Mild Oxidation of Diarylacetylenes to 1,2-Diketones Using Oxone in Trifluoroacetic Acid

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Abstract: A variety of 1,2-diaryldiketones were synthesized in 15–90% yields by treatment of diarylacetylenes with Oxone as the oxidant in trifluoroacetic acid. Oxidation of 1-nitro-2-(phenylethynyl)benzene and 2,4′-(ethyne-1,2-diyl)bis(nitrobenzene) furnished 1-benzoylbenzo[*c*]isoxazol-3(1*H*)-one and benzo[*c*]isoxazol-3-yl(4-nitrophenyl)methanone as the major products, respectively.

Key words: diarylalkyne, Oxone, oxidation, 1,2-diketone

1,2-Diketone compounds are versatile building blocks for organic syntheses. They can be used to prepare various organic compounds, such as chiral 1,2-diols,[1] imidazoles,[2] quinoxalines[3] and indolone-*N*-oxide.[4] Some of these compounds show good antitumor activity[5] or can be used as selective cyanide anion indicators.[6] Moreover, they have been widely used in industry as photoinitiators in radical polymerization and polymer grafting.[7] Over the past decade, many synthetic methods for the preparation of 1,2-diaryldiketones have been reported.[8] The direct conversion of substituted alkynes into the desired 1,2-diketones appear to be the most convenient method, however, most of the reagents used in this conversion are toxic and expensive. A recent method reported by Wan[8k] is more practical for this transformation, although the required reaction temperature is still high (105 °C). Herein, we would like to report a more convenient method for transforming diarylacetylenes into the corresponding 1,2-diaryldiketones using Oxone in trifluoroacetic acid at room temperature.

The starting diarylacetylenes **1a**–**r** were prepared by Sonogashira coupling reaction of the corresponding aryl halides and arylacetylenes.[9] Treatment of **1a**–**r** with two equivalents of Oxone in trifluoroacetic acid at 0 °C for five minutes and then at room temperature for 10–25 minutes, gave the 1,2-diketone products **2a**–**r** in 15–90% yields (Table 1). The structure of compound **2o** was further confirmed by a single crystal X-ray crystallography analysis (Figure 1).[10]

On the basis of experimental results, it could be concluded that most diarylacetylenes **1a**–**m** were transformed into the 1,2-diketones **2a**–**m** in modest to good yields (40–90%). When the phenyl ring contained electron-withdrawing groups, such as nitro, acetyl or cyano groups, the yields ranged from 75 to 90% (Table 1, entries 1–13). When the compounds contained substituents at the *ortho*-position, the diketones formed in slightly lower yields (Table 1, entries 10–13). The oxidation of 1-[4-(phenylethynyl)phenyl]ethanone (**1d**) gave two products (**2d** and **2d′**), in a ratio of 66:34. Compound **2d′** apparently forms as a further oxidation adduct of **2d** via Baeyer–Villiger oxidation. On the other hand, compounds bearing electron-donating groups on the phenyl ring, such as, methyl, methoxy or hydroxyl group, gave low yields of the products (Table 1, entry 14–17). We also found that large amounts of starting material were also recovered in the oxidation of 1-methyl-4-(phenylethynyl)benzene (**1n**) and 1,2-di(*p*-tolyl)ethyne (**1o**), even when four equivalents of Oxone were used and the reaction time was prolonged (2 h). Based on these observations, it can be concluded that electron-deficient diarylacetylenes are more suitable for this conversion.

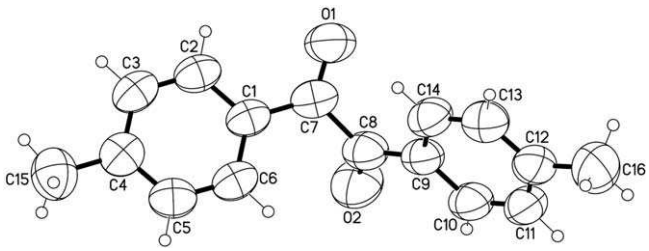
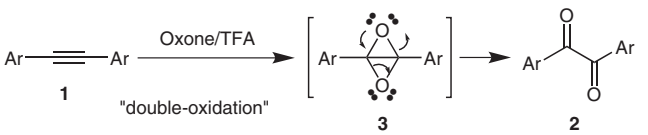


Figure 1 ORTEP drawing of compound **2o**

A proposed mechanism for the formation of 1,2-diaryldiketones from diarylacetylenes using Oxone in trifluoroacetic acid is shown in Scheme 1. The bisoxirane **3** is proposed as the key intermediate, which may be generated by the so-called 'double oxidation' mechanism.[11]

