

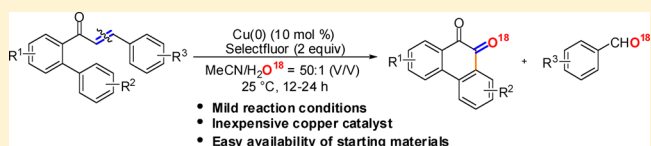
# Copper(0)/Selectfluor System-Promoted Oxidative Carbon–Carbon Bond Cleavage/Annulation of *o*-Aryl Chalcones: An Unexpected Synthesis of 9,10-Phenanthraquinone Derivatives

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## Supporting Information

**ABSTRACT:** A general and efficient protocol for the synthesis of 9,10-phenanthraquinone derivatives has been successfully developed involving a copper(0)/Selectfluor system-promoted oxidative carbon–carbon bond cleavage/annulation of *o*-aryl chalcones. A variety of substituted 9,10-phenanthraquinones were synthesized in moderate to good yields under mild reaction conditions.



## INTRODUCTION

The 9,10-phenanthraquinone scaffold is often seen in some natural, metabolic, or synthetic products which display unique biological activities.<sup>1</sup> Besides, 9,10-phenanthraquinones can serve as useful intermediates for the preparation of many biologically interesting compounds<sup>2</sup> as well as functional molecules in materials science.<sup>3</sup> Thus, the development of efficient methods for the preparation of 9,10-phenanthraquinones is highly desirable. Traditionally, 9,10-phenanthraquinones are synthesized through oxidation of phenanthrenes with a variety of oxidants.<sup>4,5</sup> Alternative methods include oxidation of several phenanthrene-originated substrates such as 9,10-dihydrophenanthrenes,<sup>6</sup> 10-hydroxyphenanthren-9(10H)-ones,<sup>7</sup> 9-phenanthrenols,<sup>8</sup> and phenanthrene-9,10-diol.<sup>9</sup> However, most of these oxidative reactions suffer from one or more limitations such as the use of expensive catalysts, the employment of toxic oxidants, and lack of generality. In addition, the construction of the 9,10-phenanthraquinone scaffold from nonphenanthrene-based precursors, e.g. 2-acetylbiphenyls,<sup>10</sup> dimethyl biphenyl-2,2'-dicarboxylate,<sup>11</sup> benzils,<sup>12</sup> benzoin, <sup>13</sup> biaryloxalic acids,<sup>14</sup> or 2,2'-dilithiobiphenyl,<sup>15</sup> has also been reported. Despite their merits, most of these methods have several drawbacks such as a narrow scope of substrates, multistep processes, and low yields. Overall, to date, general and efficient methods enabling the synthesis of different substituted 9,10-phenanthraquinones remain very limited.<sup>12d,e,14</sup> Herein we describe a general and efficient method to access a range of substituted 9,10-phenanthraquinones through a copper(0)/Selectfluor system-promoted oxidative carbon–carbon bond cleavage/annulation of *o*-aryl chalcones under mild reaction conditions (Scheme 1).<sup>16</sup>

As part of our ongoing effort to develop mild and efficient catalyst systems for the construction of useful molecules,<sup>17</sup> we have recently disclosed that the combination of copper powder and Selectfluor (1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), F-TEDA-BF<sub>4</sub>) may gen-

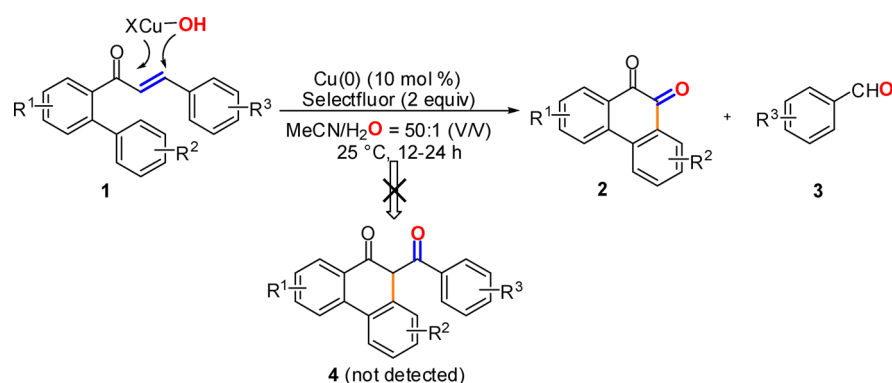
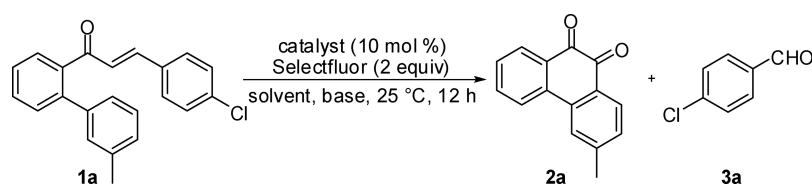
erate an active XCuOH species (X = F or BF<sub>4</sub>) which is easily able to undergo oxycupration toward carbon–carbon multiple bonds and induce successive tandem reactions.<sup>18</sup> For example, we have successfully achieved oxidative annulation of 1,5- and 1,6-enynes by the Cu(0)/Selectfluor system to access 3-formyl-1-indenones<sup>18b</sup> and fluorinated fluorenones,<sup>18c</sup> respectively. Inspired by these findings, we envisioned that the oxycupration of the C–C double bond in *o*-aryl chalcone **1** by the Cu(0)/Selectfluor system followed by a dehydrogenative cross-coupling and an oxidation of the hydroxy group would result in the formation of annulated products **4**. To our surprise, the desired products **4** were not obtained whereas 9,10-phenanthraquinones **2** were unexpectedly formed in moderate to good yields (Scheme 1).

## RESULTS AND DISCUSSION

Initially, chalcone **1a** was selected as the model substrate for the optimization of reaction conditions (Table 1; also see the Supporting Information). When **1a** was treated with Cu(0) powder (5 mol %) and Selectfluor (2.0 equiv) in acetonitrile at 25 °C for 12 h, 3-methylphenanthrene-9,10-dione **2a** was obtained in 70% yield along with the formation of aldehyde **3a** (entry 1, Table 1). It was found that base additives had no positive effect on the yield of **2a** (entries 2–5, Table 1). The reaction gave a better yield of **2a** in the presence of 10 mol % of Cu(0) powder (75%, entry 6, Table 1). Solvent screening experiments indicated that a combined CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v) solvent system proved to be the most suitable medium for the reaction (entries 6, 8–10 vs 7, Table 1). The catalytic activity of a series of copper(I) and copper(II) salts were investigated for the reaction, and it was found that their catalytic performances were inferior to that of Cu(0) powder

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Scheme 1. Unexpected Synthesis of 9,10-Phenanthraquinones via the Cu(0)/Selectfluor System-Promoted Annulation of *o*-Aryl Chalcones 1Table 1. Optimization of Reaction Conditions<sup>a</sup>

