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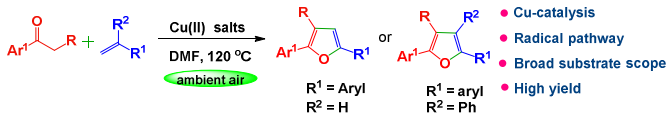
Copper-Catalyzed Regioselective Synthesis of Multisubstituted Furans by Coupling between Ketones and Aromatic Olefins

Amrita Dey, Md Ashif Ali, Sourav Jana, and Alakananda Hajra*

Department of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India



Abstract:

A regioselective synthesis of multi-substituted furan derivatives has been developed via Cu(II)-catalyzed intermolecular annulation of aryl ketones with a wide range of aromatic olefins under ambient air in good yields. This protocol is applicable to both cyclic and acyclic aryl ketones.

Introduction:

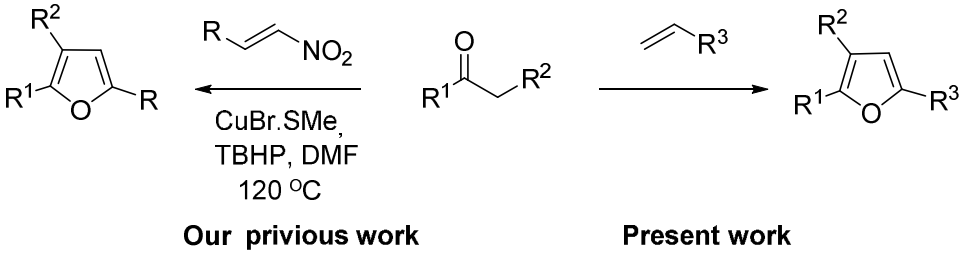
Among the five-membered heterocyclic derivatives polysubstituted furan is one of the most important motifs present in a number of pharmaceuticals and biologically active compounds and natural products.[1] Furthermore, they are the basic scaffolds of numerous therapeutic agents, optoelectronic materials and also used as building blocks in organic synthesis.

The versatile pharmacological and biological activities of furan derivatives is resulting in development of various methods for construction of polysubstituted furan derivatives.[2] Despite considerable synthetic routes for their preparation, construction of furan molecules from readily available starting materials under mild conditions till now attracts the interest of organic chemists. As for examples, the Paal–Knorr and Feist–Benary cyclocondensations from dicarbonyl compounds provide direct access to substituted furans.[3] In addition, several methodologies from prefunctionalized alkynyl, allenyl, or cyclopropyl ketone precursors involving alkyne- or allene-assisted cyclizations have been developed for the synthesis of furans.[4]

Although a number of methods have been extensively utilized for the furan synthesis, most of these approaches require either prefunctionalized substrates or multistep procedures. To the best of our knowledge the use of commercially available simple aryl ketones and olefins as precursors

has been less explored.[5] Very recently, Maiti et al. reported an efficient method of 2,3-dihydrofuran synthesis from aryl ketones and aromatic olefins by using stoichiometric amount of $Cu(OAc)_2$.[5b] On the basis of our experience in copper catalysis,[6] we envisaged that furan might be synthesized via annulation of ketones with aromatic olefins by using catalytic amount of copper salt in ambient air.[7] Transition-metal-catalyzed organic transformations have become one of the most powerful tools to prepare functionalized furan molecules during the past few years.[8] The most versatile and widely used transition-metal for the synthesis of furan derivatives are Pd, Cu, Au, Ag and Ru.[9] In general direct regioselective synthesis of substituted heterocycles from readily available and cheap chemicals as reactants is a great challenge. Recently, our group has reported a copper-catalyzed regioselective synthesis of multisubstituted furan derivatives employing ketones and nitroalkenes as the coupling partners.[10] This discovery encouraged us to search suitable conditions for synthesis of furan derivatives using simple alkene as coupling partner. Herein we report a regioselective synthesis of 2,3,5-trisubstituted furans from aryl ketones and olefins (Scheme 1).

Scheme 1. Synthesis of Multisubstituted Furans from Olefins

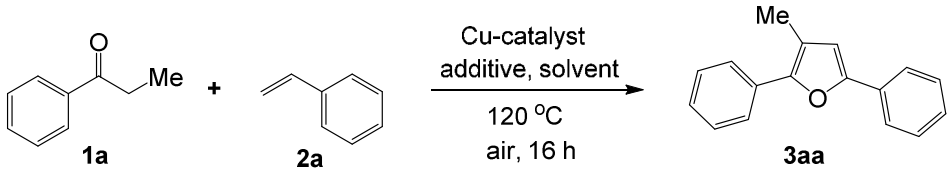


Results and Discussion:

In our initial study, we focused on the reaction of styrene with propiophenone varring different copper salts, additives and solvents to standardize reaction conditions. The 3-methyl-2,5-diphenylfuran was obtained as single regioisomer in 30% yield when we used $Cu(OAc)_2 \cdot H_2O$ (20 mol %) in DMF at 120 °C (Table 1, entry 1). The addition of perchloric acid greatly enhanced the yield of desired product (Table 1, entry 2). Other acids like trifluoroacetic acid and hydrochloric acid were effective but acetic acid was less efficient. The use of potassium acetate as an additive was not successful providing only trace amount of the product. Next we examined different copper salt and the most effective result came out when the reaction was performed with copper(II) chloride. The reaction yielded 95% of the desired product without any additives. Other copper salt like copper(I) chloride, copper(II) bromide and copper(II) triflate were also

effective but not as copper(II) chloride. The solvents like xylene, NMP and DMAc were less effective than DMF. The reaction did not work well under argon atmosphere and at 80 °C providing only 20% and trace amount of desired product respectively (Table 1, entry 14). The reaction did not proceed in water as well as under solvent-free conditions (Table 1, entries 16 and 17). Use of organic bases is not also effective for this transformation (Table 1, entry 18). There is no reaction in the absence of Cu-catalyst (Table 1, entry 19).

