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Copper-catalyzed synthesis of 1,3,5-triarylpentane-1,5-diones from α,β-unsaturated ketones†

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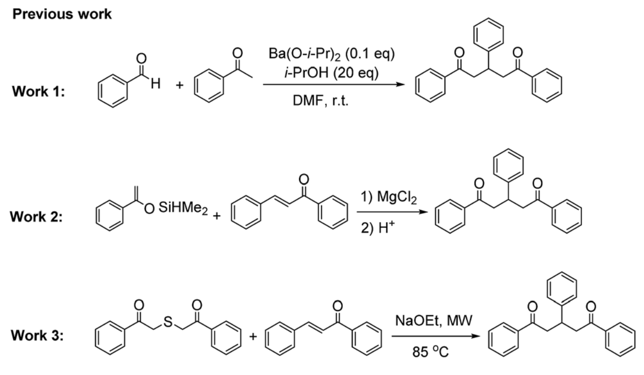
An efficient method for copper catalyzed synthesis of 1,3,5-triarylpentane-1,5-diones using α,β-unsaturated ketones as unique starting materials is described. The protocol offers several advantages such as simple, inexpensive reagents, mild reaction conditions and simple work-up procedure.

Introduction

Michael addition of α,β-unsaturated carbonyl compounds as substrates is a beneficial method to obtain 1,5-dicarbonyl compounds,[1] which are important synthetic building blocks and have attracted the attention of many organic chemists.

The reported synthetic methods for 1,3,5-triarylpentane-1,5-diones (Scheme 1) include: (1) using benzaldehyde and acetophenone as the raw materials by Michael addition reaction;[2] (2) using α,β-unsaturated ketones (or benzaldehyde) and silyl enol ethers as the starting materials in the presence of magnesium chloride (or sodium hydroxide);[3] (3) using α,β-unsaturated ketones and diphenacyl sulfides as the starting materials under microwave irradiation.[4] However, some of these methods use air- and moisture-sensitive materials and require manipulation using complex techniques; some of these methods use materials with unpleasant odors that often cause environment pollution. In this work, a novel method for the synthesis of 1,3,5-triarylpentane-1,5-diones is reported using α,β-unsaturated ketones as the unique starting materials and inexpensive cuprous iodide as the catalyst (Scheme 2).



Scheme 1 The common synthetic methods for 1,3,5-triphenylpentane-1,5-dione.

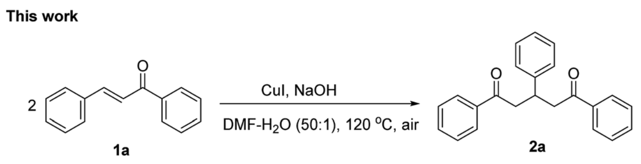
Results and discussion

Initially, the synthesis of 1,3,5-triarylpentane-1,5-diones were investigated using chalcone (**1a**) as a selected substrate. The reaction was performed under the conditions of a wide range of catalysts, bases and solvents.

It was found that the reaction desired to proceed under an appropriate catalyst (Table 1), and the copper(I) salts, such as CuCl, CuBr, CuI, CuOTf and CuCN, were revealed certain activities for the synthesis of 1,3,5-triphenylpentane-1,5-dione (**2a**) (Table 1, entries 2–6). Among them, the best yield was obtained from CuI as a catalyst (Table 1, entry 4). However, copper(II) salts and other metal compounds tested had no activations for the reaction (Table 1, entries 7–9).

The bases were also indispensable for the reaction, and NaOH, KOH, Ca(OH)$_2$, Na$_2$CO$_3$, *t*-BuONa and *t*-BuOK were tested for the reaction using CuI as a catalyst. It was found that these bases had certain effects for the reaction (Table 1, entries 4, 10–14). Among them, NaOH was the most suitable base for the reaction (Table 1, entry 4).

Meanwhile the solvents also played an important role in the reaction. It was found that the yield of **2a** could be significantly



Scheme 2 Synthesis of 1,3,5-triphenylpentane-1,5-dione from α,β-unsaturated ketone.

