RhCl_2]_2$ (2 mol %), 100 °C, 2 h.

Scheme 2. Gram-Scale Synthesis of This Method



Scheme 3. Rh(III)-Catalyzed C−H Activation/Esterification of 2-Diazo-4,4-dimethylcyclohexane-1,3-dione and 4-Methoxybenzoic Acid



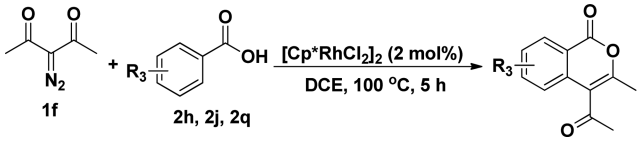
broad substrate scope with moderate to excellent yields, (iii) scalability to the gram level, and (vi) an additive-free workup process. This procedure involves domino C−H activation, cyclization, and esterification steps and releases H_2O and N_2 as byproducts. The C−H bond activation step and high atom economy are the most attractive parts of this reaction. We believe that the results will inspire the use of C−H activation to construct heterocycles in a variety of future applications.

EXPERIMENTAL SECTION

General Comments. Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. Flash chromatography was performed using 200−300 mesh silica gel with the indicated solvent system according to standard techniques. The ^1H and ^{13}C NMR data were recorded on 300 and 500 MHz NMR spectrometers unless otherwise specified. Chemical shifts (δ) in parts per million are reported relative to the residual signals of chloroform (7.26 ppm for ^1H and 77.16 ppm for ^{13}C), and all ^{13}C NMR were recorded with proton broadband decoupling and indicated as $^{13}C\{^1H\}$NMR. Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet), and the coupling constants (J) are reported in hertz. HRMS analysis with a quadrupole time-of-flight mass spectrometer yielded ion mass/charge (m/z) ratios in atomic mass units. IR spectra were measured as dry films (KBr), and the peaks are reported in terms of wavenumber (cm^{-1}).

General Procedure for the Synthesis of Isocoumarin Derivatives 3. A mixture of cyclic 2-diazo-1,3-diketones **1** (0.5 mmol), benzoic acids **2** (0.5 mmol), and $[Cp^*RhCl_2]_2$ (0.001 mmol) in DCE (2 mL) was heated in an oil bath at 100 °C for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with water. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated in vacuum. The residue was purified by flash column chromatography on silica gel (200−300 mesh) with ethyl acetate and petroleum ether (1:6−1:8, v/v) as the elution solvent to give the desired products **3**.

Scheme 4. Rh(III)-Catalyzed C−H Activation/Esterification of 3-Diazopentane-2,4-dione and Benzoic Acids



3fh: R_3 = 2-Br, 60%
3fj: R_3 = 4-Br, 65%
3fq: R_3 = 4-Cl, 63%

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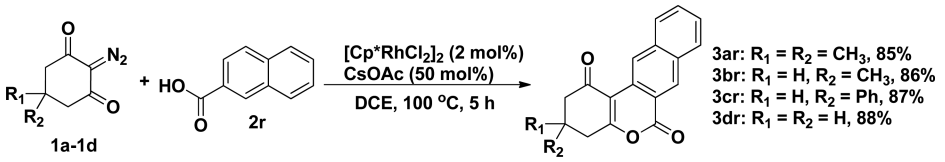
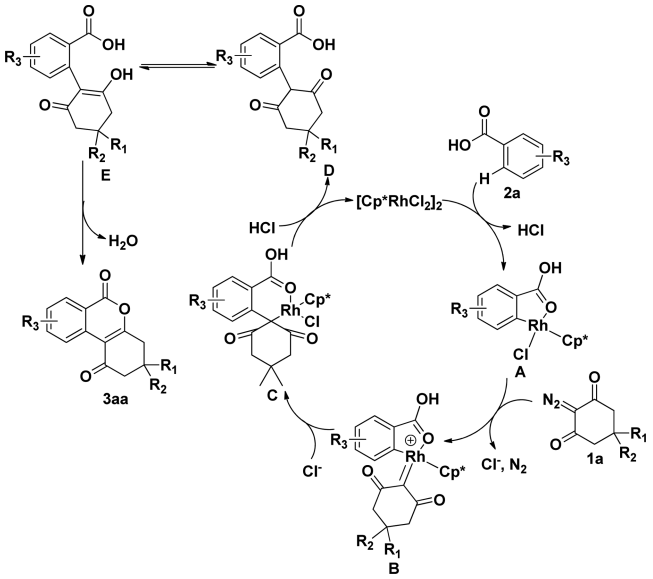
Scheme 5. Rh(III)-Catalyzed C−H Activation/Esterification of Cyclic 2-Diazo-1,3-diketones and 2-Naphthoic Acid