Table 1. Optimization of the Reaction Conditions[a]

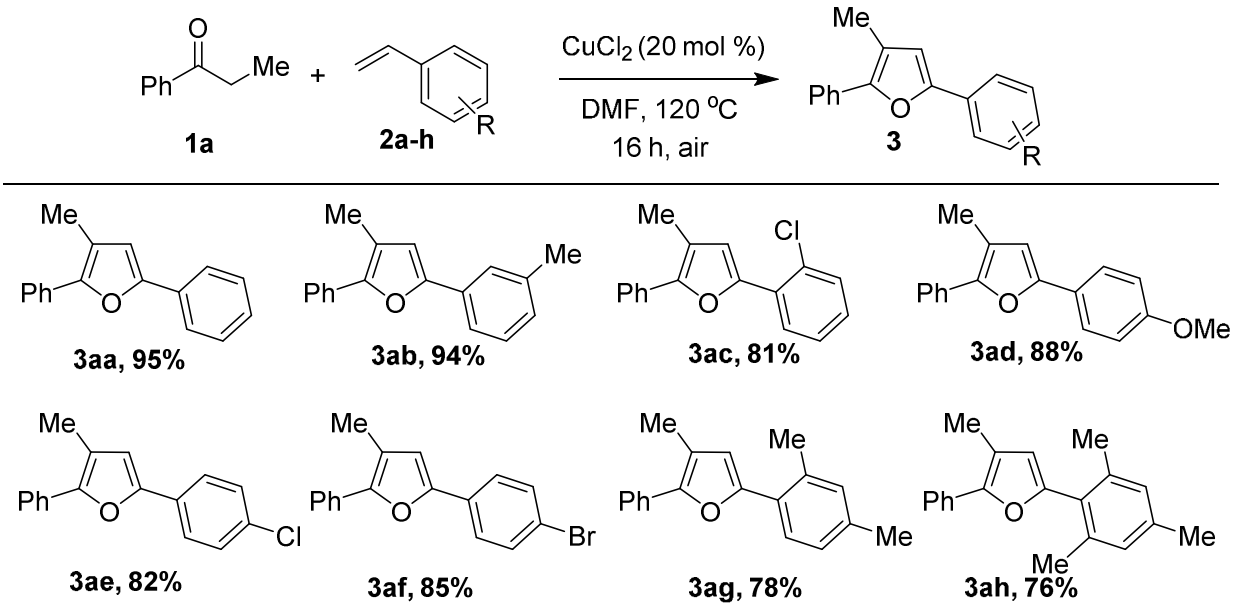


entry	catalyst (20 mol%)	additive (3 equiv.)	solvent	temp. (°C)	yield (%)
1	$Cu(OAc)_2 \cdot H_2O$	-	DMF	120	30
2	$Cu(OAc)_2 \cdot H_2O$	$HClO_4$	DMF	120	80
3	$Cu(OAc)_2 \cdot H_2O$	TFA	DMF	120	50
4	$Cu(OAc)_2 \cdot H_2O$	HCl	DMF	120	85
5	$Cu(OAc)_2 \cdot H_2O$	AcOH	DMF	120	30
6	$Cu(OAc)_2 \cdot H_2O$	KOAc	DMF	120	Trace
7	$CuCl_2$	-	DMF	120	95
8	CuCl	-	DMF	120	60
9	$CuBr_2$	-	DMF	120	85
10	$Cu(OTf)_2$	-	DMF	120	85
11	$CuCl_2$	-	Xylene	120	81
12	$CuCl_2$	-	NMP	120	90
13	$CuCl_2$	-	DMAc	120	84
14	$CuCl_2$	-	DMF	120	20[b]

15	$CuCl_2$	-	DMF	80	trace
16	$CuCl_2$	-	H_2O	100	N.R.
17	$CuCl_2$	-	-	120	N.R.
18	$CuCl_2$	DBU	DMF	120	N.R. (15^c, 58^d)
19	-	-	DMF	120	N.R.

[a]Reaction conditions: 0.5 mmol of **1a** and 0.5 mmol of **2a** in the presence of 20 mol % catalyst in 2 mL DMF at mentioned temperature for 16 h. [b]Under argon atmosphere. [c]Using DABCO. [d]Using Et_3N.

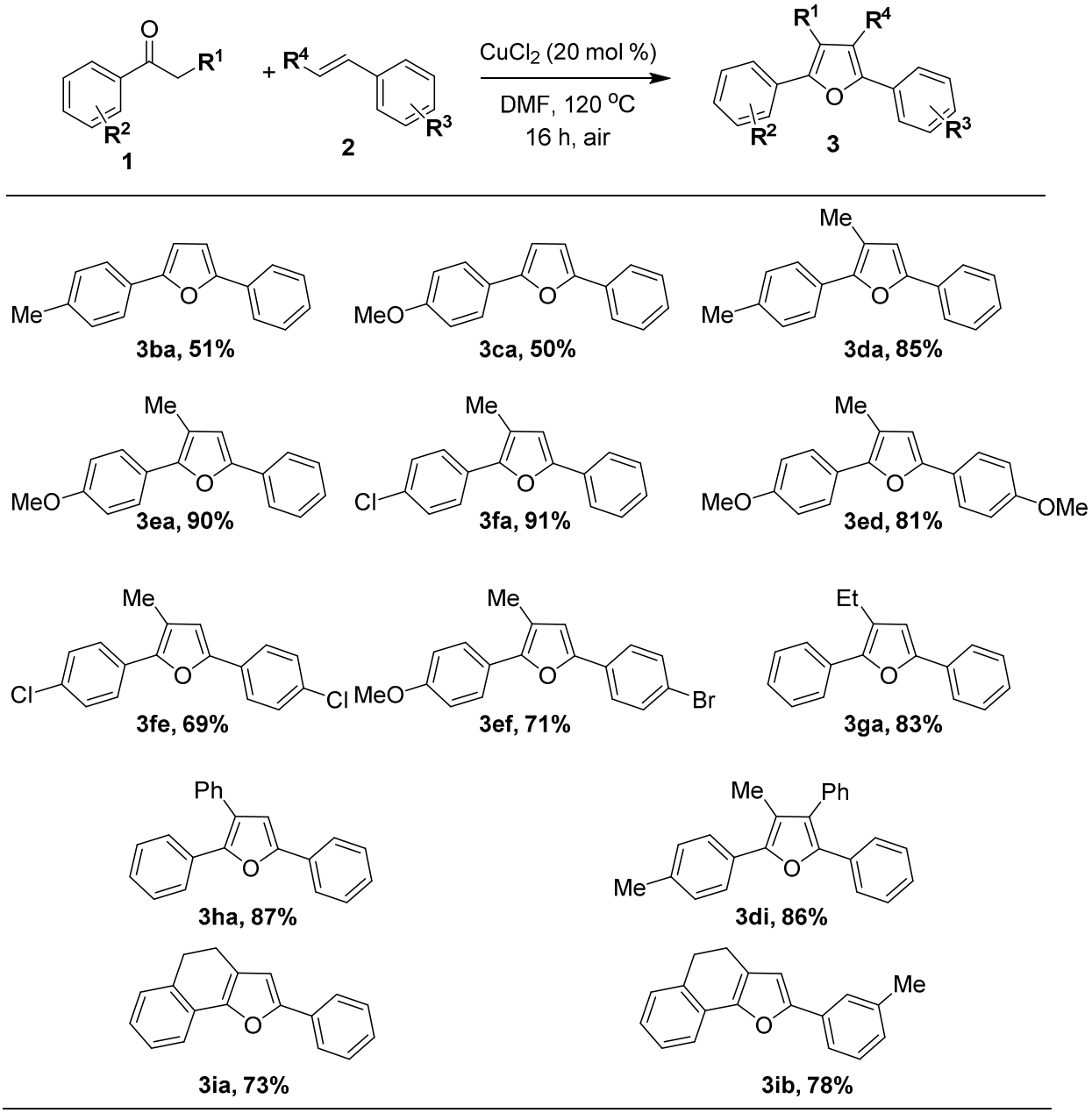
Scheme 2. Substrates Scope with Different Styrenes[a]