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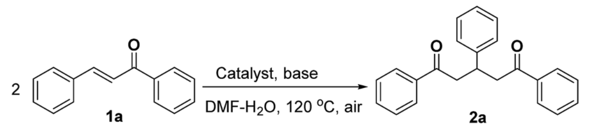
† Electronic supplementary information (ESI) available: Copies of IR, ^{1}H and ^{13}C NMR spectra of all compounds. See DOI: 10.1039/c5ra09155a

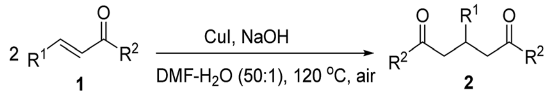
Table 1 The effect of reaction conditions on the yield of **2a**[a]

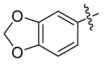
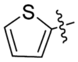


Entry	Catalyst	Base	Yield[b] (%)
1	None	NaOH	0
2	CuCl	NaOH	41
3	CuBr	NaOH	55
4	CuI	NaOH	83
5	CuOTf	NaOH	62
6	CuCN	NaOH	56
7	$Cu(OAc)_2$	NaOH	0
8	$FeCl_2$	NaOH	0
9	AgCl	NaOH	0
10	CuI	$Ca(OH)_2$	45
11	CuI	Na_2CO_3	42
12	CuI	KOH	70
13	CuI	*t*-BuONa	78
14	CuI	*t*-BuOK	76
15	CuI	None	0

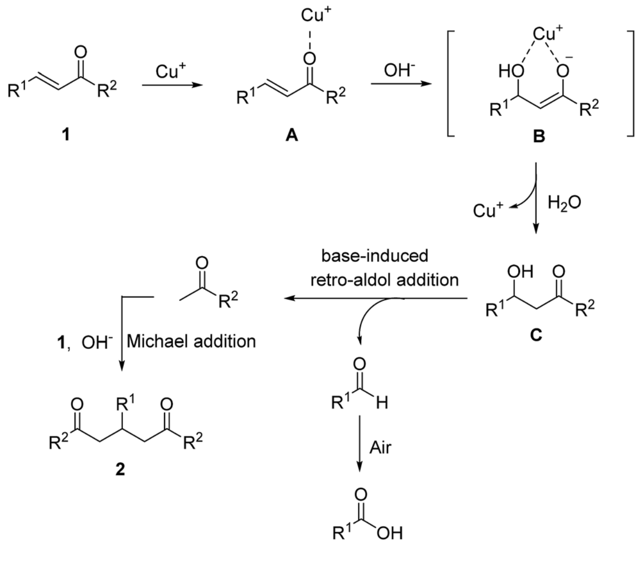
[a] Reaction condition: **1a** (0.2 mmol), base (0.6 mmol), and catalyst (0.02 mmol) were stirred at 120 °C in DMF–H_2O (50 : 1) for 8 h under air. [b] Isolated yields.

Table 2 Scope of α,β-unsaturated ketones[a]



Entry	R^1	R^2	Yield[b] (%)	Mp (°C)
1	C_6H_5	C_6H_5	83	63–65
2	$4\text{-}CH_3C_6H_4$	C_6H_5	72	102–104
3	$4\text{-}CH_3OC_6H_4$	C_6H_5	70	100–102
4	$2\text{-}CH_3OC_6H_4$	C_6H_5	68	106–108
5	$4\text{-}ClC_6H_4$	C_6H_5	65	96–98
6	$2\text{-}ClC_6H_4$	C_6H_5	67	100–102
7	$4\text{-}BrC_6H_4$	C_6H_5	58	90–92
8	C_6H_5	$4\text{-}CH_3C_6H_4$	76	104–106
9	C_6H_5	$4\text{-}CH_3OC_6H_4$	74	105–107
10	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	78	88–90
11	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	80	Oil
12	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3OC_6H_4$	78	Oil
13	$4\text{-}FC_6H_4$	$4\text{-}CH_3C_6H_4$	77	108–110
14	$2,4\text{-}Cl_2C_6H_3$	$3\text{-}CH_3OC_6H_4$	71	Oil
15		$4\text{-}ClC_6H_4$	73	86–88
16		C_6H_5	63	89–91

[a] Reaction condition: α,β-unsaturated ketones (0.2 mmol), NaOH (0.6 mmol), and CuI (0.02 mmol) in DMF (3 mL) and H_2O (0.06 mL) were stirred at 120 °C for 8 h under air. [b] Isolated yields.



