Friedel–Crafts Coupling of Electron-Deficient Benzoylacetons Tuned by Remote Electronic Effects

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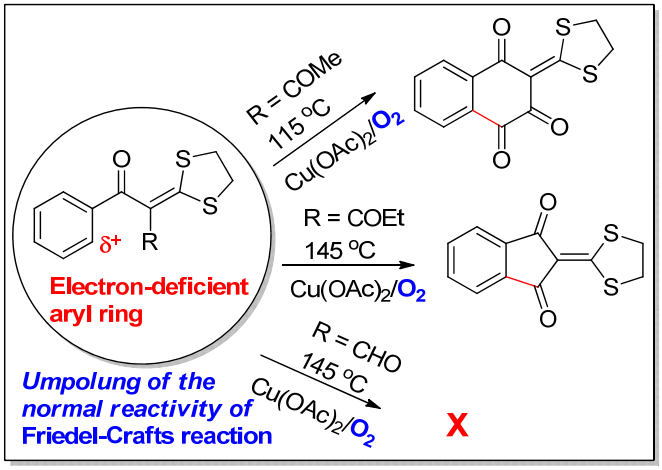
ABSTRACT: Acid-catalyzed electrophilic aromatic substitution for C–C bond-formation, commonly referred to as the Friedel–Crafts reaction in recognition of its discoverers, is one of the most useful reactions in organic chemistry for over a century. However, the Friedel–Crafts reaction can not occur on a benzene ring having a strongly electron-withdrawing group, such as an acyl group, which deactivates the aromatic ring toward electrophilic substitutions and remains a major challenge. Herein, the synthesis of naphthoquinones and 1,3-indandiones, bearing two acyl groups at *ortho*-positions to each other on a benzene ring, are demonstrated by means of copper-catalyzed intramolecular aerobic oxidative acylation of benzoylacetone derivative precursors. This unusual Friedel–Crafts reaction reveals a new activation mode for the in-situ polarity-reverse of an electron-deficient aromatic ring to a reactive, electron-rich one tuned by remote electronic effects.

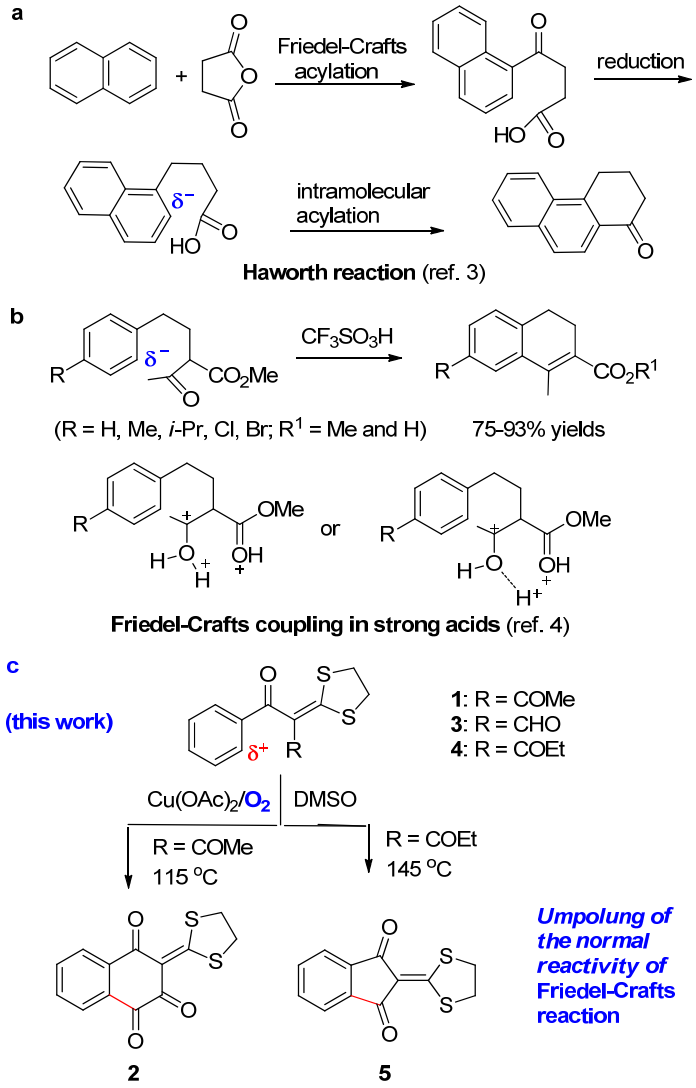


INTRODUCTION

The Friedel−Crafts reaction, an acid-catalyzed electrophilic aromatic substitution reaction first reported by Friedel and Crafts on the $AlCl_3$-catalyzed alkylation or acylation of benzene with an alkyl halide and a carboxylic acid chloride, respectively, is the most common reaction of aromatic compounds and one of the most useful synthetic methods in organic chemistry for over a century.[1] Cyclization of aromatic compounds by intramolecular attack on an aromatic ring is the intramolecular version of the Friedel−Crafts reactions,[2] such as the Haworth reaction based on a three-step synthesis of 1-tetralone derivatives through Friedel−Crafts acylation, Clemmensen reduction, and intramolecular Friedel−Crafts acylation starting from an arene and succinic anhydride (Scheme 1a).[3] Recently, Ohwada and co-workers described that arylacetoacetates can be transformed into dihydronaphthalenes (as a mixture of acid and ester) through self-condensation in the superacid, trifluoromethanesulfonic acid (TFSA, 10 equiv, Scheme 1b).[4] For this intramolecular aromatic substitution, the tricationic, superelectrophilic species was proposed to interpret the enhanced electrophilicity of the preferred keto cyclization based on the principle of superacid-promoted Friedel−Crafts reactions for the activation of electrophiles.[4,5] In 2011, Siegel and co-workers showed an intramolecular Friedel−Crafts aryl–aryl coupling of fluoroarenes,[6] which is activated by silyl cation through the exchange of C−F bond for the more stronger Si−F bond to generate active aryl carbocations from fluoroarenes.[6,7] These results[4–6] largely expanded the utility of Friedel−Crafts reaction and are in accord with the electrophilic aromatic substitution reaction for C–C bond-formation as well.[1–8]

Friedel−Crafts alkylation and acylation reactions are very useful methods for C–C bond formations. However, the Friedel−Crafts reaction can't occur on the benzene ring having the strongly electron-withdrawing acyl group, which deactivates the aromatic ring toward electrophilic substitutions. This is a strict limitation of the Friedel−Crafts reaction.[1–8] Recently, we disclosed a concept, "polarity-reversible conjugate addition", showing that the polarity of a classical Michael acceptor can

