# Oxidant-Free C(sp^2)−H Functionalization/C−O Bond Formation: A Kolbe Oxidative Cyclization Process

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S Supporting Information

ABSTRACT: An anodic oxidation/cyclization of 2-arylbenzoic acids for the synthesis of dibenzopyranones has been developed. The reaction proceeds at room temperature with no oxidant or electrolyte required and exhibits a high atom economy with H$_2$ being the only byproduct. A series of dibenzopyranones was obtained in good to excellent yields. Urolithins A, B, and C are formally synthesized by adopting this method as a key step to demonstrate its synthetic utility.
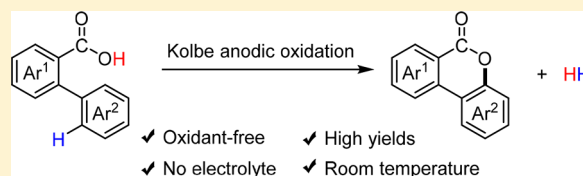
INTRODUCTION

Oxygen-containing heterocycles are privileged motifs found in numerous bioactive natural products, organic materials, agrochemicals, and pharmaceuticals.[1] The traditional approaches for constructing such heterocyclic scaffolds mainly rely on the addition of a nucleophile to a carbonyl group, to a halide or other leaving groups, electrocyclic reactions, etc.[2] However, most of these approaches involve the use of expensive reagents and harsh conditions as well as generate large amounts of waste. Although much progress has been made in recent decades in the transition metal-catalyzed cyclization of acyclic substrates for heterocycles synthesis,[3] the high cost, toxicity, and air/moisture sensitivity of some catalysts are major concerns. Consequently, new compatible and more sustainable synthetic approaches are urgently needed for the synthesis of heterocycles.

The prosperous development of organic electrochemistry has dramatically expanded chemists' toolboxes that provide a variety of opportunities to solve synthetic challenges in unique ways.[4] For example, intramolecular anodic oxidative C−O bond formation can serve as a powerful tool for the construction of oxygen-containing heterocycles (Scheme 1A). Moeller and co-workers pioneered a series of intramolecular anodic cyclization of electron-rich olefins with alcohols.[5] Intramolecular electrochemical nucleophilic attack of oxygen nucleophiles on Schiff bases reported by Zeng and other groups also provide straightforward routes to constructing oxygen-containing heterocycles.[6] The Okimoto and Lee groups described the anodic oxidation of amides or tertiary amines to generate reactive N-acyliminium cations or iminium cations, which were trapped by alcohol nucleophiles to afford cyclic N,O-acetals.[7] Very recently, the Waldvogel and Xu groups reported on the intramolecular anodic dehydrogenative coupling of aromatic C−H bonds and amide groups for the synthesis of benzoxazoles and benzoxazines, respectively.[8]

The anodic oxidation of carboxylic acid, also known as Kolbe electrolysis (or Kolbe oxidation, Kolbe dimerization) has a long

Scheme 1. Intramolecular Anodic Oxidative C−O Bond Formation and Kolbe Electrolysis
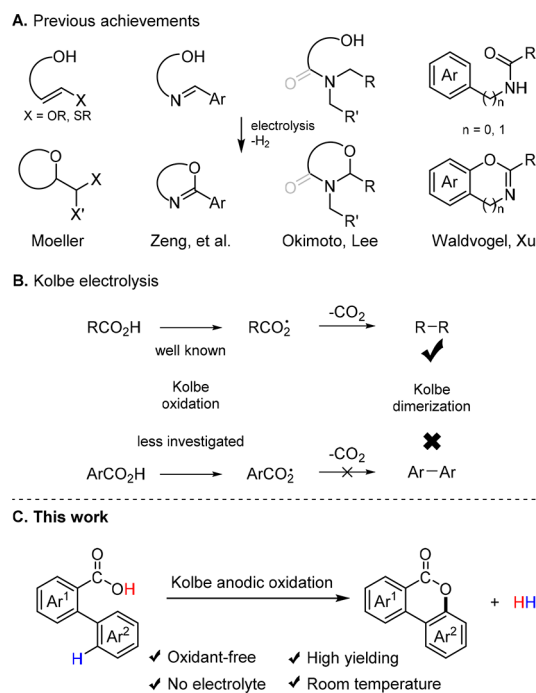
history of development since its discovery in 1849.[9] The coupling reaction of alkyl radicals generated from electrodecarboxylation of alkyl carboxylates (RCO$_2^-$) gives the Kolbe dimer R−R. However, aryl carboxylates (ArCO$_2^-$) cannot be applied in Kolbe dimerization due to the challenging decarboxylation of aroyloxy radicals. In fact, Barton has categorized ArCO$_2^\bullet$ as "nondecarboxylating acyloxy radicals",

noting that it does not decarboxylate at temperatures below 120−130 °C.[10] Thus, compared with alkyl carboxylic acids, there have been far fewer investigations of aryl carboxylic acids for the Kolbe oxidation reaction (Scheme 1B). These previous results give four reasons that the preparation of benzolactones is an ideal process for the use of Kolbe electrolysis of 2-arylbenzoic acids. First, although this has been less investigated, anodic oxidation of aromatic carboxylic acid is feasible.[11] Second, the formed aroyloxy radical does not undergo decarboxylation at ambient temperature. Third, the two consecutive electron transfers between the electrode and the substrate taking place on the same electrode (double anodic oxidation) favor implementation of the reaction. Finally, the concomitant cathodic proton reduction to hydrogen gas exactly balances the redox of the overall reaction. In this paper, we report a Kolbe electrolysis for the lactonization of 2-arylbenzoic acids at room temperature in an oxidant-free manner (Scheme 1C).

■ RESULTS AND DISCUSSION

Biaryl lactones and their derivatives are common structure motifs found in a wide variety of bioactive molecules ranging from natural products to drugs (Scheme 2).[12] They also serve

Scheme 2. Natural Products and Pharmaceuticals Containing Biaryl Lactones
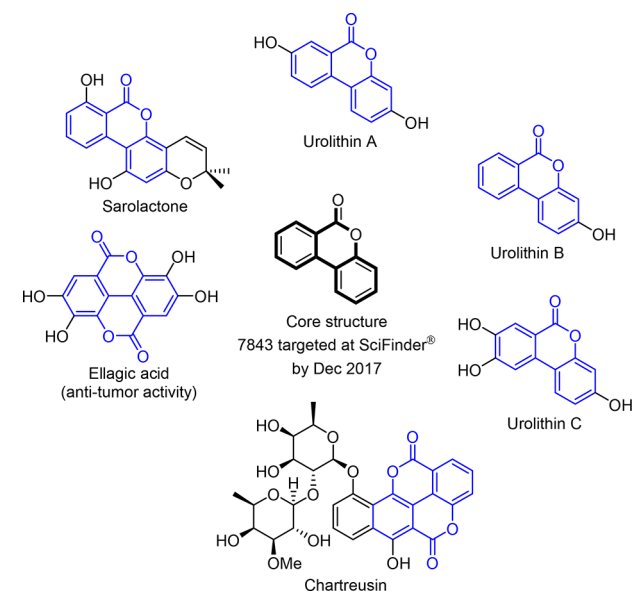

as versatile building blocks for the synthesis of various pharmaceuticals, as well as agrochemicals, fragrances, and materials.[13] In light of the importance of these biaryl lactone compounds, a variety of methods has been developed for their synthesis.

