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Copper-catalyzed regioselective synthesis of furan *via* tandem cycloaddition of ketone with an unsaturated carboxylic acid under air†

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A catalytic decarboxylative annulation has been developed for the regioselective synthesis of trisubstituted furans by the cycloaddition of ketones with α,β -unsaturated carboxylic acids under ambient air. A library of furan derivatives were obtained in good yields from the readily available substrates in the combination of a catalytic amount of Cu-salt and a stoichiometric amount of water. Water plays a crucial role in this catalytic transformation.

Introduction

Polysubstituted furans represent an important class of five-membered heterocycles ubiquitous in natural products, pharmaceuticals, and agrochemicals as well as act as useful intermediates in organic synthesis.¹ The multisubstituted furan is a basic scaffold of various biologically active alkaloids and pharmaceutical drugs, such as dantrolene and (+)-(Z)-deoxypukalide (Fig. 1).

Various methods have been reported for the synthesis of furan derivatives due to their important biological activities and usefulness.² Classical approaches such as Paal–Knorr synthesis^{3a,b} and Feist–Benary synthesis^{3c–f} have already been established for the assembly of polysubstituted furans from dicarbonyl compounds. In addition, several methodologies have been reported from the prefunctionalized acyclic ketone derivatives such as cyclopropenyl ketones,^{4a} β -acyloxy acetylenic ketones,^{4b} allenyl ketones,^{4c} *o*-alkoxyketones,^{4d,e} α -aryloxyketo-

nes^{4f} *etc.* However, the synthetic potential of these strategies is limited by the requirement of functionalized precursors, which can only be obtained through specialized protocols involving multi-step procedures. As a consequence, the development of a new synthetic route to synthesize furan derivatives from simple and commercially available starting materials is still in demand.

Transition metal-catalyzed decarboxylative coupling has emerged as a powerful tool to form carbon–carbon or carbon–heteroatom bonds starting from carboxylic acids.⁵ Use of carboxylic acid has several advantages due to its ready availability, easy handling as well as environmentally benign properties. Moreover, it produces nontoxic CO₂ as the byproduct. From the point of view of atom and process-economical chemistry, the most concise route with reduced waste and fewer steps is needed.

To the best of our knowledge, no catalytic method has been reported for the synthesis of furans *via* decarboxylative annulation reaction. Recently, Zhang *et al.* developed an elegant protocol for the synthesis of furan derivatives through a decarboxylative cyclization between ketones and α,β -unsaturated carboxylic acids.⁶ However, stoichiometric amounts of two different copper salts are required for this reaction. Catalytic decarboxylative methods are well-known and have been used in various chemical transformations.⁷ Based on our experience in copper catalysis,⁸ we envisaged that the synthesis of furans might be possible by the annulation of ketones with α,β -unsaturated carboxylic acids *via* decarboxylative cycloaddition using a catalytic amount of copper salt in the presence of a suitable oxidant. Generally, oxidants such as PIDA, K₂S₂O₈, TBHP, O₂ *etc.* are used for copper-catalyzed oxidative coupling reactions.⁹ Among them molecular O₂ is considered to be the most ideal oxidant due to its high abundance, low cost, and environment friendly nature and therefore shows a great demand in the industrial prospects.¹⁰ Moreover, water is

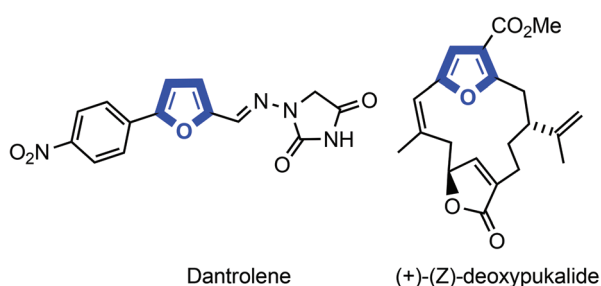
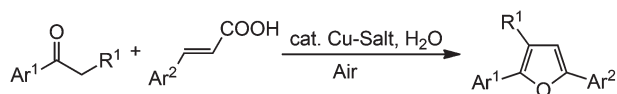


Fig. 1 Some biologically active furan containing drugs.

