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Pyridine *N*-Oxide Mediated Oxidation of Diarylalkynes with Palladium on Carbon

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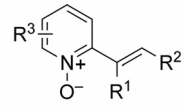
Pyridine *N*-oxide works as an effective oxidant of 1,2-diarylalkynes at 120 °C to form benzil derivatives under Pd/C-catalyzed solvent-free conditions, and Pd/C could be reused up to five times after simple filtration.

Introduction

Pyridine *N*-oxide derivatives, inexpensive and readily available reagents, are quite useful oxidants to incorporate oxygen atoms into organic frameworks because of their ease of handling and harmless reaction residue (only pyridine derivatives) after the oxidation step.[1–11] Meanwhile, direct construction methods for the preparation of the 1,2-diketone skeleton, which is valuable for the synthesis of pharmaceutical agents[12–14] and functional materials[15] as key intermediates, from alkynes has been eagerly studied as a very straightforward process.[16,17] Although the transformation of disubstituted alkynes into 2-alkenylated pyridine *N*-oxides[18] **1** by nickel(0)-catalyzed C–H functionalization at the 2-position of pyridine *N*-oxides due to the potential directing effect of the *N*-oxide moiety is known,[19] the pyridine *N*-oxide promoted synthesis of diketones from the corresponding alkynes has not been reported.

Most recently, we reported the efficient Pd/C-catalyzed synthesis of 1,2-diaryl-1,2-diketones (benzil derivatives) starting from diarylalkynes with the combination of dimethyl sulfoxide (DMSO) and molecular oxygen (O_2) as oxidants; the use of O_2 gas and DMSO is not generally accepted by process chemists because of the oxidative and explosive nature of O_2 and because of the malodorous nature of dimethyl sulfide. In this reaction, DMSO played the role of solvent and oxidant, and the zero-valent palladium [Pd^0] of Pd/C was oxidized by O_2 gas to divalent palladium [Pd^{II}] during the catalytic cycle.[20]

We now report the O_2/DMSO-free, pyridine *N*-oxide mediated oxidation of 1,2-diarylalkynes by using Pd/C to form benzil derivatives. This harmless and environmentally friendly oxidation system should garner the attention of organic and process chemists.



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Results and Discussion

Our initial attempt to replace DMSO, which is transformed into dimethyl sulfide having an unpleasant odor, with pyridine *N*-oxide readily led to the desirable benzil derivatives and established a novel oxidation method for diarylalkynes by comparing previous reports using pyridine *N*-oxides.[8,9,11]

In the presence of a catalytic amount of Pd/C and under atmospheric O_2 at 120 °C, pyridine *N*-oxide (5 equiv.) smoothly oxidized diphenylacetylene (**2a**, 0.5 mmol) to give the desired benzil (**3a**) in excellent yield (Table 1, Entry 2). The oxidation also proceeded under an atmosphere of argon (Ar) and in air without losing any reactivity (Table 1, Entries 3 and 4). Lower reactivities were observed when using 4-methoxy- or 4-nitro-substituted pyridine *N*-oxides (Table 1, Entries 5 and 6). On the other hand, the *tert*-alkylamine *N*-oxides and *tert*-butyl hydroperoxide (TBHP) were not effective for the oxidation of the diarylalkynes (Table 1, Entries 7–9).

We next examined the effect of other activated carbon supported transition metal catalysts. Au/C and Pt/C maintained moderate catalyst activities for the oxidation, but the reactions were not complete within 24 h (Table 2, Entries 2 and 3). In contrast, Ni, Ir, Ru, and Rh/C gave no reaction (Table 2, Entries 4–7). These results indicate that 10% Pd/C is the optimal catalyst for the oxidation.