Among those methods, the oxidative cyclization of 2-arylbenzoic acids via a C−H bond activation/C−O bond formation process is a commonly used cyclization method.[14] For example, Togo and Yokoyama reported on (diacetoxy-iodo)arene and iodine comediated cyclization of 2-aryl (or alkyl) benzoic acids under photo irradiation.[14b−d] In 2013, Martin and co-workers reported on Cu-catalyzed C−H functionalization/C−O bond formation assisted by carboxylic acids with dibenzoyl peroxide as the oxidant.[14e] Later, they also reported on the iodine(III)-catalyzed cyclization of 2-

arylbenzoic acid with peroxyacetic acid as the terminal oxidant.[14i] Wang and co-workers developed a Pd catalysis for the same transformation using $PhI(OAc)_2$ as the oxidant.[14f] Gevorgyan reported a Cu(II)-catalyzed title transformation using *tert*-butyl peroxybenzoate as the oxidant.[14g] Xu also achieved the same goal using a Ag(I) catalyst with $(NH_4)_2S_2O_8$ as the oxidant.[14j] In addition, the Wei group demonstrated a visible light-induced cyclization of 2-arylbenzoic acids with *N*-iodosuccinimide as the oxidant,[14h] whereas the Gonzalez−Gomez group reported on the metal-free dehydrogenative lactonization of 2-arylbenzoic acids at room temperature under visible light irradiation with [Acr$^+$-Mes] as the photocatalyst and $(NH_4)_2S_2O_8$ as the oxidant.[14k] Very recently, the Luo group[14l] and the Zhu group[14m] independently reported a photoredox and cobalt cocatalyzed C(sp^2)−H functionalization/C−O bond formation reaction toward biaryl lactone synthesis with no oxidant involved. However, the catalysis system is somewhat complicated. The most known methods use stoichiometric oxidants, since the overall process involves the removal of two hydrogens from the substrate. This will cause excessive waste generation and poor atom economy. We envisage that oxidant-free conditions might be possible if the two hydrogens can be properly handled. In this case, the generation of hydrogen gas (H_2) gives an ideal solution for the two hydrogen atoms (Scheme 3).

Scheme 3. Rationale of Kolbe Electrolysis for Cyclization of 2-Arylbenzoic Acid

A. Literature known methods for cyclization of 2-aryl benzoic acid (ref. 14)
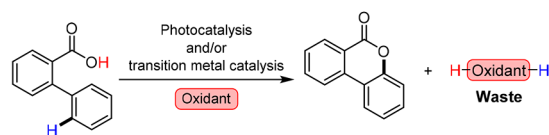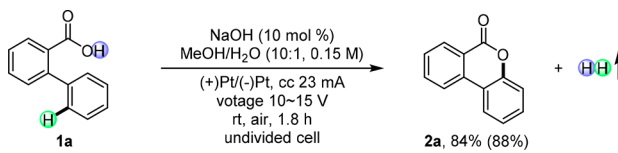
B. Rationale of this work
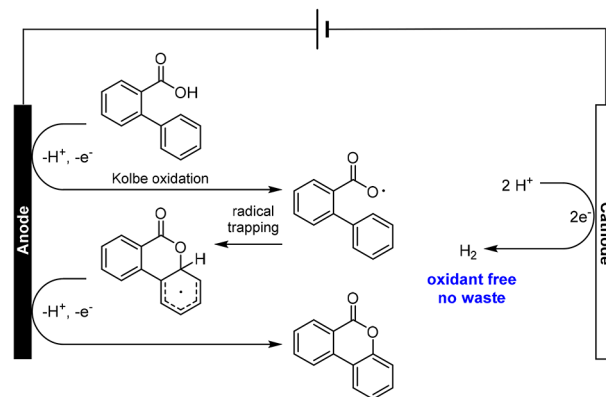
We initially studied the anodic oxidation of 2-phenylbenzoic acid (Table 1). The reaction conditions were optimized to give the desired cyclization product **2a** with 84% NMR yield and 88% isolated yield in the presence of 10% NaOH in a MeOH/H_2O mixed solvent. Platinum was used as the electrode with the reaction using the constant current mode with a current of 23 mA. The Kolbe reaction is usually performed with constant current density with the anode potential seldom needing to be controlled by a potentiostat.[9e]

The reaction proceeds quite fast as monitored by TLC and with the voltage variations with the voltage starting at 10−15 V and rising to over 20 V on completion of the reaction. Other

Table 1. Reaction Development and Optimization

| entry	deviation from the standard conditions	yield[b] (%)
1	MeCN instead of MeOH, 2.8 h	69
2	acetone instead of MeOH, 2.8 h	52
3	DMF instead of MeOH, 11 h	34
4	THF instead of MeOH, 7 h	32
5	^{i}PrOH instead of MeOH, 4 h	34
6	HFIP instead of MeOH, 3 h	79
7	under N_2, 1.8 h	80 (86)
8	1 mmol scale, 0.3 M conc, 3.3 h	76
9	50 °C, 16 h	76
10	cc 10 mA, 5 h	76
11	w/o NaOH, cv 60 V, current ca. 3−7 mA, 2 days	76
12	no electricity, 2 days	0

[a]Reaction conditions: 1a, 0.5 mmol; MeOH, 3 mL; H_2O, 0.3 mL; Pt net electrode; 1 cm × 1 cm; 52 mesh. cc = constant current. cv = constant voltage. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. Reaction time varies in each entry. The completion of the reaction was monitored by TLC and voltage. [b]Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene. Isolated yield in parentheses.

solvents, such as MeCN, acetone, and DMF, proved to be less efficient (entries 1−5), while HFIP gave a comparable yield (entry 6). The reaction is not sensitive to air or concentration (entries 7 and 8). Normally, the reaction temperature is slightly higher than room temperature, since the reaction is exothermic. Interestingly, the reaction still works well but is slower at 50 °C (entry 9). An applied current of 10 mA required a longer reaction time with a good yield (entry 10). The reaction media became less conductive (60 V, 3−7 mA) when no base was added. The yield did not drop much after 2 days of electrolysis (entry 11). The results show that the reaction is unambiguously driven by the electrical current (entry 12).

The optimal reaction conditions were then used for substrate scope studies with the results shown in Table 2. A series of benzoic acid substrates bearing substitutions on both the Ar^1 and Ar^2 rings were examined with the corresponding cyclization products isolated with good to excellent yields. This anodic oxidation reaction tolerates a variety of functional groups, such as ketone, ester, ether, alkene, halides, trifluoromethyl, and trifluoromethoxy groups. Both electron-donating and -withdrawing substituents worked well on both aromatic rings. Substituents in the *ortho* position hindered the reaction, providing 2j in a relatively low yield. *meta*-Substitution on the Ar^2 ring caused site selectivity, as shown in the case of 2k. The reaction gave a roughly 1.25:1 mixture of isomers in 90% total yield. In another example, a single isomer, 2z, was obtained with the naphthalene backbone. Heterocycles could also be accommodated under our electrochemical condition as exemplified by 2aa.
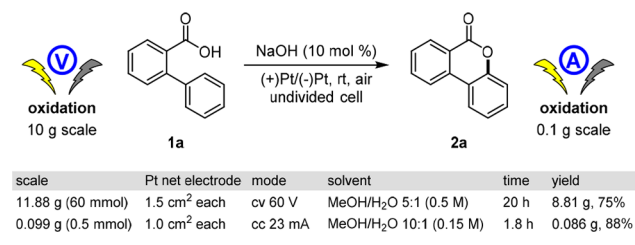
Furthermore, a 10 g scale experiment was conducted to examine the scalability of this electrochemical protocol.