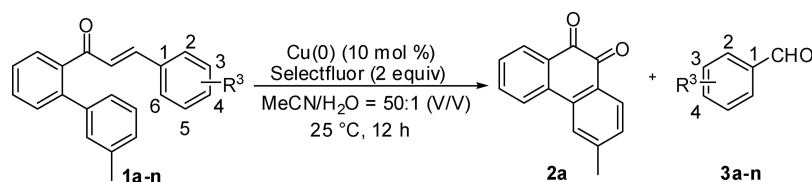
entry	catalyst	oxidant	base	solvent	yield of <b>2a</b> (%) <sup>b</sup>
1	Cu(0) <sup>c</sup>	Selectfluor	–	CH <sub>3</sub> CN	70
2	Cu(0) <sup>c</sup>	Selectfluor	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	68
3	Cu(0) <sup>c</sup>	Selectfluor	NaHCO <sub>3</sub>	CH <sub>3</sub> CN	64
4	Cu(0) <sup>c</sup>	Selectfluor	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	67
5	Cu(0) <sup>c</sup>	Selectfluor	K <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> CN	57
6	Cu(0)	Selectfluor	–	CH <sub>3</sub> CN	75
7	Cu(0)	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	80
8	Cu(0)	Selectfluor	–	acetone	0
9	Cu(0)	Selectfluor	–	methanol	0
10	Cu(0)	Selectfluor	–	DMF	0
11	CuBr	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	64
12	CuI	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	57
13	CuCl	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	55
14	CuCl <sub>2</sub>	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	60
15	Cu(OAc) <sub>2</sub>	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	50
16	Cu(0)	NFSI <sup>d</sup>	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	50
17	Cu(0)	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	40, <sup>e</sup> 62 <sup>f</sup>
18	–	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	0
19	Cu(0) <sup>g</sup>	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	69
20	Cu	Selectfluor	–	CH <sub>3</sub> CN/H <sub>2</sub> O = 50:1	55 <sup>h</sup>

<sup>a</sup>Reaction conditions: **1a** (0.3 mmol), Cu(0) powder (10 mol % based on **1a**), oxidant (2.0 equiv), solvent (3.0 mL), 25 °C for 12 h unless otherwise noted. <sup>b</sup>Isolated yield. <sup>c</sup>In the presence of 5 mol % of Cu(0) powder. <sup>d</sup>NFSI: *N*-fluorobenzenesulfonimide. <sup>e</sup>The amount of Selectfluor is 1.0 equiv. <sup>f</sup>The amount of Selectfluor is 3.0 equiv. <sup>g</sup>In the presence of 20 mol % of Cu(0) powder. <sup>h</sup>The reaction was conducted in 50 °C.

(entries 11–15 vs 7, Table 1). Among several fluorinating agents screened, Selectfluor showed the most effectiveness for the formation of **2a** (entry 16 vs 7; also see the Supporting Information). Note that the use of 2 equiv of Selectfluor is sufficient for the reaction, as excessive or deficient use of Selectfluor would lead to a lower yield of **2a** (entry 17 vs 7, Table 1). Controlled experiments showed that the reaction failed to produce **2a** in the absence of Cu(0) powder (entry 18, Table 1). Increasing the amount of Cu(0) powder (20 mol %) or the reaction temperature (50 °C) only resulted in a lower yield of **2a** (entries 19, 20, Table 1).

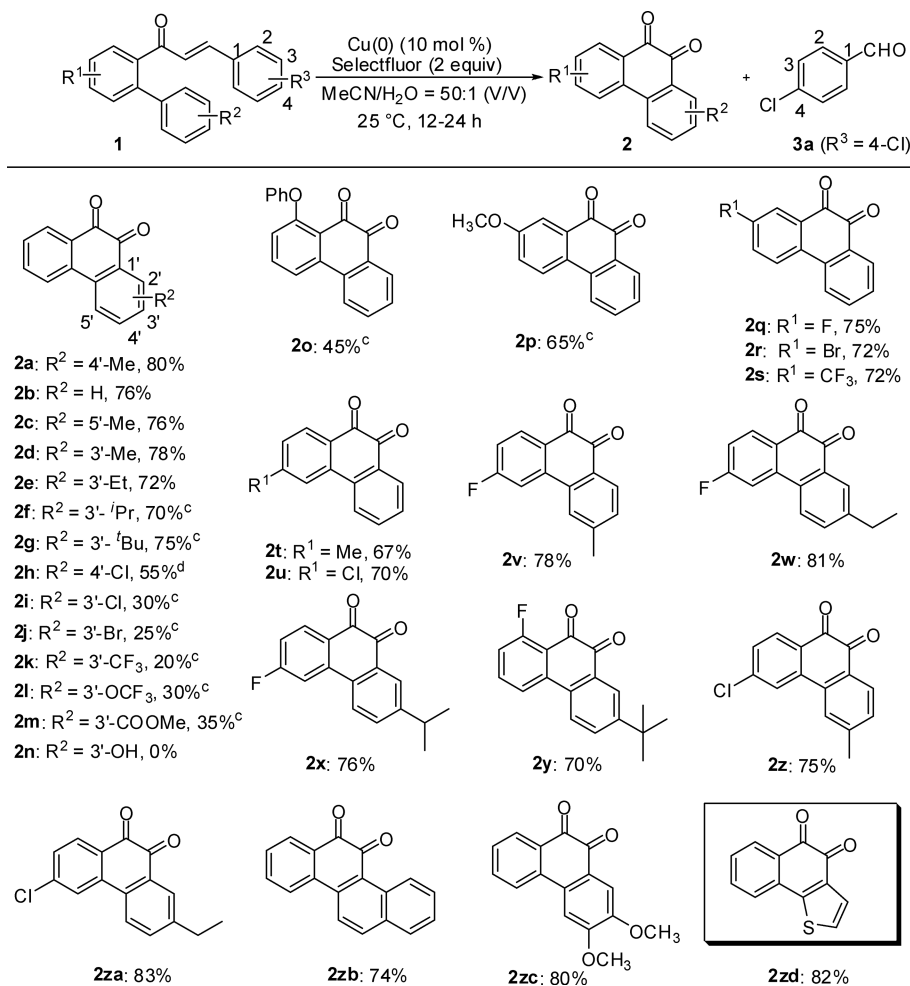
To make the reaction synthetically valuable, we further set out to investigate the effect of different benzylidene moieties in

chalcone **1a–n** on the formation of **2a** under the above optimized reaction conditions (Table 2). It was found that chalcone **1a–n** bearing benzylidene moieties substituted with electron-withdrawing groups generally reacted more smoothly and gave higher yields of **2a** than those substituted with electron-donating or electron-neutral groups (entries 2–6 vs 8 and 9, Table 2). To our surprise, chalcone **1a-6** possessing a 4-nitrobenzylidene moiety only afforded **2a** in 45% yield due to the formation of an unidentified byproduct (entry 7, Table 2). So far, chalcone **1a** bearing a 4-chlorobenzylidene moiety has proven to be the most suitable substrate for the formation of **2a** (entries 2–9 vs 1, Table 2).

