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Pd/Cu-catalyzed oxidation of alkynes into 1,2-diketones using DMSO as the oxidant

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ABSTRACT

A facile and practical method for the palladium/copper-catalyzed transformation of internal alkynes into 1,2-diketones has been described, affording the desired products in moderate to excellent yields. The mechanistic studies were also preliminarily pursued using diphenyl sulfoxide as the oxidant, and the diphenyl sulfide was isolated as the reduced product.

1. Introduction

1,2-Dicarbonyl derivatives are very useful building blocks in the construction of a variety of organic intermediates,[1] especially in the synthesis of biologically active heterocyclic compounds,[2] such as imidazoles, quinoxalines, and indolone-*N*-oxide.[3] Some of these compounds show good antitumor activity or/and can be used as selective cyanide anion indicators or photoinitiators.[4]

Over the past decade, lots of synthetic protocols for the preparation of 1,2-diaryldiketones have been reported.[5] Since the internal alkynes as the starting material could be easily accessible via Sonogashira coupling,[6] the direct oxidation of internal alkynes into 1,2-dicarbonyl derivatives appears to be one of the most straightforward methods. Great progress on this type of transformation has been made during the last few years. For example, Yusubov and Chi introduced the $PdCl_2$ catalyzed oxidation of internal alkynes in DMSO, while the scope of this reaction was quite narrow and only two examples (1-phenylprop-1-yne and 1-phenylpent-1-yne) were involved.[5m] Subsequently, Wan's group reported palladium-catalyzed synthesis of 1,2-diketones via the oxidation of internal alkynes using oxygen as the oxidant.[5d] And then, Li and co-workers described a Au/Ag-catalyzed protocol, which could undergo in mild conditions using diphenyl sulfoxide as oxidant, which enlightened us on the essence of sulfoxide in these reactions.[5b] Inspired by these promising reports, our work was focused on the direct palladium/copper-catalyzed oxidation of internal alkynes into 1,2-dicarbonyl derivatives in DMSO. In this transformation, the DMSO would also behave as an oxidant.

2. Results and discussion

In our initial study, we launched our efforts to transform 1,2-diphenylethyne (**1a**) to the benzil (**2a**), and the product (**2a**) could be obtained in a yield of 17% in DMSO after 20 h using $Pd(OAc)_2$ as the catalyst in the absence of the cocatalyst (Table 1, entry 1). Gratifyingly, with the addition of the cocatalyst (e.g., $FeCl_3$ and $CuBr_2$), the yield of the desired product could increase dramatically, albeit the reaction did not occur at all with AgOAc as the cocatalyst (Table 1, entries 2–4). Especially, with $CuBr_2$ as the cocatalyst, the benzil (**2a**) could be afforded in a yield of 99% (Table 1, entry 4), while the desired product was not observed at all in the absence of the palladium catalyst (Table 1, entry 5). These results indicated that both of the palladium and copper species played a critical role on the catalytic efficiency (Table 1, entries 1–5). However, when the reaction time or temperature decreased to 12 h and 80 °C, the reaction only gave the benzil in yields of 78% and 72%, respectively (Table 1, entries 6 and 7). This oxidative reaction could also be performed in DMSO under the nitrogen atmosphere,

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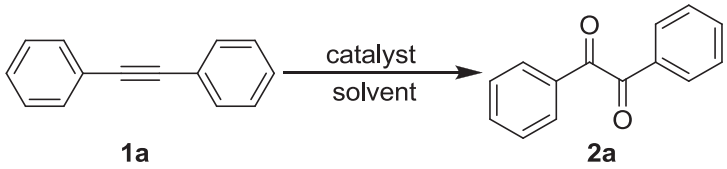
Table 1
Optimization of reaction conditions[a]



