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Microwave-assisted efficient synthesis of 1,2-diaryldiketones: a novel oxidation reaction of diarylalkynes with DMSO promoted by $FeBr_3$

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Abstract—This paper reports the oxidation of functionalized diarylalkynes with DMSO in the presence of the environmentally friendly $FeBr_3$ catalyst. This non-toxic procedure is general and has been applied successfully under microwave irradiation leading rapidly to benzil derivatives in good yields.

1. Introduction

Benzil derivatives are an important class of compounds, which have been reported for their application as inhibitors of the acid corrosion of mild steel,[1] as photosensitive agents in photocurable coatings,[2] and also as natural compounds.[3] Moreover, benzil substrates constitute useful intermediates in organic synthesis as precursors of various heterocyclic compounds such as, for example, imidazoles[4] or quinoxalines.[5] Conventionally, benzil derivatives are obtained by oxidation of benzoins[6] or hydrobenzoins.[7] However, the access to functionalized benzoins is not easy and their oxidation very often required the use of toxic and/or expensive reagents (e.g., thallium nitrate,[6d] ammonium chlorochromate–alumina,[6e] RuO_4[6g] and *N*-hydroxyphthalimide–$Co(acac)_3$).[7c] Besides other methodologies,[8,6g] by far the most important procedure for the preparation of benzils is the oxidation of diarylalkynes, which are easily prepared by Sonogashira–Linstrumelle coupling. Thus, a large number of oxidizing systems have been utilized including $Co(OAc)_2$/$Mn(OAc)_2$/NaBr,[9] $ZnCr_2O_7 \cdot 3H_2O$,[10] SO_3–dioxane complex,[11] H_5IO_6[12] and CH_3ReO_3/H_2O_2.[13] However, these reagents have several drawbacks in terms of toxicity, difficult reaction conditions, long reaction times and/or low yields. DMSO as an oxidant in the presence of an excess of NBS[14] has been successfully reported to transform diphenylacetylene into benzil. Similarly, an attractive protocol using DMSO as oxidant in the presence of $PdCl_2$ has been described by a Russian team.[15] While this transformation is a suitable method, its success was influenced by the electronic nature of the aryl substituents.[16] A recent work concerning the oxidation of alkynes into α-diketones with DMSO and $CH_3SO_3H/HCO_2H/HBr$[17] prompted us to report the results of our study. With respect to the environmental concerns, there is a strong demand for a clean, safe and highly efficient catalytic methodology for the conversion of arylalkynes to benzil derivatives.

2. Results and discussion

As a part of our programme aimed at the development of new, soft and selective oxidizing methodologies,[18] we have investigated the oxidation of various internal arylalkynes **1** with DMSO in the presence of catalytic amounts of friendly transition-metal salts. Herein, we report a simple and convenient procedure for the synthesis of a range of functionalized benzil derivatives promoted by the non-toxic and cheap $FeBr_3$.

At the outset of this work, we began our approach by screening a variety of catalysts using diarylalkyne **1a** as a model substrate in DMSO.

The results described in Table 1 showed clearly that transition-metal catalysts promoted the oxidation of **1a** while no reaction occurred without catalyst (entry 1). Whereas all studied metal salts (bromides or chlorides) were effective in a surprising way, $MnCl_2$ (two attempts) did not catalyze the oxidation reaction (entry 8) and starting alkyne **1a** was recovered unchanged. Examination of Table 1 indicates that transition-metal salt bromide catalysts were superiors

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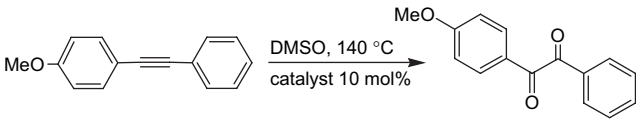
Table 1. Oxidation of diarylalkyne **1a** to benzil **2a**



1a **2a**

Entry	Catalyst	Time (h)	Yield[a] (%)
1	—	72	0
2	CuCl	72	65
3	CuBr	72	66
4	$InCl_3$	16	65
5	$InBr_3$	14	70
6	$NiCl_2$	40	72
7	$NiBr_2$	24	76
8	$MnCl_2$	36	0[b]
9	$MnBr_2$	14	75[b]
10	$Fe(acac)_3$	40	68
11	$FeCl_3$	36	73
12	$FeBr_3$	10	80
13	$FeBr_3$[c]	10	78

[a] Isolated yield.
[b] Two reproducible attempts.
[c] 1 equiv of $FeBr_3$ was used.

to the corresponding chlorides in terms of increasing yields and reducing reaction times. In all studied cases, no traces of arylalkyne **1a** were found at the end of the reaction and then purifications were easy. Of the transition-metal salts examined, $FeBr_3$ was the most efficient catalyst delivering benzil **2a** in high yield (10 h, 80%, entry 12) whereas, under the same conditions $FeCl_3$ and $Fe(acac)_3$ gave similar yields but with longer reaction times (entries 10 and 11). With CuBr, $InBr_3$, $NiBr_2$ and $MnBr_2$, the oxidation reaction was also successful but with lower yields and longer reaction times (entries 3, 5, 7 and 9). Finally, increasing the amount of the iron bromide catalyst was not efficient to observe neither a reduced reaction time nor a better yield (entry 13).