Scheme 3 Plausible mechanism.

elevated if addition of some water to organic solvents, such as DMF and DMSO. However, the highest yield for **2a** was obtained in DMF–H_2O (50 : 1). Other solvents, such as 1,4-dioxane, PhMe, MeCN and EtOH in the presence of a certain amount of water were found no effects on the reaction.

In addition, it was worthy of mentioning that keeping the reaction under air condition at 120 °C were also an essential condition for the reaction.

Based on the above findings, a series of α,β-unsaturated ketones were investigated to synthesize 1,3,5-triarylpentane-1,5-diones using CuI as a catalyst and NaOH as a base in DMF–H_2O (50 : 1) (Table 2). It was found that α,β-unsaturated ketones with electron-donating (CH_3, CH_3O) or electron-withdrawing (F, Cl, Br) groups on the aromatic rings could be successfully converted to the corresponding products in good to excellent yields. And the substituent groups at *o*-, *m*-, *p*-position on the aromatic rings did not show strong steric effects. In addition, α,β-unsaturated ketones bearing heterocyclyl such as thiophen-2-yl could also converted into the corresponding product in good yield (Table 2, entry 16).

A plausible mechanism was proposed for the synthesis of 1,3,5-triarylpentane-1,5-diones (Scheme 3). First, α,β-unsaturated ketones **1** were coordinated with Cu(I) to form Cu(I) complexes **A**. Complexes **A** were attacked by the hydroxide ion in a conjugate fashion to give the intermediates **B**. **B** were protonated to form β-hydroxy ketones **C**.[5] The base-induced retro-aldol reactions of **C** would provide the corresponding benzaldehydes and acetophenones. The resulting acetophenones could undergo base-catalyzed conjugate additions to **1** to yield the observed compounds **2**. And the benzaldehydes subsequently were oxidized by air in the system to benzoic acids, which could reduce the concentration of benzaldehydes and render the reaction equilibrium favorable to the formation of **2**.

Conclusions

A novel method for the synthesis of 1,3,5-triarylpentane-1,5-diones using α,β-unsaturated ketones as unique starting materials and copper(I) as a catalyst under air condition has been developed. The advantages of this protocol are the use of inexpensive and non-toxic raw materials, mild conditions and simple work-up procedure.

Experimental

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained with Mercury-400 BB or Mercury-600BB instrument using CDCl$_3$ as solvent and Me$_4$Si as the internal standard. Melting points were observed in an electrothermal melting point apparatus. α,β-Unsaturated ketones were prepared according to literature procedure.[6]

The general procedure for the preparation of 1,3,5-triarylpentane-1,5-diones

The mixture of α,β-unsaturated ketones (0.2 mmol), NaOH (0.6 mmol) and CuI (0.02 mmol) in DMF (3 mL) and H$_2$O (0.06 mL) was stirred under air at 120 °C for 8 h. After the completion of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate and washed with saturated sodium carbonate solution. The resulting organic phase was dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ether and ethyl acetate (30 : 1) as eluent to give pure product. The analytical data for products are given below.

1,3,5-Triphenylpentane-1,5-dione (2a)

Gray solid; Mp: 63–65 °C; IR (KBr, cm^{-1}): ν 1684; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, J = 7.2 Hz, 4H, ArH), 7.53–7.57 (m, 2H, ArH), 7.42–7.47 (m, 4H, ArH), 7.28 (d, J = 13.6 Hz, 4H, ArH), 7.19–7.20 (m, 1H, ArH), 4.06–4.11 (m, 1H, CH), 3.55 (dd, J = 7.2, 16.8 Hz, 2H, CH$_2$), 3.37 (d, J = 6.8, 16.4 Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.5, 143.8, 137.0, 133.0, 128.6, 128.5, 128.1, 127.5, 126.7, 44.9, 37.2.