Entry	Catalyst	Solvent	*t* (h)	*T* (°C)	Yield[b] (%)
1	$Pd(OAc)_2$	DMSO	20	120	17
2	$Pd(OAc)_2$/AgOAc	DMSO	20	120	0
3	$Pd(OAc)_2/FeCl_3$	DMSO	20	120	93
4	**$Pd(OAc)_2/CuBr_2$**	**DMSO**	**20**	**120**	**99**
5	$CuBr_2$	DMSO	20	120	0
6	$Pd(OAc)_2/CuBr_2$	DMSO	12	120	78
7	$Pd(OAc)_2/CuBr_2$	DMSO	84	80	72
8[c]	$Pd(OAc)_2/CuBr_2$	DMSO	20	120	95
9	$PdCl_2/CuBr_2$	DMSO	20	120	90
10	$Pd(PPh_3)_2Cl_2/CuBr_2$	DMSO	20	120	90
11	$Pd(dba)_2/CuBr_2$	DMSO	20	120	70
12	$Pd(OAc)_2/CuBr_2$	Dioxane	20	100	0
13	$Pd(OAc)_2/CuBr_2$	DMF	20	120	0
14	$Pd(OAc)_2/CuBr_2$	DMA	20	120	0

Bold values in entry 4 represents the optimal conditions.
[a] Reaction conditions: 0.5 mmol **1a** and 10 mol % of catalyst in 2 mL solvent in air.
[b] Isolated yield.
[c] Under the nitrogen atmosphere.

generating the benzil in 95% yield (Table 1, entry 8). Then, other palladium catalysts were evaluated and the benzil was formed in moderate to good yields (Table 1, entries 9–11). Some other solvents such as dioxane, DMF and DMA were also examined, and no product was detected (Table 1, entries 12–14).

With the optimized reaction conditions in hand, the scope of the oxidation of alkynes was explored (Tables 2 and 3). Generally, the substituent and electronic effects have no significant influence on this transformation, and the reaction could tolerate a broad scope of substituents such as MeO, CHO, NO_2, CN, $SiMe_3$, and F, affording the desired products in moderate to good yields (Table 2). It should be noted that the oxidation of some heterocyclic and fused aromatic ring alkynes could also afford the corresponding 1,2-dicarbonyl derivatives in good yields (Table 3, entries 1–3). However, when one of the two substituents is an alkyl group (**1r**), the oxidation only gave the product in a low yield of 33% (Table 3, entry 4).

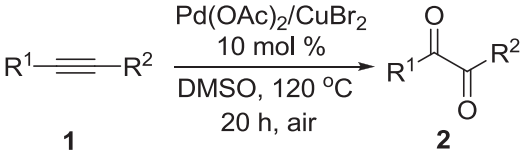
This oxidative reaction could generate the benzil in 95% yield under the nitrogen atmosphere, which suggested that the solvent (DMSO) may serve as an oxidant (Table 1, entry 8). To clarify the mechanism of the oxidation of internal alkynes, mechanistic studies were also pursued (Scheme 1). According to this hypothesis, the reductive product of DMSO would be dimethyl sulfide. But unfortunately, dimethyl sulfide is quite volatile, which is difficult to be detected. So we took diphenyl sulfoxide (**3**) instead of DMSO, and diphenyl sulfide (**4**) as the reductive product could be detected and isolated easily. However, diphenyl sulfoxide is a solid and cannot be used as the solvent, and thus the reaction was performed

Table 2
Oxidation of alkynes[a]

Entry	R^1	R^2	Substrate	Product/yield[b] (%)
1	H	Me	**1b**	**2b**, 83
2	H	*tert*-Butyl	**1c**	**2c**, 78
3	H	MeO	**1d**	**2d**, 70
4	H	n-$C_5H_{11}O$	**1e**	**2e**, 85
5	H	NO_2	**1f**	**2f**, 65
6	H	CN	**1g**	**2g**, 75
7	H	CHO	**1h**	**2h**, 88
8	H	F	**1i**	**2i**, 80
9	H	$SiMe_3$	**1j**	**2j**, 90
10	Et	Me	**1k**	**2k**, 91
11	Et	MeO	**1l**	**2l**, 87
12	n-C_5H_{11}	MeO	**1m**	**2m**, 71
13	*tert*-Butyl	CN	**1n**	**2n**, 75

[a] Reaction conditions: 0.5 mmol alkyne, 10 mol % of $Pd(OAc)_2$ and 10 mol % of $CuBr_2$ in 2 mL DMSO at 120 °C in air for 20 h.
[b] Isolated yield.