Table 2. Kolbe Anodic Cyclization via C(sp^2)−H Functionalization/C−O Formation[a]
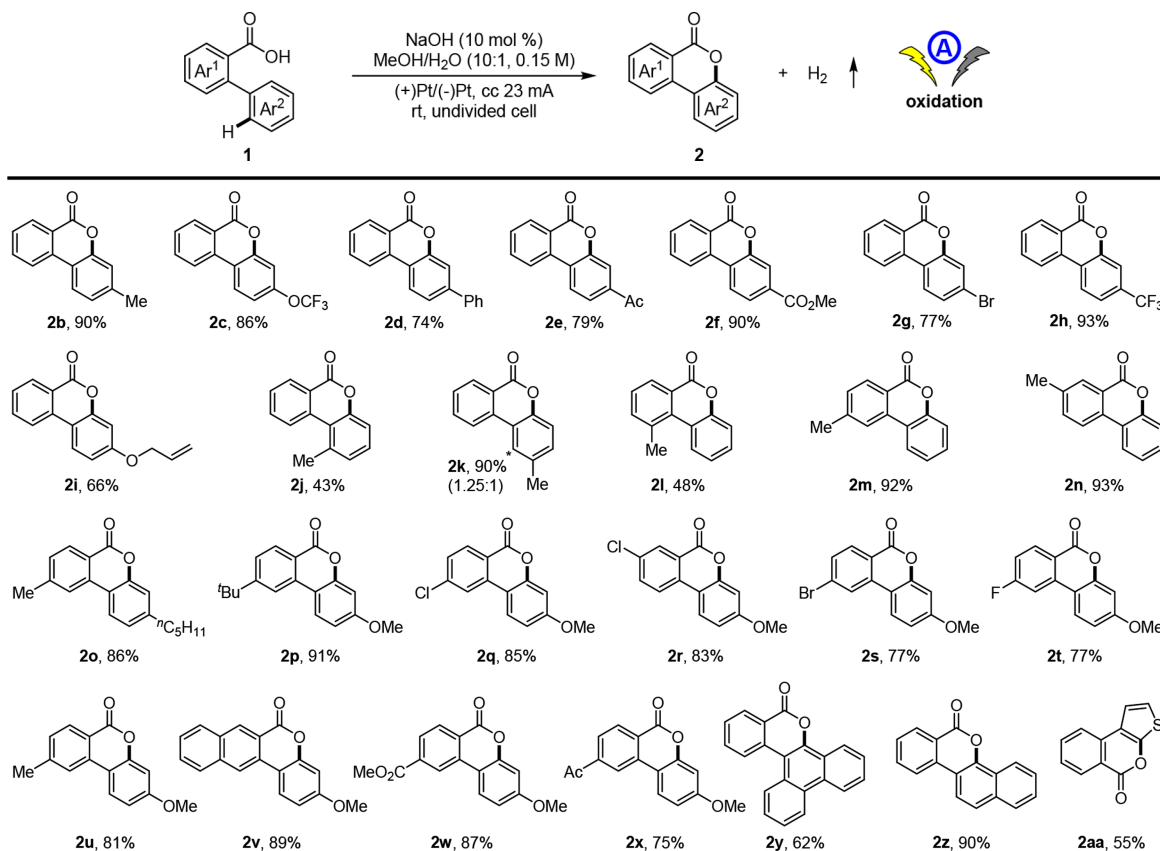
[a]Reaction conditions: 1a, 0.5 mmol; MeOH, 3 mL; H_2O, 0.3 mL; Pt net electrode; 1 cm × 1 cm; 52 mesh. cc = constant current. Isolated yields are reported.

Running the reaction at a 60 mmol scale with larger electrodes in a higher concentration (0.5 M) in a constant voltage mode (60 V) gave **2a** with 75% isolated yield (Scheme 4).

Scheme 4. Comparison of 10 Gram Scale with 0.1 Gram Scale Reactions

scale	Pt net electrode	mode	solvent	time	yield
11.88 g (60 mmol)	1.5 cm² each	cv 60 V	MeOH/H₂O 5:1 (0.5 M)	20 h	8.81 g, 75%
0.099 g (0.5 mmol)	1.0 cm² each	cc 23 mA	MeOH/H₂O 10:1 (0.15 M)	1.8 h	0.086 g, 88%

Three compounds in the Urolithin family are suitable targets for demonstrating the synthetic utility of this Kolbe oxidative cyclization reaction. Starting from the easily available substituted benzoic acid or ester, the electrochemical precursors are obtained by means of a Pd-catalyzed cross-coupling reaction or the C−H arylation reaction. An electrochemical technique was then applied to convert compounds **5** to cyclized products **6**. Finally, compounds **6a**, **6b**, and **6c** can be easily transformed to Urolithins A, B, and C following a reported procedure (Scheme 5).[15]

To probe the mechanism of this reaction, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a free radical scavenger, was introduced as an additive to the standard reaction. We found that the reaction was suppressed to a great extent. As shown in Scheme 6A, product **2a** was formed with less than 5% yield in 2 h and 17% yield in 6 h. These results support the Kolbe oxidation mechanism. Interestingly, compound **7**, which was synthesized by adopting a procedure reported by Zeng,[16] can be converted to the cyclized product **2a** in a decent yield under the standard conditions (Scheme 6B). We proposed that compound **7** be oxidized at the anode first to deliver a radical cation. Homolytic cleavage of this radical cation affords the 2-phenylbenzoic acid radical and TEMPO cation. Compound **2a** can be formed by subsequent radical trapping and reoxidation either by TEMPO⁺ or the anode. At the cathode, reduction of TEMPO⁺ back to TEMPO and hydrogen evolution are two possible reactions to balance the overall transformation. To get more insight into this reaction, we have also performed two competitive reactions between **1a** and **5b** as well as **5b** and **1w**, respectively (Scheme 6C). It was shown that **5b** is predominantly oxidized when competing with **1a**, while **5b** and **1w** are equally oxidized to give **6b** and **2w** in a ca. 1:1 ratio. These competitive experiments demonstrated that the Kolbe oxidation of benzoic acid is not likely a rate-determining step.

■ CONCLUSION

In summary, we have developed a general, practical intramolecular Kolbe oxidative cyclization method for the synthesis of dibenzopyranones.[25] This method is oxidant-free, does not involve electrolytes, has high yields, works at ambient temperature, and is scalable. Urolithins are formally synthesized by adopting this method as a key step to demonstrate its synthetic utility.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise noted, chemicals and solvents were purchased with the highest purity grade available and

Scheme 5. Kolbe Oxidative Cyclization for the Synthesis of the Urolithin Family of Natural Products
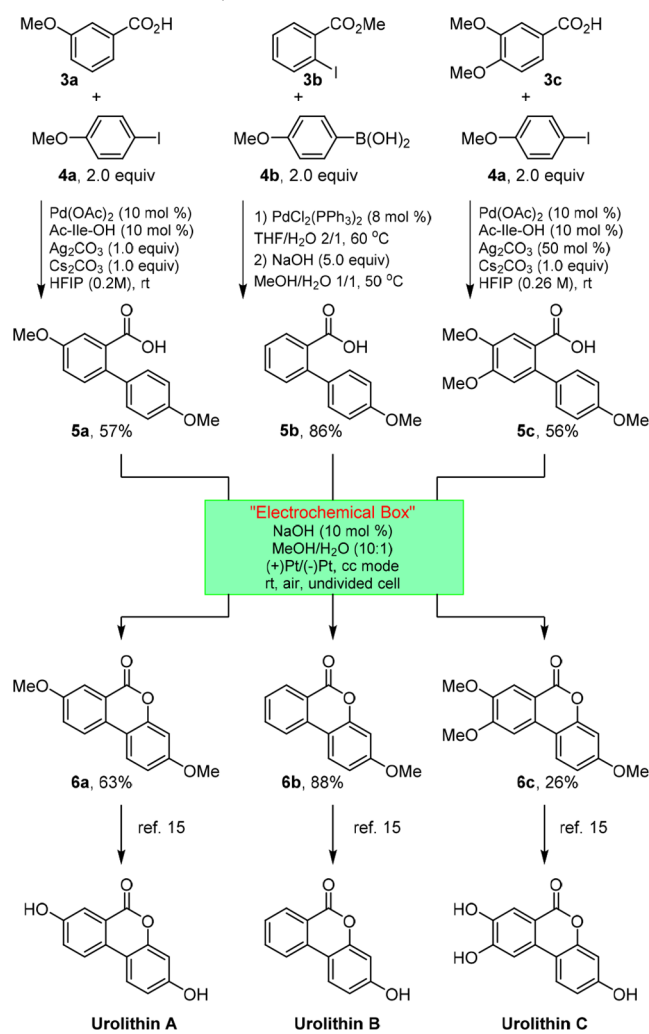

were used without further purification. Purification of products was conducted by column chromatography on silica gel (200−300 mesh, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (¹H at 400 MHz, ¹³C at 101 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as an internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), and coupling constants (J) were reported in hertz (Hz). Infrared spectra were recorded on a Thermal Fisher Nicolet iS50 Fourier transform spectrometer (FT-IR) and were reported in wave numbers (cm⁻¹). HRMS data were obtained on a VG ZAB-HS mass spectrometer and Bruker Apex IV FTMS spectrometer.

Characterization Data. *General Procedure for the Electrochemical Experiments.* A 15 mL test tube with a stir bar was charged with 0.5 mmol of 2-arylbenzoic acid **1**, followed by 3 mL of MeOH and 0.3 mL of an aqueous NaOH solution (0.167 M, 0.05 mmol). Two platinum net electrodes (1.0 cm × 1.0 cm) were set up in the tube, and the electrodes were totally immersed. The resulting mixture was electrolyzed at a constant current mode with a current of 23 mA under ambient temperature. The reaction was monitored by TLC or GC. Upon completion, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with PE/EA to give the desired product **2**.