Scheme 1. Intramolecular Friedel–Crafts Coupling



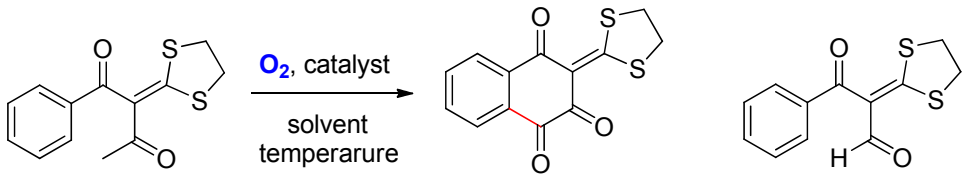
be reversed through remote electronic effects.[9] Mechanism studies[10] and related experimental results support this concept.[10,11] In our recent research on the CuI-catalyzed oxidative C–C bond cleavage reaction of methyl ketones using molecular oxygen as the oxidant,[12,13] it was found that the reaction of 4-phenylbutan-2-one gave the sequential C–C bond cleavage product, benzaldehyde, in high yield via 2-oxo-4-phenylbutanal as an intermediate.[12] An attempted extension of the C–C bond cleavage methodology in connection with our research on the ketene dithioacetal chemistry,[13–17] we found that, catalyzed by $Cu(OAc)_2$ in the presence of molecular oxygen as the oxidant, the aldehyde, 2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal **3** (Scheme 1c), is inert to further transformation. This result is similar to our previous results.[12] Interestingly, under identical reaction conditions, the 1,2-diacylbenzene derivatives, 3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3*H*)-triones **2** and

2-(1,3-dithiolan-2-ylidene)-1*H*-indene-1,3(2*H*)-diones **5**, were obtained from the reactions of 2-(1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-diones **1** and 2-(1,3-dithiolan-2-ylidene)-1-phenylpentane-1,3-diones **4**, respectively (Scheme 1c). These transformations represent the unusual modes of the Friedel−Crafts reaction involving the C–C bond formation on a benzene ring having a strongly electron-withdrawing acyl group. In this paper, we disclose the realization of the intramolecular Friedel−Crafts reaction of benzoylacetone derivatives for the concise synthesis of naphthoquinones and 1,3-indandiones in a single operation starting from readily available substrates and reveal an umpolung strategy for the polarity-reverse from an electron-deficient aromatic ring into a reactive, electron-rich one tuned by remote electronic effects, for the first time.

RESULTS AND DISCUSSION

The starting materials, 2-(1,3-dithiolan-2-ylidene)-1-arylbutane-1,3-diones **1** were readily prepared by the reaction of aroylacetones with CS_2 and $Br(CH_2)_2Br$ (or $Cl(CH_2)_2Cl$) under basic conditions or by Friedel−Crafts-type acylation of the corresponding acyl/aroyl ketene dithioacetals.[14,15] In the present research, initially, the reactions of **1** bearing a terminal acetyl group were examined with 2-(1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-dione **1a** as a model employing the catalyst system applied to the oxidative C–C bond cleavage reaction of methyl ketones.[12,13] Catalyzed by CuI in the solvent, dimethyl sulfoxide (DMSO), under oxygen atmosphere (balloon)[12,13] at 115 ^{o}C for 40 h, the reaction of **1a** gave the naphthoquinone product, 3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3*H*)-trione **2a**, in 32% yield (Table 1, entry 1). This result suggests that the formation of naphthoquinone **2a** involves the acetyl sp^3C–H bond oxidation of **1a**, similar to the oxidation of 4-phenylbutan-2-one[12] followed by intramolecular cyclization to form a six-membered ring through an unusual Csp^2–Csp^2 bonding between the *ortho*-C–H of the electron-deficient aryl ring and the terminal aldehydic C–H bond (vide infra). Encouraged by this result, the reaction conditions were then optimized as shown in Table 1. Increasing CuI loading resulted in a higher yield of **2a** (Table 1, entry 2). Similar results were obtained by using CuCl and CuBr as the catalysts, respectively (Table 1, entries 3 and 4). In comparison, $Cu(OAc)_2$ as the catalyst led to the best result for the formation of **2a** (Table 1, entry 7, along with 7% yield of 2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal **3** formed via oxidative C–C bond cleavage[12,13]).

Table 1. Catalyst screening and optimization of reaction conditions[a]



