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Synthesis of 1,2-Diketones *via* A Metal-free, Visible-light Induced Aerobic Photooxidation of Alkynes

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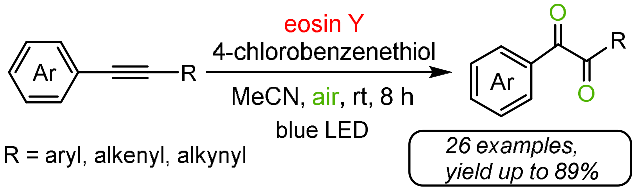


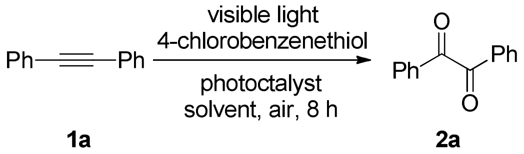
ABSTRACT: 1,2-Diketones were synthesized by the oxidation of corresponding alkynes using air as the oxidant under metal-free conditions upon irradiation of blue light. A cheap and readily available organic dye, eosin Y, was used as the photocatalyst. For various substituents on the aryl ring, the reaction proceeded smoothly to give the dicarbonylation products in moderate to good yields. Some oxidation sensitive groups such as formyl and carbon-carbon double bond tolerated under the developed reaction conditions.

1,2-Diketones are very important precursors in organic synthesis. The construction of azacyclic compounds from 1,2-diketones are well-known.[1] These compounds also play an important role in pharmaceutical chemistry. For example, they were used as the basic materials to synthesize anticonvulsant and antimicrobial drugs.[2] The oxidation of various compounds such as olefins, methylene ketones, and alkynes are generally employed for the preparation of 1,2-diketones,[3] in which the oxidations of alkynes are considered to be one of the most straightforward and practical strategies. Alkynes can be oxidized by ordinary oxidants such as potassium permanganate to the corresponding 1,2-diketones, but the tolerance to the functional groups is very limited. Mn(III) or Cu mediated oxidative decarboxylative coupling of arylboronic acids or aryl iodides with arylpropiolic acids provided new protocols for the preparation of these compounds.[4] Other than that, many efforts focused on the transition-metal catalyzed direct oxidation of alkynes to 1,2-diketones in recent years. Pd,[5] Ru,[6] Au[7], Cu,[8] *etc* were employed as the catalysts, and DMSO, Oxone, $K_2S_2O_8$ and Ph_2SO behaved as the oxidants in these transformations. Alkynes could also be oxidized to α-ketoesters, esters or amides by hypervalent iodines in the presence of alcohol or amine.[9] It is obvious that to construct chemical bonds under transition-metal-free conditions to fulfill the classic transition-metal-catalyzed reactions is highly desired, especially in pharmaceuticals industry. Thus, developing more efficient and high selective oxidation pathways is still a challenging task.

Visible light photoredox catalysis for the activation of organic molecules has received much attention in recent years.[10] Several electron-rich functional groups have enabled the oxidation *via* the single-electron oxidation pathways with visible light in the presence of photocatalysts. For example, alcohols,[11] α-haloesters,[12] arylboronic acids[13] and thiobenzanilides[14] can be oxidized to corresponding aldehydes, α-ketoesters, phenols and benzothiazoles respectively upon irradiation of visible light in the presence of photocatalysts. Recently, a nitrate radical $NO_3^{\cdot}$ was found to oxidize diphenylacetylene to generate dibenzoyl under visible light photooxidation conditions.[15] What is more, organic dyes have been introduced as photocatalysts in many visible light photoredox catalysis, and drawn greater attention.[16] In this work, we wish to report an efficient method for the synthesis of 1,2-diketones *via* visible light photooxidation of alkynes, in which O_2 was employed as the oxidant, and eosin Y as the photo-catalyst.

