

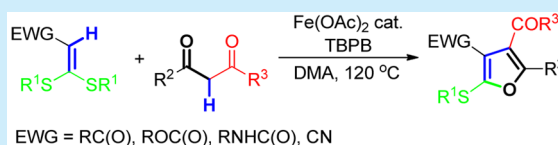
## Iron-Catalyzed Oxidative C–H Functionalization of Internal Olefins for the Synthesis of Tetrasubstituted Furans

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## Supporting Information

**ABSTRACT:** Tetrasubstituted furans were efficiently synthesized from Fe(OAc)<sub>2</sub>-catalyzed C–H/C–H cross-dehydrogenative-coupling (CDC) reactions of activated carbonyl methylenes with *S,S*-functionalized internal olefins, that is,  $\alpha$ -oxo ketene dithioacetals and analogues, under oxidative conditions.  $\beta$ -Ketoesters, 1,3-dicarbonyls,  $\beta$ -keto nitrile, and amide derivatives were used as the coupling partners.

The resultant alkylthio- and carbonyl-functionalized furans could be further transformed to diverse arylated furan derivatives and furan-fused *N*-heterocycles, respectively. The control experiments have revealed a radical reaction pathway.



The furan motif is an important structural unit abundant in many biologically active natural products, pharmaceuticals, and agrochemicals.<sup>1</sup> Continuous efforts have been devoted to the synthesis of functionalized furans and furan-based complex molecules.<sup>2</sup> In this regard, substituted furans have usually been synthesized by means of the cyclization of alkynyl- or allenyl-bearing carbonyl compounds or through reactions between alkynes and carbonyl compounds. Thus, transition-metal-catalyzed dehydrogenative heterocyclization of 2- and 3-alkynyl enones was employed to access furan-fused carbocycles or polysubstituted furans.<sup>3,4</sup> Iodocyclization was also applied for this purpose.<sup>5</sup> Intramolecular cyclization of propargylic alcohols afforded polysubstituted furans.<sup>6a,b</sup> Alkynyl epoxides,<sup>7</sup> allenyl ketones,<sup>8a</sup> allenyl or homopropargylic alcohols,<sup>8b</sup> and allene-1,3-dicarboxylic esters<sup>8c</sup> can be used for the same purpose. Copper-catalyzed heterocyclization of alkynyl ketones and imines<sup>8d</sup> and phosphine-mediated reductive condensation of  $\gamma$ -acyloxybutynoates<sup>8e</sup> readily yielded furan derivatives.<sup>4a</sup> Brønsted acid catalyzed cyclization of 1,4-diketones also gave furans.<sup>9</sup> Transition-metal-catalyzed vinylic C–H activation/[4 + 2] *O*-annulation of  $\alpha$ -aryl enones<sup>10a</sup> and oxidative cross-coupling of 1,3-dicarbonyl compounds or  $\beta$ -ketoesters<sup>10b</sup> with internal alkynes formed functionalized furans.  $\alpha$ -Diazocarbonyls<sup>11a</sup> and *N*-tosylhydrazones<sup>11b</sup> were used for metalloradical cyclization with alkynes to construct polysubstituted furans. The combination of *N*-arylimines and alkynylbenziodoxolones was utilized for the synthesis of polysubstituted furans.<sup>12</sup> A two-step reaction procedure of aldehydes with propargylic alcohols was developed to prepare highly substituted furans.<sup>13</sup>

Due to the ready C–H addition to olefinic C=C bonds to form dihydrofurans,<sup>14</sup> only a limited number of olefins have been documented for the synthesis of polysubstituted furans. Fused furans and naphthofurans were synthesized through a

copper/*P*(*t*Bu)<sub>3</sub>-mediated oxidative radical [3 + 2] cyclization between olefins or alkynes and cyclic ketones,<sup>15a</sup> and the same type of reactions occurred between styrenes and aryl alkyl ketones.<sup>15b</sup> Photocatalytic reactions of styrenes and  $\alpha$ -chloroalkyl ketones afforded polysubstituted furans.<sup>15c</sup> Manganese dioxide promoted the oxidative cyclization of enones with 1,3-dicarbonyl compounds to give 3,4-dicarbonyl-substituted furans.<sup>15d</sup> In order to avoid formation of dihydrofurans, functionalized olefins were usually reacted with carbonyl compounds. Using such a synthetic strategy, 2-siloxy-1-olefins,<sup>16a</sup> *gem*-difluoro olefins,<sup>16b</sup>  $\beta$ -nitrostyrenes,<sup>16c</sup> enamines,<sup>16d</sup> 2,3-dibromo-1-propenes,<sup>16e</sup> and  $\alpha,\beta$ -unsaturated carboxylic acids<sup>16f</sup> have been reported for substituted furan synthesis. Palladium-catalyzed intramolecular oxidative cycloisomerization of 2-cinnamyl-1,3-dicarbonyls was also applied to synthesize furan derivatives.<sup>17</sup>

