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Iron-Promoted C−C Bond Cleavage of 1,3-Diketones: A Route to 1,2-Diketones under Mild Reaction Conditions

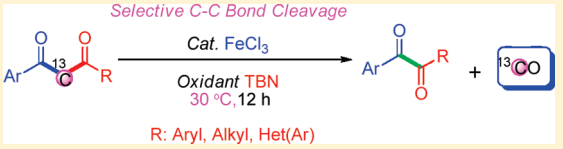
Lehao Huang,[†] Kai Cheng,[†] Bangben Yao,[†] Yongju Xie,[†] and Yuhong Zhang*[,†,‡]

[†]Department of Chemistry, Zhejiang University, Hangzhou 310027, China

[‡]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

Supporting Information

ABSTRACT: A conceptual method for the preparation of 1,2-diketones is reported. The selective C−C bond cleavage of 1,3-diketones affords the 1,2-diketones in high yields under mild reaction conditions in air by the use of $FeCl_3$ as the catalyst and *tert*-butyl nitrite (TBN) as the oxidant without the use of solvent. The possible reaction mechanism is discussed. This protocol provides an expeditious route to the useful 1,2-diketones.



INTRODUCTION

1,2-Diketones are of great importance in organic chemistry, especially in the synthesis of pharmaceuticals and functional materials.[1] Their industrial applications as corrosion inhibitors,[2] photosensitive agents,[3] and photoinitiators[4] have also been shown. Despite the wide spectrum of utilization, practical and efficient methods for their preparation are very limited.[5] Traditionally, 1,2-diketones are prepared by the oxidation of benzoins or hydrobenzoins in the presence of an excessive amount of metal oxidants. Though this method is still popular today, it suffers from several notable disadvantages, including heavy environmental pollution and difficulty accessing functionalized benzoins.[5a,6] Recent strategies for the synthesis of 1,2-diketones based on the direct oxidation of internal alkynes partially complement the classical synthetic approaches.[7] However, drawbacks such as the need for toxic and/or expensive reagents complicate the application of these methods. Very recently, the preparation of 1,2-diketones by the decarboylation of 1,3-diketones with iodide and base under irradiation of fluorescent light was reported.[8] This is really a clean method, but irradiation of 10 h by four 22 W fluorescent lamps for 0.3 mmol substrates is required to afford the moderate yields.

In recent years, the development of various transition-metal-catalyzed reactions has greatly advanced synthetic methodologies. In particular, the metal-promoted activation of the C−C bond has been explored in the field of organometallic chemistry as the promising approach for new selective and efficient protocols of complex molecules.[9−12] Herein, we report our founding on the iron-promoted C−C bond cleavage of 1,3-diketones in the presence of *tert*-butyl nitrite (TBN) oxidant. The selective cleavage of the C−C bond of 1,3-diketones affords the 1,2-diketones in good yields under mild reaction conditions, which provides an alternative for accessing the useful 1,2-diketones.

RESULTS AND DISCUSSION

We began our investigation with diphenylpropane-1,3-dione **1a** (Table 1). After much experimentation, it was discovered that the use of a combination of 20 mol % of $FeCl_3$ and 5 equiv of TBN gave benzil in 80% isolated yields at 30 °C for 12 h (Table 1, entry 1). Benzil was not observed in the absence of iron catalyst (Table 1, entry 2). The use of $FeCl_2$ and $FeCl_3 \cdot 6H_2O$ showed relatively lower efficiency, while Fe_2O_3 and $Fe(acac)_3$ were almost inactive (Table 1, entries 3−6). A copper(I) catalyst precursor CuBr also provided the product but in very low yields (Table 1, entry 7). The stronger Lewis acid $AlCl_3$ showed very low efficiency (Table 1, entry 8). Catalysts such as $Pd(OAc)_2$, $RuCl_3$, and $AuCl_3$ have little effect on the reaction. The reaction rate in solvent slowed down, and moderate yields were obtained in CH_2Cl_2, toluene, and hexane (Table 1, entries 9−11). Decreasing the amount of TBN led to the lower yield (Table 1, entry 12). No reaction was observed in the absence of TBN (Table 1, entry 13). This transformation can proceed smoothly in 71% isolated yields under nitrogen atmosphere (Table 1, entry 14). Isopentyl nitrite can also serve as the oxidant for this reaction but in relatively lower yields (Table 1, entry 15).