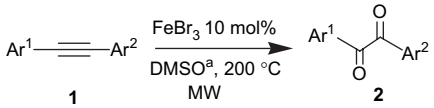
In our current work to develop rapid and efficient methods for oxidation reactions, we thought to speed up the synthesis of various benzils using microwave-assisted irradiation.[18d]

Our first efforts were focused on the optimization of the reaction temperature. When the reaction of **1a** is carried out at 140 °C (as base line control to evaluate the microwaves contribution) for 20 min, one notes that 20% of the starting product **1a** was transformed into its corresponding benzil **2a**, while only traces of **2a** (<5%, indicated by GC) were obtained by conventional thermal conditions. By increasing gradually the reaction temperature, we were pleased to observe that, using microwave irradiation at 200 °C, diarylalkyne **1a** was totally transformed into **2a** in only 20 min and with a satisfactory yield (75%).[19] It should be noted that under convention thermal heating (200 °C, 20 min, sealed tube) the reaction occurred smoothly and 50% of the starting material was recovered unchanged. $InBr_3$ (10 mol %) and $MnBr_2$ (10 mol %) were also tested, but longer reaction times, by comparison with $FeBr_3$, were required to oxidize **1a** completely (75%, 40 min and 68%, 45 min, respectively).

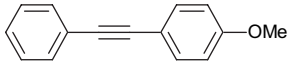
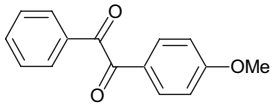
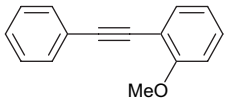
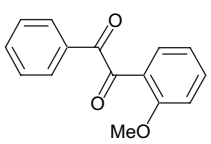
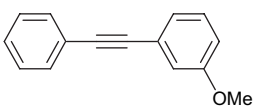
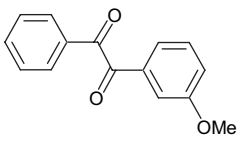
Next, we investigated the oxidizing species. When using stoichiometric amounts or slight excess (5 equiv) of DMSO, no traces of **2a** were detected even after a prolongated reaction time (48 h). A similar result was obtained when DMSO was replaced by sulfolane (tetramethylene sulfone); the oxidation reaction failed and starting alkyne **1a** was recovered unchanged. We are presently examining alternatives to DMSO for the oxygen transfer step.

To demonstrate the scope of the reaction, a series of acetylenic substrates **1a–o** were synthesized by Sonogashira–Linstrumelle coupling[20] and subjected to oxidation by the DMSO–$FeBr_3$ couple under microwave irradiation. The results of this study are summarized in Table 2.

Table 2. Oxidation of diarylalkynes **1** to benzyl derivatives **2** under microwave irradiation

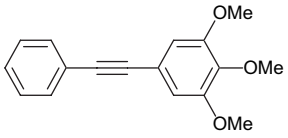
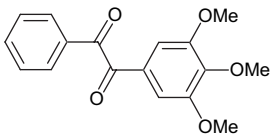
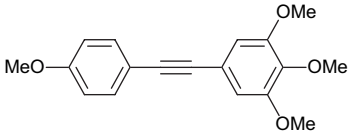
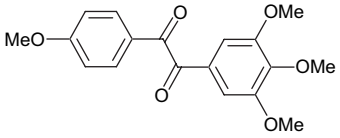
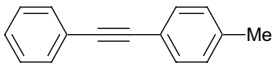
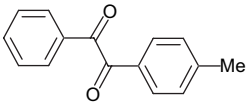
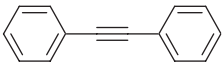
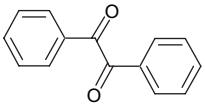
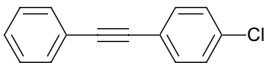
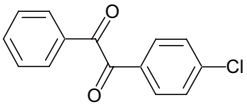
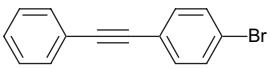
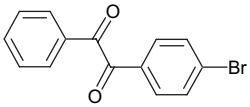
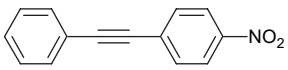
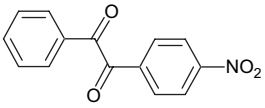
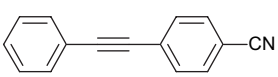
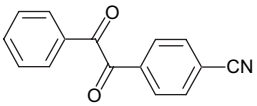
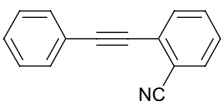
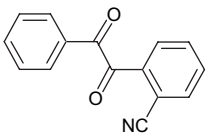
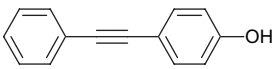
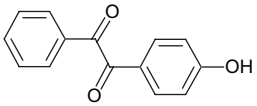
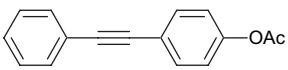
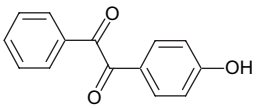
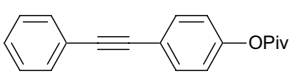
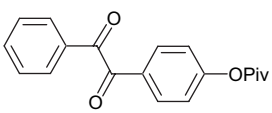