Table 2. Investigation of the Effect of Different Benzylidene Moieties in 1a–n on the Formation of 2a<sup>a</sup>

entry	R <sup>3</sup> (1a–n)	aldehyde (3a–n)	yield of 2a (%) <sup>b</sup>
1	4-Cl (1a)	3a	80
2	2-Cl (1a-1)	3a-1	66
3	3-Cl (1a-2)	3a-2	60
4	4-Br (1a-3)	3a-3	61
5	3,5-dichloro (1a-4)	3a-4	65
6	2,6-dichloro (1a-5)	3a-5	63
7	4-NO <sub>2</sub> (1a-6)	3a-6	45
8	4-CH <sub>3</sub> (1a-7)	3a-7	32
9	H (1a-8)	3a-8	60

<sup>a</sup>Reaction conditions: **1a–n** (0.3 mmol), Cu(0) powder (10 mol % based on **1a–n**), Selectfluor (2.0 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (V/V) (3.0 mL), 25 °C for 12 h. <sup>b</sup>Isolated yield.

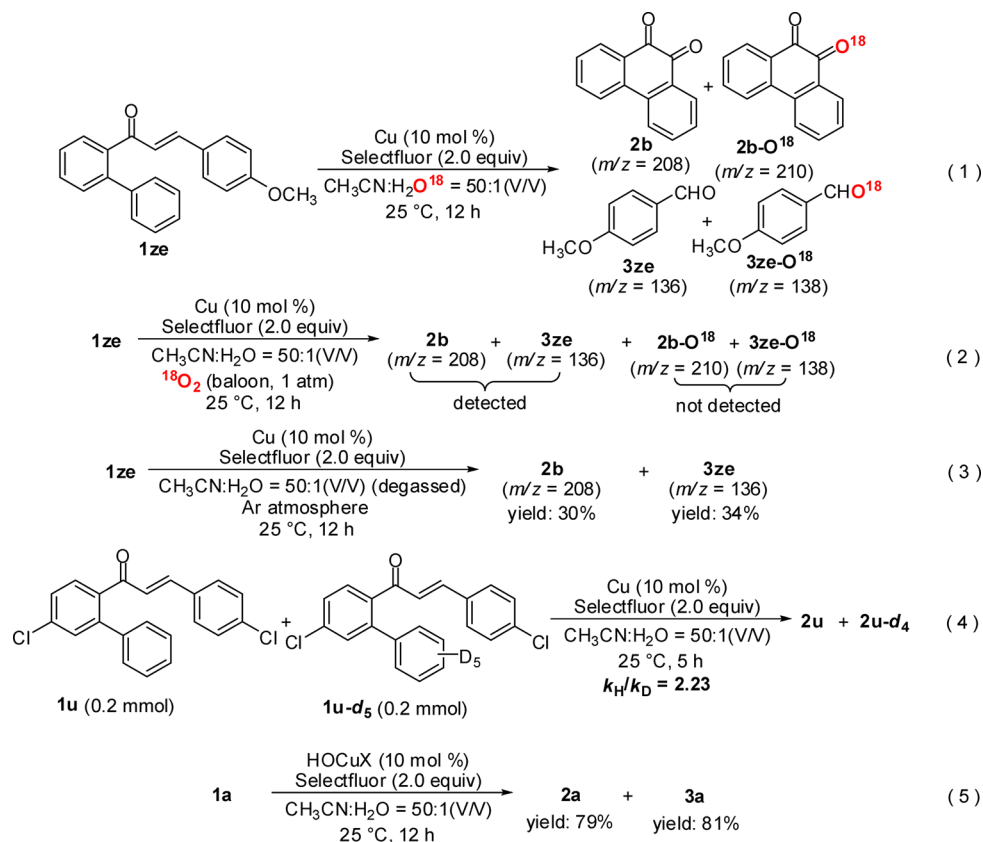
Table 3. Cu(0)/Selectfluor System-Promoted Oxidative Annulation of Chalcones **1** for the Synthesis of 2<sup>a,b</sup>

<sup>a</sup>Reaction conditions: **1** (0.3 mmol), Cu(0) powder (10 mol % based on **1**), Selectfluor (2.0 equiv), CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v) (3.0 mL), 25 °C for 12 h unless otherwise noted. <sup>b</sup>Isolated yield. <sup>c</sup>The reaction time is 24 h. <sup>d</sup>The reaction time is 18 h.

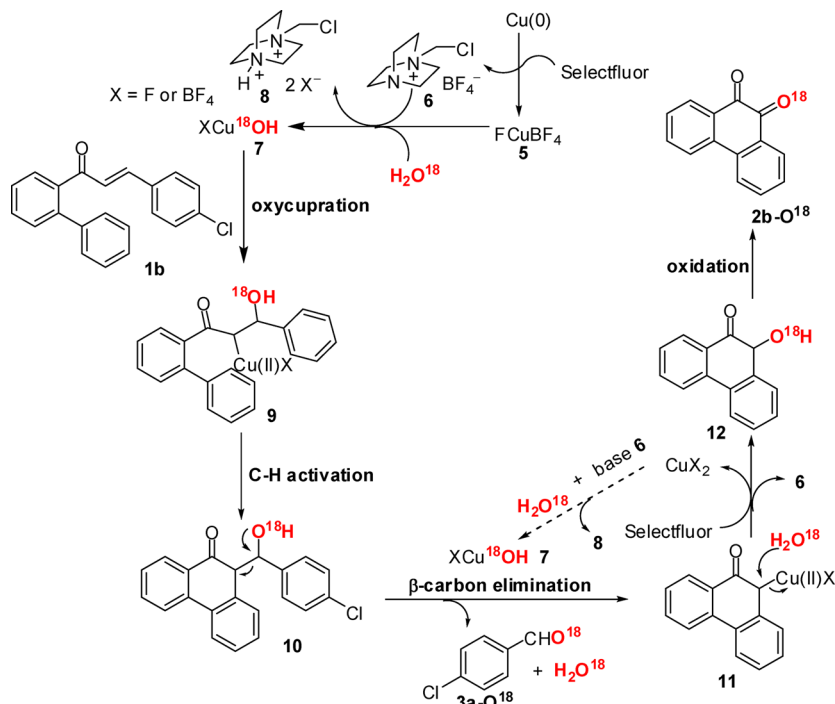
With the optimized reaction conditions and design ideas for substrates in hand, the exploration of the present protocol for the oxidative annulation of a range of *o*-aryl chalcones **1** was then carried out (Table 3). As shown in Table 3, both electron-

donating and -withdrawing substituents in the aryl ring of **1** were compatible with the reaction conditions, among which include methyl, ethyl, methoxy, isopropyl, *tert*-butyl, phenoxy, halo (F, Cl, Br), trifluoromethyl, trifluoromethoxy, and ester

Scheme 2. Preliminary Mechanistic Studies



Scheme 3. Proposed Mechanism for the Oxidative Annulation of 1b



groups. It was found that the electronic nature of  $R^2$  had a significant effect on the reaction outcome in terms of the yield. For instance, substrates bearing electron-rich substituents  $R^2$  (e.g., methyl, ethyl, isopropyl, and *tert*-butyl; **1a**, **1c–1g**, **1v–1za**, **1zc**, Table 3) reacted more smoothly and gave higher

yields of products than those bearing electron-deficient substituents  $R^2$  (e.g., Cl, Br;  $CF_3$ ,  $OCF_3$ , and  $COOMe$ , **1h–1m**, Table 3). In contrast, it seemed that the electronic property of  $R^1$  had a lesser effect on the reaction outcome than  $R^1$  did (**1p**, **1t** vs **1q–1s**, **1u**, Table 3). For substrate **1f–1p**

(except **1n**), the reaction required a prolonged time (18–24 h) in order to deliver a better yield of products. When substrate **1n** bearing a phenolic hydroxy group was used, the reaction gave complicated products and the desired product **2n** was not detected. Interestingly, naphtho[1,2-*b*]thiophene-4,5-dione **2zd**, a potential inhibitor of the protein tyrosine phosphatase (PTP) CD45,<sup>1g</sup> could also be successfully synthesized from chalcone **1zd** in 82% yield (Table 3).