Scheme 6. Proposed Mechanism for Rh(III)-Catalyzed C−H Activation/Esterification of Cyclic 2-Diazo-1,3-diketones and Benzoic Acids



*3,3-Dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3aa**):* petroleum ether/ethyl acetate 6:1; white solid; yield 88% (107 mg, 0.44 mmol); mp 125−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.06 (d, J = 6.0 Hz, 1H), 8.30 (d, J = 6.0 Hz, 1H), 7.80 (t, J = 9.0 Hz, 1H), 7.54 (t, J = 9.0 Hz, 1H), 2.81 (s, 2H), 2.53 (s, 2H), 1.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 168.4, 161.1, 136.0, 134.3, 126.2, 120.2, 111.0, 53.2, 42.9, 32.3, 28.5; IR (KBr) ν 3111, 2952, 1738, 1661, 1614, 1559, 1484, 1364, 1248, 1198, 1148, 1037, 778, 696, 530 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{14}O_3 + H]^+$ 243.1016, found 243.1022.

*3,3,7-Trimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ab**):* petroleum ether/ethyl acetate 6:1; white solid; yield 83% (106 mg, 0.42 mmol); mp 109−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (d, J = 9.0 Hz,1H), 7.67 (t, J = 9.0 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 2.81 (s, 3H), 2.77 (s, 2H), 2.52 (s, 2H), 1.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 167.9, 159.9, 143.5, 135.4, 134.9, 131.5, 127.5, 123.7, 110.7, 53.2, 42.6, 31.9, 28.2, 23.8; IR (KBr) ν 3097, 2957, 2870, 1984, 1743, 1670, 1618, 1584, 1566, 1468, 1402, 1327, 1059, 1007, 801, 694, 651, 542, 460 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}O_3 + H]^+$ 257.1172, found 257.1177.

*3,3,8-Trimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ac**):* petroleum ether/ethyl acetate 6:1; white solid; yield 82% (105 mg, 0.41 mmol); mp 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (d, J = 9.0 Hz, 1H), 8.09 (s, 1H), 7.62 (d, J = 6.0 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 2.46 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 167.2, 138.7, 136.9, 129.4, 125.8, 119.8, 110.4, 52.9, 42.5, 32.0, 28.2, 21.2; IR (KBr) ν 3133, 2952, 1965, 1725, 1673, 1616, 1495, 1464, 1402, 1366, 1323, 1246, 1153, 1057, 1035, 876, 782, 542 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}O_3 + H]^+$ 257.1172, found 257.1177.

*3,3,9-Trimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ad**):* petroleum ether/ethyl acetate 6:1; white solid; yield 84% (96 mg, 0.42 mmol); mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 2.51 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 168.1, 160.7, 147.0, 133.8, 129.5, 125.8, 117.2, 110.5, 52.9, 42.5, 31.9, 28.1, 22.4; IR (KBr) ν 3138, 1745, 1666, 1614, 1486, 1402, 1309, 1184, 1048, 987, 898, 456 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{12}O_3 + H]^+$ 229.0859, found 229.0855.

*9-Methoxy-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ae**):* Petroleum ether/ethyl acetate 6:1; white solid; yield 85% (116 mg, 0.43 mmol); mp 109−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.07 (d, J = 9.0 Hz, 1H), 3.95 (s, 3H), 2.790 (s, 2H), 2.52 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.2, 169.0, 165.5, 160.4, 136.3, 131.7, 117.1, 112.6, 110.3, 108.0, 55.7, 52.9, 42.7, 31.9, 28.1; IR (KBr) ν 3138, 2303, 1752, 1670, 1618, 1598, 1570, 1489, 1402, 1325, 1239, 1159, 1100, 1032, 989, 876, 767, 694, 654, 540 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}O_4 + H]^+$ 273.1121, found 273.1120.

*3,3-Dimethyl-8-nitro-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3af**):* Petroleum ether/ethyl acetate 6:1; white solid; yield 80% (115 mg, 0.40 mmol); mp 155−156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.47 (d, J = 6.0 Hz, 1H), 8.32 (d, J = 9.0 Hz, 1H), 2.85 (s, 2H), 2.58 (s, 2H), 1.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 169.4, 158.8, 151.9, 134.9, 131.0, 123.6, 122.2, 121.2, 109.5, 52.2, 42.2, 31.8, 27.9; IR (KBr) ν 3116, 1754, 1657, 1623, 1512, 1404, 1235, 1136, 1024, 896, 814, 756, 694 cm^{-1}; HRMS (ESI) calcd for$[C_{15}H_{13}NO_5 + H]^+$ 288.0866, found 288.0869.