More interestingly, the oxidation of 1-nitro-2-(phenylethynyl)benzene (**1r**) and 2,4′-dinitrophenylacetylene (**1s**) gave unexpected products. We found that oxidation of **1r** under the described reaction conditions, gave the



Scheme 1

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diketone **2r** in only 20% yield. The major product (40%) of this reaction was 1-benzoylbenzo[*c*]isoxazol-3(1*H*)-one (**4**; Table 1, entry 18), the structure of which was unambiguously determined by a single crystal X-ray crystallographic analysis (Figure 2).[10] On the other hand, upon oxidation of **1s**, no 2-(2-nitrophenyl)-1-(4-nitrophenyl)ethane-1,2-dione (**2s**) was observed; in this case, benzo[*c*]isoxazol-3-yl(4-nitrophenyl)methanone (**5**) was formed as the major product, along with small amounts of 1-(4-nitrobenzoyl)benzo[*c*]isoxazol-3(1*H*)-one (**6**; Table 1, entry 19).

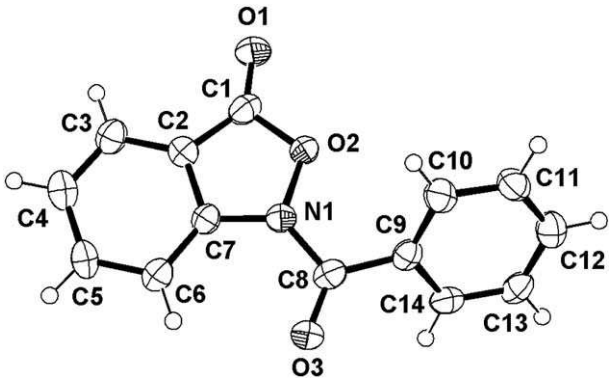
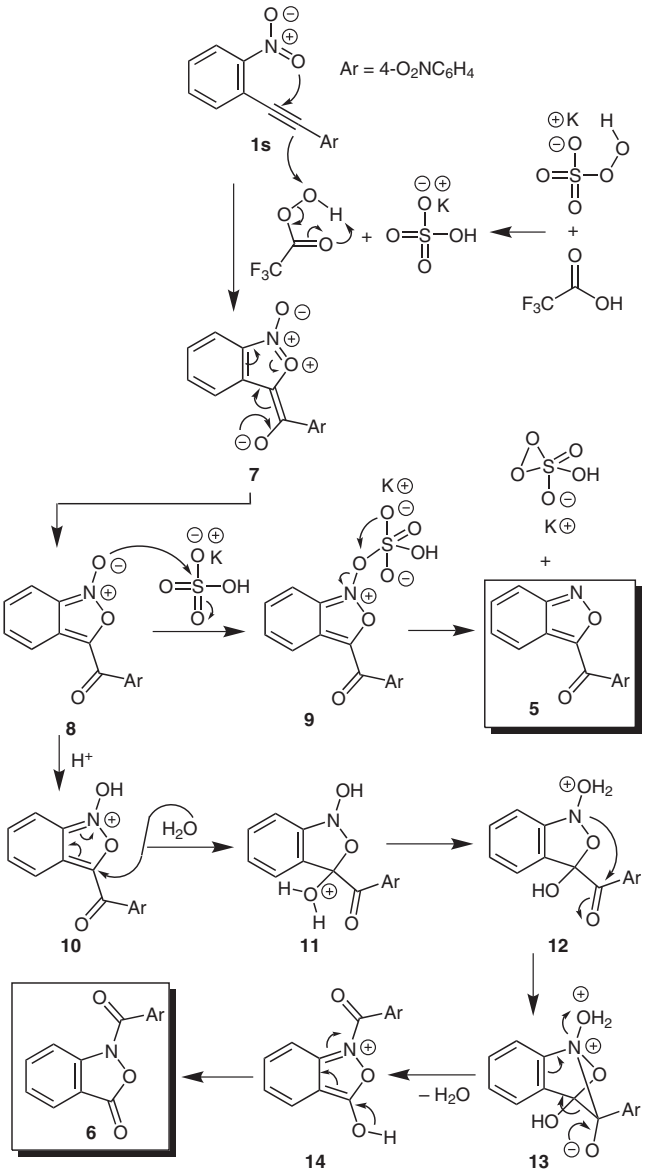


Figure 2 ORTEP drawing of compound **4**

A possible mechanism for the formation of compounds **5** and **6** is outlined in Scheme 2. Oxidation of the triple bond of **1s**, followed by cyclization through one of the oxygens of the nitro group in situ, would form intermediate **7**. Tautomerization of **7** into **8** and reduction of the *N*-oxide of isoxazole-1-oxide by potassium hydrogensulfate would generate compound **5**. On the other hand, protonation of the *N*-oxide of **8** would give **10**, which could hydrolyze to give **11**. This could be further converted into **12** through intramolecular proton transfer and nucleophilic attack of the carbonyl group by the nitrogen of **12** to give **13**. Subsequent ring-opening reaction of **13** would lead to **14**. Finally, tautomerization of **14** would give compound **6**.