1 **2**

Entry	Alkynes	1	Benzils	2	Time (min)	Yield[b] (%)
1		**1a**		**2a**	20	75[c]
2		**1b**		**2b**	40	70
3		**1c**		**2c**	9	75

(*continued*)

Table 2. (*continued*)

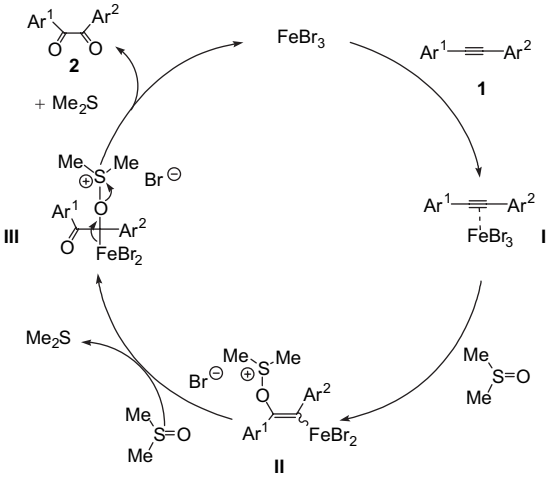
Entry	Alkynes	1	Benzils	2	Time (min)	Yield[b] (%)
4		**1d**		**2d**	25	64
5		**1e**		**2e**	30	65
6		**1f**		**2f**	11	61
7		**1g**		**2g**	20	73
8		**1h**		**2h**	9	75
9		**1i**		**2i**	9	72
10		**1j**		**2j**	15	72
11		**1k**		**2k**	21	46
12		**1l**		**2l**	16	43
13		**1m**		**2m**	120	0
14		**1n**		**2m**	9	51
15		**1o**		**2o**	8	59

[a] During this study, we did not observe a notable degradation of the DMSO[21] under microwave irradiation.
[b] Isolated yield. All compounds exhibited satisfactory spectral properties and microanalyses.
[c] No oxidation was observed when reactions were conducted without $FeBr_3$ in DMSO at 200 °C under MWI.

Arylalkynes substituted with an electron-donating group (Me, OMe) have been transformed into benzil derivatives in good yields (from 61% to 76%) and with reduced reaction times (<1 h). It should be noted that the position of the substituent (*o*, *m*, *p*) on the aromatic ring had no influence on the oxidation yield, although the *meta* benzil **2c** was obtained in a shorter reaction time (compare entry 3 with entries 1 and 2). We were also pleased to observe that halogenated substituted arylalkynes **1h** and **1i** afforded the expected benzils with reduced times and good yields (<10 min, 72–75%, entries 8 and 9). Moreover, the presence of an electron-withdrawing group on the aryl ring such as NO_2 did not affect the yield as well as the reaction time of the oxidizing process and provides benzil **2j** in 72% yield (entry 10). However, by using arylalkynes **1k** and **1l** substituted with an *ortho* or a *para* cyano group, respectively, the desired corresponding benzil derivatives **2k** and **2l** were obtained in moderate yields although totally disappearance of starting material was observed. It seems that under these conditions, the cyano group interferes with the outcome of the present reaction (non-identified hydrolyzed by-products were observed in the crude reaction mixture). One can note that the phenolic arylalkyne **1m** did not give its corresponding benzil **2m**, even after a prolongated reaction time under MW irradiation. However, when the hydroxy substituent of **1m** was protected as an acetate (**1n**), we observed the formation of **2m**, after oxidation of the triple bond followed by cleavage of the acetoxyester group. A similar result (oxidation and cleavage) has been obtained with conventional heating (70%, 7 h). On the contrary, pivaloyl substituted ester **1o** was successfully transformed into its corresponding benzil **2o**, but without removal of the bulky protecting group (entry 15). It is important to note that this new oxidation process with $FeBr_3$–DMSO is not sensitive to the electronic nature of the acetylenic substrates, unlike some others methodologies.[11]

