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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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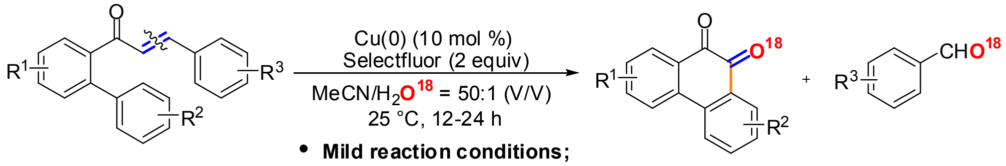
TOC graphic



- **Mild reaction conditions;**
- **Inexpensive copper catalyst;**
- **Easy availability of starting materials.**

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

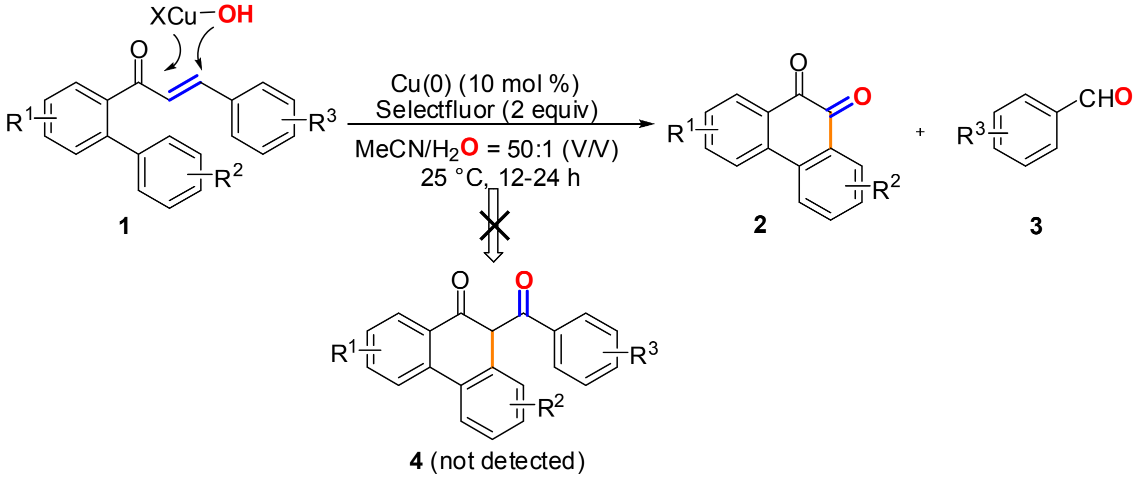
synthesized in moderate to good yields under mild reaction conditions.

Introduction

9,10-Phenanthraquinone scaffold is often seen in some natural, metabolic, or synthetic products which display unique biological activities.[1] Besides, 9,10-phenanthraquinones can serve as useful intermediates for the preparation of many biologically interesting compounds[2] as well as functional molecules in materials science.[3] 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.[4,5] Alternative methods include oxidation of several phenanthrene-originated substrates such as 9,10-dihydrophenanthrenes,[6] 10-hydroxyphenanthren-9(10*H*)-ones,[7] 9-phenanthrenols,[8] and phenanthrene-9,10-diol.[9] 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 non-phenanthrene-based precursors, e.g. 2-acetylbiphenyls,[10] dimethyl biphenyl-2,2'-dicarboxylate,[11] benzils,[12] benzoins,[13] biaryloxalic acids,[14] or 2,2'-dilithiobiphenyl,[15] has also been reported. Despite their merits, most of these methods have several drawbacks such as narrow scope of substrates, multistep processes, and low yields. Overall, up to now, general and efficient methods enabling the synthesis of different substituted 9,10-phenanthraquinones remain very limited.[12d,e,14] 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).[16]

As part of our ongoing effort to develop mild and efficient catalyst systems for the construction of useful molecules,[17] 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_4) may generate an active XCuOH species (X = F or BF_4) which is easily able to undergo oxycupration toward carbon-carbon multiple bonds and induce successive tandem reactions.[18] 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[18b] and fluorinated fluorenones,[18c] 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 formtion 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).

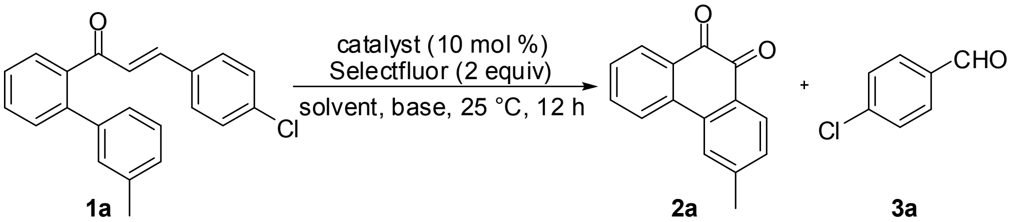
Scheme 1. Unexpected Synthesis of 9,10-Phenanthraquinones via the Cu(0)/Selectfluor System-promoted Annulation of *o*-Aryl Chalcones 1



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 ºC 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_3CN/H_2O = 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 (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 equivalents of Selectfluor is just fine for the reaction while the 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 ºC) only resulted in a lower yield of **2a** (entries 19, 20, Table 1).

