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# CuI/1,10-phen/PEG promoted decarboxylation of 2,3-diarylacrylic acids: synthesis of stilbenes under neutral and microwave conditions with an *in situ* generated recyclable catalyst†

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A series of *trans*- or *cis*-stilbenes have been synthesized in good to excellent yields *via* a functional group-dependent decarboxylation process from the corresponding 2,3-diaryl acrylic acids in a neutral CuI/1,10-phen/PEG-400 system under microwave conditions. The *in situ* generation of the recyclable catalytic complex, the use of environmentally benign solvent PEG-400, the operational simplicity, the short reaction times, as well as the functional group-dependent chemo- and stereo-selectivity have made the decarboxylation process a highly efficient and applicable protocol.

## Introduction

In recent years, stilbenes, either in *trans* or *cis* forms, have aroused the attention of medicinal chemists owing to their interesting biological activities.[1] Studies have shown that the *trans*-stilbenes, like resveratrol and pterostilbene (Fig. 1), possess antioxidant, anti-infective, anti-inflammatory, anticancer and anti-ageing (SIRT1 activating) properties, and have the potential to be used as chemopreventive, neuroprotective or nutraceutical agents,[2–5] whereas the *cis*-stilbenes such as combretastatin A-4 (CA4), AVE-8063 (Fig. 1) are renowned for potent antitubulin and antivascular activities, and are regarded as the lead compounds of vascular disrupting agents (VDAs).[6,7]

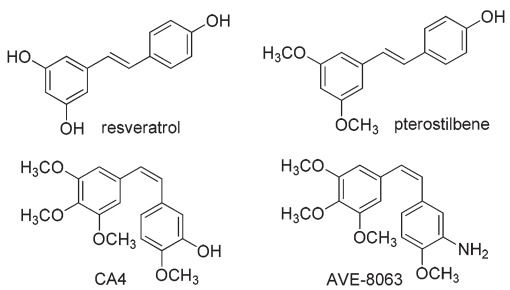


**Fig. 1** Chemical structures of resveratrol, pterostilbene, CA4 and AVE-8063.

Stilbenes can be obtained through decarboxylation of the corresponding 2,3-diarylacrylic acids, which were readily obtained *via* Perkin condensation between phenylacetic acids and benzaldehydes.[8] In fact, the decarboxylation process has emerged as an intriguing strategy in organic synthesis owing to the inducing and activating properties of the carboxylic group which could then be cleaved or decarboxylatively coupled thereafter.[9] Typically, the decarboxylation protocol for aromatic carboxylic acids had for a long time been represented by the excessive use of Cu powder and quinoline as the catalytic system at high temperatures since the initial work of Shepard in 1930 and the later applications in various carboxylic substrates.[10,11] Recently, this methodology has been improved by Goossen,[12] Larrosa,[13] Lisitsyn,[14] Kozlowski[15] and Sinha,[16] with the development of catalytic systems using $Cu_2O$/phenanthroline/NMP/quinoline, $AgOAc/K_2CO_3$/NMP, $Ag_2CO_3$/AcOH/DMSO, $Cu^{n+}$/bipy/$Ph_2O$, $(CF_3CO_2)_2Pd/CF_3CO_2H$/DMSO/DMF and [Hmim]/PTSA respectively, to achieve decarboxylation for various aromatic carboxylic acids. Among them, Sinha's method performed in ionic liquid [Hmim]/PTSA under microwave conditions is unique and impressive,[16] for it represents a metal- and quinoline-free decarboxylative protocol with a wide substrate scope. However, most of the reported

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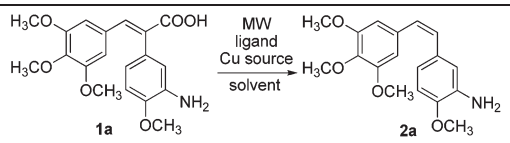
methods still suffer from disadvantages such as the use of environmentally hazardous or nondegradable solvents, prolonged reaction times, difficulty in isolating the products. Moreover, in most cases, the decarboxylative systems couldn't be recycled for the next runs. Thus, exploring for a milder, more benign and recyclable catalytic system for decarboxylation would be highly desirable.

The use of PEG as an efficient, neutral and benign solvent has grown rapidly in recent years.[17] This is due to its green properties such as ready availability, high stability, reduced flammability, nontoxicity, odorlessness, easily degradability and extensive miscibility. In 2007, Sinha and co-workers[18] reported a microwave-assisted decarboxylation process by using $NaHCO_3$(aq)/PEG/MIm and piperidine/PEG/MIm as catalysts to afford an interesting library of *para*-hydroxylated *trans*-stilbenes. The above-mentioned drawbacks as well as the clues for using PEG attracted our attention, and in continuation of our work on green synthesis of natural stilbenes and biomass-based conversion,[8a,19] we herein report a facile, efficient, environmentally benign and recyclable catalytic system for decarboxylation of 2,3-diarylacrylic acids which exhibit a broad substrate scope.