[a]Reaction conditions: 0.5 mmol of **1a** and 0.5 mmol of **2a-h** in the presence of 20 mol % $CuCl_2$ in 2 mL DMF at 120 °C for 16 h.

Having optimized reaction conditions in hand, we began to explore the substrate scope for the annulation of propiophenone with various substituted styrenes (Scheme 2). 3-Substituted styrenes such as 3-methyl and 2-substituted styrenes such as 2-chloro as well as 4-substituted styrenes like 4-methoxy, 4-chloro, and 4-bromo worked well providing very high yield of the desired products (**3ab**-**3af**). Multi-substituted styrenes such as 2,4-dimethyl and 2,4,6-trimethyl styrenes worked resulting in good yield of the expected products **3ag** and **3ah** respectively. The styrene containing strong electron withdrawing groups like $-NO_2$ and -F did not give any desired products under the standard reaction conditions.

Scheme 3. Substrates Scope with Different Aryl Ketones and Styrenes[a]

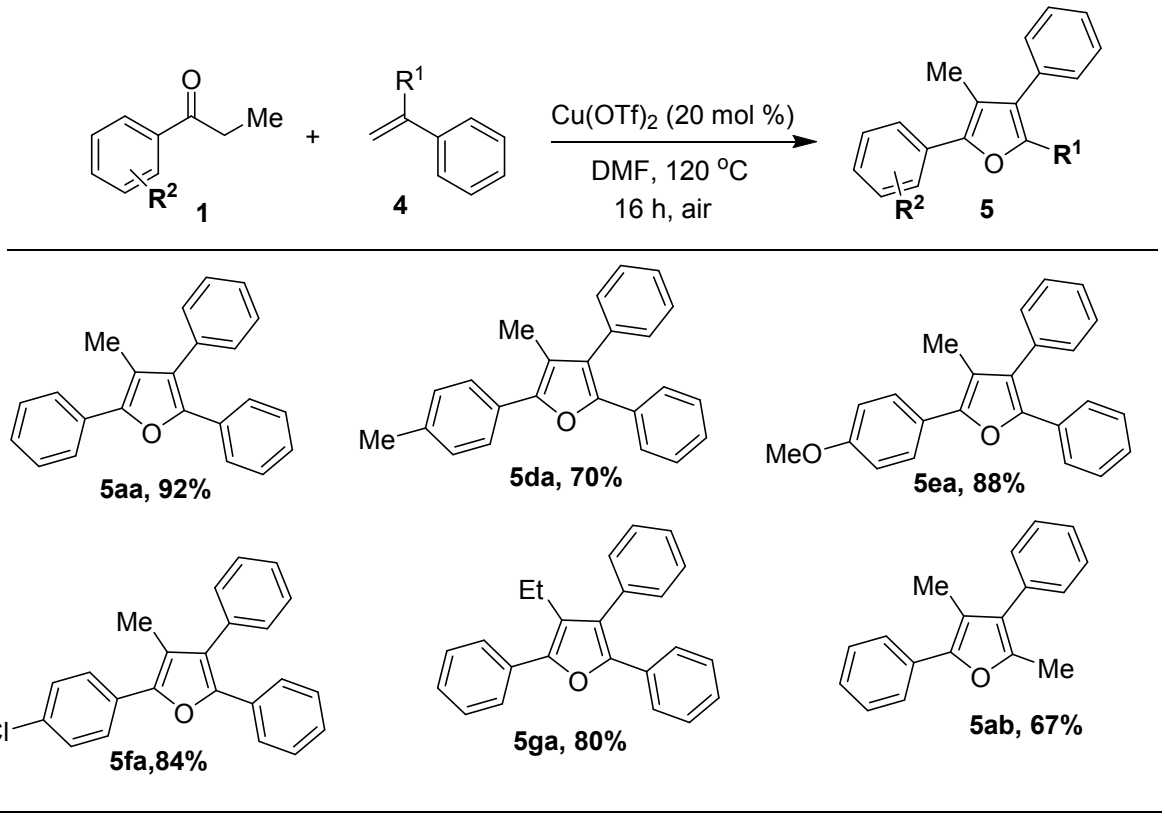


[a]Reaction conditions: 0.5 mmol of **1** and 0.5 mmol of **2** in the presence of 20 mol % $CuCl_2$ in 2 mL DMF at 120 °C for 16 h.

Next, to generalise the reaction conditions, we have performed the reaction with different aryl ketones derivatives and styrenes (Scheme 3). 4-Methyl and 4-methoxy acetophenone reacted with styrene to give the desired furan **3ba** and **3ca** 51 and 50% yield respectively. Likewise, reaction of 4-methyl, 4-methoxy, and 4-chloro propiophenones with styrene were also compatible and the desired furans **3da**, **3ea**, and **3fa** were formed in excellent yield. The reaction of substituted aryl ketones and substituted styrenes were also successful. For examples, 4-methoxy, and 4-chloro propiophenone reacted with 4-methoxy, 4-chloro, and 4-bromostyrene

and afforded corresponding furans **3ed**, **3fe**, **3ef** with excellent regioselectivity and good yield. Other aryl ketones like butyrophenone and 2-phenylacetophenone were also effective and provided the corresponding furans **3ga** and **3ha** with styrene. *Trans*-stilbene is also suitable candidate and was converted to the product **3di** with good yield. Moreover, α-tetralone was found to be effective under the reaction conditions and reacted efficiently with styrene and 3-methylstyrene to give the product **3ia** and **3ib** respectively.

