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ARTICLE TYPE

Copper-catalyzed TEMPO oxidative cleavage of 1,3-diketones and β-keto esters for synthesis of 1,2-diketones and α-keto esters

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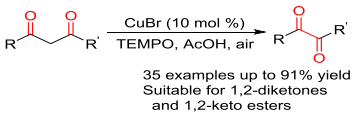


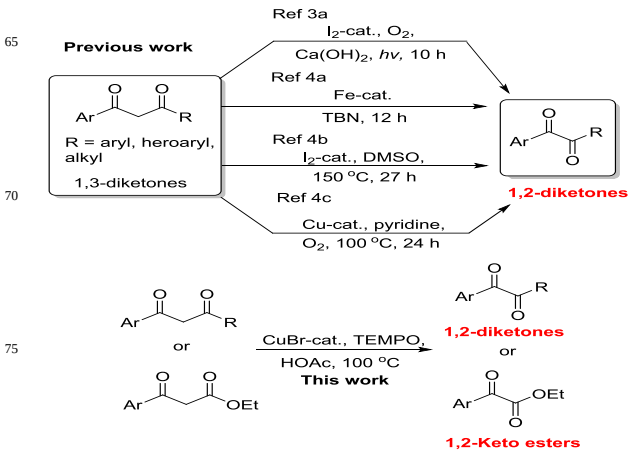
Copper-catalyzed an efficient, practical method has been developed for the synthesis of 1,2-diketones and α-keto esters. TEMPO used as radical initiator and scavenger oxidized cleavage of α-methylene of 1,3-diketones and β-keto esters to form 1,2-diketones and α-keto esters. This method provided a general way to the 1,2-dicarbonyl compounds.

Introduction

1,2-Diketones and α-keto esters serve as very useful building blocks in various bioactive molecules, and are of great important substrates for the synthesis of natural pharmaceuticals especially in heterocycles.[1] Moreover, their valuable application as photosensitive agents and photoinitiators have also been shown.[2] Although various compounds, such as α-methylene ketones, α-functionalized ketones, 1,2-diols, β-keto nitriles, alkenes, alkynes and acrylic derivatives, could be transformed to 1,2-diketones, or α-keto esters,[3] one of the most important strategies for synthesis of 1,2-dicarbonyl compounds is to use 1,3-dicarbonyl compounds as starting materials through the catalytic process. Recently, Itoh, Zhang, Yuan and Jiao's groups reported the transformation of 1,3-diketones to 1,2-diketones catalyzed by iron, iodine and copper catalysts (Scheme 1),[3a, 4] but these methods were unsuitable for synthesis of α-keto esters from β-keto esters,[5] hence development of catalytic and general way to 1,2-dicarbonyl compounds is still limited.

2,2,6,6-Tetramethylpiperidine oxide (TEMPO) is a useful mild oxidant for oxidation of alcohols, amines, aldehydes to carbonyl compounds, imines and nitriles, respectively, in laboratory and industrial production. TEMPO is also employed in the radical reaction, C–C bond formation and C–H functionalization. [6] In connection of our efforts on large-scale radical reactions,[7] herein, we disclose a copper-catalyzed method to synthesize 1,2-diketones and α-keto esters from the corresponding 1,3-diketones and β-keto esters using TEMPO as a mild oxidant through an radical pathway. This protocol provides an efficient and general process with short reaction times and mild reaction conditions.

Initially, we began our explorations in the reaction of 1,3-diphenylpropane-1,3-dione (**1a**) with TEMPO in AcOH at 100 °C. Fortunately, the desired product **2a** was isolated in 36% yield after 24 h (Table 1, entry 1). Thereafter, the ratios of **1a**/TEMPO were varied, however, the yields of **2a** were not improved obviously (Table 1, entries 2-3). To our delight, **2a** was obtained in 81% yield when CuI was added in this reaction, which indicated a Cu^{I} salt could dramatically improve the yield of product (Table 1, entry 4). Furthermore, we investigated other Cu^{I} salts such as CuCl and CuBr, and found CuBr was the most effective catalyst giving **2a** in 91% yield (Table 1, entries 5-6). Decreasing reaction temperature led to lower yields (Table 1, entries 7-9), but either shortening reaction time to 2 h or increasing the catalyst loading to 20% amount of CuBr catalyst have slight influence with 90% yield of **2a** (Table 1, entries 10-12). Moreover, the use of Cu^{II} and Fe^{II} salts also gave the desired product **2a** though the yield was relative lower (Table 1, entries 13-14). After screening the different solvents of this reaction (Table 1, entries 15-20), the optimized conditions were a combination of 1,3-diketone/TEMPO/CuBr (1:2:0.1) in AcOH for 2 h at 100 °C (Table 1, entry 11).