Table 1. Optimization of Reaction Conditions[a]



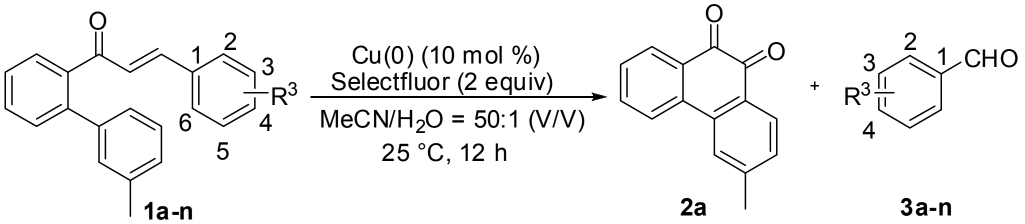
entry	catalyst	oxidant	base	solvent	yield of **2a** (%)[b]
1	Cu(0)[c]	Selectfluor	--	CH_3CN	70
2	Cu(0)[c]	Selectfluor	K_2CO_3	CH_3CN	68
3	Cu(0)[c]	Selectfluor	$NaHCO_3$	CH_3CN	64
4	Cu(0)[c]	Selectfluor	K_2CO_3	CH_3CN	67
5	Cu(0)[c]	Selectfluor	K_3PO_4	CH_3CN	57
6	Cu(0)	Selectfluor	--	CH_3CN	75

7	Cu(0)	Selectfluor	--	CH_3CN/H_2O = 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_3CN/H_2O = 50:1	64
12	CuI	Selectfluor	--	CH_3CN/H_2O = 50:1	57
13	CuCl	Selectfluor	--	CH_3CN/H_2O = 50:1	55
14	$CuCl_2$	Selectfluor	--	CH_3CN/H_2O = 50:1	60
15	$Cu(OAc)_2$	Selectfluor	--	CH_3CN/H_2O = 50:1	50
16	Cu(0)	NFSI[d]	--	CH_3CN/H_2O = 50:1	50
17	Cu(0)	Selectfluor	--	CH_3CN/H_2O = 50:1	40,[e] 62[f]
18	--	Selectfluor	--	CH_3CN/H_2O = 50:1	0
19	Cu(0)[g]	Selectfluor	--	CH_3CN/H_2O = 50:1	69
20	Cu	Selectfluor	--	CH_3CN/H_2O = 50:1	55[h]

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

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 groups or electron-neutral ones (entries 2-6 vs 8 & 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 proved 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[a]



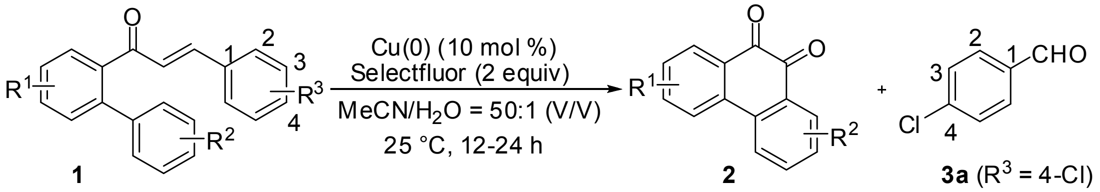
entry	R^3 (**1a-n**)	Aldehyde (**3a-n**)	yield of **2a** (%)[b]
1	4-Cl (**1a**)	**3a**	80
2	2-Cl (**1a-1**)	**3a-1**	66
3	3-Cl (**1a-2**)	**3a-2**	60

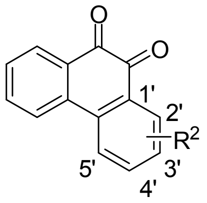
4	4-Br (**1a-3**)	**3a-3**	61
5	3,5-dichloro (**1a-4**)	**3a-4**	65
6	2,6-dichloro (**1a-5**)	**3a-5**	63
7	4-NO_2 (**1a-6**)	**3a-6**	45
8	4-CH_3 (**1a-7**)	**3a-7**	32
9	H (**1a-8**)	**3a-8**	60

[a] Reaction conditions: **1a-n** (0.3 mmol), Cu(0) powder (10 mol % based on **1a-n**), Selectfluor (2.0 equiv), CH_3CN/H_2O = 50:1 (V/V) (3.0 mL), 25 ºC for 12 h. [b].Isolated yield.

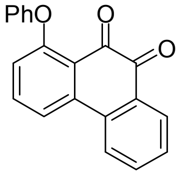
With the optimized reaction conditions and design ideas for substrates in hand, the exploration of the present protocol for the oxidative annulation of a range of *o*-aryl chalcones **1** was then carried out (Table 3). As shown in Table 3, both electron-donating and –withdrawing substituents in the 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 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 less effect on the reaction outcome than R^1 did (**1p**, **1t** vs **1q-1s**, **1u**, Table 3). For substrate **1f-1p** (except **1n**), the

Table 3. Cu(0)/Selecfluor System-promoted Oxidative Annulation of Chalcones 1 for the Synthesis of 2.[a,b]

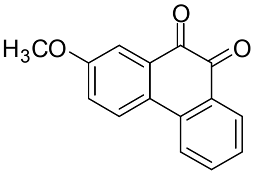




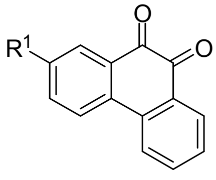
2a: R^2 = 4'-Me, 80%
2b: R^2 = H, 76%
2c: R^2 = 5'-Me, 76%
2d: R^2 = 3'-Me, 78%
2e: R^2 = 3'-Et, 72%
2f: R^2 = 3'- ^{i}Pr, 70%^{c}
2g: R^2 = 3'- ^{t}Bu, 75%^{c}
2h: R^2 = 4'-Cl, 55%^{d}
2i: R^2 = 3'-Cl, 30%^{c}
2j: R^2 = 3'-Br, 25%^{c}
2k: R^2 = 3'-CF$_3$, 20%^{c}
2l: R^2 = 3'-OCF$_3$, 30%^{c}
2m: R^2 = 3'-COOMe, 35%^{c}
2n: R^2 = 3'-OH, 0%