Scheme 4. Synthesis of 2,3,4,5-Tetrasubstituted Furans[a]

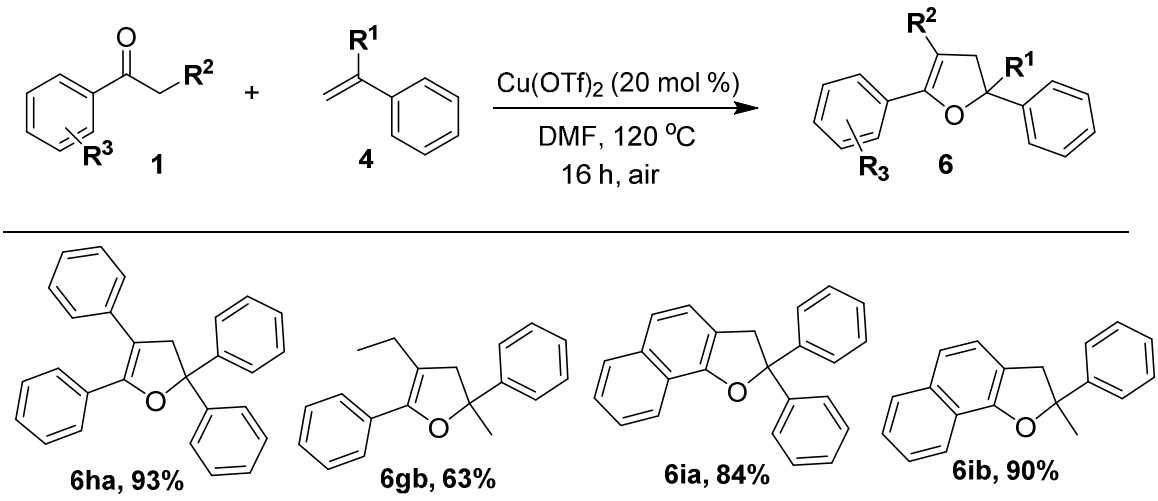


[a]Reaction conditions: 0.5 mmol of **1** and 0.5 mmol of **4** in the presence of 20 mol % $Cu(OTf)_2$ in 2 mL DMF at 120 °C for 16 h.

Although, the stilbene worked well under the standard conditions but α-substituted styrene like α-phenylstyrene did not work with copper(II) chloride. This failure led us to investigate further. Interestingly, 2,3,4,5-tetrasubstituted furans were obtained through 1,2-phenyl migration when the catalyst was changed from copper(II) chloride to copper(II) triflate under the same conditions (Scheme 4). Hence, we explored the substrate scopes with different α-substituted styrenes. For examples, α-phenylstyrene was treated with different aryl ketone such as propiophenone, 4-

methylpropiophenone, 4-methoxypropiophenone, 4-chloropropiophenone and butyrophenone to get the expected tetra-substituted furans **5aa**, **5da**, **5ea**, **5fa** and **5ga** respectively in good yield. Similarly, *α*-methylstyrene reacted well with propiophenone resulting in 67% yield of the product **5ab**. But *α*-methylstyrene did not respond well with the other substituted aryl ketones. While performing these reactions, we observed that some substrates did not give the tetra-substituted furans instead the reaction stopped at dihydrofurans (Scheme 5). The 2-phenylacetophenone gave the 2,2,4,5-tetraphenyl-2,3-dihydrofuran **6ha** in 93% yield while reacting with *α*-phenylstyrene. Similar product was obtained when butyrophenone was treated with *α*-methylstyrene (**6gb**, 63%). *α*-Tetralone was treated with *α*-phenylstyrene and *α*-methylstyrene to produce naphthodihydrofurans (**6ia**, 84% and **6ib**, 90% respectively). But the aliphatic ketones like ethylmethyl ketone, 4-phenylbutan-2-one and cyclohexanone as well as the aliphatic olefin like oct-1-ene did work at all under the present reaction conditions. The structure of 3-methyl-4,5-diphenyl-2-(*p*-tolyl)furan (**5da**) was further confirmed by the X-ray crystallography.[12]

Scheme 5. Synthesis of 2,2,4,5-Tetrasubstituted-2,3-dihydrofurans[a]

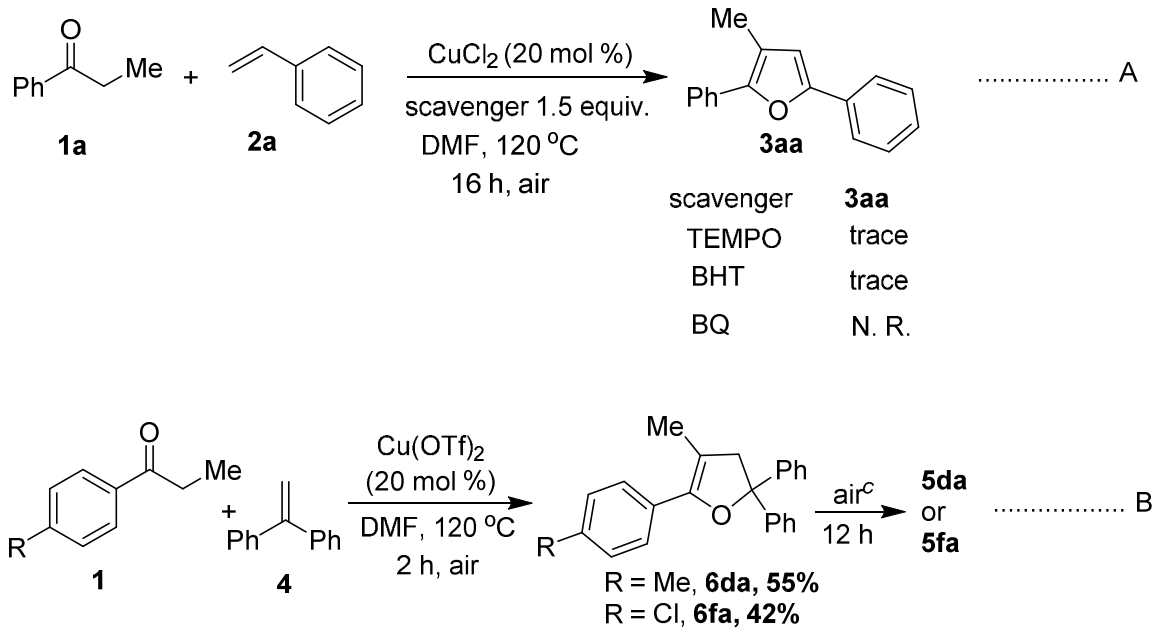


[a]Reaction conditions: 0.5 mmol of **1** and 0.5 mmol of **4** in the presence of 20 mol % $Cu(OTf)_2$ in 2 mL DMF at 120 °C for 16 h.