1,5-Diphenyl-3-*p*-tolylpentane-1,5-dione (2b)

White solid; Mp: 102–104 °C; IR (KBr, cm^{-1}): ν 1674; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, J = 7.6 Hz, 4H, ArH), 7.52–7.57 (m, 2H, ArH), 7.42–7.46 (m, 4H, ArH), 7.17 (d, J = 6.8 Hz, 2H, ArH), 7.08 (d, J = 7.2 Hz, ArH), 4.02–4.05 (m, 1H, CH), 3.48 (dd, J = 6.8, 16.4 Hz, 2H, CH$_2$), 3.32 (dd, J = 6.8, 16.4 Hz, 2H, CH$_2$), 2.28 (s, 1H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.6, 140.7, 136.9, 136.1, 133.0, 129.2, 128.5, 128.1, 127.2, 45.0, 36.8, 21.0.

3-(4-Methoxyphenyl)-1,5-diphenylpentane-1,5-dione (2c)

White solid; Mp: 100–102 °C; IR (KBr, cm^{-1}): ν 1677; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, J = 7.6 Hz, 4H, ArH), 7.53–7.56 (m, 2H, ArH), 7.42–7.46 (m, 4H, ArH), 7.19 (d, J = 8.4 Hz, 2H, ArH), 6.81 (d, J = 8.0 Hz, 2H, ArH), 4.00–4.04 (m, 1H, CH), 3.76 (s, 3H, OCH$_3$), 3.47 (dd, J = 6.8, 16.4 Hz, 2H, CH$_2$), 3.31 (dd, J = 7.2, 16.8 Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.7, 158.2, 137.0, 135.8, 133.0, 128.5, 128.4, 128.1, 114.0, 55.2, 45.1, 36.5.

3-(2-Methoxyphenyl)-1,5-diphenylpentane-1,5-dione (2d)

White solid; Mp: 106–108 °C; IR (KBr cm^{-1}): ν 1680; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, J = 7.2 Hz, 4H, ArH); 7.52–7.54 (m, 2H, ArH); 7.43–7.46 (m, 4H, ArH); 7.15–7.30 (m, 2H, ArH); 6.82–6.89 (m, 2H, ArH); 4.33–4.36 (m, 1H, CH); 3.77 (s, 3H, OCH$_3$); 3.41–3.53 (m, 4H, 2CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 199.1, 157.0, 137.0, 132.8, 131.3, 128.4, 128.1, 127.6, 120.6, 110.7, 55.1, 43.0, 32.7.

3-(4-Chlorophenyl)-1,5-diphenylpentane-1,5-dione (2e)

Yellow solid; Mp: 96–98 °C; IR (KBr, cm^{-1}): ν 1674; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, J = 7.2 Hz, 4H, ArH), 7.53–7.57 (m, 2H, ArH), 7.42–7.46 (m, 4H, ArH), 7.22–7.23 (m, 4H, ArH), 4.04–4.07 (m, 1H, CH), 3.48 (dd, J = 5.6, 16.8 Hz, 2H, CH$_2$), 3.33 (dd, J = 6.0, 16.0 Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.1, 142.3, 136.8, 133.1, 132.3, 128.9, 128.7, 128.6, 128.0, 44.7, 36.5.

3-(2-Chlorophenyl)-1,5-diphenylpentane-1,5-dione (2f)

Yellow solid; Mp: 100–102 °C; IR (KBr, cm^{-1}): ν 1677; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (d, J = 7.6 Hz, 4H, ArH), 7.50–7.54 (m, 2H, ArH), 7.39–7.43 (m, 4H, ArH), 7.30–7.33 (m, 2H, ArH), 7.14–7.18 (m, 1H, ArH), 7.08–7.11 (m, 1H, ArH), 4.48–4.55 (m, 1H, CH), 3.51 (dd, J = 7.2, 17.2 Hz, CH$_2$), 3.43 (dd, J = 6.8, 17.2 Hz, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.3, 140.8, 136.8, 133.7, 133.1, 130.0, 128.5, 128.4, 128.1, 127.7, 127.0, 42.9, 34.0.