Detailed optimization of the reaction conditions revealed that the oxidation was strongly influenced by the use of Pd/C and pyridine *N*-oxide and the reaction temperature

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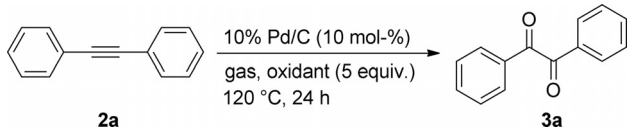
Table 1. Pyridine *N*-oxide mediated benzil (**2a**) synthesis from diphenylacetylene (**3a**) with Pd/C.[a]

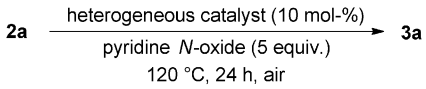


2a **3a**

Entry	Gas	Oxidant	Yield [%][b]
1	O_2	DMSO	92
2	O_2	pyridine *N*-oxide	92
3	Ar	pyridine *N*-oxide	88
4	air	pyridine *N*-oxide	94
5	air	4-methoxypyridine *N*-oxide	52
6	air	4-nitropyridine *N*-oxide	34
7	air	trimethylamine *N*-oxide	complex mixture
8	air	*N*-methylmorpholine *N*-oxide	0
9	air	TBHP	3

[a] 0.5 mmol of **2a** was used. [b] Isolated yield.

Table 2. Catalyst efficiencies of various carbon-supported catalysts.

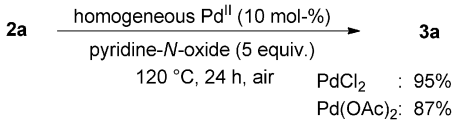


Entry	Catalyst	Ratio [%] [a] **3a**/**2a**
1	10% Pd/C	100:0
2	10% Au/C	80:20
3	10% Pt/C	37:63
4	10% Ni/C	no reaction
5	10% Ir/C	no reaction
6	10% Ru/C	no reaction
7	10% Rh/C	no reaction

[a] Ratio determined by ^{1}H NMR spectroscopy.

(Table 3). Pd/C is essential for the progress of the reaction (Table 3, Entry 1), and the use of 5 mol-% Pd/C led to an incomplete reaction even after 24 h (Table 3, Entry 2 vs. 3). On the other hand, the oxidation efficiency gradually dropped when the amount of pyridine *N*-oxide used was decreased (Table 3, Entries 4–6).[21] A reduction in the oxidation efficiency with a decrease in the reaction temperature was also observed (Table 3, compare Entries 3, 7, and 8).

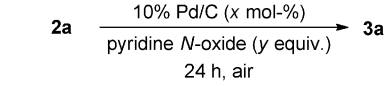
The pyridine *N*-oxide mediated oxidation also identically and effectively proceeded when using homogeneous Pd^{II} reagents [$PdCl_2$ and $Pd(OAc)_2$] instead of Pd/C [Equation (1)], which suggests that the catalytic cycle is probably mediated by a Pd^{II} species.



(1)

The proposed oxidation mechanism is illustrated in Figure 1. The Pd^0 species of Pd/C, which regularly consists of two Pd species, Pd^0 as a chief element and Pd^{II} as a minor or trace element, is initially oxidized to Pd^{II} by pyridine *N*-oxide. Following formation of vinyl Pd^{II} complex **B** via formation of Pd^{II}–π complex **A** and subsequent nucleophilic addition by pyridine *N*-oxide, the pyridine *N*-oxide-mediated oxidation of **B** gives keto alcohol intermediate **C** with concomitant elimination of pyridine. The continuous elimination of pyridine from **C** produces desired product **3a** and the Pd^{II} species.

Table 3. Optimization of reaction conditions.



Entry	*x*	*y*	*T* [°C]	Ratio[a] **3a**/**2a**
1	none	5	120	0:100
2	5	5	120	84:16
3	10	5	120	100:0
4	10	3	120	91:9
5	10	2	120	85:15
6	10	1	120	47:53
7	10	5	100	58:42
8	10	5	80	31:69

[a] Ratio was determined by ^{1}H NMR spectroscopy.

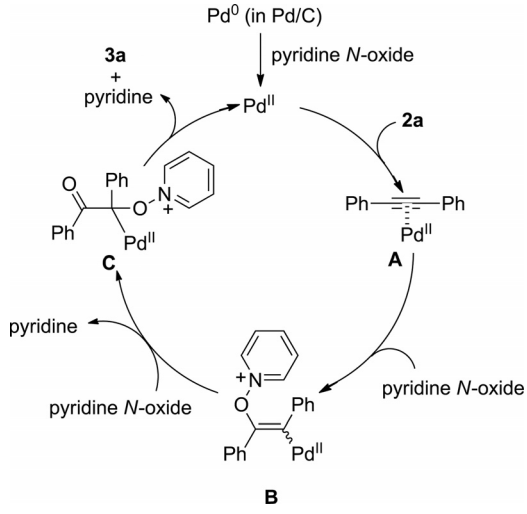


Figure 1. Proposed reaction mechanism.

