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Organocatalytic Electrochemical C–H Lactonization of Aromatic Carboxylic Acids

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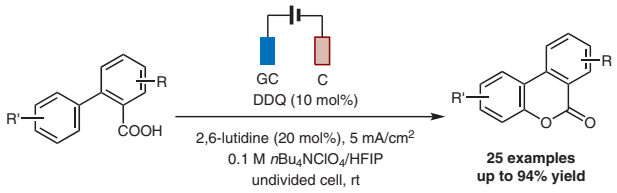

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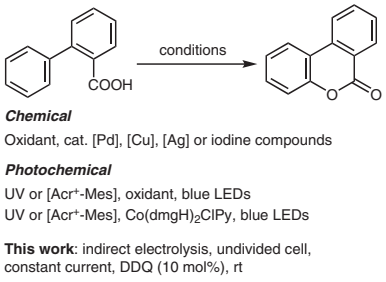
Abstract An electrochemical strategy has been developed for radical arene carbon–oxygen bond formation. This reaction utilizes DDQ as a redox mediator, with inexpensive glassy carbon electrodes to facilitate an intramolecular lactonization of biphenyl-2-carboxylic acid derivatives via aromatic carboxyl radical substitution to give 6*H*-benzo[*c*]chromen-6-ones.

Key words electrochemical oxidation, aromatic radical substitution, lactonization, 6*H*-benzo[*c*]chromen-6-one, redox mediator

Biaryl lactones and their derivatives are frequently found in many natural products and pharmaceuticals and widely used as intermediates in the total synthesis of axially chiral natural products.[1] Developing efficient new methods for their preparation is a worthwhile endeavor. 6*H*-Benzo[*c*]chromen-6-ones (benzocoumarins) are normally prepared through the dehydrogenative lactonization of biphenyl-2-carboxylic acids usually under ultraviolet irradiation[2] or using stoichiometric toxic reactants[3] thus limiting the actual applicability of these methodologies. In 2013, Wang and co-workers[4] reported the construction of biaryl lactones using Pd(II)/Pd(IV)-catalyzed carbonyl-directed C–H activation/C–O cyclization (Scheme 1). Also in 2013, Martin and Gallardo-Donaire[5] and Gevorgyan and co-workers[6] utilized the copper-catalyzed oxygenation reaction of biphenyl-2-carboxylic acid, but this protocol is only efficient for electron-neutral and electron-rich substrates. In addition to palladium and copper, silver[7] has also been shown to catalyze C–H functionalization/C–O cyclization. Notably, the first organocatalyzed procedure that enables this transformation was developed by Martin and co-workers;[8] although the use of a toxic and expensive transition-metal catalyst is avoided, a stoichiometric amount of oxidant is necessary. Visible-light photoredox catalyzed versions of the dehydrogenative lactonization of biphenyl-2-carboxylic acid have also been reported (Scheme 1). A combination of photocatalyst [Acr$^+$-Mes] with $(NH_4)_2S_2O_8$ as the terminal oxidant was used by Gonzalez-Gomez and co-workers.[9] In 2018, our group reported an oxidant-free method by utilizing a photocatalyst/cobalt catalyst system.[10] Although much progress has been made in the processes describe above, the need to use toxic and excess external co-oxidants or heavy metal catalysts does not meet the guiding principles of green and sustainable chemistry.[11]



Scheme 1 Catalytic intramolecular lactonization of biphenyl-2-carboxylic acid

Electrochemistry provides an efficient method to achieve the formation of a new chemical bond and the transformation of a functional group.[12] Kolbe electrolysis is the oldest electroorganic reaction[13] and is defined as the electrochemical one-electron oxidation of carboxylate ions that leads to radical homocoupling upon decarboxylation. This method is very specific and versatile for the synthesis of higher alkenes[14] and 1,n-diesters.[15] Due to the high oxidation potential of the carboxylates,[16] the Kolbe electrol-