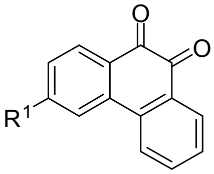
2o: 45%^{c}



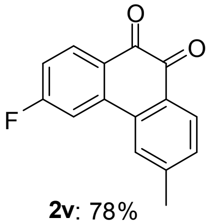
2p: 65%^{c}



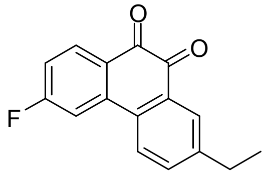
2q: R^1 = F, 75%
2r: R^1 = Br, 72%
2s: R^1 = CF$_3$, 72%



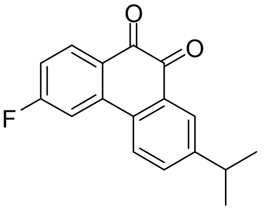
2t: R^1 = Me, 67%
2u: R^1 = Cl, 70%



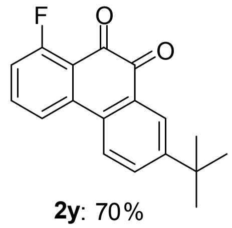
2v: 78%



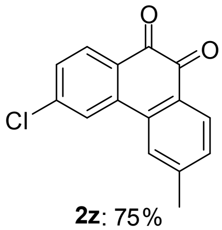
2w: 81%



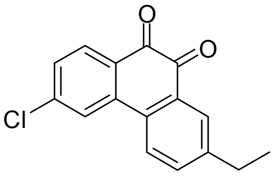
2x: 76%



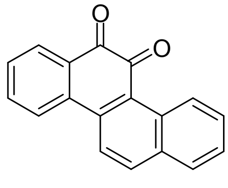
2y: 70%



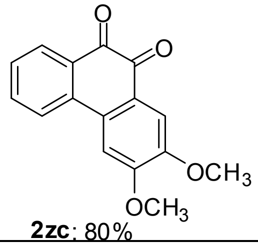
2z: 75%



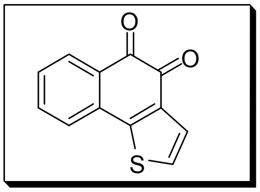
2za: 83%



2zb: 74%



2zc: 80%



2zd: 82%

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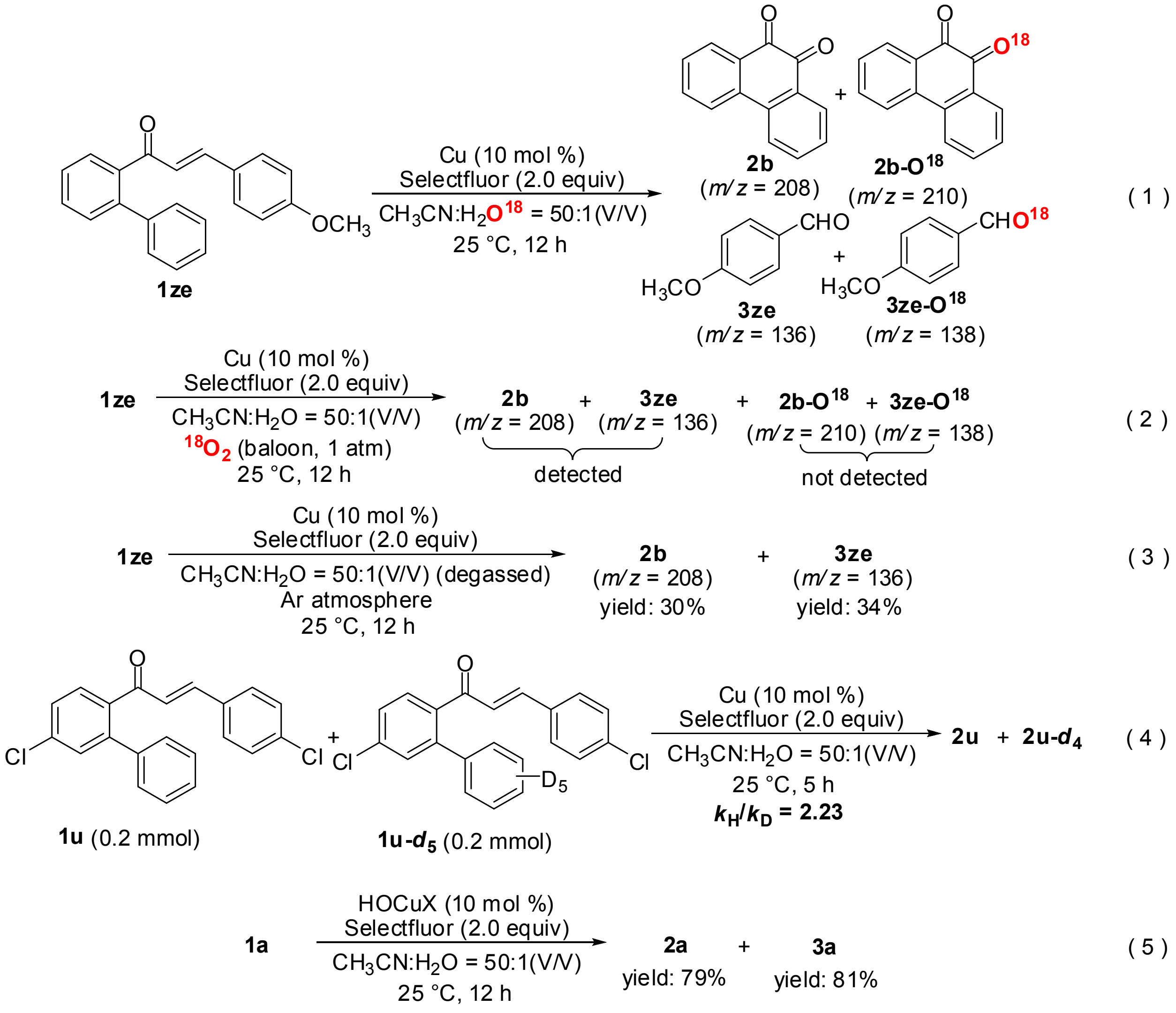
[a] Reaction conditions: **1** (0.3 mmol), Cu(0) powder (10 mol % based on **1**), Selectfluor (2.0 equiv), CH$_3$CN/H$_2$O = 50:1 (V/V) (3.0 mL), 25 ºC for 12 h unless otherwise noted. [b.]Isolated yield. [c.]The reaction time is 24 h. [c.]The reaction time is 18 h.

