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Highly Efficient Synthesis of Multisubstituted Furans through Cupric Halide-Mediated Intramolecular Halocyclization of 1-(1-Alkynyl)cyclopropyl Ketones

Mei Zhu,[a] Wei-Jun Fu,*[a] Chen Xu,[a] Guang-Long Zou,[b] Zhi-Qiang Wang,[a] and Bao-Ming Ji[a]

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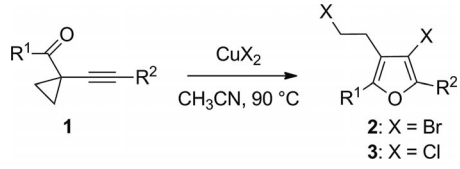
A convenient and efficient method for the synthesis of 3-halofurans was developed by using a cascade reaction between 1-(1-alkynyl)cyclopropyl ketones and cupric halide. Under mild reaction conditions, both 3-chloro- and 3-bromofuran derivatives were obtained in high yields. The reaction involves consecutive multiple bond formations, including C–O and C–Br bonds, with high regioselectivity. Mechanistic aspects are described.

Introduction

Furans represent a class of heterocycles, which occur in various natural products and biologically active compounds.[1] Moreover, they are extensively used as important reaction intermediates in the preparation of a variety of heterocyclic and acyclic compounds.[2] In particular, halofurans are of special interest, because the halogen atom provides an opportunity for further functionalization through transition-metal-catalyzed reactions to form a variety of C–C, C–N, or C–S bonds, and halofurans also serve as building blocks in combinatorial chemistry.[3] As a consequence, a number of efficient and selective methods have been developed to synthesize them.[4] Among the many methods developed in past years, the most common synthetic method for the construction of halofurans is the intramolecular electrophilic cyclization of functionally substituted alkynes, which includes the iodocyclizations of 3-alkyne-1,2-diols,[5] 2,4-dialkenyl-1,3-dicarbonyls,[6] propargylic oxirane,[7] 1,4-disubstituted but-3-yn-1-ones,[8] 2-(1-alkynyl)-alk-2-en-1-ones,[9] and (*Z*)-1,4-disubstitutedbut-1-en-3-ynyl acetates.[10] However, the chlorocyclization and bromocyclization reactions are rarely reported, most likely because the stability of the corresponding halonium intermediates decrease in the order I > Br > Cl.[11] Thus, continuous interest has been directed to the development of new and efficient syntheses for chloro- and bromofurans.

The CuX_2-mediated intramolecular halocyclization of nucleophiles,[12] such as oxygen,[13] nitrogen,[14] sulfur,[15] selenium,[16] phosphorus,[17] and sp^2-hybridized carbon,[18] with alkynes or allenes has proven to be an effective method for the syntheses of heterocyclic compounds. Many important heterocycles, such as selenophenes, thiophenes, indoles, phosphaisocoumarins, butenolides, azaanthraquinones, 5-hydroxypyrrol-2(5*H*)-ones, benzo[*b*]thiophenes, and 2,5-dihydro[1,2]oxaphosphole 2-oxides have been synthesized on the basis of this strategy. Meanwhile, 1-(1-alkynyl)cyclopropyl ketones have drawn much attention for their increasing applications in the syntheses of highly substituted furans and other cyclic compounds, using gold(I), copper(I), or rhodium(I) complexes as catalysts.[19] Recently, we reported the electrophilic cyclization of 1-(1-alkynyl)cyclopropyl ketones, using I^+ or $PhSe^+$ as the electrophilic species, to afford the efficient syntheses of substituted iodofurans and chalcogenylfurans.[20] On the basis of the above considerations and in the context of our efforts for developing new strategies toward heterocycles and related libraries,[21] we envisioned that the reaction of 1-(1-alkynyl)-cyclopropyl ketones with CuX_2 (X = Br and Cl) formed bromo- and chlorofurans (see Scheme 1).



1

2: X = Br
3: X = Cl

Scheme 1. CuX_2-mediated halocyclization of 1-(1-alkynyl)cyclopropyl ketones.

[a] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, P. R. China
Fax: +86-379-69810261
E-mail: wjfu@lynu.edu.cn
[b] School of Chemistry and Environmental Science, Guizhou University for Nationalities, Guiyang 550025, P. R. China

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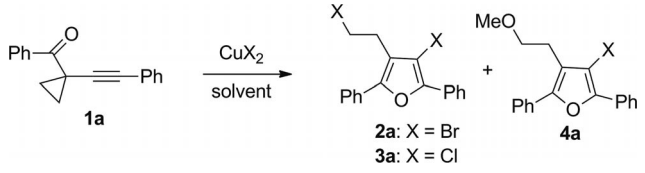
Results and Discussion

Our initial study began with the reaction of phenyl[1-(2-phenylethynyl)cyclopropyl]methanone (**1a**), NBS (*N*-bromosuccinimide, 1.0 equiv.), MeOH (10.0 equiv.), and K_2CO_3 (1.0 equiv.) in CH_2Cl_2 at room temperature. Unfortunately, NBS did not afford any furan product (Table 1, Entry 1). When the reaction was performed with $CuBr_2$ (2.5 equiv.), bromofuran **2a** was obtained in 40% yield along with a trace amount of **4a** (Table 1, Entry 2). Considering the competing reactions between MeO^- and Br^-, we then tried to use MeOH as the solvent. However, **2a** was again isolated as the major product (Table 1, Entry 3). In the absence of MeOH, bromofuran **2a** was synthesized in 60% yield within 12 h (Table 1, Entry 4). Further investigation showed that the reaction temperature and solvent were important. We found that using DMSO (dimethyl sulfoxide) as the solvent at an elevated reaction temperature (90 °C) could shorten the reaction time, and the yield showed moderate improvement (Table 1, Entry 5). To our delight, by employing CH_3CN as the solvent, **2a** was obtained in 92% yield (Table 1, Entry 6). Reducing the amount of $CuBr_2$ (1.0 equiv.) led to a decrease in the chemical yield of **2a** (Table 1, Entry 7). Solvents such as DMF (dimethylformamide), THF (tetrahydrofuran), and toluene were found to be less effective (Table 1, Entries 8–10). Additionally, under similar reaction conditions, $CuCl_2$ was used to generate chlorofuran **3a** in 90% yield (Table 1, Entry 11).