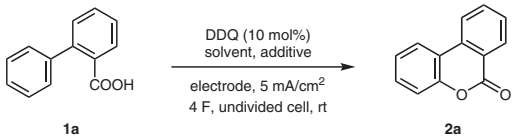
ysis must proceed under high current density and electrode potential with an expensive platinum plate electrode. In 2018, Zeng and co-workers reported the intramolecular C–H/C–O oxidative coupling of aromatic carboxylic acids using direct electrolysis.[17] Indirect electrolysis using a redox mediator catalyst is advantageous in its avoidance of electrode passivation and kinetic inhibition, lowering electrode potential, and allowing for better selectivity.[18] We exploited this redox catalyst to mediate the electrochemical oxidation for the generation of the aromatic carboxyl radicals. DDQ can be regenerated from the anodic oxidation[19] as a redox catalyst, providing an alternative strategy for the electrochemical transformations of organic compounds.[20] Herein, we describe an electrochemical synthesis of biaryl lactones via aromatic carboxyl radicals catalyzed by DDQ as a redox mediator.

We commenced our studies using biphenyl-2-carboxylic acid (**1a**) as a model substrate with the system of DDQ as the redox catalyst under controlled current electrolysis at 5 mA in an undivided cell using $LiClO_4$/MeCN as the electrolyte solution with two graphite plates as anode and cathode and this gave the desired 6*H*-benzo[*c*]chromen-6-one (**2a**) in 16% yield after passing 4 F of charge (Table 1, entry 1); **1a** was completely consumed as indicated by TLC. According to the reaction mechanism,[21] deprotonation by a base to give the carboxylate would render it more susceptible to oxidation, hence we reasoned that the presence of a base would be beneficial. To our delight, the addition of 1 equivalent of 2,6-lutidine gave an improved yield (58%) of **2a** (entry 2). The use of Na_2CO_3 or $NaHCO_3$ led to comparable yields of **2a** (entries 3 and 4), but a dramatically lower yield of **2a** was obtained in the case of K_2CO_3 (entry 5). Encouraged by this result, the search for the optimal quantity of 2,6-lutidine was undertaken. Decreasing the amount of 2,6-lutidine had no effect (entry 6). Notably, **2a** was obtained in very low yield in the absence of 2,6-lutidine, thereby demonstrating the essential role of a base in the overall transformation. We then turned our attention to solvent optimization. Comparable yields of **2a** were obtained when MeOH or TFE (2,2,2-trifluoroethanol) were used as solvents (entries 7 and 8), while the yield increased to 80% when HFIP (1,1,1,3,3,3-hexafluoropropan-2-ol) was employed (entry 9). Further screening of electrode materials demonstrated that the glass carbon plate was preferable for the reaction and **2a** was obtained in 94% yield (entry 10); Pt as the anode proved to be less active (entry 11).

With the optimized conditions in hand (Table 1, entry 10), we then explored the scope and generality of the reaction. As shown in Scheme 2, a variety of biphenyl-2-carboxylic acids **1** were cyclized to give the corresponding biaryl lactones **2** in modest to excellent yields (up to 94%). It was observed that both electron-withdrawing and electron-donating groups were tolerated in the 4′-position and the desired cyclization products **2b–f** were obtained in satisfactory 62–92% yields. In addition, the 3′-substituent has no obvious influence on the reaction, and afforded the corresponding products **2g**,**h** in good yields. Meanwhile, regardless of whether a methyl group was present in the 4-, 5-, or 6-positions, the corresponding products **2i–l** were obtained in moderate to good yields. When a phenyl group was present in the 4- or 4′-positions, the desire products **2m**,**n** were obtained in good yields. Notably, this transformation could also bear naphthalene well to give products **2o–r**. The use of 3,3-diphenylacrylic acid and 2-(2,2-diphenylvinyl)benzoic acid was examined to explore the synthetic potential of arene lactonization. 3,3-Diphenylacrylic acid (**1s**) smoothly gave 4-phenyl-2*H*-chromen-2-one (**2s**) in 91% yield and also, 2-(2,2-diphenylvinyl)benzoic acid (**1t**) gave 3-(diphenylmethylene)isobenzofuran-1(3*H*)-one (**2t**) in 63% yield; in these cases, tetrabutylammonium bromide was found to perform better than DDQ as a redox mediator.

