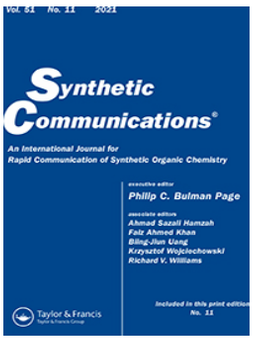

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# Copper-catalyzed synthesis of phenolic compounds with DMSO as the methylene source

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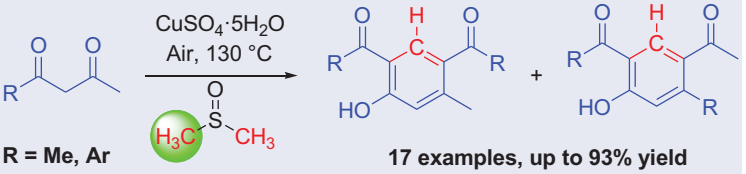
**ABSTRACT**

The application of DMSO as an ideal source of carbon is highly attractive. A simple and novel protocol has been developed for the synthesis of phenolic compounds via $CuSO_4·5H_2O$-catalyzed cyclization of 1,3-dicarbonyl compounds with DMSO. It was found that the unsymmetrical 1,3-dicarbonyl compounds always gave a mixture of two isomeric products. In addition, the deuterium-labeling experiments revealed that the C2 in benzene rings resulted from DMSO.

**GRAPHICAL ABSTRACT**

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**KEYWORDS**
$CuSO_4·5H_2O$; cyclization; 1,3-dicarbonyl; DMSO; phenolic compounds

## Introduction

Dimethyl sulfoxide (DMSO) as a cheap, relative stability, low toxicity, and common polar solvent has been widely used in organic synthesis.[1] Chemists have developed useful applications of DMSO as an oxidant, ligand, and oxygen source.[2] On the other hand, DMSO is also an important and multipurpose building block for the construction of organic frameworks. In the past decade, DMSO has been reported as the source of $=CH_2$,[3] =CH–,[4] –SMe,[3b,5] SOMe,[6] $SO_2Me$,[3b,7] $–CH_2SMe$,[8] –CHO,[9] –CN,[10] –Me,[5c,11] and $–CH_2–$[12] fragments. Although DMSO has successfully served as a carbon source, the application of DMSO for construction of more complex compounds continues to attract the interest of chemists.

Phenol and its derivatives are found in numerous natural products and drugs. In particular, biologically active compounds with a phenol motif show excellent biological and pharmaceutical activities, such as anti-inflammatory, anti-thrombotic, anti-bacterial, anti-bleeding, antioxidant, anti-fungal, and enhanced immunity.[13] They are also applied as fundamental raw materials for the synthesis functional materials and

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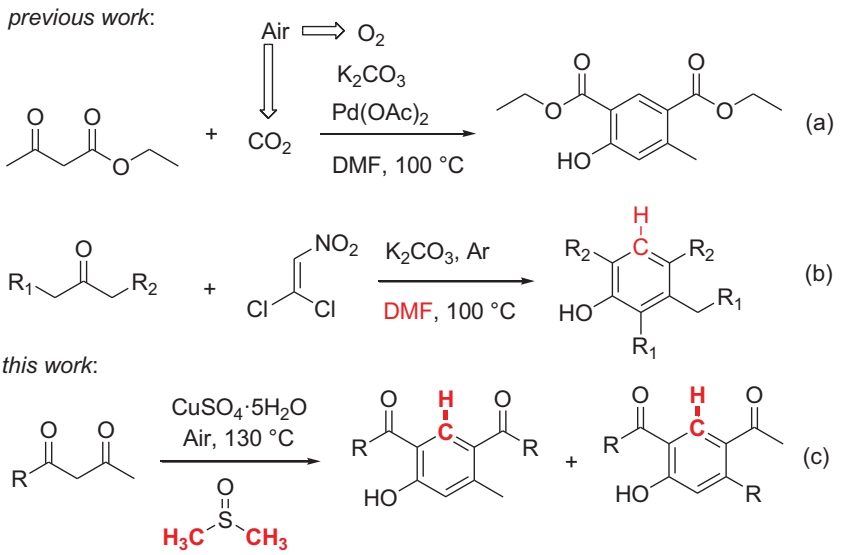