In conclusion, we have developed a new protocol for the synthesis of 1,2-diaryldiketones from diarylalkynes. The method is simple, fast and convenient, and also circumvents the use of expensive and toxic transition-metal catalysts.

^{1}H NMR spectra were measured on a 400 MHz Varian Unity plus 400 spectrometer. Natural abundance ^{13}C NMR spectra were measured using a pulse Fourier transform Varian Unity plus 400 (400 MHz NMR) spectrometer operating at 100 MHz. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants *J* in Hertz (Hz) for both nuclei; the solvent peak (usually $CDCl_3$) was used as an internal standard. The reference peak used for ^{1}H was TMS (δ = 0.00 ppm), and the central solvent peak (δ = 77.0 ppm) was used for ^{13}C NMR. MS spectra were measured using Thermo Finnigan-PolarisQ and Thermo Finnigan LCQ-Advantage spectrometers. Melting points were measured using a Barnstead International-Electrothermal melting point meter IA1101D.



Scheme 2

General Procedure

To a well-stirred solution of Oxone (2 equiv) in TFA (3 mL), was added diarylacetylene **1a–s** (100 mg, 1 equiv) at 0 °C over 5 min. The solution was then warmed to r.t. and stirred for an additional 10–25 min. The solution was diluted with CH_2Cl_2 (3 mL) and H_2O (5 mL) was added to the solution. The aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL) and the combined organic extracts were washed with sat. aq $NaHCO_3$ (2 × 5 mL) and dried over $MgSO_4$. After filtration and concentration in vacuo, the residue was purified by column chromatography to give the 1,2-diketones **2a–r**, **2d′**, and **4–6** in 15–90% yields (Table 1).

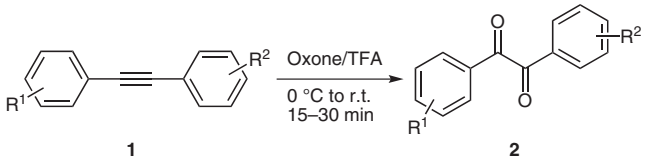
1,2-Diphenylethane-1,2-dione (2a)[8l]

Pale-yellow solid; mp 90–92 °C (Lit.[8l] 96 °C); R_f = 0.55 (*n*-hexane–EtOAc, 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.54 (m, 4 H), 7.64–7.69 (m, 2 H), 7.96–8.00 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.0 (4 × CH), 129.9 (4 × CH), 133.0 (2 × Cq), 134.9 (2 × CH), 194.6 (2 × Cq).

Table 1 Oxidation of Diarylalkynes **1** to 1,2-Diketones **2** by Oxone in TFA[a]



1 **2**

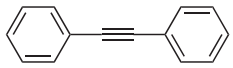
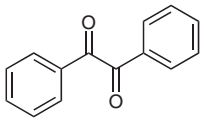
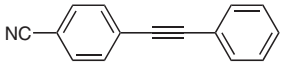
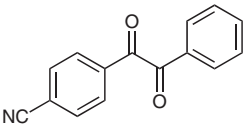
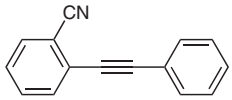
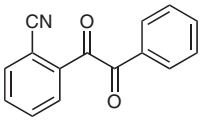
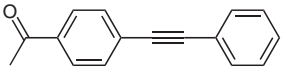
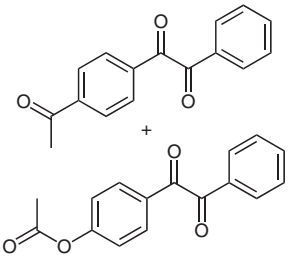
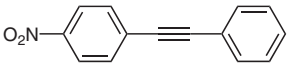
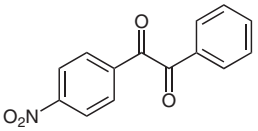
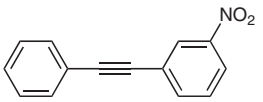
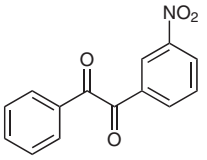
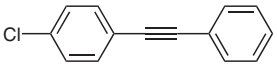
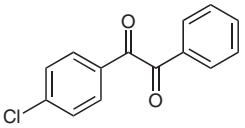
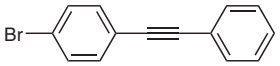
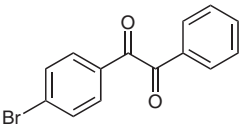
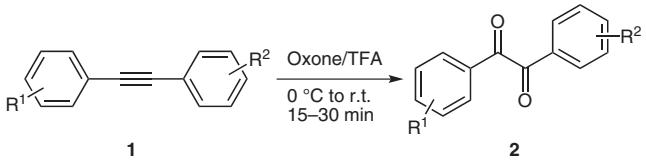
Entry	Diarylacetylene	Product	Yield (%)[b]
1	 **1a**	 **2a**	80
2	 **1b**	 **2b**	75
3	 **1c**	 **2c**	50
4	 **1d**	 **2d** + **2d′** (66:34)[c]	85
5	 **1e**	 **2e**	83
6	 **1f**	 **2f**	90
7	 **1g**	 **2g**	65
8	 **1h**	 **2h**	70