Scheme 1 Catalytic transformation of 1,3-dicarbonyl compounds to 1,2-dicarbonyl compounds

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Table 1 Optimization of the reaction conditions

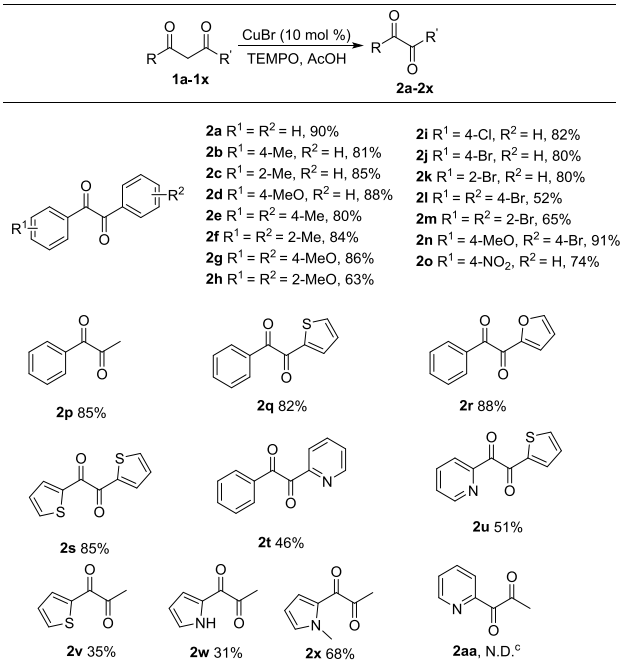
Entry	Catalyst[a]	1a:TEMPO	Temp (°C)	Time (h)	Solvent	Yield (%)[b]
1	None	1:1	100	24	AcOH	36
2	None	1:2	100	24	AcOH	43
3	None	1:0.5	100	24	AcOH	31
4	CuI	1:2	100	24	AcOH	81
5	CuCl	1:2	100	24	AcOH	90
6	CuBr	1:2	100	24	AcOH	91
7	CuBr	1:2	80	24	AcOH	86
8	CuBr	1:2	60	24	AcOH	76
9	CuBr	1:2	25	48	AcOH	38
10	CuBr	1:2	100	8	AcOH	90
11	CuBr	1:2	100	2	AcOH	90
12	CuBr	1:2	100	2	AcOH	90[c]
13	$Cu(OAc)_2$	1:2	100	4	AcOH	85
14	$Fe(OAc)_2$	1:2	100	4	AcOH	81
15	CuBr	1:2	100	30	DMF	78
16	CuBr	1:2	100	18	DMSO	48
17	CuBr	1:2	100	24	CH_3CN	N.R.[d]
18	CuBr	1:2	100	24	DCE	N.R.[d]
19	CuBr	1:2	100	24	Dioxane	N.R.[d]
20	CuBr	1:2	100	24	Toluene	N.R.[d]

[a] Using 10 mol% catalyst in the reaction. [b] Isolated yield. [c] CuBr (20 mol %). [d] N. R. means no reaction.

With the optimized conditions in hand, the scope of 1,3-diketones were explored, as shown in Table 2. In general, the corresponding 1,2-diketones were smoothly obtained in moderate to good yields. With substrates bearing electron-donating groups such as methyl and methoxy on phenyl ring, the transformation took place in good yields (Table 2, **2b**-**2g**). The product **2h** only was isolated in 63% yield due to steric hindrance of two methoxy groups located at *ortho* positions of phenyl rings. Fortunately, the introduction of one halogen, such as Cl and Br on benzene rings also afforded the desired products in good yields (Table 2, **2i**-**2k**, **2n**), which shown good tolerance of this method. However, moderate yields of **2l** (52%), **2m** (65%) and **2o** (74%) were obtained when the benzene rings contain two Br or NO_2 group. Thereby, we note that electronic effect play a significant role during transformation. Moreover, we investigated the scope of heteroaryl 1,3-diketones, a wide range of substrates produced the corresponding heteroaryl 1,2-diketones in varying yields, respectively. Substituted with one or two electron-donating heteroaryl such as thienyl and furyl group gave **2q**, **2r** and **2s** in 82%, 88% and 85% yields, respectively, however, substituted with one electron-withdrawing heteroaryl such as pyridyl gave the low yields of products **2t** (46%) and **2u** (51%). It is worthy to note that products **2v** and **2w** bearing one electron-donating heteroaryl were only isolated in 35% and 31% yields, respectively, that might be caused by methyl group replacing phenyl ring. Furthermore, no desired product **2aa** was observed for 1-pyridyl-3-methyl-1,3-diketone.