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Scheme 1 Catalytic decarboxylative synthesis of furans.

produced as the only byproduct using molecular O_2 as an oxidant. So, the construction of heterocycles from simple and readily accessible substrates using molecular O_2 is compatible with the increasing requirements for green chemistry and an efficient process.

Recently, we have reported the synthesis of arenofuran derivatives by the coupling of phenols/naphthols with nitroalkenes *via* tandem Michael addition/denitration.¹¹ In continuation of our research interest in furan synthesis as well as in coupling between nitroalkenes with various nucleophiles,¹² herein we report an efficient synthetic method for the synthesis of 2,3,5-trisubstituted furans *via* decarboxylative annulation employing a catalytic amount of copper salt in the presence of a stoichiometric amount of water under ambient air (Scheme 1).

Results and discussion

We commenced our study by choosing propiophenone and cinnamic acid (1 : 1) as the model substrates to find out the optimized reaction conditions using various copper salts, additives and solvents. The results are summarized in Table 1. Initially, the reaction was carried out employing 10 mol% $Cu(OAc)_2 \cdot H_2O$ in DMA at 120 °C under an air atmosphere. The reaction did not proceed at all even after 24 h (Table 1, entry 1). On increasing the amount of $Cu(OAc)_2 \cdot H_2O$ (20 mol%), the reaction proceeded in very low conversion (Table 1, entry 2). Encouraged by this result, we turned our attention to check the role of an acid and a base in this transformation. In the presence of various acids (1 equiv.) the desired products were obtained in low to moderate yields (Table 1, entries 3–6). Similar effects were observed in the case of bases (Table 1, entries 7 and 8). On the other hand, in the presence of 1 equiv. of water, the reaction proceeded with 44% yield (Table 1, entry 9). On increasing the amount of H_2O (3 equiv.), the desired product was obtained in 67% yield (Table 1, entry 11). The yield of the product was decreased by changing the molar ratios of the reactants (Table 1, entries 12 and 13). Different solvents like NMP, toluene, xylene, DMSO and DMF (Table 1, entries 14–18) were also screened, among them DMA gave the best result compared to others (Table 1, entry 11). Use of other Cu-salts such as $Cu(OTf)_2$, $Cu(ClO_4)_2 \cdot 6H_2O$ resulted in lower yields (Table 1, entries 19 and 20) whereas $CuCl_2$ and $CuBr_2$ were almost ineffective for this reaction (Table 1, entries 21 and 22). Finally, the optimized reaction conditions were achieved using the combination of propiophenone and cinnamic acid (1 : 1), 20 mol% $Cu(OAc)_2 \cdot H_2O$ in the presence of 3 equiv. of water at 120 °C for 7 h under ambient air (Table 1, entry 11).

To explore the general applicability, scope and limitation of this method, various cinnamic acids and ketones were

Table 1 Optimization of the reaction conditions^a

Entry	Catalyst (mol%)	Additive (equiv.)	Solvent	1a : 2a	Yield ^b (%)
1.	$Cu(OAc)_2 \cdot H_2O$ (10)	—	DMA	1 : 1	n.d. ^c
2.	$Cu(OAc)_2 \cdot H_2O$ (20)	—	DMA	1 : 1	5
3.	$Cu(OAc)_2 \cdot H_2O$ (20)	AcOH (1)	DMA	1 : 1	33
4.	$Cu(OAc)_2 \cdot H_2O$ (20)	TFA (1)	DMA	1 : 1	40
5.	$Cu(OAc)_2 \cdot H_2O$ (20)	HCl (1)	DMA	1 : 1	<5
6.	$Cu(OAc)_2 \cdot H_2O$ (20)	<i>p</i> -TSA (1)	DMA	1 : 1	8
7.	$Cu(OAc)_2 \cdot H_2O$ (20)	NaOAc (1)	DMA	1 : 1	15
8.	$Cu(OAc)_2 \cdot H_2O$ (20)	KOAc (1)	DMA	1 : 1	22
9.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (1)	DMA	1 : 1	44
10.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (2)	DMA	1 : 1	55
11.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	DMA	1 : 1	67
12.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	DMA	2 : 1	45
13.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	DMA	1 : 2	20
14.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	NMP	1 : 1	37
15.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	Toluene	1 : 1	22
16.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	Xylene	1 : 1	25
17.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	DMSO	1 : 1	32
18.	$Cu(OAc)_2 \cdot H_2O$ (20)	Water (3)	DMF	1 : 1	60
19.	$Cu(OTf)_2$ (20)	Water (3)	DMA	1 : 1	43
20.	$Cu(ClO_4)_2 \cdot 6H_2O$ (20)	Water (3)	DMA	1 : 1	45
21.	$CuCl_2$ (20)	Water (3)	DMA	1 : 1	n.d.
22.	$CuBr_2$ (20)	Water (3)	DMA	1 : 1	n.d.