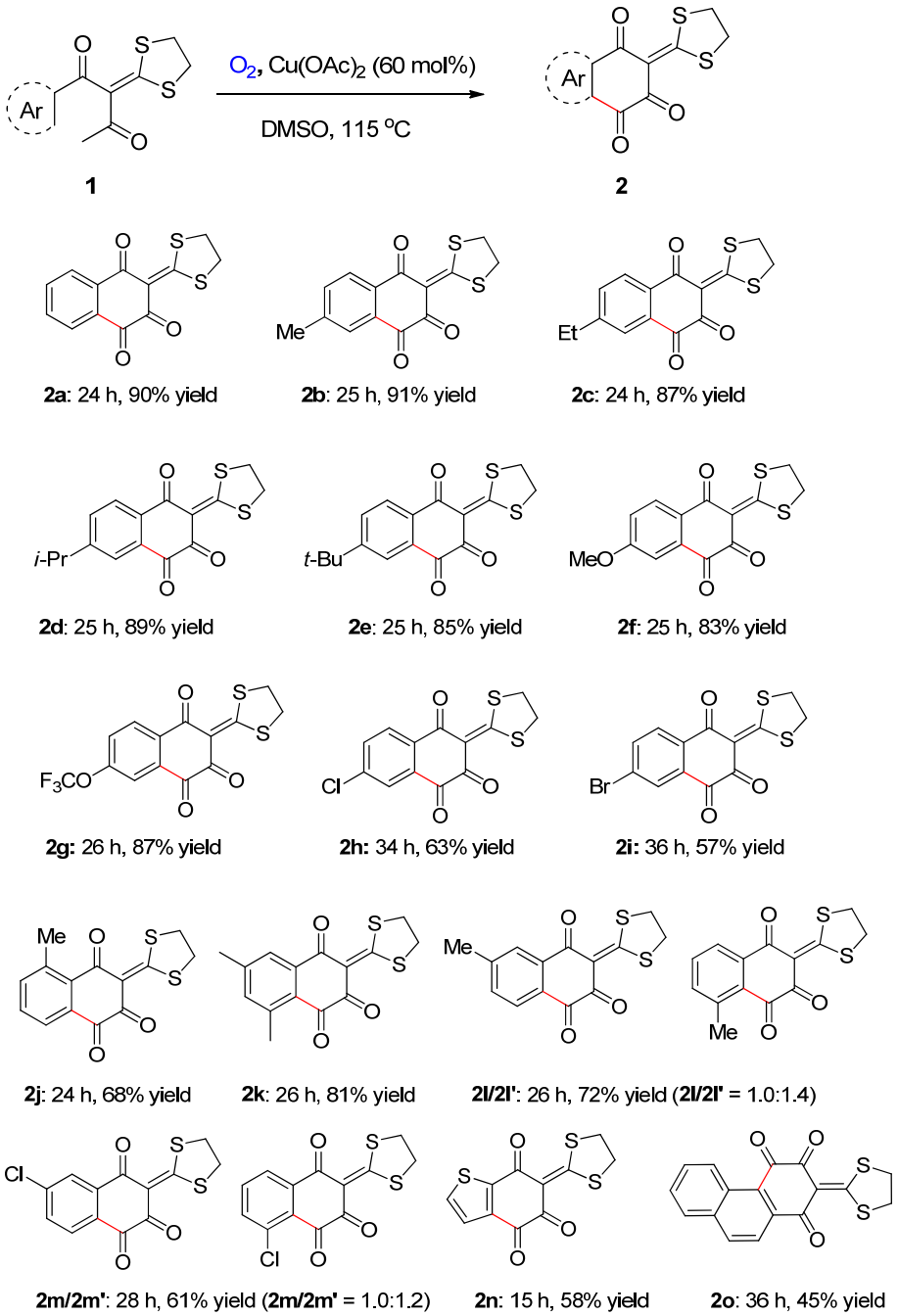
1a **2a** **3**

Entry	Catalyst (mol%)	Solvent	*T* (°C)	Time (h)	Yield (%)[b]
1	CuI (30)	DMSO	115	40	32
2	CuI (60)	DMSO	115	20	57
3	CuCl (60)	DMSO	115	64	68
4	CuBr (60)	DMSO	115	60	63
5	$CuCl_2$ (60)	DMSO	115	48	75
6	$Cu(OTf)_2$ (60)	DMSO	115	72	42
7	**$Cu(OAc)_2$ (60)**	**DMSO**	**115**	**24**	**90**
8	$Cu(OAc)_2$ (30)	DMSO	115	48	87
9	$PdCl_2$ (60)	DMSO	115	24	N.R.[c]
10	$Pd(OAc)_2$ (60)	DMSO	115	24	N.R.[c]
11	$Cu(OAc)_2$ (60)	DMF	115	24	78
12	$Cu(OAc)_2$ (60)	TCP	115	72	46
13	$Cu(OAc)_2$ (60)	DMSO	80	24	N.R.[c]
14	$Cu(OAc)_2$ (60)	DMSO	100	70	82
15	$Cu(OAc)_2$ (60)	DMSO	115	30	56[d]
16	$Cu(OAc)_2$ (60)	DMSO	115	24	NR[c,e]
17	$CuBr_2$ (60)	DMSO	115	5	24

[a]Reaction conditions: 2-(1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-dione **1a** (0.5 mmol scale), O_2 (balloon), solvent (8 mL). [b]Isolated yields. [c]No reaction was observed. [d]The reaction was performed in the open air. [e]The reaction was performed under nitrogen atmosphere.

These results indicated either the higher catalytic activity of Cu(II) than Cu(I) (Table 1, entry 3 versus entry 5) and the significant influence of the counteranion of catalysts on the transformation from **1a** to **2a** (Table 1, entry 7 versus entries 5 and 6). Under identical conditions, $PdCl_2$ and $Pd(OAc)_2$ as catalysts were ineffective (Table 1, entries 9 and 10). Among the solvents tested, DMSO gave the highest yield of **2a** (Table 1, entry 7) in comparison with dimethylformamide (DMF, Table 1, entry 11) or 1,2,3-trichloropropane (1,2,3-TCP, Table 1, entry 12). It was found that no reaction occurred at all (**1a** was recovered quantitatively) when the reaction of **1a** was performed under the optimal conditions as in Table 1, entry 7 but under a nitrogen atmosphere (Table 1, entry 16). It was also found that, catalyzed by $CuBr_2$, the reaction of **1a** could be completed in about 4 h, however gave only 24% yield of **2a** isolated from the reaction mixture (Table 1, entry 17).

Table 2. Synthesis of Naphthoquinones[a,b]



[a] Reaction conditions: 2-(1,3-dithiolan-2-ylidene)-1-aryllbutane-1,3-dione **1** (0.5 mmol scale), solvent (8 mL), O_2 (balloon) at 115 °C. [b] Isolated yields.

The transformation of **1a** to **2a** is an unusual oxidative intramolecular acylation reaction because the benzene ring of **1a** having an acyl group. This transformation is previously unknown in Friedel–Crafts reactions.[1–8] Thus, with the optimal conditions (Table 1, entry 7) in hand, the scope of the transformation from α-acetyl ketene dithioacetals **1** to naphthoquinones **2** was examined. As shown in

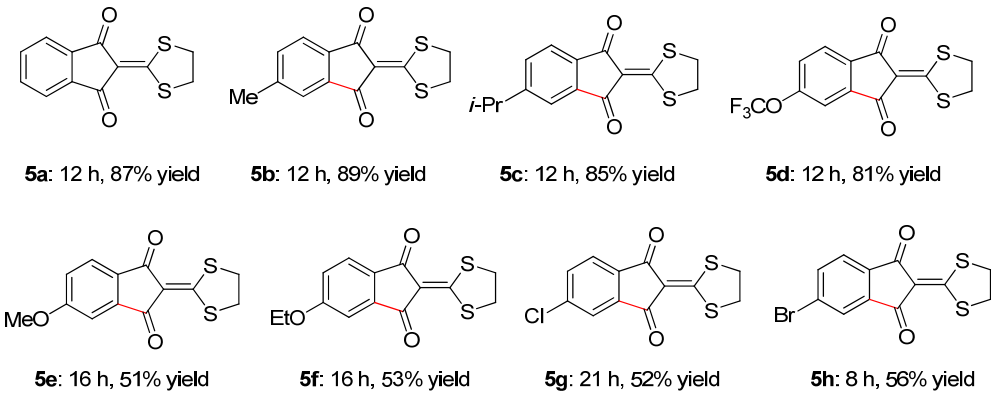
Table 2, a wide range of naphthoquinone derivatives **2** were prepared, which all participated in a straightforward manner for the unusual intramolecular acylation reaction, thereby furnishing the desired naphthoquinones **2** with high efficiency. For the aryl ketone substrates **1** with either electron-donating (**1b**−**1g**, **1j**, **1k** and **1l**) or electron-withdrawing substitutes (**1h**, **1i** and **1m**) on the aryl ring of **1** gave the corresponding acylation products **2** in good to excellent yields. In addition, the desired naphthoquinones **2n** and **2o** were also obtained in good yields from aryl ketones **1n** and **1o** having a heteraryl and a 2-naphthalenyl unit, respectively (Table 2).

Clearly, naphthoquinones **2b**−**2g**, **2j**, **2k** and **2l**/**2l'** can be prepared in high to excellent yields from those α-acetyl ketene dithioacetals **1** bearing electron-donating substituents on the aryl ring. In comparison, naphthoquinones **2h**, **2i**, **2m**/**2m'** can also be synthesized from the corresponding α-acetyl ketene dithioacetals **1** although bearing an additional electron-withdrawing substituent on the aryl ring (Table 2). These results indicate that the above *ortho*-acylation reactions are a powerful tool to expand the conventional Friedel−Crafts reactions.[1–8]

The unusual intramolecular oxidative *ortho*-acylation of aryl ketones **1** mentioned above (Table 2) provides a new and an efficient access to naphthoquinone derivatives.[18] For further understanding the unusual coupling reaction, selected experiments were performed using the readily available 2-(1,3-dithiolan-2-ylidene)-1-arylpentane-1,3-diones **4** as the substrates.[14,15] It was found that no reaction occurred when 2-(1,3-dithiolan-2-ylidene)-1-arylpentane-1,3-dione **4a** was treated under the identical reaction conditions as described for the synthesis of naphthoquinones **2** (Table 2). Whereas, when the reactions of **4** were carried at a higher temperature (145 ^{o}C) than the reaction of **1**, 2-(1,3-dithiolan-2-ylidene)-1*H*-indene-1,3(2*H*)-dione derivatives **5** were produced in good to high yields via a formal deethylation/intramolecular *ortho*-acylation sequence to form the five-membered ring (Table 3).[19] Similar to the synthesis of naphthoquinones **2**, the substrate, 2-(1,3-dithiolan-2-ylidene)-1-arylpentane-1,3-diones **4g** and **4h**, bearing an additional electron-withdrawing substituent on the aryl ring gave relatively lower yields of the 1,3-indandione

products **5g** and **5h** than 1,3-indandiones **5a**−**d** having an electron-donating substituent on the aryl ring. Interestingly, 1,3-indandiones **5e** and **5f** were produced in relatively lower yields although the corresponding substrates bearing an electron-donating methoxy and ethyoxy group, respectively.