*7-Hydroxy-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ag**):* petroleum ether/ethyl acetate 6:1; white solid; yield 90% (117 mg, 0.45 mmol); mp 122−123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.51 (d, J = 9.0 Hz, 1H), 7.70 (t, J = 9.0 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 2.80 (s, 2H), 2.52 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5, 166.9, 164.8, 161.8, 138.6, 133.8, 116.5, 116.0, 111.4, 105.4, 52.9, 42.3, 31.9, 28.1; IR (KBr) ν 3114, 2372, 1726, 1671, 1626, 1596, 1555, 1398, 1317, 1235, 1164, 1135, 917, 813, 777, 537 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{14}O_4 + H]^+$ 259.0965, found 259.0970.

*7-Bromo-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ah**):* petroleum ether/ethyl acetate 6:1; white solid; yield 93% (149 mg, 0.47 mmol); mp 128−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (d, J = 6.0 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.55 (t, J = 9.0 Hz 1H), 2.80 (s, 2H), 2.53 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 168.5, 157.2, 136.8, 135.3, 125.1, 124.6, 118.1, 110.0, 53.0, 42.4, 31.8, 28.1; IR (KBr) ν 3154, 2362, 1746, 1661, 1616, 1586, 1545, 1398, 1134, 1194, 1055, 927, 803, 786, 688, 541 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{13}BrO_3 + H]^+$ 321.0121, found 321.0123.

*8-Bromo-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ai**):* petroleum ether/ethyl acetate 6:1; white solid; yield 92% (148 mg, 0.46 mmol); mp 128−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (d, J = 9.0 Hz, 1H), 8.41 (s, 1H), 7.90 (d, J = 9.0 Hz, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 168.4, 159.6, 138.8, 132.8, 127.9, 122.4, 121.6, 110.4, 52.9, 42.7, 32.1, 28.3; IR (KBr) ν 3104, 2352, 1730, 1651, 1606, 1570, 1505, 1389, 1317, 1224, 1194, 1135, 907, 842, 776, 532 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{13}BrO_3 + H]^+$ 321.0121, found 321.0123.

*9-Bromo-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3aj**):* petroleum ether/ethyl acetate 6:1; white solid; yield 96% (154 mg, 0.48 mmol); mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.13 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 2.81 (s, 2H), 2.53 (s, 2H), 1.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 169.1, 160.2, 135.1, 131.9, 131.8, 131.0, 128.8, 118.4, 109.7, 52.7, 42.6, 32.0, 28.2; IR (KBr) ν 3109, 2355, 1731, 1641, 1609, 1568, 1505, 1389, 1317,1194, 1155, 917, 843, 777, 556 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{13}BrO_3 + H]^+$ 321.0121, found 321.0123.

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*3,3-Dimethyl-9-(trifluoromethyl)-3,4-dihydro-1H-benzo[c]-chromene-1,6(2H)-dione (**3ak**):* petroleum ether/ethyl acetate 6:1; white solid; yield 95% (147 mg, 0.48 mmol); mp 130−131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 2.83 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 168.9, 159.4, 136.5, 134.2, 130.2, 124.6 (d, J_{C-F} = 175.0 Hz), 122.0, 109.7, 52.4, 42.3, 31.8, 27.9; IR (KBr) ν 3429, 3121, 2380, 1725, 1683, 1624, 1481, 1371, 1283, 1282, 1041, 802, 777, 684, 629, 513 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_{13}F_3O_3 + H]^+$ 311.0890, found 311.0893.

*9(tert-Butyl-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3al**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (127 mg, 0.43 mmol); mp 115−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.23 (d, J = 6.0 Hz, 1H), 7.60 (d, J = 6.0 Hz,1H), 2.80 (s, 2H), 2.53 (s, 2H), 1.40 (s, 9H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 168.1, 160.8, 159.9, 133.8, 129.4, 122.5, 117.2, 110.8, 53.3, 42.6, 35.8, 32.0, 31.1, 28.2; IR (KBr) ν 3121, 2962, 1748, 1658, 1613, 1561, 1482, 1369, 1250, 1193, 1158, 1057, 778, 676, 551 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_3 + H]^+$ 299.1642, found 299.1645.

*9-Acetyl-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3as**):* petroleum ether/ethyl acetate 6:1; white solid; yield 88% (124 mg, 0.44 mmol); mp 120−121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.36 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 2.84 (s, 2H), 2.74 (s, 3H), 2.56 (s, 2H), 1.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 196.4, 168.4, 159.5, 141.9, 134.0, 129.6, 126.6, 126.3, 122.2, 109.8, 52.4, 42.2, 31.6, 27.7, 26.6; IR (KBr) ν 3137, 2313, 1753, 1672, 1628, 1599, 1587, 1499, 1412, 1325, 1229, 1169, 1110, 1032, 989, 875, 767, 654, 541 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{16}O_4 + H]^+$ 285.1082, found 285.1080.