## Results and discussion

Initially, (*E*)-2-(3-amino-4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)acrylic acid (**1a**), which served as the key intermediate for access to AVE-8063, was chosen as the model substrate to screen the optimal conditions (Table 1). Although our previously established protocol which employed Cu/1,10-phen-(1,10-phenanthroline hydrate) in quinoline under microwave conditions could afford **2a** in 73% isolated yield (Table 1, entry 1), the excessive use of Cu powder, difficulty in isolating the product from the quinoline mixture, as well as the environmental and labour security concerns associated with quinoline have made the process far from perfect and benign. Subsequently, we investigated various high boiling point solvents with greener profiles, such as triglycol, PEG-200, PEG-400, PEG-600, NMP and [Bmim]Br in place of quinoline. To our delight, experiments showed that a highly beneficial result was obtained using PEG-400 as the solvent, giving **2a** in 76% yield (entry 6). Other polymerized ethylene glycols like triglycol, PEG-200 and PEG-600 gave slightly lower or almost the same yields (entries 4, 5, 7), whereas NMP and ionic liquid [Bmim]Br were not workable (entries 2, 3). Apart from the solvent effect, the copper-containing catalyst is another crucial factor which deserves further exploration. Although the influence of different Cu sources on decarboxylation reactions has previously been investigated by Goossen *et al.* in their pioneering work,[12a,b] optimized catalytic system possessing green chemistry properties is still needed. Accordingly, we investigated a number of copper salts, including CuBr, CuI, $Cu_2O$, $Cu(OAc)_2$ and $CuSO_4$, for their catalytic behavior combined with 1,10-phen in PEG-400 (entries 8–12). Results showed that when 30 mol% of CuI was utilized, about 84% of **2a** was obtained in only 6 min reaction under microwave irradiation. Investigation on the different amounts of CuI revealed that 10 mol% of CuI was the most optimal for this reaction, giving **2a** in 83% yield (compare entries 12–15). However, no reaction occurred in the absence of CuI under otherwise identical conditions, indicating that CuI was essential for the decarboxylation processes (entry 16). In addition, 10 mol% amount of 1,10-phen proved to be the best choice for this reaction, as there was no significant improvement in yield when 15 mol% amounts of 1,10-phen were used (entry 17), whereas lower yields were obtained with 5 mol% or without 1,10-phen (entries 14, 18, 19). Other commonly-used ligands such as bipyridine, oxine and $PPh_3$ were also tested, but were shown to be less effective or essentially unworkable (entries 20–22). Further inspection of the reaction time revealed that 6 min of microwave irradiation was optimal for the reaction, while longer or shorter reaction times were found to be unfavorable (entries 14, 23–25). In comparison to microwave irradiation,

**Table 1** Screening of the reaction conditions for decarboxylation of 2,3-diarylacrylic acid (**1a**)[a]




| Entry | Solvent | Cu source (mol%) | Ligand (mol%) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Quinoline | Cu (280) | L1 (10) | 73 |
| 2 | NMP | Cu (280) | L1 (10) | Trace |
| 3[c] | Ionic liquid | Cu (280) | L1 (10) | Trace |
| 4 | Triglycol | Cu (280) | L1 (10) | 71 |
| 5 | PEG-200 | Cu (280) | L1 (10) | 72 |
| 6 | PEG-400 | Cu (280) | L1 (10) | 76 |
| 7 | PEG-600 | Cu (280) | L1 (10) | 75 |
| 8 | PEG-400 | $CuSO_4$ (30) | L1 (10) | 37 |
| 9 | PEG-400 | $Cu(OAc)_2$ (30) | L1 (10) | 41 |
| 10 | PEG-400 | $Cu_2O$ (30) | L1 (10) | 80 |
| 11 | PEG-400 | CuBr (30) | L1 (10) | 81 |
| 12 | PEG-400 | CuI (30) | L1 (10) | 84 |
| 13 | PEG-400 | CuI (20) | L1 (10) | 84 |
| 14 | PEG-400 | CuI (10) | L1 (10) | 83 |
| 15 | PEG-400 | CuI (5) | L1 (10) | 53 |
| 16 | PEG-400 | — | L1 (10) | ND |
| 17 | PEG-400 | CuI (10) | L1 (15) | 84 |
| 18 | PEG-400 | CuI (10) | L1 (5) | 51 |
| 19 | PEG-400 | CuI (10) | — | 7 |
| 20 | PEG-400 | CuI (10) | L2 (10) | 61 |
| 21 | PEG-400 | CuI (10) | L3 (10) | 48 |
| 22 | PEG-400 | CuI (10) | L4 (10) | Trace |
| 23[d] | PEG-400 | CuI (10) | L1 (10) | 79 |
| 24[e] | PEG-400 | CuI (10) | L1 (10) | 81 |
| 25[f] | PEG-400 | CuI (10) | L1 (10) | 36 |
| 26[g] | PEG-400 | CuI (10) | L1 (10) | 79 |

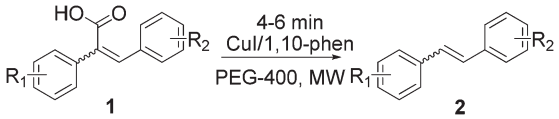
[a] Reaction conditions: **1a** (5.0 mmol), Cu source, ligand (L1: 1,10-phenanthroline hydrate, L2: bipyridine, L3: oxine, L4: $PPh_3$), solvent (20 ml), under $N_2$ atmosphere, the mixture was stirred under microwave irradiation (800 W, 180–190 °C) for 6 min (2 min irradiation for each time with a 5 min interval between). ND: no desired product. [b] Isolated yield. [c] Ionic liquid: [Bmim]Br (15 g). [d] Microwave irradiation for 10 min. [e] Microwave irradiation for 8 min. [f] Microwave irradiation for 4 min. [g] Under conventional heating (200 °C, 60 min).

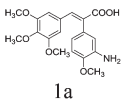
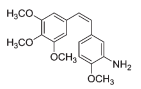
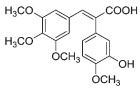
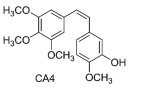
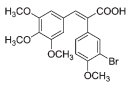
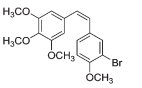
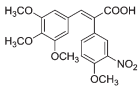
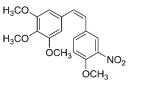
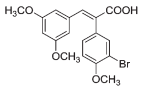
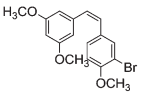
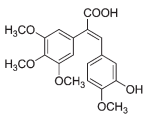
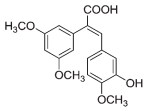
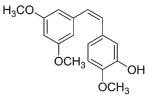
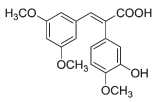
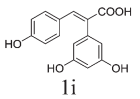
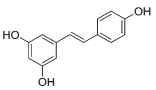
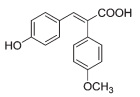
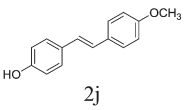
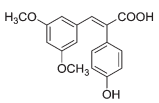
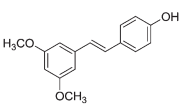
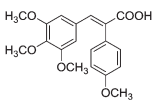
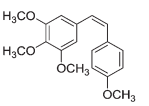
conventional heating was also studied under the same conditions, which afforded lower yield in prolonged reaction time (entry 26). The optimized reaction conditions were established as: 2,3-diaryl acrylic acid (5 mmol), CuI (10 mol%), 1,10-phen (10 mol%) in PEG-400 (20 ml) under microwave irradiation (800 W, 180–190 °C) for 6 min.