Table 1 Oxidation of Diarylalkynes **1** to 1,2-Diketones **2** by Oxone in TFA[a] (continued)



1 2

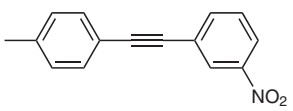
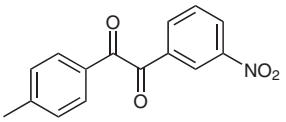
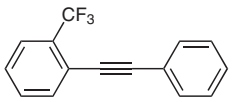
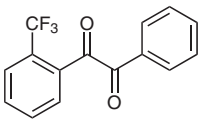
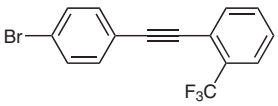
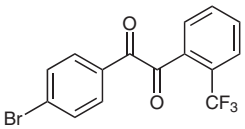
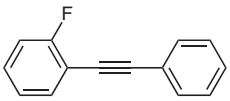
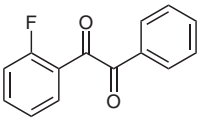
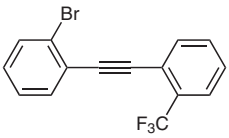
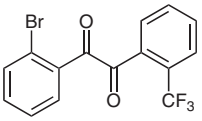
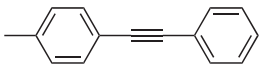
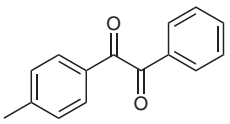
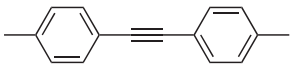
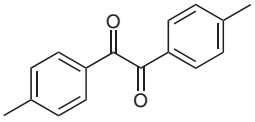
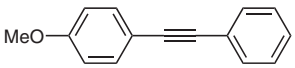
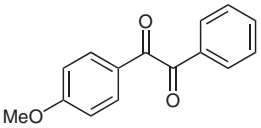
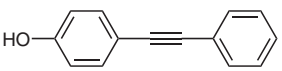
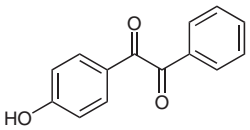
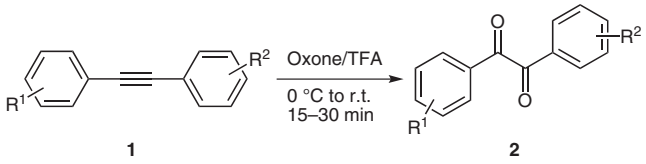
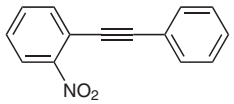
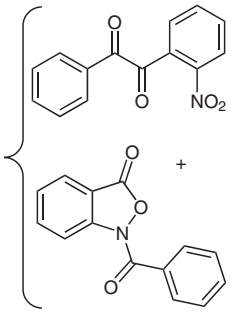
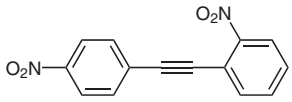
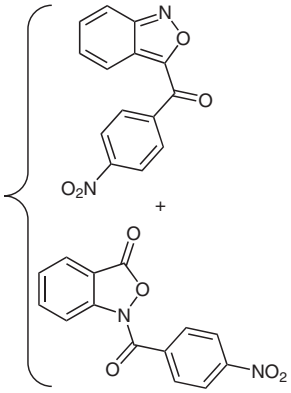
Entry	Diarylacetylene	Product	Yield (%)[b]
9	 **1i**	 **2i**	75
10	 **1j**	 **2j**	60
11	 **1k**	 **2k**	70
12	 **1l**	 **2l**	40
13	 **1m**	 **2m**	55
14	 **1n**	 **2n**	45[d]
15	 **1o**	 **2o**	35[d]
16	 **1p**	 **2p**	15
17	 **1q**	 **2q**	15