General Procedure for the 10 Gram Scale Electrochemical Experiment. A 150 mL conical flask with a stir bar was charged with 60 mmol of 2-arylbenzoic acid **1a**, followed by 100 mL of MeOH and

Scheme 6. Control Experiments

A. Radical intercept experiment

B. Electrolysis of compound 7

C. Competitive reactions
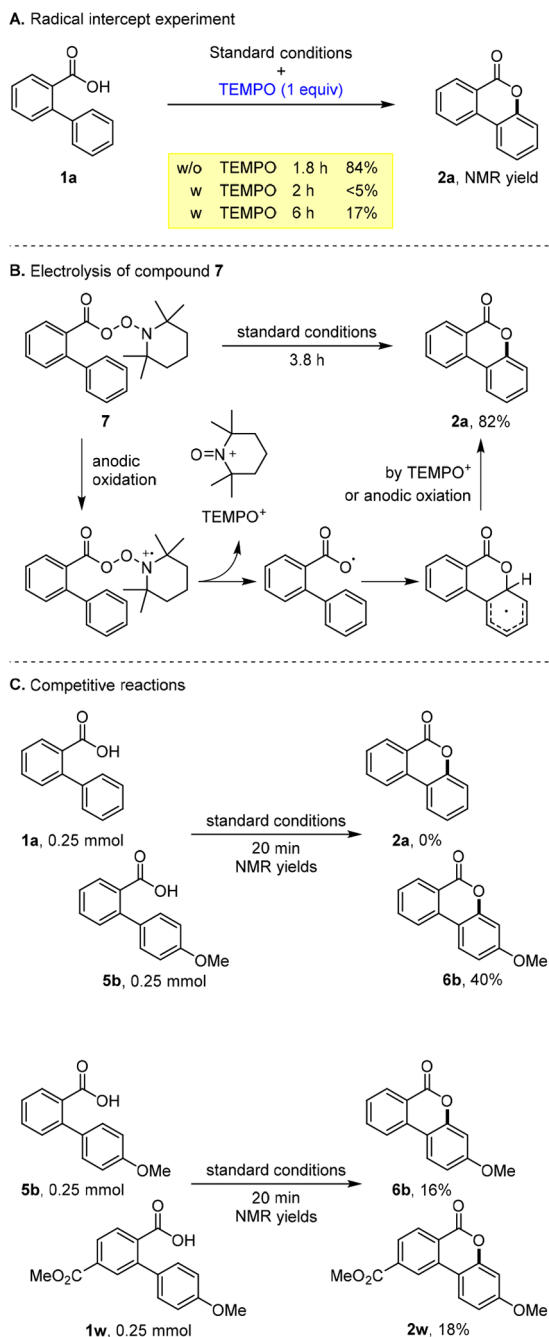
20 mL of an aqueous NaOH solution (0.3 M, 6 mmol). Two platinum net electrodes (1.5 cm × 1.0 cm) were set up in a conical flask, and the electrodes were totally immersed. The resulting mixture was electrolyzed at a constant potential mode with a potential of 60 V under ambient temperature. Note that the the reaction is exothermic. An ice water bath was used to maintain a reaction temperature between 15 and 30 °C. The reaction was monitored by TLC. Upon completion, the reaction mixture was poured into a saturated Na_2CO_3 aqueous solution. A large amount of solid product precipitated out. The solid product was filtered and washed by water. The residue was dried under heating and a vacuum to give the analytically pure product **2a**, 8.81 g, 75% yield.

Electrolysis of Compound 7. Compound **7** was synthesized by adopting a procedure reported by Zeng.[16] A 15 mL test tube with a stir bar was charged with 0.66 mmol of 2,2,6,6-tetramethylpiperidin-1-yl [1,1′-biphenyl]-2-carboperoxoate (**7**), followed by 3 mL of MeOH

and 0.3 mL of an aqueous NaOH solution (0.167 M, 0.05 mmol). Two platinum net electrodes (1.0 cm × 1.0 cm) were set up in the tube, and the electrodes were totally immersed. The resulting mixture was electrolyzed at a constant current mode with a current of 23 mA under ambient temperature. The reaction was monitored by TLC. After 3 h and 50 min, the reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with PE/EA to give the desired product **2a**, 106 mg, 82% yield.

6H-Benzo[c]chromen-6-one (2a).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 88% (86 mg); mp 90−91 °C (lit.[14e] 88−89 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.39 (d, 1H, J = 7.9 Hz), 8.10 (d, 1H, J = 8.1 Hz), 8.04 (d, 1H, J = 7.9 Hz), 7.81 (t, 1H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.7 Hz), 7.35 (d, 1H, J = 6.5 Hz), 7.33 (t, 1H, J = 8.1 Hz). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.1, 151.2, 134.8, 134.6, 130.4, 130.4, 128.8, 124.5, 122.7, 121.6, 121.1, 117.9, 117.6.

3-Methyl-6H-benzo[c]chromen-6-one (2b).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 90% (95 mg); mp 129−130 °C (lit.[16] 125−126 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (d, 1H, J = 7.9 Hz), 8.07 (d, 1H, J = 8.1 Hz), 7.93 (d, 1H, J = 8.0 Hz), 7.79 (dd, 1H, J = 3.9 Hz, J = 11.4 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.17 (s, 1H), 7.15 (d, 1H, J = 8.2 Hz), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.4, 151.3, 141.3, 135.0, 134.7, 130.6, 128.4, 125.6, 122.5, 121.4, 121.0, 117.9, 115.5, 21.4.

3-(Trifluoromethoxy)-6H-benzo[c]chromen-6-one (2c).[14g] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 86% (120 mg); mp 77−78 °C (lit.[17] 86−87 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.41 (dd, 1H, J = 7.9, 1.4 Hz), 8.09 (dd, 2H, J = 8.5, 2.3 Hz), 7.86 (ddd, 1H, J = 8.2, 7.3, 1.4 Hz), 7.62 (ddd, 1H, J = 8.2, 7.4, 1.1 Hz), 7.26−7.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.5, 151.8, 150.2, 135.2, 133.8, 130.8, 129.4, 124.2, 121.8, 120.9, 120.4 (q, J = 259 Hz), 117.0, 116.8, 110.2.

3-Phenyl-6H-benzo[c]chromen-6-one (2d).[14j] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 74% (100 mg); mp 84−86 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (dd, J = 7.9, 1.4 Hz, 1H), 8.13 (dd, J = 10.7, 8.5 Hz, 2H), 7.84 (td, J = 7.7, 1.4 Hz, 1H), 7.66 (d, J = 7.1 Hz, 2H), 7.63−7.56 (m, 3H), 7.49 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.2, 151.6, 143.4, 139.2, 134.8, 134.6, 130.6, 129.1, 128.8, 128.3, 127.0, 123.3, 123.2, 121.7, 121.1, 116.9, 115.7.

3-Acetyl-6H-benzo[c]chromen-6-one (2e).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 79% (94 mg); mp 189−191 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.46 (dd, J = 7.9, 1.4 Hz, 1H), 8.18 (t, J = 8.4 Hz, 2H), 7.97−7.92 (m, 2H), 7.90 (ddd, J = 8.2, 7.4, 1.4 Hz, 1H), 7.72−7.65 (m, 1H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 196.5, 160.6, 151.2, 138.4, 135.1, 133.7, 130.9, 130.1, 123.9, 123.2, 122.4, 122.0, 121.8, 118.0, 26.8.

Methyl 6-Oxo-6H-benzo[c]chromene-3-carboxylate (2f). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 90% (114 mg); mp 160−162 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.43 (dd, 1H, J = 7.9, 1.3 Hz), 8.17 (d, 1H, J = 8.1 Hz), 8.13 (d, 1H, J = 8.3 Hz), 7.99 (d, 2H, J = 7.6 Hz), 7.91−7.84 (m, 1H), 7.69−7.63 (m, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 165.8, 160.6, 151.0, 135.1, 133.7, 131.9, 130.8, 130.0, 125.3, 122.9, 122.4, 121.9, 121.8, 119.1, 52.6. IR: ν = 2948, 1735, 1717, 1606, 1304, 1267, 1097, 751 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{11}O_4^+$ [M + H]$^+$, 255.0652; found, 255.0646.