Under the optimized conditions, the scope of the protocol was explored using various 2,3-diaryl acrylic acids as substrates. As shown in Table 2, almost all of the tested compounds successfully produced the desired stilbenes with good to excellent yields. The results showed that the functional groups on the aryl rings exerted remarkable influences on the decarboxylation processes. Electron-deficient substrates were more favorable than electron-sufficient ones to provide the corresponding products. For example, substrates with –Br, –OH or $–NH_2$ moieties which decrease in electron withdrawing order provided product yields of 86%, 84% and 83% respectively, under our standard conditions, whereas substrates with the strong withdrawing $–NO_2$ group **1d** was efficiently decarboxylated to give an excellent yield of 94% under milder conditions (Table 2, entries 1–4). It was also evident from Table 2 that the position of the carboxylic group on ethylene scaffold had little influence on the yields (entries 2, 6–8, and 14–15). Furthermore, it was notable that the substrates with *para*-hydroxyl substitution at either aryl ring of (*E*)-2,3-diaryl acrylic acids underwent an isomerization process during decarboxylation, which led to the formation of corresponding *trans*-stilbenes in good to excellent yields (entries 9–11). The *cis* to *trans* isomerization concerning the *para*-hydroxylated substrates **1i–k** can be attributed to the formation of the *para*-quinone intermediate.[18,19a,b,20] However, when 2,3-diaryl acrylic acid without a *para*-hydroxyl group on either aryl ring like (*E*)-2-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)acrylic acid (**1l**) was decarboxylated, the reaction would retain the configuration and give rise to the *cis*-stilbene as a sole product (entry 12). Likewise, the reactions also performed well for (*Z*)-2,3-diaryl acrylic acids, which gave *trans*-stilbenes as expected with satisfactory yields (entries 13–17). It is worth mentioning that an interesting and unambiguous *ortho*-effect leading to unexpected products has been found in the synthesis of some specific stilbenes and the precursors. For example, the *ortho*-brominated substrate *E*-2-(2-bromo-3,5-dimethoxyphenyl)-3-(4-hydroxyphenyl)acrylic acid (**1s**) underwent a tandem hydroxylation/intramolecular addition/dehydrogenation process in the presence of $CuSO_4$/NaOH(aq) to give 2-(4-hydroxyphenyl)-5,7-dimethoxybenzofuran-3-carboxylic acid (**1r**). Subsequent decarboxylation of this compound under typical conditions afforded livistone C (**2r-1**),[21] a new 2-arylbenzofuran compound recently isolated from the fruits of *Livistona chinensis*, in moderate yield. In the meantime, trace amount of *E*-2,4′-dihydroxyl-3,5-dimethoxylstilbene (**2r-2**) could also be detected owing to the existence of 2-(2-hydroxy-3,5-dimethoxyphenyl)-3-(4-hydroxyphenyl)acrylic acid in the crude product of **1r**. Moreover, compound **1s** reacted under typical conditions and unexpectedly gave a lactonated isoaurostatin derivative **2s**, which might be due to the copper-catalyzed C–Br cleavage

**Table 2** Decarboxylation of 2,3-diaryl acrylic acids (**1a–1t**) under optimized conditions[a]




1 2

| Entry | Substrate | Product | Yield[b] (%) |
|---|---|---|---|
| 1 |  1a |  2a (AVE-8063) | 83 |
| 2 |  1b |  2b | 84 |
| 3 |  1c |  2c | 86 |
| 4[c] |  1d |  2d | 94 |
| 5 |  1e |  2e | 88 |
| 6 |  1f | **2b** | 82 |
| 7 |  1g |  2g | 84 |
| 8 |  1h | **2g** | 85 |
| 9 |  1i |  2i (resveratrol) | 82 |
| 10 |  1j |  2j | 89 |
| 11 |  1k |  2k (pterostilbene) | 87 |
| 12 |  1l |  2l | 83 |

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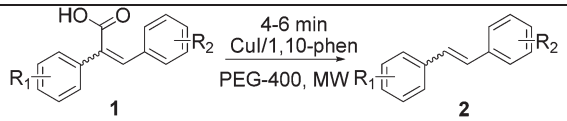


| Entry | Substrate | Product | Yield[b] (%) |
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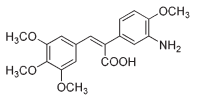
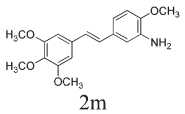
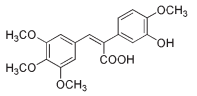
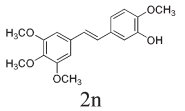
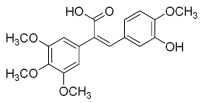
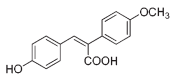
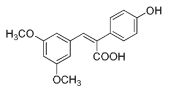
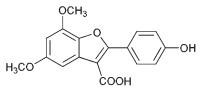
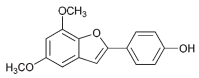
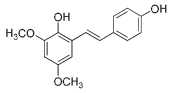
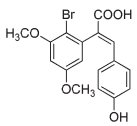
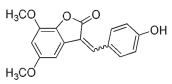
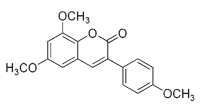
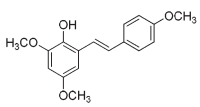
| 13 |  1m |  2m | 84 |
| 14 |  1n |  2n | 87 |
| 15 |  1o | **2n** | 86 |
| 16 |  1p | **2j** | 92 |
| 17 |  1q | **2k** | 89 |
| 18 |  1r |  2r-1 (livistone C) | 69 |
| | |  2r-2 | Trace |
| 19[d] |  1s |  2s | 63 |
| 20[e] |  1t |  2t | ND |