Table 1 Oxidation of Diarylalkynes **1** to 1,2-Diketones **2** by Oxone in TFA[a] (continued)



1 2

Entry	Diarylacetylene	Product	Yield (%)[b]
18	 **1r**	 **2r** + **4** (33:67)[c]	60
19	 **1s**	 **5** + **6** (>95:5)[c]	85

[a] Reagents and conditions: Diarylacetylene (1 equiv), Oxone (2 equiv), TFA (3 mL).
[b] Isolated yield was determined by an average of three runs.
[c] Product ratio was determined by ^{1}H NMR spectroscopy.
[d] Starting material was also recovered.

MS (EI, 70 eV): *m*/*z* (%) = 210 (8) [M$^+$], 105 (100), 77 (57).

1-(4-Cyanophenyl)-2-phenylethane-1,2-dione (2b)[8l]
Pale-yellow solid; mp 108–110 °C (Lit.[8l] 111.5 °C); R_f = 0.61 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.57 (m, 2 H), 7.71 (tt, *J* = 7.4, 0.8 Hz, 1 H), 7.82 (d, *J* = 8.2 Hz, 2 H), 7.96–7.99 (m, 2 H), 8.09 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.6 (Cq), 117.9 (Cq), 129.2 (2 × CH), 130.0 (2 × CH), 130.2 (2 × CH), 132.4 (Cq), 132.7 (2 × CH), 135.4 (CH), 135.8 (Cq), 192.4 (Cq), 193.0 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 130 [M$^+$ – 105], 150 (100), 77 (54).

1-(2-Cyanophenyl)-2-phenylethane-1,2-dione (2c)[8l]
Pale-yellow solid; mp 60–62 °C (Lit.[8l] 67.5 °C); R_f = 0.32 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.57 (m, 2 H), 7.68–7.79 (m, 3 H), 7.91–7.94 (m, 2 H), 8.02–8.04 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.0 (Cq), 117.0 (Cq), 129.2 (2 × CH), 130.2 (2 × CH), 132.4 (CH and Cq), 132.7 (CH), 134.1 (CH), 135.0 (Cq), 135.4 (CH), 135.6 (CH), 191.2 (Cq), 192.1 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 235 (2) [M$^+$], 130 (6), 105 (100), 77 (52).

1-(4-Acetylphenyl)-2-phenylethane-1,2-dione (2d)[12]
Pale-yellow solid; mp 76–78 °C; R_f = 0.44 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 3 H), 7.51–7.55 (m, 2 H), 7.68 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.96–7.99 (m, 2 H), 8.01 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.0 (CH_3), 128.7 (2 × CH), 129.1 (2 × CH), 130.0 (2 × CH), 130.1 (2 × CH), 132.6 (Cq), 135.2 (CH), 135.9 (Cq), 141.3 (Cq), 193.6 (Cq), 193.8 (Cq), 197.2 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 268 (2) [M$^+$], 163 (33), 105 (100), 77 (14).

4-(2-Oxo-2-phenylacetyl)phenyl Acetate (2d′)
Pale-yellow viscous liquid; R_f = 0.48 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.3 (s, 3 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 7.50–7.54 (m, 2 H), 7.66 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.95–7.98 (m, 2 H), 8.02 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_3), 122.3 (2 × CH), 129.0 (2 × CH), 129.9 (2 × CH), 130.5 (Cq), 131.6 (2 × CH), 132.8 (Cq), 135.0 (CH), 155.7 (Cq), 168.6 (Cq), 193.2 (Cq), 194.2 (Cq).

MS (ESI): m/z = 291 $[M + Na]^+$.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{12}O_4Na$: 291.0633; found: 291.0631.

1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (2e)[8l]
Pale-yellow solid; mp 140–142 °C (Lit.[8l] 141 °C); R_f = 0.51 (*n*-hexane–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.58 (m, 2 H), 7.71 (tt, J = 7.6, 1.2 Hz, 1 H), 7.97–8.00 (m, 2 H), 8.17 (d, J = 8.4 Hz, 2 H), 8.36 (d, J = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.1 (2 × CH), 129.2 (2 × CH), 130.1 (2 × CH), 131.0 (2 × CH), 132.3 (Cq), 135.5 (CH), 137.3 (Cq), 151.2 (Cq), 192.1 (Cq), 192.8 (Cq).

MS (EI, 70 eV): m/z (%) = 225 (4) $[M^+]$, 150 (3), 105 (100), 77 (67).