The scope of this transformation was examined with respect to a variety of 1,3-diketones, as shown in Table 2. The reaction of unsymmetrical 1,3-diketones was highly selective. For instance, subjecting 1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione to the optimal reaction conditions failed to yield the crossover products such as benzil or 1,2-bis(4-methoxyphenyl)ethane-1,2-dione. Instead, the reaction afforded selectively 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione **2b** in 80% yield (Table 2, 2b). Both electron-donating and electron-withdrawing substituents in the aryl ring of 1,3-diketones tolerated the reaction conditions well to give the corresponding 1,2-diketones in good yields (Table 2, **2b**−**2j**). It should be noted that halides such as bromide and iodide in the aryl ring were compatible with the reaction conditions, which is useful for the further functionalization (Table 2, **2g**−**2j**). In addition, the steric hindrance on aryl ring played little role in the reaction (Table 2, **2e**). 1- and 2-Naphthyl-substituted 1,3-diketones underwent the transformation

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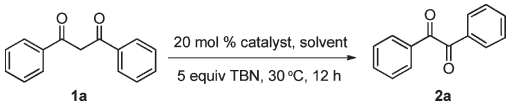
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	yield (%)
1	$FeCl_3$		80
2			
3	$FeCl_3 \cdot 6H_2O$		67
4	$FeCl_2$		64
5	$Fe(acac)_3$		
6	Fe_2O_3		
7	CuBr		29
8	$AlCl_3$		30
9	$FeCl_3$	CH_2Cl_2	68[b]
10	$FeCl_3$	toluene	73[b]
11	$FeCl_3$	hexane	67[b]
12	$FeCl_3$		72[c]
13	$FeCl_3$		0[d]
14	$FeCl_3$		71[e]
15	$FeCl_3$		48[f]

[a] Reaction conditions: 1,3-diketone (0.5 mmol), $FeCl_3$ (16 mg, 20 mol %), TBN (*tert*-butyl nitrite, 2.5 mmol, 258 mg). [b] The reaction was carried out in 1 mL of solvent. [c] TBN (2.0 mmol) was added. [d] In the absence of TBN. [e] Reaction under nitrogen atmosphere. [f] Isopentyl nitrite (5 equiv) was added as the oxidant.

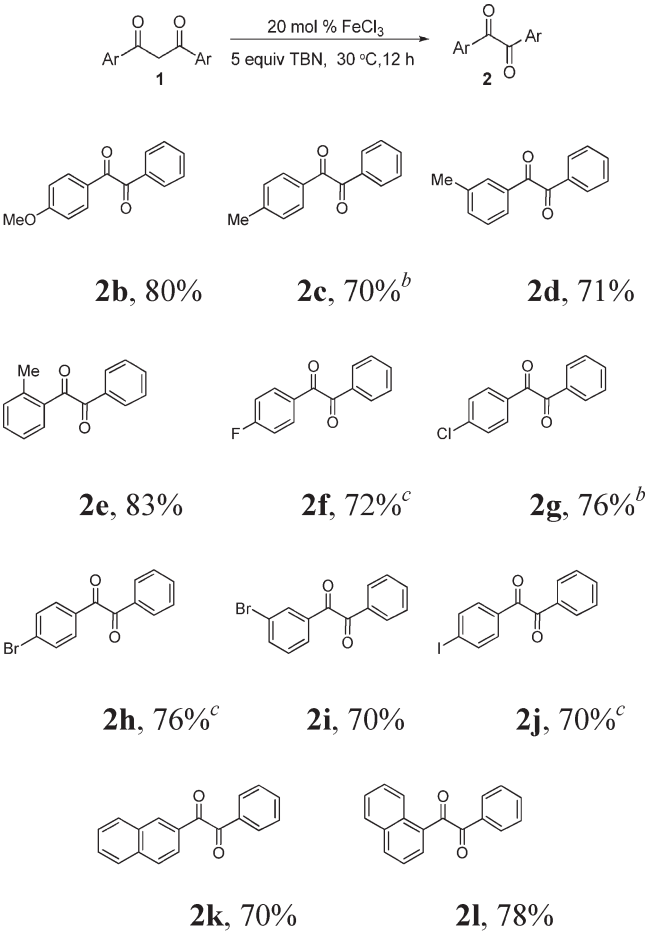
smoothly to afford the corresponding 1,2-diketones in good yields (Table 2, **2k** and **2l**).