[a] Reaction conditions: 2,3-diarylacrylic acid (5.0 mmol), CuI (10 mol%), 1,10-phen (10 mol%), PEG-400 (20 ml), under $N_2$ atmosphere, the mixture was stirred under microwave irradiation (800 W, 180–190 °C) for 6 min (2 min irradiation each time with a 5 min interval between). The configuration of *cis* and *trans*-stilbenes is confirmed by coupling constant of alkene protons ($J_{(CH=CH)}$ = 12.4 Hz for *cis*-stilbenes, and $J_{(CH=CH)}$ = 16.4 Hz for *trans*-stilbenes). ND: no desired product. [b] Isolated yields. [c] Reaction was performed at 150 °C under microwave irradiation (720 W). [d] Microwave irradiation (800 W, 180–190 °C) for 8 min. [e] Microwave irradiation (800 W, 180–190 °C) for 12 min.

followed by a sterically favorable lactone formation process. However, 3-arylcoumarin was found to be inactive for decarboxylation even in prolonged irradiation time (Table 2, entry 20).[16]

It is worth mentioning that, during the decarboxylation reactions, an appreciable amount of red crystalline powder could readily be recovered from the mixture by filtration. The low solubility in PEG-400, $H_2O$ and most organic solvents as well as the high thermostability according to thermogravimetric analysis (*ca.* 2% weight loss at 294 °C, see ESI†) suggested that it would be a CuI-related complex *in situ* generated during the reaction and therefore deserve further attention. Accordingly, analytical and spectroscopic studies have been conducted for identification of this complex. The elemental analysis and FAB-MS spectra suggested it to be a 1,10-phen-ligated CuI complex having the dimeric formula $[CuI(1,10\text{-phen})]_2$ [22] (Anal. calcd for $C_{24}H_{16}N_4Cu_2I_2$: C, 38.88; H, 2.18; N, 7.56; found: C, 39.00; H, 2.13; N, 7.51; FAB-MS: *m*/*z* 741.17 $[M + 1]^+$). In the $^1H$ NMR spectrum of the complex, note the appearance of four broad singlets in the region of aromatic protons at 9.17, 8.79, 8.23, and 8.06 ppm, corresponding to the eight symmetrical protons of 2-H, 9-H; 4-H, 7-H; 5-H, 6-H; 3-H, 8-H for 1,10-phen, respectively. The formation of singlets can be attributed to the high chemical exchange rate between a bound and unbound 1,10-phen, thus resulting in each proton signal being averaged to be a single broad band. The $^1H$ NMR spectrum also showed that all of the protons in the conjugated 1,10-phen underwent a remarkable downfield shift with respect to the free ligand due to the coordination between N–Cu–N. The IR spectra of the complex clearly showed the existence of the 1,10-phen framework, strong absorptions at 1498, 1415 $cm^{-1}$ were assigned to the $\nu_{as}$ (C=N) stretching vibration which showed a red shift compared to the free ligand (1504, 1421 $cm^{-1}$, respectively). Scanning electron microscopy (SEM) image revealed that this copper complex had a regular parallelepiped microcrystal morphology with an average crystal size of 5 × 20 × 50 μm (Fig. 2).

With the *in situ* generated $[CuI(1,10\text{-phen})]_2$ complex in hand, we were eager to find out its catalytic activity for decarboxylation by using (*E*)-2-(3,5-dimethoxyphenyl)-3-(3-hydroxy-4-methoxy-phenyl)acrylic acid (**1g**) as a model substrate. Much to our delight, this complex revealed a high efficiency in decarboxylation reactions and gave the desired (*Z*)-3′-hydroxyl-3,4′,5-trimethoxystilbene (**2g**) which had been reported to be a potent vascular disrupting agent,[23] in comparable yields over five consecutive runs (Table S1†). The structure of **2g** was confirmed by single crystal X-ray diffraction (Fig. 3). The results demonstrated that the catalytic CuI-related complex still retained its physicochemical and morphological properties during repeated reactions, and could be readily recycled and reused without significant loss of activity. To the best of our