*3,3-Dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1H-benzo[c]-chromene-9-carbonitrile (**3at**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (113 mg, 0.43 mmol); mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.37 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H),, 2.84 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 169.9, 159.5, 150.3, 134.7, 131.1, 130.7, 122.9, 119.4, 118.0, 109.7, 52.9, 42.9, 32.3, 28.4; IR (KBr) ν 3337, 2363, 1750, 1670, 1638, 1589, 1587, 1499, 1422, 1326, 1227, 1165, 1111, 1031, 982, 872, 762, 674, 548 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}NO_3 + H]^+$ 268.0929, found 268.0925.

*3-Methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ba**):* petroleum ether/ethyl acetate 6:1; white solid; yield 86% (98 mg, 0.43 mmol); mp 125−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, J = 9.0 Hz, 1H), 8.29 (d, J = 6.0 Hz, 1H), 7.79 (t, J = 9.0 Hz, 1H), 7.53 (t, J = 9.0 Hz, 1H), 2.92−2.99 (m,1H), 2.62−2.740 (m, 2H), 2.33−2.47 (m, 2H), 1.20 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 169.1, 160.8, 135.9, 134.2, 128.6, 126.2, 120.0, 111.4, 47.4, 37.1, 27.9, 21.0; IR (KBr) ν 3124, 2367, 1757, 1673, 1607, 1489, 1391, 987, 854, 656, 532 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{12}O_3 + H]^+$ 229.0859, found 229.0855.

*3,9-Dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3bd**):* petroleum ether/ethyl acetate 6:1; white solid; yield 84% (102 mg, 0.42 mmol); mp 120−121 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.87 (s, 1H), 8.18 (d, J = 6.0 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 2.90−2.98 (m, 1H), 2.61−2.74 (m, 2H), 2.51 (s, 3H), 2.32−2.45 (m, 2H), 1.20 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.9, 168.8, 160.4, 146.8, 133.7, 129.4, 125.8, 117.1, 110.9, 47.0, 36.7, 27.5, 22.3, 20.0; IR (KBr) ν 3720, 2362, 1763, 1657, 1609, 1402, 1257, 1023, 803, 776, 689, 664, 537 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{14}O_3 + H]^+$ 243.1016, found 243.1011.

*9-Methoxy-3-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3be**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (127 mg, 0.43 mmol); mp 132−133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.60 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 6.0 Hz, 1H), 3.95 (s, 3H), 2.91−2.97 (m, 1H), 2.61−2.73 (m, 2H), 2.32−2.41 (m, 2H), 1.18 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.0, 169.7, 165.3, 160.1, 136.2, 131.5, 116.8, 112.4, 110.7, 107.9, 55.6, 47.0, 36.8, 27.5, 20.7; IR (KBr) ν 3133, 2349, 1738, 1673, 1554, 1398, 1305, 1178, 1087, 1037, 989, 912, 860, 782, 685, 530 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{14}O_4 + H]^+$ 259.0965, found 259.0971.

*7-Bromo-3-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3bh**):* petroleum ether/ethyl acetate 6:1; white solid; yield 84% (129 mg, 0.42 mmol); mp 132−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.46 (t, J = 9.0 Hz, 1H), 2.83−2.89 (m, 1H), 2.53−2.67 (m, 2H), 2.25−2.34 (m, 2H), 1.12 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 169.3, 156.9, 136.8, 135.1, 125.1, 124.4, 118.0, 110.4, 47.1, 36.6, 27.3, 20.5; IR (KBr) ν 3850, 3740, 1748, 1643, 1308, 1205, 1118, 1047, 998, 783, 655, 543 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{11}BrO_3 + H]^+$ 306.9964, found 306.9959.

*8-Bromo-3-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3bi**):* petroleum ether/ethyl acetate 6:1; white solid; yield 89% (136 mg, 0.45 mmol); mp 132−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (d, J = 9.0 Hz, 1H), 8.42 (s, 1H), 7.91 (d, J = 9.0 Hz, 1H), 2.93−2.99 (m, 1H), 2.62−2.76 (m, 2H), 2.34−2.43 (m, 2H), 1.22 (d, J = 6.0 Hz, 3H); ^{13}C NMR ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 169.0, 139.5, 138.5, 131.8, 127.6, 125.1, 122.1, 121.3, 46.8, 36.6, 27.4, 20.6; IR (KBr) ν 3849, 3738, 1748, 1643, 1358, 1305, 1212, 1178, 1057, 990, 780, 686, 541 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{11}BrO_3 + H]^+$ 306.9964, found 306.9959.

*9-Bromo-3-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3bj**):* petroleum ether/ethyl acetate 6:1, light yellow solid; yield 88% (135 mg, 0.44 mmol); mp 140−141 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.28 (s, 1H), 8.12 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 2.91−2.97 (m, 1H), 2.62−2.74 (m, 2H), 2.32−2.41 (m, 2H), 1.20 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 170.0, 160.0, 135.2, 131.9, 131.7, 131.0, 128.9, 118.5, 110.0, 47.0, 36.9, 27.6, 20.8; IR (KBr) ν 3859, 3748, 1738, 1673, 1398, 1305, 1178, 1047, 782, 685, 540 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{11}BrO_3 + H]^+$ 306.9964, found 306.9959.