In our initial study, we selected diphenylethyne (**1a**) as a model substrate for the optimization of reaction conditions (Table 1). To our delight, using eosin Y as the photocatalyst upon irradiation of blue light, and in the presence of 4-chlorobenzenethiol, an oxidation product 1,2-diphenylethane-1,2-dione was obtained in 55% yield at room temperature in THF after 8 h (entry 1). However, if the reaction was carried out in dark environment, only trace product was found (entry 2). In the absence of 4-chlorobenzenethiol, photocatalyst or air (O_2), no product was generated (entries 3-5). Then, a screen of different solvents such as MeCN, DCE, DMF, toluene and DMSO were tested and MeCN was proved to be the best, and a good yield of 83% was obtained (entries 6–10). Other photocatalysts were then examined. With the transition-metal complexes such as $Ru(bpy)_3Cl_2·6H_2O$ and $Ir(ppy)_3$, the moderate yields were given (entries 11 and 12). Other organic dyes (rose bengal, fluorescein and rhodamine B) did not show better effect than that of eosin Y (entries 13–15). The presence of 2 equiv 4-chlorobenzenethiol was essential. The decrease of the amount of 4-chlorobenzenethiol to 1 equiv resulted in the lower yields (entry 16). When 4-methoxybenzenethiol was used to replace 4-chlorobenzenethiol, a lower yield of 74% was obtained (entry 17). Compared with that in air, when the reaction took place in O_2, the yield was not considerably enhanced (entry 18). The appropriate amount of the photocatalyst was 2 mol %. Increasing it to 4 mol % did not bring the obvious change of the yield, but reducing the dosage of the photocatalyst to 1 mol % led to a lower yield of 72% (entries 19 and 20). Upon irradiation of green light instead of blue light, the yield was slightly decreased (entry 21).

Table 1. Optimization of Reaction Conditions[a]



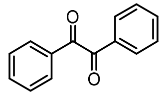
entry	photocatalyst (mol %)	solvent	yield (%)
1	eosin Y (2)	THF	55
2[b]	eosin Y (2)	THF	trace
3[c]	eosin Y (2)	THF	0
4	-	THF	0
5[d]	eosin Y (2)	THF	0
6	**eosin Y (2)**	**MeCN**	**83**
7	eosin Y (2)	DCE	26
8	eosin Y (2)	DMF	19
9	eosin Y (2)	toluene	31
10	eosin Y (2)	DMSO	13
11	$Ru(bpy)_3Cl_2·6H_2O$ (2)	MeCN	53
12	$Ir(ppy)_3$ (2)	MeCN	61
13	rose bengal (2)	MeCN	37
14	fluorescein (2)	MeCN	65
15	rhodamine B (2)	MeCN	69
16[e]	eosin Y (2)	MeCN	70
17[f]	eosin Y (2)	MeCN	74

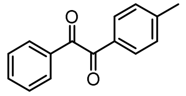
18[g]	eosin Y (2)	MeCN	84
19	eosin Y (4)	MeCN	82
20	eosin Y (1)	MeCN	72
21[h]	eosin Y (2)	MeCN	75

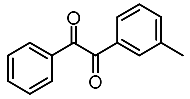
[a] Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), 4-chlorobenzenethiol (0.4 mmol), photocatalyst, solvent (2 mL), irradiation under air atmosphere at room temperature using 5 W blue LED for 8 h. [b] In the dark. [c] Without 4-chlorobenzenethiol. [d] In Ar atmosphere. [e] 4-Chlorobenzenethiol (0.2 mmol). [f] 4-Methoxybenzenethiol was used instead of 4-chlorobenzenethiol. [g] Under O_2 atmosphere (1 atm). [h] Using 5 W green LED as the light source.