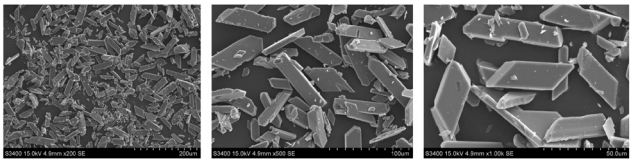


**Fig. 2** SEM of $[CuI(1,10\text{-phen})]_2$.

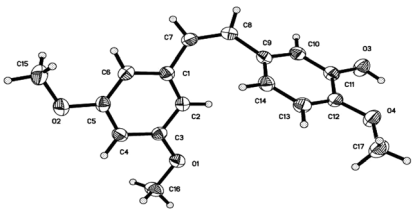
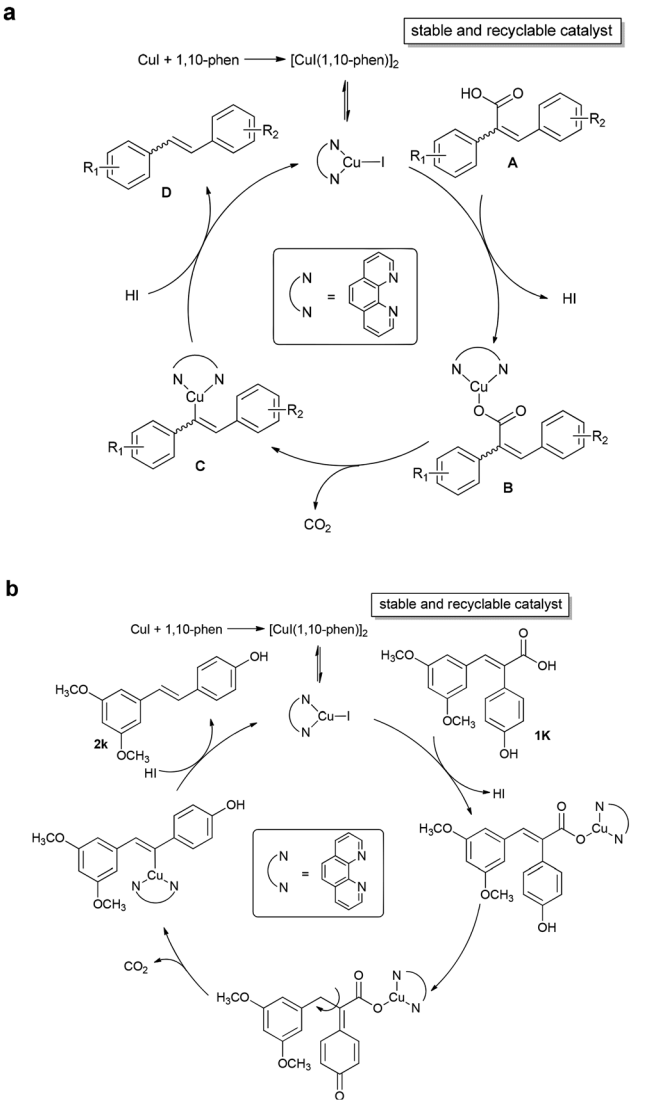


**Fig. 3** X-ray crystal structure of **2g**.[25]

knowledge, although the combinative use of CuI/1,10-phen has been widely employed as a hallmark in catalytic processes in recent years,[24] the *in situ* generation of a stable complex under reaction conditions as well as the excellent recyclability and reusability have not yet been reported.

A plausible mechanism for this decarboxylative process including the pathway for *cis*-to-*trans* isomerization is outlined in Scheme 1. The combination of CuI and 1,10-phen in PEG-400 under reaction conditions generates a monomer CuI-(1,10-phen), which would serve as an active state of the more stable dimeric complex $[CuI(1,10\text{-phen})]_2$. An initial reaction of A and CuI(1,10-phen) affords the copper carboxylate B with the loss of a hydriodic acid, followed by decarboxylation to give the organocopper intermediate C, which is subsequently protonated by hydriodic acid to yield stilbene D and regenerate the CuI(1,10-phen) catalyst. Finally, the reactive CuI(1,10-phen) species may be converted into $[CuI(1,10\text{-phen})]_2$ as the solvent cools down (Scheme 1a). On the other hand, when a substrate bearing an *para*-hydroxyl group in either of the phenyl rings like **1k** is subjected to the reaction conditions, a *para*-quinone intermediate would be generated, thus leading to the *cis* to *trans* isomerization *via* rotation around the single bond and resulting in the formation of a more stable *trans*-stilbene, like **2k** (Scheme 1b). It is noteworthy that control experiments for decarboxylation reactions catalyzed by CuI and 1,10-phen in the presence of quinoline have failed to regenerate the corresponding $[CuI(1,10\text{-phen})]_2$ complex, indicating the importance and effectiveness for using PEG-400 as the solvent in decarboxylation.




**Scheme 1** A plausible mechanism for the CuI(1,10-phen)-catalyzed decarboxylation of 2,3-diarylacrylic acids. (a) Mechanism for substrate without a *para*- and *ortho*-hydroxyl group in either of the phenyl rings, which provided a configuration-retained product. (b) Representative mechanism for substrates bearing an *para*-hydroxyl group in either of the phenyl rings, which lead to the *cis* to *trans* isomerization (taking **1k–2k** as an example).

## Conclusions

In summary, we have developed a green and efficient method for decarboxylation of 2,3-diaryl acrylic acids in the CuI/1,10-phen/PEG-400 system under microwave conditions. The results demonstrated that the *in situ* generated $[CuI(1,10\text{-phen})]_2$ complex, which could be readily recovered from the reaction mixture, revealed excellent catalytic activity, stability, and reusability. In addition, the use of environmentally benign solvent (PEG-400), the operational simplicity, short reaction times, as well as the functional group-dependent chemo- and stereoselectivity have all made the decarboxylation process a highly efficient and applicable protocol.

## Experimental section

### General information

2,3-Diaryl acrylic acids were directly obtained through Perkin reaction except **1a** and **1r**. Other reagents and chromatography grade solvents were obtained from commercial sources and used without further purification unless otherwise stated. Petroleum ether (PE) used refers to the boiling fraction of 60–90 °C. All microwave assisted reactions were carried out with a Microwave Synthesizer (WBFY-205, Gongyi City Yu Hua Instrument Co. Ltd, China), and the reaction temperature was detected using an infrared thermometer. The melting points are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were measured using a 400 MHz spectrometer ($^1$H 400 MHz, $^{13}$C 100 MHz)

using $CDCl_3$ or DMSO-$d_6$ as the solvent at room temperature. Chemical shifts are reported in parts per million (ppm) and are calibrated using residual undeuterated solvent as an internal reference. HRMS spectra were recorded using a LC-Q-TOF (ESI) apparatus. The single X-ray diffraction measurement was performed using a X-ray diffractometer. The morphology was characterized using scanning electron microscopy (SEM, 15 kV). Thermogravimetric analysis (TGA) was carried out at a heating rate of 3° $min^{-1}$ under a flowing argon atmosphere.