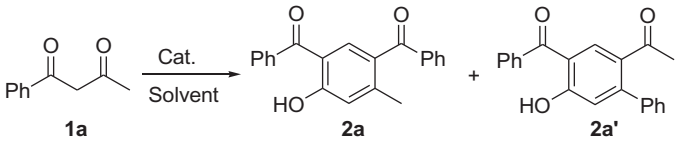

**Scheme 1.** Methods for the synthesis of phenolic compounds.

conducting polymers. Alkali melt process of aromatic sulfonate, hydrolysis of halogenated benzene, diazol method, or Friedel–Crafts reaction of phenol is the most commonly synthetic method for construction of phenol and its derivatives.[14] Recently, Liang et al. developed a novel protocol for the synthesis of phenolic compounds by $Pd(OAc)_2$-catalyzed reaction of carbonyl compound with $CO_2$ as a carbon source (Scheme 1a).[15] Li et al. described another procedure for the construction of substituted phenols via 1,1-dichloro-2-nitroethene promoted condensation of carbonyl compounds with DMF (Scheme 1b).[16] Encouraged by the results revealed in Scheme 1, we describe a novel transformation for the synthesis of phenolic compounds catalyzed by copper salts in one pot.

## Discussion

Initially, we employed 1-phenylbutane-1,3-dione **1a** as the model substrate to optimize the reaction conditions. The reaction **1a** was conducted at 130 °C in the presence of $Cu(OAc)_2$ in DMSO under air. A cyclization product **2a** was obtained in 48% yield, which an isomer product **2a′** was formed in 25% yield as a minor product (Table 1, entry 1). Further studies were screened on the catalysts. Among other copper salts such as $CuF_2$, CuO, CuI, $Cu(OTf)_2$, $CuCl_2$ and $CuSO_4·5H_2O$ were performed, $CuSO_4·5H_2O$ displayed the best reactivity and the yield of **2a** increased to 62% yield (Table 1, entries 2–7). The replacement of $CuSO_4·5H_2O$ by silver, iron, zinc, cobalt, indium and nickel salts provided low efficiency and selectivity (Table 1, entries 8–15). The reaction did not occur under the same reaction conditions in the absence of copper source (Table 1, entry 16). When increasing the amount of $CuSO_4·5H_2O$ to 20 mol%, the yield and selectivity was not significantly improved (Table 1, entry 17). However, the efficiency of this cyclization reaction decreased when the reaction was carried out at 110 °C (Table 1,

**Table 1.** Optimization of the reaction conditions.[a]




**1a** **2a** **2a'**

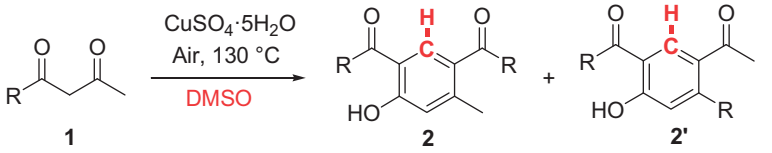
| Entry | Catalyst | Solvent | Temp (°C) | Yield (%)[b] | |
|---|---|---|---|---|---|
| | | | | **2a** | **2a′** |
| 1 | $Cu(OAc)_2$ | DMSO | 130 | 48 | 25 |
| 2 | $CuF_2$ | DMSO | 130 | – | – |
| 3 | CuO | DMSO | 130 | – | – |
| 4 | CuI | DMSO | 130 | 25 | 14 |
| 5 | $Cu(OTf)_2$ | DMSO | 130 | 52 | 22 |
| 6 | $CuCl_2$ | DMSO | 130 | Trace | – |
| 7 | $CuSO_4{\cdot}5H_2O$ | DMSO | 130 | 62 | 26 |
| 8 | $AgNO_3$ | DMSO | 130 | 12 | Trace |
| 9 | $FeCl_3$ | DMSO | 130 | 18 | 11 |
| 10 | $Fe(NO_3)_3{\cdot}9H_2O$ | DMSO | 130 | – | – |
| 11 | $ZnCl_2$ | DMSO | 130 | Trace | – |
| 12 | $Zn(OAc)_2$ | DMSO | 130 | 13 | 7 |
| 13 | $Co(OAc)_2$ | DMSO | 130 | – | – |
| 14 | $InCl_3$ | DMSO | 130 | – | – |
| 15 | $Ni(OAc)_2$ | DMSO | 130 | 20 | 9 |
| 16 | – | DMSO | 130 | – | – |
| 17[c] | $CuSO_4{\cdot}5H_2O$ | DMSO | 130 | 62 | 27 |
| 18 | $CuSO_4{\cdot}5H_2O$ | DMSO | 110 | 39 | 15 |
| 19 | $CuSO_4{\cdot}5H_2O$ | DMF | 130 | – | – |
| 20 | $CuSO_4{\cdot}5H_2O$ | $CH_3CN$ | 130 | – | – |
| 21 | $CuSO_4{\cdot}5H_2O$ | $H_2O$ | 130 | – | – |
| 22 | $CuSO_4{\cdot}5H_2O$ | Toluene | 130 | – | – |
| 23 | $CuSO_4{\cdot}5H_2O$ | 1,4-Dioxane | 130 | – | – |