^a Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), solvent: 2 mL, 120 °C, 7 h, air. ^b Isolated yield. ^c n.d. = not determined. DMA = *N,N*-dimethylacetamide. DMF = *N,N*-dimethylformamide. DMSO = dimethylsulfoxide. NMP = *N*-methyl-2-pyrrolidone.

Table 2 Decarboxylative coupling with propiophenone^a

3aa , 67%	3ab , 64%	3ac , 52%	3ad , 54%	3ae , 59%	3af , 61%
3ag , 63%	3ah , 54%	3ai , 56%	3aj , 54% ^b	3ak , 56% ^b	

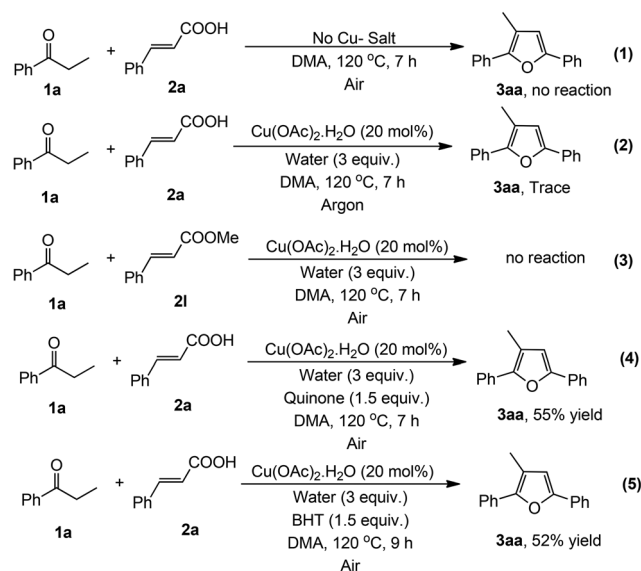
^a Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), water (0.27 mL, 3 equiv.), DMA (2 mL), 120 °C, 7 h, air. ^b 5 h; isolated yields.

investigated. At first, various cinnamic acid derivatives were examined (Table 2). Electron-donating substituents (–Me, –OMe) in cinnamic acid produced the corresponding furans in moderate to good yields (**3ab** and **3ac**). Moreover, halogen

