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Note

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Regioselective Synthesis of Multisubstituted Furans *via* Copper-Mediated Coupling between Ketones and β-Nitrostyrenes

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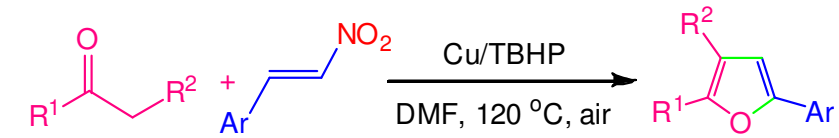


R^1 = aryl, heteroaryl, Me
R^2 = H, Me, Et, Ph, Bn
Ar = aryl, heteroaryl

Abstract:

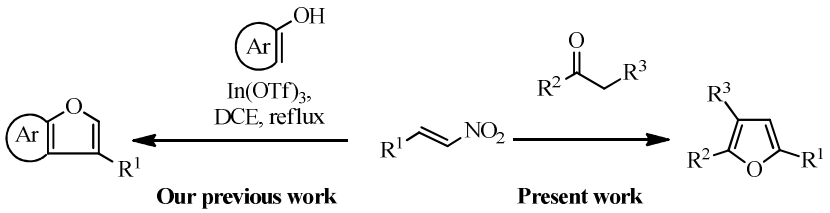
A copper-mediated intermolecular annulation of alkyl ketones and *β*-nitrostyrenes has been developed for the regioselective synthesis of multi-substituted furan derivatives in good yields. This protocol is applicable for both cyclic and acyclic ketones.

Polysubstituted furan derivatives represent an important class of five membered heterocycles ubiquitous in a number of biologically active natural products. They are the constituents of numerous therapeutic agents and also used as building blocks in organic synthesis.[1] Owing to their versatile biological activities, extensive synthetic efforts have been devoted for the construction of polysubstituted furans. The classical methods such as the Paal-Knorr synthesis[2] and Feist-Benary synthesis[3] provide rapid access to substituted furans from dicarbonyl compounds. On the other hand, many excellent methods have also been developed for the synthesis of substituted furans from acyclic ketone precursors involving alkyne- or allene-assisted cyclizations.[4] During the past decades transition metal-catalyzed inter/intra molecular condensation reactions for the synthesis of furan derivatives have provided powerful means of access to diversely substituted furans which are extensively studied.[5] Given the great importance of furans in natural and synthetic substances, the development of new synthetic method that allow more straightforward and environmentally accessible intermolecular approach from simple

and cheap chemical reagents is highly desirable. Although various dicarbonyl compounds and pre-functionalized ketones have been extensively utilized for the synthesis of furans, use of commercially available simple alkyl ketone as precursor has been less explored.[6]

Conjugated nitroolefins are widely used as Michael acceptor in organic synthesis due to the high electrophilicity of the double bond. They have attracted attention as excellent building blocks for the synthesis of various types of heterocyclic and carbocyclic compounds.[7] In this context, reactive nitroallylic acetates have also been explored for the synthesis of furan/benzofurans from dicarbonyl/phenol derivatives.[8] Recently, we have described a simple, and straight forward one-pot synthesis of benzofuran and naphthofuran derivatives from readily available nitroalkenes by coupling with phenols/naphthols *via* tandem Michael addition/denitration (Scheme 1).[9] More recently, we reported a copper-catalyzed regioselective synthesis of multisubstituted furans employing ketone and cinnamic acid as the coupling partner.[10] So far coupling between simple alkyl ketone and nitrostyrene has not been studied till now, we envisioned that commercially available ketone and easily accessible nitrostyrene would be the good choice for annulation to synthesize more structurally diversed furan derivatives. Herein, we report a regioselective synthesis of 2,3,5-trisubstituted furans from readily available simple alkyl ketones and *β*-nitrostyrenes (Scheme 1).