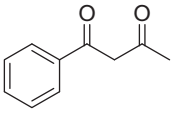
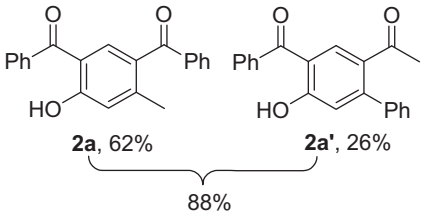
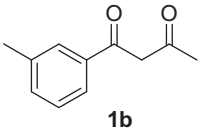
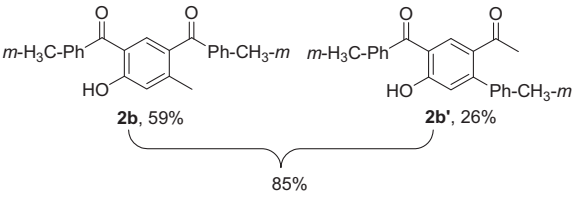
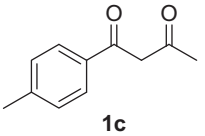
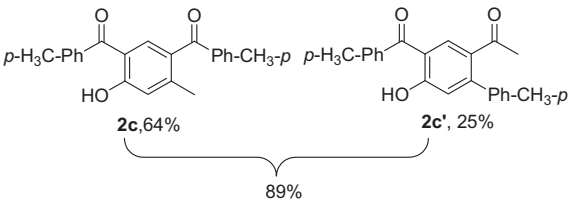
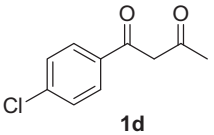
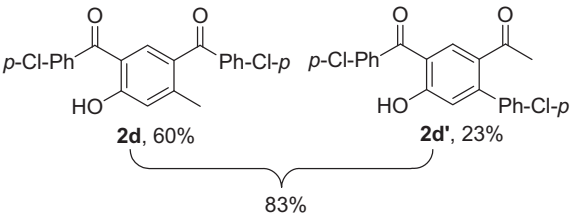
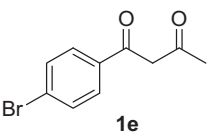
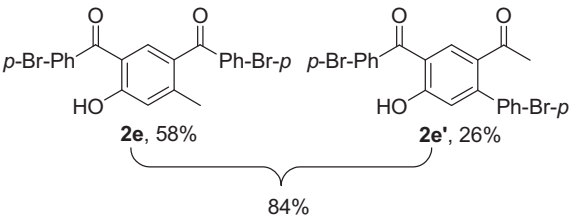
[a]Reaction conditions: **1a** (0.5 mmol) catalyst (10 mol%), solvent (2 mL), 130 °C, 6 h.
[b]Isolated yield.
[c]$CuSO_4{\cdot}5H_2O$ (20 mol%) was used.

entry 18). Subsequently, the effect of solvents on the reaction was also tested (Table 1, entries 19–23). No desired product **2a** or **2a′** was found in other solvents, such as DMF, $CH_3CN$, $H_2O$, toluene, and 1,4-dioxane. Based on these results, it is noteworthy that DMSO played a key role in the cyclization process for the formation of phenolic compounds.

