

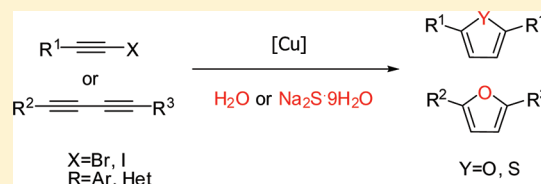
Copper(I)-Catalyzed Synthesis of 2,5-Disubstituted Furans and Thiophenes from Haloalkynes or 1,3-Diynes

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S Supporting Information

ABSTRACT: A regioselective synthesis of 2,5-disubstituted furans using copper(I) catalyst from haloalkynes in a one-pot procedure has been reported. This chemistry proceeds through the hydration reaction of 1,3-diynes, which can be readily prepared from the coupling reaction of haloalkynes in the presence of CuI. The procedure also can be used for the facile synthesis of 2,5-disubstituted thiophenes.



Substituted furans and thiophenes are ubiquitous in biologically active molecules¹ and have also been used as building blocks for both heterocyclic and acyclic compounds.² Consequently, the synthesis of furans and thiophenes has attracted extensive interest.^{3–5} One continuing challenge among existing preparative methods is general access to the 2,5-disubstituted derivatives. The discovery of new activation processes and selective transition-metal-catalyzed transformations of alkyne have significantly contributed to this field (Scheme 1).⁶ While these protocols represent stalwart advances in the preparation of 2,5-disubstituted furans, there are still opportunities to design methods with more easily accessible materials and routines.

Compared with noble-metal catalysts, copper-based methods have obvious economic attractiveness. The simple head-to-head dimerization of copper-based Glaser coupling is of special interest as a convenient way to build conjugated C4 units.⁷ The salts of copper can operate as Lewis acids activating carbon–carbon multiple bonds via π -binding and make the σ -complexes with heteroatoms in the same fashion.⁸ Lewis acids promoted hydration of alkynes to carbonyl compounds is one of the most important and fundamental functional group transformation methods,⁹ and the carbonyl compounds via alkyne hydration can be used as precursors of furans.¹⁰ Many metal complexes have proved to be useful in alkyne hydration catalysis.^{6d,i,11} However, there are few examples of copper-catalyzed hydration of alkynes.¹² During our study on the cyclization reaction involving electron-deficient alkynes for synthesis of furans,¹³ we recently focused on developing alkynes hydration to construct furans catalyzed by copper. Herein we report a novel synthesis of 2,5-disubstituted furans directly from haloalkynes or 1,3-diynes through sequential one-pot reactions. The procedure also can be used for the facile synthesis of 2,5-disubstituted thiophenes.

It has been demonstrated that haloalkynes are useful materials in organic reactions.¹⁴ Recently, our group has reported several nucleophilic additions, homocoupling reactions, and transition-metal-catalyzed bond formation reactions of haloalkynes.¹⁵ Based on our previous results, we first studied the reaction of phenylethynyl bromide in DMF using CuI as

the catalyst and 1,10-phen as the ligand. To our delight, the desired furan **3a** was obtained in 65% GC yield (Table 1, entry 1). This result prompted us to screen suitable reaction conditions (Table 1). After solvent evaluation, we found that DMSO was the best solvent and afforded **3a** with 80% GC yield (entry 2), while other solvents just led to moderate or low yields (entries 1, 3, and 4). Further investigation revealed that the base played a critical role for this transformation (entries 5–9). Cs₂CO₃, K₂CO₃, and *t*-BuOK were ineffective and NaOH just gave moderate yields, while KOH was the best choice. The amount of KOH was then examined, and the best result was obtained by using 5.0 equiv of KOH, which gave **3a** in 93% yield (entry 10). The effects of different copper salts were also studied (entries 10–13). CuI was found to be the best catalyst, and the yield reached 93% (entry 10).