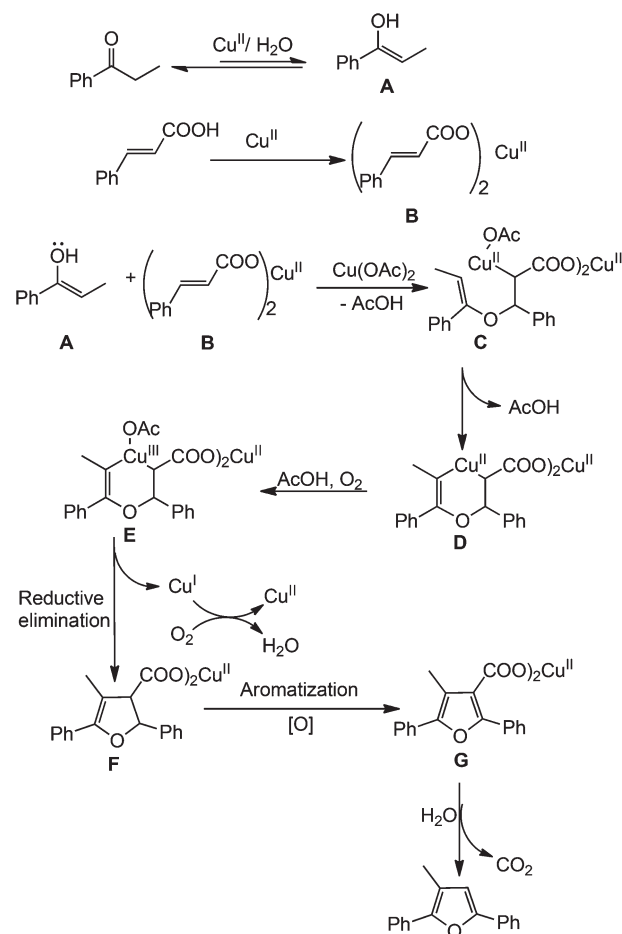
substituents in the aryl moiety also produced the furan derivatives with moderate yields (**3ae–3ai**). Substituents at the different positions in the aryl moiety slightly affected the yields of this reaction. Interestingly, in all cases only one regioisomeric product was obtained. Heteroaryl unsaturated carboxylic acids were also examined and were found to be effective for the synthesis of furan derivatives (**3aj** and **3ak**).

Furthermore, various commercially available ketones were also tested to explore the scope of the reaction (Table 3). Aryl alkyl ketones, such as butyrophenone (**3ba**, **3bd** and **3bf**) and 2-phenyl acetophenone (**3cb** and **3cf**) reacted smoothly to afford the desired products. Cyclic ketones such as α -tetralone, cyclohexanone and cyclododecanone also produced the corresponding furan derivatives (**3da**, **3ea** and **3fa**) in moderate yields. However, no reaction occurred in the case of acyclic ketones (ethylmethyl ketone and isobutylmethyl ketone) and crotonic acid.

Some controlled experiments were performed to evaluate the mechanism of this reaction (Scheme 2). When the reaction was carried out in the absence of copper, the reaction did not proceed at all (eqn (1)), which signifies that the presence of copper as a catalyst is necessary in this reaction. Only a trace amount of product was detected under an argon atmosphere (eqn (2)), which confirms that molecular O₂ (air) is essential for the completion of the catalytic cycle. It is noteworthy to mention that styrene did not produce the desired product under the optimized reaction conditions.⁶ Moreover, we did not observe the formation of styrene during this reaction. This result indicates that the reaction did not proceed through the formation of a styrene intermediate. Moreover, methyl cinnamate was unreacted under the present reaction conditions (eqn (3)). Furthermore the reaction probably does not follow a radical pathway^{6,13} as the radical scavengers like quinone and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (1.5 equiv.) did not inhibit the reaction (eqn (4) and (5)).



Scheme 2 Some controlled experiments.



Scheme 3 Probable reaction mechanism.

Table 3 Coupling of various ketones with carboxylic acids^a

$\text{R}^1\text{---}\text{C}(=\text{O})\text{---}\text{R}^2$ (1) + $\text{Ar}^2\text{---}\text{CH}=\text{CH}\text{---}\text{COOH}$ (2)		$\xrightarrow[\text{Water (3 equiv.), DMA, 120 }^\circ\text{C, 7 h}]{\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O (20 mol\%)}}$	$\text{R}^1\text{---}\text{C}(=\text{O})\text{---}\text{C}(\text{OAr}^2)=\text{CH}\text{---}\text{CH}=\text{CH}\text{---}\text{COOH}$ (3)
 3ba , 64%	 3bd , 50%	 3bf , 62%	
 3cb , 57%	 3cf , 60%	 3da , 54%	
 3ea , 40%	 3fa , 34%		

^a Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), water (0.27 mL, 3 equiv.), DMA (2 mL), 120 °C, 7 h, air; isolated yields.

On the basis of results obtained from these controlled experiments, a probable mechanism of the reaction is depicted in Scheme 3. Nucleophilic addition of the hydroxyl group in

enol **A**, *in situ* generated from ketones, to cinnamic acids in the presence of Cu(II) salt affords alkyl–Cu(II) intermediate **C**. The intermediate **C** reacts with enol to lead the intermediate **D** which is oxidized to give the C–Cu(III)–C intermediate **E**.¹⁴ The intermediate **F** is formed from **E** *via* reductive elimination and subsequently oxidative aromatization occurs to convert the furan intermediate **G**. Finally the intermediate **G** affords the desired furan derivative *via* decarboxylation.¹⁵ Although the specific role of water is not clear at the present stage, it probably facilitates the formation of enol.