Table 3
Oxidation of alkynes[a]



Entry	R^1	R^2	Substrate	Product/yield[b] (%)
1	Ph	3-Pyridyl	**1o**	**2o**, 72
2	Ph	1-Naphthyl	**1p**	**2p**, 87
3	*p*-FC_6H_4	1-Naphthyl	**1q**	**2q**, 71
4	Ph	Me	**1r**	**2r**, 33

[a] Reaction conditions: 0.5 mmol alkyne, 10 mol% of $Pd(OAc)_2$ and 10 mol% of $CuBr_2$ in 2 mL DMSO at 120 °C in air for 20 h.
[b] Isolated yield.

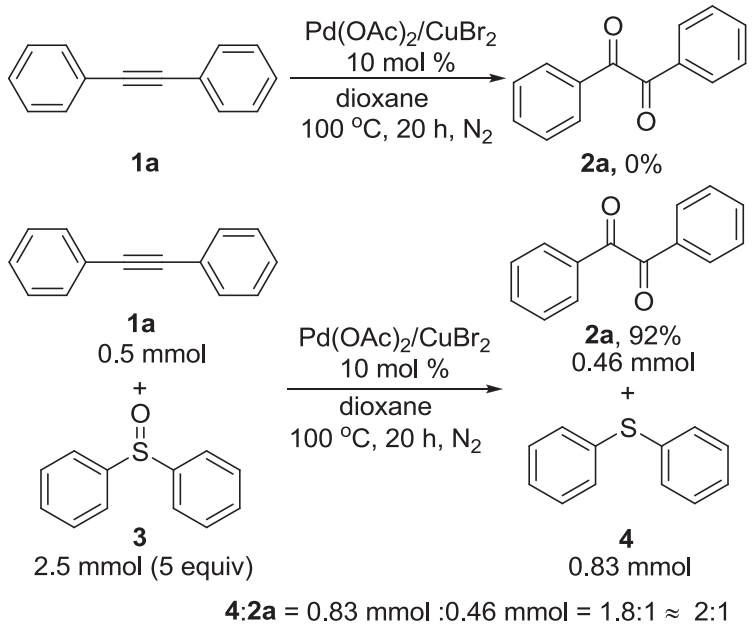
3. Conclusion

In summary, we have developed a new and facile pathway to 1,2-diketones via the Pd/Cu-catalyzed oxidation of internal alkynes in DMSO under ligand- and additive-free conditions. This catalytic system showed high efficiency and good functional group tolerance. The preliminary mechanistic studies demonstrated that the solvent of DMSO could also behave as the oxidant. Further application of this synthetic methodology is currently underway.

4. Experimental

4.1. General methods

All commercial materials were used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on



Scheme 1. Mechanistic studies of oxidation of alkynes.

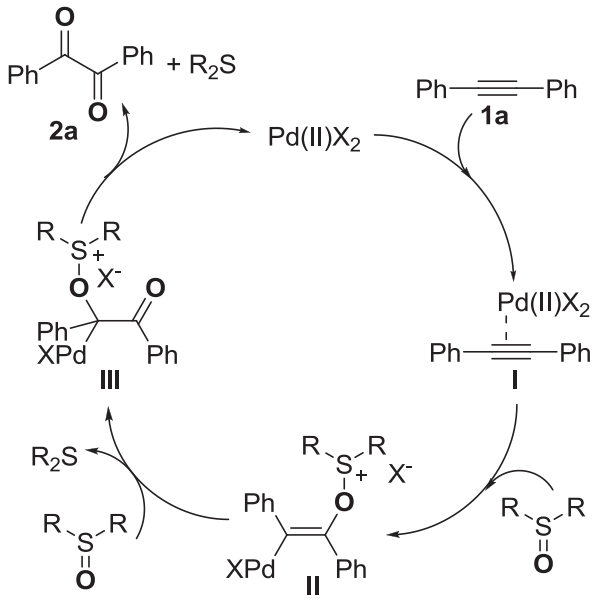
in dioxane with the addition of 5 equiv sulfoxide as the oxidant. When the reaction was carried out in dioxane under the nitrogen atmosphere in the absence of diphenyl sulfoxide, no product was observed. But with the addition of 5 equiv diphenyl sulfoxide (**3**), the isolated yield of the product (**2a**) was up to 92% (0.46 mmol), and 0.83 mmol diphenyl sulfide (**4**) was also obtained. To our delight, the mole ratio of **4**/**2a** (1.8:1) is approximately equal to 2:1, which suggests that two molecules of DMSO could oxidize one molecule of alkyne and the two oxygen atoms in the benzil (**2a**) should come from the sulfoxide.