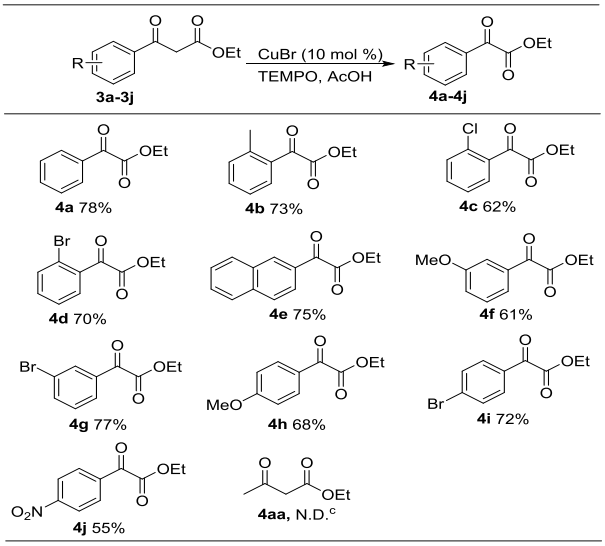
Subsequently, we took effort to investigate the substrates' scope of β-keto esters. To our delight, the corresponding α-keto esters were generated in satisfactory yield under similar reaction conditions. Substrates including electron-donating and electron-withdrawing groups on phenyl ring could be transformed to products smoothly. Substrates containing methyl and methoxy groups on phenyl ring could produce α-keto esters in moderate to good yields (Table 3, **4b**, **4f** and **4h**). Notably, compared with the halogens substituted on phenyl ring (Table 3, **4c**, **4d**, **4g** and **4i**), the strong electron-withdrawing substituent such as nitro group could decrease the yield to 55% (Table 3, **4j**). Other effort to synthesize aliphatic α-keto ester from aliphatic β-keto ester has

Table 2 Scope of 1,3-diketones[a,b]



[a] Reaction conditions: the mixture of **1** (0.5 mmol), CuBr (0.05 mmol), and TEMPO (1.0 mmol) was heated in HOAc (1.0 mL) at 100 °C for 2 h under air. [b] Isolated yield. [c] N.D. means none detected.

Table 3 Scope of β-keto esters[a,b]



[a] Reaction conditions: the mixture of **3** (0.5 mmol), CuBr (0.05 mmol), and TEMPO (1.0 mmol) was heated in HOAc (1.0 mL) at 100 °C for 3.0~5.5 h (monitored by TLC) under air. [b] Isolated yield. [c] N.D. means none detected.

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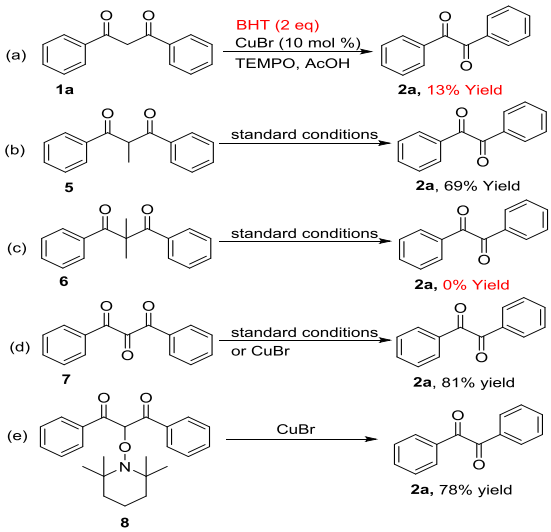
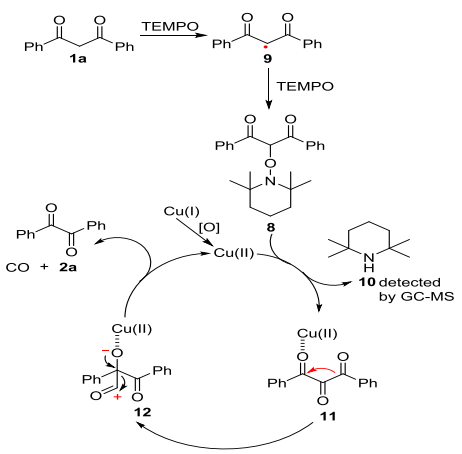
been tried, unfortunately, we didn't detect the desired product (Table 3, **4aa**).