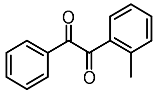
Having established the optimized reaction conditions, we then explored the generality and scope of the reaction across a series of alkynes (Table 2). As that can been seen from Table 2, different 1,2-disubstituted alkynes were oxidized to the corresponding diketones in moderate to good yields. It was showed that the diarylethynes containing electron-donating substitutes, such as methyl, *tert*-butyl, methoxyl had a high reactivity and afforded the corresponding diaryldiketones in good yields (**2a**–**2f**, **2s**–**2v**), but the presence of electron-withdrawing groups, such as halogens, nitro, cyano, trifluoromethyl, ester and carbonyl led to moderate yields, which might be because that the electron-deficiency of the triple bonds reduced their reactivity (**2g**–**2r**). It was nice to see that the easily oxidized formyl group could be preserved in this oxidation process (**2r**), this result revealed that the reaction had very good selectivity. Moreover, for naphthyl and thienyl substituted ethynes, the corresponding 1,2-diketones were also afforded in 72% and 70% yield respectively (**2w** and **2x**). In addition, from the reaction of 1,4-diphenylbuta-1,3-diyne, only a monoalkynyl oxidized product was obtained (**2y**). And for 1,4-diphenylbut-1-en-3-yne, the carbon-carbon double bond was preserved (**2z**). The reaction was suitable for various diaryl alkynes or other large conjugated alkynes. For the substrate phenylacetylene or 1-phenyl-1-hexyne, however, the complex mixture was obtained. Although the exact reason was not clear, it should be related to the stability of the intermediates.

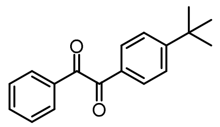
Table 2. Visible-Light-Induced Synthesis of 1,2-Dikeones[a]

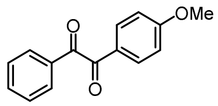

2a, 83%


2b, 84%

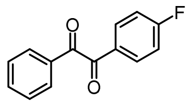

2c, 82%


2d, 81%

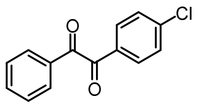

2e, 85%



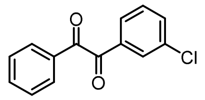
2f, 85%



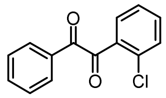
2g, 66%



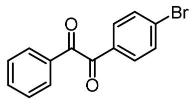
2h, 69%



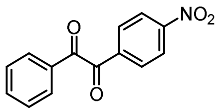
2i, 63%



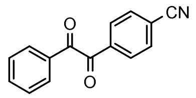
2j, 65%



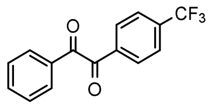
2k, 70%



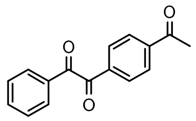
2l, 65%

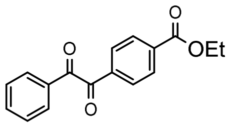


2m, 63%

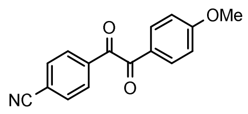


2n, 67%

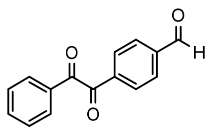

2o, 74%



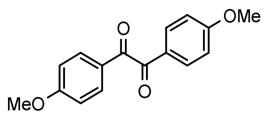
2p, 71%



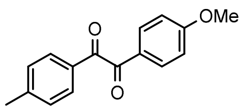
2q, 55%



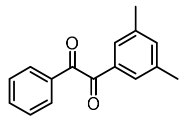
2r, 77%

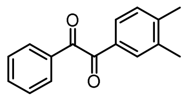


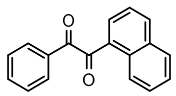
2s, 89%

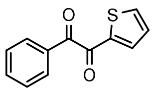


2t, 82%

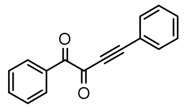

2u, 86%

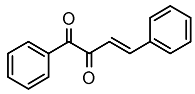

2v, 81%


2w, 72%



2x, 70%

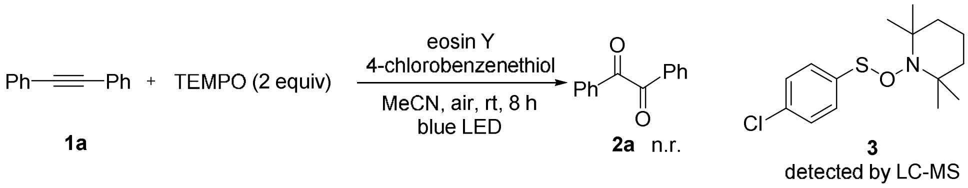

2y, 77%


2z, 68%

[a]Reaction conditions: **1** (0.2 mmol), 4-chlorobenzenethiol (0.4 mmol), eosin Y (2 mol %), MeCN (2 mL), irradiation under air atmosphere at room temperature using 5 W blue LED for 8 h. All yields are isolated ones.