3-(4-Bromophenyl)-1,5-diphenylpentane-1,5-dione (2g)

Red solid; Mp: 90–92 °C; IR (KBr, cm^{-1}): ν 1674; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, J = 6.8 Hz, 4H, ArH), 7.55–7.58 (m, 2H, ArH), 7.44–7.47 (m, 4H, ArH), 7.39 (d, J = 6.8 Hz, 2H, ArH), 7.18 (d, J = 6.8 Hz, ArH), 4.04–4.07 (m, 1H, CH), 3.49 (dd, J = 6.8, 16.8 Hz, 2H, CH$_2$), 3.33 (dd, J = 6.0, 16.8 Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.1, 142.8, 136.8, 133.2, 131.6, 129.3, 128.6, 128.1, 120.4, 44.6, 36.5.

1,5-Bis-(4-methoxyphenyl)-3-phenylpentane-1,5-dione (2h)

Yellow solid; Mp: 104–106 °C; IR (KBr, cm^{-1}): ν 1680; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, J = 6.0 Hz, 4H, ArH), 7.17–7.27 (m, 9H, ArH), 4.03–4.06 (m, 1H, CH), 3.45 (dd, J = 6.8, 16.4 Hz, 2H, CH$_2$), 3.30 (dd, J = 4.8, 14.4 Hz, 2H, CH$_2$), 2.39 (m, 6H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 198.2, 143.9, 143.8, 134.3, 129.2, 128.5, 128.2, 127.4, 126.5, 44.8, 37.2, 21.6.

1,5-Bis(4-methoxyphenyl)-3-phenylpentane-1,5-dione (2i)

White solid; Mp: 105–107 °C; IR (KBr, cm^{-1}): ν 1670; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.93 (d, J = 8.4 Hz, 4H, ArH), 7.24–7.26 (m, 4H, ArH), 7.15–7.17 (m, 1H, ArH), 6.91 (d, J = 9.0 Hz, ArH), 4.0–4.05 (m, 1H, CH), 3.84 (s, 6H, OCH$_3$), 3.42 (dd, J = 7.2, 16.2 Hz, 2H, CH$_2$), 3.27 (dd, J = 6.6, 16.2 Hz, 2H, CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 197.1, 163.4, 144.0, 130.4, 130.0, 128.5, 127.4, 126.5, 113.6, 55.4, 44.6, 37.6.

1,3,5-Tri-*p*-tolylpentane-1,5-dione (2j)

Yellow solid; Mp: 88–90 °C; IR (KBr, cm^{-1}): ν 1674; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, $J = 7.6$ Hz, 4H, ArH), 7.23 (d, $J = 7.6$ Hz, 4H, ArH), 7.16 (d, $J = 7.2$ Hz, 2H, ArH), 7.07 (d, $J = 7.2$ Hz, 2H, ArH), 3.99–4.02 (m, 1H, CH), 3.43 (dd, $J = 7.2$, 16.4 Hz, 2H, CH_2), 3.28 (dd, $J = 6.8$, 16.4 Hz, 2H, CH_2), 2.36 (s, 6H, CH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 143.7, 140.9, 136.0, 134.5, 129.2, 129.2, 128.2, 127.2, 44.9, 37.0, 21.5, 20.9.

1,3,5-Tris(4-methoxyphenyl)pentane-1,5-dione (2k)

Yellow liquid; IR (KBr, cm^{-1}): ν 1670; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 6.8$ Hz, 4H, ArH), 7.18 (d, $J = 6.8$ Hz, 2H, ArH), 6.89 (d, $J = 6.8$ Hz, 4H, ArH), 6.79 (d, $J = 6.8$ Hz, 2H, ArH), 3.97–4.00 (m, 1H, CH), 3.83 (s, 6H, OCH_3); 3.73 (s, 3H, OCH_3), 3.40 (dd, $J = 6.4$, 16.0 Hz, 2H, CH_2), 3.23 (dd, $J = 5.6$, 15.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 163.4, 158.1, 136.0, 130.4, 130.1, 128.4, 113.9, 113.7, 55.4, 55.1, 44.9, 37.0.