To gain insight of reaction features, the control experiments were conducted. As shown in Scheme 2(a), the addition of radical scavenger BHT inhibited the reaction dramatically and **2a** was only afforded in 13% yield, the result indicated that this reaction might be involved a radical pathway. Then we speculated TEMPO might abstract a hydrogen atom from α-methylene and was induced to a sp^3-carbon radical. To verify our speculation, substrates **5** and **6** were selected to proceed reaction under standard conditions (Scheme 2(b) and 2(c)). The results showed substrate **5** could convert to **2a** in 69% yield but no product was transformed by substrate **6**. Also, we prepared intermediate triketone **7,** and found that **7** could easily generate **2a** in 81% yield under standard conditions or even CuBr used only (Scheme 2(d)), based on these experimental results, the forming progress of key intermediate **7** was necessary to find out. So we hypothesized the sp^3-carbon radical which generated in situ might be captured by TEMPO, after then the intermediate **8** might produce in reaction. Thereby, we prepared compound **8** as starting substrate to conduct experiment under CuBr without TEMPO, finally the product **2a** was isolated in 78% yield as expected (Scheme 2(e)). The experimental results proved that compound **8** might be generated by a radical pathway and then converted to triketone **7**.



Scheme 2 Control experiments



Scheme 3 Proposed mechanism

On the basis of control experiments and previous reports,[3a, 4] a plausible mechanism is outlined in Scheme 3. Initially, TEMPO abstracted a hydrogen atom from α-methylene of 1,3-diketone **1a** to generate sp^3-carbon radical **9**, which was then trapped by another molecule of TEMPO to produce intermediate **8**, the fragile N-O bond was broken easily in the presence of copper salt, meanwhile triketone **7** was generated with leaving of 2,2,6,6-tetramethylpiperidine **10**, and the corresponding Cu^{II} could coordinate with **7** to form complex **11**, which underwent a 1,2-Wagner-Meerwein-type rearrangement to result in intermediate **12**, the simultaneous elimination of carbon monoxide in **12** promoting the reaction toward the 1,2-diketone **2a**.

Conclusions

In summary, we have developed an copper-catalyzed efficient and practical method for the synthesis of 1,2-diketones and α-keto esters in short time in air. The mechanism study disclosed that TEMPO played a dual function as radical initiator and scavenger, oxidizing cleavage of α-methylene of 1,3-diketones and β-keto esters to form 1,2-diketones and α-keto esters. This method provided a general way to the 1,2-dicarbonyl compounds.

Experimental section

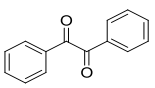
General information

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were determined with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm from internal TMS (δ); all coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300−400 mesh silica gel using flash column techniques. All of the reagents were obtained commercially and used directly unless otherwise noted.

Typical procedure for the preparation of benzil (2a).

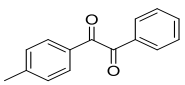
To a solution of acetic acid (1.0 mL), 1,3-diphenylpropane-1,3-dione (**1a**) (112 mg, 0.5 mmol), CuBr (7.2 mg, 0.05 mmol) and TEMPO (156 mg, 1 mmol) were added, the mixture was heated at 100 ^{o}C for 2 h, after completion of reaction (monitored by TLC), the reaction was quenched by water and then neutralized by aqueous $NaHCO_3$ solution and extracted with DCM (10 mL × 3). The combined organic fractions were dried over anhydrous $MgSO_4$, and concentrated under vacuum to obtain the crude product, which was purified by column chromatography (silica gel, 95% petroleum ether/EtOAc) to give pure benzil (**2a**).

Benzil (2a) [1].



Yellow solid, mp 100–101 ^{o}C, 81% yield (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.5 Hz, 4H), 7.65 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.6, 134.9, 132.9, 129.8, 129.0. MS (ESI-TOF) m/z: $(M+H)^+$ Calcd for $C_{14}H_{11}O_2$ 211.1, found 211.1.

1-Phenyl-2-(*p*-tolyl)ethane-1,2-dione (2b) [4a].



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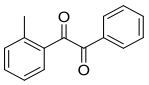
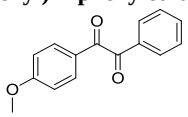
Yellow oil, 80% yield (91 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.94 (m, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.68–7.60 (m, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.9, 194.4, 146.4, 134.9, 133.2, 130.6, 130.1, 130.0, 129.9, 129.1, 22.0. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{15}H_{13}O_2$ 225.1, found 225.1.

1-Phenyl-2-(*o*-tolyl)ethane-1,2-dione (2c) [4c].