Table 1. CuX_2-mediated halocyclization of **1a** under various conditions.[a]

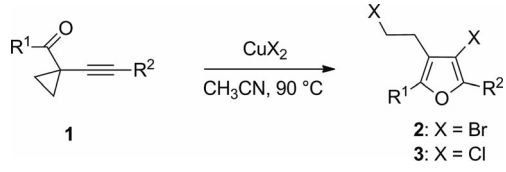


Entry	CuX_2	Solvent	T [°C]	t [h]	Yield [%][b] 2a	4a
1	none[c]	CH_2Cl_2	r.t.	24	0	
2	$CuBr_2$[d]	CH_2Cl_2	r.t.	12	40	trace
3	$CuBr_2$	CH_3OH	r.t.	12	35	trace
4	$CuBr_2$	CH_2Cl_2	r.t.	12	60	
5	$CuBr_2$	DMSO	90	3	82	
6	$CuBr_2$	CH_3CN	90	1	92	
7	$CuBr_2$	CH_3CN	90	1	43[e]	
8	$CuBr_2$	DMF	90	1	75	
9	$CuBr_2$	THF	90	3	68	
10	$CuBr_2$	toluene	90	3	70	
11	$CuCl_2$	CH_3CN	90	1	90	

[a] Reagents and conditions: **1a** (0.5 mmol), CuX_2 (2.5 equiv.), solvent (5 mL). [b] Isolated yield. [c] Reactions were performed using **1a** (0.5 mmol), NBS (2.5 equiv.), MeOH (10 equiv.), and K_2CO_3 (1.0 equiv.). [d] MeOH (10 equiv.) and K_2CO_3 (1.0 equiv.) were added. [e] $CuBr_2$ (1.0 equiv.) was used.

To establish the scope of this halocyclization protocol, we tested a wide range of 1-(1-alkynyl)cyclopropyl ketones (Table 2). First, the effect of various groups on the aromatic ring R^1 was examined. As expected, various common functionalities such as the chloro, bromo, fluoro, and methoxy groups were well tolerated to form the corresponding products in moderate to good yields. The procedure seemed insensitive to the electronic nature of the substituents on the aromatic ring. For example, cyclopropyl ketones **1** with electron-withdrawing groups on the aromatic ring such as *para*-chloro, -bromo, and -fluoro substituents gave the corresponding 3-halofurans in good yields (Table 2, Entries 3–8). Substrates with a strong electron-donating methoxy group at the *para* and *meta* positions of the aromatic ring also provided **2e**, **3e**, **2f**, and **3f** in excellent yields (Table 2, Entries 9–12). However, when a bulky 1-naphthyl group was used as in the case of **1i**, the desired products were obtained in the slightly lower yields of 76 and 72% (Table 2, Entries 17 and 18, respectively). Additionally, good results were also obtained with alkyl substituents as in **1g** and **1h** (Table 2, Entries 13–16). The molecular structure of representative product **2e** was determined by X-ray crystallography (Figure 1).[22]

Table 2. CuX_2-mediated halocyclization of **1** to halofurans.[a]



Entry	R^1	R^2	X	Yield [%][b]
1	C_6H_5	C_6H_5	Br	**2a**, 92
2	C_6H_5	C_6H_5	Cl	**3a**, 90
3	4-ClC_6H_4	C_6H_5	Br	**2b**, 88
4	4-ClC_6H_4	C_6H_5	Cl	**3b**, 74
5	4-BrC_6H_4	C_6H_5	Br	**2c**, 86
6	4-BrC_6H_4	C_6H_5	Cl	**3c**, 80
7	4-FC_6H_4	C_6H_5	Br	**2d**, 78
8	4-FC_6H_4	C_6H_5	Cl	**3d**, 73
9	4-$CH_3OC_6H_4$	C_6H_5	Br	**2e**, 93
10	4-$CH_3OC_6H_4$	C_6H_5	Cl	**3e**, 95
11	3-$CH_3OC_6H_4$	C_6H_5	Br	**2f**, 90
12	3-$CH_3OC_6H_4$	C_6H_5	Cl	**3f**, 89
13	*n*Pr	C_6H_5	Br	**2g**, 91
14	*n*Pr	C_6H_5	Cl	**3g**, 90
15	C_2H_5	C_6H_5	Br	**2h**, 90
16	C_2H_5	C_6H_5	Cl	**3h**, 92
17	1-naphthyl	C_6H_5	Br	**2i**, 76
18	1-naphthyl	C_6H_5	Cl	**3i**, 72
19	4-ClC_6H_4	4-$CH_3C_6H_4$	Br	**2j**, 84
20	4-ClC_6H_4	4-$CH_3C_6H_4$	Cl	**3j**, 88
21	C_6H_5	2-$CH_3C_6H_4$	Br	**2k**, 93
22	C_6H_5	2-$CH_3C_6H_4$	Cl	**3k**, 86
23	C_6H_5	4-$CH_3OC_6H_4$	Br	**2l**, 87[c]
24	4-$CH_3C_6H_4$	hexyl	Br	**2m**, 73
25	4-$CH_3C_6H_4$	hexyl	Cl	**3m**, **65**
26	4-$CH_3C_6H_4$	TMS	Br	–[d]

[a] Reactions were performed using **1** (0.5 mmol) and CuX_2 (2.5 equiv.) in CH_3CN (5 mL) at 90 °C. [b] Isolated yield. [c] Reaction was performed at room temperature. [d] A complex reaction mixture was obtained.

Then, we elucidated the scope of the reaction by examining the effect of various R^2 groups on the alkyne moiety. Substrates bearing *para*-methyl and -methoxy groups were subjected to the reaction conditions, and the corresponding products were obtained in moderate to excellent yields

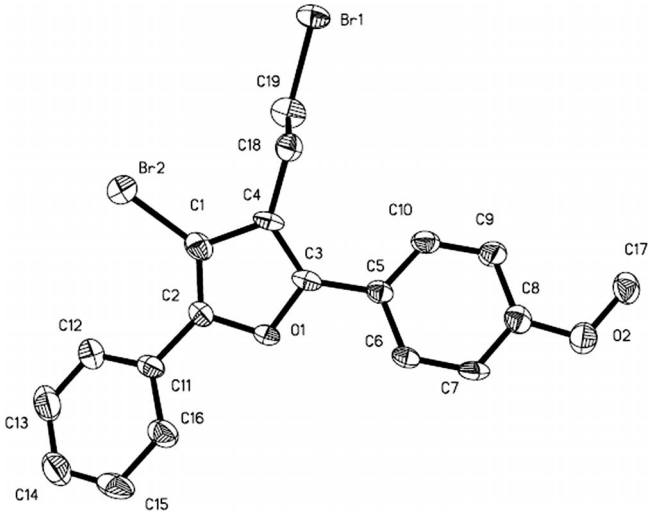
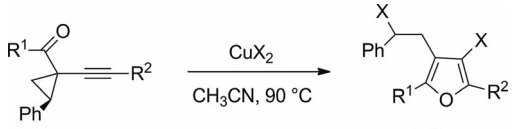


Figure 1. X-ray crystal structure of **2e**.