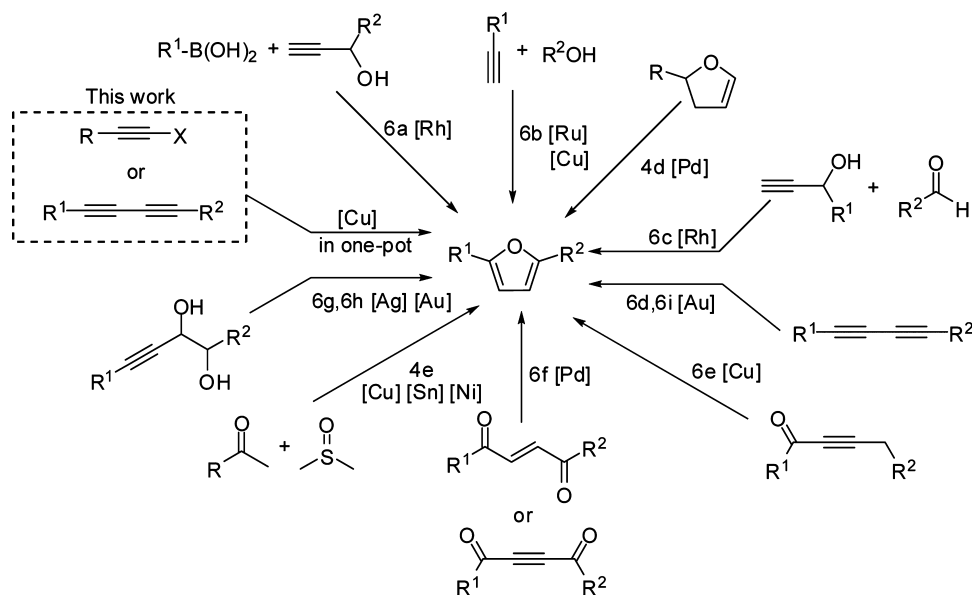
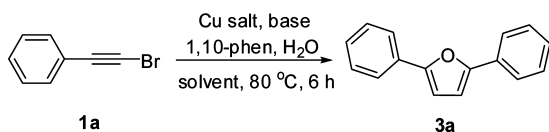
Under the optimized conditions (Table 1, entry 10), the reaction was applied to a range of different substrates smoothly giving the corresponding products with moderate to excellent yields, and the results are summarized in Table 2. Aromatic alkynyl bromides with either electron-donating or electron-withdrawing groups on the benzene ring were able to generate the corresponding products in excellent yields. The reaction conditions were compatible with alkyl, alkoxy, trifluoromethyl, and halogen groups on the benzene ring providing the corresponding products in good yields (**3b–1**). Fortunately, 2,5-diheterocyclic furans could be generated in the same way (**3m,n**). We also extended this reaction to phenylethynyl iodide as a substrate and found that the reaction occurred to give **3a** in good yield (Scheme 2).

Compared with oxygen, sulfur proved to be a better match as a nucleophile for the diaryl/heterocycle diynes. Applying Na₂S·9H₂O instead of KOH successfully afforded the corresponding 2,5-disubstituted thiophenes (Table 3). Optimum reaction conditions were determined after a short screening. The best reaction conditions used DMF as the solvent and a lower reaction temperature to 70 °C. In addition,

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Scheme 1. Synthetic Approaches to 2,5-Disubstituted Furans

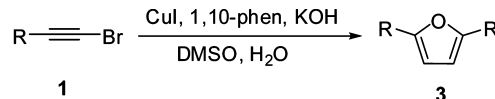
Table 1. Optimization of Reaction Conditions^a

entry	catalyst	solvent	base (X equiv)	yield ^b (%)
1	CuI	DMF	KOH (3.0)	65
2	CuI	DMSO	KOH (3.0)	80
3	CuI	1,4-dioxane	KOH (3.0)	21
4	CuI	toluene	KOH (3.0)	56
5	CuI	DMSO	K ₂ CO ₃ (3.0)	NR
6	CuI	DMSO	Cs ₂ CO ₃ (3.0)	NR
7	CuI	DMSO	<i>t</i> -BuOK (3.0)	NR
8	CuI	DMSO	NaOH (3.0)	69
9	CuI	DMSO	KOH (4.0)	85
10	CuI	DMSO	KOH (5.0)	93
11	CuCl	DMSO	KOH (5.0)	75
12	CuBr	DMSO	KOH (5.0)	72
13	CuCl ₂	DMSO	KOH (5.0)	NR