3. Mechanistic consideration

At first, an experiment was performed in which the DMSO solution was degassed. Without O_2, oxidation of **1a** was still observed with comparable yields and reaction times, implying that DMSO constitutes the oxidizing species. When **1a** was heated in DMSO without any catalysts, the oxidation occurred slowly (stirring for 72 h at 140 °C, starting alkyne **1a** (10%) was still recovered). In the plausible proposed mechanism (Scheme 1) concerning the oxidation of arylalkynes **1**, the Fe(III), acting as a Lewis acid, may activate the triple bond to generate **I** and allowed successive additions of DMSO. After a first addition, a vinyl iron species **II** (or its cationic equivalent) would be formed and then trapped by a second molecule of DMSO. The species **III** formed would evolve to afford the desired benzyl **2** together with Me_2S and regenerated the catalyst.



Scheme 1. Proposed pathway for the oxidation of arylalkynes **1**.

In order to activate better the alkyne function, the Lewis acidity of the Fe(III) catalyst should be increased. For that purpose, an additional experiment was achieved by introducing 30 mol % of trifluoromethanesulfonic acid (TfOH) to the reaction mixture (**1a**, 10 mol % of $FeBr_3$, DMSO). We were pleased to observe that under classical thermal conditions (140 °C), the oxidation proceeded in only 1 h and with a good yield (71%). In order to determine the positive influence of TfOH associated with $FeBr_3$, we performed the oxidation without $FeBr_3$, as control. Total disappearance of **1a** was observed but after 10 h of reaction. It is reasonable to think that the catalytic species formed $Fe(OTf)_3$,[22] which is a stronger Lewis acid than $FeBr_3$, activates considerably the triple bond. Other attempts were achieved with various iodine salts in the place of TfOH but unfortunately failed to give **2a** in shorter reaction times. This latest oxidation reaction involving the synergetic couple TfOH and $FeBr_3$ is currently under investigation in our laboratory.

4. Conclusion

In conclusion, we have developed a simple and efficient process for oxidation of arylalkynes using DMSO and catalytic $FeBr_3$. The use of friendly non-toxic catalytic $FeBr_3$, short reaction times, high to excellent yields, low cost and easy preparation are the obvious advantages of the present method. Under classical thermal conditions, we have demonstrated that the tandem $FeBr_3$–DMSO can be used to prepare benzil derivatives in reasonable reaction times and satisfactory yields. The microwave-assisted procedure allows for the rapid synthesis of various benzils, 20 min compared to 10 h by conventional methods. The experimental microwaves experiments described in this paper are well established and controlled and can be safely and beneficially reproduced.

5. Experimental

5.1. Materials

All glasswares were oven-dried at 140 °C and all reactions were conducted under an argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium–benzophenone ketyl. Triethylamine (TEA) was distilled from potassium hydroxide under argon prior to use.

5.2. Instrumentation

All microwave experiments were performed using an Emrys Optimizer in 2–5 mL Pyrex reaction vessels. Each contained a Teflon stir bar and Teflon coated reaction vessel cap.

The compounds were all identified by usual physical methods, i.e., ^{1}H NMR, ^{13}C NMR, IR and elemental analysis. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ with a Bruker AC 200 or Bruker ARX 400. ^{1}H NMR chemical shifts are reported in parts per million from an internal standard TMS or of residual chloroform (7.27 ppm). The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), tt (triplet of triplet). ^{13}C NMR chemical shifts are reported in parts per million from the central peak of deuteriochloroform (77.14). IR spectra were measured on a Bruker Vector 22 spectrophotometer (neat, cm^{-1}). Elemental analyses were performed with a Perkin–Elmer 240 analyzer. Mass spectra were obtained with a LCT Micromass spectrometer. Analytical TLC were performed on Merck precoated silica gel 60F plates. Merck silica gel 60 (230–400 mesh) was used for column chromatography. Melting points (mp) were recorded on a Büchi B-450 apparatus and were uncorrected.

5.3. General procedure for the preparation of arylalkynes from aryl halides

All arylalkynes except **1o** were known compounds and have been prepared according to the following procedure.