Because the present reactions were carried out at 120 °C, which is a higher temperature than the melting point of pyridine *N*-oxide (65–66 °C), the pyridine *N*-oxide and pyridine[22] generated during the reaction play efficient roles as solvents. However, the reaction rate dependently decreases over time (Figure 2, ▲), indicating a time course for the oxidation of **2a** because of catalyst poisoning resulting from the generated pyridine.[23] These results indicate that the use of a somewhat excess amount of pyridine *N*-oxide should be required to accelerate the oxidation.[24]

We next investigated the reusability of 10% Pd/C with the aim of improving the cost performance and environmental compatibility of the present oxidation process. Although 10% Pd/C has retained its catalytic properties over

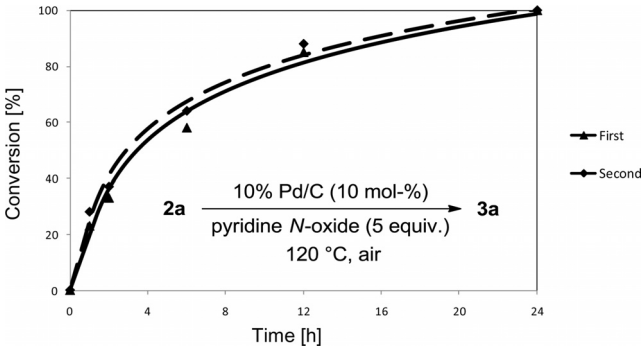


Figure 2. Time course of the oxidation of **2a**: (▲) first use of new Pd/C, (♦) second use of recovered Pd/C.

three reaction cycles, its oxidation activity gradually decreased with repeated use due to catalyst poisoning resulting from the residual amount of pyridine on the recovered Pd/C (Table 4, left column). This problem could be improved by washing the recovered Pd/C with 1 mM aqueous HCl after each oxidation to remove trace amounts of pyridine on the Pd metal, that is, the acid-washed Pd/C maintained a high catalytic activity, and the catalyst was used until at least the fifth run (Table 4, right column).[25] Furthermore, the reaction time course observed for the second use of the recovered Pd/C catalyst also indicated no loss of activity [Figure 2, dashed line (♦)].

Table 4. Reuse tests of Pd/C.[a]

Reuse number	Yield [%] Pd/C[b]	Pd/C washed with HCl[c]
1st	94	96
2nd	96	96
3rd	96	94
4th	89 (8)[d]	95
5th	84 (12)[d]	96

[a] Using 0.5 mmol of **2a** under the conditions of 5 equiv. of pyridine *N*-oxide and 10 mol-% of 10% Pd/C at 120 °C in air for 24 h. [b] The recovered Pd/C was rinsed with CH_2Cl_2. [c] The recovered Pd/C was washed with CH_2Cl_2, followed by 1 mM aqueous HCl. See the Experimental Section for details. [d] The yield of the recovered starting material is shown in parentheses.

The Pd leaching from Pd/C to the reaction mixture was next examined. After the Pd/C-catalyzed oxidation of **2a** using pyridine *N*-oxide at 120 °C for 24 h, the catalyst was removed by filtration, the filter was washed with CH_2Cl_2, and the filtrate was concentrated in vacuo. The residue was heated in the absence of Pd/C at 120 °C for another 24 h after further addition of **2a** and pyridine *N*-oxide to give desired **3a** in 90% yield and recovered **2a** in 5% yield over two steps, respectively (Figure 3). These results, including ICP-AES analysis (see Experimental Section), indicated that the leached Pd could be the actual catalyst of the oxidation reaction and that Pd/C likely acts only as a reservoir of the leached and soluble active Pd species.