*3-Methyl-9-(trifluoromethyl)-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3bk**):* petroleum ether/ethyl acetate 6:1; white solid; yield 90% (133 mg, 0.45 mmol); mp 132−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.41 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 2.94−3.01 (m, 1H), 2.65−2.77 (m, 2H), 2.35−2.43 (m, 2H), 1.22 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 170.3, 159.7, 137.0, 134.8, 130.7, 125.1 (d, J_{C-F} = 1.2 Hz), 123.8 (d, J_{C-F} = 1.8 Hz), 122.6, 110.8, 47.2, 37.1, 27.9, 21.0; IR (KBr) ν 3850, 3651, 1748, 1657, 1397, 1145, 1026, 866, 794, 543 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{11}F_3O_3 + H]^+$ 297.0733, found 297.0730.

*3-Phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ca**):* petroleum ether/ethyl acetate 6:1; white solid; yield 87% (126 mg, 0.44 mmol); mp 105−106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.12 (d, J = 6.0 Hz, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.28−7.40 (m, 6H), 3.52−3.60 (m, 1H), 3.16−3.19 (m, 2H), 2.90−2.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.8, 169.9, 160.0, 141.4, 135.3, 132.3, 131.3, 129.3, 129.2, 127.8, 126.8, 118.7, 45.9, 38.1, 36.6; IR (KBr) ν 3129, 3016, 1743, 1725, 1663, 1609, 1480, 1400, 1357, 1302, 1243, 1191, 1014, 769, 701, 558 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{14}O_3 + H]^+$ 291.1016, found 291.1015.

*7-Methyl-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3cb**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (129 mg, 0.43 mmol); mp 108−109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (d, J = 6.0 Hz, 1H), 7.66 (t, J = 9.0 Hz, 1H), 7.30−7.43 (m, 6H), 3.51−3.62 (m, 1H), 3.13 (d, J = 9.0 Hz, 2H), 2.88−2.94 (m, 2H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 168.4, 159.3, 143.3, 141.3, 135.1, 134.8, 131.5, 128.9, 127.3, 126.4, 123.6, 118.1, 111.2, 45.9, 37.7, 36.1, 23.6; IR (KBr) ν 3824, 1738, 1675, 1614, 1482, 1393, 1316, 1243, 1187, 1007, 764, 694 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{16}O_3 + H]^+$ 305.1172, found 305.1167.

*9-Methyl-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3cd**):* petroleum ether/ethyl acetate 6:1; light yellow solid; yield 84% (128 mg, 0.42 mmol); mp 168−169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 7.29−7.39 (m, 6H), 3.50−3.56 (m, 1H), 3.16 (d, J = 9.0 Hz, 2H), 2.88−2.96 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 168.8, 160.5, 147.2, 141.5, 133.8, 129.9, 129.7, 129.1, 127.5, 126.6, 126.0, 117.4, 111.3, 46.0, 38.0, 36.4, 22.6; IR (KBr) ν 3859, 1739, 1651, 1563, 1377, 1027, 784, 694 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{16}O_3 + H]^+$ 305.1172, found 305.1167.

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*9-Methoxy-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ce**):* petroleum ether/ethyl acetate 6:1; white solid; yield 83% (107 mg, 0.42 mmol); mp 132−133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63 (s, 1H), 8.21 (d, J = 9.0 Hz, 1H), 7.26−7.40 (m, 5H), 7.09 (d, J = 9.0 Hz, 1H), 3.96 (s, 3H), 3.51−3.62 (m, 1H), 3.15−3.18 (m, 2H), 2.89−2.97 (m, 2H), 2.39−2.34 (m, 2H), 1.18 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.1, 169.4, 165.4, 159.9, 141.2, 136.0, 128.9, 127.3, 126.4, 117.0, 112.5, 110.9, 108.0, 55.6, 45.8, 37.8, 36.3; IR (KBr) ν 3133, 2349, 1738, 1673, 1554, 1398, 1305, 1178, 1087, 1037, 989, 912, 860, 782, 685, 530 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{14}O_4 + H]^+$ 259.0965, found 259.0971.

*8-Bromo-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ci**):* petroleum ether/ethyl acetate 6:1; white solid; yield 86% (158 mg, 0.43 mmol); mp 175−176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (d, J = 9.0 Hz, 1H), 8.44 (s, 1H), 7.92 (d, J = 6.0 Hz, 1H), 7.31−7.40 (m, 5H), 3.51−3.63 (m, 1H), 3.18 (d, J = 9.0 Hz, 2H), 2.88−2.95 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 170.0, 160.2, 141.5, 135.4, 132.5, 132.3, 131.5, 129.4, 128.0, 126.9, 118.9, 110.8, 46.1, 38.2, 36.8; IR (KBr) ν 3705, 3627, 1757, 1673, 1624, 1519, 1505, 1467, 1316, 1277, 1080, 891, 801, 705. cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{13}BrO_3 + H]^+$ 369.0121, found 369.0115.