5.3.1. 2,2-Diethyl-propionic acid-4-phenylethynyl-phenyl ester 1o. To a mixture of 2,2 dimethyl-propionic acid-4-iodo-phenyl ester (303 mg; 1 mmol), $PdCl_2(PPh_3)_2$ (35.1 mg; 0.05 mmol), CuI (19.1 mg; 0.1 mmol) and TEA (404.8 mg; 4.0 mmol) in THF (10 mL), a solution of phenylacetylene (132.6 mg; 1.2 mmol) was added dropwise under an argon atmosphere. The mixture was stirred at room temperature for overnight. Then Et_2O (20 mL) was added to the crude and the mixture was filtered over a short pad of Celite. The organic layer was washed twice with brine (5 mL), separated, dried over $MgSO_4$, filtered and concentrated. Resulting residue was further purified by flash chromatography.

Yield: 95%; mp: 92 °C; TLC: R_f 0.61 (cyclohexane/EtOAc, 90/10, SiO_2). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52%. Found: C, 81.87; H, 6.47. IR (neat) ν_{max}/cm^{-1}: 2971, 1743, 1593, 1506, 1479, 1445, 1396, 1369, 1275, 1235, 1197, 1160, 1140, 1115, 1033, 1013, 954, 919, 897, 859, 842, 801. ^{1}H NMR for **1o** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.62–7.51 (m, 4H), 7.36–7.33 (m, 3H), 7.06 (d, 2H, J=8.7 Hz), 1.37 (s, 9H). ^{13}C NMR for **1o** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 176.7 (CO), 151.0 (C), 132.7 (2CH), 131.6 (2CH), 128.3 (2CH), 128.3 (CH), 123.2 (C), 121.6 (2CH), 120.7 (C), 89.3 (C), 88.6 (C), 39.1 (C), 27.1 ($3CH_3$).

5.4. General procedure for the preparation of benzils 2a–o from alkynes under microwave irradiation

To an Emrys Optimizer 2–5 mL Pyrex reaction vessel were added alkyne (0.5 mmol), $FeBr_3$ (15 mg; 0.05 mmol), in DMSO (2.5 mL). The reaction vessel was then placed in the Emrys Optimizer and exposed to microwave irradiation according to the following specifications: temperature: 200 °C, time (see Table 2), fixed hold time: on, sample absorption: high, pre-stirring: 60 s. After cooling to room temperature, H_2O (3 mL) was added to the crude and the mixture was extracted with EtOAc (3×2 mL). Organic layers were then washed with an aqueous saturated NH_4Cl solution, dried and concentrated. The crude mixture was then purified by column chromatography on silica gel.

5.4.1. 1-(4-Methoxyphenyl)-2-phenyl-ethane-1,2-dione 2a. Yield: 75%; mp: 65 °C; TLC: R_f 0.40 (cyclohexane/EtOAc, 80/20, SiO_2). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. Found: C, 74.81; H, 5.21. IR (neat) ν_{max}/cm^{-1}: 2938, 2842, 1666, 1649, 1594, 1569, 1509, 1450, 1422, 1320, 1303, 1268, 1214, 1182, 1162, 1110, 1020, 973, 931, 877, 841, 818, 803. ^{1}H NMR for **2a** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.98–7.92 (m, 4H), 7.69–7.66 (m, 1H), 7.52–7.44 (m, 2H), 6.96 (d, 2H, J=9 Hz), 3.87 (s, 3H). ^{13}C NMR for **2a** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.7 (CO), 193.0 (CO), 164.9 (C), 134.6 (CH), 133.7 (C), 132.2 (2CH), 129.7 (2CH), 128.8 (2CH), 125.9 (C), 114.2 (2CH), 55.5 (CH_3). m/z MS (ES+) 263.1 ($M+Na^+$).

5.4.2. 1-(2-Methoxyphenyl)-2-phenyl-ethane-1,2-dione 2b. Yield: 70%; TLC: R_f 0.63 (cyclohexane/EtOAc, 85/15, SiO_2). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. Found: C, 74.58; H, 4.95. IR (neat) ν_{max}/cm^{-1}: 2945, 1676, 1654, 1596, 1580, 1483, 1466, 1450, 1435, 1306, 1271, 1246, 1202, 1162, 1114, 1017, 875. ^{1}H NMR for **2b** ($CDCl_3$, 400 MHz, 298 K): δ, ppm 8.06 (d, 1H, J=8.0 Hz), 7.95 (d, 2H, J=8.0 Hz), 7.64–7.60 (m, 2H), 7.56 (t, 2H, J=8.0 Hz), 7.16 (t, 1H, J=8.0 Hz), 6.97 (t, 1H, J=8.0 Hz), 3.59 (s, 3H). ^{13}C NMR for **2b** ($CDCl_3$, 100 MHz, 298 K): δ, ppm 194.6 (CO), 193.5 (CO), 160.4 (C), 136.4 (CH), 133.7 (CH), 133.0 (C), 130.6 (CH), 129.3 (2CH), 128.7 (2CH), 124.0 (CH), 121.6 (CH), 112.4 (CH), 55.6 (CH_3). m/z MS (ES+) 263.0 ($M+Na^+$).