(Table 2, Entries 19, 20, and 23). The alkyne with the *ortho*-methyl aromatic group was also a good substrate for this transformation, and the desired 3-halofurans were obtained in 93% and 86% yields, respectively (Table 2, Entries 21 and 22). Besides the different aromatic substituted alkynes, we employed aliphatic and functionalized alkynes as well. In contrast, the yields were lower than the yields with the aromatic alkynes (Table 2, Entries 24 and 25). The use of the trimethylsilylalkyne, however, gave no product, and the reaction led mainly to degradation (Table 2, Entry 26).

Following the successful halocyclization of 1-(1-alkynyl)-cyclopropyl ketones, we decided to examine 2-substituted 1-(1-alkynyl)cyclopropyl ketones to expand the scope of this methodology (Table 3). In general, the reaction of 2-substituted 1-(1-alkynyl)-cyclopropyl ketones with $CuBr_2$ resulted in relatively lower yields (Table 3, Entries 1–5). This may be because of the steric effect of the phenyl group on the cyclopropane ring. Interestingly, nucleophilic addition occurred at the more substituted position of the cyclopropane ring in all cases. However, when $CuCl_2$ was used under the same conditions, no desired product was obtained.

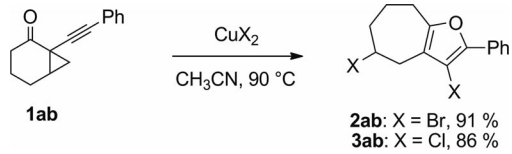
Table 3. CuX_2-mediated halocyclization of 2-substituted 1-(1-alkynyl)cyclopropyl ketones.[a]



Entry	R^1	R^2	X	Yield [%][b]
1	C_6H_5	C_6H_5	Br	**4a**, 65
2	C_6H_5	4-$CH_3OC_6H_4$	Br	**4b**, 72
3	C_6H_5	4-$CH_3C_6H_4$	Br	**4c**, 70
4	C_6H_5	4-ClC_6H_4	Br	**4d**, 58
5	*n*-C_4H_9	C_6H_5	Br	**4e**, 67
6	C_6H_5	C_6H_5	Cl	N. R.[c]
7	C_6H_5	4-$CH_3OC_6H_4$	Cl	N. R.[c]

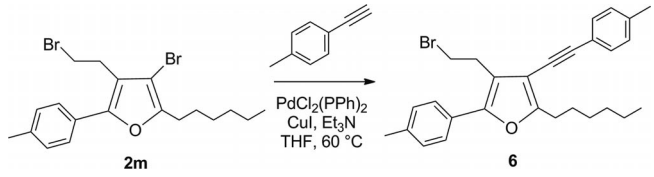
[a] Reactions were performed using 2-substituted 1-(1-alkynyl)cyclopropyl ketone (0.5 mmol) and CuX_2 (2.5 equiv.) in CH_3CN (5 mL) at 90 °C. [b] Isolated yield. [c] N. R. = no reaction.

The generality of the method was also investigated by using 1-phenylethynyl-bicyclo[4.1.0]heptan-2-one (**1ab**) under the optimized conditions (Scheme 2). Fortuitously, the expected products **2ab** and **3ab** were obtained in good yields.



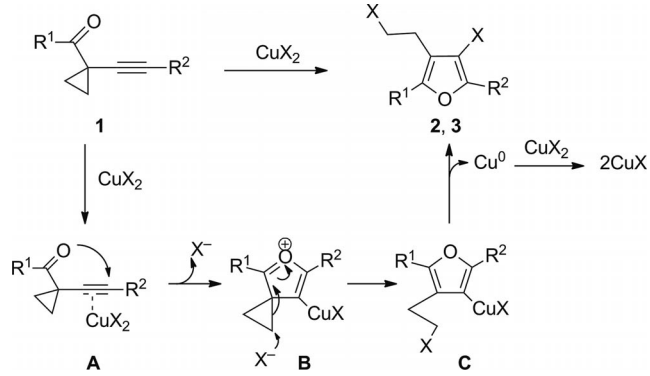
Scheme 2. Reaction between **1ab** and CuX_2.

The utility of the 3-bromofurans, produced by this chemistry, as useful synthetic intermediates for further elaboration was briefly investigated. For example, **2m** was successfully treated with 1-ethynyl-4-methylbenzene, and product **6** was obtained in 67% yield (Scheme 3).



Scheme 3. Sonogashira coupling reaction of **2m**.

On the basis of the above results, a plausible mechanism for the formation of **2** and **3** is depicted in Scheme 4. First, the CuX_2 species coordinates to the triple bond to generate intermediate **A**, which enhances the electrophilicity of the alkyne. The *anti* attack of the oxygen on the activated triple bond leads to the formation of intermediate **B**, which can be attacked by X^- in a regioselective homo-Michael-type addition to give intermediate **C**. A reductive elimination reaction of **C** provides 3-halofurans **2** or **3** and Cu^0. The Cu^0 can be oxidized by CuX_2 to produce CuX.



Scheme 4. Plausible reaction mechanism.

Conclusions

In conclusion, an efficient process for the synthesis of 3-halofurans was developed by the cascade cyclization–ad-

dition–reductive elimination reactions of 1-(1-alkynyl)cyclopropyl ketones in the presence of cupric halide. The reaction involves consecutive multiple bond formations, including C–O and C–Br bonds, with high regioselectivity. This process shows considerable synthetic advantages in terms of product diversity, mild reaction conditions, simplicity of the reaction procedure, and good-to-excellent yields. Further studies to elucidate the precise mechanism of this reaction and to extend the scope of its synthetic utility are in progress in our laboratory.