3-Bromo-6H-benzo[c]chromen-6-one (2g).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 77% (105 mg); mp 134−136 °C (lit.[16] 136−138 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.39 (dd, 1H, J = 8.0, 1.4 Hz), 8.11−8.04 (m, 1H), 7.91 (d, 1H, J = 8.5 Hz), 7.84 (ddd, 1H, J = 8.2, 7.4, 1.5 Hz), 7.61 (ddd, 1H, J = 8.2, 7.3, 1.1 Hz), 7.53 (d, 1H, J = 2.0 Hz), 7.46 (dd, 1H, J = 8.5, 2.0 Hz). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.5, 151.5, 135.1, 134.0, 130.8, 129.3, 127.9, 124.0, 123.7, 121.7, 121.0, 120.9, 117.1.

3-(Trifluoromethyl)-6H-benzo[c]chromen-6-one (2h).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 93% (123 mg); mp 127−129 °C (lit.[14e] 123.1−124.1 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.45 (d, 1H, J = 7.9 Hz), 8.18 (t, 2H, J = 8.1 Hz), 7.89 (t, 1H, J = 7.7 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.63 (s, 1H), 7.59 (d,

1H, J = 8.4 Hz). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.2, 151.0, 135.2, 133.4, 132.4, 132.1, 130.9, 130.1, 124.6, 123.6, 122.2, 122.0, 121.7, 121.2, 121.11, 121.08, 121.0, 115.3, 115.3, 115.24, 115.20.

3-(Allyloxy)-6H-benzo[c]chromen-6-one (2i).[14j] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 66% (83 mg); mp 93–94 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.31 (dd, 1H, J = 7.9, 1.3 Hz), 7.98–7.92 (m, 1H), 7.88 (d, 1H, J = 8.8 Hz, 1H), 7.75 (ddd, 1H, J = 8.4, 7.3, 1.5 Hz), 7.47 (ddd, 1H, J = 8.2, 7.3, 1.1 Hz), 6.90 (dd, 1H, J = 8.8, 2.6 Hz), 6.82 (d, 1H, J = 2.6 Hz), 6.06 (ddt, 1H, J = 17.3, 10.5, 5.3 Hz), 5.45 (dq, 1H, J = 17.2, 1.6 Hz), 5.34 (dq, 1H, J = 10.5, 1.4 Hz), 4.58 (dt, 2H J = 5.3, 1.6 Hz). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.4, 160.4, 152.5, 135.1, 134.8, 132.4, 130.5, 127.7, 123.7, 121.0, 119.9, 118.4, 112.9, 111.2, 102.5, 69.2.

1-Methyl-6H-benzo[c]chromen-6-one (2j).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 43% (45 mg); mp 159–161 °C (lit.[18] 161 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.50 (d, 1H, J = 7.9 Hz), 8.39 (d, 1H, J = 8.4 Hz), 7.83 (t, 1H, J = 7.8 Hz), 7.60 (t, 1H, J = 7.6 Hz), 7.36 (t, 1H, J = 7.8 Hz), 7.28 (d, 1H, J = 8.5 Hz), 7.17 (d, 1H, J = 7.4 Hz), 2.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.3, 152.2, 136.2, 136.1, 134.2, 130.8, 129.3, 128.8, 128.1, 126.2, 122.2, 117.5, 116.2, 25.5.

2-Methyl-6H-benzo[c]chromen-6-one (2k).[14g] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated 53 mg; mp 124–125 °C (lit.[19] 126–128 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.36 (d, 1H, J = 7.9 Hz), 8.05 (d, 1H, J = 8.1 Hz), 7.78 (m, 2H), 7.54 (t, 1H, J = 7.6 Hz), 7.23 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.3, 149.3, 134.8, 134.7, 134.1, 131.3, 130.5, 128.7, 122.7, 121.6, 121.2, 117.6, 117.4, 77.4, 77.1, 76.8, 21.1.

4-Methyl-6H-benzo[c]chromen-6-one (2k').[14g] Isolated 42 mg, white solid; mp 120–122 °C (lit.[19] 132–134 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.37 (d, 1H, J = 7.9 Hz), 8.07 (d, 1H, J = 8.1 Hz), 7.85 (d, 1H, J = 7.9 Hz), 7.78 (dt, 1H, J = 1.2 Hz, J = 7.8 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.30 (d, 1H, J = 7.3 Hz), 7.19 (t, 1H, J = 7.7 Hz), 2.47 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.2, 149.6, 135.1, 134.7, 131.8, 130.4, 128.6, 127.0, 124.0, 121.8, 121.1, 120.4, 117.6, 77.4, 77.1, 76.8, 16.0.

10-Methyl-6H-benzo[c]chromen-6-one (2l).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 46% (48 mg); mp 119–120 °C (lit.[14h] 122–124 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (d, J = 7.8 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 2.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 151.2, 139.1, 135.0, 133.6, 129.6, 129.2, 128.3, 127.2, 124.0, 122.8, 119.7, 118.0, 25.4.

9-Methyl-6H-benzo[c]chromen-6-one (2m).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 92% (97 mg); mp 84–86 °C (lit.[16] 86–88 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.26 (d, 1H, J = 8.1 Hz), 8.02 (dd, 1H, J = 7.9, 1.5 Hz), 7.91–7.85 (m, 1H), 7.46 (ddd, 1H, J = 8.5, 7.2, 1.6 Hz), 7.37 (ddd, 1H, J = 8.2, 1.6, 0.7 Hz), 7.35–7.33 (m, 1H), 7.33–7.29 (m, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.2, 151.4, 145.9, 134.6, 130.4, 130.2, 130.1, 124.4, 122.7, 121.8, 118.7, 118.0, 117.6, 22.2.

8-Methyl-6H-benzo[c]chromen-6-one (2n).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 90% (95 mg); mp 128–129 °C (lit.[16] 114–115 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (s, 1H), 7.99–7.87 (m, 2H), 7.56 (dd, J = 8.2, 2.1 Hz, 1H), 7.46–7.36 (m, 1H), 7.28 (t, J = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 150.9, 139.2, 136.0, 132.1, 130.2, 129.8, 124.4, 122.5, 121.6, 121.0, 118.1, 117.6, 21.3.

9-Methyl-3-pentyl-6H-benzo[c]chromen-6-one (2o).[14f] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 86% (120 mg); mp 60–61 °C (lit.[16] 61–63 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.24 (dd, 1H, J = 8.1, 2.1 Hz), 7.91 (dd, 1H, J = 8.0, 2.3 Hz), 7.83 (s, 1H), 7.33 (dt, 1H, J = 8.0, 1.5 Hz), 7.13 (dd, 2H, J = 9.6, 1.6 Hz), 2.68 (t, 2H, J = 7.7 Hz), 2.53 (s, 3H), 1.66 (m, 2H), 1.40–1.30 (m, 4H), 0.94–0.86 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.5, 151.5, 146.1, 145.8, 130.5, 129.6, 124.8, 122.4, 121.6, 118.4, 117.2, 115.6, 35.7, 31.4, 30.7, 22.5, 22.3, 14.0.

9-tert-Butyl-3-methoxy-6H-benzo[c]chromen-6-one (2p). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 91% (128

mg); mp 150–151 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.28 (d, 1H, J = 8.4 Hz), 7.99 (dd, 2H, J = 5.3, 3.5 Hz), 7.56 (dd, 1H, J = 8.4, 1.8 Hz), 6.92 (dd, 1H, J = 8.8, 2.6 Hz), 6.86 (d, 1H, J = 2.5 Hz), 3.88 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.6, 161.3, 158.8, 152.8, 134.9, 130.4, 125.7, 123.6, 117.5, 117.3, 112.4, 111.6, 101.6, 55.7, 35.6, 31.1. IR: ν = 2961, 2908, 1727, 1612, 1409, 1277, 1106, 1040, 776, 692 cm^{-1}. HRMS (ESI): calcd for C$_{18}$H$_{19}$O$_3^+$ [M + H]$^+$, 283.1329; found, 283.1329.