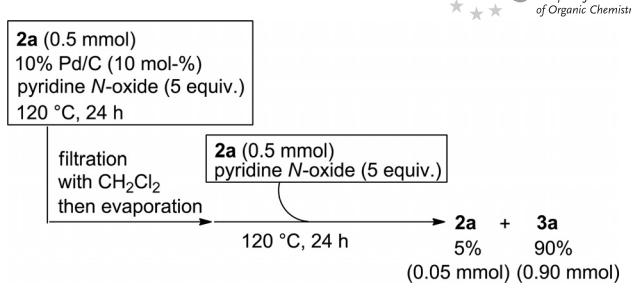


Figure 3. Pd leaching test.

The optimized reaction conditions were adapted for diarylalkynes **2b**–**r**[26,27] to construct benzil derivatives **3b**–**r** (Table 5). Substrates **2b**–**d** possessing an electron-withdrawing group (Cl, CN, or NO_2 group) on the aromatic ring were transformed into **3b**–**d** with high yields (Table 5, Entries 1–3). Electron-donating Me- or MeO-substituted substrates **2e**–**i** underwent efficient oxidation to afford corresponding benzils **3e**–**i** with high to excellent yields regardless of the steric or electronic effects at the substitution site (*ortho*,[28] *meta*, or *para* position; Table 5, Entries 4–8). Diphenylacetylenes **2j** and **2k** bearing a hydroxy and formyl group, respectively, also underwent the oxidation to afford desired benzils **3j** and **3k** without forming any oxidized side products (Table 5, Entries 9 and 10). The oxidation of diarylalkynes **2l**–**o** bearing substituents on both aromatic rings also successfully gave corresponding benzil derivatives **3l**–**o** (Table 5, Entries 11–14). Furthermore, diarylalkynes **2p**–**r** possessing a naphthyl, 2-pyridinyl, or 2-thienyl ring within the molecule tolerated the oxidation conditions without any significant deactivation of Pd/C to give **3p**–**r** in moderate to high yields (Table 5, Entries 15–17).

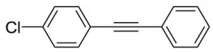
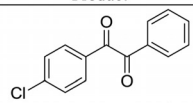
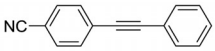
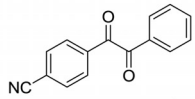
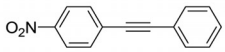
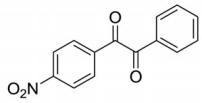
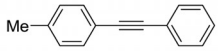
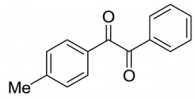
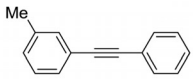
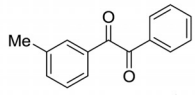
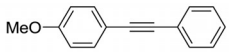
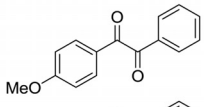
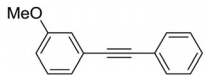
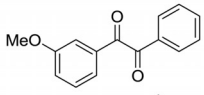
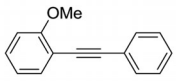
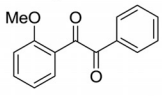
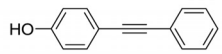
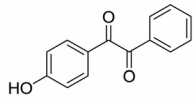
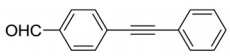
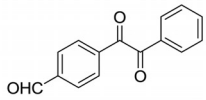
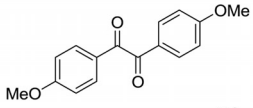
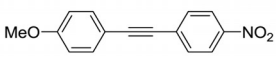
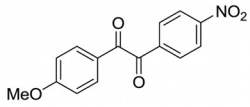
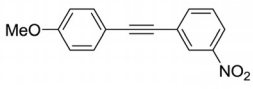
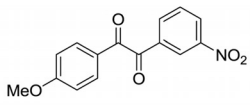
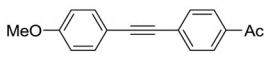
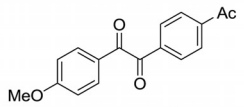
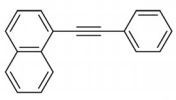
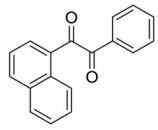
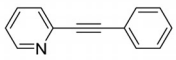
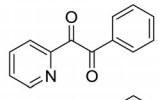
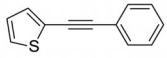
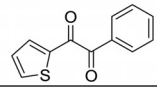
Conclusions