To gain insight into the mechanism of the oxidative carbon–carbon cleavage/annulation of *o*-aryl chalcones, several mechanistic experiments were carried out (Scheme 2). When **1ze** was subjected to the standard reaction conditions except using a CH<sub>3</sub>CN/H<sub>2</sub>O<sup>18</sup> = 50:1 (v/v) solvent system, both the <sup>18</sup>O-incorporated products **2b-O<sup>18</sup>** and **3ze-O<sup>18</sup>** were detected (eq 1, Scheme 2; also see the Supporting Information).<sup>18b,19</sup> In contrast, when **1ze** reacted under the standard reaction conditions in the presence of an <sup>18</sup>O<sub>2</sub> atmosphere, both **2b** and **3ze** were normally formed while **2b-O<sup>18</sup>** and **3ze-O<sup>18</sup>** were not detected (eq 2, Scheme 2). An attempt to run the reaction of **1ze** in a degassed solvent system under an Ar atmosphere also successfully delivered **2b** and **3ze** in 30% and 34% yield, respectively (eq 3, Scheme 2). These results unambiguously disclosed that the incorporated oxygen atoms in **2b** and **3ze** originated from water rather than dioxygen. In addition, the measurement of the intermolecular KIE between **1u** and **1u-d<sub>5</sub>** on the basis of the competitive dehydrogenative cross-coupling was carried out. The intermolecular *k<sub>H</sub>*/*k<sub>D</sub>* of **1u** to **1u-d<sub>5</sub>** was determined to be 2.23 (eq 4, Scheme 2; also see the Supporting Information), suggesting that the cleavage of the C–H bond is the rate-determining step. Note that the reaction of **1a** could also proceed smoothly and give **2a** and **3a** in 79% and 81% yield, respectively, by using the preparative HOCuX (X = F or BF<sub>4</sub>)<sup>18a</sup> as a catalyst (eq 5, Scheme 2). This result suggests that HOCuX (X = F or BF<sub>4</sub>) may be the real catalyst in the catalytic cycle.

On the basis of the above experiments and previous literature,<sup>7,18,20–22</sup> a proposed mechanism for the Cu(0)/Selectfluor system-promoted oxidative annulation of **1b** is described in Scheme 3. First, the redox reaction between copper powder and Selectfluor may generate a copper species **5** and release a base **6**.<sup>18</sup> In our previous work,<sup>18</sup> we have disclosed that **5** may be transferred into a copper species **7** in the presence of H<sub>2</sub>O<sup>18</sup> with the aid of the base **6**. Then, an oxycupration of **7** to the C–C double bond<sup>18b,c</sup> in **1b** followed by a dehydrogenative cross-coupling<sup>20</sup> would deliver an intermediate **10**. Intermediate **10** might undergo β-carbon elimination<sup>18b,21</sup> in the presence of **7** to produce an intermediate **11** and an aldehyde **3a-O<sup>18</sup>**. Furthermore, intermediate **11** might undergo an oxidative substitution reaction with H<sub>2</sub>O<sup>18</sup> to form an intermediate **12** followed by the regeneration of **7** in the presence of Selectfluor.<sup>18,22,23</sup> Finally, intermediate **12** may be transferred into **2b-O<sup>18</sup>** under the oxidative reaction conditions.<sup>7</sup>

## CONCLUSION

In summary, we have developed a general and efficient method for the construction of 9,10-phenanthraquinone derivatives involving a Cu(0)/Selectfluor system-promoted oxidative carbon–carbon cleavage/annulation of *o*-aryl chalcones. The present method for the synthesis of 9,10-phenanthraquinones has characteristic advantages of mild reaction conditions, an inexpensive catalyst, and good generality for construction of a range of substituted 9,10-phenanthraquinones.

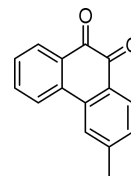
## EXPERIMENTAL SECTION

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. Melting points are uncorrected. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a spectrometer at 25 °C in CDCl<sub>3</sub> at 500 MHz (or 400 MHz) and 125 MHz (or 100 MHz), respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm, and coupling constants *J* are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with an EI source; high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with an EI or ESI source. CH<sub>3</sub>CN is dehydrated by CaH<sub>2</sub> before preparation of the combined solvent CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v).

**Preparation of the Starting Material *o*-Aryl Chalcones 1.** All *o*-aryl chalcones (**1**) were synthesized from the corresponding *o*-aryl acetophenones and benzaldehydes according to the literature procedure.<sup>24</sup> The *o*-aryl acetophenones were synthesized by the standard Suzuki–Miyaura cross-coupling reaction between an *ortho*-bromoacetophenone derivative and an arylboronic acid.<sup>25</sup>

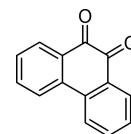
**Typical Experimental Procedure for the Synthesis of 9,10-Phenanthraquinones 2.** **1** (0.3 mmol), Cu(0) powder (1.92 mg, 10 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and a combined CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v) solvent (3 mL) were added to a 10 mL flask. Then the reaction mixture was stirred at 25 °C for 12 h. Upon completion, the resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure **2**.

**3-Methylphenanthrene-9,10-dione (2a).**<sup>26</sup> Yellow solid (53.3 mg, 80%), *R<sub>f</sub>* = 0.27 (petroleum ether–EtOAc, 6:1); mp 216–217 °C



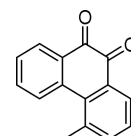
(lit.<sup>26</sup> mp 208–210 °C); IR (neat):  $\nu = 1672$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.05–8.03 (m, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.61–7.57 (m, 1H), 7.37–7.33 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 179.5, 178.7, 148.4, 134.8, 134.7, 130.0, 129.6, 129.4, 129.3, 128.4, 127.8, 123.5, 122.8, 21.3; HRMS (EI) for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>: calcd 222.0681, found 222.0685.

**Phenanthrene-9,10-dione (2b).**<sup>27</sup> Yellow solid (47.5 mg, 76%), *R<sub>f</sub>* = 0.26 (petroleum ether–EtOAc, 6:1); mp 218–220 °C (lit.<sup>27</sup> mp



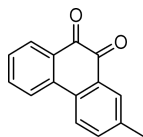
217–219 °C); IR (neat):  $\nu = 1673$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.17–8.15 (m, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.73–7.68 (m, 2H), 7.48–7.44 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 180.3, 136.0, 135.8, 131.0, 130.5, 129.6, 124.0; HRMS (EI) for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>: calcd 208.0524, found 208.0518.