During the study using 2′-halobiphenyl-2-carboxylic acids **1u–w**, the reaction gave only substitution product **2a** instead of C–H substitution product. Arene halides bearing an ortho-halide substitute including chloride, bromide, and fluoride, all underwent C-X radical substitution to give the desired products in good yields (Scheme 3). This represents a rare example of electrolysis-initiated aromatic radical substitution.

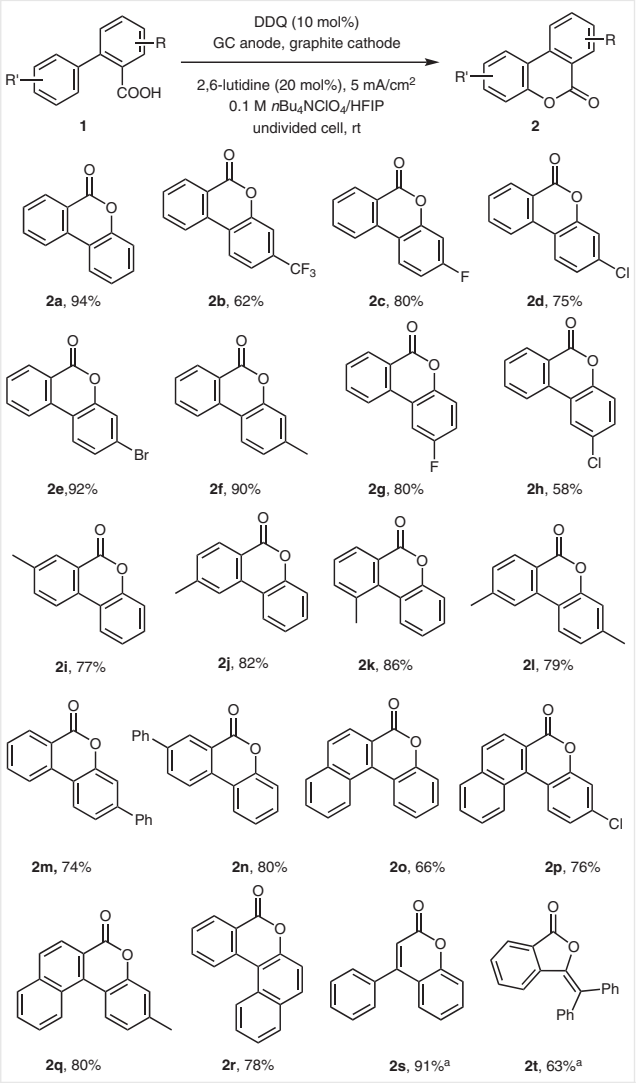
Table 1 Reaction Optimization[a]



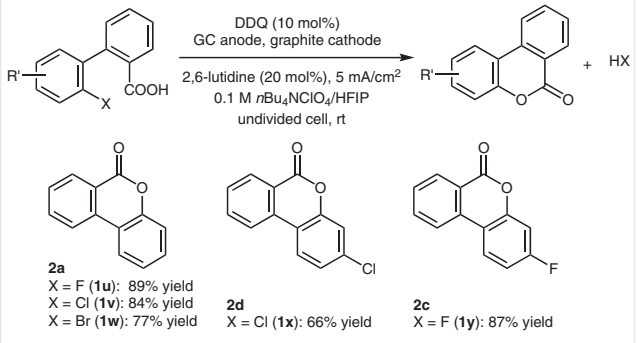
1a **2a**

Entry	Solvent	Additive	Anode	Cathode	Yield[b] (%)
1	MeCN	–	C	C	16
2	MeCN	2,6-lutidine[c]	C	C	58
3	MeCN	Na_2CO_3[c]	C	C	50
4	MeCN	$NaHCO_3$[c]	C	C	53
5	MeCN	K_2CO_3[c]	C	C	27
6	MeCN	2,6-lutidine	C	C	53
7	MeOH	2,6-lutidine	C	C	57
8	TFE	2,6-lutidine	C	C	64
9	HFIP	2,6-lutidine	C	C	80
10	HFIP	2,6-lutidine	GC	C	94
11	HFIP	2,6-lutidine	Pt	C	83

[a] General conditions: **1a** (0.10 mmol), DDQ (10 mol%), additive (20 mol%), 0.1 M supporting electrolyte solvent mixture (2.0 mL), r.t.
[b] Determined by ^{1}H NMR analysis with an internal standard.
[c] The amount of additive was 0.10 mmol (1 equiv).