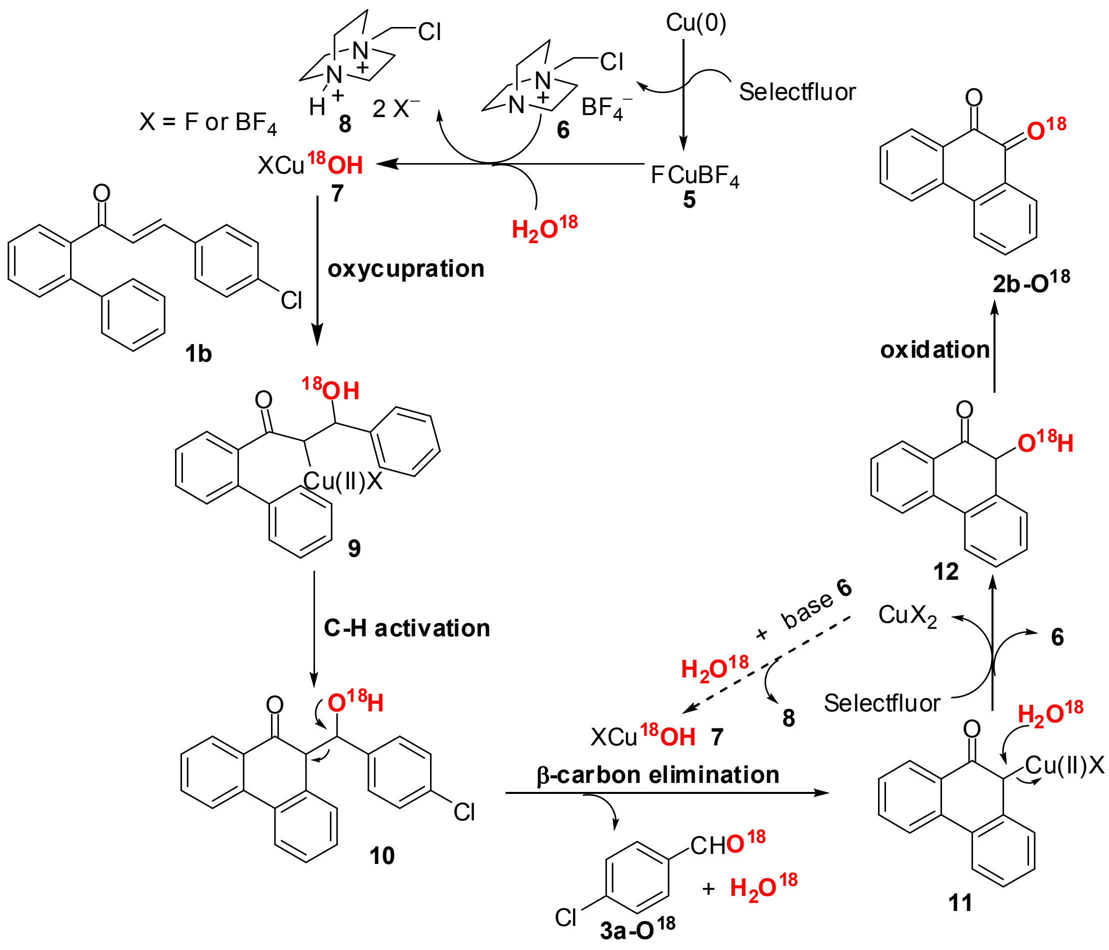
reaction required a prolonged time (18-24 h) in order to deliver a better yield of products. When substrate **1n** bearing a phenolic hydroxy group was used, the reaction gave complicated products and the desired product **2n** was not detected. Interestingly, naphtho[1,2-*b*]thiophene-4,5-dione **2zd**, a potential inhibitor of the protein tyrosine phosphatase (PTP) CD45,[1g] 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_3CN/H_2O^{18} = 50:1 (V/V) solvent system, both the ^{18}O-incorporated products **2b-O^{18}** and **3ze-O^{18}** were detected (eq. (1), Scheme 2, also see the Supporting Information).[18b,19] In contrast, when **1ze** reacted under the standard reaction conditions in the presence of an $^{18}O_2$ atmosphere, both **2b** and **3ze** were normally formed while **2b-O^{18}** and **3ze-O^{18}** 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** were originated from water rather than dioxygen. In addition, the measurement of the intermolecular KIE between **1u** and **1u-*d*$_5$** on the basis of the competitive dehydrogenative cross-coupling was carried out. The intermolecular k_H/k_D of **1u** to **1u-*d*$_5$** 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_4)[18a] as a catalyst (eq. (5), Scheme 2). This result suggests that HOCuX (X = F or BF_4) may be the real catalyst in the catalytic cycle.