To understand the possible mechanism of this reaction, some controlled experiments were carried out and the results have been summarized in Scheme 6. The reactions were nearly or totally stopped upon treatment with a radical scavenger such as TEMPO (1.5 equiv.), BHT (1.5 equiv.) and BQ (1.5 equiv.). These results are the possible indication of a radical formation

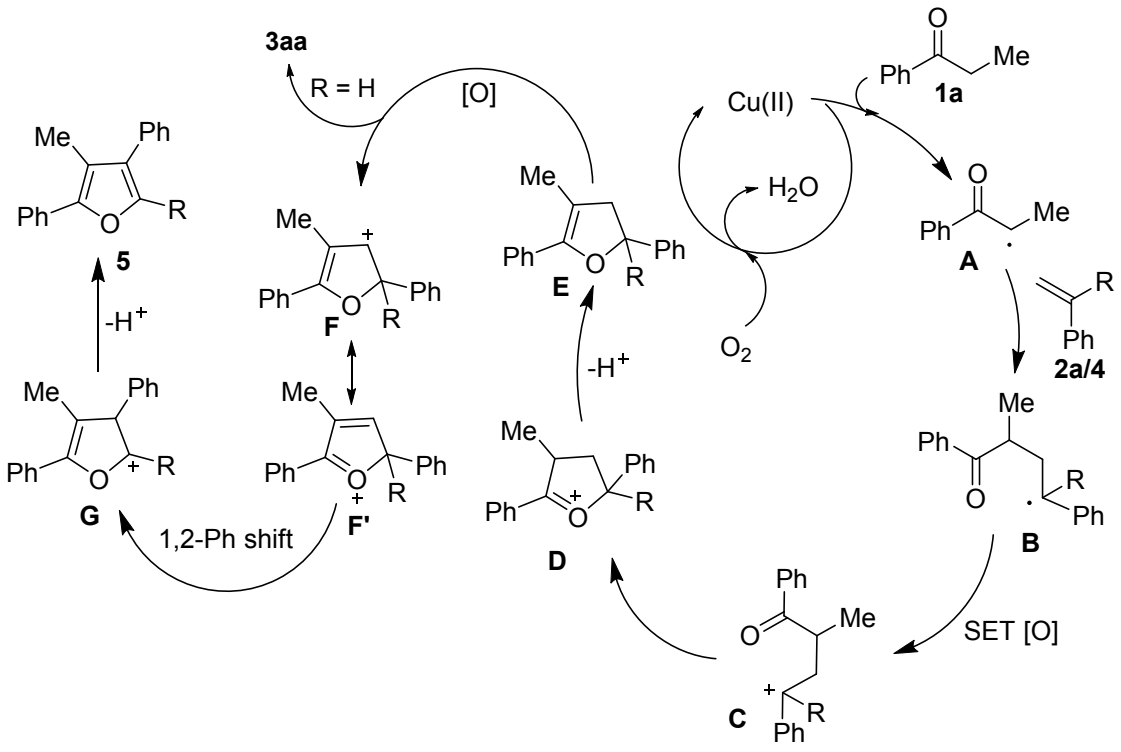
pathway. Furthermore, two reaction intermediates (**6da** and **6fa**) have been isolated after 2 h (Scheme 6, eq B) which are transformed to the corresponding furans (**5da** and **5fa**) in the presence of air only.

Scheme 6. Control Experiments[a,b]



[a]Reaction conditions for eq A: 0.5 mmol of **1a**, 0.5 mmol of **2a** and 0.75 mmol scavenger in the presence of 20 mol % $CuCl_2$ in 2 mL DMF at 120 °C for 16 h. [b]Reaction conditions for eq B: 0.5 mmol of **1** and 0.5 mmol of **4** in the presence of 20 mol % $Cu(OTf)_2$ in 2 mL DMF at 120 °C for 2 h. [c]DMF, 120 °C, 12 h.

Scheme 7. Proposed Mechanism



A plausible reaction mechanism has been outlined in Scheme 7 on the basis of the controlled experiments and literature reports.[5b-c,10,11] The propiophenone can be converted to a carbon-centered radical **A** in the presence of copper catalysts[5b-c] and air oxygen. Intermediate **A** attacks the styrene to form another carbon-centered radical **B** which is further transformed to intermediate **C** via single-electron transfer. After cyclization and tautomerization, the intermediate **C** can form the intermediate **E** which has been isolated in some cases (see Scheme 5). Upon oxidation, intermediate **E** is either converted to product **3aa** or intermediate **F** depending on the styrene derivatives. The intermediate **F** is transformed to intermediate **G** after 1,2-phenyl shift.[13] The intermediate **G** directly forms tetra-substituted furans after the removal of a proton.

Conclusion:

In conclusion, we have demonstrated the copper-catalysed annulation *via* an oxidative free-radical process from aryl ketones and aromatic olefins without using any external oxidant. These reactions provide a novel synthetic route to 2,3,5-tri-, 2,3,4,5- tetrasubstituted furan and 2,2,4,5-tetrasubstituted dihydrofurans from readily available starting materials. Complete regioselectivity, broad substrates scope and wide availablability of starting materials make this protocol synthetically useful to create a library of furan derivatives.

EXPERIMENTAL SECTION:

General Information: ^{1}H NMR spectra were determined on a 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and are referenced to tetramethylsilane (TMS) as internal standard and the signals were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and coupling constants *J* were given in Hz. Proton-decoupled $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. TLC was monitored with aluminium backed silica gel 60 (HF_{254}) plates (0.25 mm) using various organic solvent mixtures. Silica gel (60-120 mesh) was used for column chromatography. Petroleum ether (PET) refers to the fraction boiling in the range of 60-80ºC unless otherwise mentioned. All solvents were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. X-ray single crystal data were collected using MoKα (λ = 0.71073 Å) radiation with CCD area detector.

General Experimental Procedure for the Synthesis of Multisubstituted Furan (Scheme 2, Scheme 3): A mixture of **1** (0.5 mmol), styrenes (0.5 mmol), and $CuCl_2$ (0.1 mmol, 14 mg) in DMF (2 mL) was placed in a reaction tube. Then the reaction mixture was stirred at 120 °C for 16 h under ambient air. 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 Na_2SO_4. The crude residue was obtained after evaporation of the solvent in vacuum and was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether as the eluent to afford pure product.