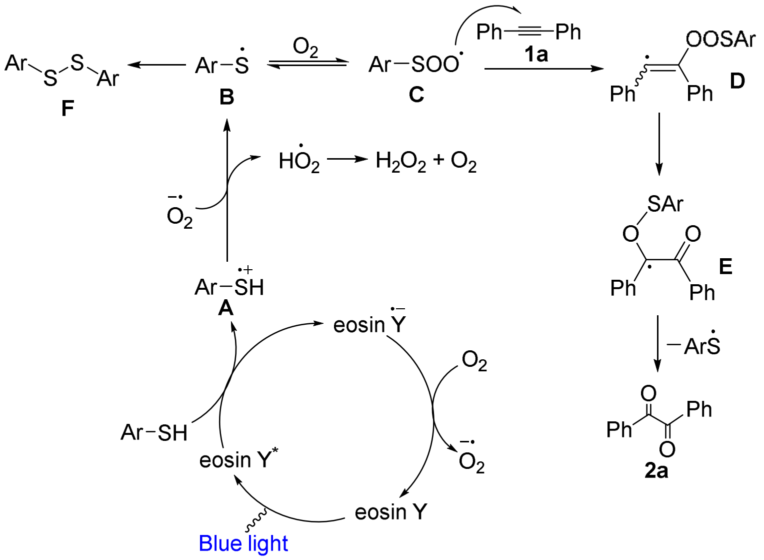
In order to study the possible mechanism of the transformation, a radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added under the standard reaction conditions. No desired product was found from the reaction mixture in the presence of 2 equiv TEMPO, meanwhile, an adduct of 4-chlorophenylthio radical with TEMPO was detected by LC-MS (Scheme 1), which indicated that the transformation might undergo through a radical pathway. By using DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) as the radical trapping agent, a characteristic signal of a superoxide radical anion ($O_2^{-\cdot}$) was clearly observed by EPR spectra (see Supporting Information).[17] This radical anion was obviously generated from the molecular oxygen by a single-electron transfer (SET) under the current reaction conditions.[18]

Scheme 1. Control Experiment



It was found by Wille *et al* that a thiylperoxyl radical could be generated by a reversible oxidation of thiophenyl radical with O_2.[19] Inspired by this report, and based on our observations as well as other related works,[16-18] a plausible reaction mechanism is described in Scheme 2. Initially, eosin Y was converted to excited state eosin Y* upon irradiation of visible light, and this eosin Y* underwent reductive quenching by thiophenol to afford the radical cation **A** and form an eosin Y radical anion. The eosin Y radical anion was oxidized to the ground state by aerobic oxygen to complete the photoredox cycle and a superoxide radical anion ($O_2^{-\cdot}$) was generated simultaneously.[18] The resulting radical cation **A** was deprotonated by $O_2^{-\cdot}$ to give the thiophenyl radical **B**. Subsequently, a thiylperoxyl radical **C** was formed through the reversible trapping of **B** with O_2. The addition of radical **C** to 1,2-diphenylethyne (**1a**) generated an vinyl radical **D**. The rearrangement of **D** *via* the homolytic O−O bond cleavage and the radical transfer formed radical intermediate **E**. The desired product 1,2-diphenylethane-1,2-dione **2a** was finally produced by the elimination of thiophenyl radical **B** from **E**. In addition, a byproduct di(4-chlorophenyl) disulfide **F** which came from the homocoupling of radical **B** was also separated from the reaction mixture.

Scheme 2. Plausible Reaction Mechanism



In summary, we have discovered a convenient pathway for the oxidation of diarylalkynes into corresponding 1,2-diketones using air as the oxidant under metal-free conditions upon irradiation of visible light. A cheap and readily available organic dye, eosin Y, was used as the photocatalyst. The reaction has a very good selectivity, various substituents on the aryl ring, including some oxidation sensitive groups such as formyl and carbon-carbon double bond tolerated under the developed reaction conditions and the dicarbonylation products were obtained in moderate to good yields.

Experimental Section

General.