Importantly, various heteroaromatic 1,3-diketones readily participated in this transformation, thus providing easy access to valuable symmetric and unsymmetric heteroaromatic 1,2-diketones (Table 3).[13] It was found that the reactivity of heteroaromatic 1,3-diketones was correlated with their aromaticity (Table 3, **2m**−**2o**). For example, 1-phenyl-3-(thiophen-2-yl)-propane-1,3-dione showed a better reactivity than 1-phenyl-3-(1*H*-pyrrol-2-yl)propane-1,3-dione and 1-(furan-2-yl)-3-phenyl-propane-1,3-dione. Notably, 1,3-diketones containing heteroaromatic rings at C1 and C3 positions participated in the reaction smoothly to give the heteroaryl 1,2-diketones **2p**, **2q**, and **2r**. This protocol provides a useful alternative for the preparation of symmetric and unsymmetric heteroaryl 1,2-diketones.

The substrate scope of aliphatic 1,3-diketones was limited. Treatment of pentane-2,4-dione failed to give any desired 1,2-diketone. Gratifyingly, 3-alkyl-1,3-diketones such as 1-phenyl-butane-1,3-dione and 1-phenylpentane-1,3-dione participated in the reaction well to give the corresponding 1,2-diketones in moderate yields (Scheme 1, **2s** and **2t**). The results indicated that an aryl group for benzoyl migration was necessary for this transformation.

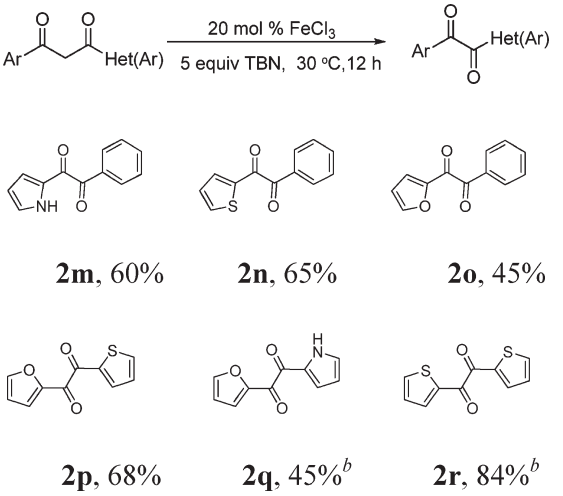
The initial mechanistic study indicates that an intermediate is formed at the beginning of the reaction and gradually transformed to the 1,2-diketone product. Fortunately, we isolated this intermediate and found it was 2-(hydroxyimino)-1,3-diphenyl-propane-1,3-dione **A** (eq 1). Interestingly, intermediate **A** fails to give benzil in the absence of iron(III) or TBN (eq 1). Treatment of intermediate **A** with 20 mol % of $FeCl_3$ and 5 equiv of TBN afforded benzil in 82% yield (eq 1). However, the use of 2-methyl-

Table 2. Iron-Promoted Selective C−C Bond Cleavage of 1,3-Diketones[a]



[a] Reaction conditions: 1,3-diketone (0.5 mmol), $FeCl_3$ (16 mg, 20 mol %), TBN (*tert*-butyl nitrite, 2.5 mmol, 258 mg). [b] TBN (3.5 mmol) was added. [c] TBN (4.5 mmol) was added.

Table 3. Iron-Promoted Reactions of Heteroaromatic 1,3-Diketones[a]



[a] The reaction conditions are the same as in Table 2. [b] TBN (3.5 mmol) in 1 mL of CH_2Cl_2 was added.

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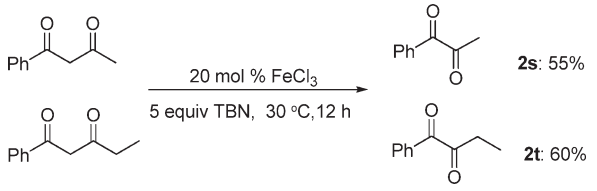
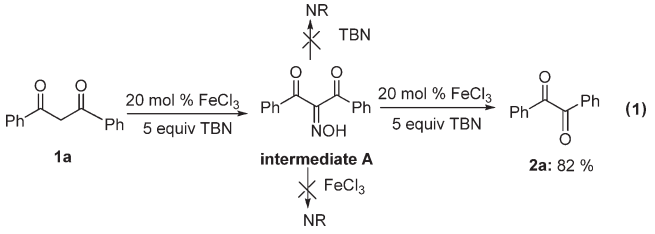
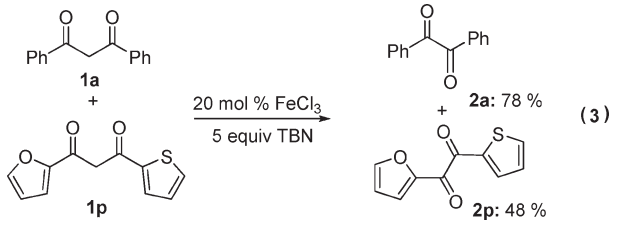
Scheme 1. Reaction of 3-Alkyl-1,3-diketones