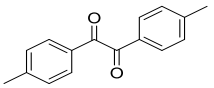
Yellow solid, mp 58–59 °C, 85% yield (97.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.94 (m, 2H), 7.70–7.60 (m, 2H), 7.54–7.45 (m, 3H), 7.34 (d, J = 7.7 Hz, 1H), 7.29–7.23 (m, 1H), 2.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.9, 195.0, 141.5, 134.8, 133.9, 133.23, 133.17, 132.7, 131.9, 130.0, 129.1, 126.2, 22.0. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{15}H_{12}NaO_2$ 247.1, found 247.1.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2d) [4a].



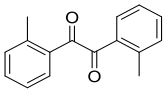
Yellow solid, mp 60–61 °C, 88% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.91 (m, 4H), 7.66–7.61 (m, 1H), 7.53–7.46 (m, 2H), 7.00–6.94 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.0, 193.3, 165.1, 134.8, 133.3, 132.5, 130.0, 129.1, 126.2, 114.5, 55.8. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{15}H_{13}O_3$ 241.1, found 241.1.

1,2-Di-*p*-tolylethane-1,2-dione (2e) [4a].



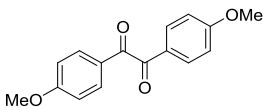
Yellow solid, mp 105–106 °C, 80% yield (95 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 4H), 7.18 (d, J = 8.0 Hz, 4H), 2.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.6, 146.1, 130.7, 130.0, 129.8, 21.9. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{15}O_2$ 239.1, found 239.1.

1,2-Di-*o*-tolylethane-1,2-dione (2f) [8].



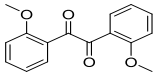
Yellow solid, mp 82–83 °C; 84% yield (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J = 7.8, 1.1 Hz, 2H), 7.47 (td, J = 7.5, 1.3 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 7.30–7.22 (m, 2H), 2.70 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 141.6, 133.7, 133.1, 132.7, 131.9, 126.1, 22.0. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{16}H_{14}NaO_2$ 261.1, found 261.1.

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (2g) [9].



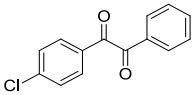
Yellow solid, mp 134–135 °C, 85% yield (114 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 9.0 Hz, 4H), 6.96 (d, J = 9.0 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6, 165.0, 132.5, 126.4, 114.4, 55.8. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{15}O_4$ 271.1, found 271.1.

1,2-Bis(2-methoxyphenyl)ethane-1,2-dione (2h) [10].



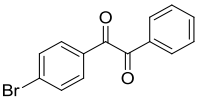
White solid, mp 130–131 °C, 63% yield (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.8, 1.7 Hz, 2H), 7.60–7.50 (m, 2H), 7.15–7.06 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H), 3.57 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.6, 160.4, 135.7, 130.4, 123.4, 121.4, 112.6, 55.9. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{16}H_{15}O_4$ 271.1, found 271.1.

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (2i) [4a].



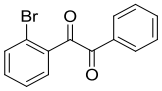
Yellow solid, mp 80–81 °C, 82% yield (101 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.88 (m, 4H), 7.66 (t, J = 7.4 Hz, 1H), 7.58–7.44 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.0, 193.2, 141.7, 135.2, 132.9, 131.4, 131.3, 130.0, 129.5, 129.2. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_9ClNaO_2$ 267.0, found 267.0.

1-(4-Bromophenyl)-2-phenylethane-1,2-dione (2j) [4c].



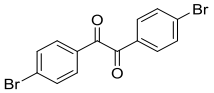
Yellow solid, mp 79–81 °C, 80% yield (116 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.4 Hz, 2H), 7.90–7.80 (m, 2H), 7.72–7.62 (m, 3H), 7.52 (t, J = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.0, 193.4, 135.2, 132.9, 132.6, 131.9, 131.4, 130.6, 130.1, 129.2. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_9BrNaO_2$ 311.0, found 311.0.

1-(2-Bromophenyl)-2-phenylethane-1,2-dione (2k) [4c].



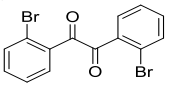
Yellow solid, mp 65–67 °C, 80% yield (116 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.04 (m, 2H), 7.85–7.79 (m, 1H), 7.70–7.61 (m, 2H), 7.57–7.51 (m, 2H), 7.50–7.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.3, 191.6, 136.2, 134.6, 134.5, 133.9, 132.8, 132.7, 130.5, 129.0, 128.0, 121.9. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_9BrNaO_2$ 311.0, found 311.0.