**4-Methylphenanthrene-9,10-dione (2c).**<sup>28</sup> Yellow solid (50.7 mg, 76%), *R<sub>f</sub>* = 0.28 (petroleum ether–EtOAc, 6:1); mp 145–146 °C



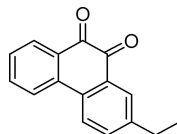
(lit.<sup>28</sup> mp 167 °C); IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.18–8.16 (m, 1H), 8.07 (d,  $J = 8.0$  Hz, 1H), 8.00 (d,  $J = 7.5$  Hz, 1H), 7.79 (s, 1H), 7.72–7.69 (m, 1H), 7.48–7.44 (m, 1H), 7.26 (d,  $J = 8.5$  Hz, 1H), 2.51 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  180.6, 179.9, 147.4, 136.0, 135.8, 131.2, 130.8, 130.5, 130.4, 129.5, 129.2, 129.0, 124.6, 123.9, 22.4; HRMS (EI) for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ : calcd 222.0681, found 222.0686.

**2-Methylphenanthrene-9,10-dione (2d).**<sup>29</sup> Yellow solid (52.0 mg, 78%),  $R_f = 0.27$  (petroleum ether–EtOAc, 6:1); mp 145–147 °C



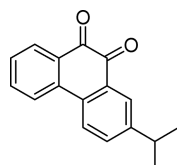
(lit.<sup>29</sup> mp 155–156 °C); IR (neat):  $\nu = 1672$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.04–8.02 (m, 1H), 7.83 (d,  $J = 8.4$  Hz, 2H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.60–7.56 (m, 1H), 7.40–7.38 (m, 1H), 7.34–7.30 (m, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  179.4, 138.9, 135.9, 135.0, 134.9, 132.2, 129.8, 129.7, 129.4, 128.1, 127.3, 123.0, 122.7, 19.9; HRMS (EI) for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ : calcd 222.0681, found 222.0689.

**2-Ethylphenanthrene-9,10-dione (2e).** Yellow solid (51.0 mg, 72%),  $R_f = 0.25$  (petroleum ether–EtOAc, 6:1); mp 122–124 °C; IR



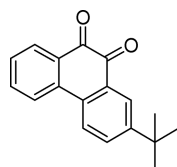
(neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.01–7.97 (m, 1H), 7.84–7.73 (m, 3H), 7.58–7.53 (m, 1H), 7.41–7.39 (m, 1H), 7.32–7.28 (m, 1H), 2.63–2.57 (q,  $J = 7.6$  Hz, 2H), 1.19 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  180.37, 180.36, 146.1, 136.02, 135.95, 135.8, 133.4, 130.9, 130.6, 130.3, 129.5, 129.1, 124.1, 123.7, 28.3, 14.9; HRMS (EI) for  $\text{C}_{16}\text{H}_{12}\text{O}_2$ : calcd 236.0837, found 236.0831.

**2-Isopropylphenanthrene-9,10-dione (2f).**<sup>30</sup> Yellow solid (52.6 mg, 70%),  $R_f = 0.28$  (petroleum ether–EtOAc, 6:1); mp 125–126 °C



(lit.<sup>30</sup> mp 134 °C); IR (neat):  $\nu = 1677$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.00–7.98 (m, 1H), 7.89 (d,  $J = 2.0$  Hz, 1H), 7.81–7.74 (m, 2H), 7.57–7.53 (m, 1H), 7.46–7.43 (m, 1H), 7.31–7.27 (m, 1H), 2.91–2.84 (m, 1H), 1.20 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  179.41, 179.39, 149.7, 135.0, 134.9, 133.5, 132.5, 129.9, 129.6, 129.3, 128.0, 127.1, 123.1, 122.7, 32.7, 22.4; HRMS (EI) for  $\text{C}_{17}\text{H}_{14}\text{O}_2$ : calcd 250.0994, found 250.0987.

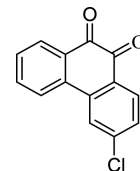
**2-tert-Butylphenanthrene-9,10-dione (2g).** Yellow solid (59.5 mg, 75%),  $R_f = 0.27$  (petroleum ether–EtOAc, 6:1); mp 127–128 °C; IR



(neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz): 8.15 (d,  $J = 2.0$  Hz, 1H), 8.11–8.09 (m, 1H), 7.92–7.86 (m, 2H), 7.73–7.70 (m, 1H), 7.67–7.63 (m, 1H), 7.41–7.37 (m, 1H), 1.37 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  180.5, 180.5, 153.1, 135.97, 135.95,

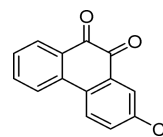
133.4, 133.2, 130.7, 130.3, 129.1, 127.1, 124.0, 123.8, 34.9, 30.9; HRMS (EI) for  $\text{C}_{18}\text{H}_{16}\text{O}_2$ : calcd 264.1150, found 264.1157.

**3-Chlorophenanthrene-9,10-dione (2h).**<sup>31</sup> Yellow solid (40.0 mg, 55%),  $R_f = 0.26$  (petroleum ether–EtOAc, 6:1); mp 265–266 °C



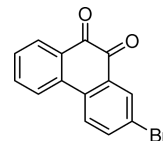
(lit.<sup>31</sup> mp 261 °C); IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.24–8.23 (m, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 8.02–7.99 (m, 2H), 7.78–7.75 (m, 1H), 7.56–7.53 (m, 1H), 7.48–7.45 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  179.8, 179.3, 143.1, 137.5, 136.1, 134.6, 132.0, 131.4, 130.8, 130.3, 129.8, 124.4, 124.1; HRMS (EI) for  $\text{C}_{14}\text{H}_7\text{ClO}_2$ : calcd 242.0135, found 242.0130.

**2-Chlorophenanthrene-9,10-dione (2i).**<sup>32</sup> Yellow solid (21.8 mg, 30%),  $R_f = 0.28$  (petroleum ether–EtOAc, 6:1); mp 226–227 °C



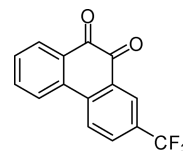
(lit.<sup>32</sup> mp 245–247 °C); IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.22–8.20 (m, 1H), 8.15 (d,  $J = 2.0$  Hz, 1H), 7.98 (d,  $J = 8.5$  Hz, 1H), 7.77–7.73 (m, 1H), 7.70–7.67 (m, 1H), 7.53–7.50 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  179.6, 179.4, 136.25, 136.21, 135.9, 135.1, 134.4, 132.2, 130.9, 130.1, 130.0, 128.8, 125.6, 124.1; HRMS (EI) for  $\text{C}_{14}\text{H}_7\text{ClO}_2$ : calcd 242.0135, found 242.0142.

**2-Bromophenanthrene-9,10-dione (2j).**<sup>33</sup> Yellow solid (21.5 mg, 25%),  $R_f = 0.26$  (petroleum ether–EtOAc, 6:1); mp 215–216 °C



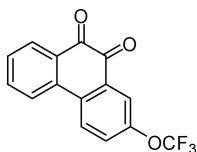
(lit.<sup>33</sup> mp 233–234 °C); IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.32 (d,  $J = 2.0$  Hz, 1H), 8.23–8.21 (m, 1H), 7.99 (d,  $J = 8.0$  Hz, 1H), 7.91 (d,  $J = 8.5$  Hz, 1H), 7.86–7.84 (m, 1H), 7.77–7.74 (m, 1H), 7.54–7.51 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  179.5, 179.3, 138.8, 136.2, 135.1, 134.7, 133.1, 132.2, 131.0, 130.9, 130.0, 125.7, 124.1, 124.0; HRMS (EI) for  $\text{C}_{14}\text{H}_7\text{BrO}_2$ : calcd 285.9629, found 285.9623.