*9-Bromo-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3cj**):* petroleum ether/ethyl acetate 6:1; white solid; yield 88% (162 mg, 0.44 mmol); mp 189−190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.14 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 6.0 Hz, 1H), 7.28−7.42 (m, 5H), 3.52−3.62 (m, 1H), 3.19 (d, J = 9.0 Hz, 2H), 2.84−3.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 169.7, 159.8, 141.2, 135.1, 132.1, 131.9, 131.1, 129.1, 129.0, 127.7, 126.6, 118.6, 110.4, 45.8, 37.9, 36.5; IR (KBr) ν 3850, 3637, 1757, 1653, 1454, 1396, 1187, 1018, 708 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{13}BrO_3 + H]^+$ 369.0121, found 369.0115.

*3-Phenyl-9-(trifluoromethyl)-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ck**):* petroleum ether/ethyl acetate 6:1; white solid; yield 92% (165 mg, 0.46 mmol); mp 189−190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.41 (d, J = 6.0 Hz, 1H), 7.78 (d, J = 6.0 Hz, 1H), 7.31−7.40 (m, 5H), 3.55−363 (m, 1H), 3.21 (d, J = 6.0 Hz, 2H), 2.87−3.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 169.7, 159.3, 141.1, 137.2, 134.3, 130.5, 129.1, 127.7, 126.6, 125.0 (d, J_{C-F} = 3.8 Hz), 123.5 (d, J_{C-F} = 3.8 Hz), 122.3, 121.5, 110.7, 45.7, 37.9, 36.4; IR (KBr) ν 3856, 37297, 1740, 1643, 1424, 1392, 1197, 1040, 913 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{13}F_3O_3 + H]^+$ 359.0890, found 359.0896.

*9-tert-Butyl-3-phenyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3cl**):* petroleum ether/ethyl acetate 6:1; white solid; yield 86% (148 mg, 0.43 mmol); mp 125−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.25 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.29−7.42 (m, 5H), 3.51−3.62 (s, 1H), 3.18 (d, J = 6.0 Hz, 2H), 2.90−2.98 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 168.5, 159.8, 141.3, 133.6, 129.5, 129.1, 127.3, 126.6, 126.3, 122.5, 117.1, 109.2, 45.9, 37.9, 36.2, 35.6, 30.9; IR (KBr) ν 3843, 2349, 1738, 1673, 1554, 1388, 1315, 1178, 1089, 1040, 988, 910, 860, 782, 685, 510 cm^{-1}; HRMS (ESI) calcd for $[C_{23}H_{22}O_3 + H]^+$ 347.1642, found 347.1642.

*3,4-Dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3da**):* petroleum ether/ethyl acetate 6:1; white solid; yield 87% (93 mg, 0.44 mmol); mp 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.06 (d, J = 9.0 Hz, 1H), 8.29 (d, J = 9.0 Hz, 1H), 7.79 (t, J = 9.0 Hz, 1H), 7.53 (t, J = 9.0 Hz, 1H), 2.94 (t, J = 6.0 Hz, 2H), 2.66 (t, J = 6.0 Hz, 2H), 2.13−2.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 169.3, 160.3, 135.4, 133.8, 129.4, 128.2, 125.9, 119.7, 111.4, 38.7, 28.8, 19.8; IR (KBr) ν 3129, 2325, 1738, 1663, 1609, 1477, 1398, 1307, 1180, 1144, 1062, 1019, 994, 782, 683, 540 cm^{-1}; HRMS (ESI) calcd for $[C_{13}H_{10}O_3 + H]^+$ 215.0703, found 215.0709.

*9-Methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3dd**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (97 mg, 0.43 mmol); mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s,1H), 8.19 (d, J = 9.0 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 2.93 (t, J = 6.0 Hz, 2H), 2.66 (t, J = 6.0 Hz, 2H), 2.52 (s, 3H), 2.13−2.21 (m,, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 169.6, 160.6, 147.0, 134.03, 129.7, 129.6, 126.1, 117.4, 111.6, 39.0, 29.0, 22.5, 20.0; IR (KBr) ν 3138, 1745, 1666, 1614, 1486, 1402, 1309, 1184, 1048, 987, 898, 773, 456 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_{12}O_3 + H]^+$ 229.0859, found 229.0855.