1,2-Bis(4-bromophenyl)ethane-1,2-dione (2l) [11].



White solid, mp 229–230 °C, 52% yield (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz, 4H), 7.67 (d, J = 8.2 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.7, 132.7, 131.7, 131.4, 130.9. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_8Br_2NaO_2$ 391.0, found 391.0.

1,2-Bis(2-bromophenyl)ethane-1,2-dione (2m) [12].



Yellow solid, mp 132–133 °C, 65% yield (121 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.95 (m, 2H), 7.74 –7.65 (m, 2H), 7.53 – 7.41 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.2, 134.7, 134.5, 134.2, 133.4, 127.7, 123.3. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_8Br_2NaO_2$ 390.9, found 390.9.

1-(4-Bromophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (2n) [13].

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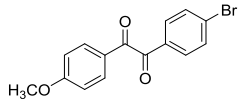
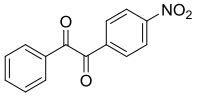


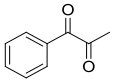
Yellow solid, mp 147–148 °C, 54% yield (83 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.90 (m, 2H), 7.87–7.81 (m, 2H), 7.68–7.61 (m, 2H), 7.01–6.95 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.7, 192.5, 165.3, 132.6, 132.5, 132.1, 131.4, 130.4, 126.0, 114.6, 55.8. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{15}H_{12}BrO_3$ 319.0, found 319.0.

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (2o) [5].



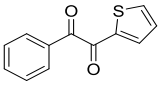
Yellow solid, mp 151–152 °C, 74% yield (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.1 Hz, 2H), 8.17 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 7.3 Hz, 2H), 7.80–7.65 (m, 1H), 7.62–7.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.0, 192.2, 151.3, 137.4, 135.6, 132.5, 131.1, 130.2, 129.4, 124.3. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{14}H_{10}NO_4$ 256.1, found 256.1.

1-Phenylpropane-1,2-dione (2p) [3a].



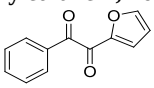
Yellow solid, mp: 102–103 °C, 85% yield (63.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.95 (m, 2H), 7.68–7.58 (m, 1H), 7.54–7.43 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 191.5, 134.7, 131.8, 130.4, 128.9, 26.4. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_9H_9O_2$ 149.0, found 149.0.

1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione (2q).



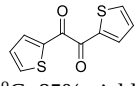
Yellow solid, mp: 69–71 °C, 82% yield (88.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.00 (m, 2H), 7.84 (dd, J = 4.9, 1.1 Hz, 1H), 7.80 (dd, J = 3.9, 1.1 Hz, 1H), 7.70–7.61 (m, 1H), 7.56–7.46 (m, 2H), 7.22–7.14 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.2, 185.7, 139.9, 137.0, 136.8, 135.0, 132.7, 130.3, 129.0, 128.9. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ calcd for $C_{12}H_8NaO_2S$ 239.0143, found 239.0144.

1-(Furan-2-yl)-2-phenylethane-1,2-dione (2r).



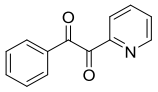
Yellow solid, mp: 45–46 °C, 82% yield (62.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.94 (m, 2H), 7.74 (d, J = 1.1 Hz, 1H), 7.67–7.59 (m, 1H), 7.54–7.44 (m, 2H), 7.36 (d, J = 3.6 Hz, 1H), 6.60 (dd, J = 3.7, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 180.5, 149.9, 149.3, 134.9, 132.6, 130.2, 129.0, 123.4, 113.1. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ calcd for $C_{12}H_8NaO_3$ 223.0371, found 223.0373.

1,2-Di(thiophen-2-yl)ethane-1,2-dione (2s) [4c].



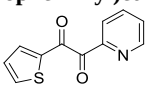
Yellow solid, mp: 88–89 °C, 85% yield (94.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 3.9, 1.1 Hz, 2H), 7.84 (dd, J = 4.9, 1.1 Hz, 2H), 7.23–7.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 182.5, 138.6, 137.6, 137.3, 128.8. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_6NaO_2S_2$ 244.9, found 244.9.

1-Phenyl-2-(pyridin-2-yl)ethane-1,2-dione (2t).



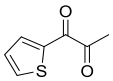
Yellow solid, mp: 72–74 °C, 46% yield (48.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70–8.64 (m, 1H), 8.24–8.17 (m, 1H), 7.97–7.90 (m, 3H), 7.67–7.61 (m, 1H), 7.56–7.45 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.3, 195.3, 151.9, 150.0, 137.4, 134.8, 133.3, 129.7, 129.1, 128.3, 123.3. HRMS (ESI-TOF) *m/z*: $(M+Na)^+$ calcd for $C_{13}H_9NNaO_2$ 234.0531, found 234.0520.