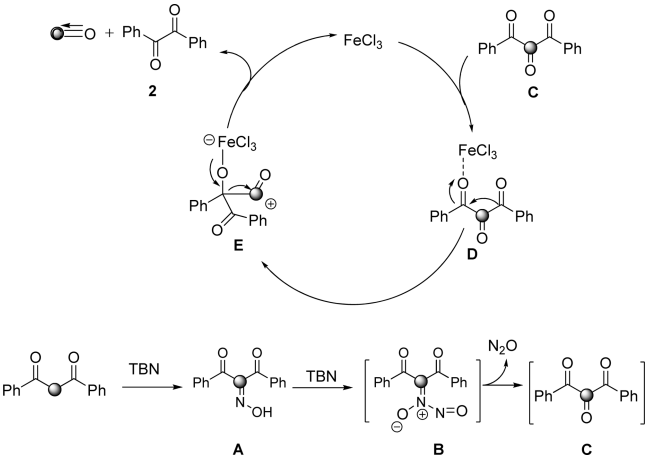
1,3-diphenylpropane-1,3-dione **1u** as substrate failed to produce benzil under the reaction conditions. In contrast, the reaction stopped at the nitrosation stage to give 2-methyl-2-nitroso-1,3-diphenylpropane-1,3-dione **2u** (eq 2), illustrating that the oxime intermediate **A** is essential to the final formation of 1,2-diketone product. The room temperature ESR (electron spin resonance) studies revealed that the addition of 1,3-diketones significantly enhanced the signal of Fe^{3+} species, showing the possibility of coordination of the diketones with iron(III) in the catalytic system.

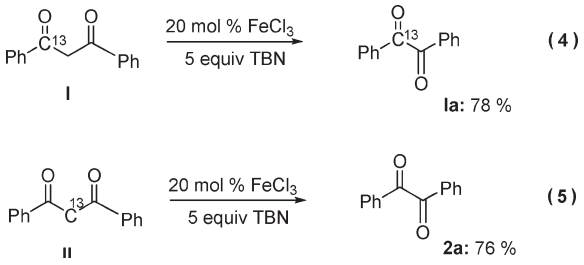


To gain insight to the reaction features, 1,3-diphenylpropane-1,3-dione and 1-(furan-2-yl)-3-(thiophen-2-yl)propane-1,3-dione were treated in one pot under the reaction conditions. Potential crossover producxts were not detected by GC−MS, showing that the transformation most possibly occurred through an intramolecular process (eq 3). In addition, carbon monoxide (CO) and nitrous oxide (N_2O) were found to be released during the reaction (monitored by a GASMET Dx4000 apparatus). In order to determine whether the central or side carbon was lost in the reaction, we performed the isotopic labeling studies. Using conditions identical to that used in Table 2, the specially labeled substrate **I** gave the labeled 1,2-diketone **Ia** (eq 4): MS analysis of the isotopic distribution showed the presence of about 92% ^{13}C-labeled product. The ^{13}C NMR results (see Supporting Information) indicated clearly that the labeled carbonyl carbon remained in the 1,2-diketone. The use of labeled 1,3-diketone (**II**) delivered the 1,2-diketone **2a** (eq 5), showing that this iron-promoted transformation of 1,3-diketones to 1,2-diketones results with loss of the central carbon.



Scheme 2. Plausible Reaction Mechanism





On the basis of the previous studies[14] and our experimental results, a plausible reaction mechanism is proposed, as shown in Scheme 2. First, the radical reaction of 1,3-diketones in the presence of TBN produces the diketone oxime **A**,[15] which is possibly converted to intermediate **B** in the presence of TBN without the use of iron chloride.[16] The release of N_2O of intermediate **B** gives the triketone **C** under the reaction conditions in situ.[16] The results of MS(ESI) and HRMS(EI) support the formation of intermediate **C** (see Supporting Information). Second, the iron chloride coordinates with the carbonyl of intermediate **C** to form intermediate **D**, which undergoes a 1,2-Wagner−Meerwein-type rearrangement of a benzoyl group with an electron pair to the electrophilic carbon resulting in the intermediate **E**.[14a] The subsequent (or simultaneous) liberation of carbon monoxide of intermediate **E** results in the 1,2-diketone products.

CONCLUSIONS

In conclusion, we have developed an iron-promoted method for the synthesis of 1,2-diketones through C−C bond cleavage. This transformation represents rare examples of iron-promoted processes for the construction of useful compounds via the selective C−C bond cleavage. Further studies of the reaction mechanism and application of the catalytic system to alternative transformations are in progress in our laboratory.