*9-Bromo-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3dj**):* petroleum ether/ethyl acetate 6:1; white solid; yield 90% (131 mg, 0.45 mmol); mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.13 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 2.95 (t, J = 6.0 Hz, 2H), 2.64 (t, J = 6.0 Hz, 2H), 2.16−2.22 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 170.4, 142.4, 136.6, 135.2, 131.1, 128.9, 125.5, 117.9, 110.2, 108.8, 38.7, 28.9, 19.8; IR (KBr) ν 3738, 1745, 1676, 1614, 1406, 1305, 1184, 1058, 988, 898, 775, 459 cm^{-1}; HRMS (ESI) calcd for $[C_{13}H_9BrO_3 + H]^+$ 292.9808, found 292.9803.

*9-(Trifluoromethyl)-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3dk**):* petroleum ether/ethyl acetate 6:1; white solid; yield 92% (130 mg, 0.46 mmol); mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.42 (d, J = 9.0 Hz, 1H), 7.77 (d, J = 6.0 Hz, 1H), 2.98 (t, J = 6.0 Hz, 2H), 2.69 (t, J = 6.0 Hz 2H), 2.16−2.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 170.6, 136.8, 134.7, 130.5, 124.9 (q, J = 7.5 Hz), 123.7 (q, J = 7.5 Hz), 122.5, 111.1, 38.9, 29.1, 20.0; IR (KBr) ν 3804, 3732, 1739, 1660, 1545, 1308, 1217, 1104, 1035, 917, 822, 755, 668, 517 cm^{-1}; HRMS (ESI) calcd for $[C_{14}H_9F_3O_3 + H]^+$ 283.0577, found 283.0571.

*7-Chloro-3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3dm**):* petroleum ether/ethyl acetate 6:1; white solid; yield 89% (123 mg, 0.45 mmol); mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.20 (d, J = 6.0 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 2.95 (t, J = 6.0 Hz, 2H), 2.67 (t, J = 6.0 Hz, 2H), 2.14−2.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 171.0, 160.1, 143.1, 135.6, 131.4, 129.4, 126.4, 118.5, 111.1, 39.2, 29.4, 20.3; IR (KBr) ν 3124, 2362, 1736, 1661, 1616, 1586, 1545, 1398, 1307, 1234, 1164, 1035, 907, 842, 803, 776, 698, 537 cm^{-1}; HRMS (ESI) calcd for $[C_{15}H_{13}ClO_3 + H]^+$ 277.0626, found 277.0622.

*9-Methoxy-4,4-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ee**):* petroleum ether/ethyl acetate 6:1; white solid; yield 44% (60 mg, 0.22 mmol); mp 110−111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 3.96 (s, 3H), 2.94 (t, J = 6.0 Hz, 2H), 2.01 (t, J = 6.0 Hz, 2H), 1.25 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 168.6, 165.5, 160.4, 137.0, 131.7, 117.3, 113.0, 109.5, 108.1, 55.9, 42.1, 33.2, 25.7, 24.6; IR (KBr) ν 3138, 2303, 1752, 1670, 1618, 1598, 1570, 1489, 1402, 1325, 1239, 1159, 1100, 1032, 989, 876, 767, 694, 654, 540 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}O_4 + H]^+$ 273.1121, found 273.1120.

*9-Methoxy-4,4-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (**3ee′**):* petroleum ether/ethyl acetate 6:1; white solid; yield 44% (60 mg, 0.22 mmol); mp 110−111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.05 (d, J = 9.0 Hz, 1H), 3.96 (s, 3H), 2.94 (t, J = 6.0 Hz, 2H), 2.01 (t, J = 6.0 Hz, 2H), 1.25 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 168.6, 165.5, 160.4, 137.0, 131.7, 117.3, 113.0, 109.5, 108.1, 55.9, 42.1, 33.2, 25.7, 24.6; IR (KBr) ν 3138, 2303, 1752, 1670, 1618, 1598, 1570, 1489, 1402, 1325, 1239, 1159, 1100, 1032, 989, 876, 767, 694, 654, 540 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{16}O_4 + H]^+$ 273.1121, found 273.1120.

*4-Acetyl-8-bromo-3-methyl-1H-isochromen-1-one (**3fh**):* petroleum ether/ethyl acetate 6:1; white solid; yield 60% (84 mg, 0.30 mmol); mp 121−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 6.0 Hz, 1H), 7.48 (t, J = 6.0 Hz, 1H), 7.24 (d, J = 9.0 Hz, 1H), 2.56 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 158.3, 153.2, 137.6, 135.3, 135.0, 125.8, 122.7, 118.5, 32.7, 18.4; IR (KBr) ν 3836, 3746, 1762, 1649, 1477, 1313, 1010, 987, 811, 520 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_9BrO_3 + H]^+$ 280.9808, found 280.9803.