Experimental Section

General Remarks: The chemicals were obtained from commercial suppliers and used without further purification. 1-(1-Alkynyl)cyclopropyl ketones **1a**–**1l** were prepared as described previously.[19a] ^{1}H and ^{13}C NMR spectroscopic data were measured in $CDCl_3$ and recorded with a Bruker Avance-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR), using TMS as the internal standard. EI-MS were determined with an HP5989B mass spectrometer. Elemental analyses were performed with an EA-1110 instrument. Melting points were measured with a microscopic apparatus.

Typical Procedure for the $CuBr_2$-Mediated Cyclization of 1-(1-Alkynyl)cyclopropyl Ketones: To a solution of phenyl[1-(2-phenylethynyl)cyclopropyl]methanone (**1a**, 0.5 mmol) in CH_3CN (5 mL) was added copper(II) bromide (2.5 equiv.). The resulting mixture was stirred at 90 °C for 1 h, and then the reaction was quenched with a saturated aqueous solution of NH_4Cl. The mixture was then extracted with diethyl ether, and the combined organic layers were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel using hexane as the eluent to afford **2a** as a colorless solid. Compounds **2b**–**2l**, **3a**–**3k**, and **4a**–**4e** were prepared by the same method.

3-Bromo-4-(2-bromoethyl)-2,5-diphenylfuran (2a): Colorless solid, m.p. 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26–3.30 (t, J = 8.0 Hz, 2 H), 3.56–3.60 (t, J = 8.0 Hz, 2 H), 7.34–7.48 (m, 6 H), 7.67–7.69 (d, J = 8.0 Hz, 2 H), 8.02–8.04 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 147.8, 130.3, 129.7, 129.1, 128.7, 128.4, 128.3, 125.9, 125.7, 120.5, 100.9, 29.9, 29.1 ppm. MS: m/z (%) = 406 (100) $[M]^+$. $C_{18}H_{14}Br_2O$ (406.11): calcd. C 53.23, H 3.47; found C 53.47, H 3.30.

3-Chloro-4-(2-chloroethyl)-2,5-diphenylfuran (3a): Colorless solid, m.p. 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.17–3.21 (t, J = 8.0 Hz, 2 H), 3.72–3.76 (t, J = 8.0 Hz, 2 H), 7.29–7.47 (m, 6 H), 7.68–7.70 (d, J = 8.0 Hz, 2 H), 7.97–7.99 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 146.3, 130.4, 129.4, 129.0, 128.7, 128.4, 128.1, 125.9, 125.2, 118.3, 114.3, 42.3, 27.8 ppm. MS: m/z (%) = 316 (100) $[M]^+$. $C_{18}H_{14}Cl_2O$ (317.21): calcd. C 68.15, H 4.45; found C 68.40, H 4.21.

3-Bromo-4-(2-bromoethyl)-5-(4-chlorophenyl)-2-phenylfuran (2b): Colorless solid, m.p. 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22–3.25 (t, J = 8.0 Hz, 2 H), 3.53–3.57 (t, J = 8.0 Hz, 2 H), 7.32–7.45 (m, 5 H), 7.58–7.60 (d, J = 8.0 Hz, 2 H), 7.99–8.01 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 134.2, 129.4, 129.3, 128.7, 128.7, 128.5, 127.0, 125.7, 120.9, 100.9, 29.7, 29.0 ppm. MS: m/z (%) = 440 (100) $[M]^+$. $C_{18}H_{13}Br_2ClO$ (440.56): calcd. C 49.07, H 2.97; found C 49.15, H 3.11.

3-Chloro-4-(2-chloroethyl)-5-(4-chlorophenyl)-2-phenylfuran (3b): Colorless solid, m.p. 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.14–3.16 (t, J = 8.0 Hz, 2 H), 3.72–3.76 (t, J = 8.0 Hz, 2 H), 7.31–7.45 (m, 5 H), 7.61–7.63 (d, J = 8.0 Hz, 2 H), 7.95–7.97 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 146.6, 134.2, 129.3, 129.2, 128.8, 128.7, 128.3, 127.0, 125.2, 118.7, 114.4, 42.3, 27.8 ppm. MS: m/z (%) = 350 (100) $[M]^+$. $C_{18}H_{13}Cl_3O$ (351.65): calcd. C 61.48, H 3.73; found C 61.42, H 3.95.

3-Bromo-4-(2-bromoethyl)-5-(4-bromophenyl)-2-phenylfuran (2c): Colorless solid, m.p. 135–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22–3.26 (t, J = 8.0 Hz, 2 H), 3.54–3.58 (t, J = 8.0 Hz, 2 H), 7.33–7.36 (m, 1 H), 7.42–7.46 (m, 2 H), 7.53–7.59 (m, 4 H), 7.99–8.01 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 148.0, 132.2, 129.4, 129.2, 128.7, 128.5, 127.3, 125.7, 122.4, 121.0, 100.9, 29.7, 29.0 ppm. MS: m/z (%) = 484 (100) $[M]^+$. $C_{18}H_{13}Br_3O$ (485.01): calcd. C 44.58, H 2.70; found C 44.66, H 2.56.

2-(4-Bromophenyl)-4-chloro-3-(2-chloroethyl)-5-phenylfuran (3c): Colorless solid, m.p. 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.14–3.18 (t, J = 8.0 Hz, 2 H), 3.72–3.76 (t, J = 8.0 Hz, 2 H), 7.33–7.35 (m, 1 H), 7.42–7.56 (m, 6 H), 7.95–7.97 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 146.6, 132.2, 129.3, 129.2, 128.8, 128.3, 127.3, 125.2, 122.4, 118.8, 114.4, 42.3, 27.7 ppm. MS: m/z (%) = 396 (100) $[M]^+$. $C_{18}H_{13}BrCl_2O$ (396.11): calcd. C 54.58, H 3.31; found C 54.47, H 3.53.

3-Bromo-4-(2-bromoethyl)-5-(4-fluorophenyl)-2-phenylfuran (2d): Colorless solid, m.p. 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.20–3.24 (t, J = 8.0 Hz, 2 H), 3.54–3.58 (t, J = 8.0 Hz, 2 H), 7.12–7.16 (t, J = 8.0 Hz, 2 H), 7.31–7.35 (t, J = 8.0 Hz, 1 H), 7.41–7.45 (t, J = 8.0 Hz, 2 H), 7.62–7.65 (t, J = 8.0 Hz, 2 H), 7.99–8.01 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 161.4 (d, J = 248.0 Hz), 148.4, 147.8, 129.5, 128.7, 128.4, 127.91, 127.83 (d, J = 8.0 Hz), 126.60, 126.57 (d, J = 3.0 Hz), 125.7, 120.2, 116.27, 116.05 (d, J = 22.0 Hz), 100.8, 29.9, 29.0 ppm. MS: m/z (%) = 424 (100) $[M]^+$. $C_{18}H_{13}Br_2FO$ (424.10): calcd. C 50.98, H 3.09; found C 51.21, H 3.26.