Scheme 2 Substrate scope. [a] Bu_4NBr was used instead of DDQ.

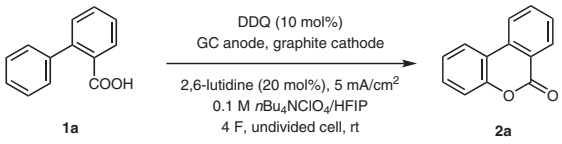


Scheme 3 C(sp^2)–X bond cleavage

To gain additional insight into the reaction mechanism, we performed a series of control experiments (Table 2). First, we attempted to perform the reaction in the absence of DDQ or 2,6-lutidine, but the yields dropped considerably (entries 1 and 2). These experiments suggest that both DDQ and 2,6-lutidine are essential for the high efficiency of reaction. Also the reaction did not occur in the absence of an electric current even in the presence of 1.5 equivalents of DDQ. The electrolysis of **1a** under the standard conditions was performed in the presence of 2.0 equivalent of BHT (3,5-di-*tert*-4-butyl-4-hydroxytoluene), a radical scavenger, and this gave a trace amount of **2a** (entry 5). While not yet conclusive, these experiments imply that the reaction involves a radical process. In addition, experiments focusing on the kinetic isotopic effect (KIE) were also conducted to gain additional insight into this reaction. The intra- and intermolecular K_H/K_D ratios were 1.19 and 1.20, respectively. This result suggests that C–H bond cleavage was not involved in the rate-determining step.

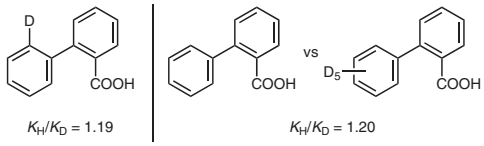
Table 2 Mechanism Studies

a. Control experiments



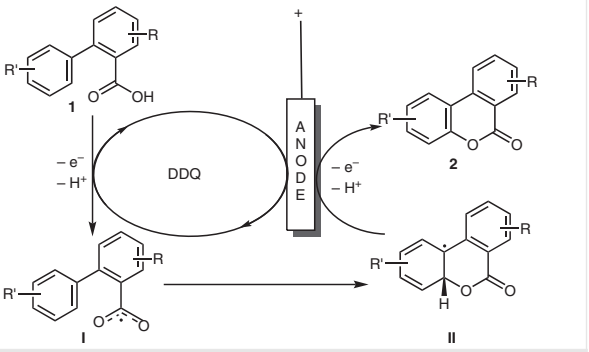
Entry	Variation from the standard conditions	Yield (%)
1	no DDQ	30
2	no 2,6-lutidine	50
3	no electric current	no reaction
4	no electric current but 1.5 equiv DDQ	no reaction
5	BHT	trace

b. Intramolecular and intermolecular KIE



Base on the mechanistic investigation above, we proposed a plausible mechanism shown in Scheme 4. The sequence begins with DDQ engaged in a homogeneous electron transfer from biphenyl-2-carboxylic acid **1** to an O-centered carboxylic radical **I**, DDQ was regenerate by the anodic oxidation. That the transformation can be mediated by DDQ is verified by the fact that that **2** is obtained in only 30% yield when **1** is electrolyzed in the absence of DDQ, while the yield is 94%, in its presence (Table 2, entry 1 and Table 1, entry 10). Carboxylic radical **I** undergoes addition to the arene ring to form an aryl radical intermediate **II**. A further anodic oxidation of aryl radical **II** then leads to **2**.

The presence of 2,6-lutidine would facilitate the deprotonation of both **1** and intermediate **II**, favoring the coupled electron-transfer.



Scheme 4 Proposed mechanism

In summary, we have developed an intramolecular lactonization of biphenyl-2-carboxylic acids by electrochemical oxidation with DDQ as the redox catalyst. This method provides a general and convenient access to 6*H*-benzo[*c*]chromen-6-ones under mild, robust and environmentally friendly conditions.