5.4.3. 1-(3-Methoxyphenyl)-2-phenyl-ethane-1,2-dione 2c. Yield: 75%; TLC: R_f 0.54 (cyclohexane/EtOAc, 80/20, SiO_2). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. Found: C, 74.88; H, 4.99. IR (neat) ν_{max}/cm^{-1}: 3074, 3010, 2838, 1658, 1592, 1484, 1467, 1453, 1429, 1337, 1321, 1298, 1259, 1203, 1174, 1157, 1079, 1033, 994, 932, 903, 874, 832, 803. ^{1}H NMR for **2c** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.87 (d, 1H, J=7.0 Hz), 7.58–7.49 (m, 1H), 7.40–7.22 (m, 5H), 7.13 (s, 1H), 7.10–7.04 (m, 1H), 3.74 (s, 3H). ^{13}C NMR for **2c** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.4 (2CO), 160.0 (C), 134.8 (CH), 134.2 (C), 133.0 (C), 130.0 (CH), 129.8 (2CH), 128.9 (2CH), 123.1 (CH), 121.8 (CH), 112.9 (CH), 55.4 (CH_3).

5.4.4. 1-Phenyl-2-(3,4,5-trimethoxyphenyl)-ethane-1,2-dione 2d. Yield: 64%; mp: 102 °C; TLC: R_f 0.48 (cyclohexane/EtOAc, 70/30, SiO_2). Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37%. Found: C, 67.91; H, 5.30. IR (neat) ν_{max}/cm^{-1}: 2932, 2834, 1664, 1581, 1504, 1460, 1450, 1413, 1343, 1317, 1283, 1233, 1180, 1157, 1129, 1076, 993, 947, 859, 819. ^{1}H NMR for **2d** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.95 (d, 2H, J=7.4 Hz), 7.66 (t, 1H, J=7.4 Hz), 7.49 (t, 2H, J=7.4 Hz), 7.11 (s, 2H), 3.93 (s, 3H), 3.85 (s, 6H). ^{13}C NMR for **2d** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.2 (CO), 193.2 (CO), 153.4 (2C), 144.2 (C), 134.7 (CH), 133.1 (C), 129.8 (2CH), 128.9 (2CH), 127.9 (C), 107.2 (2CH), 60.9 (CH_3), 56.3 ($2CH_3$). m/z MS (ES+) 323.1 ($M+Na^+$).

5.4.5. 1-(4-Methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)-ethane-1,2-dione 2e. Yield: 65%; mp: 140 °C; TLC: R_f

0.37 (cyclohexane/EtOAc, 80/20, SiO_2). Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49%. Found: C, 65.46; H, 5.59. IR (neat) ν_{max}/cm^{-1}: 2982, 1651, 1598, 1571, 1502, 1448, 1427, 1412, 1342, 1273, 1245, 1180, 1155, 1125, 1017, 998, 948, 854. ^1H NMR for **2e** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.95 (d, 2H, J=9.0 Hz), 7.23 (s, 2H), 6.98 (d, 2H, J=9.0 Hz), 3.94 (s, 3H), 3.89 (s, 3H), 3.88 (s, 6H). ^{13}C NMR for **2e** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 193.5 (CO), 192.8 (CO), 164.9 (C), 153.2 (2C), 144.1 (C), 132.3 (2CH), 128.1 (C), 126.1 (C), 114.3 (2CH), 107.2 (2CH), 60.9 (CH_3), 56.3 ($2CH_3$), 55.5 (CH_3). *m/z* MS (ES+) 353.1 ($M+Na^+$).

5.4.6. 1-Phenyl-2-*p*-tolyl-ethane-1,2-dione 2f. Yield: 61%; mp: 96 °C; TLC: R_f 0.51 (cyclohexane/EtOAc, 90/10, SiO_2). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79%. Found: C, 79.92; H, 4.81. IR (neat) ν_{max}/cm^{-1}: 1665, 1591, 1578, 1449, 1325, 1209, 1173, 998, 874. ^1H NMR for **2f** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.97 (d, 4H, J=8.0 Hz), 7.67 (m, 2H), 7.52 (d, 4H, J=8.0 Hz). ^{13}C NMR for **2f** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.0 (2CO), 134.7 (2CH), 132.9 (2CH), 129.8 (4CH), 128.9 (4CH). *m/z* MS (ES+) 233.0 ($M+Na^+$).