3-Chloro-4-(2-chloroethyl)-5-(4-fluorophenyl)-2-phenylfuran (3d): Colorless solid, m.p. 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.16–3.20 (t, J = 8.0 Hz, 2 H), 3.75–3.78 (t, J = 8.0 Hz, 2 H), 7.14–7.18 (t, J = 8.0 Hz, 2 H), 7.32–7.35 (t, J = 8.0 Hz, 1 H), 7.43–7.47 (t, J = 8.0 Hz, 2 H), 7.67–7.70 (t, J = 8.0 Hz, 2 H), 7.96–7.98 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.96, 161.48 (d, J = 248.0 Hz), 148.2, 146.4, 129.4, 128.8, 128.2, 128.0, 127.9, 127.6, 126.7, 125.8, 125.2, 118.0, 116.28, 116.06 (d, J = 22.0 Hz), 114.2, 42.4, 27.8 ppm. MS: m/z (%) = 334 (100) $[M]^+$. $C_{18}H_{13}Cl_2FO$ (335.2): calcd. C 64.50, H 3.91; found C 64.63, H 3.81.

3-Bromo-4-(2-bromoethyl)-5-(4-methoxyphenyl)-2-phenylfuran (2e): Colorless solid, m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22–3.26 (t, J = 8.0 Hz, 2 H), 3.54–3.58 (t, J = 8.0 Hz, 2 H), 3.85 (s, 3 H), 6.98–7.00 (d, J = 8.0 Hz, 2 H), 7.30–7.45 (m, 3 H), 7.59–7.61 (d, J = 8.0 Hz, 2 H), 8.00–8.02 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 149.4, 147.2, 129.8, 128.6, 128.1, 127.5, 125.6, 123.1, 119.2, 114.5, 100.8, 55.5, 30.0, 29.1 ppm. MS: m/z (%) = 436 (100) $[M]^+$. $C_{19}H_{16}Br_2O_2$ (436.14): calcd. C 52.32, H 3.70; found C 52.54, H 3.93.

3-Chloro-4-(2-chloroethyl)-5-(4-methoxyphenyl)-2-phenylfuran (3e): Colorless solid, m.p. 103–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.03–3.07 (t, J = 8.0 Hz, 2 H), 3.58–3.62 (t, J = 8.0 Hz, 2 H), 3.80 (s, 3 H), 6.94–6.96 (d, J = 8.0 Hz, 2 H), 7.22–7.38 (m, 3 H), 7.59–7.63 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 149.2, 148.5, 131.3, 128.7, 127.3, 127.1, 125.7, 124.2, 119.7, 118.2, 114.5, 55.4, 43.1, 28.3 ppm. MS: m/z (%) = 346 (100) $[M]^+$.

$C_{19}H_{16}Cl_2O_2$ (347.24): calcd. C 65.72, H 4.64; found C 65.83, H 4.90.

3-Bromo-4-(2-bromoethyl)-5-(3-methoxyphenyl)-2-phenylfuran (2f): Colorless solid, m.p. 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.26–3.30 (t, J = 8.0 Hz, 2 H), 3.56–3.60 (t, J = 8.0 Hz, 2 H), 3.86 (s, 3 H), 6.89–6.91 (d, J = 8.0 Hz, 1 H), 7.23–7.45 (m, 6 H), 8.01–8.03 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 148.9, 147.7, 131.5, 130.1, 129.6, 128.6, 128.3, 125.7, 120.7, 118.3, 114.0, 111.4, 100.9, 55.5, 29.8, 29.1 ppm. MS: m/z (%) = 436 (100) $[M]^+$. $C_{19}H_{16}Br_2O_2$ (436.14): calcd. C 52.32, H 3.70; found C 52.48, H 3.88.

3-Chloro-4-(2-chloroethyl)-5-(3-methoxyphenyl)-2-phenylfuran (3f): Colorless solid, m.p. 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18–3.22 (t, J = 8.0 Hz, 2 H), 3.74–3.77 (t, J = 8.0 Hz, 2 H), 3.86 (s, 3 H), 6.89–6.91 (d, J = 8.0 Hz, 1 H), 7.25–7.43 (m, 6 H), 7.96–7.98 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 148.7, 146.3, 131.6, 130.1, 129.4, 128.7, 128.2, 125.2, 118.5, 118.3, 114.3, 113.9, 111.6, 55.5, 42.3, 27.8 ppm. MS: m/z (%) = 346 (100) $[M]^+$. $C_{19}H_{16}Cl_2O_2$ (347.24): calcd. C 65.72, H 4.64; found C 65.90, H 4.41.

3-Bromo-4-(2-bromoethyl)-2-phenyl-5-propylfuran (2g): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–0.98 (t, J = 8.0 Hz, 3 H), 1.67–1.72 (q, J = 8.0 Hz, 2 H), 2.60–2.63 (t, J = 8.0 Hz, 2 H), 2.92–2.95 (t, J = 8.0 Hz, 2 H), 3.45–3.49 (t, J = 8.0 Hz, 2 H), 7.24–7.27 (t, J = 8.0 Hz, 1 H), 7.35–7.39 (t, J = 8.0 Hz, 2 H), 7.90–7.92 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 146.8, 130.0, 128.5, 127.7, 125.2, 118.9, 98.7, 31.4, 28.7, 28.2 21.8, 13.9 ppm. MS: m/z (%) = 372 (100) $[M]^+$. $C_{15}H_{16}Br_2O$ (372.09): calcd. C 48.42, H 4.33; found C 48.30, H 4.48.