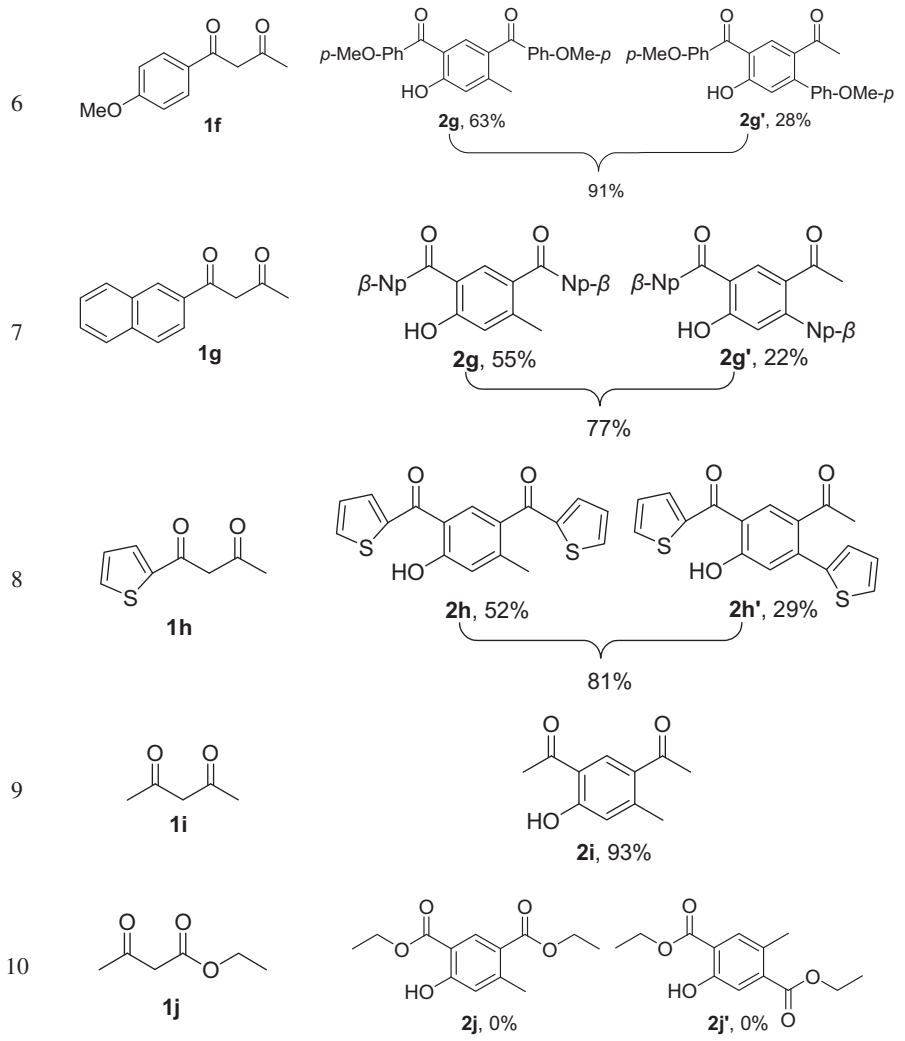
With the optimized conditions in hand, we investigated the scope and limitation of this process and the results are shown in Table 2. The unsymmetrical 1,3-dicarbonyl compounds **1a**–**1h** were examined for the reaction. When substrates **1a**–**1h** reacted with DMSO, the corresponding isomeric products **2a/2a′**–**2h/2h′** were obtained in total 77–91% yields. The ring closure isomers could be isolated by column chromatography with an approximate ratio of 2.2–2.6:1. Notably, the isomeric products **2a′**–**2h′** as new compounds were not found in previous literatures. The 1,3-dicarbonyl compounds **1b**–**1f** substituted with methyl, chloro, bromo, and methoxy groups on the benzene rings reacted smoothly with DMSO. 1-(Naphthalen-2-yl)butane-1,3-dione **1g** and 1-(thiophen-2-yl)butane-1,3-dione **1h** also worked well, generating the desired products **2g/2g′** and **2h/2h′** in total 77 and 81% yields. The reaction of symmetrical acetylacetone **2i** with DMSO generated the unique products **2i** in 93% yield. We attempted to extend