Table 3. Synthesis of 1,3-Indandiones[a,b]



5a: 12 h, 87% yield **5b**: 12 h, 89% yield **5c**: 12 h, 85% yield **5d**: 12 h, 81% yield

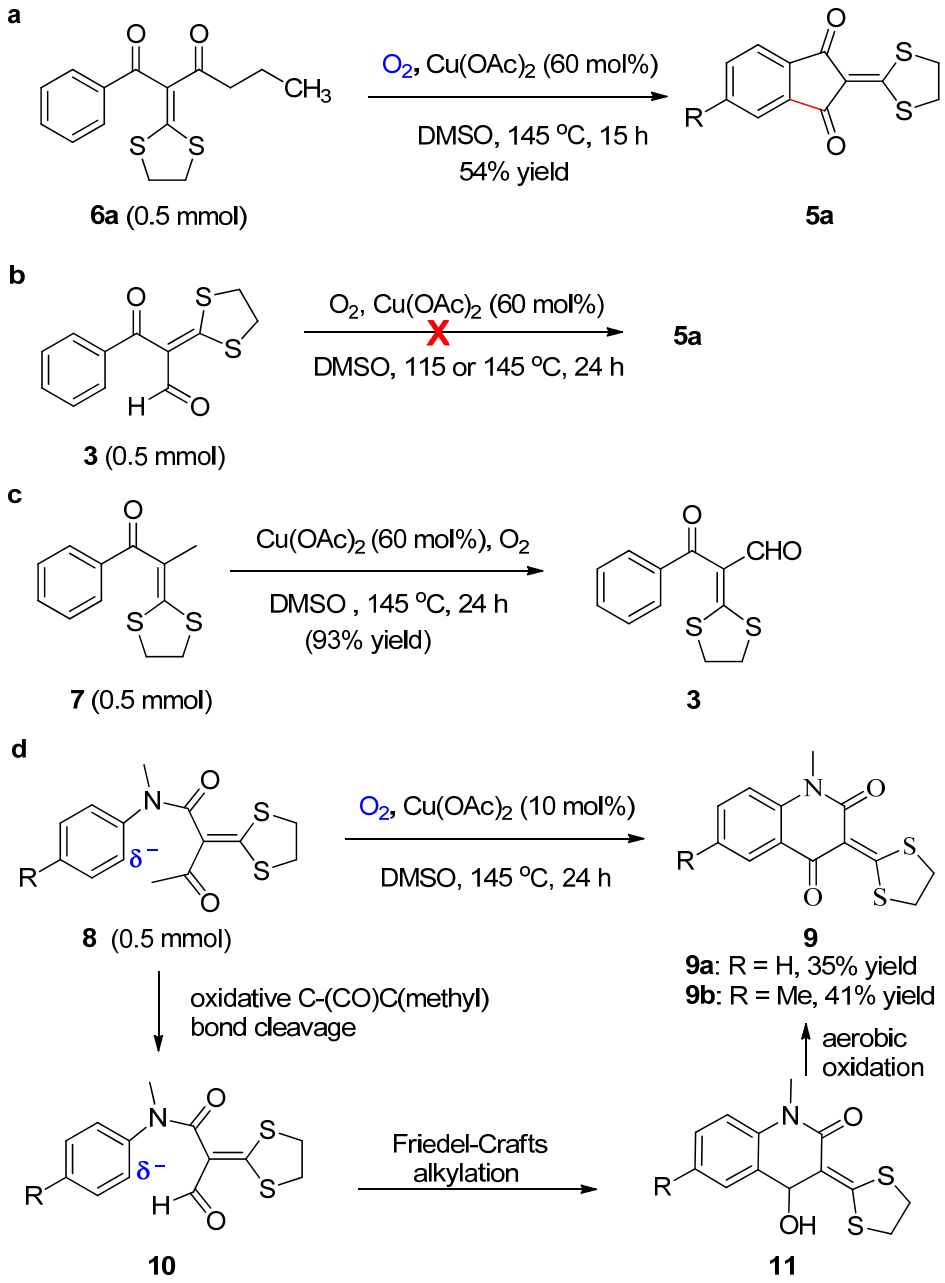
5e: 16 h, 51% yield **5f**: 16 h, 53% yield **5g**: 21 h, 52% yield **5h**: 8 h, 56% yield

[a] Reaction conditions: 2-(1,3-dithiolan-2-ylidene)-1-arylpentane-1,3-diones **4** (0.5 mmol scale), solvent (8 mL), O_2 (balloon) at 145 °C. [b]Isolated yields.

The above reactions exhibit high levels of chemoselectivity and broad functional-group tolerance. The intramolecular cyclization of 2-(1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-diones **1** forms a six-membered ring (Table 2). Whereas, the cyclization of 2-(1,3-dithiolan-2-ylidene)-1-phenylpentane-1,3-diones **4** under similar reaction conditions forms a five-membered ring (Table 3). To understand the reaction mechanisms, a series of experiments was designed and conducted.

Firstly, the cyclization reaction of 2-(1,3-dithiolan-2-ylidene)-1-phenylhexane-1,3-dione **6a** was performed to examine the influence of alkyl chain length of the aroyl ketone substrates on the synthesis of indene-1,3(2*H*)-dione derivatives **5**. As the result, **5a** was obtained in moderate yield by treatment of **6a** under identical conditions as for the synthesis of **5** (Scheme 2a). This result indicates that the cyclization reactions of **4** and **6** share the same mechanism. The relatively lower yield of **5a** from **6a** is likely due to the less reactivity of **6a** than **4a** because the former has a longer alkyl chain.