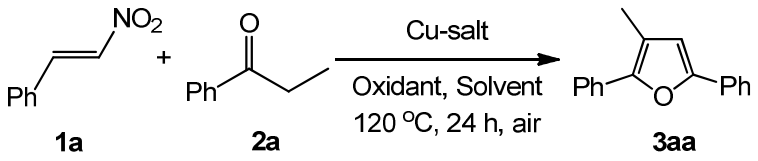
Scheme 1. Synthesis of multisubstituted furans from nitroalkenes



We commenced our study by taking a mixture of *β*-nitrostyrene (**1a)** and propiophenone (**2a)** in 1:2 molar ratio in the presence of 1 equiv. of CuBr in DMF (Table 1, entry 1) which afforded 20% yield of the corresponding furan regioselectively (**3aa)**. Replacing CuBr by $CuBr{\cdot}SMe_2$ (1 equiv.), an improvement in the yield (35%) was observed (Table 1, entry 2). Different solvents like DMA, NMP, toluene, xylene and DMSO (Table 1, entries 3-7) were also screened; among them DMF was found to be the best one. Next we turned our attention to check the effect of oxidants. Scrutinizing the various oxidants such as O_2, TBHP, DTPB, $K_2S_2O_8$ and

DDQ (Table 1, entries 8-13); TBHP (1 equiv.) has the beneficial effect to give the best yield (67%) (Table 1, entry 10). However the yield was decreased on lowering the amount of TBHP. The yield of the product was decreased with changing the molar ratio of the reactants (Table 1, entries 14 and 15). The reaction did not proceed at all in presence of other Cu-salts (Table 1, entries 16-19), such as CuCl, CuI, $CuCl_2$, $CuBr_2$. However, only trace amount of product was obtained in presence of $Cu(OAc)_2.H_2O$ (Table 1, entry 20). The reaction did not occur in absence of Cu-salt (Table 1, entries 21). Increasing the amount of Cu-salt (2 equiv.) did not improve the yield, (Table 1, entry 22) whereas decreasing the amount of Cu-salt (50 mol%) the yield was decreased (Table 1, entry 23). Finally, the optimized reaction conditions were obtained using the combination of propiophenone and *β*-nitrostyrene (2:1) in presence of 1 equiv. of $CuBr{\cdot}SMe_2$ and TBHP (1 equiv.) in DMF at 120 °C for 24 h under ambient air (Table 1, entry 10). It is noteworthy to mention that only one regioselective furan is obtained following this protocol.

Table 1. Optimization of the reaction conditions[a]



1a **2a** **3aa**

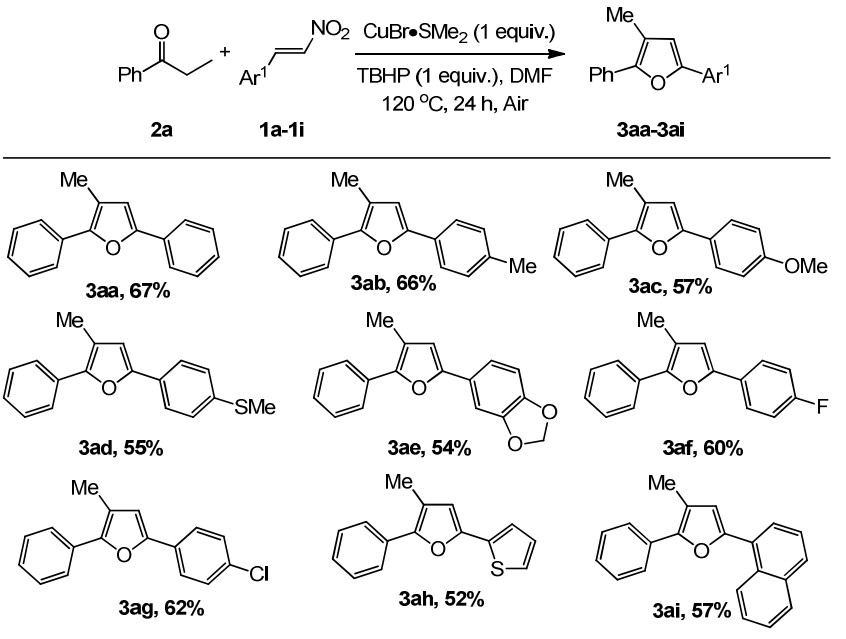
Entry	[Cu]	Oxidant	Solvent (mL)	Yield (%)
1	CuBr	-	DMF	20
2	$CuBr{\cdot}SMe_2$	-	DMF	35
3	$CuBr{\cdot}SMe_2$	-	DMA	32
4	$CuBr{\cdot}SMe_2$	-	NMP	9
5	$CuBr{\cdot}SMe_2$	-	Toluene	N.R
6	$CuBr{\cdot}SMe_2$	-	Xylene	8
7	$CuBr{\cdot}SMe_2$	-	DMSO	29
8	$CuBr{\cdot}SMe_2$	O_2 (1 atm)	DMF	35
9	$CuBr{\cdot}SMe_2$	O_2 (5 atm)	DMF	37
10	$CuBr{\cdot}SMe_2$	TBHP	DMF	67
11	$CuBr{\cdot}SMe_2$	DTBP	DMF	48
12	$CuBr{\cdot}SMe_2$	$K_2S_2O_8$	DMF	12
13	$CuBr{\cdot}SMe_2$	DDQ	DMF	8
14	$CuBr{\cdot}SMe_2$	TBHP	DMF	35[b]
15	$CuBr{\cdot}SMe_2$	TBHP	DMF	36[c]
16	CuCl	TBHP	DMF	N.R