3-Methyl-2,5-diphenylfuran (3aa):[10] White solid (95%, 115 mg), R_f 0.8 (PET), mp 46−47 °C (lit. mp 47−48 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* =7.6 Hz, 4H), 7.42-7.33 (m, 4H), 7.24-7.20 (m, 2H), 6.56 (s, 1H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 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-(*m*-tolyl)furan (3ab):[5c] Gummy colorless liquid (94%, 116 mg), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.67-7.64 (m, 2H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.43-7.38 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.72 (s, 1H), 2.53 (s, 3H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.9, 148.2, 138.3, 131.9, 130.8, 128.7, 128.6, 128.1, 126.7, 125.3, 124.4, 121.0, 118.7, 110.8, 21.6, 12.2.

(2-Chlorophenyl)-3-methyl-2-phenylfuran (3ac):[7a] Gummy liquid (81% yield, 108 mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 8.0, 1.6 Hz, 1H), 7.74-7.71 (m, 2H), 7.47-7.42 (m, 3H), 7.35-7.29 (m, 2H), 7.21-7.16 (m, 1H), 7.11 (s, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.4, 148.0, 131.6, 130.8, 130.0, 129.2, 128.7, 127.9, 127.7, 127.09, 127.00, 125.5, 118.7, 116.8, 12.2.

5-(4-Methoxyphenyl)-3-methyl-2-phenylfuran (3ad):[10] White solid (88%, 116 mg), R_f 0.6 (PET : EtOAc = 98 :2), mp 95–96 °C (lit. mp 96–97 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.67-7.63 (m, 2H), 7.45-7.40 (m, 2H), 7.28-7.24 (m, 1H), 6.96-6.91 (m, 2H), 6.48 (s, 1H), 3.85 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 151.9, 147.6, 132.0, 128.6, 126.5, 125.27, 125.21, 124.0, 118.7, 114.3, 109.4, 55.4, 12.2.

5-(4-Chlorophenyl)-3-methyl-2-phenylfuran (3ae):[7a] White solid (82 % yield, 110 mg), R_f 0.7 (PET), mp 80–82 °C (lit. 81–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.67-7.64 (m, 2H), 7.50-7.45 (m, 2H), 7.40-7.36 (m, 2H), 7.34-7.30 (m, 1H), 6.62 (s, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 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, 12.2.

5-(4-Bromophenyl)-3-methyl-2-phenylfuran (3af):[7a] White solid (85 % yield, 133 mg), R_f 0.7 (PET), mp 85–86 °C (lit. 84–85 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.58-7.55 (m, 2H), 7.52-7.49 (m, 2H), 7.46-7.42 (m, 2H), 7.31-7.27 (m, 1H), 6.61 (s, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.7, 148.7, 131.9, 131.6, 129.8, 128.7, 127.0, 125.4, 125.3, 125.2, 123.8, 121.0, 118.9, 111.4, 12.2.

5-(2,4-Dimethylphenyl)-3-methyl-2-phenylfuran (3ag): Liquid (78%, 102 mg), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.29-7.25 (m, 1H), 7.08 (d, J = 6.8 Hz, 2H), 6.47 (s, 1H), 2.54 (s, 3H), 2.36 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.8, 147.6, 137.2, 134.4, 132.1, 132.0, 128.6, 127.5, 126.9, 126.8, 126.6, 125.2, 118.3, 113.8, 22.1, 21.2, 12.2; Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92; Found: C, 86.77; H, 7.01%.

5-Mesityl-3-methyl-2-phenylfuran (3ah): Colorless liquid (76%, 105 mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 6.97 (s, 2H), 6.23 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.30 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.4, 147.7, 138.3, 138.2, 132.2, 128.6, 128.5, 128.2, 126.4, 125.1, 117.3, 115.2, 21.2, 20.9, 12.3; Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29%; Found: C, 87.13; H, 7.18%.

2-Phenyl-5-(*p*-tolyl)furan (3ba):[10] Gummy mass (51%, 60 mg), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.65-7.63 (m, 2H), 7.43-7.36 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 3.2 Hz, 1H), 6.68 (d, J = 3.6 Hz, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 129.5, 128.8, 128.7, 128.6, 128.3, 127.5, 127.3, 125.4, 123.87, 123.81, 107.3, 106.6, 21.4.

2-(4-Methoxyphenyl)-5-phenylfuran (3ca): Gummy mass (50%, 62 mg), R_f 0.8 (PET : EtOAc = 98:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.67 (m, 4H), 7.41-7.37 (m, 2H), 7.27-7.25 (m, 1H), 6.96-6.93 (m, 2H), 6.72 (d, J = 3.6 Hz, 1H), 6.60 (d, J = 3.2 Hz, 1H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 152.8, 131.0, 128.8, 128.4, 127.2, 126.7, 125.3, 123.6, 114.3, 107.3, 105.7, 55.4; Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%; Found: C, 81.31; H, 5.71%.

3-Methyl-5-phenyl-2-(*p*-tolyl)furan (3da):[10] White solid (85%, 105 mg), R_f 0.8 (PET), mp 94–95 °C (lit. 95–96 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.14-7.12 (m, 3H), 6.48 (s, 1H),2.28 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.4, 148.5, 136.5, 131.0, 129.3, 129.1, 128.7, 127.1, 125.3, 123.7, 118.0, 110.8, 21.3, 12.1.

2-(4-Methoxyphenyl)-3-methyl-5-phenylfuran (3ea):[5c] White solid, (90%, 119 mg), R_f 0.6 (PET : EtOAc = 98 :2), mp 92-93 °C (lit. 92–93 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.67-7.63 (m, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.26-7.22 (m, 1H), 7.00-6.97 (m, 2H), 6.60 (s, 1H), 3.86 (s, 3H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.6, 151.2, 148.4, 131.0, 128.7, 127.0, 126.8, 124.9, 123.6, 117.1, 114.2, 110.7, 55.4, 12.0.

2-(4-Chlorophenyl)-3-methyl-5-phenylfuran (3fa): White solid (91%, 122 mg), R_f 0.8 (PET), mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.70 (m, 2H), 7.66-7.62 (m, 2H), 7.43-7.38 (m, 4H), 7.30-7.26 (m, 1H), 6.61 (s, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.0, 147.2, 132.3, 130.6, 130.3, 128.87, 128.82, 127.5, 126.3, 123.8, 119.2, 111.0, 12.2; Anal. Calcd for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88%; Found: C, 76.10; H, 4.76%.

2,5-Bis(4-methoxyphenyl)-3-methylfuran (3ed): White solid (81%, 119 mg), R_f 0.6 (PET : EtOAc = 97:3), mp 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 4H), 6.90-6.81 (m, 4H), 6.36 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 158.4, 151.3, 147.7, 128.3, 127.3, 126.7, 125.1, 125.0, 124.2, 117.0, 114.2, 114.1, 109.2, 55.4, 12.0; Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16%; Found: C, 77.31; H, 6.04%.