^aReactions were carried out using bromoalkyne (0.5 mmol), Cu salt (5 mol %), 1,10-phen (15 mol %), H₂O (4 mmol), solvent (2.5 mL), 80 °C, 6 h. ^bDetermined by GC.

the amounts of CuI and 1,10-phen were increased to 15 and 20 mol %, respectively. Excellent regioselectivity was still observed. Both aromatic alkynyl bromides and heterocycle alkynyl bromides could generate the corresponding products in excellent yields. It is noteworthy that α -terthienyl (**4e**), which has anthelmintic and insecticidal activities, could be obtained with 78% yield in this way.

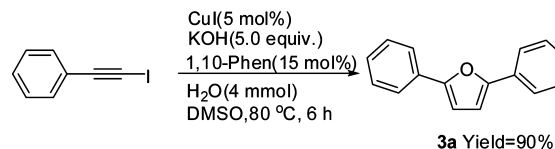
We conjectured that this reaction would occur through a 1,3-diyne intermediate. As shown in Table 4, we synthesized series of 1,3-diyne compounds. With 1,3-diyne as starting materials, the reaction successfully afforded the corresponding 2,5-disubstituted furans under the standard conditions. Unsymmetrical products can also be synthesized in this way (**3o–s**). The overall yield of 2,5-disubstituted furans are the same when alkynyl bromides were used as starting material (Table 4).

Table 2. Substrate Scope of 2,5-Disubstituted Furans via Cu-Catalyzed Reaction^a

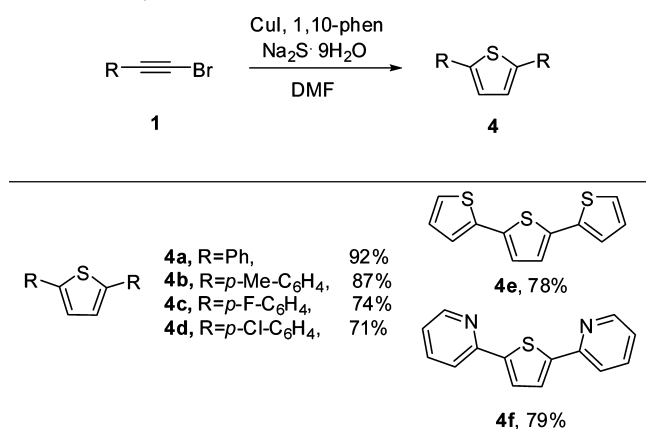
3a , R=Ph,	93%	
3b , R= <i>p</i> -Me-C ₆ H ₄ ,	90%	
3c , R= <i>m</i> -Me-C ₆ H ₄ ,	87%	
3d , R= <i>p</i> -Et-C ₆ H ₄ ,	90%	
3e , R= <i>p</i> -F-C ₆ H ₄ ,	84%	
3f , R= <i>p</i> -Cl-C ₆ H ₄ ,	85%	3m , 84%
3g , R= <i>o</i> -Cl-C ₆ H ₄ ,	75%	
3h , R= <i>m</i> -Cl-C ₆ H ₄ ,	68%	
3i , R= <i>p</i> -Br-C ₆ H ₄ ,	71%	
3j , R= <i>p</i> -CF ₃ -C ₆ H ₄ ,	74%	
3k , R= <i>p</i> -MeO-C ₆ H ₄ ,	85%	
3l , R= <i>p</i> -EtO-C ₆ H ₄ ,	71%	3n , 75%

^aReactions were carried out using bromoalkyne (0.5 mmol), CuI (5 mol %), 1,10-phen (15 mol %), KOH (5 mmol), H₂O (4 mmol), DMSO (2.5 mL), 80 °C, 6 h. ^bIsolated yields.