**2-(Trifluoromethyl)phenanthrene-9,10-dione (2k).** Yellow solid (16.6 mg, 20%),  $R_f = 0.23$  (petroleum ether–EtOAc, 6:1); mp 225–



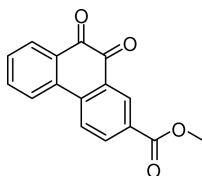
228 °C; IR (KBr, neat):  $\nu = 1661$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (DMSO, 500 MHz):  $\delta$  8.56 (d,  $J = 8.5$  Hz, 1H), 8.40 (d,  $J = 8.0$  Hz, 1H), 8.22 (d,  $J = 1.5$  Hz, 1H), 8.13–8.09 (m, 2H), 7.86–7.83 (m, 1H), 7.65–7.62 (m, 1H); HRMS (EI) for  $\text{C}_{15}\text{H}_7\text{F}_3\text{O}_2$ : calcd 276.0398, found 276.0392.

**2-(Trifluoromethoxy)phenanthrene-9,10-dione (2l).** Saffron yellow solid (26.3 mg, 30%),  $R_f = 0.23$  (petroleum ether–EtOAc, 6:1); mp 199–201 °C; IR (neat):  $\nu = 1675$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.18 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.07 (d,  $J = 8.5$  Hz, 1H), 7.99–7.96 (m, 2H), 7.77–7.74 (m, 1H), 7.55 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 2.5$  Hz, 1H), 7.50 (t,  $J = 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR



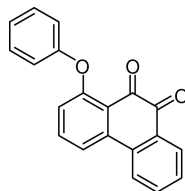
(CDCl<sub>3</sub>, 125 MHz):  $\delta$  179.4, 179.1, 150.0, 136.3, 134.7, 134.4, 132.4, 130.8, 130.7, 130.0, 128.0, 126.0, 124.2, 121.6, 120.6 (q,  $J = 257.5$  Hz); HRMS (EI) for C<sub>15</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>: calcd 292.0347, found 292.0350.

**Methyl 9,10-Dioxo-9,10-dihydrophenanthrene-2-carboxylate (2m).** Yellow solid (28.0 mg, 35%),  $R_f = 0.25$  (petroleum ether–



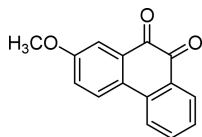
EtOAc, 6:1); mp 253–254 °C; IR (KBr, neat):  $\nu = 1713, 1677$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.83 (d,  $J = 2.0$  Hz, 1H), 8.38 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 2.0$  Hz, 1H), 8.25 (dd,  $J_1 = 7.5$  Hz,  $J_2 = 1.5$  Hz, 1H), 8.14 (d,  $J = 8.5$  Hz, 1H), 8.10 (d,  $J = 8.0$  Hz, 1H), 7.81–7.77 (m, 1H), 7.59–7.55 (m, 1H), 4.00 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  179.8, 179.6, 165.4, 139.5, 136.4, 136.2, 134.8, 131.6, 131.4, 131.3, 131.0, 130.8, 130.6, 124.7, 124.3, 52.6; HRMS (EI) for C<sub>16</sub>H<sub>10</sub>O<sub>4</sub>: calcd 266.0579, found 266.0583.

**1-Phenoxyphenanthrene-9,10-dione (2o).** Saffron yellow solid (40.5 mg, 45%),  $R_f = 0.26$  (petroleum ether–EtOAc, 6:1); mp 198–



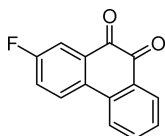
200 °C; IR (neat):  $\nu = 1662$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.17 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.25$  Hz, 1H), 8.04 (d,  $J = 8.0$  Hz, 1H), 7.78–7.72 (m, 2H), 7.59 (t,  $J = 8.3$  Hz, 1H), 7.52–7.49 (m, 1H), 7.41–7.38 (m, 2H), 7.19 (t,  $J = 7.5$  Hz, 1H), 7.10–7.08 (m, 2H), 6.91 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 0.5$  Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  181.4, 179.9, 160.4, 155.8, 138.0, 136.4, 136.1, 135.8, 130.8, 129.98, 129.95, 129.8, 124.7, 124.4, 121.8, 120.0, 119.7, 118.9; HRMS (EI) for C<sub>20</sub>H<sub>12</sub>O<sub>3</sub>: calcd 300.0786, found 300.0781.

**2-Methoxyphenanthrene-9,10-dione (2p).** Red solid (46.4 mg, 65%),  $R_f = 0.27$  (petroleum ether–EtOAc, 6:1); mp 214–215 °C; IR



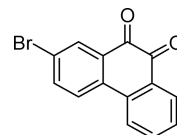
(neat):  $\nu = 1671$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.14–8.13 (m, 1H), 7.91–7.87 (m, 2H), 7.69–7.66 (m, 1H), 7.62 (d,  $J = 3.0$  Hz, 1H), 7.41–7.38 (m, 1H), 7.26–7.23 (m, 1H), 3.92 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  180.5, 180.3, 160.6, 136.3, 136.1, 132.4, 130.5, 130.2, 129.1, 128.6, 125.7, 123.7, 123.5, 112.8, 55.8; HRMS (EI) for C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>: calcd 238.0630, found 238.0625.

**2-Fluorophenanthrene-9,10-dione (2q).**<sup>34</sup> Yellow solid (50.9 mg, 75%),  $R_f = 0.28$  (petroleum ether–EtOAc, 6:1); mp 250–251 °C

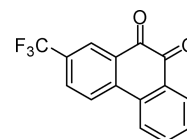


(lit.<sup>34</sup> mp 246–248 °C); IR (neat):  $\nu = 1671$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.19 (d,  $J = 7.5$  Hz, 1H), 8.04–8.02 (m, 1H), 7.95 (d,  $J = 8.0$  Hz, 1H), 7.85–7.83 (m, 1H), 7.74 (t,  $J = 7.5$  Hz, 1H), 7.50–7.41 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  179.8, 179.4 (d,  $J = 1.3$  Hz), 163.2 (d,  $J = 251.3$  Hz), 136.3, 135.2, 132.8 (d,  $J = 6.3$  Hz), 132.3 (d,  $J = 3.8$  Hz), 130.8, 130.5, 129.6, 126.4 (d,  $J = 5.0$  Hz), 124.0, 123.3 (d,  $J = 22.5$  Hz), 116.5 (d,  $J = 22.5$  Hz); HRMS (EI) for C<sub>14</sub>H<sub>7</sub>FO<sub>2</sub>: calcd 226.0430, found 226.0437.

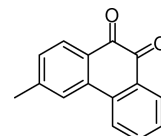
**2-Bromophenanthrene-9,10-dione (2r).** Yellow solid (62.0 mg, 72%); the structure is the same as that of 2j.