We have accomplished the novel Pd/C-catalyzed and pyridine *N*-oxide-promoted oxidation of diarylalkynes as a synthetic method to prepare benzil derivatives.[29] Pyridine *N*-oxide is inexpensive and nontoxic and may play triple roles: solvent, oxygen source for the transformation of alkynes into diketones, and oxidant of Pd^0 to Pd^{II}. Moreover, a high level of catalytic activity of the Pd species derived from Pd/C was maintained over five runs by simple acid wash after recovery. The presented reaction using Pd/C as a reservoir of the Pd species could provide an easy-to-handle, safe, and practical method for oxidation.

Experimental Section

General: 10% Pd/C, Au/C, Pt/C, Ni/C, Ir/C, Ru/C, and Rh/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). Flash column chromatography was performed using Silica Gel 60 N (Kanto Chemical Co., Inc., 63-210 μm spherical, neutral). ^1H and ^{13}C NMR spectra were recorded with a JEOL EX 400, AL 400, or ECA 500 spectrometer (^1H NMR; 400 MHz for **3b**, **3d**, **3e**, **3f**, **3i**, **3j**, **3k**, **3n**, **3o**, and **3r** or 500 MHz for **3a**, **3c**, **3g**, **3h**, **3l**, **3m**, **3p**, and **3q**; ^{13}C NMR; 100 MHz for **3f** and **3n**). Chemical shifts are intern-

Table 5. Scope of substrates.[a]

Entry	Substrate		Product		Yield [%]
1		**2b**		**3b**	84
2		**2c**		**3c**	82
3		**2d**		**3d**	78
4		**2e**		**3e**	93
5		**2f**		**3f**	81
6		**2g**		**3g**	85
7		**2h**		**3h**	84
8		**2i**		**3i**	80
9		**2j**		**3j**	82
10		**2k**		**3k**	78
11		**2l**		**3l**	76
12		**2m**		**3m**	99
13		**2n**		**3n**	97
14		**2o**		**3o**	76
15		**2p**		**3p**	56
16		**2q**		**3q**	94
17		**2r**		**3r**	87

[a] Reactions were carried out under the conditions indicated in Table 3, Entry 3.

ally referenced (δ =7.26 ppm for $CDCl_3$ for ^1H NMR and 77.0 ppm for $CDCl_3$ for ^{13}C NMR). EI mass spectra were taken with a JEOL JMS-SX102A instrument.

Typical Procedure for the Synthesis of Benzil (3a) from 1,2-Diphenylacetylene (2a): After the reaction mixture was passed through a filter paper, crude Pd/C including pyridine was washed with CH_2Cl_2 (25 mL). Subsequently, the residual pyridine on Pd/C was washed with 1 mM aqueous HCl (2.5 mL). A mixture of 1,2-diphenylacetylene (**2a**; 89.1 mg, 500 μmol), 10% Pd/C (53.2 mg, 50.0 μmol), and pyridine *N*-oxide (238 mg, 2.50 mmol) in a 15-mL test tube was stirred at 120 °C with an air balloon by using a Chemistation personal organic synthesizer (EYELA, Tokyo). After 24 h, the mixture was diluted with CH_2Cl_2 (20 mL) and water (15 mL) and then passed through a membrane filter (Millipore, Millex-LH, 0.45 μm) to remove Pd/C. The aqueous layer was separated, and the CH_2Cl_2 layer was washed successively with water (2 × 15 mL) and brine (20 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Pure benzil (**3a**) could be obtained by simple extraction (94% yield, Figure 4).

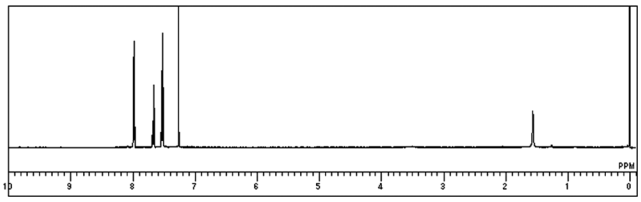


Figure 4. ^1H NMR spectrum of **3a** after the simple extraction.