EXPERIMENTAL SECTION

General. All solvents were purified and dried according to standard methods prior to use. ^1H NMR spectra were recorded at 400 or 500 MHz using TMS as internal standard (0 ppm) for $CDCl_3$ or DMSO-d_6. ^{13}C NMR spectra were recorded at 100 or 125 MHz and referenced to

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the internal solvent signals (center peak is 77.00 ppm in $CDCl_3$ or 39.90 ppm in DMSO-d_6). The multiplicities were reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonances (br). Mass spectroscopy data were collected on HRMS-EI, HRMS-ESI, and MS-ESI instruments. ESR spectra were recorded on an A 300 EPR spectrometer at the following settings: microwave power, 20 mW; microwave frequency, 9.87 GHz; field set, 3335 G; center field, 3286.85 G; sweep width, 2000.7 G; modulation frequency, 100 kHz; modulation amplitude, 1 G. CO and N_2O were collected on GASMET Dx4000. 1,3-Diketone compounds **1b**−**1r**[17] and **1s**−**1t**[18] were synthesized following the reported procedures. Other materials were purchased from common commercial sources and used without additional purification.

Preparation of 1,3-Diketones 1b−1r, I, II[17]**.** To a 100 mL three-necked round-bottom flask were added sodium hydride (60% in mineral oil, 1.0 g, 25 mmol) and then anhydrous THF (35 mL). This mixture was cooled to 0 °C, and then the corresponding ester (11 mmol) and ketone (10 mmol) were added. The suspension was heated to reflux under nitrogen for 16 h. After being cooled to room temperature, a mixture of ether and dilute hydrochloric acid was added to the vigorously stirred reaction mixture carefully. The precipitate was filtered through Celite. The ether phase was separated and washed three times with brine and dried on magnesium sulfate. After removal of ether, the residue was purified by chromatography (silica gel) to give the corresponding 1,3-diketones.

^{13}C-1,3-Diphenylpropane-1,3-dione (***I***)*:* A light yellow solid after purification by flash chromatography (eluent, ethyl acetate/petrol ether = 1/80, v/v); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 17.02 (s, 1 H), 8.02 (d, J = 6.5 Hz, 4 H), 7.57 (t, J = 7.0 Hz, 2 H), 7.50 (t, J = 7.5 Hz, 4 H), 6.89 (d, J = 4.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 185.9 (t, J = 29.7 Hz), 135.7 (t, J = 29.1 Hz), 132.7, 128.9, 127.4, 93.3 (d, J = 62.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5 (s, 2.7 C), 185.9 (t, J = 29.7 Hz, 93 C), 135.7 (t, J = 29.1 Hz, 2 C), 132.7 (s, 2 C), 128.9 (s, 4 C), 127.4 (s, 4 C), 93.3 (d, J = 62.9 Hz, 1 C); HRMS (EI) calcd for $C_{14}{}^{13}CH_{12}O_2$ (M^+) 225.0871, found 225.0876.

^{13}C-1,3-Diphenylpropane-1,3-dione (***II***)*:* A light yellow solid after purification by flash chromatography (eluent, ethyl acetate/petrol ether = 1/80, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 16.85 (d, J = 5.2 Hz, 1 H), 7.96 (d, J = 7.6 Hz, 4 H), 7.53 (t, J = 6.6 Hz, 2 H), 7.46 (t, J = 7.2 Hz, 4 H), 7.04 (s, 0.5 H), 6.63 (s, 0.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 185.4, 135.5 (d, J = 10.3 Hz), 132.4, 128.6, 127.1, 93.1 (t, J = 39.6 Hz), 50.2; HRMS (EI) calcd for $C_{14}{}^{13}CH_{12}O_2$ (M^+) 225.0871, found 225.0868.

Preparation of 1,3-Diketones 1s, 1t[18]**.** To a 100 mL three-necked round-bottom flask were added anhydrous toluene (30 mL) and sodium sand (0.552 g, 24 mmol). This mixture was cooled to 0 °C, and then a small amount of mixed solution (0.2−0.4 mL) of the corresponding ester (28 mmol) and acetophenone (1.2 g, 10 mmol) was added. After the ice bath was removed, the reaction was stirred at room temperature for 20 min. The remaining mixture was added dropwise continuously in an ice bath. After dropping, the suspension was stirred at room temperature for 2 h. After the reaction, ice was slowly added to the vigorously stirred reaction mixture to fully consume the remaining sodium sand (***Special attention***!), then acetic acid was added to neutralize the solution. The precipitate was filtered through Celite. The organic phase was separated and washed three times with saturated sodium bicarbonate and dried on anhydrous sodium sulfate. After removal of solvent, the residue was purified by chromatography (silica gel) to give the corresponding 1,3-diketones.