Scheme 2. Preliminary Mechanistic Studies



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



On the basis of the above experiments and previous literatures,[7,18, 20-22] 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**.[18] In our previous work,[18] we have disclosed that **5** may be transferred into a copper species **7** in the presence of H_2O^{18} with the aid of the base **6**. Then, an oxycupration of **7** to the C-C double bond[18b,c] in **1b** followed by a dehydrogenative cross-coupling[20] would deliver an intermediate **10**. Intermediate

10 might undergo β-carbon elimination[18b,21] in the presence of **7** to produce an intermediate **11** and an aldehyde **3a-O^{18}**. Furthermore, intermediate **11** might undergo an oxidative substitution reaction with H_2O^{18} to form an intermediate **12** followed by the regeneration of **7** in the presence of Selectfluor.[18,22,23] Finally, intermediate **12** may be transferred into **2b-O^{18}** under the oxidative reaction conditions.[7]

Conclusion

In summary, we have developed a general and efficient method for the contruction 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, inexpensive catalyst, and good generality for construction of a range of substituted 9,10-phenanthraquinones.

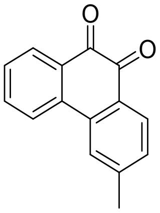
Experimental Section

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. Melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 500 MHz (or 400 MHz) and 125 MHz (or 100 MHz), respectively, with TMS as 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 EI source; high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source. CH_3CN is dehydrated by CaH_2 before preparation of the combined solvent CH_3CN/H_2O = 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.[24] The *o*-aryl acetophenones were synthesized by the standard Suzuki–Miyaura cross-coupling reaction between an *ortho*-bromoacetophenone derivative and an arylboronic acid.[25]

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_3CN/H_2O = 50:1 (V/V) solvent (3 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 25 ºC for 12 h. Upon completion, the resulting mixture was diluted with CH_2Cl_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 **2**.

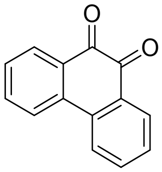
3-methylphenanthrene-9,10-dione (2a)[26]



Yellow solid (53.3 mg, 80%), R_f = 0.27 (petroleum ether-EtOAc, 6:1); m.p. 216-217 ºC (lit.[26] m.p. 208-210 ºC); IR (neat): ν = 1672 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.05-8.03 (m, 1H), 7.93 (d,

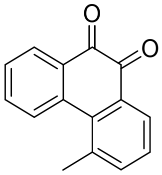
J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.61-7.57 (m, 1H), 7.37-7.33 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.5, 178.7, 148.4, 134.8, 134.7, 130.0, 129.6, 129.4, 129.3, 128.4, 127.8, 123.5, 122.8, 21.3; HRMS (EI) for $C_{15}H_{10}O_2$: calcd. 222.0681, found 222.0685.

phenanthrene-9,10-dione (2b)[27]



Yellow solid (47.5 mg, 76%), R_f = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 218-220 ºC (lit.[27] m.p. 217-219 ºC); IR (neat): ν = 1673 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 136.0, 135.8, 131.0, 130.5, 129.6, 124.0; HRMS (EI) for $C_{14}H_8O_2$: calcd. 208.0524, found 208.0518.

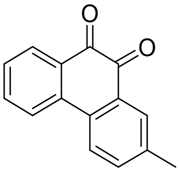
4-methylphenanthrene-9,10-dione (2c)[28]



Yellow solid (50.7 mg, 76%), R_f = 0.28 (petroleum ether-EtOAc, 6:1); m.p. 145-146 ºC (lit.[28] m.p. 167 ºC); IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 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}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{15}H_{10}O_2$: calcd. 222.0681, found

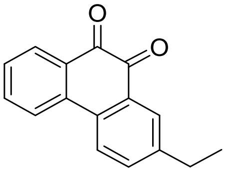
222.0686.

2-methylphenanthrene-9,10-dione (2d)[29]



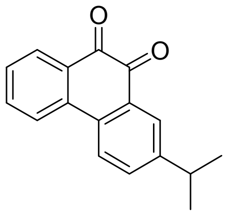
Yellow solid (52.0 mg, 78%), R_f = 0.27 (petroleum ether-EtOAc, 6:1); m.p. 145-147 ºC (lit.[29] m.p. 155-156 ºC); IR (neat): ν = 1672 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): 8.04-8.02 (m, 1H), 7.83(d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.40-7.38 (m, 1H), 7.34-7.30 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 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 $C_{15}H_{10}O_2$: calcd. 222.0681, found 222.0689.

2-ethylphenanthrene-9,10-dione (2e)



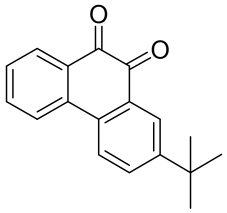
Yellow solid (51.0 mg, 72%), R_f = 0.25 (petroleum ether-EtOAc, 6:1); m.p. 122-124 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz): 8.01-7.97 (m, 1H), 7.84-7.73 (m, 3H), 7.58-7.53 (m, 1H), 7.41-7.39 (m, 1H), 7.32-7.28 (m, 1H), 2.63-2.57 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 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 $C_{16}H_{12}O_2$: calcd. 236.0837, found 236.0831.