On the basis of the above results, a possible catalytic cycle for palladium-catalyzed oxidation of alkynes is outlined in Scheme 2, which includes: (i) the coordination of Pd(II) to the triple bond of the internal alkyne (**1a**), resulting in the formation of the intermediate **I**; (ii) the attack of R_2SO to intermediate **I** to form the vinyl palladium species **II**; (iii) nucleophilic addition of another molecule of R_2SO to the intermediate **II** accompanied by the leaving of the R_2S, affording the palladium species **III**; (iv) β-elimination of the intermediate **III**, leading to the desired 1,2-dicarbonyl compound (**2a**) and another molecule of R_2S as well as the active palladium(II) species.

a Bruker DPX-400 spectrometer. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. GC analysis was performed on Agilent 4890D gas chromatograph. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High-resolution mass spectra were measured on a MALDI-FTMS. IR spectra were recorded on a Bruker Alpha FT-IR Spectrometer. Ethyl acetate and petroleum ether were used for column chromatography without purification. Other solvents were purified according to the standard methods. $Pd(OAc)_2$, $CuBr_2$, and diphenyl sulfoxide were purchased from Alfa-Aesar Chemicals and used without further purification. The other chemicals were from commercial sources and used as-received unless otherwise noted.

4.2. The general procedure for preparation of internal alkynes

Alkynes of **1b**, **1k**, **1l**, and **1r** were purchased from Alfa-Aesar Chemicals and used without further purification, other alkynes were prepared according to the reported procedure.[7] The known compounds (**1a**, **1c**–**1k**, **1o**, **1p**, **1r**) were characterized by comparing their mp, ^1H, ^{13}C NMR to those previously reported.



Scheme 2. Proposed mechanism for oxidation of alkynes.

Characterization data for the unknown internal alkynes:

*4.2.1. 1-Methoxy-4-[2-(4-pentyloxyphenyl)ethynyl]benzene (**1m**).* White solid; mp: 54–55 °C; yield: 80%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.42 (m, 4H), 6.87–6.84 (m, 4H), 3.96 (t, 2H, J=6.6 Hz), 3.81 (s, 3H), 1.79 (t, 2H, J=7.2 Hz), 1.44–1.37 (m, 4H), 0.93 (t, 3H, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.23, 158.87, 132.73, 132.71, 115.66, 115.30, 114.37, 113.82, 87.93, 87.70, 67.92, 55.16, 28.78, 28.05, 22.33, 13.89; IR (KBr, cm^{-1}): ν 2967, 2932, 2928, 2859, 2210; HRMS-ESI (m/z): [M+H]$^+$ calcd for $C_{20}H_{23}O_2$ 295.1698; found 295.1694.

*4.2.2. 4-[2-(4-tert-Butylphenyl)ethynyl]benzonitrile (**1n**).* White solid; mp: 101–102 °C; yield: 85%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (q, 4H, J=7.7 Hz), 7.47 (d, 2H, J=8.5 Hz), 7.41–7.38 (m, 2H), 1.33 (t, 9H, J=5.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.46, 131.89, 131.89, 131.43, 128.39, 125.41, 119.05, 118.47, 111.11, 93.98, 87.08, 34.78, 31.01; IR (KBr, cm^{-1}): ν 3078, 3039, 2957, 2861, 2228, 2215; HRMS-ESI (m/z): [M+H]$^+$ calcd for $C_{19}H_{18}N$ 260.1439; found 260.1436.