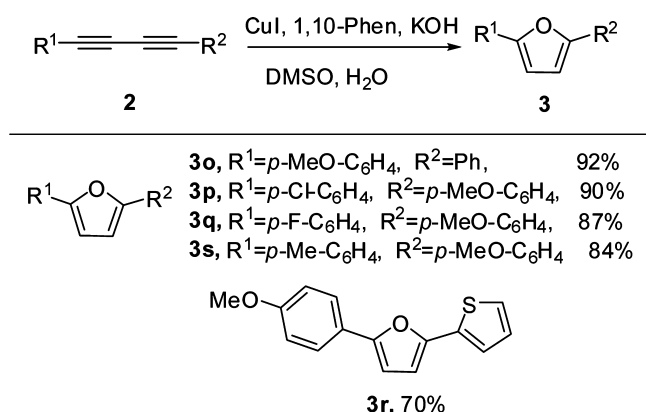
Scheme 2. Cu-Catalyzed Reaction of Iodoalkyne



To gain a mechanistic insight into the process of this reaction, a series of competition experiments were conducted to test the effect of water. When anhydrous DMSO without the addition of water was used, the yield of **3a** was low (Scheme 3), and the major product was 1,4-diphenylbuta-1,3-diyne. On the basis of previous reports^{6e,16} and our experimental data, a plausible reaction mechanism for copper-catalyzed synthesis of furans and thiophenes is illustrated in Scheme 4. First, the 1,3-diyne **B** could be generated from bromoalkyne **A** via Cu(I) catalysis. The single alkyne hydration and enol-ketone equilibrium provided **D**. Then the nucleophilic attack of carbonyl oxygen to the copper-coordinated alkyne may result in

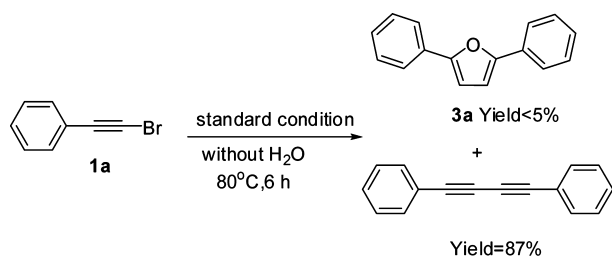
Table 3. Substrate Scope of 2,5-Disubstituted Thiophenes via Cu-Catalyzed Reaction^a

^aReactions were carried out using bromoalkynes (0.5 mmol), CuI (15 mol %), 1,10-Phen (20 mol %), Na₂S·9H₂O (2.5 mmol), DMF (2.5 mL), 70 °C, 6 h. ^bIsolated yields.

Table 4. Substrate Scope for Cu-catalyzed Reaction of 1,3-Diynes 2^a

^aReactions were carried out using 1,3-diynes (0.25 mmol), CuI (5 mol %), 1,10-Phen (15 mol %), KOH (2.5 mmol), H₂O (2 mmol), DMSO (2.5 mL), 80 °C, 6 h. ^bIsolated yields.