Scheme 2. Mechanism Studies



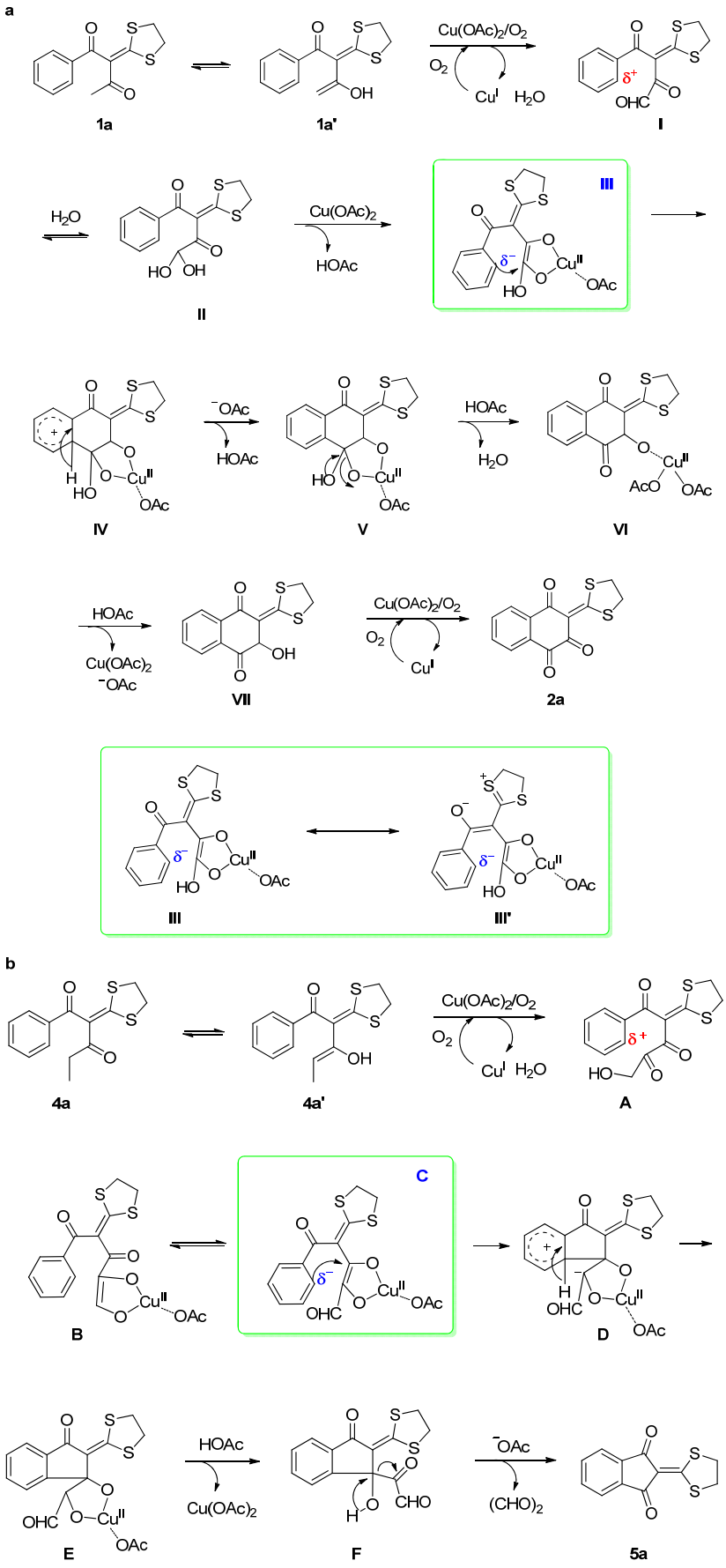
Secondly, the reaction of 2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal **3** was examined in details under the conditions for the formation of either naphthoquinones **2** (Table 2) and 1,3-indandiones **5** (Table 3), respectively. In both cases, compound **3** was inert and was recovered in nearly quantitative yield (Scheme 2b). These results imply that **3** is very stable under the reaction conditions applied. In addition, these results exclude the mechanism accounting for cross-dehydrogenative coupling (CDC) reactions to form the C–C bond[20] leading to 1,3-dione **5a**.

Thirdly, it was found that compound **3** could be prepared in excellent isolated yield by aerobic oxidation of 2-(1,3-dithiolan-2-ylidene)-1-phenylpropan-1-one **7** (Scheme 2c) under identical conditions as described in Table 3. This result give further evidence for the stability of **3** under the reaction conditions as indicated above.

Forthly, to provide further insights into the reaction mechanisms, the tandem oxidative C–C bond cleavage/intramolecular Friedel−Crafts alkylation/aerobic oxidation reaction of 2-(1,3-dithiolan-2-ylidene)-*N*-methyl-3-oxo-*N*-phenylbutanamides **8** were investigated. As the results, 3-(1,3-dithiolan-2-ylidene)-1-methylquinoline-2,4(1*H*,3*H*)-diones **9a** and **9b** were obtained in moderate yields (Scheme 2d). Although the Friedel−Crafts-type CDC process for the formation of **9** via aldehyde intermediate **10** can't be excluded,[20] a mechanism involving Friedel−Crafts cyclization[1–5] to form alcohol intermediate **11** followed by aerobic oxidation[12,13] to form **9** is preferred due to *N*-acyl anilines **8** have the electron-rich aromatic ring.

Based on the above experimental results, a mechanism for the formation of naphthoquinones **2** is proposed with the reaction of **1a** as an example (Scheme 3a). Similar as the previous work, Cu-catalyzed aerobic oxidation of **1a** gives aldehyde intermediate **I** via the enol form of **1a'**.[12,13,21] Aldehyde intermediate **I** should be inert for the intramolecular Friedel−Crafts alkylation because **I** has a strongly electron-withdrawing acyl substituent on the benzene ring[1–5] (also see Scheme 2b and Scheme 2c for the stability of **3** under the identical conditions). On the other hand, the CDC reaction[20] of **I** through Csp^2–Csp^2 bond-formation between the *ortho*-C–H bond of the aryl ring and the aldehydic C–H bond to afford naphthoquinones **2** seems impossible because the related compound **3** is very stable under the identical reaction conditions (Scheme 2b and Scheme 2c).

Scheme 3. Suggested Mechanism for Formation of Products 2 and 5



Thereby, the Cu(II) enolate complex intermediate **III** will be generated by coordination of the hydrate intermediate **II** with $Cu(OAc)_2$.[15,22] Complex **III**, as the key intermediate, the aryl ring has been tuned to the electron-rich one at this stage by the remote electron-donating enol p-π conjugation structure of the side chain.[23] As the result of the umpolung of the innate reactivity of aryl ketone **1a** at the *ortho*-position of the aryl ring, the intramolecular Friedel−Crafts reaction of intermediate **III** enables the formation of naphthoquinone **2a** through an intramolecular Friedel−Crafts reaction as the crucial step, followed by deprotonation, regeneration of the catalyst, $Cu(OAc)_2$, and $Cu(OAc)_2$-catalyzed aerobic oxidation sequence (Scheme 3a).[12,13,21] It should be mentioned that, similar to the polarity-reversible conjugate addition,[9–11] the zwitterionic resonance contribution of **III'** attributing to an S···O interaction of the α-oxo ketene dithioacetal moiety (Scheme 3a)[15,24,25] may play an important role for the remote electronic effects to make the polarity reverse of the electron-deficient aromatic ring to the electron-rich one. As described above, the formation of 1,3-indandiones **5** should follow a similar umpolung procedure, whereas leading to a five- instead of six-membered carbocycle via intramolecular Friedel−Crafts reaction (Scheme 3b).

Thus, Cu-catalyzed aerobic oxidation of ethyl ketone **5a** gives hydroxyl α-diketone intermediate **A** followed by formation of the Cu(II) enolate complex intermediate **B** in equilibrium with **C** as the key intermediate. Whereby, the intramolecular Friedel−Crafts cyclization will lead to a five-membered ring by reaction at the β-carbon of the α,β-unsaturated aldehyde moiety of the side chain. Subsequent proton elimination (transfer) of intermediate **D** results in intermediate **E**. Finally, 1,3-indandione **5a** is formed through the sequential release of $Cu(OAc)_2$ and oxalaldehyde. In comparison, intermediate **C** should be less reactive than intermediate **IV** as described in Scheme 3b due to the existence of the terminal electron-withdrawing formyl group. The transformation from

2-(1,3-dithiolan-2-ylidene)-1-phenylhexane-1,3-dione **6a** to 1,3-indandione **5a** (Scheme 2a) gives further evidence for the proposed mechanism.