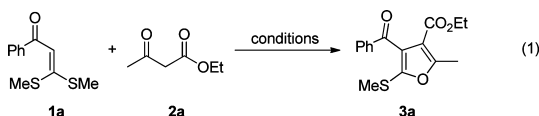
Although a variety of methods have been developed for furan synthesis, more diverse and environmentally benign procedures are strongly desired to access highly functionalized furans. In this context, C–H/C–H cross-dehydrogenative-coupling (CDC) reactions<sup>18</sup> are attractive for the establishment of a furan backbone. Gold-catalyzed alkylation of 1,3-dicarbonyl compounds with terminal alkynes efficiently proceeded to afford 3-alkynylfurans.<sup>19a</sup> Stoichiometric Ag<sub>2</sub>CO<sub>3</sub> mediated the same reactions to give 1,2,4-trisubstituted furans.<sup>19b</sup> Molecular iodine effected the oxidative cross-coupling of  $\beta$ -ketoesters and terminal alkynes to generate furan derivatives.<sup>19c</sup> During the ongoing investigation of internal olefinic C–H activation,<sup>20</sup> we were encouraged by FeCl<sub>3</sub>·H<sub>2</sub>O-catalyzed benzofuran synthesis from the arene C(sp<sup>2</sup>)-H/C(sp<sup>3</sup>)-H CDC reactions of phenols and  $\beta$ -keto esters<sup>21</sup> and the merits of iron catalysis<sup>22</sup>

Received: May 11, 2017

Published: June 1, 2017

and reasonably envisioned that  $\alpha$ -oxo ketene dithioacetals,<sup>23</sup> a class of functionalized internal olefins, might be used for the synthesis of highly functionalized furans through direct olefinic C(sp<sup>2</sup>)-H functionalization with the C(sp<sup>3</sup>)-H bond of a suitable carbonyl compound. Herein, we disclose Fe(OAc)<sub>2</sub>-catalyzed oxidative annulations of  $\alpha$ -oxo ketene dithioacetals with  $\beta$ -ketoesters and related compounds for the synthesis of tetrasubstituted furans.

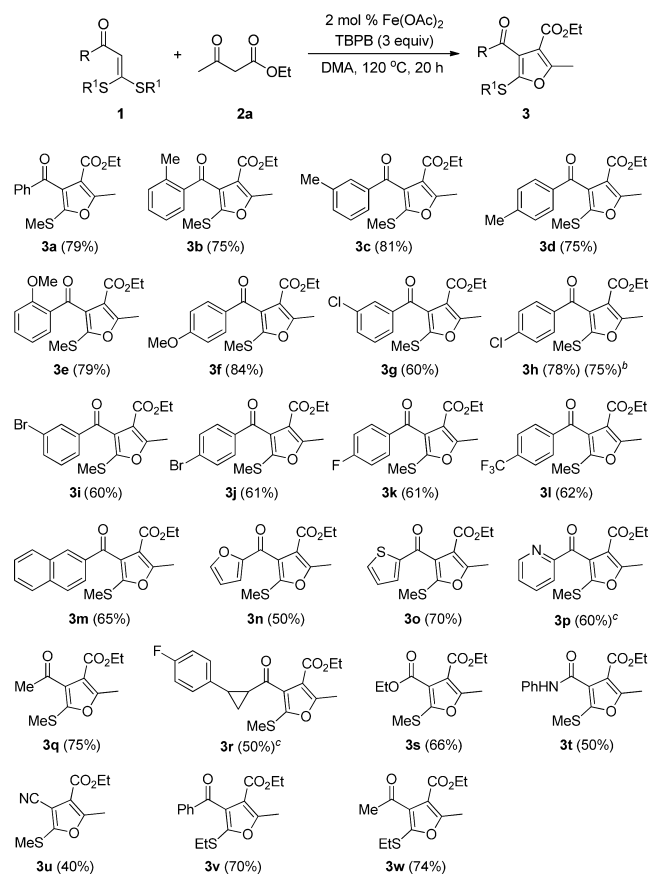
Initially, the reaction of  $\alpha$ -benzoyl ketene di(methylthio)acetal (**1a**) with ethyl acetoacetate (**2a**) was conducted to optimize the reaction conditions (eq 1) (see the Supporting