3-Chloro-4-(2-chloroethyl)-2-phenyl-5-propylfuran (3g): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96–0.99 (t, J = 8.0 Hz, 3 H), 1.68–1.74 (m, 2 H), 2.60–2.63 (t, J = 8.0 Hz, 2 H), 2.85–2.88 (t, J = 8.0 Hz, 2 H), 3.62–3.66 (t, J = 8.0 Hz, 2 H), 7.24–7.28 (m, 1 H), 7.37–7.41 (t, J = 8.0 Hz, 2 H), 7.87–7.89 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 145.3, 129.8, 128.6, 127.5, 124.7, 116.8, 112.4, 43.4, 28.7, 27.1, 21.8, 13.9 ppm. MS: m/z (%) = 282 (100) $[M]^+$. $C_{15}H_{16}Cl_2O$ (283.19): calcd. C 63.62, H 5.69; found C 63.91.30, H 5.86.

3-Bromo-4-(2-bromoethyl)-5-ethyl-2-phenylfuran (2h): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27–1.30 (t, J = 8.0 Hz, 3 H), 2.68–2.74 (q, J = 8.0 Hz, 2 H), 2.95–2.99 (t, J = 8.0 Hz, 2 H), 3.49–3.53 (t, J = 8.0 Hz, 2 H), 7.25–7.31 (m, 1 H), 7.38–7.42 (t, J = 8.0 Hz, 2 H), 7.92–7.94 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 146.8, 130.1, 128.6, 127.8, 125.7, 118.2, 98.8, 31.6, 28.2, 20.3, 13.1 ppm. MS: m/z (%) = 358 (100) $[M]^+$. $C_{14}H_{14}Br_2O$ (358.07): calcd. C 46.96, H 3.94; found C 46.85, H 4.09.

3-Chloro-4-(2-chloroethyl)-5-ethyl-2-phenylfuran (3h): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.30 (t, J = 8.0 Hz, 3 H), 2.65–2.69 (m, 2 H), 2.86–2.89 (t, J = 8.0 Hz, 2 H), 3.63–3.67 (t, J = 8.0 Hz, 2 H), 7.24–7.29 (m, 1 H), 7.38–7.42 (t, J = 8.0 Hz, 2 H), 7.87–7.89 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 145.3, 129.9, 128.6, 127.5, 124.7, 116.0, 112.5, 43.5, 27.1, 20.2, 13.0 ppm. MS: m/z (%) = 268 (100) $[M]^+$. $C_{14}H_{14}Cl_2O$ (269.17): calcd. C 62.47, H 5.24; found C 62.58, H 5.44.

3-Bromo-4-(2-bromoethyl)-5-(naphthalen-1-yl)-2-phenylfuran (2i): Colorless solid, m.p. 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.03–3.06 (t, J = 8.0 Hz, 2 H), 3.44–3.48 (t, J = 8.0 Hz, 2 H), 7.33–7.43 (m, 4 H), 7.52–7.65 (m, 3 H), 7.84–8.04 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 148.7, 133.5, 132.4, 130.2, 129.5, 128.8, 128.7, 128.7, 128.4, 127.9, 127.8, 127.5, 127.0, 126.3, 125.7, 122.9, 99.6, 30.4, 28.6 ppm. MS: m/z (%) = 456 (100) $[M]^+$. $C_{22}H_{16}Br_2O$ (456.17): calcd. C 57.92, H 3.54; found C 57.80, H 3.72.

3-Chloro-4-(2-chloroethyl)-5-(naphthalen-1-yl)-2-phenylfuran (3i): Colorless solid, m.p. 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98–3.01 (t, J = 8.0 Hz, 2 H), 3.62–3.65 (t, J = 8.0 Hz, 2 H), 7.30–7.42 (m, 3 H), 7.52–7.61 (m, 4 H), 7.89–7.99 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 147.1, 133.9, 132.3, 130.2, 129.6, 128.8, 128.7, 128.6, 128.1, 127.4, 127.0, 126.4, 125.7, 125.3, 125.2, 120.4, 113.4, 42.6, 27.6 ppm. MS: m/z (%) = 366 (100) $[M]^+$. $C_{22}H_{16}Cl_2O$ (367.27): calcd. C 71.95, H 4.39; found C 72.21, H 4.30.

3-Bromo-4-(2-bromoethyl)-5-(4-chlorophenyl)-2-*p*-tolylfuran (2j): Colorless solid, m.p. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.21–3.25 (t, J = 8.0 Hz, 2 H), 3.53–3.57 (t, J = 8.0 Hz, 2 H), 7.23–7.25 (d, J = 8.0 Hz, 2 H), 7.40–7.42 (d, J = 8.0 Hz, 2 H), 7.58–7.60 (d, J = 8.0 Hz, 2 H), 7.88–7.90 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 147.7, 138.5, 134.1, 129.4, 129.2, 128.8, 126.9, 126.7, 125.7, 120.8, 100.2, 29.7, 29.1, 21.5 ppm. MS: m/z (%) = 454 (100) $[M]^+$. $C_{19}H_{15}Br_2ClO$ (454.58): calcd. C 50.20, H 3.33; found C 50.45, H 3.51.

3-Chloro-4-(2-chloroethyl)-5-(4-chlorophenyl)-2-*p*-tolylfuran (3j): Colorless solid, m.p. 107–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 3.12–3.16 (t, J = 8.0 Hz, 2 H), 3.71–3.74 (t, J = 8.0 Hz, 2 H), 7.22–7.24 (d, J = 8.0 Hz, 2 H), 7.38–7.40 (d, J = 8.0 Hz, 2 H), 7.59–7.61 (d, J = 8.0 Hz, 2 H), 7.82–7.84 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 146.8, 138.3, 134.0, 129.4, 129.2, 128.9, 126.9, 126.4, 125.1, 118.6, 113.6, 42.3, 27.8, 21.5 ppm. MS: m/z (%) = 364 (100) $[M]^+$. $C_{19}H_{15}Cl_3O$ (365.68): calcd. C 62.41, H 4.13; found C 62.63, H 4.32.

3-Bromo-4-(2-bromoethyl)-5-phenyl-2-*o*-tolylfuran (2k): Colorless solid, m.p. 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 3.32–3.36 (t, J = 8.0 Hz, 2 H), 3.63–3.67 (t, J = 8.0 Hz, 2 H), 7.29–7.35 (m, 3 H), 7.45–7.49 (t, J = 8.0 Hz, 2 H), 7.60–7.61 (d, J = 4.0 Hz, 1 H), 7.67–7.69 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 149.6, 137.8, 131.0, 130.5, 130.3, 129.5, 129.1, 128.8, 128.3, 125.8, 125.7, 119.39, 102.6, 30.0, 29.4, 20.9 ppm. MS: m/z (%) = 420 (100) $[M]^+$. $C_{19}H_{16}Br_2O$ (420.14): calcd. C 54.32, H 3.84; found C 54.49, H 3.62.