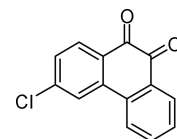
**2-(Trifluoromethyl)phenanthrene-9,10-dione (2s).** Yellow solid (59.8 mg, 72%); the structure is the same as that of 2k.



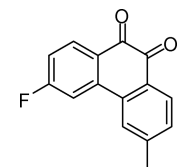
**3-Methylphenanthrene-9,10-dione (2t).** Yellow solid (44.7 mg, 67%); the structure is the same as that of 2a.



**3-Chlorophenanthrene-9,10-dione (2u).** Yellow solid (51.0 mg, 70%); the structure is the same as that of 2h.

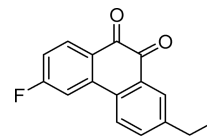


**3-Fluoro-6-methylphenanthrene-9,10-dione (2v).** Yellow solid (56.2 mg, 78%),  $R_f = 0.29$  (petroleum ether–EtOAc, 6:1); mp



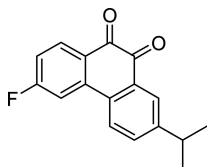
245–246 °C; IR (neat):  $\nu = 1671$  (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.14–8.11 (m, 1H), 7.99 (d,  $J = 7.6$  Hz, 1H), 7.60 (s, 1H), 7.57–7.53 (m, 1H), 7.21 (d,  $J = 8.0$  Hz, 1H), 7.07–7.03 (m, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  179.4, 178.9, 167.7 (d,  $J = 257.0$  Hz), 147.5, 139.1 (d,  $J = 10.0$  Hz), 134.5 (d,  $J = 2.0$  Hz), 133.7 (d,  $J = 10.0$  Hz), 131.2, 130.8, 129.1, 128.5, 124.7, 116.8 (d,  $J = 22.0$  Hz), 111.0 (d,  $J = 24.0$  Hz), 22.3; HRMS (EI) for C<sub>15</sub>H<sub>9</sub>FO<sub>2</sub>: calcd 240.0587, found 240.0591.

**2-Ethyl-6-fluorophenanthrene-9,10-dione (2w).** Yellow solid (61.8 mg, 81%),  $R_f = 0.26$  (petroleum ether–EtOAc, 6:1); mp



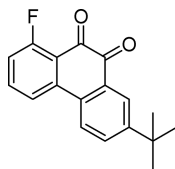
182–183 °C; IR (neat):  $\nu = 1668$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz): 8.20–8.16 (m, 1H), 7.98 (d,  $J = 1.6$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.59–7.53 (m, 2H), 7.12–7.07 (m, 1H), 2.75–2.70 (m, 2H), 1.29 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  180.0, 178.8, 167.7 (d,  $J = 257.0$  Hz), 147.0, 139.3 (d,  $J = 9.0$  Hz), 135.8, 133.7 (d,  $J = 10.0$  Hz), 132.1 (d,  $J = 2.0$  Hz), 131.1, 129.6, 127.4 (d,  $J = 3.0$  Hz), 124.2, 116.5 (d,  $J = 22.0$  Hz), 110.8 (d,  $J = 24.0$  Hz), 28.4, 14.9; HRMS (EI) for  $\text{C}_{16}\text{H}_{11}\text{FO}_2$ : calcd 254.0743, found 254.0748.

**6-Fluoro-2-isopropylphenanthrene-9,10-dione (2x).** Yellow solid (61.2 mg, 76%),  $R_f = 0.25$  (petroleum ether–EtOAc, 6:1); mp 168–



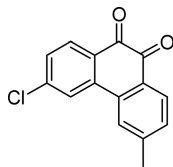
169 °C; IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.23–8.21 (m, 1H), 8.07 (d,  $J = 2.0$  Hz, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.64–7.60 (m, 2H), 7.14–7.10 (m, 1H), 3.05–2.99 (m, 1H), 1.32 (d,  $J = 7.0$  Hz, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  180.1, 179.0, 167.8 (d,  $J = 256.3$  Hz), 151.7, 139.4 (d,  $J = 10.0$  Hz), 134.5, 133.7 (d,  $J = 10.0$  Hz), 132.4 (d,  $J = 1.3$  Hz), 131.3, 128.4, 127.6 (d,  $J = 2.5$  Hz), 124.3, 116.5 (d,  $J = 22.5$  Hz), 110.8 (d,  $J = 25.0$  Hz), 33.9, 23.4; HRMS (EI) for  $\text{C}_{17}\text{H}_{13}\text{FO}_2$ : calcd 268.0900, found 268.0906.

**7-tert-Butyl-1-fluorophenanthrene-9,10-dione (2y).** Yellow solid (59.3 mg, 70%),  $R_f = 0.25$  (petroleum ether–EtOAc, 6:1); mp 178–



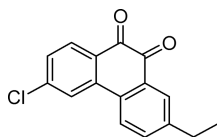
179 °C; IR (neat):  $\nu = 1672$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz): 8.08 (d,  $J = 2.0$  Hz, 1H), 7.83 (d,  $J = 8.8$  Hz, 1H), 7.72–7.65 (m, 2H), 7.60–7.54 (m, 1H), 7.04–7.00 (m, 1H), 1.29 (s, 9H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  180.4 (d,  $J = 1.0$  Hz), 178.8 (d,  $J = 1.0$  Hz), 183.9 (d,  $J = 268.0$  Hz), 153.8, 137.9, 137.2 (d,  $J = 11.0$  Hz), 133.4, 132.7 (d,  $J = 3.0$  Hz), 130.5, 127.1, 124.7, 120.0 (d,  $J = 3.0$  Hz), 119.3 (d,  $J = 6.0$  Hz), 117.4 (d,  $J = 21.0$  Hz), 35.0, 30.9; HRMS (EI) for  $\text{C}_{18}\text{H}_{15}\text{FO}_2$ : calcd 282.1056, found 282.1052.

**3-Chloro-6-methylphenanthrene-9,10-dione (2z).** Yellow solid (57.8 mg, 75%),  $R_f = 0.28$  (petroleum ether–EtOAc, 6:1); mp



215–216 °C; IR (neat):  $\nu = 1675$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz): 8.11–8.06 (m, 2H), 7.93 (d,  $J = 2.0$  Hz, 1H), 7.70 (s, 1H), 7.42–7.40 (m, 1H), 7.29 (d,  $J = 8.0$  Hz, 1H), 2.51 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  179.4, 179.2, 147.6, 142.8, 137.4, 134.4, 131.9, 131.2, 130.9, 129.6, 129.4, 129.1, 124.6, 124.1, 22.4; HRMS (EI) for  $\text{C}_{15}\text{H}_9\text{ClO}_2$ : calcd 256.0291, found 256.0297.