Information for details). With 2 mol % of FeCl<sub>3</sub> as the catalyst and 3 equiv of *tert*-butyl peroxybenzoate (TBPB) as the oxidant, the reaction of **1a** and **2a** in a 1:3 molar ratio proceeded in *N,N*-dimethylacetamide (DMA) at 120 °C for 15 h under an argon atmosphere, forming the target product, that is, tetrasubstituted furan **3a**, in 40% yield. Use of Fe(OAc)<sub>2</sub> as the catalyst remarkably enhanced the yield to 83%. Increasing the loading of TBPB to 4 equiv or using 5 mol % of the catalyst did not improve the reaction efficiency, and use of a smaller amount of the oxidant or catalyst deteriorated the product yield. Both di-*tert*-butylperoxide (DTBP) and *tert*-butyl hydroperoxide (TBHP) were not effective oxidants. Elevating the reaction temperature to 130 °C did not enhance the yield either. Extending the reaction time to 20 h improved the formation of **3a** (87%), which was thus isolated in 79% yield. Under an air or oxygen atmosphere, the product yield was lessened to 70–75%. Without the catalyst or oxidant, the desired reaction could not efficiently proceed to form **3a** (35%) or did not occur.

Under the optimized conditions, the scope of  $\alpha$ -oxo ketene dithioacetals (**1**) was explored (Scheme 1). The analogues of **1a**, that is, substituted  $\alpha$ -benzoyl ketene dithioacetals, exhibited various reactivities to form the target furan products of type **3** in good to excellent yields. No obvious steric effects were observed for the methyl and methoxy-substituted  $\alpha$ -benzoyl ketene dithioacetal substrates, and their reactions with **2a** afforded products **3b–f** (75–84%). The steric/electronic effects were obvious among the halo-substituted  $\alpha$ -benzoyl-bearing substrates. *m*-Cl (F)- and *p*-Br (F)-substituted substrates reacted with **2a** to give the corresponding products **3g** and **3i–k** in 60–61% yields, while *p*-Cl-benzoyl-bearing substrate reacted more efficiently to yield furan **3h** (78%), even reaching 75% yield from a 2 mmol scale reaction (see the SI). 4-Trifluoromethyl demonstrated an obvious negative electronic impact on the yield of **3l** (62%). The bulky  $\alpha$ -naphthoyl moiety exhibited a steric effect to render the formation of **3m** in 65% yield.  $\alpha$ -Heteroaryl ketene dithioacetals smoothly underwent the reaction to generate **3n–p** (50–70%), exhibiting various reactivities due to the different aromaticities of the *O*-, *S*-, and *N*-heteroaryl functionalities.  $\alpha$ -Acetyl ketene di(methylthio)acetal exhibited a good reactivity to afford **3q** (75%), whereas a steric effect was observed in the case of using  $\alpha$ -cyclopropylcarbonyl substrate, leading to the target product **3r** in 50% yield. Treatment of  $\alpha$ -ester, amide, and cyano ketene dithioacetals with **2a** under the standard conditions could give the target products **3s–u** (40–66%), respectively, demonstrat-

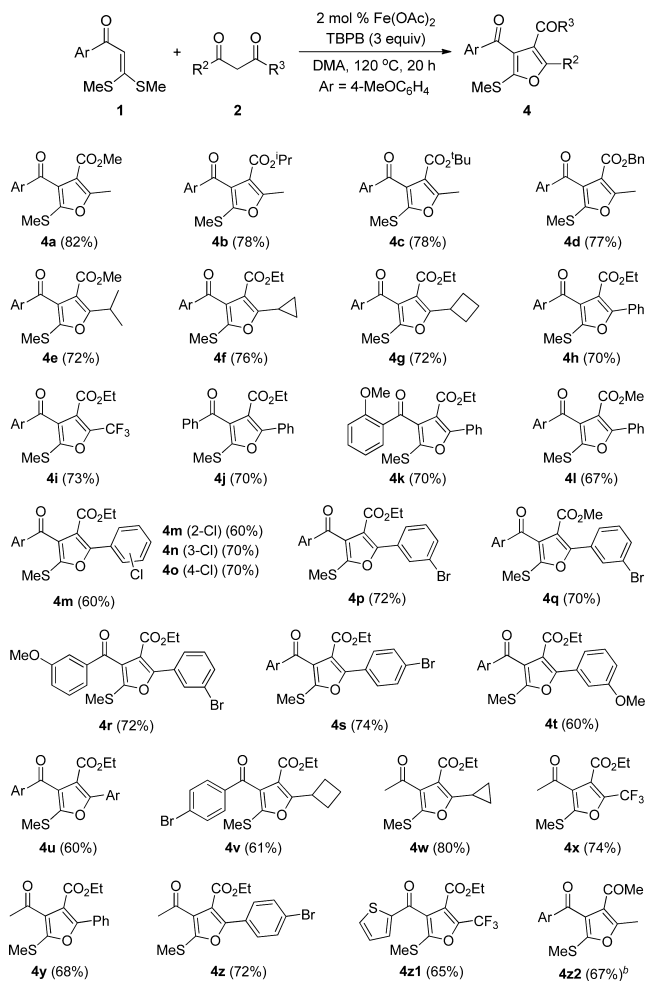
Scheme 1. Scope of Ketene Dithioacetals **1**<sup>a</sup>