Conclusions

In summary, we have developed a copper-catalyzed regioselective synthesis of 2,3,5-trisubstituted furans from the readily available ketones and α,β -unsaturated carboxylic acids *via* decarboxylative annulation. Water plays a crucial role in this transformation. Operational simplicity, broad substrates scope, low cost of the catalyst, and use of green oxidant make this protocol a practical one in diversity-oriented synthesis.

Experimental section

Typical experimental procedure for the synthesis of 3-methyl-2,5-diphenylfuran product (**3aa**)

A mixture of propiophenone (**1a**, 0.5 mmol, 67 mg), cinnamic acid (**2a**, 0.5 mmol, 74 mg), Cu(OAc)₂·H₂O (20 mol%, 19 mg) and H₂O (0.27 mL, 3 equiv.) in DMA (2 mL) was taken in a reaction vessel and stirred at 120 °C for 7 h under an open atmosphere. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature, and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether as an eluent to afford the pure product as a white solid (75 mg, 67% yield). Mp 45–46 °C (lit.⁶ 46–47 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 7.6 Hz, 4H), 7.36–7.27 (m, 4H), 7.18–7.14 (m, 2H), 6.51 (s, 1H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.7, 148.3, 131.8, 130.9, 128.7, 128.6, 127.3, 126.7, 125.3, 123.7, 118.7, 110.9, 12.2.

3-Methyl-2-phenyl-5-*p*-tolylfuran (3ab**).**⁶ White solid (79 mg, 64% yield). Mp 80–82 °C (lit. 78–79 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.28–7.24 (m, 2H), 6.60 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 147.7, 137.0, 131.8, 129.3, 128.5, 128.1, 126.5, 125.1, 123.6, 118.6, 110.1, 21.2, 12.1.

5-(4-Methoxyphenyl)-3-methyl-2-phenylfuran (3ac**).**⁶ White solid (71 mg, 54% yield). Mp 97–98 °C (lit. 98–99 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.63–7.56 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.20–7.18 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 6.40 (s, 1H), 3.76 (s, 3H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 151.9, 147.6, 132.0, 128.6, 126.5, 125.2, 125.2, 124.0, 118.7, 114.3, 109.4, 55.4, 12.2.

5-(4-Methyl-5-phenylfuran-2-yl)-benzo[1,3]dioxole (3ad**).**⁶ White solid (78 mg, 54% yield). Mp 110–112 °C (lit. 112–113 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.19–7.10 (m, 3H), 6.75 (d, J = 8.4 Hz, 1H), 6.38 (s, 1H), 5.89 (s, 2H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 148.1, 147.7, 147.0, 131.9, 128.6, 126.6, 125.4, 125.2, 118.7, 117.7, 109.8, 108.7, 104.5, 101.2, 12.2.

5-(4-Fluorophenyl)-3-methyl-2-phenylfuran (3ae**).**⁶ White solid (74 mg, 59% yield). Mp 85–86 °C (lit. 87–88 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.63–7.57 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.21–7.17 (m, 1H), 7.02–6.98 (m, 2H), 6.46 (s, 1H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.2 (d, ¹ J_{C-F} = 246 Hz), 150.9, 148.3, 131.8, 128.7, 127.2, 126.8, 125.5 (d, ² J_{C-F} = 8 Hz), 118.8, 115.8 (d, ³ J_{C-F} = 22 Hz), 110.6, 12.2.

5-(4-Chlorophenyl)-3-methyl-2-phenylfuran (3af**).**⁶ White solid (82 mg, 61% yield). Mp 81–82 °C (lit. 82–83 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.39–7.37 (m, 2H), 7.35–7.33 (m, 1H), 6.60 (s, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.7, 148.6, 132.8, 131.6, 129.3, 128.9, 128.7, 126.9, 125.3, 124.9, 118.8, 111.3, 12.1.