*4.2.3. 1-[2-(4-Fluorophenyl)ethynyl]naphthalene (**1q**).* Yellow oil; yield: 70%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, 1H, J=8.2 Hz), 7.85 (t, 2H, J=8.5 Hz), 7.73 (d, 1H, J=7.0 Hz), 7.61 (m, 3H), 7.54 (m, 1H), 7.46 (t, 1H, J=7.8 Hz), 7.08 (t, 2H, J=8.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.57 (d, J=248.1 Hz), 133.53 (d, J=8.3 Hz), 133.19, 130.35, 128.83, 128.34, 126.79, 126.45, 126.11, 125.27, 120.69, 119.48 (d, J=3.5 Hz), 115.73 (d, J=21.9 Hz), 93.17, 87.19; IR (KBr, cm^{-1}): ν 2965, 2920, 2849, 2211; HRMS-ESI (m/z): [M+H]$^+$ calcd for $C_{18}H_{12}F$ 247.0923; found 247.0928.

4.3. General procedures for oxidation of alkynes

Alkyne (0.5 mmol), $Pd(OAc)_2$ (10 mol %), and $CuBr_2$ (10 mol %) were added to DMSO (2.0 mL) in an oven-dried flask under air. The reaction mixture was heated in an oil bath at designated temperature for 20 h. After the reaction was complete, 10 mL water was added and the mixture was extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate) to afford the pure products.

*4.3.1. 1,2-Diphenylethane-1,2-dione (**2a**).*[5d] Yellow solid, mp 94–95 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, 4H, J=7.6 Hz), 7.67 (t, 2H, J=7.4 Hz), 7.52 (t, 4H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.61, 134.94, 132.94, 129.92, 129.04; MS ($C_{14}H_{10}O_2$): 210.0 (M$^+$).

*4.3.2. 1-Phenyl-2-(p-tolyl)ethane-1,2-dione (**2b**).*[5g] Yellow solid, mp 96 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (m, 2H), 7.86 (d, 2H, J=8.2 Hz), 7.64 (t, 1H, J=7.4 Hz), 7.49 (t, 2H, J=7.7 Hz), 7.30 (d, 2H, J=8.1 Hz), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.73, 194.27, 146.18, 134.74, 133.06, 129.98, 129.82, 129.80, 129.71, 128.94, 21.88; MS ($C_{15}H_{12}O_2Na$): 247.2 (M+Na$^+$).

*4.3.3. 1-(4-tert-Butylphenyl)-2-phenylethane-1,2-dione (**2c**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (m, 2H), 7.91 (d, 2H, J=8.5 Hz), 7.63 (m, 1H), 7.54–7.48 (m, 4H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.76, 194.28, 159.01, 134.74, 133.07, 130.43, 129.87, 128.94, 126.02, 35.37, 30.94; IR (KBr, cm^{-1}): ν 3077, 3039, 2955, 2928, 2860, 1665; HRMS-ESI (m/z): [M+Na]$^+$ calcd for $C_{18}H_{18}O_2Na$ 289.1204; found 289.1209.

*4.3.4. 1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (**2d**).*[5d] Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (t, 4H, J=8.7 Hz), 7.63 (t, 1H, J=7.4 Hz), 7.49 (t, 2H, J=7.7 Hz), 6.97 (d, 2H, J=8.8 Hz), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.82, 193.12, 164.967 134.67, 133.17, 132.34, 129.85, 128.91, 126.06, 114.34, 55.61; MS ($C_{15}H_{12}O_3Na$): 263.1 (M+Na$^+$).

*4.3.5. 1-(4-Pentyloxyphenyl)-2-phenylethane-1,2-dione (**2e**).*[8a] Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98–7.92 (m, 4H), 7.66–7.62 (m, 1H), 7.49 (t, 2H, J=7.7 Hz), 6.97–6.94 (m, 2H), 4.03 (t, 2H, J=6.5 Hz), 1.84–1.77 (m, 2H), 1.47–1.35 (m, 4H), 0.92 (t, 3H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.89, 193.15, 164.64, 134.65, 133.19, 132.34, 129.85, 128.90, 125.79, 114.77, 68.46, 28.64, 28.02, 22.35, 13.94; MS ($C_{19}H_{20}O_3Na$): 319.2 (M+Na$^+$).