**Table 2.** Substrate scope for the synthesis of phenolic products.[a]




| Entry | Substrate | Product/Yield[b] |
|---|---|---|
| 1 |  **1a** |  **2a**, 62% **2a'**, 26% 88% |
| 2 |  **1b** |  **2b**, 59% **2b'**, 26% 85% |
| 3 |  **1c** |  **2c**,64% **2c'**, 25% 89% |
| 4 |  **1d** |  **2d**, 60% **2d'**, 23% 83% |
| 5 |  **1e** |  **2e**, 58% **2e'**, 26% 84% |

(*continued*)




[a]Conditions: **1** (0.5 mmol), DMSO (2 mL), $CuSO_4 \cdot 5H_2O$ (10 mol%) 130 °C, 12 h.
[b]Isolated yield.

the substrate scope to acetoacetate under the standard conditions, however no desired product **2j** or **2j′** was observed.

To clarify the reaction mechanism, a few controlled experiments have been performed. The product **2i** was obtained in 90% yield when DMSO-$d_6$ was used as a solvent instead of DMSO for the reaction of acetylacetone **1i** under the standard reaction conditions (Scheme 2, eq 1). As shown in Figure 1, the absence of chemical shift in 8.15 ppm clearly confirms that C2 in the benzene ring comes from the DMSO. The model reaction did not affect the yield after introducing a radical scavenger TEMPO (Scheme 2, eq 2). The cyclization reaction of acetylacetone **1i** was unreactive when using DMF as a solvent (Scheme 2, eq 3). If formaldehyde was added, the product **2i** was isolated in 67% yield (Scheme 2, eq 4). These results confirmed that the C-source came from the $CH_2O$ generated from decomposition of DMSO.