5-(4-Bromophenyl)-3-methyl-2-phenylfuran (3ag**).** White solid (99 mg, 63% yield). Mp 84–85 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.48–7.45 (m, 2H), 7.39–7.36 (m, 1H), 7.34–7.28 (m, 1H), 6.61 (s, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.7, 148.6, 132.8, 131.6, 129.3, 129.0, 128.7, 126.9, 125.3, 124.9, 123.7, 118.8, 111.3, 12.2. Anal. Calcd for C₁₇H₁₃BrO: C, 65.19; H, 4.18%; Found: C, 65.17; H, 4.21%.

5-(2-Chlorophenyl)-3-methyl-2-phenylfuran (3ah**).**⁶ Gummy liquid (73 mg, 54% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.37–7.33 (m, 3H), 7.25–7.18 (m, 2H), 7.10–7.06 (m, 1H), 7.01 (s, 1H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.3, 147.9, 131.6, 130.8, 130.0, 129.2, 128.7, 127.8, 127.7, 127.0, 126.9, 125.5, 118.7, 116.8, 12.2.

5-(2-Bromophenyl)-3-methyl-2-phenylfuran (3ai**).** White solid (87 mg, 56% yield), Mp 81–82 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.64 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.38–7.34 (m, 3H), 7.26–7.20 (m, 2H), 7.12–7.08 (m, 1H), 7.02 (s, 1H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 148.3, 148.0, 131.6, 130.8, 130.0, 129.2, 128.7, 127.8, 127.7, 127.0, 127.0, 125.5, 118.7, 116.8, 12.2. Anal. Calcd for C₁₇H₁₃BrO: C, 65.19; H, 4.18%; Found: C, 65.17; H, 4.20%.

4-Methyl-5-phenyl-[2,2']bifuranyl (3aj**).** Colorless oil (63 mg, 54% yield); ¹H NMR (500 MHz, CDCl₃): δ 7.67 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 3H), 7.28–7.25 (m, 2H), 6.59 (d, J = 3.0 Hz, 1H), 6.50 (s, 1H), 6.47–6.46 (m, 1H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 148.1, 146.8, 144.6, 141.9, 131.6, 131.2, 128.6, 126.9, 125.4, 118.3, 111.5, 110.8, 105.2, 12.1. Anal. Calcd for C₁₅H₁₂O₂: C, 80.34; H, 5.39%; Found: C, 80.35; H, 5.42%.

3-Methyl-2-phenyl-5-thiophen-2-yl-furan (3ak**).**⁶ Colorless oil (68 mg, 56% yield); ¹H NMR (300 MHz, CDCl₃): δ 7.70 (d, J = 7.4 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.31–7.28 (m, 2H), 7.26–7.22 (m, 1H), 7.07–7.04 (m, 1H), 6.48 (s, 1H), 2.32 (s, 1H);

^{13}C NMR (75 MHz, CDCl_3): δ 147.8, 147.4, 133.8, 131.5, 128.5, 127.6, 126.7, 125.2, 124.0, 122.3, 118.6, 110.7, 12.0.

3-Ethyl-2,5-diphenylfuran (3ba). Colorless oil (79 mg, 64% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.76–7.71 (m, 4H), 7.48–7.39 (m, 4H), 7.33–7.28 (m, 2H), 6.72 (s, 1H), 2.77 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.9, 147.5, 131.7, 130.8, 128.6, 128.5, 128.4, 127.1, 126.7, 125.4, 125.3, 125.1, 123.6, 108.6, 19.2, 14.3. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}$: C, 87.06; H, 6.49%; Found: C, 87.08; H, 6.52%.

5-(4-Ethyl-5-phenylfuran-2-yl)-benzo[1,3]dioxole (3bd). Yellow oil (72 mg, 50% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.58 (d, J = 8.0 Hz, 2H), 7.36–7.31 (m, 3H), 7.19–7.11 (m, 3H), 6.75 (d, J = 8.0 Hz, 1H), 6.45 (s, 1H), 5.88 (s, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.9, 148.1, 147.1, 147.0, 131.8, 129.6, 128.6, 128.2, 126.7, 125.4, 117.6, 108.7, 107.7, 104.5, 101.2, 19.4, 14.5. Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3$: C, 78.06; H, 5.52%; Found: C, 78.09; H, 5.58%.