Typical Procedure for Reuse of Pd/C: After the reaction mixture was passed through a filter paper, crude Pd/C including pyridine was washed with CH_2Cl_2 (25 mL). Subsequently, the residual pyridine on Pd/C was washed with 1 mM aqueous HCl (5 × 2.5 mL) and MeOH (5 × 2.5 mL), and the resulting Pd/C was dried in vacuo.

General Procedure of Pd Leaching Test: After stirring a mixture of diphenylacetylene (**2a**; 89.1 mg, 500 μmol), pyridine *N*-oxide (238 mg, 2.50 mmol), and 10% Pd/C (53.2 mg, 50.0 μmol) for 24 h at 120 °C, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and then passed through a membrane filter (Millipore, Millex-LH, 0.45 μm). The filtrate was concentrated in vacuo. Diphenylacetylene (**2a**; 89.1 mg, 500 μmol) and pyridine *N*-oxide (238 mg, 2.50 mmol) were added again to the residue, and the reaction mixture was stirred at 120 °C in air by using a Chemistation personal organic synthesizer (EYELA, Tokyo). After 24 h, the mixture was diluted with CH_2Cl_2 (40 mL) and washed successively with water (3 × 20 mL) and brine (20 mL). The CH_2Cl_2 layer was dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo to give a mixture of 5% of **2a** (8.1 mg, 0.05 mmol) and 90% of **3a** (190.4 mg, 0.9 mmol). The yields were determined by ^1H NMR spectroscopy.

ICP-AES of Pd Leaching: After stirring a mixture of diphenylacetylene (**2a**; 891 mg, 5.0 mmol), pyridine *N*-oxide (2.38 g, 25.0 mmol), and 10% Pd/C (532 mg, 500 μmol) for 24 h at 120 °C, the mixture was diluted with CH_2Cl_2 (30 mL) and then passed through a glass filter with Celite. Furthermore, the filtrate was passed through a membrane filter (Millipore, Millex-LH, 0.45 μm), a second membrane filter (Millipore, Millex-LH, 0.20 μm), and then concentrated in vacuo. After the filtrate was dissolved in CH_2Cl_2 (30 mL) and extracted with water (30 mL), the aqueous layer and the CH_2Cl_2 layer were diluted with water or CH_2Cl_2, respectively, in a 50-mL volumetric flask. <10 ppm of Pd-leaching in the aqueous layer and 120 ppm of Pd leaching in the CH_2Cl_2 layer were observed by ICP-AES.

General Procedure for Synthesis of Benzils: A mixture of diarylalkyne (500 μmol), 10% Pd/C (53.2 mg, 50.0 μmol), and pyridine *N*-oxide (238 mg, 2.50 mmol) in a 15-mL test tube was stirred at 120 °C with an air balloon by using a Chemistation personal organic synthesizer (EYELA, Tokyo). After 24 h, the mixture was diluted with CH_2Cl_2 (20 mL) and water (15 mL) and then passed through a membrane filter (Millipore, Millex-LH, 0.45 μm). The aqueous as separated and the CH_2Cl_2 layer were washed successively with water (2 × 15 mL) and brine (20 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Pure products of **3a**, **3e**, **3m**, **3n**, **3q**, and **3r** were obtained by simple extraction. The yields of **3b**, **3c**, **3d**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3o**, and **3p** were determined after silica gel column chromatography (*n*-hexane/EtOAc), because these products contained a slight amount of side products.

Benzil (1,2-Diphenylethane-1,2-dione, 3a): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 6.8, 7.3 Hz, 4 H), 7.64 (t, *J* = 6.8 Hz, 2 H), 7.89 (t, *J* = 7.3 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.9, 129.8, 132.9, 134.8, 194.5 ppm. The NMR spectrum of **3a** was identical to that reported.[16t]

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (3b): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.45–7.51 (m, 4 H), 7.64 (m, *J* = 7.4 Hz, 1 H), 7.89–7.96 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.0, 129.4, 129.9, 131.1, 131.3, 132.7, 135.0, 141.5, 193.0, 193.8 ppm. The NMR spectrum of **3b** was identical to that reported.[16t]