Commercial reagents were used as received, unless otherwise indicated. ^{1}H, ^{13}C NMR spectra were measured on a NMR instrument (300, 400, or 500 MHz for ^{1}H NMR, 75, 101, or 126 MHz for ^{13}C NMR). TMS served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR.

Lactones 2; General Procedure

To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a Glass Carbon plate anode (10.0 mm × 20.0 mm), and a graphite plate cathode (10.0 mm × 30.0 mm) were added redox catalyst–DDQ (10 mol%), biphenyl-2-carboxylic acid **1** (0.10 mmol). Then electrolyte solution (0.1 M nBu$_4$NClO$_4$ in HFIP, 2.0 mL), and 2,6-lutidine (20 mol%) was added. The mixture was then stirred for 10 min. After that, the electrolysis was initiated at a control current of 5.0 mA. Each reaction was terminated upon full consumption of starting material as determined by TLC analysis. The entire mixture was then transferred to a chromatography column (silica gel, petroleum ether/EtOAc 9:1–4:1) to afford the desired product.

6*H*-Benzo[*c*]chromen-6-one (2a)[10]

White solid; yield: 18.4 mg (94%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.37 (dd, *J* = 7.9, 1.4 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.02 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.80 (td, *J* = 7.8, 1.4 Hz, 1 H), 7.60–7.53 (m, 1 H), 7.46 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1 H), 7.38–7.28 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.2, 151.3, 134.9, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.1, 117.8.

3-(Trifluoromethyl)-6*H*-benzo[*c*]chromen-6-one (2b)[10]

White solid; yield: 16.4 mg (62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (dd, *J* = 8.0, 1.7 Hz, 1 H), 8.15 (t, *J* = 7.8 Hz, 2 H), 7.88 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.75–7.63 (m, 1 H), 7.58 (dd, *J* = 10.0, 2.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 151.1, 135.3, 133.5, 132.5, 132.2, 131.0, 130.3, 124.5, 123.8, 122.3, 121.8, 121.3, 121.2, 121.1, 115.4, 115.3.

3-Fluoro-6*H*-benzo[*c*]chromen-6-one (2c)[10]

White solid; yield: 17.0 mg (80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (dd, *J* = 7.9, 1.4 Hz, 1 H), 8.00 (dd, *J* = 8.5, 6.0 Hz, 2 H), 7.81 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.58 –7.50 (m, 1 H), 7.14–6.92 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.5, 162.5, 160.8, 152.2, 152.1, 135.2, 134.3, 130.7, 128.8, 124.5, 124.4, 121.6, 120.5, 114.7, 114.6, 112.6, 112.4, 105.2, 105.0.

3-Chloro-6*H*-benzo[*c*]chromen-6-one (2d)[10]

White solid; yield: 17.2 mg (75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.39 (dd, *J* = 8.0, 1.3 Hz, 1 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 7.84 (ddd, *J* = 8.3, 7.3, 1.4 Hz, 1 H), 7.66–7.55 (m, 1 H), 7.37 (d, *J* = 2.1 Hz, 1 H), 7.31 (dd, *J* = 8.5, 2.1 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.7, 151.6, 136.1, 135.2, 134.1, 130.9, 129.3, 125.2, 123.9, 121.8, 121.0, 118.1, 116.8.

3-Bromo-6*H*-benzo[*c*]chromen-6-one (2e)[10]

White solid; yield: 25.2 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (dd, *J* = 8.0, 1.4 Hz, 1 H), 8.06 (d, *J* = 8.1 Hz, 1 H), 7.90 (d, *J* = 8.5 Hz, 1 H), 7.87–7.78 (m, 1 H), 7.67–7.56 (m, 1 H), 7.52 (d, *J* = 2.0 Hz, 1 H), 7.45 (dd, *J* = 8.5, 1.9 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.6, 151.7, 135.2, 134.2, 130.9, 129.4, 128.0, 124.1, 123.9, 121.8, 121.2, 121.1, 117.3.

3-Methyl-6*H*-benzo[*c*]chromen-6-one (2f)

White solid; yield: 19.0 mg (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 7.9 Hz, 1 H), 8.07 (d, *J* = 8.1 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.80 (td, *J* = 7.7, 7.0, 1.4 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.19–7.10 (m, 2 H), 2.45 (s, 3 H).