1-(3-Nitrophenyl)-2-phenylethane-1,2-dione (2f)[13]
Pale-yellow solid; mp 119–121 °C; R_f = 0.37 (*n*-hexane–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (t, J = 8.0 Hz, 2 H), 7.72 (tt, J = 7.2, 1.2 Hz, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 8.00–8.03 (m, 2 H), 8.33 (dt, J = 7.6, 1.2 Hz, 1 H), 8.52 (ddd, J = 8.2, 2.2, 1.0 Hz, 1 H), 8.83 (t, J = 2.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.6 (CH), 128.8 (CH), 129.2 (2 × CH), 130.1 (2 × CH), 130.3 (CH), 132.4 (Cq), 134.3 (Cq), 135.3 (CH), 135.5 (CH), 148.6 (Cq), 191.4 (Cq), 192.7 (Cq).

MS (EI, 70 eV): m/z (%) = 150 $[M^+ - 105]$, 105 (100), 77 (52).

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (2g)[8l]
Pale-yellow solid; mp 75–76 °C (Lit.[8l] 77 °C); R_f = 0.72 (*n*-hexane–EtOAc, 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.4 Hz, 2 H), 7.52 (t, J = 8.0 Hz, 2 H), 7.68 (t, J = 7.2 Hz, 1 H), 7.92 (d, J = 8.4 Hz, 2 H), 7.97 (dd, J = 7.6, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.1 (2 × CH), 129.5 (2 × CH), 130.0 (2 × CH), 131.2 (2 × CH), 131.3 (Cq), 132.8 (Cq), 135.1 (CH), 141.6 (Cq), 193.1 (Cq), 193.9 (Cq).

MS (EI, 70 eV): m/z (%) = 246 (1) $[M^+ + 2]$, 244 (3) $[M^+]$, 105 (100), 77 (61).

1-(4-Bromophenyl)-2-phenylethane-1,2-dione (2h)[8l]
Pale-yellow solid; mp 84–86 °C (Lit.[8l] 87 °C); R_f = 0.62 (*n*-hexane–EtOAc, 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, J = 8.0 Hz, 2 H), 7.67 (d, J = 8.8 Hz, 2 H), 7.68 (tt, J = 7.2, 1.2 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.96 (dd, J = 8.4, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.1 (2 × CH), 129.9 (2 × CH), 130.5 (Cq), 131.2 (2 × CH), 131.7 (Cq), 132.4 (2 × CH), 132.7 (Cq), 135.1 (CH), 193.3 (Cq), 193.9 (Cq).

MS (EI, 70 eV): m/z (%) = 290 (2) $[M^+ + 1]$, 288 (2) $[M^+ - 1]$, 185 (45), 183 (46), 105 (100), 77 (66).

1-(3-Nitrophenyl)-2-*p*-tolylethane-1,2-dione (2i)
Pale-yellow solid; mp 121–123 °C; R_f = 0.56 (*n*-hexane–EtOAc, 7:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 7.35 (dd, J = 7.8, 0.8 Hz, 2 H), 7.74 (dd, J = 8.2, 7.8 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 2 H), 8.32 (dt, J = 8.0, 1.2 Hz, 1 H), 8.51 (ddd, J = 8.0, 2.4, 1.2 Hz, 1 H), 8.82 (dd, J = 2.4, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0 (CH_3), 124.6 (CH), 128.7 (CH), 129.9 (2 × CH and Cq), 130.2 (2 × CH), 130.3 (CH), 134.4 (Cq), 135.3 (CH), 147.0 (Cq), 148.5 (Cq), 191.6 (Cq), 192.4 (Cq).

MS (ESI): m/z = 292 $[M + Na]^+$.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{11}NO_4Na$: 292.0586; found: 292.0584.

1-(2-Trifluoromethylphenyl)-2-phenylethane-1,2-dione (2j)
Pale-yellow viscous liquid; R_f = 0.46 (*n*-hexane–EtOAc, 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (tt, J = 8.0, 1.6 Hz, 2 H), 7.66–7.75 (m, 4 H), 7.82 (dd, J = 7.2, 2.0 Hz, 1 H), 8.09 (dd, J = 8.4, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.0 (Cq), 124.7 (Cq), 127.1 (q, J = 5.3 Hz, CH), 128.9 (2 × CH), 130.4 (2 × CH), 131.2 (CH), 131.9 (CH), 132.3 (Cq), 132.4 (CH), 134.4 (Cq), 134.8 (CH), 190.9 (Cq), 193.0 (Cq).

MS (ESI): m/z = 301 $[M + Na]^+$.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_9F_3O_2Na$: 301.0452; found: 301.0453.