3-Chloro-4-(2-chloroethyl)-5-phenyl-2-*o*-tolylfuran (3k): Colorless solid, m.p. 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 3.20–3.24 (t, J = 8.0 Hz, 2 H), 3.76–3.80 (t, J = 8.0 Hz, 2 H), 7.26–7.35 (m, 3 H), 7.42–7.45 (t, J = 8.0 Hz, 2 H), 7.57–7.59 (d, J = 8.0 Hz, 1 H), 7.65–7.67 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 148.1, 137.5, 131.0, 130.6, 129.8, 129.3, 129.0, 128.3, 125.7, 117.1, 115.3, 42.43, 28.0, 20.9 ppm. MS: m/z (%) = 330 (100) $[M]^+$. $C_{19}H_{16}Cl_2O$ (330.24): calcd. C 68.89, H 4.87; found C 68.63, H 4.71.

3-Bromo-4-(2-bromoethyl)-2-(4-methoxyphenyl)-5-phenylfuran (2l): Colorless solid, m.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24–3.28 (t, J = 8.0 Hz, 2 H), 3.55–3.59 (t, J = 8.0 Hz, 2 H), 3.84 (s, 3 H), 6.95–6.97 (d, J = 8.0 Hz, 2 H), 7.32–7.36 (t, J = 8.0 Hz, 1 H), 7.43–7.47 (t, J = 8.0 Hz, 2 H), 7.65–7.67 (d, J = 8.0 Hz, 2 H), 7.94–7.96 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 148.5, 147.9, 130.4, 129.0, 128.2, 127.3, 125.8, 122.5, 120.4, 114.1, 99.4, 55.4, 29.9, 29.2 ppm. MS: m/z (%) = 436 (100) $[M]^+$. $C_{19}H_{16}Br_2O_2$ (436.14): calcd. C 52.32, H 3.70; found C 52.53, H 3.85.

3-Bromo-4-(2-bromoethyl)-2-hexyl-5-*p*-tolylfuran (2m): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.92 (m, 3 H), 1.25–1.40 (m, 6 H), 1.64–1.68 (m, 2 H), 2.35 (s, 3 H), 2.62–2.66 (t, J = 7.2 Hz, 2

H), 2.92–2.96 (t, *J* = 7.2 Hz, 2 H), 3.46–3.50 (t, *J* = 7.2 Hz, 2 H), 7.18–7.20 (d, *J* = 8.0 Hz, 2 H), 7.79–7.81 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 147.0, 137.6, 129.2, 127.3, 125.2, 118.5, 98.0, 31.7, 31.4, 29.0, 28.5, 28.3, 26.8, 22.7, 21.4, 14.2 ppm. MS: *m*/*z* (%) = 428 (81) $[M]^+$. $C_{19}H_{24}Br_2O$ (428.20): calcd. C 53.29, H 5.65; found C 53.60, H 5.83.

3-Chloro-4-(2-chloroethyl)-2-hexyl-5-*p*-tolylfuran (3m): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87–0.90 (m, 3 H), 1.31–1.36 (m, 6 H), 1.64–1.68 (m, 2 H), 2.35 (s, 3 H), 2.60–2.64 (t, *J* = 7.2 Hz, 2 H), 2.84–2.88 (t, *J* = 7.2 Hz, 2 H), 3.62–3.66 (t, *J* = 7.2 Hz, 2 H), 7.19–7.23 (d, *J* = 8.0 Hz, 2 H), 7.75–7.77 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 145.5, 137.4, 129.3, 127.1, 124.7, 116.4, 111.7, 43.4, 31.7, 29.0, 28.5, 27.2, 26.7, 22.7, 21.4, 14.2 ppm. MS: *m*/*z* (%) = 338 (65) $[M]^+$. $C_{19}H_{24}Cl_2O$ (339.30): calcd. C 67.26, H 7.13; found C 67.43, H 6.95.

3-Bromo-4-(2-bromo-2-phenylethyl)-2,5-diphenylfuran (4a): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52–3.58 (m, 1 H), 3.68–3.74 (m, 1 H), 5.32–5.36 (t, *J* = 7.6 Hz, 1 H), 7.19–7.20 (m, 3 H), 7.29–7.35 (m, 4 H), 7.39–7.42 (m, 4 H), 7.57–7.59 (d, *J* = 8.0 Hz, 2 H), 7.99–8.02 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 147.7, 140.9, 130.5, 129.7, 128.8, 128.63, 128.6, 128.5, 128.4, 128.2, 127.5, 126.5, 125.7, 119.9, 100.9, 52.7, 36.0 ppm. MS: *m*/*z* (%) = 482 (78) $[M]^+$. $C_{24}H_{18}Br_2O$ (482.20): calcd. C 59.78, H 3.76; found C 60.05, H 3.49.

3-Bromo-4-(2-bromo-2-phenylethyl)-2-(4-methoxyphenyl)-5-phenylfuran (4b): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.49–3.55 (m, 1 H), 3.66–3.72 (m, 1 H), 3.78 (s, 3 H), 5.32–5.36 (t, *J* = 7.6 Hz, 1 H), 6.92–6.94 (t, *J* = 8.4 Hz, 2 H), 7.18 (br. s, 3 H), 7.30 (br. s, 3 H), 7.36–7.40 (t, *J* = 8.0 Hz, 2 H), 7.55–7.57 (d, *J* = 7.2 Hz, 2 H), 7.91–7.93 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 149.0, 147.8, 141.0, 130.6, 128.7, 128.54, 128.50, 128.1, 127.5, 127.2, 126.3, 122.5, 119.7, 114.0, 99.3, 55.4, 52.8, 35.9 ppm. MS: *m*/*z* (%) = 512 (71) $[M]^+$. $C_{25}H_{20}Br_2O_2$ (512.23): calcd. C 58.62, H 3.94; found C 58.81, H 3.76.