5-(4-Chlorophenyl)-3-ethyl-2-phenylfuran (3bf). Gummy liquid (87 mg, 62% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.71–7.65 (m, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.39–7.36 (m, 2H), 7.34–7.28 (m, 1H), 6.70 (s, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.0, 148.1, 132.8, 131.6, 129.8, 129.0, 128.7, 127.1, 125.6, 125.6, 124.9, 109.2, 19.4, 14.5. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{ClO}$: C, 76.46; H, 5.35%; Found: C, 76.50; H, 5.36%.

2,3-Diphenyl-5-*p*-tolylfuran (3cb). White solid (87 mg, 57% yield). Mp 99–100 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.40–7.37 (m, 2H), 7.32–7.28 (m, 2H), 7.26–7.20 (m, 3H), 7.17–7.13 (m, 3H), 6.67 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 147.6, 137.5, 134.5, 131.3, 129.5, 128.8, 128.7, 128.5, 127.9, 127.5, 127.3, 126.2, 124.6, 123.9, 108.9, 21.4. Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}$: C, 89.00; H, 5.85%; Found: C, 89.05; H, 5.92%.

5-(4-Chlorophenyl)-2,3-diphenylfuran (3cf). White solid (98 mg, 60% yield). Mp 93–94 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.50–7.47 (m, 2H), 7.45–7.38 (m, 4H), 7.38–7.34 (m, 2H), 7.32–7.27 (m, 2H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.6, 148.3, 134.2, 133.2, 131.0, 129.1, 129.1, 128.8, 128.8, 128.5, 127.8, 127.5, 126.3, 125.1, 124.7, 110.0. Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{ClO}$: C, 79.88; H, 4.57%; Found: C, 79.85; H, 4.60%.

2-Phenyl-4,5-dihydronaphtho[1,2-*b*]furan (3da). Colourless liquid (66 mg, 54% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.41–7.37 (m, 2H), 7.27–7.23 (m, 2H), 7.20–7.18 (m, 1H), 7.13–7.10 (m, 1H), 6.62 (s, 1H), 2.99 (t, J = 8.0 Hz, 2H), 2.77 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.3, 149.8, 134.8, 131.1, 128.8, 128.1, 128.0, 127.2, 126.9, 126.5, 123.7, 121.6, 119.2, 106.6, 29.1, 21.1. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}$: C, 87.78; H, 5.73%; Found: C, 87.75; H, 5.79%.

2-Phenyl-4,5,6,7-tetrahydrobenzofuran (3ea). Yellow liquid (40 mg, 40% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.62–7.59 (m, 2H), 7.35–7.31 (m, 2H), 7.20–7.16 (m, 1H), 6.46 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.45 (t, J = 7.6 Hz, 2H), 1.88–1.83 (m, 2H), 1.77–1.72 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.7, 150.9, 131.5, 128.6, 126.6, 123.3, 119.1, 106.1, 23.4,

23.2, 23.2, 22.2. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}$: C, 84.81; H, 7.12%; Found: C, 84.85; H, 7.19%.

2-Phenyl-4,5,6,7,8,9,10,11,12,13-decahydrocycloclododeca[*b*]-furan (3fa). Colorless liquid (48 mg, 34% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.62–7.60 (m, 2H), 7.35–7.31 (m, 2H), 7.20–7.16 (m, 1H), 6.46 (s, 1H), 2.66 (t, J = 6.8 Hz, 2H), 2.40 (t, J = 6.8 Hz, 2H), 1.82–1.76 (m, 2H), 1.69–1.62 (m, 2H), 1.36–1.32 (m, 8H), 1.27–1.24 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.6, 151.3, 131.5, 128.6, 126.6, 123.3, 121.9, 106.6, 27.7, 26.3, 24.9, 24.8, 24.5, 24.4, 23.0, 22.4, 22.3, 21.6. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}$: C, 85.06; H, 9.28%; Found: C, 85.09; H, 9.22%.

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