17	CuI	TBHP	DMF	N.R
18	$CuCl_2$	TBHP	DMF	N.R
19	$CuBr_2$	TBHP	DMF	N.R
20	$Cu(OAc)_2.H_2O$	TBHP	DMF	10
21	-	TBHP	DMF	N.R
22	$CuBr{\cdot}SMe_2$	TBHP	DMF	69[d]
23	$CuBr{\cdot}SMe_2$	TBHP	DMF	29[e]

[a]Reaction conditions: *β*-nitrostyrene (**1a**) (0.5 mmol), propiophenone (**2a**) (1.0 mmol), Cu-salt (1 equiv.), oxidant (1 equiv.), solvent (1.5 mL), 120 °C, 24 h, air. [b]**1a**:**2a** (2:1). [c]**1a**:**2a** (1:1). [d]Cu-salt (2 equiv.). [e]Cu-salt (0.5 equiv.).

Under the optimized reaction conditions, we began to explore the scope of this annulation by employing various *β*-nitrostyrenes (**1a-1i**) (Scheme 2). *β*-Nitrostyrene bearing electron donating groups such as -Me and -OMe on the phenyl ring successfully provided the corresponding furans with good yields (**3ab** and **3ac**) whereas, halogen substituted aryl nitrostyrenes gave the moderate yields (**3af** and **3ag**). Notably, the dioxole part in the aryl nitrostyrene was unaffected in the present reaction conditions to give the desired furan with moderate yield (**3ae**). Moreover, hetero-aryl substituted nitroalkene also produced the corresponding furan (**3ah**) with moderate yield. However, *β*-methyl-*β*-nitrostyrene did not give the desired furan under the present reaction conditions.

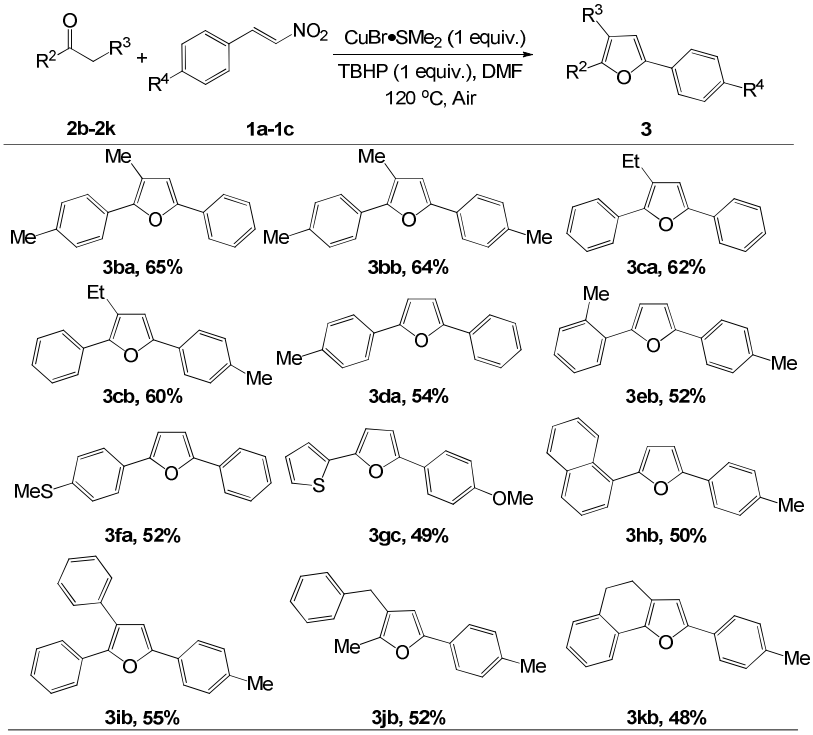
Scheme 2. Annulation of propiophenone with various *β*-nitrostyrenes[a]



[a]Reaction conditions: Propiophenone (1 mmol), *β*-nitrostyrenes (0.5 mmol), $CuBr{\cdot}SMe_2$ (0.5 mmol), TBHP (5~6M) in decane (0.1 mL, 1 equiv.), DMF (1.5 mL), 120 ^oC, 24 h, air.