*4.3.6. 1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (**2f**).*[8b] Yellow solid, mp 141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37–8.34 (m, 2H), 8.18–8.16 (m, 2H), 8.00–7.98 (m, 2H), 7.71–7.72 (m, 1H), 7.55 (t, 2H, J=7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.82, 192.05, 151.13, 137.27, 135.44, 132.35, 130.93, 130.03, 129.20, 124.09; MS ($C_{14}H_9NO_4$): 255.2 (M$^+$).

*4.3.7. 1-(4-Cyanophenyl)-2-phenylethane-1,2-dione (**2g**).*[5d] Yellow solid, mp 111–112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08–8.06 (m, 2H), 7.97–7.94 (m, 2H), 7.81–7.78 (m, 2H), 7.68–7.66 (m, 1H), 7.52 (t, 2H, J=7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.94, 192.34, 135.83, 135.34, 132.69, 132.39, 132.11, 130.15, 129.99, 129.96, 129.15, 128.58, 117.84, 117.51; MS ($C_{15}H_9NO_2$): 235.2 (M$^+$).

*4.3.8. 1-(4-Formylphenyl)-2-phenylethane-1,2-dione (**2h**).*[5d] Yellow solid, mp 64–67 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.12 (s, 1H), 8.14 (d, 2H, J=8.3 Hz), 8.03–7.97 (m, 4H), 7.69 (t, 1H, J=7.4 Hz), 7.56–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.53, 193.40, 191.29, 139.98, 136.96, 135.21, 132.55, 130.36, 129.94, 129.92, 129.11; MS ($C_{15}H_{10}NO_3$): 238.1 (M$^+$).

*4.3.9. 1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (**2i**).*[5d] Yellow solid, mp 68–70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04–8.00 (m, 2H), 7.98–7.96 (m, 2H), 7.66–7.67 (m, 1H), 7.51 (t, 2H, J=7.8 Hz), 7.18 (t, 2H, J=8.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.05, 192.71, 166.75 (d, J=256.6 Hz), 134.98, 132.81, 132.70 (d, J=10.0 Hz), 129.89, 129.47 (d, J=1.9 Hz), 129.03, 116.37 (d, J=22.1 Hz); MS ($C_{14}H_9O_2F$): 228.2 (M$^+$).

*4.3.10. 1-(4-Trimethylsilylphenyl)-2-phenylethane-1,2-dione (**2j**).* Yellow solid, mp 60–63 °C; ^{1}H NMR ($CDCl_3$, 400 MHz):

δ 7.97–7.90 (m, 4H), 7.67–7.63 (m, 3H), 7.48 (t, 2H, *J*=7.8 Hz), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.85, 194.61, 149.89, 134.79, 133.79, 133.00, 132.96, 129.83, 128.96, 128.61, -1.49; IR (KBr, cm^{-1}): ν 3066, 2957, 2897, 2802, 1675; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{18}O_2SiNa$ 305.0974; found 305.0971.

*4.3.11. 1-(4-Ethylphenyl)-2-(p-tolyl)ethane-1,2-dione (**2k**).* Yellow solid, mp 62–65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (t, 4H, *J*=8.8 Hz), 7.31–7.27 (m, 4H), 2.70 (q, 2H, *J*=7.6 Hz), 2.40 (s, 3H), 1.23 (t, 3H, *J*=7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.48, 152.13, 146.02, 130.84, 130.66, 130.07, 129.95, 129.65, 128.49, 29.12, 21.85, 15.00; IR (KBr, cm^{-1}): ν 3029, 2968, 2931, 2875, 1668; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{16}O_2Na$ 275.1048; found 275.1045.

*4.3.12. 1-(4-Ethylphenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (**2l**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94–7.89 (m, 2H), 7.86 (d, 2H, *J*=8.2 Hz), 7.29 (d, 2H, *J*=8.2 Hz), 6.96–6.92 (m, 2H), 3.85 (s, 3H), 2.69 (q, 2H, *J*=7.6 Hz), 1.22 (t, 3H, *J*=7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.59, 193.37, 164.86, 152.06, 132.29, 130.93, 130.08, 128.46, 126.14, 114.27, 55.57, 29.11, 15.00; IR (KBr, cm^{-1}): ν 2968, 2934, 2841, 1665; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{16}O_3Na$ 291.0997; found 291.0994.