Preparation of 1,3-Dione A and 2u. *tert*-Butyl nitrite (2.5 mmol, 258 mg) was added to a mixture of 1,3-dione (0.5 mmol) and $FeCl_3$ (16 mg, 20 mol %). The solution was stirred at room temperature under air for 10 min. Then ethyl acetate (2 mL) was added to the mixture and filtered through a pad of Celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (silica gel) to obtain the desired product.

2-(Hydroxyimino)-1,3-diphenylpropane-1,3-dione[15d] (***A***)*:* A white solid after purification by flash chromatography (eluent, ethyl acetate/petrol ether = 1/5, v/v); 16% yield; ^{1}H NMR (400 MHz, C_2D_6SO, TMS) δ 13.26 (s, 1 H), 8.04 (d, J = 7.2 Hz, 2 H), 7.87 (d, J = 7.2 Hz, 2 H), 7.47−7.68 (m, 2 H), 7.62−7.55 (m, 4 H); ^{13}C NMR (100 MHz, C_2D_6SO) δ 193.2, 189.7, 155.0, 136.2, 135.1, 134.8, 133.9, 130.5, 129.8, 129.2, 128.8; HRMS (EI) calcd for $C_{15}H_{11}NO_3$ (M^+) 253.0739, found 253.0743.

2-Methyl-2-nitroso-1,3-diphenylpropane-1,3-dione (***2u***)*:* The solution was stirred at room temperature under air for 12 h; a white viscous liquid after purification by flash chromatography (eluent, ethyl acetate/petrol ether = 1/20, v/v); 26% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.79 (d, J = 7.6 Hz, 4 H), 7.53 (t, J = 7.6 Hz, 2 H), 7.39 (t, J = 8.0 Hz, 4 H), 2.29 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 134.0, 133.6, 129.7, 128.7, 102.0, 22.7; HRMS (ESI) calcd for $C_{16}H_{13}NO_3$ (M^+) 267.0895, found 267.0899.

Typical Procedure for Products 2a−2t, Ia. *tert*-Butyl nitrite (2.5−4.5 mmol) was added to a mixture of 1,3-diketone (0.5 mmol) and $FeCl_3$ (16 mg, 20 mol %) at 30 °C. The solution was then stirred at 30 °C under air for 12 h. Afterward, ethyl acetate (2 mL) was added to the mixture and filtered through a pad of Celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Benzil[19] (***2a***)*:* 80% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, J = 8.4 Hz, 4 H), 7.66 (t, J = 7.2 Hz, 2 H), 7.52 (t, J = 7.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 134.9, 133.0, 129.9, 129.0; HRMS (EI) calcd for $C_{14}H_{10}O_2$ (M^+) 210.0681, found 210.0682.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione[19] (***2b***)*:* 80% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (t, J = 8.8 Hz, 4 H), 7.63 (d, J = 7.2 Hz, 1 H), 7.49 (t, J = 8.0 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 3.87 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 193.2, 165.0, 134.7, 133.1, 132.4, 129.9, 128.9, 126.0, 114.3, 55.6; HRMS (EI) calcd for $C_{15}H_{12}O_3$ (M^+) 240.0786, found 240.0786.

1-Phenyl-2-p-tolylethane-1,2-dione[19] (***2c***)*:* 70% yield; 3.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, J = 8.0 Hz, 2 H), 7.86 (d, J = 7.6 Hz, 2 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.30 (d, J = 7.6 Hz, 2 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 194.3, 146.2, 134.7, 133.0, 130.5, 130.0, 129.8, 129.7, 128.9, 21.9; HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0844.

1-Phenyl-2-m-tolylethane-1,2-dione[7f] (***2d***)*:* 71% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, J = 8.0 Hz, 2 H), 7.80 (d, J = 11.2 Hz, 2 H), 7.67 (t, J = 7.6 Hz, 1 H), 7.48−7.55 (m, 3 H), 7.41 (t, J = 7.6 Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 194.7, 139.0, 135.7, 134.8, 133.0, 132.9, 130.2, 129.9, 129.0, 128.9, 127.2, 21.2; HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0840.

1-Phenyl-2-o-tolylethane-1,2-dione[19] (***2e***)*:* 83% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (d, J = 8.0 Hz, 2 H), 7.66 (d, J = 8.0 Hz, 2 H), 7.48−7.54 (m, 3 H), 7.35 (d, J = 7.2 Hz, 1 H), 7.27 (t, J = 7.6 Hz, 1 H), 2.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 194.9, 141.3, 134.7, 133.8, 133.1, 133.0, 132.6, 131.7, 129.9, 129.0, 126.0, 21.9; HRMS (EI) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0836.