1,5-Bis(4-methoxyphenyl)-3-*p*-tolylpentane-1,5-dione (2l)

Yellow liquid; IR (KBr, cm^{-1}): ν 1670; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 7.6$ Hz, 4H, ArH), 7.16 (d, $J = 6.8$ Hz, 2H, ArH), 7.07 (d, $J = 7.2$ Hz, 2H, ArH), 6.90 (d, $J = 7.2$ Hz, 4H, ArH), 3.98–4.01 (m, 1H, CH), 3.83 (s, 6H, OCH_3), 3.42 (dd, $J = 6.8$, 16.0 Hz, 2H, CH_2), 3.24 (dd, $J = 6.4$, 16.0 Hz, 2H, ArH), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 163.4, 140.9, 136.0, 130.4, 130.1, 129.2, 127.3, 113.7, 55.4, 44.8, 37.3, 21.0.

3-(4-Fluorophenyl)-1,5-di-*p*-tolylpentane-1,5-dione (2m)

Yellow solid; Mp: 108–110 °C; IR (KBr, cm^{-1}): ν 1680; ^1H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, $J = 8.4$ Hz, 4H, ArH), 7.22–7.25 (m, 6H, ArH), 6.91–6.94 (m, 2H, ArH), 4.01–4.06 (m, 1H, CH), 3.43 (dd, $J = 7.2$, 16.8 Hz, 2H, CH_2), 3.27 (dd, $J = 7.8$, 16.8 Hz, 2H, CH_2), 2.38 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 193.3, 139.2, 134.9, 134.8, 129.6, 124.5, 124.2, 124.1, 123.5, 110.6, 110.5, 40.1, 31.9, 16.8.

3-(2,4-Dichlorophenyl)-1,5-bis-(3-methoxyphenyl)pentane-1,5-dione (2n)

Yellow liquid; IR (KBr, cm^{-1}): ν 1680; ^1H NMR (600 MHz, $CDCl_3$): δ 7.53–7.55 (m, 2H, ArH), 7.46–7.47 (m, 2H, ArH), 7.33–7.36 (m, 3H, ArH), 7.24–7.25 (m, 1H, ArH), 7.15–7.17 (m, 1H, ArH), 7.08–7.10 (m, 2H, ArH), 4.45–4.50 (m, 1H, CH), 3.82 (s, 6H, $2OCH_3$), 3.49 (dd, $J = 7.2$, 17.4 Hz, 2H, CH_2), 3.40 (dd, $J = 7.2$, 17.4 Hz, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.1, 160.0, 139.7, 138.1, 134.6, 133.0, 130.0, 129.9, 129.5, 127.5, 121.0, 120.2, 112.4, 55.7, 43.1, 33.7.

3-Benzo[1,3]dioxol-5-yl-1,5-bis(4-chlorophenyl)pentane-1,5-dione (2o)

Yellow solid; Mp: 86–88 °C; IR (KBr, cm^{-1}): ν 1681; ^1H NMR (600 MHz, $CDCl_3$): δ 7.87 (d, $J = 8.4$ Hz, 4H, ArH), 7.41 (d, $J = 8.4$ Hz, 4H, ArH), 6.74 (s, 1H, ArH), 6.67 (s, 2H, ArH), 5.88 (s, 2H, CH_2), 3.90–3.95 (m, 1H, CH), 3.39 (dd, $J = 7.2$, 16.8 Hz, 2H, CH_2), 3.23 (dd, $J = 7.2$, 16.8 Hz, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.2, 147.8, 146.3, 139.6, 137.2, 135.1, 129.5, 128.9, 120.4, 108.3, 107.7, 100.9, 45.0, 37.0.

1,5-Diphenyl-3-thiophen-2-yl-pentane-1,5-dione (2p)

Gray solid; Mp: 89–91 °C; IR (KBr, cm^{-1}): ν 1686; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, $J = 7.6$ Hz, 4H, ArH), 7.53–7.55 (m, 2H, ArH), 7.43–7.46 (m, 4H, ArH), 7.10–7.11 (m, 1H, ThH), 6.88–6.89 (m, 2H, ThH), 4.42–4.45 (m, 1H, CH), 3.53 (dd, $J = 6.8$, 16.8 Hz, 2H, CH_2), 3.42 (dd, $J = 6.8$, 16.8 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 147.4, 136.8, 133.1, 128.5, 128.1, 126.6, 124.2, 123.2, 45.5, 23.4.

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Notes and references

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