<sup>a</sup>Conditions: **1** (0.5 mmol), **2a** (1.5 mmol), Fe(OAc)<sub>2</sub> (0.01 mmol), TBPB (1.5 mmol), DMA (2.0 mL), 120 °C, 0.1 MPa argon, 20 h. Yields refer to the isolated products. <sup>b</sup>**1h** (2.0 mmol), **2a** (6.0 mmol), Fe(OAc)<sub>2</sub> (0.04 mmol), TBPB (6.0 mmol), DMA (5.0 mL). <sup>c</sup>48 h.

ing a good diversity of the present synthetic methodology.  $\alpha$ -Oxo ketene di(ethylthio)acetals also efficiently reacted with **2a** to form the target products **3v** (70%) and **3w** (74%). It is clear that the internal olefin substrates are widely substituent tolerant.

Next, the protocol generality was investigated by performing the reactions of  $\alpha$ -oxo ketene dithioacetals **1** with a variety of  $\beta$ -ketoesters **2** (Scheme 2). Under the standard conditions, the reaction of  $\alpha$ -(4-methoxybenzoyl) ketene di(methylthio)acetal (**1f**) reacted with methyl acetoacetate (**2b**) to yield the target furan product **4a** (82%), exhibiting a reactivity similar to that of ethyl acetoacetate (**2a**) as compared to the formation of **3f** (84%) (Scheme 1). Variation of the alkyl moieties to isopropyl, *tert*-butyl, and benzyl in acetoacetates **2c–e** did not obviously alter the reaction efficiency, leading to furans **4b–d** (77–78%). However, when the bulkiness of the  $\beta$ -ketoester substrates was increased, the product yields were dropped from 84% for **3f** to 70–76% for **4e–h**. It should be noted that 4,4,4-trifluoroacetoacetate (**2j**) also exhibited a decent reactivity to produce **4i** (73%). In the case of using unsubstituted ethyl (or methyl) 3-oxo-3-phenylpropanoates, the steric effect from the substituted  $\alpha$ -benzoyl moieties was not obvious, resulting in **4j–l** in 67–70% yields. However, ethyl 3-oxo-3-(2'-chlorophenyl)propanoate (**2l**) showed an obvious steric effect to deteriorate the product yield to 60% for **4m**, and *m*- or *p*-halo-substituted phenyl groups did not exhibit obvious steric/

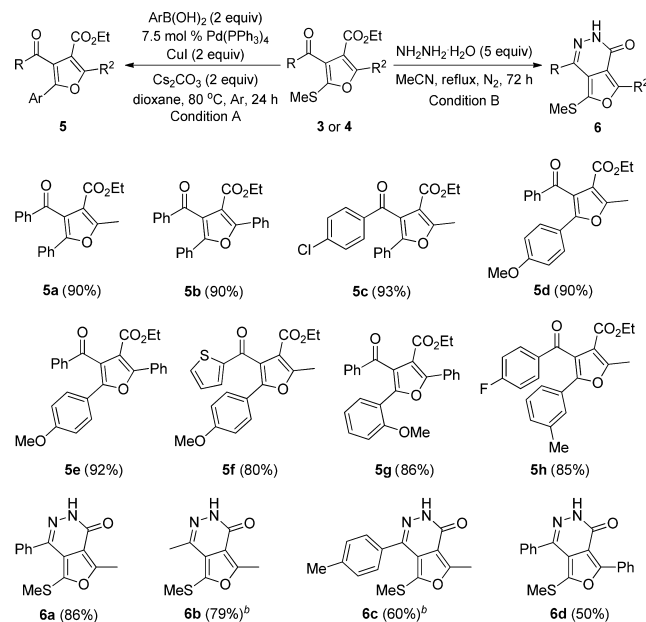
Scheme 2. Scope of  $\beta$ -Ketoesters 2<sup>a</sup>