2-isopropylphenanthrene-9,10-dione (2f)[30]



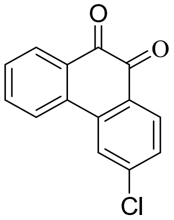
Yellow solid (52.6 mg, 70%), $R_f = 0.28$ (petroleum ether-EtOAc, 6:1); m.p. 125-126 ºC (lit.[30] m.p. 134 ºC); IR (neat): $\nu = 1677$ (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.00-7.98 (m, 1H), 7.89 (d, $J = 2.0$ Hz, 1H), 7.81-7.74 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.43 (m, 1H), 7.31-7.27 (m, 1H), 2.91-2.84 (m, 1H), 1.20 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 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 $C_{17}H_{14}O_2$: calcd. 250.0994, found 250.0987.

2-*tert*-butylphenanthrene-9,10-dione (2g)



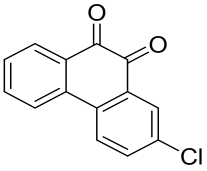
Yellow solid (59.5 mg, 75%), $R_f = 0.27$ (petroleum ether-EtOAc, 6:1); m.p. 127-128 ºC; IR (neat): $\nu =$ 1671 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.15 (d, $J = 2.0$ Hz, 1H), 8.11-8.09 (m, 1H), 7.92-7.86 (m, 2H), 7.73-7.70 (m, 1H), 7.67-7.63 (m, 1H), 7.41-7.37 (m, 1H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 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 $C_{18}H_{16}O_2$: calcd. 264.1150, found 264.1157.

3-chlorophenanthrene-9,10-dione (2h)[31]



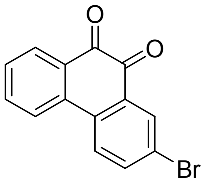
Yellow solid (40.0 mg, 55%), R_f = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 265-266 ºC (lit.[31] m.p. 261 ºC); IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.24-8.23 (m, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.02-7.99 (m, 2H), 7.78-7.75 (m, 1H), 7.56-7.53 (m, 1H), 7.48-7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{14}H_7ClO_2$: calcd. 242.0135, found 242.0130.

2-chlorophenanthrene-9,10-dione (2i)[32]



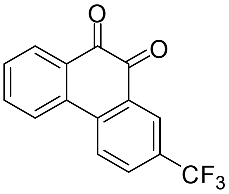
Yellow solid (21.8 mg, 30%), R_f = 0.28 (petroleum ether-EtOAc, 6:1); m.p. 226-227 ºC (lit.[32] m.p. 245-247 ºC); IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.22-8.20 (m, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.77-7.73 (m, 1H), 7.70-7.67 (m, 1H), 7.53-7.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{14}H_7ClO_2$: calcd. 242.0135, found 242.0142.

2-bromophenanthrene-9,10-dione (2j)[33]



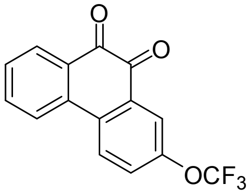
Yellow solid (21.5 mg, 25%), R_f = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 215-216 ºC (lit.[33] m.p. 233-234 ºC); IR (neat): ν = 1671 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.32 (d, *J* = 2.0 Hz, 1H), 8.23-8.21 (m, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.86-7.84 (m, 1H), 7.77-7.74 (m, 1H), 7.54-7.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{14}H_7BrO_2$: calcd. 285.9629, found 285.9623.

2-(trifluoromethyl)phenanthrene-9,10-dione (2k)



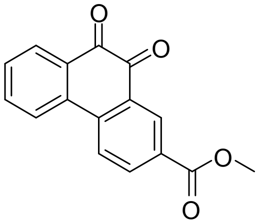
Yellow solid (16.6 mg, 20%), R_f= 0.23 (petroleum ether-EtOAc, 6:1); m.p.225–228°C; IR (KBr, neat): *ν* = 1661 (C=O) cm^{-1}; ^1H NMR (DMSO, 500 MHz): δ 8.56 (d, *J* = 8.5 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 1.5 Hz, 1H), 8.13-8.09 (m, 2H), 7.86-7.83 (m, 1H), 7.65-7.62 (m, 1H); HRMS (EI) for $C_{15}H_7F_3O_2$: calcd. 276.0398, found 276.0392.

2-(trifluoromethoxy)phenanthrene-9,10-dione (2l)



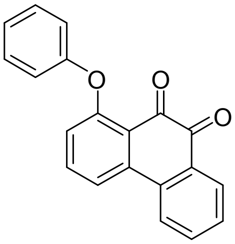
Saffron yellow solid (26.3 mg, 30%), R_f= 0.23 (petroleum ether-EtOAc, 6:1); m.p. 199–201 ºC; IR (neat): ν = 1675 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.18 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.99-7.96 (m, 2H), 7.77-7.74 (m, 1H), 7.55 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 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 $C_{15}H_7F_3O_3$: calcd. 292.0347, found 292.0350.

methyl 9,10-dioxo-9,10-dihydrophenanthrene-2-carboxylate (2m)



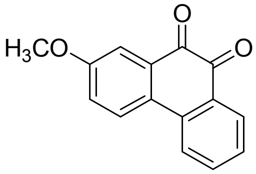
Yellow solid (28.0 mg, 35%), R$_f$ = 0.25 (petroleum ether-EtOAc, 6:1); m.p.253–254°C; IR (KBr, neat): ν = 1713, 1677 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.83 (d, J = 2.0 Hz, 1H), 8.38 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 8.25 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.81-7.77 (m, 1H), 7.59-7.55 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 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 $C_{16}H_{10}O_4$: calcd. 266.0579, found 266.0583.