### Procedure for preparing (*E*)-2-(3-amino-4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)acrylic acid (1a)

A tube equipped with a magnetic stir bar was charged with **1c** (10 mmol, 4.23 g), CuI (20 mol%, 0.38 g), ammonia water (wt = 28%, 15 ml) and PEG-400 (15 ml). The tube was sealed and the mixture was stirred at 80 °C for 48 h. The reaction mixture was cooled to room temperature, adjusted with 10% HCl solution to pH 7, the insoluble CuI was filtered off, and the resulting filtrate was further acidified to pH 5 with 10% HCl solution to give a yellow solid, which was collected by filtration to afford **1a** (3.27 g, 91.1% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 12.21 (s, 1H, COOH), 7.57 (s, 1H), 6.83 (d, $J$ = 8.4 Hz, 1H), 6.49 (s, 2H), 6.46 (d, $J$ = 1.6 Hz, 1H), 6.34 (dd, $J$ = 8.4 Hz, $J$ = 1.6 Hz, 1H), 4.43 (s, 2H, $NH_2$), 3.75 (s, 3H), 3.60 (s, 3H), 3.48 (s, 6H); MS ($m/z$): 359 ($M^+$), 344, 329, 299, 284, 269, 255, 241, 183, 156, 148, 134.

### Procedure for preparing 2-(4-hydroxyphenyl)-5,7-dimethoxybenzofuran-3-carboxylic acid (1r)

A tube equipped with a magnetic stir bar was charged with **1s** (10 mmol, 3.79 g), $CuSO_4$ (30 mmol, 4.8 g), NaOH (100 mmol, 4.0 g) and $H_2O$ (36 ml). The mixture was stirred at 120 °C for 72 h. The reaction mixture was cooled to room temperature and the insoluble substance was filtered off. The resulting filtrate was acidified to pH 4–5 using 10% HCl solution and a white solid **1r** (1.48 g, 46.8% yield) was separated by filtration. HRMS (ESI): m.p. 212–214 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 12.4 (s, COOH), 12.4 (s, OH), 7.82 (d, $J$ = 8.0 Hz, 2H), 7.01 (d, $J$ = 4.0 Hz, 1H), 6.87 (d, $J$ = 8.0 Hz, 2H), 6.58 (d, $J$ = 4.0 Hz, 1H), 3.93 (s, 3H), 3.79 (s, 3H); HRMS (ESI): $m/z$ calcd for $C_{17}H_{14}NaO_6$ $[M + Na]^+$: 337.0683; found: 337.0677.

### General procedures for decarboxylation

2,3-Diaryl acrylic acid **1** (5 mmol), CuI (0.5 mmol), 1,10-phenanthroline monohydrate (0.5 mmol) and PEG-400 (20 ml) were added into a 50 ml round bottom flask. The flask was then placed in the microwave synthesizer, charged with $N_2$, and irradiated (800 W, 180–190 °C) with stirring for 4–12 min (2 min irradiation each time with a 5 min interval between). After completion of the reaction, the mixture was cooled to r.t., water (20 ml) and ethyl acetate (20 ml) were added, the resulting red crystalline powder $[CuI(1,10\text{-phen})]_2$ was filtered off, washed with water and ethyl acetate, dried and stored for next runs. The filtrate was extracted with ethyl acetate (2 × 20 ml). The combined organic phases were washed with water, dried over anhydrous $MgSO_4$ and then concentrated to afford the crude product, which was further recrystallized from EtOAc–PE to give the desired product **2**.

### Recyclability of $[CuI(1,10\text{-phen})]_2$

Run 1: **1g** (0.05 mol, 16.5 g), the recovered $[CuI(1,10\text{-phen})]_2$ (5 mol%, 1.85 g) from the initial reaction and PEG-400 (100 ml) were added into a 250 ml round bottom flask. The flask was then placed in the microwave synthesizer, charged with $N_2$, and irradiated (800 W, 180–190 °C) with stirring for 6 min (2 min irradiation for three times with a 5 min interval between). After completion of the reaction, the mixture was cooled to r.t., water (50 ml) and ethyl acetate (50 ml) were added, the resulting red crystalline powder $[CuI(1,10\text{-phen})]_2$ was filtered off, washed with water and ethyl acetate, dried and stored for next runs. The filtrate was extracted with ethyl acetate (2 × 50 ml). The combined organic phases were washed with water, dried over anhydrous $MgSO_4$ and then concentrated to afford the crude product, which was further recrystallized from EtOAc–PE to give the pure product **2g** in 84% isolated yield. Reaction conditions of Runs 2–5 were the same as those of Run 1 with 83%, 82%, 82%, 82% yield, respectively (Table S1†).

### (*Z*)-3′-Amino-3,4,4′,5-tetramethoxystilbene (2a)[7b]

Yellow oil (yield: 1.31 g, 83%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 6.72 (d, $J$ = 8 Hz, 1H), 6.66 (d, $J$ = 1.6 Hz, 1H), 6.60 (s, 2H), 6.47 (dd, $J$ = 1.6 Hz, $J$ = 8 Hz, 1H), 6.41 (d, $J$ = 12.4 Hz, 1H), 6.31 (d, $J$ = 12.4 Hz, 1H), 4.71 (s, 2H), 3.72 (s, 3H), 3.62 (s, 3H), 3.58 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): 152.7, 146.5, 135.6, 132.9, 129.9, 128.3, 128.2, 126.2, 119.5, 115.2, 109.9, 105.9, 60.8, 56.0, 55.8; HRMS (ESI): $m/z$ calcd for $C_{18}H_{22}NO_4$ $[M + H]^+$: 316.1543; found: 316.1555.