9-Chloro-3-methoxy-6H-benzo[c]chromen-6-one (2q).[20] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 85% (110 mg); mp 190–192 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.28 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.45 (dd, J = 8.5, 2.0 Hz, 1H), 6.93 (dd, J = 8.9, 2.6 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 162.1, 160.7, 153.0, 141.8, 136.7, 132.2, 128.1, 123.9, 121.1, 118.2, 112.7, 110.0, 101.7, 55.8.

8-Chloro-3-methoxy-6H-benzo[c]chromen-6-one (2r). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 83% (108 mg); mp 160–161 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.31 (d, J = 2.3 Hz, 1H), 7.94 (d, 1H, J = 8.6 Hz), 7.89 (d, 1H, J = 8.9 Hz), 7.72 (dd, J = 8.6, 2.3 Hz), 6.92 (dd, 1H, J = 8.8, 2.6 Hz), 6.86 (d, 1H, J = 2.6 Hz), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.8, 160.4, 152.5, 135.2, 133.6, 130.0, 123.8, 122.8, 121.2, 112.8, 110.4, 101.7, 55.8. IR: ν = 2939, 2839, 1728, 1623, 1604, 1474, 1263, 1168, 775 cm^{-1}. HRMS (ESI): calcd for C$_{14}$H$_{10}$ClO$_3^+$ [M + H]$^+$, 261.0313; found, 261.0312.

9-Bromo-3-methoxy-6H-benzo[c]chromen-6-one (2s). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 77% (117 mg); mp 188–190 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.18 (d, 1H, J = 8.5 Hz), 8.10 (d, 1H, J = 1.8 Hz), 7.84 (d, 1H, J = 8.9 Hz), 7.59 (dd, 1H, J = 8.5, 1.8 Hz), 6.90 (dd, 1H, J = 8.8, 2.6 Hz), 6.83 (d, 1H, J = 2.6 Hz), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 162.1, 160.8, 153.0, 136.7, 132.2, 131.0, 130.6, 124.2, 123.9, 118.6, 112.7, 109.9, 101.7, 55.8. IR: ν = 2918, 1731, 1625, 1600, 1590, 1277, 1169, 1034, 768 cm^{-1}. HRMS (ESI): calcd for C$_{14}$H$_{10}$BrO$_3^+$ [M + H]$^+$, 304.9808; found, 304.9809.

9-Fluoro-3-methoxy-6H-benzo[c]chromen-6-one (2t). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 77% (94 mg); mp 188–189 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 (dd, 1H, J = 8.8, 5.8 Hz), 7.84 (d, 1H, J = 8.9 Hz), 7.61 (dd, 1H, J = 9.9, 2.4 Hz), 7.19 (td, 1H, J = 8.5, 2.4 Hz), 6.92 (dd, 1H, J = 8.9, 2.6 Hz), 6.86 (d, 1H, J = 2.5 Hz), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 167.1 (d, J = 256.1 Hz), 162.1, 160.6, 153.1, 138.2 (d, J = 10.7 Hz), 133.9 (d, J = 10.3 Hz), 124.0, 116.4 (d, J = 2.5 Hz), 115.9 (d, J = 23.4 Hz), 112.7, 110.5 (d, J = 2.9 Hz), 107.4 (d, J = 23.5 Hz), 101.7, 55.8. IR: ν = 2957, 2849, 1746, 1614, 1600, 1278, 1267, 1193, 1099, 832, 619 cm^{-1}. HRMS (ESI): calcd for C$_{14}$H$_{10}$FO$_3^+$ [M + H]$^+$, 245.0608; found, 245.0607.

3-Methoxy-9-methyl-6H-benzo[c]chromen-6-one (2u). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 81% (97 mg); mp 155–157 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.24 (d, 1H, J = 8.1 Hz), 7.94 (dd, 1H, J = 8.9, 1.0 Hz), 7.79 (s, 1H), 7.36–7.29 (m, 1H), 6.91 (ddd, 1H, J = 8.8, 2.6, 0.7 Hz), 6.86 (dd, 1H, J = 2.6, 0.9 Hz), 3.88 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.6, 161.4, 152.8, 145.9, 135.2, 130.6, 129.1, 123.7, 121.2, 117.6, 112.3, 111.2, 101.6, 55.7, 22.3. IR: ν = 3007, 2943, 1736, 1616, 1279, 1265, 1198, 1038, 831, 771 cm^{-1}. HRMS (ESI): calcd for C$_{15}$H$_{13}$O$_3^+$ [M + H]$^+$, 241.0859; found, 241.0858.

3-Methoxy-6H-naphtho[2,3-c]chromen-6-one (2v). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 89% (123 mg); mp 181–183 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.90 (s, 1H), 8.32 (s, 1H), 8.03 (d, 1H, J = 8.8 Hz), 7.94 (dd, 2H, J = 12.7, 8.3 Hz), 7.63 (ddd, 1H, J = 8.3, 6.8, 1.3 Hz), 7.52 (ddd, 1H, J = 8.1, 6.8, 1.1 Hz), 6.91 (dd, 1H, J = 8.8, 2.6 Hz), 6.81 (d, 1H, J = 2.5 Hz), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.7, 161.2, 152.0, 136.4, 132.8, 131.8, 130.0, 129.5, 129.5, 127.8, 126.6, 123.9, 119.5, 118.5, 112.4, 111.3, 101.8, 55.6. IR: ν = 2841, 1728, 1628, 1301, 1288, 1273, 1165, 771, 470 cm^{-1}. HRMS (ESI): calcd for C$_{18}$H$_{13}$O$_3^+$ [M + H]$^+$, 277.0859; found, 277.0859.

Methyl 3-Methoxy-6-oxo-6H-benzo[c]chromene-9-carboxylate (2w). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 87% (123 mg); mp 128−130 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.68 (d, 1H, J = 1.5 Hz), 8.42 (d, 1H, J = 8.2 Hz), 8.10 (dd, 1H, J = 8.2, 1.5 Hz), 8.05 (d, 1H, J = 8.9 Hz), 6.96 (dd, 1H, J = 8.8, 2.6 Hz), 6.89 (d, 1H, J = 2.5 Hz), 4.02 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 166.0, 162.0, 160.8, 152.8, 135.7, 135.4, 130.9, 127.8, 124.2, 122.9, 122.8, 112.8, 110.7, 101.7, 55.8, 52.8. IR: ν = 2959, 1732, 1629, 1422, 1302, 1281, 1253, 1107, 1040, 751 cm^{-1}. HRMS (ESI): calcd for C$_{16}$H$_{13}$O$_5^+$ [M + H]$^+$, 285.0758; found, 285.0756.

9-Acetyl-3-methoxy-6H-benzo[c]chromen-6-one (2x). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 75% (100 mg); mp 220−222 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.56 (d, 1H, J = 1.5 Hz), 8.45 (d, 1H, J = 8.2 Hz), 8.05 (d, 1H, J = 8.9 Hz), 8.00 (dd, 1H, J = 8.2, 1.6 Hz), 6.96 (dd, 1H, J = 8.9, 2.6 Hz), 6.88 (d, 1H, J = 2.5 Hz), 3.90 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 197.4, 162.0, 160.7, 152.8, 141.6, 135.6, 131.2, 126.7, 124.1, 122.9, 121.0, 112.8, 110.7, 101.8, 55.8, 27.1. IR: ν = 3075, 2841, 1734, 1684, 1611, 1420, 1282, 1270, 1235, 1038 cm^{-1}. HRMS (ESI): calcd for C$_{16}$H$_{13}$O$_4^+$ [M + H]$^+$, 269.0808; found, 269.0808.

10H-Tribenzo[c,f,h]chromen-10-one (2y). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 62% (92 mg); mp 154−156 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.70 (dd, 1H, J = 3.4, 6.2 Hz), 8.67 (dd, 1H, J = 3.4, 6.2 Hz), 8.63 (d, 2H, J = 8.2 Hz), 8.55 (d, 1H, J = 8.3 Hz), 8.51 (d, 1H, J = 7.9 Hz), 7.86 (dt, 1H, J = 1.1, 7.7 Hz), 7.75 (m, 1H), 7.72 (dd, 1H, J = 5.7, 6.5 Hz), 7.66 (m, 2H), 7.62 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.2, 146.7, 135.5, 134.2, 131.3, 130.6, 128.9, 128.92, 128.89, 127.7, 127.6, 127.1, 126.5, 126.1, 126.0, 123.7, 123.1, 122.51, 122.49, 110.1. IR: ν = 3066, 1735, 1496, 1479, 1312, 1200, 1113, 1084, 763, 699 cm^{-1}. HRMS (ESI): calcd for C$_{21}$H$_{13}$O$_2^+$ [M + H]$^+$, 297.0910; found, 297.0909.