1-(4-Bromophenyl)-2-(2-trifluoromethylphenyl)ethane-1,2-dione (2k)
Pale-yellow solid; mp 70–72 °C; R_f = 0.49 (*n*-hexane–EtOAc, 40:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.51 (m, 2 H), 7.67–7.76 (m, 4 H), 7.97 (d, J = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.0 (Cq), 124.8 (Cq), 127.0 (d, J = 4.6 Hz, CH), 128.8, 128.4 (Cq), 130.5 (Cq), 131.0 (Cq), 131.1 (CH), 131.8 (2 × CH), 132.0 (CH), 132.3 (2 × CH), 132.4 (CH), 134.3 (Cq), 189.5 (Cq), 192.7 (Cq).

MS (ESI): m/z = 380 $[M + Na]^+$.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_8{}^{79}BrF_3O_2Na$: 378.9557; found: 378.9555.

1-(2-Fluorophenyl)-2-phenylethane-1,2-dione (2l)[14]
Pale-yellow solid; mp 58–60 °C; R_f = 0.45 (*n*-hexane–EtOAc, 15:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (dd, J = 10.4, 8.8 Hz, 1 H), 7.35 (td, J = 7.6, 0.8 Hz, 1 H), 7.53 (t, J = 8.0 Hz, 2 H), 7.63–7.69 (m, 2 H), 7.96–7.99 (dd, J = 7.6, 1.6 Hz, 2 H), 8.06 (td, J = 7.2, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.7 (d, J = 21.3 Hz, CH), 122.3 (d, J = 10.6 Hz, Cq), 125.0 (d, J = 3.8 Hz, CH), 129.0 (2 × CH), 129.9 (2 × CH), 130.8 (d, J = 1.5 Hz, CH), 132.0 (d, J = 2.3 Hz, Cq), 134.7 (CH), 136.8 (d, J = 9.1 Hz, CH), 162.9 (d, J = 257.9 Hz, Cq), 191.9 (Cq), 193.0 (Cq).

MS (EI, 70 eV): m/z (%) = 228 (7) $[M^+]$, 123 (39), 105 (100), 77 (57).

1-(2-Bromophenyl)-2-(2-trifluoromethylphenyl)ethane-1,2-dione (2m)
Pale-yellow solid; mp 72–74 °C; R_f = 0.43 (*n*-hexane–EtOAc, 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.51 (m, 2 H), 7.67–7.76 (m, 4 H), 7.86–7.88 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.7 (Cq), 121.9 (Cq), 124.6 (Cq), 127.5 (q, J = 5.3 Hz, CH), 127.7 (CH), 129.5, 129.7 (Cq), 131.6 (CH), 131.8 (CH), 132.3 (CH), 132.5 (CH), 133.9 (CH), 134.1 (CH), 135.0 (Cq), 189.7 (Cq), 191.8 (Cq).

MS (ESI): m/z = 380 $[M + Na]^+$.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_8{}^{79}BrF_3O_2Na$: 378.9557; found: 378.9558.

1-Phenyl-2-*p*-tolylethane-1,2-dione (2n)[8l]
Pale-yellow viscous liquid; R_f = 0.41 (*n*-hexane–EtOAc, 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.48–7.53 (m, 2 H), 7.65 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.95–7.98 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (CH_3), 129.0 (2 × CH), 129.7 (2 × CH), 129.9 (2 × CH), 130.0 (2 × CH), 130.5 (Cq), 133.1 (Cq), 134.8 (CH), 146.2 (Cq), 194.3 (Cq), 194.8 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 224 (5) [M^+], 119 (100), 105 (15), 91 (41).

1,2-Di-*p*-tolylethane-1,2-dione (2o)[15]
Pale-yellow solid; mp 93–95 °C (Lit.[15] 103–105 °C); R_f = 0.41 (*n*-hexane–EtOAc, 30:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 6 H), 7.30 (d, *J* = 8.4 Hz, 4 H), 7.86 (d, *J* = 8.4 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (2 × CH_3), 129.7 (4 × CH), 130.0 (4 × CH), 130.6 (2 × Cq), 146.1 (2 × Cq), 194.5 (2 × Cq).

MS (EI, 70 eV): *m*/*z* (%) = 238 (8) [M^+], 119 (100), 91 (50).

1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (2p)[8l]
Pale-yellow solid; mp 62–64 °C (Lit.[8l] 65 °C); R_f = 0.46 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 7.51 (td, *J* = 7.2, 1.2 Hz, 2 H), 7.65 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 7.99 (dd, *J* = 7.6, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6 (CH), 114.4 (2 × CH), 126.1 (Cq), 128.9 (2 × CH), 129.9 (2 × CH), 132.4 (2 × CH), 133.2 (Cq), 134.7 (CH), 165.0 (Cq), 193.2 (Cq), 194.9 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 135 (100) [M^+ – 105], 77 (27).