^{13}C NMR 126 MHz, $CDCl_3$): δ = 161.4, 151.3, 141.3, 135.0, 134.8, 130.5, 128.4, 125.7, 122.5, 121.5, 120.9, 117.9, 115.4, 21.5.

2-Fluoro-6*H*-benzo[*c*]chromen-6-one (2g)[10]

White solid; yield: 17.1 mg (80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (dd, *J* = 7.9, 1.3 Hz, 1 H), 8.02 (d, *J* = 7.8 Hz, 1 H), 7.85 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.70 (dd, *J* = 9.1, 2.9 Hz, 1 H), 7.67–7.60 (m, 1 H), 7.34 (dd, *J* = 9.0, 4.7 Hz, 1 H), 7.19 (ddd, *J* = 9.0, 7.6, 2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.9, 160.4, 158.4, 147.5, 147.4, 135.1, 134.0, 139.9, 130.8, 129.7, 122.0, 121.3, 119.4, 119.3, 119.3, 117.9, 117.7, 109.0, 108.8.

2-Chloro-6*H*-benzo[*c*]chromen-6-one (2h)[10]

White solid; yield: 13.3 mg (58%).

^{1}H NMR 500 MHz, $CDCl_3$): δ = 8.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.85 (td, *J* = 7.7, 1.4 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.42 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 149.8, 135.2, 133.7, 130.9, 130.5, 130.2, 129.7, 122.7, 121.9, 121.4, 119.5, 119.3.

8-Methyl-6*H*-benzo[*c*]chromen-6-one (2i)[10]

White solid; yield: 16.2 mg (77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 1.9 Hz, 1 H), 8.01 (dd, *J* = 8.1, 6.5 Hz, 2 H), 7.66–7.59 (m, 1 H), 7.49–7.41 (m, 1 H), 7.37–7.28 (m, 2 H), 2.49 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.5, 151.2, 139.4, 136.2, 132.4, 130.5, 130.0, 124.6, 122.7, 121.8, 121.3, 118.4, 117.8, 21.4.

9-Methyl-6*H*-benzo[*c*]chromen-6-one (2j)[10]

White solid; yield: 17.2 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.1 Hz, 1 H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.89 (s, 1 H), 7.46 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1 H), 7.41–7.28 (m, 3 H), 2.55 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.4, 151.6, 146.0, 134.9, 130.7, 130.4, 130.3, 124.5, 122.8, 122.0, 119.0, 118.3, 117.9, 22.4.

10-Methyl-6*H*-benzo[*c*]chromen-6-one (2k)[10]

White solid; yield: 18.0 mg (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (dd, *J* = 7.9, 1.5 Hz, 1 H), 8.36–8.30 (m, 1 H), 7.66 (d, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 7.7 Hz, 2 H), 7.42 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.38–7.30 (m, 1 H), 2.92 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.8, 151.3, 139.2, 135.1, 133.6, 129.7, 129.3, 128.3, 127.3, 124.1, 122.9, 119.8, 118.0, 25.5.

3,9-Dimethyl-6*H*-benzo[*c*]chromen-6-one (2l)[10]

White solid; yield: 17.7 mg (79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.1 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.84 (s, 1 H), 7.34 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.17–7.09 (m, 2 H), 2.54 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.6, 151.6, 145.9, 141.2, 135.1, 130.7, 129.8, 125.7, 122.6, 121.7, 118.6, 118.0, 115.6, 22.4, 21.5.

3-Phenyl-6*H*-benzo[*c*]chromen-6-one (2m)[10]

White solid; yield: 20.1 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (dd, *J* = 8.0, 1.4 Hz, 1 H), 8.10 (dd, *J* = 14.3, 8.0 Hz, 2 H), 7.86–7.78 (m, 1 H), 7.65 (dd, *J* = 7.4, 1.7 Hz, 2 H), 7.60–7.55 (m, 3 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.45–7.39 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.3, 151.7, 143.5, 139.3, 135.0, 134.7, 130.7, 129.1, 128.9, 128.4, 127.1, 123.4, 123.3, 121.8, 121.2, 117.0, 115.9.