5.4.7. 1,2-Diphenyl-ethane-1,2-dione (benzil) 2g. Yield: 73%; TLC: R_f 0.27 (cyclohexane/EtOAc, 90/10, SiO_2). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39%. Found: C, 80.26; H, 5.31. IR (neat) ν_{max}/cm^{-1}: 1667, 1603, 1572, 1475, 1449, 1410, 1324, 1287, 1208, 1173, 1120, 1019, 879, 828. ^1H NMR for **2g** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.96 (d, 2H, J=7.3 Hz), 7.86 (d, 2H, J=8.0 Hz), 7.64 (t, 1H, J=7.3 Hz), 7.49 (t, 2H, J=7.3 Hz), 7.30 (d, 2H, J=8.0 Hz), 2.42 (s, 3H). ^{13}C NMR for **2g** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.7 (CO), 194.2 (CO), 146.1 (C), 134.7 (CH), 133.1 (C), 130.6 (C), 129.9 (2CH), 129.8 (2CH), 129.7 (2CH), 128.9 (2CH), 21.8 (CH_3).

5.4.8. 1-(4-Chlorophenyl)-2-phenyl-ethane-1,2-dione 2h. Yield: 75%; mp: 77 °C; TLC: R_f 0.35 (cyclohexane/EtOAc, 70/30, SiO_2). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71%. Found: C, 69.01; H, 3.75. IR (neat) ν_{max}/cm^{-1}: 1663, 1584, 1487, 1450, 1402, 1321, 1208, 1172, 1113, 1093, 1013, 873, 833. ^1H NMR for **2h** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.98–7.90 (m, 3H), 7.70–7.63 (m, 2H), 7.55–7.40 (m, 4H). ^{13}C NMR for **2h** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 193.8 (CO), 193.0 (CO), 141.5 (C), 135.0 (CH), 132.8 (C), 131.4 (C), 131.2 (2CH), 129.9 (2CH), 129.4 (2CH), 129.0 (2CH).

5.4.9. 1-(4-Bromophenyl)-2-phenyl-ethane-1,2-dione 2i. Yield: 72%; mp: 87 °C; TLC: R_f 0.61 (cyclohexane/EtOAc, 94/6, SiO_2). Anal. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%. Found: C, 58.02; H, 3.03. IR (neat) ν_{max}/cm^{-1}: 1662, 1578, 1483, 1450, 1398, 1321, 1204, 1172, 1113, 1069, 1024, 1009, 870, 829. ^1H NMR for **2i** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 7.96 (d, 2H, J=7.4 Hz), 7.84 (d, 2H, J=8.6 Hz), 7.68–7.64 (m, 3H), 7.52 (t, 2H, J=7.4 Hz). ^{13}C NMR for **2i** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 193.8 (CO), 193.2 (CO), 135.0 (CH), 132.8 (C), 132.4 (2CH), 131.8 (C), 131.2 (2CH), 130.4 (C), 129.9 (2CH), 129.0 (2CH).

5.4.10. 1-(4-Nitrophenyl)-2-phenyl-ethane-1,2-dione 2j. Yield: 72%; mp: 141 °C; TLC: R_f 0.27 (cyclohexane/EtOAc, 50/50, SiO_2). Anal. Calcd for $C_{14}H_9NO_4$: C, 65.88; H, 3.55; N, 5.49%. Found: C, 65.81; H, 3.54; N, 5.48. IR (neat) ν_{max}/cm^{-1}: 1660, 1594, 1523, 1450, 1344, 1200, 1170, 1110, 883, 859, 839. ^1H NMR for **2j** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 8.36 (d, 2H, J=8.7 Hz), 8.17 (d, 2H, J=8.7 Hz), 7.99 (dd, 2H, J=7.9, 1.0 Hz), 7.71 (tt, 1H, J=7.9, 1.0 Hz), 7.55 (t, 2H, J=7.9 Hz). ^{13}C NMR for **2j** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 192.8 (CO), 192.0 (CO), 151.1 (C), 137.3 (C), 135.4 (CH), 132.4 (C), 130.9 (2CH), 130.0 (2CH), 129.2 (2CH), 129.0 (2CH).