1-(4-Fluorophenyl)-2-phenylethane-1,2-dione[19] (***2f***)*:* 72% yield; 4.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04−7.96 (m, 4 H), 7.67 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 7.19 (t, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 192.7, 165.0 (J = 248.6 Hz), 135.0, 132.8, 132.7, 129.9, 129.0, 116.5, 116.3; HRMS (EI) calcd for $C_{14}H_9O_2F$ (M^+) 228.0587, found 228.0594.

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1-(4-Chlorophenyl)-2-phenylethane-1,2-dione[19] (***2g***): 76% yield; 3.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 (d, J = 7.6 Hz, 2 H), 7.96 (d, J = 8.8 Hz, 2 H), 7.71 (t, J = 7.6 Hz, 1 H), 7.52−7.58 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 193.1, 141.7, 135.0, 132.7, 131.3, 131.2, 129.9, 129.4, 129.0; HRMS (EI) calcd for $C_{14}H_9O_2Cl$ (M^+) 244.0291, found 244.0287.

1-(4-Bromophenyl)-2-phenylethane-1,2-dione[7f] (***2h***): 76% yield; 4.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (d, J = 8.4 Hz, 2 H), 7.85 (d, J = 8.0 Hz, 2 H), 7.66 (d, J = 8.4 Hz, 3 H), 7.52 (t, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 193.2, 135.0, 132.7, 132.4, 131.7, 131.2, 130.5, 129.9, 129.0; HRMS (EI) calcd for $C_{14}H_9O_2Br$ (M^+) 287.9786, found 287.9784.

1-(3-Bromophenyl)-2-phenylethane-1,2-dione[20] (***2i***): 70% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.13 (s, 1 H), 7.96 (d, J = 7.6 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 7.6 Hz, 1 H), 7.66 (t, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 2 H), 7.37 (t, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 192.8, 137.7, 135.1, 134.6, 132.6, 132.4 (J = 40.0 Hz), 130.6 (J = 6.3 Hz), 129.9 (J = 7.4 Hz), 129.1 (J = 7.4 Hz), 128.6 (J = 5.6 Hz), 123.3 (J = 6.4 Hz); HRMS (EI) calcd for $C_{14}H_9O_2Br$ (M^+) 287.9786, found 287.9788.

1-(4-Iodophenyl)-2-phenylethane-1,2-dione[7f] (***2j***): 70% yield; 4.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, J = 8.0 Hz, 2 H), 7.86 (d, J = 8.0 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.2 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 194.3, 146.2, 134.8, 133.0, 130.6, 130.0, 129.8, 129.7, 129.0; HRMS (EI) calcd for $C_{14}H_9O_2I$ (M^+) 335.9647, found 335.9650.

1-(Naphthalen-2-yl)-2-phenylethane-1,2-dione[21] (***2k***): 70% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.43 (s, 1 H), 8.12 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 2 H), 7.99 (t, J = 8.8 Hz, 1 H), 7.91 (t, J = 7.2 Hz, 2 H), 7.63−7.70 (m, 2 H), 7.50−7.58 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 136.4, 134.9, 133.5, 133.1, 132.3, 130.3, 130.0, 129.9, 129.6, 129.2, 129.0, 128.0, 127.2, 123.6; HRMS (EI) calcd for $C_{18}H_{12}O_2$ (M^+) 260.0837, found 260.0839.

1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione[21] (***2l***): 78% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.39 (d, J = 8.4 Hz, 1 H), 8.14 (d, J = 8.0 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 2 H), 7.97 (d, J = 7.2 Hz, 2 H), 7.79 (t, J = 8.0 Hz, 1 H), 7.64−7.71 (m, 2 H), 7.49 −7.57 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 194.6, 136.0, 135.1, 134.8, 134.1, 133.3, 130.9, 130.0, 129.5, 129.0, 128.8, 128.6, 127.1, 125.9, 124.4; HRMS (EI) calcd for $C_{18}H_{12}O_2$ (M^+) 260.0837, found 260.0835.

1-Phenyl-2-(1H-pyrrol-2-yl)ethane-1,2-dione[22] (***2m***): 60% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.72 (s, 1 H), 8.16 (d, J = 7.6 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 2 H), 7.61 −7.68 (m, 1 H), 7.52 (t, J = 8.0 Hz, 2 H), 7.29 (s, 1 H), 7.06 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 171.3, 134.6, 133.7, 133.1, 130.2, 128.8, 128.7, 128.5, 122.6, 129.0, 128.0, 127.2, 123.6; HRMS (ESI) calcd for $C_{12}H_9NO_2$ (M^+) 199.0633, found 199.0637.