1-(Pyridin-2-yl)-2-(thiophen-2-yl)ethane-1,2-dione (2u).



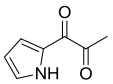
Yellow oil, 51% yield (55.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.76–8.69 (m, 1H), 8.28 (dd, J = 4.9, 1.0 Hz, 1H), 8.25–8.19 (m, 1H), 8.15 (td, J = 7.7, 1.6 Hz, 1H), 7.84–7.73 (m, 2H), 7.36–7.26 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 193.4, 188.2, 150.4, 149.9, 139.2, 138.2, 137.9, 137.4, 129.6, 129.2, 123.5. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ calcd for $C_{11}H_8NO_2S$ 218.0276, found 218.0267.

1-(Thiophen-2-yl)propane-1,2-dione (2v) [14].



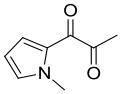
Yellow solid, mp: 56–58 °C, 35% yield (26.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, J = 3.9, 1.1 Hz, 1H), 7.80 (dd, J = 4.9, 1.1 Hz, 1H), 7.20–7.14 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 180.9, 137.7, 137.4, 137.2, 128.7, 25.4. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_7H_7O_2S$ 155.0, found 155.0.

1-(1*H*-Pyrrol-2-yl)propane-1,2-dione (2w).



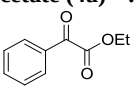
Yellow solid, mp: 57–58 °C, 31% yield (21.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.24 (br, 1H), 7.37–7.31 (m, 1H), 7.18 (s, 1H), 6.35–6.32 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 177.0, 128.1, 122.5, 112.4, 25.6. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ calcd for $C_7H_8NO_2$ 138.0555, found 138.0558.

1-(1-Methyl-1*H*-pyrrol-2-yl)propane-1,2-dione (2x).



Yellow oil, 68% yield (51.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 3.1 Hz, 1H), 6.98 (s, 1H), 6.25–6.15 (m, 1H), 3.98 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.5, 179.5, 133.4, 125.4, 124.0, 108.9, 36.1, 25.1. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ calcd for $C_8H_{10}NO_2$ 152.0712, found 152.0705.

Ethyl 2-oxo-2-phenylacetate (4a) [15].



Colorless oil, 78% yield (69.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.99 (m, 2H), 7.70–7.62 (m, 1H), 7.57–7.47 (m, 2H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.5, 163.9, 135.0, 132.6, 130.1, 129.0, 62.5, 14.2. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_{10}NaO_3$ 201.1, found 201.1.

Ethyl 2-oxo-2-(*o*-tolyl)acetate (4b) [15].

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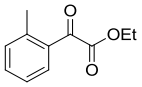
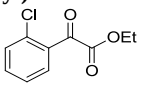


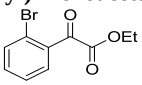
Colorless oil, 73% yield (70.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.9 Hz, 1H), 7.49 (td, J = 7.5, 1.3 Hz, 1H), 7.32 (t, J = 8.0 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 2.61 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.9, 164.8, 141.5, 133.8, 132.5, 132.4, 131.4, 126.1 , 62.4, 21.6, 14.2. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{11}H_{12}NaO_3$ 215.1, found 215.1.

Ethyl 2-(2-chlorophenyl)-2-oxoacetate (4c) [16].



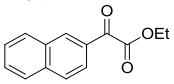
Colorless oil, 62% yield (65.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 7.7, 1.7 Hz, 1H), 7.56–7.48 (m, 1H), 7.47–7.35 (m, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.7, 163.2, 134.4, 134.0, 133.4, 131.7, 130.7, 127.4, 62.9, 14.0. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_9ClNaO_3$ 235.0, found 235.0.

Ethyl 2-(2-bromophenyl)-2-oxoacetate (4d) [15].



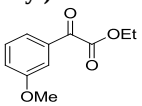
Colorless oil, 70% yield (89.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.64 (m, 1H), 7.65–7.60 (m, 1H), 7.47–7.38 (m, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 187.4, 162.5, 135.7, 134.1, 133.8, 131.9, 127.8, 121.6, 63.0, 14.0. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_9BrNaO_3$ 278.9, found 278.9.

Ethyl 2-(naphthalen-2-yl)-2-oxoacetate (4e) [15].