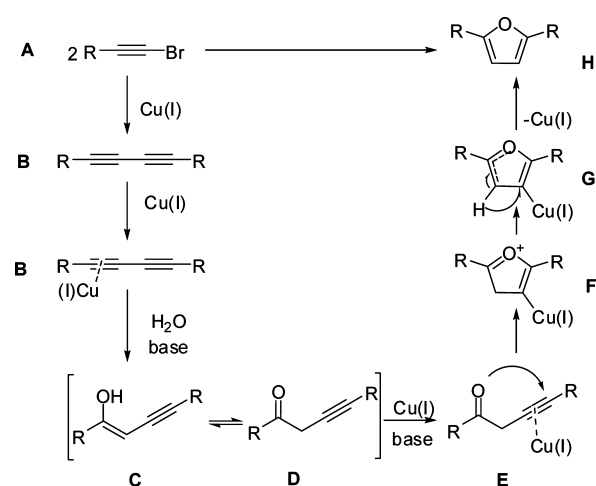
Scheme 3. Controlled Experiment



the formation of the resonance stabilized oxonium ion F, which could easily transfer to intermediate G. Finally, a rearrangement took place in which G was converted to furan product H with regeneration of the Cu(I) catalyst.

In conclusion, we have established a facile and highly stereoselective method to synthesize 2,5-disubstituted furans from haloalkynes or 1,3-diynes in the presence of the CuI catalyst. Furthermore, we have shown that the procedure can be used for the facile synthesis of 2,5-disubstituted thiophenes. This approach can tolerate a broad range of aryl and heterocyclic groups and it is particularly useful as this is an

Scheme 4. Proposed Mechanism for the Synthesis of 2,5-Disubstituted Furans



easy access to conduct reaction with simple starting material in high-yielding reactions under mild conditions.

EXPERIMENTAL SECTION

General Methods. ¹H and ¹³C NMR spectra were recorded on a 400 MHz spectrometer using CDCl₃ as solvent and TMS as an internal standard. Mass spectra were obtained with a gas chromatograph–mass spectrometer.

Typical Procedure for the Synthesis of 2,5-Disubstituted Furans or Thiophenes. A mixture of phenylethynyl bromide **1** (0.5 mmol), CuI (4.8 mg, 5 mol %), 1,10-phen (13.5 mg, 15 mol %), KOH (140 mg, 5 equiv), and H₂O (7.2 mg, 4 mmol) in DMSO (2.5 mL) was placed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred at 80 °C for 6 h. After the reaction was complete, the mixture was filtered through a glass filter and washed with ethyl acetate. The mixture was washed with brine and extracted with ethyl acetate. The organic layer was dried (MgSO₄), concentrated in vacuo, and purified by flash silica gel chromatography using petroleum ether/ethyl acetate 20:1 to give the desired products.

2,5-Diphenylfuran (3a): 51.3 mg, 93%; ¹H NMR (400 MHz, CDCl₃) δ = 7.73–7.75 (m, 4H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.24–7.28 (m, 2H), 6.72 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.4, 130.8, 128.7, 127.4, 123.8, 107.3; MS (EI) *m/z* 115, 165, 191, 220; IR ν_{max}(KBr)/cm⁻¹ 1475, 1022, 796, 757, 689.

2,5-Di-*p*-tolylfuran (3b): 55.4 mg, 90%; ¹H NMR (400 MHz, CDCl₃) δ = 7.63 (d, *J* = 8 Hz, 4H), 7.20 (d, *J* = 8 Hz, 4H), 6.65 (s, 2H), 2.37 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.2, 137.1, 129.4, 128.2, 123.6, 106.4, 21.3; MS (EI) *m/z* 129, 205, 233, 248; IR ν_{max}(KBr)/cm⁻¹ 2924, 1486, 1022, 822, 791.

2,5-Di-*m*-tolylfuran (3c): 53.9 mg, 87%; ¹H NMR (400 MHz, CDCl₃) δ = 7.54–7.56 (m, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.70 (s, 2H), 2.41 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.4, 138.3, 130.8, 128.6, 128.2, 124.3, 120.9, 107.1, 21.6; MS (EI) *m/z* 119, 129, 205, 248; IR ν_{max}(KBr)/cm⁻¹ 2920, 1478, 1026, 782, 697.