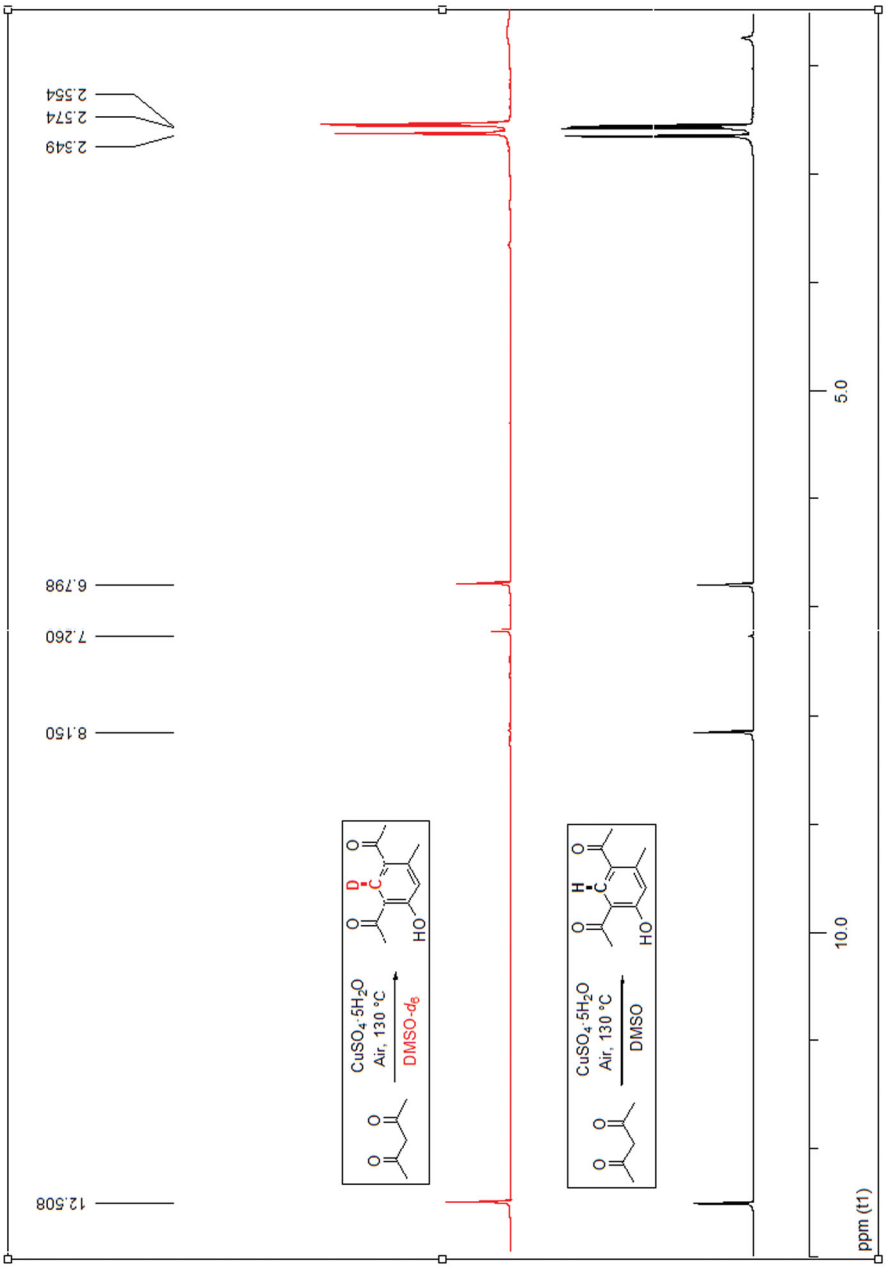
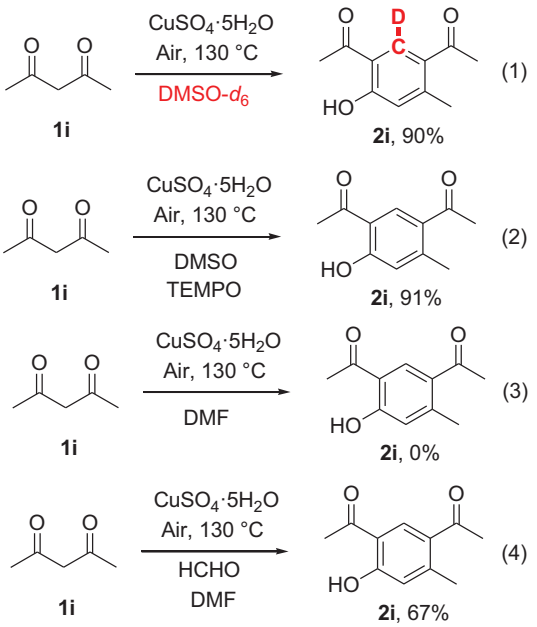
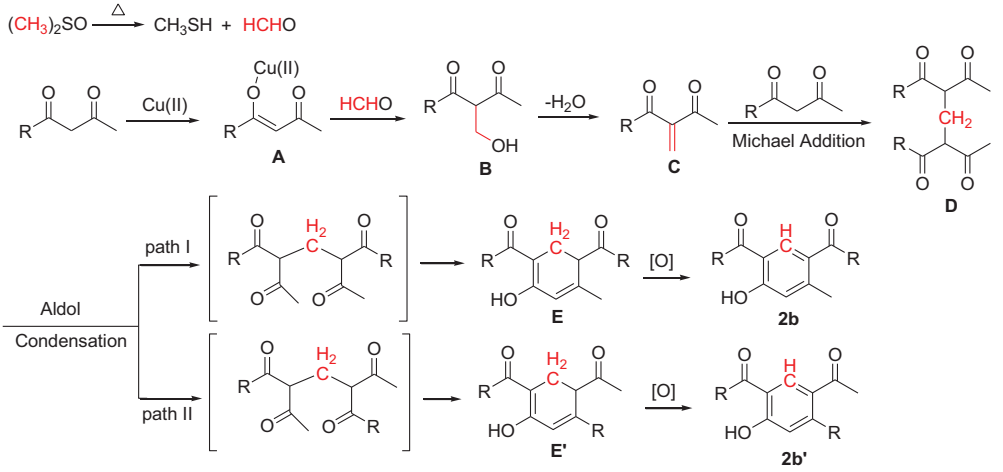