1-(4-Cyanophenyl)-2-phenylethane-1,2-dione (3c): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 8.0 Hz, 2 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 7.96 (d, *J* = 8.6 Hz, 2 H), 8.08 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.4, 117.8, 129.1, 129.9, 130.1, 132.3, 132.6, 135.2, 135.7, 192.2, 192.8 ppm. The NMR spectrum of **3c** was identical to that reported.[20]

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (3d): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 7.2, 7.7 Hz, 2 H), 7.71 (t, *J* = 7.2 Hz, 1 H), 7.99 (d, *J* = 7.7 Hz, 2 H), 8.17 (d, *J* = 8.8 Hz, 2 H), 8.34 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.1, 129.2, 130.0, 130.9, 132.4, 135.4, 137.3, 151.1, 192.0, 192.8 ppm. The NMR spectrum of **3d** was identical to that reported.[16t]

1-Phenyl-2-*p*-tolylethane-1,2-dione (3e): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.48 (dd, *J* = 7.2, 7.3 Hz, 2 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.86 (d, *J* = 8.3 Hz, 2 H), 7.96 (d, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 21.8, 128.9, 129.6, 129.7, 129.9, 130.4, 133.0, 134.7, 146.1, 194.2, 194.7 ppm. The NMR spectrum of **3e** was identical to that reported.[16t]

1-Phenyl-2-*m*-tolylethane-1,2-dione (3f): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 7.38 (dd, *J* = 7.2, 7.7 Hz, 1 H), 7.45–7.52 (m, 3 H), 7.65 (t, *J* = 7.8 Hz, 1 H), 7.75–7.78 (m, 2 H), 7.97 (d, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 127.2, 128.9, 128.9, 129.8, 130.1, 132.9, 133.0, 134.8, 135.7, 138.9, 194.7, 194.8 ppm. MS (EI): *m*/*z* = 224 (20) $[M]^+$, 51 (10), 65 (10), 91 (30), 105 (40), 119 (100), 224 (20). HRMS (EI): calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837; found 224.0841.

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (3g): ^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 7.50 (dd, *J* = 7.9, 8.0 Hz, 2 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.94–7.98

(m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 114.3, 126.1, 128.9, 129.9, 132.3, 133.2, 134.7, 165.0, 193.1, 194.7 ppm. The NMR spectrum of **3g** was identical to that reported.[16t]

1-(3-Methoxyphenyl)-2-phenylethane-1,2-dione (3h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 7.21 (dd, J = 1.6, 8.2 Hz, 1 H), 7.40 (t, J = 8.2 Hz, 1 H), 7.47–7.55 (m, 4 H), 7.66 (t, J = 7.2 Hz, 1 H), 7.97 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 112.8, 121.8, 123.1, 129.0, 129.8, 130.0, 132.9, 134.2, 134.8, 160.0, 194.4, 194.4 ppm. The NMR spectrum of **3h** was identical to that reported.[20]

1-(2-Methoxyphenyl)-2-phenylethane-1,2-dione (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (s, 3 H), 6.93 (d, J = 8.0 Hz, 1 H), 7.13 (t, J = 8.0 Hz, 1 H), 7.49 (dd, J = 1.2, 8.1 Hz, 2 H), 7.58–7.63 (m, 2 H), 7.92 (dd, J = 8.0, 8.1 Hz, 2 H), 8.03 (dd, J = 1.2, 8.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 112.4, 121.6, 123.9, 128.7, 129.3, 130.6, 133.0, 133.7, 136.4, 160.4, 193.4, 194.6 ppm. The NMR spectrum of **3i** was identical to that reported.[16s]

1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione (3j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (br. s, 1 H), 6.90 (d, J = 8.4 Hz, 2 H), 7.50 (dd, J = 7.3, 7.7 Hz, 2 H), 7.65 (t, J = 7.3 Hz, 1 H), 7.87 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.1, 125.9, 129.0, 130.0, 132.8, 133.0, 135.0, 162.0, 193.4, 195.2 ppm. The NMR spectrum of **3j** was identical to that reported.[16s]