All reactions were run in oven-dried flasks under air. Chemicals were commercially available and were used without purification. Diarylethynes and other alkynes were prepared according to the literature procedures.[20] NMR spectra were recorded at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ using TMS as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. Melting points are uncorrected. Q-TOF was used for the HRMS measurement.

General Experimental Procedure for the Synthesis of 1,2-Diphenylethane-1,2-dione (**2a**).

1,2-Diphenylethyne (**1a**) (0.2 mmol, 35.6 mg), 4-chlorobenzenethiol (0.4 mmol, 57.4 mg), and eosin Y (2 mol %, 2.8 mg) were added in MeCN (2 mL). The mixture was stirred under blue LED irradiation for 8 h under ambient air. After completion of the reaction, the reaction mixture was extracted with DCM (15 mL × 3). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (20:1) to afford the pure product **2a**.

1,2-Diphenylethane-1,2-dione (**2a**).[4b] Yellow solid (34.9 mg, 83% yield); mp 94−95 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.00 (d, J = 7.1 Hz, 4H), 7.67 (t, J = 7.4 Hz, 2H), 7.53 (t, J = 7.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.6, 134.9, 133.0, 129.9, 129.1.

1-Phenyl-2-(p-tolyl)ethane-1,2-dione (**2b**).[4b] Yellow solid (37.6 mg, 84% yield); mp 93−94 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.99 (dt, J = 8.5, 1.5 Hz, 2H), 7.89 (d, J = 8.3 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.8, 194.3, 146.2, 134.8, 133.1, 130.6, 130.0, 129.9, 129.8, 129.0, 21.9.

1-Phenyl-2-(m-tolyl)ethane-1,2-dione (**2c**).[4b] Yellow solid (36.7 mg, 82% yield); mp 56−57 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.99 (d, J = 7.1 Hz, 2H), 7.80 (dt, J = 9.7, 4.8 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.57–7.47 (m, 3H), 7.42 (t, J = 7.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.9, 194.7, 139.0, 135.8, 134.9, 133.1, 133.0, 130.2, 129.9, 129.0, 128.9, 127.2, 21.3.

1-Phenyl-2-(o-tolyl)ethane-1,2-dione (**2d**).[4b] Yellow solid (36.3 mg, 81% yield); mp 55−56 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.00 (d, J = 7.1 Hz, 2H), 7.71–7.64 (m, 2H), 7.57–7.50 (m, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 196.8, 194.9, 141.4, 134.7, 133.8, 133.1, 133.1, 132.6, 131.8, 130.0, 129.0, 126.1, 21.9.

1-(4-(Tert-butyl)phenyl)-2-phenylethane-1,2-dione (**2e**).[4b] Yellow oil (45.3 mg, 85% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.00 (d, J = 7.1 Hz, 2H), 7.93 (d, J = 8.6 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.59–7.48 (m, 4H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.8, 194.3, 159.1, 134.8, 133.1, 130.5, 129.9, 129.0, 126.1, 35.4, 31.0.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (**2f**).[4b] Yellow oil (40.8 mg, 85% yield); ^{1}H NMR

($CDCl_3$, 400 MHz): δ (ppm) 7.98 (t, J = 8.6 Hz, 4H), 7 .66 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 3.90(s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.9, 193.2, 165.0, 134.7, 133.2, 132.4, 129.9, 129.0, 126.1, 114.4, 55.7.

1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (**2g**).[8] Yellow solid (30.1 mg, 66% yield); mp 69−70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.06–8.02 (m, 2H), 8.00 (dt, J = 8.5, 1.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.24–7.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 194.1, 192.7, 166.8 (d, J = 256.7 Hz), 135.0, 132.9, 132.8 (d, J = 9.8 Hz), 130.0, 129.5, 129.1, 116.4 (d, J = 22.1 Hz).

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**2h**).[4b] Yellow solid (33.8 mg, 69% yield); mp 72−73 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.00–7.93 (m, 4H), 7.71–7.67 (m, 1H), 7.56–7.50 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 193.9, 193.1, 141.6, 135.1, 132.8, 131.4, 131.2, 130.0, 129.5, 129.1.