6H-Dibenzo[c,h]chromen-6-one (2z).[14g] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 90% (111 mg); mp 182−184 °C (lit.[14e] 181−182 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.61 (dd, 1H, J = 8.1, 1.7 Hz), 8.48 (dd, 1H, J = 7.9, 1.3 Hz), 8.21 (d, 1H, J = 8.1 Hz), 8.08 (d, 1H, J = 8.8 Hz), 7.88 (td, 2H, J = 7.6, 1.4 Hz), 7.78 (d, 1H, J = 8.7 Hz), 7.67−7.58 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.2, 147.2, 135.3, 134.9, 134.2, 130.6, 128.6, 127.8, 127.6, 127.1, 124.5, 123.8, 122.3, 122.0, 121.1, 119.1, 113.0.

5H-Thieno[2,3-c]isochromen-5-one (2aa). White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 55% (56 mg); mp 116−117 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.35 (dd, 1H, J = 0.6, 8.0 Hz), 7.80 (ddd, 1H, J = 1.3, 7.0, 8.3 Hz), 7.75 (m, 1H), 7.51 (ddd, 1H, J = 1.4, 7.1, 8.4 Hz), 7.31 (d, 1H, J = 5.9 Hz), 6.99 (d, 1H, J = 5.9 Hz). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.7, 156.1, 135.3, 134.4, 131.1, 127.6, 122.2, 119.2, 118.3, 117.0, 116.0. IR: ν = 2921, 2850, 1736, 1610, 1305, 1200, 1014, 710 cm^{-1}. HRMS (ESI): calcd for C$_{11}$H$_7$O$_2$S$^+$ [M + H]$^+$, 203.0161; found, 203.0161.

4,4′-Dimethoxybiphenyl-2-carboxylic Acid (5a). This compound was synthesized following the procedure as reported by Su.[21] Isolated yield: 57%; mp 155−156 °C (lit.[22] 156 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, J = 2.8 Hz, 1H), 7.29−7.19 (m, 3H), 7.08 (dd, J = 8.5, 2.8 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 173.5, 158.8, 158.3, 135.6, 133.1, 132.5, 130.0, 129.7, 118.6, 115.1, 113.6, 55.6, 55.3.

4′-Methoxybiphenyl-2-carboxylic acid (5b). This compound was synthesized following the procedure as reported by Wang.[14f] Isolated yield: 86%; mp 146−147 °C (lit.[23] 146−148 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (dd, J = 7.8, 1.4 Hz, 1H), 7.54 (td, J = 7.5, 1.5 Hz, 1H), 7.43−7.37 (m, 1H), 7.37−7.33 (m, 1H), 7.30−7.26 (m, 2H), 6.97−6.89 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 173.4, 159.1, 142.9, 133.4, 132.0, 131.2, 130.7, 129.7, 129.4, 126.9, 113.6, 55.3.

4,4′,5-Trimethoxybiphenyl-2-carboxylic acid (5c). This compound was synthesized following the procedure as reported by Su.[21] Isolated yield: 56%; mp 198−199 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52 (s, 1H), 7.24 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.76 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 172.4, 158.9, 151.9, 147.5, 138.3, 133.7, 129.8, 120.3, 114.0, 113.6, 113.4, 56.2, 56.1, 55.3.

3,8-Dimethoxy-6H-benzo[c]chromen-6-one (6a).[15] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 63% (81 mg); mp 147−148 °C (lit.[15] 156 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.93 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 2.8 Hz, 1H), 7.37 (dd, J = 8.8, 2.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.6 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.6, 160.7, 159.2, 151.7, 128.7, 124.5, 123.2, 122.8, 121.0, 112.4, 111.3, 111.0, 101.6, 55.8, 55.7.

3-Methoxy-6H-benzo[c]chromen-6-one (6b).[15] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 88% (99 mg); mp 128−130 °C (lit.[16] 133−135 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.34 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 6.90 (dd, J = 8.5, 2.0 Hz, 1H), 6.84 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.5, 161.4, 152.7, 135.2, 134.8, 130.6, 127.7, 123.8, 121.0, 120.0, 112.4, 111.2, 101.7, 55.7.

3,8,9-Trimethoxy-6H-benzo[c]chromen-6-one (6c).[15] White solid, using PE/EA (10:1 v/v) as an eluent. Isolated yield: 26% (37 mg); mp 176−177 °C (lit.[24] 178 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, J = 8.8 Hz, 1H), 7.68 (s, 1H), 7.31 (s, 1H), 6.89 (dd, J = 8.8, 2.6 Hz, 1H), 6.84 (d, J = 2.6 Hz, 1H), 4.08 (s, 3H), 3.99 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.4, 160.9, 155.2, 152.3, 149.3, 130.5, 123.1, 113.0, 112.3, 111.2, 110.4, 102.1, 101.5, 56.3, 56.2, 55.7.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00089.

Compound charts, equipment and experiment setup pictures, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) *Bioactive Heterocyclic Compound Classes: Agrochemicals*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012. (b) *Bioactive Heterocyclic Compound Classes: Pharmaceuticals*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2013.

(2) *Heterocyclic Chemistry*; Wiley-Blackwell: Hoboken, NJ, 2010.

(3) *Transition Metal-Catalyzed Heterocycle Synthesis via C–H Activation*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2016.

(4) (a) Moeller, K. D. *Tetrahedron* **2000**, *56*, 9527. (b) Jutand, A. *Chem. Rev.* **2008**, *108*, 2300. (c) Yoshida, J.-i.; Kataoka, K.; Horcajada, R.; Nagaki, A. *Chem. Rev.* **2008**, *108*, 2265. (d) Francke, R.; Little, R. D. *Chem. Soc. Rev.* **2014**, *43*, 2492. (e) Horn, E. J.; Rosen, B. R.; Baran, P. S. *ACS Cent. Sci.* **2016**, *2*, 302. (f) Jiang, Y.; Xu, K.; Zeng, C. *Chem. Rev.* **2017**. (g) Yan, M.; Kawamata, Y.; Baran, P. S. *Angew. Chem., Int. Ed.* **2017**. (h) Yan, M.; Kawamata, Y.; Baran, P. S. *Chem. Rev.* **2017**, *117*, 13230.

(5) For a seminal work, see: (a) Sutterer, A.; Moeller, K. D. *J. Am. Chem. Soc.* **2000**, *122*, 5636. For a recent article, see: (b) Redden, A.; Perkins, R. J.; Moeller, K. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12865. (c) Smith, J. A.; Moeller, K. D. *Org. Lett.* **2013**, *15*, 5818. (d) Campbell, J. M.; Smith, J. A.; Gonzalez, L.; Moeller, K. D. *Tetrahedron Lett.* **2015**, *56*, 3595.

(6) (a) Li, W.-C.; Zeng, C.-C.; Hu, L.-M.; Tian, H.-Y.; Little, R. D. *Adv. Synth. Catal.* **2013**, *355*, 2884. (b) Shih, Y.; Ke, C.; Pan, C.; Huang, Y. *RSC Adv.* **2013**, *3*, 7330. (c) Gao, W.-J.; Li, W.-C.; Zeng, C.-C.; Tian, H.-Y.; Hu, L.-M.; Little, R. D. *J. Org. Chem.* **2014**, *79*, 9613. (d) Singh, S.; Sharma, L. K.; Saraswat, A.; Srivastava, M. K.; Siddiqui, I. R.; Singh, R. K. P. *Chem. Heterocycl. Compd.* **2014**, *49*, 1508. (e) Xiao, H.-L.; Zeng, C.-C.; Tian, H.-Y.; Hu, L.-M.; Little, R. D. *J. Electroanal. Chem.* **2014**, *727*, 120. (f) Röse, P.; Emge, S.; Yoshida, J.-i.; Hilt, G. *Beilstein J. Org. Chem.* **2015**, *11*, 174. (g) Kang, L.-S.; Xiao, H.-l.; Zeng, C.-C.; Hu, L.-M.; Little, R. D. *J. Electroanal. Chem.* **2016**, *767*, 13.