5.4.11. 1-(4-Cyanophenyl)-2-phenyl-ethane-1,2-dione 2k. Yield: 46%; mp: 111.5 °C; TLC: R_f 0.42 (cyclohexane/EtOAc, 90/10, SiO_2). Anal. Calcd for $C_{15}H_9NO_2$: C, 76.59; H, 3.86; N, 5.95%. Found: C, 76.38; H, 3.61; N, 5.85. IR (neat) ν_{max}/cm^{-1}: 3072, 2226, 1679, 1658, 1593, 1579, 1450, 1405, 1321, 1297, 1206, 1171, 1116, 999, 971, 879, 843, 800. ^1H NMR for **2k** ($CDCl_3$, 200 MHz, 298 K): δ, ppm 8.08 (d, 2H, J=8.0 Hz), 7.96 (d, 2H, J=8.6 Hz), 7.80 (d, 2H, J=8.6 Hz), 7.69 (t, 1H, J=8.0 Hz), 7.53 (t, 2H, J=8.0 Hz). ^{13}C NMR for **2k** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 193.0 (CO), 192.4 (CO), 135.9 (C), 135.3 (CH), 132.7 (C), 132.5 (2CH), 130.2 (2CH), 130.0 (2CH), 129.2 (2CH), 117.9 (C), 117.5 (C).

5.4.12. 2-(2-Oxo-2-phenylacetyl)-benzonitrile 2l. Yield: 43%; mp: 67.5 °C; TLC: R_f 0.36 (cyclohexane/EtOAc, 70/30, SiO_2). Anal. Calcd for $C_{15}H_9NO_2$: C, 76.59; H, 3.86; N, 5.95%. Found: C, 76.47; H, 3.79; N, 5.92. IR (neat) ν_{max}/cm^{-1}: 3067, 2926, 2227, 1668, 1592, 1570, 1489, 1451, 1367, 1318, 1212, 1180, 1124, 1017, 951, 888, 869. ^1H NMR for **2l** ($CDCl_3$, 400 MHz, 298 K): δ, ppm 8.05 (d, 2H, J=8.4 Hz), 7.96–7.92 (m, 2H), 7.82–7.71 (m, 3H), 7.58 (t, 2H, J=8.4 Hz). ^{13}C NMR for **2l** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 192.1 (CO), 191.2 (CO), 135.6 (CH), 135.3 (CH), 135.1 (C), 134.0 (CH), 132.7 (CH), 132.4 (C), 132.3 (CH), 130.1 (2CH), 129.1 (2CH), 117.0 (C), 117.9 (CN), 112.0 (C).

5.4.13. 1-(4-Hydroxyphenyl)-2-phenyl-ethane-1,2-dione 2m. Yield: 51%; mp: 125 °C; TLC: R_f 0.50 (cyclohexane/EtOAc, 70/30, SiO_2). Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46%. Found: C, 74.18; H, 4.32. IR (neat) ν_{max}/cm^{-1}: 3385, 1672, 1648, 1595, 1562, 1515, 1449, 1302, 1204, 1157, 1047, 998, 878, 845. ^1H NMR for **2m** ($CDCl_3$, 400 MHz, 298 K): δ, ppm 7.88 (d, 2H, J=7.3 Hz), 7.80 (d, 2H, J=8.6 Hz), 7.57 (t, 1H, J=7.3 Hz), 7.42 (t, 2H, J=7.3 Hz), 6.82 (d, 2H, J=8.6 Hz), 6.80–6.10 (m, 1H). ^{13}C NMR for **2m** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 195.4 (CO), 193.6 (CO), 162.5 (C), 135.0 (CH), 133.0 (C), 132.7 (2CH), 129.9 (2CH), 129.0 (2CH), 125.6 (C), 116.1 (2CH).

5.4.14. 2,2-Dimethyl-propionic acid-4-(2-oxo-2-phenyl-acetyl)-phenyl ester 2o. Yield: 59%; mp: 87 °C; TLC: R_f 0.47 (cyclohexane/EtOAc, 90/10, SiO_2). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%. Found: C, 73.41; H, 5.79. IR (neat) ν_{max}/cm^{-1}: 2978, 1742, 1662, 1594, 1505, 1479, 1454, 1400, 1366, 1326, 1296, 1280, 1231, 1207, 1174, 1157, 1116, 1032, 1012, 997, 974, 904, 873, 804. ^1H NMR for **2o** ($CDCl_3$, 400 MHz, 298 K): δ, ppm 8.05–7.94 (m, 4H), 7.65 (tt, 1H, J=7.7, 1.4 Hz), 7.54–7.46 (m, 2H), 7.26–7.16 (m, 2H). ^{13}C NMR for **2o** ($CDCl_3$, 50 MHz, 298 K): δ, ppm 194.2 (CO), 193.2 (CO), 176.2 (OCO), 156.3

(C), 134.9 (CH), 132.9 (C), 131.5 (2CH), 130.3 (C), 129.9 (2CH), 129.0 (2CH), 122.2 (2CH), 93.2 (C), 27.0 ($3CH_3$).

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