*4.3.13. 1-(4-Methoxyphenyl)-2-(4-pentyloxyphenyl)ethane-1,2-dione (**2m**).* Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96–7.92 (m, 4H), 6.98–6.94 (m, 4H), 4.03 (t, 2H, *J*=6.5 Hz), 3.88 (s, 3H), 1.83–1.79 (m, 2H), 1.46–1.37 (m, 4H), 0.93 (t, 3H, *J*=7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.45, 193.39, 164.69, 164.39, 132.24, 126.19, 125.88, 114.58, 114.14, 68.33, 55.50, 28.56, 27.93, 22.26, 13.86; IR (KBr, cm^{-1}): ν 2965, 2932, 2858, 1672, 1666; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$ 349.1416; found 349.1413.

*4.3.14. 1-(4-tert-Butylphenyl)-2-(4-cyanophenyl)ethane-1,2-dione (**2n**).*[8a] Yellow solid, mp 59–62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, 2H, *J*=8.4 Hz), 7.90 (d, 2H, *J*=8.6 Hz), 7.81 (d, 2H, *J*=8.4 Hz), 7.55 (d, 2H, *J*=8.6 Hz), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.72, 192.63, 159.71, 135.98, 132.69, 130.18, 130.01, 129.87, 126.23, 117.75, 117.61, 35.47, 30.92; MS ($C_{19}H_{17}NO_2$): 291.3 (M^+).

*4.3.15. 1-Phenyl-2-(pyridin-3-yl)ethane-1,2-dione (**2o**).*[8c] Yellow solid, mp: 62–65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17(m, 1H), 8.88–8.86 (m, 1H), 8.31–8.29 (m, 1H), 8.01–7.99 (m, 2H), 7.69–7.67 (m, 1H), 7.56–7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.85, 192.69, 154.76, 151.27, 136.83, 135.22, 132.42, 129.99, 129.09, 128.64, 123.83; MS ($C_{13}H_9NO_2$): 211.2 (M^+).

*4.3.16. 1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (**2p**).*[8d] Yellow solid, mp 60–62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, 1H, *J*=8.6 Hz), 8.09 (d, 1H, *J*=8.2 Hz), 8.01–8.03 (m, 2H), 7.93–7.89 (m, 2H), 7.73–7.71 (m, 1H), 7.64–7.61 (m, 2H), 7.51–7.46 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.11, 194.52, 135.91, 135.00, 134.69, 134.03, 133.33, 130.89, 129.95, 129.39, 128.98, 128.76, 128.57, 127.07, 125.88, 124.37; MS ($C_{18}H_{12}O$): 260.3 (M^+).

*4.3.17. 1-(4-Fluorophenyl)-2-(naphthalen-1-yl)ethane-1,2-dione (**2q**).* Yellow solid, mp 67–70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.28 (d, 1H, *J*=8.6 Hz), 8.13 (d, 1H, *J*=8.2 Hz), 8.08–8.05 (m, 2H), 7.94 (d, 1H, *J*=7.9 Hz), 7.89 (d, 1H, *J*=7.2 Hz), 7.75–7.76 (m, 1H), 7.63–7.64 (m, 1H), 7.52–7.48 (m, 1H), 7.22–7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.66, 192.86, 166.65 (d, *J*=256.4 Hz), 136.11, 135.05, 134.06, 132.79 (d, *J*=9.7 Hz), 130.92, 129.83 (d, *J*=2.9 Hz), 129.51, 128.81, 128.45, 127.16, 125.86, 124.39, 116.38 (d, *J*=22.1 Hz); IR (KBr, cm^{-1}): ν 2968, 2925, 2851, 1668; HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{18}H_{11}O_2FNa$ 301.0641; found 301.0636.

*4.3.18. 1-Phenylpropane-1,2-dione (**2r**).*[8c] Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, 2H, *J*=8.0 Hz), 7.63 (t, 1H, *J*=7.4 Hz), 7.49 (t, 2H, *J*=7.7 Hz), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.47, 191.34, 134.53, 131.73, 130.26, 128.79, 26.31; MS ($C_9H_8O_2$): 148.2 (M^+).

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References and notes

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