1-phenoxyphenanthrene-9,10-dione (2o)



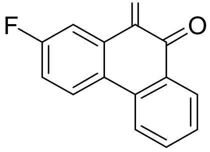
Saffron yellow solid (40.5 mg, 45%), R$_f$ = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 198–200 ºC; IR (neat): ν = 1662 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.17 (dd, J_1 = 7.8 Hz, J_2 = 1.25 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.78-7.72 (m, 2H), 7.59 (t, J = 8.3 Hz, 1H), 7.52-7.49 (m, 1H), 7.41-7.38 (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); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{20}H_{12}O_3$: calcd. 300.0786, found 300.0781.

2-methoxyphenanthrene-9,10-dione (2p)



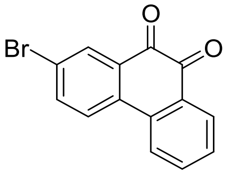
Red solid (46.4 mg, 65%), R$_f$ = 0.27 (petroleum ether-EtOAc, 6:1); m.p. 214-215 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14-8.13 (m, 1H), 7.91-7.87 (m, 2H), 7.69-7.66 (m, 1H), 7.62 (d, J = 3.0 Hz, 1H), 7.41-7.38 (m, 1H), 7.26-7.23 (m, 1H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{15}H_{10}O_3$: calcd. 238.0630, found 238.0625.

2-fluorophenanthrene-9,10-dione (2q)[34]



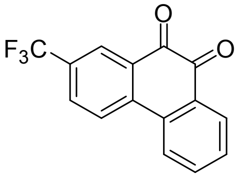
Yellow solid (50.9 mg, 75%), R$_f$ = 0.28 (petroleum ether-EtOAc, 6:1); m.p. 250-251 ºC (lit.[34] m.p. 246-248 ºC); IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, J = 7.5Hz, 1H), 8.04-8.02 (m, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.50-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 = 22.5Hz); HRMS (EI) for $C_{14}H_7FO_2$: calcd. 226.0430, found 226.0437.

2-bromophenanthrene-9,10-dione (2r)



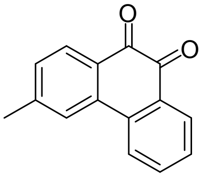
Yellow solid (62.0 mg, 72%), the structure is the same as **2j**.

2-(trifluoromethyl)phenanthrene-9,10-dione (2s)



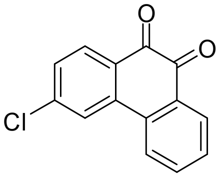
Yellow solid (59.8 mg, 72%), the structure is the same as **2k**.

3-methylphenanthrene-9,10-dione (2t)



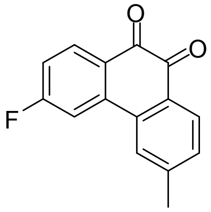
Yellow solid (44.7 mg, 67%), the structure is the same as **2a**.

3-chlorophenanthrene-9,10-dione (2u)



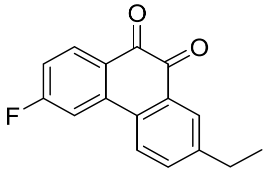
Yellow solid (51.0 mg, 70%), the structure is the same as **2h**.

3-fluoro-6-methylphenanthrene-9,10-dione (2v)



Yellow solid (56.2 mg, 78%), R$_f$ = 0.29 (petroleum ether-EtOAc, 6:1); m.p. 245-246 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 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);^{13}C NMR (CDCl$_3$, 100 MHz): δ 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 $C_{15}H_9FO_2$: calcd. 240.0587, found 240.0591.

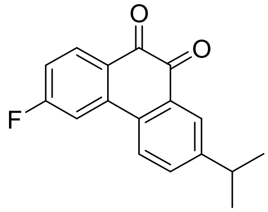
2-ethyl-6-fluorophenanthrene-9,10-dione (2w)



Yellow solid (61.8 mg, 81%), R$_f$ = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 182-183 ºC; IR (neat): ν = 1668 (C=O) cm^{-1}; ^{1}H NMR (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* = 7.6Hz, 3H);^{13}C NMR (CDCl$_3$, 100 MHz): δ 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 $C_{16}H_{11}FO_2$: calcd. 254.0743, found

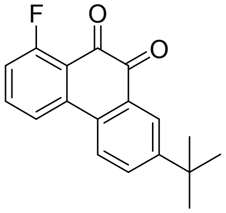
254.0748.

6-fluoro-2-isopropylphenanthrene-9,10-dione (2x)



Yellow solid (61.2 mg, 76%), R_f = 0.25 (petroleum ether-EtOAc, 6:1); m.p. 168-169 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 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}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{17}H_{13}FO_2$: calcd. 268.0900, found 268.0906.