1-(4-Formylphenyl)-2-phenylethane-1,2-dione (3k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, J = 7.7, 8.2 Hz, 2 H), 7.70 (t, J = 7.7 Hz, 1 H), 7.97–8.03 (m, 4 H), 8.14 (d, J = 8.7 Hz, 2 H), 10.1 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.0, 129.9, 129.9, 130.3, 132.4, 135.2, 136.8, 139.9, 191.3, 193.4, 193.5 ppm. The NMR spectrum of **3k** was identical to that reported.[16u]

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (3l): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 6 H), 6.97 (d, J = 9.0 Hz, 4 H), 7.96 (d, J = 9.0 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 114.2, 126.2, 132.3, 164.8, 193.4 ppm. The NMR spectrum of **3l** was identical to that reported.[20]

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethane-1,2-dione (3m): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.00 (d, J = 8.9 Hz, 2 H), 7.97 (d, J = 8.9 Hz, 2 H), 8.16 (d, J = 9.0 Hz, 2 H), 8.34 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 114.6, 124.0, 125.4, 130.9, 132.6, 137.6, 151.1, 165.5, 191.3, 192.3 ppm. The ^{1}H NMR spectrum of **3m** was identical to that reported.[30]

1-(4-Methoxyphenyl)-2-(3-nitrophenyl)ethane-1,2-dione (3n): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 6.97 (d, J = 9.0 Hz, 2 H), 7.70 (dd, J = 7.8, 8.2 Hz, 1 H), 7.93 (d, J = 9.0 Hz, 2 H), 8.27 (d, J = 7.8 Hz, 1 H), 8.45 (d, J = 8.2 Hz, 1 H), 8.76 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 114.5, 124.4, 125.2, 128.5, 130.2, 132.5, 134.4, 135.2, 148.4, 165.4, 191.0, 191.6 ppm. MS (EI): m/z = 285 (5) $[M]^+$, 44 (15), 50 (10), 64 (5), 77 (15), 92 (10), 107 (5), 135 (100), 285 (5). HRMS (EI): calcd. for $C_{15}H_{11}NO_5$ $[M]^+$ 285.0637; found 285.0631.

1-(4-Acetylphenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (3o): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 3 H), 3.90 (s, 3 H), 6.99 (d, J = 9.0 Hz, 2 H), 7.95 (d, J = 9.0 Hz, 2 H), 8.06 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.9, 55.7, 114.5, 125.8, 128.6, 130.1, 132.4, 136.2, 141.2, 165.2, 192.2, 193.8, 197.2 ppm. The NMR spectrum of **3o** was identical to that reported.[20]

1-(1-Naphthyl)-2-phenylethane-1,2-dione (3p): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.53 (m, 3 H), 7.61–7.67 (m, 2 H), 7.73–7.77 (m, 1 H), 7.92 (t, J = 8.6 Hz, 2 H), 8.04 (dd, J = 1.5, 8.6 Hz, 2 H), 8.11 (d, J = 8.0 Hz, 1 H), 9.33 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.4, 125.9, 127.1, 128.6, 128.8, 129.0, 129.4, 129.9, 130.9, 133.3, 134.1, 134.7, 135.1, 135.9, 194.6, 197.1 ppm. The NMR spectrum of **3p** was identical to that reported.[16t]

1-Phenyl-2-(2-pyridinyl)ethane-1,2-dione (3q): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.53 (m, 3 H), 7.64 (t, J = 7.5 Hz, 1 H), 7.93–7.95 (m, 3 H), 8.20 (d, J = 6.9 Hz, 1 H), 8.66 (d, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 123.1, 128.1, 128.9, 129.5, 133.1, 134.6, 137.2, 149.8, 151.7, 195.1, 196.1 ppm. The NMR spectrum of **3q** was identical to that reported.[31]

1-Phenyl-2-(2-thienyl)ethane-1,2-dione (3r): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, J = 3.8, 4.8 Hz, 1 H), 7.51 (dd, J = 7.3, 7.7 Hz, 2 H), 7.66 (d, J = 7.7 Hz, 1 H); 7.80–7.85 (m, 2 H), 8.04 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 128.8, 128.9, 130.2, 132.5, 134.8, 136.7, 136.9, 139.8, 185.6, 192.0 ppm. The NMR spectrum of **3o** was identical to that reported.[32]

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR spectra of the benzil products.

Acknowledgments

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