2,5-Bis(4-chlorophenyl)-3-methylfuran (3fe): Liquid (69%, 104 mg), R_f 0.8 (PET : EtOAc = 99:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 4H), 7.40-7.38 (m, 2H), 7.36-7.34 (m, 2H),

6.58 (s, 1H), 2.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0, 147.6, 133.1, 132.6, 130.1, 129.1, 129.0, 128.9, 126.4, 125.0, 119.3, 111.4, 12.2; Anal. Calcd for $C_{17}H_{12}Cl_2O$: C, 67.35; H, 3.99%; Found: C, 67.56; H, 3.85%.

5-(4-Bromophenyl)-2-(4-methoxyphenyl)-3-methylfuran (3ef): White solid (71%, 122 mg), R_f 0.6 (PET : EtOAc = 97:3), mp 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2H), 7.56-7.53 (m, 2H), 7.50-7.47 (m, 2H), 7.00-6.96 (m, 2H), 6.58 (s, 1H), 3.86 (s, 3H), 2.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 158.8, 150.1, 148.9, 131.9, 129.9, 126.9, 125.1, 124.6, 120.7, 117.2, 114.2, 111.3, 55.4, 12.0; Anal. Calcd for $C_{18}H_{15}BrO_2$: C, 62.99; H, 4.41%; Found: C, 63.13; H, 4.32%.

3-Ethyl-2,5-diphenylfuran (3ga):[10] Colorless oil (83% yield, 103 mg,), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.49-7.40 (m, 4H), 7.33-7.25 (m, 2H), 6.72 (s, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 147.7, 131.8, 130.9, 128.7, 128.6, 127.3, 126.9, 125.6, 125.5, 123.7, 108.7, 19.4, 14.5.

2,3,5-Triphenylfuran (3ha):[5c] White solid (87 % yield, 129 mg), R_f 0.8 (PET), mp 99–101 °C (lit. 93–94 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.60-7.56 (m, 2H), 7.45-7.42 (m, 2H), 7.39-7.35 (m, 3H), 7.34-7.31 (m, 1H), 7.30-7.19 (m, 5H), 6.78 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.6, 148.0, 134.4, 131.2, 130.6, 128.87, 128.84, 128.80, 128.5, 127.66, 127.63, 127.4, 126.2, 124.6, 123.9, 109.6.

3-Methyl-4,5-diphenyl-2-(*p*-tolyl)furan (3di): White solid (86%, 139 mg), R_f 0.8 (PET), mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.0 Hz, 2H), 7.40-7.33 (m, 4H), 7.31-7.25 (m, 3H), 7.18-7.12 (m, 4H), 7.07 (t, J = 7.6 Hz, 1H), 2.31 (s, 3H), 2.03 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 147.9, 146.8, 136.7, 134.0, 131.1, 130.2, 129.3, 128.9, 128.8, 128.3, 127.4, 126.9, 126.0, 125.5, 125.4, 118.1, 21.3, 10.4; Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21%; Found: C, 89.13; H, 6.16%.

2-Phenyl-4,5-dihydronaphtho[1,2-*b*]furan (3ia):[7a] Colourless liquid (73% yield, 90 mg,), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.81 (m, 2H), 7.70-7.67 (m, 1H), 7.52-7.46 (m, 2H), 7.38-7.34 (m, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.25-7.21 (m, 1H), 6.73 (s, 1H), 3.10 (t, J = 8.0 Hz, 2H), 2.88 (t, J = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.3, 149.8, 134.8, 128.9, 128.8, 128.5, 128.1, 128.0, 127.2, 126.8, 126.4, 124.8, 123.7, 121.6, 119.2, 106.6, 29.1, 21.1.

2-(*m*-Tolyl)-4,5-dihydronaphtho[1,2-*b*]furan (3ib): Colorless oil (78%, 101 mg), R_f 0.8 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.65 (m, 3H), 7.44-7.36 (m, 2H), 7.33-7.30 (m, 1H), 7.27-

7.23 (m, 1H), 7.21 (d, J = 6.8 Hz, 1H), 6.74 (s, 1H), 3.12 (t, J = 8.0 Hz, 2H), 2.90 (t, J = 8.4 Hz, 2H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.7, 153.5, 149.6, 138.3, 134.7, 131.0, 128.7, 128.1, 126.8, 126.4, 125.3, 125.1, 124.3, 121.5, 120.9, 120.1, 119.2, 106.5, 29.1, 21.6, 21.1; Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20%; Found: C, 87.58; H, 6.14%.

General Experimental Procedure for the Synthesis of Multisubstituted Furan (Scheme 4, Scheme 5): A mixture of **1** (0.5 mmol), styrenes (**4**) (0.5 mmol), and $Cu(OTf)_2$ (0.1 mmol, 36 mg) in DMF (2 mL) was placed in a reaction tube. Then the reaction mixture was stirred at 120 °C for 16 h under ambient air. 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 Na_2SO_4. The crude residue was obtained after evaporation of the solvent in vacuum and was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether as the eluent to afford pure product.

3-Methyl-2,4,5-triphenylfuran (5aa): White solid (92%, 142 mg), R_f 0.8 (PET), mp 99–100 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69-7.67 (m, 2H), 7.40-7.33 (m, 6H), 7.31-7.29 (m, 1H), 7.27-7.25 (m, 2H), 7.22-7.18 (m, 1H), 7.16-7.12 (m, 2H), 7.10-7.05 (m, 1H), 2.05 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8, 147.3, 134.0, 131.8, 131.1, 130.3, 128.9, 128.7, 128.4, 127.5, 127.1, 127.0, 126.1, 125.6, 125.5, 118.9, 10.5; Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%; Found: C, 89.28; H, 5.76%.

3-Methyl-4,5-diphenyl-2-(*p*-tolyl)furan (5da): White solid (70%, 113 mg), R_f 0.8 (PET), mp 147–149 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 2H), 7.50-7.44 (m, 4H), 7.42-7.39 (m, 1H), 7.38-7.35 (m, 2H), 7.29-7.22 (m, 4H), 7.20-7.15 (m, 1H), 2.42 (s, 3H), 2.14 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.0, 146.9, 136.8, 134.1, 131.2, 130.3, 129.4, 129.0, 128.9, 128.4, 127.5, 127.0, 126.0, 125.6, 125.5, 118.2, 21.4, 10.5; Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21%; Found: C, 88.77; H, 6.29%.