We then turned our attention towards the scope of various alkyl aryl ketones to prove the general applicability of the reaction (Scheme 3). A diverse range of ketones such as 4´-methyl propiophenone (**2b**), butyrophenone (**2c**), acetophenones (**2d-2h**), and 2´-phenylacetophenone (**2i**) were compatible with this condition and afforded the expected products with excellent regioselectivity. We also synthesized disubstituted furans (**3da-3hb**) from different acetophenone derivatives under the present reaction conditions. Moreover, 2-acetyl thiophene (**2g**) underwent the reaction smoothly to give the corresponding furan (**3gc**). 4-Phenyl-2-butanone successfully produced the corrosponding furan (**3jb**) with 52% yield. Interestingly, alicyclic ketone such as *α*-tetralone also produced the desired furan (**3kb**) with moderate yield. However, no reaction occurred in the case of cyclohexanone and ethyl methyl ketone.

Scheme 3. Annulation of different alkyl aryl ketones with *β*-nitrostyrenes[a]

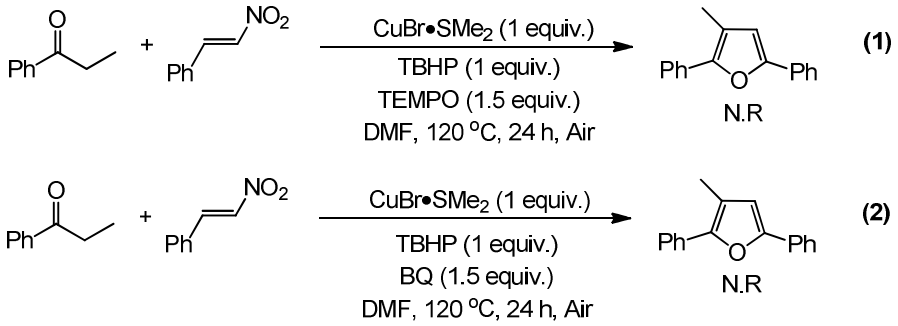


[a]Reaction conditions: Ketone (1 mmol), *β*-nitrostyrene (0.5 mmol), $CuBr{\cdot}SMe_2$ (0.5 mmol), TBHP (5~6M) in decane (0.1 mL, 1 equiv.), DMF (1.5 mL), 120 ^oC, 24 h, air.

To gain insight into the possible mechanism of this reaction, few controlled experiments were carried out (Scheme 4). It is noteworthy to mention that the reaction did not proceed at all on

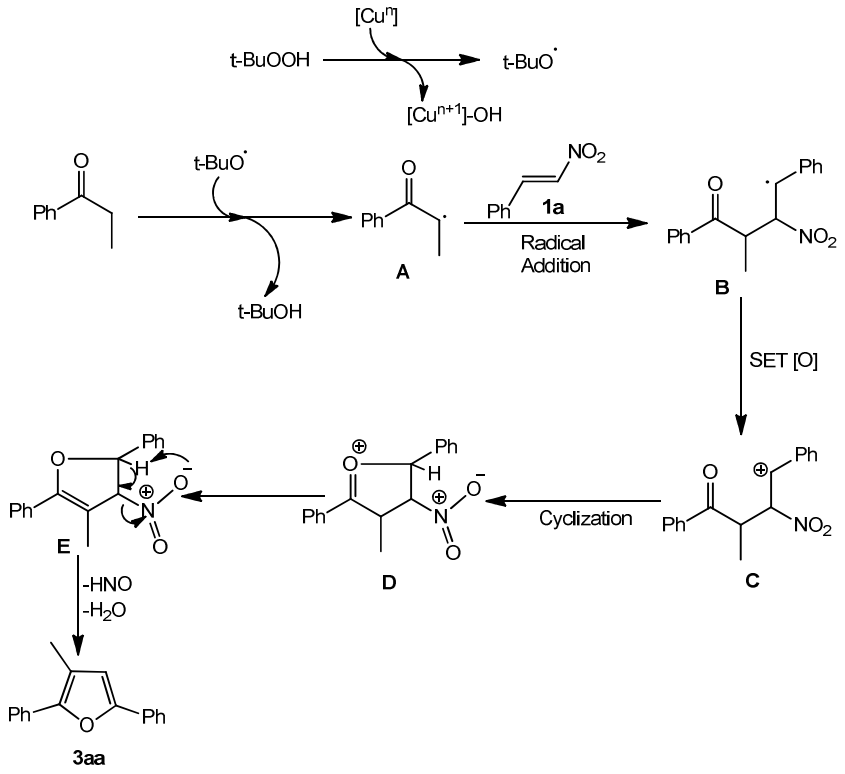
addition of radical scavengers like TEMPO (1.5 equiv.) or BQ (1.5 equiv.). These results indicate that the reaction possibly proceeds through the radical formation pathway.