*4-Acetyl-6-bromo-3-methyl-1H-isochromen-1-one (**3fj**):* petroleum ether/ethyl acetate 6:1, white solid; yield 65% (91 mg, 0.33 mmol); mp 116−117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.50 (s, 1H), 2.59 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 160.4, 154.1, 135.6, 131.5, 131.4, 130.7, 125.9, 118.3, 117.4, 32.3, 18.5; IR (KBr) ν 3835, 3745, 1760, 1648, 1476, 1313, 812, 521 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_9BrO_3 + H]^+$ 280.9808, found 280.9803.

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*4-Acetyl-6-chloro-3-methyl-1H-isochromen-1-one (**3fq**):* petroleum ether/ethyl acetate 6:1; white solid; yield 63% (75 mg, 0.32 mmol); mp 111−112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 6.0 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 7.34 (s, 1H), 2.59 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 154.3, 141.7, 135.8, 132.0, 128.7, 122.7, 118.3, 117.4, 110.1, 32.7, 18.7; IR (KBr) ν 3837, 3756, 1763, 1659, 1478, 1314, 1221, 1011, 927, 801, 522 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_9ClO_3 + H]^+$ 237.0314, found 237.0310.

*3,3-Dimethyl-3,4-dihydro-1H-naphtho[2,3-c]chromene-1,6(2H)-dione (**3ar**):* petroleum ether/ethyl acetate 6:1; white solid; yield 85% (124 mg, 0.43 mmol); mp 178−179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (s, 1H), 8.86 (s, 1H), 7.98 (t, J = 7.5 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 2.80 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 166.9, 161.0, 136.9, 132.0, 131.8, 129.6, 129.3, 129.0, 127.8, 127.2, 125.4, 118.0, 110.6, 53.0, 42.6, 32.0, 28.2; IR (KBr) ν 3836, 3746, 1748, 1640, 1497, 1313, 1212, 1016, 999, 987, 778, 821, 523, 442 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{16}O_3 + H]^+$ 293.1172, found 293.1170.

*3-Methyl-3,4-dihydro-1H-naphtho[2,3-c]chromene-1,6(2H)-dione (**3br**):* petroleum ether/ethyl acetate 6:1; white solid; yield 88% (123 mg, 0.44 mmol); mp 200−201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.92 (s, 1H), 8.02 (t, J = 9.0 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 2.94−3.00 (m, 1H), 2.65−2.79 (m, 2H), 2.37−2.46 (m, 2H), 1.23 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 167.8, 137.0, 132.1, 131.9, 129.6, 129.3, 129.2, 127.9, 127.3, 125.6, 118.2, 111.3, 47.4, 37.0, 27.8, 20.9; IR (KBr) ν 3816, 3756, 1750, 1643, 1467, 1323, 1202, 1116, 1010, 939, 907, 887, 758, 520, 440 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{14}O_3 + H]^+$ 279.1016, found 279.1019.

*3-Phenyl-3,4-dihydro-1H-naphtho[2,3-c]chromene-1,6(2H)-dione (**3cr**):* petroleum ether/ethyl acetate 6:1; white solid; yield 86% (126 mg, 0.43 mmol); mp 179−180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.94 (s, 1H), 8.03 (t, J = 9.0 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.32−7.43 (m, 5H), 3.53−3.62 (m, 1H), 3.19−3.22 (m, 2H), 2.95−3.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 167.4, 141.4, 136.8, 132.1, 131.8, 129.5, 129.2, 129.1, 129.0, 127.6, 127.4, 127.3, 126.5, 125.6, 45.9, 37.9, 36.3; IR (KBr) ν 3816, 3756, 1746, 1642, 1490, 1314, 1210, 999, 986, 777, 820, 520, 441 cm^{-1}; HRMS (ESI) calcd for $[C_{23}H_{16}O_3 + H]^+$ 341.1133, found 341.1130.

*3,4-Dihydro-1H-naphtho[2,3-c]chromene-1,6(2H)-dione (**3dr**):* petroleum ether/ethyl acetate 6:1; white solid; yield 87% (115 mg, 0.44 mmol); mp 198−199 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.88 (s, 1H), 8.00 (t, J = 7.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 2.96 (t, J = 6.0 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 168.4, 136.9, 132.0, 131.8, 129.6, 129.3, 129.1, 128.0, 127.3, 125.7, 118.1, 111.7, 39.1, 29.1, 20.1; IR (KBr) ν 3826, 3766, 1740, 1653, 1457, 1324, 1212, 1116, 1011, 939, 917, 867, 758, 521, 441 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{12}O_3 + H]^+$ 265.0859, found 265.0855.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02906.

Spectral data for all compounds and crystallographic data for compounds **3ah**, **3ej**, and **3ar** (PDF)
Crystallographic data for compound **3ah** (CIF)
Crystallographic data for compound **3ej** (CIF)
Crystallographic data for compound **3ar** (CIF)

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Notes

The authors declare no competing financial interest.

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