2-(4-Methoxyphenyl)-3-methyl-4,5-diphenylfuran (5ea): White solid (88%, 150 mg), R_f 0.6 (PET : EtOAc = 98:2), mp 132–133 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.38-7.31 (m, 5H), 7.25-7.22 (m, 3H), 7.13-7.09 (m, 2H), 6.90-6.87 (m, 2H), 3.73 (s, 3H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.7, 147.9, 146.6, 137.6, 134.1, 132.5, 131.2, 130.3, 128.8, 128.3, 127.4, 127.1, 125.4, 124.7, 117.3, 114.1, 55.4, 10.4; Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92%; Found: C, 84.48; H, 6.06%.

2-(4-Chlorophenyl)-3-methyl-4,5-diphenylfuran (5fa): White solid (84%, 145 mg), R_f 0.7 (PET), mp 137–139 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.58 (m, 2H), 7.38-7.35 (m, 3H),

7.34-7.28 (m, 4H), 7.25-7.23 (m, 2H), 7.16-7.12 (m, 2H), 7.10-7.06 (m, 1H), 2.03 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 147.5, 146.7, 133.7, 132.6, 130.9, 130.3, 130.2, 128.97, 128.92, 128.4, 128.2, 127.6, 127.3, 126.7, 126.2, 125.6, 119.4, 10.6 ; Anal. Calcd for $C_{23}H_{17}ClO$: C, 80.11; H, 4.97%; Found: C, 80.32; H, 4.89%.

3-Ethyl-2,4,5-triphenylfuran (5ga): White solid (80%, 130 mg), R_f 0.8 (PET), mp 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.66 (m, 2H), 7.38-7.30 (m, 7H), 7.29-7.25 (m, 2H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.04 (m, 1H), 2.49 (q, J = 7.6 Hz, 2H), 0.98 (t, J = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 147.35, 147.31, 134.2, 131.7, 131.1, 130.3, 128.9, 128.7, 128.4, 127.6, 127.1, 127.0, 125.7, 125.6, 125.4, 17.5, 14.7; Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21%; Found: C, 88.61; H, 6.08%.

2,4-Dimethyl-3,5-diphenylfuran (5ab): White solid (67%, 83 mg), R_f 0.8 (PET), mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 2H), 7.45-7.39 (m, 4H), 7.34-7.29 (m, 3H), 7.27-7.23 (m, 1H), 2.36 (s, 3H), 2.20 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 147.3, 147.0, 133.7, 132.0, 129.8, 128.6, 128.5, 126.8, 126.5, 125.4, 124.9, 116.5, 12.5, 10.9; Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49%; Found: C, 86.87; H, 6.52%.

2,2,4,5-Tetraphenyl-2,3-dihydrofuran (6ha): Colorless oil (93%, 174 mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.66-7.64 (m, 4H), 7.45-7.38 (m, 7H), 7.36-7.27 (m, 6H), 7.23-7.20 (m, 1H), 4.00 (d, J = 1.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 149.0, 146.4, 135.6, 131.8, 128.8, 128.4, 128.3, 128.2, 127.5, 127.3, 126.2, 126.0, 109.6, 88.5, 50.0; Anal. Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92%; Found: C, 90.13; H, 5.78%.

4-Ethyl-2-methyl-2,5-diphenyl-2,3-dihydrofuran (6gb): Colorless oil (63%, 83 mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (m, 2H), 7.49-7.46 (m, 2H), 7.38-7.25 (m, 5H), 7.24-7.20 (m, 1H), 2.98 (q, J = 15.6 Hz, 2H), 2.38-2.24 (m, 2H), 1.70 (s, 3H), 1.05 (t, J = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 148.5, 146.5, 132.4, 128.3, 128.2, 127.8, 127.2, 126.7, 124.6, 110.8, 84.3, 49.3, 29.6, 20.3, 13.2; Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%; Found: C, 86.55; H, 7.73%.

2,2-Diphenyl-2,3-dihydronaphtho[1,2-*b*]furan (6ia): Colorless oil (84%, 135mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.62-7.59 (m, 4H), 7.54-7.52 (m, 1H), 7.50-7.46 (m, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.38-7.33 (m, 5H), 7.31-7.26 (m, 2H), 4.14 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 153.9, 145.7, 134.2, 128.4, 128.0, 127.5, 126.1, 125.8, 125.5, 122.8, 121.6, 120.69, 120.62, 119.2, 93.3, 45.6; Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63%; Found: C, 89.62; H, 5.55%.

2-Methyl-2-phenyl-2,3-dihydronaphtho[1,2-*b*]furan (6ib): Colorless oil (90%, 117 mg), R_f 0.7 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.67-7.65 (m, 2H), 7.62-7.53 (m, 2H), 7.51-7.43 (m, 3H), 7.39-7.34 (m, 2H), 3.66 (q, J = 15.2 Hz, 2H), 1.98 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 147.2, 134.2, 128.5, 128.0, 127.1, 125.7, 125.3, 124.6, 123.1, 121.7, 120.7, 120.2, 119.2, 90.0, 45.8, 29.5; Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20%; Found: C, 87.82; H, 6.12%.

4-Methyl-2,2-diphenyl-5-(*p*-tolyl)-2,3-dihydrofuran (6da): Colorless oil (55%, 55 mg), R_f 0.6 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 2H), 7.43-7.40 (m, 4H), 7.24-7.20 (m, 4H), 7.15-7.11 (m, 4H), 3.41 (d, J = 1.2 Hz, 2H), 2.29 (s, 3H), 1.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.1, 137.6, 129.2, 128.9, 128.2, 127.0, 126.1, 125.9, 104.1, 87.5, 52.1, 21.4, 12.9; Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%; Found: C, 88.07; H, 6.67%.

5-(4-Chlorophenyl)-4-methyl-2,2-diphenyl-2,3-dihydrofuran (6fa): Colorless oil (42%, 73 mg), R_f 0.6 (PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.47 (m, 2H), 7.39 (d, J = 7.6 Hz, 3H), 7.27-7.19 (m, 9H), 3.41 (s, 2H), 1.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 133.4, 130.5, 128.6, 128.55, 128.50, 128.34, 128.30, 128.2, 127.2, 125.8, 105.7, 87.8, 52.1, 12.9; Anal. Calcd for $C_{23}H_{19}ClO$: C, 79.65; H, 5.52%; Found: C, 79.52; H, 5.64%.

AUTHOR INFORMATION

Corresponding Author

E-mail: alakananda.hajra@visva-bharati.ac.in

Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:.

Scanned copies of 1H and ^{13}C{^{1}H} NMR spectra of the synthesized compounds (PDF)

Crystallographic data for compound **5da** (CIF)

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