1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione[13a] (***2n***): 65% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, J = 7.2 Hz, 2 H), 7.82 (d, J = 4.4 Hz, 1 H), 7.78 (d, J = 3.6 Hz, 1 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.16 (t, J = 4.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 191.6, 143.1, 134.4, 133.2, 131.7, 130.3, 128.7, 128.6, 128.0, 127.6, 126.9; HRMS (EI) calcd for $C_{12}H_8O_2S$ (M^+) 216.0245, found 216.0247.

1-(Furan-2-yl)-3-phenylpropane-1,3-dione[13a] (***2o***): 45% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, J = 7.2 Hz, 2 H), 7.83 (d, J = 4.4 Hz, 1 H), 7.78 (d, J = 4.4 Hz, 1 H), 7.66 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.2 Hz, 2 H), 7.18 (t, J = 4.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 188.2, 155.4, 135.5, 134.7, 134.3, 130.7, 130.1, 129.3, 128.8, 128.5, 128.4; HRMS (EI) calcd for $C_{12}H_8O_3$ (M^+) 200.0473, found 200.0475.

1-(Furan-2-yl)-2-(thiophen-2-yl)ethane-1,2-dione[13a] (***2p***): 68% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.08 (d, J = 3.6 Hz, 1 H), 7.86 (d, J = 4.4 Hz, 1 H), 7.80 (s, 1 H), 7.64 (d, J = 3.6 Hz, 1 H), 7.22 (t, J = 4.4 Hz, 1 H), 6.65 (d, J = 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 177.5, 149.4, 137.4, 137.2, 128.7, 124.6, 113.0; HRMS (EI) calcd for $C_{10}H_6O_3S$ (M^+) 206.0038, found 206.0046.

1-(Furan-2-yl)-2-(1H-pyrrol-2-yl)ethane-1,2-dione (***2q***): 45% yield; 3.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, C_2D_6SO, TMS) δ 12.33 (s, 1 H), 8.10 (s, 1 H), 7.46 (d, J = 3.2 Hz, 1 H), 7.29 (s, 1 H), 6.90 (s, 1 H), 6.72 (t, J = 2.0 Hz, 1 H), 6.22 (t, J = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, C_2D_6SO) δ 180.3 (J = 2.9 Hz), 179.7 (J = 3.1 Hz), 150.7, 149.7, 129.7 (J = 17.7 Hz), 128.3 (J = 15.4 Hz), 124.2, 122.1 (J = 3.2 Hz), 113.7, 111.8 (J = 3.1 Hz); HRMS (EI) calcd for $C_{10}H_7NO_3$ (M^+) 189.0426, found 189.0424.

1,2-Di(thiophen-2-yl)ethane-1,2-dione[21] (***2r***): 84% yield; 3.5 mmol TBN was used; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (dd, J = 4.0, 0.8 Hz, 2 H), 7.84 (dd, J = 5.2, 1.2 Hz, 2 H), 7.20 (t, J = 4.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.6, 138.8, 137.7, 137.5, 128.9.

1-Phenylpropane-1,2-dione[23] (***2s***): 55% yield; 2.5 mmol TBN was used; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, J = 8.0 Hz, 2 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 2.51 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 191.3, 134.5, 131.7, 130.2, 128.8, 26.2.

1-Phenylbutane-1,2-dione[24] (***2t***): 60% yield; 2.5 mmol TBN was used; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, J = 8.4 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.50 (t, J = 7.8 Hz, 2 H), 2.92 (q, J = 7.2 Hz, 2 H), 1.20 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 192.6, 134.5, 132.0, 130.1, 128.8, 32.1, 6.7.

^{13}C-Benzyl (***Ia***): 76% yield; 2.5 mmol TBN was used; light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.97 (d, J = 7.0 Hz, 4 H), 7.64 (t, J = 7.5 Hz, 2 H), 7.49 (t, J = 7.5 Hz, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 135.1, 133.1 (q, J = 17.9 Hz) 130.0, 129.2; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8 (s, 86 C), 135.1 (s, 2 C), 133.1 (q, J = 7.5 Hz, 2 C), 130.0 (s, 4 C), 129.2 (s, 4 C); HRMS (EI) calcd for $C_{13}{}^{13}CH_{10}O_2$ (M^+) 211.0714, found 211.0712.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yhzhang@zju.edu.cn.

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