CONCLUSION

In summary, the rapid and concise synthesis of naphthoquinones **2** and 1,3-indandiones **5** in a single operation starting from readily available benzoylacetone derivative precursors has been described for the first time. It has been revealed that although the aromatic rings of 2-(1,3-dithiolan-2-ylidene)-1-arylbutane-1,3-diones **1** and 2-(1,3-dithiolan-2-ylidene)-1-arylpentane-1,3-diones **4** bear strongly electron-withdrawing groups and are not reactive for the traditional Friedel−Crafts reactions, the intramolecular Friedel−Crafts reaction of these substrates can be achieved by the umpolung of the normal reactivity of the aryl ring during the reaction. This new concept, namely electron-deficient aromatic ring umpolung, for the in-situ polarity-reverse of an electron-deficient aromatic ring to a reactive, electron-rich one tuned by electronic effects, provides new insights into the Friedel−Crafts reactions. The reactions exhibit high levels of chemoselectivity and broad functional-group tolerance. Efforts toward expanding the umpolung methodology are currently underway in our laboratory and will be reported in due course.

EXPERIMENTAL SECTION

General Information. All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel. The products were purified by column chromatography on flash silica gel. Melting points were uncorrected. NMR spectra were obtained by 500 MHz and 400 MHz for ^{1}H NMR; 125 MHz for ^{13}C NMR, with TMS as the internal standard. All chemical shifts are given in ppm. The solvent peaks were not integrated in all the NMR spectra.

High-resolution mass spectra (HRMS) were obtained using a micro TOF focus spectrometer (ESI).

General experimental procedures for the synthesis of naphthoquinones (with 2a as an example). To the solution of 2-(1,3-dithiolan-2-ylidene)-1-phenylbutane-1,3-dione **1a** (132 mg, 0.5 mmol) in DMSO (8.0 mL) was added anhydrous $Cu(OAc)_2$ (99.0 %, 55 mg, 0.3 mmol) at room temperature, then the reaction was heated up to 115 ^oC and stirred under O_2 atmosphere. After **1a** was consumed as indicated by TLC, the resulting mixture was cooled to room temperature, poured into water (30 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (dichloromethane: ethyl acetate: petroleum ether = 0.25/1/5, V/V/V) to give 3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3*H*)-trione **2a** (124 mg, 90%, 0.45 mmol).

*3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione (**2a**)*. Obtained as a yellow solid; isolated yield: 124 mg (90%); m.p. 218–219 ^oC. Eluent dichloromethane/ethyl acetate/petroleum ether (0.25/1/5, V/V/V). ^1H NMR (DMSO, 500 MHz, ppm): δ 3.57 (s, 4H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.0, 38.2, 122.8, 127.6, 127.8, 132.5, 134.1, 134.6, 135.5, 175.1, 179.3, 180.0, 192.5. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_9O_3S_2$ $[M + H]^+$: 276.9988, found: 276.9990.

*3-(1,3-dithiolan-2-ylidene)-7-methylnaphthalene-1,2,4(3H)-trione (**2b**)*. Obtained as a yellow solid; isolated yield: 132 mg (91%); m.p. 253–254 ^oC. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.51 (s, 3H), 3.52 (s, 4H), 7.64 (d, *J* = 7.5 Hz, 1H), 8.01 (s, 1H), 8.20 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 21.7, 37.7, 37.9, 122.5, 128.2, 131.7, 132.1, 136.4, 144.8, 175.1, 179.8, 179.9, 193.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{10}NaO_3S_2$ $[M+Na]^+$: 312.9964, found 312.9970.

*3-(1,3-dithiolan-2-ylidene)-7-ethylnaphthalene-1,2,4(3H)-trione (**2c**).* Obtained as a yellow solid; isolated yield: 132 mg (87%); m.p. 214–215 ^oC. Eluent dichloromethane/ethyl acetate/*n*-hexane

(0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.31 (t, *J* = 7.5 Hz, 3H), 2.80 (q, *J* = 7.5 Hz, 2H), 3.52 (s, 4H), 7.66 (d, *J* = 7.5 Hz, 1H), 8.03 (s, 1H), 8.21 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.9, 28.9, 37.7, 37.9, 122.5, 127.0, 128.2, 131.7, 132.3, 135.3, 150.9, 175.1, 179.8(2C), 193.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{15}H_{13}O_3S_2$ $[M + H]^+$: 305.0301, found 305.0292.

3-(1,3-dithiolan-2-ylidene)-7-isopropylnaphthalene-1,2,4(3H)-trione ***(2d)***. Obtained as a yellow solid; isolated yield: 141.5 mg (89%); m.p. 202–203 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.32 (d, *J* = 7.0 Hz, 6H), 3.04–3.09 (m, 1H), 3.53 (s, 4H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.06 (d, *J* =1.5 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 23.4, 34.3, 37.7, 37.9, 122.5, 125.7, 128.3, 131.8, 132.4, 134.0, 155.4, 175.2, 179.8(2C), 193.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{16}H_{15}O_3S_2$ $[M + H]^+$: 319.0457, found 319.0449.

7-(tert-butyl)-3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione ***(2e)***. Obtained as a yellow solid; isolated yield: 141 mg (85%); m.p. 212–213 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.40 (s, 9H), 3.54 (s, 4H), 7.88 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 30.7, 35.3, 37.6, 37.8, 122.3, 124.4, 127.9, 131.3, 131.9, 132.8, 157.6, 175.1, 179.6, 179.8, 193.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{17}H_{17}O_3S_2$ $[M + H]^+$: 333.0614, found 333.0604.

3-(1,3-dithiolan-2-ylidene)-7-methoxynaphthalene-1,2,4(3H)-trione ***(2f)***. Obtained as a yellow solid; isolated yield: 127 mg (83%); m.p. 189–190 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR (DMSO, 500 MHz, ppm): δ 3.55 (s, 4H), 3.93 (s, 3H), 7.45 (m, 2H), 8.11 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.0, 38.1, 56.5, 110.5, 122.3, 122.5, 128.0, 130.3, 134.4, 163.7, 175.2, 179.2, 179.5, 191.6. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{11}O_4S_2$ [M +

H]$^+$:307.0093, found 307.0098.

3-(1,3-dithiolan-2-ylidene)-7-(trifluoromethoxy)naphthalene-1,2,4(3H)-trione ***(2g).*** Obtained as a yellow solid; isolated yield: 156.6 mg (87%); m.p. 207–208 ^{o}C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.54 (s, 4H), 7.64 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.9, 38.0, 118.6, 120.2 (q, *J* = 258.9 Hz, CF_3), 122.2, 127.0, 130.7, 132.4, 133.5, 153.0, 174.2, 178.5(2C), 194.8. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_8F_3O_4S_2$ [M + H]$^+$: 360.9811, found 360.9801.

7-chloro-3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione ***(2h).*** Obtained as a yellow solid; isolated yield: 97.6 mg (63%); m.p. 220–221 ^{o}C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR (DMSO, 500 MHz, ppm): δ 3.58 (s, 4H), 7.93–7.96 (m, 2H), 8.16 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.1, 38.2, 122.6, 126.7, 130.0, 133.2, 134.1, 135.1, 139.0, 174.7, 178.1, 179.2, 192.7. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_8ClO_3S_2$ [M + H]$^+$:310.9598, found 310.9595.

7-bromo-3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione ***(2i).*** Obtained as a yellow solid; isolated yield:101 mg (57%); m.p. 243–244 ^{o}C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR (DMSO, 500 MHz, ppm): δ 3.58 (s, 4H), 8.08–8.10 (m, 3H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.1, 38.2, 122.7, 127.9, 129.6, 130.0, 133.5, 134.1, 138.0, 174.7, 178.1, 179.4, 192.7. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_8BrO_3S_2$ [M + H]$^+$: 354.9093, found 354.9102.