Scheme 4. Controlled experiments



On the basis of controlled experiments and literature reports,[11] a plausible mechanism is outlined in scheme 5. The formation of *tert*-butylperoxy radical from TBHP was facilitated in presence of Cu (I) catalyst. Consequently propiophenone was converted into the carbon-centered radical **A** in the presence of *tert*-butylperoxy radical. Intermediate **A** attacks at the β position of nitroalkene (**1a**) to form the radical intermediate **B**, which was further transformed to intermediate **C** through SET. Upon cyclization and successive elimination of HNO and H_2O,[9,12] **C** was consecutively converted to **3aa** *via* the intermediates **D** and **E**.

Scheme 5. Plausible Mechanism



Conclusion:

In summary, we have demonstrated a CuBr·SMe_2/TBHP-mediated direct synthesis of 2,3,5-trisubstituted furan derivatives regioselectively by single electron transfer (SET) radical pathway. The versatile method shows a broad functional group tolerance and is applicable to a wide range of simple alkyl ketones and nitrostyrenes. Complete regioselectivity and widely available 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 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 (double doublet), m (multiplet) and coupling constants *J* were given in Hz. $^{13}C\{^1H\}$ NMR for proton-

decoupled carbon spectra were recorded at 100 MHz. TLC was done on TLC Silica gel 60 F_{254} coated on aluminium sheets (Merck). Silica gel (60-120 mesh) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C 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.

General experimental procedure for the synthesis of 3-methyl-2,5-diphenylfuran (3aa): A mixture of propiophenone (**2a**, 1 mmol, 134 mg), β-nitrostyrene (**1a**, 0.5 mmol, 74 mg), and $CuBr{\cdot}SMe_2$ (0.5 mmol, 102 mg) in DMF (1.5 mL) were taken in a reaction vessel and TBHP (5~6 molar in decane) (1 equiv., 0.1 mL) was added drop wise. Then the reaction mixture was stirred at 120 ^oC for 24 hours 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 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 3-methyl-2,5-diphenyl-furan **(3aa)** as white solid (78 mg, 67% yield).

3-Methyl-2,5-diphenylfuran (3aa):[10] White solid (67%, 78 mg), mp 47-48 ^oC (lit. mp 45-46^oC); ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 4H), 7.61-7.54 (m, 4H), 7.44-7.43 (m, 2H), 6.73 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 148.2, 131.8, 130.8, 128.7, 128.6, 127.2, 126.6, 125.2, 123.7, 118.7, 110.9, 12.1.

3-Methyl-2-phenyl-5-*p*-tolylfuran (3ab):[10] White solid (66%, 81 mg), mp 81-83 ^oC (lit. mp 80–82 ^oC); ^1H NMR (400 MHz, $CDCl_3$): 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), 7.25 (d, *J* = 8.0 Hz, 2H), 6.60 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 147.9, 137.1, 132.0, 129.4, 128.6, 128.2, 126.6, 125.2, 123.7, 118.7, 110.2, 21.4, 12.2.