2,5-Bis(4-ethylphenyl)furan (3d): 62.1 mg, 90%; ¹H NMR (400 MHz, CDCl₃) δ = 7.65 (d, *J* = 8 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 6.66 (s, 2H), 2.66 (q, *J* = 7.2 Hz, 4H), 1.26 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.3, 143.5, 128.5, 128.2, 123.7, 106.5, 28.7, 15.6; MS (EI) *m/z* 123, 207, 246, 261, 276; IR ν_{max}(KBr)/cm⁻¹ 2924, 1362, 1223, 832, 789.

2,5-Bis(4-fluorophenyl)furan (3e): 53.7 mg, 84%; ¹H NMR (400 MHz, CDCl₃) δ = 7.67–7.70 (m, 4H), 7.07–7.11 (m, 4H), 6.65 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 162.2 (d, *J*_{CF} = 245.6 Hz), 152.5, 127.1 (d, *J*_{CF} = 3.3 Hz), 125.4 (d, *J*_{CF} = 8.0 Hz), 115.8 (d, *J*_{CF} = 21.8 Hz), 106.9; MS (EI) *m/z* 95, 123, 133, 227, 256; IR ν_{max}(KBr)/cm⁻¹ 1488, 1231, 1025, 831, 774.

2,5-Bis(4-chlorophenyl)furan (3f): 61.2 mg, 85%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.63 (d, J = 8 Hz, 4H), 7.35 (d, J = 8 Hz, 4H), 6.70 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 152.6, 133.2, 129.0, 129.0, 125.0, 107.8; MS (EI) m/z 111, 114, 149, 189, 225, 288; IR ν_{max} (KBr)/ cm^{-1} 1473, 1106, 1020, 831, 791.

2,5-Bis(2-chlorophenyl)furan (3g): 54.1 mg, 75%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.95 (d, J = 8 Hz, 2H), 7.45 (d, J = 8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.25 (s, 2H), 7.21 (t, J = 8 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 149.7, 130.1, 130.3, 128.9, 128.2, 128.0, 126.9, 113.0; MS (EI) m/z 139, 149, 189, 225, 288; IR ν_{max} (KBr)/ cm^{-1} 1597, 1464, 1421, 1026, 747.

2,5-Bis(3-chlorophenyl)furan (3h): 49.0 mg, 68%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.70 (s, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.22–7.24 (m, 2H), 6.74 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 152.4, 134.8, 132.1, 130.0, 127.5, 123.8, 121.9, 108.4; MS (EI) m/z 111, 139, 149, 189, 225, 252, 288; IR ν_{max} (KBr)/ cm^{-1} 1579, 1470, 1026, 774, 686.

2,5-Bis(4-bromophenyl)furan (3i): 67.1 mg, 71%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.59 (d, J = 8 Hz, 4H), 7.52 (d, J = 8 Hz, 4H), 6.73 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 152.7, 131.9, 129.5, 125.2, 121.3, 107.9; MS (EI) m/z 114, 157, 189, 269, 378; IR ν_{max} (KBr)/ cm^{-1} 1582, 1401, 1070, 1006, 824, 792.

2,5-Bis(4-(trifluoromethyl)phenyl)furan (3j): 65.9 mg, 74%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.82 (d, J = 8.2 Hz, 4H), 7.65 (d, J = 8 Hz, 4H), 6.86 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 152.8, 133.4, 129.4 (q, J_{CF} = 32.4 Hz), 125.8 (q, J_{CF} = 3.9 Hz), 124.1 (q, J_{CF} = 270.2 Hz), 123.9, 109.3; MS (EI) m/z 145, 183, 259, 337, 356; IR ν_{max} (KBr)/ cm^{-1} 1614, 1324, 1108, 837, 778.

2,5-Bis(4-methoxyphenyl)furan (3k): 59.5 mg, 85%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.66 (d, J = 8.8 Hz, 4H), 6.94 (d, J = 8.8 Hz, 4H), 6.57 (s, 2H), 3.84 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 158.9, 152.8, 125.0, 124.1, 114.2, 105.6, 55.4; MS (EI) m/z 140, 165, 194, 222, 250, 265, 280; IR ν_{max} (KBr)/ cm^{-1} 2924, 1601, 1508, 1252, 1043.