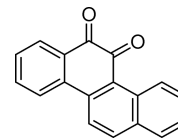
**6-Chloro-2-ethylphenanthrene-9,10-dione (2za).**<sup>35</sup> Yellow solid (67.4 mg, 83%),  $R_f = 0.26$  (petroleum ether–EtOAc, 6:1); mp 205–



206 °C (lit.<sup>35</sup> mp 210–210.5 °C); IR (neat):  $\nu = 1673$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz): 8.00 (d,  $J = 8.4$  Hz, 1H), 7.92 (d,  $J = 1.6$

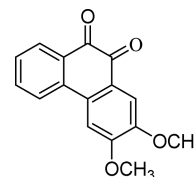
Hz, 1H), 7.82 (d,  $J = 1.6$  Hz, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.48–7.45 (m, 1H), 7.31–7.29 (m, 1H), 2.68–2.62 (m, 2H), 1.21 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  179.9, 179.4, 147.0, 142.9, 137.7, 135.9, 132.1, 131.9, 131.2, 129.8, 129.3, 129.0, 124.2, 124.0, 28.4, 14.9; HRMS (EI) for  $\text{C}_{16}\text{H}_{11}\text{ClO}_2$ : calcd 270.0448, found 270.0453.

**Chrysene-5,6-dione (2zb).** Yellow solid (57.3 mg, 74%),  $R_f = 0.25$  (petroleum ether–EtOAc, 6:1); mp 249–250 °C; IR (neat):  $\nu = 1671$



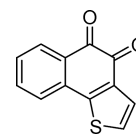
(C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.41 (d,  $J = 8.5$  Hz, 1H), 8.19–8.15 (m, 2H), 8.10 (d,  $J = 8.5$  Hz, 2H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.77–7.70 (m, 2H), 7.59–7.56 (m, 1H), 7.52–7.49 (m, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  184.3, 182.1, 137.9, 137.4, 136.7, 136.1, 133.9, 132.3, 130.9, 130.7, 130.1, 130.0, 128.7, 127.7, 127.2, 126.0, 125.3, 121.2; HRMS (EI) for  $\text{C}_{18}\text{H}_{10}\text{O}_2$ : calcd 258.0681, found 258.0685.

**2,3-Dimethoxyphenanthrene-9,10-dione (2zc).** Yellow solid (64.4 mg, 80%),  $R_f = 0.27$  (petroleum ether–EtOAc, 6:1); mp 202–203 °C;



IR (neat):  $\nu = 1671$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.08–8.07 (m, 1H), 7.83 (d,  $J = 8.0$  Hz, 1H), 7.73–7.70 (m, 1H), 7.43–7.40 (m, 1H), 7.36 (s, 1H), 7.30 (s, 1H), 4.04 (s, 3H), 4.00 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  187.0, 168.2, 152.2, 150.4, 136.4, 136.1, 129.0, 128.4, 127.4, 125.2, 123.1, 109.5, 107.9, 106.9, 56.3, 56.2; HRMS (EI) for  $\text{C}_{16}\text{H}_{12}\text{O}_4$ : calcd 268.0736, found 268.0741.

**Naphtho[1,2-b]thiophene-4,5-dione (2zd).**<sup>19</sup> Yellow solid (52.7 mg, 82%),  $R_f = 0.28$  (petroleum ether–EtOAc, 6:1); mp 218–220 °C;



IR (neat):  $\nu = 1672$  (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz): 8.04–8.02 (m, 1H), 7.60–7.56 (m, 1H), 7.51–7.48 (m, 2H), 7.41–7.37 (m, 1H), 7.24 (d,  $J = 5.6$  Hz, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  180.4, 173.8, 151.2, 136.5, 135.8, 132.4, 130.2, 129.7, 129.1, 127.7, 126.1, 124.7; HRMS (EI) for  $\text{C}_{12}\text{H}_6\text{O}_2\text{S}$ : calcd 214.0089, found 214.0086.

**Mechanistic Studies. Reaction of 1ze in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}^{18}$  (50:1, v/v).** **1ze** (94.3 mg, 0.3 mmol), Cu(0) powder (1.92 mg, 10 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}^{18} = 50:1$  (v/v, 3 mL) were added to a 10 mL flask. Then the reaction mixture was stirred at 25 °C for 12 h. Upon completion, the resulting mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure products. The resulting product **2b/2b-O<sup>18</sup>** and **3ze/3ze-O<sup>18</sup>** were sampled for MS analysis (see Figures S1–S2 in the Supporting Information).

**Reaction of 1ze in the Standard Reaction Conditions in the Presence of an  $\text{O}_2$  Atmosphere.** **1ze** (94.3 mg, 0.3 mmol), Cu(0) powder (1.92 mg, 10 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and  $\text{CH}_3\text{CN}/\text{H}_2\text{O} = 50:1$  (v/v, 3 mL) were added to a 10 mL flask. The flask was opened to the vacuum, pumped for 2–3 min, and backfilled with  $^{18}\text{O}_2$  gas using a balloon. Then the reaction mixture was stirred at 25 °C for 12 h. Upon completion, the resulting mixture was



diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure products for MS analysis. The analyses showed that both **2b** and **3ze** were normally formed while **2b-O<sup>18</sup>** and **3ze-O<sup>18</sup>** were not detected.

**Reaction of 1ze in the Standard Reaction Conditions except in a Degassed Solvent under an Argon Atmosphere.** **1ze** (94.3 mg, 0.3 mmol), Cu(0) powder (1.92 mg, 10 mol %), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v, 3 mL) were added to a 10 mL flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the resultant mixture in the sealed tube was frozen by immersion of the flask in liquid N<sub>2</sub>. When solvent was completely frozen, the flask was opened to the vacuum (high vacuum) and pumped for 2–3 min, with the flask still immersed in liquid N<sub>2</sub>. The flask was then closed and warmed until solvent completely melted. This process was repeated three times, and after the last cycle the flask was backfilled with an inert Ar gas. Then the reaction mixture was stirred at 25 °C for 12 h. Upon completion, the resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure products (**2b**: 30%; **3ze**: 34%).

**Studies on the Intermolecular Kinetic Isotope Effects (KIE) Based on Substrate 1u and 1u-d<sub>5</sub>.** **1u** (70.4 mg, 0.2 mmol), **1u-d<sub>5</sub>** (71.6 mg, 0.2 mmol), Cu(0) powder (2.56 mg, 10 mol %), Selectfluor (283.5 mg, 0.8 mmol, 2 equiv), and CH<sub>3</sub>CN:H<sub>2</sub>O = 50:1 (v/v, 4 mL) were added to a 10 mL flask. Then the reaction mixture was stirred at 25 °C for 5 h. Upon completion, the resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure products. On the basis of <sup>1</sup>H NMR spectra analysis, the intermolecular competitive KIE was calculated as  $k_H/k_D \approx 2.23$  (Figure S3).

**Reaction of 1a in the Standard Reaction Conditions except Using the Preparative HOCuX as the Catalyst.** **1a** (0.3 mmol), HOCuX (X = F or BF<sub>4</sub>, 10 mol %, prepared according to our previous work<sup>18a</sup>), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and a combined CH<sub>3</sub>CN/H<sub>2</sub>O = 50:1 (v/v) solvent (3 mL) were added to a 10 mL flask. Then the reaction mixture was stirred at 25 °C for 12 h. Upon completion, the resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using petroleum ether–EtOAc (6:1) as eluent to give pure **2a** (52.7 mg, 79%) and **3a** (34.2 mg, 81%).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02212.

Charts for mechanistic studies as well as copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products (PDF)

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### Notes

The authors declare no competing financial interest.

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