3-Bromo-4-(2-bromo-2-phenylethyl)-5-phenyl-2-*p*-tolylfuran (4c): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.48–3.54 (m, 1 H), 3.65–3.71 (m, 1 H), 5.31–5.35 (t, *J* = 7.2 Hz, 1 H), 7.13–7.19 (m, 5 H), 7.27–7.29 (m, 3 H), 7.35–7.39 (t, *J* = 7.2 Hz, 2 H), 7.54–7.56 (d, *J* = 7.6 Hz, 2 H), 7.86–7.88 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 147.9, 140.9, 138.0, 130.5, 129.3, 128.7, 128.5, 128.4, 128.1, 127.5, 126.9, 126.4, 122.6, 119.8, 100.2, 52.8, 35.9, 21.5 ppm. MS: *m*/*z* (%) = 496 (83) $[M]^+$. $C_{25}H_{20}Br_2O$ (496.23): calcd. C 60.51, H 4.06; found C 60.35, H 3.88.

3-Bromo-4-(2-bromo-2-phenylethyl)-2-(4-chlorophenyl)-5-phenylfuran (4d): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46–3.52 (m, 1 H), 3.64–3.69 (m, 1 H), 5.27–5.31 (t, *J* = 7.6 Hz, 1 H), 7.16–7.18 (m, 3 H), 7.27–7.40 (m, 7 H), 7.53–7.55 (d, *J* = 7.6 Hz, 2 H), 7.88–7.90 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 146.6, 140.9, 133.8, 130.2, 128.83, 128.81, 128.6, 128.5, 128.1, 127.5, 126.7, 126.4, 120.0, 101.4, 52.6, 35.9 ppm. MS: *m*/*z* (%) = 516 (74) $[M]^+$. $C_{24}H_{17}Br_2ClO$ (516.65): calcd. C 55.79, H 3.32; found C 55.58, H 3.60.

3-Bromo-4-(2-bromo-2-phenylethyl)-5-butyl-2-phenylfuran (4e): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99–1.02 (t, *J* = 7.2 Hz, 3 H), 1.44–1.51 (m, 2 H), 1.68–1.72 (m, 2 H), 2.85–2.88 (t, *J* = 7.6 Hz, 2 H), 3.35–3.40 (m, 1 H), 3.53–3.58 (m, 1 H), 5.02–5.06 (t, *J* = 7.6 Hz, 1 H), 7.38–7.44 (m, 5 H), 7.72–7.79 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 130.4, 130.3, 128.9, 128.7, 128.1, 127.9, 127.3, 125.4, 124.0, 108.4, 100.2, 51.8, 40.5, 35.2, 29.6, 22.0, 14.1 ppm. MS: *m*/*z* (%) = 462 (86) $[M]^+$. $C_{22}H_{22}Br_2O$ (462.21): calcd. C 57.17, H 4.80; found C 57.38, H 4.59.

3,5-Dibromo-5,6,7,8-tetrahydro-2-phenyl-4*H*-cyclohepta[*b*]furan (2ab): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66–1.69 (m, 1 H), 2.00–2.10 (m, 2 H), 2.43–2.45 (m, 1 H), 2.75–2.85 (m, 3 H), 2.96–3.00 (m, 1 H), 4.10–4.15 (m, 1 H), 7.21–7.23 (d, *J* = 8.0 Hz, 1 H), 7.34–7.38 (t, *J* = 8.0 Hz, 2 H), 7.51–7.56 (t, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 146.9, 135.9, 131.6, 128.6, 126.9, 125.6, 100.6, 41.4, 34.0, 28.3, 28.2, 24.7 ppm. MS: *m*/*z* (%) = 370 (100) $[M]^+$. $C_{15}H_{14}Br_2O$ (370.08): calcd. C 48.68, H 3.81; found C 48.81, H 3.54.

3,5-Dichloro-5,6,7,8-tetrahydro-2-phenyl-4*H*-cyclohepta[*b*]furan (3ab): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66–1.99 (m, 3 H), 2.75–3.07 (m, 5 H), 4.26–4.31 (m, 1 H), 7.22–7.24 (d, *J* = 8.0 Hz, 1 H), 7.33–7.37 (t, *J* = 8.0 Hz, 2 H), 7.51–7.56 (t, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 146.9, 135.9, 131.6, 128.6, 126.9, 125.6, 115.9, 42.3, 34.8, 28.3, 28.2, 25.8 ppm. MS: *m*/*z* (%) = 280 (100) $[M]^+$. $C_{15}H_{14}Cl_2O$ (281.18): calcd. C 64.07, H 5.02; found C 64.28, H 5.35.

3-(2-Bromoethyl)-5-hexyl-2-*p*-tolyl-4-(2-*p*-tolylethynyl)furan (6): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–0.81 (t, *J* = 8.0 Hz, 3 H), 1.38–1.40 (br. s, 6 H), 1.66–1.69 (m, 2 H), 2.28 (s, 3 H), 2.30 (s, 3 H), 2.58–2.61 (m, *J* = 7.2 Hz, 2 H), 2.67–2.70 (t, *J* = 7.6 Hz, 2 H), 3.39–3.43 (t, *J* = 7.6 Hz, 2 H), 7.02–7.04 (d, *J* = 8.0 Hz, 2 H), 7.07–7.09 (d, *J* = 7.6 Hz, 2 H), 7.24–7.26 (d, *J* = 7.6 Hz, 2 H), 7.95–7.97 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 130.4, 130.3, 128.9, 128.7, 128.1, 127.9, 127.3, 125.4, 124.0, 108.4, 100.2, 51.8, 40.5, 35.2, 29.6, 22.0, 14.1 ppm. MS: *m*/*z* (%) = 462 (86) $[M]^+$. $C_{22}H_{22}Br_2O$ (462.21): calcd. C 57.17, H 4.80; found C 57.38, H 4.59.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and ^{1}H NMR and ^{13}C NMR spectra.

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[22] The atomic coordinates for **2e** have been deposited at the Cambridge Crystallographic Data Centre. CCDC-858907 (for **2e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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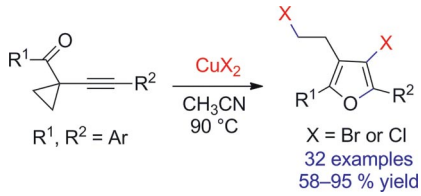
Halofuran Synthesis

The selective synthesis of functionalized furans by using the cupric halide-mediated intramolecular halocyclization of 1-(1-alkynyl)cyclopropyl ketones is described. Under mild conditions, a series of 3-chloro- and 3-bromofuran derivatives were formed in 1 h in high yields (58–95%).



Keywords: Oxygen heterocycles / Cyclopropyl ketones / Copper / Halogenation / Cyclization