<sup>a</sup>Conditions: **1** (0.5 mmol), **2** (1.5 mmol),  $\text{Fe}(\text{OAc})_2$  (0.01 mmol), TBPB (1.5 mmol), DMA (2.0 mL), 120 °C, 0.1 MPa argon, 20 h. Yields refer to the isolated products. <sup>b</sup> $\text{Fe}(\text{OAc})_2$  (0.05 mmol), acetylacetone (2.0 mmol), TBPB (2.0 mmol).

electronic effects on the reaction efficiency to render the formation of **4n–s** (70–74%). 3- and 4-methoxy substituents on the aryl moiety of  $\beta$ -ketoesters and a 4-bromo substituent on the benzoyl moiety of an  $\alpha$ -oxo ketene dithioacetal lessened the substrate reactivity to form **4t–v** (60–61%).  $\alpha$ -Acetyl ketene di(methylthio)acetal also exhibited a decent reactivity to interact with various  $\beta$ -ketoesters to give **4w–z** (68–80%).  $\alpha$ -(Thiophene-2-carbonyl) ketene di(methylthio)acetal reacted with 4,4,4-trifluoroacetoacetate to form **4z1** in 65% yield. It is noteworthy that internal olefin **1f** reacted with the 1,3-dicarbonyl compound, that is, acetoacetone, under the standard conditions to afford 3,4-dicarbonyl-tetrasubstituted furan **4z2** (67%). The molecular structures of compounds **3** and **4** were further confirmed by the X-ray single-crystal structural determination of compound **4j** (see the SI).

In contrast to most of the known substituted furans, the present tetrasubstituted furans **3** and **4** bear three readily convertible functional groups, i.e., alkythio, carbonyl, and ester, at the 2-, 3-, and 4-positions of the furan backbone. This structural feature is highly desired for furans to be used as organic synthons. Thus, derivation of furans **3** and **4** was conducted by palladium-catalyzed Liebeskind–Srogl cross-coupling reactions with arylboronic acids and condensation

with hydrazine (Scheme 3). With benzenboronic acid and its 4-chloro, 4- and 2-methoxy, and 3-methyl-substituted ana-

Scheme 3. Derivation of Furans **3** and **4**<sup>a</sup>

<sup>a</sup>Conditions A: **3** or **4** (0.15 mmol), dioxane (2.0 mL). Conditions B: **3** or **4** (0.3 mmol), MeCN (2.0 mL). Yields refer to the isolated products. <sup>b</sup>Seven days.

logues, 2-arylated tetrasubstituted furans **5a–h** were efficiently obtained (80–93%). The condensation reactions afforded potentially bioactive furan-fused pyridazinone derivatives<sup>24</sup> **6a–d** in 50–86% yields.

To probe into the reaction mechanism addition of 3 equiv of a radical scavenger such as 2,2,6,6-tetramethyl-1-piperidinyloxy or 2,6-di-*tert*-butyl-4-methylphenol to the reaction mixture of **1a** with **2a** completely inhibited the reaction, suggesting a radical pathway involved in the reaction.<sup>22</sup> The kinetic isotope effect experiments were explored by conducting the reactions of **1a** and its deuterated form **1a[D]**<sup>20e</sup> with **2a** under the standard conditions, respectively. A secondary isotope effect<sup>25</sup> was observed with  $k_{\text{H}}/k_{\text{D}} = 1.1$ , which indicates that cleavage of the internal olefinic C–H bond in **1a** is not involved in the rate-determining step of the overall catalytic cycle. On the basis of these results and the literature reports,<sup>26</sup> a plausible radical oxidative reaction mechanism is proposed (see the SI for details).

In summary, efficient iron-catalyzed direct regioselective radical oxidative annulation of *S,S*-functionalized internal olefins with  $\beta$ -ketoesters and analogues has been realized to synthesize tetrasubstituted furans. The highly functionalized furan products can be readily transformed to 2-arylfurans and 2,3-furan-fused pyridazinones through catalytic C–S cleavage and condensation with hydrazine, respectively. The present protocol provides a concise and environmentally benign route to highly functionalized furan derivatives.

## ■ ASSOCIATED CONTENT

## S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01431.

Experimental materials and procedures, NMR of compounds, and X-ray crystallographic analysis for compound **4j** (PDF)

X-ray crystallographic data for compound **4j**(CIF)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (21472185) and the National Basic Research Program of China (2015CB856600) for support of this research.

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