2,5-Bis(4-ethoxyphenyl)furan (3l): 54.7 mg, 71%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.64 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.8 Hz, 4H), 6.56 (s, 2H), 4.07 (q, J = 7.2 Hz, 4H), 1.43 (t, J = 6.8 Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 158.3, 152.8, 125.0, 124.0, 114.7, 105.5, 63.5, 14.8; MS (EI) m/z 165, 194, 223, 251, 279, 308; IR ν_{max} (KBr)/ cm^{-1} 2926, 2856, 1602, 1509, 1253, 1041.

2,5-Di(thiophene-2-yl)furan (3m): 48.7 mg, 84%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.29–7.30 (m, 2H), 7.21–7.22 (m, 4H), 7.02–7.04 (m, 2H), 6.53 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 148.6, 133.5, 127.7, 124.2, 122.7, 107.2; MS (EI) m/z 111, 121, 171, 203, 232; IR ν_{max} (KBr)/ cm^{-1} 1509, 1458, 1417, 1002, 793, 697.

2,5-Di(pyridin-2-yl)furan (3n): 41.6 mg, 75%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 8.62–8.63 (m, 2H), 7.84 (d, J = 7.6 Hz, 2H), 7.75 (t, J = 7.6 Hz, 2H), 7.21 (s, 2H), 7.17–7.20 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 154.1, 149.7, 149.1, 136.7, 122.2, 118.9, 111.1; MS (EI) m/z 78, 89, 116, 148, 193, 222; IR ν_{max} (KBr)/ cm^{-1} 1699, 1579, 1466, 1010, 777.

2-(4-Methoxyphenyl)-5-phenylfuran (3o): 57.5 mg, 92%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.2 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.22–7.26 (m, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 3.6 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 3.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 159.1, 153.5, 152.7, 130.9, 128.7, 127.1, 125.2, 123.9, 123.6, 114.2, 107.2, 105.7, 55.4; MS (EI) m/z 125, 152, 178, 235, 250; IR ν_{max} (KBr)/ cm^{-1} 2929, 1599, 1499, 1250, 1026, 832, 759.

2-(4-Chlorophenyl)-5-(4-methoxyphenyl)furan (3p): 63.9 mg, 90%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.62–7.66 (m, 4H), 7.34 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 3.6 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 3.84 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 159.3, 153.8, 151.6, 132.6, 129.4, 128.9, 125.3, 124.7, 123.7, 114.2, 107.7, 105.7, 55.4; MS (EI) m/z 178, 241, 269, 284; IR ν_{max} (KBr)/ cm^{-1} 2960, 1478, 1363, 1252, 1026, 833, 787.

2-(4-Fluorophenyl)-5-(4-methoxyphenyl)furan (3q): 58.3 mg, 87%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.64–7.70 (m, 4H), 7.08 (t, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 3.84 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ =

162.0 (d, J_{CF} = 245.3 Hz), 159.1, 153.5, 151.9, 127.3 (d, J_{CF} = 3.3 Hz), 125.3 (d, J_{CF} = 7.9 Hz), 125.2, 123.8, 115.7 (d, J_{CF} = 21.8 Hz), 114.2, 106.7, 105.7, 55.4; MS (EI) m/z 95.0, 123.0, 170.0, 196.0, 225.0, 253.0, 268.0; IR ν_{max} (KBr)/ cm^{-1} 2923, 1489, 1253, 1026, 838, 786.