5-(4-Methoxyphenyl)-3-methyl-2-phenylfuran (3ac):[10] White solid (57%, 75 mg), mp 96-97 ^oC (lit. mp 97-98 ^oC); ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 3.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 151.8, 147.6, 132.0, 128.6, 126.5, 125.2, 125.1, 124.0, 118.7, 114.2, 109.4, 55.4, 12.2.

3-Methyl-5-(4-(methylthio)phenyl)-2-phenylfuran (3ad): Colorless oil (55%, 77 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 9.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.0

Hz, 2H), 7.21-7.17 (m, 3H), 6.48 (s, 1H), 2.43 (s, 3H), 2.24 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 148.2, 137.4, 131.8, 128.7, 127.9, 126.9, 126.8, 125.3, 124.2, 118.8, 110.6, 16.0, 12.2. Anal calcd. for $C_{18}H_{16}OS$: C, 77.11; H, 5.75%; Found: C, 77.13; H, 5.79%.

5-(4-Methyl-5-phenylfuran-2-yl)-benzo[1,3]dioxole (3ae):[10] White solid (54%, 75 mg), mp 111-112 °C (lit. mp 110-112 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.19-7.10 (m, 3H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 5.89 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 148.1, 147.7, 147.0, 131.9, 128.6, 126.6, 125.4, 125.2, 118.7, 117.7, 109.9, 108.7, 104.6 , 101.2, 12.2.

5-(4-Fluorophenyl)-3-methyl-2-phenylfuran (3af):[10] White solid (60%, 75 mg), mp 85-86 °C (lit. mp 85-86 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.57 (m, 4H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.46 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^1J_{C\text{-}F}$ = 245 Hz), 150.9, 148.3, 131.8, 128.7, 127.2, 126.8, 125.5 (d, $^3J_{C\text{-}F}$ = 8 Hz), 125.3, 118.8, 115.8 (d, $^2J_{C\text{-}F}$ = 22 Hz), 110.6, 12.2.

5-(4-Chlorophenyl)-3-methyl-2-phenylfuran (3ag):[10] Colorless oil (62%, 83 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.22-7.17 (m, 1H), 6.51 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 148.6, 132.9, 131.9, 131.7, 129.4, 129.0, 128.7, 127.0, 125.4, 124.9, 118.8, 111.3, 12.2.

3-Methyl-2-phenyl-5-thiophen-2-yl-furan (3ah):[10] Light yellow oil (52%, 62 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 9.2 Hz, 2H), 7.35 (t, *J* = 8.0 Hz , 2H), 7.22-7.17 (m, 2H), 7.14 (d, *J* = 6.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.39 (s, 1H), 2.23 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.5, 131.6, 131.1, 129.3, 128.7, 127.8, 126.8, 125.3, 124.1, 122.4, 118.7, 110.8, 12.2.

3-Methyl-5-(naphthalen-1-yl)-2-phenylfuran(3ai):[6] Colorless oil (57%, 80 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.87-7.83 (m, 1H), 7.81-7.75 (m, 5H), 7.49-7.41 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.71 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 148.7, 133.7, 132.8, 131.9, 128.7, 128.4, 128.2, 127.9, 126.9, 126.6, 125.9, 125.4, 122.4, 122.0, 118.9, 111.6, 12.3.

3-Methyl-5-phenyl-2-*p*-tolylfuran (3ba): White solid (65%, 80 mg), mp 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.46-7.43 (m, 2H), 7.32-7.29 (m, 3H), 6.65 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ151.4, 148.5, 136.5, 131.0, 129.3, 129.1, 128.7, 127.1, 125.3, 123.7, 123.7, 118.0, 110.8, 21.3, 12.1. Anal calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49%; Found: C, 87.02; H, 6.55%.

3-Methyl-2,5-di-*p*-tolylfuran (3bb): White solid (64%, 83 mg), mp 98-99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.16-7.09 (m, 4H), 6.45 (s, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 , 148.2 137.0, 136.4 , 129.4, 129.3, 129.2, 128.3, 125.3, 125.0, 123.7, 117.9, 110.1, 21.4, 21.3, 12.2. Anal calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92%; Found: C, 87.02; H, 6.88%.

3-Ethyl-2,5-diphenylfuran (3ca):[10] Colorless oil (62%, 76 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.64 (m, 4H), 7.41-7.33 (m, 4H), 7.26-7.21 (m, 2H), 6.65 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1,147.7, 131.9, 130.9, 128.8, 128.7, 128.5, 127.3, 126.9, 125.6, 125.5, 125.3, 123.8, 108.8, 19.4, 14.5.