**Figure 1.** Comparison of $^{1}$H NMR of **2i** in different solvents.




**Scheme 2.** Preliminary mechanism study.




**Scheme 3.** Plausible mechanism for synthesis of phenolic products.

On the basis of above experimental results and previous literature,[17] a plausible mechanism is proposed in Scheme 3. Formaldehyde is generated via decomposition of DMSO under heating. DMSO could be used as a formaldehyde precursor for providing a one-carbon bridge. The enolate **A** could be formed after treating 1,3-dicarbonyl compounds with copper salts. The intermolecular aldol condensation between enolate **A** with formaldehyde generates the intermediate **C**. Then intermediate **C** proceeded the

Michael addition with 1,3-dicarbonyl compounds to form the intermediate **D**. The cyclization intermediates **E**/**E′** were obtained through path I or path II via intramolecular aldol condensation, which underwent oxidation reaction to generate the final phenolic products **2**/**2′**.

## Conclusion

In conclusion, a convenient and novel method has been developed for the preparation of phenol derivatives by $CuSO_4{\cdot}5H_2O$-catalyzed cyclization of 1,3-dicarbonyl compounds with DMSO. DMSO is used not only as an effective solvent, but also as the source of C2 for the construction of phenol under this reaction system. It is noteworthy that a mixture of two isomer products is found when unsymmetrical 1,3-dicarbonyl compounds are used as substrates. The present work provides a new route to synthesis highly functionalized phenol derivatives.

## Experimental section

NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 M Hz for carbon). $CDCl_3$ or DMSO-$d_6$ were used as solvents and tetramethylsilane (TMS) as an internal standard. ESI-MS spectra were measured on Finnigan Mat TSQ 7000 instruments. Elemental analyses were performed on a Heraeus elemental analyzer. TLC was performed using commercially prepared 200–300 mesh silica gel plates ($GF_{254}$), and visualization was effected at 254 nm. Melting points were measured with a Tektronix X4 apparatus and were uncorrected.

### *General procedure for the synthesis of phenol compounds*

A 25 mL of dried round-bottom flask was charged with 1,3-dicarbonyl compounds **1** (0.5 mmol), $CuSO_4{\cdot}5H_2O$ (10 mol%), and DMSO (2 mL) at 130 °C for 6 h. After completion of the reaction (monitored by TLC), the water (10 mL) was added. The aqueous solution was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (2 × 10 mL) and dried with anhydrous $MgSO_4$. The solvent was removed and the crude product was separated by column chromatography (eluted with petroleum ether/ethyl acetate = 15:1) to give a pure sample of **2** and **2′**.

#### *(4-Hydroxy-6-methyl-1,3-phenylene)bis(phenylmethanone)(2a)*

White solid, m.p. 84–85 °C. Yield: 62% (98 mg). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 12.31 (s, 1H), 7.75 (d, $J$ = 6.8 Hz, 2H), 7.66 (s, 1H), 7.66–7.62 (m, 2H), 7.58–7.56 (m, 1H), 7.57–7.51 (m, 1H), 7.49–7.39 (m, 4H), 7.01 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 200.7, 196.6, 164.7, 147.9, 138.0, 137.3, 135.6, 133.1, 132.3, 129.9, 129.5, 129.2, 128.48, 128.45, 120.8, 116.2, 21.2. ESI-MS (*m*/*z*) 317 $[M+H]^+$. Anal. calcd. C, 79.73; H, 5.10; Found: C, 79.58; H, 5.07.

### *(4-Hydroxy-6-phenyl-1,3-phenylene)-1-ethanone-3-phenylmethanone(2a′)*

Pale yellow oil. Yield: 26% (41 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 12.36 (s, 1H), 7.97 (s, 1H), 7.73 (d, $J = 7.2$ Hz, 2H), 7.64–7.61 (m, 1H), 7.56–7.52 (m, 2H), 7.46–7.45 (m, 3H), 7.38–7.35 (m, 2H), 7.08 (s, 1H), 1.92 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 201.9, 201.1, 164.7, 149.1, 139.7, 137.3, 134.9, 132.5, 131.9, 129.2, 128.92, 128.90, 128.7, 128.5, 120.0, 117.7, 30.3. ESI-MS ($m/z$) 317 $[M+H]^+$. Anal. calcd. C, 79.73; H, 5.10; Found: C, 79.60; H, 5.06.

Full experimental details, $^{1}$H and $^{13}$C NMR spectra are accessible via the "Supplementary content" section of this article's webpage.

## Funding

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