2-(4-Methoxyphenyl)-5-(thiophene-2-yl)furan (3r): 44.8 mg, 70%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.64 (d, J = 8.8 Hz, 2H), 7.28–7.29 (m, 1H), 7.20–7.21 (m, 1H), 7.02–7.04 (m, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.55 (s, 2H), 3.83 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 159.2, 153.1, 148.4, 134.0, 127.7, 125.2, 123.8, 123.7, 122.2, 114.2, 107.2, 105.6, 55.4; MS (EI) m/z 128, 152, 184, 213, 241, 25; IR ν_{max} (KBr)/ cm^{-1} 2929, 1503, 1250, 1026, 832, 783, 702.

2-(4-Methoxyphenyl)-5-*p*-tolylfuran (3s): 55.44 mg, 84%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.66 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 159.0, 153.1, 153.0, 137.0, 129.4, 128.3, 125.1, 124.0, 123.6, 114.2, 106.5, 105.6, 55.4, 21.3; MS (EI) m/z 91, 152, 178, 221, 249, 264; IR ν_{max} (KBr)/ cm^{-1} 2923, 1488, 1250, 1028, 830, 787.

2,5-Diphenylthiophene (4a): 54.3 mg, 92%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.62 (d, J = 7.6 Hz, 4H), 7.39 (t, J = 7.8 Hz, 4H), 7.26–7.29 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 143.6, 134.3, 128.9, 127.5, 125.7, 124.0; MS (EI) m/z 134, 165, 191, 202, 221, 236; IR ν_{max} (KBr)/ cm^{-1} 1452, 1329, 803, 749, 685.

2,5-Di-*p*-tolylthiophene (4b): 57.4 mg, 87%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.50 (d, J = 8.0 Hz, 4H), 7.21 (s, 2H), 7.17 (d, J = 7.6 Hz, 4H), 2.35 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 143.3, 137.3, 131.7, 129.6, 125.5, 123.5, 21.2; MS (EI) m/z 115, 171, 215, 264; IR ν_{max} (KBr)/ cm^{-1} 2917, 1457, 1366, 797.

2,5-Bis(4-fluorophenyl)thiophene (4c): 50.3 mg, 74%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.55–7.59 (m, 4H), 7.19 (s, 2H), 7.08 (t, J = 8.4 Hz, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 162.3 (d, J_{CF} = 246.0 Hz), 142.5, 130.5 (d, J_{CF} = 3.4 Hz), 127.3 (d, J_{CF} = 7.9 Hz), 124.0, 115.9 (d, J_{CF} = 21.7 Hz); MS (EI) m/z 133, 152, 176, 238, 272; IR ν_{max} (KBr)/ cm^{-1} 1513, 1456, 1408, 1101, 834, 797.

2,5-Bis(4-chlorophenyl)thiophene (4d): 54.0 mg, 71%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.53 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 7.25 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 142.7, 133.4, 132.6, 129.1, 126.8, 124.4; MS (EI) m/z 114, 155, 168, 189, 234, 304; IR ν_{max} (KBr)/ cm^{-1} 1511, 1454, 1105, 828, 799.

α -Terthienyl (4e): 48.4 mg, 78%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.16 (d, J = 9.2 Hz, 2H), 7.13 (d, J = 3.6 Hz, 2H), 7.03 (s, 2H), 6.97 (t, J = 4.4 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 137.2, 136.3, 127.9, 124.5, 124.4, 123.8; MS (EI) m/z 127, 171, 203, 216, 248; IR ν_{max} (KBr)/ cm^{-1} 1422, 1057, 831, 796, 682.

2,5-Di(pyridin-2-yl)thiophene (4f): 47.0 mg, 79%; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 8.59 (d, J = 4.8 Hz, 2H), 7.66–7.69 (m, 4H), 7.63 (s, 2H), 7.14–7.17 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 152.4, 149.6, 146.0, 136.7, 125.7, 122.1, 119.0; MS (EI) m/z 78, 89, 116, 160, 205, 238; IR ν_{max} (KBr)/ cm^{-1} 1581, 1458, 1427, 1295, 776.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR of compounds 3a–s and 4a–f. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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