3-Ethyl-2-phenyl-5-*p*-tolylfuran (3cb): Colorless oil (60%, 78 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 9.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.36-7.32 (m, 2H), 7.21-7.17 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 147.3, 137.1, 131.9, 129.4, 128.6, 128.3, 126.8, 125.6, 125.5, 123.7, 108.0, 21.4, 19.4, 14.5. Anal calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92%; Found: C, 86.89; H, 6.97%.

2-Phenyl-5-*p*-tolylfuran (3da): Colorless oil (54%, 63 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.2 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.34-7.30 (m, 2H), 7.20-7.16 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 153.1, 137.3, 131.0, 129.5, 128.8, 128.2, 127.3, 123.8, 123.7, 107.3, 106.6, 21.4. Anal calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%; Found: C, 87.16; H, 6.05%.

2-*o*-Tolyl-5-*p*-tolylfuran (3eb): Colorless oil (52%, 64 mg),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.27-7.24 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 3.6 Hz, 1H), 6.62 (d, *J* = 3.6 Hz, 1H), 2.56 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 152.8, 137.3, 134.5, 131.4, 130.3, 129.5, 128.3, 127.4, 126.9, 126.1, 123.8, 110.7, 106.3, 22.2, 21.4. Anal calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49%; Found: C, 87.01; H, 6.56%.

2-(4-(Methylthio)phenyl)-5-phenylfuran (3fa): Colorless oil (52%, 69 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 9.2 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.28-7.24 (m, 3H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 153.1, 137.7, 130.8, 128.8, 127.9, 127.4, 126.9, 124.2, 123.8, 107.4, 107.0, 16.0. Anal calcd. for $C_{17}H_{14}OS$: C, 76.66; H, 5.30%; Found: C, 76.68; H, 5.34%.

2-(4-Methoxyphenyl)-5-(thiophen-2-yl)furan (3gc): Colorless oil (49%, 62 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 4.4 Hz, 1H), 7.14 (d, *J* = 6.4 Hz,

1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.48 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 153.2, 148.8, 134.0, 127.7, 125.3, 123.9, 123.7, 122.3, 114.3, 107.3, 105.6, 55.4. Anal calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72%; Found: C, 70.22; H, 4.76%.

2-(Naphthalen-1-yl)-5-*p*-tolylfuran (**3hb**):[6] Colorless oil (50%, 71 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.84-7.81 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.57-7.50 (m, 3H), 7.25-7.22 (m, 2H), 6.81-6.79 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 152.7, 137.4, 134.1, 130.4, 129.6, 128.7, 128.5, 128.3, 126.7, 126.0, 125.7, 125.5, 123.9, 111.5, 106.3, 21.4.

2,3-Diphenyl-5-*p*-tolylfuran (**3ib**):[10] White solid (55%, 85 mg), mp 99-101 ^{o}C (lit. mp 99-100 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.37-7.34 (m, 2H), 7.29-7.25 (m, 2H), 7.23-7.17 (m, 3H), 7.14-7.10 (m, 3H), 6.65 (s, 1H), 2.27 (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.

3-Benzyl-2-methyl-5-*p*-tolylfuran (**3jb**): Colorless oil (52%, 68 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.30-7.24 (m, 2H), 7.21-7.17 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.33 (s, 1H), 3.71 (s, 2H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 147.4, 140.9, 136.5, 129.3, 128.5, 126.1, 123.5, 123.3, 120.0, 106.9, 31.3, 21.3, 11.8. Anal calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92%; Found: C, 86.95; H, 6.96%.

2-*p*-Tolyl-4,5-dihydronaphtho[1,2-*b*]furan (**3kb**): Colorless oil (48%, 62 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.13-7.11 (m, 3H), 7.10-7.09 (m, 1H), 6.57 (s, 1H), 2.99 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 149.4, 137.1, 134.7, 129.5, 128.4, 128.0, 126.8, 126.3, 124.7, 123.7, 121.6, 119.1, 105.9, 29.2, 21.4, 21.2; Anal calcd. for $C_{19}H_{16}O$: C, 87.66; H, 6.19%; Found: C, 87.65; H, 6.21%.

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Supporting information:

Scanned copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds are available as supporting information. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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