1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione (2q)[8l]
Pale-yellow solid; mp 115–117 °C; R_f = 0.61 (*n*-hexane–EtOAc, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (br s, 1 H), 6.92 (d, *J* = 9.0 Hz, 2 H), 7.49–7.53 (m, 2 H), 7.65 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.90 (d, *J* = 9.0 Hz, 2 H), 7.96–7.99 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.0 (2 × CH), 126.1 (Cq), 129.0 (2 × CH), 129.9 (2 × CH), 132.7 (2 × CH), 133.1 (Cq), 134.8 (CH), 161.7 (Cq), 193.1 (Cq), 194.9 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 226 (3) [M^+], 121 (100), 105 (13).

1-(2-Nitrophenyl)-2-phenylethane-1,2-dione (2r)[16]
Pale-yellow solid; mp 124–126 °C; R_f = 0.57 (*n*-hexane–EtOAc, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (tt, *J* = 7.6, 1.2 Hz, 2 H), 7.68 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.73–7.79 (m, 2 H), 7.86 (td, *J* = 7.6, 1.2 Hz, 1 H), 8.20–8.23 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.1 (CH), 128.6 (2 × CH), 130.8 (2 × CH), 131.1 (CH), 132.4 (CH and Cq), 133.6 (Cq), 134.5 (CH), 134.9 (CH), 150.0 (Cq), 188.0 (Cq), 189.8 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 105 (100) [M^+ – 150], 77 (60).

1-Benzoylbenzo[*c*]isoxazol-3(1*H*)-one (4)
White solid; mp 134–136 °C; R_f = 0.42 (*n*-hexane–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (td, *J* = 7.4, 0.8 Hz, 1 H), 7.53 (tt, *J* = 8.0, 1.2 Hz, 2 H), 7.63 (tt, *J* = 7.2, 1.2 Hz, 1 H), 7.85 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.95 (dt, *J* = 7.2, 0.8 Hz, 1 H), 7.99 (dd, *J* = 8.0, 1.2 Hz, 2 H), 8.25 (dd, *J* = 8.0, 0.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.7 (Cq), 115.8 (CH), 125.6 (CH), 126.1 (CH), 128.4 (2 × CH), 129.7 (2 × CH), 131.1 (Cq), 133.0 (CH), 136.5 (CH), 145.8 (Cq), 163.8 (Cq), 164.1 (Cq).

MS (ESI): *m*/*z* = 262 [M + Na]$^+$.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_9NO_3Na$: 262.0482; found: 262.0481.

Benzo[*c*]isoxazol-3-yl(4-nitrophenyl)methanone (5)[17]
White solid; mp 175–177 °C; R_f = 0.61 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (ddd, *J* = 8.8, 6.0, 0.8 Hz, 1 H), 7.47 (ddd, *J* = 9.6, 6.4, 0.8 Hz, 1 H), 7.82 (d, *J* = 9.2 Hz, 1 H), 8.18 (dt, *J* = 8.8, 1.2 Hz, 1 H), 8.44 (d, *J* = 8.8 Hz, 2 H), 8.48 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.2 (CH), 121.4 (CH), 122.2 (Cq), 123.9 (2 × CH), 129.6 (CH), 131.1 (2 × CH), 131.7 (CH), 140.6 (Cq), 150.5 (Cq), 157.5 (Cq), 159.4 (Cq), 179.6 (Cq).

MS (EI, 70 eV): *m*/*z* (%) = 268 (100) [M^+], 224 (48), 178 (22).

1-(4-Nitrobenzoyl)benzo[*c*]isoxazol-3(1*H*)-one (6)
White solid; mp 157–159 °C; R_f = 0.39 (*n*-hexane–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (td, *J* = 7.6, 0.8 Hz, 1 H), 7.90 (td, *J* = 8.0, 0.8 Hz, 1 H), 7.99 (dt, *J* = 7.6, 0.8 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 2 H), 8.28 (d, *J* = 8.4 Hz, 1 H), 8.38–8.40 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.8 (Cq), 115.8 (CH), 123.6 (2 × CH), 125.9 (CH), 126.8 (CH), 130.8 (2 × CH), 131.8 (Cq), 136.9 (CH), 145.3 (Cq), 150.0 (Cq), 161.7 (Cq), 163.1 (Cq).

MS (ESI): *m*/*z* = 307 [M + Na]$^+$.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_8N_2O_5Na$: 307.0331; found: 307.0334.

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