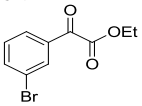
Colorless oil, 75% yield (85.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (dd, J = 8.6, 0.5 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.99 (dd, J = 7.3, 1.2 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.73–7.64 (m, 1H), 7.63–7.49 (m, 2H), 4.49 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.0, 164.7, 135.9 , 134.05, 134.01, 131.1, 129.4, 128.8, 128.3, 127.1, 125.7, 124.4, 62.5, 14.2. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{14}H_{12}NaO_3$ 251.1, found 251.1.

Ethyl 2-(3-methoxyphenyl)-2-oxoacetate (4f) [17].



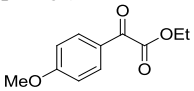
Colorless oil, 61% yield (63.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 2H), 7.41 (t, J = 7.9 Hz, 1H), 7.20 (dd, J = 8.2, 2.5 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 186.3, 163.9, 159.9, 133.7, 129.9, 123.1, 121.8, 113.3, 62.3, 55.5, 14.1. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{11}H_{12}NaO_4$ 231.1, found 231.1.

Ethyl 2-(3-bromophenyl)-2-oxoacetate (4g) [18].



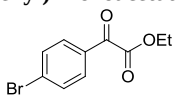
Colorless oil, 77% yield (98.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 184.5, 162.8, 137.5, 134.1, 132.6, 130.3, 128.5, 122.9, 62.5, 13.9. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_9BrNaO_3$ 278.9, found 278.9.

Ethyl 2-(4-methoxyphenyl)-2-oxoacetate (4h) [15].



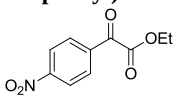
Colorless oil, 68% yield (70.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.94 (m, 2H), 7.00–6.90 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.0, 165.1, 164.3, 132.7, 125.6, 114.3, 62.3, 55.7, 14.2. MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{11}H_{13}O_4$ 209.1, found 209.1.

Ethyl 2-(4-bromophenyl)-2-oxoacetate (4i) [15].



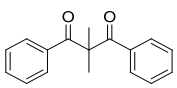
Colorless oil, 72% yield (92.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.83 (m, 2H), 7.69–7.59 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 185.1, 163.1, 132.3, 131.4, 131.3, 130.5, 62.5, 14.1. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_9BrNaO_3$ 278.9, found 278.9.

Ethyl 2-(4-nitrophenyl)-2-oxoacetate (4j) [17].



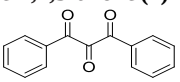
Colorless oil, 55% yield (61.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36–8.30 (m, 2H), 8.26–8.19 (m, 2H), 4.47 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 184.2, 162.4, 151.2, 137.1, 131.3, 124.0, 63.1, 14.1. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{10}H_9NNaO_5$ 246.1, found 246.1.

2,2-Dimethyl-1,3-diphenylpropane-1,3-dione (6) [19].



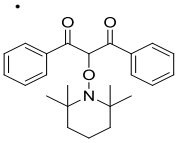
White solid, mp: 104–106 °C, 85% yield (1.07 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.7 Hz, 4H), 7.40 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.6 Hz, 4H), 1.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 135.6, 133.0, 129.2, 128.7, 59.5, 25.4. MS (ESI-TOF) *m/z*: $(M+Na)^+$ Calcd for $C_{17}H_{16}NaO_2$ 275.1, found 275.1.

1,3-Diphenylpropane-1,2,3-trione (7) [20].



White solid (the mixture of 1,3-diphenylpropane-1,2,3-trione and diphenylpropane-1,2,3-trione hydrate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.04 (m, 2H), 7.98–7.90 (m, 2H), 7.75–7.68 (m, 1H), 7.61–7.47 (m, 3H), 7.36 (t, J = 7.8 Hz, 2H), 5.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 192.6, 188.4, 135.5, 134.8, 133.7, 132.22, 132.18, 130.36, 130.33, 129.2, 128.9, 128.6, 94.2. MS (ESI-TOF) *m/z*: $(M)^+$ Calcd for $C_{15}H_{10}O_3$ 238.1, found 238.1.

1,3-Diphenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy) propane-1,3-dione (8) [20].



White solid, mp: 104–105 °C, 90% yield (102.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.16 (m, 4H), 7.58–7.50 (m, 2H),

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7.49–7.38 (m, 4H), 6.30 (s, 1H), 1.60–1.40 (m, 5H), 1.30 (m, 1H), 1.13 (s, 6H), 0.95 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.1, 134.8, 133.8, 130.3, 128.5, 99.2, 60.2, 40.1, 33.0, 20.3, 17.1. HRMS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{24}H_{30}NO_3$ 380.2234, found 380.2229.

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Notes and references

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