### (*Z*)-3′-Hydroxyl-3,4,4′,5-tetramethoxystilbene (2b)[19a]

White solid (yield: 1.33 g, 84%). m.p. 116–117 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.91 (d, $J$ = 2.0 Hz, 1H), 6.79 (dd, $J$ = 8.0 Hz, $J$ = 2.0 Hz, 1H), 6.71 (d, $J$ = 8.0 Hz, 1H), 6.51 (s, 2H), 6.45 (d, $J$ = 12.4 Hz, 1H), 6.42 (d, $J$ = 12.4 Hz, 1H), 5.49 (s, 1 H), 3.89 (s, 3H), 3.84 (s, 3H), 3.68 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 152.6, 145.7, 145.1, 136.9, 132.5, 130.3, 129.3, 128.8, 120.9, 114.9, 110.2, 105.9, 60.7, 55.7; HRMS (ESI): $m/z$ calcd for $C_{18}H_{21}O_5$ $[M + H]^+$: 317.1384; found: 317.1399.

### (*Z*)-3′-Bromo-3,4,4′,5-tetramethoxystilbene (2c)

Yellow solid (yield: 1.63 g, 86%). m.p. 76–77 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.55 (d, $J$ = 2.0 Hz, 1H), 7.19 (dd, $J$ = 8.4 Hz, $J$ = 2.0 Hz, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H), 6.50 (s, 2H), 6.45 (d, $J$ = 12 Hz, 1H), 6.42 (d, $J$ = 12 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 154.7, 152.8, 133.5, 132.1, 130.7, 129.7, 129.1, 127.7, 111.2, 110.9, 105.8, 103.2, 60.8, 56.0, 55.9; HRMS (ESI): $m/z$ calcd for $C_{18}H_{20}BrO_4$ $[M + H]^+$: 379.0539; found: 379.0546.

### (*Z*)-3′-Nitro-3,4,4′,5-tetramethoxystilbene (2d)[7b]

Yellow solid (yield: 1.62 g, 94%). m.p. 118–120 °C, $^1$H NMR (400 MHz, $CD_3COCD_3$): $\delta$ = 7.74 (d, $J$ = 2.0 Hz, 1H), 7.53–7.57

(dd, $J$ = 8.8, 2.0 Hz, 1H), 7.26 (d, $J$ = 8.8 Hz, 1H), 6.62 (d, $J$ = 12.4 Hz, 1H), 6.58 (s, 2H), 6.54 (d, $J$ = 12.4 Hz, 1H), 3.71 (s, 3H), 3.95 (s, 3H), 3.67 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.2, 151.7, 139.4, 137.6, 134.6, 131.8, 129.7, 126.8, 125.9, 113.0, 105.8, 60.9, 56.5, 56.0; HRMS (ESI): $m/z$ calcd for $C_{18}H_{19}NnaO_6$ $[M + Na]^+$: 368.1105; found: 368.1105.

### (*Z*)-3′-Bromo-3,4′,5-trimethoxystilbene (2e)

Yellow oil (yield: 1.54 g, 88%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.46 (d, $J$ = 2.4 Hz, 1H), 7.22 (dd, $J$ = 8.8 Hz, $J$ = 2.0, 1H), 7.01 (d, $J$ = 8.8 Hz, 1H), 6.50 (t, $J$ = 12.8 Hz, 2H), 6.37–6.39 (m, 3H), 3.81 (s, 3H), 3.63 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.6, 154.8, 138.7, 133.7, 130.9, 129.8, 128.5, 111.3, 111.0, 106.5, 99.9, 56.1, 55.2; HRMS (ESI): $m/z$ calcd for $C_{17}H_{17}NaBrO_3$ $[M + Na]^+$: 371.0253; found: 371.0250.

### (*Z*)-3′-Hydroxyl-3,4′,5-trimethoxystilbene (2g)[19a]

White solid (yield: 1.20 g, 84%). m.p. 93–95 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.87 (d, $J$ = 2.0 Hz, 1H), 6.77 (dd, $J$ = 8.4 Hz, $J$ = 2.0 Hz, 1H), 6.69 (d, $J$ = 8.4 Hz, 1H), 6.47 (d, $J$ = 12.4 Hz, 1H), 6.43 (d, $J$ = 2.0 Hz, 2H), 6.42 (d, $J$ = 12.4 Hz, 1H), 6.30 (t, $J$ = 2.0 Hz, 1H), 5.42 (s, 1H), 3.84 (s, 3H), 3.66 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.4, 145.8, 145.0, 139.2, 130.3, 130.1, 128.9, 121.1, 115.0, 110.2, 106.6, 99.6, 55.7, 55.1; HRMS (ESI): $m/z$ calcd for $C_{17}H_{18}NaO_4$ $[M + Na]^+$: 309.1097; found: 309.1097.

### (*E*)-3,4′,5-Trihydroxystilbene (2i)[19a]

White solid (yield: 0.93 g, 82%). m.p. 263–264 °C. $^1$H NMR (400 MHz, $CD_3COCD_3$): $\delta$ = 8.43 (s, 1H, OH), 8.23 (s, 2H, 2 × OH), 7.43 (d, $J$ = 8.8 Hz, 2H), 7.01 (d, $J$ = 16.4 Hz, 1H), 6.89 (d, $J$ = 16.4 Hz, 1H), 6.84 (d, $J$ = 8.8 Hz, 2H), 6.55 (d, $J$ = 2.0 Hz, 2H), 6.28 (t, $J$ = 2.0 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 158.6, 157.3, 139.3, 128.1, 127.9, 125.7, 115.6, 104.4, 101.8; HRMS (ESI): $m/z$ calcd for $C_{14}H_{13}O_3$ $[M + H]^+$: 229.0859; found: 229.0859.