3-(1,3-dithiolan-2-ylidene)-5-methylnaphthalene-1,2,4(3H)-trione ***(2j).*** Obtained as a yellow solid; isolated yield: 98.6 mg (68%); m.p. 224–225 ^{o}C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.87 (s, 3H), 3.50 (m, 4H), 7.58–7.63 (m, 2H), 8.14 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 23.7, 37.6, 37.7, 123.6, 126.9, 131.9,

132.5, 133.1, 139.7, 142.3, 174.9, 180.7, 182.5, 192.6. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{11}O_3S_2$ $[M + H]^+$: 291.0144, found 291.0145.

3-(1,3-dithiolan-2-ylidene)-6,8-dimethylnaphthalene-1,2,4(3H)-trione ***(2k)***. Obtained as a yellow solid; isolated yield: 123 mg (81%); m.p. 175–176 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.47 (s, 3H), 2.74 (s, 3H), 3.51 (s, 4H), 7.34 (s, 1H), 8.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 21.9, 22.7, 37.7, 37.9, 121.7, 127.1, 127.7, 135.9, 137.9, 143.1, 145.7, 175.9, 180.4, 181.1, 192.3. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{15}H_{13}O_3S_2$ $[M + H]^+$: 305.0301, found 305.0294.

3-(1,3-dithiolan-2-ylidene)-6-methylnaphthalene-1,2,4(3H)-trione ***(2l);*** *3-(1,3-dithiolan-2-ylidene)-5-methylnaphthalene-1,2,4(3H)-trione* ***(2l').*** Obtained as a yellow solid; isolated yield: 104.4 mg (72%); m.p. 125–127 °C; **2l/2l'** = 1.0:1.4. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). **2l**, ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.53 (s, 3H), 3.53 (m, 4H), 7.53–7.54 (m, 1H), 8.10– 8.11 (m, 2H); **2l'**, ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.78 (s, 3H), 3.53 (m, 4H), 7.53–7.54 (m, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 8.24 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 22.2, 22.8, 37.7, 37.9, 121.6, 122.6, 126.5, 128.3(2C), 129.6, 129.8, 134.3(2C), 134.5, 135.9, 137.2, 142.8, 147.0, 175.2, 175.6, 179.2, 180.1, 180.2, 181.7, 192.7, 193.3. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{11}O_3S_2$ $[M + H]^+$: 291.0144, found 291.0152.

6-chloro-3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione ***(2m);*** *8-chloro-3-(1,3-dithiolan-2-ylidene)naphthalene-1,2,4(3H)-trione* ***(2m').*** Obtained as a yellow solid; isolated yield: 94.5 mg (61%); m.p. 125–127 °C; **2m/2m'** = 1.0:1.2. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). **2m**, ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.54 (s, 4H), 7.68–7.75 (m, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.27 (d, *J* = 2.0 Hz, 1H); **2m'**, ^{1}H NMR ($CDCl_3$, 400 MHz, ppm):

δ 3.54 (s, 4H), 7.68–7.75 (m, 2H), 8.30 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.9, 38.0, 121.2, 122.3, 127.2, 128.1, 128.5, 129.6, 130.0, 133.6, 133.8, 134.8, 135.6, 136.7, 137.0, 142.6, 174.5, 174.9, 178.5, 178.6(2C), 179.0, 194.0, 194.7. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_8ClO_3S_2$ $[M + H]^+$: 310.9598, found 310.9581.

6-(1,3-dithiolan-2-ylidene)benzo[b]thiophene-4,5,7(6H)-trione ***(2n).*** Obtained as a yellow solid; isolated yield: 81.8 mg (58%); m.p. 210–211 °C. Eluent dichloromethane/ethyl acetate/petroleum ether (0.25/1/5, V/V/V). ^{1}H NMR (DMSO, 500 MHz, ppm): δ 3.56 (s, 4H), 7.59 (d, *J* = 5.0 Hz, 1H), 8.08 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.0, 38.2, 121.4, 126.8, 135.2, 140.2, 149.2, 173.7, 175.7, 176.2, 190.7. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{11}H_7O_3S_3$ $[M + H]^+$: 282.9552, found 282.9560.

2-(1,3-dithiolan-2-ylidene)phenanthrene-1,3,4(2H)-trione ***(2o).*** Obtained as a yellow solid; isolated yield: 73 mg (45%); m.p. 205–206 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.25/1/5, V/V/V). ^{1}H NMR (DMSO, 500 MHz, ppm): δ 3.61 (s, 4H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 9.38 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): δ 38.1, 38.3, 121.0, 123.3, 127.7, 128.3, 129.3, 129.6, 130.0, 130.7, 135.7, 135.9, 136.6, 175.5, 180.2, 182.2, 191.6. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{17}H_{11}O_3S_2$ $[M + H]^+$: 327.0144, found 327.0132.

General experimental procedures for the synthesis of 1,3-Indandiones (with 5a as an example). To the solution of 2-(1,3-dithiolan-2-ylidene)-1-phenylpentane-1,3-dione **4a** (139 mg, 0.5 mmol) in DMSO (8.0 mL) was added anhydrous $Cu(OAc)_2$ (99.0%, 55 mg, 0.3 mmol) at room temperature, then the reaction was heated up to 145 °C and stirred for 12.0 h under O_2 atmosphere. After **4a** was consumed as indicated by TLC, the resulting mixture was poured into water (30 mL) and extracted

with dichloromethane (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (dichloromethane: ethyl acetate: petroleum ether = 0.1/1/6, V/V/V) to give 2-(1,3-dithiolan-2-ylidene)-1*H*-indene-1,3(2*H*)-dione **5a** (107.9 mg, 87%) .

*2-(1,3-dithiolan-2-ylidene)-1H-indene-1,3(2H)-dione (**5a**).* Obtained as a yellow solid; isolated yield: 107.9 mg (87%); m.p. 193–194 ^{o}C. Eluent dichloromethane/ethyl acetate/petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.56 (s, 4H), 7.67–7.69 (m, 2H), 7.85–7.87 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.6, 119.1, 122.6, 134.1, 140.2, 174.6, 188.0. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{12}H_9O_2S_2$ $[M+H]^+$: 249.0038, found 249.0030.

*2-(1,3-dithiolan-2-ylidene)-5-methyl-1H-indene-1,3(2H)-dione (**5b**).* Obtained as a yellow solid; isolated yield: 116.6 mg (89%); m.p. 177–178 ^{o}C. Eluent dichloromethane/ethyl acetate/petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.50 (s, 3H), 3.55 (s, 4H), 7.48 (d, J = 7.5 Hz, 1H), 7.65 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 22.1, 37.5, 119.5, 122.6, 123.0, 134.9, 138.0, 140.7, 145.4, 173.6, 187.9, 188.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_{11}O_2S_2$ $[M + H]^+$: 263.0195, found 263.0184.