1-(3-Chlorophenyl)-2-phenylethane-1,2-dione (**2i**).[6b] Yellow oil (30.8 mg, 63% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.02–7.96 (m, 3H), 7.87–7.85 (m, 1H), 7.72–7.67 (m, 1H), 7.66–7.63 (m, 1H), 7.54 (tt, J = 7.6, 1.4 Hz, 2H), 7.50–7.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 193.6, 193.0, 135.4, 135.2, 134.8, 134.5, 132.7, 130.4, 130.0, 129.6, 129.1, 128.1.

1-(2-Chlorophenyl)-2-phenylethane-1,2-dione (**2j**).[6b] Yellow oil (31.8 mg, 65% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.05 (dd, J = 8.3, 1.1 Hz, 2H), 7.92 (dd, J = 8.1, 1.6 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.58–7.53 (m, 3H), 7.45 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 193.7, 192.1, 134.6, 134.6, 134.0, 133.9, 132.5, 132.1, 130.5, 130.2, 128.9, 127.4.

1-(4-Bromophenyl)-2-phenylethane-1,2-dione (**2k**).[6b] Yellow solid (40.5 mg, 70% yield); mp 86−87 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.00-7.97 (m, 2H), 7.88-7.85 (m, 2H), 7.72-7.67 (m, 3H), 7.56-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 193.9, 193.3, 135.1, 132.8, 132.5, 131.8, 131.3, 130.5, 130.0, 129.1.

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (**2l**).[4b] Yellow solid (33.2 mg, 65% yield); mp 137−138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.38 (d, J = 9.0 Hz, 2H), 8.19 (d, J = 9.0 Hz, 2H), 8.01 (dd, J = 8.4, 1.3 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 192.9, 192.1, 151.2, 137.3, 135.5, 132.4, 131.0, 130.1, 129.2, 124.1.

4-(2-Oxo-2-phenylacetyl)benzonitrile (**2m**).[4b] Yellow solid (29.6 mg, 63% yield); mp 98−99 °C;

^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.11 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 7.1 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 193.0, 192.4, 135.9, 135.4, 132.8, 132.5, 130.2, 130.0, 129.2, 117.9, 117.6.

1-Phenyl-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione (**2n**).[6b] Yellow solid (37.3 mg, 67% yield); mp 44−45 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.13 (d, J = 8.1 Hz, 2H), 8.00 (dd, J = 8.4, 1.3 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.59–7.52 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 193.5, 193.0, 135.9 (q, J = 32.7 Hz), 135.6, 135.3, 132.6, 130.2, 130.0, 129.2, 126.1 (q, J = 3.7 Hz), 123.3 (q, J = 271.3 Hz).

1-(4-Acetylphenyl)-2-phenylethane-1,2-dione (**2o**).[4a] Yellow solid (37.3 mg, 74% yield); mp 70−72 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.06 (s, 4H), 7.97 (d, J = 7.1 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 197.2, 193.8, 193.6, 141.3, 136.0, 135.2, 132.7, 130.1, 130.0, 129.1, 128.7, 27.0.

Ethyl 4-(2-oxo-2-phenylacetyl)benzoate (**2p**).[21] Yellow solid (40.1 mg, 71% yield); mp 75−76 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.18 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 193.8, 193.7, 165.4, 136.0, 135.7, 135.1, 132.7, 130.1, 130.0, 129.8, 129.1, 61.7, 14.3.

4-(2-(4-Methoxyphenyl)-2-oxoacetyl)benzonitrile (**2q**).[6b] Yellow oil (29.2 mg, 55% yield); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.11 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 9.0 Hz, 2H), 7.83 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 192.7, 191.5, 165.4, 136.2, 132.7, 132.6, 130.2, 125.5, 117.7, 117.7, 114.6, 55.7.

4-(2-Oxo-2-phenylacetyl)benzaldehyde (**2r**).[4b] Yellow solid (36.7 mg, 77% yield); mp 186−187 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 10.15 (s, 1H), 8.16 (d, J = 8.3 Hz, 2H), 8.05–7.99 (m, 4H), 7.74–7.66 (m, 1H), 7.56 (t, J = 7.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 193.6, 193.5, 191.3, 140.0, 137.0, 135.3, 132.6, 130.4, 130.0, 130.0, 129.2.