8-Phenyl-6*H*-benzo[*c*]chromen-6-one (2n)[10]

White solid; yield: 21.8 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 2.0 Hz, 1 H), 8.20 (d, *J* = 8.3 Hz, 1 H), 8.08 (td, *J* = 8.2, 1.7 Hz, 2 H), 7.71 (dd, *J* = 7.6, 1.7 Hz, 2 H), 7.52–7.34 (m, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.3, 151.2, 141.7, 138.9, 133.5, 133.4, 130.4, 129.2, 128.5, 128.4, 127.1, 124.7, 122.8, 122.4, 122.6, 118.0, 117.8.

6*H*-Naphtho[2,1-*c*]chromen-6-one (2o)[10]

White solid; yield: 16.2 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 8.54 (s, 1 H), 8.26–8.19 (m, 1 H), 8.03 (dd, *J* = 14.2, 8.2 Hz, 2 H), 7.69 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H), 7.60 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H), 7.48 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1 H), 7.39–7.26 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.1, 150.9, 136.3, 132.9, 132.5, 130.3, 129.7, 129.7, 129.6, 128.2, 127.3, 124.7, 123.0, 120.8, 119.3, 118.4, 118.0.

3-Chloro-6*H*-naphtho[2,1-*c*]chromen-6-one (2p)[10]

White solid; yield: 21.3 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.39 (s, 1 H), 8.06 (d, *J* = 8.3 Hz, 1 H), 7.97 (t, *J* = 7.6 Hz, 2 H), 7.68 (d, *J* = 1.3 Hz, 1 H), 7.58 (d, *J* = 1.4 Hz, 1 H), 7.34–7.27 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.0, 151.1, 136.3, 135.6, 133.2, 132.6, 130.0, 129.7, 128.9, 128.2, 127.6, 125.2, 124.0, 120.8, 118.8, 118.2, 117.1.

3-Methyl-6*H*-naphtho[2,1-*c*]chromen-6-one (2q)[10]

White solid; yield: 20.8 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 8.40 (s, 1 H), 8.02 (d, *J* = 8.1 Hz, 1 H), 7.96 (dd, *J* = 14.9, 8.3 Hz, 2 H), 7.64 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1 H), 7.57–7.51 (m, 1 H), 7.14 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.11 (s, 1 H), 2.43 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.8, 150.9, 141.0, 136.4, 132.9, 132.3, 130.0, 129.7, 129.6, 128.1, 127.0, 125.9, 122.8, 120.3, 119.2, 118.1, 115.8, 21.5.

5*H*-Dibenzo[*c*,*f*]chromen-5-one (2r)[10]

White solid; yield: 19.2 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (dd, *J* = 8.0, 1.5 Hz, 1 H), 8.39 (dd, *J* = 7.9, 1.3 Hz, 1 H), 8.08 (d, *J* = 8.1 Hz, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 7.86–7.75 (m, 2 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.52–7.59 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.2, 147.2, 135.4, 135.0, 134.3, 130.6, 128.6, 127.9, 127.7, 127.1, 124.5, 123.9, 122.3, 122.0, 121.2, 119.1, 113.0.

4-Phenyl-2*H*-chromen-2-one (2s)[10]

White solid; yield: 20.2 mg (91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.51 (m, 4 H), 7.50 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.46 (ddd, *J* = 6.2, 4.2, 2.7 Hz, 2 H), 7.42 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.26–7.21 (m, 1 H), 6.39 (s, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.9, 155.8, 154.3, 135.4, 132.1, 129.8, 129.0, 128.6, 127.2, 124.3, 119.2, 117.5, 115.4.

3-(Diphenylmethylene)isobenzofuran-1(3*H*)-one (2t)[10]

White solid; yield: 18.3 mg (63%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.6 Hz, 1 H), 7.60–7.54 (m, 2 H), 7.52 (dd, *J* = 4.8, 1.9 Hz, 3 H), 7.44–7.28 (m, 7 H), 6.30 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.3, 142.6, 139.7, 137.7, 137.5, 132.0, 130.7, 130.6, 129.5, 129.5, 128.9, 128.3, 128.3, 125.4, 125.0, 125.0, 123.7.

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Supporting Information

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