*2-(1,3-dithiolan-2-ylidene)-5-isopropyl-1H-indene-1,3(2H)-dione (**5c**).* Obtained as a yellow solid; isolated yield: 123.2 mg (85%); m.p. 147–148 ^{o}C. Eluent dichloromethane/ethyl acetate/petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.31 (d, J = 7.0 Hz, 6H), 3.03–3.08 (m, 1H), 3.55 (s, 4H), 7.54 (d, J = 7.5 Hz, 1H), 7.73 (s, 1H), 7.78 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 23.6, 34.7, 37.4, 37.5, 119.6, 120.3, 122.7, 132.7, 138.3, 140.7, 156.3, 173.5, 187.9, 188.2. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{15}H_{15}O_2S_2$ $[M + H]^+$: 291.0508, found 291.0511.

*2-(1,3-dithiolan-2-ylidene)-5-(trifluoromethoxy)-1H-indene-1,3(2H)-dione (**5d**).* Obtained as a

yellow solid; isolated yield: 134.5 mg (81%); m.p. 163–164 °C. Eluent dichloromethane/ethyl acetate/*n*-hexane (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.58 (s, 4H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.66 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.7(2C), 114.4, 118.8, 120.2 (q, *J* = 258.2 Hz, CF_3), 124.6, 126.0, 138.0, 142.4, 153.4, 176.5, 186.2, 186.4. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_8F_3O_3S_2$ $[M+H]^+$: 332.9861, found 332.9856.

*2-(1,3-dithiolan-2-ylidene)-5-methoxy-1H-indene-1,3(2H)-dione (**5e**).* Obtained as a yellow solid; isolated yield: 70.9 mg (51%);m.p. 195–196 °C. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.54 (s, 4H), 3.93 (s, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.4, 37.5, 56.0, 105.9, 119.7, 121.1, 124.4, 133.3, 143.0, 164.8, 172.6, 187.2, 187.7. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_{11}O_3S_2$ $[M+H]^+$: 279.0144, found 279.0154.

*2-(1,3-dithiolan-2-ylidene)-5-ethoxy-1H-indene-1,3(2H)-dione (**5f**).* Obtained as a yellow solid; isolated yield: 77.4 mg (53%); m.p. 185–186 °C. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.46 (t, *J* = 7.0 Hz, 3H), 3.53 (s, 4H), 4.16 (q, *J* = 7.0 Hz, 2H), 7.14 (dd, J_1= 8.0 Hz, J_2= 1.5 Hz, 1H), 7.28 (d, *J*= 1.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.6, 37.4, 37.5, 64.4, 106.3, 119.7, 121.5, 124.5, 133.2, 143.1, 164.2, 172.4, 187.2, 187.8. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{13}O_3S_2$ $[M+H]^+$: 293.0301, found 293.0309.

*5-chloro-2-(1,3-dithiolan-2-ylidene)-1H-indene-1,3(2H)-dione (**5g**).* Obtained as a yellow solid; isolated yield: 73.3 mg (52%); m.p. 198–199 °C. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/1/6, V/V/V). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.58 (s, 4H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.78–7.80 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.7(2C), 118.7, 122.9, 124.0, 134.1, 138.2, 140.6,

141.6, 176.1, 186.5, 186.8. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{12}H_8ClO_2S_2$ $[M+H]^+$: 282.9649, found 282.9638.

*5-bromo-2-(1,3-dithiolan-2-ylidene)-1H-indene-1,3(2H)-dione (**5h**).* Obtained as a yellow solid; isolated yield: 91 mg (56%); m.p. 168–169 ^oC. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/1/6, V/V/V). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.57 (s, 4H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.7(2C), 118.6, 124.1, 125.9, 129.1, 137.0, 138.7, 141.6, 176.2, 186.4, 186.9. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{12}H_8BrO_2S_2$ $[M+H]^+$: 326.9144, found 326.9166.

Synthesis of 2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal 3. To the solution of 2-(1,3-dithiolan-2-ylidene)-1-phenylpropan-1-one **7** (118 mg, 0.5 mmol) in DMSO (8.0 mL) was added anhydrous $Cu(OAc)_2$ (99.0 %, 55 mg, 0.3 mmol) at room temperature, then the reaction was heated up to 145 ^oC and stirred for 24.0 h under O_2 atmosphere. After **7** was consumed as indicated by TLC, the resulting mixture was poured into water (30 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (ethyl acetate: petroleum ether =1/6, V/V) to give 2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal **3** (116 mg, 93%) as a yellow solid. Reaction time 24.0 h.

*2-(1,3-dithiolan-2-ylidene)-3-oxo-3-phenylpropanal (**3**).* Obtained as a yellow solid; isolated yield: 116 mg (93%); m.p. 93–94 ^oC. Eluent ethyl acetate/ petroleum ether (1/6, V/V). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.42 (m, 2H), 3.50 (m, 2H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 9.71 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 37.0, 37.6, 124.2, 128.5, 129.0, 131.8, 138.3, 186.5, 187.0, 192.1. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{12}H_{11}O_2S_2$ $[M+H]^+$: 251.0195,

found 251.0201.

Synthesis of 3-(1,3-dithiolan-2-ylidene)-1-methylquinoline-2,4(1*H*,3*H*)-dione. To the solution of 2-(1,3-dithiolan-2-ylidene)-*N*-methyl-3-oxo-*N*-phenylbutanamide **8a** (146.5 mg, 0.5 mmol) in DMSO (8.0 mL) was added anhydrous $Cu(OAc)_2$ (99.0%, 9.2 mg, 0.05 mmol) at room temperature, then the reaction was heated up to 145 ^oC and stirred for 24.0 h under O_2 atmosphere. After **8a** was consumed as indicated by TLC, the resulting mixture was poured into water (30 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (dichloromethane/ethyl acetate/ petroleum ether = 0.1/2/5, V/V/V) to give 3-(1,3-dithiolan-2-ylidene)-1-methylquinoline-2,4(1*H*,3*H*)-dione **9a** (48.5 mg, 35 %) as a yellow solid. Reaction time 24.0 h.

*3-(1,3-dithiolan-2-ylidene)-1-methylquinoline-2,4(1H,3H)-dione (**9a**).* Obtained as a yellow solid; isolated yield: 48.5 mg (35%); m.p. 179–180 ^oC. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/2/5, V/V/V). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 3.42–3.44 (m, 2H), 3.47–3.50 (m, 2H), 3.63 (s, 3H), 7.21–7.25 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 29.3, 37.2, 38.1, 114.2, 116.3, 121.0, 122.3, 128.1, 134.4, 141.1, 162.0, 177.4, 190.3. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{13}H_{12}NO_2S_2$ $[M + H]^+$: 278.0304, found 278.0306.

*3-(1,3-dithiolan-2-ylidene)-1,6-dimethylquinoline-2,4(1H,3H)-dione (**9b**).* Obtained as a yellow solid; isolated yield: 59.7 mg (41%); m.p. 189–190 ^oC. Eluent dichloromethane/ethyl acetate/ petroleum ether (0.1/2/5, V/V/V). ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 2.40 (s, 3H), 3.40–3.43 (m, 2H), 3.46–3.48 (m, 2H), 3.60 (s, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 20.5, 29.3, 37.2, 38.1, 114.2, 116.4, 120.8, 128.0, 131.9, 135.3, 139.0, 161.9, 177.5,

190.0. HRMS (ESI-TOF) *m*/*z* Calcd. for $C_{14}H_{14}NO_2S_2$ $[M + H]^+$: 292.0460, found 292.0463.

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ASSOCIATED CONTENT

Supporting Information. Crystallographic data and spectral data for all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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