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (**2s**).[8] Yellow solid (48.1 mg, 89% yield); mp 99−101 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.96 (d, J = 8.9 Hz, 4H), 6.99 (d, J = 8.9 Hz, 4H), 3.90 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 193.5, 164.9, 132.4, 126.3, 114.3, 55.6.

1-(4-Methoxyphenyl)-2-(p-tolyl)ethane-1,2-dione (**2t**).[8] Yellow solid (41.7 mg, 82% yield); mp

98−99 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.96 (d, J = 8.9 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 194.6, 193.4, 164.9, 146.0, 132.4, 130.8, 130.0, 129.7, 126.2, 114.3, 55.6, 21.9.

1-(3,5-Dimethylphenyl)-2-phenylethane-1,2-dione (**2u**). Yellow oil (41.0 mg, 86% yield); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.99 (dd, J = 8.3, 1.2 Hz, 2H), 7.71−7.63 (m, 1H), 7.60 (s, 2H), 7.53 (t, J = 7.8 Hz, 2H), 7.31 (s, 1H), 2.38 (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 195.1, 194.9, 138.9, 136.7, 134.8, 133.1, 133.1, 129.9, 129.0, 127.6, 21.1; HRMS-ESI (m/z): calcd for $C_{16}H_{14}O_2Na$ [M + Na]$^+$ 261.0886, found 261.0882.

1-(3,4-Dimethylphenyl)-2-phenylethane-1,2-dione (**2v**).[22] Yellow oil (38.6 mg, 81% yield); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.99 (dd, J = 8.4, 1.3 Hz, 2H), 7.77 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 194.9, 194.7, 145.1, 137.6, 134.8, 133.2, 131.0, 130.8, 130.3, 129.9, 129.0, 127.8, 20.3, 19.7.

1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (**2w**).[4b] Yellow solid (37.5 mg, 72% yield); mp 101−102 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 9.33 (dd, J = 8.6, 0.8 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 8.10–8.01 (m, 2H), 7.99–7.88 (m, 2H), 7.77 (ddd, J = 8.6, 6.9, 1.4 Hz, 1H), 7.71–7.64 (m, 2H), 7.57–7.51 (m, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 197.2, 194.6, 136.0, 135.1, 134.8, 134.1, 133.4, 131.0, 130.0, 129.5, 129.1, 128.8, 128.6, 127.1, 126.0, 124.4.

1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione (**2x**).[4b] Yellow oil (30.3 mg, 70% yield); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.07 (dt, J = 8.5, 1.5 Hz, 2H), 7.86 (dd, J = 4.9, 1.1 Hz, 1H), 7.83 (dd, J = 3.9, 1.1 Hz, 1H), 7.71–7.64 (m, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.21 (dd, J = 4.9, 3.9 Hz, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 192.1, 185.6, 139.9, 136.9, 136.8, 134.9, 132.6, 130.3, 128.9, 128.8.

1,4-Diphenylbut-3-yne-1,2-dione (**2y**).[6b] Yellow oil (36.1 mg, 77% yield); ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.11 (dt, J = 8.5, 1.5 Hz, 2H), 7.70–7.67 (m, 3H), 7.58–7.51 (m, 3H), 7.45–7.42 (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) 188.5, 178.6, 134.9, 133.7, 131.7, 131.6, 130.5, 128.9, 128.8, 119.2, 99.2, 87.1.

(E)-1,4-Diphenylbut-3-ene-1,2-dione (**2z**).[23] Yellow oil (32.1 mg, 68% yield); ^{1}H NMR (CDCl$_3$,

400 MHz): *δ* (ppm) δ 8.07 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.74 (d, *J* = 16.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.63 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.58–7.51 (m, 2H), 7.48–7.44 (m, 3H), 7.17 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* (ppm) 193.3, 192.8, 148.9, 134.7, 134.0, 132.8, 131.6, 130.2, 129.1, 128.9, 128.9, 122.4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Copies of ^{1}H NMR and ^{13}C NMR spectra for all products (PDF).

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Notes

The authors declare no competing financial interest.

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