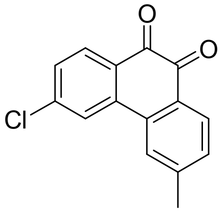
7-*tert*-butyl-1-fluorophenanthrene-9,10-dione (2y)



Yellow solid (59.3 mg, 70%), R_f = 0.25 (petroleum ether-EtOAc, 6:1); m.p. 178-179 ºC; IR (neat): ν = 1672 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 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}C NMR ($CDCl_3$, 100 MHz): δ 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

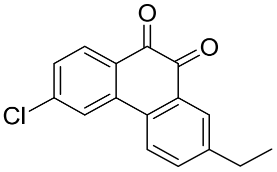
Hz), 133.4, 132.7 (d, *J* = 3.0 Hz), 130.5, 127.1, 124.7, 120.0 (d, *J* = 3.0 Hz), 119.3 (d, *J* = 6.0 Hz), 117.4 (d, *J* = 21.0 Hz), 35.0, 30.9; HRMS (EI) for $C_{18}H_{15}FO_2$: calcd. 282.1056, found 282.1052.

3-chloro-6-methylphenanthrene-9,10-dione (2z)



Yellow solid (57.8 mg, 75%), R$_f$ = 0.28 (petroleum ether-EtOAc, 6:1); m.p. 215-216 ºC; IR (neat): ν = 1675 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 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}C NMR ($CDCl_3$, 100 MHz): δ 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 $C_{15}H_9ClO_2$: calcd. 256.0291, found 256.0297.

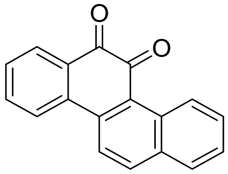
6-chloro-2-ethylphenanthrene-9,10-dione (2za)[35]



Yellow solid (67.4 mg, 83%), R$_f$ = 0.26 (petroleum ether-EtOAc, 6:1); m.p. 205-206 ºC (lit.[35] m.p. 210-210.5 ºC); IR (neat): ν = 1673 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 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}C NMR ($CDCl_3$, 100 MHz): δ 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;

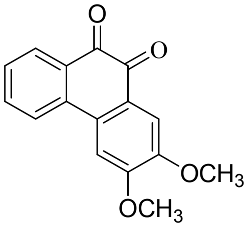
HRMS (EI) for $C_{16}H_{11}ClO_2$: calcd. 270.0448, found 270.0453.

chrysene-5,6-dione (2zb)



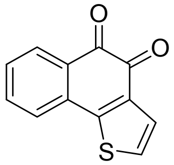
Yellow solid (57.3 mg, 74%), R_f = 0.25 (petroleum ether-EtOAc, 6:1); m.p. 249-250 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.41(d, *J* = 8.5 Hz, 1H), 8.19-8.15 (m, 2H), 8.10 (d, *J* = 8.5Hz, 2H), 7.90 (d, *J* =8.0 Hz, 1H), 7.77-7.70 (m, 2H), 7.59-7.56 (m, 1H), 7.52-7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{18}H_{10}O_2$: 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); m.p. 202-203 ºC; IR (neat): ν = 1671 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$,500 MHz): δ 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}C NMR ($CDCl_3$, 125 MHz): δ 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 $C_{16}H_{12}O_4$: calcd. 268.0736, found 268.0741.

naphtho[1,2-b]thiophene-4,5-dione (2zd)[1g]



Yellow solid (52.7 mg, 82%), R$_f$ = 0.28 (petroleum ether-EtOAc, 6:1); m.p. 218-220 ºC; IR (neat): ν = 1672 (C=O) cm^{-1}; ^{1}H NMR (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}C NMR (CDCl$_3$, 100 MHz): δ 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 $C_{12}H_6O_2S$: calcd. 214.0089, found 214.0086.

Mechanistic Studies.

Reaction of 1ze in CH$_3$CN-H$_2$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 CH$_3$CN:H$_2$O^{18} = 50:1 (V/V, 3 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 25 ºC for 12 h. Upon completion, the resulting mixture was diluted with CH$_2$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^{18}** and **3ze**/**3ze-O^{18}** were sampled for MS analysis (see Figure *S1-S2* in Supporting Information).

Reaction of 1ze in the standard reaction conditions in the presence of an 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 CH_3CN:H_2O = 50:1 (V/V, 3 mL) were added to a 10-mL flask. The flask was opened to the vacuum, pumped for 2-3 minutes and backfilled with $^{18}O_2$ gas using a balloon. Then the reaction mixture was stirred at 25 ºC for 12 h. Upon completion, the resulting mixture was diluted with CH_2Cl_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 for MS analysis. The analyses showed that both **2b** and **3ze** were normally formed while **2b-O^{18}** and **3ze-O^{18}** 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_3CN:H_2O = 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_2. When solvent was completely frozen, the flask was opened to the vacuum (high vacuum) and pumped for 2-3 minutes, with the flask still immersed in liquid N_2. 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 ºC for 12 h. Upon completion, the resulting mixture was diluted with CH_2Cl_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 (**2b**: 30%; **3ze**: 34%).

Studies on the intermolecular kinetic isotope effects (KIE) based on substrate 1u and 1u-*d*$_5$. 1u (70.4 mg, 0.2 mmol), **1u-*d*$_5$** (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_3CN:H_2O = 50:1 (V/V, 4 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 25 ºC for 5 h. Upon completion, the resulting mixture was diluted with CH_2Cl_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. On the basis of ^{1}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_4, 10 mol %, prepared according to our previous work[18a]), Selectfluor (212.6 mg, 0.6 mmol, 2 equiv), and a combined CH_3CN/H_2O = 50:1 (V/V) solvent (3 mL) were added to a 10-mL flask. Then the reaction mixture was stirred at 25 ºC for 12 h. Upon completion, the resulting mixture was diluted with CH_2Cl_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 **2a** (52.7 mg, 79%) and **3a** (34.2 mg, 81%).

Acknowledgement

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Supporting Information

Charts for mechanistic studies as well as copies of ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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