(7) (a) Okimoto, M.; Yoshida, T.; Hoshi, M.; Hattori, K.; Komata, M.; Numata, K.; Tomozawa, K. *Heterocycles* **2006**, *68*, 2563. (b) Lee, D.-S. *Tetrahedron: Asymmetry* **2009**, *20*, 2014. (c) Okimoto, M.; Ohashi, K.; Yamamori, H.; Nishikawa, S.; Hoshi, M.; Yoshida, T. *Synthesis* **2012**, *44*, 1315.

(8) (a) Gieshoff, T.; Kehl, A.; Schollmeyer, D.; Moeller, K. D.; Waldvogel, S. R. *Chem. Commun.* **2017**, *53*, 2974. (b) Gieshoff, T.; Kehl, A.; Schollmeyer, D.; Moeller, K. D.; Waldvogel, S. R. *J. Am. Chem. Soc.* **2017**, *139*, 12317. (c) Xu, F.; Qian, X.-Y.; Li, Y.-J.; Xu, H.-C. *Org. Lett.* **2017**, *19*, 6332.

(9) (a) Kolbe, H. *Justus Liebigs Ann. Chem.* **1849**, *69*, 257. (b) Vijh, A. K.; Conway, B. E. *Chem. Rev.* **1967**, *67*, 623. (c) Schäfer, H.-J. Recent contributions of kolbe electrolysis to organic synthesis. In *Electrochemistry IV*; Steckhan, E., Ed.; Springer Berlin Heidelberg: Berlin, Germany, 1990; p 91. (d) Wang, Z. Kolbe Electrolysis. In *Comprehensive Organic Name Reactions and Reagents*; John Wiley & Sons, Inc.: 2010. (e) Tanaka, H.; Kuroboshi, M.; Torii, S. Oxidation of Carboxylic Acids and Derivatives. In *Organic Electrochemistry*, 5th Edition Revised and Expanded; Hammerich, O., Speiser, B., Eds.; CRC Press: Boca Raton, FL, 2015; p 1267.

(10) (a) Barton, D. H. R.; Lacher, B.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 4321. (b) Barton, D. H. R.; Ramesh, M. *Tetrahedron Lett.* **1990**, *31*, 949.

(11) (a) Bunyan, P. J.; Hey, D. H. *J. Chem. Soc.* **1960**, 3787. (b) Wilshire, J. *Aust. J. Chem.* **1963**, *16*, 432. (c) Koyama, K.; Yoshida, K.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 516.

(12) (a) Ishiguro, K.; Yamaki, M.; Kashihara, M.; Takagi, S.; Isoi, K. *Phytochemistry* **1990**, *29*, 1010. (b) Koch, K.; Podlech, J.; Pfeiffer, E.; Metzler, M. *J. Org. Chem.* **2005**, *70*, 3275. (c) Weissman, K. *Chem. Biol.* **2005**, *12*, 512. (d) Tibrewal, N.; Pahari, P.; Wang, G.; Kharel, M. K.; Morris, C.; Downey, T.; Hou, Y.; Bugni, T. S.; Rohr, J. *J. Am. Chem. Soc.* **2012**, *134*, 18181. (e) Lazo, J. S.; Sharlow, E. R.; Epperly, M. W.; Lira, A.; Leimgruber, S.; Skoda, E. M.; Wipf, P.; Greenberger, J. S. *J. Pharmacol. Exp. Ther.* **2013**, *347*, 669.

(13) (a) Edwards, J. P.; West, S. J.; Marschke, K. B.; Mais, D. E.; Gottardis, M. M.; Jones, T. K. *J. Med. Chem.* **1998**, *41*, 303. (b) Ku, Y.-Y.; Grieme, T.; Raje, P.; Sharma, P.; King, S. A.; Morton, H. E. *J. Am. Chem. Soc.* **2002**, *124*, 4282. (c) Schmidt, J. M.; Tremblay, G. B.; Pagé, M.; Mercure, J.; Feher, M.; Dunn-Dufault, R.; Peter, M. G.; Redden, P. R. *J. Med. Chem.* **2003**, *46*, 1289. (d) Abe, H.; Nishioka, K.; Takeda, S.; Arai, M.; Takeuchi, Y.; Harayama, T. *Tetrahedron Lett.* **2005**, *46*, 3197. (e) Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. *Science* **2005**, *310*, 80. (f) Sun, W.; Cama, L. D.; Birzin, E. T.; Warrier, S.; Locco, L.; Mosley, R.; Hammond, M. L.; Rohrer, S. P. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 1468.

(14) (a) Glover, S. A.; Golding, S. L.; Goosen, A.; McCleland, C. W. *J. Chem. Soc., Perkin Trans. 1* **1981**, 842. (b) Togo, H.; Muraki, T.; Yokoyama, M. *Tetrahedron Lett.* **1995**, *36*, 7089. (c) Togo, H.; Muraki, T.; Hoshina, Y.; Yamaguchi, K.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 787. (d) Muraki, T.; Togo, H.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1713. (e) Gallardo-Donaire, J.; Martin, R. *J. Am. Chem. Soc.* **2013**, *135*, 9350. (f) Li, Y.; Ding, Y.-J.; Wang, J.-Y.; Su, Y.-M.; Wang, X.-S. *Org. Lett.* **2013**, *15*, 2574. (g) Wang, Y.; Gulevich,

A. V.; Gevorgyan, V. *Chem. - Eur. J.* **2013**, *19*, 15836. (h) Gao, P.; Wei, Y. *Synthesis* **2014**, *46*, 343. (i) Wang, X.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 11084. (j) Dai, J.-J.; Xu, W.-T.; Wu, Y.-D.; Zhang, W.-M.; Gong, Y.; He, X.-P.; Zhang, X.-Q.; Xu, H.-J. *J. Org. Chem.* **2015**, *80*, 911. (k) Ramirez, N. P.; Bosque, I.; Gonzalez-Gomez, J. C. *Org. Lett.* **2015**, *17*, 4550. (l) Yang, Q.; Jia, Z.; Li, L.; Zhang, L.; Luo, S. *Org. Chem. Front.* **2018**, *5*, 237. (m) Zhang, M.; Ruzi, R.; Li, N.; Xie, J.; Zhu, C. *Org. Chem. Front.* **2018**.

(15) Nealmongkol, P.; Tangdenpaisal, K.; Sitthimonchai, S.; Ruchirawat, S.; Thasana, N. *Tetrahedron* **2013**, *69*, 9277.

(16) Zhang, S.; Li, L.; Wang, H.; Li, Q.; Liu, W.; Xu, K.; Zeng, C. *Org. Lett.* **2018**, *20*, 252.

(17) Zhang, J.; Shi, D.; Zhang, H.; Xu, Z.; Bao, H.; Jin, H.; Liu, Y. *Tetrahedron* **2017**, *73*, 154.

(18) Grundmann, C.; Litten, E. *Chem. Ber.* **1952**, *85*, 261.

(19) Suarez-Meneses, J. V.; Oukhrib, A.; Gouygou, M.; Urrutigoity, M.; Daran, J. C.; Cordero-Vargas, A.; Ortega-Alfaro, M. C.; Lopez-Cortes, J. G. *Dalton Trans.* **2016**, *45*, 9621.

(20) Hart, D. J.; Kim, A.; Krishnamurthy, R.; Merriman, G. H.; Waltos, A.-M. *Tetrahedron* **1992**, *48*, 8179.

(21) Zhu, C. L.; Zhang, Y. F.; Kan, J.; Zhao, H. Q.; Su, W. P. *Org. Lett.* **2015**, *17*, 3418.

(22) Horner, L.; Baston, D. W. *Justus Liebigs Ann. Chem.* **1973**, *1973*, 910.

(23) Brown, P. M.; Russell, J.; Thomson, R. H.; Wylie, A. G. *J. Chem. Soc. C* **1968**, 842.

(24) Young, D. A.; Ferreira, D.; Roux, D. G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2031.

(25) While the manuscript was under preparation, a similar work was reported; see ref 16.