### (*E*)-4′-Hydroxyl-4-methoxystilbene (2j)[26]

Gray solid (yield: 1.01 g, 89%). m.p. 182–184 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48 (d, $J$ = 8.8 Hz, 2H), 7.40 (d, $J$ = 8.8 Hz, 2H), 7.10 (d, $J$ = 16.4 Hz, 1H), 6.96 (d, $J$ = 16.4 Hz, 1H), 6.92 (d, $J$ = 8.8 Hz, 2H), 6.83 (d, $J$ = 8.8 Hz, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 158.5, 157.0, 130.2, 128.4, 127.5, 127.3, 126.2, 124.8, 115.5, 114.1, 55.1; MS (EI): $m/z$ (%) 226 (100%), 221 (60), 165 (30), 113 (27).

### (*E*)-4′-Hydroxyl-3,5-dimethoxystilbene (2k)[9a]

White solid (yield: 1.11 g, 87%). m.p. 85–86 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.58 (s, 1H), 7.40 (d, $J$ = 8.4 Hz, 2H), 7.15 (d, $J$ = 16.4 Hz, 1H), 6.93 (d, $J$ = 16.4 Hz, 1H), 6.76 (d, $J$ = 8.8 Hz, 2H), 6.74 (d, $J$ = 2.4 Hz, 2H), 6.36 (t, $J$ = 2.4 Hz, 1H), 3.75 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 160.9, 155.3, 139.6, 130.1, 128.7, 128.0, 126.6, 115.6, 104.4, 99.6, 55.4; HRMS (ESI): $m/z$ calcd for $C_{16}H_{17}O_3$ $[M + H]^+$: 257.1172; found: 257.1167.

### (*Z*)-3,4,4′,5-Tetramethoxystilbene (2l)[19a]

Yellow oil (yield: 1.25 g, 83%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.21 (d, $J$ = 8.4 Hz, 2H), 6.77 (d, $J$ = 8.4 Hz, 2H), 6.49 (s, 2H), 6.48 (d, $J$ = 12.4 Hz, 1H), 6.40 (d, $J$ = 12.4 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.67 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.5, 152.7, 136.8, 132.7, 130.1, 129.4, 129.3, 128.5, 113.4, 105.7, 60.7, 55.7, 55.0; HRMS (ESI): $m/z$ calcd for $C_{18}H_{21}O_4$ $[M + H]^+$: 301.1434; found: 301.1431.

### (*E*)-3′-Amino-3,4,4′,5-tetramethoxystilbene (2m)

White solid (yield: 1.32 g, 84%). m.p. 110–112 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.03 (d, $J$ = 16.4 Hz, 1H), 6.88 (d, $J$ = 1.6 Hz, 1H), 6.85 (d, $J$ = 16.4 Hz, 1H), 6.84 (s, 2H), 6.78 (d, $J$ = 8.4 Hz, 1H), 6.74 (dd, $J$ = 1.6 Hz, $J$ = 8.4 Hz, 1H), 4.74 (s, 2H), 3.81 (s, 6H), 3.76 (s, 3H), 3.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.3, 147.4, 138.4, 136.0, 133.5, 130.3, 128.2, 126.3, 117.8, 112.2, 110.3, 103.2, 60.9, 56.0, 55.5; HRMS (ESI): $m/z$ calcd for $C_{18}H_{22}NO_4$ $[M + H]^+$: 316.1543; found: 316.1547.

### (*E*)-3′-Hydroxyl-3,4,4′,5-tetramethoxystilbene (2n)[27]

White solid (yield: 1.37 g, 87%). m.p. 102–104 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.01 (s, 1H), 7.08–7.04 (d, $J$ = 16.4 Hz, 1H), 7.01 (s, 1H), 6.97–6.89 (m, 3H), 6.86 (s, 2H), 3.81 (s, 6H), 3.77 (s, 3H), 3.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.3, 146.3, 145.7, 137.5, 133.2, 130.9, 127.7, 126.9, 119.1, 111.6, 110.6, 103.2, 60.9, 56.0, 55.9; HRMS (ESI): $m/z$ calcd for $C_{18}H_{20}NaO_5$ $[M + Na]^+$: 339.1203; found: 339.1208.

### 5,7-Dimethoxy-2-(4′-hydroxyphenyl)benzofuran (2r-1)[21]

White solid (yield: 0.93 g, 69%). m.p. 122–124 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 9.83 (s, 1H), 7.68 (d, $J$ = 8.8 Hz, 2H), 7.05 (s, 1H), 6.76 (d, $J$ = 8.8 Hz, 2H), 6.65 (d, $J$ = 2.4 Hz, 1H), 6.47 (d, $J$ = 2.4 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 158.2, 156.6, 156.3, 144.9, 130.5, 127.9, 126.2, 121.0, 115.8, 100.0, 96.6, 94.5, 55.8, 55.5; HRMS (ESI): $m/z$ calcd for $C_{16}H_{15}O_4$ $[M + H]^+$: 271.0965; found: 271.0962.

### 3-(4-Hydroxybenzylidene)-5,7-dimethoxybenzofuran-2(3*H*)-one (2s) (*Z*/*E* = 1 : 1)

Yellow solid (yield: 0.94 g, 63%). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 10.47 (s, 1H), 10.36 (s, 1H), 8.25 (d, $J$ = 8.4 Hz, 2H), 7.95 (s, 1H), 7.75 (s, 1H), 7.70 (d, $J$ = 8.4 Hz, 2H), 7.01 (d, $J$ = 2.0 Hz, 1H), 6.95 (d, $J$ = 8.8 Hz, 2H), 6.91 (d, $J$ = 2.0 Hz, 1H), 6.88 (d, $J$ = 8.8 Hz, 2H), 6.71 (d, $J$ = 2.0 Hz, 1H), 6.58 (d, $J$ = 2.0 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H); HRMS (ESI): $m/z$ calcd for $C_{17}H_{14}NaO_5$ $[M + Na]^+$: 321.0733; found: 321.0734.

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